AN INVESTIGATION INTO THE SYNTHESIS AND STRUCTURE OF SOME PENTAMETHYLCYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM, TUNGSTEN AND IRON.

by

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ABBREVIATIONS

The following abbreviations are used in this work :

Cp = η-C_5H_5 *

Cp* = η-C_5Me_5 *

THF = tetrahhdrofuran

Ph = phenyl

Me = methyl

Et = ethyl

dppm = bis diphenylphosphinomethane

dppe = bis diphenylphosphinoethane

n-Bu = n-butyl

* The IUPAC convention for maximum hapticity of unsaturated hydrocarbon rings will be used throughout this work.

ABSTRACT

The extensive series of cyclopentadienyl transition metal complexes known, has made of interest the corresponding chemistry of pentamethylcyclopentadienyl transition metal derivatives, and other substituted cyclopentdienyl species. Such compounds are of interest, since the substitution of all five hydrogens in a cyclopentadienyl ring bonded to a transition metal would be expected to have a profound effect on the reactivity and structure of the resulting metal complex, resulting from both steric and electronic effects.

Monosubstituted methyl transition metal complexes of the type $LnMCH_2X$, (Ln = other ligands and X = functional group), have been suggested as possible precursors for a number of compounds such as hydroxymethyl complexes, carbene complexes and bridging methylene complexes, all of which are models for intermediates which have been proposed in the mechanism of the Fischer-Tropsch synthesis reaction.

Two synthetic routes are described for the synthesis of new halomethyl complexes of molybdenum and tungsten. Thus the reaction of $[(\eta\text{-}C_5Me_5)M(CO)_3]^-$ and CH_2XY gives $[(\eta\text{-}C_5Me_5)M(CO)_3CH_2X]$ (M = Mo, W; X, Y = halogen).

$[(\eta\text{-}C_5Me_5)M(CO)_3CH_2OCH_3)]$ M = Mo, W gives on reaction with dry HX gas (X = Cl, Br, I) the halomethyl complexes $[(\eta\text{-}C_5Me_5)M(CO_3)CH_2X]$, (M = Mo, W; X = Cl, Br I). The new complexes were characterised by usual methods.

The reactions of $[(\eta\text{-}C_5Me_5)W(CO)_3]^-$ with CH_2Br_2 and CH_2I_2 unexpectedly gave the known complex $[(\eta\text{-}C_5Me_5)W(CO)_3CH_3]$, possible reasons for this are discussed. Also, reaction of $[(\eta\text{-}C_5Me_5)Fe(CO)_2]^-$ with $ClCH_2OCH_3$ gave $[(\eta\text{-}C_5Me_5)Fe(CO)_2CH_3]$ instead of the expected methoxymethyl product. The chloromethyl complex $[(\eta\text{-}C_5Me_5)Fe(CO)_2CH_2Cl]$ was prepared from the reaction of $[(\eta\text{-}C_5Me_5)(Fe(CO)_2]^-$ with CH_2Cl_2.

The reactions of some halomethyl transition metal complexes with PPh_3 were investigated. Thus $[(\eta\text{-}C_5Me_5)Mo(CO)_3CH_2Cl]$ gave on reaction with PPh_3 in methanol under reflux, or in acetonitrile at room temperature, the product $[(\eta\text{-}C_5Me_5)Mo(CO)_2(PPh_3)Cl]$. Reaction of $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2I]$ with PPh_3 in methanol under reflux or in acetonitrile at room temperature gave the phosphorous ylide complex $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]^+I^-$. The iron chloromethyl complex, $[(\eta\text{-}C_5Me_5)Fe(CO)_2CH_2Cl]$ gave on reaction with PPh_3 in CH_3CN, the product $[(\eta\text{-}C_5Me_5)Fe(CO)_2CH_2PPh_3]^+Cl^-$, isolated as the BPh_4^- salt, whereas the analogous reaction in methanol under reflux yielded only the methoxymethyl product, $[(\eta\text{-}C_5Me_5)Fe(CO)_2CH_2OCH_3]$.

The X-ray crystal structure of $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]^+I^-$ was investigated, the complex crystallised in the space group $P2_{1/n}$ - with unit cell parameters as follows:

$\underline{a}$ = 16.616 (8) Å

$\underline{b}$ = 11.738 (6) Å

$\underline{c}$ = 18.126 (9) Å

β = 101.74 (1)°

Z = 4

The final R for 3310 reflections was 0.076. Each ion pair was found to occupy a general position in the unit cell. The solvent of crystallisation, CH_2Cl_2, was found to be slightly disordered, and to occupy a general positions in the unit cell at S.O.F. = 0.5.

The pentamethylcyclopentadienyl ring is bonded to the tungsten atom in an η^5 manner, the average metal to ring carbon distance is W-C = 2.35 (2) Å. The tungsten atom is bonded to a methylene carbon which is in turn bonded to triphenylphosphine, giving rise to a phosphorous ylide complex. This structure is compared with the structures of other phosphorous ylide transition metal complexes.

Attempts have also been made to synthesise hydroxymethyl and carbene transition metal complexes.

CONTENTS

CHAPTER ONE

1. INTRODUCTION

1.1 The significance of the pentamethylcyclopentadienyl ligand.

Since the discovery of ferrocene in 1951,[1] the chemistry of cyclopentadienyl transition metal complexes has developed into one of the most important areas of transition metal organometallic chemistry.[2]

The replacement of some or all five hydrogens bonded to the cyclopentadienyl ring with methyl groups would at first glance appear to be a relatively minor alteration. Instead, this alteration has a profound effect on the chemistry of the resulting transition metal complexes, owing to both steric and electronic effects. Thus the pentamethylcyclopentadienyl transition metal complexes tend to exhibit altered crystallisation characteristics, are in general more soluble, have greater tendencies to form stable metal-metal bonds, exhibit different kinetic and thermodynamic stabilities and have different reactivity patterns towards attacking reagents, as compared with their unsubstituted cyclopentadienyl analogues.[3] The bonding between a transition metal atom or ion with partially filled d- orbitals, and a symmetrically planar C_5H_5 ring is described in fig 1.1.1[4].

Thus the cyclopentadienyl ring is bonded to the transition metal in an η^5 manner, the η^5 bond being composed of :

(a) A σ bond resulting from the donation of an electron pair from the filled A- orbital of the cyclopentadienyl ring, to the empty d- orbitals of the transition metal.

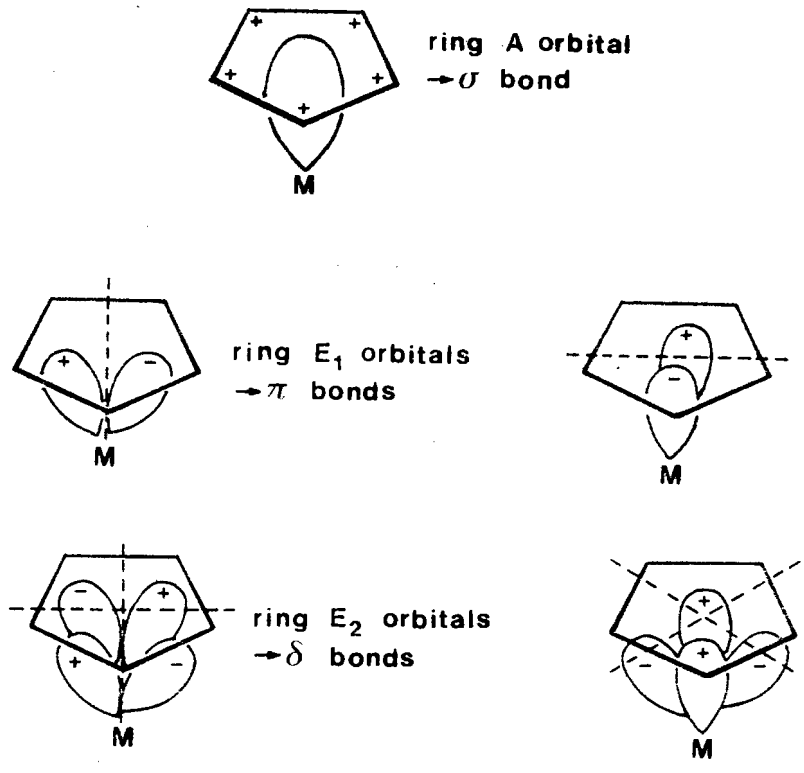


Fig 1.1.1 : The components of the bonding between a transition metal and a cyclopentadienyl ring.

(b) Two orthogonal π - bonds resulting from the donation of an electron pair from each of the two degenerate E_1 bonding orbitals of the cyclopentadienyl ring, into empty transition metal d- orbitals of appropriate symmetry.

(c) Two orthogonal reverse δ - bonds arising from the back donation of electron density from the filled transition metal d- orbitals of appropriate symmetry, into the two degenerate E_2 anti-bonding orbitals of the cyclopentadienyl ring.

The substitution of all five hydrogens on the cyclopentadienyl ring with methyl groups would be expected to strengthen the bonds between the ring and a transition metal as a result of the increased electron density in the filled A and E_1 orbitals of the ring. Thus it would be expected that the pentamethylcyclopentadienyl transition metal bond would be more stable than the bond between an unsubstituted cyclopentadienyl ring and a transition metal. As a result of the electron

releasing effects of the methyl substituents on the pentamethylcyclopentadienyl ring, there would be more electron density on the transition metal, than in the case of an unsubstituted cyclopentadienyl ring bonded to a transition metal, and thus the bonds between the transition metal and other ligands would be expected to be more stable, in most cases, and thus a more extensive range of complexes could be prepared.[2,3]

Thus Calabro *et al* [3] investigated the gas phase photo-electron spectra for molecules of the type $[(\eta\text{-}C_5H_{(5-n)}(CH_3)_n)M(CO)_3]$ (M = Mn, Re ; n = 0,1,5). The influence of the methyl substituents on the cyclopentadienyl ring was monitored by shifts in both the valence and core ionisation energies. The valence ionisation energies were found to decrease with increasing methylation of the cyclopentadienyl ring. This phenomenon was interpreted in terms of an electron releasing or inductive effect, of the methyl groups on the cyclopentadienyl ring, which tends to increase the electron charge on the ring, thereby increasing the effective basicity of the cyclopentadienyl ring.

Bordwell *et al* [5] investigated the methyl substitution effects of various unsaturated hydrocarbons on their equilibrium acidities in dimethyl sulphoxide at 25°C. Thus the substitution of 5 hydrogens on cyclopentadiene with methyl groups to give 1,2,3,4,5 pentamethylcyclopentadiene was found to result in an acid weakening effect of 7.8 pKa units relative to the pKa of cyclopentadiene. These authors attributed this to the large hyperconjugative effects of the methyl groups which tended to stabilise the undissociated acid C_5Me_5H, and also to the steric inhibition of solvation of the anion formed, viz $(C_5Me_5)^-$.

These authors[5] propose this large hyperconjugative effects of the methyl substituents on the pentamethylcyclopentadienyl ring, to be present in

pentamethylcyclopentadienyl transition metal complexes, and this hyperconjugative effect is the source of the increased electron density on the transition metal, as compared with the unsubstituted cyclopentadienyl analogue. For example, decamethyl ferrocene, Cp^*_2Fe has a lower oxidation potential than does ferrocene, resulting in a greater tendency towards spontaneous oxidation in air. Thus, although the electron releasing effects of the methyl substituents on the pentamethylcyclopentadienyl ring tend to increase the strength of the transition metal-ring bond, and also the bonds between the transition metal and other ligands, the oxidation potential of the complexes would be expected to be lower than those of the unsubstituted cyclopentadienyl analogues.

1.2 A review of pentamethylcyclopentadienyl transition metal complexes, and a comparison with their unsubstituted cyclopentadienyl analogues.

1.2.1 Pentamethylcyclopentadienyl complexes of titanium and zirconium.

The first pentamethylcyclopentadienyl transition metal complex, Cp^*TiCl_3 , was reported to result from the reactions of $TiCl_4$ with various simple hydrocarbons such as but-1-ene, but-2-ene, pent-1-ene etc.[6] This method used the transition metal , Ti, to form the pentamethylcyclopentadienyl ring system. The complex was later prepared in a more conventional manner from the reaction of $TiCl_4$ with C_5Me_5H.[2]

Titanium complexes such as $Cp_2Ti(CO)_2$ and $CpTiCl_2$ have been shown to catalytically hydrogenate alkenes and alkynes in the presence of various Grignard reagents. Various workers postulated mechanisms for these reactions, and proposed highly reactive intermediates such as "Cp_2TiH" and "Cp_2Ti", their existence however was not verified. Bercaw *et al* [7] demonstrated that the proposed intermediate

"Cp_2Ti" was in fact a titanium hydride species of formula $[(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_4)TiH]_2$. These authors proposed that if, in fact the intermediate "Cp_2Ti" were to exist, it would exhibit a tendency to re-arrange via an α-hydrogen shift from the cyclopentadienyl ring to titanium. In order to eliminate the possibility of such a re-arrangement, Bercaw *et al* [7] undertook the synthesis of Cp'_2Ti.

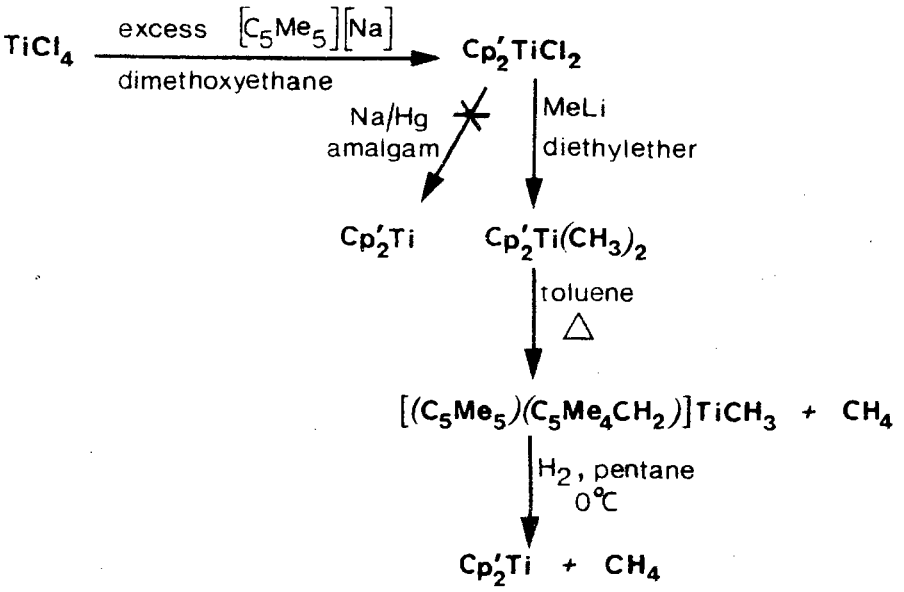


Fig 1.2.1 : The preparation of Cp'_2Ti.

The analogous unsubstituted cyclopentadienyl complex, "Cp_2Ti" , however, could not be synthesised by this route, instead a dimeric species $[Cp_2Ti]_2$ was isolated. The complexes Cp'_2Ti and $[Cp_2Ti]_2$ display a very high reactivity towards dinitrogen and dihydrogen.

The complex $Cp'_2Ti(CH_3)_2$ was shown to display a very low reactivity towards dihydrogen, as compared with that observed for the analogous cyclopentadienyl complex, $Cp_2Ti(CH_3)_2$. This was thought to be related to the greater thermal stability of the Cp' complex which could be stored for days at room temperature without decomposition, whereas the Cp complex decomposed at room temperature within minutes.

The analogous zirconium complex , viz $C\acute{p}_2Zr$ was prepared in the following manner[8]:

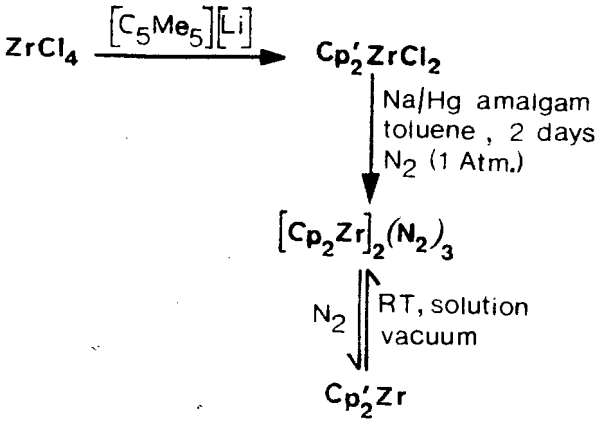


Fig 1.2.2 : Preparation of $C\acute{p}_2Zr$.

$[\{C\acute{p}_2Zr\}_2(N_2)_3]$ may be protonated to yield hydrazine in good yield.

Bercaw *et al* [9] have prepared a number of dinitrogen complexes of Ti and Zr having either Cṕ or Cp ligands and have determined their X-ray crystal structures.

These authors report the Cṕ complexes to be generally more stable than their Cp analogues, and thus more amenable to study. The Cp complexes are less soluble and more difficult to obtain in crystalline form.

Bercaw *et al* [10] reported that the complex $[\{C\acute{p}Zr(CO)\}_2N_2]$ catalyses the reduction of CO in moderate yields on treatment with HCl according to the following scheme :

$$[(C\acute{p}_2Zr(CO))_2N_2] + 4H_2 \longrightarrow [C\acute{p}_2Zr(H)(OCH_3)] + N_2$$

The reaction was proposed to go via an intermediate involving the oxidative

addition of H_2 to $Cp_2Zr(CO)_2$, generating the intermediate $[Cp_2Zr(H)_2(CO)]$. This complex was prepared via an alternate route :

$$\underset{(I)}{[(\eta\text{-}C_5Me_5)_2ZrH_2]} \xrightarrow[-80\,^{\circ}C]{CO,\ \text{toluene}} [(\eta\text{-}C_5Me_5)_2Zr(H)_2CO]$$

Fig 1.2.3 : Preparation of $[Cp_2Zr(H)_2(CO)]$

The complex (I) was found to be stable, and soluble in hydrocarbon and ether solvents, in contrast to the polymeric unsubstituted cyclpentadienyl analogue, $[Cp_2ZrH_2]_n$.

Ketene complexes of Zr have been synthesised, and reduced to enolate hydrides using hydrogen gas, according to the following scheme : [11]

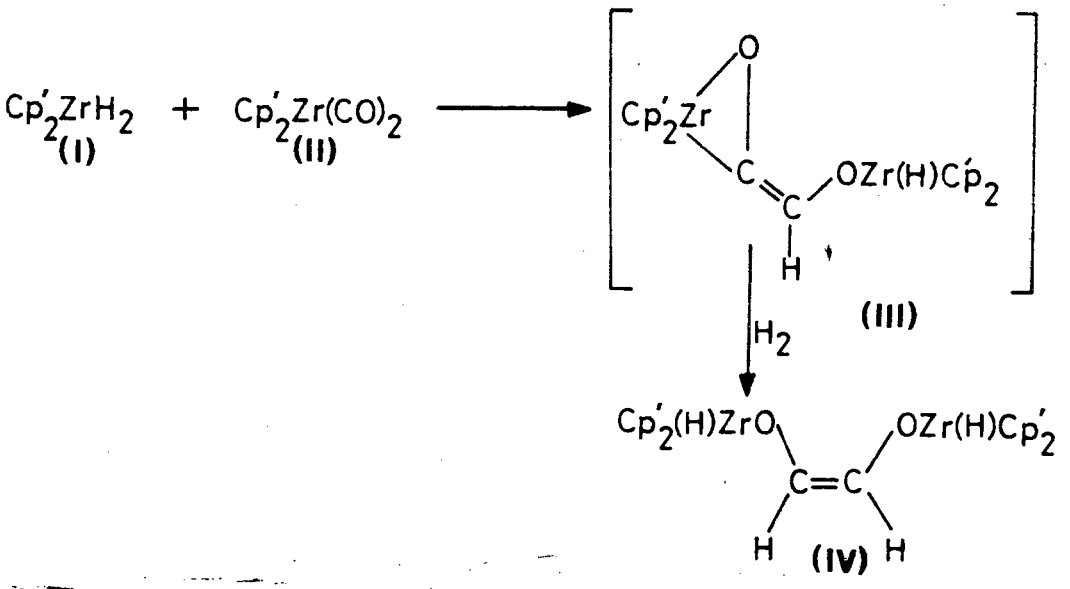


Fig 1.2.4 : Preparation of a zirconium enolate hydride.

The reaction of (I) + (II) $\longrightarrow$ (IV) was proposed to go via (III), which was then hydrogenated to give (IV). The *cis* geometry of (IV) was proposed to result from :

(a) The *cis* structure of (III) in which bulky $C\bar{p}ZrO$ moieties are sterically constrained to a *cis* arrangement.

(b) The stereospecific hydrogenation of (III) to (IV).

Stable monomeric Lewis base adducts of $\left[C\bar{p}_2Zr(C,O\text{-}\eta^2\text{-}R_2C{=}CO)\right]$; (R = H, alkyl) were prepared, $\left[C\bar{p}_2Zr(py)(C,O\text{-}\eta^2\text{-}R_2C{=}CO)\right]$; where py = pyridine.[11] These complexes are monomeric, in contrast to the unsubstituted cyclopentadienyl complexes which are dimeric and only sparingly soluble in organic solvents. Thus the bulky $C\bar{p}$ ligand appears to prevent dimerisation, as well as confer solubility on these complexes.

1.2.2 Pentamethylcyclopentadienyl complexes of niobium and tantalum.

The syntheses of the cyclopentadienyl Ta and Nb complexes $[CpMCl_4]_n$, (n >1; M = Nb, Ta) have been reported. The products were, however, extremely difficult to characterise, owing to their insolubility in organic solvents, and their high melting and sublimation points, which made mass spectra difficult to obtain.[12]

Sanner *et al* [13] synthesised the complex $C\bar{p}TaCl_4$ as a monomeric crystalline material. The complex was prepared from the treatment of a dichloromethane solution of $TaCl_4$ with $C\bar{p}Sn\text{-}(n\text{-}Bu)_3$. The product was soluble in common organic solvents, thus making ^1H nmr spectra accessible, mass spectra could also be obtained. Other $C\bar{p}Ta$ complexes, viz $C\bar{p}TaCl_4L$; (L = PMe_3, $P(OMe)_3$, dppe) ; $C\bar{p}TaMe_4$ and $C\bar{p}Ta(CH_2Ph)_2(CHPh)$ were also prepared.

Bercaw *et al* [14] investigated the X-ray crystal structure of $[C\acute{p}Ta(PMe_3)_2H_4]$. The η^5-C_5Me_5 ligand was found to be planar, the carbon atoms of the methyl groups attatched to the cyclopentadienyl ring being displaced from the mean plane of the ring away from the Ta atom. The Ta-P bond distances were found to be similar to those reported for other $Ta(PMe_3)$ structures. The geometry about the P atom was not quite tetrahedral, all the CH_3-P-CH_3 bond angles, 99° (mean), were less than the tetrahedral value.

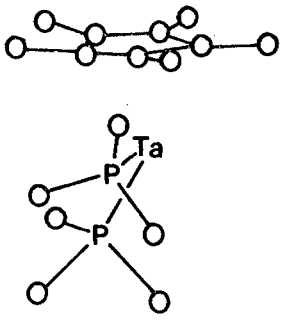


Fig 1.2.5 : The X-Ray crystal structure of $[C\acute{p}Ta(PMe_3)_2H_4]$.

The structure displayed slight asymmetry since the midpoint between the P atoms was not directly opposite the midpoint of the Cṕ ring.

These authors also investigated the ^1H nmr spectra of hydride complexes of the type $[C\acute{p}ML_2H_3X]$, (M = Ta, Nb; L = PMe_3, $P(OMe)_3$; L_2 = dppe ; X = Cl, H).

The metal atoms in these complexes are all 8 or 9 coordinate (considering the Cṕ ring as occupying 3 coordination sites on the metal). They were found to be highly fluxional at room temperature, the spectra were thus run at low temperatures in order to assign coordination geometries to these complexes.

1.2.3 Pentamethylcyclopentadienyl complexes of chromium, molybdenum and tungsten.

Simple thermal reactions of the metal carbonyls $M(CO)_6$ (M = Mo, W) with pentamethylcyclopentadiene; or with acetylpentamethylcyclopentadiene in the case of M = Cr, Mo ; gave the complexes $[C\bar{p}M(CO)_2]_2$, (M = Cr, Mo, W) , each containing a formal metal-metal triple bond. [16]

$[C\bar{p}M(CO)_2]_2$ M = Cr (V)

M = Mo (VI)

M = W (VII)

These complexes were of considerable interest, firstly, since they were different from the complexes formed with cyclopentadiene under similar conditions, viz $[CpM(CO)_3]_2$ (M = Cr, Mo, W) (VIII) and secondly, because these were the first complexes containing a cyclopentadienyl ring to have been shown to possess a metal-metal multiple bond. The analogous unsubstituted cyclopentadienyl complexes, viz $[CpM(CO)_2]_2$ (M = Cr, Mo, W) were prepared from (VIII) above. [17]

Direct experimental evidence for the metal-metal triple bonds in (V) and (VI) was obtained by X-ray crystallography. [18,19]

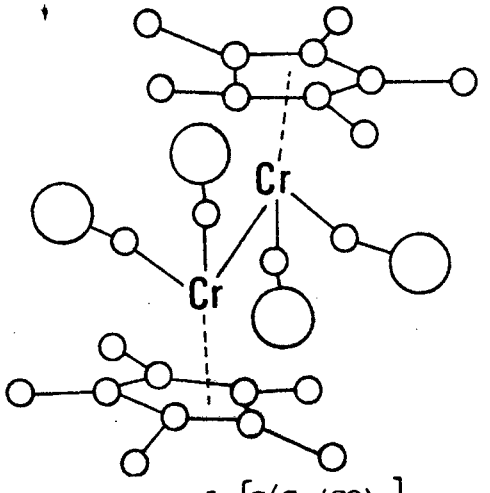


Fig 1.2.6 : X-ray crystal structure of $[C\bar{p}Cr(CO)_2]_2$

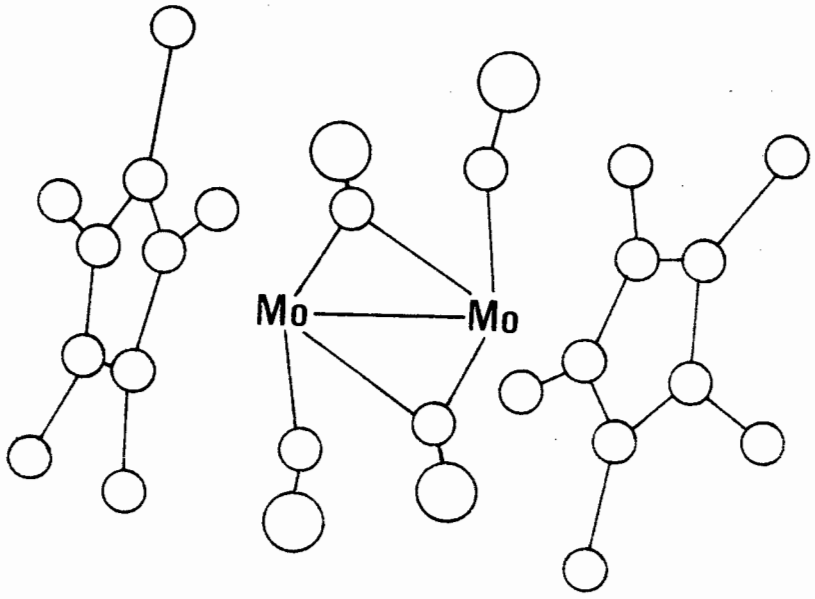


Fig 1.2.7 : X-Ray crystal structure of $[C\bar{p}Mo(CO)_2]_2$

The X-ray crystal structure of (V)[18] (see fig 1.2.6) revealed the complex as having a metal-metal triple bond, as evidenced by the fact that the Cr-Cr bond distance is 2.276 Å, which is much shorter than that found in metallic Cr (2.50 Å). The methyl groups of the $C\bar{p}$ ligands are bent away from the mean plane of the ring, and are *exo* with respect to Cr. These authors reported that attempts to saturate the metal-metal triple bond with σ or π donors such as PPh_3 or Ph_2C_2 were uncucessful. Thus the large, bulky $C\bar{p}$ rings made penetration by large molecules impossible; however, penetration by small molecules e.g. NO was possible to give the product $C\bar{p}Cr(CO)_2NO$.

King and Efrarty[16] investigated the reactivity of the Cr-Cr triple bond in (V), however none of the reactions could be interpreted in terms of being an addition to the metal-metal triple bond.

The reactivity of the complex $[CpMo(CO)_2]_2$ (IX) towards small molecules was investigated,[17] and the results compared with those obtained for (VI). For example, on reaction with I_2, (IX) gave as product $[CpMo(CO)_2I]_2$; whereas the only identifiable product obtained from the reaction of (VI) with iodine under

similar conditions was $[C\acute{p}Mo(CO)_3I]$. Thus the unsubstituted cyclopentadienyl complex (IX) appeared to be more reactive towards additions to the molybdenum-molybdenum triple bond than did (VI). This was attributed mainly to steric effects, i.e. ten methyl groups on the cyclopentadienyl rings of complex (VI) may hinder access of attacking reagents to the metal-metal triple bond.

Dahl and Huang[19] compared the crystal and molecular structures of the triple M-M bonded metal dimers $[C\acute{p}M(CO)_2]_2$ and $[CpM(CO)_2]_2$, (M = Cr, Mo). $[C\acute{p}Mo(CO)_2]_2$ consists of two identical $C\acute{p}Mo(CO)$ moieties linked by two carbonyl bridges and direct metal-metal bonding. The Mo-Mo bond distance of 2.488 Å was found to be 0.04 Å shorter than that obtained for the corresponding Cp complex, and much shorter that that obtained for the complex $[CpMo(CO)_3]_2$ which contains a formal single metal-metal bond.

This trend in bond lengths on going from $[C\acute{p}Mo(CO)_2]_2$ to $[CpMo(CO)_2]_2$ is paralled in the corresponding Cr dimers, viz $[C\acute{p}Cr(CO)_2]_2$ and $[CpCr(CO)_2]_2$.

Marked differences in the geometries of (VI) and (IX) were observed. Thus in (IX) the Cp rings are orientated to give a linear Cp(c)-Mo-Mo-Cp(ć) axis, (c,ć = centroid of ring), and all four carbonyl ligands are equivalently bent back over the Mo-Mo bond to form linear type asymmetric bridges. In (VI), however, the two centrosymmetrically related Cṕ rings are non-linear with the Mo-Mo axis, and the degree of semi-bridging is markedly different for the two pairs of carbonyl ligands in (VI) and (IX) respectively. These differences were attributed to steric effects, which gave rise to different geometries.

These authors thus concluded that the differences in reactivity patterns associated with the dimers $[C\acute{p}M(CO)_2]_2$ and $[CpM(CO)_2]_2$, (M = Cr, Mo), could not be attributed

only to the methyl groups on the pentamethylcyclopentadienyl ring blocking access to the metal-metal triple bond, but also to the energies associated with the different geometries observed for these species.

The metallocenes, $C\bar{p}_2Mo$ and $[Cp_2Mo]_n$ were found to display markedly different physical and chemical properties.[20] Thus $C\bar{p}_2Mo$ is monomeric , soluble in organic solvents and reacts readily with CO and H_2; whereas the insoluble, polymeric unsubstituted cyclopentadienyl analogue, $[Cp_2Mo]_n$ is relatively inert to $H_2$and CO.

Photolysis of the hydride complexes $[C\bar{p}M(CO)_3H]$ (M = Cr, Mo, W) and $[CpM(CO)_3H]$ (M = Cr, W) showed marked differences for the corresponding $C\bar{p}$ and Cp species.[21] (see table 1.1)

Table 1.1

A SUMMARY OF THE PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF THE HYDRIDE COMPLEXES $[(\eta\text{-}C_5R_5M(CO)_3H]$ (R = H, Me ; M = Cr, Mo, W)

HYDRIDE COMPLEX	PRODUCTS OBTAINED	REACTION TIME
M = Cr ; R = H	$[CpCr(CO)_2]_2$ (CO and H_2 evolved)	20 minutes
M = Mo ; R = H	$[CpMo(CO)_3]_2$ $[CpMo(CO)_2]_2$ (trace)	3 hours
M = W ; R = H	$[CpW(CO)_2H]_2$ (major) + $[CpW(CO)_2]_2$ $[CpW(CO)_3]_2$ (trace)	5 hours (80% conversion)

Table 1.1 (cont.)

HYDRIDE COMPLEX	PRODUCTS OBTAINED	REACTION TIME
M = Cr ; R = Me	$[C\bar{p}Cr(CO)_2]_2$	20 minutes
M = W ; R = Me	$[C\bar{p}W(CO)_2H]_2$	5 hours

The complexes $[CpW(CO)_2H]_2$ and $[C\bar{p}W(CO)_2H]_2$ contain a metal-metal double bond. Irradiation of $[C\bar{p}Mo(CO)_2]_2$ in the presence of hydrogen gas produced the hydride complex $[C\bar{p}Mo(CO)_2H]_2$.

The pentamethylcyclopentadienyl tungsten complex (VII) has been shown to react with diazo complexes, yielding μ-alkylidene complexes.[22] The reaction was shown to go via an η^2 intermediate with the diazo ligand bridging the metal-metal bond. The final product obtained contains a W-W double bond.

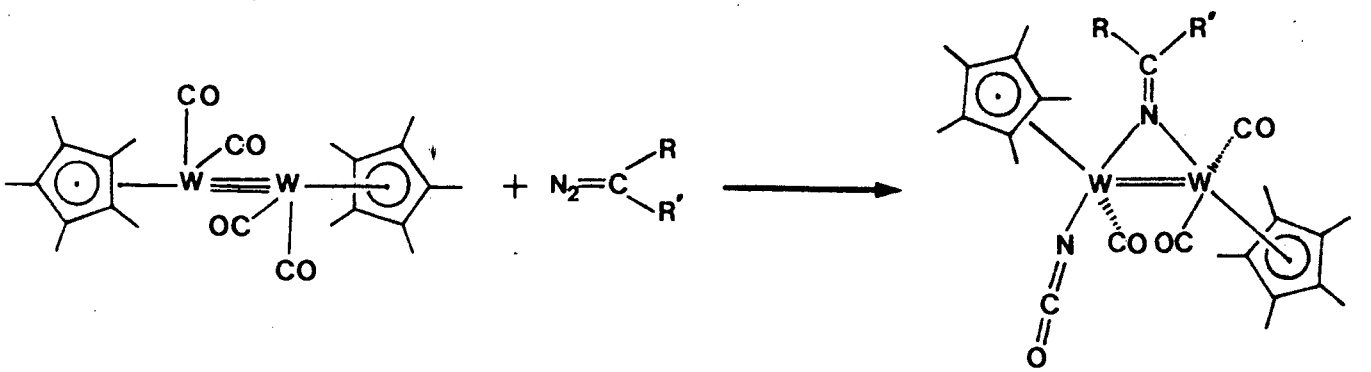


Fig 1.2.8 : Reactions of $[C\bar{p}W(CO)_2]_2$ with diazo compounds.

The products obtained from the reactions of the Mo dimer (VI) with diazo compounds could not be considered as resulting from an addition to the Mo-Mo triple bond. Instead products of the form described in fig 1.2.9 were isolated.

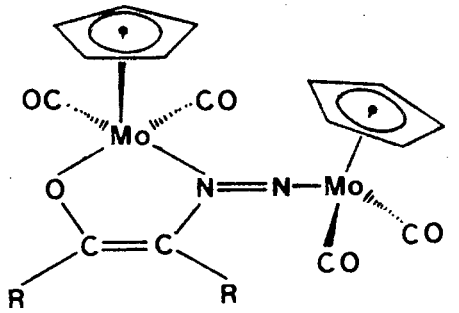


Fig 1.2.9 : Products derived from the reactions of $[CpMo(CO)_2]_2$ with diazo compounds.

Petrigani and Alper[23] investigated the reactions of α-haloketones with the complexes $[(\eta\text{-}RC_5H_4)Mo(CO)_2]_2$ (R = H, Me) and $[CpMo(CO)_2]_2$; all of which contain a Mo-Mo triple bond.

Thus the reaction of $[(\eta\text{-}RC_5H_4)Mo(CO)_2]_2$ with α-haloketones gave $[(\eta\text{-}RC_5H_4)Mo(CO)_3X]$ (X = Cl, Br, I), according to the scheme described below.

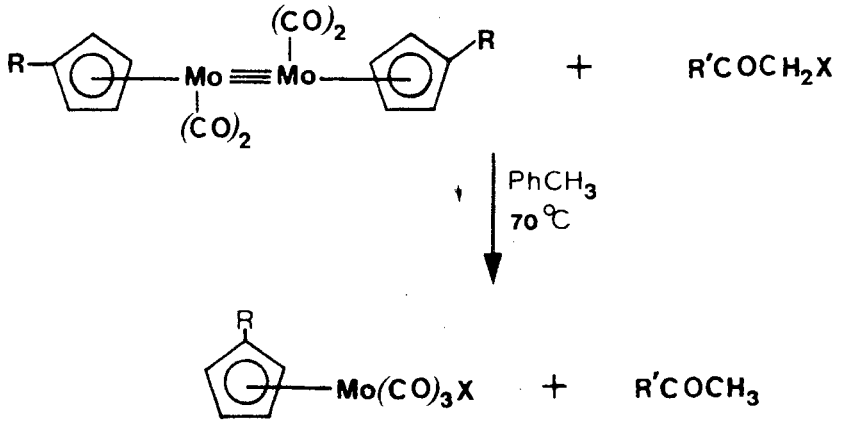
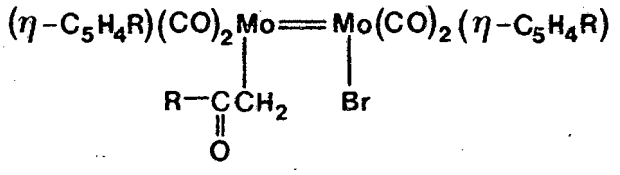


Fig 1.2.10 : Reaction of $[(\eta\text{-}RC_5H_4)Mo(CO)_2]_2$ with α-haloketones.

The yields of $R'COCH_3$ and $[(\eta\text{-}RC_5H_4)Mo(CO)_3X]$ were very similar, ranging from

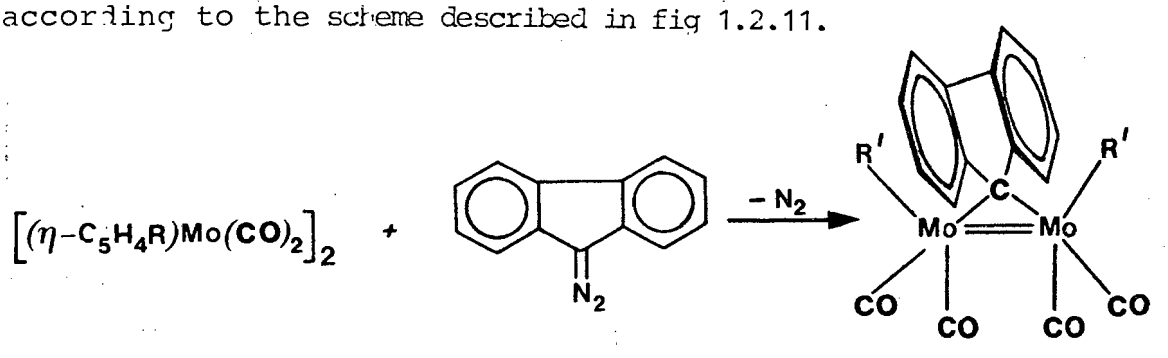
25% to 40%. No reaction occurred when the complex $[(\eta\text{-}RC_5H_4)Mo(CO)_3]_2$ containing a single Mo-Mo bond was used.

In order to determine the source of hydrogen for the product $R'COCH_3$, and also why the tricarbonyl Mo complex $[(\eta\text{-}RC_5H_4)Mo(CO)_3X]$ was produced, similar reactions were performed using the permethylated analogue, $[CpMo(CO)_2]_2$. These results clearly indicated that the hydrogen in $R'COCH_3$ arises from a second molecule of the α-haloketone, and not from the cyclopentadienyl ring. These reactions were proposed to involve as intermediates, complexes which involved additions to the Mo-Mo triple bond, such as :



(These were however, not isolated.)

Dimetallacyclopropenes, viz $[(\eta\text{-}RC_5H_4)Mo_2(CO)_4(\mu\text{-}C_{13}H_{18})]$ (R = H, Me) were isolated from the reaction of $[(\eta\text{-}RC_5H_4)Mo(CO)_2]_2$ with 9-diazoflourene according to the scheme described in fig 1.2.11.



$R' = C_5H_5$, $C_5H_4\text{-}CH_3$

Fig 1.2.11 : Reaction of $[(\eta\text{-}RC_5H_4)Mo(CO)_2]_2$ with 9-diazoflourene.

The product contains two coordinated phenyl groups "tied back" in order to prevent

complexation of the phenyl groups.[24] The structure was confirmed X-ray crystallographically for the product where R = CH_3. No evidence for an intermediate diazo complex was obtained.

1.2.4 Pentamethylcyclopentadienyl complexes of manganese and rhenium.

The complexes $[C\bar{p}M(CO)_3]$ (M = Mn, Re) were prepared from the reactions of the appropriate metal carbonyl $M_2(CO)_{10}$ (M = Mn, Re) with C_5Me_5H ; or using acetylpentamethylcyclopentadiene as starting material. The products were found to be completely analogous with their unsubstituted cyclopentadienyl analogues.[15,16]

Gladysz *et al* reported the synthesis and X-ray crystal structure of $[C\bar{p}Re(NO)(=CH_2)L]^+ \ PF_6^-$ (L = PPh_3, $P(OPh)_3$).[25]

The complex was prepared in the following manner :

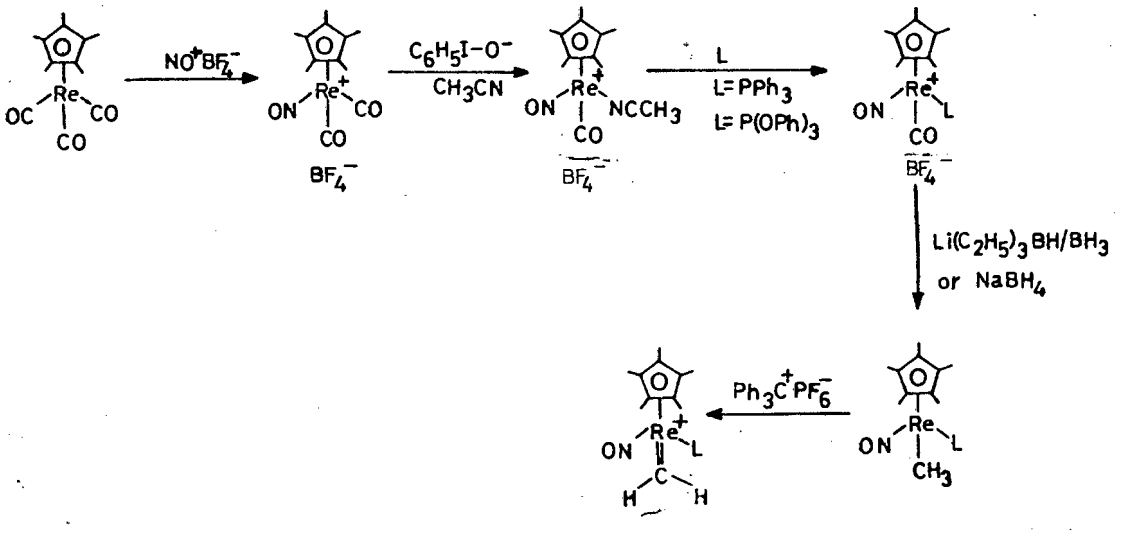


Fig 1.2.12 : Preparation of $[C\bar{p}Re(NO)L(=CH_2)]^+ \ PF_6^-$

These authors found this complex to be more stable than the cyclopentadienyl analogue, viz $[CpRe(NO)(PPh_3)(=CH_2)]^+ \ PF_6^-$, which rapidly self-coupled to give the ethylene complex, $[CpRe(NO)(PPh_3)(CH_2=CH_2)]^+ \ PF_6^-$ at room temperature. The $C\bar{p}$ complex was found to be stable to $\geq 100°C$, and could thus be studied.

These authors[25] attributed the stability of this complex to the following factors :

(a) Third row transition metals generally form stronger metal-ligand bonds than do first and second row transition metals.

(b) The complexes $[C\bar{p}Re(NO)L(=CH_2)]^+ PF_6^-$ (L = PPh_3, $P(OPh)_3$) contain two good donor ligands that are also bulky, viz C_5Me_5 and PPh_3 or $P(OPh)_3$. These ligands tend to enhance the basicity of rhenium, and hence strengthen the Re to CH_2 bond.

(c) The $C\bar{p}$ ligand sterically inhibits the facile decomposition pathway observed for the Cp complex, i.e. $[CpRe(NO)(PPh_3)(=CH_2)]^+$ decomposes to the ethylene complex.

Graham and Sweet[26] found similar trends in the Re formyl complexes. For example, $[C\bar{p}Re(CO)(NO)(CHO)]$ is a stable solid to 70°C, whereas the Cp homologue is only stable to -10°C. Thus the $C\bar{p}$ ligand dramatically enhances the stabilities of these Re complexes.

1.2.5 Pentamethylcyclopentadienyl complexes of iron, ruthenium and osmium.

$[C\bar{p}Fe(CO)_2]_2$ (X) was prepared from the reaction of C_5Me_5H with $Fe(CO)_5$, or from the reaction of $Fe_2(CO)_9$ with acetylpentamethylcyclopentadiene in a high boiling point hydrocarbon solvent.[15,16]

(X) was found to be completely analogous in structure to the unsubstituted cyclopentadienyl anaogue, $[CpFe(CO)_2]_2$. However, reduction of $[CpFe(CO)_2]_2$ with Na/Hg amalgam proceeds readily at room temperature, whereas the reduction of (X) under the same conditions requires a much longer time, and the product formed

$[C\bar{p}Fe(CO)_2]^-$ is very susceptible to air oxidation.

Astruc and Catheline[27] report that the reduction is more easily carried out using a potassium mirror. However, these authors state that the reduction cannot be done using a Na/Hg amalgam as (X) has a very negative reduction potential ($E_{\frac{1}{2}}$ = -1.80 V/SCE in dimethoxyethane and $Bu_4N^+ Br^-$). This value is 0.36 V more negative than that for $[CpFe(CO)_2]_2$. However, this reduction has been performed by King *et al* [28] who report no difficulty. (see chapter 2.3)

$[CpFe(CO)_2]_2$ and $[C\bar{p}Fe(CO)_2]_2$ have been used as catalysts for reactions involving the replacement of ligands such as CO in transition metal complexes by group V donor ligands.[29,30] Thus the reaction of $Mn_2(CO)_{10}$ with PPh_3 requires 7 hours for completion, or photochemical conditions, in the absence of a catalyst, to give the product $[Mn(CO)_4(PPh_3)]_2$. In the presence of $[CpFe(CO)_2]_2$ however, the reaction proceeds to 80% completion in 90 minutes, and in 180 minutes when the catalyst is (X).

Teller and Williams[31] investigated the crystal and molecular structure of $[C\bar{p}Fe(CO)_2]_2$, and compared it with that of the non-methylated analogue, $[CpFe(CO)_2]_2$.

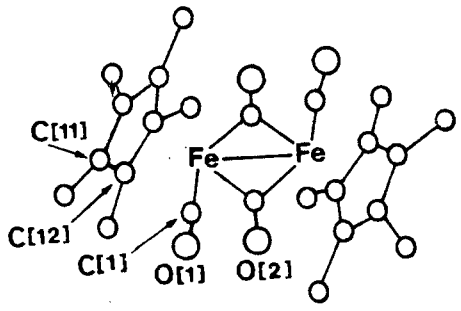


Fig 1.2.13 ; X-ray crystal structure of $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$.

The complex (X) was found to be isostructural with the non-methylated analogue

$[CpFe(CO)_2]_2$ (XI) . (X) was found to have a slightly longer Fe-Fe bond distance, this was, however, not significant, as the two studies were conducted at different temperatures. One important difference between the two structures, was that in (X), the terminal carbonyl ligand C1-O1 is eclipsed with respect to C11 of the cyclopentadienyl ring, whereas in (XI), the terminal carbonyl ligand is staggered with respect to C11 of the ring. (These structures are further discussed in chapter 4.3)

Bailey *et al* [32] compared the X-ray crystal structures and reactivity patterns of the complexes $[(\eta\text{-}C_5Me_4Et)Ru(CO)_2Br]$ (XII) and $[CpRu(CO)_2Br]$ (XIII).

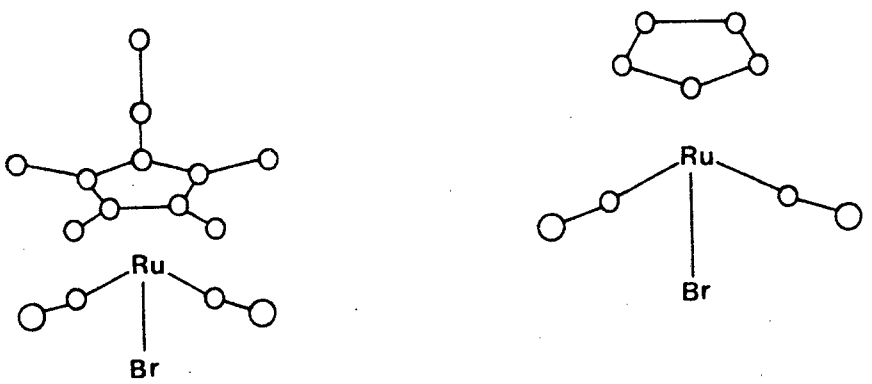


Fig 1.2.14 : X-ray crystal structures of $[CpRu(CO)_2Br]$ and $[(\eta\text{-}C_5Me_4Et)Ru(CO)_2Br]$.

Complexes (XII) and (XIII) show markedly different behaviour on reaction with bromine. Thus (XII) is oxidised by bromine to $[(\eta\text{-}C_5Me_4Et)Ru(CO)Br_3]$, formally a Ru(IV) complex, whereas (XIII) is unaffected by bromine under similar conditions. The kinetics of the reactions of (XII) and (XIII) with $P(OMe)_3$ in diglyme were investigated, (XII) was found to react eighteen times faster than (XIII) under the same conditions.

The X-ray crystal structures of (XII) and (XIII) revealed the $Ru(CO)_2Br$ fragments to be very similar, and having conventional geometries, the Ru-C (carbonyl) bond distances were very similar, despite the differences observed in the carbonyl

IR stretching frequencies. Compound (XIII) possesses a planar Cp ring, the substituted cyclopentadienyl ring in (XII), however, exhibits significant deviations from planarity. Despite the fact that the substituted cyclopentadienyl ring in (XII) would be expected to be more electron donating than the Cp ring in (XIII), little, if any, evidence was seen in this X-ray crystallographic comparison.

Reduction of $[CpRu(CO)_3]^+ BF_4^-$ with excess $NaBH_3CN$ in methanol gave the hydroxymethyl complex $[CpRu(CO)_2CH_2OH]$[33] as the major product isolated, the reaction went via a formyl complex, $[CpRu(CO)_2(CHO)]$ according to the scheme described in fig 1.2.15.

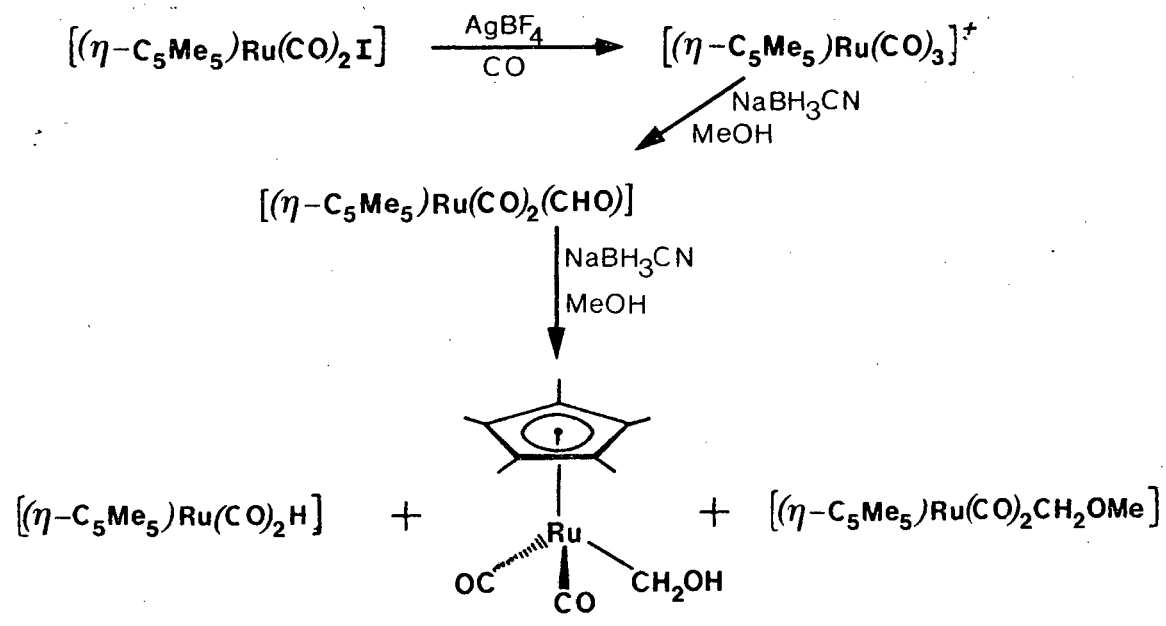


Fig 1.2.15 : The reduction of $[CpRu(CO)_3]^+ BF_4^-$.

$[CpRu(CO)_2CH_2OH]$ is the first hydroxymethyl complex of Ru to be isolated and characterised. This is of great interest, since the hydrogenation of carbon monoxide has been shown to be effected by Ru compounds.

Graham *et al* [34] prepared the osmium hydride complexes $[CpOs(CO)_2H]$ (XIV) and $[CpOs(CO)_2H]$ (XV) according to the following scheme :

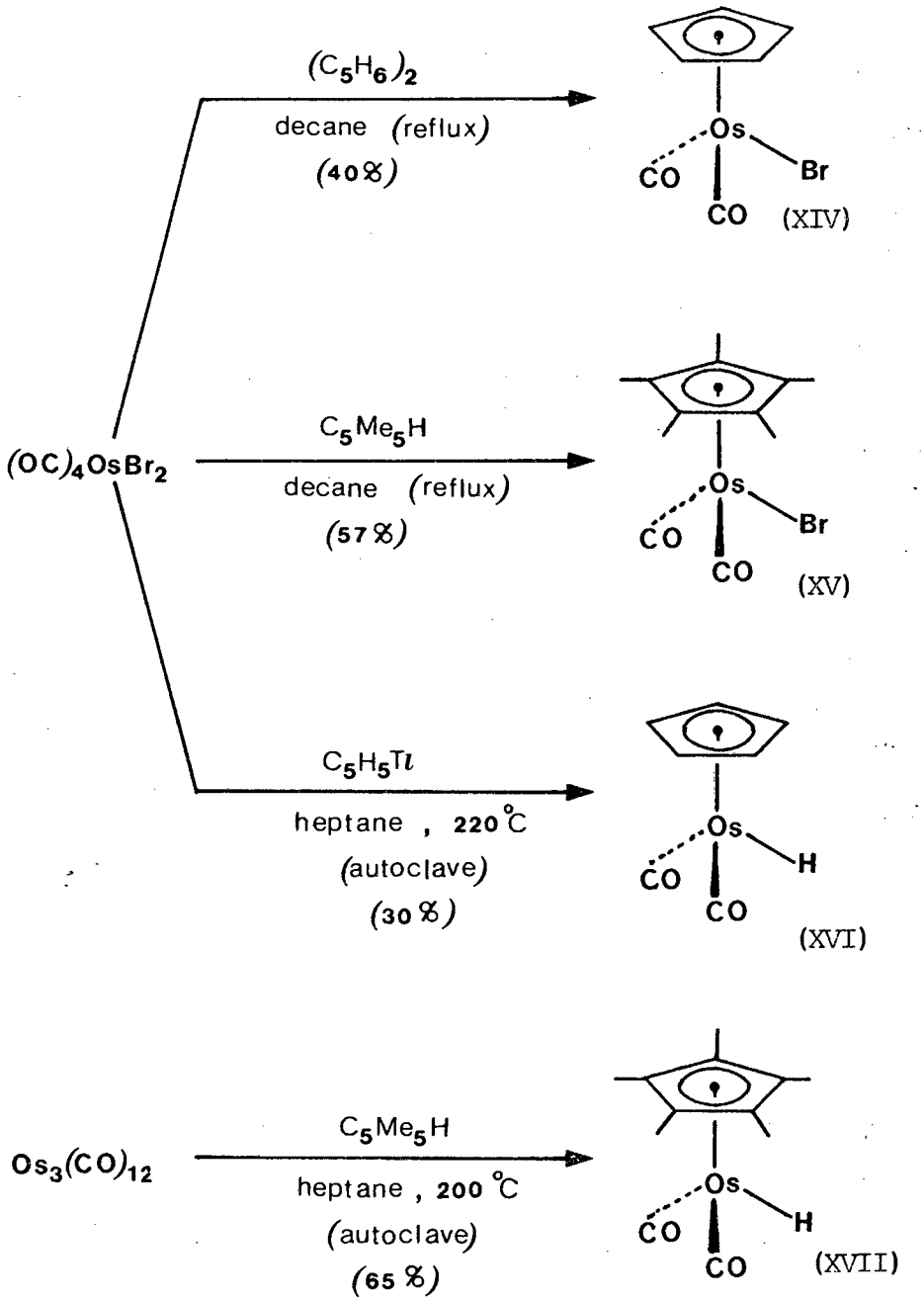
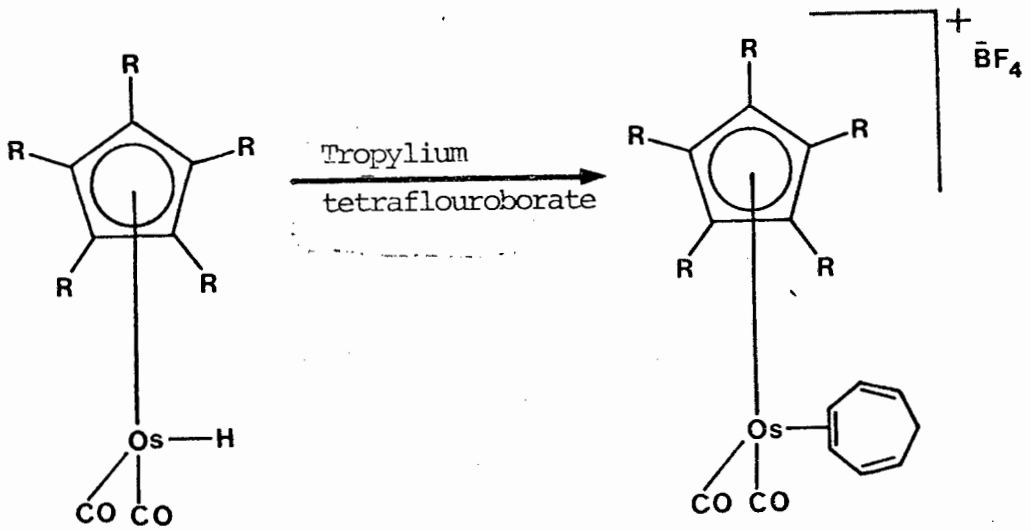


Fig 1.2.16 : Preparation of $[C\bar{p}Os(CO)_2H]$ and $[C\bar{p}Os(CO)_2H]$

these authors prepared a range of new osmium complexes, $[(\eta\text{-}C_5R_5)Os(CO)_2X]$, (R = H, Me; X = halogen), and $[(\eta\text{-}C_5R_5)Os(CO)_2L]^+$ (L = CH_3CN, THF, H_2O, CO).

For the complexes $[CpOs(CO)_2I]$ and $[C\bar{p}Os(CO)_2I]$ the $C\bar{p}$ compound was less reactive towards nucleophilic attack than the Cp analogue, probably as a result of the increased electron density on Os in the case of the $C\bar{p}$ complex; for example, the reactions of these complexes with the organolithium reagents, RLi, R = alkyl or aryl proceed faster for the Cp complex.



(XVI) R = H
(XVII) R = CH_3

(XVIII) R = H
(XIX) R = CH_3

Fig 1.2.17 : Reactions of $[CpOs(CO)_2H]$ and $C\bar{p}Os(CO)_2H$ with tropylium tetraflouroborate.

For complex (XVI) (R = H), the reaction requires six days to go to completion, whereas for (XVII) (R = Me) , the reaction goes to completion in only 5 hours. These authors attribute this phenomenon to the increased electron density on Os in (XVII), thus making the hydride ligand more "hydridic" in nature.

Complete deprotonation of (XVIII) is effected by by excess triethylamine, whereas (XIX) requires the more basic diethylamine for complete deprotonation to occur. The relative acidities of the η^2-C_7H_8 ligands in (XVIII) and (XIX) accords with the view that the $C\bar{p}$ ligand is more electron donating than the Cp ligand.

1.2.6 Pentamethylcyclopentadienyl complexes of cobalt, rhodium and iridium.

$[CpCo(CO)_2]$ was prepared from the reaction of $Co_2(CO)_8$ and acetylpentamethylcyclopentadiene,[17] the X-ray structure of this complex was later reported by Byers and Dahl.[35]

The first methylene bridged complex of Co, viz $[(C\bar{p}Co)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ was isolated from the reaction of cobaltous chloride with lithium pentamethylcyclopentadienide in THF.[36] These authors were, in fact, attempting to prepare bispentamethylcyclopentadienylcobalt from this reaction. Analytical data suggested that the product obtained from this reaction was not the desired product, but instead the first binuclear μ-methylene cobalt complex. The product was thought to arise from the lithium enolate of acetaldehyde ($Li^+CH_2CHO^-$, LEA) which was generated from the reaction of the THF solvent with n-butyllithium. This hypothesis was tested by carrying out the reaction using a stoichiometric amount of n-butyllithium, the the product so obtained was tentatively identified as $[C\bar{p}Co(\mu\text{-}Cl)]_2$. In contrast, when the reaction was performed using a stoichiometric amount of n-butyllithium and one equivalent of pre-formed LEA, the μ-methylene complex was isolated.

An X-ray crystal structure of $[(C\bar{p}Co)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ verified the proposed structure, and the metal-metal bond distance was found to be that of a Co-Co double bond.

Robbins *et al* [38] prepared a number of mixed metal clusters of cobalt from the reactions of $[C\bar{p}Co(\mu\text{-}CO)]_2$, which contains a metal-metal double bond with various species M and M' , (M = $Cr(\eta\text{-}C_6H_5Me)$, $Fe(\eta\text{-}C_4H_4)$, $Mn(\eta\text{-}C_5H_4Me$; M' = $Fe(CO)_3$, $Co(\eta\text{-}C_5H_4Me)$), as shown in fig 1.2.18.

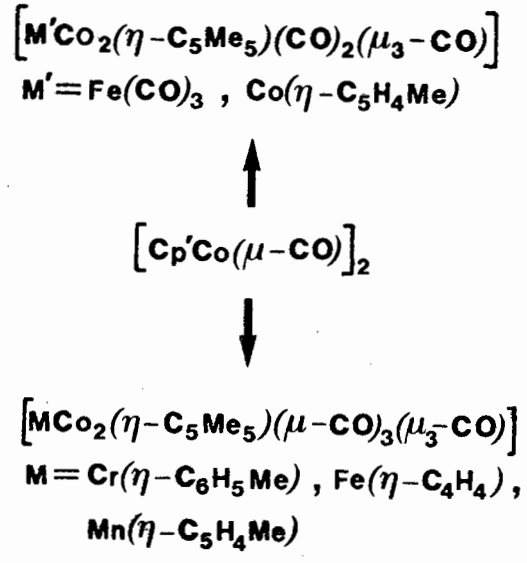


Fig 1.2.18 : Mixed metal clusters of Co.

The species M and M' were generated photochemically.

The series $[MCo_2(\eta\text{-}C_5Me_5)(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ contain one triply bridging and three doubly bridging carbonyl ligands, whilst the series $[M'Co_2(\eta\text{-}C_5Me_5)(\mu\text{-}CO)_2(\mu_3\text{-}CO)]$ contain one triply bridging and two doubly bridging carbonyl ligands. These electronically equivalent clusters, which were photogenerated under relatively mild conditions, were not able to be obtained from the corresponding thermal reactions.

The cluster $[Co_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_4Me)(\mu\text{-}CO)_2(\mu_3\text{-}CO)]$ was found to have a solid state structure completely analogous to that of the non-methylated cyclopentadienyl analogue, viz $[(\eta\text{-}C_5H_5)_2Co_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)]$.

The only difference between the two structures is that one of the Co-Co bonds in the permethylated derivative is 0.04 Å longer than in the unsubstituted cyclopentadienyl species. This lengthening of the Co-Co bond was attributed to greater steric effects in the permethylated complex.

The first pentamethylcyclopentadienyl rhodium complex, $[C\acute{p}RhCl_2]_2$ was shown by Kang and Maitlis[39] to result from the reaction of hydrated $RhCl_3$ with hexamethyl-Dewar benzene (hexamethyl bicyclo (2.2.0) hexadiene) in methanol.

A number of other Cp rhodium complexes were also characterised [39,40] viz, $[C\acute{p}RhX_2]_2$ (X = Br, I); $[C\acute{p}Rh(OCOR)_2.H_2O]$ (R = CH_3, CF_3) ; $[C\acute{p}Rh(diene)]$, (diene = 1,5 cyclo-octadiene, dicyclopentadiene etc.). Several cationic species containing bridging ligands such as $[(C\acute{p}Rh)_2(\mu\text{-}X)_3]^+$, (X = Cl, OH) were also characterised.

Several of the above complexes were shown to have catalytic activity, for example,

$[C\acute{p}Rh(1,3\ cyclohexadiene)]$ catalysed the diproportionation of 1,3 cyclohexadiene to cyclohexane and benzene. The complexes $[C\acute{p}RhX_2]_2$ (X = Cl, CO_2CH_3, CO_2CF_3) catalysed the hydrogenation of olefins under ambient conditions of temperature and pressure. The cyclopentadienyl analogues of the above complexes exhibited little or no catalytic activity. This is probably due to the fact that whereas the complexes $[C\acute{p}RhX_2]_2$ (X = halogen) were found to be stable crystalline solids which survived acidic, basic, oxidising and reducing conditions, the unsubstituted cyclopentadienyl analogues, viz $[CpRhX_2]_n$ are amorphous, probably polymeric, and are insoluble in all but the most powerfully coordinating solvents. The Cp-Rh bond is easily cleaved by a number of reagents, including hydrogen, which do not affect the Cṕ-Rh bond.

Various pentamethyl cyclopentadienyl complexes of Ir have been prepared, $[C\acute{p}Ir(CO)_2]$ was found to undergo reaction reaction with Grignard reagents such as CH_3I, to to give products of the type shown in fig 1.2.19 :

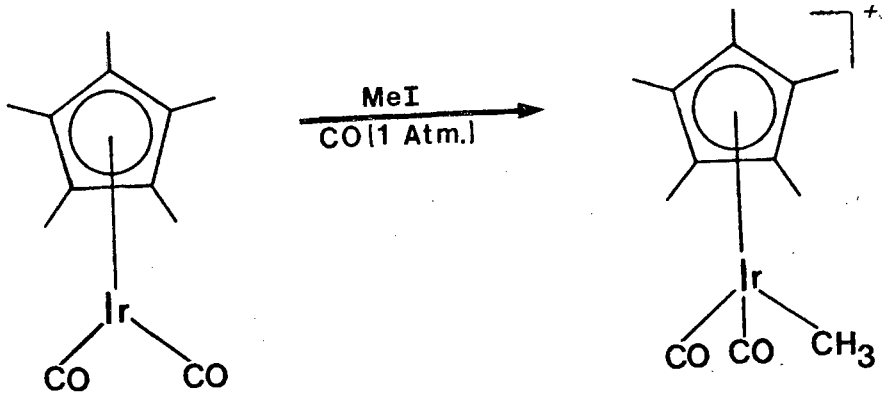


Fig 1.2.19 : Reaction of $[C\acute{p}Ir(CO)_2]$ with MeI.

The complexes $[C\acute{p}M(CO)_2]$ (M = Rh, Ir) were reported to be stable crystalline solids, in contrast to the oily, unstable Cp analogue.[40]

Kang and Maitlis[41] reported a number of iridium μ-hydrido cations, viz

$[(C\bar{p}Ir)_2(\mu\text{-}H)_3]^+$, $[(C\bar{p}Ir)_2(\mu\text{-}H)(\mu\text{-}X)_2]^+$, and $[(C\bar{p}Ir)_2(\mu\text{-}H)_2(\mu\text{-}X)]^+$, (X = CO_2CF_3, CO_2CH_3). The analogous Rh complexes , however, could not be isolated. The rhodium dimer, $[C\bar{p}Rh(\mu\text{-}CO)]_2$, which contains a Rh-Rh double bond, reacts with diazo compounds N_2CRR', to give the μ-alkylidene complexes, $[\{C\bar{p}Rh(CO)\}_2(\mu\text{-}CRR')]$.[42]

The spectral characteristics of the μ-alkylidene complexes were in close agreement with those of the previously characterised Cp analogues. These authors [42] reported the Cp̄ complexes to be moderately air sensitive and to decompose immediately on silica gel. This is in contrast to the Cp complexes which are air stable and may be chromatographed. The complex $[\{C\bar{p}Rh(CO)\}_2(\mu\text{-}CPh_2)]$ decarbonylated readily to give the product $[\{C\bar{p}Rh\}_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$, in the case of the cyclopentadienyl analogue, however, the only product derived from the decarbonylation was $[CpRh(\mu\text{-}CPh_2)]_2$.

Hermann *et al* [43] prepared a μ-methylene Rh complex $[\{C\bar{p}Rh(CO)\}_2(\mu\text{-}CH_2)]$ from the reaction of $[C\bar{p}Rh(\mu\text{-}CO)]_2$ with CH_2N_2 , thereby causing the insertion of methylene into a metal-metal bond, a reaction reported only for platinum previously.[44] previously.[44] The μ-methylene complex was reported to be thermally and photochemically very stable. The complex was treated with SO_2 to yield a co-ordinated sulphene complex, thus converting a 3-membered ring to a 4-membered ring.[45]

See fig 1.2.20.

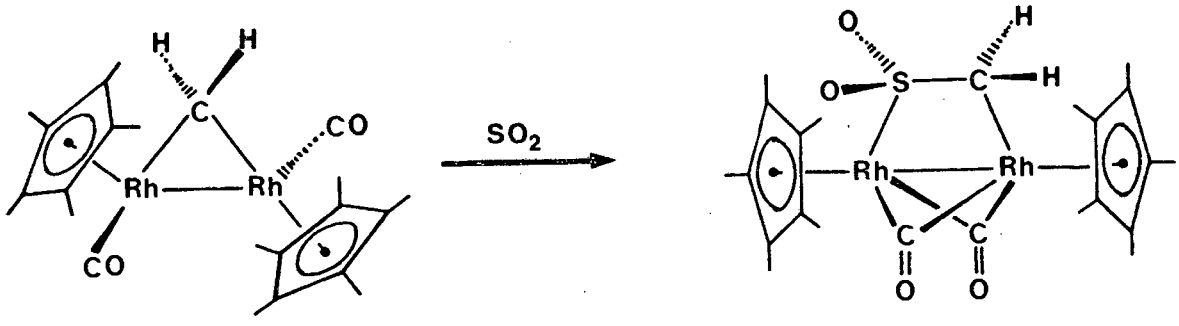


Fig 1.2.20 : Reaction of $[\{C\bar{p}Rh(CO)\}_2(\mu\text{-}CH_2)]$ with SO_2 to give a co-ordinated sulphene product.

Dickson *et al* [46] investigated the reactions of alkynes with $[C\bar{p}Rh(\mu\text{-}CO)]_2$, and determined the X-ray crystal structure of one of the products obtained, viz $[C\bar{p}_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}C\text{-}(O)C_2(CF_3)_2]$. The molecule was fluxional with the bridging $C(CF_3):C(CF_3):CO$ unit displaying a different geometry from that observed in related CpRh and $C\bar{p}Rh$ complexes.

Stone *et al* [47] investigated the reactions of $[C\bar{p}Rh(\mu\text{-}CO)]_2$ with diazoalkanes and various zerovalent platinum complexes. Clusters such as $[PtRh_2(\mu\text{-}CO)_2(PPh_3)C\bar{p}_2]$ were isolated.

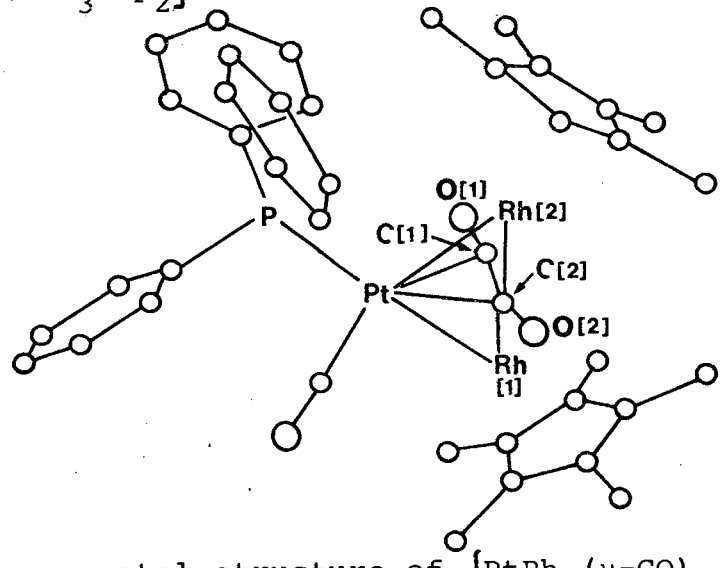


Fig 1.2.21 : X-ray crystal structure of $[PtRh_2(\mu\text{-}CO)_2(PPh_3)C\bar{p}_2]$.

The X-ray crystal structure of this complex revealed the $C\bar{p}$ and PPh_3 ligands to be staggered with respect to one another, the methyl substituents on the $C\bar{p}$ rings closest to PPh_3 showed the greatest deviation from the mean plane of the $C\bar{p}$ rings. The most dramatic effect of the steric interaction between PPh_3 and the $C\bar{p}$ ligands was shown by the lengthening of the $Pt\text{-}Rh_2$ bond, (2.691 Å).

Stone *et al* [48-50] have prepared a number of $C\bar{p}$ rhodium clusters,

including $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)C\bar{p}_2]^+ BF_4^-$, which was prepared by protonation of the cluster $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)C\bar{p}_2]$[48]; $[PtRh_4(\mu\text{-}CO)_4C\bar{p}_4]$[49] and also $[MnRh(\mu\text{-}CO)_2(CO)_2C\bar{p}Cp]$[50] which was prepared by heating $[C\bar{p}Rh(\mu\text{-}CO)]_2$ with $[CpMn(CO)_2THF]$.

Maitlis *et al* [51] determined the X-ray crystal stucture of the complex $[(C\bar{p}Rh)_3Cl_5np_3]^+ PF_6^-.\frac{1}{2}C_3H_8O$, ($np_3$ = *tris* (2-diphenylphosphinoethylamine).

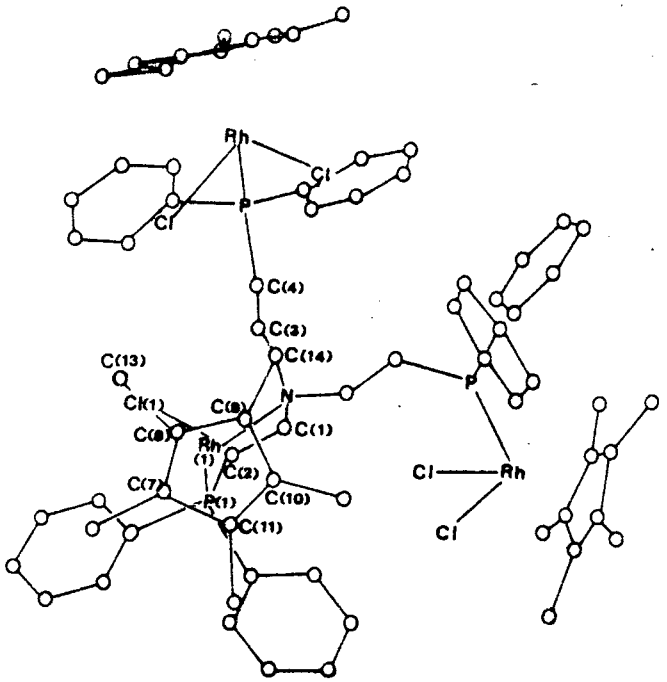


Fig 1.2.22 : X-ray crystal structure of $[(C\bar{p}Rh)_3Cl_5np_3]^+ PF_6^-.\frac{1}{2}C_3H_8O$.

The complex was prepared from the reaction of $[C\bar{p}RhCl_2]_2$ with the tetradentate ligand np_3. The complex cation of the above structure contains two $C\bar{p}RhCl_2$ units, each bonded through Rh to one P atom of the np_3 ligand, and a $C\bar{p}RhCl$ group in which Rh is bound to the third P atom and the nitrogen atom of the np_3 ligand. The two $PRhCl_2C\bar{p}$ units are not symmetrically arranged about the plane passing through the N, P and Rh atoms of the $NCH_2CH_2PRhC\bar{p}Cl$ part of the complex cation. This inequivalence was thought to be caused by the bulkiness of the

C̄pRh groups.

Basolo and Rereck [52] investigated the reactions of the species $C\bar{p}M(CO)_2$ (M = Co, Rh) with phosphines, phosphites and isocyanides. For M = Rh, the reaction was found to be first order with respect to the metal complex, and first order with respect to the incoming nucleophile. The rate is strongly dependent on the size of the incoming nucleophile. For the analogous Cp complex, however, the rate was found to be dependent on the concentration of the nucleophile only. The rate of reaction of $C\bar{p}Rh(CO)_2$ with nucleophiles was found to be of the order of 10^2 times faster than that observed for the reactions with the analogous Cp complex. This was attributed to the extra electron density on the metal on the C̄p complex, as compared with that on the metal in the Cp complex. In the case of the reaction of $[C\bar{p}Rh(CO)_2]$ with nucleophiles, the dependence of the rate on the size of the incoming nucleophile was attributed to steric effects, the large bulky, C̄p ligand prevents access of large molecules to the metal atom.

Graham *et al* [53] reported the activation of methane by $[C\bar{p}Ir(CO)_2]$. Thus a solution of this complex in perflourohexane under 8 atmospheres of methane was irradiated for 16 hours at room temperature, the complex $[C\bar{p}Ir(CO)(H)(CH_3)]$ was isolated. The unsubstituted cyclopentadienyl complex $[CpIr(CO)_2]$ was found to react with methane under similar conditions as efficiently as the C̄p complex, and the complex $[CpIr(CO)(H)(CH_3)]$ was isolated. These complexes are the first products to be isolated from the oxidative addition reactions of methane.

1.2.7 Pentamethylcyclopentadienyl complexes of copper.

Malcomber and Rausch [54] recently reported the first pentamethylcyclopentadienyl complexes of copper. Thus the complexes $[C\bar{p}CuPR_3]$ (R = C_6H_5, C_2H_5) were prepared from the following reaction :

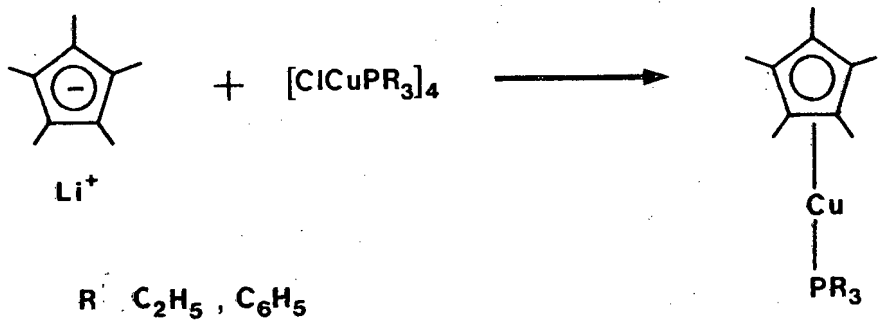


Fig 1.2.23 : Preparation of $[C\bar{p}CuPR_3]$.

An ethereal solution of $(C_5Me_5)^-Li^+$ reacted with CuCl in the presence of carbon monoxide to produce $[C\bar{p}Cu(CO)]$. A *bis* η^2-(trimethylsilyl)-acetylene copper complex was prepared :

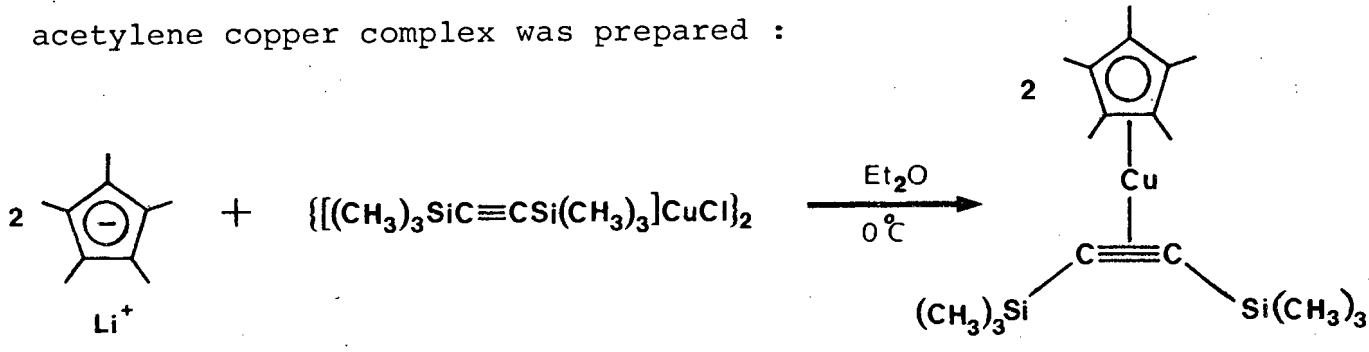


Fig 1.2.24 : Preparation of a pentamethylcyclopentadienyl copper complex containing an η^2-acetylenic ligand.

The analogous Cp complex $[CpCu(\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3)]$ was reported to be more air and temperature sensitive than the $C\bar{p}$ complex, but was easier to crystallise.

1.3 Pentamethylcyclopentadienyl complexes of the Actinides, thorium and uranium.

The complexes $[C\bar{p}_2MCl_2]$ (M = Th, U) are among the most chemically reactive and versatile organoactinide compounds prepared to date.[55] These complexes exhibit relatively low Th and U co-ordination numbers, and provide a direct comparison with the analogous series of Ti and Zr transition metal organometallic complexes.

These *bis* pentamethylcyclopentadienyl dichloro complexes of thorium and uranium may be alkylated in ether solution to yield alkyl complexes of the type $[C\bar{p}_2M(CH_3)_2]$ (M = Th, U). The alkyl compounds are air-sensitive and have been shown to be monomeric in benzene.[56] They were shown to possess high thermal stability, in contrast with the analogous unstable Cp complexes.

The uranium complex, $[C\bar{p}_2UCl_2]$ was shown to be monomeric in solution as opposed to the extensively associated complexes of uranium containing unsubstituted cyclopentadienyl ligands.[57]

Recently,[58] stable π-allylic complexes of U were reported, $[C\bar{p}U(allyl)_3]$ (allyl = η^3-C_3H_5, η^3-C_4H_7). These π-allyl complexes were reported to be thermally stable, in contrast with the unsubstituted cyclopentadienyl analogues which decomposed above 10°C. The complexes are, however, somewhat air -sensitive. An X-ray crystal structure of the complex $[C\bar{p}U(\eta^3\text{-}C_4H_7)]$ revealed the molecule as being distorted tetrahedron, with the $C\bar{p}$ ligand bonded in an η^5 manner. The methyl substituents of the ring are bent away from the U atom, out of the plane of the

ring. The methyl substituents on the allyl groups are displaced out the allyl plane towards the uranium atom. This phenomenon was not explained, it was not known whether it occurred as a result of electronic preferences, or simply packing forces within the crystal lattice.

CHAPTER TWO

2. The synthesis and characterisation of some methoxymethyl and monohalomethyl complexes of iron, molybdenum and tungsten.

2.1 Monohalomethyl and methoxymethyl transition metal complexes.

Methoxymethyl and monohalomethyl transition metal complexes may be versatile intermediates for the synthesis of complexes containing various functional groups which have been proposed as intermediates in the Fischer-Tropsch reaction, such as hydroxymethyl and carbene species.

The first methoxymethyl and halomethyl transition metal complexes were reported by Green *et al* [59]. Thus treatment of a THF solution of $[CpFe(CO)_2]^-Na^+$ with an excess of $ClCH_2OCH_3$ yielded the methoxymethyl complex $[CpFe(CO)_2CH_2OCH_3]$ (XX) as a yellow oil. Treatment of a hexane solution of (XX) with HX gas (X = Cl, Br) gave the appropriate monohalomethyl complexes $[CpFe(CO)_2CH_2X]$ (X = Cl,Br) in good yield. The complex X = Br was reported to be less stable than the chloromethyl analogue. These workers report that the complexes $[CpFe(CO)_2CH_2X]$ react readily with nucleophiles.

The complexes $[CpMo(CO)_3CH_2OCH_3]$ and $[CpW(CO)_3CH_2OCH_3]$ were prepared by a similar route. These complexes, gave on reaction with dry HCl gas the chloromethyl complexes $[CpM(CO)_3CH_2Cl]$ (M = Mo, W). The complex $[CpW(CO)_3CH_2Br]$ was prepared by a similar method, and was reported to be less stable than the chloromethyl analogue.

King and Braitsch [60] prepared the halomethyl species directly from the

reaction of the appropriate metal carbonyl anion with various dihalomethanes. Table 2.1 summarises some of the results obtained.

Table 2.1

Metal carbonyl anion	Dihalomethane with reaction time in parentheses.	Product(s) with yields in parentheses.
$CpMo(CO)_3^-$	$ClCH_2I$ (5 hours)	$[CpMo(CO)_3CH_2Cl]$ (60-70%)
$CpW(CO)_3^-$	$ClCH_2I$ (5 hours)	$[CpW(CO)_3CH_2Cl]$ (60%) $[CpW(CO)_3CH_2I]$ (12%)
$CpFe(CO)_2^-$	$ClCH_2I$ (30 mins.)	$[CpFe(CO)_2CH_2Cl]$ (13%)
$CpMo(CO)_3^-$	CH_2Br_2 (5 hours)	$[CpMo(CO)_3]_2$ + $[CpMo(CO)_3Br]$ (trace)
$CpMo(CO)_3^-$	CH_2I_2 (15 mins.)	$[CpMo(CO)_3CH_2I]$ (17%)
$CpW(CO)_3^-$	CH_2I_2 (15 mins.)	$[CpW(CO)_3CH_2I]$**

** No yield reported, we have found the yield to vary between 10 and 15%.

These workers report that the iodomethyl derivatives $[CpM(CO)_3CH_2I]$ (M = Mo, W) are very unstable. $ClCH_2I$ was used to prepare the chloromethyl derivatived directly, as the metal carbonyl anions gave no

reaction with CH_2Cl_2 , attributed to the inertness of the strong carbon-chlorine bond. Chloroiodomethane offered a good alternative, due to the fact that the C-I bond is weaker than the C-Cl bond, as evidenced by the fact that the C-I bond is cleaved, and the C-Cl bond is retained, in most cases. (see chapter 2.3)

Moss *et al* [61-63] reported the synthesis of the chloromethyl complexes $[Mn(CO)_5CH_2Cl]$, $[Re(CO)_5CH_2Cl]$ and $[CpRu(CO)_2CH_2Cl]$; the methoxymethyl complexes $[CpRu(CO)_2CH_2OCH_3]$ and $[Re(CO)_5CH_2OCH_3]$ were also isolated.

Davison *et al* [64] reported the complexes $[CpFe(CO)(PPh_3)CH_2X]$ (X = OCH_3, Cl, I). The complex $[CpFe(CO)(PPh_3)CH_2I]$ was reported to be somewhat more stable than the chloromethyl analogue.

Chloromethyl complexes of Pt and Ir have also been reported.[65,66]

In view of the relevance of these complexes to the Fischer-Tropsch reaction, which will be discussed in the following section, a brief overview of the Fischer-Tropsch reaction is now presented.

2.2 The Fischer-Tropsch reaction.

A simplistic representation of the Fischer-Tropsch process is given by :

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

The reaction of CO with H_2 takes place on a heterogeneous catalyst to give a mixture of alkanes, alkenes, alcohols, esters, acids and aromatic compounds in varying amounts. The synthesis is distinguished by a lack of selectivity that reflects a myriad of competing reactions. The products obtained from this synthesis vary markedly with the catalyst used, and with the particular reaction conditions employed, namely temperature, pressure, CO/H_2 ratio, flow rate etc.[67]

A Fischer-Tropsch synthesis reaction may be defined as a carbon monoxide hydrogenation reaction that includes at least three steps :[68]

(a) C-H bond formation

(b) C-C bond formation

(c) C-O bond scission

This definition allows for substansive mechanistic differences among Fischer-Tropsch reactions, and delineates the minimal key formal reaction steps. (Not necessarily in the order given above.)

Two main mechanisms have been proposed for the Fischer-Tropsch reaction, a carbide mechanism, and a mechanism involving unstable intermediates with C, H and O atoms bonded to metals.

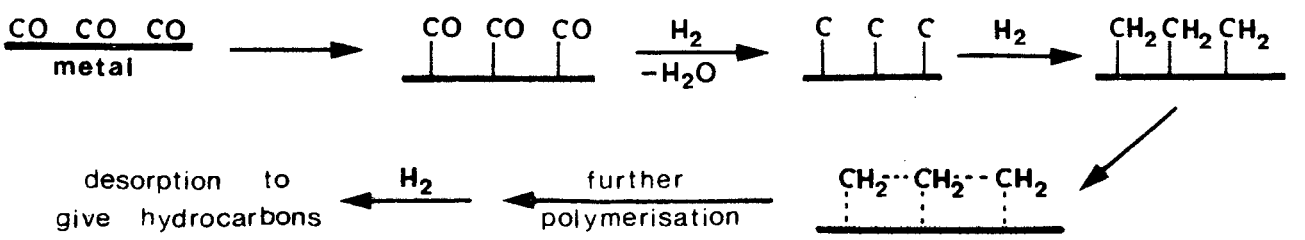


Fig 2.2.1 : The carbide mechanism of the Fischer-Tropsch reaction.[69]

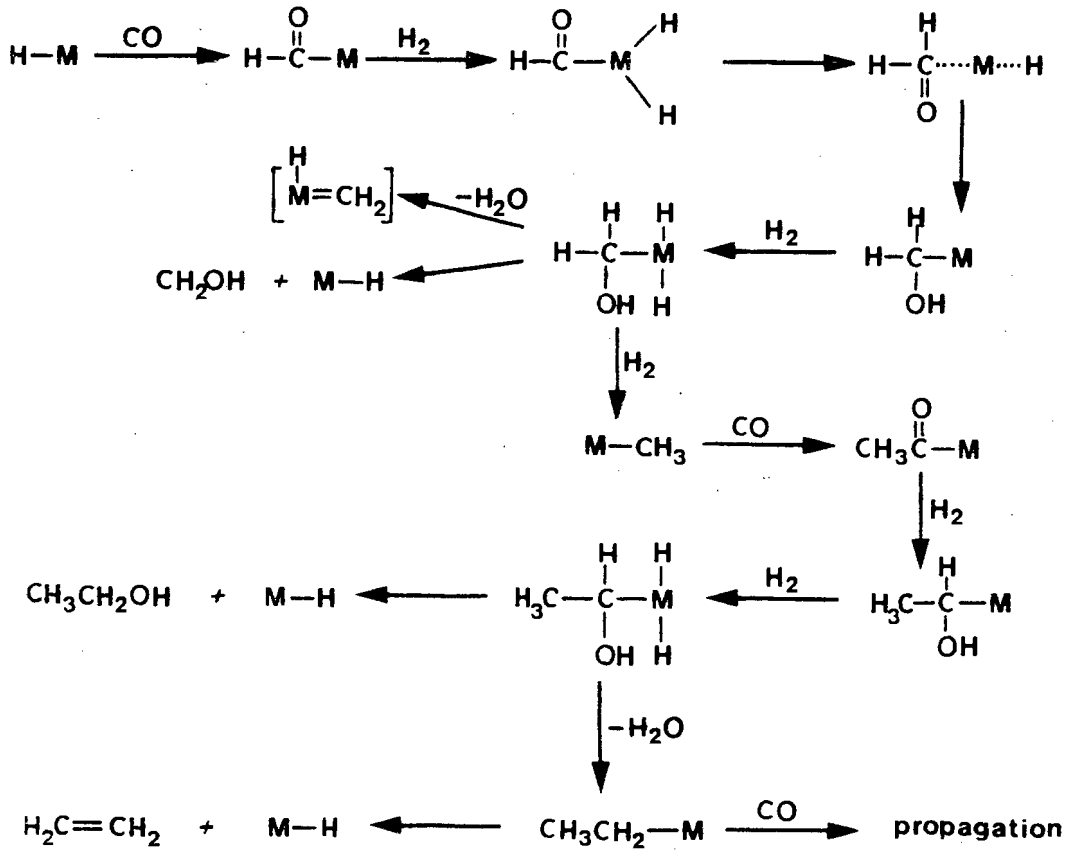


Fig 2.2.2 : A mechanism involving unstable intermediates with C, H and O atoms bonded to metals.[70]

The catalysts used in the Fischer-Tropsch reaction are heterogeneous catalysts, i.e. a solid state catalyst is exposed to the gaseous reactants, and the reaction thus occurs in a chemisorbed phase. No homogeneous catalyst has as yet been found for the Fischer-Tropsch reaction, however, many intermediates which have been proposed in this synthesis have been isolated, and studies on these compounds have led to a greater understanding of how these organic moieties behave when bonded to transition metals. The following section discusses some complexes which may be thought of as models for various intermediates which have been proposed in the Fischer-Tropsch synthesis reaction.

2.3 The synthesis of Fischer-Tropsch intermediates using monohalomethyl and methoxymethyl transition metal complexes.

Various complexes which serve as models for intermediates proposed in the Fischer-Tropsch reaction have been synthesised using mono-substituted methyl transition metal complexes, $LnMCH_2X$, (Ln = other ligands, M = transition metal, X = functional group).

Thus alkoxide abstraction from methoxymethyl iron complexes has been reported to yield transient carbene species :

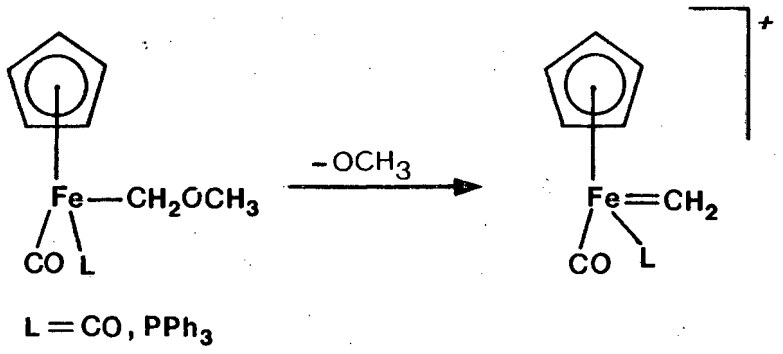


Fig 2.3.1 : Alkoxide abstraction from a methoxymethyl iron complex.

These complexes were, however, not fully characterised. These authors[72] also reported the reaction of $[CpFe(CO)_2CH_2OCH_3]$ with non co-ordinating acids such as HBF_4.

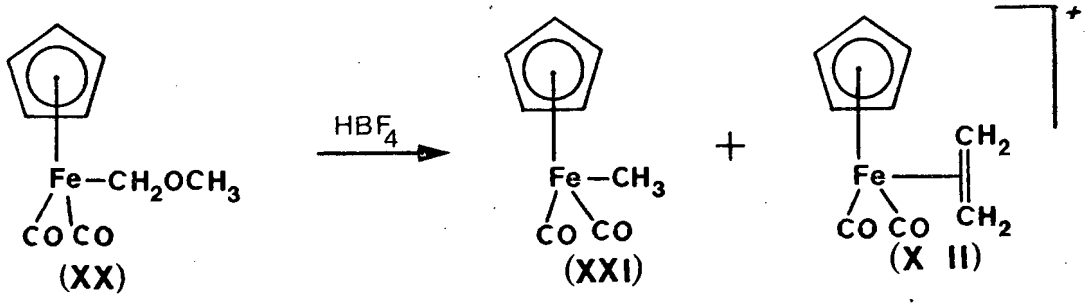


Fig 2.3.2 : Reaction of a methoxymethyl iron complex with a non co-ordinating acid.

These products were explained in terms of an intermediate carbene species. When the reaction was conducted in the presence of cyclohexene, norcarane was produced in 46% yield based on (XX), together with other

products, predominately (XXII) and $[CpFe(CO)_3]^+$. When the chloromethyl complex, $[CpFe(CO)_2CH_2Cl]$ was treated with $AgPF_6$, AgCl was precipitated, and (XXI),(XXII) and $[CpFe(CO)_3]^+$ were isolated as products. [72] This reaction was also performed in the presence of cyclohexene at low temperature, norcarane was produced, which tends to imply the intermediacy of a carbene species.

Flood *et al* [73] reported the spectroscopic characterisation of an iron

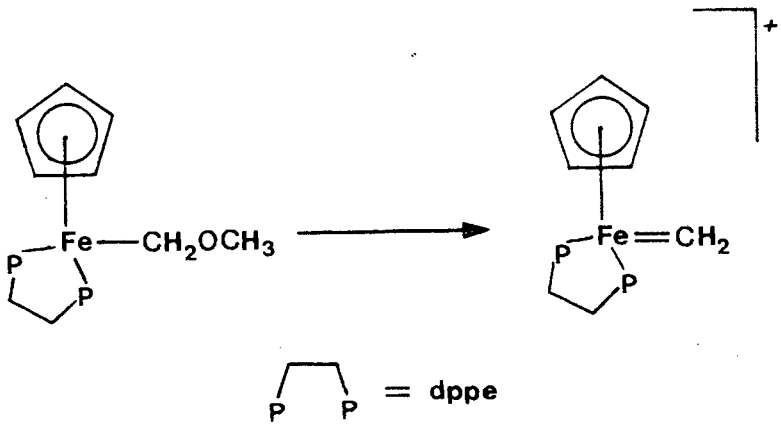


Fig 2.3.3 : Reaction of a methoxymethyl iron complex with HBF_4.

carbene species, isolated from the reaction of a methoxtmethyl iron complex with a non co-ordinating acid. The X-ray crystal structure of this complex was investigated by Pettit *et al.* [74]

Recently, Cutler *et al* [75] reported the preparation of a ligated ketene, obtained from the carbonylation of a methylidene ligand, according to the following sequence :

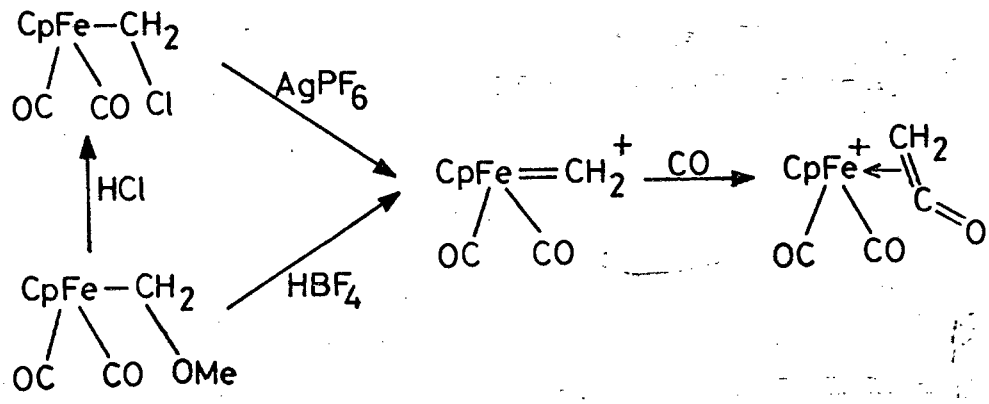


Fig 2.3.4 : Preparation of a ligated ketene complex.

Both carbene species and η^2C,C ketene complexes of the type MCH_2COM have been postulated in some mechanisms of the Fischer-Tropsch synthesis reaction, these complexes thus serve as models for intermediates in the proposed mechanism of the Fischer-Tropsch synthesis reaction.[68]

Various substituted carbene species have been prepared from the treatment of methoxymethyl complexes with trityl salts.[76]

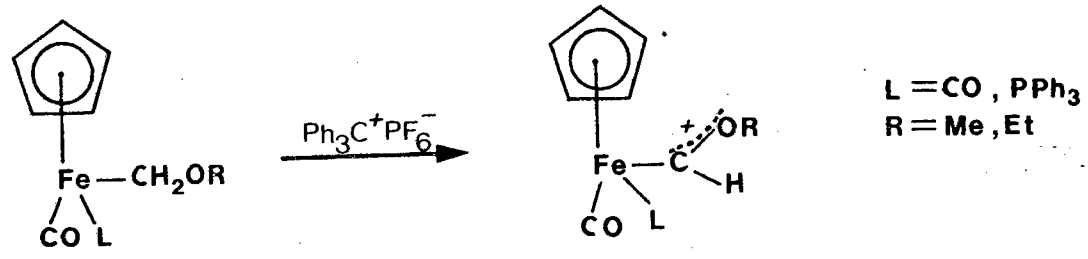


Fig 2.3.5 Preparation of substituted carbene complexes.

The products were isolated at room temperature in high yields as stable yellowish solids. The complexes where L = CO hydrolysed slowly in air. The alkoxycarbene complexes could be reduced to alkoxymethyl and methyl complexes under a variety of conditions. Similar sequences of co-ordinated ligand reactions may be involved on metal surfaces during the Fischer-Tropsch reaction, in which secondary

hydroxy carbene species are further hydrogenated to methanol or methane via hydroxymethyl or methyl ligands. See fig 2.2.2.

Brookhart *et al* [73] prepared carbene complexes of Mo by treatment of the methoxymethyl complex with a non co-ordinating acid :

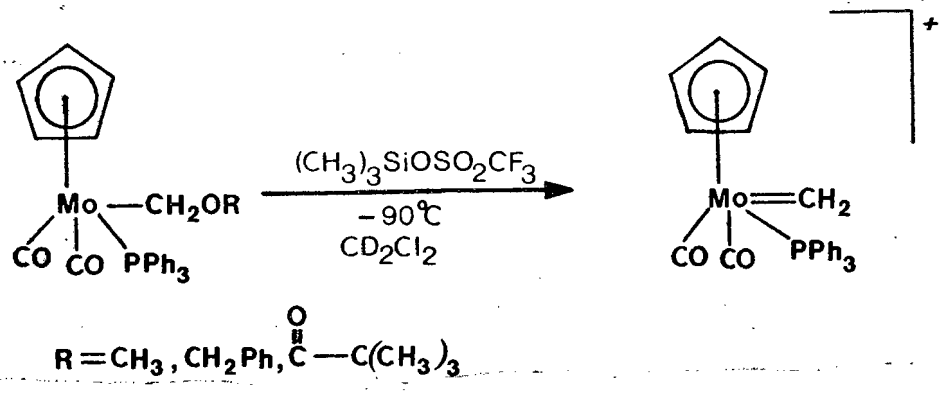


Fig 2.3.6 : Preparation of a carbene complex of molybdenum.

The molybdenum methylene complex (XXIV) was generally contaminated with small amounts of the appropriate heteroatom carbene, viz, $[CpMo(CO)_2(PPh_3)(=C<^{OR}_{H})]^+$, and also the methyl complex $[CpMo(CO)_2(PPh_3)CH_3]$. The carbene complex (XXIV) decomposed above -70°C.

A carbene complex of tungsten, $[W(=CH_2)(PMe_3)_4Cl]^+ CF_3SO$ was prepared by Schrock and Holmes.[78] These workers could not isolate this complex as a stable solid, and thus treated the complex with CO, giving rise to a phosphorous ylide complex, which was a stable solid of formula $[W(CH_2PMe_3)(CO)_2(PMe_3)_3Cl]^+ CF_3SO_3^-$. The X-ray crystal structure of this complex is discussed in chapter 4.1.

Carbene complexes of Re have been prepared from methoxymethyl complexes, thus Gladysz *et al* [25] reported that treatment of

$[CpRe(NO)(PPh_3)CH_2OCH_3]$ with CH_3SO_3F yielded the complex, $[CpRe(NO)(PPh_3)(=CH_2)]^+$.

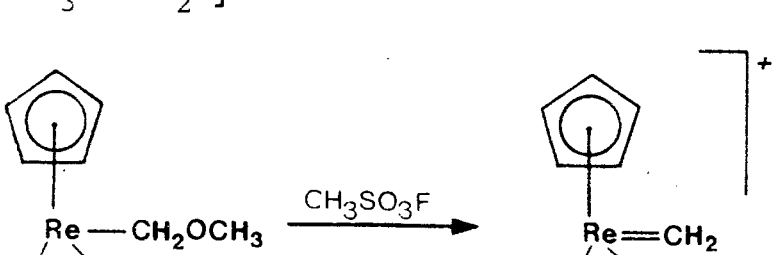


Fig 2.3.7 : Preparation of a rhenium carbene complex.

Gladysz *et al* [25] recently prepared the analogous pentamethylcyclopentadienyl complex by another route. (See chapter 1.2.4)

The reactions of a dihapto-formaldehyde complex (η^2-CHO) of osmium were investigated, and this complex was found to be a useful synthetic precursor for stable formyl, hydroxymethyl, methoxymethyl and halomethyl osmium complexes.[80-82]

The following diagram illustrates some of the complexes obtained from reactions involving this dihapto-formaldehyde complex.

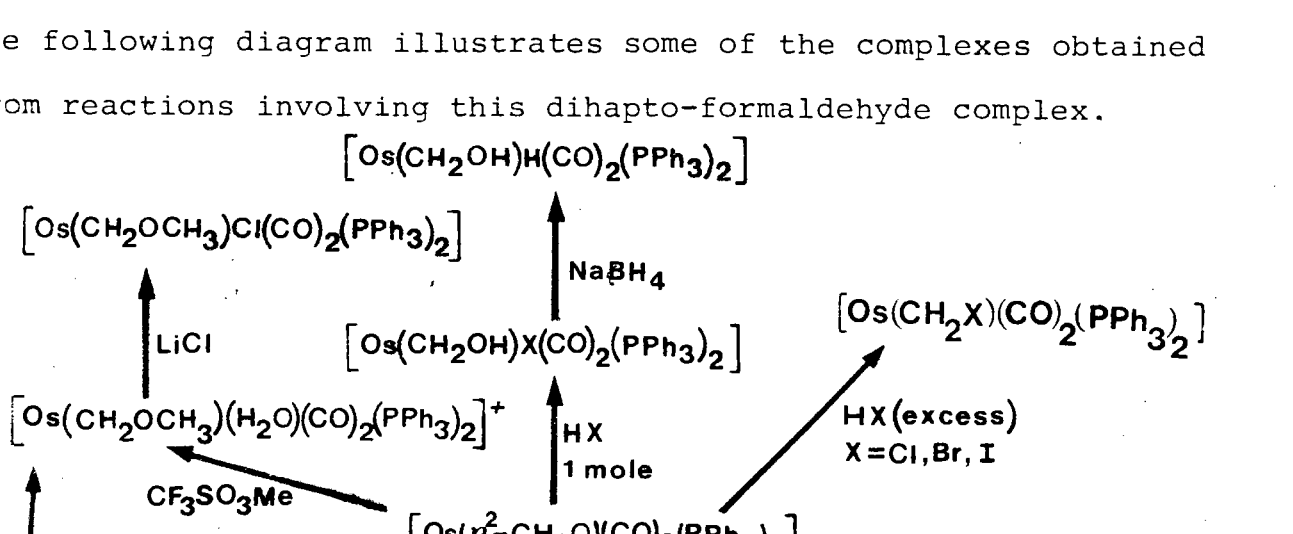


Fig 2.3.8 : Reactions of $[Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2]$.

In the above sequence of reactions, a hydroxymethyl complex is converted to a chloromethyl complex on reaction with HCl. It would thus seem plausible that a chloromethyl complex could be converted to a hydroxymethyl complex, using a source of OH^-, for example, $NaOH/H_2O$. (see chapter 3)

A μ-methylene complex $[\{CpFe(CO)\}_2(\mu\text{-}CH_2)(\mu\text{-}CO)]$ was prepared by Casey *et al* [83] from the reaction of $CpFe(CO)_2CH_2OCCH_3$ (O) with $[CpFe(CO)_2]^-$. This reaction yielded a mixture of *cis* and *trans* isomers of the μ-methylene product.

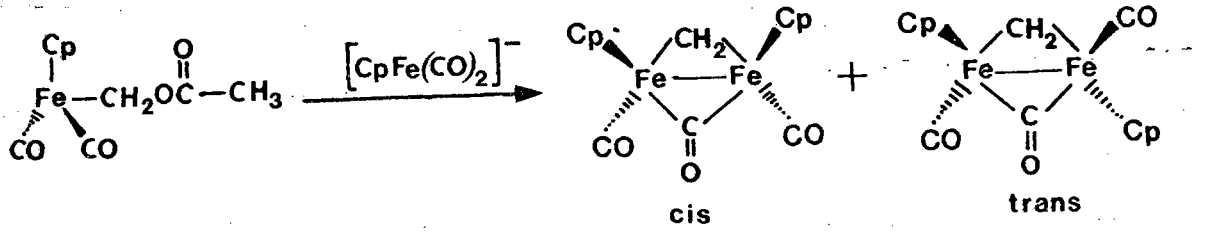


Fig 2.3.9 : Preparation of $[\{CpFe(CO)\}_2(\mu\text{-}CH_2)(\mu\text{-}CO)]$

μ-methylene complexes may be considered to be models of intermediates which have been proposed to occur during the Fischer-Tropsch reaction. The above μ-methylene complexes contain another bridging ligand (CO) and also a metal-metal bond. Many authors suggested that these features were necessary in order to stabilise μ-methylene species,[84] however, a stable μ-methylene complex of ruthenium was prepared by Lin *et al* [85], from the reaction of $[CpRu(CO)_2]^-$ with 0.5 equivalents of CH_2Cl_2. These authors do not mention an intermediate chloromethyl complex, although it seems likely that the reaction does go via this route. The μ-methylene complex $[\{CpRu(CO)_2\}_2(\mu\text{-}CH_2)]$ was found to react readily with CO affording a complex containing a $(\mu\text{-}COCH_2)$ fragment. Photolysis of

$[\{CpRu(CO)_2\}_2(\mu\text{-}CH_2)]$ was found to give a mixture of *cis* and *trans* isomers of $[\{CpRu(CO)\}_2(\mu\text{-}CH_2)(\mu\text{-}CO)]$ which contains a metal-metal bond. The μ-methylene complex was reported to be far more reactive than the analogous alkyl or metal-metal bonded μ-methylene complexes.

This reaction is of great interest since King and Braitsch[60] suggested that the carbon-chlorine bond is very strong, and would thus not easily be cleaved. However, the reaction of $[CpRu(CO)_2]^-$ with CH_2Cl_2 gave the μ-methylene complex under mild conditions, thus the mechanism of reaction of metal carbonyl anions with dihalomethanes would not appear to be a simple nucleophilic substitution reaction, but rather, to involve a more complicated mechanism, and may involve radicals.

A μ-methylene Co complex was prepared from the reaction of $[CpCo(CO)_2]^-$ with 0.5 equivalents of CH_2I_2. The product $[\{CpCo(CO)\}_2(\mu\text{-}CH_2)]$ was isolated as a mixture of *cis* and *trans* isomers.[86] A mixed metal μ-methylene complex, $[CpCo(CO)(\mu CH_2)(CO)RhCp]$ was also prepared.

Thus the syntheses of models of intermediates which are proposed to exist in the mechanism of the Fischer-Tropsch reaction are of great relevance, since the information about the reactivity of organic ligands co-ordinated to transition metals may yield information as to the design of homogeneous catalysts for the Fischer-Tropsch reaction, which may be used in the future. Methoxymethyl and halomethyl transition metal complexes appear to be good precursors for a number of complexes which are models for intermediates in the

Fischer-Tropsch reaction, and thus a study of these complexes is of great interest.

2.4 The synthesis of some new halomethyl and methoxymethyl complexes of iron, molybdenum and tungsten.

Methoxymethyl and monohalomethyl transition metal complexes are useful precursors for a number of complexes which are models for intermediates in the Fischer-Tropsch synthesis reaction.

The new monohalomethyl and methoxymethyl complexes $[C\bar{p}M(CO)_3CH_2X]$ ($X = OCH_3$, Cl, Br, I) ; and $[C\bar{p}Fe(CO)_2CH_2Cl]$ were synthesised. The reactivity of these complexes with various nucleophiles was investigated, and the results compared with those obtained for the known cyclopentadienyl analogues.[59,60]

2.4.1 Preparation of the complexes $[C\bar{p}M(CO)_3CH_2X]$ ($X = OCH_3$, Cl, Br, I ; M = Mo, W)

The methoxymethyl complexes $[C\bar{p}M(CO)_3CH_2OCH_3]$ (M = Mo, W) were prepared by the reaction of the appropriate metal carbonyl anion, $[C\bar{p}M(CO)_3]^-$ with $ClCH_2OCH_3$. The metal carbonyl anions were prepared by the reaction of the metal carbonyl $M(CO)_6$ with $(C_5Me_5)^-Li^+$ according to the method described previously.[87]

A solution of $[C\bar{p}Mo(CO)_3]^-$ in THF was cooled to 0°C, $ClCH_2OCH_3$ in THF was added slowly over a period of approximately 15 minutes, and the solution allowed to warm to room temperature. The product, $[C\bar{p}Mo(CO)_3CH_2OCH_3]$ was isolated as a yellow microcrystalline solid

Table 2.2

Characterisation data for the complexes $[C_5H_5M(CO)_3CH_2X]$, M = Mo, W; X = Cl, Br, I, OCH_3.

Complex	Carbonyl stretching frequencies (in cm^{-1}) [a]	^{1}Hnmr (in δ ppm) [b]			
		Peak Position	Relative Intensity	Multiplicity	Assignment
$[C_5H_5Mo(CO)_3CH_2OCH_3]$	2016(s) 1937(vs) 1921(s)	4.29	2	singlet	CH_2
		3.24	3	singlet	CH_3
		1.62	15	singlet	C_5Me_5
$[C_5H_5Mo(CO)_3CH_2Cl]$	2024(s) 1946(s) 1929(s)	3.91	2	singlet	CH_2
		1.54	15	singlet	C_5Me_5
$[C_5H_5Mo(CO)_3CH_2Br]$	2023(s) 1947(vs) 1929(s)	3.16 [c]	2	singlet	CH_2
		1.35	15	singlet	C_5Me_5
$[C_5H_5W(CO)_3CH_2OCH_3]$	2014(s) 1929(vs) 1913(s)	4.32	2	singlet	CH_2
		3.21	3	singlet	CH_3
		1.72	15	singlet	C_5Me_5
$[C_5H_5W(CO)_3CH_2Cl]$	2023(s) 1937(vs) 1921(s)	4.06	2	singlet	CH_2
		1.64	15	singlet	C_5Me_5
$[C_5H_5W(CO)_3CH_2Br]$	2020(s) 1935(vs) 1922(s)	3.55	2	singlet	CH_2
		1.55	15	singlet	C_5Me_5
$[C_5H_5W(CO)_3CH_2I]$	2019(s) 1934(vs) 1922(s)	2.84	2	singlet	CH_2
		1.56	15	singlet	C_5Me_5

a All IR spectra were recorded using n-hexane as solvent.
The following abbreviations are used in connection with the IR spectra:
w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

b All nmr spectra were recorded using C_6D_6 as solvent.

c The nmr spectrum showed traces of C_5Me_5H.

The analogous cyclopentadienyl complex, $[CpMo(CO)_3CH_2OCH_3]$ is an oil.[59] A small amount of $[C\bar{p}Mo(CO)_3Cl]$ was also isolated from this reaction, and identified by comparison of IR and mp data reported previously for this compound.[87] This product was shown to be a decomposition product of the chloromethyl complex $[C\bar{p}Mo(CO)_3CH_2Cl]$, which could concievably be a product from this reaction. This would be in agreement with fellow workers,[88] who found that the reaction of $ClCH_2OCH_3$ with $[CpMo(CO)_3]^-$ yielded both the methoxymethyl and the chloromethyl products, the relative proportions being dependent on the reaction conditions employed, predominately temperature.

On bubbling dry HCl gas through a hexane solution of $[C\bar{p}Mo(CO)_3CH_2OCH_3]$ (XXV), the solution darkened slightly, and a small amount of dark purple crystalline material was observed. The hexane solution contained $[C\bar{p}Mo(CO)_3CH_2Cl]$, (XXVI) contaminated with a small amount of $[C\bar{p}Mo(CO)_3Cl]$. $[C\bar{p}Mo(CO)_3Cl]$ was shown to be a decomposition product of (XXVI), thus a solution of (XXVI), on exposure to sunlight, darkens, and the chloride product $[C\bar{p}Mo(CO)_3Cl]$, is formed, in almost quantitative yield. Exposure of solid (XXVI) to sunlight also results in the formation of the chloride product, however, the process is slower than when a solution is exposed to sunlight. Exposure of solid (XXVI) to sunlight results in the formation of the chloride product in quantiative yield after 6-8 hours, whereas this process occurs in 2-3 hours if (XXVI) is in solution. The purple insoluble material was not identified, no carbonyl bands were seen in the IR spectrum of this compound.

Treatment of a hexane solution of (XXV) with dry HBr gas yielded the bromomethyl complex $[C\bar{p}Mo(CO)_3CH_2Br]$, together with it's decomposition product, $[C\bar{p}Mo(CO)_3Br]$ This bromomethyl product was found to be far less stable than the chloromethyl complex (XXVI). This is in agreement with similar observations made by Green *et al* [59] on the analogous cyclopentadienyl complexes $[CpMo(CO)_3CH_2Br]$ and $[CpFe(CO)_2CH_2Br]$.

The analogous HI reaction resulted in a mixture of $[C\hat{p}Mo(CO)_3CH_2I]$ and $[C\hat{p}Mo(CO)_3I]$ being formed in similar yields. The two products, however, could not be separated, and thus a complete characterisation of $[C\hat{p}Mo(CO)_3CH_2I]$ could not be achieved. The complex was, however, identified spectroscopically. The iodomethyl complex rapidly decomposed to the iodide complex, and was found to be much less stable than the bromo and chloro analogues. This is in agreement with observations made by other workers on the analogous cyclopentadienyl complexes. [59,60]

Reaction of $[C\hat{p}W(CO)_3]^-$ with $ClCH_2OCH_3$ gave $[C\hat{p}W(CO)_3CH_2OCH_3]$ (XXVII) in low yield, contaminated with approximately 5% $[C\hat{p}W(CO)_3Cl]$. The two products were separated by fractional crystallisation from n-hexane, or by chromatography. $[C\hat{p}W(CO)_3Cl]$ was identified by comparison of IR and mp data reported previously for this compound.[87] A large quantity of $W(CO)_6$ was obtained from this reaction, which may account, in part, for the low yield. It is not clear whether $W(CO)_6$ results from incomplete formation of the anion $[C\hat{p}W(CO)_3]^-$, which is prepared from $W(CO)_6$ and $(C_5Me_5)^-Li^+$, or a disproportionation reaction of the anion.

A solution of (XXVII) in hexane, gives, on reaction with dry HX gas, (X = Cl, Br, I), the expected $[C\hat{p}W(CO)_3CH_2X]$ species, in good yields. The bromomethyl and iodomethyl complexes were found to be remarkably stable to light and heat as compared with the molybdenum analogues, and also with the cyclopentadienyl analogues. [60] Thus the complex $[CpW(CO)_3CH_2I]$ is an unstable oil, isolated in very low yield from the reaction of $[CpW(CO)_3]^-$ with CH_2I_2, whereas the pentamethylcyclopentadienyl analogue $[C\hat{p}W(CO)_3CH_2I]$ (XXVIII) is an air stable crystalline compound. No noticeable difference in stability to air, light and heat was observed for the series $[C\hat{p}W(CO)_3CH_2X]$ (X = Cl, Br, I); whereas for the cyclopentadienyl analogues, the iodomethyl complex is far less stable to heat and light than the chloromethyl complex.[60]

The complexes, $[C\acute{p}M(CO)_3CH_2X]$, (M = Mo, W ; X = OCH_3, Cl, Br, I) were generally found to have higher melting points than their unsubstituted cyclopentadienyl analogues. For example, $[C\acute{p}W(CO)_3CH_2OCH_3]$ is a crystalline solid mp = 71-76°C, whereas $[CpW(CO)_3CH_2OCH_3]$ has a melting point of 44°C.

Characterisation data for the pentamethylcyclopentadienyl halomethyl and methoxymethyl complexes of molybdenum and tungsten are given in table 2.2. The carbonyl stretching frequencies for these complexes are approximately 12-15 cm^{-1} lower than those observed for the cyclopentadienyl analogues.[58,59]

Reactions of the halomethyl complexes $[C\acute{p}M(CO)_3CH_2X]$ (M = Mo, W ; X = Cl, Br, I) with methanol, gave as products the methoxymethyl products, (XXV) and (XXVII). See fig 2.4.1. The analogous cyclopentadienyl complexes give similar results on reaction with methanol.

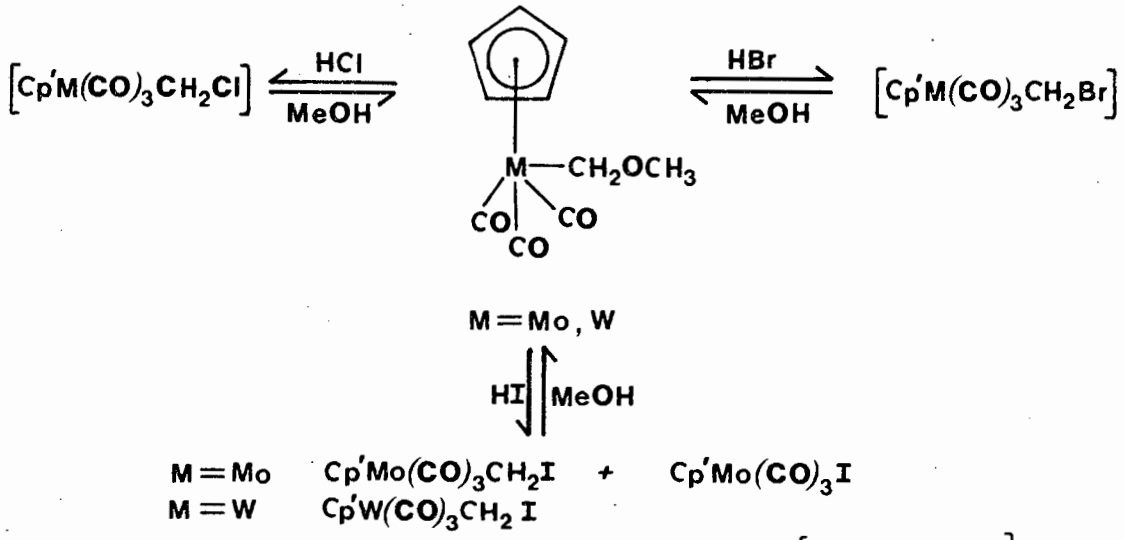


Fig 2.4.1 : Preparation of the halomethyl complexes $[C\acute{p}M(CO)_3CH_2X]$, (X = Cl, Br, I ; M = Mo, W), and their reaction with methanol to give the methoxymethyl complexes.

2.4.2 Reactions of the complexes $C\acute{p}M(CO)_3^-$ (M = Mo, W) with various dihalomethanes.

Reactions of metal carbonyl anions with dihalomethanes have been reported to

yield μ-methylene complexes.[85,86] We thus decided to investigate the reactions of the complexes $[C\bar{p}M(CO)_3]^-$ with various dihalomethanes, in order to ascertain whether we could isolate μ-methylene complexes of Mo and W in this manner. Moreover, King and Braitsch[60] investigated the reactions of $[CpM(CO)_3]^-$ (M = Mo, W) with various dihalomethanes, and found that not all of the reactions yielded the expected halomethyl complexes. We were thus interested to see what results would be obtained for the analogous Cp̄ complexes. The results obtained by King and Braitch [60] are summarised in table 2.1.

The reaction of $[C\bar{p}Mo(CO)_3]^-$ with $ClCH_2I$ in THF gave the expected product, (XXVI), completely analogous to the product obtained from the reaction of $[CpMo(CO)_3]^-$ with $ClCH_2I$. However, reaction of $[C\bar{p}W(CO)_3]^-$ with $ClCH_2I$ at room temperature gave the iodomethyl product (XXVIII) as the only product. This is in marked contrast to the results obtained previously for the cyclopentadienyl complexes. (see table 2.1). Thus King and Braitsch[60] reported that the reaction of $[CpW(CO)_3]^-$ with $ClCH_2I$ at room temperature yielded the complexes $[CpW(CO)_3CH_2Cl]$ and $CpW(CO)_3CH_2I$ in yields of 60 and 12% respectively.

(see fig 2.4.2)

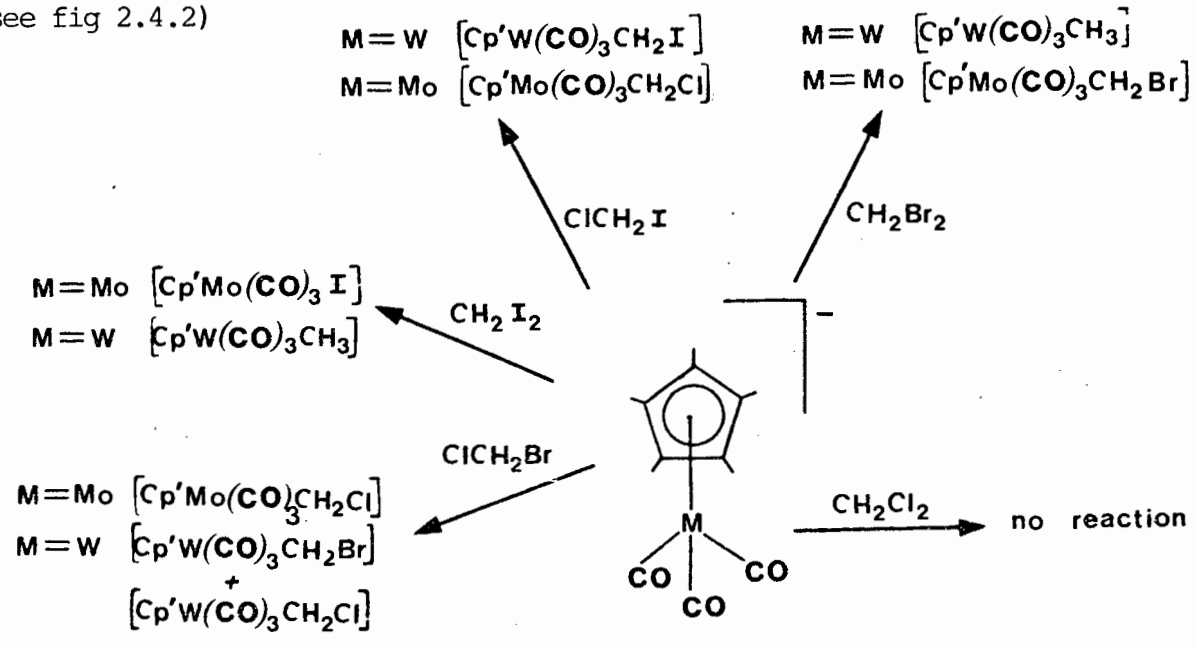


Fig 2.4.2 : The reactions of $[C\bar{p}M(CO)_3]^-$ with various dihalomethanes.

Thus reaction of $[C\bar{p}Mo(CO)_3]^-$ with CH_2Br_2 gave $[C\bar{p}Mo(CO)_3CH_2Br]$, whereas the reaction of $[C\bar{p}W(CO)_3]^-$ with CH_2Br_2 gave the complex $[C\bar{p}W(CO)_3CH_3]$ as the only product, whether the reaction was carried out using 0.5 equivalents of CH_2Br_2, or excess dibromomethane. This would seem to imply a transient carbene species, probably $[C\bar{p}W(CO)_3(=CH_2)]^+$, which extracts a hydride ion (probably from the solvent THF), to give the methyl product. This phenomenon has been noted previously.[72,79] $[C\bar{p}W(CO)_3CH_3]$ was characterised by comparison of IR and nmr spectra with those reported previously.[16] In contrast, the reaction of $[CpMo(CO)_3]^-$ with CH_2Br_2 was reported to give the dimer, $[CpMo(CO)_3]_2$, in 95% yield, plus a trace of $[CpMo(CO)_3Br]$. The reaction of $[CpW(CO)_3]^-$ with CH_2Br_2 was not reported.[60]

Reaction of $[C\bar{p}M(CO)_3]^-$ (M = Mo, W) with CH_2I_2, gave for M = Mo, $[C\bar{p}Mo(CO)_3I]$ as the only product. $[C\bar{p}Mo(CO)_3I]$ was identified by comparison of IR and mp data reported previously for this compound.[87] In the case of M = W, the methyl complex, $[C\bar{p}W(CO)_3CH_3]$ was obtained in good yield, whether 0.5 equivalents or excess CH_2I_2 were used. The product was identified as described above.

The reactions of $[CpM(CO)_3]^-$ (M = Mo, W) with CH_2I_2 were reported to yield the complexes $[CpMo(CO)_3CH_2I]$ (low yield), and $[CpW(CO)_3CH_2I]$ respectively,[60] no yield was reported for the tungsten product, we find that the yield is between 10 and 15%.

Neither $[C\bar{p}M(CO)_3]^-$, nor $[CpM(CO)_3]^-$ (M = Mo, W) react with CH_2Cl_2, even on heating the solution under reflux overnight. This was explained by King and Braitsch[60] as resulting from the great strength of the C-Cl bond, which tends to make this compound relatively inert to nucleophilic substitution, as compared with other dihalomethanes, e.g. $ClCH_2I$. However, Lin *et al*[85] found that reaction of $[CpRu(CO)_2]^-$ with CH_2Cl_2 at room temperature, gave the μ-methylene complex $[\{CpRu(CO)_2\}_2(\mu\text{-}CH_2)]$. Thus other factors must determine whether CH_2Cl_2 will

react with a metal carbonyl anion.

$[C\bar{p}M(CO)_3]^-$ (M = Mo, W) gave on reaction with $ClCH_2Br$, the chloromethyl complex (XXVI) for M = Mo; and a mixture of $[C\bar{p}W(CO)_3CH_2Cl]$ and $[C\bar{p}W(CO)_3CH_2Br]$ in a ratio of 2:3 in the case of M = W. For the reaction where M = Mo, the chloromethyl product (XXVI) was isolated in higher yield than when the reaction was performed using $ClCH_2I$.

The different products isolated from the reactions of the various dihalomethanes with either $[C\bar{p}M(CO)_3]^-$ or $[CpM(CO)_3]^-$ (M = Mo,W), do not appear to have a simple explanation. The difference in reactivity of the $[C\bar{p}M(CO)_3]^-$ relative to the $[CpM(CO)_3]^-$ anion could possibly be explained in terms of the relative nucleophilicity of these anions, for example, $[C\bar{p}Mo(CO)_3]^-$ reacted with dibromomethane to give the product $[C\bar{p}Mo(CO)_3CH_2Br]$ in good yield, whereas in the case of the unsubstituted cyclopentadienyl analogue, the anion $[CpMo(CO)_3]^-$ is oxidised to the dimer $[CpMo(CO)_3]_2$, with only a trace of $[CpMo(CO)_3Br]$ being isolated, probably resulting from the decomposition of $[CpMo(CO)_3CH_2Br]$. Kinetic studies of these reactions would be of great interest, since they would give an indication as to the mechanisms of these reactions, and thus the increased nucleophilicity of the pentamethylcyclopentadienyl metal carbonyl anion would be quantified, with respect to that of the Cp analogue.

2.4.3 Reactions of $[C\bar{p}Fe(CO)_2]^-Na^+$ with $ClCH_2OCH_3$ and CH_2Cl_2.

The reaction of $[C\bar{p}Fe(CO)_2]^-$ with $ClCH_2OCH_3$ gave the product $[C\bar{p}Fe(CO)_2CH_3]$, as major product. This compound was identified according to IR, ^1H nmr, mass spectrum and solution molecular weight determination, and the results found to be identical with those obtained previously.[18,27] This result tends to imply the intermediacy of a carbene species, which then abstracts a hydride ion from

the solvent, or another molecule of $ClCH_2OCH_3$, this has been noted previously.[72,79]

A trace of a second product was seen in the ^1H nmr spectrum, this product could not be separated from the methyl product, and could thus not be completely characterised. The ^1H nmr spectrum of this product in C_6D_6 gave peaks at 1.14 (C_5Me_5) and 0.16 δ, relative intensities approximately 7:1. The ν(CO) region of the IR spectrum in n-hexane gave peaks corresponding to $[C_5FeFe(CO)_2CH_3]$, and two weak peaks at 1979 and 1964 cm^{-1}. We would tentatively assign a μ-methylene structure to this second product, i.e. $[C_5FeFe(CO)_2]_2(\mu\text{-}CH_2)$, however no trace of this was seen in the mass spectrum. No trace of the chloromethyl or methoxymethyl products were observed, this is in marked contrast to the cyclopentadienyl analogue, which gives on reaction with $ClCH_2OCH_3$, either the methoxymethyl or the chloromethyl products, the relative proportions of which are dependent on the reaction conditions employed.[90]

$[C_5FeFe(CO)_2]^-$ reacted with CH_2Cl_2 to give the chloromethyl complex, $[C_5FeFe(CO)_2CH_2Cl]$ (XXIX). $[CpFe(CO)_2]^-$ does not react with CH_2Cl_2.[59] The methoxymethyl complex, $[C_5FeFe(CO)_2CH_2OCH_3]$ was prepared by dissolving the chloromethyl complex (XXIX) in methanol, the product formed in high yield on standing at room temperature for 2 hours. This product was identified according to characterisation data reported by Cutler *et al*[91]. The analogous cyclopentadienyl complex, $[CpFe(CO)_2CH_2Cl]$ also gives the methoxymethyl product on dissolution in methanol.[90]

2.5 Monohaloalkyl transition metal complexes and their importance as precursors for polymethylene bridged transition metal dimers.

The complexes $[CpFe(CO)_2(CH_2)_nBr]$ (n = 3, 4, 5) were synthesised from the reaction of $[CpFe(CO)_2]^-$ with the appropriate α,ω dihalomethane at -20°C. The complexes $[CpFe(CO)_2(CH_2)_nBr]$ react with $[CpFe(CO)_2]^-$ to give the binuclear polymethylene

bridged complexes $[CpFe(CO)_2]_2(\mu\text{-}CH_2)_n$ (n = 3, 4, 5) .[92]

A mixed metal polymethylene bridged complex was also prepared by reacting $[CpFe(CO)_2(CH_2)_3Br]$ with $[CpMo(CO)_3]^-$, giving the product $[CpFe(CO)_2(\mu\text{-}CH_2)_3Mo(CO)_3Cp]$.

The complexes $[CpFe(CO)_2]_2(\mu\text{-}CH_2)_n$ (n = 3-12) have been prepared directly from the reaction of $[CpFe(CO)_2]^-$ with the appropriate α,ω dihaloalkane.[93,94] The X-ray crystal structures of the complexes where n = 3,4 have been investigated. The iron atoms were found to be joined by simple chains of sigma bonded $(CH_2)_n$ ligands, with no metal-metal interaction.[93]

Bailey *et al* [95,96] showed that the reaction of $[CpMo(CO)_3]^-$ with $I(CH_2)_3I$ led to a cyclic carbene complex, (see chapter 3), and the reaction of $[CpMo(CO)_3]^-$ with $I(CH_2)_4I$ yielded the μ-methylene complex, $[CpMo(CO)_3]_2(\mu\text{-}CH_2)_4$.

The polymethylene bridged tungsten complexes, $[CpW(CO)_3]_2(\mu\text{-}CH_2)_n$ (n = 3, 4) were also prepared from the reaction of the complexes $[CpW(CO)_3(CH_2)_nX]$ (n = 3, 4; X = Br, I) with $[CpW(CO)_3]^-$.[96]

Polymethylene bridged ruthenium compounds, $[CpRu(CO)_2]_2(\mu\text{-}CH_2)_n$ (n = 2, 3, 4) were prepared from the reaction of $[CpRu(CO)_2]^-$ with the appropriate α,ω dihaloalkane. [85] These authors also prepared the methylene bridged complex, $[\{CpRu(CO)_2\}_2(\mu\text{-}CH_2)]$, containing no metal-metal bond, from the reaction of the metal carbonyl anion with dichloromethane.[85]

Polymethylene bridged complexes are of great significance, since they are models for intermediates proposed in the carbide mechanism of the Fischer-Tropsch process. (See fig 2.2.1)

2.6 The preparation of new monohaloalkyl complexes of molybdenum, tungsten and iron.

The haloalkyl complexes $[C\bar{p}M(CO)_3(CH_2)_nBr]$ (M = Mo, W; n = 3, 4) , were isolated from the reactions of the appropriate metal carbonyl anions $C\bar{p}M(CO)_3^-$ with α,ω-dibromoalkanes, $Br(CH_2)_nBr$, n = 3, 4.

The reactions were performed using 0.5 equivalents of the dibromoalkane, and the reaction mixtures heated under reflux overnight. However, the only products isolated from these reactions were the above haloalkyl complexes. No evidence for the formation of polymethylene bridged complexes, or in the case of M = Mo, and n = 3, were cyclic carbene complexes observed, as in the case of the unsubstituted cyclopentadienyl analogues.[95]

It is not known whether this is due to the bulkiness of the pentamethylcyclpentadienyl ligand blocking access by another metal carbonyl anion, thus preventing attack on the carbon atom adjacent to the bromine atom, or whether this is due to a low yield of the metal carbonyl anion in solution.

The complexes $[C\bar{p}Mo(CO)_3(CH_2)_nBr]$ (n = 3, 4) were not able to be isolated in a pure state, and were thus only identified spectroscopically. The results, however, compare well with those obtained for the analogous cyclopentadienyl complexes, and thus the assignments would appear to be correct.

The complexes are solid at room temperature, the molybdenum complexes are extremely light sensitive, and decompose to $[C\bar{p}Mo(CO)_3Br]$ on exposure to light, especially when in solution.

In contrast to the unsubstituted cyclopentadienyl complexes, the iron haloalkyl

complexes $[C\acute{p}Fe(CO)_2(CH_2)_nBr]$ (n = 3, 4), prepared from the reaction of $[C\acute{p}Fe(CO)_2]^-$ with 0.5 equivalents of α,ω dibromoalkane, were found to be crystalline solids, as opposed to the cyclopentadienyl analogues which are oils at room temperature. The complexes display remarkable stability with respect to air, temperature and light, even when in solution. No evidence for the formation of polymethylene bridged iron dimers was seen, the reason for this is not known.

Most of the reactions of $[C\acute{p}M(CO)_3]^-$ with various dihaloalkanes gave lower yields than those reported for the cyclopentadienyl complexes, this may be explained in terms of the greater nucleophilicity of the pentamethylcyclopentadienyl metal carbonyl anion in comparison with the unsubstituted cyclopentadienyl analogues.

CHAPTER THREE

3. The reactions of the complexes $[\bar{C}pM(CO)_3CH_2X]$, (M = Mo, W; X = halogen) $[\bar{C}pFe(CO)_2CH_2Cl]$ and $[\bar{C}pMo(CO)_3(CH_2)_3Br]$ with tertiary phosphines, and some attempts to prepare hydroxymethyl and carbene species.

3.1 The reactivity of halomethyl transition metal complexes towards tertiary phosphines.

Halomethyl complexes of transition metals have been found to be very susceptible to nucleophilic attack. [59] Thus Moss *et al* [62,63] investigated the reactions of cyclopentadienyl halomethyl transition metal complexes with various tertiary phosphines.

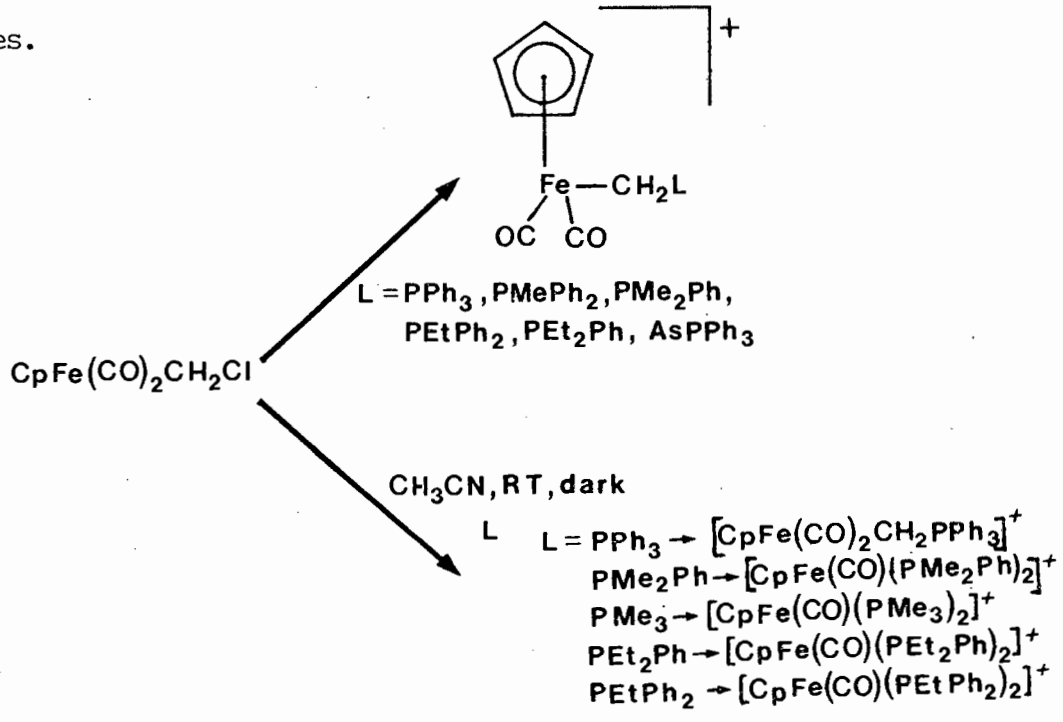


Fig 3.1.1 : A summary of the products obtained from the reactions of $[CpFe(CO)_2CH_2Cl]$ with various tertiary phosphines.

These authors found that in acetonitrile solution, less nucleophilic ligands tended to give the cationic ylide complexes, $[CpFe(CO)_2CH_2L]^+$, whereas more nucleophilic ligands gave the species $[CpFe(CO)L_2]^+$, L = tertiary phosphine ligand. The reactions of the chloromethyl complexes of Ru, Mo and W with triphenylphosphine were also investigated.

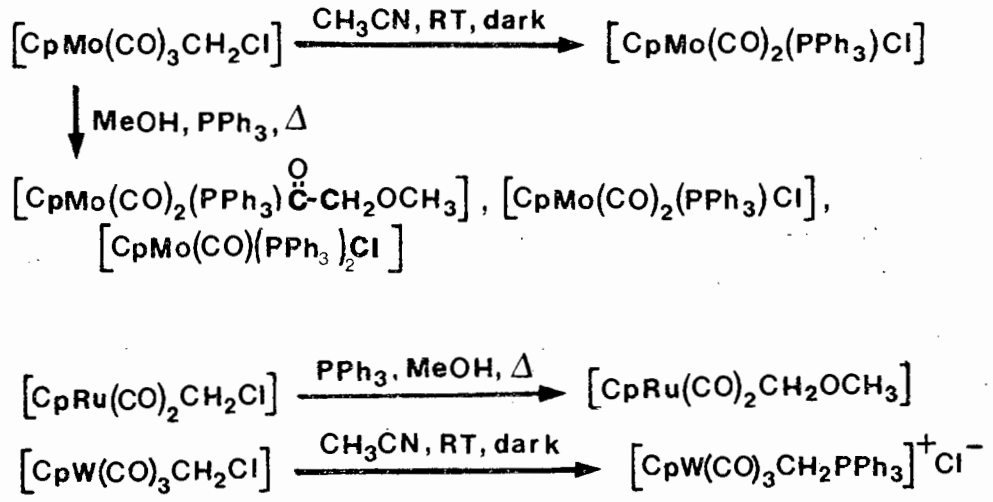


Fig 3.1.2 : The reactions of the cyclopentadienyl chloromethyl complexes of Ru, Mo and W with triphenylphosphine.

The reactions of chloromethyl complexes of platinum with PPh_3 have also been investigated, thus the cationic ylide complex *cis*-$[Pt(PPh_3)_2(CH_2PPh_3)Cl]^+$ was prepared from the reaction of *cis* or *trans*-$[Pt(PPh_3)_2(CH_2Cl)I]$ with PPh_3. This reaction involved the novel migration of Cl from a methylene group to Pt.[66]

3.2 The reactions of the complexes $[C_5Me_5Mo(CO)_3CH_2Cl]$, $[C_5Me_5W(CO)_3CH_2I]$ and $[C_5Me_5Fe(CO)_2CH_2Cl]$ with triphenylphosphine.

The reactions of the cyclopentadienyl chloromethyl complexes of Mo, W and Fe are described in the previous section.(3.1) The reactions of the analogous pentamethylcyclopentadienyl complexes with PPh_3 were investigated in order to ascertain what the difference in reactivity would be if the cyclopentadienyl ring were to be replaced by a pentamethylcyclopentadienyl ring. The reaction of $[C_5Me_5Mo(CO)_3CH_2Cl]$ (XXVI) with PPh_3 in acetonitrile in the dark for 6 days at room temperature, gave the product *cis*-$[C_5Me_5Mo(CO)_2(PPh_3)Cl]$ in moderate yield. This reaction was found to be completely analogous to that reported for the cyclopentadienyl analogue under similar conditions,[63] however , this reaction was left to

stand for 28 days, which may account for the slightly higher yield obtained, (71%) as opposed to 53% for the reaction of (XXVI) with PPh_3.

The reaction of (XXVI) with PPh_3 in methanol under reflux for 3 hours, gave the product *cis*-$[CpMo(CO)_2(PPh_3)Cl]$ in 57% yield. The methoxymethyl complex (XXV) was also isolated from this reaction in approximately 15% yield. This result was very interesting as a similar reaction with the analogous cyclopentadienyl complex gave a mixture of products, viz, $[CpMo(CO)_2(PPh_3)C(O)CH_2OCH_3]$, $[CpMo(CO)_2(PPh_3)Cl]$ and $[CpMo(CO)(PPh_3)_2Cl]$. The amounts of each complex obtained depended on the reaction time, thus a short reaction time gave mainly $[CpMo(CO)_2(PPh_3)C(O)CH_2OCH_3]$. Thus the reaction was proposed to go via the methoxymethyl complex, $[CpMo(CO)_3CH_2OCH_3]$ which then underwent carbonyl insertion, giving rise to a vacant site on the metal, at which the PPh_3 then attacked.

In the case of the reaction of (XXVI) with PPh_3 in methanol, the methoxymethyl complex was isolated as a by-product, so the reaction could conceivably go via this complex, however, carbonyl insertion would probably occur less readily than in the case of the cyclopentadienyl complex, due to steric hindrance by the methyl groups on the cyclopentadienyl ring, which would prevent access to the metal carbon bond. This would explain why a carbonyl insertion product into the methylene carbon of the methoxymethyl product was not observed.

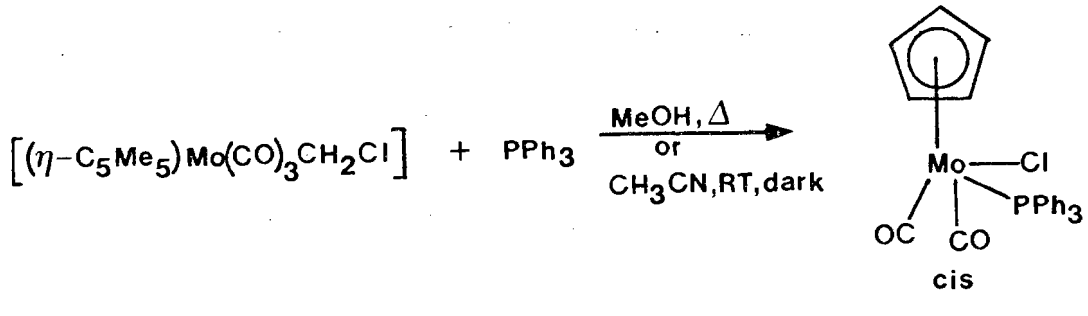


Fig 3.2.1 : Reactions of $[CpMo(CO)_3CH_2Cl]$ (XXVI) with PPh_3.

The *cis*-configuration of the product was assigned on the basis of the pattern of the carbonyl stretching frequencies in the IR spectrum, the spectrum gave bands at 1948(vs) and 1867(m) cm^{-1}, which is the same pattern as that observed for *cis*-$[CpMo(CO)_2(PPh_3)Cl]$, 1971(s) and 1883(m) cm^{-1}. [63,97]

$[C\bar{p}W(CO)_3CH_2I]$ (XXVIII) gave on reaction with PPh_3 in acetonitrile at room temperature for 18 days, the expected product, $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-$, identified according to IR, ^1H nmr and elemental analysis. The product was found to crystallise with one molecule of CH_2Cl_2 per ion pair of the salt, i.e. $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-. CH_2Cl_2$. This was verified by ^1H nmr and elemental analysis. The X-ray crystal structure of this complex was determined, see chapter 4. The X-ray crystal structure revealed that there were in fact, only 0.5 molecules of CH_2Cl_2 per molecule of the phosphorus ylide complex, a ^1H nmr spectrum of the crystals showed that the peak corresponding to the solvent of crystallisation, had, in fact, decreased by 50%. Thus it was concluded, that by leaving the crystals exposed to the atmosphere at room temperature for about one week, one half of the solvent of crystallisation had been lost.

Reaction of (XXVIII) with PPh_3 in methanol under reflux for 3 hours gave the product $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-$ in 57% yield, the methoxymethyl product (XXVII) was also isolated from this reaction in 12% yield, and (XXVIII) in 5% yield. The ionic product was recrystallised from CH_2Cl_2/hexane to give fine dark yellow needles.

These results are very similar to those obtained by Moss *et al* [62], who investigated the reactions of $[CpW(CO)_3CH_2Cl]$ with PPh_3 in methanol (reflux) and in acetonitrile in the dark at room temperature. (see fig 3.1.2)

The reaction of (XXVIII) with PPh_3 in CH_3CN was left for a shorter time than was the cyclopentadienyl complex, $[CpW(CO)_3CH_2Cl]$ [62], a slightly lower yield was obtained

for the Cp̄ complex, and a small amount of (XXVIII) was isolated. However, a direct comparison between the two reactions was not possible, as in the case of the Cp̄ complex, the iodomethyl complex was used, whereas in the Cp comp ex, reaction occurred at a chloromethyl ligand.

Graham *et al* [34] suggested that nucleophilic attack on the metal atom occurs less readily for the Cp̄ complexes as compared with the Cp complexes. Thus for the complexes $[\bar{C}pOs(CO)_2I]$ and $[CpOs(CO)_2I]$, nucleophilic attack occurred more readily on the metal atom of the Cp complex, than on the metal atom of the Cp̄ complex. See Chapter 1.2. This mat explain why the reaction of (XXVI) with PPh_3 gave only one product, viz, $[\bar{C}pMo(CO)_2(PPh_3)Cl]$, whereas in the case of the unsubstituted cyclopentadienyl analogue, three products were obtained, including $[CpMo(CO)(PPh_3)_2Cl]$, which was not detected for the Cp̄ analogue.

The reaction of (XXIX) with PPh_3 in methanol under reflux, gave the methoxymethyl product $[\bar{C}pFe(CO)_2CH_2OCH_3]$ only, in almost quantitative yield. This product was identified by comparison of the Ir and mp data with that obtained previously.[9]

The reaction of (XXIX) with PPh_3 in acetonitrile in the dark at room temperature, gave mainly starting material, (XXIX), and a small amount of hexane insoluble material. The hexane insoluble material was precipitated as the tetraphenylborate salt from methanol, giving orange needles, which were identified as $[\bar{C}pFe(CO)_2CH_2PPh_3]^+$ BPh_4^-. These results are very different from those obtained by Moss *et al* [63], who obtained $[CpFe(CO)_2CH_2PPh_3]^+$ in high yield from the reaction of $[CpFe(CO)_2CH_2Cl]$ with PPh_3 in CH_3CN in the dark at room temperature, or by heating a methanolic solution of $[CpFe(CO)_2CH_2Cl]$ and PPh_3 under reflux. Thus the methylene carbon of the halomethyl ligand would appear to be less suscepticle to nucleophilic attack in the case of the Cp̄ complex, as opposed to the Cp analogue.

3.3 Reaction of $[CpMo(CO)_3(CH_2)_3Br]$(XXX) with PPh_3.

(XXX) gave on reaction with PPh_3 in CH_3CN, after precipitation with BPh_4^-, bright orange needles as product. The product gave two bands in the ν(CO) region of the IR spectrum, of equal intensity , at 1975(s) and 1904(s) cm^{-1}. The product gave a very complicated ^1H nmr spectrum, and was thought to be a mixture of *cis* and *trans* isomers of the cyclic carbene complex shown in fig 3.3.1.

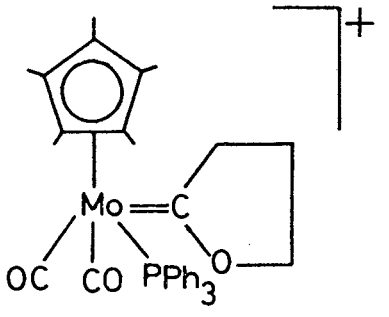


Fig 3.3.1 : Proposed product from the reaction of (XXX) with PPh_3.

Cotton and Lukehart [98] investigated the reaction of the analogous cyclopentadienyl complex, viz, $[CpMo(CO)_3(CH_2)_3Br]$ with PPh_3 .

$$[CpMo(CO)_3(CH_2)_3Br] \xrightarrow[PPh_3]{CH_3CN} [CpMo(CO)_2(PPh_3)(\eta^1\text{-}C(CH_2)_3O)]^+Br^-$$

Fig 3.3.2 : Preparation of a cyclic carbene complex.

When the reaction was performed in a concentrated solution of CH_3CN, the *cis* product precipitated out almost immediately, and was filtered off to give the *cis* cyclic carbene species in high yield, which was isolated as the BPh_4^- salt. The *trans* product was obtained by using a dilute solution of CH_3CN, the reaction mixture was stirred vigorously for one hour, and the *trans* product isolated in high yield as the BPh_4^- salt.

In the case of the Cp̄ complex, a similar route was not possible, as the product is extremely soluble in CH_3CN, and changing the amount of solvent did not appear to affect the reaction. Thus when a very concentrated solution of (XXX) in CH_3CN was used, only a small quantity of product precipitated out of solution, and was found to be identical with that obtained in previous reactions. The *cis* and *trans* isomers could not be separated, and thus a complete assignment of the ^1H nmr spectrum was not possible.

Cotton and Lukehart [98] reported *trans*-$[CpMo(CO)_2(PPh_3)(\eta^1\text{-}\overline{C(CH_2)_3O})]^+ BPh_4^-$ to give two bands in the carbonyl region of the IR spectrum at 1985(s) and 1910(vs) cm^{-1}, whereas the *cis* isomer gave peaks at 1990(vs) and 1930(s) cm^{-1}. Thus the relative intensities of the two bands in the ν(CO) region of the IR spectrum change on going from the *cis* to the *trans* isomer, the wavenumbers of the bands also shift.
In the case of the Cp̄ complex, the product exhibited two bands of equal intensity in the ν(CO) region of the IR spectrum, thus the product appears to be a mixture of *cis* and *trans* isomers.

Cotton and Lukehart [98] proposed that the reaction of $[CpMo(CO)_3(CH_2)_3Br]$ with PPh_3 went via a carbonyl insertion mechanism as described in fig 3.3.3.

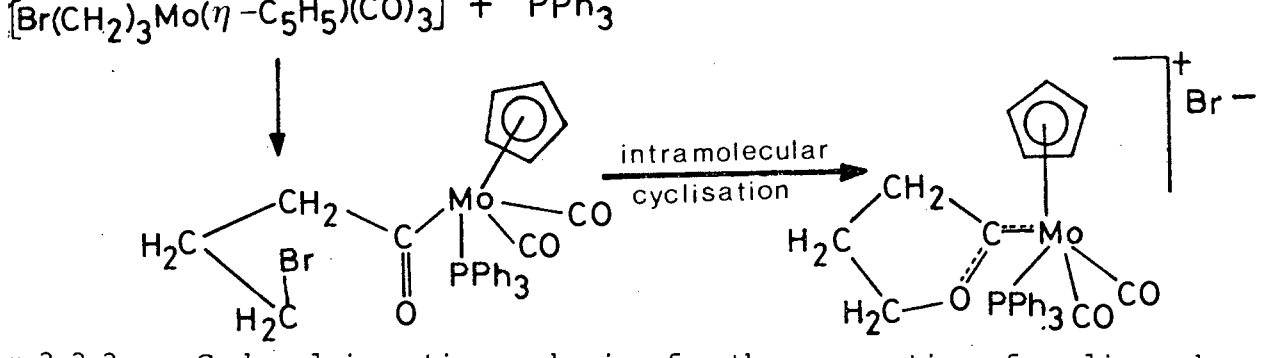


Fig 3.3.3 : Carbonyl insertion mechanism for the preparation of cyclic carbenes.

In the case of the analogous unsubstituted Cp̄ reaction, some starting material was isolated, which would seem to suggest that the reaction was slower than in the case of the Cp complex, this could be explained in terms of the Cp̄ complex(XXX)

being less susceptible to carbonyl insertion, as a result of the methyl groups on the $C\bar{p}$ ring blocking access to the metal carbon bond where carbonyl insertion occurs.

Recently, many cyclic carbene complexes of Mo have been prepared. Bailey *et al* [96] showed that the reaction of $[CpMo(CO)_3]^-$ with $I(CH_2)_3I$ in THF, or of $[CpMo(CO)_3(CH_2)_3Br]$ with LiI in THF resulted in the formation of the neutral cyclic carbene complex, $[CpMo(CO)_2I(\eta^1\text{-}\overline{C(CH_2)_3O})]$. This complex was characterised by X-ray crystallography. The complexes, $[Cp(CO)_3MoMo(CO)_2(\eta^1\text{-}\overline{C\text{-}(CH_2)_3O})Cp]$ and $[Cp(CO)_3WMo(CO)_2(\eta^1\text{-}\overline{C(CH_2)_3O})Cp]$ were also prepared.[95]

3.4 Some attempts to prepare Fischer-Tropsch intermediates.

Hydroxymethyl and carbene species have been proposed as intermediates in the Fischer-Tropsch reaction. (see chapter 2.2) The preparation of carbene species from methoxymethyl and chloromethyl transition metal complexes is described in 2.3. Hydroxymethyl transition metal complexes have not been prepared from methoxymethyl or halomethyl complexes previously, however, Roper *et al* [81,82] converted an osmium hydroxymethyl complex to a chloromethyl complex using HCl. (see fig 2.3.8). It thus seems possible that halomethyl complexes could be converted to hydroxymethyl complexes using NaOH in water. Hydroxymethyl complexes have been prepared by a number of routes, for example Nelson [33] prepared the complex $[C\bar{p}Ru(CO)_2CH_2OH]$ from the reaction of $[CpRu(CO)_3]^+$ with $NaBH_3CN$. Lin *et al* [99] prepared the analogous cyclopentadienyl complexes of iron and ruthenium, viz, $[CpFe(CO)_2CH_2OH]$ and $[CpRu(CO)_2CH_2OH]$ by a similar route. These authors converted the hydroxymethyl complexes to methoxymethyl derivatives, the hydroxymethyl derivatives, however, could not be regenerated from the methoxymethyl complexes.

3.4.1 Attempted preparation of $[CpMo(CO)_3CH_2OH]$.

A solution of (XXVI) in THF was treated with an aqueous solution of NaOH. The solution was stirred vigorously. An IR spectrum of this material showed new weak bands at 2010 and 1928 cm^{-1}, as well as strong bands due to starting material. The new product was not able to be separated from the starting material, and was therefore not characterised. More vigorous conditions led to the decomposition of the starting material, and no carbonyl containing material appeared to be present.

A similar reaction was performed using KOH instead of NaOH, the reaction proved to be very different from that described above. A hexane soluble yellow oil was isolated, which gave peaks in the ν(CO) region of the IR spectrum at 2023(w), 2012 (m), 1946(w) and 1927(s) cm^{-1}; the ^1H nmr spectrum showed many peaks between 1 and 3 δ, but the product could not be further purified, and was thus not able to be characterised.

3.4.2 Attempted preparation of $[CpMo(CO)_3CH_2OH]$.

A solution of $[CpMo(CO)_3CH_2Cl]$ in THF was treated with a solution of NaOH in water. Predominately starting material was isolated, together with a second product which displayed peaks in the carbonyl region of the IR spectrum at 2023 and 1939 cm^{-1}. The product was partially purified, the nmr spectrum, however, was very complex, exhibiting many peaks between 1.3 and 6.5 δ. The product could not be identified.

The above reaction was repeated using acetone as solvent, the IR spectrum of the product appeared to be very similar to that obtained above, as did the ^1H nmr spectrum. The product could not be identified.

3.4.3 Attempted acid hydrolysis of $[C_5H_5Mo(CO)_3CH_2OCH_3]$ (XXV) with CF_3COOH.

A solution of (XXV) in THF was treated with a mixture of CF_3COOH in water. An IR spectrum of the hexane soluble material from this reaction showed mainly starting material, with new ν(CO) bands at 2024, 1946, 1936 and 1776 cm^{-1}. The ^1H nmr spectrum gave new peaks at 5.15 and 1.47 in the ratio 1:7. This product could not be purified, but it was suspected that in fact, esterification had occurred, as the band at 1776 cm^{-1} did not disappear on treating the product with aqueous diethylamine. The reaction was repeated using different concentrations of CF_3COOH and water, the same peaks appeared each time.

In order to determine whether in fact the product was a result of an esterification reaction, a solution of (XXV) in THF was treated with CF_3COOH (excess). After quenching with aqueous diethylamine, and extraction with with n-hexane, a yellow solid was isolated, which was recrystallised from n-hexane, and identified as $[C_5H_5Mo(CO)_3CH_2OC(O)CF_3]$ according to IR, ^1H nmr and elemental analysis. The ν(CO) region of the IR spectrum was found to be identical with that obtained in previous reactions, and thus no hydrolysis had occurred, but rather esterification. Thus CF_3COOH is not a good acid to use, as it does tend to give esterification products.

3.4.4 Attempted preparation of $[C_5H_5M(CO)_3(=CH_2)]^+$, (M = Mo, W).

A solution of (XXVI) in THF was treated with $AgPF_6$. A grey precipitate appeared immediately, and the THF solution became very viscous. It appeared that, in fact, the THF solvent had polymerised, no product could be extracted from the reaction.

The reactions of (XXVI) and $[CpMo(CO)_3CH_2Cl]$ with $AgPF_6$ in acetone were investigated

CHAPTER FOUR

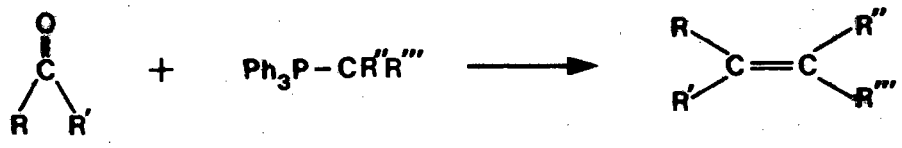
4. X-ray crystal structure of $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]^+ I^-.\frac{1}{2}CH_2Cl_2$.

4.1 Introduction

The term ylide traditionally denotes a compound in which a negatively charged carbon is bonded to a heteroatom which bears a formal positive charge.[100] Ylides in clude as heteroatom S, N, As and P.

Fig 4.1.1 : A general representation of an ylide with the ylidene resonance form.

Ylides are commonly used in organic synthesis for the preparation of alkenes from carbonyl compounds, thus forming new C-C bonds. See fig 4.1.2.



R,R',R'',R''' = alkyl, aryl or H

Fig 4.1.2 : Reaction of an organic carbonyl compound with an ylide.

Ylides have recently been used as ligands in transition metal organometallic chemistry,[100] a variety of complexation modes being known : see fig 4.1.3.

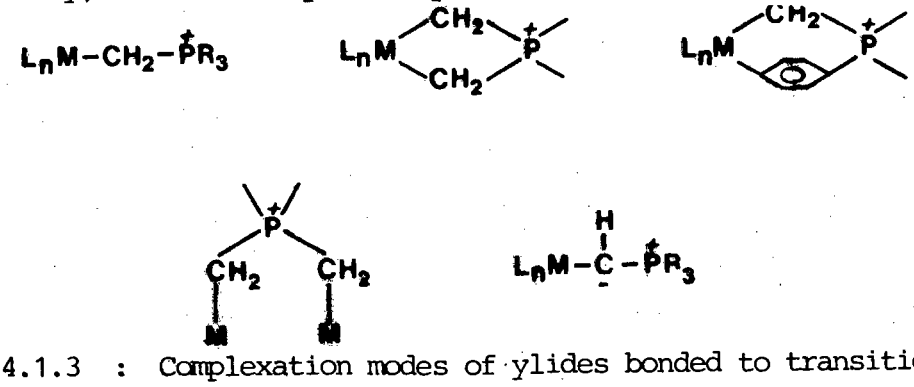
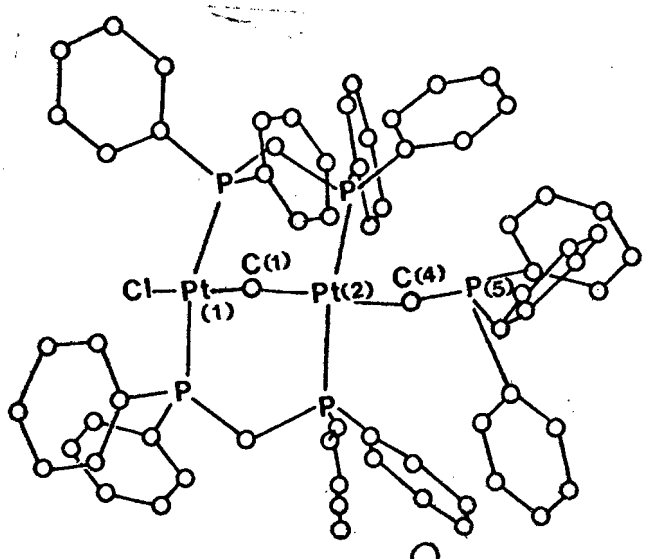


Fig 4.1.3 : Complexation modes of ylides bonded to transition metals.

Such diversity in complexation arises from the wide variety of ylide ligands known. Ylide complexes of a number of transition metals are known.[100-102]

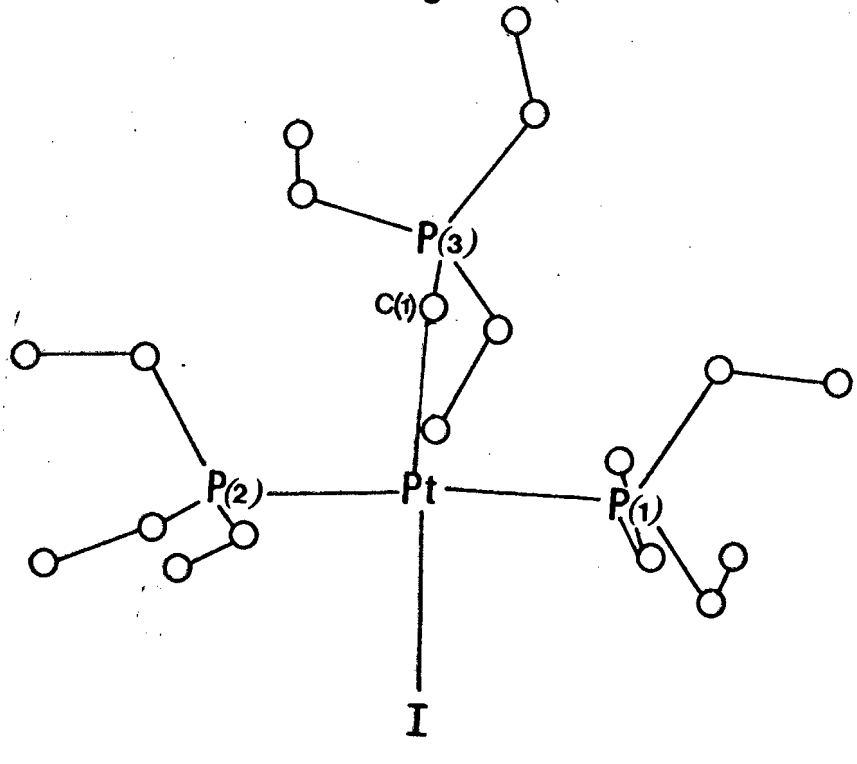
Phosphorus atoms in transition metal ylide complexes generally retain the tetrahedral geometry of the phosphonium cation, but the P-C bond of the methylene carbon is shortened, indicating a increase in bond order.[103]

In the present study, the crystal and molecular structure of the complex $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]^+ I^-.\frac{1}{2}CH_2Cl_2$ is investigated. The crystal structures of a number of phosphorus ylide complexes analogous to this structure have been investigated. See fig 4.1.4.



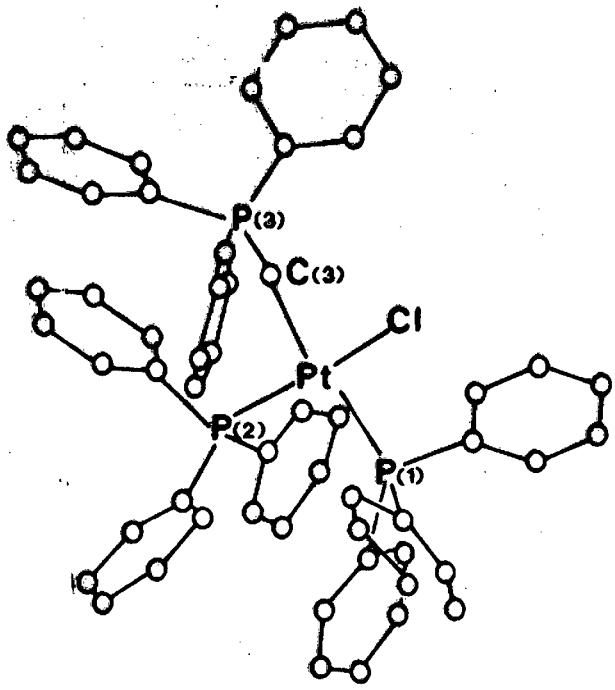
Pt(2)-C(4) = 2.10-2.12 Å
C(4)-P(5) = 1.84 Å
Pt(2)-C(4)-P(5) = 129°

(XXXI) [104]



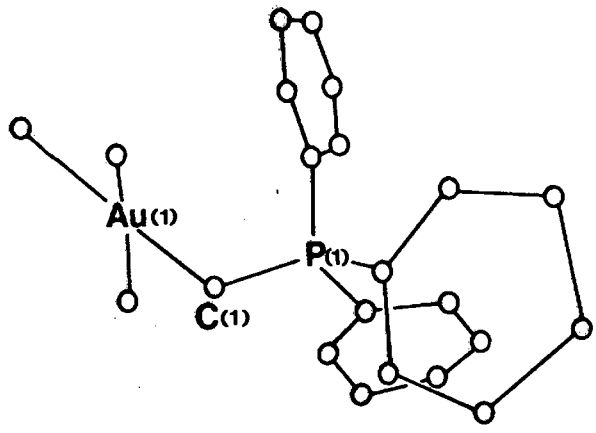
Pt(1)-C(1) = 2.08 Å
C(1)-P(3) = 1.77 Å
Pt(1)-C(1)-P(3) = 118°

(XXXII) [105]



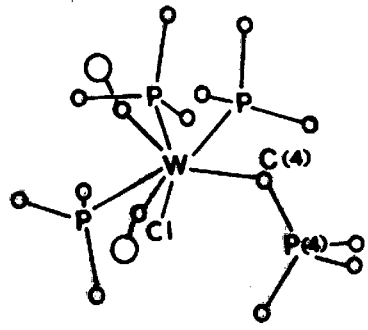
Pt(1)-C(3) = 2.12 Å
C(3)-P(3) = 1.80 Å
Pt(1)-C(3)-P(3) = 121.8°

(XXXIII) [106]



Au(1)-C(1) = 2.15 Å
C(1)-P(1) = 1.76 Å
Au(1)-C(1)-P(1) = 114.9°

(XXXIV) [107]



C(4)-P(4) = 1.75 Å
W(1)-C(4) = 2.30 Å
W(1)-C(4)-P(4) = 126.4 Å

(XXXV) [108]

Fig 4.1.4 : X-ray crystal structures of selected phosphorus ylide transition metal complexes.

The X-ray crystal structural determination of a manganese double ylide complex has also been investigated.[109]

The crystal and molecular structures of (XXXI) - (XXXV) all contain a phosphorus ylide ligand, and have many structural features in common, they will thus be discussed together.

(XXXI) was synthesised from the reaction of $[H\text{-}Pt(\mu\text{-}dppm)_2Pt(PPh_3)]^+ PF_6^-$ with excess diazomethane in dichloromethane, resulting in methylene insertion into the Pt-Pt bond, and a Pt-P bond. Pt-C bond distances for individual methylene carbons were not reported, rather the bond distances for the three Pt-methylene carbon bonds were reported to be in the range 2.10-2.12 Å.

(XXXII) was isolated from the reaction of $[Pt(PEt_3)_4]$ with CH_2I_2; (XXXIII) could be prepared either directly from the reaction of $[Pt(PPh_3)_4]$ with $ClCH_2I$, or from the reaction of $[Pt(PPh_3)_2(CH_2Cl)I]$ with PPh_3. The gold phosphorus ylide complex (XXXIV) was prepared by reacting $[(Ph_3P)AuMe_3]$ with triphenylmethylenephosphorane in ether. (XXXV) was produced by transfer of a PMe_3 ligand to the $W{=}CH_2$ system in $[W(=CH_2)(PMe_3)_4Cl]^+ CF_3SO_3^-$, when this complex was treated with CO (1 atm. pressure).

Structures (XXXI)-(XXXIV) crystallise in monoclinic space groups, while (XXXV) crystallises in the primitive space group $\bar{P}_1$. These complexes all exhibit tetrahedral geometries about the P atom of the phosphorus ylide ligand, the C-P bond distances (methylene carbon to phosphorus) are all very similar, and the M-C-P bond angles for the phosphorous ylide ligand are all larger than the expected tetrahedral value. None of the above complexes exhibit any unusual intermolecular interactions.

Complex (XXXV) is the first reported structure of a tungsten ylide complex, the W atom is 7 co-ordinate, and the bond distance W(1)-C(4) (see fig 4.1.4) of 2.30 Å is reported to be that of a single bond.

4.2 General experimental and computational procedures.

4.2.1 The synthesis of $[C\tilde{p}W(CO)_3CH_2PPh_3]^+ I^-.\frac{1}{2}CH_2Cl_2$.

$[C\tilde{p}W(CO)_3CH_2PPh_3]^+ I^-. CH_2Cl_2$ (XXXVI) was prepared by reacting $[C\tilde{p}W(CO)_3CH_2I]$ with PPh_3 (excess) in acetonitrile in the dark at room temperature for 18 days. The solution was protected from light using foil, and the orange solution gradually darkened to an orange/red colour. The solvent was removed under reduced pressure, and the oily residue recrystallised rpeatedly from mixtures of CH_2Cl_2 and n-hexane in order to obtain crystals of suitable quality. Chapter 5.6 gives detalis of the characterisation of this complex.

4.2.2 Preliminary X-ray analysis.

Single crystals obtained as in 4.2.1 above were selected, checked for reflection quality, and then cut to appropriate dimensions in order to minimise absorption effects.

Oscillation and Weissenberg (zero and first layer) photographs were taken using a non-integrating Stoe (Heidelberg) goniometer attatched to a camera of radius 28.65 mm. Ni-filtered CuK_α radiation (λ = 1.5418 Å) was used.

The X-ray generator, model Philips PW1120 was operated at 0.8 kW (20 mA and 40 kV) X-ray films (3M) were processed in the usual manner with Kodak X-ray developer and fixer solutions.

These photographs yielded the unit cell dimensions and the space group symmetry. (See table 4.1)

The density was estimated to be about 1.5 to 1.6 g/cm^3 from flotation in bromobenzene.

4.2.3 Determination of space group and unit cell parameters.

A monoclinic space group was revealed by oscillation and Weissenberg photography. The approximate cell dimensions as obtained from the photographs were :

$a = 16.93$ Å

$b = 12.40$ Å

$c = 18.33$ Å

$\beta = 78°$

$Z = 4$ *

* Z = total number of molecules in the unit cell, this was determined from the relation :

$Z \times Mr = N\ Dm\ abc \sin\beta \times 10^{-24}$

Mr = molecular mass ($g\ mol^{-1}$)

a,b,c = unit cell lenghths (Å)

N = Avogadro's number = 6.023×10^{23}

Dm = density measured ($g\ cm^{-3}$)

abc sin β = volume of unit cell ($Å^3$)

From the Weissenberg photographs, the conditions for non-extinction of reflections was determined as :

00ℓ	$\ell = 2n$
$h00$	$h = 2n$
$h0\ell$	$h+\ell = 2n$

Hence the space group is $P2_{1/n}$.[110]

Table 4.1

Crystal data and experimental and refinement parameters for $[(\eta\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]^+I^-.\frac{1}{2}CH_2Cl_2$.

Molecular formula	$C_{32}H_{32}O_3PIW.\frac{1}{2}CH_2Cl_2$
Mr (g mol^{-1})	848.80
Space group	$P2_{1/n}$
a (Å)	16.61 (8)
b (Å)	11.738 (6)
c (Å)	18.126 (9)
β (°)	101.74 (2)
V ($Å^3$)	3461 (1)
Dm (Mgm^{-3})	1.6
Dc (Mgm^{-3}, for Z = 4)	1.50
F [000]	1664
μ (Mok_α)	40.64 cm^{-1}
Melting point (K)	407 - 413
Composition	see characterisation data, chapter 5.6.4

Data collection:

Crystal dimensions (mm)	.28 x .18 x .10
Scan mode	ω-2θ
Scan width (°)	1.2
Scan speed (° s^{-1})	0.04
Range scanned (2θ°)	7 - 46
Stability of standard reflections (%)	4.8
Number of reflections collected	4647
Number of reflections observed with $I_{(rel)} > 2\sigma I_{(rel)}$	3310

Refinement :

Number of variables	207
$R = \frac{\Sigma \lvert \lvert Fo \rvert - \lvert Fc \rvert \rvert}{\Sigma \lvert Fo \rvert}$	0.076

U_{iso} of hydrogen atoms :

phenyl hydrogens ($Å^2$)	0.08 (2)
methyl hydrogens ($Å^2$)	0.08 (2)
methylene hydrogens ($Å^2$) (of ylide ligand)	0.10 (2)

Table 4.2

Fractional atomic co-ordinates ($x10^4$) and thermal parameters ($Å^2 \times 10^4$) for non hydrogen atoms.

	$x/_A$	$y/_B$	$x/_C$	U
W1	2357(1)	1940(1)	-22(1)	482 *
I1	1512(1)	5051(1)	7365(1)	720 *
P1	924(3)	1275(5)	8265(3)	414 *
Cl1	6097(10)	2372(24)	8838(9)	1316 *
Cl2	6072(11)	2222(38)	7375(10)	2238 *
O2	813(12)	3224(18)	10159(11)	1003(61)
O3	2674(12)	-679(20)	9698(12)	1028(65)
O4	1894(13)	802(20)	11365(13)	1157(73)
C1	1902(11)	1946(19)	8670(11)	476(49)
C2	1391(16)	2640(22)	10043(14)	685(69)
C3	2515(16)	286(25)	9775(14)	744(75)
C4	2068(15)	1221(23)	10809(15)	715(70)
C5	5566(29)	1993(46)	7374(27)	687(130)
C111	2996(13)	3728(19)	9986(12)	503(53)
C121	3105(12)	3280(17)	10769(11)	467(51)
C131	3630(12)	2287(17)	10769(11)	443(51)
C141	3778(12)	2132(18)	10055(11)	490(52)
C151	3397(11)	3025(19)	9568(11)	453(47)
C112	2551(14)	4816(21)	9756(13)	648(66)
C122	2851(15)	3811(23)	11401(13)	703(69)
C132	4004(15)	1640(22)	11446(13)	669(68)
C142	4351(16)	1282(23)	9854(15)	775(75)
C152	3495(15)	3286(21)	8799(12)	645(65)

	$x/_A$	$y/_B$	$z/_C$	U
C11	19(10)	2001(19)	8443(11)	517(52)
C12	-712(10)	1468(19)	8432(11)	553(58)
C13	-1379(15)	2050(23)	8500(13)	716(68)
C14	-1360(17)	3240(25)	8585(15)	830(80)
C15	-665(16)	3806(27)	8561(15)	862(83)
C16	54(15)	3202(23)	8487(13)	718(69)
C21	827(10)	1232(16)	7251(10)	414(47)
C22	162(10)	656(16)	6816(10)	549(57)
C23	49(14)	704(21)	6032(13)	634(64)
C24	540(14)	1303(20)	5708(14)	629(63)
C25	1187(15)	1948(24)	6106(14)	717(67)
C26	1330(13)	1889(21)	6893(12)	594(57)
C31	909(10)	201(15)	8579(10)	363(15)
C32	1292(10)	-999(15)	8179(10)	578(59)
C33	1307(16)	-2122(25)	8448(15)	782(75)
C34	1007(15)	-2403(24)	9058(14)	755(75)
C35	661(15)	-1643(22)	9448(14)	726(72)
C36	621(13)	-493(20)	9201(12)	557(58)

* $U_{equiv} = \frac{1}{3}\{U_{11}\sin^2\alpha + U_{22}\sin^2\beta + U_{33}\sin^2\gamma + 2U_{23}\sin\beta\sin\gamma\cos\alpha + 2U_{13}\sin\alpha\cos\beta\sin\gamma + 2U_{12}\sin\alpha\sin\beta\cos\gamma\} \div \{1+2\cos\alpha\cos\beta\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma\}$

$U = \frac{1}{3}\{$trace of the orthogonal Uij matrix$\}$

Since $\alpha = 90°$ and $\gamma = 90°$

Uequiv reduces to : $U_{equiv} = \frac{\frac{1}{3}\{U_{11}+U_{22}\sin^2\beta+U_{33}+2U_{13}\cos\beta\}}{\{1-\cos^2\beta\}}$

4.2.4 Diffractometer data collection.

Single crystals of suitable quality were mounted on brass pins using glass fibres and dental glue. Three crystals were sent to Mr J. Albain at the National Physical research Laboratory, CSIR (Pretoria) for a diffractometer data collection

The relative intensities of the reflections were measured on a Philips PW1100 computer controlled four circle diffractometer. A Philips PW1130 X-ray generator, operating at 1kW (20mA and 59kV) provided graphite monochromated MoK_{α} radiation. (λ = 0.7107 Å). Accurate cell dimensions were obtained by least squares refinement from the setting of 25 higher order reflections accurately centered on the diffractometer. The three dimensional intensity data were then collected employing the ω-2θ scan technique.

The intensities of three reference reflections were monitored every 68 reflections throughout the data collection this ensured instrument stability, and monitored any crystal decomposition. The intensities of the reference reflections remained constant to within 4.8% of their mean value. (See table 4.1)

The diffractometer data set contained 4647 unique reflections within the range $7<2\theta<46°$. Lorentz-polarisation corrections were automatically applied to all reflection data, although no corrections for absorption were made.

4.2.5 Computation.

All computations were performed on a Sperry 1100/81 computer at the University of Cape Town.

The program SHELX [111] was used for crystallographic data reduction, structure

solution and refinement. Features of this program which were utilised included data reduction, full matrix least squares refinements, geometric positioning and constrained refinement of hydrogen atoms, analysis of variance and Fourier syntheses with peak search and structure factor listings.

The agreement factor between observed (Fo) and calculated (Fc) structure factors is expressed by the conventional residual index (R) [112] defined as :

$$R = \frac{\Sigma \left| |Fo| - Fc \right|}{\Sigma |Fo|} = \frac{\Sigma |\Delta|}{\Sigma |Fo|}$$

A low value of R (<10%) is indicative of a correctly refined structure.

Atomic radii used were those of Pauling [113]. Complex neutral atom scattering factors were taken from Cromer and Mann [114] for all non-hydrogen atoms, and from Stewart, Davison and Simpson [115] for hydrogen, with dispersion corrections from Cromer and Libermann.[116]

The program XANADU [117] was used for calculations of bond distances, bond angles and least squares planes.

The program PLUTO [118] was used for the plotting of the final structure.

4.2.6 Solution and refinement of the structure.

Of the 4647 reflections collected, 3310 with $I_{rel} < 2\sigma\ I_{rel}$ were considered as observed. The standard error of $2\sigma\ I_{rel}$ in the relative integrated intensity, I_{rel}, was calculated as follows :

$$I_{rel} = (Npk + Nbg + N \cdot instr)^{\frac{1}{2}}$$

Npk = gross peak count for a specific reflection

Nbg = background count as measured on either side of the peak.

$$N\ instr = (0.02(Npk - Nbg))^2$$

A three dimensional Patterson vector map was computed in order to locate the tungsten-tungsten peaks, and hence the atomic co-ordinates. A vector grid of the general positions for the space group $P2_{1/n}$ was constructed from which vector co-ordinates were derived. [110] Thus for a tungsten atom located at the general positions x,y,z, the W x W vectors are given by :

Vector positions	Multiplicity
0 , 0 , 0	4
½ + ½X, ½ + 2y, ½ + ½z	2
½ + 2x, ½, ½ + 2z	2
½ - 2x, ½ - ½y, ½ + 2z	2
½, ½ - 2y, ½	2
2x, 2y, 2z	1
-2x, -2y, -2z	1
1 - 2x, 1 + 2y, 1 - 2z	1
1 + 2x, 1 - 2y, 1 + 2z	1

Thus the x, y, z co-ordinates of W were found, and the atom inserted in a Fourier synthesis. Subsequent difference syntheses revealed the positions of all remaining non-hydrogen atoms, except for those of the solvent of crystallisation, CH_2Cl_2. The final full matrix least squares refinement was carried out treating W, I, Cl, and P anisotropically, all remaining non-hydrogen atoms were treated isotropically. The hydrogen atoms on the phenyl rings were constrained to ride at 1.00 Å from their respective carbon atoms, their positions being dictated by the geometry of the sp^2 hybridised carbons of the phenyl rings. The methylene hydrogens of the phosphorus ylide ligand were placed at 1.00 Å from the carbon atom C1, their positions being dictated by the sp^3 hybridisation

of the carbon atom. (See 4.3, Structure description and discussion).

The hydrogen atoms of the methyl groups attatched to the cyclopentadienyl ring were incorporated, with the methyl groups being treated as rigid tetrahedral fragments. The isotropic temperature factors of the phenyl hydrogens and the hydrogens of the methylene carbon of the phosphorus ylide ligand were treated as a single parameter, as were the temperature factors of the methyl protons.

In the final cycle, the mean e.s.d. in the parameters of the non-hydrogen atoms was 100 times greater than the average parameter shift, while the difference map was smooth, except next to the tungsten and iodine atoms, where the largest residual peaks were 2.00 electrons per $\mathring{A}^3$.

4.2.7 Location of the solvent of crystallisation.

A difference map obtained after the insertion of the ion pair $[C\hat{p}W(CO)_3CH_2PPh_3]^+I^-$ revealed the solvent of crystallisation, CH_2Cl_2, to be slightly disordered, with the electron density of the Cl2 atom smeared into two peaks. (See fig 4.3.3) In addition, the electron density map showed the electron densities of the carbon and chlorine atoms to be about half the expected weight. A ^1H nmr spectrum obtained of the crystals at this stage (approximately 1 month after they had been prepared and characterised by ^1H nmr, IR, and elemental analysis) showed that the relative intensity of the CH_2Cl_2 proton peak had in fact decreased by about 50%, thus half of the solvent of crystallisation had been lost.

The solvent molecule was subsequently inserted into a difference Fourier in the following manner :
The disorder was modelled by placing the Cl2 atom at the midpoint of it's resultant electron density (see fig 4.3.3), and the entire molecule inserted

Table 4.3

Uij values for atoms treated anisotropically with estimated e.s.d.'s in parentheses. ($Å^2 x 10^4$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	533(5)	453(5)	405(5)	30(5)	-39(4)	-106(5)
I1	902(13)	474(9)	759(11)	54(9)	104(10)	35(9)
P1	440(31)	395(30)	363(28)	-30(24)	-24(23)	-4(25)
C11	709(100)	2716(293)	549(88)	-629(132)	181(75)	-449(136)
C12	700(114)	5454(607)	626(106)	-173(216)	274(88)	-580(222)

Table 4.4

Bond angles (°) for all non-hydrogen atoms with estimated e.s.d.'s in parentheses.

C2-W1-C1	87.5 (.9)
C3-W1-C1	81.0 (.9)
C3-W1-C2	126.6 (1.1)
C4-W1-C1	137.2 (.9)
C4-W1-C2	77.2 (1.1)
C4-W1-C3	77.0 (1.1)
C111-W1-C1	93.2 (.7)
C111-W1-C2	90.0 (.9)
C111-W1-C3	142.3 (.9)
C111-W1-C4	125.9 (.9)
C121-W1-C1	130.5 (.7)
C121-W1-C2	91.3 (.9)

Table 4.4 (cont.)

C121-W1-C3	134.4 (.9)
C121-W1-C4	90.1 (.9)
C121-W1-C111	37.3 (.7)
C131-W1-C1	133.4 (.7)
C131-W1-C2	125.4 (.9)
C131-W1-C3	98.4 (.9)
C131-W1-C4	86.2 (.9)
C131-W1-C111	59.3 (.7)
C131-W1-C121	36.5 (.7)
C141-W1-C1	100.0 (.7)
C141-W1-C2	147.0 (1.0)
C141-W1-C3	86.4 (.9)
C141-W1-C4	114.5 (.9)
C141-W1-C111	57.7 (.7)
C141-W1-C121	59.4 (.7)
C141-W1-C131	34.2 (.7)
C151-W1-C1	77.7 (.7)
C151-W1-C2	118.8 (.9)
C151-W1-C3	109.3 (.9)
C151-W1-C4	114.3 (.9)
C151-W1-C111	33.9 (.7)
C151-W1-C121	59.9 (.7)
C151-W1 C131	58.3 (.7)
C151-W1-C141	35.2 (.7)
C11-P1-C1	115.5 (.9)
C21-P1-C1	107.9 (.8)

Table 4.4 (cont.)

C21-P1-C11	106.7 (.9)
C31-P1-C1	110.6 (.9)
C31-P1-C11	109.1 (.9)
C31-P1-C21	106.6 (.8)
P1-C1-W1	119.0 (1.0)
O2-C2-W1	170.3 (2.2)
O3-C3-W1	174.1 (2.3)
O4-C4-W1	176.9 (2.4)
C121-C111-W1	70.0 (1.1)
C151-C111-W1	74.4 (1.3)
C151-C111-W1	109.5 (1.8)
C112-C111-W1	124.4 (1.5)
C112-C111-C121	121.7 (1.9)
C112-C111-C151	128.8 (2.0)
C111-C121-W1	72.7 (1.1)
C131-C121-W1	72.6 (1.1)
C131-C121-C111	103.8 (1.7)
C122-C121-W1	125.4 (1.5)
C122-C121-C111	127.3 (2.0)
C122-C121-C131	128.3 (1.9)
C121-C131-W1	70.9 (1.1)
C141-C131-W1	73.3 (1.2)
C141-C131-C121	109.1 (1.8)
C132-C131-W1	126.8 (1.5)
C132-C121-C121	124.4 (1.9)
C132-C131-C141	126.2 (2.0)

Table 4.4 (cont.)

C131-C141-W1	72.5 (1.2)
C151-C141-W1	73.8 (1.1)
C151-C141-C131	110.0 (1.8)
C142-C141-W1	127.7 (1.6)
C142-C141-C131	124.6 (2.0)
C142-C141-C151	124.7 (2.0)
C111-C151-W1	71.7 (1.2)
C141-C151-W1	71.0 (1.2)
C141-C151-C111	107.6 (1.7)
C152-C151-W1	129.4 (1.5)
C152-C151-C111	123.7 (2.0)
C152-C151-C141	128.1 (1.9)
C12-C11-P1	123.4 (.6)
C16-C11-P1	116.9 (1.5)
C16-C11-C12	119.1 (1.3)
C13-C12-C11	121.4 (1.4)
C14-C13-C12	121.3 (2.5)
C15-C14-C13	119.4 (2.9)
C16-C15-C14	120.2 (3.0)
C15-C16-C11	118.5 (2.4)
C22-C21-P1	118.9 (.5)
C26-C21-P1	121.3 (1.3)
C26-C21-C22	119.1 (1.1)
C23-C22-C21	118.9 (1.2)
C24-C23-C22	120.9 (2.2)
C25-C24-C23	123.3 (2.4)

Table 4.4 (cont.)

C26-C25-C24	117.0 (2.4)
C25-C26-C21	120.6 (2.1)
C36-C31-P1	121.8 (1.4)
C36-C31-C32	122.1 (1.2)
C33-C32-C31	115.0 (1.3)
C34-C33-C32	122.3 (2.6)
C35-C34-C33	122.8 (2.8)
C36-C35-C34	117.8 (2.5)
C35-C36-C31	120.0 (2.2)
Cl2-C5-Cl1	110.6 (3.0)

Table 4.5

Bond lengths in Å with e.s.d.'s in parentheses.

(for atom numbering scheme see fig 4.3.1)

W-C1	2.34 (2)
W-C2	1.83 (3)
W-C3	2.00 (3)
W-C4	1.87 (3)
W1-C111	2.35 (2)
W1-C121	2.31 (2)
W1-C131	2.34 (2)
W1-C141	2.35 (2)
W1-C151	2.38 (2)
C1-P1	1.82 (2)
C2-O2	1.23 (3)
C3-O3	1.18 (3)
C4-O4	1.21 (3)
P1-C11	1.81 (2)
P1-C21	1.81 (2)
P1-C31	1.83 (2)
C111-C121	1.49 (3)
C121-C131	1.46 (3)
C131-C141	1.38 (3)
C141-C151	1.43 (2)
C111-C151	1.38 (3)
C111-C112	1.49 (3)
C121-C122	1.44 (3)

Table 4.5 (cont.)

C131-C132	1.47 (3)
C141-C142	1.48 (3)
C151-C152	1.47 (3)
C11-C12	1.36 (1)
C12-C13	1.33 (3)
C13-C14	1.41 (4)
C14-C15	1.34 (4)
C15-C16	1.42 (3)
C11-C16	1.41 (3)
C21-C22	1.40 (1)
C22-C23	1.40 (3)
C23-C24	1.30 (3)
C24-C25	1.39 (3)
C25-C26	1.40 (3)
C21-C26	1.39 (3)
C31-C32	1.41 (1)
C32-C33	1.40 (3)
C33-C34	1.34 (3)
C34-C35	1.34 (3)
C35-C36	1.42 (3)
C31-C36	1.36 (3)

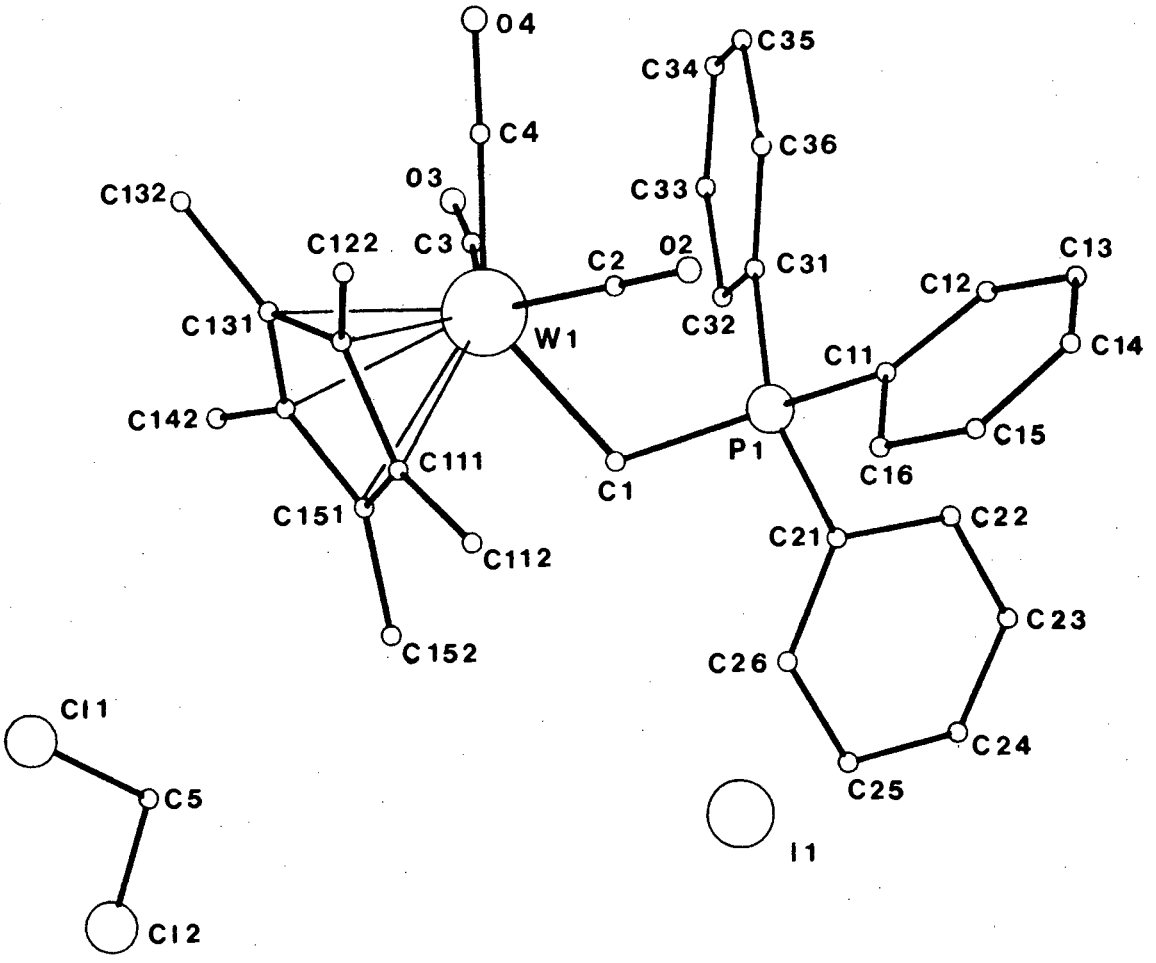


Fig 4.3.1 : Perspective view of $[C_5H_5W(CO)_3CH_2PPh_3]^+ I^-.\frac{1}{2} CH_2Cl_2$, giving atom numbering scheme.

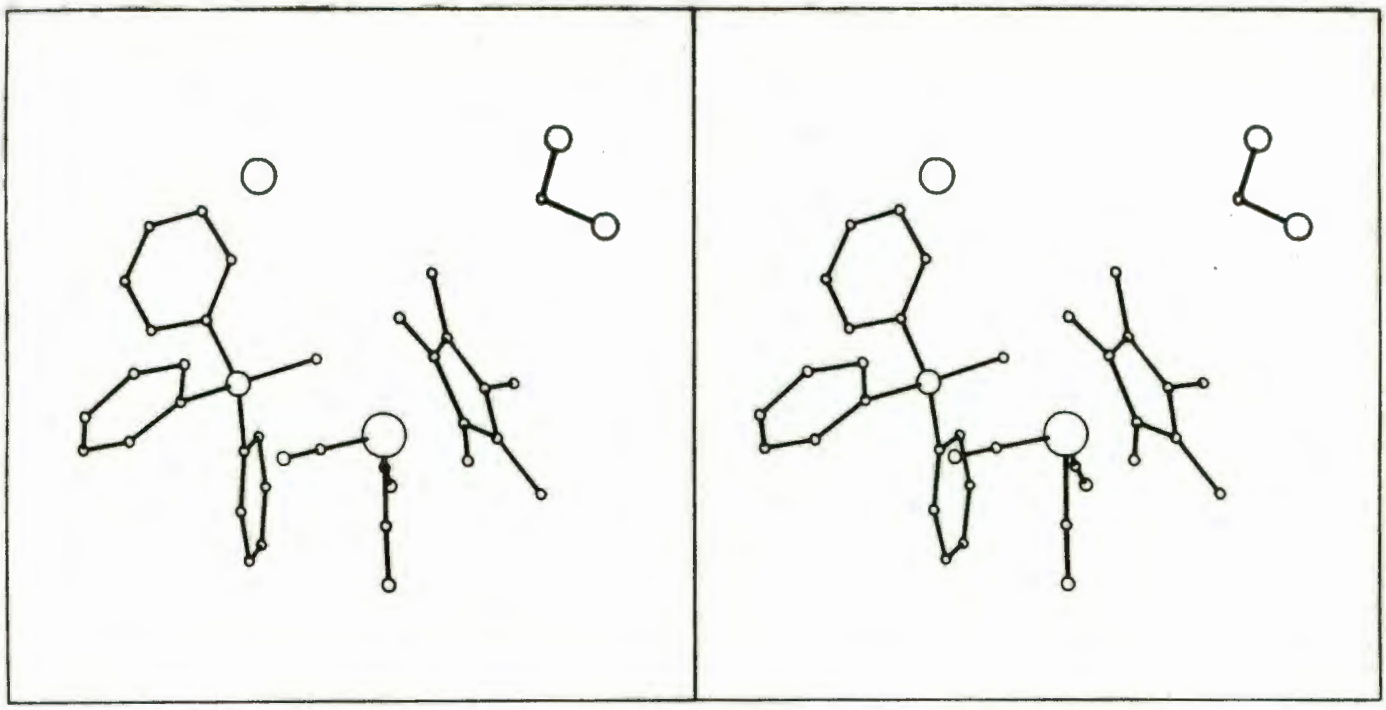


Fig 4.3.2 : Stereo view of $[CpW(CO)_3CH_2PPh_3]^+ I^- . \frac{1}{2} CH_2Cl_2$.

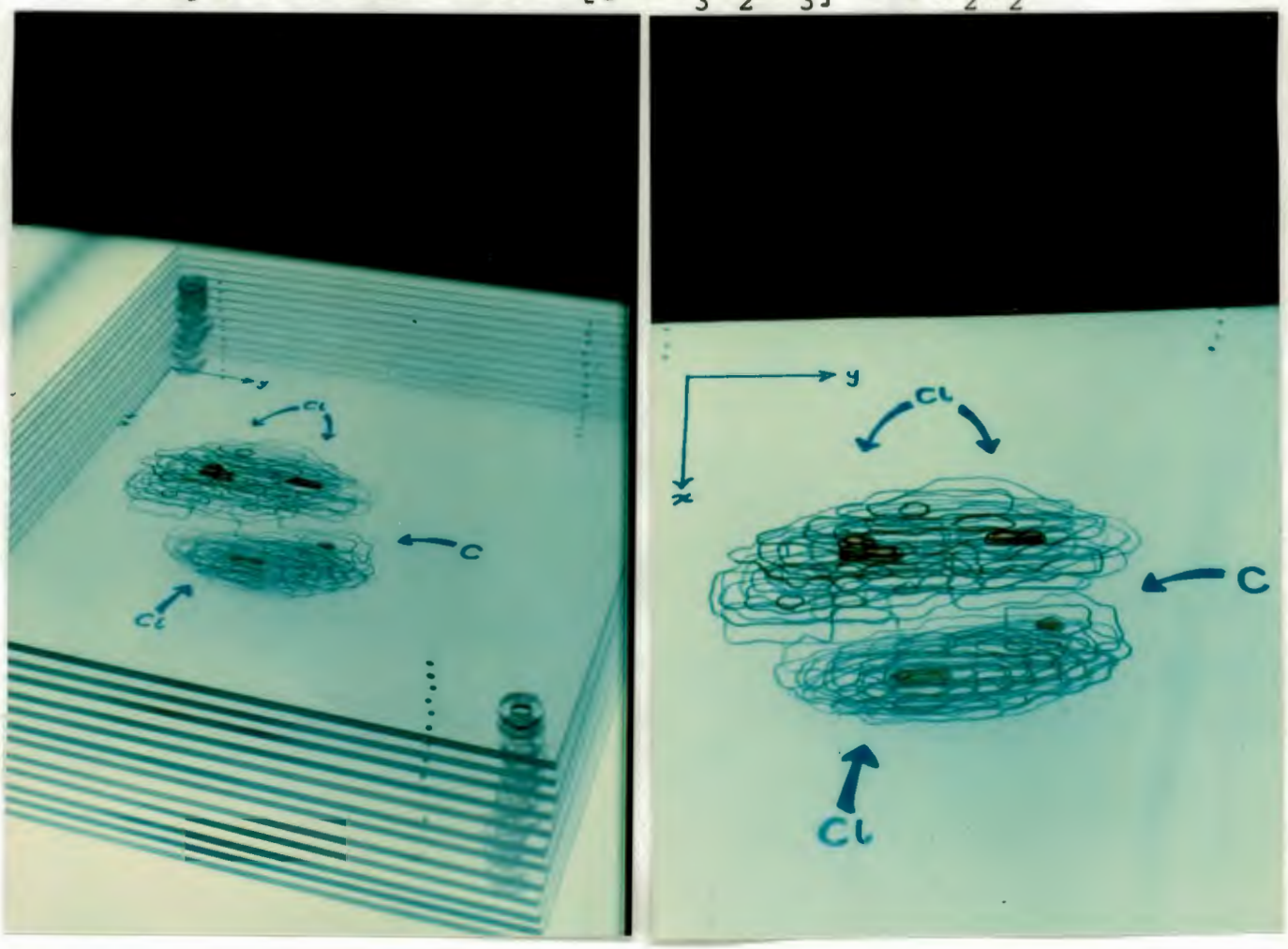


Fig 4.3.3 : Electron density map of the solvent of crystallisation, CH_2Cl_2.

at site occupancy factor one half, to account for the observed loss. The chlorine atoms were inserted anisotropically, and the carbon atom (C5, see fig 4.3.1) isotropically. The hydrogen atoms were incorporated at calculated positions, 1.00 Å from the carbon atom. Successful refinement has vindicated this approach.

4.2.8 Calculation of mean planes.

A XANADU [117] program was used to calculate the mean planes for each of the three phenyl rings on the phosphorus ylide ligand, and the mean plane described by the carbon atoms of the pentamethylcyclopentadienyl ring.

Table 4.6 gives the standard deviations from planarity (mean plane) of each carbon atom describing the pentamethylcyclopentadienyl ring, and the deviation from the mean plane of the ring of each of the methyl substituents.

4.3 Structure description and discussion.

A perspective view of $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-.\frac{1}{2}CH_2Cl_2$ is shown in figure 4.3.1, figure 4.3.2 gives a stereo view of the structure.

The structure consists of discrete ion pairs of the salt $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-$, four per unit cell in the general positions generated by the space group $P2_{1/n}$ with no unusually short intermolecular interactions. The pentamethylcyclopentadienyl ring is bonded to the tungsten atom in an η^5 manner. The $C\bar{p}$ ring formally occupies 3 co-ordination sites , thus making the W atom of the cation $[C\bar{p}W(CO)_3CH_2PPh_3]^+$ 7-co-ordinate.

The mean plane of the carbon atoms of the cyclopentadienyl ring is given in table 4.6, with no significant deviations from planarity. The methyl substituents

Table 4.6

Equation of plane of pentamethylcyclopentadienyl ring.

(See fig 4.3.1 for numbering scheme)

$$.8221X_o + .5621Y_o + .0910\ Z_o = 8.0129$$

$$13.0663X + 6.5975Y + 1.6501\ Z = 8.0129$$

(a)

Atom	Deviation from plane (A)
C111	.0091
C121	-.0148
C131	.0160
C141	-.0107
C151	.0003

(b)

C112	.1075
C122	.1079
C132	.1896
C142	.1441
C152	.1737

Mean deviation from plane = .1446

Standard deviation = .0335

on the cyclopentadienyl ring, however, show a significant deviation from the mean plane of the cyclopentadienyl ring, these are bent away from the W atom, all above the plane of the cyclopentadienyl ring. This phenomenon has been noted in many structures of complexes containing pentamethylcyclopentadienyl rings.[119] This phenomenon has been attributed to both steric and electronic effects. The bonding in the pentamethylcyclopentadienyl ring is unremarkable in terms of the W-C bond distances, the C-C bond distances within the cyclopentadienyl ring, and the ring C to methyl C bond distances. Table 4.7 compares the W-C and C-C bond distances in some structures containing the Cp-W or Cp̄-W moiety.

Three carbonyl groups are bonded to the tungsten atom, the W-C-O bond distances being very similar to those reported previously. (See references in table 4.7 and 4.8 , and other structures containing W-CO terminal bonds.)

The W atom is bonded to a methylene carbon C1, which is in turn bonded to a triphenylphosphine substituent, giving rise to a phosphorous ylide complex. The phenyl rings of the triphenylphosphine ligand are planar within the limits of experimental error.

The W1-C1 bond distance of 2.34 (2) Å is compared with the distances quoted for the tungsten to carbon single bonds in other structures in table 4.8. This bond distance is similar to the bond distance for complex (XXXV) (fig 4.1.4), which also contains a phosphorous ylide ligand bonded to tungsten in a +2 oxidation state. In the cation $[Cp\bar{W}(CO)_3CH_2PPh_3]^+$, and complex (XXXV), tungsten is seven co-ordinate, thus it would appear that this would be the best comparison to make.

The C1-P1 bond distance of 1.82(2) Å is almost identical with the P-Cph bond distances, (table 4.5, Cph = C11, C21, and C31). This is within the limits for

Table 4.7

A comparison of the W-C (ring) distances and the C-C (ring) distances in some structures containing the Cp-W or Cp̄-W moiety.

Compound	Reference	Ring C-W bond distances in Å, with estimated e.s.d.'s in parentheses	C-C bond distances in Å, with estimated e.s.d.'s in parentheses
$[CpW(H_2NNC_6H_5)]^+BF_4^-$	120	2.26(1)-2.36(1)	1.32(2)-1.49(2)
$[CpW(CO)_3\{\mu\text{-}(\eta^1,\eta^2\text{-}C_2Ph)\}W(\eta^2\text{-}C_2PhH)(CO)Cp]^+BF_4^-$	121	2.31(2)-2.42(2)	1.30(3)-1.48(4)
$[CpW(CO)_3Cl]$	122	2.26(1)-2.38(1)	1.36(2)-1.43(2)
$[CpW(CO)_3(AlMe_3)]_2$	123	2.30(2)-2.36(3)	1.28(4)-1.46(4)
$[CpW(CO)_3]_2$	124	2.31(1)-2.38(1)	1.38(1)-1.44(1)
$[Cp̄W(CO)_2NO]$	125	2.32(2)-2.37(2)	1.32(1)-1.45(1)
$[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4Cp_2]$	126	2.31(1)-2.36(1)	1.40 (2) (mean)
$[CpW(CO)_3AuPPh_3]$	127	2.32(5)-2.39(7)	1.38(8)-1.55(8)
$[CpW(CO)_3]_3Ga$	128	2.28(4)-2.39(3)	1.21(6)-1.53(7)
$[Cp̄W(CO)_3CH_2PPh_3]^+I^-.\frac{1}{2}CH_2Cl_2$		2.31(2)-2.38(2)	1.38(3)-1.49(3)

Table 4.8

A comparison of the W-C single bond distances in selected structures.

Complex	Reference	Bond distance (Å) with estimated e.s.d.'s in parentheses.
$[WMe_4(ON(Me)NO)_2]$	131	2.20 (mean)
$[W(CO)_2(\eta^2\text{-}C_3H_6)COOCF_3$ (1,2 dimethoxyethane)]	132	2.07 - 2.29
$[\{(CO)_4W\}_2HCCH{=}C(Me)_2]$	133	2.30(2) - 2.34(2)
$[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO_4(Cp)(C_6Me_6)]$	134	2.03 (1)
$[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_2]^+[CF_3SO_3]^-$	108	2.31 (1)
$[CpW(CO)_3CH_2PPh_3]\ ^+I^-.\frac{1}{2}CH_2Cl_2$		2.34 (2)

a C-P single bond distance in other structures containing a phosphorus ylide ligand. See fig 4.1.4.

The M-C-P bond angles,(M = metal), for other structures containing phosphorus ylides are given in fig 4.1.4. Thus the W1-C1-P1 bond angle of 119° is closer to the sp^2 hybridised bond angle of 120°, than to the tetrahedral angle of 109°28'. This has been noted in other phosphorus ylides, thus in fig 4.1.4, all of these complexes have a M-C-P bond angle greater than the tetrahedral value, so this result is not anomalous as compared with other structures of this type.

The co-ordination about the P atom was found to be approximately tetrahedral, (see table 4.4), as was the case in complexes (XXXI)-(XXXV), and the three phenyl rings showed very little deviation from planarity.

Although a number of structures of complexes containing the moiety $[(\eta\text{-}C_5H_5)M(CO)_n]$, (M = Mo,W) have been investigated, relatively few structures containing the analogous substituted cyclopentadienyl unit, viz, $[(\eta\text{-}C_5Me_5)M(CO)_n]$, have been studied, and only one structural study of the species $[(\eta\text{-}C_5R_5)M(CO)_2X]$, (M = Mo, W; R = H, Me). [125]

Thus Malito *et al* [125] synthesised the species, $[(\eta\text{-}C_5R_5)M(CO)_2NO]$ (R = H, Me; M = Cr, Mo, W); and investigated their crystal and molecular structures, in order to ascertain the physiochemical changes that would be exerted on the $M(CO)_2NO$ moiety on complexation with either Cp or Cṕ. The ν(CO) and ν(NO) stretching frequencies of the Cṕ compexes were found to be 10 - 20 cm^{-1} lower than those of the corresponding Cp compounds, This was attributed mainly to the greater electron donating capability of the Cṕ ligand relative to the Cp ligand.

For the series R = H, the complexes were found to be isostructural, whereas in the

series R = CH_3, only the Mo and W complexes were isostructural. In $[CpMo(CO)_2NO]$ the cyclopentadienyl groups were bonded in a symmetrical fashion, whereas in the complexes, $[C\acute{p}M(CO)_2NO]$, the rings are tilted for M = Cr, Mo. In the case of M = W, a valid comparison could not be made owing to the high standard deviations involved. The complexes containing the $C\acute{p}$ moiety showed a larger X-M-X angle, (X = C, N), than do their Cp analogues.

A considerable displacement of the ring methyl groups out of the plane of the ring, *exo* to the metal atom was noted for the complexes $[C\acute{p}M(CO)_2NO]$. In the case of these complexes, no steric considerations could be invoked, as all non-bonded interactions were greater than the sum of the van der Waals radii, this effect was thus explained in terms of the greater electron donating capability of the $C\acute{p}$ ligand relative to the Cp ligand.

Teller and Williams [130] compared the crystal and molecular structures of $[(\eta\text{-}C_5R_5)Fe(CO)_2]_2$, (R = H, Me). The orientation of the rings was found to be very similar in both complexes, as were the Fe-C-O distances. One important difference that was noted was that for the complex R = Me, the terminal carbonyl ligands were eclipsed with respect to C1 of the ring, whereas in the complex, R = H the terminal C-O groups were staggered with respect to C1 of the ring. These authors concluded that the main effect of the CH_3 groups on the ring was to alter the packing forces within the lattice. (See 1.2.13 , Chapter 1.2).

A comparison of this structure, $[C\acute{p}W(CO)_3CH_2PPh_3]^+ I^-$ with the unsubstituted cyclopentadienyl analogue would have been very interesting to show the differences engendered by the substitution of all 5 hydrogens on the cyclopentadienyl ring with methyl groups, as this would be expected to have a profound effect on the structure of this complex, owing to both steric and electronic effects.

Table 4.9

Analyses of variance.

(a) As a function of $\sin\theta$:

$\sin\theta$	.17 - .22	.22 - .25	.25 - .27	.27 - .30	.30 - .32	.32 - .34	.34 - .36	.36 - .38
N	412	329	263	441	323	345	326	357
V	675	585	585	537	551	571	655	745

(b) As a function of $\sqrt{F/F_{max}}$

$\sqrt{F/F_{max}}$	.24 - .26	.26 - .29	.29 - .31	.31 - .33	.33 - .36	.36 - .39	.39 - .44	.44 - .50
N	289	425	292	303	327	315	373	268
V	743	621	585	582	668	647	669	797

N = Number of reflections in the group.

$V = 100 \left\{ M \frac{\Sigma (w |Fo-Fc|^2)}{N\Sigma w} \right\}$ where M = total number of reflections.

The above analyses of variance exhibit no discernible trends, therefore no systematic errors appear to be present.

A comparison of the structures of the complexes $[C\hat{p}W(CO)_3CH_2PPh_3]^+ I^-$, and the unsubstituted cyclopentadienyl analogue was not possible, since suitable crystals of the cyclopentadienyl complex could not be obtained.

However, this structure is of considerable interest, since it is the first structure of a phosphorous ylide transition metal complex of this type to be investigated, and only one other tungsten ylide structure has been reported.[108]

4.4 Intramolecular non-bonded distances.

Table 4.10 list all the intramolecular non-bonded distances less than, or approximating to the sum of the van der Waals radii for the atoms concerned.

The interactions given are all less than the sum of the combined van der Waals radii for the carbon atoms viz, 3.5 Å. These would appear to be indicative of steric interactions and thus the relatively long W1-C1 bond would appear to result from steric as well as electronic effects arising from the electron releasing methyl substituents on the cyclopentadienyl ring.[2]

Table 4.10

Intramolecular non-bonded distances (Å) less than or approximating to van der Waals contracts.*

C1-C111	3.41
C1-C151	2.96
C1-C152	3.05
C1-C2	2.90
C1-C3	2.83
C1-C11	3.07
C1-C16	3.36
C1-C21	2.94
C1-C26	3.17
C1-C31	3.00

*Listed are all intramolecular distances less than 3.50 Å. The van der Waals radius for carbon is 1.75 A.

CHAPTER FIVE

5. EXPERIMENTAL SECTION.

5.1 General remarks.

All reactions were performed under nitrogen using standard Schlenk tube techniques. Solvents were generally of analytical reagent grade, and were further dried, where necessary, by distillation under nitrogen from a suitable reagent.

(a) THF was distilled from $LiAlH_4$ after standing over KOH for several days.

(b) Methanol was distilled from anhydrous $CaCl_2$.

(c) Acetonitrile was distilled from P_2O_5.

(d) Dichloromethane was distilled from anhydrous $CaCl_2$.

(e) N-hexane and petroleum ether (bp 100-120°C) were distilled from $LiAlH_4$.

$W(CO)_6$, $Mo(CO)_6$ and C_5Me_5H were obtained from Strem Chemicals Inc., $Fe(CO)_5$ was obtained from Fluka Chemicals, $ClCH_2OCH_3$ was obtained from Merck Chemical Company, $ClCH_2I$ and $AgPF_6$ were obtained from Alpha products, CH_2I_2 and CH_2Br_2 were obtained from BDH Chemicals Ltd., and all α,ω dihalomethanes were obtained from Aldrich Chemical Company. All were used without further purification.

PPh_3 was obtained from Merck Chemical Company, and further purified by recrystallisation from ethanol, and then dried at 0.05 mm Hg and 60°C for five hours.

n-butyllithium in n-hexane was obtained from Alpha Products, and standardised in the following manner :

(i) Determination of total LiOH.

A solution of n-butyllithium in n-hexane (2.0 cm^3) was added to deionised water

(20 cm^3). The LiOH so formed was titrated versus a standard solution of HCl using phenolphthalein as indicator.

(ii) Determination of suspended LiOH.

n-Hexane (20 cm^3) was saturated with N_2 and benzyl bromide (1 cm^3) was added under N_2, together with n-butyllithium in hexane (2.0 cm^3). The solution was stirred for 10 minutes. Deionised water was added and the solution titrated versus a standard solution of HCl using phenolphthalein as indicator.

All other reagents were obtained commercially, and used without further purification

$ClCH_2OCH_3$ and $Fe(CO)_5$ are extremely toxic, and were thus handled under a fume hood using disposable gloves. All residues were treated with a solution of iodine in dichloromethane.

Molecular distillations were performed on a modified Hickmann Still, and chromatography was performed using BDH silica gel (40 - 60 mesh ASTM).

Melting points were recorded on a Kofler Hot Stage microscope, and are uncorrected.

Microanalyses were performed by the University of Cape Town Microanalytical Laboratories, and by Drs. F. and E. Pascher; Microanalytisches Labatorium, Buchstrasse 54, 5300 Bonn I, Germany.

Infra-red spectra were recorded on a Perkin-Elmer 180 or 983 grating spectrometer, using solution cells with NaCl windows and 0.1 mm spacers.

^1H nmr spectra were recorded on a Varian XL100 (100 MHz), or on a Brucker WH 90

(90 MHz), operating in a Fourier transform mode. Chemical shifts are given relative to tetramethylsilane in δ ppm.

Mass spectra were recorded using a VG micromass 16F spectrometer, operating at 70eV ionising voltage.
(1eV = 1.60×10^{-19}J).

Samples were introduced into the instrument as oils, solids or hexane solutions using the direct probe.

The m/e values quoted from the mass spectum are those peaks in a peak cluster which correspond to the ions containing the metal isotope, or combination of isotopes, with the highest natural abundance.

Calculated mass spectra were obtained using a computer program prepared at the University of Alberta, Canada by Drs. R.S. Gay and E.H. Brookes. This program calculated the exact masses and isotope combinations for any particular parent ion or fragment required. Where the isotope pattern of a peak cluster is in close agreement with a particular combination of isotopes, this has been stated.

Pressures are recorded in mm Hg throughout this work.
1 mm = 101.325/760 Pa.

5.1.1 Preparation of dry HCl gas.[136]

Concentrated hydrochloric acid (10M) was added dropwise with stirring to concentrated sulphuric acid (18M). The dry HCl gas so prepared was bubbled through the required solution.

5.1.2 Preparation of dry HBr gas.

Dry HBr gas was prepared by an adaptation of the literature procedure, [137] thus tetrahydronaphthalene (1.1 g 2.0 cm^3 8.32 mmol) was placed in a 3-necked flask. Bromine (1.6 cm^3 2.65 g 16.6 mmol) was added via a dropping funnel, slowly, with vigorous stirring. The HBr gas so produced was swept up via a stream of nitrogen gas and bubbled through the required solution.

5.1.3 Preparation of dry HI gas.

Dry HI gas was prepared according to the literature procedure, [138] thus a solution of I_2 in tetrahydronaphthalene was added dropwise with vigorous stirring to a flask containing tetrahydronaphthalene under reflux. The HI gas so produced was swept up through a condenser into a bubbler, by passing a stream of dry nitrogen gas through the mixture.

5.2 Experimental section pertaining to Chapter 2 :

Preparation of pentamethylcyclopentadienyl tricarbonyl monohalomethyl and methoxymethyl complexes of molybdenum and tungsten.

5.2.1 Preparation of $(C_5Me_5)^- Li^+$.

$(C_5Me_5)^- Li^+$ was prepared according to a previously described method, [139] thus a solution of n-butyllithium in hexane (1.93 M, 4.0 cm^3, 7.72 mmol) was added dropwise with stirring to THF (80 cm^3) containing C_5Me_5H (1.0 cm^3, 0.95 g, 7 mmol). A white gelatinous precipitate of $(C_5Me_5)^- Li^+$ gradually appeared, which was used *in situ* without further purification.

5.2.2 Preparation of $[C\tilde{p}Mo(CO)_3]^- Li^+$.

$Mo(CO)_6$ (1.90 g, 7.2 mmol) was added to $(C_5Me_5)^- Li^+$ (7 mmol) suspended in THF (80 cm^3), prepared according to the method described in 5.2.1. The white cloudy mixture was heated under reflux for 24 hours, the solution became clear and deep red in colour. This solution was used *in situ* without further purification.

5.2.3 Preparation of $[C\tilde{p}W(CO)_3]^- Li^+$.

$W(CO)_6$ (2.10 g, 7 mmol) was added to a solution of $(C_5Me_5)^- Li^+$ (7 mmol) suspended in THF (80 cm^3). The cloudy white solution was heated under reflux for 3 days to give a clear deep red solution of $[C\tilde{p}W(CO)_3]^- Li^+$. This solution was used *in situ* without further purification.

5.2.4 Preparation of $[C\tilde{p}Mo(CO)_3CH_2OCH_3]$(XXV).

A solution of $[C\tilde{p}Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was prepared as in 5.2.2. This solution was added dropwise with stirring under nitrogen to a solution of $ClCH_2OCH_3$ (1.0 cm^3, 1.08 g, 13.4 mmol) in THF (5 cm^3) at 0°C. The solution was warmed to room temperature, and stirred for three hours. The deep red solution gradually went black. Removal of the solvent under reduced pressure, and subsequent extraction with portions of warm n-hexane gave a yellow/orange solution containing the product (XXV), contaminated with approximately 5% $[C\tilde{p}Mo(CO)_3Cl]$. The yellow orange hexane extracts were chromatographed, elution with 20% diethyl ether in n-hexane gave a yellow band which gave 0.47 g of yellow crystalline (XXV), 19% yield, mp 57 - 65°C.

Analysis found : C: 50.0 %

H: 5.61 %

$(C_{15}H_{20}MoO_4)$ requires : C: 50.0 %

H: 5.60 %

The mass spectrum gave peaks at :

334 $(M-CO)^+$, 304 $(M-2CO-2H)^+$, 288 $(M-2CO-H_2O)^+$, 276 $(M-3CO-2H)^+$,

259 $(M-2CO-CH_2OCH_3-2H)^+$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope of this formula.

Elution with dichloromethane gave an orange/red band from which 0.10 g orange crystalline $[C\tilde{p}Mo(CO)_3Cl]$ (5%) was isolated. The IR and mp of this complex were found to be identical with those reported previously. [139]

5.2.5 Preparation of $[C\tilde{p}Mo(CO)_3CH_2Cl]$ (XXVI).

(XXV) (prepared as in 5.2.4) (0.09 g , 0.25 mmol) was dissolved in n-hexane (10 cm^3). Dry HCl gas (see 5.1.1) was bubbled through the solution for 15 minutes at room temperature. The yellow solution gradually darkened to pale orange, with a small amount of purple insoluble material. The solution was protected from light using foil. The solution was allowed to stand for 10 minutes. The solution was filtered to remove the hexane insoluble material, removal of the solvent and subsequent extraction with n-hexane, gave after crystallisation from n-hexane at -78°C, 0.07 g of yellow/orange crystalline (XXVI); 78% yield, mp 87 - 94 °C.(decomp

Analysis found :	C: 45.75 %
	H: 4.90 %
$(C_{14}H_{17}ClMoO_3)$ requires :	C: 46.11 %
	H: 4.70 %

The mass spectrum gave peaks at :

338 $(M-CO)^+$, 302 $(M-CO-Cl)^+$, 282 $(M-3CO)^+$

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

$[C_5H_5Mo(CO)_3Cl]$ (0.1 g , 10%) was also isolated from this reaction, and separated from the product (XXVI) by crystallisation. $[C_5H_5Mo(CO)_3Cl]$ was identified on the basis of the $\nu(CO)$ bands in the IR spectrum and melting point, and the results found to be identical with those obtained previously.[139]

5.2.6 Preparation of $[C_5H_5Mo(CO)_3CH_2Br]$.

(XXV) (prepared as in 5.2.4) (0.05 g, 0.14 mmol) was dissolved in n-hexane (10 cm^3). Dry HBr gas generated as in 5.1.2 was bubbled through the solution for 5 minutes. Removal of the solvent and subsequent extraction with n-hexane gave 0.035 g $[C_5H_5Mo(CO)_3CH_2Br]$ as yellow/orange crystalline material, 70 % yield. The product was identified by IR and mp, and the results found to be identical with those obtained in 5.3.4.

A second product, viz, $[C_5H_5Mo(CO)_3Br]$ was isolated from this reaction, and separated from $[C_5H_5Mo(CO)_3CH_2Br]$ by crystallisation from n-hexane at -78°C. $[C_5H_5Mo(CO)_3Br]$ was identified by IR and mp, and the results found to be identical with those obtained previously. [139] Yield = 0.012 g, 24 %.

5.2.7 Attempted preparation of $[C_5H_5Mo(CO)_3CH_2I]$.

(XXV) (prepared as in 5.2.4) (0.30 g, 0.83 mmol) was dissloved in n-hexane (10 cm^3). Dry HI gas (prepared as in 5.1.3) was bubbled through the solution for 12 minutes at 0°C. The solution darkened rapidly to a deep-red/orange colour. Removal of the solvent, extraction with n-hexane and then cooling to -78°C gave 0.28 g of red/orange crystalline material. This red/orange material gave the following peaks

in the ν(CO) region of the IR spectrum, in hexane.

2032(s)*, 2027(m), 1963(vs)*, 1949(s) 1939(s)*, 1929(m) cm^{-1}.

* These peaks correspond to $[C\bar{p}Mo(CO)_3I]$ as reported previously.[139]

A melting point of this material showed two products, orange crystals which decomposed at 80°C, and red crystals which melted above 200°C.

These two products could not be separated, as the product with peaks at 2027, 1949 and 1929 cm^{-1} in the carbonyl region of the IR spectrum decomposed to give $[C\bar{p}Mo(CO)_3I]$, as seen in the IR spectrum.

Thus the products from this reaction would appear to be a mixture of $[C\bar{p}Mo(CO)_3I]$ and $[C\bar{p}Mo(CO)_3CH_2I]$.

5.2.8 Preparation of $[C\bar{p}W(CO)_3CH_2OCH_3]$(XXVII).

A THF solution of $[C\bar{p}W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was prepared as described in 5.2.3. This deep red solution was added dropwise with stirring to a solution of $ClCH_2OCH_3$ (1.0 cm^3, 1.08 g, 13.4 mmol) in THF (5 cm^3). The solution was stirred for three hours at room temperature, and the deep red solution gradually went black. Removal of the solvent under reduced pressure, and subsequent extraction with n-hexane gave, after removal of the solvent, a yellow orange oil. The oil was chromatographed, elution with 40% diethyl ether in n-hexane, gave after crystallisation from n-hexane at -78°C, 0.55 g of yellow microcrystalline material, mp 71 - 76 °C, identified as (XXVII), 18 % yield.

Analysis found :	C: 42.05 %
	H: 4.8 %
($C_{15}H_{20}WO_4$) requires :	C: 40.20 %
	H: 4.50 %

The mass spectrum gave peaks at :

420 $(M-CO)^+$, 403 $(M-CO-OH)^+$, 390 $(M-2CO-2H)^+$, 373 $(M-2CO-2H-OH)^+$,

364 $(M-3CO)^+$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

The ^1H nmr spectrum of this compound revealed small peaks corresponding to that of C_5Me_5H. This would explain the inaccurate elemental analysis.

$W(CO)_6$ (0.05 g) was also isolated from this reaction. It is not known whether this arose from incomplete reaction with $(C_5Me_5)^- Li^+$, to form $[C\hat{p}W(CO)_3]^- Li^+$, or from a disproportionation reaction.

5.2.9 Preparation of $[C\hat{p}W(CO)_3CH_2Cl]$.

(XXVII) (0.14 g, 0.55 mmol) (prepared as described in 5.2.8), was dissolved in n-hexane (15 cm^3). Dry HCl gas (prepared as in 5.1.1) was bubbled through the solution for 15 minutes at room temperature. The yellow solution became slightly paler, and a small amount of black insoluble material was formed. The solution was protected from light using foil. The solution was allowed to stand for 10 minutes at room temperature before filtration and removal of the solvent under reduced pressure. Subsequent extraction with n-hexane, and crystallisation from n-hexane at -78°C gave 0.14 g of yellow crystalline material, mp 114 - 122°C (decomp). The product was identified as $[C\hat{p}W(CO)_3CH_2Cl]$, 94 % yield.

Analysis found :	C: 37.70 %	
	H: 4.0 %	
$(C_{14}H_{17}ClWO_3)$ requires :	C: 37.15 %	
	H: 3.79 %	

A small amount of hexane impurities were detected in the ^{1}H nmr spectrum, this would explain the slightly high C and H analysis.

The mass spectrum gave peaks at :
452 $(M)^{+}$, 424 $(M-CO)^{+}$, 396 $(M-2CO)^{+}$, 368 $(M-3CO)^{+}$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

5.2.10 Preparation of $[C\tilde{p}W(CO)_3CH_2Br]$.

(XXVII) (0.11 g, 0.41 mmol) (prepared as described in 5.2.8) was dissolved in n-hexane (10 cm^3). Dry HBr gas (prepared as described in 5.1.2) was bubbled through the solution for 10 minutes. Removal of the solvent and subsequent extraction with n-hexane, gave after cooling to -78°C, 0.12 g of orange red crystalline material, mp 110 - 113°C, 98 % yield.

The product was contaminated with approximately 5 % $[C\tilde{p}W(CO)_3Br]$ identified on the basis of the IR spectrum, [139] which could not be separated from the product $[C\tilde{p}W(CO)_3CH_2Br]$. Elemental analysis was therefore not obtained.

The mass spectrum gave peaks at :
496 $(M-CO)^{+}$, 482 $(M-CH_2-CO)^{+}$, 468 $(M-2CO)^{+}$, 454 $(M-2CO-CH_2)^{+}$,
440 $(M-3CO)^{+}$.

5.2.11 Preparation of $[C\tilde{p}W(CO)_3CH_2I]$ (XXVIII)

(XXVII) (0.12 g, 0.27 mmol) was dissolved in n-hexane (10 cm^3). Dry HI gas (generated as in 5.1.3) was bubbled through the solution for 30 minutes. The yellow

solution gradually darkened to brown/red. Removal of the solvent and subsequent extraction with n-hexane, gave after cooling to -78°C, 0.11 g of red crystalline material. The material was chromatographed, a yellow band was eluted with 20 % CH_2Cl_2 in n-hexane, which after removal of the solvent was identified as (XXVIII) by IR and mp, and the results found to be identical with those obtained in 5.3.6. A red band was eluted with CH_2Cl_2, this product was identified as $[C_5H_5W(CO)_3I]$ by comparison of the IR and mp with that obtained previously.[139]

$[C_5H_5W(CO)_3CH_2I]$ yield = 0.105 g , 73 %

$[C_5H_5W(CO)_3I]$ yield = 0.03 g , 21 %

5.3 Experimental section pertaining to Chapter 2 :

Reactions of $[C_5H_5M(CO)_3]^- Li^+$ (M = Mo, W) with dihalomethanes.

5.3.1 Reaction of $[C_5H_5Mo(CO)_3]^- Li^+$ with $ClCH_2I$.

$[C_5H_5Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was prepared as in 5.2.2. The deep red solution was added dropwise with stirring to a solution of $ClCH_2I$ (1.0 cm^3, 2.4 g, 1.37 mmol) in THF (5 cm^3). The solution gradually went black on stirring for three hours at room temperature. Removal of the solvent and subsequent extraction with n-hexane, gave, after cooling the solution to -78°C, 0.60 g of yellow crystalline material, identified as (XXVI), 24 % yield.

The product was identified by IR, ^1H nmr and mass spectrum, and the results compared with those obtained in 5.2.5.

$[C_5H_5Mo(CO)_3Cl]$ 0.06 g was also isolated from this reaction, the two products were separated by fractional crystallisation from n-hexane. Thus $[C_5H_5Mo(CO)_3Cl]$ crystallised out of solution at 0°C, the solution was filtered and cooled to -78°C, where the

product (XXVI) crystallised out of solution.

5.3.2 Reaction of $[C_5Me_5Mo(CO)_3]^- Li^+$ with $ClCH_2Br$.

This reaction was performed in the same manner as that described in 5.3.1. Thus $[C_5Me_5Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a mixture of $ClCH_2Br$ (1.0 cm^3) in THF (5 cm^3), the solution was stirred for three hours. After removal of the solvent and subsequent extraction with n-hexane, (XXVI) was isolated as yellow crystalline material, 1.27 g, 40 % yield. The product was found to be identical with an authentic sample prepared in 5.2.5.

5.3.3 Reaction of $[C_5Me_5Mo(CO)_3]^- Li^+$ with CH_2Cl_2.

This reaction was performed in the same manner as that described in 5.3.1. Thus $[C_5Me_5M(CO)_3]^- Li^+$ (7 mmol) in THF (5 cm^3) was added to a solution of CH_2Cl_2 (1.0 cm^3, 1.32 g, 15.52 mmol) in THF (5 cm^3). No reaction occurred on stirring the solution for three hours at room temperature, nor on heating the solution under reflux overnight, the reaction mixture was thus discarded.

5.3.4 Reaction of $[C_5Me_5Mo(CO)_3]^- Li^+$ with CH_2Br_2.

The reaction was performed as described in 5.3.1. Thus $[C_5Me_5Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a solution of CH_2Br_2 (1.0 cm^3, 2.50 g, 14.36 mmol) in THF (5 cm^3). The solution was stirred for two hours at room temperature. Removal of the solvent under reduced pressure and subsequent extraction with n-hexane, gave after crystallisation from n-hexane at -78°C, 0.43 g of an oily orange crystalline material, mp 75 - 85°C (decomp). The product was identified as $[C_5Me_5Mo(CO)_3CH_2Br]$, 30 % yield. The product was contaminated with C_5Me_5H, and thus elemental analysis was not obtained. The product was not able to be purified further as it

decomposed on attempted chromatography.

The mass spectrum gave peaks at :

382 $(M-CO)^+$, 368 $(M-CO-CH_2)^+$, 354 $(M-2CO)^+$, 340 $(M-2CO-CH_2)^+$, 326 $(M-3CO)^+$.

The isotope pattern of this complex was in close agreement with a computer simulated isotope pattern of this formula.

5.3.5 Reaction of $[C_5H_5Mo(CO)_3]^- Li^+$ with CH_2I_2.

This reaction was performed in the same manner as that in 5.3.1. Thus $[C_5H_5Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a solution of CH_2I_2 (1.0 cm^3, 3.4 g, 12.4 mmol) in THF (5 cm^3). The solution was stirred at room temperature for 1 hour. Removal of the solvent and subsequent extraction with n-hexane, gave after cooling the solution to 0°C, 0.38 g of red crystalline material, 25 % yield of $[C_5H_5Mo(CO)_3I]$, identified on the basis of IR and mp, and the results compared with those obtained previously. [139]

5.3.6 Reaction of $[C_5H_5W(CO)_3]^- Li^+$ with $ClCH_2I$.

$[C_5H_5W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added dropwise with stirring under nitrogen to a solution of $ClCH_2I$ (1.0 cm^3, 2.4 g, 13.7 mmol) in THF (5 cm^3). The solution was stirred for 2 hours at room temperature. Removal of the solvent and subsequent extraction with n-hexane, gave, after crystallisation from n-hexane, bright yellow crystalline material, 0.63 g, mp 88 - 92 °C. The product was identified as (XXVIII), yield 17 %.

Analysis found : C: 31.3 %

H: 3.3 %

($C_{14}H_{17}IO_3W$) requires : C: 30.9 %

H: 3.15 %

The mass spectrum gave peaks at :

532 $(M-CH_2)^+$, 516 $(M-CO)^+$, 502 $(M-CO-CH_2)^+$, 488 $(M-2CO)^+$, 458 $(M-3CO-2H)^+$,

444 $(M-3CO-CH_2-2H)^+$, 389 $(M-CO-I)^+$, 373 $(M-CO-I-CH_2-2H)^+$, 345 $(M-2CO-I-CH_2-2H)^+$.

The isotope patterns of the higher mass peak clusters (< 400) were in close agreement with a computer simulated isotope pattern of that particular formula.

5.3.7 Reaction of $[C\bar{p}W(CO)_3]^- Li^+$ with $ClCH_2Br$.

This reaction was performed in a similar fashion to that described in 5.3.6. Thus $[C\bar{p}W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to $ClCH_2Br$ (1.0 cm^3, 1.86 g, 15.0 mmol) in THF (5 cm^3). This reaction mixture was stirred for two hours at room temperature. Removal of the solvent and subsequent extraction with n-hexane gave orange crystalline material, 0.80 g. An IR spectrum of this product revealed that it was in fact a mixture of $[C\bar{p}W(CO)_3CH_2Cl]$ and $[C\bar{p}W(CO)_3CH_2Br]$, in the ratio approximately 2:3. The products could not be separated by chromatography, sublimation or fractional crystallisation, but were however separated by preparative TLC on alumina plates. The IR and mp's of these products were found to be identical with those obtained in 5.2.9 and 5.2.10

5.3.8 Reaction of $[C\bar{p}W(CO)_3]^- Li^+$ with CH_2Cl_2.

This reaction was performed in a similar fashion to that described in 5.3.6. Thus $[C\bar{p}W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a solution of CH_2Cl_2 (1.0 cm^3, 1.32 g. 15.52 mmol) in THF (5 cm^3). No reaction occurred on stirring the solution for three hours at room temperature, nor on heating the solution under reflux for 24 hours.

5.3.9 Reaction of $[C_5H_5W(CO)_3]^- Li^+$ with CH_2Br_2.

This reaction was performed in a similar manner to that described in 5.3.6, thus $[C_5H_5W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a solution of CH_2Br_2 (1.0 cm^3, 2.50 g, 14.36 mmol) in THF (5 cm^3). The reaction mixture was stirred for 2 hours. After removal of the solvent and subsequent extraction with n-hexane, yellow crystalline material was obtained, identified as $[C_5H_5W(CO)_3CH_3]$ from IR and nmr, and the results compared with those obtained previously.[16]

Yield = 1.21 g, 42 %.

5.3.10 Reaction of $[C_5H_5W(CO)_3]^- Li^+$ with CH_2I_2.

This reaction was performed in a similar fashion to that described in 5.3.6, thus $[C_5H_5W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to CH_2I_2 (1.0 cm^3, 3.4 g, 13.4 mmol) in THF (5 cm^3), and the reaction mixture stirred for 2 hours. Removal of the solvent and subsequent extraction with n-hexane, gave after cooling the n-hexane extracts to -78°C, $[C_5H_5W(CO)_3CH_3]$, 1.32 g, 45 % yield. The product was identified according to the IR and nmr spectra, and the results compared with those obtained previously.[16]

5.4 Reactions of $[C_5H_5M(CO)_3]^- Li^+$, (M = Mo, W) with α,ω-dihalomethanes.

5.4.1 Reaction of $[C_5H_5Mo(CO)_3]^- Li^+$ with $Br(CH_2)_3Br$.

$[C_5H_5Mo(CO)_3]^- Li^+$ prepared as in 5.1.3 (7 mmol) in THF (80 cm^3) was added dropwise with stirring to $Br(CH_2)_3Br$ (0.71 g, 3.5 mmol). The reaction mixture was heated under reflux for 24 hours, the deep-red solution gradually turned black during this period. Removal of the solvent and extraction with portions of warm n-hexane, gave after crystallisation from n-hexane at 0°C, orange crystalline material, 0.864 g,

mp 65 - 69 °C. The product was identified as $[C_5Me_5Mo(CO)_3(CH_2)_3Br]$, yield = 58 % (based on $Br(CH_2)_3Br$). No evidence for the polymethylene bridged species $[(C_5Me_5Mo(CO)_3)_2(\mu\text{-}CH_2)_3]$ was observed.

Elemental analysis was not obtained as the product contained traces of some organic material which could not be removed, as the complex decomposed on attempted chromatography. The complex was however identified spectroscopically :

ν(CO) (hexane) 2008(s) 1924(vs) cm^{-1}

^1H nmr (C_6D_6) 0.585δ(m, 2p, CH_2); 1.145δ(s, 15p, C_5Me_5); 1.905δ(m, 2p, CH_2); 2.885δ(t, 2p, CH_2).

The mass spectrum gave peaks at :

438 $(M)^+$, 419 $(M\text{-}CO)^+$, 382 $(M\text{-}2CO)^+$, 354 $(M\text{-}3CO)^+$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

5.4.2 Reaction of $[C_5Me_5Mo(CO)_3]^- Li^+$ with $Br(CH_2)_4Br$.

This experiment was performed in a similar manner to that described for 5.4.1. Thus a solution of $[C_5Me_5Mo(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to a solution of $Br(CH_2)_4Br$ (0.76 g, 3.5 mmol) in THF (5 cm^3). The solution was heated under reflux for 24 hours. Removal of the solvent and extraction with n-hexane, gave, after cooling to -78°C, 0.966 g of orange crystalline material, mp 60 - 63 °C. The product was identified as $[C_5Me_5Mo(CO)_3(CH_2)_4Br]$, yield = 51 % (based on $Br(CH_2)_4Br$. No evidence for the polymethylene bridged species $[(C_5Me_5Mo(CO)_3)_2(\mu\text{-}CH_2)_4]$ was seen.

This product was very unstable, and rapidly decomposed to $[C_5Me_5Mo(CO)_3Br]$, and thus elemental analysis was not obtained.

ν(CO) (hexane) 2006(s) 1921(vs) cm^{-1}.

^{1}H nmr (C_6D_6) : 0.56δ(m, 2p, CH_2); 0.92δ(m, 2p, CH_2); 2.68δ(t, 2p, CH_2); 1.13δ(s, 15p, C_5Me_5); 1.82δ(m, 2p, CH_2).

The mass spectrum gave peaks at :

452 $(M)^+$, 424 $(M-CO)^+$, 396 $(M-2CO)^+$, 368 $(M-3CO)^+$.

The highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

5.4.3 Reaction of $[CpW(CO)_3]^- Li^+$ with $Br(CH_2)_3Br$.

$[CpW(CO)_3]^- Li^+$ prepared as in 5.1.4 (7 mmol) in THF (80 cm^3) was added to $Br(CH_2)_3Br$ (0.71 g, 3.5 mmol) in THF (5 cm^3). The solution was heated under reflux for 24 hours, during which time the solution darkened to black. Removal of the solvent under reduced pressure, and extraction with n-hexane gave a yellow/orange solution. On cooling this solution to 0 °C, yellow crystalline material precipitated mass = 1,368 g, mp = 80 - 87 °C(decomp). The product was identified as $[CpW(CO)_3(CH_2)_3Br]$, yield = 74 % (based on 1,3 dibromopropane).

Analysis found :	C: 36.55 %
	H: 4.00 %
($C_{16}H_{21}BrO_3W$) requires :	C: 36.60 %
	H: 4.03 %

ν(CO) (hexane) 2005(s) 1913(vs) cm^{-1}.

^{1}H nmr (C_6D_6) gave peaks at :

0.77δ(t, 2p, CH_2); 1.55δ(s, 15p, C_5Me_5); 2.20δ(m, 2p, CH_2); 3.18δ(t, 2p, CH_2).

The mass spectrum gave peaks at :

525 $(M)^+$, 497 $(M-CO)^+$, 483 $(M-CO-CH_2)^+$, 469 $(M-2CO)^+$, 457 $(M-2CO-CH_2)^+$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

No evidence for the formation of a polymethylene bridged species $[(C\hat{p}W(CO)_3)_2(\mu\text{-}CH_2)_3]$ was seen.

5.4.4 Reaction of $[C\hat{p}W(CO)_3]^- Li^+$ with $Br(CH_2)_4Br$.

This experiment was performed in a similar fashion to that described in 5.4.3. Thus $[C\hat{p}W(CO)_3]^- Li^+$ (7 mmol) in THF (80 cm^3) was added to $Br(CH_2)_4Br$ (0.76 g, 3.5 mmol) in THF (5 cm^3). The solution was heated under reflux for 24 hours. Removal of the solvent and subsequent extraction with n-hexane, gave on cooling the solution to -78 °C, 0.98 g of orange crystalline material, mp 78 - 82 °C. The product was identified as $[C\hat{p}W(CO)_3(CH_2)_3Br]$, yield = 52 % (based on 1,4 dibromobutane).

Satisfactory elemental analysis was not obtained for this product as it contained an organic impurity, as seen in the ^1H nmr spectrum.

ν(CO) (hexane) 2004(s) 1923(vs) cm^{-1}.

^1H nmr (C_6D_6) gave peaks at :

0.68δ(m, 2p, CH_2); 1.53δ(s, 15p, C_5Me_5); 1.67δ(m, 2p, CH_2); 2.10δ(m, 2p, CH_2).

The mass spectrum gave peaks at :

539 $(M)^+$, 511 $(M\text{-}CO)^+$, 455 $(M\text{-}3CO)^+$.

The isotope pattern of the highest mass peak cluster was in close agreement with a computer simulated isotope pattern of this formula.

No evidence for a polymethylene bridged species was seen.

5.5 Reactions of $[C\hat{p}Fe(CO)_2]^- Na^+$ with α,ω-dihaloalkanes and $ClCH_2OCH_3$.

5.5.1 Preparation of $[C_5Me_5Fe(CO)_2]_2$.

$[C_5Me_5Fe(CO)_2]_2$ was prepared by a modification of the literature method.[15] C_5Me_5H (2.0 g, 14.71 mmol) was dissolved in petroleum ether, (bp 100-120 °C) (80 cm^3). $Fe(CO)_5$ (4.0 cm^3 27 mmol) was added and the solution heated under reflux for 48 hours. The solution gradually darkened from pale yellow to maroon/black. Removal of the solvent under high vacuum gave a black crystalline solid, which was recrystallised from CH_2Cl_2/hexane at 0 °C. The red/black crystalline solid was found to be identical with that reported previously.

5.5.2 Preparation of $[C_5Me_5Fe(CO)_2]^- Na^+$.

A solution of $[C_5Me_5Fe(CO)_2]_2$ prepared as in 5.5.1 (0.63 g, 1.27 mmol) in THF (100 cm^3) was stirred over a dilute Na/Hg amalgam for 12 hours. The solution changed colour from deep red/black to grey during this period. The product, $[C_5Me_5Fe(CO)_2]^-$ was not further purified.

5.5.3 Reaction of $[C_5Me_5Fe(CO)_2]^- Na^+$ with CH_2Cl_2.

$[C_5Me_5Fe(CO)_2]^- Na^+$ (2.54 mmol) prepared as in 5.5.2 in THF (100 cm^3) was added to CH_2Cl_2 (0.11 g, 1.27 mmol). The solution was stirred for 3 hours, during which time slight darkening was noted. Removal of the solvent, and subsequent extraction with n-hexane, gave after cooling to -78 °C, pale yellow crystalline material, 0.37 g, mp 80 - 89 °C (decomp). The product was identified as $[C_5Me_5Fe(CO)_2CH_2Cl]$, yield = 98 %, based on CH_2Cl_2.

Analysis found :	C: 52.6 %
	H: 5.8 %
($C_{13}H_{17}ClFeO_2$) requires :	C: 52.65 %
	H: 5.78 %

ν(CO) (hexane) 2004(s) 1953(s) cm^{-1}.

^{1}H nmr (C_6D_6) gave peaks at :

1.23δ(s, 15p, C_5Me_5); 3.96δ(s, 2p, CH_2).

The mass spectrum gave peaks at :

296 $(M)^+$, 268 $(M-CO)^+$, 240 $(M-2CO)^+$

5.5.4 Reaction of $[C_pFe(CO)_2]^- Na^+$ with $Br(CH_2)_3Br$.

This reaction was performed in a similar manner to that described in 5.5.3, thus $[C_pFe(CO)_2]^- Na^+$ (1.36 mmol) in THF (50 cm^3) was added to $Br(CH_2)_3Br$ (0.13 g, 0.68 mmol). The solution was stirred for 3 hours. Removal of the solvent and subsequent extraction with n-hexane gave, after cooling, yellow crystalline material, 0.20 g, 80 % yield of $[C_pFe(CO)_2(CH_2)_3Br]$, Based on 1,3 dibromopropane, mp 98 - 102 °C.

Analysis found : C: 48.9 %

H: 5.85 %

($C_{15}H_{21}BrFeO_2$) requires : C: 48.81 %

H: 5.74 %

ν(CO) (hexane) 1992 (s) 1939 (s) cm^{-1}.

^{1}H nmr (C_6D_6) gave peaks at :

0.84δ(t, 2p, CH_2); 1.35δ(s, 15p, C_5Me_5); 2.07δ(m, 2p, CH_2); 3.40δ(t, 2p, CH_2).

The mass spectrum gave peaks at :

369 $(M)^+$, 341 $(M-CO)^+$, 313 $(M-2CO)^+$.

5.5.5 Reaction of $[C_pFe(CO)_2]^- Na^+$ with $Br(CH_2)_4Br$.

This reaction was performed in a similar fashion to that described in 5.5.3, thus $[C_pFe(CO)_2]^- Na^+$ (1.74 mmol) in THF (50 cm^3) was added to $Br(CH_2)_4Br$ (0.19 g, 0.87

mmol). The solution was stirred for 3 hours. Removal of the solvent and extraction with n-hexane gave, after cooling, yellow crystalline material, 0.27 g, mp 100 - 103 °C. The product was identified as $[C\bar{p}Fe(CO)_2(CH_2)_4Br]$, yield = 81 %, based on 1,4 dibromobutane.

Analysis found : C: 51.1 %

H: 6.3 %

$(C_{16}H_{23}BrFeO_2)$ requires : C: 50.16 %

H: 6.05 %

ν(CO) (hexane) : 1989 (s) 1935 (s) cm^{-1}.

^1H nmr (C_6D_6) gave peaks at :

0.82δ(t, 2p, CH_2); 1.32δ(s, 15p, C_5Me_5); 1.82δ(m, 2p, CH_2); 2.10δ(m, 2p, CH_2) 3.35δ(t, 2p, CH_2)

The mass spectrum gave peaks at :

383 $(M)^+$, 355 $(M-CO)^+$, 327 $(M-2CO)^+$, 299 $(M-2CO-2CH_2)^+$,

247 $(M-2CO-Br)^+$.

5.5.6 Reaction of $[C\bar{p}Fe(CO)_2]^- Na^+$ with $ClCH_2OCH_3$.

$[C\bar{p}Fe(CO)_2]^- Na^+$ prepared as in 5.5.2 (2.52 mmol) in THF (80 cm^3) was added to $ClCH_2OCH_3$ (0.5 cm^3 6.21 mmol) in THF (5 cm^3). The solution was stirred for 4 hours at room temperature. Removal of the solvent under reduced pressure and extraction with n-hexane gave a clear yellow solution, on cooling, this solution, 0.49 g of yellow crystalline material, mp 51 - 56 °C was isolated. The product was identified by nmr and IR as $[C\bar{p}Fe(CO)_2CH_3]$, and the results found to be identical with those reported previously.[27] Yield = 67 %.

5.6 Reactions of $[C_5^*Mo(CO)_3CH_2Cl]$ (XXVI) and $[C_5^*W(CO)_3CH_2I]$ (XXVII) with PPh_3.

5.6.1 Reaction of (XXVI) with PPh_3 in acetonitrile at room temperature.

(XXVI) prepared as in 5.2.5 (0.25 g, 0.69 mmol) was dissolved in CH_3CN (5 cm^3). PPh_3 (0.22 g, 0.82 mmol) in CH_3CN (10 cm^3) was added under nitrogen. The solution was placed in the dark, and allowed to stand for 6 days. The solution gradually changed colour from yellow/orange to deep red. The solvent was removed under reduced pressure, and the oily red product recrystallised from CH_2Cl_2/hexane to give fine orange needles; 0.13 g of *cis*-$[C_5^*Mo(CO)_2(PPh_3)Cl]$, 53 % yield , mp 140 - 146 °C.

Analysis found : C: 60.2 %

H: 5.2 %

($C_{30}H_{30}ClMoO_2$) requires : C: 61.6 %

H: 5.17 %

ν(CO) (CH_2Cl_2) 1948 (vs) 1863 (s) cm^{-1}

^1H nmr ($CDCl_3$) 1.74δ(s, 15 p, C_5Me_5) ; 7.39δ(m, 15p, PPh_3).

(The integration for the $CHCl_3$ impurity in $CDCl_3$ could not be completely separated from the integration for the protons of the PPh_3 ligand).

5.6.2 Reaction of (XXVI) with PPh_3 in methanol under reflux.

(XXVI) prepared as in 5.2.5 (0.26 g, 0.71 mmol) was dissolved in methanol (30 cm^3). PPh_3 (0.24 g, 0.93 mmol) was added and the solution heated under reflux for 3 hours. The solution darkened from yellow/orange to red/orange during this time. The solvent was removed under reduced pressure, and the oily residue recrystallised from CH_2Cl_2/hexane, to give 0.15 g $[C_5^*Mo(CO)_2(PPh_3)Cl]$, 75 % yield.

The product was identified by mp, IR, and ^{1}H nmr, and the results found to be identical with those obtained in 5.6.1.

$[C\bar{p}Mo(CO)_3CH_2OCH_3]$ was isolated from this reaction as a by product in 15 % yield.

5.6.3 Reaction of (XXVIII) with PPh_3 in methanol under reflux.

(XXVIII) (0.21 g, 0.39 mmol) was dissolved in methanol (10 cm^3). PPh_3 (0.31 g , 0.39 mmol) was added, and the solution heated under reflux for three hours. The solution darkened from yellow to dark orange during this time. The solvent was removed under reduced pressure to give an orange oil. The oil was extracted with n-hexane, (XXVIII) and (XXVII) were present in 5 and 12 % yields respectively, identified on the basis of the ν(CO) bands in the IR spectrum, in hexane, and the values compared with those obtained in 5.2.11 and 5.2.8 respectively. The hexane insoluble material was twice recrystallised from CH_2Cl_2/hexane to give orange/yellow prisms, mp 134 - 140 °C (decomp), identified as $[C\bar{p}W(CO)_3CH_2PPh_3]^+ I^-$. $\frac{1}{2}$ CH_2Cl_2 , yield = 57 %.

Analysis found : C: 44.4 %

H: 3.8 %

$(C_{33}H_{34}Cl_2IO_3PW)$ requires : C: 44.4 %

H: 3.84 %

ν(CO) (CH_2Cl_2) 2023 (s) 1934 (s) 1920 (sh) cm^{-1}.

^{1}H nmr ($CDCl_3$) gave peaks at :

1.62δ(d, 2p, CH_2(ylide ligand) ; 2.16δ(s, 15p, C_5Me_5) ; 5.34δ(s, 2p, CH_2Cl_2) ; 7.73δ(m, 15p, PPh_3).

J(PH) = 17.0 Hz.

5.6.4 Reaction of (XXVIII) with PPh_3 in acetonitrile at room temperature.

(XXVIII) (0.17 g, 0.32 mmol) was dissolved in CH_3CN (10 cm^3). PPh_3 (0.09 g, 0.36 mmol) was added and the solution stirred vigorously until all the PPh_3 had dissolved. The solution was allowed to stand in the dark for 20 days. The solution gradually darkened, and a small amount of yellow crystalline precipitate appeared. The solvent was removed under reduced pressure, and the red oily residue extracted with n-hexane to give a mixture of (XXVIII) and $[C\bar{p}W(CO)_3I]$ in approximately 5 % yield each.

The hexane insoluble material was recrystallised from CH_2Cl_2/hexane to give yellow crystalline material, mass = 0.23 g, identical with that obtained in 5.6.3, 79 % yield, mp 136 - 142 °C (decomp).

5.7 Reactions of $[C\bar{p}Mo(CO)_3(CH_2)_3Br]$ and $[C\bar{p}Fe(CO)_2CH_2Cl]$ with PPh_3.

5.7.1 Reaction of $[C\bar{p}Mo(CO)_3(CH_2)_3Br]$ (XXX) with PPh_3.

(XXX) (0.12 g, 0.28 mmol) was dissolved in CH_3CN (5 cm^3). PPh_3 (0.09 g, 0.34 mmol) in CH_3CN (5 cm^3) was added, and the solution stirred for 10 minutes. The solution darkened slightly, and a small amount of orange crystalline material precipitated out of solution. Removal of the solvent under reduced pressure gave an orange/red oil. Trituration with n-hexane gave a yellow solution, with n-hexane insoluble orange oily crystals. The hexane solution was evaporated under reduced pressure to give 0.02 g (17 % yield) of (XXX), identified on the basis of the ν(CO) bands in the IR spectrum. The hexane insoluble material was dissolved in methanol, and precipitated as the BPh_4^- salt, the orange crystalline precipitate was filtered and dried, to give 0.24 g bright orange needles, mp 164 - 169 °C (decomp). This product was identified as a mixture of *cis* and *trans* isomers of

$[C_5H_5Mo(CO)_2(PPh_3)(\eta^1\text{-}\overline{C\text{-}(CH_2)_3\text{-}O})]^+ BPh_4^-$, yield = 90 %.

Analysis found C: 74.20 %

H: 6.01 %

$(C_{58}H_{56}BPO_3Mo)$ requires : C: 73.9 %

H: 5.90 %

$\nu(CO)$ (CH_2Cl_2) 1975 (s) 1904 (s) cm^{-1}.

^1H nmr $(CDCl_3)$ gave peaks at :

1.7δ(s, 15p, C_5Me_5) ; unresolved multiplets between 2.0 and 3.7δ, 0.86δ(m);

1.28δ(m) , total integration for these peaks was 6p.

6.95δ(m, 20p, BPh_4^-) ; 7.26δ(m, 15p, PPh_3).

5.7.2 Reaction of $[C_5H_5Fe(CO)_2CH_2Cl]$ (XXIX) with PPh_3 in methanol under reflux.

(XXIX) (0.21 g, 0.71 mmol) was dissolved in methanol (5 cm^3). PPh_3 (0.80 g, 3.05 mmol) in methanol (5 cm^3) was added, and the solution heated under reflux for three hours. $[C_5H_5Fe(CO)_2CH_2OCH_3]$ was isolated from this reaction as the only product, 0.20 g, 95 % yield. The product was identified by comparison of the IR and mp data with that obtained previously. [91]

5.7.3 Reaction of (XXIX) with PPh_3 in CH_3CN.

(XXIX) (0.16 g, 0.54 mmol) was dissolved in CH_3CN (5 cm^3). PPh_3 (0.70 g, 2.67 mmol) in CH_3CN (5 cm^3) was added, and the solution left to stand in the dark for 17 days. The solution darkened slightly during this time. Removal of the solvent under reduced pressure gave a yellow/orange oil. Trituration with n-hexane gave a yellow solution and mustard hexane insoluble crystalline material. The hexane solution was filtered, removal of the hexane under reduced pressure gave (XXIX) 0.11 g, 69 % yield. This product was identified by comparison of IR and mp

data with an authentic sample prepared in 5.5.4.

The hexane insoluble material was dissolved in methanol, and precipitated as the BPh_4^- salt, to give dark yellow crystalline material, 0.04 g, mp 200 - 212 °C (decomp). The product was identified as $[C\bar{p}Fe(CO)_2CH_2PPh_3]^+ BPh_4^-$, yield = 10 %.

$\nu(CO)$ (CH_2Cl_2) 2012 (s) 1952 (s) cm^{-1}.

^1H nmr ($CDCl_3$) gave peaks at :

1.68δ(d, 2p, CH_2) , 1.92δ(s, 15p, C_5Me_5) , 6.80δ(m, 20p, BPh_4^-) ,

7.48δ(m, 15p, PPh_3).

J(PH) = 14.0 Hz.

Elemental analysis was not obtained for this product as it was contaminated with a small quantity of triphenylphosphine oxide, which could not be separated from the product by crystallisation, as the product decomposed rapidly in solution.

5.8 Some attempts to prepare models for Fischer-Tropsch intermediates.

5.8.1 Attempted acid hydrolysis of (XXV) with triflouroacetic acid.

(XXV) prepared as in 5.2.3 (0.18 g, 0.48 mmol) was dissolved in THF (15 cm^3). CF_3COOH (0.04 g, 0.52 mmol) in water (1 cm^3) was added in one portion. The yellow solution was stirred for three hours during which time it darkened to brown/yellow. The solvent was removed under reduced pressure to give a brown/black oil, which was extracted with n-hexane to give a deep-yellow solution, which gave a yellow oil (0.07 g) on removal of the solvent. An IR spectrum in n-hexane showed mainly peaks due to (XXV), with new peaks at 2027 (m), 1946 (m), 1936 (m) and 1176 (w) cm^{-1}, a small peak at 1779 cm^{-1} was noticed, this was attributed to a small amount of CF_3COOH. A ^1H nmr in C_6D_6 gave new peaks at 5.15 and 1.47δ, ratio 1 : 7.

The product could not be purified, and was therefore not characterised.

The reaction was repeated in the same manner, using water (5 cm^3), and extracting the product with n-hexane, the same product was obtained, but could not be characterised as it could not be purified.

5.8.2 Attempted acid hydrolysis of (XXV) with triflouroacetic acid.

(XXV) prepared as in 5.2.3 (0.15 g, 0.42 mmol) was dissolved in THF (15 cm^3). CF_3COOH (0.20 cm^3) was added together with water (1 cm^3) at 0 °C. The solution was allowed to warm to room temperature, and then stirred at room temperature for three hours. The solution darkened slightly during this time. 25 % (w/v) trimethylamine in water (5 cm^3) was added to the solution, and the solvent removed under reduced pressure, and then dried on a vacuum pump (0.1 mm Hg) for one hour to remove the water. The residue was extracted with n-hexane to give a green/yellow solution, which on removal of the solvent gave a yellow oil (0.12 g). An IR spectrum in n-hexane showed this oil to be (XXV) only, no new peaks were present.

5.8.3 Attempted esterification of (XXV).

(XXV) (0.23 g, 0.64 mmol) was dissolved in THF (15 cm^3). CF_3COOH (0.50 cm^3) was added to the orange/yellow solution, with vigorous stirring. The solution was protected from light with foil, and stirred overnight. The solution became slightly paler. Triethylamine (0.7 cm^3 25 % solution with water) was added dropwise with stirrring. The solvent was removed under reduced pressure with gentle warming to give an orange/red residue which contained water. The residue was extracted with n-hexane to give a clear yellow solution, which became green cloudy on standing. The hexane solution was filtered, and the solvent removed under reduced pressure. The yellow/orange residue was recrystallised fron n-hexane at -78 °C to give small orange crystals, 0.16 g, mp 55 -

64 °C (decomp).

Analysis found : C: 45.3 %

H: 4.5 %

Analysis expected for $[CpMo(CO)_3CH_2OC(O)CF_3]$:

C: 43.5 %

H: 3.9 %

ν(CO) (hexane) 2024 (s) 1947 (s) 1936 (s) 1779 (m) cm^{-1}.

^1H nmr (C_6D_6) gave peaks at :

1.47δ(s, 15p, C_5Me_5) ; 5.16δ(s, 2p, CH_2).

5.8.4 Reaction of (XXVI) with $AgPF_6$ in THF.

(XXVI) (0.14 g, 0.39 mmol) was dissolved in THF (30 cm^3). The Schlenk tube was protected from light with foil. $AgPF_6$ (0.11 g, 0.42 mmol) was added under nitrogen with vigorous stirring, the solution darkened immediately, and a grey precipitate appeared, after 30 minutes the solution was filtered, the THF was sticky and very viscous, and could not be filtered easily. The reaction mixture was placed on a rotavapor, and the volume reduced to a sticky oil, no product could be extracted from the oil. The reaction was repeated to give the same result, an IR spectrum in CH_2Cl_2 showed very weak carbonyl bands.

The reaction was repeated with $[CpMo(CO)_3CH_2Cl]$, to give a similar result.

5.8.5 Reaction of $[CpMo(CO)_3CH_2Cl]$ with $AgPF_6$ in acetone.

$[CpMo(CO)_3CH_2Cl]$ (0.20 g, 0.68 mmol) was dissolved in acetone (10 cm^3). $AgPF_6$ (0.14 g, 0.57 mmol) was added under nitrogen, the solution was protected from light with foil. The yellow/orange solution went cloudy on addition of the $AgPF_6$ and went purple/brown within 2 minutes. After 30 minutes, the solution had darkened to deep red and cloudy. The solution was filtered and the solvent

removed under reduced pressure to give a red oil. An IR spectrum in CH_2Cl_2 gave peaks at 2066 (m) , 2057 (w) , 1981 (vs) , 1674 (m) cm^{-1}. The product was recrystallised from CH_2Cl_2/hexane to give a small amount of crystalline material. A ^1H nmr in $CDCl_3$ gave peaks at 1.26δ(s) and 5.82δ(s) . The product was not able to be purified and decomposed readily, and was therefore not characterised.

5.8.6 The reaction of (XXVI) with NaOH in THF/water.

(XXVI) (0.11 g, 0.29 mmol) was dissolved in THF (10 cm^3). NaOH pellets (0.57 g, 12.8 mmol) and water (2 cm^3) were added and the solution stirred for 16 hours. The solution changed colour from yellow/orange to pale yellow and cloudy, The solution was filtered and the solvent removed under reduced pressure. The residue was extracted with n-hexane to give a yellow oil after removal of the solvent. An IR spectrum in n-hexane showed mainly bands due to (XXVI), and new peaks at 2010 and 1928 cm^{-1}. The new product , about 20 % as seen from the relative intensities of the peaks in the carbonyl region of the IR spectrum, could not be separated from (XXVI). The product could thus not be characterised.

The reaction was repeated under reflux overnight, the material decomposed, and no carbonyl containing material could be detected.

5.8.7 The reaction of (XXVI) with KOH/water.

(XXVI) (0.41 g, 1.13 mmol) was dissolved in N_2 saturated THF (10 cm^3) and water (2 cm^3). KOH pellets (0.24 g, 4.3 mmol) was added under nitrogen, and the solution stirred vigorously. The solution was protected from light with foil. The solution was stirred for 18 hours. After removal of the solvent, and subsequent extraction with n-hexane, 0.14 g yellow oil was obtained.

An IR spectrum in n-hexane showed bands at 2023 (w) , 2012 (m) , 1946 (w) , 1927 (s) cm^{-1}. This IR spectrum is very different from that of (XXVI). A ^1H nmr spectrum in C_6D_6 gave many peaks between 1 and 3δ. The material could not be purified, and was thus not characterised.

5.8.8 Attempted preparation of $[CpW(CO)_3(=CH_2)]^+ PF_6^-$.

(XXVIII) (0.22 g, 0.40 mmol) was dissolved in THF (10 cm^3). $AgPF_6$ (0.20 g, 0.79 mmol) was added. The solution went cloudy immediately after the addition of the silver salt. The solution was filtered under nitrogen after three minutes to give an orange/brown solution which darkened immediately it was exposed to the atmosphere. Removal of the solvent under reduced pressure gave a brown oily material, which went blue within 10 minutes. An IR spectrum of this product in CH_2Cl_2 gave two bands in the carbonyl region, at 1927 (s) and 1867 (m) cm^{-1}. The product was not able to be purified due to it's instability in solution, and was therefore not characterised.

5.8.9 Attempted preparation of $[CpW(CO)_3CH_2OH]$.

(XXVIII) (0.18 g, 0.33 mmol) was dissolved in THF (10 cm^3). A solution of NaOH in water (0.1 M, 5 cm^3) was added, and the mixture stirred very vigorously. The solution went slightly cloudy, removal of the solvent and extraction with n-hexane gave (XXVIII) in 60 % yield. A small amount of brown hexane insoluble material remained, this was, however, not characterised.

5.8.10 Attempted preparation of $[CpW(CO)_3CH_2OH]$.

(XXVII) (0.11 g, 0.25 mmol) was dissolved in THF (5 cm^3). CF_3COOH (0.01 g,

0.09 mmol) in water (2 cm^3) was added, and the solution stirred vigorously for 2 hours. The solution was quenched with aqueous diethylamine, and the THF layer removed. Removal of the THF and subsequent extraction with n-hexane gave a yellow oil. The carbonyl region of the IR spectrum in n-hexane showed weak bands at 2010 and 1962 cm^{-1}. The product was, however, not able to be purified, and was thus not characterised.

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APPENDIX

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[(C_5Me_5)W(CO)_3CH_2PPh_3]^+I^-.\frac{1}{2}CH_2Cl_2$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	107	-62	2	3	0	53	33	8	5	0	29	-14	3	8	0	32	-37	6	12	0	56	54
6	0	0	179	-164	3	3	0	304	299	9	5	0	110	110	4	8	0	179	-188	-17	0	1	57	46
8	0	0	208	193	5	3	0	119	-120	11	5	0	71	-68	5	8	0	55	58	-15	0	1	111	-107
10	0	0	132	-118	6	3	0	60	54	13	5	0	47	45	6	8	0	96	94	-13	0	1	77	84
12	0	0	96	88	8	3	0	52	-51	15	5	0	60	-55	8	8	0	79	-78	-11	0	1	23	-11
2	1	0	57	17	9	3	0	34	-35	0	6	0	233	242	14	8	0	40	29	-9	0	1	38	28
3	1	0	112	103	10	3	0	42	47	1	6	0	144	-146	1	9	0	34	-33	-7	0	1	192	-186
5	1	0	72	59	11	3	0	105	103	2	6	0	110	-113	2	9	0	36	35	-5	0	1	196	193
6	1	0	111	-127	12	3	0	57	-59	3	6	0	188	203	3	9	0	53	51	-3	0	1	77	-136
7	1	0	185	-170	13	3	0	118	-109	5	6	0	62	-64	4	9	0	49	-52	3	0	1	53	92
8	1	0	174	160	15	3	0	68	55	7	6	0	71	67	6	9	0	60	62	5	0	1	81	-94
9	1	0	111	99	16	3	0	32	-33	8	6	0	58	55	7	9	0	61	-67	7	0	1	139	-138
10	1	0	109	-106	17	3	0	25	-20	9	6	0	93	-96	8	9	0	45	-44	9	0	1	176	174
11	1	0	31	24	0	4	0	111	113	10	6	0	91	-93	9	9	0	48	48	11	0	1	138	-136
12	1	0	59	54	1	4	0	201	206	11	6	0	31	22	10	9	0	50	54	13	0	1	120	111
14	1	0	98	-89	2	4	0	220	-119	12	6	0	57	-54	12	9	0	53	-54	15	0	1	37	-25
15	1	0	27	-17	3	4	0	215	-219	15	6	0	25	12	0	10	0	148	156	17	0	1	46	43
16	1	0	69	64	4	4	0	91	-90	1	7	0	63	-63	2	10	0	109	-113	-13	1	1	51	48
0	2	0	231	-206	5	4	0	179	185	3	7	0	108	106	3	10	0	51	-59	-12	1	1	26	-27
1	2	0	161	-174	6	4	0	110	177	4	7	0	29	33	5	10	0	40	37	-11	1	1	41	-44
2	2	0	80	96	7	4	0	188	-184	5	7	0	65	-79	7	10	0	30	-29	-10	1	1	46	-40
3	2	0	81	68	8	4	0	100	104	6	7	0	56	-55	8	10	0	69	66	-9	1	1	85	93
4	2	0	63	-86	9	4	0	100	97	7	7	0	46	-48	9	10	0	26	30	-8	1	1	147	154
5	2	0	145	-138	10	4	0	96	-93	8	7	0	65	55	10	10	0	62	-56	-7	1	1	122	-132
6	2	0	196	192	11	4	0	41	-45	9	7	0	24	-16	3	11	0	26	20	-6	1	1	132	-139
7	2	0	124	117	13	4	0	35	27	10	7	0	74	-72	6	11	0	36	-38	-5	1	1	206	180
8	2	0	106	-106	15	4	0	33	-25	11	7	0	74	69	7	11	0	38	-29	-4	1	1	151	-152
9	2	0	48	-50	1	5	0	67	-85	12	7	0	40	42	8	11	0	54	54	-3	1	1	255	-260
10	2	0	23	-22	2	5	0	29	28	13	7	0	66	-63	9	11	0	30	32	-2	1	1	45	-37
11	2	0	43	37	3	5	0	53	63	14	7	0	27	-22	1	12	0	62	-67	2	1	1	158	-166
13	2	0	58	-51	4	5	0	36	34	15	7	0	36	28	2	12	0	25	13	3	1	1	350	310
14	2	0	41	34	5	5	0	78	88	0	8	0	40	-42	3	12	0	43	55	4	1	1	233	227
16	2	0	31	-26	6	5	0	33	-30	1	8	0	28	-32	4	12	0	48	-44	5	1	1	110	-132
1	3	0	129	-143	7	5	0	149	-150	2	8	0	97	100	5	12	0	40	-36	6	1	1	82	-81

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	1	1	108	114	12	2	1	72	62	-13	4	1	27	31	-1	5	1	120	-131	13	6	1	38	30
8	1	1	61	-66	13	2	1	93	-86	-12	4	1	87	88	0	5	1	185	197	14	6	1	61	-50
10	1	1	36	-32	14	2	1	57	-56	-11	4	1	29	24	2	5	1	273	-271	-15	7	1	28	-12
11	1	1	86	78	15	2	1	81	74	-10	4	1	91	-90	4	5	1	207	206	-13	7	1	34	23
12	1	1	81	77	16	2	1	38	30	-9	4	1	34	-39	5	5	1	93	91	-12	7	1	37	-29
13	1	1	25	-25	17	2	1	54	-45	-8	4	1	98	92	6	5	1	64	-75	-11	7	1	56	-53
15	1	1	27	14	-17	3	1	28	-7	-7	4	1	100	-99	8	5	1	42	40	-10	7	1	47	43
16	1	1	24	-4	-14	3	1	59	49	-6	4	1	74	-74	10	5	1	61	-52	-9	7	1	92	86
-17	2	1	34	-29	-12	3	1	90	-82	-5	4	1	184	162	11	5	1	32	-23	-8	7	1	40	28
-16	2	1	53	-44	-11	3	1	61	65	-4	4	1	113	109	12	5	1	62	58	-7	7	1	67	-64
-14	2	1	57	55	-10	3	1	64	58	-3	4	1	21	19	14	5	1	51	-42	-6	7	1	40	29
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-4	1	3	197	225	-1	2	3	152	149	6	3	3	70	62	15	4	3	28	-25	-5	6	3	78	-77
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-2	1	3	238	-242	1	2	3	134	-114	8	3	3	61	-64	-14	5	3	53	-54	-2	6	3	73	58
-1	1	3	371	334	3	2	3	25	-16	9	3	3	51	45	-12	5	3	72	62	-1	6	3	92	88
1	1	3	327	-305	4	2	3	139	120	10	3	3	98	95	-11	5	3	31	26	0	6	3	25	-26
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4	7	3	104	-102	0	9	3	47	-45	5	11	3	43	-41	-2	1	4	33	46	4	2	4	253	-245
5	7	3	97	-95	1	9	3	111	112	6	11	3	69	-70	-1	1	4	109	-102	5	2	4	89	-86
6	7	3	50	47	2	9	3	62	62	7	11	3	55	47	0	1	4	104	-95	6	2	4	221	210
7	7	3	104	100	3	9	3	88	-93	8	11	3	61	52	1	1	4	214	-207	7	2	4	142	138
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-7	1	5	167	-182	-3	2	5	120	118	6	3	5	193	197	-3	5	5	32	29	10	6	5	56	-56
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-1	12	7	32	27	4	1	8	83	76	14	2	8	32	31	-4	4	8	21	-21	-11	6	8	42	-46
-14	0	8	29	-43	5	1	8	129	123	-15	3	8	61	56	-3	4	8	189	186	-10	6	8	75	-72
-12	0	8	44	50	6	1	8	74	-77	-14	3	8	33	-38	-2	4	8	76	-72	-9	6	8	28	29
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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