THE SYNTHESIS AND REACTIVITY OF BINUCLEAR μ- HYDROCARBYL COMPLEXES OF SOME TRANSITION METALS

by

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B.Sc.(Hons)

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ABSTRACT

The new μ-(1,n)-alkanediyl compounds $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$, (R = H, n = 3 -10 and R =Me, n =3 - 6), $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (M = Mn, n = 4-6 and M = Re, n= 3 and 4) have been prepared using essentially two synthetic routes. Thus the iron compounds were synthesized by the reaction of $Na[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]$ with the appropriate dibromoalkane. The manganese and rhenium compounds on the other hand, were prepared by the decarbonylation of the corresponding diacyl compounds of the type, $[M(CO)_5]_2\{\mu\text{-}CO(CH_2)_nCO\}$ (M = Mn or Re). These diacyl species in turn were synthesized by the reaction of $Na[M(CO)_5]$ with diacyl chlorides.

All the new compounds have been fully characterized by microanalysis, infrared, ^1H and ^{13}C nmr spectroscopy. The mass spectra of the compounds have been investigated and the fragmentation patterns are discussed and compared with other known polymethylene compounds.

An extensive investigation into the reactivity of the new alkanediyl compounds has been carried out. Thus for example the reactivity of the compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ with nucleophiles such as tertiary phosphines and isocyanides, yield diacyl compounds of the type $[CpFe(CO)L]_2\{\mu\text{-}CO(CH_2)_nCO\}$ (Cp = C_5H_4Me or C_5Me_5) and (L = tertiary phosphine or isocyanide). Similar ligand induced CO insertion reactions were observed for the manganese and rhenium alkanediyl compounds. The products from these reactions were characterized using the analytical techniques mentioned earlier. The reactions are discussed and compared with those of mononuclear alkyl compounds of manganese, rhenium and iron.

The reactions of some polymethylene bridged compounds with synthesis gas have also been investigated. This reaction is of importance in view of the fact that polymethylene bridged compounds have been implicated in a number of catalytic processes e.g the Fischer- Tropsch reaction. The reaction with synthesis gas was found to yield bifunctional alcohols of the type $HO(CH_2)_nOH$.

In a separate study, the binuclear μ-phthaloyl compounds of manganese, rhenium,iron,molybdenum,cobalt and rhodium were prepared and characterized. The phthaloyl compounds of manganese, rhenium and iron were decarbonylated to form the corresponding μ-phenylene compounds. The reactions of some of these compounds with nucleophiles and electrophiles have been studied and the results compared with that of the corresponding mononuclear benzoyl and phenyl compounds.

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ABBREVIATIONS

The following abbreviations are used in this thesis:

APT	:attached proton test
Cp	: $(\eta^5\text{-}C_5H_5\ )$
Cp′	: $(\eta^5\text{-}C_5H_4Me)$
Cp^*	: $(\eta^5\text{-}C_5Me_5)$
ether	: diethyl ether
h	: hour(s)
IR	: infrared
Me	: methyl group
M^+	: molecular ion
m/e	: mass to charge ratio
nmr	: nuclear magnetic resonance
Ph	: phenyl group
PR_3	: tertiary phosphine
ppm	: parts per million
py	: pyridine
R	: an alkyl group
rt	: room temperature
t-BuNC	: tertiary butylisocyanide
THF	: tetrahydrofuran
TMS	: tetramethylsilane

CONTENTS

CHAPTER ONE.

1. INTRODUCTION:

1.1 DEFINITION OF μ-HYDROCARBYL COMPOUNDS AND GENERAL MOTIVATION FOR THE STUDY THEREOF

μ-Hydrocarbyl compounds are organometallic species in which two or more metal centres are bridged by hydrocarbyl or hydrocarbon ligands. There are a number of different types of hydrocarbyl compounds [1,2]. These compounds are normally classified in terms of the nature of the bridging ligand. In this work, we will only be considering two types of μ-hydrocarbyl compounds viz μ(1,n)-alkanediyl and μ-phenylene compounds.

μ(1,n)-alkanediyl compounds (also known as polymethylene bridged compounds) are binuclear species in which the metal centres are bridged by an alkyl chain via the latter's two terminal carbon atoms. There are two types of μ(1,n)-alkanediyl compounds, viz those without a metal-metal bond, type 1, and those with a metal-metal bond, type 2, (Figure 1.1) [3,4]

$L_nM\text{-}(CH_2)_n\text{-}ML_n$

Type 1

$L_nM\overset{(CH_2)_n}{\text{———}}ML_n$

Type 2

(L_nM = metal and its associated ligands, $n > 2$.)

Figure 1.1 Types of μ-alkanediyl compounds.

μ-Phenylene compounds are binuclear compounds in which the two metal centres are bridged by a benzene ring (Figure 1.2).

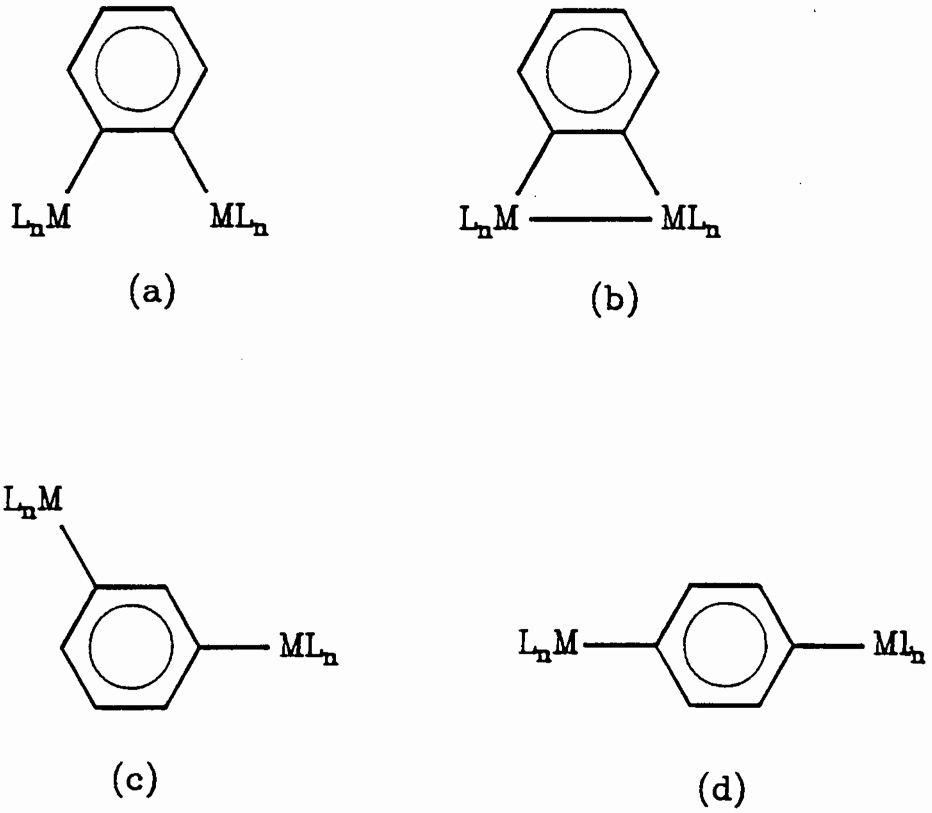


Figure 1.2 Types of μ-phenylene compounds.

There are many different ways in which a benzene ring can bridge two metal centres, some of these are depicted in Figure. 1.2. In this work we will only be dealing with μ-(p-phenylene) compounds i.e. compounds in which the metals are attached in a 1,4 fashion to a benzene ring (Figure 1.2d).

Recently there has been an increased interest in binuclear μ-hydrocarbyl compounds, because of their possible role in catalytic processes. It is thought that some of these compounds could be models for intermediates in a number of catalytic reactions. An example of a catalytic process in which μ-hydrocarbyl compounds have been invoked as intermediates is the Fischer-Tropsch (F-T) reaction [5]. This process involves initial gasification of coal to form a mixture of H_2 and CO. The CO/H_2 (syngas) mixture is then converted to long chain hydrocarbons, olefins as well as oxygenated products such as aldehydes and alcohols (Equation 1.1)

$$CO + H_2 \xrightarrow{\text{Catalyst}} CH_4\text{, alkanes, olefins and oxygenates} \quad (1.1)$$

The Fischer-Tropsch synthesis is a heterogeneous process and can be catalyzed by different metals such as Fe, Co, Ni and Ru supported on alumina [6].Cobalt promoted by chromium oxides have also been employed. The types of products obtained depend on the nature of the catalyst as well as the reaction conditions. Thus for example, a cobalt based catalyst will give mainly long chain alkanes, while a rhodium based catalyst tends to produce oxygenates such as alcohols and aldehydes.

Catalytic processes such as the Fischer-Tropsch reaction, are becoming increasingly important, because of the need to develop alternatives to petroleum feedstocks [7]. Presently the production costs of synfuels from syngas are fairly high, however it is expected to fall as technological advances are made. At the moment South Africa is the only country which operates a commercially viable synfuel industry on a large scale at its SASOL plants.

A number of different mechanisms have been proposed for the F-T reaction. Among the more favoured, is the one originally put forward by Fischer and Tropsch [8]. This mechanism, known as the "Carbide Mechanism", was extended by Craxford and Rideal [9]. The later work of Pettit [10] as well as that of Sachtler [11] has led to further refinement of the mechanism. The basic features of the carbide mechanism as it is known today are shown in Figure 1.3.

From Figure 1.3, it can be seen that the initial step in the reaction involves the adsorption of CO onto the catalyst surface followed by dissociation to form a surface carbide and an adsorbed oxygen. The latter can be transformed into water or CO_2.In the second step, the surface carbides are reduced in the presence of H_2, to give adsorbed methylene or methyl groups. The methylene groups then undergo oligomerization to form a hydrocarbon chain which is adsorbed on the metal surface. The oligomerization process is initiated by the interaction of an adsorbed methyl with an adsorbed methylene group. Further chain propagation results via repeated insertion of methylene groups. The process is terminated when β-elimination followed by desorption of the alkene product occurs.

Examining the proposed mechanism of Fischer and Tropsch, it is evidently clear that hydrocarbyl complexes play an important role. Thus terminal methylene as well as bridging methylene compounds have been invoked as model compounds for the F-T reaction. Similarly μ-alkanediyl compounds can be models for chain extension.

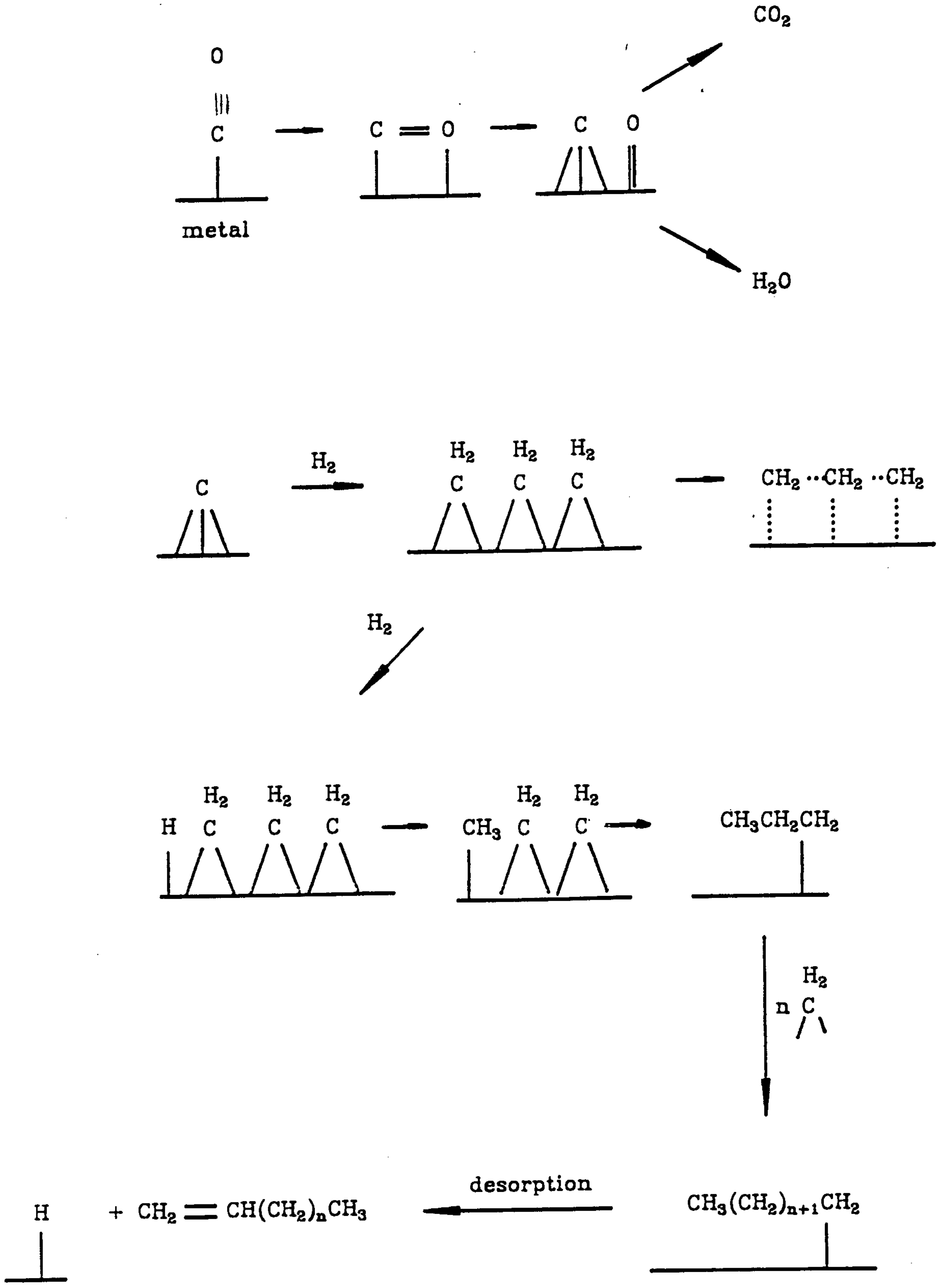
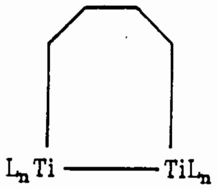
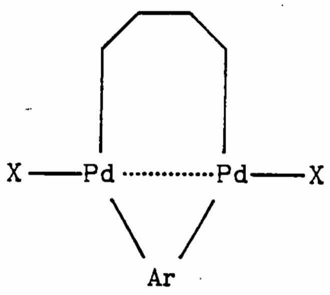


Figure 1.3: The carbide mechanism for the F-T reaction.

Besides the F-T reaction, μ-hydrocarbyl compounds have been implicated in other catalytic processes. Thus μ-alkanediyl compounds have been proposed as intermediates in a number of alkene oligomerization reactions [12, 13]. In this regard, species of the type **1-I** and **1-II** have been linked respectively to intermediates in ethene disproportionation (catalyzed by a titanium compound) [12] and the dimerization of ethene to 1-butene (catalyzed by a palladium compound) [13].



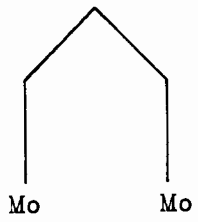
1–I



1–II

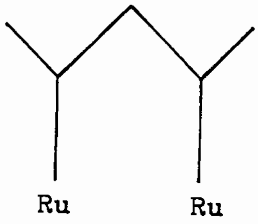
μ-Alkanediyl compounds have also been envisaged as intermediates in olefin polymerization processes, such as the Ziegler-Natta reaction [14] and μ(alkanediyl) compounds of type 2, i.e. dimetallocycles, are believed to be chain propagating entities in the olefin metathesis process [15, 16].

Tanaka *et al* have invoked a binuclear 1,3-propanediyl molybdenum species, **1-III**, as an intermediate in the homologation of ethene using $MoO_3/SnMe_4$ supported on silica as catalyst [17].



1–III

A similar ruthenium species, **1-IV**, has been implicated in the hydrogenolysis of pentenes (branched and linear) on a Ru/SiO_2 catalyst [18].



1–IV

From the afore-going discussion it is clear that μ-alkanediyl complexes play a central role in a variety of catalytic processes. Thus a study of these compounds could provide insight into the mechanism of some catalytic processes.

Besides the catalytic importance of these μ-hydrocarbyl compounds, they are also of interest in their own right. These binuclear compounds may be expected to show different reactivity patterns to mononuclear metal compounds. Thus for example, bridging hydrocarbyl ligands which are bonded to two metal centres, may be involved in rearrangements which are not possible for simple mononuclear analogues. Therefore a study of the reactivity of these compounds is of importance.

1.2 A BRIEF SUMMARY OF KNOWN μ(1,n)-ALKANEDIYL COMPOUNDS OF TRANSITION METALS:

A number of excellent and in depth reviews dealing with μ(1,n)-alkanediyl compounds have appeared in recent years [1,3,4]. The review by Lappert *et al* [1] deals with μ-hydrocarbyl compounds in general, while the later reviews by Moss and Scott [3], and the 1986 review by Casey and Audett [4], deal specifically with polymethylene bridged compounds. Because the subject matter is dealt with extensively in these articles, it is therefore not necessary to give an in depth review in this thesis. However, to give a brief overview of the field, a summary of the known μ(1,n)-alkanediyl compounds prepared over the years is to be found in Table 1.1. Basically Table 1.1 lists the known compounds and also indicates the synthetic routes to these compounds. In addition to the table a brief update of recent work on polymethylene bridged compounds is also given.

Not many reports on polymethylene bridged compounds have appeared subsequent to Casey's review [4]. In fact, most of these have originated from our laboratory at the University of Cape Town. Among the compounds reported recently were a series of dinuclear polymethylene bridged cobaloximes of the type $[Co(DH)_2py]_2\{\mu\text{-}(CH_2)_n\}$, where n = 4-8 and DH = mono-anion of dimethylglyoxime [19]. These compounds can be prepared by the reaction of mononuclear bromoalkyl cobaloximes, $[Co(DH)_2py(CH_2)_nX]$ with an equimolar quantity of $[Co(DH)_2pyCl]$ in the presence of $NaBH_4$ (Equation 1.2). These complexes can also be prepared by the reaction of $[Co(DH)_2pyCl]$ and the corresponding dihaloalkane in a 2:1 mole ratio (Equation 1.3). This is an extension of the work of Schrauzer and Windgassen who first reported the synthesis of the 1,3-propanediyl and the 1,4-butanediyl compounds, however these compounds were not fully characterized by these workers [20].

$$\begin{tikzcd}[Co(DH)_2pyCl] + Br(CH_2)_nBr \arrow[r, "NaBH_4"] & {[Co(DH)_2py(CH_2)_nBr]} \arrow[d, "{[Co(DH)_2pyCl]}"] \\ & {[py(DH)_2Co(CH_2)_nCo(DH)_2py]} \\ & n = 4\text{-}6\end{tikzcd} \qquad (1.2)$$

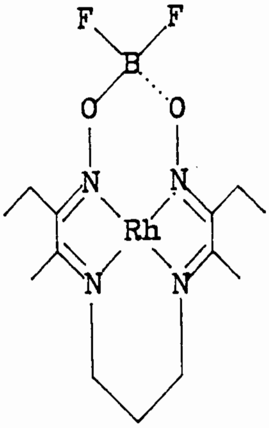
$$2[Co(DH)_2pyCl]+Br(CH_2)_nBr \xrightarrow{NaBH_4} [py(DH)_2Co(CH_2)_nCo(DH)_2py] \qquad (1.3)$$

These polymethylene-bridged cobaloximes together with polymethylene-bridged compounds of vitamin B_{12} [21] are the only examples of μ-(1,n)-alkanediyl compounds of cobalt with no metal-metal bond. It would appear that the surrounding macrocyclic ligands afford stability to these cobalt complexes.

The synthesis of polymethylene bridge macrocyclic dirhodium compounds of the type, **1-V**, have been reported by Collman [22]. These compounds are formed via the oxidative addition of α,ω-dihalides to a macrocyclic rhodium(I) complex (Equation 1.4)

$$2Rh(I) + X(CH_2)_nX \longrightarrow \underset{\textbf{1-V}}{XRh(CH_2)_nRhX}$$

Rh =



(1.4)

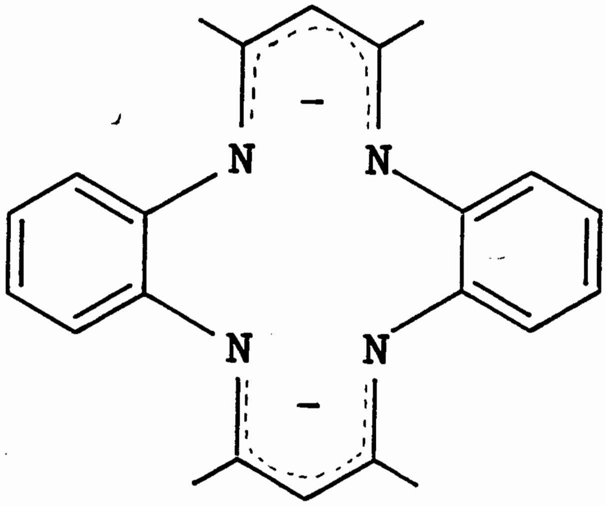
The binuclear rhodium compounds are formed via an intermediate mononuclear halo-alkyl compound which can be isolated. Collman found that the ratio of mononuclear to binuclear product appears to be solvent dependent. Thus the ratio of binuclear to mononuclear compound is found to be about 2:1 when the reactions are carried out in THF or DME with 50% excess of substrate. Increasing the substrate excess six-fold, leads to a reversal of the ratio of mononuclear and binuclear products. When the ethers are substituted by solvents such as acetonitrile or acetone, the dimer/monomer ratio is reduced to 1:9. It is believed that the variations in product ratios in going from one solvent to another are due to changes in the solubility of the Rh(I) macrocycle.

An analogous 1,2-ethanediyl compound **1-VI**, also containing a rhodium macrocycle, was reported by Van Voorhees and Wayland [23]. This compound was prepared by the reaction of $[Rh(TMTAA)]_2$ with ethene (Equation 1.5)

$$[Rh(TMTAA)]_2 + CH_2{=}CH_2 \longrightarrow (TMTAA)Rh\text{-}CH_2CH_2\text{-}Rh(TMTAA) \quad (1.5)$$

1-VI

TMTAA = dibenzotetramethylaza [14] annulene dianion

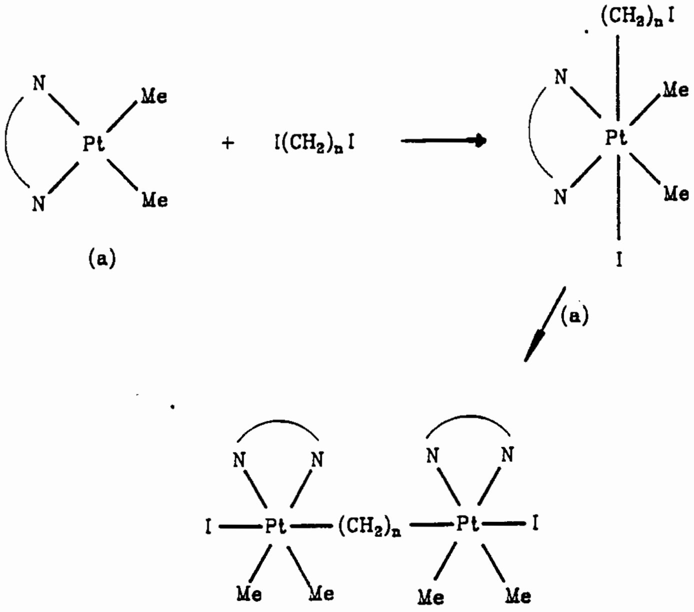


TMTAA

If the reaction in Equation 1.5 is repeated in the presence of hydrogen, then the μ(1,n)-ethanediyl compound is not obtained, but rather a mononuclear ethyl species (Equation 1.6)

$$[Rh(TMTAA)]_2 + H_2 + 2CH_2{=}CH_2 \longrightarrow 2Rh(TMTAA)(CH_2CH_3) \quad (1.6)$$

Puddephatt and co-workers have done extensive studies on $\mu(1,n)$-alkanediyl complexes of platinum. These compounds were generally prepared by the addition of diiodoalkanes, $I(CH_2)_nI$, to compounds such as dimethyl(1,10-phenanthroline)platinum (II) and other similar species [24-26]



N⌒N = 1,10-phenanthroline, n = 2 - 5

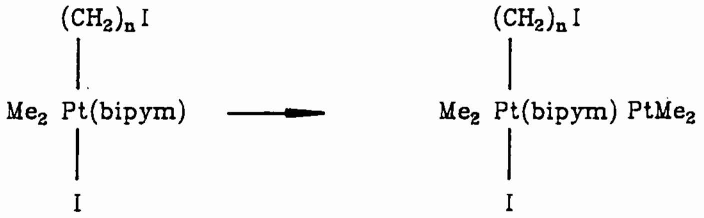
N⌒N = biphen, n = 3 - 5

N⌒N = 2,2′-bipyrimidine, n = 3 - 5.

(1.7)

As can be seen from Equation 1.7, the reactions proceed via a mononuclear iodoalkyl complex, which reacts further to produce the binuclear alkanediyl bridged complex. The mononuclear compounds are found to be the only product if a large excess of $I(CH_2)_nI$ is used.

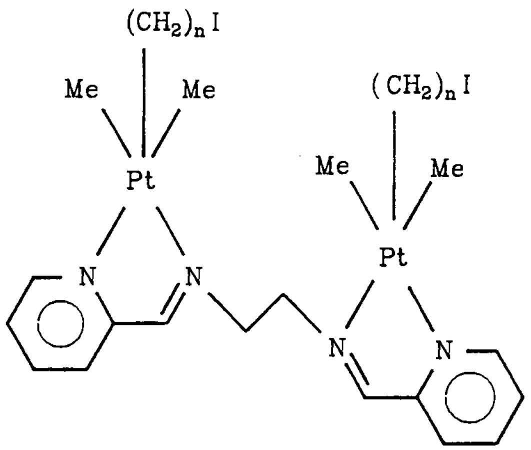
In the case of the complexes where the chelating ligand, N-N, is 2,2′-bipyrimidine, the intermediate mononuclear iodoalkyl compound can undergo two possible reactions [25]. Firstly it can react with a second moiety of (a) to form the μ-alkanediyl dimer as is depicted in Equation 1.7. A second possible reaction, is where the free nitrogen atoms of the bipym ligand are linked to a second $PtMe_2$ unit to give a binuclear compound of type (b) (Equation 1.8)



(b) (1.8)

Compounds of the type (b) are rare examples of mixed oxidation state Pt(II)-Pt(IV) complexes. A tetranuclear mixed oxidation state Pt(II)-Pt(IV) complex, with a μ-alkanediyl bridge can be formed by the reaction of the dinuclear polymethylene bridged compound with $Pt_2Me_2(\mu\text{-}SMe_2)_2$. No intramolecular oxidation of the $Pt(CH_2)I$ group to the dimethyl-platinum (II) centre of (b) has been observed which may be a result of the rigidity of the bipyrimidine system.

Similar oxidative-addition reactions were attempted with a bis(2-pyridyl)ethylenediimine system, however no polymethylene bridged compounds were isolated. Only iodoalkyls of the type **1-VII** were observed [26].



μ-(1,n)-Alkanediyl compounds of the type, $[CpRu(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 5-10) have been prepared in our laboratory at the University of Cape Town [27]. These compounds were prepared using the synthetic route shown in Equation (1.9).

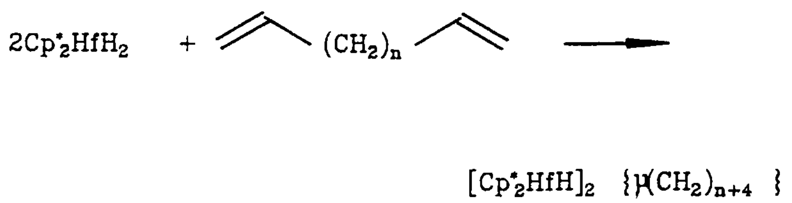
$$2Na[CpRu(CO)_2] + I(CH_2)_nI \longrightarrow [CpRu(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + 2NaI \quad n = 5 - 10 \tag{1.9}$$

These compounds have been found to be extremely stable at room temperature. A crystal structure determination of the compound where n = 5, revealed that the two cyclopentadienyl rings are *cis* to each other. This is different to what has been found for the iron compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ [28]. A study of the reactivity of some members of the series of ruthenium μ-alkanediyl compounds, show that these complexes are far less reactive than the analogous iron compounds. Thus for example, the ruthenium compounds only undergo carbonyl insertion reactions under much more vigorous conditions than their iron counterparts. The reaction of the alkanediyl compounds with tertiary phosphines yield phosphine substituted diacyl compounds (Equation 1.10)

$$[CpRu(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + 2PR_3 \xrightarrow[\text{xylene}]{\text{reflux}}$$

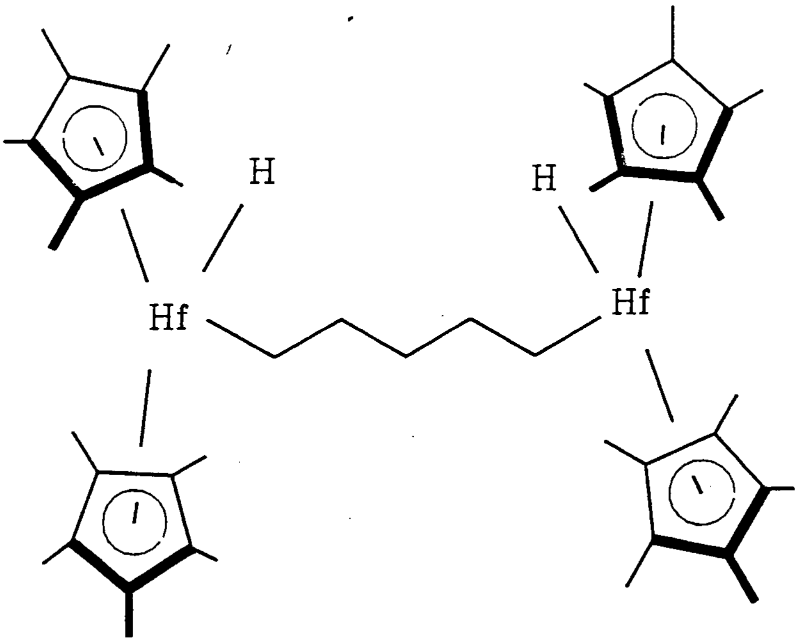
$$Cp(PR_3)(CO)RuCO(CH_2)_nCORu(CO)(PR_3)Cp \tag{1.10}$$

Moss and Bercaw [29] have prepared polymethylene bridged compounds of hafnium by the reaction of dienes with $Cp^*{}_2HfH_2$ (Equation 1.11)



(1.11)

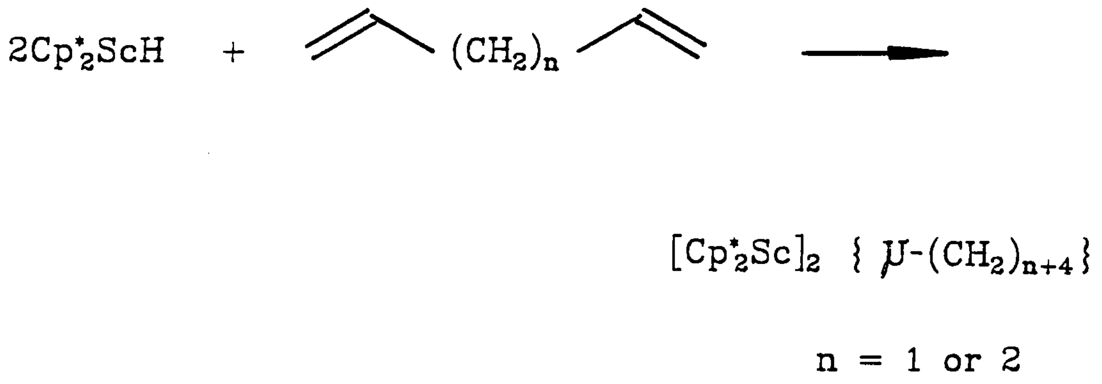
These hafnium compounds are the first examples of hydrido alkanediyl compounds i.e. a compound which has polymethylene bridge as well as a hydride bonded to the metal centres **(1-VIII)**



1–VIII

These hydrido alkanediyl compounds of hafnium although extremely air-sensitive, are relatively stable thermally.

The reaction of Cp^*_2ScH with dienes (2:1) also leads to alkanediyl compounds (Equation 1.12)



(1.12)

Table 1.1 Summary of μ-Alkanediyl Compounds.

COMPOUND	SYNTHESIS	REMARKS	REF
$[Cp^*{}_2Sc]_2\{\mu\text{-}(CH_2)_n\}$	$2Cp^*ScH$ + diene	n = 5 and 6	29
$[Cp^*{}_2HfH]_2\{\mu\text{-}(CH_2)_n\}$	$2Cp^*HfH_2$ + diene	n = 4 - 7	29
$M_2Cp_4\{\mu\text{-}(CH_2)_2\}(ClAlEt_3)_2$	$[M(Cp)_2Cl_2]$ + $AlEt_3$	M = Ti or Zr	30, 31
$Zr_2Cp_4\{\mu\text{-}(CH_2)_2\}Cl_2$	$[ZrCp_2Cl_2]$ + Al_2Et_6		32
$[CpMo(CO)_3]_2\{\mu\text{-}(CH_2)_n\}$	$[CpMo(CO)_3]^-$ + $X(CH_2)_nX$	X = Br, I n = 4 and 10	33, 34
$[CpM(CO)_3]_2\{\mu\text{-}(CH_2)_2\}$	$[CpM(CO)_3]^-$ + $[CpM(CO)_3(C_2H_4)]^+$	M = Mo, W	35, 36
$[CpW(CO)_3]_2\{\mu\text{-}(CH_2)_n\}$	$[CpW(CO)_3]^-$ + $I(CH_2)_nI$	n = 3 - 5	37, 38
$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_2\}$	$[Mn(CO)_5]^-$ + $Mn(CO)_5(C_2H_4)^+$		39
$[L_nM(CH_2)_2Re(CO)_5]$	$Re(CO)_5(C_2H_4)^+$ + $[L_nM]^-$	L_nM = $Cp(CO)_3W$, $Cp(CO)_3Mo$ $Mn(CO)_5$ $Re(CO)_5$	36, 39
$(CO)_5ReCH_2CH(CH_3)Re(CO)_5$	$[(CO)_5Re(CH_2=CHCH_3)]$ + $[Re(CO)_5]^-$		39
$[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$	$2[CpFe(CO)_2]^-$ + $Br(CH_2)_nBr$	n = 3 - 12	40, 41

Table 1.1/Continued....

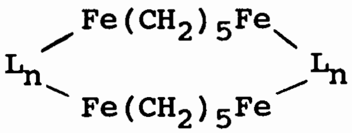
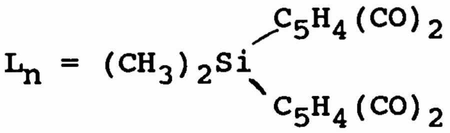
	$(CH_3)_2Si[C_5H_4Fe(CO)_2]_2^{2-}$ + $I(CH_2)_5I$	 $L_n = (CH_3)_2Si\begin{matrix}C_5H_4(CO)_2\\C_5H_4(CO)_2\end{matrix}$	42, 43
$[CpRu(CO)_2]_2\{\mu-(CH_2)_n\}$	$2[CpRu(CO)_2]^-$ + $X(CH_2)_nX$	X = Cl, n = 2	
		X = Br, I, n 3, 4	43, 44
		X = I, n = 5 - 10	27
$Cp(CO)_2Ru(CH_2)_nFe(CO)_2Cp$	$Cp(CO)_2Fe(CH_2)_nI$ + $[CpRu(CO)_2]^-$	n = 3 and 4	43, 27
$FpCH(Me)CH_2CH_2Fp$	$2[CpFe(CO)_2]^-$ + $ICH(Me)CH_2CH_2I$	Fp = $CpFe(CO)_2$	43

Table 1.1/Continued....

$FpCH(Me)CH_2CH_2CH_2Fp$	$2[CpFe(CO)_2]^-$ + $BrCH(Me)CH_2CH_2CH_2Br$	$Fp = CpFe(CO)_2$	56
$(CO)_4\overline{Os(CH_2)_nOs}(CO)_4$	$[Os_2(CO)_8]^{2-}$ + $I(CH_2)_nI$	$n = 2$ and 3	45
$[Co(DH)_2py]_2\{\mu\text{-}(CH_2)_n\}$	$2[Co(DH)_2pyCl]$ + $Br(CH_2)_nBr$ in presence of $NaBH_4$	DH = monoanion of dimethylglyoxime $n = 4 - 8$	19, 20
$(CO)Cp\overline{Co(CH_2)_nCo}Cp(CO)$	$[Cp_2(CO)_2Co_2]^{2-}$ + $I(CH_2)_nI$	$n = 3$ and 4 the carbonyl ligands bridge the two metal centres	46, 47

1.3 μ-PHENYLENE COMPOUNDS:

Although there are many aryl complexes known of the type M-C_6H_5, there have been very few reports of μ-phenylene compounds of transition metal elements. Most of these reports have dealt with μ-(*o*-phenylene) compounds which contain a metal-metal bond and some examples of these type of compounds are shown in Figure 1.4. Compound **I-IX** was prepared via a double oxidative addition of benzene to CpIr(CO)$_2$ [48] (Equation 1.13)

$$2CpIr(CO)_2 \xrightarrow{h\nu} "2CpIr(CO)" \xrightarrow{C_6H_6} \mathbf{1\text{-}IX} + H_2 \qquad (1.13)$$

The formation of **1-IX** is one of the few examples where double C-H activation occurs on the same organic molecule. These compounds such as **1-IX** and **1-X** [49] are important in relation to homogeneous catalytic activation of carbon-hydrogen bonds [50].

A second type of μ-(*o*-phenylene) compound has no metal-metal bond and again there are very few examples of this. Nesmeyanov and co-workers [51], prepared binuclear manganese and rhenium compounds in which the two metal centres were bridged by a phenyl group in the *ortho* position (see **1-XI** in Figure 1.5). These compounds were prepared by reaction of phthaloyl dichloride with the appropriate metal anion, followed by thermal decarbonylation (Equation 1.14).

$$M(CO)_5^- + C_6H_4\text{-}1,2\text{-}(COCl)_2 \longrightarrow C_6H_4\text{-}1,2\text{-}[COM(CO)_5]_2$$

$$\downarrow -2\ CO$$

$$C_6H_4\text{-}1,2\text{-}[M(CO)_5]_2$$

1-XI

M = Mn,Re

(1.14)

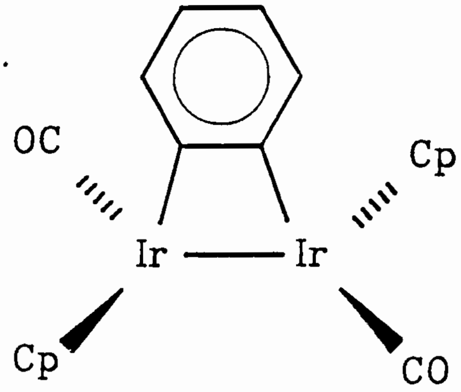
Another example of a μ-(*o*-phenylene) compound, is the nickel species, $[Ni_2(\mu\text{-}C_6H_4\text{-}o)_2(PEt_3)_4]$ (I-XII) which can be prepared by the reaction of *trans*-chloro(2-bromophenyl)-*bis*-(triethylphosphine)-nickel(II) with lithium metal [52] (Equation 1.15).

$$2[Ni(PEt_3)_2Cl(C_6H_4Br)] + 4Li \longrightarrow [C_6H_4Ni(PEt_3)_2]_2 + 2LiCl + 2LiBr \qquad (1.15)$$

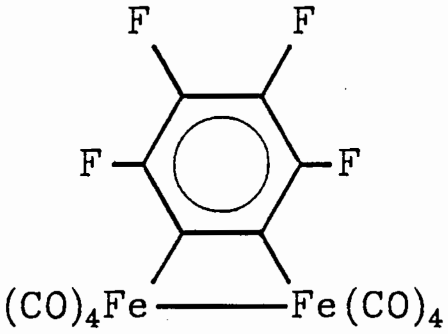
Not many examples of μ-(*p*-phenylene) compounds are to be found in the literature. The first known reports of μ-(*p*-phenylene) compounds of transition metal elements were those of the manganese and rhenium, compounds **1-XIII** and **1-XIV** respectively [51]. These were prepared in a similar fashion to those of the analogous μ-(*o*-phenylene) compounds discussed earlier. Cohen [53] reported the synthesis of the tetra-fluorobenzene bridged compound, $[Fe_2(Cp)_2(\mu\text{-}C_6F_4)(CO)_4]$, **1-XV**, by the route outlined in Equation 1.16

$$2\ CpFe(CO)_2I + Li_2C_6F_4 \longrightarrow [Fe_2(Cp)_2(\mu\text{-}C_6F_4)(CO)_4] + 2\ LiI$$

1-XV (1.16)

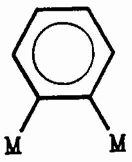


1–IX



1–X

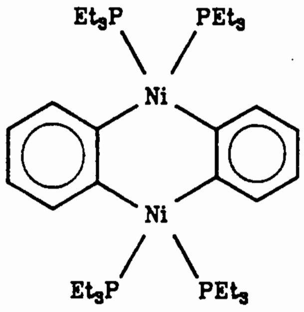
Figure 1.4: Some μ-(*o*-phenylene) complexes.



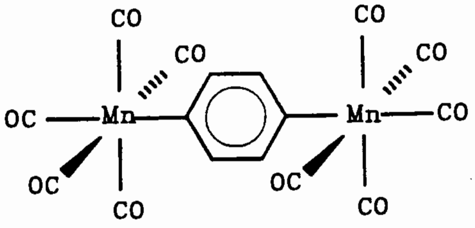
M = $Mn(CO)_5$ or

$Re(CO)_5$

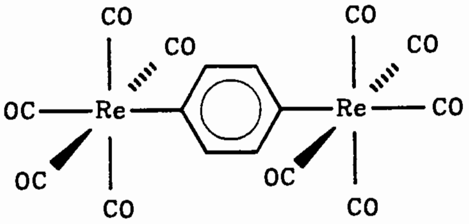
1-XI



1 - XII



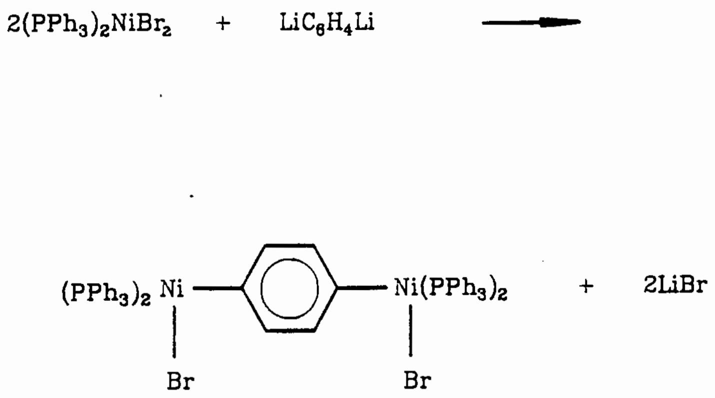
1-XIII



1-XIV

Figure 1.5: Some examples of μ-phenylene compounds.

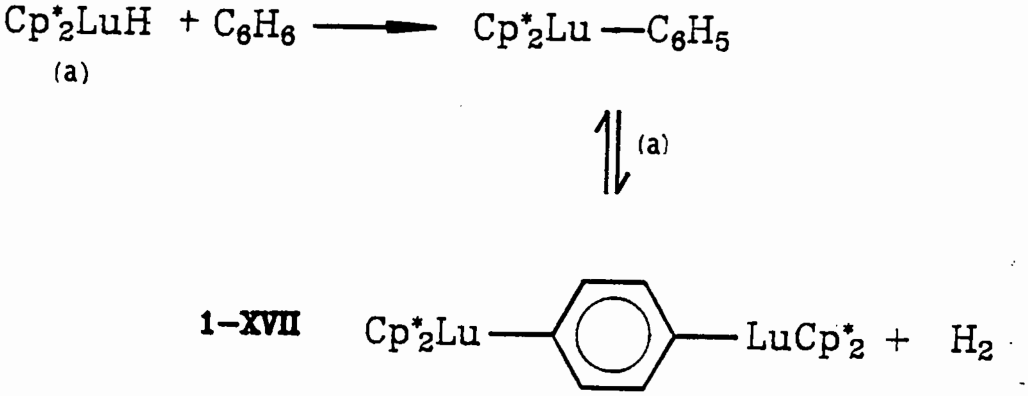
Uhlig *et al* [54], reported the preparation of a μ-(*p*-phenylene) compound of nickel, (**1-XVI**) (Equation 1.17).



1-XVI

(1.17)

Watson and Parshall [55] reported the synthesis of the μ-(*p*-phenylene) compound of lutetium, **1-XVII**, by the reaction of the lutetium hydride, $Cp^*{}_2LuH$, with benzene (Equation 1.18).



1-XVII

(1.18)

Compound 1-XVII has a greatly distorted structure which is thought to be a result of the interaction of the electrophilic metal and the *ortho* C-H bonds.

1.4 SCOPE OF THIS THESIS:

In this work, the synthesis and characterization of new alkanediyl compounds of iron, manganese and rhenium are reported. All these compounds were characterized using a combination of analytical techniques such as microanalysis, IR, ^{1}H and ^{13}C nmr and mass spectrometry. An extensive reactivity study of the compounds was also carried out. Thus for example the alkanediyl compounds were reacted with nucleophiles such as tertiary phosphines and isocyanides as well as with electrophilic reagents such as halogens and sulfur dioxide. Investigations of the reactions of some of the alkanediyl compounds with synthesis gas were also carried out. The results obtained in all of these reactions are compared with those of mononuclear alkyls and other related compounds.

In a separate study, a series of μ-phenylene and μ-phthaloyl compounds were prepared and characterized. The reactivity of some of these compounds was also investigated and was again compared with mononuclear phenyl and benzoyl compounds.

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CHAPTER TWO.

2. SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NEW μ-ALKANEDIYL COMPLEXES OF IRON.

2.1 SYNTHESIS AND CHARACTERIZATION OF μ-ALKANEDIYL COMPLEXES OF THE TYPE $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ WHERE R=H, n=3-10 AND R=Me, n=3-6.

The first [1] and now most extensive [2] series of alkanediyl transition metal complexes to be prepared are the cyclopentadienyl iron complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (Where n = 3-12). The structures [4], decomposition [2], reactivity [5] and spectroscopic data [2,4] of some members of this series have been reported fully in the literature.

Over the last few years, it has been demonstrated that substituting H for Me in cyclopentadienyl compounds can have a dramatic effect on the types of complexes that are formed and also on their reactivity and stability [3,6,7]. These effects can be attributed to a combination of steric and electronic factors. The substitution of the hydrogens on the cyclopentadienyl ring with methyl groups can be expected to lead to an increased bond strength of the bonds between the η^5- Cp ring and the transition metal.

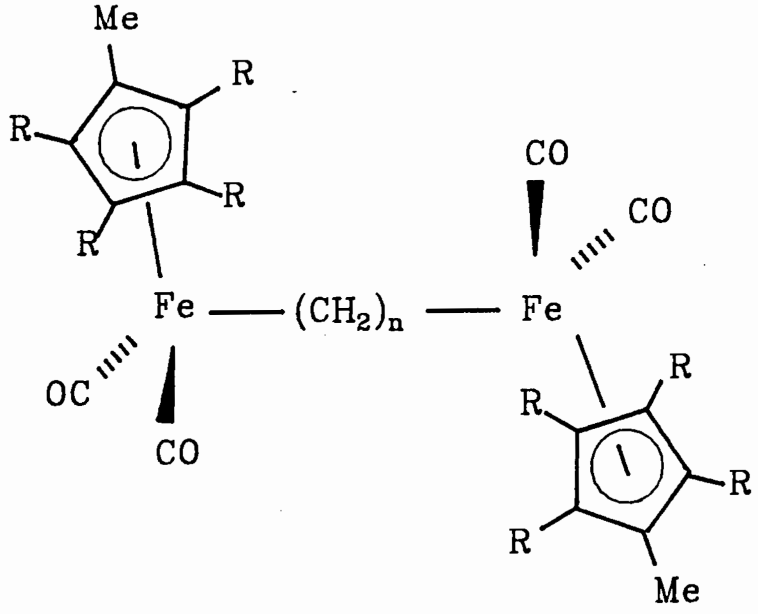
In general pentamethylcyclopentadienyl transition metal complexes show different crystallization characteristics. Thus it is often possible to obtain suitable crystals for crystal structure determination. Another property of these substituted cyclopentadiene complexes, is that in most cases they are more soluble than the unsubstituted cyclopentadienyl compounds.

With these factors in mind, we investigated the synthesis of some methylcyclopentadienyl and pentamethylcyclopentadienyl complexes of the type $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (where R=H or Me). The complexes $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (R = H, n = 3-10 and R = Me, n=3-6) were prepared using essentially the same method that was employed to prepare the analogous cyclopentadienyl complexes [1,2]. This involves the reaction of the metal anion with the appropriate dibromoalkane in a 2:1 molar ratio(Equation 2.1).

$$2Na[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2] + Br(CH_2)_nBr \xrightarrow{THF} [(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\} \qquad (2.1)$$

In this way the compounds <u>1</u> - <u>12</u> were prepared. All of these compounds are new, except for <u>11</u> which has previously been prepared and for which some data has been reported [8]. Although some polymethylene bridged complexes, for example $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3 - 10) can be obtained in fairly high yields by reacting the sodium salt of the anion, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-$ with the appropriate diiodoalkane [9,10], the reaction of $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ with $I(CH_2)_nI$ (n = 3-5) is found not to yield the required polymethylene bridged complex but rather a mixture of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2I]$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. This emphasizes the importance of the choice of halogen in the dihaloalkane for such reactions [9,11].

The compounds 1 - 12 were all obtained in moderate yields (see Tables 2.1 and 2.2), with the only by-product being the dimers, $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2$, (R=H or Me) which could be easily separated from the other products. The C_5Me_5 compounds were all obtained as yellow crystalline solids and the C_5H_4Me compounds were obtained as yellow-brown oils where n is odd and yellow crystalline solids where n is even. All the compounds 1 - 12 are stable at room temperature when pure but decompose fairly rapidly in solution on exposure to air yielding a brown solid which showed no ν(CO) bands in its infra-red spectrum. Solutions of the compounds are perfectly stable when kept under an inert atmosphere. All the compounds have been fully characterized by elemental analysis, IR, ^{1}H nmr and mass spectroscopy. The data for compounds 1 - 12 are presented in Tables 2.1 - 2.5



COMPOUND NUMBER	R	n
1	H	3
2	H	4
3	H	5
4	H	6
5	H	7
6	H	8
7	H	9
8	H	10
9	Me	3
10	Me	4
11	Me	5
12	Me	6

Figure 2.1: μ-alkanediyl complexes of the type $[\eta^5\text{-}(C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

Table 2.1: Yields, m.p.s. and analytical data for compounds $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

COMPOUND		m.p./	YIELD/	ANALYSIS^b			
No	n^a	°C	%	C	H	(C)	(H)
1	3	oil	54	53.8	4.7	(53.6)	(4.6)
2	4	65-66	51	54.5	5.1	(54.7)	(5.0)
3	5	oil	48	55.8	5.3	(55.4)	(5.3)
4	6	84-86	43	56.6	5.6	(56.4)	(5.6)
5	7	oil	50	57.5	5.8	(57.4)	(6.3)
6	8	47-48	46	58.3	6.1	(58.2)	(6.3)
7	9	oil	62	59.1	6.4	(58.7)	(6.8)
8	10	45-46	47	59.6	6.5	(59.5)	(6.6)

a n is the number of methylene groups in the polymethylene chain.

b calculated values in parentheses.

Table 2.2: Yields, m.p.s. and analytical data for compounds $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

COMPOUND		m.p./	YIELD/	ANALYSIS[b]			
No	n[a]	°C	%	C	H	(C)	(H)
<u>9</u>	3	155-161(dec)	48	60.5	6.7	(60.2)	(6.5)
<u>10</u>	4	210-216(dec)	42	61.1	6.9	(60.9)	(6.9)
<u>11</u>	5	150-153	34	61.7	7.1	(61.5)	(7.0)
<u>12</u>	6	171-174	41	62.3	7.3	(62.4)	(7.1)

[a] n is the number of methylene groups in the polymethylene chain.

[b] calculated values in parentheses.

MELTING POINTS AND THERMAL STABILITY OF THE COMPOUNDS OF THE TYPE, $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$, R=H and Me:

In the study of the compounds $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (where n=3-12) [2], it was found that there was a smooth variation of melting point with the value of n. Also the melting points for n (odd) and n (even) lay on two straight lines and that the line for n (odd) was below that for n (even) [2]. In the C_5H_4Me compounds where n is even, there is random variation of melting points and where n is odd, the products are all oils. Thus the only correlation for these C_5H_4Me compounds is that the compounds where n is odd have lower melting points than those where n is even, as is found in the C_5H_5 series. For the C_5Me_5 compounds (<u>9</u> - <u>12</u>), the melting points appear to follow the same trends as has been observed for the C_5H_5 compounds (see Table 2.3), at least for the few members of the C_5Me_5 homologous series that have been investigated. As is the case with many other cyclopentadienyl compounds, it was found that the C_5Me_5 compounds have higher melting points than their C_5H_5 analogues (See Table 2.3) whereas the C_5H_4Me compounds have lower melting points.

INFRA-RED SPECTRA OF COMPOUNDS <u>1</u> - <u>12</u>:

Compounds <u>1</u> - <u>12</u> all show two strong $\nu(CO)$ bands in their infra-red spectra as do the analogous C_5H_5 compounds [1,2]. The $\nu(CO)$ for the

C_5Me_5 compounds are about $18cm^{-1}$ lower than that for the C_5H_4Me compounds, which in turn are about $6cm^{-1}$ lower than that for the C_5H_5 complexes. This behaviour has been observed previously for C_5Me_5 and C_5H_4Me compounds and explained in terms of there being greater electron density on the metal for the substituted compounds, which results in increased back-bonding to the carbonyl groups and hence lower $\nu(CO)$ values arise [12]. Within each of the three series of compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ where Cp= C_5H_5, C_5H_4Me and C_5Me_5, there is little variation in $\nu(CO)$ with changes in the length of the hydrocarbon chain (see Tables 2.4 and 2.5).

Table 2.3: Comparison of m.p. data (°C) for the compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

n	$Cp=C_5H_5$[a]	$Cp=C_5H_4Me$	$Cp=C_5Me_5$
3	104-105	c	155-161
4	125-126,112-115[b]	65-66	210-216
5	83-85	c	150-153
6	100-103	84-86	171-174

a. data from ref. 2.

b. m.p.s. correspond to two different forms

c. oil at room temperature.

Table 2.4: IR and ^1H nmr data for the compounds of the type

$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

COMPOUND No	n^a	$\nu(CO)/cm^{-1}$ ^{b}	^1H NMR^c / δ ppm $C_5H_4{}^d$	$CH_3{}^e$	$CH_2{}^f$
<u>1</u>	3	2004s 1950vs 1919sh	4.54(8H)	1.86(6H)	1.42(6H)
<u>2</u>	4	2003s 1950vs 1919sh	4.52(8H)	1.90(6H)	1.42(8H)
<u>3</u>	5	2004s 1950vs 1920sh	4.56(8H)	1.90(6H)	1.40(10H)
<u>4</u>	6	2004s 1950vs 1919sh	4.60(8H)	1.90(6H)	1.41(12H)
<u>5</u>	7	2001s 1948vs 1918sh	4.56(8H)	1.88(6H)	1.38(14H)
<u>6</u>	8	2004s 1951vs 1919sh	4.52(8H)	1.92(6H)	0.40;1.32(16H)
<u>7</u>	9	2002s 1949vs 1919sh	4.56(8H)	1.88(6H)	0.86;1.30(18H)
<u>8</u>	10	2003s 1950vs 1919sh	4.52(8H)	1.88(6H)	0.40;1.30(20H)

a n is the number of methylene groups in the polymethylene chain
b measured in hexane, s strong, vs very strong.
c measured in $CDCl_3$
d signals are multiplets
e signals are sharp singlets.
f signals are broad singlets.

Table 2.5: IR and ^1H nmr data for the compounds of the type

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

COMPOUND		$\nu(CO)/cm^{-1}$ [b]		^1H NMR[c] / δ ppm		
No	n[a]			CH_3[d]	CH_2[e]	
9	3	1988s	1931vs	1.72(30H)	1.47(2H)	0.99(4H)
10	4	1985s	1931vs	1.72(30H)	1.46(4H)	0.98(4H)
11	5	1986s	1931vs	1.72(30H)	1.38(6H)	1.00(4H)
12	6	1986s	1931vs	1.69(30H)	1.34(8H)	0.98(4H)

a n is the number of methylene groups in the polymethylene chain

b measured in hexane, s strong, vs very strong.

c measured in $CDCl_3$

d signals are sharp singlets

e signals are broad and unresolved.

^{1}H NMR SPECTRA OF COMPOUNDS 1 - 12:

The ^{1}H nmr spectra for the C_5H_4Me compounds 1 - 8, show three sets of signals (see Table 2.4). There is no significant variation in the chemical shifts of these peaks on changing the length of the polymethylene chain. Two peaks are observed for the four ring protons due to magnetic inequivalence but it was not possible to obtain values for coupling constants from the spectra. The methylene protons for 1 - 5 all show a broad singlet whereas for 6 - 8 two broad singlets are observed. For the C_5Me_5 compounds 9 - 12, two sets of signals are observed (see Table 2.5), a singlet for the methyl protons and two broad singlets for the methylene protons. Neither set of peaks shows significant variation with changing n. The observation of two broad signals for all the methylene protons of the C_5Me_5 compounds 9 - 12, contrasts with the corresponding C_5H_5 [1,4] compounds where one broad singlet is observed for all the methylene protons. The reason for two signals being observed for the C_5Me_5 compounds, may be due to the increased electron density on the metal which causes a shift to higher field of about 1 ppm for the methylene groups closest to the iron atoms. It has previously been demonstrated that the singlet observed for all the methylene protons in each of the compounds of the type $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ is due to accidental equivalence of the chemical shifts of the methylene protons in these complex systems [4].

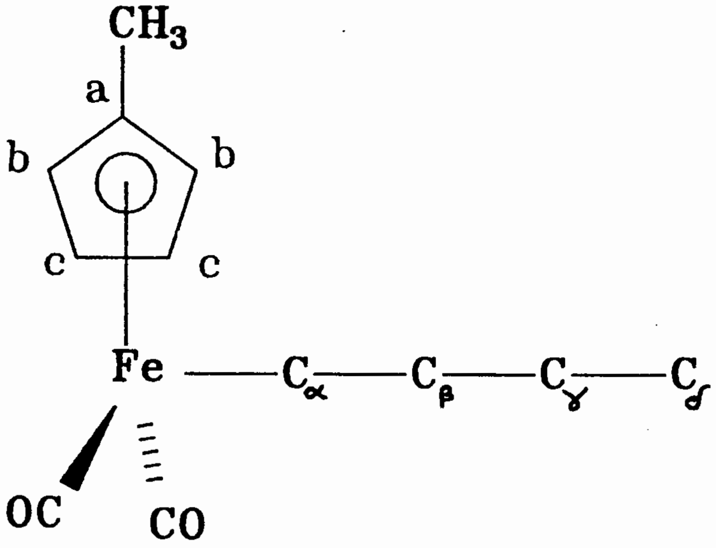


Figure. 2.2 labeling of the carbon atoms in compounds of the type $[\eta^5\text{-}(C_5H_4Me)Fe(CO)_2]_2\{(CH_2)_n\}$

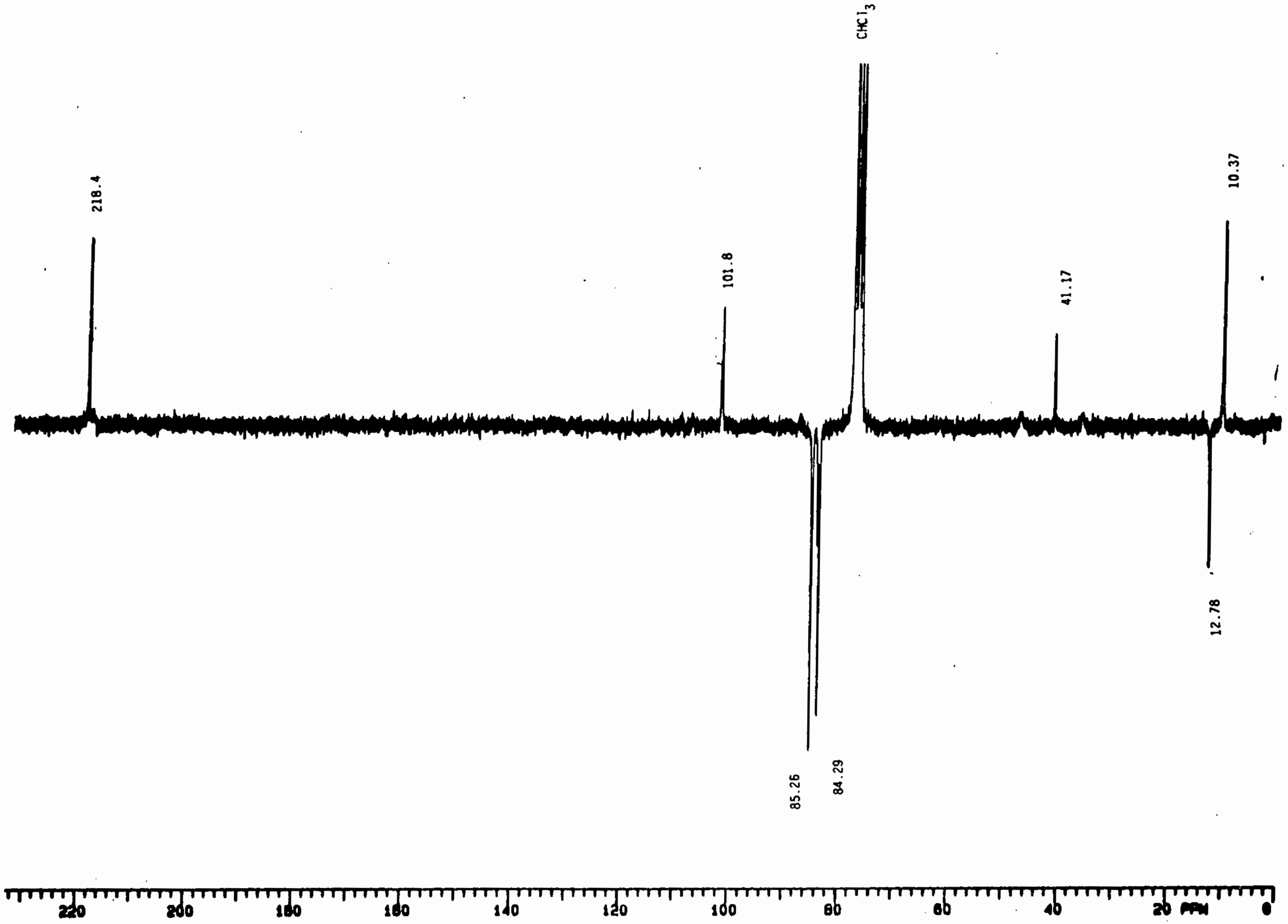


Figure 2.3: The ^{13}C APT nmr spectrum of $[Cp'Fe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$.

Table 2.6: ^{13}C nmr data for compounds of the type $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$.

COMPOUND		$^{13}C\{^1H\}$ nmr/δ ppm								
No	n^a	CO	CH_3	$C_a{}^c$	$C_b{}^c$	$C_c{}^c$	C_α	C_β	C_γ	C_δ
1	3	218.2	12.8	101.8	85.3	84.3	10.4	41.2	-	
2	4	218.0	12.9	101.7	85.4	84.2	5.7	41.1	-	
3	5	218.0	12.6	101.7	85.2	84.0	5.9	34.1	38.0	
4	6	217.7	12.8	101.5	85.1	84.0	5.8	34.7	38.2	
5	7	218.0	12.6	101.6	85.1	84.0	5.7	35.1	38.1	29.1
6	8	218.1	12.7	101.7	85.2	84.1	5.8	35.1	38.2	29.5
7	9	217.9	12.5	101.5	85.0	83.9	5.6	35.0	38.0	29.0
8	10	218.1	12.7	101.7	85.2	84.1	5.8	35.1	38.0	29.4 29.75

a n is the number of methylene groups in the polymethylene chain

b measured in $CDCl_3$

c These refer to carbon atoms of the cyclopentadienyl ring (see Figure 2.2)

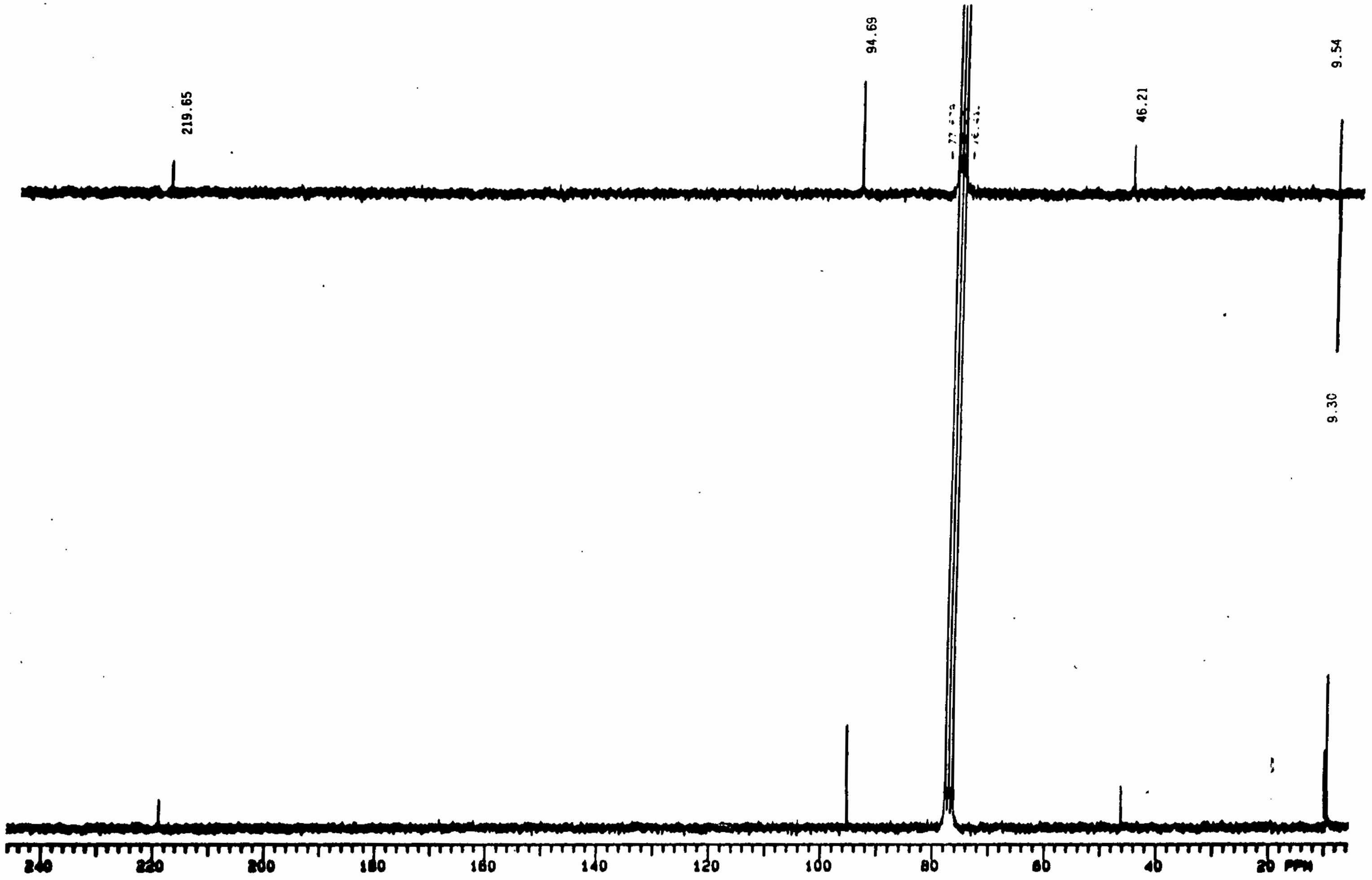


Figure 2.4: The ^{13}C APT nmr spectrum of $[Cp^{*}Fe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$.

^{13}C NMR SPECTRA OF COMPOUNDS OF THE TYPE $[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3-10):

The proton-decoupled ^{13}C nmr spectra of the above complexes were recorded in $CDCl_3$ and referenced to TMS. The assignments of the peaks in the ^{13}C nmr spectra were confirmed by employing the attached proton test (APT) [13] and are given in Tables 2.6 and 2.7.

The spectrum of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$ is depicted in Figure 2.3 and shows four bands in the cyclopentadienyl region. The signal at δ12.7 can be assigned to the carbon atom which is directly bonded to the methyl substituent. The remaining carbons of the cyclopentadienyl ring give rise to two singlets at δ85.3 and 84.3 respectively. The carbon atoms of the the propanediyl bridge, give rise to two signals which appear at δ10.4 and 41.1 (see Table 2.6 and Figure 2.3). These were assigned the α and β carbons respectively, by comparison with the analogous cyclopentadienyl compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$ [4]. The pentanediyl and hexanediyl complexes, both show three signals in the saturated hydrocarbon region (see Tables 2.6). The assignments of the β and γ carbons have been made by comparing the relative peak heights. An interesting observation in the spectra of these compounds, is the fact that the signals for the δ - carbons appear at values lower than that of both the β and γ carbons. A similar effect has been observed in other alkanediyl compounds [10, 14, 15], as well as in simple alkanes [16].

Table 2.7: ^{13}C nmr data for compounds of the type $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

COMPOUND		$^{13}C\{^1H\}$ nmr[b]/δ ppm					
No	n[a]	CO	CH_3	$\underline{C}_5CH_3$	C_α	C_β	C_γ
9	3	219.7	9.3	94.7	9.5	46.2	
10	4	219.7	9.3	94.6	14.4	44.7	
11	5	219.3	9.3	94.5	14.3	37.5	42.0
12	6	219.5	9.2	94.6	14.2	35.8	38.0

a n is the number of methylene groups in the polymethylene chain.

b measured in $CDCl_3$

The ^{13}C nmr spectra of the compounds $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$, (n=3-5), show fewer peaks relative to the C_5H_4Me compounds as expected. The assignments of these peaks are given in Table 2.7.

MASS SPECTRA FOR THE COMPOUNDS 1 - 12

Molecular ions of low intensity are observed in the mass spectra of compounds 1 - 12 (see Tables 2.8 and 2.9). All the spectra show peaks corresponding to $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]^+$ (R = H or Me) and other fragments showing the loss CO groups. A peak corresponding to the ion $[(\eta^5\text{-}C_5R_4Me)_2Fe]^+$ is observed in all the spectra and is analogous to the ion $[Cp_2Fe]^+$ (m/e 186) found in the mass spectra of the Cp compounds. This latter ion is thought to arise from the ionization of ferrocene [2]. The intensities and probable assignments for the other major peaks of high mass in the spectra of compounds 1 - 12 are given in Tables 2.8 and 2.9. The results show that the three series of compounds of the type $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]\{\mu\text{-}(CH_2)_n\}$ (where R_5=H, H_4Me and Me_5) have similar fragmentation pathways. For the $(\eta^5\text{-}C_5H_4Me)$ and $(\eta^5\text{-}C_5Me_5)$ compounds, the fragmentation route involving the complete loss of the hydrocarbon bridge from the parent ion followed by sequential loss of four carbonyl groups appears to be the major pathway. The second fragmentation pathway involving the sequential loss of carbonyl group from the parent ion appears to be less significant in these complexes than it is for Cp analogues [2].

Table 2.8: Mass spectral data for the compounds 1 - 8, of the type $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

ION[a]	RELATIVE PEAK INTENSITY[b]							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
M	1	0.5	3	1	2	2	3	1
M-CO	0.5	-	1	0.5	5	2	6	2
M-2CO	1	0.5	4	1	4	2	3	4
M-3CO	0.5	1	3	2	17	4	7	3
M-4CO	1	1	0.5	4	3	3	4	2
M-4CO-H_2	1	1	3	1	10	3	6	5
M-C_nH_{2n}	3	0.5	1	2	1	3	-	2
M-CO-C_nH_{2n}	9	1	0.5	4	8	-	6	12
M-2CO-C_nH_{2n}	3	1	1	1	0.1	6	6	21
M-3CO-C_nH_{2n}	12	7	15	12	4	41	66	11
M-4CO-C_nH_{2n}	4	5	11	4	1	6	8	22
M-CO-$(C_5H_4Me)Fe(CO)_2$	-	58	65	25	26	9	45	37
M-2CO-$(C_5H_4Me)Fe(CO)_2$	40	58	19	21	8	7	16	3
M-CO-C_5H_5Me	-	-	1	-	4	2	4	1
M-2CO-C_5H_5Me	-	1	18	12	1	8	29	14
M-3CO-C_5H_5Me	3	11	-	13	4	8	12	6
M-4CO-C_5H_5Me	10	21	56	15	12	18	13	6
M-4CO-C_5H_5Me-H_2	2	11	15	4	2	-	20	14
M-CO-$(C_5H_4Me)Fe(CO)_2$-C_nH_{2n}	40	37	30	28	9	33	34	31
M-2CO-$(C_5H_4Me)Fe(CO)_2$-C_nH_{2n}	100	100	100	100	100	100	100	96

[a] $M=(C_5H_4Me)_2Fe_2(CO)_4(C_nH_{2n})$; all ions have a single positive charge. Ion refers to suggested assignments, low resolution spectra.

[b] peak intensities are relative to the base peak at m/e 135 unless otherwise stated.

[c] relative to base peak at m/e 194.

Table 2.9: Mass spectral data for the compounds <u>9</u> - <u>12</u>, of the type $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

ION[a]	RELATIVE PEAK INTENSITY			
	9[b]	10[c]	11[d]	12[e]
M	15	7	5	1
M-CO	-	-	-	-
M-2CO	-	-	-	0.5
M-3CO	-	4	3	6
M-4CO	-	15	-	4
M-4CO-H_2	-	-	-	-
M-C_nH_{2n}	25	7	7	6
M-CO-C_nH_{2n}	79	4	8	4
M-2CO-C_nH_{2n}	4	15	62	28
M-3CO-C_nH_{2n}	2	3	7	5
M-4CO-C_nH_{2n}	13	-	-	30
M-CO-$(C_5Me_5)Fe(CO)_2$	40	75	56	73
M-2CO-$(C_5Me_5)Fe(CO)_2$	63	100	1	3
M-CO-C_5Me_5H	1	-	-	-
M-2CO-C_5Me_5H	0.4	0.5	2	-
M-3CO-C_5Me_5H	1	0.3	1	4
M-4CO-C_5Me_5H	2	2	6	7
M-4CO-C_5Me_5H-H_2	1	6	4	11
M-CO-$(C_5Me_5)Fe(CO)_2$-C_nH_{2n}	65	75	42	45
M-2CO-$(C_5Me_5)Fe(CO)_2$-C_nH_{2n}	100	93	69	11

a. $M=(C_5Me_5)_2Fe(CO)_4(C_nH_{2n})$; all ions have a single positive charge. Ions refer to suggested assignments, low resolution spectra.

b. peak intensities relative to base peak at m/e 191

c. peak intensities relative to base peak at m/e 247

d. peak intensities relative to base peak at m/e 259

e. peak intensities relative to base peak at m/e 273

2.2 REACTIVITY OF THE COMPLEXES OF THE TYPE $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

2.2.1 REACTIONS OF $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ WITH TERTIARY PHOSPHINES:

The binuclear iron polymethylene bridged complexes $[CpFe(CO)_2]_2\text{-}\{\mu\text{-}(CH_2)_n\}$ (Cp = C_5H_5, n = 3-12) are known to react with tertiary phosphines, PR_3, to give either monosubstituted or disubstituted phosphine diacyl complexes [5]. Under the conditions of our experiments, we find that the reactions of <u>2</u> with tertiary phosphines in a 1:2 mole ratio yields the disubstituted diacyl species. Thus for example the reaction of PPh_2Me with the complex $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$ – $\{\mu\text{-}(CH_2)_4\}$ yields the diacyl compound <u>13</u> (Equation 2.2) The reaction was carried out in refluxing tetrahydrofuran and was found to be significantly slower than the reaction of the analogous cyclopentadienyl compound, $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$(Cp = C_5H_5) [5]. The latter reaction is found to be complete after refluxing for 6 hours in tetrahydrofuran. The reduced reactivity of the C_5H_4Me compounds towards phosphines, can be ascribed to the electron releasing effect of the methyl group and also to its steric hinderance.

The reaction of <u>2</u> with $PPhMe_2$ similarly yields the disubstituted diacyl species <u>14</u>. This reaction appears to be slightly faster than that of PPh_2Me with compound <u>2</u> and is probably due to the lower steric bulk of

$PPhMe_2$ relative to PPh_2Me. Also $PPhMe_2$ is more nucleophilic than PPh_2Me, which will favour the reaction.

$$[Cp'Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\} + 2\ PR_3 \xrightarrow{\text{refluxing THF}} Cp'(CO)(PR_3)FeCO(CH_2)_4COFe(PR_3)(CO)Cp'$$

<u>13</u>. Cp′ = η^5-C_5H_4Me, PR_3 = PPh_2Me

<u>14</u> Cp′ = η^5-C_5H_4Me, PR_3 = $PPhMe_2$ (2.2)

Compounds <u>13</u> and <u>14</u> were isolated as orange-yellow solids which are stable in the solid state but they decompose fairly rapidly in solution when air is present . Both compounds show only two bands in the ν(CO) region of their infra-red spectra. The band around 1905 cm^{-1} represents the single terminal carbonyl group on each iron atom, while the lower frequency band at about 1590 cm^{-1} represents the acyl carbonyl, the latter appears as a broad band of medium intensity.

The ^1H nmr spectrum of compound <u>13</u>, shows six distinct signals (see Table 2.10). The spectrum confirms that the product contains a $CO(CH_2)_4CO$ bridge. The bridge protons give rise to two signals *viz* a broad multiplet at δ2.47 and a broad multiplet at δ1.02. The former can be assigned to the protons attached to the carbon atoms directly bonded to the acyl group, while the latter is due to the central carbon atoms of the polymethylene bridge. The ^1H nmr spectrum of <u>14</u> is similar to that of <u>13</u> and the assignments of the peaks are given in Table 2.10.

Table 2.10: ^{1}H nmr data for the compounds of the type

$[Cp'(CO)(PR_3)FeCO(CH_2)_4COFe(PR_3)(CO)Cp']$ $(Cp' = C_5H_4CH_3)$

COMPOUND	PR_3	^{1}H nmr / δ ppm[a]					
		CH_2CO[b]	$-CH_2-$[b]	$C_5\underline{H}_4-CH_3$[c]	$C_5H_4-C\underline{H}_3$[d]	$P-CH_3$[e]	P-Ph[b]
13	PPh_2Me	2.47(4H)	1.02(4H)	4.15(8H)	1.31(6H)	1.85(6H)	7.32(20H)
14	PPh_2Me	2.72(4H)	1.31(4H)	4.13(8H)	1.44(6H)	1.78(12H)	7.38(10H)

a measured in $CDCl_3$

b signals are broad multiplets.

c broad singlet.

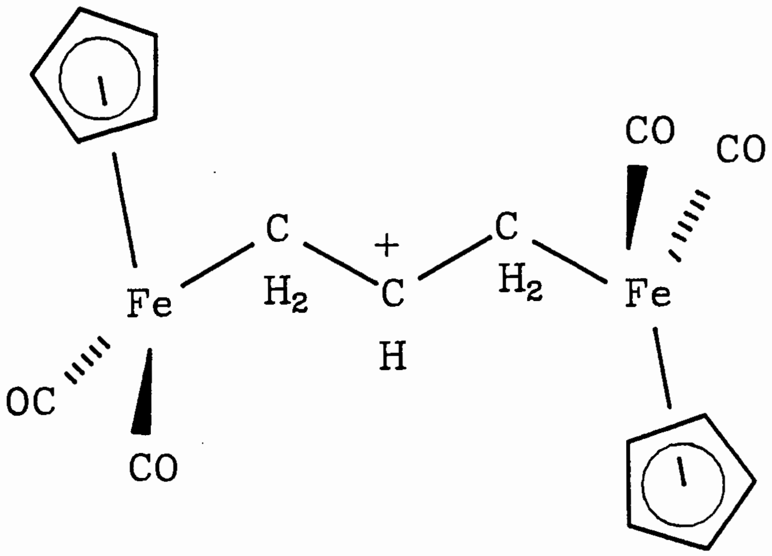
d singlet.

e doublet with $^2J_{PH}$ = 9 Hz.

2.2.2 REACTION WITH THE TRITYL SALT Ph_3CPF_6:

Mononuclear iron-alkyl complexes of the type $(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{-}R$ are known to undergo β-hydride abstraction to give the cationic species $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(olefin)]^+$, when treated with triphenylmethyl salts [17,18]. King and Bisnette [19] also reported an analogous reaction with the binuclear μ-propanediyl di-iron complex, $[\eta^5\text{-}(C_5H_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$. This complex reacts with triphenylmethyl hexafluorophosphate to yield an orange cationic species $[CpFe(CO)_2CH_2CH{=}CH_2\text{-}Fe(CO)_2Cp][PF_6]$. The ^1H nmr of the compound shows only a single cyclopentadienyl resonance indicating that the two iron atoms are equivalent. King concluded that the complex existed as the carbonium ion **2-I** (Figure 2.5) with the positive charge located on the central carbon atom of the three-carbon chain.

Moss and Johnson [20] subsequently investigated the reactions of longer chain polymethylene bridged complexes with trityl salt. The reactions of the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (where n = 4-6) with Ph_3CPF_6 in dichloromethane gave yellow crystalline complexes of the formula $\{[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2[\mu\text{-}(C_nH_{2n-1})]\}PF_6$. These cationic complexes have structures in which one iron atom is π-bonded and the other σ-bonded to the alkyl chain.



2–I

Figure 2.5: The structure of $\{[CpFe(CO)_2]_2[\mu\text{-}(C_3H_5)]\}^+$ [20]

In this section, the reactions of the analogous complexes $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 6) with trityl-PF_6 were investigated (see experimental section for details). The reactions of these alkanediyl complexes, yield microcrystalline yellow solids <u>15</u> and <u>16</u> (Equation 2.3)

$$[Cp'Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + Ph_3CPF_6 \xrightarrow{CH_2Cl_2} \{[Cp'Fe(CO)_2]_2[\mu\text{-}(C_nH_{2n-1})]\}PF_6$$

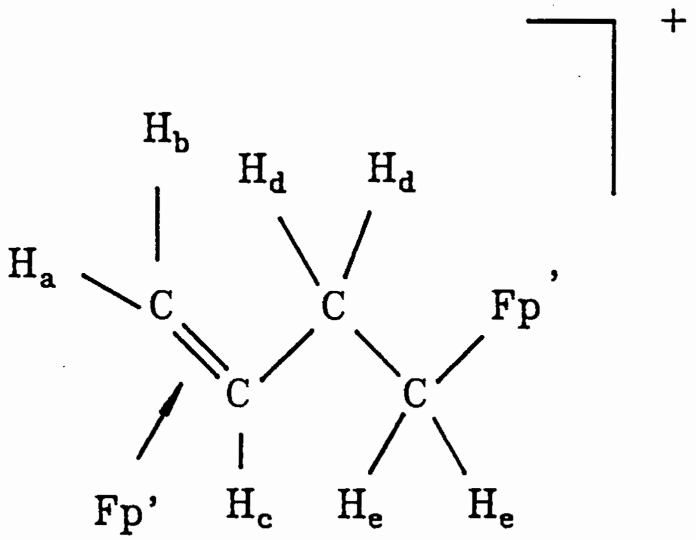
Cp′ = C_5H_4Me, <u>15</u> n=4

<u>16</u> n=6

(2.3)

The infra-red spectrum of complex <u>15</u> (CH_2Cl_2 solution) shows four bands in the carbonyl region at 2068, 2030, 1997 and 1937 cm^{-1} corresponding to the carbonyls attached to the cationic iron and neutral iron atoms respectively. The ^1H nmr spectrum of the compound at room temperature shows two broad signals at $\delta5.37$ and $\delta4.58$ corresponding to the two Cp rings attached to the nonequivalent iron atoms. The alkenyl chain protons give rise to fairly complex signals, but the following features are discernable:

The CH_2 group of the olefinic functionality resonates as a doublet of doublets, centred at $\delta3.62$ (J_{H-H} = 8 Hz) and $\delta3.08$ (J_{H-H} = 14 Hz) corresponding to H_a and H_b in Figure 2.6. The methine proton H_c, being highly deshielded gives rise to a broad multiplet at $\delta5.26$. The protons of the other two CH_2 groups give rise to signals at $\delta2.32$ (H_d) and $\delta1.17$ (H_e).



Fp′ = $C_5H_4MeFe(CO)_2$

Figure 2.6: The proposed structure of the compound $\{[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2[\mu\text{-}(C_4H_7)]\}PF_6$

2.2.3 REACTION WITH LIQUID SULFUR DIOXIDE:

The binuclear complex $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$ was found to react with SO_2 to yield a mixture of the monosulfinato and disulfinato complexes as shown in Equation 2.4 [22].

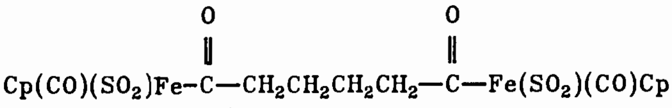
$$[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_3\} + SO_2 \longrightarrow [CpFe(CO)_2]_2\{SO_2(CH_2)_3\} + [CpFe(CO)_2]_2\{\mu\text{-}SO_2(CH_2)_3SO_2\} \qquad (2.4)$$

We now find that the corresponding reaction of compound 2 with liquid sulfur dioxide at room temperature readily yields the disulfinato derivative 17 (Equation 2.5).

$$\underset{\mathbf{2}}{[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}} + SO_2 \longrightarrow \underset{\mathbf{17}}{[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}SO_2(CH_2)_4SO_2\}} \qquad (2.5)$$

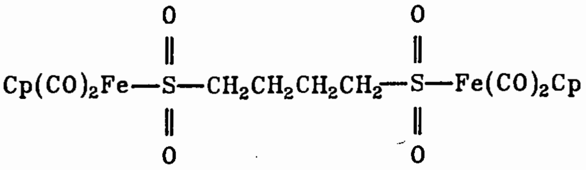
Compound 17 was isolated as a yellow microcrystalline solid and was characterized by micro-analysis, IR and ^{1}H nmr spectroscopy as described in the experimental section. The compound is stable in the solid state provided it is kept under vacuum but solutions show gradual decomposition in the presence of air.

The infra-red spectrum of compound 17, shows only two strong ν(CO) bands at 2054 and 2005 cm^{-1}. The absence of acyl CO bands, indicates that the product is an iron-sulfinato derivative and not an acyl sulfur dioxide compound (Figure 2.7 a). Also, the two bands in the terminal CO region of the IR spectrum, suggests that the disulfinato complex (Fig. 2.7 b) rather than the monosulfinato complex (Fig. 2.7 c) was obtained. The solid state infra-red spectrum (Nujol mull) of compound 17, shows two strong bands in the region 1200-1000cm^{-1} corresponding to the symmetric and asymmetric SO stretching frequencies. Similar bands have been observed in the sulfinato derivatives of mononuclear alkyl compounds of the type $CpFe(CO)_2R$ [22]. This region of the spectrum also resembles the IR spectra of common organic sulfones [23], however the SO of bands 17 occur at frequencies which are lower by about 120cm^{-1}. This is as a result of the strong π bonding between the metal and the SO_2 group (see Figure 2.8) [23].



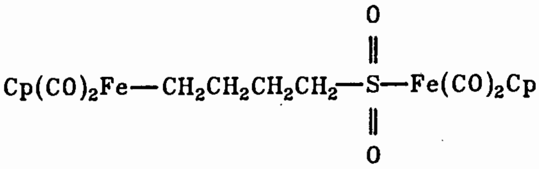
$$\mathrm{Cp(CO)(SO_2)Fe{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_2CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}Fe(SO_2)(CO)Cp}$$

(a) Acyl sulfur dioxide complex



$$\mathrm{Cp(CO)_2Fe{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2CH_2CH_2CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Fe(CO)_2Cp}$$

(b) Disulfinato derivative



$$\mathrm{Cp(CO)_2Fe{-}CH_2CH_2CH_2CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Fe(CO)_2Cp}$$

(c)Mono-sulfinato derivative

Figure 2.7 Possible structure for SO_2 derivatives of $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$.

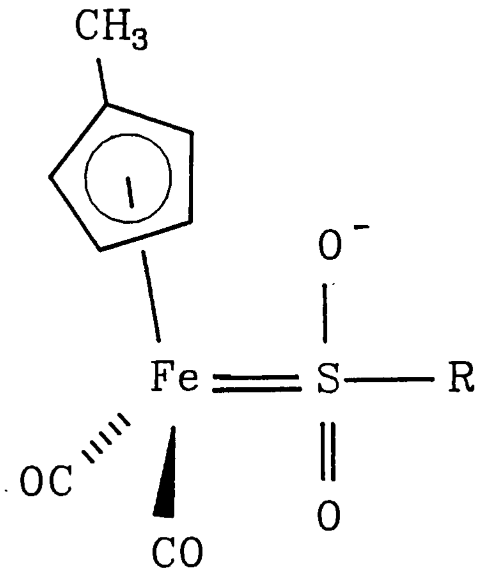


Figure 2.8: Resonance hybrid showing π bonding between the SO_2 group and the metal.

The absence of an iron-alkyl linkage in compound <u>17</u> is confirmed by its ^1H nmr spectrum, which shows only two signals for the protons of the hydrocarbon chain. The one signal occurs at $\delta 3.06$ and is due to the protons of the methylene group adjacent to the SO_2 moiety. The other signal appears at $\delta 1.96$ and can be assigned to the protons attached to the central carbons of the polymethylene chain. The ^1H nmr data is consistent with the structure in Figure. 2.9.

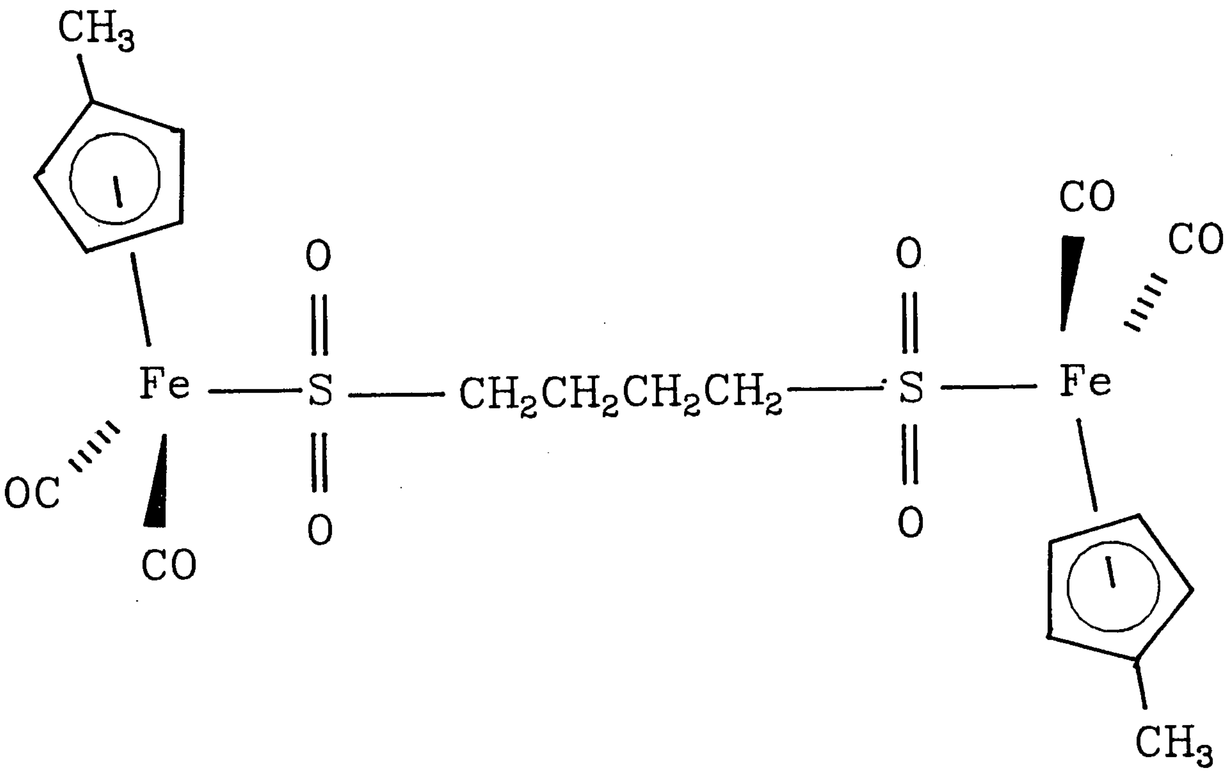
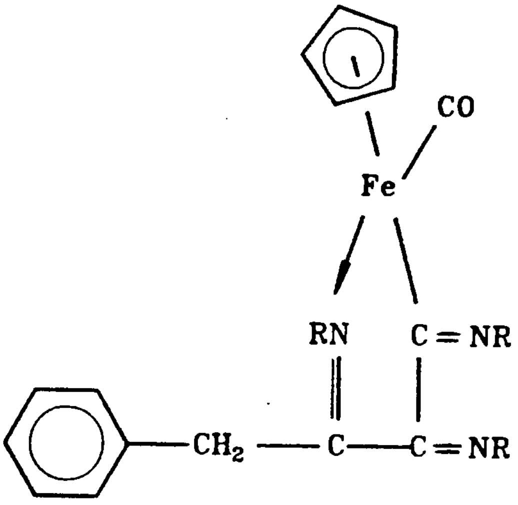


Figure 2.9: Proposed structure of the product of the reaction of $[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ with SO_2.

2.2.4 REACTION WITH t-BUTYL ISOCYANIDE:

Cyclopentadienyl dicarbonyl iron alkyl compounds are known to react with alkyl isocyanides. The products obtained are dependant on the type of iron-alkyl compound as well as the alkyl isocyanide. The compound, $CpFe(CO)_2CH_3$ reacts with both cyclohexyl isocyanide and t-butyl isocyanide to yield an acyl alkylisocyanide substituted derivative of the type $Cp(CO)(CNR)FeCOCH_3$ (R = t-butyl or cyclohexyl) [25]. On the other hand the reaction of the benzyl iron complex, $CpFe(CO)_2CH_2C_6H_5$ with t-butyl isocyanide, does not yield the acyl compound, but rather the compound $CpFe(CO)[CNC(CH_3)_3]CH_2Ph$ [25]. In this case there is substitution of one of the terminal carbonyl groups by t-butyl isocyanide.

The reaction of the benzyl-iron complex with cyclohexyl isocyanide is different to the above reaction. In this case a "triple insertion" product, $CpFe(CO)(CNC_6H_{11})_3CH_2C_6H_5$ is isolated [25]. The product has the structure shown in Figure. 2.10.



$R = C_6H_{11}$

Figure 2.10: The triple insertion product of the reaction $CpFe(CO)_2CH_2Ph$ and $C_6H_{11}NC$.

A similar "triple insertion" complex $CpFe(CO)(CNC_6H_{11})_3CH_2C_6H_4Cl$*p* has been isolated from the reaction of cyclohexyl isocyanide with the *p*-chlorobenzyl iron compound $CpFe(CO)_2CH_2C_6H_4Cl$*p*[25]. In both reactions, no mono-*o*-bis-imino complexes are isolated. Varying the ratio of the parent benzyl iron complex to cyclohexyl isocyanide results only in the "triple insertion" product being isolated.

In this section, the reactions of the μ-alkanediyl complexes $[(\eta^5\text{-}C_5H_4Me)Fe(CO_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 6) with t-butyl isocyanide were investigated and compared with those of mononuclear cyclopentadienyl iron alkyls. Both the 1,4-butanediyl and the 1,6-hexanediyl complexes react with t-butyl isocyanide to give the corresponding isocyanide substituted products 18 and 19 (Equation 2.6)

$$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + 2t\text{-BuNC} \xrightarrow{\text{reflux THF}}$$

$$[(\eta^5\text{-}C_5H_4Me)Fe(CO)(t\text{-BuNC})]_2\{\mu\text{-}CO(CH_2)_nCO\}$$

<u>18</u> n = 4

<u>19</u> n = 6

(2.6)

Compounds <u>18</u> and <u>19</u> were isolated as a yellow oils. These compounds are stable in the pure form when kept in the dark but solutions decompose rapidly to unidentified products. Prolonged exposure of the compounds to light also leads to decomposition.

The infra-red spectrum of compound <u>18</u> shows three ν(CO) bands at 2121s, 1937vs and 1610m-s cm^{-1}. The band at 2121cm^{-1} can be assigned to the C$\equiv$N stretching frequency of the isocyanide group, the band at 1937cm^{-1} to the terminal carbonyl group, while the low frequency band is assignable to an acyl carbonyl group. The infra-red data is consistent with a isocyanide substituted diacyl species (Figure 2.11).

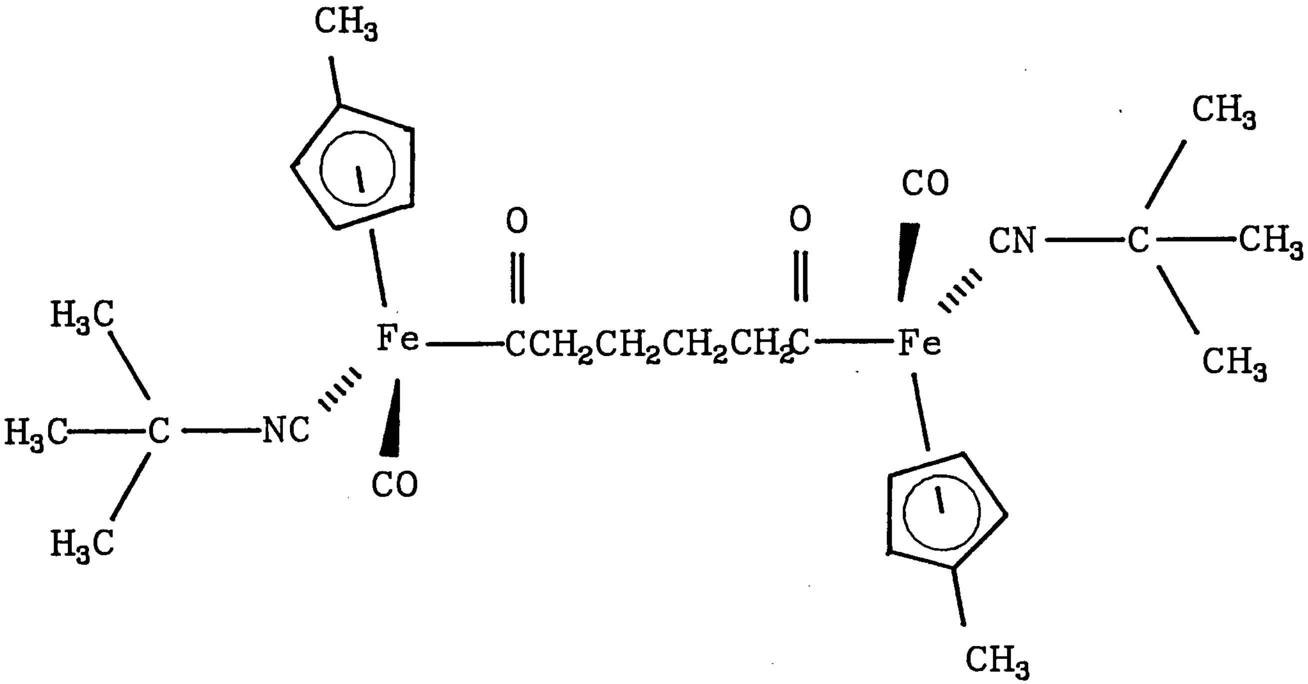


Figure 2.11: Product of the reaction of $[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ with t-butylisocyanide.

The ^1H nmr spectrum ($CDCl_3$ solution) of <u>18</u>, shows a broad multiplet at δ4.4 - δ4.29 due to the cyclopentadienyl protons and a triplet at δ2.74 due to the protons of the methylene groups which are bonded to the acyl carbonyls. The spectrum also shows a broad singlet at δ1.86, a multiplet at δ1.26 - δ1.50 and a singlet at δ1.42. The latter is due to the methyl groups of the t-butyl isocyanide ligand. The signal at δ1.86 can be assigned to the methyl substituent on the cyclopentadienyl ring while the multiplet at δ1.26- δ1.50 is due to the protons of the central methylene groups of the hydrocarbon chain.

The proton decoupled ^{13}C nmr spectrum of <u>18</u> (see experimental) is quite complex showing a number of resonances. The peak assignments were confirmed by means of an APT experiment . The weak and slightly broad peak at δ218.6 can be assigned to the two terminal carbonyls, while the peak at δ269.8 can be assigned to the acyl carbonyl. The nitrile carbon atom of the isocyanide ligand resonates at δ167.6. This has been assigned by comparing it with ^{13}C spectra of other compounds containing the $C\equiv N$ group e.g. $[Cp_2Fe_2(CO)_3(t\text{-}BuNC)]$ [26]. The three carbons of the methyl group of tertiary butyl isocyanide give rise to an intense peak at δ30.9, while the tertiary carbon of the isocyanide yields a signal at δ57.2. The carbon atoms of the butanediyl bridge give rise to two signals *viz* at δ65.0 and δ24.8. The peak at δ65.0 is due to the carbon atoms of the methylene groups bonded to the acyl carbonyls while the peak at δ24.8 is due to the central carbon atoms of the butyl chain.

The 1,6-hexanediyl complex $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_6\}$ reacts in a similar fashion to once again yield a diisocyanide diacyl derivative <u>19</u>, which was characterized by micro-analysis, infra-red and ^{1}H nmr spectroscopy (see Experimental section for details).

2.2.5 <u>REACTIONS WITH BROMINE AND IODINE</u>

Like most electrophilic cleavages of transition metal-carbon σ bonds, halogen cleavage is useful for both synthetic purposes as well as the characterization of organometallic compounds [27]. Normally the reaction of halogens with transition metal alkyl complexes results in the formation of a metal halide and alkyl halide (Equation 2.7)

$$RML_n + X_2 \longrightarrow RX + XML_n \qquad (2.7)$$

In this work, the reactions of μ-alkanediyl complexes of iron with halogens were investigated and compared with those of mononuclear alkyls,as well as with the binuclear cyclopentadienyl μ-alkanediyl analogues. The complexes $[(C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 5) were reacted with halogens, X_2 (X = Br and I) using a 1:2 mole ratio. (Equation 2.8). All the reactions proceed rapidly at room temperature to give products of the type $X(CH_2)_nX$ and $(C_5H_4Me)Fe(CO)_2X$.

$$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + 2X_2 \xrightarrow{THF} 2(\eta5\text{-}C_5H_4Me)Fe(CO)_2X + X(CH_2)_nX$$

(X = Br and I) ; n = 4 and 5

(2.8)

The alkanediyl complexes react rapidly with halogens and halo-alkyl intermediates, of the type $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2(CH_2)_nX$, were not detected. The products obtained in Equation 2.8 were identified by infra-red and ^{1}H nmr spectroscopy by comparison with the spectra of authentic samples.

2.3 REACTIVITY OF THE COMPLEXES OF THE TYPE $[Cp^*Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

The reactions of the Cp^* complexes of the above type with $[Ph_3C]PF_6$, sulfur dioxide and halogens gave similar products to those obtained from reactions of the $(\eta^5\text{-}C_5H_4Me)$ analogues with the same reagents as reported in Section 2.2.

Thus, $[Cp^*Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, <u>10</u>, reacts with $[Ph_3C]PF_6$ to yield the cationic complex, $[Cp^*(CO)_2Fe(CH_2)_2CH{=}CH_2Fe(CO)_2Cp^*]PF_6$, <u>20</u>. The characterisation data for this compound are to be found in the experimental section.

The reaction of compound <u>10</u> with SO_2 at room temperature, readily yields the disulfinato derivative, $[Cp^*Fe(CO)_2SO_2]_2\{\mu\text{-}(CH_2)_4\}$, <u>21</u> which was isolated as a yellow microcrystalline solid and was characterized by micro-analysis IR and ^{1}H nmr spectroscopy (see experimental section for details). The reaction of the Cp^* complex is slightly faster than that of the methylcyclopentadienyl complex. This result compares reasonably well with that obtained by Jacobson and Wojcicki in their study of mononuclear alkyl complexes [28]. These workers found that an enhancement in the rate of the SO_2 reaction can be effected by increasing the degree of methyl substitution on the cyclopentadienyl ring.

Compounds <u>10</u> and <u>12</u> react readily with iodine or bromine to yield the expected Fe-CH_2 bond cleavage products. The reactions of the Cp^* analogue proceed slightly faster than both the methylcyclopentadienyl and cyclopentadienyl complexes. Thus, the reaction of $[Cp^*Fe(CO)_2]_2\{\mu-(CH_2)_4\}$ with bromine is almost instantaneous, whereas that of $[CpFe(CO)_2]_2\{\mu-(CH_2)_4\}$ with the same reagent, takes about 20 minutes [5]. This is probably a as result of the high electron density on the metal in the case of the Cp^* compounds.

REACTION OF $[(\eta^5-C_5Me_5)Fe(CO)_2]_2\{\mu-(CH_2)_4\}$ <u>10</u> WITH CARBON MONOXIDE.

Compound <u>10</u> is extremely reluctant to undergo CO insertion. Thus the starting material was recovered unchanged after stirring compound <u>10</u> for several days under an atmosphere of CO. Increasing the CO pressure to 15 atmospheres, leads to a small conversion of the starting material to the diacyl species (as detected by IR spectroscopy). At higher CO pressures (30 - 40 atm), a mixture of starting material and the diacyl species, $Cp^*(CO)_2FeCO(CH_2)_4COFe(CO)_2Cp^*$ <u>22</u> , was obtained. Compound <u>22</u>

was isolated as a yellow crystalline compound in 25% yield and the characterization data can be found in the experimental section. Several attempts were made to decarbonylate 22 to reform the original μ-alkanediyl compound. Thus 22 was refluxed in benzene for 36 hours and during this time, extensive decomposition to $[Cp^*Fe(CO)_2]_2$ occurs and formation of 10 was not observed. Using the high boiling solvent, xylene, leads to decomposition to the dimer. However, in this case a small amount of the compound 10 is detected by IR spectroscopy (Equation 2.9).

$$\underset{\underline{22}}{Cp^*(CO)_2FeCO(CH_2)_4COFe(CO)_2Cp^*} \longrightarrow [Cp^*Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\} + 2CO \qquad (2.9)$$

Photolysis of 22 in benzene as solvent leads to large - scale decomposition of the starting material with the only isolable product being the dimer, $[Cp^*Fe(CO)_2]_2$.

ATTEMPTED REACTION OF $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ WITH PPh_2Me.

$[Cp^*Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ was reacted with PPh_2Me in a 1:2 mole ratio. The reaction is extremely slow in refluxing tetrahydrofuran and does not go to completion. After four days, there is only about 20% conversion to a phosphine substituted product as judged by the IR spectrum of the reaction mixture. Attempts to separate the phosphine substituted product from the starting material were not successful.

The reluctance of compound <u>10</u> to undergo ligand induced CO insertion, is probably a result of both steric and electronic effects. The methyl substituents on the cyclopentadienyl ligand, cause an increase in the electron density on the metal and this makes reaction with a nucleophilic ligand more difficult. Steric factors also play a role in these ligand induced insertions, since the approach of the bulky tertiary phosphine ligand is hindered.

2.4 CONCLUSIONS

The μ-alkanediyl complexes of the type $[(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\ \{\mu\text{-}(CH_2)_n\}$ (where R = H, n = 3-10 and R = Me, n = 3-6) have been prepared successfully using the general synthetic route:

$$2\ [(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]Na + X(CH_2)_nX \longrightarrow [(\eta^5\text{-}C_5R_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\} + 2NaX \quad (X = Br\ or\ I)$$

This route is analogous to that used previously to prepare the cyclopentadienyl compounds $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3-12) [1,2]. From our experience, it has been found that the choice of the halogen in the dihalo-alkane is quite important. Thus the reaction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]Na$ with $I(CH_2)_4I$, does not yield the expected alkanediyl compound but $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$ instead. The 1,4-dibromobutane on the other hand yields the required 1,4-butanediyl product.

The two series of compounds show differences in their reactivity patterns. Thus for example the $\eta^5\text{-}C_5H_4Me$ complexes react with tertiary phosphines (PR_3) to yield diacyl disubstituted phosphine compounds of the type $Cp'(CO)(L)FeCO(CH_2)_nCOFe(L)(CO)Cp'$ ($Cp' = \eta^5\text{-}C_5H_4Me$, L = tertiary phosphine), whereas the $\eta^5\text{-}C_5Me_5$ compounds are extremely reluctant to undergo ligand induced carbonyl insertion reactions. If one compares the η^5-C_5H_5, η^5-C_5H_4Me and η^5-C_5Me_5 compounds, then it is clear that a reduction in the rate of ligand induced insertion is effected by increasing the degree of methyl substitution on the cyclopentadienyl ring. Thus the following order of reactivity exists η^5-C_5H_5 > η^5-C_5H_4Me >> η^5-C_5Me_5. This order of reactivity is exactly the same as that which can be predicted taking steric and electronic factors into consideration.

Electrophilic reactions of the compounds prepared in this chapter, not surprisingly, tend to show the reverse order of reactivity to that of nucleophilic reactions. Thus for example the η^5-C_5Me_5 compounds show a great tendency to undergo electrophilic cleavage of the Fe-C bond. All compounds prepared, also react readily with the trityl salt Ph_3CPF_6 to form cationic olefin species and all of these reactions proceed faster than those of the η^5-C_5H_4Me and η^5-C_5H_5 analogues. This is to be expected since an increase in electron density will favour electrophilic reactions.

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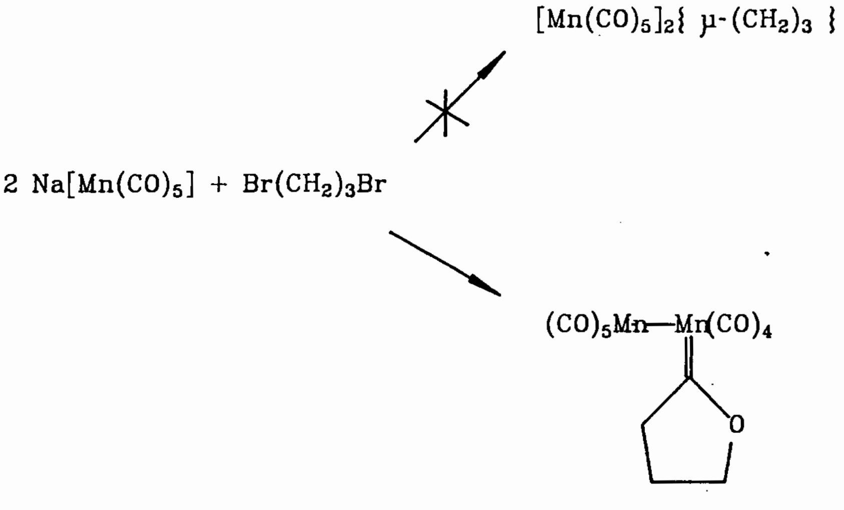
CHAPTER THREE.

3. SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF μ-ALKANEDIYL COMPLEXES OF MANGANESE AND RHENIUM

3.1 ALKANEDIYL COMPLEXES OF MANGANESE:

3.1.1 SYNTHESIS AND CHARACTERIZATION:

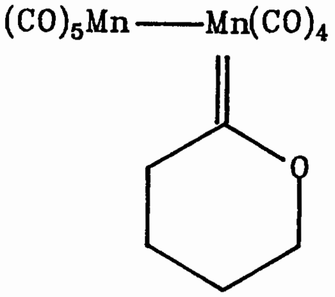
As seen in Section 2.1, the iron alkanediyl complexes $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (Cp = C_5H_5, C_5H_4Me and C_5Me_5) could be prepared by the reaction of $Na[CpFe(CO)_2]$ with the appropriate 1,n-dihaloalkanes. Attempts to prepare related polymethylene bridged complexes of manganese from $Na[Mn(CO)_5]$ and dihaloalkanes have proved to be unsuccessful. These attempts resulted only in the formation of cyclic carbene species. For example the reaction of $Na[Mn(CO)_5]$ with 1,3 dibromopropane yields the complex **3-I** as shown below [1].



3–I

(3.1)

Similarly the reaction of the 1,4 -dibromobutane is thought to yield an analogous six-membered cyclic carbene species **3-II**.



3–II

Until now, the only known alkanediyl bridged manganese complex has been the μ-(1,2)-ethanediyl species, $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_2\}$, which was prepared by the reaction of $[(CO)_5Mn(C_2H_4)]^+$ with $Na[Mn(CO)_5]$ [2].

The synthesis of the new μ-(1,n)-alkanediyl complexes, $(CO)_5Mn(CH_2)_nMn(CO)_5$ (n = 4-6), is now reported. These complexes were prepared by the decarbonylation of the corresponding diacyl species, $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$, which in turn are readily obtainable from the reaction of the metal carbonyl anion $[Mn(CO)_5]^-$ with the appropriate 1,n-diacyl chloride (Equation 3.2). The diacyl compounds where n=4 and 5 have been previously reported by Kraihanzel [3].

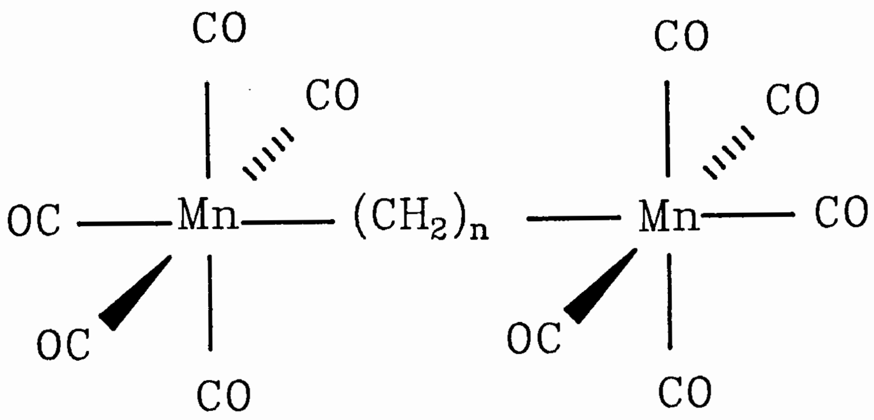
$$2\ Na[Mn(CO)_5] + ClCO(CH_2)_nCOCl \xrightarrow[25^\circ C]{THF}$$

$$(CO)_5MnCO(CH_2)_nCOMn(CO)_5 + 2NaCl$$

$$\text{reflux hexane}$$

$$(CO)_5Mn(CH_2)_nMn(CO)_5 + 2CO$$

(3.2)



COMPOUND	n
23	4
24	5
25	6

Figure 3.1 μ-(1,n) alkanediyl complexes of manganese

In this way compounds 23 - 25 were prepared.

Attempts to prepare the μ-(1,3)-propanediyl complex of manganese starting from $Na[Mn(CO)_5]$ and glutaryl chloride proved unsuccessful.

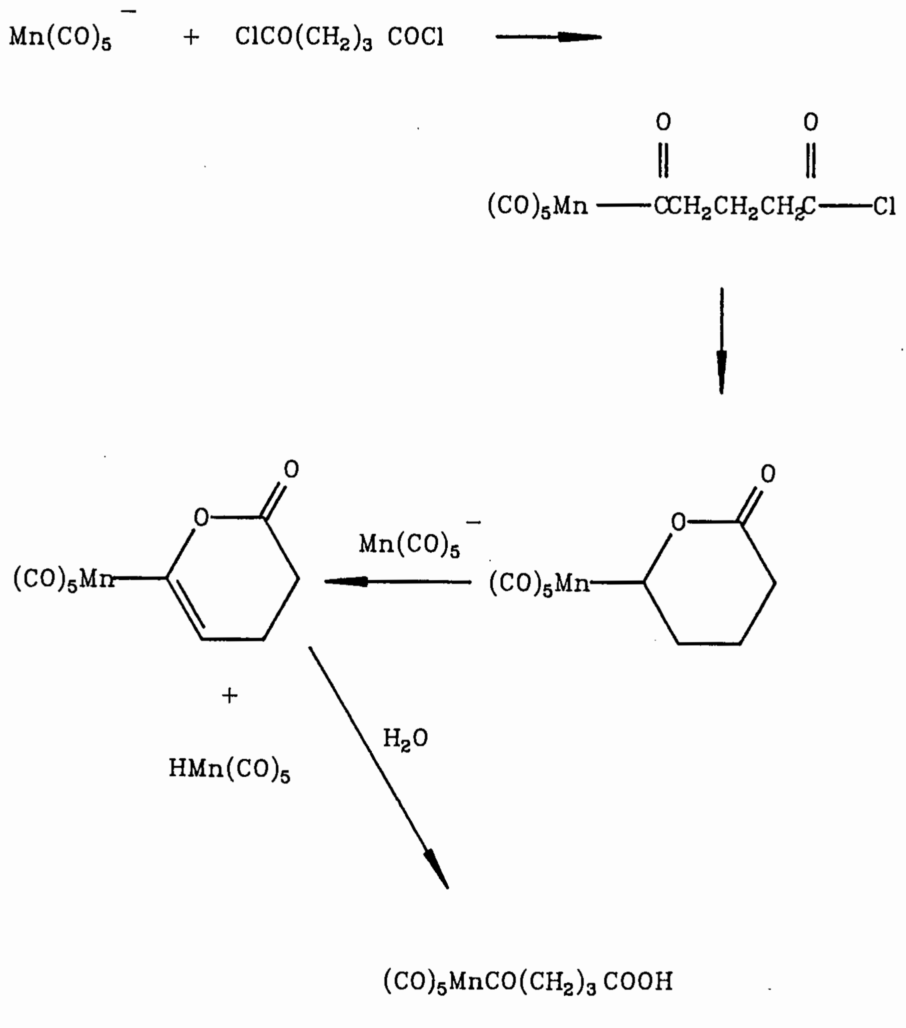


Figure 3.2: Possible mechanism for the formation of $(CO)_5MnCO(CH_2)_3COOH$ [3].

This is due to the inability of manganese to form the expected diacyl complex $(CO)_5MnCO(CH_2)_3COMn(CO)_5$. The only product isolated in the reaction is the complex $(CO)_5MnCO(CH_2)_3COOH$. This result is in agreement with that previously obtained by Kraihanzel and Herman [3], who suggested a mechanism for the formation of the carboxylic acid species as outlined in Figure 3.2.

Compounds <u>23</u> - <u>25</u> were all isolated as white microcrystalline solids which are stable in air for at least several months. They are also fairly stable in solution when kept under an atmosphere of nitrogen. The stability of the compounds is remarkable in comparison with mononuclear alkyl complexes of manganese pentacarbonyl which contains β-hydrogens. Ethyl manganese pentacarbonyl for example is reported to decompose slowly even when kept in the dark, in vacuo and at -10°C [4].

Compounds <u>23</u> - <u>25</u> have been fully characterized by IR, ^1H and ^{13}C nmr, mass spectroscopy and micro-analysis aned the data are listed in Tables 3.1 - 3.3.

The infrared spectra of the μ-(1,n) alkanediyl manganese complexes generally show two bands in the $\nu(CO)$ region; a weak band around $2105cm^{-1}$ and a very strong band about $2010cm^{-1}$. This is completely analogous to the spectrum obtained for mononuclear alkyl manganese pentacarbonyl complexes [5].

In the ^1H nmr spectra of the compounds **23** - **25**, the methylene protons give rise to two signals, one a broad triplet at about δ 1.10 and a broad multiplet between δ1.40 and δ1.80. The signal at δ1.1ppm, corresponds to the protons of the $-CH_2$ groups attached to the metal centres. the broad multiplet can be assigned to the central $-CH_2-$ groups. These assignments were made by comparing the spectra with those of other μ-alkanediyl complexes as well as spectra of compounds of the type, $RMn(CO)_5$ (R=Me or Et). There is no significant variation in the chemical shifts of the methylene protons, on changing the length of the polymethylene chain.

The proton decoupled ^{13}C nmr spectra of the complexes are relatively simple, showing either two or three signals in the methylene region. For example, the spectrum of the complex $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$, shows only two signals in the methylene region. These occur at δ6.2 and δ43.3. The signal at δ6.2 can be assigned to the carbon of the methylene groups which are directly bonded to the manganese atoms. This assignment was accomplished by comparison with the assignments for polymethylene bridged compounds of iron [7]. In these iron systems, the α-carbon atom was assigned the smallest chemical shift value. This is because the α-carbon atom is strongly shielded by the nearby metal centre. The second signal in the methylene region at δ43.3 is assigned to the β-carbon atoms. The spectra of the μ-(1,5)-pentanediyl and μ-(1,6)-hexanediyl complexes are similar to that of the μ-(1,4)-butanediyl compound. The ^{13}C nmr spectra of all three compounds show a weak and broad signal around δ213 characteristic of the terminal carbonyl groups.

TABLE 3.1:Yields and m.p.s. and analytical data for compounds 23 -25.

COMPOUND		m.p.	yield	ANALYSIS[b]			
No	n[a]	°C	(%)	C	H	(C)	(H)
23	4	136-140 (decomp)	90	37.45	1.75	(37.66)	(1.81)
24	5	122-126	76	38.90	2.15	(39.16)	(2.19)
25	6	116-144	72	40.25	2.70	(40.53)	(2.55)

a n is the number of methylene groups in the polymethylene chain.

b calculated values in parentheses.

TABLE 3.2: IR and ^1H nmr data for compounds 23 - 25.

COMPOUND		$\nu(CO)^b/cm^{-1}$			^1H nmr$^c/\delta$	
No·	n[a]				$-CH_2M$	CH_2-
23	4	2104w	2008vs	1980sh	1.06(4H)[d]	1.72(4H)[e]
24	5	2105w	2007vs		1.08(4H)[d]	1.68(6H)[e]
25	6	2105w	2009vs	1979sh	1.12(4H)[d]	1.44(8H)[e]

a n is the number of methylene groups in the polymethylene chain.

b measured in $CHCl_3$.

c measured in $CDCl_3$.

d signals are broad multiplets.

TABLE 3.3: ^{13}C nmr data for the compounds of the type $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$.

			$^{13}C\{^1H\}$nmr/ppm[b].		
COMPOUND			C_1	C_2	C_3
No.	n[a]	CO	M-$\underline{C}H_2$	M-$CH_2\underline{C}H_2$	-$\underline{C}H_2$-
<u>23</u>	4	213.5	6.2	43.3	-
<u>24</u>	5	213.5	6.7	36.5	41.3
<u>25</u>	6	213.0	6.9	35.0	37.2

a n refers to the number of methylene groups in the polymethylene chain.

b measured in $CDCl_3$.

Molecular ions are observed in the mass spectra of compounds 23 - 25. However these are of low intensity (Table 3.4). These complexes show three fragmentation patterns. The first involves the successive loss of carbon monoxide from the parent ion. A second decomposition pathway, involves the initial loss of the hydrocarbon bridge to form the species $[Mn_2(CO)_{10}]^+$. The μ-(1,5)-pentanediyl complex 24, does not show this pathway in its mass spectrum. A third fragmentation route, involves the complete loss of a $Mn(CO)_5$ unit from the parent ion to form $[(CO)_5Mn(C_nH_{2n})]^+$. The observation of this fragment is indicative of the absence of a Mn-Mn bond in the μ-(1,n)-alkanediyl complexes. The intensities and assignments of the major peaks in the spectra of the compounds 23 - 25 are listed in Table 3.4

TABLE 3.4: Mass spectral data for the compounds 23-25.

ION[a]	RELATIVE PEAK INTENSITIES		
	23 n=4	24 n=5	25 n=6
M	1.0	0.3	0.7
M-CO	0.1	0.3	0.6
M-2CO	0.4	0.9	-
M-3CO	0.9	1.0	4.7
M-4CO	0.9	2.0	7.0
M-5CO	1.0	6.0	15.0
M-6CO	3.0	5.5	8.0
M-7CO	94.0	8.0	10.0
M-8CO	41.0	1.0	87.0
M-9CO	39.0	24.0	55.0
M-10CO	20.0	13.0	20.0
M-10CO-Mn	-	4.0	21.0
M-C_nH_{2n}	0.4	-	4.7
M-CO-C_nH_{2n}	0.9	-	7.0
M-2CO-C_nH_{2n}	0.9	-	15.0
M-3CO-C_nH_{2n}	1.0	-	8.0
M-4CO-C_nH_{2n}	3.0	-	10.0
M-5CO-C_nH_{2n}	94.0	32.0	87.0
M-6CO-C_nH_{2n}	41.0	12.0	55.0
M-7CO-C_nH_{2n}	39.0	2.0	20.0
M-8CO-C_nH_{2n}	20.0	2.0	4.0

Table 3.4/continued....

Table 3.4:/continued.....

M-9CO-C_nH_{2n}	19.0	15.0	29.0
M-10CO-C_nH_{2n}	69.0	19.0	56.0
M-10CO-C_nH_{2n}-Mn	100.0	100.0	100.0
M-10CO-Mn-C_2H_4	77.0	-	21.0
M-C_nH_{2n}-Mn$(CO)_5$	97.0	40.0	35.0

a M = $Mn_2(CO)_{10}C_nH_{2n}$; all ions have a single positive charge; ion refers to suggested assignments.

b peak intensities relative to base peak at m/e 55.

3.1.2 REACTIONS OF THE COMPLEXES $[Mn(CO)_5]_2\{\mu-(CH_2)_n\}$ (n=4-6):

3.1.2(a) REACTIONS WITH TERTIARY PHOSPHINES:

Mononuclear manganese alkyls of the type, $RMn(CO)_5$, are known to react readily with tertiary phosphines PR_3, to yield phosphine substituted products, $RCOMn(CO)_4PR_3$ [8].

In an analogous way, we find that the binuclear complexes of the type, $(CO)_5Mn(CH_2)_nMn(CO)_5$ (n=4-6), react with tertiary phosphines in a 1:2 molar ratio to give the disubstituted phosphine diacyl compounds, 26-36 (Equation 3.3).

The phosphine substitued complexes were isolated as either white microcrystalline solids or clear oils. They were characterized by microanalysis, IR and ^1H nmr spectroscopy (see Tables 3.5 - 3.7). The infra-red spectra of the diacyl phosphine substituted species are similar to those of mononuclear compounds of the type, *cis*-$R'COMn(CO)_4(PR_3)$ [10], showing four bands in the $\nu(CO)$ region. This suggests that the binuclear compounds have C_s local symmetry and hence *a cis* configuration (Figure 3.4). In the reactions of $CH_3Mn(CO)_5$ with tertiary phosphines, it has been reported that *cis*-$CH_3Mn(CO)_5$ is formed initially and then isomerizes in solution to form mixtures of *cis* and *trans* isomers [11]. No such isomerization is observed in the case of the binuclear μ-alkanediyl compounds.

$$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\} \xrightarrow[25°C]{PR_3,\,THF}$$

$$(CO)_4(PR_3)MnCO(CH_2)_nCOMn(PR_3)(CO)_4$$

26 $n{=}4; PR_3 = PPh_3$

27 $n{=}4; PR_3 = PPh_2Me$

28 $n{=}4; PR_3 = PPhMe_2$

29 $n{=}4; PR_3 = PMe_3$

30 $n{=}5; PR_3 = PPh_3$

31 $n{=}5; PR_3 = PPh_2Me$

32 $n{=}5; PR_3 = PPhMe_2$

33 $n{=}6; PR_3 = PPh_3$

34 $n{=}4; PR_3 = PPh_2Me$

35 $n{=}4; PR_3 = PPhMe_2$

36 $n{=}4; PR_3 = PMe_3$

(3.3)

Table 3.5: Yields, m.p.s. and analytical data for the compounds **26**-**36**

Compounds		PR_3	Yield	m.p.			Analysis[b]	
No	n[a]		(%)	(°C)	C	H	(C)	(H)
26	4	PPh_3	64	118-122	61.2	3.90	(61.50)	(3.95)
27	4	PPh_2Me	80	95-96	49.90	4.25	(49.88)	(4.19)
28	4	$PPhMe_2$	66	117-120	56.45	4.40	(56.75)	(4.05)
29	4	PMe_3	83	104-108	40.45	4.50	(40.15)	(4.38)
30	5	PPh_3	68	oil	61.80	4.35	(62.21)	(4.09)
31	5	PPh_2Me	74	oil	56.75	4.40	(57.22)	(4.20)
32	5	$PPhMe_2$	69	oil	50.35	4.20	(50.56)	(4.38)
33	6	PPh_3	55	112-119	62.14	4.36	(62.54)	(4.24)
34	6	PPh_2Me	68	oil	57.30	4.15	(57.67)	(4.36)
35	6	$PPhMe_2$	61	58-61	51.20	4.55	(51.22)	(4.57)
36	6	PMe_3	58	oil	41.95	4.60	(42.19)	(4.83)

a n is the number of methylene groups in the polymethylene chain.
b calculated values in parentheses.

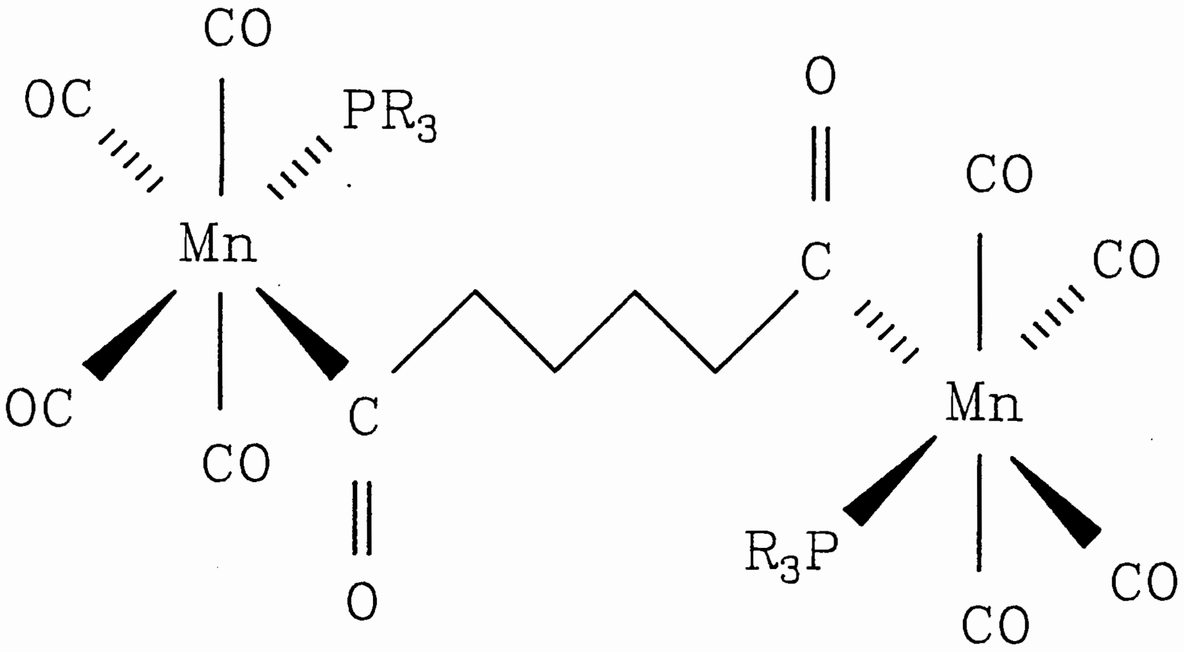


Figure 3.3: The structure of the diacyl, disubstituted phosphine complexes <u>26</u> -<u>29</u>.

As is the case for mononuclear alkyl manganese pentacarbonyl complexes, the reactions of the μ-alkanediyl complexes with tertiary phosphines are most likely to proceed via the reaction pathway outlined in the Equation 3.4.

$$(CO)_5Mn(CH_2)_nMn(CO)_5$$

$$\Big\downarrow \mathrm{S}$$

$$(CO)_4(S)MnCO(CH_2)_4COMn(S)(CO)_4$$

<u>37</u>

$$\Big\downarrow \mathrm{PR_3}$$

$$(PR_3)(CO)_4MnCO(CH_2)_nCOMn(CO)_4(PR_3)$$

S = tetrahydrofuran

(3.4)

Evidence for the metal complex - solvent intermediate, <u>37</u>, is the fact that carbonyl insertion is observed when $(CO)_5Mn(CH_2)_4Mn(CO)_5$ is dissolved in tetrahydrofuran and allowed to stand. This can be clearly be seen by using infra-red spectroscopy since an acyl band appears at 1640 cm^{-1}. Proton nmr can also be used to confirm the existence of this acyl intermediate. A spectrum of the polymethylene bridge compound in tetrahydrofuran-d_8, shows that the resonance due to the protons of the methylene group adjacent to the metal has shifted down field to δ2.47. This is indicative of a CH_2 group adjacent to an acyl group. This tetrahydrofuran adduct is extremely unstable and in the presence of air, it rapidly decomposes to an unidentified non-carbonyl containing species.

The ^1H nmr spectra of the PR_3 substituted diacyl compounds are similar to spectra reported for $R'COMn(CO)_4(PR_3)$ complexes [8]. Thus for example the triphenylphosphine complex <u>26</u>, shows a broad singlet at δ7.38 (Ph protons), a triplet at δ2.66 (CH_2CO protons) and a broad multiplet at δ0.88-δ1.24 ($-CH_2-$ protons). These signals are in the ratio 30:4:4 respectively as expected for <u>26</u>

On a qualitative basis, there is an increase in the rate of ligand induced CO insertion reaction in going from PPh_3 to PMe_3. This can be attributed to increase in the nucleophilicity and a reduction of the steric bulk of the tertiary phosphine ligand. The greater the nucleophilicity and the less the steric bulk of the phosphine ligand, the more facile the akyl- migration reaction. This effect is observed for the reactions of μ-(1,n) alkanediyl complexes of manganese where the order of the reactivity with various tertiary phosphine ligands is as follows:

$$PPh_3 < PPh_2Me < PPhMe_2 < PMe_3$$

Table 3.6: ^{1}H nmr data for compounds **26** - **36**.

Compounds		PR$_3$		^{1}H nmr (δ ppm[b])		
No	n[a]		P-Ph[c]	CH$_2$COM[d]	P-CH$_3$[e]	-CH$_2$-[f]
26	4	PPh$_3$	7.38(30H)	2.66(4H)	-	0.88-1.24(4H)
27	4	PPh$_2$Me	7.38(20H)	2.58(4H)	2.06(6H)	1.10(4H)
28	4	PPhMe$_2$	7.36(10H)	2.73(4H)	1.79(12H)	1.25(4H)
29	4	PMe$_3$	-	2.88(4H)	1.46(18H)	1.24(4H)
30	5	PPh$_3$	7.42(30H)	2.54(4H)	-	0.74-1.64(6H)
31	5	PPh$_2$Me	7.39(20H)	2.66(4H)	2.11(6H)	0.88-1.26(6H)
32	5	PPhMe$_2$	7.38(10H)	2.74(4H)	1.78(12H)	1.24(6H)
33	6	PPh$_3$	7.40(30H)	2.75(4H)	-	1.11(8H)
34	6	PPh$_2$Me	7.38(20H)	2.64(4H)	2.05(6H)	1.12(8H)
35	6	PPhMe$_2$	1.40(10H)	2.78(4H)	1.82(12H)	1.16(8H)
36	6	PMe$_3$	-	2.63(4H)	1.48(18H)	1.20(8H)

a n refers to the number of CH$_2$ groups in the polymethylene chain.

b measured in CDCl$_3$

c signals are broad singlets

d signals are broad triplets

e signals are doublets (J_{H-P} = 9Hz)

f signals are broad multiplets.

Table 3.7: IR data for compound 26 - 36.

Compound		PR$_3$	ν(CO)/cm^{-1} [b]			
No	n[a]					
26	4	PPh$_3$	2067m,	1994s,	1962vs,	1604mbr
27	4	PPh$_2$Me	2067m,	1991s,	1962vs,	1603mbr
28	4	PPhMe$_2$	2056sh,	1985s,	1960vs,	1603mbr
29	4	PMe$_3$	2057m,	1990m,	1963s,	1605mbr
30	5	PPh$_3$	2068m,	1995s,	1962vs,	1604mbr
31	5	PPh$_2$Me	2068m,	1991s,	1962vs	1600mbr
32	5	PPhMe$_2$	2055m,	1985sh,	1957s,	1603mbr
33	6	PPh$_3$	2068m,	1996s,	1962vs	1606mbr
34	6	PPh$_2$Me	2067m,	1993m,	1963s,	1599mbr
35	6	PPhMe$_2$	2065m,	1988s,	1962vs,	1601mbr
36	6	PMe$_3$	2057m,	2007s,	1963vs,	1603mbr

[a] n refers to the number of the -CH$_2$- groups in the polymethylene chain.

[b] measured in CHCl$_3$
s = strong, vs = very strong, m = medium, sh = shoulder,
mbr = medium broad, w = weak.

3.1.2 (b) DECARBONYLATION OF COMPOUNDS 26 - 29:

The tertiary phosphine substituted diacyl compounds 26 - 29 were decarbonylated thermally to form the tertiary phosphine substituted μ-(1,4)-butanediyl compounds 38 - 41. The reaction proceeds smoothly and quantitatively at about 65°C (Equation 3.5)

$$(CO)_4(PR_3)MnCO(CH_2)_4COMn(PR_3)(CO)_4 \xrightarrow[\text{hexane}]{\text{reflux}} (CO)_4(PR_3)Mn(CH_2)_4Mn(PR_3)(CO)_4 + 2CO$$

38 $PR_3 = PPh_3$

39 $PR_3 = PPh_2Me$

40 $PR_3 = PPhMe_2$

41 $PR_3 = PMe_3$

(3.5)

The phosphine substituted μ-(1,4)-butanediyl compounds were isolated as white microcrystalline solids. The compounds are stable in the solid state only decomposing in solution after prolonged exposure to air. The infra-red spectra of compounds 38 - 41 (see Table 3.9) again shows four bands in the ν(CO) region, suggesting that the compounds exist as *cis-cis* isomers (Figure 3.4).

Table 3.8: Yields, m.p.s. and analytical data for the complexes of the type $[Mn(CO)_4(PR_3)]_2(\mu-(CH_2)_4\}$

Compound	PR_3	Yield (%)	m.p. (°C)	Analysis[a] C	H	(C)	(H)
38	PPh_3	81	137-140	62.75	4.30	(63.03)	(4.16)
39	PPh_2Me	88	116-121(dec)	57.35	3.95	(57.68)	(4.30)
40	$PPhMe_2$	64	128-131	50.15	4.30	(50.46)	(4.50)
41	PMe_3	77	123-126	39.55	4.70	(39.86)	(4.80)

a. calculated values in parentheses

Table 3.9: IR data for complexes of the type $[Mn(CO)_4(PR_3)]_2\{\mu-(CH_2)_4\}$

Compound	PR_3	$\nu(CO)/cm^{-1}$ [a]				
38	PPh_3	2051w,	1978m,	1964s,	1935m	
39	PPh_2Me	2052m,	1980m,	1963s,	1936m,	
40	$PPhMe_2$	2052w,	1978m,	1961s,	1944sh,	1931m
41	PMe_3	2052w,	1977m,	1961s,	1934m	

a. measured in hexane
m = medium, s = strong, w = weak.

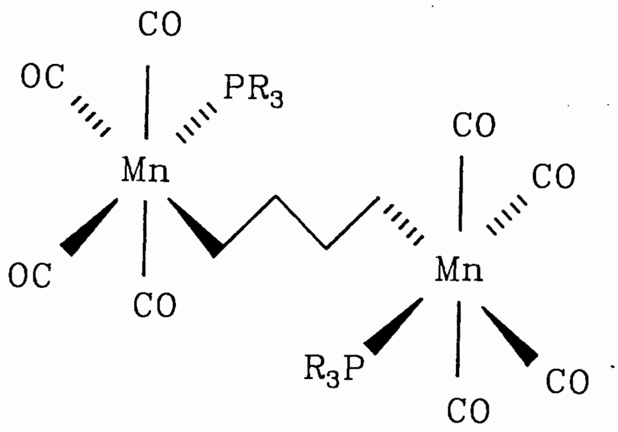


Figure:3.4 The μ-(1,4)-butanediyl phosphine disubstituted complexes of manganese

The ^{1}H nmr spectra of the phosphine substituted μ-(1,4)-butanediyl complexes are analogous to the spectra of simple mononuclear phosphine substituted alkyl complexes of manganese [8]. The triphenylphosphine complex shows three signals at δ7.30 (30H), δ0.30 (4H) and δ1.24 (4H). The signal at δ7.10 is due to the aromatic protons of the triphenylphosphine ligand. The broad multiplet at δ0.30 can be assigned to the protons of the methylene groups which are directly bonded to the manganese atoms, while the broad multiplet at δ1.24 is due to the protons of the central carbons in the hydrocarbon chain. The spectra of the other phosphine compounds, with the exception of the PMe_3 compound, show four signals in (see Table 3.10). An examination of the spectra of compounds <u>38</u>-<u>41</u>, shows that the resonances of the protons of the α-CH_2 groups vary with changing the PR_3 ligands. The general trend observed is an increase in the chemical shifts of the α-CH_2 prontons as we sequentially substitute Ph with Me on PPh_3. Similary a downfield

Table 3.10: ^{1} H nmr data for the complexes of the type $[Mn(CO)_4(PR_3)]_2\{\mu\text{-}(CH_2)_4\}$

		^{1}H nmr (δ ppm)[a]			
Compound	PR_3	P-Ph[b]	CH_2-Mn[c]	$-CH_2-$[d]	$P-CH_3$[e]
38	PPh_3	7.10(30H)	0.30(4H)	1.24(4H)	-
39	PPh_2Me	7.34(20H)	0.45(4H)	1.38(4H)	1.86(6H)
40	$PPhMe_2$	7.36(10H)	0.54(4H)	1.50(4H)	1.74(12H)
41	PMe_3	-	0.80(4H)	1.88(4H)	1.26(18H)

a measured in $CDCl_3$

b signals are broad singlets

c signals are broad multiplets

d signals are broad multiplets

e signals are doublets ($^2J_{PH}$ = 9Hz) shift in the β-CH_2 protons is observed in going from PPh_3 to PMe_3 compound. In both cases, the observed trend can be ascribed to the anisotropic shielding effects of the aromatic rings of the phosphine ligands.

3.1.2(c) REACTIONS OF $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ WITH HALOGENS:

There are hardly any reports in the literature on the reactions of mononuclear alkyl complexes of manganese with halogens. On the other hand, the reactions of both mononuclear iron and μ-(1,n) alkanediyl di-iron complexes have been investigated extensively [9, 12-16].

Treatment of $(CO)_5Mn(CH_2)_n\ Mn(CO)_5$ (n = 4 and 5) with Br_2 and I_2 in a 1:2 mole ratio in tetrahydrofuran, gave adipic acid and an unidentified inorganic product. This is in contrast to what is obtained in the case of the analogous iron compounds [9]. The isolation of adipic acid can be accounted for by the fact that tetrahydrofuran being a good coordinating solvent promotes initial CO insertion to form a THF-adduct, compound <u>37</u> (Equation 3.6).

$$\begin{tikzcd}
(CO)_5Mn(CH_2)_4Mn(CO)_5 \arrow[d, "\text{THF}"] \\
(THF)(CO)_4MnCO(CH_2)_4COMn(CO)_4(THF) \atop \underline{37} \arrow[d, "X_2"] \\
XOC(CH_2)_4COX + \text{unidentified inorganic product} \arrow[d, "\text{Hydrolysis (on work up)}"] \\
HOOC(CH_2)_4COOH
\end{tikzcd} \qquad (3.6)$$

It is thought that the THF-adduct <u>37</u> undergoes Mn-C bond cleavage in the presence of X_2, yielding the corresponding acid dihalide, which is then hydrolyzed during the subsequent work-up procedure.

A similar reaction occurs when μ-(1,5)-pentanediyl bis (manganese pentacarbonyl) is reacted with halogens in THF. Again a bifunctional organic acid is isolated viz pimelic acid. When the above reactions are repeated in methylene chloride, the expected cleavage products are obtained in high yields (Equation 3.7).

$$(CO)_5Mn(CH_2)_nMn(CO)_5 + 2X_2 \xrightarrow[rt]{CH_2Cl_2} 2Mn(CO)_5X + X(CH_2)_nX$$

$X = Br, I$

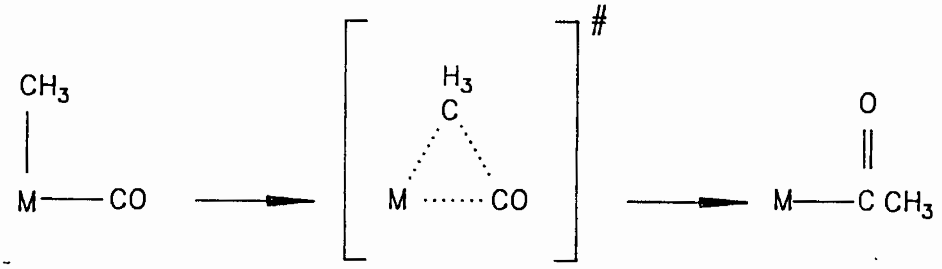
$n = 4$ and 5

(3.7)

The products from the above reactions were all identified by their IR and ^{1}Hnmr spectra and comparing these with the spectra of authentic samples. Reactions 3.6 and 3.7 demonstrate that bifunctional organic compounds can result from reactions of the μ-(1,n)-alkanediyl complexes of manganese.

3.1.2(d) REACTIONS OF $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ WITH CO:

The reactions of mononuclear manganese alkyl complexes of the type, $RMn(CO)_5$, with carbon monoxide are well documented [17, 18]. These complexes have been found to undergo carbonyl insertion readily to form the acyl derivatives $RCOMn(CO)_5$. Thus for example methyl manganese pentacarbonyl undergoes CO insertion to form $CH_3COMn(CO)_5$. The mechanism for this reaction has been investigated extensively [19]. It has been found that the reaction can best be described as a 1,2-migration of an alkyl group to a co-ordinated CO ligand which is in a *cis* position relative to the alkyl group. It is thought that this migration proceeds via a three centred transition state :



By analogy with mononuclear systems, the μ-alkanediyl complexes would thus be expected to react with carbon monoxide to produce acyl complexes. The reactions of compounds <u>23</u> and <u>24</u> with CO (1 atm) were therefore investigated. As expected the reactions readily yield the diaycl compounds as shown in Equation 3.8

$$(CO)_5Mn(CH_2)_nMn(CO)_5 \xrightarrow[THF]{CO(1\ atm)} (CO)_5MnCO(CH_2)_nCOMn(CO)_5$$

n=4 and 5

(3.8)

The above reaction proceeds rapidly at room temperature. This is to be expected as studies on mononuclear alkyl complexes of manganese pentacarbonyl have shown that carbonyl insertion becomes easier as the electron releasing ability of the alkyl group increases [20,21,22]. Cawse and co-workers [22] determined the rate of CO insertion of a number of mononuclear alkyl complexes of manganese pentacarbonyl. From this study, it would appear that a Taft σ-p correlation can be established for the alkyl migration (CO insertion) reaction. The rates of insertion increases as the electron releasing ability of the substituent increases i.e. in the reaction:

$$RMn(CO)_5 + CO \longrightarrow RCOMn(CO)_5$$

the rate increases in the order:

$$CF_3 < CFH_2 < CH_3 < C_2H_5 < C_3H_7.$$

The μ-(1,n) alkanediyl ligand is fairly electron releasing and it can therefore be expected that CO insertion in the alkanediyl complexes to be facile as is observed.

3.1.2(e) REACTION OF $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ WITH SYNTHESIS GAS:

The catalytic hydrogenation of carbon monoxide to yield organic compounds such as hydrocarbons ,alcohols and a host of other oxygenates is of great industrial importance. This conversion is catalyzed by transition metal complexes. The increased interest in this process has arisen as a result of the need to develop alternative sources of fuel. An example of a process which deals with the conversion of carbon monoxide and hydrogen to hydrocarbons is the so called Fischer-Tropsch process [23] which was first developed in the 1920s. Presently South Africa with its SASOL operations, is the only country which has large scale Fischer-Tropsch synthesis plants [23].

Other examples of catalytic processes which involve the hydrogenation of carbon monoxide includes methanol synthesis [24], the hydroformylation reaction [25] and the production of polyalcohols [26].

A great deal of research has been carried out on the reaction of transition metal complexes with synthesis gas (CO/H_2) [24-31]. The purpose of these studies was to gain a better understanding of the mechanisms of a variety of catalytic processes. This in turn could lead to the development of more efficient and selective catalysts. In addition these complexes may also serve as models for heterogeneous hydrogenation of carbon monoxide on metal surfaces [31].

There are quite a few examples in the literature dealing with the reaction of mononuclear alkyl transition metal complexes with synthesis gas. Dombek [32] for example investigated the reactions of a number of simple mononuclear alkyls of the type $RMn(CO)_5$ with synthesis gas in sulfolane as solvent. When methyl manganese pentacarbonyl was reacted with synthesis gas, acetaldehyde could be isolated as the only organic product. On the other hand the reaction of $CH_3Mn(CO)_5$ with H_2 only leads to the isolation of ethanol as the major organic product. Other alkyl complexes react in a similar fashion yielding either the aldehyde or the corresponding alcohol. The reaction of acyl manganese pentacarbonyls with synthesis gas has also been investigated . Freudenberger and Orchin [33] found that in hexane, syngas becomes incorporated into the acyl compounds to form alkoxycarbonyl species as shown below:

$$RCOMn(CO)_5 \xrightarrow{H_2/CO} RCH_2OC(O)Mn(CO)_5$$

In this thesis, the reaction of μ-(1,n)-alkanediyl complexes of manganese with synthesis gas is discussed and compared with those of mononuclear manganese alkyls.

The μ-(1,4)-butanediyl complex $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ was reacted with syngas (50/50 mixture CO and H_2) at 40 atmospheres and at 70°C, using THF as solvent. The reaction yields the diol, $HOCH_2(CH_2)_4CH_2OH$ as the only isolable organic product. A small amount of an aldehydic species, ν(CO) 1720cm^{-1}, was also detected. However it was not possible to isolate this compound. The formation of 1,6-hexanediol can be explained using Figure 3.5.

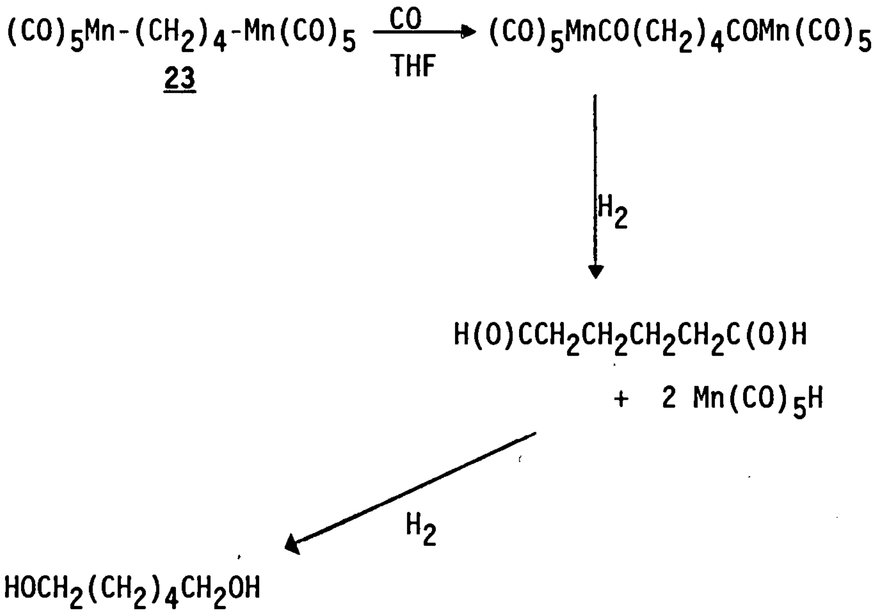


Figure 3.5. The formation 1,6-hexanediol from the 1,4-butanediyl complex $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$

The step in which the acyl intermediate $(CO)_5MnCO(CH_2)_4COMn(CO)_5$ is reduced to the dialdehyde has been confirmed by reacting the acyl species with hydrogen in a separate experiment. The product of this reaction is again the diol $HOCH_2(CH_2)_4CH_2OH$.

As can be seen from Figure 3.5, $HMn(CO)_5$ is proposed to be a product of the reaction, however it is not isolated or detected. Instead, the only organometallic compound isolated is $Mn_2(CO)_{10}$. It is however known that $Mn_2(CO)_{10}$ is the main decomposition product of $HMn(CO)_5$. Indirect evidence for $HMn(CO)_5$ formation has been obtained by repeating the reaction using CH_2Cl_2 instead of THF as solvent. In this case the only organometallic species isolated is $Mn(CO)_5Cl$ which may be formed by the reaction of $HMn(CO)_5$ with the chlorinated solvent. Similar results as above are obtained using the higher homoloques $(CO)_5Mn(CH_2)_5Mn(CO)_5$ and $(CO)_5Mn(CH_2)_6Mn(CO)_5$. The former yields $HOCH_2(CH_2)_5CH_2OH$, while the latter yields $HOCH_2(CH_2)_6CH_2OH$. In no case is complete incorporation of synthesis gas into the μ-alkanediyl compound observed i.e. no alkoxy-carbonyl compounds of the type $(CO)_5MnC(O)\text{-}O(CH_2)_n\text{-}O(O)CMn(CO)_5$ were observed. All the reactions were carried out at moderate temperatures and pressures (70°C/40 atm). Running the reactions at lower pressures and/or temperatures results in incomplete reactions yielding mixtures of products. For example when the reaction is run at 30°C, a mixture of the diol and an aldehydic species is obtained. It is not possible to separate these species, with the result that we were not able to fully characterize them. Reactions performed at low pressures (5 atm) yield only a mixture of $(CO)_5Mn\text{-}(CH_2)_n\text{-}Mn(CO)_5$ and $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$. From the results obtained, it can be seen that the reactions of

μ-(1,n)-alkanediyl complexes could be models for the termination step in a catalytic conversion of hydrocarbons to oxygenated species such as aldehydes and alcohols.

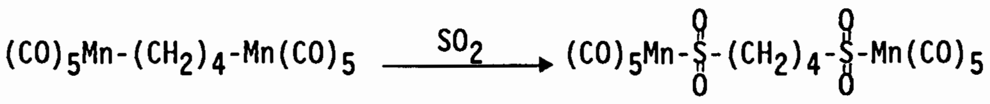
3.1.2(f) REACTION OF $[Mn(CO)_5]_2\{\mu-(CH_2)_4\}$ WITH SO_2:

Hartman and Wojcicki [35] have demonstrated that mononuclear manganese alkyl complexes of the type $RMn(CO)_5$ ($R=CH_3$ and C_2H_5) undergo reaction with sulfur dioxide to yield the corresponding S-sulfinato complexes (Equation 3.9).

$$(CO)_5Mn\text{-}R + SO_2 \longrightarrow (CO)_5Mn(SO_2R) \qquad (3.9)$$

The reactions proceed cleanly with the sulfinato derivatives being formed in fairly high yields.

In this section, the reaction of the 1,4-butanediyl complex with sulfur dioxide is discussed and compared with mononuclear analogues. Unlike ethyl or methyl manganese pentacarbonyl, the μ-(1,4)-butanediyl complex reacts very sluggishly with liquid sulfur dioxide. After 48h refluxing in SO_2 at room temperature, only about 40% of the starting material is consumed and mixture of the sulfinato derivative and starting material is isolated. However if the reaction is carried out at 70°C (19h) then almost complete conversion to a binuclear S-sulfinato derivative <u>42</u> achieved. (Equation 3.10)



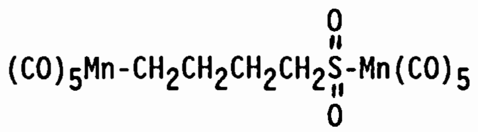
$$(CO)_5Mn\text{-}(CH_2)_4\text{-}Mn(CO)_5 \xrightarrow{SO_2} (CO)_5Mn\text{-}\overset{O}{\underset{O}{S}}\text{-}(CH_2)_4\text{-}\overset{O}{\underset{O}{S}}\text{-}Mn(CO)_5$$

23 **42**

(3.10)

The sulfinato compound **42** , was isolated as a pale yellow microcrystalline solid which is insoluble in almost all organic solvents, but only slightly soluble in acetone. The compound appears to be fairly hygroscopic becoming very sticky on prolonged exposure to air.

The infra-red spectrum of compound **42**, exhibits three main bands in the carbonyl region at 2137 w, 2048 s and 2021 msh cm^{-1}. The spectrum shows no sign of an acyl carbon band which tends to suggest that the compound is not an acyl-sulfur dioxide derivative but rather a S-sulfinato complex. An acyl-sulfur dioxide complex could have been formed if the SO_2 induced an alkyl migration of the hydrocarbon chain onto one of the terminal carbonyls (Figure 3.6), but evidently this does not occur. The infra-red spectrum of the complex does not exhibit any bands which resemble those of the original starting material which tends to suggest that the complex is the disulfinato rather than the monosulfinato complex:



$$(CO)_5Mn\text{-}CH_2CH_2CH_2CH_2\overset{O}{\underset{O}{S}}\text{-}Mn(CO)_5$$

In addition to the bands in the terminal carbonyl region, the solid state spectrum of the complex shows bands at 1120 and 1038 cm^{-1}, corresponding to $\nu(SO)_{sym}$ and $\nu(SO)_{asym}$ respectively. The sulfinato derivatives of mononuclear pentacarbonyl alkyl compounds exhibit bands in the region 1040 - 1200 cm^{-1}, which have been assigned as $\nu(SO)$ bands [36].

Because of the low solubility of the sulfinato compound, it was not possible to obtain a suitable nmr spectrum. However acceptable analytical data were obtained which help to confirm the proposed formulation of the compound (see experimental section for the figures).

From the results obtained, it can be seen that SO_2 insertion into the manganese-carbon bond of the μ-(1,4)-butanediyl complex is much slower than carbonyl insertion into the same bond. The reaction with carbon monoxide is quantitative at room temperature whereas the SO_2 reaction yields only about 40% of the expected product at this temperature. Heating the reaction mixture, however, results in almost complete conversion to the sulfinato derivative.

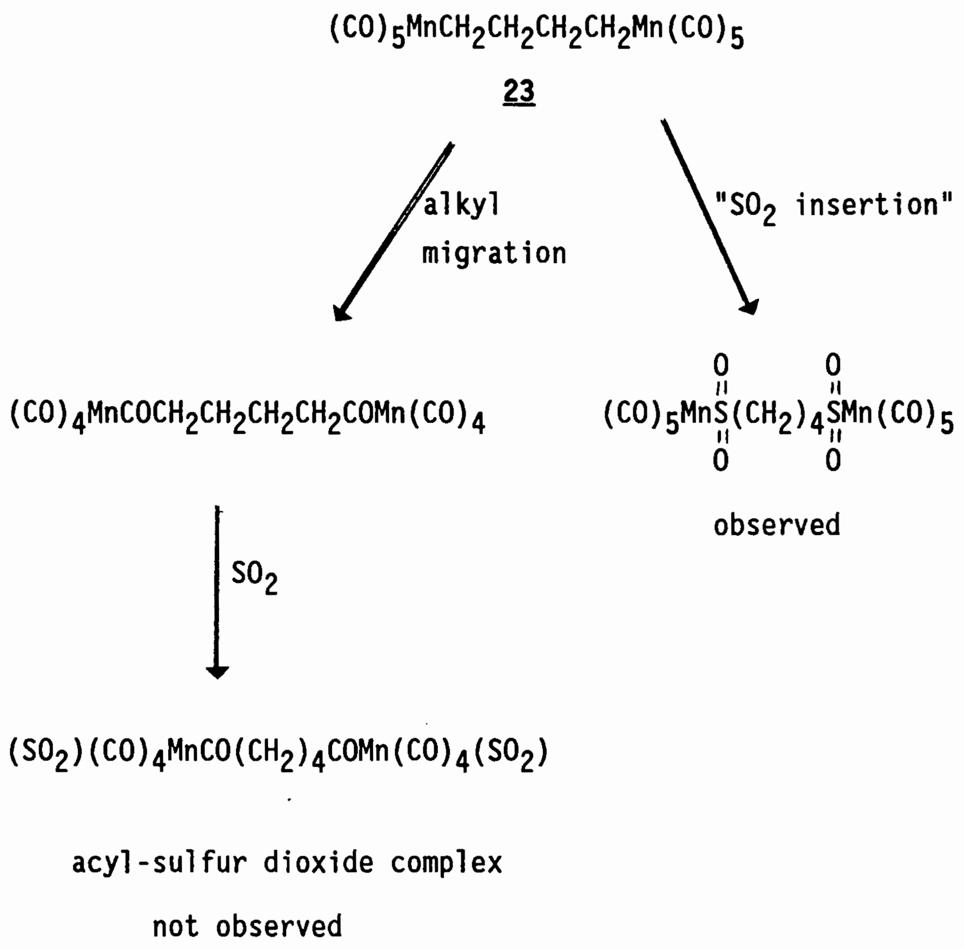


Figure 3.6 Possible reaction pathway for SO_2 reaction with compound 23

3.2 μ-ALKANEDIYL COMPLEXES OF RHENIUM:

3.2.1 SYNTHESIS AND CHARACTERIZATION

Until now, the only known μ-alkanediyl complex of rhenium pentacarbonyl has been μ-(1,2)-ethanediyl bis (rhenium pentacarbonyl) which can be prepared by the reaction of $\mathrm{Na[Re(CO)_5]}$ with $\mathrm{[(CO)_5Re(C_2H_4)]^+}$ [37]. The compounds <u>44</u> and <u>45</u> are thus new members of the homologous series. Compound <u>44</u>, the 1,4-butanediyl complex was prepared using a method analogous to that of the alkanediyl complexes of manganese. Thus the diacyl compound <u>43</u> was first prepared and subsequently decarbonylated to yield <u>44</u> (Equation 3.11).

$$2\mathrm{Na[Re(CO)_5]} + \mathrm{ClCO(CH_2)_4COCl} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{THF}}$$

$$\begin{tikzcd}
\mathrm{(CO)_5ReCO(CH_2)_4CORe(CO)_5} + 2\mathrm{NaCl} \arrow[d, "\underline{43}\quad \mathrm{Reflux\ Toluene}"] \\
\underset{\underline{44}}{\mathrm{(CO)_5Re(CH_2)_4Re(CO)_5}} + 2\mathrm{CO}
\end{tikzcd} \qquad (3.11)$$

The 1,3-propanediyl complex <u>45</u>, was however prepared by the reaction of $\mathrm{Na[Re(CO)_5]}$ with the appropriate triflate. (Equation 3.12)

$$2Na[Re(CO)_5] + Z(CH_2)_3Z \xrightarrow[25^\circ C]{THF} (CO)_5Re(CH_2)_3Re(CO)_5 + 2NaZ$$

45

$(Z = OSO_2CF_3)$

(3.12)

Both compounds **44** and **45** were isolated as white microcrystalline solids which are stable in air. In solutions which are exposed to air, the compounds tend to decompose to non-carbonyl species,however they are quite stable in solution when kept under nitrogen.

The polymethylene bridged rhenium complexes also exhibit three bands in the $\nu(CO)$ region at (see Table 3.12). This is similar to the spectrum of methyl rhenium pentacarbonyl [5].

Table 3.11: Yields, mps and analytical data for the compounds **44** and **45**

Compound No	n^a	mp/ (°C)	Yield (%)	ANALYSIS[b] C	H	(C)	(H)
45	3	118-121	49[c]	22.15	0.85	(22.48)	(0.87)
44	4	171-172	78[d]	23.75	1.15	(23.73)	(1.14)

a n is the number of methylene groups in the polymethylene chain

b calculated values in parentheses

c prepared by the reaction of $Re(CO)_5^-$ with $Z(CH_2)_3Z$ ($Z=OSO_2CF_3$)

d prepared from $(CO)_5ReCO(CH_2)_4CORe(CO)_5$

Table 3.12: IR and ^{1}Hnmr data compounds **44** and **45**:

Compound No	n^a	$\nu(CO)/cm^{-1}$ [b]			^{1}Hnmr/δppm[c] $-CH_2M$	$-CH_2-$
45	3	2118w	2012vs	1974m	1.02(4H)[d]	2.12(2H)[d]
44	4	2121w	2011vs	1976m	1.01(4H)[d]	1.78(4H)[d]

a n is the number of methylene groups in the polymethylene chain.

b measured in $CHCl_3$.

c measured in $CDCl_3$.

d signals are broad multiplets.

In the ^{1}Hnmr spectra of compounds <u>44</u> and <u>45</u>, two signals are observed, *viz* a broad triplet at about δ1.00 and a broad multiplet between δ1.80 and δ2.00 . The former corresponds to those protons of the methylene groups directly bonded to the metal centres, while the latter is due to the protons of the central methylene groups of the hydrocarbon chain (see Table 3.12). These assignments were made by comparison with the analogous manganese compounds.

The proton decoupled ^{13}C nmr spectra (Table 3.13) of compounds <u>44</u> and <u>45</u> show only four signals. The terminal carbonyl groups give rise to two signals appearing at δ186 and δ181.5 . The observation of two signals is a result of two of the carbonyl groups being *trans* to the alkyl chain. while the remaining eight carbonyls are *cis* to the alkyl chain. The signal at δ186 can be assigned to the *cis* carbonyls while the signal at δ181.5 is due to the *trans* carbonyls. These assignments were made on the basis of relative intensities of the peaks, which in this case was found to be approximately 4:1. This compares well with what is obtained for other complexes of the type $Re(CO)_5X$ [6]. The other two signals observed in the spectra of the μ-(1,n)-alkanediyl complexes of rhenium are due to the carbon atoms of the hydrocarbon bridge. In the case of the μ-(1,3)-propanediyl complex, these two signals appear at δ49.7 and δ0.2 . The latter is due to the α-carbon atoms while the former is due to the β-carbons. In the case of the μ-(1,4)-butanediyl complex, the bridge carbon signals appear at δ47.0 (β-carbons) and δ9.7 (α-carbons).

Table 3.13: ^{13}C nmr data for compounds 44 and 45.

Compound		$^{13}C\{^1H\}$nmr/ppm[b]		
		CO	C_α	C_β
No	n[a]		Re-$\underline{C}H_2$	Re-$CH_2\underline{C}H_2$
45	3	186.1/181.6	0.2	47.0
44	4	186.1/181.5	9.7	49.7

a n refers to the number of methylene groups in the polymethylene chain

b measured in $CDCl_3$.

These assignments were made by comparison with the $^{13}C\{^{1}H\}$ spectra of alkanediyl complexes of other metals.

Table 3.14 gives the relative intensities and assignments of the major peaks in the mass spectra of compounds <u>44</u> and <u>45</u>. The m/e values given are for ions containing ^{186}Re. Both compounds show molecular ions in their mass spectra. The fragmentation pattern of compound <u>44</u>, generally resembles that of the μ-(1,n)-alkanediyl complexes of manganese. Like those compounds, <u>44</u> shows a sequential loss of 28 mass units from the parent ion and the subsequent fragment ions. This is attributed to the loss of CO units from the parent ion which appears to be the major decomposition pathway for this compound. No ion is observed for the species in which the hydrocarbon chain has been lost from the parent ion. Thus it would appear that this route is not significant for compound <u>44</u>. The mass spectrum of compound <u>45</u> shows a molecular ion of low intensity and unlike other μ-(1,n)-alkanediyl complexes, such as $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ [38] and $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ [39], it does not decompose via successive loss of CO from the parent ion. Instead the major decomposition pathway appears to be one where elimination of the C_3H_6 bridge occurs followed by step-wise loss of CO to ultimately give the species $[Re_2]^+$ (m/e 372). Analogous to the manganese complexes, compounds <u>44</u> and <u>45</u> also decompose via the loss of a $M(CO)_5$ fragment (M = Re) to give $[(CO)_5Re(C_nH_{2n})]^+$. Again this appears to be a minor decomposition route.

Table 3.14: Mass spectral data for the compounds of the type $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3 and 4):

Ion[a]	Relative Peak Intensities	
	n=3[b]	n=4[c]
M	5	10
M-CO	-	7
M-2CO	-	-
M-3CO	-	8
M-4CO	-	17
M-5CO	-	32
M-6CO	-	32
M-7CO	-	33
M-8CO	-	32
M-9CO	-	28
M-10CO	8	26
$M\text{-}C_nH_{2n}$	49	-
$M\text{-}CO\text{-}C_nH_{2n}$	5	-
$M\text{-}2CO\text{-}C_nH_{2n}$	11	-
$M\text{-}3CO\text{-}C_nH_{2n}$	100	32
$M\text{-}4CO\text{-}C_nH_{2n}$	-	32
$M\text{-}5CO\text{-}C_nH_{2n}$	36	3
$M\text{-}6CO\text{-}C_nH_{2n}$	44	33

Table 3.14:/continued...

Table 3.14:/continued...

$M\text{-}6CO\text{-}C_nH_{2n}$	44	33
$M\text{-}7CO\text{-}C_nH_{2n}$	30	28
$M\text{-}8CO\text{-}C_nH_{2n}$	34	26
$M\text{-}9CO\text{-}C_nH_{2n}$	23	4.6
$M\text{-}10CO\text{-}C_nH_{2n}$	44	23
$M\text{-}10CO\text{-}C_nH_{2n}\text{-}Re$	9	47
$M\text{-}10CO\text{-}Re\text{-}C_2H_4$	15	46
$M\text{-}C_nH_{2n}\text{-}Re(CO)_5$	57	100
$M\text{-}C_nH_2n\text{-}Re\text{-}6CO$	37	94
$M\text{-}C_nH_{2n}\text{-}Re\text{-}7CO$	24	38
M-10CO-Re	11	27
$M\text{-}C_nH_{2n}\text{-}Re\text{-}8CO$	16	68
$M\text{-}C_nH_{2n}\text{-}Re\text{-}9CO$	17	45
$M\text{-}C_nH_{2n}\text{-}Re\text{-}10CO$	9	47
$M\text{-}Re(CO)_5$	22	27
$M\text{-}Re(CO)_5\text{-}CO$	8	13
$M\text{-}Re(CO)_5\text{-}2CO$	23	11
$M\text{-}Re(CO)_5\text{-}3CO$	6	30
$M\text{-}Re(CO)_5\text{-}4CO$	7	24

---

[a] $M = Re_2(CO)_{10}C_nH_{2n}$; all ions have a single positive charge; ion refers to suggested assignments, low resolution spectra.

[b] peak intensities relative to base peak at m/e 568.

[c] peak intensities relative to base peak at m/e 326.

3.2.2 REACTIONS OF THE COMPLEX $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$:

3.2.2 (a) REACTION WITH TERTIARY PHOSPHINES

The reactions of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 45 with tertiary phosphines do not proceed so smoothly as the reactions of the analogous manganese μ-(1,4)-butanediyl complex. 45 does not react with tertiary phosphines in tetrahydrofuran at room temperature, even after stirring for prolonged periods. On refluxing with tetrahydrofuran some reaction does occur however, the reaction is still sluggish. The reaction with triphenylphosphine phosphine , yields $[(CO)_4(PPh_3)Re]_2\{\mu\text{-}(CH_2)_4\}$ 46, after refluxing for 42 hours. The reaction is rather complicated, as is evident when it is monitored by IR spectroscopy and it would seem that initially the disubstituted diacyl complex $(CO)_4(PPh_3)ReCO(CH_2)_4CORe(PPh_3)(CO)_4$ is formed which is quickly converted to the phosphine substituted μ-alkanediyl complex. Thus during the initial stages of the reaction, we have a complex mixture of at least three compounds, viz the starting material, the disubstituted phosphine diacyl complex and the disubstituted phosphine μ-alkanediyl complex. Prolonged heating of the reaction mixture leads to the complete conversion to complex 46. The overall reaction is shown in Equation 3.13.

$$[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\} + 2\ PR_3 \xrightarrow[THF]{reflux} [Re(CO)_4(PR_3)]_2\{\mu\text{-}(CH_2)_4\}$$

46 $PR_3 = PPh_3$
47 $PR_3 = PPh_2Me$
48 $PR_3 = PPhMe_2$

(3.13)

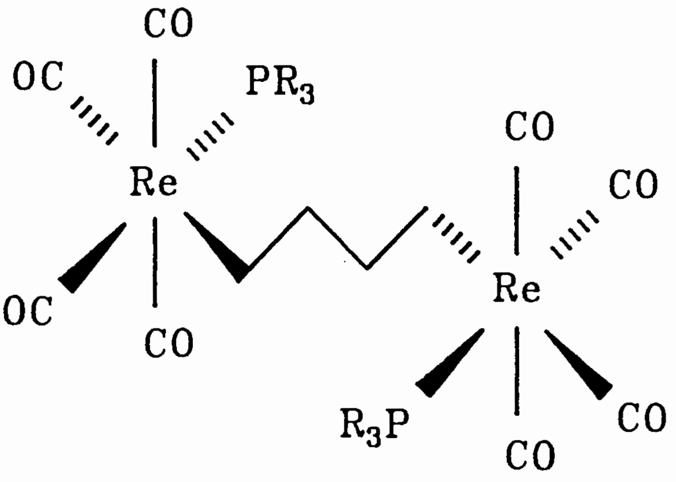
The reactions of PPh_2Me and $PPhMe_2$ respectively are even more sluggish with the former taking 72h and the latter 6 days to go to completion. In the case of the $PPhMe_2$ reaction, it is possible to isolate the intermediate disubstituted diacyl complex, $(CO)_4(PPhMe_2)ReCO(CH_2)_4CORe(PPhMe_2)(CO)_4$ (see experimental section).

The tardiness of the reactions of the rhenium μ-alkanediyl complex in the comparison with those of manganese, is in agreement with the general observation that alkyl complexes of third row transition metal elements undergo alkyl migrations and substitution reactions at rates much slower than those of first row metals [36].

The reactions appear to be faster in refluxing acetonitrile, for example the reaction of $PPhMe_2$ with μ-(1,4)-butanediyl complex of rhenium (2:1 mole ratio) yields the diacyl disubstituted phosphine complex $(CO)_4(PPhMe_2)ReCO(CH_2)_4CORe(PPhMe_2)(CO)_4$ after 4.5h refluxing as compared to 3 days refluxing in tetrahydrofuran. This rate enhancement in acetonitrile agrees with what has previously been observed for other substitution reactions.Thus it has been found that the rate varies markedly with the dielectric constant and with the nucleophilic power of the solvent. For example the sequence CH_3CN >> $(CH_3)_2CO$ > THF > $CHCl_3$ > C_6H_6 has been reported for the reaction of $MeMn(CO)_5$ with the tertiary phosphines [40]. Similar trends have been observed for the insertion reactions of $CpFe(CO)_2R$ and $CpMo(CO)_3R$ type complexes [41-43].

Compounds 46 - 48 were isolated as white microcrystalline solids which are stable at room temperature in the solid state. Solutions of the compounds are stable provided they are kept under an inert atmosphere but in the presence of air, they show extensive decomposition to unidentified non-carbonyl compounds.

All three compounds 46, 47 and 48 show four bands in the ν(CO) region of their IR spectra which is indicative of a *cis*,*cis* configuration (Figure 3.7). This resembles the analogous manganese μ-(1,n) alkanediyl complexes which also show *cis*,*cis* configurations. Prolonged heating of the compounds in tetrahydrofuran shows no change in the ν(CO) region. This suggests that there is no isomerization to the *trans* isomer, which we would expect to show only one strong bond in the terminal νCO region of the IR spectrum. The lack of *cis-trans* isomerization is an indication of the Re-C bond strength (Re-CO bond cleavage is expected to precede isomerization).



46 $PR_3 = PPh_3$

47 $PR_3 = PPh_2Me$

48 $PR_3 = PPhMe_2$

Figure 3.7: The μ-(1,4)-butanediyl phosphine substituted complexes of rhenium.

TABLE 3.15: Yields, m.p.s and analytical data for compounds **46** - **48**.

COMPOUND	PR_3	Yield %	m.p. (°C)	ANALYSIS[a] C	H	(C)	(H)
46	PPh_3	68	154-159	49.30	3.55	(48.98)	(3.25)
47	PPh_2Me	60	148-154	43.30	3.15	(43.34)	(3.25)
48	$PPhMe_2$	56	92-98	36.45	3.50	(36.20)	(3.30)

a calculated values in parentheses.

TABLE 3.16: IR data for compounds **46** - **48**.

COMPOUND	PR_3	$\nu(CO)/cm^{-1}$ (CH_2Cl_2)			
46	PPh_3	2073m	1980ssh	1969vs	1922s
47	PPh_2Me	2072m	1978ssh	1968vs	1922m
48	$PPhMe_2$	2071m	1978ssh	1969vs	1920m

Table 3.17: ^1H nmr data for the compounds **46** - **48**

COMPOUND			^1H nmr/δ ppm^a		
Number	PR_3	$P\text{-}C_6H_5$^{b}	$CH_2\text{-}Re$^{c}	$\text{-}CH_2\text{-}$^{c}	$P\text{-}CH_3$^{d}
46	PPh_3	7.28(30H)	0.41(4H)	1.39(4H)	-
47	PPh_2Me	7.33(20H)	0.50(4H)	1.49(4H)	2.02(6H)
48	$PPhMe_2$	7.40(10H)	0.56(4H)	1.60(4H)	1.84(12H)

a measured in $CDCl_3$.

b signals are broad singlets.

c signals are broad multiplets.

d signals are doublets ($^2J_{PH}$ = 9 Hz).

The ^1H nmr spectra of compounds <u>46</u> - <u>48</u> (Table 3.17) are in accord with these compounds having polymethylene bridges. The bridge protons appear as two distinct signals, one around δ0.45 - 0.50 and the other around δ1.40 - 1.60 . Both appear as broad multiplets. The high field signal is due to the protons attached to the carbon atoms directly bonded to the metal centres. These protons are shielded and thus resonate at lower chemical shift values. The low field signal is due to the protons attached to the central carbon atoms of the polymethylene chain; they experience less shielding and therefore have lower chemical shifts.

An examination of the reaction times for the preparation of the compounds of the type $[(CO)_4(PR_3)Re]_2\{\mu\text{-}(CH_2)_4\}$, reveals that the reaction rates increase in the order:

$$PPhMe_2 < PPh_2Me < PPh_3$$

This is the reverse to what is obtained in the case of the μ-(1,n)-alkanediyl complexes of iron [9]. When the complexes $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ were reacted with tertiary phosphines, it was found that $PPhMe_2$ for example reacted much faster than PPh_3. This is explained by the fact that in the case of the rhenium system, we are dealing with a decarbonylation (retro-insertion) process in the final step, while in the case of the iron system, the rate determining step is a CO insertion process. The two processes are outlined in the reaction scheme in Figure 3.8.

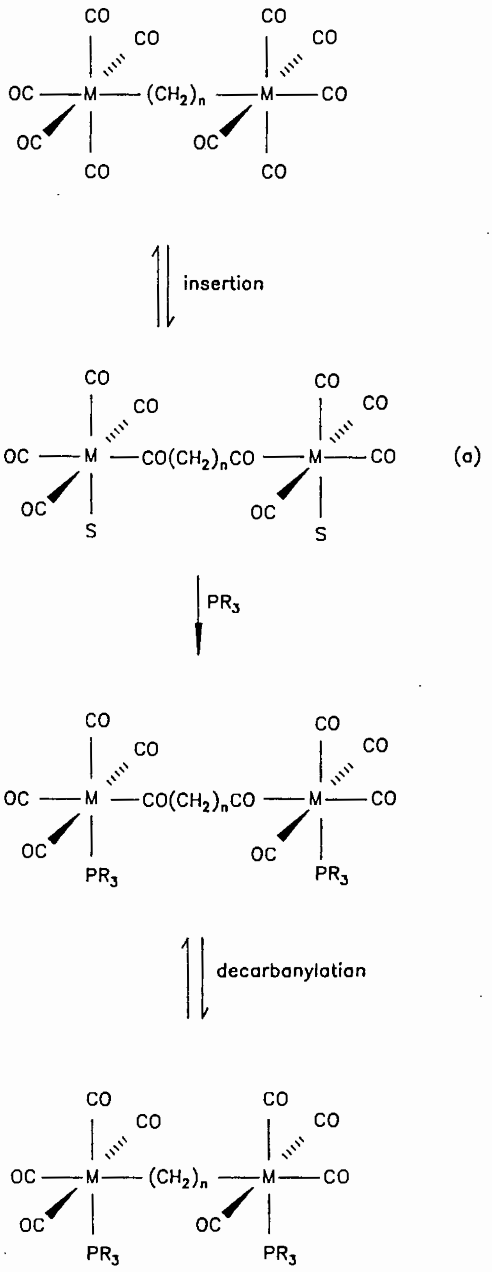


Figure 3.8: Insertion follwed by decarbonylation in metal alkanediyl compounds.(M = Mn, Re)

From Figure 3.8, it can be seen that the CO insertion reaction proceeds via intermediate (a) which further reacts with the tertiary phosphine to form the phosphine substituted diacyl complex. The rate of the CO insertion reaction is influenced by the nucleophilicity and steric bulk of the tertiary phosphine (PR_3). The greater the nucleophilicity and the less the steric bulk, the faster CO insertion will occur. In the decarbonylation process however, these two factors (nucleophilicity and steric bulk) have the opposite effect. Thus an increase in steric bulk and a lower nucleophilicity will enhance the decarbonylation process.

3.2.2 (b) REACTIONS OF $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ WITH HALOGENS:

The reactions of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ with bromine or iodine,lead to the cleavage of the Re-C bonds of the alkyl bridge (Equation 3.14).

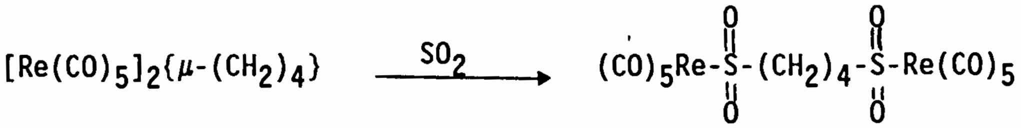
$$\underset{\underline{44}}{[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}} + 2X_2 \xrightarrow[25°C]{THF} 2Re(CO)_5X + X(CH_2)_4X \quad (X{=}Br,\ I)$$

(3.14).

As can be seen from Equation 3.14, the reactions were performed in tetrahydrofuran as solvent. In contrast to the reactions of μ-(1,4)-butanediylbis(manganese pentacarbonyl) with halogens, the formation of adipic acid is not observed. This is because the rhenium polymethylene bridge complex does not readily form a THF-acyl adduct as is the case with the manganese complex. The reason for this is that rhenium alkyls, $RRe(CO)_5$, are not so susceptible to CO insertion as manganese alkyls [36]. Rhenium is a third row element and as discussed in section 3.2.1, carbonyl insertion for third row elements is much slower than for the analogous first row elements. The cleavage products in Equation 3.14 were identified using infra-red and ^1H nmr spectroscopy.

3.2.2 (c) REACTIONS OF $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ WITH SO_2:

$[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ undergoes SO_2 insertion in the same way as the analogous manganese compound to yield a bis-S-sulfinato derivative 49 (Equation 3.15).



$$[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\} \xrightarrow{SO_2} (CO)_5Re-\overset{O}{\underset{O}{S}}-(CH_2)_4-\overset{O}{\underset{O}{S}}-Re(CO)_5$$

49

(3.15)

The SO_2 insertion product 49, was isolated as a white micro-crystalline solid which is extremely stable in the solid state, decomposing only at a temperature exceeding 200°C.

The infra-red spectrum of the compound 49, shows four bands in the carbonyl region at 2154w, 2097vw, 2051s and 2025msh cm^{-1} . The solid state spectrum also shows two bands at 1183 cm^{-1} and 1045 cm^{-1} which can

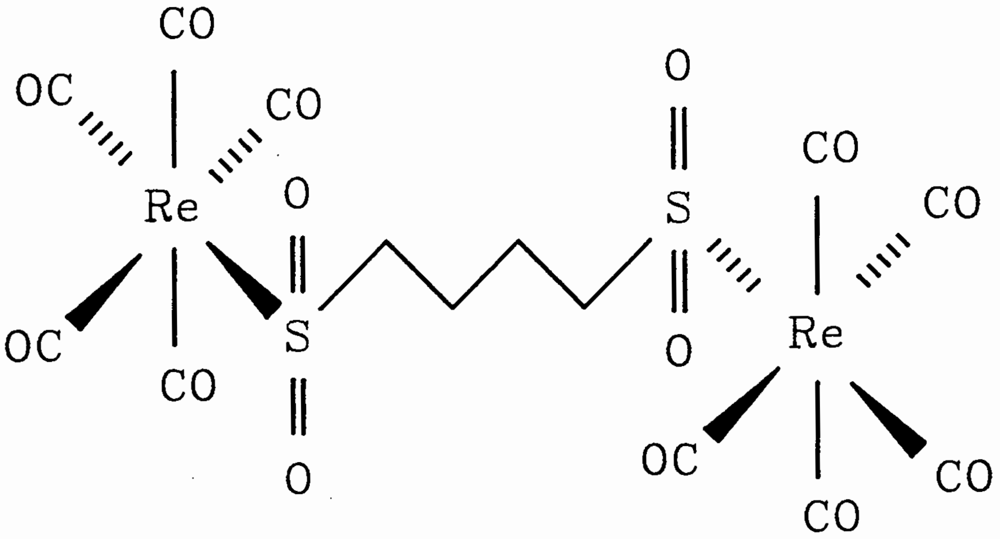


Figure 3.9 Possible structure of the S-sulfinato compound, $[Re(CO)_5]_2\{\mu\text{-}SO_2(CH_2)_4SO_2\}$

be assigned to the symmetric and asymmetric S-O stretching frequencies respectively. The spectrum closely resembles that of the analogous methyl derivative, $(CO)_5ReSO_2CH_3$ [37]. It can thus be assumed that the compound has the structure shown in Figure 3.9. The sulfinato derivative **49**, was found to be insoluble in all the common organic solvents. This precluded any nmr characterization of the complex. Analytical was found to be satisfactory for the proposed structure (see experimental section).

Although the reaction of $(CO)_5Re\text{-}(CH_2)_4\text{-}Re(CO)_5$ with liquid sulfur dioxide yields the sulfinato complex, the reaction appears to be much slower than that of methyl rhenium pentacarbonyl.

3.2.2(d) REACTION OF $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ WITH CARBON MONOXIDE:

Relative to mononuclear alkyl manganese complexes, very little work has been done on the carbonylation reactions of simple mononuclear alkyls of rhenium. These latter reactions are normally very slow and require fairly vigorous reaction conditions. Even ligand induced carbonylations tend to proceed at a slow rate and in some cases,CO substitution is favoured over CO insertion into the rhenium-akyl bond

Like its mononuclear analogues, the binuclear μ-(1,4-butanediyl complex of rhenium, reacts very sluggishly with carbon monoxide to yield the diacyl compound $(CO)_5ReCO(CH_2)_4CORe(CO)_5$. For example when the μ-(1,4)-butanediyl complex is reacted with CO (40 atm) for 24h, only about 30%

of the diacyl product is obtained. The major portion of the reaction mixture is unreacted starting material. A similar result is obtained in the reaction of the μ-(1,3-propanediyl) complex with carbon monoxide.

3.2.2(e) REACTION OF $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ WITH SYNTHESIS GAS:

The rhenium binuclear alkyl, $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ was reacted with CO/H_2 (1:1) to see if the reaction would yield 1,6-hexanediol as was found in the case of the analogous manganese compound. However the reaction was not so straightforward as for the manganese case. Reaction of the μ-butanediyl compound with CO/H_2 (40 atm, 70°C) yields a complex mixture which from the infra-red spectrum appears to contain at least four components. The major portion of the product appears to be unreacted starting material. Other products identified tentatively from the infra-red spectrum are the diacyl species $(CO)_5ReCO(CH_2)_4CORe(CO)_5$ and 1,6-hexanediol. There is also a sign of a second organic product showing a strong band at 1720 cm-^{1}. It is thought that this may be an aldehydic species, since the carbonyl band of aliphatic aldehydes normally appears between 1700-1725 cm-^{1}. It is speculated that this compound is the bifunctional aldehyde $H(O)C(CH_2)_4C(O)H$. It is however not possible to separate these products, with the result that they could not be fully characterized. The reason for the reaction being more complex than the manganese reaction is again probably due to the reluctance of the rhenium alkyl-bridge compound to undergo carbonyl insertion. It is thought that the initial step in these syngas reactions, is carbonyl insertion into the metal carbon bond of the bridging hydrocarbon chain. Since this process is so slow for rhenium alkyls, the subsequent steps to produce 1,6-hexanediol via bifunctional aldehydes are also slowed down resulting in a complex mixture of products.

3.3 CONCLUSION:

The manganese and rhenium μ-alkanediyl complexes of the type, $[M(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (M = Mn, Re) can now be synthesized by a route not previously used for other μ-alkanediyl complexes. Previous attempts to produce the manganese μ-alkanediyl complexes using the conventional reaction of the metal anion and a dihaloalkane were not successful. The only product isolated was a cyclic carbene species. The synthetic approach described in this section, thus overcomes the problems previously encountered using the conventional route to μ-alkanediyl compounds. Using the indirect method i.e. the method involving the decarbonylation of the diacyl species of the type $(CO)_5MCO(CH_2)_nCOM(CO)_5$, we were able to synthesize a number of new μ-alkanediyl of manganese and rhenium.

The reactivity of the two series of compounds, differs considerably. The manganese compounds have been found to be extremely susceptible to nucleophilic reactions. They, for example easily undergo carbonyl insertions in the presence of Lewis bases such as tertiary phosphines. The rhenium μ-alkanediyl compounds, on the other hand, show a great reluctance to undergo CO insertion reactions. Substitution reactions are favoured instead. The ease of carbonyl insertion of the manganese compounds over that of rhenium is further demonstrated in the reactions of μ-alkanediyl compounds with halogens using tetrahydrofuran as solvent. In the case of the manganese compounds, the cleavage products are bifunctional carboxylic acids, while in the case of the rhenium compounds, the products are dihaloalkanes.

μ-Alkanediyl compounds can be models for hydrocarbon fragments bound to two active sites on a catalyst surface. The reactions of these compounds may therefore give some insight into the behaviour of such hydrocarbon fragments on the catalyst surface. Thus for example, the reaction of μ-alkanediyl compounds with synthesis gas, may have some relevance to reactions that lead to the formation of oxygenates in catalytic processes. The results obtained in this section, would tend to suggest that a catalyst based on manganese, may yield oxygenates more readily than one based on rhenium. This is because CO insertion is more facile for manganese akyls than is the case for the rhenium analogues.

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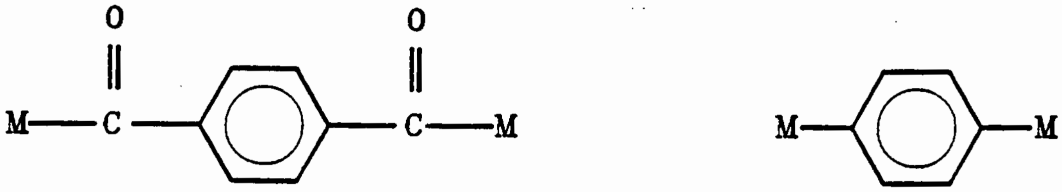
CHAPTER FOUR.

4. THE SYNTHESIS AND CHARACTERIZATION OF μ-(p-PHTHALOYL) AND μ-(*p*-PHENYLENE) COMPLEXES OF TRANSITION METALS

4.1 INTRODUCTION

μ-(*p*-Phthaloyl) and μ-(*p*-phenylene) complexes are binuclear compounds in which two metal centres are bridged by a bifunctional aroyl, **4-I** or aryl group, **4-II** (Figure 4.1).



4–I

4–II

Figure 4.1 μ-(*p*-phthaloyl) and μ-(*p*-phenylene) complexes.

These complexes could be significant in a hypothetical catalytic conversion of aromatic compounds to bifunctional aromatic acids, aldehydes and alcohols. An example of a bifunctional aromatic compound which could be a possible product is terephthalic acid, C_6H_4-1,4-$(COOH)_2$. Phthalic acids are produced on a large scale industrially and are important feedstocks for a wide range of products e.g. polyester fibres, plasticizers and dyes [1,2].

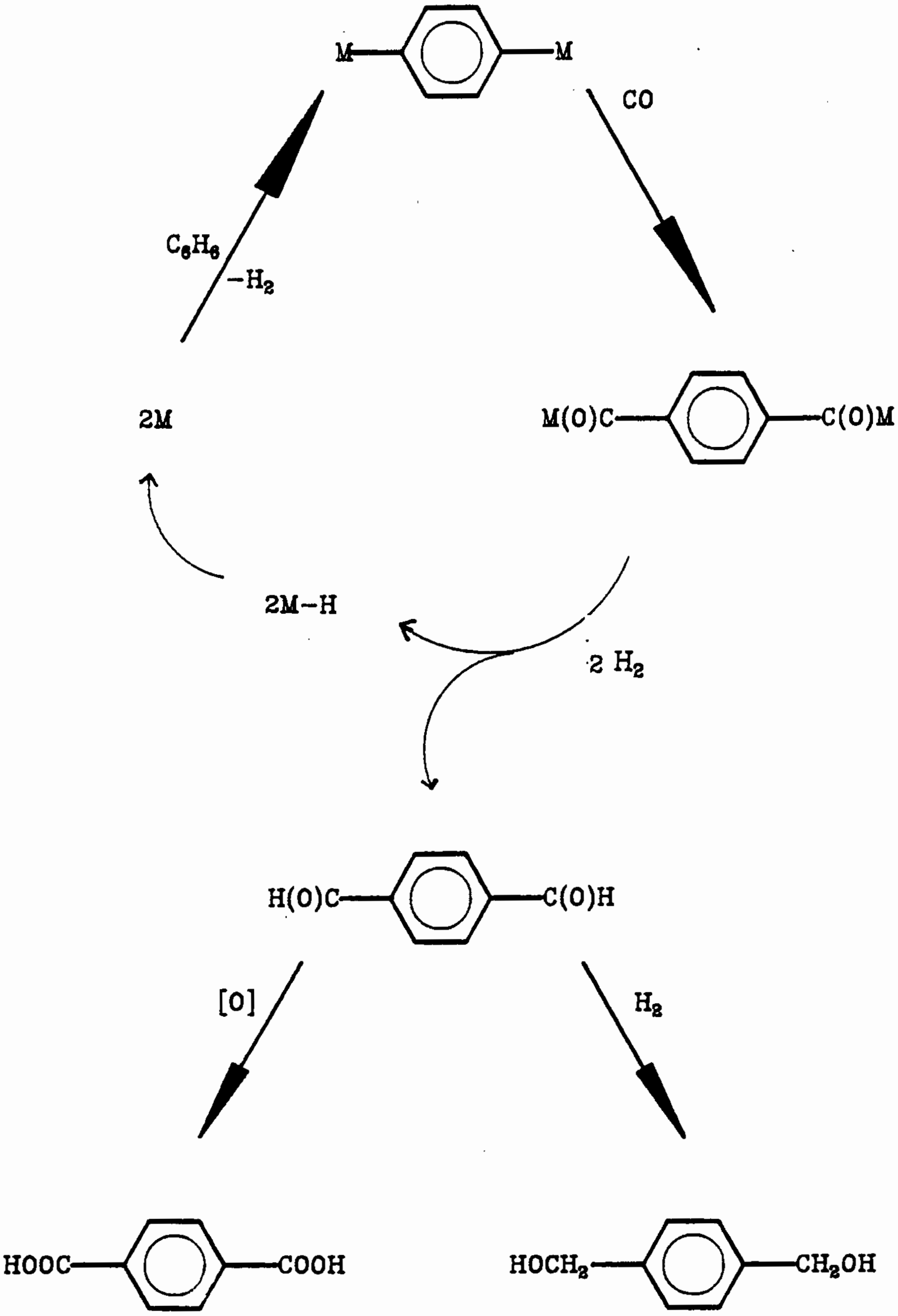


Figure 4.2: A hypothetical catalytic cycle for the formation of bifunctional aromatic compounds.

A hypothetical catalytic cycle for the formation of bifunctional aromatic compounds is outlined in Figure 4.2. The first step in the hypothetical cycle involves the activation of two C-H bonds of an aromatic ring. C-H bond activation of the benzene ring has been reported previously [3]. The second step of the cycle, involves the insertion of carbon monoxide into a metal-carbon bond. This type of reaction has been reported before [4], hence this step is quite feasible in our catalytic cycle. In the final step, we have cleavage of the M-C bond to yield a bifunctional aromatic compound. Again M-C (acyl) bond cleavage of this type is known [5].

It can thus be seen that if such a catalytic process as the one in Figure 4.2 was to be possible, then the μ-(*p*-phthaloyl) and the μ-(*p*-phenylene) complexes would be important model compounds. A study of these complexes would give some insight into the feasibility of the proposed mechanism for the formation of the bifunctional compounds.

At present, there are very few examples of μ-(*p*-phthaloyl) and μ-(*p*-phenylene) complexes in the literature. The only examples known are those of manganese and rhenium pentacarbonyl, together with a nickel complex, $Ni_2(\mu\text{-}C_6H_4)(PPh_3)_4Br_2$ [6] and a lutetium compound, $Lu_2(\mu\text{-}C_6H_4)Cp^*{}_4$ [7]. The manganese and rhenium complexes were first reported by Nesmeyanov *et al* [8]. Although these workers describe the synthesis of these compounds, they give no characterization data besides elemental analysis. Furthermore, the reactivity of these complexes are completely unknown. It was therefore decided to repeat the preparation of the manganese and rhenium compounds in order to fully characterize them and to study their reactivity. In addition to preparing, these complexes, new μ-(*p*-phthaloyl) complexes of iron, cobalt, molybdenum and rhodium were also prepared and characterized. The preparation of a μ-(*p*-phenylene) complex of iron, although in low yield is also reported in this section·

4.2 μ-(p-PHTHALOYL) COMPLEXES:

4.2.1 SYNTHESIS AND CHARACTERIZATION OF (μ-*p*-PHTHALOYL) COMPLEXES OF Mn,Re, Fe, AND Co.

The μ-(*p*-phthaloyl) complexes of Mn, Re, Fe and Co were prepared by reacting the appropriate metal anion with phthaloyl dichloride in tetrahydrofuran at room temperature (Equation 4.1).

$$2Na^+M^- + C_6H_4\text{-}1,4\text{-}(COCl)_2 \xrightarrow{THF} C_6H_4\text{-}1,4\text{-}(COM)_2 + 2NaCl \qquad (4.1)$$

50 M = $Mn(CO)_5$

51 M = $Re(CO)_5$

52 M = $CpFe(CO)_2$

53 M = $Co(CO)_3(PPh_3)$

Compounds 50 -53 were isolated as microcrystalline solids. The manganese, rhenium and iron complexes are extremely air stable for prolonged periods (several months). The cobalt complex however appears to be slightly air sensitive, decomposing slowly over several days. During this decomposition, the compound changes colour from pale yellow through greenish-yellow to green. The final decomposition product is insoluble in common organic solvents. A solid state infra-red spectrum shows that the green solid does not contain any carbonyl ligands. Due to the insolubility of the decomposition product, it was not possible to characterize it. The cobalt *μ*-(*p*-phthaloyl) compound appears to be fairly stable when stored under nitrogen.

The *μ*-(*p*-phthaloyl) complexes are extremely stable thermally, decomposing only at elevated temperatures (see Table 4.1). For example, the iron complex, compound 52, decomposes between 154-161°C. In all cases, the decomposition occurs without the compound melting. All the *μ*-(*p*-phthaloyl) complexes with the exception of the cobalt complex, are extremely insoluble in common organic solvents. The iron compound is moderately soluble in methylene chloride. The cobalt complex is completely soluble in a number of polar organic solvents such as methylene chloride, acetone, ethanol and chloroform. It is insoluble in hexane and benzene. The insolubility of the manganese and the rhenium complexes, precludes nmr characterization of these compounds. It was however possible to obtain ^{1}H nmr spectra of both the iron and cobalt complexes. The compounds were further characterized by infra-red spectroscopy, micro-analysis and mass spectroscopy. The characterization data for the complexes appear in Tables 4.1 - 4.3.

Table 4.1: M.p.s, yields and analytical data for the compounds of the type, C_6H_4-1,4-$(COM)_2$, where M = $Mn(CO)_5$, $Re(CO)_5$, $CpFe(CO)_2$, $Co(CO)_3(PPh_3)$ $CpMo(CO)_3$ and $Rh(PPh_3)_2Cl_2$.

COMPOUND		m.p./°C	YIELD/	ANALYSIS+			
M	No		%	C	H	(C)	(H)
$Mn(CO)_5$	50	120-125 (dec)	85	41.40	0.90	(41.4)	(0.77)
$Re(CO)_5$	51	210-218 (dec)	44	27.80	0.70	(27.55)	(0.51)
$CpFe(CO)_2$	52	154-161 (dec)	64	54.65	2.95	(54.40)	(2.90)
$Co(CO)_3(PPh_3)$	53	204-212 (dec)	23	63.26	3.80	(63.71)	(3.64)
$CpMo(CO)_3$	54	131-138 (dec)	7	45.95	2.20	(46.32)	(2.28)
$Rh(PPh_3)_2Cl_2$	55	206-211 (dec)	74	62.50	4.60	(62.85)	(4.22)

+ Calculated values in brackets.

TABLE 4.2: IR data for the compounds of the type, C_6H_4-1,4-(COM)$_2$, where M = $Mn(CO)_5$, $Re(CO)_5$, $CpFe(CO)_2$, $Co(CO)_3(PPh_3)$, $CpMo(CO)_3$ and $Rh(PPh_3)_2Cl_2$.

COMPOUND M	No.	ν(CO)/cm^{-1}					
$Mn(CO)_5$[a]	**<u>50</u>**	2117w	2050w-m	2033m	2004s	1988vs	1588m
$Re(CO)_5$[a]	**<u>51</u>**	2133w	2060w-m	2018msh	2002s	1976vs	1566m
$CpFe(CO)_2$[b]	**<u>52</u>**	2024vs	1967s			1608mbr	
$Co(CO)_3(PPh_3)$[b]	**<u>53</u>**	2051w	1983s	1966s		1622mbr	
$CpMo(CO)_3$[b]	**<u>54</u>**	2024m	1938s			1607mbr	
$Rh(PPh_3)_2Cl_2$[a]	**<u>55</u>**				1701m	1665w	

KBr

a Nujol mull, Kbr plates.

b CH_2Cl_2 solution.

w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad.

Table 4.3 ^1H nmr data for complexes of the type, C_6H_4-1,4-(COM)$_2$, M = CpFe(CO)$_2$, CpMo(CO)$_3$ and Co(CO)$_3$(PPh$_3$).

				1H nmr/δ ppm[a]
M	No	Ph-CO	C_5H_5	P-Ph
CpFe(CO)$_2$	<u>52</u>	7.42(4H)	4.88(10H)	-
Co(CO)$_3$(PPh$_3$)	<u>53</u>	7.72(4H)	-	7.44(30H)
CpMo(CO)$_3$	<u>54</u>	7.44(4H)	5.54(10h)	_

a measured in $CDCl_3$.

The infra-red spectra of both the manganese and rhenium complexes show six bands in the ν(CO) region. In both cases the position of the bands are similar to those of the mononuclear complexes of the type $(CO)_5MCOC_6H_5$ (M = Mn and Re) [9]. The infra-red spectrum of the iron complex, **52**, exhibit three bands in the carbonyl region (see Table 4.2) . Again these bands appear in similar positions to those found in the spectrum of $Cp(CO)_2FeCOPh$ [10]. The cobalt complex shows four distinct bands in the ν(CO) region of the infra-red spectrum, viz a weak high frequency band at 2051 cm^{-1}, two very strong bands at 1984 and 1966 cm^{-1} and a weak acyl band at 1622 cm^{-1}.

As stated earlier, it was not possible to obtain ^1H nmr spectra for the manganese and rhenium μ-(*p*-phthaloyl) complexes as a result of the insolubility of these complexes. The iron and cobalt complexes on the other hand were sufficiently soluble to obtain reasonable spectra and in both cases, the ^1H nmr spectrum shows two signals. Thus the spectrum of the iron compound consists of a singlet at δ7.38 and a singlet at δ4.87. The low field signal is due to the four protons of the bridging phthaloyl ring. The fact that these protons give rise to a singlet is indicative of a symmetrical 1,4-disubstituted benzene ring. The signal at δ4.87 is due to the cyclopentadienyl protons.

The ^1H nmr spectrum of the cobalt complexes, **53**, also shows two signals which occur at δ7.44 and δ7.72. The signal at δ7.44 corresponds to four protons and is due to the phenyl ring protons while the downfield signal at δ7.72 is due to the thirty protons of the triphenylphosphine ligands.

The mass spectra of compounds **50**, **51** and **52** do not show a parent ion, instead the highest mass peak represents the fragment (M^+-2CO). Thus the spectra are identical to that of the corresponding μ-(p-phenylene) complexes. The mass spectra of these complexes are discussed in section 4.3.3

4.2.2 PREPARATION AND CHARACTERIZATION OF $[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$

The synthesis of the μ-(p-phthaloyl) complex of molybdenum was attempted using an analogous synthetic approach as for the complexes of manganese and rhenium. However the reaction is not very successful with only about 7% of the expected product being isolated. The major isolable product is the dimer, $[CpMo(CO)_3]_2$ which was isolated in 78% yield.

$$2\ CpMo(CO)_3^-Na^+ \ + \ C_6H_4\text{-}1,4\text{-}(COCl)_2 \xrightarrow{THF}$$

$$\underset{\mathbf{54}}{Cp(CO)_3Mo\text{-}COC_6H_4CO\text{-}Mo(CO)_3Cp} \qquad (4.2)$$

The inability to prepare the μ-(p-phthaloyl) complex in reasonable amounts, is probably due to the instability of the compound. The analogous mononuclear benzoyl compound of molybdenum is not very stable and rapidly decomposes to the compounds $[C_6H_5C_5H_4Mo(CO)_3]_2$ and $[C_6H_5C_5H_4(CO)_3Mo\text{-}Mo(CO)_3C_5H_5]$ [11]. In the case of the reaction of terephthaloyl chloride with the molybdenum anion, the only decomposition product obtained is the dimeric species, $[C_5H_5Mo(CO)_3]_2$. No migration of the phenyl group onto the cyclopentadienyl ring is observed. It is believed that the decomposition occurs via simple homolytic cleavage of the metal acyl bonds as shown in Figure 4.3.

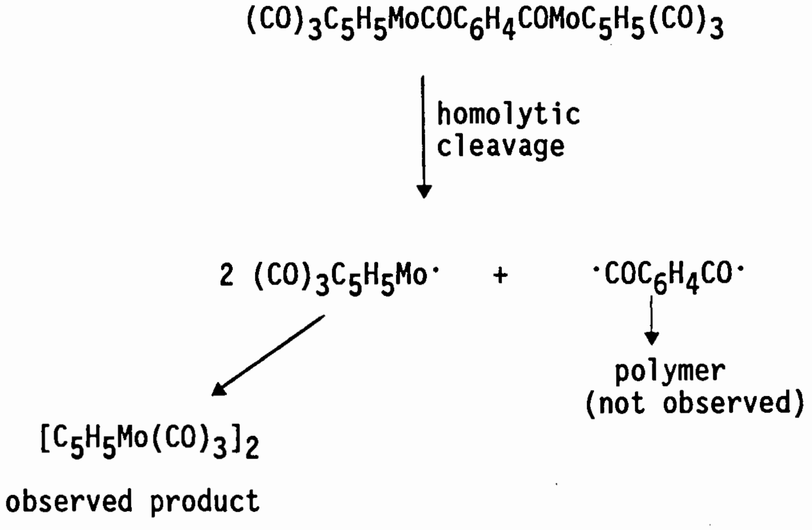


Figure 4.3: Decomposition of the *μ*-(*p*-phthaloyl) complex of molybdenum

The organic product is expected to be some sort of polymeric species formed from the diradical, $\cdot COC_6H_4CO\cdot$, however no such species was observed.

The *μ*-(*p*-phthaloyl) complex <u>54</u>, was isolated as a yellow-orange microcrystalline solid which has only limited stability in the solid state, while in solution, it decomposes rapidly. The infra-red spectrum (CH_2Cl_2 solution) of the compound shows three bands in the $\nu(CO)$ region. These are a medium band at 2024 cm^{-1} , a strong band at 1938 cm^{-1} and a weak broad band at 1607 cm^{-1}. The latter is due to the acyl groups of the bridging phthaloyl ligand. The spectrum closely resembles that of the benzoyl compound, $C_6H_5COMo(CO)_3C_5H_5$ [11].

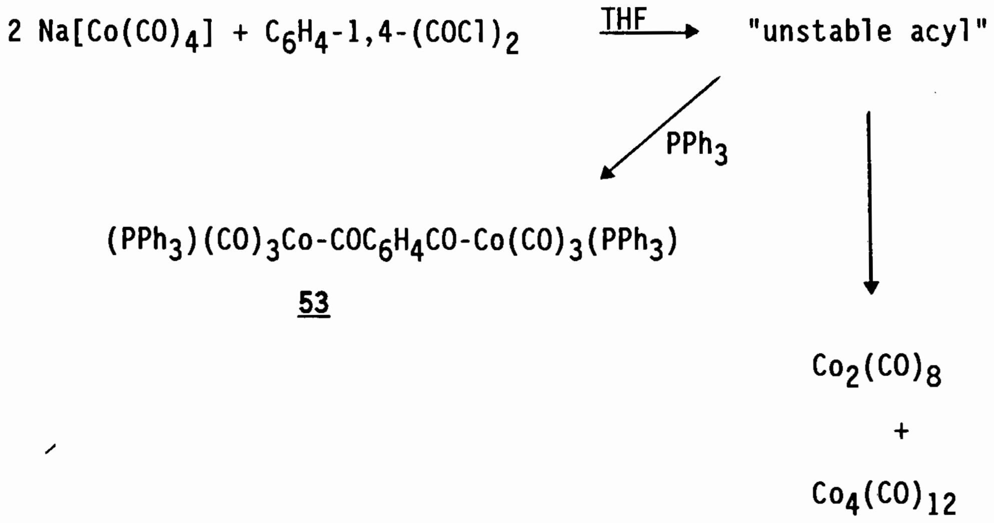
The proton nmr spectrum of the compound shows two signals, *viz* a singlet at δ7.44, integrating for four protons which can be assigned to the bridging phthaloyl group, while the singlet at δ5.54 is due to the ten protons of the two cyclopentadienyl groups. The fact that a singlet is observed for the four protons of the phthaloyl group is indicative of a symmetrical para substituted benzene ring.

4.2.3 ATTEMPTED PREPARATION OF $[Co(CO)_4]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$

$Na[Co(CO)_4]$ reacts with C_6H_4-1,4-$(COCl)_2$ to produce an extremely air-sensitive compound. All attempts to isolate the product were unsuccessful, resulting in rapid decomposition to $Co_2(CO)_8$ and $Co_4(CO)_{12}$. These decomposition products were identified by comparing the infra-red spectra of the compounds with those found in the literature [12]. An infra-red spectrum of the reaction mixture, shows bands at 2106s, 2048s, 2026s, 2004vs and 1695m cm^{-1} which are consistent with an acyltetracarbonylcobalt type species [13].

The instability of the product is not surprising, since mononuclear alkyl as well as aryl derivatives of the type $RCo(CO)_4$, are known to be extremely unstable and in fact very few mononuclear cobalt complexes of this type have been isolated. Those which have been isolated, often contain strong electronegative substituents on the alkyl chain. These electron withdrawing groups seem to stabilize the mononuclear alkyls and aryls [14].

Because of the inability to isolate a stable binuclear acyl, it was decided to add triphenylphosphine to the reaction mixture in a bid to stabilize the product. This strategy has been employed before in the case of unstable cobalt acyls [15]. Indeed the addition of the tertiary phosphine results in a relatively stable compound being isolated. this compound is in fact identical to compound <u>53</u>, which was discussed in section 4.2.1. Thus this is an indirect route to compound <u>53</u> (Equation 4.3).



(4.3)

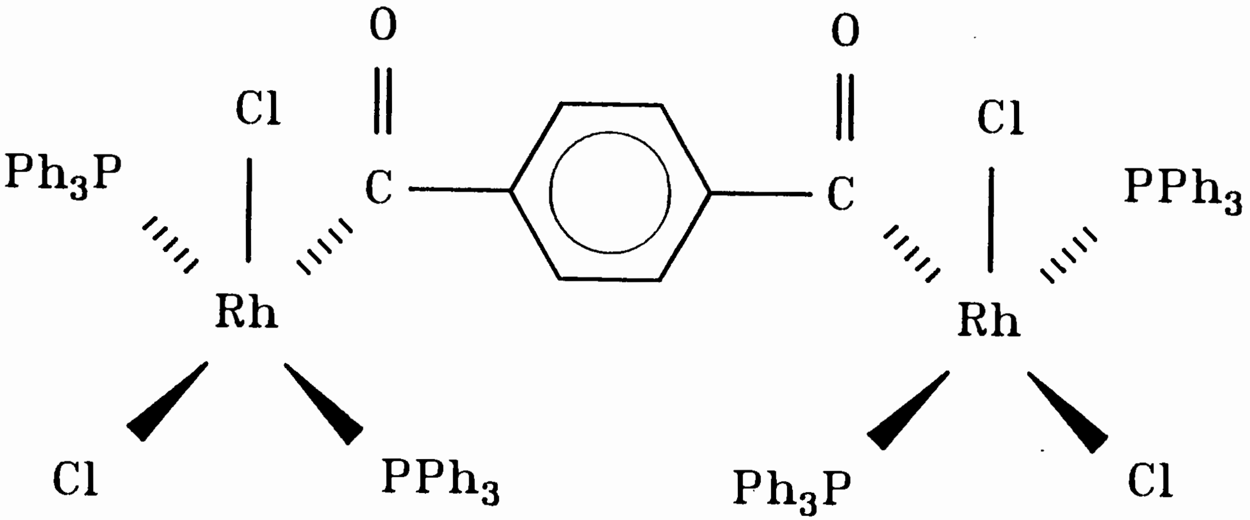
The yield of compound <u>53</u>, is however lower using this indirect route. Thus this synthetic pathway has no real advantage over that discussed in section 4.2.1. The fact that <u>53</u> is isolated, tends to suggest that the "unstable acyl" is probably $[Co(CO)_4]_2\{\mu\text{-}(COC_6H_4CO)\}$.

4.2.4 SYNTHESIS OF $[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(COC_6H_4CO)\}$

It has been found that the reactions of acyl or aroyl chlorides, RCOCl, with $Rh(PPh_3)_3Cl$ yield compounds of the type $RCORh(PPh_3)_2Cl_2$ and in most cases ,the isomer that is formed initially, contains *cis*-triphenylphosphine and *cis*-chlorine ligands [16]. This then isomerizes to a species in which the triphenylphosphine ligands are mutually trans. In some instances, this latter five-coordinate acyl species rearranges to form a six-coordinate alkyl compound of the type $RRh(PPh_3)_2(CO)Cl_2$ [16].

The μ-(*p*-phthaloyl) complex <u>55</u>, was prepared in a an analogous way by the reaction of $Rh(PPh_3)_3Cl$ with terephthaloyl dichloride (Equation 4.4)

$$2Rh(PPh_3)_3Cl + C_6H_4\text{-}1,4\text{-}(COCl)_2 \xrightarrow{CH_2Cl_2\ (r\ t)} \underset{\underline{55}}{[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(COC_6H_4CO)\}} + 2PPh_3 \qquad (4.4)$$



55

Figure 4.4: The μ-phthaloyl complex, $[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$

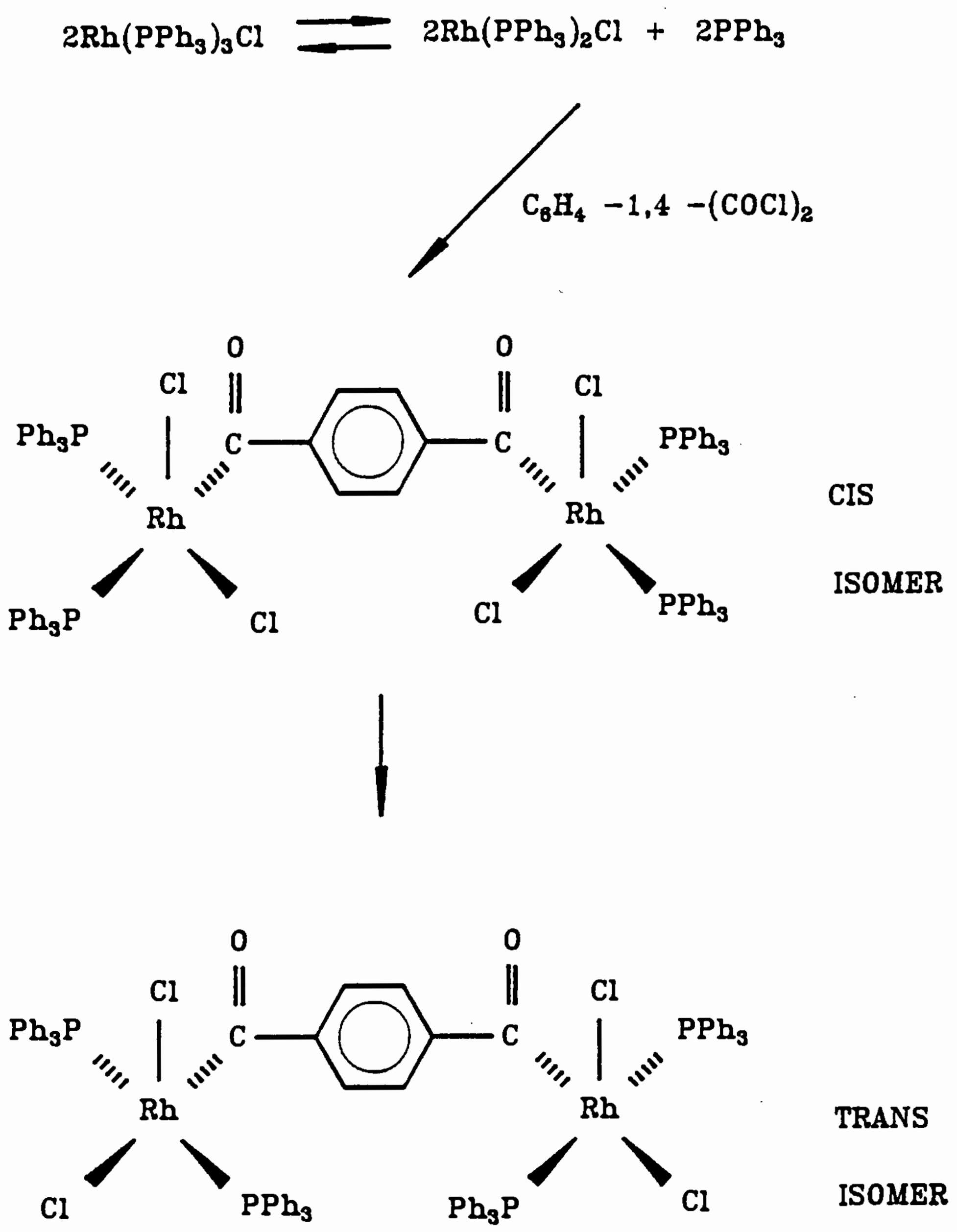


Figure 4.5: A possible mechanism for the formation of *trans* - $[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$.

Compound 55 was isolated as a yellow solid which is extremely air stable almost indefinitely. It also shows remarkable thermal stability, only decomposing at a temperature above 200°C. The compound is totally insoluble in all the common organic solvents and this therefore precludes nmr studies on it. It was thus only partially characterized by infra-red spectroscopy (solid state) and micro-analysis (see Table 4.1). The infra-red spectrum in the carbonyl region shows a fairly strong band at 1701 cm^{-1} which is due to the acyl carbonyl group.

The far infra-red spectrum of the compound shows two bands at 356 and 324 cm^{-1} respectively and can be assigned to the ν(Rh-Cl) frequencies. The positions of these bands are typical for Rh-acyl complexes of the type $RCORh(PPh_3)_2Cl_2$, where the two triphenylphosphine groups are *trans* to each other [17].

The reaction of terephthaloyl dichloride with chlorotris-(triphenylphosphine)rhodium (I), involves a double oxidative addition of the bifunctional acid chloride to two molecules of the low valent rhodium (I) complex. A possible mechanism for the reaction is outlined in Figure 4.5.

4.3 μ-(p-PHENYLENE) COMPLEXES:

4.3.1 SYNTHESIS AND CHARACTERIZATION OF μ-(*p*-PHENYLENE) COMPLEXES OF MANGANESE AND RHENIUM:

The μ-(*p*-phthaloyl) complexes of manganese and rhenium, compounds **50** and **51** respectively, can be converted to the corresponding μ-(*p*-phenylene) complexes by decarbonylation. In both cases, decarbonylation can be effected thermally. Thus for example complex **50** can be converted to the corresponding μ-(*p*-phenylene) complex **56** by refluxing the aroyl compound in toluene for 1 hour (Equation 4.5).

$$\underset{\mathbf{50}}{[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}} \xrightarrow[\text{toluene}]{\text{reflux}} \underset{\mathbf{56}}{C_6H_4\text{-}1,4\text{-}[Mn(CO)_5]_2} + 2CO \qquad (4.5)$$

Decarbonylation can also be brought about by heating the aroyl complex in the solid state, however the yield of the μ-(*p*-phenylene) compound in this case, is much lower due to extensive decomposition occurring.

The analogous rhenium μ-(*p*-phenylene) complex, **57**, can be prepared by refluxing the μ-(*p*-phthaloyl) analogue in methyl isobutyl ketone (Equation 4.6) but the yield of 56% is lower than that of the manganese complex.

$$[Re(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\} \xrightarrow[\text{MIBK}]{\text{reflux}}$$

<u>51</u>

$$C_6H_4\text{-}1,4\text{-}[Re(CO)_5]_2 + 2CO$$

<u>57</u>

(4.6)

The μ-(*p*-phenylene) complexes of manganese and rhenium were isolated as white microcrystalline solids. The compounds are stable in the solid state for prolonged periods, decomposing only at relatively high temperatures (> 150°). Both compounds <u>56</u> and <u>57</u> were fully characterized by infra-red, ^1H and ^{13}C nmr and mass spectroscopy. Satisfactory micro-analyses were also obtained for both compounds. The spectral data are listed in Tables 4.4 - 4.6.

The infra-red spectrum of the manganese compound <u>56</u>, shows three bands in the ν(CO) region and resembles that of the analogous phenyl complex [9]. The spectrum of the rhenium compound <u>57</u>, also shows three bands in the ν(CO) region (see Table 4.5). Again the spectrum is very similar to that of the corresponding mononuclear phenyl complex [18]. The ^1H nmr spectra of both complexes <u>56</u> and <u>57</u> show, a broad singlet at about δ7.30 due to the four phenyl protons as is expected for a benzene ring that is symmetrically substituted in the *para* position.

Table 4.4: M.p.s., yields and analytical data for μ-(p-phenylene) complexes of the type C_6H_4-1,4-$(M)_2$, M = $Mn(CO)_5$, $Re(CO)_5$ and $CpFe(CO)_2$.

COMPOUND		M.P./°C	YIELD/	ANALYSIS+			
M	No		%	C	H	(C)	(H)
$Mn(CO)_5$	**56**	178-185 (dec)	74	41.15	0.95	(41.23)	(0.87)
$Re(CO)_5$	**57**	210-215 (dec)	56	26.50	0.70	(26.38)	(0.55)
$CpFe(CO)_2$	**58**	156-163 (dec)	26	56.15	3.05	(55.86)	(3.28)

\+ Calculated values in brackets.

Table 4.5: IR data for the compounds of the type C_6H_4-1,4-$(M)_2$, where M = $Mn(CO)_5$, $Re(CO)_5$ and $CpFe(CO)_2$

COMPOUND				
M	No	νCO / cm^{-1} [a]		
$Mn(CO)_5$	56	2110w-m	2019vs	1994m-sh
$Re(CO)_5$	57	2128w	2020s	1986w-sh
$CpFe(CO)_2$	58	2015s		1959vs

a CH_2Cl_2 as solvent.

w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

Table 4.6 ^{1}H and ^{13}C nmr data for the compounds of the type C_6H_4-1,4-$(M)_2$ where

M = $Mn(CO)_5$, $Re(CO)_5$ and $CpFe(CO)_2$.^{a}

COMPOUND		^{1}H nmr/δ ppm^{b}			^{13}C nmr/ ppm^{c}		
M	No	C_6H_4^{d}	C_5H_5 ^{e}	CO	$C_{1+1'}$^{f}	$C_{2+2'}$^{f}	other (assignment)
$Mn(CO)_5$	**56**	7.21(4H)		210.8^{e}	138.1	145.1	
$Re(CO)_5$	**57**	7.26(4H)		183.4/181.5^{g}	134.3	146.1	
$CpFe(CO)_2$	**58**	7.01(4H)	4.80(10H)	216.5	133.9	145.3	85.7(C_5H_5)

a Chemical shifts in ppm relative to TMS;

b CD_2Cl_2 as solvent.

c $CDCl_3$ as solvent.

d Signal is a broad singlet.

e Singlet

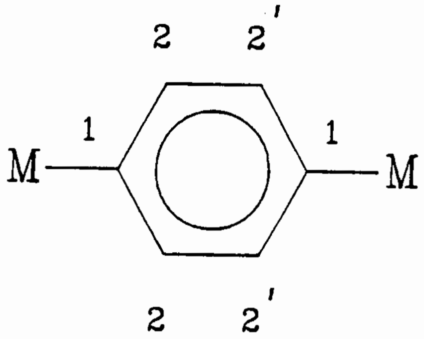
e Broad singlet

f See fig. 4.6 for assignment of phenyl carbons.

g Two signals observed for the carbonyls cis and trans to phenyl group.

The $^{13}C\{^1H\}$ nmr spectrum of C_6H_4-1,4-$[Mn(CO)_5]_2$, exhibits three peaks;. the carbons of the ten carbonyl groups resonate as a broad singlet at δ210.8 as a result of the quadrupole moment of ^{55}Mn (I = 5/2) [19]. The carbons of the bridging phenyl group give rise to only two signals which appear at δ145.1 and δ138.1 respectively. The signal at δ145.1 can be assigned to all carbon atoms which are *ortho* to the two metal centres (C_2 in Figure 4.6). The remaining signal at δ138.1 is due to the carbon atoms which are directly bonded to the manganese atoms. Assignments of the phenyl ring resonances were made on the basis of relative intensities and were confirmed using the attached proton test.

The $^{13}C\{^1H\}$ spectrum of the rhenium compound <u>57</u>, is similar to that of the manganese analogue, but two resonances are observed for cis and trans carbonyls. The assignments for compounds <u>56</u> and <u>57</u> are summarized in Table 4.6.



M = $Mn(CO)_5$, $Re(CO)_5$and $CpFe(CO)_2$

Figure 4.6 Assignments of the phenylene carbons.

4.3.2 ATTEMPTS TO PREPARE THE μ-(*p*-PHENYLENE) COMPLEX, C_6H_4-1,4-$[CpFe(CO)_2]_2$:

The μ-(*p*-phthaloyl) iron complex 52, is extremely resistant to decarbonylation. Several attempts were made to thermally decarbonylate the complex, both in solution and in the solid state. In all instances, extensive decomposition occurs without any of the μ-(*p*-phenylene) complex being observed. Since all attempts to thermally decarbonylate complex 52 failed, an attempt was made at photochemical decarbonylation. King and Bisnette reported the photochemical decarbonylation of the mononuclear benzoyl complex to yield the phenyl analogue [20]. In our case a toluene solution of the μ-(*p*-phthaloyl) complex 52, was subjected to broad band u.v. photolysis for 1 hour at room temperature. During this time extensive decomposition occurs with a dark brown solid precipitating out of solution. The photolytic reaction yields a small amount of a yellow solid, the infra-red spectrum of which shows two strong bands in the ν(CO) region at 2017 and 1959 cm^{-1}. No acyl band is observed in the spectrum of the compound. The ^1H nmr (CD_2Cl_2 solution) shows two singlets at δ7.01 and δ4.80. This differs from the starting material in that the two singlets occur at slightly higher chemical shifts. This is what one would expect if we convert an aroyl compound to an aryl compound. In this particular case, the phenyl protons of the μ-(*p*-phenylene) complex has been shifted up field by about 0.4 ppm (δ7.01 as against δ7.42 for the μ-(*p*-phthaloyl) complex). The yellow μ-(*p*-phenylene) complex 58, is a stable microcrystalline solid. Solutions of the compound decompose slowly over several hours, yielding a non carbonyl containing species which was not identified. In addition to being stable at room temperature, the compound is also relatively stable thermally, decomposing only at about 160°C. The other products isolated from the photolytic reaction are $[CpFe(CO)_2]_2$ and unreacted starting material (Equation 4.7).

$$\underset{\underline{52}}{[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}} \xrightarrow[\text{toluene}]{h\nu} \underset{\underline{58}}{C_6H_4\text{-}1,4\text{-}[CpFe(CO)_2]_2} + 2CO \qquad (4.7)$$

Although photolytic decarbonylation of the μ-(*p*-phthaloyl) iron complex leads to the required μ-(*p*-phenylene) complex **58**, the yield (12%), is low and an alternative route to the complex was sought.

Chemical decarbonylation of the μ-(*p*-phthaloyl) complex **52**, was investigated. There are many examples in the literature [21-22] where transition metal acyl complexes have been decarbonylated chemically. The most useful decarbonylating agent seems to be $Rh(PPh_3)_3Cl$, (Wilkinson's complex). Nesmeyanov for example reported the decarbonylation of $CpMo(CO)_2(PPh_3)COC_6H_4F$ using this reagent [24]. Wilkinson's complex and its bromo and iodo analogues have also been employed to abstract carbon monoxide from several transition metal carbonyl complexes of iron [21, 22, 25]. These rhodium complexes readily remove a carbon monoxide moiety from organic compounds [26] as well as from organometallic acyls. Other platinum group metal complexes have also been employed as decarbonylating agents. These include complexes such as $Ir(PPh_3)_3Cl$ and $Ru(PPh_3)_3Cl_2$ [27]. However these are not so successful as $Rh(PPh_3)_3X$ (X = Cl, Br).

Since chemical decarbonylation was possible for the benzoyl complex $Cp(CO)_2FeCOC_6H_5$, the reaction of the μ-(p-phthaloyl) iron complex with Wilkinson's complex as well as its bromo analogue was investigated. The μ-(p-phthaloyl) complex 52, was initially reacted with $Rh(PPh_3)_3Cl$ in a 1:2 mole ratio using methylene chloride as a solvent. A rapid reaction occurs at room temperature. The major product isolated from the reaction is the rhodium complex $Rh(CO)(PPh_3)_2Cl$ (71%). The compound was identified by its infra-red spectrum and melting point. The isolation of this compound clearly indicates that carbonyl abstraction had occurred. The other products of the reaction are the μ-(p-phenylene) iron complex 58 together with some phosphine substituted adduct. The μ-(p-phenylene) complex was isolated in 26% yield. The yield of the phosphine-adduct was small and this product was not fully characterized.

The reaction of compound 52 with $Rh(PPh_3)_3Br$ was also investigated. The reaction occurs readily at room temperature in both CH_2Cl_2 and benzene. The major product isolated in both reactions is the rhodium (I) complex $Rh(CO)(PPh_3)_2Br$. Again the isolation of this compound is an indication that carbonyl abstraction had taken place. When the reaction is carried out in methylene chloride, 26% of the μ-(p-phenylene) complex, C_6H_4-1,4-$[CpFe(CO)_2]_2$ is isolated. The reaction appears to be more complex in benzene. A third product besides C_6H_4-1,4-$[CpFe(CO)_2]_2$ and $Rh(CO)(PPh_3)_2Br$ is observed. This third component is isolated as a yellow-orange microcrystalline solid. The infra-red spectrum of this compound shows three bands in the $\nu(CO)$ region at 2107s, 1961s and 1916m-s cm^{-1}. There is also a weak and broad acyl band at 1558 cm^{-1}.

This product has been further characterized using ^1H nmr and microanalysis as the monosubstituted phosphine complex $Cp(CO)_2Fe\text{-}C_6H_4CO\text{-}Fe(PPh_3)(CO)Cp$ **59**. The ^1H nmr spectrum of the compound shows two signals for the cyclopentadienyl rings. The one, a singlet, occurs at $\delta 4.82$ while the other, a doublet, appears at $\delta 4.52$. The splitting of one of the cyclopentadienyl signals into a doublet, is a result of P-H coupling. This type of behaviour is also observed for mononuclear phosphine substituted benzoyl complex, $CpFe(PPh_3)(CO)C_6H_5$ [25].The appearance of two cyclopentadienyl signals is consistent with the two cyclopentadienyl rings being in different environments. The protons of the bridging phenyl ring are also no longer equivalent giving rise to two distinct signals which are complex multiplets. The one signal appears at $\delta 6.90$ - $\delta 6.80$ and is due to the two protons which are ortho to the iron atom which does not have a phosphine group attached to it. The second multiplet at $\delta 7.30$, is due to the two protons which are ortho to the acyl group. The signal for these latter protons appears downfield from that of the other two protons, because of the deshielding of the acyl group.

The isolation of a phosphine substituted acyl species is analogous to the reaction observed when the acyl species, $Cp(CO)_2FeC(O)CH_3$ was decarbonylated using $Rh(PPh_3)_3Cl$ [22]. Alexander and Wojcicki explained the formation of the phosphine substituted species $Cp(CO)(PPh_3)FeC(O)CH_3$ as follows:

Initally $Rh(PPh_3)_3Cl$ dissociates PPh_3 to give "$Rh(PPh_3)_2Cl$", which is thought to be the active decarbonylating agent. Evidence for this is the fact that CO abstraction is depressed by the addition of PPh_3 [27]. Once formed, "$Rh(PPh_3)_2Cl$" removes a terminal CO from the acyl species $Cp(CO)_2FeCOCH_3$ to form the coordinatively unsaturated intermediate $CpFe(CO)COCH_3$. The fact that the CO abstracted is a terminal carbonyl and not the acyl carbonyl, has been confirmed by ^{13}C labeling of the acyl group [25]. The coordinatively unsaturated intermediate is highly reactive and can undergo two possible reactions. The first reaction is the facile migration of the alkyl group from the acyl carbonyl to the metal centre resulting in the formation of an alkyl compound. The second possible reaction is attack of free PPh_3 (from $Rh(PPh_3)_3Cl$ dissociation) on the coordinatively unsaturated intermediate. This results in the formation of a phosphine substituted acetyl complex.

The reaction of the μ-(*p*-phthaloyl) complex, which is bifunctional, can be expected to be more complicated than that of any mononuclear acyl complex. Thus if the same steps as are to be applied to the binuclear μ-(*p*-phthaloyl) complex, we see that there are at least four possible products (see Figure 4.7). Product A (Figure 4.8) is formed when the intermediate (I) reacts with one mole of PPh_3 to form a monophosphine substituted diacyl compound. Formation of product B, involves an aryl migration at one metal centre to give a mono-acyl species. Product C is formed when the intermediate (II) undergoes an aryl migration, resulting in the μ-(*p*-phenylene) compound. Finally product D is a result of intermediate (II) reacting with free PPh_3 to form a monophosphine substituted mono-acyl compound.

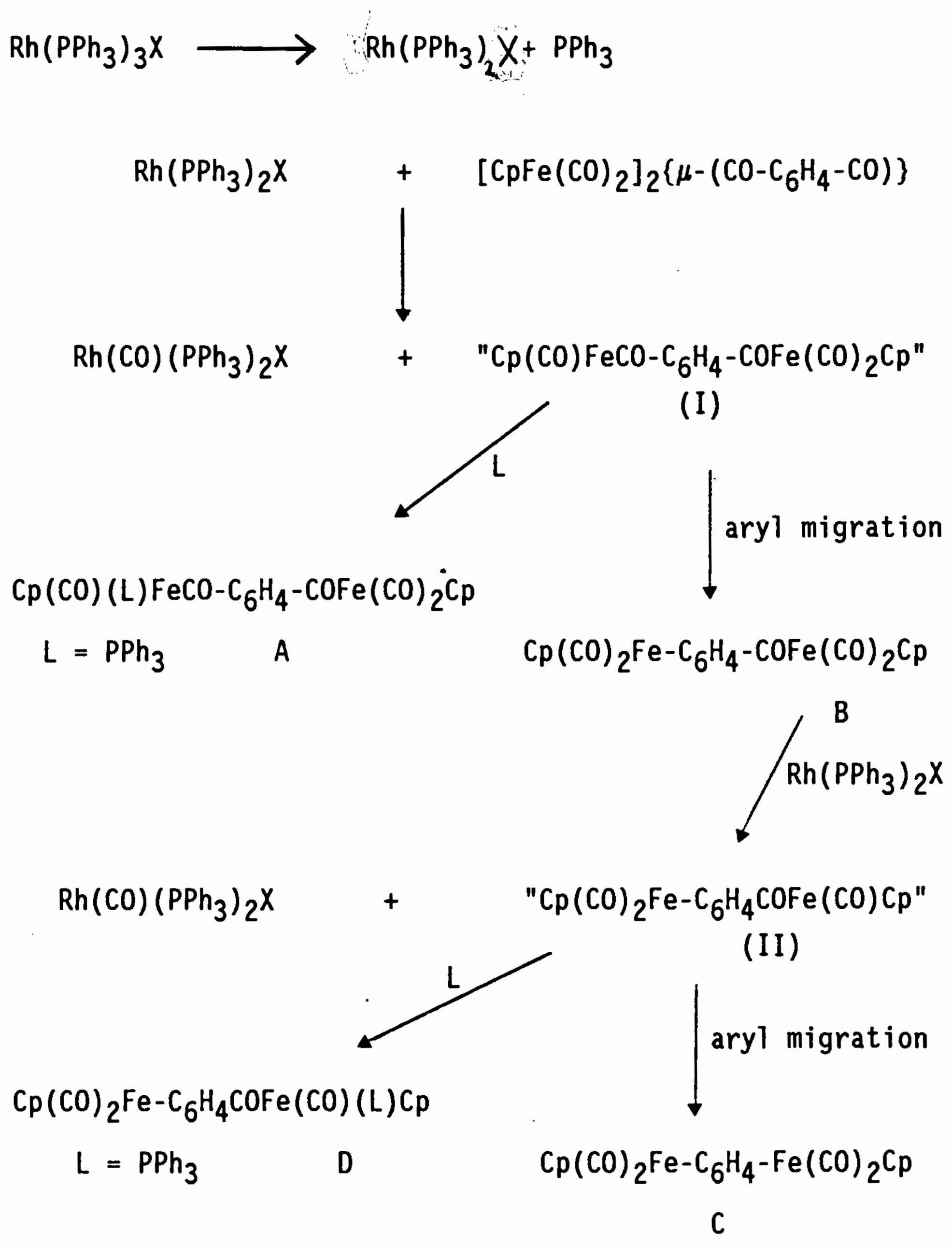


Figure 4.7 Possible products from the reaction of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ with $Rh(PPh_3)_3X$, (X = Cl,Br)

The only compounds isolated in this reaction were products C and D. No signs of the other two possible products were observed. An interesting observation is that a higher yield of the μ-p-phenylene complex is obtained when the reaction is carried out in methylene chloride as a solvent than when it is performed in benzene.

$[Rh(PPh_3)_2Cl]_2$ is known to be an effective decarbonylating agent, and in this case decarbonylation occurs without PPh_3 substitution [27]. This was confirmed by reacting the μ-(p-phthaloyl) complex with $[Rh(PPh_3)_2Cl]_2$ in a 1:1 mole ratio. The reaction does yield some of the μ-(p-phenylene) complex (Equation 4.8) but no phosphine substituted adduct is observed.

$$[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO\} + [Rh(PPh_3)_2Cl]_2 \xrightarrow{CH_3CN} \underset{\underline{58}}{C_6H_4\text{-}1,4\text{-}[CpFe(CO)_2]_2} + Rh(CO)(PPh_3)_2Cl \qquad (4.8)$$

Although the above reaction produces the μ-(p-phenylene) complex <u>58</u>, the yield is not better than that from the reaction of $Rh(PPh_3)_3Cl$ with the μ-(p-phthaloyl) complex.

An attempt was also made to synthesize the μ-(p-phenylene) iron complex <u>58</u>, directly by reaction of a 1,4-dihalobenzene. Thus, initially the reaction of $Na[CpFe(CO)_2]$ with 1,4-dibromobenzene (2:1 mole ratio) in refluxing THF was attempted. Very little reaction occurs even after 24 hours refluxing. The only products isolated from the reaction were $[CpFe(CO)_2]_2$ (80%) and $[CpFe(CO)_2(4\text{-}BrC_6H_4)]$ (1.6%) (Equation 4.9).

$$Na[CpFe(CO)_2] + 1,4\text{-}C_6H_4Br_2 \xrightarrow[THF]{reflux} \underset{\underline{60}}{[CpFe(CO)_2(4\text{-}BrC_6H_4)]} + NaBr \qquad (4.9)$$

The formation of the *μ*-(*p*-phenylene) complex <u>58</u>, was not observed in this reaction. The *p*-bromo-phenyl complex <u>60</u> was characterized by micro-analysis, IR and ^1H nmr spectroscopy (see experimental section). The failure to produce the *μ*-(*p*-phenylene) iron complex or even a reasonable yield of the *p*-bromo phenyl iron complex is probably due to the reluctance of the 1,4-dibromobenzene to undergo nucleophilic displacement reactions even with a fairly strong nucleophile such as $[CpFe(CO)_2]^-$.

Due to the inability of the 1,4-dibromobenzene to undergo nucleophilic displacement, the reaction of $Na[CpFe(CO)_2]$ with 1,4-diiodobenzene in a 2:1 mole ratio was attempted. This reaction in refluxing THF yields only the mononuclear compound, $[CpFe(CO)_2(4\text{-}IC_6H_4)]$ <u>61</u> (Equation 4.10).

$$\mathrm{Na[CpFe(CO)_2]} + \mathrm{1,4\text{-}C_6H_4I_2} \xrightarrow[\mathrm{THF}]{\mathrm{reflux}} \underset{\underline{\mathbf{61}}}{\mathrm{[CpFe(CO)_2(4\text{-}IC_6H_4)]}} + \mathrm{NaI} \qquad (4.10)$$

4.3.3 MASS SPECTROSCOPY OF μ- (p-PHENYLENE) COMPLEXES OF THE TYPE C_6H_4-1,4-$[M]_2$ WHERE M = $Mn(CO)_5$, $Re(CO)_5$ AND $CpFe(CO)_2$

The intensities and probable assignments of the high mass peaks in the mass spectra of compounds 56 - 58 are given in Tables 4.7 - 4.9. Fragmentation pathways for these compounds are shown in Figures 4.8 - 4.10. It should be noted that the assignments are only probable due to the fact that we recorded only low resolution spectra. The fragmentation pattern for each complex is discussed below.

4.3.3(a) MASS SPECTRUM OF C_6H_4-1,4-$[Mn(CO)_5]_2$ 56:

The mass spectrum of compound 56, exhibits a molecular ion, however it is of fairly low intensity. A prominent feature of the mass spectrum of compound 56, is the sequential loss of ten CO groups from the parent ion. This is in line with what has been found for many metal carbonyl compounds [28].

The sequential loss of CO appears to be the major fragmentation pathway which ultimately leads to the ion $[Mn_2(C_6H_4)]^+$ (m/e 186) i.e. an ion in which two "naked" manganese centres are bridged by a phenyl ring. The intensity of this ion is quite high. This ion then breaks down further by loss of a manganese atom followed by loss of the phenyl group to give $[Mn]^+$ (m/e 55) which is the base peak in the spectrum. An alternative but minor fragmentation pathway involves the complete loss of a $[Mn(CO)_5]$ fragment from the molecular ion to form $[Mn(CO)_5(C_6H_4)]^+$. This ion subsequently undergoes stepwise loss of CO to form $[Mn(C_6H_4)]^+$ (m/e 131).

Weak peaks in the spectrum at (m/e 56) and (m/e 84), can be attributed to the ions $[HMn]^+$ and $[HMn(CO)]^+$ respectively. These ions have previously been observed in the mass spectra of other manganese pentacarbonyl derivatives [28]. It is thought that these ions are formed by hydrogen transfer from the aryl ring to the metal centre and that the transfer initially involves an ion of the type $[C_6H_4Mn(CO)_n]^+$ $(1 < n < 5)$. The fragmentation scheme of compound 56 is outlined in Figure 4.8, while the actual mass spectrum appears in Figure 4.11.

4.3.3(b) MASS SPECTRUM OF C_6H_4-1,4-$[Re(CO)_5]_2$ 57:

A molecular ion peak at (m/e 728) is observed in the mass spectrum of compound 57 and is of moderate intensity. As is the case for the analogous manganese complex, the mass spectrum of C_6H_4-1,4-$[Re(CO)_5]_2$, shows sequential loss of carbon monoxide from the parent ion. However this is not the major fragmentation pathway. The major route by which the compound fragments, is one where a complete $Re(CO)_5$ unit is lost

Table 4.7: Peak intensities and assignments in the mass spectrum of C_6H_4-1,4-[Mn(CO)$_5$]$_2$

m/e	ION[a]	RElATIVE PEAK INTENSITY (%)[b]
466	M	15
438	M-CO	4
410	M-2CO	29
382	M-3CO	9
354	M-4CO	10
326	M-5CO	46
298	M-6CO	73
271	M-5CO-Mn	6
270	M-7CO	28
243	M-6CO-Mn	3
242	M-8CO	24
215	M-7CO-Mn	3
214	M-9CO	28
187	M-8CO-Mn	5
186	M-10CO	80
131	M-10CO-Mn	49
110	M-10CO-C_6H_4	17
93	M-10CO-Mn-C_3H_2	37
84	M-9CO-Mn-C_6H_3	22
56	M-10CO-Mn-C_6H_3	13
55	M-10CO-Mn-C_6H_4	100

a. M= C_6H_4-1,4-[Mn(CO)$_5$]$_2$; all ions have a single positive charge; ion refers to suggested assignments.

b. peak intensities relative to base peak at m/e 55.

Table 4.8 Peak intensities and assignments in the mass spectrum of C_6H_4-1,4-$[Re(CO)_5]_2$

m/e	ION[a]	Relative peak intensity (%)b
728	M	39
700	M-CO	6
672	M-2CO	12
652	M-C_6H_4	<0.2
644	M-3CO	14
624	M-C_6H_4-CO	<0.2
616	M-4CO	22
596	M-C_6H_4-2CO	<0.2
588	M-5CO	10
568	M-C_6H_4-3CO	12
560	M-6CO	8
540	M-C_6H_4-4CO	5
532	M-7CO	24
512	M-C_6H_4-5CO	3
504	M-8CO	23
434	M-C_6H_4-6CO	4
476	M-9CO	16
456	M-C_6H_4-7CO	3
448	M-10CO	30
428	M-C_6H_4-8CO	7

Table 4.8/continued...

Table 4.8/continued...

402	M-5CO-Re	50
400	M-C_6H_4-9CO	<0.2
374	M-6CO-Re	17
372	M-C_6H_4-10CO	6
346	M-7CO-Re	36
318	M-8CO-Re	60
290	M-9CO-Re	65
262	M-10CO-Re	81
186	M-10CO-C_6H_4-Re	18
76	M-10CO-2Re	38

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a. The m/e values are for ions containing 186^{Re}.

b. M = C_6H_4-1,4-$[Re(CO)_5]_2$, all ions have a single positive charge; ion refers to suggested assignments.

c. peak intensity relative to base peak at m/e 28.

Table 4.9 Peak intensities and assignments in the mass spectrum of C_6H_4-1,4-$[(C_5H_5)Fe(CO)_2]_2$

m/e	ION[a]	RELATIVE PEAK INTENSITY (%)[b]
430	M	28
402	M-CO	26
374	M-2CO	16
346	M-3CO	28
318	M-4CO	66
262	M-4CO-Fe	24
261	M-4CO-Fe-H	100
253	M-$(C_5H_5)Fe(CO)_2$	4
225	M-CO-$(C_5H_5)Fe(CO)_2$	47
197	M-2CO-$(C_5H_5)Fe(CO)_2$	21
141	M-4CO-2Fe-(C_5H_5)	22

a. M = C_6H_4-1,4-$[(C_5H_5)Fe(CO)_2]_2$; all ions have a single positive charge; ion refers to suggested assignments.

b. peak intensities relative to base peak at m/e 261.

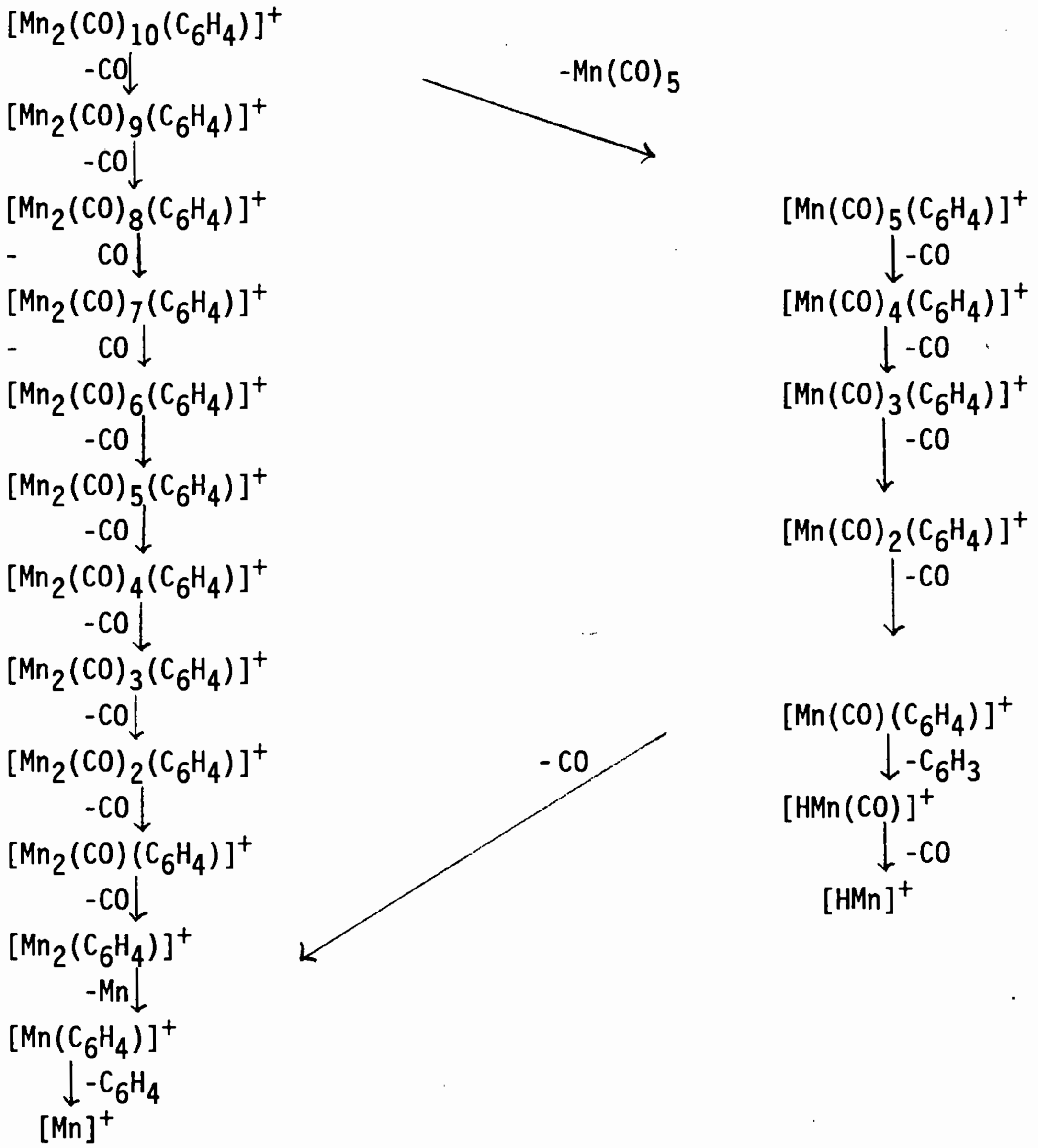


Figure 4.8: Fragmentation scheme of C_6H_4-1,4-$[Mn(CO)_5]_2$.

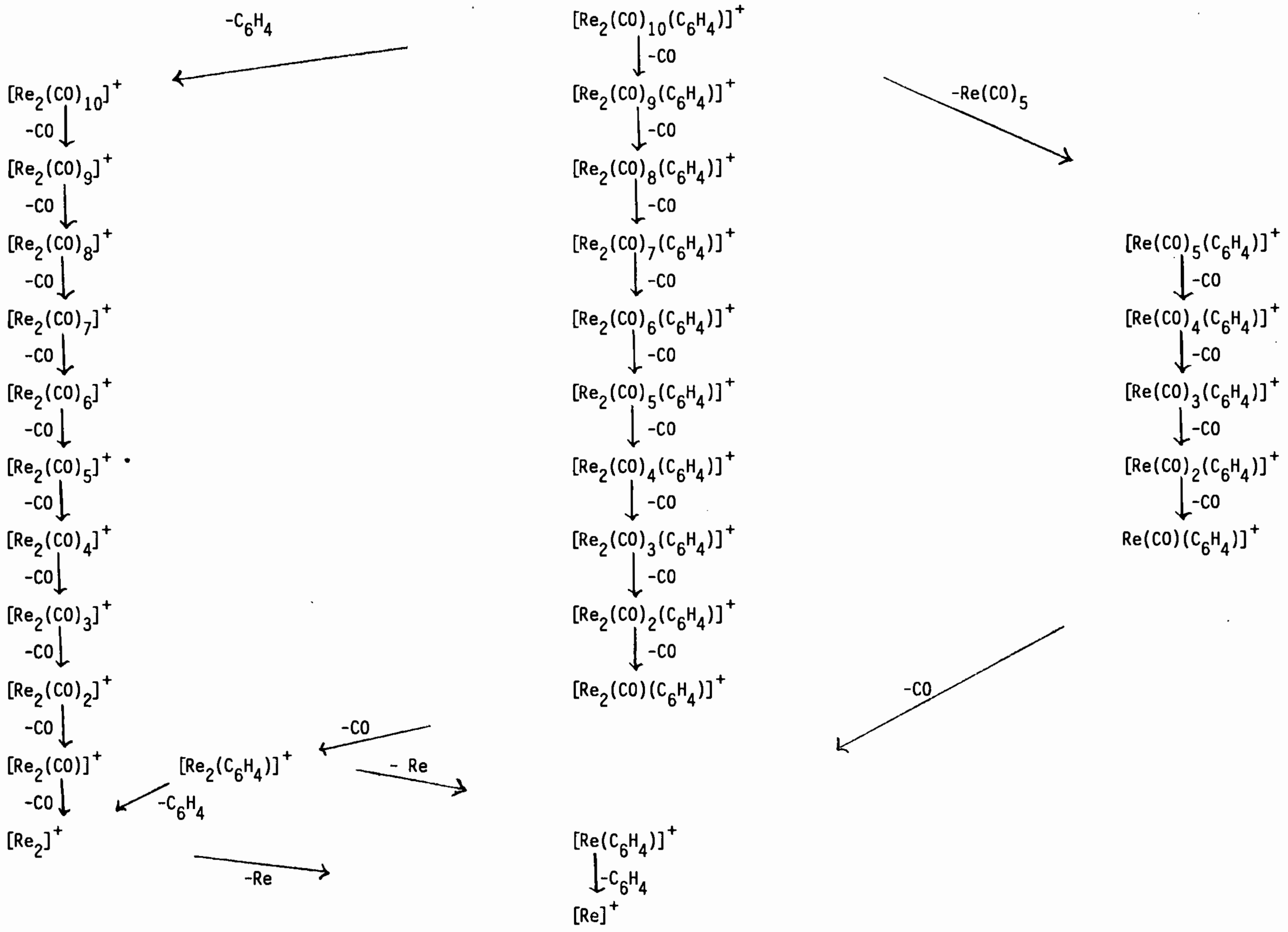


Figure 4.9: Fragmentation scheme of C_6H_4-1,4-$[Re(CO)_5]_2$.

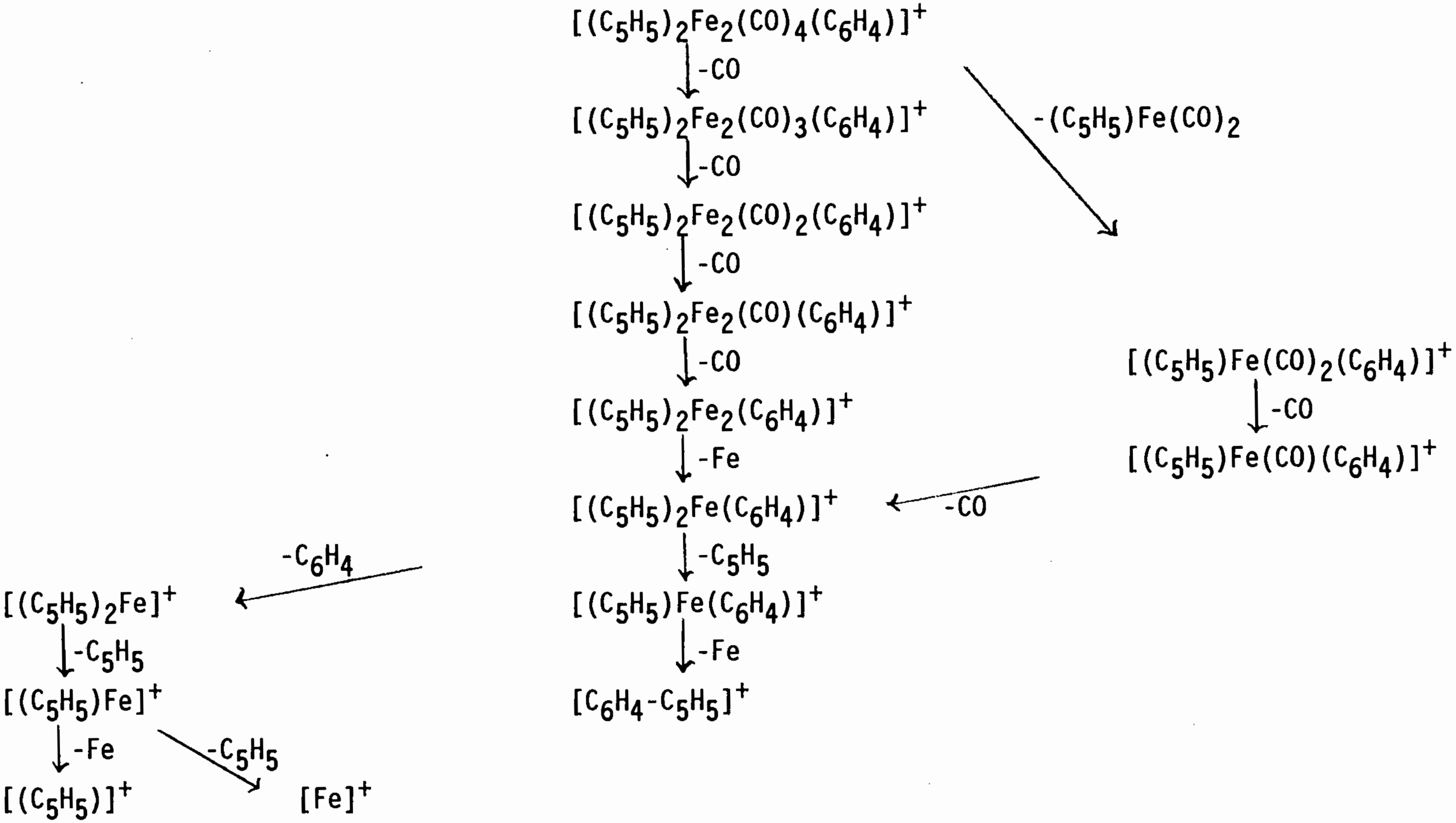


Figure 4.10 Fragmentation scheme of C_6H_4-1,4-$[CpFe(CO)_2]_2$.

from the molecular ion to form the ion, $[Re(CO)_5(C_6H_4)]^+$ (m/e 402). This then undergoes sequential loss of carbon monoxide to ultimately form $[Re(C_6H_4)]^+$(m/e 262). Unlike the analogous manganese complex, the rhenium complex, C_6H_4-1,4-$[Re(CO)_5]_2$, exhibits a third decomposition pathway. This involves the initial elimination of the bridging phenyl group from the molecular ion to yield, $[Re_2(CO)_{10}]^+$. The fragmentation of this ion resembles that of $Re_2(CO)_{10}$ and shows stepwise loss of 10 carbonyl groups to ultimately form $[Re_2]^+$. Of the three possible decomposition pathways, the latter route proves to be the minor (judging from the relative intensities). From the afore-going observations, it can be seen that the rhenium and manganese μ-(*p*-phenylene) complexes differ in their fragmentation pathways.

4.3.3 (c) MASS SPECTRUM OF C_6H_4-1,4-$[CpFe(CO)_2]_2$ 58:

The mass spectrum of compound 58, shows a fairly strong molecular ion peak at m/e 430. The spectrum (Figure 4.13) also exhibits a number of peaks which are characteristic of compounds that contain the $CpFe(CO)_2$ group [30,31,32]. These peaks can be assigned to the ions $[CpFe(CO)_2]^+$ (m/e 177), $[CpFe(CO)]^+$ (m/e 149), $[CpFe]^+$ (m/e 121), $[(C_5H_3)Fe]^+$ (m/e 95), $[Cp]^+$ (m/e 65) and $[Fe]^+$ (m/e 56). A strong peak is also observed at (m/e 186). This can be assigned to the ion $[Cp_2Fe]^+$ which has been found to be prominent in the mass spectra of many mononuclear cyclopentadienyl iron dicarbonyl compounds. It is thought to result from the ionization of ferrocene which is formed by fragmentation and rearrangement of the sample. In the case of some mononuclear cyclopentadienyl iron dicarbonyl compounds, the presence of a ferrocene ion in the spectrum is thought to be a result of thermal decomposition of the sample in the ion source [31]. In our case the ion source temperature (ca 110°C) was far below the decomposition point of the compound, with the result that ferrocene formation is unlikely to be due to thermal decomposition.

The intensities and likely assignments of the other peaks in the spectrum are given in Table 4.9. The fragmentation scheme for compound 58 is outlined in Figure 4.10. This shows that the compound fragments via two competitive routes. The first pathway, as is found for many metal carbonyl compounds, involves sequential loss of carbon monoxide from the parent ion. This process leads to the ion, $[Cp_2Fe_2(C_6H_4)]^+$ (m/e 318). The ion at m/e 318 then loses a Fe atom to form $[Cp_2Fe(C_6H_4)]^+$, m/e 262. This ion can then fragment further via two possible routes. The first route involves the loss of the phenyl group to form $[Cp_2Fe]^+$ which finally breaks down to $[Fe]^+$. The second route involves the loss of a cyclopentadienyl group to form $[CpFe(C_6H_4)]^+$ (m/e 197). The latter loses a Fe atom with a concomitant migration of the aryl group to the cyclopentadienyl ring.

There is an alternative pathway by which the parent ion, $[Cp_2Fe_2(CO)_4(C_6H_4)]^+$ can fragment. This involves the loss of a complete $CpFe(CO)_2$ unit to form $[CpFe(CO)_2(C_6H_4)]^+$ (m/e 253), which then undergoes subsequent loss of its two carbonyl groups in the normal stepwise fashion. The resulting ion $[CpFe(C_6H_4)]^+$, then decomposes as described earlier.

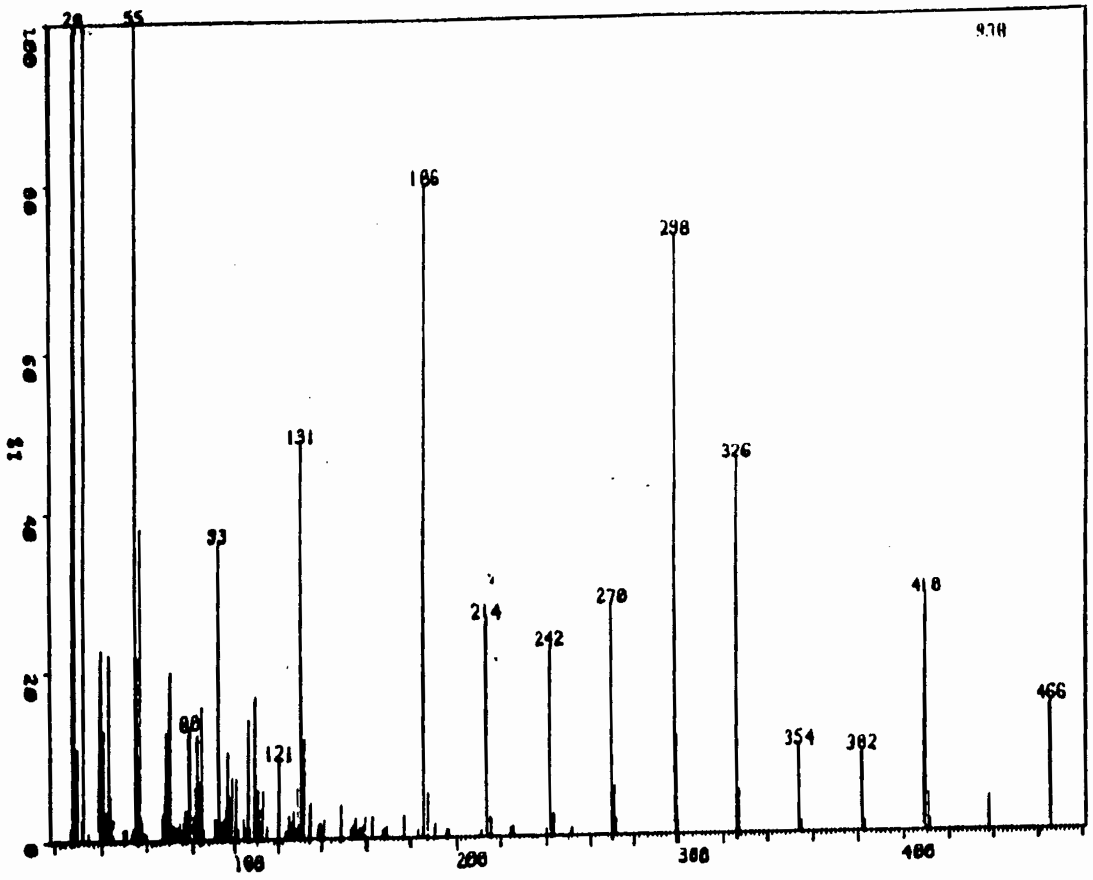


Figure 4.11: The low resolution mass spectrum of C_6H_4-1,4-$[Mn(CO)_5]_2$.

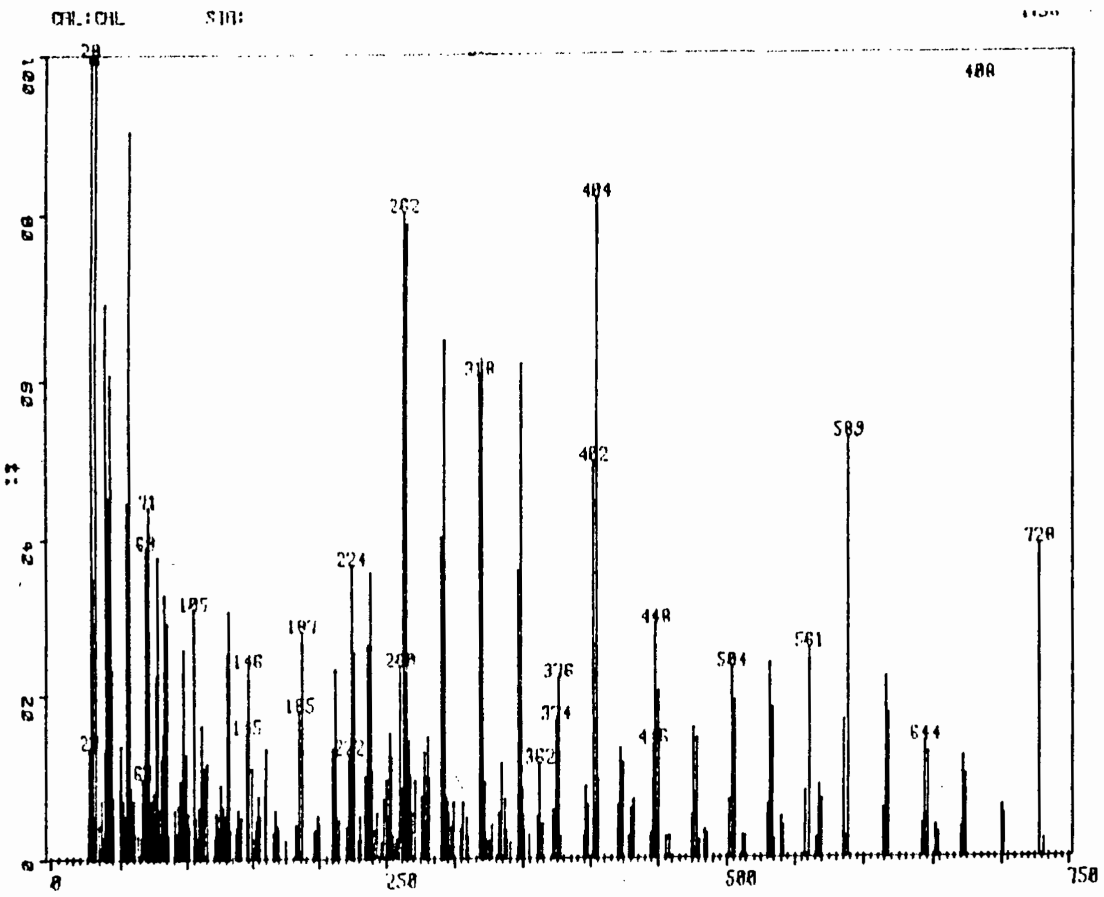


Figure 4.12: The low resolution mass spectrum of C_6H_4-1,4-$[Re(CO)_5]_2$.

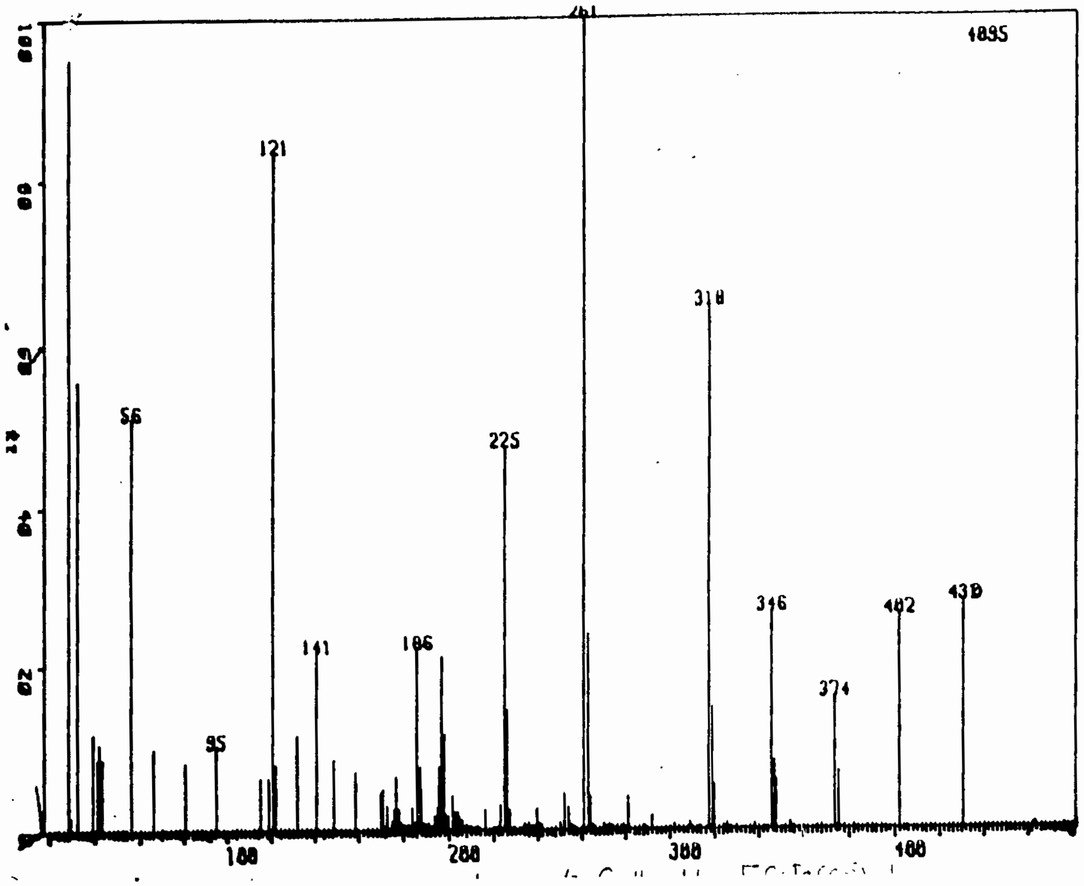
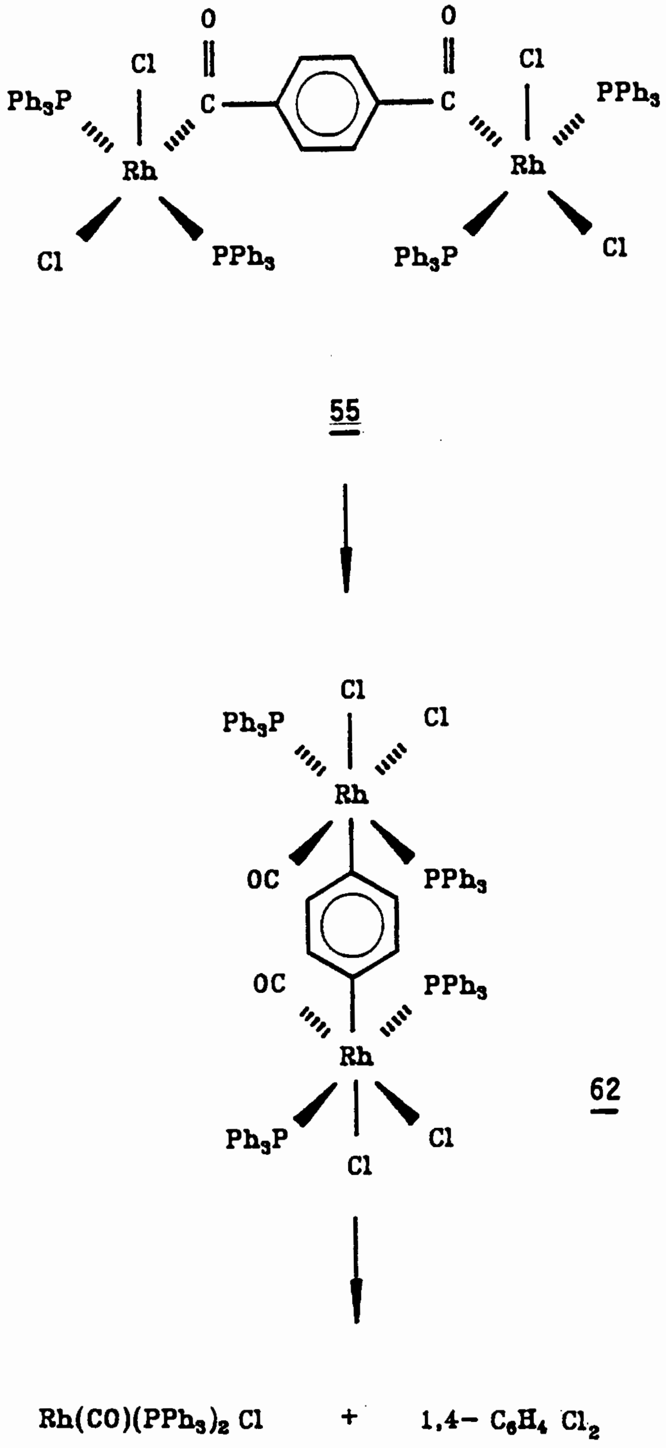


Figure 4.13: The low resolution mass spectrum of C_6H_4-1,4-$[CpFe(CO)_2]_2$.

As can be seen from the afore-going account, the *μ*-(*p*-phenylene) compound of iron shows a similar behaviour to that of the analogous manganese complex which also fragments via these two routes described above.

4.3.4 ATTEMPTS TO PREPARE THE *μ*-(*p*-PHENYLENE) COMPLEX C_6H_4-1,4-[Rh(PPh$_3$)$_2$(CO)Cl$_2$]$_2$.

The *μ*-(*p*-phthaloyl) complex, [Rh(PPh$_3$)$_2$Cl$_2$]$_2${*μ*-CO-C_6H_4-CO)} **55** was allowed to stir in chloroform for several days at room temperature. Infra-red spectra of aliquots of the reaction mixture were measured periodically to monitor the formation of any new species. After about 18 hours, the IR. spectrum of the reaction mixture shows the appearance of a second band at 2073 cm^{-1}, in addition to the original band at 1705 cm^{-1} which is due to the starting material. The new band is a result of the suspected formation of the *μ*-(*p*-phenylene) complex, C_6H_4-1,4-[Rh(PPh$_3$)$_2$(CO)Cl$_2$]$_2$ **62**. After about 30 hours stirring, a third band appears at 1969 cm^{-1}. This can be assigned to Rh(CO)(PPh$_3$)$_2$Cl. It would appear that the reaction mixture at this stage contains three species which are depicted in Figure 4.14.



$Rh(CO)(PPh_3)_2Cl$ + 1,4- $C_6H_4Cl_2$

Figure 4.14: Products of the reaction of $Rh(PPh_3)_3Cl$ and terephthaloyl chloride

The reaction mixture was heated to about 50°C, in an attempt to produce more of the μ-(p-phenylene) complex **62** and indeed a slight increase in the amount of **62**, is observed. However any further variations in the reaction temperature or reaction time had no real effect on the amount of the μ-(p-phenylene) complex **62** produced. Thus the reaction always yielded a mixture of **55**, **62**, and $Rh(CO)(PPh_3)_2Cl$. The mixture contains about 15% of **62**. It was not possible to separate the μ-(p-phenylene) complex from the μ-(p-phthaloyl) complex. This precluded the complete characterization of the μ-(p-phenylene) complex.

4.3.5 AN ATTEMPT TO PREPARE A μ-(PHENYLENE) COMPLEX OF MOLYBDENUM:

An attempt to prepare the μ-(p-phenylene) complex, C_6H_4-1,4-$[CpMo(CO)_3]_2$ by thermal decarbonylation of the μ-(p-phthaloyl) complex, $[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ **54** was not successful. Refluxing **54** in benzene for 30 minutes, results in the complete decomposition of the compound. No μ-(p-phenylene) species is isolated or even detected while monitoring the reaction by infra-red spectroscopy. The only product isolated from the reaction, was the molybdenum carbonyl dimer, $[CpMo(CO)_3]_2$ (Equation 4.11).

$$\underset{\mathbf{54}}{[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}} \xrightarrow[\text{benzene}]{\text{reflux}} [CpMo(CO)_3]_2 \qquad (4.11)$$

The isolation of $[CpMo(CO)_3]_2$, would seem to suggest that the μ-(p-phenylene) complex, if it exists, is not too stable. The results obtained here, are somewhat similar to those obtained for the mononuclear benzoyl complex, $Cp(CO)_3MoCO\text{-}C_6H_5$, which could not be transformed to the phenyl complex [11]. Nesmeyanov and co-workers found that refluxing $Cp(CO)_3MoCO\text{-}C_6H_5$, in benzene results in phenyl migration onto the cyclopentadienyl ring to form the compound, $[(C_6H_5C_5H_4Mo(CO)_3]_2$. From the results obtained for the work on mononuclear as well as binuclear systems, it would appear that the Mo-aryl (σ) bond is not too stable and the preparation of the molybdenum phenyl and phenylene complexes is not possible by this route.

4.4 CONCLUSIONS

The μ-(p-phthaloyl) and μ-(p-phenylene) complexes of a number of transition metal elements have been successfully prepared using different synthetic approaches. In general the μ-(p-phthaloyl) compounds can be synthesized by the following route:

$$2Na^+(ML_n)^- + C_6H_4\text{-}1,4\text{-}(COCl)_2 \longrightarrow C_6H_4\text{-}1,4\text{-}[CO(ML_n)]_2 + 2NaCl$$

These μ-(p-phthaloyl) complexes can be isolated in fairly high yields, the exceptions being the cobalt and molybdenum compounds. The low yields of the cobalt and molybdenum compounds are probably a result of the inherently high kinetic lability of these products towards decomposition. All the μ-(p-phthaloyl) compounds isolated, show high thermal stability.

The μ-(p-phenylene) compounds are difficult to make and were prepared in only moderate yields. The manganese and rhenium compounds can be produced by thermal decarbonylation of the corresponding *μ*-(*p*-phthaloyl) compounds. The iron *μ*-(*p*-phenylene) compound is not easily synthesized. A number of synthetic approaches were tried. These included, thermal, photolytic and chemical decarbonylation of the *μ*-(*p*-phthaloyl) compound. Of these methods, the chemical decarbonylation was the most successful. However the yield was still low, being around 26%. A disadvantage of this latter method, is the production of a phosphine substituted adduct, which has to be separated from the required product. Finally attempts to synthesize the iron *μ*-(*p*-phenylene) directly by the reaction of $Na[CpFe(CO)_2]$ with 1,4-dihalobenzenes were not successful, yielding only compounds of the type, $[Cp(CO)_2Fe(4\text{-}XC_6H_4)]$, where X = I or Br. This is probably due to the reluctance of halo-benzenes to undergo nucleophilic substitution reactions.

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CHAPTER FIVE.

5. REACTIVITY OF μ-PHTHALOYL AND μ-PHENYLENE COMPLEXES

5.1 REACTIVITY OF μ-PHTHALOYL COMPLEXES:

5.1.1 REACTIONS WITH HALOGENS

Electrophilic cleavage of transition metal-carbon σ bonds using a variety of reagents such as protic acids, halogens and mercury(II) halides has been widely studied for a number of different metal systems [1]. As stated in Chapter 2, these cleavage reactions can be synthetically useful [2].

As far as halogens are concerned, cleavage of the metal-carbon σ bond usually results in the formation of a transition metal halide complex and an alkyl halide or an acyl halide depending on whether the starting material is transition metal-alkyl or acyl complex (Equation 5.1)

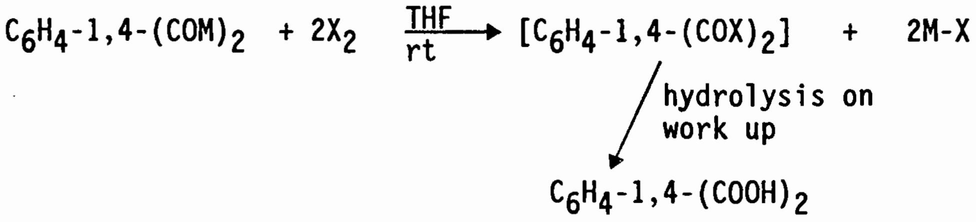
$$RML_n + X_2 \longrightarrow RX + XML_n$$

R = alkyl/aryl or acyl/aroyl

(5.1)

There are many examples of cleavage reactions in the literature, however most of these concern the cleavage of metal-alkyl bonds [3].

In this work, the reactions of binuclear μ-(p-phthaloyl) complexes with halogens X_2 (X = Br and I) have been carried out. The expected cleavage products are the metal carbonyl halide and terephthaloyl dichloride. The μ-(p-phthaloyl) complexes of manganese, rhenium and iron were all subjected to cleavage reactions by halogens. These reactions were carried out using a 2:1 mole ratio of halogen to substrate (Equation 5.2).



$$C_6H_4\text{-}1,4\text{-}(COM)_2 + 2X_2 \xrightarrow[rt]{THF} [C_6H_4\text{-}1,4\text{-}(COX)_2] + 2M\text{-}X$$
$$[C_6H_4\text{-}1,4\text{-}(COX)_2] \xrightarrow{\text{hydrolysis on work up}} C_6H_4\text{-}1,4\text{-}(COOH)_2$$

X = Br, I

M = $Mn(CO)_5$, $Re(CO)_5$ and $CpFe(CO)_2$

(5.2)

In the case of the manganese compound, it was found that the cleavage reactions proceed very slowly at room temperature and are only partially complete, even after prolonged reaction times. Thus, for example, when $[Mn(CO)_5]_2\{\mu\text{-}CO(C_6H_4)CO\}$ was reacted with a four fold excess of bromine for three days at room temperature, a 42% of the starting acyl complex was recovered. The products of the reaction are $Mn(CO)_5Br$ and terephthalic acid. Presumably the latter is derived from terephthaloyl dichloride which is hydrolyzed during the work up of the reaction. Similar results are obtained for the reactions of the μ-(p-phthaloyl) complexes of rhenium and iron, however these reactions are much more facile than that of the manganese compound. For example, the bromination of the μ-phthaloyl complex of iron is complete within 20 minutes at room temperature.

Table 5.1 Results of the halogen cleavage reactions of complexes of the type C_6H_4-1,4-$(COM)_2$ at room temperature.

Compound No	M	Electrophile[a] Conditions	% Yield[b] Metal Halide	% Yield Tere-phthalic Acid	% Recovery of Starting Material
<u>50</u>	$Mn(CO)_5$	Br_2(4) 70h	44	48	42
<u>50</u>	$Mn(CO)_5$	I_2(4) 57h	32	43	48
<u>51</u>	$Re(CO)_5$	Br_2(2) 2h	74	83	-
<u>51</u>	$Re(CO)_5$	I_2(2) 16h	69	87	12
<u>52</u>	$CpFe(CO)_2$	Br_2(2) 20min	85	92	-
<u>52</u>	$CpFe(CO)_2$	I_2(2) 3h	77	88	-

a. THF as solvent, metal acyl ca $2x10^{-2}M$, the molar ratio of the electrophile to metal-akyl is given in brackets..

b. based on the *μ*-(*p*-phthaloyl) complex.

The products $CpFe(CO)_2Br$ and C_6H_4-1,4-$(COOH)_2$ were isolated in high yields viz 85 and 92% respectively. The yields of the various products from the halogenation reactions are listed in Table 5.1. The metal carbonyl halides were identified using infra-red spectroscopy and comparing the spectra with those of authentic samples.

From Table 5.1, it can be seen that the order of reactivity of the μ-(*p*-phthaloyl) complexes of the type, C_6H_4-1,4-$(COM)_2$ with halogens is $CpFe(CO)_2$ > $Re(CO)_5$ > $Mn(CO)_5$. This order can be explained by the fact that the metal-carbon bond cleavage is an electrophilic process. The electron density on the metal is much greater in the case of the $CpFe(CO)_2$ compound than it is in the case of both $Re(CO)_5$ and $Mn(CO)_5$ compounds. Of the last two compounds, the rhenium compound has the higher electron density. The greater the electron density, the more facile electrophilic reactions tend to be. This is clearly borne out by the observed reactivity order. Further evidence for the electrophilic nature of the reaction can be seen by the fact that the reactions with iodine appear to be slower than those with bromine. Bromine being more electronegative than iodine, will participate more readily in electrophilic reactions.

5.1.2 REACTION OF $[CpFe(CO)_2]_2\{\mu\text{-}(COC_6H_4CO)\}$ 52 WITH PPh_3:

(a) *In refluxing xylene*

Compound 52 was reacted with PPh_3 in an attempt to effect CO substitution. However no reaction was observed even after prolonged (3 days) heating. Thus the only species isolated from the reaction mixture, was the starting material which was recovered in 78% yield. Although no reaction was observed, some decomposition was however evident to give a brown solid with no $\nu(CO)$ band in its IR spectrum.

(b) *In the presence of U.V. light.*

U.V. irradiation of compound 52 at room temperature in the presence of PPh_3, results in the reaction mixture showing extensive decomposition. However small amounts of the disubstituted triphenylphosphine μ-(*p*-phenylene) complex, $C_6H_4\text{-}1,4\text{-}[CpFe(CO)(PPh_3)]_2$, 63, (9%) together with $C_6H_4\text{-}1,4\text{-}[CpFe(CO)_2]_2$ (6%) were isolated (Equation 5.3). The starting material was also recovered in 53% yield.

$$2\ [CpFe(CO)_2]_2\{\mu\text{-}CO\text{-}(C_6H_4)\text{-}CO\} + 2\ PPh_3 \xrightarrow[\text{toluene}]{h\nu(4h)}$$

52

$$C_6H_4\text{-}1,4\text{-}[CpFe(CO)_2]_2$$

$$+$$

$$C_6H_4\text{-}1,4\text{-}[CpFe(CO)(PPh_3)]_2 \quad + \quad 6\ CO$$

63

(5.3)

Compound 63 was isolated as a microcrystalline orange solid which was characterized by micro-analysis, infra-red and ^1H nmr spectroscopy. The IR spectrum exhibits a single band in the ν(CO) region at 1913 cm^{-1} and is indicative of a phosphine substituted iron aryl species [4]. The ^1H nmr shows only three signals viz at δ7.34, δ6.54 and δ4.36. The signal at δ7.34, is a broad multiplet and can be assigned to the protons of the triphenylphosphine groups. The broad singlet at δ6.54 is due to the four protons of the bridging phenylene group. The signal at δ4.36 is split into two broad peaks and is due to the 10 protons of the cyclopentadienyl ligands. The observation of more than one signal for the protons of the cyclopentadienyl protons, is probably due to P-H coupling.

From the result obtained, it is clear that compound 52 is not too susceptible to CO substitution even under severe conditions. The fact that the disubstituted phosphine μ-(*p*-phenylene) and not the phosphine substituted μ-(*p*-phthaloyl) compound is isolated, would suggest that the photolysis initially leads to the decarbonylation of the starting aroyl compound to form the μ-phenylene compound, C_6H_4-1,4-[CpFe(CO)$_2$]$_2$. This then undergoes a substitution of CO by PPh_3 (Figure 5.1). The isolation of C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ from the photolysis reaction of [CpFe(CO)$_2$]$_2$\{μ-(CO-C_6H_4-CO)\} seems to substantiate this.

The photolytic reaction of the μ-(*p*-phthaloyl) complex of iron with triphenylphosphine differs slightly from that of the analogous mononuclear benzoyl complex, Cp(CO)$_2$FeCOC$_6$H$_5$. Nesmeyanov and co-workers [5], found that the U.V.irradiation of a mixture of the benzoyl complex

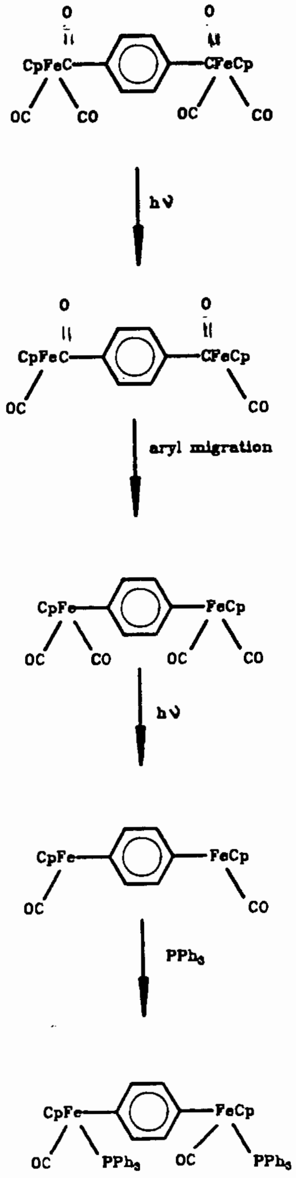


Figure 5.1: Possible reaction pathway for the photolytic reaction of [CpFe(CO)$_2${μ-(CO-C$_6$H$_4$-CO)} with PPh$_3$.

and triphenylphosphine results in the formation of both $Cp(CO)(PPh_3)Fe-C_6H_5$ and $Cp(CO)(PPh_3)FeCOC_6H_5$. In our case, we do not observe the formation of the phosphine substituted μ-(*p*-phthaloyl) species.

5.1.3 REACTIONS OF μ-PHTHALOYL COMPLEXES WITH REDUCING AGENTS:

INTRODUCTION:

The reduction of organic carbonyl compounds by group III hydrides and other related compounds is well known [6]. However until recently, the reduction of the carbonyl group (acyl or terminal) in organometallic compounds has not been widely studied. Masters and co-workers [7], reported the successful conversion of an acyl carbonyl to a methylene group using $BH_3.THF$ as a reducing agent. The systems they studied were the iron-acetyl complexes of the type $CpFe(CO)(L)COCH_3$ ($L = CO, PPh_3$). These authors found that there is a clean conversion to the ethyl complex $CpFe(CO)(L)CH_2CH_3$. The employment of reducing agents such as $NaBH_4$ and $LiAlH_4$ leads either to the recovery or decomposition of the acyl compound and no ethyl complex formation is observed. Davies [8] has reported a similar reduction of acyl complexes to alkyl complexes. In this case though $LiAlH_4$and $NaBH_4$ were used successfully as reducing agents.It should be noted though that the tertiary phosphine ligand in this case was PMe_3 and not PPh_3.

There have also been reports of the reduction of terminal carbonyl groups to yield either hydroxymethyl methyl or methyl complexes. Lapinte and Astruc for example have reported the reduction of the cationic complex $[C_5Me_5Fe(CO)_3]^+$ with $NaBH_4$ [9]. The reaction yields different products depending on reaction conditions. In CH_2Cl_2, there is a quantitative conversion of the cation to the hydroxymethyl complex $C_5Me_5Fe(CO)_2CH_2OH$. If on the other hand, the reaction is carried out in tetrahydrofuran, then the methyl complex $C_5Me_5Fe(CO)_2Me$ can be isolated in high yields. Finally when the reaction is performed in an aqueous medium, the hydrido complex $C_5Me_5Fe(CO)_2H$, is isolated as the major product.

In this work the attempted reactions of μ-(*p*-phthaloyl) complexes of manganese, rhenium and iron with a number of reducing agents are described.

(a) *Reactions of μ-(p-phthaloyl) complexes with K-Selectride:*

K-Selectride (potassium tri- sec-butylborohydride) has previously been used to selectively reduce organic carbonyls [10]. It is a fairly efficient reducing agent giving clean reactions.

A solution of $[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ in tetrahydrofuran was reacted with K-Selectride in a 1:2 mole ratio. Reaction occurs almost immediately at -78°C. An infra-red spectrum of the reaction mixture shows two strong bands at 1886 cm^{-1} and 1557 cm^{-1}. The former band can be assigned to the monoanion $[Mn(CO)_5]^-$, while the latter is thought to be due to an intermediate which could be a formyl species. The exact formulation of this species is not known, but it is speculated that it could possibly be a di-anion of the type, **64**, (see Figure 5.2). This species is extremely unstable and was not isolated, although the IR spectrum resembles that of known formyl complexes [11].

The above reaction shows similarities to that of benzoyl manganese pentacarbonyl with $Li(Et)_3BH$ which was investigated by Gladysz *et al* [11]. These authors found that the reaction leads to the formation of a kinetically unstable formyl complex. This formyl species then decomposes to $[Mn(CO)_5]^-$. It is thought that a similar reaction occurs for the binuclear μ-phthaloyl complex. A possible pathway for this reaction is outlined in Figure. 5.2 and it is suggested, that the initial reaction is the attack of H^- on the terminal carbonyl groups. This leads to the formation of a doubly charged anionic formyl species **64**. The anionic formyl could then be transformed to di-anion **65** which could rapidly decompose to $K[Mn(CO)_5]$ and terephthalaldehyde. The former is an observed product of the reaction. The bifunctional aldehyde was however not detected or isolated. Work up of the reaction mixture yields $Mn_2(CO)_{10}$ as the only observed product which comes from the oxidation of $[Mn(CO)_5]^-$.

The iron μ-phthaloyl complex also reacts rapidly with K-Selectride. Monitoring the reaction by infra-red spectroscopy shows three strong peaks at 1880, 1862 and 1587 cm^{-1}. The lower frequency band may be due to some sort of anionic formyl species.As was suggested for the manganese reaction, the anionic formyl could be formed by attack of H^- on a terminal carbonyl. Work-up of the reaction mixture, leads to the isolation of the metal carbonyl dimer $[CpFe(CO)_2]_2$ (65%). The reaction of the μ-(*p*-phthaloyl) complex of iron with K-Selectride is much slower than that of the manganese μ-(p-phthaloyl) complex. The latter reacts almost immediately with K-Selectride. In the case of the iron compound, the reaction mixture still shows a significant amount of the starting material after 2h stirring at room temperature.

(b) *Reaction of* $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ *with* $LiAlH_4$:

Lithium aluminium hydride is extensively used in organic chemistry to reduce ketonic and aldehydic functionalities to alcohols. It was stated earlier that $LiAlH_4$ has been employed to reduce carbonyl groups to alkyl ligands [8]. This conversion was found to occur under fairly mild conditions. With this in mind, the reaction of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ with $LiAlH_4$ was attempted. The aim was to try and reduce the acyl groups to methylene groups to form the μ-*p*-xylene-α,α'-diyl iron complex, $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2C_6H_4CH_2)\text{-}p\}$. The μ-(*p*-phthaloyl) compound <u>52</u>, was reacted with $LiAlH_4$ in a 1:2 mole ratio. The reaction appears to be fairly slow since after 20h stirring at room temperature, there is still unreacted starting material present in the reaction mixture. The major product isolated from the reaction is $[CpFe(CO)_2]_2$ (67%). No organic product was isolated or even observed. Monitoring the reaction mixture by infra-red spectroscopy, shows no sign of acyl carbonyl reduction. The only species detected during the reaction is $[CpFe(CO)_2]^-$. This anion is oxidized to the dimer $[CpFe(CO)_2]_2$, which is the only isolable decomposition product of the reaction.

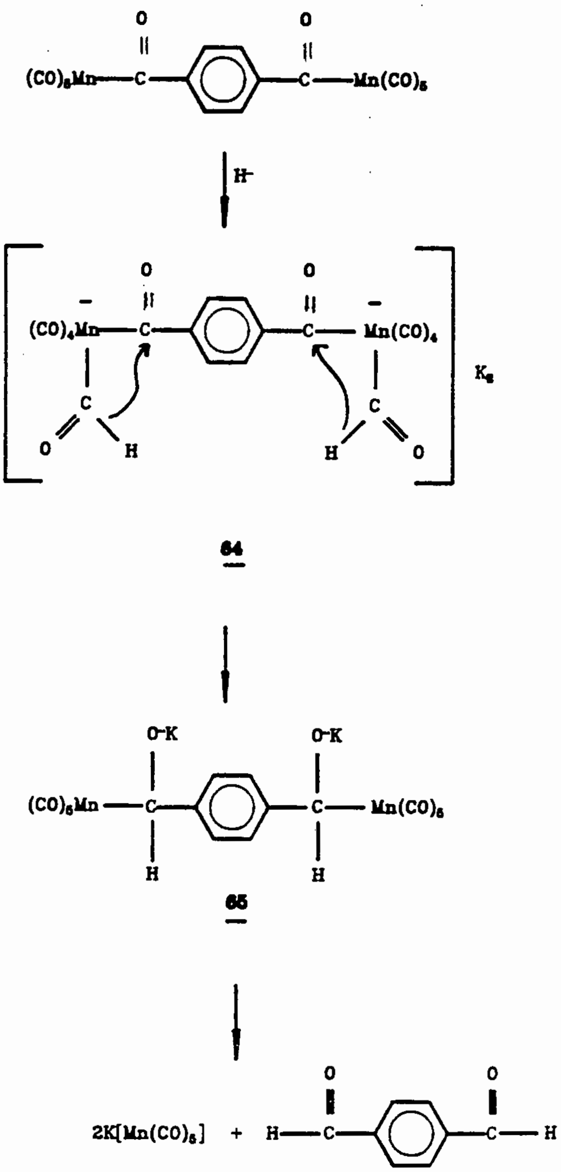


Figure 5.2: Proposed reaction pathway for the reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ with K-Selectride.

(c) *Reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ with $LiBEt_3H$:*

Lithium triethylborohydride, also known as "superhydride", is an exceptionally powerful reducing agent. It has previously been used to convert terminal carbonyls into formyl groups [11]. Because of this, it was thought that this reagent might readily reduce an acyl carbonyl to initially a hydroxymethyl group and then subsequently to a methylene group. The μ-(*p*-phthaloyl) compound $[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ was thus reacted with "superhydride" using a 1:2 mole ratio at room temperature. Extensive decomposition of the starting material was observed during the reaction. Monitoring the reaction by infra-red spectroscopy shows the presence of $[Mn(CO)_5]^-$ and a species which may be an anionic formyl species. Again $Mn_2(CO)_{10}$ is the only isolable inorganic product.

(d) *Reactions of μ-(p-phthaloyl) complexes with BH_3*

The addition of a solution of BH_3 in tetrahydrofuran to a suspension of the μ-(*p*-phthaloyl) complex $[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$,shows no observable reaction even when stirring at room temperature for 21 hours and using a four-fold excess of the reducing agent. Attempts to induce a reaction by refluxing the reaction mixture leads only to the decarbonylation of the starting material to yield the μ-(*p*-phenylene) complex $C_6H_4\text{-}1,4\text{-}[Mn(CO)_5]_2$. This latter compound is also obtained when the reaction is repeated in the absence of BH_3. In a similar way, the μ-(*p*-phthaloyl) complexes of both rhenium and iron, remain unaffected by excess BH_3. The expected products for these BH_3 reactions are the μ-*p*-xylene-α,α'-diyl complexes of the type $M\text{-}CH_2C_6H_4CH_2\text{-}M$. This type of product could be obtained, if the acyl carbonyls were reduced to -CH_2- moieties. It is not too surprising that these attempted reductions failed since Van Doorn and Masters [7], have shown that BH_3 reductions, unlike those of other reducing agents are electrophilic in nature. Attack of the BH_3 will therefore tend to occur at the site of highest electron density. In the acyl compounds, this is the oxygen atom of the acyl carbonyl group. In the case of the μ-(*p*-phthaloyl) complexes, the electron density on the acyl oxygen is reduced by the electron withdrawing action of the bridging aryl ring. Thus the reduction does not take place. At elevated temperatures, the only reaction observed, is the decarbonylation of the compounds to form the corresponding μ-(*p*-phenylene) compounds. In all of the reactions, there is no evidence of BH_3 attack at the terminal carbonyl groups, neither is there any sign of the production of the metal carbonyl hydrides, $Mn(CO)_5H$, $Re(CO)_5H$ and $CpFe(CO)_2H$. The complete reluctance of the μ-(*p*-phthaloyl) compound of iron to undergo any reduction is a bit surprising, since it contains the fairly electron rich C_5H_5Fe group. This compound shows no reaction even when using a five-fold excess of BH_3 in refluxing tetrahydrofuran.

5.2 REACTIVITY OF μ-(p-PHENYLENE) COMPLEXES:

5.2.1 REACTIONS WITH CARBON MONOXIDE:

INTRODUCTION

The reaction of organometallic complexes with carbon monoxide is one of the fundamental reactions in many catalytic processes. Examples of this are the Fischer-Tropsch process [12], the hydroformylation process [13] and the Monsanto acetic acid process [14]. It is well known that transition metal alkyl and aryl complexes react with carbon monoxide to undergo a so called "carbonyl insertion" reaction. Mechanistic studies have shown that the reaction is in fact an alkyl or aryl migration [15]. In Chapter 3, we have seen that the carbonyl insertion reaction, occurs fairly readily for binuclear polymethylene complexes, the products being the analogous diacyl compounds. It was also seen that this CO insertion reaction is most facile for the manganese system, with the reaction being quantitative at room temperature and atmospheric pressure.

The reaction of carbon monoxide with mononuclear phenyl complexes, L_nM-Ph (L_nM is a transition metal and its associated ligands) has not been so widely studied as the corresponding alkyl compounds. Calderazzo [16] however has reported the reaction of $PhMn(CO)_5$ with CO. This author found that the rate of insertion into the Mn-Ph bond was slightly faster than the rate of insertion into the Mn-Me bond. Thus, it may be expected that the binuclear μ-phenylene complexes would undergo carbonyl insertion reaction.

Reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ with CO:

Initially the above reaction was attempted using a CO pressure of 1 atm at room temperature. No reaction was observed using these condition, even after stirring for 48h. The reaction was repeated under CO pressure (30atm). Monitoring the reaction by infra-red spectroscopy, shows that about 30% conversion of the μ-phenylene complex to the μ-phthaloyl complex had taken place. The reaction is almost complete (85% conversion) after stirring for 22h under these conditions (see Equation 5.4).

$$C_6H_4\text{-1,4-}[Mn(CO)_5]_2 \xrightarrow[THF]{CO(30atm)} (CO)_5\,MnCO\text{-}C_6H_4\text{-}CO\text{-}Mn(CO)_5 \qquad (5.4)$$

It is clear from these results that the μ-(*p*-phenylene) complex of manganese is extremely reluctant to undergo carbonyl insertion. This behaviour is in contrast to the μ(1,n)-alkanediyl complexes of manganese which undergoes carbonyl insertion within 10 minutes at atmospheric pressure (see Chapter 3).

Reactions of other μ-(p-phenylene) complexes with carbon monoxide:

Carbonyl insertion reactions were also attempted with the μ-(*p*-phenylene) complexes of rhenium and iron. In these cases the reaction is even slower than that of the manganese analogue. The rates of CO insertion for the μ-(*p*-phenylene) complexes of the type C_6H_4-1,4-$(M)_2$, shows the following order:

$$M = Mn(CO)_5 > M = Re(CO)_5 >> M = CpFe(CO)_2$$

It should in fact be noted that no CO insertion was observed for the iron complex, while in the case of the rhenium compound only about 20% of the μ-(p-phthaloyl) complex was isolated after 48h reaction (30atm at room temperature). From the above results, it would appear that the rate of carbonyl insertion into the metal-aryl bond is inversely proportional to the strength of this bond. This trend was also found for other systems such as mononuclear alkyls [17] and also the binuclear μ-alkanediyl complexes (see Chapters 2 and 3).

5.2.2 REACTIONS WITH SYNTHESIS GAS

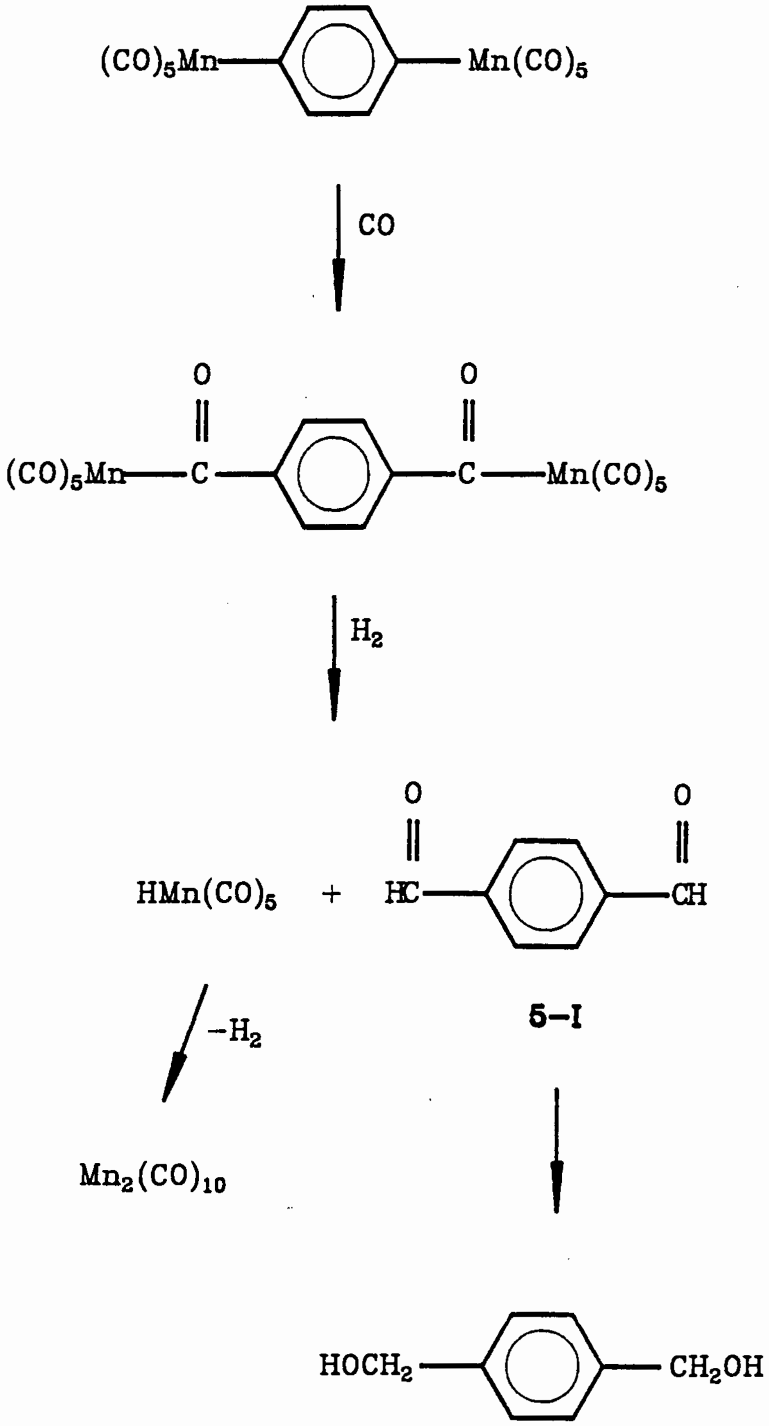
As was discussed in Chapter 3, the reaction of synthesis gas with transition metal complexes to produce hydrocarbons and oxygenated organic species, are of great catalytic importance. These reactions can be used to model processes such as the Fischer-Tropsch reaction or the hydroformylation reaction. Both of these industrially important reactions yield oxygenated products such as aldehydes and alcohols. Dombek [18] found that the reaction of mononuclear alkyl transition metal complexes with synthesis gas leads to aldehydes and in some cases alcohols. Thus for example, the reaction of $CH_3Mn(CO)_5$ with H_2/CO yields CH_3CHO as the major organic product [18]. It was also found that under more severe conditions, the aldehydes can be further reduced to the corresponding alcohols. In Chapter 3 of this work, it was shown that this type of reaction could be extended to binuclear alkyl bridged complexes to yield diols. In this section, the reactions of μ-(p-phenylene) complexes are investigated.

Reaction of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ with synthesis gas:

A solution of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ in tetrahydrofuran was reacted with synthesis gas (1:1 CO/H_2) at 40 atmospheres and 70°C. The reaction gave C_6H_4-1,4-(CH_2OH)$_2$ as the only isolable organic product (yield 69%) (see Equation 5.5).

$$C_6H_4\text{-}1,4\text{-}[Mn(CO)_5]_2 + H_2/CO(40atm) \xrightarrow[70°(3.5h)]{THF} C_6H_4\text{-}1,4\text{-}(CH_2OH)_2 + Mn_2(CO)_{10} \qquad (5.5)$$

The diol, C_6H_4-1,4-(CH_2OH)$_2$ was identified by comparison of its, IR, ^1H nmr and mass spectra with published spectra [19,20]. The only organometallic compound isolated from the reaction was $Mn_2(CO)_{10}$. The reaction appears to be analogous to that of the μ-alkanediyl complexes of manganese [21]. A possible reaction scheme is outlined in Figure 5.3. The intermediate aldehyde, **5-I** (Figure 5.3) was not detected, however it is thought that under the reaction conditions, it is rapidly reduced to the diol, **5-II** (Figure 5.3). In a separate experiment, the reaction of [Mn(CO)$_5$]$_2${μ-(CO-C_6H_4-CO)} with H_2 (40atm) was shown to give the diol C_6H_4-1,4-(CH_2OH)$_2$.



5–I

5–II

Figure 5.3: Possible pathway for the reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ with syngas.

$Mn_2(CO)_{10}$ is the only inorganic product isolated from the reaction of both the *μ*-(*p*-phenylene) *oσ* *μ*-(*p*-phthaloyl) complexes of manganese with syngas and is presumed to be formed from the decomposition of $HMn(CO)_5$ under the conditions of the experiment.

Attempted reactions of other μ-(p-phenylene) complexes with syngas:

The reactions of C_6H_4-1,4-$[CpFe(CO)_2]_2$ and C_6H_6-1,4-$[Re(CO)_5]_2$with syngas were attempted, however these reactions were not as successful as that of the manganese compound. The rhenium compound for example shows some reaction with syngas (40atm) at 70°C but the reaction mixture after 8 hours under these conditions, contains at least four components (from the IR spectrum of the reaction mixture). Some of the products which were identified in the mixture are, the *μ*-(*p*-phenylene) starting material,the *μ*-(*p*-phthaloyl) complex and the diol C_6H_4-1,4-$(CH_2OH)_2$. An aldehydic species - ν(CO) 1720 cm^{-1} - was also observed but attempts to separate these components were not successful. Repeating the reaction at 100°C gave a similar result, although there was less of the *μ*-(*p*-phthaloyl) species in the reaction mixture.

C_6H_4-1,4-$[CpFe(CO)_2]_2$ is even less reactive. Thus, reacting this species with syngas under the same conditions as above, gave no expected diol or even the intermediate acyl species. The fact that the diol, *p*-dihydroxy-α,α'-xylene, is not observed, is probably due to the inability of the *μ*-(*p*-phenylene) compound of iron to undergo carbonyl insertion which is thought to be the first step in the syngas reaction. It was seen earlier (section 5.2.1), that these μ-(*p*-phenylene) compounds are extremely reluctant to undergo CO insertion.

5.2.3 REACTIONS OF μ-(p-PHENYLENE) COMPLEXES WITH LIQUID SULFUR DIOXIDE:

As discussed earlier in Chapters 2 and 3, transition metal alkyl complexes readily undergo SO_2 insertion to yield S-sulfinato derivatives. Similarly mononuclear aryl complexes have been found to react with SO_2 to form the corresponding S-sulfinates [22,23]. However, compared to alkyl complexes, these mononuclear aryl compounds undergo SO_2 insertion at a much slower rate and under more vigorous reaction conditions. For example methylmanganese pentacarbonyl inserts SO_2 at -5°C, while phenylmanganese pentacarbonyl only reacts at about 40°C [22]. Even under these conditions the yield of the S-sulfinato derivative of $PhMn(CO)_5$, is only 24%.

Reaction of C_6H_4-1,4-$[CpFe(CO)_2]_2$ with SO_2:

The μ-(*p*-phenylene) complex of iron reacts with liquid sulfur dioxide at room temperature to yield the expected S-sulfinato derivative (Equation 5.6). The reaction is however is only complete after 38h stirring at room temperature and is thus slower than the reaction of the μ(1,n)-alkanediyl complexes of iron with liquid sulfur dioxide [24]. It is also much slower than the reaction of the mononuclear phenyl complex with SO_2. This reaction of the phenyl compound is complete within 2h at -40°C [25].

$$C_6H_4\text{-}1,4\text{-}(M)_2 + SO_2\ (\text{liquid}) \xrightarrow{25°C} C_6H_4\text{-}1,4\text{-}(SO_2M)_2 \quad \underline{66}\quad M = CpFe(CO)_2 \qquad (5.6)$$

The S-sulfinato derivative <u>66</u>, was isolated as a yellow microcrystalline solid which appears to be stable in the solid state. Solutions of the compound, in the absence of an inert atmosphere, show fairly rapid decomposition to an unidentified species which show no bands in the ν(CO) region of the IR spectrum. Compound <u>66</u> is thermally stable, decomposing only above 174°C. The infra-red spectrum of <u>66</u>, shows only two strong bands in the ν(CO) region at 2054 and 2011 cm^{-1} which are about 30 wavenumbers above those of the μ-(*p*-phenylene) compound, $C_6H_4\text{-}1,4\text{-}[CpFe(CO)_2]_2$. This shift to higher frequencies is indicative of the electron withdrawing nature of the SO_2 groups. The IR spectrum in the region 1250-1000 cm^{-1}, shows two bands at 1193 and 1045 cm^{-1}, which can be assigned to S-O stretching frequencies. The infra-spectrum of <u>66</u>, resembles the spectra of S-sulfinato derivatives of mononuclear aryl compounds of iron [25].

The ^1H nmr spectrum of <u>66</u>, exhibits two signals which occur at δ5.10 and δ7.38. The singlet at δ5.10,is due to the protons of the cyclopentadienyl ring while the broad singlet at δ7.38 can be attributed to the four protons of the bridging phenyl group. The fact that the phenyl protons appear as singlet, indicates that it is the binuclear disulfinato and not the binuclear mono-sulfinato derivative that has been prepared.

Reaction of C_6H_4-1,4-$[Re(CO)_5]_2$ with SO_2:

The reaction of the μ-(*p*-phenylene) complex, C_6H_4-1,4-$[Re(CO)_5]_2$ with liquid SO_2 at room temperature does not yield the expected S-sulfinato derivative, instead the starting material is quantitatively recovered, even after stirring for 72h at room temperature. When the reaction was repeated at 80°C, about 30% conversion to the S-sulfinato derivative does occur (Equation 5.7).

$$C_6H_4\text{-1,4-}[Re(CO)_5]_2 + SO_2\ \text{(liquid)} \xrightarrow[48h]{80°C} C_6H_4\text{-1,4-}[SO_2Re(CO)_5]_2 \quad (5.7)$$

<u>67</u>

The difference in reactivity of the iron and rhenium systems, reflects the difference in electron density of the two compounds. The iron μ-(*p*-phenylene) compound having a greater electron density, would be expected to be more susceptible to electrophilic attack by SO_2.

The S-sulfinato compound of rhenium <u>67</u>, was obtained as a white microcrystalline solid, which is stable in the solid state but decomposes at about 200°C (see Table 5.2). The carbonyl region of the infra-red spectrum of <u>67</u>, shows one strong band at 2045 cm^{-1} and a weak

Table 5.2: M.p.s., yields and analytical data for the complexes of the type C_6H_4-1,4-$(SO_2M)_2$, M = CpFe$(CO)_2$, Re$(CO)_5$ and Mn$(CO)_5$.

COMPOUND		m.p.s.	YIELD	ANALYSIS*			
No	M	(°C)	(%)	C	H	(C)	(H)
66	CpFe$(CO)_2$	174-181 (dec)	77	42.70	2.40	(43.04)	(2.53)
67	Re$(CO)_5$	198-203 (dec)	33	21.95	0.49	(22.43)	(0.47)
68	Mn$(CO)_5$	166-173 (dec)	18	32.88	0.73	(32.34)	(0.68)

* Calculated values in parentheses.

Table 5.3 IR data for the complexes of the type, C_6H_4-1,4-$(SO_2M)_2$ M = $CpFe(CO)_2$, $Re(CO)_5$ and $Mn(CO)_5$

COMPOUND NO	M	νCO/cm^{-1} [a]				ν(SO) [b]	
66	$CpFe(CO)_2$			2054s	2011vs	1193s	1045s
67	$Re(CO)_5$	2158w		2045s		1186s	1045s
68	$Mn(CO)_5$	2137m	2085w	2051s	2022m	1190s	1030s

a measured in CH_2Cl_2 soln

b measured as a Nujol mull

band at 2158 cm^{-1}. In addition to the ν(CO) bands, the solid state spectrum (Nujol) shows absorbances at 1186 and 1048 cm^{-1} which can be assigned to the S-O stretching frequencies. The spectrum closely resembles that of other sulfinato complexes of rhenium [22]. Due to the low solubility of <u>67</u>, we were unable to obtain nmr evidence for the compound.

Reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ with SO_2:

The reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ with SO_2, is extremely slow, thus when the compound is refluxed in neat liquid sulfur dioxide in a sealed tube at room temperature, most of the starting material is recovered unchanged. The infra-red spectrum of the mixture isolated shows weak bands which can be attributed to the expected product. Heating the reaction mixture at 80°C for 60h results in about 20% of the starting material being consumed and converted into the S-sulfinato derivative (Equation 5.8).

$$C_6H_4\text{-1,4-}[Mn(CO)_5]_2 + SO_2 \xrightarrow[60h]{80^\circ C} C_6H_4\text{-1,4-}[SO_2Mn(CO)_5]_2 \quad (18\%) \tag{5.8}$$

<u>68</u>

Compound <u>68</u> was isolated as a pale yellow microcrystalline solid, which is extremely insoluble in all common organic solvents with the exception of ethanol in which it is sparingly soluble. The IR spectrum of the compound shows ν(CO) bands at 2137m, 2085w, 2051brs and 2022m cm^{-1}.. The spectrum closely resembles that of the sulfinato derivative of the analogous phenyl compound [22]. Once again the low solubility of the compound 68, precludes an nmr investigation.

5.2.4 REACTIONS OF μ(p-PHENYLENE) COMPLEXES WITH HALOGENS.

Unlike the corresponding μ-(*p*-phthaloyl) complexes, the μ-(*p*-phenylene) compounds react readily with halogens to yield transition metal carbonyl halides and the appropriate 1,4-dihalobenzene (Equation 5.9).

$$C_6H_4\text{-}1,4\text{-}(M)_2 + 2X_2 \xrightarrow[rt]{THF} 2\ M\text{-}X + 1,4\text{-}XC_6H_4X$$

$M = Mn(CO)_5$, $CpFe(CO)_2$ X = Br or I

or $Re(CO)_5$

(5.9)

The products of the reaction in Equation 5.9 were identified on the basis of their infra-red and ^1H nmr spectra by comparison with those reported in the literature and of authentic samples. The rate of metal-carbon bond cleavage with a particular halogen follows the following order: $CpFe(CO)_2$ > $Re(CO)_5$ > $Mn(CO)_5$. This is exactly the same order found for the cleavage of the μ-phthaloyl complexes described in section 5.1.1. This order reflects the order of decrease in the electron density on the metal.

THe slower rate of M-C bond cleavage in the *μ*-(*p*-phthaloyl) compounds relative to the *μ*-(p-phenylene) compounds, can be attributed to the acyl carbonyl in the *μ*-(*p*-phthaloyl) compounds being fairly electron withdrawing. This decreases the electron density on the metal and makes the acyl compounds less susceptible to electrophilic attack by halogens.

The cleavage reactions of the *μ*-(*p*-phenylene) compounds with iodine, proceeds slower than the corresponding reactions with bromine which is a reflection of the electrophilic nature of these halogen cleavage reactions.

5.2.5 <u>REACTIONS OF *μ*-(*p*-PHENYLENE) COMPLEXES WITH</u> <u>TERTIARY PHOSPHINES</u>:

Reaction of C_6H_4*-1,4-[Mn(CO)*$_5$*]*$_2$ *with* PPh_2Me

Phenyl manganese pentacarbonyl is known to undergo reaction with tertiary phosphines, PR_3, to yield phosphine substituted products of the type, $PhMn(CO)_4(PR_3)$ [26]. In a similar way, the reaction of the *μ*-(*p*-phenylene) complex, C_6H_4-1,4-$[Mn(CO)_5]_2$ with PPh_2Me in a 1:2 mole ratio, yields a disubstituted phosphine derivative <u>69</u> (Equation 5.10).

$$C_6H_4\text{-}1,4\text{-}[Mn(CO)_5]_2 + 2PPh_2Me \xrightarrow[25^\circ C]{THF} C_6H_4\text{-}1,4\text{-}[Mn(CO)_4(PPh_2Me)]_2 + 2CO$$

<u>69</u>

(5.10)

The reaction proceeds relatively slowly at room temperature and only 23% of the starting material was converted to product after 20h. Compound **69**, was isolated as a pale yellow microcrystalline solid and was characterized by micro-analysis, infra red and ^1H nmr spectroscopy. The compound is stable in the solid state at room temperature but solutions decompose fairly rapidly in the presence of air to a product which shows no bands in the ν(CO) region of its IR spectrum.

The infra-red spectrum of the phosphine substituted compound **69**, is very similar to spectra of the compounds obtained from the reactions of manganese μ-alkanediyl complexes with tertiary phosphines [27]. Thus the IR spectrum of **69**, shows four bands in the ν(CO) region. This is indicative of a *cis* configuration at each of the manganese centres. The high frequency band at 2065 cm^{-1} corresponds to the symmetric stretch of the two mutually *trans* carbonyl groups, while the strong band at 1988 cm^{-1} can be assigned to the asymmetrical stretching mode of the same two carbonyl groups [28]. These assignments were made by comparison with the assignments in the IR spectrum of the mononuclear phenyl compound, $PhMn(CO)_4\{P(OPh)_3\}$ [29]. The absence of a band in the infra-red spectrum of the compound assignable to an aroyl (PhCOMn) suggest that the product is not a phosphine substituted μ-phthaloyl complex.

The ^1H nmr spectrum for the complex shows three signals, viz a doublet (J_{PH} = 9Hz) at δ1.67 due to the methyl groups of the PPh_2Me ligand, a singlet at δ6.90 due to the bridging C_6H_4 group and a multiplet centred at δ7.38 which can be assigned to the phenyl groups of the tertiary phosphine ligands.

Table 5.4: Yields, m.p.s. and analytical data for compounds of the type C_6H_4-1,4-$[Mn(CO)_4PR_3]_2$

COMPOUND	PR_3	YIELD	m.p.	ANALYSIS[a]			
		(%)	(°C)	C	H	(C)	(H)
69	PPh_2Me	64	161-164	58.75	3.80	(59.1)	(4.00)
71	PPh_3	76	148-153	64.60	3.45	(64.25)	(3.67)

a. calculated values in parentheses

Table 5.5: I.R. and ^1H nmr data for compounds of the type C_6H_4-1,4-$[Mn(CO)_4(PR_3)]_2$

		$\nu(CO)/cm^{-1}$ [a]				^1H nmr/δ ppm[b]		
COMPOUND	PR_3					PhP[c]	$-C_6H_4-$[d]	P-Me[e]
69	PPh_2Me	2065m	1989ssh	1969vs	1943ssh	7.38	6.90	1.67
71	PPh_3	2059m	1986ssh	1972vs	1942s	7.32	6.74	

a measured in CH_2Cl_2

b measured in $CDCl_3$

c signals are broad multiplets

d signals are broad singlets

e doublet (J_{PH} = 9Hz)

Reaction of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ with PPh_2Me in the presence of Me_3NO:

In an attempt to improve the yield of the phosphine substituted product <u>69</u>, the reaction of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ with PPh_2Me was carried out in the presence of Me_3NO.

Trimethylamine N-oxide has previously been employed in the preparation of substituted metals carbonyl complexes. For example, it has been used to prepare substituted metal carbonyl clusters under mild conditions [30]. Hutchings and co-workers have also used this reagent to prepare isocyanide substituted metal dimers which are not easily accessible via other routes [31]. Finally Brown *et al* [32] used Me_3NO to synthesize the substituted phenyl compound PhMn(CO)$_4$(PPh$_3$).

C_6H_4-1,4-[Mn(CO)$_5$]$_2$ was thus reacted with PPh_2Me in the presence of Me_3NO in a 1:2:2 mole ratio and a rapid reaction was observed. Monitoring the reaction by infra-red spectroscopy, revealed that all the starting material had been consumed after about 40 minutes stirring at room temperature. The product was isolated as a pale yellow microcrystalline solid and was characterized by elemental analysis, IR and ^{1}H nmr spectroscopy. It was found to be identical to the product isolated earlier when C_6H_4-1,4-[Mn(CO)$_5$]$_2$ was reacted with PPh_2Me in tetrahydrofuran. As was found for the mononuclear phenyl compound [32], the reaction probably proceeds via an intermediate trimethylamine compound. Further support for this was obtained by repeating the reaction in the absence of the tertiary phosphine. The IR spectrum of the reaction mixture shows new bands at 2033, 1935 and 1908 cm^{-1} which are due to the trimethylamine complex, C_6H_4-1,4-[Mn(CO)$_4$(Me$_3$N)]$_2$. On adding the diphenylmethylphosphine to the above solution, these bands disappear and are replaced by the bands of the phosphine substituted compound, C_6H_4-1,4-[Mn(CO)$_4$(PPh$_2$Me)]$_2$ (2065, 1988, 1969 and 1946 cm^{-1}). The sequence of reactions for this substitution process is outlined in Equations 5.11 and 5.12.

$$C_6H_4\text{-1,4-}[\mathrm{Mn(CO)_5}]_2 + 2\ \mathrm{Me_3NO} \xrightarrow[\mathrm{rt}]{\mathrm{CH_2Cl_2}} \underset{\underline{70}}{C_6H_4\text{-1,4-}[\mathrm{Mn(CO)_4(Me_3N)}]_2} + 2\mathrm{CO_2} \qquad (5.11)$$

$$\underset{\underline{70}}{C_6H_4\text{-1,4-}[\mathrm{Mn(CO)_4(Me_3N)}]_2} + 2\ \mathrm{PPh_2Me} \longrightarrow \underset{\underline{69}}{C_6H_4\text{-1,4-}[\mathrm{Mn(CO)_4(PPh_2Me)}]_2} + 2\ \mathrm{Me_3N} \qquad (5.12)$$

Attempts to isolate the intermediate trimethylamine complex, 70, were not successful.

Reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ with PPh_3 in the presence of Me_3NO:

C_6H_4-1,4-$[Mn(CO)_5]_2$ undergoes a similar Me_3NO assisted substitution reaction with triphenylphosphine as shown in Equation 5.13

$$C_6H_4\text{-}1,4\text{-}[Mn(CO)_5]_2 + 2\ PPh_3 + 2\ Me_3NO \xrightarrow[rt]{CH_2Cl_2} C_6H_4\text{-}1,4\text{-}[Mn(CO)_4(PPh_3)]_2 + 2\ CO_2 + 2\ Me_3N \qquad (5.13)$$

71

Compound 71, was isolated as a yellow microcrystalline solid (76%). It was characterized by infra-red, ^1H nmr spectroscopy and micro-analysis (see Tables 5.4 and 5.5).

The infra-red spectrum of the compound shows four bands in the ν(CO) at 2059, 1986, 1972 and 1942 cm^{-1} indicative of a *cis* arrangement at each of the manganese centres. The absence of an acyl band in the IR spectrum, suggests that we have prepared a μ-phenylene and not a μ-phthaloyl compound.

The ^1H nmr spectrum of 71, shows a multiplet at δ7.32 (P-Ph) and a broad singlet at δ6.74 (-C_6H_4-).

From the results obtained for the reactions of PPh_3 and the PPh_2Me with 56 , it is clear that the Me_3NO assisted reactions give higher yields of the phosphine substituted products. Also the reactions proceed at much faster rates. In neither case are acyl products observed, this would tend to suggest that we have direct substitution of CO with PR_3 and not aryl migration.

Attempted reaction of C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ with PPh_3:

(a) In refluxing benzene.

A mixture of the μ-(*p*-phenylene) complex C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ and triphenylphosphine was refluxed in benzene for 48h, however no reaction is observed during this time. Using the higher boiling point solvent xylene, leads only to decomposition of the starting material.

(b) In the presence of U.V. light.

During the irradiation of a mixture of the μ-(*p*-phenylene) complex, C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ and PPh_3 with a U.V. source, considerable decomposition of the iron complex is observed. The reaction yields a mixture, consisting of the starting μ-phenylene compound, some of the phosphine substituted product, C_6H_4-1,4-[CpFe(CO)(PPh$_3$)]$_2$ and the iron dimer [CpFe(CO)$_2$]$_2$.

$$C_6H_4\text{-1,4-}[CpFe(CO)_2]_2 + 2PPh_3 \xrightarrow[\text{benzene}]{h\nu(rt)} \underset{\underline{63}}{C_6H_4\text{-1,4-}[CpFe(CO)(PPh_3)]_2} + 2CO \qquad (5.14)$$

The phosphine substituted compound was isolated in 11% yield as an orange microcrystalline solid and was found to be identical to compound <u>63</u>, prepared earlier (see section 5.1.2).

(c) In the presence of Me_3NO:

The μ-(*p*-phenylene) iron compound was thus reacted with PPh_3 in the presence of Me_3NO (1:2:2 mole ratio) with the aim of facilitating the CO substitution reaction, however no reaction is observed even after prolonged stirring at room temperature. Heating the reaction mixture has little effect besides leading to decomposition of the starting material. Thus, it appears that the carbonyl groups in the μ-(*p*-phenylene) compound of iron are not susceptible to attack by Me_3NO. From this result and the result of the reaction of the μ-(*p*-phenylene) compound of manganese, it is apparent that Me_3NO is a selective reagent. Hutchings and Coville reported a similar sort of selectivity for the reaction of Me_3NO with the mixed dimer $Cp(CO)_2Fe\text{-}Mn(CO)_5$ [31]. These authors found that substitution occurred at the carbonyl groups attached to manganese and not at those attached to iron. This is thought to be a consequence of the stronger Fe-CO relative to the Mn-CO bonds.

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CHAPTER SIX.

6. EXPERIMENTAL

6.1 GENERAL

All reactions were performed under an atmosphere of high purity nitrogen using standard Schlenk tube techniques unless stated otherwise.

$[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$,$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $[Co_2(CO)_8]$ were purchased from Strem Chemicals Inc., and were used without further purification, while $RhCl_3{\cdot}xH_2O$ was obtained on loan from Johnson Matthey Ltd. The tertiary phosphines with the exception of PMe_3 were obtained either from Merck or Strem Chemicals Inc, except PMe_3,which was produced by the method of Mann and Wells [1]. The compounds $I(CH_2)_nI$, $Br(CH_2)_nBr$ and $ClCO(CH_2)_nCOCl$ were purchased from Aldrich Chemical Corporation, Ventron or Ega Chemie. t-BuNC and $(CF_3SO_2)_2O$ were obtained from Fluka AG Chemicals.

The compounds $Rh(PPh_3)_3X$ (X = Cl,Br) were prepared by the method reported by Wilkinson [2]. $Co_2(CO)_6(PPh_3)_2$ was prepared by the method of Manning [3]. The triflates $Z(CH_2)_nZ$ ($Z = CF_3SO_2O$ and n = 3 and 4) were prepared as reported by Linder [4].

The solvents used, were generally analytical grade and were purified as follows: THF, benzene, hexane and toluene were dried by distilling under a nitrogen atmosphere from Na/benzophenone; dichloromethane was distilled from anhydrous $CaCl_2$, while CH_3CN was distilled from P_2O_5. Nitrogen was bubbled through the solvents for *ca* 10 minutes prior to use.

Column chromatography was carried out using neutral aluminium oxide (70-80 Mesh) or Florosil (60-100 Mesh) obtained from Merck. The aluminium oxide was deactivated as follows: a 50% slurry of the aluminium oxide in water, was prepared and allowed to stand for 2h at room temperature. The water was then decanted and the alumina allowed to dry in the oven at 120°C for 18h.

Infra-red spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells with NaCl windows or as Nujol mulls between NaCl or CsI plates. The following abbreviations are employed in the description of infra-red spectra: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder and br = broad.

^1H and ^{13}C nmr spectra were recorded on a Varian XL 100, Varian VXR 200 or on a Bruker WH 90 nmr instrument. In all cases tetramethylsilane was used as an internal reference and chemical shifts are reported in downfield of TMS(δ0.00).

Low resolution electron impact mass spectra were recorded on a VG Micromass 16 F spectrometer, operating at 70eV and using an accelerating voltage of 4 kV. The data were analyzed on a VG 200 Digital data system.

Melting points were determined on a Kofler hotstage microscope (Reichert Thermovar) and are uncorrected.

Microanalyses were performed by Mr. W.T. Hemsted and Mr. G.D. Benin-Casa in the microanalytical laboratory of the Department of Chemistry at the University of Cape Town.

Photochemical reactions were carried out using a Hanovia 125 W photochemical reactor in a 500ml flask under nitrogen.

High pressure gas reactions were carried out in a 250ml Berghof autoclave.

6.2 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 2:

6.2.1. General Synthetic Route to the Compounds $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ where n = 3-10

A solution of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$ (0.50g, 1.31 mmol) in tetrahydrofuran (20ml) was stirred over a sodium amalgam (0.10g Na in 2ml Hg) for 2h at room temperature. The resulting solution of $Na[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]$ (2.62 mmol) was transferred by syringe to a Schlenk tube and the dibromoalkane $Br(CH_2)_n$ Br (n = 3-10) (1.31 mmol) was added dropwise with stirring. During this time, the solution changed colour from brown to green. The reaction mixture was stirred for 45 minutes at room temperature, after which the solvent was removed under reduced pressure. The green residue was extracted with dichloromethane (3 x 10ml), the resulting solution filtered and the solvent removed to leave a brown oil. The residue was extracted with warm hexane (20ml), the extract filtered and the filtrate cooled to -15°C. In the case of the compounds where n is even, the product was obtained as a yellow solid.

This was filtered off and recrystallized from hexane. In the case of the compounds where n is odd, the hexane solution was cooled to -78°C and this resulted in the formation of yellow crystals. The supernatant was removed by syringe and the yellow crystals washed with ice-cold hexane (2 x 10ml). The yellow crystals were then allowed to warm to room temperature. On doing so the solid melts yielding a yellow-brown oil. This was dried under reduced pressure. Yields, melting points, elemental analysis and spectroscopic data are given in Tables 2.1, 2.4 and 2,6 (see Section 2.1).

6.2.2. General Synthetic Route to the Compounds $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ where n = 3-6

A solution of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (0.30g, 0.61 mmol) in tetrahydrofuran (20ml) was stirred with a sodium amalgam (0.10g Na in 2 ml Hg) overnight at room temperature. The resulting solution of $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ (1.22 mmol) was transferred by syringe to a Schlenk tube and the dibromoalkane $Br(CH_2)_nBr$ (0.61 mmol) (n = 3-6) was added dropwise with stirring. The reaction mixture was stirred for 18h at room temperature, after which the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (4 x 10 ml), the resulting solution filtered and the solvent removed to leave a brown oil. Addition of hexane (20 ml) and cooling resulted in the formation of a yellow solid. Recrystallization of this yellow solid from warm hexane gave the required products as yellow crystals. Yields, melting points, elemental analysis and spectral data are given in Tables 2.2, 2.5 and 2.7 (see Section 2.1).

6.2.3 Reactions of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ with Tertiary Phosphines:

General Procedure:

A mixture of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ (0.46 mmol) and the tertiary phosphine (0.92 mmol) in tetrahydrofuran (15 ml) was refluxed under nitrogen. The course of the reaction was monitored by infra-red spectroscopy in the region (2200-1600 cm^{-1}). During this time the bands at 2003 and 1950 cm^{-1} gradually disappear while two new bands appear at 1909 and 1594 cm^{-1}. Heating was continued until no further change in the infra-red spectrum of the reaction mixture was observed. The orange solution was then allowed to cool and the solvent removed under reduced pressure. The orange oily residue obtained was extracted with hexane (30ml). The extract was filtered giving a bright orange filtrate which was reduced to half its original volume and then cooled to - 15°C. This resulted in the precipitation of a yellow-orange solid which was filtered off and dried. The yields, melting points, micro-analysis and spectral data for the phosphine substituted products $[Cp'(CO)(PR_3)FeCO(CH_2)_4COFe(PR_3)(CO)Cp']$ (PR_3 = PPh_2Me and $PPhMe_2$; Cp' = $\eta^5\text{-}C_5H_4Me$) are given in Table 6.1 and Table 2.10 (see Section 2.2.1)

Table 6.1 Reaction times, yields m.p.s and analytical data for the formation of the compounds [$Cp'(CO)(PR_3)FeCO(CH_2)_4COFe(PR_3)(CO)Cp'$], $Cp' = (\eta^5\text{-}C_5H_4Me)$.

COMPOUND	PR_3	REACTION TIME(h)	YIELD (%)	m.p. (°C)			ANALYSIS[a]	
					C	H	(C)	(H)
13	PPh_2Me	17	73 (dec)	142-148	65.70	5.45	(65.89)	(5.77)
14	$PPhMe_2$	12	80	97-102	60.35	5.90	(60.53)	(6.21)

a calculated values in brackets.

6.2.4 Reactions of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 6) with Ph_3CPF_6:

Reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$:

A solution of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ (0.11g, 0.24 mmol) in dichloromethane (5 ml) was added to a solution of Ph_3CPF_6 (0.093g, 0.24 mmol) in dichloromethane (2 ml). The reaction mixture was stirred for 12h at room temperature. The solution was filtered and the filtrate was evaporated to half its original volume. Diethyl ether (4 ml) was added and the mixture was then cooled to -78°C. A fine yellow solid precipitates out of solution. The supernatant liquid was syringed off and the yellow solid was washed with cold diethyl ether (3 x 5 ml). The product was dried under reduced pressure to yield yellow microcrystals (0.062g, 43%), m.p. 115-123°C decomp. Found: C, 41.10; H, 3.30%. $C_{20}H_{21}F_6Fe_2O_4P$ requires: C, 41.27; H, 3.63%. IR(CH_2Cl_2) ν(CO) 2068 s, 2030 s, 1997 s, 1937 s cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 5.37 (4H br d, C_5H_4), δ5.26 (1H, br m, = CH), δ4.58 (4H br d, C_5H_4), δ3.62 (1H, d, = CH_2, J = 7.5 Hz), δ3.06 (1H, d, = CH_2, J = 14.0 Hz), δ2.32 (2H, m, CH_2), δ2.03 (3H, 5, CH_3), δ1.86 (3H, s, CH_3), δ1.17 (2H, m, CH_2Fe).

Reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_6\}$:

The compound $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_6\}$ (0.10g, 0.21 mmol) was reacted with Ph_3CPF_6 (0.08g, 0.21 mmol) in dichloromethane (7 ml). The product, $\{[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(C_6H_{11})]\}PF_6$, was obtained as yellow microcrystals (0.068g, 53%), m.p. 108-113 °C decomp. Found : C, 42.95; H, 3.90%. $C_{22}H_{25}F_6Fe_2O_4P$ requires: C, 43.30; H, 4.13%. IR (CH_2Cl_2) ν(CO) 2070 s, 2032 s, 1997 vs, 1936 vs cm^{-1}; ^1H nmr ($CDCl_3$) δ5.36 4H, br s, C_5H_4), δ5.27 (1H, br m, = CH), δ4.52 (4H, br d, C_5H_4), δ3.64 (1H, d, = CH_2, J = 8Hz), δ3.22 (1H, d, = CH_2, J = 14 Hz, δ2.36 (2H, brm, $C\underline{H}_2$ - CH = CH_2), δ1.36 (4H, br m, CH_2) δ0.90 (2H, brm CH_2Fe).

6.2.5. Reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2))_4\}$ with Liquid Sulphur Dioxide:

A Carius tube, fitted with a teflon tap, was charged with $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}CH_2)_4\}$(0.1g, 0.23 mmol). Liquid SO_2 (10ml) was condensed onto the solid and the tube sealed via its teflon tap. The mixture was stirred for 20.5h at room temperature after which time the excess SO_2 was allowed to evaporate, leaving a red-brown residue. This was extracted with chloroform (30ml) and filtered. The filtrate was reduced to *ca* 5ml and hexane was added until the solution goes cloudy. The mixture was cooled to -15°C, resulting in a yellow microcrystalline solid precipitating out of solution. This was filtered to yield (0.069g, 53%) of the S-sulfinato compound, $[(\eta^5\text{-}C_5H_4Me)(CO)_2Fe(SO_2)]_2\{\mu\text{-}(CH_2)_4\}$, <u>17</u>, m.p. 169-173°C. Found: C, 41.95; H, 3.75%. $C_{20}H_{22}Fe_2O_8S_2$ requires: C, 42.43; H, 3.92%.
IR ($CHCl_3$) ν(CO) 2054 vs, 2005 s cm^{-1}; ν(SO) (Nujol) 1196 m and 1040 m cm^{-1}; ^1H nmr ($CDCl_3$) δ5.12 (4H, br s, C_5H_4), δ4.86 (4H, br s, C_5H_4), δ3.06 (4H, br t, CH_2SO_2), δ2.00 (6H,s, CH_3), δ1.96 (4H, br m, CH_2).

6.2.6 Reactions of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 6) with t-BuNC.

(a) *Reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$*

$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ (0.10g. 0.23 mmol) was dissolved in THF (8 ml) and to this was added a solution of t-BuNC (0.038g, 0.46 mmol) in THF (2 ml). This mixture was refluxed under nitrogen and the reaction was monitored by infra-red spectroscopy in the region 2200-1550 cm^{-1}. Heating was continued until no further change in the infra-red spectrum of the reaction mixture could be detected (43h). The mixture was allowed to cool and the solvent removed under reduced pressure. The oily orange residue was extracted with hexane (15ml) and filtered. The filtrate was cooled to -78°C. This resulted in a yellow-orange solid precipitating out of solution. The hexane was syringed off and the solid then washed with cold hexane (3 x 5ml). The solid was allowed to warm up to room temperature and on doing so, it melts to form a yellow-orange oil. This was dried under reduced pressure to yield the isocyanide derivative: $[\eta^5\text{-}C_5H_4MeFe(CO)(t\text{-}BuNC)]_2\{\mu\text{-}(CO\text{-}(CH_2)_4\text{-}CO)\}$, (0.11g, 79%). Found: C, 59.25; H, 6.60; N, 4.60. $C_{30}H_{40}Fe_2N_2O_4$ requires: C, 59.60; H 6.67; N, 4.64%. IR (CH_2Cl_2) ν(CO) 1937 vs, 1610 m cm^{-1}; ν(CN) 2124 br s, 2076 sh cm^{-1}; ^1H nmr ($CDCl_3$) δ4.4 - 4.29 (8H br m, C_5H_4), δ2.74 (4H, br t CH_2CO), δ1.86 (6H, s, $C\underline{H}_3\text{-}C_5H_4$), δ1.42 (18H, s, $(CH_3)_3C$), δ1.5 - 1.26 (4H, m, CH_2).

Reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_6\}$:

$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_6\}$ (0.11g, 0.24 mmol) and t-BuNC (0.04g, 0.48mmol) in THF (10ml) were reacted together in a similar fashion to that described above. The product, $[\eta^5\text{-}C_5H_4MeFe(CO)(t\text{-}BuNC)]_2\text{-}\{\mu\text{-}(CO\text{-}(CH_2)_6\text{-}CO)]$, was obtained as a yellow-orange oil (0.08g, 53%). Found: C, 60.45; H, 7.20; N, 4.73%, $C_{32}H_{44}Fe_2N_2O_4$ requires: C, 60.77; H, 7.01; N, 4.43%. IR (CH_2Cl_2) ν(CO) 1936 vs, 1608 m cm^{-1}; ν(CN) 2128 br s, 2080 sh cm^{-1}; ^{1}H nmr ($CDCl_3$) δ4.42 (8H, C_5H_4), δ2.74 (4H, br t CH_2CO), δ1.86 (6H, s, $CH_3\text{-}C_5H_4$), δ1.44 (18H, s $(CH_3)_3C$) δ1.30 (4H, m, $COCH\underline{H}_2$), δ0.86 (4H, m, - CH_2CH_2-).

6.2.7 Reactions of $\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}(n = 4 \text{ and } 5)$ with bromine and iodine:

Reactions of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ 2, with X_2 (X = Br or I)

Addition of a solution of Br_2 (0.26 mmol) in THF (2ml) to a solution of 2 (0.13 mmol) in THF (5ml) gave a red-brown reaction mixture which was stirred at room temperature for 10 minutes. The solvent was then removed under reduced pressure leaving a brown residue which was dissolved in CH_2Cl_2 (3ml) and the solution chromatographed on an alumina column (made up with hexane). A pale yellow band was eluted with hexane and gave a pale yellow, almost colourless, oil on evaporation. This was identified as $Br(CH_2)_4Br$, by comparing its IR and ^{1}H nmr spectra with those of an authentic sample.

A second dark red band was eluted with CH_2Cl_2/hexane (1:1), followed by pure CH_2Cl_2. Evaporation of this solution yielded a dark red solid, the infra-red and ^1H nmr spectra of which were identical to those of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2Br]$ [5] (85% yield).

The reaction of 2 with I_2 in THF was performed in the same way as the reaction with Br_2. The work up of the reaction mixture resulted in two products which were identified on the basis of their infra-red and ^1H nmr spectra as $I(CH_2)_4I$ and $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ [6] (73%).

Reactions of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_5\}_2$ 3, with X_2 (X = Br or I)

I_2 (0.26mmol) was added to a solution of 3 (0.13mmol) in THF at room temperature. The work up of the reaction mixture as described above, gave two products. An almost colourless band eluted with hexane, gave a pale yellow oil on evaporation. The infra-red and ^1H nmr spectra of this showed that it was $I(CH_2)_5I$. A brown band was eluted with CH_2Cl_2/hexane (1:1). Evaporation of the solution yielded a dark red solid, the infra-red and ^1H nmr spectra of which were identical to those of the compound $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ (69%).

The reaction of 3 with Br_2 was carried out in the same way and gave $Br(CH_2)_5Br$ and $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2Br]$(76%).

6.2.8 REACTION OF $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ WITH Ph_3CPF_6.

A solution of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4)\}$ (0.07g, 0.13 mmol) in dichloromethane (5ml) was added to a solution of Ph_3CPF_6 (0.05g, 0.13 mmol) in dichloromethane (2ml). The reaction mixture was stirred for 3h at room temperature. The solution was filtered and the filtrate was reduced to half its original volume. Diethyl ether (4ml) was added and the mixture cooled to -15°C. This resulted in a yellow solid precipitating out of solution. The solution was filtered to give, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(C_4H_7)]\}PF_6$, as yellow microcrystals (0.048g, 53%), m.p. 158-164 °C decomp. Found: C, 48.75; H, 5.37%; $C_{28}H_{37}F_6Fe_2O_4P$ requires: C, 48.44; H, 5.37. IR(CH_2Cl_2) ν(CO) 2052vs, 2013s, 1983s, 1925vs cm^{-1}; ^1H nmr ($CDCl_3$) δ3.98(1H, brm, =CH),d3.08(1H, d, $=CH_2$, J = 8Hz),δ2.76(1H, d, $=CH_2$, J = 14Hz), δ1.88(15H, s, C_5Me_5), 1.70 (15H, s, C_5Me_5),δ 2.14(2H, brm, $C\underline{H}_2\text{-}CH{=}CH_2$), δ1.15(2H, brm, CH_2Fe).

6.2.9 REACTION OF $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4)\}$ WITH SO_2:

A Carius tube, fitted with a teflon stopcock, was charged with $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4)\}$ (0.064g, 0.12mmol). Liquid SO_2 (10ml) was condensed onto the solid and the tube sealed immediately via its teflon tap. The mixture was stirred for 8h at room temperature after which the excess SO_2 allowed to evaporate. This resulted in a red-brown residue being obtained which was extracted with methylene chloride (15ml) and filtered. The resulting filtrate was evaporated leaving a brown sticky residue. This was triturated with hexane (3x10ml). On doing so a yellow solid was obtained which was then filtered off. Recrystallization of this from CH_2Cl_2/hexane gave $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2SO_2]_2\{\mu\text{-}(CH_2)_4)\}$ as a microcrystalline yellow solid (52%), m.p. 203-211 °C decomp. Found: C, 49.25; H, 5.60%. $C_{28}H_{38}Fe_2O_8S_2$ requires: C, 49.58; H, 5.65%. IR (CH_2Cl_2) ν(CO) 2024s, 1975s cm^{-1}; ν(SO) 1182m, 1038m cm^{-1}; ^1H nmr ($CDCl_3$) δ2.96(4H, brt, CH_2SO_2),δ1.86(30H, s, CH_3), δ1.68-1.26(4H, brm, CH_2).

6.2.10 REACTIONS OF $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n)\}$ (n = 4 AND 6) WITH BROMINE AND IODINE:

These reactions were performed using the same general procedure as for the reactions of the (η^5-C_5H_4Me) analogues. (See Section 6.2.7.).

Reactions of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4)\}$,10, *with* X_2.

Addition of a solution of Br_2 (0.36 mmol) in THF (2ml) to a solution of 10 (0.18 mmol) in THF (5 ml) gave a brown reaction mixture. The work up of the reaction mixture as described in Section 6.2.7, gave two products, viz $Br(CH_2)_4Br$ and a dark brown solid which was shown to be $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2Br]$ (93%) [7].

A similar reaction of 10 with I_2 yields $I(CH_2)_4I$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2I]$ (80%) [7] .

Reactions of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$]$_2${μ-(CH$_2$)$_6$)}, 12, with Halogens.

I_2(0.54 mmol) was added to a solution of 12 (0.27 mmol) in THF at room temperature. The work up of the reaction mixture was similar to that described in Section 6.2.7 and yielded two products, $I(CH_2)_6I$ and [(η^5-C_5Me_5)Fe(CO)$_2$I] (69%).

The reaction of 12 with Br_2 was carried out in a similar fashion and yielded $Br(CH_2)_6Br$ and [(η^5-C_5Me_5)Fe(CO)$_2$Br] (73%).

6.2.11 Reaction of [(η^5-C_5Me_5)Fe(CO)$_2$]$_2${μ-(CH$_2$)$_4$)}, 12, with Carbon Monoxide:

12 (0.05g) 0.09mmol) was dissolved in THF (6ml) and CO bubbled through the reaction mixture for 30 mins. The mixture was then stirred for a further 18h under an atmosphere of CO. No reaction was observed during this time, as monitored by IR spectroscopy.

The reaction mixture above was transferred to an autoclave which was sealed and then pressurized with CO (30atm) The reaction mixture was stirred at room temperature for 23h after which time the autoclave was vented and the reaction mixture taken to dryness. The infra-red spectrum of the resulting yellow-brown solid, showed that it was a mixture of starting material and an acyl compound. The yellow solid was extracted with CH_2Cl_2 (10 ml) and chromatographed on an alumina column made up in CH_2Cl_2. A yellow band was eluted with CH_2Cl_2 and on evaporation gave a yellow solid, the IR and ^{1}Hnmr of which was identical to the starting material (70% recovery). A second bright yellow band was eluted with a CH_2Cl_2/methanol (1:1) mixture, followed by pure methanol. Evaporation of the solution yields a dark yellow solid. This was identified as the acyl compound, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}CO(CH_2)_4CO)\}$ <u>22</u>, (25%).

M.p. 71-76 C^o. Found: C, 59.75; H, 6.20% $C_{30}H_{38}Fe_2O_6$ requires: C, 59.43; H, 6.32%. IR(CH_2Cl_2) ν(CO) 2001 s, 1943 vs cm^{-1}; ^{1}H nmr ($CDCl_3$) δ2.77 (4H, br t CH_2CO), δ1.76 (30H, s, CH_3), δ1.48 (4H, br m, CH_2).

6.2.12 <u>Attempts to Decarbonylate $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CO(CH_2)_4CO)\}$</u>

<u>Thermal Decarbonylation.</u>

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CO(CH_2)_4CO)\}$ (0.02g, 0.033 mmol) was suspended in xylene (10ml). The mixture was heated for 18h, during which time the reaction was monitored by infra-red spectroscopy. This shows that <u>22</u>, undergoes extensive decomposition yielding mainly $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (85%). A small percentage of the μ-alkanediyl compound, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$ (<10%) is also detected.

<u>Photolysis:</u>

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CO(CH_2)_4CO)\}$ (0.02g, 0.033 mmol.) was dissolved in benzene (150ml). The mixture was subjected to U.V. irradiation for 2h at room temperature. During this time the pale yellow solution goes dark red. The solvent was removed under reduced pressure, leaving a dark red residue which was shown to be $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (93%).

6.2.13 Attempted Reaction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}\}$ 10 with PPh_2Me.

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}\}$ (0.1g, 0.18 mmol) was dissolved in THF (8ml). To this was added a solution of PPh_2Me (0.07g, 0.36 mmol) in THF (2ml) and the mixture was refluxed for 4 days. During this time, the reaction was monitored by infra-red spectroscopy. This showed that the reaction is extremely slow and that after 4 days, only about 20% of the starting material was consumed. The solvent was removed leaving a yellow solid residue which was extracted with hexane and filtered. Cooling the filtrate results in a yellow solid precipitate which was filtered off and dried. An infra-red spectrum of this solid, shows, it to be a mixture of mainly starting material and an unidentified acyl product. Attempts to separate the mixture failed.

6.3 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 3:

6.3.1 The preparation of $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$ (n = 4-6).

General Procedure:

The above compounds were prepared using modified literature procedure [8,9] as outlined below:

$Mn_2(CO)_{10}$ (1.5g, 3.85 mmol) in tetrahydrofuran (25ml) was stirred over a sodium amalgam (0.3g Na in 6ml Hg) for 2h at room temperature. The resulting solution of Na[Mn(CO)$_5$] (7.70 mmol) was transferred by syringe to a Schlenk tube and the diacyl chloride ClCO(CH$_2$)$_n$COCl (n = 4-6) (3.85 mmol) was added with rapid stirring. The reaction mixture was stirred for 3h at room temperature after which the solvent was removed leaving a yellow residue. This was extracted with warm chloroform (50cm^3) and filtered. The filtrate was concentrated to 10ml and hexane added until the solution goes cloudy. Cooling (-15°C) results in the formation of the diacyl complexes (CO)$_5$MnCO(CH$_2$)$_n$COMn(CO)$_5$ (n= 4-6).

(CO)$_5$MnCO(CH$_2$)$_4$COMn(CO)$_5$:

This was isolated a white microcrystalline solid (60%) m.p. 141-144°C decomp. Found: C, 38.10; H, 1.80%. $C_{16}H_8Mn_2O_{12}$ requires: C, 38.19; H 1.61%. IR(CHCl$_3$) 2114 w, 2050 sh, 2014 vs, 1638 w br cm^{-1}; ^{1}H nmr (CDCl$_3$) δ2.94 (4H, br t, CH$_2$CO), δ1.42(4H, br m, CH$_2$)

(CO)$_5$MnCO(CH$_2$)$_5$COMn(CO)$_5$:

The above compound was isolated as white micro-crystals (36%) m.p. 131-133°C. Found: C, 39.35; H, 1.80%. $C_{17}H_{10}Mn_2O_{12}$ requires: C, 39.58; H, 1.95%. IR(CHCl$_3$) 2115W, 2052 w, 2014 vs, 1636 m br cm^{-1}; ^{1}H nmr (CHCl$_3$) δ2.88 (4H, br t, CH$_2$CO), δ1.33 (4H, br m, CH$_2$)

$(CO)_5MnCO(CH_2)_6COMn(CO)_5$:

This was obtained as a white microcrystalline solid (40%); m.p. 97-100°C. Found: C, 40.50; H 2.25%, $C_{18}H_{12}Mn_2O_{12}$ requires: C, 40.78; H, 2.28%, IR($CHCl_3$) 2115 w, 2053 w, 2013 vs, 1636 w br cm^{-1}; ^1H nmr ($CDCl_3$) δ2.89 (4H, br m, CH_2CO), δ1.34 (4H, br m, CH_2).

6.3.2. General Synthetic Route to μ-alkanediyl complexes of the type $[Mn(CO)_5]_2\{\mu-(CH_2)_n\}$ (n = 4-6) i.e. Compounds 23 - 25

The diacyl compounds $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$ (n = 4-6) were converted to the corresponding μ(1,n)-alkanediyl compounds by simple decarbonylation. In a typical preparation, $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$ (2 mmol) was suspended in hexane (150 ml). The mixture was then refluxed for 15 minutes under nitrogen. The reaction can be followed by IR spectroscopy, by monitoring the disappearance of the acyl band around 1625 cm^{-1}. Removal of the hexane leaves a cream coloured solid which can be recrystallized by dissolving in a minimum of chloroform and adding hexane. Cooling to -15°C, results in the formation of a white microcrystalline solid. The yields, melting points, elemental analysis and spectroscopic data are given in Tables 3.1 - 3.4. (See Chapter 3).

6.3.3 Synthesis of $(CO)_5ReCO(CH_2)_4CORe(CO)_5$: 43.

$Re_2(CO)_{10}$ (1.00g, 1.53 mmol) in tetrahydrofuran (30ml) was stirred over sodium amalgam (0.20g Na in 4 ml Hg) for 2h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (2.06 mmol) was transferred by syringe to a

Schlenk tube. Adipoyl dichloride (0.28g; 1.53 mmol) was added dropwise with rapid stirring. The solution goes cloudy almost immediately with a precipitate forming. The mixture was stirred for 3 hours at room temperature. The solvent was removed leaving a creamy-white residue which was then extracted with methylene chloride and filtered. The filtrate was taken to dryness leaving a white solid which was recrystallized from warm acetone. The resulting white micro-crystalline solid was filtered off to give 0.70g (60%) of $(CO)_5ReCO(CH_2)_4CORe(CO)_5$, m.p. 143-147°C. Found: C, 24.8; H 1.1%. $C_{16}H_8O_{12}Re_2$ requires: C, 25.1; H 1.1%. IR ($CHCl_3$) ν(CO) 2133 w, 2023 vs and 1605 w br; ^1H nmr ($CDCl_3$) δ2.68 (4H, t, CH_2CO), δ1.38 (4H, m, CH_2).

6.3.4. Preparation of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 44

$(CO)_5ReCO(CH_2)_4CORe(CO)_5$ (0.70g; 0.92 mmol) was suspended in toluene (100ml) and the mixture was refluxed for 1h under N_2. The reaction mixture was filtered while hot and the filtrate reduced to *ca* 30 ml. It was then cooled (-15°C), resulting in the formation of white crystals. This was filtered off to give the μ-alkanediyl complex. The yield and characterization data are recorded in Tables 3.11 - 3.14 (See Chapter 3).

6.3.5. Preparation of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$ 45

A solution of $CF_3O_2SO(CH_2)_3OSO_2CF_3$ [4] (0.26g, 0.77 mmol) in tetrahydrofuran (5ml) was added dropwise with rapid stirring to a solution of $Na[Re(CO)_5]$ (1.54 mmol) in THF. The reaction mixture was stirred for 3h at room temperature, after which the solvent was removed, leaving a light yellow residue. This was extracted with chloroform (40 ml) and filtered. The filtrate was taken to dryness leaving a white residue which was recrystallized from chloroform/hexane to yield **45** (49%). The characterization data for **45** are listed in Tables 3.11 - 3.14 (Chapter 3).

6.3.6. Reactions of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4-6), 23 - 25, with Tertiary Phosphines, PR_3 (1:2 mole ratio).

General Procedure.

$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (0.45 mmol) was dissolved in tetrahydrofuran (10 ml). To this was added a solution of the tertiary phosphine (0.90 mmol) in tetrahydrofuran (2 ml). The mixture was stirred at room temperature for between 45 - 90 mins. The reaction was monitored by IR spectroscopy and continued until no more starting material remained. The solvent was removed leaving a colourless oily residue. This was extracted with chloroform and filtered. The filtrate was taken to dryness, leaving a sticky residue. In the case of the compounds where (n = 4) and (n = 6, PR_3 = $PPhMe_2$ and PMe_3), the compounds could be purified by adding hexane to the oil. This results in a white micro-crystalline solid being obtained. In the cases where (n = 5 or 6 and PR_3 = PPh_2Me), the products are oils at room temperature and were purified by adding hexane to the oily residue and then cooling to -78°C. This resulted in a white solid precipitating out of solution. The supernatant was removed by syringe and the white solid washed with ice-cold hexane (3 x 5 ml). The washings were then syringed off and the solid was allowed to warm up to room temperature. On doing so the solid melts to yield a colourless oil. The product was dried under vacuum. The yields and the characterization data of compounds 26 - 36 are given in Tables 3.5 - 3.7 (Chapter 3).

6.3.7. Preparation of the compounds $[Mn(CO)_4(PR_3)]_2\{\mu-(CH_2)_4\}$ i.e. compounds 38 - 41

The phosphine substituted diacyl compounds 26 - 29 were converted to the corresponding phosphine substituted μ-alkanediyl compounds 38 - 41.

General Procedure:

$(CO)_4(PR_3)MnCO(CH_2)_4COMn(PR_3)(CO)_4$ (0.1g) was suspended in hexane (20 ml) and the mixture refluxed for about 1h. The reaction was monitored by IR spectroscopy in the region (2200 - 1550 cm^{-1}). Heating was continued until the acyl band at 1605cm^{-1} had completely disappeared. The reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The oily pale yellow residue was dissolved in a minimum of CH_2Cl_2 and filtered. The addition of hexane and cooling (-15°C), resulted in a white microcrystalline solid being obtained. This was identified as $[Mn(CO)_4(PR_3)]_2\{\mu-(CH_2)_4\}$ (38 - 41). The melting points and elemental analysis of the products are given in Table 3.8 and the IR and ^1H nmr data in Tables 3.9 and 3.11 respectively (Chapter 3).

6.3.8. Reactions of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 45 with Tertiary Phosphines: (1:2 mole ratio)

General Method:

A solution of the tertiary phosphine (1 mmol) in tetrahydrofuran (2 ml) was added to a solution of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (0.5 mmol) in tetrahydrofuran (10 ml). The mixture was refluxed under nitrogen and the course of the reaction was followed by infra-red spectroscopy in the region 2200-1550 cm^{-1}. The reaction was continued until the infra-red spectrum showed no further change. The reaction is extremely slow and takes between 2 - 6 days to reach completion, depending on the tertiary phosphine used. The reaction mixture was allowed to cool and the solvent removed. This leaves an oily residue which was extracted with dichloromethane and filtered. The filtrate was taken to dryness to yield a sticky residue. This was triturated with hexane (5 ml), resulting in a white solid precipitating out of solution. The solid was filtered and dried. Analytically pure samples can be obtained by recrystallization from CH_2Cl_2/hexane at -78°C. The yield, elemental analysis and spectral data are to be found in Tables 3.15 - 3.17 (Chapter 3). The reaction times with the different phosphines are: PPh_3 (42h), PPh_2Me (72h) and $PPhMe_2$ (6 days).

6.3.9 Reactions of $[M(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (M = Mn, n = 4-6, M = Re, n = 4) with Halogens, X_2 (X = Br and I).

Reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 23 *with* Br_2 *and* I_2 *in Tetrahydrofuran:*

$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (0.1g, 0.22 mmol) was dissolved in tetrahydrofuran (10 ml). A solution of Br_2 (0.44 mmol) in tetrahydrofuran (2 ml) was added with rapid stirring. The mixture was stirred for 1h at room temperature. The solvent was removed leaving a brown residue. Methylene chloride (15 ml) was added to the residue resulting in a fine off-white solid precipitating out of solution. The solid was filtered off and washed with a minimum of dichloromethane. This was dried on the water pump to yield 0.022g (69%) of adipic acid. The acid was identified by comparing its IR and ^{1}H nmr spectra with those of authentic samples.

The filtrate obtained above was taken to dryness leaving a brown residue. An infra-red spectrum of this residue reveals that it is a non-carbonyl containing species, which was not identified.

A similar result to the above was obtained when 23 was reacted with I_2 in tetrahydrofuran. The organic product isolated was again adipic acid (56%).

The reaction of 24 with Br_2 was also performed in tetrahydrofuran. This yields pimelic acid, $HOOC(CH_2)_5COOH$ (60%) which was identified on the basis of its IR and ^{1}H nmr spectra.

Reaction of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 44, with Halogens X_2

A solution of Br_2 (0.4 mmol) in THF (2 ml) was added to a solution of 44 (0.14g, 0.2 mmol) in THF (10ml) at room temperature. The solvent was removed leaving a yellow residue. This was dissolved in *ca.* 3 ml CH_2Cl_2 and the solution chromatographed on a silica gel column (made up in hexane). Elution with CH_2Cl_2/hexane (1:1), gave a yellow oil on evaporation of the eluted solution. This was identified as $Br(CH_2)_4Br$ on the basis of the IR and ^1H nmr spectra of the compound. A second faint yellow band was eluted with pure CH_2Cl_2. This yielded a yellow solid, which was identified as $Re(CO)_5Br$ (72% yield) [10].

Similarly the reaction of 44 with I_2 in THF, yielded $I(CH_2)_4I$ and $Re(CO)_5I$ (68% yield) [10].

Reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 23 with X_2 in methylene chloride.

$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (0.1g, 0.22 mmol) was dissolved in anhydrous methylene chloride (10 ml). A solution of Br_2 (0.44 mmol) in CH_2Cl_2 (2 ml) was added with rapid stirring at room temperature. The orange-red solution was stirred for 1h at room temperature. The volume of the reaction mixture was reduced to *ca.* 3 ml. This solution was then chromatographed on a silica gel column (made up in hexane). A pale yellow band eluted with CH_2Cl_2/hexane (1:1) gave a pale yellow oil on removal of the solvent. This was identified as $Br(CH_2)_4Br$ on the basis of its IR and ^1H nmr spectra. A yellow-orange band was eluted with a 20% hexane/CH_2Cl_2 solution. This yielded a yellow solid on evaporation of the solution. The IR spectrum of the compound was identical to that of $Mn(CO)_5Br$ [11], (74% yield).

The reaction of 23 with I_2 in CH_2Cl_2 was carried out in an analogous fashion. The products isolated from the reaction were, $I(CH_2)_4I$ and $Mn(CO)_5I$ [11] (82% yield).

6.3.10 Reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4 and 5) with Carbon Monoxide:

General Procedure:

$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\}$ (0.15g, 0.34 mmol) was dissolved in THF (20 ml). CO was then bubbled through the reaction mixture for 30 minutes. The reaction mixture was then stirred for an additional 1.5h at room temperature and the solvent removed to yield a white solid. This was recrystallized from $CHCl_3$/hexane to yield the diacyl species $(CO)_5MnCO(CH_2)_nCOMn(CO)_5$; yields,

n = 4; 90%

n = 5; 84%

The products were identified by comparing their IR and ^1H nmr spectra with those of authentic samples.

6.3.11 Reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 23, with synthesis gas:

The above reaction was carried out in a 250 ml Berghof autoclave, which was charged with $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (0.1g, 0.22 mmol) and tetrahydrofuran (15 ml). The autoclave was sealed and then pressurized with synthesis gas (1:1

CO/H_2) until a pressure of 40 atm was reached. The mixture was then heated at 70 C for 3.5h. The autoclave was allowed to cool to room temperature and then vented. A dark brown mixture was obtained which was filtered yielding a pale yellow filtrate. The solvent was removed from the filtrate, leaving a pale yellow oil. An IR spectrum (neat film) of the oily residue shows that it is a mixture of $HOCH_2(CH_2)_4CH_2OH$ and $Mn_2(CO)_{10}$, with the diol being the major component. The oil was dissolved in a minimum of a 1:1 mixture of CH_2Cl_2/hexane. The solution was then filtered through a short (5 cm) alumina column (made up with hexane). Two bands are observed on the column, a faint yellow (almost colourless) band and a bright yellow band. The pale yellow band was eluted with 10% CH_2Cl_2/hexane and on evaporation gave a pale yellow oil. This was identified as $HOCH_2(CH_2)_4CH_2OH$ on the basis of its IR [12] and ^1H nmr [13] spectra (69%). The second yellow band was eluted with CH_2Cl_2 and evaporation of this solution produced a trace of a yellow solid, the IR spectrum of which was identical to that of $Mn_2(CO)_{10}$. (71%).

The reaction of $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_5\}$ with synthesis gas was carried out in the same way and the work up of the reaction gave two products which were identified on the basis of their infra-red and ^1H nmr spectra as $HOCH_2(CH_2)_5CH_2OH$ (53%) and $Mn_2(CO)_{10}$ (64%).

6.3.12 Reaction of $[Re(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ 44, with Carbon Monoxide:

44 (0.1g, 0.14 mmol) was dissolved in THF (15 ml). CO was bubbled through the reaction mixture for 30 minutes. The reaction mixture was then stirred for a further 22h under a positive atmosphere of CO (1 atm). Monitoring the reaction by infra-red spectroscopy, showed no change during this time.

The reaction mixture prepared above, was transferred to an autoclave which was sealed and then pressurized with CO to 30 atm. The reaction mixture was stirred at room temperature for 24h. The autoclave was vented and the reaction mixture filtered. An infra-red spectrum of the filtrate, showed that it contained a mixture of unreacted starting material and the diacyl species, $(CO)_5ReCO(CH_2)_4CORe(CO)_5$. The latter made up about 30% of the mixture, judging from the IR spectrum of the mixture.

6.3.13 Reactions of $[M(CO)_5]_2\{\mu\text{-}(CH_2)_4\}$ (M = Re, Mn) with SO_2

Reaction of $[Re(CO)_5]\{\mu\text{-}(CH_2)_4\}$ 44 , with SO_2:

44 (0.10g, 0.14 mmol) was charged into a Carius tube, which was fitted with a teflon stopcock. SO_2 (15ml) was condensed onto the solid and the tube sealed immediately via the teflon tap. The mixture was stirred for 21h at room temperature. During this time, the solid gradually dissolves to give a colourless solution. The excess SO_2, was then allowed to evaporate, leaving a creamy residue which was extracted with CH_2Cl_2 (3 x 50 ml) and filtered. The filtrate was taken to dryness, leaving a white solid. This was identified as the S-sulfinato compound $[Re(CO)_5SO_2]_2\{\mu\text{-}(CH_2)_4\}$ (64%) m.p. 215 - 223°C decomp. Found: C, 19.8; H, 0.88%; $C_{14}H_8O_{14}Re_2S_2$ requires: C, 20.1; H, 0.96%. IR (CH_2Cl_2) ν(CO) 2154 w, 2097 vw, 2051 m, 2025 wsh cm^{-1}; (Nujol) ν(SO) 1183 m, 1045 m cm^{-1}.

Reaction of [Mn(CO)$_5$]$_2${μ-(CH$_2$)$_4$} 23 with SO$_2$:

Compound 23 (0.10g, 0.22 mmol) was charged into a Carius tube and SO_2 (10ml) was condensed onto the solid. The tube was sealed via its teflon tap and then heated at 70°C for 19h. During this time, the solid gradually dissolved and gave a yellow solution. The SO_2 was then evaporated to leave a yellow residue which was extracted with acetone (3 x 30 ml) and filtered. The solvent was removed from the filtrate leaving a pale yellow solid. This was washed with CH_2Cl_2 (3 x 5 ml) and dried to give a yellow microcrystalline solid. This was identified as $[Mn(CO)_5SO_2]_2\{\mu\text{-}(CH_2)_4\}$ (77%). m.p. 265 - 278°C decomp. Found: C, 29.15; H, 1.85%. $C_{14}H_8Mn_2O_{14}S_2$ requires: C, 29.30; H, 2.16% IR (acetone) ν(CO) 2137 w, 2090 vw, 2048 s, 2021 sh cm^{-1}; (Nujol) ν(SO) 1120 m and 1038 m cm^{-1}.

6.4 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 4

6.4.1 PREPARATION OF THE μ-(p-PHTHALOYL) COMPLEXES, C_6H_4-1,4-(COM)$_2$, M = Mn(CO)$_5$, Re(CO)$_5$ and CpFe(CO)$_2$.

General procedure

A solution of the sodium salt of the anion M^- [where M = $Mn(CO)_5$, $Re(CO)_5$, $CpFe(CO)_2$] (2mmol) in THF (30ml) was added dropwise to a solution of 1,4-terephthaloyl dichloride (1mmol) in THF (5ml) with rapid stirring. The reaction mixture was then stirred for 3h at the addition temperature. The solvent was removed and the residue triturated with water (4x30ml). The product was then filtered off, washed with diethyl ether (5x30ml) and the solid dried on the vacuum pump. The μ-(p-phthaloyl) compounds of Mn and Re are insoluble in organic solvents and cannot be recrystallized. Analytically pure samples were obtained by washing the products with large volumes of diethyl ether. The μ-(p-phthaloyl) compound of Fe can be recrystallized from hot acetone. The yields, melting points, analytical and spectral data are listed in Tables 4.1 - 4.3 (see Chapter 4).

6.4.2 SYNTHESIS OF $[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 54:

A solution of $Na[CpMo(CO)_3]$ (2.04mmol) was added to a solution of C_6H_4-1,4-$(COCl)_2$ (0.21g, 1.02mmol) in THF (2ml) which was cooled to -78°C. The reaction mixture was stirred at -78°C for 30 minutes after which, it was allowed to warm up to room temperature (30 minutes). The solvent was removed leaving a brown residue which was extracted with CH_2Cl_2 (50ml) and filtered. The filtrate was evaporated, resulting in an orange-red residue. This was dissolved in 5ml benzene and chromatographed on an alumina column (made up with benzene). A red band eluted with benzene gave a bright red solid on evaporation, the infra-red and ^1H nmr spectra of which were identical to those of $[CpMo(CO)_3]_2$ (78% yield). An orange band was eluted with 20% CH_2Cl_2/benzene and produced an orange-yellow solid on evaporation. The solid can be recrystallized from CH_2Cl_2/hexane to yield the compound, $[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ (7%), m.p. 131-138 °C decomp. The analytical and spectral data are to be found in Tables 4.1-4.3 (Chapter 4).

6.4.3 PREPARATION OF $[Co(CO)_3(PPh_3)]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 53.

$[Co(CO)_3(PPh_3)]_2$ (0.5g, 0.62mmol) was suspended in THF (20ml) and the mixture stirred over a sodium amalgam (0.1g Na in 2ml Hg) for 18h at room temperature. The resulting green solution of $Na[Co(CO)_3(PPh_3)]$ (1.24mmol) was added to a solution of C_6H_4-1,4-$(COCl)_2$ (0.13g, 0.62mmol) in THF (2ml) and the mixture stirred for 18h at room temperature. The solvent was removed leaving a green residue. This was extracted with CH_2Cl_2 (60ml) and filtered. The filtrate was reduced to *ca* 10ml and chromatographed on a Florosil column (made up with hexane). A pale yellow band was eluted initially using CH_2Cl_2/hexane(1:1), followed by pure CH_2Cl_2 . Evaporation of the solvent, yielded an off-white solid. This was found to contain a mixture of C_6H_4-1,4-$(COCl)_2$ and C_6H_4-1,4-$(COOH)_2$. The latter is thought to be a result of hydrolysis of the unreacted diacyl chloride. A bright yellow band was eluted with CH_2Cl_2/ethanol (1:1) and gave a yellow solid on evaporation. This was recrystallized from CH_2Cl_2/hexane to give the compound, $[Co(CO)_3(PPh_3)]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ as yellow microcrystals (23%). The m.p., analytical and spectral data are listed in Tables 4.1-4.3.

6.4.4 ATTEMPTED REACTION OF $Na[Co(CO)_4]$ WITH C_6H_4-1,4-$(COCl)_2$:

$Co_2(CO)_8$ (1g, 2.93mmol) was suspended in THF (30ml) and stirred over a sodium amalgam (0.2g Na in 4ml Hg) for 2h at room temperature. The resulting grey solution of $Na[Co(CO)_4]$ (5.86mmol) was added to solution of C_6H_4-1,4-$(COCl)_2$ (0.6g, 2.95mmol) in THF (5ml). The mixture was stirred for 26h at room temperature. An infra-red spectrum of the reaction mixture showed bands at 2106 s, 2048 s, 2026 s, 2004 vs and 1695 m cm^{-1}. The spectrum resembles that of acyltetracarbonyl cobalt compounds. The product appears extremely air sensitive. Removal of the solvent, left a dark brown residue which was extracted with CH_2Cl_2 and filtered. Evaporation of the filtrate gave a brown solid, the infra-red spectrum of which, showed it to be mainly $Co_2(CO)_8$ and a trace of $Co_4(CO)_{12}$ [14].

Addition of PPh_3 to reaction mixture:

The above reaction was repeated, using the same amount of reagents. After stirring for 18h at room temperature, PPh_3 (1.5g, 5.86mmol) was added. The reaction mixture was stirred for a further 3 hours at room temperature. The solvent was removed, leaving a green residue. This was extracted with CH_2Cl_2 and filtered. The filtrate was reduced to *ca*. 10ml and chromatographed on a Florosil column (made up with hexane). A dark orange-brown band was eluted using CH_2Cl_2/hexane (1:1) and gave a brown solid on evaporation. This was identified as unreacted $Co_2(CO)_8$ (60%). A yellow band was eluted using 30% ethanol/CH_2Cl_2. Evaporation of this solution gave a yellow solid, which was identified as $[Co(CO)_3(PPh_3)]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ <u>53</u> (8%). A third band (brown) could not be removed from the column.

6.4.5 SYNTHESIS OF $[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 55 :

To a solution of chlorotris(triphenylphosphine)rhodium(I) (0.5g, 0.54mmol) in CH_2Cl_2 (10ml) was added a solution of C_6H_4-1,4-$(COCl)_2$ (0.055g, 0.27mmol) in CH_2Cl_2 (2ml). The reaction mixture was stirred for 6.5h at room temperature. During this time, the solution changed colour from red to yellow, with a fine precipitate forming. The reaction was quenched by the addition of hexane (100ml). The mixture was filtered and the orange-yellow precipitate was washed with CH_2Cl_2 (4x10ml). This yielded $[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ as yellow microcrystals (74%). The m.p., analytical and infra-red data are listed in Tables 4.1 and 4.2 (Chapter 4).

6.4.6 PREPARATION OF C_6H_4-1,4-$[Mn(CO)_5]_2$ 56 :

$[Mn(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ (0.12g, 0.24mmol) was suspended in toluene (10ml). The reaction mixture was refluxed for 1h under N_2. The pale yellow solution was then filtered while still hot. The filtrate was evaporated to ~5ml and then cooled to -15°C. A white solid precipitates out of solution which was filtered off yielding 56 as a white microcrystalline solid (74%). The m.p., analytical and spectral data are listed in Tables 4.4 - 4.6 (see Chapter 4).

6.4.7 PREPARATION OF C_6H_4-1,4-$[Re(CO)_5]_2$ 57:

$[Re(CO)_5]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ (0.05g, 0.064mmol) was suspended in methyl isobutyl ketone (5ml). The mixture was refluxed for 35 minutes and then filtered while still hot. The filtrate was reduced to about 3ml and then cooled (-15°C). A white solid precipitated out of solution and was filtered to give 57 as white microcrystals (56%). The m.p., analytical and spectral data are listed in Tables 4.4 - 4.6.

6.4.8 ATTEMPTS TO DECARBONYLATE $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 52:

Thermolysis

(a) *In Toluene*

A suspension of 52 (0.1g, 0.21mmol) in toluene (10ml) was heated for 24h. During this time no change occurred as monitored by infra-red spectroscopy. Removal of the solvent left a yellow solid, which was identified as unreacted starting material (96%).

(b) *In Xylene*

A suspension of 52 (0.1g, 0.21mmol) in xylene (10ml) was refluxed for 22h. During this time extensive decomposition of starting material occurred. The solvent was removed leaving a dark brown residue. This was extracted with benzene and chromatographed on an alumina column (made up with benzene). Elution with benzene/CH_2Cl_2 (3:1) gave a yellow solution, which on evaporation yielded a yellow solid. This was identified as unreacted starting material (26%). A red band was eluted with CH_2Cl_2 and on evaporation gave a dark red solid, identified as $[CpFe(CO)_2]_2$ (60%).

Photolysis

Compound **52** (0.2g,0.42mmol) was dissolved in toluene (200ml) and the mixture irradiated with a broad band u.v. source for 1h at room temperature. The solution, which was originally yellow and clear, became cloudy and a dark brown precipitate formed. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The yellow solid was extracted with benzene and then chromatographed on an alumina column (made up with benzene). Elution with 10% CH_2Cl_2/benzene gave a faint yellow solid on evaporation. This was identified as unreacted starting material. A second yellow band eluted with CH_2Cl_2/benzene (1:1), gave C_6H_4-1,4-$[CpFe(CO)_2]_2$ as a yellow microcrystalline solid (12%). The m.p., analytical and spectral data are found in Tables 4.4 - 4.6.

Chemical decarbonylation with $XRh(PPh_3)_3$ (X = Cl,Br)

General procedure:

A mixture of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ (0.21mmol) and $XRh(PPh_3)_3$ (0.42mmol) in CH_2Cl_2 or benzene (10ml) was stirred at room temperature. The reaction was monitored by infra-red spectroscopy in the region 2200 - 1600cm^{-1}.

Stirring was continued until no further change in the infra-red spectrum was detected. The colour of the solution changed from red to orange with a fine precipitate forming. This was filtered off to give a yellow solid, which was identified as Rh(CO)$(PPh_3)_2$X by comparison of its IR spectrum with that reported in the literature . The solvent was removed from the filtrate leaving a brown residue. This was extracted with benzene and chromatographed on an alumina column (made up with benzene). Elution with benzene/CH_2Cl_2 separated the reaction products. The eluted solutions were evaporated under reduced pressure and the products identified by infra-red, ^{1}H nmr and microanalysis.

Reaction of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ <u>52</u>, *with* $Rh(PPh_3)_3Cl$.

The reaction of <u>52</u> (0.21 mmol) with $ClRh(PPh_3)_3$ (0.42 mmol) in CH_2Cl_2 (10 ml) for 23h at room temperature gave an orange mixture. This was worked up as described above. A yellow band eluted with CH_2Cl_2/benzene gave a yellow solid on evaporation. This was identified as C_6H_4-1,4-$[CpFe(CO)_2]_2$. (20%). The characterization data are listed in Tables 4.4 - 4.6. A red band remained immobile on the column and could not be eluted.The yield of Rh(CO)$(PPh_3)_2$Cl obtained from reaction was 71%.

Reaction of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 52 *with* $Rh(PPh_3)_3Br$:

The reaction of <u>52</u> (0.43 mmol) with $Rh(PPh_3)_3Br$ in CH_2Cl_2 (10ml) for 2h at room temperature gave an orange mixture. The reaction was worked up as described above. Rh(CO)$(PPh_3)_2$Br (84%) was obtained by filtering the reaction mixture. Evaporation of the filtrate, followed by extraction and chromatography on an alumina column separated two products. A yellow band eluted with CH_2Cl_2/benzene (1:1), gave a mixture containing mainly C_6H_4-1,4-$[CpFe(CO)_2]_2$ and a trace of $Rh(CO)(PPh_3)_2Br$. A second yellow band was eluted with pure CH_2Cl_2 and on evaporation gave a yellow residue. This contained mainly $Rh(CO)(PPh_3)_2Br$ and a trace of an unidentified acyl species. The fraction containing C_6H_4-1,4-$[CpFe(CO)_2]_2$, was triturated with small portions of CH_2Cl_2. The insoluble $Rh(CO)(PPh_3)_2Br$ was filtered off, leaving a yellow filtrate. Removal of the solvent gave C_6H_4-1,4-$[CpFe(CO)_2]_2$ as a yellow microcrystalline solid (26%) (see Tables 4.4 - 4.6 for characterization data).

The reaction of 52 with $Rh(PPh_3)_3Br$ in benzene was carried out in a similar fashion. The work up of the reaction mixture yielded three products: $Rh(CO)(PPh_3)_2Br$ (7%), C_6H_4-1,4-$[CpFe(CO)_2]_2$ (15%) and $Cp(CO)_2Fe$-C_6H_4-$COFe(CO)(PPh_3)Cp$ 59, (21%). m.p. 117-121°C. Found: C, 66.30; H, 4.4% $C_{38}H_{29}Fe_2O_4P$ requires: C,65.93; H, 4.2%. IR (CH_2Cl_2) 2017 vs, 1961 s, 1916 m, 1554 m; ^1H nmr ($CDCl_3$) δ7.30 17H, m, aryl), δ6.94 - 6.80 (2H, m, ArCOFe), δ4.82 (5H s, C_5H_5), δ4.50 (5H, d, C_5H_5).

Chemical decarbonylation of 52, with $[Rh(PPh_3)_2Cl]_2$

A mixture of 52 (0.2g, 0.41 mmol) and $[Rh(PPh_3)_2Cl]_2$ (0.54g, 0.41 mmol) in benzene (10ml) was stirred for 22h at room temperature. The solvent was removed under reduced pressure leaving a brown residue. Methylene chloride was added to the residue, resulting in a yellow solid precipitating out of solution. This was filtered off to yield a yellow microcrystalline solid, which was identified as $ClRh(CO)(PPh_3)_2$ (85%). The filtrate was taken to dryness and dissolved in ~5 ml benzene. The solution was chromatographed on an alumina column (made up with benzene). A yellow band eluted with benzene/CH_2Cl_2 (1:1) gave a yellow solid on evaporation. The infra-red and ^1H nmr spectra of this compound was identical to that of C_6H_4-1,4-$[CpFe(CO)_2]_2$ (18% yield). A brown band could not be eluted even using polar solvents such as chloroform and methanol, with the result that this portion decomposed on the column.

6.4.9 Reaction of $Na[CpFe(CO)_2]$ with 1,4-Dibromobenzene:

To a solution of $Na[CpFe(CO)_2]$ (5.6 mmol) in THF (30 ml), was added a solution of 1,4-dibromobenzene (2.8 mmol) in THF (5 ml). The mixture was refluxed for 24h under nitrogen. The reaction was allowed to cool and the solvent evaporated under reduced pressure. The brown residue was extracted with CH_2Cl_2 and filtered giving a dark brown filtrate. This was evaporated under reduced pressure. The residue obtained, was extracted with hexane and chromatographed on an alumina column (made up with hexane). A pale yellow band was eluted with hexane/benzene (1:1) and gave a creamy solid on evaporation. The infra-red and ^1H nmr of this portion showed that it contained mainly 1,4-dibromobenzene. A second yellow band eluted with 30% hexane/benzene, yielded a yellow solid on evaporation. Recrystallization from hexane (-15°C) gave yellow crystals of $[CpFe(CO)_2(4\text{-}BrC_6H_4)]$ (1.7%). m.p. 105-109°C. Found: C, 46.75; H, 2.60%, $C_{13}H_9BrFeO_2$ requires: C, 46.89; H, 2.72%. IR (CH_2Cl_2) ν(CO) 2019 s,1964 s cm^{-1}; ^1H nmr ($CDCl_3$) δ7.16 (4H, m, C_6H_4), δ4.83 (5H, s, C_5H_5).

A red band was eluted with benzene and gave a red solid on evaporation. This was identified as $[CpFe(CO)_2]_2$ (80%).

6.4.10 Reaction of $Na[CpFe(CO)_2]$ with 1,4 - Diiodobenzene.

A solution of 1,4-diiodobenzene (2.83 mmol) in THF (5 ml) was added to a solution of $Na[CpFe(CO)_2]$ (5.66 mmol) in THF (30 ml). The reaction mixture was heated under reflux for 19h. It was then allowed to cool and the solvent evaporated under reduced pressure. The red-brown residue was extracted with CH_2Cl_2 and filtered. The filtrate was taken to dryness, leaving a brown residue. This was extracted with benzene and chromatographed on an alumina column (made up with hexane). A pale yellow band was eluted with hexane and gave a pale yellow solid on evaporation of the solvent. This was identified as 1,4-diiodobenzene on the basis of its infra-red and ^1H nmr spectra. A second yellow band eluted with hexane/benzene (1:1) gave a bright yellow solid. Recrystallization of the solid from hexane (-15°C) gave $CpFe(CO)_2(4\text{-}IC_6H_4)$ as yellow microcrystals (3.5%). m.p. 109-111°C. Found: C, 45.20; H, 2.40. $C_{13}H_9FeIO_2$ requires: C, 44.87; H, 2.61. IR(CH_2Cl_2) ν(CO) 2019 s, 1964 s cm^{-1} ; ^1H nmr ($CDCl_3$) δ7.14 (4H, m, C_6H_4), δ4.81 (4H, s, C_5H_5).

6.4.11 Attempts to prepare $C_6H_4\text{-}1,4\text{-}[Rh(PPh_3)_2(CO)Cl_2]_2$ 62.

$[Rh(PPh_3)_2Cl_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 55 (0.2g, 0.13 mmol) was suspended in chloroform (15 ml). The mixture was stirred at room temperature for 3 days. During this time, the reaction was monitored by withdrawing small aliquots and measuring the IR spectrum. At the start of the reaction, the spectrum of the reaction mixture, showed only one band, which appeared at 1703 cm^{-1}. This is due to the acyl species <u>55</u>. After about 18h at room temperature, a second band at 2075 cm^{-1} was observed. This band is thought to be due to the μ-phenylene compound <u>62</u>. After 2 days stirring at room temperature, there was not much change in the IR spectrum of the reaction mixture. It was therefore decided to heat the mixture at 50°C (4h). This resulted in a slight increase in the amount of both C_6H_4-1,4-$[Rh(PPh_3)_2Cl_2]_2$ and $ClRh(CO)(PPh_3)_2$. The reaction was heated until no further change in the infra-red spectrum of the reaction mixture could be detected. The solvent was removed, leaving a orange solid. This is insoluble in common organic solvents, with the result it was not possible to separate the mixture. Judging from the IR spectrum, the mixture contained about 15% of the μ-phenylene complex <u>62</u>.

6.4.12 <u>Attempted Thermal Decarbonylation of</u> <u>$[CpMo(CO)_3]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$</u>

A suspension of $[CpMo(CO)_3]_2\{\mu\text{-}COC_6H_4\text{-}CO)\}$ (20mg, 0.032 mmol) in benzene (10 ml) was refluxed under N_2. The reaction was monitored by IR spectroscopy in the region 2200-1600 cm^{-1} and heating was continued until no more starting material remained (*ca.*30 mins). The reaction mixture was reduced to about 3 ml and then chromatographed on an alumina column (made up in benzene). A red band was eluted with benzene and evaporation of the solution gave a red solid which was identified as $[CpMo(CO)_3]_2$ (77%). A brown band was also observed, but it was not possible to remove it from the column.

6.5 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 5:

6.5.1 Reactions of μ-(p-phthaloyl) complexes with Halogens:

Reactions of $[Mn(CO)_5]_2\{\mu-(CO-C_6H_4-CO)\}$ 50 with X_2 (1:4)

50 (0.19 mmol) was suspended in THF (5 ml). To this was added a solution of Br_2 (0.76 mmol) in THF (2 ml). The brown solution was stirred for 70 h at room temperature. The mixture was filtered and gave a yellow solid which was identified as unreacted starting material (42%). The filtrate obtained was evaporated and this gave an orange oily residue. This was washed with CH_2Cl_2 (5 ml). On doing so a fine white solid precipitates out of solution. This was filtered off to give C_6H_4-1,4-$(COOH)_2$ [12] (48%) and an orange filtrate, which on evaporation gave an orange solid. This was identified as $Mn(CO)_5Br$ (44%).

The reaction of 50 with I_2 (57 h) was carried out in the same way and the work up of the reaction yielded, unreacted starting material (48%), C_6H_4-1,4-$(COOH)_2$ (43%) and $Mn(CO)_5I$ (32%).

Reactions of $[Re(CO)_5]_2\{\mu-(CO-C_6H_4-CO)\}$ 51 with X_2 (1:2)

51 (0.13 mmol) was suspended in THF (5 ml). A solution of Br_2 (0.26 mmol) in THF (2 ml) was added and the mixture stirred at room temperature for 2h. During this time, the solid dissolved and gave a dark brown solution. The solvent was removed under reduced pressure, leaving a yellow-brown residue. This was washed with CH_2Cl_2, resulting in an off-white solid precipitating out

of solution. This was filtered off to give C_6H_4-1,4-$(COOH)_2$ (83%). The filtrate obtained was evaporated and this gave a pale yellow (almost colourless) solid, the IR spectrum of which, showed it to be $Re(CO)_5Br$ (74%).

The reaction of 51 with I_2 was performed in a similar fashion. The addition of I_2 (0.26 mmol) to a solution of 51 (0.13 mmol) in THF (5 ml) gave a dark brown solution. This was stirred at room temperature for 16h. The solvent was removed leaving a brown residue. This was washed with CH_2Cl_2 (5 ml). A white solid precipitated out of solution and was filtered off to give C_6H_4-1,4-$(COOH)_2$ (87%). The filtrate was filtered through a short alumina column to get rid of any excess I_2. The eluate was taken to dryness leaving a pale yellow solid which was identified as $Re(CO)_5I$ (69%).

Reactions of [CpFe(CO)$_2$]$_2${CO-C$_6$H$_4$-CO)} 52 *with X$_2$*

To a solution of 52 (0.21 mmol) in THF (5 ml), was added a solution of Br_2 (0.42 mmol) in THF (2 ml). The mixture was stirred for 20 minutes at room temperature. During this time the solution went dark red in colour. The solvent was removed leaving a red residue. CH_2Cl_2 (5 ml) was added to the residue resulting in a pale yellow solid precipitating out of solution. This was filtered off and washed with acetone to give a white solid which was identified as C_6H_4-1,4-$(COOH)_2$ (94%). The CH_2Cl_2 filtrate obtained earlier was evaporated leaving a red solid which was identified on the basis of its IR and ^1H nmr as $CpFe(CO)_2Br$ (85%).

The reaction of 52 with I_2 was carried out in a similar manner. Adding I_2 (0.20 mmol) to a solution of 52 (0.10 mmol) in THF (5 ml), gave a brown solution. This was stirred for 3 h at room temperature. The solvent was removed leaving a black residue. CH_2Cl_2 (5 ml) was added to the residue. This resulted in an off-white solid precipitating out of solution. The mixture was filtered and the white solid washed with CH_2Cl_2 (2 x 2ml). The white solid was identified as C_6H_4-1,4-$(COOH)_2$ (88%). The filtrate was then passed through a short alumina column to get rid of excess I_2. The eluted solution was evaporated and gave a brown solid. This was identified as $CpFe(CO)_2I$ (77%).

6.5.2. Reaction of $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 52 with PPh_3:

In refluxing Xylene

A mixture of 52 (0.2g, 0.41 mmol) and PPh_3 (0.215g, 0.82 mmol) in xylene (20 ml) was refluxed under N_2. The reaction was monitored by IR spectroscopy in the region 2200-1600 cm^{-1}. No reaction was detected even after heating for 3 days, however a fair amount of decomposition of the starting material took place. Removal of the solvent gave a yellow brown solid. This was washed with diethyl ether giving a yellow solid which was identified as unreacted starting material (78%). The filtrate was devoid of any carbonyl containing material.

In the presence of U.V. light.

A mixture of 52 (0.2g, 0.41 mmol) and PPh_3 (0.215g, 0.82 mmol) in toluene (200 ml) was photolyzed for 4h at room temperature. The reaction mixture was filtered and the solvent removed from the filtrate. The residue was extracted with benzene and chromatographed on an alumina column (made up with benzene). An orange band was eluted with benzene and on evaporation gave a sticky orange residue. This was triturated with hexane (10 ml), resulting in an orange solid coming out of solution. The mixture was filtered and the orange solid obtained was recrystallized from CH_2Cl_2/hexane. This gave C_6H_4-1,4-[CpFe(CO)(PPh_3)]$_2$ as orange microcrystals (9%) m.p. 98 - 107°C. Found: C, 72.45; H, 4.75%, $C_{54}H_{44}Fe_2O_2P_2$ requires: C, 72.18; H, 4.94%, IR (CH_2Cl_2) ν(SO) 1913 s; ^{1}H nmr ($CDCl_3$) δ7.34 (30 H, br m, P-C_6H_5), δ6.54 (4H, br s C_6H_4), 4.36 (10 H, br d).

A yellow band eluted with 10% CH_2Cl_2/benzene gave a yellow solid on evaporation. This was identified as C_6H_4-1.4-[CpFe(CO)$_2$]$_2$ (6%). A second yellow band was eluted with CH_2Cl_2/benzene (1:1), followed by pure CH_2Cl_2. Evaporation of the solution gave a yellow solid which was identified as unreacted starting material (53%).

6.5.3 Reactions of μ-(p-phthaloyl) complexes with K-Selectride.

Reaction of [Mn(CO)$_5$]$_2${μ-(CO-C$_6$H$_4$-CO)} 50 *with K-Selectride.*

A suspension of 50 (0.2g, 0.38 mmol) in THF (5 ml) was cooled to -78°C. To this was added K-Selectride (0.76 ml of a 1M THF Solution) via a syringe. The reaction mixture changed colour from yellow to orange almost immediately. Monitoring the reaction by IR spectroscopy in the region 2200-1500 cm^{-1}, showed strong bands at 1886 and 1557 cm^{-1}. The reaction was allowed to stir at -78°C for 30 mins, after which time it was slowly warmed up to room temperature (45 mins). On doing so, the band at 1557 cm^{-1} gradually disappeared, while the band at 1886 cm^{-1} became stronger. The solvent was removed and the residue extracted with CH_2Cl_2 and filtered. Removal of the solvent from the filtrate left a yellow solid which was identified as $Mn_2(CO)_{10}$ (61%).

Reaction of [CpFe(CO)$_2$]$_2${μ-(CO-C$_6$H$_4$-CO)} 52 *with K-Selectride.*

K-Selectride (0.82ml of a 1M THF solution) was added to a suspension of 52 (0.2g, 0.41mmol) in THF (10ml). The mixture was stirred at room temperature for 22h. During this time, the reaction was monitored by IR spectroscopy in the region 2200-1500 cm^{-1}. The IR spectrum showed bands at 1880, 1862, and 1587 cm^{-1}, in addition to the bands of the starting material. A second portion of K-Selectride (0.82ml) was then added and the mixture, stirred for an additional 2h at room temperature. The solvent was removed, leaving a brown residue. This was extracted with CH_2Cl_2 and filtered through a short alumina column. The eluted solution was evaporated to give a red solid which was identified as $[CpFe(CO)_2]_2$ (65%).

6.5.4 REACTION OF $[CpFe(CO)_2]_2\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ 52 WITH $LiAlH_4$.

52 (0.21g, 0.42mmol) was suspended in THF (10ml). To this was added $LiAlH_4$ (0.032g, 0.84mmol). The mixture was stirred for 20h at room temperature. During this time, the spectrum was monitored by IR spectroscopy in the region 2200-1500 cm^{-1}. The only species observed after 20h stirring were unreacted starting material and some $Na[CpFe(CO)_2]$ (1880 and 1860 cm^{-1}). The solvent was removed leaving a brown residue. This was extracted with benzene and chromatographed on an alumina column (made up with benzene). A red band eluted with CH_2Cl_2/benzene (1:1) gave a red solid on evaporation. This was identified as $[CpFe(CO)_2]_2$ (67%). A yellow-brown residue remained after extraction with benzene for chromatography. This was washed with diethyl ether (3x5ml) to give a yellow solid. The IR spectrum of this showed that it was unreacted starting material (29%).

6.5.5 REACTION OF $[Mn(CO)_5]_2\{\mu\text{-}CO\text{-}C_6H_4\text{-}CO)\}$ 50 WITH $LiBEt_3H$.

To a suspension of 50 (0.1g, 0.19mmol) in THF (10ml) was added $LiBEt_3H$ (0.38ml of a 1M THF solution). The mixture was stirred at room temperature for 24h. The reaction was monitored by IR spectroscopy in the region 2200-1500 cm^{-1}.

This showed bands at 1880 and 1560 cm^{-1} in addition to the bands of the starting material. The intensity of the band at 1880 cm^{-1} gradually increased with time, however after 24h stirring there was still a lot of starting material left (~40% judged from the IR spectrum of the reaction mixture). The solvent was removed leaving a yellow-brown solid. This was extracted with CH_2Cl_2 (a yellow insoluble material remained) and filtered. The filtrate was taken to dryness leaving a bright yellow solid which was identified as $Mn_2(CO)_{10}$ (54%). The yellow residue remaining after CH_2Cl_2 extraction contained unreacted starting material.

6.5.6 ATTEMPTED REACTION OF *μ*-(*p*-phthaloyl) COMPOUNDS WITH THF·BH_3.

$[Mn(CO)_5]_2\{\mu\text{-}(COC_6H_4CO)\}$ (0.2g, 0.38mmol) was suspended in THF (15ml) at -78°C. To this was added THF·BH_3 (0.76mmol). The mixture was stirred at -78°C for 1h. The reaction was monitored by IR spectroscopy in the region 2200-1500 cm^{-1}. No reaction was observed while stirring at -78°C. The reaction mixture was then allowed to warm up to room temperature over a period of 30 minutes. It was then stirred for a further 19h at this temperature. Still no reaction was observed under these conditions. The reaction mixture was then refluxed for 45 minutes. During this time, the solid dissolves and the colour changes from pale yellow to bright yellow. Monitoring the reaction by IR spectroscopy, showed that no more starting material remained after about 40 minutes refluxing. The reaction mixture was allowed to cool and the solvent removed under reduced pressure. The residue was extracted with CH_2Cl_2 and filtered. Evaporation of the filtrate gave a pale yellow residue which was found to consist solely of the μ-(*p*-phenylene) complex, C_6H_4-1,4-$[Mn(CO)_5]_2$ (60%).

The same product is isolated in the absence of THF.BH_3. Thus the reducing agent plays no role in the reaction.

The attempted reactions of C_6H_4-1,4-$[CpFe(CO)_2]_2$ and C_6H_4-1,4-$[Re(CO)_5]_2$ with THF.BH_3, showed that the latter had no effect on the μ-(*p*-phthaloyl) compounds.

6.5.7 Reactions of μ-(*p*-phenylene) compounds with Carbon Monoxide:

Reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ 56 with CO:

A 250 ml autoclave was charged with C_6H_4-1,4-$[Mn(CO)_5]_2$ (0.05g, 0.11 mmol) and THF (10ml). The autoclave was then pressurized with CO until a pressure of 30 atm was reached. The mixture was stirred at room temperature for 22h. The autoclave was vented leaving a pale yellow mixture containing a yellow precipitate. The solvent was removed leaving a pale yellow residue which was washed with diethyl ether leaving a white solid which was identified as [Mn(CO)5]2{1-(CO-C6H4-CO)} (84%).

Reaction of C_6H_4-1,4-$[Re(CO)_5]_2$ 57 with CO:

57 (0.1g, 0.14 mmol) and THF (10 ml) was charged into an autoclave which was then pressurized with CO until a pressure of 30 atm was reached. The reaction mixture was stirred at room temperature for 48h. The autoclave was

vented and the reaction mixture filtered. A white insoluble solid was obtained. This was washed with small portions of CH_2Cl_2 (3 x 2 ml) and dried to yield, $[Re(CO)_5]\{\mu\text{-}(CO\text{-}C_6H_4\text{-}CO)\}$ (20%). The filtrate was found to contain unreacted starting material.

The reaction of C_6H_4-1,4-$[CpFe(CO)]_2$ (0.23 mmol) with CO under similar conditions, yielded only unreacted starting material (98%) after 24h.

6.5.8 Reactions of μ-(*p*-phenylene) compounds with synthesis gas:

Reaction of C_6H_4-1,4-$[Mn(CO)_5]_2$ 56 with synthesis gas.

An autoclave was charged with C_4H_4-1,4-$[Mn(CO)_5]_2$ (0.1g, 0.21 mmol) and THF (10 ml). The autoclave was then pressurized with H_2/CO (1:1) until a pressure of 40 atm. was reached. The mixture was then heated at 70°C for 3.5h. The autoclave was allowed to cool to room temperature and then vented. The yellow reaction mixture was filtered and the solvent removed from the filtrate. The yellow residue obtained was extracted with hexane. On doing so, a fair amount of a white insoluble material was obtained. This was filtered off and dried to give a white powder, the IR, ^1H nmr and mass spectra of which were identical to those reported for C_6H_4-1,4-$(CH_2OH)_2$ [12,13], (69% yield). The filtrate obtained from the extraction with hexane was evaporated and gave a bright yellow solid, which was identified as $Mn_2(CO)_{10}$ (71%).

A similar reaction of C_6H_4-1,4-$[Re(CO)_5]_2$ 57 (0.14 mmol) with H_2/CO (1:1) under the same conditions as above yielded a complex mixture of products which could not be separated completely. Some of the products detected in the reaction mixture were unreacted starting material, the analogous μ-(*p*-phthaloyl) complex, C_6H_4-1,4-$(CH_2OH)_2$ and also an aldehydic species.

The reaction of the iron complex, C_6H_4-1,4-$[CpFe(CO)_2]_2$ 58 (0.23 mmol) with H_2/CO for 8h, yielded only unreacted starting material (58%) and some $[CpFe(CO)_2]_2$ (37%).

6.5.9 Reactions of μ-(*p*-phenylene) compounds with Sulfur Dioxide.

Reaction of C_6H_4-1,4-$[CpFe(CO)_2]_2$ 58, SO_2:

A thick-walled Carius tube, fitted with a teflon tap, was charged with 58 (0.03g, 0.07 mmol). SO_2 (*ca.* 10 ml) was condensed onto the solid and the tube sealed immediately via its teflon tap. The mixture was stirred at room temperature for 38h. Evaporation of the excess SO_2 gave a sticky orange residue. This was extracted with CH_2Cl_2, filtered and the filtrate evaporated leaving a yellow solid. This was recrystallized from CH_2Cl_2/hexane to give C_6H_4-1,4-$[CpFe(CO)_2SO_2]_2$ (77%) m.p. 174-181°C decomp. Found: C, 42.7; H 2.40%. $C_{20}H_{14}Fe_2O_8S_2$ requires: C, 43.04; H, 2.53%. IR (CH_2Cl_2) ν(CO) 2054 s, 2011 vs cm^{-1}; (Nujol) ν(SO) 1193 m, 1045 m cm^{-1}. ^1H nmr ($CDCl_3$) δ7.38 (4H, br s, C_6H_4), δ5.10 (10H, br s, C_5H_5).

Reaction of C_6H_4-1,4-[Re(CO)$_2$]$_2$ 57, with SO_2:

A mixture of 57 (0.05g, 0.07 mmol) in SO_2 (10 ml) was heated at 80°C for 48h in a sealed Carius tube. Evaporation of the SO_2 gave a creamy residue which was extracted with CH_2Cl_2 (4 x 20 ml) and filtered. The filtrate was taken to dryness leaving a white solid. This was recrystallized by dissolving in hot chloroform and adding hexane. Cooling the mixture at -15°C, gave C_6H_4-1,4-[Re(CO)$_5$SO$_2$]$_2$ as a white microcrystalline solid (33%). m.p. 198-210°C decomp. Found: C, 21.95; H 0.49%, $C_{16}H_4O_{14}Re_2S_2$ requires: C, 22.43; H, 0.47%. IR(CH_2Cl_2) ν(CO) 2158 w, 2045 vs cm^{-1}; (Nujol) ν(SO) 1186 s and 1048 ms cm^{-1}.

Reaction of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ 56 with SO_2:

The reaction of 56 (0.1g, 0.21 mmol) in SO_2 (*ca.*10 ml) was carried out in a similar fashion to that described above. After stirring for 60h at 80° C, the SO_2 was allowed to evaporate. This gave a pale yellow residue which was extracted with ethanol (3 x 20 ml) and filtered. The filtrate was taken to dryness leaving a yellow residue, an IR spectrum of which showed it to be a mixture of starting material and the expected sulfinato product. The residue was washed with CH_2Cl_2 (4 x 10 ml) and filtered to give a yellow microcrystalline solid. This was identified as C_6H_4-1,4-[Mn(CO)$_5$SO$_2$]$_2$ (18%) m.p. 166-173°C. Found C, 31.95; H, 0.68%. $C_{16}H_4O_{14}Mn_2S_2$ requires: C, 32.34; H, 0.68 IR (CH_2Cl_2) ν(CO) 2137 m, 2085 w, 2051 s, 2022 m, cm^{-1}; (Nujol) ν(SO) 1190 s, 1030 m cm^{-1}.

6.5.10 Reactions of μ-(*p*-phenylene) compounds with Halogens.

Reactions of C_6H_4*-1,4-[Mn(CO)*$_5$*]*$_2$ *56 with Halogens* X_2 *(1:2)*

56 (0.11g, 0.23 mmol) was dissolved in THF (8 ml). To this was added a solution of Br_2 (0.44 mmol) in THF (2 ml). The mixture was stirred at room temperature for 2.5h. The solvent was removed leaving a yellow residue. This was extracted with CH_2Cl_2 and chromatographed on an alumina column (made up with hexane). A yellow band was eluted with 10% ether/hexane and evaporation of the solvent gave a cream coloured solid. This was identified as 1,4-dibromobenzene, by comparison of its IR and ^1H nmr spectra with those of an authentic sample, (62% yield). A second yellow band was eluted with ether/hexane (1:1) gave a yellow solid on evaporation, the IR spectrum of which was identical to that of $Mn(CO)_5Br$ (74%).

The reaction of 56 (0.05g, 0.11 mmol) with I_2 (0.11 mmol) in THF (10 ml) was performed in a similar way. The brown solution obtained was stirred for 20h at room temperature. The work up of the reaction mixture was the same as that described above and this separated two products. A pale yellow band eluted with 10% ether/hexane gave a creamy solid on evaporation. The IR and ^1H nmr of this was the same as that of 1,4-diiodobenzene (54% yield). An orange band was eluted with ether/hexane (1:1), followed by 100% ether. Evaporation of the solution gave an orange solid, which was identified as $Mn(CO)_5I$ (61%).

Reaction of C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ 58 with Halogens X_2 (1:2).

A solution of Br_2 (0.46 mmol) in THF (2 ml) was added to a solution of <u>58</u> (0.1g, 0.23 mmol) in THF (10 ml). The brown mixture was stirred for 30 minutes at room temperature. The solvent was removed leaving a red-brown residue. This was extracted with CH_2Cl_2 and chromatographed on an alumina column (made up with hexane). A pale yellow band was eluted with 10% CH_2Cl_2/hexane. Evaporation of the solution gave a pale yellow solid. This was identified as 1,4-dibromobenzene (85%). A red band was eluted with CH_2Cl_2/hexane (1:1) and gave a red solid on evaporation, identified as CpFe(CO)$_2$Br by IR spectroscopy (82%).

The reaction of <u>58</u> with I_2 was carried out in the same way and the work up of the reaction mixture yielded two products, which were identified as 1,4 diiodobenzene (60%) and CpFe(CO)$_2$I (62%).

Reaction of C_6H_4-1,4-[Re(CO)$_5$]$_2$, 57 with Br_2

Addition of a solution of Br_2(0.28 mmol) in THF (2 ml) to a solution of 57 (0.1g, 0.14 mmol) in THF (10 ml), gave a dark brown reaction mixture, which was stirred at room temperature for 1.5h. The solvent was removed leaving a brown residue. This was chromatographed on an alumina column (made up with hexane). Elution with 10% CH_2Cl_2/hexane gave a pale yellow band. Evaporation of the eluted solution gave a cream solid which was identified as 1,4-dibromobenzene (76%). A second yellow band was eluted with CH_2Cl_2/hexane (1:1) followed by pure CH_2Cl_2. Removal of the solvent from the solution gave a pale yellow (almost colourless) solid. This was identified as $Re(CO)_5Br$ (81%).

6.5.11 Reactions of C_6H_4-1,4-[$Mn(CO)_5$]$_2$ 56 with Tertiary Phosphines:

Reaction of 56 with PPh_2Me:

A mixture of 56 (0.1g, 0.21 mmol) and PPh_2Me (0.084g, 0.42 mmol) in THF (10 ml) was stirred at room temperature for 20h. During this time the solution changed colour from colourless to pale yellow. The solvent was removed leaving a yellow oily residue. This was extracted with benzene and chromatographed on a Florosil column (made up with benzene). A colourless band was eluted with benzene and evaporation of the solution gave a white solid. This was found to be unreacted starting material (68%). A yellow band eluted with 20% diethyl ether/benzene followed by pure diethyl ether gave a sticky yellow residue. Hexane was added to the oily residue and the mixture cooled to -78°C. A pale yellow solid precipitated out of solution. The supernatant was syringed off and the solid washed with ice-cold hexane (3 x 5 ml). The washings were also syringed off and the solid allowed to warm up to room temperature. The product was dried in vacuo. This yielded C_6H_4-1,4-[$Mn(CO)_4(PPh_2Me)$]$_2$ as a pale yellow microcrystalline solid (23%), m.p. 161-164°C. Found: C, 58.95; H 3.80, $C_{40}H_{32}Mn_2O_8P_2$ requires: C, 59.40; H, 3,73, IR (CH_2Cl_2) ν(CO) 2065 m, 1988 ssh, 1969 vs, 1946 s cm^{-1}. ^1H nmr ($CDCl_3$) δ7.38 (20H, br m, C_6H_5) δ6.90 ppm (4H, s, C_6H_4), δ1.67 (6H, d, J = 9Hz, CH_3).

Reaction of 56 with PPh_2Me in the presence of Me_3NO:

56 (0.06g, 0.13 mmol) and PPh_2Me (0.052g, 0.26 mmol) were dissolved in CH_2Cl_2 (10 ml). Trimethylamine N-oxide dihydrate (0.03g, 0.26 mmol) was added with vigorous stirring. The reaction was followed by IR spectroscopy in the region 2200-1600 cm^{-1} and was continued until no further change in the IR spectrum of the reaction mixture could be detected. The volume of the reaction mixture was reduced to *ca.*4 ml. The CH_2Cl_2 solution was chromatographed on an alumina column (made up in hexane). A pale yellow band was eluted with 10% CH_2Cl_2/hexane. An IR spectrum of this portion showed no carbonyl bands in the region 2200-1600 cm^{1}. A second yellow band was eluted with CH_2Cl_2/hexane (1:1). Evaporation of the eluted solution gave a yellow residue was recrystallized from CH_2Cl_2/hexane to give C_6H_4-1,4-[Mn(CO)$_4$(PPh_2Me)]$_2$ (65%).

6.5.12 Reaction of C_6H_4-1,4-[Mn(CO)$_5$]$_2$ 56 with PPh_3 in the presence of Me_3NO:

56 (0.05g, 0.11 mmol) and PPh_3 (0.06g, 0.22 mmol) were dissolved in CH_2Cl_2 (10 ml). Me_3NO (0.024g, 0.22 mmol) was added with rapid stirring. The solution went yellow almost immediately. After *ca.*1h stirring at room temperature, no more starting material remained, as judged by IR spectroscopy. Removal of the solvent gave a yellow oily residue. This was dissolved in a 1:1 mixture of hexane/CH_2Cl_2. The solution was chromatographed on an alumina column (made up in hexane). A pale yellow band was eluted with 10% CH_2Cl_2/hexane and on evaporation gave a cream coloured solid (identified as PPh_3). A second yellow band was eluted with CH_2Cl_2/hexane (1:1). Evaporation of the

eluted solution gave a yellow solid. Recrystallization from CH_2Cl_2/hexane gave C_6H_4-1,4-[Mn(CO)$_4$(PPh$_3$)]$_2$ as a yellow microcrystalline solid (76%). m.p. 148-153°C. Found: C, 64.60; H, 3.45%, $C_{50}H_{34}Mn_2O_8P_2$ requires: C, 64.25; H, 3.67% IR (CH_2Cl_2) ν(CO) 2059 m, 1986 ssh, 1972 vs, 1942 s, ^{1}H nmr ($CDCl_3$) δ7.32 (30H, m, C_6H_5), δ6.74 (4H, s, C_6H_4)

6.5.13 Reaction of C_6H_4-1,4-[CpFe(CO)$_2$]$_2$ 58 with PPh$_3$:

A mixture of 58 (0.1g, 0.23 mmol) and PPh$_3$ (0.12g, 0.46 mmol) in benzene (150 ml) was photolyzed for 2h at room temperature. A fair amount of decomposition was observed during this time. The reaction mixture was filtered leaving an orange-red filtrate. This was reduced to *ca.* 5 ml. The solution was then chromatographed on an alumina column (made up with benzene). An orange band was eluted with pure benzene and gave an orange solid on evaporation. Recrystallization of the orange solid gave microcrystals of C_6H_4-1,4-[CpFe(CO)(PPh$_3$)]$_2$ (11%). (See Section 6.5.2 for characterization data). A yellow band was eluted with 10% CH_2Cl_2/benzene. Evaporation of the eluted solution gave a yellow solid, which was identified as unreacted starting material (71%). A red band was eluted with pure CH_2Cl_2 and gave a red solid on removal of the solvent. The IR spectrum of this showed it to be [CpFe(CO)$_2$]$_2$ (15%).

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