Preparation and Reactions of Some Organic Derivatives of Manganese Carbonyl Compounds

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of the requirements of the Degree of
Doctor of Philosophy in Chemistry
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by

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Abstract

New orthomanganated aryl ketones of type 1 (Figure 1) have been prepared, including some in which the donor ketone carbonyl group is incorporated into a fused ring. Analogous derivatives of benzoates and heteroaromatic carboxylic acid esters are also described, together with several orthorheniated compounds. Single crystal X-ray structure determinations of η^2-5-(1,4-benzopyronyl)tetracarbonylmanganese **(13)** and η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium **(32)** are reported.

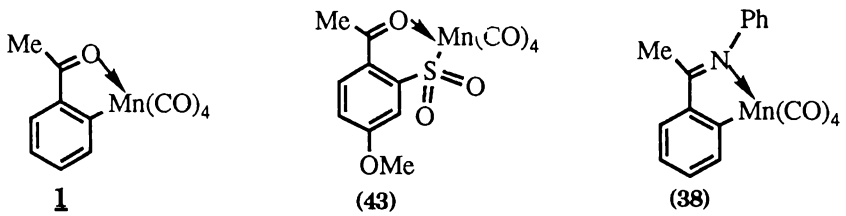


Figure 1

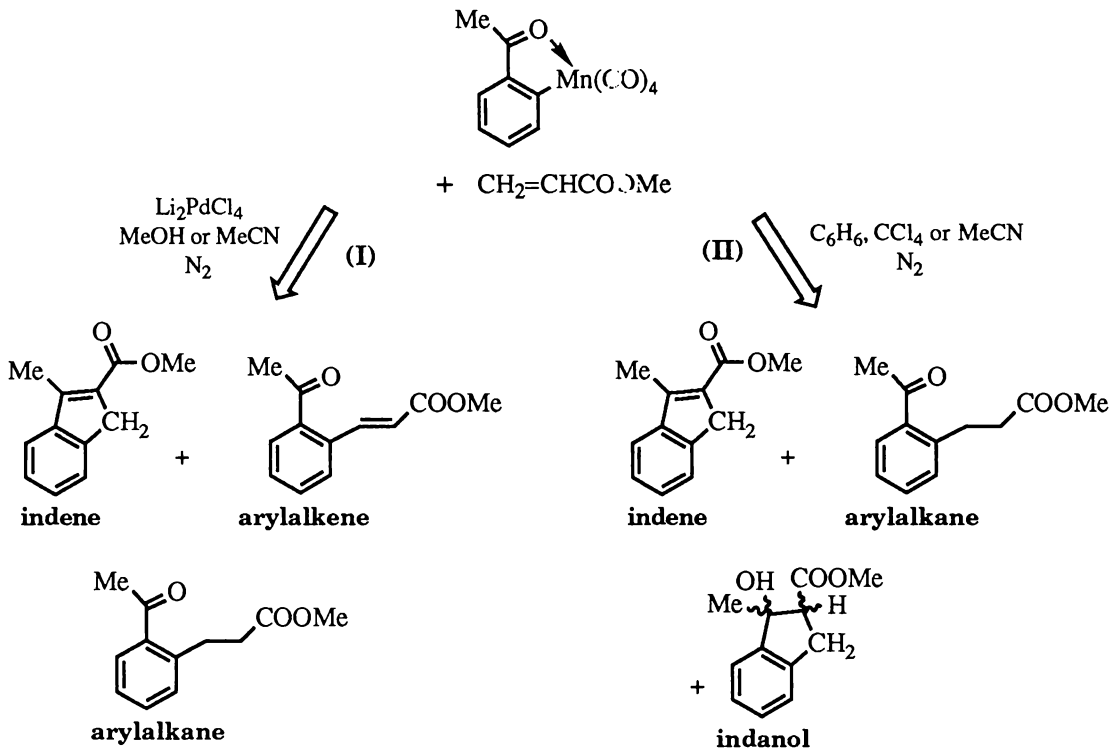
Reactions of orthomanganated aryl ketones with SO_2 and with the electronically and structurally related cumulenes, *N*-sulfinylaniline (PhN=S=O), *N*-sulfinylbenzenesulfonamide ($PhS(O)_2N=S=O$) and the disulfonylsulfodiimide $[PhS(O)_2N]_2S$ have been investigated. SO_2 inserts efficiently into the Mn-C_{aryl} bond of a range of orthomanganated ketones, to give the corresponding S-sulfinato complex e.g. **(43)** (Figure 1). The X-ray crystal structure of **(43)** was determined and it is the first reported example of a six-membered metallocycle incorporating an O, Mn and S atom.

In contrast, reaction of PhN=S=O with a number of orthomanganated acetophenones led to the corresponding orthomanganated imines e.g. **(38)** (Figure 1). The structure of η^2-3-chloro-2-[1-(*N*-phenylimino)ethyl]-phenyl-tetracarbonylmanganese **(44)** was determined by single crystal X-ray diffraction.

$PhS(O)_2NSO$ and $[PhS(O)_2N]_2S$ did not react with orthomanganated *p*-methoxyacetophenone **(39)** under similar conditions.

The palladium- and thermally-promoted coupling reactions of orthomanganated aryl ketones and esters with alkenes have been explored in detail.

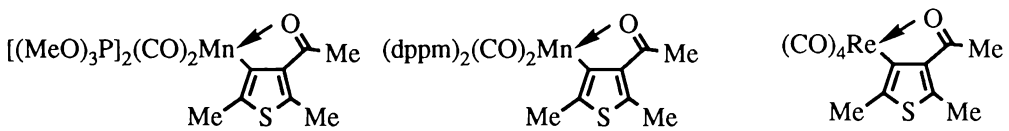
In the presence of Pd(II), η^2-(*o*-acetylaryl)tetracarbonylmanganese compounds undergo coupling reactions with methyl acrylate, methyl vinyl ketone, acrylonitrile, acrolein, vinyl acetate and allyl alcohol. The coupling reactions normally proceed in excellent yield and produce three main products, arylalkene, arylalkane and indene, the ratios of which vary with reaction conditions and substrate (Scheme 1; Path (I)).



Scheme 1

Orthomercurated aryl ketones obtained via transmetalation of orthomanganated ketones with mercuric chloride allowed a comparison of the product distribution for Pd(II)-promoted methyl acrylate coupling of an orthomercurated precursor 4-acetyl-2,5-dimethylthien-3-ylmercury(II) chloride **(112)** and the corresponding orthomanganated precursor η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)** under identical conditions. Cyclisation to give the indene-type product methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate **(53)** (whose crystal structure is reported) was found to be much more strongly favoured in the Mn than the Hg case precluding the possibility that the only role of both

replaced metals is in transmetalation with palladium prior to alkene coupling. This conclusion is supported by similar reactions with phosphite or phosphine derivatives of cyclomanganated aryl ketones e.g. **(145)**, **(146)** (Figure 2), and by reactions of orthorheniated substrates e.g. **(32)** (Figure 2).

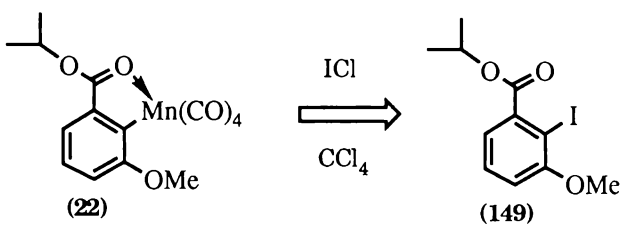


(145) **(146)** **(32)**

Figure 2

In the absence of Pd(II), alkenes were also found to insert efficiently into the Mn-C_{aryl} bond of orthomanganated ketones at *ca* 80 °C. In this case, the major products were found to be arylalkane, indene and a mixture of the diastereoisomeric indanols (Scheme 1; Path (II)). Arylalkene products were formed in very small or indetectable amounts. Possible reaction pathways for both the Pd(II) and the thermally initiated reactions are presented.

Several sterically crowded 3-substituted orthomanganated esters and ketones were reacted with ICl to give the corresponding 2-iodo-3-substituted compounds (e.g. Equation 1). 3-Substituted 2-iodo esters formed via this route are of interest as potential precursors for the formation of 5-substituted 9-oxo-9H-xanthene-4-acetic acid (XAA) compounds, which exhibit antitumour activity.



(22) **(149)**

Equation 1

Acknowledgements

I would like to thank my supervisors, Assoc. Prof. L. Main and Assoc. Prof. B. K. Nicholson, for their guidance and encouragement throughout the course of this investigation. Their relaxed attitude to life and wonderful sense of humour have made my time as a graduate student very enjoyable.

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Finally, special thanks to Jamie and Mitchell for their support, encouragement and understanding.

All numbered compounds appear in the fold out section
at the rear of this thesis

Note on Nomenclature

For convenience and brevity, throughout this thesis orthomanganated compounds are named using a η^2 naming convention to specify that both the aryl carbon and the oxygen are coordinated. Strictly speaking this should be specified with a η^2-(C,O) nomenclature, or more correctly using the κ notation, so that for example η^2-(2-acetylphenyl)tetracarbonyl-manganese **(2)** should be 2-acetyl-κO-phenyl-κC^1-tetra(carbonyl-κC)-manganese(I).

Contents

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Abbreviations

br	-	broad
Bu	-	butyl
Cp	-	η^5-cyclopentadienyl
1D	-	one-dimensional
2D	-	two-dimensional
δ	-	chemical shift (ppm)
d	-	doublet
DMSO	-	dimethyl sulphoxide
dppm	-	bis(diphenylphosphino)methane
Et	-	ethyl
FAB	-	fast atom bombardment
FID	-	free induction decay
GC	-	gas chromatograph
IR	-	infrared
J	-	coupling constant (Hz)
m	-	medium
m	-	multiplet
M^+	-	molecular ion
Me	-	methyl
MS	-	mass spectrum/spectroscopy
NMR	-	nuclear magnetic resonance
NOE	-	nuclear Overhauser effect
Ph	-	phenyl
p.l.c.	-	preparative layer chromatography
Pr	-	propyl
q	-	quartet
s	-	strong
s	-	singlet
t	-	triplet
THF	-	tetrahydrofuran
t.l.c.	-	thin layer chromatography
υ	-	stretching frequency (IR)
vs	-	very strong
w	-	weak

Chapter One

Introduction: Cyclometalation

Over the past two to three decades cyclometalated complexes have attracted increasing attention from researchers, as evident from the many comprehensive reviews now available [1-4].

Metallacycles are successfully used in organic synthesis [5], catalysis [6], asymmetric synthesis [7] and photochemistry [8]. They mimic some key intermediates in catalytic transformations [9] and show promise as potential biologically active materials [10,11].

1.1 Definition

Cyclometalated complexes are defined by Omae [1] as organometallic intramolecular-coordination compounds with a metal-carbon bond of the configuration shown in Figure 1.1.

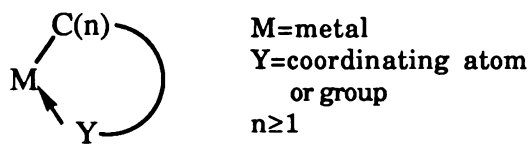


Figure 1.1

Although Omae's definition excludes compounds which contain a non-carbon atom in the ring, there are numerous examples of such complexes in the literature [12,13], and it is therefore appropriate to include them in this review.

Omae describes two types of coordination: σ-coordination and π-coordination, depending on the mode of coordination of Y to the metal.

When Y is a π-coordinating group the compounds mainly have vinylene, π-allyl, cyclopentadienyl, or aryl as the coordinating group.

The Y in the σ-coordination compounds represents N, P, As and Sb in Group 15, O and S in Group 16, and Cl, Br, and I in Group 17, but is much more commonly restricted to N, P, As, O and S than the other elements.

1.2 History

The earliest examples of cyclometalated compounds were cited by Bähr and Müller [14-16] in 1955, with a report of several complexes described as "Metallorganische Innerkomplexe" (Figure 1.2).

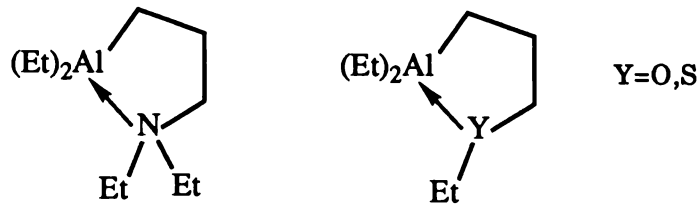
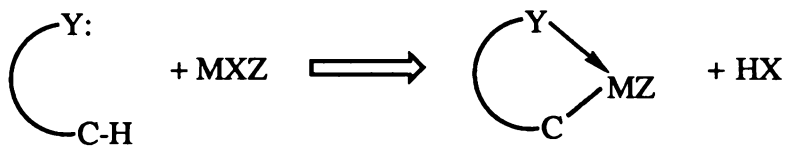


Figure 1.2

Some bicyclic beryllium analogues were also described.

The term "cyclometalation" was introduced by Trofimenko [17] in 1973, to describe the ring formation reaction of cyclometalated compounds (Equation 1.1).



Equation 1.1

The predominantly reported examples in the literature involve selective metalation in an aromatic ring position *ortho* to the donor function Y, and this has given rise to the term "orthometalation".

The first examples of orthometalation were provided by Kleiman and Dubeck [18] in 1963 who reported an azobenzene complex of nickel, $CpNi\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_5$, and by Cope and Siekman [19] in 1965 with an analogous complex of palladium $[C_6H_5N{=}N\text{-}C_6H_4\text{-}PdCl]_2$.

1.3 Ring Size

Cyclometalated complexes, except for π-coordinated compounds, generally form a chelate ring which possesses three to seven members, with the five-membered ring structure being most prevalent [9,20]. Almost all

compounds containing an oxygen or nitrogen donor atom, with no available d-orbitals, form the five-membered ring structure. It is widely believed that this configuration is most stable because it gives the closest to the ideal geometry (bond angles and bond lengths) of all the possible ring sizes. X-ray crystallographic studies have illustrated the considerable ring strain associated with three- and four-membered rings [21], for instance as in the structure in Figure 1.3.

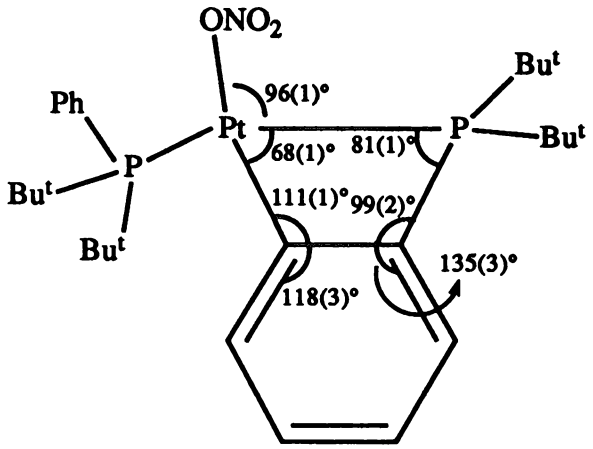


Figure 1.3

The tendency to form five-membered rings is illustrated by the ligands $C_6H_5(CH_2)_nNMe_2$ where n may be 0, 1, 2 or 3, since only the benzylamine (n=1) undergoes metalation with $PdCl_2$. The other amines, which would form four-, six-, or seven-membered rings by *ortho* substitution, give only the complexes $[C_6H_5(CH_2)_nNMe_2]_2PdCl_2$ [20]. Similarly *N*,*N*-dimethyl-1-naphthylamine, which could in theory ring close at either the 2-position (giving a four-membered ring) or at the 8-position (giving a five-membered ring) is found to form only the five-membered ring structure [9].

It has been observed, however, that organometallic intramolecular-coordination compounds having sulphur or phosphorus donor atoms, show an increasing tendency to form three- or four-membered rings. Omae suggests that this is due to the increased size of the atoms, and the possibility of d-orbital participation in the bonding with the metal, leading to small chelate rings with less strain [1].

1.4 Donor Atoms

While cyclometalation reactions are known for many combinations of metal and organic substrate [1,3], they are perhaps best developed for Pd(II) with N-donor substrates, as is evident from the number of articles and reviews reported in the literature to date [22,23].

Although in this thesis the focus will be on orthomanganated compounds with carbonyl-oxygen donor functions, a brief overview of all the principal donor atoms involved in σ–coordination compounds will be given, in addition to a more detailed account of the carbonyl-oxygen donor functions.

1.4.1 Nitrogen

Cyclometalated compounds with a nitrogen donor ligand, can be divided into ten groups, depending on the nature of the ligand: benzylamines, tolylamines, benzoylamines, ferrocenylmethylamines, benzylideneamines, azobenzenes, phenyldiazenes, heteroaromatic compounds, alkylamines and imines. To date cyclometalated compounds of a wide range of transition metals including Ti [22], Cr [23], W [23], Fe [23], Mo [23], Mn [24], Re [22,24], Ru [22], Os [22], Rh [22], Ir [23], Ni [18], Pd [19], Pt [19], Cu [1] and Au [22] incorporating a N-donor ligand have been reported.

1.4.2 Phosphorus

As phosphorus is in the same group of the Periodic Table as nitrogen, organometallic intramolecular-coordination compounds containing a phosphorus donor ligand form many chelate compounds which are analogous to their nitrogen counterparts. P-donor ligands include phenylphosphanes, benzylphosphanes, *o*-tolylphosphanes, 1-naphthylphosphanes, aryl phosphites, 2-alkoxyphenylphosphanes and propylphosphanes, and complexes are known for Mn [25], Ru [26], Rh [1], Ir [1], Pt [1], Pd [4], Ni [1], Fe [26], Au [26], Re [25] and Os [1].

Despite the ring stability of chelate complexes decreasing in the order of five->six->four-membered ring, a relatively large number of four-membered ring compounds containing a phosphorus donor ligand have

been reported compared to those containing a nitrogen donor ligand. This difference has been attributed to the size of the P atom and the possibility of d-orbital participation in the bonding with the metal [1].

1.4.3 Arsenic

Relatively few examples of metalated As donor ligands have been described [27].

Three-, four-, five- and six-membered ring compounds have been reported, but the five-membered ring structures, similar to those of the corresponding phosphane compounds, are preferred. They are generally more difficult to synthesize and are more labile than their corresponding phosphane analogues.

1.4.4 Oxygen

In organometallic intramolecular-coordination compounds containing an oxygen atom, the ligand groups are in most cases carbonyl groups or, in a small number of cases, alkoxy groups. There are a few examples also of nitro [28], hydroxy [29], phosphoryl [30], nitrato [31] or sulfinyl [32] groups as ligands. Examples of these unusual compounds are shown in Figure 1.4.

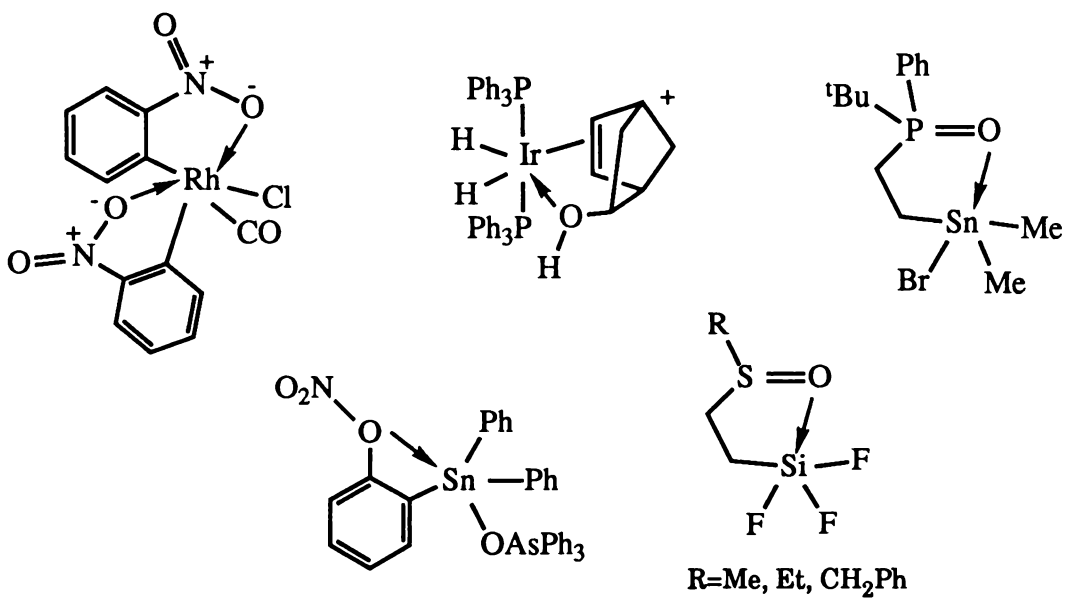


Figure 1.4

1.4.4.1 Carbonyl-oxygen ligands

Cyclometalated compounds containing carbonyl-oxygen donor ligands are comprised principally of ketone, amide and ester functionalities, and more rarely, aldehydes.

1.4.4.1.1 Ketones

A growing number of complexes containing a ketone carbonyl group coordinated to a metal atom via an oxygen-metal σ-donor bond are becoming known.

Early reports include the structures of Figure 1.5. (A) is obtained by treatment of *cis*-(2-oxacyclopentylidene)nonacarbonyldimanganese with butyl lithium followed by treatment with acetyl chloride [33], (B) is one of the products obtained in the addition of $MeMn(CO)_5$ to *o*-styryl-(diphenyl)phosphine [34], and (C) is obtained in the addition of $MeM(CO)_5$ or $HM(CO)_5$ (M=Mn or Re) to acetylenes [35].

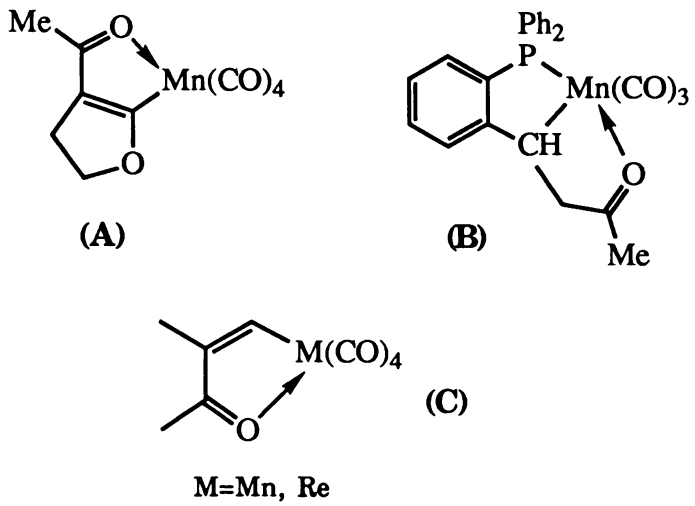
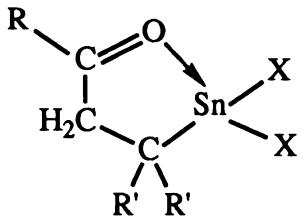
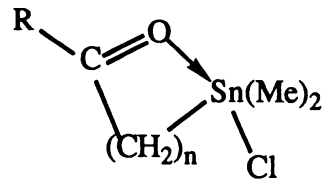


Figure 1.5

Examples of other types of metal complexes containing the chelated keto group include a series of tin compounds [1] (Figure 1.6), an iridium complex [36] (Figure 1.7), and several five-membered ring examples incorporating W [37], Te [38], Se [38] or Fe [39].



R=Me, Et, n-Pr, Ph
R'=H, Me
X=Cl, Br, I



R=Me, Ph
n=2,3

Figure 1.6

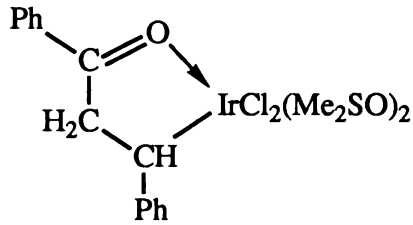
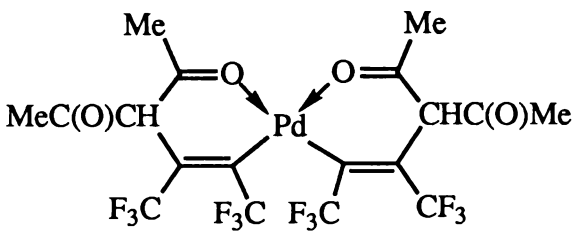
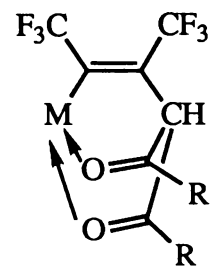


Figure 1.7

Bicyclic six-membered ring compounds are known for Pd, Rh and Ir [1], Figure 1.8.

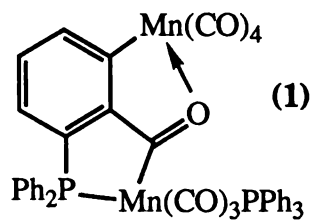




R=Me, CMe_3
M=Rh[L], Ir[L]

Figure 1.8

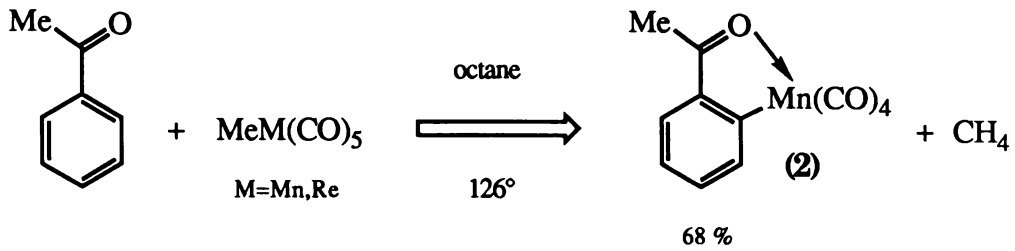
The formation of secondary metalation products such as **(1)** [40,41] (Figure 1.9), led Kaesz into the area of direct metalation of aromatic ketones and



(1)

Figure 1.9

quinones, which gave rise to the first reports of *ortho*-substitution by a transition metal of an aromatic system in which an oxygen functionality directs the metalation [42] (Equation 1.2).



Equation 1.2

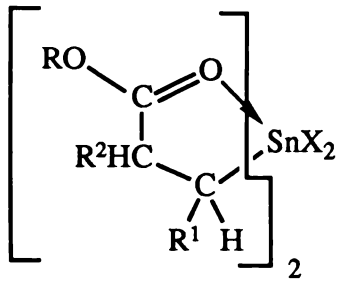
The Kaesz group has subsequently reported similar reactions involving benzophenones [43], acetylferrocenes [44], anthraquinones [43] and a variety of substituted acetophenones [43].

More recently the scope of the reaction has been extended to include various acetyl-thiophenes, -furans and -*N*-methylpyrroles [45].

To date, only manganese, rhenium [41,43,46] (an expensive manganese mimic) and a small number of ruthenium [47,48] orthometalated keto-donor compounds have been reported. Other metals that react routinely with N, P or S donor ligands are not orthometalated [17,49]. The reasons for the distinctive behaviour of manganese towards aromatic ketones is still not clear.

1.4.4.1.2 Esters

The first proven examples of cyclometalated compounds containing an ester oxygen donor ligand were provided in the early 60's by Matsuda and his co-workers who reported the synthesis of a series of five-membered cyclometalated tin compounds [50] (Figure 1.10).

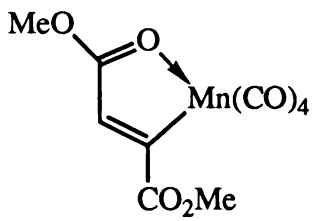


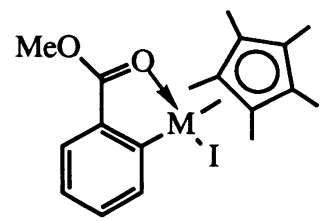
R=alkyl, aryl
R^1,R^2=H, Me
X=Cl, Br, I

Figure 1.10

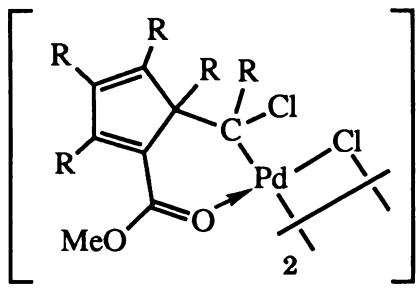
Related six-membered ring systems have also been reported.

A number of Mn [51], Mo [52], Ru [53], Rh [54], Ir [54], Re [51], Ti [2], Sb [2] and Pt [55] five-membered ring ester complexes have also been described in the literature, along with a report of a six-membered ring Pd compound [56] (Figure 1.11).





M=Rh, Ir



R=COOMe

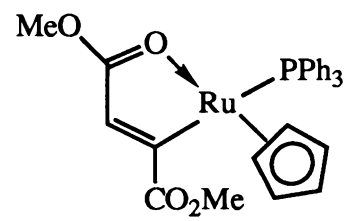


Figure 1.11

The successful orthomanganation of isopropyl benzoate (85 %) and methyl benzoate (4 %) by Cabral in 1981 [57] were the first examples of orthomanganated aromatic esters formed by direct metalation. We have also reported the orthomanganation of methyl 3,4,5-trimethoxybenzoate in high yield (73 %) [58]. The reason for the vast difference in the reactivity

between methyl benzoate and the other two alkyl benzoates is unclear. It is not due to any instability of the product, since Casey and Bunnel [59] have prepared **(3)** by an indirect route and once formed the compound is stable and has similar properties to other cyclomanganated species. This will be discussed further in Chapter Two in the context of further work done in this area as part of this project.

Woodgate *et al* have also recently reported the orthomanganation of a 13-methoxycarbonyl diterpenoid derivative [60].

1.4.4.1.3 Amides

An amide ligand can interact with a metal to form a cyclometalated complex in two possible ways. Disregarding any nitrogen-metal interaction, the two possibilities are a metallacycle that contains the nitrogen atom, and one that excludes it (Figure 1.12).

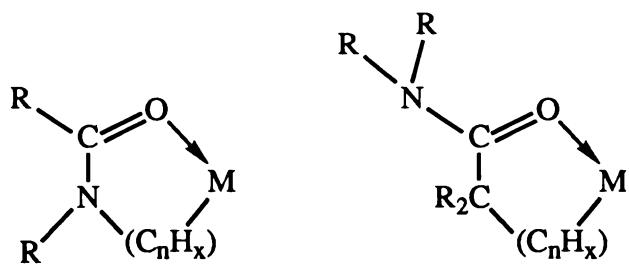


Figure 1.12

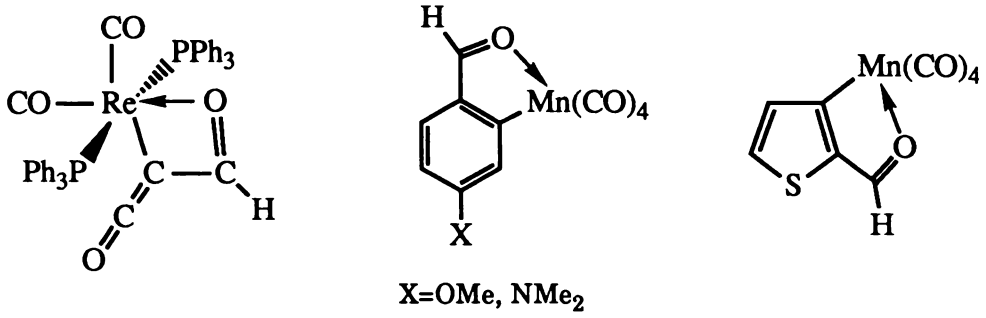
Examples related to the former group have been reported by Cowie and Ibers for Rh [61], Roat *et al* for Pt [62] and more recently by Robinson [13] for a number of Mn compounds.

Cyclometalated amides with the nitrogen atom outside the metallocycle, were known prior to 1989 in only a few cases. Omae describes several tin(II) species in his review [1], but more recently Robinson has prepared and characterised a wide variety of these novel cyclometalated complexes for manganese [13,63].

1.4.4.1.4 Aldehydes

Previous accounts of cyclometalated aldehydes in the literature are few. Hillhouse reports a four-membered ring aldehyde for Re [64], while Robinson has recently prepared several substituted orthomanganated

benzaldehydes and orthomanganated thiophenecarboxaldehydes [13] (Figure 1.13).



X=OMe, NMe_2

Figure 1.13

Depree also claims to have successfully orthomanganated indole-3-carboxaldehyde and its *N*-methyl analogue [65]. Definitive assignment, however, is awaiting a single crystal X-ray structure determination of the latter compound. Woodgate's group has also prepared a substituted orthomanganated benzaldehyde [66] and several analogous cyclomanganated diterpenoid-derived aldehydes [60].

1.4.4.2 Alkoxy oxygen ligands

There have been relatively few articles published on cyclometalated complexes containing an alkoxy oxygen ligand.

The ether oxygen is capable of coordination to a metal to form a chelate compound, but this metal-oxygen bond is rather labile since it reacts readily with a number of reagents, and these compounds are therefore not as stable as those containing a carbonyl oxygen bond.

Omae reviews a number of these alkoxy ligands, including alkyl ethers, ferrocenyl ethers, methoxybenzene, 1-methoxynaphthalene and norbornene alkyl ethers [1].

1.4.5 Sulphur

As sulphur belongs to the 6th group of the Periodic Table, it shows similar character to oxygen. However in contrast to oxygen, the sulphur 3d orbitals may take part in bond formation with metals, leading to many more reports of three-membered ring intramolecular-coordination

compounds, compared with those containing an oxygen or nitrogen donor ligand. Omae [67] suggests that the low energy sulphur d orbitals enable these compounds to form three-membered rings with less strain. The sulphur donor ligand can be an alkane thioether, alkene thioether, benzyl thioether, or thiobenzophenone, and complexes are known for Al [1] and Be [66] as well as for a range of transition metals including Fe [68], Mn [69], Re [67], Pd [2], Pt [4], W [1], Mo [1] and Rh [67].

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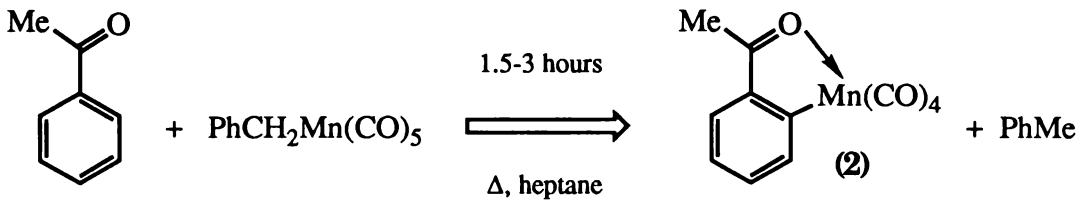
Chapter Two

Ortho-Functionalisation of Aromatic Ketones and Esters via Manganation and Rheniation

2.1 Introduction

Cyclomanganation of a range of simple aromatic and heterocyclic ketones is now well documented [1-9].



Equation 2.1

The reaction proceeds smoothly in refluxing heptane under nitrogen to give the cyclomanganated product, generally in high yield. The use of benzylpentacarbonylmanganese rather than methylpentacarbonyl-manganese as the metalating agent is now standard, requiring less forcing reaction conditions, giving rise to fewer decomposition products, and in most cases studied resulting in a higher yield of the cyclometalated product [3,10].

It has been shown that cyclometalated aryl ketones are useful intermediates in the synthesis of a number of novel organic and organometallic compounds, providing an important method for activating the carbon at the *ortho* site [5,9].

With a view to exploring in more depth the value of cyclomanganated products in synthesis, we have prepared a wider variety of cyclomanganated compounds, including some in which the donor ketone carbonyl group is incorporated into a fused ring, along with a variety of benzoates and heterocyclic acid esters. To provide a comparison, several orthorheniated compounds have also been prepared.

These new compounds have been fully characterised by spectroscopic and,

where appropriate, X-ray structure methods.

2.2 Discussion of Results

2.2.1 General

The yields of and workup procedures for the orthomanganated and orthorheniated compounds prepared in this study are given in Table 2.1. Experimental conditions, melting points, elemental analysis data and spectral data are given in section 2.6.

2.2.2 Orthomanganations

2.2.2.1 Orthomanganation of Ketones

The successful orthomanganation of thioxanthen-9-one, thiochroman-4-one, 1,2,3,4,9,10-hexahydro-9-acridone, 10-methyl-9(10H)-acridone, 2-chlorothioxanthen-9-one, dibenzosuberone and dibenzosuberenone shows that orthometalation proceeds normally, and generally in good yield when the carbonyl group is incorporated into a fused ring.

2.2.2.1.1 Regioselectivity Studies

For 2-chlorothioxanthen-9-one metalation affords two isomers (Figure 2.1), one with the manganese *ortho* to the chloro group [**(7)**; 39 %] and the other showing metalation at the unsubstituted aryl ring [**(6)**; 51 %]. Regioselectivity is not great in this reaction. On repeating it, while the overall yield remained similar, the ratio was found to be ~1:1.

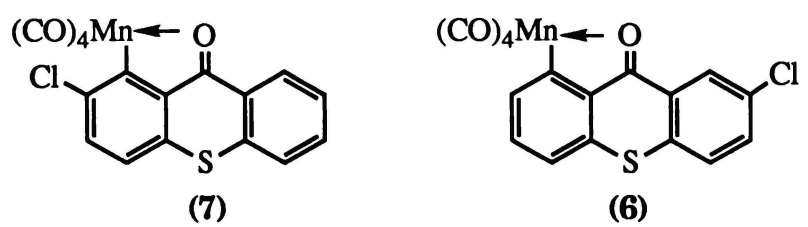


Figure 2.1

Orthomanganation of 3'-chloroacetophenone also gave similar yields of both the 2,6-disubstituted [**(14)**; 42 %] and 2,4-disubstituted [**(15)**; 37 %]

Table 2.1 Orthometalated Compounds Prepared in this Study

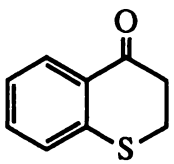
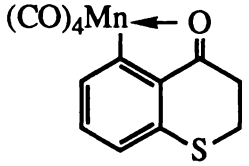
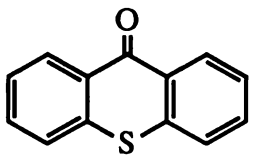
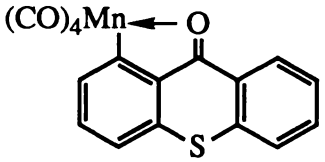
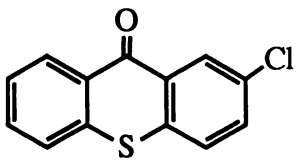
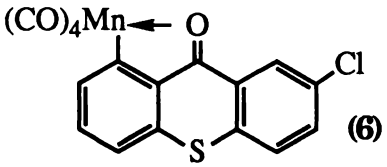
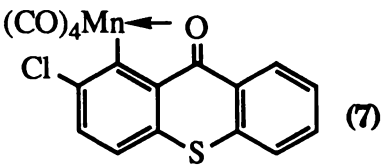
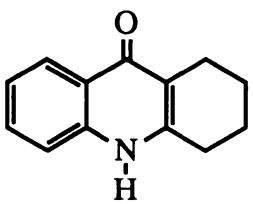
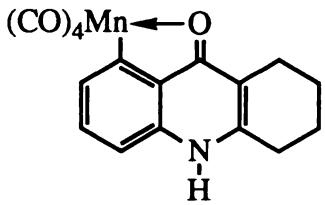
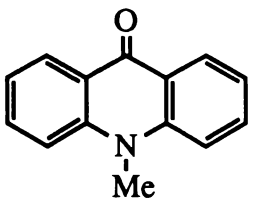
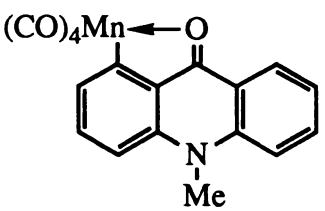
Starting Compound	Products	Yield	Method of Purification
	 (4)	51 %	A
	 (5)	96 %	A
	 (6)	51 %	B
	 (7)	39 %	B
	 (8)	62 %	C
	 (9)	88 %	D

Table 2.1 continued

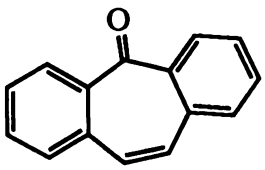
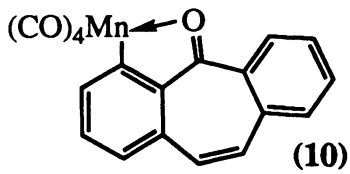
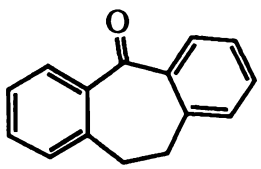
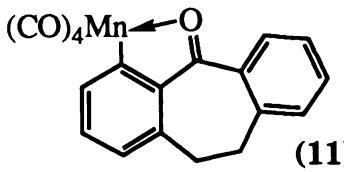
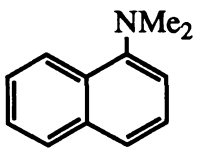
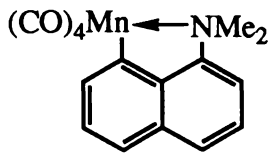
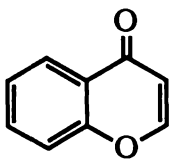
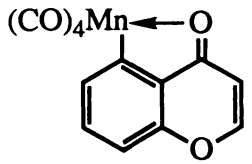
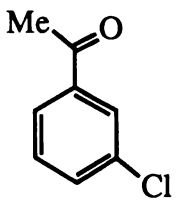
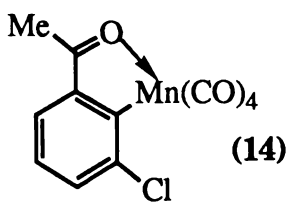
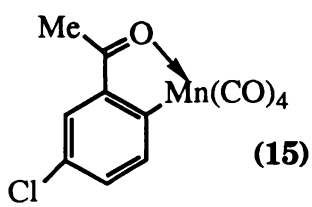
Starting Compound	Products	Yield	Method of Purification
	 **(10)**	100 %	A
	 **(11)**	100 %	A
	 **(12)**	88 %	E
	 **(13)**	96 %	A
	 **(14)**	42 %	F
	 **(15)**	37 %	F

Table 2.1 continued

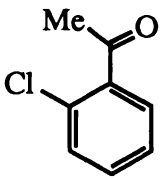
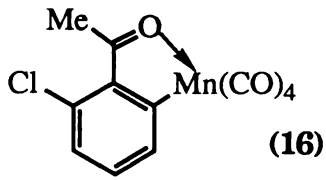
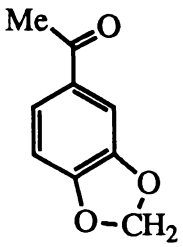
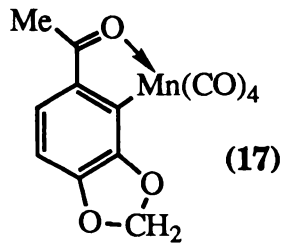
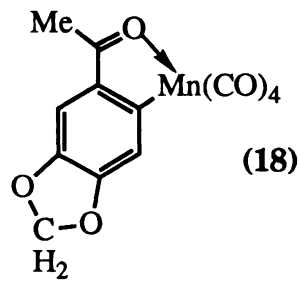
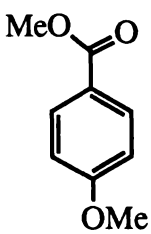
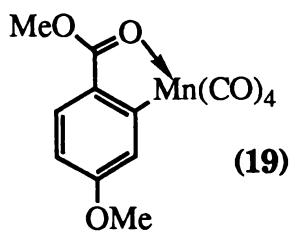
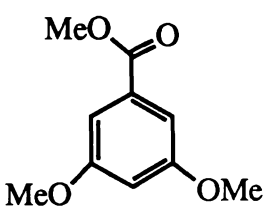
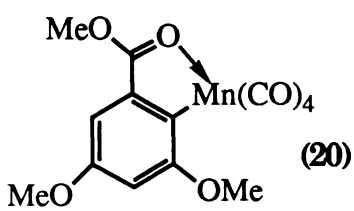
Starting Compound	Products	Yield	Method of Purification
	 **(16)**	86 %	F
	 **(17)**	86 %	A
	 **(18)**	~4 %	A
	 **(19)**	74 %	A
	 **(20)**	87 %	A

Table 2.1 continued

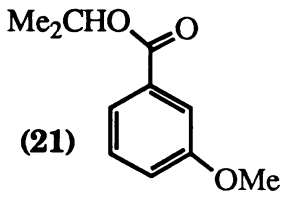
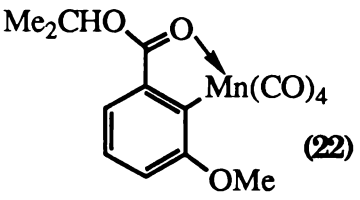
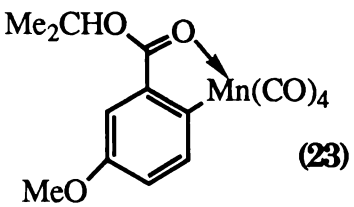
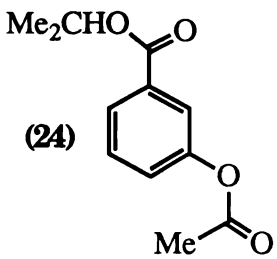
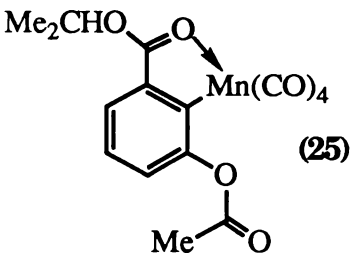
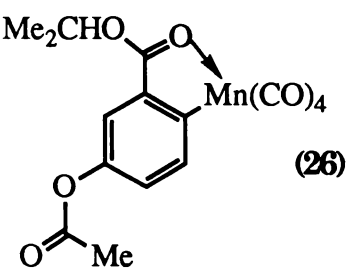
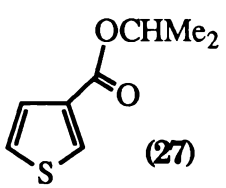
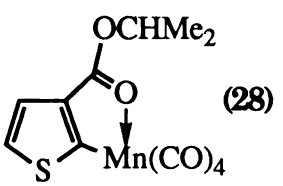
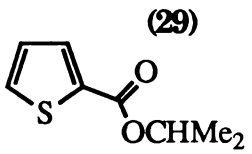
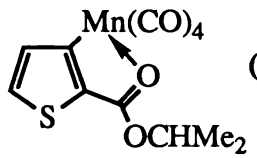
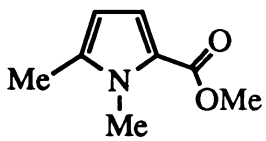
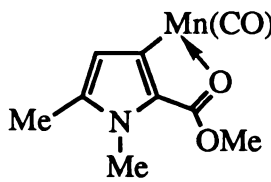
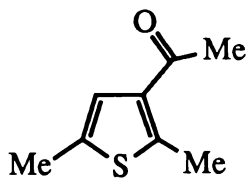
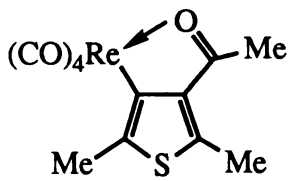
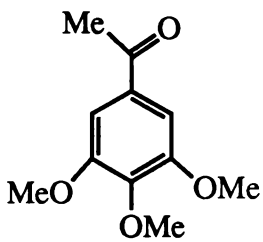
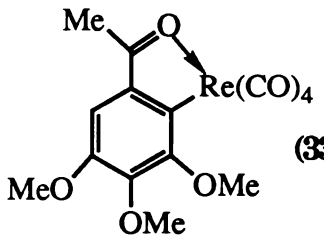
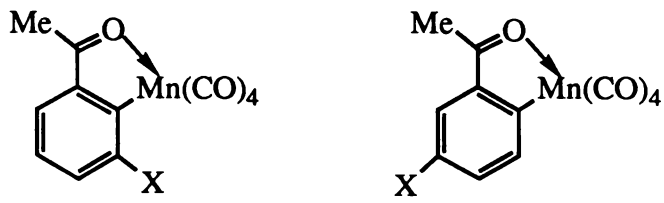
Starting Compound	Products	Yield	Method of Purification
 (21)	 (22)	53 %	B
	 (23)	39 %	B
 (24)	 (25)	79 %	B
	 (26)	10 %	B
 (27)	 (28)	62 %	B

Table 2.1 continued

Starting Compound	Products	Yield	Method of Purification
(29) 	 (30)	38 %	B
	 (31)	4 %	A
	 (32)	36 %	A
	 (33)	41 %	D

A=P.l.c. (1:10 v/v ether/petroleum spirit)
B=P.l.c. petroleum spirit
C=solid filtered and recrystallized from hot chloroform
D=P.l.c. (1:5 v/v ethyl acetate/petroleum spirit)
E=P.l.c. (1:5 v/v ether/petroleum spirit)
F=P.l.c. (1:20 v/v ethyl acetate/petroleum spirit)

manganated products (Figure 2.2).

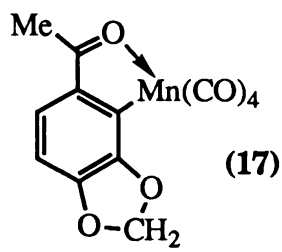


(14) X=Cl **(15)** X=Cl

(A) **(B)**

Figure 2.2

Liebeskind has subsequently published corresponding data as part of an independent study into regioselective metalation of acetophenones and reports similar results [9]. He concluded that there is an electronic directing effect favouring metalation at the 2'-site which diminishes with increasing size of X. Upon manganation of a series of 3'-substituted acetophenones the ratio of isomers A:B is 4.5:1 (X=F), 1.05:1 (X=Cl) and 0.69:1 (X=Br). For X=Me or CF_3 only isomer (B) is isolated, although the Kaesz group report a trace of the former in the crude reaction mixture and have recorded the infrared spectrum [2]. For X=OMe the more sterically crowded 2,6-disubstituted isomer (A) is the dominant one formed [2,6], also indicating an electronic directing effect from the methoxy substituent, possibly via lone-pair coordination to the entering metal. Gommans has reported that for 3',4'-dimethoxyacetophenone metalation preferentially takes place (in a ratio of 3:1) at the less-hindered 6'-site [4], probably because the 4'-OMe group now sterically prevents the 3'-OMe freely rotating to direct a lone pair towards the 2'-position. Our results for the cyclometalation of 3',4'-(methylenedioxy)acetophenone support this steric interpretation, as attack reverts predominantly to the 2' site, giving isomer [**(17)**; 86 %] (Figure 2.3), with only a trace (~4 %) of the other possible isomer **(18)**.



(17)

Figure 2.3

2.2.2.1.2 Manganation Via Reaction at C-H Versus Reaction at C-Cl

The orthometalation of 2'-chloroacetophenone was of interest to determine whether reaction at C-H or C-Cl is favoured, following reports that the phosphane $P(o\text{-}ClC_6H_4)Ph_2$ undergoes orthometalation in Rh compounds, by C-Cl rather than C-H labilization yielding Rh(III) species which contain a four-atom metallocycle (Figure 2.4) [11].

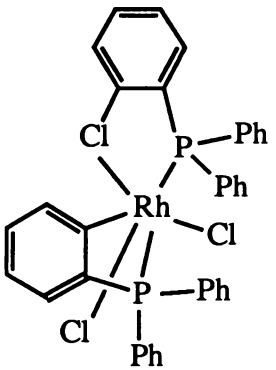


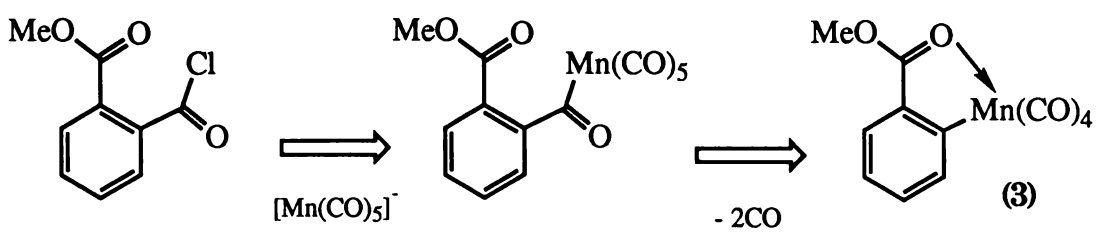
Figure 2.4

The reaction afforded only the chlorinated cyclometalated complex, η^2-(2-acetyl-3-chlorophenyl)tetracarbonylmanganese [**(16)**; 86 %], indicating that replacement of Cl is not favoured over replacement of H in orthomanganation.

2.2.2.2 Orthomanganation of Esters

2.2.2.2.1 Effect of Electron-Donating Substituents on Reactivity

Cabral has reported that methyl benzoate gives only a trace of the orthomanganated ester **(3)** under the usual conditions [3]. This is not due to any instability of the product since Casey and Bunnell [12] have prepared **(3)** by an indirect route, outlined in Equation 2.2 and once formed the compound is stable and has similar properties to other cyclomanganated species.



Equation 2.2

The successful orthomanganation of methyl 4-methoxybenzoate (74 %), was in accord with results obtained by Robinson [13,14], who found that a 4-OMe substituent on the aromatic ring of benzaldehyde allows metalation to proceed with good yield, when in its absence (benzaldehyde) no reaction occurs. We have also previously reported the orthomanganation of methyl 3,4,5-trimethoxybenzoate in high yield (73 %) [6], though in this case it is not clear that the crowded 4-methoxy group could become coplanar with the ring to provide electron-donation to increase the donor ability of the ketone carbonyl oxygen. There is still further unpredictability with substituent effects in this area in our finding that methyl 3,5-dimethoxybenzoate is also effectively orthometalated (87 %) in spite of having no 4-OMe group. Furthermore, isopropyl benzoate does give good yields of the orthomanganated complex with benzylpentacarbonyl-manganese in spite of the absence of an electron-donating 4-substituent [3].

2.2.2.2.2 Effect of Alkyl Substitution of the Donor Carbonyl Group on Reactivity

One possible explanation for the difference in behaviour between the methyl and isopropyl esters is related to the observation that if a cyclic compound is in equilibrium with an open-chain derivative it appears to be the almost invariable rule that alkyl substitution favours the ring form [15]. This phenomenon can be rationalized in terms of the Thorpe-Ingold effect for three- and four-membered rings, while the proposals of Allinger and Zalkow are generally invoked to rationalize similar trends in five- and six-membered rings.

Allinger and Zalkow [16] suggest the enthalpy of ring-closure is more favourable for alkyl-substituted n-hexanes because of the increased number of gauche interactions in the open-chain compared with the cyclic product. The entropy of ring-closure is more favourable also, because branching reduces the rotational entropy of the open-chain form significantly more than that of the ring which has built in restrictions to internal rotation.

We would therefore expect the isopropyl ester to be more effective at promoting ring closure (ie. undergoing orthomanganation) than its

corresponding methyl analogue, reflecting the increased alkyl substitution.

Robinson has previously shown that methyl thiophene-2-carboxylate afforded no cyclometalated product [17], so for comparison we prepared and reacted isopropyl thiophene-2-carboxylate **(29)** and isopropyl thiophene-3-carboxylate **(27)** with benzylpentacarbonylmanganese. Both gave cyclometalated derivatives, albeit in rather low yield in the case of isopropyl thiophene-2-carboxylate (38 %). Their formation provides further support for the premise that increasing alkyl substitution does indeed assist ring formation.

2.2.2.2.3 Regioselectivity Studies

Isopropyl 3-methoxybenzoate **(21)** was also prepared and orthomanganated in good yield. The sterically crowded 2,6-disubstituted isomer **(22)** was found to be the principal derivative, 53 % versus 39 % for the 2,4-disubstituted isomer **(23)**, in accord with regioselectivity results reported for 3'-methoxyacetophenone [2,6].

Similarly isopropyl 3-acetoxybenzoate **(24)** was prepared and subsequently orthomanganated in high yield (89 %). Regioselectivity was even more pronounced in this case, a ratio of ~8:1 in favour of the sterically crowded isomer being observed. Clearly the donor ability of the alkoxy oxygens is not the only factor involved, as we would expect the methoxy oxygen to be a better electron donor than the corresponding oxygen in the acetoxy group (Figure 2.5), and yet the sterically crowded isomer is more favoured for the acetoxy group.

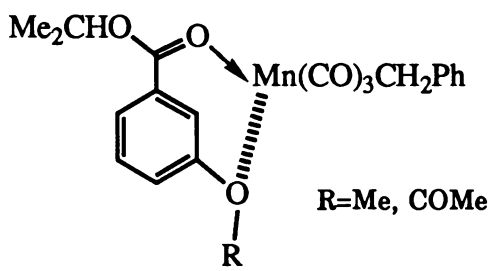


Figure 2.5

Although it is difficult to make too much of this observation as very little is known about the mechanism of orthomanganation, we could imagine a transition state in which the carbonyl oxygen of the acetoxy group acts as

a two-electron donor, effectively creating for the manganese a geometry more favourable to ring metalation than possible with a 3-methoxy group for which ring-size constraints might influence transition state energy (Figure 2.6).

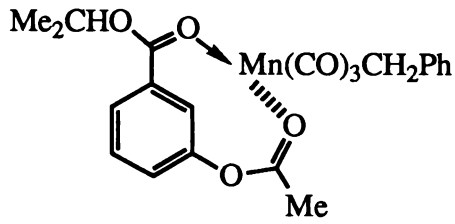


Figure 2.6

This reaction was also of interest as it represented a competition between an ester carbonyl and acetoxy carbonyl donor groups. Examination of the infrared spectra of the orthomanganated products revealed a shift to lower energy of 122 cm^{-1} for the ester carbonyl stretching frequency from that of the corresponding absorption in the originating non-manganated compound, while the acetoxy carbonyl stretch showed only a 9 cm^{-1} downward shift. The minor isomer showed no shift in the acetoxy carbonyl stretch, but a shift to lower energy of 122 cm^{-1} for the ester carbonyl stretch. These findings are in accord with literature reports of a characteristic downward shift of ~150 cm^{-1} for metal-coordinated carbonyl absorptions [2,8] and confirm that it is the aryl ester carbonyl group which is coordinated in a five-membered ring rather than the acetoxy carbonyl in a six-membered ring.

2.2.2.3 Orthomanganation of a N-donor Compound

Reaction of *N,N*-dimethyl-1-naphthylamine with benzylpentacarbonylmanganese gave η^2-(8-dimethylamino-1-naphthyl)tetracarbonylmanganese **(12)** in high yield. This compound was prepared primarily as a substrate for subsequent coupling reactions (see Chapter Four), as although this compound had not previously been prepared, previous work has shown that *N,N*-dimethyl-1-naphthylamine readily undergoes cyclometalation with various metals [18].

2.2.3 Orthorheniations

Both 3-acetyl-2,5-dimethylthiophene and 3',4',5'-trimethoxyacetophenone gave the expected cyclometalated products on treatment with benzylpentacarbonylrhenium. The orthorheniation reactions generally required more forcing reaction conditions and were lower yielding than their manganese counterparts.

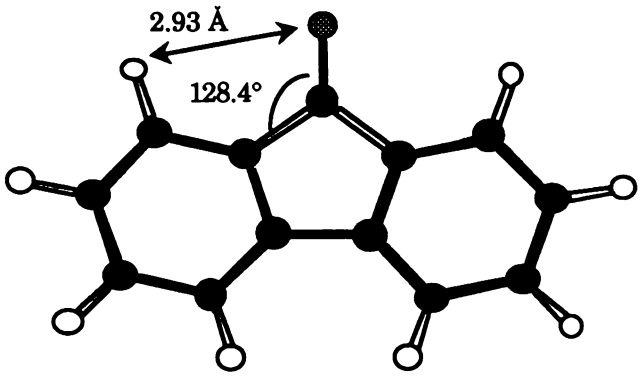
2.2.4 Unsuccessful Orthometalations

No orthomanganation occurred with 9-fluorenone, 1-indanone and phenanthrenequinone. For the former two, presumably this is due to steric constraints imposed by the angle of the fused carbonyl group with respect to the *ortho* site on the aromatic ring. To illustrate this, the structures of 9-fluorenone, 1-indanone and phenanthrenequinone were generated by molecular mechanics and compared with those generated for compounds which were known to undergo orthomanganation readily (Figure 2.7).

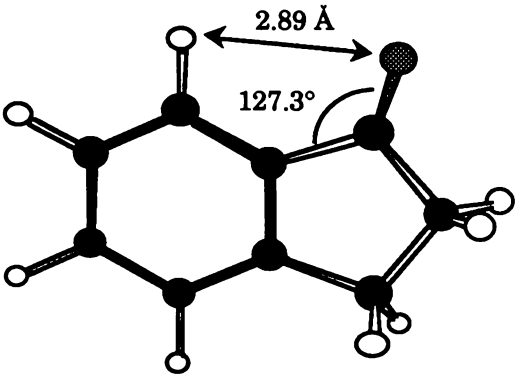
The crystal structure of 9-fluorenone has been reported in the literature [19]. The quoted C-C-O bond angle of 127.1(3)° is in good agreement with the molecular-mechanics-generated bond angle of 128.4°. Examination of Figure 2.7 shows that for both 9-fluorenone and 1-indanone, the angle of the fused carbonyl group with respect to the *ortho* site on the aromatic ring and the distance from the donor oxygen atom to the *ortho* hydrogen are considerably larger than for those examples where orthomanganation proceeds readily. It may be that these steric constraints do not provide a suitable geometry for the incoming manganese, thus precluding cyclometalation.

Phenanthrenequinone did not undergo cyclometalation even though the aforementioned geometry would appear to be favourable to replacement by the incoming manganese. The chemical properties of this compound however are completely different from those of the other fused ring systems containing a donor carbonyl group which have been examined. The quinones are known to be strong oxidising agents, and it is therefore probable that the unstable, highly coloured product formed upon reaction of phenanthrenequinone with benzylpentacarbonylmanganese was a radical species formed via a redox reaction. It has previously been shown

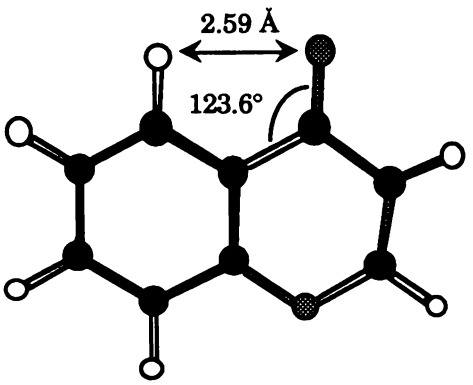
Figure 2.7 Molecular Mechanics Generated Structures of a Range of Potential Substrates for Orthometalation in which the Donor Ketone Carbonyl Group is Incorporated into a Fused Ring



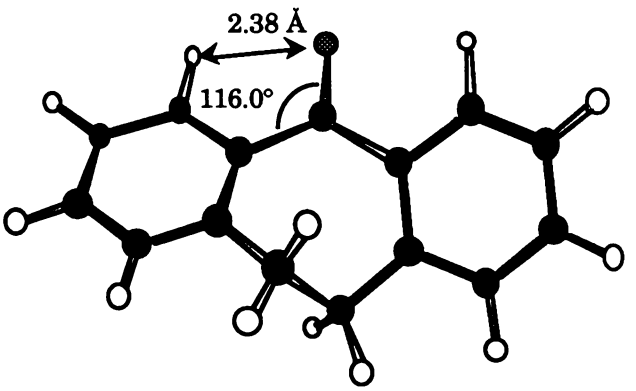
9-Fluorenone



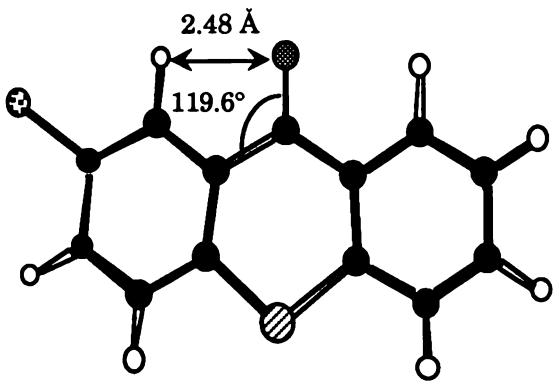
1-Indanone



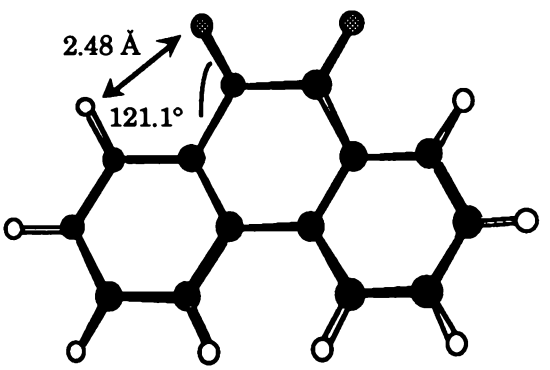
Chromone



Dibenzosuberone



2-Chlorothioxanthen-9-one



Phenanthrenequinone

that phenanthrenequinone reacts with decacarbonyldimanganese to form a radical species in which the manganese atom is equally coordinated to the two oxygen atoms of the quinone [20]. It has also previously been noted that both duroquinone and anthraquinone proved to be exceedingly reactive to methylpentacarbonylmanganese producing highly air-sensitive green solids [2]. For anthraquinone however cyclometalation did occur with methylpentacarbonylrhenium to yield a mono-rheniated and two di-rheniated isomers [3]. This is presumably due to the fact that rhenium compounds are generally less susceptible to oxidation than are manganese compounds.

The failure of methyl 2,5-dimethyl-3-furoate to orthometalate is not surprising in light of the lack of success Robinson reported with the attempted manganation of methyl thiophene-2-carboxylate [17]. It has been shown that for various acetyl-thiophenes, -furans and *N*-methylpyrroles, yields of orthomanganated products are satisfactory only for the thiophenes [4].

9-Acetylanthracene was treated with benzylpentacarbonylmanganese in order to establish the favourability of the formation of a six-membered metallocycle. Infrared spectra of the crude reaction mixture showed only decacarbonyldimanganese and the reaction was abandoned. Robinson [13] also found that for amides the six-membered ring is less favoured than its five-membered analogue, since acetanilide, exalgin (*N*-methylacetanilide) and *N*-(phenylacetyl)pyrrolidine all failed to yield any isolable cyclometalated product.

2.3 Properties of Orthomanganated and Orthorheniated Complexes

2.3.1 General

All of the orthomanganated and orthorheniated complexes prepared in this study are easily handled. They are mostly yellow-to-orange crystalline solids with sharp melting points, although some have been isolated only as oils. They are generally air stable and can be stored in a refrigerator for extended periods of time without any appreciable decomposition. With the exception of η^2-1-(5,6,7,8,9,10-hexahydro-9-acridinonyl)tetracarbonyl-manganese (**8**), the cyclometalated compounds tend to dissolve readily in

all organic solvents, which means there are no constraints for spectroscopy and reactivity studies.

2.3.2 Infrared Spectra

Most of the cyclometalated complexes prepared in this study exhibit three absorptions in the metal carbonyl region, with the exception of several of the cyclometalated esters and the orthorheniated compounds for which four bands are usually observed.

For a *cis*-$L_2M(CO)_4$ group, four bands are predicted in the υCO region of the spectrum. There is usually a medium intensity band at about 2080 cm^{-1}, two intense bands near 2000 cm^{-1}, which are often not resolved, and a strong band around 1945 cm^{-1}.

Since the high energy bands of this pattern are well resolved from those of benzylpentacarbonylmanganese and from the side by-product decacarbonyldimanganese, the progress of the reaction may be followed spectroscopically.

We have observed that in reactions where two isomers are possible, the position of the metal carbonyl absorption band at lowest wavenumber is particularly diagnostic (Table 2.2).

Where metalation occurs at a position with a substituent *ortho* to the metal resulting in a 2,6-disubstituted orthomanganated complex, the lowest band is shifted to higher wavenumber when compared to the less sterically crowded 2,4-disubstituted isomer. This trend is observed for all the orthomanganated species prepared in this study and related compounds described in the literature with the exception of one case, the metalation of 3'-methylacetophenone.

Although it is not known whether this phenomenon is due to steric or electronic effects, it is interesting to note that in the case where this shift is not observed, the substituent is a +I group (-Me) as opposed to the remainder of cases which involve -I/+R substituent groups (-OMe, -OCOMe, -Cl). It is also worth noting that within this range of good to poor electron donors there does not appear to be any trend in the size of the metal carbonyl frequency shift. The shift is however useful in that it

Table 2.2 Variation of M-CO Frequency with Substitution Pattern in the Aromatic Ring

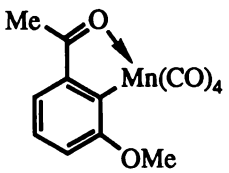
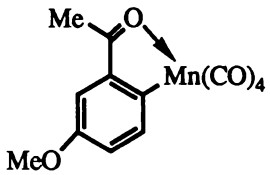
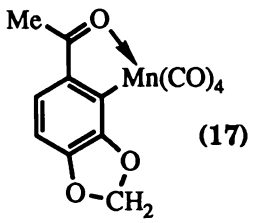
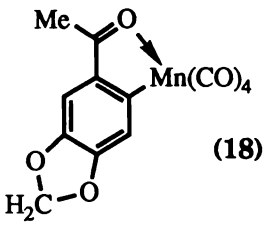
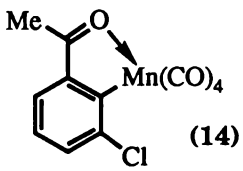
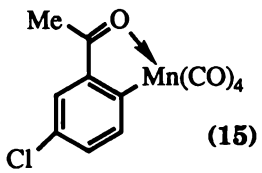
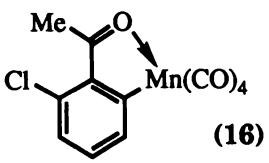
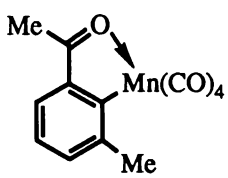
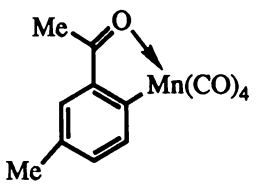
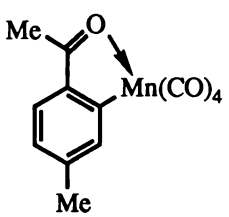
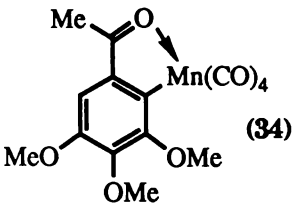
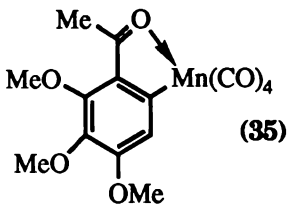
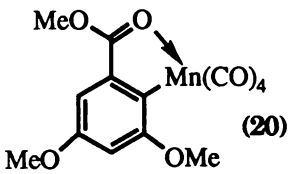
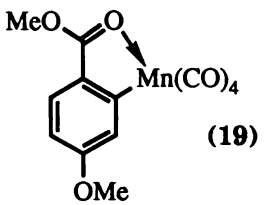
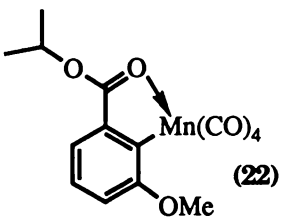
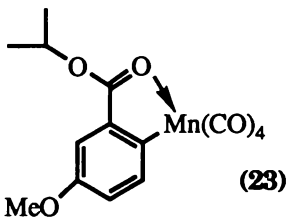
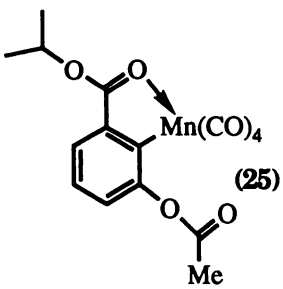
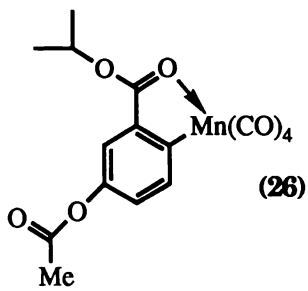
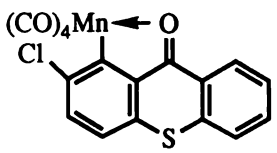
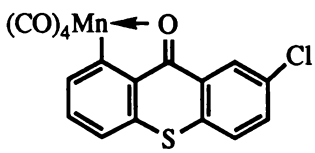
2,6-disubstituted type	υ(M-CO) cm^{-1}	2,4-disubstituted type	υ(M-CO) cm^{-1}
	2083, 1995, 1959		2082, 1998, 1947
 (17)	2086, 1997, 1960	 (18)	2082, 1997, 1944
 (14)	2088, 1998, 1961	 (15)	2085, 1997, 1949
	cf.	 (16)	2085, 1997, 1949
	2080, 1993 1944		2082, 1997, 1947
	cf.		2082, 1996, 1945

Table 2.2 continued

2,6-disubstituted type	υ(M-CO) cm^{-1}	2,4-disubstituted type	υ(M-CO) cm^{-1}
 (34)	2080, 1993, 1987, 1953 cf.	 (35)	2080, 1990, 1932 (CH_2Cl_2)
 (20)	2084, 1992, 1954 cf.	 (19)	2085, 1996, 1944
 (22)	2083, 1993, 1955	 (23)	2083, 1994, 1991, 1944
 (25)	2090, 2006, 1994, 1948	 (26)	2083, 1995, 1944
 (7)	2085, 1999, 1958	 (6)	2083, 1997, 1946

allows us to estimate the ratios of cyclometalated isomers by IR, while the reaction is still in progress.

2.3.3 ^{1}H-NMR Spectra

The Kaesz group has previously analysed and discussed the ^{1}H-NMR spectra of a number of orthomanganated acetophenones [2], and a self-consistent pattern of chemical shifts for these compounds is now well established.

For our polycyclic complexes, however, assignment was not so straightforward, and to enable definitive assignments to be made a combination of NMR techniques was employed.

The general procedure for assigning these spectra was as follows. First, ^{1}H-NMR spectra were tentatively assigned on the basis of chemical shift, multiplicities and coupling constants. These assignments were then unambiguously confirmed by two-dimensional homonuclear correlation spectroscopy (COSY) and difference NOE experiments.

As an example Figure 2.8 shows the ^{1}H-NMR spectrum of η^2-4-(dibenzosuberonyl)tetracarbonylmanganese **(11)**.

Clearly the singlet at 3.15 ppm can be assigned to the 4 H's at H-10 and H-11. From closer examination of the aromatic region (Figure 2.8b) the coupling constants displayed by these protons identifies the two doublet of doublets at 8.06 ppm (^{3}J=7.4 Hz, ^{4}J=0.9 Hz) and 6.98 ppm (^{3}J=7.4 Hz, ^{4}J=0.9 Hz) (H-1 or H-3) coupled to the triplet at 7.30 ppm (^{3}J=7.4 Hz, H-2). The remaining two doublet of doublets at 8.00 ppm (^{3}J=7.5 Hz, ^{4}J=1.5 Hz) and 7.27 ppm (^{3}J=7.5 Hz, ^{4}J=1.3 Hz) must correspond to either protons H-6 or H-9 and the two triplet of doublets at 7.52 ppm (^{3}J=7.5 Hz, ^{4}J=1.5 Hz) and 7.38 ppm (^{3}J=7.5 Hz, ^{4}J=1.3 Hz) to protons H-7 or H-8. However, further assignment is not possible from this spectrum alone.

COSY

Figure 2.9 shows a contour plot of the COSY spectrum of the aromatic region of **(11)**.

Figure 2.8 ***^{1}H-NMR Spectrum of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)***

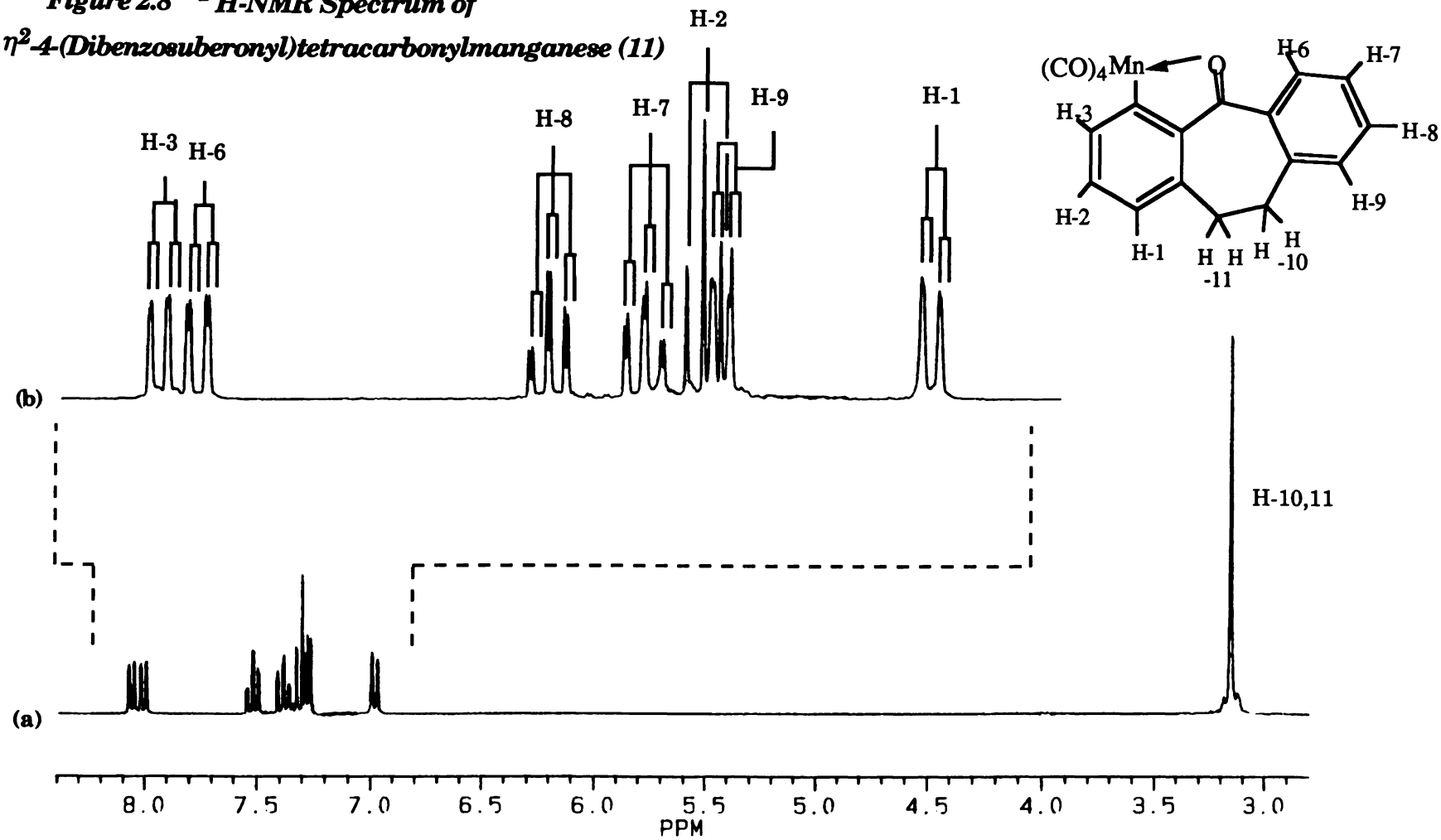
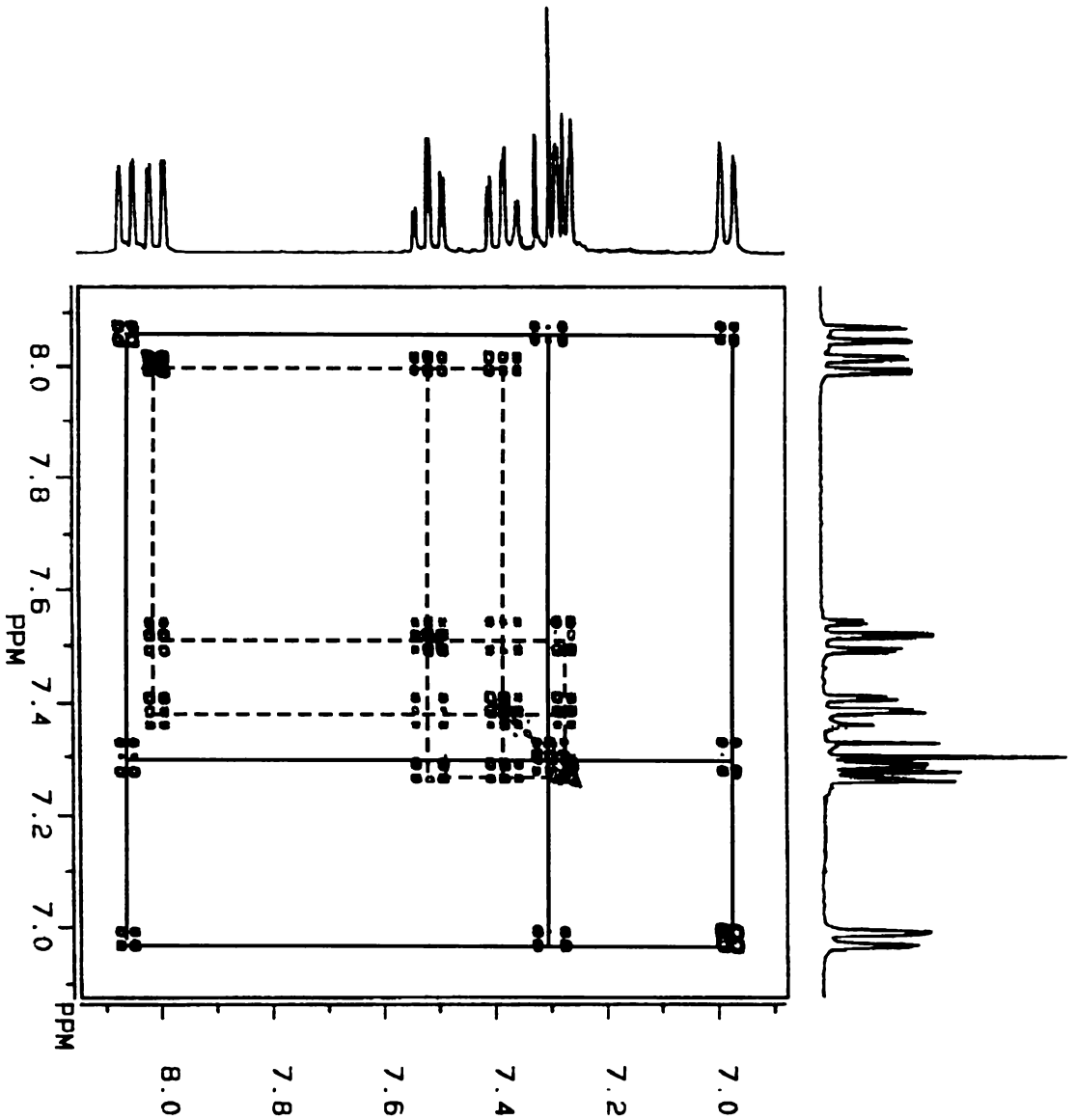


Figure 2.9 COSY Spectrum of
η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)



By tracing the crosspeak connectivities, two separate spin systems are readily identifiable. System A (—) exhibits coupling between the doublet of doublets at 8.06 ppm, the triplet at 7.30 ppm and the doublet of doublets at 6.98 ppm and clearly must be attributable to the manganese substituted ring, confirming our earlier assignment of H-2.

Spin system B (---) comprises four proton resonances as expected. The doublet of doublets at 8.00 ppm and 7.27 ppm both show correlations with the triplet of doublets at 7.52 ppm and 7.38 ppm, which again confirms our earlier assignments but still does not allow us to make distinctions within each pair.

In this case definitive assignment requires further (1D) experiments.

NOE's

The NOE is a change in the intensity of an NMR resonance when the transitions of another associated nucleus are perturbed. By strongly irradiating one nucleus using a double irradiation transmitter, the nuclear spin populations are grossly perturbed. Relaxation processes attempt to return the population to equilibrium and in so doing absorb much more energy than is normal from the irradiated nucleus. Nuclei which lie close in space to the irradiated nucleus provide some of this energy and undergo nuclear transitions which alter the populations of their spin states also. Generally for H-H NOE effects, enhancements are observed. The maximum value that the Overhauser effect can have is determined by the nature of the nuclear species involved. Since the phenomenon is controlled by relaxation processes, it falls off as approximately r^{-6}, where r is the distance between the nuclei concerned, and so is important only if the nuclei are in close proximity [21]. This technique provides a useful means therefore of identifying nearest neighbours to a nucleus giving a particular resonance.

In order to optimise detection of enhancements, the NOE difference method is employed. The NOE is generated using gated decoupling to facilitate comparison of perturbed and unperturbed spectra. Having accumulated some scans with the system perturbed, an equal number are obtained without the perturbation, by shifting the irradiation frequency well away from the resonances. Subtraction of the unperturbed FID,

followed by Fourier transformation of the resulting difference FID, generates a spectrum in which only signals which differ between the two are evident, the saturated signal being inverted.

Figure 2.10 shows the difference NOE spectrum obtained by irradiation of the methylene protons at 3.15 ppm. The significant enhancements of the signals at 6.98 ppm and 7.27 ppm identify these signals as being from the protons H-1 and H-9 respectively, which are closest in space to the methylene signals being irradiated. By elimination we can then assign the doublet of doublets at 8.06 ppm to H-3 and the remaining doublet of doublets at 8.00 ppm to H-6.

Irradiation of the signal at 8.00 ppm leads to enhancement of the triplet of doublets at 7.38 ppm, identifying the signal as H-7. This assignment is confirmed by irradiation of the triplet of doublets itself, which enhances both the doublet of doublets at 8.00 ppm, H-6, and the remaining triplet of doublets at 7.52, H-8. Further confirmation comes from irradiation of the proton at 7.52 ppm, leading to enhancement of both the signals at 7.38 and 7.27 ppm and thus completing the ^{1}H-NMR assignment.

2.3.4 ^{13}C-NMR Spectra

^{13}C-NMR data have been reported for a limited range of orthometalated ketones [4,6,8].

The orthomanganated derivatives generally show four signals around δ 200 ppm, three broad ones of intensity 1:1:2 which can be assigned to the terminal CO groups, and the fourth, sharp signal to the carbon of the ketone group, thus having been shifted by 12-21 ppm to lower field on coordination. In the case of the cyclomanganated esters the chemical shift of the coordinated carbonyl is as expected at higher field, usually in the range 170-180 ppm. The aryl carbon atom bonded to manganese is normally found in the range 190-210 ppm, although it can be as low as 166 ppm; when compared with the free ketones, it appears that coordination shifts the signal of the metalated carbon by 60-75 ppm to lower field, those on either side by 9-14 ppm to lower field, with only small shifts for the remaining aryl carbon signals.

The orthorheniated complexes prepared in this study exhibit similar ^{13}C-NMR spectra to their orthomanganated counterparts. The most apparent

Figure 2.10 Difference NOE Spectrum of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)

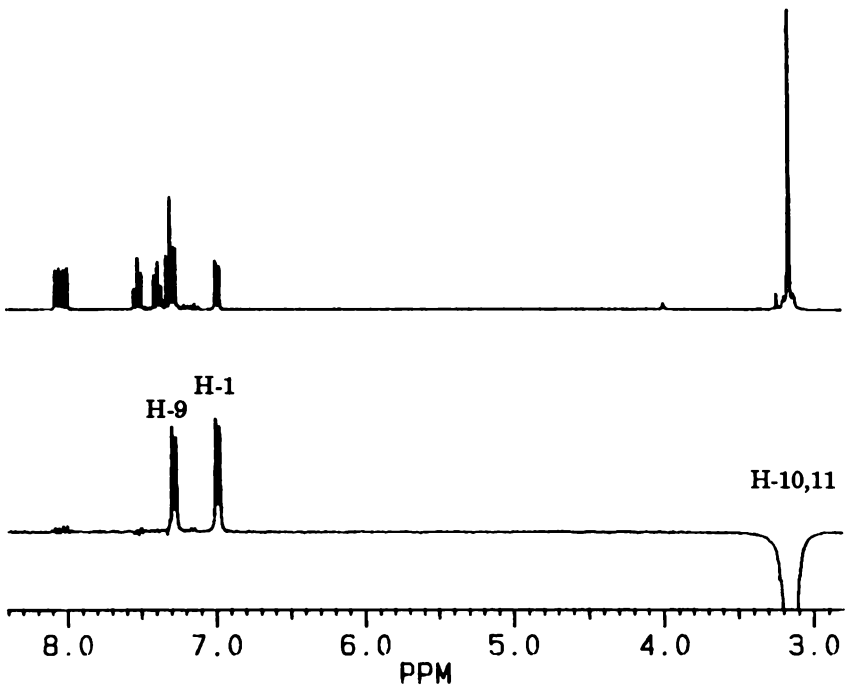
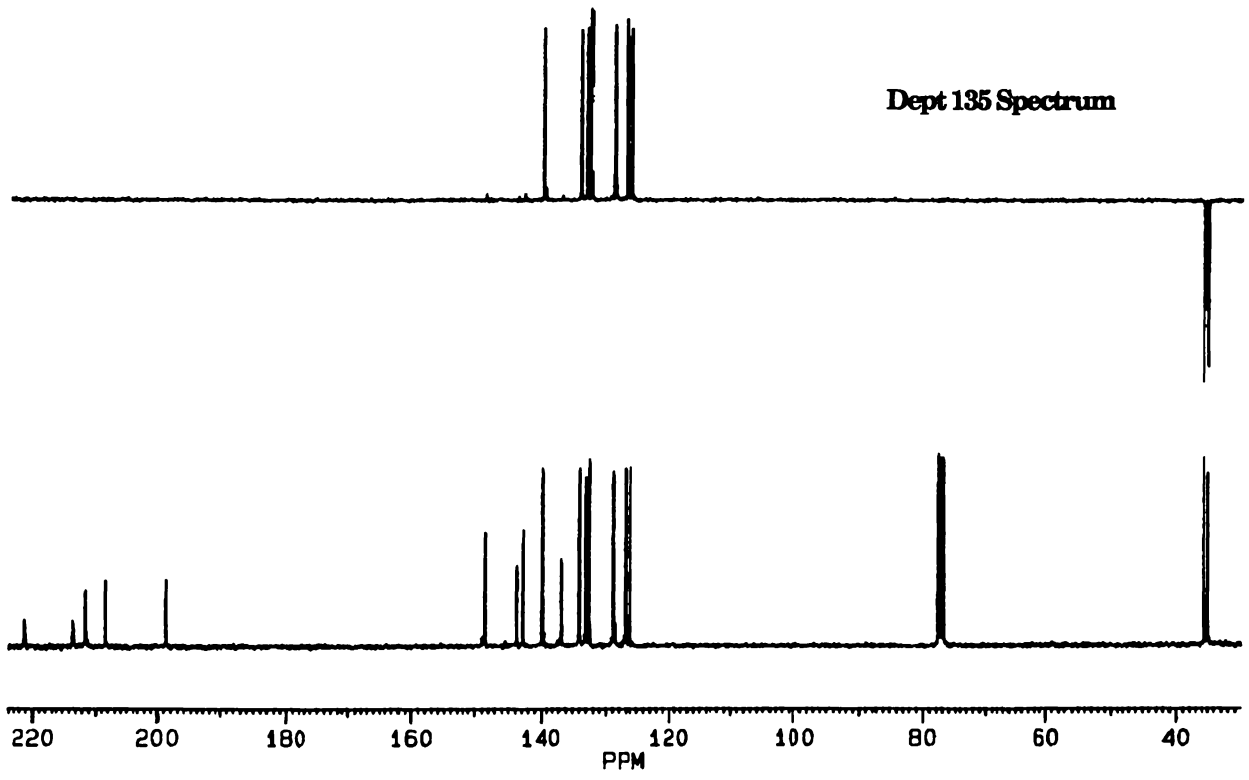


Table 2.3 NOE Data for η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)

Proton Irradiated (ppm)	Protons Enhanced (ppm)
8.06	7.30 (6.1)
8.00	7.38 (6.1)
7.52	7.38 (2.1), 7.27 (3.3)
7.38	8.00 (7.8), 7.52 (4.8)
7.30	8.06 (6.1), 6.98 (3.9)
7.27	7.52 (4.1), 3.15 (3.7)
6.98	7.30 (6.6), 3.15 (5.8)
3.15	7.27 (3.6), 6.98 (3.9)

Figure 2.11 ^{13} *C-NMR Spectra of*
η^2*-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)*



difference is a shift to higher field of the metal carbonyl signals by approximately 20-30 ppm. This upfield shift is a recognized phenomena as one progresses down a given group of the periodic table [22] and is due to the increased diamagnetic shielding caused by the larger number of electrons introduced by the heavier atom. Our results follow the same trends as those observed for simpler organomanganese and rhenium compounds, for example benzylpentacarbonylmanganese (211.1 ppm equatorial; 209.1 ppm axial [23];. compared to benzylpentacarbonyl-rhenium 185.1 ppm equatorial; 181.0 ppm axial).

X-H

Once the ^{1}H-NMR spectra are fully assigned, the assignment of the signals of protonated carbons in the ^{13}C-NMR spectra is straightforward by means of heteronuclear 2D correlation spectroscopy. This is illustrated in Figure 2.12 for **(11)** in which the ^{13}C-NMR spectrum on the vertical axis is assigned from the cross-correlation peaks to the previously assigned ^{1}H-NMR spectrum, on the horizontal axis. Figure 2.13 shows an enlargement of the aromatic region for clarity.

Long-Range Coupling Experiments

To assign the quarternary carbon signals it is necessary to use a C-H shift correlation experiment which is optimised for long-range magnetization transfer. The 2D maps obtained using this technique enable us to establish C-C connectivities since they show correlations between carbons and protons which are separated by two or three bonds. Unfortunately, many one-bond correlations are often visible, complicating spectral interpretation, and sometimes overlapping and obscuring the long-range correlations. In an attempt to overcome this problem a number of pulse sequences have been designed to suppress directly bonded C-H correlations from the long-range experiment [24].

As part of our signal assignment of **(11)** we compare the results of our standard long range C-H experiment, to that incorporating a BIRD pulse sequence (the XHBIRD experiment) and the BIRDTRAP experiment.

Figure 2.12 X-H Spectrum of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)

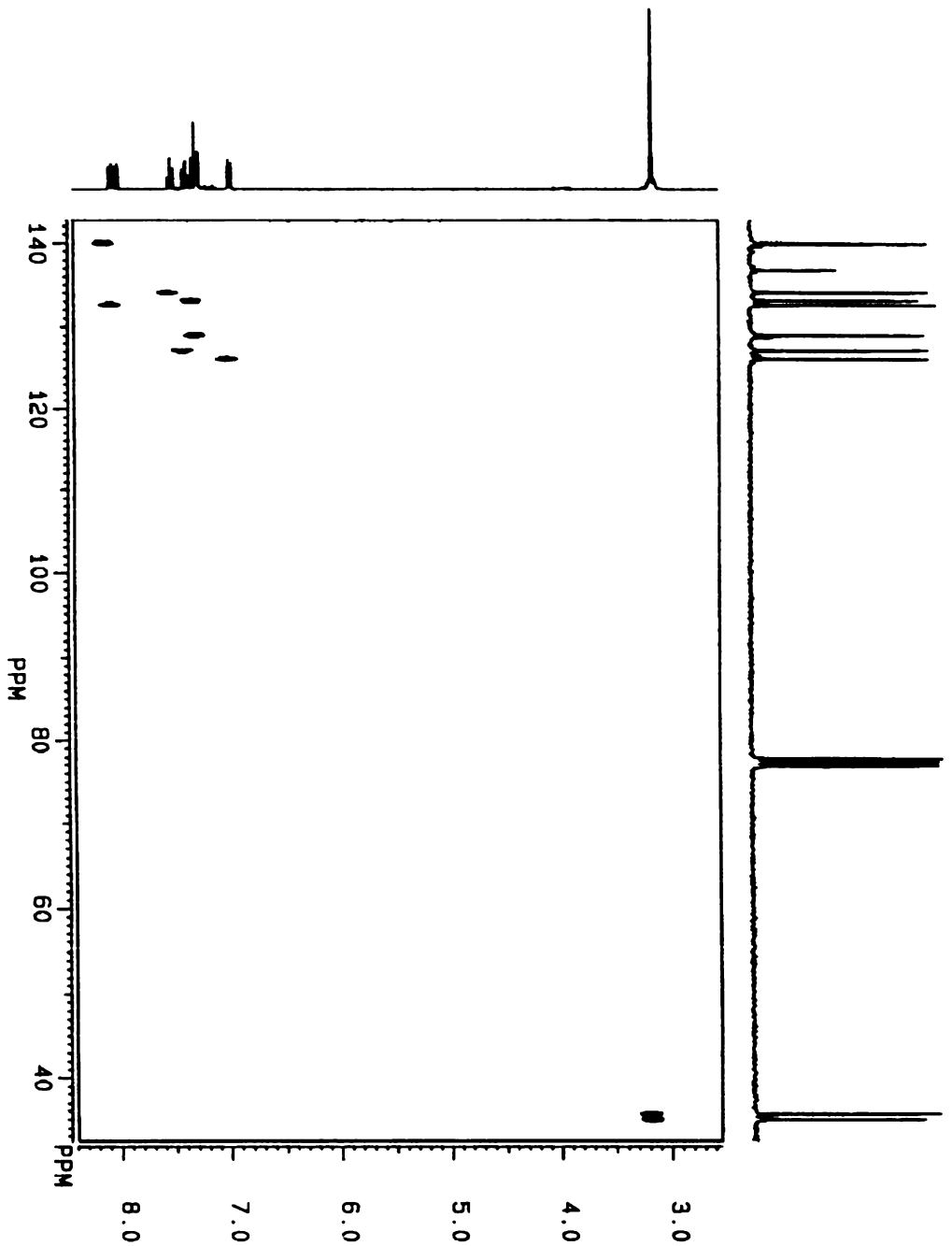
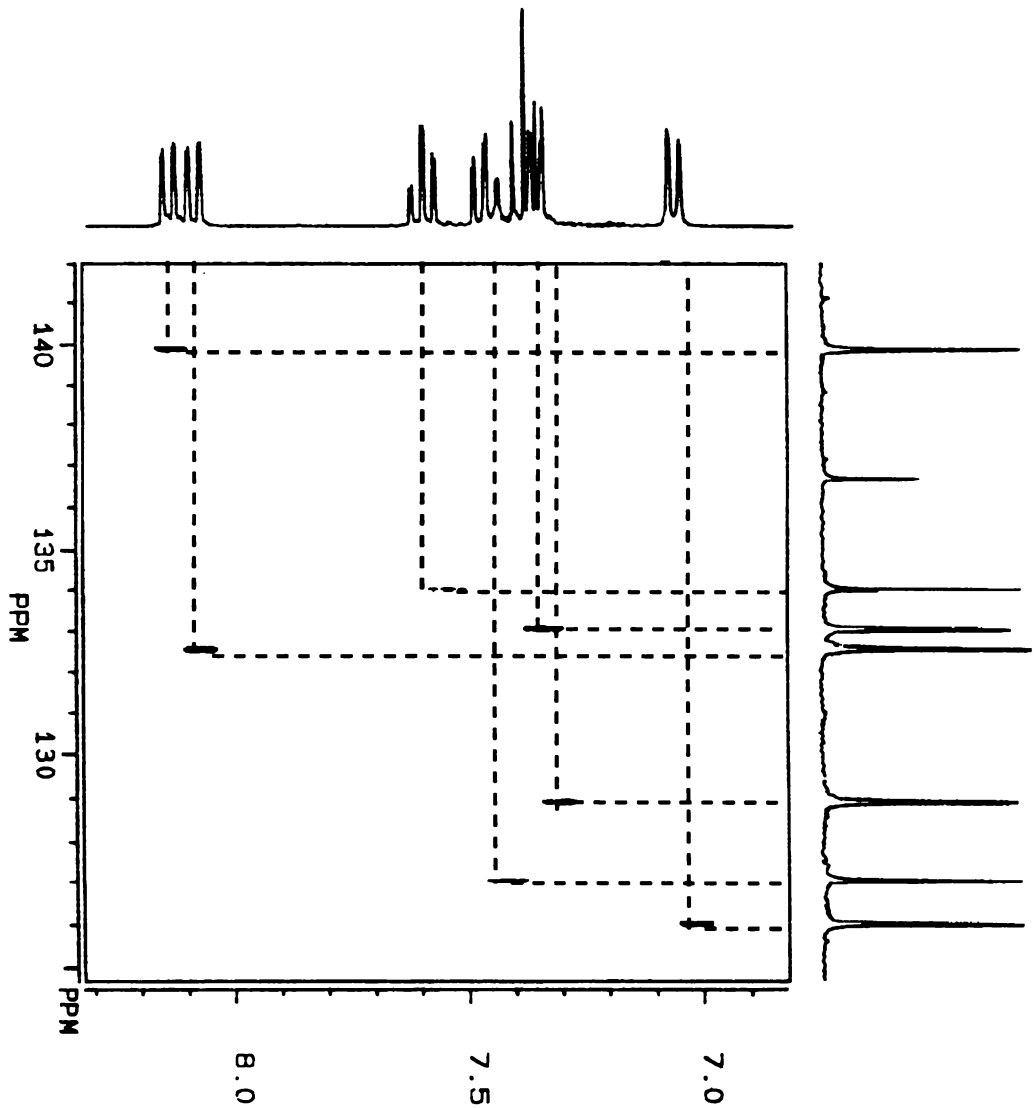


Figure 2.13 X-H Spectrum of the Aromatic Region of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)

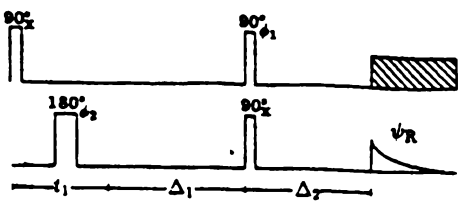


Experimental

The experiments were carried out on a Bruker AC300 spectrometer. 512 scans, using 1K data points were accumulated for each value of t_1 to complete the phase cycles. The 2D data sets were aquired with 64 increments of t_1.

The Standard Long-Range Experiment

The pulse sequence for the long-range heteronuclear chemical shift correlation experiment [24] is shown in Figure 2.14.



t_1=a combination of pulse time and switching time for the first two pulses

$\tau=1/2{}^1J_{CH}{}^{nom}$=3.7 MS

Δ_1=50 MS

Δ_2=30 MS

Figure 2.14

In contrast to regular heteronuclear shift correlation experiments in which only directly bonded C-H correlations are observed, the delays Δ_1 and Δ_2 are optimised for long-range couplings so that both direct and long-range correlations are displayed in the spectra.

XHBIRD

It has been shown that incorporating a BIRD pulse sequence [24] (Figure 2.15) in the middle of the refocusing period Δ_2 significantly improves the efficiency of the basic long-range experiment.

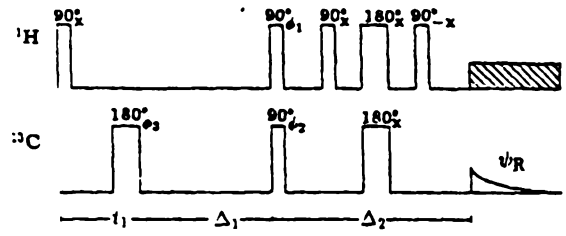


Figure 2.15

Besides decreasing the intensity of the directly bonded correlation peaks, the BIRD pulse sequence suppresses one-bond modulation effects which can otherwise attenuate long range responses. However in samples where the compound has a wide range of C-H coupling constants, the suppression of one-bond correlations is far from complete.

BIRDTRAP

In order to increase the suppression efficiency of the BIRD experiment, a two-step J filter purge (TRAP) sequence is incorporated at the front end of the sequence. This pulse sequence is referred to as the BIRDTRAP sequence [24] and is shown in Figure 2.16.

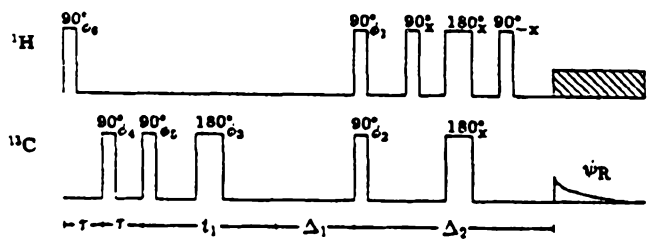


Figure 2.16

The two-step J filter sequence purges the directly bonded correlations from the 2D map by transferring the magnetizations of protons directly bonded to ^{13}C nuclei into multiple-quantum coherences. The purge sequence makes use of the large difference in the magnitudes of direct and long-range coupling constants.

Shown in Figure 2.17 are the f_1 slices at the carbon peaks of **(11)** obtained using the three sequences. The cross sections for a given carbon are

Figure 2.17 The f_1 Slices from the 2D map of (11) Obtained with a Standard Long-Range Sequence, a BIRD Sequence and the BIRDTRAP sequence.

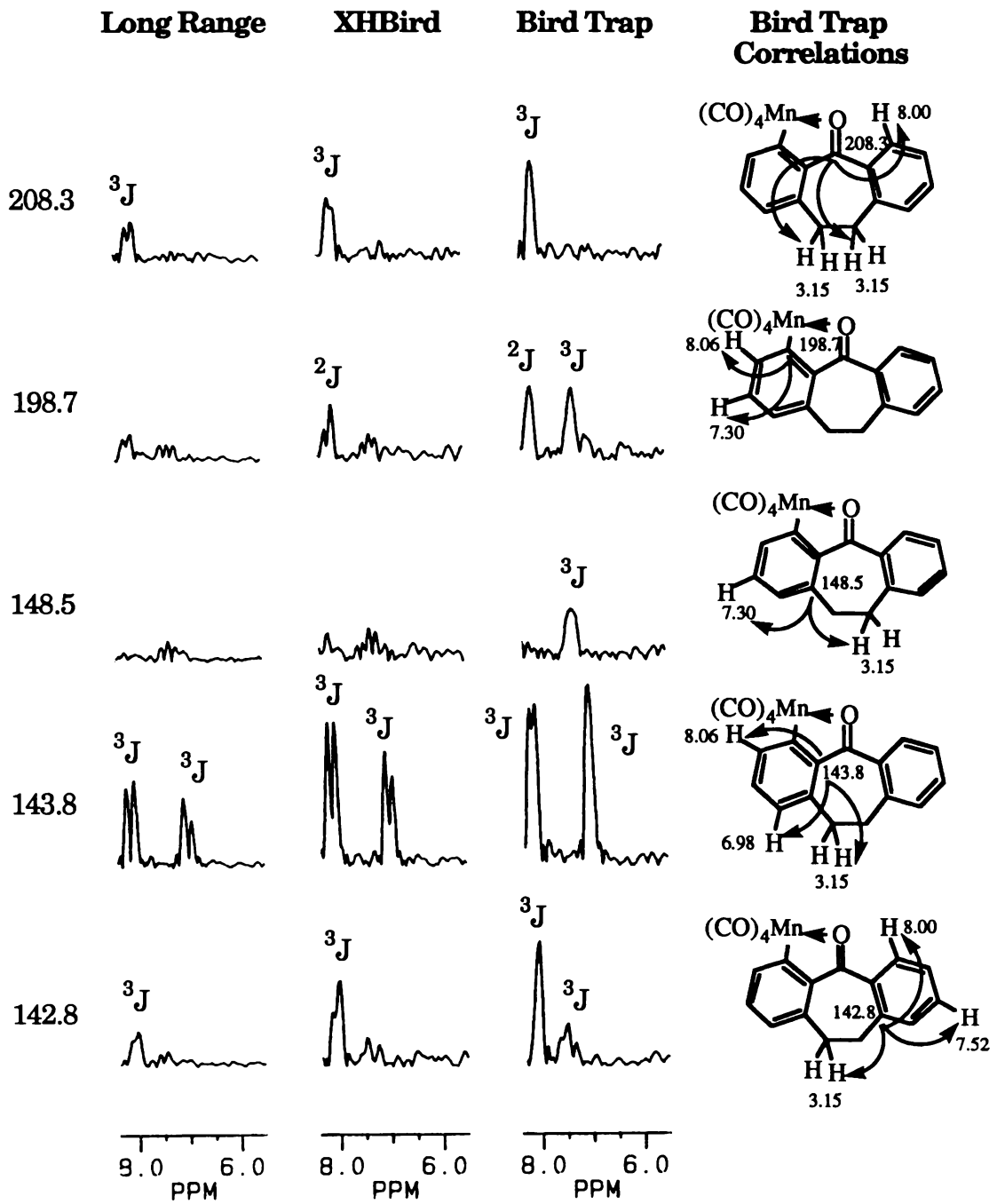


Figure 2.17 continued

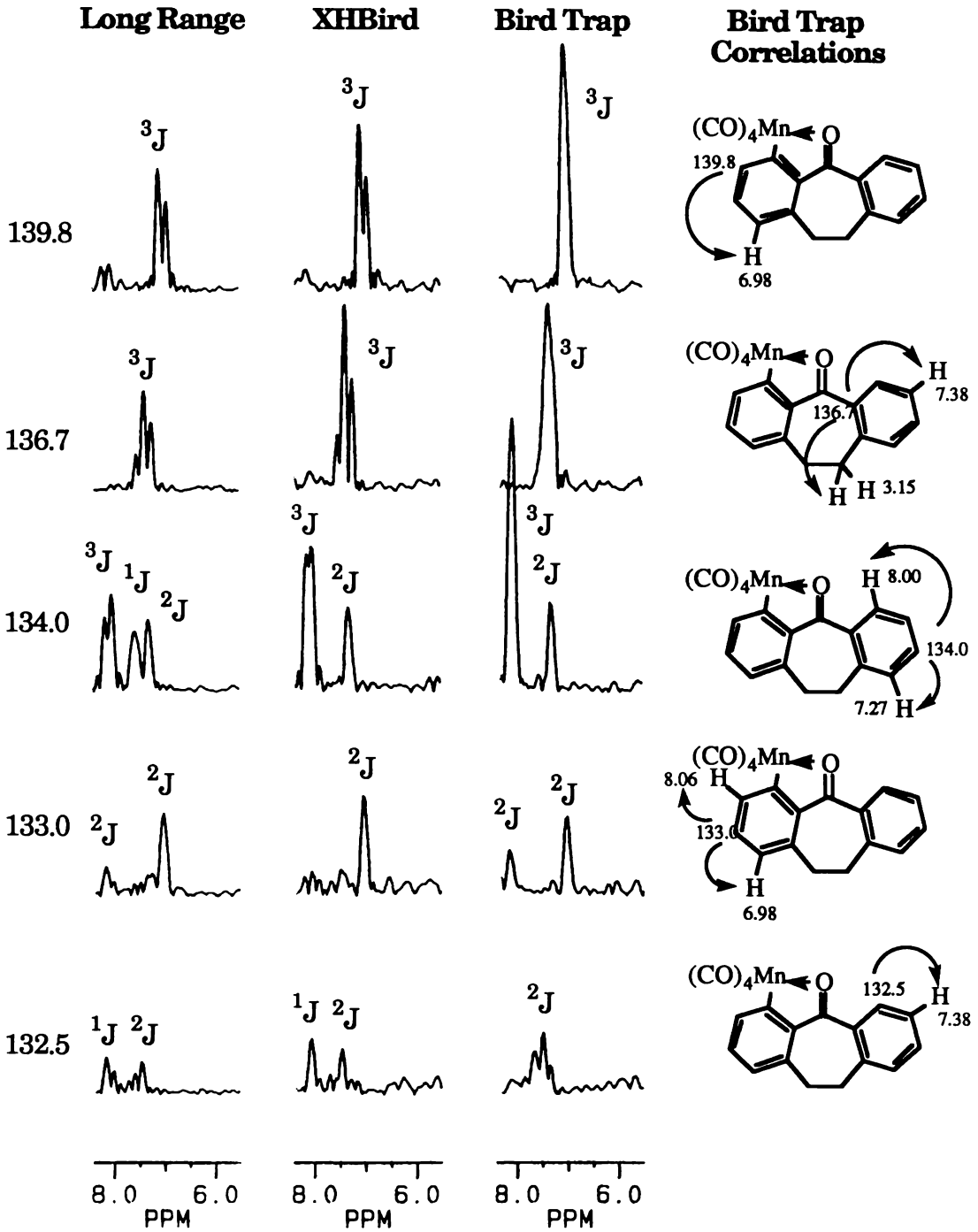
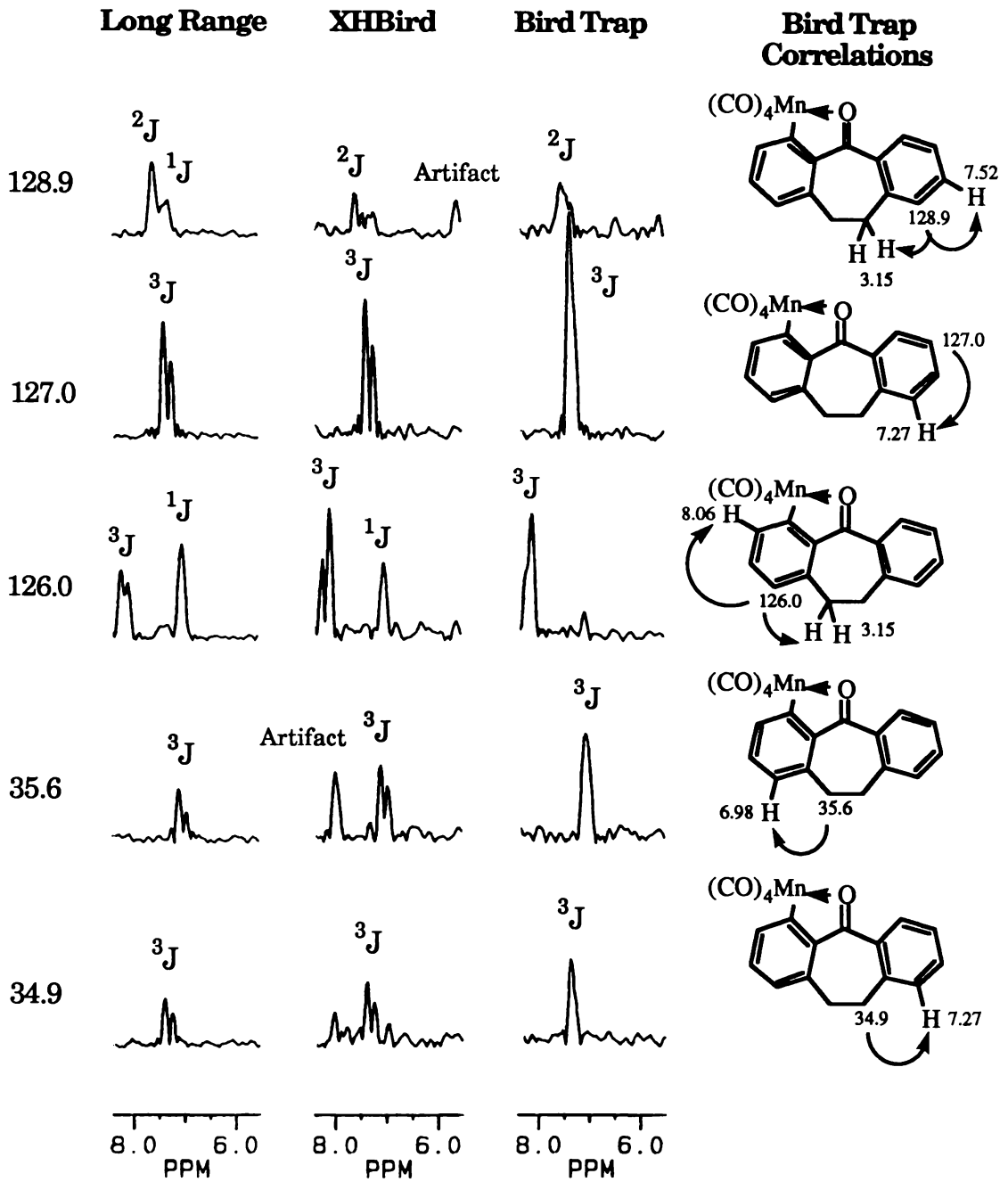


Figure 2.17 continued



plotted at the same absolute intensity in order to allow comparison of the sensitivities of each method.

It is apparent that the BIRDTRAP experiment exhibits higher sensitivity than both the XHBIRD and the standard long-range experiment. Long-range peaks are more intense in the BIRDTRAP spectra, while the directly bonded correlations are virtually eliminated (compare C-1 126.0 ppm). While the XHBIRD experiment is clearly an improvement on the standard long-range experiment, it is neither as sensitive nor as effective at suppressing directly bonded correlations as the BIRDTRAP pulse sequence. It does however appear to exhibit higher resolution than the BIRDTRAP experiment, for reasons which are not apparent. While the loss of the finer detail of the proton signals was not a problem in this case, it is sometimes useful to be able to obtain coupling constants in these types of experiments to confirm assignments. We generally found that the XHBIRD experiment exhibited sufficient sensitivity for our purposes and had the added advantage of reasonable resolution, and so was usually the type of long-range experiment employed. For this example the BIRDTRAP experiment was used to assign the quarternary carbons as it exhibited several extra correlations not revealed by the XHBIRD pulse sequence.

Assignments are made by mapping correlations between ^{13}C and ^{1}H signals. For our compounds, experience has shown that ^{3}J coupling correlations predominate, with ^{2}J correlations usually being of weaker intensity, and ^{4}J correlations being only rarely observed. ^{1}J's can of course be easily identified by comparison with the XH experiment. Assignment then is simply a matter of mapping the correlations, assuming ^{3}J connectivity initially, but modifying this to ^{2}J or ^{4}J if need be, until a self-consistent set of assignments eventuates. In this manner we can assign the quarternary carbons as follows: 208.3 C-5, 198.7 C-4, 148.5 C-11a, 143.8 C-4a, 142.8 C-9a and 136.7 C-5a. The two triplet carbons at 35.6 and 34.9 ppm can also be assigned as C-11 and C-10 respectively as the former reveals a ^{3}J correlation to H-1 while the latter exhibits ^{3}J connectivity with H-9.

The ^{1}H- and ^{13}C-NMR spectra listed in the experimental section were assigned by the same techniques as those described in the above example. Where assignments were not definitive the interchangeable signals are indicated.

2.4 X-Ray Crystal Structure of η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese (13)

The crystal structure of η^2-5-(1,4-benzopyronyl)tetracarbonylmanganese **(13)** (orthomanganated chromone) was determined to study the effect that the coordinated manganese might have on the aromaticity of the chromone molecule and to identify any constraints on the metallocycle ring arising from the incorporation of the donor carbonyl group into a fused ring system.

2.4.1 Results of Preliminary Studies

Yellow/orange rectangular crystals were obtained by recrystallization from ether/hexane (1:20) at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 A°) indicated triclinic symmetry, so the space group $P\bar{1}$ was assumed and was confirmed by the successful refinement.

2.4.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -135 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{13}H_5O_6Mn$

M_r=312.12

Crystal class=triclinic; Space group=$P\bar{1}$

a=7.035 (1), b=8.043 (1), c=10.923 (3) Å

α=91.66 (2)°, β=92.39 (2)°, γ=94.71 (1)°

U=615.10 $Å^3$

D_{calc}=1.63 g cm^{-3}

Z=2

F(000)=312

μ(Mo-K_α)=10.22 cm^{-1}

A total of 2251 unique reflections in the range $2°<\theta<26°$ was collected. These were corrected for Lorentz and polarisation effects and for linear absorption by a Ψ scan method. Of these, 1920 had $I \geq 2\sigma(I)$ and were used in all calculations.

2.4.3 Solution and Refinement

The position of the Mn atom was revealed by automatic analysis of the Patterson map using SHELXS-86. All other non-hydrogen atoms were revealed by a subsequent difference map phased on the Mn atom. In the final cycle of full-matrix least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R=0.0317, R_w=0.0362 where $w=[\sigma(F)^2 + 0.001F^2]^{-1}$ and with no parameter shifting more than 0.001σ. A final difference map showed no peaks or troughs greater than 0.27 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 2.4 and 2.5. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix II.

Figure 2.18 shows the metalated chromone molecule.

2.4.4 Discussion of the Structure

The structure is essentially planar (with the exception of the two axial CO ligands) consisting of a chromone (1,4-benzopyrone) system with a tetracarbonylmanganese unit attached at the 5-position. The acyl oxygen group is coordinated to the manganese atom giving rise to a six-coordinate manganese and a five-membered cyclometalated ring.

In Table 2.6 for comparison are summarised some relevant bond length

Figure 2.18 Perspective View of
η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese (13)

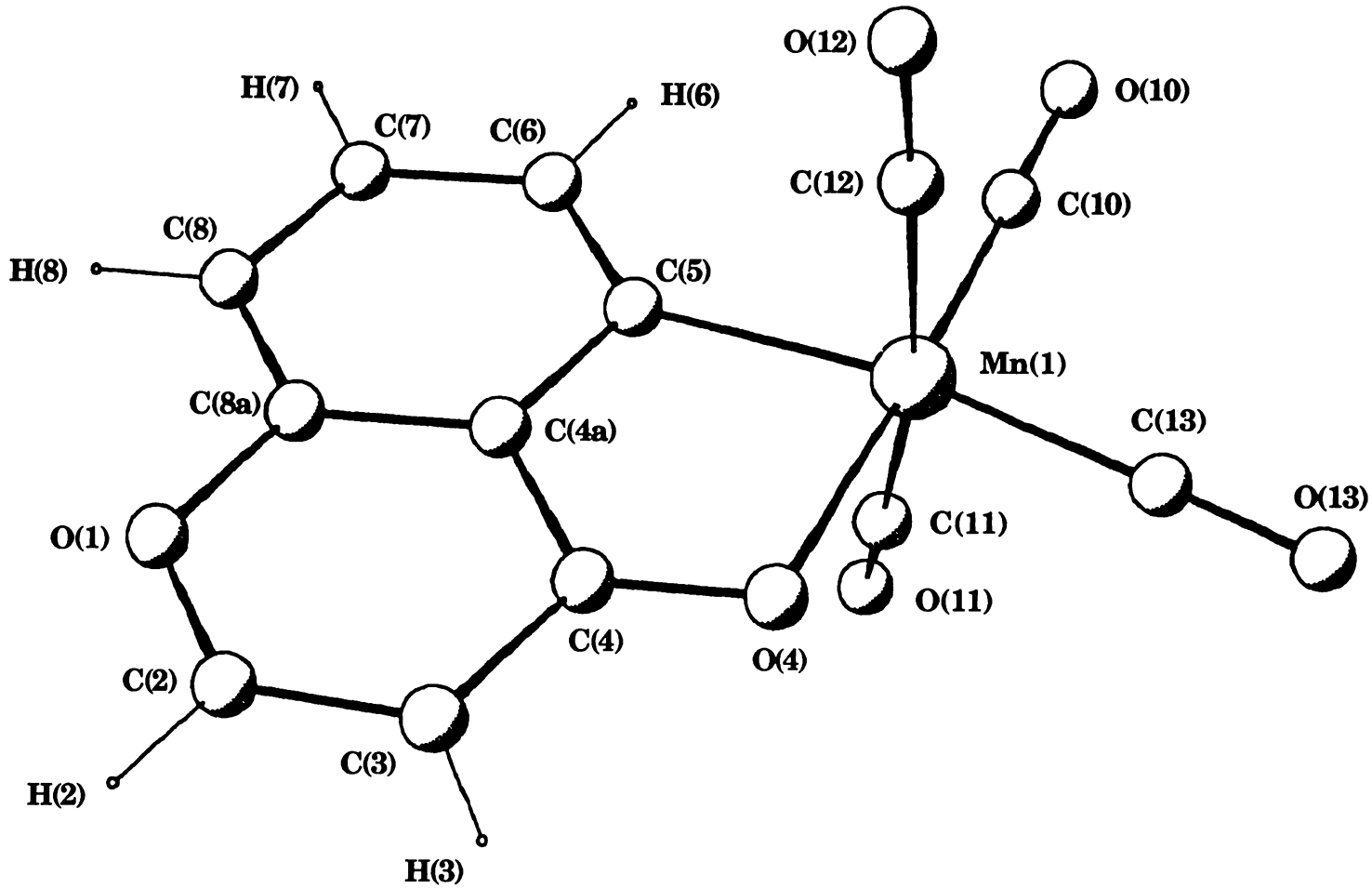


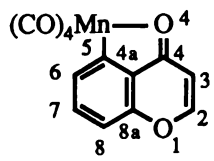
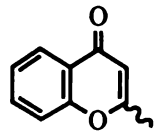
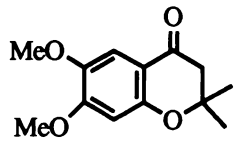
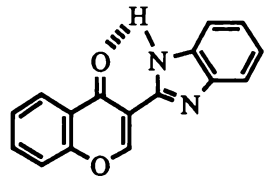
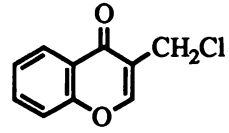
Table 2.4 Bond Lengths (Å) for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese (13)

Mn(1)	---C(5)	2.039(2)	C(5)	---C(6)	1.388(4)
Mn(1)	---C(9)	1.837(3)	C(4a)	---C(8a)	1.387(3)
Mn(1)	---C(10)	1.788(3)	C(2)	---O(1)	1.340(3)
Mn(1)	---C(11)	1.858(3)	C(8)	---C(8a)	1.389(4)
Mn(1)	---C(12)	1.851(3)	C(8)	---C(7)	1.377(4)
Mn(1)	---O(4)	2.079(2)	C(8a)	---O(1)	1.371(3)
C(3)	---C(4)	1.432(3)	C(7)	---C(6)	1.392(4)
C(3)	---C(2)	1.343(4)	C(9)	---O(9)	1.148(3)
C(4)	---C(4a)	1.424(4)	C(10)	---O(10)	1.143(3)
C(4)	---O(4)	1.260(3)	C(11)	---O(11)	1.133(3)
C(5)	---C(4a)	1.414(3)	C(12)	---O(12)	1.130(3)

Table 2.5 Bond Angles (°) for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese (13)

C(5)	-Mn(1)	-C(10)	96.2(1)	Mn(1)	-C(5)	-C(4a)	109.6(2)
C(5)	-Mn(1)	-C(9)	170.2(1)	Mn(1)	-C(5)	-C(6)	134.8(2)
C(5)	-Mn(1)	-C(12)	85.8(1)	C(4a)	-C(5)	-C(6)	115.6(2)
C(5)	-Mn(1)	-C(11)	84.6(1)	C(4)	-C(4a)	-C(5)	117.1(2)
C(5)	-Mn(1)	-O(4)	81.3(1)	C(4)	-C(4a)	-C(8a)	120.3(2)
C(9)	-Mn(1)	-C(10)	93.2(1)	C(5)	-C(4a)	-C(8a)	122.6(2)
C(9)	-Mn(1)	-C(12)	97.0(1)	C(3)	-C(2)	-O(1)	125.5(2)
C(9)	-Mn(1)	-C(11)	93.2(1)	C(8a)	-C(8)	-C(7)	117.1(2)
C(9)	-Mn(1)	-O(4)	89.4(1)	C(4a)	-C(8a)	-C(8)	120.7(2)
C(10)	-Mn(1)	-C(12)	88.6(1)	C(4a)	-C(8a)	-O(1)	120.5(2)
C(10)	-Mn(1)	-C(11)	87.6(1)	C(8)	-C(8a)	-O(1)	118.8(2)
C(10)	-Mn(1)	-O(4)	176.7(1)	C(8)	-C(7)	-C(6)	122.7(3)
C(11)	-Mn(1)	-C(12)	169.2(1)	C(5)	-C(6)	-C(7)	121.3(2)
C(11)	-Mn(1)	-O(4)	94.2(1)	Mn(1)	-C(9)	-O(9)	177.7(3)
C(12)	-Mn(1)	-O(4)	89.1(1)	Mn(1)	-C(10)	-O(10)	179.2(3)
C(4)	-C(3)	-C(2)	118.2(3)	Mn(1)	-C(11)	-O(11)	174.4(3)
C(3)	-C(4)	-C(4a)	117.0(2)	Mn(1)	-C(12)	-O(12)	176.4(2)
C(3)	-C(4)	-O(4)	124.1(2)	C(2)	-O(1)	-C(8a)	118.4(2)
C(4a)	-C(4)	-O(4)	118.9(2)	Mn(1)	-O(4)	-C(4)	113.1(2)

Table 2.6 Bond Length Data (Å) for Selected Chromones and Chromanones

	 (13)	(A)  2-((1R,2S,3S,4R)-1,2:3,4-Diepoxy-1-methylpentyl)-chromone [25]	(B)  6,7-Dimethoxy-2,2-dimethyl-4-chromanone [26]	(C)  3-(2-Benzimidazoyl)-4H-(1)benzopyran-4-one [27]	(D)  3-(Chloromethyl)chromen-4-one [28]
O(1)-C(2)	1.340(3)	1.361	1.461(5)	1.352	1.355(3)
C(2)-C(3)	1.343(4)	1.329	1.524(7)	1.344	1.339(5)
C(3)-C(4)	1.432(3)	1.430	1.523(7)	1.449	1.460(3)
C(4)-C(4a)	1.424(4)	1.464	1.447(6)	1.478	1.472(4)
C(4)-O(4)	1.260(3)	1.202	1.218(6)	1.237	1.234(4)
C(4a)-C(5)	1.414(3)	1.415	1.414(6)	1.404	1.404(4)
C(5)-C(6)	1.388(4)	1.346	1.361(6)	1.386	1.371(4)
C(6)-C(7)	1.392(4)	1.396	1.428(6)	1.392	1.392(6)
C(7)-C(8)	1.377(4)	1.360	1.375(6)	1.377	1.369(4)
C(8)-C(8a)	1.389(4)	1.391	1.384(6)	1.397	1.390(4)
C(8a)-C(4a)	1.387(3)	1.382	1.381(6)	1.383	1.392(4)
C(8a)-O(1)	1.371(3)	1.382	1.380(5)	1.377	1.384(3)
		esd= 0.005-0.01 Å		no esds quoted	

data from the crystal structures of related systems.

Examination reveals that the most significant structural features of the orthomanganated chromone are the differences in the C(4)-O(4), C(4a)-C(4), C(3)-C(2) and O(1)-C(2) bond lengths, compared with (A), (B), (C) and (D).

The C(4)-O(4) bond length is lengthened significantly on coordination to manganese, 1.260 Å compared with 1.202 Å in (A), which is the most relevant example available for comparison. This indicates a decrease in double bond character, as would be expected due to the donation of electron density from the acyl oxygen to the coordinatively unsaturated manganese atom. Comparison with the equivalent bond in (C) suggests that the effect of the manganese coordination on the carbonyl functionality of the ketone group is considerably stronger than that of the intramolecular H-bonding interaction, the bond length only increasing by some 0.035 Å in this structure when compared to (A).

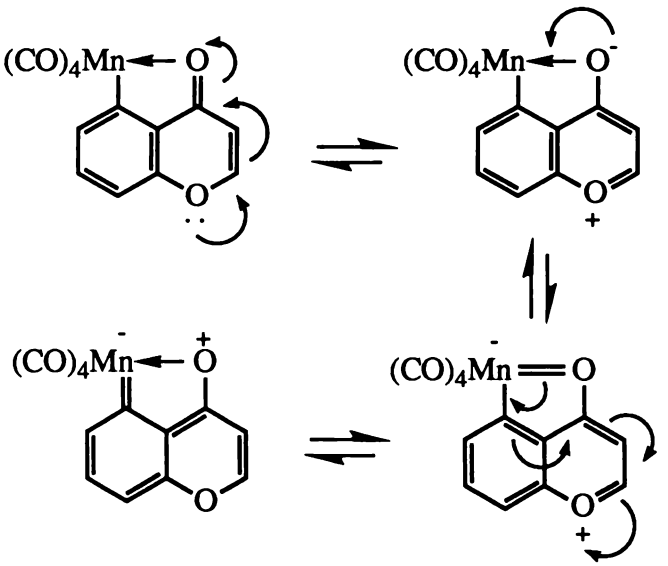
There is a marked decrease in the bond length of the C(4a)-C(4) bond. This bond is significantly shorter, (by some 0.038 Å) than the equivalent bond length in (A). This is in accord with lengthening of C(4)-O(4) and the establishment of aromaticity in the cyclometalated ring, and is also reflected in the Mn-C(5) distance (2.039 Å) which appears to be shorter than expected for a single bond (>2.1 Å) suggesting that there is significant multiple bonding.

The O(1)-C(2) bond length is shortened to some degree in the orthomanganated chromone (1.341 Å cf. 1.361 Å in (A)) indicating a small increase in multiple bond character. This is supported by comparison with the O(1)-C(2) bond length of (B) (1.461 Å) which exhibits predominately single bond character.

The C(2)-C(3) bond length is slightly longer however, 1.343 Å compared with 1.329 Å in (A). These trends are consistent with delocalisation of electron density from the available electron lone pair on O(1) over the pyrone ring onto the acyl oxygen. This trend is also shown in (C), although to a lesser extent, as would be expected for the weaker intramolecular H-bonding interaction.

The O(1)-C(8a) and remaining C-C bond lengths remain reasonably constant within the experimental errors of the figures quoted, suggesting that there is little change in aromaticity over these bonds.

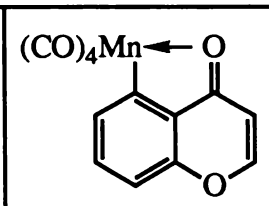
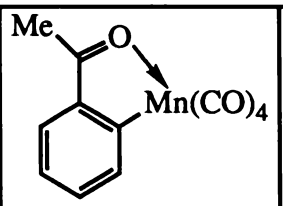
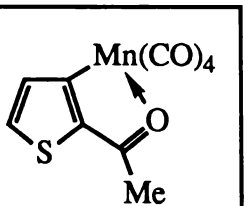
An extensively delocalised π -bonding system over both the cyclometalated and pyrone rings is therefore indicated (Scheme 2.1).



Scheme 2.1

The C(5)-Mn-O(4) bite angle of 81.2° is very similar to the corresponding angles observed for other cyclomanganated structures, while the relative Mn-CO distances and C-Mn-C angles of the $Mn(CO)_4$ group fall into the pattern established for other orthomanganated complexes [8,29].

Table 2.7 C-Mn-O Bite Angles (°) for Selected Orthomanganated Complexes

			
C-Mn-O bite angle °	81.2(1)	79.4(2)	79.9(2)

The uniformity in geometry of the cyclometalated ring is perhaps a reflection of the steric requirements that need to be met for successful cyclometalation (see section 2.2.4).

2.5 X-Ray Crystal Structure of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32)

The structure of the orthorheniated thiophene was determined to provide a direct comparison between an orthomanganated and orthorheniated complex. A crystallographic study was also of interest due to the paucity of good quality crystallographic data reported in the literature for rhenium containing cyclometalated compounds incorporating an oxygen donor atom.

2.5.1 Results of Preliminary Studies

Yellow rectangular crystals were obtained by recrystallization from pentane/chloroform at -20 °C. Preliminary precession photography indicated triclinic symmetry, so the space group $P\bar{1}$ was assumed and was confirmed by the successful refinement.

2.5.2 Data Collection

Intensity data were obtained on a Enraf-Nonius CAD4 automatic four-circle diffractometer at the University of Auckland.

Crystal Data

Formula=$C_{12}H_9O_5ReS$

M_r=451.467

Crystal class=triclinic; Space group=$P\bar{1}$

a=8.064 (2), b=9.026 (3), c=10.999 (6) Å

α=101.06 (4)°, β=111.44 (3)°, γ=102.65 (2)°

U=693.8(5) $Å^3$

D_{calc}=2.16 g cm^{-3}

Z=2

F(000)=424

μ(Mo-K_α)=90 cm^{-1}

A total of 2575 reflections in the range $0°<\theta<25°$ was collected at 23 °C, corresponding to 2424 unique reflections. 2375 data with $I>2\sigma(I)$ after correction for Lorentz, polarisation and absorption effects were used for all calculations.

2.5.3 Solution and Refinement

The position of the rhenium atom was located by Patterson methods. All other non-hydrogen atoms were revealed by a subsequent difference map phased on the rhenium atom. In the final cycle of full-matrix least-squares refinement all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in their calculated positions.

The refinement converged with R=0.0649, R_w=0.0663 where $w=[\sigma(F)^2 + 0.009031F^2]^{-1}$. No parameter shifted more than 0.1σ in the final cycle, other than those associated with the orientation of the methyl group. A final difference map revealed a ripple of electron density associated with the rhenium atom, +/-3.9 e $Å^{-3}$, but was otherwise unremarkable.

Bond lengths and angles are presented in Tables 2.8 and 2.9. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix III.

The structure is shown in Figure 2.19.

2.5.4 Discussion of the Structure

The molecule consists of two coplanar five-membered heterocycles with essentially octahedral coordination about the rhenium atom, although the small "bite" of the chelating ligand gives rise to a C(9)-Re-O(5) angle of

Figure 2.19 Perspective View of η^2-(4 -Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32)

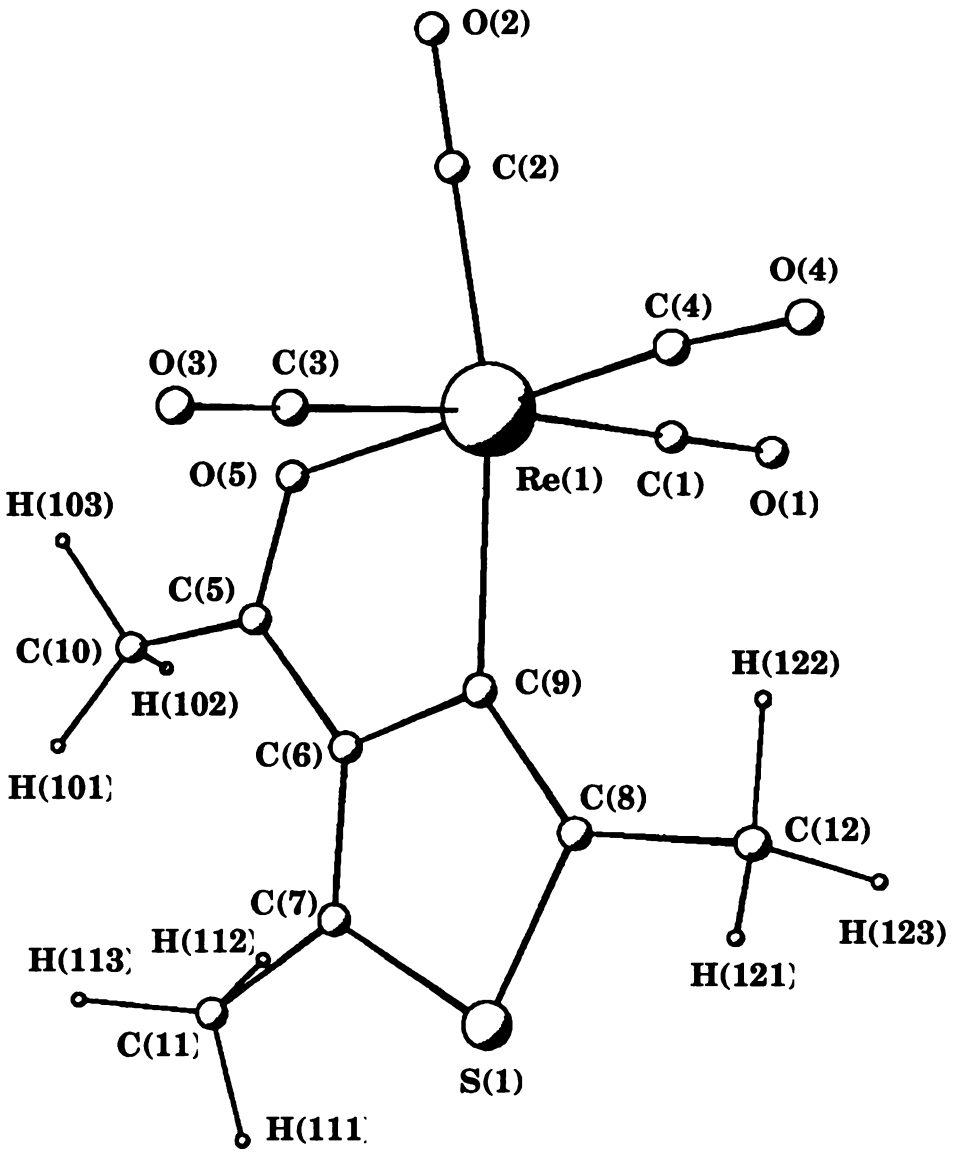


Table 2.8 Bond Lengths (Å) for η^2-(4 -Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32)

Re(1)	---C(1)	2.01(2)	C(3)	---O(3)	1.14(2)
Re(1)	---C(2)	1.98(1)	C(4)	---O(4)	1.22(2)
Re(1)	---C(3)	1.98(2)	C(5)	---C(6)	1.43(2)
Re(1)	---C(4)	1.85(2)	C(5)	---C(10)	1.48(2)
Re(1)	---C(9)	2.17(1)	C(5)	---O(5)	1.25(1)
Re(1)	---O(5)	2.17(1)	C(6)	---C(7)	1.39(1)
S(1)	---C(7)	1.69(1)	C(6)	---C(9)	1.46(2)
S(1)	---C(8)	1.72(1)	C(7)	---C(11)	1.52(1)
C(1)	---O(1)	1.12(2)	C(8)	---C(9)	1.37(2)
C(2)	---O(2)	1.13(2)	C(8)	---C(12)	1.53(2)

Table 2.9 Bond Angles (°) for η^2-(4 -Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32)

C(1)	-Re(1)	-C(2)	93.2(5)	Re(1)	-C(3)	-O(3)	178(1)
C(1)	-Re(1)	-C(3)	173.2(3)	Re(1)	-C(4)	-O(4)	174(2)
C(1)	-Re(1)	-C(4)	90.1(6)	C(6)	-C(5)	-C(10)	125(1)
C(1)	-Re(1)	-C(9)	87.8(5)	C(6)	-C(5)	-O(5)	117(1)
C(1)	-Re(1)	-O(5)	87.6(4)	C(10)	-C(5)	-O(5)	117(1)
C(2)	-Re(1)	-C(3)	93.4(5)	C(5)	-C(6)	-C(7)	130.9(9)
C(2)	-Re(1)	-C(4)	91.0(7)	C(5)	-C(6)	-C(9)	115(1)
C(2)	-Re(1)	-C(9)	164.6(5)	C(7)	-C(6)	-C(9)	113(1)
C(2)	-Re(1)	-O(5)	89.7(4)	S(1)	-C(7)	-C(6)	110.3(7)
C(3)	-Re(1)	-C(4)	87.9(6)	S(1)	-C(7)	-C(11)	121.2(8)
C(3)	-Re(1)	-C(9)	86.3(5)	C(6)	-C(7)	-C(11)	128(1)
C(3)	-Re(1)	-O(5)	94.3(4)	S(1)	-C(8)	-C(9)	112.5(8)
C(4)	-Re(1)	-C(9)	104.3(6)	S(1)	-C(8)	-C(12)	118.3(9)
C(4)	-Re(1)	-O(5)	177.7(4)	C(9)	-C(8)	-C(12)	129(1)
C(9)	-Re(1)	-O(5)	75.0(4)	Re(1)	-C(9)	-C(6)	112.3(8)
C(7)	-S(1)	-C(8)	93.7(5)	Re(1)	-C(9)	-C(8)	137.7(8)
Re(1)	-C(1)	-O(1)	176(1)	C(6)	-C(9)	-C(8)	110(1)
Re(1)	-C(2)	-O(2)	178(1)	Re(1)	-O(5)	-C(5)	119.8(8)

75.0°, and the out-of-plane *trans*-CO ligands are folded slightly towards the C(9) atom (C(9)-Re-C(1) 87.8°, C(9)-Re-C(3) 86.3°). The equatorial carbonyl C(4)-O(4) shows distortion away from its expected octahedral geometry (C(9)-Re-C(4) 104.3°), while only minor distortions are observed for the other equatorial carbonyl.

Further evidence of strained geometry is reflected in the C(5)-C(6)-C(7) and Re-C(9)-C(8) angles which are both larger than expected (130.9 and 137.7°, respectively), while the methyl groups are bent towards the sulphur atom to give C(6)-C(7)-C(11) and C(9)-C(8)-C(12) angles of 128.4 and 129.1° respectively. These distortions probably arise more from the crowding in the tetrasubstituted ring than from difficulties in fusing two five-membered rings, as the related structure of orthomanganated 2-acetylthiophene which also incorporates two coplanar five-membered heterocycles exhibits little evidence of strain [6,8].

Although the large esds, due to the dominance of the scattering by the rhenium atom, preclude rigorous analysis of bond lengths, several trends are apparent.

The C(5)-C(6) distance (1.429 Å) is shortened by ~0.03 Å with respect to an average sp^2-sp^2 distance of 1.46 Å [30], while the C(6)-C(7) distance (1.393 Å) and the C(5)-O(5) distance (1.253 Å) are both lengthened slightly (~0.03 Å) with respect to typically observed bond lengths [31].

The C(7)-S bond is noticeably shorter than the C(8)-S bond (1.687 vs 1.719 Å) indicating that the C(7)-S bond has more double bond character.

The Re-C(9) bond (2.170 Å) is almost midway between Re-C_{sp2} single (~2.22 Å) and double (~2.09 Å) bonds [32] suggesting that there is significant multiple bonding.

The variations in C-C bond lengths within the molecule can be understood in terms of contributions from both resonance forms (Figure 2.20), indicating a delocalised π–bonding network over both rings.

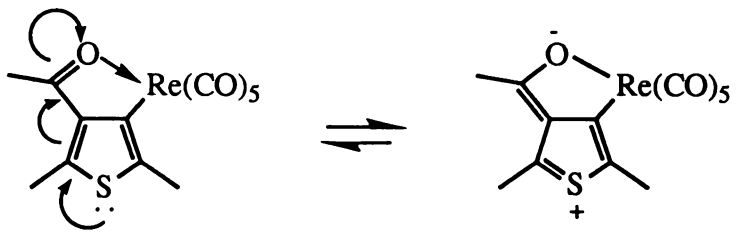
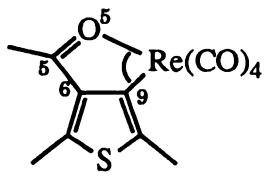
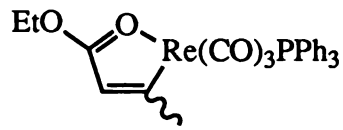


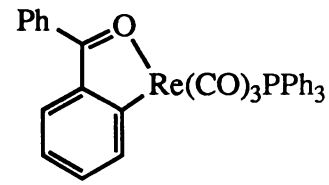
Figure 2.20

A comparison of our structure with bond lengths and angles of similar bonds in two other rhenium metallocycles whose structures have been previously determined, show that the metallocyclic ring is very similar in all three species.

Table 2.10 Bond Lengths (Å) and Chelate Angle (°) Data for Selected Rhenium Compounds







	***fac*-Tricarbonyl[1-ethoxy -4-(trimethylsilyl)-1-oxo-2-butenyl-C^3,O]-(triphenyl phosphine)rhenium**	**(2-Benzoylphenyl) tricarbonyl(triphenyl phosphine)rhenium**
Re-C(9)	2.170(12)	2.162(2)	2.199(10)
C(5)-O(5)	1.253(14)	1.244(4)	1.240(17)
O(5)-Re	2.170(10)	2.191(2)	2.174(9)
O(5)-Re-C(9)	75.0(4)	75.65(15)	74.4(4)

A comparison of bond lengths (Figure 2.21) and angles (Figure 2.22) between the orthorheniated and orthomanganated [4,8] analogues of 3-acetyl-2,5-dimethylthiophene also reveals very little change in bond lengths and angles bar those expected for increasing atom size on moving down the period from manganese to rhenium, an increase in atomic radii of 0.11 Å. This is reflected in the increased Re-CO (Re-C(1) +0.15 Å, Re-C(2) +0.14 Å, Re-C(3) +0.13 Å, Re-C(4) +0.07 Å), Re-C(9) (+0.13 Å) and Re-O(5) (+0.12 Å) bond lengths, although why the Re-C(4) bond length appears shorter than expected is unclear.

Figure 2.21 Selected Bond Lengths of Orthorheniated (A) and Orthomanganated (B) 3-Acetyl-2,5-dimethylthiophene

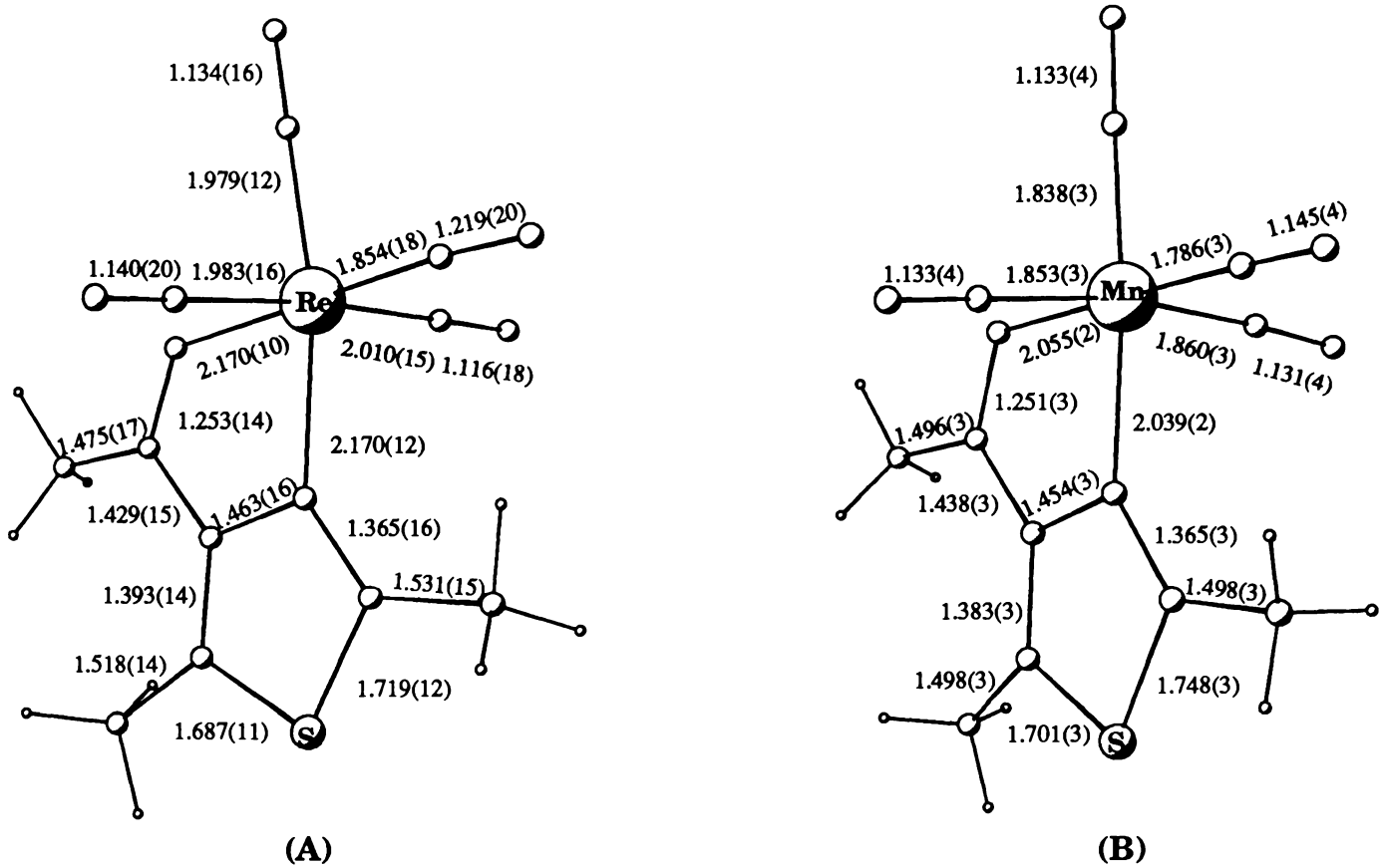
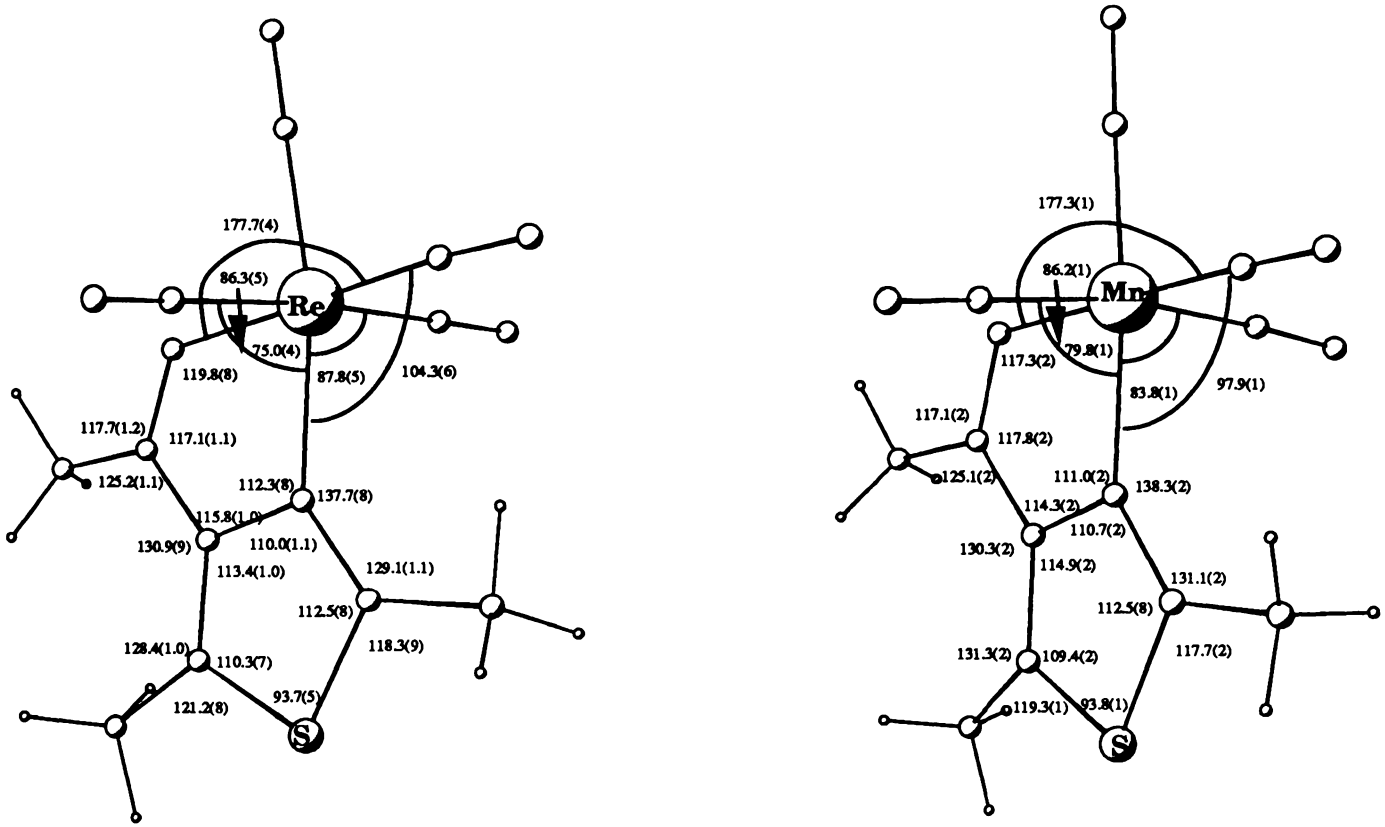


Figure 2.22 Selected Bond Angles (°) of Orthorheniated (A) and Orthomanganated (B) 3-Acetyl-2,5-dimethylthiophene



The smaller chelate bite angle for the rhenium compound (75.0° for O(5)-Re-C(9) vs 79.8° for O(5)-Mn-C(9)) suggests increased strain in the metallocyclic ring showing even further deviation from ideal geometry than for manganese. It is interesting that for rhenium the small chelate bite angle seems to be compensated for almost entirely by the large C(9)-Re-C(4) bond angle of 104.3°. If this distortion was due solely to steric interaction between the C(4) carbonyl and the C(12) methyl group we would expect a bigger distortion for the manganese structure than for rhenium, reflecting the closer interaction between the two ligands due to the smaller atom size. Clearly this is not the case, as the C(4) carbonyl distortion is ~6° larger for rhenium than for manganese. It may be worth noting that both the O(5)-Re-C(4) and O(5)-Mn-C(4) bond angles are reasonably linear (177.7 and 177.3°, respectively), and so perhaps the C(4) distortion is fulfilling a requirement for linearity in this vector. The large C(9)-Re-C(4) bond angle may therefore be a function of the larger C(5)-O(5)-Re angle (119.8° cf. 117.3° for manganese) which is necessary to accommodate the bulky rhenium atom in the metallocycle ring.

2.6 Experimental Section

2.6.1 Preparation of Starting Materials

Preparation of Benzylpentacarbonylmanganese

$PhCH_2Mn(CO)_5$ was prepared by the standard method of Closson *et al* [35,36] m.p. 34.5-36 °C. (lit., 37.5-38.5 °C [35]) IR: (hexane) ν(CO) 2108 (s), 2009 (vs, br), 1992 (vs) cm^{-1}.

Preparation of Benzylpentacarbonylrhenium

$PhCH_2Re(CO)_5$ was prepared by the method of Hieber *et al* [37] m.p. 30-31 °C (lit., 33-34 °C [37]). IR: (hexane) ν(CO) 2127 (m), 2018 (vs), 2014 (vs) 1986 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.25 (2H, *t*, $^3J_{3',2'}=^3J_{3',4'}=^3J_{5',4'}=^3J_{5',6'}$= 7.5 Hz, H-3',5'), 7.13 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=7.5 Hz, H-2',6'), 6.93 (1H, *t*, $^3J_{4',3'}=^3J_{4',5'}$=7.5 Hz, H-4') 2.53 (2H, *s*, H-1). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 185.1 (*s*, $C{\equiv}O_{eq}$), 181.0 (*s*, $C{\equiv}O_{ax}$), 155.0 (*s*, C-1'), 128.4 (*d*, C-3',5'), 125.5 (*d*, C-2',6'), 122.5 (*d*, C-4'), -2.2 (*t*, C-1).

Preparation of Isopropyl thiophene-2-carboxylate (29)

2-Thiophenecarboxylic acid (5.0 g, 0.039 mol) was added to isopropyl alcohol (30 ml, 0.39 mol) with a catalytic amount of conc. H_2SO_4 (0.5 ml). The mixture was refluxed gently for 24 h. The excess alcohol was distilled off using a water bath as heat source and the residue was allowed to cool before pouring into a separating funnel containing H_2O (100ml)/diethyl ether (40ml) and further extracted with diethyl ether (2 x 10 ml). The ethereal solution was washed with saturated $NaHCO_3$ soln., then H_2O and dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure to give a brown oil. The oil was distilled and *isopropyl thiophene-2-carboxylate* was collected as a colourless liquid (1.25 g, 19 %), b.p. 220 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.77 (1H, *dd*, $^3J_{3,4}$=3.8 Hz, $^4J_{3,5}$=1.2 Hz, H-3), 7.52 (1H, *dd*, $^3J_{5,4}$=5.0 Hz, $^4J_{5,3}$=1.2 Hz, H-5), 7.08 (1H, *dd*, $^3J_{4,5}$=5.0 Hz, $^3J_{4,3}$=3.8 Hz, H-4), 5.21 (1H, *m*, ^{3}J=6.2 Hz, 2-COOC<u>H</u>$(CH_3)_2$), 1.36 (6H, *d*, ^{3}J=6.2 Hz, 2-COOCH(C<u>H</u>$_3)_2$).

Preparation of Isopropyl thiophene-3-carboxylate (27)

Similarly 3-thiophenecarboxylic acid (3.49 g, 0.027 mol), isopropyl alcohol (21 ml, 0.27 mol) and conc. H_2SO_4 (0.5 ml) were refluxed for 48 h. Workup yielded a brown oil, which was distilled. *Isopropyl thiophene-3-carboxylate* was collected as a colourless liquid (2.06 g, 45 %), b.p. 218-220 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 8.07 (1H, *dd*, $^4J_{2,4}$=2.9 Hz, $^4J_{2,5}$=1.2 Hz, H-2), 7.52 (1H, *dd*, $^3J_{5,4}$=5.3 Hz, $^4J_{5,2}$=1.2 Hz, H-5), 7.27 (1H, *dd*, $^3J_{4,5}$=5.3 Hz, $^4J_{4,2}$=2.9 Hz, H-4), 5.20 (1H, *m*, ^{3}J=6.2 Hz, 3-COOC<u>H</u>$(CH_3)_2$), 1.34 (6H, *d*, ^{3}J=6.2 Hz, 3-COOCH(C<u>H</u>$_3)_2$).

Preparation of Isopropyl 3-hydroxybenzoate (36)

Similarly 3-hydroxybenzoic acid (30 g, 0.217 mol), isopropyl alcohol (170 ml, 2.17 mol) and conc. H_2SO_4 (2.7 ml) were refluxed for 18.5 h. Workup yielded an off-white crystalline solid which was recrystallized from hot ethanol to give *isopropyl 3-hydroxybenzoate* as white chunky crystals, m.p. 55.5-57 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.61 (1H, *dt*, $^3J_{6,5}$=7.9 Hz, $^4J_{6,4}$=$^4J_{6,2}$=1.3 Hz, H-6), 7.55 (1H, *dd*, $^4J_{2,4}$=2.7 Hz, $^4J_{2,6}$=1.3 Hz, H-2), 7.30 (1H, *t*, $^3J_{5,4}$=$^3J_{5,6}$=7.9 Hz, H-5), 7.04 (1H, *ddd*, $^3J_{4,5}$=7.9 Hz, $^4J_{4,2}$=2.7 Hz, $^4J_{4,6}$=1.3 Hz, H-4), 5.39 (1H, *s*, br, 3-OH), 5.24 (1H, *m*, ^{3}J=6.2 Hz,

1-COOC<u>H</u>$(CH_3)_2$), 1.36 (6H, *d*, ^3J=6.2 Hz, 1-COOCH(C<u>H</u>$_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 166.9 (*s*, 1-<u>C</u>OOCH$(CH_3)_2$), 156.2 (*s*, C-3), 131.9 (*s*, C-1), 129.7 (*d*, C-5), 121.7 (*d*, C-6), 120.4 (*d*, C-4), 116.5 (*d*, C-2), 69.2 (*d*, 1-COO<u>C</u>H$(CH_3)_2$), 21.9 (*q* , 1-COOCH(<u>C</u>$H_3)_2$).

Preparation of Isopropyl 3-methoxybenzoate (21)

Isopropyl 3-hydroxybenzoate (4 g, 0.022 mol), K_2CO_3 (6.06 g, 0.044 mol) and MeI (2.75 ml, 0.044 mol) were refluxed in acetone (AR, 100 ml) overnight. The solution was filtered and the acetone was removed on the rotary evaporator. The residue was poured into a separating funnel containing H_2O (100 ml)/ether (40 ml) and further extracted with ether (2 x 20 ml). The ethereal solution was washed with NaOH (2 mol l^{-1}), then H_2O and dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure to give *isopropyl 3-methoxybenzoate* as a colourless liquid (3.20 g, 75 %), pure by ^{1}H nmr. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.62 (1H, *dt*, $^3J_{6,5}$=8.0 Hz, $^4J_{6,4}$=$^4J_{6,2}$=1.2 Hz, H-6), 7.55 (1H, *dd*, $^4J_{2,4}$=2.7 Hz, $^4J_{2,6}$=1.2 Hz, H-2), 7.32 (1H, *t*, $^3J_{5,6}$=$^3J_{5,4}$=8.0 Hz, H-5), 7.07 (1H, *ddd*, $^3J_{4,5}$=8.0 Hz, $^4J_{4,2}$=2.7 Hz, $^4J_{4,6}$=1.2 Hz, H-4), 5.24 (1H, *m*, ^3J=6.2 Hz, 1-COOC<u>H</u>$(CH_3)_2$), 3.83 (3H, *s*, 3-OCH_3), 1.36 (6H, *d*, ^3J=6.2 Hz, 1-COOCH(C<u>H</u>$_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 165.9 (*s*, 1-<u>C</u>OOCH$(CH_3)_2$), 159.6 (*s*, C-3), 132.3 (*s*, C-1), 129.3 (*d*, C-5), 121.9 (*d*, C-6), 119.0 (*d*, C-4), 114.1 (*d*, C-2), 68.4 (*d*, 1-COO<u>C</u>H$(CH_3)_2$), 55.3 (*q*, 3-OCH_3), 21.9 (*q* , 1-COOCH(<u>C</u>$H_3)_2$).

Preparation of Isopropyl 3-acetoxybenzoate (24)

Isopropyl 3-hydroxybenzoate (4.16 g, 0.023 mol) and acetic anhydride (3.27 ml, 0.035 mol) were stirred overnight in pyridine (10 ml). The residue was poured into a separating funnel containing H_2O (100 ml)/ether (40 ml) and further extracted with ether (2 x 20 ml). The ethereal solution was washed with HCl (2 mol l^{-1}), H_2O, NaOH (2 mol l^{-1}), then H_2O and dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure to give *isopropyl 3-acetoxybenzoate* as a very pale yellow liquid (4.05 g, 79 %), pure by ^{1}H nmr. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.91 (1H, *dt*, $^3J_{6,5}$=7.9 Hz, $^4J_{6,4}$=$^4J_{6,2}$=1.2 Hz, H-6), 7.73 (1H, *dd*, $^4J_{2,4}$=2.5 Hz, $^4J_{2,6}$=1.2 Hz, H-2), 7.43 (1H, *t*, $^3J_{5,6}$=$^3J_{5,4}$=7.9 Hz, H-5), 7.26 (1H, *ddd*, $^3J_{4,5}$=7.9 Hz, $^4J_{4,2}$=2.5 Hz, $^4J_{4,6}$=1.2 Hz, H-4), 5.24 (1H, *m*, ^3J=6.3 Hz, 1-COOC<u>H</u>$(CH_3)_2$), 2.31 (3H, *s*, 3-$OCOCH_3$), 1.35 (6H, *d*, ^3J=6.3 Hz, 1-COOCH(C<u>H</u>$_3)_2$).

^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 169.3 (*s*, 3-O<u>C</u>OCH$_3$), 165.1 (*s*, 1-<u>C</u>OOCH(CH$_3$)$_2$), 150.6 (*s*, C-3), 132.5 (*s*, C-1), 129.3 (*d*, C-5), 127.0 (*d*, C-6), 126.1 (*d*, C-4), 122.8 (*d*, C-2), 68.8 (*d*, 1-COO<u>C</u>H(CH$_3$)$_2$), 21.9 (*q*, 1-COOCH(<u>C</u>H$_3$)$_2$), 21.1 (*q* , 3-OCO<u>C</u>H$_3$).

2.6.2 The Standard Method for Orthometalation

Preparation of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11)

Dibenzosuberone (0.230 g, 1.104 mmol) and $PhCH_2Mn(CO)_5$ (0.347 g, 1.215 mmol) were dissolved in heptane (AR, 25-30 ml) and the solution degassed and flushed with nitrogen several times. After refluxing under nitrogen for three hours, the heptane was removed under vacuum. The resultant yellow solid was dissolved in dichloromethane and chromatographed on silica gel plates with 1:10 v/v diethyl ether/petroleum spirit b.p. 60-80 °C as the eluant. A broad bright yellow band of *η^2-4-(dibenzosuberonyl)-tetracarbonylmanganese* **(11)** was collected (0.412 g, 100 %). Spectral and other physical data are given in section 2.6.2. Products are reported in order of increasing polarity.

The workup procedures and yields of other orthomanganated compounds prepared in this study are given in Table 2.1.

The orthorheniation reactions employed the same general method as for the orthomanganation reactions, but required more forcing conditions and longer reaction times. The solvent of choice was AR petroleum spirit of b.p. 120-160 °C and heating was provided by an oil bath at 130 °C.

Orthomanganation of Thiochroman-4-one

Similarly prepared from $PhCH_2Mn(CO)_5$ (270 mg, 0.942 mmol) and thiochroman-4-one (129 mg, 0.785 mmol) under reflux over 2 h was *η^2-5-(thiochroman-4-onyl)tetracarbonylmanganese* [**(4)**; 133 mg, 51 %] which crystallized from hexane/diethyl ether as tiny yellow blocks, m.p. 116.5 °C (dec). Anal. Found: C, 47.93; H, 2.50 %; $C_{13}H_7O_5MnS$ calcd: C, 47.29; H, 2.14 %. IR: (hexane) ν(CO) 2084 (m), 1997 (vs, br), 1949 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.80 (1H, *d*, $^3J_{6,7}$=7.5 Hz, H-6), 7.22 (1H, *t*, $^3J_{7,6}$=$^3J_{7,8}$= 7.5 Hz, H-7), 7.01 (1H, *d*, $^3J_{8,7}$=7.5 Hz, H-8), 3.20-3.16 (2H, *m*, H-2a,2b), 3.05-3.00 (2H, *m*, H-3a,3b). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 220.8

(*s*, br, C≡O), 212.8 (*s*, br, C≡O), 212.4 (*s*, C-4), 211.2 (*s*, 2xC≡O), 197.0 (*s*, C-5), 145.9 (*s*, C-8a), 139.0 (*s* , C-4a), 137.7 (*d*, C-6), 133.7 (*d*, C-7), 122.5 (*d*, C-8), 38.4 (*t*, C-3), 27.3 (*t*, C-2). MS: 330 (5.2, P^+), 246 (7.4, P^+-84, P^+-3C≡O), 218 (100, P^+-112, P^+-4C≡O).

Orthomanganation of Thioxanthen-9-one

Similarly prepared from $PhCH_2Mn(CO)_5$ (214 mg, 0.748 mmol) and thioxanthen-9-one (132 mg, 0.624 mmol) under reflux over 3 h was *η^2-1-(thioxanthen-9-onyl)tetracarbonylmanganese* [(**5**); 236 mg, 96 %] which crystallized from petroleum spirit as yellow needles, m.p. 129.5 °C (dec). Anal. Found: C, 54.23; H, 1.85 %; $C_{17}H_7O_5MnS$ calcd: C, 53.98; H, 1.87 %. IR: (hexane) ν(CO) 2083 (m), 1995 (vs, br), 1945 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.55 (1H, *d*, $^3J_{8,7}$=8.2 Hz, H-8), 8.12 (1H, *d*, $^3J_{2,3}$=6.9 Hz, H-2), 7.74-7.66 (2H, *m*, H-5,6), 7.53-7.48 (2H, *m*, H-3,7) 7.40 (1H, *d*, $^3J_{4,3}$=8.0 Hz, H-4). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.0 (*s*, br, C≡O), 213.4 (*s*, br, C≡O), 211.4 (*s*, br, 2xC≡O), 194.4 (*s*, C-9), 193.2 (*s*, C-1), 140.1 (*s* , C-4a,10a), 138.6 (*d*, C-2), 137.4 (*s*, C-9a), 133.1 (*d*, C-6), 132.2 (*d*, C-3), 129.5 (*d*, C-8), 127.9 (*s*, C-8a), 126.4 (*d*, C-7), 126.0 (*d*, C-5), 120.1 (*d*, C-4). MS: 378 (3.3, P^+), 294 (9.6, P^+-84, P^+-3C≡O), 266 (100, P^+-112, P^+-4C≡O).

Orthomanganation of 2-Chlorothioxanthen-9-one

Similarly prepared from $PhCH_2Mn(CO)_5$ (175 mg, 0.613 mmol) and 2-chlorothioxanthen-9-one (126 mg, 0.511 mmol) under reflux over 1.5 h was (i) *η^2-1-(7-chlorothioxanthen-9-onyl)tetracarbonylmanganese* [(**6**); 108 mg, 51 %] which crystallized from petroleum spirit as orange feathers, m.p. 143.5-145 °C. Anal. Found: C, 49.29; H, 1.62 %; $C_{17}H_6O_5ClMnS$ calcd: C, 49.48; H, 1.47 %. IR: (hexane) ν(CO) 2083 (m), 1997 (vs, br), 1946 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.52 (1H, *dd*, $^4J_{8,6}$=2.1 Hz, $^5J_{8,5}$=0.9 Hz, H-8), 8.14 (1H, *dd*, $^3J_{2,3}$=7.1 Hz, $^4J_{2,4}$= 1.0 Hz, H-2), 7.64-7.63 (2H, *m*, H-5,6), 7.51 (1H, *dd*, $^3J_{3,4}$=8.0 Hz, $^3J_{3,2}$= 7.1 Hz, H-3), 7.39 (1H, *dd*, $^3J_{4,3}$=8.0 Hz, $^4J_{4,2}$=1.0 Hz, H-4). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.0 (*s*, br, C≡O), 213.2 (*s*, br, C≡O), 211.2 (*s*, 2xC≡O), 194.3 (*s*, C-9), 193.5 (*s*, C-1), 139.9 (*s* , C-4a), 139.0 (*d*, C-2), 138.2 (*s*, C-10a), 137.1 (*s*, C-9a), 133.4 (*d*, C-6), 132.8 (*s*, C-7), 132.5 (*d*, C-3), 128.9 (*s*, C-8a), 128.9 (*d*, C-8), 127.5 (*d*, C-5), 120.2 (*d*, C-4); and (ii) *η^2-1-(2-chlorothioxanthen-9-onyl)tetracarbonylmanganese* [(**7**); 82 mg, 39 %] which crystallized from petroleum spirit as yellow needles, m.p.

136 °C (dec). Anal. Found: C, 49.51; H, 1.26 %; $C_{17}H_6O_5ClMnS$ calcd: C, 49.48; H, 1.47 %. IR: (hexane) ν(CO) 2085 (m), 1999 (vs, br), 1958 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.53 (1H, *dt*, $^3J_{8,7}$=8.2 Hz, $^4J_{8,6}$=$^5J_{8,5}$=0.9 Hz, H-8), 7.72-7.69 (2H, *m*, H-5,6), 7.61 (1H, *d*, $^3J_{3,4}$=8.4 Hz, H-3), 7.56-7.51 (1H, *m*, H-7), 7.35 (1H, *d*, $^3J_{4,3}$=8.4 Hz, H-4). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 219.6 (*s*, br, C≡O), 214.8 (*s*, br, C≡O), 210.6 (*s*, 2xC≡O), 194.7 (*s*, C-9), 189.3 (*s*, C-1), 146.2 (*s*, C-2), 139.4 (*s*, C-10a), 138.1 (*s*, C-9a), 137.9 (*s*, C-4a), 133.4 (*d*, C-6), 133.3 (*d*, C-3), 129.8 (*d*, C-8), 127.8 (*s*, C-8a), 126.7 (*d*, C-7), 126.0 (*d*, C-5), 122.4 (*d*, C-4).

Orthomanganation of 1,2,3,4,9,10-Hexahydroacridin-9-one

Similarly prepared from $PhCH_2Mn(CO)_5$ (224 mg, 0.783 mmol) and 1,2,3,4,9,10-hexahydroacridin-9-one (130 mg, 0.652 mmol) under reflux over 2 h was *η^2-1-(5,6,7,8,9,10-hexahydro-9-acridinonyl)tetracarbonyl-manganese* [(**8**); 238 mg, 62 %] which crystallized from hot chloroform as a yellow powder. IR: ($CHCl_3$) ν(CO) 2076 (m), 1991 (vs, br), 1925 (s) cm^{-1}.

Orthomanganation of *N*-methyl-9,10-dihydro-9-acridinone

Similarly prepared from $PhCH_2Mn(CO)_5$ (244 mg, 0.855 mmol) and *N*-methyl-9,10-dihydro-9-acridinone (149 mg, 0.712 mmol) under reflux over 1.25 h was *η^2-1-(N-methyl-9,10-dihydro-9-acridinonyl)tetracarbonyl-manganese* [(**9**); 267 mg, 88 %] which crystallized from hexane/diethyl ether as yellow feathers, m.p. 140 °C (dec). IR: (hexane) ν(CO) 2079 (m), 1992 (vs, br), 1940 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.45 (1H, *dd*, $^3J_{8,7}$=8.1 Hz, $^4J_{8,6}$=1.7 Hz, H-8), 7.95 (1H, *dd*, $^3J_{2,3}$=6.9 Hz, $^4J_{2,4}$=0.7 Hz, H-2), 7.80 (1H, *ddd*, $^3J_{6,5}$=8.8 Hz, $^3J_{6,7}$=6.9 Hz, $^4J_{6,8}$=1.7 Hz, H-6), 7.68 (1H, *dd*, $^3J_{3,4}$=8.5 Hz, $^3J_{3,2}$=6.9 Hz, H-3), 7.64 (1H, *d*, $^3J_{5,6}$=8.8 Hz, H-5), 7.35 (1H, *ddd*, $^3J_{7,8}$=8.1 Hz, $^3J_{7,6}$=6.9 Hz, $^4J_{7,5}$=1.0 Hz, H-7), 7.25 (1H, *d*, $^3J_{4,3}$=8.5 Hz, H-4), 3.96 (3H, *s*, N-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.4 (*s*, br, C≡O), 214.1 (*s*, br, C≡O), 212.6 (*s*, 2xC≡O), 189.2 (*s*, C-1*), 188.8 (*s*, C-9*), 143.3 (*s*, C-10a), 141.7 (*s*, C-4a), 134.4 (*d*, C-3,6), 134.0 (*d*, C-2), 132.4 (*s*, C-8a), 127.0 (*d*, C-8), 121.8 (*d*, C-7), 120.2 (*s*, C-9a), 115.2 (*d*, C-5), 108.7 (*d*, C-4), 33.3 (*q*, N-CH_3).

Orthomanganation of Dibenzosuberenone

Similarly prepared from $PhCH_2Mn(CO)_5$ (200 mg, 0.698 mmol) and dibenzosuberenone (120 mg, 0.582 mmol) under reflux over 1.25 h was η^2-*4-(dibenzosuberenonyl)tetracarbonylmanganese* [**(10)**; 217 mg, 100 %] which crystallized from hexane/diethyl ether as yellow needles, m.p. 129-131 °C. IR: (diethyl ether) ν(CO) 2080 (m), 1993 (vs, br), 1964 (m), 1939 (m) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.74 (1H, *d*, $^3J_{6,7}$=8.1 Hz, H-6), 8.37 (1H, *d*, $^3J_{3,2}$=7.3 Hz, H-3), 7.76 (1H, *t*, $^3J_{8,7}$=$^3J_{8,9}$=7.4 Hz, H-8), 7.66 (1H, *d*, $^3J_{9,8}$=7.4 Hz, H-9), 7.64 (1H, *m*, H-7), 7.61 (1H, *t*, $^3J_{2,1}$=$^3J_{2,3}$=7.3 Hz, H-2), 7.44 (1H, *d*, $^3J_{1,2}$=7.3 Hz, H-1), 7.21 (1H, *m*, H-11), 7.17 (1H, *m*, H-10). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.0 (*s*, br, C≡O), 213.5 (*s*, br, C≡O), 211.4 (*s*, 2xC≡O), 202.0 (*s*, C-5), 195.8 (*s*, C-4), 144.5 (*s*, C-4a), 142.0 (*d*, C-3), 140.0 (*s*, C-11a), 136.1 (*s*, C-9a), 134.7 (*d*, C-11), 134.1 (*s*, C-5a), 133.8 (*d*, C-8), 133.3 (*d*, C-9), 132.8 (*d*, C-6), 132.3 (*d*, C-2), 132.1 (*d*, C-10), 129.1 (*d*, C-7), 129.0 (*d*, C-1).

Orthomanganation of Dibenzosuberone

Similarly prepared from $PhCH_2Mn(CO)_5$ (347 mg, 1.215 mmol) and dibenzosuberone (230 mg, 1.104 mmol) under reflux over 3 h was η^2-*4-(dibenzosuberonyl)tetracarbonylmanganese* [**(11)**; 412 mg, 100 %] which crystallized from hexane/diethyl ether as orange feathers, m.p. 105-107 °C. Anal. Found: C, 60.75; H, 2.69 %; $C_{19}H_{11}O_5Mn$ calcd: C, 60.98; H, 2.96 %. IR: (hexane) ν(CO) 2080 (m), 1994 (vs, br), 1943 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.06 (1H, *dd*, $^3J_{3,2}$=7.4 Hz, $^4J_{3,1}$=0.9 Hz, H-3), 8.00 (1H, *dd*, $^3J_{6,7}$=7.5 Hz, $^4J_{6,8}$=1.5 Hz, H-6), 7.52 (1H, *td*, $^3J_{8,7}$=$^3J_{8,9}$=7.5 Hz, $^4J_{8,6}$=1.5 Hz, H-8), 7.38 (1H, *td*, $^3J_{7,6}$=$^3J_{7,8}$=7.5 Hz, $^4J_{7,9}$=1.3 Hz, H-7), 7.30 (1H, *t*, $^3J_{2,1}$=$^3J_{2,3}$=7.4 Hz, H-2), 7.27 (1H, *dd*, $^3J_{9,8}$=7.5 Hz, $^4J_{9,7}$=1.3 Hz, H-9), 6.98 (1H, *dd*, $^3J_{1,2}$=7.4 Hz, $^4J_{1,3}$=0.9 Hz, H-1), 3.15 (4H, *s*, H-10,11). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.1 (*s*, br, C≡O), 213.4 (*s*, br, C≡O), 211.5 (*s*, 2xC≡O), 208.3 (*s*, C-5), 198.7 (*s*, C-4), 148.5 (*s*, C-11a), 143.8 (*s*, C-4a), 142.8 (*s*, C-9a), 139.8 (*d*, C-3), 136.7 (*s*, C-5a), 134.0 (*d*, C-8), 133.0 (*d*, C-2), 132.5 (*d*, C-6), 128.9 (*d*, C-9), 127.0 (*d*, C-7), 126.0 (*d*, C-1), 35.6 (*t*, C-11), 34.8 (*t*, C-10).

Orthomanganation of *N,N*-dimethyl-1-naphthylamine

Similarly prepared from $PhCH_2Mn(CO)_5$ (299 mg, 1.044 mmol) and *N,N*-dimethyl-1-naphthylamine (149 mg, 0.870 mmol) under reflux over 4 h was *η^2-(8-dimethylamino-1-naphthyl)tetracarbonylmanganese* [**(12)**; 293 mg, 88 %] which crystallized from hexane/diethyl ether as yellow feathers, m.p. 115-117 °C. Anal. Found: C, 57.12; H, 3.79; N, 4.24 %; $C_{16}H_{12}O_4MnN$ calcd: C, 56.99; H, 3.59; N, 4.15 %. IR: (hexane) ν(CO) 2071 (m), 1982 (vs, br), 1976 (s), 1939 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.88 (1H, *d*, $^3J_{2,3}$=7.6 Hz, H-2), 7.72 (1H, *d*, $^3J_{5,6}$=7.5 Hz, H-5), 7.56 (1H, *d*, $^3J_{4,3}$=7.6 Hz, H-4), 7.45 (1H, *t*, $^3J_{3,2}$=$^3J_{3,4}$=7.6 Hz, H-3), 7.38 (1H, *t*, $^3J_{6,5}$=$^3J_{6,7}$=7.5 Hz, H-6), 7.30 (1H, *d*, $^3J_{7,6}$=7.5 Hz, H-7), 3.24 (6H, *s*, 8-N(CH_3)$_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.1 (*s*, br, C≡O), 214.1 (*s*, br, 3xC≡O), 164.4 (*s*, C-1), 155.8 (*s*, C-8), 140.9 (*s*, C-8a), 137.9 (*d*, C-2), 134.4 (*s*, C-4a), 128.2 (*d*, C-3), 127.8 (*d*, C-5), 124.5 (*d*, C-6), 122.4 (*d*, C-4), 114.9 (*d*, C-7), 60.6 (*q*, 8-N(CH_3)$_2$).

Orthomanganation of Chromone

Similarly prepared from $PhCH_2Mn(CO)_5$ (215 mg, 0.753 mmol) and chromone (100 mg, 0.684 mmol) under reflux over 2 h was *η^2-5-(1,4-benzopyronyl)tetracarbonylmanganese* [**(13)**; 213 mg, 96 %] which crystallized from hexane/diethyl ether as yellow/orange rectangular crystals, m.p. 99-101.5 °C. Anal. Found: C, 49.86; H, 1.90 %; $C_{13}H_5O_6Mn$ calcd: C, 50.03; H, 1.61 %. IR: (hexane) ν(CO) 2082 (m), 1994 (vs), 1945 (s) cm^{-1}. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 7.98 (1H, *d*, $^3J_{6,7}$=7.0 Hz, H-6), 7.93 (1H, *d*, $^3J_{2,3}$=5.9 Hz, H-2), 7.63 (1H, *dd*, $^3J_{7,8}$=8.2 Hz, $^3J_{7,6}$=7.0 Hz, H-7), 7.17 (1H, *d*, $^3J_{8,7}$=8.2 Hz, H-8), 6.50 (1H, *d*, $^3J_{3,2}$=5.9 Hz, H-3). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 221.2 (*s*, br, C≡O), 213.2 (*s*, br, C≡O), 211.5 (*s*, 2xC≡O), 191.8 (*s*, C-5), 186.2 (*s*, C-4), 157.5 (*s*, C-8a), 157.2 (*d*, C-2), 137.6 (*d*, C-6*), 134.7 (*d*, C-7*), 134.0 (*s*, C-4a), 111.1 (*d*, C-3#), 109.9 (*d*, C-8#). MS: 312 (3.2, P^+), 256 (2.2, P^+-56, P^+-2C≡O), 228 (9.0, P^+-84, P^+-3C≡O), 200 (100, P^+-112, P^+-4C≡O).

Orthomanganation of 3'-Chloroacetophenone

Similarly prepared from $PhCH_2Mn(CO)_5$ (397 mg, 1.389 mmol) and 3'-chloroacetophenone (179 mg, 1.158 mmol) under reflux overnight was (i) *η^2-(2-acetyl-4-chlorophenyl)tetracarbonylmanganese* [**(15)**; 137 mg, 37 %]

which crystallized from hexane/diethyl ether as small yellow/orange regular crystals, m.p. 131-133 °C (lit. 132-134 °C [9]) IR: (hexane) ν(CO) 2085 (m), 1997 (vs, br), 1949 (s) cm^{-1}. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 8.02 (1H, *d*, $^3J_{6,5}$=7.9 Hz, H-6), 7.81 (1H, *d*, $^4J_{3,5}$=2.1 Hz, H-3), 7.39 (1H, *dd*, $^3J_{5,6}$=7.9 Hz, $^4J_{5,3}$=2.1 Hz, H-5), 2.61 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 221.0 (*s*, br, C≡O), 216.2 (*s*, 2-$\underline{C}OCH_3$), 211.0 (*s*, br, 2xC≡O), 191.6 (*s*, C-1), 146.4 (*s*, C-2), 142.4 (*d*, C-6), 133.7 (*d*, C-5), 130.9 (*d*, C-3), 130.5 (*s*, C-4), 24.7 (*q*, 2-CO$\underline{C}H_3$); 1 metal carbonyl signal not observed; and (ii) *η^2-(2-acetyl-6-chlorophenyl)tetracarbonylmanganese* [**(14)**; 156 mg, 42 %] which crystallized from hexane/diethyl ether as small yellow/orange regular crystals, m.p. 106-107.5 °C (lit. 105-107 °C [9]). IR: (hexane) ν(CO) 2088 (m), 1998 (vs, br), 1961 (s) cm^{-1}. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 7.73 (1H, *d*, $^3J_{3,4}$=7.6 Hz, H-3), 7.53 (1H, *d*, $^3J_{5,4}$=7.6 Hz, H-5), 7.12 (1H, *t*, $^3J_{4,3}$=$^3J_{4,5}$=7.6 Hz, H-4), 2.60 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 219.7 (*s*, br, C≡O), 217.2 (*s*, 2-$\underline{C}OCH_3$), 210.8 (*s*, br, 2xC≡O), 189.9 (*s*, C-1), 149.5 (*s*, C-6), 146.4 (*s*, C-2), 134.6 (*d*, C-5), 129.5 (*d*, C-3), 125.8 (*d*, C-4), 25.1 (*q* , 2-CO$\underline{C}H_3$); 1 metal carbonyl signal not observed.

Orthomanganation of 2'-Chloroacetophenone

Similarly prepared from $PhCH_2Mn(CO)_5$ (406 mg, 1.420 mmol) and 2'-chloroacetophenone (183 mg, 1.184 mmol) under reflux over 2.5 h was *η^2-(2-acetyl-3-chlorophenyl)tetracarbonylmanganese* [**(16)**; 327 mg, 86 %] which crystallized from hexane/diethyl ether as regular yellow prisms, m.p. 82.5-83.5 °C. Anal. Found: C, 44.84; H, 1.84 %; $C_{12}H_6O_5ClMn$ calcd: C, 44.96; H, 1.89 %. IR: (hexane) ν(CO) 2085 (m), 1997 (vs, br), 1949 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.97 (1H, *dd*, $^3J_{6,5}$=7.5 Hz, $^4J_{6,4}$=1.1 Hz, H-6), 7.28 (1H, *t*, $^3J_{5,4}$=$^3J_{5,6}$=7.5 Hz, H-5), 7.18 (1H, *dd*, $^3J_{4,5}$=7.5 Hz, $^4J_{4,6}$=1.1 Hz, H-4), 2.88 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.4 (*s*, br, C≡O), 216.6 (*s*, 2-$\underline{C}OCH_3$), 212.6 (*s*, br, C≡O), 210.7 (*s*, br, 2xC≡O), 198.5 (*s*, C-1), 141.4 (*s*, C-2), 139.8 (*d*, C-6), 137.9 (*s*, C-3), 133.5 (*d*, C-5), 127.0 (*d*, C-4), 32.2 (*q* , 2-CO$\underline{C}H_3$).

Orthomanganation of 3',4'-(Methylenedioxy)acetophenone

Similarly prepared from $PhCH_2Mn(CO)_5$ (303 mg, 1.060 mmol) and 3',4'-(methylenedioxy)acetophenone (145 mg, 0.883 mmol) under reflux over 2.5 h was (i) *η^2-(2-acetyl-4,5-methylenedioxyphenyl)tetracarbonylmanganese*

[**(18)**; 11 mg, ~4 %] a yellow oil. IR: (hexane) ν(CO) 2082 (m), 1997 (vs, br), 1944 (s) cm^{-1}; and (ii) *η^2-(6-acetyl-2,3-methylenedioxyphenyl)tetracarbonyl-manganese* [**(17)**; 251 mg, 86 %] which crystallized from hexane/diethyl ether as yellow feathers, m.p. 121-122.5 °C. Anal. Found: C, 47.30; H, 2.19 %; $C_{13}H_7O_7Mn$ calcd: C, 47.30; H, 2.14 %. IR: (hexane) ν(CO) 2086 (m), 1997 (vs), 1960 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.58 (1H, *d*, $^3J_{5,4}$=8.0 Hz, H-5), 6.67 (1H, *d*, $^3J_{4,5}$=8.0 Hz, H-4), 6.09 (2H, *s*, 2-OCH_2O-3), 2.53 (3H, *s*, 6-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 219.9 (*s*, br, C≡O), 213.4 (*s*, 6-$\underline{C}OCH_3$), 211.0 (*s*, br, 2xC≡O), 163.1 (*s*, C-1), 157.9 (*s*, C-2), 149.8 (*s*, C-3), 141.2 (*s*, C-6), 129.4 (*d*, C-5), 105.4 (*d*, C-4), 100.7 (*t*, 2-OCH_2O-3), 24.2 (*q*, 6-$CO\underline{C}H_3$); 1 metal carbonyl signal not observed. MS. 330 (6.7, P^+), 274 (7.5, P^+-56, P^+-2C≡O), 246 (15.0, P^+-84, P^+-3C≡O), 218 (100, P^+-112, P^+-4C≡O).

Orthomanganation of Methyl 4-methoxybenzoate

Similarly prepared from $PhCH_2Mn(CO)_5$ (233 mg, 0.816 mmol) and methyl 4-methoxybenzoate (113 mg, 0.680 mmol) under reflux over 3 h was *η^2-(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese* [**(19)**; 226 mg, 74 %] which crystallized from hexane/diethyl ether as yellow feathers, m.p. 105-107 °C. Anal. Found: C, 46.83; H, 2.69 %; $C_{13}H_9O_7Mn$ calcd: C, 47.01; H, 2.73 %. IR: (hexane) ν(CO) 2085 (m), 1996 (vs, br), 1944 (s) cm^{-1}. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 7.66 (1H, *d*, $^3J_{3,4}$=8.8 Hz, H-3), 7.45 (1H, *d*, $^4J_{6,4}$=2.3 Hz, H-6), 6.63 (1H, *dd*, $^3J_{4,3}$=8.8 Hz, $^4J_{4,6}$=2.3 Hz, H-4), 3.93 (3H, *s*, 2-$COOCH_3$*), 3.92 (3H, *s*, 5-OCH_3*). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 221.4 (*s*, br, C≡O), 213.2 (*s*, br, C≡O), 212.0 (*s*, br, 2xC≡O), 187.8 (*s*, C-1), 179.9 (*s*, 2-$\underline{C}OOCH_3$), 163.9 (*s*, C-5), 130.7 (*d*, C-3), 127.0 (*s*, C-2), 124.2 (*d*, C-6), 111.4 (*d*, C-4), 55.3 (*q* , 5-OCH_3), 53.9 (*q* , 2-$COO\underline{C}H_3$). MS. 332 (4.2, P^+), 276 (4.2, P^+-56, P^+-2C≡O), 248 (17.5, P^+-84, P^+-3C≡O), 220 (100, P^+-112, P^+-4C≡O).

Orthomanganation of Methyl 3,5-dimethoxybenzoate

Similarly prepared from $PhCH_2Mn(CO)_5$ (234 mg, 0.820 mmol) and methyl 3,5-dimethoxybenzoate (134 mg, 0.683 mmol) under reflux over 2.75 h was *η^2-(2,4-dimethoxy-6-methoxycarbonylphenyl)tetracarbonyl-manganese* [**(20)**; 247 mg, 87 %] which crystallized from hexane/diethyl ether as orange blocky crystals, m.p. 108-109 °C. Anal. Found: C, 46.44; H,

2.87 %; $C_{14}H_{11}O_8Mn$ calcd: C, 46.43; H, 3.06 %. IR: (hexane) ν(CO) 2084 (m), 1992 (vs, br), 1954 (s) cm^{-1}. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 6.92 (1H, *d*, $^4J_{5,3}$=2.1 Hz, H-5*), 6.60 (1H, *d*, $^4J_{3,5}$=2.1 Hz, H-3*), 3.95 (3H, *s*, 6-$COOCH_3$#), 3.82 (3H, *s*, 2-OCH_3#), 3.80 (3H, *s*, 4-OCH_3#). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 220.8 (*s*, br, C≡O), 214.3 (*s*, br, C≡O), 211.9 (*s*, br, 2xC≡O), 180.4 (*s*, 6-$\underline{C}OOCH_3$), 168.1 (*s*, C-2*), 161.1 (*s*, C-1*), 159.4 (*s*, C-4), 134.8 (*s*, C-6), 104.5 (*d*, C-5#), 104.3 (*d*, C-3#), 55.5 (*q*, 2,4-OCH_3), 54.2 (*q*, 6-$COO\underline{C}H_3$). MS. 362 (2.6, P^+), 306 (1.9, P^+-56, P^+-2C≡O), 278 (13.3, P^+-84, P^+-3C≡O), 250 (100, P^+-112, P^+-4C≡O).

Orthomanganation of Isopropyl 3-methoxybenzoate

Similarly prepared from $PhCH_2Mn(CO)_5$ (564 mg, 1.971 mmol) and isopropyl 3-methoxybenzoate **(21)** (319 mg, 1.642 mmol) under reflux over 5 h was (i) *η^2-(2-methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese* [**(22)**; 313 mg, 53 %] which crystallized from hexane/diethyl ether as yellow needles, m.p. 82.5-83.5 °C. IR: (hexane) ν(CO) 2083 (m), 1993 (vs), 1955 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.38 (1H, *d*, $^3J_{5,4}$=7.6 Hz, H-5), 7.12 (1H, *t*, $^3J_{4,3}$=$^3J_{4,5}$=7.6 Hz, H-4), 6.91 (1H, *d*, $^3J_{3,4}$=7.6 Hz, H-3), 5.20 (1H, *m*, ^3J=6.2 Hz, 6-$COOC\underline{H}(CH_3)_2$), 3.85 (3H, *s*, 2-$OCH_3$), 1.35 (6H, *d*, ^3J=6.2 Hz, 6-$COOCH(C\underline{H}_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.6 (*s*, br, C≡O), 214.3 (*s*, br, C≡O), 211.9 (*s*, br, 2xC≡O), 179.9 (*s*, C-1), 170.9 (*s*, 6-$\underline{C}OOCH(CH_3)_2$), 167.6 (*s*, C-2), 136.4 (*s*, C-6), 125.5 (*d*, C-4), 121.7 (*d*, C-5), 113.8 (*d*, C-3), 72.1 (*d*, 6-$COO\underline{C}H(CH_3)_2$), 55.5 (*q* , 2-$OCH_3$), 21.8 (*q* , 6-$COOCH(\underline{C}H_3)_2$); and (ii) *$\eta^2$-(4-methoxy-2-isopropoxycarbonylphenyl)-tetracarbonylmanganese* [**(23)**; 229 mg, 39 %] a yellow oil which failed to crystallize. IR: (hexane) ν(CO) 2083 (m), 1994 (vs), 1991 (s), 1944 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.82 (1H, *d*, $^3J_{6,5}$=8.1 Hz, H-6), 7.28 (1H, *d*, $^4J_{3,5}$=2.6 Hz, H-3), 7.15 (1H, *dd*, $^3J_{5,6}$=8.1 Hz, $^4J_{5,3}$=2.6 Hz, H-5), 5.23 (1H, *m*, ^3J=6.2 Hz, 2-$COOC\underline{H}(CH_3)_2$), 3.83 (3H, *s*, 4-$OCH_3$), 1.35 (6H, *d*, ^3J=6.2 Hz, 2-$COOCH(C\underline{H}_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.5 (*s*, br, C≡O), 213.0 (*s*, br, C≡O), 212.1 (*s*, br, 2xC≡O), 179.6 (*s*, C-1), 171.5 (*s*, 2-$\underline{C}OOCH(CH_3)_2$), 157.5 (*s*, C-4), 141.2 (*d*, C-6), 135.2 (*s*, C-2), 122.6 (*d*, C-5), 113.1 (*d*, C-3), 72.3 (*d*, 2-$COO\underline{C}H(CH_3)_2$), 55.4 (*q*, 4-$OCH_3$), 21.8 (*q*, 2-$COOCH(\underline{C}H_3)_2$).

Orthomanganation of Isopropyl 3-acetoxybenzoate

Similarly prepared from $PhCH_2Mn(CO)_5$ (595 mg, 2.079 mmol) and isopropyl 3-acetoxybenzoate **(24)** (385 mg, 1.732 mmol) under reflux over 3 h was (i) *η^2-(4-acetoxy-2-isopropoxycarbonylphenyl)tetracarbonylmanganese* [**(26)**; 69 mg, 10 %] a yellow oil which failed to crystallize. IR: (hexane) ν(CO) 2083 (m), 1995 (s, br), 1944 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.93 (1H, *d*, $^3J_{6,5}$=8.0 Hz, H-6), 7.46 (1H, *d*, $^4J_{3,5}$=2.4 Hz, H-3), 7.17 (1H, *dd*, $^3J_{5,6}$=8.0 Hz, $^4J_{5,3}$=2.4 Hz, H-5), 5.23 (1H, *m*, ^3J=6.2 Hz, 2-COOC<u>H</u>$(CH_3)_2$), 2.31 (3H, *s*, 4-OCOC<u>H</u>$_3$), 1.35 (6H, *d*, ^3J=6.2 Hz, 2-COOCH(C<u>H</u>$_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.2 (*s*, br, C≡O), 212.7 (*s*, br, C≡O), 211.5 (*s*, br, 2xC≡O), 180.2 (*s*, C-1), 179.3 (*s*, 4-O<u>C</u>OCH$_3$), 169.7 (s, 2-<u>C</u>OOCH$(CH_3)_2$), 148.1 (*s*, C-4), 141.4 (*d*, C-6), 135.6 (*s*, C-2), 127.2 (*d*, C-5), 121.6 (*d*, C-3), 72.6 (*d*, 2-COO<u>C</u>H$(CH_3)_2$), 21.8 (*q* , 2-COOCH(<u>C</u>H$_3)_2$), 21.2 (*q*, 4-OCO<u>C</u>H$_3$); and (ii) *η^2-(2-acetoxy-6-isopropoxycarbonylphenyl)-tetracarbonylmanganese* [**(25)**; 533 mg, 79 %] a yellow oil which failed to crystallize. Anal. Found: C, 49.74; H, 3.53 %; $C_{16}H_{13}O_8Mn$ calcd: C, 49.50; H, 3.38 %. IR: (hexane) ν(CO) 2090 (m), 2006 (s), 1994 (s), 1948 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.65 (1H, *m*, 2nd order coupling, H-5), 7.21-7.15 (2H, *m*, 2nd order coupling, H-3,4), 5.23 (1H, *m*, ^3J=6.2 Hz, 6-COOC<u>H</u>$(CH_3)_2$), 2.30 (3H, *s*, 2-OCOC<u>H</u>$_3$), 1.36 (6H, *d*, ^3J=6.2 Hz, 6-COOCH(C<u>H</u>$_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.9 (*s*, br, C≡O), 213.5 (*s*, br, C≡O), 210.5 (*s*, br, 2xC≡O), 179.7 (*s*, C-1), 172.6 (*s*, 2-O<u>C</u>OCH$_3$), 170.6 (*s*, 6-<u>C</u>OOCH$(CH_3)_2$), 160.4 (*s*, C-2), 137.1 (*s*, C-6), 127.5 (*d*, C-5), 127.0 (*d*, C-4), 125.5 (*d*, C-3), 72.7 (*d*, 6-COO<u>C</u>H$(CH_3)_2$), 21.8 (*q* , 6-COOCH(<u>C</u>H$_3)_2$), 21.1 (*q*, 2-OCO<u>C</u>H$_3$).

Orthomanganation of Isopropyl thiophene-3-carboxylate

Similarly prepared from $PhCH_2Mn(CO)_5$ (462 mg, 1.616 mmol) and isopropyl thiophene-3-carboxylate **(27)** (250 mg, 1.469 mmol) under reflux over 4.5 h was *η^2-(3-isopropoxycarbonylthien-2-yl)tetracarbonylmanganese* [**(28)**; 306 mg, 62 %] which crystallized from hexane/diethyl ether as yellow needles, m.p. 57.5-58 °C. Anal. Found: C, 43.09; H, 2.91 %; $C_{12}H_9O_6MnS$ calcd: C, 42.87; H, 2.70 %. IR: (hexane) ν(CO) 2093(m), 2007 (vs), 2002 (s), 1957 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.42 (1H, *d*, $^3J_{5,4}$=5.0 Hz, H-5), 7.36 (1H, *d*, $^3J_{4,5}$=5.0 Hz, H-4), 5.19 (1H, *m*, ^3J= 6.2 Hz, 3-COOC<u>H</u>$(CH_3)_2$), 1.35 (6H, *d*, ^3J=6.2 Hz, 3-COOCH(C<u>H</u>$_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.3 (*s*, br, C≡O), 213.0 (*s*, br, C≡O), 209.8 (*s*, br,

2xC≡O), 196.5 (*s*, C-2), 175.5 (*s*, 3-$\underline{C}OOCH(CH_3)_2$), 136.8 (*s*, C-3), 132.5 (*d*, C-4), 125.1 (*d*, C-5), 71.7 (*d*, 3-COO$\underline{C}H(CH_3)_2$), 21.9 (*q* , 3-COOCH($\underline{C}H_3)_2$).

Orthomanganation of Isopropyl thiophene-2-carboxylate

Similarly prepared from $PhCH_2Mn(CO)_5$ (494 mg, 1.726 mmol) and isopropyl thiophene-2-carboxylate **(29)** (267 mg, 1.569 mmol) under reflux over 5 h was *η^2-(2-isopropoxycarbonylthien-3-yl)tetracarbonylmanganese* [**(30)**; 202 mg, 38 %] a yellow oil which failed to crystallize. Anal. Found: C, 43.20; H, 3.01 %; $C_{12}H_9O_6MnS$ calcd: C, 42.87; H, 2.70 %. IR: (hexane) ν(CO) 2088 (m), 2001 (vs), 1996 (s), 1950 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.85 (1H, *d*, $^3J_{4,5}$=4.6 Hz, H-4*), 7.47 (1H, *d*, $^3J_{5,4}$=4.6 Hz, H-5*), 5.19 (1H, *m*, ^{3}J=6.3 Hz, 2-COOC$\underline{H}(CH_3)_2$), 1.35 (6H, *d*, ^{3}J=6.3 Hz, 2-COOCH($C\underline{H}_3)_2$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 221.5 (*s*, br, C≡O), 212.9 (*s*, br, C≡O), 210.9 (*s*, br, 2xC≡O), 194.3 (*s*, C-3), 175.4 (*s*, 2-$\underline{C}OOCH(CH_3)_2$), 137.3 (*d*, C-5*), 136.4 (*d*, C-4*), 127.8 (*s*, C-2), 72.3 (*d*, 2-COO$\underline{C}H(CH_3)_2$), 21.9 (*q* 2-COOCH($\underline{C}H_3)_2$).

Orthomanganation of Methyl 1,5-dimethyl-2-pyrrolecarboxylate

Similarly prepared from $PhCH_2Mn(CO)_5$ (370 mg, 1.293 mmol) and methyl 1,5-dimethyl-2-pyrrolecarboxylate (165 mg, 1.077 mmol) under reflux over 3 h was *η^2-(N,5-dimethyl-2-methoxycarbonylpyrrol-3-yl)tetracarbonyl-manganese* [**(31)**; 15 mg, 4 %] a yellow oil which failed to crystallize. IR: (hexane) ν(CO) 2086 (m), 2017 (m), 2000 (vs, br), 1937 (s) cm^{-1}.

Orthorheniation of 3-Acetyl-2,5-dimethylthiophene

Similarly prepared from $PhCH_2Re(CO)_5$ (636 mg, 1.525 mmol) and 3-acetyl-2,5-dimethylthiophene (224 mg, 1.453 mmol) under reflux over 5 h was *η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium* [**(32)**; 236 mg, 36 %] which crystallized from pentane/chloroform as small yellow plates m.p. 143-145.5 °C. Anal. Found: C, 31.85; H, 2.01 %; $C_{12}H_9O_5SRe$ calcd: C, 31.93; H, 2.01 %. IR: (hexane) ν(CO) 2093 (m), 1989 (s), 1983 (s) 1937 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 2.74 (3H, *s*, 5-CH_3), 2.59 (3H, *s*, 2-CH_3), 2.41 (3H, *s*, 4-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ

207.9 (*s*, 4-$\underline{C}OCH_3$), 194.0 (*s*, br, C≡O), 192.0 (*s*, br, C≡O), 188.3 (*s*, br, 2xC≡O), 161.6 (*s*, C-3), 154.6 (*s*, C-5), 149.3 (*s*, C-4), 136.0 (*s*, C-2), 27.3 (*q*, 4-CO$\underline{C}H_3$), 16.7 (*q*, 2-CH_3), 15.5 (*q*, 5-CH_3).

Orthorheniation of 3',4',5'-Trimethoxyacetophenone

Similarly prepared from $PhCH_2Re(CO)_5$ (477 mg, 1.143 mmol) and 3',4',5'-trimethoxyacetophenone (200 mg, 0.952 mmol) under reflux over 6 h was *η^2-(6-acetyl-2,3,4-trimethoxyphenyl)tetracarbonylrhenium* [**(33)**; 239 mg, 41 %] which crystallized from pentane/chloroform as small yellow crystals m.p. 144.5-146 °C. Anal. Found: C, 35.77; H, 2.83 %; $C_{15}H_{13}O_8Re$ calcd: C, 35.50; H, 2.58 %. IR: (hexane) ν(CO) 2093 (m), 1989 (vs), 1983 (s) 1946 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.23 (1H, *s*, H-5), 4.05 (3H, *s*, 2-OCH_3), 3.89 (3H, *s*, 3-OCH_3), 3.83 (3H, *s*, 4-OCH_3), 2.66 (3H, *s*, 6-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 217.7 (*s*, 6-$\underline{C}OCH_3$), 192.6 (*s*, br, C≡O), 191.8 (*s*, br, C≡O), 187.8 (*s*, br, 2xC≡O), 168.3 (*s*, C-1), 159.7 (*s*, C-2), 151.1 (*s*, C-4), 150.0 (*s*, C-3), 140.0 (*s*, C-6), 112.3 (*d*, C-5), 61.0 (*q*, 2-OCH_3), 60.0 (*q*, 3-OCH_3), 56.4 (*q*, 4-OCH_3), 25.0 (*q*, 6-CO$\underline{C}H_3$).

A number of orthomanganation reactions did not yield any isolable metalated product; details of the attempts are given below.

9-Acetylanthracene

Standard procedure from $PhCH_2Mn(CO)_5$ (0.185 g, 0.648 mmol) and 9-acetylanthracene (0.119 g, 0.540 mmol) in refluxing heptane (20 ml) over 48 h failed to yield any cyclometalated product. An infrared spectrum of the crude reaction mixture showed only $Mn_2(CO)_{10}$.

9-Fluorenone

Similarly, $PhCH_2Mn(CO)_5$ (0.230 g, 0.806 mmol) and 9-fluorenone (0.121 g, 0.671 mmol) under reflux overnight gave no orthomanganated product. Again infrared spectroscopy of the crude reaction mixture showed only $Mn_2(CO)_{10}$.

1-Indanone

Reaction of $PhCH_2Mn(CO)_5$ (0.322 g, 1.126 mmol) and 1-indanone (0.124 g, 0.938 mmol) with refluxing over 4.5 h, showed some signs of orthomanganation by infrared spectroscopy and t.l.c., but chromatography yielded no isolable metalated product.

Methyl 2,5-dimethyl-3-furoate

Reaction of $PhCH_2Mn(CO)_5$ (0.322 g, 1.126 mmol) and methyl 2,5-dimethyl-3-furoate (0.130 g, 0.843 mmol) with refluxing overnight showed no signs of metalated product.

Phenanthrenequinone

Standard procedure from $PhCH_2Mn(CO)_5$ (0.514 g, 1.796 mmol) and phenanthrenequinone (0.170 g, 0.816 mmol) under reflux over 3 h, followed by workup by the normal method, gave a purple oil which decomposed upon chromatography (p.l.c., 1:10 ether/petroleum spirit).

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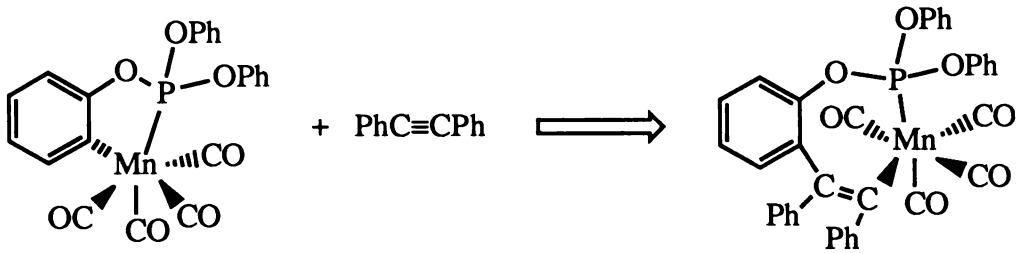
Chapter Three

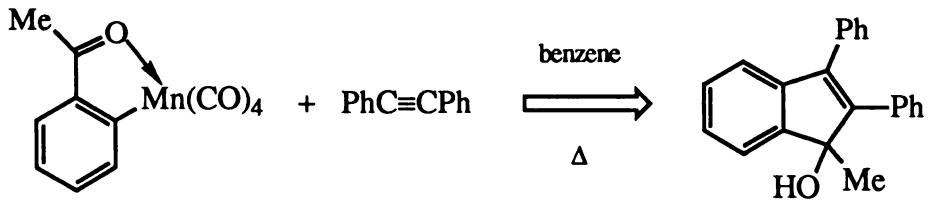
Reaction of Orthomanganated Ketones with SO_2 and Related Cumulenes

3.1 Introduction

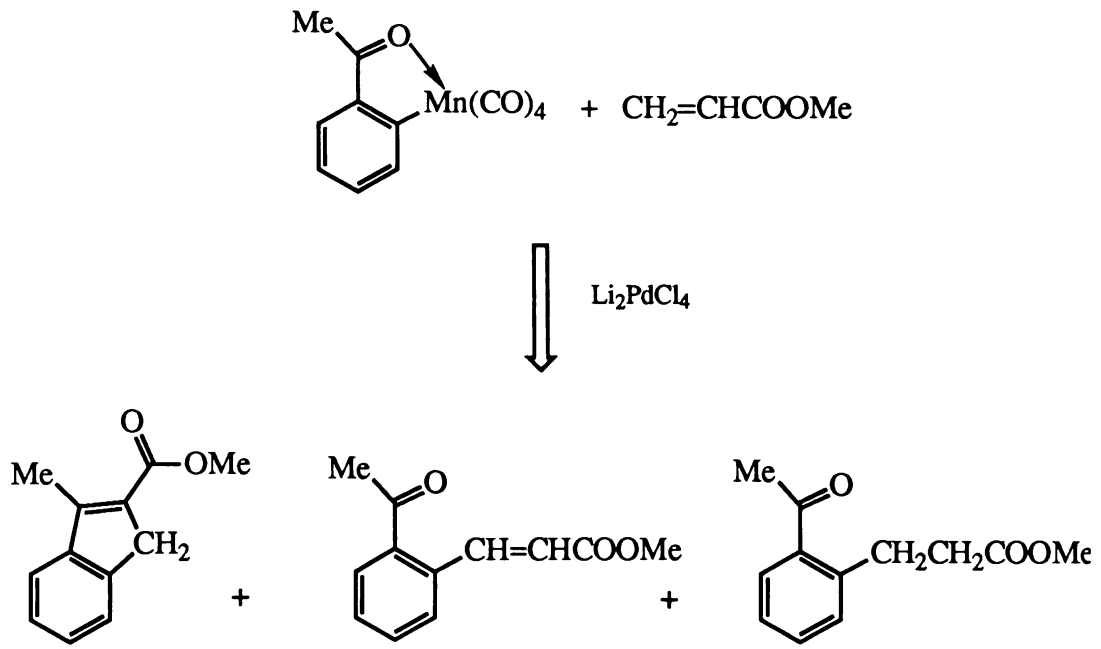
Insertion of unsaturated species into the manganese-carbon bond of orthomanganated triphenyl phosphite has been reported for an alkyne (Equation 3.1) [1], and has been implicated in the coupling reactions of orthomanganated acetophenones with alkynes [2,3] (Equation 3.2), alkenes [4] (Equation 3.3) and isocyanates [5] (Equation 3.4).



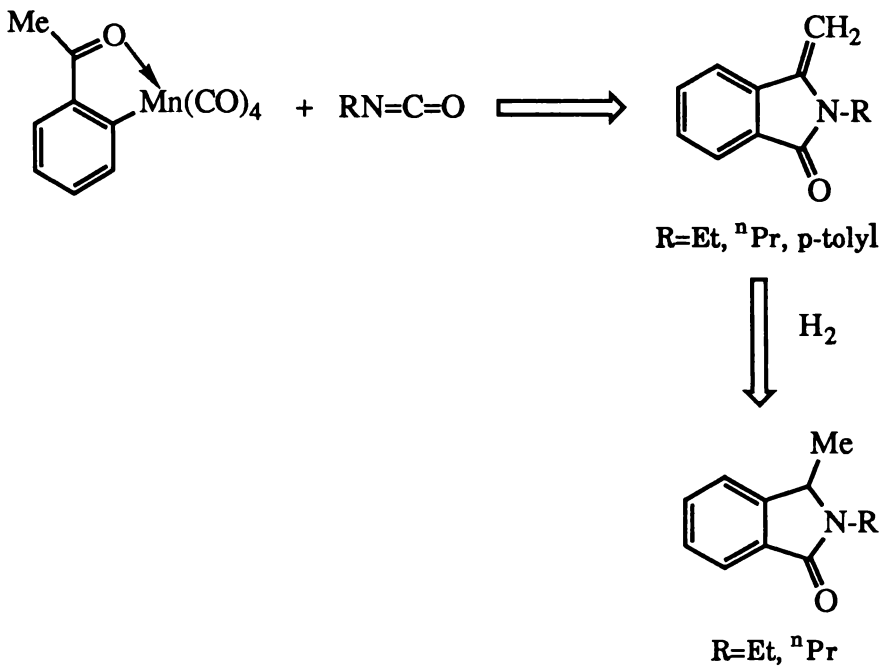
Equation 3.1



Equation 3.2



Equation 3.3



Equation 3.4

To extend the range of this type of reaction, we turned our attention to SO_2 and unsaturated molecules that are related to SO_2.

The cumulenes *N*-sulfinylamines (RN=S=O), the more electrophilic *N*-sulfinylsulfonamides ($RS(O)_2N=S=O$) and disufinylsulfur diimides

($RS(O)_2N{=}S{=}NS(O)_2R$), may be regarded as close electronic and structural analogues of sulphur dioxide.

The insertion of SO_2 into the metal-carbon bond of coordinatively saturated transition metal alkyls and aryls is one of the most systematically studied and best understood reactions in organotransition-metal chemistry [6]. In contrast to CO insertion, SO_2 insertion can, in principle, generate several types of linkages (Figure 3.1).

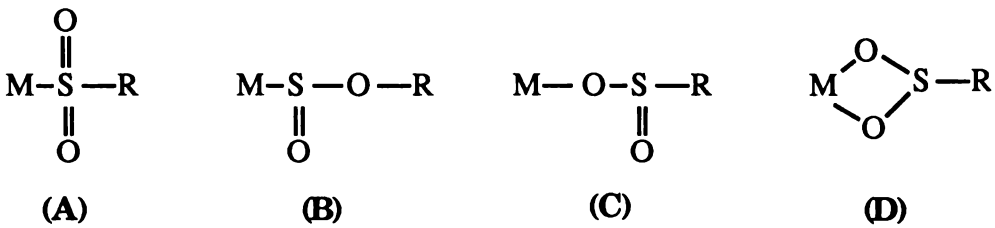
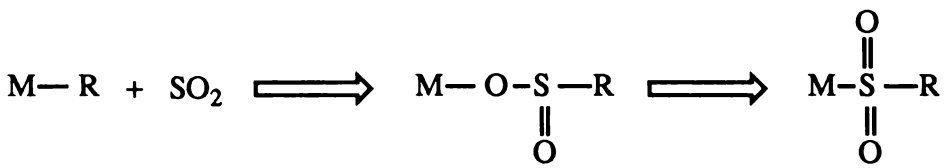


Figure 3.1

Although the usual product is the S-sulfinate (A), the O-alkyl-S-sulfoxylate (B), the O-sulfinate (C) or the O,O'-sulfinate (D) may also be formed [6].

Wojcicki has reported striking similarities in the chemistry of the O=S=O, -N=S=O and -N=S=N- cumulene systems in insertion reactions into the metal-carbon σ-bond of several types of transition metal-alkyl complexes.

SO_2 was found [7] to insert readily into the metal-alkyl carbon bond of $RM(CO)_5$ (M=Mn, R=Me, Et, CH_2Ph; M=Re, R=Me, CH_2Ph) to yield the S-sulfinato-pentacarbonyl-manganese(I) and -rhenium(I) complexes $RS(O)_2Mn(CO)_5$ and $RS(O)_2Re(CO)_5$. In contrast, $PhMn(CO)_5$ gave an insertion product in low yield only under forcing conditions. Alkyl- and aryl-cyclopentadienyliron dicarbonyls were also found to react with SO_2 to give the corresponding S-sulfinato complexes [8]. Insertion is believed to go via the O-sulfinate, which is too unstable to be isolated, before isomerising to give the S-bonded sulfinate (Equation 3.5).

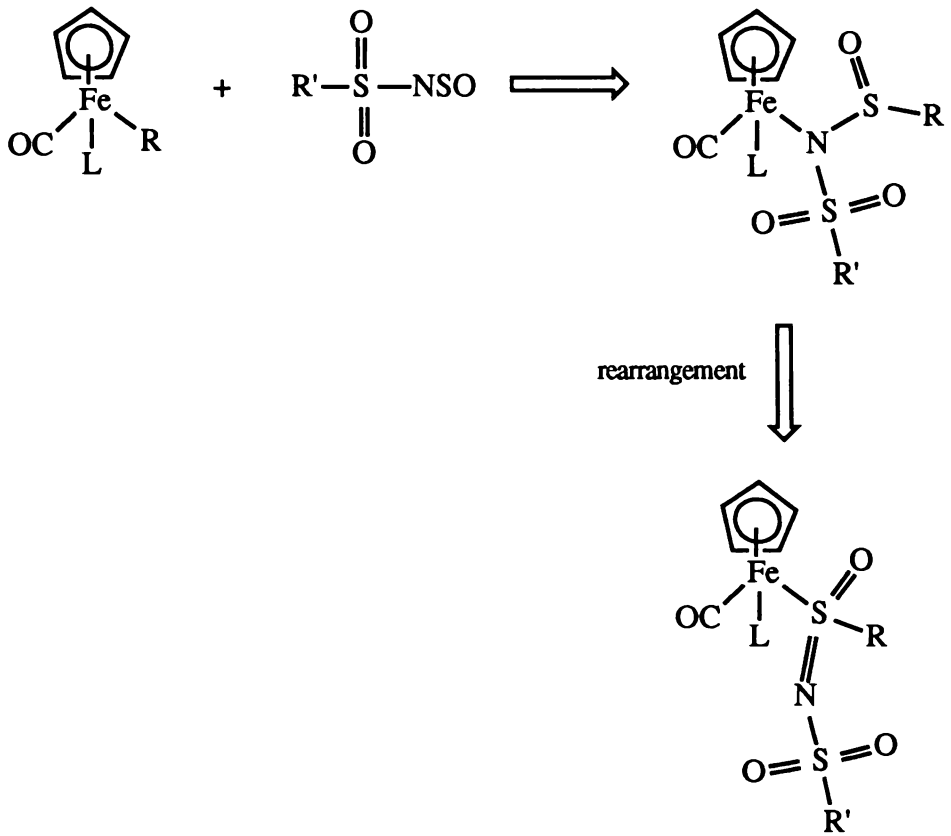


Equation 3.5

The *N*-sulfinylamines, $C_6H_{11}NSO$ and PhNSO, do not react with $MeFe(CO)_2Cp$ at ambient temperature; $C_6H_{11}NSO$ reacts with

$MeFe(CO)_2Cp$ in the presence of BF_3 but no stable products have been isolated [9].

By contrast under comparable conditions, the more electrophilic *N*-sulfinylsulfonamides $R'S(O)_2NSO$ insert into the Fe-R σ-bond of $RFe(CO)(L)Cp$ (L=CO, PPh_3, $P(OPh)_3$) to yield N-bonded $M'\{N[S(O)_2R']S(O)R\}$ analogous to the $M'[OS(O)R]$ from the SO_2 insertion [9] (Equation 3.6).



Equation 3.6

These complexes rearrange upon warming or column chromatography to isolable S-bonded linkage isomers, the propensity for which increases with increasing basicity of the ligand, i.e. $L=CO<P(OPh)_3<PPh_3$.

Reaction between $MeMn(CO)_5$ and $MeS(O)_2NSO$ afforded an insertion product only stable at low temperature and assumed to contain an $Mn\{N[S(O)_2Me]S(O)Me\}$ fragment [10] (Figure 3.2).

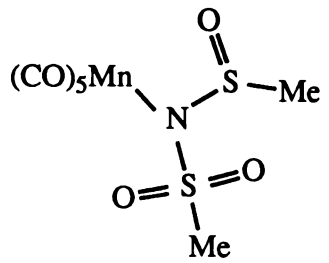


Figure 3.2

Reaction of *cis*-$MeMn(CO)_4(PPh_3)$ with $MeS(O)_2NSO$ gave a moderately stable compound (Figure 3.3), which has been proposed to arise from disproportionation of $MeS(O)_2NSO$ to SO_2 and $[MeS(O)_2N]_2S$ followed by insertion of the latter into the Mn-Me bond [10].

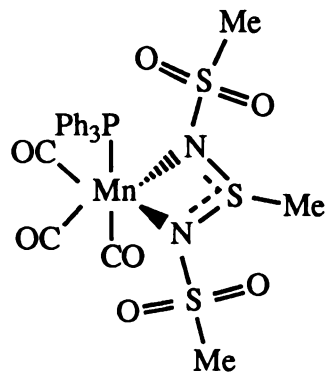
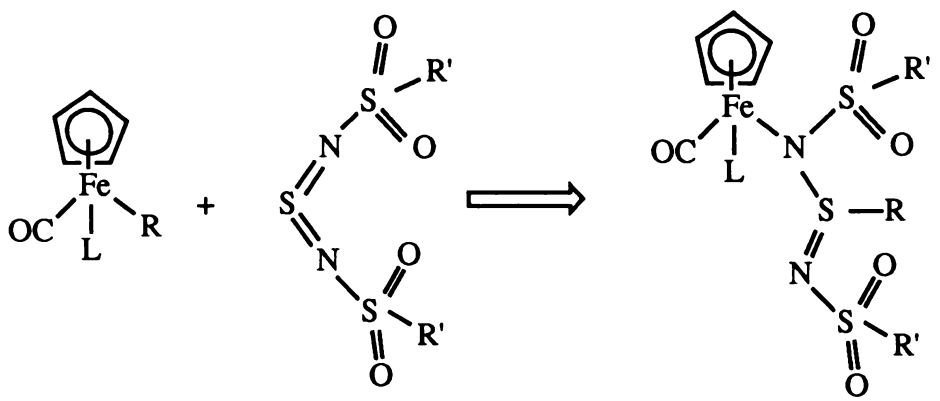


Figure 3.3

Insertion of $[R'S(O)_2N]_2S$ into M'-R bonds almost invariably yields $M'\{N[S(O)_2R']S(R)NS(O)_2R'\}$ products [10] (Equation 3.7).



Equation 3.7

Unlike $M'[OS(O)R]$ and $M'\{N[S(O)_2R'S(O)R\}$, these complexes display no tendency to undergo linkage rearrangement to the corresponding S-bonded isomers upon heating.

$Mn(CO)_4(L)\{N[S(O)_2Me]S(Me)NS(O)_2Me\}$ (L=CO, PPh_3) convert at room temperature to the chelates $(CO)_3(L)\overline{Mn\{N[S(O)_2Me]S(Me)N}S(O)_2Me\}$ probably due to the lability of the ligated CO [10].

Herberhold and coworkers [11] also report the formation of *N*-(tosyl)toluenesulphinimidato-S complexes $[MCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$ from the sixteen electron compounds $[MRCl(CO)(PPh_3)_2]$ (M=Ru, Os; R=C_6H_4Me-4) with $RS(O)_2NSO$ and tosyl-NSO. These are believed to be stabilised by weak coordination of a sulphimide group.

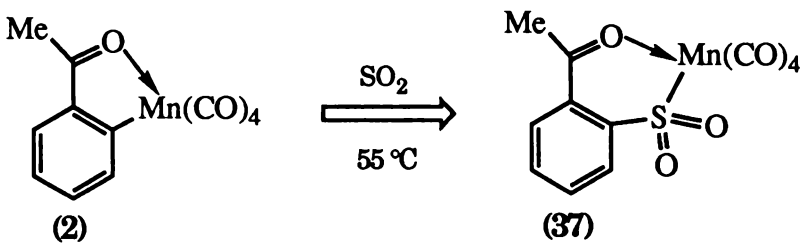
No reaction was observed with the less electrophilic R'NSO (R'=C_6H_4Me-2, C_6H_4Me-4, ferrocenyl).

3.2 Discussion of Results

3.2.1 Reactions with SO_2

Unlike the insertion reactions of SO_2 and *N*-sulfinyl-amines or -amides into iron-carbon σ-bonds described by Wojcicki [10,12], orthomanganated complexes behave differently towards SO_2 and its related cumulenes.

SO_2 was found to insert efficiently into the Mn-C_{aryl} bond of orthomanganated acetophenone **(2)** (Equation 3.8), orthomanganated *p*-methoxyacetophenone **(39)** and the orthomanganated thiophene η^2-(2-acetylthien-3-yl)tetracarbonylmanganese **(40)**, to give the corresponding S-sulfinato complex incorporating a six-membered chelate ring.



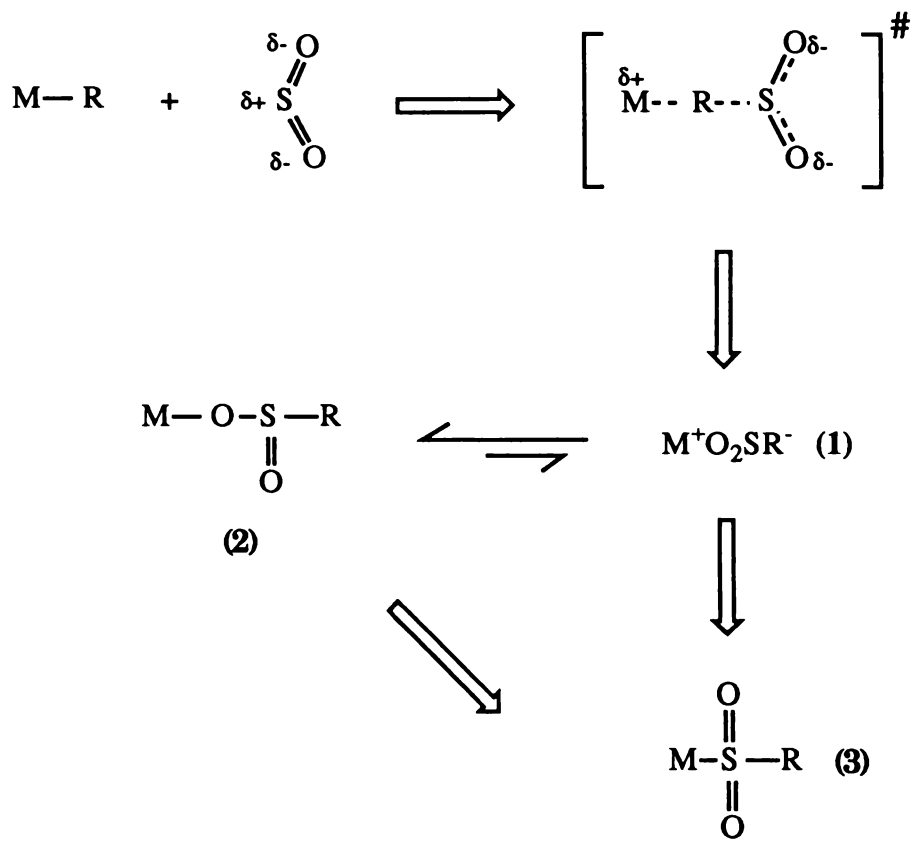
(2) (37)

Equation 3.8

This reaction appears to be reversible, as ^{13}C-NMR overnight indicated reversion of ~ 25 % of the product back to the orthomanganated precursor due to extrusion of SO_2. No such reversion was observed when the

S-sulfinato complexes were stored at low temperature either in the crystalline form or in solution.

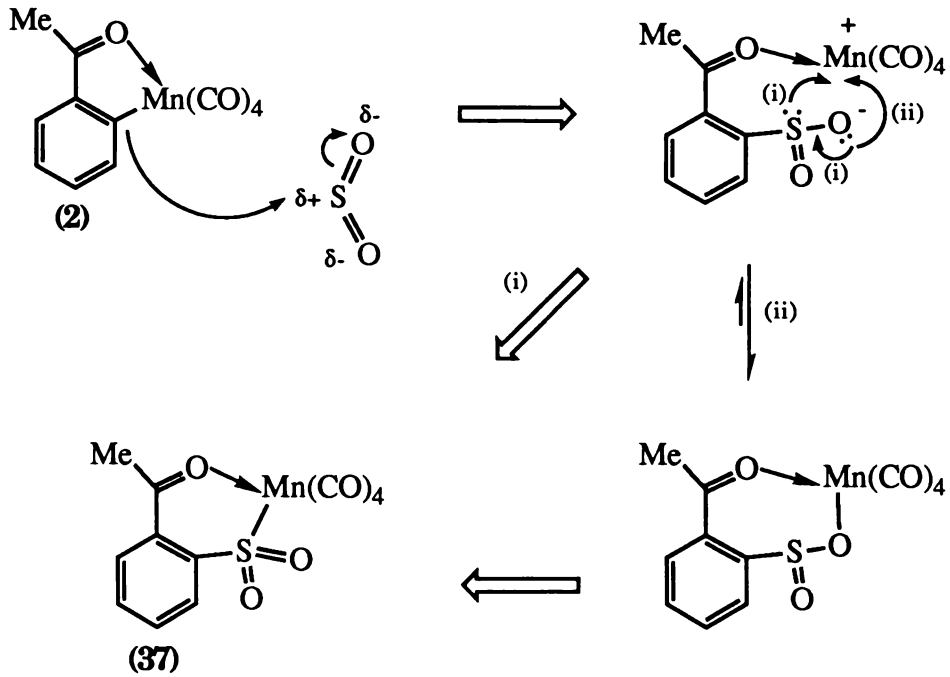
The insertion product is believed to be formed by an electrophilic cleavage process, involving backside electrophilic attack of SO_2 at the α-carbon [6]. This is depicted in Scheme 3.1. The resultant ion-pair (1) then combines to yield the neutral product (3) directly or via an intermediate O-bonded complex (2), this O-sulfinate being too unstable to be isolated [8].



Scheme 3.1

A similar reaction scheme can also be envisaged for the insertion of SO_2 into the Mn-C_{aryl} bond of orthomanganated ketones (Scheme 3.2).

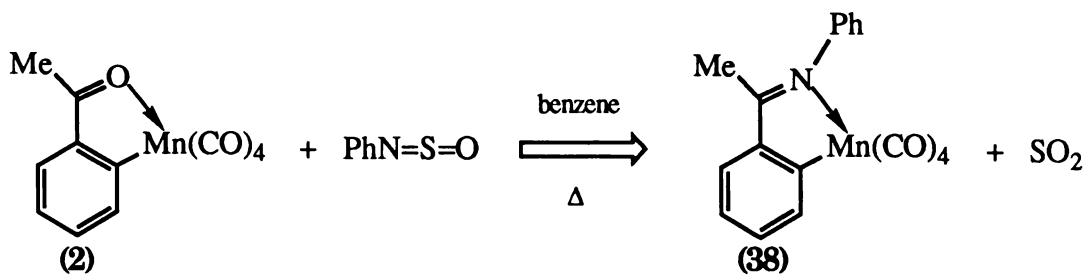
The facile insertion of SO_2 into the Mn-C_{aryl} bond of the orthomanganated ketone contrasts with the sluggish insertion of SO_2 into the Mn-C_{aryl} bond of $PhMn(CO)_5$ reported by Wojcicki *et al* [7]. Presumably this is due to the increased electron density at the aryl carbon for the orthomanganated compound as a result of coordination to manganese by the oxygen which is a π-donor rather than a π-acceptor.



Scheme 3.2

3.2.2 Reactions with PhNSO

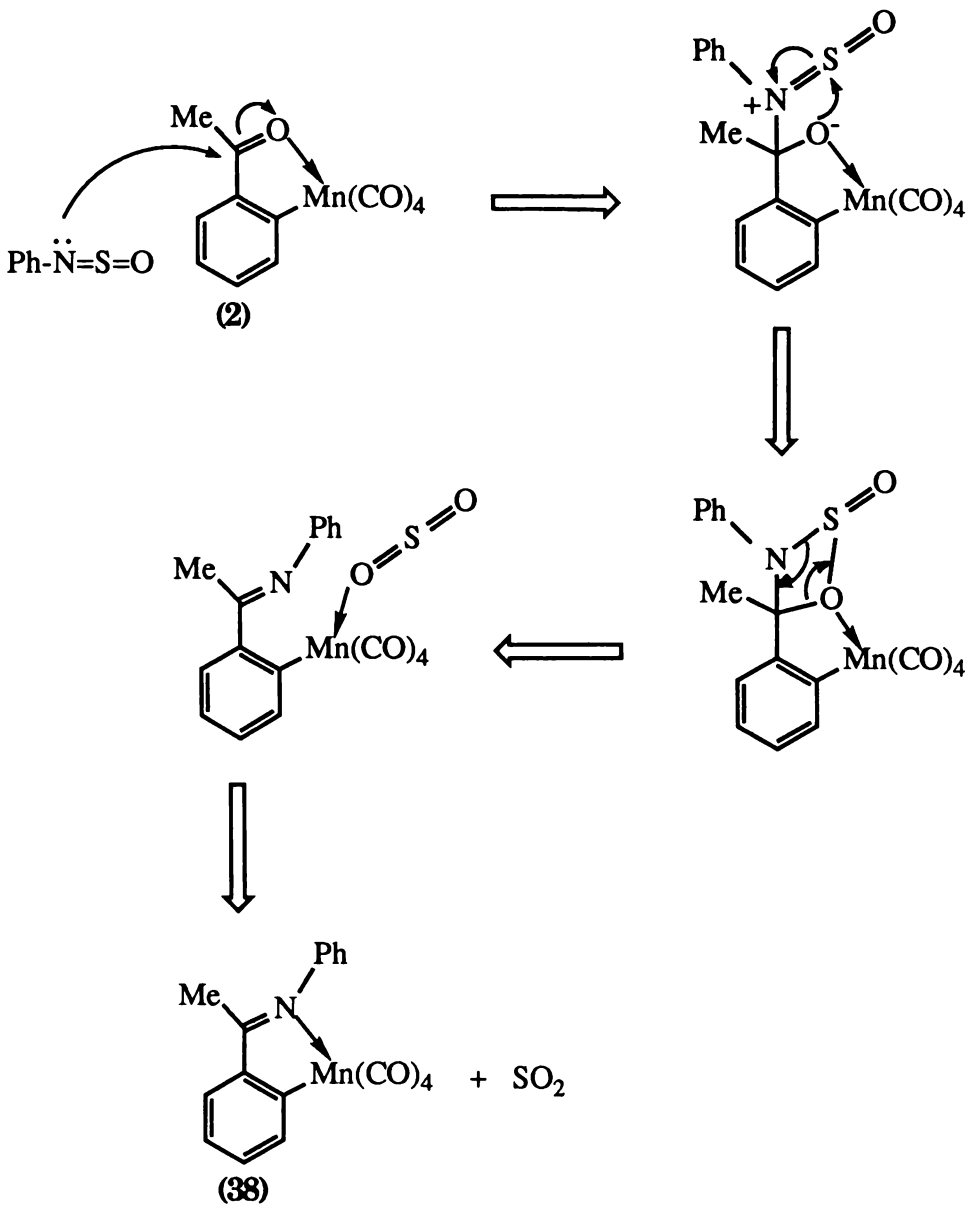
In contrast, reaction of PhNSO with a number of orthomanganated acetophenones led to the formation of the corresponding orthomanganated imine presumably via SO_2 elimination (Equation 3.9).



Equation 3.9

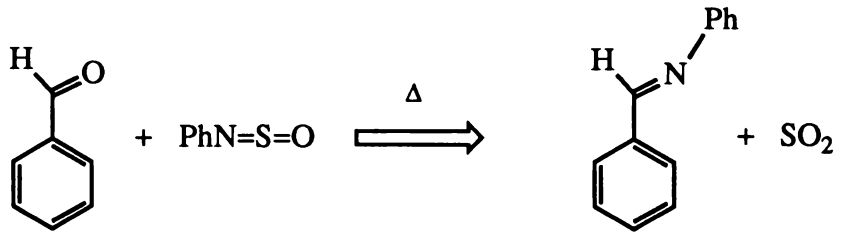
In this case, therefore, attack at the carbonyl functional group takes precedence over insertion into the Mn-C_{aryl} bond. This is possibly due to the fact that for PhNSO the nitrogen atom is a better nucleophile than the oxygen in SO_2. The carbon atom of the donor carbonyl group would also be particularly susceptible to nucleophilic attack, electron density being drawn away by the manganese atom.

The formation of the orthomanganated imine may occur by the route depicted in Scheme 3.3.



Scheme 3.3

A similar reaction has been reported for *N*-sulfinylaniline with benzaldehyde on heating to give benzylideneaniline [13] (Equation 3.10). However we found that the corresponding reaction with acetophenone did not proceed. This is perhaps not surprising as aldehydes generally undergo nucleophilic attack more readily than ketones. Coordination of the carbonyl group to manganese may polarise the ketone carbonyl to render it sufficiently susceptible to nucleophilic attack.



Equation 3.10

An alternative reaction that must be considered is the hydrolysis of the moisture sensitive PhNSO to $PhNH_2$ followed by nucleophilic attack at the ketone carbon to give the same product. Under the reaction conditions employed, however, this would be extremely unlikely, the reactions being conducted under nitrogen in rigorously dried and degassed solvent. This is further supported by the results of another worker at Waikato [14] who found that under identical conditions, reaction of orthomanganated acetophenone and aniline fails to afford the corresponding imine, the starting materials and $Mn_2(CO)_{10}$ only being recovered.

To ascertain the generality of the imine-forming reaction a range of orthomanganated compounds were reacted with PhNSO but with only limited success.

The orthomanganated acetophenones η^2-(2-acetylphenyl)-tetracarbonylmanganese **(2)**, η^2-(2-acetyl-3-chlorophenyl)tetracarbonyl-manganese **(16)**, η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** and η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese **(35)** all afforded the corresponding orthomanganated imine in reasonable yield.

It was somewhat surprising then that η^2-(6-acetyl-2,3-methylenedioxy-phenyl)tetracarbonylmanganese **(17)** failed to yield the expected product. There does not appear to be any reason for the difference in reactivity between this compound and the other substituted acetophenones.

There also appears to be no obvious reason for the failure of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese **(40)** to react. Reaction was observed for η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)**, though the resulting imine proved to be unstable, decomposing on workup.

η^2-(1-Phenylbut-1-ene-3-on-1-yl)tetracarbonylmanganese **(42)** also failed to react, implying there is no corresponding reactivity in α,β-unsaturated ketone systems.

Benzophenone systems are also not reactive if the polycyclic example, η^2-4-(dibenzosuberonyl)tetracarbonylmanganese **(11)** is typical of this class of substrate.

The orthomanganated ester, η^2-(5-methoxy-2-methoxycarbonylphenyl)-tetracarbonylmanganese **(19)**, failed to react as is consistent with lower reactivity of esters than ketones with nucleophiles.

Reaction of $PhCH_2Mn(CO)_5$ and PhNSO in refluxing benzene gave rise to an unstable insertion product, which decomposed within a matter of hours. The IR spectrum in the ν(CO) region showed absorption bands at 2076 (w), 1993 (vs), 1977 (s) and 1936 (s) cm^{-1}, consistent with the presence of a *cis*-tetracarbonyl species.

A similar reaction between $MeMn(CO)_5$ and $MeS(O)_2NSO$ at -25 °C reported by Wojcicki [10], also gave an unstable insertion product assumed to contain an Mn{N[S(O)$_2$Me]S(O)Me} fragment (Figure 3.5).

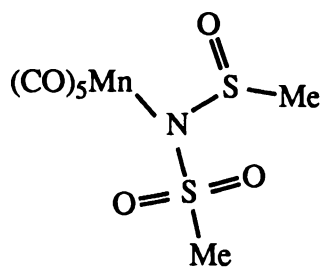


Figure 3.5

On this basis, we can suggest formation of an analogous intermediate followed by chelation with loss of a CO ligand to give a *cis*-tetracarbonyl species (Figure 3.6). This is conceivable as more forcing reaction conditions were employed than those used by Wojcicki, but were necessary for any reaction to occur at all.

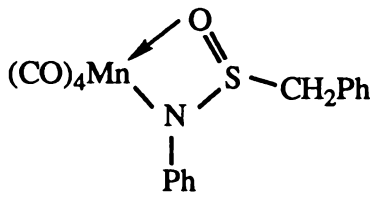


Figure 3.6

Another possibility is the structure shown in Figure 3.7. Wojcicki reported a complex of this type following the reaction of $MeMn(CO)_4PR_3$ and $MeS(O)_2NSO$ [10]. This reaction product was assumed to arise from the disproportionation of SO_2 and $[MeS(O)_2N]_2S$ followed by insertion of the latter into the Mn-Me bond. The same complex was obtained by direct reaction of $[MeS(O)_2N]_2S$ and $MeMn(CO)_4PR_3$. $MeMn(CO)_5$ and $[MeS(O)_2N]_2S$ also afforded a complex of this type with absorption bands in the ν(CO) region at 2145 (w), 2045 (s), 1950 (s) and 1930 (s) cm^{-1}.

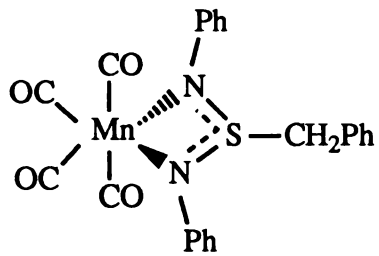


Figure 3.7

Since Wojcicki found that substitution of $L=PR_3$ for a CO group resulted in the formation of stable $MeS(O)_2NSO$ insertion products for $MeM(CO)_2(L)Cp$ (M=Mo, W) and $MeMn(CO)_4(L)$, the reaction of *cis*-$PhCH_2Mn(CO)_4PPh_3$ with PhNSO was conducted in an attempt to isolate an analogous complex. However this reaction was not successful, the starting materials only being recovered.

Reaction of $PhMn(CO)_5$ and PhNSO also failed to afford any insertion product. This was however not unexpected as aryl-metal bonds are generally less reactive than alkyl-metal bonds towards insertion reactions.

3.2.3 Reactions with $PhS(O)_2NSO$ and $[PhS(O)_2N]_2S$

Reaction of *N*-sulfinylsulfonamide and the disulfinylsulfur diimide with orthomanganated *p*-methoxyacetophenone **(39)** showed no reaction under

the conditions employed. If our assumption that the analogous reaction with PhNSO occurs by nucleophilic attack is correct, this is hardly surprising as electron withdrawal by the sulfonamide group would appreciably decrease the nucleophilic character of the nitrogen atom.

N-sulfinylsulfonamides have been reported to react on heating with aldehydes having no α-hydrogen atoms, to give SO_2 elimination and the *N*-sulfonylimine [15] (Equation 3.11).

$$R\text{-}SO_2\text{-}NSO + R'\text{-}CH{=}O \longrightarrow R\text{-}SO_2\text{-}N{=}CH\text{-}R' + SO_2$$

Equation 3.11

The reaction is often catalysed by $AlCl_3$, BF_3, HCl or similar substances, all of which would render the aldehyde more susceptible to nucleophilic attack.

The only sulfodiimides whose reactions with polar multiple bonds have so far been investigated are the di-t-alkyl-substituted compounds. The sulfodiimides, like the *N*-sulfinylsulfonamides also react with aromatic aldehydes to form imines [13] (Equation 3.12).

$$R\text{-}N{=}S{=}N\text{-}R + Ar\text{-}CH{=}O \longrightarrow R\text{-}N{=}CH\text{-}Ar + O{=}S{=}N\text{-}R$$

R=t-alkyl

Equation 3.12

3.3 X-Ray Crystal Structure of η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonyl-manganese (43)

The X-ray crystal structure of η^2-(2-acetyl-5-methoxyphenylsulphonyl)-tetracarbonylmanganese **(43)** was determined to characterise the reaction product between orthomanganated *p*-methoxyacetophenone **(39)** and liquid SO_2. The structure was of interest, as an SO_2 insertion reaction would give a novel six-membered chelate ring incorporating an O, Mn and S atom. No related structures of this type have been previously reported.

3.3.1 Results of Preliminary Studies

Yellow plates were obtained by crystallization by vapour diffusion of pentane into a saturated dichloromethane solution of **(43)** at 4 °C. Preliminary precession photography indicated triclinic symmetry, $P\bar{1}$ was assumed to be the space group and this was confirmed by the successful refinement.

3.3.2 Data Collection

Intensity data were obtained on a Enraf-Nonius CAD4 automatic four-circle diffractometer at the University of Auckland.

Crystal Data

Formula=$C_{13}H_9O_8MnS$

M_r=380.23

Crystal class=triclinic; Space group=$P\bar{1}$

a=6.426 (1), b=9.045 (4), c=13.767 (2) Å

α=97.37 (2)°, β=103.16 (1)°, γ=78.45 (2)°

U=760.6 (4) $Å^3$

D_{calc}=1.66 g cm^{-3}

Z=2

F(000)=384

μ(Mo-K_α)=9.69 cm^{-1}

A total of 2798 reflections in the range $0°<\theta<25°$ was collected of which 2576 were unique. These were corrected for Lorentz and polarisation effects and for linear absorption by a Ψ scan method. Of these, 2392 had $I \geq 2\sigma(I)$ and were used in all calculations.

3.3.3 Solution and Refinement

The position of the Mn atom was revealed by automatic analysis of the Patterson map using SHELXS-86. All other non-hydrogen atoms were revealed by a subsequent difference map phased on the Mn atom. In the final cycle of full-matrix least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R=0.0401, R_w=0.0413 where $w=[\sigma(F)^2 + 0.000174F^2]^{-1}$ and with no parameter shifting more than 0.02σ. A final difference map was featureless bar a ripple of electron density around the manganese atom ± 0.8 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 3.1 and 3.2. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix IV.

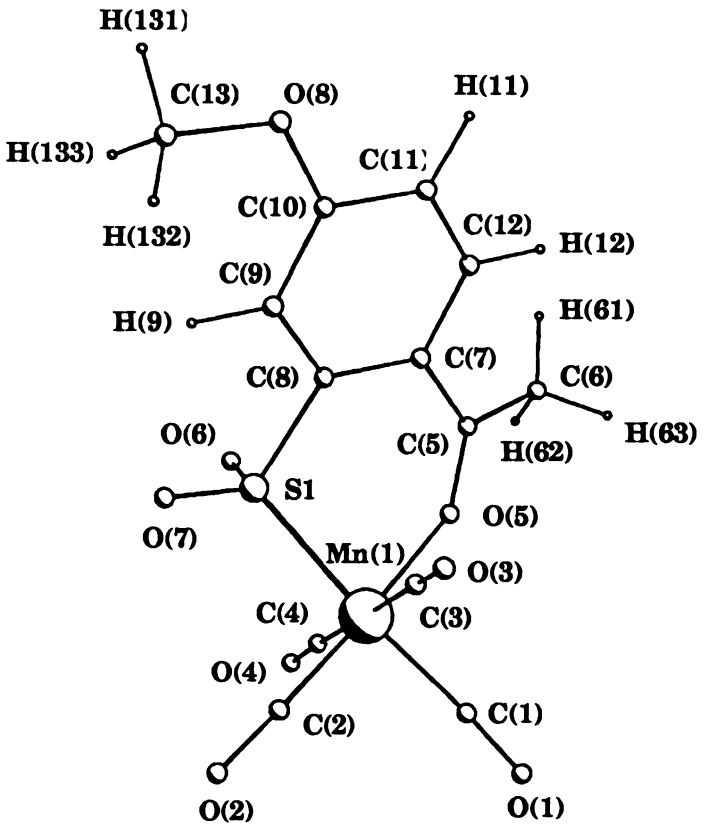
Figure 3.8 shows perspective and side views of **(43)** and illustrates the atom labelling scheme.

3.3.4 Discussion of the Structure

Insertion of SO_2 into the Mn-C_{aryl} bond of orthomanganated *p*-methoxy-acetophenone **(39)** leads to the formation of a six-membered metallocyclic ring which differs considerably in geometry from that of its five-membered precursor.

Previously reported orthomanganated compounds incorporating a five-membered chelate ring are all essentially planar and exhibit remarkably constant geometry about the metallocycle. In contrast the metallocyclic ring of **(43)** shows considerable deviation from planarity (see Figure 3.8 side view). The ring can be defined by two planes: plane 1 comprising the atoms C(5), C(7), C(8) and S, and plane 2 defined by the atoms S, Mn, O(5), C(2), O(2), C(1) and O(1) with a dihedral angle between the planes of 50.05(7)°. This pronounced fold presumably arises from the requirement for the S atom to assume tetrahedral geometry. As a result the metallocycle can no

Figure 3.8 Perspective and Side Views of η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese (43)



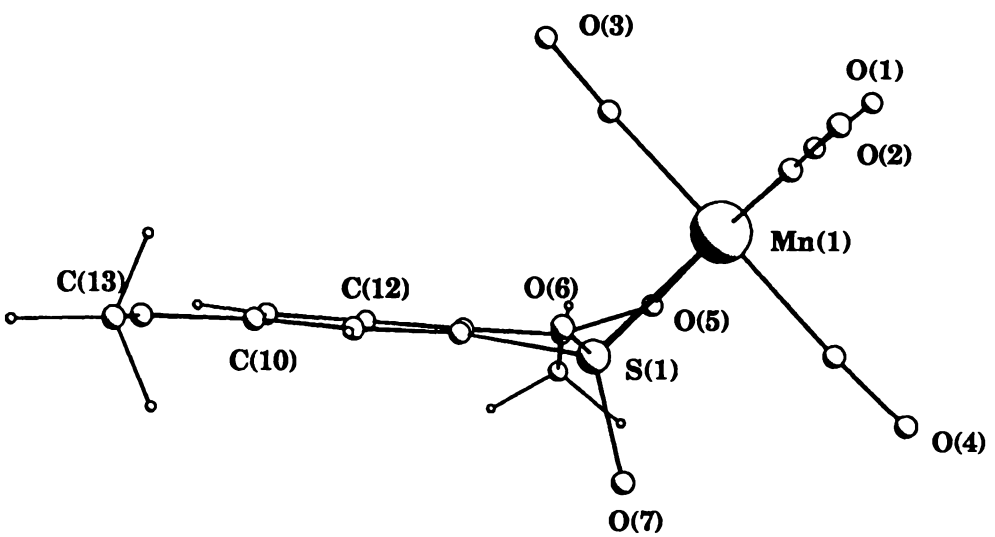


Table 3.1 Bond Lengths (Å) for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese (43)

Mn(1)	---S(1)	2.270(1)	O(4)	---C(4)	1.123(4)
Mn(1)	---O(5)	2.023(2)	O(5)	---C(5)	1.244(3)
Mn(1)	---C(1)	1.873(3)	O(8)	---C(10)	1.353(4)
Mn(1)	---C(2)	1.788(3)	O(8)	---C(13)	1.432(4)
Mn(1)	---C(3)	1.882(3)	C(5)	---C(6)	1.504(3)
Mn(1)	---C(4)	1.883(3)	C(5)	---C(7)	1.464(4)
S(1)	---O(6)	1.456(2)	C(7)	---C(8)	1.406(3)
S(1)	---O(7)	1.460(2)	C(7)	---C(12)	1.400(4)
S(1)	---C(8)	1.820(3)	C(8)	---C(9)	1.379(4)
O(1)	---C(1)	1.124(4)	C(9)	---C(10)	1.393(4)
O(2)	---C(2)	1.157(4)	C(10)	---C(11)	1.395(4)
O(3)	---C(3)	1.121(4)	C(11)	---C(12)	1.369(4)

Table 3.2 Bond Angles (°) for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese (43)

S(1)	-Mn(1)	-O(5)	83.5(1)	Mn(1)	-O(5)	-C(5)	136.4(2)
S(1)	-Mn(1)	-C(1)	173.8(1)	C(10)	-O(8)	-C(13)	118.1(3)
S(1)	-Mn(1)	-C(2)	93.2(1)	Mn(1)	-C(1)	-O(1)	176.3(3)
S(1)	-Mn(1)	-C(3)	90.0(1)	Mn(1)	-C(2)	-O(2)	178.5(3)
S(1)	-Mn(1)	-C(4)	88.3(1)	Mn(1)	-C(3)	-O(3)	175.5(3)
O(5)	-Mn(1)	-C(1)	90.4(1)	Mn(1)	-C(4)	-O(4)	176.4(3)
O(5)	-Mn(1)	-C(2)	175.7(1)	O(5)	-C(5)	-C(6)	116.3(2)
O(5)	-Mn(1)	-C(3)	93.6(1)	O(5)	-C(5)	-C(7)	123.1(2)
O(5)	-Mn(1)	-C(4)	88.2(1)	C(6)	-C(5)	-C(7)	120.6(2)
C(1)	-Mn(1)	-C(2)	92.8(1)	C(5)	-C(7)	-C(8)	122.5(2)
C(1)	-Mn(1)	-C(3)	91.7(1)	C(5)	-C(7)	-C(12)	120.3(2)
C(1)	-Mn(1)	-C(4)	90.1(1)	C(8)	-C(7)	-C(12)	117.2(2)
C(2)	-Mn(1)	-C(3)	89.0(1)	S(1)	-C(8)	-C(7)	121.3(2)
C(2)	-Mn(1)	-C(4)	89.0(1)	S(1)	-C(8)	-C(9)	116.8(2)
C(3)	-Mn(1)	-C(4)	177.4(1)	C(7)	-C(8)	-C(9)	121.7(2)
Mn(1)	-S(1)	-O(6)	111.8(1)	C(8)	-C(9)	-C(10)	119.4(3)
Mn(1)	-S(1)	-O(7)	115.9(1)	O(8)	-C(10)	-C(9)	124.5(3)
Mn(1)	-S(1)	-C(8)	104.7(1)	O(8)	-C(10)	-C(11)	115.5(3)
O(6)	-S(1)	-O(7)	115.0(1)	C(9)	-C(10)	-C(11)	120.0(3)
O(6)	-S(1)	-C(8)	103.4(1)	C(10)	-C(11)	-C(12)	119.9(3)
O(7)	-S(1)	-C(8)	104.2(1)	C(7)	-C(12)	-C(11)	121.8(3)

longer be viewed as a pseudoaromatic species exhibiting delocalised π-bonding over a planar ring.

The phenyl ring and *p*-methoxy group form a planar system (plane 3) which is almost coplanar with plane 1, leading to a dihedral angle of only 3.08(8)°.

Coordination about the manganese atom is essentially octahedral, distortions from ideal geometry being far less pronounced than for previously reported cyclomanganated species with five-membered rings.

The axial carbonyls are essentially perpendicular to the plane defined by the equatorial ligands about manganese, with deviation from 90° of only 2.6°. This contrasts with most other C_{ax}-Mn-C_{ax} bond angles reported for orthomanganated complexes where the folding of the axial carbonyls towards the ring carbon bonded to manganese is usually very pronounced. C_{ax}-Mn-C_{ax} bond angles of 169.6(1)° [16,17], 168.9(2)° [18] and 168.7(2)° [18] are usually typical of these compounds.

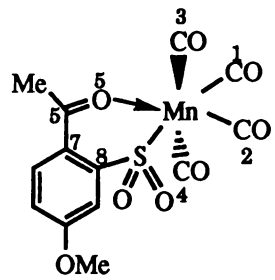
The six-membered ring allows a wider chelate bite (83.5(1)°) than those reported for corresponding five-membered chelate ring incorporating structures (78-80°). In Table 3.3, the bond distances and angles about the metal coordination sphere are tabulated and compared with the corresponding distances and angles reported for orthomanganated acetophenone **(2)** and the cyclic S-sulfinate $(OC)_4\overline{MnPPh_2(CH_2)_3SO_2}$.

The C(5)-O(5)-Mn bond angle of 136.4(2)° in **(43)** is markedly different from that reported for (A) 116.5(2)°, and deviates considerably from that expected for ideal sp^2 hybridised geometry. This opening of the bond angle suggests an increase in s-character in the C(5)-O(5) and O(5)-Mn bonds, which would account for some shortening over these bonds.

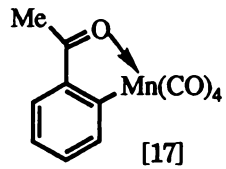
The geometry about manganese can be rationalised by the replacement of the sp^2 C in (A) by the more electronegative SO_2 group in **(43)**. This would have the effect of withdrawal of electron density from manganese, making it a better σ-acceptor from oxygen leading to the shortest yet reported Mn-O distance in a cyclomanganated complex.

The withdrawal of electron density from manganese would make it a poorer π-donor. This is evident from the longer Mn-CO distances in this compound,

Table 3.3 Selected Bond Lengths (Å) and Bond Angles (°) of η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese (43) and Related Compounds

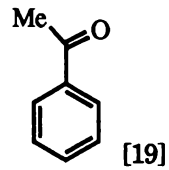


(43)

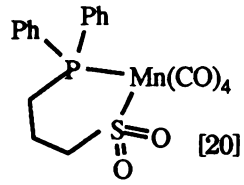


(2)

(A)



(B)



(C)

Mn-S	2.270(1)			
Mn-O(5)	2.023(2)	2.055(2)		
C(5)-O(5)	1.244(3)	1.244(3)	1.216(2)	2.312(2)
C(5)-C(7)	1.464(4)	1.455(3)	1.494(2)	
C(7)-C(8)	1.406(3)			
Mn-C(1)	1.873(3)	1.849(3)		1.807(9)
Mn-C(2)	1.788(3)	1.786(3)		1.820(9)
Mn-C(3)	1.882(3)	1.857(3)		1.852(9)
Mn-C(4)	1.883(3)	1.856(3)		1.889(9)
O(5)-Mn-X	83.5(1)	79.4(1)		
(X=S,C)				
C(5)-O(5)-Mn	136.4(2)	116.5(2)		
C(7)-C(5)-O(5)	123.1(2)	117.5(2)		

and also presumably from both the constant upfield shift in the ^{13}C-NMR resonances of the metal-carbonyls, and the shift to higher wavenumbers in the metal-carbonyl region of the IR spectrum which reflects an increase in the CO bond order (Table 3.4).

Table 3.4 ^{13}C-NMR and Infrared M-C≡O Data for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese (43) and Related Compounds

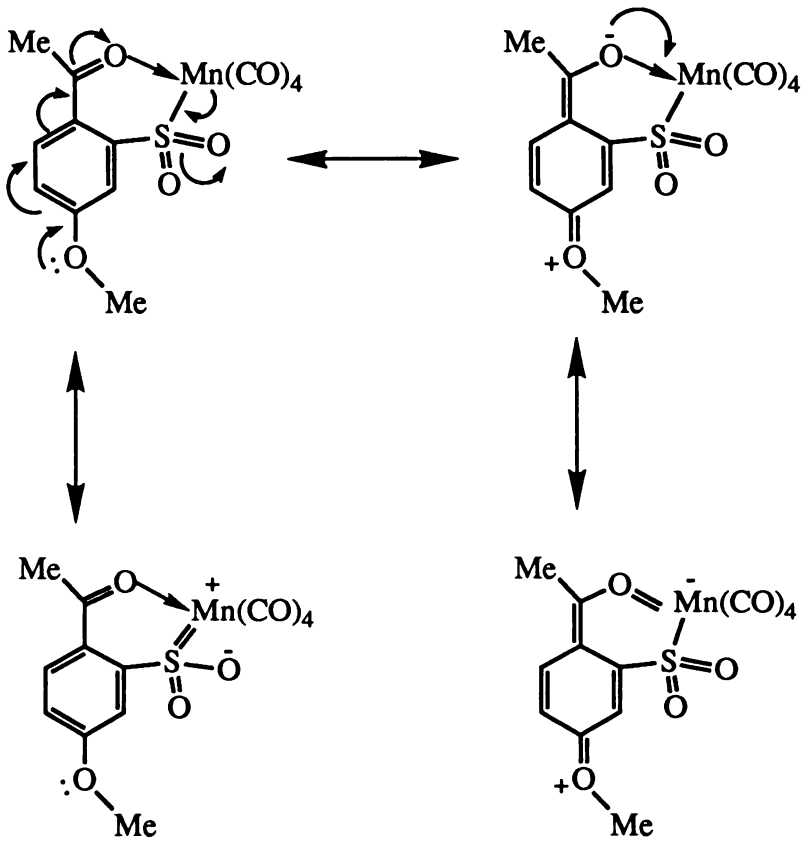
	^{13}C-NMR M-C≡O ($CDCl_3$) δ	Infrared M-C≡O ν(CO) cm^{-1}
(43)	214.6, 209.1, 2x 205.8	2111 (m), 2039 (s), 2020 (s), 1986 (s) (CH_2Cl_2)
(A)	221.0, 213.6, 2x 211.6	2081 (m), 1993 (vs), 1945 (s) (hexane)
(C)		2095 (m), 2040 (s), 2003 (vs), 1991 (s) (CH_2Cl_2/CCl_4 1/1)

The Mn-S distance of 2.270(1) Å is considerably shorter than that reported for the six-membered cyclic S-sulfinate (C), 2.312(2) Å. Presumably this is due to increased electron withdrawal from manganese to sulphur in **(43)**, as a result of coordination to electronegative oxygen in **(43)** compared to the larger and less electronegative phosphorus atom in (C).

The C(5)-O(5) bond length of 1.233(3) Å is ~0.03 Å longer than the uncoordinated carbonyl distance in free acetophenone, and is identical to that reported for (A). Whereas this decrease in double bond character is rationalised by π-delocalisation over the entire metallocycle in (A), for **(43)** it may be explained by electron withdrawal to manganese due to the effect of the electronegative SO_2 group, tempered with a shortening of the bond due to the widening of the C(5)-O(5)-Mn bond angle implying increased s-character in the bonding hybridisation scheme.

The geometry over the remainder of the molecule in **(43)** is similar to other delocalised organic systems, and suggests delocalisation over the planar part of the molecule.

The complete structure may be rationalised by the following contributing resonance forms (Scheme 3.4).



Scheme 3.4

As the ketone carbonyl group is rotated 24.5(1)° out of the plane defined by the atoms C(7), C(5) and O(5), we would not expect a great degree of delocalisation of electron density from the *p*-methoxy group through to the ketone oxygen atom due to poor p-orbital overlap. Nevertheless, bond length data seems to suggest some overlap is possible as is evident from the short C(10)-O(8) and C(7)-C(5) bonds.

3.4 X-Ray Crystal Structure of η^2-3-Chloro-2-[1-(*N*-phenylimino)ethyl]-phenyltetracarbonylmanganese (44)

The crystal structure of η^2-3-chloro-2-[1-(*N*-phenylimino)ethyl]-phenyltetracarbonylmanganese **(44)** was determined to characterise the reaction product between orthomanganated 2'-chloroacetophenone **(16)** and PhNSO.

3.4.1 Results of Preliminary Studies

Yellow prismatic crystals were obtained by recrystallization from chloroform/hexane (1:10) at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated monoclinic symmetry with systematic absences appropriate for the space group $P2_1/c$.

3.4.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -105 °C with monochromated Mo-K_α radiation.

Crystal Data

Formula=$C_{18}H_{11}O_4ClNMn$

M_r=395.69

Crystal class=monoclinic; Space group=$P2_1/c$

a=8.564(2), b=21.544(6), c=10.055(4) Å

β=111.98(2) °

U=1720(1) $Å^3$

D_{calc}=1.53 g cm^{-3}

Z=4

F(000)=800

μ(Mo-K_α)=8.78 cm^{-1}

A total of 4887 reflections in the range $4°<2\theta<50°$ was collected, corresponding to 3020 unique reflections. These were corrected for Lorentz and polarisation effects and for linear absorption by a Ψ scan method. Of these, 2532 had $I \geq 3\sigma(I)$ and were used in all calculations.

3.4.3 Solution and Refinement

The heavy atom positions (all 25 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. The refinement converged with R=0.0282, R_w=0.0276 where $w=[\sigma^2(F) + 0.000122\ F^2]^{-1}$. No parameter shifted by more than 0.006σ in the final cycle. The final difference map showed no peak or trough of electron density greater than 0.30 e Å.

Bond lengths and angles are presented in Tables 3.5 and 3.6. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix V.

Side and perspective views of the structure are illustrated in Figure 3.9, along with the atom labelling scheme.

3.4.4 Discussion of the Structure

On solving the crystal structure it was apparent that the insertion product of the reaction was an orthomanganated imine and that insertion into the $Mn\text{-}C_{aryl}$ bond had not occurred. This is the first crystal structure of a cyclomanganated imine derived from an aryl ketone, the only other closely related compound being a cyclomanganated imine formed from the Schiff base benzylideneaniline [21].

In the resulting complex **(44)**, the manganese atom is coordinated in a distorted octahedral configuration with the chelate ligand and two carbonyl ligands in the equatorial plane, while the axial positions are occupied by the other two carbonyl ligands. The ligand is bound via a metal-nitrogen bond

Figure 3.9 Side and Perspective Views of η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese (44)

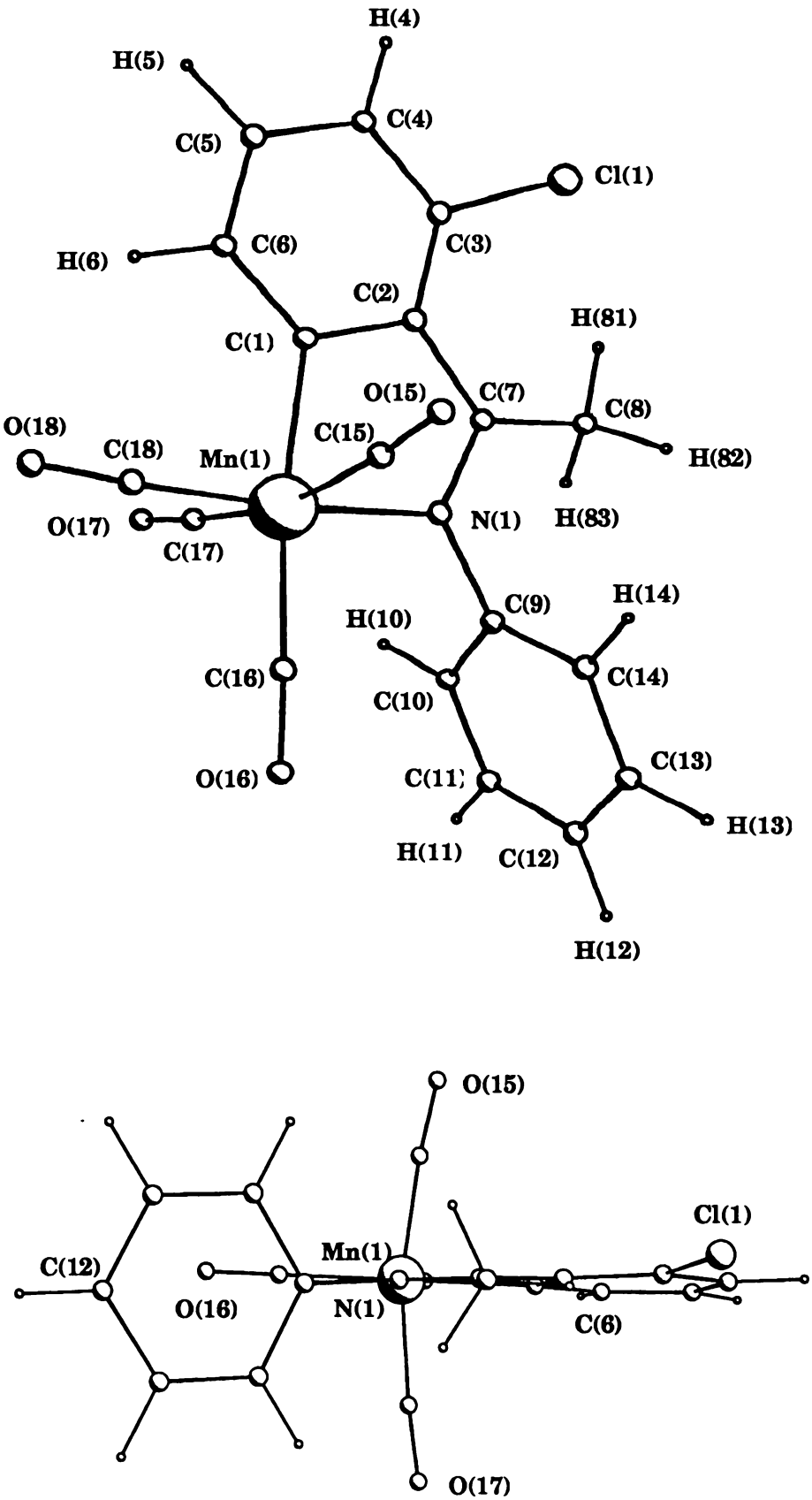


Table 3.5 Bond Lengths (Å) for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese (44)

Mn(1)	---N(1)	2.041(2)	C(4)	---C(5)	1.381(3)
Mn(1)	---C(1)	2.040(2)	C(5)	---C(6)	1.383(3)
Mn(1)	---C(15)	1.843(2)	C(7)	---C(8)	1.499(3)
Mn(1)	---C(16)	1.854(2)	C(9)	---C(10)	1.390(3)
Mn(1)	---C(17)	1.848(2)	C(9)	---C(14)	1.379(3)
Mn(1)	---C(18)	1.804(2)	C(10)	---C(11)	1.384(3)
Cl(1)	---C(3)	1.750(2)	C(11)	---C(12)	1.381(3)
N(1)	---C(7)	1.300(3)	C(12)	---C(13)	1.382(4)
N(1)	---C(9)	1.439(3)	C(13)	---C(14)	1.386(3)
C(1)	---C(2)	1.422(3)	C(15)	---O(15)	1.143(3)
C(1)	---C(6)	1.401(3)	C(16)	---O(16)	1.137(3)
C(2)	---C(3)	1.399(3)	C(17)	---O(17)	1.137(3)
C(2)	---C(7)	1.477(3)	C(18)	---O(18)	1.154(2)
C(3)	---C(4)	1.386(3)			

Table 3.6 Bond Angles (°) for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese (44)

N(1)	-Mn(1)	-C(1)	78.1(1)	C(3)	-C(2)	-C(7)	127.8(2)
N(1)	-Mn(1)	-C(15)	90.2(1)	Cl(1)	-C(3)	-C(2)	123.6(2)
N(1)	-Mn(1)	-C(16)	94.4(1)	Cl(1)	-C(3)	-C(4)	114.6(2)
N(1)	-Mn(1)	-C(17)	90.0(1)	C(2)	-C(3)	-C(4)	121.8(2)
N(1)	-Mn(1)	-C(18)	173.7(1)	C(3)	-C(4)	-C(5)	119.2(2)
C(1)	-Mn(1)	-C(15)	83.2(1)	C(4)	-C(5)	-C(6)	120.6(2)
C(1)	-Mn(1)	-C(16)	172.4(1)	C(1)	-C(6)	-C(5)	121.2(2)
C(1)	-Mn(1)	-C(17)	84.7(1)	N(1)	-C(7)	-C(2)	113.5(2)
C(1)	-Mn(1)	-C(18)	95.7(1)	N(1)	-C(7)	-C(8)	121.7(2)
C(15)	-Mn(1)	-C(16)	96.6(1)	C(2)	-C(7)	-C(8)	124.8(2)
C(15)	-Mn(1)	-C(17)	167.6(1)	N(1)	-C(9)	-C(10)	119.3(2)
C(15)	-Mn(1)	-C(18)	89.2(1)	N(1)	-C(9)	-C(14)	119.8(2)
C(16)	-Mn(1)	-C(17)	95.7(1)	C(10)	-C(9)	-C(14)	120.6(2)
C(16)	-Mn(1)	-C(18)	91.9(1)	C(9)	-C(10)	-C(11)	119.3(2)
C(17)	-Mn(1)	-C(18)	89.3(1)	C(10)	-C(11)	-C(12)	120.4(2)
Mn(1)	-N(1)	-C(7)	119.8(1)	C(11)	-C(12)	-C(13)	119.9(2)
Mn(1)	-N(1)	-C(9)	118.6(1)	C(12)	-C(13)	-C(14)	120.2(2)
C(7)	-N(1)	-C(9)	121.6(2)	C(9)	-C(14)	-C(13)	119.6(2)
Mn(1)	-C(1)	-C(2)	114.7(1)	Mn(1)	-C(15)	-O(15)	175.0(2)
Mn(1)	-C(1)	-C(6)	126.8(2)	Mn(1)	-C(16)	-O(16)	178.4(2)
C(2)	-C(1)	-C(6)	118.5(2)	Mn(1)	-C(17)	-O(17)	175.7(2)
C(1)	-C(2)	-C(3)	118.6(2)	Mn(1)	-C(18)	-O(18)	179.2(2)
C(1)	-C(2)	-C(7)	113.7(2)				

and a metal-carbon σ-bond to the *ortho* position of the chlorine substituted phenyl ring.

The chelate five-membered ring (Mn-N-C(7)-C(2)-C(1)) is only slightly puckered, deviating from planarity by ~0.3 Å. The two phenyl rings are each essentially planar, with the aniline phenyl ring (C(9)-C(14)) twisted by 131.81(8)° from the chelate plane. The chlorine-substituted phenyl ring (C(1)-C(6)) and the chelate ring are also non-coplanar, giving rise to a dihedral angle of 21.40(5)°.

The coordination about the manganese atom is distorted octahedral, the principal distortions being related to the chelate bite angle of 78.1(1)° and to the non linearity of the C(15)-Mn-C(17) vector. The latter distortion involves an angular displacement of C(15) and C(17) away from C(16) and towards C(1), with a resulting C(17)-Mn-C(15) angle of 167.6(1)°. The O(15)-C(15)-Mn and O(17)-C(17)-Mn vectors also deviate slightly from linearity with bond angles of 175.0(2)° and 175.7(2)° respectively.

In Table 3.7 for comparison are summarised some relevant structural data from the crystal structures of related systems.

The C=N bond is lengthened upon coordination to manganese, from 1.237(3) Å in the related benzylidineaniline (A) to 1.300(3) Å, while the C(2)-C(7) bond length appears to be shortened slightly (1.477(3) in **(44)** compared to 1.496(3) Å in (A)).

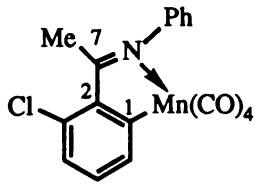
The Mn-C(1) and Mn-N distances are at the shorter end of ranges found in related molecules, (see Table 3.7) but are otherwise unremarkable.

The structure is consistent with π-delocalised bonding over the chelate ring, analogous to that described for other orthomanganated arenes for which structures have been determined.

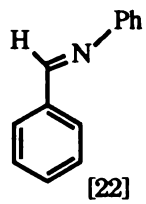
The C-C distances within both phenyl rings are comparable, neither showing any significant deviation from the norm.

Following the pattern established for O-donor orthomanganated complexes, some variation in the individual Mn-C≡O bond lengths is observed, the shortest being to the carbonyl *trans* to the donor atom, in this case a nitrogen.

Table 3.7 Selected Bond Lengths (Å) and Angles (°) of η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese (44) and Related Compounds

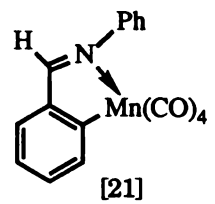


(44)



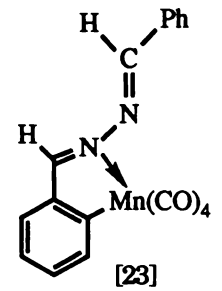
[22]

Benzylidene aniline (A)



[21]

Tetracarbonyl-2-(*N*-phenyl formidoyl) phenylmanganese (B)



[23]

(2-Benzylidene hydrazonomethyl phenyl-C'N)tetra carbonylmanganese (C)

Mn-N	2.041(2)		2.070(7)	2.120(50
Mn-C(1)	2.040(2)		2.060(8)	2.068(5)
C(1)-C(2)	1.422(3)		1.418(11)	1.389(9)
C(2)-C(7)	1.477(3)	1.496(3)	1.443(10)	1.446(9)
C(7)-N	1.300(3)	1.237(3)	1.285(10)	1.295(8)
C(1)-Mn-N	78.1(1)		79.4(3)	79.3(2)

A comparison of the ^{13}C-NMR M-C≡O resonances for **(44)** and the corresponding orthomanganated acetophenone **(16)** reveal little variation in chemical shift between these two compounds (Table 3.8), suggesting that in this environment the O and N atoms are comparable π-donors.

Table 3.8 ^{13}C-NMR and M-C≡O Bond Length Data for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonyl-manganese (44) and Related Compounds

	^{13}C-NMR M-C≡O ($CDCl_3$) δ	M-C≡O Bond Lengths (Å)
(44)	219.7, 213.2, 2x 211.8	M-C(15) 1.843(2); M-C(16) 1.854(2); M-C(17) 1.848(2); M-C(18) 1.804(2)
(16)	220.4, 212.6, 2x 210.7	
(2)		M-C(15) 1.857(3); M-C(16) 1.849(3); M-C(17) 1.856(3); M-C(18) 1.786(3)

Examination of the individual M-C≡O bond lengths for **(44)** and **(2)** [17] (Table 3.8), the most closely related orthomanganated acetophenone for which a structure has been determined, shows little variation in the metal-carbon bond lengths for the axial carbonyls (M-C(15), M-C(17)) and the carbonyl group *trans* to the aromatic ring (M-C(16)) between the two structures. There does however appear to be some variation in the metal-carbon bond length for the carbonyl *trans* to the coordinated donor atom (M-C(18)), this bond being slightly shorter in the case of the orthomanganated acetophenone.

3.5 Experimental Section

The cumulenes *N*-sulfinylaniline (PhN=S=O) [24], *N*-sulfinylbenzene-sulfonamide ($PhS(O)_2N=S=O$) and the disulfonylsulfodiimide ($[PhS(O)_2N]_2S$) [13] were prepared by established literature methods.

cis-$PhCH_2Mn(CO)_4PPh_3$ was prepared by the method reported by Drew *et al* [25] m.p. 153-155 °C (lit. 155 °C [25])

Sulphur dioxide (BDH Chemicals) was used as supplied.

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with SO_2

η^2-(2-Acetylphenyl)tetracarbonylmanganese [**(2)**; 200 mg, 0.699 mmol] was placed in an ampoule, degassed and treated with liquid SO_2 (~ 10 ml) which had previously been degassed by two cycles of freeze-pump-thawing using standard vacuum line techniques. The ampoule was sealed, and placed in a Carius tube maintained at 55 °C overnight. The ampoule was opened and the excess SO_2 allowed to evaporate in the fumehood whereupon the residue was extracted with dichloromethane. An infrared spectrum showed complete conversion to the SO_2 insertion product, *η^2-(2-acetylphenylsulphonyl)tetracarbonylmanganese* **(37)** by the absence of the peaks at 2083 (m), 1996 (vs), 1948 (s) cm^{-1} and the appearance of the peaks at 2112 (m), 2040 (s), 2020 (s), 1980 (s) cm^{-1}. The compound was an oil which failed to crystallize. IR: (CH_2Cl_2) ν(CO) 2112 (m), 2040 (s), 2020 (s), 1980 (s) cm^{-1}.

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with SO_2

Similarly, η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 200 mg, 0.633 mmol] was treated with SO_2 (~ 10 ml) and left to react overnight at 55 °C. An infrared spectrum showed complete conversion to the SO_2 insertion product, *η^2-(2-acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese* **(43)**. Vapour diffusion of pentane into a saturated dichloromethane solution of **(43)** at 4 °C afforded small yellow plates in 84 % yield, m.p. 115 °C (dec). IR: (CH_2Cl_2) ν(CO) 2111 (m), 2039 (s), 2020 (s), 1986 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.84 (2H, br, *s*), 7.04 (1H, br, *s*), 4.02 (3H, *s*, 5-OCH_3), 2.77 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 214.6 (*s*, br, C≡O), 210.0 (*s*, 2-$\underline{C}OCH_3$), 209.1 (*s*, br, C≡O), 205.8 (*s*, br, 2xC≡O), 166.0 (*s*, C-5), 154.3 (*s*, C-1), 135.2 (*d*, C-3), 123.6 (*s*, C-2), 117.2 (*d*, C-4), 105.8 (*d*, C-6), 56.4 (*q*, 5-OCH_3), 29.5 (*q*, 2-$CO\underline{C}H_3$).

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with SO_2

Following the standard procedure, η^2-(2-acetylthien-3-yl)tetracarbonylmanganese [**(40)**; 115 mg, 0.394 mmol] was treated with SO_2 (~ 10 ml) and left to react overnight at 55 °C. An infrared spectrum showed complete conversion to the SO_2 insertion product, *η^2-(2-acetylthien-3-ylsulphonyl)tetracarbonylmanganese* **(45)**. Vapour diffusion of pentane into a saturated dichloromethane solution of **(45)** at 4 °C afforded small yellow/orange crystals in 74 % yield. IR: (CH_2Cl_2) ν(CO) 2115 (m), 2040 (vs), 2027 (s), 1987 (s) cm^{-1}.

Reaction of η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with PhNSO

A degassed solution of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese [**(35)**; 200 mg, 0.532 mmol] in dichloromethane (8 ml) was treated with PhNSO (0.06 ml, 0.532 mmol) and stirred under nitrogen for an hour. Preliminary infrared spectroscopy showed only starting material in the metal carbonyl region, and so the mixture was refluxed for an hour. An infrared spectrun still showed no sign of reaction, so an excess of PhNSO (0.1 ml, 0.888 mmol) was added. After a total of 150 min refluxing no sign of

reaction was evident by infrared spectrum or t.l.c. and the reaction was abandoned.

A degassed solution of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese [**(35)**; 215 mg, 0.572 mmol] in benzene (8 ml) was mixed with PhNSO (0.32 ml, 2.86 mmol) and stirred under nitrogen for 30 min. A preliminary infrared spectrum once again showed only starting material. The reaction mixture was refluxed for 3 h after which time the two bands at highest energy in the metal carbonyl region had shifted downfield ~10 wavenumbers. The benzene was removed under vacuum. The resultant yellow oil was dissolved in dichloromethane and chromatographed on silica plates with diethyl ether/petroleum spirit (1:10) as the eluant. A broad yellow band of *η^2-3,4,5-trimethoxy-2-[1-N(phenylimino)ethyl]-phenyltetracarbonylmanganese* [**(46)**; 285 mg, 60 %] was collected, m.p. 113-114.5 °C. Anal. Found: C, 55.88; H, 4.15; N, 3.17 %; $C_{21}H_{18}O_7NMn$ calcd: C, 55.89; H, 4.02; N, 3.17 %. IR: (hexane) ν(CO) 2073 (m), 1985 (vs), 1942 (s) 1566 (w), 1536 (w) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.42 (2H, *t*, $^3J_{3',2'}=^3J_{3',4'}=^3J_{5',4'}=^3J_{5',6'}$=7.6 Hz, H-3',5'), 7.23 (1H, *t*, $^3J_{4',3'}=^3J_{4',5'}$=7.6 Hz, H-4'), 7.23 (1H, *s*, H-6), 6.89 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=7.6 Hz, H-2',6'), 4.00 (3H, *s*, -OCH_3), 3.96 (3H, *s*, -OCH_3), 3.85 (3H, *s*, -OCH_3), 2.32 (3H, *s*, 2-C(NPh)$\underline{C}H_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.4 (*s*, br, C≡O), 214.1 (*s*, br, C≡O), 212.3 (*s*, br, 2xC≡O), 182.9 (*s*, 2-$\underline{C}$=NPh), 178.8 (*s*, C-1), 155.8 (*s*, C-5*), 155.7 (*s*, C-3*), 153.3 (*s*, C-1'), 138.8 (*s*, C-2), 133.7 (*s*, C-4), 129.7 (*d*, C-3',5'), 125.9 (*d*, C-4'), 121.6 (*d*, C-2',6'), 118.1 (*d*, C-6), 61.0 (*q*, 5-OCH_3), 60.7 (*q*, 4-OCH_3), 55.9 (*q*, 3-OCH_3), 21.6 (*q*, 2-C(NPh)$\underline{C}H_3$).

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with PhNSO

A degassed solution of η^2-(2-acetylphenyl)tetracarbonylmanganese [**(2)**; 208 mg, 0.727 mmol] in benzene (8 ml) was treated with PhNSO (0.41 ml, 3.64 mmol) and refluxed under nitrogen for one hour. An infrared spectrum showed only the shifted metal carbonyl stretches, indicating that the reaction had gone to completion. The reaction mixture was worked up by the normal method and chromatographed (p.l.c., 1:10 ether/petroleum spirit) to yield *η^2-2-[1-N(phenylimino)ethyl]-phenyltetracarbonylmanganese* [**(38)**; 263 mg, 53 %], m.p 108-110 °C. Anal. Found: C, 60.12; H, 3.62; N, 4.01 %; $C_{18}H_{12}O_4NMn$ calcd: C, 59.85; H, 3.35; N, 3.88 %. IR: (hexane) ν(CO) 2074

(m), 1985 (vs), 1947 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.06 (1H, *d*, $^3J_{6,5}$=7.4 Hz, H-6), 7.66 (1H, *d*, $^3J_{3,4}$=7.4 Hz, H-3), 7.48 (2H, *t*, $^3J_{3',2'}=^3J_{3',4'}=^3J_{5',4'}=^3J_{5',6'}$=7.6 Hz, H-3',5'), 7.36 (1H, *t*, $^3J_{5,4}=^3J_{5,6}$=7.4 Hz, H-5), 7.30 (1H, *t*, $^3J_{4',3'}=^3J_{4',5'}$=7.6 Hz, H-4'), 7.21 (1H, *t*, $^3J_{4,3}=^3J_{4,5}$=7.4 Hz, H-4), 6.95 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=7.6 Hz, H-2',6'), 2.24 (3H, *s*, 2-C(NPh)C$\underline{H}_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.4 (*s*, br, C≡O), 214.1 (*s*, br, C≡O), 212.6 (*s*, br, 2xC≡O), 183.1 (*s*, 2-$\underline{C}$=NPh), 182.3 (*s*, C-1), 152.9 (*s*, C-1'), 148.8 (*s*, C-2), 141.5 (*d*, C-6), 131.3 (*d*, C-5), 129.8 (*d*, C-3',5'), 128.9 (*d*, C-3), 126.3 (*d*, C-4'), 123.5 (*d*, C-4), 121.2 (*d*, C-2',6'), 17.9 (*q*, 2-C(NPh)$\underline{C}H_3$).

Reaction of η^2-(2-Acetyl-3-chlorophenyl)tetracarbonylmanganese (16) with PhNSO

Similarly η^2-(2-acetyl-3-chlorophenyl)tetracarbonylmanganese [**(16)**; 174 mg, 0.542 mmol] and PhNSO (0.31 ml, 2.71 mmol) refluxed in benzene (8 ml) over 2 h afforded *η^2-3-chloro-2-[1-N(phenylimino)ethyl]-phenyl-tetracarbonylmanganese* [**(44)**; 215 mg, 62 %], m.p. 109-109.5 °C. Anal. Found: C, 54.77; H, 2.79; N, 3.66 %; $C_{18}H_{11}O_4ClNMn$ calcd: C, 54.64; H, 2.80; N, 3.54 %. IR: (hexane) ν(CO) 2076 (m), 1989 (vs), 1950 (s) 1575 (w), 1566 (w) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.89 (1H, *m*, H-6), 7.46 (2H, *t*, $^3J_{3',2'}=^3J_{3',4'}=^3J_{5',4'}=^3J_{5',6'}$=7.4 Hz, H-3',5'), 7.28 (1H, *t*, $^3J_{4',3'}=^3J_{4',5'}$=7.4 Hz, H-4'), 7.18 (2H, *m*, H-4,5), 6.88 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=7.4 Hz, H-2',6'), 2.51 (3H, *s*, 2-C(NPh)C$\underline{H}_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 219.7 (*s*, br, C≡O), 213.2 (*s*, br, C≡O), 211.8 (*s*, br, 2xC≡O), 186.9 (*s*, 2-C=NPh), 184.1 (*s*, C-1), 153.3 (*s*, C-1'), 143.8 (*s*, C-2), 139.8 (*d*, C-6), 135.4 (*s*, C-3), 131.0 (*d*, C-5), 130.0 (*d*, C-3',5'), 127.4 (*d*, C-4), 126.4 (*d*, C-4'), 121.0 (*d*, C-2',6'), 24.3 (*q*, 2-C(NPh)$\underline{C}H_3$).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with PhNSO

Similarly η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 200 mg, 0.633 mmol] and PhNSO (0.36 ml, 3.17 mmol) refluxed in benzene (8 ml) over 2 h afforded *η^2-5-methoxy-2-[1-N(phenylimino)ethyl]-phenyl-tetracarbonylmanganese* [**(47)**; 248 mg, 47 %], m.p. 131-133 °C. Anal. Found: C, 58.55; H, 3.65; N, 3.59 %; $C_{19}H_{14}O_5NMn$ calcd: C, 58.33; H, 3.61; N, 3.58 %. IR: (CH_2Cl_2) ν(CO) 2073 (m), 1985 (vs), 1935 (s) 1575 (w), 1547 (w) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.59 (1H, *d*, $^3J_{3,4}$=7.9 Hz, H-3),

7.55 (1H, *s*, H-6), 7.44 (2H, *t*, $^3J_{3',2'}=^3J_{3',4'}=^3J_{5',4'}=^3J_{5',6'}$=7.4 Hz, H-3',5'), 7.26 (1H, *t*, $^3J_{4',3'}=^3J_{4',5'}$=7.4 Hz, H-4'), 6.92 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=7.4 Hz, H-2',6'), 6.69 (1H, *d*, $^3J_{4,3}$=7.9 Hz, H-4), 3.93 (3H, *s*, 5-OCH_3), 2.17 (3H, *s*, 2-C(NPh)C$\underline{H}_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 220.4 (*s*, br, C≡O), 214.2 (*s*, br, C≡O), 212.7 (*s*, br, 2xC≡O), 185.4 (*s*, 2-$\underline{C}$=NPh), 181.6 (*s*, C-1), 161.4 (*s*, C-5), 153.0 (*s*, C-1'), 142.0 (*s*, C-2), 130.1 (*d*, C-3), 129.7 (*d*, C-3',5'), 126.1 (*d*, C-4'), 125.3 (*d*, C-6), 121.6 (*d*, C-2',6'), 109.9 (*d*, C-4), 55.2 (*q*, 5-OCH_3), 17.8 (*q*, 2-C(NPh)$\underline{C}H_3$).

Reaction of η²-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with PhNSO

The standard procedure from η²-(2-acetylthien-3-yl)tetracarbonylmanganese [**(40)**; 220 mg, 0.753 mmol] and PhNSO (0.42 ml, 3.77 mmol) in refluxing benzene (8 ml) showed no bands in the metal carbonyl region by infrared spectrum after 4 h. However, chromatography (p.l.c., 1:10 diethyl ether/petroleum spirit) afforded no major organic products, and the reaction was not pursued.

Reaction of η²-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese (17) with PhNSO

η²-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese [**(17)**; 97 mg, 0.294 mmol] and PhNSO (0.17 ml, 1.47 mmol) in refluxing benzene (8 ml) overnight showed only the starting materials by t.l.c. and infrared spectrum.

Reaction of η²-(5-Methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese (19) with PhNSO

Reaction of η²-(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese [**(19)**; 138 mg, 0.416 mmol] and PhNSO (0.23 ml, 2.08 mmol) in refluxing benzene (8 ml) after 5.5 h showed no bands in the metal carbonyl region by infrared spectroscopy. T.l.c. indicated no major organic products, and therefore the reaction was abandoned.

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with PhNSO

Standard procedure from η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 250 mg, 0.781 mmol] and PhNSO (0.44 ml, 3.90 mmol) in refluxing benzene (8 ml) showed the downward shift of the metal carbonyl bands in the infrared after 2 h characteristic of the formation of manganated imine. The reaction mixture was worked up by the normal method. However, chromatography (p.l.c., 1:10 diethyl ether/petroleum spirit) led to decomposition of the metalated complex.

Reaction of η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese (11) with PhNSO

η^2-4-(Dibenzosuberonyl)tetracarbonylmanganese [**(11)**; 412 mg, 1.10 mmol] and PhNSO (0.62 ml, 5.51 mmol) were refluxed in benzene (8 ml) for 5 h. Infrared spectroscopy of the crude reaction mixture showed only $Mn_2(CO)_{10}$ in the metal carbonyl region, and therefore the reaction was abandoned.

Reaction of η^2-(1-Phenylbut-1-ene-3-on-1-yl)tetracarbonylmanganese (42) with PhNSO

Similarly, η^2-(1-phenylbut-1-ene-3-on-1-yl)tetracarbonylmanganese [**(42)**; 71 mg, 0.227 mmol] and PhNSO (0.13 ml, 1.14 mmol) in refluxing benzene (8 ml) for 4 h showed only $Mn_2(CO)_{10}$ in the infrared spectrum.

Reaction of Benzylpentacarbonylmanganese with PhNSO

Benzylpentacarbonylmanganese (297 mg, 1.04 mmol) and PhNSO (0.12 ml, 1.04 mmol) were stirred in benzene (5 ml) for 2 h. Infrared spectroscopy and t.l.c. showed no sign of reaction, so excess PhNSO (0.12 ml, 1.04 mmol) was added and the mixture left to reflux overnight. An infrared spectrum showed the presence of four new bands in the metal carbonyl region, so the mixture was filtered and worked up by the usual method. Chromatography (p.l.c., 1:10 diethyl ether/petroleum spirit) afforded a bright yellow band which on extraction gave a yellow solid (58 mg) which decomposed within a matter of hours and was therefore not completely characterised. IR: (hexane) ν(CO) 2076 (w), 1993 (vs), 1977 (s), 1936 (s) cm^{-1}.

Reaction of Phenylpentacarbonylmanganese with PhNSO

Phenylpentacarbonylmanganese (203 mg, 0.76 mmol) and PhNSO (0.09 ml, 0.82 mmol) were stirred in benzene (5 ml) for 2 h. Infrared spectroscopy and t.l.c. showed no sign of reaction so the reaction mixture was refluxed overnight. An infrared spectrum and t.l.c. indicated only the starting materials.

Reaction of *cis*-Benzyltetracarbonyltriphenylphosphinemanganese with PhNSO

Similarly *cis*-benzyltetracarbonyltriphenylphosphinemanganese (144 mg, 0.28 mmol) and PhNSO (0.03 ml, 0.30 mmol) were stirred in benzene (5 ml) for 2 h. Infrared spectroscopy and t.l.c. showed no sign of reaction so the reaction mixture was refluxed for 4 h. An infrared spectrum and t.l.c. showed only the starting materials.

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with $PhS(O)_2NSO$

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 127 mg, 0.40 mmol] and $PhS(O)_2NSO$ (245 mg, 1.20 mmol) were stirred in benzene (6 ml) for 40 min, after which time there was no sign of reaction by t.l.c. or infrared spectroscopy in the metal carbonyl region. The mixture was refluxed for an hour and then evaporated to dryness under reduced pressure. An infrared spectrum of the residue showed only η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)**.

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with $[PhS(O)_2N]_2S$

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 100 mg, 0.32 mmol] and $[PhS(O)_2N]_2S$ (253 mg, 0.74 mmol) were stirred in benzene (5 ml) for an hour, after which time there was no visible reaction by t.l.c. or infrared spectroscopy in the metal carbonyl region. The mixture was refluxed for an hour, after which time an infrared spectrum showed all the orthomanganated starting material had been consumed. T.l.c. showed no major products and the reaction was abandoned.

Reaction of Phenylpentacarbonylmanganese with $[PhS(O)_2N]_2S$

Phenylpentacarbonylmanganese (167 mg, 0.61 mmol) and $[PhS(O)_2N]_2S$ (234 mg, 0.68 mmol) were stirred in benzene (5 ml) for 2 h. Infrared spectroscopy and t.l.c. showed no sign of reaction so the reaction mixture was refluxed for 5 h. An infrared spectrum showed only $PhMn(CO)_5$.

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Chapter Four

Reactions of Orthomanganated and Orthorheniated Aryl Carbonyl Compounds with Alkenes

4.1 Introduction

Much of the justification for the study of orthomanganated compounds lies in their synthetic potential. This potential can be attributed to the replaceability of the manganese by another metal or by a nonmetal, thus providing new routes to the *ortho* directed construction of carbon-carbon bonds, an area which is of prime interest to the synthetic organic chemist.

The *ortho*-functionalisation of aryl ketones via manganation is of particular interest as the carbonyl function is *meta*-directing in electrophilic aromatic substitution, an otherwise useful method for entry into aryl functionalisation. Electrophilic attack may also occur preferentially at the ketone α-carbon.

To date, directed metalation *ortho* to a ketone function is known only for manganese, rhenium [1,2] and for a small number of ruthenium complexes [3,4], so that the coupling reactions of alkenes at the metal-activated aryl carbon, which make aryl complexes of Hg, Pd, Sn, Pb, Tl and other elements so synthetically useful [5a,6], are not applicable to *ortho*-functionalisation of aryl ketones.

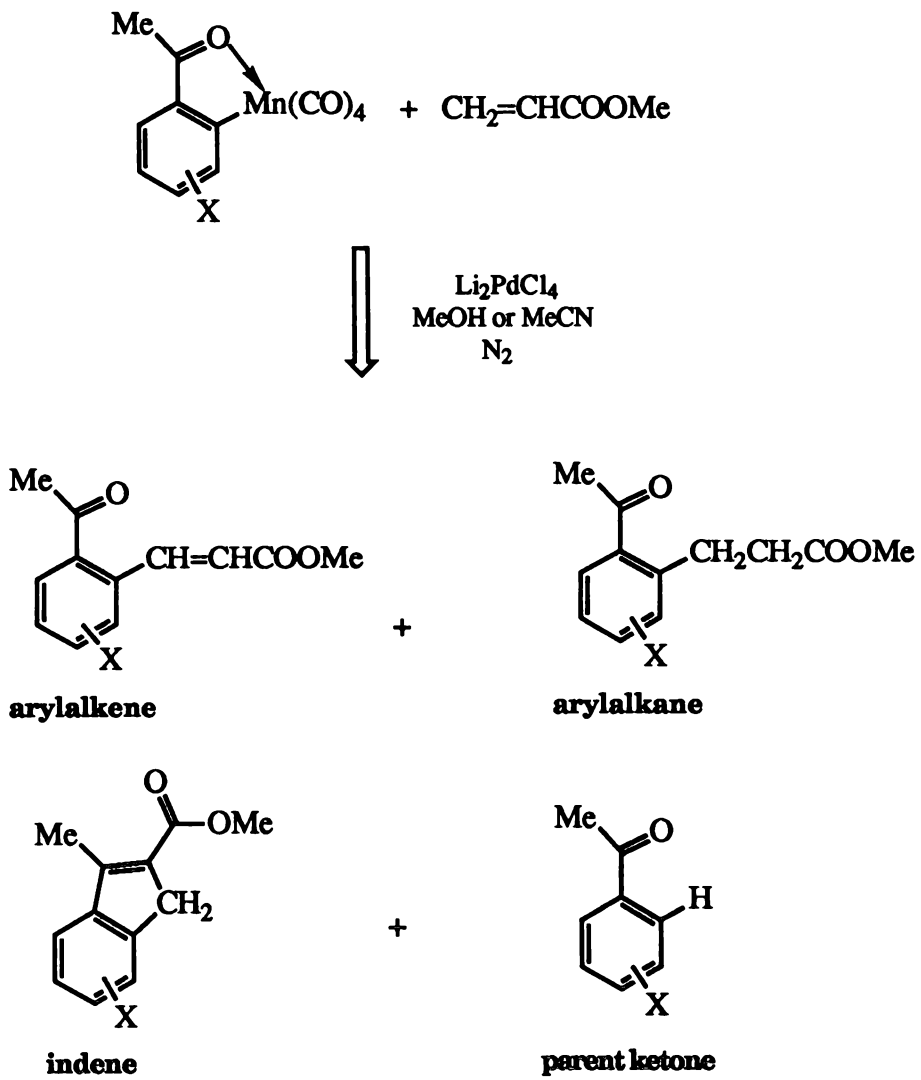
Activation by directed metalation *ortho* to other aryl carbonyl functions is known for some metals, but is inapplicable to ketones. For example, orthothalliation is well known for benzoate esters and benzoic acids, with Pd-promoted coupling of alkenes in the latter case providing a convenient route to isocoumarins [7].

Ortholithiation of benzamides is also well established [8] and that of benzoic acids is indirectly available through protection of the acid as an oxazoline, the N-atom of which provides the directive effect [8].

Aryl halogenation also provides activation for Pd(0)-catalysed coupling with alkenes [5a,9], but the general inaccessibility of halo-ketones, other

than via the orthomanganated complex itself, is a major limitation for *ortho*-functionalisation.

Gommans [10] first reported in 1987 that orthomanganated ketones couple with alkenes in the presence of Pd(II), as in the Heck reactions of aryl-mercury and -halo compounds. The coupling reactions normally proceed in excellent yield and produce three main coupling products, arylalkene (the normal Heck product), arylalkane and indene (Equation 4.1), the ratios of which vary with reaction conditions and substrate. Often a fourth minor product is the parent ketone formed by demetalation at the aryl carbon.



Equation 4.1

This reaction shows considerable synthetic potential as it not only provides a route to the *ortho*-functionalisation of aromatic ketones, but it also yields a cyclised indene-type product, inaccessible by the Heck method.

A literature search revealed only one other reaction with the potential to give such cyclisation: the Pd(0)-promoted coupling of *o*-bromoacetophenone with methyl acrylate [11]. However, this reaction was reported to give a high yield of the normal Heck product, the arylated alkene, and there was no cyclisation.

It was the aim of this study to explore more fully the reactivity patterns of these reactions and to optimise synthetic methods.

4.2 Discussion of Results

4.2.1 Palladium-Promoted Coupling Reactions

In 1987 Gommans [10] reported that palladium(II) reagents promote an extensive range of synthetically valuable coupling reactions of alkenes at the aryl-manganese centre of orthomanganated aryl ketones. Since that time considerable work has been done in this area, both at this university and by other research groups.

In this section is summarised the results of work on reactions of orthomanganated aryl carbonyl compounds with alkenes in the presence of palladium(II).

4.2.1.1 Exploration of Coupling Reaction Conditions

Our initial investigations into coupling reactions of orthomanganated compounds with alkenes in the presence of Li_2PdCl_4 were carried out principally with η^2-(2-acetylthien-3-yl)tetracarbonylmanganese **(40)** and the alkenes, methyl vinyl ketone and methyl acrylate. This orthomanganated thiophene was chosen because it afforded two main coupling products in good yield, the Heck-type insertion products **(48)** or **(49)** and the corresponding saturated adducts **(50)** or **(51)**. Methyl vinyl ketone and methyl acrylate were the alkenes of choice, as previous work had indicated these two olefins consistently gave the highest yields of coupled products [12].

Reaction conditions were explored and the coupling product ratios analysed with a view to optimising experimental methods, while also attempting to gain an overall understanding of reactivity patterns.

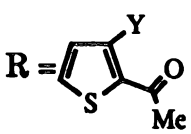
In these comparative reactions any differences in yields of less than 5 % should not be considered significant because of the inherent inaccuracy owing to losses in working up small quantities,

4.2.1.1.1 Effect of Temperature on the Coupling Reaction

To investigate what effect temperature might have on the coupling reaction η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (40) was treated with methyl vinyl ketone in the presence of Li_2PdCl_4 (i) in refluxing acetonitrile (b.p. 81.6 °C), and (ii) in acetonitrile stirred at ambient temperature. The reactions were repeated using methyl acrylate as the olefin. Results are summarised in Table 4.1.

Table 4.1 Products (%) as a Function of Temperature for the Reactions of (40) with Methyl Vinyl Ketone and Methyl Acrylate in Acetonitrile in the Presence of Li_2PdCl_4

CH_2=CH-X	Products (R-Y)	Yield at 81.6 °C	Yield at 20 °C
X=COMe	R-CH_2CH_2COMe (50)	60	56
	R-CH=CHCOMe (48)	20	39
	R-H (52)	-	-
X=COOMe	R-CH_2CH_2COOMe (51)	27	-
	R-CH=CHCOOMe (49)	66	-
	R-H (52)	5	-



Our results showed that, for methyl vinyl ketone, refluxing gave a 3:1 preference for the arylalkane 4-(2-acetylthien-3-yl)-butan-2-one (50) over the arylalkene E-4-(2-acetylthien-3-yl)-but-3-en-2-one (48), compared to a

1.4:1 preference when the reaction was performed at ambient temperature. This latter reaction under less forcing conditions, gave a higher overall yield of coupling products.

When the olefin was changed to methyl acrylate, however, no sign of reaction was observed at ambient temperature. The coupling products methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate (**49**) and methyl 3-(2-acetylthien-3-yl)-propanoate (**51**) were afforded in high overall yield at the higher temperature, preference for the arylalkene over the arylalkane being observed in a ratio of 2.4:1, the reverse situation to that applying for methyl vinyl ketone.

Later work showed that for the majority of orthomanganated ketones and alkenes in the presence of Li_2PdCl_4, coupling reactions in acetonitrile required refluxing. For this solvent, therefore, refluxing was adopted as the standard method.

4.2.1.1.2 Order of Mixing of Reactants

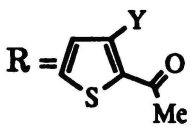
To ascertain whether adding the alkene prior or subsequent to the orthomanganated ketone had an effect on coupling product ratios, two experiments were performed under identical conditions (Table 4.2). These reactions were of importance to establish whether any initial palladium-olefin interactions [13] interfere with subsequent reactions involving the manganese complex.

The variance in coupling product ratios between the two experiments was not great suggesting that any prior interaction between the metal and the olefin were not important. The overall yields were also similar, so neither method appeared to be advantageous.

To be consistent, for subsequent coupling reactions, the alkene was always added after the addition of the orthomanganated compound. Due to the volatile nature of the alkenes concerned and their distinctive odour, it was considered preferable to add these by syringe subsequent to addition of the crystalline orthomanganated compound, the transfer of which took a little more time.

Table 4.2 Effect of the Order of Mixing Reagents in the Reaction of (40) with Methyl Vinyl Ketone in Methanol in the Presence of Li_2PdCl_4 at 20 °C

Products (R-Y)	Alkene Added Prior to Mn Compound (%)	Alkene Added Subsequent to Mn Compound (%)
R-CH_2CH_2COMe (50)	66	55
R-CH=CHCOMe (48)	24	32
R-H (52)	6	10



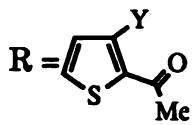
4.2.1.1.3 The Importance of Dry Solvent

Heck has reported that small amounts of water do not interfere in the Pd(0) catalysed coupling reactions of aryl halides with alkenes. In some cases, even aqueous organic solvents are employed [14a]. It was of interest then to establish whether the palladium-mediated coupling reactions of orthomanganated precursors with alkenes, also displayed the same insensitivity to water, thus precluding the need for rigorous drying of solvents.

Our results (Table 4.3) suggest that for protic solvents such as methanol, a small amount (3 %) of water in the reaction system has a minor effect on product ratios, enhancing the yield of the arylalkane slightly at the expense of the arylalkene, while protiodemetalation also becomes significant. A far more dramatic change is observed for the aprotic solvent acetonitrile where small amounts of water (3 %) give a pronounced effect. This is consistent with the need in the formation of the arylalkane for a proton source.

Table 4.3 Products (%) as a Function of Solvent Composition for the Reaction of (40) with Methyl Vinyl Ketone and Methyl Acrylate in the Presence of Li_2PdCl_4 in Wet and Dry Solvent

CH_2=CH-X	Solvent & Reaction Conditions	Products (R-Y)	Dry Solvent	100:3 v/v Solvent:H_2O
X=COMe	MeOH (20 °C)	R-CH_2CH_2COMe (50)	66	76
		R-CH=CHCOMe(48)	26	8
		R-H (52)	-	14
X=COOMe	MeCN (81.6 °C)	R-CH_2CH_2COOMe (51)	27	67
		R-CH=CHCOOMe(49)	66	13
		R-H (52)	5	14



De Wit [15] has reported that for the palladium-promoted coupling reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with methyl vinyl ketone in refluxing acetonitrile, addition of a limited amount of water (0.3 ml in 15 ml MeCN) led to different coupling product ratios. The yields of indene (120) and arylalkene (155) decreased from 52 % and 6 % respectively to 0 % on the addition of water, while the arylalkane (119) and parent ketone (56) increased from 25 % and 0 %, to 63 % and 21 % respectively.

It therefore appears that solvents employed in these reactions should be as dry as possible in order to maximise the yield of the arylalkene product.

4.2.1.1.4 Do Reactions Need to be Carried Out Under a Nitrogen Environment?

The Heck reaction is reported not only to be insensitive to oxygen but also to be catalytic with respect to $PdCl_2$ when employing cupric chloride, air and hydrogen chloride as a reoxidising system [14].

It was of interest to establish whether our coupling reactions showed the same insensitivity to oxygen.

Our initial results for the palladium-promoted coupling reactions of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese **(40)** with methyl vinyl ketone in methanol at ambient temperature showed no significant variation in product ratios irrespective of whether the reaction was performed under nitrogen or in the presence of air.

(40) with methyl acrylate in refluxing acetonitrile in the presence of Li_2PdCl_4 showed a decrease in the yield of arylalkane **(51)** when the reaction was performed in air, but almost identical yields for the arylalkene **(49)** and parent ketone **(52)** for both reaction conditions.

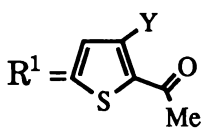
To determine whether the presence of air had a bearing on the yield of indene-type product, a comparison was made between the palladium-promoted coupling reactions of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)** with methyl acrylate in refluxing acetonitrile in the presence and in the absence of air. In the course of this study, this reaction was performed a number of times, affording a range of results, as indicated in Table 4.4. Although the actual yields are somewhat erratic for this system, there is a clear trend towards increased indene yield when the reaction is carried out in the presence of air.

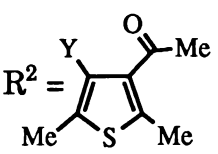
This trend was not observed, however, in a similar comparison with η^2-(2-acetylphenyl)tetracarbonylmanganese **(2)**. The yield of indene **(60)** was virtually identical for reaction both in the presence and absence of air, while the yields af arylalkene **(58)** and arylalkane **(57)** as well as the parent ketone **(59)**, all increased when the reaction was carried out in air.

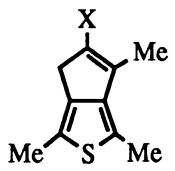
These results were difficult to rationalise, as any trends in product ratios were not consistent between different orthomanganated ketones and alkenes. As it was not clear what effect the presence of air was having on the reaction mechanism, it was decided to exclude air routinely, and all reported coupling reactions were performed under nitrogen except where specifically stated.

Table 4.4 Effect of Oxygen on the Reaction of Selected Orthomanganated Ketones with Methyl Vinyl Ketone or Methyl Acrylate in Methanol or Acetonitrile in the Presence of Li_2PdCl_4

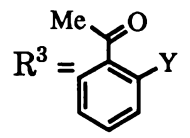
Mn Compound	CH_2=CH-X	Solvent & Reaction Conditions	Products (R-Y)	Nitrogen Atmosphere (%)	Air ($CaCl_2$ Drying Tube) (%)
(40)	X=COMe	MeOH (20 °C)	R^1-CH_2CH_2COMe (50)	66	67
			R^1-CH=CHCOMe (48)	26	26
	X=COOMe	MeCN (81.6 °C)	R^1-CH_2CH_2COOMe (51)	27	11
			R^1-CH=CHCOOMe (49)	66	65
			R^1-H (52)	5	3
(41)	X=COOMe	MeCN (81.6 °C)	R^2-CH_2CH_2COOMe (55)	10, 19	-, 5[a]
			R^2-CH=CHCOOMe (54)	60, 57	60, 35[a]
			R^2-H (56)	5, 17	5, 2[a]
			R^2-indene (53)	5, 5	22, 58[a]
(2)	X=COOMe	MeCN (81.6 °C)	R^3-CH_2CH_2COOMe (57)	10	15
			R^3-CH=CHCOOMe (58)	34	44
			R^3-H (59)	-	14
			R^3-indene (60)	8	9

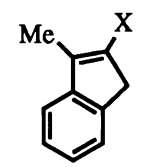






R^2-indene





R^3-indene

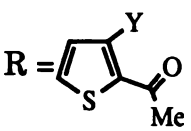
[a] actual yields not calculated; relative yields based on GC integral values (see section 4.2.1.5.2)

4.2.1.1.5 Workup Method

In order to determine the most efficient method of workup (ether/water extraction or filtration through a silica column), a reaction was repeated under identical conditions to one previously performed using the standard workup procedure. The reaction mixture was instead extracted with ether/water and worked up as described in section 4.4. Overall yields of the two reactions are compared in Table 4.5.

Table 4.5 Products (%) as a Function of Workup Method for the Reaction of (40) with Methyl Vinyl Ketone in Methanol in the Presence of Li_2PdCl_4 at 20 °C

Products (R-Y)	Ether/Water Extraction	Silica Column
R-CH_2CH_2COMe (**50**)	54	66
R-CH=CHCOMe (**48**)	21	26



Clearly, the overall yield is higher when a silica column is employed to remove precipitated palladium(0) as compared to separation via ether/water extraction. The latter method was also more time consuming, extraction from water necessitating drying of the combined ether extracts before subsequent workup.

All ensuing palladium-promoted coupling reactions therefore employed filtration through a silica colum as the standard method.

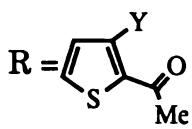
4.2.1.1.6 Solvent Effects

In four separate experiments, (**40**) in the presence of Li_2PdCl_4 was treated with methyl vinyl ketone and stirred at ambient temperature in (i) methanol, (ii) acetonitrile, (iii) tetrahydrofuran and (iv) acetone. All four reactions were repeated using methyl acrylate as the alkene. These solvents, although all reasonably polar, a requirement for the solubility of

Li_2PdCl_4, represented a range of dielectric constants (ε) from 7.6 to 37.5, and also provided a comparison between protic and aprotic solvents.

Table 4.6 Products (%) as a Function of Solvent for the Reaction of (40) with Methyl Vinyl Ketone and Methyl Acrylate in the Presence of Li_2PdCl_4

CH_2=CH-X	Products (R-Y)	MeOH ε=32.7	MeCN ε=37.5	THF ε=7.6	Acetone ε=20.7
X=COMe	R-CH_2CH_2COMe (50)	66	61	33	60
	R-CH=CHCOMe (48)	26	32	46	33
	R-H (52)	-	-	7	-
X=COOMe	R-CH_2CH_2COOMe (51)	7	27	19	19
	R-CH=CHCOOMe (49)	72	66	62	38
	R-H (52)	-	5	-	-



Reaction of **(40)** with methyl vinyl ketone gave the arylalkane **(50)** in greater yield than the Heck-type insertion product, the arylalkene **(48)** (2-2.5:1) for all solvents with the exception of tetrahydrofuran. Conversely, reaction of **(40)** with methyl acrylate showed greater preference for the arylalkene **(49)** over the arylalkane **(51)** (2-10:1) in all cases, this preference being most pronounced for methanol as solvent. For this system, no reaction was observed at ambient temperature when acetonitrile or tetrahydofuran were employed as solvent. Both reactions however showed almost immediate palladium precipitation upon refluxing. When these reactions are performed in methanol, the solvent can act as the proton donor required for the production of arylalkane. However, when the reactions are performed in the anhydrous aprotic solvents acetonitrile, tetrahydrofuran and acetone, there is no proton source of comparable acidity, yet the arylalkane is still formed.

Mechanistic implications and the potential sources of the reducing hydrogen will be discussed in section 4.2.1.5.1.

Methanol and acetonitrile were therefore selected as the solvents of choice as both gave consistently higher overall yields of coupling products.

4.2.1.1.7 Other Alkenes

η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese **(40)** was reacted with a range of alkenes to compare the types of aryl functionalisation obtainable from aryl-manganese precursors with those previously reported for Heck's reactions of aryl-mercury and aryl-halogen compounds. The results are depicted in Scheme 4.1.

Table 4.7 shows a comparison with results previously reported for aryl-mercury coupling reactions; aryl-halogen results [5,9] are generally identical to those for mercury and are therefore excluded from the table. The comparison is not an exact one because of differences in reaction conditions, but it does reveal some synthetically-exploitable variation in the nature of the coupling product in the manganese as opposed to the mercury (or halogen) cases. Possible explanations for these reactivity differences are considered in section 4.2.1.3.

4.2.1.2 Palladium-Promoted Coupling Reactions of a Range of Orthomanganated Aryl Ketones and Esters

Table 4.8 summarises the results of my work on coupling reactions of a wide variety of orthomanganated aryl carbonyl compounds with alkenes in the presence of palladium.

Scheme 4.1

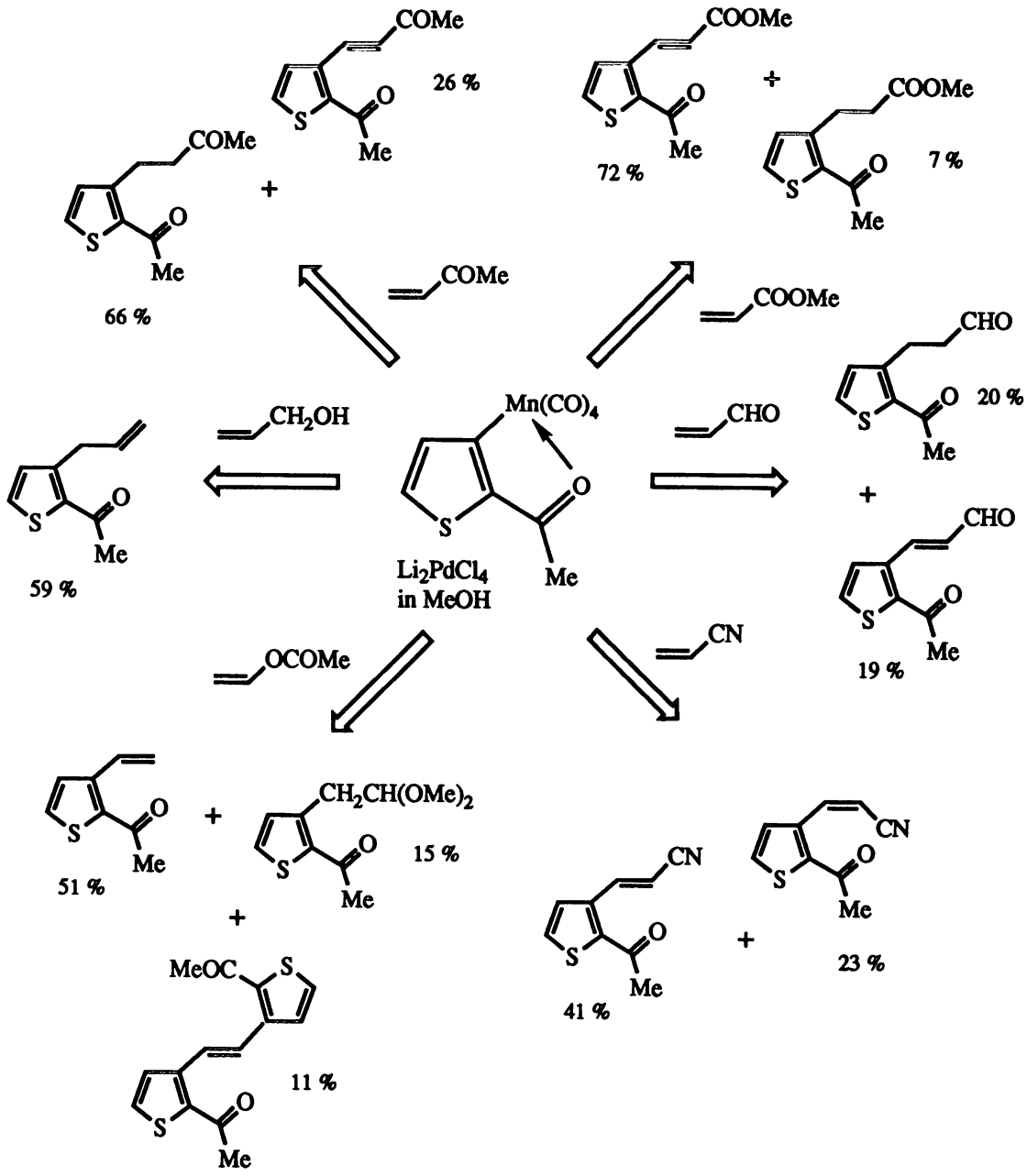

COMe
26 %
COMe
+
Me
66 %
COMe
COOMe
+
COOMe
72 %
Me
7 %
Me
COOMe
CHO
20 %
Me
+
CHO
Me
19 %
CH2OH
Mn(CO)4
CHO
59 %
Li2PdCl4
in MeOH
Me
OCOMe
CN
51 %
CH2CH(OMe)2
15 %
Me
+
MeOC
11 %
Me
CN
CN
41 %
Me
+
23 %
Me

Table 4.7 Comparison of Functional Groups Introduced by Pd(II)-Promoted Coupling of Alkenes at Aryl Carbon Substituted by Manganese and by Mercury

CH_2=CH-X	X=COMe	X=COOMe	X=CN	X=CHO	X=CH_2OH	X=OCOMe
Ar-Mn[a]	-CH_2CH_2COMe >-CH=CHCOMe	-CH=CHCOOMe >-CH_2CH_2COOMe	-E-CH=CHCN >-Z-CH=CHCN	-CH_2CH_2CHO -CH=CHCHO	-CH_2CH=CH_2	-CH=CH_2 >-CH_2CH$(OMe)_2$ >-CH=CH-Ar
Ar-Hg[b]	-CH=CHCOMe[c] (-CH_2CH_2COMe[d])	-CH=CHCOOMe[c]	-CH=CHCN[c]	-CH=CHCHO[c]	-CH_2CH_2CHO[e]	-CH=CH-Ar >CH_2CHO >CH=CH_2[f]

[a] Based on results for the orthomanganated ketone **(40)** in MeOH.

[b] For arylmercuric chloride and diarylmercury compounds, commonly in MeCN and MeOH, in some cases with $CuCl_2$.

[c] References 14a and 5b.

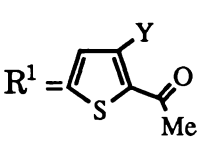
[d] Reference 5d. A two phase $CH_2Cl_2/HCl_{(aq)}$ system with $(n\text{-}Bu)_4NCl$ is employed.

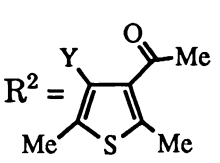
[e] References 14b and 5c.

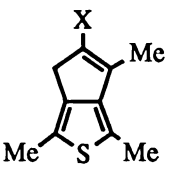
[f] Reference 14d.

Table 4.8 Yields (%) of Products from Li_2PdCl_4-Promoted Coupling of Orthomanganated Ketones and Esters with a Range of Alkenes in Methanol and Acetonitrile

Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	In MeOH	In MeCN
(40)	X=COMe	R^1-CH_2CH_2COMe (50)	66	61
		R^1-CH=CHCOMe (48)	26	32
	X=COOMe	R^1-CH_2CH_2COOMe (51)	7	27
		R^1-CH=CHCOOMe (49)	72	66
		R^1-H (52)	-	5
	X=CN	R^1-Z-CH=CHCN (61)	23	
		R^1-E-CH=CHCN (62)	41	
		R^1-H (52)	9	
	X=CHO	R^1-CH_2CH_2CHO (63)	20	
		R^1-CH=CHCHO (64)	19	
	X=OCOMe	R^1-CH=CH_2 (65)	51	
		R^1-CH_2CH$(OMe)_2$ (66)	15	
		R^1-CH=CH-R^1 (67)	11	
	X=CH_2OH	R^1-Mn(CO)$_4$ (40)	21	
		R^1-CH_2CH=CH_2 (68)	59	
(41)	X=COOMe	R^2-CH_2CH_2COOMe (55)		10, 19
		R^2-CH=CHCOOMe (54)		60, 57
		R^2-H (56)		5, 17
		R^2-indene (53)		5, 5



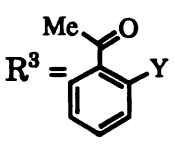


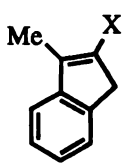


R^2-indene

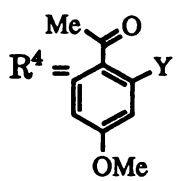
Table 4.8 Continued

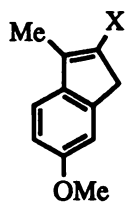
Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	In MeOH	In MeCN
(2)	X=COMe	R^3-Mn(CO)$_4$ (2)	7	-
		R^3-CH=CHCOMe (69)	-	14
		R^3-indene (70)	57	61
	X=COOMe	R^3-CH_2CH_2COOMe (57)		10
		R^3-CH=CHCOOMe (58)		34
		R^3-indene (60)		8
(39)	X=COMe	R^4-Mn(CO)$_4$ (39)	30	-
		R^4-CH=CHCOMe (71)	-	10
		R^4-H (72)	27	21
		R^4-indene (73)	11	46
		R^4-COOMe (74)	11	-
	X=COOMe	R^4-Mn(CO)$_4$ (39)	25	
		R^4-CH_2CH_2COOMe (75)	10	
		R^4-CH=CHCOOMe (76)	18	
		R^4-H (72)	20	
		R^4-indene (77)	10	





R^3-indene



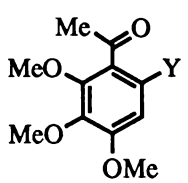


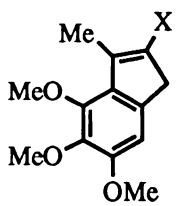
R^4-indene

Table 4.8 Continued

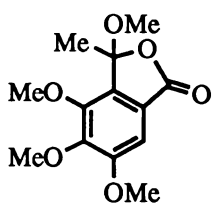
Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	In MeOH	In MeCN
(35)	X=COMe	R^5-Mn(CO)$_4$ (35)	43	-
		R^5-CH_2CH_2COMe (78)	-	3
		R^5-CH=CHCOMe (79)	-	12
		R^5-H (80)	22	-
		R^5-indene (81)	3	80
		R^5-lactone (82)	8	-
	X=COOMe	R^5-Mn(CO)$_4$ (35)	13	
		R^5-CH=CHCOOMe (83)	37	
		R^5-H (80)	23	
		R^5-indene (84)	22	
(34)	X=COOMe	R^6-CH_2CH_2COOMe (85)	}8	
		R^6-CH=CHCOOMe (86)	}	
		R^6-H (87)	71	
		R^6-indene (88)	10	
	X=CN	R^6-E-CH=CHCN (89)		24
		R^6-indene (90)		33

R^5 =



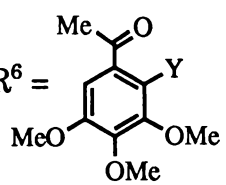


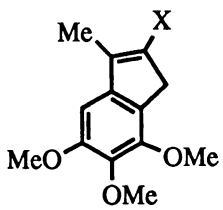
R^5-indene



R^5-lactone

R^6 =

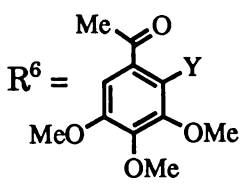


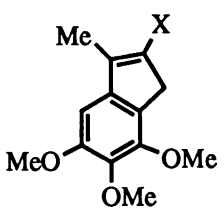


R^6-indene

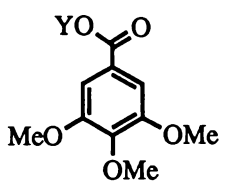
Table 4.8 Continued

Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	In MeOH	In MeCN
(34)	X=CHO	R^6-H (87)		3
		R^6-indene (91)		55
		R^6-ester (Y=Et) (92)		4
		R^6-ester (Y=Me) (93)		5
	X=CH_2OH	R^6-H (87)		57
		R^6-indene (X=CHO) (91)		31
(13)	X=COMe	R^7-Mn(CO)$_4$ (13)	4	-
		R^7-CH_2CH_2COMe (94)	35	47
		R^7-CH=CHCOMe (95)	-	14
		R^7-H (96)	36	25
(10)	X=COOMe	R^8-Mn(CO)$_4$ (10)		5
		R^8-CH_2CH_2COOMe (97)		17
		R^8-CH=CHCOOMe (98)		5
		R^8-H (99)		11
		R^8-indene (100)		14

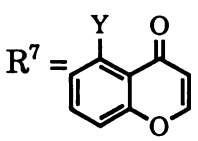


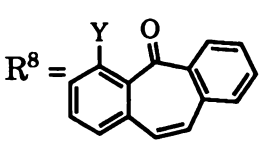


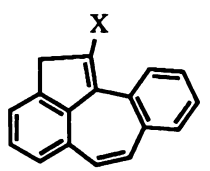
R^6-indene



R^6-ester



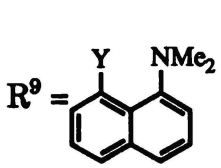


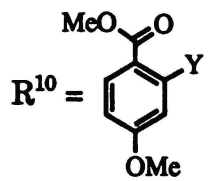


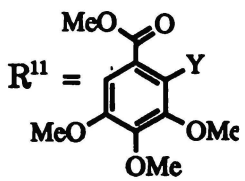
R^8-indene

Table 4.8 Continued

Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	In MeOH	In MeCN
(12)	X=COMe	R^9-H (101)	81	
	X=COOMe	R^9-H (101)		*
(19)	X=COOMe	R^{10}-Mn(CO)$_4$ (19)	12	
		R^{10}-CH_2CH_2COOMe (102)	50	
		R^{10}-CH=CHCOOMe (103)	11	
		R^{10}-H (104)	15	
(105)	X=COMe	R^{11}-CH_2CH_2COMe (106)		76
		R^{11}-H (107)		11







* = only product by t.l.c. therefore reaction abandoned

4.2.1.2.1 Palladium-Promoted Coupling Reactions with Methyl Vinyl Ketone and Methyl Acrylate

4.2.1.2.1.1 Aryl Methyl Ketones

The palladium-promoted reaction of η^2-(2-acetylthien-3-yl)tetracarbonyl-manganese **(40)** with methyl vinyl ketone in methanol at ambient temperature afforded the arylalkane 4-(2-acetylthien-3-yl)-butan-2-one **[(50)**; 66 %] and the Heck-type insertion product, the arylalkene E-4-(2-acetylthien-3-yl)-but-3-en-2-one **[(48)**; 26 %]. Changing the solvent to refluxing acetonitrile had little bearing on the product ratios, the saturated coupling product again being the major isolated species **[(50)**; 61 %], along with the arylalkene **[(48)**; 32 %]. Both coupling products were readily identifiable by ^{1}H- and ^{13}C-NMR spectroscopy, and were fully characterised (see section 4.2.4).

Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (40) with methyl acrylate in methanol at ambient temperature in the presence of palladium gave principally the arylalkene methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [(49); 72 %] with the arylalkane methyl 3-(2-acetylthien-3-yl)-propanoate [(51); 7 %] isolated in only minor yield. The same reaction performed in refluxing acetonitrile gave the arylalkene in major yield [(49); 66 %], the arylalkane [(51); 27 %] and the demetalated product, the parent ketone [(52); 5 %]. As for the coupling products obtained upon treatment of the orthomanganated ketone with methyl vinyl ketone, the esters (49) and (51) were readily characterised by ^{1}H- and ^{13}C-NMR spectroscopy.

The arylalkene was again the major product observed when η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) was treated with methyl acrylate in refluxing acetonitrile in the presence of palladium [(54); 60, 57 %]. The arylalkane was also isolated [(55); 10, 19 %] along with the indene-type species methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [(53); 5, 5 %].

The palladium-promoted reaction of η^2-(2-acetylphenyl)tetracarbonyl-manganese (2) with methyl vinyl ketone in methanol at ambient temperature afforded the indene 1-(3-methylinden-2-yl)-ethanone [(70); 57 %] as the sole coupling product. A small amount of the orthomanganated starting material [(2); 7 %] was also isolated, suggesting that the reaction had not gone fully to completion despite a three day reaction period. Changing the solvent to refluxing acetonitrile gave a similar yield of the indene species [(70); 61 %], in addition to the arylalkene E-4-(2-acetylphenyl)-but-3-en-2-one [(69); 14 %].

Treatment of η^2-(2-acetylphenyl)tetracarbonylmanganese (2) with methyl acrylate under similar reaction conditions afforded the arylalkene methyl E-3-(2-acetylphenyl)-prop-2-enoate [(58); 34 %], the arylalkane methyl 3-(2-acetylphenyl)-propanoate [(57); 10 %] and the indene methyl (3-methylinden-2-yl)-carboxylate [(60); 8 %].

Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with methyl vinyl ketone in methanol at ambient temperature in the presence of palladium gave principally demetalated product [(72); 27 %]. Also isolated in minor yield were the indene 1-(6-methoxy-3-methylinden-2-yl)-ethanone [(73); 11 %] and methyl 2-acetyl-5-methoxybenzoate [(74);

11 %] the origin of which will be discussed in section 4.2.1.3. The orthomanganated ketone (39) was also returned in 30 % yield despite a reaction time of two days. The same reaction performed in refluxing acetonitrile again gave the parent ketone 4'-methoxyacetophenone [(72); 21 %], but afforded as the major product, the indene 1-(6-methoxy-3-methylinden-2-yl)-ethanone [(73); 46 %]. The arylalkene E-4-(2-acetyl-5-methoxyphenyl)-but-3-en-2-one [(71); 10 %] was also detected in minor yield.

A two day reaction time was also required for the palladium-promoted coupling reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonyl-manganese (39) with methyl acrylate in methanol at ambient temperature. As for the methyl vinyl ketone case, a considerable amount of unreacted orthomanganated starting material was recovered [(39); 25 %]. Also isolated was the arylalkane methyl 3-(2-acetyl-5-methoxyphenyl)-propanoate [(75); 10 %], the arylalkene methyl E-3-(2-acetyl-5-methoxyphenyl)-prop-2-enoate [(76); 18 %], the indene methyl (3-methyl-6-methoxyinden-2-yl)-carboxylate [(77); 10 %] and the parent ketone [(72); 20 %].

Coupling of methyl vinyl ketone with η^2-(2-acetyl-3,4,5-trimethoxy-phenyl)tetracarbonylmanganese (35) in methanol at ambient temperature in the presence of palladium also met with little success, the orthomanganated starting material [(35); 43 %] and parent ketone [(80); 22 %] being the major compounds isolated. Also detected, albeit in minor yield, was the indene 1-(4,5,6,-trimethoxy-3-methylinden-2-yl)-ethanone [(81); 3 %] and the lactone 3,4,5,6-tetramethoxy-3-methylbenzo[c]-2,5-dihydrofuran-2-one [(82); 8 %], the origin of which will be discussed in section 4.2.1.3. For this reaction, solvent choice was critical, as changing to refluxing acetonitrile afforded the indene in good yield [(81); 80 %] along with a mixture of the arylalkane 4-(2-acetyl-3,4,5-trimethoxyphenyl)-butan-2-one [(78); 3 %] and the arylalkene E-4-(2-acetyl-3,4,5-trimethoxy-phenyl)-but-3-en-2-one [(79); 12 %].

The palladium-promoted reaction of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)-tetracarbonylmanganese (35) with methyl acrylate in methanol at ambient temperature gave in addition to orthomanganated starting material [(35); 13 %], the indene species methyl (4,5,6-trimethoxy-3-methylinden-2-yl)-

carboxylate [(84); 22 %], parent ketone [(80); 23 %] and the arylalkene methyl E-3-(2-acetyl-3,4,5-trimethoxyphenyl)-prop-2-enoate [(83); 37 %].

Treatment of η^2-(6-acetyl-2,3,4-trimethoxyphenyl)tetracarbonylmanganese (34) with methyl acrylate in methanol at ambient temperature in the presence of palladium gave as the major product, the parent ketone [(87); 71 %]. This may be due either to steric crowding of the reaction centre leading to retardation of the alkene insertion step, and/or to release of steric strain by homolysis of the metal-carbon bond followed by proton abstraction from the solvent, a reaction which is not very subject to steric demand. Also isolated in minor yield were the indene methyl (5,6,7-trimethoxy-3-methylinden-2-yl)-carboxylate [(88); 10 %] and a mixture of the arylalkane methyl 3-(6-acetyl-2,3,4-trimethoxyphenyl)-propanoate (85) and the arylalkene methyl E-3-(6-acetyl-2,3,4-trimethoxyphenyl)-prop-2-enoate (86) (a combined yield of 8 %) which failed to separate. It is interesting to note that any steric effects are not insuperable, as Gommans [10,12] reports the indene species is formed in high yield (89 %) when the reaction is performed in refluxing acetonitrile in the presence of air.

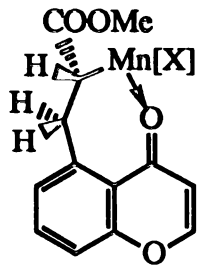
4.2.1.2.1.2 Polycyclic Compounds

The palladium-promoted coupling reaction of η^2-5-(1,4-benzopyronyl)-tetracarbonylmanganese (13) with methyl vinyl ketone in methanol at ambient temperature afforded the arylalkane 4-(1,4-benzopyron-5-yl)-butan-2-one [(94); 35 %] and parent ketone [(96); 36 %] in addition to a small return of orthomanganated starting material [(13); 4 %]. Changing the solvent to refluxing acetonitrile gave again the parent ketone [(96); 25 %], along with the arylalkane [(94); 47 %] and the arylalkene E-4-(1,4-benzopyron-5-yl)-but-3-en-2-one [(95); 14 %].

The difficulty of indene-type formation from benzopyranone-type precursors may result from the carbonyl group not being free to rotate to expose its antibonding π-molecular orbital to the neighbouring reactant metalated centre (Figure 4.1).

It is interesting to note in this context that Liebeskind found no cyclisation product from orthomanganated tetralone with alkynes whereas with increased flexibility for twisting the carbonyl group in the

seven-membered ring of benzosuberone, cyclisation to form indenol did occur [16].



cf.

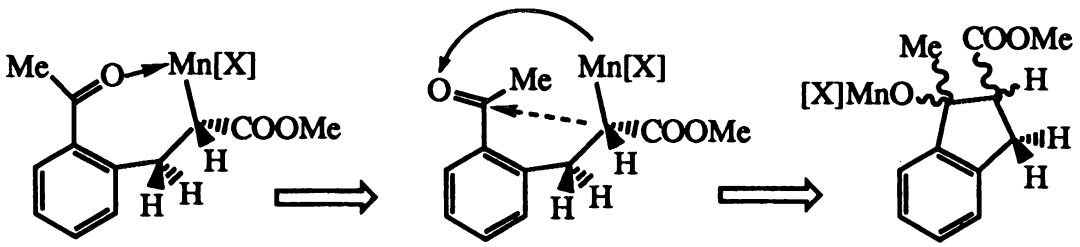


Figure 4.1

In accord with Liebeskind's results, we also found that cyclisation to the indene-type product occurred, albeit in minor yield [**(100)**; 14 %] when the seven-membered cyclic species η^2-(dibenzosuberenonyl)tetracarbonyl-manganese **(10)** was treated with methyl acrylate in refluxing acetonitrile in the presence of palladium. Also afforded were the orthomanganated starting material [**(10)** 5 %], parent ketone [**(99)**; 11 %] and the arylalkane methyl 3-(dibenzosuberenon-4-yl)-propanoate [**(97)**; 17 %] and arylalkene methyl E-3-(dibenzosuberenon-4-yl)-prop-2-enoate [**(98)**; 5 %].

The attempted coupling reactions of the related N-donor naphthylmanganese compound η^2-(8-dimethylamino-1-naphthyl)-tetracarbonylmanganese **(12)** with methyl vinyl ketone and methyl acrylate were of interest because, if successful, there existed the possibility of interaction between the nitrogen lone pair of the amine group and the β-carbon of the α,β-unsaturated carbonyl functionality of the anticipated product (Figure 4.2).

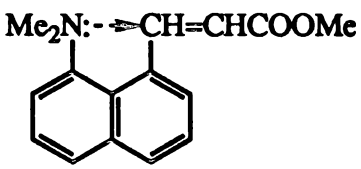
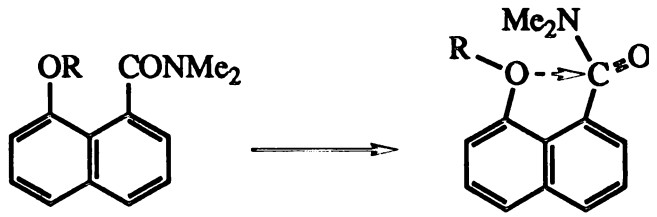


Figure 4.2

The possibility of such an interaction was recognized in light of observations made by Dunitz and co-workers [17] in the crystal structure analyses of *N,N*-dimethyl-8-hydroxynaphthalene-1-carboxamide and the corresponding methoxy derivative (Figure 4.3).



R=H, Me

Figure 4.3

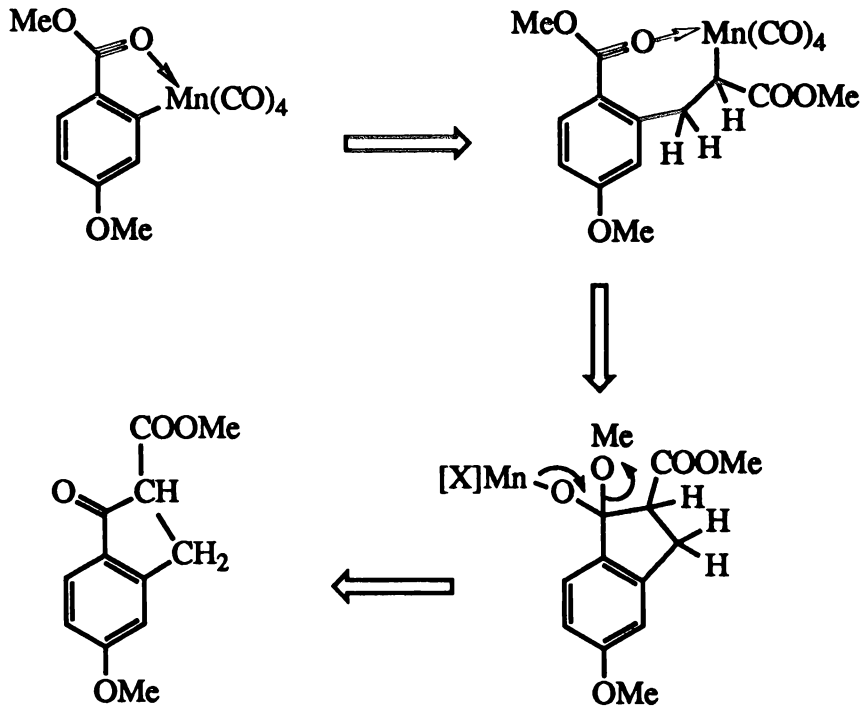
They report that the amide function is perpendicular to the aromatic ring, and is splayed outward while the C-OR bond is inward, i.e. towards the carbonyl group. The carbonyl naphthalene bond is bent in such a way to allow an alignment of the lone pair orbital to the π^* orbital of the carbonyl system which is in accord with the optimal interaction based on stereoelectronic considerations.

It was unfortunate then that η^2-(8-dimethylamino-1-naphthyl)-tetracarbonylmanganese (**12**) failed to afford any coupling product with methyl acrylate or with methyl vinyl ketone in either methanol or acetonitrile as solvent. The thermally promoted reaction of (**12**) with methyl acrylate in refluxing benzene gave the arylalkane methyl 3-(8-dimethylamino-1-naphthyl)-propanoate [(**108**); 8 %] in minor yield (see section 4.2.2.2), but no sign of the arylalkene was detected under these conditions. An X-ray crystal structure determination of the arylalkene would have been of interest from the point of view of the optimal orientation of the amino nucleophile with the β-carbon of an α,β-unsaturated carbonyl system.

Although alkene coupling with the orthomanganated derivative was not successful, another possible route to the arylalkene of interest is via alkene coupling of the orthopalladiated analogue which has been previously prepared [18].

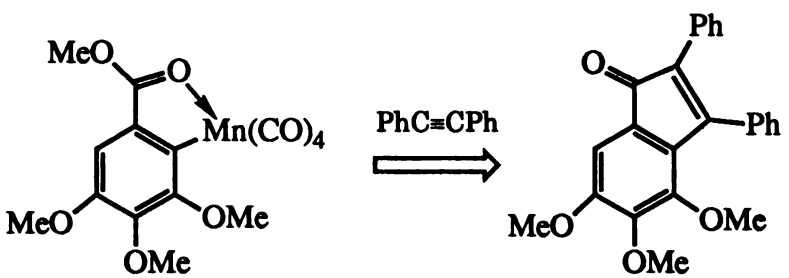
4.2.1.2.1.3 Esters

If cyclisations analogous to those with orthomanganated ketones could be made to occur, orthomanganated esters should give indanones by ester substitution (Scheme 4.2) as is found in the thermally promoted reactions



Scheme 4.2

of both orthomanganated esters and amides with alkynes to afford indenones [19] (Equation 4.2).



Equation 4.2

To date, only a few studies of Pd(II)-promoted reactions of orthomanganated esters with alkenes have been made. The palladium-promoted reaction of η^2-(5-methoxy-2-methoxycarbonylphenyl)-tetracarbonylmanganese (19) with methyl acrylate in methanol at ambient temperature, gave in addition to orthomanganated starting material [(19);

12 %], parent ester [(104); 15 %], the arylalkane methyl 3-(5-methoxy-2-methoxycarbonylphenyl)-propanoate [(102); 50 %] and the arylalkene methyl E-3-(5-methoxy-2-methoxycarbonylphenyl)-prop-2-enoate [(103); 11 %]. The reaction of the methyl 3,4,5-trimethoxybenzoate derivative (105) with methyl vinyl ketone in refluxing acetonitrile gave neither indanone nor arylalkene. Only the arylalkane 4-(2,3,4-trimethoxy-6-methoxycarbonylphenyl)-butan-2-one [(106); 76 %] and parent ketone [(107); 11 %] were recovered.

4.2.1.2.2 Palladium-Promoted Coupling Reactions with Other Alkenes

4.2.1.2.2.1 Reactions in Methanol

(i) Acrylonitrile

Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (40) with acrylonitrile in methanol at ambient temperature in the presence of palladium, gave in addition to parent ketone [(52); 9 %], E-3-(2-acetylthien-3-yl)-prop-2-enenitrile [(62); 41 %] and Z-3-(2-acetylthien-3-yl)-prop-2-enenitrile [(61); 23 %]. These isomers were readily distinguishable by examination of the olefinic coupling constant in the ^{1}H-NMR (see section 4.2.4). Inexplicably, the same reaction was reported by Gommans [10,12] to give only methyl 2-(2-acetylthien-3-yl)-acetate [(109); 29 %].

(ii) Acrolein

Our results for the coupling reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (40) with acrolein in methanol at ambient temperature are also at variance with those reported by Gommans [10,12]. While we isolated only the arylalkane 3-(2-acetylthien-3-yl)-propanal [(63); 20 %] and arylalkene E-3-(2-acetylthien-3-yl)-prop-2-enal [(64); 19 %], Gommans reported the formation of the dimethyl acetal of 3-(2-acetylthien-3-yl)-propanal [(110); 85 %] and the *o*-methyl enol of 3-(2-acetylthien-3-yl)-propanal [(111); ~5 %].

(iii) Vinyl Acetate

The palladium-promoted reaction of η^2-(2-acetylthien-3-yl)tetracarbonyl-manganese **(40)** with vinyl acetate in methanol gave as the major products 2-acetyl-3-vinylthiophene [**(65)**; 51 %], and a mixture of the dimethyl acetal of 2-(2-acetylthien-3-yl)-ethanal [**(66)**; 15 %] and the bis-aryl ethene 2-acetyl-3-(2-(2-acetylthien-3-yl)-vinyl)-thiophene [**(67)**; 11 %]. Yields were calculated by integration of the ^{1}H-NMR. Fractional crystallization of the mixture by vapour diffusion of hexane into a saturated chloroform solution at 4 °C afforded white plates of the bis-aryl ethene compound, but the remaining oil, comprising principally the dimethyl acetal, could not be purified sufficiently to give satisfactory elemental analysis.

These products are of the type reported by Heck for arylmercury compounds [14d] but there is a reversed order of preference (see Table 4.7), and a much higher overall yield in the manganese case. Mechanisms of the type suggested by Heck [14d] may be equally applicable for arylmanganese precursors and are not repeated here.

(iv) Allyl Alcohol

The palladium-promoted reaction of η^2-(2-acetylthien-3-yl)tetracarbonyl-manganese **(40)** with allyl alcohol in methanol afforded 2-acetyl-3-prop-2-enylthiophene **(68)** in 59 % yield, in addition to unreacted orthomanganated ketone [**(40)**; 21 %]. The introduction of the allyl group contrasts with the reactivity of aryl-mercury and -halo compounds which introduce instead the function $-CH_2CH_2CHO$ (see Table 4.7). The formation of this compound will be discussed further in section 4.2.1.3.

4.2.1.2.2.2 Reactions in Acetonitrile

(i) Acrylonitrile

The coupling reaction of η^2-(6-acetyl-2,3,4-trimethoxyphenyl)tetracarbonyl-manganese **(34)** with acrylonitrile in refluxing acetonitrile in the presence of palladium gave the indene 5,6,7-trimethoxy-3-methylindene-2-carbonitrile [**(90)**; 33 %] and the E-alkene E-3-(6-acetyl-2,3,4-trimethoxy-phenyl)-prop-2-enenitrile [**(89)**; 24 %]. Traces of the Z-isomer were observed by GC-MS as a very minor component of the E-isomer product.

(ii) Acrolein

The palladium-promoted reaction of η^2-(6-acetyl-2,3,4-trimethoxyphenyl)-tetracarbonylmanganese **(34)** with acrolein in refluxing acetonitrile gave principally the cyclised product 5,6,7-trimethoxy-3-methylindene-2-carbaldehyde [**(91)**; 55 %]. Minor yields of the esters ethyl 3,4,5-trimethoxybenzoate [**(92)**; 4 %] and methyl 3,4,5-trimethoxybenzoate [**(93)**; 5 %] were also detected in addition to the parent ketone [**(87)**; 3 %]. We can offer no feasible mechanism to explain the formation of either of these products.

(iii) Allyl Alcohol

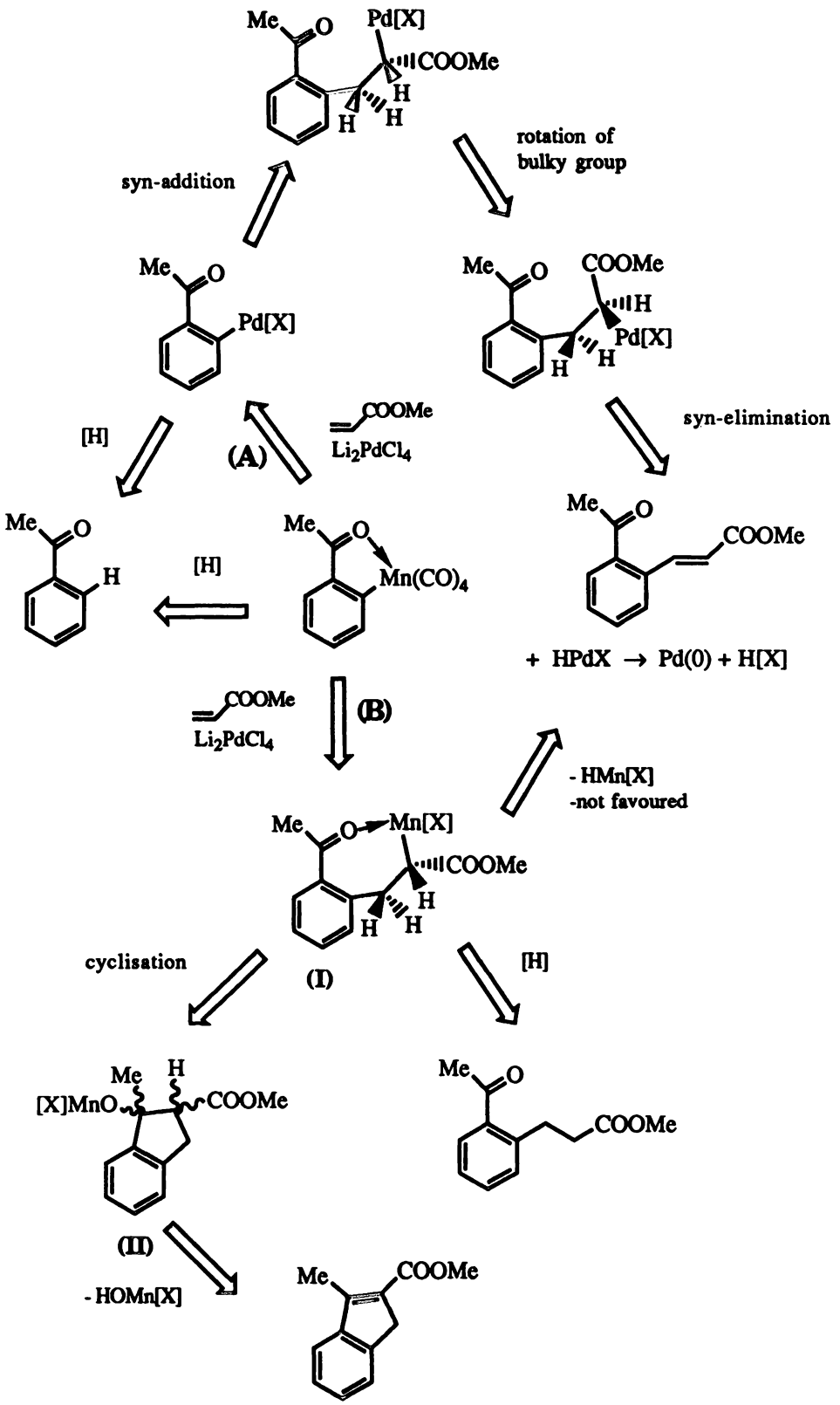
The coupling of η^2-(6-acetyl-2,3,4-trimethoxyphenyl)tetracarbonyl-manganese **(34)** with allyl alcohol in refluxing acetonitrile gave the parent ketone [**(87)**; 57 %] and the indene 5,6,7-trimethoxy-3-methylindene-2-carbaldehyde [**(91)**; 31 %]. The latter compound, like the Heck product reported for reactions of aryl-mercury and -halogen compounds with allyl alcohol (see Table 4.7), comprises a reduced double bond and oxidised alcohol functionality, in contrast to the manganese case for allyl alcohol in methanol (see above).

4.2.1.3 Reaction Scheme for Palladium-Promoted Coupling

Scheme 4.3 illustrates possible routes to the formation of arylalkene, arylalkane, indene and demetalation products for orthomanganated compounds reacted with alkenes in the presence of palladium.

Route (A) is as proposed by Heck for the arylation of alkenes. Addition of the arylpalladium complex to the alkene is syn, followed by rotation of the aryl group and syn-elimination of [X]PdH. When R is bulky (e.g. COOMe, COMe etc.) the most stable conformation for syn-elimination would orientate the bulky aryl ring *trans* to the alkene R group, leading exclusively to the E-isomer. For smaller R groups (e.g. CN) both E- and Z-isomers are formed [20].

Scheme 4.3


Me
O
Pd[X]
COOMe
H
H
H
rotation of
bulky group
syn-addition
Me
O
Pd[X]
Me
O
COOMe
H
Pd[X]
H
H
[H]
(A)
COOMe
Li_2PdCl_4
syn-elimination
Me
O
H
[H]
Me
O
$Mn(CO)_4$
Me
O
COOMe
+ HPdX → Pd(0) + H[X]
COOMe
Li_2PdCl_4
(B)
- HMn[X]
-not favoured
Me
O
Mn[X]
COOMe
H
H
H
cyclisation
(I)
[H]
Me
H
[X]MnO
COOMe
Me
O
COOMe
(II)
- HOMn[X]
Me
COOMe

Formation of arylalkane products has not been detected in any of Heck's reactions, with one exception. Arylmercury (and aryltin) compounds were reported [21] to give arylalkanes with enones instead of the normal arylalkenes, in a Pd(II)-promoted reaction in a two-phase $CH_2Cl_2/HCl_{(aq)}$ system incorporating $(n\text{-}Bu)_4NCl$. Here the added acid present however may be involved in directing the coupling to the arylalkane product by acid cleavage of Pd-C.

Arylalkane formation would therefore seem to be a distinguishing feature of alkene coupling with orthomanganated precursors. On this basis we may propose that arylalkane formation may occur via intermediates different from that proposed for the arylalkene coupling product.

Our results could be explained by insertion of the alkene into the $Mn\text{-}C_{aryl}$ bond of the orthomanganated ketone, followed by protonolysis, to give the arylalkane, rather than transmetalation by $PdCl_2$ and subsequent alkene insertion. The arylalkene could also in theory be formed via this route by elimination of a HMn[X] species. This step however would appear to be unfavourable based on our results for thermally promoted coupling reactions carried out in the absence of palladium, where arylalkenes were rarely detected, and then only in small yields (see section 4.2.2).

Normally β-elimination of metal hydride for Mn-alkyls is facile. However, β-elimination of metal hydride may be blocked when the alkyl group is part of a chelate ring, as explains the stability of the palladocycle [22] (Figure 4.4) compared to its acyclic analogue $Pd(Bu^n)_2(dppe)$). This is

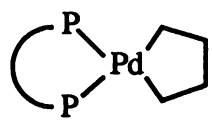


Figure 4.4

because the geometric constraints imposed by the ring lead to an unfavourable M-C-C-H dihedral angle preventing close approach of H_β to the metal. The optimum angle is presumably close to zero (Figure 4.5). If

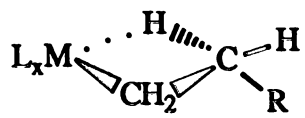


Figure 4.5

the manganese remains coordinated to the donor ketone carbonyl oxygen upon insertion of the alkene to form a seven-membered ring structure, this may explain why the arylalkene is not generally formed. When palladium is present, however, insertion of the alkene into the Pd-C_{aryl} bond would impose no such geometric constraints allowing facile β-elimination to form the arylalkene (Figure 4.6).

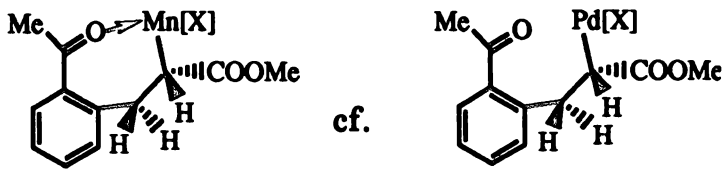


Figure 4.6

Protonolysis is possibly mediated when R is a carbonyl function by initial protonation at carbonyl oxygen, with subsequent ketonisation of the enolic product. The source of this putative H is still not clear, as good yields of the arylalkane products were obtained in both anhydrous protic and aprotic solvents. Potential sources will be discussed in section 4.2.1.5.1.

Indene formation could also be envisaged via the same route proposed for arylalkane formation. Manganese may remain coordinated (Scheme 4.3, (I)) or become recoordinated to the donor ketone carbonyl oxygen and by electron withdrawal increase the susceptibility of the ketone carbonyl to addition by the manganated carbon. Loss of Mn[X] would then yield the indene. If [Mn] is more effective at coordinating to oxygen and polarising the carbonyl bond than [Pd], this may explain why the indene product is often formed in large excess over arylalkenes under suitable conditions for orthomanganated precursors.

This is supported by the absence of indene formation in the Pd(0)-promoted coupling reaction of *o*-bromoacetophenone with methyl acrylate, referred to in section 4.1, suggesting that a cyclised intermediate of the type (II) but with palladium as metal rather than manganese is either not formed, or is formed reversibly and does not lead to indene product, at least under the conditions concerned.

The report [23] that *ortho*-palladiated benzaldehyde N-t-butylimine affords 2-acetylindene on reaction with methyl vinyl ketone is relevant. The O→M bond is proposed to be much weaker than the N→M bond where M is a soft metal such as palladium or platinum [24]. This is supported by the fact

that Trofimenko has reported [25] that no cyclo-palladiated products could be observed with methyl benzyl ether, acetophenone or *N,N*-dimethylbenzamide. The stronger N→Pd bond therefore may polarise the C=N bond sufficiently to promote cyclisation, unlike the weaker O→Pd bond.

Reaction of *ortho*-palladiated benzaldehyde *N*-t-butylimine with methyl acrylate, however, gave only an arylalkene coupling product [23].

Formation of the indene product is generally better achieved in acetonitrile under reflux as solvent, rather than in methanol. One possible explanation for this is as follows:-

Under thermal conditions, labilisation of carbon monoxide followed by coordination of solvent acetonitrile to the coordinatively unsaturated manganese is possible (Figure 4.7).

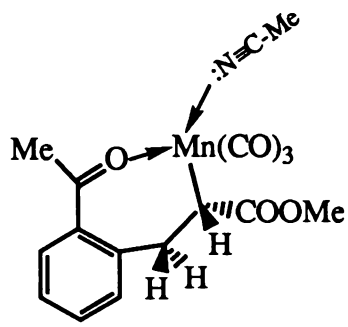


Figure 4.7

If replacing a CO by the better σ–donor serves to lower the effective electronegativity of the manganese atom (see section 4.2.3.1), this would lead to a less polar Mn-C_{aryl} bond, thereby increasing the carbanionic character of the manganated carbon, and so promoting cyclisation.

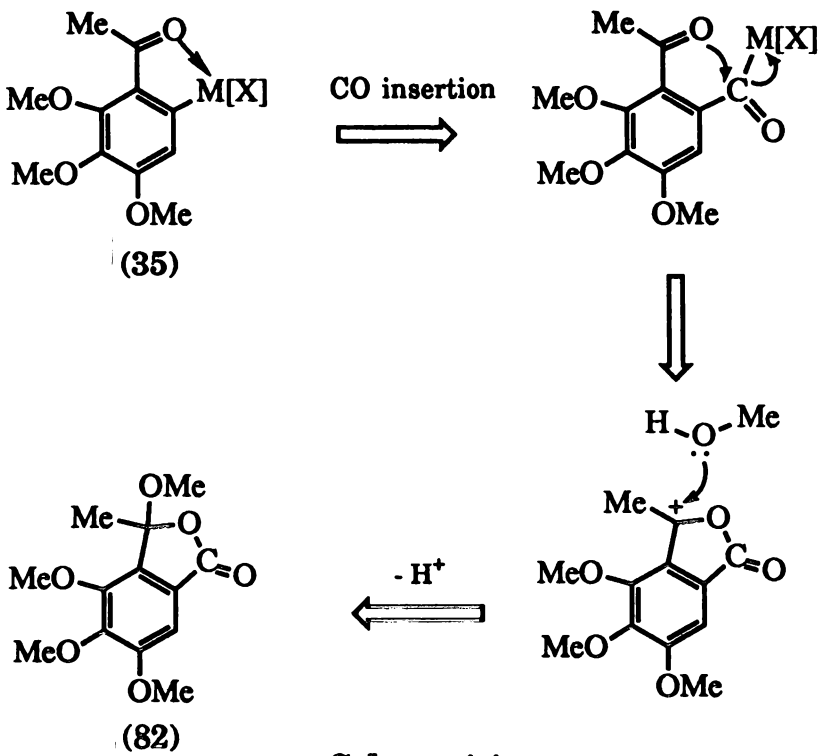
Demetalation to form the parent ketone occurs to a variable degree in both protic and aprotic solvents, presumably via protolytic cleavage of the tetracarbonylmanganese complex or of the transmetalated palladium derivative. As for the arylalkane coupling product, the source of reducing hydrogen has not been established (see section 4.2.1.5.1).

Formation of the allylic product $ArCH_2CH{=}CH_2$ upon reaction of **(40)** with allyl alcohol in methanol, contrasts with the reactivity of aryl-mercury and -halo compounds which introduce instead the function $-CH_2CH_2CHO$ in which the double bond is reduced and the alcohol oxidised. Heck has

proposed in the mercury case the elimination from $ArCH_2CH(PdCl)CH_2OH$ of ClPdH to form $ArCH_2CH{=}CHOH$, the enolic form of $ArCH_2CH_2CHO$. If a similar intermediate is involved in the manganese case, then it must instead be ClPdOH which is eliminated to form $ArCH_2CH{=}CH_2$ under our reaction conditions. Why a similar intermediate would behave so differently under these conditions is unclear, but it suggests the possibility that a displaced manganese function coordinates to oxygen and promotes its elimination.

The structures of unknown minor products have not generally been pursued. However several products which may arise from carbonyl insertion into the aryl-metal bond have been isolated. These compounds generally form when the reaction is performed in methanol as solvent, and the reaction is slow, as adjudged by the amount of unreacted orthomanganated starting material recovered.

The lactone 3,4,5,6-tetramethoxy-3-methylbenzo[c]-2,5-dihydrofuran-2-one (82) formed in the palladium-promoted reaction of (35) with methyl vinyl ketone in methanol, presumably arises from carbonyl insertion into the aryl-metal bond with subsequent cyclisation to form the five-membered ring (Scheme 4.4).

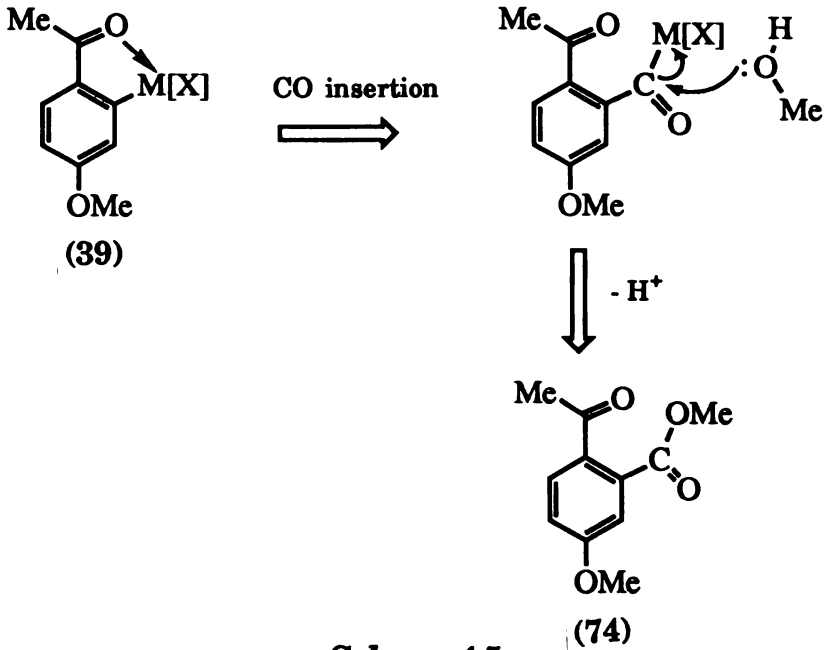


Scheme 4.4

Oxidatively induced carbonyl insertion into a manganese-carbon bond to form a lactone has been previously reported [26,27]. However, it is uncertain whether (82) is formed via insertion of carbon monoxide into an aryl-manganese bond or (after transmetalation) into a aryl-palladium bond, since σ-complexes of either metal are known to react in this way.

Similarly, insertion of carbon monoxide into the aryl carbon-metal bond may account for the formation of the ester methyl 2-acetyl-5-methoxybenzoate (74) (Scheme 4.5).

It is unclear, however, why in this case cyclisation to give the lactone should not occur.



Scheme 4.5

4.2.1.4 Summary: Coupling Reactions in the Presence of Pd(II)

1. Palladium-mediated coupling reactions of alkenes with orthomanganated ketones may therefore involve two competing reactions.

(a) Aryl transmetalation from manganese to palladium, insertion of the alkene and elimination of HPd[X] to yield the arylalkene coupling product, analogous to the Heck reaction, and

(b) insertion of alkene into the carbon-manganese bond followed by either protonolysis to afford the arylalkane, or cyclisation and elimination

of [X]MnOH to yield the indene. Elimination of HMn[X} to give the arylalkene would also be possible by this route, but does not appear to be favoured, perhaps because cyclic compounds such as (I) (Scheme 4.3) are generally less prone to M-C cleavage through β-elimination than their linear counterparts.

Protonolysis of either the orthomanganated precursor or the transmetalated palladium derivative could afford the demetalated parent ketone.

2. Indene-type product formation is more favoured in acetonitrile under reflux than in methanol at room temperature.

3. Arylalkenes of E rather than Z configuration are formed as is consistent with similar couplings with aryl-mercury compounds [5,14]. An exception is the result for acrylonitrile which gives both isomers.

4. Of the five olefins used, methyl vinyl ketone and methyl acrylate consistently gave the highest yields of coupled products. Reaction with methyl vinyl ketone tended to give the arylalkane in higher yield than the arylalkene in both protic and non-protic solvent, in contrast to aryl-mercury compounds where only formation of the arylalkene is reported. Methyl acrylate however showed preference for the arylalkene over the arylalkane.

5. While coupling reactions for the olefins CH_2=CHX (X=CHO, CN, CH_2OH, OCOMe) gave much lower yields than for the aforementioned alkenes (X=COMe, COOMe), these reactions are nevertheless of value as they afford products that differ from those obtained from aryl-mercury and -halo compounds.

4.2.1.5 Mechanistic Implications

4.2.1.5.1 Source of Proton

Formation of both the arylalkane and the parent ketone requires a proton source. This is clearly not entirely solvent dependent, as both products are detected in anhydrous protic and aprotic solvents alike. Potential proton sources are now considered:-

Since formation of the arylalkene generates one molar equivalent of [X]PdH (or [X]MnH), and subsequently Pd(0) and HCl, this process can lead to one molar equivalent of the saturated analogue, the arylalkane. It is clear, however, that the amount of arylalkane can not exceed the amount of arylalkene unless protic solvents or contaminants (e.g. H_2O, possibly not until workup) take the place of HCl. As the yields of arylalkane far exceeds that of the arylalkene for many of our reactions, including those performed in aprotic solvents, clearly this source of proton does not account for all of the reducing capability of the reaction. This is particularly evident for a number of thermally promoted reactions (see section 4.2.2) where often the arylalkane is formed in good yield in aprotic solvents and the arylalkene is not detected at all.

The Woodgate group has reported [28] that reductive cleavage occurs during the course of the reaction and not at the quenching stage (ie. during workup). This conclusion was reached following the absence of deuterium in the arylalkane and parent ketone in a reaction quenched with CD_3CO_2D. They also report that coupling in deuterated acetonitrile as solvent did not give any deuterium-labelled products providing support for the argument that the proton source does not come from the solvent.

The only remaining source of proton able to lead to reduced products is the excess of alkene. This premise could be investigated by the use of deuterated alkenes in coupling reactions.

4.2.1.5.2 Does the Palladium Chloride Function as a Transmetalating Agent?

If palladium-promoted coupling reactions of alkenes with aryl-metal precursors involve only one pathway, i.e. the formation of the alkene-inserted palladiated intermediate, it would be expected in the case of orthometalated ketones that any potential for the cyclisation of the palladiated carbon to the ketone carbonyl would be realised irrespective of the metal in the precursor.

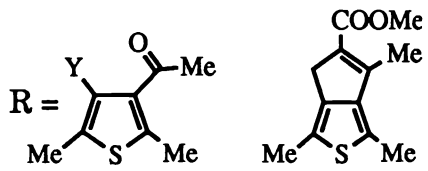
The availability of orthomercurated aryl ketones, via transmetalation of orthomanganated ketones with mercuric chloride [29], allowed us to determine the product distribution for methyl acrylate coupling with an orthomercurated precursor (analogous to the Heck reaction) and to

compare it with that for the corresponding orthomanganated precursor under identical conditions. Orthomercurated **(112)** and orthomanganated 3-acetyl-2,5-dimethylthiophene **(41)** in acetonitrile as solvent in the presence of air were used for this study because we knew there to be in the manganese case, a good balance between the indene-type product and the arylalkane, so that any product ratio difference for the mercury case could be readily detected. These conditions also approximated those described for the Heck reaction.

Our results (Table 4.9) show cyclisation to be much more strongly favoured in the manganese than the mercury case.

Table 4.9 Product Proportions for the Pd(II)-Promoted Coupling Reaction in Acetonitrile of Methyl Acrylate with the Orthomanganated (41) and Orthomercurated (112) Derivatives of 3-Acetyl-2,5-dimethylthiophene

Orthometalated ketone	**Products (R-Y) (M_r; retention time / s)**			
	Indene R-indene	Arylalkene [a] R-CH_2CH_2COOMe	Arylalkane R-CH=CHCOOMe	Parent ketone R-H
	(53)	**(54)**	**(55)**	**(56)**
	(222; 940)	(238; 960)	(240; 830)	(156; 260)
$ArMn(CO)_4$ **(41)**	58	35	5	2
ArHgCl **(112)**	3	85	3	9



R-indene

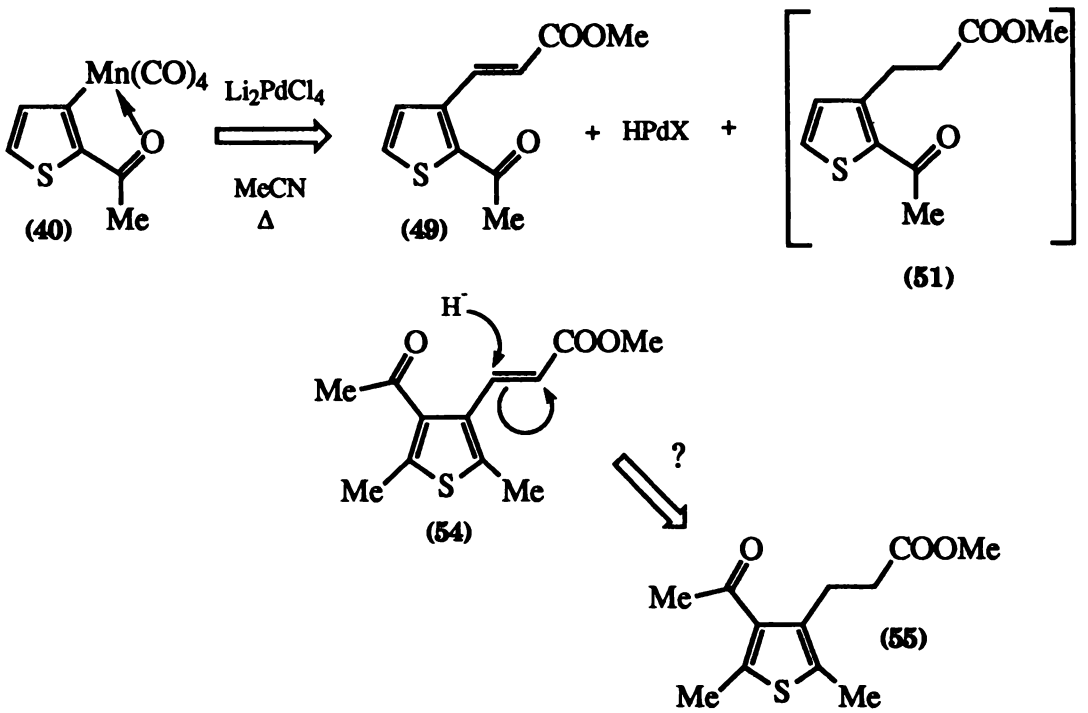
[a] *E*-isomer. Another product (M_r 238; retention time 780 s) was, from its identical fragmentation pattern, the *Z*-isomer, but it was present in <0.5% yield in both the Mn and Hg cases.

It is therefore highly unlikely that a sole reaction pathway involving transmetalation by palladium at the aryl carbon prior to alkene coupling is occurring for both manganese and mercury.

For manganese, therefore, a second pathway leading to the indene-type product seems likely (see Scheme 4.3).

4.2.1.5.3 Is Arylalkene a Source of Arylalkane by Hydride Transfer from HPdX Eliminated in Arylalkene Formation?

η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (**40**) was treated with methyl acrylate in the presence of Li_2PdCl_4 in refluxing acetonitrile. Immediately upon reaction, E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate (**54**) was added. The aim was to establish whether the alkene coupling product once formed can lead to the arylalkane coupling product via HPdX as the reducing agent providing H^- (Scheme 4.6).



Scheme 4.6

Our results revealed only the presence of the expected arylalkene and arylalkane coupling products (**49**) and (**51**), in addition to the arylalkene (**54**) we had added. There was no sign that the arylalkene (**54**) had reacted on further to give the arylalkane (**55**).

This result lends credence to our suggestion that the arylalkane is formed directly and not from the arylalkene.

4.2.1.5.4 Does the Indene Come From an Arylalkane Precursor?

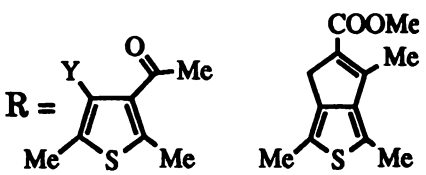
(i) Does Increasing the Reflux Time Lead to an Increase in the Yield of Cyclised Product at the Expense of Arylalkane?

There existed the possibility that the arylalkane once formed, was the indene precursor (Cl^- in the dipolar aprotic solvent acetonitrile might be basic enough to promote the condensation). If this was the case, we might expect the yield of indene to increase with increasing reaction time.

The palladium-promoted reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)** with methyl acrylate in refluxing acetonitrile was chosen to determine the effect that the length of reflux time might have on the yield of indene-type product. Refer to Table 4.10.

Table 4.10 Products (%) as a Function of Time for the Reaction of (41) with Methyl Acrylate in Acetonitrile in the Presence of Li_2PdCl_4

Products (R-Y)	3 Hours (duplicate run)	43 Hours
R-CH_2CH_2COOMe (55)	10, (19)	16
R-CH=CHCOOMe (54)	60, (57)	49
R-H (56)	5, (17)	20
R-indene (53)	5, (5)	4



R-indene

Our results however show virtually no change in the yield of cyclised product between a reaction refluxed for three hours compared to that refluxed for forty three hours.

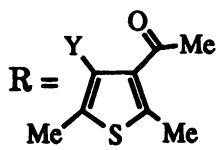
It is also unlikely that Cl^- in methanol would promote cyclisation of the arylalkane to form the indene-type species because of its low basicity when solvated by protic solvents.

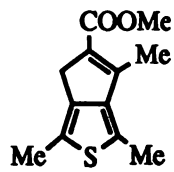
(ii) Can the Base Cl^- Promote Aldol-Type Cyclisation in the Dipolar Aprotic Solvent Acetonitrile?

The palladium-promoted reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with methyl acrylate in refluxing acetonitrile was chosen to examine whether an increase in the concentration of LiCl affected the yield of cyclised product. Refer to Table 4.11.

Table 4.11 Products (%) as a Function of LiCl Concentration for the Reaction of (41) with Methyl Acrylate in Acetonitrile in the Presence of Li_2PdCl_4

Products (R-Y)	LiCl in MeCN 0.084 mol l^{-1} (duplicate run)	LiCl in MeCN 0.168 mol l^{-1}
R-CH_2CH_2COOMe (55)	10, (19)	16
R-CH=CHCOOMe (54)	60, (57)	48
R-H (56)	5, (17)	20
R-indene (53)	5, (5)	5





R-indene

Our results show no change in the yield of indene when the concentration of LiCl is doubled.

If the indene was formed via a condensation reaction promoted by abstraction of H^+ from the arylalkane by Cl^-, we would expect the yield of indene to increase with increasing concentration of Cl^-.

There seems therefore to be little support for the arylalkane being the precursor to the indene. A reaction scheme such as that suggested in section 4.2.1.3, depicting both being formed from a common intermediate would seem more likely in the face of our experimental evidence.

4.2.2 Thermally Promoted Coupling Reactions

4.2.2.1 Thermally Promoted Coupling Reactions of a Range of Orthomanganated Aryl Ketones

It was first noted by Gommans [30] that coupling of methyl acrylate with orthomanganated 3',4',5'-trimethoxyacetophenone (**34**) to form an indene product is possible in the absence of palladium. The yield, however, was only low and the attempted separation of other unstable products was not achieved. This was followed up by Robinson [19,31] who reported that reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese with diphenylacetylene in refluxing benzene gave 2,3-diphenyl-1-methylinden-1-ol in excellent yield. This method has also been adopted by the Woodgate group who have initiated investigations into the coupling of tetracarbonylmanganese complexes derived from podocarpic acid with substituted alkenes and alkynes without palladium as the catalyst [28,32,33].

Work at Waikato has also continued in this area, the results of which are summarised in Table 4.12.

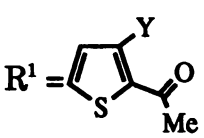
4.2.2.1.1 Thermally Promoted Coupling Reactions with Methyl Vinyl Ketone and Methyl Acrylate

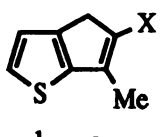
Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**40**) with methyl acrylate in refluxing carbon tetrachloride afforded the arylalkane methyl 3-(2-acetylthien-3-yl)-propanoate [(**51**); 25 %], the arylalkene methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [(**49**); 10 %] and the indene-type compound methyl 6-methyl-4H-cyclopenta[d]thiophene-5-carboxylate [(**113**); 37 %].

Although cyclisation across the 3,4 bond of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (**41**) had been routinely observed in the course of our coupling reaction investigations, this was the first time that cyclisation across the 2,3 double bond of the thiophene had been found. Satisfactory elemental analysis results have not yet been obtained for this compound. However the ^{1}H and ^{13}C-NMR and MS data were all consistent with the proposed structure.

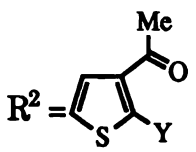
Table 4.12 Yields (%) of Products from Thermally Promoted Coupling of Orthomanganated Ketones with a Range of Alkenes in Benzene, Carbon tetrachloride and Acetonitrile

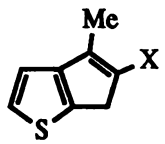
$Ar\text{-}Mn(CO)_4$	Alkene CH_2=CH-X	Products (R-Y)	C_6H_6	CCl_4	MeCN
(40)	X=COOMe	R^1-CH_2CH_2COOMe (51)		25	
		R^1-CH=CHCOOMe (49)		10	
		R^1-indene (113)		37	
(114)	X=COOMe	R^2-CH_2CH_2COOMe (115)	83	48	
		R^2-indene (116)	-	trace	
		R^2-(4S*,5R*) indanol (117)	-	32	
		R^2-(4R*,5R*) indanol (118)	-	5	
(41)	X=COMe	R^3-CH_2CH_2COMe (119)	15	14	
		R^3-indene (120)	74	63	
		R^3-(4S*,5R*) indanol (121)	-	}~20	
		R^3-(4R*,5R*) indanol (122)	-	}	



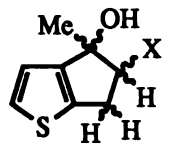


R^1-indene

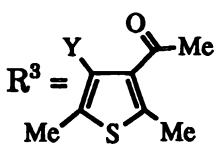


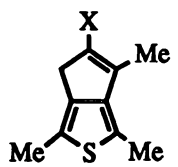


R^2-indene

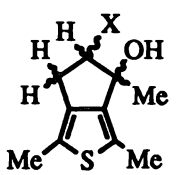


R^2-indanol





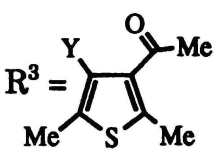
R^3-indene

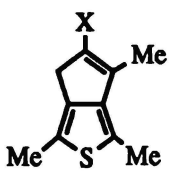


R^3-indanol

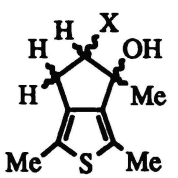
Table 4.12 Continued

$Ar\text{-}Mn(CO)_4$	Alkene $CH_2{=}CH\text{-}X$	Products (R-Y)	C_6H_6	CCl_4	MeCN
(41)	X=COOMe	$R^3\text{-}CH_2CH_2COOMe$ (55)		3	
		$R^3\text{-}CH{=}CHCOOMe$ (54)		~1	
		R^3-indene (53)		12	13
		R^3-(4S*,5R*) indanol (123)		47	17
		R^3-(4R*,5R*) indanol (124)		18	12
		R^3-nitrile insertion product (125)			8
(41)	X=CN	$R^3\text{-}CH_2CH_2CN$ (126)		5	
		R^3-indene (127)		~1	
		R^3-(4S*,5S*) indanol (128)		50	
		R^3-(4R*,5S*) indanol (129)		21	
	X=CHO	R^3-indene (130)	16		
(2)	X=COMe	R^4-indene (70)	84		
	X=COOMe	R^4-indene (60)		67	

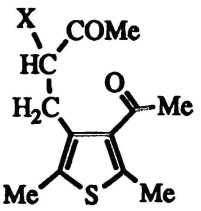




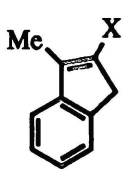
R^3-indene



R^3-indanol



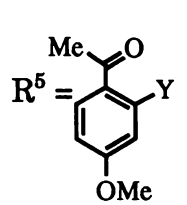
R^3-nitrile insertion product

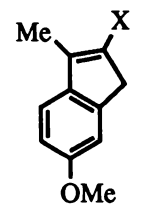


R^4-indene

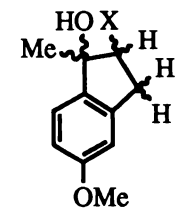
Table 4.12 Continued

Ar-Mn(CO)$_4$	Alkene CH_2=CH-X	Products (R-Y)	C_6H_6	CCl_4	MeCN
(39)	X=COMe	R^5-indene (73)		94	
	X=COOMe	R^5-CH_2CH_2COOMe (75)		11	
		R^5-H (72)		6	
		R^5-(1S*,2R*) indanol (131)		57	
		R^5-(1R*,2R*) indanol (132)		14	
(35)	X=COOMe	R^6-indene (84)	24		
		R^6-indene-H (133)	8		
(12)	X=COOMe	R^7-Mn(CO)$_4$ (12)	23		
		R^7-CH_2CH_2COOMe (108)	8		
		R^7-H (101)	23		

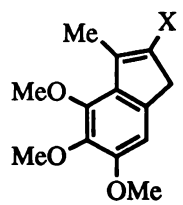




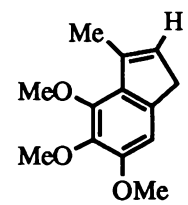
R^5-indene



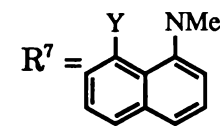
R^5-indanol



R^6-indene

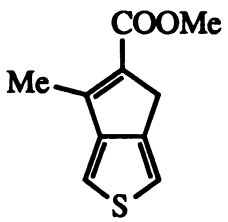


R^6-indene-H

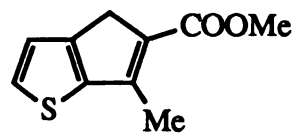


It had previously been suggested that cyclisation across this bond was not observed due to the ring strain that fusion might induce [34]. Data obtained from molecular mechanics calculated structures (Table 4.13) suggests that cyclisation across the 3,4 bond of the thiophene ring (A) results in a more stable structure than cyclisation across the 2,3 bond (B). The latter structure experiences greater angle-bending strain and a diminished electrostatic term, due either to fewer attractive interactions or more repulsive interactions.

Table 4.13 MM2* Calculated Energies for Indene-type Structures Formed via Cylisation Across the 3,4 Bond (A) and the 2,3 Bond (B)



(A)



(B)

Energy	141.18 kJ/mol	162.96 kJ/mol
Stretch	3.43	2.93
Prop Torsion	32.93	35.44
Electrostatic	-17.94	-4.41
Van der Waals	12.37	12.89
Bend	107.66	115.93
Cross Terms	2.72	0.17

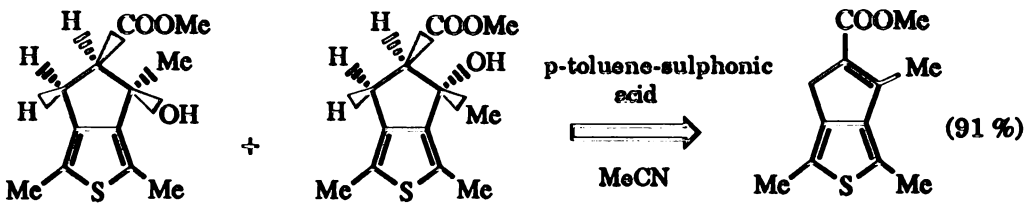
Reports that cyclisation across the 2,3 thiophene bond occurs in good yield via an intramolecular Friedel-Crafts reaction [35] suggests that the strain of fusing two five-membered rings together does not preclude cyclisation.

This ring fusion was not unique to the 2-acetylthiophene system. Reaction of η^2-(3-acetylthien-2-yl)tetracarbonylmanganese (114) in refluxing carbon tetrachloride with methyl acrylate in addition to the major coupling product, the arylalkane methyl 3-(3-acetylthien-2-yl)-propanoate [(115);

48 %], also afforded products resulting from cyclisation across the 2,3-double bond. In this case, however, only a trace of the indene-type product **(116)** was observed, the major cyclised product being instead the cyclopentanol methyl (4S*, 5R*)-4-hydroxy-4-methyl-5,6-dihydro-4H-cyclopenta[d]-thiophene-5-carboxylate [**(117)**; 32 %]. Its diastereoisomer [**(118)**; 5 %] was also observed, but only in minor yield and was not fully characterised. Solvent choice was critical for this reaction, as the same reaction performed under identical conditions, but in refluxing benzene, afforded only the arylalkane coupling product **(115)**.

In contrast the indene-type species 1-(1,3,6-trimethyl-4H-cyclopenta[c]-thien-5-yl)-ethanone [**(120)**; 74 %] was the major product isolated from the reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)** with methyl vinyl ketone in refluxing benzene. The arylalkane 4-(4-acetyl-2,5-dimethyl-thien-3-yl)-butan-2-one [**(119)**; 15 %] was also detected in small yield. Solvent choice was not as critical in this reaction, as changing to refluxing carbon tetrachloride, led only to a slight decrease in the yield of indene-type product [**(120)**; 63 %] while the arylalkane yield remained virtually unchanged [**(119)**; 14 %]. However, unlike the benzene reaction, for carbon tetrachloride the cyclopentanols (4S*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(121)** and (4R*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(122)** were also detected, albeit as minor products.

Changing the alkene to methyl acrylate while maintaining carbon tetrachloride as solvent as for the methyl vinyl ketone case, afforded the cyclised species as the major reaction products, but with the yield of the cyclopentanols methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate [**(123)**; 47 %] and methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate [**(124)**; 18 %] far exceeding that of the indene-type compound methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 12 %]. The arylalkane methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 3 %] was isolated in only low yield, with traces of the arylalkene methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; ~1 %] also being detected. Acid-catalysed elimination of water from the mixture of diastereoisomeric cyclopentanols **(123)** and **(124)** to give the indene-type product **(53)** was achieved in high yield (91 %) (Equation 4.3).



(123) (124) (-2 H_2O) (53)

Equation 4.3

The reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with methyl acrylate was repeated in refluxing acetonitrile as solvent. The overall yield was not as good as for carbon tetrachloride (only 50 %), but again the cyclised species were the major products. Yields of the two cyclopentanols (123) and (124) and the indene-type product (53) were similar. Also detected was methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [(125); 8 %], the origin of which will be discussed in section 4.2.2.3.

Coupling of η^2-(2-acetylphenyl)tetracarbonylmanganese (2) with methyl vinyl ketone in refluxing benzene gave only the indene, 1-(3-methylinden-2-yl)-ethanone [(70); 84 %]. The same compound with methyl acrylate in refluxing carbon tetrachloride also afforded indene (60) as the sole coupling product (67 %).

The indene 1-(6-methoxy-3-methylinden-2-yl)-ethanone [(73); 94 %] was again the sole reaction product when η^2-(2-acetyl-5-methoxyphenyl)-tetracarbonylmanganese (39) was treated with methyl vinyl ketone in refluxing carbon tetrachloride. Changing the alkene to methyl acrylate while maintaining the same solvent afforded the parent ketone [(72); 6 %], the arylalkane [(75); 11 %] and a mixture of the two diastereoisomeric indanols methyl (1S*, 2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate [(131); 57 %] and methyl (1R*, 2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate [(132); 14 %].

Reaction of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with methyl acrylate in refluxing benzene gave the indene methyl (4,5,6-trimethoxy-3-methylinden-2-yl)-carboxylate [(84); 24 %] and its elimination product 4,5,6-trimethoxy-3-methylindene [(133); 8 %], the origin of which will also be discussed in section 4.2.2.3.

4.2.2.1.2 Thermally Promoted Coupling Reactions with Other Alkenes

(i) Terminal Alkenes

Reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with acrylonitrile in refluxing carbon tetrachloride afforded the indene-type product 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carbonitrile [(127); ~1 %], the arylalkane 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanenitrile [(126); 5 %] and a mixture of the two diastereoisomeric cyclopentanols (4S*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile [(128); 50 %] and (4R*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile [(129); 21 %].

The coupling reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonyl-manganese (41) with acrolein in refluxing benzene gave only the indene-type product 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carbaldehyde [(130); 16 %] in poor yield.

(ii) Chalcones

The thermally promoted coupling reactions of orthomanganated aryl ketones with substituted chalcones was investigated following reports by Tully [36] that reaction of various substituted chalcones with benzylpentacarbonylmanganese in refluxing hexane gave not only a cyclomanganated enone, but also a cyclopentenol presumably formed by insertion of the free chalcone into the carbon-manganese bond of the orthomanganated enone followed by cyclisation (Figure 4.8).

Where ring manganation of the chalcone occurred he also noted in one instance a minor amount of a novel orthomanganated structure incorporating a cyclopentanol ring, formed presumably via insertion of the alkene double bond of the ring-manganated chalcone into the aryl carbon-manganese bond of another molecule of the ring-manganated chalcone (Figure 4.9).

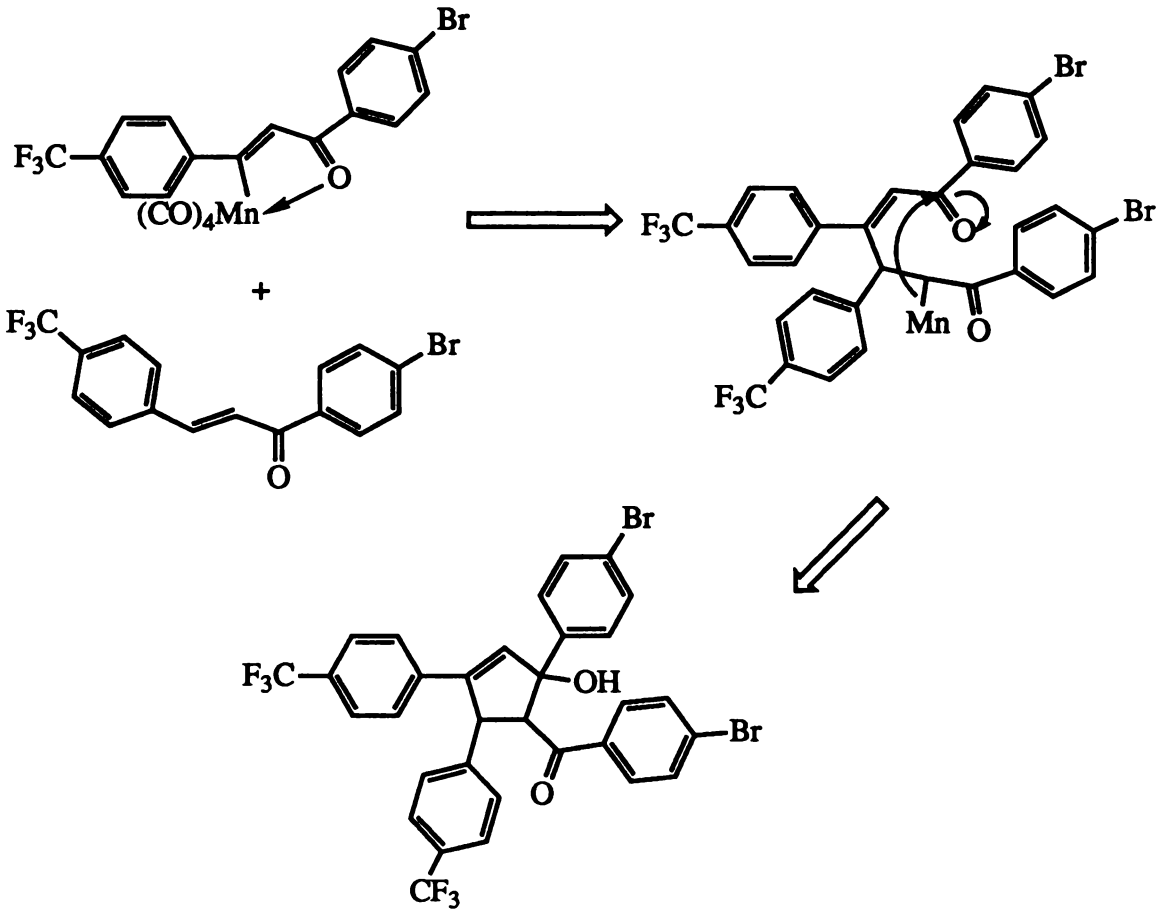


Figure 4.8

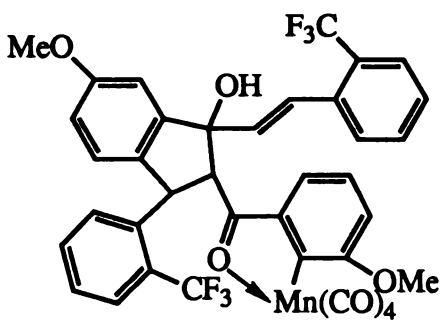


Figure 4.9

These reactions showed obvious similarities to our thermally promoted coupling reactions of orthomanganated aryl ketones with terminal olefins such as methyl acrylate and methyl vinyl ketone. It was of interest, therefore, to establish whether the simple orthomanganated aryl ketone showed a similar reactivity to the chalcone double bond.

Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** with 1-(3-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one

(134) in refluxing hexane over three hours afforded principally the starting materials, but also a small yield of one diastereoisomer of the cyclopentanol 3-methoxyphenyl 3-(2-trifluoromethylphenyl)-1-hydroxy-5-methoxy-1-methylindan-2-yl ketone [**(135)**; 9 %]. The chemical shift of the methyl group at C-1" (28.3 ppm) suggests a *trans* diequatorial arrangement between the methyl group and the bulky substituents on the adjacent carbons at C-2" and C-7a" but stereochemistry has not been definitively assigned.

In an attempt to improve the yield of the cyclopentanol species, a similar reaction was performed using longer reflux time. η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** was treated with 1-(4-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one **(136)** in refluxing hexane overnight. In addition to starting materials, the demetalated orthomanganated ketone **(72)** was recovered in 21 % yield, along with the cyclopentanol 4-methoxyphenyl 3-(2-trifluoromethyl-phenyl)-1-hydroxy-5-methoxy-1-methylindan-2-yl ketone [**(137)**; 13 %], and a novel diketone 3-(2-trifluoromethylphenyl)-1,5-di(4-methoxyphenyl)-pentane-1,5-dione [**(138)**; 8 %].

Again the stereochemistry of the cyclopentanol was not established. However a *trans*-diequatorial arrangement between the methyl group at C-1" and the adjacent bulky groups was once more assumed on the basis of the ^{13}C-NMR 1"-CH_3 chemical shift (see section 4.2.4).

The formation of **(138)** is difficult to explain given the reaction conditions employed. The product (Figure 4.10) formally resembles that expected

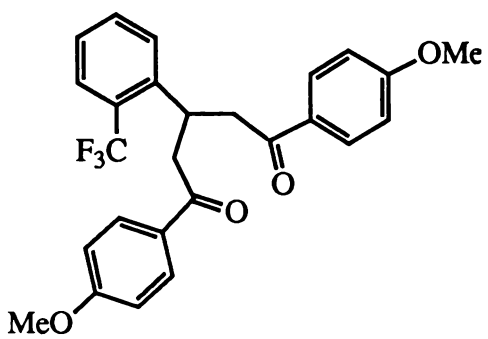


Figure 4.10

from a Michael addition of the orthomanganated ketone **(39)** and the chalcone **(136)** followed by demetalation. However for this type of reaction, in general, the compound from which the carbanion is generated must be

fairly acidic. Possibly the acidity of the methyl protons is significantly increased by carbonyl coordination to manganese, but it seems that in the absence of basic conditions it would be unlikely that η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** would fulfil this requirement. A possible alternative is that homolytic cleavage of the C-Mn bond gives an aryl radical which abstracts a methyl hydrogen to form a Ar-$CO\dot{C}H_2$ radical which could lead to a radical-initiated Michael-type addition. However, there was no sign of a biaryl dimeric product which might also be expected in this case. The structure was deduced primarily from NMR studies and confirmed by GC-MS analysis. The mass spectrum showed the expected molecular ion corresponding to $C_{26}H_{23}O_4F_3$, and gave a satisfactory fragmentation pattern.

More forcing reaction conditions, achieved by employing a higher boiling point solvent, also failed to improve the yield of coupled products. The reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** with 1-(3,4,5-trimethoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one **(139)** in refluxing heptane overnight led to the demetalation product 4'-methoxyacetophenone **(72)** and 3',4',5'-trimethoxyacetophenone **(87)** formed by decomposition of the starting chalcone. A number of minor products were also observed, but were not characterised.

Changing the solvent system to carbon tetrachloride was also unsuccessful. η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** was treated with 1-(4-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one **(136)** in refluxing carbon tetrachloride overnight and afforded the starting chalcone [**(136)**; 53 % return], demetalated ketone [**(72)**; 13 %] and the dimer 2-(2-acetyl-5-methoxyphenyl)-4-methoxyacetophenone [**(140)**; 28 %] possibly formed via radical dimerisation after homolytic cleavage of the C-Mn bond in the parent compound. Such dimeric products have not been found in measureable amounts in other more facile coupling reactions, however. Again a number of minor products were observed but not characterised.

Treatment of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese **(39)** with ethyl cinnamate **(141)** in refluxing hexane overnight failed to yield any coupled products. In addition to the starting materials only the demetalated parent ketone [**(72)**; 10 %] was isolated.

Chemical activation of the orthomanganated aryl ketone **(39)** by oxidative decarbonylation with trimethylamine *N*-oxide prior to reaction with the chalcone **(142)** was also attempted. Extensive demetalation resulted, 4'-methoxyacetophenone **(72)** being isolated in 80 % yield.

Our results indicate that although the double bond of the chalcone can insert into the aryl carbon-manganese bond of the orthomanganated ketone under certain reaction conditions, this process is not very efficient. Presumably the presence of the bulky terminal phenyl ring leads to retardation of this insertion step. This is supported by other workers in this area who report that in general the yields of coupled adducts decreases as olefin-substitution increases [28] [H_2C=CHX > RCH=CHX ~ CH_2=C(R)X >> RCH=CHR].

4.2.2.2 Attempted Coupling of an Orthomanganated Arylamine

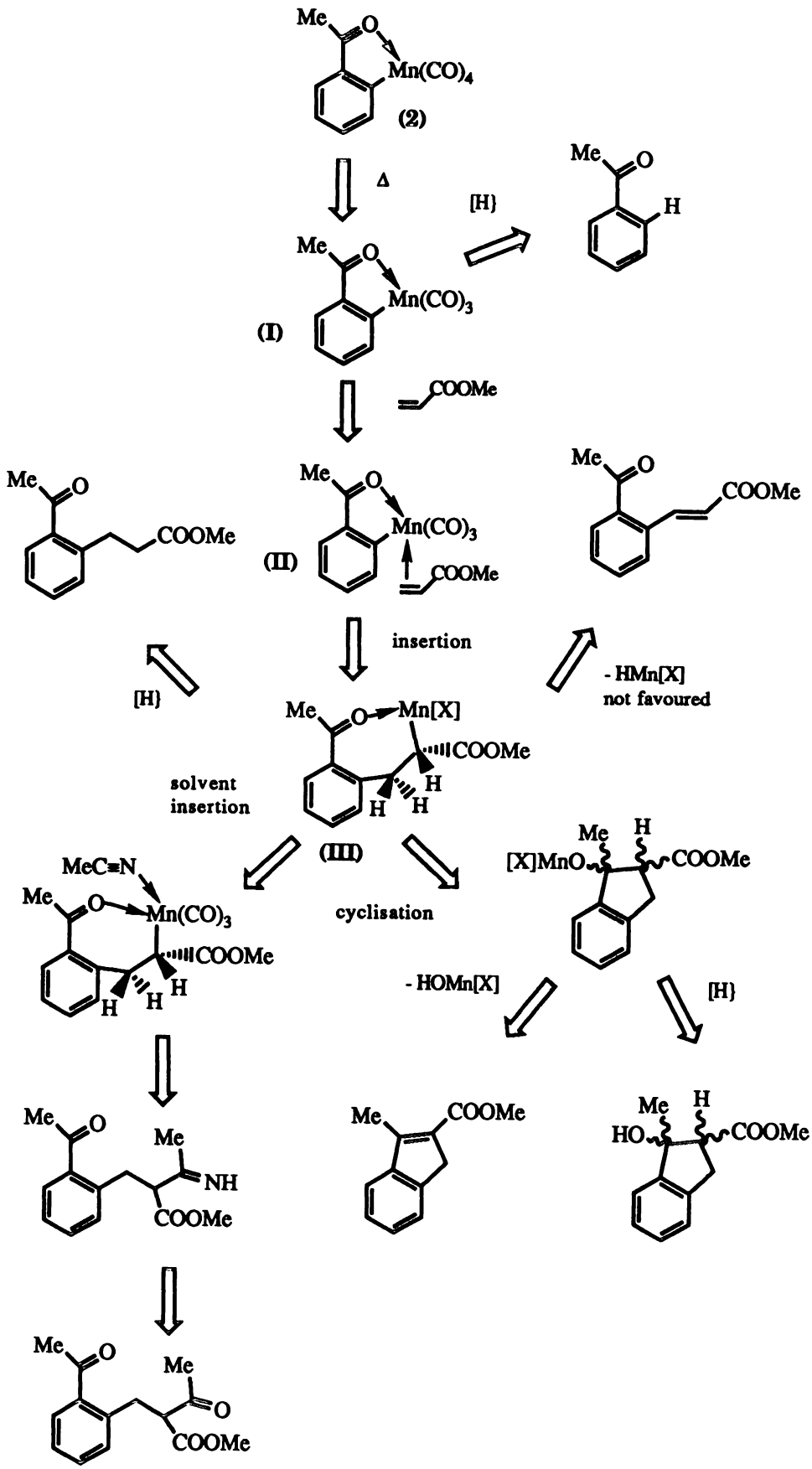
Only one thermally promoted coupling reaction between an orthomanganated arylamine and an alkene was attempted and then with only limited success.

The reaction of η^2-(8-dimethylamino-1-naphthyl)tetracarbonylmanganese **(12)** with methyl acrylate in refluxing benzene afforded the parent arylamine [**(101)**; 23 %], unreacted orthomanganated starting material [**(12)**; 23 %] and the arylalkane coupling product methyl 3-(8-dimethylamino-1-naphthyl)-propanoate [**(108)**; 8 %]. Although the coupling product was afforded in very low yield, the result was of interest as palladium-promoted coupling reactions involving this system had afforded only the parent arylamine.

4.2.2.3 Reaction Scheme for Thermally Promoted Coupling Reactions

Thermally induced decarbonylation of **(2)** presumably gives the coordinatively unsaturated intermediate; (Scheme 4.7 (I)) and then the alkene complex (II), which undergoes insertion into the aryl carbon manganese bond, forming (III).

Scheme 4.7


Me
O
Mn(CO)4
(2)
Δ
[H]
Mn(CO)3
(I)
COOMe
(II)
insertion
- HMn[X]
not favoured
Mn[X]
(III)
solvent
insertion
cyclisation
MeC≡N
- HOMn[X]
[H]
[X]MnO
HO
NH

Cyclisation of this σ-alkyl complex affords a mixture of diastereoisomeric manganese alkoxides which would decompose on workup, forming cyclopentanols; or eliminate HMnO[X] to give the indene-type product.

Cleavage of the carbon-manganese bond in intermediate (III) gives rise to the arylalkane, while similar reaction on complex (I) leads to the formation of the parent ketone.

Elimination of HMn[X] from (III) would give the E-arylalkene, although as discussed in section 4.2.1.3 this elimination does not occur to any significant extent for reactions carried out in the absence of palladium.

The formation of methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate **(125)** probably arises from insertion of solvent acetonitrile into the carbon-manganese bond of (III), to form the imine, which upon workup could hydrolyse to the ketone. Support for this explanation comes from coupling reactions performed in propionitrile as solvent (see section 4.2.3.1), which afforded a propanoyl insertion product **(143)**. There is no sign of acylation at the aryl carbon indicating such insertion does not occur at the aryl-manganese centre of (I).

The formation of a compound such as 4,5,6-trimethoxy-3-methylindene **(133)** from **(35)** and methyl acrylate is not unprecedented. Woodgate [28] has also observed a similar species during the course of investigations into coupling reactions promoted by trimethylamine *N*-oxide with methyl acrylate and orthomanganated compounds. The product corresponds to that expected formally from the reaction of the orthomanganated compound with ethene followed by loss of water. Woodgate has proposed a demethoxycarbonylation reaction mediated by manganese after the olefin has inserted into the carbon-manganese bond.

4.2.2.4 Summary: Coupling Reactions in the Absence of Pd(II)

Although these results illustrate the unpredictable nature of these coupling reactions, we can take several points from this study.

1. Alkenes can insert efficiently into the aryl carbon-manganese bond, i.e. transmetalation by palladium is not a necessary prerequisite to alkene coupling.

2. When palladium is not present arylalkene is formed in very small or indetectable amounts.

3. Reaction in benzene tends to afford either the indene-type product and/or the arylalkane, while carbon tetrachloride as solvent favours the formation of the indene-type product and/or the cyclopentanols with little arylalkane formation.

4. Acetonitrile as solvent may become incorporated via insertion as an acetyl group into coupling products.

5. The major cyclopentanol isomer formed in all cases but one, was established as having a *trans* diequatorial arrangement of the bulky alkene substituent and the methyl group. The exception was the reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese **(41)** with methyl vinyl ketone for which a *cis* relationship between the methyl group and the equatorial acetyl was established **(121)**.

6. Of the olefins used, methyl acrylate and methyl vinyl ketone gave higher yields of coupled products than acrylonitrile or acrolein.

7. An aryl substituent on the terminal carbon of the alkene as in chalcones seem to significantly reduce the yield.

4.2.3 Changing the Reactivity of the Metal Centre

Earlier results suggested that coupling reactions of orthomanganated ketones do not proceed solely via transmetalation at the aryl-manganese centre by palladium. We sought to provide further evidence for this premise by changing the reactivity of the manganese centre and comparing the ratios of coupled products obtained. The reactivity of the metal was altered by changing either the ligands on the metal or the metal itself.

4.2.3.1 Changing the Ligand

A di-phosphine and several mono- and di-phosphite derivatives of orthomanganated complexes were prepared by the reaction of the orthomanganated ketone with the appropriate ligand in refluxing heptane.

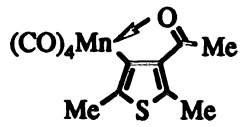
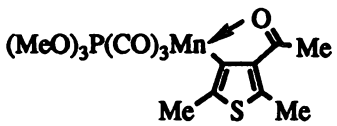
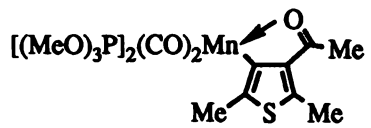
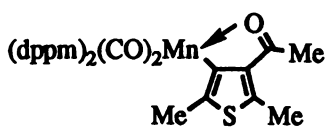
Tertiary phosphines and phosphites are much stronger Lewis bases than CO, i.e. better σ-donors, but they are generally poorer π-acceptors. The π-bonding differs from that for CO in that the π-acceptor orbitals are the phosphorus 3d orbitals. Hence the bonding can be designated as dπ-dπ whereas that of CO is dπ–pπ*. The extent of both donation to metal from the lone pair on the P atom and back-donation from metal to P depends on the nature of the groups attached to P. Electronegative substituents tend to reduce σ-donor character and enhance π-bonding capacity. Tertiary phosphites are therefore stronger π-acceptors than tertiary phosphines, but both are appreciably weaker than CO. This is reflected in the metal-carbonyl vibrational spectra of a series of substituted orthomanganated complexes prepared in this study (Table 4.14).

Replacing CO by ligands with less back-accepting ability means that the remaining CO groups must accept dπ electrons from the metal to a greater extent to prevent the accumulation of negative charge on the metal atom. An increase in the M-C bond order causes a corresponding decrease in the C-O bond order, which in turn causes a drop in the CO vibrational frequency.

If the nett effect is such that replacing a CO by a better σ–donor lowers the effective electronegativity of the manganese atom, this would lead to a less polar Mn-C_{aryl} bond. This would be manifested as a longer Mn-C_{aryl} bond length and presumably more electron density about the aryl carbon atom giving it more carbanionic character.

As yet there is no good crystallographic data to support this argument. The structure of orthomanganated benzophenone with one CO group substituted by a triphenyl arsine ligand has been reported in the literature, and a comparison of the Mn-C_{aryl} bond length with that reported for orthomanganated acetophenone would have been of interest. However for the benzophenone complex there is some suspicion that a centrosymmetric structure in true space group $P\bar{1}$ has been refined in a non-centrosymmetric space group (P1), so individual bond lengths may be inaccurate. There are also many errors in the published tables of bond parameters (see Cambridge Crystallographic data base entry DELHEH).

Table 4.14 Metal-Carbonyl Vibrational Spectra ν(M-CO) cm^{-1} of a Series of Substituted Orthomanganated Complexes

Orthomanganated Compound *		ν(M-CO) cm^{-1} (in $CHCl_3$)		
	(41)	2081,	1997,	1935
	(144)	2018,	1939,	1897
	(145)	1937,	1854	
	(146)	1915,	1819	

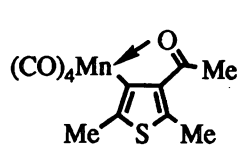
* Compound (144) is the *fac* isomer as shown by IR spectroscopy. (145) and (146) (in which the dppm ligands are monodentate) both have phosphorus donors *trans* as shown by IR spectroscopy and ^{31}P-NMR.

The results of a series of experiments comparing the palladium-promoted and thermally promoted alkene coupling reactions of an orthomanganated ketone with several of its phosphite- and phosphine-substituted analogues, are summarised in Table 4.15. All of the reactions were performed with identical reactant mole ratios and reflux times in acetonitrile or propionitrile under a nitrogen atmosphere.

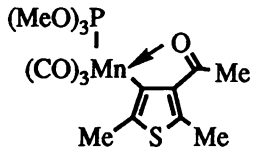
It is evident that for palladium-promoted coupling reactions, there is a steady progression towards increased yield of cyclised product as the extent of substitution of CO by trimethylphosphite increases.

Reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with methyl acrylate in the presence of lithium tetrachloropalladiate afforded the arylalkene methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [(54); 57 %], the arylalkane methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [(55); 19 %], the indene-type product methyl 1,3,6-trimethyl-

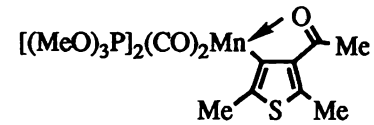
Table 4.15 Yields (%) for Palladium- and Thermally-Promoted Coupling Reactions of a Series of Substituted Orthomanganated Complexes with Methyl Acrylate in Refluxing Acetonitrile and Propionitrile



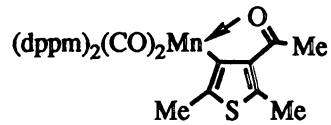
(41)



(144)

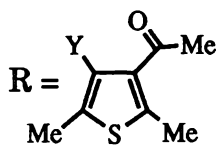


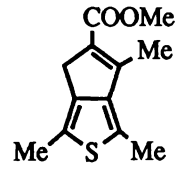
(145)



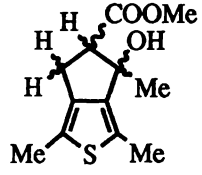
(146)

Products (R-Y)	Refluxing Acetonitrile Pd	Refluxing Acetonitrile No Pd	Refluxing Acetonitrile Pd	Refluxing Acetonitrile No Pd	Refluxing Acetonitrile Pd	Refluxing Acetonitrile No Pd	Refluxing Propionitrile Pd	Refluxing Propionitrile No Pd	Refluxing Acetonitrile Pd	Refluxing Acetonitrile No Pd	Refluxing Propionitrile Pd	Refluxing Propionitrile No Pd
R-CH=CHCOOMe (54)	57	-	64		19	-		-		-		-
R-CH_2CH_2COOMe (55)	19	-	-		-	-		6		13		13
R-H (56)	17	-	15		3	-		-		-		-
R-indene (53)	5	13	3		5	9		6		-		-
R-(4S*,5R*)-indanol (123)	-	17	8		47	17		19		44		50
R-(4R*,5R*)-indanol (124)	-	12	2		19	11		25		26		27
R-nitrile insertion product X=Me (125)[a], X=Et (143)[b]	-	8[a]	-		-	37[a]		36[b]		13[a]		-
R-Mn$(CO)_2[P(OMe)_3]_2$ (145)	-	-	-		9	-		-		-		-

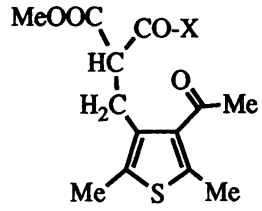




R-indene



R-indanol



R-nitrile insertion product

4H-cyclopenta[c]thiophene-5-carboxylate [(53); 5 %] and the parent ketone [(56); 17 %].

Substitution of one carbonyl ligand by a trimethylphosphite group (144) resulted in similar yields of the arylalkene [(54); 64 %], parent ketone [(56); 15 %] and indene-type product [(53); 3 %], but no yield of arylalkane (55). The cyclopentanols methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate [(123); 8 %] and methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(124); 2 %] were also isolated.

Substitution of two carbonyl ligands by trimethylphosphite (145) showed an even greater change in the reactivity of the orthomanganated ketone. The major products were now the cyclopentanols methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate [(123); 47 %] and methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate [(124); 19 %], while the yield of arylalkene (54) decreased to 19 %. Also detected were the parent ketone [(56); 3 %] and the indene-type species [(53); 5 %].

The nature of the ligand then clearly influences the alkene coupling product distribution ratios. As for the manganese versus mercury example (see section 4.2.1.5.2) these results suggest that transmetalation by palladium is not the sole pathway to formation of coupled products.

As for the thermally promoted coupling reactions reported in section 4.2.2, reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41), η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)-manganese (145) and η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(η^1-dppm)manganese (146) with methyl acrylate afforded either arylalkane (55) and cyclised coupling products [(53), (123), (124)], or in two of the cases, the solvent insertion product methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate (125). In none of these reactions was the arylalkene (54) detected.

It is interesting to note that for η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(η^1-dppm)manganese (146), where the back donation of the metal to the substituted ligand is poorest, the yield of cyclised product is greatest.

If, as discussed earlier, the nett effect of replacing a CO by a ligand which is a better σ-donor and poorer π-acceptor leads to a metal-bonded aryl carbon atom which shows increased carbanionic character, presumably the same would also hold true for the metal-bonded alkyl carbon atom following insertion of the alkene into the metal aryl carbon bond (Figure 4.11).

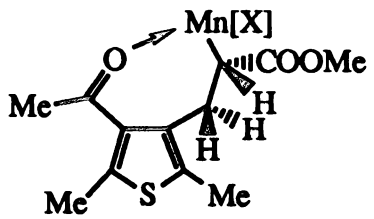


Figure 4.11

Increased electron density at the metal-bonded alkyl carbon could then promote cyclisation across to the acyl carbonyl carbon atom, which may be particularly susceptible to nucleophilic attack due to donation of electron density from the carbonyl oxygen to the metal atom.

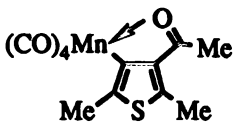
4.2.3.2 Changing the Metal from Manganese to Rhenium

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (**32**) was prepared to enable us to determine the product distribution for methyl acrylate coupling with an orthorheniated precursor and compare it with that for the corresponding orthomanganated precursor under identical conditions.

The results obtained from the palladium-promoted and thermally promoted coupling reactions of both the manganese and rhenium orthometalated compounds with methyl acrylate performed in refluxing acetonitrile are given in Table 4.16.

For the palladium-promoted reactions, the yields of arylalkane (**55**), arylalkene (**54**) and parent ketone (**56**) are reasonably similar. It is significant however that for rhenium we do not observe the indene-type product.

Table 4.16 Yields (%) for Palladium- and Thermally-Promoted Coupling Reactions of Orthomanganated (41) and Orthorheniated (32) 3-Acetyl-2,5-dimethylthiophene with Methyl Acrylate in Refluxing Acetonitrile



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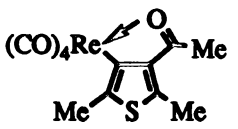
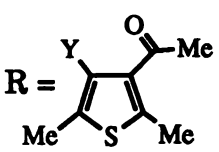
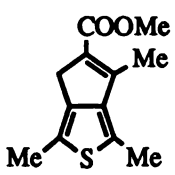


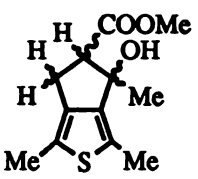
(32)

Products (R-Y)	Pd	No Pd	Pd	No Pd
R-CH=CHCOOMe (54)	57	-	66	-
R-CH_2CH_2COOMe (55)	19	-	16	17
R-H (56)	17	-	15	31
R-indene (53)	5	13	-	-
R-(4S*,5R*) indanol (123)	-	17	-	4
R-(4R*,5R*) indanol (124)	-	12	-	3
R-nitrile insertion product (125)	-	8	-	12

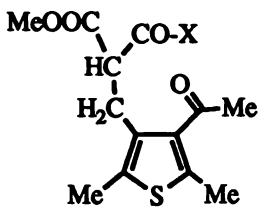




R-indene



R-indanol



R-nitrile insertion product

Although the yield of indene (53) for manganese was small (5 %), its absence in the case of rhenium provides further evidence that coupling reactions do not proceed solely via a common aryl-palladiated intermediate.

More variation in product ratios is observed between the two metals for the thermally promoted reactions. Table 4.16 shows cyclisation [(53), (123), (124)] to be much more strongly favoured in the manganese case (42 %

overall) than the rhenium case (7 % overall), while demetalation to give the parent ketone (56) occurs only for rhenium.

This difference in reactivity between the two metals may be rationalised in terms of the difference in electron density about the rhenium atom compared with manganese, and the relative strengths of the M-C bonds.

It is generally accepted from thermochemical data for transition-metal organometallics that transition metal-C σ–bond energies (in contrast to main group-C bond energies) increase with increasing atomic number.

Table 4.17 shows a comparison of the M-Me bond enthalpies of derivatives of manganese and rhenium calculated using Calvet microcalorimetry [37].

Table 4.17 Bond Enthalpies (kJ mol^{-1}) for Methylpentacarbonyl-manganese and Methylpentacarbonylrhenium

Compound	$\dot{E}(M^{\sigma}C)$ kJ mol^{-1}
$MeMn(CO)_5$	187
$MeRe(CO)_5$	220

This also parallels the generally accepted observation of the decreasing lability of CO bonded to rhenium compared to manganese.

Another pertinent factor may be the higher Pauling electronegativity of Re (1.9) compared with Mn (1.6). This difference in electronegativity between the Mn and Re atoms may also be used to rationalise the increased yield of cyclised coupling product for Mn over Re. The $M\text{-}C_{alkyl}$ bond is formally regarded as a polar $M^{\delta+}\text{-}C^{\delta-}$ bond. It is reasonable then to assume that a more electronegative metal atom (Re) would lead to increasing polarisation of the electron density towards the metal atom, thereby reducing the carbanionic character of the metal-bonded carbon atom. If formation of the indene-type product and the diastereoisomeric cyclopentanols occurs via nucleophilic attack of the carbanionic metal-bonded carbon at the acyl carbonyl carbon atom as we suggest (see section 4.2.1.3), for Re this attraction would be diminished. We would therefore predict a decreased yield of cyclised product for Re, which is in accord with our experimental results.

4.2.3.3 Summary

1. For both palladium-promoted and thermally promoted alkene coupling reactions, the yield of cyclised products increases as the extent of substitution of CO by L increases (where L is a ligand that is a better σ-donor and poorer π-acceptor than CO). These results can be rationalised in terms of increased electron density at the metal-bonded alkyl carbon atom promoting cyclisation across to the acyl carbonyl carbon atom.

2. Cyclisation is more strongly favoured for manganese than for rhenium. The more electronegative Re atom would decrease the carbanionic character of the metal-bonded alkyl carbon atom, thereby reducing the likelihood of addition across the carbonyl bond.

The nature of both the ligands and the metal itself clearly influence reactivity. For palladium-promoted coupling reactions it is therefore unlikely that the sole reaction pathway occurs via transmetalation from manganese to palladium prior to insertion of the alkene.

4.2.4 NMR

In this section are described the methods by which the major coupling products isolated in this study were identified by NMR spectroscopy.

Arylalkane (50)

The arylalkane 4-(2-acetylthien-3-yl)-butan-2-one **(50)** exhibited two triplets at 3.15 ppm and 2.70 ppm, showing mutual vicinal coupling of 7.4 Hz. The upfield signal (lower ppm) was assigned as H-3, while the downfield signal was designated H-4. These assignments were confirmed by NOE-difference experiments and a heteronuclear 2D correlation experiment.

Irradiation of the triplet at 3.15 ppm led to a strong NOE enhancement of the aromatic proton assigned as H-4', in addition to the triplet at 2.70 ppm. Irradiation of this latter signal showed, as expected, enhancement of its neighbouring $-CH_2$ group, but more importantly strong enhancement of the methyl singlet at 2.06 ppm (H-1) and only weak enhancement of the doublet at H-4'. These NOE effects are in agreement with those predicted from a molecular mechanics calculated structure of the arylalkane

(Figure 4.12), considering free rotation of the methylene protons about the sp^3 hybridised carbon atoms C-3 and C-4. Although it has been reported that an NOE enhancement is rarely useful over a distance of more than about 4 Å [38], in practise we have found that 3 Å is perhaps a more realistic limit given the sensitivity of the equipment employed.

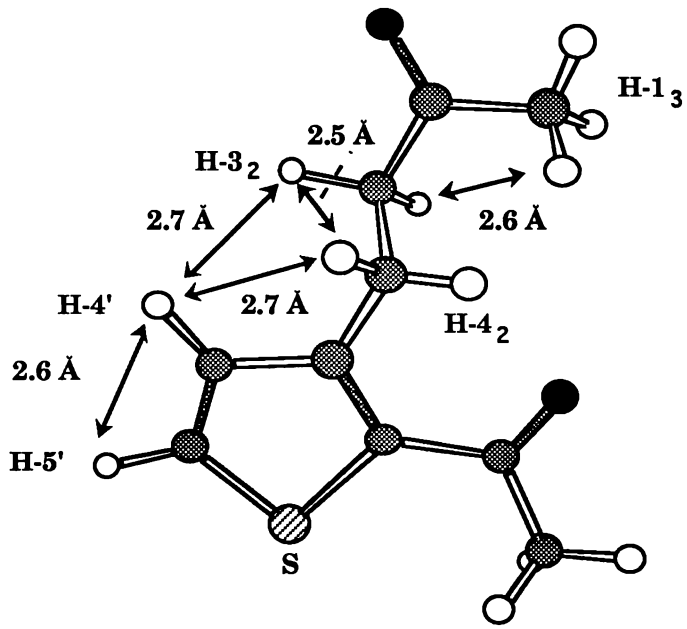


Figure 4.12 Molecular Mechanics Calculated Representation of 4-(2-Acetylthien-3-yl)-butan-2-one (50)

An X-H experiment revealed $^1J_{C\text{-}H}$ connectivity between the protons assigned as H-3 and a triplet-carbon at 43.5 ppm, and the H-4 protons with the remaining triplet-carbon at 24.5 ppm. These correlations are in accord with the chemical shifts expected for an alkyl ketone of this nature [39]. The positive polarisation of the carbonyl carbon is slightly attenuated by the electron releasing effect of the α-alkyl groups (+I effect), resulting in deshielding of the α-carbons, and a shift in the ^{13}C-NMR resonance to lower field (higher ppm). This deshielding effect is more pronounced for C-3 than C-4 due to the larger electron withdrawing capacity of the carbonyl functionality compared to the 2-acetylthiophene group.

Arylalkene (48)

^{1}H-NMR of the arylalkene E-4-(2-acetylthien-3-yl)-but-3-en-2-one **(48)** exhibited two olefinic doublets in the aromatic region in addition to those

associated with the thiophene ring. The coupling constant of 16.7 Hz was consistent with only the E-isomer being formed. The doublet at lower field, 8.41 ppm, was assigned as H-4, while the upfield doublet at 6.56 ppm was assigned as H-3, in accord with previous assignments made for α,β-unsaturated ketones. The deshielding of the β-olefinic proton may be rationalised in terms of the following contributing resonance forms (Figure 4.13):-

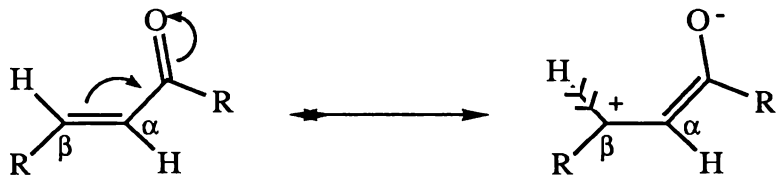


Figure 4.13

Irradiation of the α-proton in a difference NOE experiment showed only enhancement of the aromatic proton at H-4', again in accordance with the intramolecular distances predicted from a molecular mechanics calculated structure (Figure 4.14).

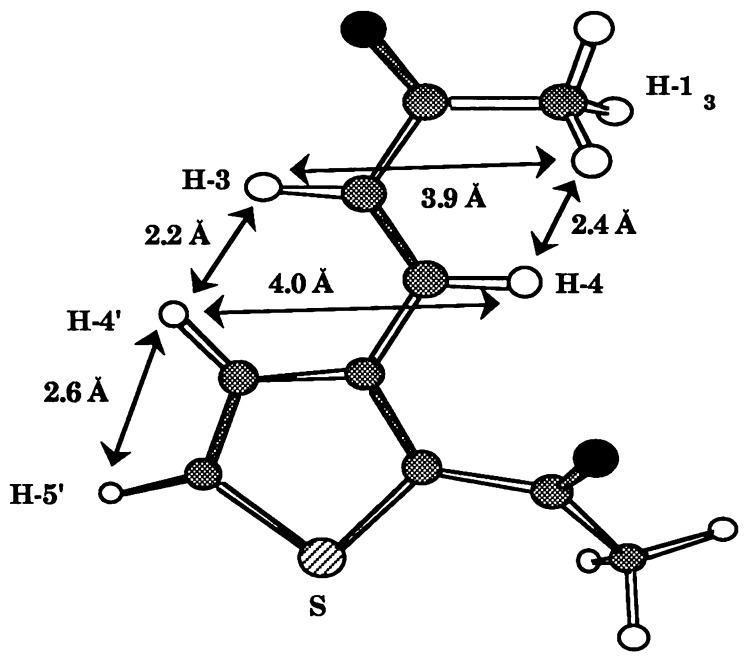


Figure 4.14 Molecular Mechanics Calculated Representation of E-4-(2-Acetylthien-3-yl)-but-3-en-2-one (48)

E- and Z-Isomers of the Arylalkene (61) (62)

The E- and Z-isomers of the arylalkene 3-(2-acetylthien-3-yl)-prop-2-enenitrile were readily distinguishable by examination of the olefinic coupling constant in the ^{1}H-NMR. The less polar isomer showed the olefinic hydrogen resonances as doublets at 8.09 and 5.56 ppm (J=12.2 Hz) consistent with a Z-isomeric alkene. The more polar isomer was consistent with an E-isomeric alkene, displaying two olefinic doublets at 8.33 and 5.88 ppm (J=16.6 Hz).

Indene-type Compounds (53) and (70)

(53)

^{1}H-NMR of the indene-type compound methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate **(53)** showed a two-proton broadened singlet at 3.23 ppm which was assigned to H-4. Signal broadening was due to long range homoallylic coupling with the methyl group (6-CH_3) which appeared as part of a six-proton multiplet at 2.54 ppm. This compound was also characterised by X-ray crystallography (see section 4.3).

(70)

The ^{1}H-NMR spectrum of 1-(3-methylinden-2-yl)-ethanone **(70)** showed better resolution than that for methyl 1,3,6-trimethyl-4H-cyclopenta[c]-thiophene-5-carboxylate **(53)**. The two-proton resonance due to H-1' appeared as a quartet (J=2.3 Hz) coupled to the protons assigned as 3'-CH_3, which gave rise to a triplet at 2.52 ppm.

Cyclopentanols (117) (121) (122) (123) (124) (131) (132) (128) (129)

(117)

The ^{1}H-NMR spectrum of methyl (4S*,5R*)-4-hydroxy-4-methyl-5,6-dihydo-4H-cyclopenta(d)thiophene-5-carboxylate **(117)** showed three doublets of doublets between 3.63 ppm and 3.04 ppm. Two of these signals (3.46, 3.09) shared a large geminal coupling (15.9 Hz) and were therefore assigned to H-6_2. The doublet of doublets at 3.61 ppm showed two similar vicinal coupling constants and was assigned to H-5.

Irradiation of this latter signal in a difference NOE experiment led to enhancement of the doublet of doublets at 3.09 ppm and the methyl singlet at 1.76 ppm, consistent with a cis relationship between these three groups. A molecular mechanics calculated structure (Figure 4.15) orientates the bulky ester group in the equatorial position at C-5 as would be expected. The thiophene ring is planar, while the cyclopentaannulated ring is slightly puckered, C-5 being pushed down out of the plane of the rest of the molecule. H-5 adopts an axial position, lying below the plane of the ring. Due to the slightly puckered conformation of the cyclopentanol ring, one of the hydrogens assigned as H-6 adopts a pseudo-equatorial position, while the other adopts a pseudo-axial position lying above the plane of the ring. Minimum distance calculations (Figure 4.16) between the proton assigned as H-5 and the two H-6 protons reveal an intermolecular distance of less than 3 Å, (the distance within which it would be expected to observe an NOE enhancement effect) only for the pseudo equatorial hydrogen. This hydrogen must therefore give rise to the doublet of doublets at 3.09 ppm, and it was assigned as H-6b. The doublet of doublets at 3.46 ppm was assigned as H-6a accordingly.

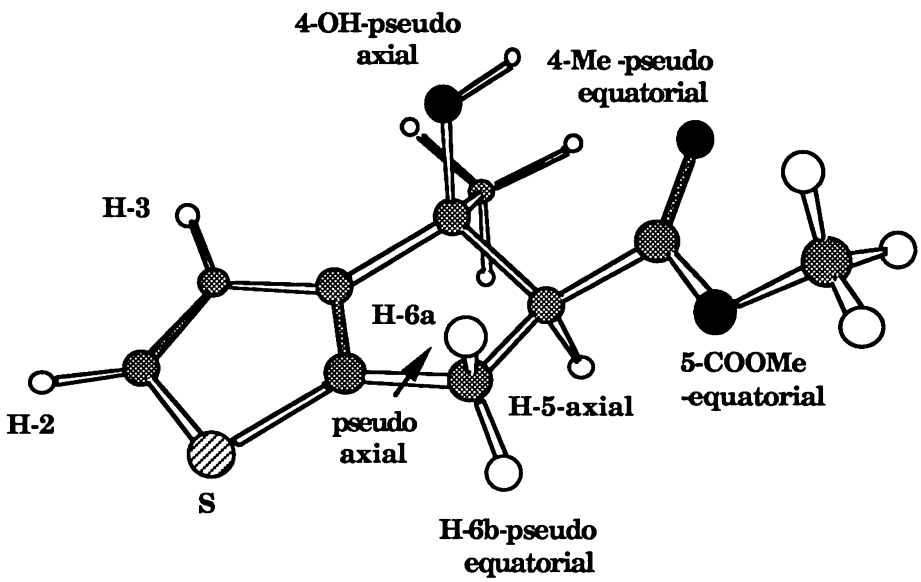


Figure 4.15 Molecular Mechanics Calculated Representation of Methyl (4S*,5R*)-4-hydroxy-4-methyl-5,6-dihydo-4H-cyclopenta(d)thiophene-5-carboxylate (117)

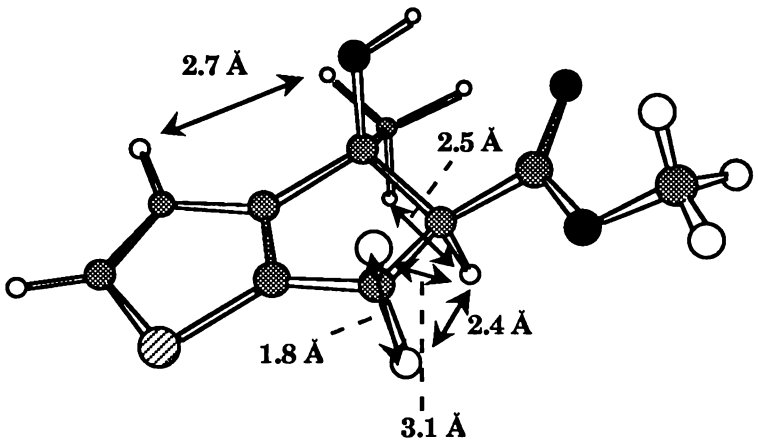


Figure 4.16

NOE experiments confirm that the methyl group at C-4 must also lie in the equatorial plane. Irradiation of this signal led to enhancement of the doublet of doublets at 3.61 ppm (H-5) as expected, and the doublet at 6.89 ppm, arising from the proton on the thiophene ring assigned as H-3. Examination of the structure generated from molecular mechanics suggests that the methyl group adopts a pseudo equatorial position, while the hydroxyl group occupies a pseudo axial position above the plane of the molecule. Again minimum distance calculations agree with the results obtained from our NOE experiments.

Further evidence for the methyl group assuming an equatorial orientation comes from a comparison of the ^{13}C-NMR chemical shifts of the methyl groups from both diastereoisomers. It is now generally accepted that for cycloalkanes, equatorial methyl group carbons typically resonate at significantly lower field (i.e. higher ppm) than carbon nuclei of axial methyl groups [39]. For the (4S*, 5R*) isomer, in which we have assigned the methyl group as pseudo equatorial, we observe the methyl group carbon at 29.7 ppm, while for the (4R*, 5R*) isomer, in which the methyl group would be orientated in a pseudo axial position, the quarternary carbon signal is observed at 24.7 ppm. The difference in chemical shift of the methyl group carbon proved to be a useful means of determining the relative stereochemistry of other cyclopentanols isolated during the course of this investigation.

(121) (122)

The cyclopentanols (4S*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(121)** and (4R*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(122)** were characterised only by ^{13}C-NMR. Relative stereochemistry was established by comparison of the chemical shift of the methyl group carbon. The major diastereoisomer **(121)** exhibited a resonance at 23.1 ppm, suggesting a *cis* relationship between the methyl group and the equatorial acetyl group at C-5', and was therefore assigned as (4R*, 5R*). The methyl carbon of the minor diastereoisomer **(122)** was observed at 27.0 ppm and was accordingly assigned as (4S*, 5R*).

(123) (124)

The cyclopentanols methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate **(123)** and methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate **(124)** were separated by fractional recrystallization and assigned structures individually.

The major isomer **(123)** was assigned as (4S*, 5R*) on the basis of the chemical shift of the methyl group in the ^{13}C-NMR spectrum. It was observed at 26.2 ppm, considerably downfield from that observed for the methyl signal in the minor isomer **(124)**, which gave rise to a signal at 23.9 ppm and was accordingly assigned as the (4R*, 5S*) isomer. Confirmation of the assignment of the relative stereochemistry of these cyclopentanols came from examination of the ^{1}H-NMR spectra of these compounds combined with difference NOE experiments.

^{1}H-NMR of the major isomer **(123)** revealed two doublet of doublets at 2.95 and 2.74 ppm and a triplet at 3.37 ppm. The two doublets of doublets shared a large geminal coupling (15.8 Hz) and the same vicinal coupling (8.5 Hz) and were easily assigned as H-6. Irradiation of the triplet at 3.37 ppm (H-5) in a difference NOE experiment led to enhancement of the doublet of doublets at 2.74 ppm and the methyl signal singlet at 1.75 ppm, thus establishing a *cis* relationship between these three groups. The bulky ester group at C-5, being the largest substituent on the cyclopentanol ring, would be most stable in an equatorial position. The proton assigned as H-5

would therefore occupy an axial position lying below the plane of the ring. We can therefore assign the doublet of doublets at 2.74 ppm to the proton at H-6 occupying the equatorial position (H-6b), and the doublet of doublets at 2.95 ppm to the hydrogen occupying the axial position above the plane of the ring (H-6a). The methyl group must also adopt an equatorial configuration, leaving the hydroxyl group, which gives rise to a broad singlet at 2.91 ppm, in a axial position lying above the plane of the ring.

Definitive confirmation that protons H-6b, H-5 and the methyl group 4-Me lie in the plane of the ring comes from further NOE experiments. Irradiation of the former led to enhancement of the doublet of doublets at 2.95 ppm (H-6a), as expected for a proton attached to the same carbon, and also the triplet at 3.37 ppm (H-5) and the methyl singlet assigned as 1-Me. An NOE effect was also observed between the methyl group 3-Me and the equatorial methyl group 4-Me, when the latter was irradiated.

A molecular mechanics calculated structure (Figure 4.17) gave intermolecular distances in accord with the NOE effects observed. As for methyl (4S*, 5R*)-4-hydroxy-4-methyl-5,6-dihydro-4H-cyclopenta[d]-thiophene, the cyclopentanol ring is puckered at C-5, pushing the substituents at C-4 and C-6 into pseudo axial and equatorial positions.

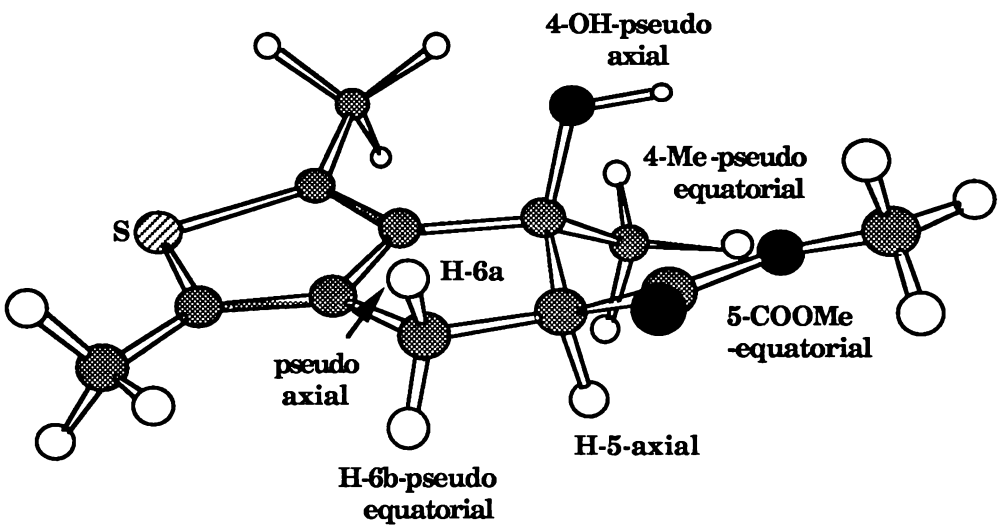


Figure 4.17 Molecular Mechanics Calculated Representation of Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate (123)

^{1}H-NMR of the minor isomer **(124)**, assigned as (4R*, 5R*), displayed a doublet of doublets at 3.49 ppm and a two proton multiplet at 2.74 ppm. The former showed two similar vicinal coupling constants (10.1 Hz, 8.5 Hz) and was therefore assigned as H-5, while we were unable to distinguish between the protons at H-6. Irradiation of the H-5 proton in a NOE experiment led to enhancement of the H-6 multiplet but no enhancement of the 4-Me singlet at 1.37 ppm, suggesting a *trans* relationship between the H-5 and 4-Me groups. An axial configuration for the 4-Me group was further confirmed by the absence of any NOE effects upon irradiation of the aforementioned group. If the methyl group lay in the plane of the ring in an equatorial position we would have expected to observe NOE enhancements of the 3-Me and 5-H groups.

Again a molecular mechanics calculated structure (Figure 4.18) gave intermolecular distances which agreed with the observed NOE effects.

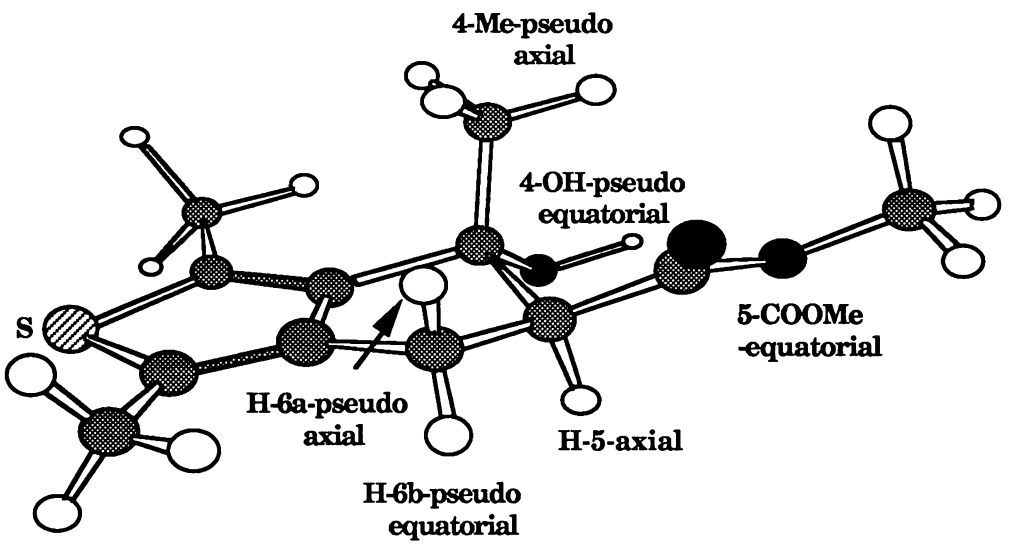


Figure 4.18 Molecular Mechanics Calculated Representation of Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carboxylate (124)

(131) (132)

The major isomer methyl (1S*, 2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate **(131)** was fully characterised and the relative stereochemistry assigned as described for earlier examples. A *trans*

diequatorial relationship between the ester group at C-2 and the methyl group at C-1 was again observed.

Likewise, the relative stereochemistry of the minor isomer methyl (1R*, 2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate **(132)** was established as (1R*, 2R*) indicating a *cis* equatorial axial arrangement between the ester and methyl groups respectively.

(128) (129)

The stereochemistry of the major isomer (4S*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile **(128)** was established as involving a *trans* diequatorial arrangement between the cyano group at C-5 and the methyl group at C-4 (Figure 4.19).

NMR studies of the minor isomer (4R*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile **(129)** confirmed a *cis* equatorial-axial relationship between the cyano group and the methyl group (Figure 4.20).

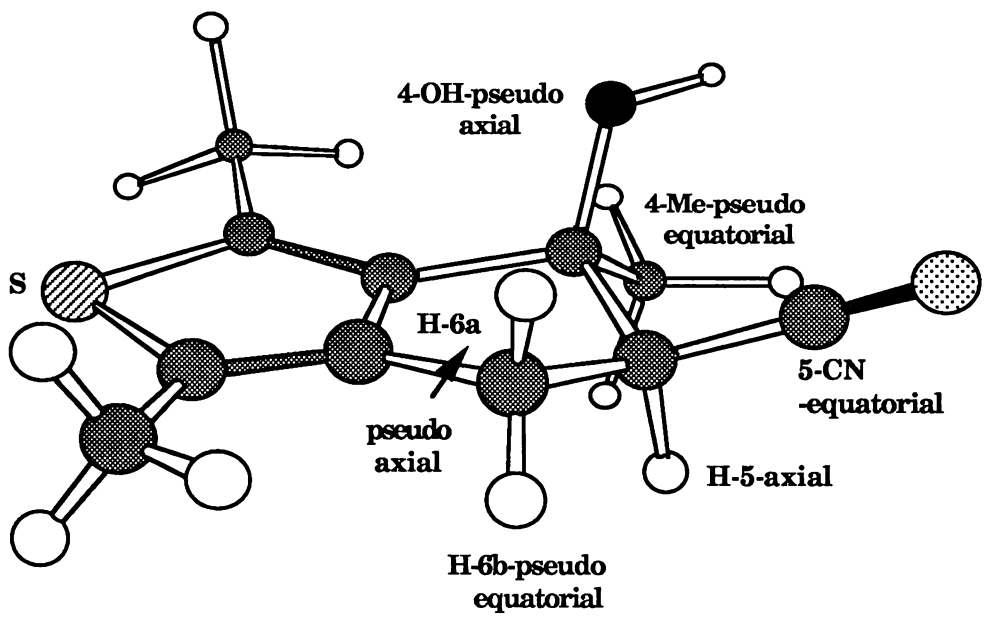


Figure 4.19 Molecular Mechanics Calculated Representation of (4S*, 5S*)-4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile (128)

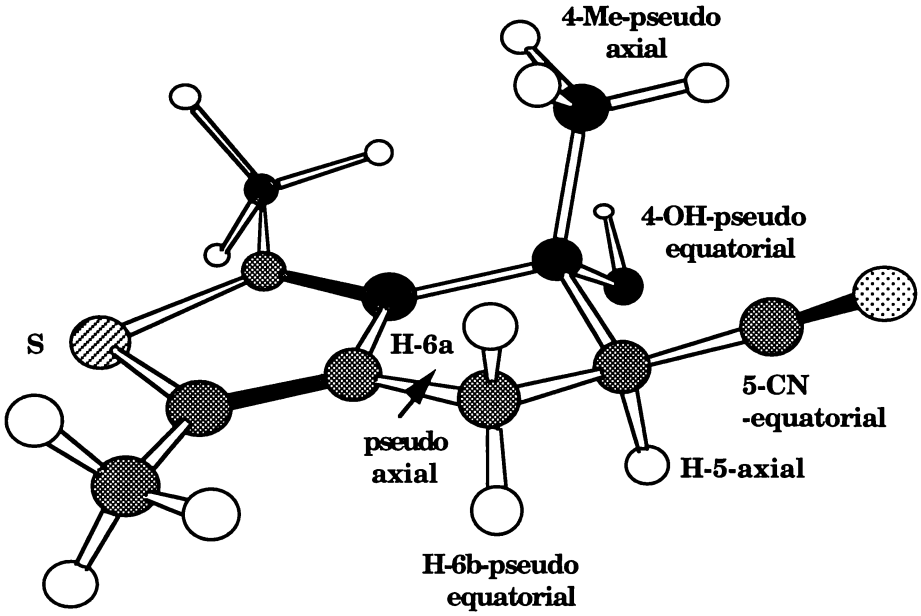


Figure 4.20 Molecular Mechanics Calculated Representation of (4R, 5S*)-4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene-5-carbonitrile (129)*

4.3 X-Ray Crystal Structure of Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate (53)

The X-ray crystal structure of the bicyclic thiophene was determined to examine the geometry of this novel structure which incorporates two fused five-membered rings.

4.3.1 Results of Preliminary Studies

White equidimensional irregular crystals were obtained by recrystallization from hexane at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated monoclinic symmetry with systematic absences appropriate for the space group $P2_1/c$

4.3.2 Data Collection

Intensity data were obtained on a Nicolet R3 four circle diffractometer at -110 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{12}H_{14}O_2S$

M_r=222.3

Crystal class=monoclinic; Space group=$P2_1/c$

a=7.520 (2), b=11.625 (4), c=13.025 (4) Å

β=101.66 (2)°

U=1117.4 $Å^3$

D_{calc}=1.32 g cm^{-3}

Z=4

F(000)=472

μ(Mo-K_α)=2.5 cm^{-1}

A total of 2193 unique reflections was collected by ω-scans in the range $4°<2\theta<52°$, of which 1801 with $I>2\sigma$ were treated as observed.

4.3.3 Solution and Refinement

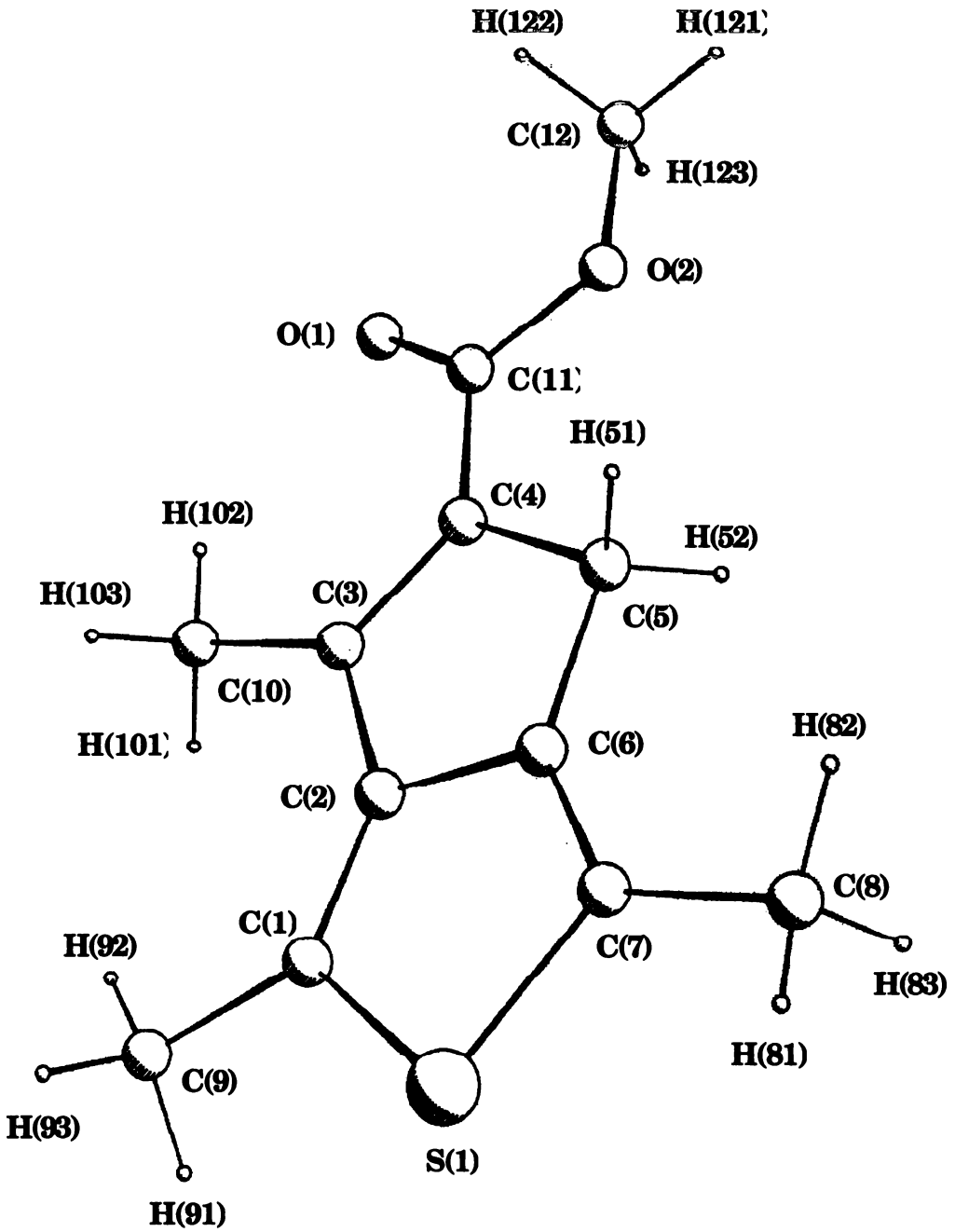
The structure was solved by Patterson methods and routinely developed. In the final cycles of full-matrix least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in their calculated positions with a common isotropic temperature factor for each type.

The refinement converged with R=0.0447, R_w=0.0499 where $w=[\sigma(F)^2 + 0.001F^2]^{-1}$. A final difference map showed no features greater than 0.28 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 4.18 and 4.19. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix VI.

The structure of the bicyclic thiophene derivative is shown in Figure 4.21.

Figure 4.21 Perspective and Side Views of Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate (53)



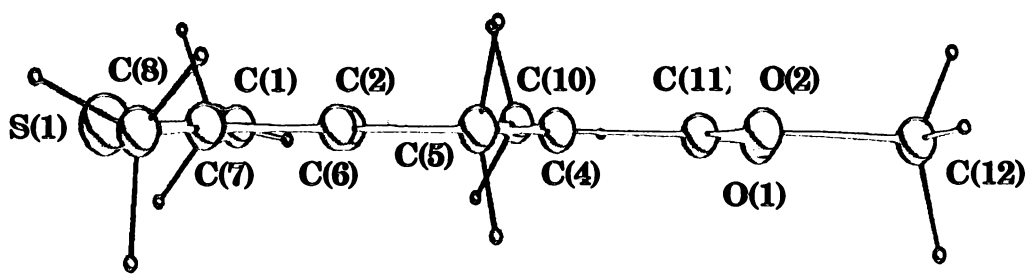


Table 4.18 Bond Lengths (Å) for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate (53)

S(1)	---C(1)	1.736(2)	C(4)	---C(5)	1.521(3)
S(1)	---C(7)	1.740(2)	C(4)	---C(11)	1.463(3)
C(1)	---C(2)	1.366(3)	C(5)	---C(6)	1.492(3)
C(1)	---C(9)	1.501(3)	C(6)	---C(7)	1.358(3)
C(2)	---C(3)	1.460(3)	C(7)	---C(8)	1.500(3)
C(2)	---C(6)	1.431(3)	C(11)	---O(1)	1.211(3)
C(3)	---C(4)	1.361(3)	C(11)	---O(2)	1.343(3)
C(3)	---C(10)	1.495(3)	C(12)	---O(2)	1.441(3)

Table 4.19 Bond Angles (°) for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate (53)

C(1)	-S(1)	-C(7)	94.1(1)	C(5)	-C(4)	-C(11)	122.0(2)
S(1)	-C(1)	-C(2)	108.8(2)	C(4)	-C(5)	-C(6)	101.5(2)
S(1)	-C(1)	-C(9)	119.9(2)	C(2)	-C(6)	-C(5)	109.6(2)
C(2)	-C(1)	-C(9)	131.3(2)	C(2)	-C(6)	-C(7)	114.2(2)
C(1)	-C(2)	-C(3)	137.5(2)	C(5)	-C(6)	-C(7)	136.1(2)
C(1)	-C(2)	-C(6)	114.0(2)	S(1)	-C(7)	-C(6)	108.9(2)
C(3)	-C(2)	-C(6)	108.5(2)	S(1)	-C(7)	-C(8)	122.1(2)
C(2)	-C(3)	-C(4)	107.9(2)	C(6)	-C(7)	-C(8)	128.9(2)
C(2)	-C(3)	-C(10)	124.2(2)	C(4)	-C(11)	-O(1)	126.9(2)
C(4)	-C(3)	-C(10)	127.9(2)	C(4)	-C(11)	-O(2)	111.0(2)
C(3)	-C(4)	-C(5)	112.4(2)	O(1)	-C(11)	-O(2)	122.1(2)
C(3)	-C(4)	-C(11)	125.6(2)	C(11)	-O(2)	-C(12)	116.0(2)

4.3.4 Discussion of the Structure

The molecule is essentially planar with no non-H atom more than 0.07 (1) Å from the least squares plane. This planarity has forced a narrow angle C(4)-C(5)-C(6) of 101.5(2)° at the formally sp^3 C(5) but allows delocalised π-bonding to extend from the thiophene ring over the enone part of the molecule (i.e. over C(2), C(3), C(4), C(11), O(1)) as shown by short C(2)-C(3) and C(4)-C(11) bonds. The strain of fusing the two small rings together is manifestated by C(1)-C(2)-C(3) and C(5)-C(6)-C(7) angles of 137.5(2)° and 136.1(2)° respectively, while the methyl groups at the 2,5 positions of the thiophene ring are displaced towards the S atom to give C(2)-C(1)-C(9) and C(6)-C(7)-C(8) angles of *ca* 130° presumably to lower steric interactions between all four substituents on the thiophene carbon atoms.

4.4 Experimental Section

4.4.1 Preparation of Starting Materials

Preparation of 4-Acetyl-2,5-dimethylthien-3-ylmercury(II) chloride (112)

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 461 mg, 1.44 mmol] and $HgCl_2$ (429 mg, 1.58 mmol) were added to nitrogen-saturated methanol (15 ml) and the solution refluxed for two hours. After cooling, the white precipitate was collected by filtration, washed with cold methanol, and air dried to give *4-acetyl-2,5-dimethylthien-3-ylmercury(II) chloride* [**(112)**; 442 mg, 79 %], m.p. 198-200 °C. Anal. Found: C, 24.43; H, 2.56 %; $C_8H_9ClHgOS$ calcd: C, 24.88; H, 2.33 %. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 2.51 (3H, *s*, $-CH_3$), 2.30 (3H, *s*, $-CH_3$), 2.24 (3H, *s*, $-CH_3$). ^{13}C NMR: (22.50 MHz) (10 % C_5D_5N in $CDCl_3$) δ 194.3 (*s*, 4-$\underline{C}OCH_3$), 147.3 (*s*), 146.6 (*s*), 142.1 (*s*), 139.8 (*s*), 30.2 (*q*, 4-CO$\underline{C}H_3$), 18.4 (*q*, 2-CH_3), 17.1 (*q*, 5-CH_3). ^{199}Hg NMR: (Jeol) ($CDCl_3$) δ -1066.0 ppm.

Preparation of *fac*-η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tricarbonyl-(trimethylphosphite)manganese (144)

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 214 mg, 0.67 mmol] and $P(OMe)_3$ (0.08 ml, 0.67 mmol) were added to nitrogen-saturated heptane (20 ml). The solution was refluxed for 1.5 h and the

heptane was removed under vacuum. The orange residue was chromatographed (p.l.c., 1:8 diethyl ether/petroleum spirit) to yield two main bands.

The band at highest R_f was unreacted orthomanganated starting material [**(41)**; 5 mg, 2 %]. IR: ($CHCl_3$) ν(CO) 2081 (m), 1997 (s), 1935 (s) cm^{-1}.

The main band was *fac-η²-(4-acetyl-2,5-dimethylthien-3-yl)tricarbonyl-(trimethylphosphite)manganese* [**(144)**; 230 mg, 83 %]. Recrystallization from hexane/diethyl ether 20:1 gave orange-yellow prismatic crystals, m.p. 86-88 °C. Anal. Found: C, 40.44; H, 4.48 %; $C_{14}H_{18}O_7MnPS$ calcd: C, 40.40; H, 4.36 %. IR: (heptane) ν(CO) 2022 (s), 1946 (s), 1903 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 3.49 (9H, *d*, $^3J_{HP}$=10.5 Hz, -OCH_3), 2.70 (3H, *s*, *br*, 5-CH_3), 2.50 (3H, *d*, $^5J_{HP}$=2.4 Hz, 2-CH_3), 2.46 (3H, *d*, $^6J_{HP}$=1.9 Hz, 4-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 225.9 (*d*, $^2J_{CP}$=37.7 Hz, C≡O), 217.5 (*d*, $^2J_{CP}$=25.3 Hz, C≡O), 216.4 (*d*, $^2J_{CP}$=47.2 Hz, C≡O), 204.3 (*d*, $^4J_{CP}$=2.1 Hz, 4-$\underline{C}OCH_3$), 173.7 (*d*, $^2J_{CP}$=32.7 Hz, C-3), 149.0 (*s*, C-5), 147.9 (*s*, C-4),133.1 (*d*, $^3J_{CP}$=3.8 Hz, C-2), 51.6 (*d*, $^2J_{CP}$=4.8 Hz, -OCH_3), 27.1 (*q*, 4-$CO\underline{C}H_3$), 16.9 (*q*, 2-CH_3), 15.4 (*q*, 5-CH_3). ^{31}P NMR: (Jeol) ($CDCl_3$) δ 171.2. FAB MS: (m/e) 624 (3.7, P^++208, P^++$P(OCH_3)_3(CO)_2$), 596 (24.1, P^++180, P^++$P(OCH_3)_3(CO)_2$), 540 (20.4, P^++124, P^++$P(OCH_3)_3$), 416 (22.2, P^+), 332 (100.0, P^+-84, P^+-$(CO)_3$), 208 (38.9, P^+-208, P^+-$P(OCH_3)_3(CO)_3$).

Preparation of η²-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese (145)

η²-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 242 mg, 0.76 mmol] and $P(OMe)_3$ (0.18 ml, 1.51 mmol) were added to nitrogen-saturated heptane (20 ml). The solution was refluxed for 1 h and the heptane was removed under vacuum. The resulting red/orange residue was chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) and the plate was developed several times to achieve separation.

The band at highest R_f was *fac*-η²-(4-acetyl-2,5-dimethylthien-3-yl)tricarbonyl(trimethylphosphite)manganese [**(144)**; 12 mg, 4 %]. IR: ($CHCl_3$) ν(CO) 2018 (s, br), 1939 (s, vbr), 1897 (s, br) cm^{-1}.

The major component was *η²-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese* [**(145)**; 338 mg, 87 %]. It was recrystallized from hexane/chloroform to give red crystals, m.p.

157.5-158 °C. Anal. Found: C, 37.56; H, 5.36 %; $C_{16}H_{27}O_9MnP_2S$ calcd: C, 37.51; H, 5.31 %. IR: ($CHCl_3$) ν(CO) 1937 (s, br), 1854 (s, br) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 3.48 (18H, *t*, J=5.2 Hz, $-OCH_3$), 2.69 (3H, *s, br*, 5-CH_3), 2.55 (3H, *t*, $^5J_{HP}$=2.3 Hz, 2-CH_3), 2.44 (3H, *t*, $^6J_{HP}$=2.1 Hz, 4-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 229.4 (*t*, $^2J_{CP}$=36.0 Hz, C≡O), 220.9 (*t*, $^2J_{CP}$=27.5 Hz, C≡O), 203.0 (*s*, 4-$\underline{C}OCH_3$), 179.6 (*t*, $^2J_{CP}$=33 Hz, C-3), 148.5 (*s*, C-4), 147.1 (*s*, C-5), 132.3 (*s*, C-2), 51.3 (*q*, $-OCH_3$), 26.9 (*q*, 4-$CO\underline{C}H_3$), 17.3 (*q*, 2-CH_3), 15.3 (*q*, 5-CH_3). ^{31}P NMR: (Jeol) ($CDCl_3$) δ 181.2. FAB MS: (m/e) 720 (1.8, P^++208, P^++$P(OCH_3)_3(CO)_3$), 596 (1.8, P^++84, P^++$(CO)_3$), 540 (3.6, P^++28, P^++CO), 512 (7.3, P^+), 481 (3.6, P^+-31, P^+-OCH_3), 456 (7.3, P^+-56, P^+-$(CO)_2$), 425 (7.3, P^+-87, P^+-$OCH_3(CO)_2$), 332 (100.0, P^+-180, P^+-$P(OCH_3)_3(CO)_2$), 208 (38.9, P^+-304, P^+-$(P(OCH_3)_3)_2(CO)_2$).

Preparation of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(η^1-dppm)-manganese (146)

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [(**41**); 415 mg, 1.30 mmol] and bis(diphenylphosphino)methane (dppm) (498 mg, 1.30 mmol) were added to nitrogen-saturated heptane (40 ml). After five hours at reflux, infrared spectroscopy of the reaction solution showed three bands in the metal carbonyl region consistent with a tricarbonyl species. IR: (hexane) ν(CO) 2011 (s), 1942 (s), 1890 (s) cm^{-1}. A further quantity of dppm was added (415 mg, 1.30 mmol) and the solution was refluxed overnight to give a red-orange crystalline precipitate. The precipitate was collected and recrystallized from chloroform/petroleum spirit to afford red-orange crystals of *η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(η^1-dppm)manganese* [(**146**); 950 mg, 71 %], m.p. 156.5-162 °C. Anal. Found: C, 69.77; H, 5.17 %; $C_{60}H_{53}O_3MnP_4S$ calcd: C, 69.57; H, 5.17 %. IR: ($CHCl_3$) ν(CO) 1915 (s, br), 1819 (s, br) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.66-6.86 (40H, *m*, Ar-H dppm), 3.19 (2H, *dd*, J=15.6 Hz, J=3.0 Hz, $-CH_2$ dppm), 2.99 (2H, *ddd*, J=15.6 Hz, J=3.7 Hz, J=3.5 Hz, $-CH_2$ dppm), 2.42 (3H, *t*, J=2.7 Hz, $-CH_3$), 2.16 (3H, *s*, $-CH_3$), 0.96 (3H, *t*, J=1.9 Hz, $-CH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 235.0 (*t*, $^2J_{CP}$=24.9 Hz, C≡O), 226.6 (*t*, $^2J_{CP}$=17.6 Hz, C≡O), 201.0 (*s*, 4-$\underline{C}OCH_3$), 187.6 (*t*, $^2J_{CP}$=23.6 Hz, C-3), 149.4 (*s*, C-4), 146.1 (*s*, C-5), 141.1-127.1 (*m*, dppm, C-2), 27.8 (*t*, J=10.4 Hz, $-CH_2$ dppm), 27.4 (*t*, J=10.4 Hz, $-CH_2$ dppm), 25.5 (*q*, 4-$CO\underline{C}H_3$), 18.3 (*q*, 2-CH_3), 14.8 (*q*, 5-CH_3). ^{31}P NMR: (Jeol) ($CDCl_3$) δ 69.7 (*m*), -26.7 (*m*). FAB MS: (m/e) 1033 (weak, P^+), 593 (100, P^+-440, P^+-$(CO)_2$dppm).

Preparation of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)dicarbonyl-bis(trimethylphosphite)manganese (147)

η^2-(6-Acetyl-2,3,4-trimethoxphenyl)tetracarbonylmanganese [(34); 287 mg, 0.76 mmol] and $P(OMe)_3$ (0.58 ml, 4.92 mmol) were added to nitrogen-saturated heptane (20 ml) and refluxed overnight. The heptane was removed under vacuum and the resulting red-orange residue was chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to yield two bands.

The band at highest R_f was *fac*-η^2-(6-acetyl-2,3,4-trimethoxyphenyl)-tricarbonyl(trimethylphosphite)manganese [(148); 55 mg, 15 %]. Recrystallization from hexane/chloroform gave yellow feathers, m.p. 84-86.5 °C. Anal. Found: C, 42.70; H, 4.74 %; $C_{17}H_{22}O_{10}MnP_2$ calcd: C, 43.24; H, 4.70 %. IR: (hexane) ν(CO) 2021 (s), 1945 (s), 1913 (s) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.18 (1H, *s*, H-5), 4.00 (3H, *s*, 2-OCH_3), 3.92 (3H, *s*, 3-OCH_3), 3.87 (3H, *s*, 4-OCH_3), 3.49 (9H, *t*, J_{HP}=10.7 Hz, -OCH_3), 2.52 (3H, *t*, J_{HP}=2.9 Hz, 6-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 224.1 (*d*, $^2J_{CP}$=40.3 Hz, C≡O), 217.6 (*d*, $^2J_{CP}$=25.1 Hz, C≡O), 216.1 (*d*, $^2J_{CP}$=40.6 Hz, C≡O), 212.0 (*d*, J_{CP}=3.1 Hz, 6-$\underline{C}OCH_3$), 185.8 (*d*, $^2J_{CP}$=31 3 Hz, C-1), 160.9 (*d*, $^3J_{CP}$=1.8 Hz, C-2), 150.5 (*s*, C-4), 147.7 (*d*, $^4J_{CP}$=1.8 Hz, C-3), 139.4 (*s*, C-6), 110.4 (*d*, C-5), 60.6 (*q*, 2-OCH_3), 59.9 (*q*, 3-OCH_3), 56.2 (*q*, 4-OCH_3), 51.7 (*d*, $^2J_{CP}$=4.7 Hz, -OCH_3), 24.4 (*d*, J_{CP}=1.5 Hz, 6-$CO\underline{C}H_3$). ^{31}P NMR: (Jeol) ($CDCl_3$) δ 171.3.

The major component was *η^2-(6-acetyl-2,3,4-trimethoxyphenyl)dicarbonyl-bis(trimethylphosphite)manganese* [(147); 341 mg, 79 %]. Recrystallization from hexane/chloroform afforded chunky red crystals, m.p. 107-108.5 °C. Anal. Found: C, 40.13; H, 5.23 %; $C_{19}H_{31}O_{12}MnP_2$ calcd: C, 40.15; H, 5.50 %. IR: ($CHCl_3$) ν(CO) 1942 (s, br), 1862 (s, br) cm^{-1}. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.10 (1H, *s*, H-5), 3.96 (3H, *s*, 2-OCH_3), 3.91 (3H, *s*, 3-OCH_3), 3.82 (3H, *s*, 4-OCH_3), 3.43 (18H, *t*, J_{HP}=5.3 Hz, -OCH_3), 2.48 (3H, *t*, J_{HP}=3.1 Hz, 6-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 227.7 (*t*, $^2J_{CP}$=34.9 Hz, C≡O), 221.1 (*t*, $^2J_{CP}$=27.8 Hz, C≡O), 209.5 (*t*, J_{CP}=3.2 Hz, 6-$\underline{C}OCH_3$), 194.4 (*t*, $^2J_{CP}$=30 1 Hz, C-1), 161.8 (*s*, C-2), 149.9 (*s*, C-4),146.2 (*s*, C-3), 139.2 (*s*, C-6), 109.0 (*d*, C-5), 60.1 (*q*, 2-OCH_3), 59.4 (*q*, 3-OCH_3), 56.0 (*q*, 4-OCH_3), 51.3 (*q*, -OCH_3), 24.1 (*q*, 6-$CO\underline{C}H_3$). ^{31}P NMR: (Jeol) ($CDCl_3$) δ 181.0.

4.4.2 General Procedures for Reactions of Alkenes with Orthomanganated Compounds in the Presence of Li_2PdCl_4

$PdCl_2$ (1 mol equivalent) and LiCl (2-4 mol equivalent) were stirred in dry solvent (10 ml) for 3 hours to solubilise the $PdCl_2$ as Li_2PdCl_4. The alkene (5 mol equivalent) and the orthomanganated complex (1 mol equivalent) were added and the mixture stirred at ambient temperature or refluxed as appropriate for 30 min to several days. Upon reaction the solution turned black with the precipitation of palladium metal. The mixture was filtered to remove metal, the filtrate run through a short silica column and the solvent evaporated. The residue was chromatographed on a silica layer (400 x 200 x 2 mm) using either diethyl ether/petroleum spirit or ethyl acetate/petroleum spirit as eluant; products are reported in order of increasing polarity.

4.4.3 Coupling Reactions of η^2-(2-Acetylthien-3-yl)-tetracarbonylmanganese (40) with Li_2PdCl_4 and Alkenes to Explore Reaction Conditions and Product Ratios

4.4.3.1 Effect of Temperature

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Acetonitrile at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (116 mg, 2.7 mmol) in dry acetonitrile (10 ml) were treated with methyl vinyl ketone (0.29 ml, 3.4 mmol) and the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol]. The mixture was stirred at ambient temperature for 1.5 h, and the solution worked up by the normal method and chromatographed (p.l.c., 1:3 ethyl acetate/petroleum spirit).

4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 75 mg, 56 %], a colourless oil which after recrystallization from hexane gave white prismatic crystals, m.p. 36-37.5 °C. Anal. Found: C, 61.34; H, 6.44 %; $C_{10}H_{12}O_2S$ calcd: C, 61.20; H, 6.16 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.34 (1H, *d*, $^3J_{5',4'}$=5.0 Hz, H-5'), 6.94 (1H, *d*, $^3J_{4',5'}$=5.0 Hz, H-4'), 3.15 (2H, *t*, $^3J_{4,3}$=7.4 Hz, H-4), 2.70 (2H, *t*, $^3J_{3,4}$=7.4 Hz, H-3), 2.45 (3H, *s*, 2'-$COCH_3$), 2.06 (3H, *s*, H-1).^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 207.8 (*s*, C-2), 190.8 (*s*, 2'-$\underline{C}OCH_3$), 148.7 (*s*, C-

3'), 135.5 (*s*, C-2'), 132.1 (*d*, C-4'), 129.8 (*d*, C-5'), 43.5 (*t*, C-3), 29.8 (*q*, C-1), 29.6 (*q*, 2'-CO$\underline{C}H_3$), 24.5 (*t*, C-4). MS m/e 196 (P^+).

E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 52 mg, 39 %], a white solid which after recrystallization from hexane gave white needles, m.p. 96-96.5 °C. Anal. Found: C, 62.08; H, 5.42 %; $C_{10}H_{10}O_2S$ calcd: C, 61.83; H, 5.19 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.41 (1H, *d*, $^3J_{4,3}$=16.7 Hz, H-4), 7.48 (1H, *d*, $^3J_{5',4'}$=5.2 Hz, H-5'), 7.39 (1H, *d*, $^3J_{4',5'}$=5.2 Hz, H-4'), 6.56 (1H, *d*, $^3J_{3,4}$=16.7 Hz, H-3), 2.58 (3H, *s*, 2'-$COCH_3$), 2.41 (3H, *s*, H-1). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 199.5 (*s*, C-2), 191.2 (*s*, 2'-$\underline{C}OCH_3$), 141.5 (*s*, C-3'), 138.9 (*s*, C-2'), 136.8 (*d*, C-4), 131.8 (*d*, C-3), 130.2 (*d*, C-5'), 127.6 (*d*, C-4'), 30.1 (*q*, 2'-CO$\underline{C}H_3$), 26.4 (*q*, C-1). MS m/e 194 (P^+).

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

The reaction was repeated using identical mole ratios of all reactants, whereupon it was refluxed for 5 hours. Work up by the normal method and chromatography (p.l.c., 1:5 diethyl ether/petroleum spirit) gave rise to two major bands plus several trace bands at higher R_f which were not pursued.

4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 80 mg, 60 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 27 mg, 20 %]

4.4.3.2 Order of Mixing of Reactants

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

In two separate experiments $PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry methanol (10 ml) were treated with: (i) methyl vinyl ketone (0.29 ml, 3.4 mmol) followed by the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] and (ii) the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] followed by methyl vinyl ketone (0.29 ml, 3.4 mmol). Both mixtures were stirred at ambient temperature for 30 minutes, and the solutions worked up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit). Products obtained were as follows:

(i)
The parent ketone 2-acetylthiophene [**(52)**; 5 mg, 6 %]
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 88 mg, 66 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 32 mg, 24 %]

(ii)
The parent ketone 2-acetylthiophene [**(52)**; 9 mg, 10 %]
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 74 mg, 55 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 43 mg, 32 %]

4.4.3.3 The Importance of Dry Solvent

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry methanol (10 ml) were treated with the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] and methyl vinyl ketone (0.29 ml, 3.4 mmol) followed by the addition of H_2O (0.3 ml). The mixture was stirred at ambient temperature for 3 hours, and the solution worked up by the normal method, dried over $MgSO_4$ and chromatographed (p.l.c, 1:10 diethyl ether/petroleum spirit) to give:

The parent ketone 2-acetylthiophene [**(52)**; 12 mg, 14 %]
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 102 mg, 76 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 10 mg, 8 %]

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] and methyl acrylate (0.31 ml, 3.4 mmol) followed by the addition of H_2O (0.3 ml). The mixture was refluxed for 3 hours, and the solution worked up by the normal method, dried over $MgSO_4$ and chromatographed (p.l.c, 1:10 diethyl ether/petroleum spirit) to give:

The parent ketone 2-acetylthiophene [**(52)**: 12 mg, 14 %]

Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 98 mg, 67 %], a white solid which after recrystallization from hexane gave white plates, m.p. 37.5-38 °C. Anal. Found: C, 56.67; H, 5.96 %; $C_{10}H_{12}O_3S$ calcd: C, 56.58; H, 5.70 %. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 7.41 (1H, *d*, $^3J_{5',4'}$=5.0 Hz, H-5'), 7.02 (1H, *d*, $^3J_{4',5'}$=5.0 Hz, H-4'), 3.66 (3H, *s*, 1-OCH_3), 3.30 (2H, *t*, $^3J_{3,2}$=7.3 Hz, H-3), 2.65 (2H, *t*, $^3J_{2,3}$=7.3 Hz, H-2), 2.54 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 190.9 (*s*, 2'-$\underline{C}OCH_3$), 173.4 (*s*, C-1), 148.0 (*s*, C-3'), 135.8 (*s*, C-2'), 131.8 (*d*, C-4'), 129.8 (*d*, C-5'), 51.6 (*q*, 1-OCH_3), 34.0 (*t*, C-2), 29.7 (*q*, 2'-CO$\underline{C}H_3$), 25.6 (*t*, C-3). MS m/e 212 (P^+).

Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 18 mg, 13 %] a white solid which after recrystallization from hexane gave white prismatic crystals, m.p. 103-103.5 °C. Anal. Found: C, 57.35; H, 5.13 %; $C_{10}H_{10}O_3S$ calcd: C, 57.12; H, 4.79 %. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 8.46 (1H, *d*, $^3J_{3,2}$=16.1 Hz, H-3), 7.48 (1H, *d*, $^3J_{5',4'}$=5.3 Hz, H-5'), 7.37 (1H, *d*, $^3J_{4',5'}$=5.3 Hz, H-4'), 6.37 (1H, *d*, $^3J_{2,3}$=16.1 Hz, H-2), 2.58 (3H, *s*, 2'-$COCH_3$), 3.81 (3H, *s*, 1-OCH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 190.8 (*s*, 2'-$\underline{C}OCH_3$), 167.0 (*s*, C-1), 140.8 (*s*, C-3'), 139.2 (*s*, C-2'), 137.5 (*d*, C-3), 130.1 (*d*, C-5'), 127.7 (*d*, C-4'), 122.3 (*d*, C-2), 51.8 (*q*, 1-OCH_3), 30.1 (*q*, 2'-CO$\underline{C}H_3$). MS m/e 210 (P^+).

4.4.3.4 Do Reactions Need to be Carried Out Under a Nitrogen Environment?

These reactions were not performed under a nitrogen atmosphere. Moisture was excluded by the use of a $CaCl_2$ drying tube.

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (91 mg, 0.51 mmol) and LiCl (44 mg, 1.03 mmol) in dry methanol (10 ml) were treated with the orthomanganated thiophene [**(40)**; 150 mg, 0.51 mmol] and methyl vinyl ketone (0.21 ml, 2.57 mmol). The mixture was stirred at ambient temperature for 5 h, worked up by the standard method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 68 mg, 67 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 26 mg, 26 %]

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (91 mg, 0.51 mmol) and LiCl (44 mg, 1.03 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated thiophene [**(40)**; 150 mg, 0.51 mmol) and methyl acrylate (0.23 ml, 2.57 mmol). The mixture was reluxed for 3 h, worked up by the standard method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

The parent ketone 2-acetylthiophene [**(52)**; 2 mg, 3 %]
Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 12 mg, 11 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 70 mg, 65 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated thiophene [**(41)**; 135 mg, 0.42 mmol) and methyl acrylate (0.19 ml, 2.11 mmol). The mixture was reluxed for 3 h, worked up by the standard method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 21 mg, 22 %], was recrystallized from hexane/chloroform as white needles, m.p. 80-81.5 °C. Anal. Found: C, 65.03; H, 6.06 %; $C_{12}H_{14}O_2S$ calcd: C, 64.84; H, 6.35 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.78 (3H, *s*, 5-$COOCH_3$), 3.23 (2H, *s*, br, H-4), 2.54 (6H, *m*, 1,6-CH_3), 2.31 (3H, *s*, br, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 167.0 (*s*, 5-$\underline{C}OOCH_3$), 149.2 (*s*, C-6), 146.2 (*s*, C-6a), 141.1 (*s*, C-3a), 132.2 (*s*, C-5), 128.0 (*s*, C-1), 125.0 (*s*, C-3), 51.1 (*q*, 5-COO$\underline{C}H_3$), 31.5 (*t*, C-4), 14.0 (*q*, 6-CH_3), 13.1 (*q*, 1-CH_3), 13.0 (*q*, 3-CH_3). MS m/e 222 (P^+).

The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 3 mg, 5 %]

Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 60 mg, 60 %] was recrystallized from petroleum spirit as prismatic white crystals, m.p. 30-31.5 °C. Anal. Found: C, 60.61; H, 6.12 %; $C_{12}H_{14}O_3S$ calcd: C, 60.48; H, 5.92 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.67 (1H, *d*, $^3J_{3,2}$=16.1 Hz, H-3), 5.89 (1H, *d*, $^3J_{2,3}$=16.1 Hz, H-2), 3.77 (3H, *s*, 1-OCH_3),

2.46 (3H, *s*, -CH_3), 2.43 (3H, *s*, -CH_3), 2.41 (3H, *s*, -CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 198.7 (*s*, 4'-$\underline{C}OCH_3$), 167.2 (*s*, C-1), 139.9 (*s*), 139.2 (*s*), 138.2 (*d*, C-3), 137.6 (*s*), 131.7 (*s*), 120.6 (*d*, C-2), 51.7 (*q*, 1-OCH_3), 31.7 (*q*, 4'-$CO\underline{C}H_3$), 14.8 (*q*, -CH_3), 14.2 (*q*, -CH_3). MS m/e 238 (P^+).

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (124 mg, 0.70 mmol) and LiCl (59 mg, 1.40 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated ketone [(**2**); 200 mg, 0.70 mmol] and methyl acrylate (0.32 ml, 3.50 mmol). The mixture was reluxed for 3 h, worked up by the standard method and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl (3-methylinden-2-yl)-carboxylate [(**60**); 12 mg, 9 %] was recrystallized from hexane as white feathers, m.p. 63.5-65 °C. Anal. Found: C, 76.80; H, 6.22 %; $C_{12}H_{12}O_2$ calcd: C, 76.57; H, 6.43 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.52-7.47 (2H, *m*, H-4,7), 7.37-7.35 (2H, *m*, H-5,6), 3.84 (3H, *s*, 2-$COOCH_3$), 3.65 (2H, *q*, $^5J_{1,3\text{-}CH_3}$=2.3 Hz, H-1), 2.56 (3H, *t*, $^5J_{3\text{-}CH_3,1}$=2.3 Hz, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 166.4 (*s*, 2-$\underline{C}OOCH_3$), 151.8 (*s*, C-3), 145.3 (*s*, C-3a), 143.5 (*s*, C-7a), 129.5 (*s*, C-2), 127.8 (*d*, C-6), 126.6 (*d*, C-5), 124.0 (*d*, C-7), 121.2 (*d*, C-4), 51.2 (*q*, 2-$COO\underline{C}H_3$), 38.8 (*t*, C-1), 12.4 (*q*, 3-CH_3). MS m/e 188 (P^+).

The parent ketone acetophenone [(**59**);12 mg, 14 %]

Methyl 3-(2-acetylphenyl)-propanoate [(**57**); 22 mg, 15 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 7.70 (1H, *m*, H-3'), 7.32 (3H, *m*, H-4',5',6'), 3.65 (3H, *s*, 1-OCH_3), 3.17 (2H, *t*, $^3J_{3,2}$=7.6 Hz, H-3), 2.64 (2H, *t*, $^3J_{2,3}$=7.6 Hz, H-2), 2.59 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 201.5 (*s*, 2'-$\underline{C}OCH_3$), 173.4 (*s*, C-1), 141.0 (*s*, C-1'), 137.8 (*s*, C-2'), 131.7 (*d*, C-4'), 131.5 (*d*, C-5'), 129.6 (*d*, C-3'), 126.5 (*d*, C-6'), 51.4 (*q*, 1-OCH_3), 35.7 (*t*, C-2), 29.6 (*t*, C-3), 29.6 (*q*, 2'-$CO\underline{C}H_3$). MS m/e 206 (P^+).

Methyl E-3-(2-acetylphenyl)-prop-2-enoate [(**58**); 63 mg, 44 %] was recrystallized from hexane as prismatic white crystals, m.p. 34.5-35 °C. Anal. Found: C, 70.49; H, 5.92 %; $C_{12}H_{12}O_3$ calcd: C, 70.58; H, 5.92 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 8.15 (1H, *d*, $^3J_{3,2}$=15.9 Hz, H-3), 7.74 (1H, *dd*, $^3J_{3',4'}$=7.4 Hz, $^4J_{3',5'}$=1.6 Hz, H-3'), 7.59 (1H, *dd*, $^3J_{6',5'}$=7.4 Hz, $^4J_{6',4'}$=1.6

Hz, H-6'), 7.52 (1H, *td*, $^3J_{4',3'}$=$^3J_{4',5'}$=7.4 Hz, $^4J_{4',6'}$=1.6 Hz, H-4'), 7.46 (1H, *td*, $^3J_{5',4'}$=$^3J_{5',6'}$=7.4 Hz, $^4J_{5',3'}$=1.6 Hz, H-5'), 6.28 (1H, *d*, $^3J_{2,3}$=15.9 Hz, H-2), 3.81 (3H, *s*, 1-OCH_3), 2.62 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 200.8 (*s*, 2'-$\underline{C}OCH_3$), 167.0 (*s*, C-1), 144.2 (*d*, C-3), 138.3 (*s*, C-1'), 134.9 (*s*, C-2'), 132.0 (*d*, C-4'), 129.5 (*d*, C-5'), 129.3 (*d*, C-3'), 128.4 (*d*, C-6'), 120.6 (*d*, C-2), 51.8 (*q*, 1-OCH_3), 29.3 (*q*, 2'-$CO\underline{C}H_3$). MS m/e 204 (P^+).

4.4.3.5 Workup Method

Reaction of η²-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry methanol (10 ml) were treated with methyl vinyl ketone (0.29 ml, 3.4 mmol) and the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol]. The mixture was stirred at ambient temperature for 5 hours, and the solution poured into a separating funnel containing H_2O (100 ml)/diethyl ether (40 ml), and further extracted with diethyl ether (2 x 30 ml). The ethereal solution was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a pale brown oil. The oil was dissolved in dichloromethane and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 72 mg, 54 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 28 mg, 21 %]

4.4.3.6 Solvent Efects

Reaction of η²-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Vinyl Ketone in a Range of Solvents at Ambient Temperature

In four separate experiments $PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry solvent (10 ml) [(i) methanol, (ii) acetonitrile, (iii) tetrahydrofuran and (iv) acetone] were treated with the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] and methyl vinyl ketone (0.29 ml, 3.4 mmol). All four mixtures were stirred at ambient temperature for 5 hours, and the solutions worked up by the normal method and

chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit). Products were as follows:

(i) Methanol
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 83 mg, 66 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 32 mg, 26 %]

(ii) Acetonitrile
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 67 mg, 61 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 35 mg, 32 %]

(iii) Tetrahydrofuran
The parent ketone 2-acetylthiophene [**(52)**; 6 mg, 7 %]
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 44 mg, 33 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 61 mg, 46 %]

(iv) Acetone
4-(2-Acetylthien-3-yl)-butan-2-one [**(50)**; 72 mg, 60 %]
E-4-(2-Acetylthien-3-yl)-but-3-en-2-one [**(48)**; 39 mg, 33 %]

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Acrylate in a Range of Solvents at Ambient Temperature

In four separate experiments $PdCl_2$ (121 mg, 0.69 mmol) and LiCl (58 mg, 1.4 mmol) in dry solvent (10 ml) [(i) methanol, (ii) acetonitrile, (iii) tetrahydrofuran and (iv) acetone] were treated with the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol] and methyl acrylate (0.31 ml, 3.4 mmol). Solutions (i) and (iv) were stirred at ambient temperature for 5 hours. However solutions (ii) and (iii) showed no signs of Pd precipitation after 90 minutes stirring and were refluxed for 3 hours. Pd precipitation was immediate. All four mixtures were worked up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit). Products were as follows:

(i) Methanol
Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 10 mg, 7 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 104 mg, 72 %]

(ii) Acetonitrile

The parent ketone 2-acetylthiophene [**(52)**; 4 mg, 5 %]
Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 39 mg, 27 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 95 mg, 66 %]

(iii) Tetrahydrofuran

Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 27 mg, 19 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 89 mg, 62 %]

(iv) Acetone

Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 28 mg, 19 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 54 mg, 38 %]

4.4.3.7 Other Alkenes

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Acrylonitrile in Methanol at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (116 mg, 2.7 mmol) in dry methanol (10 ml) were treated with acrylonitrile (0.23 ml, 3.4 mmol) and the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol]. The mixture was stirred at ambient temperature overnight, and the solution worked up by the normal method and chromatographed (p.l.c., 1:4 ethyl acetate/petroleum spirit) to give:

The parent ketone 2-acetylthiophene [**(52)**; 18 mg, 9 %]

Z-3-(2-Acetylthien-3-yl)-prop-2-enenitrile [**(61)**; 28 mg, 23 %], a colourless oil which after crystallization from hexane/chloroform gave white needles of m.p. 129-132 °C. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 8.09 (1H, *d*, $^3J_{3,2}$=12.2 Hz, H-3), 8.07 (1H, *d*, $^3J_{4',5'}$=5.3 Hz, H-4'*), 7.57 (1H, *d*, $^3J_{5',4'}$=5.3 Hz, H-5'*), 5.56 (1H, *d*, $^3J_{2,3}$=12.2 Hz, H-2), 2.59 (3H, *s*, 2'-$COCH_3$).^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 190.9 (*s*, 2'-$\underline{C}OCH_3$), 142.3 (*d*, C-3), 139.8 (*s*, C-3'*), 139.3 (*s*, C-2'*), 130.2 (*d*, C-5'), 128.8 (*d*, C-4'), 117.2 (*s*, C-1), 97.9 (*d*, C-2), 29.9 (*q*, 2'-CO$\underline{C}H_3$). MS m/e 177 (P^+).

E-3-(2-Acetylthien-3-yl)-prop-2-enenitrile [**(62)**; 50 mg, 41 %], a white solid which was recrystallized from hexane/chloroform to give white needles, m.p. 130.5-133 °C. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 8.33 (1H, *d*, $^3J_{3,2}$=16.6

Hz, H-3), 7.54 (1H, *d*, $^3J_{5',4'}$=4.8 Hz, H-5'), 7.35 (1H, *d*, $^3J_{4',5'}$=4.8 Hz, H-4'), 5.88 (1H, *d*, $^3J_{2,3}$=16.6 Hz, H-2), 2.59 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 190.9 (*s*, 2'-$\underline{C}OCH_3$), 143.5 (*d*, C-3), 139.4 (*s*, C-2'*), 138.9 (*s*, C-3'*), 130.5 (*d*, C-5'), 126.6 (*d*, C-4'), 118.3 (*s*, C-1), 100.2 (*d*, C-2), 29.8 (*q*, 2'-CO$\underline{C}H_3$). MS m/e 177 (P^+).

Reaction of η²-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Acrolein in Methanol at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (116 mg, 2.7 mmol) in dry methanol (10 ml) were treated with acrolein (0.23 ml, 3.4 mmol) and the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol). The mixture was stirred at ambient temperature overnight, and the solution worked up by the normal method and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

3-(2-Acetylthien-3-yl)-propanal [**(63)**; 25 mg, 20 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 9.79 (1H, *s*, 1-H), 7.43 (1H, *d*, $^3J_{5',4'}$=5.3 Hz, H-5'), 7.02 (1H, *d*, $^3J_{4',5'}$=5.3 Hz, H-4'), 3.30 (2H, *t*, $^3J_{3,2}$=7.0 Hz, H-3), 2.78 (2H, *t*, $^3J_{2,3}$=7.0 Hz, H-2), 2.53 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 201.3 (*s*, C-1), 190.7 (*s*, 2'-$\underline{C}OCH_3$), 147.8 (*s*, C-3'), 135.4 (*s*, C-2'), 131.7 (*d*, C-4'), 129.8 (*d*, C-5'), 43.7 (*t*, C-2), 29.5 (*q*, 2'-CO$\underline{C}H_3$), 22.8 (*t*, C-3).

E-3-(2-Acetylthien-3-yl)-prop-2-enal [**(64)**; 24 mg, 19 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 9.76 (1H, *d*, $^3J_{1\text{-}H,2}$=7.9 Hz, 1-H), 8.45 (1H, *d*, $^3J_{3,2}$=16.1 Hz, H-3), 7.53 (1H, *d*, $^3J_{5',4'}$=5.3 Hz, H-5'), 7.42 (1H, *d*, $^3J_{4',5'}$=5.3 Hz, H-4'), 6.61 (1H, *dd*, $^3J_{2,3}$=16.1 Hz, $^3J_{2,1\text{-}H}$=7.9 Hz, H-2), 2.61 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 194.2 (*s*, C-1), 191.0 (*s*, 2'-$\underline{C}OCH_3$), 144.8 (*d*, C-3), 140.8 (*s*, C-3'), 139.5 (*s*, C-2'), 132.2 (*d*, C-2), 130.1 (*d*, C-5'), 127.7 (*d*, C-4'), 30.0 (*q*, 2'-CO$\underline{C}H_3$).

Reaction of η²-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Vinyl Acetate in Methanol at Ambient Temperature

$PdCl_2$ (121 mg, 0.69 mmol) and LiCl (116 mg, 2.7 mmol) in dry methanol (10 ml) were treated with vinyl acetate (0.32 ml, 3.4 mmol) and the orthomanganated thiophene [**(40)**; 200 mg, 0.68 mmol]. The mixture was stirred at ambient temperature for 30 minutes, and the solution worked

up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

2-Acetyl-3-vinylthiophene [**(65)**; 53 mg, 51 %], a colourless oil. Anal. Found: C, 63.60; H, 5.27 %; C_8H_8OS calcd: C, 63.13; H, 5.30 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.56 (1H, *dd*, $^3J_{trans}$=17.7 Hz, $^3J_{cis}$=11.0 Hz, 3-C<u>H</u>=CH_2), 7.40 (1H, *d*, $^3J_{5,4}$=5.2 Hz, H-5), 7.33 (1H, *d*, $^3J_{4,5}$=5.2 Hz, H-4), 5.74 (1H, *dd*, $^3J_{trans}$=17.7 Hz, $^2J_{gem}$=1.2 Hz, 3-CH=C(H)<u>H</u>), 5.45 (1H, *dd*, $^3J_{cis}$=11.0 Hz, $^2J_{gem}$=1.2 Hz, 3-CH=C(<u>H</u>)H), 2.54 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 191.3 (*s*, 2-<u>C</u>OCH_3), 144.6 (*s*, C-3), 135.9 (*s*, C-2), 130.9 (*d*, 3-<u>C</u>H=C(H)H), 129.8 (*d*, C-5), 127.5 (*d*, C-4), 118.7 (*t*, 3-CH=<u>C</u>(H)H), 30.1 (*q*, 2-CO<u>C</u>H_3). MS m/e 152 (P^+).

A mixture of 2-acetyl-3(2-(2-acetylthienyl)-vinyl)-thiophene **(67)** and the dimethyl acetal of 2-(2-acetylthien-3-yl)-ethanal **(66)** (42 mg).

2-Acetyl-3(2-(2-acetylthienyl)-vinyl)-thiophene [**(67)**; 20 mg, 11 %] was obtained pure by vapour diffusion of hexane into a saturated chloroform solution to give white needles, m.p. 158-159 °C (lit. 158-160 °C [12]). ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.17 (2H, *s*, 2-C<u>H</u>=C<u>H</u>-), 7.59 (2H, *d*, $^3J_{5,4}$=5.2 Hz, H-5), 7.44 (2H, *d*, $^3J_{4,5}$=5.2 Hz, H-4), 2.57 (6H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 191.5 (*s*, 2-<u>C</u>OCH_3), 144.5 (*s*, C-3), 135.7 (*s*, C-2), 129.8 (*d*, C-4), 127.7 (*d*, C-5*), 127.6 (*d*, 2-<u>C</u>H=<u>C</u>H-*), 30.2 (*q*, 2'-CO<u>C</u>H_3). MS m/e 183 (P^+-31).

The dimethyl acetal of 2-(2-acetylthien-3-yl)-ethanal [**(66)**; 22 mg, 15 %], a colourless oil. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.41 (1H, *d*, $^3J_{5,4}$=5.0 Hz, H-5), 7.08 (1H, *d*, $^3J_{4,5}$=5.0 Hz, H-4), 4.57 (1H, *t*, ^3J=5.6 Hz, 3-CH_2C<u>H</u>$(OCH_3)_2$), 3.36 (6H, *s*, 3-$CH_2CH(OC$<u>H</u>$_3)_2$), 3.33 (2H, *d*, ^3J=5.6 Hz, 3-C<u>H</u>$_2CH(OCH_3)_2$), 2.55 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 191.5 (*s*, 2-<u>C</u>OCH_3), 144.3 (*s*, C-3), 136.4 (*s*, C-2), 132.8 (*d*, C-4), 129.5 (*d*, C-5), 104.5 (*d*, 3-CH_2<u>C</u>$H(OCH_3)_2$), 53.9 (*q*, 3-$CH_2CH(O$<u>C</u>$H_3)_2$), 34.1 (*t*, 3-<u>C</u>$H_2CH(OCH_3)_2$), 29.8 (*q*, 2-CO<u>C</u>H_3). MS m/e 276 (P^+)

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Allyl Alcohol in Methanol at Ambient Temperature

$PdCl_2$ (82 mg, 0.46 mmol) and LiCl (39 mg, 0.92 mmol) in dry methanol (10 ml) were treated with allyl alcohol (0.16 ml, 2.31 mmol) and the orthomanganated thiophene [**(40)**; 135 mg, 0.46 mmol]. The mixture was

stirred at ambient temperature for 1 h, and the solution worked up by the normal method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

Recovered η^2-(2-acetylthien-3-yl)tetracarbonylmanganese [**(40)**; 28 mg, 21 %]

2-Acetyl-3-prop-2-enylthiophene [**(68)**; 45 mg, 59 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.40 (1H, *d*, $^3J_{5,4}$=4.0 Hz, H-5), 6.99 (1H, *d*, $^3J_{4,5}$=4.0 Hz, H-4), 5.97 (1H, *m*, 3-CH_2-C<u>H</u>=CH_2), 5.05 (2H, *d*, ^{3}J=12.5 Hz, 3-CH_2-CH=C<u>H</u>$_2$), 3.77 (2H, *d*, ^{3}J=5.9 Hz, 3-C<u>H</u>$_2$-CH=CH_2), 2.52 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 191.0 (*s*, 2-<u>C</u>OCH_3), 147.1 (*s*, C-3), 135.9 (*s*, C-2), 135.9 (*d*, 3-CH_2-<u>C</u>H=CH_2), 131.6 (*d*, C-4), 129.9 (*d*, C-5), 116.2 (*t*, 3-CH_2-CH=<u>C</u>H$_2$), 34.5 (*t*, 3-<u>C</u>H$_2$-CH=CH_2), 29.7 (*q*, 2-CO<u>C</u>H$_3$). MS m/e 166 (P^+).

4.4.4 Palladium-Promoted Coupling Reactions of a Range of Orthomanganated Aryl Ketones and Esters

4.4.4.1 Palladium-Promoted Coupling Reactions with Methyl Vinyl Ketone and Methyl Acrylate

4.4.4.1.1 Aryl Methyl Ketones

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (124 mg, 0.70 mmol) and LiCl (59 mg, 1.40 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl vinyl ketone (0.29 ml, 3.5 mmol) and the orthomanganated ketone [**(2)**; 200 mg, 0.70 mmol] were added, and the mixture stirred at ambient temperature for 3 days. The solution was worked up by the normal method and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Recovered η^2-(2-acetylphenyl)tetracarbonylmanganese [**(2)**; 15 mg, 7 %]

1-(3-Methylinden-2-yl)-ethanone [**(70)**; 68 mg, 57 %], a colourless oil, was crystallized from petroleum spirit as large white blocks, m.p. 29.5-30 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.50 (1H, *m*, H-4'), 7.47 (1H, *m*, H-7'), 7.36 (2H, *m*, H-5',6'), 3.64 (2H, *q*, $^5J_{1',3'\text{-}CH_3}$=2.3 Hz, H-1'), 2.52 (3H, *t*, $^5J_{3'}$-

$CH_{3,1'}$=2.3 Hz, 3'-CH_3), 2.42 (3H, *s*, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 196.8 (*s*, C-1), 150.1 (*s*, C-3'), 145.5 (*s*, C-3a'), 143.2 (*s*, C-7a'), 137.7 (*s*, C-2'), 128.1 (*d*, C-6'), 126.9 (*d*, C-5'), 124.1 (*d*, C-7'), 121.7 (*d*, C-4'), 39.3 (*t*, C-1'), 30.3 (*q*, C-2), 13.0 (*q*, 3'-CH_3). MS m/e 172 (P^+).

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (124 mg, 0.70 mmol) and LiCl (118 mg, 2.8 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl vinyl ketone (0.29 ml, 3.5 mmol) and the orthomanganated ketone [**(2)**; 200 mg, 0.70 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

1-(3-Methylinden-2-yl)-ethanone [**(70)**; 73 mg, 61 %]

E-4-(2-Acetylphenyl)-but-3-en-2-one [**(69)**; 18 mg, 14 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 8.10 (1H, *d*, ^{3}J=16.4 Hz, H-4), 7.87-7.77 (1H, *m*, Ar-H), 7.61-7.43 (3H, *m*, Ar-H), 6.49 (1H, *d*, ^{3}J=16.4 Hz, H-3), 2.64 (3H, *s*, 2-$COCH_3$), 2.40 (3H, *s*, H-1). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 200.7 (*s*, 2'-$\underline{C}OCH_3$), 198.8 (*s*, C-2), 143.4 (*d*, C-4), 137.8 (*s*, C-1'), 135.2 (*s*, C-2'), 132.2 (*d*, C-4'), 130.2 (*d*, C-3), 129.7 (*d*, C-5'), 129.6 (*d*, C-3'), 128.4 (*d*, C-6'), 29.1 (*q*, 2'-CO$\underline{C}H_3$), 26.8 (*q*, C-1).

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (124 mg, 0.70 mmol) and LiCl (118 mg, 2.8 mmol) were stirred in dry acetonitrile (10 ml) for 2 hours. Methyl acrylate (0.32 ml, 3.5 mmol) and the orthomanganated ketone [**(2)**; 200 mg, 0.70 mmol] were added, and the mixture stirred for 70 mins. At this time there was no sign of reaction, indicated by the absence of any Pd(0), and the solution was refluxed for 3.5 hours, and worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl (3-methylinden-2-yl)-carboxylate [**(60)**; 10 mg, 8 %]
Methyl 3-(2-acetylphenyl)-propanoate [**(57)**; 15 mg, 10 %]

Methyl E-3-(2-acetylphenyl)-prop-2-enoate [(**58**); mg, 34 %]

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (112 mg, 0.63 mmol) and LiCl (54 mg, 1.26 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl vinyl ketone (0.26 ml, 3.2 mmol) and the orthomanganated ketone [(**39**); 200 mg, 0.63 mmol] were added, and the mixture stirred at ambient temperature for 2 days. The solution was worked up by the normal method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [(**39**); 60 mg, 30 %]

The parent ketone 4'-methoxyacetophenone [(**72**); 26 mg, 27 %]

1-(6-Methoxy-3-methylinden-2-yl)-ethanone [(**73**); 14 mg, 11 %] was recrystallized from hexane/chloroform as small white crystals, m.p. 53.5-54 °C. Anal. Found: C, 77.02; H, 7.12 %; $C_{13}H_{14}O_2$ calcd: C, 77.20; H, 6.98 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.44 (1H, *d*, $^3J_{4',5'}$=8.2 Hz, H-4'), 7.04 (1H, *d*, $^4J_{7',5'}$=2.2 Hz, H-7'), 6.93 (1H, *dd*, $^3J_{5',4'}$=8.2 Hz, $^4J_{5',7'}$=2.2 Hz, H-5'), 3.86 (3H, *s*, 6'-OCH_3), 3.66 (2H, *q*, $^5J_{1',3'\text{-}CH_3}$=2.3 Hz, H-1'), 2.53 (3H, *t*, $^5J_{3'\text{-}CH_3,1'}$=2.3 Hz, 3'-CH_3), 2.43 (3H, *s*, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 196.4 (*s*, C-1), 160.7 (*s*, C-6'), 150.6 (*s*, C-3'), 145.6 (*s*, C-7a'), 138.7 (*s*, C-3a'), 136.1 (*s*, C-2'), 122.6 (*d*, C-4'), 113.3 (*d*, C-5'), 109.7 (*d*, C-7'), 55.6 (*q*, 6'-OCH_3), 39.2 (*t*, C-1'), 30.1 (*q*, C-2), 13.3 (*q*, 3'-CH_3). MS m/e 202 (P^+).

Methyl 2-acetyl-5-methoxybenzoate [(**74**); 15 mg, 11 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.57 (1H, *d*, $^3J_{3,4}$=8.6 Hz, H-3), 7.14 (1H, *d*, $^4J_{6,4}$=2.6 Hz, H-6), 6.99 (1H, *dd*, $^3J_{4,3}$=8.6 Hz, $^4J_{4,6}$=2.6 Hz, H-4), 3.89 (3H, *s*, 1-$COOCH_3$), 3.86 (3H, *s*, 5-OCH_3), 2.51 (3H, *s*, 2-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 199.4 (*s*, 2-$\underline{C}OCH_3$), 168.9 (*s*, 1-$\underline{C}OOCH_3$), 161.7 (*s*, C-5), 133.6 (*s*, C-1), 132.0 (*s*, C-2), 130.1 (*d*, C-3), 116.1 (*d*, C-4), 114.2 (*d*, C-6), 55.7 (*q*, 5-OCH_3), 52.8 (*q*, 1-$COO\underline{C}H_3$), 28.5 (*q*, 2-$CO\underline{C}H_3$).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (112 mg, 0.63 mmol) and LiCl (107 mg, 2.5 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl vinyl ketone (0.26 ml, 3.2 mmol) and the orthomanganated ketone [**(39)**; 200 mg, 0.63 mmol] were added, and the mixture refluxed for 3 hours, and worked up as usual. Chromatographed (p.l.c., 1:5 diethyl ether/pet spirit) to give:

The parent ketone 4'-methoxyacetophenone [**(72)**; 20 mg, 21 %]

1-(6-Methoxy-3-methylinden-2-yl)-ethanone [**(73)**; 59 mg, 46 %]

E-4-(2-Acetyl-5-methoxyphenyl)-but-3-en-2-one [**(71)**; 14 mg, 10 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 8.22 (1H, *d*, $^3J_{4,3}$=16.4 Hz, H-4), 7.82 (1H, *d*, $^3J_{3',4'}$=8.5 Hz, H-3'), 7.05 (1H, *d*, $^4J_{6',4'}$=2.3 Hz, H-6'), 6.96 (1H, *dd*, $^3J_{4',3'}$=8.5 Hz, $^4J_{4',6'}$=2.3 Hz, H-4'), 6.43 (1H, *d*, $^3J_{3,4}$=16.4 Hz, H-3), 3.88 (3H, *s*, 5'-OCH_3), 2.59 (3H, *s*, 2'-$COCH_3$), 2.41 (3H, *s*, C-1). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 198.6 (*s*, 2'-$\underline{C}OCH_3$*), 198.4 (*s*, C-2*), 162.7 (*s*, C-5'), 143.8 (*d*, C-4), 138.7 (*s*, C-1'), 132.3 (*d*, C-3'), 131.9 (*s*, C-1'), 130.6 (*d*, C-3), 114.7 (*d*, C-4'), 114.0 (*d*, C-6'), 55.7 (*q*, 5'-OCH_3), 29.7 (*q*, 2'-$CO\underline{C}H_3$), 26.5 (*q*, C-1).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Li_2PdCl_4 and Methyl Acrylate in Methanol at Ambient Temperature

$PdCl_2$ (112 mg, 0.63 mmol) and LiCl (54 mg, 1.3 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl acrylate (0.29 ml, 3.2 mmol) and the orthomanganated ketone [**(39)**; 200 mg, 0.63 mmol] were added, and the mixture stirred for 2 days. The solution was worked up as usual and chromatographed (p.l.c, 1:10 diethyl ether/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 50 mg, 25 %]

Methyl (3-methyl-6-methoxyinden-2-yl)-carboxylate [**(77)**; 14 mg, 10 %] a white powder was recrystallized from hexane/choroform as tiny white crystals, m.p. 89.5 °C. Anal. Found: C, 71.43; H, 6.24 %; $C_{13}H_{14}O_3$ calcd: C, 71.54; H, 6.47 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.39 (1H, *d*, $^3J_{4,5}$=8.4 Hz, H-4), 7.03 (1H, *d*, $^4J_{7,5}$=2.0 Hz, H-7), 6.91 (1H, *dd*, $^3J_{5,4}$=8.4 Hz, $^4J_{5,7}$=2.0

Hz, H-5), 3.84 (3H, *s*, 6-OCH_3), 3.81 (3H, *s*, 2-$COOCH_3$), 3.61 (2H, *q*, $^5J_{1,3\text{-}CH_3}$=2.3 Hz, H-1), 2.52 (3H, *t*, $^5J_{3\text{-}CH_3,1}$=2.3 Hz, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 166.4 (*s*, 2-$\underline{C}OOCH_3$), 160.3 (*s*, C-6), 151.9 (*s*, C-3), 145.7 (*s*, C-7a), 138.4 (*s*, C-3a), 127.3 (*s*, C-2), 121.9 (*d*, C-4), 112.9 (*d*, C-5), 109.7 (*d*, C-7), 55.6 (*q*, 6-OCH_3), 51.0 (*q*, 2-$COO\underline{C}H_3$), 38.7 (*t*, C-1), 12.6 (*q*, 3-CH_3). MS m/e 218 (P^+).

The parent ketone 4'-methoxyacetophenone [**(72)**; 19 mg, 20 %]

Methyl 3-(2-acetyl-5-methoxyphenyl)-propanoate [**(75)**; 16 mg, 10 %], a colourless oil. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.76 (1H, *d*, $^3J_{3',4'}$=9.1 Hz, H-3'), 6.79-6.78 (2H, *m*, H-4',6'), 3.83 (3H, *s*, 5'-OCH_3), 3.65 (3H, *s*, 1-OCH_3), 3.20 (2H, *t*, $^3J_{3,2}$=7.6 Hz, H-3), 2.64 (2H, *t*, $^3J_{2,3}$=7.6 Hz, H-2), 2.54 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 199.3 (*s*, 2'-$\underline{C}OCH_3$), 173.7 (*s*, C 1), 162.6 (*s*, C-5'), 144.6 (*s*, C-1'), 133.0 (*d*, C-3'), 129.5 (*s*, C-2'), 117.1 (*d*, C 4'), 111.3 (*d*, C-6'), 55.4 (*q*, 5'-OCH_3), 51.6 (*q*, 1-OCH_3), 35.4 (*t*, C-3), 30.5 (*t*, C-2), 29.1 (*q*, 2'-$CO\underline{C}H_3$). MS m/e 236 (P^+).

Methyl E-3-(2-acetyl-5-methoxyphenyl)-prop-2-enoate [**(76)**; 26 mg, 18 %] was recrystallized from hexane/chloroform as prismatic white crystals, m.p. 49-51 °C.Anal. Found: C, 66.87; H, 6.23 %; $C_{13}H_{14}O_4$ calcd: C, 66.66; H, 6.02 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 8.24 (1H, *d*, $^3J_{3,2}$=15.8 Hz, H-3), 7.77 (1H, *d*, $^3J_{3',4'}$=8.5 Hz, H-3'), 6.98 (1H, *d*, $^4J_{6',4'}$=2.3 Hz, H-6'), 6.92 (1H, *dd*, $^3J_{4',3'}$=8.5 Hz, $^4J_{4',6'}$=2.3 Hz, H-4'), 6.20 (1H, *d*, $^3J_{2,3}$=15.8 Hz, H-2), 3.85 (3H, *s*, 5'-OCH_3), 3.78 (3H, *s*, 1-OCH_3), 2.55 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 198.8 (*s*, 2'-$\underline{C}OCH_3$), 167.0 (*s*, C-1), 162.4 (*s*, C-5'), 145.3 (*d*, C-3), 138.1 (*s*, C-1'), 132.3 (*d*, C-3'), 130.3 (*s*, C-2'), 120.5 (*d*, C-2), 114.3 (*d*, C-4'), 113.9 (*d*, C-6'), 55.6 (*q*, 5'-OCH_3), 51.8 (*q*, 1-OCH_3), 28.6 (*q*, 2'-$CO\underline{C}H_3$). MS m/e 219 (P-15).

Reaction of η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (141 mg, 0.80 mmol) and LiCl (68 mg, 1.6 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl vinyl ketone (0.33 ml, 4.0 mmol) and the orthomanganated ketone [**(35)**; 300 mg, 0.80 mmol] were added. The solution was stirred at ambient temperature for 6 hours. The reaction

mixture was worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Recovered η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese [**(35)**; 130 mg, 43 %]

The parent ketone 2',3',4'-trimethoxyacetophenone [**(80)**; 36 mg, 22 %]

3,4,5,6-Tetramethoxy-3-methylbenzo[c]-2,5-dihydrofuran-2-one [**(82)**; 18 mg, 8 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.11 (1H, *s*, H-7), 3.98 (3H, *s*, 4-OCH_3), 3.94 (3H, *s*, 6-OCH_3*), 3.91 (3H, *s*, 5-OCH_3*), 3.11 (3H, *s*, 3-OCH_3), 1.87 (3H, *s*, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 167.9 (*s*, C-1), 156.8 (*s*, C-6), 148.4 (*s*), 147.5 (*s*), 132.3 (*s*), 122.8 (2x *s*), 102.8 (*d*, C-7), 61.2 (*q*, 4,5-OCH_3), 56.5 (*q*, 6-OCH_3), 51.3 (*q*, 3-OCH_3), 24.3 (*q*, 3-CH_3).

1-(4,5,6,-Trimethoxy-3-methylinden-2-yl)-ethanone [**(81)**; 6 mg, 3 %] was recrystallized from hexane/chloroform as prismatic white crystals, m.p. 92-93 °C. Anal. Found: C, 68.44; H, 6.81 %; $C_{15}H_{18}O_4$ calcd: C, 68.69; H, 6.92 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 6.79 (1H, *s*, H-7'), 3.92 (3H, *s*, 4'-OCH_3), 3.88 (3H, *s*, 6'-OCH_3), 3.84 (3H, *s*, 5'-OCH_3), 3.58 (2H, *q*, $^5J_{1',3'\text{-}CH_3}$=2.3 Hz, H-1'), 2.70 (3H, *t*, $^5J_{3'\text{-}CH_3,1'}$=2.3 Hz, 3'-CH_3), 2.37 (3H, *s*, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 196.1 (*s*, C-1), 154.8 (*s*, C-6'), 151.4 (*s*, C-3'), 150.7 (*s*, C-4'), 141.7 (*s*, C-5'), 140.3 (*s*, C-7a'), 135.8 (*s*, C-2'), 130.6 (*s*, C-3a'), 103.6 (*d*, C-7'), 61.3 (*q*, 4'-OCH_3), 60.9 (*q*, 5'-OCH_3), 56.1 (*q*, 6'-OCH_3), 39.7 (*t*, C-1'), 30.2 (*q*, C-2), 15.1 (*q*, 3'-CH_3). MS m/e 262 (P^+).

Reaction of η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (94 mg, 0.53 mmol) and LiCl (90 mg, 2.1 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl vinyl ketone (0.2 ml, 2.6 mmol) and the orthomanganated ketone [**(35)**; 200 mg, 0.53 mmol] were added. After 40 minutes stirring there was no sign of palladium precipitation and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

1-(4,5,6-Trimethoxy-3-methylinden-2-yl)-ethanone [**(81)**; 139 mg, 80 %]

The band at lower R_f (21 mg) was identified spectroscopically and by GC-MS as a mixture of 4-(2-acetyl-3,4,5-trimethoxyphenyl)-butan-2-one (**78**) and E-4-(2-acetyl-3,4,5-trimethoxyphenyl)-but-3-en-2-one (**79**):

4-(2-Acetyl-3,4,5-trimethoxyphenyl)-butan-2-one [(**78**); 3 % by NMR integration]. ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 154.4 (*s*), 134.2 (*s*), 109.1 (*d*, C-6'), 45.8 (*t*, C-3), 29.8 (*q*, C-1), 27.5 (*t*, C-4) (5 singlets and 4 quartets not observed). MS m/e 280 (P^+).

E-4-(2-Acetyl-3,4,5-trimethoxyphenyl)-but-3-en-2-one [(**79**); 12 % by NMR integration]. ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 202.6 (*s*, 2'-$\underline{C}OCH_3$), 198.4 (*s*, C-2), 154.8 (*s*, C-5'), 151.3 (*s*, C-3'), 143.6 (*s*, C-4'), 140.5 (*d*, C-4), 130.2 (*s*, C-1'), 129.3 (*d*, C-3), 127.9 (*s*, C-2'), 105.8 (*d*, C-6'), 61.6 (*q*, 3'-OCH_3), 60.9 (*q*, 4'-OCH_3), 55.2 (*q*, 5'-OCH_3), 32.7 (*q*, 2'-$CO\underline{C}H_3$), 26.9 (*q*, C-1). MS m/e 278 (P^+).

Ratios were calculated on the intensity of the C-6' doublet in the ^{13}C NMR spectrum.

Reaction of η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with Li_2PdCl_4 and Methyl Acrylate in Methanol at Ambient Temperature

$PdCl_2$ (94 mg, 0.53 mmol) and LiCl (90 mg, 2.13 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl acrylate (0.24 ml, 2.66 mmol) and the orthomanganated ketone [(**35**); 200 mg, 0.53 mmol] were added. The solution was stirred overnight, worked up as usual, and chromatographed (p.l.c., 1:8 ethyl acetate/petroleum spirit) to give:

Recovered η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese [(**35**); 25 mg, 13 %]

Methyl (4,5,6-trimethoxy-3-methylinden-2-yl)-carboxylate [(**84**); 33 mg, 22 %] was recrystallized from petroleum spirit as white feathers, m.p. 100-101.5 °C. (lit. m.p. 99-100 °C [12]). ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 6.81 (1H, *s*, H-7), 3.95 (3H, *s*, 4-OCH_3), 3.89 (3H, *s*, 6-OCH_3), 3.87 (3H, *s*, 5-OCH_3), 3.80 (3H, *s*, 2-$COOCH_3$), 3.57 (2H, *q*, $^5J_{1,3\text{-}CH_3}$≈2.3 Hz, H-1), 2.71 (3H, *t*, $^5J_{3\text{-}CH_3,1}$≈2.3 Hz, 3-CH_3). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 166.2 (*s*, 2-$\underline{C}OOCH_3$), 154.5 (*s*, C-6), 152.8 (*s*, C-3), 150.2 (*s*, C-4), 141.5 (*s*, C-5), 140.6 (*s*, C-7a), 130.5 (*s*, C-3a), 127.2 (*s*, C-2), 103.6 (*d*, C-7), 61.4 (*q*, 4-OCH_3), 60.9

(*q*, 5-OCH_3), 56.2 (*q*, 6-OCH_3), 50.9 (*q*, 2-$COO\underline{C}H_3$), 39.2 (*t*, C-1), 14.5 (*q*, 3-CH_3). MS m/e 278 (P^+).

The parent ketone 2',3',4'-trimethoxyacetophenone [**(80)**; 26 mg, 23 %]

Methyl E-3-(2-acetyl-3,4,5-trimethoxyphenyl)-prop-2-enoate [**(83)**; 57 mg, 37 %], a colourless oil. ^1H NMR: (89.55 MHz) ($CDCl_3$) δ 7.57 (1H, $^3J_{3,2}$=15.8 Hz, H-3), 6.88 (1H, *s*, H-6'), 6.26 (1H, $^3J_{2,3}$=15.8 Hz, H-2), 3.89 (9H, *s*, 3',4',5'-OCH_3), 3.76 (3H, *s*, 1-OCH_3), 2.52 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 202.5 (*s*, 2'-$\underline{C}OCH_3$), 166.7 (*s*, C-1), 154.6 (*s*, C-5'), 150.9 (*s*, C-3'), 143.4 (*s*, C-4'), 141.5 (*d*, C-3), 130.3 (*s*, C-2'), 127.5 (*s*, C-1'), 119.7 (*d*, C-2), 105.8 (*d*, C-6'), 61.4 (*q*, 3'-OCH_3), 60.9 (*q*, 4'-OCH_3), 56.1 (*q*, 5'-OCH_3), 51.6 (*q*, 1-OCH_3), 32.6 (*q*, 2'-$CO\underline{C}H_3$).

Reaction of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)tetracarbonylmanganese (34) with Li_2PdCl_4 and Methyl Acrylate in Methanol at Ambient Temperature

$PdCl_2$ (94 mg, 0.53 mmol) and LiCl (45 mg, 1.06 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl acrylate (0.24 ml, 2.65 mmol) and the orthomanganated ketone [**(34)**; 200 mg, 0.53 mmol] were added. The solution was stirred at ambient temperature overnight, worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Methyl (5,6,7-trimethoxy-3-methylinden-2-yl)-carboxylate [**(88)**; 14 mg, 10 %) was recrystallized from petroleum spirit as white feathers, m.p. 86-87.5 °C (lit. 85-86 °C [12]). Anal. Found: C, 64.53; H, 6.49 %; $C_{15}H_{18}O_5$ calcd: C, 64.74; H, 6.52 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 6.79 (1H, *s*, H-4), 4.00 (3H, *s*, 7-OCH_3), 3.88 (3H, *s*, 6-OCH_3), 3.92 (3H, *s*, 5-OCH_3), 3.82 (3H, *s*, 2-$COOCH_3$), 3.65 (2H, *q*, $^5J_{1,3\text{-}CH_3}$=2.4 Hz, H-1), 2.51 (3H, *t*, $^5J_{3\text{-}CH_3,1}$=2.4 Hz, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 166.1 (*s*, 2-$\underline{C}OOCH_3$), 153.7 (*s*, C-5), 151.5 (*s*, C-3), 149.4 (*s*, C-7), 142.1 (*s*, C-3a*), 141.2 (*s*, C-6*), 129.4 (*s*, C-7a+), 127.2 (*s*, C-2+), 100.3 (*d*, C-4), 61.2 (*q*, 7-OCH_3), 60.2 (*q*, 6-OCH_3), 56.4 (*q*, 5-OCH_3), 51.2 (*q*, 2-$COO\underline{C}H_3$), 36.6 (*t*, C-1), 12.6 (*q*, 3-CH_3).

The parent ketone 3',4',5'-trimethoxyacetophenone [**(87)**; 79 mg, 71 %]

A mixture (12 mg, ~8 %) of similar amounts of methyl E-3-(6-acetyl-2,3,4-trimethoxyphenyl)-prop-2-enoate **(86)** and methyl 3-(6-acetyl-2,3,4-trimethoxyphenyl)-propanoate **(85)**:

Methyl E-3-(6-acetyl-2,3,4-trimethoxyphenyl)-prop-2-enoate **(86)**. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.82 (1H, *d*, $^3J_{3,2}$=16.1 Hz, H-3), 6.82 (1H, *s*, H-5'), 6.35 (1H, *d*, $^3J_{2,3}$=16.1 Hz, H-2), 3.90 (9H, *s*, br, 2',3',4'-OCH_3), 3.78 (3H, *s*, 1-OCH_3), 2.49 (3H, *s*, 6'-$COCH_3$).

Methyl 3-(6-acetyl-2,3,4-trimethoxyphenyl)-propanoate **(85)**. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 6.93 (1H, *s*, H-5'), 3.88 (3H, *s*, 2'-OCH_3*), 3.87 (3H, *s*, 4'-OCH_3*), 3.84 (3H, *s*, 3'-OCH_3), 3.67 (3H, *s*, 1-OCH_3), 3.04 (2H, *t*, $^3J_{3,2}$=8.0 Hz, H-3), 2.57 (2H, *t*, $^3J_{2,3}$=8.0 Hz, H-2), 2.55 (3H, *s*, 6'-$COCH_3$).

4.4.4.1.2 Polycyclic Compounds

Reaction of η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese (13) with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

$PdCl_2$ (114 mg, 0.64 mmol) and LiCl (109 mg, 2.56 mmol) were stirred in dry methanol (10 ml) for 2 hours. Methyl vinyl ketone (0.27 ml, 3.21 mmol) and orthomanganated 1,4-benzopyranone [**(13)**; 200 mg, 0.64 mmol] were added, and the solution stirred overnight. The reaction mixture was worked up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Recovered η^2-5-(1,4-benzopyronyl)tetracarbonylmanganese [**(13)**; 7 mg, 4 %]

The parent ketone 1,4-benzopyranone [**(96)**; 34 mg, 36 %]

4-(1,4-Benzopyron-5-yl)-butan-2-one [**(94)**; 49 mg, 35 %] was recrystallized from hexane/chloroform as small white feathers, m.p. 68.5-69 °C. Anal. Found: C, 71.92; H, 5.73 %; $C_{13}H_{12}O_3$ calcd: C, 72.21; H, 5.59 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.69 (1H, *d*, $^3J_{2',3'}$=5.7 Hz, H-2'), 7.43 (1H, *t*, $^3J_{7',6'}$=$^3J_{7',8'}$=7.9 Hz, H-7'), 7.22 (1H, *d*, $^3J_{8',7'}$=7.9 Hz, H-8'), 7.09 (1H, *d*, $^3J_{6',7'}$=7.9 Hz, H-6'), 6.17 (1H, *d*, $^3J_{3',2'}$=5.7 Hz, H-3'), 3.40 (2H, *t*, $^3J_{4,3}$=7.4 Hz, H-4), 2.71 (2H, *t*, $^3J_{3,4}$=7.4 Hz, H-3), 2.08 (3H, *s*, H-1). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 208.4 (*s*, C-2), 179.1 (*s*, C-4'), 158.1 (*s*, C-8a'), 153.8 (*d*, C-2'),

143.7 (*s*, C-1'), 133.0 (*d*, C-7'), 127.8 (*d*, C-6'), 122.7 (*s*, C-4a'), 117.0 (*d*, C-8'), 114.1 (*d*, C-3'), 45.1 (*t*, C-3), 29.8 (*q*, C-1), 29.7 (*t*, C-4). MS m/e 216 (P^+).

Reaction of η^2 5-(1,4-Benzopyronyl)tetracarbonylmanganese (13) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (114 mg, 0.64 mmol) and LiCl (55 mg, 1.3 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl vinyl ketone (0.27 ml, 3.2 mmol) and orthomanganated 1,4-benzopyranone [**(13)**; 200 mg, 0.64 mmol] were added, and the solution refluxed for 4.5 hours.The reaction mixture was worked up by the normal method and chromatographed (p.l.c., 1:3 ethyl acetate/petroleum spirit). The plate was developed several times to achieve separation of the following:

The parent ketone 1,4-benzopyranone [**(96)**; 23 mg, 25 %]

4-(1,4-Benzopyron-5-yl)-butan-2-one [**(94)**; 65 mg, 47 %]

E-4-(1,4-Benzopyron-5-yl)-but-3-en-2-one [**(95)**; 19 mg, 14 %], was recrystallized from hexane/chloroform as white feathers, m.p. 117.5-119.5 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 8.92 (1H, *d*, $^3J_{4,3}$=16.4 Hz, H-4), 7.81 (1H, *d*, $^3J_{2',3'}$=5.8 Hz, H-2'), 7.63 (1H, *t*, $^3J_{7',6'}$=$^3J_{7',8'}$=7.9 Hz, H-7'), 7.49 (1H, *d*, $^3J_{8',7'}$=7.9 Hz, H-8'*), 7.46 (1H, *d*, $^3J_{6',7'}$=7.9 Hz, H-6'*), 6.43 (1H, *d*, $^3J_{3,4}$=16.4 Hz, H-3), 6.31 (1H, *d*, $^3J_{3',2'}$=5.8 Hz, H-3'), 2.46 (3H, *s*, H-1). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 199.5 (*s*, C-2), 179.1 (*s*, C-4'), 157.6 (*s*, C-8a'), 154.4 (*d*, C-2'), 144.2 (*d*, C-4), 137.3 (*s*, C-5'), 133.3 (*d*, C-7'), 133.1 (*s*, C-4a'), 131.2 (*d*, C-6'), 124.7 (*d*, C-3), 120.0 (*d*, C-8'), 114.3 (*d*, C-3'), 26.4 (*q*, C-1). MS m/e 199 (P-15).

Reaction of η^2-4-(Dibenzosuberenonyl)tetracarbonylmanganese (10) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (91 mg, 0.51 mmol) and LiCl (43 mg, 1.02 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.23 ml, 2.55 mmol) and the orthomanganated compound [**(10)**; 190 mg, 0.51 mmol] were added, and the mixture refluxed for 3 hours. The solution was cooled, worked up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Recovered η^2-4-(dibenzosuberenonyl)tetracarbonylmanganese [**(10)**; 10 mg, 5 %]

The parent ketone dibenzosuberenone [**(99)**; 12 mg, 11 %]

Methyl 2H-dibenzo[cd,h]azulene-1-carboxylate [**(100)**; 19 mg, 14 %] was recrystallized from petroleum spirit/chloroform as yellow feathers, m.p. 140-142 °C. Anal. Found: C, 82.92; H, 5.43 %; $C_{19}H_{14}O_2$ calcd: C, 83.19; H, 5.14 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.51 (1H, *dd*, ^{3}J=8.0 Hz, ^{4}J=1.5 Hz, H-11), 7.34-7.21 (5H, *m*), 7.12 (1H, *d*, ^{3}J=7.4 Hz), 6.52-6.42 (2H, *m*, H-6,7), 3.85 (2H, *s*, H-2), 3.78 (3H, *s*, 1-$COOCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 168.1 (*s*, 1-$\underline{C}OOCH_3$), 150.8 (*s*, C-11b), 146.6 (*s*, C-11c), 143.5 (*s*, C-2a), 136.4 (*s*, C-7a), 133.1 (*s*, C-11a), 132.9 (*d*), 132.8 (*d*), 131.9 (*d*), 131.7 (*s*, C-5a), 130.8 (*d*, C-9), 130.1 (*d*), 129.7 (*s*, C-1), 128.6 (*d*, C-8), 128.4 (*d*, C-10), 127.7 (*d*, C-11), 123.7 (*d*, C-5), 51.4 (*q*, 1-COO$\underline{C}H_3$), 41.2 (*t*, C-2).

Methyl 3-(dibenzosuberenon-4-yl)-propanoate [**(97)**; 25 mg, 17 %], was recrystallized from hexane/chloroform as white feathers, m.p. 49-50 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.85 (1H, *dd*, $^3J_{6',7'}$=7.2 Hz, $^4J_{6',8'}$=1.8 Hz, H-6'), 7.55 (1H, *td*, $^3J_{8',7'}=^3J_{8',9'}$=7.2 Hz, $^4J_{8',6'}$=1.8 Hz, H-8'), 7.51 (1H, *td*, $^3J_{7',6'}=^3J_{7',8'}$=7.2 Hz, $^4J_{7',9'}$=1.7 Hz, H-7'), 7.46 (1H, *dd*, $^3J_{9',8'}$=7.2 Hz, $^4J_{9',7'}$=1.7 Hz, H-9'), 7.43 (1H, *m*, H-2'), 7.39 (1H, *dd*, $^3J_{3',2'}$=7.1 Hz, $^4J_{3',1'}$=2.0 Hz, H-3'), 7.36 (1H, *dd*, $^3J_{1',2'}$=7.1 Hz, $^4J_{1',3'}$=2.0 Hz, H-1'), 7.01 (2H, *m*, H-10',11'), 3.68 (3H, *s*, 1-OCH_3), 3.16 (2H, *t*, $^3J_{3,2}$=7.9 Hz, H-3), 2.80 (2H, *t*, $^3J_{2,3}$=7.9 Hz, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 197.6 (*s*, C-5), 173.5 (*s*, C-1), 141.2 (*s*, C-4'), 139.9 (*s*, C-11a'*), 137.9 (*s*, C-9a'*), 134.4 (*s*, C-5a'+), 133.2 (*s*, C-4a'+), 131.2 (*d*, C-10'#), 131.0 (*d*, C-3'), 130.9 (*d*, C-8'), 130.6 (*d*, C-11'#), 130.1 (*d*, C-2'), 129.0 (*d*, C-9'), 128.8 (*d*, C-7'), 128.1 (*d*, C-1'), 127.6 (*d*, C-6'), 51.7 (*q*, 1-OCH_3), 36.4 (*t*, C-2), 29.7 (*t*, C-3).

Methyl E-3-(dibenzosuberenon-4-yl)-prop-2-enoate [**(98)**; 8 mg, 5 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.98 (1H, *dd*, $^3J_{6',7'}$=7.1 Hz, $^4J_{6',8'}$=1.8 Hz, H-6'), 7.97 (1H, *d*, $^3J_{3,2}$=15.7 Hz, H-3), 7.70 (1H, *dd*, ^{3}J=6.2 Hz, ^{4}J=2.6 Hz), 7.60 (1H, *td*, ^{3}J=7.1 Hz, ^{4}J=1.8 Hz), 7.57 (1H, *dd*, ^{3}J=7.4 Hz, ^{4}J=1.8 Hz), 7.56-7.52 (2H, *m*), 7.50 (1H, *dd*, ^{3}J=7.2 Hz, ^{4}J=1.8 Hz), 7.10-7.02 (2H, *m*, H-10',11'), 6.40 (1H, *d*, ^{3}J=15.7 Hz, H-2), 3.84 (3H, *s*, 1-OCH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 196.0 (*s*, C-5), 167.1 (*s*, C-1), 144.1 (*d*, C-3), 140.6 (*s*), 135.1 (*s*), 134.8 (*s*), 133.4 (2x *s*), 131.6 (*d*), 131.4 (*d*), 131.2 (*d*), 130.6 (2x *d*), 129.5 (*d*), 129.1 (*d*), 128.3 (2x *d*), 120.5 (*d*, C-2), 51.8 (*q*, 1-OCH_3).

Reaction of η^2-(8-Dimethylamino-1-naphthyl)tetracarbonylmanganese (12) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Methanol

$PdCl_2$ (112 mg, 0.63 mmol) and LiCl (107 mg, 2.5 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl vinyl ketone (0.26 ml, 3.2 mmol) and the orthomanganated compound [**(12)**; 213 mg, 0.63 mmol] were added, and the mixture refluxed for 5 hours. The solution was cooled, worked up by the normal method and chromatographed (p.l.c., 1:3 ethyl acetate/petroleum spirit) to give:

The parent ketone *N,N*-dimethyl-1-naphthylamine [**(101)**; 87 mg, 81 %]

The reaction was repeated at ambient temperature in methanol, but the orthomanganated material was reluctant to go into solution. The demetalated compound was again the only product recovered.

Reaction of η^2-(8-Dimethylamino-1-naphthyl)tetracarbonylmanganese (12) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (105 mg, 0.59 mmol) and LiCl (101 mg, 2.4 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.27 ml, 3.0 mmol) and the orthomanganated compound [**(12)**; 200 mg, 0.59 mmol] were added, and the mixture refluxed for 3 hours. By t.l.c. the reaction appeared only to yield the demetalated product and was therefore abandoned.

4.4.4.1.3 Esters

Reaction of η^2-(5-Methoxy-2-methoxycarbonylphenyl)tetracarbonyl-manganese (19) with Li_2PdCl_4 and Methyl Acrylate in Methanol at Ambient Temperature

$PdCl_2$ (112 mg, 0.63 mmol) and LiCl (54 mg, 1.3 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl acrylate (0.29 ml, 3.2 mmol) and the orthomanganated ester [**(19)**; 210 mg, 0.63 mmol] were added, and the solution stirred at ambient temperature for 3 days. The reaction mixture was worked up by the normal method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to yield 4 bands. Separation was achieved by developing the plate 2-3 times and gave:

Recovered η^2-(5-methoxy-2-methoxycarbonylphenyl)tetracarbonyl-manganese [**(19)**; 26 mg, 12 %]

The parent ester methyl 4-methoxybenzoate [**(104)**; 16 mg, 15 %]

Methyl 3-(5-methoxy-2-methoxycarbonylphenyl)-propanoate [**(102)**; 79 mg, 50 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.91 (1H, *d*, $^3J_{3',4'}$=8.5 Hz, H-3'), 6.76 (1H, *d*, $^4J_{6',4'}$=2.7 Hz, H-6'), 6.74 (1H, *dd*, $^3J_{4',3'}$=8.5 Hz, $^4J_{4',6'}$=2.7 Hz, H-4'), 3.82 (3H, *q*, 5'-OCH_3), 3.79 (3H, *q*, 2'-$COOCH_3$), 3.63 (3H, *q*, 1-OCH_3), 3.25 (2H, *t*, $^3J_{3,2}$=7.8 Hz, H-3), 2.63 (2H, *t*, $^3J_{2,3}$=7.8 Hz, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 173.5 (*s*, C-1), 167.0 (*s*, 2'-$\underline{C}OOCH_3$), 162.5 (*s*, C-5'), 145.4 (*s*, C-1'), 133.4 (*d*, C-3'), 121.3 (*s*, C-2'), 116.5 (*d*, C-4'), 111.7 (*d*, C-6'), 55.3 (*q*, 5'-OCH_3), 51.7 (*q*, 1-OCH_3*), 51.5 (*q*, 2'-$COO\underline{C}H_3$*), 35.5 (*t*, C-3), 30.4 (*t*, C-2).

Methyl E-3-(5-methoxy-2-methoxycarbonylphenyl)-prop-2-enoate [**(103)**; 17 mg, 11 %] was recrystallized from hexane/diethyl ether as white feathers, m.p. 65-67 °C. Anal. Found: C, 61.98; H, 5.86 %; $C_{13}H_{14}O_5$ calcd: C, 62.39; H, 5.64 %. ^{1}H NMR: (90 MHz) ($CDCl_3$) δ 8.51 (1H, *d*, $^3J_{3,2}$=16.1 Hz, H-3), 7.97 (1H, *d*, $^3J_{3',4'}$=8.6 Hz, H-3'), 7.03 (1H, *d*, $^4J_{6',4'}$=2.6 Hz, H-6'), 6.91 (1H, *dd*, $^3J_{4',3'}$=8.6 Hz, $^4J_{4',6'}$=2.6 Hz, H-4'), 6.26 (1H, *d*, $^3J_{2,3}$=16.1 Hz, H-2), 3.89 (3H, *q*, 2'-$COOCH_3$*), 3.87 (3H, *q*, 5'-OCH_3*), 3.81 (3H, *q*, 1-OCH_3*). ^{13}C NMR: (22.3 MHz) ($CDCl_3$) δ 166.8 (*s*, 2'-$\underline{C}OOCH_3$*), 166.7 (*s*, C-1*), 162.7 (*s*, C-5'), 144.3 (*d*, C-3), 139.0 (*s*, C-1'), 133.1 (*d*, C-3'), 122.2 (*s*, C-2'), 120.8 (*d*, C-2), 114.7 (*d*, C-4'), 113.2 (*d*, C-6'), 55.5 (*q*, 5'-OCH_3), 51.9 (*q*, 1-OCH_3+), 51.6 (*q*, 2'-$COO\underline{C}H_3$+). MS m/e 250 (P^+).

Reaction of η^2-(2,3,4-Trimethoxy-6-methoxycarbonylphenyl)tetracarbonyl-manganese (105) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (90 mg, 0.51 mmol) and LiCl (87 mg, 2.0 mmol) were stirred in dry acetonitrile (10 ml) for 2 hours. Methyl vinyl ketone (0.21 ml, 2.6 mmol) and the orthomanganated ester [**(105)**; 200 mg, 0.51 mmol] were added, and the mixture refluxed for 3 hours, at which time there appeared to be no orthomanganated starting material left by t.l.c. The solution was cooled, worked up by the normal method and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

The parent ester methyl 3,4,5-trimethoxybenzoate [(**107**); 13 mg, 11 %]

4-(2,3,4-Trimethoxy-6-methoxycarbonylphenyl)-butan-2-one [(**106**); 115 mg, 76 %] was recrystallized from petroleum spirit as white needles, m.p. 53-53.5 °C. Anal. Found: C, 60.86; H, 6.72 %; $C_{15}H_{20}O_6$ calcd: C, 60.80; H, 6.80 %. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 7.36 (1H, *s*, H-5'), 3.92 (3H, *s*, 6'-$COOCH_3$), 3.87 (9H, *s*, 2',3',4'-OCH_3), 3.14 (2H, *t*, $^3J_{4,3}$=7.6 Hz, H-4), 2.68 (2H, *t*, $^3J_{3,4}$=7.6 Hz, H-3), 2.17 (3H, *s*, C-1). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 207.8 (*s*, C-2), 167.2 (*s*, 6'-$\underline{C}OOCH_3$), 152.1 (*s*, C-2'*), 151.2 (*s*, C-4'*), 145.7 (*s*, C-3'), 130.0 (*s*, C-6'), 124.8 (*s*, C-1'), 109.9 (*d*, C-5'), 60.8 (*q*, 2'-OCH_3), 60.4 (*q*, 3'-OCH_3), 56.0 (*q*, 4'-OCH_3), 51.7 (*q*, 6'-$COO\underline{C}H_3$), 44.5 (*t*, C-4), 29.2 (*t*, C-3), 21.6 (*q*, C-1). MS m/e 296 (P^+).

4.4.4.2 Palladium-Promoted Coupling Reactions with Other Alkenes

Reaction of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)tetracarbonylmanganese (34) with Li_2PdCl_4 and Acrylonitrile in refluxing acetonitrile

$PdCl_2$ (94 mg, 0.53 mmol) and LiCl (45 mg, 1.06 mmol) were stirred in dry acetonitrile (10 ml) for 2 hours. Acrylonitrile (0.18 ml, 2.66 mmol) and the orthomanganated ketone [(**34**); 200 mg, 0.53 mmol] were added. The solution was refluxed overnight, worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

5,6,7-Trimethoxy-3-methylindene-2-carbonitrile [(**90**); 43 mg, 33 %], a white solid which was recrystallized from petroleum spirit/chloroform as white feathers, m.p. 94-94.5 °C. Anal. Found: C, 68.49; H, 6.03; N, 5.72 %; $C_{14}H_{15}O_3N$ calcd: C, 68.56; H, 6.16; N, 5.71 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 6.73 (1H, *s*, H-4), 3.97 (3H, *s*, 7-OCH_3), 3.91 (3H, *s*, 5-OCH_3), 3.87 (3H, *s*, 6-OCH_3), 3.56 (2H, *q*, $^5J_{1,3\text{-}CH_3}$=2.4 Hz, H-1), 2.36 (3H, *t*, $^5J_{3\text{-}CH_3,1}$=2.4 Hz, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 156.2 (*s*, C-3), 154.3 (*s*, C-5), 149.3 (*s*, C-7), 142.5 (*s*, C-6), 138.6 (*s*, C-3a), 127.1 (*s*, C-7a), 117.2 (*s*, 2-CN), 109.2 (*s*, C-2), 100.1 (*d*, C-4), 61.2 (*q*, 7-OCH_3), 60.4 (*q*, 6-OCH_3), 56.4 (*q*, 5-OCH_3), 37.3 (*t*, C-1), 13.1 (*q*, 3-CH_3). MS m/e 245 (P^+).

E-3-(6-Acetyl-2,3,4-trimethoxyphenyl)-prop-2-enenitrile [(**89**); 33 mg, 24 %], white feathers which were recrystallized from petroleum spirit/chloroform as white needles, m.p. 114-114.5 °C. Anal. Found: C, 64.17; H, 5.82; N, 5.37 %; $C_{14}H_{15}O_4N$ calcd: C, 64.36; H, 5.79; N, 5.36 %. ^{1}H

NMR: (300.13 MHz) ($CDCl_3$) δ 7.53 (1H, *d*, $^3J_{3,2}$=16.7 Hz, H-3), 6.90 (1H, *s*, H-5'), 6.06 (1H, *d*, $^3J_{2,3}$=16.7 Hz, H-2), 3.92 (3H, *s*, -OCH_3), 3.90 (3H, *s*, -OCH_3), 3.83 (3H, *s*, -OCH_3), 2.54 (3H, *s*, 6'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 200.9 (*s*, 6'-$\underline{C}OCH_3$), 154.3 (*s*, C-4'*), 153.6 (*s*, C-2'*), 145.0 (*s*, C-3'), 144.8 (*d*, C-3), 135.9 (*s*, C-6'), 119.8 (*s*, C-1'÷), 118.8 (*s*, C-1÷), 108.0 (*d*, C-5'), 100.8 (*d*, C-2), 61.1 (*q*, 2'-OCH_3), 60.8 (*q*, 3'-OCH_3), 56.3 (*q*, 4'-OCH_3), 30.1 (*q*, 6'-$CO\underline{C}H_3$). MS m/e 261 (P^+) (Traces of the Z isomer were also observed by GC-MS).

Reaction of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)tetracarbonylmanganese (34) with Li_2PdCl_4 and Acrolein in Refluxing Acetonitrile

$PdCl_2$ (90 mg, 0.51 mmol) and LiCl (86 mg, 2.02 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Acrolein (0.17 ml, 2.53 mmol) and the orthomanganated ketone [**(34)**; 190 mg, 0.51 mmol] were added. The solution was refluxed for 3 hours, worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Ethyl 3,4,5-trimethoxybenzoate [**(92)**; 5 mg, 4 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 7.30 (2H, *s*, H-2,6), 4.38 (2H, *q*, ^{3}J=7.0 Hz, 1-$COOC\underline{H}_2CH_3$), 3.91 (9H, *s*, 3,4,5-OCH_3), 1.40 (3H, *t*, ^{3}J=7.0 Hz, 1-$COOCH_2C\underline{H}_3$). MS m/e 240 (P^+).

Methyl 3,4,5-trimethoxybenzoate [**(93)**; 6 mg, 5 %]

The parent ketone 3',4',5'-trimethoxyacetophenone [**(87)**; 3 mg, 3 %]

5,6,7-Trimethoxy-3-methylindene-2-carbaldehyde [**(91)**; 69 mg, 55 %], a colourless oil. ^{1}H NMR: (89.55 MHz) ($CDCl_3$) δ 10.14 (1H, *s*, 2-COH), 6.87 (1H, *s*, H-4), 4.00 (3H, *s*, 7-OCH_3), 3.94 (3H, *s*, 5-OCH_3), 3.91 (3H, *s*, 6-OCH_3), 3.64 (2H, *q*, $^5J_{1,3\text{-}CH_3}$=2.3 Hz, H-1), 2.52 (3H, *t*, $^5J_{3\text{-}CH_3,1}$=2.3 Hz, 3-CH_3). ^{13}C NMR: (22.50 MHz) ($CDCl_3$) δ 186.5 (*s*, 2-COH), 155.7 (*s*, C-3*), 154.0 (*s*, C-5*), 149.7 (*s*, C-7), 143.2 (*s*, C-3a÷), 140.6 (*s*, C-6÷), 139.5 (*s*, C-2), 128.4 (*s*, C-7a), 100.7 (*d*, C-4), 61.1 (*q*, 7-OCH_3), 60.2 (*q*, 6-OCH_3), 56.4 (*q*, 5-OCH_3), 33.7 (*t*, C-1), 10.8 (*q*, 3-CH_3).

Reaction of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)tetracarbonylmanganese (34) with Li_2PdCl_4 and Allyl Alcohol in Refluxing Acetonitrile

$PdCl_2$ (94 mg, 0.53 mmol) and LiCl (90 mg, 2.13 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Allyl alcohol (0.18 ml, 2.66 mmol) and the orthomanganated ketone [(**34**); 200 mg, 0.53 mmol] were added. The solution was refluxed for 3 hours, worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

The parent ketone 3',4',5'-trimethoxyacetophenone [(**87**); 64 mg, 57 %]
5,6,7-Trimethoxy-3-methylindene-2-carbaldehyde [(**91**); 41 mg, 31 %]

4.4.5 Mechanistic Implications

4.4.5.1 Does the Palladium Chloride Function as a Transmetalating Agent?

Comparison of Product Ratios for the Pd(II)-Promoted Coupling of Methyl Acrylate at the 3-Metalated Aryl Carbons in η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) and 4-Acetyl-2,5-dimethylthien-3-ylmercury(II) chloride (112) in Acetonitrile

Coupling reaction conditions. The following method was used for the aryl-mercury compound and the reaction was repeated under identical conditions with the same molar quantities for the aryl-manganese analogue.

To 4-acetyl-2,5-dimethylthien-3-ylmercury(II) chloride [(**112**); 300 mg, 0.77 mmol] were added in succession LiCl (131 mg, 3.07 mmol), methyl acrylate (331 mg, 3.84 mmol), acetonitrile (10 ml) and $PdCl_2$ (136 mg, 0.77 mmol). After heating under reflux with exclusion of moisture ($CaCl_2$) for 5 h, the mixture was cooled, filtered, run onto a short column of silica gel and washed through with acetonitrile (3 x 10 ml) to complete elution.

Analysis by GCMS with ion-trap detection.

Products were analysed on a Varian 3700 gas chromatograph fitted with a 12 m S.G.E. brand BPI column (1 μ film; 0.25 mm internal diameter) using helium carrier (40 cm s^{-1}) with purged splitless injection. Column temperature was 100 °C at injection, increasing at 5° min^{-1}. A Finnigan

MAT 700 ion-trap detector linked to a data station provided parent-ion mass values and integrated peak areas. The latter were used to calculate the product ratios which are only semi-quantitative in the absence of calibration to establish response factors for the individual components, but which provide for the comparison (Mn vs Hg) required. Assignments were made by correlation of retention time and mass for the known compounds ((**53**), (**54**), and the parent ketone (**56**)) or for (**55**), in the absence of an authentic sample, by mass [m/e 240 (P^+), 197 (P^+-COMe), and 153 (P^+-CH_2CH_2COOMe)]. Overall yields were not determined here although that in the Mn case was high (87 %) in a previous experiment [see section 4.2.3.5] under similar conditions. By comparison of total product peak areas, the total yield for the Hg reaction was estimated to be similar to that for Mn, although the Hg reaction product did contain a number of unidentified minor (< 2%) products whereas the Mn reaction was much cleaner.

Orthometalated ketone	**Products (R-Y) (M_r; retention time / s)**			
	Indene	Arylalkene [a]	Arylalkane	Parent ketone
	R-indene	$R\text{-}CH_2CH_2COOMe$	R-CH=CHCOOMe	R-H
	(53)	**(54)**	**(55)**	**(56)**
	(222; 940)	(238; 960)	(240; 830)	(156; 260)
$ArMn(CO)_4$ **(41)**	58	35	5	2
ArHgCl **(112)**	3	85	3	9

[a] *E*-isomer. Another product (M_r 238; retention time 780 s) was, from its identical fragmentation pattern, the *Z*-isomer, but it was present in <0.5% yield in both the Mn and Hg cases.

4.4.5.2 Is Arylalkene a Source of Arylalkane by Hydride Transfer from HPdX Eliminated in Arylalkene Formation?

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (121 mg, 0.68 mmol) and LiCl (58 mg, 1.36 mmol) in dry acetonitrile (10 ml) were treated with methyl acrylate (0.31 ml, 3.40 mmol) and the orthomanganated thiophene [(**40**); 200 mg, 0.68 mmol]. The mixture was

refluxed for 3.5 hours. Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 43 mg, 0.18 mmol] was added to the reaction mixture immediately upon Pd(0) formation. The solution was worked up by the normal method and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit). One large band was removed from the plate (162 mg) and analysed by ^{13}C NMR. Yields were based on ^{13}C integral.

Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 36 mg, 25 %]
Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 95 mg, 66 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 31 mg, 72 % return]

4.4.5.3 Does the Indene Come From an Arylalkane Precursor?

(i) Does Increasing the Reflux Time Lead to an Increase in the Yield of Cyclised Product at the Expense of Arylalkane?

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated thiophene [**(41)**; 135 mg, 0.42 mmol] and methyl acrylate (0.19 ml, 2.11 mmol). The mixture was reluxed for 43 h, worked up by the standard method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 4 mg, 4 %]
The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 13 mg, 20 %]
Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 16 mg, 16 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 50 mg, 49 %]

(ii) Can the Base Cl⁻ Promote Aldol-Type Cyclisation in the Dipolar Aprotic Solvent Acetonitrile?

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (72 mg, 1.68 mmol) in dry acetonitrile (10 ml) were treated with the orthomanganated thiophene [**(41)**; 35 mg, 0.42 mmol] and methyl acrylate (0.19 ml, 2.11 mmol). The mixture was reluxed for 3 h, worked up by the standard method and chromatographed (p.l.c., 1:10 diethyl ether/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 5 mg, 5 %]
The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 13 mg, 20 %]
Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 16 mg, 16 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 48 mg, 48 %]

4.4.6 Thermally Promoted Coupling Reactions

4.4.6.1 Themally Promoted Coupling Reactions of a Range of Orthomanganated Aryl Ketones

4.4.6.1.1 Themally Promoted Coupling Reactions with Methyl Vinyl Ketone and Methyl Acrylate

Reaction of η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese (40) with Methyl Acrylate in Refluxing Carbon tetrachloride

η^2-(2-Acetylthien-3-yl)tetracarbonylmanganese [**(40)**; 185 mg, 0.63 mmol] in carbon tetrachloride (10 ml) was treated with methyl acrylate (0.29 ml, 3.17 mmol) and refluxed for 5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl 3-(2-acetylthien-3-yl)-propanoate [**(51)**; 33 mg, 25 %]

Methyl 6-methyl-4H-cyclopenta[d]thiophene-5-carboxylate [**(113)**; 46 mg, 37 %], a white solid, was recrystallized from pentane/dichloromethane as

tiny white plates, m.p. 66-67.5 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.40 (1H, *d*, $^3J_{3,2}$=4.8 Hz, H-3), 7.06 (1H, *d*, $^3J_{2,3}$=4.8 Hz, H-2), 3.80 (3H, *s*, 5-$COOCH_3$), 3.51 (2H, *q*, $^5J_{4,6\text{-}CH_3}$=2.1 Hz, H-4), 2.53 (3H, *t*, $^5J_{6\text{-}CH_3,4}$=2.1 Hz, 6-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 165.9 (*s*, 5-$\underline{C}OOCH_3$), 149.2 (*s*, C-6), 148.7 (*s*, C-3a), 148.1 (*s*, C-6a), 129.7 (*s*, C-5), 129.5 (*d*, C-3), 122.6 (*d*, C-2), 51.1 (*q*, 5-COO$\underline{C}H_3$), 36.2 (*t*, C-4), 14.6 (*q*, 6-CH_3). MS m/e 194 (P^+).

Methyl E-3-(2-acetylthien-3-yl)-prop-2-enoate [**(49)**; 13 mg, 10 %]

Reaction of η^2-(3-Acetylthien-2-yl)tetracarbonylmanganese (114) with Methyl Acrylate in Refluxing Benzene

η^2-(3-Acetylthien-2-yl)tetracarbonylmanganese [**(114)**; 130 mg, 0.45 mmol] in benzene (10 ml) was treated with methyl acrylate (0.21 ml, 2.23 mmol) and refluxed for 3.5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl 3-(3-acetylthien-2-yl)-propanoate [**(115)**; 78 mg, 83 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.34 (1H, *d*, $^3J_{5',4'}$=5.3 Hz, H-5'*), 7.06 (1H, *d*, $^3J_{4',5'}$=5.0 Hz, H-4'*), 3.66 (3H, *s*, 1-OCH_3), 3.44 (2H, *t*, $^3J_{3,2}$=7.4 Hz, H-3), 2.70 (2H, *t*, $^3J_{2,3}$=7.4 Hz, H-2), 2.49 (3H, *s*, 2'-$COCH_3$). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 193.9 (*s*, 3'-$\underline{C}OCH_3$), 172.9 (*s*, C-1), 152.0 (*s*, C-2'), 135.9 (*s*, C-3'), 129.1 (*d*, C-4'), 122.1 (*d*, C-5'), 51.7 (*q*, 1-OCH_3), 34.9 (*t*, C-2), 29.9 (*q*, 3'-CO$\underline{C}H_3$). 25.2 (*t*, C-3). MS m/e 212 (P^+).

Reaction of η^2-(3-Acetylthien-2-yl)tetracarbonylmanganese (114) with Methyl Acrylate in Refluxing Carbon tetrachloride

η^2-(3-Acetylthien-2-yl)tetracarbonylmanganese [**(114)**; 130 mg, 0.45 mmol] in carbon tetrachloride (10 ml) was treated with methyl acrylate (0.21 ml, 2.23 mmol) and refluxed for 3.5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl 3-(3-acetylthien-2-yl)-propanoate [**(115)**; 45 mg, 48 %]

Methyl (4S*, 5R*)-4-hydroxy-4-methyl-5,6-dihydro-4H-cyclopenta[d]-thiophene-5-carboxylate [**(117)**; 30 mg, 32 %] was recrystallized from

petroleum spirit as tiny white crystals, m.p. 44.5-46 °C. Anal. Found: C, 56.32; H, 5.44 %; $C_{10}H_{12}O_3S$ calcd: C, 56.58; H, 5.70 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.20 (1H, *d*, $^3J_{2,3}$=5.0 Hz, H-2), 6.89 (1H, *d*, $^3J_{3,2}$=5.0 Hz, H-3), 3.78 (3H, *s*, 5-$COOCH_3$), 3.61 (1H, *t*, $^3J_{5,6a}$=$^3J_{5,6b}$=8.0 Hz, H-5), 3.46 (1H, *dd*, $^2J_{6a,6b}$=15.9 Hz, $^3J_{6a,5}$=7.6 Hz, H-6a), 3.09 (1H, *dd*, $^2J_{6b,6a}$=15.9 Hz, $^3J_{6b,5}$=8.4 Hz, H-6b), 2.52 (1H, *s*, br, 4-OH), 1.75 (3H, *s*, 4-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 172.5 (*s*, 5-$\underline{C}OOCH_3$), 149.9 (*s*, C-6a), 142.3 (*s*, C-3a), 129.3 (*d*, C-2), 120.1 (*d*, C-3), 78.3 (*s*, C-4), 59.7 (*d*, C-5), 52.0 (*q*, 5-COO$\underline{C}H_3$), 29.7 (*t*, C-6), 27.4 (*q*, 4-CH_3). MS m/e 212 (P^+).

Methyl (4R*, 5R*)-4-hydroxy-4-methyl-5,6-dihydro-4H-cyclopenta[d]-thiophene-5-carboxylate [**(118)**; 5 mg, 5 %], a colourless oil. ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 172.5 (*s*, 5-$\underline{C}OOCH_3$), 149.8 (*s*, C-6a), 140.0 (*s*, C-3a), 129.3 (*d*, C-2), 120.0 (*d*, C-3), 80.6 (*s*, C-4), 62.9 (*d*, C-5), 51.9 (*q*, 5-COO$\underline{C}H_3$), 29.7 (*t*, C-6), 24.7 (*q*, 4-CH_3).

Methyl 4-methyl-6H-cyclopenta[d]thiophene-5-carboxylate [**(116)**; trace amount]. MS m/e 194 (P^+).

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Methyl Vinyl Ketone in Refluxing Benzene

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in benzene (10 ml) was treated with methyl vinyl ketone (0.18 ml, 2.18 mmol) and refluxed for 1.5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

1-(1,3,6-Trimethyl-4H-cyclopenta[c]thien-5-yl)-ethanone [**(120)**; 64 mg, 74 %], which after recrystallization from hexane/chloroform gave white needles, m.p. 68.5-70 °C. Anal. Found: C, 70.05; H, 6.83 %; $C_{12}H_{14}OS$ calcd: C, 69.86; H, 6.84 %. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 3.28 (2H, *m*, br, H-4'), 2.55 (3H, *s*, H-2), 2.53 (3H, *t*, $^5J_{6'\text{-}CH_3,4'}$=2.3 Hz, 6'-CH_3), 2.35 (3H, *s*, 1'-CH_3), 2.33 (3H, *s*, br, 3'-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 197.8 (*s*, C-1), 147.6 (*s*, C-6'), 146.5 (*s*, C-6a'), 140.8 (*s*, C-3a'), 140.5 (*s*, C-5'), 129.2 (*s*, C-1'), 125.1 (*s*, C-3'), 32.1 (*t*, C-4'), 30.2 (*q*, C-2), 14.7 (*q*, 6'-CH_3), 13.3 (*q*, 1'-CH_3), 13.1 (*q*, 3'-CH_3). MS m/e 206 (P^+).

4-(4-Acetyl-2,5-dimethyl-thien-3-yl)-butan-2-one [**(119)**; 14 mg, 15 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 2.83 (2H, *t*, $^{3}J_{4,3}$=7.7 Hz, H-4), 2.61 (2H, *t*, $^{3}J_{3,4}$=7.7 Hz, H-3), 2.58 (3H, *s*, -CH_3), 2.47 (3H, *s*, -CH_3), 2.27 (3H, *s*, -CH_3), 2.13 (3H, *s*, -CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 208.5 (*s*, C-2), 197.8 (*s*, 4'-$\underline{C}OCH_3$), 140.7 (*s*), 139.0 (*s*), 136.8 (*s*), 130.7 (*s*), 44.1 (*t*, C-3), 31.8 (*q*, 4'-CO$\underline{C}H_3$), 29.9 (*q*, C-1), 22.2 (*t*, C-4), 16.1 (*q*, -CH_3), 12.5 (*q*, -CH_3).

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Methyl Vinyl Ketone in Refluxing Carbon tetrachloride

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in carbon tetrachloride (10 ml) was treated with methyl vinyl ketone (0.18 ml, 2.18 mmol) and refluxed for 1.5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

1-(1,3,6-trimethyl-4H-cyclopenta[c]thien-5-yl)-ethanone [**(120)**; 55 mg, 63 %]

4-(4-acetyl-2,5-dimethylthien-3-yl)-butan-2-one [**(119)**; 13 mg, 14 %]

A mixture of the indanols (4S*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(121)** and (4R*, 5R*)-1-(4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(122)**. [a combined yield of 19 mg, 20 %]:

(4S*, 5R*)-1-(4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(121)**. ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 210.3 (*s*, C-1), 145.9 (*s*, C-3a'), 138.4 (*s*, C-6a'), 128.5 (*s*, C-3'), 125.7 (*s*, C-1'), 77.3 (*s*, C-4'), 66.5 (*d*, C-5'), 30.7 (*q*, C-2), 27.0 (*q*, 4'-CH_3), 26.7 (*t*, C-6'), 13.0 (*q*, 1'-CH_3), 12.4 (*q*, 3'-CH_3).

(4R*, 5R*)-1-(4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone **(122)**. ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 207.9 (*s*, C-1), 146.6 (*s*, C-3a'), 140.1 (*s*, C-6a'), 127.4 (*s*, C-3'), 126.1 (*s*, C-1'), 79.6 (*s*, C-4'), 70.6 (*d*, C-5'), 30.8 (*q*, C-2), 24.6 (*t*, C-6'), 23.1 (*q*, 4'-CH_3), 12.8 (*q*, 1'-CH_3), 11.9 (*q*, 3'-CH_3).

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Methyl Acrylate in Refluxing Carbon tetrachloride

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in carbon tetrachloride (10 ml) was treated with methyl acrylate (0.19 ml, 2.18 mmol) and refluxed overnight. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 53 mg, 3 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.62 (3H, *s*, 1-OCH_3), 2.89 (2H, *t*, $^3J_{3,2}$=7.8 Hz, H-3), 2.51 (3H, *s*, -CH_3), 2.45 (2H, *t*, $^3J_{2,3}$=7.9 Hz, H-2), 2.45 (3H, *s*, -CH_3), 2.26 (3H, *s*, -CH_3).^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 197.6 (*s*, 4'-$\underline{C}OCH_3$), 173.5 (*s*, C-1), 140.7 (*s*), 138.8 (*s*), 136.3 (*s*), 131.1 (*s*), 51.5 (*q*, 1-OCH_3), 34.5 (*t*, C-2), 31.7 (*q*, 4'-$CO\underline{C}H_3$), 23.2 (*t*, C-3), 16.0 (*q*, -CH_3), 12.5 (*q*, -CH_3). MS m/e 240 (P^+).

Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 1 mg, ~1 %]

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 11 mg, 12 %]

Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 47 mg, 47 %], recrystallized from hexane as prismatic white crystals, m.p. 84-85 °C. Anal. Found: C, 59.92; H, 6.70 %; $C_{12}H_{16}O_3S$ calcd: C, 59.97; H, 6.71 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.76 (3H, *s*, 5-$COOCH_3$), 3.37 (1H, *t*, $^3J_{5,6}$=8.5 Hz, H-5), 2.95 (1H, *dd*, $^2J_{6b,6a}$=15.8 Hz, $^3J_{6b,5}$=8.5 Hz, H-6b), 2.91 (1H, *s*, br, 4-OH), 2.74 (1H, *dd*, $^2J_{6a,6b}$=15.8 Hz, $^3J_{6a,5}$=8.5 Hz, H-6a), 2.40 (3H, *s*, 3-CH_3), 2.23 (3H, *s*, 1-CH_3), 1.75 (3H, *s*, 4-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 173.3 (*s*, 5-$\underline{C}OOCH_3$), 145.5 (*s*, C-3a), 140.6 (*s*, C-6a), 128.9 (*s*, C-3), 125.6 (*s*, C-1), 77.3 (*s*, C-4), 60.0 (*d*, C-5), 51.9 (*q*, 5-$COO\underline{C}H_3$), 26.9 (*t*, C-6), 26.2 (*q*, 4-CH_3), 13.0 (*q*, 1-CH_3), 12.5 (*q*, 3-CH_3). MS m/e 240 (P^+).

Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 18 mg, 18 %], recrystallized from hexane as prismatic white crystals, m.p. 81-82 °C. Anal. Found: C, 59.94; H, 6.59 %; $C_{12}H_{16}O_3S$ calcd: C, 59.97; H, 6.71 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.78 (3H, *s*, 5-$COOCH_3$), 3.49 (1H, *dd*, ^{3}J=10.1 Hz, ^{3}J=8.5 Hz, H-5), 2.74 (2H, *m*,

H-6a,6b), 2.49 (1H, *s*, br, 4-OH), 2.40 (3H, *s*, 3-CH_3), 2.23 (3H, *s*, 1-CH_3), 1.37 (3H, *s*, 4-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 172.6 (*s*, 5-$\underline{C}OOCH_3$), 145.5 (*s*, C-3a), 138.1 (*s*, C-6a), 128.0 (*s*, C-3), 126.1 (*s*, C-1), 79.3 (*s*, C-4), 62.7 (*d*, C-5), 51.8 (*q*, 5-COO$\underline{C}H_3$), 25.9 (*t*, C-6), 23.9 (*q*, 4-CH_3), 12.9 (*q*, 1-CH_3), 12.0 (*q*, 3-CH_3). MS m/e 240 (P^+).

A mixture of the indanols **(123)** and **(124)** [49 mg, 0.20 mmol] was treated with a catalytic amount of *p*-toluenesulphonic acid in acetonitrile (10 ml) and stirred overnight to give methyl 1,3,6-trimethyl-4H-cyclopenta[c]-thiophene-5-carboxylate [**(53)**; 41 mg, 91 %].

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Methyl Acrylate in Refluxing Acetonitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in acetonitrile (10 ml) was treated with methyl acrylate (0.19 ml, 2.18 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 12 mg, 13 %]

Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 18 mg, 17 %]

Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 13 mg, 12 %]

Methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(125)**; 11 mg, 8 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.91 (1H, *m*, H-2), 3.64 (3H, *s*, 1-OCH_3), 3.13 (2H, *m*, H-3), 2.57 (3H, *s*, -CH_3), 2.48 (3H, *s*, -CH_3), 2.27 (3H, *s*, -CH_3), 2.19 (3H, *s*, -CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 203.4 (*s*, 2-$\underline{C}OCH_3$), 197.2 (*s*, 4'-$\underline{C}OCH_3$), 170.1 (*s*, C-1), 142.3 (*s*, C-4'), 138.2 (*s*, C-3'), 134.2 (*s*, C-5'), 132.5 (*s*, C-2'), 59.2 (*d*, C-2), 52.3 (*q*, 1-OCH_3), 31.9 (*q*, 4'-CO$\underline{C}H_3$), 29.8 (*q*, 2-CO$\underline{C}H_3$), 26.5 (*t*, C-3), 16.6 (*q*, 2'-CH_3), 12.7 (*q*, 5'-CH_3).

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Methyl Vinyl Ketone in Refluxing Benzene

η^2-(2-Acetylphenyl)tetracarbonylmanganese [**(2)**; 190 mg, 0.66 mmol] in benzene (10 ml) was treated with methyl vinyl ketone (0.28 ml, 3.32 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:7 diethyl ether/petroleum spirit) to give:

1-(3-Methylinden-2-yl)-ethanone [**(70)**; 96 mg, 84 %]

Reaction of η^2-(2-Acetylphenyl)tetracarbonylmanganese (2) with Methyl Acrylate in Refluxing Carbon tetrachloride

η^2-(2-Acetylphenyl)tetracarbonylmanganese [**(2)**; 155 mg, 0.54 mmol] in carbon tetrachloride (10 ml) was treated with methyl acrylate (0.25 ml, 2.71 mmol) and refluxed for 8 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl (3-methylinden-2-yl)-carboxylate [**(60)**; 68 mg, 67 %]

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Methyl Vinyl Ketone in Refluxing Carbon tetrachloride

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 151 mg, 0.48 mmol] in carbon tetrachloride (10 ml) was treated with methyl vinyl ketone (0.20 ml, 2.39 mmol) and refluxed for 2 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:3 diethyl ether/petroleum spirit) to give:

1-(6-Methoxy-3-methylinden-2-yl)-ethanone [**(73)**; 91 mg, 94 %]

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Methyl Acrylate in Refluxing Carbon tetrachloride

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 180 mg, 0.57 mmol] in carbon tetrachloride (10 ml) was treated with methyl acrylate (0.26 ml, 2.85 mmol) and refluxed overnight. The solution was evaporated

to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

The parent ketone 4'-methoxyacetophenone [**(72)**; 5 mg, 6 %]

Methyl 3-(2-acetyl-5-methoxyphenyl)-propanoate [**(75)**; 15 mg, 11 %]

Methyl (1S*,2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate [**(131)**; 77 mg, 57 %], a colourless oil, which was crystallized from petroleum spirit/diethyl ether as white regular blocks, m.p. 66.5-69 °C. Anal. Found: C, 66.09; H, 7.04 %; $C_{13}H_{16}O_4$ calcd: C, 66.09; H, 6.83 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.26 (1H, *d*, $^3J_{7,6}$=8.3 Hz, H-7), 6.80 (1H, *dd*, $^3J_{6,7}$=8.3 Hz, $^4J_{6,4}$=2.4 Hz, H-6), 6.77 (1H, *d*, $^4J_{4,6}$=2.4 Hz, H-4), 3.78 (3H, *s*, 5-OCH_3*), 3.77 (3H, *s*, 2-$COOCH_3$*), 3.40 (1H, *dd*, $^2J_{3a,3b}$=15.7 Hz, $^3J_{3a,2}$=8.2 Hz, H-3a), 3.21 (1H, *t*, $^3J_{2,3a}$=$^3J_{2,3b}$=8.2 Hz, H-2), 3.04 (1H, *dd*, $^2J_{3b,3a}$=15.7 Hz, $^3J_{3b,2}$=8.2 Hz, H-3b), 2.70 (1H, *s*, br, 1-OH), 1.74 (3H, *s*, 1-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 173.3 (*s*, 2-$\underline{C}OOCH_3$), 160.5 (*s*, C-5), 142.6 (*s*, C-3a), 138.5 (*s*, C-7a), 123.7 (*d*, C-7), 113.5 (*d*, C-6), 109.7 (*d*, C-4), 80.7 (*s*, C-1), 55.4 (*q*, 5-OCH_3), 55.1 (*d*, C-2), 51.9 (*q*, 2-$COO\underline{C}H_3$), 32.8 (*t*, C-3), 26.8 (*q*, 1-CH_3). MS m/e 236 (P^+).

Methyl (1R*, 2R*)-(1-hydroxy-5-methoxy-1-methylindan-2-yl)-carboxylate [**(132)**; 19 mg, 14 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.24 (1H, *d*, $^3J_{7,6}$=8.3 Hz, H-7), 6.80 (1H, *dd*, $^3J_{6,7}$=8.3 Hz, $^4J_{6,4}$=2.4 Hz, H-6), 6.73 (1H, *d*, $^4J_{4,6}$=2.4 Hz, H-4), 3.78 (3H, *s*, 5-OCH_3*), 3.77 (3H, *s*, 2-$COOCH_3$*), 3.34 (1H, *dd*, $^3J_{2,3a}$=9.6 Hz, $^3J_{2,3b}$=8.2 Hz, H-2), 3.20 (1H, *dd*, $^2J_{3a,3b}$=15.7 Hz, $^3J_{3a,2}$=9.6 Hz, H-3a), 3.04 (1H, *dd*, $^2J_{3b,3a}$=15.7 Hz, $^3J_{3b,2}$=8.2 Hz, H-3b), 2.48 (1H, *s*, br, 1-OH), 1.36 (3H, *s*, 1-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 173.2 (*s*, 2-$\underline{C}OOCH_3$), 160.2 (*s*, C-5), 140.5 (*s*, C-3a), 139.4 (*s*, C-7a), 123.3 (*d*, C-7), 113.5 (*d*, C-6), 109.7 (*d*, C-4), 82.3 (*s*, C-1), 58.5 (*d*, C-2), 55.4 (*q*, 5-OCH_3), 51.8 (*q*, 2-$COO\underline{C}H_3$), 32.0 (*t*, C-3), 25.2 (*q*, 1-CH_3). MS m/e 236 (P^+).

Reaction of η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (35) with Methyl Acrylate in Refluxing Benzene

η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese [**(35)**; 160 mg, 0.43 mmol] in benzene (10 ml) was treated with methyl acrylate (0.19 ml, 2.13 mmol) and refluxed for 2 hours. The solution was evaporated to

dryness under reduced pressure and chromatographed (p.l.c, 1:10 ethyl acetate/petroleum spirit) to give:

4,5,6-Trimethoxy-3-methylindene [**(133)**; 7 mg, 8 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 6.84 (1H, *d*, H-7), 5.96 (1H, *m*, H-2), 3.92 (3H, *s*, 4-OCH_3), 3.88 (3H, *s*, 6-OCH_3*), 3.87 (3H, *s*, 5-OCH_3*), 3.23 (2H, *m*, H-1), 2.29 (3H, *m*, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 151.8 (*s*, C-6), 148.1 (*s*, C-4), 141.2 (*s*, C-5*), 141.1 (*s*, C-3*), 139.9 (*s*, C-7a), 131.3 (*s*, C-3a), 126.9 (*d*, C-2), 104.4 (*d*, C-7), 61.7 (*q*, 4-OCH_3), 61.0 (*q*, 5-OCH_3), 56.4 (*q*, 6-OCH_3), 38.0 (*t*, C-1), 15.7 (*q*, 3-CH_3). MS m/e 220 (P^+).

Methyl (4,5,6-trimethoxy-3-methylinden-2-yl)-carboxylate [**(84)**; 28 mg, 24 %]

4.4.6.1.2 Thermally Promoted Coupling Reactions with Other Alkenes

(i) Terminal Alkenes

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Acrylonitrile in Refluxing Carbon tetrachloride

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol) in carbon tetrachloride (10 ml) was treated with acrylonitrile (0.14 ml, 2.11 mmol) and refluxed for 1.5 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:3 diethyl ether/petroleum spirit) to give:

1,3,6-Trimethyl-4H-cyclopenta[c]thiophene-5-carbonitrile [**(127)**; 1 mg, ~1 %] was recrystallized from hexane/chloroform as white feathers, m.p. 111-112 °C. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 3.19 (2H, *s*, br, H-4), 2.50 (3H, *s*, 1-CH_3), 2.36 (3H, *t*, $^5J_{6\text{-}CH_3,4}$=2.3 Hz, 6-CH_3), 2.30 (3H, *s*, 3-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 153.1 (*s*, C-6), 143.5 (*s*, C-6a), 140.1 (*s*, C-3a), 128.5 (*s*, C-1), 126.3 (*s*, C-3), 117.6 (*s*, 5-CN), 112.2 (*s*, C-5), 32.3 (*t*, C-4), 14.6 (*q*, 6-CH_3), 13.1 (*q*, 1-CH_3), 13.0 (*q*, 3-CH_3). MS m/e 189 (P^+).

3-(4-Acetyl-2,5-dimethylthien-3-yl)-propanenitrile [**(126)**; 4 mg, 5 %]. MS m/e 207 (P^+).

(4R*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carbonitrile [**(129)**; 18 mg, 21 %], a colourless oil. ^{1}H NMR:

(300.13 MHz) ($CDCl_3$) δ 3.42 (1H, *dd*, ^3J=9.6 Hz, ^3J=8.3 Hz, H-5), 2.98 (1H, *dd*, ^2J=15.3 Hz, ^3J=8.3 Hz, H-6), 2.75 (1H, *s*, br, 4-OH), 2.66 (1H, *dd*, ^2J=15.3 Hz, ^3J=9.6 Hz, H-6), 2.38 (3H, *s*, 3-CH_3), 2.23 (3H, *s*, 1-CH_3), 1.65 (3H, *s*, 4-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 144.0 (*s*, C-3a), 136.9 (*s*, C-6a), 129.1 (*s*, C-3), 127.0 (*s*, C-1), 119.5 (*s*, br, 5-CN), 78.8 (*s*, C-4), 48.1 (*d*, C-5), 28.4 (*t*, C-6), 24.4 (*q*, 4-CH_3), 12.9 (*q*, 1-CH_3), 12.0 (*q*, 3-CH_3).

(4S*, 5S*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carbonitrile [**(128)**; 44 mg, 50 %], a colourless oil. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 3.34 (1H, *t*, $^3J_{5,6}$=8.2 Hz, H-5), 2.90 (2H, *m*, H-6a,6b), 2.54 (1H, *s*, br, 4-OH), 2.39 (3H, *s*, 3-CH_3), 2.23 (3H, *s*, 1-CH_3), 1.72 (3H, *s*, 4-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 143.3 (*s*, C-3a), 138.8 (*s*, C-6a), 130.0 (*s*, C-3), 127.0 (*s*, C-1), 119.5 (*s*, br, 5-CN), 77.0 (*s*, C-4), 47.9 (*d*, C-5), 28.2 (*t*, C-6), 25.4 (*q*, 4-CH_3), 13.0 (*q*, 1-CH_3), 12.5 (*q*, 3-CH_3).

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Acrolein in Refluxing Benzene

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in benzene (10 ml) was treated with acrolein (0.14 ml, 2.11 mmol) and refluxed for 6 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

1,3,6-Trimethyl-4H-cyclopenta[c]thiophene-5-carbaldehyde [**(130)**; 13 mg, 16 %], a colourless oil. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 10.10 (1H, *s*, 5-COH), 3.20 (2H, *s*, br, H-4), 2.57 (3H, *s*, 1-CH_3), 2.52 (3H, *t*, $^5J_{6\text{-}CH_3,4}$=2.1 Hz, 6-CH_3), 2.32 (3H, *s*, 3-CH_3). MS m/e 192 (P^+).

(ii) Chalcones

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with 1-(3-Methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one (134) in Refluxing Hexane

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 89 mg, 0.28 mmol] and the chalcone [**(134)**; 86 mg, 0.28 mmol] were refluxed in hexane (10 ml) for 3 hours. The solution was evaporated to dryness under reduced

pressure and chromatographed (p.l.c., 1:3 dichloromethane/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 64 mg, 73 % return]

1-(3-Methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(134)**; 63 mg, 72 % return]. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 8.13 (1H, *dd*, J=15.6 Hz, J=2.1 Hz, H-3), 7.81 (1H, *d*, J=7.7 Hz, H-6''), 7.70 (1H, *d*, J=7.7 Hz, H-3''), 7.58 (2H, *m*, H-4'',6'), 7.54 (1H, *d*, J=2.6 Hz, H-2'), 7.47 (1H, *t*, J=7.7 Hz, H-5''), 7.40 (1H, *d*, J=15.6 Hz, H-2), 7.38 (1H, *t*, J=7.8 Hz, H-5'), 7.12 (1H, *dd*, J=7.8 Hz, J=2.6 Hz, H-4'), 3.84 (3H, *s*, 3'-OCH_3).

3-Methoxyphenyl 3-(2-trifluoromethylphenyl)-1-hydroxy-5-methoxy-1-methylindan-2-yl ketone [**(135)**; 12 mg, 9 %] which was recrystallized from petroleum spirit/chloroform as white granular crystals, m.p. 95-97 °C. Anal. Found: C, 68.27; H, 5.47 %; $C_{26}H_{23}O_4F_3$ calcd: C, 68.41; H, 5.08 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.59 (1H, *d*, $^3J_{3''',4'''}$=7.6 Hz, H-3'''), 7.49 (1H, *t*, $^3J_{4''',5'''}$=$^3J_{4''',3'''}$=7.6 Hz, H-4'''), 7.36-7.27 (3H, *m*, H-5''',7'',2'), 7.26-7.21 (2H, *m*, H-5',6'), 7.19 (1H, *d*, $^3J_{6''',5'''}$=7.5 Hz, H-6'''), 7.04 (1H, *dt*, $^3J_{4',5'}$=7.2 Hz, ^{4}J=2.3 Hz, ^{4}J=1.9 Hz, H-4'), 6.89 (1H, *dd*, $^3J_{6'',7''}$=8.3 Hz, $^4J_{6'',4''}$=1.8 Hz, H-6''), 6.35 (1H, *d*, $^4J_{4'',6''}$=1.8 Hz, H-4''), 5.39 (1H, *d*, $^3J_{3'',2''}$=7.4 Hz, H-3''), 4.33 (1H, *d*, $^3J_{2'',3''}$=7.4 Hz, H-2''), 3.79 (3H, *s*, 3'-OCH_3), 3.71 (3H, *s*, 5''-OCH_3), 3.61 (1H, *s*, br, 1''-OH), 1.76 (3H, *s*, 1''-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 201.2 (*s*, C-1), 160.9 (*s*, C-5''), 159.8 (*s*, C-3'), 146.7 (*s*, C-3a''), 142.3 (*s*, C-1'''), 139.6 (*s*, C-7a''), 139.3 (*s*, C-1'), 132.3 (*d*, C-4'''), 129.8 (*d*, C-6'''), 129.4 (*d*, C-5'), 127.0 (*d*, C-5'''), 125.8 (*m*, J=5.5 Hz, C-3'''), 123.5 (*d*, C-7''), 121.1 (*d*, C-6'), 120.1 (*d*, C-4'), 114.6 (*d*, C-6''), 112.6 (*d*, C-2'), 110.0 (*d*, C-4''), 81.5 (*s*, C-1''), 65.3 (*d*, C-2''), 55.5 (*q*, 5''-OCH_3*), 55.4 (*q*, 3'-OCH_3*), 48.6 (*d*, C-3''), 28.3 (*q*, 1''-CH_3) (C-2''' and 2'''-CF_3 were not observed).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with 1-(4-Methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one (136) in Refluxing Hexane

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 201 mg, 0.64 mmol] and 1-(4-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(136)**; 195 mg, 0.64 mmol] were refluxed in hexane (10 ml) overnight.

The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:3 dichloromethane/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 31 mg, 15 % return]

The parent ketone 4'-methoxyacetophenone [**(72)**; 20 mg, 21 %]

3-(2-Trifluoromethylphenyl)-1,5-di(4-methoxyphenyl)-pentane-1,5-dione [**(138)**; 24 mg, 8 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.95 (4H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=8.9 Hz, H-2',6'), 7.62 (1H, *d*, $^3J_{3'',4''}$=7.8 Hz, H-3''), 7.56 (1H, *d*, $^3J_{6'',5''}$=7.6 Hz, H-6''), 7.50 (1H, *dd*, $^3J_{5'',6''}$=7.6 Hz, $^3J_{5'',4''}$=7.5 Hz, H-5''), 7.29 (1H, *dd*, $^3J_{4'',3''}$=7.8 Hz, $^3J_{4'',5''}$=7.5 Hz, H-4''), 6.91 (4H, *d*, $^3J_{3',2'}=^3J_{5',6'}$=8.9 Hz, H-3',5'), 4.44 (1H, *m*, H-3), 3.83 (6H, *s*, 4'-OCH_3), 3.52 (2H, *dd*, $^2J_{2a,2b}$=16.2 Hz, $^3J_{2a,3}$=7.5 Hz, H-2a), 3.25 (2H, *dd*, $^2J_{2b,2a}$=16.2 Hz, $^3J_{2b,3}$=6.5 Hz, H-2b). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 196.7 (*s*, C-1,5), 163.6 (*s*, C-4'), 142.8 (*s*, C-1''), 132.0 (*d*, C-5''), 130.6 (*d*, C-2',6'), 129.9 (*s*, C-1'), 128.1 (*d*, C-6''), 126.6 (*d*, C-4''), 126.3 (*m*, J=5.5 Hz, C-3''), 113.8 (*d*, C-3',5'), 55.5 (*q*, 4'-OCH_3), 44.4 (*t*, C-2,4), 33.3 (*d*, C-3) (C-2'' and 2''-CF_3 were not observed). MS m/e 456 (P^+).

4-Methoxyphenyl 3-(2-trifluoromethylphenyl)-1-hydroxy-5-methoxy-1-methylindan-2-yl ketone [**(137)**; 39 mg, 13 %] was crystallized by vapour diffusion of heptane into a saturated benzene solution at 4 °C as pale yellow globular balls, m.p. 158-161 °C. Anal. Found: C, 68.40; H, 5.27 %; $C_{26}H_{23}O_4F_3$ calcd: C, 68.41; H, 5.08 %. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.71 (2H, *d*, $^3J_{2',3'}=^3J_{6',5'}$=8.9 Hz, H-2',6'), 7.57 (1H, *d*, $^3J_{3''',4'''}$=7.7 Hz, H-3'''), 7.50 (1H, *dd*, $^3J_{4''',3'''}$=7.7 Hz, $^3J_{4''',5'''}$=7.4 Hz, H-4'''), 7.35 (1H, *d*, $^3J_{7'',6''}$=8.4 Hz, H-7''), 7.31 (1H, *dd*, $^3J_{5''',6'''}$=7.8 Hz, $^3J_{5''',4'''}$=7.4 Hz, H-5'''), 7.23 (1H, *d*, $^3J_{6''',5'''}$=7.8 Hz, H-6'''), 6.88 (1H, *dd*, $^3J_{6'',7''}$=8.4 Hz, $^4J_{6'',4''}$=1.9 Hz, H-6''), 6.79 (2H, *d*, $^3J_{3',2'}=^3J_{5',6'}$=8.9 Hz, H-3',5'), 6.34 (1H, *d*, $^4J_{4'',6''}$=1.9 Hz, H-4''), 5.34 (1H, *d*, $^3J_{3'',2''}$=7.9 Hz, H-3''), 4.27 (1H, *d*, $^3J_{2'',3''}$=7.9 Hz, H-2''), 4.18 (1H, *s*, br, 1''-OH), 3.81 (3H, *s*, 4'-OCH_3), 3.70 (3H, *s*, 5''-OCH_3), 1.75 (3H, *s*, 1''-CH_3). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 200.1 (*s*, C-1), 163.9 (*s*, C-4'), 160.8 (*s*, C-5''), 147.0 (*s*, C-3a''), 142.3 (*s*, C-1'''), 139.6 (*s*, C-7a''), 132.2 (*d*, C-4'''), 131.2 (*s*, C-1'), 130.9 (*d*, C-2',6'), 129.9 (*d*, C-6'''), 127.0 (*d*, C-5'''), 125.7 (*m*, J=5.6 Hz, C-3'''), 123.4 (*d*, C-7''), 114.4 (*d*, C-6''), 113.7 (*d*, C-3',5'), 110.2 (*d*, C-4''), 81.3 (*s*, C-1''), 64.4 (*d*, C-2''), 55.5 (*q*, 4',5''-OCH_3), 48.8 (*d*, C-3''), 27.9 (*q*, 1''-CH_3) (C-2''' and 2'''-CF_3 were not observed). MS m/e 438 (P-18, P-H_2O).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with 1-(3,4,5-Trimethoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one (139) in Refluxing Heptane

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 227 mg, 0.72 mmol] and 1-(3,4,5-trimethoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(139)**; 263 mg, 0.72 mmol] were refluxed in heptane (10 ml) overnight. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:3 dichloromethane/petroleum spirit) to give:

The parent ketone 4'-methoxyacetophenone [**(72)**; 61 mg, 56 %]
3',4',5'-Trimethoxyacetophenone [**(87)**; 73 mg, 48 %]

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with 1-(4-Methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one (136) in Refluxing Carbon tetrachloride

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 205 mg, 0.65 mmol and 1-(4-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(136)**; 199 mg, 0.65 mmol] were refluxed in carbon tetrachloride (10 ml) overnight. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:2 dichloromethane/petroleum spirit) to give:

Recovered 1-(4-methoxyphenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(136)**; 106 mg, 53 % return]. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 8.10 (1H, *dd*, ^{3}J=15.7 Hz, J=2.0 Hz, H-3), 8.02 (2H, *d*, ^{3}J=8.6 Hz, H-2',6'), 7.82 (1H, *d*, ^{3}J=7.7 Hz, H-6"), 7.72 (1H, *d*, ^{3}J=7.7 Hz, H-3"), 7.60 (1H, *t*, ^{3}J=^{3}J=7.7 Hz, H-4"), 7.49 (1H, *t*, ^{3}J=^{3}J=7.7 Hz, H-5"), 7.42 (1H, *d*, ^{3}J=15.7 Hz, H-2), 6.99 (2H, *d*, ^{3}J=8.6 Hz, H-3',5'), 3.89 (3H, *s*, 4'-OCH_3).

The parent ketone 4'-methoxyacetophenone [**(72)**; 13 mg, 13 %]

2-(2-Acetyl-5-methoxyphenyl)-4-methoxyacetophenone [**(140)**; 27 mg, 28 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.89 (2H, *d*, $^3J_{6',5'}$=8.7 Hz, H-6'), 6.91 (2H, *dd*, $^3J_{5',6'}$=8.7 Hz, $^4J_{5',3'}$=2.6 Hz, H-5'), 6.64 (2H, *d*, $^4J_{3',5'}$=2.6 Hz, H-3'), 3.82 (6H, *s*, 4'-OCH_3), 2.26 (6H, *s*, H-2).^{13}C NMR: (75.34 MHz) ($CDCl_3$) δ 199.1 (*s*, C-1), 161.7 (*s*, C-4'), 144.2 (*s*, C-2'), 131.5 (*d*,

C-6'), 130.7 (*s*, C-1'), 116.0 (*d*, C-5'), 112.4 (*d*, C-3'), 55.5 (*q*, 4'-OCH_3), 28.8 (*q*, C-2). MS m/e 255 (P-43, P-$COCH_3$).

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with Ethyl E-3-phenylpropenoate (ethyl cinnamate) (141) in Refluxing Hexane

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 344 mg, 1.09 mmol] and ethyl cinnamate [**(141)**; 192 mg, 1.09 mmol] were refluxed in hexane (10 ml) overnight. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 182 mg, 53 % return]

Returned ethyl E-3-phenylpropenoate (ethyl cinnamate) [**(141)**; 119 mg, 62 % return]. ^1H NMR: (300.13 MHz) ($CDCl_3$) δ 7.68 (1H, *d*, $^3J_{1,2}$=16.0 Hz, H-1), 7.51-7.48 (2H, *m*, H-3',5'), 7.36-7.34 (3H, *m*, H-2',6'), 6.43 (1H, *d*, $^3J_{2,1}$=16.0 Hz, H-2), 4.25 (2H, *q*, $^3J_{4,5}$=7.1 Hz, H-4), 1.32 (3H, *t*, $^3J_{5,4}$=7.1 Hz, H-5). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 167.0 (*s*, C-1), 144.7 (*d*, C-3), 134.5 (*s*, C-1'), 130.2 (*d*, C-4'), 128.9 (*d*, C-3',5'), 128.1 (*d*, C-2',6'), 118.3 (*d*, C-2), 60.5 (*t*, 1-O$\underline{C}H_2CH_3$), 14.4 (*q*, 1-$OCH_2\underline{C}H_3$).

The parent ketone 4'-methoxyacetophenone [**(72)**; 16 mg, 10 %]

Reaction of η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (39) with 1-(4-Bromophenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one (142) and Me_3NO in Refluxing Acetonitrile

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 190 mg, 0.60 mmol] and Me_3NO (45 mg, 0.60 mmol) were stirred in acetonitrile (10 ml) for 5 minutes and then treated with 1-(4-bromophenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(142)**; 214 mg, 0.60 mmol]. The solution was refluxed overnight, evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:2 dichloromethane/petroleum spirit) to give:

Recovered η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese [**(39)**; 9 mg, 5 % return]
The parent ketone 4'-methoxyacetophenone [**(72)**; 72 mg, 80 %]
Recovered 1-(4-bromophenyl)-3-(2-trifluoromethylphenyl)-prop-2-en-1-one [**(142)**; 180 mg, 84 % return]

4.4.6.2 Attempted Coupling of an Arylamine

Reaction of η^2-(8-Dimethylamino-1-naphthyl)tetracarbonylmanganese (12) with Methyl Acrylate in Refluxing Benzene

η^2-(8-Dimethylamino-1-naphthyl)tetracarbonylmanganese [**(12)**; 226 mg, 0.67 mmol] in benzene (10 ml) was treated with methyl acrylate (0.30 ml, 3.36 mmol) and refluxed overnight. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

The parent arylamine *N,N*-dimethyl-1-naphthylamine [**(101)**; 26 mg, 23 %]

Methyl 3-(8-dimethylamino-1-naphthyl)-propanoate [**(108)**; 14 mg, 8 %], a colourless oil. ^{1}H NMR: (300.13 MHz) ($CDCl_3$) δ 7.70 (1H, *dd*, $^3J_{7',6'}$=7.6 Hz, $^4J_{7',5'}$=1.9 Hz, H-7'), 7.58 (1H, *dd*, $^3J_{4',3'}$=8.0 Hz, $^4J_{4',2'}$=1.0 Hz, H-4'), 7.39 (1H, *t*, ^3J=7.7 Hz), 7.37-7.27 (3H, *m*), 3.65 (2H, *t*, $^3J_{3,2}$=7.8 Hz, H-3), 3.64 (3H, *s*, 1-OCH_3), 2.67 (6H, *s*, 1'-$N(CH_3)_2$), 2.53 (2H, *t*, $^3J_{2,3}$=7.8 Hz, H-2). ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 174.3 (*s*, C-1), 152.0 (*s*, C-1'), 137.4 (*s*, C-8'), 136.7 (*s*, C-4a'), 129.2 (*d*, C-5), 128.2 (*d*, C-7'), 127.7 (*s*, C-8a'), 125.4 (*d*, C-3',6'), 125.3 (*d*, C-4'), 117.3 (*d*, 2'), 51.4 (*q*, 1-OCH_3), 46.0 (*q*, 1'-$N(CH_3)_2$), 36.8 (*t*, C-2), 32.9 (*t*, C-3). MS m/e 257 (P^+).

Recovered η^2-(8-dimethylamino-1-naphthyl)tetracarbonylmanganese [**(12)**; 52 mg, 23 %]

4.4.7 Changing the Reactivity of the Metal Centre

4.4.7.1 Changing the Ligand

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.19 ml, 2.11 mmol) and the orthomanganated ketone [**(41)**; 135 mg, 0.42 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:8 diethyl ether/petroleum spirit to give:.

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 5 mg, 5 %]
The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 11 mg, 17 %]
Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 19 mg, 19 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 57 mg, 57 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (41) with Methyl Acrylate in Refluxing Acetonitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese [**(41)**; 135 mg, 0.42 mmol] in acetonitrile (10 ml) was treated with methyl acrylate (0.19 ml, 2.18 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [**(53)**; 12 mg, 13 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 18 mg, 17 %]
Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 13 mg, 12 %]
Methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(125)**; 11 mg, 8 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tricarbonyl(trimethylphosphite)manganese (144) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.19 ml, 2.11 mmol) and the orthomanganated ketone [(**144**); 175 mg, 0.42 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [(**53**); 3 mg, 3 %]
The parent ketone 3-acetyl-2,5-dimethylthiophene [(**56**); 10 mg, 15 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [(**54**); 64 mg, 64 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**123**); 9 mg, 8 %]
Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**124**); 2 mg, 2 %]

Reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese (145) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.19 ml, 2.11 mmol) and the orthomanganated ketone [(**145**); 216 mg, 0.42 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [(**53**); 5 mg, 5 %]
The parent ketone 3-acetyl-2,5-dimethylthiophene [(**56**); 2 mg, 3 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [(**54**); 19 mg, 19 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**123**); 47 mg, 47 %]

Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**124**); 20 mg, 19 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese (145) with Methyl Acrylate in refluxing Acetonitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)-manganese [(**145**); 216 mg, 0.42 mmol] in acetonitrile (10 ml) was treated with methyl acrylate (0.19 ml, 2.18 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [(**53**); 8 mg, 9 %]
Recovered η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese [(**145**); 19 mg, 9 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**123**); 17 mg, 17 %]
Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [(**124**); 11 mg, 11 %]
Methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [(**125**); 49 mg, 37 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)manganese (145) with Methyl Acrylate in Refluxing Propionitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethylphosphite)-manganese [(**145**); 200 mg, 0.39 mmol] in propionitrile (10 ml) was treated with methyl acrylate (0.18 ml, 1.95 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate [(**53**); 5 mg, 6 %]

Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [(**55**); 6 mg, 6 %]

Methyl 2-propanoyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(143)**; 39 mg, 36 %] a colourless oil. ^{13}C NMR: (75.47 MHz) ($CDCl_3$) δ 206.2 (*s*, 2-$\underline{C}OCH_2CH_3$), 197.2 (*s*, 4'-$\underline{C}OCH_3$), 170.1 (*s*, C-1), 142.2 (*s*, C-4'), 138.3 (*s*, C-3'), 134.2 (*s*, C-5'), 132.5 (*s*, C-2'), 58.1 (*d*, C-2), 52.2 (*q*, 1-OCH_3), 36.4 (*t*, 2-$CO\underline{C}H_2CH_3$), 31.9 (*q*, 4'-$CO\underline{C}H_3$), 26.7 (*t*, C-3), 16.5 (*q*, -CH_3), 12.7 (*q*, -CH_3), 7.6 (*q*, 2-$COCH_2\underline{C}H_3$).

Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 18 mg, 19 %]

Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 23 mg, 25 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethyl-phosphite)manganese (145) with Li_2PdCl_4 and Methyl Acrylate in Methanol at Ambient Temperature

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry methanol (10 ml) for 3 hours. Methyl acrylate (0.19 ml, 2.11 mmol) and the orthomanganated ketone [**(145)**; 216 mg, 0.42 mmol] were added, and the solution was stirred at ambient temperature for three days. The reaction mixture was worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 32 mg, 49 %]
Recovered η^2-(4-acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethyl-phosphite)manganese [**(145)**; 40 mg, 19 %]
A number of other bands were not identified.

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonylbis(trimethyl-phosphite)manganese (145) with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl vinyl ketone (0.18 ml, 2.11 mmol) and the orthomanganated ketone [**(145)**; 216 mg, 0.42 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 diethyl ether/petroleum spirit) to give:

1-(1,3,6-Trimethyl-4H-cyclopenta[c]thien-5-yl)-ethanone [**(120)**; 8 mg, 9 %]
4-(4-Acetyl-2,5-dimethylthien-3-yl)-butan-2-one [**(119)**; 14 mg, 14 %]
E-4-(4-Acetyl-2,5-dimethylthien-3-yl)-but-3-en-2-one [(); 14 mg, 15 %]
(4S*, 5R*)-1-(4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone [**(121)**; 4 mg, 5 %]
(4R*, 5R*)-1-(4-Hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]thien-5-yl)-ethanone [**(122)**; 16 mg, 17 %]
A number of other bands were not identified.

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonyl(dppm)$_2$-manganese (146) with Methyl Acrylate in Refluxing Acetonitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonyl(dppm)$_2$manganese [**(146)**; 305 mg, 0.30 mmol] in acetonitrile (10 ml) was treated with methyl acrylate (0.13 ml, 1.48 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 9 mg, 13 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 31 mg, 44 %]
Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 18 mg, 26 %]
Methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(125)**; 13 mg, 13 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonyl(dppm)$_2$-manganese (146) with Methyl Acrylate in Refluxing Propionitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)dicarbonyl(dppm)$_2$manganese [**(146)**; 305 mg, 0.30 mmol] in propionitrile (10 ml) was treated with methyl acrylate (0.13 ml, 1.48 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 9 mg, 13 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 35 mg, 50 %]

Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 19 mg, 27 %]

Reaction of η^2-(6-Acetyl-2,3,4-trimethoxyphenyl)dicarbonylbis(trimethyl-phosphite)manganese (147) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (78 mg, 0.44 mmol) and LiCl (37 mg, 0.88 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.20 ml, 2.20 mmol) and the orthomanganated ketone [**(147)**; 250 mg, 0.44 mmol] were added, and the solution was heated under reflux for 24 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:5 ethyl acetate/petroleum spirit) to give:

Methyl (3-methyl-5,6,7-trimethoxyinden-2-yl)-carboxylate [**(88)**; 7 mg, 6 %]
A number of trace bands which were not further investigated.

4.4.7.2 Changing the Metal from Manganese to Rhenium

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32) with Li_2PdCl_4 and Methyl Acrylate in Refluxing Acetonitrile

$PdCl_2$ (75 mg, 0.42 mmol) and LiCl (36 mg, 0.84 mmol) were stirred in dry acetonitrile (10 ml) for 3 hours. Methyl acrylate (0.19 ml, 2.11 mmol) and the orthorheniated ketone [**(32)**; 190 mg, 0.42 mmol] were added, and the solution was heated under reflux for 3 hours. The reaction mixture was cooled, worked up as usual and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 10 mg, 15 %]
Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 17 mg, 16 %]
Methyl E-3-(4-acetyl-2,5-dimethylthien-3-yl)-prop-2-enoate [**(54)**; 66 mg, 66 %]

Reaction of η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium (32) with Methyl Acrylate in Refluxing Acetonitrile

η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium [**(32)**; 190 mg, 0.42 mmol] in acetonitrile (10 ml) was treated with methyl acrylate (0.19 ml, 2.18 mmol) and refluxed for 3 hours. The solution was evaporated to dryness under reduced pressure and chromatographed (p.l.c., 1:10 ethyl acetate/petroleum spirit) to give:

The parent ketone 3-acetyl-2,5-dimethylthiophene [**(56)**; 20 mg, 31 %]
Methyl 3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(55)**; 17 mg, 17 %]
Methyl (4S*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(123)**; 4 mg, 4 %]
Methyl (4R*, 5R*)-4-hydroxy-1,3,4-trimethyl-5,6-dihydro-4H-cyclopenta[c]-thiophene-5-carboxylate [**(124)**; 3 mg, 3 %]
Methyl 2-acetyl-3-(4-acetyl-2,5-dimethylthien-3-yl)-propanoate [**(125)**; 14 mg, 12 %]

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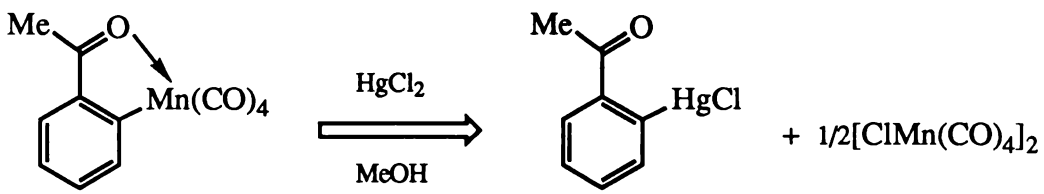
Chapter Five

Iodination via Manganation at Sterically Crowded *Ortho*-Sites

5.1 Introduction

The reactions of orthomanganated aryl ketones with electrophiles such as $HgCl_2$, Br_2, I_2 and ICl are now well established.

Mercuric chloride reacts with orthomanganated aryl ketones in refluxing methanol to give the corresponding aryl mercury(II) chlorides in good yields, with the mercury specifically *ortho* to the ketone function (Equation 5.1) [1].



Equation 5.1

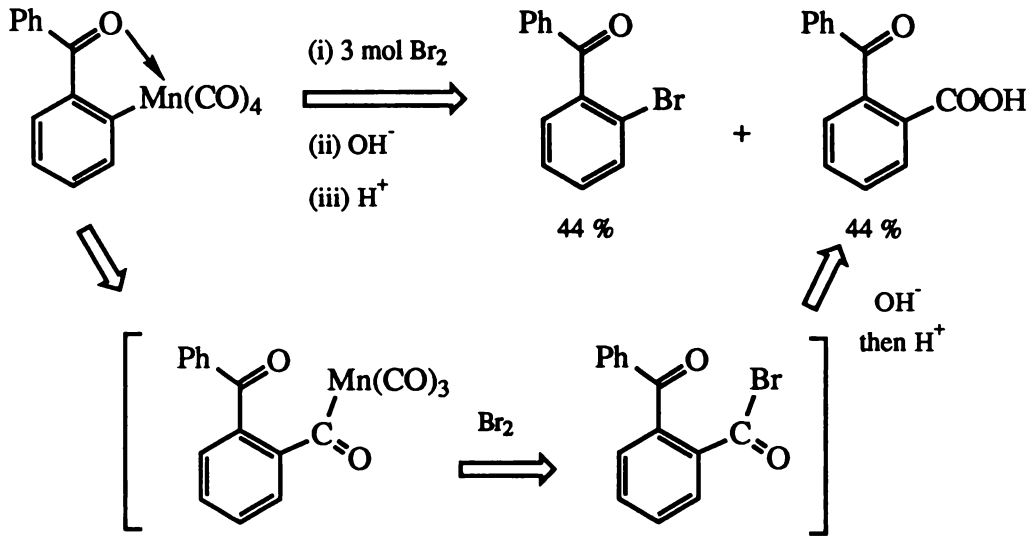
The transmetalation reaction is quite general for orthomanganated complexes, giving mercurated acetophenones, benzophenones, methyl benzoates and acetyl thiophenes by use of the appropriate orthomanganated species.

The mercuration reaction shows considerable synthetic potential as mercurated acetophenones are not otherwise available; direct mercuration gives attack at the methyl group, and preparations via aryl lithium or Grignard reagents are precluded by the presence of the ketone group.

The oxidation of orthomanganated aryl compounds by Br_2 is not straightforward.

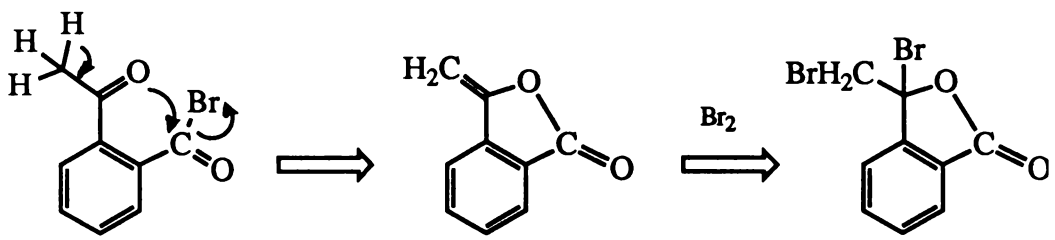
Crawford first reported the use of bromine in carbon tetrachloride for bromodemanganation [2]. Orthomanganated benzophenone gave, with a three mole excess of bromine and after workup involving aqueous alkaline

extraction, 2-bromobenzophenone and 2-benzoylbenzoic acid. The latter was envisaged as derived from the acyl bromide formed by bromodemetalation at the acyl carbon after carbonyl insertion into the C-Mn bond (Scheme 5.1).



Scheme 5.1

Repetition of the reaction with orthomanganated acetophenone gave the dibromide of vinylphthalide rather than the 2'-bromoacetophenone [2]. The latter is probably formed from the acyl bromide (Equation 5.2).

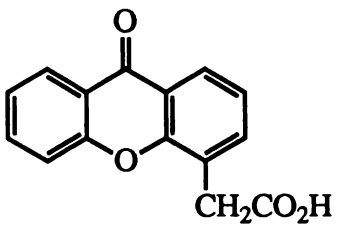


Equation 5.2

When electrophilic attack at the manganated aryl carbon is activated by electron-donating methoxy groups, good yields of orthobromo-ketones are obtained. If however an unsubstituted ring position is activated moreso than the manganated ring position, bromodeprotonation occurs more readily than bromodemanganation [3,4]. This resistance of the C-Mn group to substitution is a synthetic limitation in that the Br group is not introduced *ortho* to the ketone function, the whole point of the initial metalation. Direct bromination of the parent ketones without manganation would probably give the same products in better yield.

Iodine appears to give no reaction with orthomanganated ketones at all [4], but iodine chloride in carbon tetrachloride reacts cleanly even though it is much less reactive than bromine. It appears to have the advantage over bromine in that it almost always reacts exclusively to substitute the metal rather than a ring proton, even if the unsubstituted ring position is more activated to electrophilic attack [3,4].

Our attention was focused on the synthetic potential of these iodination reactions following reports in the literature [5] that selected 5-substituted and 5,6-disubstituted 9-oxo-9H-xanthene-4-acetic acid (XAA) compounds (Figure 5.1) exhibit antitumour activity against *in vivo* colon 38 tumour in mice.



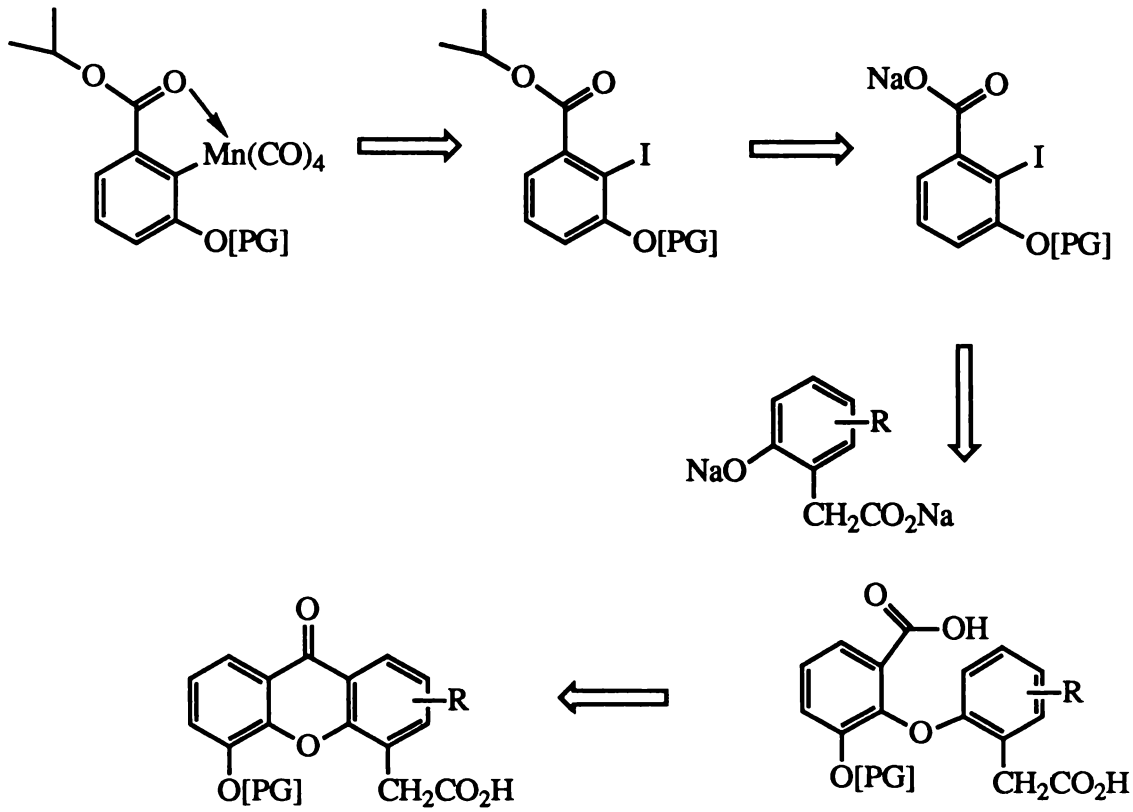
(XAA)

Figure 5.1

The ability of ICl to specifically substitute manganese could be utilized by iodinating 3-substituted orthomanganated esters to form the key precursor required for the formation of XAA (Scheme 5.2).

A range of derivatives with groups of different length or size in the key 5-position could then be achieved by replacing the protective group on oxygen by various alkyl groups.

It was therefore the aim of this study to establish whether substitution of manganese by bulky iodine at a sterically crowded site to give the desired 2-iodo-3-substituted ester was synthetically feasible.



Scheme 5.2

5.2 Discussion of Results

Reaction of η^2-(2-methoxy-6-isopropoxycarbonylphenyl)tetracarbonyl-manganese **(22)** with iodine chloride yielded 74 % of isopropyl 2-iodo-3-methoxybenzoate **(149)** after a six day reaction time. Also recovered was unreacted starting material [**(22)**; 20 %] and $[IMn(CO)_4]_2$.

The *ortho*-iodinated compound, isopropyl 3-acetoxy-2-iodobenzoate [**(150)**; 49 %] was similarly prepared. The yield of unreacted starting material [**(25)**; 35 %] would suggest that a three day reaction time was not sufficient for this compound. Also isolated were $IMn(CO)_5$ and $[IMn(CO)_4]_2$.

Although we have iodinated only a limited number of 3-substituted orthomanganated esters in this study, our preliminary findings would suggest that a sterically crowded *ortho* position does not preclude substitution of manganese by bulky iodine. The potential for synthesising a range of 3- and 3,4-disubstituted 2-iodo esters would therefore seem to be unlimited.

As previously discussed, the sodium salts of the acids of these compounds form the precursor required for the formation of XAA (Scheme 5.1). Coupling with the appropriately substituted sodium salt of 2-hydroxyphenylacetic acid, followed by acid-catalysed cyclodehydration, removal of the protective group and substitution on O of the desired R group would yield selected 5-substituted 9-oxo-9H-xanthene-4-acetic acid (XAA) compounds.

Studies of structure-activity relationships among monosubstituted XAA analogues (Figure 5.2) showed that small lipophilic substituents in the 5-position enhanced dose potency and efficacy *in vivo* against the colon 38 tumour in mice [5].

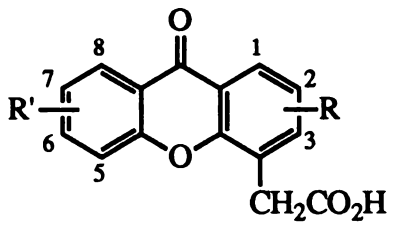


Figure 5.2

Further studies demonstrated the best overall effects were achieved with the 5,6-dimethyl and 5-methyl-6-methoxy derivatives of XAA. The pharmacokinetic and metabolic profiles of the former compound are presently being evaluated [5].

η^2-(2-Acetyl-6-methoxyphenyl)tetracarbonylmanganese **(151)** and η^2-(6-acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese **(17)** were also iodinated during the course of this study.

Reaction of the former with ICl over six days gave 2'-iodo-3'-methoxyacetophenone **(152)** in 89 % yield. Also recovered were $IMn(CO)_5$ and $[IMn(CO)_4]_2$.

Reaction of the latter gave the expected 2'-iodo substituted compound, 2'-iodo-3',4'-methylenedioxyacetophenone **[(153)**; 63 %] in addition to unreacted starting material **[(17)**; 12 %], but also showed traces of an iodinated isomer.

For orthomanganated 3',4'-methylenedioxyacetophenone **(17)**, the *o,p*-directing oxy groups and meta-directing ketone group would activate the

unsubstituted ring position C-4 to electrophilic attack moreso than the manganated ring position C-1 (Figure 5.3).

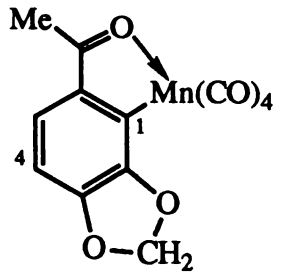


Figure 5.3

Despite this, it is the 2'-iodo derivative which is isolated as the major product, in accord with previously reported results, which showed that iodine chloride reacts specifically to substitute the metal rather than an activated ring proton [3,4]. In this case however, there was also a minor isomer, which was surprising given that Gommans reports a quantitative yield of 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-6'-iodoacetophenone upon iodination of orthomanganated 2'-t-butyldimethylsiloxy-3',4'-dimethoxyacetophenone with ICl [4]. For his compound, the 6-position (Figure 5.4) would be even more electronically activated to electrophilic attack than for compound **(17)**, yet no trace of the 5'-iodo isomer was observed in this instance.

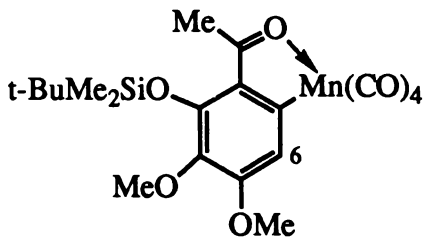
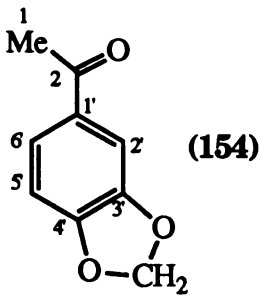


Figure 5.4

Examination of the ^{1}H- and ^{13}C-NMR of the minor iodinated isomer from **(17)** failed to reveal conclusively whether iodination has taken place at the 4'- or 5'-position, although it is clear that manganese is no longer present.

Comparison of the ^{1}H-NMR chemical shifts for this compound with those calculated by increment [6] for iodinated 3',4'-(methylenedioxy)-acetophenone shows convincing agreement for neither the 5'- nor the 6'-iodinated isomer (Table 5.1).

Table 5.1 ^{1}H-NMR Calculated Chemical Shifts for Iodinated 3',4'-(Methylenedioxy)acetophenone (154)



(154)

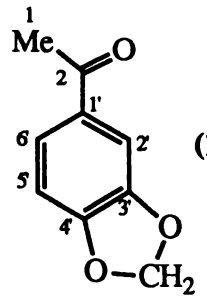
	H-2'	H-5'	H-6'
(154)	7.42	6.83	7.54
I-5'	0	-	0.39
Predict	7.42(s)	-	7.93(s)
I-6'	-0.21	0.39	-
Predict	7.21(s)	7.22(s)	-
Observe	7.04(s)	7.35(s)	-
I-2'	-	0	-0.21
Predict	-	6.83(d)	7.33(d)
Observe	-	6.77(d)	7.28(d)

Correlation for the 6'-iodinated isomer is closer, however, this assignment is by no means definitive.

For comparison the predicted and observed proton resonances for the 2'-iodinated isomer are also given, and for this isomer we observe a good correlation between the observed and predicted chemical shifts of the aromatic protons.

A similar comparison of the ^{13}C-NMR spectrum also points to the 6'-iodinated isomer, the agreement between the observed and calculated [7] resonances of the aryl doublets being much closer for this isomer than for the 5'-iodinated isomer (Table 5.2).

Table 5.2 ^{13}C-NMR Calculated Chemical Shifts for Iodinated 3',4'-(Methylenedioxy)acetophenone (154)



(154)

	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
(154)	132.2	108.0*	148.2	151.8	107.8*	124.8
I-5	2.6	-0.4	2.6	9.9	-32.3	9.9
Predict	134.8(s)	107.6(d)	150.8(s)	161.7(s)	75.5(s)	134.7(d)
I-6	9.9	2.6	-0.4	2.6	9.9	-32.3
Predict	142.1(s)	110.6(d)	147.8(s)	154.4(s)	117.7(d)	92.5(s)
Observe	136.3(s)	109.0(d)	148.2(s)	150.3(s)	120.4(d)	81.5(s)
I-2	9.9	-32.3	9.9	2.6	-0.4	2.6
Predict	142.1(s)	75.7(s)	158.1(s)	154.4(s)	107.4(d)	127.4(d)
Observe	134.7(s)	69.9(s)	151.1(s)	148.3(s)	107.4(d)	125.6(d)

It is difficult to rationalise these results in the absence of a definitive assignment. Although the NMR points towards the 6'-iodinated isomer, electronically we would expect the 5'-iodinated isomer to be favoured. It is also unlikely that the 6'-iodinated isomer comes from iodination of the orthomanganated isomer η^2-(2-acetyl-4,5-methylenedioxyphenyl)-tetracarbonylmanganese **(18)**, given that this has never been observed in more than trace amounts, while the yield of the minor iodinated product was ~13 %.

5.3 Experimental Section

Reaction of η^2-(2-Methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese (22) with ICl

η^2-(2-Methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [**(22)**; 0.194 g, 0.540 mmol] was dissolved in 5 ml of N_2-saturated CCl_4. A freshly prepared solution of ICl (0.35 mol l^{-1}, 1.54 ml, 0.540 mmol) was added slowly to this solution. The reaction vessel was tightly stoppered and stirred at ambient temperature for six days. The CCl_4 was removed under vacuum and the oily residue chromatographed (p.l.c., 3:2 petroleum spirit/dichloromethane) to yield three bands.

Recovered η^2-(2-methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [**(22)**; 0.038 g, 18 %]

$[IMn(CO)_4]_2$ (0.003 g) IR: (hexane) ν(CO) 2088 (w), 2035 (s), 2010 (m), 1979 (m) cm^{-1} (lit. 2087 (w), 2033 (s), 2009 (m), 1976 (m) cm^{-1} [8]).

Isopropyl 2-iodo-3-methoxybenzoate [**(149)**; 0.128 g, 74 %], a colourless oil. ^{1}H-NMR (300.13 MHz) ($CDCl_3$) δ 7.29 (1H, *t*, $^3J_{5,4}=^3J_{5,6}$=7.9 Hz, H-5), 7.14 (1H, *dd*, $^3J_{6,5}$=7.9 Hz, $^4J_{6,4}$=1.3 Hz, H-6), 6.86 (1H, *dd*, $^3J_{4,5}$=7.9 Hz, $^4J_{4,6}$=1.3 Hz, H-4), 5.25 (1H, *m*, ^3J=6.3 Hz, 1-COOC<u>H</u>$(CH_3)_2$), 3.85 (3H, *s*, 3-OCH_3), 1.37 (6H, *d*, ^3J=6.3 Hz, 1-COOCH(C<u>H</u>$_3)_2$). ^{13}C-NMR (75.47 MHz) ($CDCl_3$) δ 167.3 (*s*, 1-<u>C</u>OOCH$(CH_3)_2$), 158.6 (*s*, C-3), 139.8 (*s*, C-1), 129.3 (*d*, C-5), 122.0 (*d*, C-6), 112.7 (*d*, C-4), 86.2 (*s*, C-2), 69.7 (*d*, 1-COO<u>C</u>H$(CH_3)_2$), 56.8 (*q*, 3-OCH_3), 21.9 (*q*, 1-COOCH(<u>C</u>H$_3)_2$). MS m/e 278 (P^+-42, P^+-C$(CH_3)_2$).

Reaction of η^2-(2-Acetoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese (25) with ICl

η^2-(2-Acetoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [**(25)**; 0.327 g, 0.842 mmol] was dissolved in 5 ml of N_2-saturated CCl_4, and reacted with ICl following the standard procedure. After three days the solution was worked up and chromatographed (p.l.c., 3:2 petroleum spirit/dichloromethane) to give three bands.

A mixture of $IMn(CO)_5$ and $[IMn(CO)_4]_2$ (0.023 g) by IR.

$IMn(CO)_5$ IR: (hexane) ν(CO) 2127 (w), 2046 (s), 2005 (m) cm^{-1} (lit. 2125 (m), 2043 (s), 2003 (m) cm^{-1} [9]).

Recovered η^2-(2-acetoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [**(25)**; 0.114 g, 35 %]

Isopropyl 3-acetoxy-2-iodobenzoate [**(150)**; 0.144 g, 49 %], a colourless oil. ^{1}H-NMR (300.13 MHz) ($CDCl_3$) δ 7.53 (1H, *dd*, $^3J_{6,5}$=7.9 Hz, $^4J_{6,4}$=1.5 Hz, H-6), 7.36 (1H, *t*, $^3J_{5,4}$=$^3J_{5,6}$=7.9 Hz, H-5), 7.15 (1H, *dd*, $^3J_{4,5}$=7.9 Hz, $^4J_{4,6}$=1.5 Hz, H-4), 5.25 (1H, *m*, ^{3}J=6.3 Hz, 1-COOC<u>H</u>$(CH_3)_2$), 2.36 (3H, *s*, 3-$OCOCH_3$), 1.37 (6H, *d*, ^{3}J=6.3 Hz, 1-COOCH(C<u>H</u>$_3)_2$). ^{13}C-NMR (75.47 MHz) ($CDCl_3$) δ 168.5 (*s*, 3-O<u>C</u>OCH_3), 166.1 (*s*, 1-<u>C</u>$OOCH(CH_3)_2$), 152.1 (*s*, C-3), 138.9 (*s*, C-1), 129.1 (*d*, C-5), 127.8 (*d*, C-6), 125.3 (*d*, C-4), 91.6 (*s*, C-2), 69.9 (*d*, 1-COO<u>C</u>$H(CH_3)_2$), 21.9 (*q*, 1-$COOCH(\underline{C}H_3)_2$), 21.3 (*q*, 3-$OCO\underline{C}H_3$). MS m/e 289 ($P^+$-59, P^+-$OCH(CH_3)_2$).

Reaction of η^2-(2-Acetyl-6-methoxyphenyl)tetracarbonylmanganese (151) with ICl

η^2-(2-Acetyl-6-methoxyphenyl)tetracarbonylmanganese [**(151)**; 0.133 g, 0.421 mmol] was dissolved in 10 ml of N_2-saturated CCl_4, and reacted with ICl following the standard procedure. After five days the ICl had decolourised and the solution was worked up and chromatographed (p.l.c., 3:2 petroleum spirit/dichloromethane) to give two bands.

A mixture of $IMn(CO)_5$ and $[IMn(CO)_4]_2$ (0.012 g) by IR.

2'-Iodo-3'-methoxyacetophenone [**(152)**; 0.103 g, 89 %], a colourless oil. Anal. Found: C, 39.63; H, 3.36; I, 46.05 %; $C_9H_9O_2I$ calcd; C, 39.16; H, 3.29; I, 45.97 %. ^{1}H-NMR (300.13 MHz) ($CDCl_3$) δ 7.31 (1H, *t*, $^3J_{5',4'}$=$^3J_{5',6'}$=8.0 Hz, H-5'), 6.88 (1H, *dd*, $^3J_{6',5'}$=8.0 Hz, $^4J_{6',4'}$=1.1 Hz, H-6'), 6.84 (1H, *dd*, $^3J_{4',5'}$=8.0 Hz, $^4J_{4',6'}$=1.1 Hz, H-4'), 3.87 (3H, *s*, 3'-OCH_3), 2.56 (3H, *s*, H-2). ^{13}C-NMR (75.47 MHz) ($CDCl_3$) δ 203.4 (*s*, C-1), 158.3 (*s*, C-3'), 148.0 (*s*, C-1'), 129.8 (*d*, C-5'), 119.5 (*d*, C-6'), 112.1 (*d*, C-4'), 83.0 (*s*, C-2'), 56.8 (*q*, 3'-OCH_3), 30.1 (*q*, C-2). MS m/e 276 (P^+).

Reaction of η^2-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonyl-manganese (17) with ICl

η^2-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese [**(17)**; 0.251 g, 0.760 mmol] was dissolved in 10 ml of N_2-saturated CCl_4, and reacted with ICl following the standard procedure. After five days the solution was worked up and chromatographed (p.l.c., 3:2 petroleum spirit/dichloromethane) to give three bands.

A mixture of $IMn(CO)_5$ and $[IMn(CO)_4]_2$ (0.048 g), by IR.

Recovered η^2-(6-acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese [**(17)**; 0.029 g, 12 %].
The major band (0.165 g, 75 %) was identified as a mixture (*ca* 5:1) of the two iodinated isomers by ^1H and ^{13}C-NMR spectroscopy. Pure white crystals of the principal isomer 2'-iodo-3',4'-methylenedioxyacetophenone **(153)** were obtained by fractional crystallization with benzene/heptane, m.p. 114 °C. Anal. Found: C, 37.34; H, 2.77; I, 43.62 %; $C_9H_7O_3I$ calcd; C, 37.27; H, 2.43; I, 43.75 %. ^1H-NMR (300.13 MHz) ($CDCl_3$) δ 7.29 (1H, *d*, $^3J_{6',5'}$=8.1 Hz, H-6'), 6.77 (1H, *d*, $^3J_{5',6'}$=8.1 Hz, H-5'), 6.10 (2H, *s*, 3'-CH_2-4'), 2.59 (3H, *s*, H-2). ^{13}C-NMR (75.47 MHz) ($CDCl_3$) δ 198.0 (*s*, C-1), 151.1 (*s*, C-3'*), 148.3 (*s*, C-4'*), 134.7 (*s*, C-1'), 125.6 (*d*, C-6'), 107.4 (*d*, C-5'), 101.0 (*t*, 3'-CH_2-4'), 69.9 (*s*, C-2'), 28.8 (*q*, C-2). MS m/e 290 (P^+).

The remaining oil could not be purified sufficiently for complete characterisation, but showed the following spectral features: ^1H-NMR (300.13 MHz) ($CDCl_3$) δ 7.35 (1H, *s*), 7.04 (1H, *s*), 5.99 (2H, *s*, -CH_2-), 2.52 (3H, *s*, -$COCH_3$). ^{13}C-NMR (75.47 MHz) ($CDCl_3$) δ 199.7 (*s*, -$\underline{C}OCH_3$), 150.3 (*s*), 148.2 (*s*), 136.3 (*s*), 120.4 (*d*), 109.0 (*d*), 102.4 (*t*), 81.5 (*s*), 29.2 (*q*, -CO$\underline{C}H_3$), and was either the 5'- or 6'-iodinated isomer of 3',4'-(methylenedioxy)-acetophenone.

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Appendix I

General Experimental

All reactions and recrystallizations of air-sensitive compounds were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

Heptane and acetonitrile were dried by distillation from CaH_2 under nitrogen. THF and diethyl ether were dried by distillation from sodium/benzophenone under nitrogen. Benzene was dried by distillation from CaH_2 and was stored over sodium wire. Methanol was dried using the following procedure: dry magnesium turnings and iodine were added to A.R. methanol and stirred until all the iodine disappeared and all the magnesium was converted to its methoxide. Reagent grade methanol was added and, after refluxing for two to three hours, it was distilled off, excluding moisture from the system. Petroleum spirit was of analytical grade quality and of boiling point range 60-80 °C. All other solvents were of analytical grade quality and were stored over 4-A molecular sieves.

All glassware was routinely cleaned in chromic acid and thoroughly dried in an air oven.

NMR spectra were recorded in $CDCl_3$ as solvent. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on either a Bruker AC300 instrument or a Jeol FX-90Q instrument. Chemical shifts were referenced internally with TMS using the following standard resonances for deuterated chloroform: ^{1}H: 7.25 ppm; ^{13}C: 77.06 ppm. ^{31}P-NMR and ^{199}Hg-NMR spectra were recorded on a Jeol FX-90Q instrument. ^{31}P-NMR spectra were externally referenced to 85 % H_3PO_4 while ^{199}Hg-NMR spectra were externally referenced to $HgMe_2$.

Chemical shifts (δ) are in parts per million (ppm) and coupling constants are in Hertz (Hz). Spin multiplicities are indicated by the following symbols: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet).

Full NMR assignments were made using 2D-COSY [1], XHCORR [2], BIRDTRAP [3], XHBIRD [3], and NOE [4] experiments.

Infrared spectra were recorded in solution cells (KBr windows) with hexane as solvent on either a Digilab FTS-45 FTIR instrument or a Perkin Elmer 180B instrument.

Mass spectra were recorded on either a Varian MAT CH5 instrument at Ruakura Agricultural Research Centre or on a VG ZAB 2HF FAB-MS at the University of Adelaide.

GC-MS samples were analysed on a Hewlett Packard 5890 gas chromatograph fitted with a 15 m HP1 column (0.33 μm film thickness; 0.2 mm internal diameter) using helium carrier (15 p.s.i. head pressure; flow rate 90 ml min^{-1}). A Hewlett Packard 5970 Series Mass Selective Detector linked to a data station provided parent-ion mass values.

All melting points were determined on a Reichert thermopan melting point apparatus and are uncorrected.

Elemental analyses were performed by the University of Otago Microanalytical Laboratory.

Thin layer chromatography (t.l.c.) was carried out on Merck Kieselgel $60F_{254}$ silica gel backed by aluminium sheets (layer thickness 0.2 mm). Preparative layer chromatography (p.l.c.) was carried out on Merck Kieselgel $60PF_{254+366}$ silica gel coated glass plates poured to a thickness of 1 mm.

Molecular modelling was performed on:

(i) A Macintosh IIfx running Chem3D Plus V3.0, Cambridge Scientific Computing. Structural minimisation was performed using supplied parameters for MM2 and Tinker forcefields.

(ii) A Silicon Graphics IRIS Indigo XS24 workstation running MacroModel V3.5x [5]. Structural minimisation was performed using MacroModel-implemented MM2* forcefield.

For both Chem3D and MacroModel, minimisations were converged to default convergence criteria.

Energy: The energy term is the sum of all the other terms, but can not be thermodynamically measured. We can, however, compare differences in energy.

Bond Stretching: This term is associated with deformation of a bond from its standard equilibrium length. For small displacements from equilibrium, a harmonic function is often used.

Bond Angle Bending: This term is associated with the deformation of an angle from its normal value. For small displacements from equilibrium, a harmonic function is often used.

Van der Waals: This term describes the repulsive forces keeping two nonbonded atoms apart at close range and the attractive force drawing them together at long range.

Electrostatic: This term describes the classical nonbonded electrostatic interactions of charge distributions.

Proper Torsion (Dihedrals): This term is associated with the tendency of dihedral angles to have a certain *n*-fold symmetry and to have minimum energy for the *cis*-, *gauche*-, or *trans*-conformation, etc.

Bond Stretch and Angle Bending Cross Term: This term is associated with the coupling between bond stretching and angle bending (opening a bond angle may tend to lengthen the bonds involved).

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Appendix II

Thermal and Positional Parameters for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese

Table AII.1 Final Positional and Equivalent Thermal Parameters for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.2228(1)	0.3231(1)	0.3104(1)	0.027
C(5)	0.2762(3)	0.1068(3)	0.2211(2)	0.027
C(4a)	0.2355(3)	0.1197(3)	0.0940(2)	0.025
C(4)	0.1680(3)	0.2722(3)	0.0542(2)	0.027
C(3)	0.1352(4)	0.2878(3)	-0.0750(2)	0.030
C(2)	0.1644(4)	0.1571(3)	-0.1493(2)	0.034
C(8a)	0.2583(3)	-0.0089(3)	0.0098(2)	0.028
C(8)	0.3194(4)	-0.1595(3)	0.0482(3)	0.035
C(7)	0.3586(4)	-0.1734(3)	0.1719(3)	0.037
C(6)	0.3389(4)	-0.0443(3)	0.2569(2)	0.033
C(10)	0.3031(4)	0.2645(4)	0.4593(3)	0.038
C(9)	0.1501(4)	0.5244(3)	0.3673(2)	0.036
C(12)	0.4725(4)	0.3956(3)	0.2803(2)	0.036
C(11)	-0.0115(4)	0.2107(3)	0.3396(2)	0.033
O(4)	0.1424(3)	0.3846(2)	0.1332(1)	0.030
O(1)	0.2201(3)	0.0104(2)	-0.1129(2)	0.033
O(10)	0.3562(4)	0.2282(3)	0.5544(2)	0.058
O(9)	0.0987(4)	0.6477(3)	0.4033(2)	0.056
O(12)	0.6276(3)	0.4318(3)	0.2634(2)	0.055
O(11)	-0.1467(3)	0.1353(3)	0.3644(2)	0.048

Table AII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese

Atom	X/A	Y/B	Z/C	U11
H(2)	0.1429(4)	0.1702(3)	-0.2376(2)	0.034
H(3)	0.0929(4)	0.3911(3)	-0.1084(2)	0.034
H(6)	0.3698(4)	-0.0604(3)	0.3439(2)	0.034
H(7)	0.4023(4)	-0.2784(3)	0.2013(3)	0.034
H(8)	0.3341(4)	-0.2519(3)	-0.0102(3)	0.034

Table AII.3 Thermal Parameters for η^2-5-(1,4-Benzopyronyl)tetracarbonylmanganese

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0366(2)	0.0243(2)	0.0216(2)	0.0021(1)	0.0015(1)	0.0046(2)
C(5)	0.027(1)	0.027(1)	0.027(1)	0.005(1)	0.003(1)	0.003(1)
C(4a)	0.025(1)	0.023(1)	0.028(1)	0.003(1)	0.0060(9)	0.0031(9)
C(4)	0.026(1)	0.029(1)	0.026(1)	0.003(1)	0.0030(9)	0.004(1)
C(3)	0.033(1)	0.032(1)	0.025(1)	0.005(1)	0.001(1)	0.004(1)
C(2)	0.036(1)	0.041(2)	0.024(1)	0.002(1)	0.003(1)	-0.003(1)
C(8a)	0.024(1)	0.027(1)	0.033(1)	-0.002(1)	0.007(1)	-0.0009(9)
C(8)	0.033(1)	0.024(1)	0.049(2)	-0.003(1)	0.012(1)	0.003(1)
C(7)	0.031(1)	0.025(1)	0.058(2)	0.011(1)	0.010(1)	0.008(1)
C(6)	0.032(1)	0.030(1)	0.039(1)	0.011(1)	0.002(1)	0.006(1)
C(10)	0.047(2)	0.034(2)	0.032(1)	0.003(1)	-0.002(1)	0.005(1)
C(9)	0.051(2)	0.033(2)	0.024(1)	0.003(1)	0.008(1)	-0.001(1)
C(12)	0.049(2)	0.026(1)	0.033(1)	0.004(1)	0.001(1)	0.006(1)
C(11)	0.044(2)	0.031(1)	0.025(1)	-0.005(1)	0.003(1)	0.006(1)
O(4)	0.044(1)	0.0243(9)	0.0245(8)	0.0031(7)	0.0022(7)	0.0133(8)
O(1)	0.039(1)	0.033(1)	0.0280(9)	-0.0049(8)	0.0070(8)	-0.0008(8)
O(10)	0.078(2)	0.065(2)	0.032(1)	0.011(1)	-0.011(1)	0.008(1)
O(9)	0.090(2)	0.031(1)	0.048(1)	-0.004(1)	0.029(1)	0.008(1)
O(12)	0.044(1)	0.046(1)	0.074(2)	0.012(1)	0.009(1)	-0.001(1)
O(11)	0.052(1)	0.048(1)	0.041(1)	-0.010(1)	0.010(1)	-0.010(1)

Appendix III

Thermal and Positional Parameters for η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium

Table AIII.1 Final Positional and Equivalent Thermal Parameters for η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium

Atom	X/A	Y/B	Z/C	Ueq
Re(1)	1.03153(3)	0.28152(3)	0.14957(3)	0.036
S(1)	1.0243(4)	0.2775(4)	0.5778(3)	0.049
C(1)	0.834(2)	0.390(1)	0.120(1)	0.050
C(2)	0.993(2)	0.234(2)	-0.044(1)	0.056
C(3)	1.237(2)	0.187(2)	0.203(1)	0.055
C(4)	1.213(2)	0.475(2)	0.195(2)	0.064
C(5)	0.766(2)	0.025(1)	0.188(1)	0.047
C(6)	0.871(2)	0.131(1)	0.324(1)	0.039
C(7)	0.857(1)	0.123(1)	0.445(1)	0.040
C(8)	1.117(2)	0.355(1)	0.477(1)	0.036
C(9)	1.020(2)	0.270(1)	0.342(1)	0.036
C(10)	0.610(2)	-0.123(1)	0.146(2)	0.059
C(11)	0.712(2)	0.004(2)	0.466(1)	0.058
C(12)	1.287(2)	0.507(1)	0.546(1)	0.045
O(1)	0.732(2)	0.458(2)	0.107(1)	0.076
O(2)	0.972(2)	0.204(1)	-0.155(1)	0.065
O(3)	1.358(2)	0.135(2)	0.235(1)	0.081
O(4)	1.329(1)	0.6056(9)	0.235(1)	0.080
O(5)	0.812(1)	0.061(1)	0.0972(9)	0.049

Table AIII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium

Atom	X/A	Y/B	Z/C	U11
H(101)	0.531(2)	-0.095(1)	0.202(2)	0.110
H(102)	0.636(2)	-0.234(1)	0.154(2)	0.110
H(103)	0.532(2)	-0.134(1)	0.039(2)	0.110
H(111)	0.748(2)	0.030(2)	0.574(1)	0.110
H(112)	0.761(2)	-0.093(2)	0.435(1)	0.110
H(113)	0.562(2)	-0.031(2)	0.409(1)	0.110
H(121)	1.259(2)	0.600(1)	0.605(1)	0.110
H(122)	1.295(2)	0.537(1)	0.457(1)	0.110
H(123)	1.419(2)	0.494(1)	0.608(1)	0.110

Table AIII.3 Thermal Parameters for π^2-(4-Acetyl-2,5-dimethylthien-3-yl)tetracarbonylrhenium

Atom	U11	U22	U33	U23	U13	U12
Re(1)	0.0419(3)	0.0371(3)	0.0276(3)	0.0073(2)	0.0147(2)	0.0111(2)
S(1)	0.056(2)	0.066(2)	0.033(1)	0.015(1)	0.024(1)	0.026(1)
C(1)	0.046(6)	0.042(5)	0.034(5)	0.006(4)	0.002(5)	-0.005(5)
C(2)	0.072(8)	0.056(7)	0.045(7)	0.017(6)	0.029(6)	0.020(6)
C(3)	0.067(8)	0.046(6)	0.036(6)	0.004(5)	0.017(6)	0.002(6)
C(4)	0.054(7)	0.08(1)	0.07(1)	0.039(8)	0.028(7)	0.027(7)
C(5)	0.050(6)	0.052(6)	0.045(6)	0.017(5)	0.025(5)	0.021(5)
C(6)	0.043(5)	0.031(5)	0.035(5)	0.008(4)	0.012(4)	0.010(4)
C(7)	0.052(5)	0.038(4)	0.046(5)	0.017(4)	0.031(5)	0.020(4)
C(8)	0.037(5)	0.034(5)	0.030(6)	0.002(4)	0.013(4)	0.008(4)
C(9)	0.042(5)	0.030(5)	0.034(5)	0.008(4)	0.015(5)	0.012(4)
C(10)	0.063(7)	0.045(6)	0.054(7)	0.005(5)	0.017(6)	0.009(5)
C(11)	0.058(7)	0.071(7)	0.066(7)	0.036(6)	0.042(6)	0.025(5)
C(12)	0.038(5)	0.040(5)	0.037(5)	0.001(4)	0.005(4)	0.005(4)
O(1)	0.072(7)	0.063(6)	0.073(7)	0.004(5)	0.006(5)	0.037(5)
O(2)	0.090(9)	0.060(6)	0.048(7)	0.014(5)	0.035(7)	0.023(6)
O(3)	0.068(7)	0.091(8)	0.087(8)	0.029(7)	0.021(6)	0.051(6)
O(4)	0.072(6)	0.039(4)	0.101(8)	0.026(5)	0.018(5)	-0.004(4)
O(5)	0.055(5)	0.047(4)	0.039(4)	0.004(3)	0.020(4)	0.014(4)

Appendix IV

Thermal and Positional Parameters for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)-tetracarbonylmanganese

Table AIV.1 Final Positional and Equivalent Thermal Parameters for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	1.0411(1)	0.2375(1)	0.3237(1)	0.032
S(1)	0.7826(1)	0.0899(1)	0.2955(1)	0.035
O(1)	1.4079(4)	0.4114(2)	0.3771(2)	0.057
O(2)	0.7221(4)	0.5062(2)	0.2568(2)	0.063
O(3)	1.0893(4)	0.1662(3)	0.1102(2)	0.071
O(4)	0.9588(4)	0.3284(3)	0.5312(2)	0.063
O(5)	1.2415(3)	0.0476(2)	0.3735(1)	0.034
O(6)	0.7566(3)	0.0412(2)	0.3881(2)	0.050
O(7)	0.5801(3)	0.1441(2)	0.2267(2)	0.054
O(8)	0.7129(4)	-0.3621(3)	0.0277(2)	0.058
C(1)	1.2743(4)	0.3427(3)	0.3551(2)	0.039
C(2)	0.8492(5)	0.4019(3)	0.2839(2)	0.044
C(3)	1.0779(5)	0.1880(3)	0.1909(2)	0.043
C(4)	0.9906(4)	0.2896(3)	0.4543(2)	0.041
C(5)	1.2622(4)	-0.0906(3)	0.3477(2)	0.033
C(6)	1.4529(4)	-0.1900(3)	0.4068(2)	0.042
C(7)	1.1137(4)	-0.1563(3)	0.2640(2)	0.033
C(8)	0.8980(4)	-0.0849(3)	0.2309(2)	0.033
C(9)	0.7595(4)	-0.1490(3)	0.1525(2)	0.038
C(10)	0.8347(5)	-0.2879(3)	0.1044(2)	0.044
C(11)	1.0490(5)	-0.3601(3)	0.1351(2)	0.048
C(12)	1.1829(5)	-0.2962(3)	0.2143(2)	0.043
C(13)	0.4930(6)	-0.2919(5)	-0.0085(3)	0.068

Table AIV.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese

Atom	X/A	Y/B	Z/C	U11
H(61)	1.4411(4)	-0.2969(3)	0.4040(2)	0.087
H(62)	1.4781(4)	-0.1473(3)	0.4767(2)	0.087
H(63)	1.5744(4)	-0.1815(3)	0.3771(2)	0.087
H(9)	0.6095(4)	-0.0974(3)	0.1309(2)	0.057
H(11)	1.1035(5)	-0.4563(3)	0.1000(2)	0.057
H(12)	1.3314(5)	-0.3499(3)	0.2368(2)	0.057
H(131)	0.4398(6)	-0.3687(5)	-0.0600(3)	0.087
H(132)	0.4761(6)	-0.1966(5)	-0.0386(3)	0.087
H(133)	0.4094(6)	-0.2758(5)	0.0444(3)	0.087

Table AIV.3 Thermal Parameters for η^2-(2-Acetyl-5-methoxyphenylsulphonyl)tetracarbonylmanganese

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0273(2)	0.0233(2)	0.0456(3)	0.0069(2)	0.0109(2)	0.0010(2)
S(1)	0.0250(3)	0.0306(4)	0.0483(4)	0.0016(3)	0.0113(3)	-0.0007(3)
O(1)	0.047(1)	0.041(1)	0.089(2)	0.003(1)	0.020(1)	-0.016(1)
O(2)	0.048(1)	0.043(1)	0.095(2)	0.028(1)	0.017(1)	0.016(1)
O(3)	0.075(2)	0.096(2)	0.048(2)	0.009(1)	0.021(1)	-0.015(2)
O(4)	0.072(2)	0.063(2)	0.057(2)	-0.009(1)	0.027(1)	-0.013(1)
O(5)	0.0296(9)	0.0265(9)	0.046(1)	0.0060(8)	0.0077(8)	-0.0010(7)
O(6)	0.056(1)	0.048(1)	0.057(1)	0.000(1)	0.028(1)	-0.017(1)
O(7)	0.029(1)	0.047(1)	0.073(2)	0.000(1)	0.000(1)	0.0075(9)
O(8)	0.062(1)	0.051(1)	0.053(1)	-0.010(1)	0.001(1)	-0.013(1)
C(1)	0.035(1)	0.028(1)	0.056(2)	0.009(1)	0.016(1)	0.003(1)
C(2)	0.038(2)	0.037(2)	0.059(2)	0.009(1)	0.018(1)	-0.001(1)
C(3)	0.038(2)	0.038(2)	0.054(2)	0.010(1)	0.011(1)	-0.001(1)
C(4)	0.036(1)	0.027(1)	0.058(2)	0.002(1)	0.013(1)	-0.002(1)
C(5)	0.028(1)	0.028(1)	0.044(2)	0.008(1)	0.013(1)	-0.001(1)
C(6)	0.037(2)	0.030(1)	0.055(2)	0.013(1)	0.001(1)	0.001(1)
C(7)	0.030(1)	0.028(1)	0.040(2)	0.005(1)	0.010(1)	-0.001(1)
C(8)	0.032(1)	0.027(1)	0.041(2)	0.005(1)	0.010(1)	-0.002(1)
C(9)	0.035(1)	0.036(1)	0.043(2)	0.005(1)	0.007(1)	-0.005(1)
C(10)	0.052(2)	0.038(2)	0.041(2)	0.001(1)	0.009(1)	-0.011(1)
C(11)	0.054(2)	0.034(2)	0.051(2)	-0.006(1)	0.014(1)	-0.001(1)
C(12)	0.040(2)	0.032(1)	0.054(2)	0.004(1)	0.011(1)	0.005(1)
C(13)	0.065(2)	0.068(2)	0.063(2)	-0.002(2)	-0.008(2)	-0.020(2)

Appendix V

Thermal and Positional Parameters for η^2-3-Chloro-2-[1-(*N*-phenylimino)ethyl]-phenyltetracarbonylmanganese

Table AV.1 Final Positional and Equivalent Thermal Parameters for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.7975(1)	0.3816(1)	1.0595(1)	0.017
Cl(1)	0.1168(1)	0.3009(1)	0.8097(1)	0.030
N(1)	0.6191(2)	0.3905(1)	0.8578(2)	0.017
C(1)	0.5888(3)	0.3468(1)	1.0848(2)	0.020
C(2)	0.4440(3)	0.3423(1)	0.9559(2)	0.018
C(3)	0.2988(3)	0.3146(1)	0.9613(2)	0.022
C(4)	0.2900(3)	0.2945(1)	1.0893(2)	0.029
C(5)	0.4288(3)	0.3015(1)	1.2148(2)	0.035
C(6)	0.5768(3)	0.3263(1)	1.2128(2)	0.029
C(7)	0.4676(3)	0.3698(1)	0.8301(2)	0.018
C(8)	0.3319(3)	0.3758(1)	0.6839(2)	0.027
C(9)	0.6649(3)	0.4204(1)	0.7497(2)	0.019
C(10)	0.6564(3)	0.4847(1)	0.7381(2)	0.025
C(11)	0.7150(3)	0.5139(1)	0.6432(2)	0.033
C(12)	0.7832(3)	0.4796(1)	0.5622(2)	0.037
C(13)	0.7912(3)	0.4156(1)	0.5744(2)	0.037
C(14)	0.7304(3)	0.3858(1)	0.6674(2)	0.029
C(15)	0.8303(3)	0.2999(1)	1.0224(2)	0.022
C(16)	0.9694(3)	0.4144(1)	1.0111(2)	0.021
C(17)	0.7306(3)	0.4564(1)	1.1107(2)	0.023
C(18)	0.9372(3)	0.3703(1)	1.2435(2)	0.023
O(15)	0.8452(2)	0.2480(1)	1.0063(2)	0.033
O(16)	1.0771(2)	0.4345(1)	0.9848(2)	0.029
O(17)	0.6851(2)	0.5005(1)	1.1472(2)	0.041
O(18)	1.0251(2)	0.3626(1)	1.3614(1)	0.035

Table AV.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese

Atom	X/A	Y/B	Z/C	U11
H(4)	0.1865(3)	0.2756(1)	1.0903(2)	0.035
H(5)	0.4225(3)	0.2890(1)	1.3064(2)	0.035
H(6)	0.6756(3)	0.3292(1)	1.3024(2)	0.035
H(81)	0.2314(3)	0.3948(1)	0.6912(2)	0.032
H(82)	0.3039(3)	0.3344(1)	0.6413(2)	0.032
H(83)	0.3724(3)	0.4018(1)	0.6234(2)	0.032
H(10)	0.6093(3)	0.5091(1)	0.7966(2)	0.035
H(11)	0.7069(3)	0.5591(1)	0.6331(2)	0.035
H(12)	0.8273(3)	0.5005(1)	0.4972(2)	0.035
H(13)	0.8390(3)	0.3912(1)	0.5165(2)	0.035
H(14)	0.7343(3)	0.3405(1)	0.6751(2)	0.035

Table AV.3 Thermal Parameters for η^2-3-Chloro-2-[1-(N-phenylimino)ethyl]-phenyltetracarbonylmanganese

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0166(2)	0.0155(2)	0.0172(2)	0.0003(1)	0.0048(1)	-0.0009(1)
Cl(1)	0.0187(3)	0.0360(3)	0.0338(3)	-0.0069(2)	0.0068(2)	-0.0065(3)
N(1)	0.020(1)	0.0143(8)	0.0162(8)	0.0017(7)	0.0063(7)	0.0015(8)
C(1)	0.020(1)	0.017(1)	0.024(1)	0.0027(8)	0.0085(9)	-0.003(1)
C(2)	0.020(1)	0.013(1)	0.023(1)	0.0009(8)	0.0088(9)	0.0019(9)
C(3)	0.018(1)	0.016(1)	0.030(1)	0.0002(9)	0.006(1)	0.002(1)
C(4)	0.025(1)	0.024(1)	0.040(1)	0.008(1)	0.015(1)	-0.001(1)
C(5)	0.035(2)	0.040(1)	0.032(1)	0.015(1)	0.015(1)	-0.001(1)
C(6)	0.027(1)	0.033(1)	0.025(1)	0.009(1)	0.005(1)	-0.003(1)
C(7)	0.021(1)	0.013(1)	0.020(1)	-0.0024(8)	0.0058(9)	0.0021(9)
C(8)	0.025(1)	0.026(1)	0.022(1)	0.0035(9)	0.002(1)	-0.003(1)
C(9)	0.018(1)	0.023(1)	0.0143(9)	0.0019(8)	0.0030(8)	-0.002(1)
C(10)	0.027(1)	0.023(1)	0.024(1)	0.0028(9)	0.010(1)	0.000(1)
C(11)	0.034(2)	0.029(1)	0.032(1)	0.010(1)	0.008(1)	-0.004(1)
C(12)	0.036(2)	0.053(2)	0.025(1)	0.013(1)	0.015(1)	-0.002(1)
C(13)	0.043(2)	0.050(2)	0.026(1)	0.001(1)	0.020(1)	0.006(1)
C(14)	0.037(1)	0.028(1)	0.021(1)	0.002(1)	0.011(1)	0.006(1)
C(15)	0.015(1)	0.024(1)	0.021(1)	0.0033(9)	0.0009(9)	-0.002(1)
C(16)	0.023(1)	0.016(1)	0.021(1)	-0.0007(8)	0.0055(9)	0.001(1)
C(17)	0.024(1)	0.024(1)	0.024(1)	-0.0001(9)	0.012(1)	-0.004(1)
C(18)	0.022(1)	0.022(1)	0.028(1)	-0.0014(9)	0.012(1)	-0.006(1)
O(15)	0.033(1)	0.0190(9)	0.0401(9)	-0.0027(7)	0.0047(8)	0.0022(8)
O(16)	0.0275(9)	0.0256(9)	0.0389(9)	-0.0021(7)	0.0187(8)	-0.0051(8)
O(17)	0.049(1)	0.027(1)	0.057(1)	-0.0087(8)	0.032(1)	0.0016(9)
O(18)	0.033(1)	0.045(1)	0.0193(8)	0.0035(7)	0.0013(7)	-0.0038(9)

Appendix VI

Thermal and Positional Parameters for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate

Table AVI.1 Final Positional Parameters for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate

Atom	X/A	Y/B	Z/C
S(1)	0.14060(8)	0.09464(5)	0.40224(5)
C(1)	0.2576(3)	0.1500(2)	0.5203(2)
C(2)	0.2573(3)	0.2673(2)	0.5141(2)
C(3)	0.3295(3)	0.3639(2)	0.5811(2)
C(4)	0.2803(3)	0.4626(2)	0.5266(2)
C(5)	0.1728(3)	0.4397(2)	0.4167(2)
C(6)	0.1647(3)	0.3114(2)	0.4153(2)
C(7)	-0.0922(3)	0.2293(2)	0.3452(2)
C(8)	0.0183(3)	0.2436(2)	0.2367(2)
C(9)	0.3401(3)	0.0699(2)	0.6072(2)
C(10)	0.4408(3)	0.3517(2)	0.6892(2)
C(11)	0.3212(3)	0.5794(2)	0.5662(2)
C(12)	0.2874(3)	0.7766(2)	0.5231(2)
O(1)	0.3990(3)	0.6064(2)	0.6533(1)
O(2)	0.2588(2)	0.6579(1)	0.4922(1)

Table AVI.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate

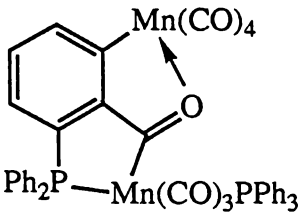
Atom	X/A	Y/B	Z/C	U11
H(51)	0.2362(3)	0.4692(2)	0.3635(2)	0.041
H(52)	0.0511(3)	0.4736(2)	0.4061(2)	0.041
H(81)	-0.0065(4)	0.1731(2)	0.1975(2)	0.096
H(82)	0.0254(4)	0.3092(2)	0.2017(2)	0.096
H(83)	-0.1462(4)	0.2555(2)	0.2398(2)	0.096
H(91)	0.2462(4)	0.0162(2)	0.6195(2)	0.096
H(92)	0.3846(4)	0.1147(2)	0.6708(2)	0.096
H(93)	0.4410(4)	0.0266(2)	0.5887(2)	0.096
H(101)	0.3781(3)	0.3017(2)	0.7310(2)	0.096
H(102)	0.4687(3)	0.4255(2)	0.7252(2)	0.096
H(103)	0.5538(3)	0.3148(2)	0.6803(2)	0.096
H(121)	0.2462(4)	0.8258(2)	0.4619(2)	0.096
H(122)	0.4155(4)	0.7925(2)	0.5525(2)	0.096
H(123)	0.2146(4)	0.7924(2)	0.5758(2)	0.096

Table AVI.3 Thermal Parameters for Methyl 1,3,6-trimethyl-4H-cyclopenta[c]thiophene-5-carboxylate

Atom	U11	U22	U33	U23	U13	U12
S(1)	0.0366(4)	0.0224(3)	0.0360(4)	-0.0067(2)	0.0025(3)	-0.0042(2)
C(1)	0.028(1)	0.022(1)	0.032(1)	-0.0009(9)	0.0031(9)	-0.0005(9)
C(2)	0.025(1)	0.022(1)	0.027(1)	-0.0001(9)	0.0032(9)	-0.0012(9)
C(3)	0.022(1)	0.022(1)	0.027(1)	-0.0012(9)	0.0022(9)	-0.0009(8)
C(4)	0.025(1)	0.024(1)	0.023(1)	-0.0008(9)	0.0017(9)	0.0008(9)
C(5)	0.028(1)	0.023(1)	0.026(1)	0.0002(9)	0.0005(9)	0.0001(9)
C(6)	0.024(1)	0.024(1)	0.026(1)	-0.0007(9)	0.0013(9)	0.0008(9)
C(7)	0.028(1)	0.028(1)	0.030(1)	-0.0030(9)	0.0032(9)	-0.0025(9)
C(8)	0.041(2)	0.043(2)	0.030(1)	-0.006(1)	-0.002(1)	-0.004(1)
C(9)	0.045(2)	0.022(1)	0.044(2)	0.007(1)	0.000(1)	0.002(1)
C(10)	0.038(1)	0.029(1)	0.027(1)	0.001(1)	-0.004(1)	-0.002(1)
C(11)	0.028(1)	0.025(1)	0.029(1)	0.0012(9)	0.0035(9)	0.0004(9)
C(12)	0.048(2)	0.018(1)	0.046(2)	-0.003(1)	0.005(1)	-0.001(1)
O(1)	0.072(1)	0.0260(9)	0.032(1)	-0.0040(7)	-0.0117(9)	-0.0038(9)
O(2)	0.043(1)	0.0165(8)	0.0350(9)	-0.0004(7)	-0.0019(7)	0.0019(7)

Appendix VII

List of Compounds by Numbers and NMR Numbering Scheme



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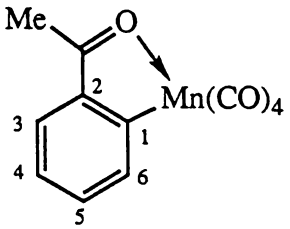

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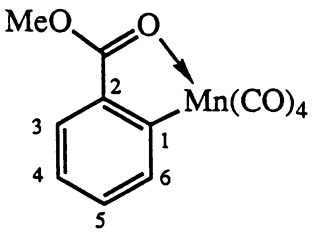

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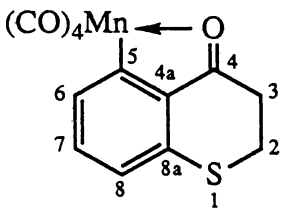

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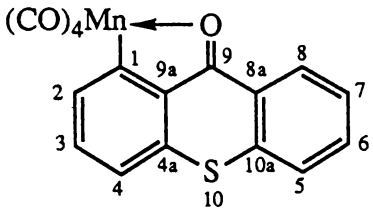

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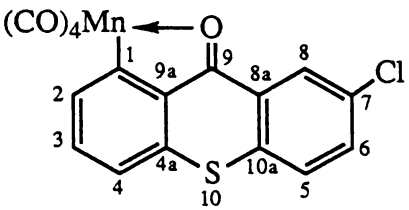

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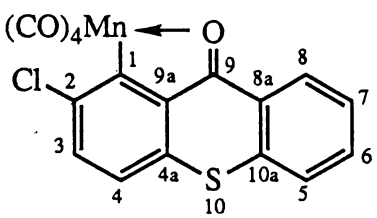

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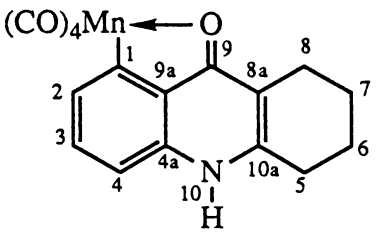

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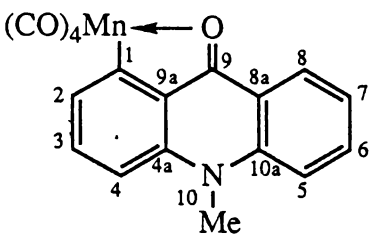

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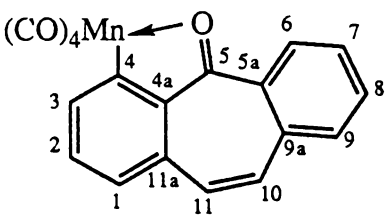

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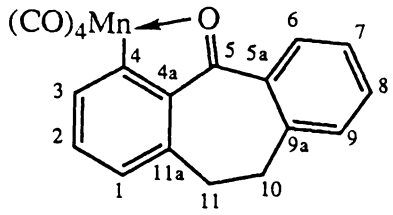

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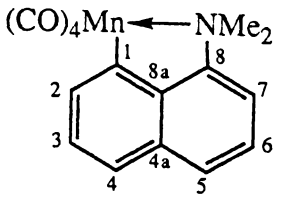

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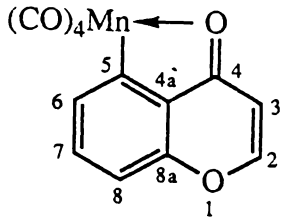

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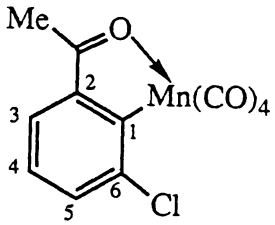

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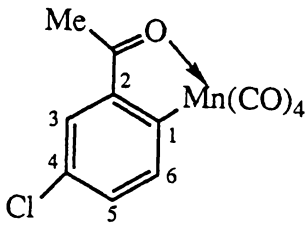

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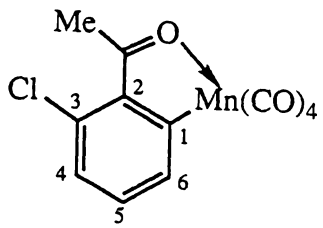

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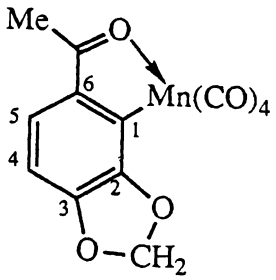

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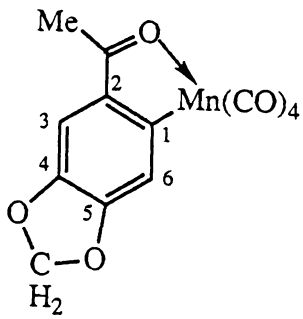

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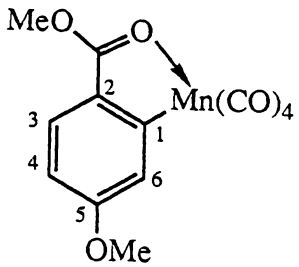

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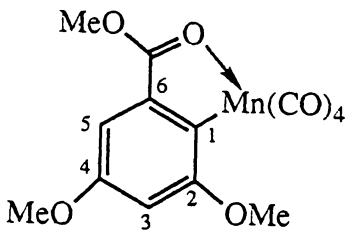

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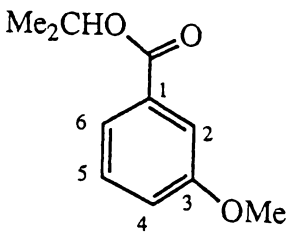

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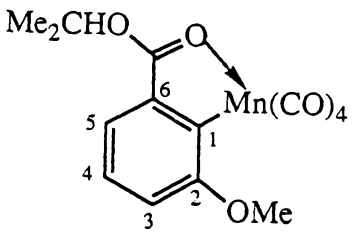

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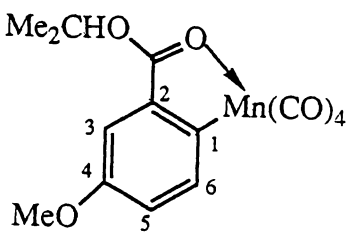

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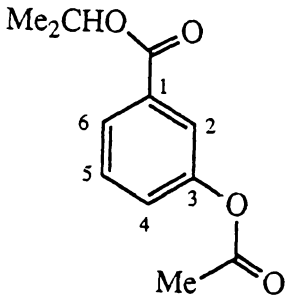

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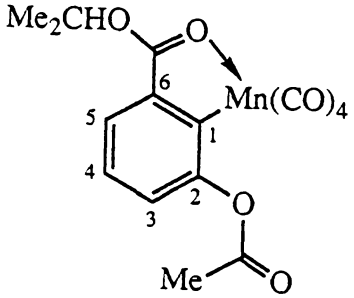

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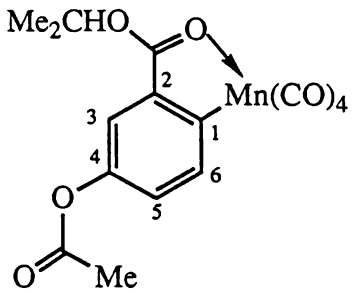

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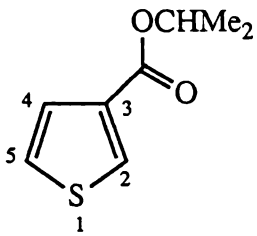

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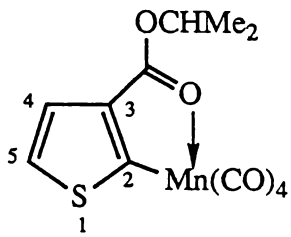

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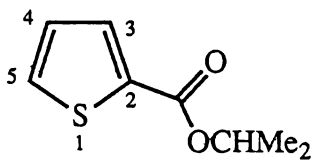

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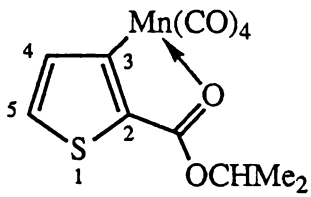

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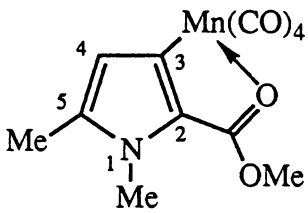

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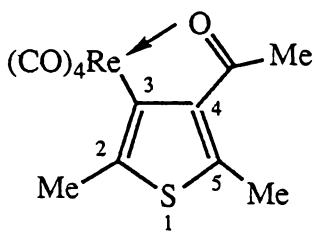

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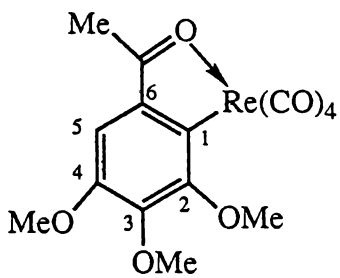

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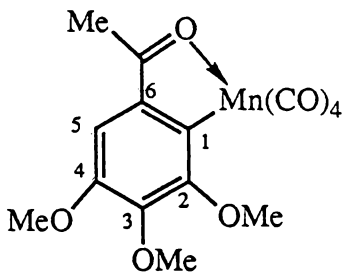

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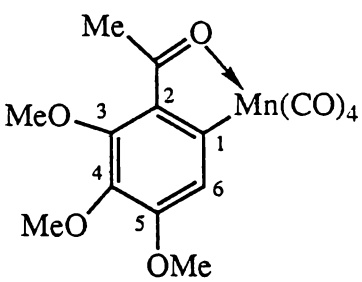

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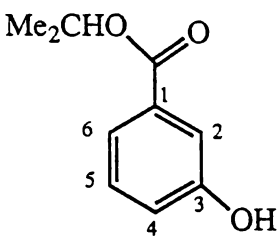

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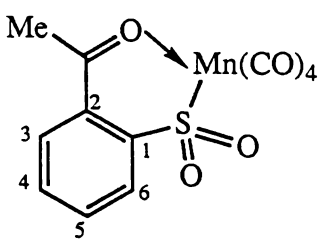

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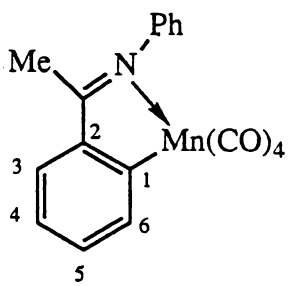

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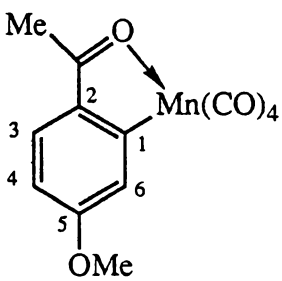

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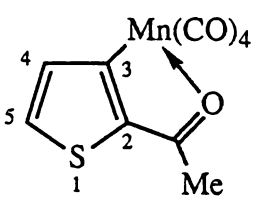

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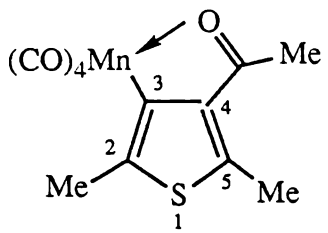

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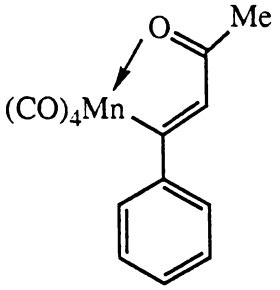

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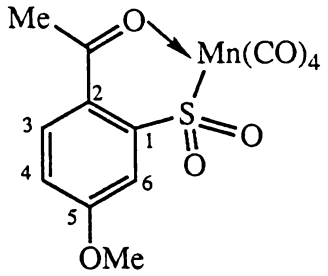

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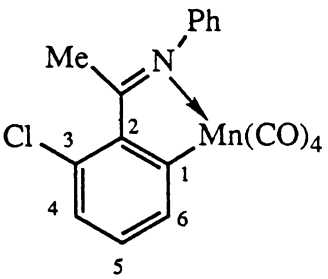

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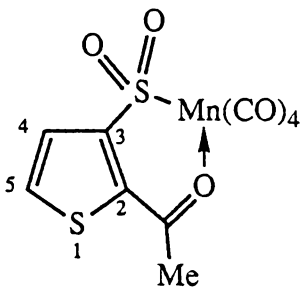

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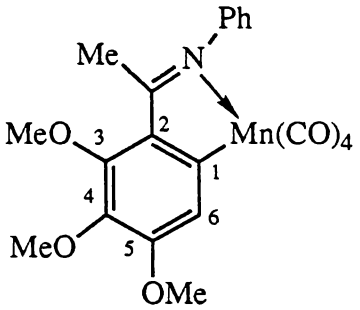

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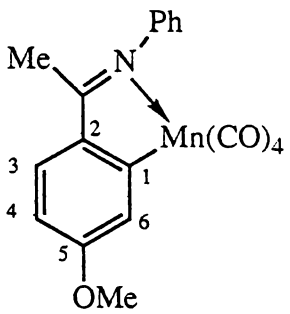

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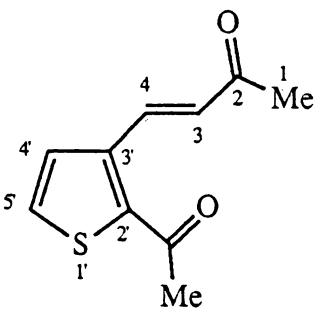

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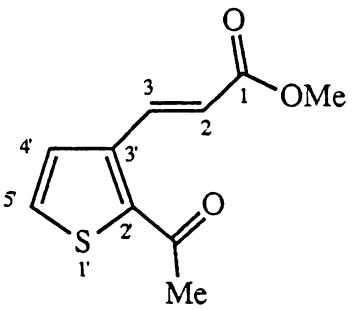

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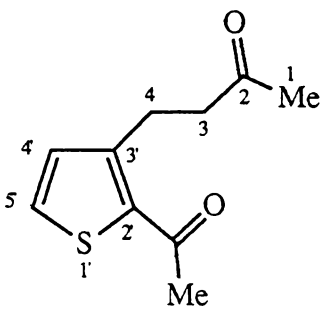

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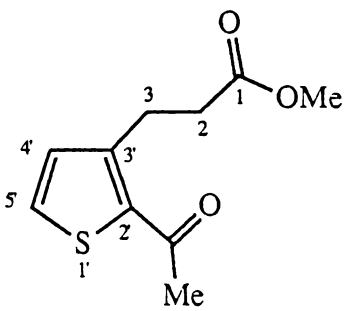

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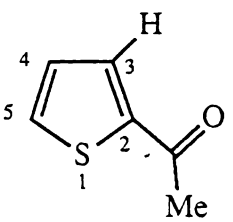

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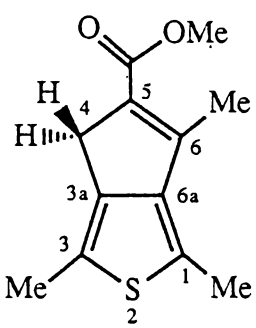

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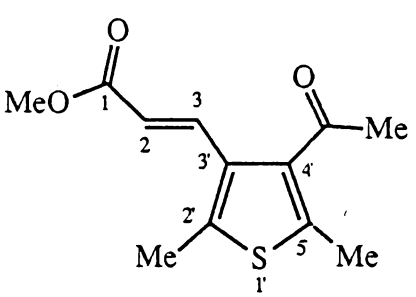

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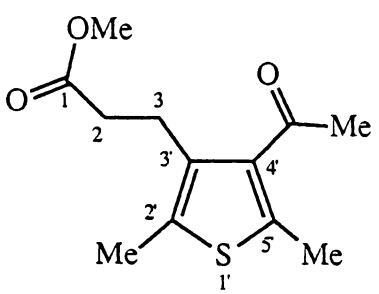

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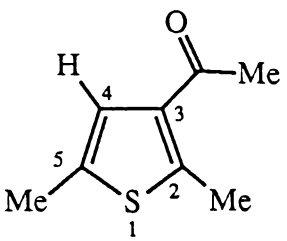

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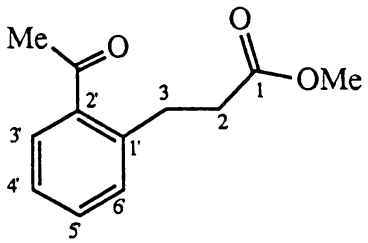

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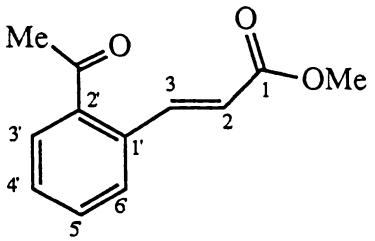

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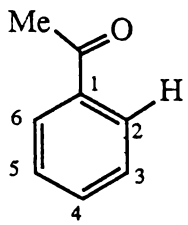

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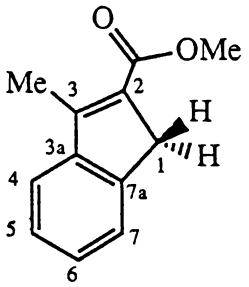

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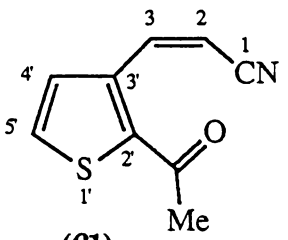

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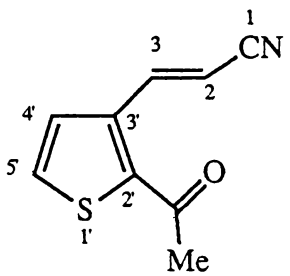

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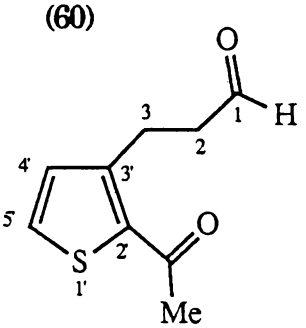

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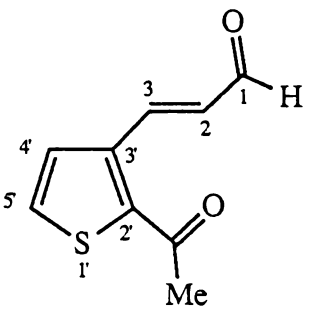

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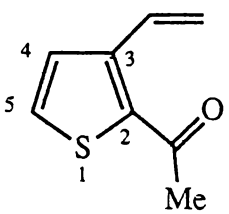

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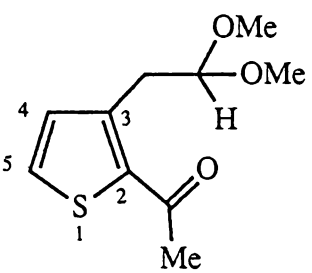

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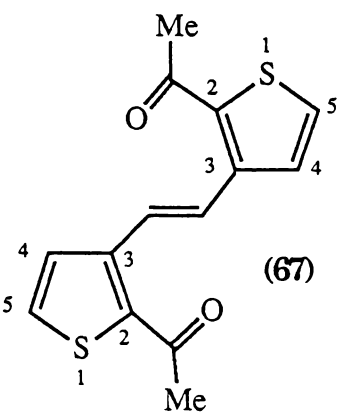

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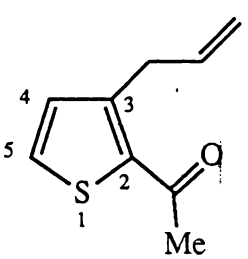

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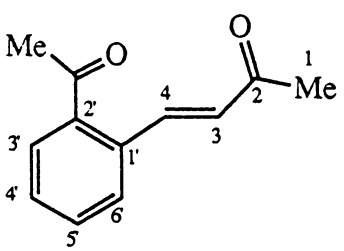

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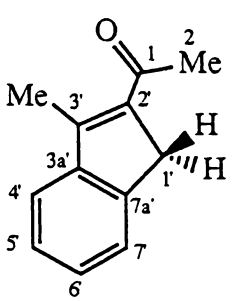

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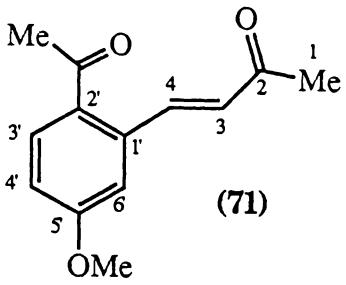

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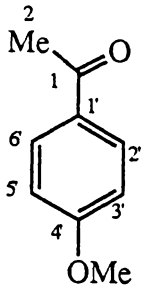

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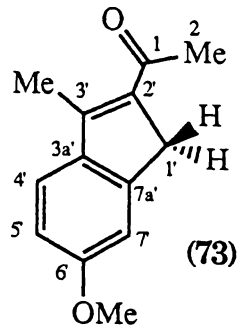

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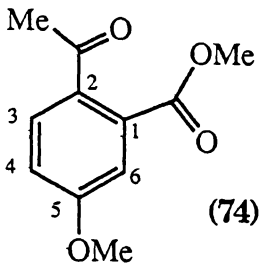

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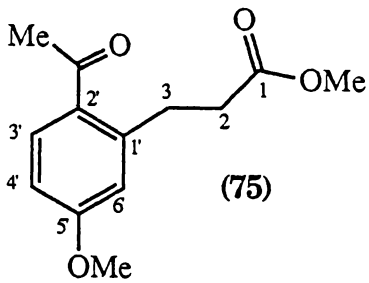

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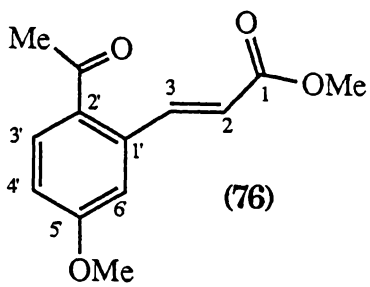

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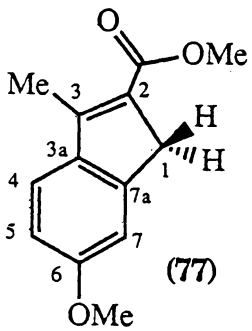

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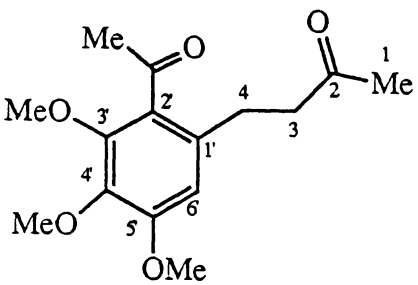

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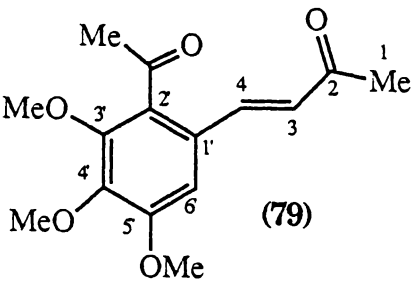

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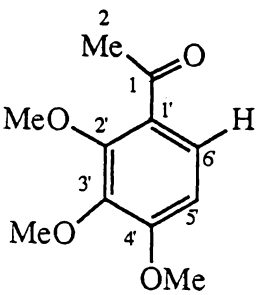

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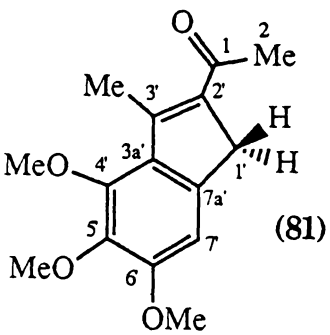

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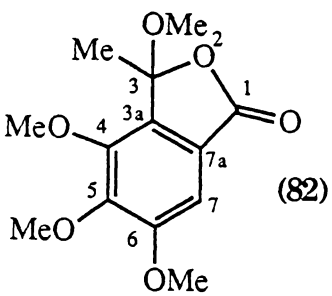

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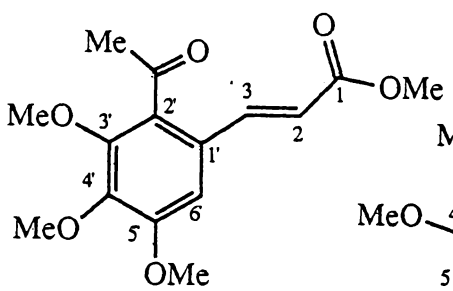

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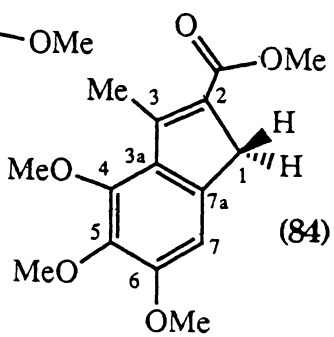

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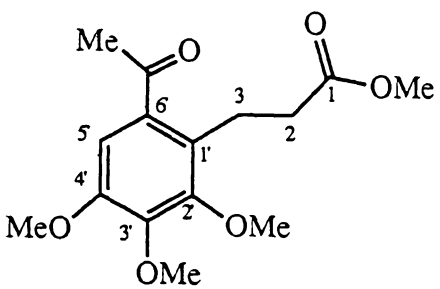

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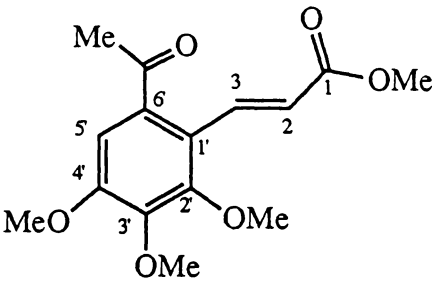

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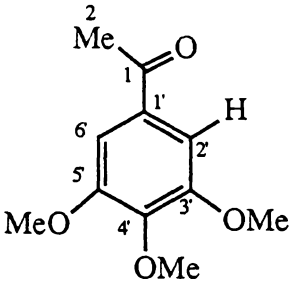

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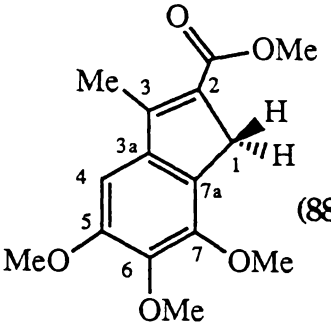

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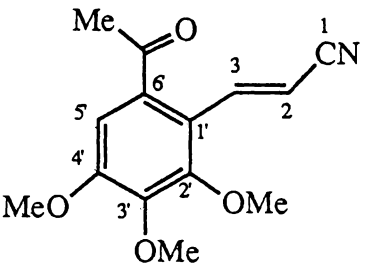

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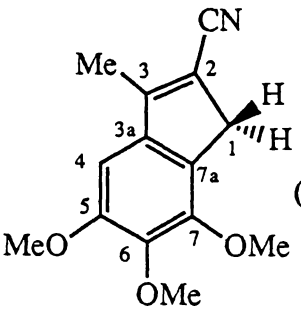

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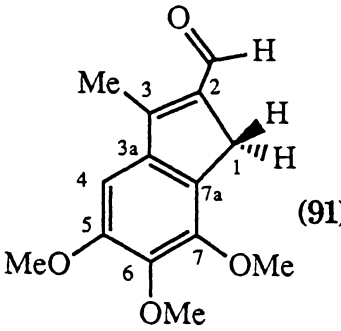

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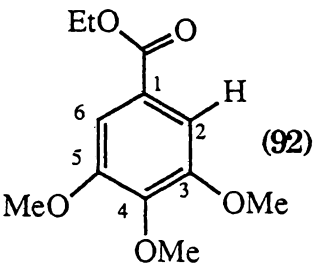

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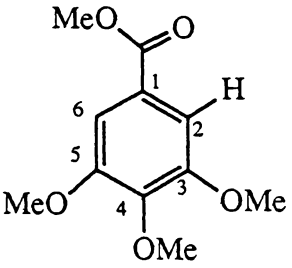

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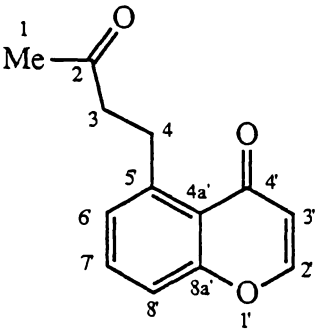

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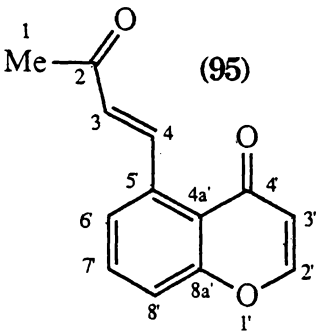

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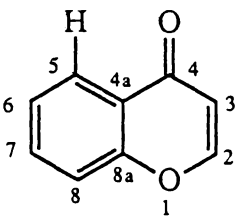

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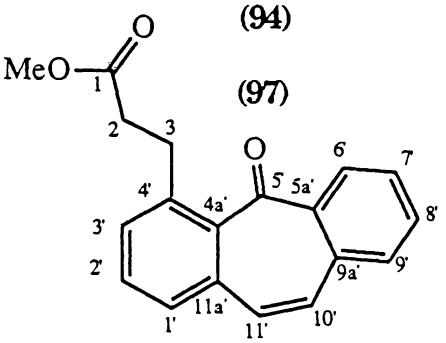

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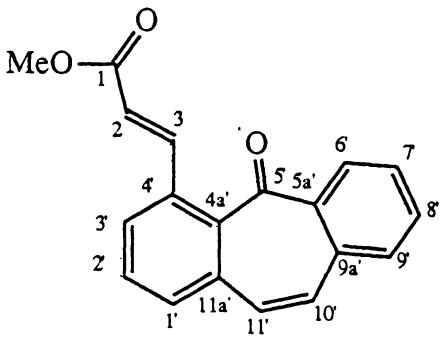

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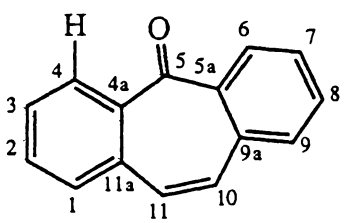

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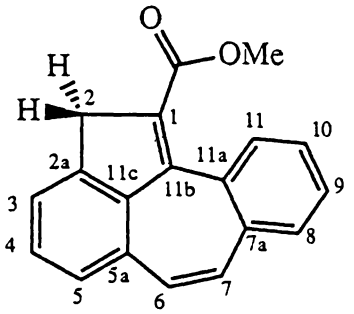

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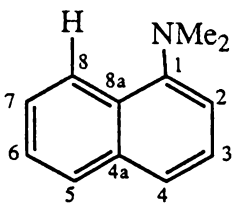

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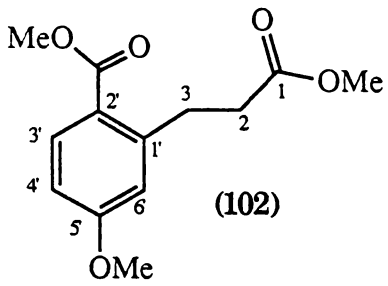

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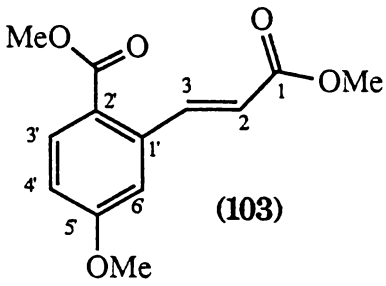

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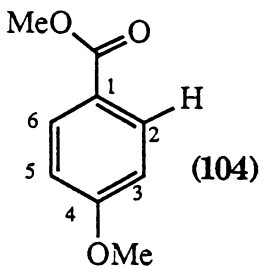

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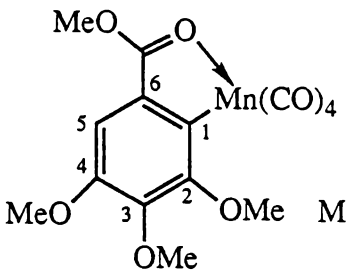

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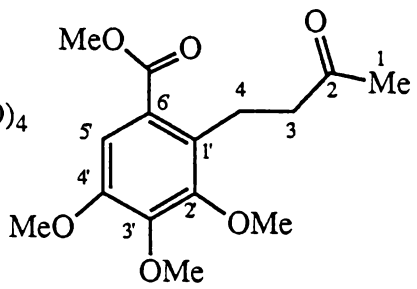

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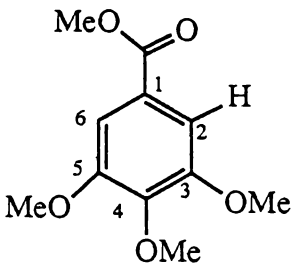

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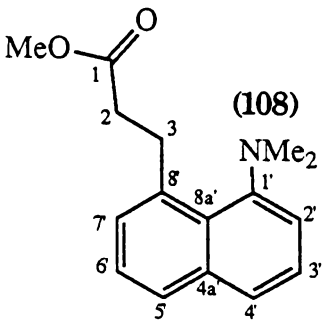

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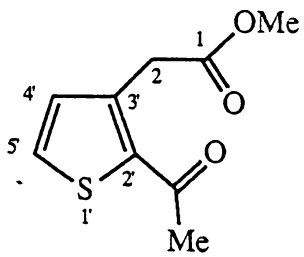

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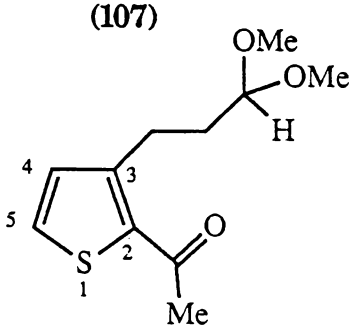

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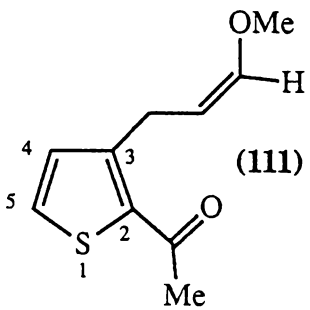

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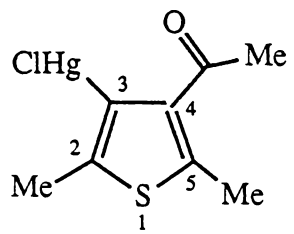

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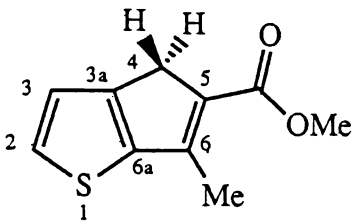

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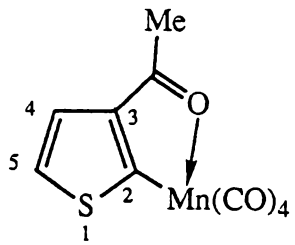

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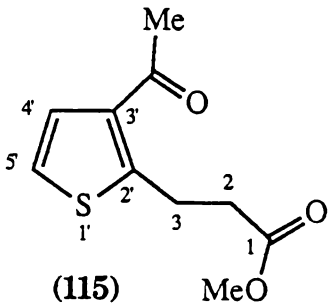

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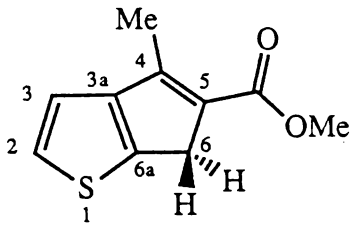

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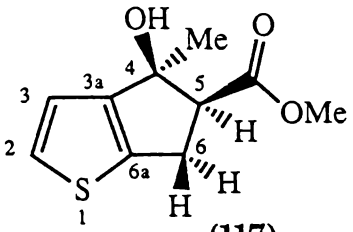

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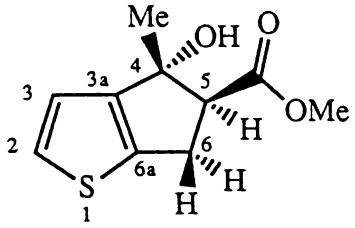

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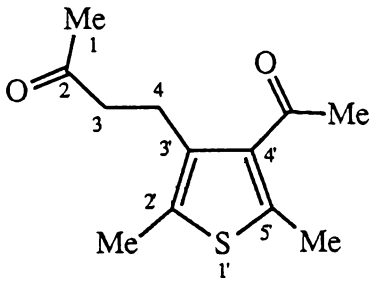

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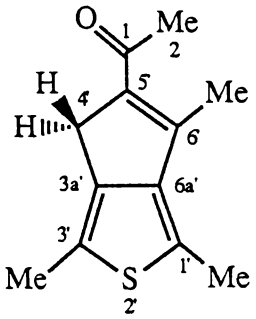

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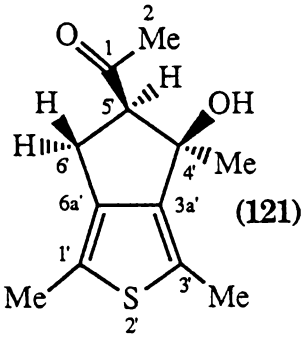

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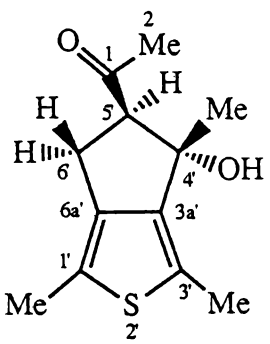

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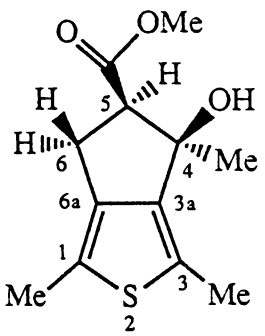

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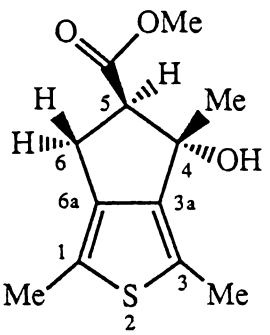

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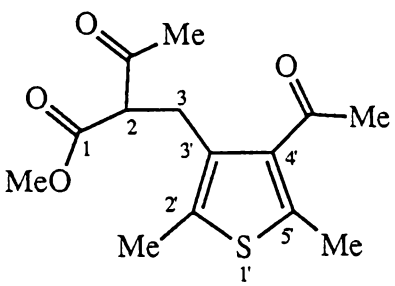

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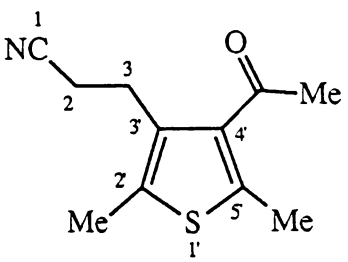

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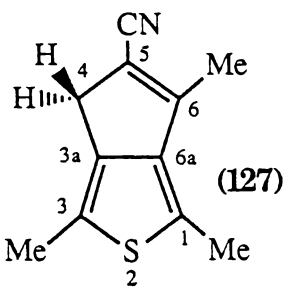

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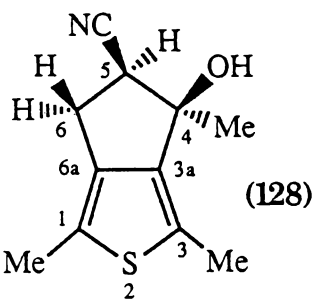

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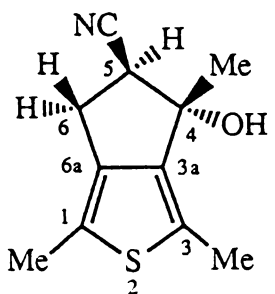

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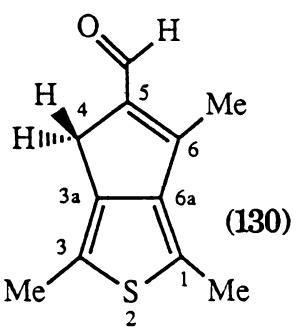

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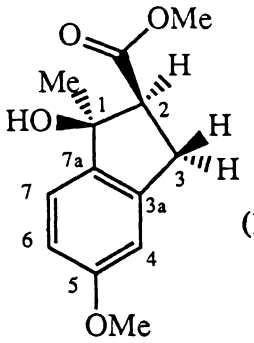

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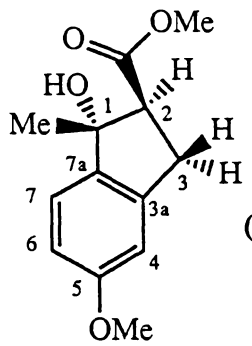

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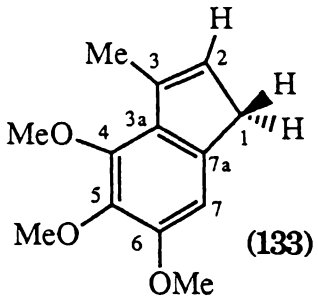

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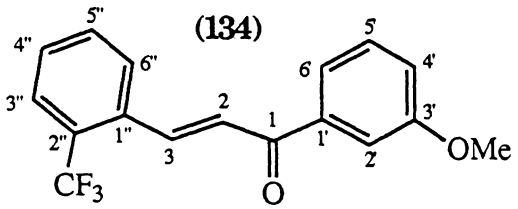

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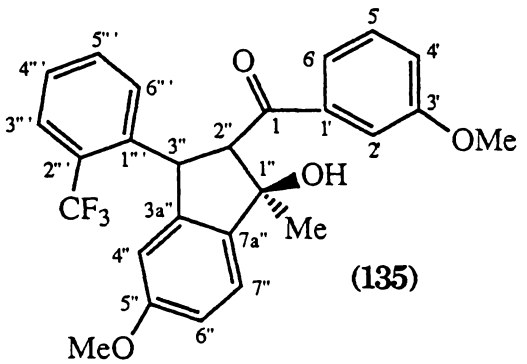

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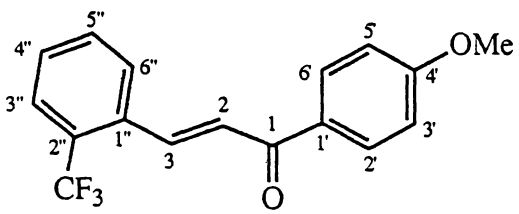

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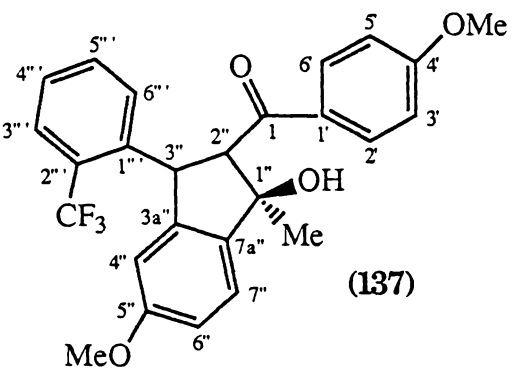

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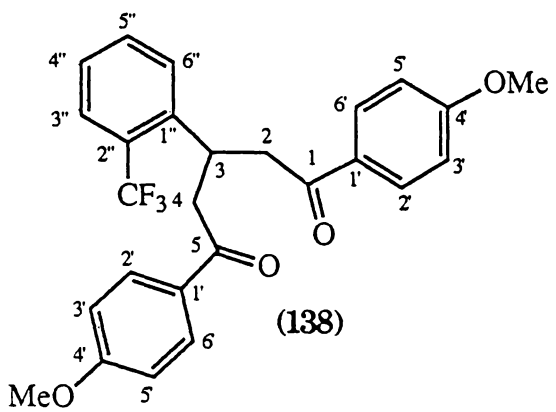

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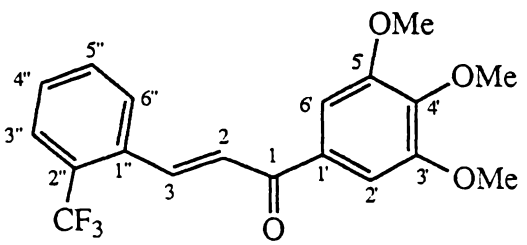

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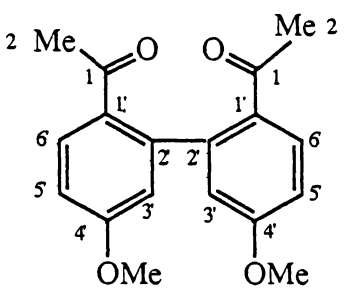

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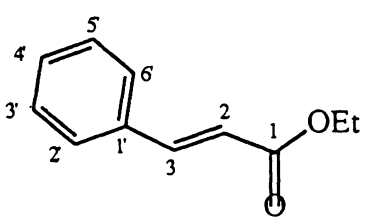

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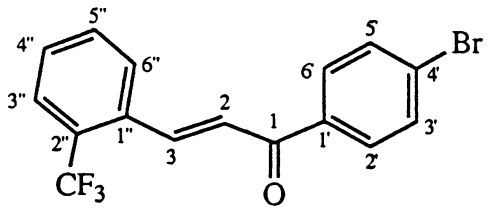

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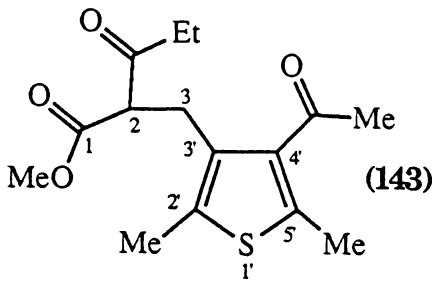

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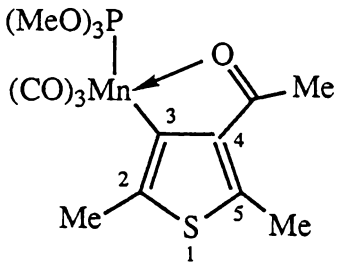

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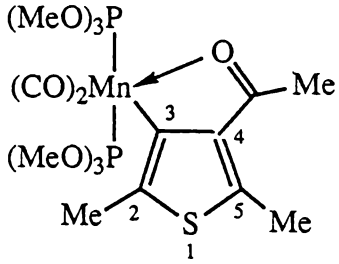

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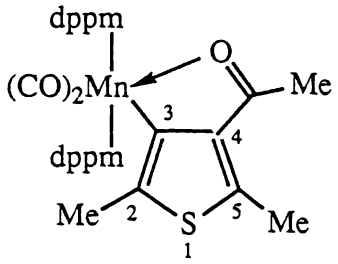

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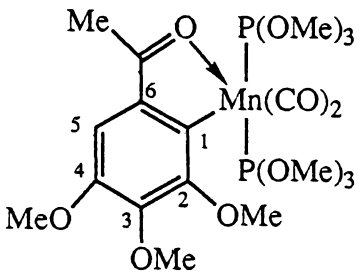

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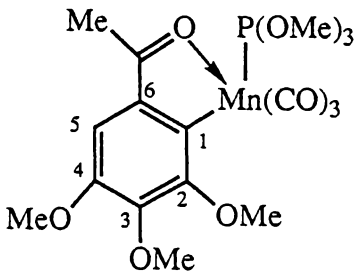

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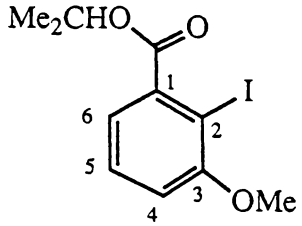

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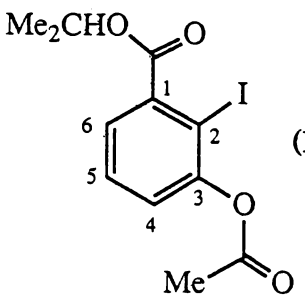

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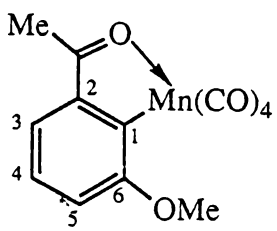

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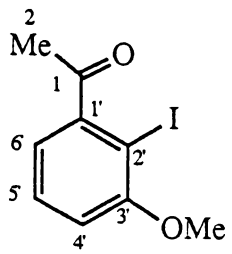

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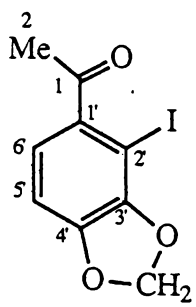

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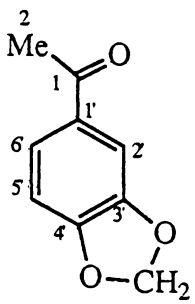

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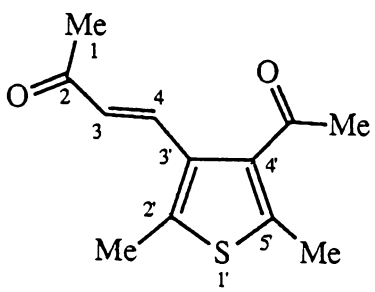

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