THE UNIVERSITY OF CALGARY

The Reactions of $Mn(CO)_5^-$ with Organic Halides

by

Andrew Peter Masters

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

JULY, 1987

THE UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, " The Reactions of $Mn(CO)_5^-$ with Organic Halides " submitted by Andrew Peter Masters in partial fulfillment for the degree of Doctor of Philosophy.

Ted Sorensen

Supervisor, Dr. T.S. Sorensen
(Chemistry)

Thomas G Back

Dr. T.G. Back (Chemistry)

Michael Benn

Dr. M.H. Benn (Chemistry)

Peter Bayliss

Dr. P. Bayliss
(Geology and Geophysics)

Dennis Tanner

Dr. D. Tanner
(University of Alberta)

(Date) *July 20 1987*

-ii-

ABSTRACT

The reactions of pentacarbonylmanganate anion with α-haloesters (XCR^1R^2COOEt), primary and secondary allylic halides, 2-bromoacyl halides (XCR^1R^2COX) and β, γ and δ-bromoacyl halides ($XCH_2(CH_2)nCOCl$, n = 1,2,3,) are described. These reactions were investigated using ^{55}Mn-N.M.R spectroscopy.

On reaction with $Mn(CO)_5^-$, ethyl 2-chloroethanoate and ethyl 4-chloro-2-butenoate give high yields of the corresponding σ-bonded alkyl and allyl enolate complexes by nucleophilic substitution. In contrast, α-bromo and α-iodoesters give significant yields of the non-substitution products $Mn(CO)_5X$ and $Mn_2(CO)_{10}$ in addition to substitution products. When these reactions are carried out in deuterochloroform, the organic by-products $DCRR^2COOEt$ are observed. The reaction of $Na^+[Mn(CO)_5^-]$ with ethyl 4-bromo-2-butenoate in tetrahydrofuran gives, in addition to the η^1-allyl complex (34%), $Mn(CO)_5Br$ (25%) and $Mn_2(CO)_{10}$ (42%). From this reaction four organic products were isolated: (a) ethyl 2-(2-carboethoxycyclopropyl)-3-butenoate, (b) ethyl 6-carbethoxy-2,6-heptadienoate, (c) ethyl 4-(2´-carboethoxycyloproyl)-2-butenoate, and (d) ethyl 2,6-octadien-1,8-dioate. The formation of the non-substitution products $Mn(CO)_5X$ and $Mn_2(CO)_{10}$ is discussed in terms of electron-transfer and halogen-metal exchange mechanisms, the latter mechanism providing the most likely explanation for the results.

The reaction of the pentacarbonylmanganate anion with 2-bromoacyl halides gives ketenes and $Mn(CO)_5Br$ exclusively, rather than the expected α-bromoacyl complexes. This reaction was developed into a

convenient method for preparing mono-alkyl, vinyl and methylene ketenes in high yields. The mechanism of this reaction was investigated by theoretical calculations based on the Hartree-Fock-Slater method which suggest that halogen-metal-exchange takes place.

Pentacarbonylmanganate anion reacts with β, γ and δ-bromoacyl halides ($XCH_2(CH_2)nCOCl$, n = 1,2,3,) to give the corresponding acyl complexes. These comlexes give debrominated alkenes on heating; however, the γ-bromoacyl complex gives some cyclopropane. The formation of cyclopropane from this complex is discussed in terms of a metallocycle intermediate.

The a, β-unsaturated η^1-bonded enolate complex, 4-oxo-4-ethoxy-2-butenyl manganese pentacarbonyl decarbonylates on heating to give the corresponding η^3-complex, which on further heating gives the η^5-bonded oxo-allyl complex. The structures of these complexes were determined by X-ray crystallography.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1   Introduction

1.1   Historical Background[1,2]

Organometallic compounds are defined as substances containing carbon-metal bonds and the earliest examples of these species are the alkyl zinc complexes Frankland[3] discovered in 1840 and a platinum olefin complex described by Zeiss[4] in 1827.

The first metal carbonyl complex $[PtCl_2CO]_2$ was described in 1868 by Schutzenberger[5], and in 1890 Mond[6] prepared $Ni(CO)_4$, and used this preparation as a means of purifying nickel. Shortly after this, in 1891, Mond[7] prepared $Fe(CO)_5$.

The bonding in metal carbonyl comlexes remained vauge for some time. It was not until 1951 that a suitable model was described for the bonding in such complexes, and the discovery of ferrocene[8,9,10] in the same year assured the future growth of organometallic chemistry.

In contrast to other transition metals, the history of manganese organometallics is not as comprehensive[11]. The first organometallic compound of manganese to be fully characterized was dimanganese decacarbonyl, whhich was first prepared[12] in 1949, but not described fully[13] until 1954. At this time manganese pentacarbonyl iodide[13], sodium pentacarbonyl manganate[13], manganocene[14,15] and cyclopentadienyl

manganese tricarbonyl[15,16] were also described. The first fully
characterized manganese (carbonyl) alkyl complex, methyl manganese
pentacarbonyl was described[17] in 1957.

1.2 Transition Metal Organometallics in Organic Synthesis

The potential of transition metal organometallics to mediate
novel organic reactions has led to some applications in organic
synthesis[18,19]. Transition metal carbonyl alkyl complexes have been
proposed as reagents for organic transformations, and this has been
explored in particular by Cooke[20] and Collman[21] for the chemistry
involving $Fe(CO)_4^{2-}$ $\underline{1}$, and its derivatives, $\underline{2}$ and $\underline{3}$. Such complexes
undergo reactions specific to transition metal compounds, like
oxidative addition/reductive elimination, and
carbonylation/decarbonylation as summarised below.

$$RFe(CO)_4^- \xleftarrow{\;RX\;} Fe(CO)_4^{2-} \xrightarrow{\;RX,\ CO\;} R\overset{O}{\overset{\|}{C}}Fe(CO)_4^-$$

$$\underline{2} \qquad\qquad \underline{1} \qquad\qquad \underline{3}$$

$$R'X \searrow \qquad \swarrow R'X$$

$$RCOR'$$
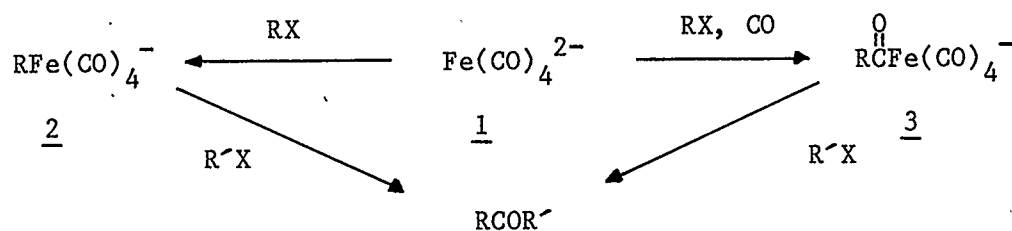
Somewhat similar chemistry has been developed by Heck[22] using
$Co(CO)_4^-$. Some organic reactions have also been developed
using[23] $CpFe(CO)_2^-$.

1.3 The Synthesis of Transition Metal (Carbonyl)

Alkyl and Acyl Complexes

There are a number of general methods for preparing acyl and alkyl transition metal carbonyl complexes, and some of these are described by reactions (1)-(7) below.

This thesis is concerned with the preparation and reactions of alkyl, acyl and allyl manganese carbonyl complexes produced by nucleophilic substitution reactions shown as numbers (5) and (1)[23]. A number of other methods for preparing alkyl and acyl manganese carbonyl complexes have been described.

(1)   M-X + R$^-$ M$^-$ + R-X   (2)

M-R

(3) M-H   R$^-$ N$^-$ M$^+$ (4)   R$^-$

$$M-\overset{\overset{O}{\|}}{C}-R$$

(5) M$^-$ + R$\overset{\overset{O}{\|}}{C}$-X   R$^-$ M$^+$-CO   (6)

M + R-X $\longrightarrow$ M$\underset{X}{\overset{R}{<}}$ (7)
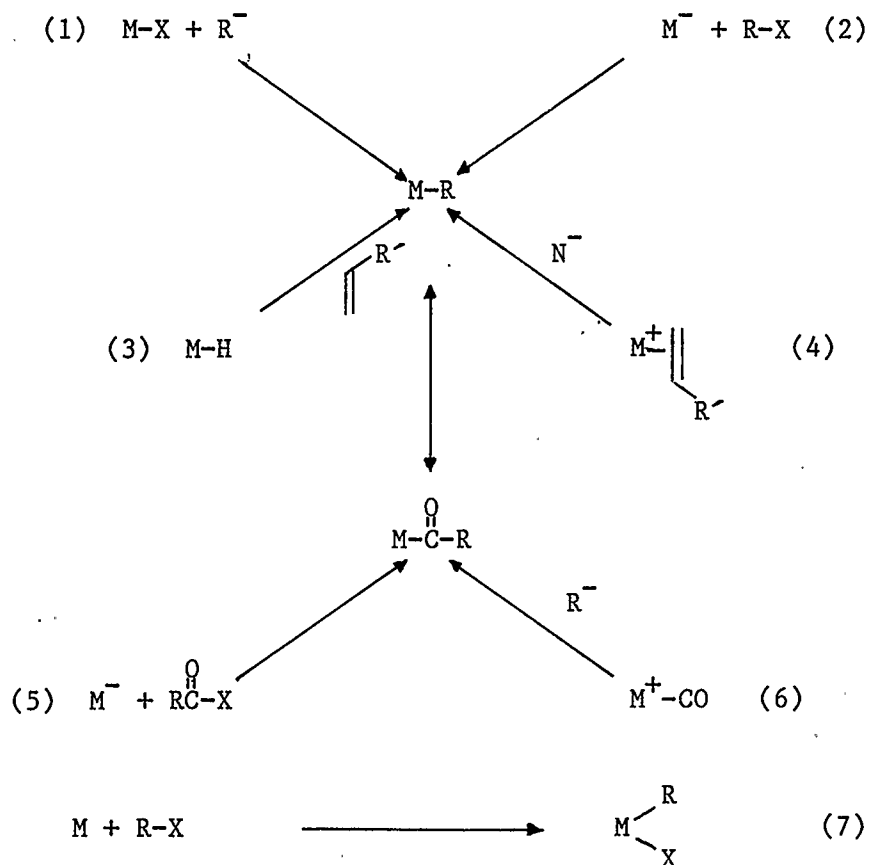
Treatment of metal halides with carbanions[24,25,26] (1) has been applied in manganese carbonyl chemistry but only for a limited number of cases and these are shown below.

$$(CO)_5MnBr + RLi \longrightarrow (CO)_5MnR + LiBr \qquad (8)$$
$$R = C_6H_5, \ CH_2SiMe_3 \qquad \underline{4}$$

$$(CO)_5MnBr + Ph_2PCH_2CH_2CH_2MgBr \xrightarrow{-CO}$$

$$+ \ MgBr_2 \qquad (9)$$
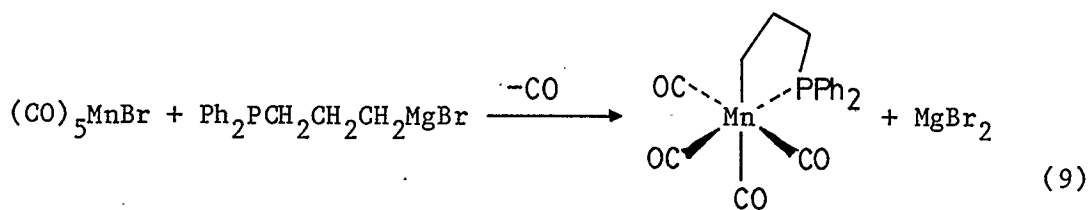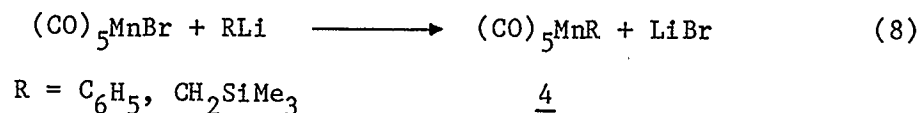
$$\underline{5}$$

This reaction is limited by the availability of suitable carbanions and is therefore not particularly general. This is reinforced by the fact that attack can occur at a carbonyl ligand rather than at the metal center to give anionic carbene complexes, $\underline{6}$, rather than the desired alkyl complex[27].

$$(CO)_5MnBr + MeLi \longrightarrow$$

$$\qquad (10)$$
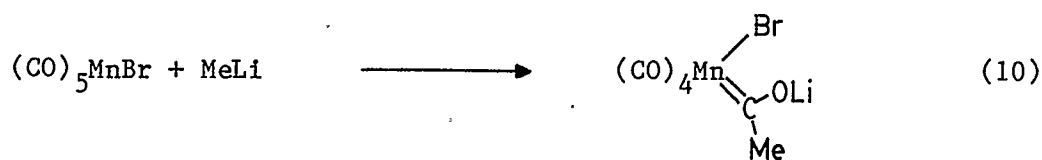
$$\underline{6}$$

Carbanions can also be used to prepare acyl complexes, for example, $\underline{7}$ shown below[28].

$$(CO)_6Mn^+X^- + PhCH_2MgCl \longrightarrow (CO)_5MnCOCH_2Ph + MgClX \quad (11)$$

$$\underline{7}$$
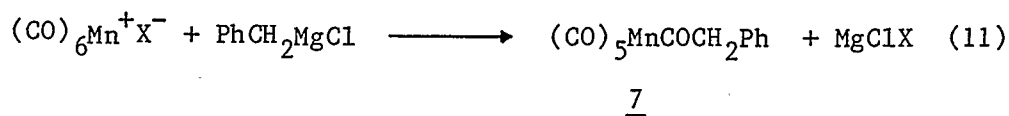
Treatment of alkenes and polyalkenes with metal hydrides has been used in a number of preparations, and in particular it can be used to prepare allyl complexes[29], for example, $\underline{8}$.

$$Mn(CO)_5H + \quad\quad \longrightarrow \quad\quad Mn(CO)_5 \quad\quad (12)$$

$$\underline{8}$$

This method is potentially useful, however manganese pentacarbonyl hydride is not readily available and is somewhat difficult to purify[30].

The other methods (reactions (4) and (7)) have not been applied in manganese chemistry, although the potential is there. The reaction of cationic alkene complexes with nucleophiles (4) has been studied[31] for iron complexes and has led to some useful transformations.

1.4 Overview and Objectives

The main aim of this thesis concerns the reactions of manganese pentacarbonyl anion and organic halides with a view to preparing manganese alkyl, acyl and allyl complexes as described in the previous section. This study develops into two broad areas, firstly the

general reactivity of $Mn(CO)_5^-$, and finally some of the reactions of

the acyl and allyl complexes generated using $Mn(CO)_5^-$. The

organization of this thesis reflects these themes, and although this

work is all related, topics have been separated into chapters, each

with a general introduction, results section and discussion. These

chapters address the following subjects:

Chapter 2: The reactions of $Mn(CO)_5^-$ with alkyl and allyl halides.

An original aim of this work was the preparation of allylic manganese

complexes, 9, which are potential precursors for functionalized η^3-

allyl compounds, 10, as shown below.

$$Na^+[Mn(CO)_5^-] + \quad\quad\quad \longrightarrow \quad\quad\quad \underline{9} \;+\; X^- \tag{13}$$
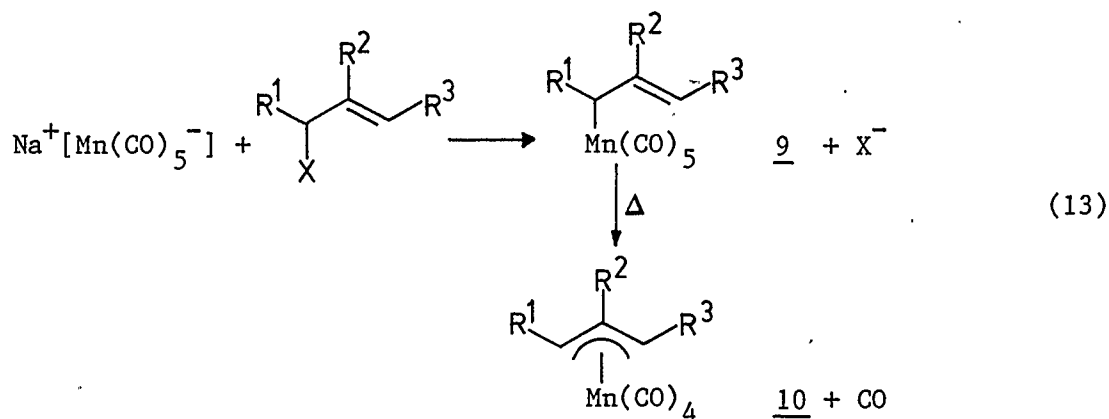
Examples of such reactions are well known [29,32] and it was

expected that this reaction would be reasonably general and would

therefore give high yields of both the η^1 and η^3 compounds, using a

variety of R substituents. However, an observation by Sorensen and

Oudeman[33], in this laboratory, that ethyl 4-bromo-2-butenoate ($R^1=R^2=H$

$R^3=COOEt$) reacts with $Mn(CO)_5^-$ to give only dimanganese decacarbonyl,

prompted a reinvestigation of $Mn(CO)_5^-$ reactions, since these appeared to be not as general as previously supposed. Using ^{55}Mn-N.M.R. as the primary tool of analysis, this reaction was found to give the desired allyl manganese complex, along with substantial amounts of manganese pentacarbonyl bromide as well as dimanganese decacarbonyl. This leads to the topic of Chapter Two, a study of the preparation of alkyl and allyl manganese carbonyl complexes using $Mn(CO)_5^-$, with the following objectives:

(a) To examine the reactivity of $Mn(CO)_5^-$ with akyl and allyl halides.

(b) To explore the factors which influence the yield of alkyl and allyl complexes from this reaction.

(c) To study the mechanism of the reaction.

This problem was approached by looking at the reactions of $Mn(CO)_5^-$ with 2-halo esters, with reference to three possible mechanisms: normal S_N2 displacement, halogen displacement with electron transfer (E.T.), and halogen metal exchange (H.M.E.).

Chapter 3 A second major objective of this thesis concerns the preparation of α, β, γ and δ-bromoacyl complexes of the general type, 11.

$$Mn(CO)_5^- + BrCH_2(CH_2)_n\overset{O}{\overset{\|}{C}}Cl \longrightarrow BrCH_2(CH_2)_n\overset{O}{\overset{\|}{C}}Mn(CO)_5 + Cl^- \quad (14)$$

$$\underline{11} \ n = 0,1,2,3.$$
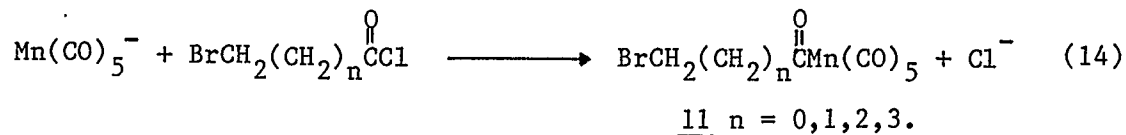
It was expected that 2-haloacyl complexes, $\underline{11}$ where n=0, could serve as precursors to methylene manganese complexes, $\underline{12}$ or $\underline{13}$.

$$XCH_2\overset{O}{\overset{\|}{C}}Mn(CO)_5 \quad\begin{array}{l} \nearrow \quad CH_2=\overset{X}{\overset{|}{Mn}}(CO)_4 + 2CO \\ \quad\quad\quad\quad \underline{12} \\ \\ \searrow \quad CH_2=Mn^+(CO)_5 + X^- + CO \\ \quad\quad\quad\quad \underline{13} \end{array} \qquad (15)$$
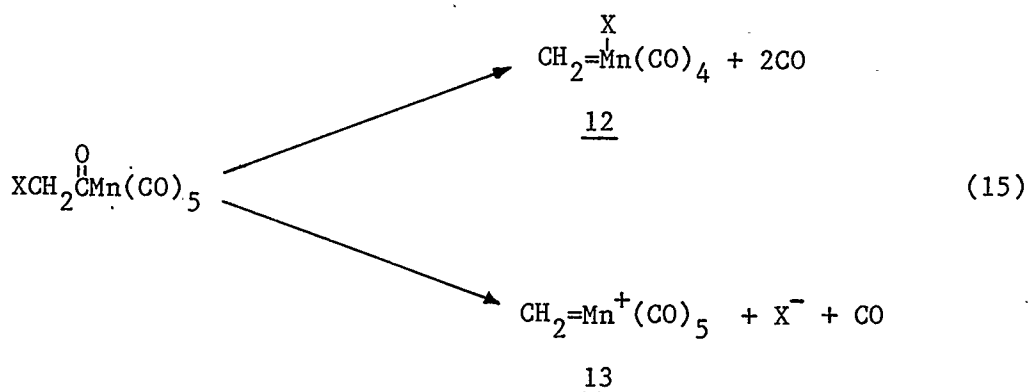
The reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides does not yield the desired acyl complex, $\underline{11}$, n=1, X=Br, but gives manganese pentacarbonyl bromide and ketenes, $\underline{14}$, instead:

$$Mn(CO)_5^- + BrCRR'COX \longrightarrow Mn(CO)_5Br + \overset{O}{\underset{R\quad R'}{\overset{\|}{\underset{\diagup\quad\diagdown}{C}}}} + X^- \quad (16)$$

$$\underline{14}$$
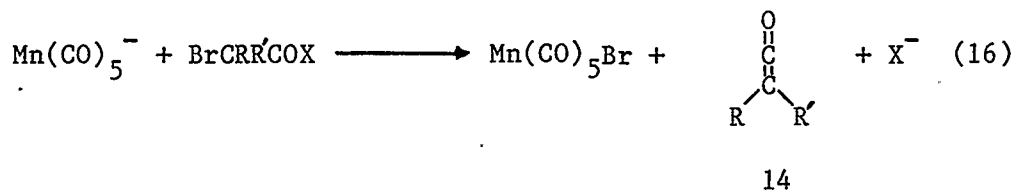
This is related to the reactions described in Chapter Two, but in this case $Mn(CO)_5Br$ is the sole product.

Acyl complexes with more remote bromine substitution $\underline{15}$, can however be prepared and this allowed a return to the original objective $\underline{i.e.}$ to see if the system would oxidatively add the carbon-bromine bond in an intra-molecular fashion, in this case to possibly give a metallocycle intermediate $\underline{16}$. This is a potentially useful reaction since a subsequent ring closure by reductive elimination would be subject to stereochemical factors as a result of using the metal center as an intermediate "template" in the cyclisation (17).

$$\text{BrCH}_2(\text{CH}_2)_n\text{CMn(CO)}_5 \xrightarrow{\ -\text{CO}\ }$$

$$\underline{15}\ n = 1,2,3$$

$$\underline{16}$$
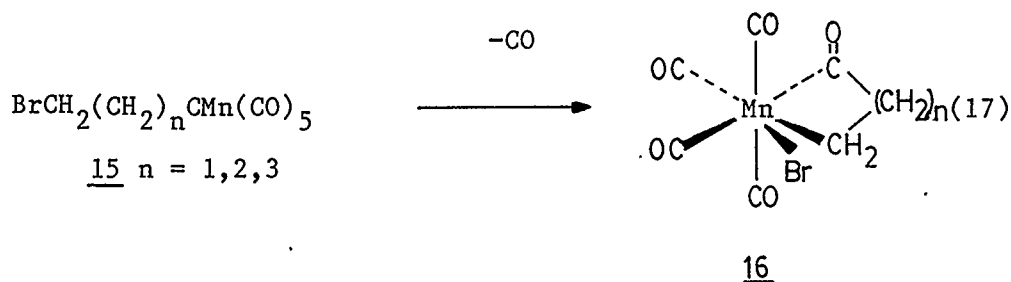
Chapter 4   The reaction of Mn(CO)_5^- with 2-bromoacyl halides is a potentially useful way of preparing ketenes. Thus it was decided to investigate this reaction as a practical ketene synthesis. Since the products of this reaction were straightforward, the mechanistic details of the reaction are treated separately, but it should be noted that the conclusions formed fit with the reactivity patterns of Mn(CO)_5^- in a more general sense. Theoretical calculations were carried out on this reaction and are included in the discussion.

Chapter 5   The final objective of this thesis relates to the structure and reactivity of complexes resulting from the thermal decarbonylation of manganese allyl esters as shown below.

$$\text{(18)}$$
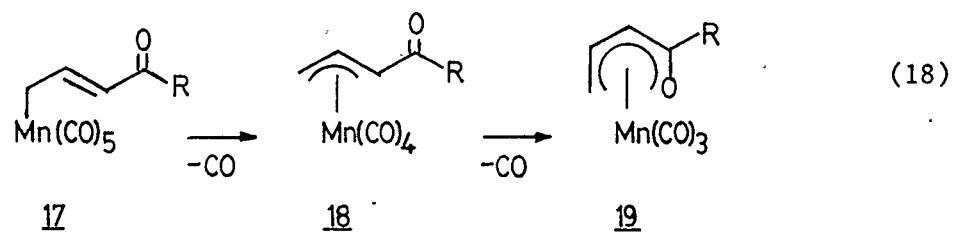
Since η^1, η^3 and η^5 bonding modes (complexes 17, 18, and 19 respectively) would all be accessible for the same ligand using this sequence, a full characterization of these complexes by X-ray crystallography was sought.

Chapter 2

2.1 Introduction: The Reactivity of $Mn(CO)_5^-$ with Organic Halides

The reaction of $Na^+[Mn(CO)_5^-]$ with organic halides to give

substitution products has been successfully used to prepare a number

of alkyl 20 and acyl 21 complexes in high yields[34].

$$(19)$$
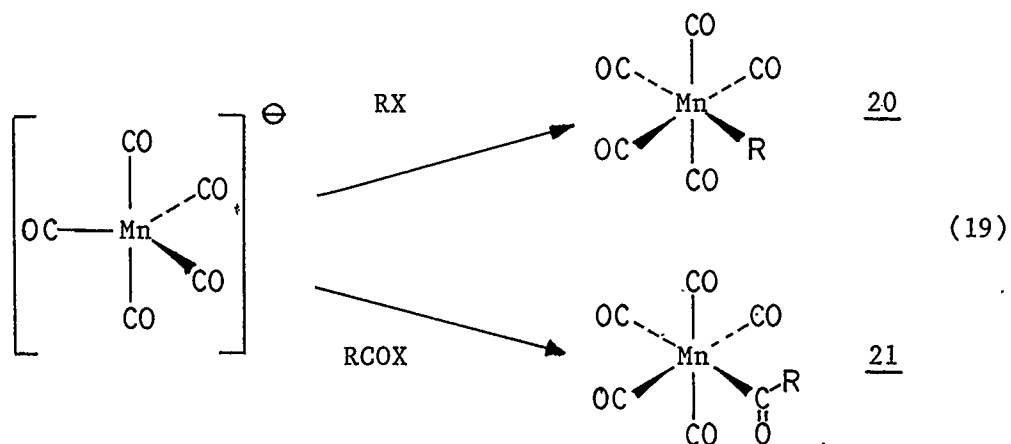
Such complexes are of interest since they can conceivably

undergo reactions such as carbonylation[35] (20) decarbonylation[36] (21),

addition/reductive elimination[37] (22), addition (23)[38] and the alkyl

ligand is readily decomplexed by treatment with acid (24)[39,40].

$$(CO)_5Mn-R \;\; \underset{-CO}{\overset{CO}{\rightleftharpoons}} \;\; (CO)_5Mn\overset{O}{\overset{\|}{C}}R \qquad (20),(21)$$

$$(CO)_5Mn-R \;\; \xrightarrow{R'M} \;\; (CO)_4\underset{COR'}{\overset{R}{Mn}}{}^- \;\; \xrightarrow{L} \;\; (CO)_4MnL^- + RCOR' \qquad (22)$$

$$(CO)_5Mn-R \xrightarrow{CO} (CO)_5Mn\overset{O}{\overset{\|}{C}}R \xrightarrow{\text{/==\\}} (CO)_5Mn-\overset{\overset{\displaystyle O\diagdown CR}{|}}{\underset{|}{}} \qquad (23)$$

$$(CO)_5Mn-R \xrightarrow{HX} (CO)_5MnX + R-H \qquad (24)$$

The substitution reactions of $Mn(CO)_5^-$ with organic halides are illustrated by the reaction of $Na^+[Mn(CO)_5^-]$ with methyl iodide and acetyl chloride, the latter reaction being described in <u>Inorganic Synthesis</u>[41], to give the methyl[17] and acyl complexes <u>22</u> and <u>23</u>, respectively.

$$Na^+[Mn(CO)_5^-] + CH_3I \longrightarrow CH_3-Mn(CO)_5 + NaI \qquad (25)$$
$$\underline{22}$$

$$Na^+[Mn(CO)_5^-] + CH_3\overset{O}{\overset{\|}{C}}Cl \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-Mn(CO)_5 + NaCl \qquad (26)$$
$$\underline{23}$$

The reaction is also successful for a number of functionalized organic halides; allyl and benzyl chloride or bromide react to give the corresponding substitution products[29,42] <u>24</u> and <u>25</u>,

$$Na^+[Mn(CO)_5^-] \quad \begin{array}{c} \xrightarrow{PhCH_2Cl} \quad PhCH_2-Mn(CO)_5 + Cl^- \\ \underline{25} \\ \\ \xrightarrow{\diagup\diagdown Cl} \quad \diagup\diagdown Mn(CO)_5 + Cl^- \\ \underline{24} \end{array} \qquad (27)$$

and similarly 2-chloro carbonyl compounds and chloro ethers

give $\underline{26}$ and $\underline{27}$[43,44].

$$\text{Na}^+[\text{Mn(CO)}_5^-] \quad \begin{array}{c} \overset{\text{O}}{\overset{\|}{\text{R}\text{C}\text{CH}_2\text{Cl}}} \nearrow \\[2em] \searrow \\ \text{ROCH}_2\text{Cl} \end{array} \quad \begin{array}{l} \overset{\text{O}}{\overset{\|}{\text{R}\text{C}}}\text{CH}_2\text{-Mn(CO)}_5 \ + \ \text{Cl}^- \\ \underline{26} \\[2em] \text{ROCH}_2\text{-Mn(CO)}_5 \ + \ \text{Cl}^- \\ \underline{27} \end{array} \qquad (28)$$

Thus the reaction seems quite general and Mn(CO)_5^- tolerates a number

of functional groups. However, Mn(CO)_5^- does not react[34] with vinyl

or aryl halides and simple secondary and tertiary alkyl halides are

reported to give only $\text{Mn}_2(\text{CO})_{10}$ and hydrocarbon[45] when treated with

Mn(CO)_5^-. This problem can be overcome by forming the corresponding

acyl complex first followed by decarbonylation and this is illustrated

by the preparation of phenyl manganese pentacarbonyl.

$$\text{Na}^+[\text{Mn(CO)}_5^-] + \text{PhCOCl} \longrightarrow (\text{CO})_5\text{MnCOPh}$$
$$\downarrow \Delta \qquad\qquad\qquad (29)$$
$$(\text{CO})_5\text{Mn-Ph} + \text{CO}$$
$$\underline{28}$$
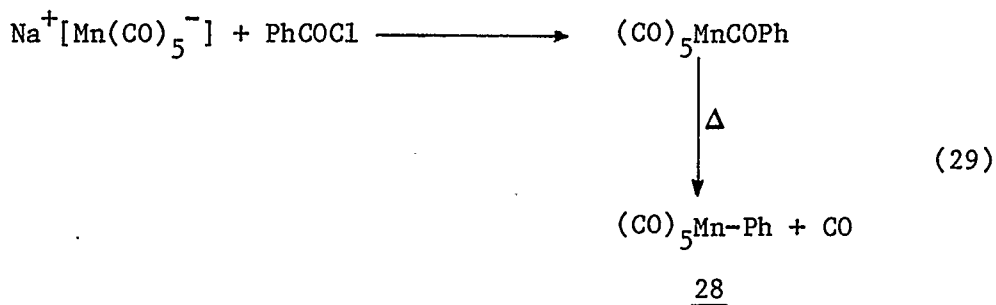
The mechanism of the substitution of halide by Mn(CO)_5^- has not

received a great deal of attention, although metalate anions in

general have been studied thoroughly[46,47], particularly Fe(CO)_4^{2-} and

CpFe(CO)_2^-. Pearson[48] has shown that in the reaction of optically

active (−) $BrCH_3CHCOOEt$ with $Na^+[Mn(CO)_5^-]$ there is 60% inversion, from which it was concluded, by analogy with other metal carbonyl anions, that the reaction follows an S_N2 mechanism[49].

$$(-)MeCHBrCO_2Et + Mn(CO)_5^- \xrightarrow{\text{inversion}} MeCH(COOEt)Mn(CO)_5 + Br^- \quad (30)$$

$$[\alpha]_D \quad -6.0°$$

$$Br_2 \downarrow \text{retention}$$

$$(+)MeCHBrCOOEt$$
$$[\alpha]_D \quad +1.0°$$
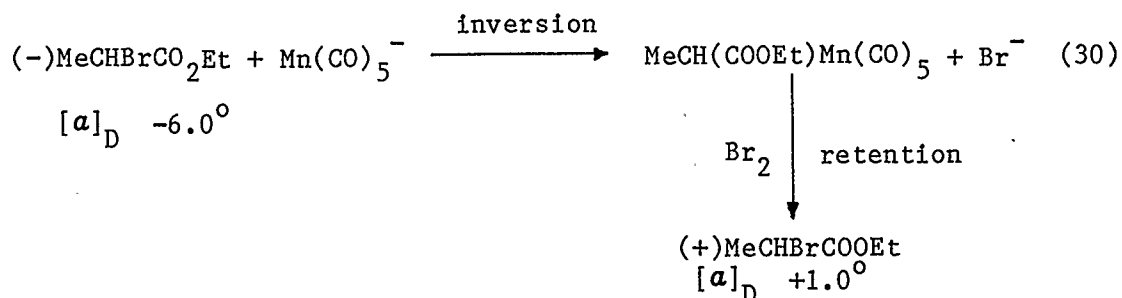
In a more recent study Pearson measured the relative rates of substitution for the reaction of various metalate anions with methyl iodide and methyl tosylate, including the reaction of $Na^+[Mn(CO)_5^-]$, and found evidence for an electron transfer component in the substitution reaction with methyl iodide[50].

The generality and reactivity of $Mn(CO)_5^-$ in substitution reactions has not been systematically studied. One would predict that the rate of substitution would depend on structural and electronic effects in a way associated with the S_N2 mechanism, with possible modifications if electron transfer is the preferred mode.

Some guide to the nucleophilicity of $Mn(CO)_5^-$ relative to other transition metal carbonyl anions comes from the rate data of Pearson[50,51], for the reaction of these anions with methyl iodide, given in Table 2.1. From this Table it is clear that $Mn(CO)_5^-$ is a relatively poor nucleophile, particularly when compared to $CpFe(CO)_2^-$; however, it is only ca. 10^2 times less reactive than

$Fe(CO)_4{}^{2-}$ and is more reactive than $Co(CO)_4{}^-$, two anions which have been used extensively to make alkyl complexes[21,22].

Anion	Rate Constant ($M^{-1}s^{-1}$)
$CpFe(CO)_2{}^-$	2.8×10^6
$CpRu(CO)_2{}^-$	3.0×10^5
$CpNi(CO)^-$	2.2×10^5
$Re(CO)_5{}^-$	1.0×10^3
$Fe(CO)_4{}^{2-}$	5.0×10^2
$Mn(CO)_5{}^-$	7.4
$CpW(CO)_3{}^-$	2.4
$CpMo(CO)_3{}^-$	1.5
$CpCr(CO)_3{}^-$	7.5×10^{-2}
$Co(CO)_4{}^-$	4.4×10^{-2}

Table 2.1   Nucleophilic Reactivities for Selected Carbonyl Metallate Anions with Methyl Iodide in Tetrahydrofuran[50].(Rate constants,$M^{-1}s^{-1}$).

The work outlined above leads one to expect that the substitution reactions of $Mn(CO)_5{}^-$ would be quite general in giving high yields of substitution products, at least for substrates

activated towards S_N2 nucleophilic substitution.

Some work carried out in the mid 1950's and early 1960's implies that there might be some competing reactions[34], for instance $Mn(CO)_5^-$ was found to react with tropylium bromide to give bitropyl and not the substitution product[52].

$$+ Na^+[Mn(CO)_5^-] \longrightarrow \qquad (31)$$

$$+Mn_2(CO)_{10} + 2NaBr$$
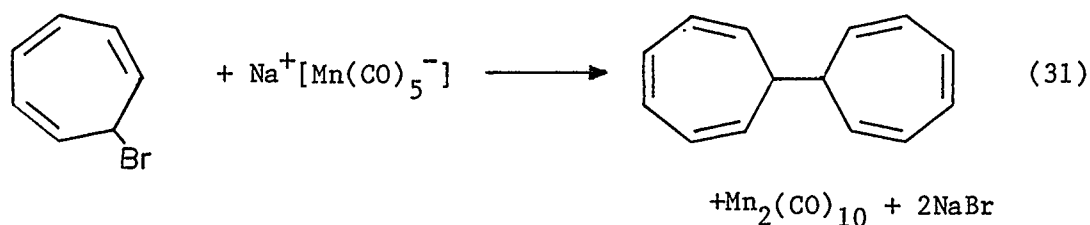
Also, the reaction of $Mn(CO)_5^-$ with some fluoroalkyl iodides yielded non-substitution products, giving coupling[53](32), elimination[54](33) and halogen exchange[55](34) instead:

$$Na^+[Mn(CO)_5^-] \xrightarrow{2CF_3I} F_3C\text{-}CF_3 + Mn(CO)_5I + NaI \qquad (32)$$

$$Na^+[Mn(CO)_5^-] \xrightarrow{IFC(CF_3)_2} \underset{F_3C}{\overset{F}{>}}C=CF_2 + Mn(CO)_5I + NaF \qquad (33)$$

$$Na^+[Mn(CO)_5^-] \xrightarrow{C_6F_5I} C_6F_5^-Na^+ + Mn(CO)_5I \qquad (34)$$
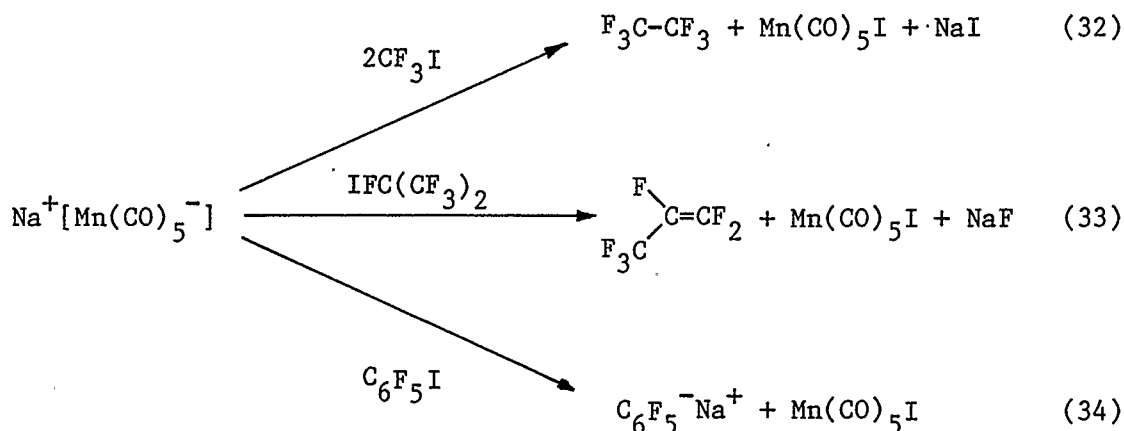
These early observations show that non-substitution products can be formed, but the dependence of these side reactions on the structure of the organic halide and the reaction conditions have not been defined. The original explanations for these non-substitution products were

based on the stability of the product, for instance tropylium

manganese pentacarbonyl was expected to decompose to give the observed

products. The products of the fluoroalkyl iodides with $Mn(CO)_5^-$ on

the other hand have been explained in terms of the reversal of

polarity of the C-I bond due to the inductive effects of fluorine

substitution[34,35].

More recent studies have dealt with the reactions of $Mn(CO)_5^-$

which give the desired substitution products, some of which were

described earlier, although Basolo[32] recently found that the reaction

of 2- and 3-t-butylallyl bromide with $Na^+[Mn(CO)_5^-]$ gave $Mn(CO)_5Br$ and

$Mn_2(CO)_{10}$ as by-products.

$$Mn(CO)_5^-$$ (35)
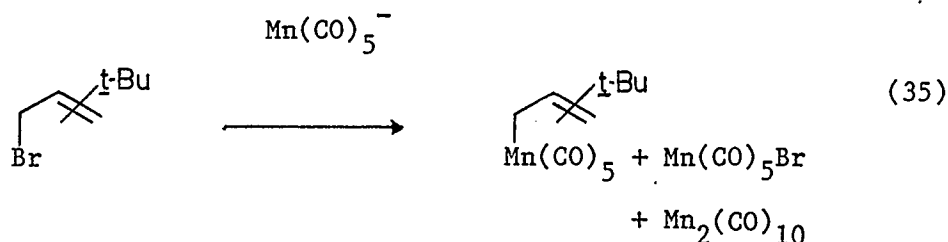
The yields of $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$ were not reported, nor was

the mechanism for their production discussed, but this does confirm

the earlier observation by Sorensen and Oudeman that the substitution

reaction of primary allylic halides with $Mn(CO)_5^-$ (see Section 1) may

not be as general as one might expect.

With these features in mind, this work has two main objectives:

(1) to look further at the generality of the substitution reaction of

$Mn(CO)_5^-$ with organic halides and (2) to try and find experimental

conditions which minimize side reactions (and by-products) in order to

enhance the possible synthetic utility of organo-manganese

intermediates

2.2 ^{55}Mn-N.M.R. Spectroscopy

In order to assess the efficiency of the reaction of Mn(CO)$_5^-$ with organic halides a suitable method was required to determine the yield of the alkyl products and to identify and quantify any biproducts in the reaction.

As was previously mentioned in Section 2.1, such reactions of Mn(CO)$_5^-$ might be expected to give manganese pentacarbonyl halides 30, Mn$_2$(CO)$_{10}$ 31, as by-products either exclusively or in addition to the alkyl or acyl complex 32.
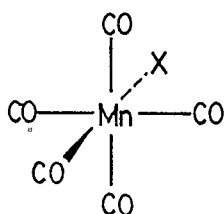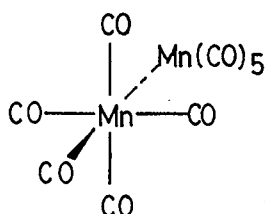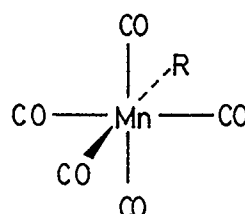
X = Cl, Br, I   R = alkyl, acyl
        30   31   32

Since alkyl complexes are frequently unstable under a number of work-up conditions, a method was sought which circumvented their isolation as a means of determining their yields. The classical technique, widely used for the identification of metal carbonyl complexes, is infra-red spectroscopy. While the carbonyl stretch region in the infra-red spectrum can give a great deal of information concerning the geometry of carbonyls at the metal center[56,57], this method is not always suited to the study of mixtures of structurally

related complexes such as 30, 31, and 32.

In contrast, ^{55}Mn-N.M.R., spectroscopy is very sensitive to the electronic environment of the manganese nucleus and resonances associated with 30, 31, and 32 are quite unique and widely separated in the ^{55}Mn-N.M.R. spectrum[58]. Thus, ^{55}Mn-N.M.R. was investigated as a technique for determining the yields of alkyl and acyl complexes in the reactions of Mn(CO)$_5$$^-$ with organic halides.

The nuclear magnetic properties of ^{55}Mn are listed in Table 2.2 along with those for ^{1}H and ^{13}C for comparison[59]. Clearly, ^{55}Mn is not a difficult nucleus to observe by N.M.R. spectroscopy, having 100% natural abundance and a sensitivity ca. 10^3 times that for ^{13}C. However, having a spin I=5/2 it has a quadrupole moment and so broad signals are expected, particularly for less symmetric complexes.

	^{1}H	^{13}C	^{55}Mn	
Spin:	1/2	1/2	5/2	
Natural Abudance:	99.98	1.11	100	(%)
Quadrupole moment:	–	–	0.55×10^{-28}m^2	
Receptivity:	5676	1.0	994	(/^{13}C)
Frequency:	200	50.3	49.34	(MHz)

Table 2.2. Nuclear Magnetic Properties of ^{55}Mn

The ^{55}Mn-N.M.R. chemical shifts of alkyl, acyl and halo manganese pentacarbonyl complexes were first investigated by Calderazzo[60] et al. in

1967 and the chemical shifts and line widths for these complexes are given in Table 2.3. There is a general trend in chemical shift associated with the polarity of the L-Mn bond, thus $ClMn(CO)_5$ (formally Mn(1)) is at low field, -985 ppm; $Mn_2(CO)_{10}$ (formally Mn(0)) at -2281 ppm and $Me_3SiMn(CO)_5$ (formally Mn(-1)) at high field, -2660 ppm. This wide range of chemical shifts is particularly useful and illustrates the sensitivity of metal nuclei in general to changes in the ligand. Since this early study, there have been a number of other manganese systems measured[58,59,60,61], particularly complexes of the general type $(CO)_5MnMR_3$ (M = Sn, Si, Ge)[62] and $HMn(CO)_{5-n}(PF_3)_n$[63]; however ^{55}Mn-N.M.R. spectroscopy has not been widely used in manganese carbonyl chemistry. Attempts to correlate the ^{55}Mn N.M.R. chemical shifts of manganese complexes with electronic parameters have been made[64,65], although in general chemical shift/structure relationships remain essentially empirical.

2.2.1 The Chemical Shifts of $Mn(CO)_5X$, $Mn_2(CO)_{10}$, $Mn(CO)_4X_2^-$ and $Mn(CO)_5^-$.

Some of the chemical shift data obtained in the present work is given in Table 2.4 and there is reasonably good agreement with the chemical shifts reported by Calderazzo[60] (Table 2.3). The chemical shift of $Mn_2(CO)_{10}$ in THF was determined from its measured frequency from $KMnO_4$ (in D_2O), although both signals could not be observed in the same

Table 2.3   [55]Mn-N.M.R. Chemical Shifts for Manganese Carbonyl

Complexes Reported by Calderazzo (in THF).

[a] with respect to $KMnO_4$ in D_2O

	Shift[a]	$W_{1/2}$ /Hz
$(CO)_5MnCl$	-1004	331
$(CO)_5MnBr$	-1160	688
$(CO)_5MnI$	-1485	1013
$(CO)_4 MnI_2^-$	-1020	4675
$(CO)_5MnCF_3$	-1850	3329
$(CO)_5MnCOCHF_2$	-1885	3729
$(CO)_5MnCOCH_2F$	-2010	4675
$(CO)_5MnCOCH_3$	-1895	3838
$(CO)_5MnCF_3$	-1850	3201
$(CO)_5MnCHF_3$	-1970	4183
$(CO)_5MnCH_2F$	-2130	4328
$(CO)_5MnCH_3$	-2265	3040
$(CO)_5MnCOCH_2Cl$	-1855	6365
$(CO)_5MnCOCHMe_2$	-1885	5184
$(CO)_5MnCOCH_2Et$	-1900	5820
$(CO)_5MnCOCH_2Me$	-1950	5002
$(CO)_5MnCOCH_2Ph$	-2035	9331
$(CO)_5MnH$	-2630	4347
$Na[Mn(CO)_5^-]$	-2780	10585
$(CO)_3MnCp$	-2225	10039
$Mn_2(CO)_{10}$	-2325	83

	Shift[a]	$W_{1/2}$ (Hz)
$(CO)_5MnCl$	-985	450
$(CO)_5MnBr$	-1156	790
$(CO)_5MnI$	-1450	1156
$(CO)_4MnBr_2^-$	-618	3800
$(CO)_4MnI_2^-$	-1011	4810
$(CO)_5MnH$	-2500	4105
$PPN^+[Mn(CO)_5^-]$	-2690	6500
$Li^+[Mn(CO)_5^-]$	-2694	6500
$Na^+[Mn(CO)_5^-]$	-2675	7100
$K^+[Mn(CO)_5^-]$	-2666	6800
$Mn_2(CO)_{10}$	-2281(-2325)[b]	74(83)[b]

Table 2.4 ^{55}Mn-N.M.R. Chemical Shift Data

for Manganese Carbonyls in THF

[a] ppm with respect to $KMnO_4$ in D_2O, $\pm$ 4 ppm.

[b] literature value[60]

spectrum. (The maximum spectral width obtainable on the Varian XL-200 is 50kHz or ca. 1000 ppm). Because of this, $Mn_2(CO)_{10}$ was used in this work as a more convenient secondary reference. As a further consequence of this limited spectral window, where signals are more than 1000 ppm apart, the signal outside the region being observed is "folded back" into the observed spectrum. This effect can be taken into account and "folded" signals easily recognized.

The disparity between the chemical shift for $Mn_2(CO)_{10}$ reported here (-2281 ppm) and that reported in the literature[60] (-2325 ppm, a difference of 44 ppm) deserves some comment. Since the published chemical shifts also used $Mn_2(CO)_{10}$ as a secondary reference signal, a correction factor of 44 ppm should be applied to make the two sets of data compatible. Differences in the chemical shifts for other compounds are variable, even when the correction factor is applied, but the values are generally within +90 ppm. Of course, the published data is now quite old and N.M.R. spectrometers are somewhat more accurate today, having improved field stability.

The differences in the reported and observed line widths (the reported line widths for manganese pentacarbonyl halides are substantially lower than those reported here) can be explained since there are field dependent T_1 (T_2) relaxation times and these relaxation times are expected to be faster at the stronger fields used in the present work.

2.2.2 The ^{55}Mn-N.M.R. Chemical Shifts for Alkyl, Acyl and Allyl Manganese Carbonyl Complexes

The chemical shifts determined in this work for a variety of alkyl, acyl and allyl manganese carbonyl complexes are given in Tables 2.4 and 2.5.

Some refinements in structure/chemical shift correlations can now be made additional to those discussed earlier. Unsaturation in the ligand deshields the manganese nucleus by about 54 ppm from $CH_3Mn(CO)_5$, i.e. data for η^1-allyl manganese pentacarbonyl. This effect is even stronger in oxo-analogues such as the ester complex $(CO)_5MnCH_2COOEt$, which is 92 ppm to lower field of the methyl complex. Further alkyl substitution at the carbon bonded to manganese results in a further downfield shift, as in $(CO)_5MnCH(CH_3)COOEt$, which is shifted downfield from $CH_3Mn(CO)_5$ by 122 ppm. However, on the whole the chemical shifts for alkyl and acyl manganese pentacarbonyl complexes come in a relatively narrow range.

Loss of a carbonyl ligand and formation of the η^3-allyl complex has the reverse effect, illustrated by a 210 ppm upfield shift on going from η^1-$(CO)_5Mn$-$CH_2CH=CH_2$ 33 to η^3-$(CO)_4MnCH_2CHCH_2$ 34.

33 -2065ppm   34 -2275ppm

	Shift[a]	$W_{1/2}$(Hz)	solvent
$(CO)_5MnCH_3$	(-2265)	(3040)	THF
$(CO)_5MnCH_2CH=CH_2$	-2065	2010	THF
$(CO)_5MnCH_2CH=CHC_6H_5$	-2043	3050	THF
$(CO)_5MnCH_2CH=CHCOOEt$	-1949	3400	THF
$(CO)_5MnCH_2CH=CHCOOC_6H_5$	-1929	3800	THF
$(CO)_5MnCH_2CH=CHCOMe$	-1939	3000	THF
$(CO)_5MnCH_2COOC_2H_5$	-1929	2250	THF
$(CO)_5MnCH_2COOC_2H_5$	-1921	2900	$CHCl_3$
$(CO)_5MnCHCH_3COOC_2H_5$	-1900	2010	THF
$(CO)_5MnCHCH_3COOC_2H_5$	-1891	2600	$CHCl_3$
$\eta^3-(CO)_4MnCH_2CHCH_2$	-2275	1600	THF
$\eta^3-(CO)_4MnCH_2CHCHCOOC_2H_5$	-1981	3000	THF
$\eta^3-(CO)_4MnCH_2CHCHCOOC_6H_5$	-1941	3100	THF
$(CO)_3MnCp$	-2195	9200	THF
$(CO)_3MnCpMe$	-2188	10560	THF

Table 2.5 ^{55}Mn-N.M.R. Chemical Shift Data for Alkyl

and Allyl Manganese Carbonyl Complexes

a ppm with respect to $KMnO_4$ in D_2O, ± 4 ppm.

b corrected literature values[60].

c solution also contained $PPN^+ Cl^-$.

	Shift[a]	$W_{1/2}$ (Hz)
$(CO)_5MnCOCH_3$	(-1851)[b]	(3838)[b]
$(CO)_5MnCOCH_2Cl$	(-1855)	(6365)[b]
$(CO)_5MnCOCH_2CH_2Br$	-1842	6100
$(CO)_5MnCOCH_2CH_2CH_2Br$	-1874	7250
$(CO)_5MnCOCH_2CH_2CH_2CH_2Br$	-1888	7300
$(CO)_5MnCOC_6H_5$	-1827	5040
$(CO)_5MnCOCH_2CH=CH_2$	-1859	4610
$(CO)_5MnCOCH_2CH=CH-CH=CH_2$	-1857	5562
$(CO)_5MnCOCH=CH-CH_3$	-1877	7150
$(CO)_5MnCOCH=CH$	-1862	5410

Table 2.6 ^{55}Mn-N.M.R. Chemical Shift Data

for Acyl Manganes-Pentacarbonyl Complexes

in THF, 25°C.

[a] ppm with respect to $KMnO_4$ in D_2O ±4ppm.

[b] corrected literature values[60]

This effect is partially cancelled by electron withdrawing

substituents on the allyl ligand, with only a 32 ppm upfield shift on

going from 35 to 36.

| 35 -1949ppm | 36 -1981ppm |

Acyl complexes (RCOMn(CO)$_5$) also have resonances which come in a relatively narrow range of chemical shift in ^{55}Mn-N.M.R. spectroscopy, as the results in this work show (Table 2.5), although there is some overlap with values for alkyl and allyl complexes.

One feature that does appear to be general is that alkyl complexes are about 100 ppm to higher field than acyl complexes; this is illustrated by the 206 ppm difference on going from 37 to 38.

$$(CO)_5MnCOCH_2CH=CH_2 \xrightarrow{\;-CO\;} (CO)_5MnCH_2CH=CH_2 \qquad (36)$$

-1859 ppm   -2065 ppm

37   38

The chemical shift data obtained in this work is summarized in Figure 2.1.

2.2.3 Line widths in ^{55}Mn-N.M.R. Spectroscopy

As previously mentioned, ^{55}Mn-N.M.R. linewidths are very sensitive to the symmetry of the attached ligands, due to the

Figure 2.1 Summary of ^{55}Mn-N.M.R. Chemical Shifts

quadrupole moment of the nucleus. This is illustrated dramatically by the changes on going from the tetrahedral MnO_4^- 39 to "octahedral" $Mn(CO)_5Cl$ 40 to the "piano stool" complex $CpMn(CO)_3$ 41.

39

$W_{1/2} = 9Hz$

40

$W_{1/2} = 450Hz$

41

$W_{1/2} = 9200Hz$

The relationship between structure and the observed linewidth $(W_{1/2})$ of ^{55}Mn-N.M.R. signals is somewhat ill-defined, only broad generalizations like those made above can be made from the data presented here. Other workers have noted that for related complexes there is a relationship between chemical shift and linewidth[60,62], a feature which is observed for $Mn(CO)_5X$, (X=I,Br,Cl,H). For the alkyl and acyl complexes described here there is little correlation, the linewidth appears to be very sensitive to subtle changes in the attached ligand. The linewidth of ^{55}Mn-N.M.R. resonances is of practical significance, since in some complexes the signal is sufficiently broad that it cannot be distinguished from baseline noise. For example, it was not possible to observe a signal for the η^5-complex 42.

$$\underline{42}$$

By analogy with $CpMn(CO)_3$ one would expect the complex $\underline{42}$ to give a broad signal which would explain why no signal was observed.

2.3 The Preparation of Manganese Pentacarbonyl Anion

Many anionic transition metal complexes can be prepared by reduction of the corresponding metal carbonyl halide or bimetallic carbonyl complex. Manganese pentacarbonyl anion $\underline{43}$ is no exception and can be obtained by reduction of the readily available dimanganese decacarbonyl[66].

$$Mn_2(CO)_{10} \xrightarrow[\text{THF, 25}^\circ\text{C}]{\text{Reductant (2e}^-\text{)}} 2Mn(CO)_5^- \qquad (37)$$

Suitable reducing agents are lithium metal[67], dilute sodium amalgam[68,69], sodium potassium alloy[70] and lithium triethylborohydride[71,72]. Since the anion was required in this study with different alkali metal counterions, all these reducing agents were used and so their relative merits can be discussed.

Lithium wire is not very convenient to use since its surface must be constantly stripped in order to achieve reduction, simply stirring

the solution over freshly cut wire in THF at 25°C did not give any

$Li^+[Mn(CO)_5^-]$ even after stirring vigorously for 24 hours. Coarse

lithium sand on the other hand did effect reduction but frequently

required an unpredictable induction period, after which the reduction

was very rapid. Once the reduction had commenced it was quite

difficult to control, and if insufficient care was not taken, partial

or even complete decomposition of the anion took place.

Lithium or sodium triethylborohydride effects the reduction in a

fairly clean fashion, the by-products of the reduction being hydrogen

gas and volatile triethyl boron.

$$Mn_2(CO)_{10} + 2LiEt_3BH \xrightarrow[0° - 25°C]{1 \text{ hour}} 2Li^+[Mn(CO)_5^-] + H_2 + 2BEt_3 \qquad (38)$$

However, solutions prepared in this manner invariably contained 5

- 10% unreduced $Mn_2(CO)_{10}$ (determined by ^{55}Mn-N.M.R.) even after

prolonged reaction times. In order to achieve this degree of

conversion a 25% excess of the reducing agent is required[71], and since

$LiEt_3BH$ is a very efficient reductant for alkyl halides, this

introduces an unnecessary complication, particularly in mechanistic

studies.

The potassium salt of manganese pentacarbonyl anion can be

obtained by the room temperature reduction of $Mn_2(CO)_{10}$ using liquid

sodium-potassium alloy ($NaK_{2.8}$). This is a fairly convenient method,

but requires up to 5 hours to achieve complete reduction in THF.

Dilute (1%) sodium amalgam was found to be the most convenient

reducing agent for preparing $Na^+[Mn(CO)_5^-]$. Complete reduction is

possible after only 30 minute in THF, and the solution is easily separated from the mercury by transfer needle and filtering. A number of studies[73], including one carried out in this laboratory and discussed later, have shown that the solution can be contaminated with up to 10% of mercury salts. This problem can be eliminated by ensuring that all mercury is removed prior to use.

For preparative purposes $Na^+[Mn(CO)_5^-]$ was used exclusively, however in some cases this salt was converted into the μ-nitrido bistriphenylphoshine (+1) salt[74,75] (PPN$^+$) $\underline{44}$.

$$Na^+[Mn(CO)_5^-] + [Ph_3P=N=PPh_3]Cl^- \qquad (39)$$

$$\downarrow THF, 25^\circ C$$

$$[Ph_3P=N=PPh_3][Mn(CO)_5^-] + NaCl$$

$$\underline{44} \qquad 85 - 90\%$$

This salt has a number of advantages, since replacing sodium ion with a bulky counterion makes the salt much more stable to air oxidation[74]. $Na^+[Mn(CO)_5^-]$ can be isolated as a white microcrystalline salt from THF solutions but it is extremely air sensitive, decomposing exothermically upon brief exposure to the atmosphere. The PPN$^+$ salt on the other hand can be exposed to air for up to 2 hours before showing signs of decomposition and if stored under argon is stable indefinitely.

2.4 The Reduction of $Mn_2(CO)_{10}$ with Methyl Lithium

During a study carried out in the present work concerning the reaction of methyl lithium with alkyl manganese complexes, some

$Mn(CO)_5^-$ was observed in the reaction mixtures. This was eventually attributed to the reduction of $Mn_2(CO)_{10}$ impurity formed in in-situ preparations of these alkyl complexes. Since this is a potentially useful way of preparing $Li^+[Mn(CO)_5^-]$, the reaction was explored further. Treatment of a THF solution of $Mn_2(CO)_{10}$ with 2 equivalents of methyl lithium (as a LiBr complex in diethyl ether), at 25°C, resulted in the rapid formation of $Li^+[Mn(CO)_5^-]$ confirmed by the infra-red spectrum (ν_{co}1861 cm^{-1} and 1895 cm^{-1}) and ^{55}Mn-N.M.R. (δ= -2694 ppm).

The reaction was accompanied by the steady evolution of 0.7 - 0.9 equivalents (determined by gas burrette) of methane (identified by G.C. gas analysis), containing traces of ethane (7%) and ethylene (3%).

The yield of the anion was established by reaction with an excess of iodine (reaction (40)), from which $Mn(CO)_5I$ was isolated by flash chromatography in 54% yield and suggesting that the reaction is not as clean as the spectral data implied. Reaction of $Na^+[Mn(CO)_5^-]$, prepared using sodium amalgam, with iodine followed by flash chromatography gives a 92% yield of $Mn(CO)_5I$, and the Inorganic Synthesis preparation[76], using the same reagents, reports a 82% yield isolating the product by recrystallization. Some intractable polar material remained after the work-up of the methyl lithium reaction. Although this residue was soluble in THF the I.R.-spectrum of such a solution was broad and featureless.

$$Li^+[Mn(CO)_5^-] + I_2 \longrightarrow Mn(CO)_5I + LiI \qquad (40)$$

The formation of methane in this reaction is somewhat surprising since it implies that C-H bond cleavage takes place at some stage in the reaction. There is precedent[77] that the first step in this reaction involves attack at a carbonyl to give the carbene complex 45.

$$Mn_2(CO)_{10} + MeLi \longrightarrow Mn(CO)_5-\underset{\underset{Me}{\overset{\displaystyle C}{\diagup}}\overset{}{\diagdown}OLi}{\overset{\displaystyle ||}{Mn}}(CO)_4 \qquad (41)$$

$$\underline{45}$$

This carbene complex would be expected[78] to be in equilibrium with $Mn(CO)_5^-$ and $Mn(CO)_5Me$ as shown below:

$$Mn(CO)_5-\underset{\underset{Me}{\overset{\displaystyle C}{\diagup}}\overset{}{\diagdown}OLi}{\overset{\displaystyle ||}{Mn}}(CO)_4 \rightleftharpoons Li^+[Mn(CO)_5^-] + Mn(CO)_5Me \qquad (42)$$

In the present work no $Mn(CO)_5Me$ was observed in the I.R. or in ^{55}Mn-N.M.R. spectra taken during the reaction, even when after only one equivalent of methyl lithium had been added to the $Mn_2(CO)_{10}$. This mechanism would require that $Mn(CO)_5Me$ reacts further with methyl lithium to give methane, a reaction for which there is no precedent,

indeed attack at a carbonyl seems more likely[37].

$$Mn(CO)_5Me \xrightarrow{\text{MeLi}} Mn(CO)_5\overset{\ominus}{C}H_2 + CH_4 \qquad (43)$$

46

One could speculate that methyl lithium attacks the methyl group preferentially to give the carbanion **46** which either decomposes or reacts further to give the intractable products observed.

2.5 The Reaction of $Na^+[Mn(CO)_5^-]$ with Primary Alkyl Halides

Both methyl iodide and ethyl iodide have been shown[17,79] to react with $Mn(CO)_5^-$ to give the corresponding alkyl manganese complexes. In the present work solutions of 1-chlorobutane, 1-bromobutane or 1-bromoethane in THF did not react with $Na^+[Mn(CO)_5^-]$ at $25^{\circ}C$ even after four hours. The signal corresponding to $Na^+[Mn(CO)_5^-]$ remained unchanged in the ^{55}Mn-N.M.R. spectrum.

Because of this absence of reactivity the reaction of $Mn(CO)_5^-$ with substrates which are not activated towards S_N2 reactions was not investigated further.

2.6 The Reaction of $Na^+[Mn(CO)_5^-]$ with Primary Allylic Halides

The reaction of $Mn(CO)_5^-$ with allyl chloride or allyl bromide was described in 1961 by McClellan et al.[29], where it was found to give good yields of the allyl complex 24. Such complexes undergo thermal decarbonylation to give η^3-allyl complexes, which are potentially useful synthetic intermediates. This decarbonylation is more fully described in Chapter 5.

The reaction of allyl chloride and allyl bromide with $Na^+[Mn(CO)_5^-]$ was repeated in this study and the in situ yield of the allyl complex 24 determined by ^{55}Mn-N.M.R. spectroscopy. Tetrahydrofuran solutions of $Na^+[Mn(CO)_5^-]$ were rapidly mixed with neat allyl bromide or allyl chloride and the ^{55}Mn-N.M.R. spectrum measured. The immediate formation of a precipitate of sodium halide in both solutions indicated that a very rapid reaction took place and this was confirmed in the ^{55}Mn-N.M.R. spectrum, the signal corresponding to $Na^+[Mn(CO)_5^-]$ had disappeared within ten minutes and a new signal was observed at -2065 ppm corresponding to the allyl complex 24. The only other signal in the ^{55}Mn-N.M.R. spectrum corresponded to a trace of $Mn_2(CO)_{10}$ present in the $Na^+[Mn(CO)_5^-]$ solution to begin with. The allyl complex 24 was subsequently isolated and purified and shown to give the same ^{55}Mn-N.M.R. signal observed in the in situ experiment.

Similar results were also obtained for the reaction of $Na^+[Mn(CO)_5^-]$ with 3-chloro or 3-bromo-1-phenyl-1-butene 47, (this reaction has been described previously[80]).

$$\text{Na}^+[\text{Mn(CO)}_5^-] + \underset{\underset{X = \text{Cl or Br}}{\underset{47 \ R = Ph \ or \ H}{}}}{X}\diagup\!\!\!\diagdown\diagup R \longrightarrow \underset{24 \ >95\%}{\text{Mn(CO)}_5}\diagup\!\!\!\diagdown\diagup R + \text{NaX} \qquad (44)$$

The success of these reactions prompted a reinvestigation of the reaction of $\text{Na}^+[\text{Mn(CO)}_5^-]$ with ethyl 4-bromo-2-butenoate 48, previously observed by Sorensen and Oudeman to give only $\text{Mn}_2(\text{CO})_{10}$. This reaction was repeated in this study and ^{55}Mn-N.M.R. spectroscopy indicated that the reaction gave several products. Rapidly mixing of ethyl 4-bromo-2-butenoate with a THF solution of $\text{Na}^+[\text{Mn(CO)}_5^-]$ at 25°C resulted in the immediate formation of a precipitate of sodium bromide, and the ^{55}Mn-N.M.R. spectrum of this solution contained three resonances (see Figure 2.2). Resonances at -1156 ppm and -2281 ppm correspond to $\text{Mn(CO)}_5\text{Br}$, and $\text{Mn}_2(\text{CO})_{10}$ and a resonance at -1929 ppm was subsequently assigned to the allyl complex 49. The yields of these products were determined by integration of the ^{55}Mn-N.M.R. spectrum.

$$\underset{48}{\underset{Br}{}\diagup\!\!\!\diagdown\diagup\!\!\!\diagdown\overset{\overset{O}{\|}}{C}\text{OEt}} \quad \xrightarrow[\substack{\text{THF } 25^{\circ}\text{C} \\ 10 \text{ min.}}]{\text{Mn(CO)}_5^-} \quad \underset{\substack{49 \\ 34\%}}{\text{Mn(CO)}_5}\diagup\!\!\!\diagdown\diagup\!\!\!\diagdown\overset{\overset{O}{\|}}{C}\text{OEt} + \underset{25\%}{\text{Mn(CO)}_5\text{Br}} + \underset{42\%}{\text{Mn}_2(\text{CO})_{10}} \quad (45)$$

The products of this reaction could be separated and isolated by flash chromatography (silica/CH_2Cl_2) and the formation of $\text{Mn(CO)}_5\text{Br}$ and $\text{Mn}_2(\text{CO})_{10}$ was confirmed. The new compound 49 was isolated as a pale yellow air sensitive oil in 20% yield, and ^{55}Mn-N.M.R. spectroscopy confirmed that this product was responsible for the

Figure 2.2 <u>In situ</u> ^{55}Mn-N.M.R. Spectra for the Reaction of $Mn(CO)_5^-$

with Ethyl 4-halo-2-butenoate (THF, 25°C)

resonance at -1929 ppm in the [55]Mn-N.M.R. spectrum of the crude

reaction mixture. The full characterization of this compound is given

in Chapter 5.

Further elution of the flash chromatography column with diethyl

ether yielded a colourless oil. This material did not contain any

bands in the infra-red spectrum associated with metal carbonyls and

G.C. analysis indicated that it consisted of four organic products.

These products were separated by preparative G.C. and the mass spectra

indicated that these products all had a probable molecular ion at m/e

226, corresponding to dimerization of the ethyl butenoyl fragment.

The [1]H-N.M.R. spectra of these products were consistent with the

structures 50,51,52, and 53.

50 14%

51 21%

52 21%

53 43%

(ca 23% overall yield)

The diesters 50 and 51 are known, and the [1]H-N.M.R. spectra

obtained agree with those reported in the literature[81] for the same

compounds. The cyclopropyl diesters 52 and 53 are unreported, however

the protons of the cyclopropyl rings give characteristic high field

multiplets with chemical shifts similar to those reported for other substituted carbethoxy cyclopropanes[82].

The ^{1}H-N.M.R. spectrum of 52 contained resonances at 0.70 - 0.95 ppm and 1.45 ppm (multiplets) which were assigned to the protons of the cyclopropyl ring.

Compound 53 was isolated as an unequal mixture of diasteriomers which were only partially resolved in the G.C., but sufficient of each could be obtained for ^{1}H-N.M.R. analysis. Both isomers had similar spectra, the resonances for the cyclopropyl protons appearing at 0.82-0.92ppm, 1.48-1.63ppm and 1.75-1.79ppm.

Extensive double resonance experiments on all these compounds were also consistent with the structures 52 and 53.

2.7 The Effect of Solvent and Counterion on the Reaction of $Mn(CO)_5^-$ with Ethyl 4-halo-2-butenoate

Since the reaction of $Na^+[Mn(CO)_5^-]$ with ethyl 4-bromo-2-butenoate only gave a 34% yield of the corresponding alkyl complex, conditions were sought to improve this yield. The effect of changing the leaving group to chloride was considered first. In contrast to the reaction of ethyl 4-bromo-2-butenoate 48 with $Na^+[Mn(CO)_5^-]$, ethyl 4-chloro-2-butenoate 54 reacted rapidly to give an 85% yield of the corresponding alkyl complex 49.

$$\underset{\underset{54}{}}{Cl\diagdown\diagup\diagdown\overset{\overset{O}{\|}}{C}OEt} \quad \xrightarrow[\substack{THF\ 25^\circ C \\ 10\ min.}]{Mn(CO)_5^-} \quad \underset{\underset{49}{85\%}}{Mn(CO)_5\diagdown\diagup\diagdown\overset{\overset{O}{\|}}{C}OEt} \quad + \quad \underset{15\%}{Mn_2(CO)_{10}} \qquad (46)$$

This reaction was still not entirely clean since a 15% yield of $Mn_2(CO)_{10}$ was observed in the ^{55}Mn-N.M.R. spectrum of the crude reaction mixture. Subsequent work-up of this reaction mixture yielded a small amount (ca. 4%) of the organic products observed for the corresponding bromo ester. In this case the non-cyclopropyl adducts predominated (G.C. analysis indicated they were formed in the following proportions: 50, 30%; 51, 55%; 52, 5%; and 53, 10%). Since neither the chloride 54 nor the corresponding bromide gave the expected >95% yields observed for the reaction of $Na^+[Mn(CO)_5^-]$ with allyl chloride or allyl bromide as described earlier, it was decided to see what effect changing the counterion M^+ in $M^+[Mn(CO)_5^-]$ had on the yield of the alkyl complex 49. The degree of association of cation and anion is known to effect the rate of the nucleophilic substitution reactions of metalate anions. Reactions of $M^+[Mn(CO)_5^-]$ were carried out for $M^+ = K^+$, Na^+, Li^+ and PPN^+. In the case of the sodium salt the effect of adding the crown ether, 18-crown-6 and hexamethylphosphoramide was also investigated since these are expected to decrease association of the cation and anion. The results of these reactions are given in Table 2.7.

These results show that there is little difference in the reactivity of $Na^+[Mn(CO)_5^-]$ and $K^+[Mn(CO)_5^-]$, but using $Li^+[Mn(CO)_5^-]$ the amount of allyl complex is substantially reduced for the reaction with ethyl 4-chloro-2-butenoate and zero for ethyl 4-bromo-2-butenoate. In contrast, changing the counterion to PPN^+

$M^+[Mn(CO)_5{}^-]$ + $XCH_2CH=CHCOOEt$				
Solvent = Tetrahydrofuran , 25°C, concentration= 0.12M				

M^+	X	$XMn(CO)_5$	$RMn(CO)_5$	$Mn_2(CO)_{10}$
K	Cl	0	85	15
K	Br	27	42	31
Na	Cl	0	88	12
Na	Br	25	34	42
Na/18c6[a]	Br	*	(86)	(14)
Li	Cl	0	67	33
Li	Br	*	0	56[b]
PPN	Cl	0	98	2
PPN	Br	21	78	1
PPN[c]	Br	24	53	24

Table 2.7   Products for the Reaction of Manganese Pentacarbonyl
Anion with Ethyl 4-Halo-2-Butenoate.

(Determined by ^{55}Mn-N.M.R.,% Manganese.)

[a]One equivalent of the crown ether 18-crown-6 added to the anion
solution.Addition of 5% dimethyl formamide or hexamethylphosphor
-amide had the same effect.

[b]Determined by isolation.

[c]In $CDCl_3$

*Signal corresponding to $Mn(CO)_4Br_2{}^-M^+$ was observed,but not quantified

increased the yield of alkyl complex in both cases, in fact the
reaction of $PPN^+[Mn(CO)_5^-]$ with ethyl 4-chloro-2-butenoate gives a
better than 95% yield of the allyl complex, and for the reaction with
ethyl 4-bromo-2-butenoate very little $Mn_2(CO)_{10}$ is produced.

The addition of 18-crown-6, or 5% hexamethylphophoramide to the
solution of $Na^+[Mn(CO)_5^-]$ prior to reaction with ethyl 4-bromo-2-
butenoate resulted in an apparent increase in the amount of allyl
complex produced in this reaction. However, observing the ^{55}Mn-N.M.R.
spectra of these reaction mixtures very quickly after the reaction had
commenced showed that $Mn(CO)_5Br$ was in fact formed initially. The
signal corresponding to $Mn(CO)_5Br$ very rapidly disappeared and was
replaced by a new signal in the ^{55}Mn-N.M.R. spectrum at -618 ppm,
which was assigned to $Na^+[Mn(CO)_4Br_2^-]$ 54. A similar observation was
made in the reaction of $Li^+[Mn(CO)_5^-]$ with ethyl 4-bromo-2-butanoate.
This secondary reaction could be reproduced by treating a solution of
$Mn(CO)_5Br$ in THF with lithium bromide or sodium bromide/18-crown-6. The
signal corresponding to $Mn(CO)_5Br$ in the ^{55}Mn-N.M.R. spectrum of this
solution disappeared over several hours, and a new signal at -620 ppm
appeared. The product 54 decomposed to $Mn_2(CO)_8Br_2$ during attempts to
isolate it; however the I.R.-spectrum of the crude reaction mixture
was consistent with that reported[83] for the same complex.

$$Mn(CO)_5Br + Br^- \longrightarrow [Mn(CO)_4Br_2^-] + CO \qquad (47)$$

$$\underline{54}$$

The reaction of $PPN^+[Mn(CO)_5^-]$ with the ethyl 4-halo-2-butanoate compounds in chloroform was also investigated. In this case the reaction with ethyl 4-bromo-2-butenoate gives a slight improvement in yield of the allyl complex, but the product ratio is quite similar to the reaction of $Na^+[Mn(CO)_5^-]$ in THF with the same compound. When this reaction was carried out in THF both bromo and chloro esters gave higher yields of the allyl complex. Under these conditions the yield of $Mn_2(CO)_{10}$ was less than 2%, in strong contrast to the same reaction carried out with the sodium salt of $Mn(CO)_5^-$.

The effect of changing the ratio of reactants was investigated for the reaction of $Na^+[Mn(CO)_5^-]$ with these halo-esters , and the results are given in Table 2.8.

Solvent = Tetrahydrofuran , 25°C, concentration= 0.12M				
Ratio = $Na^+[Mn(CO)_5^-]$:$XCH_2CH=CHCOOEt$				
Ratio	X	$XMn(CO)_5$	$RMn(CO)_5$	$Mn_2(CO)_{10}$
1:1	Cl	0	85	15
1:2	Cl	0	88	12
1:0.5	Br	0	21	79
1:1	Br	25	34	42
1:2	Br	51	35	14

Table 2.8 Variation of Products with Stoichiometry for the Reaction of Manganese Pentacarbonyl Anion with Ethyl 4-Halo-2-butenoate.(Determined by [55]Mn-N.M.R.,% Manganese.)

Using an excess of halo-ester has little effect on the relative yield of the allyl complex, but it does increase the amount of $Mn(CO)_5Br$ formed. Conversely, no $Mn(CO)_5Br$ was observed when an excess of $Na^+[Mn(CO)_5^-]$ was used.

2.8 The Reaction of $Na^+[Mn(CO_5^-]$ with Secondary Allylic Halides

The possibility of preparing secondary allylic manganese complexes using $Mn(CO)_5^-$ was investigated using 4-chloro-2-pentene 55.

A mixture of an unfiltered solution of $Na^+[Mn(CO)_5^-]$ (prepared using 1% sodium amalgam) and 4-chloro-2-pentene in THF remained unchanged after several hours at room temperature. However, on standing for several days, large bright yellow plates formed in the solution. These crystals were found to be quite insoluble in THF, hydrocarbons, chloroform, methylene chloride and alcohols, and decomposed without melting at 180°C. They were quite stable to air oxidation. Mass spectral analysis indicated the characteristic isotopic abundance associated with mercury, suggesting the compound was $Hg(Mn(CO)_5)_2$ 56. The parent ion was not observed, however ions with m/e = 395 and 397 correspond to M-195 or loss of $Mn(CO)_5$. This formulation was confirmed by elemental analysis (C = 20.32%, H = 0.00%; calculated for $HgMn_2C_{10}O_{10}$, C = 20.34%, H = 0.00%), and the crystals were isolated in 6% yield.

$$Mn(CO)_5^- \xrightarrow{\text{Hg}} [Mn(CO)_5]_2Hg + 2e- \qquad (48)$$

56

The formation of $Hg[Mn(CO)_5]_2$ has been observed before by King[73] in the reaction of 1,3-dibromopropane with $Na^+[Mn(CO)_5^-]$, (prepared

using sodium amalgam) where it was isolated in 11% yield.

The reaction of $Na^+[Mn(CO)_5^-]$ with 4-chloro-2-pentene was repeated, this time using a solution of $Na^+[Mn(CO)_5^-]$ which had been filtered, in this case no $Hg[Mn(CO)_5]_2$ was formed even after one week. Changing to a better leaving group, bromide, was then considered. The reaction of 4-bromo-2-pentene 57 with $Na^+[Mn(CO)_5^-]$ was very rapid, a white precipitate of sodium bromide immediately forming in the solution. Subsequent analysis by $^{55}Mn-$ N.M.R. spectroscopy showed signals due to $Mn(CO)_5Br$ (δ, -1156 ppm) and $Mn_2(CO)_{10}$ (δ, -2281 ppm) with no other signals present, implying that no alkyl complex was formed in this reaction. Manganese pentacarbonyl bromide (24%) and $Mn_2(CO)_{10}$ (64%) were isolated from the reaction mixture. The organic products from this reaction could not be isolated owing to their volatility, i.e. they were not separated from the large solvent G.C. peak of the distilled reaction mixture. $^{13}C-$ N.M.R. spectroscopy carried out on the crude reaction mixture showed resonances at 18.2 ppm, 114.5 ppm, 130.2 ppm, 135.5 ppm and 138.2 ppm. These compare very well with those for E-1,3-pentadiene 58 (δ,THF, 18.2 ppm, 114.6 ppm, 130.1 ppm, 133.6 ppm and 138.2 ppm, determined for authentic commercial 1,3-pentadiene as a mixture of E and Z isomers, the shifts corresponding to the E isomer were assigned by comparison with published data[84]).

$$Na^+[Mn(CO)_5^-] + \underset{\underline{57}}{\overset{Br}{\diagup\!\!\!\diagdown\!\!\!\diagdown}} \xrightarrow[\substack{25°C \\ 10 \text{ min.}}]{THF} \underset{\text{major}}{\diagup\!\!\!\diagdown\!\!\!\diagup} + \begin{matrix} Mn(CO)_5Br & 24\% \\ + Mn_2(CO)_{10} & 64\% \end{matrix} \qquad (49)$$

<u>58</u>

The reaction of $Mn(CO)_5^-$ with 3-bromo-1,3-diphenyl-1- propene 59

was also carried out. ^{55}Mn - N.M.R. spectroscopy on a mixture of

$Na^+[Mn(CO)_5^-]$ and 3-bromo-1,3-diphenyl-1-propene indicated that a very

rapid reaction took place but only one signal was observed and this

corresponded to $Mn_2(CO)_{10}$. In this case it was possible to isolate

the organic product since the $Mn_2(CO)_{10}$ could be preferentially

sublimed, leaving white crystals of 1,3,4,6-tetraphenyl-1,5-hexadiene

60 as a 1:1 mixture of diasteriomers.

This product was recrystallized to give a 92% yield of white needles

and its physical and spectroscopic properties agreed with those

reported in the literature[85]. The diasteriomers of 60 could be

separated by fractional recrystallization.

2.9 The Effect of Solvent, Counterion and Structure on the Reaction of $Mn(CO)_5^-$ with 2-Haloesters

Another class of organic halides, considered to be activated towards S_N2 nucleophilic displacement, are 2-halo carbonyl compounds. Examples of the reaction of $Mn(CO)_5^-$ with such organic halides have been reported[43] and these were mentioned earlier in Section 2.1. These reactions might be expected to be general and to take place according to the following scheme:

$$Mn(CO)_5^- + \underset{60}{X-CR^1R^2COR^3} \longrightarrow \underset{61}{(CO)_5MnCR^1R^2COR^3} + X^- \qquad (51)$$

Manganese complexes of the general type $\underline{61}$ are potentially useful since in principle they could undergo carbonylation to give the corresponding acyl complex $\underline{62}$, which contains a 1,3-dicarbonyl fragment and

$$\underset{61}{(CO)_5Mn-CR^1R^2COR^3} \overset{CO}{\longrightarrow} \underset{62}{(CO)_5Mn-\overset{O}{\overset{\|}{C}}-CR_1R_2COR^3} \qquad (52)$$

they might also serve as precursors for oxo-allyl complexes[86]. The factors influencing the yields of complexes of the general type $\underline{61}$, from the reaction of $Mn(CO)_5^-$ with 2-halo carbonyl compounds as given in reaction (51), have not been fully investigated, so it was decided to carry out a more thorough investigation of these reactions.

Primary, secondary and tertiary 2-haloesters $\underline{63-71}$ are readily available and are suitable models for determining the factors which influence the yield of the alkyl complex in reaction (51).

	XCH_2COOEt	$XCHCH_3COOEt$	$XC(CH_3)_2COOEt$
X= Cl	63	64	65
Br	66	67	68
I	69	70	71

All three halides of each ester could be conveniently prepared in high yields using halogen exchange reactions starting from the corresponding bromo esters. The reaction of $Na^+[Mn(CO)_5^-]$ with these esters in THF was considered first since $Mn(CO)_5^-$ is conveniently prepared in this solvent by reduction of $Mn_2(CO)_{10}$ using sodium amalgam. The PPN^+ salt was also considered, primarily because of its stability to air oxidation and therefore ease of handling, but also to see what effects changing the counterion has on the yield of alkyl complex. Using $PPN^+[Mn(CO)_5^-]$ also made it possible to carry the reaction out in a chlorinated hydrocarbon solvent, chloroform, as well as in THF, to see what effect the solvent might have on the reaction.

The reactions were carried out by rapidly mixing one equivalent of $Mn(CO)_5^-$ with one equivalent of the 2-halo ester at room temperature and the yield of alkyl complex determined using [55]Mn-N.M.R. spectroscopy.

2.9.1 The Reactions of Na$^+$[Mn(CO)$_5$$^-$] with 2-Halo Esters in THF

The manganese products of the reaction of Na$^+$[Mn(CO)$_5$$^-$] with the 2-halo esters are given in Table 2.9. With the exception of ethyl 2-chloropropanoate and the tertiary substrates, X(CH$_3$)$_2$CCOOEt, the reactions were very rapid, a precipitate of sodium halide forming in the solution immediately and no Mn(CO)$_5$$^-$ being detected in the reaction mixture after five minutes. After two hours a mixture of ethyl 2-chloropropanoate and Na$^+$[Mn(CO)$_5$$^-$] remained unchanged, however after 5 hours a weak signal corresponding to the alkyl complex was observed, indicating that the reaction was very slow. A solution of 2-chloro-2-methylpropanoate and Na$^+$[Mn(CO)$_5$$^-$] remained unchanged after eight hours. The tertiary bromo and iodo esters, X-(CH$_3$)$_2$CCOOEt reacted over a period of one hour, no detectable amounts of Na$^+$[Mn(CO)$_5$$^-$] remaining after this time.

Ethyl 2-chloroethanoate $\underline{63}$ reacts rapidly with Na$^+$[Mn(CO)$_5$$^-$] to give the corresponding alkyl product $\underline{72}$ in high yield, no Mn(CO)$_5$Cl being present in the reaction mixture.

$$Na^+[Mn(CO)_5^-] + ClCH_2COOEt \longrightarrow (CO)_5MnCH_2COOEt + NaCl \qquad (53)$$

$$\underline{63} \qquad\qquad\qquad \underline{72}\ 94\%$$
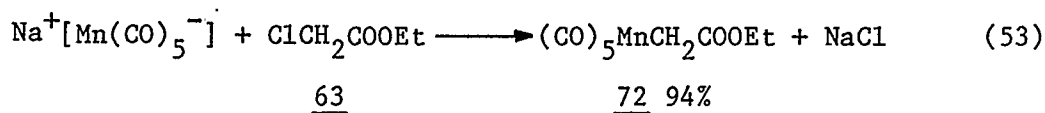
The alkyl complex $\underline{72}$ was isolated in 62% yield by flash chromatography as a colourless, air sensitive oil. The I.R.-spectrum, (in chloroform, cm^{-1}: 2120w, 2025s, 1968sh, 1685w) and the

^{1}H-N.M.R. spectrum, (in deuterochloroform: t, 1.14ppm, J=6.8Hz, 3H; s, 1.33ppm, 2H; q, 3.99ppm, J=7Hz, 2H.) are as expected for complexes of this type[43].

In contrast, the 2-bromo and 2-iodoesters give significant amounts of $Mn(CO)_5X$ and $Mn_2(CO)_{10}$, and as a result much

$M^+[Mn(CO)_5^-]$ + $X-CR_1R_2COOEt$ $M^+ = Na^+$, Solvent = Tetrahydrofuran, R = $-CR_1R_2COOEt$, 25°C					
R_1	R_2	X	$XMn(CO)_5$	$RMn(CO)_5$	$Mn_2(CO)_{10}$
H	H	Cl	0	94	6
H	H	Br	39	39	22
H	H	I	74	0	26
H	CH_3	Cl	No Reaction[a]		
H	CH_3	Br	6	63	31
H	CH_3	I	33	35	32
CH_3	CH_3	Cl	No Reaction		
CH_3	CH_3	Br	0	0	100
CH_3	CH_3	I	40	0	60

Table 2.9 Products for the Reaction of Sodium Pentacarbonyl Manganate with 2-Haloesters in Tetrahydrofuran. (Determined by ^{55}Mn-N.M.R., %Manganese.)

[a]Some alkyl product was observed after prolonged reaction times.

lower yields of the corresponding alkyl complexes.

$$XCH_2COOEt \xrightarrow[\text{THF, 25}^\circ\text{C, 5 min.}]{Na^+[Mn(CO)_5^-]} (CO)_5MnCH_2COOEt + Mn(CO)_5X + Mn_2(CO)_{10} \quad (54)$$

| | X=Br 39% | 39% | 22% |
| | X=I 0% | 74% | 26% |

<u>72</u>
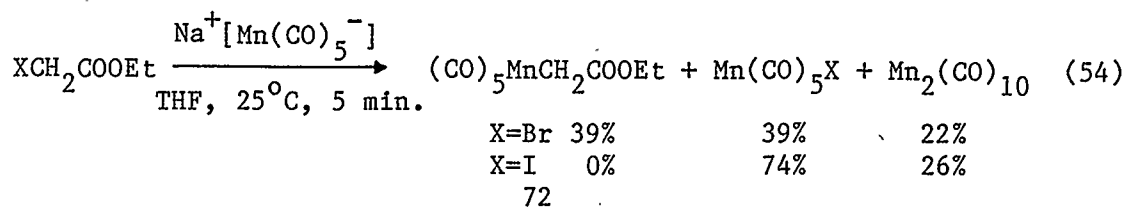
$Na^+[Mn(CO)_5^-]$ reacted very slowly with the secondary cloride <u>64</u> but some alkyl complex was formed from the reaction with secondary bromides and iodides, along with manganese pentacarbonyl halides and dimanganese decacarbonyl.

$$\overset{CH_3}{X\overset{|}{C}HCOOEt} \xrightarrow[\text{THF, 25}^\circ\text{C, 5 min.}]{Na^+[Mn(CO)_5^-]} (CO)_5Mn\overset{CH_3}{\overset{|}{C}HCOOEt} + Mn(CO)_5X + Mn_2(CO)_{10} \quad (55)$$

| | X=Br 63% | 6% | 31% |
| | X=I 35% | 33% | 32% |

<u>73</u>

The alkyl complex <u>73</u> was isolated as an air-sensitive oil in 44% yield by flash chromatography (I.R.-spectrum, in chloroform, cm^{-1}: 2117w, 2023s, 1999sh, 1686w; [1]H-N.M.R. spectrum, in deuterochloroform: t, 1.27ppm, J=6.8Hz, 3H; d, 1.58ppm, J=6.7Hz, 3H; q, 2.32ppm, J=6.9Hz, 1H; q, 4.15ppm, J=6.9Hz, 3H.)

The reaction of $Na^+[Mn(CO)_5^-]$ with ethyl 2-iodoethanoate was unusual in that no alkyl complex was formed. Carrying out the reaction with an excess of the iodoester had no effect on the yield of the alkyl complex, although this did increase the relative amount of $Mn(CO)_5I$ formed. Conversely, only Mn_2CO_{10} was formed when less than one equivalent of the iodoester was used:

$$Na^+[Mn(CO)_5^-] + \cdot ICH_2COOEt \quad\quad Mn(CO)_5I + Mn_2CO_{10}$$

Ratio:	1	:	2	86%	14%
	1	:	1	74%	26%
	1	:	0.5	0	100%

Attempts to separate the organic by-products from the organometallic species present in the solution were only successful for reactions involving the tertiary halo-esters. It was not possible to separate the products by low temperature distillation when the alkyl complexes were present, and no non-organometallic species could be isolated by chromatography. Interestingly, G.C.-analysis of the crude reaction mixture of $Mn(CO)_5^-$ with ethyl 2-iodoethanoate was uninformative. There was evidence in the G.C that a very low yield ($<5\%$) of diethyl succinate was formed in this reaction but no other peaks were present. Similar results were obtained for the reaction mixture where a two-fold excess of the iodo-ester had been used, and only 8% unreacted ethyl 2-iodoethanoate remained. In contrast, G.C.-analysis of the crude reaction mixture of ethyl 2-bromo-2-methyl propanoate with $Na^+[Mn(CO)_5^-]$ indicated that a number of products were formed in this reaction, and unreacted bromo-ester remained (25%). G.C.-mass spectrometry of a distillate from this solution indicated that the products were ethyl 2-methylpropanoate 74 (the major product), ethyl 2-methyl-2-propenoate 75, and diethyl 2,2,3,3,- tetramethylsuccinate 76. A number of non-volatile products (6% of the total products) were also formed but these were not identified since they could not be separated from the organometallic residue.

$$\text{Na}^{+}[\text{Mn(CO)}_5^{-}] \quad + \quad \underset{\text{Br}}{\overset{}{\longmapsto}}\text{—COOEt} \quad \longrightarrow \tag{55}$$

$$\underline{74} \; 36\% \qquad \underline{75} \; 16\% \qquad \underline{76} \; 14\% \qquad \underline{77} \; 1\%$$
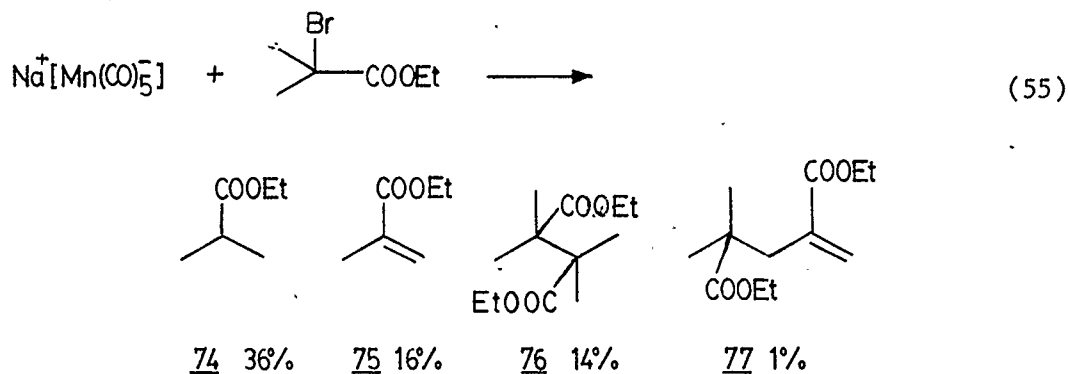
Some trends can be seen in the amount of alkyl complex produced in the reactions given in Table 2.9. Clearly the yield of alkyl complex increases as the leaving group is changed Cl>Br>I. This is particularly so for the primary esters where no alkyl complex is observed for the reaction of $\text{Na}^{+}[\text{Mn(CO)}_5^{-}]$ with ethyl 2-iodoethanoate. This is anomalous since the secondary iodide, ethyl 2-iodopropanoate gives a 35% yield of the corresponding alkyl complex. The relative amounts of $\text{Mn(CO)}_5\text{X}$ (X=Br,I) also follow a trend, changing the leaving group from bromide to iodide favors the formation of $\text{Mn(CO)}_5\text{X}$ over $\text{Mn}_2(\text{CO})_{10}$.

2.9.2 The Reaction of $\text{PPN}^{+}[\text{Mn(CO)}_5^{-}]$ with 2-Halo Esters in THF

The manganese products of the reaction of $\text{PPN}^{+}[\text{Mn(CO)}_5^{-}]$ with 2-halo esters are given in Table 2.10. The reaction times for these were the same as described for $\text{Na}^{+}[\text{Mn(CO)}_5^{-}]$ in the previous section, with the exception that the tertiary substrates $\text{X(CH}_3)_2\text{CCOOEt}$ (X=Br,I) required four hours to go to completion and there was evidence that some $\text{PPN}^{+}[\text{Mn(CO)}_5^{-}]$ remained after this time (infra-red analysis).

$$M^+[Mn(CO)_5^-] \;+\; X\text{-}CR_1R_2COOEt$$

$M^+ = PPN^+$, Solvent = Tetrahydrofuran , $R = -CR_1R_2COOEt$, $25^{\circ}C$

R_1	R_2	X	$XMn(CO)_5$	$RMn(CO)_5$	$Mn_2(CO)_{10}$
H	H	Cl	0	99	1
H	H	Br	0	100	0
H	H	I	15[a]	85	0
H	CH_3	Cl	No Reaction[b]		
H	CH_3	Br	24[a]	76	0
H	CH_3	I	32[a]	68	0
CH_3	CH_3	Cl	No Reaction		
CH_3	CH_3	Br	100[c]	0	0
CH_3	CH_3	I	100[c]	0	0

Table 2.10 Products for the Reaction of PPN Pentacarbonyl Manganate with 2-Halo Esters in Tetrahydrofuran. (Determined by [55]Mn-N.M.R., %Manganese.)

[a]Signal rapidly disappeared due to conversion to $[Mn(CO)_4X_2^-]PPN^+$.

[b]Some alkyl product was observed after prolonged reaction times.

[c]The only signals observed for these reactions corresponded to $[Mn(CO)_4X_2^-]PPN^+$, and unreacted $PPN^+[Mn(CO)_5^-]$.

Changing the counterion from sodium ion to PPN^+ has two effects

on the manganese products formed in these reactions. Firstly,

essentially no $Mn_2(CO)_{10}$ is observed in any of the reactions (1% was

detected in one case), and secondly, the yields of the alkyl complexes

are consistently higher for the primary and secondary substrates.

This is particularly true for the primary 2-haloesters where

manganese pentacarbonyl halide is only observed in the reaction of

$PPN^+[Mn(CO)_5^-]$ with ethyl 2-iodoethanoate (56).

$$PPN^+[Mn(CO)_5^-] + ICH_2COOEt \longrightarrow (CO)_5MnCH_2COOEt + Mn(CO)_5I + NaI \quad (56)$$
$$\underline{72} \quad 85\% \qquad\qquad 15\%$$
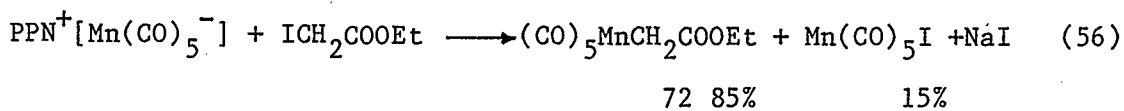
The secondary substrate ethyl 2-chloropropanoate reacted very slowly

with $PPN^+[Mn(CO)_5^-]$; however this resembled the same reaction with

$Na^+[Mn(CO)_5^-]$ in that some alkyl product was observed after several

hours. No reaction was observed between $PPN^+[Mn(CO)_5^-]$ and ethyl

2-chloro-2-methylpropanoate.

The ^{55}Mn-N.M.R. resonances for manganese pentacarbonyl halides

formed in the reactions of 2-bromo and 2-iodoesters rapidly

disappeared, new resonances appearing at −618 ppm for the bromide and

−1011 ppm for the iodide. These chemical shifts were assigned to

$PPN^+[Mn(CO)_4Br_2^-]$ and $PPN^+[Mn(CO)_4I_2^-]$ respectively. For the tertiary

substrates $X(CH_3)_2CCOOEt$ (X=Br,I) these were the only signals

observed in the ^{55}Mn-N.M.R. spectra for these reactions. In the

attempted isolation of $PPN^+[Mn(CO)_4Br_2^-]$, the material was obtained as

an impure yellow oil which would not crystallize. However, the infra-

red spectrum of the oil (THF, cm^{-1}, 2081 w, 2007s, 1973s, 1925s, 1907sh) is consistent with that reported[87] for related complexes.

The organic by-products of the reaction of PPN$^+$[Mn(CO)$_5^-$] with ethyl 2-bromo-2-methylpropanoate were analysed by G.C. and G.C.-mass spectrometry using a distillate from the reaction mixture. The products were found to be similar to those observed in the reactions of Na$^+$[Mn(CO)$_5^-$], as described in the previous section.

$$PPN^+Mn(CO)_5^- \ + \ \overset{Br}{\underset{}{\diagup\!\!\!\diagdown}}\!\!-COOEt \longrightarrow$$

74 35%   75 6%   76 36%   77 3%

(57)
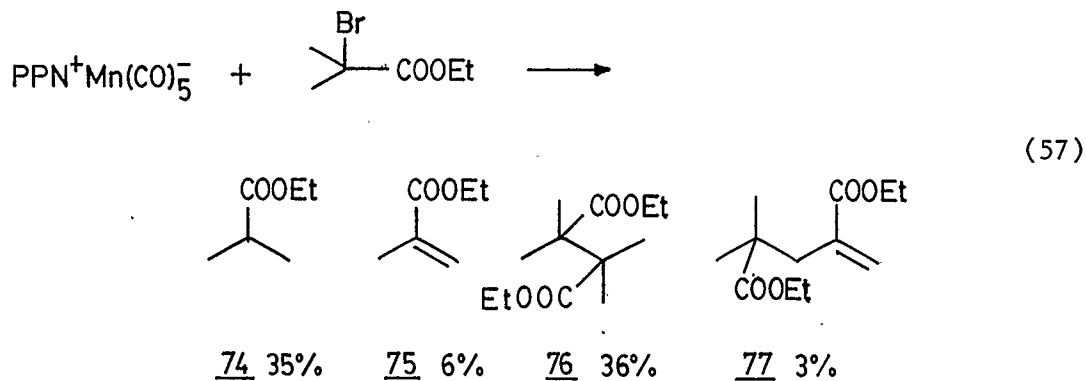
No unreacted ethyl 2-bromo-2-methylpropanoate remained in the solution and the overall yield of these products was ca. 80%.

In all the cases where Mn(CO)$_5$X was observed, I.R. analysis indicated that some unreacted PPN$^+$[Mn(CO)$_5^-$] remained in the solution, but this could not be quantified by ^{55}Mn-N.M.R. spectroscopy with any certainty because of the large linewidth observed for the resonance of this complex.

In contrast to the reactions of Na$^+$[Mn(CO)$_5^-$] discussed in the previous section, there is a decrease in the amount of alkyl complex observed in going from the primary substrates to the secondary ones, although, as mentioned earlier, the yields of alkyl complex are all

significantly higher.

2.9.3 The Reaction of PPN$^+$[Mn(CO)$_5^-$] with 2-Haloesters in Deuterochloroform

The manganese products for the reactions of PPN$^+$[Mn(CO)$_5^-$] with 2-haloester 63 - 71 are given in Table 2.11.

M$^+$[Mn(CO)$_5^-$] + X-CR$_1$R$_2$COOEt M$^+$ = PPN$^+$, Solvent = Deuterochloroform , R = -CR$_1$R$_2$COOEt , 25°C					
R$_1$	R$_2$	X	XMn(CO)$_5$	RMn(CO)$_5$	Mn$_2$(CO)$_{10}$
H	H	Cl	0	99	1
H	H	Br	14	75	11
H	H	I	17	67	16
H	CH$_3$	Cl	No Reaction[a]		
H	CH$_3$	Br	4	39	57
H	CH$_3$	I	20	56	24
CH$_3$	CH$_3$	Cl	No Reaction		
CH$_3$	CH$_3$	Br	5	0	95
CH$_3$	CH$_3$	I	77	0	23

Table 2.11 Products for the Reaction of PPN Pentacarbonyl Manganate with 2-Haloesters in Deuterochloroform.(Determined by ^{55}Mn-N.M.R., % Manganese.)

[a]Some alkyl product was observed after prolonged reaction times.

These results are similar to those observed for the reactions of $Na^+[Mn(CO)_5^-]$ in THF, except that $PPN^+[Mn(CO)_5^-]$ reacts with ethyl 2-iodoethanoate to give a 67% yield of the alkyl complex where none was formed using $Na^+[Mn(CO)_5^-]$. These reactions also differ in that there is a decrease in the relative amount of alkyl complex formed on going from primary to secondary substrates.

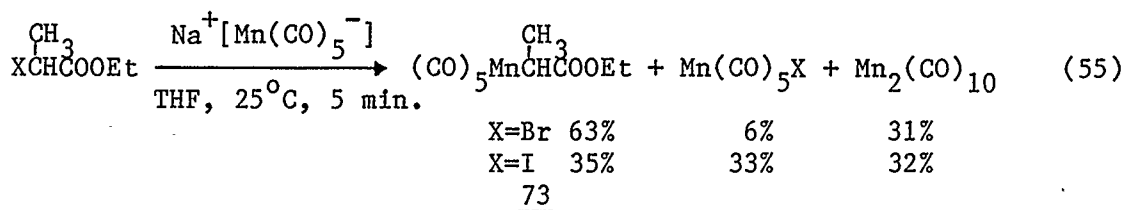Again, for all but the primary chloro ester, ethyl 2-chloroethanoate, there were significant yields of $Mn_2(CO)_{10}$ and manganese pentacarbonyl halides when bromide or iodide were the leaving group. The reaction of $PPN^+[Mn(CO)_5^-]$ with ethyl 2-chloropropanoate was very slow. At least four hours were required before any signal was observed in the [55]Mn-N.M.R. spectrum corresponding to the alkyl complex 73. The tertiary chloride failed to react, a fact which in this case could be confirmed by [1]H-N.M.R. spectroscopy carried out on the crude reaction mixture. The rates of the other reactions were similar to those observed for the reactions of $Na^+[Mn(CO)_5^-]$ in THF.

The yields of the alkyl complex and organic by-products for these reactions were determined by in situ [1]H-N.M.R. (see Table 2.12) spectroscopy. The yields of the alkyl complexes 72 and 73 determined in this way agree (within experimental error) with those determined by [55]Mn-N.M.R. spectroscopy (Table 2.11). The [1]H-N.M.R. spectrum for the reaction of $PPN^+[Mn(CO)_5^-]$ and ethyl 2-bromoethanoate contained resonances corresponding to the alkyl complex 72 (the major product), unreacted ethyl 2-bromoethanoate, and a triplet at 1.91 ppm (J=2.5Hz) which was assigned to DCH_2COOEt 78.

$$PPN^+[Mn(CO)_5^-] + BrCH_2COOEt \longrightarrow (CO)_5MnCH_2COOEt + DCH_2COOEt \quad (58)$$

$$\underline{71} \quad 71\% \qquad \underline{78} \quad 19\%$$

$$+ PPN^+Br^-$$

			$M^+[Mn(CO)_5^-]$ + X-CR$_1$R$_2$COOEt		
M^+ = PPN$^+$, Solvent = Deuterochloroform , R = -CR$_1$R$_2$COOEt , 25°C					
R$_1$	R$_2$	X	XCR$_1$R$_2$COOEt	DCR$_1$R$_2$COOEt	RMn(CO)$_5$
H	H	Cl	11	0	89
H	H	Br	10	19	71
H	H	I	0	25	75
H	CH$_3$	Cl	100	0	0
H	CH$_3$	Br	49	19	32
H	CH$_3$	I	20	16	64
CH$_3$	CH$_3$	Cl	100	0	0
CH$_3$	CH$_3$	Br	46	54	0
CH$_3$	CH$_3$	I	26	74	0

Table 2.12 Products for the Reaction of PPN Pentacarbonyl

Manganate with 2-Haloesters in Deuterochloroform.(Determined by

[1]H-N.M.R.±3%)

This resonance consisted of three lines of equal intensity, as one

would expect for deuterium coupling. It was not possible to separate

78 from the solvent by G.C.; however it was possible to distill the product from the alkyl complex and obtain the ^{1}H-N.M.R. spectrum for pure 78. Similar results were obtained for the reaction involving ethyl 2-iodoethanoate.

Evidence for deuterium substitution was also found for the reaction of $PPN^+[Mn(CO)_5^-]$ with the secondary and tertiary bromo and iodoesters. In these cases separation by G.C. was possible.

$$CH_3CHXCOOEt \quad \xrightarrow{PPN^+[Mn(CO)_5^-]} \quad CH_3CHDCOOEt + (CO)_5MnCHCH_3COOEt \quad (59)$$

$$X=Br,I$$
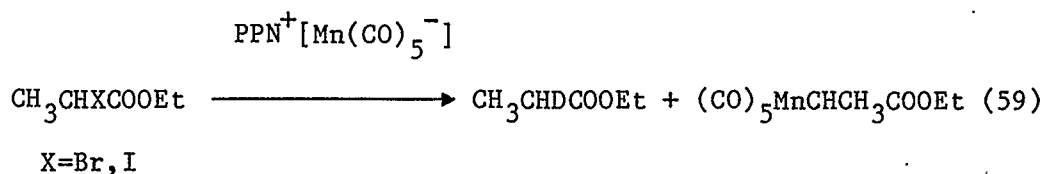
$$\underline{79} \qquad \underline{73}$$

The deutero compound 79 distilled from the alkyl complex 73 along with solvent, and G.C. mass-spectrometry indicated a single product with a probable molecular ion at m/e 103. The ^{1}H-N.M.R. spectrum of this distillate consisted of: dd, 1.15 ppm, J=7.6Hz, J_{DH}=1.0Hz, 3H; tq, 2.34 ppm, J=7.6Hz, J_{DH}=2.7Hz, 1H; t, 1.27 ppm, J=7.3Hz, 3H; q, 4.18 ppm, J=7.2Hz, 2H.

For the reaction of $PPN^+[Mn(CO)_5^-]$ with ethyl 2-bromo-2-methyl propanoate the ^{1}H-N.M.R. spectrum of the crude reaction mixture indicated that the solution contained unreacted bromo ester and a "triplet" at 1.17 ppm (J=1Hz) which was assigned to the deutero ester 80 (the major product).

$$(CH_3)_2CBrCOOEt \quad \xrightarrow{PPN^+[Mn(CO)_5^-]} \quad (CH_3)_2CDCOOEt \qquad (60)$$

$$\underline{80} \quad 54\%$$
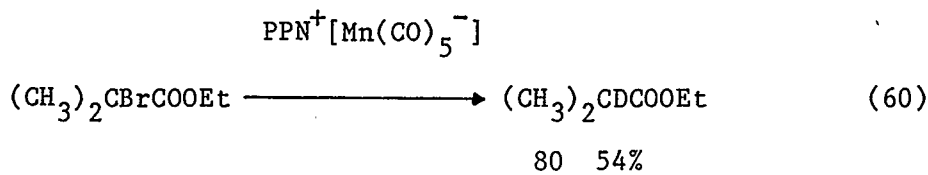
This product was isolated as a chloroform solution and G.C. - mass spectrometry indicated that the single product had a probable molecular ion at m/e 117 confirming deuterium incorporation. Again, similar results were obtained for the reaction of $PPN^+[Mn(CO)_5^-]$ with ethyl 2-iodo-2-methylpropanoate where the deuterium substitution took place with 74% yield.

Ratio = $Mn(CO)_5^-$:$X-CR_1R_2COOEt$						
ratio	R_1	R_2	X	$XMn(CO)_5$	$RMn(CO)_5$	$Mn_2(CO)_{10}$
1:0.5	H	CH_3	Br	0	40	60
1:1	H	CH_3	Br	4	39	57
1:2	H	CH_3	Br	4	50	45
1:4	H	CH_3	Br	5	54	41
1:1	H	CH_3	I	20	56	24
1:2	H	CH_3	I	18	66	16
1:1	CH_3	CH_3	Br	7	0	93
1:2	CH_3	CH_3	Br	10	0	90
1:1	CH_3	CH_3	I	77	0	23
1:2	CH_3	CH_3	I	83	0	7

Table 2.13 Variation of Products with Stoichiometry for the Reaction of $PPN^+[Mn(CO)_5^-]$ with 2-Haloesters in Deuterochloroform. (Determined by ^{55}Mn-N.M.R., % Manganese.)

The effect of changing the initial ratio of $PPN^+[Mn(CO)_5^-]$ to 2-haloesters was also investigated, and the results are given in Tables

2.13 above. In general these results show that there is a decrease in the amount of $Mn_2(CO)_{10}$ produced in the reaction as the initial concentration of the 2-halo ester is increased. This is accompanied by a slight increase in the amount of alkyl complex formed in the reaction.

2.10 Discussion: The Preparation of Alkyl and Allyl Manganese Complexes using $Mn(CO)_5^-$

The results obtained in this work support the view that $Mn(CO)_5^-$ is a relatively poor nucleophile when compared to other metalate anions. This is illustrated by the fact that $Fe(CO)_4^{2-}$ reacts rapidly with primary alkyl chlorides[46], whereas $Mn(CO)_5^-$ fails to react (or reacts only slowly)[88] with primary alkyl bromides. Simple alkyl manganese complexes must be prepared from primary alkyl iodides, e.g. methyl[17] and ethyl[79] manganese pentacarbonyl can be obtained by nucleophilic substitution, or via the corresponding acyl complex.

With substrates which are activated towards S_N2 nucleophilic displacement, the rate of substitution by $Mn(CO)_5^-$ dramatically increase. This is demonstrated by the very rapid reaction (<5 minutes) between allyl chloride (or allyl bromide) and $Mn(CO)_5^-$ to give the corresponding allyl complex in essentially quantitative yield.

For the organic chlorides studied in this work, the reactivity pattern observed follows what one would expect for a S_N2 type substitution mechanism. Thus, primary allylic chlorides, and primary 2-chloro esters react very rapidly with $Mn(CO)_5^-$ to give the corresponding alkyl (or allyl) complexes. From a synthetic point of

view the reaction is unsuccessful for secondary allylic chlorides, very slow for secondary 2-chloro esters, and no reaction is observed with tertiary 2-chloro esters.

The effect of changing the leaving group from chloride to bromide (or iodide) is more difficult to assess since this also promotes the formation of non-substitution products. Secondary 2-bromo and 2-iodo esters react with $Mn(CO)_5^-$ to give the non-substitution products $Mn_2(CO)_{10}$ and $Mn(CO)_5X$ in addition to the substitution product. This is also true for the secondary allylic compound 4-bromo-2-pentene, where no substitution product is observed on reaction with $Na+[Mn(CO)_5^-]$ although a reaction does take place. However, the secondary 2-bromo ester, ethyl 2-bromopropanoate does react with $Mn(CO)_5^-$ to give at least some substitution product, whereas the reaction was very slow for the corresponding chloro ester. These results are in keeping with quantitative rate data reported by others[89] where allyl and benzyl bromides were found to react about an order of magnitude faster with $Mn(CO)_5^-$ than the corresponding chlorides.

The limiting factor from a preparative point of view is that non-substitution reactions appear to have an even larger discrimination between halogens with Br>>Cl. Therefore, if one changes from Cl to Br, the expected faster S_N2 reaction has to compete in some of the cases described in the present work with an even faster non-substitution process.

The formation of non-substitution products is dependent on the structure of the organic halide as well as the leaving group, but the

presence of a, β-unsaturation in the organic halide is an important factor. However it is not the only one since allyl bromide reacts "normally" whereas the secondary substrate 5-bromo-2-pentene gives non-substitution products exclusively.

Possible Mechanisms for the Reaction of $Mn(CO)_5^-$ with Organic Halides

In its reaction with organic halides three possible fates of the $Mn(CO)_5^-$ species are observed, the formation of $R-Mn(CO)_5$, $Mn(CO)_5X$ (X=Br,I) and $Mn_2(CO)_{10}$. Depending on the organic halide and reaction conditions any one or a combination of these reactions can take place.

The compounds, $R-Mn(CO)_5$, correspond to S_N2 - type substitution products, normally expected to be the only product of the reaction of $Mn(CO)_5^-$ with organic halides. The key features of an S_N2 reaction are, of course, inversion of configuration at the carbon center, predictable rate changes with changes of substrate structure, leaving group, solvent and so on. For a number of metalate anions such features have in fact been observed[46,47], and as discussed above the organic chlorides studied in the present work generally follow the expected trends. More recently, researchers have determined[90,91] that in some substitution reactions, the S_N2 pathway is not the only mechanism involved. Contributions from or replacement by an initial electron transfer process (E.T.) have been proposed. These two processes are illustrated below.

$$Mn(CO)_5^- \quad \overset{\backslash}{\underset{/}{C}}-X \longrightarrow \left[(CO)_5\overset{\delta^-}{Mn}\cdots\cdots\overset{\backslash/}{\underset{|}{C}}\cdots\cdots\overset{\delta^-}{X} \right]^{\ddagger} \qquad (61)$$

$$\text{Mn(CO)}_5^- + \,\diagdown\!\!\text{C}\!-\!\text{X} \longrightarrow \left[\text{(CO)}_5\text{Mn}^\bullet + \,\diagdown\!\!\text{C}\!-\!\text{X}^{\overline{\bullet}}\right] \longrightarrow \left[\text{(CO)}_5\text{Mn}^\bullet + \,\diagup\!\!\text{C}^\bullet + \text{X}^-\right] \quad (62)$$
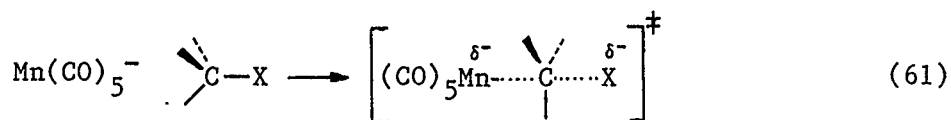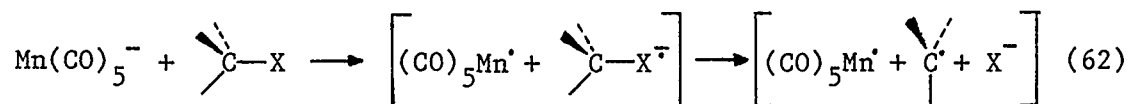
The key features of the E.T. mechanism are that it would not necessarily involve inversion of configuration[92] and rate changes are not governed by the factors controlling rates in the S_N2 mechanism. However, in this thesis, as far as the substitution products R-Mn(CO)$_5$ are concerned, this study is not attempting to distinguish between a true S_N2 and an E.T. mechanism. The E.T. mechanism was initially considered because it provided the possibility of explaining all three manganese products starting with a single process, as shown below.

$$\left[\text{(CO)}_5\text{Mn}^\bullet + \,\diagup\!\!\text{C}^\bullet + \text{X}^-\right]_{\text{cage}}$$

$$\text{(CO)}_5\text{Mn-}\diagup\!\!\text{C}\diagdown + \text{X}^- \longrightarrow \text{(CO)}_5\text{Mn}^\bullet + \,\diagup\!\!\text{C}^\bullet + \text{X}^- \quad (63)$$

$$\text{(CO)}_5\text{Mn}^\bullet + \,\diagup\!\!\text{C}^\bullet \longrightarrow \text{(CO)}_5\text{Mn-}\diagup\!\!\text{C} \quad (64)$$

$$\text{(CO)}_5\text{Mn}^\bullet + \text{X-}\diagup\!\!\text{C}\diagdown \longrightarrow \text{(CO)}_5\text{Mn-Br} + \,\diagup\!\!\text{C}^\bullet \quad (65)$$

$$2\,\diagup\!\!\text{C}^\bullet \longrightarrow \,\diagdown\!\!\text{C-C}\diagup \quad (66)$$

$$\diagup\!\!\text{C}^\bullet + \diagdown\!\!\underset{\text{H}}{\text{C-C}}\diagup \longrightarrow \,\diagdown\!\!\text{C-H} + \,\diagdown\!\!\text{C=C}\diagup \quad (67)$$

$$2\text{Mn(CO)}_5 \longrightarrow \text{Mn}_2\text{(CO)}_{10} \quad (68)$$
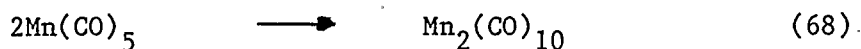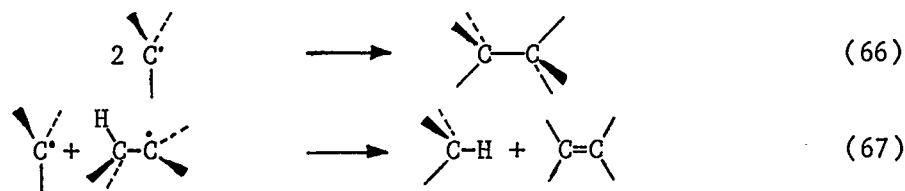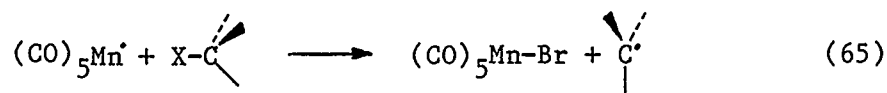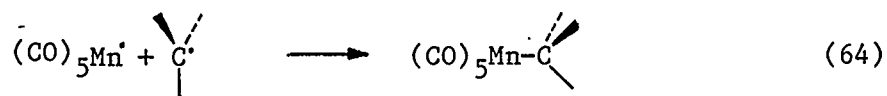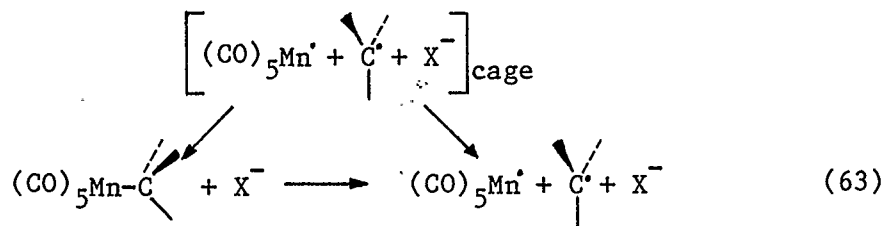
The key ingredient in these reactions is the formation of intermediate radicals. Thus, a mixture of cage and typical non-cage free radical reactions could lead to all three manganese products observed. The abstraction of bromine by $(CO)_5Mn$, (65), is known to occur for simple halo and polyhalo alkyl compounds, and in some cases occurs at a rate close to the diffusion control limit[93]. The other steps illustrated above (64), (66), (67) and (68) are typical radical reactions, but it is worth pointing out that (64) gives the substitution product, and is indistinguishable from the cage recombination product. Hydrogen atom abstraction from solvent would lead to products derived from the solvent radicals which could of course undergo typical reactions themselves.

The stoichiometry with respect to substitution (and $Mn_2(CO)_{10}$ formation) based on these steps is 1:1 for the reactants $(Mn(CO)_5^-:R-X)$. However, for a pure $Mn(CO)_5X$ forming reaction the stoichiometry is 1:2, as shown below

$$2RBr + Mn(CO)_5^- \longrightarrow Mn(CO)_5Br + Br^- + 2R \qquad (69)$$
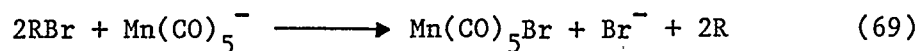
Therefore, mixed product reactions will not involve simple stoichiometric ratios of the reactants, $Mn(CO)_5^-$ and R-X.

The mechanism described above is conceptually attractive since it involves one unifying process, i.e. initial electron transfer, to explain the formation of all the manganese products.

This explanation relies heavily on the diffusion of radicals being competitive with cage recombination, and there is evidence that

this could explain non-substitution products in some related reactions[92,94]. However, it does not readily explain all of the results described in this work (see below), although one cannot rule out the possibility that some of the reaction involving $Mn(CO)_5^-$ proceeds in this way.

An alternative explanation involves two competing reactions. Some researchers have proposed[95,96] that substitution reactions involving metalate anions can also proceed via a carbanion intermediate involving halogen metal exchange (H.M.E.).

$$Mn(CO)_5^- + X-C\diagup \longrightarrow (CO)_5Mn-X + \ ^-C\diagup \longrightarrow (CO)_5Mn-C\diagup + X^- \quad (70)$$
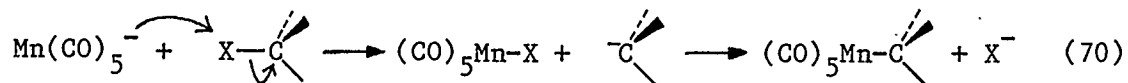
Such a process, as written above, does of course give the substitution product. However, attack by $Mn(CO)_5^-$ on halogen could take place to give carbanion intermediates in a separate non-substitution reaction as shown below[97].

$$Mn(CO)_5^- + X-C\diagup$$

$$S_N2 \text{ or E.T.} \diagdown \qquad \diagup \text{H.M.E}$$

$$(CO)_5Mn-C\diagup + X^- \qquad\qquad Mn(CO)_5X + \ ^-C\diagup \quad (71)$$
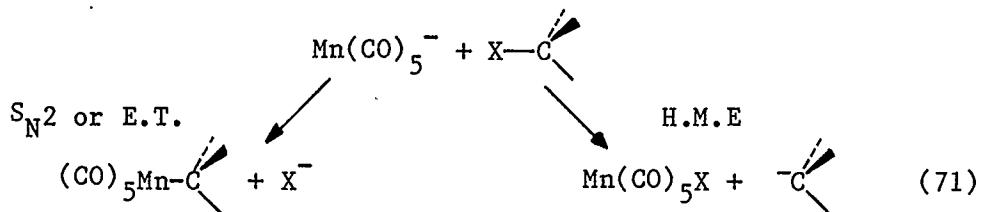
Such intermediate carbanions (or enolates) could then undergo reactions with more organic halide in the expected fashion, such as

substitution (72) or elimination (73).

$$\overset{\backslash}{\underset{/}{C}}{}^{-} + \overset{\backslash}{\underset{/}{C}}-X \longrightarrow \overset{\backslash}{\underset{/}{C}}-\overset{/}{\underset{\backslash}{C}} + X^{-} \qquad (72)$$

$$\overset{\backslash}{\underset{/}{C}}{}^{-} + \overset{H}{\underset{/}{C}}-\overset{/}{\underset{X}{C}} \longrightarrow \overset{\backslash}{\underset{/}{C}}-H + \overset{}{\underset{/}{C}}=\overset{/}{\underset{\backslash}{C}} + X^{-} \qquad (73)$$
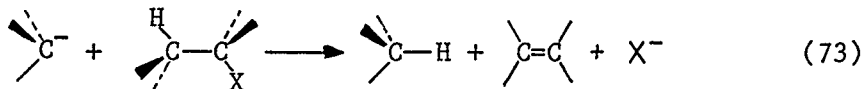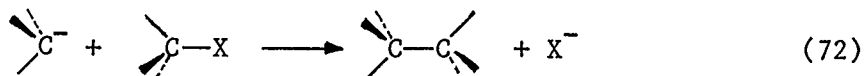
Obviously, the key feature distinguishing these alternative mechanisms is that one involves organic radical intermediates while the other involves carbanions. It was initially thought that the observed formation of $Mn_2(CO)_{10}$ could only be consistent with the radical pathway, since the steps outlined above for H.M.E. do not explain the formation of this product. The stoichiometry of the E.T. based mechanism would also require that where $Mn(CO)_5Br$ is formed, unreacted $Mn(CO)_5^{-}$ should remain for an initial 1:1 mixture of reactants. This is significant since for all cases described in this work where $Mn(CO)_5$ halides and $Mn_2(CO)_{10}$ were formed, no unreacted $Mn(CO)_5^{-}$ was observed when equimolar mixtures of the reactants were used, except for the reactions using $PPN^{+}[Mn(CO)_5^{-}]$ in tetrahydrofuran.

The absence of unreacted $Mn(CO)_5^{-}$ prompted a search for other reactions that the anion could undergo with the products obtained. One possibility, for which there is precedent[98], is that the anion can react with $Mn(CO)_5Br$ as follows

$$Mn(CO)_5^{-} + Mn(CO)_5Br \longrightarrow Mn_2(CO)_{10} + X^{-} \qquad (74)$$

Indeed, when $Na^{+}[Mn(CO)_5^{-}]$ was reacted with $Mn(CO)_5Br$ in THF a

very rapid reaction took place and ^{55}Mn-N.M.R. and I.R.-spectroscopies

confirmed the quantitative formation of $Mn_2(CO)_{10}$. Further

investigation showed the reaction also took place between

$PPN^+[Mn(CO)_5^-]$ and both $Mn(CO)_5Br$ and $Mn(CO)_5I$ in chloroform. In this

case a competitive reaction was also carried out where $PPN^+[Mn(CO)_5^-]$

was reacted with a mixture of $Mn(CO)_5Br$ and $Mn(CO)_5I$. The results of

this experiment (see Table 2.14) indicate that this reaction is

somewhat faster with $Mn(CO)_5I$.

	$BrMn(CO)_5$	$IMn(CO)_5$	$Mn_2(CO)_{10}$
Initial ratio[a]: Ratio after addition of 0.2372 mmole $PPN^+[Mn(CO)_5^-]$:	1.000(1[b]) 1.00	0.9592(0.99[b]) 0.82	0 2.50(2.34[c])

Table 2.14 Competitive Experiment for the Reaction of $PPN^+[Mn(CO)_5^-]$ with Manganese Pentacarbonyl Halides.

[a]0.2571 mmoles $BrMn(CO)_5$ and 0.2466 mmoles $IMn(CO)_5$ in 2mls. chloroform.
[b]Ratio observed by ^{55}Mn-N.M.R. before addition of anion.
[c]Calculated.

Surprisingly, the reaction of $PPN^+[Mn(CO)_5^-]$ with $Mn(CO)_5Br$ in

THF was considerably slower, the reaction required about 4 hours to go

to completion. Under these conditions the reaction was accompanied by

the evolution of gas, and as $Mn(CO)_5Br$ was consumed, the remaining

$Mn(CO)_5Br$ was converted to $PPN^+[Mn(CO)_4Br_2^-]$ (assigned from the ^{55}Mn-

N.M.R. and IR spectra). Thus the overall reaction was

$$Mn(CO)_5^- + 2Mn(CO)_5Br \xrightarrow[\substack{THF \\ 25^\circ C}]{4\ hrs} Mn_2(CO)_{10} + Mn(CO)_4Br_2^- + CO \quad (75)$$
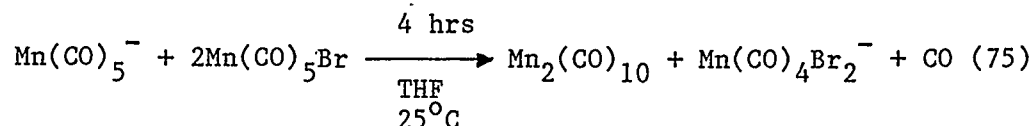
In the light of these results it is clear that this reaction could

explain some (if not all) of the $Mn_2(CO)_{10}$ formed in the reactions

described in this work. It also provides a convenient explanation for

the variation in the relative amounts of $Mn_2(CO)_{10}$ and $Mn(CO)_5X$

products in experiments where the ratio of the reactants is varied.

Obviously, where $Mn(CO)_5^-$ is used in excess, any $Mn(CO)_5X$ formed will

further react to give $Mn_2(CO)_{10}$ as the major product, as one observes.

This reaction also changes the overall stoichiometry of the E.T.

based mechanism. It now becomes:

$$Mn(CO)_5^- + R-X \longrightarrow 1/2Mn_2(CO)_{10} + R + X^- \quad (76)$$
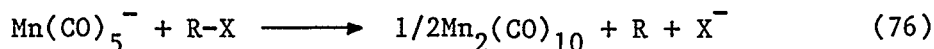
This is regardless of whether the $Mn_2(CO)_{10}$ is formed directly by

coupling of $Mn(CO)_5$ or indirectly from $Mn(CO)_5X$ formed by abstraction.

Thus a pure E.T. mechanism as written above would not be consistent

with all of the results described, i.e. $Mn(CO)_5X$ cannot be a final

product where equimolar quantities of reagents are employed.

In contrast the formation of $Mn(CO)_5X$ via a H.M.E. process would

not necessarily require that the reaction would conform to the same

stoichiometry. In this case the relative amounts of $Mn_2(CO)_{10}$ and

$Mn(CO)_5X$ would depend on the relative rates of the $Mn_2(CO)_{10}$ forming

reaction and the initial H.M.E. step. Thus initial equimolar mixture

of reactants, $Mn_2(CO)_{10}$ would be the sole non-substitution product

only if all the carbanion formed reacted with one equivalent of the

organic halide reactant. If this were not the case, then simple

stoichiometries need not follow.

More direct evidence for the mechanism comes from the organic

products observed for some of the reactions described in this work.

Considering the general schemes described above for the E.T. and

H.M.E. mechanisms, one would not necessarily expect any differences in

the observed organic products.

The reaction of $Na^+[Mn(CO)_5^-]$ with 1,3-diphenyl-3-bromo-1-propene

59 to give the dimer 60 is in contrast to the related reactions of

benzyl bromide[42] and 1-phenyl-3-bromo-1-propene, where substitution is

observed exclusively. The bromide 59 is not necessarily a good

substrate for S_N2 reactions, in fact some dissociation to give the

carbocation 81 would be expected, and this would be a good acceptor

for electron-transfer as shown below.

(77)

59   81
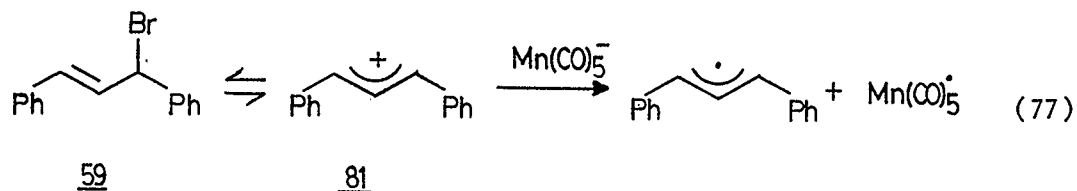
The ability of $Mn(CO)_5^-$ to undergo electron transfer reactions with

carbocations is well documented[99,100].

The absence of any substitution product from the reaction of

$Mn(CO)_5^-$ with 3-bromo-2-pentene and the formation of 1,3-pentadiene

could be explained by either H.M.E. or E.T. processes; however, both

these mechanisms would require that 2-pentene is also formed.

(78)

(79)
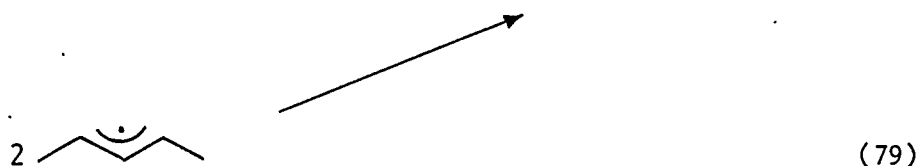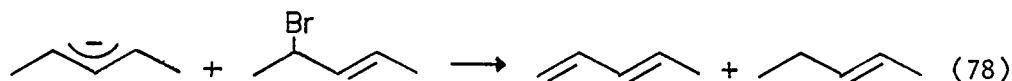
One is tempted to conclude that other products are formed in this

reaction to give the required stoichiometry, but for some reason they

do not show up in the ^{13}C-N.M.R. spectrum of the crude reaction

mixture.

For the reaction of $Mn(CO)_5^-$ with ethyl 4-bromo-2-butenoate 48,

one could argue that the formation of the cyclopropane derivatives 52

and 53 are more likely to have arisen from the enolate intermediate

82. Based on the known reaction of 4-bromo-2-butenoate esters with

related stabilized enolates[82], thiolates[101], and carbanions[102] one can

rationalize the formation of these products via Michael addition with

cyclization (80).

(80)
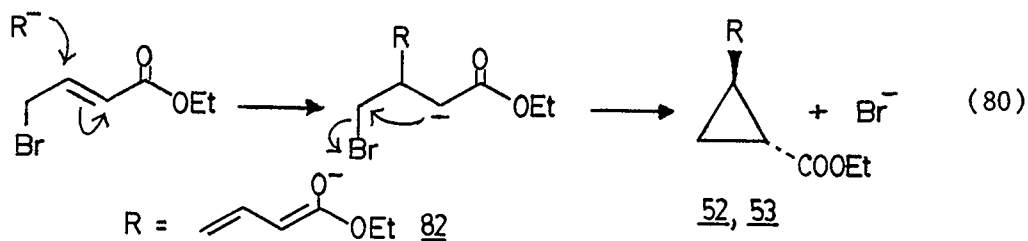
In order to test the likelihood of this reaction involving the enolate 82, this was prepared from ethyl-2-butenoate using lithium diisopropyl amide (in THF/HMPA) and reacted with 48. The major product of this reaction was identified as the diene 83, presumably arising from substitution followed by rearrangement.

$$\text{(81)}$$

83   70%
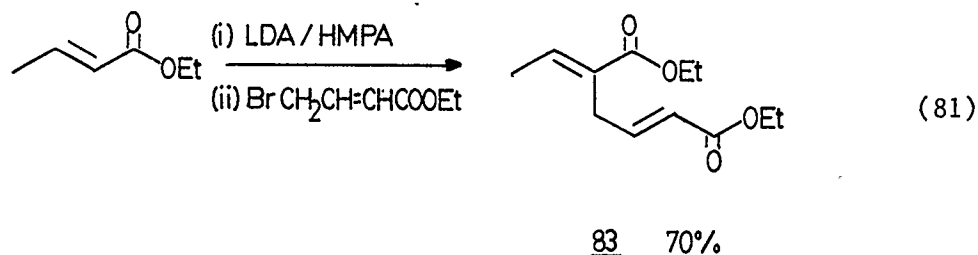
No evidence for the formation of the cyclopropyl aducts 52 and 53 was observed in the G.C. of the crude reaction mixture. This reaction has in fact been observed by other researchers[82], where it was also found that for other enolates the presence of HMPA retarded the formation of cyclopropyl derivatives over substitution products. Attempts in the present work to prepare the enolate 82 in the absence of HMPA and subsequent reaction with ethyl 4-bromo-2-butenoate gave complex mixtures of products. None of the products formed corresponded to the products observed in the $Mn(CO)_5^-$ reaction nor was there evidence for any of the diene 83. It was subsequently found that the method of preparation of the enolate 82 using LDA requires the addition of HMPA[103].

A similar mechanism involving a free radical addition reaction with cyclization can also be written:

$$\text{(82)}$$

$$R = \quad \underline{84}$$
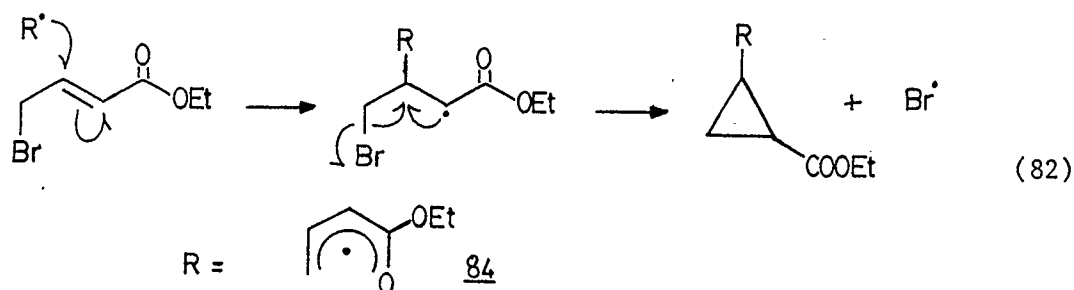
Such a reaction would form bromine radicals which could combine with $Mn(CO)_5$ to give $Mn(CO)_5Br$, although this would not be the only option open to this reactive species. The γ-bromo radical above would not normally be expected to undergo such a cyclization, intermolecular processes such as abstraction and coupling would normally dominate. For this reason the feasability of such a process was tested by generating the radical $\underline{84}$ in the presence of ethyl 4-bromo-2--butenoate. This was achieved by the photolysis of $Mn_2(CO)_{10}$ in the presence of ethyl 4-bromo-2-butenoate. The photolysis of $Mn_2(CO)_{10}$ is known to .give $Mn(CO)_5$ by homolytic cleavage of the metal-metal bond[104]:

$$Mn_2(CO)_{10} \xrightarrow{\ h\nu\ } 2Mn(CO)_5^{\bullet} \qquad (83)$$
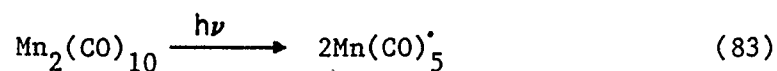
Generation of these radicals in the presence of an alkyl halide is expected[93,105] to result in halogen abstraction to give $Mn(CO)_5X$ and alkyl radicals.

$$Mn(CO)_5^{\bullet} + R-X \longrightarrow Mn(CO)_5X + R^{\bullet} \qquad (84)$$
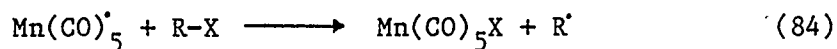
The formation of the coupled product $Mn(CO)_5R$ is not expected to interfere in this case since this species is also readily cleaved

homolytically upon photolysis[106].

The products of the reaction were identified by G.C.-mass spectrometry and ^{1}H-N.M.R. of the crude residue remaining after evaporation of the reaction mixture. The simple dimers 50 and 51 were found to be the only organic products formed in this reaction.

$$Mn_2(CO)_{10} + \text{(structure)} \xrightarrow[\text{THF}]{h\nu} \quad 64\% \text{ (50)} \quad 36\% \text{ (51)} \qquad (85)$$
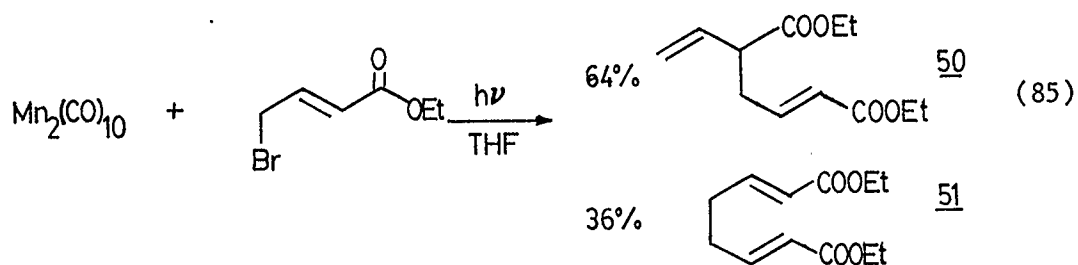
No evidence for the formation of the cyclopropyl adducts 52 and 53 was observed. Clearly, this reaction does not entirely reproduce the conditions of the $Mn(CO)_5^-$ reaction, however from these results it would seem unlikely that free radical cyclization would occur readily.

The deuterium substitution in the reaction of $PPN^+[Mn(CO)_5^-]$ with 2-halo esters could also be explained initially in terms of either radical or enolate intermediates. For the H.M.E. initiated process, the intermediate enolate would react with somewhat acidic chloroform to give the observed product and trichloromethyl anions:

$$R^1R^2C=C \overset{O^-}{\underset{OEt}{<}} \xrightarrow{CDCl_3} R^1R^2CDCOOEt + {}^-CCl_3 \qquad (86)$$

$$\downarrow$$

$$:CCl_2 + Cl^-$$
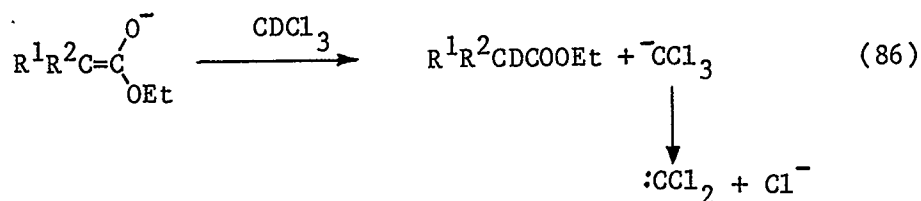
The trichloromethyl anion formed could then eliminate chloride to give dichlorocarbene. In order to trap any dichlorocarbene formed by such

·a process, the reaction of $PPN^+[Mn(CO)_5^-]$ with primary, secondary and tertiary 2-iodo-esters was carried out in the presence of a large excess of cyclohexene. No evidence for the presence of the adduct of the cyclohexene with dichlorocarbene was observed. There is evidence, however, that trihalomethyl anions do not always eliminate halide to give carbenes[107]. However, since it was not possible to observe any readily identifiable major products derived from either CCl_3^- or CCl_2, this is not confirmed by the results described.

The alternative possibility, i.e. that deuterium incorporation could be explained by a free radical intermediate, was also explored. In this case one can rationalize the formation of the observed product via free radical abstraction as shown below

$$R^\cdot + CDCl_3 \longrightarrow {}^\cdot CCl_3 + R\text{-}D \qquad (87)$$
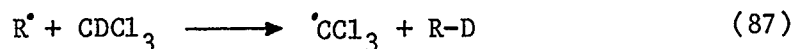
The formation of trichloromethyl radicals in this step would be expected to give at least some hexachloroethane by simple coupling. This product was not observed in reaction mixtures carried out in deuterochloroform, a fact which was confirmed by comparing the G.C. analysis with that of authentic material.

The possibility that radicals could abstract deuterium from chloroform was tested by irradiating a mixture of $Mn_2(CO)_{10}$ and each of the 2-bromo esters described for the $Mn(CO)_5^-$ reactions. In the case of ethyl 2-bromoethanoate, diethyl succinate 85 was observed as the major product along with a low yield of ethyl acetate 86 as shown below.

$$\text{BrCH}_2\text{COOEt} + \text{Mn}_2(\text{CO})_{10} \xrightarrow[\text{CDCl}_3]{h\nu} \text{EtOOCCH}_2\text{CH}_2\text{COOEt} + \text{CH}_3\text{COOEt} \quad (88)$$

$$\underline{85} \ 50\% \qquad\qquad \underline{86} \ 11\%$$
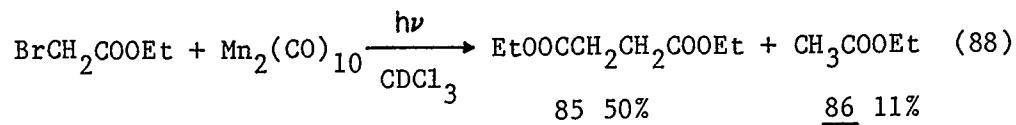
The products of this reaction were identified by gas chromatography and [1]H-N.M.R. spectroscopy of the crude reaction mixture. The final manganese products of this reaction were unidentified since considerable decomposition took place during the irradiation. All that remained at the end of the experiment was a white insoluble powder, although the I.R.-spectrum of the reaction mixture taken during the irradiation implied that $\text{Mn(CO)}_5\text{Br}$ was formed initially. Some unreacted ethyl 2-bromoethanoate remained while no $\text{Mn}_2(\text{CO})_{10}$ remained. There was evidence that the singlet corresponding to the methyl group in ethyl ethanoate in the [1]H-N.M.R. spectrum overlapped with a weak triplet corresponding to DCH_2COOEt. However, integration of these signals indicated that even if this was a correct assignment the deuterium incorporation was less than 3% of the total ethyl acetate present.

Similar results were obtained for the photolysis of $\text{Mn}_2(\text{CO})_{10}$ and ethyl 2-bromopropanoate in deuterochloroform. In addition to 27% unreacted ethyl 2-bromopropanoate, the major product was found to be diethyl 2,3-dimethyl succinate $\underline{87}$.

The products from the photolysis of $\text{Mn}_2(\text{CO})_{10}$ with ethyl 2-bromo-2-methyl propanoate were apparently more complex than the cases described above. Again the major product was identified as the dimer of the intermediate radicals expected from this reaction.

$$Mn_2(CO)_{10} + CH_3CHBrCOOEt \xrightarrow[CDCl_3]{h\nu} \underset{EtOOC}{\overset{COOEt}{\diagup}} + CH_3CH_2COOEt \quad (89)$$

87 47% **88** 21%

$$Mn_2(CO)_{10} \quad (CH_3)_2CBrCOOEt \xrightarrow[CDCl_3]{h\nu} \overset{COOEt}{\diagup} \quad \overset{COOEt}{\diagup} \quad (90)$$

74 13% **75** 5%

76 36% **77** 4% **89** 9%
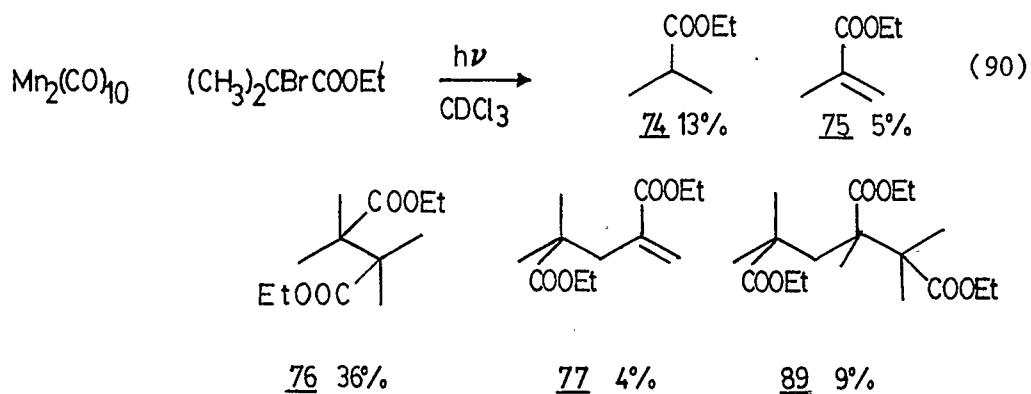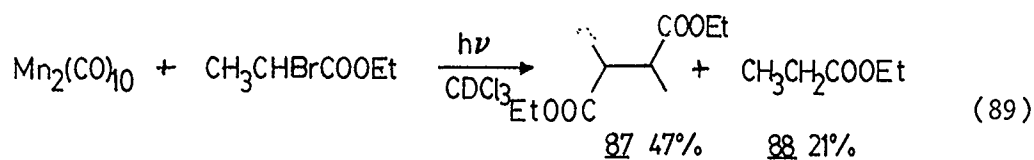
In this case the products were assigned by G.C.-mass spectrometry and ^{1}H-N.M.R. spectroscopy of fractions isolated by preparative G.C. The assignment of the trimer **89** is tentative since although the mass spectrum was consistent with trimer, the ^{1}H-N.M.R. of this product is open to a number of interpretations. A similar pattern of products was observed when this reaction was carried out in tetrahydrofuran.

The full interpretation of these experiments is somewhat more complex than the simple steps outlined for an E.T. mechanism described earlier. For example, the formation of ethyl ethanoate in the photolysis of $Mn_2(CO)_{10}$ with ethyl 2-bromoethanoate implies that other processes take place under these conditions. They do suggest though that abstraction of deuterium by the radicals is an unlikely process.

The formation of 2,2,3,3,-tetramethyl succinate **76** in the reaction of $Na^+[Mn(CO)_5^-]$ (and the PPN$^+$ salt) with ethyl 2-bromo-2-methyl

propanoate in THF is at first sight an unlikely product from enolate intermediates. However the reaction of the lithium enolate $\underline{90}$ has been shown by others[108] to undergo this reaction in respectable yields, indicating that these products are possible in a H.M.E. mechanism.

$$(91)$$
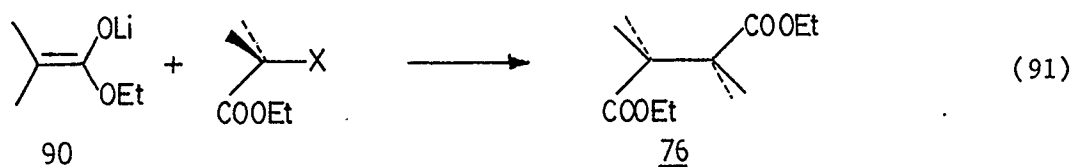
The results of the present work showed that the formation of $\underline{76}$ was accompanied by ethyl 2-methylpropanoate $\underline{74}$ and lesser amounts of ethyl 2-methyl-2-propenoate $\underline{75}$. These could arise by elimination:

$$(92)$$
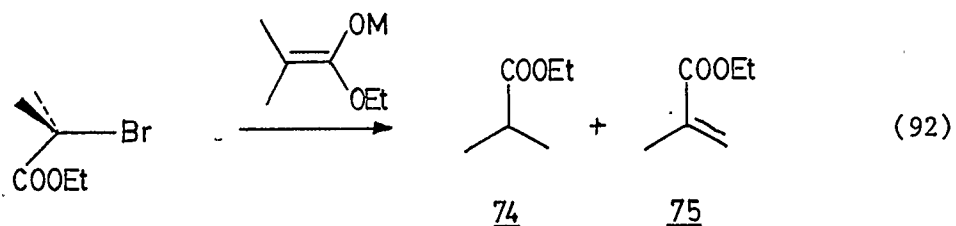
In this mechanism one would have to assume that $\underline{75}$ underwent other reactions (Michael addition for example) to explain why $\underline{74}$ and $\underline{75}$ are not formed in equal amounts. However, small amounts of the unsaturated dimer $\underline{77}$ was also observed in these reaction mixtures (a product which was also observed in the photolysis experiments described above)

and it is difficult to see how this could arise from an enolate intermediate. Since this product is formed in the photolysis experiments described above this suggests that there may be some free radical component for this particular substrate. However, this would not appear to be the case for the reaction of $Na^+[Mn(CO)_5^-]$ with the primary substrate ethyl 2-iodoethanoate where the expected free radical, product diethyl succinate, is practically absent. The absence of this product could also be used to argue against intermediate enolates where, diethyl succinate, would also be the expected product[108], although in this case a number of other options may be possible.

It is evident from the reactions carried out between $Mn(CO)_5^-$ and 2-halo esters that (Tables 2.9, 2.10 and 2.11) the structure of the organic halide plays an important role in determining the relative yields of substitution and non-substitution products. This is illustrated in particular by the somewhat surprising results for the reaction of $Na^+[Mn(CO)_5^-]$ with 2-bromo and 2-iodo esters in THF (see Table 2.9). For these conditions the observed yield of non-substitution products decreases tertiary > primary > secondary. The results show that for the 2-iodo esters the substitution product is only observed in the reaction with the secondary substrate. This observation is not entirely unexpected if one considers the effects which are likely to effect H.M.E. reactions If one assumes that the rate of the H.M.E. reaction follows the order of stability of the intermediate enolate, then it should be favored for primary

substrates. Thus, one could explain the observed pattern of reactivity by assuming that the H.M.E. reaction is more sensitive to the structure of the organic halide than a competing S_N2-type substitution mechanism. On the other hand one would predict that any E.T. component in the overall mechanism would be least favorable for primary substrates[109], resulting in the opposite trend to what is observed.

The effect of changing the counterion from Na^+ to PPN^+ in this reaction is to increase the overall yields of the substitution product for primary and secondary 2-halo esters. In this case the yield of the substitution product follows the "expected" trend with an increase tertiary < secondary < primary. This would correspond to a situation where nucleophilic substitution dominates the observed pattern of products, i.e. the structural factors affecting the rate of the H.M.E. reaction are smaller than those effecting bimolecular nucleophilic substitution. In the case of the reaction of $Mn(CO)_5^-$ with ethyl 4-bromo-2-butenoate (see Table 2.7) a similar effect is observed, i.e. changing the counterion from Na^+ to PPN^+ increases the amount of the substitution product. This is expected since substitution is more favorable where ion association is reduced, and the degree of association between $Mn(CO)_5^-$ and PPN^+ is expected[110] to be less than that with the Na^+ cation. For this reaction the trend can be extended, the observed yield of substitution product increasing $Li^+ < Na^+$ $K^+ < PPN^+$ for reactions carried out in THF. The degree of ion association in $M^+[Mn(CO)_5^-]$ has been shown to be less for $Li^+[Mn(CO)_5^-]$ than $Na^+[Mn(CO)_5^-]$, a fact which can be explained by the degree of

coordination of the alkali metal cation by THF[89,111,112]. Clearly

this is not reflected by the results described in the present work for

the yield of the substitution product since little substitution took

place when the counterion was Li^+. This pattern would be consistent

though with a competing H.M.E. process, since the intermediate enolate

is stabilized by association with the counterion, and one would expect

this association to decrease in the order $Li^+ > Na^+ > K^+ > PPN^+$.

The effect of changing the solvent from THF to chloroform in the

reactions of $PPN^+[Mn(CO)_5^-]$ with halo esters is to give an overall

decrease in the observed relative amount of the substitution product.

Whether this effect corresponds to a relative decrease in the rate of

nucleophilic substitution or an increase in the rate of the H.M.E.

reaction is unclear. Both solvents are of similar polarity (the

dielectric constant for chloroform is 4.7 compared with 7.4 for THF),

thus one would not expect this to be an important factor. It is

possible that the degree of association of PPN^+ with $Mn(CO)_5^-$ is less

in THF than in chloroform (PPN^+ salts are generally more soluble in

chloroform than in THF), which would explain why substitution

dominates in THF.

Conclusions

As a method for preparing alkyl complexes, the reaction of

$Mn(CO)_5^-$ with alkyl halides is limited to compounds which are

activated towards nucleophilic substitution. However, from a synthetic

point of view, changing to a better halogen leaving group results in

poor yields of the desired product. The reaction of the PPN^+ salt in

THF gives the best yield of the desired products, and is the method of choice where alkyl bromides or iodides are needed.

With some reservations, the formation of non-substitution products is best explained by a halogen metal exchange reaction. In theory, this process could be used to advantage since it might form the basis of a method for preparing carbanions under neutral conditions.

Chapter 3

3.1 Introduction

Based on the known reactivity of $Mn(CO)_5^-$ with acyl halides[11],
its reaction with haloacyl halides $\underline{91}$ is expected to give the
corresponding haloacyl complexes $\underline{92}$ by nucleophilic substitution

$$Mn(CO)_5^- + Cl\overset{O}{\overset{||}{C}}(CH_2)_nCR^1R^2X \longrightarrow Mn(CO)_5\overset{O}{\overset{||}{C}}(CH_2)_nCR^1R^2X + Cl^- \quad (93)$$

$$\underline{91} \qquad\qquad\qquad \underline{92}$$
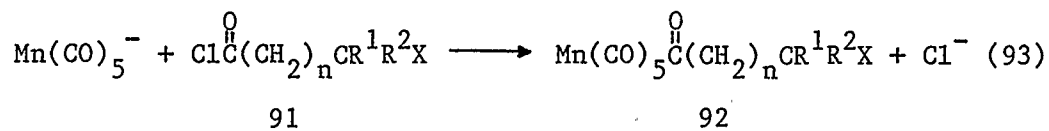
This reaction would give acyl complexes $\underline{92}$ with a variety of halides
X, R substituents and chain length n. However, there are relatively
few examples of this reaction, and these deal with cases where X =
chloride. For example the a-chloroacyl manganese complex $\underline{93}$ can be
prepared using this method[113]:

$$Mn(CO)_5^- + Cl\overset{O}{\overset{||}{C}}CH_2Cl \longrightarrow Mn(CO)_5\overset{O}{\overset{||}{C}}CH_2Cl + Cl^- \quad (94)$$

$$\underline{93}$$
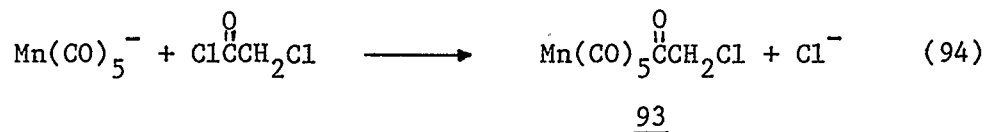
This reaction is also applicable to cases with more remote chloride
substitution[114] as in $\underline{94}$:

$$Mn(CO)_5^- + Cl\overset{O}{\overset{||}{C}}CH_2CH_2CH_2Cl \longrightarrow Mn(CO)_5\overset{O}{\overset{||}{C}}CH_2CH_2CH_2Cl + Cl^- \quad (95)$$

$$\underline{94}$$
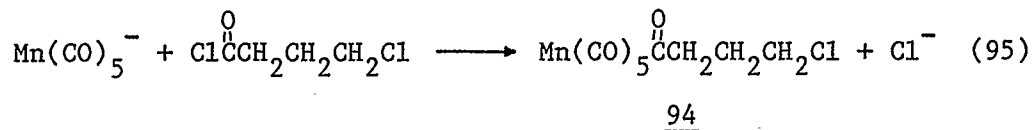
The possibility that this reaction could be used for other halogens
(other than fluoride[11]) has not been investigated for manganese. In
this thesis, the interest in preparing complexes $\underline{92}$, particularly

where X=Br arose from the possibility that such complexes could

undergo intramolecular oxidative addition of the C-Br bond (see

reaction (17), Chapter 1).

This leads to two related objectives, the preparation of 2-haloacyl

complexes (92, n=0) as precursors for a-haloalkyl complexes.

Secondly, to investigate the possibility that for complexes 92, where

n > 0, cyclometalation can occur. These are described below.

a-Haloalkyl Manganese Complexes

a-Haloalkyl manganese complexes 95 are potentially useful since

in principle they could undergo either loss of halide or halide

migration to give alkylidene complexes 96 and 97 respectively.

$$XCR^1R^2Mn(CO)_5 \quad \overset{\displaystyle \nearrow \; CR^1R^2 \overset{X}{=} Mn(CO)_4 + CO}{\underset{\displaystyle \searrow \; CR^1R^2 = Mn(CO)_5 + X^-}{}}$$

$$\begin{array}{lll} \underline{95} & \underline{96} & \\ & \underline{97} & \end{array} \tag{96}$$
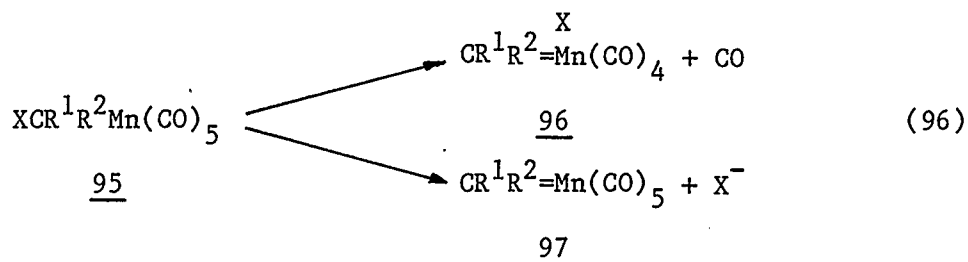
Alkylidene complexes similar to 11 have been postulated as

intermediates in the cyclopropanation of alkenes by methoxymethyl iron

complexes [115], and there has been recent interest in halo analogues of

95 ($R_1=R_2$=Halogen)[116]. The preparation of a-haloalkyl complexes 95 has

been achieved by a number of methods, including the reaction of

$Mn(CO)_5^-$ with chloroiodomethane[117,118] to give 98:

$$Mn(CO)_5^- + ClICH_2 \longrightarrow Mn(CO)_5CH_2Cl + I^- \tag{97}$$

$$\underline{98}$$
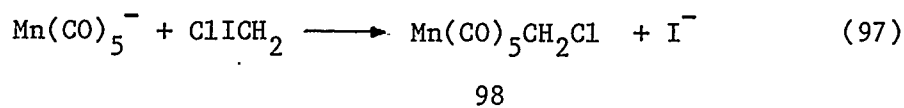
A somewhat different approach involves halogen exchange using boron trihalide and fluoromethyl complexes[116], for example α-bromomethyl manganese pentacarbonyl 99 can be made from the fluoro analog 100.

$$Mn(CO)_5CH_2F + 1/3BBr_3 \longrightarrow Mn(CO)_5CH_2Br + 1/3BF_3 \qquad (98)$$
$$\underline{100} \qquad\qquad\qquad \underline{99}$$
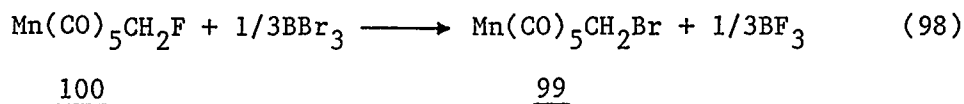
This reaction can also be used to prepare di and trihalomethyl complexes of manganese.

α-Iodomethyl manganese pentacarbonyl 102 has been prepared[119] by the reaction of the methoxymethyl complex 101 with trimethylsilyl iodide:

$$Mn(CO)_5CH_2OMe \xrightarrow{Me_3SiI} Mn(CO)_5CH_2I \qquad (99)$$
$$\underline{101} \qquad\qquad\qquad \underline{102}$$
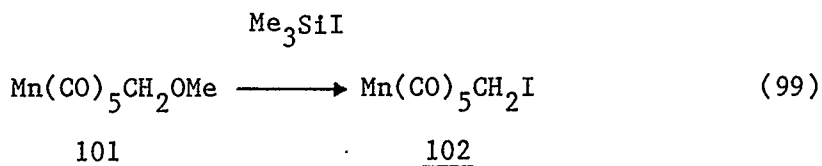
All three complexes 98, 99, and 102 are reasonably stable, although 102 decomposes to $Mn(CO)_5I$ in methylene chloride over several days.

Another approach, which has not received a great deal of attention, would be to prepare α-haloalkyl complexes via the corresponding α-haloacyl complex 104.

$$XCR^1R^2\overset{O}{\overset{\|}{C}}Cl + Mn(CO)_5^- \xrightarrow{-Cl^-} XCR^1R^2\overset{O}{\overset{\|}{C}}Mn(CO)_5 \xrightarrow{-CO} XCR^1R^2Mn(CO)_5 \qquad (100)$$
$$\underline{103} \qquad\qquad\qquad \underline{104} \qquad\qquad\qquad \underline{95}$$
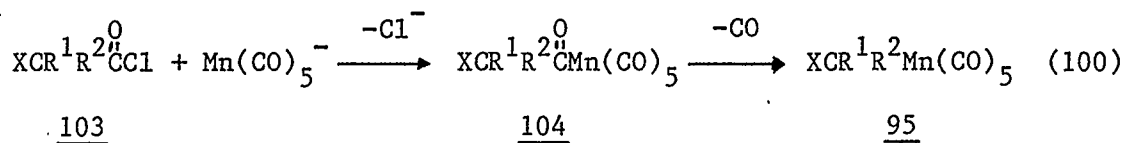
There would be some advantage to preparing the α-haloacyl complex 104 first, for instance the formation of 104 is not expected to be

affected by the substituents R^1, R^2 or the halide X. Thus, in theory a wide variety of a-haloalkyl complexes 95 could be obtained.

Cyclometallation

The β, γ and δ-halomanganese complexes 15 are potentially useful since in principle they could undergo oxidative addition to give metallocycle products (or intermediates) 16 and 105.

$$\text{Mn(CO)}_5\text{CO(CH}_2)_n\text{CH}_2\text{Br} \quad \begin{array}{c} \xrightarrow{-CO} \\[40pt] \xrightarrow{-2CO} \end{array}$$

16

105

(101)
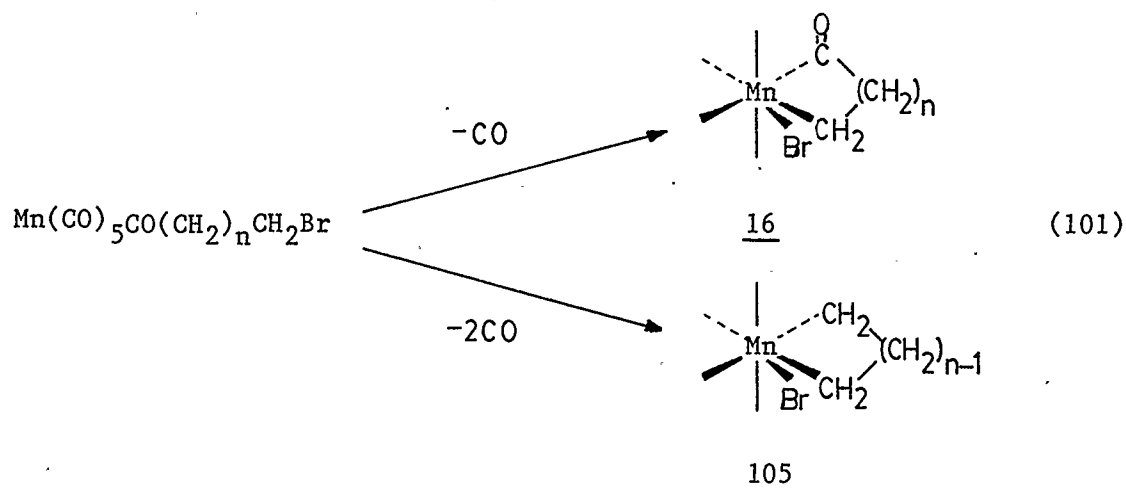
To form 16, a CO would be first lost from the manganese coordination, while with 105, one would first propose an acyl-alkyl manganese conversion followed by another CO loss from the manganese coordination shell and then cyclization. Because of the fixed coordination of the manganese, this reaction might be expected to afford some control over the stereochemistry of the ring closure. The complexes 16 and 105 could then undergo reductive elimination to give cyclized products 106 and 107. Metallocycle

complexes themselves are important in other ways, since they are

involved in olefin metathesis and dimerization reactions to name only

two.[1]

$$16 \xrightarrow{\text{CO}} Mn(CO)_5Br \; + \; \underset{CH_2}{\overset{O}{\underset{|}{\overset{\|}{C}}}} \hspace{-0.5em} {}^{(CH_2)_n} \quad \underline{106} \tag{102}$$

$$105 \xrightarrow{\text{CO}} Mn(CO)_5Br \; + \; \underset{CH_2}{\overset{CH_2}{\underset{|}{}}} \hspace{-0.5em} {}^{(CH_2)_{n-1}} \; \underline{107}$$
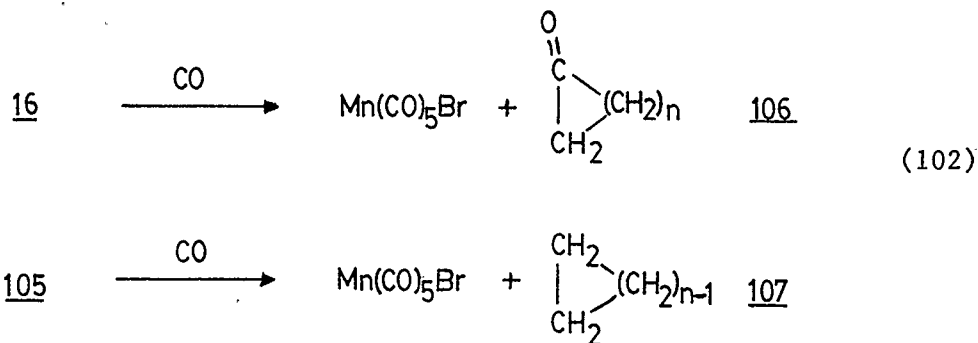
Metallocycle complexes can be prepared in a number of ways,

insertion into C-C bonds of strained cycloalkanes[120], the reaction of

dilithio-alkanes with dihalo metal complexes[121], the coupling of

alkenes or alkynes at a metal center,[122] and through cyclometallation

reactions [123]. Cyclometallation requires prior coordination of the

organic ligand to the metal center followed by ring closure by

oxidative addition. One example of this reaction is

orthometallation[124], where the ligand is coordinated to the metal

center through a benzylic heteroatom and ring closure takes place by

insertion into a C-H bond in the ortho position of the aromatic ring.

An example of such a reaction is given below[125].

$$\tag{103}$$
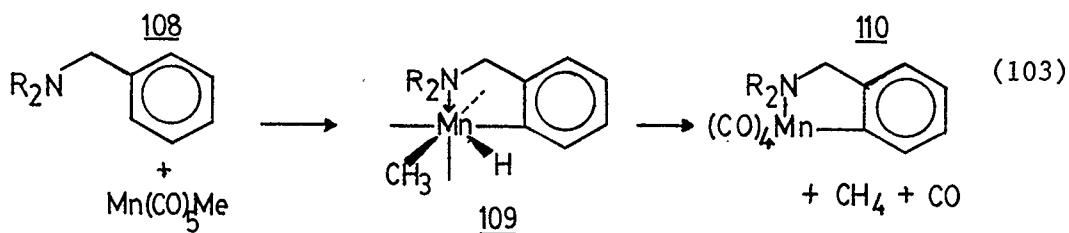
Further elaboration on this reaction using a number of reagents is
then possible followed by decomplexation of the organic fragment. A
potentially more useful cyclometallation reaction is the insertion of
the metal into an unactivated C-H bond in the alkyl ligand.
Whitesides[126] has shown that bis-neopentyl substituted platinum
complexes <u>111</u> will cyclometallate in this fashion to give the
platinocyclobutane product[23] <u>112</u>:

$$\text{(104)}$$

$$+ \ CMe_4$$

<u>111</u>   <u>112</u>
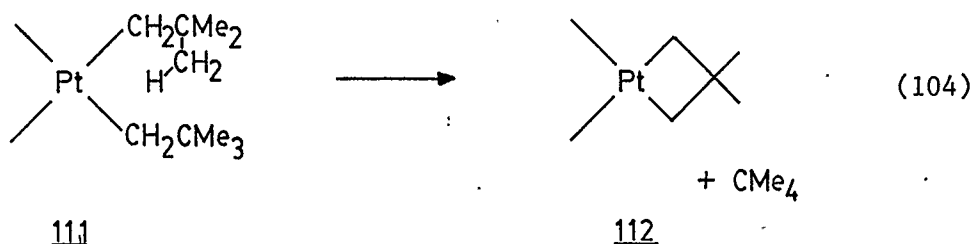
This reaction is interesting in that a remote C-H bond is activated,
but dialkyl substitution in the β-position is essential since
otherwise the reaction is dominated by β-hydride elimination to give
an alkene. A similar reaction has been described by Tulip and
Thorn[127] where they have shown that treatment of $[^{+}Ir(PMe_3)_4]Cl^{-}$ with
$LiCH_2CMe_3$ produces the iridiometallocyclobutane analogous to <u>112</u>
directly.

The reactions described above suffer from the disadvantage that
they are only appropriate for ligands which can be introduced onto the
metal center with β-substitution. However, they do illustrate how
cyclometallation can be achieved.

The possibility that the synthetic utility of these reactions
might be enhanced by cyclization involving a remote activated bond

i.e. in the haloacyl manganese complexes 15, has not been investigated. (There are examples of orthometallation using C-Br oxidative addition[128]). Such a cyclometallation would be advantageous since oxidative addition in this case could conceivably compete with side reactions such as β-elimination.

One possible complication in this strategy is that initial decarbonylation of the haloacyl manganese complex could compete with cyclization, illustrated by the decarbonylation[114] of 94 to give 113.

$$Mn(CO)_5\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2Cl \longrightarrow Mn(CO)_5CH_2CH_2CH_2Cl + CO \qquad (104)$$

$$\underline{94} \qquad\qquad\qquad \underline{113}$$
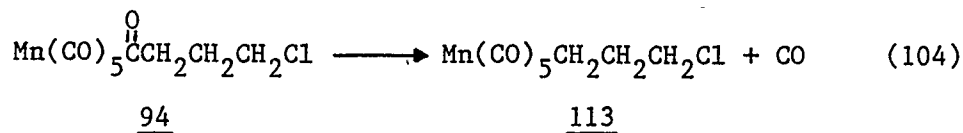
However, with bromine rather than chlorine substitution it is possible that cylcometallation would be the preferred mode.

The ability of metallocycles to reductively eliminate to give cycloalkanes is illustrated by the thermal decomposition of the nickel complexes below[129]:

$$(105)$$
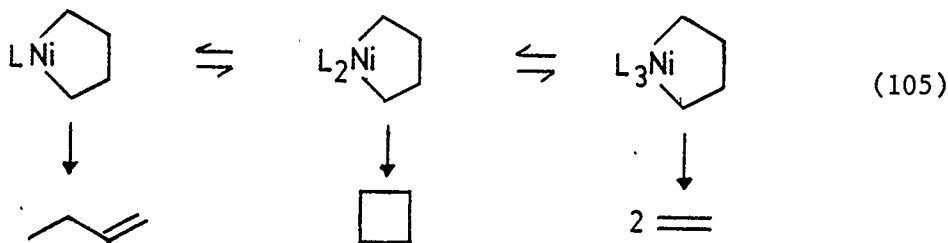
This illustrates a further complication, that is that β-hydride elimination can also complete with cyclization even at the metallocycle stage, i.e. the formation of alkenes above.

3.2 Results

3.2.1 The Reaction of $Mn(CO)_5^-$ with 2-Bromoacyl Halides

Preliminary studies on the reaction of $Na^+[Mn(CO)_5^-]$ with 2-bromoethanoyl chloride $\underline{25}$ in THF using ^{55}Mn-N.M.R. spectroscopy indicated that $Mn(CO)_5Br$ was the only product formed.

$$Na^+[Mn(CO)_5^-] + BrCH_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow[25^{\circ}C]{THF} Mn(CO)_5Br + NaCl \qquad (106)$$

$$\underline{114}$$
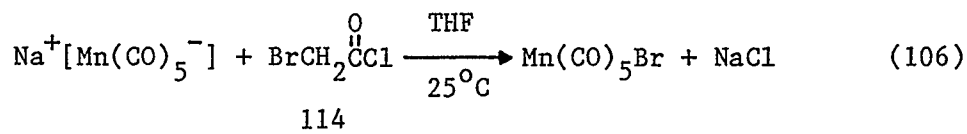
No resonances were observed in either the acyl or the alkyl region of the ^{55}Mn-N.M.R. spectrum, although a trace of $Mn_2(CO)_{10}$ was present. The reaction was carried out at temperatures ranging from $-78^{\circ}C$ to room temperature without any change in the product observed (the solution was allowed to warm to room temperature before the ^{55}Mn-N.M.R. spectrum was measured). At ambient temperatures the reaction proceeded very rapidly (<5 minutes). Similar results were obtained for the reaction of $PPN^+[Mn(CO)_5^-]$ with 2-bromoethanoyl chloride $\underline{114}$ in both THF and $CDCl_3$. Interestingly, no resonances (other than those for unreacted starting material and PPN^+Cl^-) were observed for reactions carried out in $CDCl_3$. Only $Mn(CO)_5Br$ could be isolated from these reaction mixtures (80-90% yield). Since it seemed likely that the reaction was giving a very volatile product, the reaction of $PPN^+[Mn(CO)_5^-]$ with 2-bromoethanoyl chloride was carried out in $CDCl_3$ in a sealed N.M.R. tube. In this case a sharp singlet was observed at 2.35 ppm in the ^1H-N.M.R. spectrum of the solution. This resonance was tentatively assigned to ketene $\underline{115}$, although the chemical

shift was not considered to be very characteristic, and the yield of the species responsible for this resonance was apparently very low.

$$PPN^+[Mn(CO)_5^-] + BrCH_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow{CDCl_3} Mn(CO)_5Br + \underset{H \nearrow \overset{O}{\overset{\|}{C}} \nwarrow H}{} + PPN^+Cl^- \qquad (107)$$

<u>115</u>
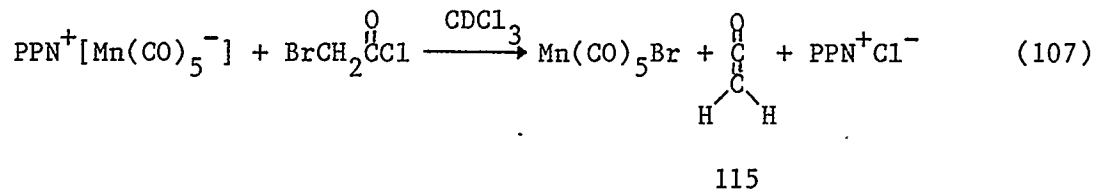
The fact that $Mn(CO)_5Br$ appeared to be the only manganese product formed in this reaction, prompted an investigation of the reaction of $Mn(CO)_5^-$ with other 2-bromoacyl halides. Using ^{55}Mn-N.M.R. spectroscopy, 2-bromopropanoyl chloride <u>116</u> was also found to react with $Na^+[Mn(CO)_5^-]$ in THF to give $Mn(CO)_5Br$ as the only manganese containing product. This reaction was also carried out using $PPN^+[Mn(CO)_5^-]$ in deuterochloroform at $-78^\circ C$ in a sealed N.M.R. tube. The reaction was followed using ^1H-N.M.R spectroscopy as the solution warmed up in the N.M.R. spectrometer probe. The resonances associated with the starting material <u>116</u> disappeared rapidly at <u>ca</u>. $-30^\circ C$ and were replaced by broad resonances consisting of a "doublet" at 1.57 ppm (J=8 Hz) and a "quartet" at 2.60 ppm. These resonances disappeared rapidly on warming to room temperature, and were replaced by a more complex N.M.R. spectrum. The ^1H-N.M.R. spectrum of the transient species is not consistent with that expected for the acyl complex, confirming the ^{55}Mn-N.M.R. spectroscopy observations. Since these observations implied that the initial product formed in this reaction is quite unstable at room temperature, the reaction was carried out in such a way that the product could be distilled as
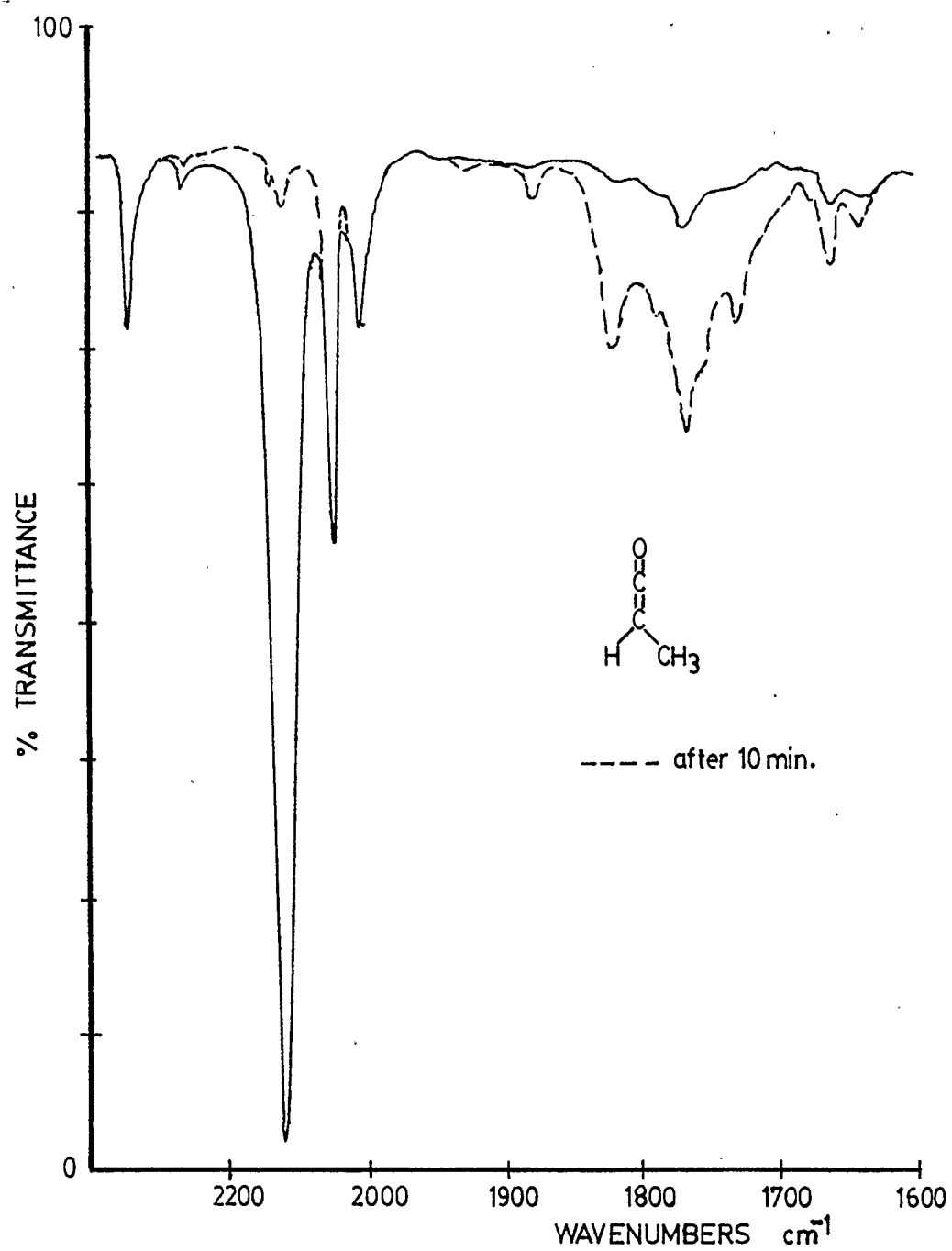
Figure 3.1 Infra-red Spectrum of Methyl Ketene (THF,solvent subtracted)

formed along with solvent into a liquid nitrogen cooled trap. Thus, a solution of 2-bromopropanoyl chloride 116 in THF was added dropwise into a slurry of $Na^+[Mn(CO)_5^-]$ in THF under vacuum, distilling the THF into a cooled trap attached to the vessel. The infra-red spectrum of the pale green distillate contained an intense band at 2117 cm^{-1} which disappeared as the solution warmed up in the infra-red cell (see Figure 3.1). This decomposition was accompanied by the appearance of several new bands in the infra-red spectrum between 1660 and 1820 cm^{-1} and a colour change from pale green to very pale yellow. From this solution compound 117 was isolated by preparative G.C. and identified by ^{1}H-N.M.R. spectroscopy and mass spectrometry.

$$Na^+[Mn(CO)_5^-] + BrCHCH_3COCl \longrightarrow \quad 118 \longrightarrow \quad 117 \ (64\%) \tag{108}$$
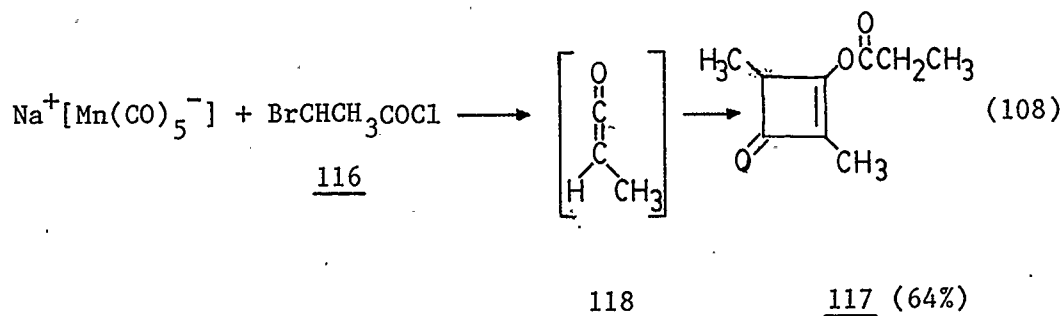
The "trimer" 117 is a characteristic product from the dimerization and trimerization of methyl ketene[130] 118. The band at 2117 cm^{-1} initially present in the infra-red spectrum of the distillate is also consistent with the intitial product being a ketene[131].

3.2.2 The Preparation of β, γ and δ-Bromoacyl Manganese Complexes

In contrast to the reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides described above, treatment of 3-bromopropanoyl chloride 119, 4-

bromobutanoyl chloride 120, and 5-bromopentanoyl chloride 121 with

$Na^+[Mn(CO)_5^-]$ yielded the corresponding haloacyl complexes 122, 123,

and 124.

$$Na^+[Mn(CO)_5^-] + BrCH_2(CH_2)_n\overset{O}{\overset{||}{C}}Cl \longrightarrow BrCH_2(CH_2)_n\overset{O}{\overset{||}{C}}Mn(CO)_5 + NaCl \quad (109)$$

n=1	119	122
n=2	120	123
n=3	121	124
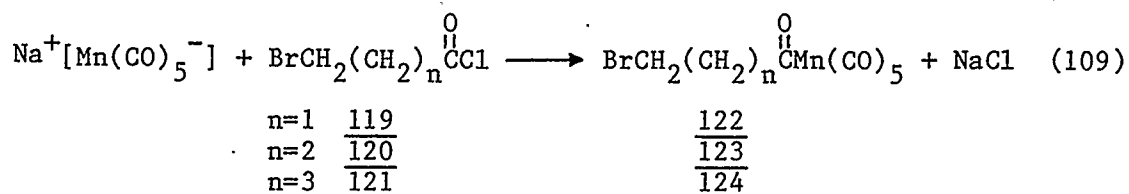
The ^{55}Mn-N.M.R. and infra-red spectra of solutions from these

reactions indicated that the reactions were essentially quantitative

(95%) although some $Mn_2(CO)_{10}$ (ca. 4%) was also present.

The acyl complexes 122 and 124 were isolated in 50% - 71% yields

as white solids and were only slightly air sensitive. Unexpectedly,

unlike 122 and 124 (and acyl complexes in general), 4-bromobutanoyl

manganese pentacarbonyl 123 was somewhat air sensitive. On exposure

to air, solid 123 readily decomposed to $Mn(CO)_5Br$, resulting in a

characteristic colour change from pale yellow to orange. Extraction

of the residue after decomposition gave a 56% yield of

γ-butyrolactone 125 and a 74% yield of $Mn(CO)_5Br$.

$$\underline{123} \xrightarrow{O_2/H_2O} Mn(CO)_5Br + \quad \underset{\underline{125} \ 56\%}{\text{(lactone)}} \quad (110)$$
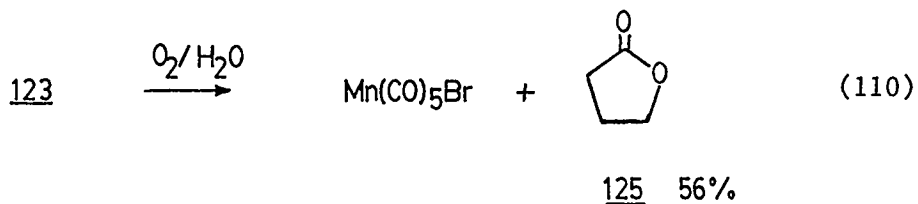
This decomposition could be avoided using the usual techniques for

handling air sensitive compounds. All three acyl complexes 122,

123, and 124 were found to be thermally unstable in THF solutions.

Heating samples of these complexes (at atmospheric pressure) prepared

in-situ from $Na^+[Mn(CO)_5^-]$ and the haloacyl halides 119, 120, and 121

to 50°C resulted in clean conversion to $Mn(CO)_5Br$ after 30 minutes.

The ^{55}Mn-N.M.R. spectra indicated that this was the major product of

the decomposition, no signals were observed in the alkyl region of the

spectrum during heating and $Mn(CO)_5Br$ was subsequently isolated from

the solutions in 80-86% yields. The infra-red spectra of these

solutions measured during the decomposition indicated that the

characteristic·acyl carbonyl stretch band (1650 cm^{-1}) disappeared, but

no new carbonyl bands other than those for $Mn(CO)_5Br$ were observed.

3.2.3 The Thermal Decomposition of 3-Bromopropanoyl Manganese Pentacarbonyl

Heating solid 3-bromopropanoyl manganese pentacarbonyl 34 above

its melting point resulted in evolution of gas at 62°C. The sample

quickly solidified with a colour change from pale yellow to orange.

Subsequent thin layer chromatography and infra-red analysis of a

solution from the residue indicated that $Mn(CO)_5Br$ was formed.

The thermal decomposition was also carried out in

deuterochloroform solution and the products formed monitored by ^1H-

N.M.R. spectroscopy. As shown in Figure 3.2, on heating the sample

to 75°C a resonance appeared in the ^1H-N.M.R. spectrum at 5.38 ppm

which corresponds to the formation of ethene. Gas analysis by G.C.

showed that ethene (72%) and, carbon monoxide (28%) were in fact
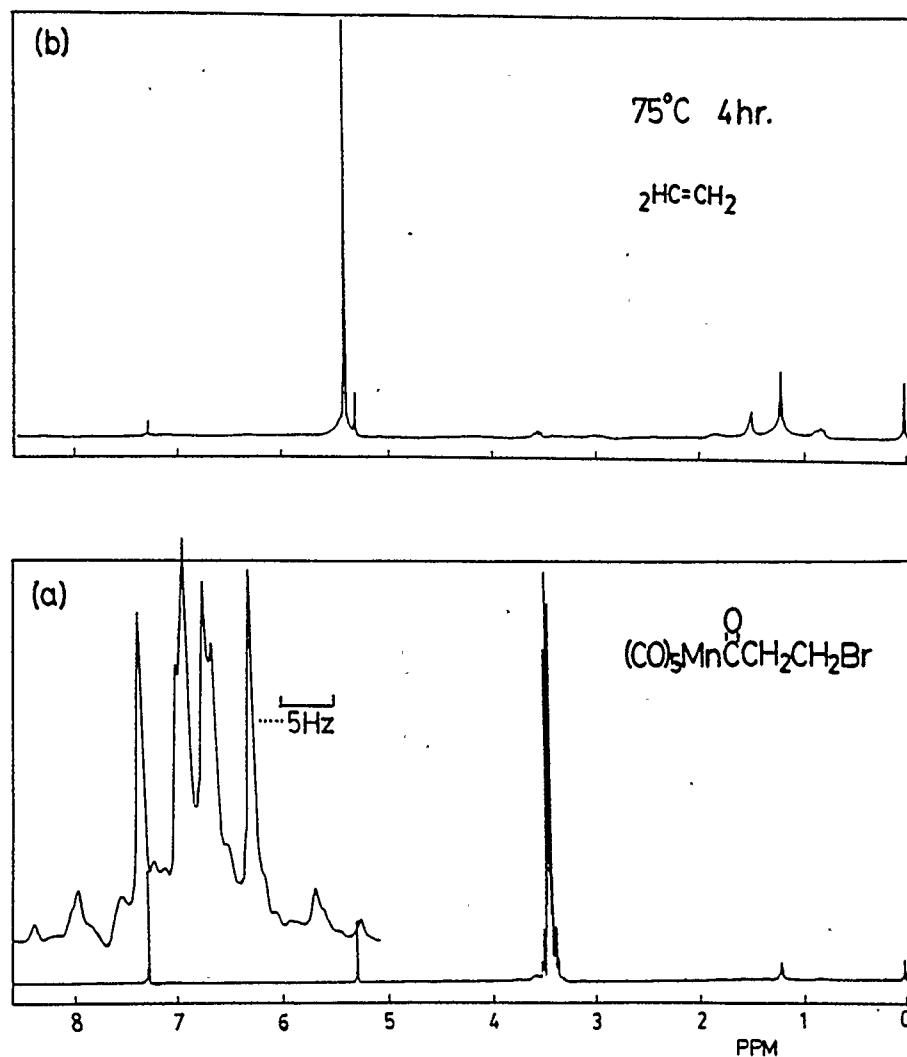
Figure 3.2 ^{1}H-N.M.R. Spectrum Measured During the Thermal

Decomposition of 3-Bromopropanoyl Manganese Pentacarbonyl (CDCl$_3$).

    (a) Spectrum of 3-Bromopropanoyl Manganese Pentacarbonyl

        (inset is a scale expansion = 35Hz).

    (b) Spectrum measured after heating to 75°C for 4 hours

formed. Subsequent infra-red analysis of the orange solution

indicated that $Mn(CO)_5Br$ was the only manganese containing species

present in the solution.

$$BrCH_2CH_2\overset{\overset{O}{\|}}{C}Mn(CO)_5 \xrightarrow[75^\circ C, \ 4hrs.]{CDCl_3} H_2C=CH_2 + Mn(CO)_5Br \qquad (111)$$
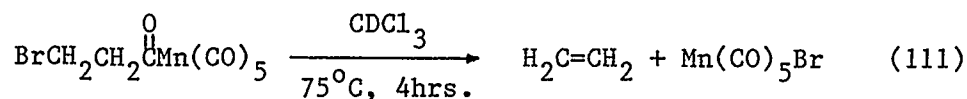
The overall yield of ethene in the decomposition is difficult to

asseses due to its high volatility, however the absence of other

resonances in the ^{1}H-N.M.R. spectrum suggests the reaction is

quantitative.

This decomposition was also carried out in tetrahydrofuran d_8.

In this case the reaction was somewhat faster, almost 50% of the

starting material having disappeared after ten minutes at $60^\circ C$

(compared to 10% at $75^\circ C$ in $CDCl_3$). Heating for 70 minutes resulted

in complete decomposition of the 3-bromopropanoyl chloride and again

an estimated quantitative yield of ethene.

3.2.4 The Thermal Decomposition of 4-Bromobutanoyl Manganese

Pentacarbonyl

In a similar fashion to 3-bromopropanoyl manganese pentacarbonyl,

heating solid 4-bromobutanoyl manganese pentacarbonyl <u>123</u> to $70^\circ C$

resulted in gas evolution and the formation of $Mn(CO)_5Br$. Thin layer

chromatography indicated the formation of another bright orange

product. This species was also present when a concentrated solution

of <u>123</u> was refluxed in chloroform. Flash chromatography of this

solution gave manganese pentacarbonyl bromide (81%) and an orange

solid (4%). This product had a characteristic infra-red spectrum

(chloroform, ν_{CO}: 2097(m); 2027 (sh); 2013(5); 1967(5) cm^{-1}) and ^{1}H-

N.M.R. spectrum (CDCl$_3$, δ ,: dt, 2.09 ppm, 2H; t, 4.18 ppm, J-7.9

Hz, 2H; t, 5.21 ppm, J=8.0 Hz, 2H), consistent with the carbene

complex $\underline{126}$.

$$\underset{\underline{123}}{BrCH_2CH_2CH_2\overset{\overset{O}{\|}}{C}Mn(CO)_5} \xrightarrow[\text{reflux}]{CDCl_3} \underset{\underline{126}\ \ 4\%}{(CO)_4 Mn} \tag{112}$$
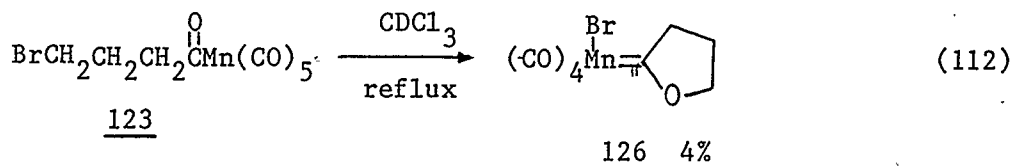
This spectral data is very similar to that reported[114] for the iodo-

analogue of $\underline{126}$. The carbene complex $\underline{126}$ was also formed by treating

4-bromobutanoyl manganese pentacarbonyl with an excess of lithium .

bromide in refluxing THF. In this case however the yield was very low

(<2%), manganese pentacarbonyl bromide being the major product. This

product was also formed, in low yield, when a chloroform solution of

4-bromobutanoyl manganese pentacarbonyl was irradiated (25°C) with a

sun-lamp. However, this also resulted in a great deal of

decomposition although some Mn(CO)$_5$Br was formed (14%).

In contrast to these reactions above, which were carried out at

atmospheric pressure, heating a chloroform solution of 4-bromo-

butanoyl chloride in deuterochloroform in a sealed tube (3 hours,

75°C) gave the corresponding alkyl complex $\underline{127}$. Although isolation of

the alkyl complex was not attempted, the ^{1}H-N.M.R. spectrum of the

solution (Figure 3.3) after heating was characteristic[114] of the alkyl

complex $\underline{127}$. (^{1}H-N.M.R. spectrum, CDCl$_3$: t, 0.9 ppm, J=8.0 Hz, 2H,

Mn-CH$_2$-; dt, 2.16 ppm, 2H; t, 3.34 ppm, J=7.5 Hz, 2H, -CH$_2$-Br).
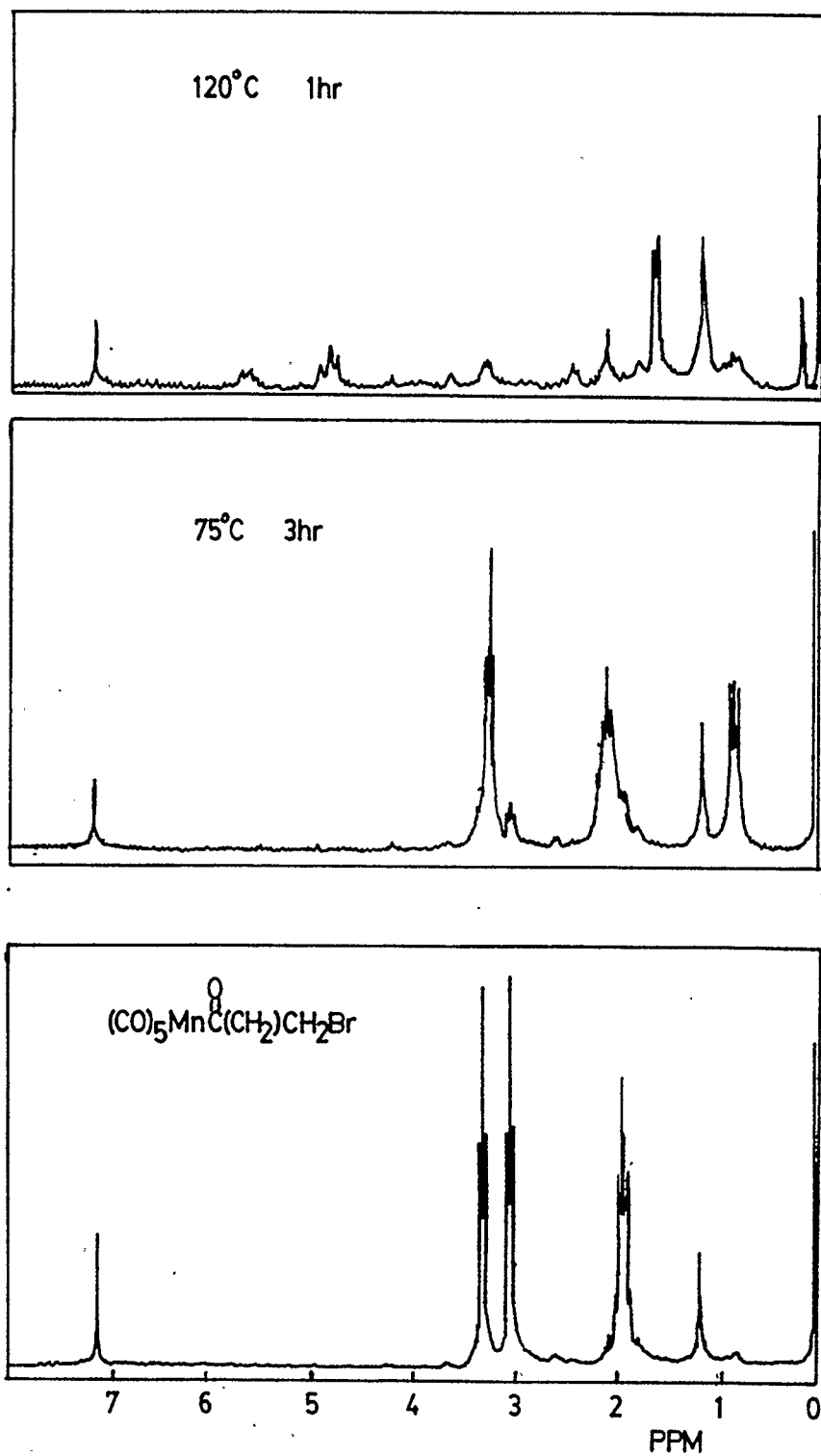
Figure 3.3 [1]H-N.M.R. Spectra Measured During the Thermal

Decomposition of 4-Bromobutanoyl Manganese Pentacarbonyl (CDCl_3)

$$\underset{\underline{123}}{BrCH_2CH_2CH_2\overset{\overset{O}{\parallel}}{C}Mn(CO)_5} \xrightarrow[75°C]{CDCl_3} \underset{\underline{127}}{BrCH_2CH_2CH_2Mn(CO)_5} + CO \qquad (113)$$
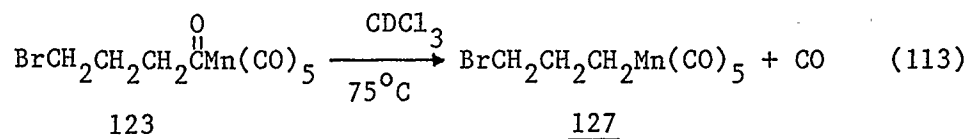
Allowing this solution to stand overnight resulted in partial conversion back to the haloacyl complex $\underline{123}$. Continued heating (125°C, 1 hour) of a solution containing mainly haloalkyl complex $\underline{127}$ resulted in a great deal of decomposition. During this decomposition the manganese containing species were converted to an insoluble brown powder of unknown composition. The ^{1}H-N.M.R. spectrum of this solution consisted of a number of resonances (see Figure 3.3). A singlet at 0.24 ppm was assigned to cyclopropane $\underline{128}$ (literature[132] ^{1}H-N.M.R. spectrum: singlet 0.25 ppm in carbon tetrachloride). The other resonances d, 1.72 ppm, J=6.2 Hz, 3H; d, 4.95 ppm and 5.05 ppm, J = 12 Hz and 19 Hz, 2H; m, 5.88 ppm, 1H) were assigned to propene $\underline{129}$ from double resonance experiments and comparison of the chemical shifts with those reported in the literature[133]. Integration of the ^{1}H-N.M.R. spectrum at low temperature (-60°C) indicated that cyclopropane was produced in 12% yield and propene in 38% yield.

$$\underset{\underline{123}}{(CO)_5Mn\diagdown\diagup\diagdown Br} \xrightarrow[125°C\ 1hr.]{CDCl_3} \underset{38\%}{\diagup\diagdown} + \underset{12\%}{\triangle} \qquad (114)$$
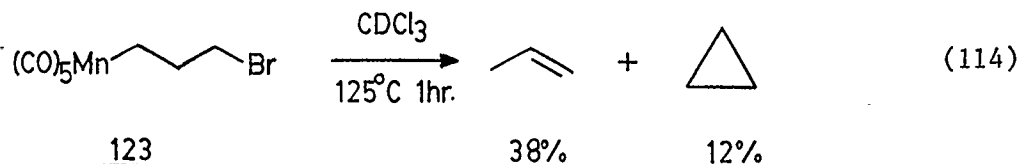
Heating 4-bromobutanoyl manganese pentacarbonyl in tetrahydrofuran d_8

(60°C, 2 hours) resulted in the formation of propene directly in this case with only a trace of cyclopropane (<1%) being formed. Infra-red analysis of the solution after heating indicated that $Mn(CO)_5Br$ was formed.

3.2.5 The Thermal Decomposition of 5-Bromopentanoyl Manganese Pentacarbonyl

Heating solid 5-bromopentanoyl manganese pentacarbonyl 124 to 70°C gave manganese pentacarbonyl bromide.

Heating a deuterochloroform solution of the complex to 75°C for 3 1/2 hours in a sealed N.M.R. tube resulted in the clean conversion of 124 to the corresponding haloalkyl complex (see Figure 3.4) 130.

$$\underset{124}{BrCH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}Mn(CO)_5} \xrightarrow[75°C, 3hrs.]{CDCl_3} \underset{130}{BrCH_2CH_2CH_2CH_2Mn(CO)_5} + CO \quad (115)$$
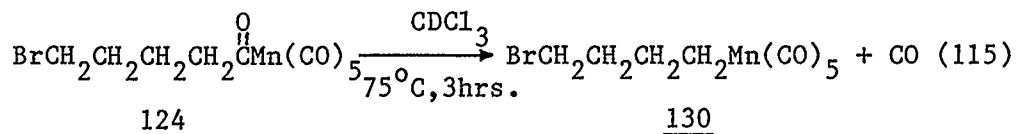
The assignment of the haloalkyl was based on the [1]H-N.M.R. spectrum observed ($CDCl_3$, δ : t 0.97 ppm, J=7.5 Hz, $Mn-CH_2-$; m, 1.90 ppm, 4H; t, 3.43 ppm, J-6.5 Hz, 2H, $-CH_2-Br$). This interpretation is consistent with similar complexes, in particular the characteristic high field resonance at 0.97 ppm for the protons a to the manganese. This decarbonylation was reversible, leaving the solution overnight at room temperature resulted in partial conversion back to the acyl complex 124. Heating the solution to 120°C for 1 hour gave 1-butene 131 as the major organic product (ca. 85%) and complete decomposition of the manganese containing species to an unidentified insoluble brown
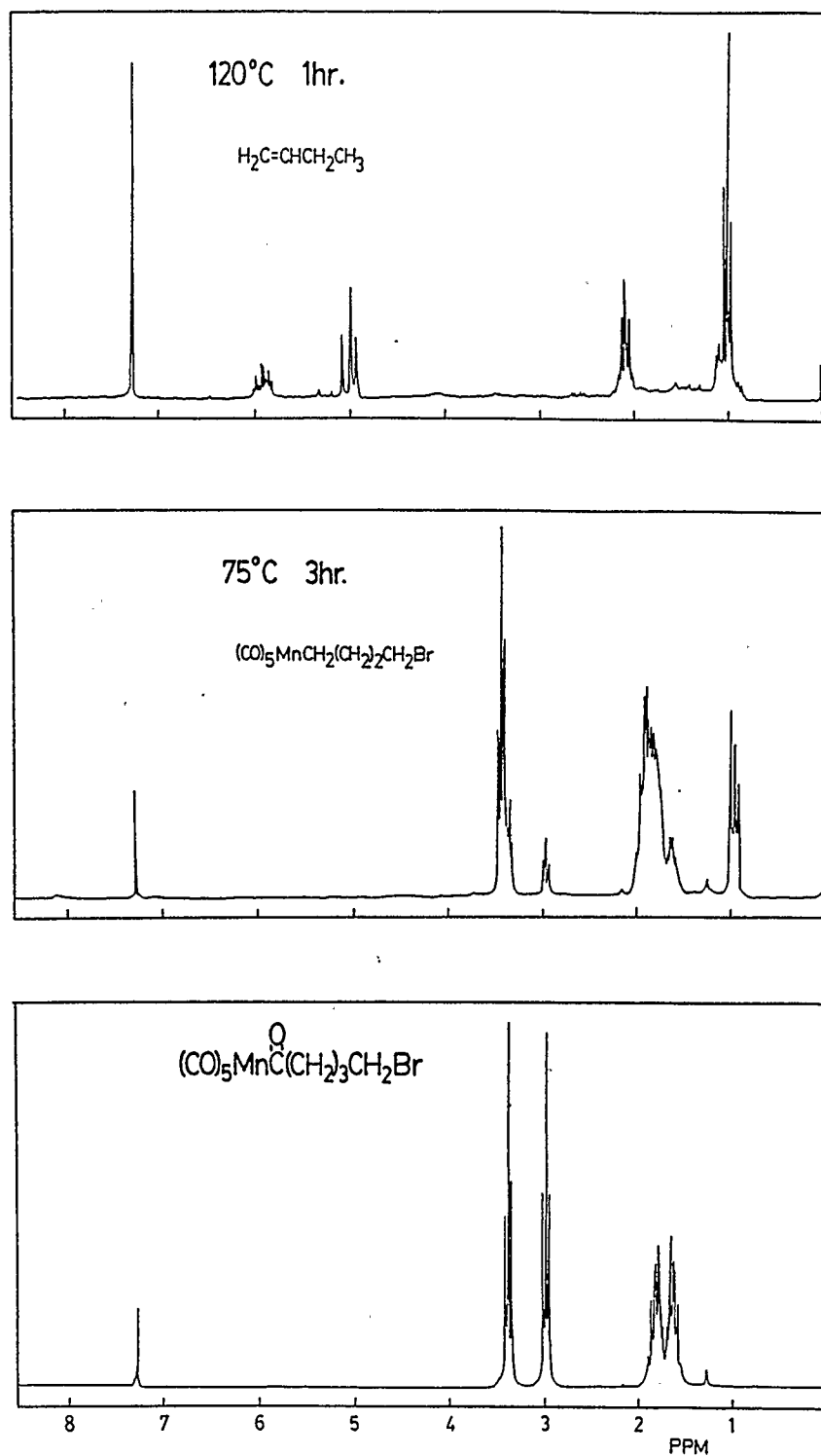
Figure 3.4 ^{1}H-N.M.R. Spectrum Measured During the Thermal

Decomposition of 5-Bromopentanoyl Manganese Pentacarbonyl (CDCl$_3$).

powder. The assignment of the organic product was based on G.C. gas

analysis and the [1]H-N.M.R. spectrum for the resulting solution (CDCl$_3$,

δ: t, 0.98 ppm, J=7.5 Hz, 3H; dq, 2.05 ppm, 2H; d, 4.90 ppm and 4.95

ppm, J= 8.2 and 19 Hz, 2H; m, 5,85 ppm, 14), which compares well with

that reported in the literature[134]. There was no evidence of any

cyclobutane from the [1]H-N.M.R. spectrum.

(116)

$\underline{124}$ $\underline{130}$
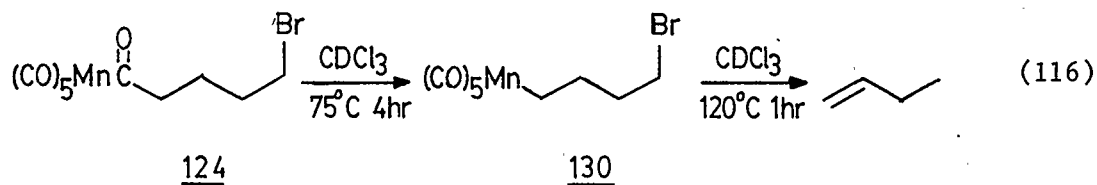
The complex $\underline{124}$ was also heated in tetrahydrofuran d$_8$ in a sealed

N.M.R tube. Under these conditions heating to 60°C for 4 hours .

resulted in the direct conversion of $\underline{124}$ to 1-butene (ca. 90% yield).

Again in this case there was no evidence of any cyclobutane formed.

(117)

$\underline{124}$
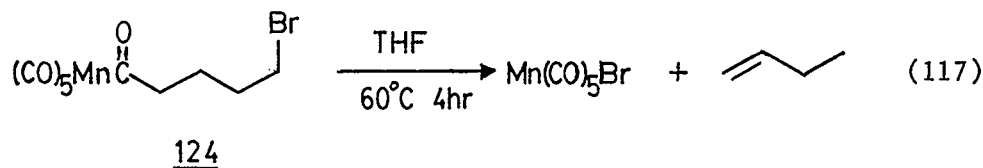
Infra-red analysis of the solution after heating indicated that

Mn(CO)$_5$Br was the major organometallic product formed in the reaction.

3.3 Discussion

The reaction of $Mn(CO)_5^-$ with 2-bromo acyl chlorides is clearly in strong contrast to its reaction with acyl chlorides with more remote bromine substitution. The reaction of $Mn(CO)_5^-$ with β, γ and δ-bromoacyl halides gives the expected substitution product. In these cases, and for the reaction of $Mn(CO)_5^-$ with acyl halides in general one can assume that the reaction proceeds via the tetrahedral mechanism.

$$Na^+[Mn(CO)_5^-] + Cl\overset{O}{\underset{\|}{C}}(CH_2)_nCH_2Br \longrightarrow Cl-\overset{O^-}{\underset{\underset{5}{Mn(CO)}}{\overset{|}{C}}}-(CH_2)_nCH_2Br \quad \underline{132} \quad (118)$$

$$\downarrow$$

$$(CO)_5Mn\overset{O}{\underset{\|}{C}}(CH_2)_nCH_2Br + Cl^-$$

$$\underline{11}$$
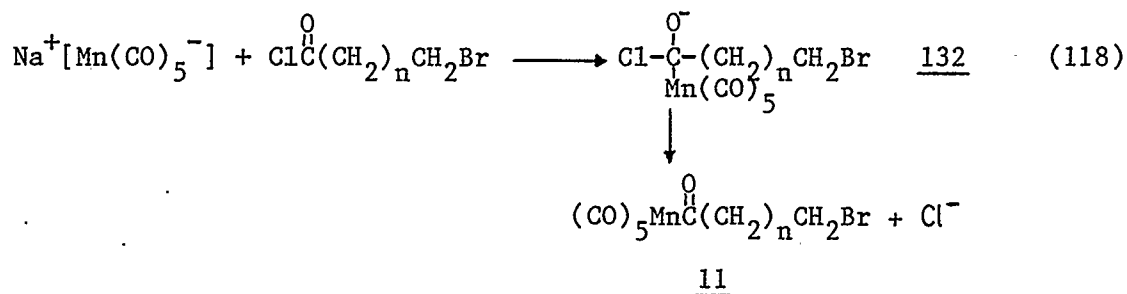
One is tempted to relate the behavior of 2-bromoacyl halides when reacted with $Mn(CO)_5^-$ to the observed behavior of β, γ and δ-bromoacyl manganese complexes when heated. This would suggest that formation of a transient acyl complex $\underline{11}$ (or possibly intermediate $\underline{132}$) is followed by decomposition to give ketenes and $Mn(CO)_5Br$. However, a more attractive analogy is that of the reaction of $Mn(CO)_5^-$ with α-bromoacyl esters as described in Chapter 2 , suggesting that in the ketene forming reaction intermediate acyl complexes need not be involved. Since the reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides was considered to be a potentially useful way of preparing ketenes, this reaction was more fully explored. A full discussion of the mechanistic implications of this reaction is therefore deferred to

Chapter 4.

In order to explain the observed products from the thermal

decomposition of β, γ and δ-bromoacyl manganese complexes a number of

mechanisms were considered. One major difference between the reaction

of $Mn(CO)_5^-$ with 2-bromoacyl halides and the observed thermal

decomposition of β, γ and δ-bromoacyl manganese complexes 122, 123 and

124, is that the latter occurs with decarbonylation. This is

illustrated by the products, both intermediate alkyl complexes

observed and the alkenes (and cyclopropane from 123) ultimately formed.

Indeed acyl complexes in general are expected to undergo

decarbonylation upon heating, a process believed to involve initial

loss of a cis CO ligand followed by an acyl alkyl interconversion as

shown below

(119)
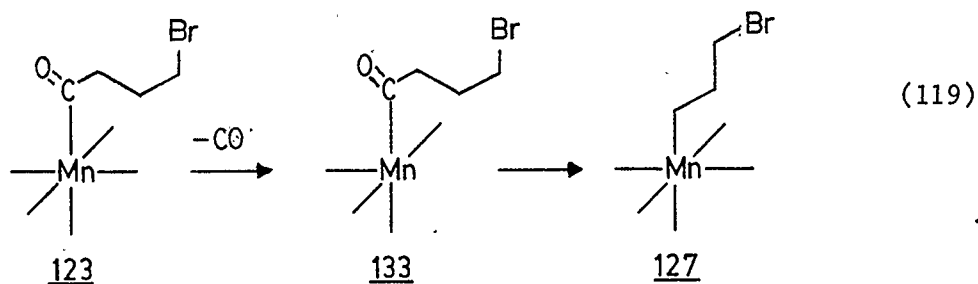
This indicates that alkyl migration by the unsaturated

intermediate 133 is prefered over intramolecular oxidative addition of

the remote carbon-bromine bond in these complexes.

However, there is evidence that some cyclometallation does take

place after the acyl-alkyl interconversion. The formation of

cyclopropane during the heating of 4-bromobutanoyl manganese

pentacarbonyl 123, (and the corresponding alkyl complex 127) can be

explained by an intermediate metallocyclobutane 135.

$$\text{(diagram of scheme 120)}$$

(120)

127   134   135
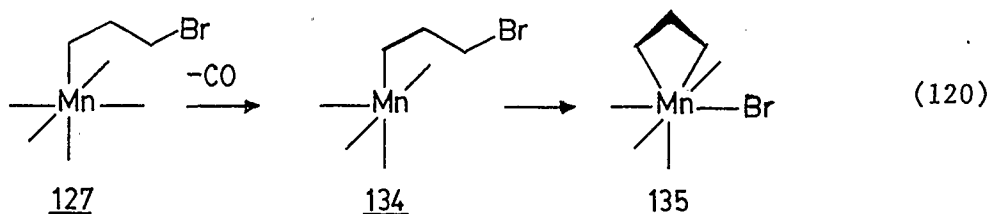
In this mechanism loss of CO from the alkyl complex 127 would give the

unsaturated intermediate 134 which would undergo cyclometallation to

give 135. Reductive ellimination from 135 with gain of CO would give

cyclopropane and $Mn(CO)_5Br$.

The formation of the metallocycle 135 can also explain the propene

formed in this reaction. Loss of CO from 135 followed by hydride

migration with reductive elimination (β-hydride elimination) gives the

observed product.

$$\text{(diagram of scheme 121)}$$

135   136   137   138

(121)

$$Mn(CO)_5Br + \text{(propene)}$$
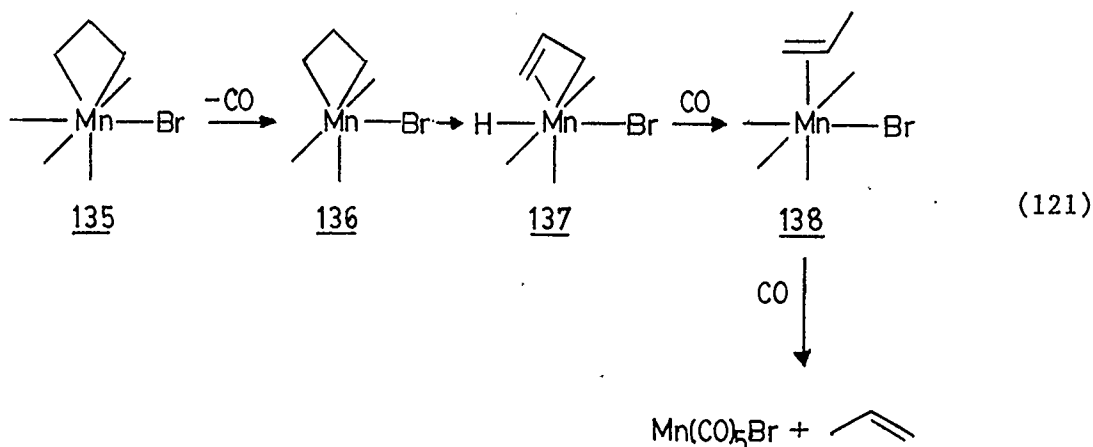
Such steps would require further loss of CO to give the rather

ungainly intermediate 137, but such a process is known to compete with

cycloalkane formation from other metallocycles[135].

These processes also explain the formation of 1-butene from the

decomposition of 5-bromobutanoyl manganese pentacarbonyl 124 where an

analogous metallocyclopentane 139 would form.

(122)
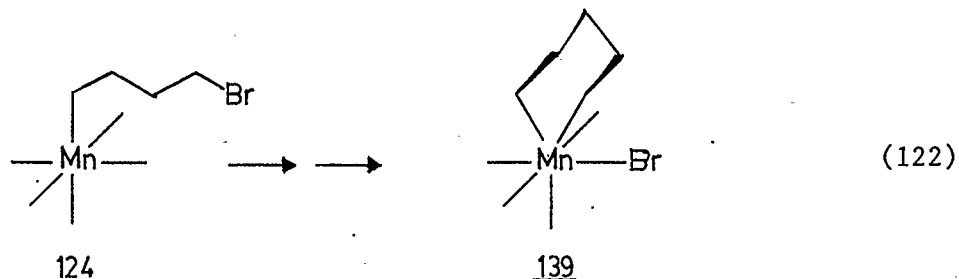
In this case though one would have to assume that the analogous reductive ellimination to give cyclobutane cannot compete with β-hydride elimination, i.e. β-hydride elimination is faster overall for metalocyclopentanes than metallocyclobutanes. There is some evidence to support this for other metals[136], however the amount of β-hydride elimination vs reductive elimination is very sensitive to the environment of the metal center and not the ring size. An alternative explanation that the initial cyclometallation is suppressed in the case of 124 can be ruled out, since one would expect that there would be some preference for the formation of a metallocyclopentane over a metallocyclobutane. This argument relies on organic analogues where ring strain is the dominant factor in the formation of of the transition state (with an entropy contribution as well) leading to cyclization. There is evidence from other work that this is true for metallocycle formation, ie. where there is a choice in ring size metallocyclopentanes form preferentially[137].

The amount of β-hydride elimination which takes place in metalocycles is expected to be considerably reduced when compared to simple alkyl complexes. This is a result of the requirement that the M-C-C-H dihedral angle is 0° for elimination to take place and

this accounts for the stability of metallocycles over non cyclic alkyl complexes[137]. This suggests that if β-hydride elimination occurs at all, it is more likely to take place prior to cyclometallation. This would be particularly true for the manganese metallocycles proposed here where one might expect the formation of a sterically unfavorable 7-coordinate species to be reversible.

$$\underline{127} \xrightarrow{-CO} \underline{134} \longrightarrow \underline{140} \xrightarrow{CO} Mn(CO)_5H + \underset{Br}{\diagup\!\!\!\!\diagup}$$ (123)
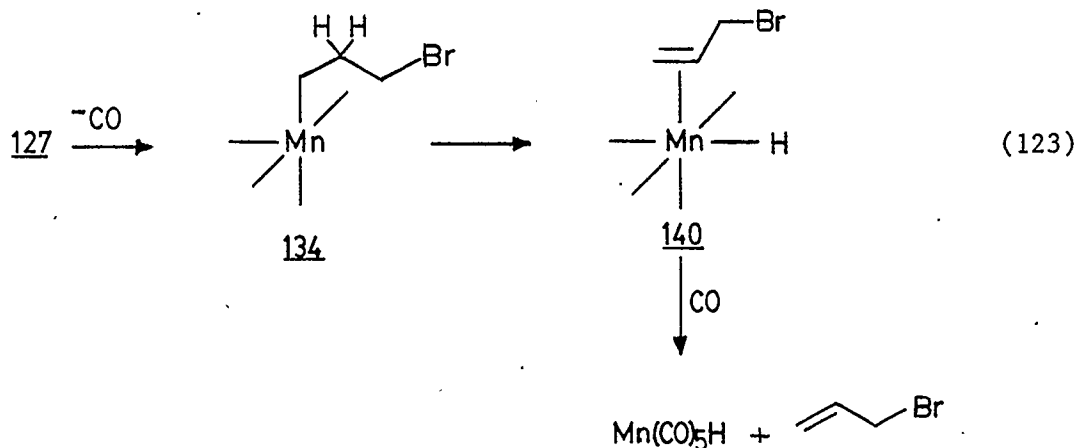
In this case β-hydride elimination would take place from the unsaturated species $\underline{134}$ to give manganese pentacarbonyl hydride and a bromo-alkene.

Such a process would not give the observed debrominated product directly. However, manganese pentacarbonyl hydride is known to rapidly reduce organic halides, which would result in the observed products[138].

$$\underset{Br}{\diagup\!\!\!\!\diagup} + Mn(CO)_5H \longrightarrow Mn(CO)_5Br + \diagup\!\!\!\!\diagdown$$ (124)

The reduction involving $Mn(CO)_5H$ described above could certainly explain the behavior of the bromoacyl complexes in tetrahydrofuran, but chloroform might be expected to compete since this would also be a suitable substrate for reduction. It is conceivable that the intermediate 140 could undergo intramolecular reduction with the same result, a process which could compete with the large excess of chloroform present.

Alternatively a series of carbon-carbon double bond migrations could take place via β-hydride elimination[139,140], to give a β-bromoalkyl complex 143 . This intermediate can undergo a β-bromide elimination which would also give the observed alkene products.
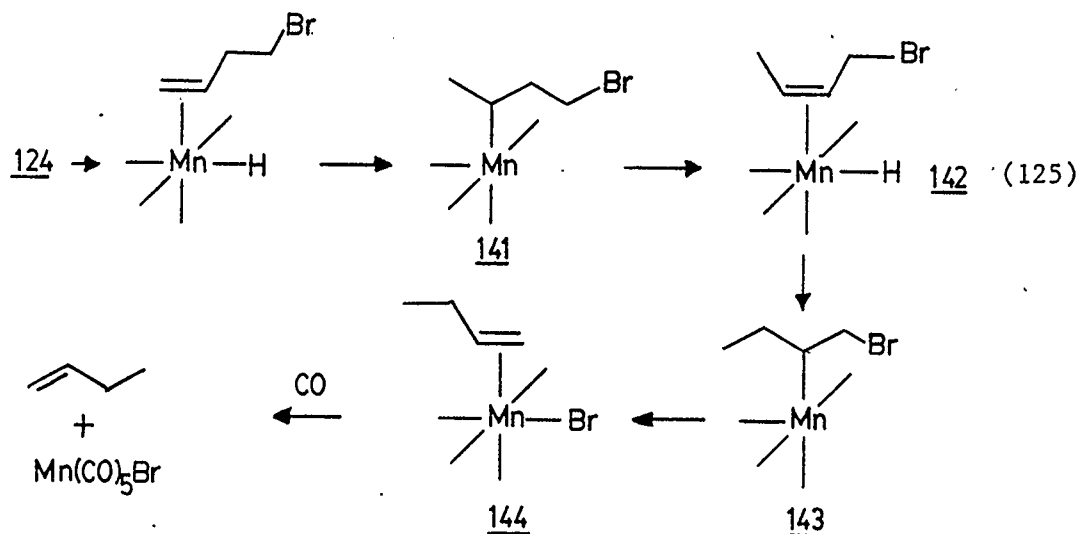
These steps are less likely to account for the results since decomplexation of the alkene could take place at any stage during the migrations, which would lead to mixed alkene products.

The steps outlined above, i.e. β-hydride elimination followed by

reduction, would not explain why 3-bromopropanoyl manganese

pentacarbonyl 122 underwent facile ethene formation. In this case

though, β-bromide elimination could occur directly after acyl/alkyl

interconversion rather than β-hydride elimination. Such a process

would be similar and is shown below:

$$
\underset{\underline{122}}{\underset{\overset{O}{\underset{C}{\diagdown}}-CH_2CH_2Br}{-Mn-}} \quad \xrightarrow{-2CO} \quad \underset{\underline{145}}{\underset{\overset{CH_2CH_2Br}{|}}{-Mn}} \quad \longrightarrow \quad \underset{\underline{146}}{\underset{\overset{H_2C=CH_2}{|}}{-Mn-Br}} \quad (126)
$$
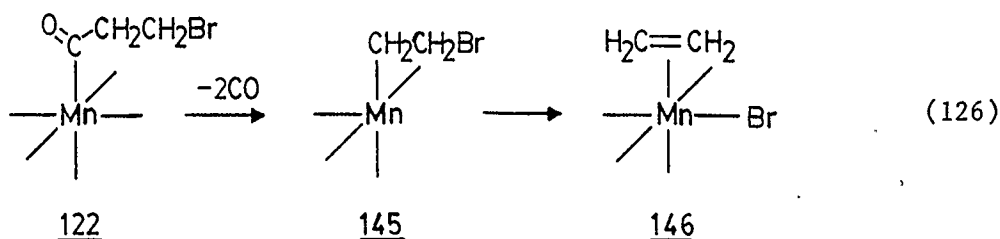
This reaction would explain why no intermediate alkyl complex was

observed in this case. The analogous β-bromide elimination would be

thermodynamically favored over β-hydride elimination since C-Br bonds

are about 30 kcal mole^{-1} weaker than C-H bonds[141]. Additionally the

Mn-Br bond in Mn(CO)$_5$Br (58 kcal mole^{-1}) is slightly stronger[142] than

the Mn-H bond in Mn(CO)$_5$H (51 kcal mole^{-1}). Thus alkyl complexes

having a β-bromo substituent would decompose faster than unsubstituted

alkyl complexes.

This β-bromide reaction could also be described by analogy with

the decarboxylation of carboxylic acids, suggesting that the reaction

could be written in one step.

$$
\underset{\underline{122}}{\underset{\overset{O}{\underset{C}{\diagdown}}CH_2CH_2Br}{-Mn-}} \quad \longrightarrow \quad \left[\underset{}{\overset{\oplus}{-Mn-}} + Br^- \right] + H_2C=CH_2 \quad (127)
$$

$$
\downarrow
$$

$$
Mn(CO)_5Br + CO
$$
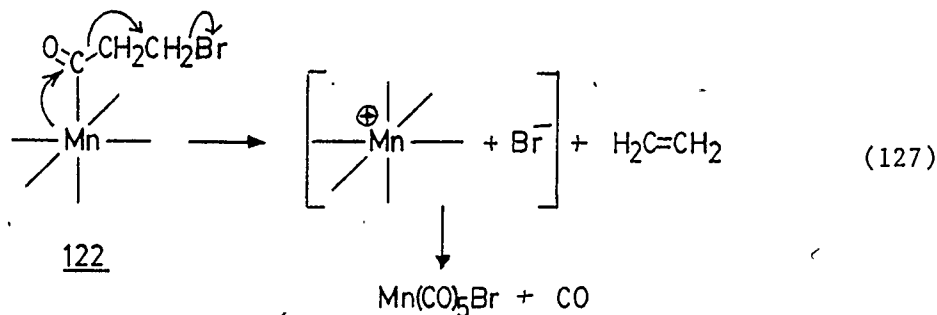
This mechanism would not involve the formation of an intermediate alkyl complex and would also explain why the reaction proceeds with such ease compared to the other complexes.

The fact that using tetrahydrofuran solvent rather than chloroform accelerates alkene formation for all the acyl complexes described here can be explained by comparing the coordinating powers of the two solvents. Tetrahydrofuran, unlike chloroform, is able to coordinate unsaturated $16e^-$ species and therefore stabilizes them by maintaining the $18e^-$ rule. This is a relatively weak interaction so the solvent is easily displaced. This would explain why intermediate alkyl complexes were not observed (there was some evidence of its transient formation in one case) when tetrahydrofuran was used.

$$\text{—Mn} + \text{THF} \quad \rightleftharpoons \quad \text{—Mn—O} \qquad (128)$$

<u>147</u>
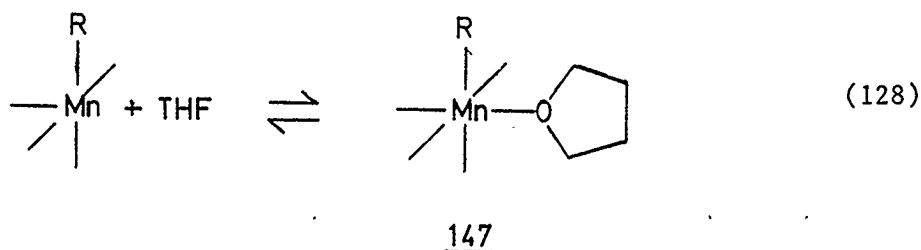
The accelerating effects of solvents such as tetrahydrofuran on reactions involving initial loss of CO from the metal is known for a number of other reactions[143].

The Formation of γ-Butyrolactone from 4-Bromobutanoyl Manganese Pentacarbonyl

Acyl complexes of manganese are not normally air-sensitive, indeed, samples of 5-bromopentanoyl manganese pentacarbonyl can be

left exposed to the atmosphere for a number of hours without signs of decomposition. Thus, 4-bromobutanoyl manganese pentacarbonyl is unusual in that it decomposes rapidly to give γ-butyrolactone

Such a decomposition is characteristic of carbene complexes[144] and the formation of γ-butyrolactone can be rationalized by the steps given below:

$$\text{(129)}$$
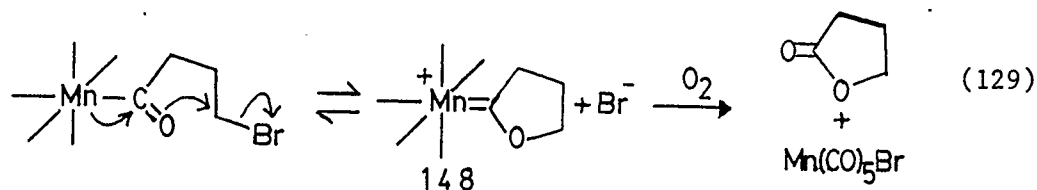
Although the carbene intermediate 148 was not observed directly, a related complex has been prepared by others[114] from the chloro analogue of 123 using silver tetrafluoroborate. It is possible that with a better leaving group like bromide that the reaction is spontaneous, although the equilibrium shown above would have to be far to the left.

The carbene 148 could also explain the formation of the neutral carbene complex 126. Loss of CO from 148 either thermally or photochemically, followed by re-attack by bromide ion gives 126:

$$\text{(130)}$$
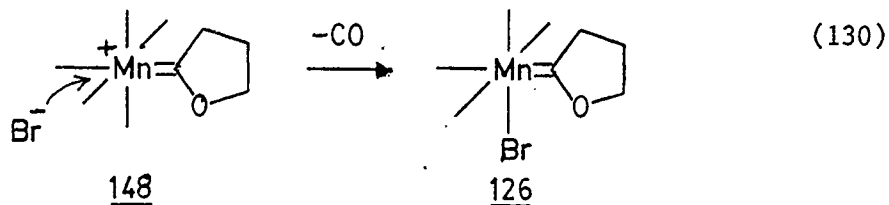
This product could also arise autocatalytically via bromide attack[114]

on the coordinatively unsaturated intermediate acyl species <u>133</u>

(131)

<u>133</u>   ⟶   <u>126</u>
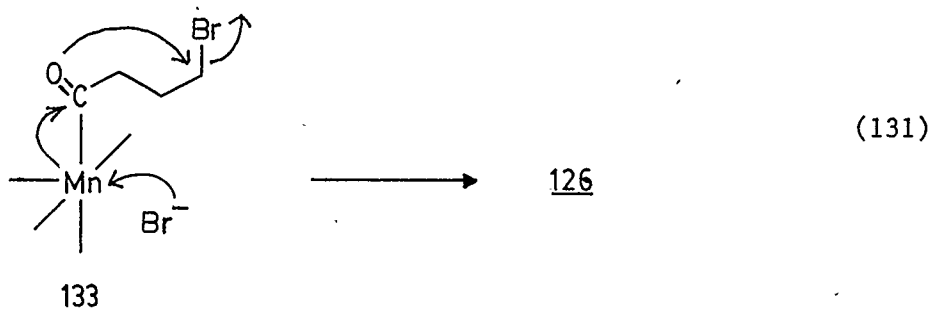
Conclusions

The reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides is not an appropriate route to the corresponding 2-bromoacyl manganese complexes, at least under the conditions used in this work. There is little doubt that this reaction gives ketenes. The infra-red spectroscopic evidence and observed dimerization products are very characteristic of these products.

The products obtained on heating the β, γ and δ-bromoacyl manganese complexes can be conveniently explained by the intermediacy of metallocycles. However, it seems more likely that β-hydride elimination is taking place before cyclometallation. It might be possible to distinguish these alternatives by blocking the β-position with alkyl groups to prevent β-hydride elimination prior to cyclometallation. The behavior of the unsymmetrical substituted acyl complex shown below would be particularly informative.

<u>149</u>
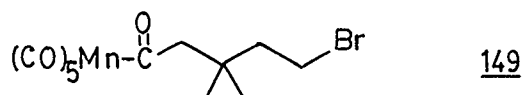
The cyclometallation process might be further enhanced by using a ligand with a remote bond more activated towards oxidative addition, a C-I bond for example.

Although some success was achieved in performing the desired cyclometallation, this was restricted to the formation of 3-membered rings. The outcome of the other reaction can be generalized as:

(132)

$$\underset{Cl}{\overset{O}{\underset{\|}{C}}}-CH_2-CH_2-(CH_2)_n Br \xrightarrow[\text{(ii) }\Delta]{\text{(i) Mn(CO)}_5^-} CH_2{=}CH-(CH_2)_{n-1}-CH_3$$
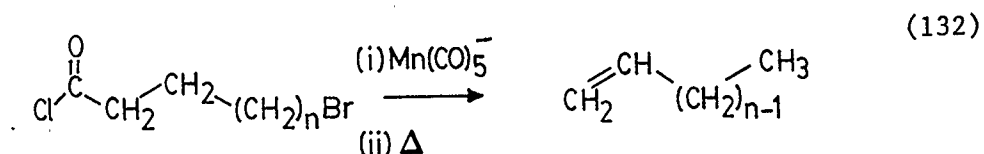
This reaction is effectively a decarboxylative elimination with reduction of a remote carbon-bromine bond.

Chapter 4

The Dehalogenation of 2-Bromoacyl Halides by $Mn(CO)_5^-$

4.1 Introduction

Ketenes $\underline{14}$ have been used in organic synthesis in a number of ways[145], one example being the $[\pi^2 + \pi^2]$ cycloaddition reaction with activated alkenes to give cyclobutanones $\underline{150}$:

(133)
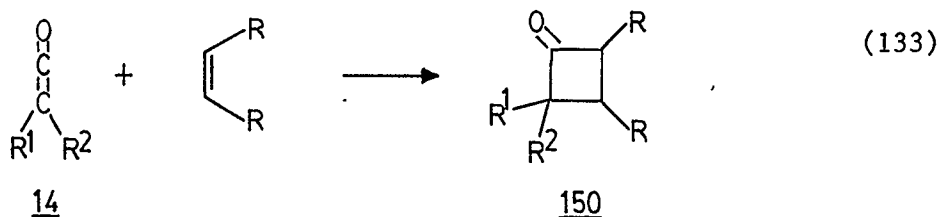
There are many methods available for the preparation of ketenes[146]: the Wolf rearrangement of α-diazocarbonyl compounds[147]; dehalogenation of 2-bromoacyl bromides using activated zinc (the Staudinger method) or triphenylphosphine[148]; the dehydrohalogenation of acid chlorides using amines[149]; the pyrolysis of carboxylic acids[150], anhydrides[151], ketones[152], ketene dimers[153], ketene acylals[154], alkoxyalkynes[155] and 2,5 diazidoquinones[156], to name the more widely used methods.

One characteristic reaction of ketenes is their self dimerization to give cyclobutanediones $\underline{151}$, or in the case of ketene itself (R =R' =H) the β-lactone, diketene $\underline{152}$:

$$(134)$$
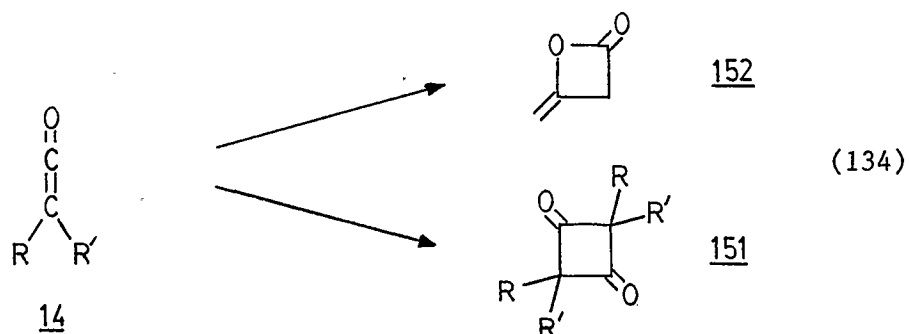
With the exception of ketene and most dialkyl and diaryl ketenes this dimerization is rapid at room temperature, and for this reason only a relatively small number of ketenes have in fact been isolated. Ketenes are generally generated in situ or as components of a pyrolysis stream[146].

Solutions of ketenes can be obtained by the treatment of readily available 2-bromoacyl bromides 5 with activated zinc, (the Staudinger synthesis).

$$BrCR^1R^2\overset{\overset{O}{\parallel}}{C}Br \xrightarrow{\quad Zn \quad} \quad + \quad ZnBr_2 \qquad (135)$$

$$\underline{153} \qquad\qquad\qquad \underline{14}$$
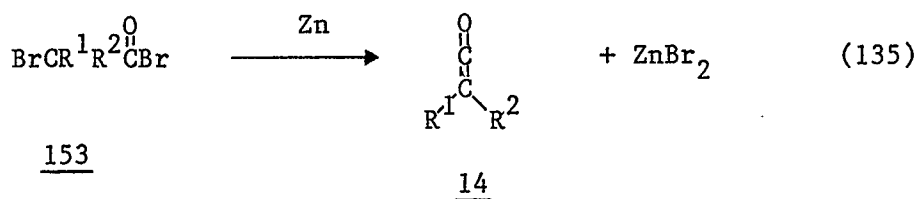
This is in fact the oldest method for preparing ketenes[157] and is a good way to prepare the more stable aryl and dialkyl ketenes[158]. For example the Organic Synthesis preparation of dimethyl ketene $(R_1=R_2=Me)$ is based on this reaction[159].

The possibility of extending this reaction to the preparation of more reactive ketenes has been explored for mono-alkyl ketenes $(R_1=H, R_2=alkyl)$, however the yields are often low[130]. Modified procedures

where the ketenes are rapidly distilled from the reaction mixture as the reaction proceeds and collected in a cold trap have had some degree of success[130].

The Staudinger reaction described above is clearly analogous to the reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides described in the preceding chapter. It was proposed that the high reactivity and homogeneous conditions of the $Mn(CO)_5^-$ reaction would extend the usefulness of the dehalogenation of 2-bromoacyl halides as a method for preparing more reactive ketenes. Thus the $Mn(CO)_5^-$ reaction was tested for a variety of alkyl substituted 2-bromoacyl halides 154 and vinylogs 155 as a potentially useful method for preparing ketenes 14, vinyl ketenes 156, and methylene ketenes 158.

$$BrCR'RCX \quad \xrightarrow{Mn(CO)_5^-} \quad \qquad \qquad (136)$$

154   14

$$\qquad \longrightarrow \qquad (137)$$

155   156

$$\qquad \longrightarrow \qquad (138)$$

157   158
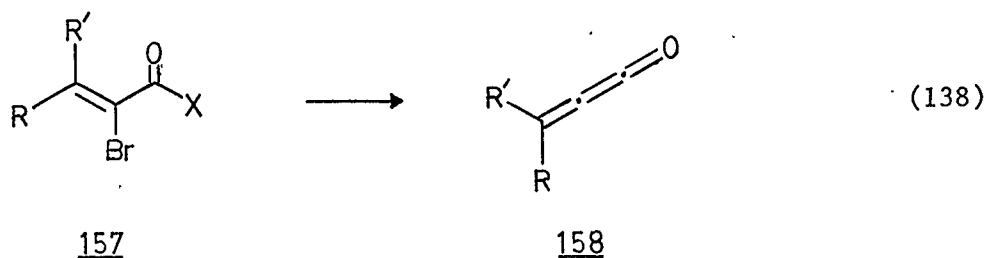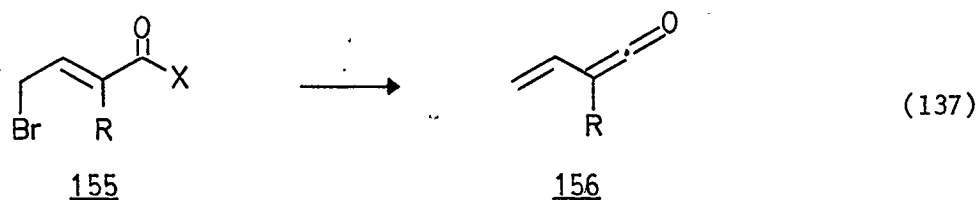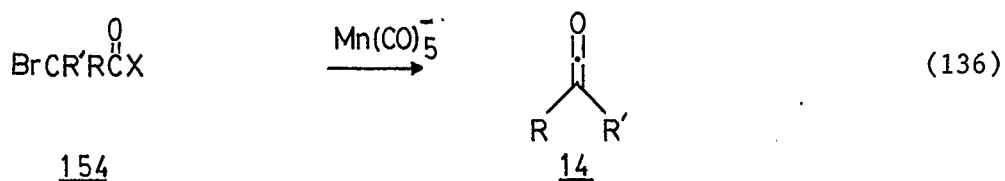
There are no useful examples of "nucleophilic" metal anions being used as dehalogenating agents in the reactions described above, although some related reactions have been described[160,161].

4.2 Results

4.2.1 The Preparation of Ketene and Dimethyl Ketene

Ketene 115 is generally prepared by pyrolysis[162], and Fieser and Fieser describes the pyrolysis of diketene 152 as being the method of choice[163]. Clearly, there would be some advantage to developing a non-pyrolytic method for preparing ketene and thus some effort was made to generate 115 using $Mn(CO)_5^-$.

The preliminary study described earlier (Chapter 3) indicated that a very rapid reaction took place between 2-bromoethanoyl chloride 114 and $Na^+[Mn(CO)_5^-]$ in tetrahydrofuran. However, the formation of ketene was not confirmed in this case, in part because of the volatility of ketene (bp $-41°C$). These results indicated a similar reaction took place between 2-bromoethanoyl chloride 16 and $PPN^+[Mn(CO)_5^-]$ in deuterochloroform. Since $PPN^+[Mn(CO)_5^-]$ is more convenient to use (it can be weighed in air and is soluble in a variety of organic solvents), it was decided to explore the reactions of this salt as a potential reagent for preparing ketenes. Deuterochloroform was chosen as the solvent for exploratory purposes since it allowed the products to be determined by ^1H-N.M.R. spectroscopy.

Because of the high volatility of ketene the reaction of

$PPN^+[Mn(CO)_5^-]$ with 2-bromoethanoyl chloride was carried out in a

closed vessel. This was achieved by layering solutions of

$PPN^+[Mn(CO)_5^-]$ and 2-bromoethanoyl chloride at liquid nitrogen

temperature, evacuating the apparatus to <u>ca</u> 0.1mmHg and then allowing

it to warm to room temperature. The solvent/ketene mixture was then

distilled from the $Mn(CO)_5Br$ and PPN^+Cl^- produced in the reaction into

a side arm receiver cooled with liquid nitrogen. The product of the

reaction was then determined by low temperature ($-50°C$) ^{1}H-N.M.R.

spectroscopy, using <u>p</u>-dibromobenzene as an internal standard. The ^{1}H-

N.M.R. spectrum (Figure 4.1) of the distillate contained a singlet at

2.46 ppm in addition to those for <u>p</u>-dibromobenzene and chloroform.

This value is close to that reported for neat ketene (2.47 ppm)[164]

indicating that this is indeed the product of the reaction.

Integration indicated that the ketene was formed in better than 95%

yield. On standing, a <u>ca</u> 1M solution prepared in this way remained

essentially unchanged after standing overnight at room temperature.

Characteristic resonances[165] in the ^{1}H-N.M.R. spectrum corresponding

to diketene <u>152</u> were observed after this time, but integration of the

signals indicated less than 5% dimerization had taken place.

$$BrCH_2COCl \xrightarrow[\text{CDCl}_3,\ 0°C]{PPN^+[Mn(CO)_5^-]} \qquad (139)$$

<u>16</u>

<u>115</u> 95%
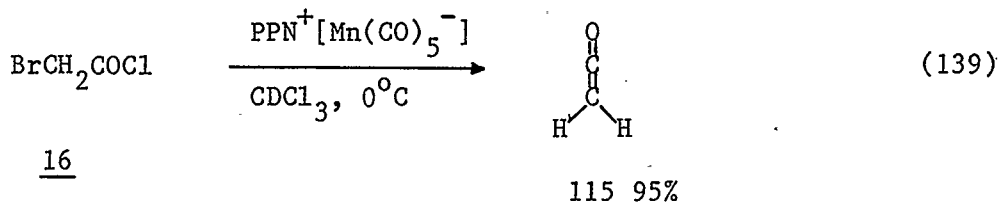
Since dimethyl ketene <u>159</u> also dimerizes slowly at room

temperature, this method was also found to be appropriate for this ketene. Following the method outlined above for the preparation of ketene, a colourless solution was obtained from the reaction of 2-bromo-2-methylpropanoyl chloride 160 or bromide 161. The ^{1}H-N.M.R. spectrum of this soelution consisted of a singlet at 1.58 ppm assigned to 159, and integration indicated a 87-95% yield of this compound in very high purity (see Figure 4.1) .

$$BrC(CH_3)_2COX \xrightarrow[CDCl_3, \ 0^{\circ}C]{PPN^+[Mn(CO)_5^-]} \quad \overset{O}{\underset{CH_3 \ CH_3}{\overset{\|}{\underset{}{C}}}} \qquad (140)$$

160 X=Cl
161 X=Br

159 87-95%
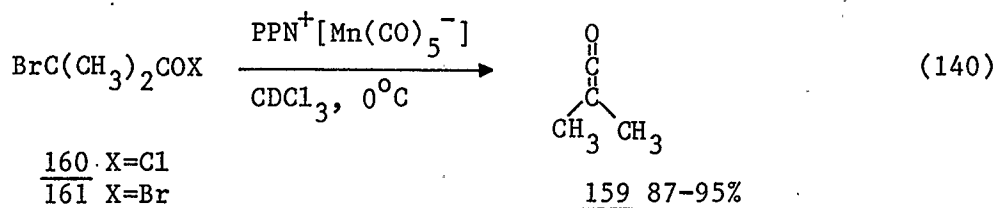
The dimethyl ketene formed under these conditions dimerized over a period of about 20 hours at room temperature to give the tetramethylcyclobutanedione 162 exclusively, identified by ^{1}H-N.M.R. spectroscopy (singlet 1.26ppm)[166] and mass spectrometry (parent ion m/e 140).

$$159 \xrightarrow[20\,hrs.]{CDCl_3 \quad 25^{\circ}C} \qquad (141)$$
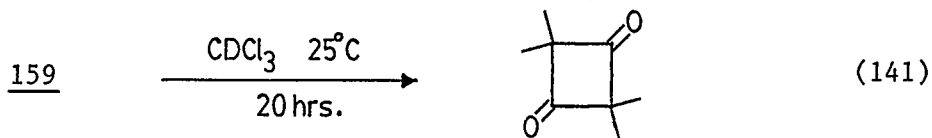
162
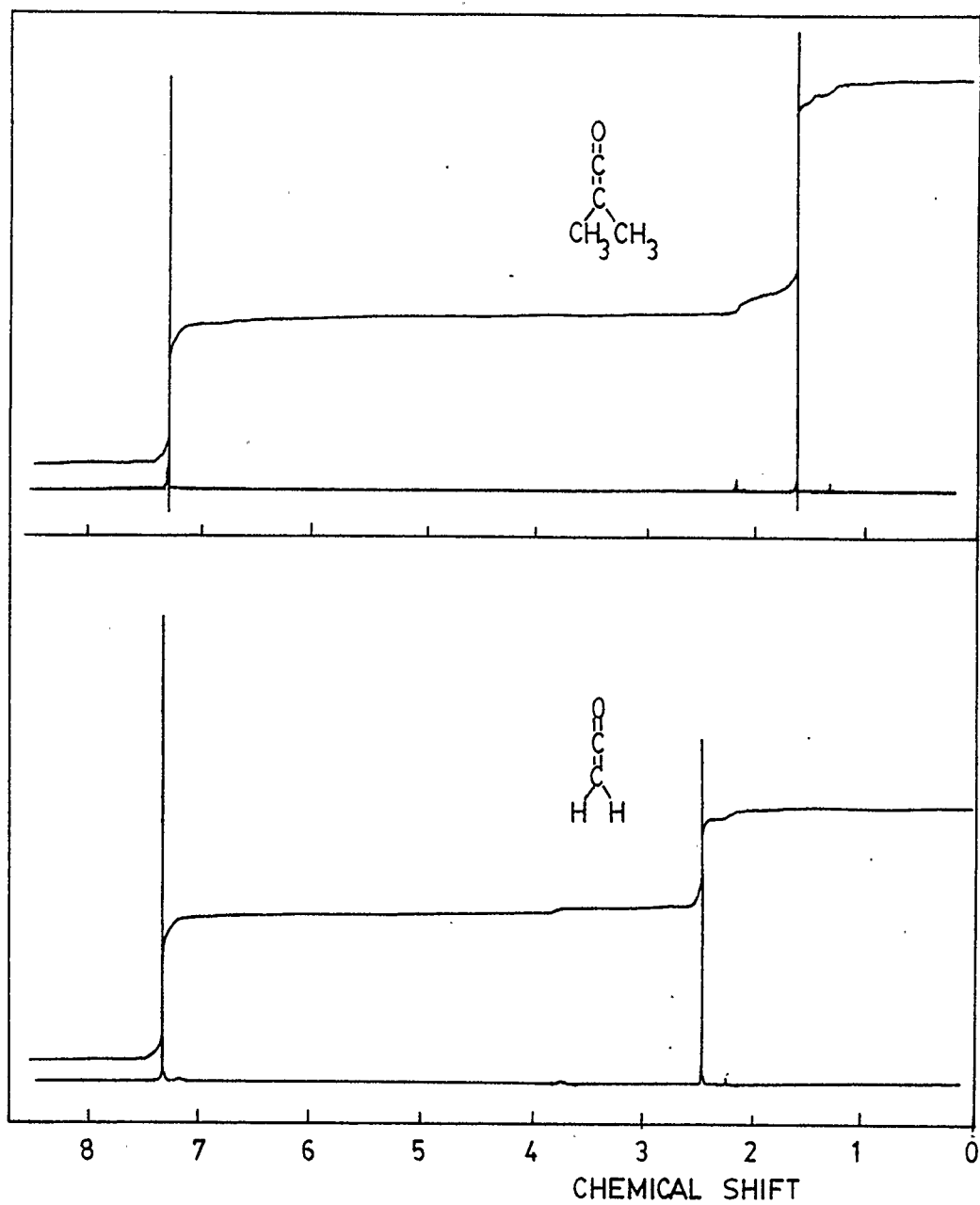
Figure 4.1 [1]H-N.M.R. Spectra of Ketene and Dimethyl Ketene (CDCl$_3$)

4.2.2 The Preparation of Mono-alkyl Ketenes

Monoalkyl ketenes are usually prepared by the dehydrohalogenation of acyl halides[167], a reaction which is normally carried out _in situ_. Solutions of methyl and ethyl ketenes have been obtained using the Staudinger procedure[130] where in this case the reaction is carried out under conditions of continuous distillation. Under these conditions the ketene solution is cooled sufficiently to prevent dimerization (and trimerization), which occurs rapidly at room temperature for this class of ketenes.

The technique of continuous distillation was modified in the present work for the reaction of $PPN^+[Mn(CO)_5^-]$ with 2-bromopropanoyl chloride and 2-bromobutanoyl bromide 116 and 163 in deuterochloroform. In these cases a chloroform solution of 116 or 163 was rapidly added to a concentrated chloroform solution of $PPN^+[Mn(CO)_5^-]$ by syringe in a sealed vessel initially evacuated to _ca._ 0.1 mmHg. The solution of $PPN^+[Mn(CO)_5^-]$ was initially frozen using liquid nitrogen, the apparatus evacuated and then warmed to _ca._ $0^{\circ}C$. At this point the solvent and formed ketenes (as the addition takes place) rapidly distill into a liquid nitrogen cooled receiver attached to the vessel. Very pale green solutions of methyl 118 and ethyl 164 ketenes were obtained in this way in 80% yield. The low temperature ^{1}H-N.M.R. spectra ($-40^{\circ}C$) were consistent with the formation of these ketenes and indicated that these were the only species present, other than known solvent impurities (see Figure 4.2).

On standing at room temperature, very rapid trimerization of the ketenes was observed, to give 117 and 165 respectively.
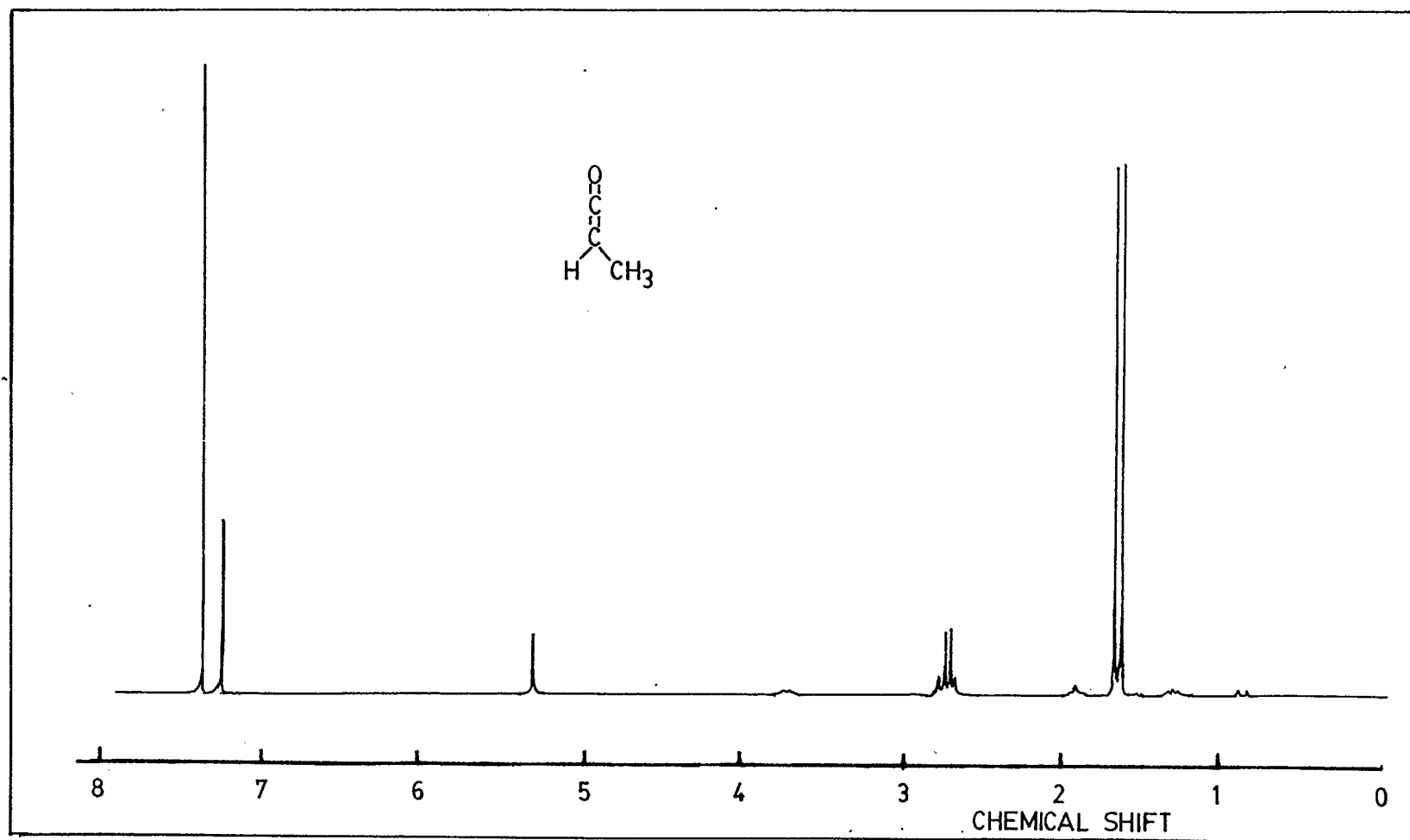
Figure 4.2 ^{1}H-N.M.R. Spectrum of Methyl Ketene (CDCl$_3$, -40°C)

$$BrCHRCOX \xrightarrow[\text{CDCl}_3, \ 0^\circ C]{PPN^+[Mn(CO)_5^-]} \quad \underset{H \quad R}{\overset{O}{\underset{\|}{\overset{\|}{C}}}} \xrightarrow[20^\circ C]{10 \text{ min.}} \quad \text{(structure)} \quad (143)$$

116 R=Me, X=Cl
163 R=Et, X=Br

118 R=Me   84-91%
164 R=Et   80%

117   100%
165
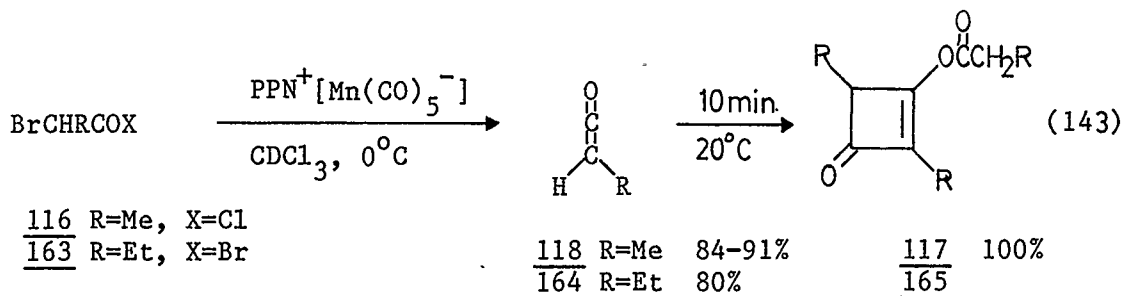
This technique was also applied to the preparation of less reactive iso-propyl ketene 167 and t-butyl ketene 169 in 57% and 76-80% yields respectively. In these cases the subsequent dimerization was much slower and the technique described earlier for preparing dimethyl ketene could also be applied here, although the yields were generally 5-10% lower.

$$BrCHRCOBr \xrightarrow[\text{CDCl}_3, \ 0^\circ C]{PPN^+[Mn(CO)_5^-]} \quad \underset{H \quad R}{\overset{O}{\underset{\|}{\overset{\|}{C}}}} \quad (144)$$

166   R=i-Pr
168   R=t-Bu

167 R=i-Pr   57%
169 R=t-Bu   76-80%
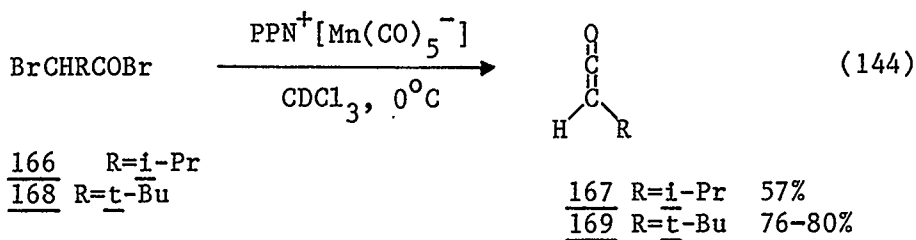
4.2.3 The Preparation of Vinyl Ketenes

The success of the preparation of monoalkyl ketenes suggested a more stringent test for the technique, the preparation of highly reactive vinyl ketene.

Vinyl ketene 170 is generally prepared in-situ by the

dehydrohalogenation of a,β unsaturated acyl halides[168,169], although

it has been isolated from the pyrolysis of 2-cyclobutenones[170] and

crotonic anhydride[171]. The latter reaction gives the ketene in 40%

yield along with substantial amounts of by-products. The possibility

that it could be obtained by a dehalogenation reaction has not been

reported.

In the present study, initial reactions were carried out at

ambient temperature and the products of the reaction determined by

[55]Mn-N.M.R. spectroscopy. The spectra for the reaction of 4-bromo-2-

butenoyl chloride $\underline{171}$ with both $Na^+[Mn(CO)_5^-]$ in THF and $PPN^+[Mn(CO)_5^-]$

in deuterochloroform indicated that $Mn(CO)_5Br$ was the sole product of

the reaction. The [1]H-N.M.R. spectrum of the crude reaction mixture

with the PPN salt was uninstructive. It could not be readily

interpreted in terms of dimerization products of vinyl ketene.

However, it was clear that no unreacted 4-bromo-2-butenoyl chloride

remained, and there was no evidence of acyl (or alkyl) manganese

products.

Using the distillation procedure described earlier for mono-alkyl

ketenes, evidence for vinyl ketene formation came from the IR-spectrum

for the reaction of $Na^+[Mn(CO)_5^-]$ in THF. A band was observed at

$2117 cm^{-1}$ which rapidly disappeared as the solution warmed in the I.R.-

cell. Similar experiments performed in deuterochloroform using the

PPN^+ salt allowed the reaction products to be determined using [1]H-

N.M.R. spectroscopy.

In these cases a characteristic spectrum for vinyl ketene was

observed, the resonances being close to those reported in the

literature[171]. However, the yield was poor (5-10%), but under more

exacting conditions this yield could be improved. Very rapidly

distilling the chloroform/ketene from an almost dry slurry of

$PPN^+[Mn(CO)_5^-]$ (in excess in this case) gave a yellow solution of

vinyl ketene in 35% yield. The [1]H-N.M.R. spectrum of a solution

prepared in this manner is shown in Figure 4.3.

$$\underset{\underline{171}}{\overset{O}{\underset{Br}{\parallel}}} \quad \xrightarrow[\text{CDCl}_3, \; 0°C]{PPN^+[Mn(CO)_5^-]} \quad \underset{\underline{170} \quad 35\%}{\overset{O}{\parallel}} \qquad (145)$$
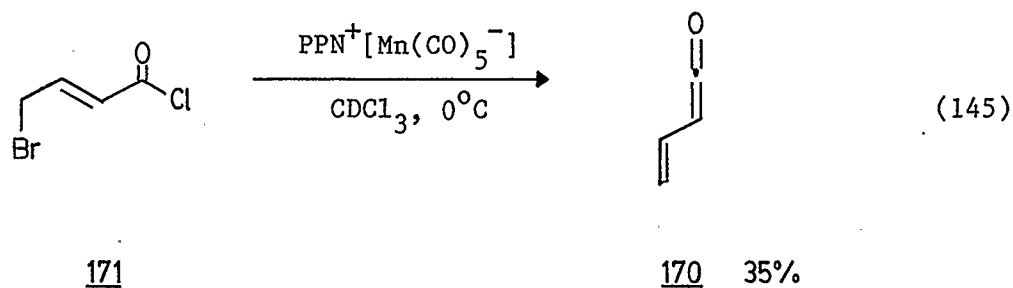
On standing at room temperature the majority of the vinyl ketene (80%)

disappeared almost immediately. A complex [1]H-N.M.R. spectrum which

defied interpretation was observed for this solution. Analysis by

G.C. indicated many products were present in the solution, although it

should be pointed out that other workers[171] have indicated that the

dimerization products are thermally unstable and so this analysis may

not be truly representative of the components present in the solution.

In contrast to vinyl ketene described above, methyl vinyl ketene

·172 could be prepared from 4-bromo-2-methyl-2-butenoyl chloride 173

without any particular precaution. This ketene could be obtained in

80% yield by reacting the bromoacyl chloride 173 in a similar fashion

to the preparation of dimethyl ketene described earlier, and was

identified by [1]H-N.M.R. spectroscopy. The yellow solutions of this

ketene showed no signs of decomposition even after several hours at
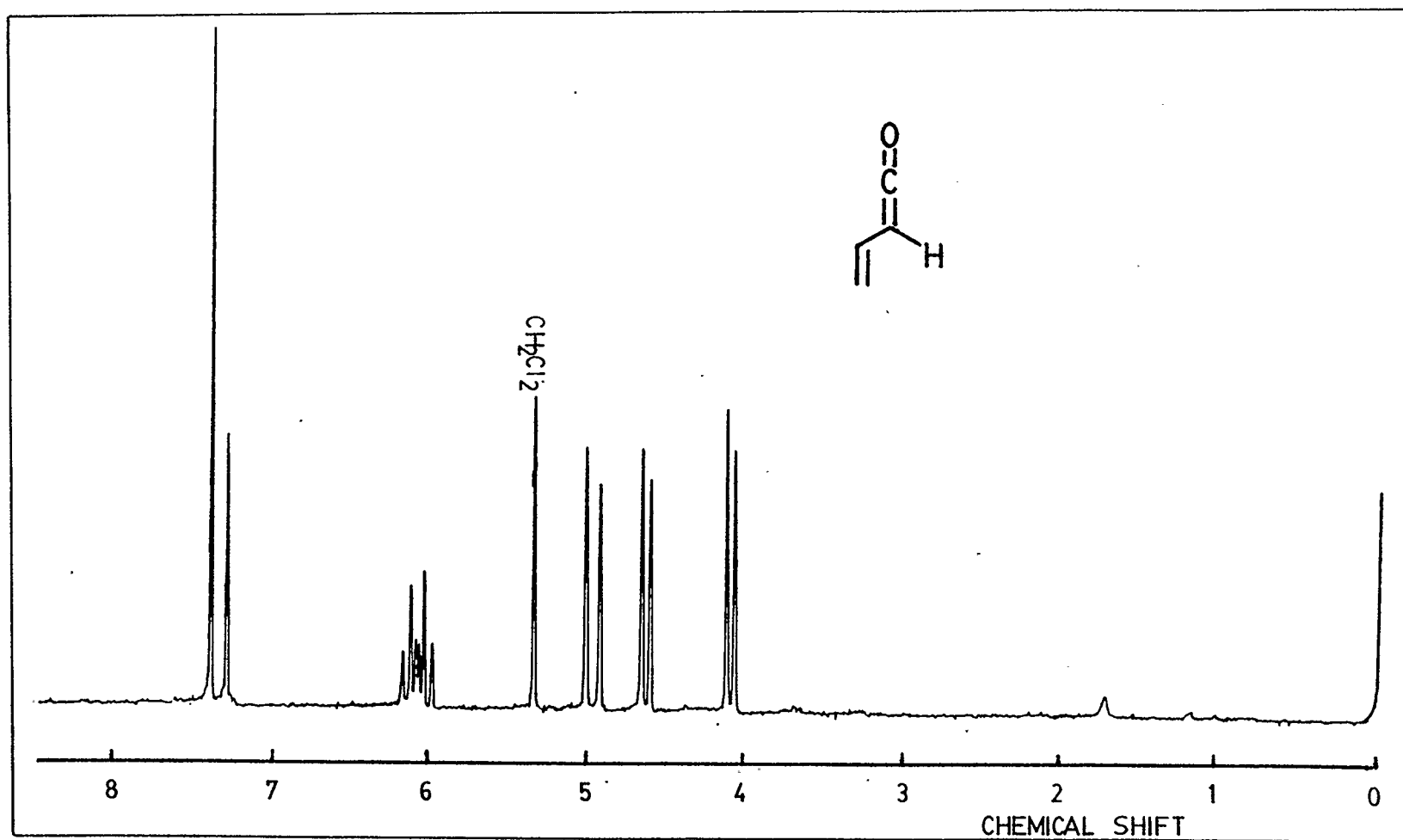
Figure 4.3 [1]H-N.M.R. Spectra of Vinyl Ketene (CDCl$_3$)

room temperature, although on heating to 50°C in chloroform solution

some degradation of the product was apparent.

(146)

173   172
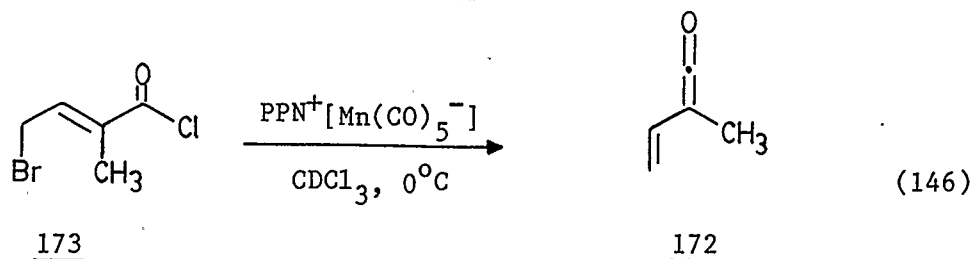
The Preparation of Cyclobutyl Ketene

There are relatively few reports concerning the attempted

isolation of cyclobutyl ketene 174. It has been made by the pyrolysis

of a Meldrum's acid derivative[172], and its dimerization to give the

dione 175 observed.

(147)

174   175
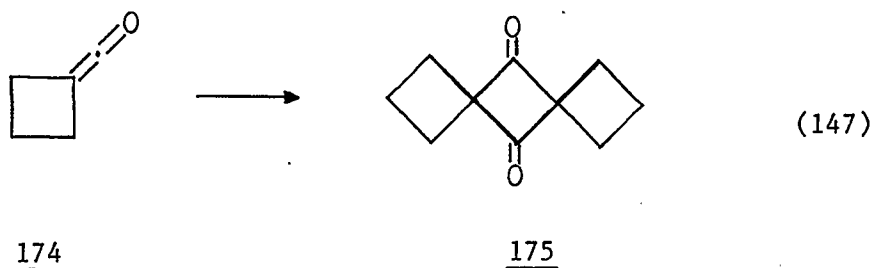
For the most part reports have concerned the preparation[173] of

175, and there are no reports regarding its properties. Both

cyclopentyl ketene and cyclohexyl ketene can be prepared by the

Staudinger method and they dimerize sufficiently slowly at room

temperature that no particular precautions need be taken[158].

The 2-bromoacyl bromide, 1-bromocyclobutylcarbonyl bromide 176

was found to react very rapidly with both $Na^+[Mn(CO)_5^-]$ in THF and
$PPN^+[Mn(CO)_5^-]$ in chloroform to give $Mn(CO)_5Br$. The ^{55}Mn-N.M.R.
spectra of these reaction mixtures were quite consistent with this.

However, a number of attempts to observe the ^1H-N.M.R. spectrum
of cyclobutyl ketene in chloroform solutions distilled under various
conditions from the reaction of $PPN^+[Mn(CO)_5^-]$ with 176 were quite
unsuccessful. Either no resonances or resonances corresponding to
traces of unreacted 176, and known solvent impurities, were observed
in the ^1H-N.M.R. spectrum of these distillates.

In a reaction carried out using $Na^+[Mn(CO)_5^-]$ in THF with 176, a
strong band at $1740cm^{-1}$ in the infra-red spectrum of the reaction
solution was assigned to the formation of dispiro [3.1.3.1].decane-
5,10-dione 175.

(148)

176   175   75-85%
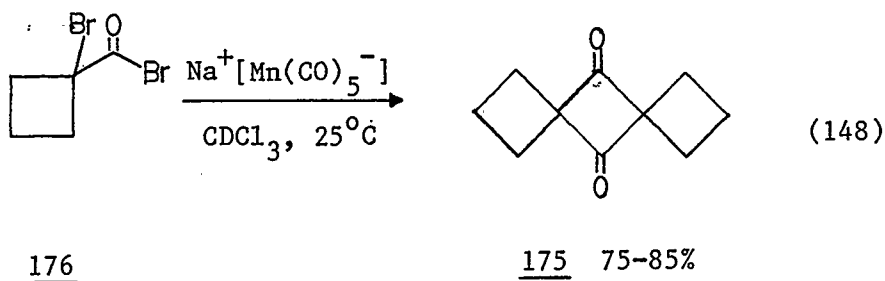
The dispiro compound 175 was isolated from this reaction mixture
in 75-85% yield and comparison of its spectroscopic and physical
properties with those reported in the literature confirmed this
assignment.

The work-up procedure for this reaction is worth noting. The
solvent was removed from the reaction mixture and replaced by hexane
and the solution refluxed. This procedure converts the $Mn(CO)_5Br$

formed in this reaction into insoluble $Mn_2(CO)_8Br_2$, aiding the isolation of the organic product.

$$2\,Mn(CO)_5Br \longrightarrow Mn_2(CO)_8Br_2 + 2CO \qquad (149)$$

The $Mn_2(CO)_8Br_2$ can be simply filtered from the hexane solution and the organic product purified by conventional means.

The Preparation of Methylene Ketene

Methylene ketenes 158 have been proposed as intermediates in a few reactions, however for the most part their isolation is restricted to the work of Brown and Eastwood[174]. These workers have prepared a number of methylene ketenes by the pyrolysis of Meldrum's acid derivatives[175]. There are also some photolytic routes to these extremely reactive species[176]. The possibility that they might be prepared by a mild low temperature method would be of some advantage.

Methylene ketenes 158 dimerize very rapidly at sub-ambient temperatures to give 2,4-alkylidenecyclobutane-1,3-diones 177:

$$(150)$$

158   177
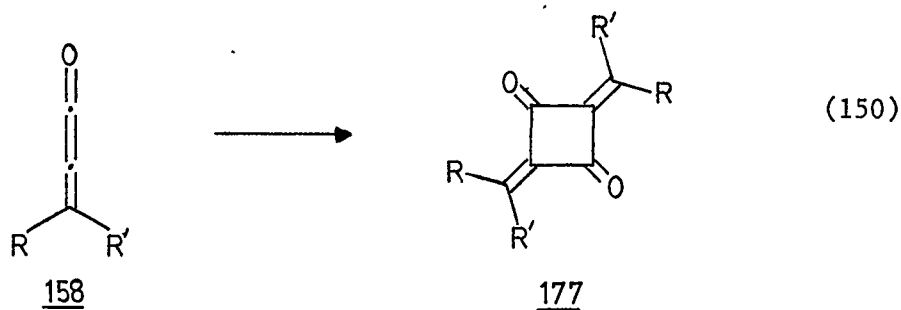
The preparation of the parent molecule, methylene ketene 9

$(R^1=R^2=H)$, was not considered since its dimerization product 158

$(R^1=R^2=H)$, a reasonable way of deducing the intermediacy of 177, is

itself unstable and polymerizes readily at room temperature[176]. There

is also some evidence (albeit rather loose) that substitution at the

3-position in methylene ketenes does give some stability towards

dimerization, although in this case one would clearly not expect this

to be as dramatic as in ketenes[174]. Thus as an exploratory experiment

the preparation of dimethylmethylene ketene 158 $(R^1=R^2=CH_3)$ was

considered.

Treatment of 2-bromo-2-butenoyl chloride 178 with $PPN^+[Mn(CO)_5^-]$

in chloroform under conditions of continuous distillation yielded no

observable dimethylmethylene ketene (or any other products) in the

distillate, even under exacting conditions. However, intense bands in

the infra red spectrum of a solution of the residue from these

reactions were observed at 1632 cm^{-1} and 1694 cm^{-1} and these are

characteristic of the dimer 179.

$$\text{178} \quad \xrightarrow[\text{CDCl}_3,\ 25^\circ\text{C}]{\text{Na}^+[\text{Mn(CO)}_5^-]} \quad \text{179} \tag{151}$$
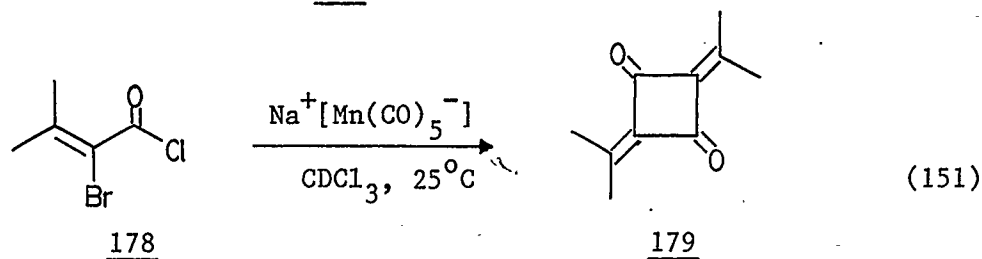
Isolating the product from the residue was not successful.

However, similar bands were observed in the infra-red spectrum from

the reaction of $Na^+[Mn(CO)_5^-]$ with 178 in THF. In this case the

product could be isolated in a low yield (ca 40%) by flash

chromatography. It was subsequently found that 179 partially

decomposed on the silica column used for this separation, accounting
for the low yield. The reaction could be quantified by IR-
spectroscopy however, and the results suggest that the product was
initially formed in >95% yield. Where $Na^+[Mn(CO)_5^-]$ was used in this
reaction, $Mn(CO)_5Br$ could be isolated in 80-90% yield.

O=C=CRR´		Yield %	Starting Material	^{1}H-NMR Spectrum
R	R´			
H	H	95	$BrCH_2COCl$	2.46(s),2H
CH_3	H	84-91	$BrCHCH_3COCl$	1.56(d),3H,J=7.4, 2.67(q),1H
CH_3CH_2	H	80	$BrCH(Et)COBr$	1.06(t),3H,J=7.4, 2.04(d of q),2H, 2.80(t),1H,J=6.9
i-Pr	H	57	$BrCH(i-Pr)COBr$	1.07(d),3H,J=6.7, 2.82(d),3H,J=5.7 2.49(d of q),1H,J=6.6
t-Bu	H	75	$BrCH(t-Bu)COBr$	1.19(s),9H, 2.81(s),1H
CH_3	CH_3	87-95	$BrC(CH_3)_2COX$ X=Br or Cl	1.58(s),6H
vinyl	H	35	$BrCH_2CH=CHCOCl$	4.09(d),1H,J=10, 4.66(d),1H,J=11 4.95(d),1H,J=18, 6.06(d of d of d),1H
vinyl	CH_3	82	$BrCH_2CH=CCOCl$ CH_3	1.76(s),3H 4.77(d of d),1H,J=0.5,11 4.76(d of d),1H,J=0.5, 16.6 6.30(d of d),1H,J=10.8, 16.6

Table 4.1 Summary of Yields and [1]H-N.M.R. Spectral Data for Ketenes
Prepared Using Reaction of $Mn(CO)_5^-$ with 2-Bromoacyl Halides (Chemical
shifts in ppm and coupling constants in Hz)

4.3 Discussion

The results described in this work show that the reaction of $Mn(CO)_5^-$ with 2-bromoacyl halides and their vinylogs to give ketenes is very general. The results are consistent with an initial quantitative yield of ketenes. In most cases the reactions were accompanied by a >90% yield of $Mn(CO)_5Br$, and where stable ketenes were involved, the yield of these products was very high. The actual isolated yield of ketenes as solutions follow the expected stability of the ketene with respect to dimerization.

The observed high reactivity of cyclobutyl ketene towards dimerization is surprising. This ketene was expected to exibit similar reactivity to that of other dialkyl ketenes (for example dimethyl ketene). This result suggests that cyclobutyl ketene has reactivity approaching that of cyclopropyl[177] and methylene ketenes[174].

In considering the mechanism of ketene formation, one is tempted to propose reaction steps based on the expected reaction between $Mn(CO)_5^-$ and 2-bromacyl halide, i.e. nucleophilic substitution. The bifunctional nature of 2-bromoacyl halides leads to two possible sites

of attack by $Mn(CO)_5^-$. Attack at the 2-position to give the corresponding alkyl complex via S_N2 nucleophilic substitution is probably the least likely since the ketene forming reaction appears to be equally facile with vinyl and tertiary substrates as with primary ones.

$$Mn(CO)_5^- + \underset{R'}{\overset{O=C}{\underset{R}{\overset{Cl}{\underset{}{}}}}} C\text{—}Br \quad \xrightarrow{\text{}^-Br^-} \quad (CO)_5Mn\text{-}C \underset{\underline{181}}{\overset{Cl}{\underset{R}{\overset{C=O}{\underset{R'}{}}}}} \quad (153)$$
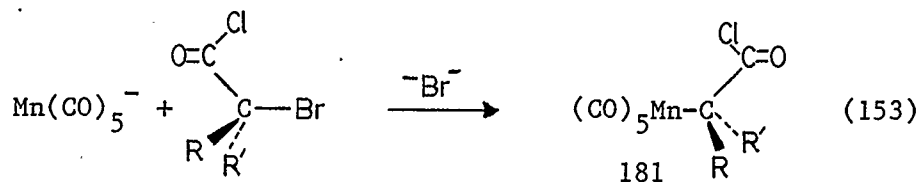
Also, the proposed formation of the akyl complex $\underline{181}$ is not an obvious precursor for the formation of $Mn(CO)_5Br$, although a related reaction was considered and is described later in this discussion.

Substitution at the acyl carbon would certainly not be strongly dependent on the steric congestion at the α-carbon. This substitution would be expected to proceed via the tetrahedral mechanism to give the acyl complex $\underline{182}$.

$$MnCO)_5^- + \underset{Cl}{\overset{O}{\overset{\|}{C}}}C\underset{Br}{\overset{R'}{\underset{R}{}}} \quad \longrightarrow \quad (CO)_5Mn\overset{O}{\overset{\|}{C}}C\underset{Br}{\overset{R'}{\underset{R}{}}} \quad (154)$$
$$\underline{182}$$

$$\Big\downarrow -CO$$

$$\underset{\underline{184}}{\overset{O}{\overset{\|}{C}}}Mn\text{-}\overset{O}{\overset{\|}{C}}\underset{Br\,R\,R'}{} \quad \longleftarrow \quad (CO)_4Mn\overset{O}{\overset{\|}{C}}C\underset{Br}{\overset{R\,R'}{\underset{}{}}}$$
$$\underline{183}$$
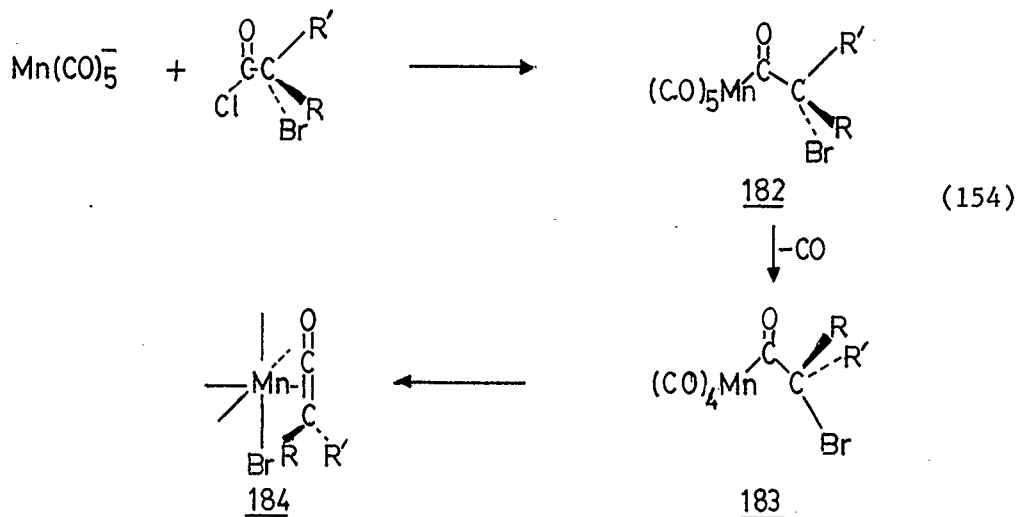
One can, based on known reaction steps, then formulate a mechanism which gives the observed products, ketene and $Mn(CO)_5Br$, as shown above. Loss of CO from the intermediate complex 182 could take place followed by migration of bromide to the unsaturated metal center. The resulting ketene complex 184 could then undergo a substitution reaction with CO, liberating ketene to form $Mn(CO)_5Br$.

Gladysz has recently speculated[178] on a similar mechanism in a reaction involving the debromination of 2-halo esters with $(CO)_5MnSiMe_3$, and the pyrolysis of a 2-chloroacyl molybdenum complex analogous to 182 has been shown to give some ketene[113]. However, in order to explain the extremely facile formation of ketenes using $Mn(CO)_5^-$ the decomposition of the acyl intermediate 182 would have to be very fast. There have been unsuccessful attempts to make 2-iodoacyl manganese complexes by a somewhat different route, but in this case the difficulties encountered might be attributed to instability of the precursor and not instability of the complex itself[119]. Evidence that the decomposition of 182 would not be facile comes from the fact that the corresponding chloro complex 185 is reasonably stable[113,179]. In the present work 185 could be prepared from $Mn(CO)_5^-$ and either 2-chloroethanoyl chloride 186 or 2-chloroethanoyl bromide 187:

$$Mn(CO)_5^- + ClCH_2COX \xrightarrow[25°C, \ 5 \ min.]{THF} Mn(CO)_5COCH_2Cl + Mn(CO)_5X + X^- \quad (155)$$

$$\underline{186} \ X=Cl \qquad\qquad \underline{185}$$
$$\underline{187} \ X=Br$$
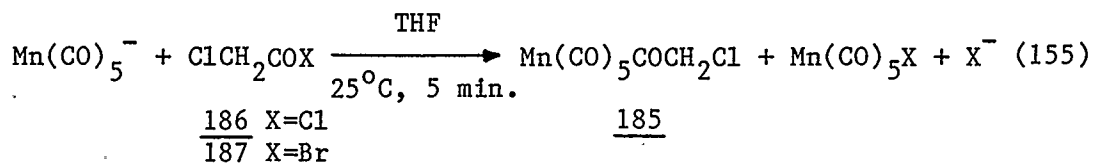
In both of these reactions the acyl complex 185 was the major product (65 - 74% yield, determined·by ^{55}Mn-N.M.R. spectroscopy), the

remainder of manganese containing products being manganese
pentacarbonyl halides. The formation of these halide by-products could
be attributed to some ketene formation by a mechanism analogous to
that observed for 2-bromoacyl halides, but the solutions of the
reactions described above remained unchanged on standing for several
hours. A sample of pure 185 prepared in this way was heated to 80°C in
deuterochloroform in a sealed tube. The reaction was monitored by [1]H-
N.M.R. spectroscopy, which indicated that conversion to the chloro
methyl complex 98 took place.

$$Mn(CO)_5COCH_2Cl \xrightarrow[80°C]{CDCl_3} Mn(CO)_5CH_2Cl + CO \qquad (156)$$

185   98
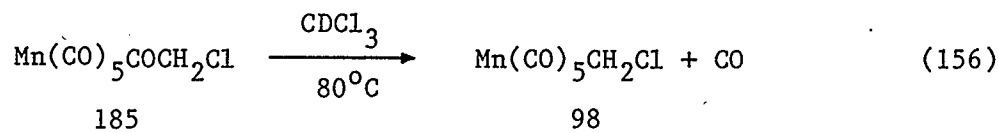
The α-chloromethyl complex 98 was not isolated. The
identification was based on a singlet in the [1]H-N.M.R. spectrum. The
decarbonylation was not entirely clean. After heating, other high
field resonances were present in the [1]H-N.M.R. spectrum. However,
there was no evidence for ketene (or diketene) formation.

The formation of the chloromethyl complex 98 from the acyl
complex 185 is of course the normal type of behavior for this type of
compound. These results imply that the ketene forming β-bromide
elimination reaction would have to be orders of magnitude faster for
the bromoacyl complex 182 than β-chloride elimination in 185. Also
this mechanism does not provide a likely explanation for vinyl ketene
formation from 4-bromo-2-butenoyl chloride and $Mn(CO)_5^-$. In the
formation of vinyl ketenes by this mechanism, an

intermediate acyl complex <u>188</u> would leave the bromine and manganese on opposite sides of a double bond, making migration of the bromine onto the metal center an unlikely process.

$$\text{Mn(CO)}_5^- + \quad \xrightarrow{\quad\quad} \xrightarrow{\quad\quad} \quad \underset{\underline{188}}{} \qquad (157)$$
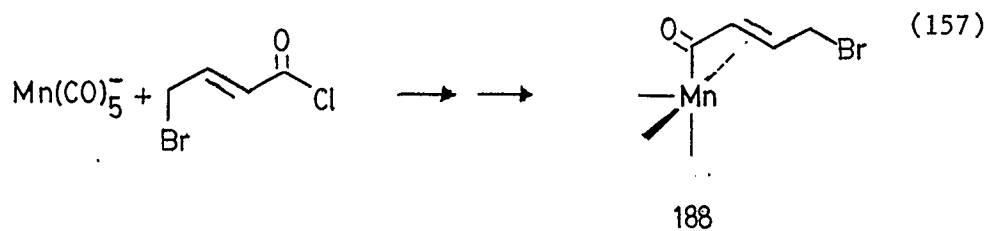
Nucleophilic substitution reactions between Mn(CO)_5^- and acyl halides is normally a fast reaction (the reaction between Mn(CO)_5^- and 2-chlorethanoyl halides described above was complete within five minutes), and there is no reason to expect that the corresponding reaction with 2-bromoacyl halides would be any different in this respect. The implication that the ketene forming reaction does not proceed via an acyl complex intermediate means that any competing process would necessarily have to be fast, and this is in fact what one observes, the ketene forming reaction proceeds rapidly at temperatures as low as -40°C.

Since mechanisms based on nucleophilic substitution are unlikely explanations for the ketene forming reaction, other processes were considered. A more attractive mechanism is halogen metal exchange (H.M.E.), since this would presumably be just as favorable with both 2-bromoacyl halides and their vinylogs.

Halogen metal exchange between Mn(CO)_5^- and a 2-bromoacyl halide,

would give the enolate <u>189</u> which could then eliminate halide to give

ketene:

$$Mn(CO)_5^- + Br-C\overset{COCl}{\underset{R}{\overset{\diagup}{\diagdown}}}R' \xrightarrow{\text{H.M.E.}} \overset{-O}{\underset{R}{\overset{\diagup}{\diagdown}}}C\overset{Cl}{\underset{R'}{\overset{\diagup}{\diagdown}}} + Mn(CO)_5Br \qquad (158)$$

$$\underset{189}{\Big\downarrow}$$

$$\overset{O}{\underset{R}{\overset{\parallel}{\text{C}}}}\overset{C}{\underset{R'}{\overset{\parallel}{\text{C}}}} + Cl^-$$
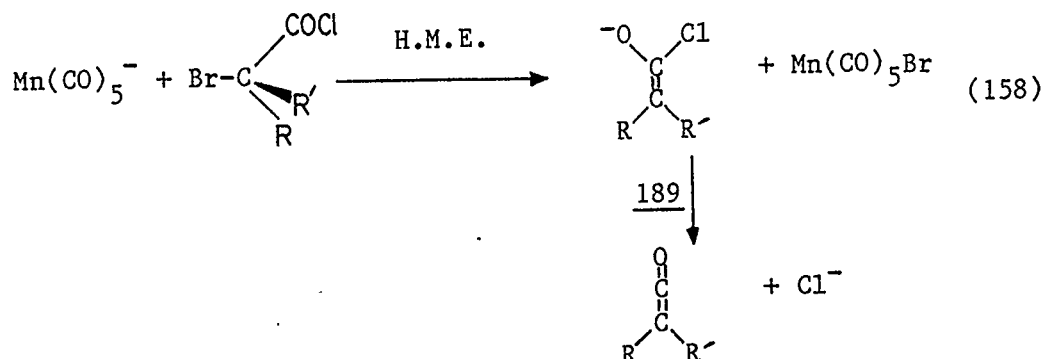
This H.M.E. mechanism is analogous to that presented in Chapter 2 to

explain the formation of non-substitution products ($Mn(CO)_5X$ and

$Mn_2(CO)_{10}$) in the reaction of $Mn(CO)_5^-$ with 2-haloesters.

$$(CO)_5MnCRR'COOEt \xleftarrow{\text{S}_N2 \text{ or E.T.}} Mn(CO)_5^- + XCRR'\overset{O}{\underset{OEt}{\overset{\diagup}{\diagdown}}} \xrightarrow{\text{H.M.E.}} \overset{R}{\underset{R'}{\overset{\diagup}{\diagdown}}}C=C\overset{O^-}{\underset{OEt}{\overset{\diagup}{\diagdown}}}$$
$$+ X^- \qquad\qquad\qquad\qquad\qquad + Mn(CO)_5Br$$
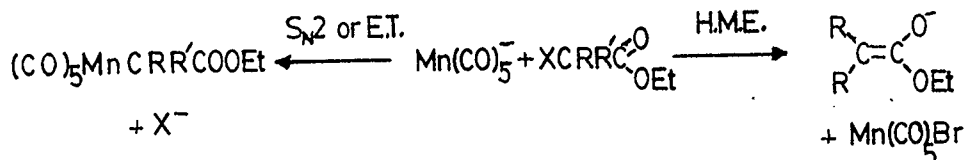
This non-substitution reaction exhibits a similar dependence on the

halogen as the reaction between $Mn(CO)_5^-$ and 2-haloacyl halides does

(i.e. the non-substitution pathway is favored when the α-halogen is

changed from chloride to bromide). However in the case of 2-haloacyl

halides there is an even bigger difference, since no substitution

products are observed at all when 2-bromoacyl chlorides or bromides

are used, and this is irrespective of the structure of the acyl

halide. This may well be because the reaction between $Mn(CO)_5^-$ and 2-

haloacyl halides to give ketenes takes place in a concerted fashion

i.e. formation of the enolate 189 takes place with simultaneous loss

of the halide on the acyl carbon, providing an additional driving

force to the reaction. This could account for the unique ease with

which the reaction takes place.

However, although the H.M.E. reaction is well know, and takes

place with number of common anions[180], there are relatively few cases

where it is explicitly implied in reactions involving metallate

anions. For this reason, and because of the unique ease with which the

ketene forming reaction takes place, exploratory theoretical

calculations were carried out on the ketene forming reaction.

Theoretical Calculations on the Reaction of $Mn(CO)_5^-$ with 2-Haloacyl Halides

Exploratory calculations using the Hartree-Fock-Slater method[181]

in collaboration with T. Ziegler[182] were carried out to investigate

the observations described in this work. The primary objective of

these calculations was to determine the reaction enthalpy for the

formation of the enolate 189 from $Mn(CO)_5^-$ and 2-bromoethanoyl

chloride, a parameter which can be reasonably well estimated by the

H.F.S.- method[183]. Direct attack by $Mn(CO)_5^-$ on the α-bromine of 2-

bromoethanoyl chloride was considered, however this approach also

suggested an alternative mechanism in which the formation of an

intermediate π-complex 190 is involved, and these steps were also

explored.

(160)
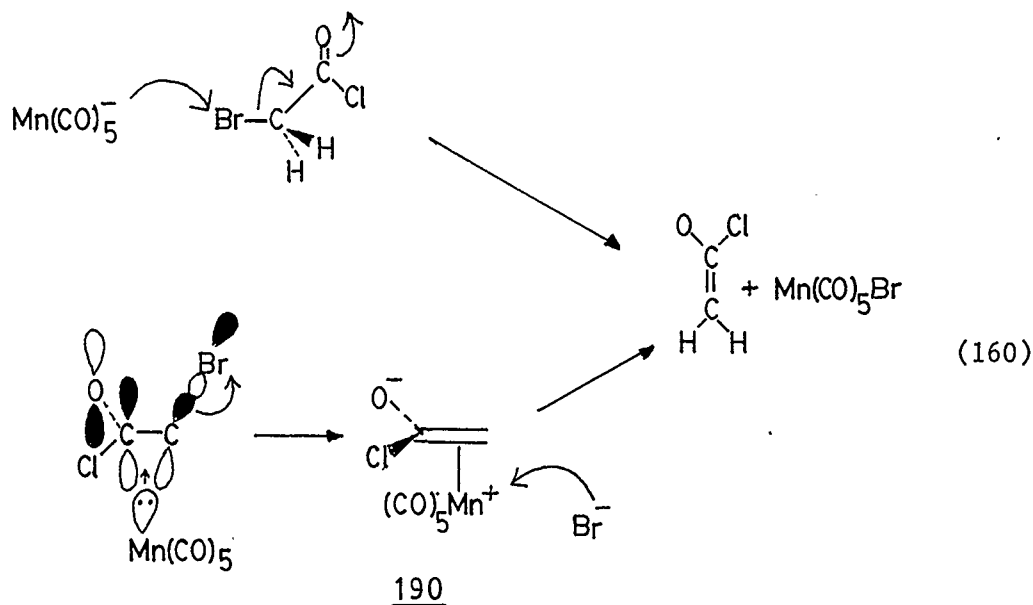
The calculated energy levels for the molecular orbitals of 2-bromoethanoyl chloride are represented in Figure 4.4 (using a double ζ-STO basis set). For this calculation the C-Br bond in the molecule was oriented perpendicular to the O-C-Cl plane, since this is the expected preferred conformation[184].

These orbitals can be conveniently constructed from chlorocarbonyl 191 and CH_2Br 192 fragments. The LUMO 197 of 2-bromoethanoyl chloride is thus the in-phase combination of π^{*}_{CO} and σ^{*}_{CBr} orbitals 193 and 195. Further calculations gave an estimate of the contributions of these fragment orbitals to this LUMO of (65% π^{*}_{CO} and 35% σ^{*}_{CBr}). The corresponding out-of-phase combination of these fragments gives the NLUMO 198 of 2-bromoethanoyl chloride an orbital which plays an important role in the bromine abstraction mechanism. The HOMO of 2-bromoethanoyl chloride 119 and the orbitals having energies close to this HOMO are essentially lone pairs on the

Figure 4.4 Calculated Energy Levels of 2-Bromoethanoyl chloride.

Cl, Br and O atoms.

LUMO	NLUMO	$"\sigma"_{CBr}$
<u>197</u>	<u>198</u>	<u>196</u>
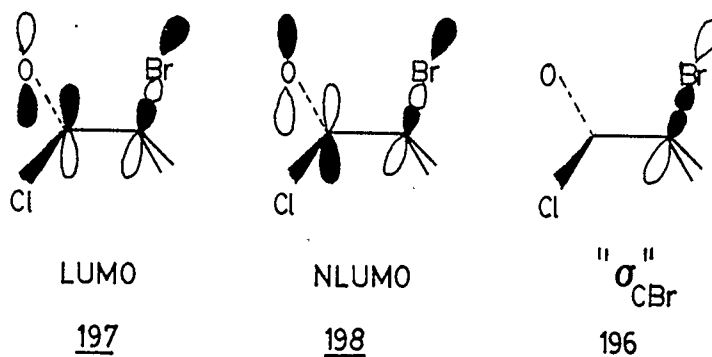
The HOMO of the $Mn(CO)_5^-$ molecule is represented by the d_{z^2} orbital on manganese.

<u>200</u>
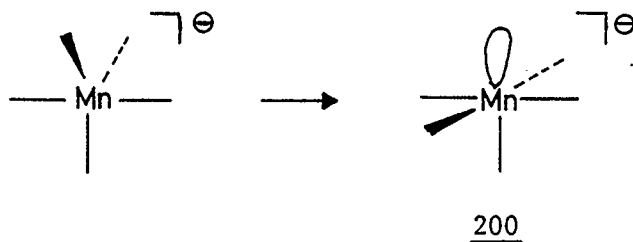
For the purposes of these calculations this molecule was distorted from the C_{3v} geometry that it is known to adopt[185], a distortion which is expected to be a low energy process.

As one can see from the schematic representation of the LUMO <u>197</u> of 2-bromoethanoyl chloride, the carbonyl-CBr bond has some π-character. This led to the idea that in treating the reaction as a HOMO-LUMO interaction, attack by $Mn(CO)_5^-$ could take place on this "π-bond". Initial calculations in which the unrelaxed organic framework was approached by the $Mn(CO)_5^-$ nucleophile indicated that a weak

adduct could be formed with a gain of 6 kcal mole^{-1}.

$$\Delta = 0.5\text{Å}$$

$$r = 3.1\text{Å}$$

(161)

201
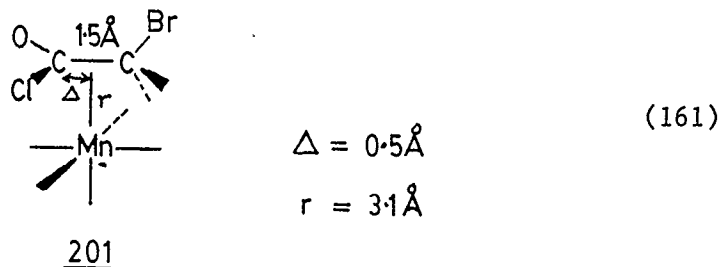
At this postulated point in the reaction profile a charge of 0.25 e-
is donated from the HOMO of $Mn(CO)_5^-$ to the LUMO of 2-bromoacetyl
bromide, indicating that an adduct could indeed be formed. The
possbility that this could proceed with smooth loss of Br$^-$ and
formation of a -complex was then considered.

201 $\longrightarrow$

$$\Delta = 0.7\text{Å}$$

$$r = 2.8\text{Å}$$

190

+ Br$^-$

(162)
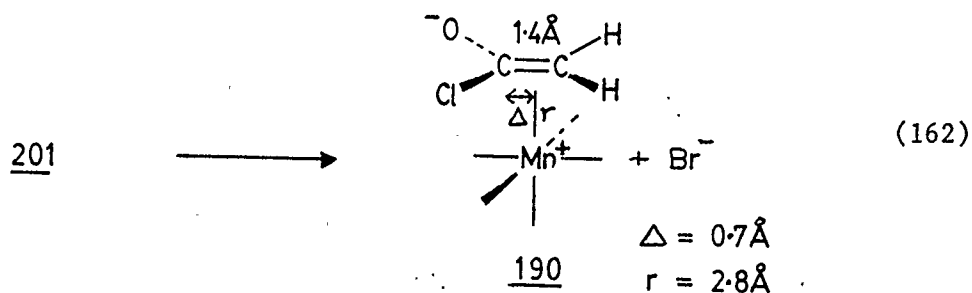
The adduct 190 is analogous to cyclopentadienyliron complexes[186] and
cationic alkene manganese complexes have been isolated[187]. The
overall process is also the reverse of the well known reaction, the
attack of alkene complexes by nucleophiles[188]. This process also
corresponds to the Dewar mechanism for the solvolysis of α-halocarbonyl
compounds[189].

The complexed enolate intermediate 190 is attractive since re-
attack by the bromide ion would release the enolate, which could then

collapse to give ketene, chloride ion and $Mn(CO)_5Br$ (reaction 160).
This intermediate would be compatible with ketene, vinyl ketene and
methylene ketene formation as shown by the structures 202,203 and 204.

202   203   204
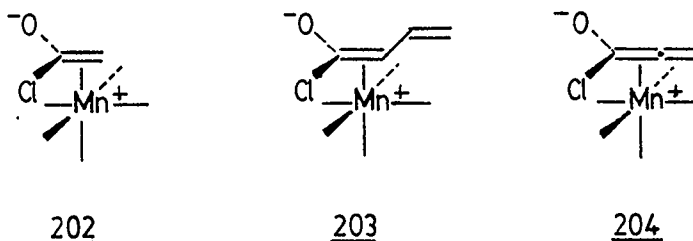
Calculations on the structure 190, in which $Mn(CO)_5^-$ was bonded to
$ClOCCH_2$, indicated a strong donor-acceptor interaction with $1.5e^-$
being donated from manganese to the organic fragment. However,
unoptimized calculations indicate that the overall process of forming
the π-adduct 190 from $Mn(CO)_5^-$ and 2-bromoethanoyl chloride would
require 50 kJ/mole, although one cannot rule out that the structure
190 represents a transition-state. This destabilization is a result of
steric factors, there would be significant interaction between the
equatorial CO ligands of the manganese complex and the coordinated
enolate ligand. This could only be worsened by alkyl substitution in
the 2-position of the 2-bromoacyl halide substrate. Moreover,
calculations indicate that displacing the manganese along the C-C bond
of the enolate ligand is stabilizing with respect to the reactants.

190 $\longrightarrow$ (163)

205
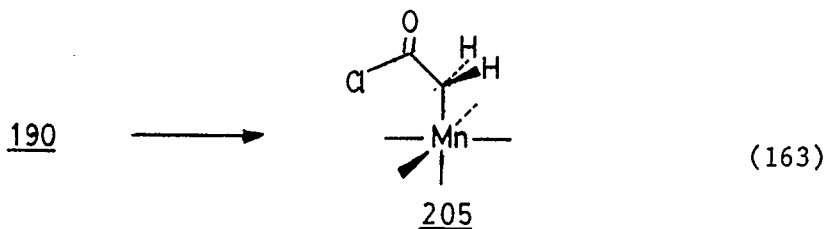
This suggests that formation of the alkyl complex <u>205</u> is a likely product from this interaction.

Re-examination of the LUMO of 2-bromoethanoyl chloride suggests another HOMO-LUMO interaction, the direct abstraction of Br by $Mn(CO)_5^-$. Such a process would be similar to the presumed mechanism for the Staudinger reaction.
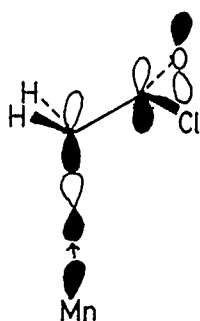
(164)

A calculation of the energy for the system in which $Mn(CO)_5^-$ is positioned along the axis of the C-Br bond at a distance of 3.06 Å, without relaxing the acyl molecule, indicated a stabilization with respect to the free reactants of 42 kJ mole^{-1}.
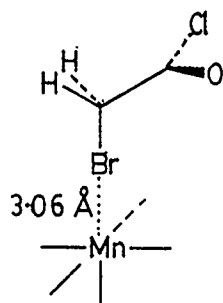
$$\Delta E = 42 \text{ kJ mole}^{-1}$$

The driving force for the reaction at this point is a donor-acceptor interaction between the HOMO of $Mn(CO)_5^-$ and the LUMO and NLUMO of 2-bromoethanoyl chloride. As the Mn-Br distance is progressively shortened (whilst optimizing the C-Br bond length and relaxing the

remaining geometrical parameters) there is a gradual reduction in
energy, and the calculated energy of the system $\underline{vs}$ the Mn-Br distance
is shown in Figure 4.5. The overall process exhibits a reaction
enthalpy of -118 kJ mol^{-1} and does not have any activation barrier.
It is interesting, if not somewhat surprising, that destabilizing
occupied orbital-orbital interactions are completely overridden by the
donor-acceptor interaction described above. There is of course a two
orbital four electron destabilizing interaction between the HOMO of
Mn(CO)$_5^-$ and the occupied orbital $\underline{196}$, which is essentially composed
of the σ_{CBr} orbital. This can be reduced by mixing in the empty
σ^*_{CBr} orbital.
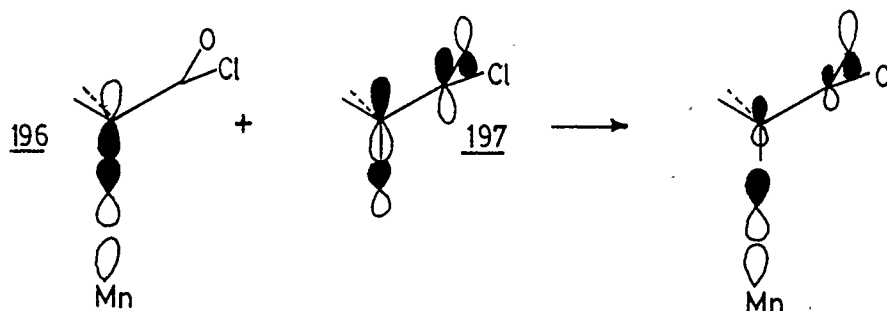
This is illustrated by constructing a correlation diagram for the
four key orbitals (see Figure 4.6). The electron pair occupying the
σ_{CBr}-orbital $\underline{196}$ correlates smoothly with σ_{MnBr} on the product side
by in-phase admixtures of the NLUMO $\underline{197}$ and LUMO $\underline{198}$ of 2-
bromoethanoyl chloride.

The other electron pair involved in the reaction occupies the
HOMO $\underline{206}$ of Mn(CO)$_5^-$, and has an intended correlation with the
unoccupied σ^*_{MnBr} orbital $\underline{207}$ on the product side. This can be avoided

Figure 4.5 Calculated Energy Profile for the Abstraction Reaction as a
Function of the Manganese-bromine Distance (the carbon-bromine
distance was optimised while the remaining parameters were
interpolated linearly).

$Mn(CO)_5^- + BrCH_2\overset{\overset{O}{\parallel}}{C}Cl$ $Mn(CO)_5Br + CH_2\overset{\overset{O^-}{\mid}}{=}\overset{}{C}Cl$
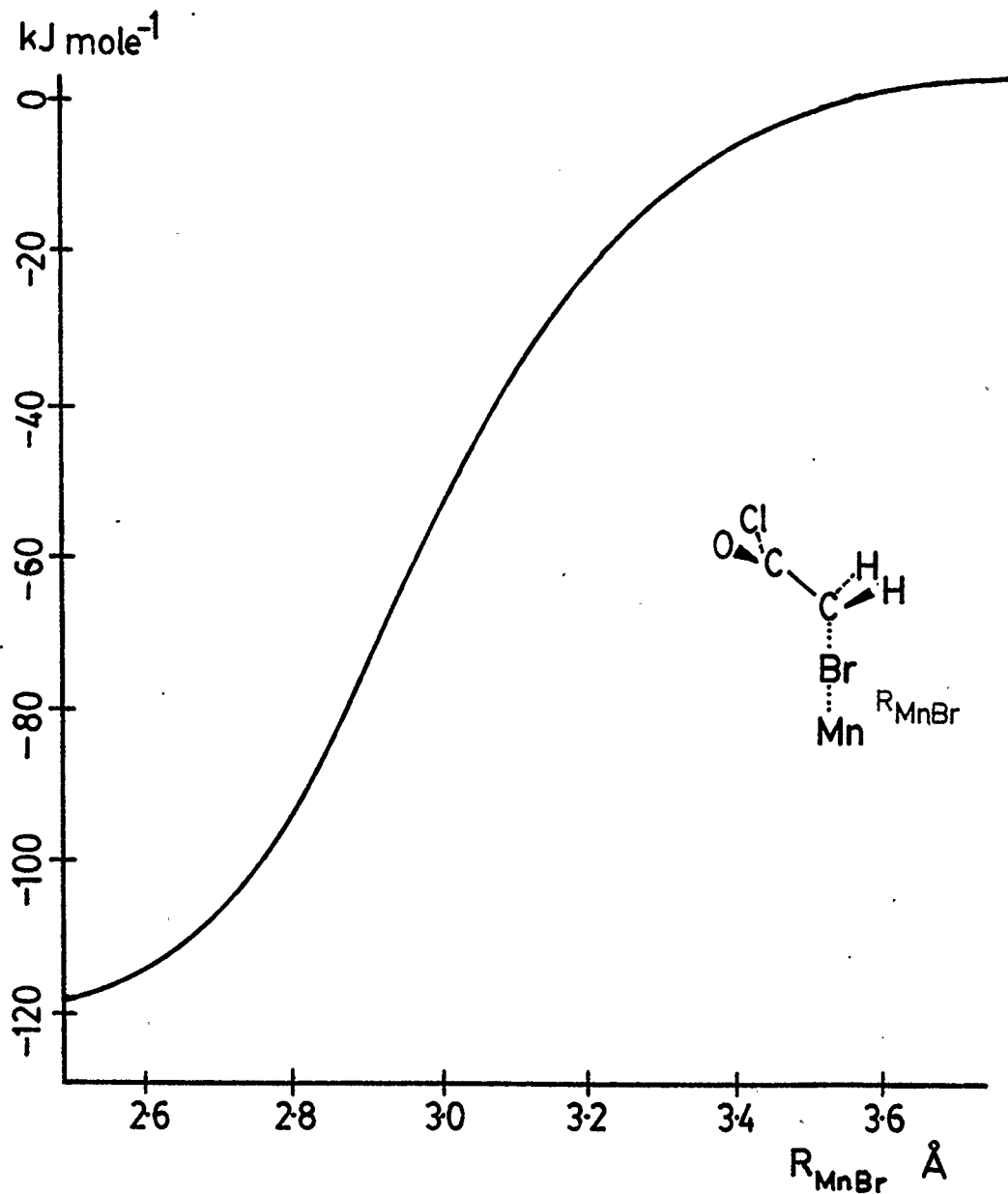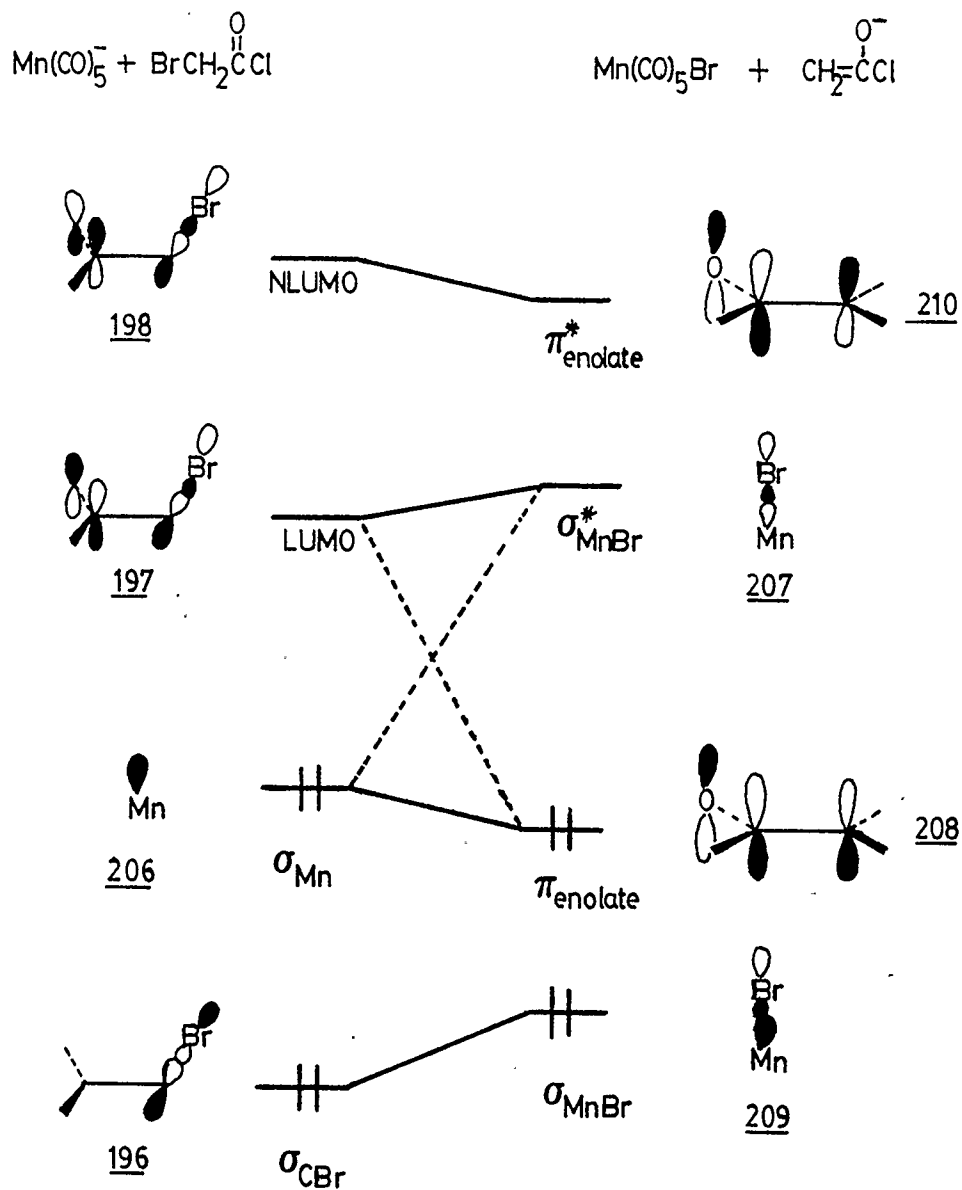
Figure 4.6 Correlation Diagram[a] for the Abstraction of Bromine from 2-Bromoethanoyl chloride by $Mn(CO)_5^-$.

[a] Solid lines indicate actual correlations, dashed lines intended correlations.

by the linear combination of $_{CBr}$196 + NLUMO 197 and LUMO 198 which

evolves into the occupied π-orbital of the enolate 208. This

combination drops in energy early on in the reaction profile, avoiding

an activation barrier for the reaction.
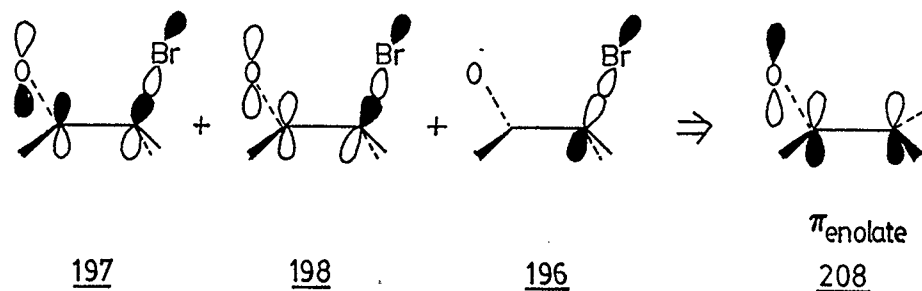
This approach explains why the reaction proceeds with such

ease, and the dependence of this explanation on contributions from the

σ^*_{CO} to the NLUMO of bromoacyl halides explains why other alkyl

bromides undergo nucleophilic substitution rather than bromine

abstraction. Ultimately though, for -halocarbonyl compounds, the

formation of the (more stable) enolate is a strong driving force in

the bromine abstraction reaction.

The difference in reactivity between 2-bromoethanoyl chloride and

2-chloroethanoyl chloride can be related to the donor-acceptor

interaction described above.

The σ^*_{CCl} orbital in 2-chloroethanoyl chloride is of higher

energy and has a smaller amplitude than the σ^*_{CBr} bond in the

corresponding bromo compound. This is due to the larger

electronegativity of chlorine. As a consequence 2-chloroethanoyl

chloride has a more σ^*_{CO}-like LUMO (91%) and a more σ^*_{CX} like NLUMO,

the latter also being of higher energy (See Figure 4.7).
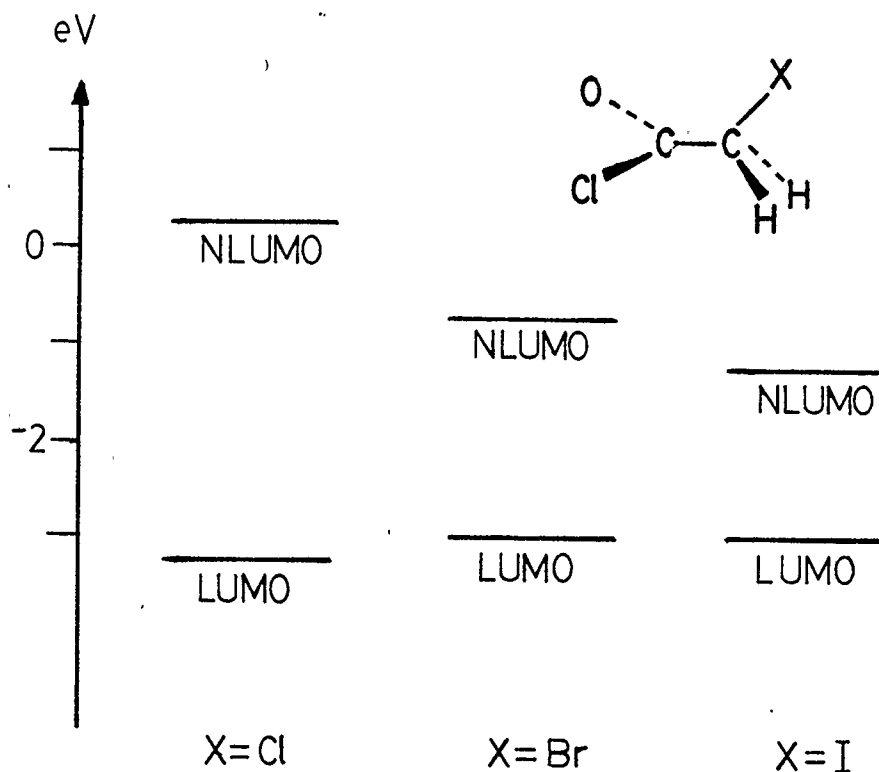
Figure 4.7 Orbital Energies for the LUMO and NLUMO of

2-Haloethanoyl chlorides

The NLUMO also has a smaller amplitude on chlorine. These

differences result in a weaker donor acceptor interaction in the early

stages of the interaction, since there is a larger gap and poorer

overlap between the donor and acceptor orbitals. Based on these

qualitative arguments one would predict that 2-iodoethanoyl chloride

would be even more prone to halogen abstraction than the bromo

compound. In this case, σ^*_{CI} is of lower energy and has a larger

amplitude than σ^*_{CBr} and σ^*_{CCl}; thus the NLUMO in the iodo compound

is the NLUMO of lowest energy and it also has the largest contribution

from σ^{*}_{CI} in the LUMO.

Conclusions

The dehalogenation of 2-bromoacyl halides and their vinylogs by $Mn(CO)_5^-$ is potentially a very useful way of preparing reactive ketenes and methylene ketenes on a small scale. This potential comes from the essentially quantitative yield of the reaction, and the very high purity with which the ketene solutions can be obtained. Although it was not specifically explored in this work, this reaction should be useful for in-situ preparations as well, particularily where the ketene is too reactive to be distilled from the reaction mixture. The reaction would be well-suited to in-situ preparations since it takes place under mild, neutral conditions.

The theoretical calculations carried out on this reaction suggest that the reaction procedes via halogen metal exchange, and although the the possibility that the reaction procedes via an intermediate π-complex cannot be ruled out, H.M.E. is the most straightforward alternative.

The potential that other di-halo compounds could be dehalogenated by $Mn(CO)_5^-$ would certainly be worth exploring further.

Chapter 5

The Preparation and Structure of η^1, η^3 and η^5 Allylester Complexes of Manganese Carbonyl

5.1 Introduction

The decarbonylation of η^1-bonded allylic transition metal carbonyl complexes to give η^3-bonded complexes is one of the oldest routes to these complexes[29].

$$Na^+[Mn(CO)_5^-] + Br\!\!\!\diagup\!\!\!\diagdown \longrightarrow Mn(CO)_5 \qquad\qquad (165)$$

211
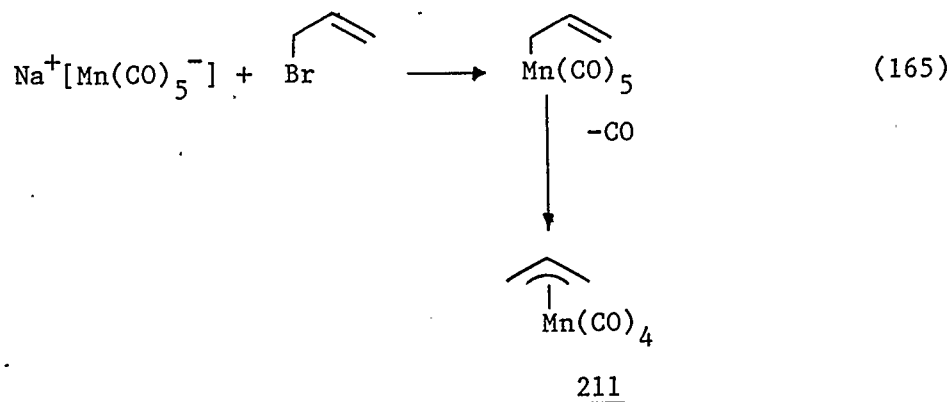
This reaction has been extended to a number of substituted complexes[54]. The preparation of η^3-allyl manganese complexes has also been achieved by the treatment of η^1-acetylene compounds with alcohols[190], $Mn(CO)_5Br$ with allylic halides and phase transfer catalysts[191], the reaction of $Mn(CO)_5H$ with dienes[29], and the photolysis of $Mn_2(CO)_{10}$ with dienes[192], to name some methods.

The addition of alkyl manganese pentacarbonyl compounds to dienes is another route[193] to η^3-complexes, in this case carbonyl-substituted complexes 212 are obtained. These compounds can be furthur decarbonylated[194] to give η^5-bonded "enolate" complexes 213.

$$\text{Mn(CO)}_5\text{Ph} + \text{(butadiene)} \xrightarrow[-\text{CO}]{} \underset{\underline{212}}{\text{(acyl)Mn(CO)}_4} \xrightarrow[-\text{CO}]{\Delta} \underset{\underline{213}}{\text{(dienyl)Mn(CO)}_3} \qquad (166)$$
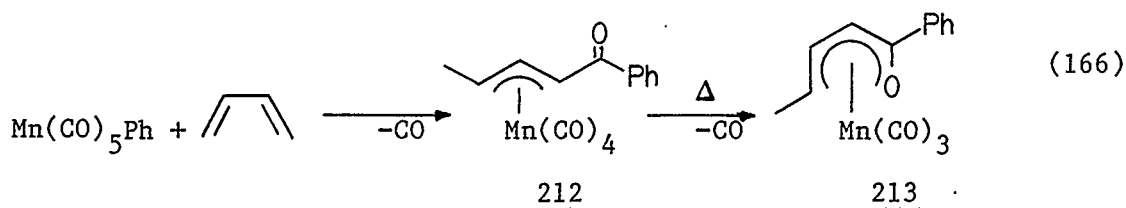
Complex $\underline{213}$ is an example of an "open" η^5-bonded ligand analogous to the η^5-cyclopentadienyl group (Cp) which is ubiquitous in organometallic chemistry. This type of ligand is of interest[195,196] since its more flexible nature (than Cp) gives it the potential to easily interconvert between η^1, η^3 and η^5 bonding modes $\underline{214}$, $\underline{215}$, and $\underline{216}$ respectively

$$X = O, CR_2$$

$$\underset{\underline{214}}{\text{Mn(CO)}_5} \underset{-\text{CO}}{\overset{\text{CO}}{\rightleftarrows}} \underset{\underline{215}}{\text{Mn(CO)}_4} \underset{-\text{CO}}{\overset{\text{CO}}{\rightleftarrows}} \underset{\underline{216}}{\text{Mn(CO)}_3} \qquad (167)$$
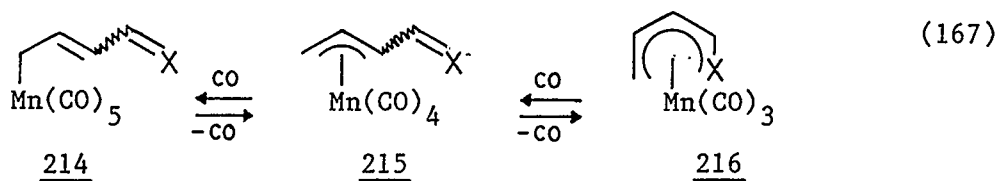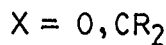
The open analogue of cyclopentadienyl manganese tricarbonyl, $\underline{217}$ has recently been prepared[197] from trialkyltin pentadiene $\underline{218}$.

$$\text{Mn(CO)}_5\text{Br} + \underset{\underline{218}}{\text{SnR}_3} \xrightarrow{-2\text{CO}} \underset{\underline{217}}{\text{Mn(CO)}_3} + \text{SnR}_3\text{Br} \qquad (169)$$
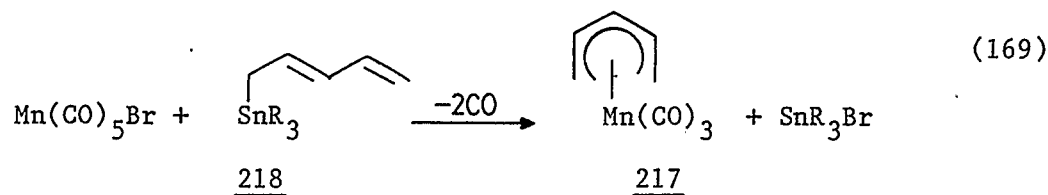
A photochemical route to complexes similar to 217 has also been described.[198]

There are few examples reported for the preparation of the η^5-bonded enolate complexes 213 of manganese, in addition to the example described above the only other reported route is a somewhat unusual reaction shown below[199]

$$\text{Mn(CO)}_5\text{Me} \xrightarrow{\hspace{3cm}} \underset{\underline{219}}{} \tag{170}$$
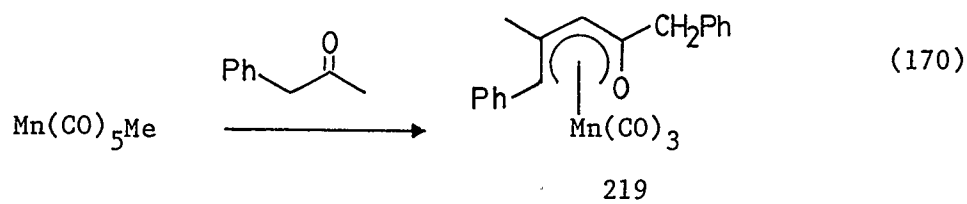
In the present work it was proposed to prepare η^1-bonded α, β-unsaturated ester complexes 210 and by subsequent decarbonylation to obtain the corresponding η^3 and η^5 complexes 211 and 212

$$\underset{\underline{220}}{\text{Mn(CO)}_5} \xrightarrow[-\text{CO}]{} \underset{\underline{221}}{\text{Mn(CO)}_4} \xrightarrow[-\text{CO}]{} \underset{\underline{222}}{\text{Mn(CO)}_3} \tag{171}$$
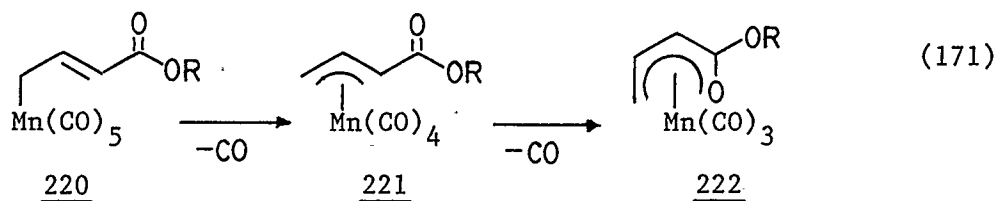
This synthetic strategy has the advantage that all three bonding modes are available from the same starting materials, making it possible to take advantage of different chemical properties of the three complexes.

5.2 Results

The formation of the σ-complex 49 from the reaction of $Mn(CO)_5^-$

and ethyl 4-chloro-2-butenoate was described earlier in this thesis.

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (172)$$

49 R = Et

223 R = Ph
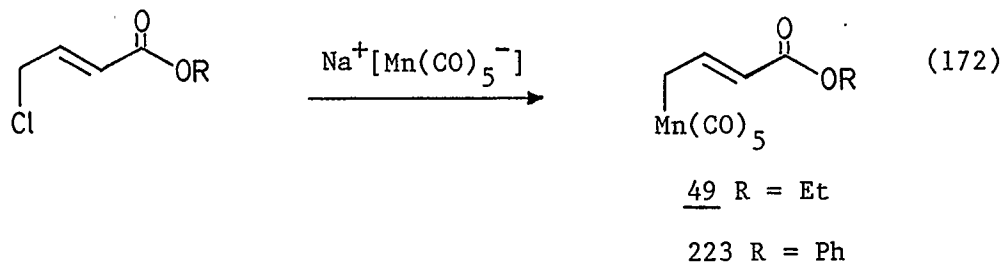
The complex, 49, was initially isolated in low yield (15%) from a

reaction carried out with ethyl 4-bromo-2-butenoate, and could be

separated from the $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$ byproducts also formed, by

flash chromatography. Much better isolated yields of 49 were obtained

using the corresponding chloro-ester. The complex 49 was isolated as

an air sensitive pale yellow oil which could be furthur purified by

low temperature recrystalization (m.p. ca -5°C) from pentane.

Since characterization of this complex (and the η^3 and η^5

complexes subsequently formed from it) by X-ray crystallography was

sought, the corresponding phenyl ester was also prepared. It was

suspected that this ester would give a product with a higher melting

point and this was found to be the case. The complex 223 could be

isolated directly from the reaction mixture by crystallization and was

obtained in 83% yield as a pale yellow crystalline solid which was

somewhat less air sensitive than the corresponding ethyl ester.

Both the ethyl and phenyl esters 49 and 223 decarbonylated

smoothly on heating to 80°C and the η^3-bonded compounds 224 and 225

were cleanly formed.

$$\text{(173)}$$

224 R=Et

225 R=Ph
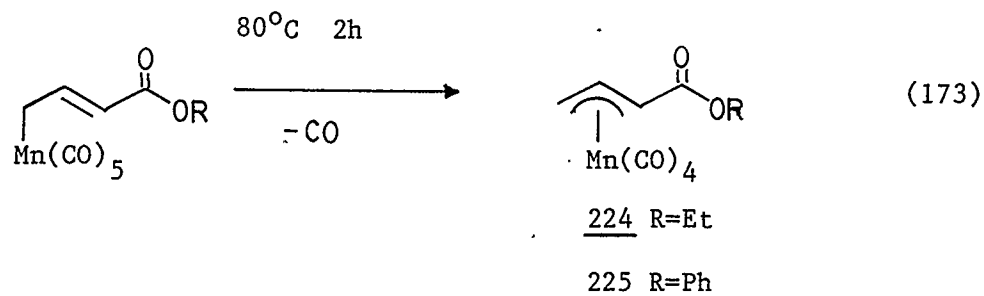
Examination of the crude product from this decarbonylation by T.L.C. and IR-spectroscopy indicated the conversion was essentially quantitative. Purification of these complexes was achieved by flash chromatography in the case of the ethyl ester, and recrystallization in the case of the phenyl ester. Both complexes appeared to be slightly less air sensitive than the corresponding η^1-bonded complexes. The phenyl ester 225 was also substantially more soluble in hydrocarbons than the corresponding η^1-complex 223.

Heating neat samples of 224 and 225 to 120°C resulted in further evolution of carbon monoxide, but in this case the decarbonylation was accompanied by considerable decomposition. The infra-red spectrum of a solution from this reaction did indicate some formation of a new complex, and T.L.C. indicated that a non-polar bright yellow species was present. Attempts to achieve this decarbonylation by U.V.-irradiation (250W GE sunlamp) of hexane solutions of 224 also resulted in considerable decomposition. However, the decarbonylation could be achieved cleanly by extended refluxing in cyclohexane, and the η^5-complexes 226 and 227 could be obtained as the major products.

$$\text{(scheme)} \xrightarrow[\text{10-20h}]{C_6H_{12} \text{ reflux}} \text{(scheme)} \quad (174)$$

$$\underline{225} \ R=Et$$

$$\underline{227} \ R=Ph$$
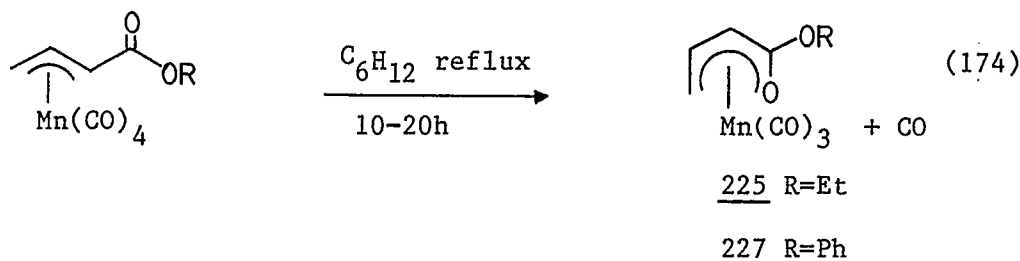
Both complexes $\underline{226}$ and $\underline{227}$ were isolated in high yield by flash chromatography, $\underline{226}$ a dark yellow oil which was very air sensitive and the phenyl ester $\underline{227}$ as an orange/yellow solid. Both complexes were extremely soluble in organic solvents, the phenyl ester $\underline{227}$ being recrystallized with some difficulty from pentane.

5.3 Spectroscopic and X-Ray Crystallographic Characterization of the η^1, η^3 and η^5 complexes

All three complexes (both phenyl and ethyl esters) exhibit typical ν_{co} stretch frequencies in their IR-spectra for the carbonyl ligands, and are similar to those for analogous complexes (see Figure 5.1).

In the η^1 and η^3-bonded complexes the weaker bond assigned to the carbonyl strech of the ester functionality is similar to that for uncomplexed a, β-unsaturated esters. Bands were observed at 1738 cm^{-1} for $\underline{223}$ and 1736 cm^{-1} for $\underline{225}$, which are close to that for phenyl 2-butenoate (1739 cm^{-1}). A weak bond at 1618 cm^{-1} in the η^1-complex $\underline{223}$ was assigned to the streching mode of the free double bond. This band, as one would expect, is not observed in the η^3-complex. No band which could be unambiguously assigned to the complexed ester function
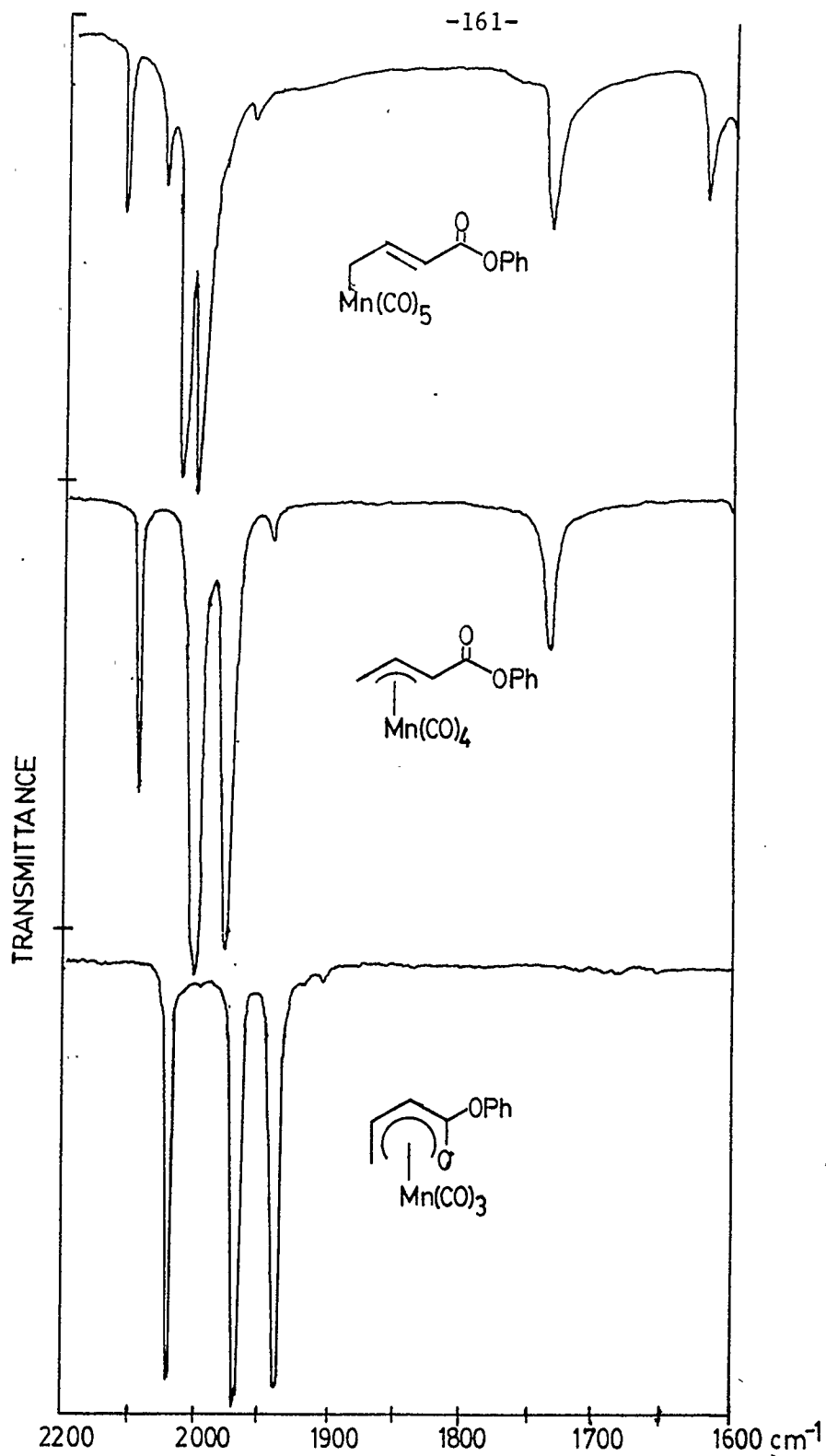
Figure 5.1 Infra-red Spectra of $\eta^1 \eta^3$ and η^5 Complexes 223, 225 and 227

(in hexane, solvent subtracted)

in the η^5 complexes 226 and 227 was observed.

The ^{1}H-N.M.R. spectrum of the η^1-complexes 49 and 223 were as expected (see Table 5.1), the doublet at 1.94 ppm (J=9.7 Hz) being assigned to the protons of the methylene attached to manganese. The proton decoupled ^{13}C-N.M.R. for 223 (see Table 5.1) contained a high field resonance (8.1 ppm) typical of the shielded carbon attached to manganese.

The ^{1}H-N.M.R. spectrum of the η^3-complex 223 consisted of a multiplet at 5.79 ppm assigned to Hc and three higher field doublets Ha, Hb and Hd, the assignments of which are given in Table 6.1. This assignment assumes that the product is the anti-isomer, a fact which is confirmed by the solid state structure described later in this discussion. It is worth noting that the observed coupling constants J_{HaHc}, J_{HbHc} and J_{HdHc} are almost identical to those recently reported by others[200] for an analogous syn-η^3 pentadienyl complex.

Comparing the ^{1}H-N.M.R. spectra for the η^1 and η^3 complexes there is a general shift of the resonances to higher field, corresponding to an increase in electron density in the allyl ligand on conversion to the η^3-complex. The ^{13}C-N.M.R. spectrum of the η^3-complex 14 is considerably more "symmetrical" than that for the η^1-complex 12, the central carbon (C_2) appearing at low field and C_1 and C_3 appearing at high field with similar chemical shifts (see Table 6.1). This assignment is based on comparison with the ^{13}C-N.M.R. chemical shifts for related complexes[200].

The methylene protons of the ethyl group in the η^3-complex 224 are diastereotopic. This can be inferred from the ^{1}H-N.M.R. spectrum
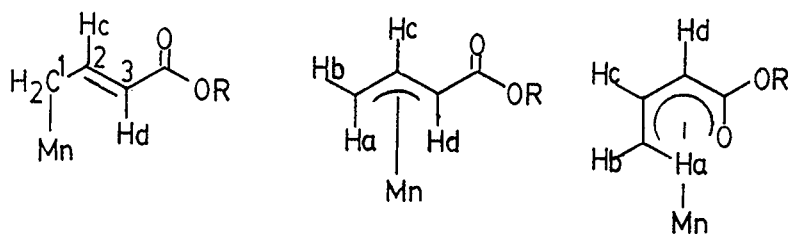
	Ha	Hb	Hc	Hd
$\underline{49}, \eta^1, R=Et$	1.88 d $J_{ac}=9.6$		7.45 dt	5.65 d $J_{dc}=15$
$\underline{223}, \eta^1, R=Ph$	1.94 d, $J_{ac}=9.7$		7.65 m	5.81 d $J_{dc}=15$
$\underline{224}, \eta^3, R=Et$	2.26 d $J_{ac}=13$ $J_{ab}=2$	2.99 d $J_{bc}=8$	5.67 m	2.53 d $J_{dc}=10$
$\underline{225}, \eta^3, R=Ph$	2.34 d $J_{ac}=14$ $J_{ab}=2$	3.09 d $J_{bc}=7$	5.97 m	2.70 d $J_{dc}=10$
$\underline{226}, \eta^5, R=Et$	1.93 d $J_{ab}=14$	3.54 d $J_{bc}=10$	5.46 m	4.86 d $J_{dc}=7$
$\underline{227}, \eta^5, R=Ph$	2.03 d $J_{ab}=13$	3.61 d $J_{bc}=10$	5.58 m	5.12 d $J_{dc}=7$

^{13}C-N.M.R.:

	C1	C2	C3
$\underline{223} \; \eta^1$	8.2	110	161
$\underline{225} \; \eta^3$	47	97	45
$\underline{227} \; \eta^5$	62	106	57

<u>Table 5.1</u> ^{1}H and ^{13}C-N.M.R. Data for the η^1, η^3, and η^5 Allylester Complexes

of this complex , where the resonance associated with these protons appears as a more complex multiplet than the expected quartet (see Figure 5.2). This feature is not observed in the η^5-complex __226__.

In the ^{1}H-N.M.R. spectrum of the η^5-bonded complex __227__ there is a shift in the resonance for Hd to considerably lower field when compared to the η^3-complex __225__. This is accompanied by a reduction in the coupling constant J_{HcHd} (10.3 Hz in the η^3-complex compared to 6.7 Hz in the η^5-complex). This is consistant with the syn structure assigned to this complex, a fact which is confirmed by its crystal structure.

X-Ray Crystallographic Structures for the η^1, η^3 and η^5-Complexes

Suitable crystals for X-ray crystallography were obtained from the phenyl esters __223__, __225__ and __227__ by slow crystallization from hydrocarbon solvent. The data was collected and the structures solved using the Patterson method by Dr. J. Richardson of this department[201] and some details of this are given in the experimental section.

Ortep diagrams for the complexes __223__, __225__ and __227__ are given in Figures 5.3, 5.4 and 5.5. With the exception of the n^1-complex __12__ (Figure 5.3) the metal-carbon bonds have been omitted for clarity. These structures confirm the conclusions of the spectroscopic evidence that the η^3-complex is the anti-isomer and the η^5-complex adopts the syn or "U" structure. Selected bond lengths and angles for these structures are given in Tables 5.2-5.7, estimated standard deviations in the least significant digits for these values are shown in parenthesis.
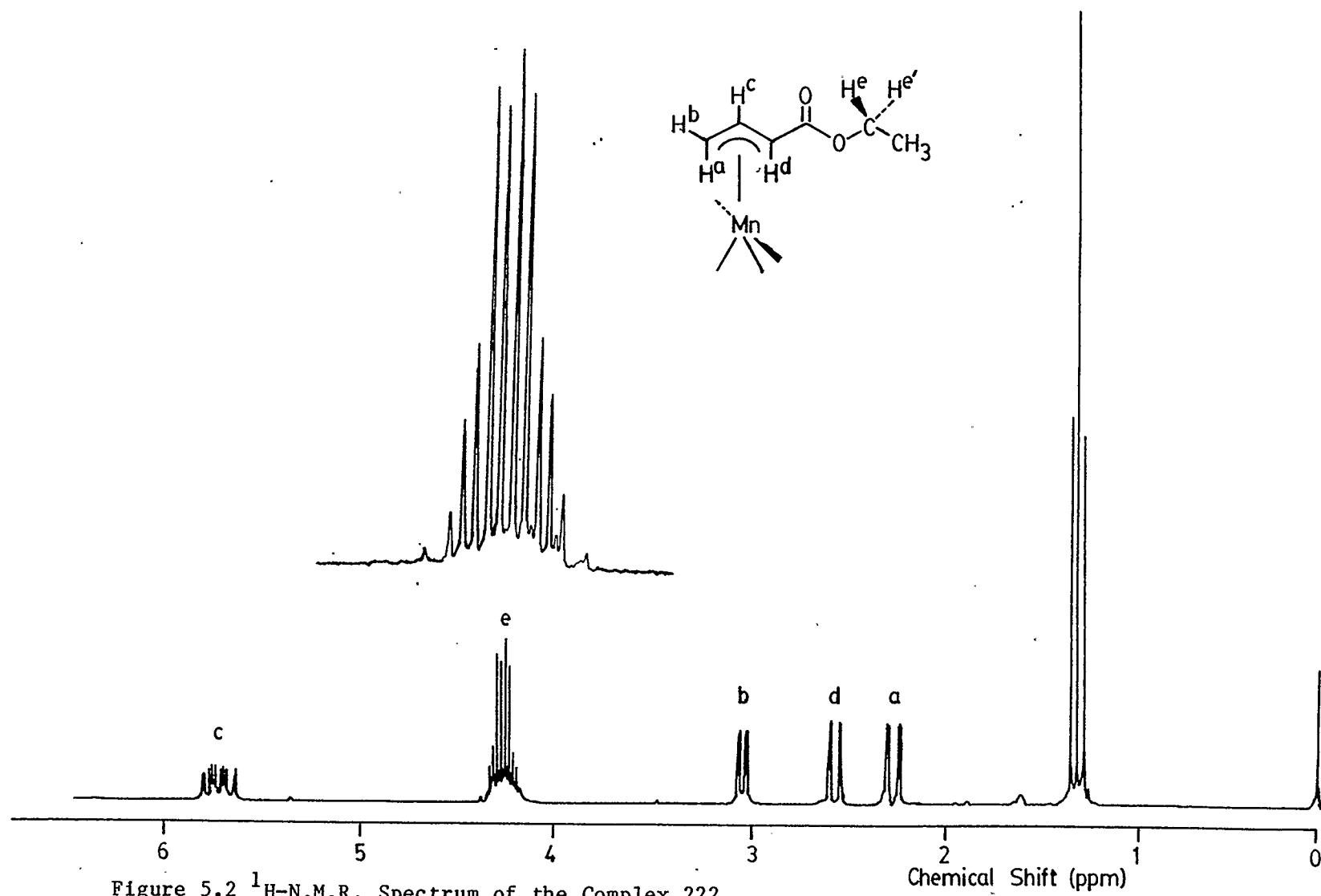
Figure 5.2 ^{1}H-N.M.R. Spectrum of the Complex 222.

Figure 5.3 ORTEP diagram of the η^1-Bonded Complex 223
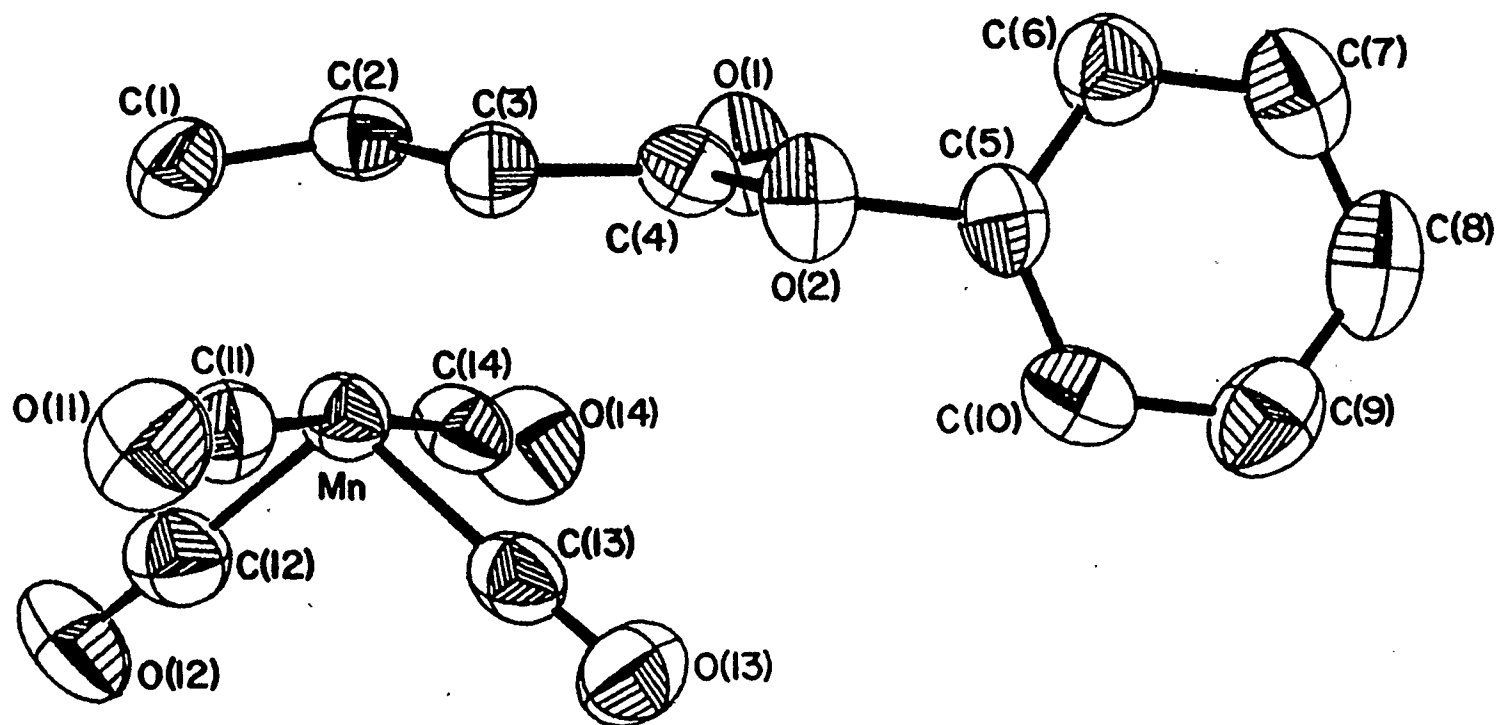
Figure 5.4 ORTEP diagram of the η^3-Bonded Complex 225

Figure 5.5 ORTEP diagram of the η^5-Bonded Complex 227

Mn-C(1)	2.214(3)		

Mn-C(11)	1.865(4)	C(11)-O(11)	1.130(4)
Mn-C(12)	1.825(4)	C(12)-O(12)	1.129(4)
Mn-C(13)	1.825(4)	C(13)-O(13)	1.131(4)
Mn-C(14)	1.845(4)	C(14)-O(14)	1.133(4)
Mn-C(15)	1.868(4)	C(15)-O(15)	1.124(4)

C(1)-C(2)	1.453(5)
C(2)-C(3)	1.324(5)
C(3)-C(4)	1.456(5)
C(4)-O(1)	1.189(5)
C(4)-O(2)	1.365(4)
O(2)-C(5)	1.410(5)

Table 5.2 Selected Bond Lengths (Å) for the η^1-Complex 223.

C(1) Mn C(11)		82.5(1)
C(1) Mn C(12)		88.5(1)
C(1) Mn C(13)		84.5(1)
C(1) Mn C(14)		175.2(1)
C(1) Mn C(15)		91.4(1)
C(1) C(2) C(3)		126.7(3)
C(2) C(3) C(4)		119.6(3)
C(3) C(4) O(1)		127.4(3)
C(3) C(4) O(2)		111.2(3)
O(2) C(4) O(2)		121.4(3)
C(4) O(2) C(5)		115.9(3)
C(11) Mn C(12)		90.5(2)
C(11) Mn C(13)		93.1(1)
C(11) Mn C(14)		173.8(1)
C(11) Mn C(15)		172.5(2)
C(12) Mn C(13)		93.5(2)
C(12) Mn C(14)		88.5(1)
C(12) Mn C(15)		93.7(2)
C(13) Mn C(14)		89.0(2)
C(13) Mn C(15)		93.7(2)
C(14) Mn C(15)		89.0(2)

Table 5.3 Selected Bond Angles for the η^1-Complex 223 (deg.).

Mn-C(1)	2.254(3)		
Mn-C(2)	2.137(4)		
Mn-C(3)	2.186(3)		

Mn-C(11)	1.893(5)	C(11)-O(11)	1.127(5)
Mn-C(12)	1.813(4)	C(12)-O(12)	1.144(5)
Mn-C(13)	1.816(4)	C(13)-O(13)	1.138(4)
Mn-C(14)	1.826(4)	C(14)-O(14)	1.135(5)

C(1)-C(2)	1.381(6)
C(2)-C(3)	1.412(5)
C(3)-C(4)	1.460(5)
C(4)-O(1)	1.198(5)
C(4)-O(2)	1.367(4)
O(2)-C(5)	1.409(5)

Table 5.4 Selected Bond Lengths (Å) for the η^3-Complex 225.

C(1) Mn C(3)	66.9(1)		C(2) Mn C(11)	103.9(2)
C(1) Mn C(11)	83.8(2)		C(2) Mn C(12)	123.4(2)
C(1) Mn C(12)	94.2(1)		C(2) Mn C(13)	131.5(2)

C(1) Mn C(13)	161.0(1)
C(1) Mn C(14)	101.9(2)

C(3) Mn C(11)	90.4(2)
C(3) Mn C(12)	160.8(2)
C(3) Mn C(13)	96.3(1)
C(3) Mn C(14)	94.0(2)
C(11) Mn C(12)	90.9(2)
C(11) Mn C(13)	87.6(2)
C(11) Mn C(14)	173.8(2)
C(12) Mn C(13)	102.9(2)
C(12) Mn C(14)	86.3(2)
C(13) Mn C(14)	87.6(2)
C(1) C(2) C(3)	122.5(4)
C(2) C(3) C(4)	118.6(3)
C(3) C(4) O(1)	126.4(3)
C(3) C(4) O(2)	111.2(3)
O(2) C(4) O(2)	122.3(3)
C(4) O(2) C(5)	116.8(3)

Table 5.5 Selected Bond Angles for the η^3-Complex 225 (deg.).

Mn-C(1)	2.152(4)
Mn-C(2)	2.097(4)
Mn-C(3)	2.160(4)
Mn-C(4)	2.369(4)
Mn-O(1)	2.159(3)

Mn-C(11)	1.751(5)	C(11)-O(11)	1.151(6)
Mn-C(12)	1.810(5)	C(12)-O(12)	1.138(6)
Mn-C(13)	1.824(5)	C(13)-O(13)	1.136(6)

C(1)-C(2)	1.400(7)
C(2)-C(3)	1.400(7)
C(3)-C(4)	1.441(7)
C(4)-O(1)	1.237(6)
C(4)-O(2)	1.352(6)
O(2)-C(5)	1.410(5)

Table 5.6 Selected Bond Lengths (Å) for the η^5-Complex 227.

C(1) Mn C(11)	87.1(2)		C(2) Mn C(11)	123.2(2)
C(1) Mn C(12)	167.3(2)		C(2) Mn C(12)	138.6(2)
C(1) Mn C(13)	102.0(2)		C(2) Mn C(13)	88.4(2)
C(3) Mn C(11)	154.9(2)		C(4) Mn C(11)	132.0(2)
C(3) Mn C(12)	102.9(2)		C(4) Mn C(12)	88.1(2)
C(3) Mn C(13)	103.9(2)		C(4) Mn C(13)	138.0(2)

O(1) Mn C(11)	100.9(2)
O(1) Mn C(12)	89.9(2)
O(1) Mn C(13)	169.3(2)
C(1) Mn C(3)	69.6(2)
C(11) Mn C(12)	89.8(2)
C(11) Mn C(13)	89.7(2)
C(12) Mn C(13)	98.2(2)
C(1) C(2) C(3)	122.9(4)
C(2) C(3) C(4)	120.8(4)
C(3) C(4) O(1)	122.2(4)
C(3) C(4) O(2)	114.8(4)
O(2) C(4) O(2)	122.8(4)
C(4) O(2) C(5)	118.7(3)

Table 5.7 Selected Bond Angles for the η^5-Complex 227 (deg.).

The structure of the η^1-complex is close to an ideal octahedral arrangement of the carbonyl and organic ligands (see Tables 5.2 and 5.3). There is a slight distortion of the equatorial carbonyl ligands towards the organic ligand as shown by the C(1)Mn-carbonyl angles (93-93.7° compared to the ideal 90°). The Mn-C(1) bond is comparable in length (2.214(3)Å) with the sum of the covalent radii of manganese[202] and carbon (2.23Å) and is only slightly longer than that determined[203] for MeMn(CO)$_5$ (2.185(11)Å).

In the η^3 and η^5-bonded complexes 225 and 227 the Mn(CO)$_4$ and Mn(CO)$_3$ fragments are quite distorted from ideal (see Tables 5.4-5.7). The structure of the complex 225 is similar to those reported for related complexes[200,204,205]. For the η^5-complex 227 C(1) is trans to C(13), C(3) is trans to C(12) and O(1) is trans to C(11) with these atoms forming a very distorted octahedron. The bond length of C(4)-O(1) is somewhat longer in the η^5-complex than that found for both the η^3 and η^1-bonded complexes.

The Reaction of the η^5-complex 227 with Triphenylphosphine

The possibility that η^5-pentadienyl complexes react with donor ligands, maintaining the syn geometry of the organic ligand has been shown by other workers[200] for η^5-pentadienyl manganese tricarbonyl.

In the present work the complex 227 was found to react with triphenylphosphine in a similar fashion. The reaction was extremely

facile, and gave high yields of the <u>syn-</u> η^3-complex <u>228</u>.

$$\text{(174)}$$
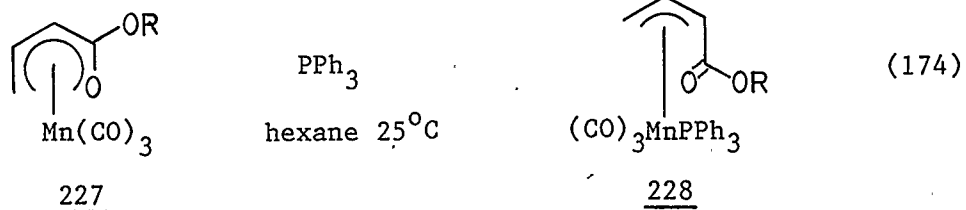
The assignment of <u>228</u> as the <u>syn-isomer</u> was based on coupling

constants in the ^{1}H-N.M.R. spectrum measured for this product

(J_{ac}=13Hz, J_{bc}=8.2Hz, J_{dc}=6.7Hz), although in this case proton-

phosphorous coupling made the assignment more complex.

EXPERIMENTAL

All procedures involving organometallic species were performed under an atmosphere of argon or nitrogen (purified by passing the gases through columns of silica gel and molecular seives). A combination of syringe, transfer needle and Schlenk techniques were used.[206,207]

Infra-red analysis was performed using a Perkin-Elmer 467 or a Nicolet 5DX FT instrument using 0.1mm path lengthm NaCl liquid cells. Mass spectrometric analyses were obtained on a Kratos MS80, and ^{1}H and ^{13}C-N.M.R. spectra on a Varian XL-200, with some [1]H-N.M.R. spectra on a Hitachi Perkin Elmer R21B. Gas chromatography analyses were performed on a Hewlett-Packard 5890 using either "530μ series" columns (10m carbowax 20M or methyl silicone capilary columns, "530μ series" is a trademark of Hewlett-Packard) or 2m x 2mm glass columns packed with either 3% OV17, or 3% OV1. Gas analysis was performed on a Carle gas chromatograph.

All m.p. and b.p. values are reported uncorrected. Flash chromatography was performed according to literature procedures[208,209], using 0.040 - 0.063mm silica gel (E. Merck 9385) and methylene chloride (distilled from P_2O_5) as eluent (unless otherwise noted).

THF was distilled from benzophenone ketyl under nitrogen. Deuterated solvents were dried over molecular sieve dust prior to use. The majority of compounds were available from commercial sources and were used without further purification, except ethyl 4-bromo-2-butenoate which was obtained as techical grade and distilled prior to use (spinning band), and where noted below.

Infra-red spectra are reported in the format wave numbers(intensity), using the following abbreviations for intensity: w-weak, m-medium, s-strong, vs-very strong, sh-shoulder.

[1]H-N.M.R. spectra are reported in the format: chemical-shift (multiplicty, coupling constant, integration ratio).

[55]Mn-N.M.R. Spectroscopy

This was performed on a Varian XL200. The chemical shifts are reported with respect to potassium permanganate in D_2O, and were calculated from the frequency of the signal for dimanganese decacarbonyl in THF, determined from the frequency offset to which the instrument was set. The majority of spectra were obtained without a lock.

Integration of signals was performed using manually set parameters. The values obtained were adjusted using calibration parameters determined for mixtures of organometallic species of known concentration.

The Reaction of $M^+[Mn(CO)_5^-]$ with Ethyl 4-halo-2-butenoate: [55]Mn-N.M.R. Spectroscopy of In-Situ Reactions

The anions $Na^+[Mn(CO)_5^-]$ and $K^+[Mn(CO)_5^-]$ were prepared according to literature procedures[68,70] from $Mn_2(CO)_{10}$ (ca. 0.25g) in THF (10mL) to give ca. 0.128 mole L^{-1} solutions, which were filtered prior to use. The salt $Li^+[Mn(CO)_5^-]$ was prepared by reduction of $Mn_2(CO)_{10}$ with lithium triethylborohydride[71] or lithium sand. The solutions were used without standardization, their purity being assessed by infra-red and [55]Mn-N.M.R. spectroscopies which indicated >98% conversion in all cases.

The solutions were transferred to a nitrogen purged graduate cylinder fitted with a rubber septum and known volumes (ca. 2mL) of the solution transferred by syringe into a 10mm N.M.R. tube containing a known amount of ethyl 4-bromo or 4-chloro-2-butenoate and rapidly shaken. Where the reaction was carried out in the presence of 18-crown-6 (Aldrich, used without purification) or hexamethylphosphoramide, these were added to the anion solution prior to the reaction.

Ethyl 4-chloro-2-butenoate[210] 54

Ethyl 2-butenoate (20g 0.175mole) was placed in a 100mL three necked round bottom flask and nitrogen was bubbled through it for 15 minutes. To this, 10g (0.092 mole) of t-butyl hypochlorite was added and the mixture irradiated with a sun-lamp (250W) for 8 hours. The reaction mixture was then distilled on a spinning-band column, and after considerable fore-run yielded 2g (15% yield) of ethyl 4-chloro-

2-butenoate which was pure by G.C. (2mm x 2m glass column containing 3% OV17) and [1]H-N.M.R spectroscopy. B.p. 70.0-70.2°C/7mm.

Infra-red (neat): 1725cm^{-1}.

[1]H-N.M.R. (CDCl$_3$): 1.25(t,J=7.0Hz,3H);

4.0(d,J=6.4Hz) and 4.12(q,J=6.9Hz) (4H);

5.92(d,J=13Hz,1H); 6.8(dt,J=6.4 and 14Hz, 1H).

This compound was also prepared by treatment of ethyl 4-bromo-2-butenoate with lithium chloride in dimethylformamide. In a 50mL Erlenmeyer flask 4g (0.09 mole) of anhydrous lithium chloride was stirred with 20mL of dimethylformamide for ten minutes. To this mixture, 2g (0.01 mole) of ethyl 4-bromo-2-butenoate was then added and the solution stirred for a further ten minues, and then 20mL of water added. The mixture was then extracted with 50mL of pentane, the extract washed with 2 x 100mL of water, dried with magnesium sufate and evaporated to give 1.3g of the title compound (88% yield). This was pure by G.C. and [1]H-N.M.R. spectroscopy and was used without further purfication.

The Preparation of PPN$^+$[Mn(CO)$_5$]$^-$[74,75] 44

In a 250mL side-arm flask, 2.0g (5.13 mmole) of dimanganese decacarbonyl was reduced with 6mL of 1% sodium amalgam in 40mL of THF for 25 minutes. The solution was then transferred rapidly via a long hollow needle to an argon purged 250mL round bottom flask (fitted with a septum) containing 6.0g (10.46 mmole) of PPN$^+$Cl$^-$ dissolved in the

minimum of methylene chloride. The reaction mixture was then stirred

for one hour and filtered through a filter tube fitted with a course

porosity frit. After washing the filter tube with 5mL of THF, 15mL of

decane was added to the filtrate and the flask attached to a vacuum.

Slow evaporation of the THF yields the product as bright yellow

crystals which were filtered, washed with 100mL of pentane and dried

under vacuum (0.1 mmHg) overnight. Yield 7.1g (94%). Infra-red (THF,

cm^{-1}): 1861 (s), 1894 (s).

The Reaction of $Na^+[Mn(CO)_5^-]$ with Ethyl 4-bromo-2-butenoate: Organic By-products

In a 10mL round bottom flask fitted with a rubber septum, 4mL of

$Na^+[Mn(CO)_5^-]$ solution (prepared from 0.96g of $Mn_2(CO)_{10}$ (0.245 mmole)

in 4mL of THF) was added with stirring to 0.96g (0.50 mmole) of ethyl

4-bromo-2-butenoate in 2mL of THF. The reaction mixture was then

stirred for 30 minutes after which the solvent removed at reduced

pressure and the residue then extracted with 2 x 5mL of pentane. The

extracts were combined and the solvent evaporated. The residue was

applied to a 1 x 15cm flash chromatography column and eluted with

methylene chloride. After initial bands of $Mn_2(CO)_{10}$ followed by

$Mn(CO)_5Br$ and a small quantity (0.001g) of the η^3-complex 222, the

η^1-complex 49 eluted as a broad pale yellow band (0.0492g). The

infra-red and ^{1}H-N.M.R. of the last fraction indicated that the sample

was pure (33% yield). Furthur elution of the column with diethyl

ether yielded 0.0135g of a colourless liquid, the G.C. of which (3%

OV17, 2mm x 2m glass column) indicated the presence of four organic

products.

The organic products could be more conveniently isolated from a larger scale reaction in which the ^{1}-complex <u>49</u> was converted to the less polar η^3-complex <u>222</u>. In this reaction 1g (5.18 mmole) of ethyl 4-bromo-2-butenoate was stirred with a solution of $Na^+[Mn(CO)_5^-]$ (prepared from 1g (2.56 mmole) of $Mn_2(CO)_{10}$ in 35mL of THF) for 30 minutes. The reaction mixture was then evaporated at reduced pressure to give a yellow oily residue which was heated to 80 - 100°C for 2 1/2 hours, at which point the evolution of carbon monoxide ceased. The liquid residue was then extracted with 3 x 6mL of pentane, filtered and flash-chromatographed to yield 0.23g $Mn_2(CO)_{10}$ (first yellow band) and 0.54g of the η^3-complex <u>222</u> (second yellow band). The column was then eluted with diethyl ether from which was obtained 0.096g of a pale yellow oil, the G.C. of which indicated that it contained the same organic products described above. Samples of these were isolated by G.C. (3% OV17, 4mm x 2m glass column) and identified as follows:

<u>Ethyl 2-(2-carboethoxycyclopropyl)-3-butenoate</u> <u>53</u> (43%):

^{1}H-N.M.R. (CDCl$_3$):

<u>Diastereomer A</u>

1.22 (t, J=7.1Hz,3H); 1.24 (t, J=7.0Hz, 3H);

2.58("t", J=8Hz, 1H) 4.13(q, J=7.0Hz, 2H);

4.18(q, J=7.0Hz, 2H); 5.1 and 5.2(dx2, J=16.4 and 11.2Hz, 2H);

5.85(m, 1H); 0.82(m, 2H); 1.63(m, 1H); 1.75(m, 1H).

Diastereomer B

1.24 (t, J=7.2Hz, 3H); 1.26(t, J=7.1Hz, 3H);

2.54 ("t", J=8Hz, 1H); 4.16(q, J=7.0Hz, 2H);

4.19(q, J=7.0Hz, 2H); 5.18 and 6.0 (dx2, J-16.8 and 10Hz, 2H);

5.88 (m, 1H); 0.92(m, 2H); 1.48 (m, 1H); 1.79 (m, 1H).

G.C.-Mass Spectrum (m/e, % base peak): 226(1,M^+), 181(22), 153(73),

125(24), 113(41), 107(48), 98(27), 97(31), 85(73), 81(97), 81(97),

80(70), 79(100), 78(39), 77(40), 67(82), 55(66).

Ethyl 6-carbethoxy-2,6-heptadienoate[81] 51 (21%):

^{1}H-N.M.R. (CDCl$_3$):   1.24(t, J=7.3Hz, 3H); 1.26 (t, J=7.2, 3H);

2.34-2.8(m, 2H); 3.17(dt, J=8.1 and 6.2Hz, 1H);

4.18(1, J=7.2Hz, 2H); 4.2(q, J=7.1Hz, 2H);

5.21(m, 2H); 5.72-5.96(m, 2H);

6.88(dt, J=10 and 15Hz, 1H).

G.C.-Mass Spectrum (m/e, % base peak): 226(3,M^+), 181(55), 180(68),

153(81), 152(78), 134(66), 125(69), 113(70), 108(35), 107(88),

106(73), 97(67), 85(97), 81(92), 80(79), 79(100), 78(76), 77(77),

69(35), 68(82), 67(79), 57(64), 55(61), 54(47), 53(67), 43(49),

41(78).

Ethyl 4-(2'-carboethoxycyclopropyl)-2-butenoate 52 (21%):

^{1}H-N.M.R. (CDCl$_3$): 1.25(t, J=6.9Hz, 3H); 1.28(t, J=7.1Hz, 3H);

2.2(m, 2H); 4.14(q, J=7.0Hz, 2H);

4.21(q, J=7.0Hz, 2H); 5.849(d, J=15.6Hz, 1H);

6.94 (dt, J-6.4 and 15.6Hz, 1H);

0.70-0.95(m, 2H); 1.45(m, <u>ca</u> 1H).

G.C.-Mass Spectrum (m.e, % base peak): 226(1,M[+]), 181(80), 153(45), 152(80), 135(29), 134(73), 125(37), 123(28), 107(79), 106(63), 98(66), 97(80), 85(55), 81(100), 80(47), 79(92), 78(79), 77(48), 68(65), 67(46), 66(27), 57(30), 55(90), 54(38), 53(65), 43(30), 41(50).

Ethyl 2,6-octadien-1,8-dioate[81] <u>50</u> (14%):

[1]H-N.M.R. (CDCl$_3$): 1.28(t, J=7.1Hz, 6H); 2.37("d", J=6.8Hz, 4H); 4.17(q, J=7.2Hz, 4H); 5.85 (d, J=15.5Hz, 2H); 6.96(dt, J=6.7 and 15.7Hz, 2H).

G.C.-Mass Spectrum (m/e, % base peak): 226(1,M[+]), 181(87), 153(56), 152(94), 135(30), 134(28), 125(42), 114(25), 113(25), 111(38), 107(80), 106(30), 97(28), 86(44), 85(100), 76(77), 75(30), 74(92), 73(54), 72(35), 69(25), 68(95), 67(48), 57(77), 55(68), 53(40), 43(28), 41(55).

4-Chloro-2-pentene[211] <u>55</u>

This was prepared from 3-penten-2-ol using phosphorus pentachloride and distilled. B.p. 92°C (lit.[212] 103°C).

[1]H-N.M.R. (CDCl$_3$): 1.45(d, J=7.0Hz, 3H); 1.55(d, J=7.0Hz, 3H); 4.35(m, 1H); 5.2-5.8(m, 2H).

4-Bromo-2-pentene[212] 57

This was prepared from 3-penten-2-ol using phosphorus tribromide and distilled. B.p. 26°C/15mm (lit.[213] 22°C/8mm).

^{1}H-N.M.R. (CDCl$_3$): 1.5("d", 6H); 4.5(m, 1H); 5.2-5.7(m, 2H).

{^{1}H}^{13}C-N.M.R. (CDCl$_3$): 18.0 (CH$_3$), 26.8 (CH$_3$), 50.9 (CH),

127.8 (CH), 134.9 (CH).

The Reaction of Na$^+$[Mn(CO)$_5^-$] with 4-Chloro-2-pentene

In a 10mm N.M.R.-tube, 2mL of Na$^+$[Mn(CO)$_5^-$] solution (prepared from 0.25g Mn$_2$(CO)$_{10}$ in 10mL of THF) was added to 0.03g (0.29mmole) of 3-chloro-2-pentene and the solution allowed to stand for 3 days. Large, clear yellow crystals formed after this time, which were filtered from the solution, washed with THF and identified[73] as Hg^{2+}[Mn(CO)$_5^-$]$_2$. Yield 4.5mg, 6%.

Infra-red (KBr): 1880 (m, broad)

Mass-spectrum (m/e, %base peak): 399(3), 397(13), 396(7), 395(10), 394(8), 393(4), 313(4), 311(14), 310(7), 309(11), 308(9), 307(4), 249(65), 221(70), 204(15), 202(60), 201(30), 200(55), 199(40), 198(18) 165(43), 139(20), 109(70), 83(40), 55(100)

Elemental analysis, calculated for HgMn$_2$C$_{10}$O$_{10}$

C, 20.34%; H, 0.00%. Found: C, 20.32%; H, 0.00%

3-Bromo-1,3-diphenyl-1-propene 59

This was prepared from the corresponding alcohol using phosphorus

tribromide and recrystallized from hexane. M.p.49-50°C.

^{1}H-N.M.R. (CDCl$_3$): 5.7("d", 1H); 6.5(m, 1H); 7.0-7.5(m, 11H).

$\{^1H\}^{13}$C-N.M.R. (CDCl$_3$): 55.4, 126.8, 127.6, 128.4, 128.7, 129.3,

132.1.

1,3,4,5-Tetraphenyl-1,5-hexadiene[213] 60

In a 50mL round bottom flask, 5mL of Na$^+$[Mn(CO)$_5$$^-$] solution
(prepared from 0.1g Mn$_2$(CO)$_{10}$, 0.13mmole, in 5mL of THF) was added by
syringe to 0.065g (0.24mmole) of 3-bromo-1,3-diphenyl-1-propene, and
the mixture stirred for 30 minutes. The solvent was then removed at
reduced pressure, and the yellow solid residue sublimed (30°C/0.2mm).
The sublimate was identified as Mn$_2$(CO)$_{10}$ (^{55}Mn-N.M.R. spectroscopy
and infra-red analysis). The residue was extracted with 20mL of
hexane, filtered and cooled to ca. 0°C and gave 0.043g of a
microcrystalline solid identified[213] as mixture of diasteriomers 60,
m.p. 108-112°C. (92%yield). The mass spectrum of this material
contained a peak at m/e 193.

^{1}H-N.M.R. of the mixture (CDCl$_3$, 60MHz): 3.7(broad s, 2H);

6.0 and 6.2 (broad singlets, 4H);

6.5-7.2 (m, 20H).

$\{^1H\}^{13}$C-N.M.R. (CDCl$_3$): 55.2 and 55.3, 126.1, 126.2, 126.5, 126.9,

127.0, 128.2, 128.4, 128.6, 131.1 and 131.4,

131.9 and 132.1.

One of the diasteriomers could be isolated pure by furthur recrystallization from hexane, 10mg of fine white needles were obtained in this way, m.p. 121-2°C.

^{1}H-N.M.R. (CDCl$_3$,200MHz): 3.9 ("d", 2H); 6.05-6.6(m, 2H); 7.0-7.5(m, 20H).

The Reaction of Na$^+$[Mn(CO)$_5$$^-$] and PPN$^+$[Mn(CO)$_5$$^-$] with 2-Haloesters

^{55}Mn-N.M.R. Spectroscopy of In-Situ Reactions.

These reactions were carried out in a similar fashion to the reaction of ethyl 4-halo-2-butenoate described earlier. In a typical reaction 0.15-0.19g (0.20-0.26 mmole) of PPN$^+$[Mn(CO)$_5$$^-$] was dissolved in 2mL of THF or deuterochloroform and rapidly transferred to a 10mm N.M.R. tube containing a known amount of a 2-haloester. The ^{55}Mn-N.M.R. spectrum of the solution was then measured.

Ethyl 2-chloro-2-methylpropanoate 65

In a 50mL conical flask 15mL of dimethylformamide was added to 3g (0.07 mole) of anhydrous lithium chloride and the mixture stirred for ten minutes. To this was added 2g(0.01 mole) of ethyl 2-bromo-2-methylpropanoate and the mixture stirred for two weeks. After this time 40mL of water was added, and the solution extracted with 50mL of pentane, the extract washed with 2x100mL of water, dried with magnesium sulfate and evaporated to give 1.4g of the title compound as

a colourless liquid which was pure by G.C. (3% OV101, 2mm x 2m glass column) and ^{1}H-N.M.R. spectroscopy (93% yield).

Infra-red (neat, cm^{-1}): 1742, 1280, 1176, 1120, 1024.

^{1}H-N.M.R. (CDCl$_3$): 1.30(t, J=7.0Hz, 3H); 1.75(s, 6H);

4.20(q, J=7.0Hz, 2H).

Preparation of Ethyl 2-Iodoethanoate 69

To a saturated solution of 18.0g (0.12 mole) of anhydrous sodium iodide in acetone, cooled to 0°C, 10g (0.06 mole) of ethyl 2-bromo-ethanoate was added dropwise with stirring. The solution was allowed to warm to room temperature and stirred for twenty minutes, by which time G.C. analysis (10m methyl silicone column) indicated complete conversion had taken place. The solvent was removed and the solid residue extracted with 2x50mL of hexane and the combined extracts filtered and evaporated to yield 11.1g (86% yield) of colourless liquid. G.C. analysis and 200 MHz N.M.R. spectroscopy indicated the product was better than 95% pure, although the product darkened on storage.

Infra-red (neat, cm^{-1}): 1736, 1265, 1096, 1026.

^{1}H-N.M.R. (CDCl$_3$): 1.28(t, 3H, J=7.1Hz); 3.68(s, 2H);

4.20(q, 2H, J=7.0Hz).

[H^1-N.M.R. of the corresponding methyl ester[214]: 3.63(s, 2H)]

Preparation of Ethyl 2-Iodo-2-methylethanoate 70

This was prepared in a similar fashion to ethyl 2-iodoethanoate

described above, and was obtained in 91% yield as a pale yellow oil.

This material decomposed on attempted distillation, however G.C.

analysis (10m methyl silicone column) and 200 MHz ^{1}H-N.M.R.

spectroscopy indicated that it was >95% pure.

Infra-red (neat, cm^{-1}): 1734, 1447, 1370, 1330, 1256, 1208, 1134,

1058, 1021.

^{1}H-N.M.R. (CDCl$_3$): 1.29(t, J=7.1Hz, 3H); 1.95(d, 7.0Hz, 3H);

4.19(q, J=7.1Hz, 2H);

4.36(q, J=7.0Hz, 1H).

[H^1-N.M.R. of the corresponding methyl ester[214]: 1.93(d,J=6.8Hz)

4.43(q)]

Preparation of Ethyl 2-Iodo-2,2-dimethylethanoate 71

To a saturated solution of 11.7g (0.078 mole) of anhydrous sodium

iodide in acetone, 5g (0.026 mole) of ethyl 2-bromo-2,2-

dimethylethanoate was added and the solution refluxed overnight.

After the reaction mixture was evaporated the resulting black oily

residue was extracted with 3x25ml hexane and the combined extracts

filtered and evaporated to give 1.1g pale brown oil (18% yield).

After trap to trap distillation the product was determined to be >90%

pure by 200MHz ^{1}H-N.M.R. spectroscopy and G.C. analysis (10m methyl

silicone column).

Infra-red (neat, cm^{-1}): 1732, 1462, 1212, 1159, 1103, 1026

^{1}H-N.M.R. (CDCl$_3$): 1.31(t, J=7.1Hz, 3H); 2.08(s, 6H);

4.22(t, J=7.1Hz, 2H).

[H^1-N.M.R. of the corresponding methyl ester[214]: 2.05(s)]

<u>The Reaction of Ethyl 2-bromo-2-methylpropanoate with $PPN^+[Mn(CO)_5^-]$</u>

<u>in THF</u>

In a 10mm N.M.R. tube 0.11g, (0.15 mmole) of $PPN^+[Mn(CO)_5^-]$ was added to 0.05g (0.26 mmole) of ethyl 2-bromo-2-methylpropanoate in 3mL of THF , and the mixture shaken. The mixture was then allowed to stand for five hours. G.C.- analysis of the crude reaction mixture indicated that <u>74,75,76</u> and <u>77</u> were formed in the reaction. These were identified from the G.C.-mass spectrum obtained for a distillate (trap to trap, <u>ca.</u> 0.1mmHg) from the reaction mixture (c.f. the photolysis of ethyl 2-bromo-2-methylpropanoate with $Mn_2(CO)_{10}$). The residue from this distillation was dissolved in 4mL of THF, filtered and pentane slowly added to the filtrate. Oily material formed which was separated by decantation, washed with pentane. This oil solidified to a resinous material (0.04g) which could not be crystallized. The infra-red of this oil contained bands (in THF) at 2081(w), 2007(s), 1973(s), 1925(s) and 1907(sh) which probably correspond to $PPN^+[Mn(CO)_4Br_2^-]$.

<u>Ethyl 2-methylpropanoate 74</u>

G.C.-M.S. (m/e, % base peak): 116(50); 89(51); 88(55); 73(55);

71(70); 43(100).

<u>Ethyl 2-methyl-2-propanoate 75</u>

G.C.-M.S. (m/e, % base peak): 114(52); 99(55); 86(68); 70(60);

69(100); 41(90).

Diethyl 2,2,3,3-tetramethylsuccinate 76

G.C.-M.S. (m/e, % base peak): 185(40), 157(46), 116(100), 88(90),

87(99), 85(90), 69(72), 59(62), 43(80),

41(95).

Diethyl 2,2-dimethyl-4-methylenepentadioate 77

G.C.-M.S. (m/e, % base peak): 288(10), 155(85), 154(70), 127(40),

109(98), 81(100), 69(40), 59(50),

43(50), 41(99).

Ethyl 2-(manganese pentacarbonyl) ethanoate 72

In a 10mL Schlenk flask, $Na^+[Mn(CO)_5^-]$ solution (prepared from

0.1g (0.26 mmole) of dimanganese decacarbonyl in 4mL of THF) was added

to 0.063g (0.51 mmole) of ethyl 2-chloroethanoate rapidly with

stirring. The reaction mixture was stirred for a further ten minutes,

evaporated under reduced pressure and the residue extracted with

pentane. The extract was filtered and concentrated and flash

chromatography (silica/methylene chloride) yielded 0.089g of the title

compound (62% yield) as an air sensitive pale yellow oil.

Infra-red (chloroform, cm^{-1}): 2120(m), 2046(2), 2025(s), 1968(w),

1686(w).

[I.R. of the corresponding methyl ester, in hexane: 2215(m),2055(m),

2018(vs),1944(s), 1655(s)][43]

H^1-N.M.R. $(CDCl_3)$: 1.20(t, J=7.0Hz, 3H); 1.45(s, 2H);

4.13(q, J=7.1Hz, 2H).

[^{1}H-N.M.R.of the corresponding methyl ester: 1.24ppm][43]

Ethyl 2-(manganese pentacarbonyl)propanoate[48]73

In a 10mL Schlenk flask, Na$^+$[Mn(CO)$_5$$^-$] solution (prepared from 0.1g (0.26 mmole) of dimanganese decacarbonyl in 4mL of THF) was added to 0.093g (0.51 mmole) of ethyl 2-bromopropanoate. The reaction mixture was stirred for a further ten minutes, evaporated under reduced presure and the residue extracted with pentane. The extract was filtered and concentrated and flash chromatography (silica/methylene chloride) yielded 0.058g dimanganese decacarbonyl (first band) and 0.070g of the title compound (46% yield, second band) as a colourless oil.

Infra-red (chloroform, cm^{-1}): 2117(m), 2057(w), 2023(s), 1999(w),

1686(m), 1178(m).

(lit.[48]: 2108(m), 2047(m),

2023(s), 1996(s), 1700(m))

^{1}H-N.M.R. (CDCl$_3$): 1.27 (t, J=6.8Hz, 3H); 1.58(d, J=6.7Hz, 3H);

2.32(q, J=6.9Hz, 1H); 4.15(q, J=6.9Hz, 2H).

The reaction of Ethyl 4-bromo-2-butenoate with Lithium 3-carboethoxypropenyl (-1).[82]

In a 250mL round bottom flask fitted with a rubber septum and magnetic stirring bar, 0.57g (5.0 mmole) of ethyl 2-butenoate in 70mL of THF was added to 5 mmole lithium diisopropylamide (prepared from diisopropylamine and n-butyllithium in 8mL of THF and 2mL of hexamethylphosphoramide) dropwise over twenty minutes maintaining the

reaction mixture at dry ice/acetone temperature. To this, 0.97g (5 mmole) of ethyl 4-bromo-2-butenoate in 20mL of THF was added (over ten minutes) and the reaction quenched in 250mL of water/ice. This mixture was extracted with 3x100mL of light petroleum ether, the extracts combined, washed with water, dried over magnesium sulfate and evaporated to give 0.8g pale yellow oil. G.C.-analysis of this product indicated that it contained unreacted ethyl 4-bromo-2-butenoate (15%) and ethyl 5-carboethoxy-2,5-hexadienoate 83 (70%). A pure sample of the diene 83 (as a single isomer) was obtained by preparative G.C. (3% OV17, 4mm x 2m glass column) and identified[82] from the [1]H-N.M.R. and mass-spectrum given below.

[1]H-N.M.R. (CDCl$_3$): 1.28 ("t", J=7.0Hz, 6H); 1.80(d, J=7.1Hz, 3H);

3.22(d, J=7.3Hz, 2H); 4.17(m, 4H);

5.80(d, J=15.6Hz, 1H); 5.80-7.10(m, 2H).

G.C.-Mass Spectrum (m/e, % base peak): 226(15,M[+]), 181(70), 180(90), 153(70), 152(75), 134(80), 123(80), 108(85), 107(95), 97(70), 81(90), 80(80), 79(100), 68(75), 67(71), 55(90), 54(80), 53(90).

The Photolysis of Dimanganese Decacarbonyl and Ethyl 4-bromo-2-butenoate.

In a Pyrex tube containing 8mL of THF 0.2g (0.51 mmole) of dimanganese decacarbonyl and 0.2g (1.04 mmole) of ethyl 4-bromo-2-butenoate were mixed. The tube was fitted with a rubber septum and magnetic stirring bar and placed in a water-cooled jacket and irradiated with a sun-lamp (G.E. 250W) for 4 1/2, hours by which time

G.C.-analysis indicated all the ethyl 4-bromo-2-butenoate had been consumed. The infra-red spectrum of the crude reaction mixture consisted of bands corresponding to $Mn(CO)_5Br$ (2138w, 2052s and 2010s cm^{-1}) and weaker overlapping bands at 2103 and 1964cm^{-1}, which probably correspond to $Mn_2(CO)_8Br_2$. A considerable amount of an insoluble white solid had formed. After removing the THF solvent, the residue which was left was extracted with 3x20mL of pentane, the extracts combined, filtered and evaporated to give 0.08g yellow oil from which flash chromatography (silica/methylene chloride) yielded 0.07g colourless oil after extended elution. The G.C. (10m methyl silicone column) and ^{1}H-N.M.R. spectrum of this fraction indicated that it contained ethyl 5-carboethoxy-2,6-heptadienoate 51 (64%) and ethyl 2,6-octadien-1,8-dioate 50 (36%).

The Photolysis of Ethyl 2-bromoethanoate with Dimanganese Decacarbonyl in Deuterochloroform

In a 1.0cm x 10cm Pyrex test tube, 0.1g(0.26 mmole) of dimanganese decacarbonyl, and 0.081 (0.49 mmole) of ethyl 2-bromoethanoate in 3mL of deuterochloroform (degassed by bubbling nitrogen through it) were irradiated with a sun-lamp (G.E. 250W) for three hours. By this time T.L.C. indicated no dimanganese decacarbonyl remained, the solution was essentially colourless and a white insoluble solid had formed. The solution was filtered and the products determined by ^{1}H-N.M.R. spectroscopy of the crude solution. A singlet at 2.63 ppm was assigned to diethyl succinate (50% yield) and this was confirmed by G.C. analysis (3% OV1, 2mm x 2m glass

column) and comparison with authentic material. Unreacted ethyl 2-bromoethanoate was also present (29%). A singlet at 2.06 ppm was assigned to ethyl ethanoate (11%). One resonance in the [1]H-N.M.R. spectrum (singlet, 3.28 ppm, 8% of the total integration as $-CH_2-$ protons) remained unidentified.

The Photolysis of Ethyl 2-bromopropanoate with Dimanganese Decacarbonyl in Deuterochloroform

This photolysis was carried out in the same way as that described above for ethyl 2-bromoethanoate using 0.1g (0.26 mmole) of dimanganese decacarbonyl and 0.09g (0.50 mmole) of ethyl 2-bromopropanoate.

The [1]H-N.M.R. spectrum of the crude reaction mixture contained resonances which were assigned to diethyl 2,3-dimethylsuccinate (m, 2.75 ppm, 47%), unreacted ethyl 2-bromopropanoate (21%) and ethyl propanoate (q, 2.32 ppm, 21%). The assignments were confirmed by comparison with authentic materials (G.C. and [1]H-N.M.R. analysis).

The Photolysis of Ethyl 2-bromo-2-methylpropanoate with Dimanganese Decacarbonyl in Deuterochloroform and THF

In a 1x10cm Pyrex test tube, 0.05g (0.13 mmole) of dimanganese decacarbonyl, and 0.05g (0.13 mmole) of ethyl 2-bromo-2-methylpropanoate in 3 mL of freshly distilled THF were irradiated for thirty minutes with a sun-lamp (250W). The solvent was then removed under reduced pressure and the oily residue extracted with hexane, filtered and evaporated (0.13g). G.C. analysis indicated that the

extract contained six components, including some unreacted starting
material (8% by G.C.), ethyl 2-methylpropanoate 74 (17%) and ethyl 2-
methyl-2-propanoate 75 (12%). These were identified by G.C.-mass
spectrometry. The other products formed in this reaction could be
isolated by G.C. (3% OV17, 2m x 4mm glass column) and were identified
as diethyl 2,2,3,3-tetramethyl succinate 76 (45%), diethyl 2,2-
dimethyl-4-methylene-penta-1,5-dioate 77 (5%) and tentatively assigned
diethyl 3-carboethoxy-2,2,3,5,5-pentamethylhexa-1,6-dioate 89 (13%).
These compounds were identified by ^{1}H-N.M.R. spectroscopy and G.C.-
mass spectrometry.

Ethyl 2-methylpropanoate 74

G.C.-mass spectrum (m/e, % base peak): 116(10), 89(7), 88(8), 71(40),
56(6), 55(5), 43(100), 41(45).

Ethyl 2-methyl-2-propanoate 75

G.C.-mass spectrum (m/e, % base peak): 114(13), 99(18), 86(32),
69(100), 58(10), 41(95).

Diethyl 2,2,3,3,-tetramethylsuccinate[108] 76

^{1}H-N.M.R. (CDCl$_3$): 1.23(s, 12H); 1.26(t, J=7.1Hz, 6H);
4.10(q, J=7.1Hz, 4H).

G.C.-Mass Spectrum (m/e, % base peak): 185(50), 157(51), 116(97),
88(90), 87(100), 84(55), 83(90), 70(50), 69(85), 59(77), 57(45),
55(60), 43(90), 42(47), 41(95).

Diethyl 2,2-dimethyl-4-methylenepenta-1,5-dioate <u>77</u>.

^{1}H-N.M.R. (CDCl$_3$): 1.18(s, 6H);

1.264 and 1.31 (tx2, J=7.1, 7.1Hz, 6H);

2.64(s, 2H); 4.11(q, J=7.1Hz, 2H);

4.2(q, J=7.1, 2H); 5.53("s", 1H);

6.22(d, J=1.6Hz, 1H).

G.C.-Mass Spectrum (m/e, % base peak): 228(4), 155(59), 154(50),

127(25), 109(87), 81(100), 68(30), 67(32), 59(37), 43(45), 41(94).

Diethyl 3-carbethoxy-2,2,3,5,5-pentamethylhexa-1,6-dioate <u>89</u>

^{1}H-N.M.R.(CDCl$_3$): 1.05(s, 6H); 1.18(s, 3H); 1.21(s, 3H);

1.26v (t J=7.0Hz, 3H); 1.27(s, 3H);

1.29(t, J=7.0Hz, 3H);

2.13 and 2.58 ("doublets", J=14.5Hz, 2H);

4.11(m, 6H).

G.C. Mass-Spectrum (m/e, % base peak): 298(32), 270(40), 268(55),

229(30), 206(42), 183(40), 155(35), 116(100), 88(33), 70(28), 88(32),

59(30), 55(38), 43(60), 41(82).

A similar pattern of products was observed when the photolysis was

carried out in deuterochloroform (G.C.-mass spectrum) although the

products were not isolated in this case.

The Reaction of Na$^+$[Mn(CO)$_5$$^-$] with 2-Bromopropanoyl Chloride in

THF

In a 20mL Schlenk flask, 0.1g (0.26 mmole) of dimanganese

decacarbonyl was reduced with 1% Na(Hg) in 5mL of THF and transferred via a filter tube to a 100mL three necked round bottom flask. The flask was fitted with a septum and a side-arm trap, and evacuated to remove most of the THF to give a slurry of $Na^+[Mn(CO)_5^-]$, and then the stopcock to the vacuum source was closed. The side-arm trap was immersed partially in liquid nitrogen and 0.09g (0.52 mmole) of 2-bromopropanoyl chloride in 2mL of THF slowly transferred by syringed into the flask. Throughout the addition the solvent distilled into the trap, aided by immersing the flask in a bath of water ($20^\circ C$). The addition took five minutes. When the addition was complete the remaining THF was allowed to distill into the trap and the trap was then removed and sealed. A sample of the green solution was rapidly transferred to an I.R.-cell and the I.R. spectrum was rapidly measured. A strong peak at $2117cm^{-1}$ corresponding to 1-propen-1-one was observed which rapidly disappeared at room temperature (ca. 5 minutes), and new bands at 1789, 1767, 1740 and $1662cm^{-1}$ appeared. On standing overnight at room temperature the solution became pale yellow in colour and after the solvent was removed 30mg of pale yellow oil was collected. The G.C. analysis of this oil (3% OV17, 2mm x 2m glass column) indicated one major product (80%) identified as 2,4-dimethyl-3-oxocyclobut-1-enyl propionate 113 (literature I.R.: 1790, 1765 and $1665cm^{-1}$)[130]. This component could be isolated by G.C. and the mass-spectrum and [1]H-N.M.R. spectrum are described below. The latter is similar to the reported spectrum[130].

^{1}H-N.M.R., (CDCl$_3$):   1.20(d, J=7.0Hz, 3H);

1.23(t,J=7.4Hz, 3H); 1.61(d,J=2.0Hz, 3H);

2.58(q, J=7.6Hz,2H); 3.75(m, 1H).

Mass Spectrum (m/e, % base peak): 168(M$^+$, 20), 140(15), 112(95), (85), 83(85), 69(45), 67(50), 57(100), (56), 55(90).

The residue from this reaction was dissolved in 10 mL of methylene chloride and 4mL of hexane added and slowly evaporated. Orange crystals of manganese pentacarbonyl bromide (0.13g, 92% yield) were isolated giving an I.R.-spectrum identical to that of authentic material.

3-Bromopropanoyl Manganese Pentacarbonyl 122

Dimanganese decacarbonyl (0.20g, 0.51 mmole) was reduced with 1% sodium amalgam in 10 mL of THF. The solution was transferred by syringe to 0.18g of 3-bromopropanoyl chloride (1.05 mmole) in 2 mL of THF and stirred for thirty minutes at room temperature, by which time a white precipitate had formed in the yellow solution. The solvent was then removed at reduced pressure and the oily residue extracted with two 10 mL aliquots of hexane, filtered and the volume of the combined extracts reduced to ca. 10 mL. The product crystallized upon cooling to 0°C and after filtering and washing with cold hexane yielded 0.19 g white needles (57% yield), m.p. 57-59°C.

Infra-red (hexane, cm^{-1}):   2117(m), 2055(m), 2016(s), 1648(m).

^{1}H-N.M.R., (CDCl$_3$): 3.45 ppm (m, -CH$_2$CH$_2$-).

$\{^1H\}^{13}C$-N.M.R., (CDCl$_3$): 25.8 ppm (-CH$_2$CO), 67.5 ppm (-CH$_2$Br)

144 ppm (CO).

^{55}Mn-N.M.R., (THF): -1830 ppm, W$_{1/2}$=6100 Hz.

Elemental analysis, calculated for C$_8$H$_4$BrMnO$_6$

C, 29.03%; H, 1.22%. Found: C, 27.58%; H, 1.41%

(The elemental analysis of this compound was not improved by repeted

recrystallization.)

4-Bromobutanoyl Manganese Pentacarbonyl 123

This complex was prepared in a similar way to that of 3-
bromopropanoyl manganese pentacarbonyl. Thin layer chromatography
indicated that the yellow solid isolated was contaminated with
manganese pentacarbonyl bromide. Flash chromatography (methylene
chloride/silica) of the crude material, followed by recrystallization
from hexane gave pale yellow needles in 19% yield, m.p. 55-6°C.

Infra-red (methylene chloride, cm^{-1}): 2117(m), 2052(m), 2013(s),

1638(m).

^{1}H-N.M.R., (CDCl$_3$): 2.01 (dt, 2H); 3.12 (t, J=6.7Hz, 2H);

3.39 (t, J=6.3Hz, 2H).

^{55}Mn-N.M.R., (THF): -1874 ppm, W$_{1/2}$=7250 Hz.

·Elemental analysis, calculated for C$_9$H$_6$BrMnO$_6$

C, 31.33%; H, 1.75%. Found: C, 31.45%; H, 1.81%

5-Bromopentanoyl Manganese Pentacarbonyl 124

The procedure followed for the preparation of this compound was

the same as that described for 3-bromopropanoyl manganese

pentacarbonyl. White needles were isolated in 71% yield,

m.p. 52-55°C.

Infra-red (hexane, cm^{-1}): 2115(m), 2052(m), 2009(s), 1659(m).

^{1}H-N.M.R., (CDCl$_3$,): 1.5-1.9 (m, 4H); 2.96 (t, J = 6.7Hz, 2H);

3.35 (t, J = 6.6 Hz, 2H).

{^{1}H}^{13}C-N.M.R., (CDCl$_3$): 23.2 (-CH$_2$CO), 31.9 (-CH$_2$-), 33.2 (-CH$_2$-),

65.9 (-CH$_2$Br), 143.9 (CO).

^{55}Mn-N.M.R., (THF):   -1880 ppm, W$_{1/2}$=7300 Hz

Elemental analysis, calculated for C$_{10}$H$_8$BrMnO$_6$

C, 33.45%; H, 2.25%. Found: C, 32.47%; H, 2.29%

(The elemental analysis of this compound was not improved by repeted

recrystallization.)

The In-Situ Thermal Decomposition of Bromoalkanoyl Manganese

Pentacarbonyl Complexes 122, 123 and 124

3-Bromo propanoyl chloride 119, 4-bromo butanoyl chloride 120 and

5-bromo pentanoyl chloride 121, were placed (0.22mmole) in individual

10mm N.M.R. tubes. Two mL of a THF solution of sodium pentacarbonyl

manganate (0.105 M) was then introduced into each tube by syringe.

The tubes were occasionally shaken over a period of half an hour and

the ^{55}Mn-N.M.R. spectrum measured. Signals were observed at -1842 ppm

-1874 ppm, and -1888 ppm respectively. All three solutions contained

4% dimanganese decacarbonyl. The tubes were then placed in a water

bath at 50°C for one hour.

The Thermal Decomposition of 3-Bromopropanoyl

Manganese Pentacarbonyl 122

In 5 mm N.M.R. tubes, 20 mg (0.06 mmole) of 3-bromo propanoyl manganese pentacarbonyl 122 was dissolved in 0.5 mL of deuterochloroform or 0.5 mL of THF d_8. The solutions were degassed by several freeze-thaw cycles and sealed under vacuum (0.1 mmHg.) and then placed in an oil bath at 75°C. The decomposition was followed by [1]H-N.M.R. (200 MHz.), the tubes being inverted and centrifuged prior to running the spectrum. When the decomposition was complete, the samples were opened while connected to a manifold, and the released gases analysed by G.C.

The Thermal Decomposition of 4-Bromobutanoyl Manganese

Pentacarbonyl and 5-Bromopentanoyl Manganese Pentacarbonyl

This was carried out in a similar fashion to the experiment described above for 3-bromopropanoyl manganese pentacarbonyl. In these cases, 5 mg (0.01 mmole) of freshly recrystallized 4-bromobutanoyl manganese pentacarbonyl and 25 mg (0.07 mmole) of 5-bromopentanoyl manganese pentacarbonyl were used. The solutions were first heated to 75°C, and then 120°C until no further reaction took place.

Ketene Synthesis

The apparatus used to prepare the ketenes described in this thesis is shown in Figure 6.1. This consists of a modified Schlenk flask to which was attached either a simple glass tube or a 5mm N.M.R. tube using a teflon adaptor, as a receiver for ketene distillations.
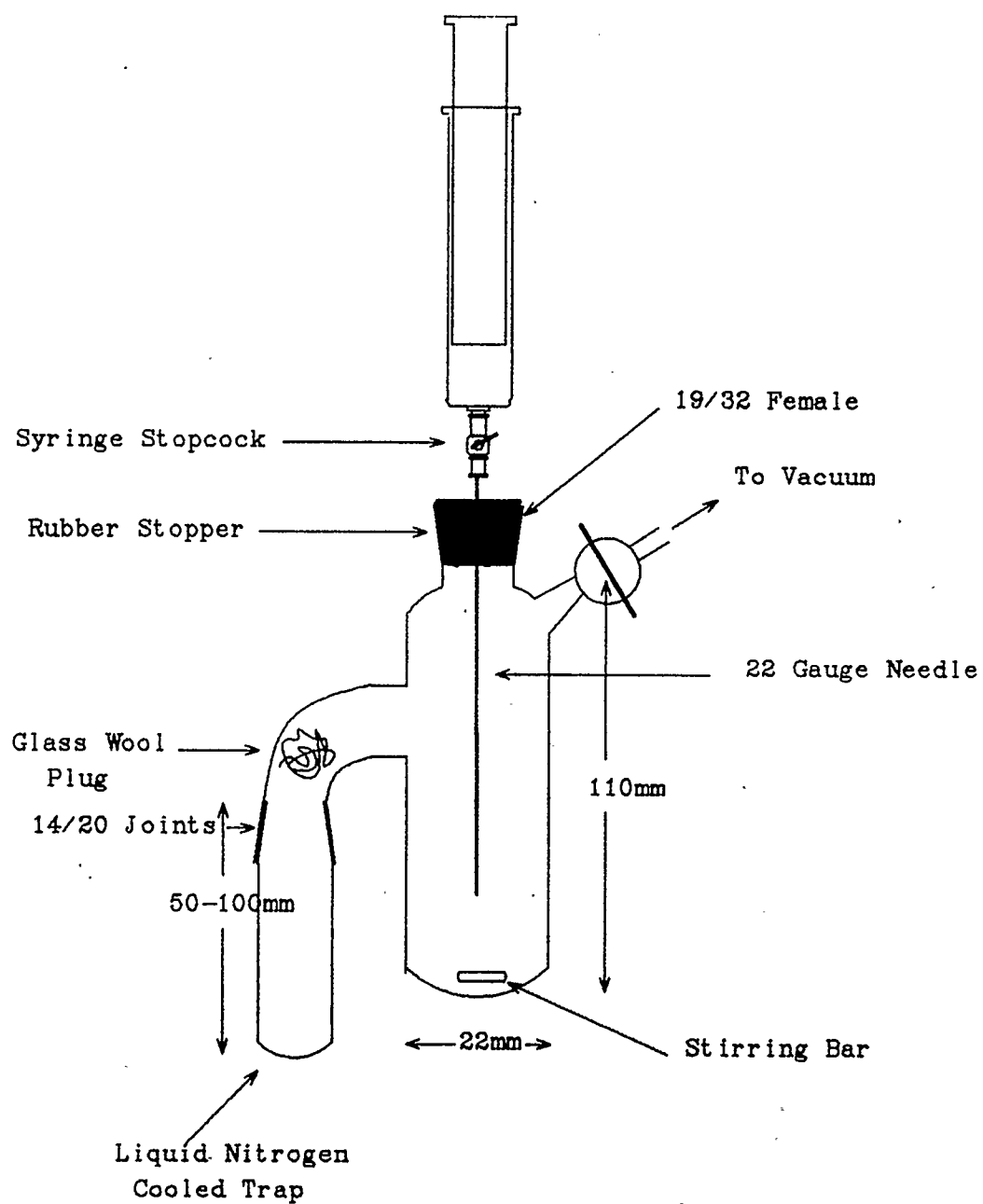
Figure 6.1 Diagram of the Apparatus used to Prepare Ketenes

Solutions were introduced into the flask via a syringe fitted with a
brass syringe stopcock (Aldrich) attached with standard luer lock
fittings.

Ethenone 115

The ketene apparatus was fitted with a 5mm N.M.R. tube containing
0.0369g p-dichlorobenzene and charged with 0.15g (0.205 mmole) of
$PPN^+[Mn(CO)_5^-]$ and the system was purged with nitrogen. To this was
added 0.6mL of deuterochloroform and the solution cooled with liquid
nitrogen and the system evacuated. To this, 0.03g (0.206 mmole) of 2-
bromoethanoyl chloride in 0.5mL of deuterochloroform was added slowly
by syringe, layering the solution on the $PPN^+[Mn(CO)_5^-]$ while
maintaining the solution at liquid nitrogen temperature. The system
was evacuated to ca. 0.1mmHg and the solutions allowed to warm to $0^{\circ}C$.
At this point the N.M.R. tube attached to the side-arm was partially
immersed in liquid nitrogen and the colourless solvent/ketene mixture
distilled over. The 5mm N.M.R. tube was then flame-sealed and the low
temperature $(-50^{\circ}C)$ 200MHz ^1H-N.M.R. spectrum was measured. The yield
of ethenone, determined by integration of the ^1H-N.M.R. spectrum with
respect to p-dichlorobenzene internal standard, was 95%. ^1H-
N.M.R.,$(CDCl_3,-50^{\circ}C)$: 2.46(s,2H).

2-Methyl-1-propen-1-one 159

In the apparatus was placed 0.15g (0.205 mmole) of $PPN^+[Mn(CO)_5^-]$
and 0.3mL of deuterochloroform and the solution cooled with liquid
nitrogen and the system evacuated to 0.1mmHg. To this, 0.035g (0.19

mmole) of 2-bromo-2-methylpropanoyl chloride in 0.3mL of deuterochloroform was added via syringe and the mixture allowed to warm to ca. 0°C. After stirring for 10 minutes, the solvent/ketene mixture (a colourless solution) was distilled into a 5mm N.M.R. tube by cooling the tube with liquid nitrogen. The tube was then flame-sealed and the ^{1}H-N.M.R. spectrum measured. The yield of the title ketene, determined by integration of the ^{1}H-N.M.R. spectrum with respect to p-dichlorobenzene internal standard, was 105%. In a similar experiment using 0.15g (0.205 mmole) of PPN$^+$[Mn(CO)$_5^-$] and 0.0429g (0.186 mmole) of 2-bromo-2-methylpropanoyl bromide and using p-dibromobenzene as an internal standard, the yield was 93%.

^{1}H-N.M.R., (CDCl$_3$): 1.58 (s, 6H).

On standing at room temperature this product dimerized to 2,2,4,4-tetramethylcyclobuta-1,3-dione (^{1}H-N.M.R., 1.26 ppm, singlet).[166]

1-Propen-1-one 118

In the apparatus was placed 0.152g (0.207 mmole) of PPN$^+$[Mn(CO)$_5^-$] and 0.5mL of deuterochloroform. The solution was then cooled with liquid nitrogen and the system evacuated to 0.1mmHg and then allowed to warm to ca. 0°C. At this point the side-arm trap was immersed partially in liquid nitrogen and addition via syringe of 0.0301g (0.176 mmole) of 2-bromopropanoyl chloride in 0.5mL of deuterochloroform commenced. The addition was made in increments over

a two minute period, maintaining steady distillation of the pale green ketene/solvent until the reaction mixture was dry. The ketene solution was then quickly transferred to a 5mm N.M.R. tube containing p-dibromobenzene as an integration standard. The solution was maintained at dry ice/acetone temperature and the low temperature (-20 - -40°C) ^{1}H-N.M.R. spectrum was measured. The yield of the title compound was 91%. The use of slightly more solvent (a total of 1.5mL of deuterochloroform) gave a yield of 84%.

^{1}H-N.M.R., (CDCl$_3$): 1.56(d, J=7.4Hz, 3H);

2.67(q, J=7.5Hz, 1H).

Infra-red (THF): 2117cm^{-1}.

1-Buten-1-one 164

This was prepared in the same way as 1-propen-1-one described above, In this case 0.1670g (0.28 mmole) of PPN$^+$[Mn(CO)$_5^-$] was reacted with 0.052g (0.224 mmole) of 2-bromobutanoyl bromide in a total of 1mL of deuterochloroform and the title compound was obtained in 80% yield (determined by ^{1}H-N.M.R. spectroscopy at -40°C).

^{1}H-N.M.R., (CDCl$_3$): 1.06(t, J=7.4Hz, 3H);

2.04 (dq, 2H); 2.80(t, J=6.9Hz, 1H).

3-Methyl-1-buten-1-one 167

This was prepared in the same way as 1-propen-1-one described above. In this case 0.10g (0.136 mmole) of PPN$^+$[Mn(CO)$_5^-$] was reacted

with 0.0316g (0.1295 mmole) of 2-bromo-3-methylbutanoyl bromide in a
total of 1mL of deuterochloroform, and the title compound was obtained
in 57% yield (determined by [1]H-N.M.R. spectroscopy at 20°C).

[1]H-N.M.R., (CDCl$_3$):   1.07(d, J=6.7Hz, 6H);

2.82(d, J=5.7Hz, 1H); 2.49(dq, J=6.6Hz, 1H).

3,3-Dimethyl-1-buten-1-one 169

This was prepared in the same way as 1-propen-1-one described
above. In this case 0.15g (0.205 mmole) of PPN$^+$[Mn(CO)$_5$$^-$] was reacted
with 0.050g (0.194 mmole) of 3,3-dimethylbutanoyl bromide in a total
of 1mL of deuterochloroform. The title compound was obtained in 75%
yield (determined by [1]H-N.M.R. spectroscopy at 20°C).

[1]H-N.M.R. (CDCl$_3$):   1.19(s, 9H); 2.81(s, 1H).

1,3-Butadien-1-one 170

In the ketene apparatus was placed 0.1995g (0.2614mmole) of
PPN$^+$[Mn(CO)$_5$$^-$] dissolved in 0.2mL of deuterochloroform. The system was
slowly evacuated to 0.1mm to remove most of the solvent. 4-Bromo-2-
butenoyl chloride, 0.0246g (0.1338mmole) dissolved in 0.75mL of
deuterochloroform was introduced onto the stirred PPN$^+$ salt in four
ca. equal amounts over a period of 45 seconds. After each addition,
the liquid nitrogen was moved up several centimeters on the receiver
to expose a fresh cold surface and cause rapid distillation of the
solvent-ketene solution. After the addition was complete, the

distillation was continued for two minutes. The title compound was

obtained in 35% yield (determined by [1]H-N.M.R. spectroscopy at -40°C).

[1]H-N.M.R., (CDCl$_3$, -40°C): 4.09(d, J=10Hz, 1H); 4.66(d, J=11Hz, 1H);

4.95(d, J=18Hz, 1H);

6.06(d of d of d, 1H).

2-Methyl-1,3-butadien-1-one 172

This ketene was prepared in a similar fashion to 2-methyl-1-
propen-1-one 159 described earlier. To 0.1500g (0.205mmole) of PPN$^+$
salt in 0.3mL of deuterochloroform was added 0.0382g (0.1934mmole) of
4-bromo-2-methyl-2-butenoyl chloride in 0.3mL of deuterochloroform.
The bright yellow ketene solution was distilled to give the title
compound in 75-82% yield.

[1]H-N.M.R., (CDCl$_3$, 20°C): 1.76(s, 3H);

4.77(d of d, J=0.5Hz and 11.0Hz, 1H);

4.76(d of d, J=0.5Hz and 16.6Hz, 1H);

6.30(d of d, J=10.8 and 16.6Hz, 1H).

Dispiro[3.1.3.1]decane-5,10-dione 175

In a 50mL round bottomed flask fitted with a rubber septum,
Na$^+$[Mn(CO)$_5$$^-$] solution (prepared from 0.2g (0.51 mmole) of Mn$_2$(CO)$_{10}$
in 10mL of THF) was added to a stirred solution of 0.2g (1.01 mmole)
of 1-bromocyclobutylcarbonyl bromide in 2mL of THF. When the addition
was complete (five minutes), the solvent was removed from the reaction

mixture at reduced pressure and 10mL of cyclohexane was added to the brown sticky residue. This mixture was then refluxed for thirty minutes, by which time T.L.C. (silica/methylene chloride) indicated all the $Mn(CO)_5Br$ had decomposed. The solution was filtered and the pale yellow filtrate concentrated (5mL) and left at $-20^\circ C$ overnight. The product crystallized as large plates which were filtered to give 0.060g (72% yield with respect to 1-bromocyclobutylcarbonyl bromide). The melting point was $85.5^\circ C$ (literature[173] $86^\circ C$).

Infra-red (CH_2Cl_2, cm^{-1}): 1738.

[1]H-N.M.R., ($CDCl_3$): 2.44(t, 4H, J=7.8Hz) 1.97(m, 2H).

Mass-Spectrum (m/e, % base peak): 164(9), 135(7), 108(15), 93(5), 82(45), 80(20), 79(21), 54(100), 53(35).

2,4-Di-(1′-methyl-1′-ethylidene)cyclobutane-1,3-dione 177

In a 20mL Schlenk flask, $Na^+[Mn(CO)_5^-]$ solution (prepared from 0.19g (0.49 mmole) of $Mn_2(CO)_{10}$ in 10mL of THF) was added to a stirred solution of 0.2g (1.01 mmole) of 2-bromo-3-methyl-2-butenoyl chloride in 5mL of THF over a period of five minutes. When the addition was complete the reaction mixture was stirred for a further five minutes, the solvent evaporated at reduced pressure and the residue dissolved in 5mL of methylene chloride. This deep orange solution was filtered and the volume reduced to 2mL and applied directly to a 1cm diameter flash-chromatography column. Elution with methylene chloride yielded $Mn_2(CO)_{10}$ (first band, 0.01g, 5% yield); $Mn(CO)_5Br$ (second band,

0.21g, 83% yield) and an orange powder (third band, 0.04g).

Considerable streaking in the column occurred during this separation.

The orange powder was dissolved in 2mL of hexane and cooled to -20°C

for 2 hours and on filtration yielded 0.031g (39% yield) of the title

compound as orange needles, m.p. 150°C (reported[215], 135°C and 143°C).

Infra-red (methylene chloride, cm^{-1}): 1630(s), 1691(s); reported[215]

(nujol): 1621, 1680.

^{1}H-N.M.R., (CDCl$_3$): 2.26(s); reported[215]: 2.25(s).

Mass-Spectrum (m/e, % base peak): 164(61, M$^+$), 136(55), 93(70),

83(64), 67(100); reported[215]: 164(36, M$^+$), 67(100).

2-Bromo-3-methyl-2-butenoyl chloride 178

This was prepared[216] by treatment of 2-bromo-3-methyl-2-butenoic

acid[217] (m.p. 90-92°C) with thionyl chloride and was obtained in 79%

yield. B.p. 60-62°C/8mm (lit.[216] 78-80°/15mm).

Infra-red (neat): 1751cm^{-1} (lit.[216] 1757cm^{-1}).

^{1}H-N.M.R., (CDCl$_3$): 2.11(s, 3H); 2.13(s, 3H).

1-Bromocyclobutanecarbonyl bromide[218] 176

This was prepared by the reaction of cyclobutanecarboxylic acid

(Aldrich) with phosphorus tribromide and bromine for 12 hours at 120°C

and was obtained in 51% yield. B.p. 67°C/7mm.

^{1}H-N.M.R., (CDCl$_3$): 1.91(m, 1H); 2.28(m, 1H); 2.62(m, 2H);

2.94(m, 2H).

2-Chloroethanoyl bromide 187

This was prepared in 72% yield by treatment of 2-chloroethanoic acid with phosphorus tribromide. B.p. 124-128°C.

^{1}H-N.M.R., (CDCl$_3$): 4.55ppm (s).

2-Bromopropanoyl chloride[219] 116

This was prepared in 81% yield by treatment of 2-bromopropanoic acid with thionyl chloride. B.p. 125-130°C. (lit.[219] 131-133°C).

Infra-red (neat): 1779cm^{-1}.

^{1}H-N.M.R., (CDCl$_3$): 1.9(d, J=7Hz, 3H); 4.6(q, J=7Hz, 1H).

2-Bromobutanoyl bromide[220] 163

This was prepared in 58% yield by treatment of butanoic acid with phosphorus and bromine at 100°C for three hours. B.p. 54°C/8mm. (lit.[220] 172-174°C)

^{1}H-N.M.R., (CDCl$_3$): 1.10(t, J=7.3Hz, 3H);

2.18(dq, J=7.0 and 7.3Hz, 2H);

4.54(t, J=7.1Hz, 1H).

2-Bromo-3,3-dimethylbutanoyl bromide 168

This was prepared in 67% yield by treatment of 3,3-dimethylbutanoic acid with phosphorus and bromine. B.p. 72°C/7mm.

^{1}H-N.M.R., (CDCl$_3$): 1.15(s, 9H); 4.5(s, 1H).

2-Bromo-2-methylpropanoyl bromide[221] 161

This was prepared by treatment of propanoic acid with phosphorus and bromine. B.p. 51-53°C/8mm (lit.[159] 162-164°C).

^{1}H-N.M.R., (CDCl$_3$): 2.0(s).

4-Bromo-2-butenoyl chloride[221] 171

This was prepared in 36% yield by treatment of 4-bromo-2-butenoic acid[222] with thionyl chloride. B.p. 95-96°C/14mm (lit.[221] 90-100°C/12mm).

Infra-red (neat, cm^{-1}): 1758, 1692, 1022
^{1}H-N.M.R., (CDCl$_3$): 4.06(d, J=7.2Hz, 2H); 6.30(d, J=14Hz, 1H);
7.26(dt, J=14.5 and 7.1Hz, 1H).

4-Bromo-2-methyl-2-butenoyl chloride 173

This was prepared by treatment of 4-bromo-2-methyl-2-butenoic acid[222] with thionyl chloride, and was obtained in 20% yield as a single isomer. B.p. 92°C/12mm.

^{1}H-N.M.R., (CDCl$_3$): 2.0(s, 3H); 4.1(d, J=7Hz, 2H);

5.34(t, J=7Hz, 1H).

Infra-red (neat): 1751cm^{-1}

2-Bromo-3-methylbutanoyl bromide 166

This was prepared by the reaction of 3-methylbutanoic acid with phosphorus tribromide and bromine for 2 hours at 110°C and obtained in 60% yield. B.p. 62°C/8mm.

^{1}H-N.M.R., (CDCl$_3$): 1.11(d, J=6.6Hz, 3H); 1.16(d, J=6.6Hz, 3H);

2.43(m, 1H); 4.46(d, J=6.6Hz, 1H).

a-Chloroacetyl Manganese Pentacarboynl 185

This was prepared in 15% isolated yield from 2-chloroethanoic acid according to a literature procedure[179], and purified by flash chromatography and recrystallized from hexane. M.p. 35-8°C.

^{1}H-N.M.R., (CDCl$_3$): 4.35(s) (lit.[179] 4.37).

Infra-red (CDCl$_3$, cm^{-1}): 2123(w), 2054(m), 2024(s), 1658(w).

(lit.[179],in heptane, cm^{-1}: 2117,2055,2014,2007,1654)

The Thermal Decomposition of *a*-Chloroacetyl Manganese Pentacarbonyl

In a 5mm N.M.R. tube, 10mg of 185 was dissolved in 0.5mL of deuterochloroform and the tube was sealed. The tube was then immersed in a heating bath and the ^{1}H-N.M.R. was spectrum periodically measured. After 5 minutes at 80°C, 50% of the acyl complex 185 had been converted to -chloromethyl manganese pentacarbonyl,

identified[117] from the N.M.R. spectrum (3.6ppm, s). After heating for 30 minutes, little acyl complex 185 remained. However, new resonances at 3.0ppm, 2.2ppm and 1.85ppm had appeared (a total of 60% of the integration) in addition to the resonance at 3.6ppm.

η^1-4-Oxo-4-ethoxy-2-butenyl Manganese Pentacarbonyl 49

In a 50mL side-arm flask, 0.2g (0.51mmole) of dimanganese decacarbonyl was dissolved in 10mL of THF and reduced with 1mL of 1% sodium amalgam. This solution was transferred by syringe into a 20mL round bottom flask containing 0.15g (1mmole) of ethyl 4-chloro-2-butenoate and the mixture stirred for 30 minutes. After this time the solvent was removed under reduced pressure and the yellow residue was extracted with 10mL of methylene chloride, the extract filtered and evaporated to 2mL. Flash-chromatography (1cm diameter column) on this solution yielded 0.01g dimanganese decacarbonyl (first band) and after extended elution 49. This product was isolated as a pale yellow air sensitive oil (0.15g, 49%) which could be recrystallized from hexane (m.p. ca -5°C).

Infra-red (methylene chloride, cm^{-1}): 2110(w), 2018(m), 2005(s),
1690(w), 1610(w)

^{1}H-N.M.R. (CDCl$_3$): 1.27(t, J=7.1Hz, 3H); 1.88(d, J=9.6Hz, 2H);
4.17(d, J=7.0Hz, 2H); 5.65(d, J=15.1Hz, 1H);
7.45(dt, 1H).

{^{1}H}^{13}C-N.M.R., (CDCl$_3$): 8.1(CH$_2$), 14.4(CH$_3$), 59.7(CH$_2$), 111.5(CH),
158.5(CH).

Mass spectrum (m/e, %base peak): 224(5), 196(30), 168(80), 124(45),

100(95), 68(80), 55(100).

Elemental Analysis, calculated for $C_{11}H_9MnO_7$

C, 42.88%; H, 2.94%. Found: C, 39.78%; H, 3.25%.

The elemental analysis for this compound could not be improved, even by

repeted purification.

η^3-4-Oxo-4-ethoxy-2-butenyl Manganese Tetracarbonyl 224

In a 20mL round bottom flask attached to a bubbler, 0.1g of 49

was heated to 80°C for one hour, by which time the evolution of gas

had ceased. The yellow oil which was left was dissolved in 1mL of

methylene chloride and purified by flash chromatography (1cm diameter

column) to yield 224 (this complex was considerably less polar than

49) as an air sensitive yellow oil (0.08g, 88% yield).

Infra-red (methylene chloride, cm^{-1}): 2090(m), 2000(s),

1970(s), 1710(m).

^{1}H-N.M.R., $(CDCl_3)$: 1.30(t, J=7.2Hz, 3H); 2.26(d, J=12.9, 1H);

2.53(d, J=10.4, 1H); 2.99(d, J=8.5Hz, 1H);

4.22(tq, 2H); 5.67(ddd, 1H).

$\{^1H\}^{13}$C-N.M.R., $(CDCl_3)$: 14.4(CH_3), 45.3(CH_2), 46.8(CH),60.5(CH_2),

96.1(CH).

Mass spectrum (m/e, %base peak): 224(1), 196(5), 168(10), 124(4),

100(20), 68(12), 55(23), 43(100).

Elemental Analysis, calculated for $C_{10}H_9MnO_6$

C, 42.88%; H, 3.24%. Found: C, 40.11%; H, 3.04%.

The elemental analysis for this compound could not be improved, even by repeted purification.

η^5-4-Oxo-4-ethoxy-2-butenyl Manganese Tricarbonyl 226

In a 25mL round bottom flask 0.05g (0.18mmole) of 224 was dissolved in 5mL of cyclohexane and the flask fitted with a reflux condenser and the solution refluxed under a slow stream of nitrogen overnight. The resulting dark yellow solution was evaporated to ca 2mL and applied directly to a 1cm diameter flash chromatography column. The product 226 eluted as the first deep yellow band, and yielded 0.036g dark yellow oil (76%). This product was air sensitive and decomposed slowly in solution even at reduced temperature.

Infra-red (methylene chloride, cm^{-1}): 2050(s), 1960(s), 1935(s).

^{1}H-N.M.R., (CDCl$_3$): 1.22(t, J=7.1Hz, 3H); 1.93(d, J=14, 1H);

3.54(d, J=9.5, 1H); 3.92(q, J=7.2Hz, 2H);

4.86(d, J=7.0Hz, 1H); 5.46(ddd, 1H).

$\{^1$H$\}^{13}$C-N.M.R., (CDCl$_3$): 14.1(CH$_3$), 57.0(CH), 60.3(CH$_2$), 61.9(CH$_2$),

105.7(CH).

Phenyl 2-butenoate[223]

In a 250mL round-bottom flask, 15mL of 2-butenoyl chloride was added dropwise to 20g (0.21 mole) of crystalline phenol. The reaction mixture was stirred for thirty minutes with warming to give a steady evolution of hydrogen chloride. The reaction mixture was washed with 3x100mL of water, diluted with diethyl ether and washed with saturated

sodium bicarbonate solution, dried with magnesium sulfate and the
solvent removed. The residue was distilled to give 21g colourless
oil, boiling point 116-119°C/12mm (lit.[223]:114°C/14mm) and was pure by
G.C. (OV17 column) and ^{1}H-N.M.R. spectroscopy (d, 1.95ppm, J=8Hz, 3H;
m, 5.8-7.6ppm, 7H).

Infra-red: 1736cm^{-1}.

Phenyl 4-Bromo-2-Butenoate

In a 250mL round bottom flask fitted with a reflux condenser,
5.0g (0.03 mole) of phenyl 2-butenoate, and 8.0g (0.045 mole) of N-
bromosuccinimide were added to 100mL of dry carbon tetrachloride, and
the mixture irradiated with stirring with a 650W quartz-halogen lamp.
During the irradiation the solution refluxed and after 2 hours all the
N-bromosuccinimide had been consumed. The solution was cooled to 0°C
and the solid succinimide filtered and the filtrate evaporated. The
brown oily residue was purified by flash chromatography (silica, 1:1
pentane/methylene chloride eluent, 5cm diameter column) in 2g
portions. This yielded 2.1g of pale yellow oil (4th band) which was
>90% pure by G.C. (3% OV-17, 2mm x 2m glass column). This product
decomposed upon attempted distillation (0.1mmHg).

Infra-red (neat, cm^{-1}): 1740, 1653, 1592, 1492, 1195.
^{1}H-N.M.R., (CDCl$_3$): 4.07(d, 2H, J=7Hz); 6.22(d, 1H), J=15Hz);
              7.06-7.50 (m, 6H).
{^{1}H}^{13}C-N.M.R., (CDCl$_3$): 28.9 (CH$_2$), 121.4 (CH), 123.9 (CH),

125.9 (CH), 129.5 (CH), 143.6(CH),

150.5 (C), 163.8 (C).

Mass-Spectrum: 242/240(2,M), 149/147(70), 121/119(10), 94(30),

68(70), 89(100).

High Resolution Mass: 241.9779 and 239.9806

(calculated for $C_{10}H_9BrO_2$ 241.9766 and 239.9786)

Elemental Analysis, calculated for $C_{10}H_9BrO_2$

C, 49.82%; H, 3.76%. Found: C, 47.96%; H, 3.60%.

Phenyl 4-chloro-2-butenoate

An excess of anhydrous lithium chloride (1.4g, 0.033 mole) was

added to 10mL of dimethylformamide and stirred for ten minutes.

Phenyl 4-bromo-2-butenoate (2.0g, 0.008 mole) was then added to this

mixture and the solution was stirred for a further ten minutes. The

reaction mixture was then added to 100mL of water, extracted with

2x50mL of hexane, the extracts combined, washed with water, dried

($MgSO_4$) and evaporated. Analysis by G.C. (3% OV17, 2mm x 2m glass

column) indicated that complete conversion had taken place (>95%

pure), giving 1.54g (94% yield) of the product as a colourless oil.

Infra-red (neat, cm^{-1}): 1741, 1676, 1660, 1592, 1492, 1197.

^{1}H-N.M.R., (CDCl$_3$): 4.15(d, 2H, J=7Hz); 6.1-6.4(m, 2H);

6.8-7.5(m, 5H).

$\{^1H\}^{13}$C-N.M.R., (CDCl$_3$): 42.4 (CH$_2$), 121.6 (CH), 123.3 (CH),

125.9 (CH), 143.7 (CH), 150.5 (C).

Preparation of η^1-4-Oxo-4-phenoxy-2-butenyl Manganese Pentacarbonyl 223

In a 100mL, round-bottomed flask 0.5g (1.28 mmole) of dimanganese decacarbonyl was dissolved in 40mL of THF under a slow stream of argon. To this, 2mL of 1% Na(Hg) was added, the flask sealed with a rubber septum and the solution was stirred for twenty minutes at room temperature. This solution was decanted via a transfer needle into a 250mL round-bottomed flask containing 0.5g (2.54 mmole) of phenyl-4-chloro-2-butenoate in 5mL of THF and the reaction mixture stirred for ten minutes, after which some sodium chloride had precipitated from the deep yellow solution. The solvent was removed on a rotory evaporator, and the orange/yellow powder residue was extracted with 4x50mL of warm (40°C) hexane. The extracts were then combined, filtered through a fine porosity glass frit, flushed with argon and the solution concentrated under high vacuum to a volume of 100mL. The solution was placed in the refrigerator at -10°C for two hours and 0.75g of fine, off-white cubic crystals were collected by filtration, m.p. 95-96°C (decomposed).

Infra-red (hexane, cm^{-1}): 2113 (m), 2052 (w), 2021 (vs), 1999 (s), 1738 (m), 1618 (w).

^{1}H-N.M.R., (CDCl$_3$): 7.65(dt, 1H, J-15Hz and 9.6 Hz); 7.1-7.5 (m, 5H); 5.81(d, 1H, J=15Hz); 1.94(d, 2H, J=9.7Hz).

{^{1}H}^{13}C-N.M.R., (CDCl$_3$): 161.1, 129.3, 125.3, 121.8, 110.2, 8.2.

Mass-Spectrum (m/e): 328(1, M-CO) 300(1), 272(1),

244(1), 216(40), 148(66), 94(72)

Elemental Analysis, Calculated for $C_{15}H_9MnO_7$: C, 50.58%; H, 2.55%.
Found: C, 50.01%; H, 2.31%.

Because of the air-sensitive nature of this compound, a good elemental analysis could not be obtained.

Preparation of η^3-4-Oxo-4-phenoxy-2-butenyl Manganese Tetracarbonyl 225

In a 20mL Schlenk flask attached to a gas burette 0.34g (0.94 mmole) of η^1-4-oxo-4-phenoxy-2-butenyl manganese pentacarbonyl 223, was heated to 85-90°C for thirty minutes, by which time the evolution of carbon monoxide had ceased (23.8mL). The resulting semisolid yellow residue was then dissolved in 20mL of hexane, filtered and cooled (-20°C) overnight. From this solution 0.19g of fine yellow needles were obtained, from which 0.17g (55% yield) analytically pure product was recrystallized (m.p. 66-67°C).

Infra-red (hexane, cm^{-1}): 2084 (s), 2021 (w), 2001 (vs),
$\qquad$ 1975 (s), 1736 (m).

Infra-red (methylene chloride, cm^{-1}): 2083 (m), 2053 (w),
$\qquad$ 1995 (vs), 1968 (s), 1723 (m).

^{1}H-N.M.R., (CDCl$_3$, ppm): 7.12-7.53 (m, 5H); 5.79 (cdd, 1H);
$\qquad$ 3.09 (d, 1H, J=7.3Hz); 2.70(d, 1H, J=10.3Hz);
$\qquad$ 2.37(d, 1H, J=14Hz).

$\{^1$H$\}^{13}$C-N.M.R., (CDCl$_3$, ppm): 22.7, 45.2(CH), 46.5(CH$_2$), 96.5(CH),
$\qquad$ 121.7(CH), 125.8(CH), 129.4(CH), 150.7.

Mass-Spectrum (m/e, %): 300(0.5, M-CO), 272(1), 244(17), 217(11),
216(80), 149(9), 148(98), 94(143), 69(14),
68(31), 66(12), 65(13), 56(10), 55(100), 40(21).

Elemental Analysis, calculated for $C_{14}H_9MnO_6$: C, 51.24%; H, 2.76%.
Found: C, 51.07%; H, 2.76%.

Preparation of η^5-4-oxo-4-phenoxy-2-butenyl Manganese Tricarbonyl 227

In a 20mL Schlenk flask 0.49g (1.49 mmole) of η^3-4-oxo-4-
phenoxy-2-butenyl manganese tetracarbonyl was dissolved in 5mL of
cyclohexane. A condenser was attached and the solution refluxed for
ten hours under a slow stream of nitrogen. The resulting deep
yellow/orange solution was then concentrated to 2mL under high vacuum
and applied directly to a 2cm x 20cm silica flash chromatography column.
The column was eluted with methylene chloride and the product
collected (first dark yellow band, T.L.C. using silica/methylene
chloride R_f=0.85). Evaporation of the solvent yielded a deep orange
oil which formed a mass of large orange crystals (plates) under a
stream of nitrogen. The product was further subjected to a high
vacuum to remove traces of solvent to yield 0.38g (84% yield) orange
solid (m.p. 48°C) which was analytically pure.

Crystals suitable for X-ray crystallographic analysis were
obtained by placing a concentrated hexane solution of the product in
the freezer (-20°C) overnight, rapidly decanting the mother liquor
from the crystals by pipette and immediately removing residual solvent
under high vacuum.

Infra-red (methylene chloride, cm^{-1}): 2036 (s), 1959 (s), 1932 (s).

^{1}H-N.M.R., (CDCl$_3$, ppm): 6.9-7.45 (m, 5H);

5.58(ddd, 1H);

5.12(d, 1H, J=6.7Hz); 3.61 (d, 1H, J=9.6Hz);

2.03 (d, 1H, J=13.6Hz).

$\{^1$H$\}^{13}$C-N.M.R., (CDCl$_3$, ppm): 57.0 (CH), 62.0 (CH$_2$), 105.7 (CH),

121.2 (CH), 126.6 (CH), 129.7 (CH).

Mass-Spectrum (m/e, %): 300(0.1, M), 272(1), 244(12), 216(61),

148(79), 94(47), 69(10), 68(36), 66(12),

65(13), 55(81), 40(20).

Elemental Analysis, calculated for C$_{13}$H$_9$MnO$_5$: C, 52.02%; H, 3.02%;

Found: C, 52.10%; H, 3.04%.

η^3 4-Oxo-4-phenoxy-2-butenyl Manganese Tricarbonyl Triphenylphosphine

228

In a round bottom flask, 0.1g (0.33mmole) of 227 was dissolved in 20mL of hexane. To this solution, 0.08g (0.32mmole) of finely ground triphenylphosphine was added in small portions with stirring. The reaction was accompanied by an immediate colour change, and formation of a yellow precipitate. The mixture was filtered, and the solid dissolved in methylene chloride and purified by flash chromatography to give 0.17g (94% yield) of the title compound 228 as analytically pure yellow microcrystals. M.p. 120°C.

Infra-red (methylene chloride, cm^{-1}): 2014(s), 1945(s), 1918(s),

1715(m).

^{1}H-N.M.R., (CDCl$_3$): 2.98(dd, J=6.7Hz, J$_{HP}$=3.2Hz, 1H);

3.17(d, J=8.2Hz, 1H);

3.52(d, J=13.4Hz, 1H);

4.33(m, J$_{HP}$=13.1Hz, 1H);

7.04-7.44(m, 5H);

7.44-7.60(m, 15H).

Elemental Analysis, calculated for C$_{31}$H$_{24}$MnO$_5$P: C, 66.20%; H, 4.30%;

Found: C, 66.04%; H, 4.54%.

X-Ray Crystallography.

The X-ray radiation employed was MoK_α with a graphite monochromator, and the data were collected at $21^\circ C$. Other parameters are given in Tables 6.1, 6.2, 6.3 and 6.4 below.

	η^1	η^3	η^5
Space Group:	$P2_1/a$	$Pna2_1$	Pbca
Unit Cell Dimensions: a (A)	18.834(5)	17.7845(14)	12.5681(13)
b (A)	6.563(1)	7.0454(8)	11.3523(8)
c (A)	12.730(3)	11.3030(11)	18.1003(15)
α (deg.)	90.0	90.0	90.0
β (deg.)	91.58(1)	90.0	90.0
γ (deg.)	90.0	90.0	90.0
Volume (A^3):	1572.6(6)	1416.2(2)	2582.5(3)
Density (gcm^{-3}):[a]	1.504	1.539	1.544
Z :[b]	4	4	8
R :[c]	0.040	0.037	0.042
R_w:[d]	0.031	0.029	0.033

<u>Table 6.1</u> X-Ray Crystallographic Parameters for η^1, η^3, η^5, Complexes <u>223</u>,<u>225</u> and <u>227</u>

[a]Calculated. [b]Formula units in unit cell. [c]$R=\Sigma(||Fo|-|Fc||)/\Sigma|Fo|$.
[d]$R_w=[\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

	x/a	y/b	z/c
Mn	3732(0)	455(1)	1120(0)
C(1)	2657(2)	-491(5)	569(3)
C(2)	2430(2)	685(5)	-347(3)
C(3)	1958(2)	2180(6)	-375(3)
C(4)	1806(2)	3243(5)	-1359(3)
C(5)	1070(2)	5712(6)	-2169(3)
C(6)	1343(2)	7603(8)	-2300(4)
C(7)	1158(3)	8693(8)	-3168(6)
C(8)	699(4)	7939(11)	-3898(5)
C(9)	418(3)	6072(10)	-3733(4)
C(10)	604(2)	4928(6)	-2878(4)
C(11)	3445(2)	-729(5)	2370(3)
C(12)	4071(2)	-2036(5)	668(3)
C(13)	3290(2)	2908(5)	1457(3)
C(14)	4591(2)	1233(5)	1687(3)
C(15)	3928(2)	1515(5)	-186(3)
O(1)	1259(1)	4588(4)	-1260(2)
O(2)	2099(1)	3042(4)	-2168(2)
O(11)	3277(1)	-1497(4)	3118(2)
O(12)	4270(1)	-3550(4)	374(2)
O(13)	3045(1)	4434(4)	1615(2)
O(14)	5121(1)	1721(4)	2040(2)
O(15)	4062(1)	2173(4)	-978(2)

Table 6.2 Atomic Positional Parameters for the η^1-Complex 223.
(The values have been multiplied by 10^4).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	51(0)	44(0)	49(0)	-3(0)	5(0)	-1(0)
C(1)	58(2)	71(2)	57(2)	-19(2)	-5(2)	3(2)
C(2)	50(2)	62(2)	60(2)	-7(2)	1(2)	-8(2)
C(3)	55(2)	79(3)	55(2)	7(2)	3(2)	-4(2)
C(4)	47(2)	68(3)	70(3)	8(2)	3(2)	-3(2)
C(5)	52(2)	69(3)	64(3)	9(2)	5(2)	-5(2)
C(6)	62(3)	78(3)	122(4)	-4(3)	-11(3)	-9(3)
C(7)	96(4)	88(4)	166(6)	11(3)	29(4)	42(4)
C(8)	141(6)	155(7)	95(4)	57(5)	25(4)	54(5)
C(9)	137(5)	153(5)	75(4)	14(4)	-40(3)	-2(4)
C(10)	92(3)	74(3)	89(3)	-12(2)	-17(3)	-6(3)
C(11)	54(2)	55(2)	54(2)	0(2)	0(2)	-7(2)
C(12)	64(3)	53(2)	54(2)	-12(2)	3(2)	3(2)
C(13)	67(2)	50(2)	63(2)	-11(2)	14(2)	3(2)
C(14)	66(3)	57(2)	58(2)	-5(2)	7(2)	-10(2)
C(15)	49(2)	53(2)	63(3)	-5(2)	5(2)	-5(2)
O(1)	70(2)	96(2)	64(2)	28(2)	5(1)	-2(2)
O(2)	76(2)	109(2)	67(2)	31(2)	27(2)	13(2)
O(11)	87(2)	87(2)	61(2)	-2(1)	12(2)	22(2)
O(12)	90(2)	53(2)	108(2)	2(1)	23(2)	-16(2)
O(13)	101(2)	48(1)	120(2)	3(2)	49(2)	1(2)
O(14)	66(2)	109(2)	97(2)	-22(2)	-6(2)	-26(2)
O(15)	88(2)	96(2)	62(2)	-8(2)	18(2)	18(2)

Table 6.3   Thermal Parameters for the η^1-Complex <u>223</u>

	x/a	y/b	z/c
Mn	1822(0)	1374(1)	2500(0)
C(1)	1467(2)	4444(4)	2571(5)
C(2)	2048(2)	4031(5)	3340(3)
C(3)	2744(2)	3292(5)	2953(3)
C(4)	3262(2)	2524(5)	3833(3)
C(5)	4437(2)	995(6)	4058(4)
C(6)	4867(2)	2015(7)	4818(4)
C(7)	5388(3)	1075(9)	5511(4)
C(8)	5458(3)	-847(10)	5444(5)
C(9)	5020(3)	-1855(7)	4658(5)
C(10)	4504(3)	-934(6)	3961(4)
C(11)	1964(2)	1861(6)	929(5)
C(12)	880(3)	503(5)	2210(3)
C(13)	2398(2)	-732(5)	2307(3)
C(14)	1665(2)	587(6)	4082(4)
O(1)	3917(1)	1929(4)	3319(2)
O(2)	3149(1)	2382(4)	4874(2)
O(11)	2056(2)	2122(4)	-51(3)
O(12)	279(2)	-13(4)	2049(3)
O(13)	2800(2)	-1971(4)	2174(2)
O(14)	1561(2)	16(4)	4999(3)

Table 6.4 Atomic Positional Parameterss for the η^3-complex __225__.

(The values have been multiplied by 10^4).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	48(0)	47(0)	38(0)	-2(0)	-2(0)	-1(0)
C(1)	59(2)	51(2)	62(2)	14(2)	2(3)	-1(3)
C(2)	55(2)	45(2)	45(2)	-3(2)	1(2)	-7(2)
C(3)	48(2)	50(2)	45(2)	5(2)	-2(2)	-4(2)
C(4)	50(2)	53(2)	44(2)	-5(2)	3(2)	-5(2)
C(5)	37(2)	65(3)	41(2)	2(2)	3(2)	6(2)
C(6)	60(3)	66(3)	54(2)	3(2)	-4(2)	-5(3)
C(7)	57(3)	98(4)	63(3)	1(3)	-10(3)	-7(3)
C(8)	59(3)	104(4)	59(3)	24(3)	0(3)	18(3)
C(9)	70(3)	64(3)	75(3)	8(3)	11(3)	13(3)
C(10)	56(3)	61(3)	60(3)	-13(2)	2(2)	-4(2)
C(11)	54(2)	55(2)	48(3)	10(2)	0(2)	-6(2)
C(12)	77(3)	59(2)	49(3)	-6(2)	-4(2)	0(2)
C(13)	60(2)	51(2)	38(2)	-9(2)	-9(2)	0(2)
C(14)	53(2)	57(2)	56(3)	-15(2)	-4(2)	-1(2)
O(1)	47(1)	82(2)	41(1)	12(1)	6(1)	3(1)
O(2)	53(2)	95(2)	40(1)	12(1)	3(1)	-5(1)
O(11)	99(2)	83(2)	46(2)	11(2)	4(2)	4(2)
O(12)	62(2)	111(2)	85(2)	-28(2)	-20(2)	-4(2)
O(13)	82(2)	56(2)	70(2)	14(1)	-9(2)	-6(1)
O(14)	82(2)	89(2)	48(2)	-11(2)	8(2)	20(2)

Table 6.5 Thermal Parameters for the η^3-Complex 225.

	x/a	y/b	z/c
Mn	3290(1)	5689(1)	2154(0)
C(1)	1893(3)	5696(4)	2841(3)
C(2)	1861(4)	6606(4)	2319(3)
C(3)	1951(3)	6410(4)	1558(3)
C(4)	1971(3)	5230(4)	1264(3)
C(5)	1805(4)	4047(4)	187(2)
C(6)	897(4)	3451(5)	16(3)
C(7)	982(5)	2427(6)	-387(4)
C(8)	1958(6)	2017(5)	-601(3)
C(9)	2855(5)	2631(6)	-423(3)
C(10)	2785(4)	3666(5)	-24(3)
C(11)	3922(4)	4813(4)	2865(3)
C(12)	4287(4)	5498(5)	1432(3)
C(13)	3972(4)	6935(4)	2471(3)
O(1)	2301(2)	4381(3)	1627(1)
O(2)	1682(3)	5141(2)	547(2)
O(11)	4308(3)	4338(3)	3349(2)
O(12)	4924(3)	5404(4)	990(2)
O(13)	4424(2)	7745(3)	2691(2)

Table 6.6 Atomic Positional Parameters for the η^5-Complex 227.
(The values have been multiplied by 10^4).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	50(0)	47(0)	46(0)	1(0)	7(0)	-1(0)
C(1)	61(3)	82(3)	69(3)	-15(3)	33(3)	-19(4)
C(2)	46(3)	51(3)	90(4)	5(3)	13(3)	-19(3)
C(3)	59(4)	48(3)	67(3)	7(3)	1(3)	0(3)
C(4)	35(3)	59(3)	52(3)	-7(2)	7(2)	-8(3)
C(5)	68(4)	53(3)	38(3)	0(3)	-4(3)	9(2)
C(6)	68(4)	78(4)	84(4)	-9(3)	9(3)	-18(3)
C(7)	97(5)	89(5)	99(5)	-28(5)	0(5)	-29(4)
C(8)	137(6)	64(4)	52(3)	-4(4)	0(4)	-9(3)
C(9)	99(5)	76(4)	48(3)	26(4)	2(3)	0(3)
C(10)	59(4)	72(4)	50(3)	-1(3)	-3(3)	4(3)
C(11)	83(4)	47(3)	60(3)	3(3)	11(4)	-5(3)
C(12)	42(3)	85(4)	52(3)	3(3)	-6(2)	-7(3)
C(13)	58(4)	48(3)	67(3)	3(3)	3(3)	0(3)
O(1)	69(2)	36(2)	49(2)	3(2)	1(2)	0(2)
O(2)	65(2)	53(2)	58(2)	7(2)	-6(2)	-1(2)
O(11)	127(3)	79(3)	69(2)	16(3)	-15(2)	17(2)
O(12)	53(2)	160(4)	66(3)	-2(3)	16(2)	-19(3)
O(13)	79(3)	73(2)	98(3)	-15(2)	-3(2)	-3(2)

Table 6.7 Thermal Parameters for the η^5-Complex 227.

REFERENCES

1. J.P. Collman and L.S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, CA, 1980.

2. J.S. Thayler, Adv. Organomet. Chem., 13, 1 (1975).

3. E. Frankland, J. Chem. Soc.; 2, 263 (1840).

4. W.C. Zeiss, Ann. Phys., 9, 932 (1827).

5. M.P. Schutzenburger, Annalen, 15, 100 (1868).

6. L. Mond, J. Chem. Soc., 57, 749 (1890).

7. L. Mond and C. Langer, J. Chem. Soc., 59, 1090 (1891)

8. T.J. Kealy and P.J. Pauson, Nature (London), 168, 1039 (1951).

9. S.A. Miller, J.A. Tebboth and J.F. Tremaine, J. Chem. Soc., 632 (1952).

10. G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, J. Am. Chem. Soc., 74, 2125 (1952).

11. P.M. Treichel, "Comprehensive Organometallic Chemistry", Ed. G. Wilkinson, F.G.A. Stone and E.W. Abel, Vol. 5, Pergamon, New York, 1980.

12. D.T. Hund, G.W. Sentell and F.J. Norton, J. Am. Chem. Soc., 71, 1899 (1949).

13. E.O. Brimon, M.A. Lynch and W.J. Sesny, J. Am. Chem. Soc., 76, 3831 (1954).

14. G. Wilkinson and F.A. Cotton, Chem. Ind. (London), 307 (1954).

15. E.O. Fisher and R. Jira, Z. Naturforsch., 9B, 618 (1954).

16. G. Wilkinson, F.A. Cotton and J.M. Birmingham, J. Inorg. Chem., 2, 95 (1956).

17. R.D. Closson, J. Kozikowski and T.H. Coffield,

    J. Org. Chem., 22, 598 (1957).

18. S.G. Davies, "Organotransition Metal Chemistry: Applications to

    Organic Synthesis", Pergamon Press, New York, 1982.

19. H.M. Colquhoun, "New Pathways for Organic Synthesis: Practical

    Applciations of Transition Metals",

    Plenum Press, New York, 1982.

20. M.P. Cooke, J. Am. Chem. Soc., 92, 6080 (1970).

21. J.P. Collman, Acc. Chem. Res., 8, 342 (1975).

22. R.F. Heck. "Organic Synthesis via Metal Carbonyls" Eds.

    I. Wender and P. Pino, Volume I, Wiley Interscience,

    New York, pp 373, 1968.

23. M. Rosenblum, Acc. Chem. Res., 7, 122 (1974).

24. P.M. Treichel, M.A. Chandhari and F.G.A. Stone,

    J. Organomet. Chem., 1, 98 (1963).

25. G. Yagupski, W. Mowat, A. Shortland and G. Wilkinson,

    J. Chem. Soc. Chem. Commun., 1369 (1979).

26. E. Lindner, G. Funk and S. Hoelme,

    Angew. Chem. Int. Ed. Engl., 18, 535 (1979).

27. K.P. Darst and C.M. Lukehart,

    J. Organomet. Chem., 171, 65 (1979).

28. D. Drew, M.Y. Darensbourg and D.J. Darensbourg,

    J. Organomet. Chem., 85, 73 (1975).

29. W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and

    B.W. Hawk, J. Am. Chem. Soc., 83, 1601 (1961).

30. J.A. Gladysz, W. Tam, G.M. Williams, D.L. Johnson and

D.W. Parker, Inorg. Chem., 18, 1163 (1979).

31. P. Lennon, A. M. Rosan and M. Rosenblum,

    J. Am. Chem. Soc., 99, 8426 (1977).

32. G.T. Palmer and F. Basolo, J. Am. Chem. Soc., 107, 3122 (1985).

33. T.S. Sorensen and A. Oudeman, personal communication.

34. R.B. King, Acc. Chem. Res., 3, 417 (1970).

35. A. Wojiki, Adv. Organomet. Chem., 11, 87 (1973).

36. J.N. Cawse, R.A. Fiato and R.L. Pruett,

    J. Organomet. Chem., 172, 405 (1975).

37. C.P. Casey and D.M. Scheck, J. Am. Chem. Soc., 102, 2728 (1980).

38. P. DeShong and G.A. Slough, Organometallics, 3, 636 (1984).

39. A. Davidson, W. McFarlane, L. Prat and G. Wilkinson,

    J. Chem. Soc., 3653 (1962).

40. M.L.H. Green, A.G. Massey, J.H. Melwyn-Hughes and

    P.L.I. Nagy, J. Organomet. Chem., 8, 511 (1967).

41. C.M.Lukehart, G. Torrence and J.V. Zeile,

    Inorg. Synth., 18, 57 (1978).

42. W. Heiber and G. Wagner, Ann. Chem., 618, 24 (1958).

43. J. Engelbrecht, T. Greiser and E. Weiss,

    J. Organomet. Chem., 204, 79 (1981).

44. B.D. Dombek, J. Am. Chem. Soc., 101, 6466 (1979).

45. R.B. King, Adv. Organomet. Chem., 2, 207 (1964).

46. J.P. Collman, R.G. Finke, J.N. Cawse and J.I. Brauman,

    J. Am. Chem. Soc., 99, 2515 (1977).

47. G.M. Whitesides and D.J. Beschetta,

    J. Am. Chem. Soc., 93, 1529 (1971).

48. R.W. Johnson and R.G. Pearson, Chem. Comm., 986 (1970).

49. D. Doug, D.A. Slack and M.C. Baird,

    Inorg. Chem., 18, 188 (1979).

50. R.G. Pearson and P.E. Figdore,

    J. Am. Chem. Soc., 102, 1541 (1980).

51. R.E. Dessy, R.L. Phol and R.B. King,

    J. Am. Chem. Soc., 88, 5121 (1966).

52. E.W. Abel, M.A. Bennett, R. Burton and G. Wilkinson,

    J. Chem. Soc., 4559 (1958).

53. W.R. McClellan, J. Am. Chem. Soc., 83, 1598 (1961).

54. W. Beck, W. Hieber and H. Tengler, Chem. Ber., 94, 862 (1961).

55. H.D. Kaesz, R.B. King and F.G.A. Stone,

    Z. Naturforsch., 15B, 763 (1960).

56. F.A. Cotten, "Chemical Applications of Group Theory", Wiley

    Interscience, New York, 1971.

57. K.F. Purcell and J.C. Kotz, "Inorganic Chemistry", Saunders,

    New York, 1977.

58. R.G. Kidd and R.J. Goddfellow in "N.M.R. and the Periodic Table",

    Eds. R.K. Harris and B. Mann, Academic Press, New York, 1978.

59. C. Brenard and P. Granger, "Handbook of High Resolution

    Multinuclear N.M.R.", Wiley Interscience, New York, 1981.

60. F. Calderazzo, E.A.C. Lucken and D.F. Williams,

    J. Chem. Soc. (A), 154 (1967).

61. J.D. Dechter, "Progress in Inorganic Chemistry", Ed.

    S.J. Lippard, Vol. 33, J. Wiley and Sons, New York, pp 393, 1985.

62. G.M. Bancroft, H.C. Clark, R.G. Kidd, A.T. Rake and

H.G. Spinney, Inorg. Chem., 12, 728 (1973).

63. W.J. Miles, B.B. Garrett and R.J. Clark,

    Inorg. Chem., 8, 2817 (1969).

64. D. Rehder, H.C. Bechtold, A. Koceci, H. Schmidt and M. Siewing,

    Z. Naturforsch., 37B, 631 (1982).

65. R.G. Kidd, Ann. Rep. N.M.R. Spectroscopy, 10A, 1 (1980).

66. F. Calderazzo, Inorg. Chem., 4, 293 (1965).

67. T.L. Brown and C.D. Pribalen,

    J. Organomet. Chem., 71, 415 (1974)

68. R.B. King and F.G.A. Stone, Inorg. Synth., 7, 196 (1963).

69. W. Heiber and G. Wagner, Z. Naturforsch., 13B, 339 (1959).

70. J.E. Ellis and E.A. Flour, J. Organomet. Chem., 99, 263 (1975).

71. J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker

    and J.C. Selover, Inorg. Chem., 18, 553 (1979).

72. J.A. Gladysz, G.M. Williams, D. Tan and D.L. Johnson

    J. Organomet. Chem., 140, C1 (1977).

73. R.B. King, J. Inorg. Nucl. Chem., 25, 1296 (1963).

74. D.N. Duffy and B.K. Nicholson,

    J. Organomet. Chem., 164, 227 (1979).

75. J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker

    and J.C. Selover, Inorg. Chem., 18, 553 (1979).

76. K.J. Reimer, A. Shaver, M.H. Quick and R.J. Angelici,

    Inorg. Synth., 19, 158 (1979).

77. E.O. Fischer and E. Offhaus, Chem. Ber., 102, 2449 (1969).

78. C.P. Casey, C.R. Cyr, R.L. Aderson and D.F. Marten,

    J. Am. Chem. Soc., 97, 3053 (1975).

79. M.L.H. Green and P.L.I. Nagy, J. Organomet. Chem., 1, 58 (1963).

80. F.A. Hartman and A. Wojcicki, Inorg. Chem., 7, 1504 (1968).

81. Y. Ito, T. Konoike, T. Harada and T. Saegusa,

J. Am. Chem. Soc., 99, 1487 (1977).

82. P. Prempree, S. Radviroongit and Y. Thebtaramonth,

J. Org. Chem., 48, 3553 (1983).

83. M.F. Farona and L.M. Frazee,

J. Inorg. Nucl. Chem., 29, 1814 (1967).

84. J.W. De Haan and L.J.M. Van de Ven,

Org. Mag. Res., 5, 147 (1973).

85. S. Sustman and C. Ruchardt, Chem. Ber., 3043 (1975).

86. E.R. Burkhardt, J.J. Doney, R.G. Bergman and C.H. Heathcock,

J. Am. Chem. Soc., 109, 2022 (1987).

87. R.J. Angelici, Inorg. Chem., 3, 1099 (1964).

88. R.B. King, J. Am. Chem. Soc., 85, 1922 (1963).

89. M.Y. Darensbourg, D.J. Darensbourg, D. Burns and D.A. Drew,

J. Am. Chem. Soc., 98, 3127 (1976).

90. (a) R. Poli, G. Wilkinson, M. Motevalli and M.B. Hursthouse,

J. Chem. Soc. Dalton. Trans., 931 (1985).

(b) E.C. Ashby, Wei-Yang Su and T.N. Pham,

Organometallics, 4, 1493 (1985).

91. P.J. Fagan and J. San Filippo, J. Am. Chem. Soc., 99, 250 (1977).

92. R.D Guthrie. "Comprehensive Carbanion Chemistry" Part A, Eds.

E. Buncel and T. Durst, Elsevier, New York, p 197, 1980.

93. R.S. Herrick, T.R. Herrington, H.W. Walker and T.L. Brown,

Organometallics, 4, 42 (1985).

94. M.S. Alnajjar and H.G. Kuivila,

    J. Am. Chem. Soc., 107, 416 (1985).

95. G.S. Koermer, M.L. Hall and T.G. Traylor,

    J. Am. Chem. Soc., 94, 7205 (1972).

96. P.B.D. de la Mare and B.E. Swedland, "The Chemistry of the

    Carbon-Halogen Bond", Part 1, Ed. S. Patai, p 534,

    Wiley Interscience, New York, 1973.

97. C. Windus, S. Sujishi and W.P. Giering,

    J. Organomet. Chem., 101, 279 (1975).

98. D.L. Morse and M. Wrighton, J. Organomet. Chem., 125, 71 (1977).

99. R.P. Hughes, J.M.J. Lambert, J.W. Reisch and W.L. Smith,

    Organometallics, 1, 1403 (1982).

100. J.A. Armstead, D.J. Cox, R. Davies,

    J. Organomet. Chem., 236, 213 (1982).

101. R.D. Little and J.R. Dawson, J. Am. Chem. Soc., 100, 4607 (1978).

102. E. Gheta and Y. Ben-David, Tetrahedron Lett., 4603 (1979).

103. J.L. Herrmann, G.R. Kieczykowski and R.H. Schlessinger,

    Tetrahedron Lett., 2433 (1973).

104. G.L. Geoffroy and M.S. Wrighton, "Organometallic Photochemistry",

    Academic Press, New York, p 89, 1972.

105. S.A. Hallock and A. Wojcicki,

    J. Organomet. Chem., 182, 521 (1979).

106. A. Hudson, M.F. Lappert, P.W. Lednor, B.K. Nicholson,

    J. Chem. Soc. Chem. Commun., 966 (1974).

107. R.T. Arnold and S.T. Kulenovic, J. Org. Chem., 43, 3687 (1978).

108. N. Petragnani and M. Yonashiro, Synthesis, 710 (1980).

109. J.F. Garst, "Free Radicals", Vol 1, Ed. J.K. Kochi, Wiley,

New York, 1973.

110. M. Darensbourg, H. Barros and C. Borman,

J. Am. Chem. Soc., 99, 1647 (1977).

111. M.Y. Darensbourg, "Progress in Inorganic Chemistry". Ed.

S.J. Lippard, Vol 33, J. Wiley and Sons, New York, p 221, 1985.

112. M.Y. Darensbourg, P. Jimenez and J.R. Sacket,

J. Organomet. Chem., 202, C68 (1980).

113. M. Dilgassa and M.D. Curtis,

J. Organomet. Chem., 172, 177 (1979).

114. C.H. Game, M. Green, J.R. Moss and F.G.A. Stone,

J. Chem. Soc. Dalton Trans., 351 (1974).

115. M. Brookhart, J.R. Tucker, T.C. Flood and J. Jensen,

J. Am. Chem. Soc., 102, 1203 (1980).

116. T.G. Richmond and D.F. Shriver, Organometallics, 3, 305 (1984).

117. C. Botha, J.R. Moss and S. Pelling,

J. Organomet. Chem., 220, C21-24 (1981).

118. T.R. Moss and S. Pelling, J. Organomet. Chem., 236, 213 (1982).

119. K.C. Brinkman, G.D. Vaughn and J.A. Gladysz,

Organometallics, 1, 1056 (1982).

120. J. Rajaram and J.A. Ibers, J. Am. Chem. Soc., 100, 829 (1978).

121. J.Y. McDermott, J.C. White and G.M. Whitesides,

J. Am. Chem. Soc., 98, 6521 (1976).

122. S.D. Chappell and D.J. Cole-Hamilton,

Polyhedron, 1, 739 (1982).

123. G.W. Parshall, Acc. Chem. Res., 3, 139 (1970).

124. E.C. Constable, Polyhedron, _3_, 1039 (1984).

125. R.L. Bennett, M.I. Bruce and I. Matsuda,

Aust. J. Chem., _12_, 844 (1973).

126. P. Foley, R. Di Cosimo and G.M. Whitesides,

J. Am. Chem. Soc., _102_, 6713 (1980).

127. T.H. Tulip and D.L. Thorn, J. Am. Chem. Soc., _103_, 2448 (1981).

128. K. Nakatsn, K. Knoshita, H. Kanda, K. Isobe, Y. Nakamura and

S. Kawaguchi, Chem. Lett., 913 (1980).

129. R.H. Grubbs, A. Miyashita, M. Kiu and P. Burk,

J. Am. Chem. Soc., _100_, 2418 (1978).

130. C.C. McCarney and R.S. Ward,

J. Chem. Soc., Perkin I, 1600 (1975).

131. J.W. Munsen. "The Chemistry of Ketenes, Allenes and Related

Compounds", Part 1, Ed. S. Patai, John Wiley and Sons,

New York, p 165, 1980.

132. D.J. Patel, M.E.H. Howden and J.D. Roberts,

J. Am. Chem. Soc., _85_, 3218 (1963).

133. A.A. Botherby and C. Naar-Colin,

J. Am. Chem. Soc., _83_, 231 (1961).

134. K.B. Wiberg and B.J.Nist, J. Am. Chem. Soc., _83_, 1226 (1961).

135. T.H. Johnson and S. Cheng, J. Am. Chem. Soc., _101_, 5277 (1979).

136. J.Y. McDermott, J.F. White and G.M. Whitesides,

J. Am. Chem. Soc., _98_, 6521 (1976).

137. R. Di Cosimo, S.S. Moore, A.F. Sowinski and G.M. Whitesides,

J. Am. Chem. Soc., _104_, 124 (1982).

138. B.L. Booth and R.N. Haszeldine, J. Chem. Soc. (A), 157 (1966).

139. C.P. Casey, C.R. Cyr and J.A. Grant,

Inorg. Chem., 13, 910 (1974).

140. C.P. Casey, W.R. Brunsvold and J. Koch,

Inorg. Chem., 15, 1991 (1976).

141. J.A. Connor, M. Zafarani-Moattar, J. Bickerton, N.I. El Saied,

S. Suradi, R. Carson, G.A. Takhin, H.A. Skinner,

Organometallics, 1, 1166 (1982).

142. J. Halpern, Acc. Chem. Res., 15, 238 (1982).

143. J.D. Atwood, "Inorganic and Organometallic Reaction Mechanisms",

Brooks/Cole Publishing Company, Monterey, Calif., 1985.

144. C.P. Casey, R.A Boggs and R.L. Anderson,

J. Am. Chem. Soc., 94, 8947 (1972).

145. W.T. Brady, "The Chemistry of Ketenes, Allenes and Related

Compounds" part 1, Ed. S. Patai, John Wiley and Sons,

New York, p 279, 1980.

146. R.S. Ward. Reference 145, p223.

147. H. Meier and K.P. Zeller,

Angew. Chem. Int. Edn. Eng., 14, 32 (1975).

148. S.D. Darling and R.L. Kidwell,

J. Org. Chem., 33, 3974 (1968).

149. W.T. Brady and L. Smith, J. Org. Chem., 36, 1637 (1971).

150. D.C. England and C.A. Krespan,

J. Am. Chem. Soc., 88, 5582 (1966).

151. H. Staudinger, E. Anthes and H. Schneider,

Chem. Ber., 46, 3539 (1913)

152. C.D. Hurd, Organic Synth., Coll. Vol. 1, 330 (1941).

153. V. Sankaran, Y. Venkateswarln and S. Bai,

Chem. Ind., 1592 (1969).

154. C.D. Hurd and S. Mayao, J. Am. Chem. Soc., 76, 5563 (1954).

155. M.A. Pericas and F. Serratosa, Tetrahedron Lett., 4437 (1977).

156. W. Weyler, W.G. Duncan, M.B. Liewen and H.W. Moore,

Organic Synth., 55, 32 (1976).

157. H. Staudinger, Chem. Ber., 38, 1735 (1905).

158. L.M. Baigrie, D. Lenoir, H.R. Seikaly and T.T. Tidwell,

J. Org. Chem., 50, 2105 (1985).

159. W.C. Smith and D.G. Norton, Organic Synthesis Coll. Vol. 4,

p348, Wiley, New York, 1963.

160. T. Bauch, A. saunders, C.V. Magatti, P. Waterman D. Judelson and

W.P. Giering, J. Organomet. Chem., 99, 269 (1975).

161. K.R. Wursthorn, H.G. Kuivila and G.F. Smith,

J. Am. Chem. Soc., 100, 2779 (1978).

162. S. Andreades and H.D. Carlson, Organic Synthesis Coll. Vol. 4,

p 679, Wiley, New York, 1963.

163. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis",

Vol. 1, John Wiley and Sons. Inc., New York, p 528, 1967.

167. W.T. Brady and T.C. Cheng, J. Org. Chem., 42, 2336 (1977).

168. R.L. Danheiser, S.K. Gee and H. Sand,

J. Am. Chem. Soc., 104, 7670 (1982).

169. D.A. Jackson, M. Rey and A.S. Dreiding,

Helv. Chim. Acta., 66, 2330 (1983).

170. H. Mayr, Angew. Chem. Int. Ed. Engl., 14, 500 (1975).

171. W.S. Trahanovsky, B.W. Surber, M.C. Wilkes and M.M. Preckel,

J. Am. Chem. Soc., 104, 6779 (1982).

172. G.J. Baxter, R.F.C. Brown, F.W Eastwood, K.H. Harrington,
     Tetrahedron Lett., 4283 (1975).

173. C.M. Sharts, M.E. McKee, R.F. Steed,
     J. Fluorine Chem, 14, 351 (1979).

174. R.F.C. Brown an F.W. Eastwood, "The Chemistry of Ketenes,
     Allenes and Related Commpounds´, Part 2, Ed. S. Patai,
     John Wiley and Sons, New York, pp 757, 1980.

175. O.L. Chapman, C.C. Chang, J. Kolc, N.R. Rosenquist and
     H. Tomioka, J. Am. Chem. Soc., 97, 6586 (1975).

176. J.L. Ripoll and M. Lasne, Tetrahedron Lett., 5201 (1978).

177. R.D. Brown, P.D. Godfrey, B. Kleibomer, R. Champion and
     P.S. Elmes, J. Am. Chem. Soc., 106, 7715 (1984).

178. M. Marsi, K.C. Brinkman, C.A. Lisensky, G.D. Vaughn and
     J.A. Gladysz, J. Org. Chem., 50, 3396 (1985).

179. F. Calderazzo, K. Noack, V. Schaerer,
     J. Organomet. Chem., 6, 265 (1966).

180. P.B.D. de La Mare and B.E. Swedland, "The Chemistry of the
     Carbon-Halogen Bond", Part 1, Ed. S. Patai, Wiley Interscience,
     New York, pp 534, 1973.

181. E.J. Baerends, D.E. Ellis and P. Raos,
     Chem. Phys., 2, 41 (1973).

182. T. Ziegler, personal communication.

183. T. Ziegler, L. Versluis and V. Tschinke,
     J. Am. Chem. Soc., 108, 612 (1986).

184. D. Bach, B.A. Coddens and G.J. Wolber,

J. Org. Chem., 51, 1030 (1986)

185. B.A. Frenz and J.A. Ibers, Inorg. Chem., 11,1109 (1972).

186. W.P. Giering, M. Rosenblum and J. Tancreole,

    J. Am. Chem. Soc., 94, 7170 (1972).

187. M.L.H. Green, A.G. Massey, J.T. Moelwyn-Hughes and P.L.J Nagy,

    J. Organomet. Chem., 8, 511 (1967).

188. O. Eisensten and R. Hoffmann,

    J. Am. Chem. Soc., 103, 4308 (1981).

189. J.W. Thorpe and J. Warkentin, Can. J. Chem., 51, 972 (1973).

190. C. Charrier, J. Colin, J.Y. Merour and J.L. Roustan,

    J. Organomet. Chem., 162, 57 (1978).

191. D.H. Gibson, W. Hsu and F.V. Ahmed,

    J. Organomet. Chem., 215, 379 (1981).

192. M. Leyendecker and C.G. Kreiter,

    J. Organomet. Chem., 249, C31 (1983).

193. W.D. Banister, M. Green and R.N. Hazeltine,

    J. Chem. Soc. (A), 194 (1966).

194. M. Green and R.I. Hancock, J. Chem. Soc. (A), 109 (1968).

195. R.D. Ernst, Acc. Chem. Res., 18, 56 (1985).

196. D.R. Wilson, R.D. Ernst, T.H. Cymbaluk,

    Organometallics, 2, 1220 (1983)

197. D. Seyferth, E.W. Goldman and J. Pornet,

    J. Organomet. Chem., 208, 189 (1981).

198. C.G. Kreiter and M. Leyendecke,

    J. Organomet. Chem., 162, 225 (1985).

199. M.J. Bennett and M.I. Bruce, Aust. J. Chem., 28, 1141 (1975).

200. M. de los Angeles Paz-Sandoval and P. Powel,

    Organometallics, 3, 1026 (1984).

201. J.F. Richardson, personal communication.

202. M.R. Churchill, K.N. Amoh and H.J. Wasserman,

    Inorg. Chem., 20, 1609 (1981).

203. H.M. Seip and R.Seip, Acta Chem. Scand., 24, 3431 (1970).

204. C.F. Putnick, J.J. Welter, G.D. Stucky, M.J. D'Anilo,

    B.A. Sosinsky, J.F. Kirner and E.L. Muetterties,

    J. Am. Chem. Soc., 100, 4107 (1978).

205. B.J. Brisdon, D.A. Edwards, J.W. White, M.G.B. Drew,

    J. Chem. Soc. Dalton Trans., 2129 (1980).

206. D.F. Shriver "The Manipulation Of Air Sensitive Compounds",

    McGraw-Hill, New York, 1969.

207. G.W. Cramer, A.B. Levy and M.M. Midland "Organic Synthesis via

    Boranes" , Ed. H.C. Brown, John Wiley, New York, 1975.

208. W.C. Still, M. Kahn and A. Mitra,

    J. Org. Chem., 43, 2923 (1978).

209. K.A.M. Kremer and P. Helquist, Organometallics, 3, 1743 (1984).

210. R.M. Hoyte and D.B. Denney, J. Org. Chem., 39, 2607 (1974).

211. F.L. Cohen and C.D.Hurd, J. Am. Chem. Soc., 53, 1920 (1931).

212. K. Dittmer, S.J. Cristol and H.L. Goering,

    J. Am. Chem. Soc., 70, 3315 (1948).

213. S. Sustman and C. Ruchardt, Chem. Ber., 3043 (1975).

214. Y. Ogata and S. Watanabe, J. Org. Chem., 45, 2831 (1980).

215. (a) R.F.C. Brown, F.W. Eastwood and K.J. Harrington,

    Aust. J. Chem.,27, 2373 (1974).

(b) B. Rosebeek, PH.D. Thesis, Rijksuniversiteit Groningen (1961).

216. M.V. Newman and J.A. Cella, J. Org. Chem., 39, 2084 (1974).

217. L.N. Owen and M.V.S. Suttanbwa, J. Chem. Soc,, 3089 (1949).

218. W.H. Perkin and W. Sinclair, J. Chem. Soc., 61, 41 (1892).

219. K. Frendenberg and L. Markert Ber., 60, 2447 (1927).

220. R. Phillips, J. Chem. Soc., 2981 (1926).

221. F. Bohlman and C. Zdelro, Chem. Ber., 106, 3774 (1973).

222. A. Loffler, F. Noris, W. Taub, K.L. Svanholt and A.S. Dreiding, Helv. Chim. Acta, 53, 403 (1970).

223. J. Colonge and R. Chambard, Compt. Rend., 223, 1461, (1951).