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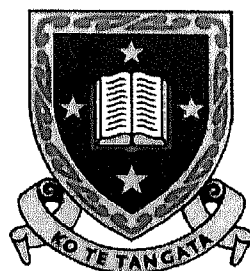
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Organomanganese Compounds in Organic Synthesis



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A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Philosophy

At the University of Waikato by

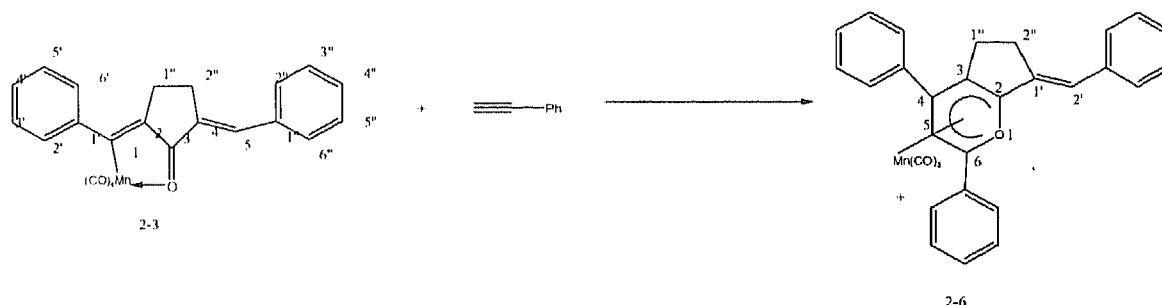
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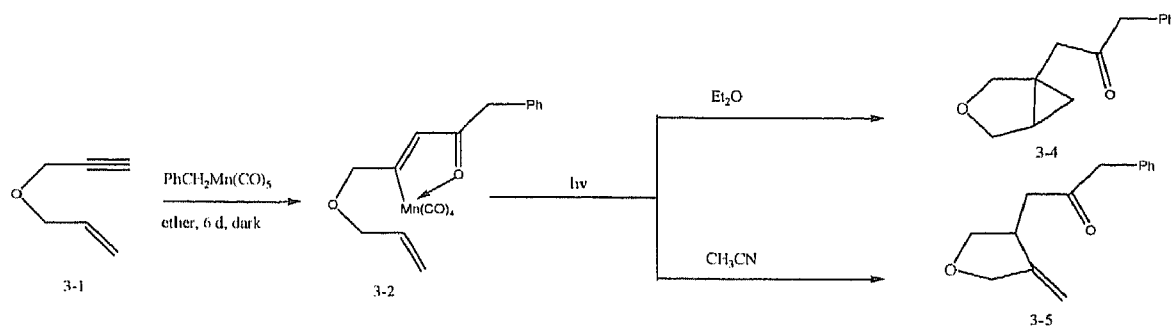
Abstract

This thesis describes the preparation and reactions of some cyclomanganated chalcones, dienones and aryl ketones.

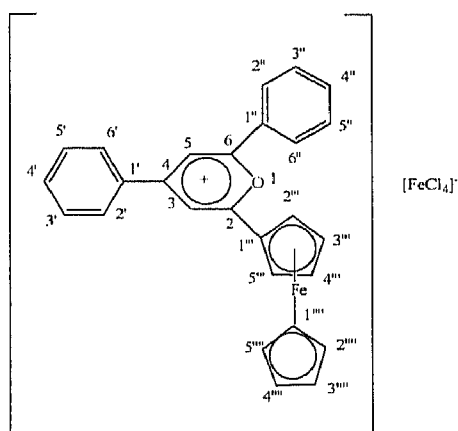
Investigation has previously been undertaken into the reaction of cyclomanganated chalcones and dienones with alkynes to give both pyranyl and cycloheptadienyl $\text{Mn}(\text{CO})_3$ complexes. In the current study, the reaction was further investigated with a cyclomanganated dienone derived from a cyclic ketone which gave only the (pyranyl) $\text{Mn}(\text{CO})_3$ complex (2-6) and not the cycloheptadienyl product as consistent with a mechanism previously proposed.



Also extended in the current study was previous work involving the methylmanganese pentacarbonyl-mediated transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond. In the current study, benzylmanganese pentacarbonyl was used instead of methylmanganese pentacarbonyl under similar conditions. In the current study however, the type of product that formed in diethyl ether (3-4) was the one dominant in acetonitrile in the $\text{MeMn}(\text{CO})_5$ study, and that formed in acetonitrile (3-5) was the dominant product type in diethyl ether (3-4). There was no apparent explanation for this reverse reactivity.



Ferrocenyl pyrylium salts of the type 5-5 have been prepared using a new route to ferrocenyl pyrylium from cyclomanganated chalcones and ferrocenylethyne. UV-visible and electrochemical properties of the pyrylium salts have been investigated.



5-5

The ferrocenyl pyrylium salt (5-5) was obtained by the oxidation of [2-ferrocenyl-4,6-diphenyl- η^5]-pyranyltricarbonylmanganese (5-6). The crystal structure of 5-6 was also determined.

Acknowledgments

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List of Abbreviations

M	metal atom	Tol	4-tolyl
TM	transition metal atom	Xy	2,6-xylyl
R	organic substituent	Mes	2,4,6- mesityl
L	ligand	Cp	cyclopentadienyl
X	halogen	dppe	1,2-(diphenyldiphosphino)ethane
Me	methyl	dmpe	1,2-(dimethyldiphosphino)ethane
Et	ethyl	DMAD	dimethyl acetylenedicarboxylate
Pr ^l	<i>iso</i> -propyl	THF	tetrahydrofuran
Bu	butyl	DMSO	dimethyl sulfoxide
Bu ^l	<i>tert</i> -butyl	Ether	diethyl ether
Cy	cyclohexyl		
Ar	aryl substituent		
Ph	phenyl		

ESMS	electrospray mass spectroscopy
IR	infra-red spectroscopy
EI-GC/MS	electron impact gas chromatography coupled mass spectroscopy
P.L.C.	preparative layer chromatography

M	molecular ion (EI-GC/MS), ESMS)	<i>J</i>	coupling constant (NMR)
s	singlet (NMR), strong (IR)	<i>m/z</i>	mass to charge ratio
d	doublet (NMR)	b.p.	boiling point
m	medium (IR), multiplet (NMR)	m.p.	melting point
br	broad (IR, NMR)		
t	triplet (NMR)		
vs	very strong (IR)		
ppm	chemical shift (NMR)		

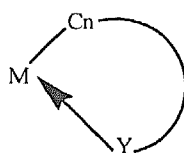
Chapter 1. Introduction

1.1 Cyclometalation

Cyclometalated complexes have been of increasing interest to researchers over the past 30 years or so as is evident from the many comprehensive reviews that are available^{1,2,3,4}. Cyclometalated complexes have a wide variety of uses in organic synthesis⁵, catalysis⁶, asymmetric transformations⁷, and photochemistry⁸. They also mimic some intermediates in catalytic transformations⁹ and show promise as potential biologically active materials¹⁰.

1.1.1 Definition

The formation of a cyclometalated complex involves the coordination of a ligand (Y) to a metal centre (M) to form a stable ring (figure 1.1).



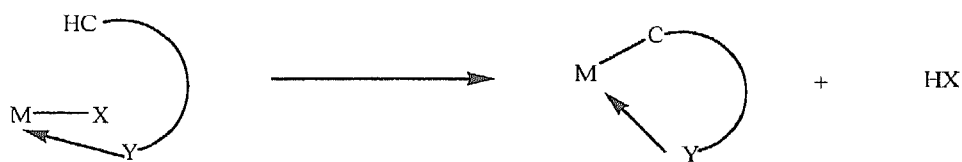
M- Metal

Y- Coordinating atom or group

$n \geq 1$

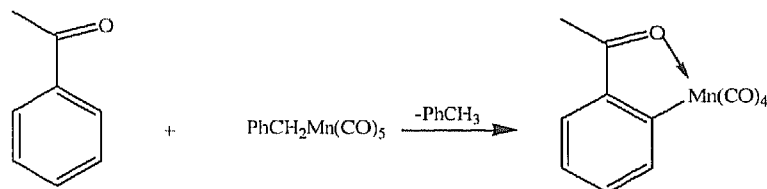
Figure 1.1: Cyclomanganated complex involving the coordination of a ligand (Y) to a metal centre (M)

The ligand (Y) is bonded to the metal (M) by the M-C sigma bond, with Y acting as a donor group. The M-C bond is possibly formed by the intramolecular rupture of a C-H bond within the coordination complex as shown by the following equation, (X=halogen or alkyl).



The preparation of a cyclomanganated complex normally involves the reaction of an organic precursor with a manganese carbonyl complex such as methylmanganese pentacarbonyl ($\text{MeMn}(\text{CO})_5$) or benzylmanganese pentacarbonyl ($\text{PhCH}_2\text{Mn}(\text{CO})_5$). Some other indirect routes are available.

It was in 1975 that Kaesz's group^{11,12,13,14} reported the preparation of the first orthomanganated aromatic ketone. Metalation of aromatic substrates normally occurs in the position *ortho* to the donor function Y and this has given rise to the term "orthometalation". The preparation of the orthomanganated acetophenone is shown by Equation 1.1.



Equation 1.1: Preparation of cyclomanganated acetophenone

In the case of orthomanganated complexes, the coordinating group directs the manganese to the carbon *ortho* to the functional group. Varieties of functional groups have been used in the preparation of cyclomanganated complexes including aldehydes¹⁵, ketones¹⁶, esters, thioesters¹⁷, imines¹⁸, imidazoles¹⁹ and benzamides¹⁵. A range of triphenylphosphine chalcogenides²⁰ and triphenylphosphites²¹ has also been orthomanganated. Figure 1.2 gives some such examples:

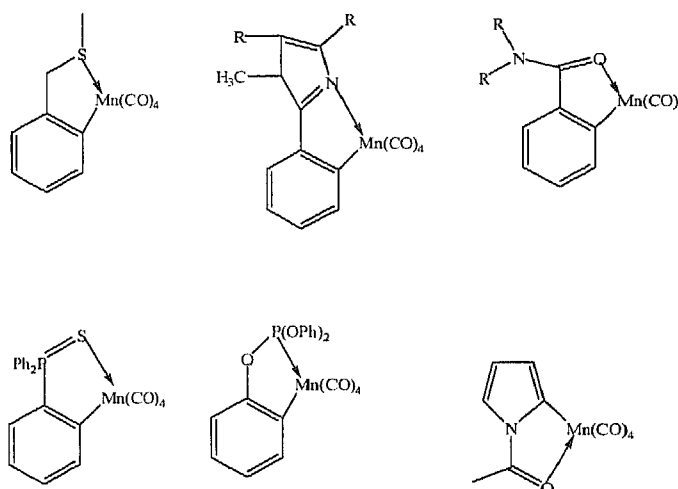


Figure 1.2: Cyclomanganated complexes of a variety of functional groups

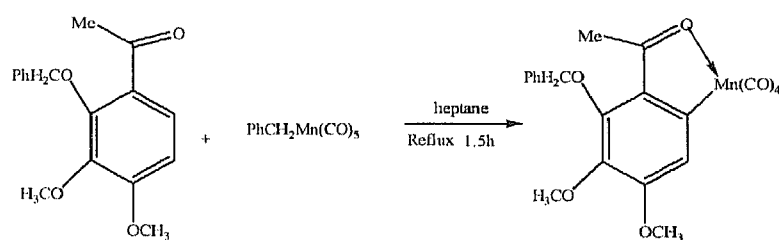
Because of the favourable geometry and entropy considerations, the five-membered ring is the most common amongst the cyclomanganated complexes. X-ray crystal structure studies have shown that the five-membered ring configuration has closest to the ideal geometry (bond angles and bond lengths) of all the possible rings². However, cyclomanganated complexes having sulphur or phosphorus as the donor atom have shown an increasing tendency to form three- or four-membered rings compared to corresponding complexes having oxygen or nitrogen donor atoms. Platinum and palladium appear to be the metals found most commonly in cyclometalated compounds because of their widespread use in organic synthesis.

1.1.2 Cyclomanganated Aryl Compounds

Kaesz and co-workers²² were the first to perform the preparation of cyclomanganated aryl ketones. Before the work of the Kaesz group, the ortho-directing effects of oxygen functional groups in the metallation of aromatic rings were established only for main group metals such as lithium²³ or thallium²⁴. Kaesz and co-workers tried to metallate various aromatic ketones and quinones with $\text{MeM}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$).

Cyclometallation reactions²⁵ of arenes with *N*-donor groups were amongst the first to be done with $\text{PhCH}_2\text{Mn}(\text{CO})_5$. Bruce *et al.*³ noticed that the benzyl compound was more efficient at promoting these reactions than the methyl compound and the benzyl compound also gave higher yields.

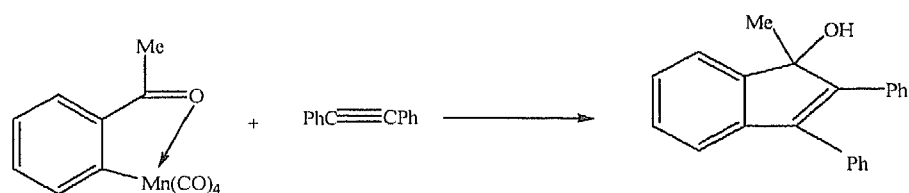
A considerable number of manganated aryl ketones have been prepared since then. These include those prepared by Gommans²⁶, Robinson²⁷, and Cooney²⁸ using $\text{PhCH}_2\text{Mn}(\text{CO})_5$ instead of $\text{CH}_3\text{Mn}(\text{CO})_5$. An example is the reaction²⁶ of 3-benzyloxy-4,5-dimethoxyacetophenone with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ to give the manganated product (Equation 1.2).



Equation 1.2: Reaction of 3-benzyloxy-4,5-dimethoxyacetophenone with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ to give the manganated product

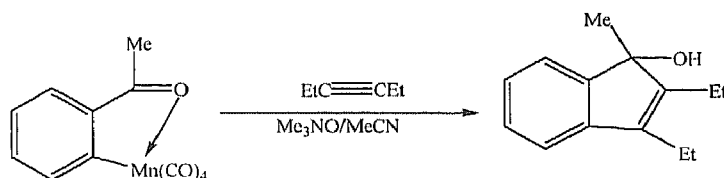
1.1.3 Reactions of Cyclomanganated Aryl compounds

Robinson²⁷ showed that the uncatalysed reaction of cyclomanganated aryl ketones with alkynes like diphenylacetylene gave indenols (Equation 1.3).



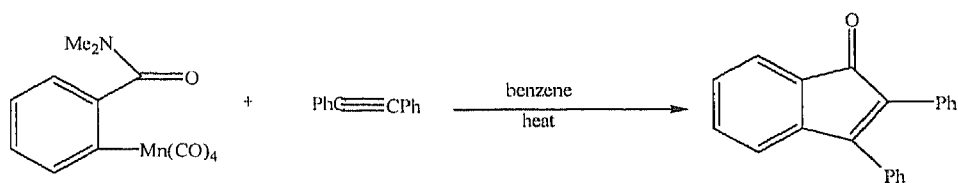
Equation 1.3: Reaction of cyclomanganated aryl ketones with alkynes like diphenylacetylene to give indenols

The Liebeskind³¹ group obtained similar results by oxidative decarboxylation with trimethylamine oxide (Equation 1.4)



Equation 1.4: Oxidative decarboxylation of manganted acetophenone with trimethylamine oxide

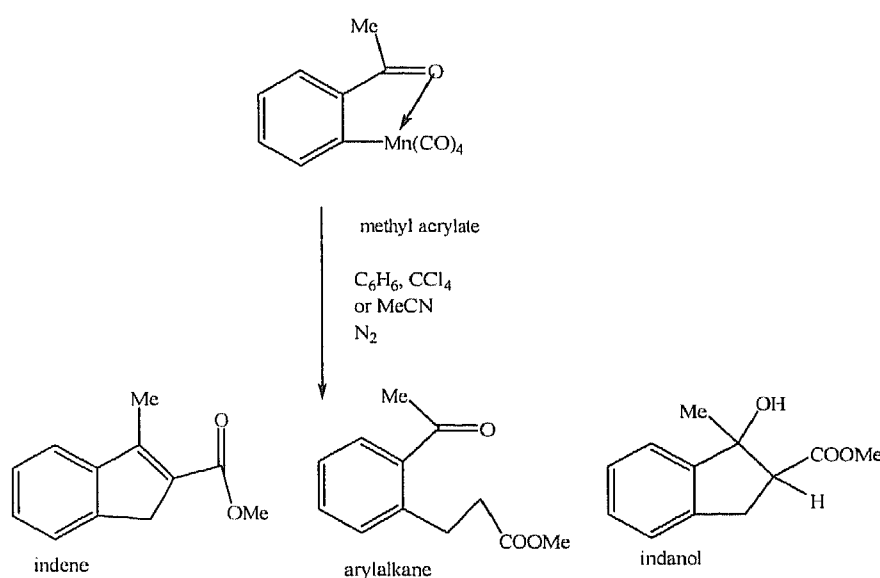
Robinson²⁷ also showed that reactions of alkynes with cyclomanganated benzamides did not form indenols but indenones (Equation 1.5)



Equation 1.5: Reactions of alkynes with cyclomanganated benzamides to form indenones

1.1.4 Uncatalysed reactions of alkenes with cyclomanaganated compounds

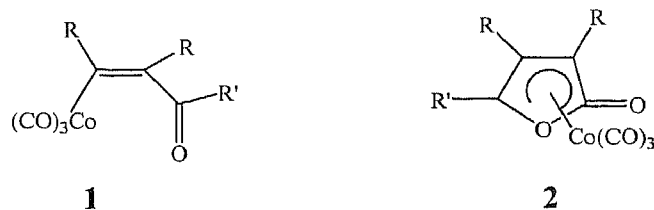
Previous studies²⁸ have found that cyclomanaganated aryl ketones couple effectively with alkenes like methyl acrylate. Depending on the solvents used, three main products formed. When benzene was used as the solvent, indene and/or arylalkanes formed and in carbon tetrachloride, indenenes and indanols were formed predominantly. (Equation 1.6)



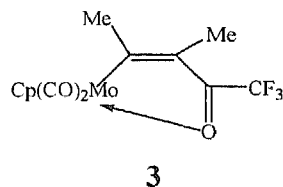
Equation 1.6: Reaction of cyclomanaganated aryl ketones (manganated acetophenone) with methyl acrylate in different solvents²⁸

1.1.5 Cyclometallated enones

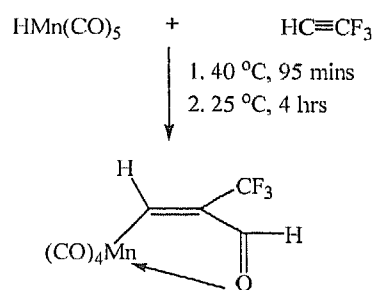
One of the first known cyclometallated enones other than of manganese was formed by the reaction of acyl compounds $R'COCo(CO)_4$ with acetylenes^{29,30}. The products were η^3 -bonded lactonyl complexes of the type **2** generated from the intermediates of type **1**¹³.



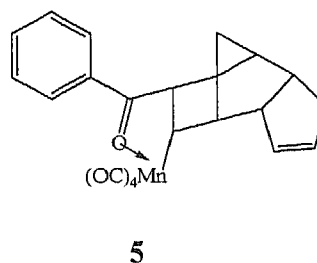
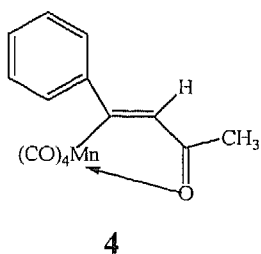
Stone³² later carried out reactions of acetylenes with $\text{RM}(\text{CO})_3\text{Cp}$ and $\text{RC}(\text{O})\text{M}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Mo}, \text{W}$). Stone's reaction of $\text{CF}_3\text{Mo}(\text{CO})_3\text{Cp}$ with but-2-yne in hexane gave **3**.



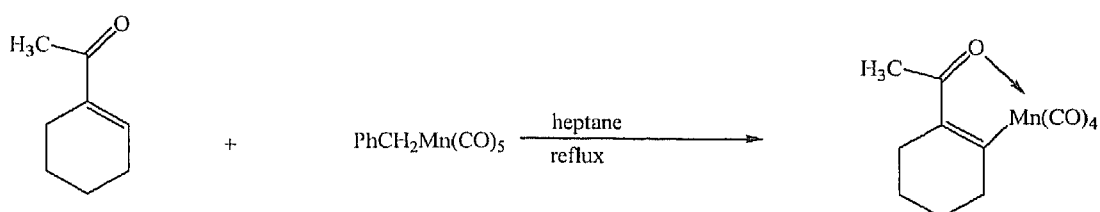
Cyclometallated enones for a variety of other metals like tungsten, nickel, ruthenium and platinum are also known. The equation below gives one of the initial syntheses of manganated enones.



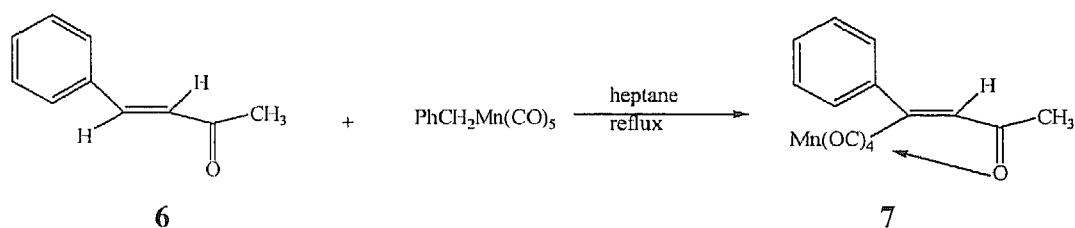
The work was extended by Booth and Hargreaves^{33,34} using $\text{RMn}(\text{CO})_5$ ($\text{R} = \text{Me}, \text{Ph}$) with alkynes. Such reactions when carried out in diethyl ether at room temperature in glass ampoules over a period of 4-10 days gave cyclomanganated enones of type **4**. Similar successful reactions were also carried out by Booth *et al.*³³ involving $\text{Ph}(\text{CO})\text{Mn}(\text{CO})_5$ with alkenes to give cyclomanganated products like **5**. This reaction involved dicyclopentadiene, in hexane, at 20°C for 7 days in a sealed ampoule.



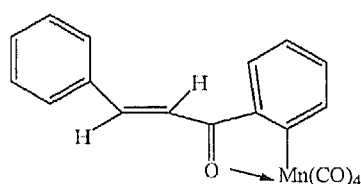
Amongst later studies, Cabral³⁵ reported the first direct preparation of a cyclomanganated enone. This was prepared by refluxing 1-acetyl-1-cyclohexene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane.



Similarly, Robinson²⁷ carried out the reaction that led to the preparation of **7** in 35% yield.



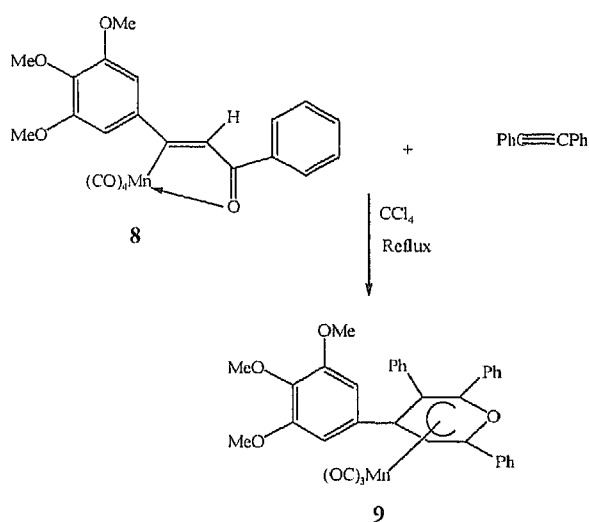
A second product was later isolated by Woodgate *et al.*³⁶ from the manganation of the chalcone where the methyl group is replaced by a benzene in **6** above. This was the ring manganated chalcone below.



In section 1.1.7, an example of a cascade reaction by Lee *et al.*³⁹ is discussed. The reaction also involves the formation of a manganated enone by the reaction of an enyne with $\text{PhCH}_2\text{Mn}(\text{CO})_5$. This work is discussed in detail in chapter 3 of this thesis.

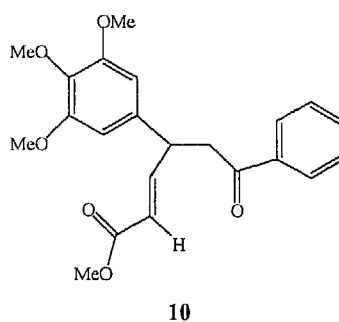
1.1.6 Reactions of Cyclomanganated Enones

Apart from the work done by Tully³⁷, few investigations into the reactions of cyclomanganated enones have been carried out. Equation 1.7 for example shows the reaction of diphenylacetylene with a cyclomanganated enone **8** to give a tricarbonylmanganese complex **9**.

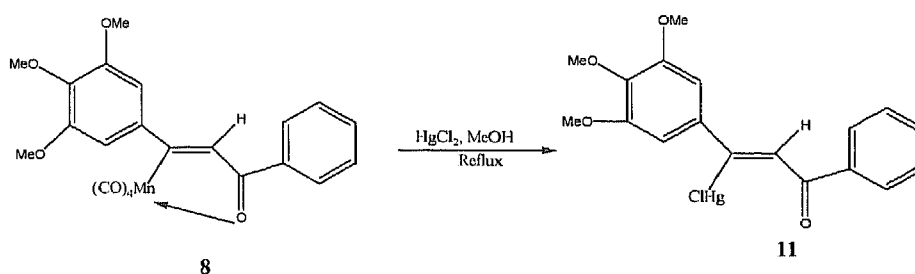


Equation 1.7: Reaction of phenylacetylene with a cyclomanganated enone to give a tricarbonylmanganese complex

8 was reacted with methyl acrylate in carbon tetrachloride to give **10** in high yield.



8 reacted with mercury (II) chloride³⁷ to give [1-phenyl-3-(3,4,5- trimethoxyphenylprop-2-en-yl- κC^3 -1-one mercury(II) chloride (**11**), equation 1.8.

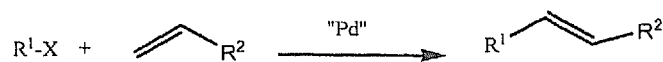


Equation 1.8: Reaction of a cyclomanganated enone with mercury

1.1.7 Cascade reactions

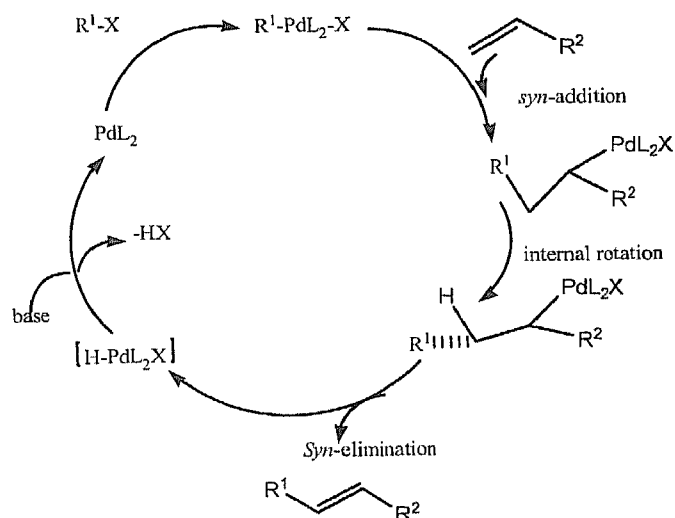
Cascade reactions provide valuable pathways especially for the construction of various carbo- and heterocyclic systems with two or more annelated rings. This area of cascade chemistry is long established for palladium and has only recently been extended to manganese.

The following Scheme (Scheme 1.9) shows the reaction modes of palladium-carbon bonds. The initial step of the Heck reaction involves the formation of a new metal carbon bond. This bond in principle can undergo any of the typical σ -M-C bond reactions. If the β -hydride elimination is slow or if it could be totally suppressed, the palladium species can undergo a number of reactions with new C-C bonds forming. If appropriate substrates are chosen, the transformations can occur as a sequence of events in a single synthetic operation.



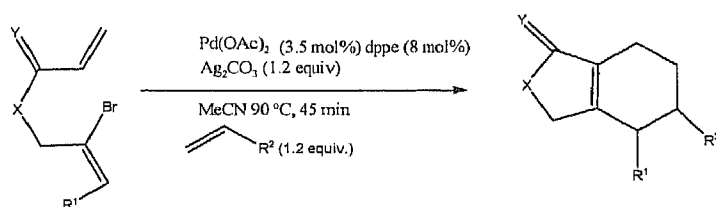
R^1 = alkenyl, aryl, allyl, alkynyl, benzyl, alkoxy carbonylmethyl

R^2 = alkyl, alkenyl, aryl, CO_2R^1 , OR^1 , SiR_3 etc



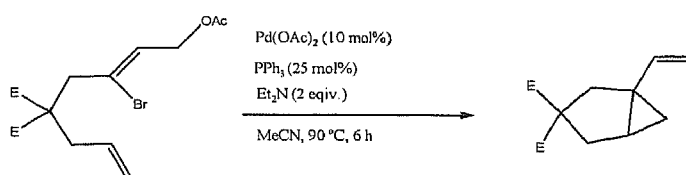
Scheme 1.9: The reaction modes of palladium-carbon bonds (the mechanism of the Heck reaction)

Given below are two examples of cascade processes of the type to be considered in the current research. Further examples are discussed in chapter 3. An example is of heteroatom-containing 2-bromo-1,6-diene reacting in the presence of dienophiles to give heterocycles in good yields³⁸.



Scheme 1.10: Reaction of a heteroatom-containing 2-bromo-1,6- dienes reacting in the presence of a dienophile to give a heterocycle.

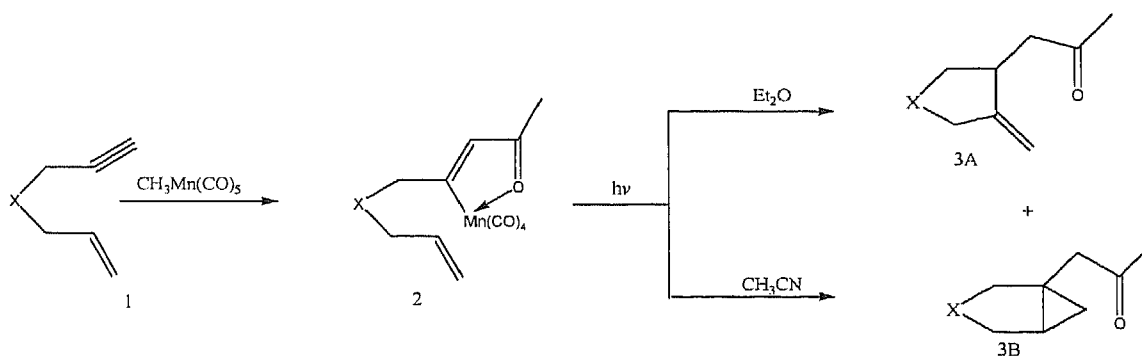
On the other hand treating the 1-acetoxymethyl-2-bromo-1,6-diene with $\text{Pd}(\text{OAc})_2$ gives the vinylbicyclo[3.1.0]hexane derivatives as shown by the following scheme. The mechanism of this transformation is however not clear³⁸.



Scheme 1.11: Treatment of the 1-acetoxymethyl-2-bromo-1,6- diene with $\text{Pd}(\text{OAc})_2$ to give the vinylbicyclo[3.1.0]hexane derivative

The use of manganese in such cyclisation reactions has been rare. Two examples are briefly given here and these are further discussed in chapter 3 where some reaction schemes are also discussed.

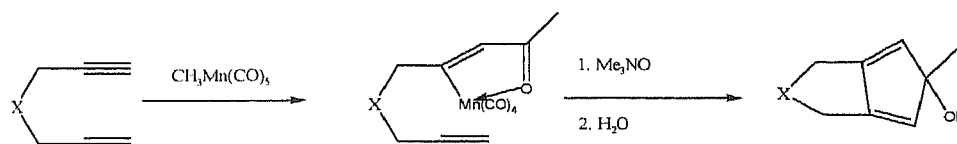
Lee *et al.*³⁹ reported the transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond using methylmanganese pentacarbonyl. The following scheme shows the general transformation that was carried out by Lee *et al.*³⁹. The dominant products in ether and acetonitrile are shown.



Scheme 1.12: The transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond using methylmanganese pentacarbonyl

Once the starting enyne **1** is reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$, it forms a manganated enone similar to those discussed in section 1.1.5 as reported by Tully³⁷. The difference is the presence of the intramolecular alkene within the Lee *et al.*³⁹ manganated enone which reacts further to give cyclised products as shown in Scheme 1.12.

Chung⁴⁰ and his team reported the carbonylative $\text{MeMn}(\text{CO})_5$ mediated carbocyclisation of 1,6-diynes to give [2,3]-fused bicyclic cyclopentadiene derivatives by incorporating carbon monoxide as hydroxyl and the methyl group as shown by scheme 1.13.

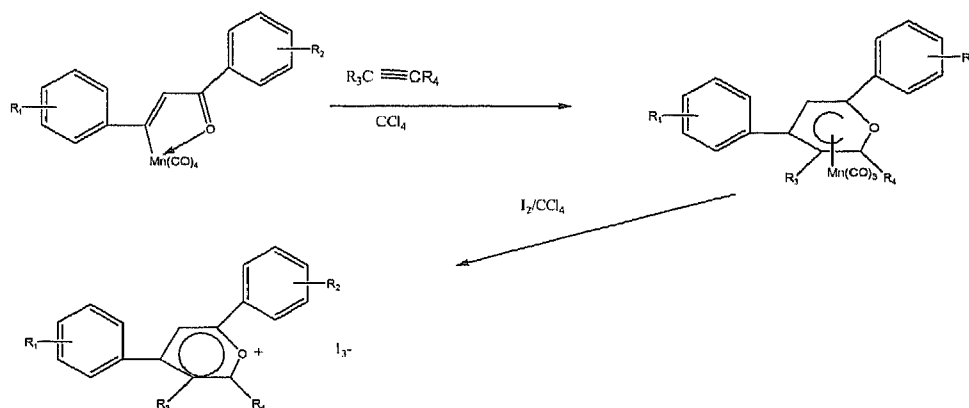


Scheme 1.13: The carbonylative $\text{MeMn}(\text{CO})_5$ mediated carbocyclisation of 1,6-diynes to give [2,3]-fused bicyclic cyclopentadiene derivatives by incorporating carbon monoxide and a methyl group as hydroxyl and methyl group

1.1.8 Pyrylium salts

Pyrylium salts function as intermediates for an extraordinary variety of syntheses. They are interesting to study in themselves as the replacement of CH in the benzene ring by O^+ modifies the electron distribution.

Pyrylium salts were prepared by Tully *et al.*⁴¹ from (pyranyl) $\text{Mn}(\text{CO})_3$ complexes by reacting them with iodine to give pyrylium iodide salts. The pyranyl complexes were prepared from β -manganated chalcones with alkynes like phenyl acetylene. These pyranyl complexes provide a ready source of pyrylium salts. Scheme 1.14 gives the general equation for the reaction by which the pyrylium triiodide salts were prepared.



Scheme 1.14: Reaction of (pyranyl) $\text{Mn}(\text{CO})_3$ complexes by iodine to give pyrylium triiodide salts

Unlike other ring systems, the pyrylium ring is as easily opened as it is formed. Pyrylium and pyrone rings as well as the benzo derivatives of the systems appear in many natural products and thus are of interest to natural product chemists. Later in chapter five, more is discussed on the pyrylium ions, in particular the preparations, properties and reactions of the ferrocenyl-substituted pyrylium ions.

However, it is worth mentioning here that ferrocenyl-substituted pyrylium ions have interesting electrochemistry. Apart from synthesizing and characterizing pyrylium ions from cyclomanganated chalcones and ferrocenylethyne, their electrochemistry was to be studied in the current study. An example of such a study was by Shaw *et al.*⁴² which involved the synthesis and electrochemistry of iron-pyrylium complexes. An example of their iron-pyrylium complex is given by figure 10 below.

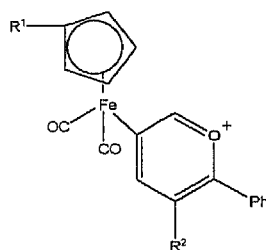


Figure 10: An example of an iron-pyrylium complex

Figure 11 shows the cyclic voltammogram of the complex (when R^1 is Ph and R^2 is a CH_3) in THF at 22°C and at scan rates larger than 400 mV/s it reveals a chemically irreversible reduction at -1.49 V versus Cp_2Fe . In comparison, $Fp-CH_3$ is reduced at a more negative potential which suggests that the pyrylium ring is reduced first).

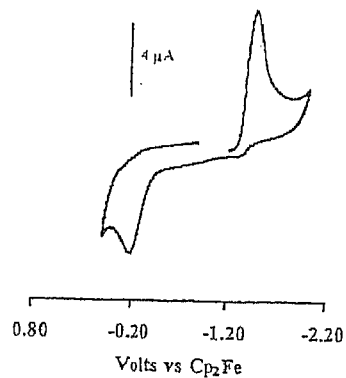


Figure 11: Cyclic voltammograms of the complex in figure 10 in THF at 22°C, Shaw, M. J. et. al⁴²

Chapter 1 References

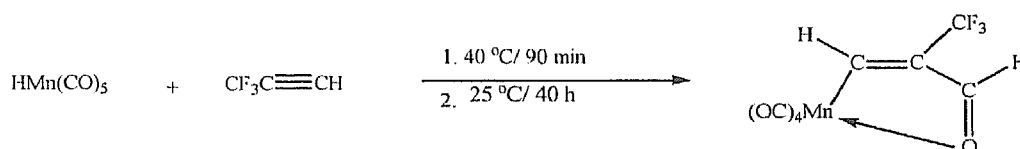
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Chapter 2: Pyranyl Complexes from Manganated Enones and Dienones

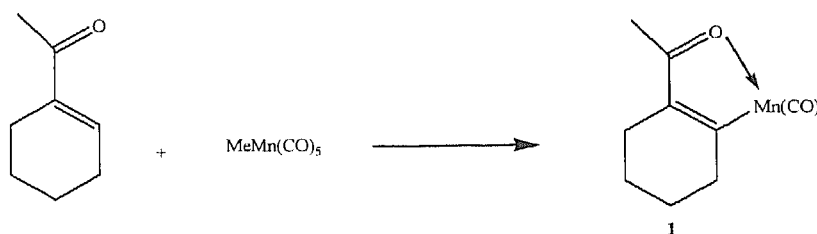
2.1 Introduction

Scheme 1 shows the preparation of one of the first reported cyclomanganated enones. It was prepared from the reaction of $\text{HMn}(\text{CO})_5$ with 3,3,3-trifluoropropyne¹. The most probable sequence of this reaction leading to the formation of the final product is the initial formation of the formyl group by the insertion of CO into the Mn-H bond. This is followed by the insertion of the alkyne group to form the acyl-coordinated manganocycle.



Scheme 1: Preparation of one of the first reported cyclomanganated enones from the reaction of $\text{HMn}(\text{CO})_5$ with 3,3,3-trifluoropropyne¹

This work was later extended to a wide range of $\text{RMn}(\text{CO})_5$ / alkyne combinations². Cabral³ reported the first direct cyclomanganation of an enone. Heating 1-acetylcyclohexene and $\text{MeMn}(\text{CO})_5$ in heptane gave **1** (Scheme 2) in good yield. The same process was applied by Robinson⁴ and Tully⁵ in the cyclomanganation of 4-phenylbut-3-en-1-one and of 1,3-diarylprop-2-en-1-ones respectively forming **2** and **3** (Figure 1).



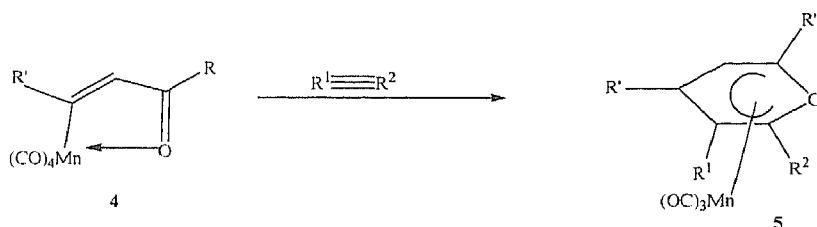
Scheme 2: Heating 1-acetylcyclohexene and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane to give **1**



Figure 1: Cyclomanganation products of 4-phenyl-3-en-1-one and of 1,3-diarylprop-2-en-1-ones

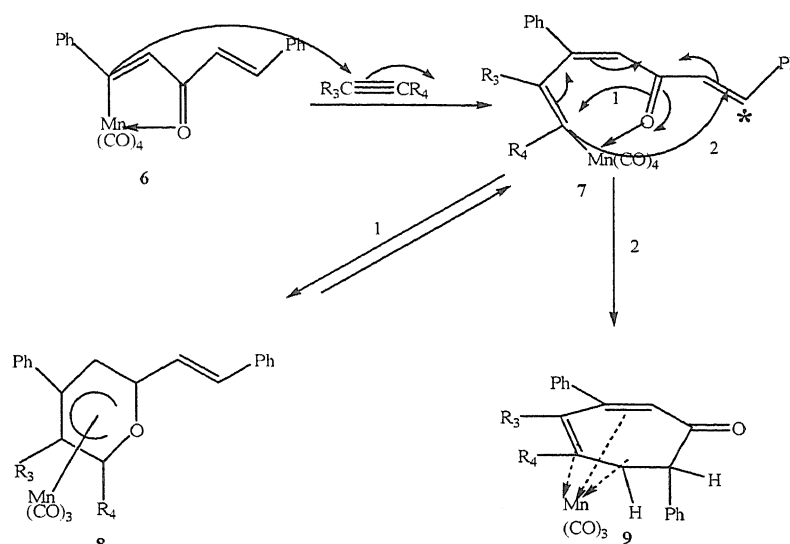
Manganation reactions of 1,3-diarylprop-2-en-1-ones can form two products, with manganation occurring either at the β -carbon or α -aryl carbon sites. Altering the substituents on either of the aryl rings can influence the manganation sites⁶.

Tully⁷ described a reaction of cyclomanganated enones of the type **4** with alkynes to form (pyranyl) $\text{Mn}(\text{CO})_3$ complexes **5** (Scheme 3), which were analogous to the pyranyl products obtained in low yield from the reaction of $\text{RMn}(\text{CO})_5$ with excess alkynes⁸. This type of product therefore was not unexpected.



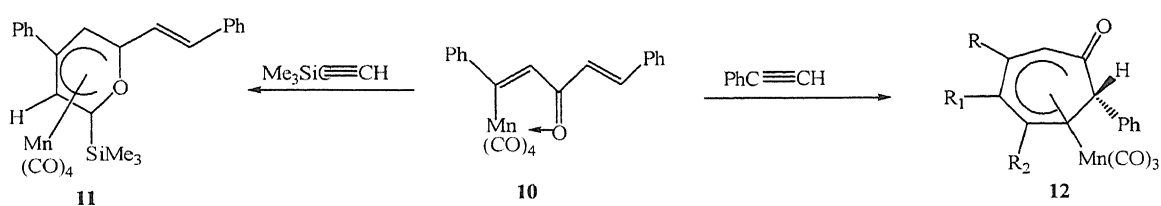
Scheme 3: Reaction of cyclomanganated enones of the type **4** with alkynes to form (pyranyl) $\text{Mn}(\text{CO})_3$ complexes **5**⁷

Similarly, the coupling with alkynes of manganated dienones (**6**, Scheme 4), led to the two primary products^{5,9} **8** and **9** (Scheme 4). Note that pyranyl complexes can also be considered as oxocyclohexadienido complexes in which the ligand formally has a negative rather than a positive charge. The O does not coordinate to the metal and the carbon chemical shifts are similar to cyclopentadienyl carbon shifts.



Scheme 4: The coupling with alkynes of manganated dienones

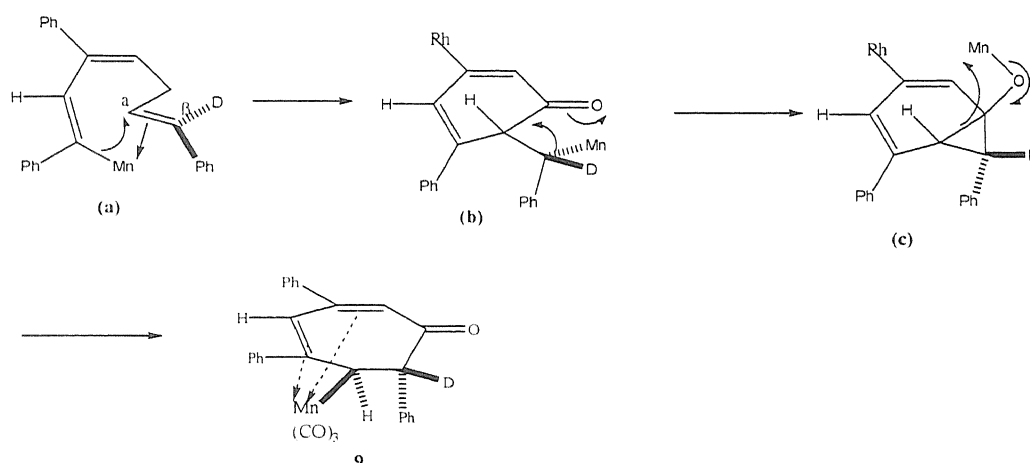
Mace^{10a} in his studies attempted to determine the factors influencing the production of the two products, pyranyl (**8**, Scheme 4) and oxocycloheptadienyl, (**9**, Scheme 4) which was earlier studied by Tully⁵. He found that the products formed depended on the diarylpentadienone and the alkyne used in the reaction¹⁰. The cyclomanganated diphenylpentadienone (**10**, Scheme 5a) reacts with trimethylsilyl acetylene to form the pyranyl product (**11**, Scheme 5a), similar to that seen for the diarylpropenones. When **10** (Scheme 5a) was reacted with phenyl acetylene under the same conditions, the cycloheptadienyl product (**12**, Scheme 5a) formed.



Scheme 5a: Formation of the pyranyl or the cycloheptadienyl product depends on the alkyne used¹⁰

Mace¹¹ used deuterium-labeled dienone to confirm the mechanism originally considered by Tully⁹ for the formation of **9** (Scheme 4). The mechanism in which the rearrangement occurs via initial alkene addition to form a 6-membered ring followed by ring expansion through addition of the manganated carbon in b (Scheme 5b) to the ketone CO with subsequent elimination to reopen the cyclopropyl ring of c (Scheme 5b). Here the Ph

group does not migrate, rather the carbon atom with attached phenyl group (and H, or D as shown) exchanges position to move adjacent to ketone CO).



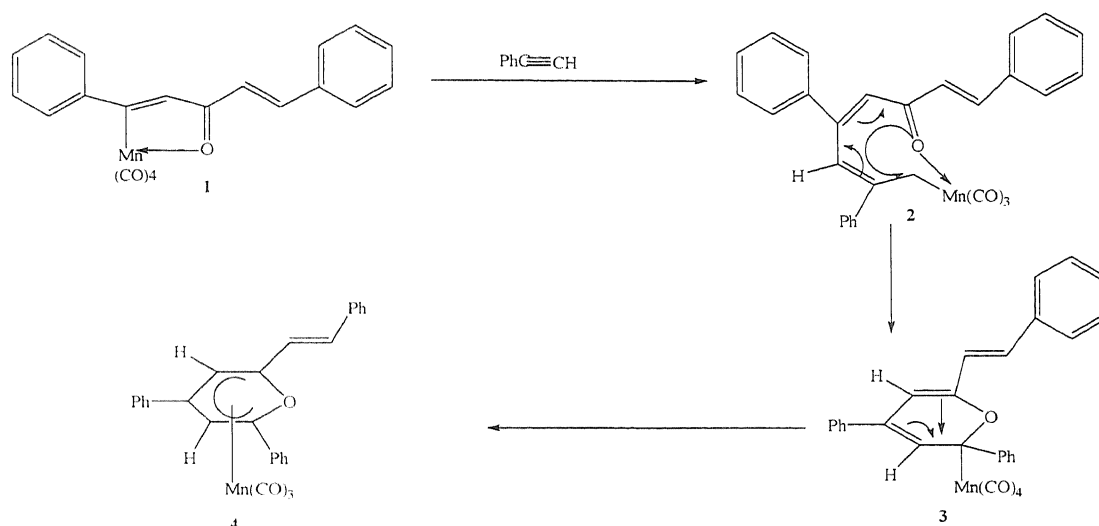
Scheme 5b: Mechanism (involving rearrangement) for the formation of the oxocycloheptadienyl complex¹¹.

In the study by Tully⁵ when a solution of phenyl acetylene and **6** (Scheme 4) was stirred in CCl_4 at ambient temperature for 8 hours, the pyranyl product formed (**8**, Scheme 4) and almost all the starting material was used up with only traces of the oxocycloheptadienyl **9** forming.

When the pyranyl product was heated in heptane at reflux, the IR peaks for the pyranyl product disappeared in just one hour¹⁰. New IR peaks for the oxocycloheptadienyl product (**9**, Scheme 4) appeared instead. After the repetition of a selection of these reactions, it was confirmed that the pyranyl product dominated under milder conditions and the oxocycloheptadienyl product formed at more forcing conditions (i.e. at reflux and with extended reaction times). This suggests that the pyranyl product is formed faster (kinetic control) but the oxocycloheptadienyl product comes to dominate under reversible conditions at higher temperatures (thermodynamic control).

Similarly, when manganated 1,5-diarylpenta-1,4-dien-3-ones were reacted with alkynes, the corresponding $(\text{pyranyl})\text{Mn}(\text{CO})_3$ formed but the seven-membered oxocycloheptadienyl product is also formed^{5,11}. Both the manganated 1,3-diphenylprop-

2-en-1-ones and manganated 1,5-diaryl-penta-1,4-dien-3-ones reacting with alkynes¹⁰ like phenylacetylene give (pyranyl)Mn(CO)₃ complexes with the addition of the manganated C to the triple bond occurring at the alkene C remote from the Ph group (Scheme 6). This orientation result is similar to that obtained by the Liebeskind's group¹² with the formation of the indenols with the orthomanganated substrates.



Scheme 6: The addition of the manganated C to the triple bond occurring at the alkene C remote from the Ph group^{5, 11}

The figure below (Figure 2) shows the ¹H NMR and ¹³C NMR signals for the (pyranyl)Mn(CO)₃ formed (**4**, Scheme 6) when (**1**, Scheme 6) was reacted with phenyl acetylene in an earlier study¹⁰. These NMR data are used later in this chapter to help characterize the product formed when (**1**, Scheme 6) was reacted with methyl propiolate. The ¹³C NMR signals are given in italics.

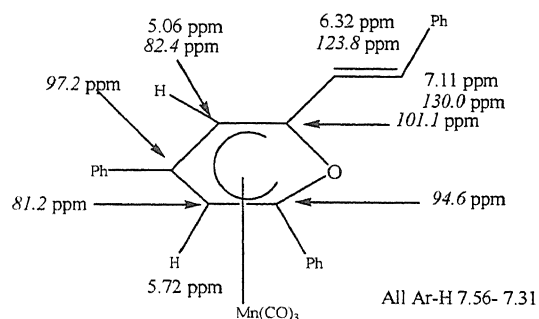
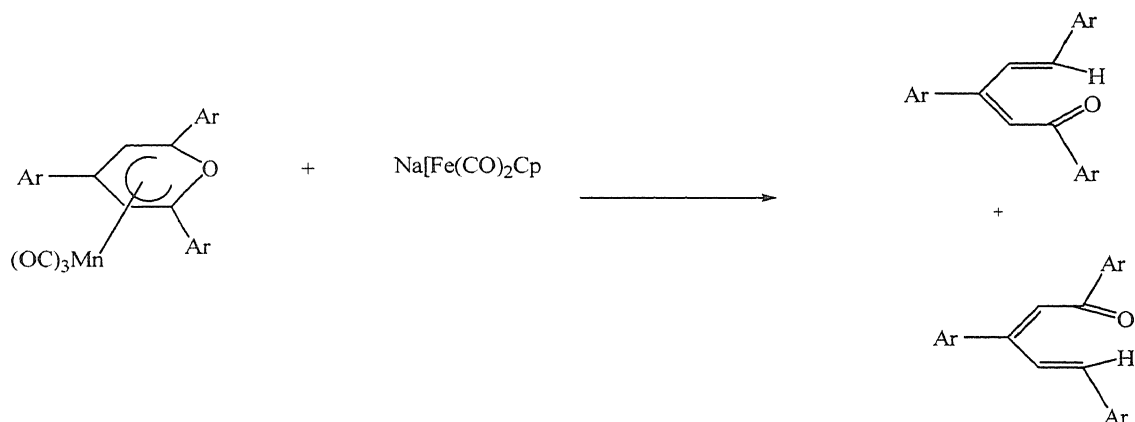


Figure 2: ^1H NMR and ^{13}C NMR signals for the (pyranyl) $\text{Mn}(\text{CO})_3$ formed (4, Scheme 6)

Attempts were also made to transmetallate the (pyranyl) $\text{Mn}(\text{CO})_3$ complexes with $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$ in an effort to replace the $\text{Mn}(\text{CO})_3$ unit with FeCp to give a compound with a sandwich structure analogous to ferrocene⁵.

This did not happen. Instead the pyranyl ring opened giving a mixture of 1,3,5-triaryl-penta-2,4-dien-1-one isomers (Scheme 7). This appeared more like a protonation by adventitious water rather than a reaction with NaFp .

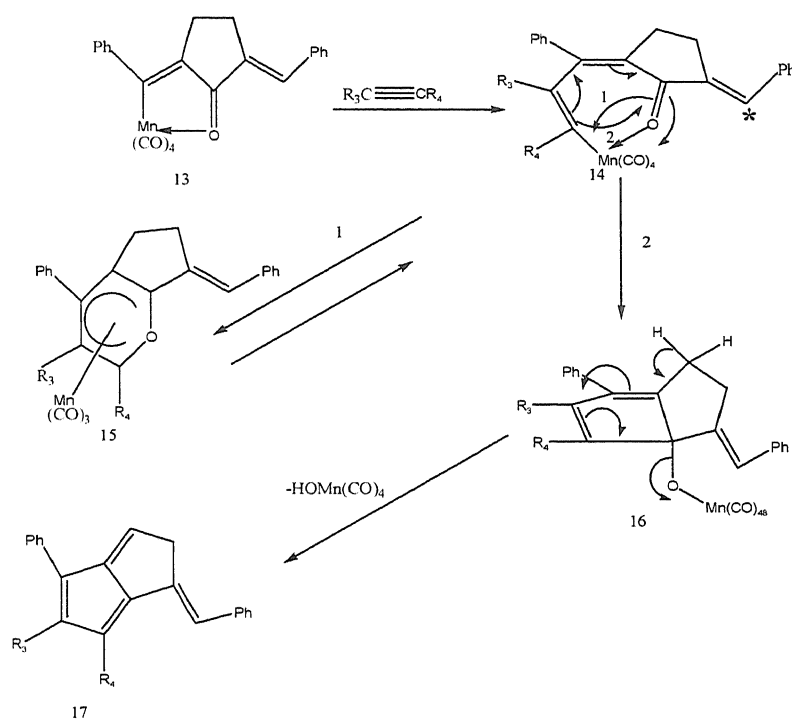


Scheme 7: Attempted transmetallation of the (pyranyl) $\text{Mn}(\text{CO})_3$ complexes with $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$

2.2 Aims of the present study

2.2.1 Dienones derived from cyclic ketones

It was found that coupling with alkynes of manganated dienones led to two primary products^{5,9} as shown in scheme 4, section 2.1. In the current study, this work was to be extended to dienones derived from cyclic ketones similar to **13** (Scheme 8). The aim was to see if alternative cyclisation occurred giving a new cyclic fulvene precursor **16** (Scheme 8) along with the bicyclic pyranyl compound **15** (Scheme 8) because of the inaccessibility of bonding site for cyclisation to the 7-membered ring in **14** (Scheme 8).



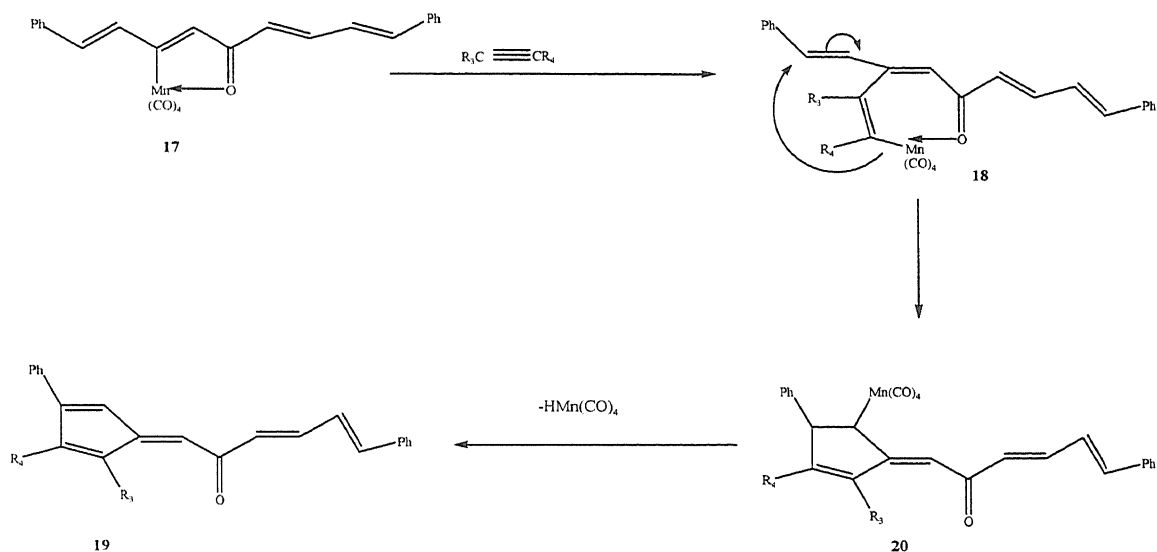
Scheme 8: Reaction of a manganated dienone derived from a cyclic ketone with phenyl acetylene

Note that the 7-membered ring in **14** (Scheme 8) cannot form because the bonding site marked * is no longer accessible as it is in **7** (Scheme 4). This is because of the introduction of the ring which bonds to the carbon adjacent to the *C.

2.2.2 Tetraenones of open chain type and analogues of 13

In the current study, the work by Tully^{5,9} was also to be extended to tetraenones of the type 17 (Scheme 9) as well as the tetraenone analogue of 13.

The tetraenone of the open chain type could cyclise according to Scheme 4 but has alternative options, e.g. as shown in Scheme 9 in which a fulvene is formed.



Scheme 9: The possible cyclisation of the manganated open chain type tetraenone

Another goal was to extend this section of work to coupling with alkenes and other unsaturated molecules like isocyanates¹² in place of alkynes to mimic the chemistry previously found for other manganated carbonyl compounds^{5, 10}.

2.2.3 Reaction of manganated chalcones with methyl propiolate

It was previously found that the reaction of η^2 -(2-acetylphenyl)tetracarbonylmanganese with asymmetrical alkynes gave indenols¹². With the formation of the indenols, the alkyne inserts with the bulkier group becoming oriented in the reverse way from normal as observed for the reactions of alkynes (like phenylacetylene) with orthomanganated aryl-compounds, giving rise to indenols with the bulky group next to the ring. Methyl propiolate is an alkyne with a stronger electron withdrawing –COOMe group on one end of the molecule when compared to alkynes like phenylacetylene. The goal of the present study was to determine if methyl propiolate reacted in the same way as other alkynes with manganated dienones and orthomanganated aryl- compounds to give (pyranyl)Mn(CO)₃ complexes or whether it would insert in the reverse way as it did with the formation of indenols¹².

2.2.4 Reaction of 3,5-diphenyl-1-(1'-phenylethenyl)-1',2-cyclopenta-pyranyl- η^5 -tricarbonylmanganese (2-6) with Na[Fe(CO)₂Cp]

Attempted transmetalation of (pyranyl)Mn(CO)₃ complex [2,4,6-triphenylpyranyl- η^5]tricarbonylmanganese, **8** (Scheme 4) with Na[Fe(CO)₂Cp] in an earlier study⁵ opened the pyranyl ring giving a mixture of penta-2,4-dien-1-one isomers(Scheme 7). In the current study, the goal was to determine if the same applied with the (pyranyl)Mn(CO)₃ complex (2-6) obtained from the dienone from cyclic ketones.

2.3 Results and Discussions

2.3.1. Dienones derived from cyclic ketones

Reaction of 2,5-dibenzylidenecyclopentanone (Figure 3) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ gave [2,5-dibenzylidenecyclopenta-1-yl- κ^3 -1-one- κO]tetracarbonylmanganese (Figure 4). Figure 3 and figure 4 are referred to as 2-1 and 2-3 in section 2.4, experimental) The manganated product (figure 4, 78.3%) showed the usual IR metal carbonyl pattern with signals at 2077, 1994 and 1958 cm^{-1} for $\text{Mn}(\text{CO})_4$ complexes as observed by Tully⁵ for his manganated chalcones.

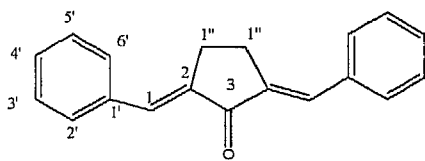


Figure 3: 2,5-dibenzylidenecyclopentanone (2-1)

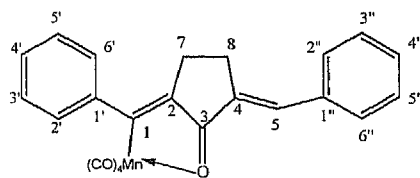


Figure 4: [2,5-dibenzylidenecyclopenta-1-yl- κ^3 -1-one- κO]tetracarbonylmanganese (2-3)

The ^1H NMR spectrum of the manganated product 2-3 (figure 4) showed some downward shift of the hydrogen signals for H2', H4', and H6' as well as for H1'' when compared to the ^1H NMR spectrum of 2-1 (figure 3) (Section 2.4) (refer to numbering of compounds, section 2.4). The ^{13}C NMR spectrum showed the usual $\text{MnC}=\text{O}$ (metal

carbonyl bands) at around 210 ppm (for 2-3) and there is a large downward shift observed for C1 when compared to the ^{13}C NMR spectrum of 2-1 (Section 2.4).

The ^1H NMR and ^{13}C NMR shifts of [2,5-dibenzylidenecyclopentan-1-yl- κ^3 -1-one- κO]tetracarbonylmanganese were again consistent with those observed by Tully⁵ for his manganated dienones. The structure of 2-3 was further confirmed by x-ray crystal structure analysis (discussed in section 2.5).

In this study, a solution of phenylacetylene and 2-3 (Figure 4) was first stirred in CCl_4 under nitrogen at ambient temperature for several hours. The reaction was monitored by IR and t.l.c. No reaction took place. Tully⁵ also found that no reaction took place at ambient temperature when manganated dienones in his study were reacted with phenylacetylene in CCl_4 . The reaction mixture was then refluxed for two hours during which 2-3 was completely converted to the (pyranyl) $\text{Mn}(\text{CO})_3$ product 3,5-diphenyl-1-(1'-phenylethenyl)-1',2-cyclopentapyranyl- η^5 -tricarbonylmanganese 2-6 (figure 5). The pyranyl product was characterized using IR, ESMS, and NMR (discussed later in the chapter). The reaction mixture was then refluxed overnight. There were no new products formed, i.e the pyranyl product remained unchanged. This showed that no alternative oxocycloheptadienyl product or any fulvene of the type suggested in scheme 8 formed.

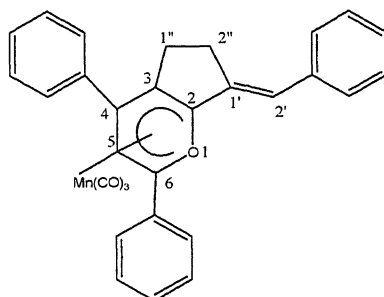


Figure 5: 3,5-diphenyl-1-(1'-phenylethenyl)-1',2-cyclopentapyranyl- η^5 -tricarbonylmanganese (2-6)

The pyranyl product progressing to the oxocycloheptadienyl product or the pyranyl product reversing to **16** (Scheme 8) and then forming the η^5 -cycloheptadienyl product,

does not happen when dienones derived from cyclic ketones are involved. Similarly, no alternative cyclisation occurred to give any novel products as was anticipated. As discussed earlier, the inaccessibility of a bonding site to give a seven membered ring similar to **9** (Scheme 4) was not possible with **14** (Scheme 8). There was however a possibility of an alternative cyclisation of **14** to give the intermediate **16** (Scheme 8) followed by the loss of the $\text{Mn}(\text{CO})_4$ to give the fulvene **17** (Scheme 8). The most likely reason for no alternative products forming is that the pyranyl product that forms cyclic ketones remains at higher temperatures and there is no reversible of **15** to **14** as shown in scheme 8. Even if this reverse reaction (i.e. **15** reversing to **14**) is taking place, it again reverts to **15**. The possible reason for this happening is discussed in section 2.2.1 (Scheme 8).

Despite continued refluxing, the (pyranyl) $\text{Mn}(\text{CO})_3$ complex (**2-6**) obtained in this study remained unchanged (as monitored by IR). This suggested that **2-6** was not getting converted into any other product. The (pyranyl) $\text{Mn}(\text{CO})_3$ complex obtained (**2-6**, 63%) showed the characteristic IR pattern for such tricarbonyl complexes⁵. The IR signals appeared at 2011, 1948 and 1930 cm^{-1} .

A ^1H NMR signal for **2-6** appeared at 5.5 ppm for H5 (expected between 5.0 and 5.7 ppm^{5,7}, refer to fig. 2 page 23). The ^{13}C NMR signals were present at 80.5 and 80 ppm for C5 and C3 and these were expected between 80 and 90 ppm. The ^{13}C NMR signals For C2, C4 and C6 appeared at 101.7, 99.0 and 98.6 ppm respectively. These signals appeared at around 95.0 ppm as expected for η^5 -pyranyltricarbonylmanganese complexes prepared from cyclomanganated chalcones and alkynes⁷. (refer to section 2.4 for numbering of the structures of the compounds).

If any 7-membered oxocycloheptadienyl product formed, then the observed IR pattern would have been 2030, 1967 and 1956 cm^{-1} . This was observed by Tully⁵ for his (cycloheptadienyl- η^5 -1-one) $\text{Mn}(\text{CO})_3$ complexes.

The ^1H NMR signals¹¹ would appear at around 4.8, 6.6 and 4.0 ppm for H2, H4 and H6 for oxocycloheptadienyl product if present and not between 5.0 and 5.7 ppm as for H3 and H5 for the (pyranyl) $\text{Mn}(\text{CO})_3$ complex.

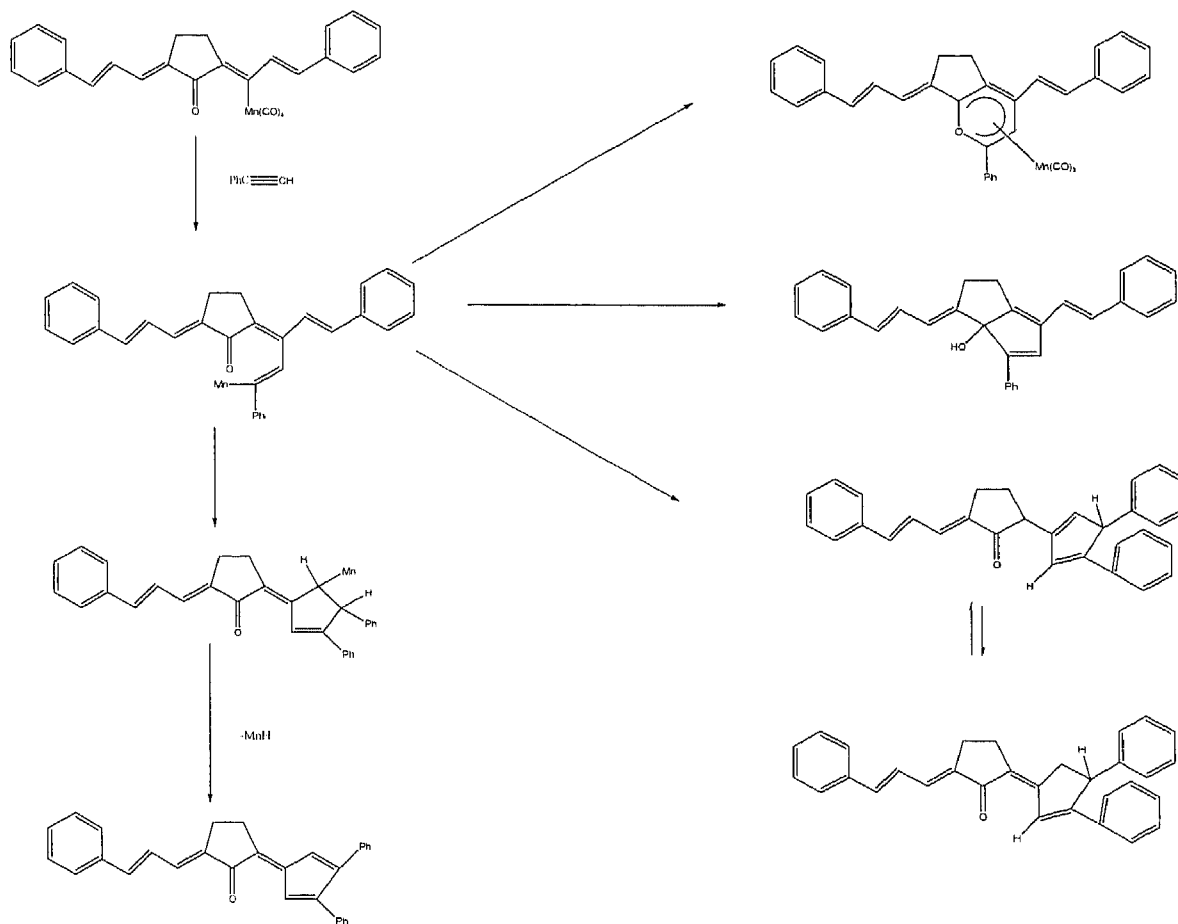
The ^{13}C NMR spectrum of the oxocycloheptadienyl product would show signals at around 115 ppm for C3 and C5 and around 75, 95 and 60 ppm for C2, C4 and C6 respectively. The NMR signals were consistent with those observed in earlier studies^{5,10} for similar (pyranyl) $\text{Mn}(\text{CO})_3$ compounds. None of these signals was observed in the ^1H NMR and ^{13}C NMR spectra of 2-6 thus confirming that no 7-membered oxocycloheptadienyl product was formed. The formation of the kinetically stable product in this case was simply a proof of what was expected.

2.3.2. Tetraenones of open chain type and analogues of 13

Tetraenones, as in scheme 9 and the cyclic analogue of **17** were successfully prepared. Reactions of the tetraenones with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane gave manganated products as seen from their IR spectra. However, the manganated products proved difficult to isolate in their pure form for full characterization, especially for getting good clean NMR spectra. Since no stable manganated products could be isolated, it became impossible to extend work in this area.

Apart from the polyenone systems being unstable and susceptible to random nucleophilic attack, and possible isomerism, it was also possible that the C-Mn bond, if uncoupled temporarily from coordination to the ketone ($\text{C}=\text{O}$) could potentially be able to cyclise to diene centres on the opposite side of the molecule. This could happen during isolation, thereby possibly giving one or more manganated cyclisation products which themselves could react further intermolecularly or intramolecularly giving fairly random Mn-containing and non-Mn products. These most likely accounts for the multiple NMR signals in the isolated product that initially seemed like a reasonable discrete band off the plate.

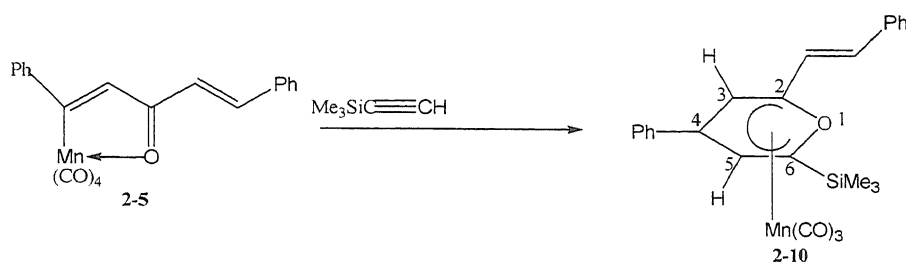
Reactions of the unpurified manganated tetraenones with alkynes and alkenes did not give any products which could be isolated and characterized fully. The main product of the reactions was the brown solid forming in the reaction vessel, which pointed to the decomposition of the starting manganated tetraenone. The solid was dissolved in CH_2Cl_2 and plated but nothing moved from the base. However, reaction of the manganated tetraenone with alkynes like phenyl acetylene could also result in multiple products and this could possibly account for multiple minor bands on the PLC. Some possible products from such a reaction are shown by the following scheme. Similarly, one-pot reactions of the tetraenones with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and alkynes in different solvents did not give any positive results. All the starting materials broke down instead. This area of work was therefore abandoned.



Scheme 11: The possible products resulting from the reaction of manganated tetraenones with alkynes

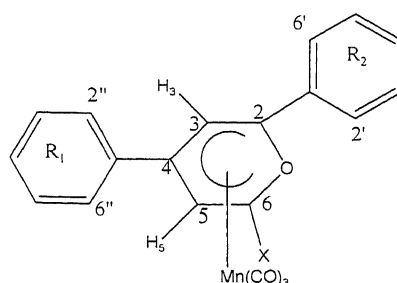
2.3.3. Reactions of manganated chalcone (2-4) and manganated dienone (2-5) with methyl propiolate

The (pyranyl)Mn(CO)₃ is formed as the result of the manganated C adding to the unsubstituted alkyne carbon (the carbon with H) most likely because of steric reasons as has been observed in the previous study¹⁰. Similarly, when 2-5 was reacted with trimethylsilylacetylene⁵, 2-10 was formed in 4 hours at reflux (Scheme 12).



Scheme 12: Reaction of 2-5 with trimethylsilylacetylene

The general structure of the (pyranyl)Mn(CO)₃ complexes is given below. This has been mentioned elsewhere in this chapter but is given here once again with the general structure to enable the reader to better follow the NMR signals listed in the tables that follow.



The table below lists the ^1H NMR chemical shifts of the protons around the pyranyl ring of the (pyranyl) $\text{Mn}(\text{CO}_3)$ complexes studied by Tully⁵.

			^1H NMR chemical shifts (ppm)	
X	R ₁	R ₂	H ₅	H ₃
Ph	3'', 4'', 5''- (OMe ₃)	4''-Cl	5.56	5.52
Ph	4''- CF ₃	H	5.63	5.63
Ph	H	H	5.63	5.63
Ph	4''CF ₃	4'- Cl	5.61	5.61
SiMe ₃	3'', 4'', 5''- (OMe ₃)	4'- Cl	5.32	5.03

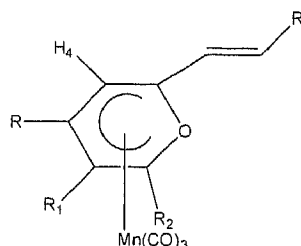
Table 1: ^1H NMR chemical shifts of the protons around the pyranyl ring⁵

The following table lists the ^{13}C NMR chemical shifts of the carbons around the pyranyl ring.

			^{13}C NMR chemical shifts (ppm)				
X	R ₁	R ₂	C2	C3	C4	C5	C6
Ph	3'', 4'', 5''- (OMe ₃)	4''-Cl	96.0	81.6	92.5	81.3	98.7
Ph	4''- CF ₃	H	96.4	80.6	94.6	80.6	96.4
Ph	H	H	95.3	81.0	97.5	81.0	95.3
Ph	4''CF ₃	4'- Cl	93.9	80.8	94.9	80.4	97.5
SiMe ₃	3'', 4'', 5''- (OMe ₃)	4'- Cl	101.9	81.5	95.4	92.2	88.8

Table 2: ^{13}C NMR chemical shifts of the carbons around the pyranyl ring⁵

Similarly, Mace¹⁰ synthesized a few pyranyl complexes, the ¹H NMR shifts of which are listed in the table below



			¹ H NMR shift of H if R ₁ = H	¹ H NMR of H ₃
R	R ₁	R ₂	R ₂ = H	H ₃
Ph	H	Ph	5.06	5.72
Ph	Ph	Ph	---	4.93
Ph	H	SiMe ₃	4.62	4.85

Table 3: ¹H NMR chemical shifts of the protons around the pyranyl ring¹⁰

The following table lists the ¹H NMR shifts around the η⁵-pyranyl ring of the products 2-7 and 2-8 resulting from the reactions of 2-5 and 2-4 with methyl propiolate in the current study. The structures of 2-4, 2-5, 2-7 and 2-8 (as numbered in section 2.4, the experimental section, are given as figures 6, 7, 8, and 9 below.

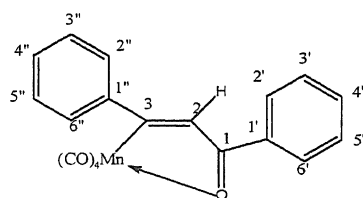


Figure 6: Structure of compound 2-4

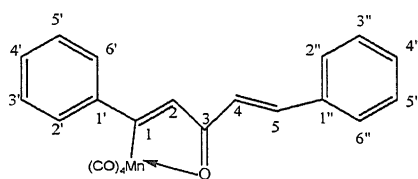


Figure 7: Structure of compound 2-5

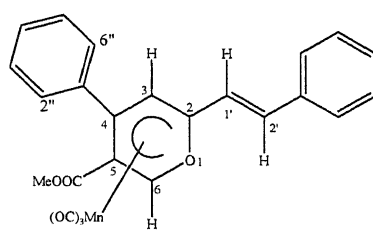


Figure 8: Structure of compound 2-7

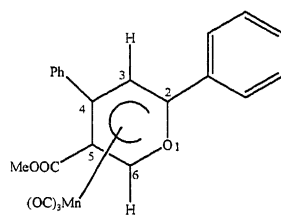


Figure 9: Structure of compound 2-8

Substrates	Comp.	ppm	
		H3	H6
2-5, methyl propiolate	2-7	4.53	6.30
2-4, methyl propiolate	2-8	5.31	6.30

Table 4: ^1H NMR shifts of the protons around the η^5 -pyranyl ring 2-7 and 2-8.

A trimethylsilyl substituent has the effect of slightly lowering the ^1H NMR shifts of both the η^5 -pyranyl ring protons when compared to the phenyl substituent. Changing the substituents has only a minor effect on the chemical shifts of individual carbons. The (pyranyl) $\text{Mn}(\text{CO})_3$ complexes formed again showed almost similar ^1H NMR and ^{13}C NMR shifts for the protons and carbons around the η^5 -pyranyl ring as listed in tables 1, 2 and 3.

While the ^1H NMR shifts ranged from 4.6 to 5.7 ppm, the ^{13}C NMR shifts ranged from 81.2 to 104.7 ppm for the (pyranyl) $\text{Mn}(\text{CO})_3$ complexes in the study by Tully⁵. This shows that changing the substituents around the η^5 -pyranyl ring did not affect the NMR chemical shifts of the protons and the carbons around the η^5 -pyranyl ring.

In the current study, 2-5 as well as 2-4 (1,3-diphenylprop-2-en-3-yl- κ^3 -1-one- κO) tetracarbonyl manganese was reacted with methyl propiolate in CCl_4 . 2-7 (64%) and 2-8 (74%) were obtained respectively and showed the usual IR metal carbonyl bands with signals at 2015, 1956 and 1934 cm^{-1} .

However, when the ^1H NMR shifts of the (pyranyl) $\text{Mn}(\text{CO})_3$ products 2-7 and 2-8 were compared with the ^1H NMR shifts of the (pyranyl) $\text{Mn}(\text{CO})_3$ products formed in the earlier studies^{5,10}, some of which have already been discussed earlier in this section, it was noted that a signal appeared at around 6.30 ppm. This signal at 6.30 ppm, for one proton, was further downfield than those observed for the (pyranyl) $\text{Mn}(\text{CO})_3$ products formed in the study by Tully⁵ and Wade¹⁰. This value of 6.30 ppm was not within the range of 5.0 and 5.7 ppm for the two protons at the α -positions on the η^5 -pyranyl ring as

has been observed earlier. The ^1H NMR signal at 6.30 ppm is for H6 which is on C6 of the pyranyl ring. C6 is adjacent to O which results in a more downward ^1H NMR signal at 6.30 ppm. Based on the ^1H NMR assignments of 2-7 and 2-8, the following structures (figures 10 and 11) for the two compounds is proposed.

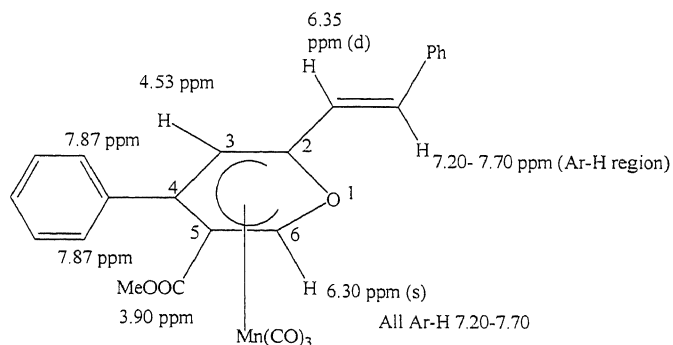


Figure 10: The proposed structure of the (pyranyl) $\text{Mn}(\text{CO})_3$ complex 2-7 based on the ^1H NMR shifts

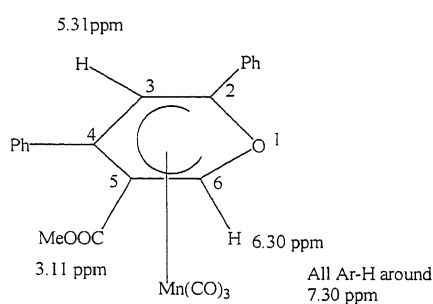


Figure 11: The proposed structure of the (pyranyl) $\text{Mn}(\text{CO})_3$ complex 2-8 based on the ^1H NMR shifts

The following table lists the ^{13}C NMR shifts around the η^5 -pyranyl ring of the products 2-7 and 2-8 resulting from the reactions of 2-5 and 2-4 with methyl propiolate in the current study.

Substrates	Compound	ppm				
		C2	C3	C4	C5	C6
2-5, methyl propiolate	2-7	101.2	79.0	119.8	121.6	87.3
2-4, methyl propiolate	2-8	101.6	77.4	107.5	124.0	87.7

Table 5: ^{13}C NMR shifts of the protons around the η^5 -pyranyl ring of 2-7 and 2-8.

From the ^{13}C NMR signals of (pyranyl) $\text{Mn}(\text{CO})_3$ from previous studies ^{5,10}, it has been noted that the carbons of the phenyl substituents, if present, have their carbon shifts starting at around 123 ppm upwards to around 150, 160 ppm depending on the other substituents that are present on the η^5 -pyranyl ring. The ^{13}C NMR signals for the carbons on the η^5 -pyranyl ring however range between around 81.0 ppm and 102 ppm.

For the products, 2-7 and 2-8, this was however not observed. A considerable ^{13}C NMR chemical shift for carbons around the η^5 -pyranyl ring was observed, mostly a downfield shift for the carbons. The ^{13}C NMR chemical shifts for 2-7 and 2-8 are assigned as listed in table 5. Based on the ^{13}C NMR assignments of 2-7 and 2-8, the following structures (figures 12 and 13) for the two compounds are proposed.

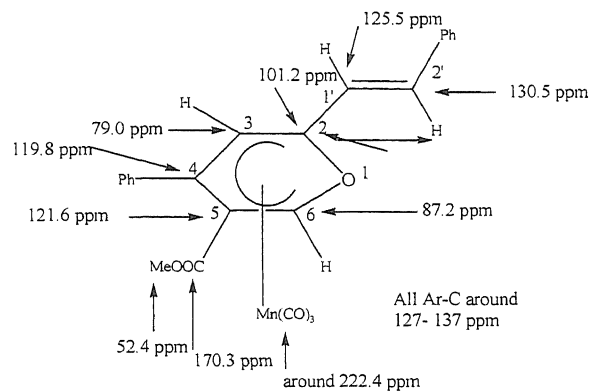


Figure 12: The proposed structure of the (pyranyl) $\text{Mn}(\text{CO})_3$ complex 2-7 based on the ^{13}C NMR shifts

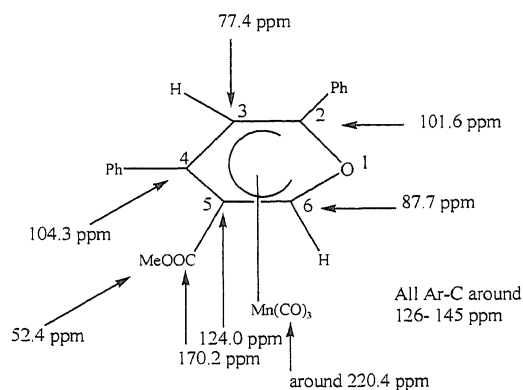


Figure 13: The proposed structure of the (pyranyl) $\text{Mn}(\text{CO})_3$ complex 2-8 based on the ^{13}C NMR shifts

In the current study therefore, the NMR data suggests that methyl propiolate inserts in the reverse way to what was observed for alkynes like phenyl acetylene when reacted with manganated dienones like 2-5. It is however consistent with the observations made by Liebeskind's group¹² with the formation of indenols (discussed earlier) from methyl propiolate and o-manganated acetophenones.

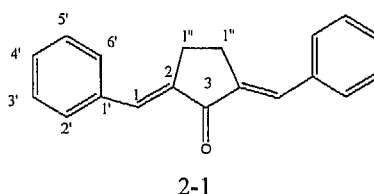
2.3.4 Reaction of 2-6 with Na[Fe(CO)₂Cp]

A product from this reaction was isolated but could not be sufficiently purified to give a good NMR spectrum. However, the result from this reaction is discussed in the experimental section.

2.4 Experimental

2.4.1 Preparation of 2,5-Dibenzylidenecyclopentanone (2-1)

Ethanol (10 mL) and a solution of sodium hydroxide (2 g) in water (15 mL) were mixed in a flask immersed in crushed ice. A solution of cyclopentanone (0.65 mL, 7.4 mmol) of benzaldehyde (15.0 mL, 14.8 mmol) was added while stirring and maintaining the temperature at 25 °C. After stirring for a further hour, the product which had precipitated was collected and washed with water (until the washings were neutral to litmus). The crude product was dried under vacuum and recrystallised from ethyl acetate in 80% yield.



M.p 188-190 °C

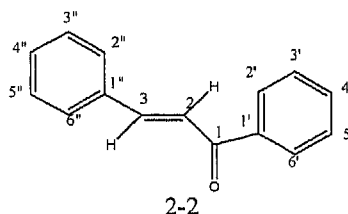
^1H NMR⁵: (300 MHz, CDCl_3) δ 7.62 (s, 2H, H1), 7.42 (m, 10H, Ar-H), 3.14 (4H, s, H1'')

^{13}C NMR⁵: (300 MHz, CDCl_3) δ 162.4 (C3), 137.4 (C1), 135.9 (C1'), 133.9 (C4'), 130.8 (C3', 5'), 129.5 (C2', C6'), 128.8 (C2).

2.4.2 Preparation of 1,3-diphenylprop-2-en-1-one

A solution of sodium hydroxide (2.2 g) in water (20 mL) and ethanol (12.5 mL) was stirred in a flask immersed in a bath of crushed ice. The flask was then removed from the crushed ice and placed on a hot plate. Acetophenone (5210 mg, 43 mmol) and benzaldehyde (4570 mg, 43 mmol) were added successively while maintaining the temperature at 25 °C. After stirring for 4 hours at 25 °C, the mixture was cooled and left at -8 °C overnight. The crude product was filtered, washed with water (until the washings

were neutral to litmus) and then washed with a little ethanol (3x2 mL). A single recrystallization from ethanol gave 1,3-diphenylprop-2-en-1-one (2-2) (6.98 g, 78%), pure by ^1H NMR⁵ and used for manganoation without further purification.

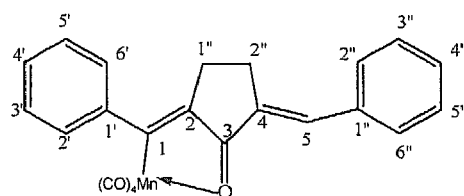


^1H NMR: (300 MHz, CDCl_3) δ 8.06 (d, 2H, $J=8.0\text{Hz}$, H2', 6'), 7.82 (d, 1H, $J=15.5\text{Hz}$, H3) 7.55 (m, 3H, H3', 4', 5), 7.51 (d, 1H, $J=15.5\text{Hz}$, H2), 7.45 (m, 5H, H2'', 3'', 4'', 5'', 6'')

^{13}C NMR: (300 MHz, CDCl_3) δ 190.7 (C1), 139.5 (C3), 138.3 (C1'), 135.0 (C1''), 129.5 (C2', C6'), 129.0 (C5'), 132.9 (C4'), 128.6 (C2), 128.9 (C3'), 126.3 (C2'', C6''), 128.5-128.9 (C3'', 4'', 5'').

2.4.3 Cyclomanganation of (2-1)

2-1 (100 mg, 0.384 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (132 mg, 0.464 mmol) were transferred to a Schlenk flask containing heptane (20 mL) under nitrogen. The solution was heated under reflux until such time as the reaction was deemed complete through disappearance of the 2106 cm^{-1} peak due to $\text{PhCH}_2\text{Mn}(\text{CO})_5$. After approximately 60 minutes, the reaction was stopped and the solvent removed under vacuum. The residue was chromatographed (p.l.c., ethyl acetate: hexane, 1:3) to afford the product, [1,5-diphenyl-2,4-cyclopenta-1,4-dien-1-yl- κC^1 -3-one- κO]tetracarbonylmanganese (2-3), R_f of 0.8, as red oil (100 mg, 63 %). The product was recrystallised by diffusion from dichloromethane and pentane to give red crystals: m.p. 107°C .



2-3

IR(hexane) 2077 (m) 1994 (vs,br) 1958 (s) cm^{-1}

ESMS (MeOH/NaOMe); (CV +20 V) m/z 449 (70% $[\text{M}+\text{Na}]^+$), 875 (65% $[2\text{M}+\text{Na}]^+$)
(MeOH/NaOMe, (Cone -20 V) m/z 457 (100% $(\text{M}+\text{OMe})^-$)

^1H NMR (300 MHz, CDCl_3) δ 7.11-7.56 (10H, m, Ar-H), 6.99 (1H, s, H5), 3.28 (2H, d, H1'), 2.68 (2H, d, H2')

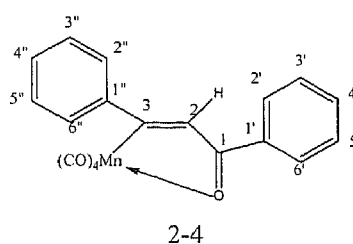
^{13}C NMR (300 MHz, CDCl_3) δ 219.4 (C1), 211.8-213.9 (MnC=O), 196.6 (C3), 123.6-151.9 (Ar-Cs), 149.6 (C5), 31.5 (C6), 26.7 (C9)

Elemental analysis calculated for $\text{C}_{23}\text{H}_{15}\text{MnO}_5$: C, 64.78 ;H, 3.55

Found: C, 64.94; H, 3.67

2.4.4 Manganation of 1,3-diphenylprop-2-en-1-one and (E,E)-1,5-diarylpenta-1,4-dien-3-one

1,3-diarylprop-2-en-1-one (200 mg, 0.96 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (330 mg, 1.15 mmol) were refluxed in nitrogen-saturated heptane for 3 h. The reaction mixture was cooled and the solvent removed under vacuum. The residue was chromatographed PLC., 1:1 CH_2Cl_2 /petroleum spirits) to afford one red band, R_f 0.8. The red band was eluted and the solvent removed to provide pure product, 2-4 as red oil, (300 mg, 78.3 %).



IR (heptane): 2081 (m), 1996(vs), 1934 (s) cm^{-1}

ESMS: (MeOH/NaOMe; (CV +20 V) m/z 397 (70% $[\text{M}+\text{Na}]^+$), 771 (65% $[2\text{M}+\text{Na}]^+$)
(MeOH/NaOMe, (Cone -20 V) m/z 405 (100% $(\text{M}+\text{OMe})^-$)

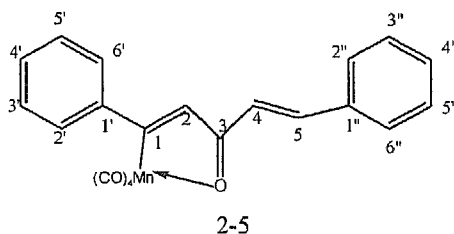
^1H NMR: (300 MHz, CDCl_3) δ 7.75 (s, 1H, H2), 7.18- 8.07 (m, 10H, Ar-H)

^{13}C NMR: (300 MHz, CDCl_3) δ 219.0 (C1), 214.0(CO), 210.3(CO), 210.0 (CO), 204.7 (C1), 135.2 (C2), 150.4 (C1''), 135.2 (C1'), 130.8 (C2', 6'), 130.1 (C2'', C6''), 133.5 (C4') 129.4-130.8(3C, C3'', 4'', 5''), 129.2 (C3'), 131.4 (C5').

No microanalyses data was obtained for 2-3.

A commercial sample of the dienone for making the cyclomanganated compound 2-5 was made available from an earlier study⁵.

The procedure for synthesis of 2-5 was similar to that for 2-3. This compound has been prepared previously⁵. The yield of 2-5 in this study was comparable to that reported earlier⁵. Consistent NMR data were obtained and are listed here.



m.p.⁵ 116 °C

IR⁵ 2082 (m), 1997 (vs, br) 1942 (s) cm⁻¹

¹H NMR⁵ (300 MHz, CDCl₃) δ 7.72 (d, 1H, J= 16.1Hz, H5), 7.59 m, 2H, H2'', 6''). 7.45 (m, 8H, H2', H6', H3', H5', H4', H3'', H5'', H4''), 7.33 (s, 1H, H2), 6.99 (d, 1H, J= 16.1 Hz, H4).

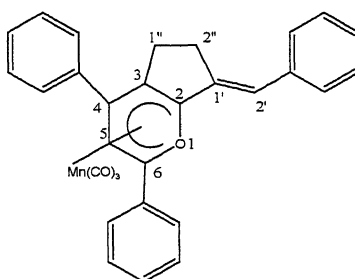
¹³C NMR⁵ (300 MHz, CDCl₃) δ 251.2(C1), 219.5(CO), 214.1(CO), 210.4(CO), 203.9 (C3), 150.2(C1'), 145.4(C5), 134.6(C1''), 133.9 (C2), 131.1 (C4''), 129.1 (C3'', C5''), 128.7 (C4'), 128.6 (C2'', C6''), 128.4 (C3', 5'), 125.3 (C2', 6'), 123.6(C4).

Elemental Analysis calculated for C₂₁H₁₃O₅Mn: C, 63.02; H, 3.27

Found: C, 62.95, H, 2.98

2.4.5 Reaction of 1,5-diphenylcyclopenta-1,4-dien-1-yl- κ C'-3-one- κ O)tetracarbonylmanganese (2-3) with phenylacetylene

2-3 (208 mg, 0.488 mmol) and phenylacetylene (1.22 mmol, 0.125 g, 130 μ L) were dissolved in nitrogen-saturated CCl_4 and the solution was refluxed under nitrogen. A brick-red colour appeared. The heating was continued until such time as the reaction was deemed to be complete by the disappearance of the 2080 cm^{-1} IR peak of 2-3. After approximately 2 h, the reaction was stopped and the solvent removed under vacuum and dichloromethane (10 mL) and deactivated neutral alumina (4 g, activity 2) were added to the dark red oil. The mixture was stirred while the dichloromethane was removed under vacuum. The adsorbed product was transferred into a column (2 x 12 cm) of neutral alumina (activity II). Elution with hexane did not produce any bands but as the polarity of the solvent was increased with dichloromethane, a large red band started to move. This was collected and the solvent removed under vacuum to give 3,5-diphenyl-1-(1'-phenylethenyl)-1',2-cyclopentapyranyl- η^5 -tricarbonylmanganese as a red oil (150 mg, 63 %). This was crystallized by diffusion from dichloromethane/ pentane as red crystals.



2-6

IR (CCl_4): 2011(vs), 1948(s), 1930 (m) cm^{-1}

ESMS (MeOH/NaOMe ; cone + 20 V) m/z 361 (100%, $[\text{M}-\text{Mn}(\text{CO})]^+$)

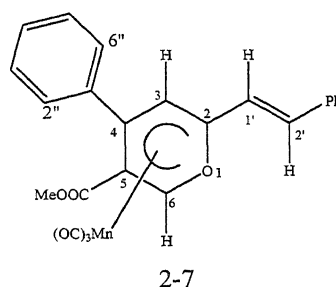
^1H NMR⁵ (300 MHz, CDCl_3) δ 5.49 (s, 1H, H5), 7.10 (s, 1H, H2'), 7.35- 7.93 (m, 15H, All Ar-H), 2.90 (t, 2H, H1''), 2.60 (t, 2H, H2'').

^{13}C NMR⁵ (300 MHz, CDCl_3) δ 224,0 (MnC=O), 137.2 (Ar-C), 136.8 (Ar-C), 136,7 (Ar-C), 130.6 (C2'), 126.9- 129.3 (Ar-C), 125.9 (C1'), 101.7 (C2), 99.0 (C4), 98.6 (C6), 80.5 (C5), 80.0 (C3), 29.7 (C1''), 29.3 (C2'').

Elemental Analysis: calculated for $\text{C}_{27}\text{H}_{21}\text{MnO}_4$: C, 71.86, H, 4.42
 Found: C, 70.51, H, 4.49

2.4.6 Reaction of 2-5 with methyl propiolate in CCl_4

2-5 (193 mg, 0.84 mmol) and methyl propiolate (269 μL , 2.47 mmol) were refluxed in nitrogen-saturated carbon tetrachloride for 4 h. The carbon tetrachloride was removed under vacuum to give a red oil. Dichloromethane (10 mL) and deactivated neutral alumina (4 g, activity II) were added to the dark red oil. The mixture was stirred while the dichloromethane was removed under vacuum. The adsorbed product was transferred onto a column (2 x 12 cm) of neutral alumina (activity II). Elution with hexane did not produce any bands but as the polarity was increased with dichloromethane, a large red band started to move. This was collected to give 2-7 as a red oil (240 mg, 64 %). This was crystallised by the solvent diffusion method (dichloromethane/pentane) as red crystals.



IR (CCl_4): 2015 (vs), 1956 (s), 1934 (m) cm^{-1}

ESMS: (MeOH/NaOMe; Cone -20 V) m/z 487 (100%, [M+ OMe]⁻), 455 (17%, [M-H]⁻)
(MeOH, Cone +20 V) m/z 317 (100%, [M-Mn(CO)₃]⁺)

¹H NMR: (300 MHz, CDCl₃) δ 7.87 (d, 2H, H2'',6''), 7.28- 7.58 (m, 10H, All Ar-H), 7.20(d, 1H, H2', J= 16 Hz), 6.30 (s, 1H, H6), 4.53 (s, 1H, H3), 6.35 (d, 1H, H1', J= 16 Hz), 3.90 (s, 3H, CH₃).

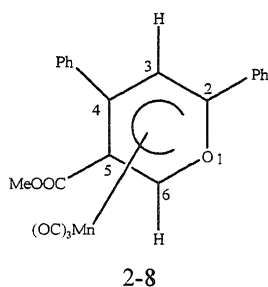
¹³C NMR: (300 MHz, CDCl₃) δ 222.4 (Mn-CO), 170.3 (CO), 127.9- 136.7 (all Ar-C) 121.6 (C5), 119.8 (C4), 130.5 (C2'), 125.5 (C1'), 101.2 (C2), 87.2(C6), 79.0 (C3).

Elemental analysis calculated for C₂₄H₁₇MnO₆ : C, 63.16; H, 3.75

Found : C, 63.69; H, 4.25

2.4.7 Reaction of 2-4 with methyl propiolate in CCl₄

2-4 (133 mg, 0.36 mmol) and methyl propiolate (126 μL, 1.45 mmol) were refluxed in nitrogen-saturated carbon tetrachloride for 4 h. The carbon tetrachloride was removed under vacuum to give a red oil. Dichloromethane (10 mL) and deactivated neutral alumina (4 g, activity II) were added to the dark red oil. The mixture was stirred while the dichloromethane was removed under vacuum. The adsorbed product was transferred onto a column (2x 12 cm) of neutral alumina (activity II). Elution with hexane did not produce any bands but as the polarity was increased with dichloromethane, a large red band started to move. This was collected to give 2-8 as a red oil (110 mg, 74 %). This was crystallised by the solvent diffusion method (dichloromethane/ pentane) as red crystals.



IR (CCl₄): 2015 (vs), 1956 (s) 1934 (m) cm⁻¹.

ESMS: (MeOH/NaOMe; Cone -20 V) m/z 487 (100%, [M+ OMe]⁺), 455 (17%, [M-H]⁻)
(MeOH, Cone +20 V) m/z ([M-Mn(CO)₃]⁺).

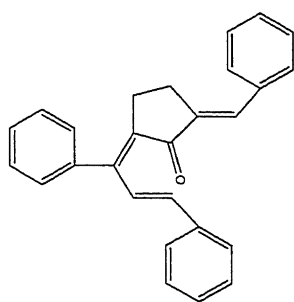
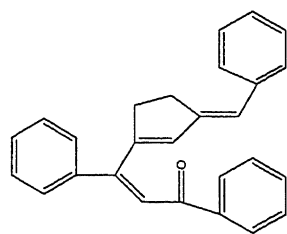
¹H NMR: (300 MHz, CDCl₃) α 7.30 (m, 10H, all Ar-H), 5.31 (s, 1H, H3), 6.30 (s, 1H, H6), 3.11 (s, 3H, CH₃).

¹³C NMR: (300 MHz, CDCl₃) α 222.4 (MnC=O), 170.2 (CO), 126.8- 144.9 (all Ar-C), 124.0 (C5), 104.3 (C4), 101.6 (C2), 87.7 (C6), 77.4 (C3), 52.4 (OCH₃).

No microanalyses data obtained for 2-8.

2.4.8 Reaction of 3,5-diphenyl-1-(1'-phenylethenyl)-1',2-(cyclopenta-pyranyl- η^5 -tricarbonylmanganese (2-6) with Na[Fe(CO)₂Cp]

3,5-Diphenyl-1-(1'-phenylethenyl)-1',2-(cyclopentapyranyl- η^5 -tricarbonylmanganese (2-6), (110 mg, 0.22mmol) and Na[Fe(CO)₂Cp] (110 mg, 0.55 mmol) were refluxed in nitrogen saturated THF (20 mL) overnight. THF was removed under vacuum and the residual oil was chromatographed (CH₂Cl₂/hexane, 1:1) to give two bands at R_f of 0.8 and R_f of 0.9. The band at R_f of 0.8 was identified by IR and MS as the dimer [Fe(CO)₂Cp]₂, (99 mg). Removal of the band at R_f of 0.8 followed by extraction with dichloromethane gave a yellow solid (27 mg). Repeated attempts to crystallize the product did not yield any crystals. As a result, no clean NMR or elemental analysis of the product could be obtained. If the reaction occurred as was observed in an earlier study⁵ then the expected products would have been the two isomers drawn below.



2-9

Table 2.5 Crystal Data and Structural Refinement of 2-3

Identification code	npcp
Empirical formula	C ₂₃ H ₁₅ Mn O ₅
Formula weight	426.29
Temperature	-110(2) C
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /n
Unit cell dimensions	a = 7.6741(7) Å alpha = 90 deg. b = 23.775(2) Å beta = 98.8600(10) deg. c = 10.9639(10) Å gamma = 90 deg.
Volume	1976.5(3) Å ³
Z, Calculated density	4, 1.433 Mg/m ³
Absorption coefficient	0.699 mm ⁻¹
F(000)	872
Crystal size	64 x .53 x .41 mm
Theta range for data collection	2.07 to 26.44 deg.
Limiting indices	-9<=h<=9, -29<=k<=29, -13<=l<=13
Reflections collected / unique	24799 / 4059 [R(int) = 0.0232]
Completeness to theta =	26.44 99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.8015
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4059 / 0 / 262
Goodness-of-fit on F ²	1.275

Final R indices [$I > 2\sigma(I)$] $R1 = 0.0519$, $wR2 = 0.1313$

R indices (all data) $R1 = 0.0530$, $wR2 = 0.1320$

Largest diff. peak and hole 0.339 and $-0.506 \text{ e. \AA}^{-3}$

Crystal data and structure refinement for [1,5-diphenylcyclopenta-1,4- diene-1-yl- $\kappa C'$ -3-one- κO] tetracarbonylmanganese (2-3).

The orange-red crystals were shown to be monoclinic of space group $P2_1/n$ with four molecules in the unit cell. Crystal and structure refinement data are given in the table in section 2.5. An ORTEP perspective view showing the atom-labeling scheme is given in figure 14.

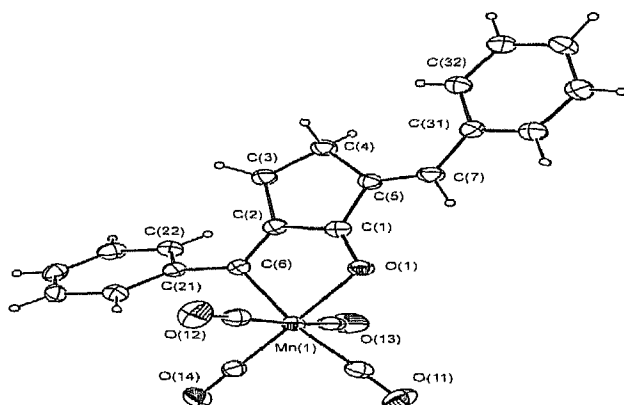


Figure 14: ORTEP perspective view showing the atom-labeling of [1,5-diphenylcyclopenta-1,4- diene-1-yl- $\kappa C'$ -3-one- κO] tetracarbonylmanganese

Cyclomanganated complexes of this type incorporate a five-membered ring which are essentially planar and constant geometry.

The following figures show the bond lengths of the manganocyclic ring of the orthomanganated acetophenone⁵ and of the cyclomanganated [1,5-diphenylcyclopentane-1,4- diene-1-yl- κ C'-3-one- κ O] tetracarbonylmanganese (2-3).

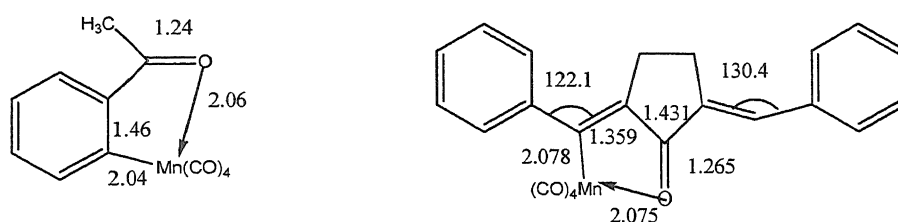


Figure 15: Bond lengths of the manganocyclic ring of the orthomanganated acetophenone⁵ and of the cyclomanganated [1,5-diphenylcyclopentane-1,4- diene-1-yl- κ C'-3-one- κ O] tetracarbonylmanganese

All the bond lengths of the manganocyclic ring in the cyclomanganated enone are longer than that of the bond lengths of the manganocyclic ring of the orthomanganated acetophenone except for the C=C bond which is 1.359 Å. This is shorter than the 1.46 Å C-C bond of the aryl ring.

The phenyl ring (C21- C26) attached to C6 is twisted about the C-C bond from the rest of the molecule at an angle of 46.59°. This twisting out of plane of this phenyl ring is most likely due to steric reasons. The electron rich and bulky Mn(CO)₄ pushes away the phenyl ring away from it thus forcing the phenyl ring out of plane. O1 Mn1 C6 angle is 80.60°, very similar to those reported for similar angles for compounds like the dimanganated 1,5-diphenyl-3-(2-pyridyl)pentane-1,5-dione⁵ and for orthomanganated acetophenone¹³.

Listed below are the C-C bond lengths (Å) between the cyclopentanone ring and the two phenyl rings of the [1,5-diphenylcyclopentane-1,4-diene-1-yl- κ C'-3-one- κ O] tetracarbonylmanganese (2-3). Also listed are the Mn-C and the C=O bonds.

C1 – C2	1.431(4)		
C2 – C6	1.359 (4)	C5 - C7	1.348 (4)
C6 – C21	1.480 (4)	C7 – C31	1.468 (4)
Mn1- C11	1.862 (3)	Mn1- C12	1.875 (3)
Mn1- C13	1.849 (3)	Mn1- C14	1.801 (3)
O11- C11	1.141 (4)	O12- C12	1.136 (4)
O13- C13	1.136 (4)	O14- C14	1.150 (4)

The C6-C21 bond is the longest amongst the four bonds of interest here. The most likely reason for this again is because of the steric effects of the $\text{Mn}(\text{CO})_4$ onto the adjacent phenyl group. Because of the repulsion between the two groups mentioned above, the C6-C21 bond is lengthened to maximize the distance between the two electron rich bulky groups systems. The Mn-C and the C=O bonds in the $\text{Mn}(\text{CO})_4$ group do not show significant variations from those reported in earlier studies for similar compounds. The bond length of C2- C6 is longer than that of C5-C7. This is because the phenyl ring adjacent to the $\text{Mn}(\text{CO})_4$ is twisted out of plane at C21 and is no longer in conjugation with the C2- C6 double bond. Because of resonance, the C2-C6 and C6- C21 bonds lengths show more of a one and a half bond character.

Similarly, the bond angles C2- C6- C21 and C5- C7- C31 are 122.1° (2) and 130.4° (3) respectively.

The C2- C6- C21 angle is smaller when compared to the C5- C7- C31 angle again because the $\text{Mn}(\text{CO})_4$ which is attached to C6 pushes away the adjacent phenyl group maximizing the distance between the two groups which makes the angle C2- C6- C21 smaller when compared to the angle C5- C7- C31 . In short, it can be said that because of steric reasons as a result of the presence of the $\text{Mn}(\text{CO})_4$ and the adjacent phenyl group, the molecule has the shape it has and also explains why one phenyl group is twisted out of plane when compared to the rest of the molecule.

2.5 Conclusions

The current study demonstrates that only the (pyranyl)Mn(CO)₃ product is formed when cyclomanganated dienones, derived from cyclic ketones like 2-3, are reacted with alkynes like phenylacetylene. Once the (pyranyl)Mn(CO)₃ product is formed, it probably opens under more forcing conditions but is not able to cyclise to form the 7-membered oxocycloheptadienyl product. The alternative cyclisation to give the fulvene did not take place as was anticipated. This is because of the inaccessibility of the bonding site for cyclisation to a 7-membered ring. The current study further endorses the mechanisms proposed in earlier studies^{9,11} as has been discussed in this chapter.

When tetraenones were studied, no viable results were obtained. While some tetraenones were successfully prepared in the laboratory, manganation of these tetraenones and any further reactions did not prove productive and these therefore have little synthetic potential at this stage.

The reaction of the manganated chalcones with alkynes like methyl propiolate provides a means of producing (pyranyl)Mn(CO)₃ complexes with the alkyne inserting in the reverse manner to that observed by Tully⁵. This area can be developed into producing a new set of compounds.

2.6 References

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12. Liebeskind, L. S., Gasdaska, J. R., McCallum, J. S., *J. Org. Chem*, **54**, 669, (1989).

Chapter 3

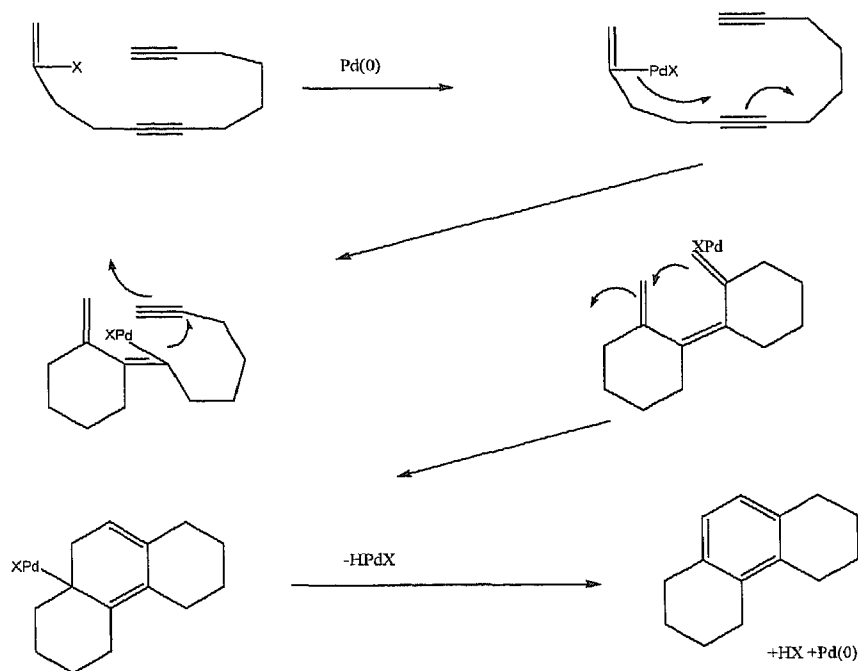
3.0 Application of the Principles of “Cascade” Reactions to Cyclomanganated Compounds

3.1 Introduction

3.1.1 Definition:

Cascade reactions are multi-step reactions where one ring system forms after another giving a multiple ring system in the final product. Cascade reactions provide valuable strategies, especially for the construction of various carbo- and heterocyclic systems with two or more annealated rings ¹.

The following reaction ² (Scheme 3. 1) is a simple example of a cascade reaction from an enediyne (X = Cl, Br, I) resulting in 3 rings in the final product. The final step in the reaction scheme involves β -elimination (loss of HPdX) to give the 3-membered ring product.



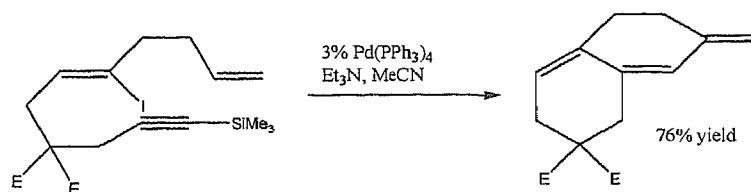
Scheme 3.1: The cyclisation of an enediyne (X= Cl, Br, I) giving a tricyclic product²

3.1.2 Different transition metals in cascade reactions

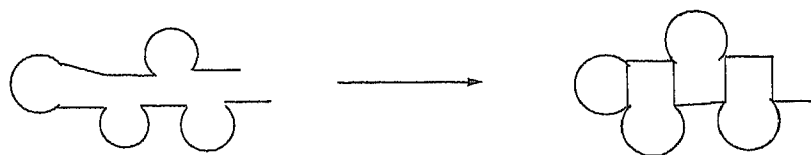
Transition metals have been widely used in a wide range of cyclisation reactions. This use of transition metals in organic synthesis covers a large area and it is not possible to discuss all the reactions. However, an effort has been made in this chapter to present examples of some reactions that have used transition metals to synthesise bicyclic compounds. The main reason for discussing reactions giving bicyclic products is that in the current study, effort has been made to synthesise bicyclic compounds using manganese. The use of methylmanganese carbonyl complex to synthesise cyclopentanoids via enyne cycloaddition in an earlier study by Lee *et al.*³ is discussed later in the chapter and forms the basis of the current study. Some reactions related to the current study, not necessarily cascade, have also been mentioned.

3.1.2.1 Palladium cascades

Palladium is amongst the most widely used metal in organic synthesis. Alkenes and alkynes represent some of the most reactive groups towards palladium. An example of the cyclic carbopalladation process performed by Zang and Negishi⁴ giving rise to a bicyclic product is given by Scheme 3.2a. The process involved in the reaction is referred to as the “zipper” mode cascade. The term “zipper” refers to the manner in which new bonds are formed and the way the cyclisation occurs. Scheme 3.2b shows diagrammatically how the zipper mode cascade reaction occurs. Later in the chapter, some similar terms like “spiro” mode cascade have also been used to indicate the manner in which cyclisations occur to give the final products from their starting materials. The final step in this reaction as for many cascades also involves β -elimination, in this case the loss of HSiMe_3 .

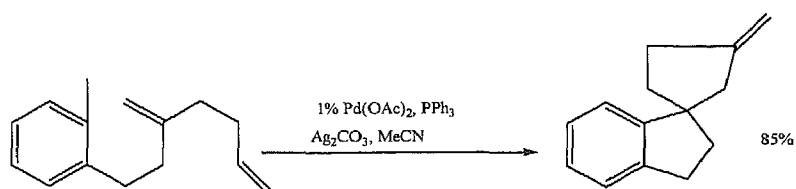


Scheme 3.2a: Example of a “zipper” mode cascade resulting in a bicyclic product⁴



Scheme 3.2b: The diagrammatic representation of the “zipper mode” cascade

These reaction types are applicable to both alkynes and alkenes but reactions involving alkenes are prone to β -elimination and other side reactions. Scheme 3.3 gives an example of the “spiro” mode cascade, readily applicable to only alkenes resulting in a tricyclic compound^{5,6}.

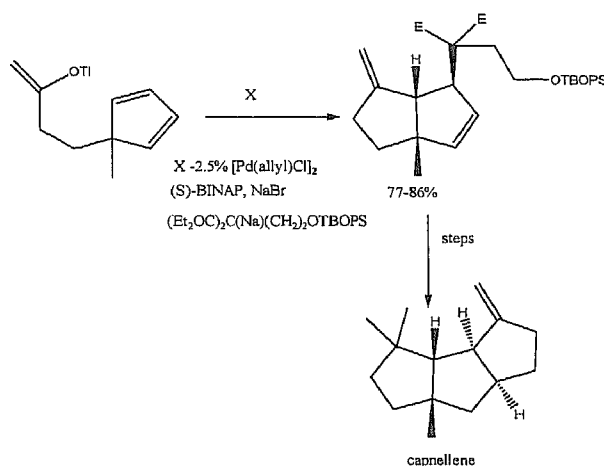


Scheme 3.3: Example of a “spiro” mode cascade resulting in a tricyclic product^{5,6}

Overman⁶ and Shibasaki^{7a} developed an asymmetrical cyclic Heck reaction in 1989. These and other groups^{7b, 7c, 7d} have since developed the reaction as a useful tool for

asymmetric synthesis of complex natural products. Scheme 3.4 gives a representative example^{7e}.

Note: E= CO₂Et or CO₂Me in this scheme and the other schemes that follow.

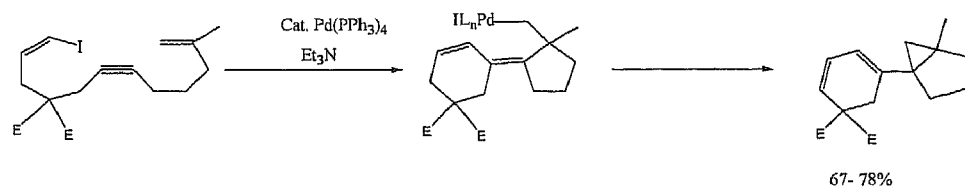


Scheme 3.4: Example of asymmetric synthesis of complex natural products^{8e}

The work that was carried out by Grigg and Sridharan⁸ involved the heating of aryl iodide with norbornene in boiling acetonitrile in the presence of 10 mol% palladium acetate, 20 mol% triphenylphosphine and trimethylamine (2 mol) to yield a single cyclopropanated norbornene stereoisomer in 40% yield.

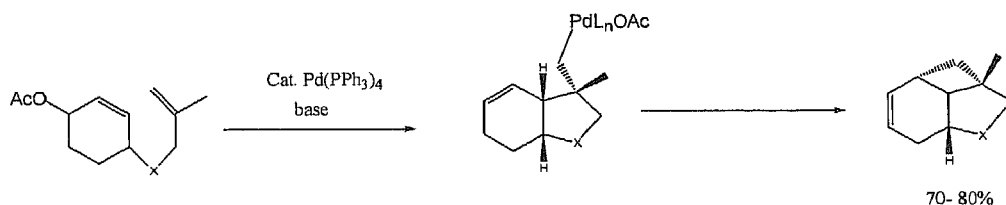
The work by Shibasaki and his group⁷ involved the synthesis of the *cis*-decalin derivative having a chiral quarternary carbon. Their strategy involved enantiotopic group selective ring closure of prochiral mono-cyclic compounds catalysed by a palladium catalyst with a chiral ligand.

An example where the cyclopropylcarbanyl palladium species can undergo β -dehydropalladation rather than decarbopalladation to undergo ring expansion giving cyclopropyl-alkenes⁴ is shown for the iodo reactant in Scheme 3.5.



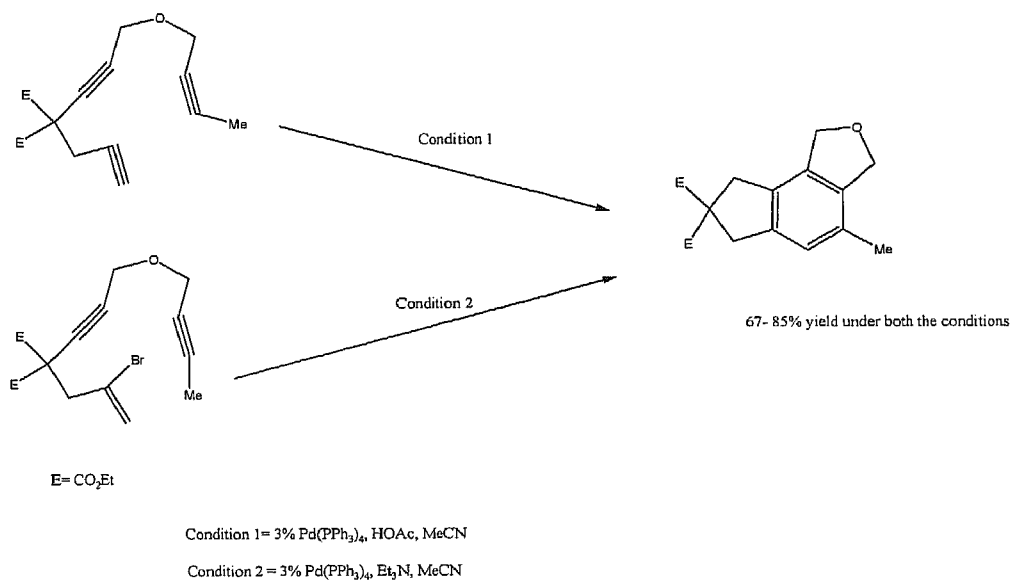
Scheme 3.5: Cyclopropylcarbinyl palladium species undergoing dehydropalladation giving cyclopropyl-alkene⁴

Similarly, Scheme 3.6 shows the formation of cyclopropanes via homoallylpalladium derivatives⁹.



Scheme 3.6: An example of the formation of a cyclopropane via a homoallylpalladium derivative⁹

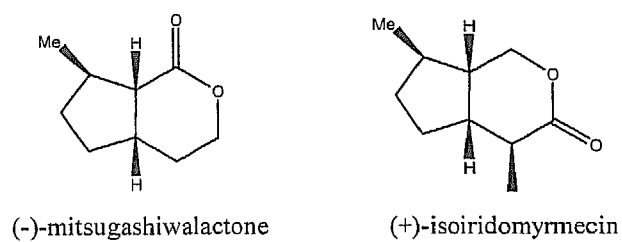
Benzene derivatives can be synthesized via all-intramolecular processes. In most cases, these are via cascade cyclisation as shown by the Scheme 3.7².



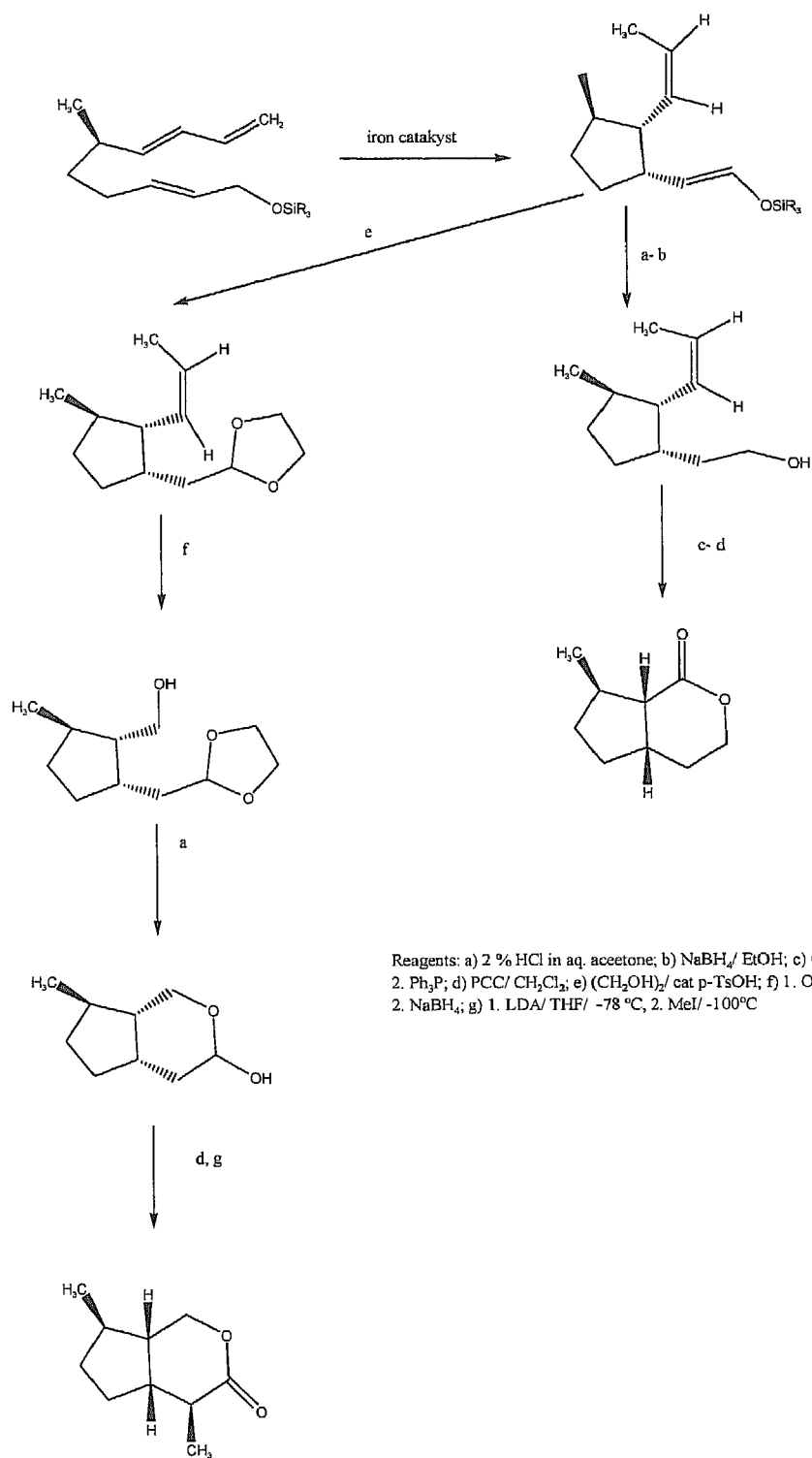
Scheme 3.7: Synthesis of benzene derivatives via all-intramolecular processes²

3.1.2.2 Iron

The iron-catalysed [4 + 4]ene cyclisation of trienes have been extensively studied as well^{10, 11}. For example, the iron [4 + 4]ene cyclisation has been successfully applied in the synthesis of (-)-mitsugashiwalactone and (+)-isoiridomyrmecin¹².



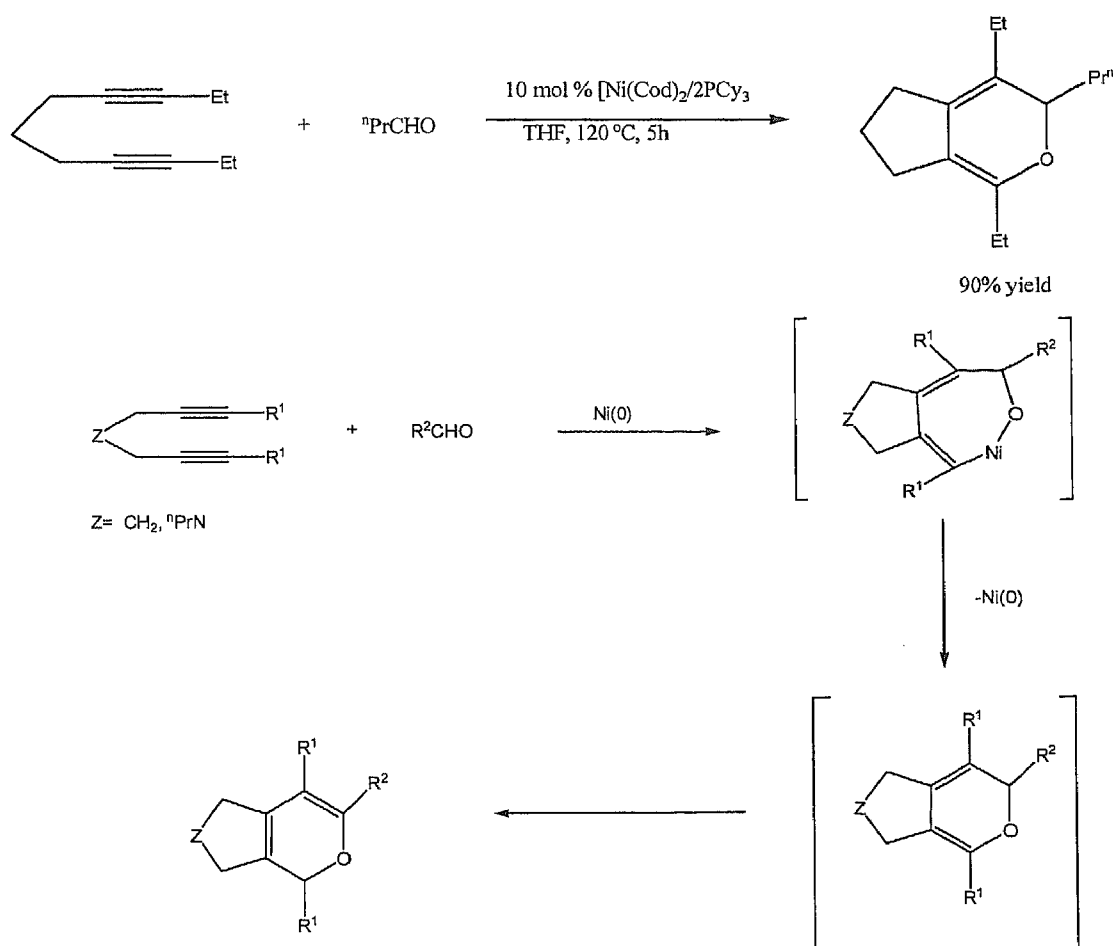
Scheme 3.8 shows how the reaction occurs from the starting materials.



Scheme 3.8: Synthesis of (-)-mitsugashiwalactone and (+)-isoiridomymecine via iron [4 + 4] ene cyclisation¹² using a combination of Fe(acac)₃ and Et₃Al as the catalyst.

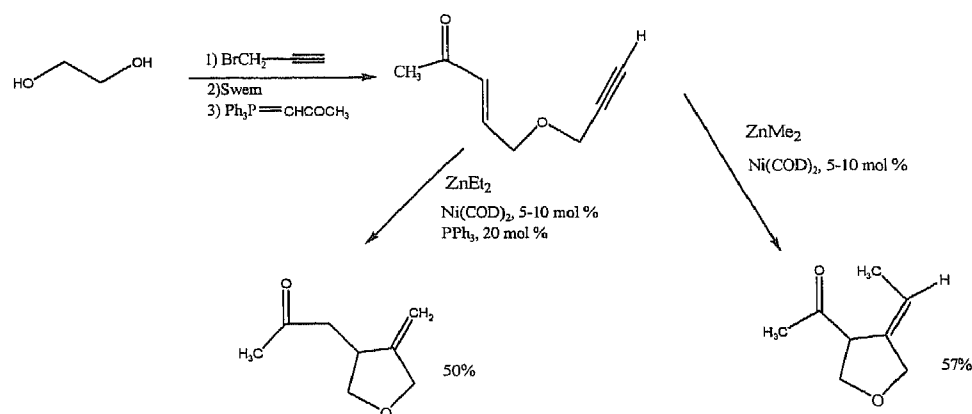
3.1.2.3 Nickel

An example of nickel-promoted cyclisation reaction is the cycloaddition of substituted diynes with aldehydes¹³ which takes place in the presence of nickel(0)-phosphine catalysts to afford the corresponding bicyclic α -pyrones. Scheme 3.9 shows the general equation of the reaction involved and the general mechanism via which the reaction occurs.



Scheme 3.9: Cycloaddition of substituted diynes with aldehydes in the presence of nickel(0)-phosphine catalysts to afford the corresponding bicyclic α -pyrones¹³

Montgomery *et al.*¹⁴ carried out the nickel-catalysed alkynyl-enone cyclisation to prepare a variety of heterocyclic ring systems as shown by Scheme 3.10. One of the products is the same as the one obtained by Lee *et al.*³ using enynes and $\text{MeMn}(\text{CO})_5$ (see scheme 3.17, section 3.1.2.7).



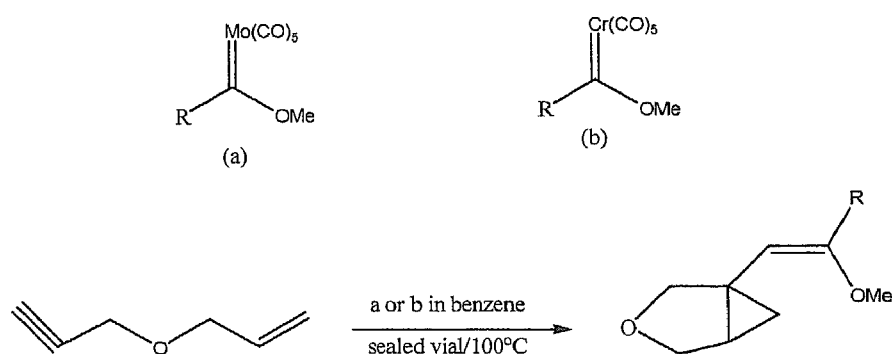
Scheme 3.10: An example of the nickel-catalysed alkynyl-enone cyclisation to prepare a variety of heterocyclic ring systems¹⁴

In scheme 3.10, alkylative cyclisation with $\text{Ni}(\text{COD})_2$ in the absence of triphenylphosphine employing dimethylzinc generated *in situ* from methyl lithium and zinc chloride led to single isomers of trisubstituted exocyclic alkenes with a *cis* orientation between the carbonyl and the substituent derived from the organozinc reagent. Reductive cyclisations with 1:4 $\text{Ni}(\text{COD})_2$: PPh_3 employing commercial diethylzinc led to the exomethylene cycloadduct.

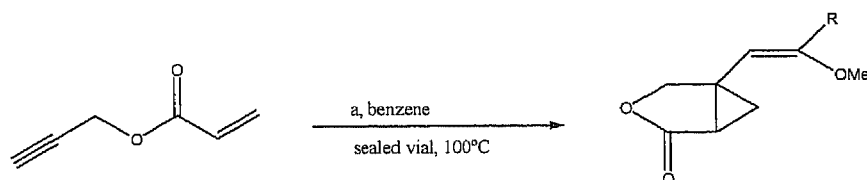
3.1.2.4 Chromium and Molybdenum

Harvey *et al.*¹⁵ carried out a range of cyclization reactions of molybdenum and chromium carbene complexes. The reactions below were used to prepare bicyclic heterocycles using an ether linkage between the alkyne and the alkene as shown by Schemes 3.11 and 3.12.

The structures of the molybdenum and chromium complexes (a and b) used in the reactions given in the schemes are shown as part of scheme 3.11.

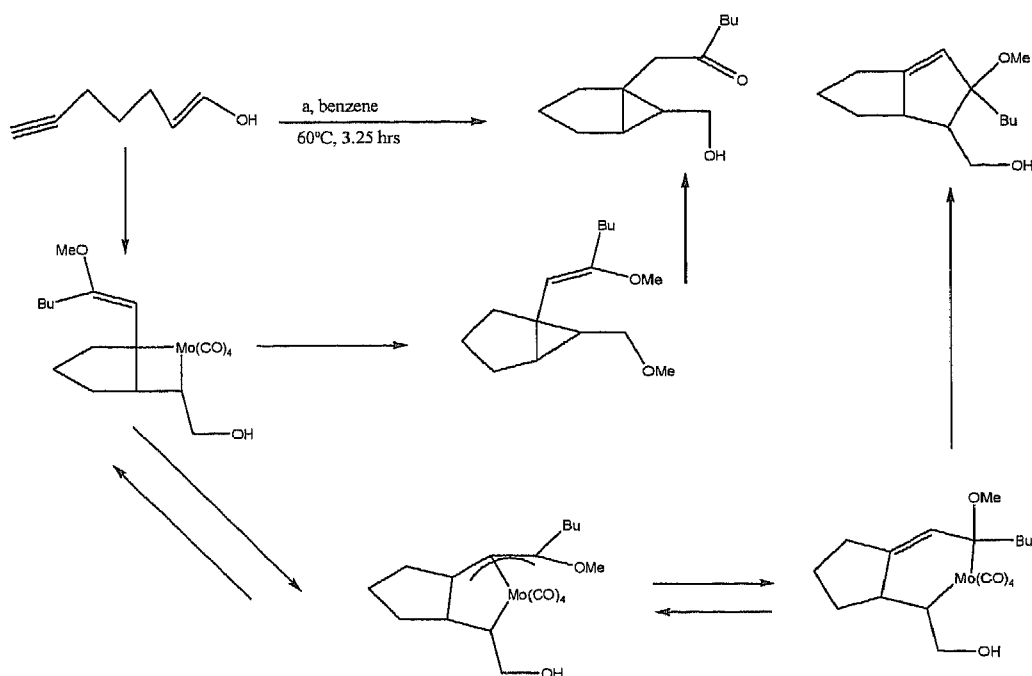


Scheme 3.11: Use of molybdenum and chromium carbene complexes to generate bicyclic heterocycles¹⁵



Scheme 3.12: Use of molybdenum and chromium carbene complexes to generate bicyclic heterocycles¹⁵

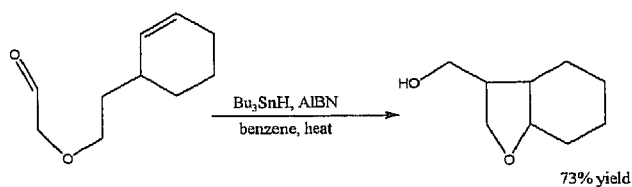
In the same study, the possibility of using an external alcohol rather than ether was also investigated. Treatment of the alcohol for a little over 3 hours at 60 °C gave the cyclopropanation product along with bicyclooctene product (Scheme 3.13). The mechanisms as proposed by Harvey *et al.*¹⁵ for the reactions are also given.



Scheme 3.13: Using an alcohol to generate the cyclopropanation product along with bicyclooctene product ¹⁵.

3.1.2.5 Tin

The work of Parsons *et al.* ¹⁶ demonstrated that aldehydes and α , β -unsaturated ketones can undergo radical cyclisation to form tetrahydrofurans, tetrahydropyrans, chromonols, quinolines and related compounds on reaction with tributyltin hydroxide. An example is the syntheses of bicyclic compounds as illustrated by the cyclisation of the cyclohexenyl aldehyde (Scheme 3.14) to give octahydrobenzofuran in a 73% yield.



Scheme 3.14: Cyclisation of the cyclohexenyl aldehyde to give octahydrobenzofuran¹⁶

3.1.2.6 Titanium

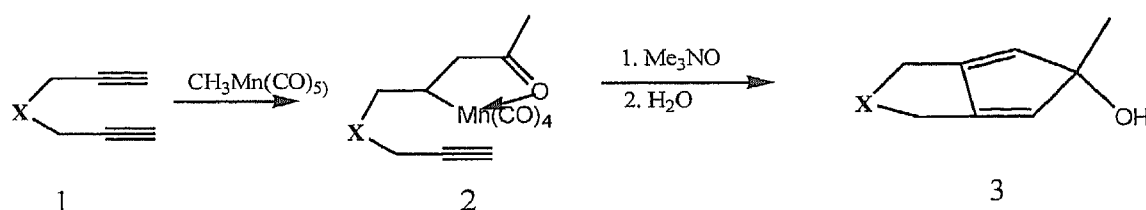
Titanium complexes have received limited attention as catalysts for carbocyclisations.

One successful Ti-catalysed carbocyclisation using $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ is that of the 1,6- and 1,7-enynes in the presence of tert-butyldimethylsilyl cyanide¹⁷. The reaction gave bicyclo[n.3.0] alkenones which serve as useful intermediates in the synthesis of a variety of cyclopentane natural products.

3.1.2.7 Manganese

Cascade reactions are a little studied area in manganese chemistry although it is well established in palladium chemistry. However, the treatment of alkyl- and aryl-manganese pentacarbonyl complexes with alkenes reportedly yielded butenolides and cyclised compounds¹⁸.

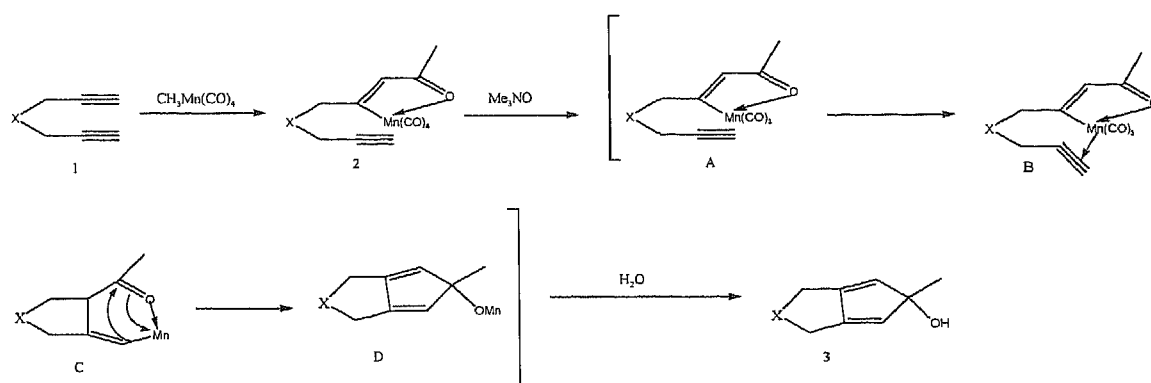
Hong *et al.*¹⁹ synthesized [2,3]-fused bicyclic cyclopentadiene derivatives by the cycloaddition reaction of diynes with methylmanganese pentacarbonyl. The study involved the carbonylative $\text{MeMn}(\text{CO})_5$ mediated carbocyclisation of 1,6-diynes giving [2,3] fused bicyclic cyclopentadiene derivatives as shown by Scheme 3.15.



Scheme 3.15: The carbonylative $\text{MeMn}(\text{CO})_5$ mediated carbocyclisation of 1,6-diynes giving [2,3]-fused bicyclic cyclopentadiene derivatives¹⁹

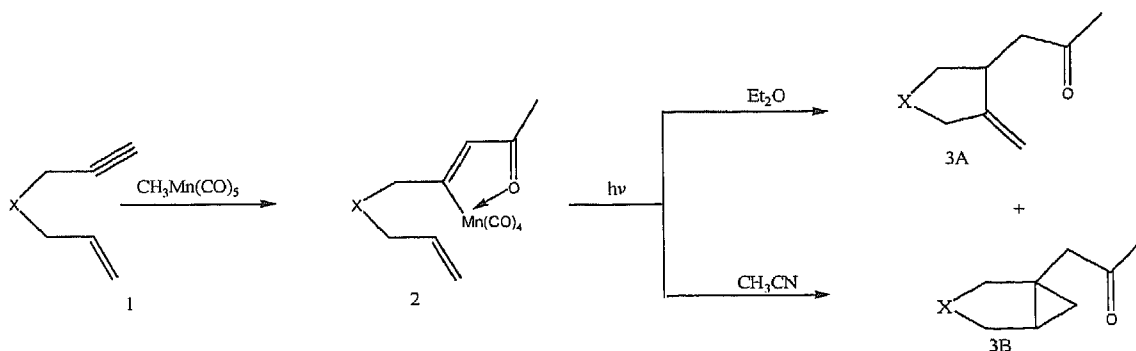
The proposed reaction pathway for the cyclisation of the 1,6-diynes¹⁹ is given by the Scheme 3.16. It shows that treating 2 with Me_3NO generates complex 2A which coordinates to the free triple bond to form 2B. 2B then undergoes intramolecular

cyclisation to give C, followed by the migration of the manganese carbonyls to afford D. Demetallation of D via hydrolysis gives 3.



Scheme 3.16: The proposed reaction pathway for the cyclisation of the 1,6-diynes¹⁹ to give bicyclic cyclopentadiene derivatives

Lee *et al.*³ attempted to use manganese compounds to search for a manganese-mediated cyclisation of enynes. They carried out the transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond (general scheme 3.17, where $\text{X} = \text{O}$, NTs, NBn).

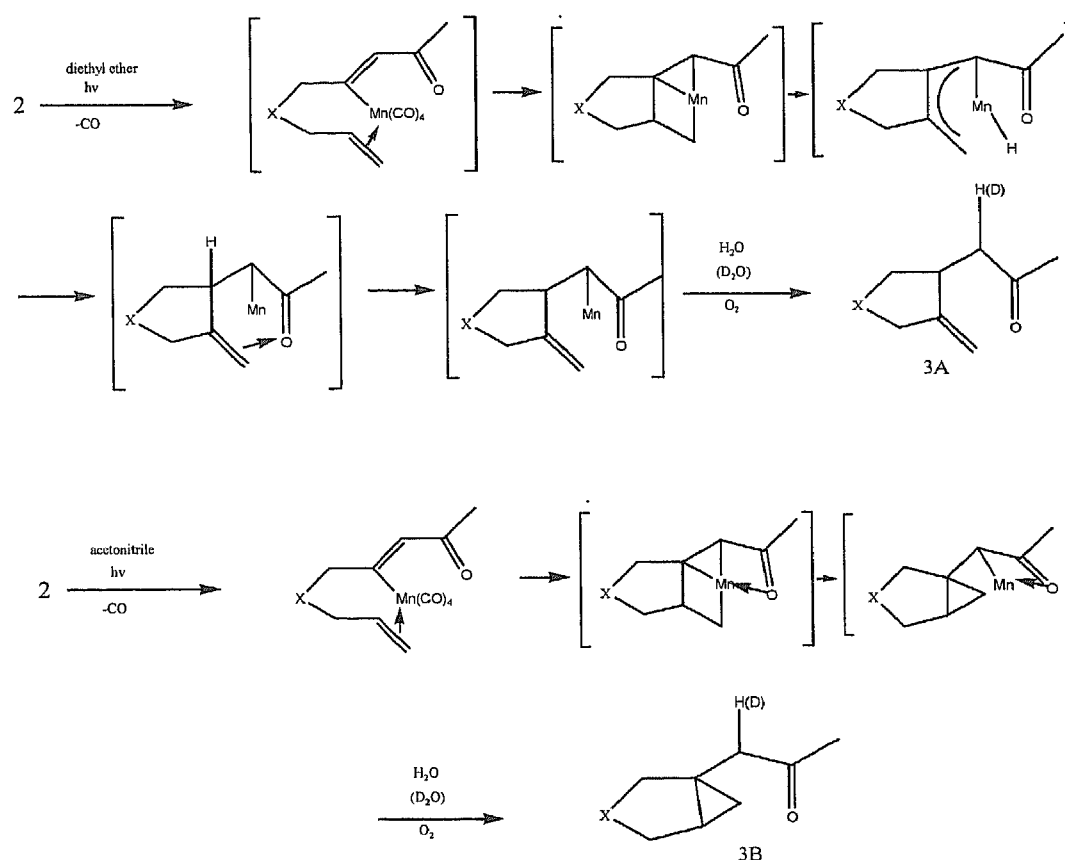


Scheme 3.17: Manganese mediated transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond³

The $\text{Mn}(\text{CO})_4$ complex, 2 (scheme 3.17), was prepared as a potential cascade precursor by reacting the enynes 1 and $\text{CH}_3\text{Mn}(\text{CO})_5$ in diethyl ether at room temperature for a period of 3 days. Compound 2 (scheme 3.17) was then dissolved in diethyl ether and the

solution irradiated with a medium pressure mercury lamp (UV) for 1.5 hours in an effort to initiate cyclisation of the manganated enone. This was then repeated in acetonitrile. The solutions in both cases were then exposed in air. 3A was predominantly obtained from the diethyl ether reaction and 3B predominantly from the acetonitrile reaction after purification using PLC.

The most likely sequence involved to give the two products as proposed by Lee *et al.*³ is the loss of CO to give a 16-electron species, followed by coordination of the double bond as an η^2 ligand, subsequent intramolecular cyclisation and metal replacement to give A or B as shown in the Scheme 3.18.

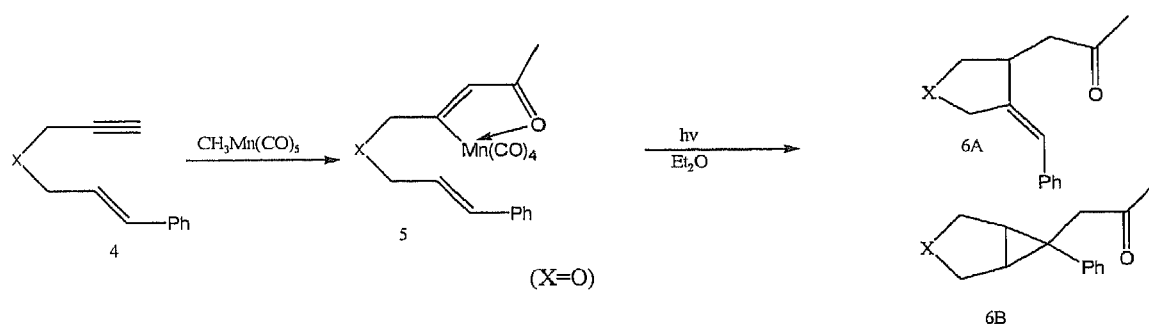


Scheme 3.18: Proposed mechanism³ for the manganese-mediated transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond¹³

The pathway to 3A may involve an intramolecular cyclisation followed by the formation of η^3 -alkylmanganese hydride, the subsequent migration of the hydride and finally demetallation to give A whereas the pathway to 3B may involve an intramolecular cyclisation, cyclopropanation and finally demetallation to give B.

Table 1 shows the stereochemistry of the products 3A and 3B as deduced from the NMR spectra.

When 3-(prop-2-ynyloxy)prop-1-enylbenzene, 4 (X=O), (Scheme 3.19) was reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$, 5 (X=O) was obtained (Scheme 3.19). Irradiation of 5 (Scheme 3.19), in diethyl ether gave predominantly 3A and 3B but in acetonitrile, decomposition products as a result of bond cleavage at X (O in this case) of the starting enyne 1 were obtained (Scheme 3.19).



Scheme 3.19: Products obtained as result of reacting 3-(prop-2-ynyloxy)prop-1-enylbenzene with $\text{CH}_3\text{Mn}(\text{CO})_5$ and subsequent U.V. irradiation in diethyl ether¹³

Table I also shows the results obtained by Lee *et al.*³ using the two enynes which were to be considered in the current study.

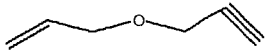
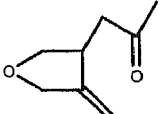
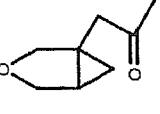
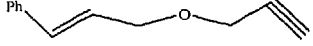
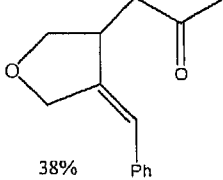
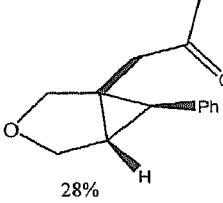
	Enyne	Yield % of A & B	Yield % of 3			
			Diethyl ether		Acetonitrile	
			A	B	A	B
1		78	3A  58%	0	0	3B  66%
2		92	6A  38%	 28%	0	6B b

Table 1: Results obtained by Lee *et al.*³ for the enynes considered in the current study

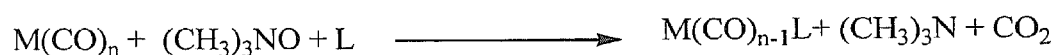
3.2 *Aims of the present study*

3.2.1 Mechanistic understanding in relation to solvent effects

One of the objectives of this section of work was to extend the earlier work by Lee³ and his group and the work done at Waikato by Nicholson, B.K.^{18a-c} and his group. It was anticipated that better mechanistic understanding of the cascade reactions presented would be achieved and that further synthetic applications of the Lee *et al.*³ work could also be worked out.

3.2.2 Methods of Activation

There has been no other reported method of activation apart from U.V. irradiation by Lee *et al.*³ to initiate cyclisation of a cyclomanganated compounds involving an intramolecular alkene. In the current study, the aim was to use heating, (CH₃)₃NO and Li₂PdCl₄ as methods of activation as previously used for other types of alkene coupling²¹. In organometallic chemistry, (CH₃)₃NO is employed as a decarboxylation agent according to the following stoichiometry.



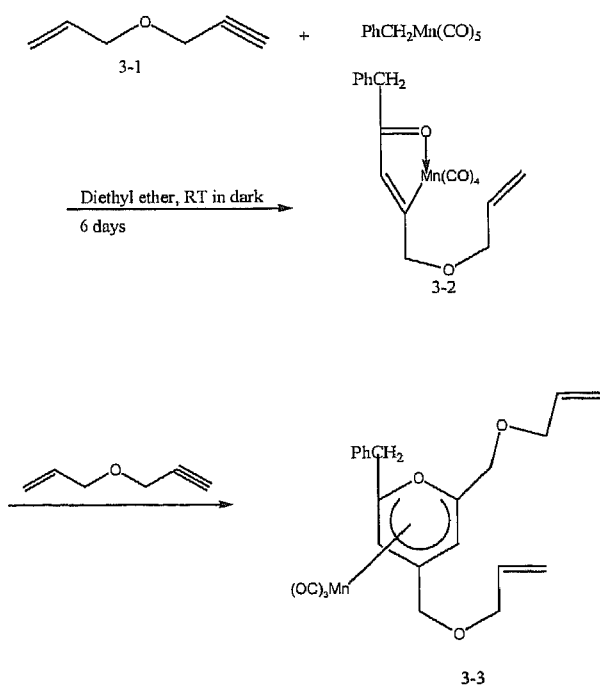
The manganated enones were to be reacted with an alkene (methyl acrylate) and an alkyne (phenylacetylene) to see if normal coupling products of the types previously obtained^{21,22} were formed and if any intervention (coupling, insertion and cyclisation) of the alkene present in the manganated enone occurred to give some novel products.

3.3 Results and Discussion

3.3.1 Reaction of 4-oxa-6-heptyn-1-ene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in ether

Reaction of the 4-oxahept-1-en-6-yne, 3-1 (Scheme 3.20) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ gave two products. The first product was identified as the $\text{Mn}(\text{CO})_4$ product, [5-(propenyl-3-oxy)-1-phenylpent-3-en-4-yl- κC^4 -2-one- κO]tetracarbonylmanganese (3-2, Scheme 3.20 and 3.22).

This $\text{Mn}(\text{CO})_4$ product (3-2, scheme 3.20 and 3.22) was similar to the methyl analogue (2, scheme 3.17) of Lee *et al.*³ which they prepared using $\text{CH}_3\text{Mn}(\text{CO})_5$ and is similar to the Hong *et al.* $\text{Mn}(\text{CO})_4$ compound¹⁹ (Scheme 3.15). The preparation of the cyclomanganated compounds in the current study involved stirring the starting enyne with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in ether, at room temperature and in dark, for 6 days. Similar pentacarbonyl molybdenum and chromium complexes have also been prepared by Harvey *et al.*¹⁵. The second product isolated as a brownish yellow oil was identified as the (pyranyl) $\text{Mn}(\text{CO})_3$ product (3-3, Scheme 3.20)

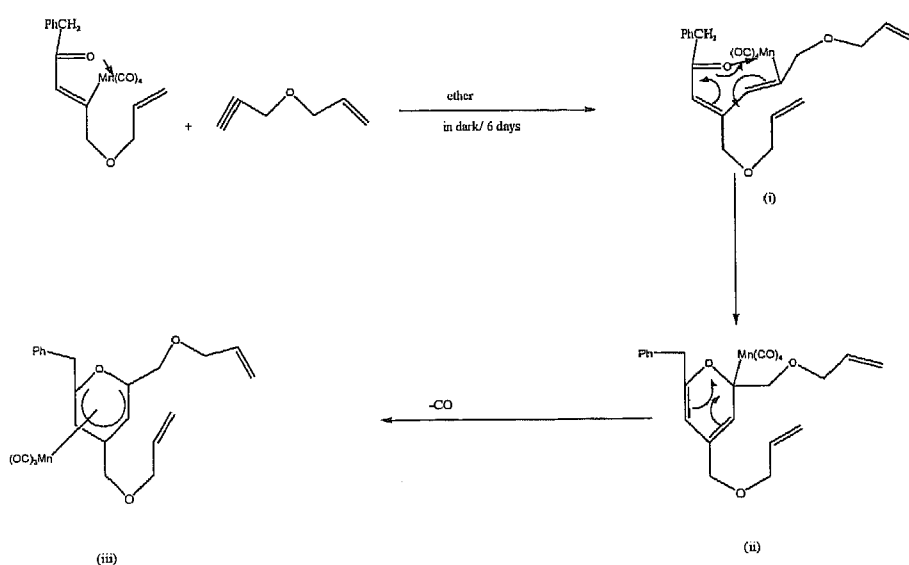


Scheme 3.20: Reaction of 4-oxa-6-heptyn-1-ene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in ether

The products were characterized by IR, ESMS, HRMS and NMR by comparison to structurally similar compounds found in literature. Where possible, the structures of the reference compounds are also given in the experimental section 3.5.

The (pyranyl)Mn(CO)₃ product (3-3) was the alkyne-coupling product of the type obtained in earlier studies^{22,23} from the coupling of manganated chalcones with alkynes. As the Mn(CO)₄ complex, 3-2 was formed in the reaction of 3-1 with PhCH₂Mn(CO)₅, 3-2 coupled with the starting alkyne 3-1 to give 3-3 (Scheme 3.20).

The previously proposed mechanism²³ (Scheme 3.21) for the formation of the (pyranyl)(Mn(CO)₃) complex analogous to 3-3 involves the initial insertion of the alkyne (3-1) into the Mn-C bond giving the intermediate (i). Cyclisation by formation of a C-O bond between the oxygen and the alkyne carbon next to the manganese comes about by rearrangement of the π -electrons giving the cyclic intermediate (ii). Coordination of the full π system to Mn together with the loss of a carbonyl group results in the formation of the (pyranyl)Mn(CO)₃ complex (iii).



Scheme 3.21: The proposed mechanism²³ for the formation of the (pyranyl)(Mn(CO)₃) complex 3-3

The IR spectrum of the $\text{Mn}(\text{CO})_3$ complex in the ν (CO) region showed the expected three band pattern of lower frequency than that of the $\text{Mn}(\text{CO})_4$ group. This was observed for the (pyranyl) $\text{Mn}(\text{CO})_3$ complex at 2011 cm^{-1} (vs) and two overlapping bands at 1946 cm^{-1} (s, br). For the $\text{Mn}(\text{CO})_4$ complex (3-2), the IR bands were observed at 2081 (m), 1995 (vs), and 1942 cm^{-1} (s). These observed IR bands for the (pyranyl) $\text{Mn}(\text{CO})_3$ complex and for the $\text{Mn}(\text{CO})_4$ complex were similar to those observed by Tully^{18a} for manganated chalcones and for the (pyranyl) $\text{Mn}(\text{CO})_3$ complexes resulting from the reactions of the manganated chalcones with alkynes like phenyl acetylene.

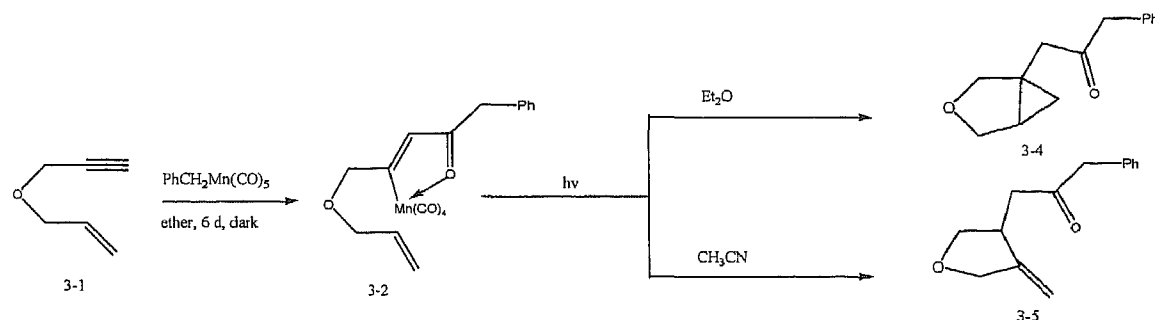
The ^1H NMR and ^{13}C NMR assignments used to characterize the $\text{Mn}(\text{CO})_4$ (3-2) and the (pyranyl) $\text{Mn}(\text{CO})_3$ (3-3) complexes are listed in section 3.5. The chemical shifts are consistent with those observed by Tully^{18a} for the $\text{Mn}(\text{CO})_4$ complexes (manganated chalcones) and for the (pyranyl) $\text{Mn}(\text{CO})_3$ complexes resulting from the reaction of manganated chalcones with alkynes.

The ^1H NMR and ^{13}C NMR spectra of 3-2 are given after the NMR signal assignments in section 3.5 to show the purity of 3-2 that was used for further reactions. When comparing the ^1H NMR of the starting material 3-1 with the manganated product 3-2, there is a large observed downward shift for the H1 in 3-1 which is H3 in 3-2 (refer to numbering of the structures in section 3.5). This is consistent with the ^1H NMR shifts observed by Tully^{18a} with the cyclomanganated chalcones. As for the ^{13}C NMR spectrum, the MnC=O (metal carbonyl) bands appear around 220 ppm for 3-2 typical for cyclomanganated compounds²². The ^1H NMR and the ^{13}C NMR spectra of pyranyl($\text{Mn}(\text{CO})_3$) complexes are discussed later in the chapter.

3.3.2 Solvent effects

Irradiation of 3-2 with a medium pressure lamp (U.V.) in diethyl ether gave predominantly 3-4 (26.5% versus 51%) (Scheme 3.22). When 3-2 was irradiated with a medium pressure mercury lamp in acetonitrile, predominantly 3-5 (27% versus 54%)

(Scheme 3.22) was obtained. Yields were lower than those reported by Lee *et al.*³ for the MeMn(CO)_5 alternative reaction.



Scheme 3.22: Reaction of the 4-oxa-6-heptyn-1-ene with $\text{PhCH}_2\text{Mn(CO)}_5$ and subsequent irradiation of 3-2 with U.V. in diethyl ether and acetonitrile

The solvent effect is the reverse of that observed by Lee *et al.*³ using the methyl analogue (2, Scheme 3.17) of 3-2 derived from MeMn(CO)_5 . Only the diethyl ether product was the cascade product and the product obtained in acetonitrile was because of a single cyclisation. A possible route to two products alternative to the one proposed by Lee *et al.*³ (Scheme 3.18) is given in section 3.3.3 (Scheme 3.24). Since no constructive data is available to propose a definite mechanism, the proposed mechanism (Scheme 3.24) seems like a viable alternative. The characterization of the two products involved the use of IR, NMR, GC-MS, MicroTOF and ESMS data.

The methyl analogues of these two products resulting from the photolysis experiments in this study have been prepared by Lee *et al.*³ as discussed earlier in the chapter. They also proposed the likely mechanism for the formation of their methyl analogues. While it is likely that similar sequence of steps led to the formation of the products obtained in the current study, it is unclear why the cascade product was obtained in diethyl ether while the product because of a single cyclisation was obtained in acetonitrile, the reverse solvent effect of that observed by Lee *et al.*³.

How exactly solvents determine the types of products formed has not been cited in literature on similar sorts of study. However, both the solvents used in the current study were aprotic with the acetonitrile being the more polar. The polar acetonitrile, for some

reason appears not to allow the second cyclisation to give a bicyclic product as obtained in diethyl ether. Acetonitrile is known to coordinate to metal centres like Mn and this could replace a CO thus affecting the coupling chemistry at the metal centre²⁴. Acetonitrile has the potential to coordinate to the metal centres via nitrogen or via the triple bond (pi electrons)²⁴. On the other hand, diethyl ether could also weakly coordinate to Mn via the oxygen atom as well thus affecting its coordination chemistry in some other way²⁵. Irrespective of the solvent ligand effects, it is not clear at all why changing diethyl ether for acetonitrile should reverse the preferred product for the benzyl vs methyl case.

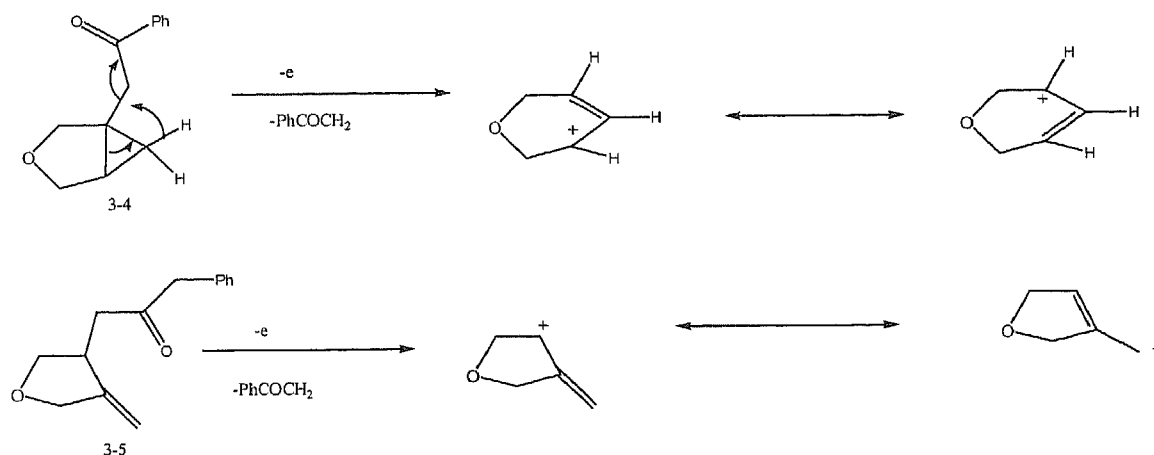
For both the products (3-4 and 3-5) to form, a proton source is required (after demetallation, refer to mechanisms) if the mechanisms proposed in this study, and as proposed by Lee *et al.*³ are to be believed.

It was originally suggested by Woodgate *et al.*²⁶, and later by Cooney²¹ that excess alkene could be a source of proton in similar coupling reactions involving cyclomanganated compounds with methyl acrylate. This followed the observation²⁶ through the use of deuterio-acetonitrile solvent, that solvent is not the source of proton. The manganated enones considered in the current study do have an alkene present, so these could be the source of proton intermolecularly in the final stages of the reactions. In the same study Cooney²¹ also demonstrated in alkene coupling studies that acetonitrile could insert into the carbon-manganese bond to form the imine which could hydrolyse to give the ketone during work-up. Although no such acetonitrile insertion products were observed here, this indicates the potential for effective coordination of acetonitrile to the Mn centre which could have affected the product type observed in the solvent.

On the other hand, Lee *et al.*³ suggested that the protons are most likely coming from water during work-up. This was confirmed by carrying out the demetallation in the presence of D₂O and finding deuterium at the α -methylene position to the ketone (Scheme 3.18, section 3.1.2.7). The two suggestions however need further investigation. ,

3.3.2.1 ESMS and EI-GCMS studies of the compounds 3-4 and 3-5

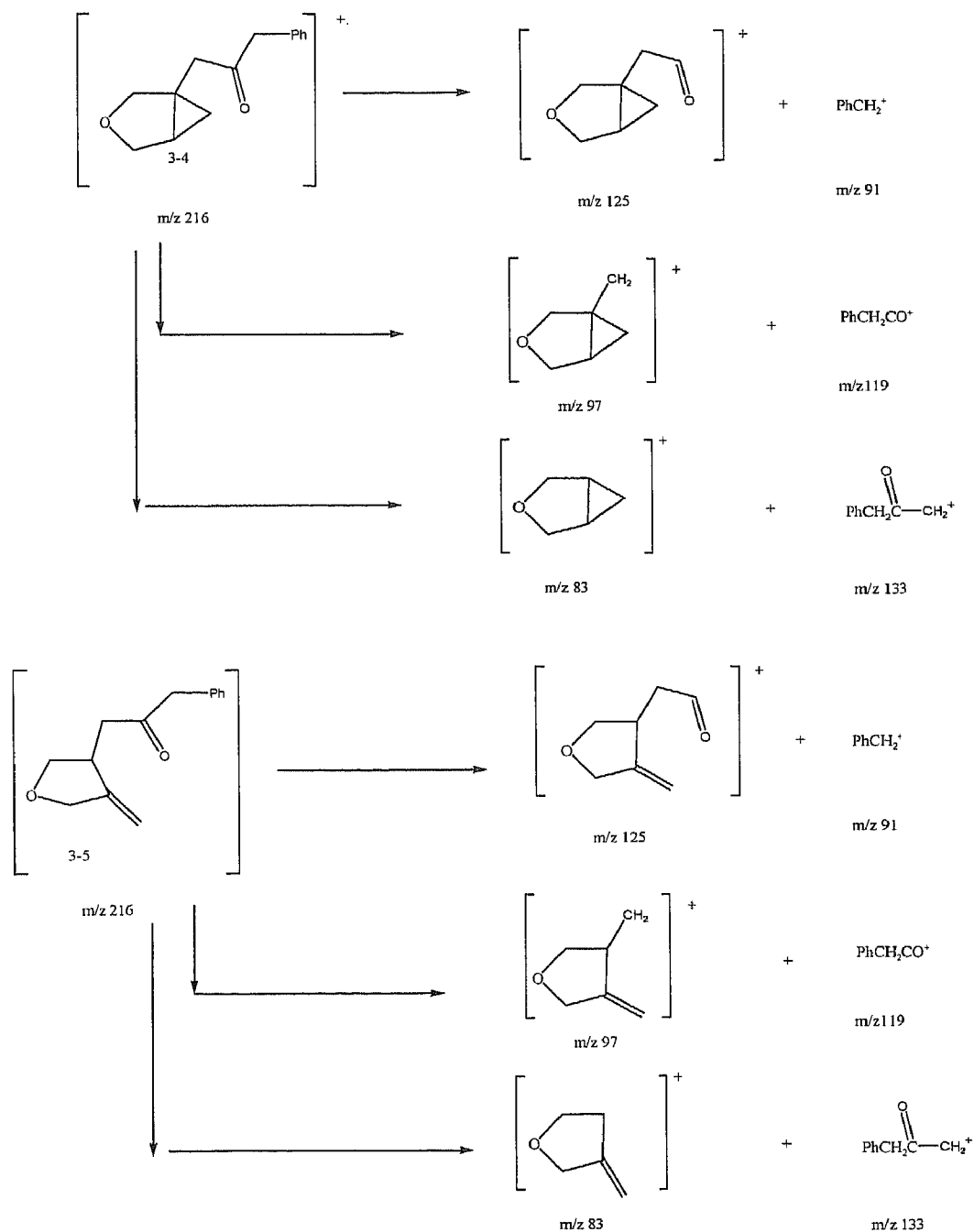
The ESMS spectra of the two compounds, 3-4 and 3-5 (Scheme 3.22) were identical as shown by figures 1. Both the compounds showed $[M+Na]^+$ and $[2M+Na]^+$ ions (figure 1). This information was of little use in the characterization of the products. Similarly, the EI-GCMS spectra (figure 2) of the two compounds (3-4 and 3-5, scheme 3.22) gave a strong signal at m/z 91 and the parent ion at 216 (figure 2). The m/z peak at 125 was due to the fragment resulting from the splitting $[M-C_7H_9O_2]$. The signal for the fragment $C_7H_9O_2$ showing at 125 and the peak at 91 for C_7H_7 . Similarly the signals at m/z 97 for C_6H_9O and 118 for $C_9H_{10}O$ are due to the fragmentation $[M-C_9H_{10}O]$. Refer to the fragmentation patterns shown in Scheme 3.23. These results are of little help in distinguishing between the two compounds. However, there is a signal at 83 in one of the EI-GCMS spectra as shown in figure 2. This signal could result from the products 3-4 and 3-5 fragmenting in the following alternative ways.



If 3-5 fragmented to give the cyclic carbocation, not shown by experiment, it will not be planar at C^+ because of the fused 5-membered ring. This carbocation will be unstable so may not be seen until it formed the second product with the double bond thus forming a stable allyl cation.

The fragmentation of 3-4 is accompanied by a hydride transfer in which the 3-membered ring opens with release of ring strain to form an allylic cation. For 3-4, fragmentation

more likely to be present and seen in the EI-GCMS spectra of 3-4, the first spectra. The possible EI-GCMS fragmentations of 3-4 and 3-5 are shown in Scheme 3.23.



Scheme 3.23: The EI-GCMS fragmentation patterns of 3-4 and 3-5

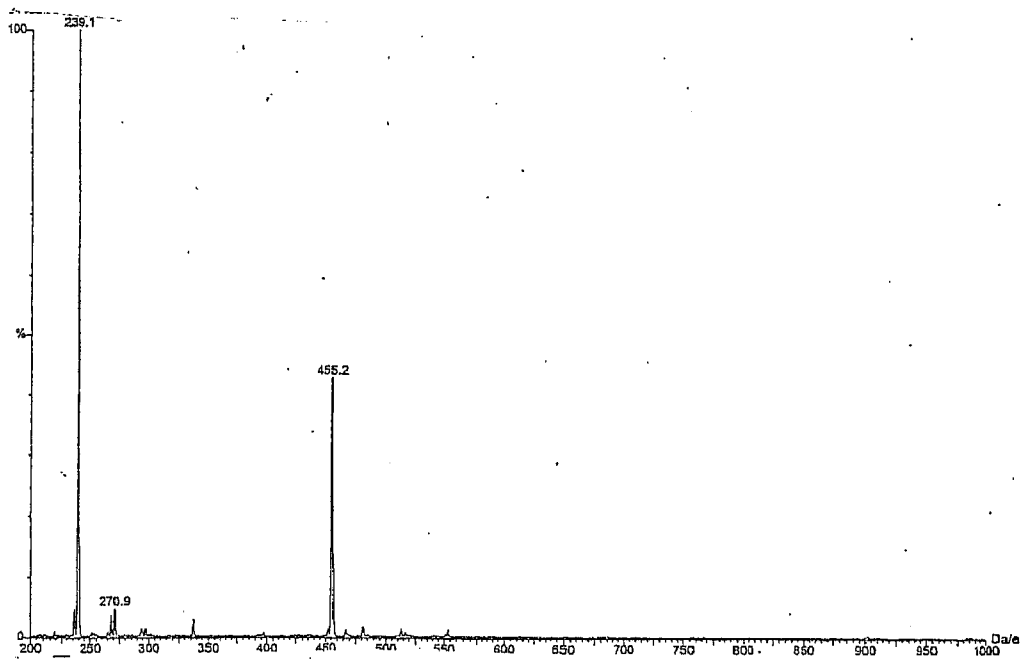
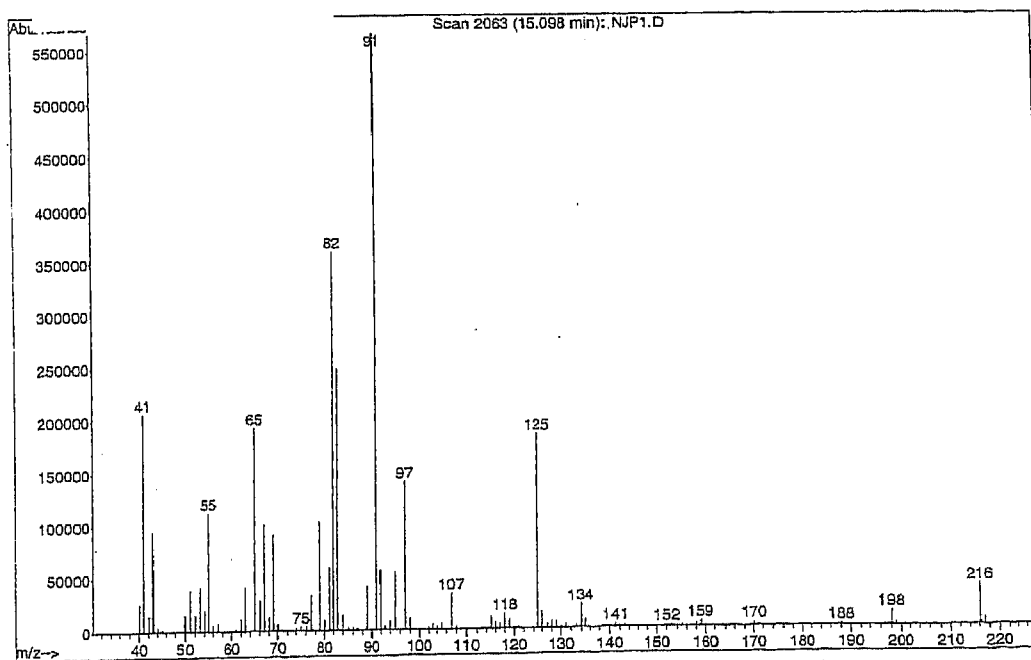


Figure 1 – ESMS of 3-4/3-5 at cone voltage +20 V in MeOH/NaOMe



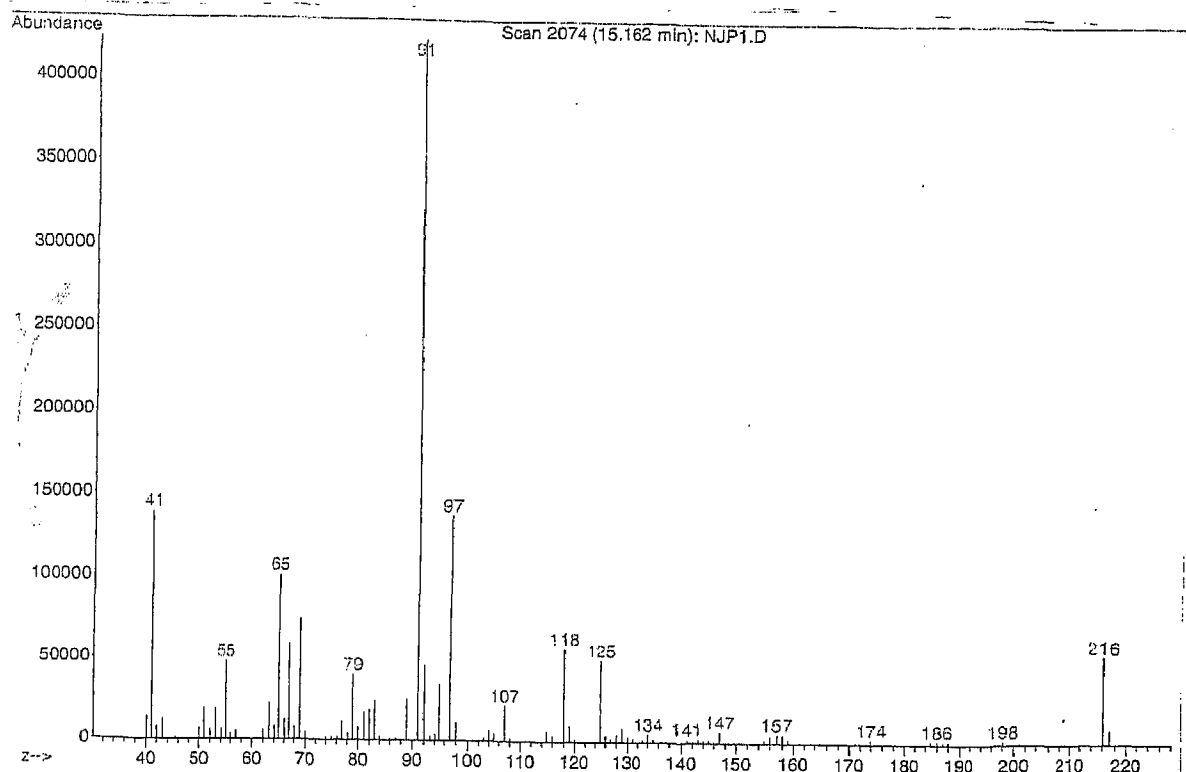


Figure 2- EI-GCMS of 3-4 and 3-5

3.3.2.2 ^1H NMR and ^{13}C NMR spectra

The products were characterized using ^1H NMR and ^{13}C NMR spectra (Section 3.5). A characteristic difference in the ^1H NMR of the two products was the missing alkene signals between 5.0 ppm and 6.0 ppm in the product out of diethyl ether (figure 3). These signals were still present in the spectrum of the acetonitrile product at around 4.90 ppm (figure 5). Similarly, the ^{13}C NMR signals for the alkene were present only in the acetonitrile product (3-5) at 104.4 and 151.4 ppm (figure 6) and not in the diethyl ether product (3-4) (figure 4).

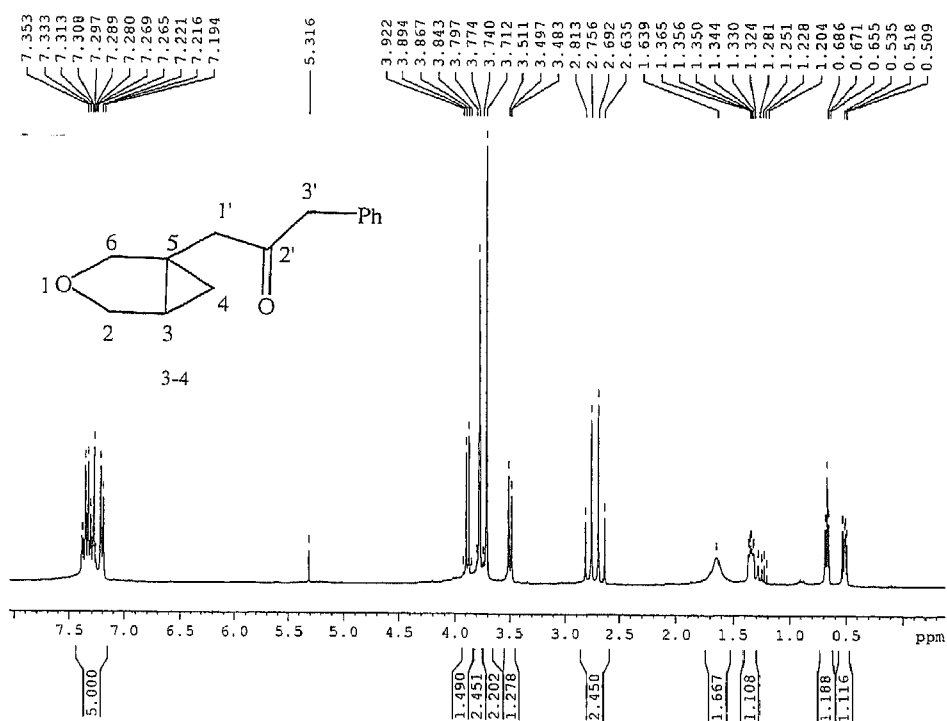


Figure 3- ¹H NMR spectrum of 3-4 (300 MHz, CDCl₃)

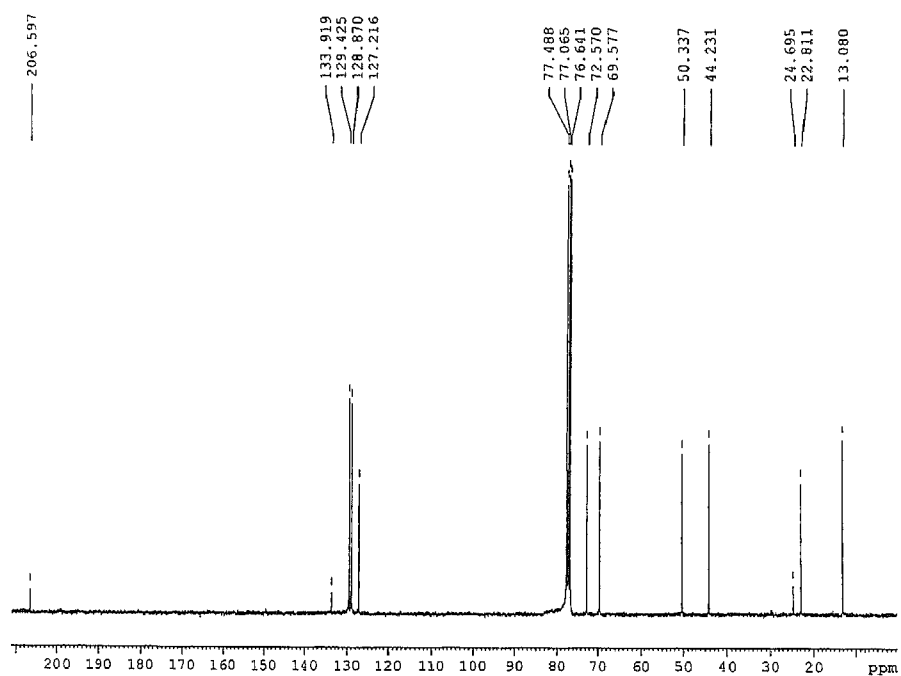


Figure 4- ¹³C NMR spectrum of 3-4 (300 MHz, CDCl₃)

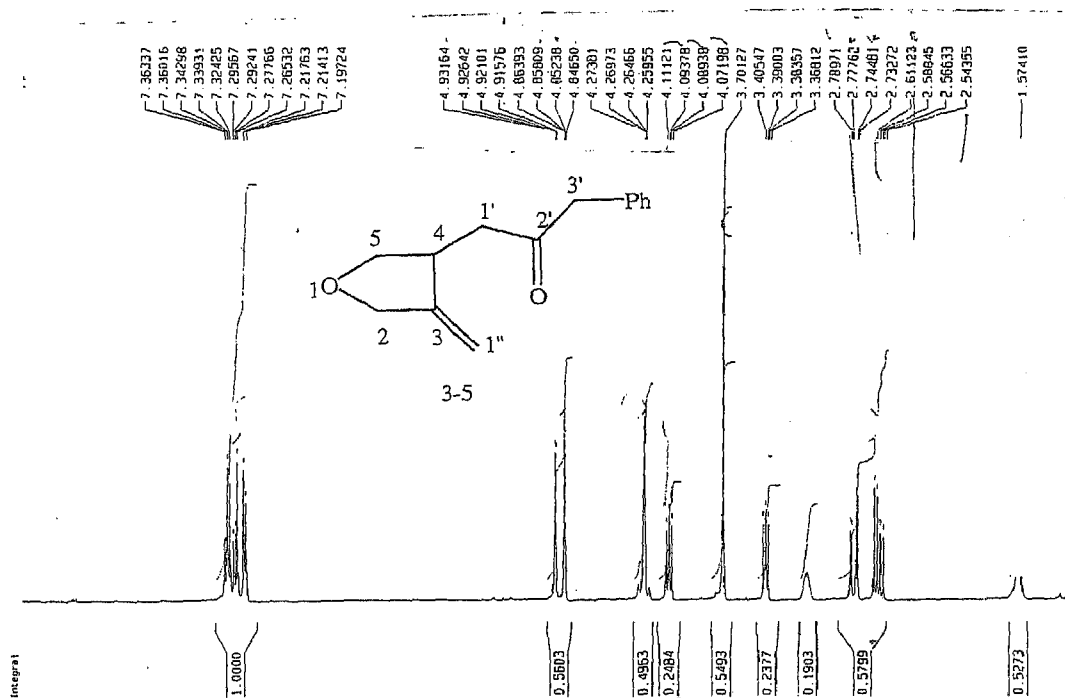


Figure 5- ^1H NMR spectrum of 3-5 (300 MHz, CDCl_3)

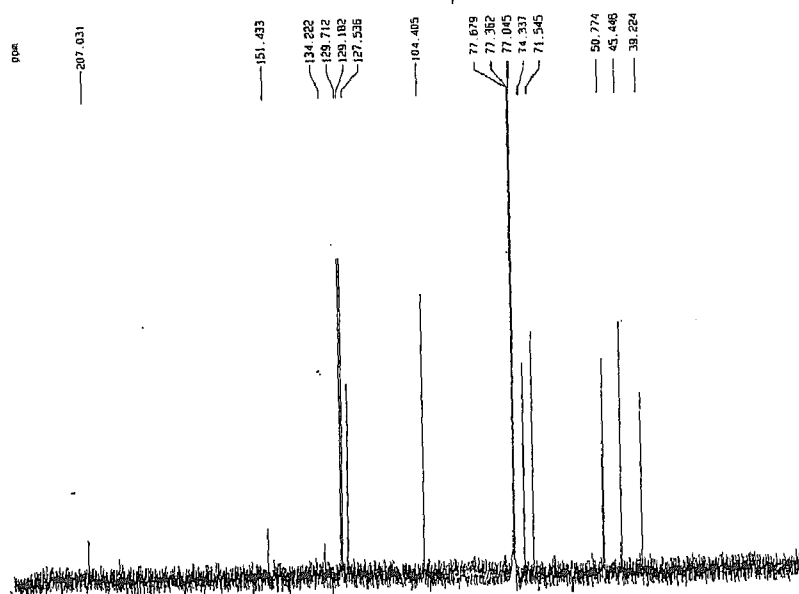


Figure 6- ^{13}C NMR spectrum of 3-5 (300 MHz, CDCl_3)

3.3.3 Different methods of activation of the coupling reactions of intramolecular alkene and the tetracarbonylmanganese complex (3-2)

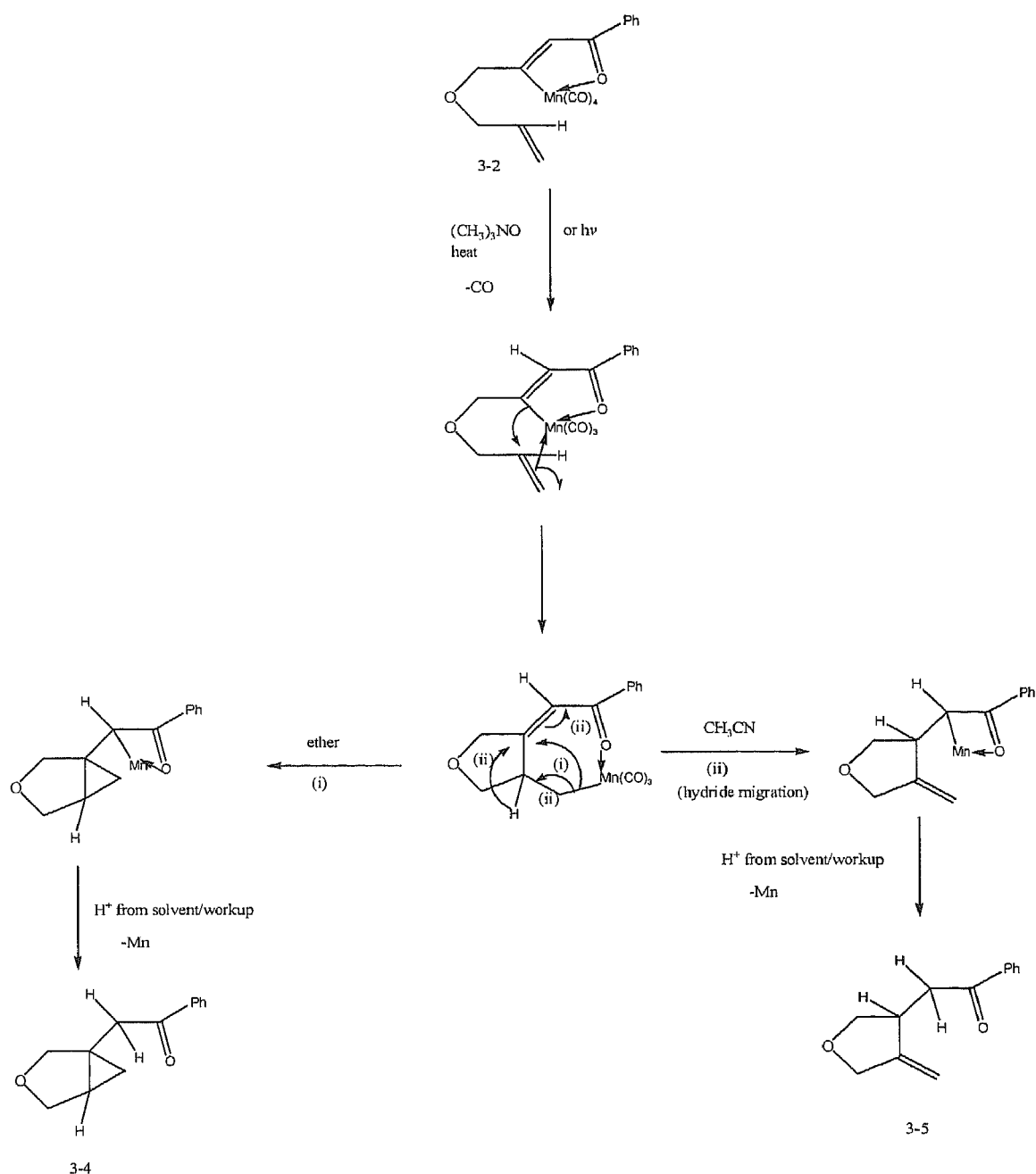
In six different experiments, (3-2) was stirred at ambient temperature in diethyl ether and acetonitrile, heated in diethyl ether and acetonitrile, as well as stirred in the presence of Li_2PdCl_4 in both diethyl ether and acetonitrile at ambient temperature. All these experiments were carried out in the dark. In another two separate experiments, 3-2 was irradiated in tetrahydrofuran and dichloromethane.

No reaction occurred when 3-2 was heated in diethyl ether and acetonitrile in two separate experiments. Similarly no reactions occurred when 3-2 was stirred in diethyl ether and acetonitrile at room temperature in the presence of $(\text{CH}_3)_3\text{NO}$ in another two experiments. Trimethylamine oxide has the ability to oxidize metal-coordinated CO to CO_2 , releasing a metal coordination site for alkene or other π -donors¹⁹.

However, stirring 3-2 in diethyl ether and acetonitrile in the presence of $(\text{CH}_3)_3\text{NO}$ followed by heating gave results similar to the U.V. irradiation experiments, i.e. 3-4 was obtained in diethyl ether and 3-5 was obtained in acetonitrile. Several minor bands were observed during PLC to separate the products and these bands were ignored and no attempts were made to extract these. This was obvious from the very low yields obtained for the main products. It was noted that most of the material put onto the base of the plate (PLC) did not move and remained at the base. The use of $(\text{CH}_3)_3\text{NO}$ therefore did not promote any reactions until the reaction mixture was heated.

This probably means the $\text{Mn}(\text{CO})_3$ complex similar to that suggested in an earlier study³ was only generated when the reaction mixture was irradiated with U.V. and heated in the presence of $(\text{CH}_3)_3\text{NO}$. Once the $\text{Mn}(\text{CO})_3$ complex was generated, this coordinatively unsaturated manganese complex could coordinate with the free double bond, followed by cyclisations to give the two products. However, none of the intermediates has been isolated and characterized to confirm the proposed mechanism.

In diethyl ether, a second cyclisation occurs followed by protonation to give the final cascade product (3-4). In acetonitrile, an intramolecular hydride migration is involved followed by protonation to give the final product (3-5). Possible routes to the two products can be proposed (Scheme 3.24). This mechanism is simpler to that of Lee *et al.*³. However, for the formation of 3-5, a Mn-H intermediate is involved for the transfer of hydrogen in the mechanism proposed by Lee *et al.*³ where as in our proposed mechanism, it is a 1,2-hydride shift to an electrophilic carbon is involved (reaction labeled (ii) for acetonitrile solvent. There is nothing in either mechanism to explain the solvent effect.



Scheme 3.24: The proposed mechanism for the formation of 3-4 and 3-5

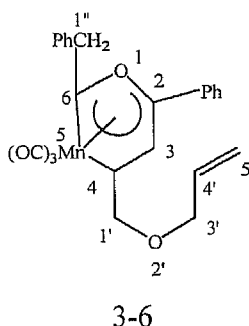
Stirring 3-2 in diethyl ether and acetonitrile in the presence of Li_2PdCl_4 gave products that could not be isolated in the pure form and fully characterized. TLC showed multiple spots and multiple bands were seen on the PLC. Extracting some of these bands gave very minor amounts and insufficient for further characterization. No reactions were

observed when 3-2 was irradiated in tetrahydrofuran and dichloromethane in two separate experiments..

3.3.4 Attempted coupling reactions of the $\text{Mn}(\text{CO})_4$ complex (3-2) with external alkenes and alkynes

3-2 was reacted with phenylacetylene in nitrogen-saturated carbon tetrachloride and benzene. The reaction in refluxing CCl_4 did not afford any dominant products. TLC of the reaction mixture showed multiple spots so the reaction was abandoned.

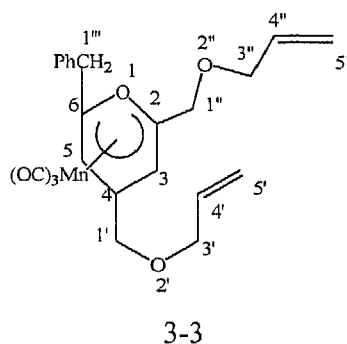
The reaction of 3-2 in refluxing benzene afforded one major product. Light orange crystals obtained by recrystallisation from dichloromethane and pentane by vapour diffusion were analysed by IR, NMR and elemental analysis. The product was identified as the (pyranyl) $\text{Mn}(\text{CO})_3$ complex 3-6 as shown below and in section 3.5, similar to those obtained by Tully²² in his reactions of manganated chalcones with phenylacetylene.



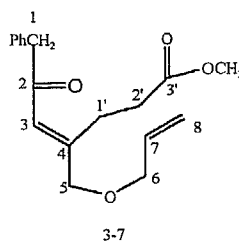
The pyranyl($\text{Mn}(\text{CO})_3$) was easily distinguished from that of from tetracarbonyl 3-2 by having distinct IR bands at around 2010 (vs), (metal carbonyl) as observed by Tully²².

Similarly both these compounds 3-3 (shown below), i.e. the tricarbonyl product formed from the reaction of 3-2 and the starting enyne 3-1 and 3-6 had ^1H NMR signals between 5.0 and 5.7 ppm for H3 and H5 (refer to numbering of the structures in section 3.5). The ^{13}C NMR signals were present at between 80 and 90 ppm for C3 and C5 at around 95 ppm for C2, C4, and C6 (again refer to compound numbering in section 3.5). These NMR

signals are consistent with those observed by Tully²² for (pyranyl)Mn(CO)₃ complexes obtained by the reactions of manganated chalcones with phenyl acetylene. This suggests that the alkyne inserted in the same way as it did for Tully²² compounds, i.e., the bulkier Ph group going closer to the O in the pyranyl ring. This also suggested that the alkene present within 3-2 does not take part in any intramolecular reaction when an external alkyne was present in the reaction mixture.



Reaction of 3-2 with methyl acrylate in refluxing carbon tetrachloride gave one main product in a very small amount. The ESMS spectrum (figure 7) of this main fraction suggested that 3-7, the arylalkane analogue from an earlier study²¹ was formed. The ¹H NMR spectrum also supported that 3-7 was the most likely compound that was formed. A reasonable ¹H NMR was obtained but a clean ¹³C NMR spectra could not be obtained with the quantity available. The product therefore could not be fully characterized. However, the intramolecular alkene appeared not to have been involved in any coupling reaction at the Mn centre. Various other minor bands on the plate were ignored.



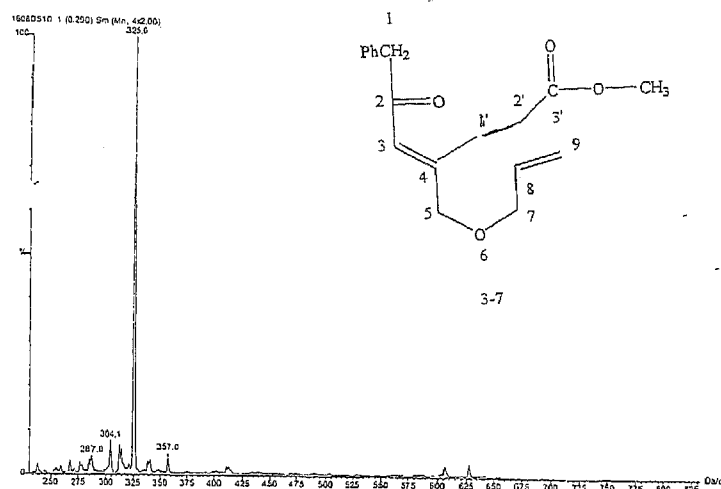
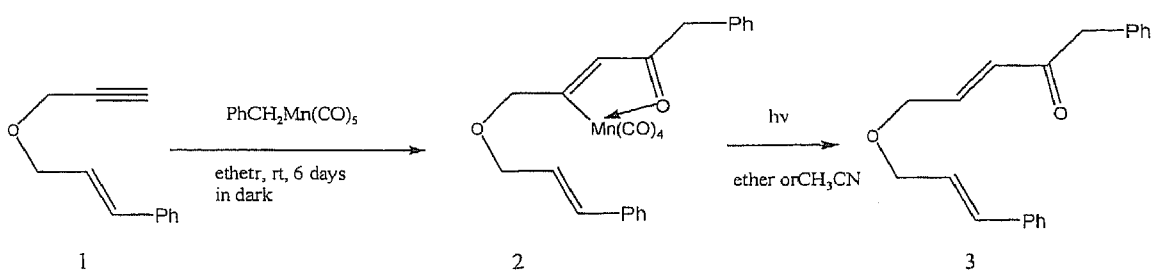


Figure 7: ESMS Spectrum of 3-7 in MeOH/NaOMe, CV +20 Volts

3.4 Reactions of the second enyne 3-(prop-2-ynyloxy)prop-1-enylbenzene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and the subsequent irradiation of the product formed

Reaction of 3-(prop-2-ynyloxy)prop-1-enylbenzene (1, Scheme 3.25) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in the same way as 4-oxa-6-heptyn-1-ene gave the manganated product 2 (Scheme 3.25). The manganated precursor, 2, (Scheme 3.25) was isolated in very low yields and could not be fully purified even after repeated plating. When the unpurified manganated enone 2 was irradiated in diethyl ether and acetonitrile and the reaction mixture worked up as before, no cascade products were isolated.

However, one major product was isolated. ^1H NMR studies of the product showed that the demetallated 3 (Scheme 3.25) had formed. This reaction was abandoned as no cascade products were isolated.



Scheme 3.25: Reaction of 3-(prop-2-ynyloxy)prop-1-enylbenzene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and subsequent irradiation with U.V.

Attempts were also made to manganate propargyl acrylate in the same way as the manganation of 3-1. A reasonably pure sample of the manganated product 3-8 was obtained as was seen from its ^1H NMR and ^{13}C NMR spectra (refer to section 3.5). However, attempts to carry out further reactions with the manganated product, including U.V. irradiation experiments in diethyl ether and acetonitrile were not successful. This section of work was therefore abandoned as well.

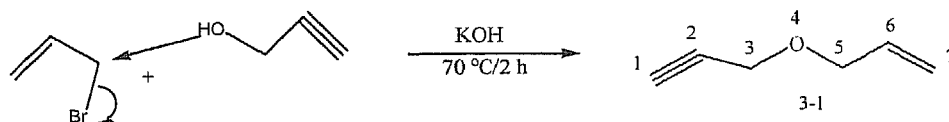
Harvey *et al.*¹⁵ successfully prepared bicyclic heterocycles from esters of this type in yields of around 24%. The reactions involved treating esters like the propargyl acrylate with a molybdenum complex in benzene at 100 °C in a sealed vial for 15 hours (refer to Scheme 3.11). The success of the propargyl acrylate reaction in this study would have given an alternative method of preparing compounds similar to those prepared by Harvey *et al.*¹⁵.

3.5 Experimental

Note: The ^1H NMR and ^{13}C NMR spectral assignments of the compounds in this section were made by comparisons with available literature data of closely related compounds. References are noted with each set of NMR data listed for the individual compounds and the literature values are given in italics, next to current assignments. Wherever possible, the structures of compounds used from literature to assign NMR signals of compounds in this study are also depicted with signals annotated for clarity. This has only been done for compounds that required only one literature compound to fully assign the NMR signals.

3.5.1 Preparation of 4-oxahept-1-en-6-yne (3-1)

To 3-bromo-1-propene (allyl bromide) (400 mg, 0.033 mol, 2.90 mL) was added prop-2-yn-1-ol (propargyl alcohol) (236 mg, 0.0420 mol, 2.48 mL), and the mixture was cooled in ice-bath. The mixture was removed from the ice-bath and KOH (10.4 mL, 4 mol L⁻¹) was added slowly over a period of about 15 minutes. During this time, the mixture was heated slowly. It was then heated for 4 hours at 70 °C. The mixture was then cooled, the oily layer decanted and washed with water twice. The oily layer was then dried over MgSO₄ to give almost pure (3-1) as seen from NMR spectra.

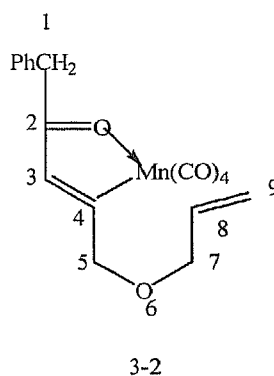


^1H NMR¹⁵: (300 MHz, CDCl₃) δ 2.42, 2.42 (1H, t, J =2.2Hz, H1), 4.04, 4.06 (2H, d, = 5.7Hz, H5), 4.13, 4.14 (2H, d, J =2.2Hz, H3), 5.21, 5.21 (1H, d, J = 10.3Hz, H7), 5.31, 5.30 (1H, d, J = 17.1, H7), 5.88, 5.89 (1H, m, H6)

^{13}C NMR¹⁵: (300 MHz, CDCl₃) δ 57.8, 57.0 (C3), 71.0, 70.5 (C5), 73.6, 74.3 (C1), 78.8, 79.6 (C2), 117.4, 117.9 (C6), 133.9, 133.8 (C5)

3.5.2 Manganation of 4-oxahept-1-en-6-yne (3-1)

4-oxahept-1-en-6-yne (100 mg, 1.04 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (358 mg, 1.25 mmol) were added to a 100 mL Schlenk flask under nitrogen. The mixture was then dissolved in diethyl ether and stirred under nitrogen in dark over a period of 5 days. During this time, the reaction mixture turned yellow and a brown solid precipitated. The reaction mixture was filtered to remove the solid. The ether was then removed under vacuum (rotary evaporator) and the residue, a yellow oil (150 mg), chromatographed (PLC, 1:1 dichloromethane:ether) to yield two major bands at R_f 0.8 and 0.2. The bands were removed, extracted with dichloromethane and the solvent was removed under vacuum. The first fraction at R_f 0.8, obtained as a yellow oil, was identified as the manganated [5-(propenyl-3-oxy)-1-phenylpent-3-en-4-yl- κC^4 -2-one- κO tetracarbonylmanganese] (3-2, 40 mg, 10.1 %. The ^1H NMR and ^{13}C NMR spectra of 3-2 are also reproduced after the list of NMR signal assignments below.

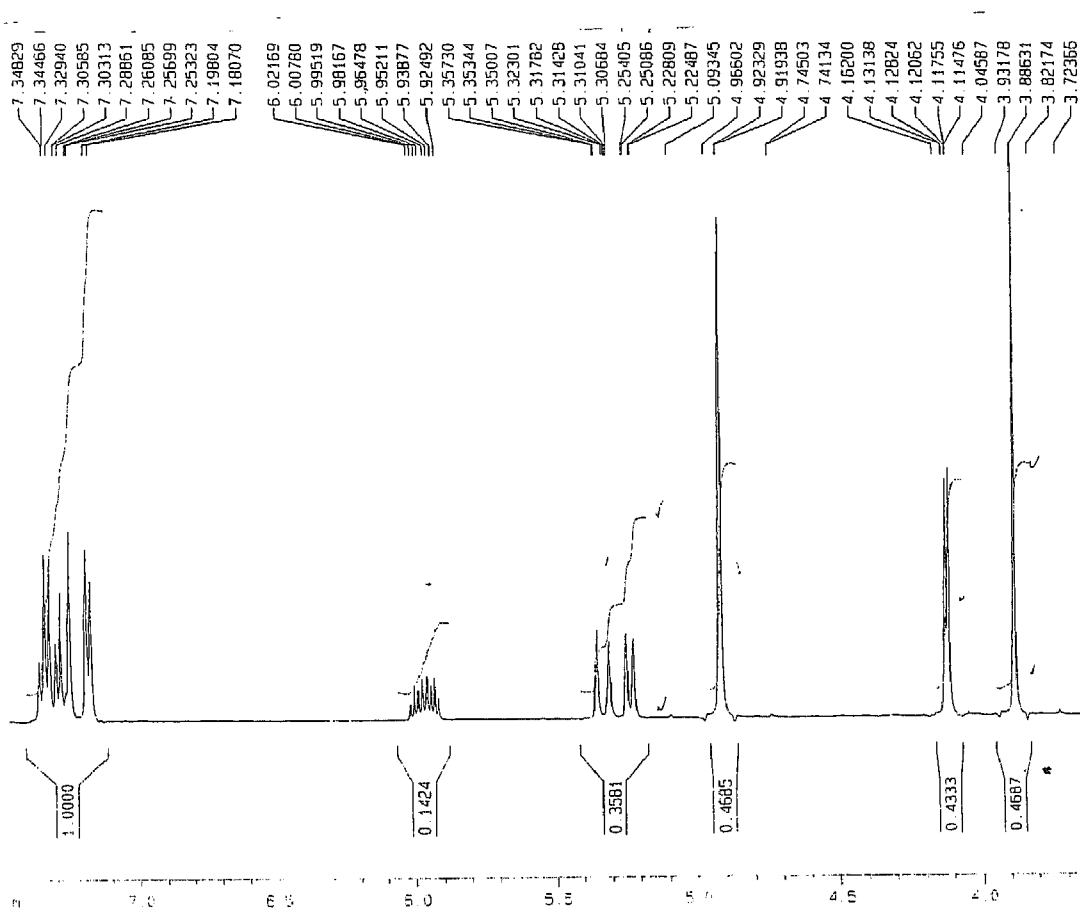


IR^{22} (ether) 2081, 2082(m), 1995, 1997(vs), 1942, 1942 cm^{-1} (s) Note: The IR values for metal carbonyl bands differ slightly for $\text{Mn}(\text{CO})_4$ complexes like manganated enones but are normally always close to the listed values here.

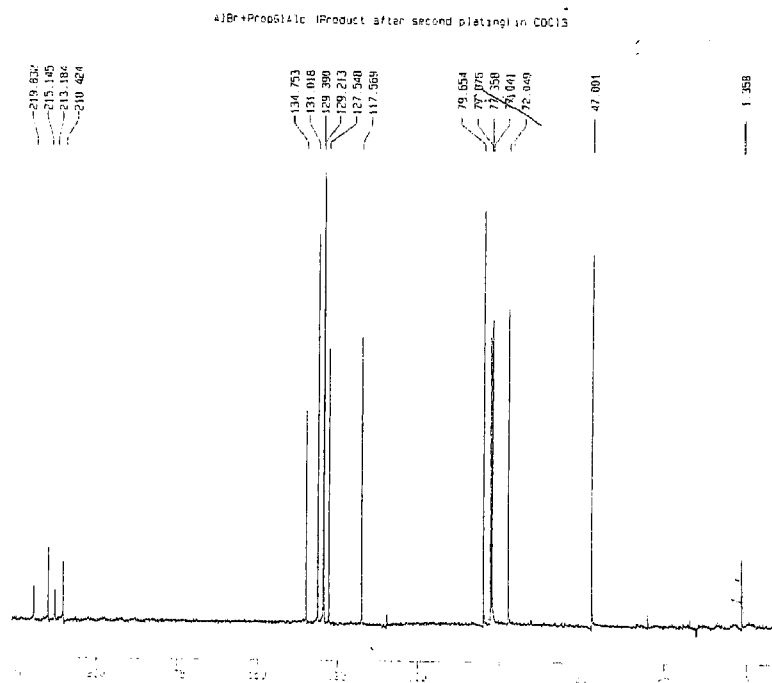
ESMS: (MeOH/NaOMe, cone + 20 V) m/z 405 (100%, $[\text{M}+\text{Na}]^+$), 382.6 (50%., $[\text{M}]^+$)

^1H NMR^{16,22}: (300 MHz, CDCl_3) δ 3.88, 4.09 (2H, s, H5), 4.12, 4.14 (2H, d, H7), 4.96, 2.30 CH_3 (2H, s, H1), 5.23, 5.36 (2H, dd, H9), 5.96, 5.80 (1H, m, H8), 7.33 (6H, m, all Ar-H, H3)

^{13}C NMR^{16,22}: (300 MHz, CDCl_3) δ 213.0-219.0, 213.0-219.0 (4MnC=O), 210.0, 204.0(C2), 134.8, 134.8(C3), 131.0, 130.1 (C8), 127.0-129.0 (all Ar-C), 117.6, 117.5 (C9), 79.8, 71.7 (C5), 72.0, 68.6 (C7), 47.0 ($-\text{COCH}_2\text{Ph}$, 27.2- CH_3 (C1).

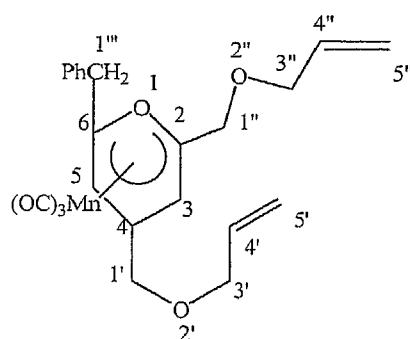


^1H NMR spectrum of 3-2



^{13}C NMR spectrum of 3-2

The second fraction at R_f 0.2, obtained as a light brownish-yellow oil, was identified as 3-3 (50 mg, 10.6%).



3-3

IR (ether) 2011(vs), 1946(s) cm^{-1} , $\text{Mn}(\text{CO})$.

ESMS: (MeOH/NaOMe, cone + 20 V), m/z 473.0 (100%, $[\text{M}+\text{Na}]^+$), 921.7 (50%, $[2\text{M}+\text{Na}]^+$); (MeOH/NaOMe, cone - 20V), m/z 449.0 (100%, $[\text{M}-\text{H}]^-$)

^1H NMR^{16, 22}: (300 MHz, CDCl_3) δ 4.03, 4.00- 4.09 (4H, m, H3', 3'') 4.17, 4.14- 4.22 (4H, s, H1', H1''), 4.74, 2.31(CH_3) (2H, s, H1'''), 5.87, 5.63 (2H, s, H3, H5), 5.34, 5.19- 5.36 (2x2H, m, H5', 5''), 6.10, 5.8-6.0 (2x 1H, m, H4', H4''), 7.29-7.39, m, all Ar-H)

^{13}C NMR^{16, 22}: (300 MHz, CDCl_3) δ 35.9, 27.2 (CH_3) ($\text{C1}'''$), 70.9, 69.4, 68.6 ($\text{C1}'$, $\text{C1}''$), 71.8, 72.1, 71.7 ($\text{C3}'$, $\text{C3}''$), 80.6, 80.6(C3), 81.2, 80.6 (C5), 91.8, 94.6 (C4), 94.4, 94.6 (C2 , C6), 117.5, 117.5($\text{C5}'$, $\text{C5}''$), 134.4, 134.0($\text{C4}'$, $\text{C4}''$), 125.0-129.0 (all Ar-C), 222.0, 221.9 ($\text{Mn}(\text{CO})_3$).

HRMS for $\text{C}_{23}\text{H}_{23}\text{O}_6\text{MnNa}$ Calculated: 473.0753

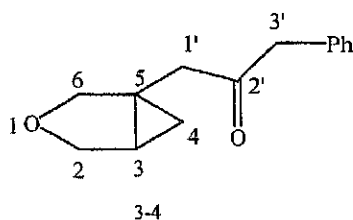
Found: 473.0716

3.5.3 Irradiation of [5-(Propenyl-3-oxy)-1-phenylpent-3-en-4yl- κC^4 -2-one- κO] tetracarbonylmanganese) (3-2) in Ether

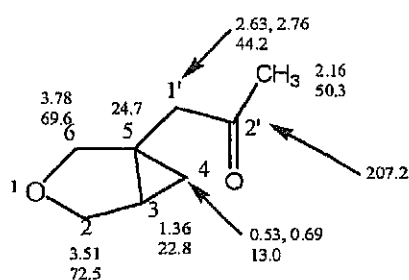
3-2 (87 mg, 0.23 mmol) was dissolved in diethyl ether (30 mL) and the solution was irradiated with medium pressure mercury lamp for 1.5 h. The reaction mixture was then exposed to air. The solution turned brown and a brown precipitate formed. After filtration of the brown precipitate, the diethyl ether was removed under vacuum (rotary evaporator) and the residue, a colourless oil, was chromatographed (PLC, hexane: ether, 1:1) to give one major band at R_f 0.7. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave 3-4 as colourless oil (13 mg, 26.5%).

Similarly 3-2 (125 mg, 0.33 mmol) was dissolved in diethyl ether. Trimethylamine oxide (24 mg, 0.33 mmol) was added to the reaction mixture which was stirred for 2 h. The reaction was monitored by IR and TLC. No obvious reaction occurred during this time but the colour of the reaction mixture turned orange. The reaction mixture was then heated slowly and then heated to reflux for about 1.5 h. The reaction mixture was then exposed to air. The solution turned brown and a brown precipitate formed. After filtration of the brown precipitate, the diethyl ether was removed under vacuum and the residue, a colourless oil, was chromatographed (PLC, hexane: ether, 1:1) to give one major band at

R_f 0.7. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave 3-4 as a colourless oil (16 mg, 25.5%). It is noted here that a substantial amount of material remained immobile at the base of the plate.



Note: The diagram below is the reference compound¹⁵ for ¹H NMR and ¹³C NMR assignments for compound 3-4.



IR (CH₂Cl₂): 1718 cm⁻¹ (CO)

ESMS: (MeOH/NaOMe, cone +20V) m/z 239.1 (100%, [M+Na]⁺), 455.3 (50%, [2M+Na]⁺)

^1H NMR¹⁵: (300 MHz, CDCl_3) δ 0.53, 0.69, 0.59, 0.69 (2H, dd, H4), 1.36, 1.37 (1H, m, H3), 2.63, 2.59 (1H, d, $J=17\text{Hz}$, H1'), 2.76, 2.76 (1H, d, $J=17\text{Hz}$, H1'), 3.51, 3.52 (1H, d, $J=8.0\text{Hz}$, H2) 3.77, 2.16- CH_3 (2H, s, H3') 3.79, 3.78 (2H, s, H6) 3.90, 3.89 (1H, d, $J=8.0\text{Hz}$, H2), 7.19-7.38 (5H, m, all Ar-H).

^{13}C NMR¹⁵: (300 MHz, CDCl_3) δ 13.0, 13.0 (C4), 22.8, 22.8 (C3), 24.7, 24.7 (C5), 44.2, 46.1(1'), 50.3, 50.3 (C3'), 69.6, 69.5 (C6), 72.5, 72.5 (C2), 127.2-133.9 (all Ar-C), 206.7, 207.2(C2')

HRMS for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na}$ Calculated: 239.1043

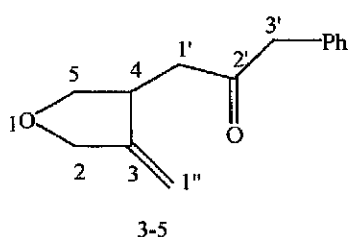
Found: 239.1045

3.5.4 Irradiation of [5-(Propenyl-3-oxy)-1-phenylpent-3-en-4yl- κC^4 -2-one- κO] tetracarbonylmanganese) (3-2) in Acetonitrile

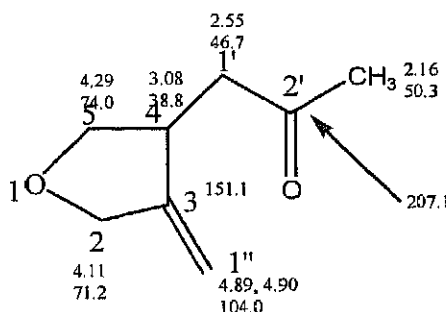
3-2 (66 mg, 0.17 mmol) was dissolved in acetonitrile (30 mL) and the solution was irradiated with medium pressure mercury lamp for 1.5 h. The solution was then exposed to air. The solution turned brown and a precipitate formed when the solution was exposed to air. After filtration of the precipitate, the acetonitrile was removed under vacuum and the residue, a colourless oil was chromatographed (PLC, hexane: ether, 1:1) to give one major band at R_f 0.8. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave 3-5 as a colourless oil (10 mg, 27.0%).

Similarly 3-2 (100 mg, 0.26 mmol) was dissolved in acetonitrile. Trimethylamine oxide (19.6 mg, 0.26 mmol) was added to the reaction mixture and stirred for 2 h. The reaction was monitored by IR and TLC. No reaction occurred during this time but reaction mixture turned slightly orange. The reaction mixture was then heated slowly and then heated to reflux for about 1.5 h. The reaction mixture was then exposed to air. The solution turned brown and a precipitate formed when the solution was exposed to air. After filtration of the precipitate, the diethyl ether was removed under vacuum and the

residue, a colourless oil was chromatographed (PLC, hexane: ether, 1:1) to give one major band at R_f 0.8. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave 3-5 as a colourless oil (13 mg, 23.2%). It is noted here that a substantial amount of material remained immobile at the base of the plate.



Note: The diagram below is the reference compound¹⁴ for ^1H NMR and ^{13}C NMR assignments for compound 3-5.



IR (CH_2Cl_2): 1718 cm^{-1} (CO)

ESMS: (MeOH/NaOMe, cone + 20 V) m/z 239.1 (100%, $[\text{M}+\text{Na}]^+$), 455.3 (50%, $[2\text{M}+\text{Na}]^+$)

^1H NMR¹⁴: (300 MHz, CDCl_3) δ 2.58, 2.55 (1H, dd, $J=17\text{Hz}$, 9Hz, $\text{H1}'$), 2.77, 2.73 (1H, dd, $J=18\text{Hz}$, 6Hz, $\text{H1}'$), 3.08, 3.08 (1H, m, H4), 3.70 (2H, s, $\text{H3}'$) 4.27, 4.29 (2H, m, H5), 4.11, 4.11 (2H, d, H2), 4.85, 4.89 (1H, dd, $J=2.1\text{Hz}$, $\text{H1}''$), 4.92, 4.90 (1H, q, $J=2.1\text{Hz}$, $\text{H1}''$) 7.19-7.36 (m, all Ar-H).

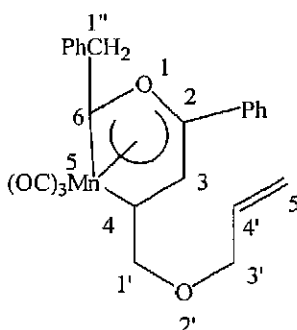
^{13}C NMR¹⁴: (300 MHz, CDCl_3) δ 39.2, 38.8(C4), 45.4, 46.7 ($\text{C1}'$), 50.7 ($\text{C3}'$), 74.3, 74.0 (C5), 71.5, 71.2 (C2), 127.0-134.0 (all Ar-C), 104.4, 104.0 ($\text{C1}''$) 151.4, 151.1 (C3), 207.0, 207.1 ($\text{C2}'$),

HRMS for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na}_1$ Calculated: 239.1043

Found: 239.1056

3.5.4 Reaction of [5-(Propenyl-3-oxy)-1-phenylpent-3-en-4yl- κC^4 -2-one- κO] tetracarbonylmanganese (3-2) with Phenylacetylene in Benzene

3-2 (110 mg, 0.29 mmol) and phenylacetylene (90 mg, 0.88 mmol) were dissolved in nitrogen-saturated benzene and the solution was refluxed for 4 h. Benzene was removed under vacuum and the residue, a yellow-orange oil was chromatographed (PLC, ether:hexane, 1:2) to give one major yellow-orange band at R_f 0.8. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave a yellow-orange oil. The oil was crystallised by solvent diffusion (dichloromethane, pentane) to give 3-6 as yellow-orange crystals (40 mg, 30.8%)



3-6

IR (benzene) 2008 (MnCO), 1816 (C-O-C) cm^{-1}

ESMS (MeOH/NaOMe, cone + 20 V) m/z 479 (100%, $[\text{M}+\text{Na}]^+$); (MeOH/NaOMe, cone - 20V) m/z 455 (100%, $[\text{M}-\text{H}]^-$)

^1H NMR^{16, 22}: (300 MHz, CDCl_3) δ 4.29, 4.14-4.22 (2H, m, H3'), 4.18, 4.14-4.22 (2H, s, H1'), 4.74, 2.30 (CH_3) (2H, s, H1''), 5.09, 5.00-5.60 (2H, s, H3, 5), 5.37, 5.19- 5.36 (2H, m, H5'), 6.02, 5.8-6.0 (m, 1H, H4'), 7.28-7.35 (10H, m, all Ar-H).

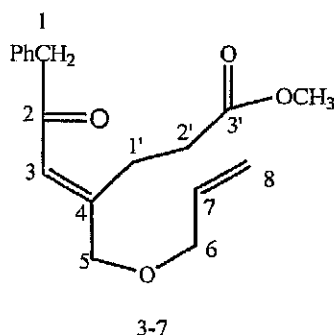
^{13}C NMR^{16, 22}: (300 MHz, CDCl_3) δ 40.2, 27.2 (CH_3) (C1''), 71.2, 68.6 (C1'), 72.7, 71.7 (C3'), 81.4, 80.8 (C3), 82.7, 80.8 (C5), 94.0, 94.9 (C6), 95.2, 95.1 (C2), 104.2, 98.0 (C4), 130.0, 130.1 (C4') 118.0, 117.5 (C5''), 123-136.0 (all Ar-C), 222.0, 221.9 (Mn(CO)₃)

Elemental analysis: Calculated for $\text{C}_{24}\text{H}_{21}\text{O}_5\text{Mn}$	C, 65.94%;	H, 4.42%
Found	C, 65.52%	H, 4.90%

3.5.5 Reaction of [5-(Propenyl-3-oxy)-1-phenylpent-3-en-4yl- κC^4 -2-one- κO] tetracarbonylmanganese) (3-2) with methyl acrylate in acetonitrile

3-2 (95 mg, 0.25 mmol) and methyl acrylate (84 μl , 0.75 mmol) were dissolved in nitrogen-saturated acetonitrile and the solution was refluxed for 1 h. Acetonitrile was removed under vacuum and the residue, a colourless oil was chromatographed (PLC, ether:petroleum spirits, 1:1, bp 60-80 $^\circ\text{C}$) to give one major colourless band at R_f 0.7. Several other minor bands were ignored. Removal and extraction of the band with dichloromethane followed by solvent removal under vacuum gave a colourless oil tentatively assigned by ^1H NMR as 3-7 (10 mg, 13%).

dichloromethane followed by solvent removal under vacuum gave a colourless oil tentatively assigned by ^1H NMR as 3-7 (10 mg, 13%).



IR (acetonitrile) 1712 (CO), 1737 cm^{-1} (COOMe)

ESMS (MeOH/NaOMe, (cone + 20 V) m/z 325.0 (100%, $[\text{M}+\text{Na}]$).

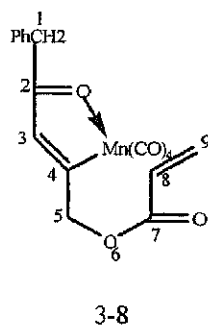
^1H NMR^{16, 21} (300 MHz, CDCl_3) δ 7.20- 7.40 (5H, all Ar-H), 6.8 (1H, s, H3), 5.82 (1H, s, H7), 5.26 (2H, m, H8), 3.92 (s, 2H, H5), 3.72 (2H, d, H6), 3.71 (3H, s, OCH_3), 3.44 (2H, t, H2'), 3.38 (t, 2H, H3'), 2.80 (2H, s, H1).

^{13}C NMR^{16, 21} (300 MHz, CDCl_3) A strong and clean enough ^{13}C NMR spectrum could not be obtained. While impurity signals made assignments difficult, carbon signals were not strong enough.

3.5.6 Manganation of propargyl acrylate

Propargyl acrylate (100 mg, 0.91 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (312 mg, 1.09 mmol) were added to a 100ml schlenk flask under nitrogen. The mixture was then dissolved in diethyl ether and stirred under nitrogen in dark over a period of 5 days. During this time, the reaction mixture turned yellow. It was filtered to remove the brown solid that had formed. The ether was then removed under vacuum (rotary evaporator) and the residue, a yellow oil (70 mg) chromatographed (PLC, 1:1 dichloromethane:ether) to yield one major band at R_f 0.8. The band was then removed, extracted with dichloromethane and the solvent

was removed under vacuum. The main fraction at R_f 0.8, obtained as a yellow oil, was identified as the manganated species 3-8 (0.041 g, 11.4%) by NMR spectroscopy.



^1H NMR^{16, 22} (300 MHz, CDCl_3) δ 5.60, 4.09 (2H, s, H5), 3.87, 2.30 CH_3 (2H, s, H1), 5.88, 5.36 (2H, dd, H9), 6.19, 5.36 (1H, m, H9), 6.45, 5.80 (1H, m, H8), 7.01- 7.53 (6H, m, all Ar-H, H3)

^{13}C NMR^{16, 22} (300 MHz, CDCl_3) δ 212.7-219.1, 213.0-219.0 ($\text{MnC}=\text{O}$), 209.5, 204.0 (C2), 165.4 (C7), 134.2, 134 (C3), 132.4, 130.1 (C8), 128.0-132.0 (all Ar-C), 127.4, 117.5 (C9), 76.6, 71.7 (C5), 72.0, 68.6 (C7), 46.7, 27.2- CH_3 (C1).

3.7 Conclusions

The current study demonstrated that enynes can be used to prepare cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond using benzylmanganese pentacarbonyl mediated transformations. This is similar to what was observed by Lee *et al.*³ using $\text{MeMn}(\text{CO})_5$. The study however did not give yields of products comparable to those observed by Lee *et al.*³. Our yields were much lower and the products were reversed, i.e. the Lee methyl analogue in ether was obtained in acetonitrile and the acetonitrile analogue was obtained in ether.

When compared to our yields, much better yields of similar products were obtained by Harvey *et al.*¹⁵, Montgomery *et al.*¹⁴ and by Parson¹⁶ and his team. They used different methods to synthesize products similar to Lees³ and to those synthesized in this study.

It is difficult at this stage to say how good the manganese method is for the synthesis of the types of compounds considered in the current study, as not much comparable data is available apart from the ones already discussed. The yields in the current study were low and the reagents used for synthesis were expensive

In the current study, the major loss of products came via the large amounts of the brown material that formed. The plating of the crude product to isolate our products was certainly contributing to the loss of the desired products as noted by the large difference in the masses of the crude product and the isolated product.

The study of the cyclomanganated complex 3-2 with phenylacetylene gave the pyranyl($\text{Mn}(\text{CO})_3$) as observed in an earlier study by Tully¹². The study showed that the external alkyne preferentially reacts with the manganated 3-2 over the intramolecular alkene. Similarly, the reaction of 3-2 with methyl acrylate gave the aryl alkane analogue of Cooney's²¹ compound even though in only low yields. Again, the intramolecular alkene was not involved in any cyclisation reactions.

It seems likely that the generally expected efficiency of the intramolecular reaction did not offset the intermolecular reaction possibly because of the constraints of achieving the required transition state geometry for the intramolecular reaction.

Failure to repeat the Lee *et al.*³ work using $\text{MeMn}(\text{CO})_5$ and the failure to generate any results with the additional enynes tried in the current study puts a limit onto what generalizations can confidently be made here. There is however scope for lot more work in this area to establish the effects solvents have on product types, to determine accurate reaction paths and to establish if the manganese method is of some real synthetic value.

3.6 References

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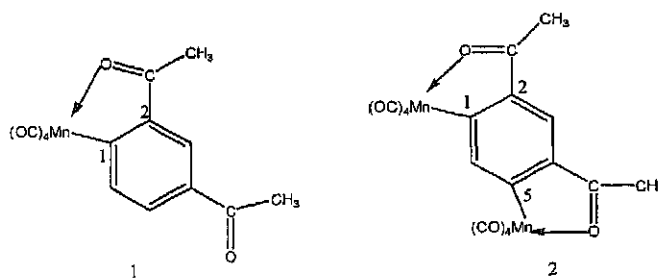
Chapter 4

4.0 Study aimed at di-manganation and subsequent coupling chemistry and new coupling substrates to provide bicyclic systems of the non-fused-aromatic type.

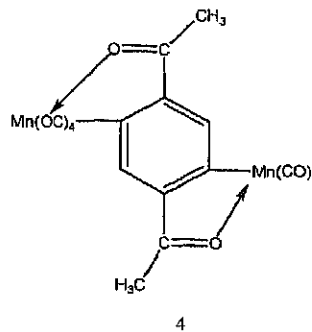
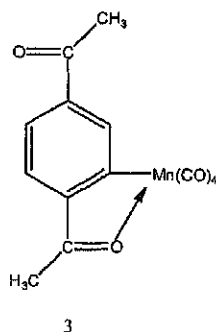
4.1 Introduction

Considerable work has been done at Waikato on manganated arylcarbonyl compounds that couple to form open chain and bicyclic derivatives of aryl ketones. This work was extended to manganated non-aryl carbonyl compounds (chalcones and dienones) by Tully¹. The previous work done at Waikato, including that by Tully¹ has already been discussed in some detail in Chapters one and two in this thesis. This work and the work discussed below forms the basis of the studies in this chapter.

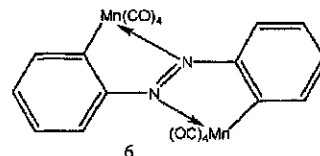
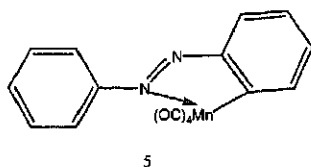
Robinson² did some work on dimanganation involving manganation at aryl carbon only. Discussed below in is some of the work done by Robinson². The reaction of 1,3-diacetylbenzene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ gave the mono-manganated **1** and the dimanganated **2**.



Similarly, the reaction of 1,4-diacetylbenzene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ gave the mono-manganated **3** and the dimanganated **4** in a 2:1 ratio.

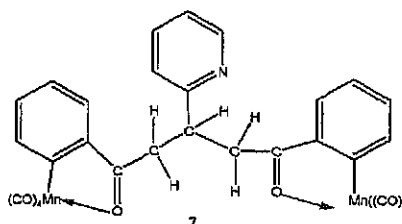


As in the case of the 1,3-diacetylbenzene, only the less sterically crowded di-manganated isomer was formed. The two reactions suggested that the acetyl groups were acting independently of each other. In an earlier study, Bruce³ and his team studied the mono- and dimanganation of azobenzene, which gave compounds **5** and **6**.

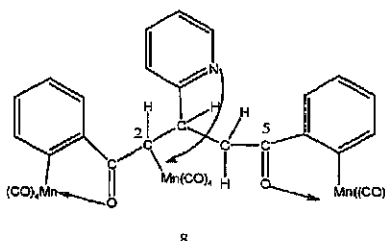


They also demonstrated that **6** reacted with azobenzene to give **5** in high yield. This demonstrated that there was an intermolecular transfer of the $\text{Mn}(\text{CO})_4$ group. Robinson² attempted to see if the same process occurred with the acetyl benzene. **2** was refluxed with 1,3-diacetylbenzene in heptane. It was found that after 2.5 hours, 31% of **2** remained, 35% of **1** was present and 33% of the free ligand was consumed. This was consistent with some $\text{Mn}(\text{CO})_4$ transfer but partial demetallation of **2** could not be ruled out because of the low yields of the products. In the study by Robinson² however, no coupling reactions of the di-manganated products were reported.

In the study by Tully¹, when a 2:1 molar excess of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ was used with 1,5-diphenyl-3-(2-pyridyl)pentane-1,5-dione, $[\text{1,5-diphenyl-}\kappa\text{C}^2-\kappa\text{C}^{2'''}\text{-3-(2-pyridyl)pentane-1,5-dione-}\kappa\text{O}^1-\kappa\text{O}^1]\text{bistetracarbonylmanganese}$, **7** was formed in 15% yield.

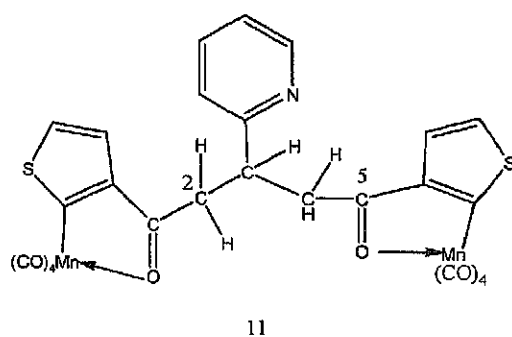
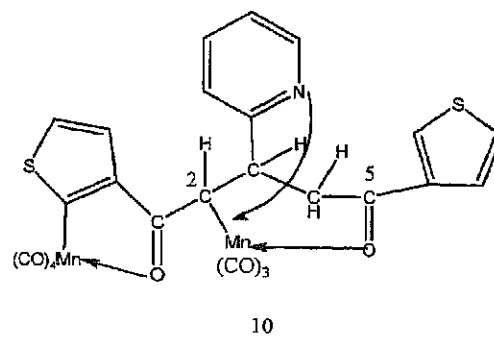
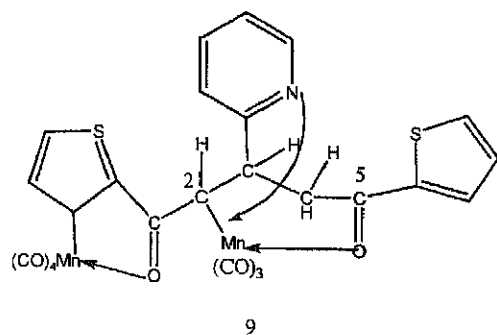


When the mole ratio of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ was increased to 3:1, a third manganation occurred giving **8**, a trimanganated complex as well.



It appears likely that once the C2 carbon becomes manganated an orientation is reached allowing a second manganese group to also become coordinated to the remaining oxygen. Once the second manganation has occurred, **8** is produced when there is excess $\text{PhCH}_2\text{Mn}(\text{CO})_5$ present.

Tully¹ also prepared similar compounds by replacing the phenyl groups with thienyl groups. When 3-(2-pyridyl)-1,5-di-(3-thienyl)pentane-1,5-dione was manganated, compounds **9**, **10** and **11** were formed.



Tully¹ however did not attempt any coupling reactions of the di-manganated and the tri-manganated products in his study.

4.2 Aims of the current study

4.2.1 Study aimed at di-manganation and subsequent coupling chemistry

Di-manganated products with metals at remote sites are known but there has been little systematic study of substrates designed to encourage manganation at closely neighbouring centres apart from the work of Robinson² at Waikato involving manganation at aryl carbon only. In the current study, some possible new substrates were to be tried for the di-manganation and the work extended to subsequent coupling chemistry in an effort to produce some novel compounds.

4.2.2 New coupling substrates to provide bicyclic systems of the non-fused aromatic type

Considerable work has been done at Waikato on manganated arylcarbonyl compounds that couple to form open chain and bicyclic derivatives of aryl ketones. Tully¹ extended the work to manganated non-aryl compounds (chalcones and dienones). However a host of structurally different compounds of the non-aryl type remain unstudied and have considerable potential for organic synthesis by coupling. Some new substrates of the non-aryl type were to be considered for manganation and for subsequent coupling reactions with alkynes and alkenes in this study. It was anticipated that this would provide an understanding of the reactivity differences of these sorts of compounds in their coupling chemistry with alkynes and alkenes. It was also anticipated that if this area turned out to be as productive as it has been in the aromatic area, it would lead to valuable new synthetic methodology.

4.3 Results and Discussion

4.3.1 Dimanganation and subsequent coupling chemistry

4.3.1.1 Manganation of dibenzoylcyclopropane

When *trans*-dibenzoylcyclopropane and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (1:3) were refluxed in hexane for 8 hours, two products were isolated when the residue was plated. The first fraction having R_f value of 0.8 was identified as the di-manganated product 4-2 (21.7 %) and the second fraction at R_f of 0.6 was identified as the mono-manganated product 4-3 (11.5 %). The figure below shows the structures of 4-2 and 4-3.

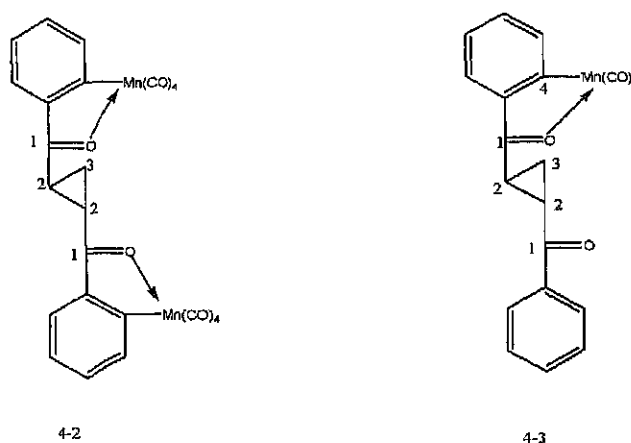


Figure 4-1: Structures of compounds 4-2 and 4-3.

The products were characterized by IR, ESMS, and NMR. The crystal structure of 4-2 was also determined. The IR of the di-manganated and the mono-manganated products 4-2 and 4-3 showed the usual¹ metal carbonyl pattern with signals at around 2080 (m), 1990 (s), 1930 (s) cm^{-1} as shown by the figure 4-2.

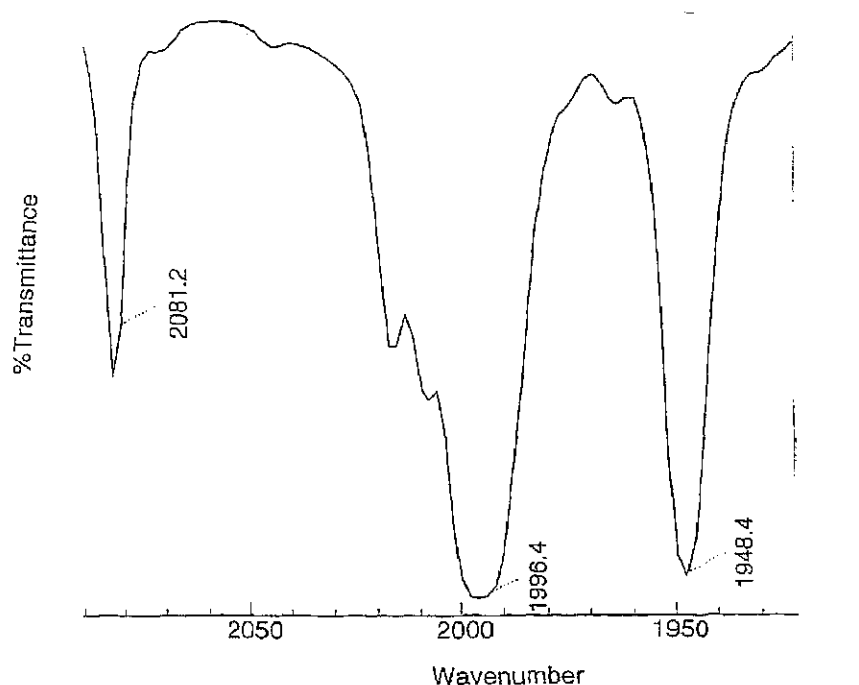


Figure 4-2: Infrared spectrum showing the metal carbonyl region of 4-2 and 4-3

The ^1H NMR and the ^{13}C NMR data also supported the structures of 4-2 and 4-3 in particular with the usual metal carbonyl signals at around 220 ppm. The crystal structure of 4-2 is discussed in detail in section 4.5.

Initially, when a 2:1 molar excess of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ was used, the di-manganated and the mono-manganated products formed in the ratios as already stated. When the molar ratio of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ to trans-1,2-dibenzoylcyclopropane was increased to as much as 4:1, the ratios of the products did not change much. This was done in an attempt to get more of the di-manganated product to form. Instead, lots of the $\text{PhCH}_2\text{Mn}(\text{CO})_5$ remained and the products formed started to decompose when the reaction times were increased.

4.3.1.2 Further reactions of the di-manganated (4-2) and the mono-manganated (4-3) products

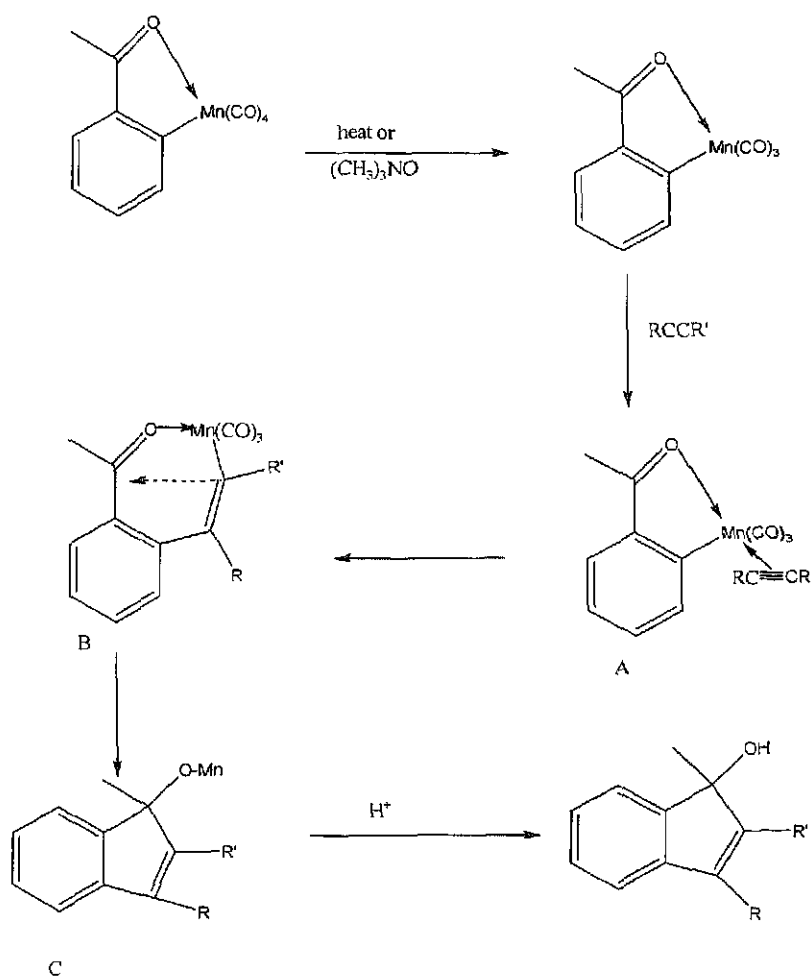
The di-manganated product (4-2) and the mono-manganated product (4-3) were reacted with alkynes like phenylacetylene and diphenylacetylene^{1,4}, alkenes like methyl acrylate⁴, as well as dimethylacetylene dicarboxylate (DMAD)⁵, HgCl₂⁴, SO₂⁶, ICl⁷ and 4-oxa-6-heptyn-1-ene amongst others. These reactions were carried out in an effort to see if the usual products obtained in earlier studies at Waikato or some other novel products were obtained. Decomposition of the starting materials was noted in most of these reactions.

The reaction of both, 4-2 and 4-3 with 4-oxa-6-heptyn-1-ene was carried out to see if the presence of both, an alkyne and an alkene in the same molecule influenced the types of products formed as well as on the ratio of the products that formed. Most of the reactions in this section of work were repeated several times and different solvents were tried. This was done in an effort to confirm the preliminary results obtained in the reactions, many of which looked promising. The difficulty however was with the isolation of the products in their pure form. Once the products appeared reasonably pure, attempts to crystallize them led to their decomposition. Apart from getting lots of reasonable IR and ESMS data, no further data like NMR and elemental analysis could be obtained.

However, when the mono-manganated product (4-3) was reacted with DMAD in CH₃CN, the indenol product (4-4, section 4.4) was obtained. The product was similar to those obtained by Depree⁵ with reactions of DMAD with manganated compounds like η^2 -(2-benzoylphenyl)-tetracarbonylmanganese.

This product (4-4) was characterized by IR, NMR, ESMS and HRMS. No elemental analysis data was obtained. The IR, NMR, ESMS and the HRMS data are listed in section 4.4. The proposed general mechanism⁵ for the formation of indenols is given below (Scheme 4.1). The steps involved are firstly, the coordination of the alkyne to the Mn to give A followed by a regiospecific migration of the aryl carbon to the nearest alkyne carbon to form a seven-membered ring B. The indenol is presumably formed via the

carbon to form a seven-membered ring B. The indenol is presumably formed via the collapse of the seven-membered ring to generate a manganese alkoxide species C followed by demetallation to give the final product.



Scheme 4-1: The proposed general mechanism⁵ for the formation of indenols

4.3.1.3 Cyclomanganation reactions of 5-methyl-3-hexen-2-one and 1-acetylcyclohexene.

This section of work was intended to extend the work done earlier at Waikato on manganated aryl compounds and on non-arylcarbonyl compounds like chalcones and dienones¹. The intent was to work on more of the non-aryl carbonyl compounds structurally different to those that have already been tried. For example, the 5-methyl-3-hexen-2-one would be one of the methyl analogues of the chalcones that Tully¹ worked on. It was hoped that a host of new compounds would be formed and would be of great potential for organic synthesis using manganese.

5-methyl-3-hexen-2-one was reacted with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in both hexane and heptane in an attempt to cyclomanganate it. While the IR spectrum showed that the cyclomanganated 5-methyl-3-hexen-2-one was formed, it broke down as the reaction proceeded. Attempts to chromatograph the residue gave one band. Removing the band and extracting it with CH_2Cl_2 gave a yellowish-grey oil. The oil was collected and NMR was done of the oil (both ^1H NMR and ^{13}C NMR). A reasonable NMR spectrum of the product could not be obtained. Attempts to crystallize the product by solvent diffusion using different solvent combinations failed.

“One-pot” reactions of 5-methyl-3-hexen-2-one with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and alkynes and alkenes were also attempted. This was attempted in an effort to use up the manganated product as it formed and to see if the usual alkyne and alkene insertion products, as observed in earlier studies^{1,6} formed or some novel products formed instead.

Reaction of 5-methyl-3-hexen-2-one and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in the presence of phenylacetylene was carried out in CCl_4 . As the reaction proceeded at reflux, the metal carbonyl IR bands for the $\text{PhCH}_2\text{Mn}(\text{CO})_5$ disappeared slowly and the metal carbonyl bands for the $(\text{pyranyl})\text{Mn}(\text{CO})_3$ appeared at 2012, 1947 and 1932 cm^{-1} . These metal carbonyl bands were consistent with those observed by Tully¹ for the $(\text{pyranyl})\text{Mn}(\text{CO})_3$ complexes formed when manganated chalcones and dienones were reacted with a variety of alkynes.

The NMR data also supported this with ^1H NMR signals at 5.02 ppm, a singlet for H5, and at 4.30 ppm, a singlet for H3 (refer to structure 4-5, section 4.4). The ^{13}C NMR spectra showed the Mn-CO signal at around 223 ppm and at 81.4 ppm for C5 and at 79.8 ppm for C3. These signals were again consistent with those observed by Tully¹. The ESMS data was also convincing.

Attempts were also made to cyclomanganate 1-acetylcyclohexene. Cabral⁸ has already done this successfully in a yield of 61 %. The solvents used were hexane and heptane, and reaction was attempted at ambient temperature followed by increasing the temperature to reflux. This was to establish the best conditions for the manganation of the 1-acetylcyclohexene and to maximize the yield of the manganated product. After repeated attempts, the best yield of the manganated product, yellow oil, was 65 %. However, this oil would not give reasonable NMR spectra. Attempts to crystallize the oil by solvent diffusion also failed. However, the ^1H NMR data of the cleanest spectrum are listed in the experimental section (Section 4.4). No ^{13}C NMR data was obtained. Since no crystals formed, no elemental analysis data was obtained. Similarly, attempts to generate sensible ESMS and HRMS data failed.

Efforts were made to carry out several “one pot reactions” of 1-acetylcyclohexene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and with alkynes and alkenes with no success. Finally, this section of work had to be abandoned.

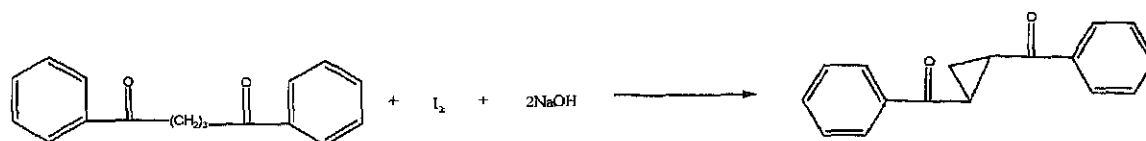
4.4 Experimental

4.4.1 Preparation of trans-1,2-dibenzoylcyclopropane

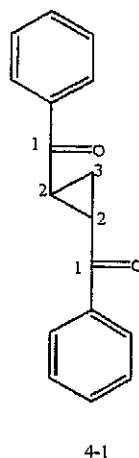
While a commercial sample of trans-1,2-dibenzoylcyclopropane was available initially, more of it had to be prepared later for use in the current study. The method used for the preparation of trans-1,2-dibenzoylcyclopropane was as follows:

To a three-necked round bottom flask equipped with a magnetic stirrer and a dropping funnel was added 1.96 g (777 mmol) of 1,3-dibenzoylpropane with a solution of sodium hydroxide in methanol (0.64 g in 23 mL of methanol). The mixture was warmed to 45 °C with stirring to dissolve the diketone (1,3-dibenzoylpropane). The reaction mixture was then cooled to 40 °C and a solution of iodine (2 g in 11.5 mL of methanol) was then added slowly with rigorous stirring. The iodine was added at a rate to allow the colour to be immediately discharged. After the addition of the iodine was completed, the reaction mixture was stirred for 1.5 h while a solid formed. The white solid was filtered, washed with four portions of 10 mL of water and dried under high vacuum to give 1.0719 g (55% yield) of trans-1,2-dibenzoylcyclopropane. The filtrate was placed in a round-bottom flask, dried under vacuum and was treated with 10% sodium bisulfite. The solid was then recrystallised to give a further 0.10 g of the product.

The purity of the product trans-1,2-dibenzoylcyclopropane (4-1) was determined by NMR. The following equation 4-1 summarizes the reaction for the formation of trans-1,2-dibenzoylcyclopropane from 1,3-dibenzoylpropane.



Equation 1-4: Reaction for the formation of trans-1,2-dibenzoylcyclopropane from 1,3-dibenzoylpropane.



^1H NMR: (CDCl_3 , 300 MHz) δ 7.28- 8.09 (10H, m, all Ar-H), 3.44 (2H, m, H2, J = 16 Hz) 1.84 (2H, dd, H3, J = 16 Hz)

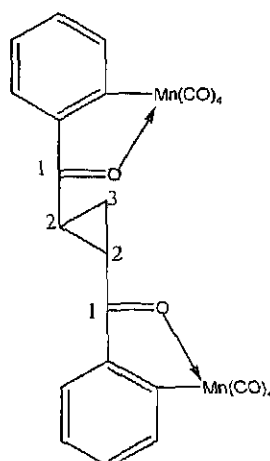
^{13}C NMR: (CDCl_3 , 300 MHz) δ 197.6 (C1), 128.3 – 137.0 (all Ar-C), 28.5(C2), 20.4 (C3).

HRMS for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{Na}$	Calculated: 273.0897
	Found: 273.0864

4.4.2 Manganation of trans-1,2-dibenzoyl cyclopropane

trans-1,2-Dibenzoyl cyclopropane, 4-1, (200 mg, 0.80 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (458 mg, 1.60 mmol) were refluxed for 13 h in nitrogen-saturated heptane. The reaction mixture was concentrated *in vacuo* and the residue was plated (PLC, dichloromethane: petroleum spirits, 1:1) to gave 2 bands at R_f 0.90 and R_f 0.8. The band at R_f 0.90 was recrystallised from CH_2Cl_2 / pentane to give yellowish-orange crystals and was identified as the dimanganated product 4-2 (100 mg, 21.7%). The second band at R_f 0.8 was also

recrystallised from CH_2Cl_2 / pentane to give yellowish-orange crystals and was identified as the dimanganated product 4-2 (100 mg, 21.7%). The second band at R_f 0.8 was also recrystallised from CH_2Cl_2 / pentane to give yellowish-orange crystals as well and was identified as the mono-manganated product 4-3 (40 mg, 11.5%).



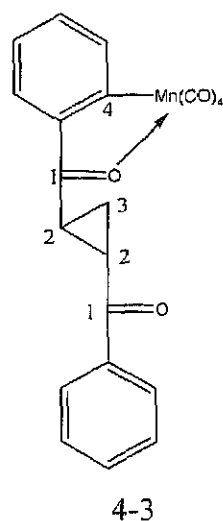
4-2

IR (heptane): 2080 (m), 1994 (s), 1933 (s), 1734 (s, br) CO.

^1H NMR: (CDCl_3 , 300 MHz) δ 7.18- 8.21 (8H, m, all Ar-H), 1.87 -2.12 (2H, dd, H3), 3.43-3.60- (2H, m, H2)

^{13}C NMR (CDCl_3 , 300 MHz) δ 220 (MnCO), 194.7 (C1), 131.7 – 144.8 (all Ar-C), 28.4 (C2), 22.1 (C3).

Elemental analysis: Calculated for $\text{C}_{25}\text{H}_{12}\text{Mn}_2\text{O}_{10}$:	C, 51.57%; H, 2.08%
Found:	C, 51.76%; H, 2.04%



IR(heptane): 2080 (m), 1994 (s), 1933 (s) cm^{-1} , 1734 (s, br) CO.

ESMS: (MeOH/NaOMe) (Cone +40 V) m/z 388.0 (25% $[\text{M}-\text{CO}]^+$, 331.9 (50%, $[\text{M}-3\text{CO}]^+$ 439.3 (40%, $[\text{M} + \text{Na}]^+$, 855.5 (100% $[\text{2M} + \text{Na}]^+$.

(Cone -40 V) m/z 391.1 $[\text{M} + \text{OMe} - 2\text{CO}]^-$, 419.4 $[\text{M} + \text{OMe} - \text{CO}]^-$, 335.4 $[\text{M} + \text{OMe} - 4\text{CO}]^-$.

^1H NMR: (CDCl_3 , 300 MHz) δ 7.20- 8.14 (9H, m, all Ar-H), 3.43 (2H, m, H2), 1.84 (2H,dd, H3).

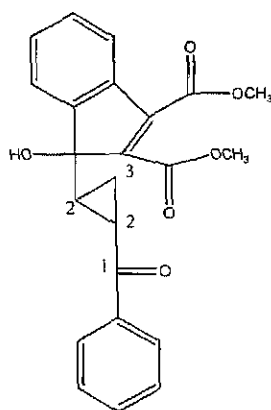
^{13}C NMR: (CDCl_3 , 300 MHz) δ 221.3 (C4), 214.2, 213.1, 211.6, 211.3 (MnC=Os), 196.6, 193.7 (2C=O), 29.6 (C2), 27.6 (C2), 21.4 (C3).

Elemental Analysis, Calculated for $\text{C}_{21}\text{H}_{13}\text{MnO}_6$: C, 60.61 %; H, 3.15 %

Found : C. 60.60 %; H, 3.48 %

4.4.3 Reaction of 4-3 with DMAD

4-3 (65 mg, 0.16 mmol) and DMAD (33 mg, 0.24 mmol) were dissolved in nitrogen-saturated CCl_4 and the solution was refluxed for 2 h. During this time, the IR metal carbonyl bands for the $\text{Mn}(\text{CO})_4$ disappeared. The CCl_4 was then removed under vacuum and the residue, a yellowish brown oil was chromatographed (PLC, CH_2Cl_2 : hexane, 1:2) to give one major band (purple under U.V. lamp) at R_f 0.2. Removal and extraction of the band with CH_2Cl_2 followed by solvent removal under vacuum gave a whitish yellow oil (21.6 mg, 35.3%) which did not crystallize. Spectral data were consistent with the following structure.



4-4

^1H NMR: (CDCl_3 , 300 MHz) δ 7.50 (9H, m, all Ar-H), 4.60 (OH), 3.96 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 3.72 (H,s, OH), 2.87 (2H, s, H3), 1.98 (2H, dd, H2).

^{13}C NMR: (CDCl_3 , 300 MHz) δ 199.2 (C=O), 164.8 (C=O), 164.3 (C=O), 132.0- 147.0 (All Ar-C), 85.01 (C-OH), 35.40 (C2), 31.33 (C2), 31.07 (C3).

HRMS Calculated for $\text{C}_{23}\text{H}_{20}\text{NaO}_6$

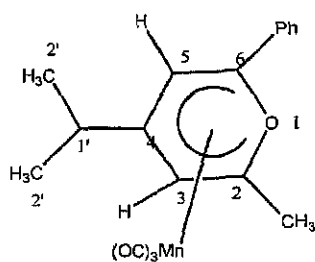
415.1152 $[\text{M} + \text{Na}]^+$

Found

415.1174 $[\text{M} + \text{Na}]^+$

4.4.4 Reaction of 5-methyl-3-hexen-2-one with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and phenylacetylene in CCl_4

5-Methyl-3-hexen-2-one (200 mg, 1.79 mmol), $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (610 mg, 2.14 mmol) and phenylacetylene (210 mg, 2.14 mmol) were refluxed in nitrogen-saturated CCl_4 for 3 h. During this time the metal carbonyl bands for $\text{PhCH}_2\text{Mn}(\text{CO})_5$ disappeared as seen by I.R. and the reaction mixture turned yellowish red in colour. The CCl_4 was then removed under vacuum and the residue, a yellowish-red oil was chromatographed (PLC, CH_2Cl_2 : petroleum spirits, 1:1) to give one red band at R_f 0.8. The band was then removed, extracted with CH_2Cl_2 and the solvent removed under vacuum to give a red oil which was identified as 4-5 (100 mg, 16%). Attempts to crystallize the product by solvent diffusion failed.



4-5

IR (benzene): 2012 (vs), 1947 (s), 1932 (m) cm^{-1}

ESMS: (MeOH/NaOMe) (Cone -10 V) m/z 351 (100% $[\text{M}-\text{H}]^-$), 382 (20% $[\text{M}+\text{OMe}]^-$); (Cone -20v) m/z 382 (80% $[\text{M}+\text{OMe}]^-$).

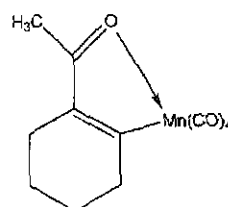
(MeOH/NaOMe) (Cone +20 V) m/z 374 (20% $[M-CO]^+$, 298 (60% $[M-2CO]^+$, 267 (90% $[M-2CO-2H]^+$

1H NMR: ($CDCl_3$, 300 MHz) δ 7.25 (5H, m, all Ar-H, 5.02 (1H, s, H5), 4.30 (1H, s, H3), 3.24 (1H, m, H1') 2.00 (3H, s, CH_3), 1.50 (6H, m, H2').

^{13}C NMR: ($CDCl_3$, 300 MHz) δ 223.1 ($MnCO$), 136.5 ($C1''$), 122.6- 128.5 (All Ar- C), 107.0 ($C4$), 101.6 ($C6$), 90.0 ($C2$), 81.4 ($C5$), 79.8 ($C3$), 32.1 ($C1'$), 24.6 ($C2'$), 24.4 ($C2''$).

4.4.5 Manganation of 1-acetyl-1-cyclohexene

1-Acetyl-1-cyclohexene (100 mg, 0.81 mmol) and $PhCH_2Mn(CO)_5$ (270 mg, 0.97 mmol) were refluxed in nitrogen-saturated hexane (20 mL) for 5 h. During this time, the metal carbonyl bands for $PhCH_2Mn(CO)_5$ disappeared and the reaction mixture turned yellow. A lot of brown solid also formed during this time. The brown solid was filtered and ignored. The hexane was removed under vacuum and the residue, a yellow oil was chromatographed (PLC, ethylacetate: X_4 , 1:6) to yield one band at R_f 0.8. The band was removed, extracted with CH_2Cl_2 and the solvent removed under vacuum. The yellow oil was identified as 4-6 (150 mg, 65%). Attempts to crystallize the product 4-6 by solvent diffusion failed. While a reasonable 1H NMR spectrum was obtained, attempts to get a reasonable ^{13}C NMR spectrum failed.



4-6

IR(heptane): 2080 (m), 1994 (s), 1933 (s) cm^{-1}

^1H NMR: (CDCl_3 , 300 MHz) δ 3.96 (3H, s, CH_3), 1.98- 2.87 (8H, cyclohexene Hs).

4.5 Crystal structure of 4-2

Crystal data and structure refinement for np3c.

Identification code	np3c
Empirical formula	C ₂₅ H ₁₂ Mn ₂ O ₁₀
Formula weight	582.23
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2/n
Unit cell dimensions	a = 13.86(7) Å alpha = 90° b = 5.85(3) Å beta = 95.45°(9). c = 14.16(7) Å gamma = 90°
Volume	1143(10) Å ³
Z, Calculated density	2, 1.692 Mg/m ³
Absorption coefficient	1.166 mm ⁻¹
F(000)	584
Crystal size	0.61 x 0.20 x 0.11 mm
Theta range for data collection	2.89 to 26.91 deg.
Limiting indices	-17<=h<=17, -6<=k<=7, -17<=l<=17
Reflections collected / unique	6634 / 2350 [R(int) = 0.0341]
Completeness to theta =	26.91° 94.6 %
Absorption correction	Empirical
Max. and min. transmission	0.8825 and 0.5366
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2350 / 0 / 176
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0949
R indices (all data)	R1 = 0.0411, wR2 = 0.0990
Largest diff. peak and hole	0.475 and -0.509 e.Å ⁻³

4.5 X-ray crystal structure 4-2

The orange crystals (needles) were shown to be monoclinic of space group $P2_1/n$ with 2 molecules in the unit cell. Crystal and structure refinement data are given in the table in section 4.5. An ORTEP perspective view showing the atom-labeling scheme is given in figure 5-5.

The structure was solved by direct methods and routinely refined. The H-atoms were in fixed positions except for the Hs on the cyclopropyl ring were located and refined. The molecule was found to lie on a 2-fold rotation axis. Cyclomanganated complexes of this type incorporate a five membered ring, which are essentially planar and constant geometry.

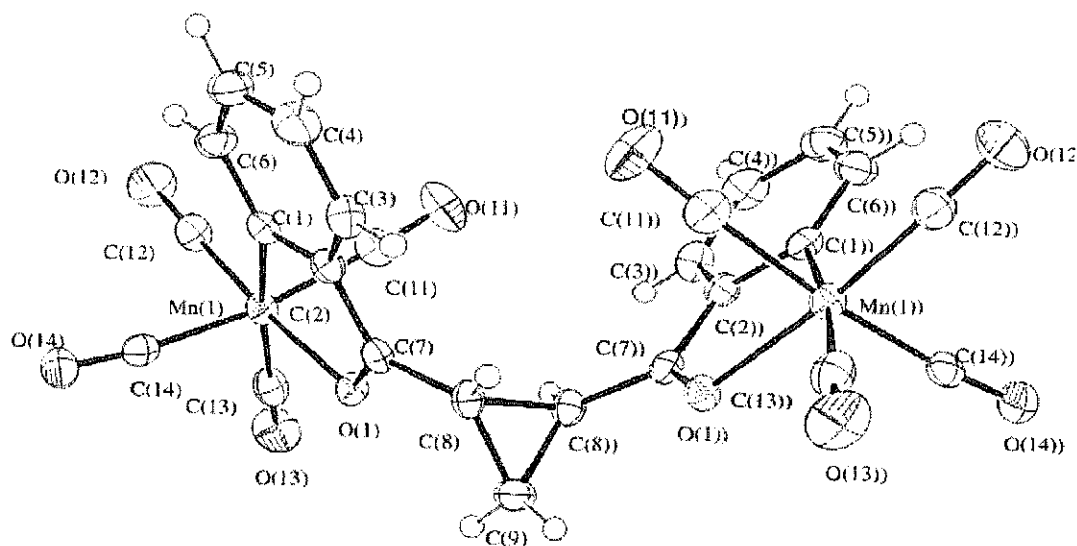


Figure 4-3: An ORTEP perspective view showing the atom-labeling scheme of 4-2

The following figures show the bond lengths of the manganocyclic ring of the dimanganated product 4-2, orthomanganated acetophenone⁵ and of the cyclomanganated [1,5-diphenylcyclopentane-1,4-diene-1-yl- κ C'-3-one- κ O]tetracarbonylmanganese¹ for comparison purposes.

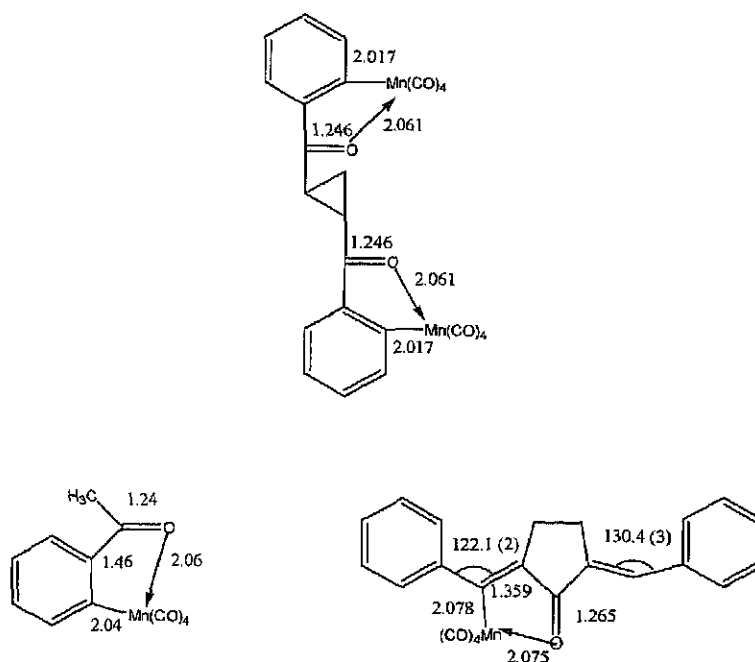
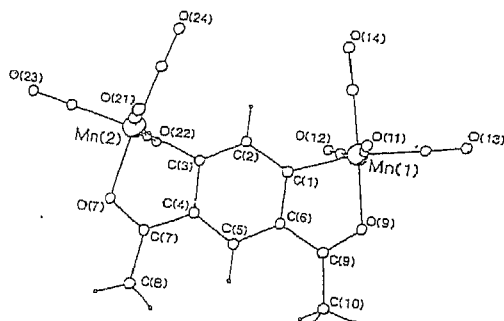


Figure 4-4: The bond lengths of the manganocyclic ring of the dimanganated product 4-2, orthomanganated acetophenone⁵ and of the cyclomanganated [1,5-diphenylcyclopentane-1,4- diene-1-yl- κ C'-3-one- κ O] tetracarbonylmanganese¹

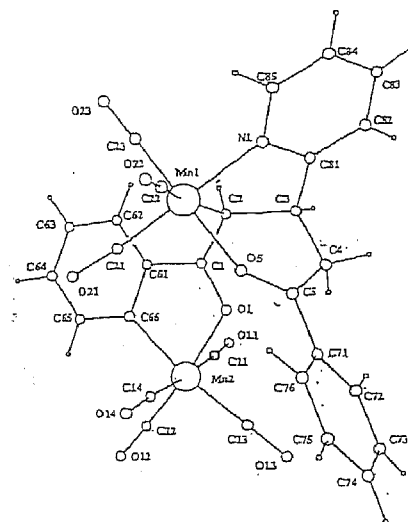
The bond lengths of the manganocyclic ring in the dimanganated product 4-2 are very similar to the bond lengths of the manganocyclic ring of the orthomanganated acetophenone. However, the bond lengths of the manganocyclic ring of the manganated dienone where it does not involve ring manganation, are slightly longer than the bond lengths of the manganocyclic rings of the dimanganated product 4-2 and of the orthomanganated acetophenone. The most likely reason for this would be the shift of the

electron cloud around the benzene ring towards the ring thus pulling the atoms bonded to the ring towards the ring.

The table below lists the bond lengths between Mn and the donor atoms of η^2 , η^2 -4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese)² (4-7), [1,5-diphenyl- κC^2 -3-(2-pyridyl- κN)-pentan-2-yl κC^5 -1,5-dione- $\kappa O^1 \kappa O^5$]-tetracarbonyltricarbonylmanganese⁹ (4-8) and 4-2. Figure 4.5 gives the crystal structure diagrams of the two compounds respectively for comparison purposes. The bond lengths between Mn and the C (aryl) are also listed.



4-7



4-8

Figure 4-5: Crystal structure diagrams of of η^2 , η^2 -4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese)² and [1,5-diphenyl- κC^2 -3-(2-pyridyl- κN)-pentan-2-yl κC^5 -1,5-dione- $\kappa O^1 \kappa O^5$]-tetracarbonyltricarbonylmanganese⁹

Compound	Bond lengths	
4-7	Mn(1)- O(9)	2.047(2)
	Mn(2)- O(7)	2.062(2)
	Mn- C aryl	2.042(2)
4-8	Mn(2)- O(1)	2.04(2)
	Mn(1)- N(1)	2.06(3)
	Mn(1)- O(5)	2.05(2)
	Mn- C aryl	2.19(3)
4-2	Mn(1)- O(1)	2.061(8)
	Mn- C aryl	2.017(7)

All three donor- atom to metal bond lengths are similar. This indicates that there is little effect of changing the donor atom or increasing the ring size on the donor atom to metal bond lengths.

The Mn-C aryl bond lengths, i.e the bond lengths between the carbon on the benzene ring and Mn are almost similar in compounds 4-7 and 4-2 but is slightly longer in compound 4-8. This difference is most likely due to the minimum interaction between the two Mn groups in 4-7 and 4-2. However, the interaction between the two Mn groups in 4-8 appears to be greater thus giving a larger Caryl-Mn bond length.

The octahedral geometry around the manganese atoms in compounds 4-8 and 4-2 are distorted in both cases. The larger deviation from 90° for the C(66)-Mn(2)-O(1) bond angle (79.1°) in 10 and the C(1)-Mn(1)-O(1) bond angle (78.6°) in 4-2 are due to the unsaturation in the five-membered ring imposing geometric constraints and compares closely with that found⁴ for orthomanganated acetophenone (79.4°). Overall then the cyclopropyl unit provides a useful bridge between the two orthomanganated rings, but has no effect on the bond parameters involving the manganese centres.

4.6 Conclusions

Reaction of trans-1,2-dibenzoylcyclopropane with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane gave the desired dimanganated product 4-2 and the mono-manganated 4-3. The manganation occurred on the two benzene rings therefore having the two $\text{Mn}(\text{CO})_4$ groups close together. Attempted coupling reactions of the dimanganated 4-2 and 4-3 did not give the desired results of producing some novel compounds. While many reactions initially looked promising, the products could not be isolated pure for final characterization. The products formed appeared highly unstable and to break down when attempting crystallization.

Extension of the work done by Tully¹ on manganated chalcones and dienones to other compounds of non-aryl type like 5-methyl-3-hexene-1-one and 1-acetyl-1-cyclohexene also did not prove too fruitful. The manganation of 5-methyl-3-hexene-2-one appeared to progress well as seen by the IR spectra as the reaction progressed. However, the manganated product could not be isolated and characterized. When phenylacetylene was present with the 5-methyl-3-hexene-1-one and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in the same reaction, the pyranyl($\text{Mn}(\text{CO})_3$) complex did however form as was observed by Tully¹ for the reaction of the manganated chalcones and dienones with alkynes. Similarly, not much could be achieved when attempts were made to manganate 1-acetyl-1-cyclohexene and to carry out one pot reactions of 1-acetyl-1-cyclohexene with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and alkynes or alkenes.

The limited success with the manganation of the compounds of the non-aryl type considered in this study and with their subsequent coupling reactions needs further investigation. It appears however that electronic factors come into play when electron-rich phenyl rings are not present in the compounds to be manganated. It is likely that when phenyl rings are present, they provide potential sites for manganation and also provide stability to the manganated compounds.

4.7 References

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Chapter 5: Ferrocenyl Pirylium Ions

5.1 Introduction

5.1.1 Pirylium Ions- Definition and Uses

A pyrylium salt is a salt formed by a conjugated six-membered carbon ring system with one carbon atom replaced by positively charged oxygen and a negatively charged counter ion (Figure 1).⁽¹⁾

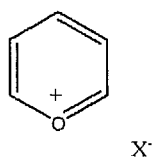


Figure 1: A pyrylium salt is a salt formed by a conjugated six-membered carbon ring system with one carbon atom replaced by positively charged oxygen and a negatively charged counter ion (Figure 1).⁽¹⁾

The replacement of a CH in benzene by O⁺ modifies the electron distribution much more than any other heteroatom or any other substituent R in CR or NR⁺. The resonance energy in pyrylium is smaller than in benzene or pyridine. Unlike benzene or pyridine, the pyrylium ring can be opened under drastic conditions such as high temperature or high pH.

Pyrylium salts can function as intermediates for a variety of syntheses. The key role of pyrylium salts depends on the high formation tendency of the pyrylium salts and their high reactivity towards nucleophiles. The organic compounds that can be synthesized from pyrylium intermediates include nitrobenzenes, pyridines, thiopyryliums, phosphobenzenes and 2,4-pentadienones⁽¹⁾. Despite the widespread interest in purely organic pyrylium salts, organometallic pyrylium salts are rare compounds and their chemistry has been little developed. Pyrylium salts are widely used in organic synthesis and have

regular applications in dyes, laser dyes, photosensitizers and corrosion-inhibiting additives in paint. ⁽¹⁾ Pyrylium ions have rich oxidation- reduction chemistry and form stable radicals or pyran compounds on reduction, depending on steric factors and on the reducing agent.

5.1.2 General synthetic methods of Pyrylium Ions

Pyrylium salts can be synthesized via various methods. Balaban et al.¹ have discussed a wide range of organic synthetic methods for pyrylium salts using commonly available starting materials under three main headings: one-component synthesis, two-component synthesis and three-component synthesis. Their methods did not involve the use of any metals. Figure 2 summarises the main routes to the pyrylium cation synthesis. An example each of one-component synthesis, two-component synthesis and three-component synthesis are discussed there after.

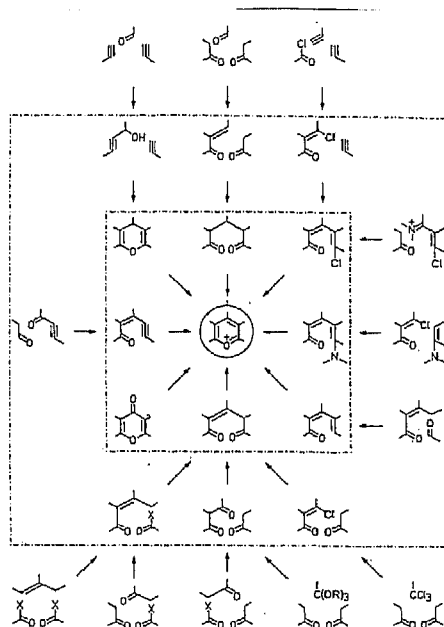
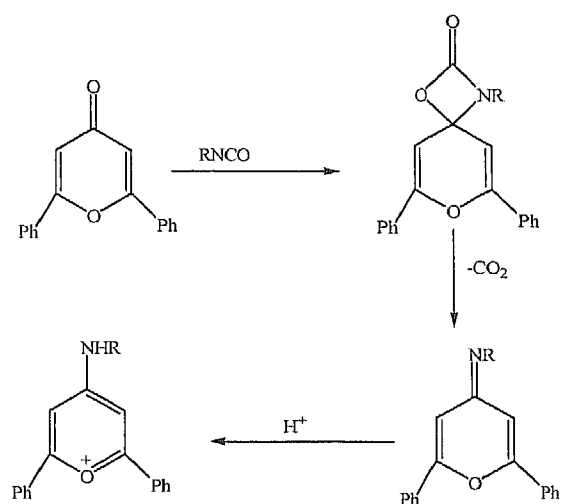


Figure 2: Synthetic main routes to the pyrylium cation (the inner field contains one-component synthesis, followed by two- and three component synthesis).

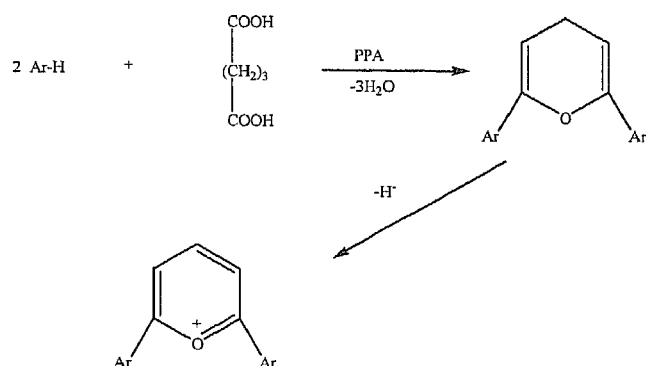
(Reference: Balaban, A.T.; Dinculescu, A.; Dorofeenko, G.N.; Fischer, G.W.; Koblik, A.V.; Mezheritskii, V.V.; Schroch, W. *Pyrylium Salts: Syntheses, Reactions and Physical Properties: Advances in Heterocyclic Chemistry: Supplement 2*: Academic Press: New York, 1982.)

An example of a one-component method is a convenient route to 4-aminopyrylium salts as suggested by Van Allan et al.² This involves the reaction between 4-pyrones (or flavones) with activated isocyanates, RCNO (R = COCCl₃, SO₂Cl, SO₂C₆H₄CH₃, CPh) followed by treatment of the primarily formed pyroneimines with mineral acid (Scheme 1).



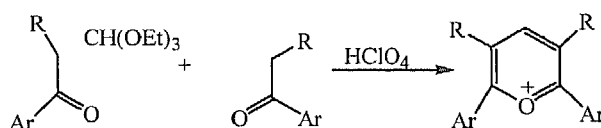
Scheme 1: An example of a one-component method is a convenient route to 4-aminopyrylium salts

An example of a two component synthesis of pyrylium salts is the synthesis of 2,6-diaryl pyrylium salts from phenol ethers and glutaric acid in the presence of polyphosphoric acid (PPA)^{3,4}. The reaction probably also involves oxidative dehydrogenation of the 4H-pyran intermediate as shown in Scheme 2.



Scheme 2: An example of a two component synthesis of pyrylium salts is the synthesis of 2,6-diaryl pyrylium salts from phenol ethers and glutaric acid in the presence of polyphosphoric acid (PPA)^{3,4}.

An example of a three-component synthesis is the reaction of ethyl orthoformate with two moles of an arylmethyl(ene) ketone in the presence of HClO₄ or BF₃.Et₂O which directly gives 2,6-diarylpyrylium salts unsubstituted at the γ -position (Scheme 3)^{5,6,8}.

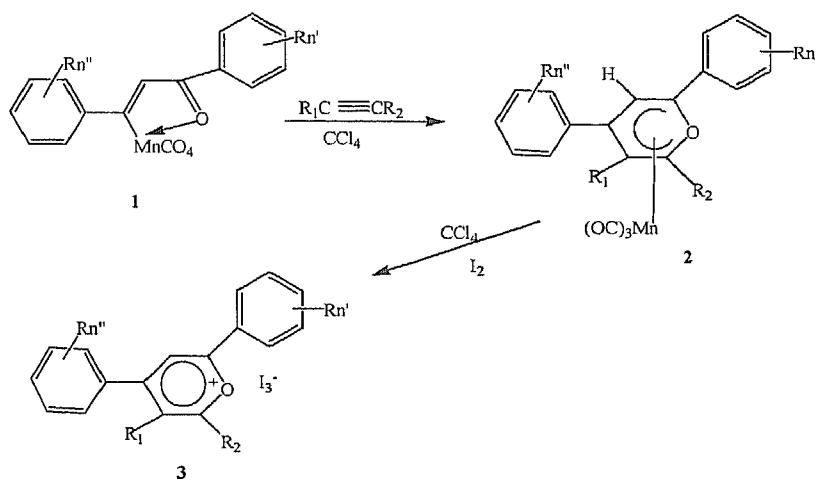


Scheme 3: An example of a three-component synthesis^{5,6,8}

5.1.3 Organomanganese pyrylium ion preparations

Tully¹⁴ reported the preparation of η^5 -pyranilcarbonylmanganese complexes and pyrylium triiodide salts from cyclomanganated chalcones and alkynes. β -Manganated chalcones were prepared by reacting the chalcones with PhCH₂Mn(CO)₅ (**1**, Scheme 4). Reaction of the β -manganated chalcones with alkynes gave the η^5 -pyranyltricarboxylmanganese derivative (**2**, Scheme 4). The pyranyl complex (**2**) was a ready source of pyrylium salts (**3**, Scheme 4) by reaction with iodine. Table 1 gives the

structures and yields of some pyranyltricarbonylmanganese complexes and pyrylium triiodide salts prepared by Tully^{12,14}.



Scheme 4: The preparation of η^5 -pyranylcarbonylmanganese complexes and pyrylium triiodide salts from cyclomanganated chalcones and alkynes.

Table 1: Substitution patterns and yields of pyranyltricarbonylmanganese complexes and pyrylium triiodide salts

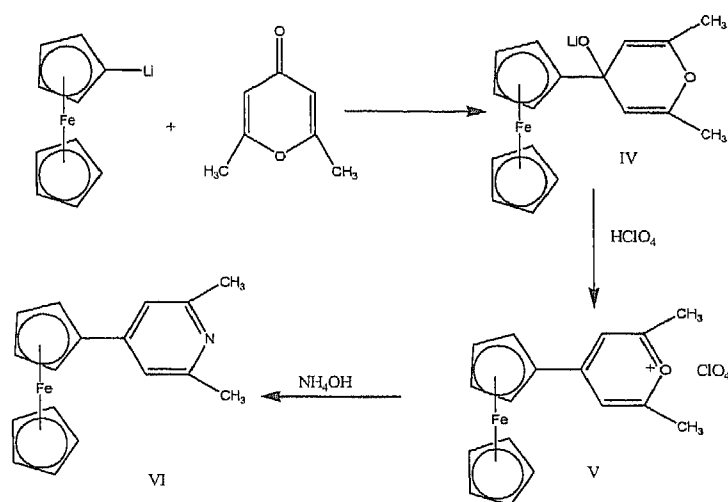
β -Manganated chalcone(1)		Alkyne		Pyranyl complex (II)	Pyrylium salt (III)
R''_n	R'_n	R_1	R_2	(Yield %)	(Yield %)
3'',4'',5''-(OMe) ₃	4''-Cl	H,	Ph	62%	92%
4''-CF ₃	H	H,	Ph	72%	82%
H	H	H,	Ph	72%	72%
4''-CF ₃	4'-Cl	H,	Ph	52%	79%
3'',4'',5''-(OMe) ₃	4'-Cl	H,	SiMe ₃	48%	85%
4''-OMe	3', 4', 5'(OMe) ₃	Me,	Pr	39%	87%
		(Pr,	Me)	5%	87%
4''-CF ₃	4'-Cl	Ph,	Ph	46%	64%
4''-CF ₃	H	Ph,	Ph	61%	84%

(Ref. Tully, W.; Main, L.; Nicholson, B.K. *J. Organometallic Chem.*, **503** (1995), 75-92)

5.1.4 Synthesis of ferrocenyl-substituted pyrylium cations

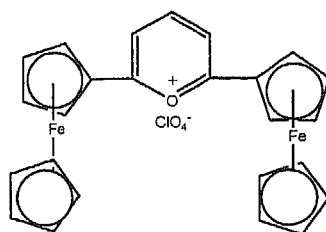
Ferrocenyl-substituted pyrylium cations have been successfully prepared before^{13,23}. However, their detailed studies have not been reported in the literature so far. Ferrocenyl-substituted pyrylium ions have two redox centres thus making them interesting compounds to study for their redox and electrochemical properties.

Dorofeenko and Krasnikov¹³ obtained 4-ferrocenyl-2,6-dimethylpyrylium perchlorate (V) when ferrocenyllithium was reacted with 2,6-dimethyl- γ -pyrone with the subsequent treatment of the carbinolate (IV) with perchloric acid (Scheme 5).



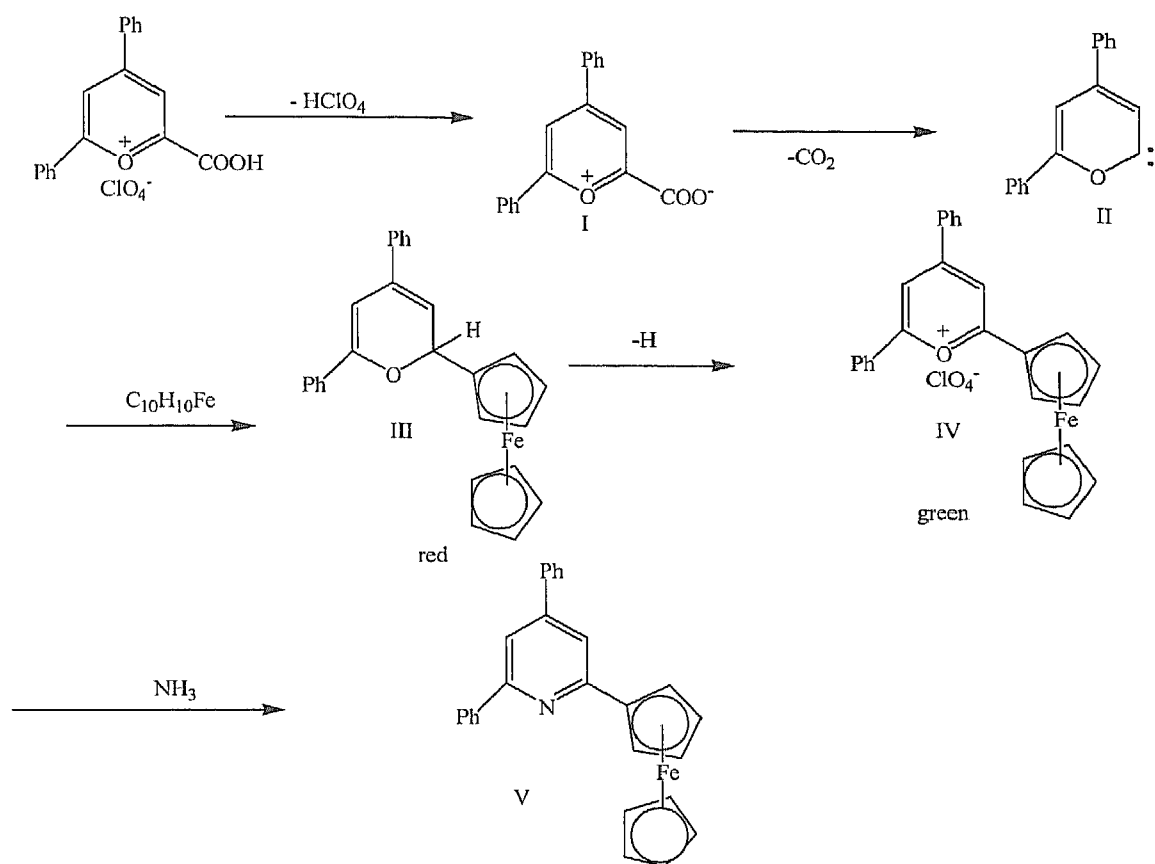
Scheme 5: The formation of 4-ferrocenyl-2,6-dimethylpyrylium perchlorate (V) when ferrocenyllithium was reacted with 2,6-dimethyl- γ -pyrone with the subsequent treatment of the carbinolate (IV) with perchloric acid ¹³

In an alternative approach, acetylferrocene was reacted with orthoformic ester in the presence of 70% perchloric acid. 2,6-diferrocenylpyrylium perchlorate (5-1) was obtained as green crystals.



5-1

In another reaction, Krasnikov²³ and his team synthesized the neutral red coloured 2-ferrocenyl-4,6-diphenylpyran (III, Scheme 6) . In the same study the treatment of the 2-ferrocenyl-4,6-diphenylpyran with perchloric acid gave green coloured 2-ferrocenyl-4,6-diphenylphenylpyrylium perchlorate (IV, Scheme 6) which was converted to yellow coloured 2-ferrocenyl-4,6-diphenylpyridine (V, Scheme 6) when treated with 25% ammonia solution.

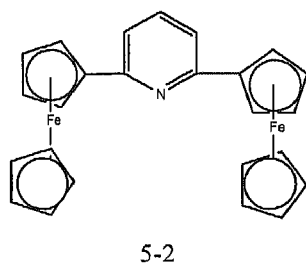


Scheme 6: The preparation of 2-ferrocenyl-4,6-diphenylpyran, 2-ferrocenyl-4,6-diphenylphenylpyrylium perchlorate and 2-ferrocenyl-4,6-diphenylpyridine²³.

5.1.5 Reactions of ferrocenyl-substituted pyrylium ions

5.1.5.1 Preparation of the pyran and the pyridine derivatives of pyrylium salts

Dorofeenko and Krasnikov ¹³ also synthesized pyridine derivatives from ferrocenyl pyrylium salts. When the pyrylium salt (V, Scheme 5) was treated with 25% ammonia solution, 4-ferrocenyl-2,6-dimethylpyridine, a yellow solid (VI, Scheme 5), was obtained. Similarly, yellow 2,6-diferrocenylpyridine (5-2) was obtained when 2,6-diferrocenylpyrylium perchlorate (5-1) was boiled with ammonium acetate in glacial acetic acid.

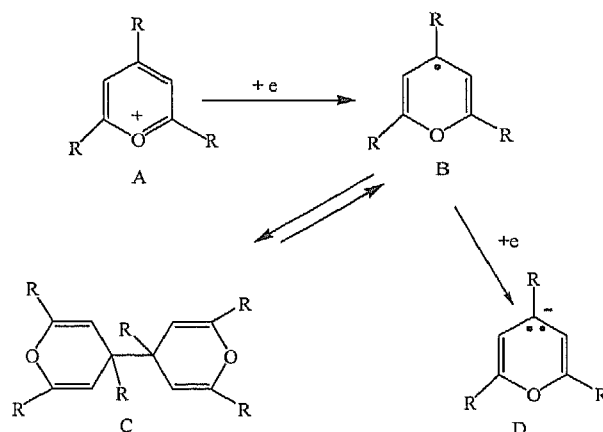


From the study by Dorofeenko and Krasnikov ¹³, it was found that pyrylium salts of ferrocene with methyl groups present at carbons 2 and 4 of the pyrylium ring were coloured blue and the pyridine derivatives of the pyrylium salts with ferrocene were coloured yellow. Krasnikov²³ and his team found that the phenyl substituted pyrylium salts of ferrocene (at carbons 4 and 6) were coloured green and their pyran derivatives were coloured red.

5.1.5.2 Oxidation and reduction reactions of pyrylium salts

Oxidation-reduction of pyrylium salts usually destroys the pyrylium ring. However in some instances, the destruction is useful for structural determinations. An example of such oxidation is that of the trinitration product obtained from 2,4,6-triphenylpyrylium perchlorate that afforded a mixture of m- and p-benzoic acids in a ratio consistent with p-nitration of the 4-phenyl group and the m-nitration of 2- and 6-phenyl groups^{9,10}.

In the electrochemical reduction of 2,4,6-trimethylpyrylium salts (perchlorate, tetrachloroferrate and iodide) no proton is involved and the product of the reaction was isolated and shown to be identical to the hexasubstituted 4,4''-bi-4H-pyran (C, scheme 7). This can also be prepared with zinc dust in water-ether or in ethanol¹.



Scheme 7: Electrochemical reduction of 2,4,6-trimethylpyrylium salts (perchlorate, tetrachloroferrate and iodide).

In the reaction, a free radical is involved which is stable if R = Ph. The reversibility of the bipyrane formation can be demonstrated by chemical oxidation of C to A, with chromium trioxide, perchloric acid or by electro-oxidation on a rotating platinum electrode in

acetonitrile with potassium perchlorate as electrolyte. The clean 4, 4'-dimerisation without any detectable 2,2'- or 2,4' dimers indicates the high spin density on the 4-position of the free radical (B) .

In another similar study²⁰, it was found that the pyrylium cations similar to A with a variety of R groups were electrochemically reduced in well shaped waves between $E_{1/2} = -0.22$ V and -0.63 V. The two waves correspond to the cathodic reduction of the pyrylium ion. The first reduction is responsible for the formation of the radical B (which may dimerise to C) and the second reduction would give the anion D. The solvent used in the study was acetonitrile at 25°C.

According to Beddoes²¹ and his team, unsubstituted triphenylpyrylium salts in acetonitrile get first electrochemically reduced to the radical at -0.31 V and then to the anion at -1.45 V. The radical formed by the first reduction can undergo dimerisation to give the bipyran as in scheme 7. Pyranyl radicals in which the substituents are small (such as H, Me, or Et) undergo irreversible dimerisation while radicals with large substituents (such as Bu^t and Ph) are in dynamic equilibrium with the bipyran¹¹. The pyranyl radicals are very sensitive to oxygen. The oxygen oxidizes the pyranyl radicals to the parent pyrylium ions.

5.2 Aims of the current research

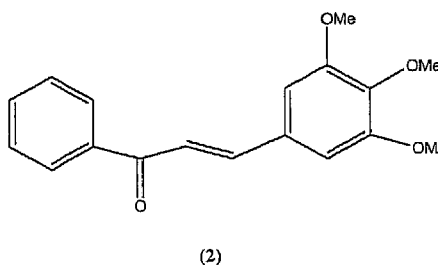
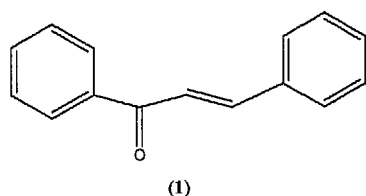
The objective of the present section of work was to make use of the Tully¹⁴ method with cyclomanganated chalcones and ferrocenylethyne to prepare compounds similar to those prepared by Dorofeenko and Krasnikov¹³ and Krasnikov²³ and his team for full physical analysis. Tully's work involved the synthesis of pyrylium ions using cyclomanganated chalcones and alkynes but not with ferrocenylethyne.

The current study intends to prepare ferrocenyl pyrylium ions with two redox centres, similar to those prepared by Dorofeenko and Krasnikov¹³ and to study their UV-visible and electrochemical properties. It was also intended to see if introducing other substituents like methoxy groups on the benzene ring (at carbons labeled 3'', 4'' and 5'') at the 4th carbon on the pyranyl ring (5-11) influenced the UV- Visible spectroscopy and the electrochemistry of the ferrocenyl pyrylium ions.

Dorofeenko and Krasnikov's¹³ study also involved the preparation of the pyridine derivative of the pyrylium ions whereas Krasnikov²³ and his team prepared both the pyran and the pyridine derivatives of a phenyl substituted pyrylium ion.

However, all these were only preliminary studies and no detailed studies were carried out.

Chalcone (1), 1,3-diphenyl-prop-2-en-1-one and chalcone (2), 1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one were chosen for the study.



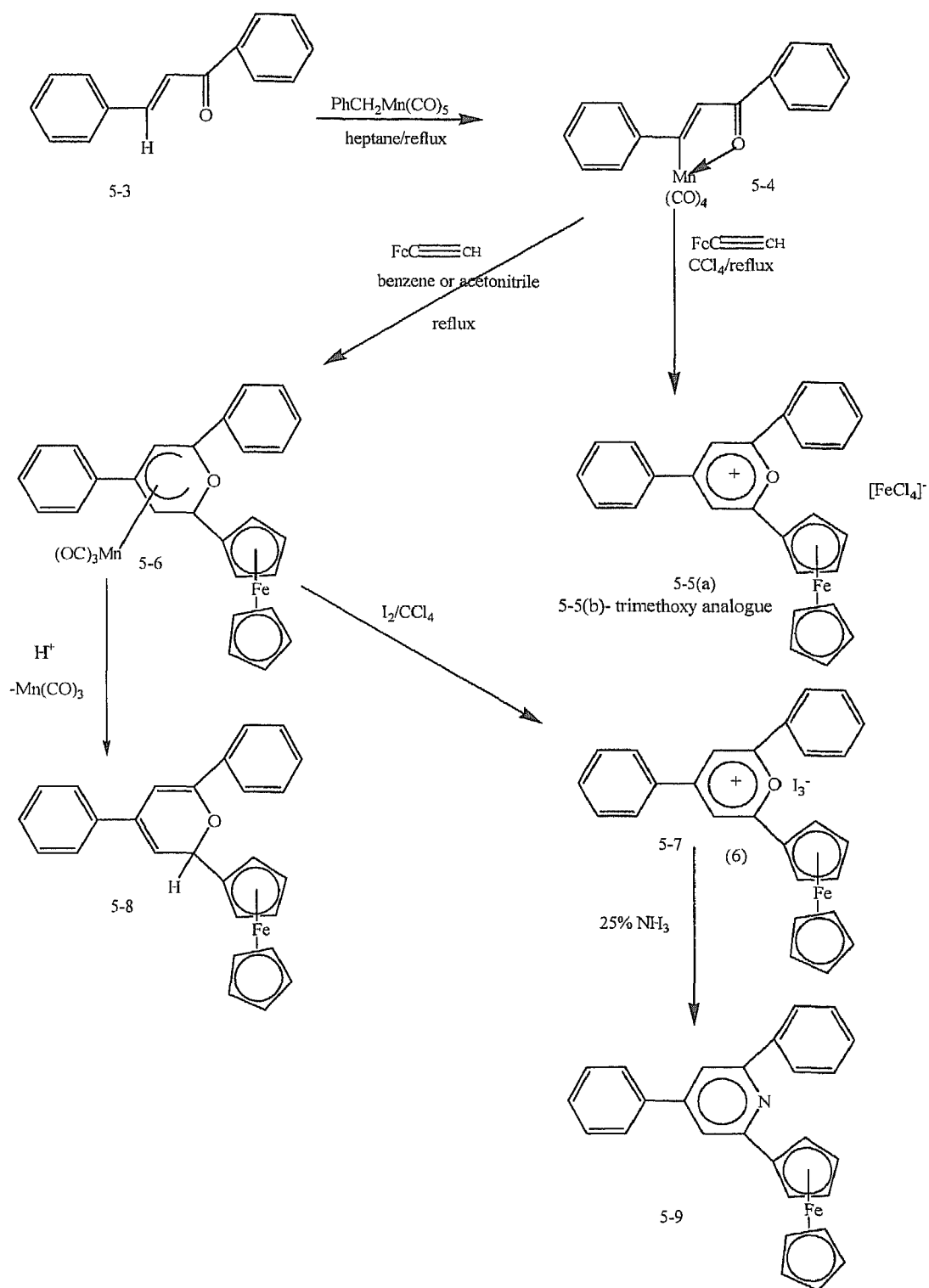
Cooney¹⁵, followed by Tully¹⁴ studied the influence of different solvents on the yields and types of products formed when alkynes and alkenes were coupled with orthomanganated aryl compounds and manganated enones. It was therefore of interest in the present study to see if a change of solvent would affect the type of products formed or the yields of the products formed.

Carbon tetrachloride, benzene and acetonitrile were the solvents chosen for the coupling reactions in the study. These solvents have been used routinely and successfully in coupling reactions of alkynes with cyclomanganated compounds and have had a considerable influence on the product types and their yields.

5.3 Results and Discussion

Chalcone (1, section 5.2), 1,3-diphenylprop-2-en-1-one and chalcone (2, section 5.2), 1-phenyl-3-(3,4,5 trimethoxyphenyl)prop-2-en-1-one were reacted with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane to give the cyclomanganated chalcones (5-4, Scheme 8). Most further reactions were carried out with the manganated chalcone (5-4, Scheme 8), i.e. with [1,3-diphenylprop-2-en-3-yl- κC^3 -1-one- κO]tetracarbonylmanganese, and in some cases with the manganated chalcone (2, section 5.2), i.e. with [1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-3-yl- κC^3 -1-one- κO]tetracarbonyl-manganese for comparison purposes.

Scheme 8 summarizes the reactions that were carried out in the current study and reference is made to it in the discussions that follow.



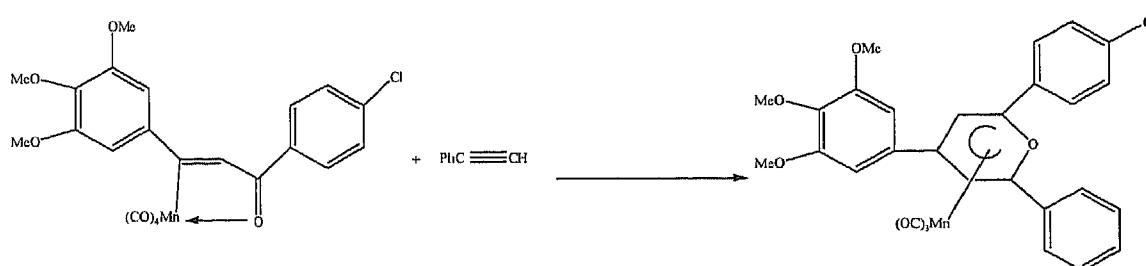
Scheme 8: Reactions done in the current study

The reactions in the scheme were essentially the same for 1-phenyl-3-(3,4,5 trimethoxyphenyl)prop-2-en-1-one (5-10, pg 180) as the starting material instead of (5-3).

5.3.1 The effect of different solvents on product types

The cyclomanganated chalcone, (5-4, Scheme 8), was reacted with ferrocenylethyne in carbon tetrachloride, benzene and acetonitrile. The time taken for all these reactions in the different solvents was about three hours at reflux and the reactions were monitored by I.R. and t.l.c.

Reaction of the cyclomanganated chalcone, 5-4, Scheme 8, with ferrocenylethyne in carbon tetrachloride afforded a green powdery product. The green colour of the product obtained in this study was similar to the green coloured 2-ferrocenyl-4,6-diphenylpyrylium perchlorate and 2,4-diferrocenylpyrylium perchlorate obtained by Krasnikov²³ and his team. This suggested that the green coloured product obtained in this study was most likely a 2-ferrocenyl-4,6-diphenylpyrylium salt. This is the expected stereochemistry of the product based on the products obtained by Tully¹² which involved reacting cyclomanganated chalcones with alkynes. An example of Tully's reaction is the reaction of [1(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-3-yl- κC^3 -1- κO]tetracarbonylmanganese with phenylacetylene to give [6-(4-chlorophenyl)-2-phenyl-4(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese, i.e the phenyl group from the alkyne ending at position 2 on the pyranyl ring as shown by Scheme 9.



Scheme 9: Reaction of [1(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-3-yl- κC^3 -1- κO]tetracarbonylmanganese with phenylacetylene to give [6-(4-chlorophenyl)-2-phenyl-4(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese, i.e the phenyl group from the alkyne ending at position 2 on the pyran ring .

ESMS studies of this green product in the positive ion mode (section 5.3.2) further suggested that the product was a salt of the 2-ferrocenyl-4,6-diphenyl pyrylium ion (5-5), Scheme 8) as it gave a very strong signal corresponding to the pyrylium ion (Figure 1, Section 5.3.2). A strong signal seen in the negative ion mode was for that of the $[\text{FeCl}_4]^-$ complex. This suggested that the counter anion formed in the reaction was $[\text{FeCl}_4]^-$. The chlorine in the $[\text{FeCl}_4]^-$ was most likely coming from CCl_4 and the Fe from the breakdown of ferrocene. Good NMR of the green product could not be obtained. This was not unexpected because Fe^{3+} ion is a d^5 high spin ion and is paramagnetic and would not allow good NMR.

The elemental analysis of the green product, $\text{C}_{27}\text{H}_{21}\text{Fe}_2\text{OCl}_4$, which had a yield of 67.1% was also performed for carbon and hydrogen. The values for carbon and hydrogen were 51.34% and 3.93% respectively. These values were close to the calculated values for the green product of 52.73 % for carbon and 3.44 % for hydrogen and hydrogen respectively. This clearly showed that the sample was reasonably pure.

Attempts were made to crystallize the product using $\text{Na}[\text{BPh}_4]$ and $\text{Na}[\text{PF}_6]$. It was anticipated that the addition of the anions $[\text{BPh}_4]^-$ and $[\text{PF}_6]^-$ would form either the 2-ferrocenyl-4,6-diphenylpyrylium tetraphenylborate or the 2-ferrocenyl-4,6-diphenyl pyrylium hexafluorophosphate, and would crystallize. However, no crystals formed.

In contrast, the reaction of the cyclomanganated chalcone, (5-4, Scheme 8) with ferrocenylethyne in benzene or acetonitrile gave a red coloured reaction mixture. The red colour of the reaction mixture suggested that it could contain either the red coloured 2-ferrocenyl-4,6-diphenyl pyran, as obtained in an earlier study²³, or [2-ferrocenyl-4,6-diphenyl- η^5 -tricarbonylmanganese] similar to the red coloured (pyranyl) $\text{Mn}(\text{CO})_3$ complexes obtained by Tully^{12,14}.

Chromatographing the residue (p.l.c., dichloromethane: hexane, 1:1) gave two major bands. A red band at R_f of 0.8 was obtained as a red oil and was recrystallised from

ether/pentane by diffusion to give red needle-like crystals. This was identified by IR having similar metal carbonyl bands for similar compounds in an earlier study^{12,14} as the (pyranyl)Mn(CO)₃ complex, i.e. the [2-ferrocenyl-4,6-diphenyl-η⁵-pyranyltricarboxylmanganese] (5-6, Scheme 8) the identity confirmed by NMR (section 5.3.2 and section 5.4). The crystal structure of 5-6 was also determined (section 5.3.5).

It was noted however that this band at R_f of 0.8 left behind a streak of green product over the plate as it moved up. This suggested that the red [2-ferrocenyl-4,6-diphenylpyranyl-η⁵]tricarbonylmanganese] was getting oxidized to the green 2-ferrocenyl-4,6-diphenylpyrylium ion as it moved up the plate. This most likely was the result of the exposure of [2-ferrocenyl-4,6-diphenylpyranyl-η⁵]tricarbonylmanganese to air and oxygen was most probably the oxidizing agent in this case.

The other red band at R_f of about 0.2 was identified as the 2-ferrocenyl-4,6-diphenylpyran (5-8, Scheme 8) using IR, NMR and elemental analysis (section 5.3.2 and section 5.4). A possible route to the formation of the 2-ferrocenyl-4, 6-diphenylpyran could be the protonation of 5-6 followed by its demetallation as shown in scheme 8. Alternatively, 5-8 could also be formed by the oxidation of the [2-ferrocenyl-4, 6-diphenylpyranyl-η⁵]tricarbonylmanganese (5-6, Scheme 8) to give the 2-ferrocenyl-4, 6-diphenylpyrylium ion which then gets reduced in the reaction mixture to give the red coloured 2-ferrocenyl-4,6-diphenylpyran (5-8, Scheme 8). This also possibly explains why no green 2-ferrocenyl-4,6-diphenylpyrylium salt (5-5, Scheme 8) was isolated from the reaction mixture of [1,3-diphenyl-prop-2-ene-3-yl-κC³-1-one-κO] tetracarboxylmanganese with ferrocenylethyne in benzene or acetonitrile. The oxidizing and the reducing agents involved in the reactions could possibly be coming from the breakdown of the manganated starting material 5-3 but this has not been confirmed.

Three other minor bands were ignored and this probably explains why the yield of the (pyranyl)Mn(CO)₃ complex, i.e. of the [2-ferrocenyl-4,6-diphenyl-η⁵-

pyranyltricarbonylmanganese] obtained in this study was lower to the yields obtained by Tully^{12,14}.

The reactions of 1-phenyl-3-(3,4,5 trimethoxyphenyl)prop-2-en-1-one (2, section 5.2) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ followed by its reaction with ferrocenylethyne in carbon tetrachloride, benzene and acetonitrile gave results similar to the reactions of chalcone (1), the 1,3-diphenyl-prop-2-en-1-one.

5.3.2 Spectroscopic and mass spectrometric characterization of the products

5.3.2.1 IR, NMR and MS studies

The red band at R_f of 0.8 obtained from the reaction of cyclomanganated chalcone (5-4) with ferrocenylethyne in benzene showed three metal carbonyl bands at 2012, 1951 and 1931 cm^{-1} . The IR bands are characteristic of the $(\text{pyranyl})\text{Mn}(\text{CO})_3$ complexes as seen in the study by Tully^{12, 14}. The IR data suggested that the product was most likely the [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese (5-6, Scheme 8).

The ^1H NMR signals at about δ 5.71 ppm, two singlets for two protons arise from the two protons directly bonded to the pyranyl ring. This was consistent with the ^1H NMR signals of the two protons bonded to the pyranyl ring of $(\text{pyranyl})\text{Mn}(\text{CO})_3$ complexes studied by Tully^{12, 14}. The ferrocene ^1H NMR signals were observed and were consistent with those observed in the earlier study¹³. The ^1H NMR evidence suggested that the product was the [2-ferrocenyl-4, 6-diphenylpyranyl- η^5]tricarbonylmanganese (5-6, Scheme 8). Elemental analysis also supported the I.R. and the ^1H NMR evidence. The ESMS spectrum of 5-6 in the positive ion mode showed a strong signal for the oxidized pyrylium cation (discussed later) suggesting that 5-6 was getting oxidized in the instrument.

[2-ferrocenyl-4, 6-diphenylpyranyl- η^5]tricarbonylmanganese was reacted with iodine in carbon tetrachloride to give the 2-ferrocenyl-4, 6-diphenylpyrylium triiodide (identified by its ESMS data). The green 2-ferrocenyl-4, 6-diphenylpyrylium salt, $C_{27}H_{21}Fe_2OCl_4$, from the carbon tetrachloride reaction was also reacted with ammonia to give the 2-ferrocenyl-4,6-diphenylpyridine. However the product isolated from the reaction of these with zinc in ether could not be fully characterized. All the products were characterized using IR, NMR, electrospray mass spectroscopy and elemental analysis thus further confirming the structure of the [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese and the other compounds discussed here (sections 5.3.3 and 5.4). The structure of the [2-ferrocenyl-4, 6-diphenyl- η^5 -pyranyl]tricarbonylmanganese (5-6, Scheme 8) was finally confirmed by its crystal structure (section 5.3.5).

The second band at $R_f=0.2$ obtained from the reaction of [1, 3-diphenyl-prop-2-ene-3-yl- κC^3 -1-one- κO]tetracarbonylmanganese with ferrocenylethyne in benzene did not have any IR metal carbonyl signals. The elemental analysis of this product (section 5.4) confirmed its formula and was consistent with the formula of 2-ferrocenyl-4,6-diphenylpyran (5-8, Scheme 8). The 1H NMR signals at around δ 5.71 ppm (two singlets for two protons) resulting from the two protons bonded directly to the pyranyl ring of [2-ferrocenyl-4, 6-diphenyl- η^5 -tricarbonylmanganese] (5-6, Scheme 8) now disappeared. However, three 1H NMR signals²¹, two doublets and a singlet for three protons appeared at around 7.86, 6.78 and 6.20 (section 5.4). These signals were due to the lone proton (C2) bonded to the carbon to which the ferrocene was bonded and to the other two protons on the same ring (i.e. C3 and C5).

The ESMS of the green products (5-5 and 5-11) in MeOH gave very strong signals in the positive ion mode. These signals (figure 1 and 2) corresponded to the respective pyrylium cations. Similar results were obtained for the triiodide salts of the two pyrylium ions and of the (pyranyl) $Mn(CO)_3$ complexes ([2-ferrocenyl-4, 6-diphenylpyranyl- η^5]tricarbonylmanganese and 2-ferrocenyl-4-(3,4,5- trimethoxyphenyl)-6-phenylpyranyl- η^5]tricarbonylmanganese]. The ESMS results for the two (pyranyl) $Mn(CO)_3$ complexes

suggested that these were getting oxidized in the instrument. Figures 3(a) and 4 show the ESMS of the pyrylium ions in MeOH at cone voltage +20 volts. Figures 3(b) and 3 (c) are the microTOF (HRMS) spectra of the 2-ferrocenyl-4,6-diphenyl pyrylium ion (5-5) and of the $[\text{FeCl}_4]^-$ counter anion. Figure 3(b)(1) shows the observed MicroTOF spectrum and the simulated isotope pattern of the 2-ferrocenyl-4,6-diphenyl pyrylium ion (5-5) and Figure 3(b)(2) shows the observed isotope pattern of the 2-ferrocenyl-4,6-diphenyl pyrylium ion (5-5). The simulated isotope pattern is the same to the observed isotope pattern further confirming the structure of the 2-ferrocenyl-4,6-diphenyl pyrylium ion.

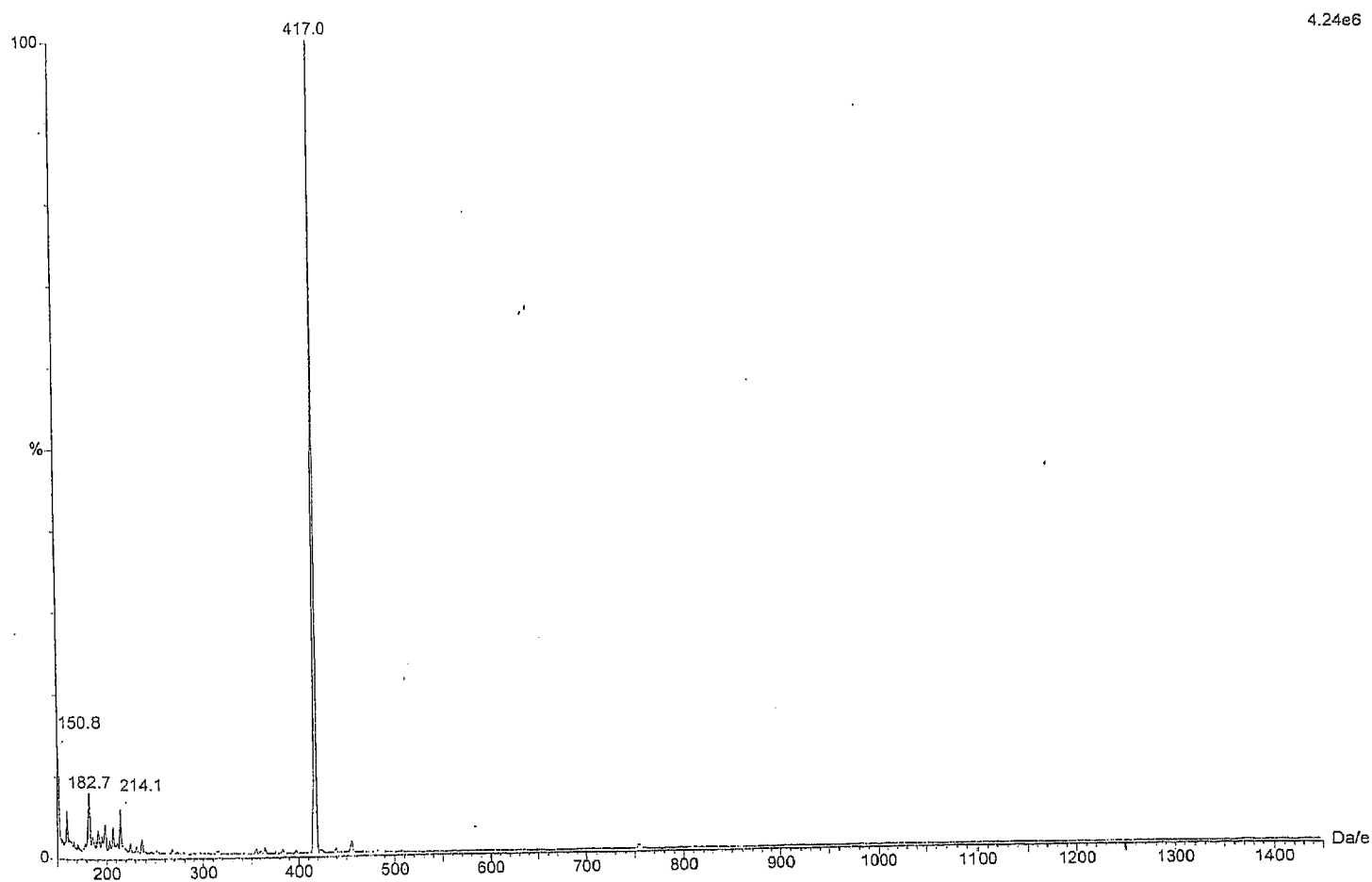


Figure 3(a): ESMS spectrum of the green 2-ferrocenyl-4, 6-diphenyl pyrylium salt showing the intense peak for the pyrylium cation

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	80.0 V	Set Pulsar Pull	400 V
Scan Begin	100 m/z	Hexapole RF	150.0 V	Set Pulsar Push	400 V
Scan End	800 m/z	Skimmer 1	24.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

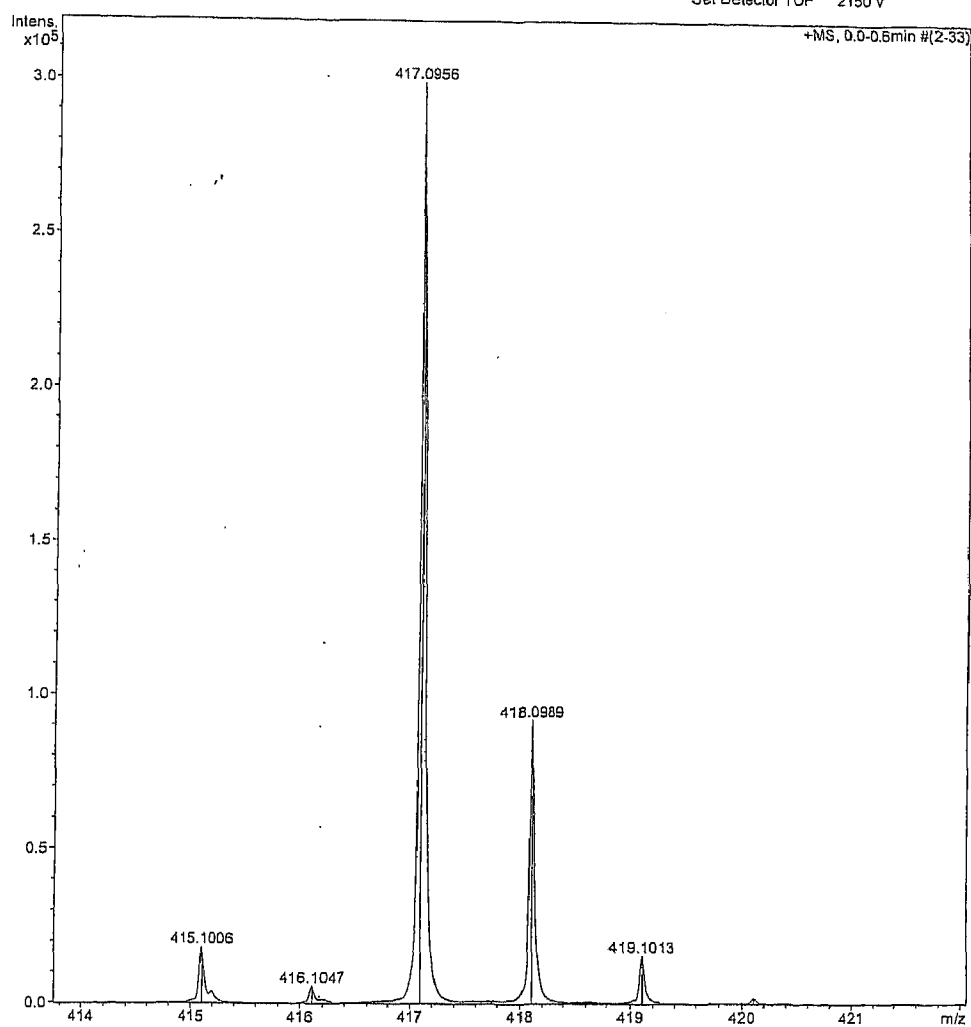
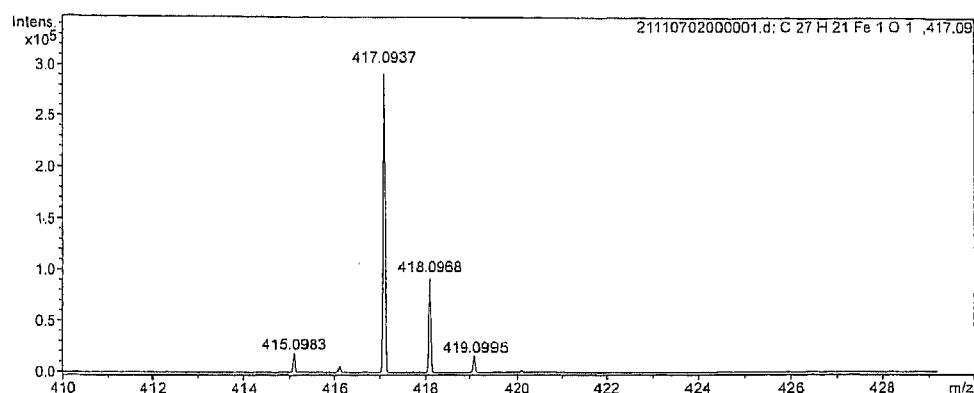
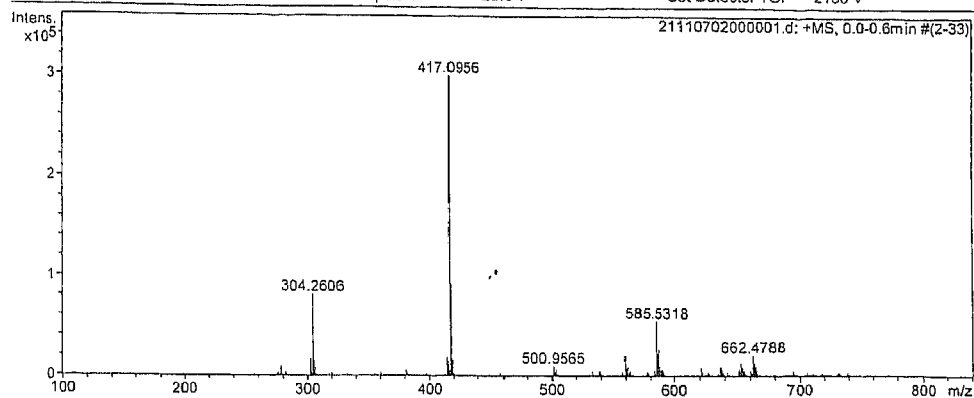


Figure 3(b) (1): The MicroTOF (HRMS) +ve ion spectrum of the green 2-ferrocenyl-4, 6-diphenyl pyrylium salt showing the intense peak for the pyrylium cation and the simulated isotope pattern

Mass Spectrum Molecular Formula Report

Analysis Info				Acquisition Date 11/21/2007 1:33:45 PM	
Analysis Name	D:\Data\Narendra\21110702000001.d				
Method	Na_formate_pos_n.m			Operator	administrator
Sample Name	ClacferAc1			Instrument	micrOTOF 89
Comment	ChalconeFErAC1 green in MEOH				
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	80.0 V	Set Pulsar Pull	400 V
Scan Begin	100 m/z	Hexapole RF	150.0 V	Set Pulsar Push	400 V
Scan End	800 m/z	Skimmer 1	24.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdB	N Rule	e ⁻
C 27 H 21 Fe 1 O 1	0.00	417.0936	-4.70	-4.77	17.50	ok	even

Figure 3(b) (2): The MicrOTOF (HRMS) +ve ion spectrum of the green 2-ferrocenyl-4, 6-diphenyl pyrylium salt showing the intense peak for the pyrylium cation and the observed characteristic isotope pattern

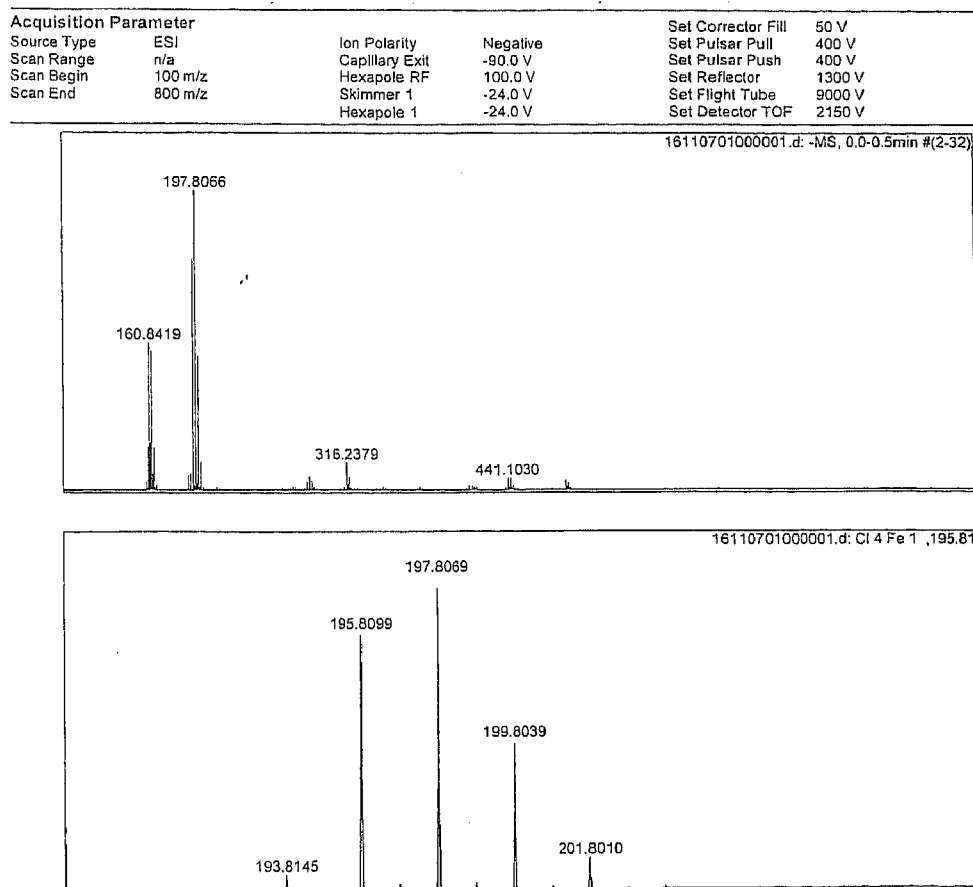


Figure 4: The MicroTOF (HRMS) –ve ion spectrum of the green 2-ferrocenyl-4, 6-diphenyl pyrylium salt showing the intense peak for the $[\text{FeCl}_4]^-$ counter anion

5.3.2.2 UV-Visible studies of the products

The UV-visible bands listed in the table below are weak and broad bands. These are the low intensity, charge transfer bands similar to those observed in earlier studies^{22,24}. The UV-visible bands for the two pyrylium salts show obvious solvent shifts. However, both the pyrylium salts show almost similar absorption bands. The other bands observed were for the phenyl and the trimethoxy phenyl groups, i.e. around 350- 450 nm²² and for ferrocene around 200 to 350 nm, assigned with comparison with the UV-visible spectrum of ferrocene (Figures 5 to 9, section 5.3.2). The intervalence charge transfer bands listed in the Table 2 are missing from the UV-visible spectra of [2-ferrocenyl-4,6-diphenyl- η^5 -tricarbonylmanganese], 2-ferrocenyl-4,6-diphenylpyran and ferrocene UV-visible spectra. (Figures 5, 6 and 7).

Table 2: UV-visible absorption maxima of ferrocenyl pyrylium ions in different solvents showing the intervalence charge transfer bands

Compound	Solvent		
	Dichloromethane	Acetone	Benzene
X	695	665	682
Y	691	655	685

Compound (X): 2-ferrocenyl-4,6-diphenylpyrylium ion

Compound (Y): 2-ferrocenyl-4-(3, 4, 5-trimethoxyphenyl)-6-phenyl pyrylium ion.

The UV-Visible bands listed in the table as seen for the two-ferrocenyl pyrylium ions are most likely due to the electron transfer that is taking place between the two-redox centres that are present in the pyrylium ions. These bands are most probably due to the electron transition occurring between the neutral Fe and the cation. These electron transfer bands also show solvent effects²². In the neutral pyran and the pyridines, these bands are missing because of the absence of the two redox centres.

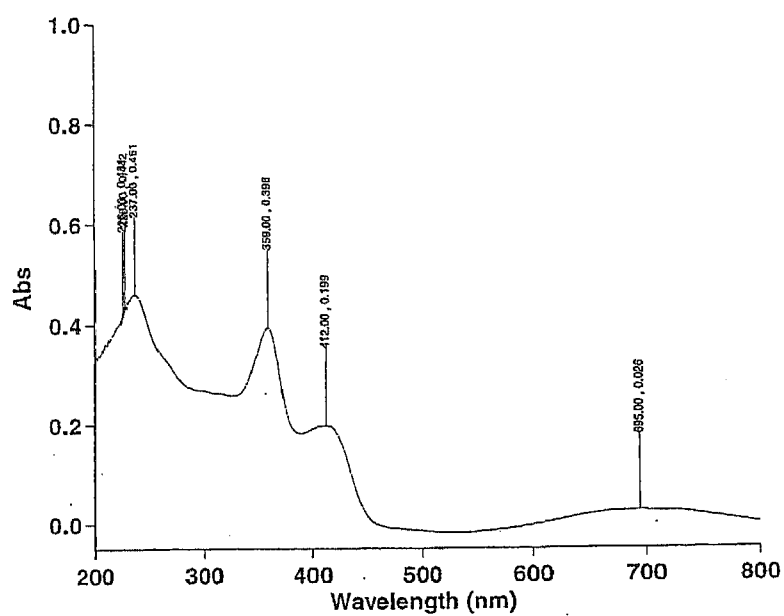


Figure 5: UV-Visible spectrum of 2-ferrocenyl-4,6-diphenyl pyrylium ion in CH_2Cl_2

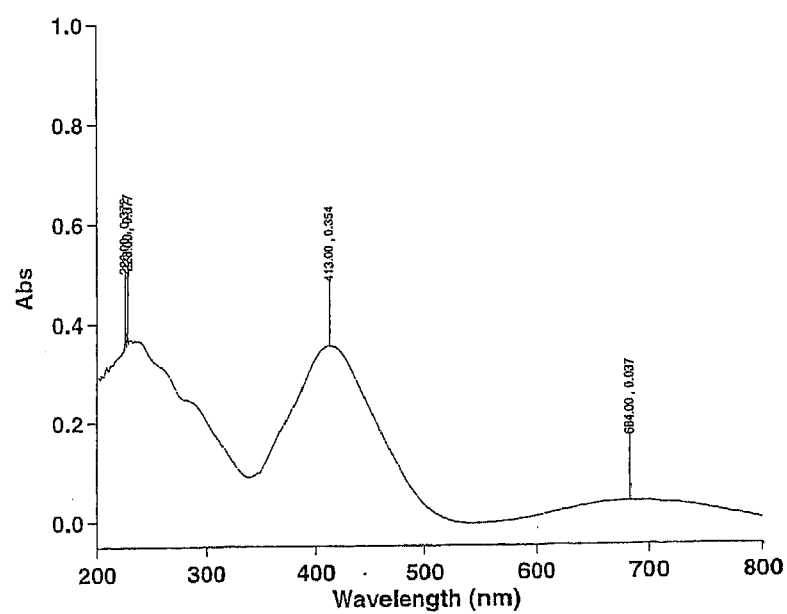


Figure 6: UV-Visible spectrum of 2-ferrocenyl-4-(3, 4, 5 trimethoxyphenyl)-6-phenylpyrylium ion in CH_2Cl_2

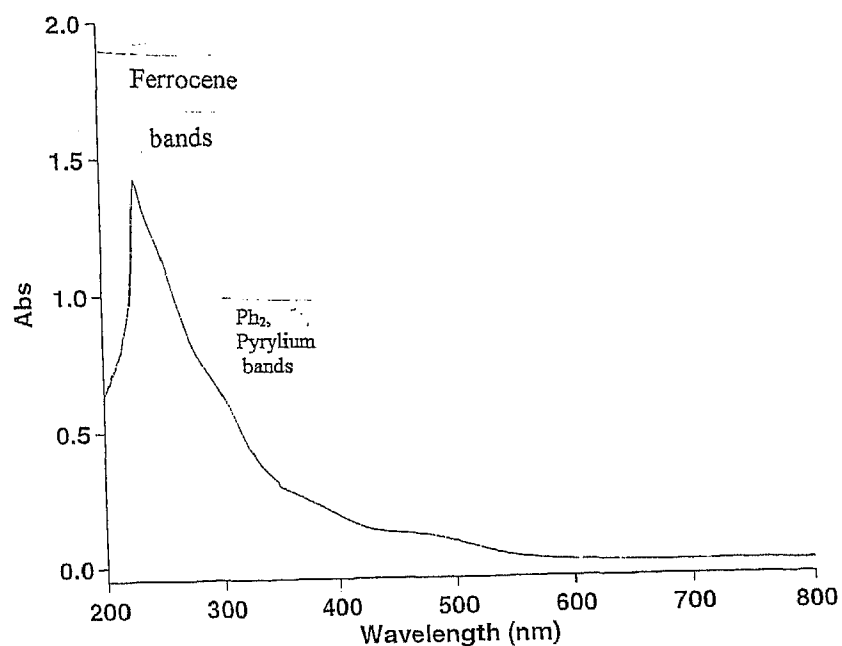


Figure 7: UV-Visible spectrum of [2-ferrocenyl-4, 6-diphenylpyranyl- η^5]tricarbonylmanganese in CH_2Cl_2

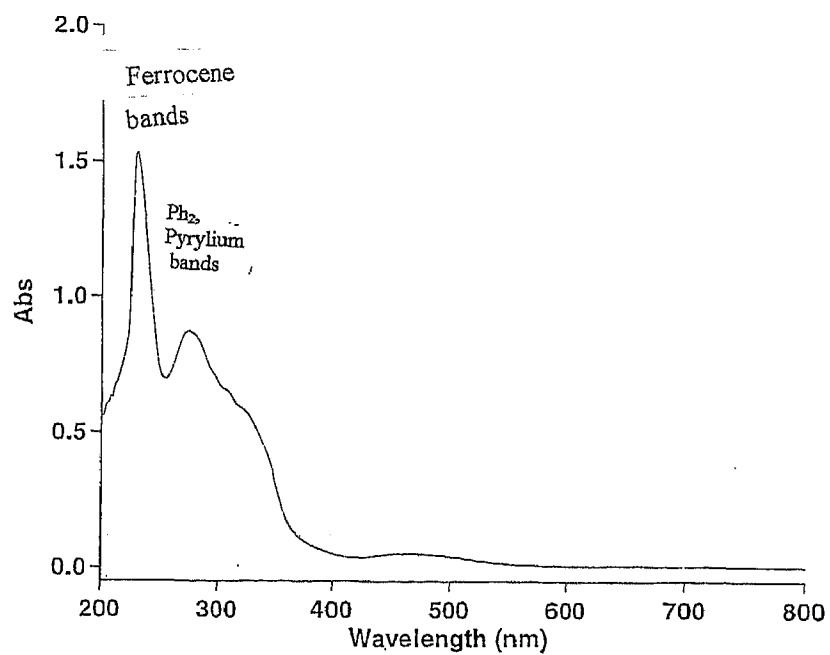


Figure 8: UV-Visible spectrum of 2-ferrocenyl-4, 6-diphenylpyran in CH_2Cl_2

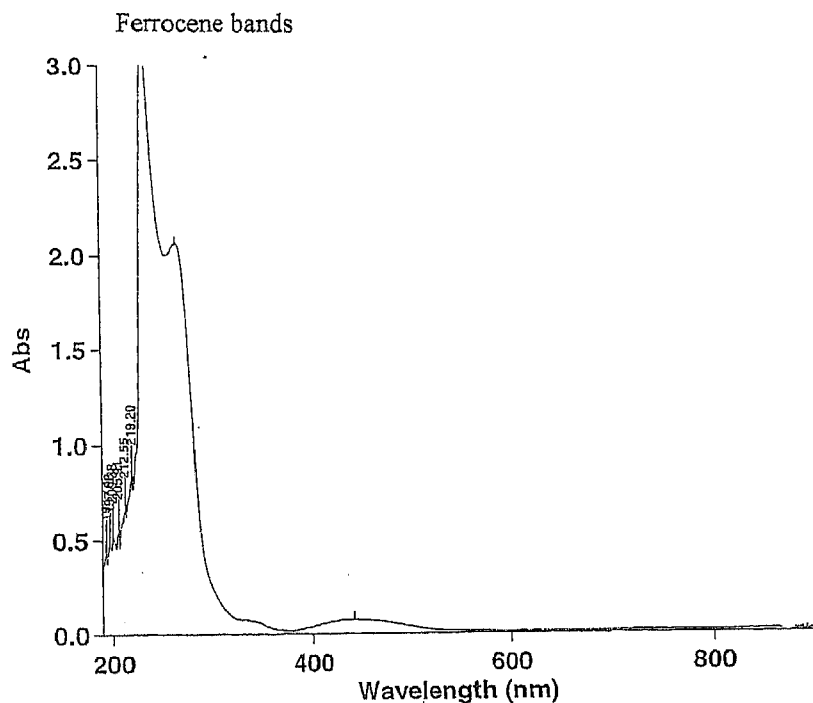
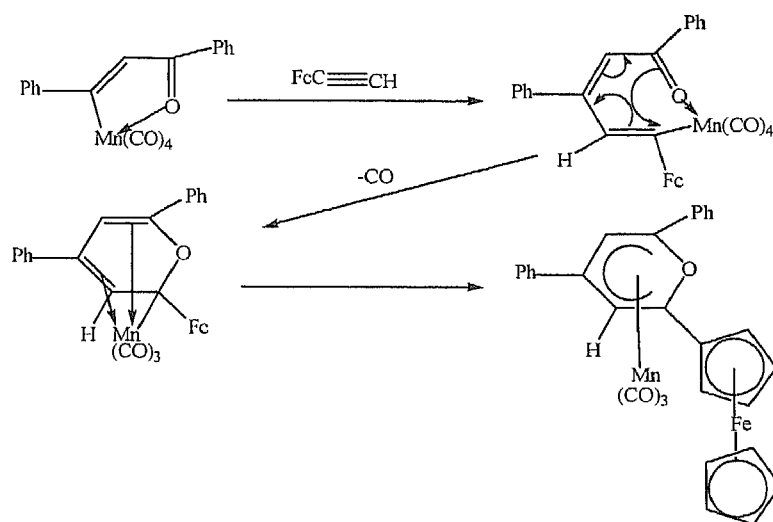


Figure 9: UV-Visible spectrum of ferrocene in CH_2Cl_2

5.3.3 Reactions of the manganated chalcones, (pyranyl) $\text{Mn}(\text{CO})_3$ complex and the pyrylium ions

The red [2-ferrocenyl-4, 6-diphenylpyranyl- η^5 -tricarbonylmanganese] (5-6, Scheme 8) was obtained by reacting [1,3-diphenyl-prop-2-en-3-yl- κC^3 -1-one- κO] tetracarbonylmanganese with ferrocenylethyne in benzene or acetonitrile. A possible route to the formation of 5-6, from the β -manganated 5-4 can be proposed (Scheme 10) as suggested by Booth and Hargreaves¹⁸ and later adapted by Tully^{12,14}. It involves the insertion of the alkyne (ferrocenylethyne), rearrangement of the π system as the enone oxygen bonds across the seven-membered ring to the manganated carbon, followed by coordination of the remaining two π bonds to the metal with expulsion of CO. The bulkier group, in this case the ferrocene finishing on the carbon bonded to the pyranyl O-atom.



Scheme 10: A possible route to the formation of 5-6, from the β -manganated 5-4.

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The red [2-ferrocenyl-4,6-diphenylpyran-5⁺-tricarbonylmanganese] (5-6, Scheme 8), was reacted with iodine in CCl_4 at room temperature. This reaction gave the intense green 2-ferrocenyl-4,6-diphenylpyrylium triiodide (5-7, Scheme 8). The product was identified by its intense green colour¹³. It also gave a very strong ESMS signal in the positive ion mode which corresponded to the 2-ferrocenyl-4,6-diphenylpyrylium ion (section 5.3.2). Clean NMR data for this product could not be obtained as this product failed to crystallize.

Reaction of the 2-ferrocenyl-4,6-diphenylpyrylium triiodide (5-7, Scheme 8) and of the 2-ferrocenyl-4,6-diphenylpyrylium salt (5-5, Scheme 8) with 25% aqueous ammonia gave the yellow¹³ 2-ferrocenyl-4,6-diphenylpyridine (5-9, Scheme 8). The yellow colour was used to identify the product. Full characterization involved HRMS, NMR and elemental analysis (section 5.4). The ^1H NMR signal, a singlet at 6.91 ppm (expected as two singlets) for two protons bonded directly to the pyridine ring was observed and was consistent with that observed for 4-ferrocenyl-2,6-dimethylpyridine¹³.

The green 2-ferrocenyl-4,6-diphenylpyrylium salt (5-5, Scheme 8) was also reacted with zinc in ether at room temperature. This reaction gave a product that could not be fully

characterized. It was expected that the green 2-ferrocenyl-4,6-diphenylpyrylium salt would get reduced to 2-ferrocenyl-4,6-diphenylpyran. However, ESMS studies (section 5.4) did not support this and a good NMR of the product could not be obtained.

The reactions of 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyran- η^5]tricarbonylmanganese in the same way as for [2-ferrocenyl-4,6-diphenylpyran- η^5]tricarbonylmanganese produced identical results in terms of the types of products that were obtained.

5.3.4 The Electrochemistry of the Pyrylium Ions

Electrochemistry of triarylpyrylium salts have been well studied and generally show two cathodic processes associated with reduction firstly to the radical P^\cdot then the anion $P^{\cdot-}$ ^{20,21,26,27,28}. For the unsubstituted triphenylpyrylium these occur at -0.31 and -1.45 V (vs SCE/MeCN). The radical formed from the first reduction can undergo dimerisation reaction, the bipyrene product generating an anodic feature (-0.7 V) on the reverse scan²⁰.

Cations 5-5a and 5-5b show evidence of similar behaviour to their tripyrylium counterparts as shown in figures 10 and 11. The ferrocenyl group is a much better electron donor than phenyl thus we expect it to help stabilize the pyrylium cation making the first reduction process more difficult. For 5-5a (figure 10(a) and 10(b)) this is borne out in results with the first reduction occurring at -0.38 V. A i_a/i_c of 0.7 for this process and a new feature occurring at about 0.7 V on the anodic sweep is consistent with a chemical reaction that may be dimerisation of 5.5a $^\cdot$. The ferrocenyl redox couple occurs at 0.96 V consistent with the attachment of a strongly electron withdrawing group. The effect on redox potentials of the trimethoxybenzene group in 5-5b is minor (figure 11). It would appear however that this group stabilizes the radical species 2b $^\cdot$ with respect to the chemical reaction that generates the feature at 0.7 V, presumably dimerisation to the bipyrene. The process occurring at about 0.1 V is associated with the non-innocent counterion $[\text{FeCl}_4]^-$.

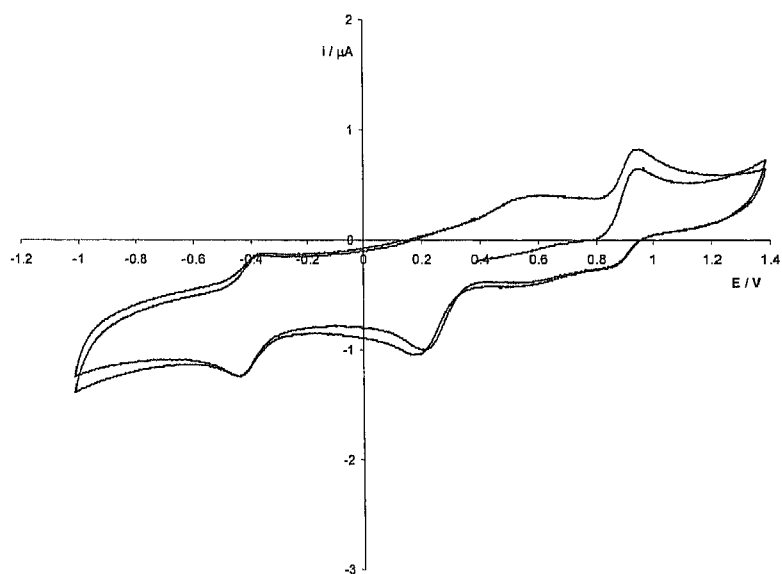


Figure 10(a): CV of Fc-(phenyl)₂-pyrylium salt (A). MeCN/TEAP/Pt/100 mVs⁻¹

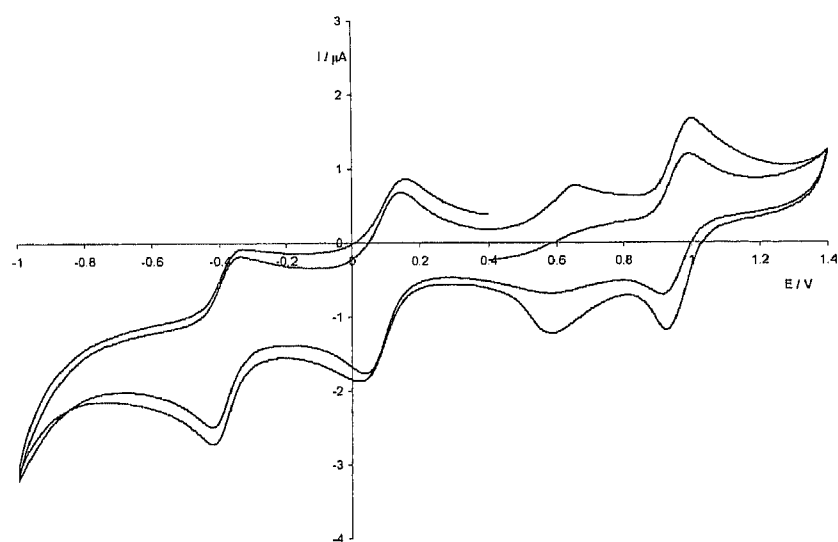


Figure 10(b): CV of Fc-(phenyl)₂-pyrylium salt (A). CH₂Cl₂/TBAPF₆/Pt/100 mVs⁻¹

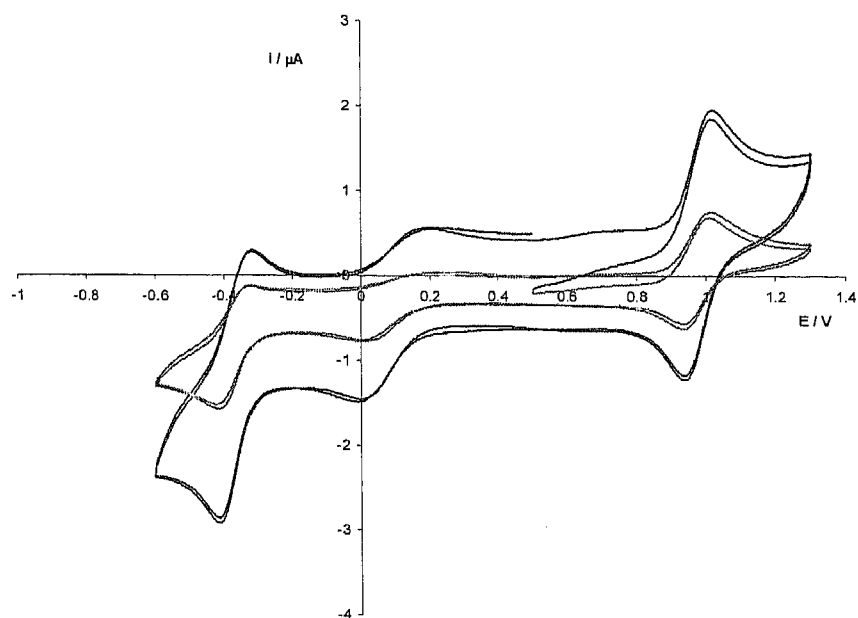


Figure 11: CV of Fc-phenyl-trimethoxybenzene-pyrylium salt (**B**).
 $\text{CH}_2\text{Cl}_2/\text{TBAPF}_6/\text{Pt}/100 \text{ \& } 500 \text{ mVs}^{-1}$

5.3.5 Crystal Data and Structural Refinement Table

5.3.5.1 Crystal data and structure refinement for [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese

Empirical formula	C ₃₀ H ₂₁ FeMnO ₄
Formula weight	556.26
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a= 7.417(2) Å b= 14.716(4) Å β = 94.396(15)° c= 21.750(6) Å
Cell volume	2366.8(12) Å ³
Z	4
Density	1.561 g cm ⁻³
Absorption coefficient	1.183 mm ⁻¹
F(000)	1136
Theta range for data collection	2.75 to 27.50°
Index ranges	-9 ≤ h ≤ 14, -19 ≤ k ≤ 19, -28 ≤ l ≤ 28
Size	1.08 x 0.32 x 0.20 mm
Reflections collected	34245
Independent reflections	5435 (R _{int} = 0.029)

Observed reflections ($I > 2\sigma(I)$)	4871
Completeness to θ 27.5°	99.9%
Tmin/Tmax	0.671 and 1.000
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	5435/0/325
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0254$, $wR_2 = 0.0695$
R indices (all data)	$R_1 = 0.0305$, $wR_2 = 0.0653$
Largest diff. peak and hole	$\pm 0.38 \text{ e } \text{\AA}^{-3}$

5.3.5.2 Tables of selected bond lengths and bond angles of [2-ferrocenyl-4,6-diphenyl- η^5]-pyranyltricarbonylmanganese

Table 3.3.5.2(a) Table of selected bond lengths (\AA) of [2-ferrocenyl-4,6-diphenyl- η^5 -pyranyltricarbonylmanganese]

Mn1 -C1 2.2747(16)	O1 -C1 1.3974(18)
Mn1 -C2 2.1243(16)	O1 -C5 1.4105(18)
Mn1 -C3 2.0949(16)	O6 -C6 1.122(2)
Mn1 -C4 2.0982(16)	O7 -C7 1.137(2)
Mn1 - C5 2.1895(16)	O8 -C8 1.141(2)
Mn1 -C6 1.7669(17)	C1 -C2 1.365(2)
Mn1- C7 1.7843(17)	C2 -C3 1.410(2)
Mn1- C8 1.8152(18)	C3 -C4 1.411(2)
	C4 -C5 1.381(2)
	C1-C11 1.430(2)

Table 3.3.5.2(b): Table of selected bond angles of [2-ferrocenyl-4,6-diphenyl- η^5]-pyranyltricarbonylmanganese

C3-Mn1-C4	39.33(6)	C3-Mn1-C2	39.04(6)	C4-Mn1-C2	68.54(6)
C3-Mn1-C5	68.41(6)	C4-Mn1-C5	66.64(6)	C2-Mn1-C5	76.83(6)
C3-Mn1-C1	66.42(6)	C4-Mn1-C1	75.47(6)	C2-Mn1-C1	35.96(5)
C5-Mn1-C1	59.89(6)	C1-O1-O5	105.14(11)	C2-C1-O2	119.93(13)

5.3.5.3 X-ray crystal structure of [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese]

The dark red crystals were shown to be monoclinic of space group $P2_1/C$ with four molecules in the unit cell. Crystal and structure refinement data are given in the table in section 5.3.5.1. An ORTEP perspective view showing the atom labeling scheme is given in figure 12.

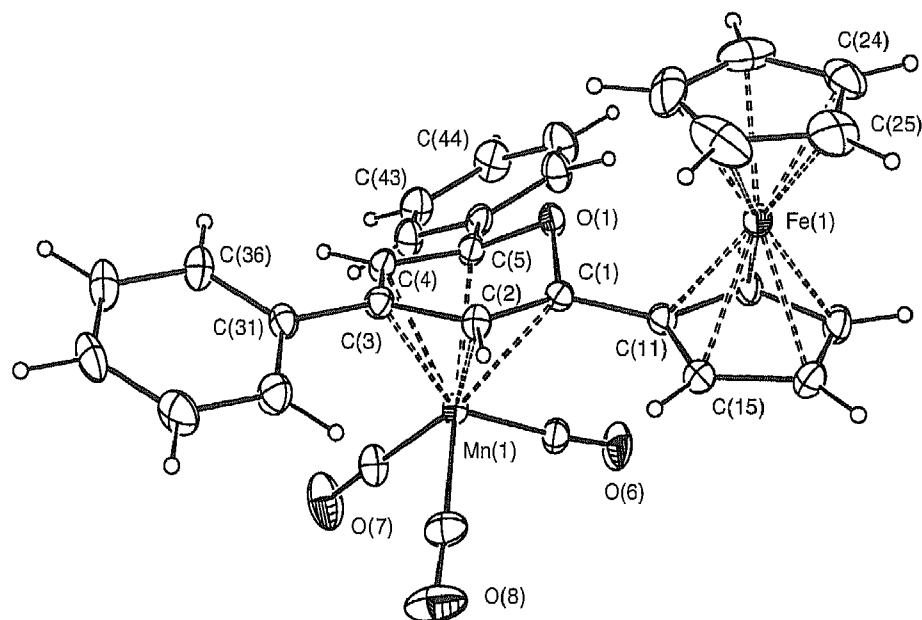


Figure 12: An ORTEP perspective view showing the atom labeling scheme of [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese

The structure shown in figure 13 illustrates the structure of [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese determined by Tully¹⁵ and is an example of a structurally characterized η^5 -pyranyl complex¹⁴ for comparison purposes.

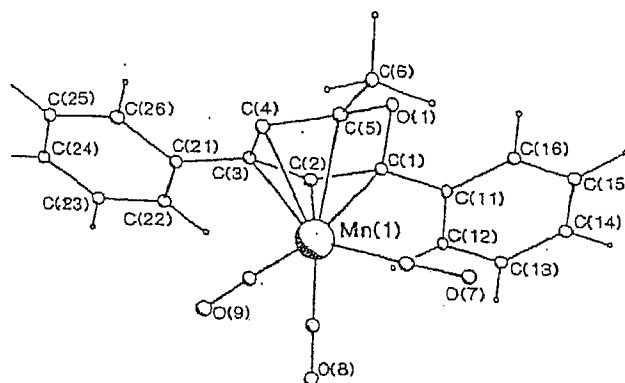


Figure 13: Structure of [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese determined by Tully¹⁵

The molecules consist of a $\text{Mn}(\text{CO})_3$ fragment bonded in η^5 fashion to the five carbon atoms in the pyranyl ring. The $\text{Mn}(\text{CO})_3$ group is tilted so that the plane defined by the three carbonyl-carbon atoms is at an angle of 9.1° to the plane defined by the C(1).....C(5) atoms. This compares closely with the angle of 10.0° for [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese.

The individual Mn-C bond length distances to the pyranyl ring vary from 2.0949(16) [to C(3)] and 2.2747(16) Å [to C(1)] so the coordination is unsymmetrical. For [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonyl-manganese the Mn-C bond lengths are slightly longer, i.e. 2.157(9) (to C(2) and 2.280(9) Å (to C(5)) (figure 9). The ring oxygen atom is displaced from the pyranyl ring, away from the Mn atom so that the plane defined by C(1)-O(1)-C(5) atoms make an angle of 44.54° to that of the rest of the ring. This angle was 47.0° for [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese.

The bond lengths around the pyranyl ring system are not equal with C(3)-C(4) being the largest and C(1)-C(2) being the shortest (as shown in figure 14).

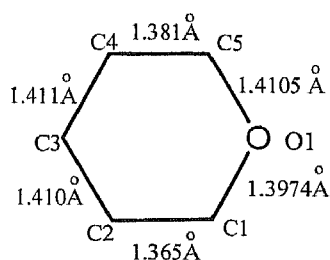


Figure 14:

This diagram (figure 15) corresponds to the resonance form shown in figure 14.

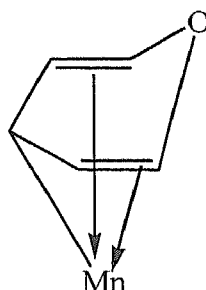


Figure 15

The phenyl groups are also twisted out of the plane of the pyranyl ring. The angle made by the phenyl ring formed by C31 to C36 with the pyranyl ring is 22.50° whereas this angle is 24.75° for the phenyl ring formed by C41 to C46. The Fe(1)-C bond lengths vary between $1.991(2) \text{ \AA}$ to C(22) and $2.0393(18) \text{ \AA}$ to C(24). The average Fe-C bond length for Fe-C (11-15) is 2.028 \AA and for Fe-C (21-25) the average bond length is 2.020 \AA . This compares well with the average Fe-C bond lengths for ferrocene²² which ranges from $2.01(4) \text{ \AA}$ to $2.055(2) \text{ \AA}$ for Fe-C (11-15) and from $2.026(11) \text{ \AA}$ to $2.056(6)$ for Fe-C (21-25) for a range of compounds. The C (1-11) bond length is $1.430(2) \text{ \AA}$, slightly shorter to those reported in an earlier study²⁵ for similar compounds and the ferrocene is bonded at an angle of $10.32^\circ (2)$ to the pyrylium ring.

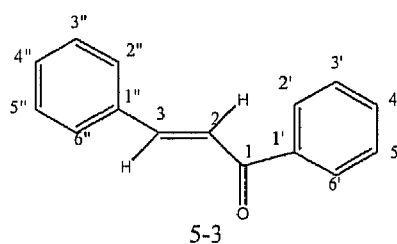
5.4 Experimental

Note: ^1H NMR and ^{13}C NMR spectral assignments of the compounds in this section were made by comparisons with available literature data for closely related compounds. References are noted with each set of NMR data listed for individual compounds.

Spectral and Instrumental methods used in this section are discussed separately in chapter 6.

5.4.1 Example of Preparation of 1,3-diphenylprop-2-en-1-one¹³.

A solution of sodium hydroxide (2.2 g) in water (20 ml) and ethanol (12.5 ml) was stirred in a flask immersed in a bath of crushed ice. The flask was then removed from the crushed ice and placed on a hot plate. Acetophenone (4.98 ml, 5.21 g, 43 mmol) and benzaldehyde (4.40 mls, 4.57 g, 43 mmol) were added successively while maintaining the temperature at 25°C. After stirring for 4 hours at 25°C, the mixture was cooled and left at -8°C overnight. The crude product was filtered, washed with water (until the washings were neutral to litmus) and then washed with a little ethanol (3x2 ml). A single recrystallizaion from ethanol gave 1,3-diphenylprop-2-en-1-one (5-3) (6.98 g, 78%), pure by ^1H NMR and used for manganation without further purification.



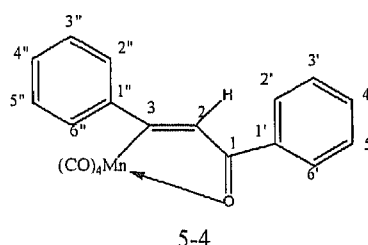
M.p. 55°C

^1H NMR¹⁴: (300 MHz, CDCl_3) δ 8.06 (d, 2H, $J=8.0$ Hz, H2', 6'), 7.82 (d, 1H, $J=15.5$ Hz, H3) 7.55 (m, 3H, H3', 4', 5'), 7.51(d, 1H, $J=15.5$ Hz, H2), 7.45(m, 5H, H2'', 3'', 4'', 5'', 6'')

^{13}C NMR¹⁴: (300 MHz, CDCl_3), δ 190.7 (C1), 139.5 (C3), 138.3 (C1'), 135.0 (C1''), 129.5 (C2', C6'), 129.0 (C5'), 132.9 (C4'), 128.6 (C2), 128.9 (C3'), 126.3 (C2'', C6''), 128.5- 128.9 (3C, C3'', 4'', 5'').

5.4.2 Manganation of 1,3-diphenylprop-2-en-1-one¹²

1,3-diphenylprop-2-en-1-one (200 mg, 0.96 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (330 mg, 1.15 mmol) were refluxed in nitrogen- saturated heptane for 3 hours. The reaction mixture was cooled and the solvent removed under high vacuum. The residue was chromatographed (p.l.c., 1:1 dichloromethane/petroleum spirits) to afford one red band, R_f 0.8. The red band was eluted and the solvent removed to provide pure product, 5-4 as red oil, (304 mg, 84.6 %)



M.p. 145°C

IR¹⁴: (heptane) 2081 (m), 1996(vs), 1934 (s) cm^{-1} .

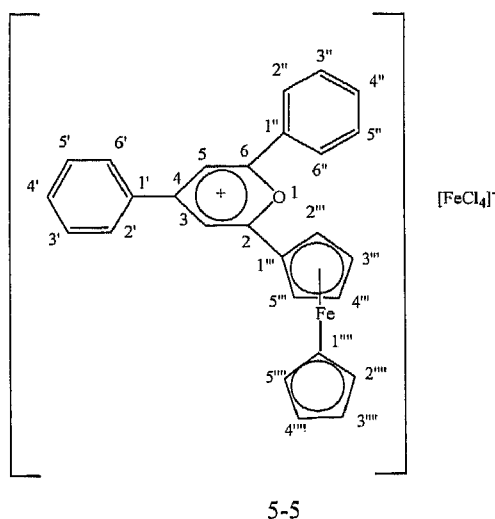
ESMS: (MeOH/NaOMe), (Positive ion) m/z 397 (70% $[\text{M}+\text{Na}]^+$), 771 (65% $[2\text{M}+\text{Na}]^+$)
(Negative ion) m/z 405 (100% $[\text{M}+\text{OMe}]^-$)

^1H NMR¹⁴: (300 MHz, CDCl_3) δ 7.75 (s, 1H, H2), 7.18-8.07 (m, 10H, Ar-H)

^{13}C NMR¹⁴: (300 MHz, CDCl_3) δ 219.0 (CO), 214.0 (CO), 210.3 (CO), 210.0 (CO), 204.7 (C1), 150.4 (C1''), 135.3 (C2), 135.2 (C1'), 133.5 (C4'), 131.8 (C3', C5'), 131.4 (C2', 6'), 130.8 (2C, C3'', 4''), 129.4 (C2'', C6''), 129.2 (5'').

5.4.3 Reaction of (5-4) with ferrocenylethyne in carbon tetrachloride

[1,3-diphenylprop-2-en-3-yl- κC^3 -1-one- κO]tetracarbonylmanganese (5-4) (106 mg, 0.28 mmol) and ferrocenylethyne (119 mg, 0.56 mmol) were refluxed in nitrogen-saturated carbon tetrachloride (30mls) for 1 hour. During this time, the colour of the reaction mixture changed from yellow to green and I.R. showed that all starting (5-4) had completely reacted. On cooling the reaction mixture, the product precipitated. This green precipitate was filtered to give the product as a green powder (82 mg, 47.6%). Clean NMR spectra of the product were not obtained. However, the intense green colour of the product suggested that it was a salt of the 2-ferrocenyl-2,6-diphenyl pyrylium ion (5-5). Similar green coloured ferrocenyl pyrylium salts have been synthesized in an earlier study²³. This was confirmed by the intense ESMS peak in the positive ion mode in methanol corresponding to the 2-ferrocenyl-4,6-diphenylpyrylium ion (figure 1, section 5.3.2). In the negative ion mode, peaks corresponding to $[\text{FeCl}_4]^-$ and $[\text{FeCl}_3]$ were observed. This suggested that the counter anion formed in the reaction was $[\text{FeCl}_4]^-$. The high resolution mass of the 2-ferrocenyl-4,6-diphenylpyrylium ion and the $[\text{FeCl}_4]^-$ was also determined.



HRMS

Calculated for $[\text{C}_{27}\text{H}_{21}\text{OFe}]^+$: 417.0937 $[\text{M}]^+$

Found: 417.0956 $[\text{M}]^+$

HRMS

Calculated for $[\text{FeCl}_4]^-$ 195.8098 $[\text{M}]^-$

Found: 195.8069 $[\text{M}]^-$

HRMS

Calculated for $[\text{FeCl}_3]^-$ 160.8410 $[\text{M}]^-$

Found: 160.8419 $[\text{M}]^-$

Elemental Analysis:

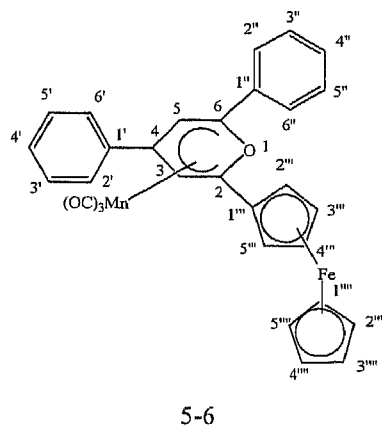
Calculated for $\text{C}_{27}\text{H}_{21}\text{Fe}_2\text{OCl}_4$: C 52.73%, H 3.44%

Found: C 51.34% H 3.93%

5.4.4 Reaction of (5-4) with ferrocenylethyne in benzene

[1,3-diphenylprop-2-en-3-yl- κC^3 -1-one- κO]tetracarbonylmanganese (5-4) (106 mg, 0.28 mmol) and ferrocenylethyne (119 mg, 0.32 mmol) were refluxed in nitrogen-saturated benzene for 2½ hours. During this time the colour of the reaction mixture had changed from yellow to red and I.R. spectra showed that all the starting (5-4) had reacted since the metal carbonyl bands for 5-4 had disappeared. The reaction mixture was cooled and solvent removed under vacuum. The residue, red oil, was chromatographed [p.l.c., dichloromethane/hexane (1:1 v/v)] to afford two major bands, a red band at R_f 0.8 and an orange band at R_f 0.2. Removal of the bands and extraction with dichloromethane followed by solvent removal under vacuum gave 5-6, [2-ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese (from red band at R_f 0.8) as a red oil, (47.0 mg, 29.8 %) and product 5-8, 2-ferrocenyl-4,6-diphenylpyran (from the band at R_f 0.2) as an orange oil

(10.0 mg, 8.4 %). Both products 5-6 and 5-8 were recrystallised by diffusion (ether/pentane) to give red and orange crystals respectively.



M.p. 182°C

IR: (benzene) 2012 (vs), 1951 (m), 1931(m) cm^{-1} .

^1H NMR^{5,14}: (300 MHz, CDCl_3) δ 7.50 (d, 2H, $J = 8.6$ Hz, $\text{H}2''$, $\text{H}6''$), 7.28- 7.58 (m, 8H, Ar-H), 5.72 (s, 1H, $\text{H}3$), 5.71, (s, 1H, $\text{H}5$), 4.80, (dd, $J = 1.6$ Hz, 2H, $\text{H}2'''$, $\text{H}5'''$), 4.43 (dd, $J = 1.6$ Hz, 2H, $\text{H}3'''$, $4'''$), 4.19 (s, 5H, C_5H_5)

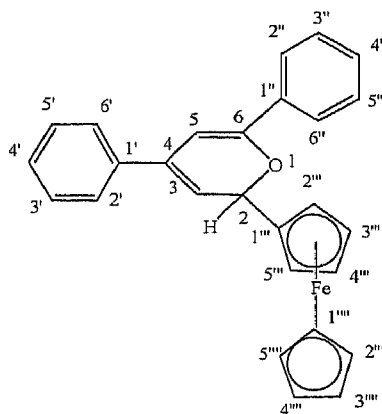
^{13}C NMR^{5,14}: (300 MHz, CDCl_3) δ 137.4 ($\text{C}1'$), 137.0, ($\text{C}1''$), 129.2, ($\text{C}3'$, $5'$), 128.7, ($\text{C}3''$, $\text{C}5''$), 128.5, ($\text{C}4'$), 128.5, ($\text{C}4''$), 127.5, ($\text{C}2'$, $\text{C}6'$), 122.7, ($\text{C}2''$, $6''$), 111.1 ($\text{C}2$), 96.8, ($\text{C}4$), 93.4, ($\text{C}6$), 85.0 ($\text{C}3$), 80.6, ($\text{C}5$), 78.3 ($\text{C}1'''$), 69.9 (C_5H_5), 67.4 (C_5H_4 , $\text{C}2'''$, $5'''$), 64.7 (C_5H_4 , $\text{C}3'''$, $\text{C}4'''$).

Elemental Analysis:

Calculated for $\text{C}_{30}\text{H}_{21}\text{FeMnO}_4$: C 64.78%, H 3.81%

Found : C 64.80% H 3.81%

ESMS: (MeOH), (positive ion) m/z 417 (100%, $[\text{M}-\text{Mn}(\text{CO})_3]^+$)



5-8

ESMS: (MeOH),(positive ion) m/z 418.0 (100%, [M+H]⁺

¹H NMR ^{5,12,24}: (300 MHz, CDCl₃) 7.86 (d, 1H, H3, J=21.0 Hz), δ 7.32 (m, 10H, all Ar-H), 6.78 (s, 1H, H5), 6.20 (d, 1H, H2, J= 21.0 Hz), 4.75 (dd, 2x 1H, H2''', H5'''), 4.71 (dd, 2x 1H, H3''', H4''), 4.11 (s, 5x 1H, C₅H₅),

¹³C NMR ^{5,12,24}: (300 MHz, CDCl₃), δ 151.3 (C6), 148.3 (C1'), 142.3 (C4), 123.6 (C3) 120.5 (C5), 77.0 (C2), 120.0-128.0 (all Ar-C), 69.6 (C₅H₅), 69.2 (C₅H₄), 66.7 (C₅H₄), 66.9 (C₅H₄).

Elemental Analysis

Calculated for C₂₇H₂₂OFe: C 77.52% H 5.30%

Found : C 76.83% H 5.32%

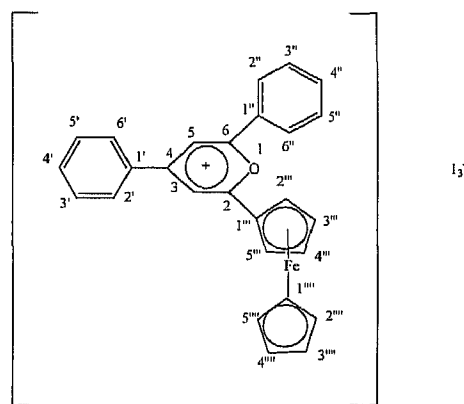
HRMS

Calculated for C₂₇H₂₂OFe: 418.1220 [M]⁺

Found: 418.1253 [M]⁺

5.4.5 Preparation of 2-ferrocenyl-4,6-diphenylpyrylium triiodide

[2-Ferrocenyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese (5-6) (50 mg, 0.090 mmol) and iodine (46 mg, 0.36 mmol) were stirred in nitrogen-saturated carbon tetrachloride for 1 hour. The colour of the reaction mixture changed from yellow to green and I.R. spectra showed that all 5-6 had reacted (disappearance of the metal carbonyl bands). The carbon tetrachloride was removed from the reaction mixture under vacuum to leave green solid (40 mg, 55.8 %). Attempts were made to crystallize the product by the solvent diffusion method using acetonitrile and ether. However, no crystals formed. Clean NMR of the product could not be obtained. The identity of the product was determined by its ESMS signal in the positive ion mode and cone voltage +20V corresponding to the 2-ferrocenyl-4,6-diphenyl pyrylium ion (figure 1). In the same way as for compound 5-5, the pyridine derivative of 5-7 was prepared and characterized to confirm its identity.



5-7

ESMS: (MeOH),(positive ion) m/z 417.0 (100%, $[M]^+$)

ESMS: (MeOH),(negative ion) m/z 380.2 (100% I_3^-)

5.4.6 Reaction of the pyrylium salt, $C_{27}H_{21}Fe_2OCl_4$, (5-5) with zinc in ether

2-Ferrocenyl-4,6-diphenylpyrylium salt, $C_{27}H_{21}Fe_2OCl_4$, (5-5) (50 mg, 0.06 mmol) and zinc (4.1 mg, 0.06 mmol) were stirred in nitrogen-saturated diethyl ether overnight. During this time the reaction mixture turned from green to red. The solid that had formed was filtered and the ether removed under vacuum to give red oil. The residual red oil was chromatographed (p.l.c., dichloromethane/hexane, 1:1) to give one major red band at R_f 0.2. Removal of the band and extraction with dichloromethane gave red oil. This product however did not form any crystals and a clean NMR of the product could not be obtained. However, The HRMS values for the product are listed below. The values show that the product has one additional oxygen atom when compared to 2-ferrocenyl-4,6-diphenylpyranylpyran (5-8). Note that the anion used here and in section 5.4.7 is $FeCl_4^-$.

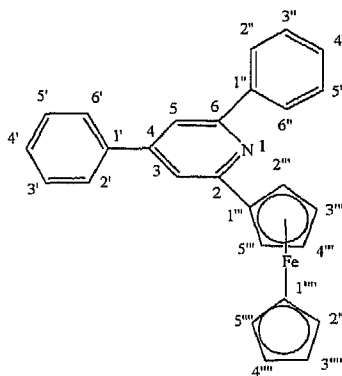
HRMS

Calculated for $C_{27}H_{22}O_2Fe_1Na_1$: 457.0861 $[M+Na]^+$

Found: 457.0819 $[M+Na]^+$

5.4.7 Reaction of 2-Ferrocenyl-4,6-diphenylpyrylium salt, $C_{27}H_{21}Fe_2OCl_4$, (5-5) with ammonia

2-Ferrocenyl-4,6-diphenylpyrylium salt, $C_{27}H_{21}Fe_2OCl_4$, (5-5) (40 mg, 0.05 mmol) was treated with a few drops of 30% ammonia²³ in a small round-bottom flask for 1 hour. Note that the ammonia was added directly to the salt and no solvent was used for the reaction. The resulting residue was chromatographed (p.l.c, 1:2 ethyl acetate/hexane) to afford one major yellow band at R_f 0.8. Removal of the band and extraction with dichloromethane gave 5-9 as yellow oil (12 mg, 44 %). Attempts to recrystallise the yellow oil did not produce any crystals.



5-9

ESMS: (MeOH),(positive ion) m/z 416.5 (100%, $[M+H]^+$)

^1H NMR^{5,14}: (300 MHz, CDCl_3) δ 7.28- 8.21 (m, 10H, all Ar-H), 6.91 (s, 2H, H3, H5), 5.10 (dd, 2H, J= 2.4 Hz, H2''', H5'''), 4.45 (dd, 2H, J=2.4 Hz, H3''', H4'''), 4.11 (s, 5H, C_5H_5). Note that the resonances for H3 and H5 were not confirmed.

^{13}C NMR^{5,14}: (300 MHz, CDCl_3) δ 127.0-130.0 (10C, all Ar-C), 159.5 (C6), 149.2 (C4), 139.8 (C1'), 139.3 (C2), 139.1 (C1''), 116.5 (C3), 115.6 (C5), 84.0 (C1'''), 69.9 (C2''', C5'''), 69.7 (C_5H_5), 67.1 (C3''', C4''').

H.R.M.S

Calculated for $\text{C}_{27}\text{H}_{21}\text{NFe}$: 415.1018 $[M]^+$

Found : 415.1047 $[M]^+$

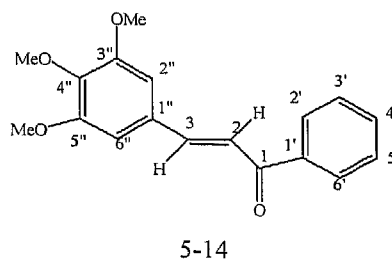
Calculated for $\text{C}_{27}\text{H}_{22}\text{NFe}$: 416.1104 $[M+H]^+$

Found : 416.1096 $[M+H]^+$

Calculated for $\text{C}_{27}\text{H}_{21}\text{NFeNa}$: 438.0916 $[M+\text{Na}]^+$

Found : 438.0953 $[M+\text{Na}]^+$

Note: 1-phenyl-3-(3, 4, 5-trimethoxyphenyl)prop-2-en-1-one was made available for use from an earlier study¹⁴. The purity was determined by NMR before it was used for further reactions.



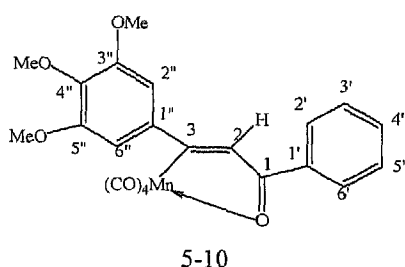
M.p. 68°C

¹H NMR¹⁴: (300 MHz, CDCl₃) δ 8.06 (d, 2H, J=8.0 Hz, H2', 6'), 8.03 (d, 1H, J=15.5 Hz, H3) 7.55 (m, 3H, H3', 4', 5'), 7.61(d, 1H, J=15.5 Hz, H2), 7.76 (s, 2H, H2'', 6''), 3.91 (s, 3H, OMe), 3.92(s, 6H, 2 x OMe)

¹³C NMR¹²: (300 MHz, CDCl₃) δ 190.6 (C1), 145.0 (C3), 138.3 (C1'), 132.7 (C1''), 130.4 (C2', C6'), 130.4 (C5'), 140.5 (C4'), 128.6 (C2), 128.9 (C3'), 126.3 (C2'', C6''), 128.5- 128.9 (3C, C3'', 4'', 5'').

5.4.8 Mangnation of 1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-ene-1-one

1-Phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (5-14) (200 mg, 0.96 mmol) and PhCH₂Mn(CO)₅ (200 mg, 0.67 mmol) were refluxed in nitrogen-saturated heptane for 3 hours. The reaction mixture was cooled and the solvent removed under vacuum. The residue was chromatograhed (p.l.c., 1:1 dichloromethane/petroleum spirits) to afford one red band, R_f 0.8. The band was eluted and the solvent removed to provide pure product (as seen by NMR), 5-10 as red oil, (113 mg, 36%)



M.p. 195°C

I.R. (heptane) 2081 (m), 1996(vs), 1934 (s) cm^{-1}

ESMS: (MeOH/NaOMe, CV +20V) m/z 487 (70% $[\text{M}+\text{Na}]^+$), 951 (65% $[2\text{M}+\text{Na}]^+$)
(MeOH/NaOMe, Cone -20V) m/z (495 ($\text{M}+\text{OMe}$) $^-$)

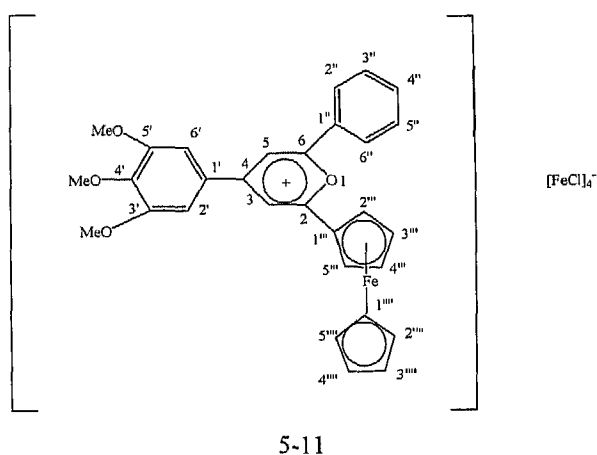
^1H NMR^{5,14}: (300 MHz, CDCl_3) δ 7.75 (s, 1H, H2), 7.18- 8.07 (m, 7H, Ar-H), 4.00 (s, 3H, OMe), 3.97 (s, 6H, 2 x OMe)

^{13}C NMR^{5,14}: (300 MHz, CDCl_3) δ 214.0 (CO), 210.3 (CO), 210.0 (CO), 204.6 (C1), 152.9 (C1''), 141.9-145.6 (3C, C3'', 4'', 5''), 135.3 (C2), 133.5 (C1'), 131.4 (C5'), 130.9 (C2', 6'), 129.3 (C2'', C6''), 128.8 (C3'), 128.3 (C4') 56.3 (OMe), 61.0 (2x OMe).

5.4.0 Reaction of (5-10) with ferrocenylethyne in carbon tetrachloride

5-10 (106 mg, 0.28 mmol) and ferrocenylethyne (119 mg, 0.57 mmol) were refluxed in nitrogen-saturated carbon tetrachloride for 1 hour. During this time, the colour of the reaction mixture changed from yellow to green and I.R. monitoring showed that all the starting (5-10) had reacted. On cooling the reaction mixture, the product precipitated as a green powder. This was filtered to give the product as a green powder (0.087g, 51.3 %). The purity of the product could not be determined as clean NMR spectra of the product

were not obtained. The product was identified as 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium ion (5-11) in the same way as the 2-ferrocenyl-4,6-diphenylpyrylium ion. The pyridine derivative of this pyrylium salt were also prepared and characterized to confirm the identity of 5-11. In the negative ion mode, a peak corresponding to $[\text{FeCl}_4]^-$ was observed. This suggested that the counter anion formed in the reaction was $[\text{FeCl}_4]^-$.



HRMS

Calculated for $[\text{C}_{30}\text{H}_{27}\text{O}_4\text{Fe}]^+$: 507.1254 $[\text{M}]^+$

Found: 507.1289 $[\text{M}]^+$

HRMS

Calculated for $[\text{FeCl}_4]^-$: 195.8098 $[\text{M}]^-$

Found: 195.8131 $[\text{M}]^-$

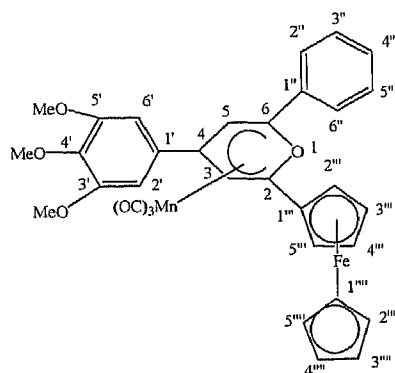
HRMS

Calculated for $[\text{FeCl}_3]^-$: 160.8410 $[\text{M}]^-$

Found: 160.8411 $[\text{M}]^-$

5.4.11 Reaction of (5-10) with ferrocenylethyne in benzene

5-10 (120 mg, 0.23 mmol) and ferrocenylethyne (65 mg, 0.31 mmol) were refluxed in nitrogen-saturated benzene for 2½ hours. During this time the colour of the reaction mixture had changed from yellow to red and I.R. monitoring showed that all the starting $\text{Mn}(\text{CO})_4$ had reacted. The reaction mixture was cooled and solvent removed under vacuum. The residue was chromatographed (p.l.c., 1:1 CH_2Cl_2 /hexane) to afford two major bands, a red band at R_f 0.8 and an orange band at R_f 0.2. Removal of the bands and extraction with dichloromethane followed by solvent removal under vacuum gave 5-12 as red oil (56 mg, 39.8 %) and product 5-13 as orange oil (31 mg, 28 %). Both products 5-12 and 5-13 were recrystallised by diffusion (ether/pentane) to give red and orange crystals respectively.



5-12

IR: (benzene) 2012 (vs), 1951 (m), 1931(m) cm^{-1} .

¹H NMR^{5,12,16}: (300 MHz, CDCl₃) δ 7.50 (d, 2x 1H, J= 8.6 Hz, H2'', H6''), 7.28- 7.58 (m, 5H, Ar-H), 7.13 (s, 2H, H2', 6'), 5.63 (s, 1H, H3), 5.32 (s, 1H, H5), (4.80, dd, J=

1.6Hz, 2H, H2''', H5'''), 4.43 (dd, J= 1.6Hz, 2H, C3''',4'''), 4.19 (s, 5H, C₅H₅), 4.03 (s, 3H, 4'OMe), 3.97 (s, 6H, 3', 5' OMe)

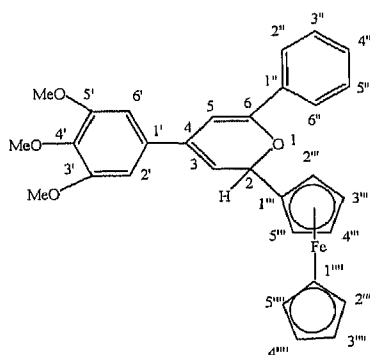
¹³C NMR^{5,12,16}: (300 MHz, CDCl₃) δ 142.3 (C1'), 137.0 (C1''), 131.3 (C3', 5'), 128.9 (C3'', C5''), 128.6 (C4'), 127.5 (C2'), 126.5 (C2', C6'), 123.0 (C2'', 6''), 110.7(C2), 96.8 (C4), 93.4 (C6), 85.0 (C3), 80.9 (C5), 78.2 (C1'''), 69.9 (C₅H₅), 97.8 (C1'''), 67.4 (C₅H₄), 64.7 (C₅H₄), 56.5 (OMe), 60.4 (2x OMe).

ESMS: (MeOH), (positive ion) m/z 507 (100%, [M-Mn(CO)₃]⁺)

Elemental Analysis

Calculated for C₃₃H₂₇O₇Fe₁Mn₁ C 60.39 H 4.15%

Found : C 60.41 H 4.20%



5-13

ESMS: (MeOH), (positive ion) m/z 509.6 (100%, [M+H]⁺)

¹H NMR^{5,12,16}: (300 MHz, CDCl₃) δ 7.32 (m, 5H, Ar-H), 7.12 (d, 1H, H3, J= 21.0Hz), 6.74 (s, 1H, H5), 6.68 (s, 2H, H2'', 6''), 6.10 (d, 1H, H2, J=21.0 Hz), 4.80 (dd, 2x 1H,

H2''', H5'''), 4.45 (dd, 2x 1H. H3''', H4'''), 4.27 (s, 5x 1H, (C₅H₅), 3.94 (s, 3H, OMe), 3.85 (s, 6H, 2 x OMe)

¹³C NMR^{5,12,16}: (300 MHz, CDCl₃), δ 153.7 (C6), 151.3 (C1'), 148.4 (C4), 123.6 (C3), 120.6 (C5), 77.4 (C2), 120.0-128.0 (all Ar-C), 69.6, (C₅H₅), 66.2 (C₅H₄) 66.7 (C₅H₄), , 66.9 (C₅H₄), 56.2 (OMe), 60.9 (2x OMe).

Elemental Analysis

Calculated for C₃₀H₂₈O₄Fe₁: C 70.88% H 5.55%

Found : C 70.29% H 6.81%

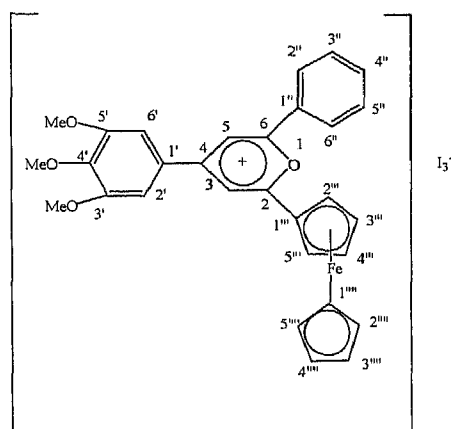
HRMS

Calculated for C₂₀H₂₈O₆Fe₁: 508.1332 [M]⁺

Found: 508.1368 [M]⁺

5.4.12 Preparation of 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium triiodide

[2-Ferrocenyl-3-(3,4,5 trimethoxyphenyl)-6-phenylpyran-yl-η⁵] tricarbonyl-manganese (5-12) (50 mg, 0.90 mmol) and iodine (46 mg, 0.36 mmol) were stirred in nitrogen-saturated carbon tetrachloride for 1 hour. The colour of the reaction mixture changed green and the I.R. showed that all starting Mn(CO)₃ had reacted. The carbon tetrachloride was removed from the reaction mixture under vacuum to leave a green solid (38 mg, 55.4 %). Attempts were made to recrystallize the product by the solvent diffusion method using acetonitrile and ether. However, no crystals formed. Clean NMR of the product could not be obtained. The identity of the product was determined by the intense ESMS signal in the positive ion mode and cone voltage +20V corresponding to 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium ion (figure 5-14). The pyridine and the pyran derivatives of the triiodide were also prepared and characterized to confirm the identity of 5-14.



5-14

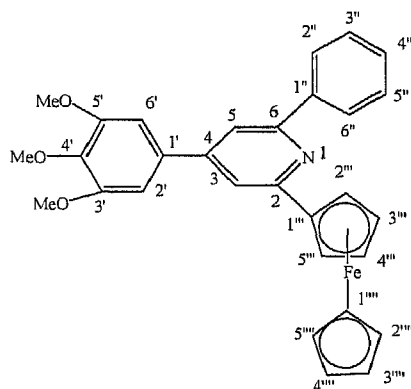
ESMS: (MeOH),(positive ion) m/z 507.0 (100%, $[M]^+$)

ESMS: (MeOH),(negative ion) m/z 380.2 (100% I_3^-)

:

5.4.13 Reaction of the pyrylium salt, $C_{30}H_{27}OFe_2Cl_4$, (5-11) with ammonia

2-Ferrocenyl-4-(3,4,5 trimethoxyphenyl)-6-phenylpyrylium salt, $C_{30}H_{27}OFe_2Cl_4$, (5-11) (50 mg, 0.06 mmol) was treated with a few drops of 30% ammonia in a small round bottom flask. Note that the ammonia was added directly to the salt and no solvent was used for the reaction. The resulting residue was chromatographed (p.l.c, 1:2 ethylacetate/hexane) to afford one major yellow band at R_f 0.8. Removal of the band and extraction with dichloromethane gave 5-15, yellow oil (19 mg, 49.7 %). The yellow oil was recrystallised by diffusion (dichloromethane/pentane) to give yellow crystals.



5-15

ESMS: (MeOH), (positive ion) m/z 506.6 (100%, $[M+H]^+$)

^1H NMR 5,12,16 : (300 MHz, CDCl_3) δ 7.28- 8.21 (m, 10H, all Ar-H), 6.91 (s, 2x 1H, H3, H5), 5.10 (dd, 2x 1H, $J = 2.4$ Hz, H2''', H5'''), 4.45 (dd, 2x 1H, $J = 2.4$ Hz, H3''', H4'''), 4.11 (s, 5x 1H, C_5H_5), 4.00 (s, 3H, OMe), 3.97 (s, 6H, 2 x OMe).

^{13}C NMR 5,12,16 : (300 MHz, CDCl_3) δ 127.0- 130.0 (10C, Ar-C), 157.0, (C6), 153.8 (C4), 139.8 (C1'), 139.6 (C2), 139.1 (C1''), 116.5 (C3), 115.6 (C5), 84.0 (C1'''), 69.9 (C2''', C5'''), 69.7 (C_5H_5), 67.1 (C3''', C4'''), 56.5 (OMe), 60.4 (2x OMe).

Elemental Analysis

Calculated for $\text{C}_{30}\text{H}_{27}\text{NFeO}_3$	C 71.30%	H 5.38%	N 2.77%
Found :	C 70.79%	H 5.71%	N 2.77%

Calculated for $\text{C}_{30}\text{H}_{27}\text{NFeO}_3$:	506.1445 $[M+H]^+$
Found :	506.1413 $[M+H]^+$

5.5 Conclusion

A new synthesis of ferrocenyl-substituted pyrylium salts has been established, which shows more ready variation of substituents than the previous routes [3]. It also avoids the strongly acid conditions used in the usual syntheses [1] which may be an advantage for some substituents. By varying the solvent, intermediate species can be isolated. The ferrocenyl-pyrylium cations incorporate both the reducible and the oxidisable centre and both redox processes are clearly seen in electrochemical measurements. The UV-visible spectra shows a broad band at *ca* 680 nm which arises from an internal charge transfer from the ferrocenyl moiety to the pyrylium ring.

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Chapter 6. General Experimental Procedures and Preparation of Precursors

6.1 General Experimental Techniques

Most reactions in the current study were carried out under inert atmosphere of oxygen free nitrogen. This was essential as most compounds, especially the cyclomanganated ones and most coupling products were moisture and oxygen sensitive. Standard Schlenk line techniques were used for the handling and reaction of such compounds¹.

Silicon and petroleum oil baths were used for most reactions requiring constant heating.

Melting point determinations were carried out on a Reichert Thermovar apparatus.

All elemental analysis of the compounds in the current study was performed at the microanalytical laboratory based at the University of Otago, Dunedin.

6.1.1 Chromatography

Preparative layer chromatography (PLC) plates were prepared by mixing silica gel (Merck Kieselgel 60PF₂₅₄) with twice its weight of distilled water. The resulting slurry was spread onto 20 x 20 cm glass plates to a depth of 1- 1.5 mm and allowed to air dry prior to activation at 100°C. The mixture to be separated was applied as a CH₂Cl₂ solution by pipette as a thin line near the base of the plate. The plates were developed in tanks containing the required solvent mixture. Coloureless bands were identified using UV light. Bands to be collected were removed from the plates and the products eluted from silica with CH₂Cl₂ or Et₂O or both used one after the other.

Column chromatography was used for some separations, for example, when alumina was required. Packing material BDH alumina oxide (Brockman Grade, activity II) was slowly poured into a column with the required solvent. The column was previously fitted with a cotton wool plug below a 5 mm layer of acid washed sand. Mixtures to be separated were added as solutions, and allowed to run into the column before developing. Where

mixtures were insoluble in the chromatography solvent, they were dissolved in CH_2Cl_2 and adsorbed onto 2-4 g of alumina. CH_2Cl_2 was removed under vacuum, with the adsorbed material transferred to the column and developed. Bands were collected according to colour.

6.1.2 Chemicals

Unless mentioned below, chemicals were used as received.

Solvents were generally purified prior to use to remove oxygen and water, by distillation over a drying agent under nitrogen atmosphere (Table 6-1).

Table 6-1 Purification of general solvents

Solvent	Purification (in nitrogen atmosphere)
Acetonitrile	Distilled from CaH_2
Benzene	Distilled from sodium
Carbon tetrachloride	
Diethylether	Distilled from sodium/benzophenone
Dichloromethane	Distilled from CaH_2
Heptane	Distilled from CaH_2
Hexane	Distilled from CaH_2
Petroleum Spirits (60-80° fraction)	Distilled from CaH_2
Tetrahydrofuran	Distilled from sodium/benzophenone

Note: In the later stages of the research, diethylether, dichloromethane, THF and hexane were purified by the solvent purification system purchased the Chemistry department towards the middle of 2007.

6.2. Instrumental Techniques

6.2.1 Infrared spectroscopy

Infrared spectroscopy was carried out on a Bio-Rad Digilab Division FTS-40 FTIR, using Bio-Rad Win-IR Ver. 4.4 software.

Solution spectra were obtained using a solution cell 0.1 mm path length and KBr windows.

Observations were made of the metal carbonyl region (1800- 2400 cm^{-1}). Chemical information was obtained from the number, pattern, intensity and position of the peaks in the region.

In the instances where organic products were prepared, observations were made between 1800-1600 cm^{-1} , the region where the C=O stretch would be expected.

6.2.2 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy was performed using either a brucker Avance DRX 300 and Avance DRX 400 spectrometer XWIN-NMR software V. 3.0 or V. 3.1 respectively. This software was later changed to Topspin.

Deuterated chloroform was used as the solvent with ^1H NMR and ^{13}C NMR spectra referenced to TMS (Me_4Si).

6.2.3 *Mass spectroscopy*

6.2.3.1 ESMS

Electrospray mass spectra was obtained on a Fisons Instruments VG Platform II using MassLynx V. 2.0 software. Analyses were conducted over a range of cone voltages in both positive and negative modes.

Methanol was used as the mobile phase. Approximately 1 mg of the compound was dissolved in 0.5 ml of methanol (the mobile phase), then immediately injected in the machine. For most samples, a few drops of a methanol solution of NaOMe was added to the sample, as an ionization aid².

Volatile, thermally stable compounds, especially for the cascade products in Chapter 3, were also analysed by coupled gas chromatography/mass spectroscopy (EI-GCMS). Electron impact mass spectra were collected on a Hewlett- Packard 5970 mass selective detector coupled to a HP 5890A gas chromatograph. Spectra were processed and analysed using HP enhanced Chemstation 61701 AA V. A. 03.00 software.

Compounds were dissolved in CH₂Cl₂ for direct injection analysis by GC/MS.

6.2.3.2 High resolution Mass Spectroscopy (MicroTOF)

The MicroTOF required calibration every time it was to be used. Sodium formate was used for calibration. The calibration range was dependant on the expected masses of the products in the samples.

The rate of flow of the mobile phase was set at 180 μ L/ h. The pump however could be fast-forwarded to speed up the sample initially to the detector.

In almost all the cases, methanol was used as the mobile phase for the analysis of the samples in this study. Samples were prepared by dissolving as little as about 1 mg of the

product in about 1.0 mL of methanol. Unlike sample preparation for ESMS, samples for MicroTOF analysis had to be very dilute.

The following steps were followed for running a sample for data analysis.

1. The sample details were entered into the sample information window.
2. When sample spectra had stabilized on the screen, the spectra/data acquisition was started by clicking on the green acquire arrow
3. Acquisition was done for about 0.5 m
4. The acquisition was then stopped followed by stopping the syringe pump

For data analysis, the following steps were involved

1. The data analysis window was opened
2. Individual users opened their own files
3. A trace appeared and a right drag was made through the trace
4. Right clicked in the MS window and copied to compound mass spectra.

6.2.4 X-ray crystallography

Preliminary investigations were undertaken by precession photography using Nickel-filtered Cu- $K\alpha$ X-ray radiation. This gave an indication of crystal quality, and allowed the determination of space group and unit cell dimensions.

For full crystal structure determination, intensity data sets were collected by University of Canterbury or University of Auckland. Both the Universities are equipped with a Siemens SMART CCD diffractometer. Structure solution and refinement was carried out using the SHELX program³, running under the WINGX⁴ suite of program.

Complete tables of bond lengths, bond angles, final position parameters and thermal parameters are presented on CD (inside back cover) in the form of the CIF files. The program Mercury⁵ can be used to view the structures.

6.3 Preparation of Reaction Precursors

Most of the preparations in the study were found in the literature. In general, the published methods were altered for reasons of convenience or scale.

Those preparations that are not referenced are syntheses based on similar preparations in the literature. The purity of all compounds was confirmed using NMR.

6.3.1 Preparation of benzylmanganesepentacarbonyl⁶

An amalgam of mercury (5 mL) and sodium (0.7 g) was prepared in a Schlenk flask (100 mL) under nitrogen. To the Schlenk flask was added THF (60 mL) followed by $\text{Mn}_2(\text{CO})_{10}$ (2 g, 5.1 mmol), and the solution was stirred vigorously for 2 hours. The pale grey/green solution was decanted under nitrogen into a second Schlenk flask containing benzyl bromide (1.1 mL). The solution was stirred for a further 10 minutes, then run through a short silica column, and washed through with THF (2x 10 mL). The solvent was removed from the pale yellow solution under reduced pressure. The resulting yellow oil was sublimed using a cold finger (0.5 mm Hg, 50 °C), affording pale yellow crystals of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (2.3 g, 78%, $\nu(\text{CO})$ (dichloromethane) 2108(m), 2011(vs, br), 1990(s, br) cm^{-1}).

Alternatively, after stirring the solution for a further 10 minutes, the solution was transferred to a 500 mL round bottom flask and the solvent removed under vacuum (rotary evaporator). The residue was then extracted with hexane three times and the solution transferred to a second 500 mL round bottom flask. The hexane was then removed under vacuum and the resulting yellow oil was sublimed as above to give pale yellow crystals in equally good yields.

6.3.2 Preparation of cyclomanganated precursors

A ratio of 1:1.2 of the compound to be cyclomanganated and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ was transferred to a Shlenk flask containing the reaction solvent (heptane or hexane unless stated) and refluxed under nitrogen. The ratio was changed to 1:2 or more where two or more possible manganation sites were possible on the compound to be cyclomanganated. The progress of the reaction was monitored by observation of the carbonyl region of the infrared spectrum, and the reaction was deemed complete with the disappearance of the 2108 cm^{-1} peak (of $\text{PhCH}_2\text{Mn}(\text{CO})_5$).

The hot reaction mixture was transferred to a 100 mL round bottom flask and the solvent removed under vacuum (rotary evaporator). The residue was plated (PLC) to isolate the major product(s). Attempts were made to crystallize the products, however, when this failed (as was the case in most instances), the oil was characterized and used for further reactions.

The IR spectra of compounds prepared in the current study were compared to the IR values of similar compounds found in literature. Purity was confirmed by NMR spectroscopy.

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