SOME CHEMISTRY
OF
ORTHOMANGANATED KETONES

A thesis
submitted in partial fulfilment
of the requirements for the Degree
of
Doctor of Philosophy in Chemistry
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by
LOUIE HERMAN PETER GOMMANS

*****

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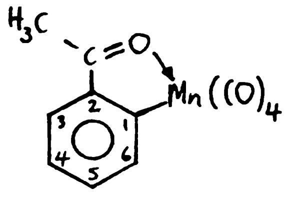
To Carey

and our parents

ABSTRACT

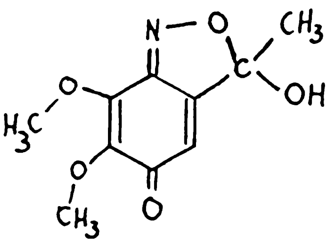
The major part of this thesis describes the preparation and reactions of orthomanganated aromatic ketones, such as (1), diagram. Among the new species characterised are substituted acetophenones, analogues of (1), namely : 3,4,5-trimethoxy (3); 4,5,6-trimethoxy (4); 3-t-butyldimethylsiloxy-4,5-dimethoxy (5); 4,5-dimethoxy (6); 5,6-dimethoxy (7); 3-benzyloxy-4,5-dimethoxy (8); and 3-t-butyldimethylsiloxy (9).



(1)

Hetero aromatic ketones have been used to prepare the corresponding orthomanganated compounds (10), (11), (12), (14) and (15) from the respective ketones 2-acetylthiophene, 3-acetyl-2,5-dimethylthiophene, 2-acetyl-N-methylpyrrole, 3-acetylindole and 2-acetylfuran. The crystal structure of η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (11) has been determined. The 5-manganated derivative (13) of flavanone has also been made. Attempted orthometallations of acetophenones with $C_6H_5CH_2Co(CO)_4$, $C_6H_5CH_2Fe(CO)_2Cp$ and $Pd(OAc)_2$ were unsuccessful.

Reaction of (4) with Br_2 in carbon tetrachloride gave the orthobromoacetophenone 2'-bromo-3',4',5'-trimethoxyacetophenone (21) plus $[Mn(CO)_4Br]_2$. The corresponding orthoiodoacetophenone (28) and $[Mn(CO)_4Cl]_2$ was obtained using ICl. Other orthohalogenated ketones were obtained similarly. The reactions were sometimes unsuccessful (e.g. for (1)) or complicated (e.g. (5) competitive ring bromination). Oxidation of (1) or (4) with cerium (IV) ammonium nitrate (0.5 mol) in CD_3CO_2D gives the corresponding orthomonodeuterio acetophenones (19) or (20). A by-product from the oxidation of (4), the cyclic hemiketal, (36), was identified by X-ray crystal structure analysis, and one other product, the lactone, (37) was identified spectrally.



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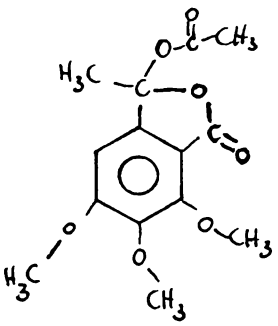

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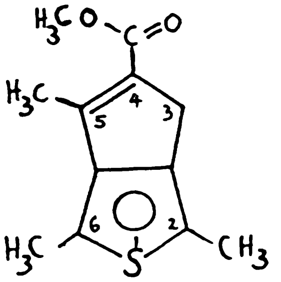
Determination by ^{1}H-NMR of the ratio of the 3-deuterio- (**1a**) to 3-protio- (**1**) formed in the orthometallation of orthomonodeuterio acetophenone (**19**) by $C_6H_5CH_2Mn(CO)_5$ gave a hydrogen isotope effect of 3.6. Similarly, for 2'-deuterio-3',4',5'-trimethoxyacetophenone (**20**) the value was 2.9. However, when the orthodeuterioacetophenone (**19**) was reacted with cis-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ the product *fac*-η^2-(2-acetylphenyl)tricarbonyltriphenylphosphinomanganese (**16**)/(**16a**) showed a D/H ratio of only 1.1. Implications of these isotope effects for mechanisms are discussed.

Reactions of orthomanganted ketones with vinyl reagents in the presence of Pd(II) were studied in two solvents. In methanol, (**1**) with methyl acrylate ($H_2C{=}CHCOOCH_3$) and Li_2PdCl_4 (1 mol) gave methyl E-3-(2-acetylphenyl)acrylate (**38**). Similarly η^2-(2-acetylthien-3-yl)-tetracarbonylmanganese (**10**) gave methyl E-3-(2-acetylthien-3-yl) acrylate (**40**). A variety of other products from coupling reactions with vinyl acetate, acrylonitrile, styrene, methyl vinyl ketone, acrolein and allyl alcohol are reported, and possible mechanisms for coupling reactions are discussed. In acetonitrile as solvent, under reflux, with $PdCl_2$ (1 mol) and excess LiCl, some of the orthomanganated ketones provided new routes to indenes in their reaction with methyl acrylate. Thus (**4**) gave methyl 3-methyl-5,6,7-trimethoxyindene-2-carboxylate (**53**), and (**2**) and (**3**) gave the corresponding indenes

[(51) and (49)]. The thiophene derivative η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (11) also gave the corresponding bicyclic compound, methyl 2,5,6-trimethyl-3H-cyclopenta-[c]-thiophene-4-carboxylate, (54) but the major product was the arylated acrylate ester (55) in this case.



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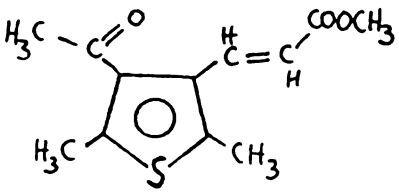

(55)

In reaction of (2) with $HgCl_2$ in refluxing methanol, transmetallation occurs to form chloro(2-acetyl-5-methoxyphenyl)mercury(II) (57). The corresponding mercuric chloride of (1), that is, chloro(2-acetylphenyl)mercury(II) (56), has also been prepared and its crystal structure is reported.

In a separate study dodecahydrotriphenylene ($C_{18}H_{24}$) (58) has been used to prepare the isoelectronic metal arene π-complexes η^6-($C_{18}H_{24}$)Cr(CO)$_3$ (59) and η^6-($C_{18}H_{24}$)Mn(CO)$_3^+$ (60). The crystal structures of the former and of the two distinct crystalline modifications of the latter, as BF_4^- salts are reported and compared.

ACKNOWLEDGEMENTS

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Finally, special thanks to my wife Carey, and our parents and families, for their concern, continued support and encouragement over the last three years of university education.

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Abbreviations

TBMSC	t-butyldimethylsilylchloride
Me	methyl
Ph	phenyl
Ac	acetyl
Bu^t	tertiary butyl
NMR	nuclear magnetic resonance
δ	chemical shift (ppm)
J	coupling constant (Hz)
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
br	broad
THF	tetrahydrofuran
D_2O	deuterium oxide
p.l.c	preparative layer chromatography
$W_{1/2}$	half band width at half peak height

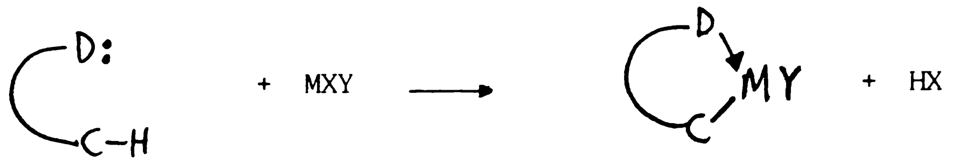
CHAPTER ONE

General Aspects of Orthometallation

1.1 Introduction

This thesis is largely focussed on compounds described as being *cyclometallated* or *orthometallated.*

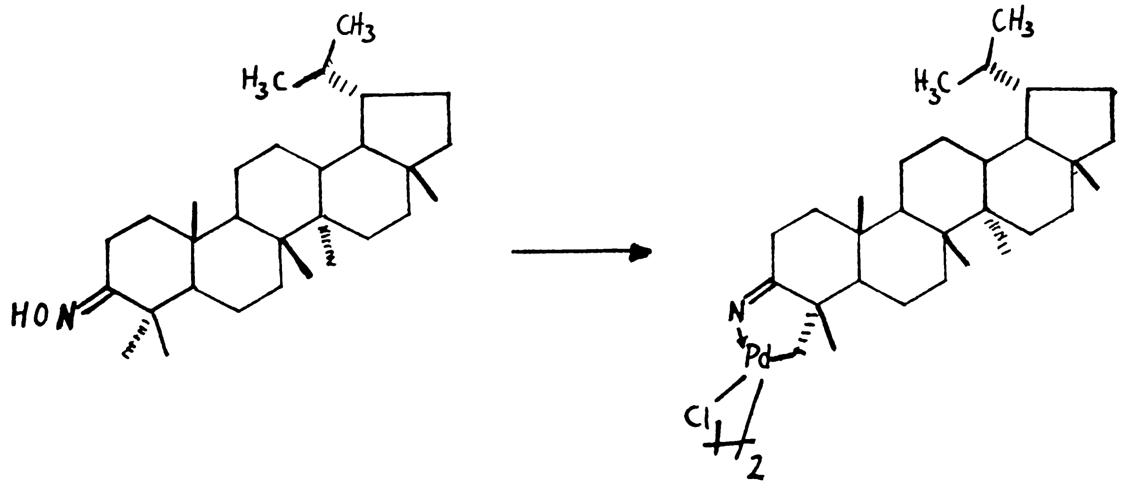
Cyclometallation is a reaction (equation 1.1) of a metal (M) reagent (MXY) and an organic molecule with a donor atom (D) to form a metal-carbon bond in a chelate ring, with elimination of HX (equation 1.1), or of another molecule if the metal replaces an atom other than H.



Equation 1.1

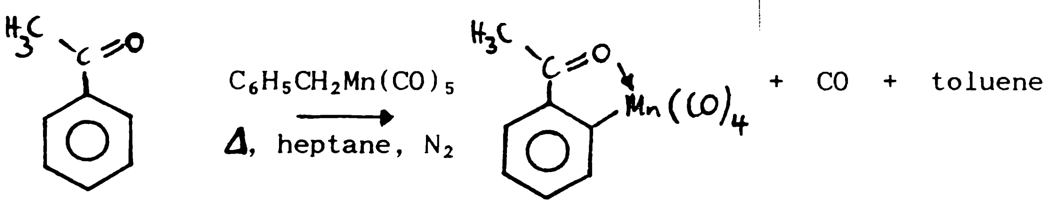
There are excellent general reviews on cyclometallation by Carty,[1] Bruce,[2] Dehand and Pfeffer,[3] Omae[4] and Abicht and Issleib.[5] Specific reviews on cyclometallation involvihg N,[4,6] P,[4,7] As[4,8], O[4,9] and S[4,10] are available.

Cyclometallation can occur with aliphatic C-H bonds (e.g. equation 1.2)[11] and some aspects of such reactions have recently been reviewed by Crabtree.[12]



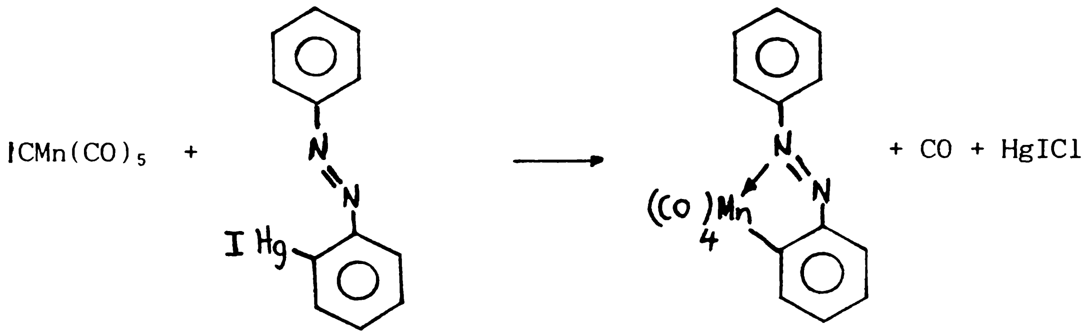
Equation 1.2

Cyclometallation of aryl systems is of more relevance to the current study. The example in equation 1.3[13] shows the substitution by metal in the ring postion *ortho* to the donor function: hence arises the term orthometallation for this special case of cyclometallation.

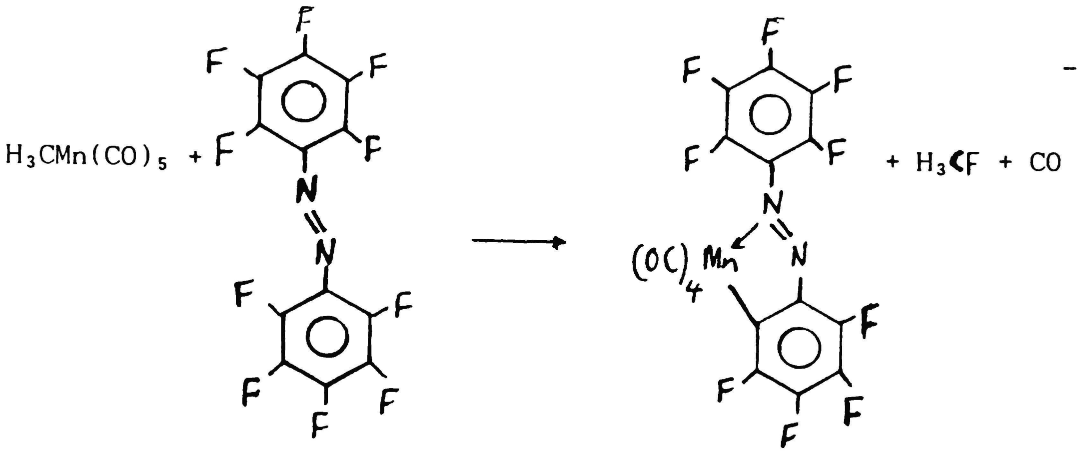


Equation 1.3

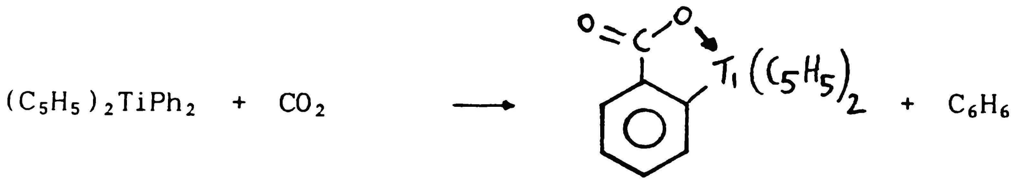
Orthometallation products can also be prepared by replacement of ortho-substituents other than H[14,15] (equations 1.4 and 1.5) as well as by indirect methods in some cases, e.g. as in equation 1.6.[16]



Equation 1.4

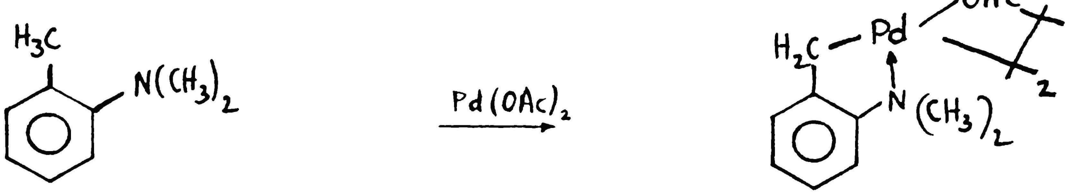


Equation 1.5

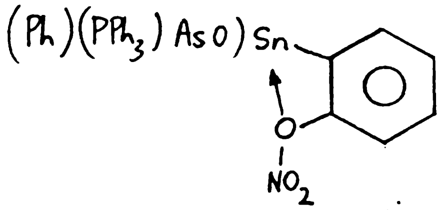


Equation 1.6

All of the above cyclometallation products have chelate rings which are five membered. This us usual if there is a choice (compare equations 1.7 and 1.8),[17,18] but there are examples of ring sizes of 3,4,6 and 7.



Equation 1.7



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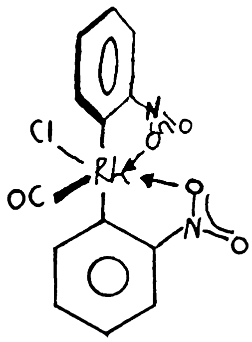

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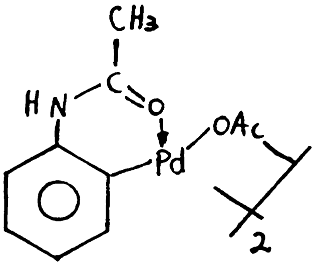

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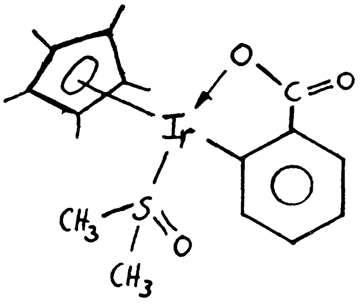

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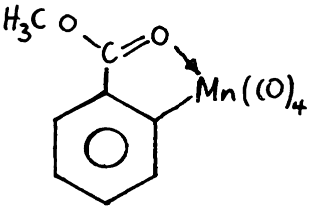

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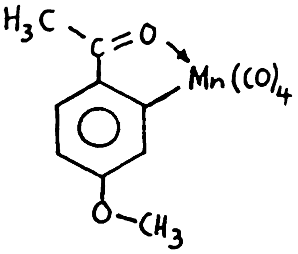

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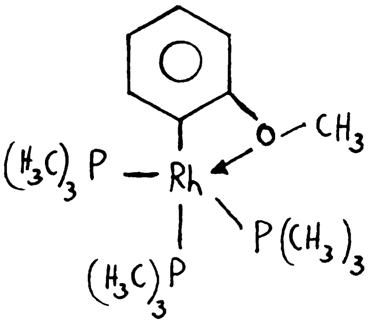

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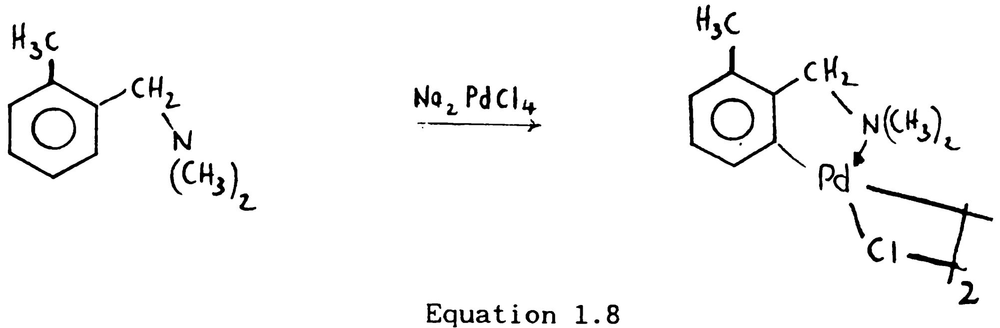


Equation 1.8

Orthometallation compounds with O-donor functions, into which group most of the compounds in the present study fall, are known for Sn[19] and Tl[20] as well as a range of transition metals including Ti,[16] Mn,[13] Re,[13] Ru,[21,22] Ir,[23] Rh,[23,24] Os[23] and Pd.[25] The O-donor group can be nitrato (i)[19], nitro (ii),[24] amido (iii),[25] carboxylate (iv),[20] carboalkoxy (v),[26] keto (vi)[13] or alkoxy (vii).[27]

Information on both the synthesis and the reactions of orthometallated compounds is so extensive that in this thesis it has been centred around manganese and is covered as required in the introductions to the separate chapters (see below).

The mechanisms of orthometallation are little understood and this area is reviewed for manganese in Chapter Three.

1.2 Outline of the Present Study

The major findings in the present study are outlined chapter by chapter as the following:

Chapter Two: A range of new orthomanganated aromatic and heteroaromatic compounds have been synthesised. Some of these orthomanganated compounds find use in organic synthesis (refer to chapters four and five)

Chapter Three : Hydrogen isotope effects for the manganation of orthomonodeuterioacetophenones by $C_6H_5CH_2Mn(CO)_5$ and $C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ are reported and mechanistic implications are discussed.

Chapter Four : A range of *ortho*-bromo and *ortho*-iodo aryl ketones have been prepared by reaction of orthomanganated ketones with bromine and iodinechloride respectively. Oxidation of several orthomanganated ketones with Ce(IV) in deuterio-acetic acid provides a simple route to orthomonodeuterioacetophenones.

Chapter Five : Orthomanganated ketones react with alkenes in methanol in the presence of Pd(II) to form coupled aryl alkenes and other products. Reaction of some orthomanganated ketones with methyl acrylate and palladium(II) in acetonitrile under reflux affords carbomethoxy indenes. 2'-Mercurated acetophenones have been prepared by reaction of orthomanganated ketones with mercury(II) chloride or mercury(II) acetate.

Chapter Six : $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ and $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ have been prepared and the crystal structures of these isoelectronic species are discussed.

References

(1) A. J. Carty,

Organomet. Chem. Rev., Sect. **A7**, 191, **1971**

(2) M. I. Bruce,

Angew. Chem. Int. Ed. Engl., **16**, 73, 1977

(3) J. Dehand and M. Pfeffer,

Co-ord. Chem. Rev., **18**, 327, **1976**

(4) I. Omae,

"Organometallic Intramolecular Co-ordination Compounds", J. Organomet. Chem. Lib. 18.

Elsevier, Amsterdam, 1986

(5) H. Abicht and K. Issleib,

Z. Chem., **17**, 1, **1977**

(6) E. C. Constable,

Polyhedron, **3**, 1037, **1984**

I. Omae,

Chem. Rev., **79**, 287, **1979**

G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer.

Chem. Rev., **86**, 451, **1986**

(7) I. Omae,

Co-ord. Chem. Rev., **32**, 235, **1980**

(8) I. Omae,

Co-ord. Chem. Rev., **42**, 245, **1982**

(9) I. **Omae**,

J. Jpn. Chem., **33**, 767, **1979**.

(10) I. **Omae**,

Co-ord. Chem. Rev., **28**, 97, **1979**

(11) J. E. Baldwin, R. H. Jones, C. Najera and M. Yus,

Tetrahedron, **41**, 699, **1985**

(12) R. H. Crabtree,

Chem. Rev. **85**, 245, **1985**

(13) R. J. McKinney, G. Firestein and H. D. Kaesz,
Inorg. Chem., **14**, 2057, **1975**

(14) R. J. Cross and N. H. Tennent,
J Organomet. Chem., **72**, 21, **1974**.

(15) M. I. Bruce, B. L. Goodall, G. L. Sheppard and F. G. A. Stone,
J. Chem. Soc. Dalton Trans., 591, **1975**.

(16) I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbochevskaya,
G. G. Aleksandrov, Y. T. Struchkov and M. E. Volpin
J. Chem. Soc., Chem. Commun., 972, **1971**.

(17) C. Mutet, M. Pfeffer,
J. Organomet. Chem., **171**, C34, **1979**.

(18) B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson and
J. Lewis,
J. Chem. Soc. Dalton Trans., 404, **1973**.

(19) R. McCrindle, E. C. Alyea, S. A. Dias and A. J. McAlees,
J. Chem. Soc. Dalton Trans., 640, **1979**.

(20) A. McKillop and E. C. Taylor, in
"Comprehensive Organmetallic Chemistry", ed.
G. Wilkinson, F. G. A. Stone, E. W. Abel,
Pergamon Press, Oxford, **1982**, Vol 7, p. 465

(21) Z. Dauter, R. J. Mawby, C. D. Reynolds and D. J. Saunders
J. Chem. Soc. Dalton Trans., 1235, **1985**.

(22) M. F. McGuiggan and L. H. Pignolet,
Inorg. Chem., **21**, 2523, **1982**.

(23) J. M. Kisenyi, J. A. Cabeza, A. J. Smith, H. Adams, G. J. Sunley,
N. J. S. Salt and P. M. Maitlis,
J. Chem. Soc., Chem. Commun., 770, **1985**.

(24) J. Vicente, J. Martin, M. Chicolte, X. Solans and C. Miravitlles,
J. Chem. Soc., Chem. Commun., 1004, **1985**.

(25) H. Horino and N. Inoue,
J. Org. Chem., **46**, 4416, **1981**.

(26) C. P. Casey and C. A. Bunnell,
Inorg. Chem., **14**, 796, **1975**.

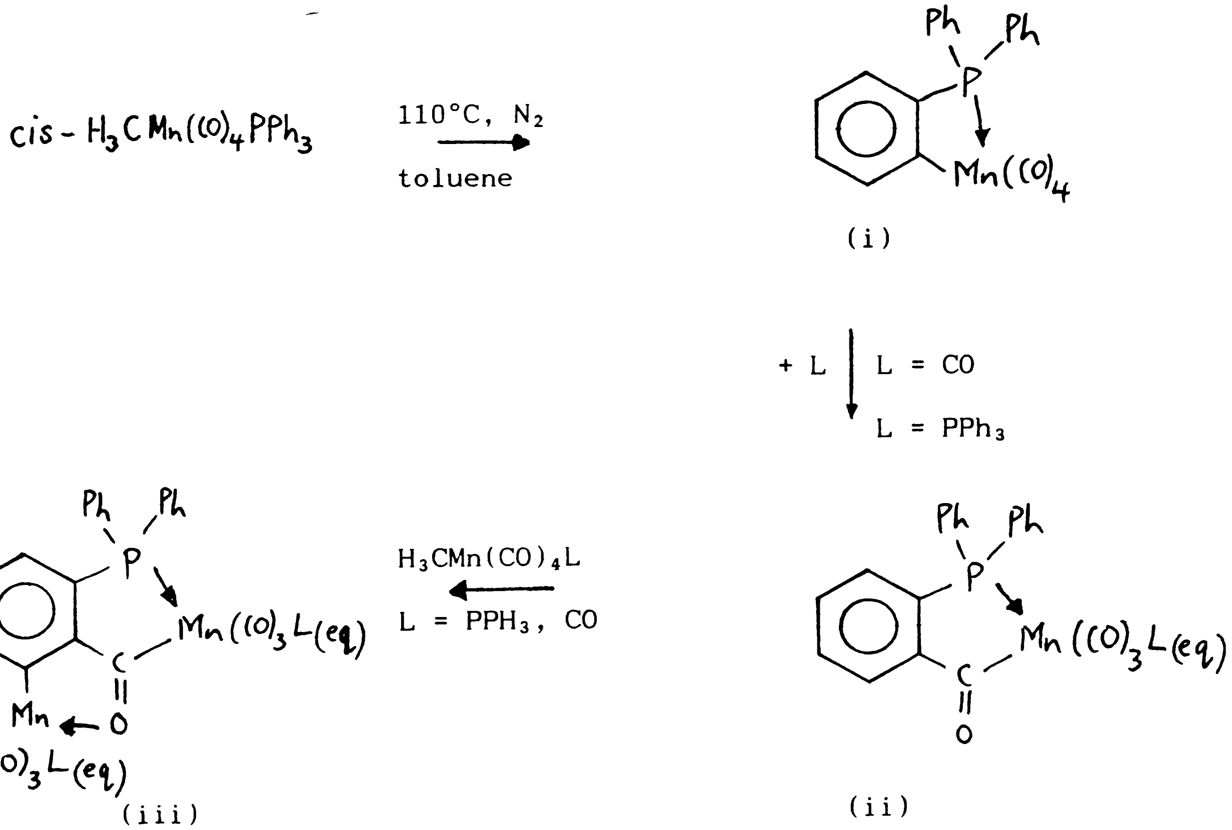
(27) R. A. Jones and G. Wilkinson,
J. Chem. Soc., Dalton Trans., 472, **1979**.

CHAPTER TWO

Synthesis of orthomanganated acetophenones

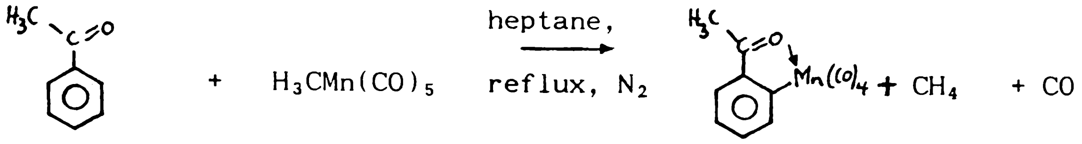
2.1 Brief literature survey of preparative methods for C,O co-ordinated orthomanganated arenes

A variety of complex cyclometallated products are formed when cis-$H_3CMn(CO)_4PPh_3$ is heated at reflux in toluene under N_2 (see scheme 2.1).[1,2,3,4]



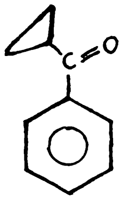
scheme 2.1

The formation of (iii) from the phenacyl product (ii) led Kaesz and co-workers to examine the possible orthomanganation of other organic phenacyl products. They found that a range of acetylferrocenes,[5] benzophenones,[6] acetophenones[6] and anthraquinones[1,6] can be orthomanganated by $H_3CMn(CO)_5$ (equation 2.1).



equation 2.1

More recently Cabral[7] has succeeded in cyclomanganating a few more novel ketones such as cyclopropyl phenyl ketone (iv), cyclohexyl phenyl ketone (v) and 1-acetylcyclohexene (vi) with $C_6H_5CH_2Mn(CO)_5$.



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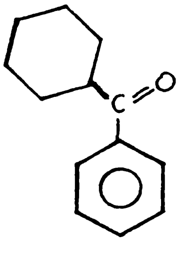

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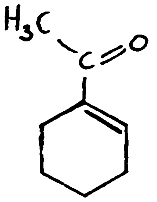
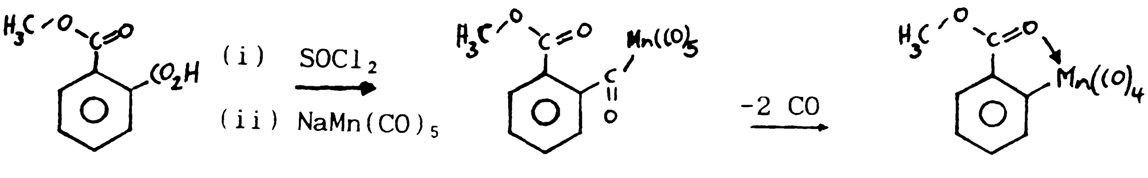


(vi)

Methyl benzoate,[7] isopropyl benzoate[7] and methyl 3,4,5-trimethoxybenzoate[8] can be cyclomanganated with $C_6H_5CH_2Mn(CO)_5$ in yields of 4%, 85%, and 75% respectively. The reason for the vast differences in reactivity between methyl benzoate and the other two alkyl benzoates is still unclear. However, Casey and co-workers[9] have prepared η^2-(2-carbomethoxyphenyl)tetracarbonylmanganese by an indirect procedure (see scheme 2.2)



scheme 2.2

A new method for the synthesis of cyclomanganated benzophenones and alkyl phenyl ketones has appeared recently.[10] This method utilises diphenylmercury and substituted alkyl-manganese carbonyls and is capable of producing the required cyclomanganated product in yields typically greater than 80% (see scheme 2.3).

$$R\text{-}Mn(CO)_{5-n}L_n \quad + \quad (C_6H_5)_2Hg$$

$$\Big\downarrow \text{reflux, } N_2 \text{, toluene}$$

$$R\text{-}CO\text{-}(o\text{-}C_6H_4)Mn(CO)_{4-n}L_n \quad + \quad Hg(0)$$

for $n = 0$ $R = CH_3, C_2H_5, C_3H_7, C_6H_5CH_2$

$n = 1$ $L = E(C_6H_5)_3$ where $E = P, As, Sb$; $R = C_6H_5$

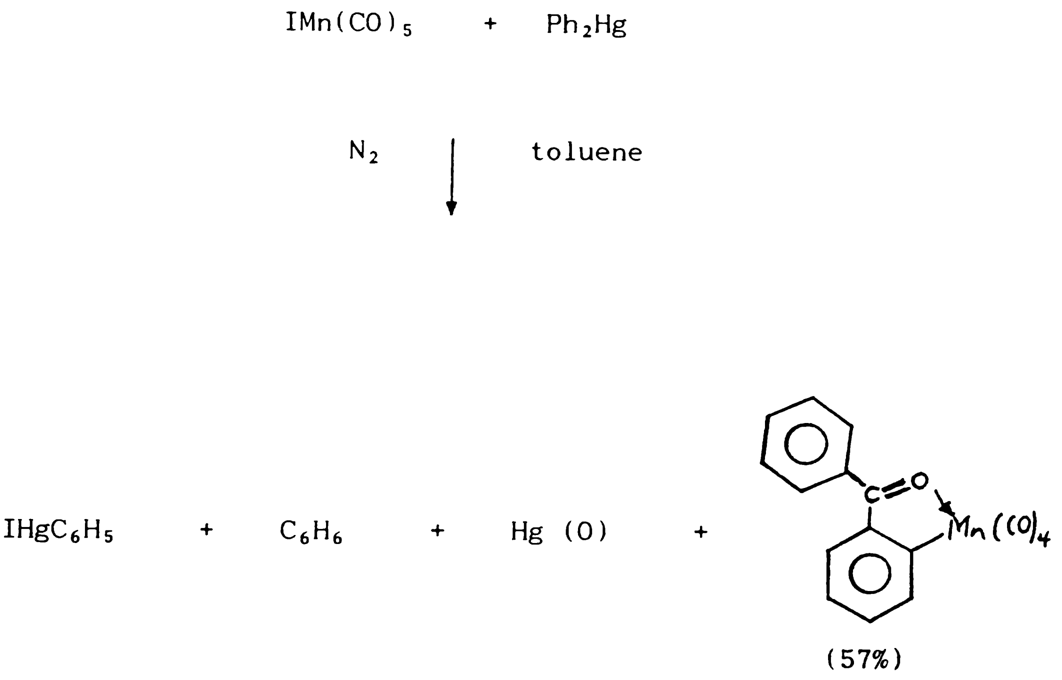
$n = 2$ $L = P(OR')_3$ where $R' = C_6H_5, CH_3, CH_2CH_3, C_3H_7$

$R = C_6H_5$

(scheme 2.3)

The chief advantage of this procedure is that the diorganomercurials and the substituted $RMn(CO)_{5-n}L_n$ complexes are easily prepared, whereas the parent aromatic ketones needed for the alternative routes are often not readily available.

The same authors[10] have developed a method for the preparation of cyclomanganated benzophenones by reaction of diphenylmercury with iodomanganesepentacarbonyl (see scheme 2.4).

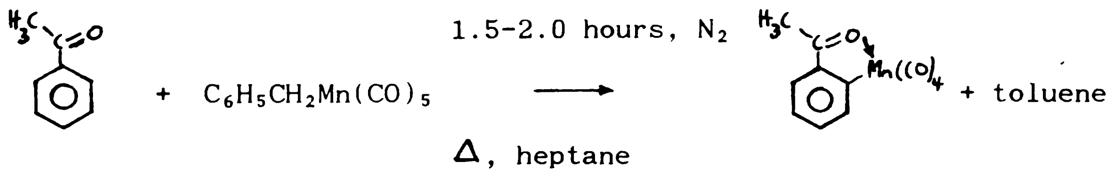


(scheme 2.4)

The use of chloromanganesepentacarbonyl (instead of iodomanganesepentacarbonyl) failed to yield the expected orthomanganated product, instead moderate yields of $Hg[Mn(CO)_5]_2$ and $ClHgC_6H_5$ were obtained.[10]

2.2 Experimental Section

We have prepared a variety of cyclomanganated substituted aryl ketones by reacting $C_6H_5CH_2Mn(CO)_5$ (1 mole) with the ketone in refluxing heptane under nitrogen (see equation 2.2).



equation 2.2

A typical preparation and purification procedure is illustrated in the preparation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) from 3',4',5'-trimethoxyacetophenone.

2.2.1 Preparation of benzylpentacarbonylmanganese[11]

Dried THF (60 ml) was syringed into a Schlenk flask containing sodium amalgam (55 g, 0.7%). The THF was purged with N_2 and manganese carbonyl (2.0 g, 5.13 mmol) was added to the flask. The flask was tightly stoppered and stirred for two hours at ambient temperature. The green solution of $NaMn(CO)_5$ was decanted from the amalgam into a Schlenk flask containing benzyl bromide (1.25 ml, 10.45 mmol). A white precipitate formed immediately and after stirring for 5 minutes the solution was passed through a short column of silica gel (60 - 120 mesh), which was washed with THF (20 ml X 2). The THF was removed under vacuum leaving a yellow oily product. The oil sublimed (1 mm Hg, 50°C) onto a cold finger yielding off white crystalline $C_6H_5CH_2Mn(CO)_5$ (2.40 g, 84%), m.p = 34-35.5°C (lit.[11] 37.5-38.5°C).

^{1}H-NMR ($CDCl_3$) δ 7.28 (s, 5H, H-Ar), 2.45 (s, 2H, $-CH_2$)

Infrared spectrum ; ν (CO) (hexane) 2105 (s), 2010 (vs, br), 1990 (vs, br), 1948 (w).

Mass spectrum (m/e value with relative abundance in parentheses)
286 (2), 258 (5), 230 (5), 202 (4), 191 (6), 174 (3), 146 (65), 91 (100), 55 (40)

2.2.2 The standard method for orthomanganation : Preparation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)-tetracarbonylmanganese (4)

3',4',5'-trimethoxyacetophenone (0.20 g, 0.95 mmol) and benzylpentacarbonylmanganese (0.28 g, 0.98 mmol) were dissolved in nitrogen saturated heptane (15 ml). This solution was refluxed under N_2 for 1.5 hours. The heptane was removed under vacuum, dichloromethane (5 ml) and deactivated neutral alumina (3 g, activity V - 15% added H_2O) were added to the bright yellow residue. The mixture was shaken vigorously while the dichloromethane was evaporated under vacuum. The absorbed product was transferred onto a 2 X 15 cm column containing neutral alumina (activity V). Elution with hexane removed a trace of unreacted benzylpentacarbonylmanganese and as the polarity of the eluent was gradually increased with dichloromethane a thick bright-yellow band of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) was collected (0.33 g, 92%).

Infrared spectrum ; ν (CO) (hexane) 2080 (m), 1993 (vs), 1987 (vs), 1953 (s); ^{1}H-NMR (CDCl$_3$) δ 7.26 (s, 1H), 4.07 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 2.58 (s, 3H); ^{13}C-NMR (CDCl$_3$) δ 220.06 (s, br), 214.27* (s), 213.81 (s, br), 211.54 (s, br), 172.85$^\#$ (s), 160.56 (s), 151.32 (s), 149.05 (s), 138.49 (s), 111.40 (d), 60.87 (q), 60.02 (q), 56.32 (q), 24.65 (q); Mass spectrum 376 (5.3), 320 (20.0), 292 (15.2), 264 (100.0), 234 (24.6), 210 (5.0), 195 (6.3), 132 (5.5), 55 (32.2).

The experimental conditions, workup procedures and the yields of other manganated ketones prepared using the above standard method in this study are given in table 2.1.

All of the orthomanganated ketones prepared by us apart from η^2-(2-acetylphenyl)tetracarbonylmanganese (1) and η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) are new compounds. The orthomanganated products are yellow, air stable crystalline solids and can be stored in a refridgerator for extended periods without any appreciable decomposition.

2.2.3 Preparation of 2'-t-butyldimethylsiloxy-3',4'-dimethoxyacetophenone (**17**)

This product was prepared by following a general literature procedure.[12]

2'-hydroxy-3',4'-dimethoxyacetophenone (0.392 g, 2 mmol) was added to a benzene solution (20 ml) containing DBU (0.366 g, 2.40 mmol) and TBDMSC (0.333 g, 2.22 mmol). The benzene solution was refluxed for 2 hours, cooled and the solution transferred to a 100 ml separating funnel. The benzene layer was washed sequentially with

Table 2.1 Orthomanganated ketones prepared in this study

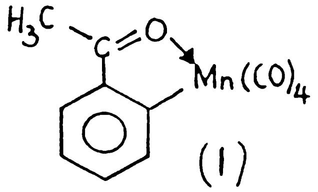
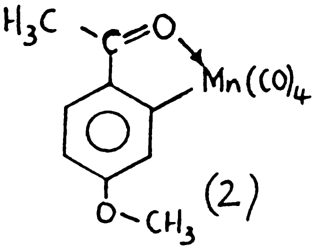
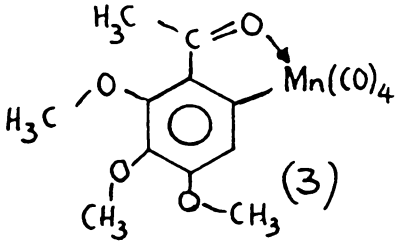
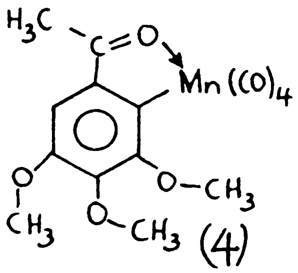
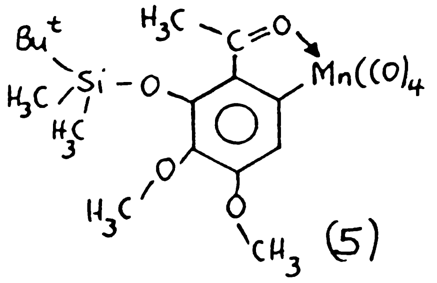
Product	Yield	Method of Purification
 (1)	85%	A
 (2)	86%	A
 (3)	80%	C
 (4)	86%	C
 (5)	80%	B

Table 2.1 (cont.)

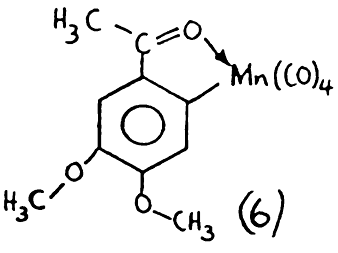
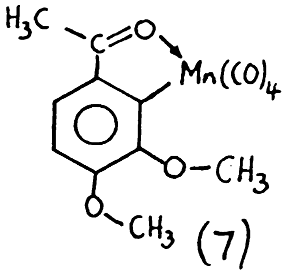
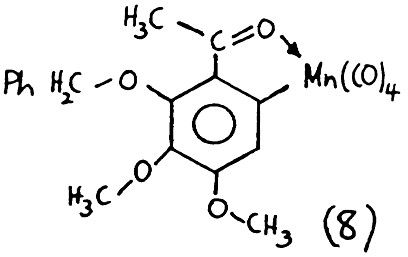
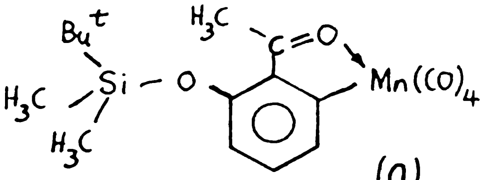
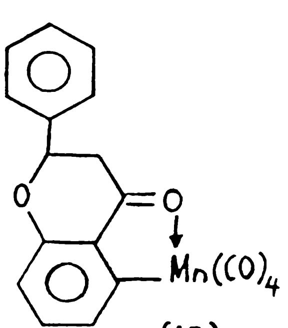
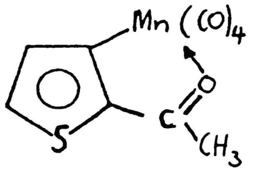
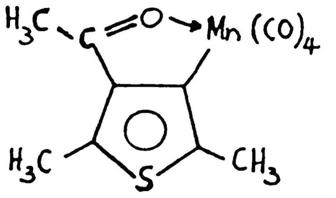
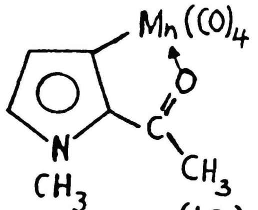
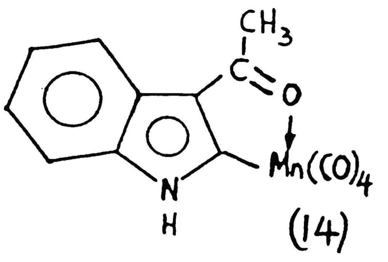
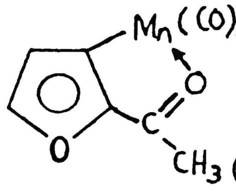
	Yield	Method of Purification
 (6)	60%	B
 (7)	20%	B
 (8)	90%	D
 (9)	86%	B
 (13)	90%	A

Table 2.1 (cont.)

	Yield	Method of Purification
 (10)	75%	A
 (11)	70%	A
 (12)	28%	B
 (14)	90%	B
 (15)	18%	B

A:column chromatographed neutral alumina, elution with hexane, polarity gradually increased with dichloromethane

B: P.l.c. (1:9 ether/petroleum spirit)

C:column chromatographed, neutral alumina (activity (V)), elution with hexane, polarity gradually increased with dichloromethane

D:column chromatographed; neutral alumina (activity III), elution with hexane, polarity gradually increased with dichloromethane.

distilled water (1 X 10 ml), 0.1 mole/l hydrochloric acid (2 X 10 ml), saturated sodium bicarbonate (3 X 10 ml) and water (2 X 10ml) sequentially. The benzene solution was dried over magnesium sulphate, filtered and the solvent removed under vacuum to yield 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-acetophenone (**17**) (0.444 g - 72%) as a colourless oil.

^{1}H-NMR ($CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 1H, 6'-H), 6.65 (d, J = 8.0 Hz, 1H, 5'-H), 3.90 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 2.57 (s, 3H, $COCH_3$), 1.00 (s, 9H, $-C(CH_3)_3$), 0.15 (s, 6H, $(CH_3)_2Si$).

^{13}C-NMR ($CDCl_3$) δ 198.92 (s, CO), 156.33 (s, 4'-C), 148.46 (s, 2'-C), 140.07 (s, 3'-C), 126.42 (s, 1'-C), 124.60 (d, 6'-C), 104.70 (d, 5'-C), 60.02 (q, OCH_3), 55.47 (q, OCH_3), 29.98 (q, $COCH_3$), 25.49 (q, $(CH_3)_3$), 18.14 (s, $C(CH_3)_3$), -4.67 (q, $(CH_3)_2Si$); Mass spectrum (m/e) 295 (4.4), 253 (100), 238 (13.3), 224 (13.6), 209 (23.2), 180 (6.4), 73 (8.5).

2.2.4 2'-t-butyldimethylsiloxyacetophenone (**18**)

This was prepared in 82% yield by the same procedure as used to prepare (**17**).A colourless oil was obtained with the following spectral characteristics.

^{1}H-NMR ($CDCl_3$) δ 7.94-6.84 (m, 4H, H-Ar), 2.55 (s, 3H, $COCH_3$), 1.00 (s, 9H, $C(CH_3)_3$), 0.25 (s, 6H, $(CH_3)_2Si$); ^{13}C-NMR ($CDCl_3$) δ 199.70 (s, CO), 154.25 (s, 2'-C), 132.46 (d, #), 131.10 (s, 1'-C), 129.60 (d, #), 120.89 (d, #), 119.91 (d, #), 30.83 (q, $COCH_3$), 25.56 (q, $C(CH_3)_3$), 18.08 (s, $C(CH_3)_3$), -4.35 (q, $(CH_3)_2Si$); # carbons not assigned; Mass spectrum (m/e) 253 (3.0), 235 (4.6), 209 (1.0), 193 (100).

2.3 Discussion of orthomanganated product yields

The manganation of most acetophenones (apart from 2'-hydroxy-acetophenones) including sterically congested ketones such as 2',3',4'-trimethoxyacetophenone and 3',4',5'-trimethoxyacetophenone proceeded smoothly and in high yield. Attempts to manganate 2'-

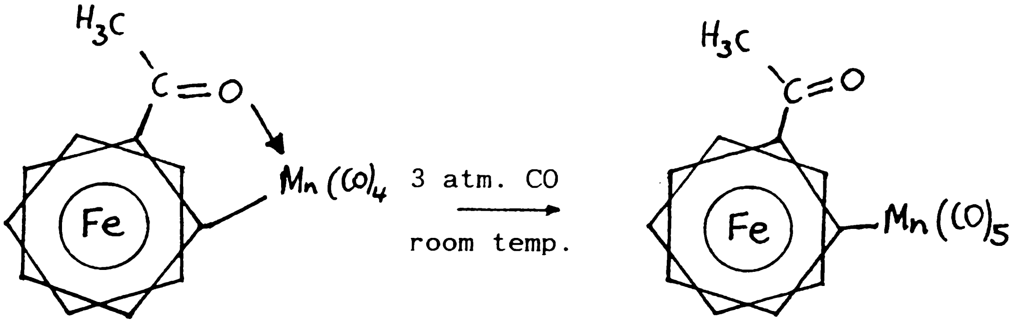
hydroxyl hydrogen-bonded ketones such as 2'-hydroxy-4'-methoxyacetophenone failed. For this reason the hydroxyl functional group of some substituted 2'-hydroxyacetophenones was protected with benzyl and t-butyldimethylsilyl groups. Some protected 2'-hydroxyacetophenones including 2'-benzyl-3',4'-dimethoxyacetophenone, 2'-t-butyl-dimethylsiloxyacetophenone and 2'-t-butyldimethyl siloxy-3',4'-dimethoxyacetophenone were manganated in excellent yield.

Metallation of 3',4'-dimethoxyacetophenone afforded two isomers namely η^2-(2-acetyl-4,5-dimethoxyphenyl)tetracarbonylmanganese (**6**) and η^2-(2-acetyl-5,6-dimethoxyphenyl)tetracarbonylmanganese (**7**). These isomers can be separated by p.l.c. (1:4 ether/petroleum spirit). It was found that the sterically less congested isomer (**6**) was the major product (refer to table 2.1). Flavanone was also manganated and afforded η^2-(5-flavanonyl)tetracarbonylmanganese (**13**) in excellent yield.

After having orthomanganated a variety of aryl methyl ketones our studies were extended to include orthomanganation of some heteroaromatic methyl ketones. Manganation of 2-acetylthiophene, 3-acetyl-2,5-dimethylthiophene and 3-acetylindole proceeded in good yield (Table 2.1). Two heterocycles, 2-acetylfuran and N-methyl-2-acetylpyrrole could not be orthomanganated in good yield, for reasons which were not obvious.

In some related work Kaesz and co-workers have established that orthomanganation of some acetyl-substituted cyclopentadienyl rings is a difficult process.[5] For example, manganation of benzoylferrocene with $H_3CMn(CO)_5$ proceeds exclusively at the phenyl ring, with no ferrocenyl manganation being observed. Furthermore, manganation of acetyl-ferrocene with $H_3CMn(CO)_5$ produces the required manganated ferrocene in a yield of only 32%. Attempts to manganate η^5-acetylpentadienyl-(tricarbonyl)manganese have failed completely.[5]

There is also some chemical evidence which suggests that the manganated acetyl cyclopentadienyl ring is rather strained. The orthomanganated acetyl ferrocene (equation 2.3) can be carbonylated with ease in 80% yield, while η^2-(2-acetylphenyl)tetracarbonylmanganese (1) is not carbonylated even at 60-70°C for 36 hours under 3 atmospheres of CO (g).[5]



equation 2.3

We have found that variously substituted aryl aldehydes such as 3',4',5'-trimethoxybenzaldehyde and p-methoxybenzaldehyde cannot be cyclomanganated by $C_6H_5CH_2Mn(CO)_5$.

2.4 Spectral Data of the cyclometallated complexes

The full assignments, where possible, of the ^{1}H- and ^{13}-NMR chemical shifts for all orthomanganated ketones can be found in appendix I. For ^{13}C-NMR, the carbonyl and metallated aryl carbon signals are identified below with the symbols * and # respectively.

η^2-(2-acetylphenyl)tetracarbonylmanganese (1)

^{1}H-NMR (d^6-acetone) δ 8.05 (d, br, J ≃ 9 Hz, 2H), 7.50 (td, J = 7.3 Hz of J = 1.5 Hz, 1H), 7.24 (td, J = 7.3 Hz of J = 1.5 Hz, 1H).

^{13}C-NMR (d^6-acetone) δ 219.43 (s, br), 213.13* (s, br), 192.12$^\#$ (s), 146.93 (s), 142.05 (d), 135.35 (d), 133.53 (d), 125.14 (d), 25.32 (q).

Mass spectrum 286 (8.3), 230 (9.8), 203 (41.0), 174 (100), 146 (11.3), 131 (29.5), 105 (30.9), 91 (49.4), 55 (90.0).

Infrared spectrum ν (CO) (hexane) 2081 (m), 1993 (vs, br), 1945 (s).

η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2)

^{1}H-NMR (CDCl$_3$) δ 7.78 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 6.66 (dd, J = 8.5 Hz of J = 2.4 Hz, 1H), 3.95 (s, 3H), 2.53 (s, 3H).

^{13}C-NMR (CDCl$_3$) δ 218.04 (s, br), 213.03* (s, br), 211.60 (s, br), 197.46$^\#$ (s), 163.58 (s), 138.77 (s), 133.34 (d), 124.27 (d), 111.43 (d), 55.44 (q), 24.06 (q).

Mass spectrum 316 (7.6), 260 (6.4), 232 (15), 204 (100), 135 (12.5), 121 (7), 102 (9).

Infrared spectrum ν (CO) (CH$_2$Cl$_2$) 2079 (m), 1991 (vs, br), 1933 (ms).

η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (3)

^{1}H-NMR (CDCl$_3$) δ 7.26 (s, 1H), 4.06 (s, 3H), 4.05 (s, 3H), 3.85 (s, 3H), 2.65 (s, 3H).

^{13}C-NMR (CDCl$_3$) δ 220.98 (s, br), 213.36* (s, br), 211.67 (s, br), 211.34 (s, br), 191.32$^\#$ (s), 158.87 (s), 157.44 (s), 138.12 (s), 131.42 (s), 117.38 (d), 60.80 (q, br), 56.19 (q), 29.27 (q).

Mass spectrum 376 (1), 292 (1), 264 (100), 234 (12.6), 206 (10.9), 195 (7.1), 132 (7.9), 55 (50.8).

Infrared spectrum ν (CO) (CH$_2$Cl$_2$) 2080 (ms), 1990 (vs, br), 1932 (ms).

η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5-dimethoxyphenyl)-tetracarbonylmanganese (5)

^{1}H-NMR (CDCl$_3$) δ 7.27 (s, 1H), 4.07 (s, 3H), 3.77 (s, 3H), 2.67 (s, 3H), 0.95 (s, 9H), 0.31 (s, 6H).

^{13}C-NMR (CDCl$_3$) δ 220.80 (s, br), 212.71* (s,br), 211.80 (s, br), 191.05$^\#$ (s), 158.61 (s), 153.73 (s), 136.56 (s), 131.55 (s), 115.95 (d), 60.41 (q), 55.99 (q), 29.46 (q), 26.21 (q), 19.24 (s), -2.86 (q).

Mass spectrum 476 (2), 364 (100), 292 (10.3), 253 (33), 209 (7.5), 146 (13.5), 75 (23.1)

Infrared spectrum ν (CO) (CH_2Cl_2) 2079 (m), 1990 (vs, br), 1931 (s)

η^2-(2-acetyl-4,5-dimethoxyphenyl)tetracarbonylmanganese (**6**)

^{1}H-NMR ($CDCl_3$) δ 7.50 (s, 1H), 7.30 (s, 1H), 4.06 (s, 3H), 3.89 (s, 3H), 2.54 (s, 3H).

η^2-(2-acetyl-5,6-dimethoxyphenyl)tetracarbonylmanganese (**7**)

^{1}H-NMR ($CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H), 3.85 (s, 3H), 2.52 (s, 3H).

η^2-(2-acetyl-3-benzyloxy-4-,5-dimethoxyphenyl)tetracarbonylmanganese (**8**)

^{1}H-NMR ($CDCl_3$) δ 7.35 (s, br, 6H), 5.26 (s, 2H), 4.00 (s, 3H), 3.83 (s, 3H), 2.46 (s, 3H).

^{13}C-NMR ($CDCl_3$) δ 220.90 (s, br), 213.49* (s), 212.90 (s, br), 211.54 (s, br), 191.18$^{\#}$ (s), 158.80 (s), 156.20 (s), 138.32 (s), 136.82 (s), 131.94 (s), 128.37 (d, br), 117.51 (d), 75.69 (t), 60.86 (q), 56.05 (q), 29.46 (q).

Mass spectrum 452 (5.5), 368 (12), 340 (100), 310 (22.5), 244 (40), 206 (10), 181 (28), 135 (12).

Infrared spectrum ν (CO) (CH_2Cl_2) 2079 (m), 1991 (vs, br), 1932 (m).

η^2-(2-acetyl-3-t-butyldimethylsiloxyphenyl)tetracarbonylmanganese (**9**)

^{1}H-NMR ($CDCl_3$) δ 7.50 (d, J = 7.4 Hz, 1H), 7.60 (m, 1H), 6.48 (d, J = 8.1 Hz, 1H), 2.62 (s, 3H), 0.96 (s, 9H), 0.31 (s, 6H).

^{13}C-NMR ($CDCl_3$) δ 220.91 (s), 215.51* (s), 213.10 (s, br), 211.67 (s, br), 195.74$^{\#}$ (s), 160.30 (s), 136.30 (s), 134.74 (d), 133.70 (d), 114.26 (d), 31.02 (q), 26.08 (q), 18.79 (s), -3.51 (q).

Mass spectrum 332 (7.0), 304 (100), 193 (16.6), 73 (7.0).

Infrared spectrum ν (CO) (CH_2Cl_2) 2079 (m), 1990 (vs, br), 1933 (ms).

η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10)

^{1}H-NMR ($CDCl_3$) δ 8.10 (d, J = 4.8 Hz, 1H), 7.75 (d, J = 4.8 Hz, 1H), 2.25 (s, 3H).

^{13}C-NMR ($CDCl_3$) δ 221.23 (br, s), 213.03 (br, s), 210.37 (s,br), 208.03* (s), 204.26$^{\#}$ (s), 141.70 (s), 138.90 (d), 138.64 (d), 24.97 (q).

Mass spectrum 292 (26.2), 236 (20.7), 208 (73.4), 180 (100), 138 (93.8), 111 (30.3), 55 (56.5).

Infrared spectrum ν (CO) (CH_2Cl_2) 2085 (m), 1998 (vs, br), 1942 (s).

η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (11)

^{1}H-NMR ($CDCl_3$) δ 2.73 (s, 3H), 2.50 (s, 3H), 2.48 (s, 3H).

^{13}C-NMR ($CDCl_3$) δ 222.27 (br, s), 213.62 (br, s), 211.67 (s, br), 205.62* (s), 165.95$^{\#}$ (s), 151.26 (s), 147.10 (s), 134.61 (s), 27.18 (q),16.58 (q), 15.48 (q).

Mass spectrum 320 (3.2), 305 (0.5), 264 (2.4), 236 (12.3), 208 (100), 174 (12.8), 139 (11.8), 88 (18.7), 55 (44.2).

Infrared spectrum ν (CO) (CH_2Cl_2) 2078 (m), 1987 (vs, br), 1930 (s).

η^2-(2-acetyl-1-methylpyrrole-3-yl)tetracarbonylmanganese (12)

^{1}H-NMR ($CDCl_3$) δ 7.07 (d, J = 1.8 Hz, 1H), 6.59 (d, J = 1.8 Hz, 1H), 3.88 (s, 3H), 2.49 (s, 3H).

Mass spectrum 289 (20), 261 (3.3), 233 (9.5), 205 (6.8), 177 (100), 108 (3.3), 55 (2.7).

Infrared spectrum ν (CO) (CH_2Cl_2) 2079 (m), 1990 (vs, br), 1930 (ms).

η^2-(5-flavanonyl)tetracarbonylmanganese (13)

^{1}H-NMR ($CDCl_3$) δ 7.48 (m, 7H), 6.69 (d, J = 8.1 Hz, 1H), 5.38 (dd, J = 10.3 Hz of J = 5.5 Hz, 1H), 3.01 (m, 2H).

^{13}C-NMR ($CDCl_3$) δ 221.09 (s, br), 212.90 (s, br), 211.60 (s, br), 211.34 (s, br), 209.13* (s), 193.33$^{\#}$ (s), 164.07 (s), 138.06 (s), 137.60 (d), 134.22 (d), 131.62 (s), 128.89 (d, br), 126.22 (d), 111.39 (d), 79.85 (d), 42.60 (t).

Mass spectrum 390 (3.4), 334 (2.5), 306 (1.3), 278 (100), 260 (6.2), 205 (6.0), 55 (16.0).

Infrared spectrum ν (CO) (hexane) 2083 (m), 1995 (vs), 1949 (ms).

η^2-(3-acetylindole-2-yl)tetracarbonylmanganese (14)

^{1}H-NMR ($CDCl_3$) δ 9.57 (s, br, 1H), 7.59 (m, br, 1H), 7.22 (m, br,3H), 2.64 (s, 3H).

^{13}C-NMR ($CDCl_3$) δ 212.68 (s, br), 210.90* (s, br), 209.76 (s, br), 201.85$^{\#}$ (s), 143.77 (s), 129.47 (s), 126.47 (s), 122.21 (d), 121.84 (d), 117.34 (d), 110.51 (d), 24.92 (d).

Infrared spectrum ν (CO) (CH_2Cl_2) 1989 (w),1998 (vs, br), 1937 (ms).

Mass spectrum 325 (13.2), 284 (2.0), 269 (4.1), 241 (3.4), 213 (100), 144 (4.1), 107 (2.8).

η^2-(2-acetylfuran-3-yl)tetracarbonylmanganese (15)

^{1}H-NMR ($CDCl_3$) δ 7.79 (d, J = 1.1 Hz, 1H), 7.05 (d, J = 1.1 Hz, 1H), 2.46 (s, 3H).

Mass spectrum 276 (14.1), 220 (13.1), 192 (36.6), 164 (100), 122 (58.6), 92 (14.8).

Infrared spectrum ν (CO) (CH_2Cl_2) 2089 (m), 2000 (vs, br), 1944 (ms).

2.5 Discussion of spectroscopic data

The ^{1}H-NMR spectra of several orthomanganated acetophenones including η^2-(2-acetylphenyl)tetracarbonylmanganese (1) and

η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) have been analysed and discussed by Kaesz et al.[6] It was found that the protons ortho to the manganese and the acyl group resonate at the lowest field strength (highest ppm). These findings are in accord with the recorded ^{1}H-NMR spectra of several iron orthometallated thiobenzophenones.[13]

The mass spectra of the cyclomanganated ketones prepared in this study show both parent and successive CO loss fragmentation ions. These findings are in accord with the mass spectra of cyclomanganated complexes reported in the literature.[6]

A representative infrared spectrum of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) is illustrated in figure 2.1. The three ν(CO) absorptions of the tetracarbonyl manganese unit are characteristic and vary little with substituents effects on the aryl ring. Although four absorptions are expected for a cis-$L_2M(CO)_4$ derivative[14] only three are usually observed. This is because two of the four absorptions are degenerate.

To the best of our knowledge no ^{13}C-NMR spectra of any ortho-manganated ketones have been reported in the literature, so a more detailed discussion is warranted. The most interesting part of the ^{13}C-NMR spectra for these structures is the low field (high ppm) area. For clarity the low field regions of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (4) and *fac*-η^2-(2-acetylphenyl)tricarbonyltriphenylphosphinomanganese (**16**) are illustrated in figures 2.2 and 2.3. η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (4) (figure 2.2) has four absorptions in the carbonyl chemical shift region (i.e. > 200 ppm). Three of these absorptions are broad (peak height ratio 2 : 1 : 1), and these are assigned be the four carbonyls of the tetracarbonylmanganese unit. The signals are probably broadened by coupling with the ^{17}O and ^{55}Mn quadrupoles.[15] The single sharp

Figure 2.1 Infrared spectrum of

η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2)

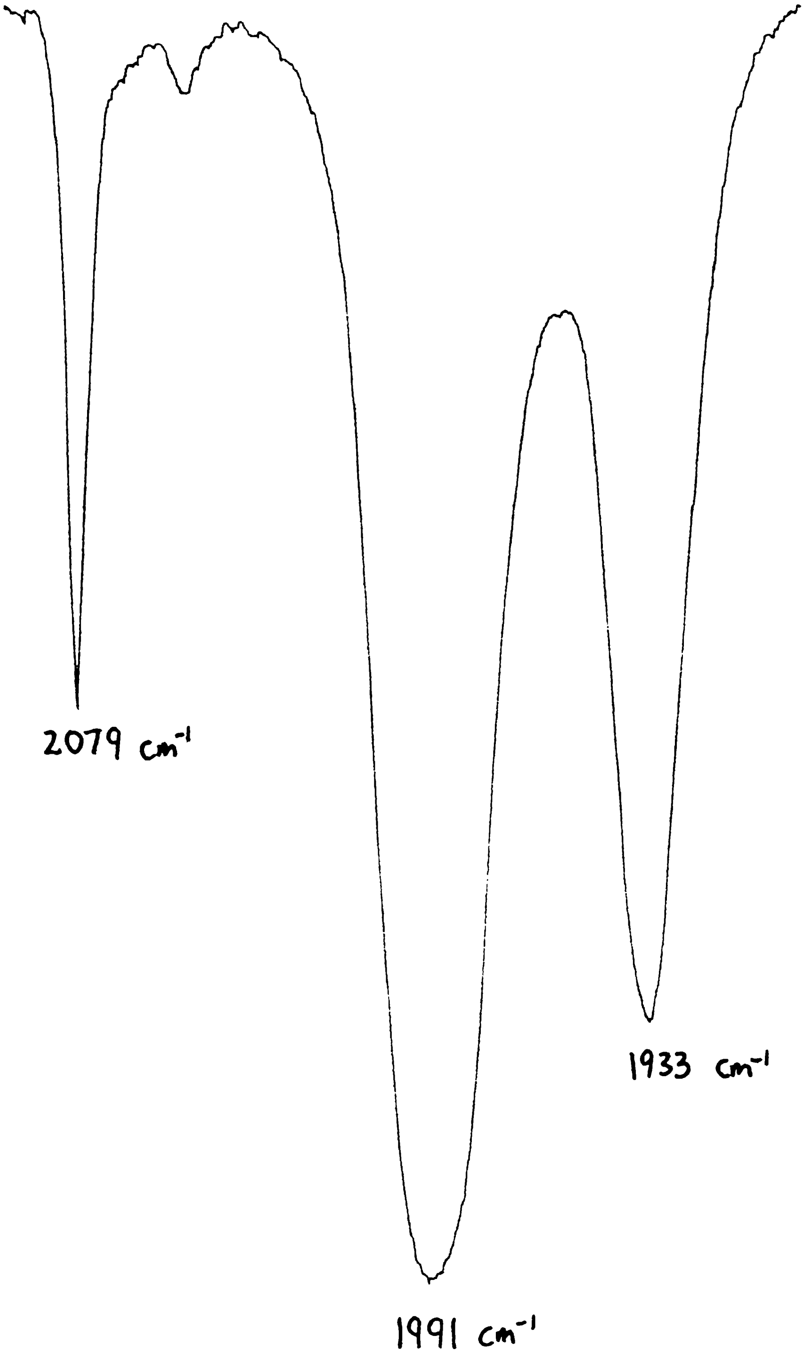


Figure 2.2 ^{13}C-NMR spectrum of

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**)

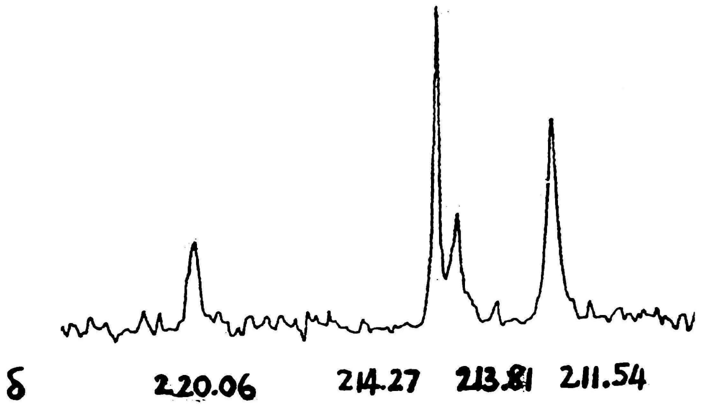
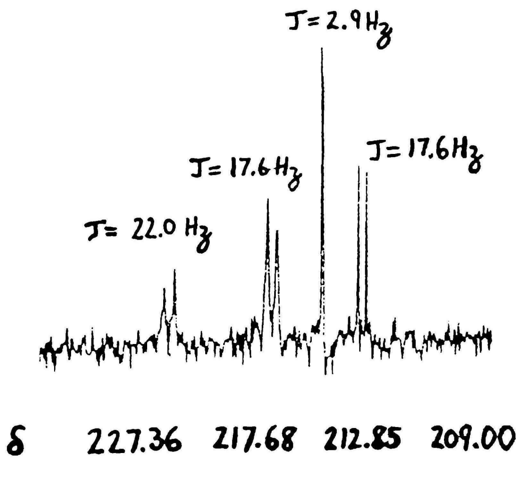


Figure 2.3 ^{13}C-NMR spectrum of

η^2-(2-acetylphenyl)factricarbonylphosphinomanganese (**16**)



absorption can then be assigned to the acetyl carbonyl. These chemical shift assignments can be confirmed by analysis of the low field spectrum of *fac*-η^2-(2-acetylphenyl)tricarbonyltriphenylphosphinomanganese (16) (figure 2.3). This has three carbonyl carbons which are easily assigned as they are strongly coupled to the phosphorus with coupling constants of 17.6 Hz (X2) and 22.0 Hz. The sharp acetyl carbonyl is only weakly coupled to the phosphorus with a coupling constant of 2.9 Hz. By comparison the acetyl carbonyl resonances for all other orthomanganated compounds are assigned (these chemical shifts are marked with an asterisk) in the preceding tabulations.

Mann and Taylor[16] have pointed out that a good correlation exists between carbonyl stretching force constants and carbonyl chemical shifts. The lower the carbonyl force constant the higher the carbonyl chemical shift. Structural studies on η^2-(2-acetylphenyl)tetracarbonylmanganese (1) and η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (11) indicate that the C-O bond orders (and therefore the force constants) of the carbonyls *trans* to the O-donor and aryl carbon are diminished with respect to the other two carbonyls. The carbonyl *trans* to the O-donor has the weakest bond and therefore this carbonyl is assigned to the one which resonates at lowest field (220.06 ppm). By analogy, the chemical shift of the carbonyl trans to the aryl donor is assigned at 213.82 ppm, with the other two carbonyls resonating at 211.54 ppm.

The chemical shifts of the aryl carbons bonded to the manganese (refer to chemical shift tabulations) are marked with a symbol #. These C-Mn chemical shifts are sensitive to the electronic and steric nature of the ligands attached to the manganese. For example the chemical shift of the C-Mn carbon in η^2-(2-acetylphenyl)tetracarbonylmanganese (1) resonates at 192.12 ppm whereas the metallated carbon in

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (4) resonates at 172.85 ppm. Most C-Mn carbons, however, resonate in the 190-210 ppm range (refer to appendix I for assignments).

2.6 X-ray crystal structure of η^2-(3-acetyl-2,5-dimethylthien-4-yl)-tetracarbonylmanganese (11)

The crystal structure of η^2-(3-acetyl-2,5-dimethylthien-4-yl)-tetracarbonylmanganese (11) is reported. We were interested in the effect that the co-ordinated manganese might have on the aromaticity of the thiophene ring.

Yellow cubic crystals were obtained by recrystallisation from ether/hexane (1:4) at -20°C. Preliminary precession photography (Cu-K_α ,λ = 1.5418 Å) indicated orthorhombic symmetry with systematic absences appropriate for the space group Pbca. Intensity data were obtained on a Nicolet XRD P3 four circle diffractometer with monochromated Mo-K_α radiation.

Crystal data

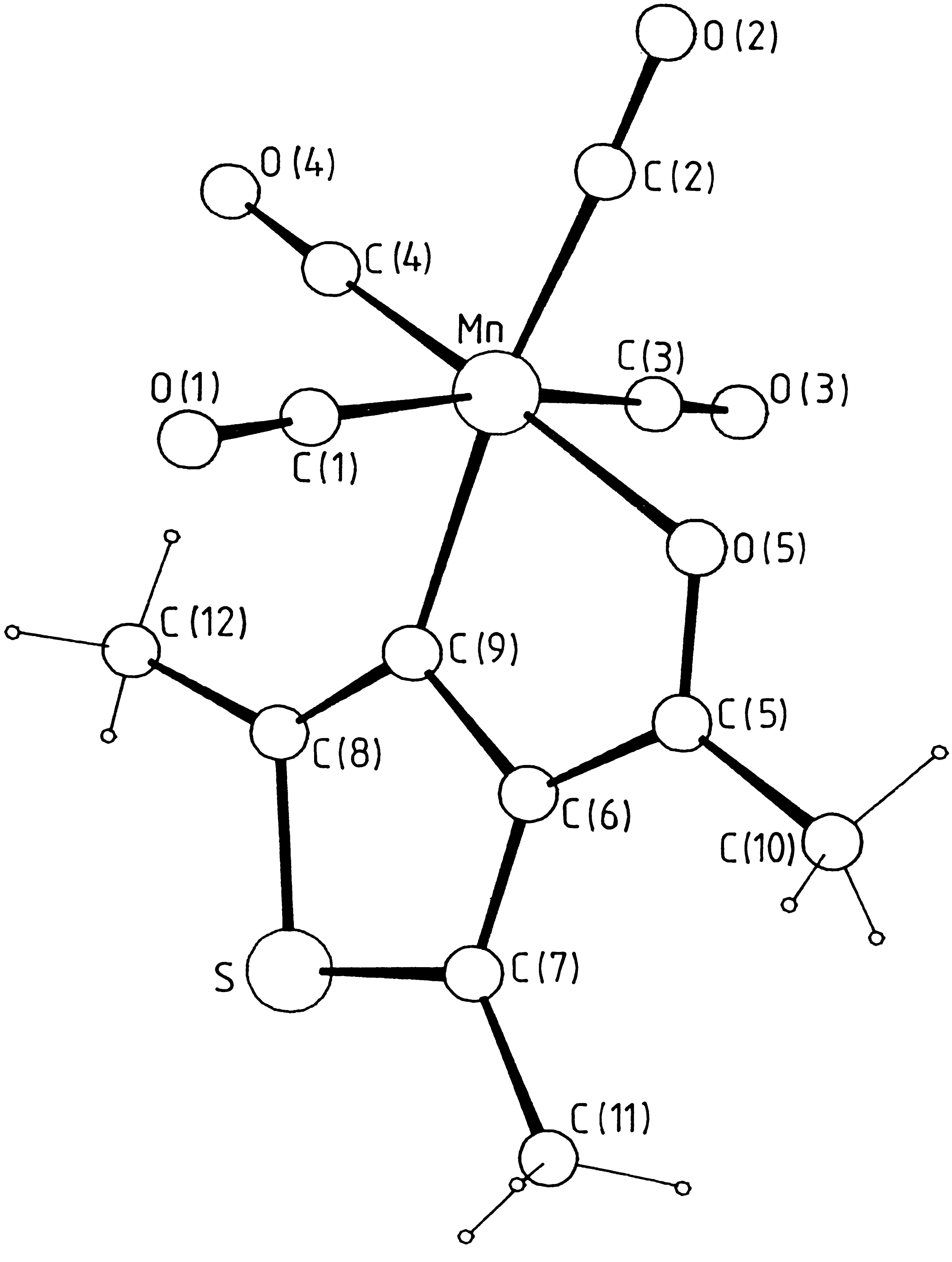
$C_{12}H_9O_5MnS$, M=320.20, orthorhombic, space group Pbca (No 61), a 9.601(2), b 13.913(3), c 19.918(10) Å , U 2660 Å^3 , D_c 1.55 g cm^{-1} for Z=8, F(000) = 1288, μ (Mo-K_α) = 9.57 cm^{-1}.

Intensity data were collected at -135°C in the range of $5° < 2\theta < 55°$ using a θ-2θ scan technique. A total of 3434 unique data were collected and after correction for Lorentz, polarisation and absorption effects, the 2758 data for which $I > 2\sigma(I)$ were used in all calculations.

Solution and Refinement

The structure was solved by direct methods using the program MULTAN[17] utilising 203 reflections with the highest values of E. An E-map based on these reflections revealed most of the structure. A subsequent difference electron density map revealed the three missing non-hydrogen atoms. The model was refined using full-matrix, least-

Figure 2.4 Perspective view of η^2-(3-acetyl-2,5-dimethylthien-4-yl)-tetracarbonylmanganese (11)



squares refinement with the manganese, sulphur and oxygen atoms being assigned anisotropic temperature factors. The hydrogen atoms were included in their calculated positions with each different type of hydrogen assigned separate isotropic temperature factors. The refinement converged with R = 0.0495 and R_w = 0.0611 where w = $[\sigma^2(F) + 0.0008 F_0{}^2]^{-1}$ with no parameter shifting more than 0.5σ in the final cycle of least squares refinement. The final difference map showed a little residual electron density around C(10) (ca. 0.40 e $Å^3$), assignable to a small degree of anisotropy.

Bond angles and bond lengths appear in tables 2.2 and 2.3 The atomic positions of all atoms, the thermal parameters for all non-hydrogen atoms and the positional and thermal parameters of the hydrogen atoms can be found in appendix II.

Figure 2.4 illustrates (along with the numbering scheme) a clear view of the metallated thiophene molecule.

2.6.1 Discussion of the structure

In table 2.4 for comparison, we have summarised some relevant bond length data from the crystal structures of other orthomanganated oxygen donor compounds.[18,19,20,21,22]

The most striking structural features of the manganated thiophene (11) are the differences in the 'aromatic' sulphur to carbon and carbon to carbon bond lengths. The S-C(7) bond is significantly shorter than the S-C(8) bond (1.701Å vs. 1.748 Å) indicating that the S-C(7) bond has more double bond character. The C(6)-C(7) bond is definitely longer (by some 0.018Å) than the C(8)-C(9) bond while the C(5)-C(6) and C(5)-O(5) bonds deviate considerably (shorter and longer respectively) from the bond lengths observed in a structure such as acetophenone (II). This is not be a true comparison but we could not find reference to any crystal structures of 3-acetyl thiophenes for further comparison. This information suggests that a considerable

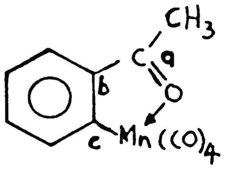
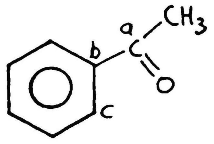
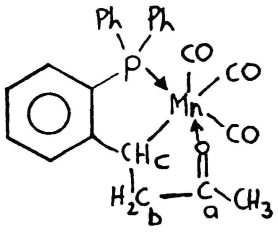
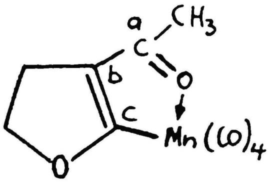
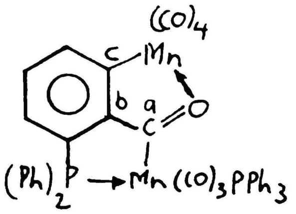
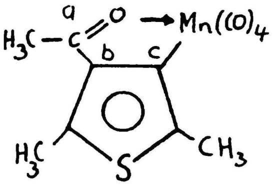
Table 2.2 Bond angles (°) for η^2-(3-acetyl-2,5-dimethylthien-4-yl)-tetracarbonylmanganese (11)

C(2) -Mn -C(1)	94.7 (1)
C(3) -Mn -C(1)	169.6 (1)
C(3) -Mn -C(2)	95.6 (1)
C(4) -Mn -C(1)	90.5 (1)
C(4) -Mn -C(2)	91.7 (1)
C(4) -Mn -C(3)	88.1 (1)
O(5) -Mn -C(1)	90.8 (1)
O(5) -Mn -C(2)	90.6 (1)
O(5) -Mn -C(3)	90.2 (1)
O(5) -Mn -C(4)	177.3 (1)
C(9) -Mn -C(1)	83.8 (1)
C(9) -Mn -C(2)	170.3 (1)
C(9) -Mn -C(3)	86.2 (1)
C(9) -Mn -C(4)	97.9 (1)
C(9) -Mn -O(5)	79.8 (1)
C(8) -S -C(7)	93.8 (1)
O(1) -C(1) -Mn	177.3 (3)
O(2) -C(2) -Mn	178.7 (3)
O(3) -C(3) -Mn	177.1 (3)
O(4) -C(4) -Mn	178.0 (3)
C(6) -C(5) -O(5)	117.0 (2)
C(10) -C(5) -O(5)	117.8 (2)
C(10) -C(5) -C(6)	125.1 (2)
C(5) -O(5) -Mn	117.3 (2)
C(7) -C(6) -C(5)	130.3 (2)
C(9) -C(6) -C(5)	114.3 (2)
C(9) -C(6) -C(7)	114.9 (2)
C(6) -C(7) -S	109.4 (2)
C(11) -C(7) -S	119.3 (1)
C(11) -C(7) -C(6)	131.3 (2)
C(9) -C(8) -S	111.2 (2)
C(12) -C(8) -S	117.7 (2)
C(12) -C(8) -C(9)	131.1 (2)
C(6) -C(9) -Mn	111.0 (2)
C(8) -C(9) -Mn	138.3 (2)
C(8) -C(9) -C(6)	110.7 (2)

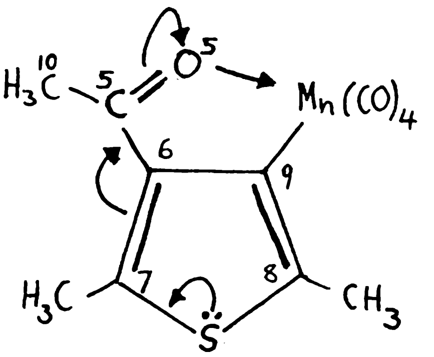
Table 2.3 Bond lengths (Å) for η^2-(3-acetyl-2,5-dimethylthien-4-yl)-tetracarbonylmanganese (11)

C(1) -Mn	1.860 (3)
C(2) -Mn	1.838 (3)
C(3) -Mn	1.853 (3)
C(4) -Mn	1.786 (3)
C(9) -Mn	2.039 (2)
C(7) -S	1.701 (3)
C(8) -S	1.748 (3)
C(1) -O(1)	1.131 (4)
C(2) -O(2)	1.133 (4)
C(3) -O(3)	1.133 (4)
C(4) -O(4)	1.145 (4)
Mn -O(5)	2.055 (2)
C(5) -O(5)	1.251 (3)
C(5) -C(6)	1.438 (3)
C(6) -C(7)	1.383 (3)
C(6) -C(9)	1.454 (3)
C(8) -C(9)	1.365 (3)
C(5) -C(10)	1.496 (3)
C(7) -C(11)	1.498 (3)
C(8) -C(12)	1.498 (3)

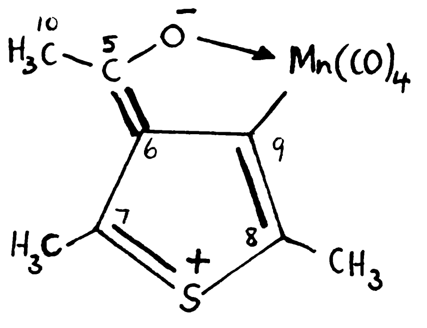
Table 2.4 Comparison of bond lengths (Å) of some orthomanganated ketones

Structure	C=O	C_a-C_b	C_b-C_c	C_c-Mn	Mn-O
 (I)	1.244(3)	1.455(3)	1.406(3)	2.042(2)	2.055(2)
 (II)	1.216(2)	1.494(2)			
 (III)	1.23(1)			2.146(10)	2.067(7)
 (IV)	1.29(1)	1.38(1)	1.36(1)	1.99(1)	2.06(1)
 (V)	1.257(8)			2.045(7)	2.053(5)
 (11)	1.251(3)	1.439(3)	1.454(3)	2.039(2)	2.055(2)

amount of π-electron density is delocalised from the sulphur atom onto the acyl oxygen [(vii),(viii)].



(vii)



(viii)

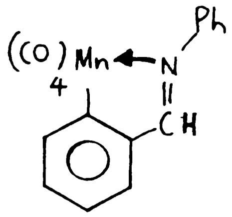
The postulation of a resonance-form such as (viii) nicely accounts for the sequential bond alternation observed in the S-C(7), C(7)-C(6), C(6)-C(5) and C(5)-O(5) bonds. Similar extended π-delocalisation has been used to rationalise the trends in the C_a-C_b, C_b-C_c, and C-O bond lengths observed in η^2-(3-acetyl-4,5-dihydrofuran-2-yl)tetracarbonylmanganese (structure IV, table 2.4).

The C_a-C_b bond (structure IV) is considerably shorter than the equivalent bond (C(6)-C(5)) found in the manganated thiophene (11). This may be related to the extent to which the O and S lone electron pairs are delocalised onto the acyl oxygen. The lone electron pair for the thiophene structure (11) will be the least accessible for delocalisation as it is tied up with the aromaticity of the molecule. No such problems would exist for the metallated dihydrofuran. Therefore this delocalisation of electron density is probably more complete for structure (IV) as compared with (11). In agreement with this shorter C_b-C_c and longer C(6)-C(7) bonds are found for structures (IV) and (11) respectively.

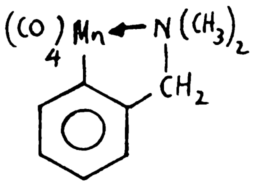
For structures (11), (I) and (V) the aryl-ring serves as a source of π-electron density which is delocalised around the cyclometallated ring. This can be verified by comparing the structures of (I), (IV), (V) and (11) with (III). For structure (III) (where no electron delocalisation is possible) notice that the Mn-O bond is longer and the C-O (acyl) bond is much shorter than in (I), (IV), (V) and (11). This is a clear indication that π-electron density is delocalised around the five- membered cyclometallated ring.

In our discussion of the ^{13}C-NMR spectra of the orthomanganated ketones (section 2.5) we note that one carbonyl absorbs at a much lower field strength than the others. This carbonyl was assigned as being *trans* to the oxygen donor.In such a configuration more electron density (from the donor oxygen) will be donated through manganese into the π^*-antibonding orbitals of the CO ligand. This would lower the bond order of the carbonyl bond whilst increasing the bond order of the Mn-C bond. This is exactly what is observed in the crystal structure of (11). The effect is less noticeable for the Mn-C and CO bonds trans to the aryl ring. No change in the carbonyl bond order is observed but this is not too surprising as carbonyls are known to be insensitive to such a small changes in bond order.

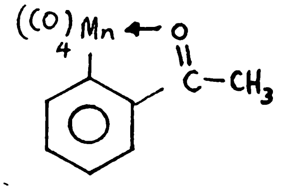
The acetylthiophene shares a distorted octahedral arrangement with the carbonyls about manganese. The C(9)-Mn-O(5) bite angle of 79.8(1)° is very similiar to the corresponding angles observed for other cyclomanganated structures (ix)[23] 79.8(2)°, (x)[24] 80.2(2)° and (xi)[18] 79.4(2)°.



(ix)



(x)



(xi)

The tetracarbonylmanganese fragment is mildly distorted away from its expected octahedral geometry. The major distortion being the folding of the axial carbonyls (C1-O1, C3-O3) towards the C9 atom [C9-Mn-C1 83.8°(1), C9-Mn-C3 86.2°(1)]. Only minor distortions are observed for the other equatorial carbonyls.

2.7 Attempted orthometallation of aryl phenyl ketones by $C_6H_5CH_2Co(CO)_4$ and $C_6H_5CH_2Fe(CO)_2$-(η-C_5H_5)

Preliminary studies have indicated that acetophenone and 3',4',5'-trimethoxyacetophenone cannot be orthometallated by $C_6H_5CH_2Co(CO)_4$ or $C_6H_5CH_2Fe(CO)_2(\eta\text{-}C_5H_5)$. Under the same reaction conditions as used for the orthomanganation of acetophenones no traces of any orthometallated products were observed. For the cobalt system complete decomposition of $C_6H_5CH_2Co(CO)_4$ occurs. However, for iron the metallating reagent appears to be transformed into $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ (identified by infrared spectroscopy).

References

(1) R. J. McKinney,

"Intramolecular Metalation Products Derived from Methylmanganese and Methylrhenium Carbonyl Complexes"

Ph. D. Thesis, University of California, 1974.

(2) R. J. McKinney, B. T. Huie, C. B. Knobler and H. D. Kaesz,
J. Am. Chem. Soc., **95**, 633, **1973**.

(3) R. J. McKinney, R. Hoxmeier and H. D. Kaesz,
J. Am. Chem. Soc., **97**, 3059, **1975**.

(4) R. J. McKinney and H. D. Kaesz,
J. Am. Chem. Soc., **97**, 3066, **1975**.

(5) S. Schreiber Crawford and H. D. Kaesz,
Inorg. Chem., **16**, 3193, **1977**.

(6) R. J. McKinney, G. Firestein and H. D. Kaesz,
Inorg. Chem., **14**, 2057, **1975**.

(7) A. W. Cabral,

"The Cyclometallation of Ketones and Quinones by Alkyl Pentacarbonyl Complexes : Mechanisitc and Synthetic Studies"

Ph. D. Thesis, University of California, **1981**.

(8) J. Cooney, personal communication, University of Waikato.

(9) C. P. Casey and C. A. Bunnell,
Inorg. Chem., **14**, 796, **1975**.

(10) H. J. Haupt, G. Lohmann and U. Florke,
Z. Anorg, Allg. Chem., **526**, 103, **1985**.

(11) T. E. Gismondi and M. D. Rausch,
J. Organomet. Chem., **284**, 59, **1985**.
R. D. Closson, J. Kozikowski and T. H. Coffield,
J. Org. Chem., **22**, 598, **1957**.

(12) J. M. Aizpurua and C. Palomo,
Tet. Letts., **26**, 475, **1985**.

(13) H. Alper and A. S. K. Chan,
J. Am. Chem. Soc., **95**, 4905, **1973**.

(14) F. A. Cotton,
Inorg. Chem., **3**, 702, **1964**.

(15) A. Oudeman and T. S. Sorensen,
J. Organomet. Chem., **156**, 259, **1978**.

(16) B. E. Mann and B. F. Taylor,
"^{13}C NMR Data for Organometallic Compounds",
Academic Press, London, **1981**, p. 15

(17) P. Main, L. Lessinger and M. M. Woolfson,
MULTAN78, University of York, **1977**.

(18) C. B. Knobler, S. Schreiber Crawford and H. D. Kaesz,
Inorg. Chem., **14**, 2062, **1975**.

(19) Y. Yanimoto, H. Kobayashi, S. Nagakura and Y. Saito,
Acta Crystallogr., Sect. B, **29**, 1822, **1973**.

(20) M. A. Bennett, G. B. Robertson, R. Watt and P. O. Whimp,
J. Chem. Soc., Chem. Commun., 752, **1971**.

(21) R. J. McKinney, B. T. Huie, C. B. Knobler and H. D. Kaesz,
J. Am. Chem. Soc., **95**, 633, **1973**.

(22) C. P. Casey, R. A. Boggs, D. F. Marten and J. C. Calabrese,
J. Chem. Soc., Chem Commun., 243, **1973**.

(23) R. G. Little and R. J. Doedens,
Inorg. Chem., **12**, 840, **1973**.

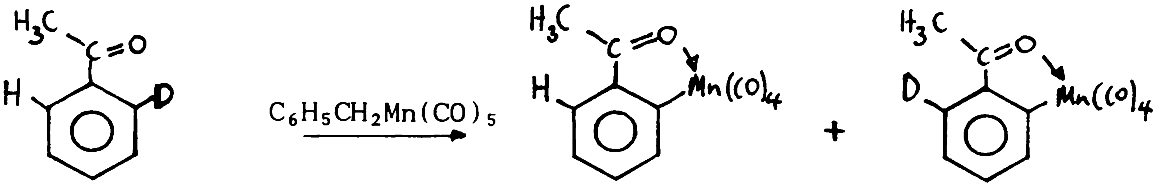
(24) R. G. Little and R. J. Doedens,
Inorg. Chem., **12**, 844, **1973**.

CHAPTER THREE

Hydrogen isotope effects in the orthomanganation of acetophenones

3.1 Introduction

In chapter four is reported the convenient preparation of pure orthomonodeuterioacetophenones by oxidation of orthomanganated acetophenones using cerium(IV) ammonium nitrate in CD_3COOD. It was recognised that these compounds provided a simple means for determining the hydrogen isotope effect for orthomanganation from the ratio of protio to deuterio products (equation 3.1).



equation 3.1

This ratio could be determined by integration of the proton NMR spectrum as long as signals were sufficiently well separated.

Apart from simplicity, this method has additional advantages over isotope effects established from kinetic measurements on separate protio and deuterio acetophenones in that even if an early step of the mechanism preceding breaking of the aryl C-H bond is rate-limiting, the product isotope effect still records the selectivity of H over D in the subsequent C-H bond breaking step. Information in some cases not accessible from kinetics may be obtained.

We therefore decided to establish that this method was viable by measuring isotope effects for orthomanganation with $C_6H_5CH_2Mn(CO)_5$ and, for comparison, with $C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$. Before discussing the results, and as a basis for consideration of where isotope effects arise and how they might assist in distinguishing mechanisms,

mechanisms previously proposed for orthomanganation, and the results of some kinetic measurements and isotope effect measurements previously carried out will be discussed. These will provide a lead-in to discussion of our results and subsequent consideration of how isotope effects may be valuable in helping to establish orthometallation mechanisms in general.

3.2 Mechanisms proposed for orthometallation by alkylmanganesepentacarbonyls

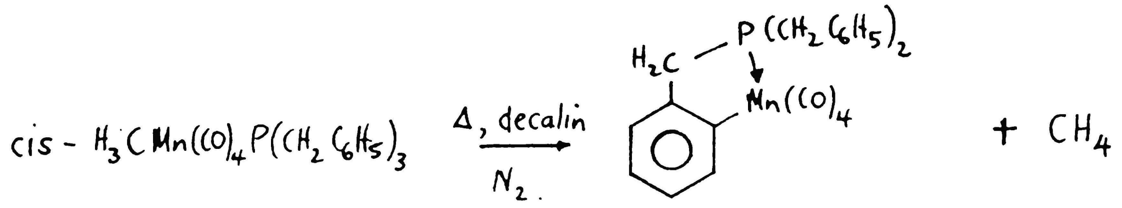
Two mechanisms have been proposed. The first[1] (Scheme 3.1) involves oxidative addition and reductive elimination steps and is referred to here as the oxidative addition mechanism. Oxidative addition occurs from the co-ordinatively unsaturated Mn(I) 16-electron intermediate (IB) to give the Mn(III) 18-electron intermediate (IC). This reductively eliminates alkane to give (ID) which picks up CO to form the orthomanganated product.

The second[2] (scheme 3.2) is referred to here as the concerted mechanism because metal-arene and alkyl-hydrogen bonds are formed in a concerted process involving a 4-membered ring transition state, as shown; there is no metal hydride bonding in any intermediate, unlike the oxidative addition mechanism.

Described now are some studies which have bearing upon mechanisms of orthomanganation. The interpretations are those originally given which have often not been considered in light of the variety of alternative mechanisms which are possible.

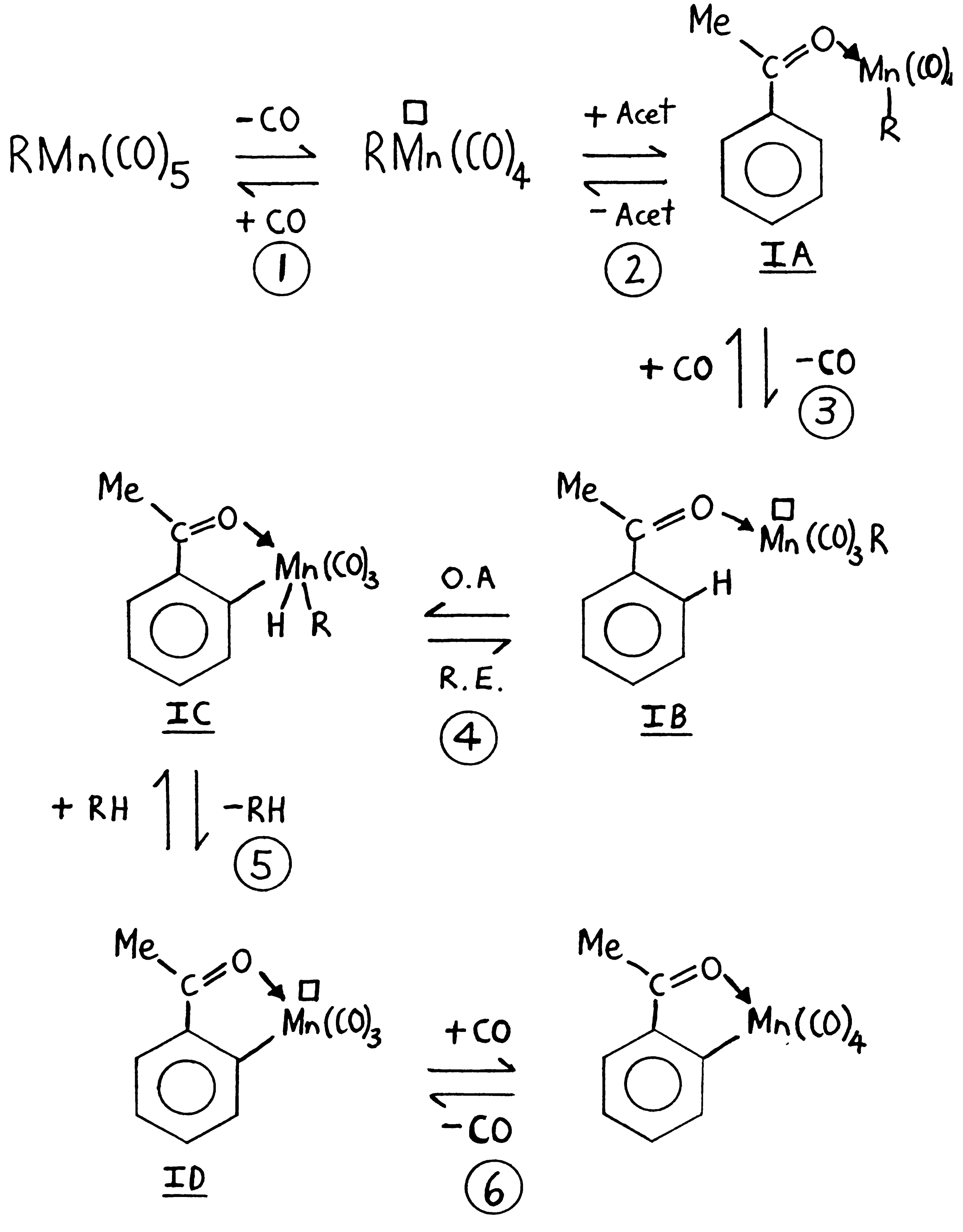
3.3 Studies of orthomanganations of relevance to mechanisms

The only system for which kinetic data is available is the internal metallation of *cis*-$H_3CMn(CO)_4P(CH_2C_6H_5)_3$ (equation 3.2) for which $\Delta S^{\ddagger}$ = 11.9 e.u. and $\Delta H^{\ddagger}$ = 32.7 kcal mol^{-1}.[3]

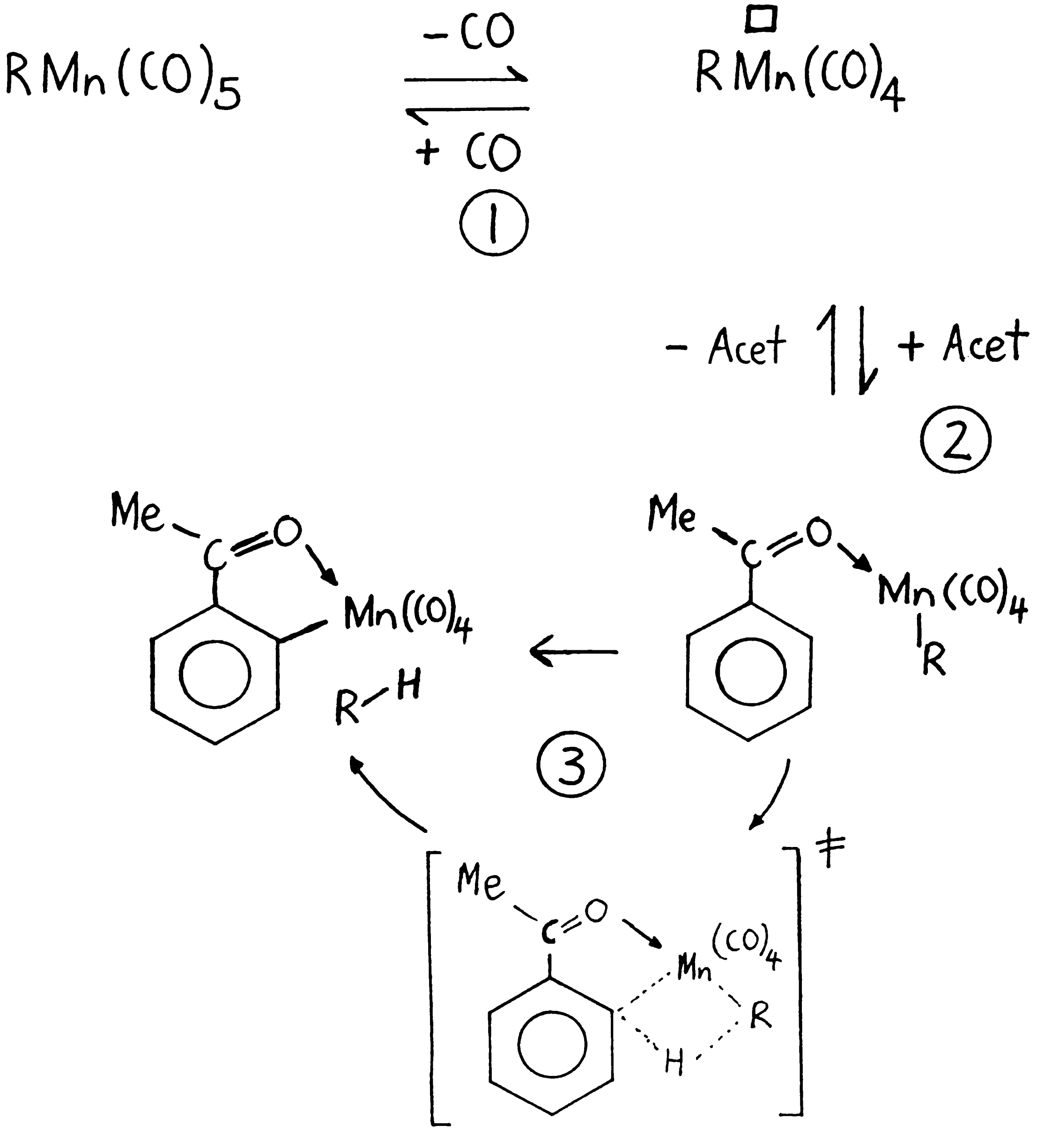


equation 3.2

Scheme 3.1 Oxidative addition mechanism for orthomanganation of acetophenone



Scheme 3.2 Concerted mechanism for orthomanganation of acetophenone

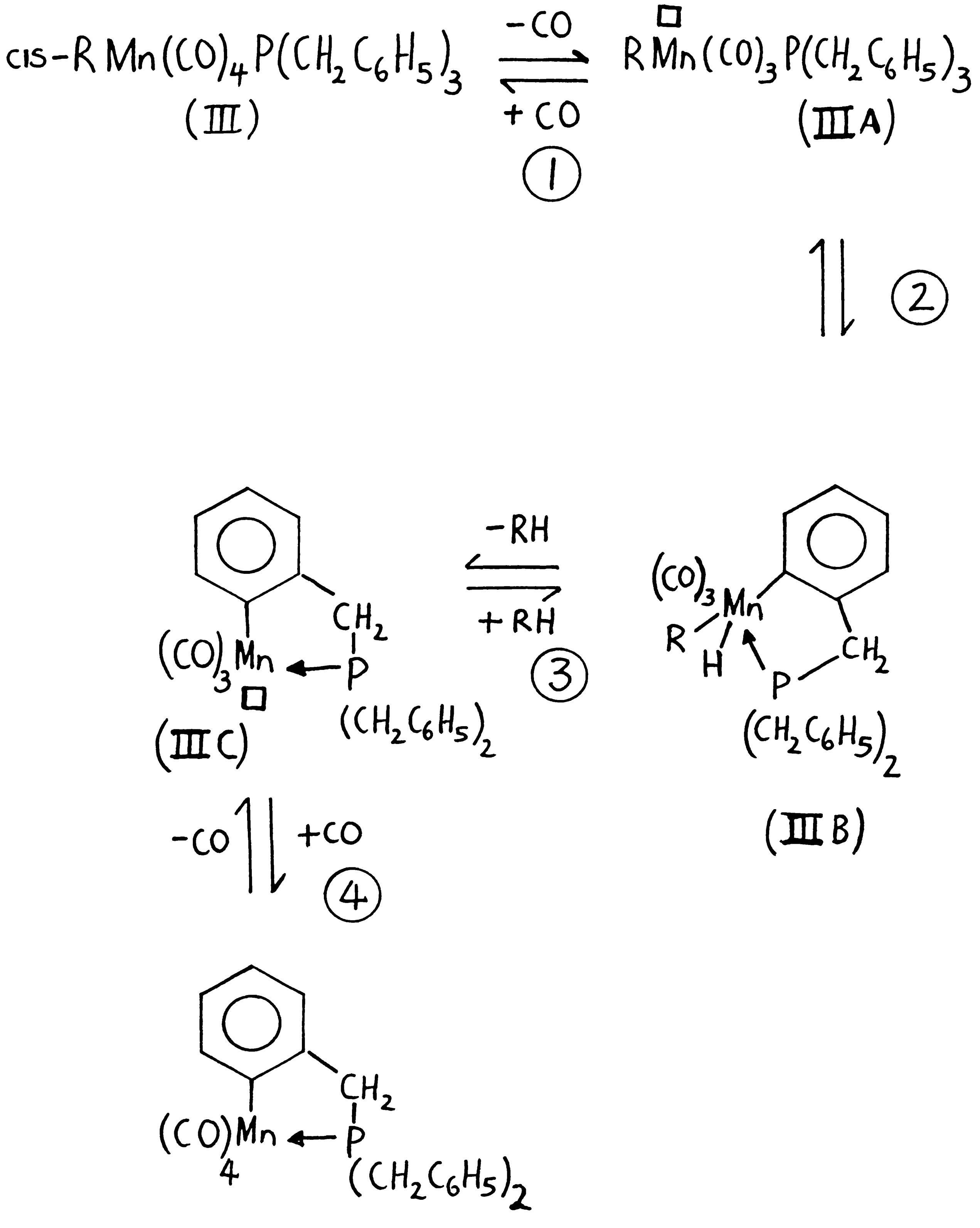


Jarvinen proposed an oxidative addition mechanism to account for this reaction (scheme 3.3). A radical mechanism involving aryl-H abstraction by a preformed alkyl/benzyl radical was discounted since the orthomanganation of *cis*-$C_6H_5CH_2Mn(CO)_4P(CH_2C_6H_5)_3$ proceeded sixteen times faster than the orthomanganation of *cis*-$H_3CMn(CO)_4$-$P(CH_2C_6H_5)_3$[3]. Bond energy calculations predict that abstraction of an aryl proton by a methyl radical ($H_3C^\bullet$) would be slightly exothermic, while abstraction of an aryl proton by a benzyl radical ($C_6H_5CH_2^\bullet$) would be strongly endothermic and slow. This is inconsistent with the higher reactivity of the benzyl compound.[3]

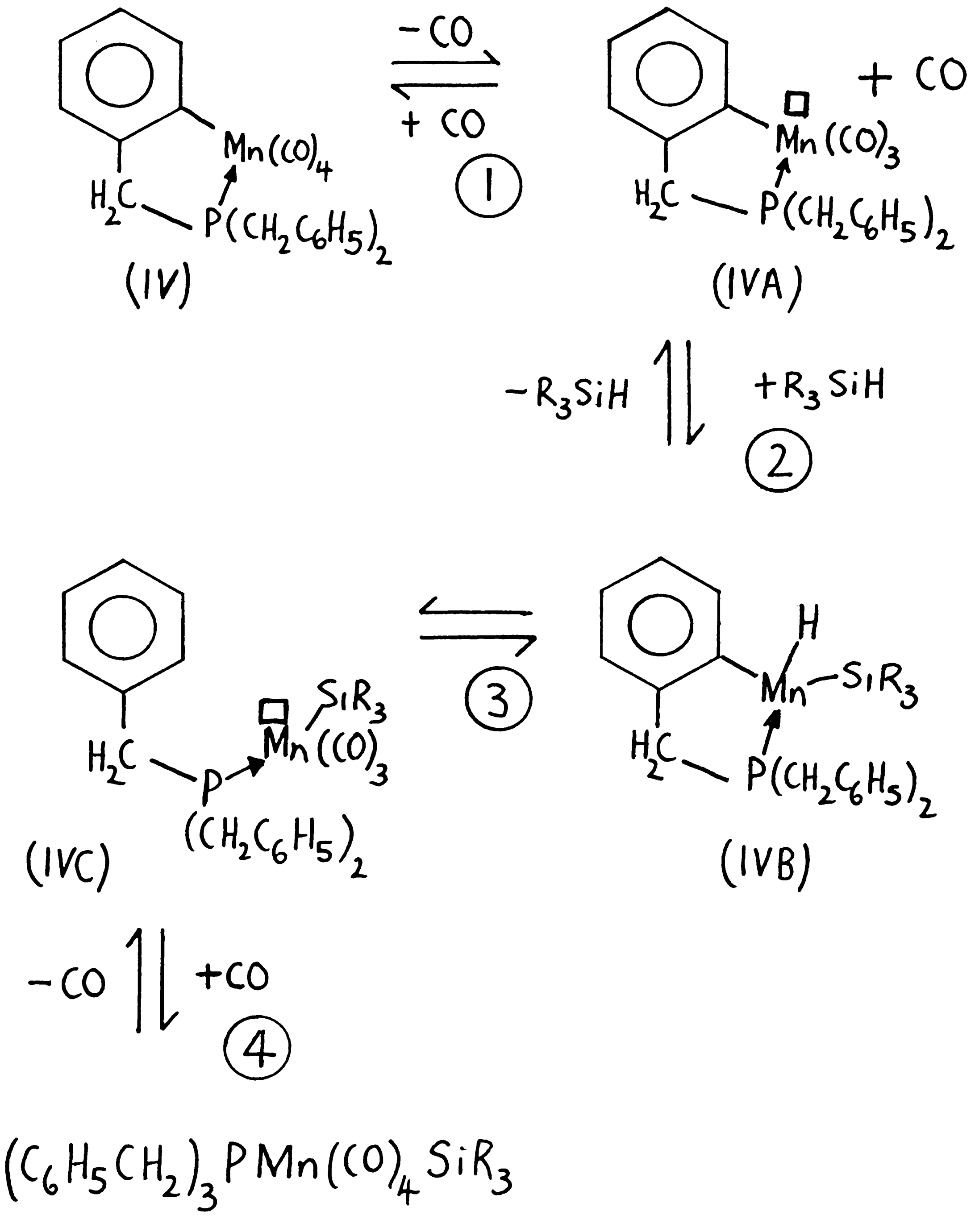
The positive $\Delta S^{\ddagger}$ suggests that the rate-determining step is a dissociative process. The rate of orthomanganation of the parafluorobenzylphosphine complex [*cis*-$H_3CMn(CO)_4P(p\text{-}CH_2C_6H_4F)_3$] was, within experimental error, identical to that of the unsubstituted benzylphosphine complex. Significant differences in rates would only be expected if attack by the metal on the ring was rate-limiting. For these reasons Jarvinen proposed that the initial dissociation of CO from (III) (scheme 3.3) was the rate-limiting step.[3]

More evidence taken as support for the oxidative addition / reductive elimination sequence was that the final product, the orthomanganated benzylphosphine complex, itself undergoes addition reactions with R_3SiH (R = C_6H_5, C_2H_5), forming *trans*-$R_3SiMn(CO)_4$-$P(CH_2C_6H_5)_3$. These addition reactions are thought to proceed through co-ordinatively unsaturated intermediates (IVA) and (IVC) (scheme 3.4)[3] with oxidative addition and reductive elimination steps. Related intermediates are implicated in the oxidative addition mechanism of orthomanganation. Concerted mechanisms for these reactions were not given consideration.

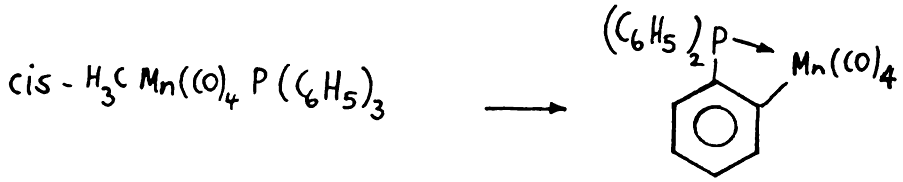
Scheme 3.3 Oxidative addition mechanism for orthomanganation of cis-RMn(CO)$_4$P(CH$_2$C$_6$H$_5$)$_3$ [R = CH$_3$ or CH$_2$C$_6$H$_5$]



Scheme 3.4 Exchange reactions of $(OC)_4\overline{MnC_6H_4CH_2P}(CH_2C_6H_5)_2$



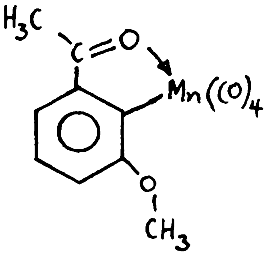
In contrast to this mechanism involving rate limiting CO dissociation, are the results of another study in which a kinetic hydrogen isotope effect was measured, implying rate limiting C-H bond breaking. The reaction studied was the internal orthomanganation in equation 3.3 for which $k_H/k_D = 2.4 \pm 0.3$.[4]



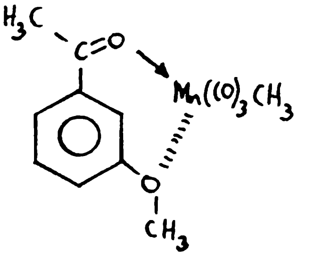
equation 3.3

In this case there was an aryl para-substituent effect on the rate (CH_3 > H > F) indicating what could be described as electrophilic characteristics.[5] There are indications here, then, of a difference in the rate-limiting step, if not the mechanism type, between these two intramolecular orthometallation reactions.

It is known that the manganation of 3'-methoxyacetophenone with $H_3CMn(CO)_5$ proceeds with the predominant formation (>95%) of the sterically more congested isomer (i).[6]



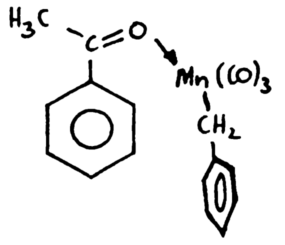
(i)



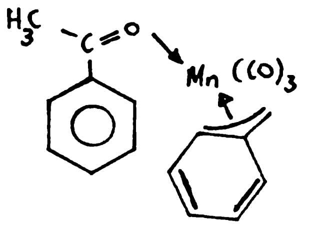
(ii)

Cabral[7] has suggested that the formation of (i) implicates an oxidative addition mechanism. He suggested that the 16 electron intermediate [(ii); cf. (IB) in scheme 3.1] can be stabilised by the methoxy oxygen (acting as a two electron donor) effectively locking the manganese into a particular geometry prior to oxidative addition. However the predominant formation of (i) could be explained in terms of a concerted mechanism (scheme 3.2) if the inductive effect (-I) of the methoxy oxygen were important. Cabral did not consider this.

In contrast, as described in chapter two, manganation of 3',4'-dimethoxyacetophenone with $C_6H_5CH_2Mn(CO)_5$ affords only 25% of the sterically more congested isomer (**7**) and 75% of (**6**), showing that the orientation control does not apply to the same extent in this case. Possibly, there is a difference between $H_3CMn(CO)_5$ and $C_6H_5CH_2Mn(CO)_5$ and we need to check the latter with 3'-methoxyacetophenone on this count. If a difference is found, a possible reason (as suggested by Cabral[7] to account for differences in rates between these two reagents) is that the 16-electron intermediate (IB) (refer to scheme 3.1) can be stabilised by the benzyl group undergoing a η^1-η^3 transformation; a similar stabilisation is not possible for the $H_3CMn(CO)_5$ intermediate (see (iii) and (iv)).



(iii)



(iv)

Such η^1-η^3 equilibria are known for other transition metal compounds, such as η^3-$C_6H_5CH_2Mo(CO)_2$-(η-C_5H_5)[8] and η^3-$C_6H_5CH_2Co(CO)_3$.[9]

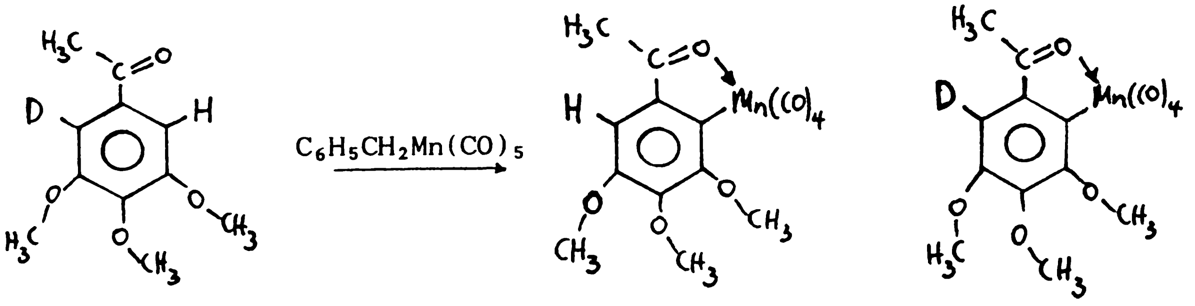
In summary then, there is no evidence which directly supports the concerted mechanism (scheme 3.2). However, it does avoid the formation of the 7-co-ordinate Mn(III) species (IC) which on steric and electronic grounds would be expected to be highly unstable. Apart from the above results there is also some unpublished hydrogen isotope effect data for orthomanganations and these are referred to for comparison with the results reported in the next section.

3.4 Results of product hydrogen isotope effects measured in the present study

3.4.1 Orthomonodeuterioacetophenone (19) and orthomonodeuterio-3',4',5'-trimethoxyacetophenone (20) with $C_6H_5CH_2Mn(CO)_5$

The orthomonodeuterioacetophenones (19) and (20) were orthomanganated in 85% and 87% yield respectively. These products were then analysed for their deuterium content by ^{1}H-NMR. The magnitude of the isotope effect for the orthomanganation of orthomonodeuterio-3',4',5'-trimethoxyacetophenone (20; > 99% D) is outlined. The ^{1}H-NMR spectrum of the manganated product (**4**/**4a**) is illustrated in figure 3.1.

For the reaction



[fraction $(1-f_x)$] [fraction (f_x)]

(20) (**4**) (**4a**)

the product isotope effect, i.e. the H/D selectivity in the product-forming steps, is given by the product ratio (**4a**)/(**4**). If the fractions of (**4a**) and (**4**) are represented as (f_x) and $(1-f_x)$ respectively, then:

$$\text{Product isotope effect} = (\mathbf{4a})/(\mathbf{4}) = (f_x)/(1-f_x)$$

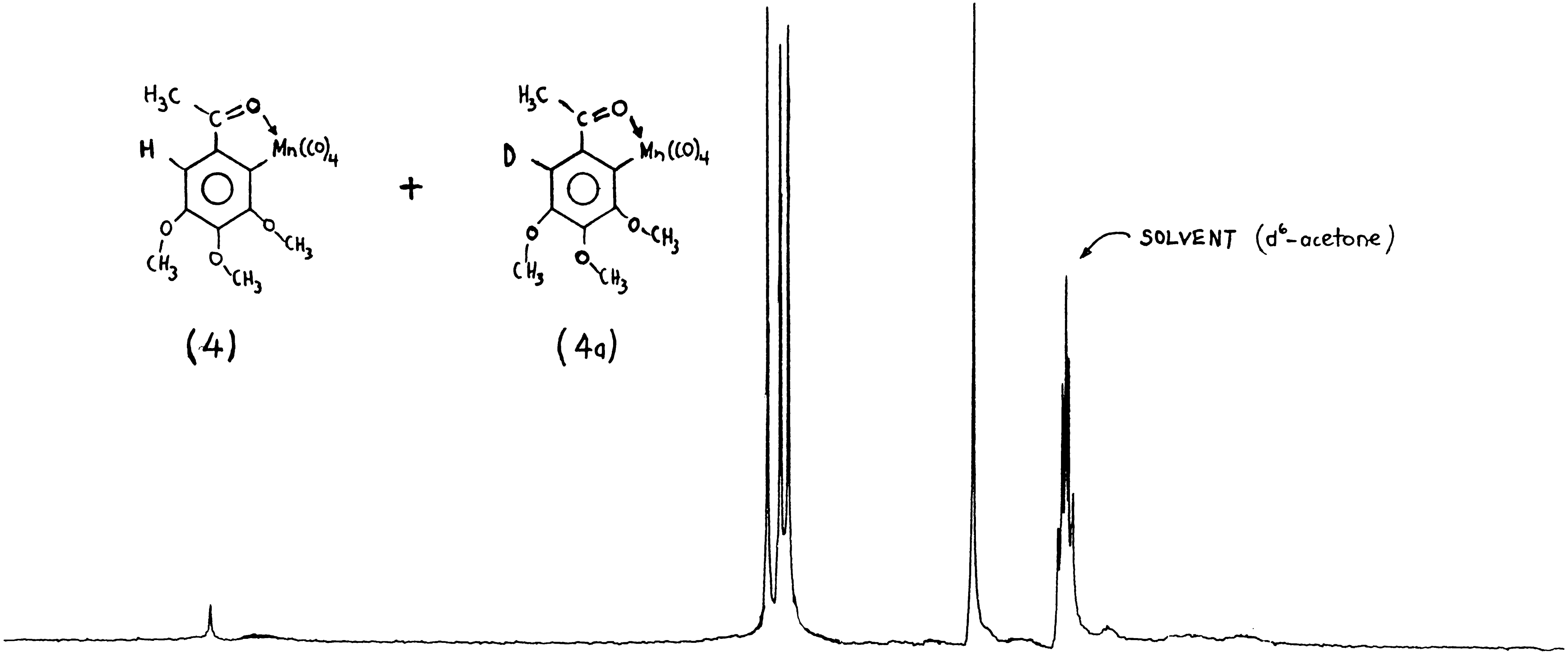


Figure 3.1 ^{1}H-NMR spectrum of (4)/(**4a**)

It remains to calculate (f_X) from the ^{1}H-NMR integral data. For a mixture of (**4**) and (**4a**)

average number ArH protons per molecule = $(1-f_X)$

number $COCH_3$ protons per molecule = 3

$(1-f_X)/3$ = weight ArH signal/weight $COCH_3$ signal

= 0.0072/0.0840

$(1-f_X)$ = 3(0072)/0.0840

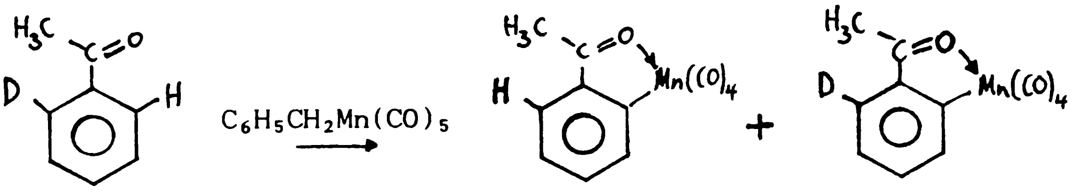
= 0.257

and (f_X) = 0.743

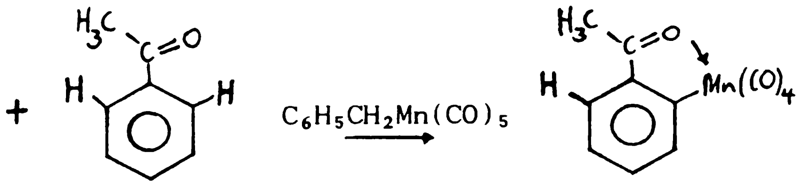
Product isotope is therefore = 0.743/0.257 = 2.9

Assuming in this case an error of 5% in the integral ratio value, the experimental error in the isotope effect is 10%.

For the compound (**19**), the ^{1}H-NMR integral indicated 88% purity, with the additional 12% being the all-protio ketone. The orthomanganation can therefore be represented as follows, using a total of 100 molecules to simplify calculations.



(**19**) 88 molecules (1) $88(1-f_X)$ (1a) $88(f_X)$



12 molecules (1) 12 molecules

The terms (f_X) and ($1-f_X$) again represent respectively the fractions of product, in this case from (**19**) alone, of (**1a**) and (**1**).

Product isotope effect = (**1a**) formed from (**19**)

(**1**) formed from (**19**)

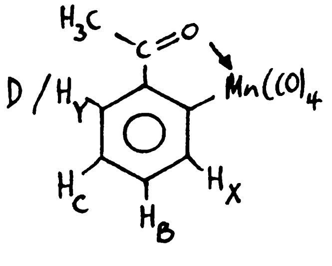
= $(f_X)/(1-f_X)$

The ratio of (**1a**)/(**1**) in the actual product, including 12 molecules from the all-protio ketone

= $88(f_X)/[88(1-f_X) + 12]$

and it is this ratio which can be equated to the experimentally determined ratio from ^{1}H-NMR to obtain the value of (f_X) required.

The experimental ratio is determined as follows. The spectrum of (**1**)/(**1a**) recorded in CD_2Cl_2 is essentially identical with that of (**1**) recorded in $CDCl_3$. That is, the H_X and H_Y protons resonate at lowest field (δ 7.8), and the H_B and H_C protons at higher field (δ 7.3).



Integrated intensity H_X/H_Y multiplet = 72 units

Integrated intensity H_B/H_C multiplet = 110 units

Integrated intensity for one proton (by reference to H_B/H_C signals) = 55 units

The H_X/H_Y signal represents 72/55 protons, and subtracting for H_X (which is always H, not D)

H_γ signal = $[(72/55) - 1]$

$= 0.31$ protons

Ratio (1a)/(1) in product = $[1 - 0.31]/0.31$

$= 0.69/0.31$

$= 2.23$

Equating,

$$88(f_X)/[88(f_X) + 12] = 2.23$$

$$88(f_X) = 196.2 - 196.2(f_X) + 26.8$$

$$284.2(f_X) = 223$$

$$(f_X) = 0.784$$

$$[1 - (f_X)] = 0.216$$

Product isotope effect = 3.6

Because of the large experimental error associated with subtraction, the H_γ integral value is estimated to have an error of up to 20%, which will be reflected in the uncertainty of the product isotope effect value.

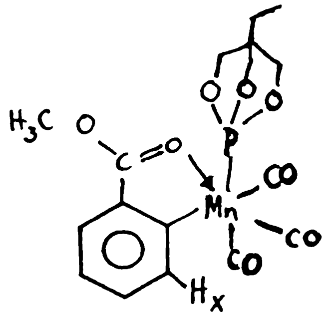
After this work was completed we became aware of an unpublished study whereby the product isotope (by a similar internal competition method) for the manganation of (**19**) by $C_6H_5CH_2Mn(CO)_5$ had been recorded as 3.4 ± 0.1,[7] in good agreement with the value which we obtained. The isotope effect for the manganation of d^5-benzophenone was also measured[7] (3.9 ± 0.1 for $C_6H_5CH_2Mn(CO)_5$ and 2.9 ± 0.1 for $H_3CMn(CO)_5$).

3.4.2 Orthodeuterioacetophenone with *cis*-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$

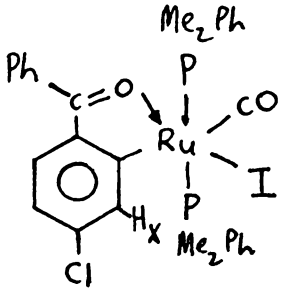
To see if the product isotope effect for manganation was affected by the ligands attached to the metal, (**19**; 88% D) was manganated with *cis*-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$. A mixture of protio (**16**) and deuterio (**16a**) compounds was obtained in 50% yield. The all-protio compound (**16**) had previously been obtained by reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (**1**) with triphenylphosphine.[10]

The ^{1}H-NMR spectrum (200 MHz) of the aromatic region of the manganated product is illustrated in figure 3.2. Although the ^{1}H-NMR spectrum of (**16**) has been reported in the literature (at 100 MHz) no proton resonances were uniquely assigned.[10] For this reason this spectrum will be discussed in more detail.

There are two distinct absorbances at low field which are separate from the multiplets centred at δ 7.40 and δ 7.55. The resonance at lowest field (δ 7.99) is assigned to H_X; it is a doublet $^3J(H_B$, 7.4 Hz) of doublets $^3J(H_C$, 1.3 Hz) of doublets $^4J(^{31}P$, 1.3 Hz) broadened by a $^5J(H_Y$, D) coupling. Assignment of a $^4J(^{31}P)$ coupling is not unreasonable as similar couplings have been observed for other orthometallated compounds, for example the following.[11,12]



$^4J(H_X - {}^{31}P)$ 1.8 Hz



$^4J(H_X - {}^{31}P)$ 1.0 Hz

The resonance at δ 7.55 is almost half the intensity of the H_X signal and is assigned to H_Y. This evidence combined with the observed multiplet pattern [doublet ^2J (H_C, 7.7 Hz) of doublets ^3J (H_B, 1.5 Hz) of doublets ^5J (H_X, 0.7 Hz)] confirms the assignment. H_B and H_C would be expected to be broadened triplets and must appear at higher field strength, obscured by the triphenylphosphine proton signals.

The ^{1}H-NMR integral of (**19**) indicated 88% purity, with the other additional 12% being the all protio-ketone. The product isotope effect is calculated by the method used previously for the orthomanganation of (**19**) by $C_6H_5CH_2Mn(CO)_5$ (refer to section 3.4.1).

The aromatic signals H_X and H_Y were enlarged, cut out and weighed.

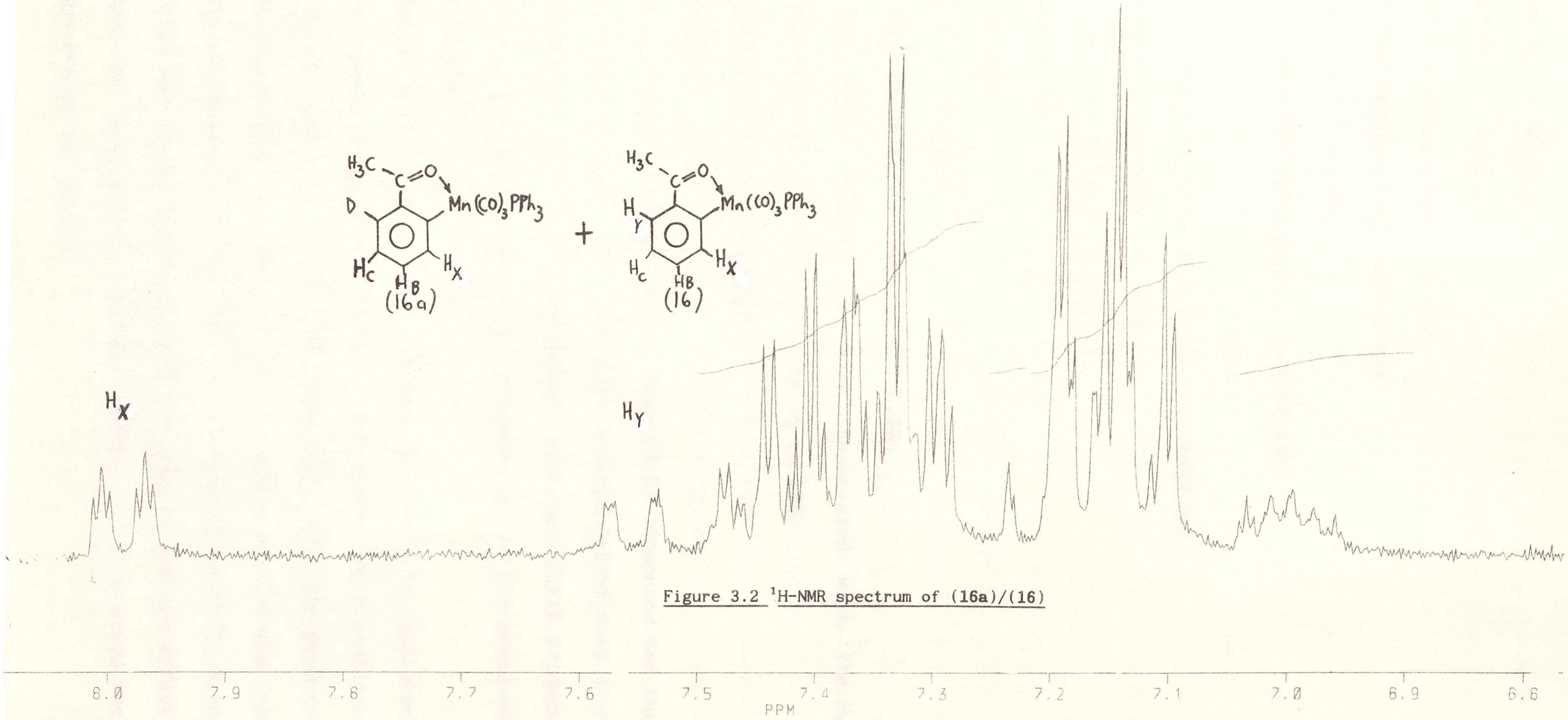


Figure 3.2 ^{1}H-NMR spectrum of (16a)/(16)

weight of H_X = 0.52 g

weight of H_Y = 0.28 g

weight of one proton (H_X) = 0.52 g

The H_Y signal represents 0.28/0.52 protons

H_Y signal = 0.538 protons

Ratio of (**16a**)/(**16**) in product = 0.462/0.538

= 0.86

Equating (refer to section 3.4.1 for a discussion)

$88(f_X)/[88(1 - f_X) + 12] = 0.86$

$88(f_X) = 75.68 - 75.68(f_X) + 10.32$

$163.68(f_X) = 86$

$(f_X) = 0.525$

$[1 - (f_X)] = 0.475$

Product isotope effect is therefore = 1.10

Because of the large experimental error associated with the H_Y integral value the error is estimated to be up to 20%.

3.5 Origin of the product isotope effect

3.5.1 $C_6H_5CH_2Mn(CO)_5$

The large product isotope effect (ca. 3.0) observed for the manganation of both (**19**) and (**20**) indicates a large selectivity of H over D bond breaking. The steps consistent with such large product isotope effects will be discussed with reference to the two proposed mechanisms in schemes 3.1 and 3.2.

The oxidative addition mechanism (scheme 3.1) will be discussed first. We have assumed that step 5 is non-reversible. Two situations could exist. First, if step 4 is non-reversible, then the product isotope effect will just be the ratio of rates of C-H and C-D oxidative addition. However, if IC is in equilibrium with IB, with step 5 being slow and rate—limiting, then the product isotope effect will depend upon the equilibrium isotope effect in step 4 and the kinetic isotope effect for step 5.

The only step consistent with a large product isotope effect for the concerted mechanism will be step 3. The product isotope effect will just be the ratio of rates of manganation at C-H and C-D.

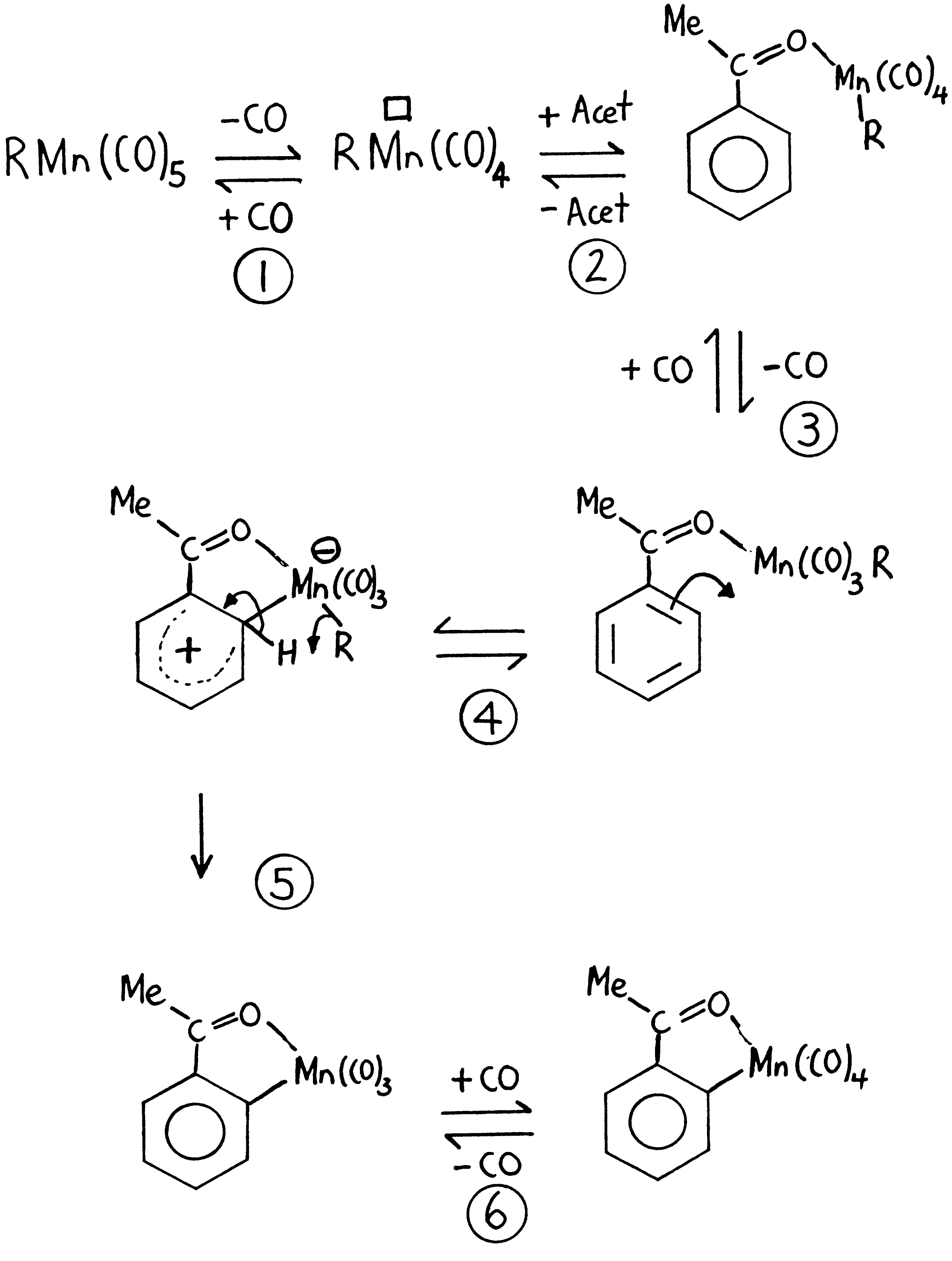
3.5.2 *cis*-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$

The low product isotope effect of ca 1.0 for this orthomanganation shows that there is little selectivity beween C-H and C-D bond breaking. This isotope effect can be explained in terms of the oxidative addition mechanism if the rate-determining step occurs prior to step 4, the most likely rate-determining step being step 3, with the oxidative addition being fast and non-selective between C-H or C-D bond cleavage.

Similar arguments apply for the concerted mechanism, with the rate-determining step occurring prior to step 3, which is fast and non-selective between H and D.

Another mechanism is possible where the Mn-aryl bond is formed prior to C-H/C-D bond breaking (electrophilic mechanism; scheme 3.5). If the electrophilic step is rate-limiting (step 4) and not reversed, then the H/D product ratio will be determined in this step and there will be little selection between H or D. Such electrophilic attack will be slower for $C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ than $C_6H_5CH_2Mn(CO)_5$ because the phosphine increases the electron density on the metal and would make it less electrophilic. Possibly then, for $C_6H_5CH_2Mn(CO)_5$, step 4 is faster and reversible, and the large product isotope effect is associated with step 5 becoming rate-limiting. Alternatively, the two reagents might react by different mechanisms. The electrophilic mechanism has been mentioned because there is some evidence from substituent effects that the intramolecular metallation of $H_3CMn(CO)_4P(C_6H_5)_3$ is electrophilic (refer to section 3.2). It should also be recognised that any electrophilic mechanism need not proceed exactly as in scheme 3.3 and that, for instance, the carbocation

Scheme 3.5 Electrophilic mechanism for orthomanganation of acetophenone



intermediate formed by electrophilic attack could lead instead to an oxidative addition by H^+ transfer first to Mn, rather than directly to the alkyl group.

Further detailed discussion of mechanisms is not justified with the small amount of data available, but it is clear that differences in isotope effects like the ones reported here have potential as mechanistic criteria, and this is good reason for their routine measurement.

3.6 Experimental

cis-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ was prepared by a literature procedure.[13] It had m.p. 152-155°C (lit.[13] 155°C).

Preparation of *fac*-η^2-(2-acetylphenyl)tricarbonyltriphenylphosphinomanganese(**16**)

cis-$C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ (0.467 g, 0.9 mmol) and excess acetophenone (0.20 g, 1.67 mmol) were added to a nitrogen-saturated heptane solution (15 ml). The solution was then refluxed for 1 hour and the heptane was removed under vacuum. The resulting yellow-orange residue was absorbed onto a small quantity of neutral alumina and transferred onto a column of alumina (2 cm X 15 cm). Elution with hexane/ether (20:1) removed a yellow-orange band. This material was rechromatographed (p.l.c., 1:9 ether/petroleum spirit). The plate had to be developed three times to separate three components. The first colourless component was unreacted acetophenone, while the second was *fac*-η^2-(2-acetylphenyl)tricarbonyltriphenylphosphinomanganese (**16**; 0.22 g, 47 %). It was recrystallised from hexane/THF (20:1) to give red-orange crystals, m.p. 164-165°C (lit.[10] 166°C).

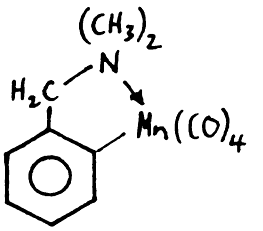
Mass spectrum (m/e) 520 (0.5), 436 (90.5), 262 (100), 183 (85.4), 174 (92.4), 108 (27.8), 55 (21.5); ^{13}C-NMR ($CDCl_3$) δ 227.36 (d, $^2J(^{31}P)$ 22.0 Hz), 217.68 (d, $^2J(^{31}P)$ 2.9 Hz), 209.00 (d, ^2J (^{31}P) 17.6 Hz), 145.54 (s), 141.44 (d), 133.73 (d, $J(^{31}P)$ 10.3 Hz), 131.94 (s, J(^{31}P) 35.0 Hz), 131.55 (d), 129.61 (d, ^{4}J(^{31}P) 2.9 Hz), 127.94 (d, J(^{31}P) 10.3 Hz), 121.93 (d), 23.74 (q) (see appendix I for chemical shift assignments); Infrared spectrum ν(CO) (cyclohexane) 2005 (vs, sharp), 1925 (vs, br), 1891 (vs, br); ^{31}P-NMR δ (referenced to 85 % H_3PO_4) +57.6 ($W_{1/2}$ 10.5 Hz).

In analogous fashion, orthomonodeuterioacetophenone (**19**) was metallated with $C_6H_5CH_2Mn(CO)_4P(C_6H_5)_3$ forming (**16/16a**) in 50 % yield. The product had m.p. 163-165°C.

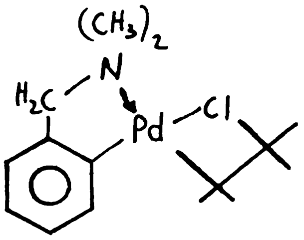
3.7 Appendix : Attempted Preparation of 2-deuterio-benzyldimethylamine

3.7.1 Introduction

Benzyldimethylamine is one of the few reagents that can be orthometallated by both manganese ($H_3CMn(CO)_5$)^{14} and palladium (Li_2PdCl_4)^{15} to form (v) and (vi) respectively.



(v)

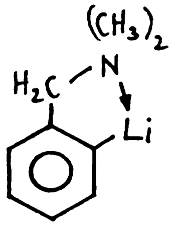


(vi)

Because Pd(II) shows electrophilic character in metallation,$^{15-19}$ any differences in the magnitudes of the product isotope effects for palladiation and manganation might supply valuable information about their respective mechanisms. We therefore attempted to prepare 2-deuterio-benzyldimethylamine for such a comparative study.

3.7.2 Attempted preparation of 2-deuterio-benzyldimethylamine

In the literature there are two claims that lithiation of benzyldimethylamine with n-butyllithium occurs exclusively in the ortho-position to form 2-lithio-benzyldimethylamine (vii).[20,21]



(vii)

Subsequent deuteriation of (vii) with D_2O is reported to form 2-deuterio-benzyldimethylamine in quantitative yield.[20]

Benzyldimethylamine was prepared from benzylchloride and aqueous dimethylamine using a literature procedure.[22] The amine was dried over KOH pellets and triply distilled before use (b.p. 180-182°C).

Benzyldimethylamine (3.2 g, 0.024 mol) and ether (ca. 50 ml) were were placed in an oven—dried Schlenk flask. n-Butyllithium (31.25 ml; 1.6 mol/l in hexane; 0.05 mol) was syringed into the flask through a stream of N_2. The colour of the solution changed from colourless to light yellow. The reaction mixture was set aside for three days while a thick crystalline mass of yellow crystals of ortho-lithiated amine formed. The mixture was cooled in an icebath and D_2O (3 ml, 0.166 mol) was pipetted into the reaction vessel. A vigorous reaction ensued but subsided after a few minutes leaving a residue of lithium deuterioxide. The ether solution was stirred for one hour, then filtered and dried ($MgSO_4$). The ether was removed under vacuum and the crude amine obtained was then doubly distilled. A small sample 1.2 g (37 %) was collected as a middle fraction from the second distillation and this was analysed for its deuterium content by ^{1}H-NMR. ^{1}H-NMR (neat) δ 7.30 (m, 4.05 H), 3.42 (s, 2 H), 2.24 (s, 6 H).

Integration of the ^{1}H-NMR spectrum was consistent with 4.05 aromatic protons, suggesting a 95 % pure sample of 2-deuterio-benzyldimethylamine.

3.7.3. Reaction of 2-deuterio-benzyldimethylamine with $C_6H_5CH_2Mn(CO)_5$

$C_6H_5CH_2Mn(CO)_5$ (0.28 g, 1.02 mmol) and 2-deuterio-benzyldimethylamine (0.136 g, 1.03 mmol) were added to 20 ml of N_2-saturated heptane. The solution was refluxed under N_2 for 150 minutes. The heptane was removed under vacuum and the residue chromatographed (p.l.c., 1:9 ether/petroleum spirit). The metallated amine was recrystallised from petroleum spirit to give yellow flakey crystals of η^2-(2-dimethylaminobenzyl)tetracarbonylmanganese (0.150 g, 49 %), m.p. 70-71°C (lit [14] 73°C). ^{1}H-NMR (CDCl$_3$) δ 7.78 (d, J 7.5 Hz), 7.14 (t, J 7.5 Hz), 7.03 (m), 3.67 (s, 2 H), 2.68 (s, 6 H).(refer to figure 3.); ^{13}C-NMR (CDCl$_3$) δ 219.47 (s, br, CO), 214.34 (s, br, CO), 213.62 (s, br, CO), 167.91 (s, C1), 147.29 (s, C2), 141.31 (d, #)), 127.00 (d, #), 123.49 (d, #), 122.84 (d, #), 75.57 (t, -CH$_2$), 56.97 (q, N(CH$_3$)$_2$); # carbons unassigned; Infrared spectrum ν(CO) (CH$_2$Cl$_2$) 2066 (m), 1972 (s, br), 1931 (ms).

The aromatic region of the ^{1}H-NMR spectrum of the manganated amine is illustrated in figure 3.3. The integrated intensity of H_A (broadened doublet) represents only 0.84 of a proton relative to NMe$_2$ and CH$_2$ signals. Clearly some deuterium label must be incorporated into this meta site. This shows that the deuterium label is scrambled around the aromatic ring, and not solely positioned at the ortho site. Probably this occurs under the basic conditions in the preparation of

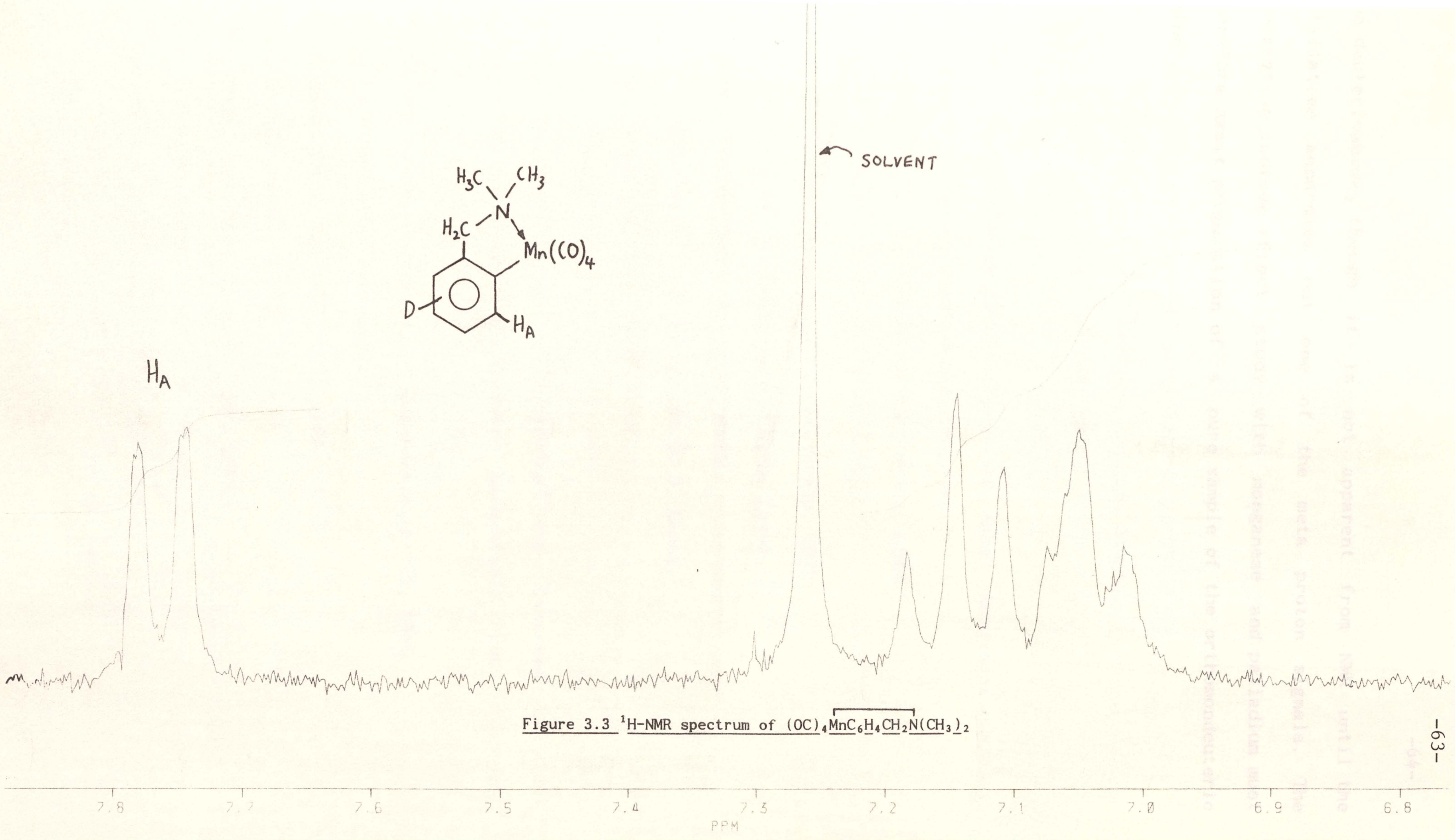


Figure 3.3 ^{1}H-NMR spectrum of $(OC)_4MnC_6H_4CH_2N(CH_3)_2$

the deuterioamine, though it is not apparent from NMR until the metallation separates out one of the meta proton signals. The comparative isotope effect study with manganese and palladium must therefore await preparation of a pure sample of the orthomondeuterio amine.

References

(1) P. M. Treichel, in

"Comprehensive Organometallic Chemistry", ed.

G. Wilkinson, F. G. A. Stone, E. W. Abel,

Pergamon Press, Oxford, 1982, Vol. 4, p. 79.

(2) R. L. Bennett, M. I. Bruce and F. G. A. Stone,

"J. Organomet. Chem., **94**, 65, **1975**.

(3) G. W. Jarvinen,

"The Cyclometallation Reaction of Alkyl Manganese Carbonyl Complexes: Mechanistic and Synthetic Studies."

Ph. D. Thesis, University of California, **1981**.

(4) R. J. Hoxmeier,

Ph. D. Thesis, University of California, **1972**.

(5) R. J. M^{c}Kinney, R. Hoxmeier and H. D. Kaesz,

J. Amer. Chem. Soc., **97**, 3061, **1975**.

(6) R. J. M^{c}Kinney, G. Firestein and H. D. Kaesz,

Inorg. Chem.,**14**, 2057, **1975**.

(7) A. W. Cabral,

"The Cyclometallation of Ketones and Quinones by Alkyl Manganese Pentacarbonyl Complexes: Mechanistic and Synthetic Studies"

Ph. D. Thesis, University of California, p. 73, **1981**.

(8) R. B. King and A. Fronzaglia,

J. Amer. Chem. Soc., **88**, 709, **1966**.

(9) V. Galamb and G. Palyi,

J. Chem. Soc. Chem. Commun., 487, **1982**.

(10) S. Schreiber Crawford and H. D. Kaesz,

Inorg. Chem., **16**, 3200, **1977**.

(11) C. P. Casey and C. A. Bunnell,
Inorg. Chem., **14**, 796, **1975**.

(12) Z. Dauter, R. J. Mawby, C. D. Reynolds and D. J. Saunders,
J. Chem. Soc. Dalton Trans., 1236, **1985**.

(13) D. Drew, M. Y. Darensbourgh and D. J. Darensbourgh,
J. Organomet. Chem., **85**, 73, **1975**.

(14) R. L. Bennett, M. I. Bruce and F. G. A. Stone,
Aust. J. Chem., **28**, 1265, **1975**.

(15) A. C. Cope and E. C. Friedrich,
J. Amer. Chem. Soc., **90**, 909, **1968**.

(16) A. D. Ryabov, I. K. Sakodinskaya and A. K. Yatsimirsky,
J. Chem. Soc. Dalton Trans., 2629, **1985**.

(17) S. Hietkamp, D. J. Stufkens and K. Vrieze,
J. Organomet. Chem., **168**, 351, **1979**.

(18) M. I. Bruce,
Angew. Chem. Int. Ed. Engl., **16**, 73, **1977**.

(19) J. Dehand and M. Pfeffer,
Co-ord. Chem. Reviews, **18**, 327, **1976**.

(20) F. N. Jones, M. F. Zinn and C. R. Hauser,
J. Org. Chem. **28**, 663, **1963**.

(21) C. T. Viswanathan and C. A. Wilkie,
J. Organomet. Chem. **54**, 1, **1973**.

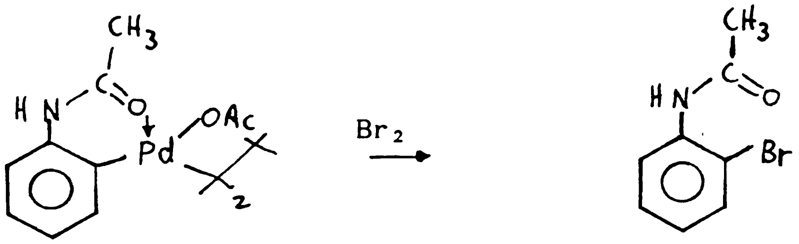
(22) Chem. Abstracts 59,8669c

CHAPTER FOUR

Oxidation of some orthomanganated ketones

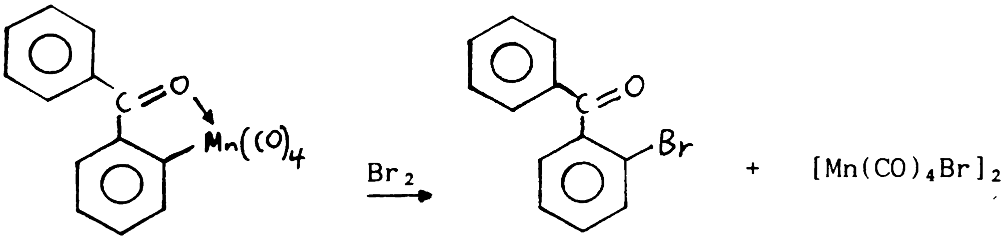
4.1 Introduction

The oxidation of some orthometallated aryl compounds by halogens has been studied by a small number of research groups. Orthopalladiated compounds react with halogens to form otherwise inaccessible o-halogenated products.[1] One example is the reaction of the orthopalladiated acetanilide with bromine to afford o-bromoacetanilide in 70 % yield (equation 4.1),[2] in contrast to direct



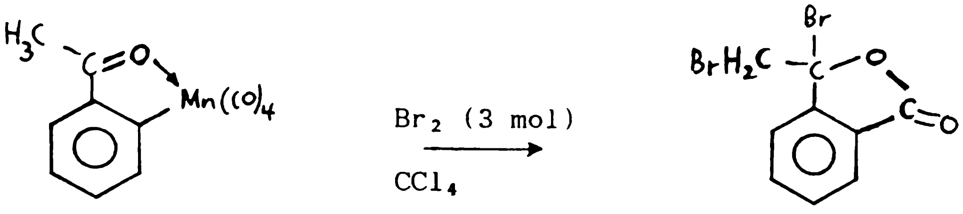
equation 4.1

bromination of acetanilide which proceeds exclusively in the para-position.[3] Similarly, there is an unpublished report of bromination of η^2-(2-benzoylphenyl)tetracarbonyl manganese giving o-bromobenzophenone in 44 % yield (equation 4.2).[4]



equation 4.2

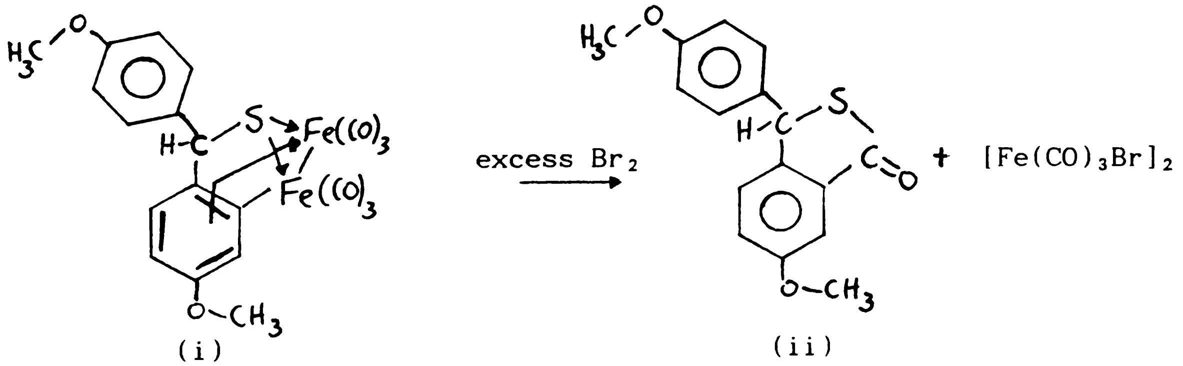
However, some reactions of halogens with orthometallated compounds do not always yield the expected o-halogenated product. An example is the bromination[4] shown in equation 4.3 which produces the dibromide of vinylphthalide rather than 2'-bromoacetophenone.



(58%)

<u>equation 4.3</u>

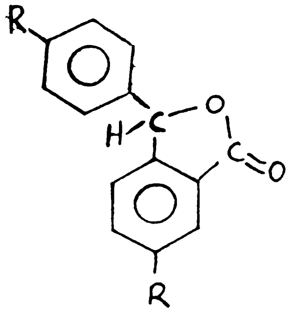
Alper has studied the reaction of some orthometallated thiobenzophenones with a number of different oxidising agents. Some useful one step transformations can be effected. For example oxidation of the orthometallated iron compound (i) with bromine produces the bromothiolactone (ii) (equation 4.4).[5]



(i) (ii)

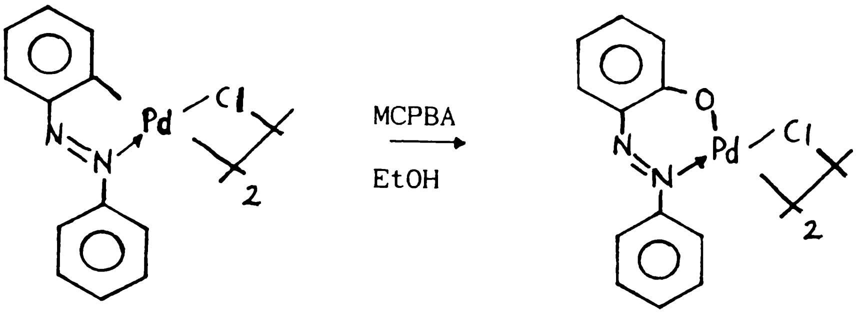
<u>equation 4.4</u>

Other thiolactones can be prepared either by treatment of orthometallated thiobenzophenones with cerium ammonium nitrate or by photolysis in ethanol.[5] Treatment of substituted orthometallated thiobenzophenones with *meta*-chloroperbenzoic acid or hydrogen peroxide produces the corresponding lactones (iii) in good yield.[5]



(iii)

However, treatment of orthopalladiated azobenzenes with *meta*-chloroperbenzoic acid results in a metaloxylation reaction (insertion of oxygen into the carbon to palladium σ-bond) (equation 4.5).[6]



equation 4.5

This reaction is of considerable interest to the synthetic organic chemist as it introduces a hydroxyl group into the original palladium position.

We have extended previous studies by investigating the reactions of substituted η^2-(2-acetylphenyl)tetracarbonylmanganese compounds with a variety of oxidising compounds including I_2, ICl, Br_2, MeI, Ce (IV) and Mn (III).

4.2 Experimental

Brominations

General Comments

All brominations were performed in AR carbon tetrachloride which was saturated with nitrogen before use. The standard method of bromination is illustrated for the preparation of 2'-bromo-3',4',5'-trimethoxyacetophenone (21).

4.2.1 Preparation of 2'-bromo-3',4',5'-trimethoxyacetophenone (21)

A freshly prepared solution of bromine in CCl_4 (0.34 mol/l ; 0.78 ml, 0.266 mmol) was added dropwise to a solution of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (4; 0.10 g, 0.266 mmol) in CCl_4. Almost instantaneously a thick orange precipitate formed with the decolourisation of the bromine. The solution was stoppered for five minutes and filtered. The precipitate proved to be $[Mn(CO)_4Br]_2$[7] having the following spectral characteristics: IR ν(CO) (CH_2Cl_2) 2099 (w), 2041 (s), 2009 (m), 1972 (m) (lit.[7] ν(CO) (CCl_4) 2099 (w), 2042 (s), 2011 (m), 1975 (m).); mass spectrum (m/e) 438 (1.1) $[M - 2\ CO]^+$, 412 (7.7), 410 (14.6), 408 (7.7). $[M - 3\ CO]^+$, 384 (9.2), 382 (18.2), 380 (9.7) $[M - 4\ CO]^+$, 356 (4.0), 354 (7.1), 352 (3.7) $[M - 5\ CO]^+$, 328 (4.6), 326 (9.1), 324 (4.8) $[M - 6CO]^+$, 300 (11.1), 298 (23.4), 296 (12.8) $[M - 7\ CO]^+$, 272 (17.0), 270 (37.0), 268 (19.0) $[M - 8\ CO]^+$, 134 (9.4), 136 (9.0), 55 (100).

The carbon tetrachloride was removed under vacuum and the oily residue was chromatographed [p.l.c.,3:7 ether/petroleum spirit] yielding two bands. The band at R_f 0.6 proved to be $BrMn(CO)_5$, by comparison of the infrared spectrum with an authentic sample. The major band at R_f 0.40 proved to be 2'-bromo-3',4',5'-trimethoxyacetophenone (**21**; 0.080 g, 104%) contaminated with a trace of 2,2'-dibromo-3',4',5'-trimethoxyacetophenone (as ajudged by a small signal at δ 4.43 in the ^{1}H-NMR spectrum of the crude product). This oil was recrystallised from hexane/diethyl ether (5 1) to yield white crystals of m.p. 44-46°C (lit.[8] 34.5-35°C).

^{1}H-NMR ($CDCl_3$) δ 6.76 (s, 1H, 6'-H), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 2.65 (s, 3H, $COCH_3$).

^{13}C-NMR ($CDCl_3$) δ 200.87 (s, CO), 152.82 (s, 3'-C), 151.06 (s, 5'-C), 145.14 (s, 4'-C), 137.27 (s, 1'-C), 107.88 (d, 6'-C), 106.39 (s, 2'-C), 61.06 (q, OCH_3), 61.02 (q, OCH_3), 56.25 (q, OCH_3), 30.56 (q, $COCH_3$).

Mass spectrum (m/e) 290 (31.3), 288 (31.3), 275 (52.1), 273 (53.1), 260 (8.5), 232 (9.2), 230 (9.9), 202 (7.4), 151 (8.7), 123 (12.2), 93 (25.8), 77 (25.1), 65 (18.9), 43 (100.0).

Anal. Calcd. for $C_{11}H_{13}BrO_4$: C, 45.70; H, 4.53. Found: C, 45.14;

H, 4.32 %.

4.2.2 Preparation of 3'-bromo-4',5',6'-trimethoxyacetophenone (22)

η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (3; 0.157 g, 0.42 mmol) was brominated, worked up and chromatographed (p.l.c., 4:1 petroleum spirit/ethylacetate) by the standard method described above for (21). The first yellow band at R_f 0.95 was not analysed. The second, major, band at R_f 0.80 proved to be slightly impure 3'-bromo-4',5',6'-trimethoxyacetophenone (22; 0.082 g, 68%), the impurity probably being a trace of the α,3'-dibrominated product, less than 5 % as indicated by ^{1}H-NMR. Attempts to recrystallise this sample from hexane/ether (50 : 1) failed, but a pure sample was obtained by vacuum sublimation (0.1 mm Hg, 40°C): white crystals m.p 45-47.5°C. (lit.[9] 53.5-54.0°C). ^{1}<u>H-NMR</u> ($CDCl_3$) δ 7.67 (s, 1H, 2'-H), 3.96 (s, 6H, OCH_3), 3.91 (s, 3H, OCH_3), 2.59 (s, 3H, $COCH_3$). ^{13}<u>C-NMR</u> ($CDCl_3$) δ 196.62 (s, CO), 154.48 (s, 4'-C), 153.55 (s, 6'-C), 147.16 (s, 5'-C), 128.85 (s, 1'-C), 127.60 (d, 2'-C), 111.41 (s, 3'-C), 61.13 (q, OCH_3), 60.75 (q, br, OCH_3), 30.69 (q, $COCH_3$); <u>Mass spectrum</u> 290 (7.3), 288 (7.4), 275 (3.8), 273 (4.2), 210 (36.3), 195 (100), 180 (13.3), 152 (30.8), 137 (13.1), 77 (11.8).

Anal. Calcd. for $C_{11}H_{13}BrO_4$: C, 45.70: H, 4.53; Br, 27.64. Found: C, 45.57; H, 4.56; Br, 27.62 %.

The last band at R_f 0.7 was 2',3',4'-trimethoxyacetophenone (0.015 g, 17%) as determined by comparison of the ^{1}H-NMR spectrum with an authentic sample.

4.2.3 Preparation of 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (23)

η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5 dimethoxyphenyl)tetracarbonylmanganese (0.25 g, 0.526 mmol) was reacted with bromine (0.084 g; 0.526 mmol) worked up and chromatographed (p.l.c., 3:7 ether/petroleum spirit) using the standard methods described, yielding 3 major bands.

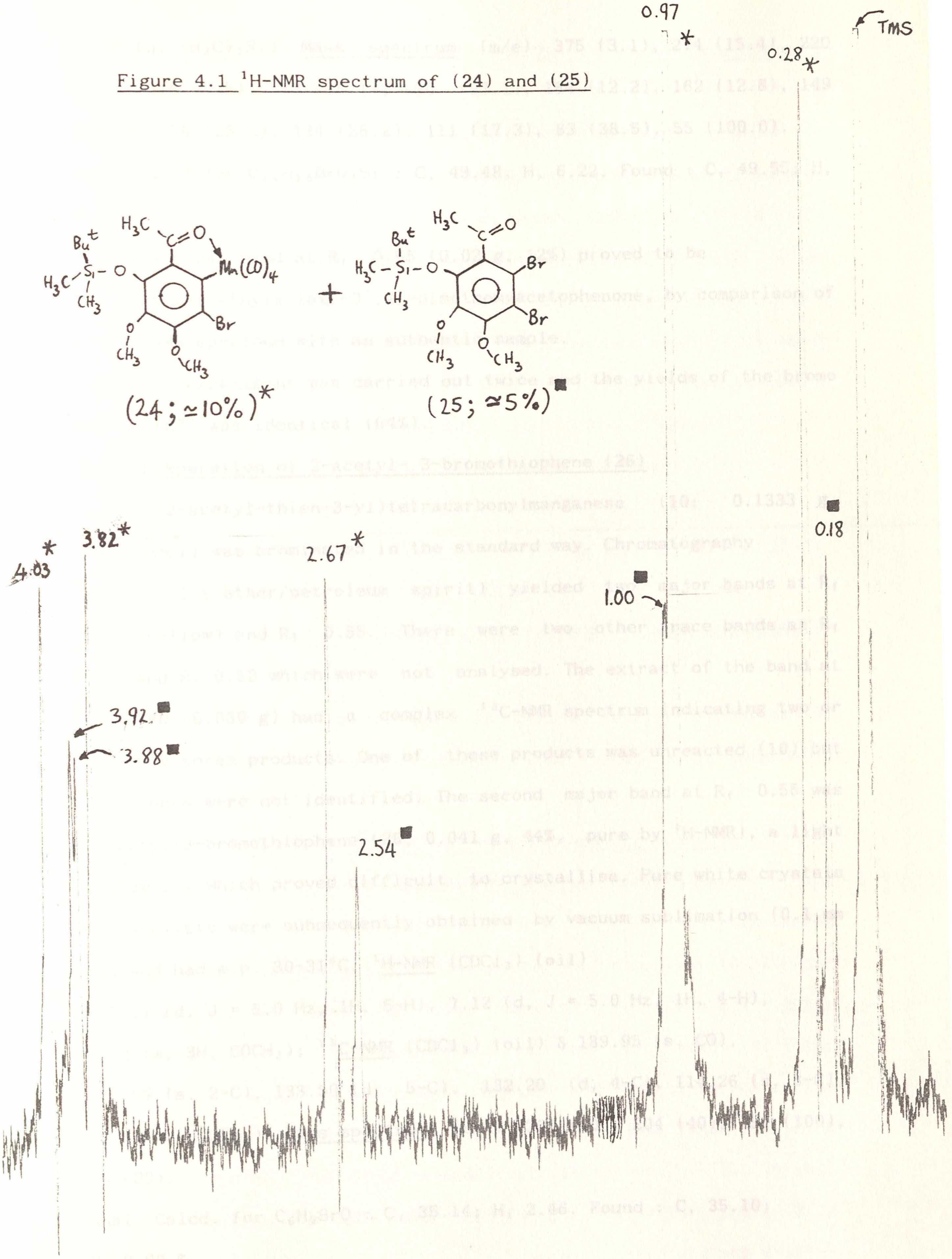
The band of highest R_f 0.85 was yellow and gave on extraction 0.04 g of material with a complex ^{1}H-NMR spectrum: δ ($CDCl_3$) 4.03, 3.92, 3.88, 3.82, 2.67, 2.54, 0.99 (br), 0.28, 0.18 (see figure 4.1). This indicates a mixture of two products in approximately a 12 : 5 ratio based on integration of the acetyl protons. The most distinguishing feature of the spectrum is the lack of any aromatic proton signal. Given the colour of the material and its infrared spectrum, which was found to be identical to that of (**5**) in the metal carbonyl region, one of the products can be assigned as η^2-(2-acetyl-3,4,5-trimethoxy-6-bromophenyl)tetracarbonylmanganese (**24**).

Observation of the following molecular ions [556 (2), 554 (2) M^+ , 472 (5), 470 (5),$[M-3CO]^+$] in the mass spectrum of the mixture support this structure. The mass spectrum also showed an ion of mass 453 with a dibromo isotope pattern [i.e. 451 (1), 453 (2), 455 (1)]. This peak was assigned to be a $[M-15]^+$ (-Me) fragmentation ion of 2',3'-dibromo-4',5'-dimethoxy-6'-t-butyldimethylsiloxyacetophenone (25).

The ^{1}H-NMR chemical shifts for the postulated structures can be assigned quite easily by comparison with the chemical shifts observed for the ^{1}H-NMR spectra of (**3**) and (**5**) (refer to figure 4.1 for the chemical shift assignments).

The band at R_f 0.80 was 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (**23**; 0.13 g, 64%), a colourless oil which we could not crystallise. <u>^{1}H-NMR</u> ($CDCl_3$) δ 7.53 (s, 1H, 2'-H), 4.00 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.58 (s, 3H, $COCH_3$), 1.00 (s, 9H, $C(CH_3)_3$), 0.16 (s, 6H, $(H_3C)_2Si$); <u>^{13}C-NMR</u> ($CDCl_3$) δ 198.60 (s, CO), 153.79 (s, 4'-C), 148.20 (s, 2'-C), 145.86 (s, 3'-C), 130.06 (s, 1'-C), 127.07 (d, 6'-C), 109.12 (s, 5'-C), 60.61 (q, OCH_3), 30.37 (q, $COCH_3$), 25.62 (q, $C(\underline{C}H_3)_3$), 18.40 (s, $\underline{C}(CH_3)_3$),

Figure 4.1 ^{1}H-NMR spectrum of (24) and (25)



-4.42 (q, $(H_3C)_2Si$); Mass spectrum (m/e) 375 (3.1), 274 (15.4), 220 (7.9), 218 (7.5), 192 (28.1), 190 (27.1), 164 (12.2), 162 (12.8), 149 (14.3), 136 (26.2), 134 (26.2), 111 (17.3), 83 (38.5), 55 (100.0). Anal. Calcd for $C_{16}H_{25}BrO_4Si$: C, 49.48; H, 6.22. Found : C, 49.55; H, 6.45 %.

The final band at R_f 0.65 (0.02 g, 12%) proved to be 2'-t-butyldimethylsiloxy-3',4'-dimethoxyacetophenone, by comparison of its ^{1}H-NMR spectrum with an authentic sample.

This experiment was carried out twice and the yields of the bromo ketone (**23**) was identical (64%).

4.2.4 Preparation of 2-acetyl- 3-bromothiophene (**26**)

η^2-(2-acetyl-thien-3-yl)tetracarbonylmanganese (**10**; 0.1333 g, 0.456 mmol) was brominated in the standard way. Chromatography (p.l.c., 1:9 ether/petroleum spirit) yielded two major bands at R_f 0.80 (yellow) and R_f 0.55. There were two other trace bands at R_f 0.65 and R_f 0.50 which were not analysed. The extract of the band at R_f 0.80 (0.030 g) had a complex ^{13}C-NMR spectrum indicating two or possibly three products. One of these products was unreacted (**10**) but the others were not identified. The second major band at R_f 0.55 was 2-acetyl-3-bromothiophene (**26**; 0.041 g, 44%, pure by ^{1}H-NMR), a light yellow oil which proved difficult to crystallise. Pure white crystals for analysis were subsequently obtained by vacuum sublimation (0.1 mm Hg) and had m.p. 30-31°C. ^{1}H-NMR ($CDCl_3$) (oil) δ 7.51 (d, J = 5.0 Hz, 1H, 5-H), 7.12 (d, J = 5.0 Hz, 1H, 4-H), 2.70 (s, 3H, $COCH_3$); ^{13}C-NMR ($CDCl_3$) (oil) δ 189.95 (s, CO), 138.97 (s, 2-C), 133.50 (d, 5-C), 132.20 (d, 4-C), 114.26 (s, 3-C), 29.53 (q, $COCH_3$); Mass spectrum (m/e) 206 (40), 204 (40), 191 (100), 75 (20).

Anal. Calcd. for C_6H_5BrO : C, 35.14; H, 2.46. Found : C, 35.10; H, 2.60 %.

4.2.5 Preparation of 3'-bromo- 4',5'-dimethoxy-6'-hydroxyacetophenone (27)

2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (23; 0.12 g, 0.308 mmol) was dissolved up in a 10 ml mixture of methanol (25%) / acetic acid (50%) / water (25%) and stirred for 3 hours at room temperature. The reaction was followed by t.l.c.. After this time a large excess of water (ca. 30 ml) was added to the mixture which was then extracted with ether. The ether was washed with water and dried over $MgSO_4$. Removal of the ether under vacuum yielded a crude oil of > 95% purity (as evident from ^1H and ^{13}C-NMR).

^{1}H-NMR ($CDCl_3$) δ 12.81 (s, 1H, OH), 7.88 (s, 1H, H-Ar), 4.13 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 2.66 (s, 3H, $COCH_3$).

^{13}C-NMR ($CDCl_3$) δ 202.69 (s, CO), 157.18 (s, 4'-C), 155.49 (s, 2'-C), 141.44 (s, 3'-C), 128.56 (d, C-Ar), 116.92 (s, 1'-C), 105.35 (s, 5'-C), 60.99 (q, OCH_3), 60.74 (q, OCH_3), 26.40 (q, $COCH_3$).

4.3 Iodinations

A typical iodination procedure is outlined for the preparation of 2'-iodo-3',4',5'-trimethoxyacetophenone (**28**) from the manganated ketone (**4**).

4.3.1 Preparation of 2'-iodo- 3',4',5'-trimethoxyacetophenone (28)

η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.1512 g, 0.4 mmol) was dissolved in 2 ml of nitrogen saturated carbon tetrachloride. Iodinechloride (0.065 g, 0.4 mmol dissolved in nitrogen saturated CCl_4) was added to this solution. The flask was tightly stoppered and left at room temperature for four days. After this time all of the iodine chloride had decolourised and a bright orange precipitate was visible: IR ν(CO) (CH_2Cl_2) 2099 (w), 2046 (vs), 2009 (m), 1972 (m). This infrared fingerprint pattern matches fairly well with that reported for the dimer $[Mn(CO)_4Cl]_2$[7] : ν (CO) (CCl_4) 2104 (w), 2045 (s), 2012 (m), 1977 (m). The orange solid did not analyse well by mass spectroscopy as no parent ion, successive CO loss, nor chlorine isotope patterns were observed. This solution was worked up and chromatographed as usual [refer to the standard bromination of (4)] to yield 2'-iodo-3',4',5'-trimethoxyacetophenone (**28**; 0.125 g, 93%) as a colourless oil. This oil was recrystallised from hexane and vacuum sublimed (0.1 mm Hg) to give white needles, m.p 53-54°C. ^{1}H-NMR (CDCl$_3$) δ 6.75 (s, 1H, 6'-H), 3.86 (s, 3H, OCH$_3$), 3.84 (s, 6H, OCH$_3$), 2.58 (s, 3H, COCH$_3$); ^{13}C-NMR (CDCl$_3$) δ 201.98 (s, CO), 153.79 (s, 3'-C), 153.47 (s ,5'-C), 147.78 (s, 4'-C), 140.98 (s, 1'-C), 107.82 (d, 6'-C), 79.79 (s, 2'-C), 60.93 (q, OCH$_3$), 60.80 (q, OCH$_3$), 56.25 (q, OCH$_3$), 29.79 (q, COCH$_3$); Mass spectrum 336 (98.8), 321 (100.0), 278 (17.6), 263 (8.7), 179 (17.5), 151 (21.9), 123 (22.8).

Anal. Calcd. for $C_{11}H_{13}IO_4$: C, 39.31; H, 3.90. Found C, 39.35 ; H, 3.97 %.

4.3.2 Preparation of 2'-benzyloxy -3',4'-dimethoxy-6'-iodoacetophenone (29)

This was prepared by the reaction of η^2-(2-acetyl-3-benzyloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (**8**; 0.311 g, 0.688 mmol) with iodine chloride in the normal way over four days. After this time not all of the iodine chloride had decolourised. Workup in the normal way (excess ICl removed under vacuum) followed by (p.l.c.,3:7 ether/petroleum spirit) afforded two bands. At R$_f$ 0.85 was predominantly unreacted manganated ketone (0.09 g, ≃ 29%) and at R$_f$ 0.7 2'-benzyloxy-3',4'-dimethoxy-6'-iodoacetophenone [(29 ; 0.178 g, 63%)] as off white crystals, recrystallisation of which from hexane yielded pure white crystals of m.p. 86.5-87.5°C. ^{1}H-NMR (CDCl$_3$) δ 7.37 (s, br, 5H, Ar-H), 7.09 (s, 1H, 5'-H), 5.03 (s, 2H, O-CH$_2$), 3.86 (s, 6H, OCH$_3$), 2.43 (s, 3H, COCH$_3$); ^{13}C-NMR (CDCl$_3$) δ 202.57 (s, CO), 154.44 (s, 4'-C), 148.98 (s, 2'-C), 142.41 (s, 3'-C), 136.50 (s, 1'-C), 128.24 (d, H_2C-Ph), 128.04 (d, H_2C-Ph), 118.29 (d, 5'-C), 81.74 (s, 6'-C), 76.21 (t, OCH_2), 60.74 (q, OCH_3), 56.19 (q, OCH_3), 31.02 (q, $COCH_3$); Mass spectrum (m/e) 412 (2), 370 (40), 336 (50), 321 (85), 265 (18), 151 (18), 91 (100).

Anal. Calcd. for $C_{17}H_{17}IO_4$: C, 49.53 ;H, 4.16. Found: C, 49.64 ; H, 4.33 %

4.3.3 Preparation of 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-6'-iodoacetophenone (30)

η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5-dimethoxyphenyl)-tetracarbonylmanganese (**5**; 0.112 g, 0.235 mmol) was iodinated with ICl in the normal way and left stoppered for four days at room temperature. After workup and chromatography we obtained slightly impure 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-6'-iodoacetophenone [(**30**): 0.100 g, 100%]. Recrystallisation of the crude product from hexane gave thick white crystals of m.p. 115-117°C. ^{1}H-NMR ($CDCl_3$) δ 7.10 (s, 1H, H-Ar), 3.92 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 2.56 (s, 3H, $COCH_3$), 0.97 (s, 9H, $(H_3C)_3C$-), 0.16 (s, 6H, $(H_3C)_2Si$). ^{13}C-NMR ($CDCl_3$) δ 203.08 (s, CO), 154.18 (s, 4'-C), 145.86 (s, 2'-C), 140.20 (s, 3'-C), 133.57 (s, 1'-C), 116.27 (d, 5'-C), 82.33 (s, 6'-C), 60.41 (q, OCH_3), 56.18 (q, OCH_3), 31.35 (q, $COCH_3$), 25.75 (q, $(H_3C)_3C$), 18.40 (s, $(H_3C)_3C$), -4.48 (q, $(H_3C)_2Si$); Mass spectrum (m/e) 421 (2), 379 (100), 349 (5), 252 (10), 237 (8), 194 (6), 167 (7), 73 (50).

Anal. Calcd for $C_{16}H_{25}IO_4Si$: C, 44.04 ; H, 5.77. Found : C, 44.11 ; H, 5.83%.

4.3.4 Preparation of 2'-iodo-4',5',6'-trimethoxyacetophenone (31)

This was prepared by reaction of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (**3**; 0.183 g, 0.488 mmol) with iodine chloride in the normal way over 15 hours. After this time not all of the iodine chloride had decolourised. The solution was worked up and chromatographed (p.l.c.,1:1 ether/petroleum spirit) in the normal way. The band at R_f 0.65 afforded after extraction, an oil, 2'-iodo-4',5',6'-trimethoxyacetophenone (**31**; 0.088 g, 53 %) which we could not crystallise. This product was identified from spectral data only and no elemental analysis has been done. ^{13}C-NMR ($CDCl_3$) δ 202.96 (s, CO), 154.64 (s, 4'-C), 150.35 (s, 6'-C), 142.28 (s, 5'-C), 134.68 (s, 1'-C), 118.22 (d, 3'-C), 81.74 (s, 2'-C), 61.84 (q, OCH_3), 60.80 (q, OCH_3), 56.32 (q, OCH_3), 31.15 (q, $COCH_3$).

4.3.5 Preparation of 3-acetyl-2,5-dimethyl-4-iodothiophene (32)

Iodination of η^2-(2,5-dimethyl-4-acetylthien-3-yl)tetracarbonylmanganese (**11**; 0.032 g, 0.1 mmol) with iodine chloride in the normal way over one day yielded (after workup and chromatography) 3-acetyl-2,5-dimethyl-4-iodothiophene (**32**; 0.028 g, 100%) as a white solid. This solid was recrystallised from hexane to give fine white needles m.p. 45.5-46.5°C. ^{1}H-NMR ($CDCl_3$) δ 2.62 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.42 (s, 3H, CH_3); ^{13}C-NMR (d^6-acetone) δ 198.01 (s, CO), 142.74 (s, 5-C), 140.20 (s, 2-C*), 136.63 (s, 3-C*), 79.33 (s, 4-C), 18.08 (q, 5-CH_3), 14.89 (q, 2-CH_3). (methyl ketone quartet was obscured beneath d^6-acetone septet); ^{13}C-NMR ($CDCl_3$) δ 198.21 (s, CO), 141.63 (s, 5-C*), 140.27 (s, 2-C*), 135.98 (s, 3-C), 31.48 (q, $COCH_3$), 18.14 (q, 5-C*), 15.15 (q, 2-CH_3) (aryl-iodo singlet was obscured under $CDCl_3$ triplet). * indicates assignments interchangeable; Mass spectrum (m/e) 280 (75), 265 (100), 110 (40).

Anal. Calcd. for C_8H_9IOS: C, 34.30 ; H, 3.24. Found : C, 34.53 ; H, 3.11%.

4.3.6 Preparation of 2-acetyl-3-iodothiophene (33)

Iodination of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**) (0.12 g, 0.41 mmol) in the normal way stoppered for 24 hours gave after workup and chromatography 2-acetyl-3-iodothiophene (**33**; 0.078 g, 75%, pure by ^{1}H-NMR), a light yellow solid. This sample was recrystallised from hexane to yield off-white crystals m.p. 59-60°C.

^{1}H-NMR (CDCl$_3$) δ 7.45 (d, J = 4.8 Hz, 5-H), 7.25 (d, J = 4.8 Hz, 4-H), 2.67 (s, 3H, COCH$_3$); ^{13}C-NMR (CDCl$_3$) δ 189.56 (s, CO), 140.27 (s, 2-C), 139.62 (d, 4-C), 132.92 (d, 5-C), 83.56 (s, 3-C), 29.46 (q, COCH$_3$); Mass spectrum (m/e) 252 (80), 237 (100), 110 (14), 82 (9).

Anal. Calcd. for C_6H_5IOS: C, 28.59; H, 2.00. Found : C, 28.52; H, 2.02 %.

4.3.7 Preparation of 2'-t-butyldimethylsiloxy-6'-iodoacetophenone (34)

Normal iodination of η^2-(2-acetyl-3-t-butyldimethylsiloxyphenyltetracarbonylmanganese (**9**) over 1 day was not effective as evident from only trace amounts of [Mn(CO)$_4$Cl]$_2$ formed. Only 5% of the required iodinated product (**34**) was produced, with recovery of ca. 90% of unreacted (**9**). However when we exposed a solution of (**9**) (0.104 g, 0.25 mmol) and ICl to strong sunlight (ca. 6 hours) a large amount of [Mn(CO)$_4$Cl]$_2$ precipitated out of solution. The solution was left to stand overnight and was worked up the next day. P.l.c (3:17 ether/petroleum spirit) afforded two major bands. The band at R$_f$ 0.95 (0.045 g) was almost all unreacted starting material, although there were traces of a second component. The second major band at R$_f$ 0.80 was 2'-t-butyldimethylsiloxy-6'-iodo-acetophenone (**34**; 0.042 g, 45%), a colourless oil which would not recrystallise. ^{1}H-NMR (CDCl$_3$) δ 7.43 (dd, J = 7.0 Hz, J = 1.50 Hz, H-Ar), 6.90 (m, 2H, H-Ar), 2.54 (s, 3H, COCH$_3$), 0.97 (s, 9H, (H$_3$C)$_3$C), 0.23 (s, 6H, (H3C)$_2$Si); ^{13}C-NMR (CDCl$_3$) δ 203.80 (s, CO), 151.84 (s, 2'-C), 139.29 (s, 1'-C), 131.62 (d, 4'-C*), 130.71 (d, 5'-C*), 118.61 (d, 3'-C), 90.06 (s, 6'-C), 30.82 (q, COCH$_3$), 25.49 (q, (H$_3$C)$_3$C), 18.01 (s, (H$_3$C)$_3$C), -4.36 (q, (H$_3$C)$_2$Si). * Indicates assignments interchangeable.

Anal. Calcd. for $C_{14}H_{21}IO_2Si$: C, 44.68 ; H, 5.62. Found : C, 46.36 ; H, 6.25%. This data is to be checked on a repurified sample.

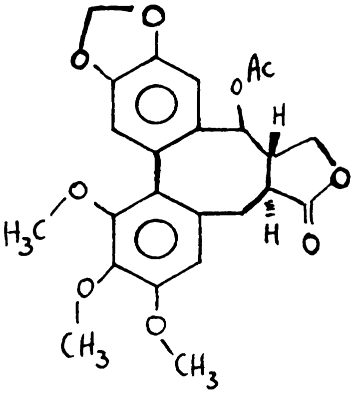
4.3.8 Preparation of 2-acetyl-3-iodofuran (35)

η^2-(2-acetylfuran-3-yl)tetracarbonylmanganese (**10**; 0.032 g, 0.08 mmol) was dissolved in N_2 saturated CCl_4 and iodinated in the normal way. The solution was left at ambient temperature for twelve hours and after workup and chromatography afforded 2-acetyl-3-iodofuran (**35**; 0.020 g, 100 %, pure by ^{1}H-NMR) as a off-white solid (m.p. not recorded). ^{1}H-NMR ($CDCl_3$) δ 7.50 (d, J = 1.8 Hz, 1H, 5-H), 6.72 (d, J = 1.8 Hz, 1H, 5-H), 2.54 (s, 3H, $COCH_3$). No elemental analysis has been recorded on this compound.

4.4 Discussion of bromination reactions

Bromination of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) proceeds readily with the formation of 2'-bromo-3',4',5'-trimethoxyacetophenone (**21**) and $[BrMn(CO)_4]_2$. The latter is probably formed by dimerisation of $[BrMn(CO)_4]$ as postulated by Crawford[4] for the formation of *ortho*-bromobenzophenone from η^2-(2-benzoylphenyl)tetracarbonylmanganese. The *ortho* bromo ketone (**21**) has previously been prepared by a four step synthesis (refer to scheme 4.1).[8]

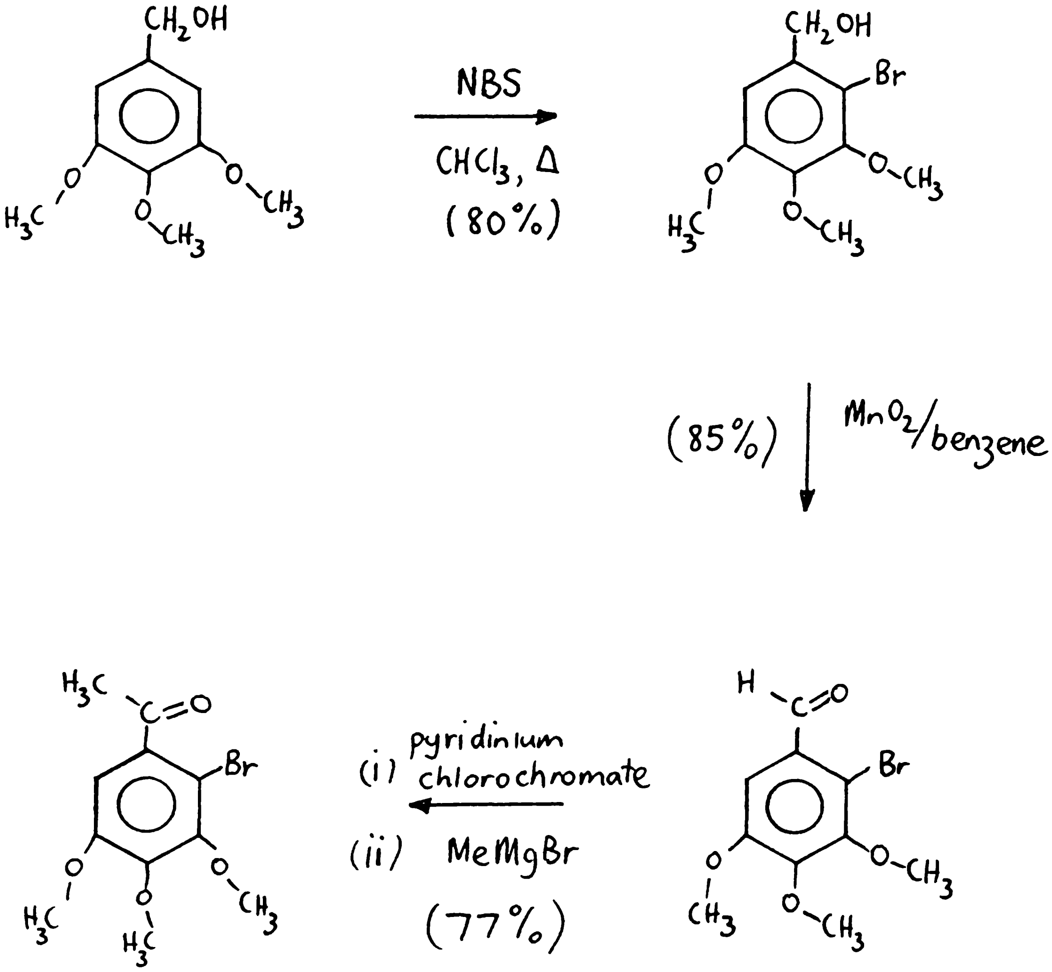
Importantly, 2'-bromo-3',4',5'-trimethoxyacetophenone (**21**) is a key intermediate used for the preparation of antileukemic lactones such as steganacin (iv).[8]



(iv)

The bromination of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)-tetracarbonylmanganese (**3**) and η^2-(2-acetyl-3-t-butyldimethylsiloxy-

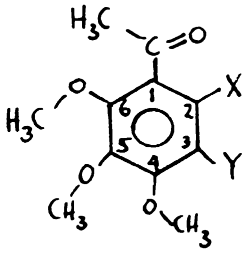
Scheme 4.1


NBS
$CHCl_3$, Δ
(80%)
(85%)
MnO_2/benzene
(i) pyridinium chlorochromate
(ii) MeMgBr
(77%)
CH_2OH
Br
H_3C
O
CH_3
H
C=O

4,5-dimethoxyphenyl)tetracarbonylmanganese (5) was less successful. Unexpectedly, they yielded not the o-bromo compounds but rather 3'-bromo-4',5',6'-trimethoxyacetophenone (22) and 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (23) as evident from the following.

First, the predicted ^{13}C-NMR chemical shifts (as calculated by additive substituent increments[10]) of 3'-bromo-4',5',6'-trimethoxyacetophenone (22) match well with the observed spectral data. Especially convincing is the agreement between the calculated and the observed aryl doublet (see table 4.1).

Table 4.1 Calculated ^{13}C-NMR chemical chemical shifts of (22)

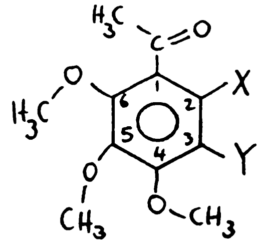


for	C1	C2	C3	C4	C5	C6
X = Br, Y = H	116.4	129.2	107.4(d)	152.0	129.0	147.6
X = H, Y = Br	117.7	125.8(d)	101.3	154.0	132.5	145.1
observed chemical shifts						
for (22)	128.85	127.07(d)	111.41	154.48	147.16	153.55

The ^{13}C-NMR chemical shifts of 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (23) parallel that of 3'-bromo-4',5',6'-trimethoxyacetophenone (22) indicative of the same bromination pattern. A close examination of the methoxy-carbon chemical shifts of (22) and (23) shows that all of the methoxy carbons resonate above 60.0 ppm. This establishes that all of the methoxy groups are in out-of-plane conformations[11] and implies steric crowding in the 3'- position.

We can confirm the assignments of structures (22) and (23) by a study of the predicted and observed ^{13}C-chemical shifts for 2′-iodo-4′,5′,6′-trimethoxyacetophenone (31) which was prepared by site specific iodination of the manganated ketone (3) as described earlier in this chapter (see table 4.2).

Table 4.2 Calculated ^{13}C-NMR chemical shifts of (31)



	C1	C2	C3	C4	C5	C6
X = I, Y = H	126.1	90.5	117.1(d)	153.6	130.6	149.2
X = H, Y = I	118.8	132.7(d)	74.9	160.9	133.6	146.2
observed spectrum (31)	134.68	81.74	118.22(d)	154.64	142.28	150.35

The agreement between the calculated and the observed chemical shifts of the aryl doublet for (31) is very good. Furthermore only two methoxy's are in out-of-plane conformations (i.e. only two chemical shifts greater than 60.0 ppm) indicative of the absence of steric crowding by a substituent in the 3′-position. Finally the literature melting point and ^{1}H-NMR spectrum of 3′-bromo-4′,5′,6′-trimethoxyacetophenone (22) are in close agreement with our data.

A number of minor products were observed when η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (5) was brominated. These products were identified as η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5-dimethoxy-6-bromophenyl)tetracarbonylmanganese

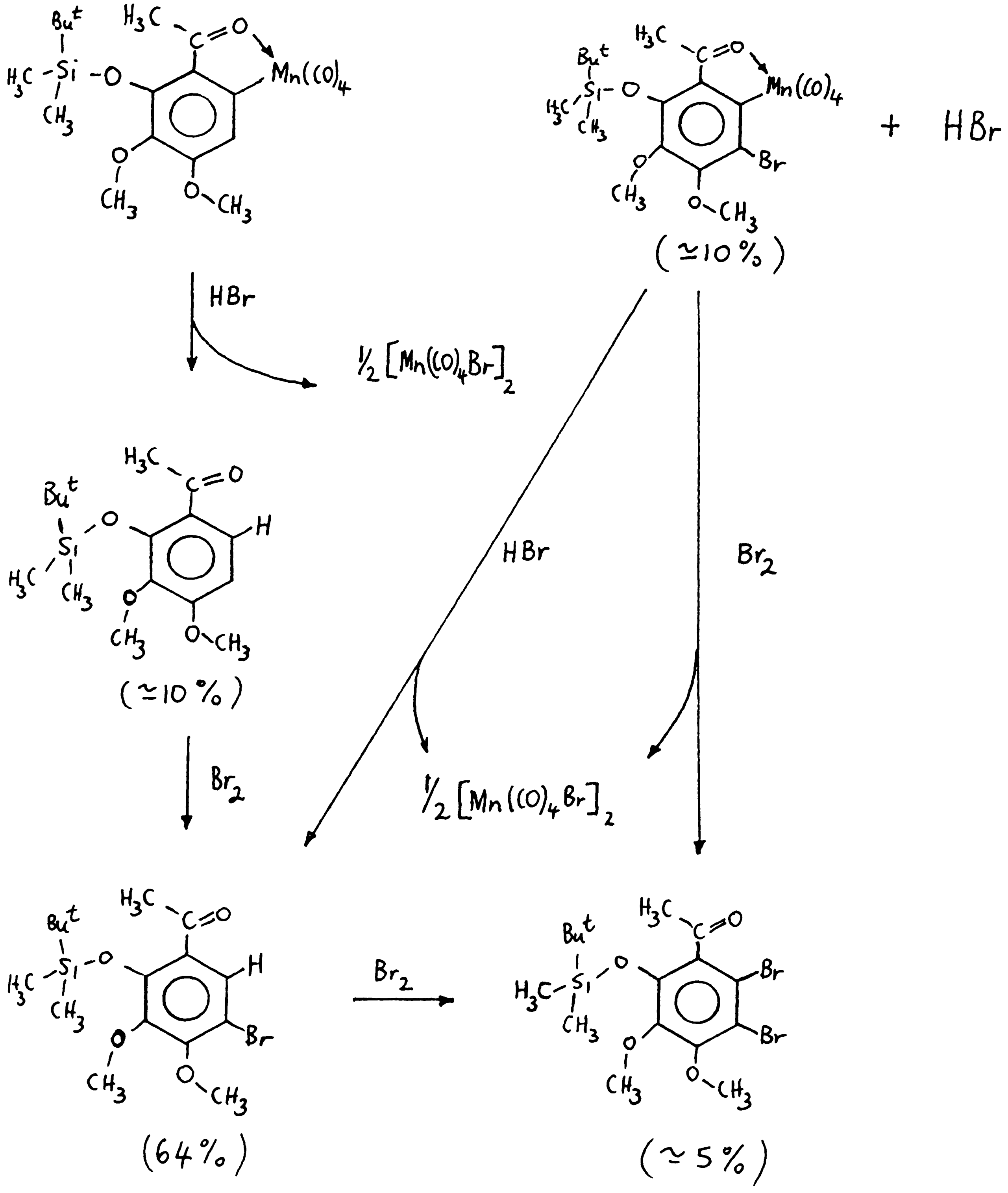
(24; ≃ 10 %), 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5',6'-dibromoacetophenone (25; ≃ 5 %) and 2'-t-butyldimethylsiloxy-3',4'-dimethoxyacetophenone (≃ 10 %)(refer to experimental section). A sequence of steps which can account for the major and by-products formed in this reaction are outlined in scheme 4.2. The proton which displaces the manganese is presumably derived from the HBr released in bromination at the 5'-position.

In conclusion the brominations of the tetracarbonylmanganese compounds (3) and (5) are not very clean reactions. They also have little synthetic potential as 3'-bromo-4',5',6'-trimethoxyacetophenone (22) can be prepared either by treatment of 2',3',4'-trimethoxyacetophenone with N-bromosuccinimide[9] or with Br_2 and sodium acetate in acetic acid.[12] However, 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-5'-bromoacetophenone (23) is a new compound.

Several attempts were made to brominate less activated metallated compounds such as η^2-(2-acetylphenyl)tetracarbonylmanganese (1). However, when the bromine solution was added to a solution of the metallated ketone a large amount of a colourless gas (CO ?) was given off. After leaving the solution for five minutes a t.l.c. showed at least five products of similar R_f . Performing the reaction at lower temperatures (in a slush bath of 1,1,1 trichloroethane and liquid N_2 using $CHCl_3$ as the reaction solvent) did not reduce the number of products. We did however manage to separate and tentatively identify (by mass spectroscopy) some vinyl phthalide, o-bromoacetophenone, $BrMn(CO)_5$ and unreacted manganated ketone (1) along with some unidentified products. This reaction was not pursued further.

The bromination of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) was also attempted and a modest yield of 2-acetyl-3-bromothiophene (26; 44%) was obtained. It was possible that the brominated thiophene that we had obtained was in fact

Scheme 4.2


Bu^t
H_3C
C=O
$Mn(CO)_4$
Si
O
CH_3
+ HBr
Br
(≃10%)
HBr
½[$Mn(CO)_4Br$]$_2$
H
HBr
Br_2
(≃10%)
Br_2
½[$Mn(CO)_4Br$]$_2$
(64%)
Br_2
(≃5%)

2-acetyl-5-bromo-thiophene, formed by ring bromination of (10) in the 5 position followed by cleavage of the tetracarbonylmanganese fragment by H-Br. However, the melting point of 2-acetyl-5-bromothiophene is 94-5°C[13] therefore we can be sure of our structural assignment. This bromo thiophene (**26**) has previously been prepared by acetylation of 3-bromo-thiophene with acetic anhydride and orthophosphoric acid (no yield cited).[14]

4.5 Discussion of iodination reactions

Our first attempt at an iodination of an orthometallated acetophenone was to react η^2-(2-acetyl-4,5,6-trimethoxyphenyl)-tetracarbonylmanganese (**4**) with molecular iodine in CCl_4. No reaction was observed even after stirring the solution for 48 hours at room temperature. Much better results were obtained when iodine chloride (ICl) was used as the iodinating reagent. The iodinations were performed in analogous fashion to the brominations discussed in section 4.2.1. The iodinations were much slower reactions (reaction flasks containing ICl and metallated ketone were typically stoppered for 24 to 96 hours at room temperature). In most cases the iodinations did not reach completion.

Reaction of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonyl-manganese (**4**) with iodine chloride yielded 93% of 2'-iodo-3',4',5'-trimethoxyacetophenone (**28**). However on a previous occasion under similar experimental conditions the yield of the iodo acetophenone (**28**) was only 65 %, the reasons for this difference in yield are not clear. In analogous fashion 2'-benzyloxy-3',4'-dimethoxy-6'-iodo-acetophenone (**29**), 2'-iodo-4',5',6'-trimethoxyacetophenone (**31**) and 2'-t-butyldimethylsiloxy-3',4'-dimethoxy-6'-iodoacetophenone (**30**) were prepared from the manganated ketones (**8**), (**3**) and (**5**) in yields of 63 %, 55 % and 100 % respectively. As discussed above, bromine preferentially substitutes the ring proton in these ketones, rather than the metal, and this difference between Br_2 and the more bulky ICl may have a steric origin.

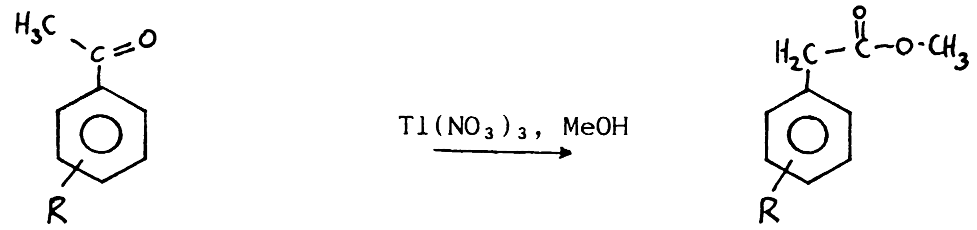
The non-activated metallated ketone η^2-(2-acetyl-3-t-butyldimethylsiloxyphenyl)tetracarbonylmanganese (**9**) was also iodinated with ICl in 45 % yield; however, the reaction proceeded only in bright sunlight. Two orthomanganated thiophenes (**10**) and (**11**) have been iodinated in excellent yield to produce 2-acetyl-3-iodothiophene (**33**; 75 %) and 3-acetyl-2,5-dimethyl-4-iodothiophene (**32**; 100 %). Similarly, η^2-(2-acetylfuran-3-yl)tetracarbonylmanganese (**15**) was iodinated in 100 % yield to produce 2-acetyl-3-iodofuran (**34**).

To the best of our knowledge all of the iodinated products that we have prepared are new compounds. An important point to stress is that the manganese from the halogenation reactions is converted into $[BrMn(CO)_4]_2$ or $[ClMn(CO)_4]_2$. These halo-bridged dimers can be converted back into $Mn_2(CO)_{10}$ making the reaction more cost efficient and essentially catalytic in manganese carbonyl.

4.6 Synthetic potential of manganated ketones

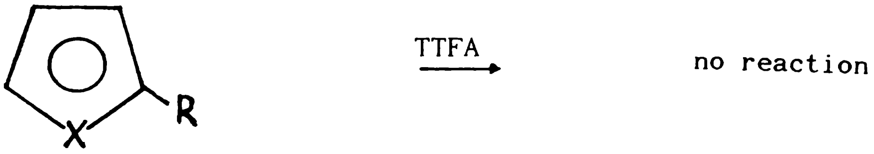
At this point it seems appropriate to consider orthomanganated acetophenones in relation to other orthometallated systems which have proven synthetic potential. The most obvious comparison to be drawn is between orthothalliated and orthomanganated O-donor compounds.

A wide range of O-donor aryl compounds can be orthothalliated by thallium(III) trifluoroacetate (TTFA) including methyl benzoate, benzoic acid, benzyl alcohol, 2-phenylethanol to name a few.[15] However, benzophenone, fluorenone, xanthone and N-methyl-acridone cannot be orthothalliated by TTFA.[16] Since benzophenone,[17] anthraquinone[17] and flavanone (this work) can be orthomanganated in good yield presumably some of the aforementioned oxygenated compounds can also be orthomanganated. Furthermore, 3-acetylindole is the only example that we are aware of whereby a methyl phenyl ketone has been orthothalliated by TTFA[18] (in the 4-position), possibly because of alternative reactions of the type observed when acetophenones are converted into methyl phenylacetates (see equation 4.6).[19]



equation 4.6

Hollins[18] has reported that 2-substituted thiophenes and 2-substituted furans cannot be orthothalliated by TTFA (see scheme 4.3).



X = S, R = CHO, CO_2H, CO_2Et, OAc

X = O, R = CO_2Et, CH_2OH

scheme 4.3

However, we have observed that 2-acetylfuran, 2-acetylthiophene and N-methyl-2-acetylpyrrole can be be orthomanganated by $C_6H_5CH_2Mn(CO)_5$ (refer to chapter 2).

The point that we are emphasising here, is that some O-donors which cannot be orthothalliated can be orthomanganated thereby broadening the synthetic potential of the O-donor metallation reaction. In this regard our iodination studies on orthomanganated acetophenones look particularly promising. More promising still are the oxidation reactions described in section 4.3 and the reactions outlined in chapter 5.

4.7 Oxidation of some orthomanganated acetophenones using Ce(IV) and Mn(III)

Experimental

4.7.1 Oxidation of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) by cerium(IV) ammonium nitrate in d^1-acetic acid.

Freshly opened AR acetic anhydride (10 ml, 0.105 mol) and deuterium oxide (99.7 % D atom; 1.90 ml, 0.105 mol) were refluxed for 20 minutes (protected from moisture by a calcium chloride drying tube). After cooling to room temperature η^2-(2-acetylphenyl)-tetracarbonylmanganese (1; 0.941 g, 3.29 mmol) was added with stirring. Cerium(IV) ammonium nitrate (0.90 g, 1.64 mmol) was then added in small proportions over a period of approximately 30 minutes. The acetic acid solution was poured into a large excess of water and extracted with ether (3 X 20 ml). The combined ether extract was washed thoroughly with sodium bicarbonate solution (5 %; 5 X 10 ml). The ether was then dried over $MgSO_4$, filtered and the solvent removed under vacuum. The resulting oil was chromatographed (p.l.c., 1:4 ether /petroleum spirit) affording a colourless band at R_f 0.6 which after extraction yielded orthomonodeuterioacetophenone (**19**; 0.194 g, 49 %). There was a considerable number of minor products at lower R_f but these were not analysed. ^{1}H-NMR (d^6-acetone) δ 7.55 (m, br, 1.11 H, 2′,6′-H), 7.10 (s, br, 3 H, 3′,4′,5′-H), 2.63 (s, 3 H, $COCH_3$). ^{2}H-NMR ($CHCl_3$) (referenced to external D_2O), δ 3.22 (s, br). ^{13}C-NMR ($CDCl_3$) δ 197.75 (s, CO), 137.93 (s, 1′-C), 133.57 (d, 4′-C), 129.21 (d, 3′-C*), 128.82 (d, 2′-C*), 128.59 (t, ^1J (C-D) = 24.2 ± 1.5 Hz, 2′-CD), 26.59 (q, $COCH_3$).

* indicates assignments interchangeable. The aryl proton integral

(1.11 H) indicates an isotropic purity of 89%.

4.7.2 Oxidation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) by cerium(IV) ammonium nitrate in acetone

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.239 g, 0.63 mmol) was dissolved in 10 ml of dry acetone. Cerium(IV) ammonium nitrate (0.348 g, 0.65 mmol) was added in small proportions over a period of 30 minutes. The solution was then stirred for a further 10 minutes and then the acetone was removed under vacuum. Distilled water (30 ml) and ether (30 ml) were added to the residue. The ether extract was dried over $MgSO_4$, filtered and the solvent removed under vacuum to yield slightly impure 3',4',5'-trimethoxyacetophenone (0.11 g, 83 %).

4.7.3 Oxidation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) by manganese(III) triacetate in methanol

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.2 g,0.53 mmol) was dissolved in 15 ml of methanol. Manganese(III) triacetate dihydrate (0.15 g, 0.56 mmol) was added slowly, however no reaction occurred as indicated by t.l.c. The solution was therefore heated at reflux for 2 hours, during which time a black insoluble precipitate had formed. The solution was cooled to room temperature and filtered through a plug of silica gel. Removal of the solvent under vacuum followed by chromatography (p.l.c.,1:1 ether/petroleum spirit) afforded two bands. At R_f 0.6 was a trace of unreacted manganated ketone (**4**), and at R_f 0.45 was 3',4',5'-trimethoxyacetophenone (0.104 g, 93 %, pure by ^{1}H-NMR).

4.7.4 Oxidation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) with cerium(IV) ammonium nitrate in acetic acid

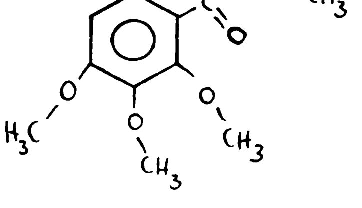
η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**, 0.29 g, 0.77 mmol) was dissolved in 10 ml of nitrogen saturated glacial acetic acid. Cerium ammonium nitrate (previously oven dried)

(0.21 g, 0.386 mmol) was added in small portions over a period of 30 minutes with stirring. During this time the solution had changed colour from yellow to red oxide. The acetic acid solution was poured into an excess of water and extracted with ether (3 X 20 ml). The combined extracts were thoroughly washed with 5% sodium hydrogen carbonate solution (5%; 5 X 20 ml). The ether solution was then dried over magnesium sulphate, filtered and the solvent removed under vacuum leaving a bright red oil.

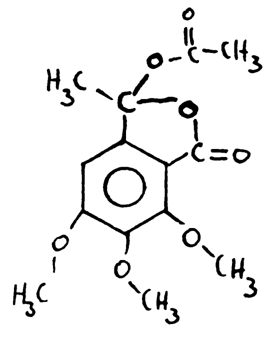
The oil was chromatographed (p.l.c., ether/petroleum spirit) to yield three bands. The yellow band at R_f 0.85 (0.005 g) was a trace of unreacted manganated ketone (4). The second colourless band at R_f 0.25 was 3',4',5'-trimethoxyacetophenone (0.073 g, 45%), while the third band at R_f 0.1 (0.070 g) was a mixture of three products as ajudged from its ^{1}H-NMR spectrum with one product (assignments asterisked) dominant: δ ($CDCl_3$) 7.00 (s), 6.77 (s), 6.30 (s)*, 5.54 (br), 4.20 (s)*, 4.13 (s), 3.96 (s), 3.83 (s)*, 2.52 (s), 2.03 (s), 1.92 (s), 1.75 (s)*.

Two products were obtained by fractional recrystallisation from hexane/diethyl ether (4 1) at -20°C. Some impure-looking white crystals plus some dark material had formed. We decanted off the hexane/ether solution into a new vial and almost immediately bright cherry red needles dropped out of this solution.

The off-white crystals had a molecular weight of 296 mass units and a composition of $C_{14}H_{16}O_7$ (exact mass calculation), two structures (v) and (vi) were considered for this minor product.



(v)



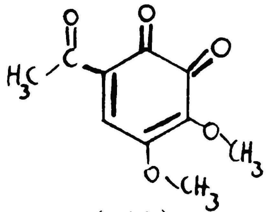
(vi)

Structure (v) (an anhydride) was thought to be most unlikely as the compound would have been expected to hydrolyse to 2-acetyl-4,5,6-trimethoxybenzoic acid under the workup conditions. Furthermore the chemical shift of the acetyl-methyl protons are not consistent with the reported literature chemical shifts for such a product.[20] On this basis the minor product was tentatively assigned as the lactone (vi). By integration of the ^{1}H-NMR spectrum of the crude product (before recrystallisation) the yield of the lactone was estimated to be 5%. The off white crystals (m.p. 75-85°C) had the following spectral characteristics. ^{1}H-NMR (CDCl$_3$) δ 6.77 (s, 1H, H-Ar), 4.16 (s, 3H, OCH$_3$), 3.96 (s, 3H, OCH$_3$), 3.88 (s, 3H, OCH$_3$), 2.04 (s, 3H, COOCH$_3$), 1.93 (s, 3H, C-CH$_3$); mass spectrum 296 (0.2), 254 (1.5), 237 (41.3), 193 (12.7), 177 (31.8), 165 (100), 150 (67.5), 136 (86.2), 122 (88.3), 109 (66.4).

Exact mass calcd. for $C_{14}H_{16}O_7$: m/e 296.0902. Found m/e 296.0920.

The cherry red crystals (**36**) had m.p. 85-86°C, and were analysed by ^{13}C-NMR, ^{1}H-NMR and mass spectroscopy. Assignments made subsequent to a crystal structure determination are given at this point for convenience [refer later to structure of (**36**)]. ^{1}H-NMR (CDCl$_3$) δ 6.39 (s, 1H, H-Ar), 4.22 (s, 1H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 1.78 (s, 3H, C-CH$_3$); ^{13}C-NMR (CDCl$_3$) δ 182.67 (s, CO), 150.02 (s, $\underline{C}$-OCH$_3$), 147.88 (s, $\underline{C}$-OCH$_3$), 145.47 (s, C=N), 140.79 (s, $\underline{C}$-C(CH$_3$)(OH)), 122.12 (d, C-Ar), 108.34 (s, $\underline{C}$(OH)(CH$_3$)), 61.32 (q, OCH$_3$) 61.00 (q, OCH$_3$), 24.00 (q, C($\underline{C}$H$_3$)(OH)); mass spectrum (single crystal) (m/e) 225 (42.3), 211 (25.4), 192 (27.5), 180 (26.7), 166 (33.9), 152 (30.5), 137 (41.5), 122 (55.9), 109 (46.3), 81 (65.2), 69 (100), 53 (91.5).

Because of the relatively simple ^{1}H-NMR spectrum and the red colour we initially thought that we had prepared the ortho-quinone (vii).



(vii)

However 225 mass units is fifteen units too high for the formulated structure. Furthermore the proposed chemical shift of the acetyl protons at δ 1.78 is not consistent with literature ketone chemical shifts.[20]

Given a molecular weight of 225 mass units we calculated the yield to be approximately 25% but we still did not know what we had prepared, and we obtained a suitable crystal for X-ray crystallography.

4.8 X-ray crystal structure of (**36**)

Bright cherry red needle shaped crystals were obtained by vapour diffusion ($CHCl_3$/hexane recrystallisation of a small quantity of (**36**). Preliminary precession photography (Cu-K_α ,λ = 1.5418 Å) indicated monoclinic symmetry with systematic absences uniquely defining the space group, $P2_1/c$ (h0l l = 2n + 1, 0k0 k = 2n + 1). Intensity data were collected on a Nicolet XRD P3 four circle diffractometer at -150°C with monochromated Mo-K_α radiation. A crystal of dimensions 0.35 x 0.08 x 0.09 mm was used for data collection.

Crystal data $C_{10}H_{11}NO_5$, M = 225.20, monoclinic, space group $P2_1/c$ (No. 14), a 11.052 (4), b 6.324 (2), c 18.010 (6) Å. , β = 124.89 (2) , U = 1033 $Å^3$. D_c 1.45 g cm^{-1} for Z = 4, D_o 1.30 g cm^{-1} (measured by flotation in saturated $ZnBr_2$ solution). F(000) = 472, μ(Mo-K_α) = 0.75 cm^{-1}

Intensity data were collected in the range of $2° < 2\theta < 55°$ using a θ - 2θ scan technique. A total of 2007 unique reflections were collected. After correction for Lorentz and polarisation effects 1265 reflections for which $I > 2\sigma(I)$ were used in all calculations. No absorption correction was deemed necessary.

Solution and refinement The structure was solved by direct methods (MULTAN) using the 200 reflections with the highest values of E . An

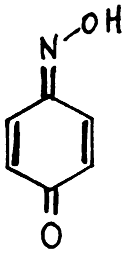
E map based upon these reflections revealed the carbon, oxygen and nitrogen atoms. In the final cycles of least-squares refinement the oxygen atoms and one methoxy carbon atom were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. Each type of hydrogen atom was assigned a common temperature factor. The proton bonded to O(5) was located in a sensible position in the difference map but attempts to refine it failed. Therefore this proton was omitted from the final cycles of full-matrix least squares refinement. The refinement converged at $R = 0.0546$ with $R_w = 0.0576$ where $w = 3.57/[\sigma^2 F + 0.000186\ F_o^2]$. In the final difference map the highest peak was near O(5) (ca. 0.38 e Å^3).

Two views of (**36**) can be seen in figures 4.2 and 4.3. The numbering scheme is also outlined in figure 4.2.

Bond angles and bond lengths can be found in tables 4.3 and 4.4. Positional parameters and thermal parameters of all atoms can be found in appendix III.

4.8.1 Discussion of structure (36)

A number of structures of the general form (viii) (p-quinone-4-oximes) have been examined crystallographically.



(viii)

Unfortunately most of these X-ray structures were investigated in the late 1950's and early 1960's so the accuracy of the reported bond angles and bond lengths leaves much to be desired. However, the X-ray

Table 4.3 Bond angles (°) of (36)

C(3)	-C(2)	-C(1)	114.9 (2)
O(1)	-C(2)	-C(1)	109.5 (3)
O(1)	-C(2)	-C(3)	114.4 (3)
O(5)	-C(2)	-C(1)	107.1 (3)
O(5)	-C(2)	-C(3)	101.4 (2)
O(5)	-C(2)	-O(1)	108.9 (2)
C(4)	-C(3)	-C(2)	132.1 (3)
C(8)	-C(3)	-C(2)	106.2 (3)
C(8)	-C(3)	-C(4)	121.7 (3)
C(5)	-C(4)	-C(3)	118.3 (3)
C(6)	-C(5)	-C(4)	119.5 (3)
O(2)	-C(5)	-C(4)	120.4 (3)
O(2)	-C(5)	-C(6)	120.1 (3)
C(7)	-C(6)	-C(5)	121.4 (3)
O(3)	-C(6)	-C(5)	116.8 (3)
O(3)	-C(6)	-C(7)	121.6 (3)
C(8)	-C(7)	-C(6)	116.9 (3)
O(4)	-C(7)	-C(6)	130.2 (3)
O(4)	-C(7)	-C(7)	112.9 (3)
C(7)	-C(8)	-C(3)	122.1 (3)
N	-C(8)	-C(3)	112.6 (3)
N	-C(8)	-C(7)	125.3 (3)
O(5)	-N	-C(8)	109.6 (3)
C(10)	-O(3)	-C(6)	115.1 (3)
C(9)	-O(4)	-C(7)	121.0 (3)
N	-O(5)	-C(2)	110.2 (2)

Table 4.4 Bond lengths (Å) of (36)

C(1)	-C(2)	1.496 (4)
C(2)	-C(3)	1.494 (4)
C(3)	-C(4)	1.334 (4)
C(4)	-C(5)	1.465 (4)
C(5)	-C(6)	1.480 (4)
C(6)	-C(7)	1.355 (4)
C(3)	-C(8)	1.366 (4)
C(7)	-C(8)	1.451 (4)
N	-C(8)	1.293 (4)
C(2)	-O(1)	1.387 (4)
C(5)	-O(2)	1.230 (4)
C(6)	-O(3)	1.362 (4)
C(10)	-O(3)	1.418 (4)
C(7)	-O(4)	1.340 (4)
C(9)	-O(4)	1.430 (4)
C(2)	-O(5)	1.491 (4)
N	-O(5)	1.388 (4)

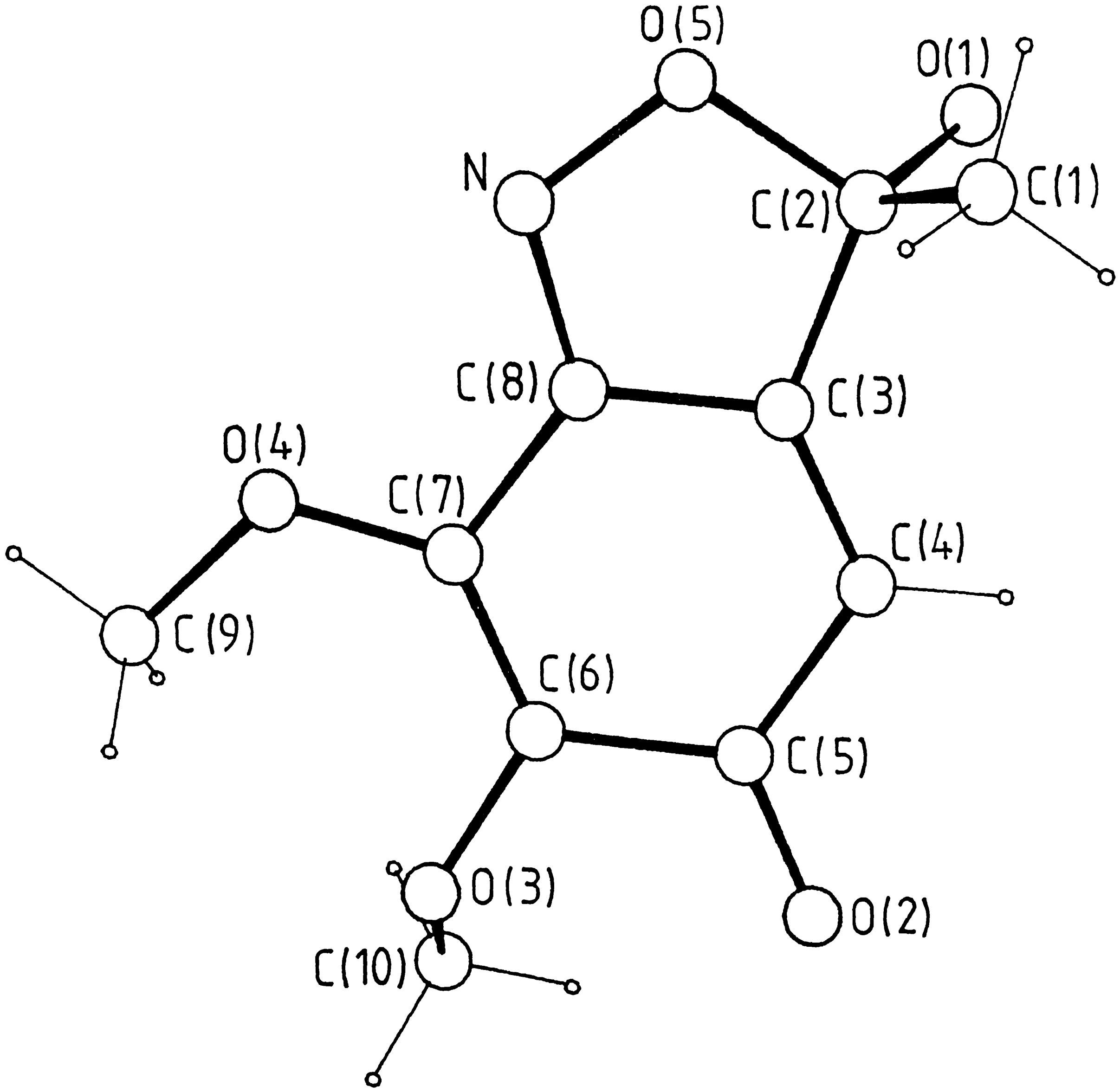


Figure 4.3 Plan elevation of (36)

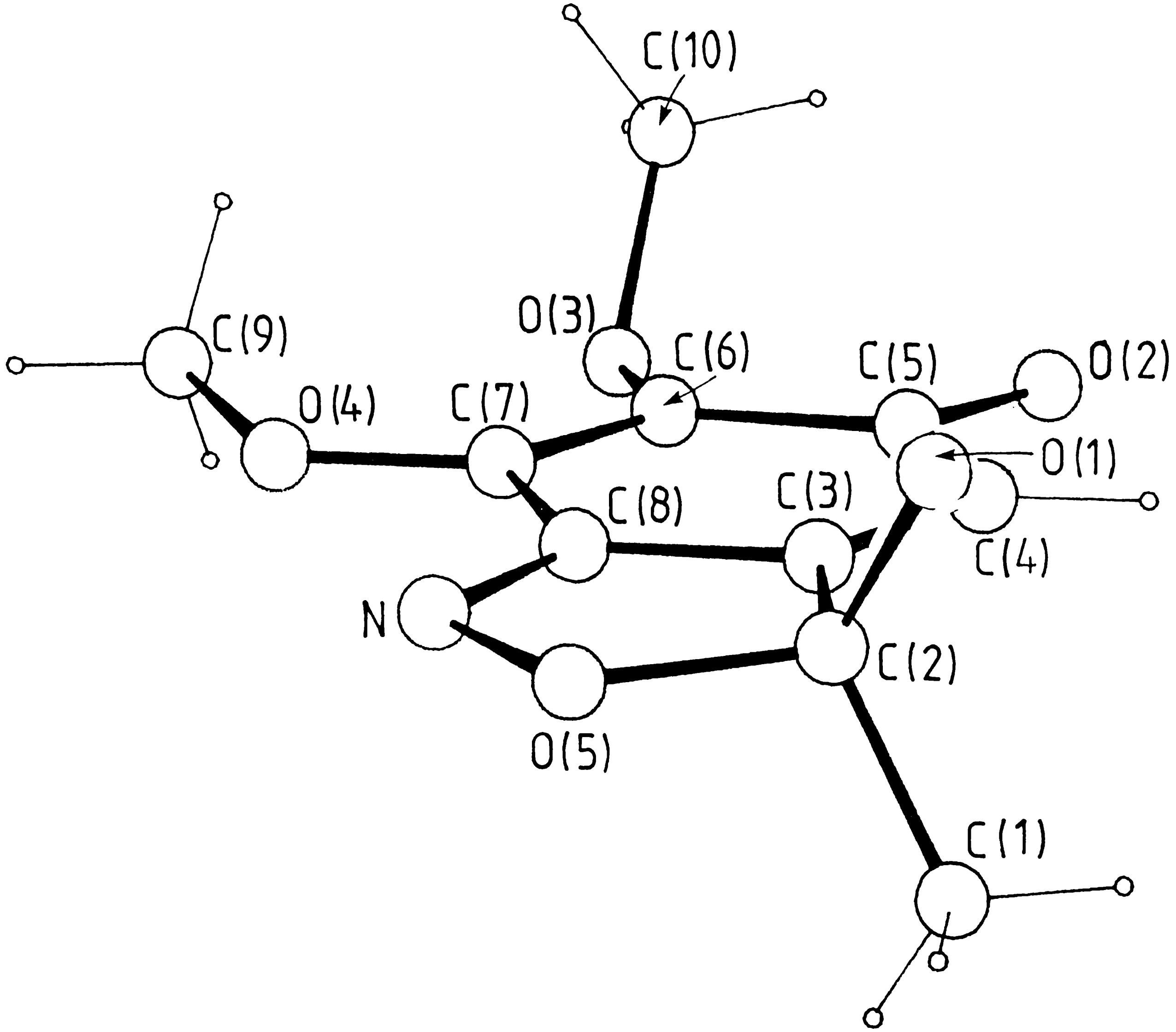
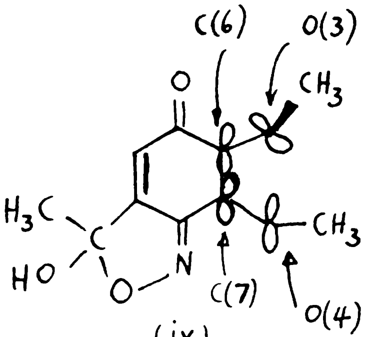


Figure 4.2 Side elevation of (**36**)

structure of the model compound (viii)[21] has recently been reported and provides a useful comparison for (**36**) [bond angle and bond length data for (viii) are summarised in tables 4.5 and 4.6 together with those for (**36**)].

There are several noticeable features about the structure (**36**) which require some discussion. Firstly there are two 'quinonoid' bonds namely C(5)-C(6), C(6)-C(7) which are 'stretched' and are considerably longer than those observed for structure (viii). The corresponding bond lengths for C(3)-C(4) and C(4)-C(5) are normal and are identical with those observed for structure (viii). We consider that the 'stretching' of these bonds is due to the steric and electronic repulsive interactions between these two methoxy groups. Clearly some repulsive forces between the methoxy groups are operative as the C(6)-C(7)-O(4) bond angle (130.2°) and the C(8)-C(7)-O(4) bond angle (112.9°) are 'opened' and 'closed' as compared with the expected bond angles of ca. 120°. Observe also that the C(6)-O(3) bond 1.362 (4) Å is considerably longer than the C(7)-O(4) bond 1.340 (4) Å. The difference in these C-O bond lengths can be explained by considering the conformation of the C10 methoxy group [bond angle C(6)-O(3)-C(10) (115.1°)]. This methoxy group is bent up away from the plane of the quinonoid ring. In such a conformation the overlap populations of the carbon and oxygen π orbitals (i.e. C(6) and O(3) π orbitals) will be severely reduced. This is because the O(3) pπ orbital is almost perpendicular to the C(6) bonding pπ orbital (ix).



(ix)

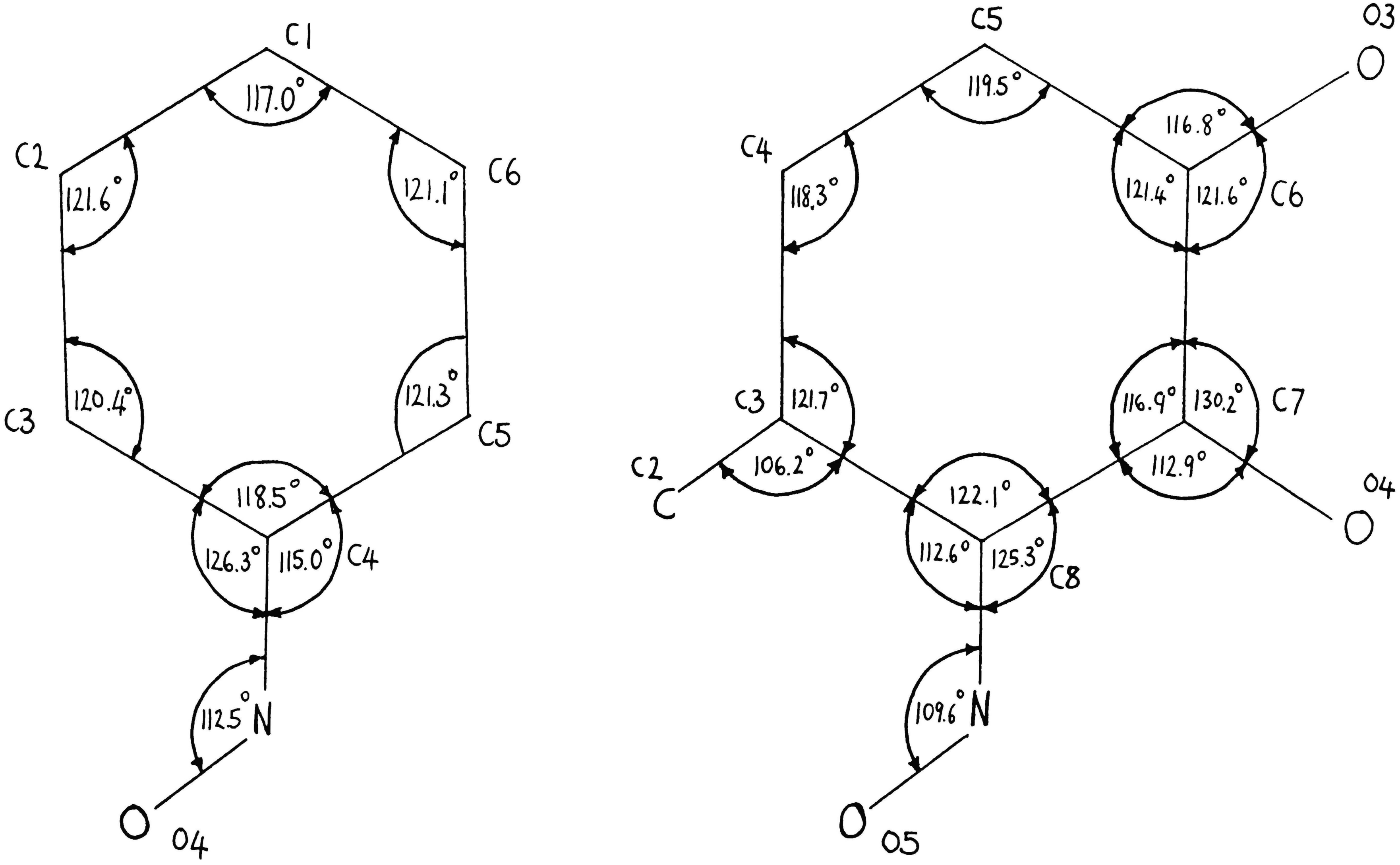
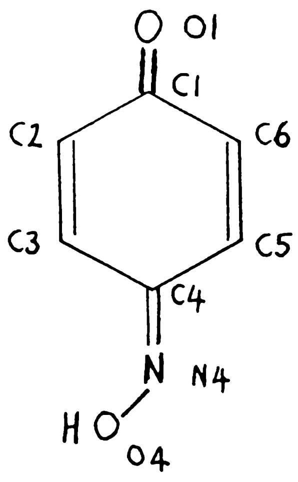
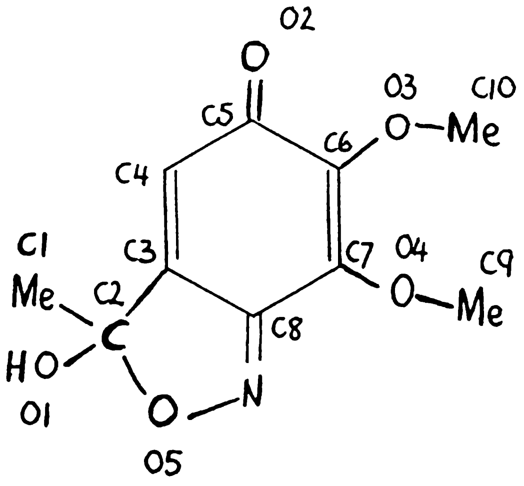


Table 4.5 Comparison of the bond angles of (36) with p-quinone-4-oxime

Table 4.6 Comparison of the bond lengths of (36) with

p-quinone-4-oxime



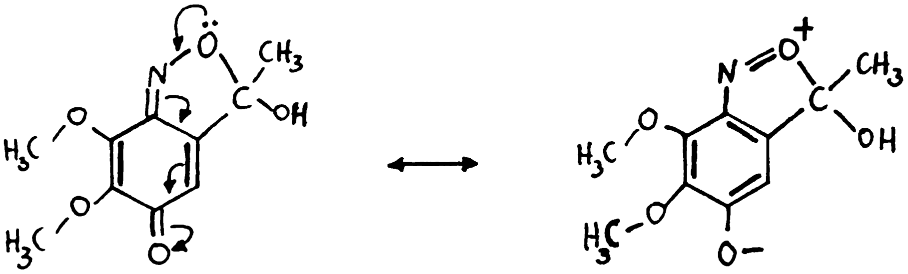


O1-C1	1.238 (3)	C5-O2	1.230 (4)
O4-N4	1.366 (3)	N- O5	1.388 (3)
N4-C4	1.306 (3)	N- C8	1.293 (4)
C1-C2	1.463 (4)	C4-C5	1.465 (4)
C2-C3	1.332 (4)	C3-C4	1.334 (4)
C3-C4	1.440 (4)	C3-C8	1.436 (4)
C4-C5	1.445 (5)	C7-C8	1.451 (4)
C5-C6	1.330 (4)	C6-C7	1.355 (4)
C6-C1	1.449 (4)	C5-C6	1.480 (4)

No such problem exists for the C(7)-O(4) bond.

The C(5)-O(2) and C(8)-N bond lengths are normal with the C(8)-N bond being slightly shorter as compared with the bond lengths observed for structure (viii). From the plan view of (36) observe that the C(7)-C(8)-N (125.5°) and the C(4)-C(3)-C(2) (132.1°) are opened out presumably to allow more favourable bonding interactions between O(5) and C(2).

The oxime N-O(5) bond is longer than we would expect (1.388 Å versus 1.371 Å).. This probably is a result of ring strain although it could reflect less delocalisation of electron density by resonance from O(5) onto O(2) (see canonical forms below).



4.9 Miscellaneous reactions

4.9.1 Reaction of η^2-(2-acetyl-4,5-dimethoxyphenyl)-tetracarbonylmanganese with lithium triethylborohydride

η^2-(2-acetyl-4,5-dimethoxyphenyl)tetracarbonylmanganese (6; 0.17 g, 0.49 mmol) was dissolved in dry THF (10 ml) and cooled to -78 °C under an atmosphere of N_2. $LiBEt_3H$ (1.0 mol/l in THF; 0.56 ml, 0.56 mmol) was added dropwise to this solution over a period of 5 minutes. After the addition was complete the THF solution was kept at -78 °C for 45 minutes and then left to warm to room temperature over night. The solution turned black. The excess $LiBEt_3H$ was destroyed by careful addition of wet butanol. The THF and butanol was removed under vacuum leaving a black oil. T.l.c. showed such a multitude of products that no attempt was made to isolate or characterise them.

4.9.2 Reaction of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)-tetracarbonylmanganese (**4**) with iodomethane

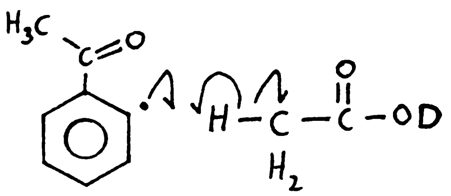
η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**: 0.082 g, 0.218 mmol) was dissolved in a small quantity of N_2 saturated CCl_4. Iodomethane (0.5 ml, 8 mmol) was added to this solution which was then refluxed for 20 minutes. The flask was cooled to room temperature and then tightly stoppered. After 3 weeks at room temperature the colour of the solution had faded and a white precipitate, possibly MnI_2, had formed. The solution was filtered and the solvent removed under vacuum. The colourless oil was chromatographed (p.l.c., 2:3 ether/petroleum spirit). The first band at R_f 0.60 was 2'-iodo-3',4',5'-trimethoxyacetophenone (**27**; 0.04 g, 55 %). The second band at R_f 0.55 was 3',4',5'-trimethoxyacetophenone (0.015 g, 33 %).

4.10 Discussion of oxidation reactions

Oxidation of η^2-(2-acetylphenyl)tetracarbonylmanganese (**1**) in dry ether under a nitrogen atmosphere had been attempted but no reaction occurred after 6 hours at room temperature.[4] We have examined the oxidation of some cyclometallated acetophenones with the oxidising agents Ce(IV), H_2O_2, Mn(III) and meta-chloroperbenzoic acid.

Oxidation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) by Ce(IV) in glacial acetic acid gives four products, of these three have been identified. 3',4',5'-Trimethoxyacetophenone was obtained in 45 % yield along with the cyclic hemiketal (**36**; ≈25 %) and the lactone (**37**; 5 %). The crystal structure of the cyclic hemiketal (**36**) is discussed in section 4.3.

Replacement of the acetic acid with deuterio-acetic acid should provide a means to prepare ortho-monodeuterioacetophenones. Indeed this did prove to be the case. Oxidation of η^2-(2-acetylphenyl)-tetracarbonylmanganese (**1**) in d^1-acetic acid with Ce(IV) gives ortho-monodeuterioacetophenone (**19**) in 49 % yield. The deuterium content in the ortho-position was established as being 89 %. However oxidation of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) in d^4-acetic acid (Fison, > 99.5 % D) gave ortho-monodeuterioacetophenone (**19**) with > 99 % deuterium incorporated in the ortho-site. The oxidation of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) in d^1-acetic acid has been performed many times and in each case the deuterium content has always been 88-90 %. A possible explanation is that η^2-(2-acetylphenyl) tetracarbonylmanganese (1) is oxidised to a phenyl radical (x) which sometimes abstracts an acetate proton in preference to carboxylic deuteron. This may apply irrespective of whether the major pathway to o-protonation is via the radical as indicated or otherwise.



(x)

One mole of the manganated ketone was always reacted with only 0.5 mole of Ce(IV) oxidising agent in acetic acid. By electron balance this would suggest that we were 1/2 mole short of the oxidising agent (equation 4.7). Experimentally, however, all of the metallated ketone was consumed. Possibly a free radical chain reaction is set up in the solvent which ensures that the orthomanganated product is fully oxidised to organic products, but the acceptor of further electrons is not clear.

$$\mathrm{ArMn(CO)_4} + \mathrm{H^+} - e \longrightarrow \mathrm{ArH} + \mathrm{Mn^{2+}} + 4\,\mathrm{CO} \quad [\mathrm{O}]$$

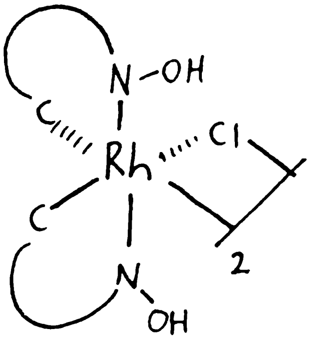
$$\mathrm{Ce^{4+}} + e \longrightarrow \mathrm{Ce^{3+}} \quad [\mathrm{R}]$$

equation 4.7

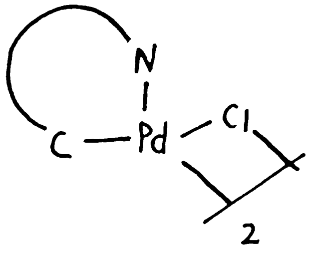
The oxidation of the manganated ketones (1) and (4) by Ce(IV) in acetic acid are not very clean reactions. A cleaner oxidation of (4) into 3',4',5'-trimethoxyacetophenone can be effected by performing the oxidation with Ce(IV) in acetone. Similarly oxidation of (4) with Mn(III) acetate (1 mol) in dry methanol (under reflux) affords the ketone in a yield of 94 %.

In summary, orthomanganated ketones can be oxidised to their parent ketones with two oxidising agents Ce(IV) and Mn(III). This procedure has been used to prepare the ortho-monodeuterioacetophenones (19) and (20) by oxidation in deuterio-acetic acid with Ce (IV). The logical extension to our work would be to oxidise manganated ketones with Ce(IV) or Mn(III) in d^6-acetone or d^4-methanol. By these suggested methods better yields of isotopically pure orthomonodeuterioketones should be obtained.

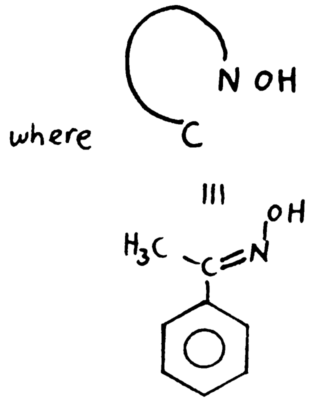
At this stage it is appropriate to summarise some literature procedures which have been used to prepare site specific ortho-deuteriated acetophenones. Treatment of rhodium(III) (xi)[22] or palladium (II) acetophenone oxime (xii)[23] complexes with $LiAlH_4$ yields 1, 2'-D_2-1-phenylethylamine. This amine can be oxidised to ortho-monodeuterioacetophenone (19) with 1,4-di-t-butyl-1,4-benzoquinone.[22] However the palladium route gives only 80 % isotopic (D_2) purity at the amine stage and for rhodium multiple ring deuteriation occurs. In conclusion, then, neither of these routes is capable of producing isotopically pure ortho-deuterioacetophenones.



(xi)



(xii)



Attempts by Crawford[4] to prepare ortho-monodeuterioacetophenone from orthomanganated acetophenone (1) have been unsuccessful: reaction of (1) with D_2 (7 atmospheres, 90-100°C, hexane) results in the formation of ortho-monodeuterioacetophenone and 1,2'-D_2-1-phenylethylalcohol (ratio 1:4; by gas chromatography). However, considerable amounts of higher deuterio analogues of both products were indicated by mass spectroscopy and ^{1}H-NMR. Reaction of (1) with hydrogen at room temperature (12 atmospheres, heptane) gave no discernable reaction.

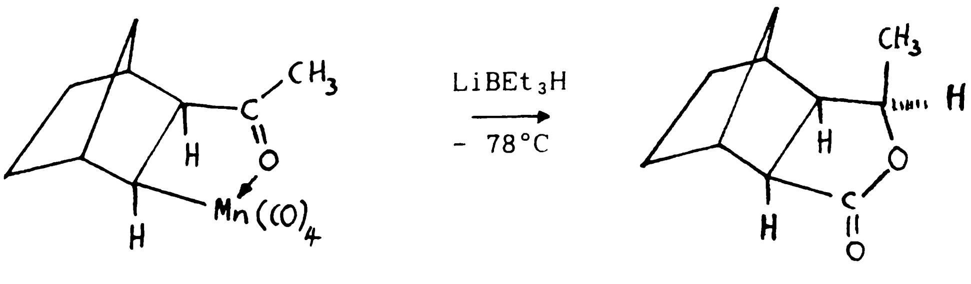
Cabral[24] has prepared ortho-monodeuterioacetophenone (**19**) by a three step sequence in an overall yield of 6 % (see scheme 4.4).

Clearly from this brief discussion it is obvious that the oxidative methods that we have described for the preparation of ortho-monodeuterioacetophenone have advantages over those described in the literature.

Oxidation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) with a large excess of 30 % hydrogen peroxide in acetic anhydride was unsuccessful as was the oxidation of (**4**) with m-chloroperbenzoic acid in $CHCl_3$. No reaction occurred for either of these oxidations.

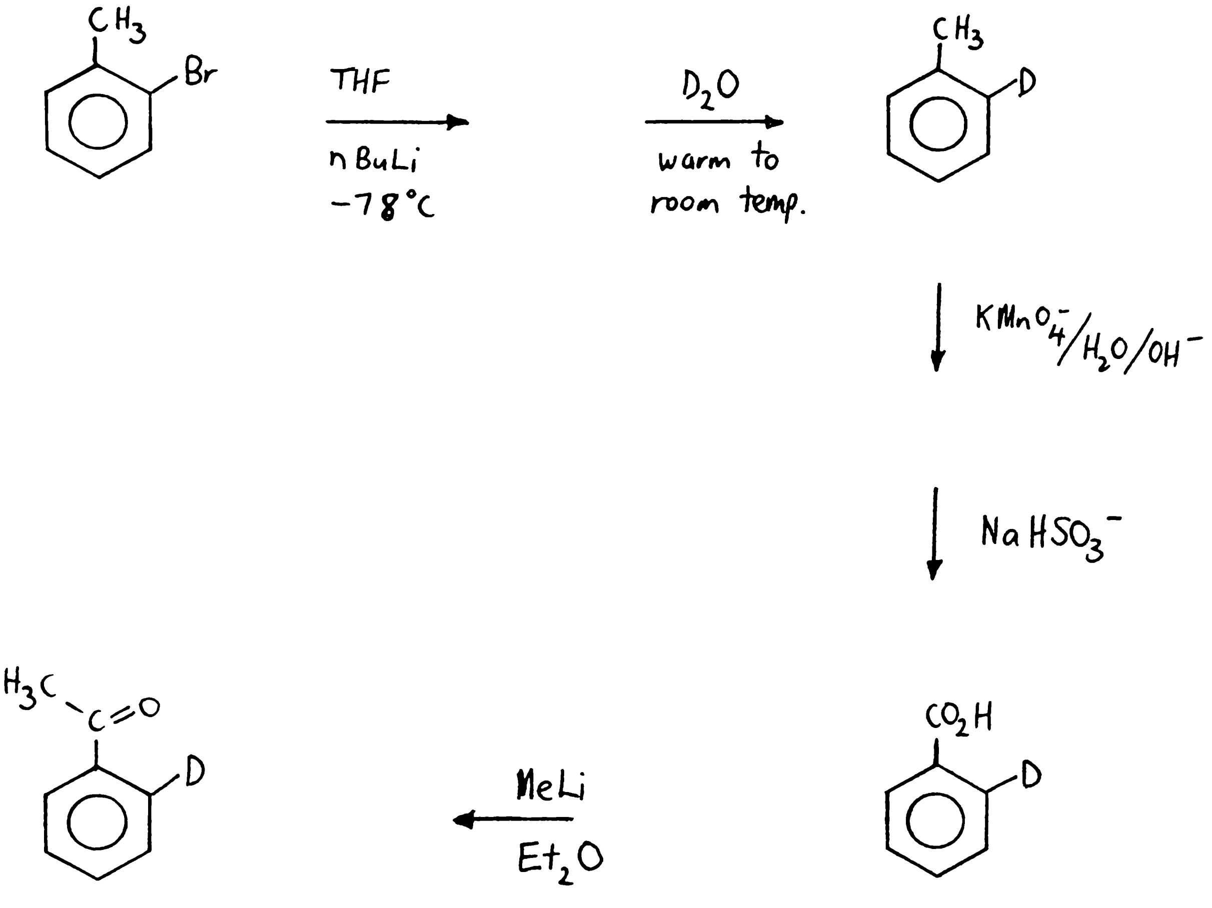
4.11 Miscellaneous reactions of orthomanganated ketones

There is a report that the orthomanganated compound (xiii)[25] can be converted into the lactone (xiv) by reduction with $LiBEt_3H$ (no experimental details were given).



(xiii) (xiv)

Scheme 4.4



88% D incorporation

6% Yield overall

We attempted to react η^2-(2-acetyl-4,5-dimethoxyphenyl)tetracarbonylmanganese (**6**) with $LiBEt_3H$ at -78°C in THF. The reaction was unsuccessful with a multitude of products being obtained, however this is one reaction in particular which should be examined in more detail.

Reaction of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) with methyl iodide (approx 3 weeks at room temperature) gave 2'-iodo-3',4',5'-trimethoxyacetophenone (**28**; 55 %) and 3',4',5'-trimethoxyacetophenone (33 %). No traces of 2'-methyl-3',4',5',-trimethoxyacetophenone were observed. The formation of **28** from the manganated ketone (**4**) with methyl iodide is difficult to understand.

References

(1) A. D. Ryabov,

Synthesis, 233, **1985**.

(2) H. Horino and N. Inoue,

J. Org. Chem., **46**, 4416, **1981**.

(3) A. I. Vogel,

"A Textbook of Practical Organic Chemistry"

Third Edition, Longman, London, p. 580, 1956.

(4) S. A. Crawford,

"Ortho-metallated Phenyl Ketones and Metallated 2-Substituted Ferrocenes : Structural and Synthetic Studies"

Ph. D. Thesis, University of California, p. 56-60, 1975.

(5) H. Alper and A. S. K. Chan,

J. Am. Chem. Soc., **95**, 4905, **1973**.

H. Alper and C. K. Foo,

Inorg. Chem., **14**, 2928, **1975**.

H. Alper, W. G. Root,

J. Am. Chem. Soc., **97**, 4251, **1975**.

(6) A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay and A. Chakravorty,

J. Chem. Soc., *Chem. Commun.*, 999, **1984**.

Inorg. Chem., **25**, 2214, **1986**.

(7) M. A. El-Sayed and H. D. Kaesz,

Inorg. Chem., **1**, 158, **1963**.

(8) F. E. Ziegler, I. Chliwner, K. W. Fowler, S. J. Kanfer, S. J. Kuo and N. D. Sinha,

J. Am. Chem. Soc., **102**, 790, **1980**.

(9) J. M. Blatchly, R. J. S. Green, J. F. W. McOmie and J. B. Searle,

J. Chem. Soc., *(C)*, 1353, **1969**.

(10) E. Breitmaier and W. Voelter,

"^{13}C-NMR Spectroscopy : Methods and Application",

Verlag Chemie, p. 213-214, 1978.

(11) A. Makriyannis and S. Fesik,
J. Am. Chem. Soc., **104**, 6463, **1982**.
J. J. Knittel and A. Makriyannis,
Tet. Letts., **30**, 2753, **1979**.

(12) C. Mannich and F. L. Hahn,
Ber., **44**, 1551, **1911**.

(13) *"CRC Handbook of Chemistry and Physics"*,
64th edition, CRC press, Florida, C-534.

(14) S. Gronowitz, T. Dahlgren, J. Namtvedt, C. Roos, G. Rosen,
B. Sjoberg and U. Forsgren,
Acta Pharm. Suecica, **8**, 623, **1971**.

(15) A. McKillop and E. C. Taylor, in
"Comprehensive Organometallic Chemistry",
ed. G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, Oxford, **1982**, Vol. 7, p. 501.

(16) R. A. Hollins and V. M. Salim,
Tetrahedron Letts., 591, **1979**.

(17) R. J. McKinney, R. Hoxmeier and H. D. Kaesz,
J. Am. Chem. Soc., **97**, 3059, **1975**.

(18) R. A. Hollins, L. A. Colnago, V. M. Salim and M. C. Seidl,
J. Heterocycl. Chem., **16**, 993, **1979**.

(19) E. C. Taylor, C. S. Chiang, A. McKillop and J. F. White,
J. Am. Chem. Soc., **98**, 6750, **1976**.
A. McKillop, B. P. Swann and E. C. Taylor,
J. Am. Chem. Soc., **93**, 4919, **1971**.
A. McKillop, B. P. Swann and E. C. Taylor,
J. Am. Chem. Soc., **95**, 3340, **1973**.

(20) L. M. Jackman and S. Sternhell,
"Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"

2nd edition, Pergamon Press, N. Y., p. 164, **1969**.

(21) H. J. Talberg,

Acta Chem. Scandinavica, A28, 910, **1974**.

(22) H. Onoue and I. Moritani,

J. Organomet. Chem., **44**, 189, **1972**.

(23) H. Onoue, K. Minami and K. Nakagawa,

Bull. Chem. Soc. Jpn., **43**, 3480, **1970**.

(24) A. W. Cabral,

"The Cyclometallation of Ketones and Quinones by Alkyl Manganese Pentacarbonyl Complexes : Mechanistic and Synthetic Studies."

Ph. D. Thesis, University of California, p. 41, **1981**.

(25) P. DeShong and G. A. Slough,

Organometallics, **3**, 636, **1984**.

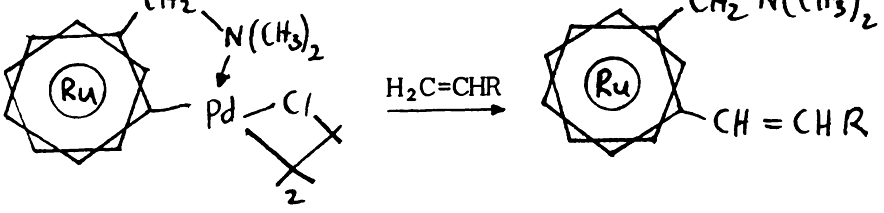
CHAPTER FIVE

Coupling reactions of orthomanganated aryl methyl ketones with alkenes promoted by palladium(II)

5.1 Introduction

Heck[1] found that a variety of alkenes including ethylene, acrolein, methyl vinyl ketone, methyl acrylate, acrylonitrile and styrene can be coupled with aryl mercury (Ar_2Hg, ArHgCl), aryl lead (Ar_4Pb) and aryl tin (Ar_4Sn) compounds to form aryl alkenes and other products. These reactions are promoted by selected metal salts such as $RuCl_3$, $RhCl_3.\ 3H_2O$, $NiBr_2$, $LiPdCl_3$ and Li_2PdCl_4. Yields varied from poor to quantitative. Some specific examples include the coupling of chlorophenylmercury(II), diphenylmercury(II), tetraphenyltin and tetraphenyllead with methyl acrylate (scheme 5.1).

It was assumed that these reactions proceed through the series of steps illustrated in scheme 5.2.[1] Further evidence for these reactions proceeding by such routes comes from the study of stable, isolable orthopalladiated compounds with alkenes.[2] One example of many reported is outlined in equation 5.1.[3]

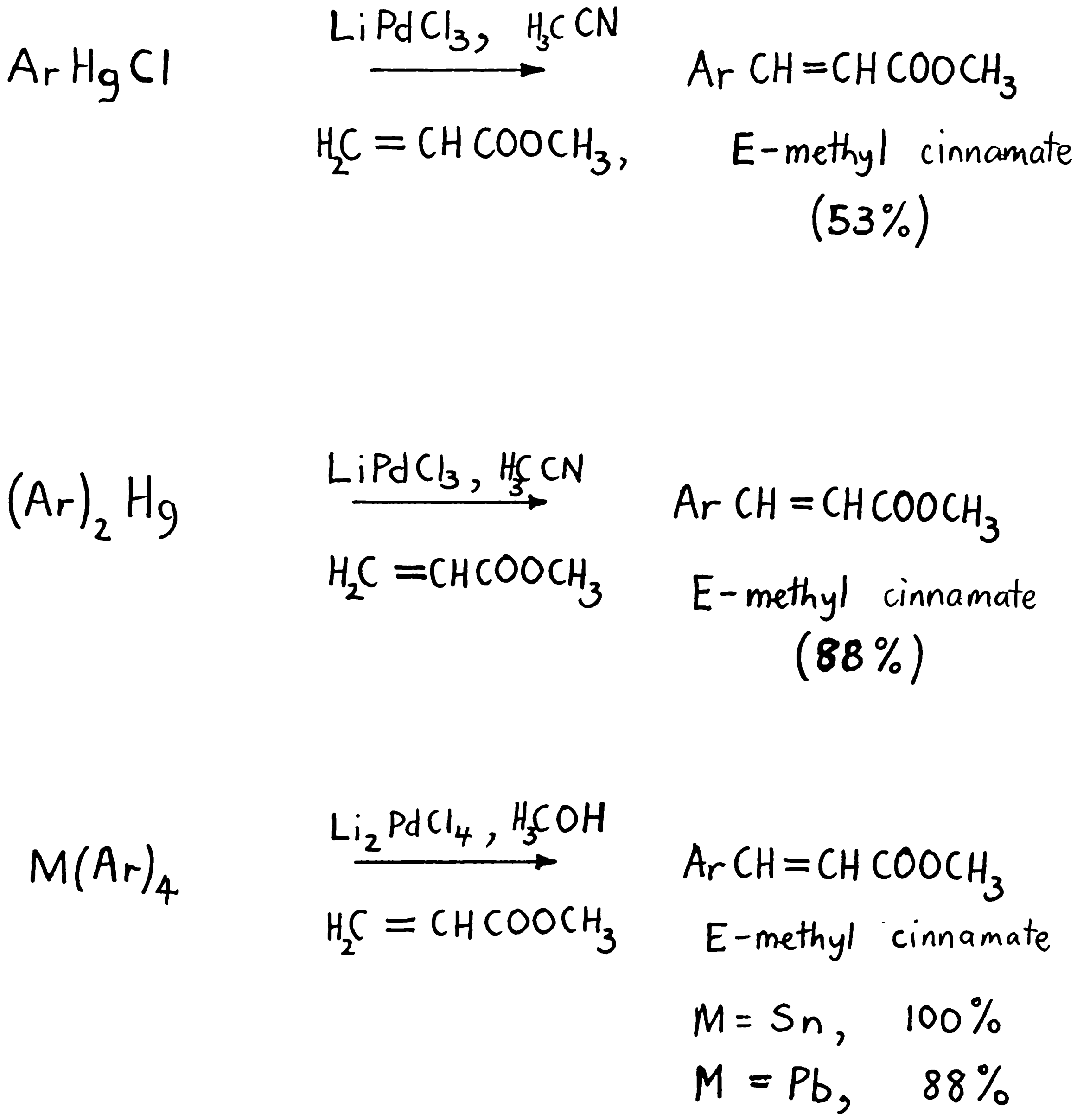


where R = $-COCH_3$, $-COOCH_3$

equation 5.1

Some coupling reactions, however, are not as clean or as simple as the ones previously discussed. For example, the reaction of chlorophenylpalladium(II) (generated from chlorophenylmercury(II) and $LiPdCl_3$ in acetonitrile) with allyl alcohol[4] was especially

Scheme 5.1



$$\mathrm{ArHgCl}\ \xrightarrow[\mathrm{H_2C=CHCOOCH_3},]{\mathrm{LiPdCl_3},\ \mathrm{H_3CCN}}\ \mathrm{ArCH=CHCOOCH_3}$$

E-methyl cinnamate (53%)

$$\mathrm{(Ar)_2Hg}\ \xrightarrow[\mathrm{H_2C=CHCOOCH_3}]{\mathrm{LiPdCl_3},\ \mathrm{H_3CCN}}\ \mathrm{ArCH=CHCOOCH_3}$$

E-methyl cinnamate (88%)

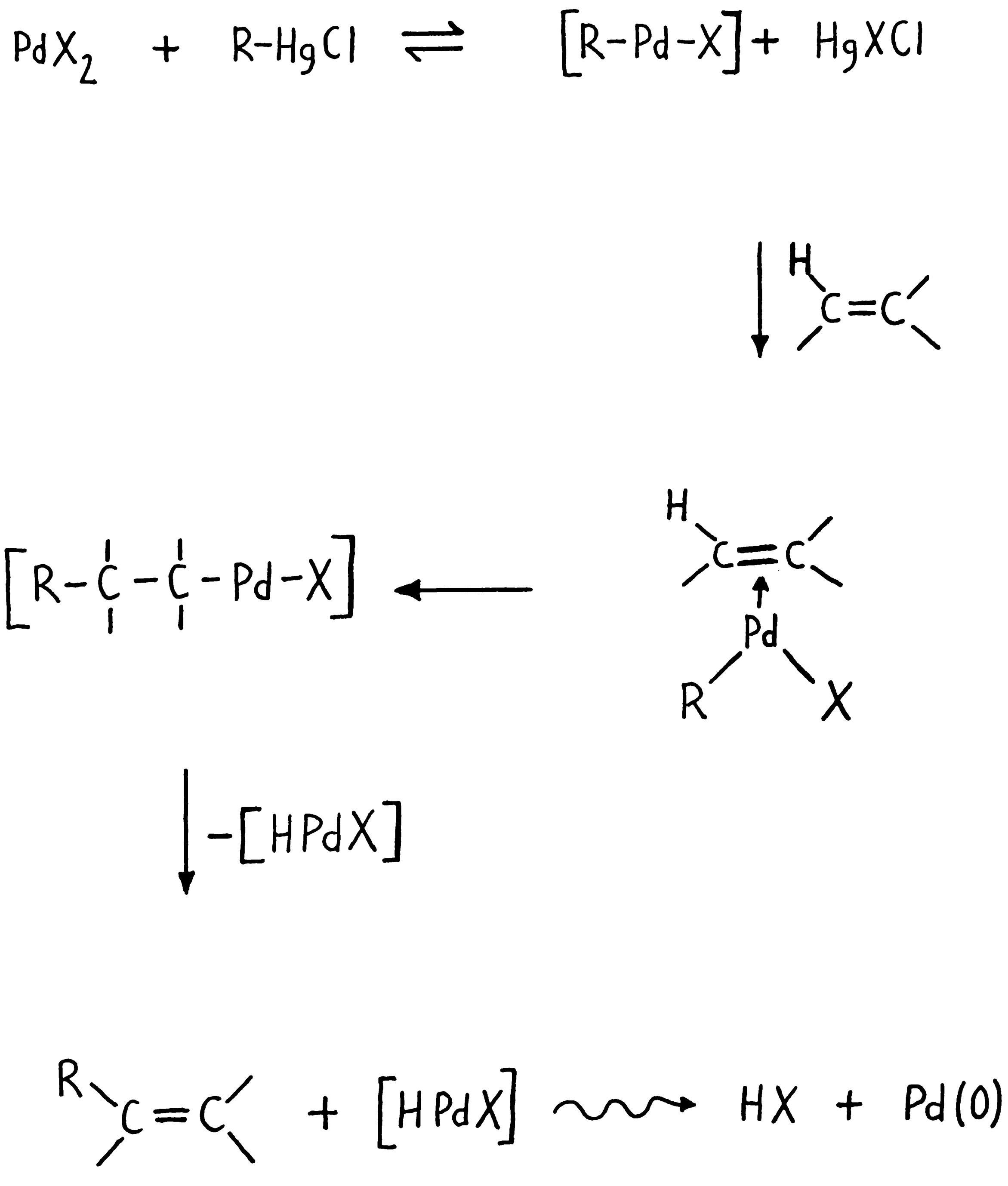
$$\mathrm{M(Ar)_4}\ \xrightarrow[\mathrm{H_2C=CHCOOCH_3}]{\mathrm{Li_2PdCl_4},\ \mathrm{H_3COH}}\ \mathrm{ArCH=CHCOOCH_3}$$

E-methyl cinnamate

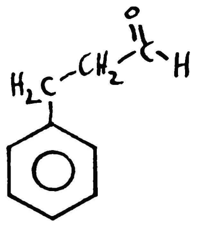
M = Sn, 100%

M = Pb, 88%

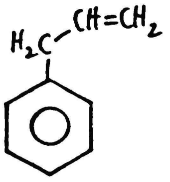
Scheme 5.2



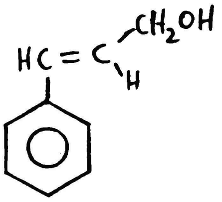
interesting. Three products were observed: 3-phenylpropanal (35%),(i); 3-phenylpropene (12%),(ii); and 3-phenylprop-2-en-1-ol (4%),(iii).



(i)



(ii)



(iii)

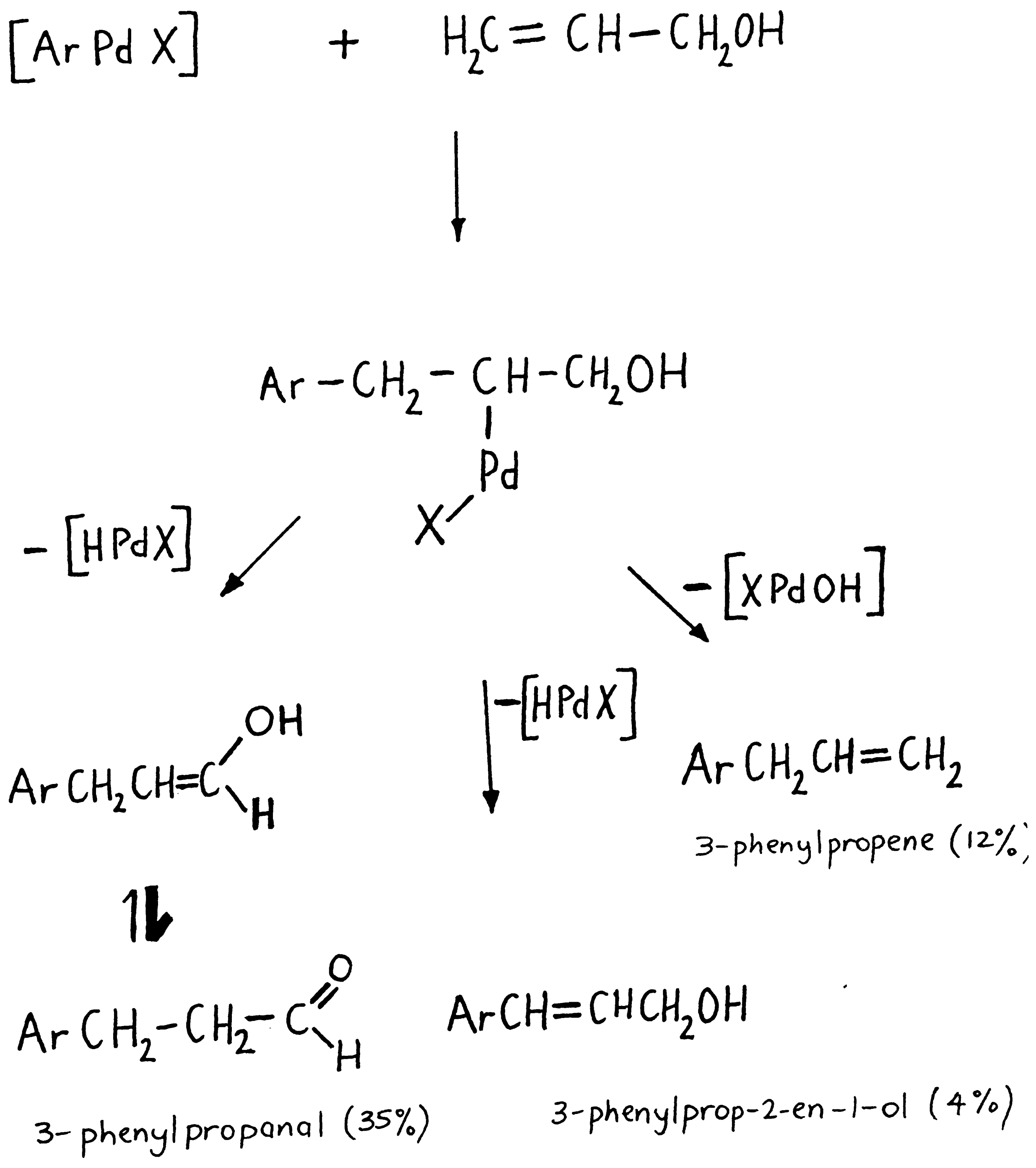
Heck[4] postulated a mechanism which could account for the formation of the observed products (see scheme 5.3). Heck also suggested that the phenylpropene might alternatively be formed by arylation of allyl chloride which can be formed from allyl alcohol under the reaction conditions. Subsequently Heck[5] showed that the reaction of chlorophenylpalladium(II) and allyl chloride did in fact form phenylpropene.

The reaction of vinyl acetate with chlorophenylpalladium(II) in acetic acid proved to be more complex.[6] The observed products were phenylacetaldehyde (33%), phenylacetaldehyde enol acetate (30%), styrene (3%), and E-stilbene (34%). A mechanism which can account for the observed products has been postulated by Heck (scheme 5.4).[6]

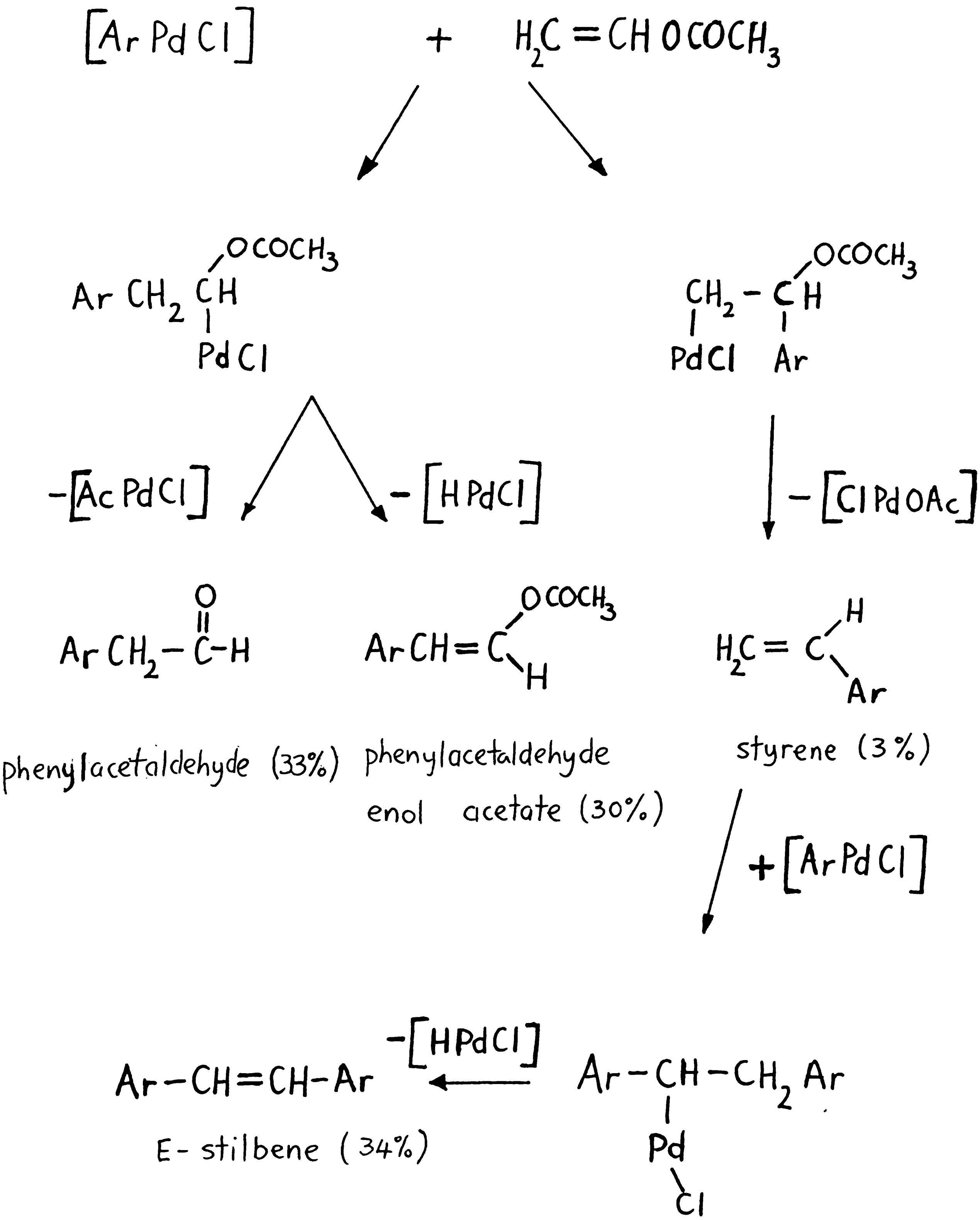
In a later study Heck[7] found that arylation of chlorophenylpalladium(II) in neat vinyl acetate (with palladium acetate) increased the yield of phenylacetaldehyde enol acetate to 91% (E:74% and Z:17%) with styrene (5%) and E-stilbene (1%) but not phenylacetaldehyde being also formed.

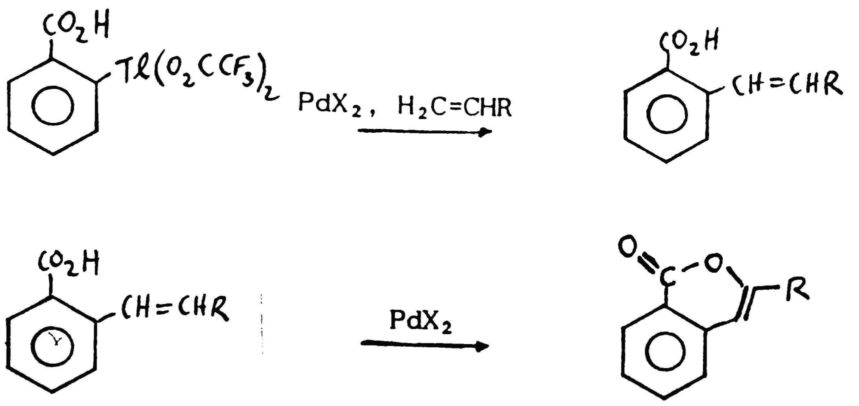
More recently Larock[8] has used the palladium catalysed vinylation of orthothalliated benzoic acids to prepare some isocoumarins (iv). This reaction is believed to proceed by the following steps (equation 5.2).[8]

Scheme 5.3


[ArPdX]
+
H₂C=CH−CH₂OH
Ar−CH₂−CH−CH₂OH
Pd
X
−[HPdX]
−[XPdOH]
−[HPdX]
ArCH₂CH=C(OH)H
ArCH₂CH=CH₂
3-phenylpropene (12%)
ArCH₂−CH₂−CHO
ArCH=CHCH₂OH
3-phenylpropanal (35%)
3-phenylprop-2-en-1-ol (4%)

Scheme 5.4

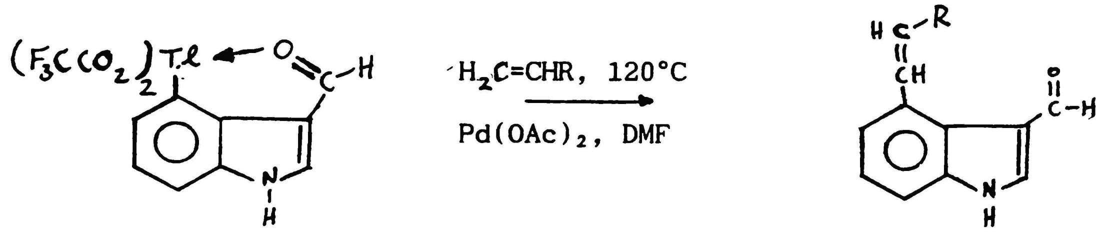

[ArPdCl]
+
H2C=CHOCOCH3
-[AcPdCl]
-[HPdCl]
-[ClPdOAc]
phenylacetaldehyde (33%)
phenylacetaldehyde enol acetate (30%)
styrene (3%)
+[ArPdCl]
-[HPdCl]
Ar-CH=CH-Ar
E-stilbene (34%)
Ar-CH-CH2Ar
Pd
Cl



(iv)

equation 5.2

A further example involving an orthothalliated compound is the vinylation in high yield (>85%) of 4-thalliated-3-formylindoles (equation 5.3 ; R = COOMe or COMe).[9]



equation 5.3

Importantly, only catalytic quantities of palladium(II) are needed for these reactions of thallium(III) compounds. This is because the Pd(0) formed during the process is reoxidised to Pd(II) by the Tl(III) formed in the initial transmetallation step.[8,9]

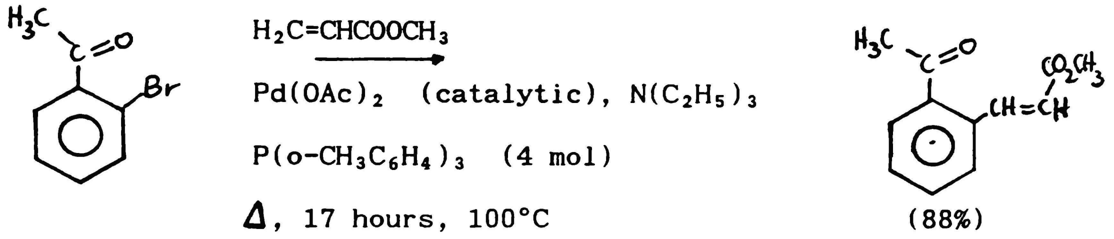
Some organocobalt(III) compounds can also be vinylated. Two illustrative examples are given (scheme 5.5 ; dmg = dimethylglyoxime).[10]

$$MeCo(dmg)_2.H_2O \xrightarrow[Li_2PdCl_4\ (2\ mol)]{styrene\ (4\ mol)} \text{3-phenylpropene } (64\%)$$

$$\mathrm{MeCo(dmg)_2.py} \xrightarrow[\mathrm{Li_2PdCl_4}\ (2\ \mathrm{mol})]{\text{hex-1-ene}\ (4\ \mathrm{mol})} \underset{(32\%)}{\text{hept-2-ene}}$$

scheme 5.5

Coupling of alkenes with aryl bromo and iodo compounds is also catalysed by a variety of palladium(II) salts.[11] One example, showing the reaction conditions needed to effect such coupling, is illustrated in the preparation of methyl E-3-(2-acetylphenyl)-acrylate from 2-bromoacetophenone (scheme 5.6).[11]



$H_2C{=}CHCOOCH_3$

$Pd(OAc)_2$ (catalytic), $N(C_2H_5)_3$

$P(o\text{-}CH_3C_6H_4)_3$ (4 mol)

Δ, 17 hours, 100°C

(88%)

scheme 5.6

Mechanistic considerations and a full review of this most useful and interesting reaction are published.[11]

Even benzene and monosubstituted benzenes[12] react with palladium acetate under fairly forcing conditions in the presence of alkenes to afford aryl alkenes (equation 5.4).

$$C_6H_6 \quad + \quad H_2C{=}CHR \quad \xrightarrow[\text{AcOH, reflux}]{Pd(OAc)_2} \quad ArCH{=}CHR$$

equation 5.4

Only styrene reacted cleanly and in good yield, forming stilbene. Other alkenes tested (acrylonitrile, vinyl acetate, ethyl vinyl ether) formed the required aryl alkene in low yields (<25%) together with complex coupling and dimerisation products.[12] The reaction therefore, has limited general synthetic potential.

We have found that a variety of alkenes can be coupled with orthomanganated aryl methyl ketones to form aryl alkenes and other products.

5.2 Experimental

5.2.1 Standard procedure for reactions in methanol:

Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) with Li_2PdCl_4 and methyl acrylate in dry methanol

A methanolic solution of Li_2PdCl_4 was prepared by stirring palladium chloride (0.1 g, 0.564 mmol) and anhydrous lithium chloride (0.05 g, 1.18 mmol) in 10 ml of dry methanol for ca. 3 hours, until the solution became homogeneous. Methyl acrylate (0.4 ml, 4.4 mmol) was then syringed into the methanol solution followed by the orthomanganated ketone (1; 0.162 g, 0.566 mmol). The solution immediately turned black with the precitation of palladium metal. The solution was stirred for 30 minutes whereupon it was filtered (to remove Pd(0)) and run through a plug of silica gel. The solvent and excess ester were removed under vacuum and the residual oil was chromatographed (p.l.c.,1:9 ethyl acetate/petroleum spirit) to give one major band at R_f 0.55. Extraction gave a compound which from spectral data was methyl E-3-(2-acetylphenyl)-acrylate [(38 ; 0.087 g, 75 %, pure by ^{1}H-NMR). Recrystallisation from hexane/chloroform (50:1) gave white needles, m.p. 47-48°C. ^{1}H-NMR ($CDCl_3$) (oil) δ 8.12 (d, J = 16 Hz, 1H, β-H), 7.73 (m, 1H, Ar-H), 7.53 (m, 3H, Ar-H), 6.23 (d, J = 16.0 Hz, 1H, α-H), 3.79 (s, 3H, $COOCH_3$), 2.61 (s, 3H, $COCH_3$); ^{13}C-NMR ($CDCl_3$) (oil) δ 200.74 (s, $\underline{C}OCH_3$), 166.93 (s, $\underline{C}OOCH_3$), 144.16 (d, β-C),138.25 (s, 2-C), 134.80 (s, 1-C), 131.94 (d, #), 129.41 (d, #), 129.31 (d, #), 128.37 (d, #), 120.56 (d, α-C), 51.70 (q, $COOCH_3$), 29.26 (q, $COCH_3$). #: carbons not assigned; Mass spectrum (m/e) 204 (0.1), 189 (2.1), 173 (2.4), 161 (4.4), 145 (100), 131 (9.9), 115 (7.3), 102 (5.8), 91 (3.6), 76 (3.6), 59 (4.1).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.62; H, 5.92. Found: C, 70.83; H, 5.88 %.

5.2.2 Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) with Li_2PdCl_4 and styrene in dry methanol

Li_2PdCl_4 (0.41 mmol) and excess styrene (0.5 ml, 4.3 mmol) were reacted with η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2; 0.13 g, 0.41 mmol) using the standard methods described. Addition of the metallated ketone to the other reagents in methanol resulted in the instantaneous formation of Pd(0) and a lump of what we took to be polystyrene. The reaction mixture was worked up by the standard method and the residue chromatographed on silica gel (p.l.c., 1:3 ethyl acetate/petroleum spirit) affording two bands. The band at highest R_f (0.8) was unreacted metallated ketone (2; 0.094 g, 73 % recovery). The colourless band at R_f 0.5 was E-1-(2-acetyl-5-methoxyphenyl)-2-phenylethene (**39** ; 0.030 g, 29 %, pure by ^{1}H-NMR), a colourless oil which would not crystallise. The assignment is based upon spectral data alone; a satisfactory analysis is yet to be obtained. ^{1}H-NMR ($CDCl_3$) (200 MHz) δ 7.85 (d, J = 16.2 Hz, 1H, β-H), 7.77 (d, J = 8.8 Hz, 1H, 3-H), 7.55 (d, J = 7.3 Hz, 2H, 2,6-H'), 7.32 (m, 3H, 3,4,5-H'), 7.17 (d, J = 2.4 Hz, 1H, 6-H), 6.94 (d, J = 16.2 Hz, 1H, α-H), 6.85 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H, 4-H), 3.91 (s, 3H, OCH_3), 2.59 (s, 3H, H_3CCO). ^{13}-NMR ($CDCl_3$) δ 199.74 (s, CO), 162.18 (s, 5-C), 140.72 (2-C), 137.31 (s, 1-C), 132.18 (d, ArCH=*), 131.32 (d, ArCH=*), 129.70 (s, C-1), 128.58 (d, 3,5'-C), 128.36 (d, 3-C), 127.77 (d, 4'-C), 126.84 (d, 2,6'-C), 112.66 (d, 4-C*), 112.37 (d, 5-C*), 55.44 (q, OCH_3), 29.30 (q, $COCH_3$). For assignment purposes the unsubstituted phenyl ring protons and carbons are labelled with a ('). Also protons and carbons labelled α are assigned α to the unsubstituted ring. * Indicates interchangeable assignments; Mass spectrum (m/e) 252 (100), 237 (52.0), 209 (46.8), 194 (31.2), 175 (72.2), 165 (52.0), 139 (8.3), 115 (8.3), 77 (17.3), 63 (11.4).

5.2.3 Reaction of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**) with Li_2PdCl_4 and methyl acrylate in dry methanol

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.22 g, 0.585 mmol), Li_2PdCl_4 (0.585 mmol) and methyl acrylate (0.5 ml, 5.5 mmol) were reacted in methanol by the standard procedure. An immediate precipitation of palladium metal did not occur unlike most other cases so the reaction mixture was stirred for a further two hours, the extent of the reaction being followed by t.l.c. After workup and chromatography (p.l.c., 1:2 ethyl acetate/petroleum spirit) two fractions were obtained. From a band at R_f 0.5 was extracted η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.024 g, 11 % recovery). From a band at R_f 0.4 we obtained 3',4',5'-trimethoxy-acetophenone (0.100 g, 81 %, pure by ^{1}H-NMR).

5.2.4 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) with Li_2PdCl_4 and methyl acrylate in methanol

To a homogeneous solution of Li_2PdCl_4 (0.565 mmol) in dry methanol (10 ml) was added methyl acrylate (0.5 ml, 5.5 mmol) and then the metallated ketone (**10**; 0.165 g, 0.565 mmol). After five minutes the solution was worked up and chromatographed (p.l.c., 1:20 ethyl acetate/petroleum spirit). There were two major bands. At highest R_f (0.85) was unreacted manganated ketone (**10**; 0.040 g, 24 % recovery). The other band at R_f 0.35 was methyl E-3-(2-acetyl-3-thienyl)-acrylate (**40** ; 0.075 g, 63 %, pure by ^{1}H-NMR), a colourless oil which after recrystallisation from $CHCl_3$/hexane (1:50) had m.p. 99-100.5°C.

^{1}H-NMR ($CDCl_3$) (oil) δ 8.44 (d, J = 16.4 Hz, 1H, β-H), 7.45 (d, J = 5.3 Hz, 1H, Ar-H), 7.36 (d, J = 5.3 Hz, 1H, Ar-H), 6.36 (d, J = 16.4 Hz, 1H, α-H), 3.81 (s, 3H, $COOCH_3$), 2.58 (s, 3H, $COCH_3$).

^{13}C-NMR ($CDCl_3$) (oil) δ 190.54 (s, $COCH_3$), 166.93 (s, $COOCH_3$), 140.53 (s, 2-C), 139.03 (s, 3-C), 137.34 (d, C-β), 129.99 (d, 4-C), 127.52 (d, 5-C), 122.06 (d, α-C), 51.63 (q, $COOCH_3$), 29.85 (q, $COCH_3$); Mass spectrum (m/e) 210 (1.1), 179 (4.1), 167 (48.6), 151 (100), 137 (20.1).

Anal. Calcd. for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79. Found: C, 57.23; H, 4.84 %.

5.2.5 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) with Li_2PdCl_4 and methyl vinyl ketone in methanol

Li_2PdCl_4 (0.565 mmol), methyl vinyl ketone (0.5 ml, 6.0 mmol) and the manganated ketone (**10**; 0.165 g, 0.565 mmol) were reacted and worked up by the normal procedure. After chromatography (p.l.c., 1:9 ethyl acetate/petroleum spirit) a colourless oil of 4-(2-acetyl-3-thienyl)-butan-2-one (**41**; 0.115 g, 104 %, pure by ^{1}H-NMR) was obtained. ^{1}H-NMR ($CDCl_3$) (oil) δ 7.41 (d, J = 5.1 Hz, 1H, 5-H), 7.01 (d, J = 5.1 Hz, 1H, 4-H), 3.17 (t, J = 7.0 Hz, 2H, Ar-CH_2), 2.81 (t, J = 7.0 Hz, 2H, CH_2COOCH_3), 2.54 (s, 3H, $COCH_3$), 2.13 (CH_2-$COCH_3$); ^{13}C-NMR ($CDCl_3$) (oil) δ 207.23 (s, CH_2-$COCH_3$), 190.55 (s, Ar-$COCH_3$), 148.35 (s, 2-C), 135.24 (s, 3-C), 131.77 (d, 4-C), 129.61 (d, 5-C), 43.20 (t, Ar-$\underline{C}H_2$), 29.44 (q, H_2C-$COCH_3^*$), 29.33 (q, Ar-$COCH_3^*$), 24.24 (t, $H_2\underline{C}$-$COCH_3$). * indicates assignments interchangeable; Mass spectrum (m/e) 196 (31.0), 166 (54.4), 153 (100), 139 (45.5), 125 (14.1), 111 (18.9), 97 (19.6).

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 61.68 ;H, 6.45 %.

5.2.6 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) with Li_2PdCl_4 and propenal (acrolein) in methanol

Li_2PdCl_4 (0.565 mmol), propenal (0.5 ml, 7.5 mmol) and the manganated thiophene (**10**; 0.165 g, 0.565 mmol) were reacted by the standard method. After workup and chromatography (p.l.c., 1:9 ethyl acetate/petroleum spirit) three compounds were obtained. From the band at highest R_f (0.85) we collected unreacted manganated thiophene (**10**; 0.008 g, 5 %). From the next band at R_f 0.6 we obtained a product which has tentatively been assigned as (**42**; 5 %) the O-methyl enol of 3-(2-acetyl-3-thienyl)propanal on the basis of ^{1}H-NMR and mass spectral data. ^{1}H-NMR ($CDCl_3$) (oil) δ 7.40 (d, J = 4.9 Hz, 1H, 5-H), 7.03 (d, J = 4.9 Hz, 1H, 4-H), 6.45 (d, 1H, J = 12.8 Hz, =C(OCH_3)(H)), 4.91 (dt, d, J = 12.8 Hz, t, J = 7.3 Hz, 1H, H_2C-CH=), 3.63 (d, J = 7.3 Hz, 2H, Ar-CH_2), 3.52 (s, 3H, OCH_3), 2.54 (s, 3H, $COCH_3$); Mass spectrum (m/e) 196 (53.1), 166 (37.9), 153 (35.5), 151 (100), 139 (41.0), 138 (53.8), 121 (24.5), 111 (18.6), 97 (26.6).

The major band of lowest R_f 0.35 was the dimethyl acetal (**43**) of the saturated aldehyde, 3-(2-acetyl-3-thienyl)-propanal, obtained as an oil (0.110 g, 85 %). The assignment is based on spectral data alone and no elemental analysis has been obtained. ^{1}H-NMR ($CDCl_3$) (oil) δ 7.43 (d, J = 4.4 Hz, 1H, 5-H), 7.00 (d, J = 4.4 Hz, 1H, 4-H), 4.40 (m, 2H, CH_2-C(H)(OCH_3)$_2$), 3.32 (s, 6H, OCH_3), 3.04 (m, 2H, Ar-CH_2), 2.52 (s, 3H, $COCH_3$);

^{13}C-NMR ($CDCl_3$) δ 190.27 (s, CO), 148.78 (s, 2-C), 135.32 (s, 3-C), 131.36 (s, 4-C), 129.41 (d, 5-C), 103.59 (d, HC(OCH_3)$_2$), 52.22 (q, OCH_3), 32.38 (t, CH_2C(H)(OCH_3)$_2$), 29.26 (q, $COCH_3$), 25.10 (t, Ar-CH_2); Mass spectrum (m/e) 228 (1.1), 213 (1.0), 196 (100), 166 (13.9), 151 (93.0), 139 (86.8), 123 (64.9), 101 (29.8), 89 (5.5).

5.2.7 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**) with Li_2PdCl_4 and allyl alcohol

Li_2PdCl_4 (0.565 mmol), η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**; 0.165 g, 0.565 mmol) and allyl alcohol were coupled by the normal procedure. After workup and p.l.c. (petroleum spirit) two fractions were obtained. At highest R_f (0.5) we collected unreacted manganated ketone (**10**; 0.057 g, 35 %), while at lower R_f (0.3) 2-acetyl-3-prop-2-enylthiophene (**44**; 0.055 g, 55 %) was obtained as a colourless oil. We have been unable to get this compound sufficiently pure for a satisfactory analysis. ^{1}H-NMR ($CDCl_3$) δ 7.43 (d, J = 5.1 Hz, 1H, 5-H), 7.01 (d, J = 5.1 Hz, 1H, 4-H), 6.00 (m, 1H, CH=CH_2), 5.09 (dm, d J = 12.8 Hz, 2H, CH=CH_2), 3.78 (d, br, J = 6.4 Hz, 2H, Ar-CH_2), 2.53 (s, 3H, $COCH_3$); ^{13}C-NMR ($CDCl_3$) δ 190.47 (s, CO), 146.62 (s, 2-C), 135.62 (s, 3-C), 131.29 (d, 4-C), 129.61 (d, 5-C), 115.82 (t, CH=CH_2), 34.13 (t, Ar-CH_2), 29.33 (q, $COCH_3$): Mass spectrum (m/e) 166 (11.1), 151 (100), 123 (13.8), 97 (100).

Anal. Calcd. for $C_9H_{10}S$: C, 65.03; H, 6.06. Found C, 65.98; H, 6.39 %.

5.2.8 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) with Li_2PdCl_4 and vinyl acetate in methanol

Li_2PdCl_4 (0.565 mmol), η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**; 0.165 g, 0.564 mmol) and vinyl acetate (0.5 ml, 5.4 mmol) were reacted by the normal procedure. After stirring for five minutes the product was worked up by the normal method and chromatographed (p.l.c., 1:19 ethyl acetate/petroleum spirit). From a band at R_f 0.70 we obtained by extraction 2-acetyl-3-vinylthiophene (**45**; 0.050 g, 55 %, pure by ^{1}H-NMR). We were unable to crystallise this compound and an elemental analysis has not been performed. ^{1}H-NMR ($CDCl_3$) δ 7.70 (dd, J = 17.6 Hz, J = 11.0 Hz, 1H, -CH=CH_2), 7.48 (s, br, 2H, H-Ar), 5.82 (d, br, J = 17.6 Hz, 1H, trans-CH=C(H)(H)), 5.53 (d, br, J = 11.0 Hz, 1H, cis-CH=C(H)(H)), 2.57 (s, 3H, $COCH_3$). ^{13}C-NMR ($CDCl_3$) δ 191.12 (s, CO), 144.43 (s, C-2), 135.78 (s, C-3), 130.77 (d, C-4), 129.73 (d, C-5), 127.33 (d, CH=CH_2), 118.61 (t, -CH_2), 29.98 (q, $COCH_3$); Mass spectrum (m/e) 152 (77.9), 151 (100), 137 (72.4), 109 (39.3).

A thick band at R_f 0.30 (0.040 g) contained two compounds as indicated by ^{13}C-NMR and ^{1}H-NMR spectroscopy. Both products were identified by G.C/M.S. The yields of the products 2-acetyl-3-(2-(2-acetylthienyl)-vinyl)-thiophene (**46**; 10%) and the dimethyl acetal of 2-(2-acetyl-3-thienyl)-ethanal (**47**; 25%) were calculated by integration of the aryl protons in the ^{1}H-NMR spectrum of the marterial. The two compounds have the following spectral characteristics: 2-acetyl-3-(2-(2-

acetylthienyl)-vinyl)-thiophene (**46**) ^{1}<u>H-NMR</u> ($CDCl_3$) (oil) δ 8.16 (s, 1H, <u>H</u>C=Ar), 7.59 (d, J = 5.3 Hz, 1H, H-5), 7.44 (d, J = 5.3 Hz, 1H, H-4), 2.57 (s, 3H, $COCH_3$); ^{13}<u>C-NMR</u> ($CDCl_3$) δ 191.07 (s, CO), 144.18 (s, 2-C), 135.57 (s, 3-C), 132.61 (d, 4-C), 129.69 (d, 5-C), 127.38 (d, Ar-CH=), 29.69 (q, $COCH_3$); <u>Mass spectrum</u> (m/e) 276 (100), 261 (29.1), 219 (11.8), 151 (30.0), 138 (11.8), 111 (21.8), 69 (16.3).

Dimethyl acetal of 2-(2-acetyl-3-thienyl)-ethanal (**47**)

^{1}<u>H-NMR</u> ($CDCl_3$) δ 7.42 (d, J= 5.0 Hz, 1H, 5-H), 7.08 (d, J = 5.0 Hz, 1H, 4-H), 4.57 (t, J = 5.6 Hz, 1H, <u>H</u>C(OCH_3)$_2$), 3.35 (s, 6H, OCH_3), 3.30 (d, J = 5.6 Hz, 2H, $-CH_2$), 2.55 (s, 3H, $COCH_3$); ^{13}<u>C-NMR</u> ($CDCl_3$) 190.88 (s, CO), 143.99 (s, 2-C), 136.08 (s, 3-C), 132.61(d, 4-C), 129.31 (d, 5-C), 104.28 (d, <u>C</u>(H)(OCH_3)$_2$), 53.63 (q, OCH_3), 33.83 (t, -CH_2), 29.57 (q, $COCH_3$); <u>Mass spectrum</u> (m/e) 214 (4.1), 183 (100), 166 (48.3), 139 (37.4), 125 (37.2), 97 (49.6).

<u>5.2.9 Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**) with Li_2PdCl_4 and acrylonitrile in dry methanol</u>

Li_2PdCl_4 (0.565 mmol), and η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**; 0.165 g, 0.565 mmol) and acrylonitrile (0.5 ml, 7.6 mmol) were reacted in the normal way. Upon addition of the manganated ketone to the methanol solution containing the reactants no visible reaction occurred. The solution was left stirring for 24 hours at ambient temperature then worked up and chromatographed (p.l.c.,1:4 ethyl acetate/petroleum spirit). To get separation the plate had to be developed three times after which there were four bands at R_f's of 0.80, 0.70, 0.50 and 0.45. Only one was major (R_f 0.50). The other bands contained less than 5 mg each of product(s) which were not analysed. The band at R_f 0.50 on extraction gave methyl 2-(2-acetyl-3-thienyl)-acetate (**48**; 0.033 g, 29 %) a colourless oil. ^{1}<u>H-NMR</u> ($CDCl_3$) δ 7.41 (d, J = 5 Hz, 1H, H-5), 7.02 (d, J = 5.0 Hz, 1H, H-4), 4.01 (s, 2H, Ar-CH_2), 3.65 (s, 3H, $COOCH_3$), 2.45 (s, 3H, $COCH_3$). ^{13}C-NMR ($CDCl_3$) δ 190.74 (s, CO), 170.86 (s, $COOCH_3$), 140.12 (s, C-2), 136.60 (s, C-3), 131.99 (d, C-4), 129.58 (d, C-5), 51.79 (q, $COOCH_3$), 35.05 (t, Ar-CH_2), 29.22 (q, $COCH_3$); Mass spectrum (m/e) 198 (11.2), 166 (100), 139 (59.3), 125 (27.6), 111 (15.9), 97 (28.2).

Anal. Calcd. for $C_9H_{10}O_3$: C, 54.53; H, 5.08. Found : C, 54.39; H, 5.29 %.

5.2.10 Reaction of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (3) with $LiPdCl_3$ and methyl acrylate in acetonitrile

Palladium chloride (0.1 g, 0.565 mmol) and anhydrous lithium chloride (0.05 g, 1.19 mmol) were stirred in acetonitrile for three hours. Methyl acrylate (0.5 ml, 5.5 mmol) and η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (**3**; 0.212 g, 0.564 mmol) were then added. After stirring the reaction mixture for ten minutes some palladium metal was precipitating but t.l.c. showed that no obvious reaction had occurred. After then heating the solution at reflux for 10 minutes, t.l.c. showed that there were three compounds at lower R_f than the starting compound (**3**) which was still present. After 90 minutes at reflux the solution was cooled, filtered and run through a plug of silica. The acetonitrile was removed under vacuum and the residue was chromatographed (p.l.c.,3:17 ethyl acetate/petroleum spirit). The plate had to be developed three times for separation. The band at highest R_f 0.95 yielded after extraction methyl 3-methyl-4,5,6-trimethoxyindene-2-carboxylate (**49**; 0.104 g, 66 %, pure by ^{1}H-NMR). This solid was recrystallised from petroleum spirit to give chunky white crystals of m.p. 99-100°C. ^{1}H-NMR ($CDCl_3$) δ 6.77 (s, br, 1H, Ar-H), 3.91 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.76 (s, 3H, $COOCH_3$), 3.50 (q, br, J = 2 Hz, 2H, Ar-CH_2), 2.68 (t, J = 2.6 Hz, 3H, H_3CC=). ^{13}C-NMR ($CDCl_3$) δ 165.69 (s, $COOCH_3$, 154.18 (s, 6-C), 152.43 (s, 4-C), 149.83 (s, 5-C), 141.11 (s, 8-C*), 140.27 (s, 9-

C*), 129.99 (s, 3-C*), 126.74 (s, 2-C), 103. 33 (d, C-7), 61.00 (q, OCH$_3$), 60.54 (q, OCH$_3$), 55.74 (q, OCH$_3$), 50.53 (q, COOCH$_3$), 38.82 (t, Ar-CH$_2$), 14.24, (q, H$_3$CC=). * indicates assignments interchangeable. Mass spectrum (m/e) 278 (100), 263 (33.0), 247 (34.0), 231 (9.0), 219 (43.0), 204 (30.5), 189 (11.1), 158 (25.0).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found C, 64.51; H, 6.48 %.

We could not identify the products from the second minor band (R$_f$ 0.85; 0.012 g) nor the third band (R$_f$ 0.75, 0.005 g). The final band at R$_f$ 0.70 (0.021 g) was methyl E-3-(2-acetyl-3,4,5-trimethoxyphenyl)-acrylate (50, an oil, 12 %) as determined from spectra alone. ^{1}H-NMR (CDCl$_3$) δ 7.57 (d, J = 15.8 Hz, 1H, β-H), 6.86 (s, 1H, H-Ar), 6.26 (d, J = 15.8 Hz, 1H, α-H), 3.87 (s, 9H, OCH$_3$), 3.76 (s, 3H, COOCH$_3$), 2.52 (s, 3H, COCH$_3$). ^{13}C-NMR (CDCl$_3$) δ 202.66 (s, CO), 166.76 (s, COOCH$_3$), 154.60 (s, 5-C), 150.96 (s, 3-C), 143.39 (s, 4-C), 141.50 (d, β-C), 130.35 (s, 1-C*), 127.55 (s, 2-C*), 119.78 (d, α-C), 105.67 (d, Ar-H), 61.75 (q, OCH$_3$), 60.99 (q, OCH$_3$), 56.15 (q, OCH$_3$), 51.76 (q, COOCH$_3$), 32.77 (q, COCH$_3$). * indicates assignments interchangeable.

5.2.11 Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) with LiPdCl$_3$ and methyl acrylate in acetonitrile

Excess lithium chloride (0.085 g, 2.0 mmol), palladium chloride (0.10 g, 0.585 mmol), methyl acrylate (0.5 ml, 4.9 mmol) and η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2; 0.185 g, 0.585 mmol) were added to 10 ml of dry acetonitrile. The solution was kept at reflux for 3 hours, cooled, worked up by the normal method and chromatographed (p.l.c.,1:9 ethyl acetate/petroleum spirit). The band of highest R$_f$ was methyl 3-methyl-6-methoxyindene-2-carboxylate (51; 0.097 g, 76 %, pure by ^{1}H-NMR). Recrystallisation from petroleum spirit gave off-white plates of m.p. 91-92°C. ^{1}H-NMR (CDCl$_3$) δ 7.48-

6.80 (m, 3H, H-Ar), 3.85 (s, 6H, $COOCH_3$, OCH_3), 3.63 (s, br, 2H, -CH_2), 2.52 (s, 3H, C-CH_3). ^{13}C-NMR ($CDCl_3$) δ 165.82 (s, $COOCH_3$), 160.03 (s, #), 151.39 (s, #), 145.27 (s, #), 137.92 (s, #), 126.07 (s, #), 121.47 (d, #), 112.50 (d, C-5*), 109.25 (d, C-7*), 55.01 (q, OCH_3), 50.53 (q, $COOCH_3$), 38.24 (t, Ar-CH_2), 12.10 (q, $H_3\underline{C}C$=). # carbons not assigned; * assignments are interchangeable; Mass spectrum (m/e) 218 (93.1), 203 (6.8), 187 (26.5), 159 (100), 144 (22.1), 115 (23.4).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found C, 71.41; H, 6.50 %.

At lower R_f was a broad band which contained one major product, assigned as methyl E-3-(2-acetyl-5-methoxyphenyl)-acrylate (**52**; 0.012 g, < 8%) as determined by ^{13}C-NMR analysis. ^{13}C-NMR ($CDCl_3$) δ 198.72 (s, $COCH_3$), 166.93 (s, $COOCH_3$), 162.31 (s, 5-C), 145.21 (d, β-C), 138.05 (s, 2-C), 132.20 (s, 3-C), 130.32 (s, 1-C), 120.36 (d, α-C), 114.19 (d, 4-C*), 113.86 (d, 6-C*), 55.47 (q, OCH_3), 51.69 (q, $COOCH_3$), 28.55 (q, $COCH_3$). * indicates that assignments interchangeable.

5.2.12 Reaction of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (4) with $LiPdCl_3$ and methyl acrylate in acetonitrile.

η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**; 0.22 g, 0.585 mmol), palladium chloride (0.104 g, 0.588 mmol), excess lithium chloride (0.085 g, 2.0 mmol) and methyl acrylate (0.5 ml, 4.9 mmol) were added to 10 ml of dry acetonitrile. The solution was refluxed for 5 hours, cooled , worked up by the normal method and chromatographed (p.l.c.,1:3 ethyl acetate/petroleum spirit). The band at R_f 0.60 was methyl 3-methyl-5,6,7-trimethoxyindene-2-carboxylate (**53**; 0.146 g, 89 %, pure by ^{1}H-NMR). Recrystallisation from petroleum spirit gave white needles of m.p. 85-86 °C. ^{1}H-NMR ($CDCl_3$) δ 6.80 (s, 1H), 4.00 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.82

(s, 3H, H_3COCO), 3.65 (q, br, 2H, J = 2.2 Hz, Ar-CH_2), 2.52 (t, br, 3H, J = 2.2 Hz, $H_3CC=$); ^{13}C-NMR ($CDCl_3$) δ 165.46 (s, $COOCH_3$), 153.34 (s, #), 151.03 (s, #), 148.94 (s, #), 141.66 (s, #), 140 72 (s, #), 128.89 (s, #), 126.68 (s, #), 99.88 (d, C-Ar), 60.67 (q, OCH_3), 59.70 (q, OCH_3), 55.92 (q, OCH_3), 50.63 (q, $COOCH_3$), 36.13 (t, Ar-CH_2), 12.07 ($H_3\underline{C}C=$). # carbons not assigned ; Mass spectrum (m/e) 278 (100), 263 (37.2), 247 (22.0), 235 (10.6), 219 (37.9), 204 (17.9), 189 (8.3), 161 (12.7), 59 (10.3).

Anal. Calcd. For $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found : C, 64.49; H, 6.65 %.

5.2.13 Reaction of η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (11) with $LiPdCl_3$ and methyl acrylate in acetonitrile

η^2-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (**11**; 0.22 g, 0.688 mmol), lithium chloride (0.10 g, 2.3 mmol), palladium chloride (0.122 g, 0.689 mmol) and methyl acrylate (0.5 ml, 4.9 mmol) were added to 10 ml of dry acetonitrile. The solution was refluxed for 5 hours, cooled, worked up by the normal method and chromatographed (p.l.c.,1:9 ethyl acetate/petroleum spirit). The band at R_f 0.80 was methyl 2,5,6-trimethyl-3H-cyclopenta-[c]-thiophene-4-carboxylate (**54** ; 0.049 g, 34 %, pure by ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$) δ 3.66 (s, 3H, $COOCH_3$), 3.03 (s, br, 2H, $-CH_2$), 2,40 (s, br, 6H, $-CH_3$), 2.18 (s, br, 3H, $-CH_3$) ; ^{13}C-NMR ($CDCl_3$) δ 166.70 (s, H_3COCO), 149.01 (s, #), 145.99 (s, #), 140.95 (s, #), 132.01 (s, #), 127.75 (s, #), 124.76 (s, #), 50.85 (q, $COOCH_3$), 31.34 (t, Ar-CH_2), 13.85 (q, Ar-CH_3), 12.84 (q, br, Ar-CH_3); # carbons not assigned; Mass spectrum (m/e) 222 (40.3), 191 (9.6), 163 (100), 148 (15.8), 59 (25.5).

Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Found : C, 64.76; H, 6.59 %.

The only other major product, obtained by extraction of a band at R_f 0.50, was methyl E-3-(2,5-dimethyl-4-acetyl-3-thienyl)-acrylate (55

; 0.090 g, 55 %). It was obtained as white prismic crystals m.p. 30-31.5°C by recrystallisation from petroleum spirit. ^{1}H-NMR (CDCl$_3$) δ 7.69 (d, J = 16.5 Hz, 1H, β-H), 5.89 (d, J = 16.5 Hz, 1H, α-H), 3.77 (s, 3H, COOCH$_3$), 2.48 (sh, s, 3H, COCH$_3$), 2.44 (s, 3H, -CH$_3$), 2.40 (s, 3H, -CH$_3$); ^{13}C-NMR (CDCl$_3$) δ 197.75 (s, CO), 166.67 (s, COOCH$_3$), 139.55 (s, #), 138.77 (s, #), 137.86 (d, β-C), 137.01 (s, #), 131.42 (s, #), 120.17 (d, α-C), 51.24 (q, COOCH$_3$), 31.21 (q, COCH$_3$), 14.31 (q, -CH$_3$), 13.72 (q, -CH$_3$). # carbons not assigned; Mass spectrum (m/e) 238 (17.9), 195 (15.5), 179 (100), 164 (34.5), 135 (13.8), 91 (10.3), 59 (53.8).

Anal. Calcd . for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found : C, 60.71; H, 6.05 %.

5.2.14 Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) with mercury(II) acetate in dichloromethane.

η^2-(2-acetylphenyl)tetracarbonylmanganese (1; 0.878 g, 3.07 mmol) and mercury(II) acetate (1.00 g, 3.13 mmol) were dissolved in dichloromethane (75 ml). The yellow solution was degassed by evacuation, purged with N$_2$ and left stirring at room temperature for ten days. After this time the yellow solution had decolourised and there was some mercury precipitated. The mixture was filtered and the dichloromethane solution evaporated on a rotary evaporator. The white residue was then recrystallised from acetone/chloroform (1:3) to yield a white powder (0.35 g). Mass spectroscopy (figure 5.1) showed that this was a mixture of di-(2-acetylphenyl)mercury(II) and chloro-(2-acetylphenyl)mercury(II) (56). However, by slow recrystallisation of the white powder from chloroform we were able to obtain long white rectangular needles of (56), m.p. 209-211°C. We did not work out the yield of (56), but from the weight of the crude product it was less than 30 %. ^{1}H-NMR (d^6-acetone/d^6-DMSO) δ 8.38 - 7.79 (m, 4H, Ar-H), 2.73 (s, 3H, COCH$_3$); ^{13}C-NMR (d^6-acetone/d^6-DMSO δ

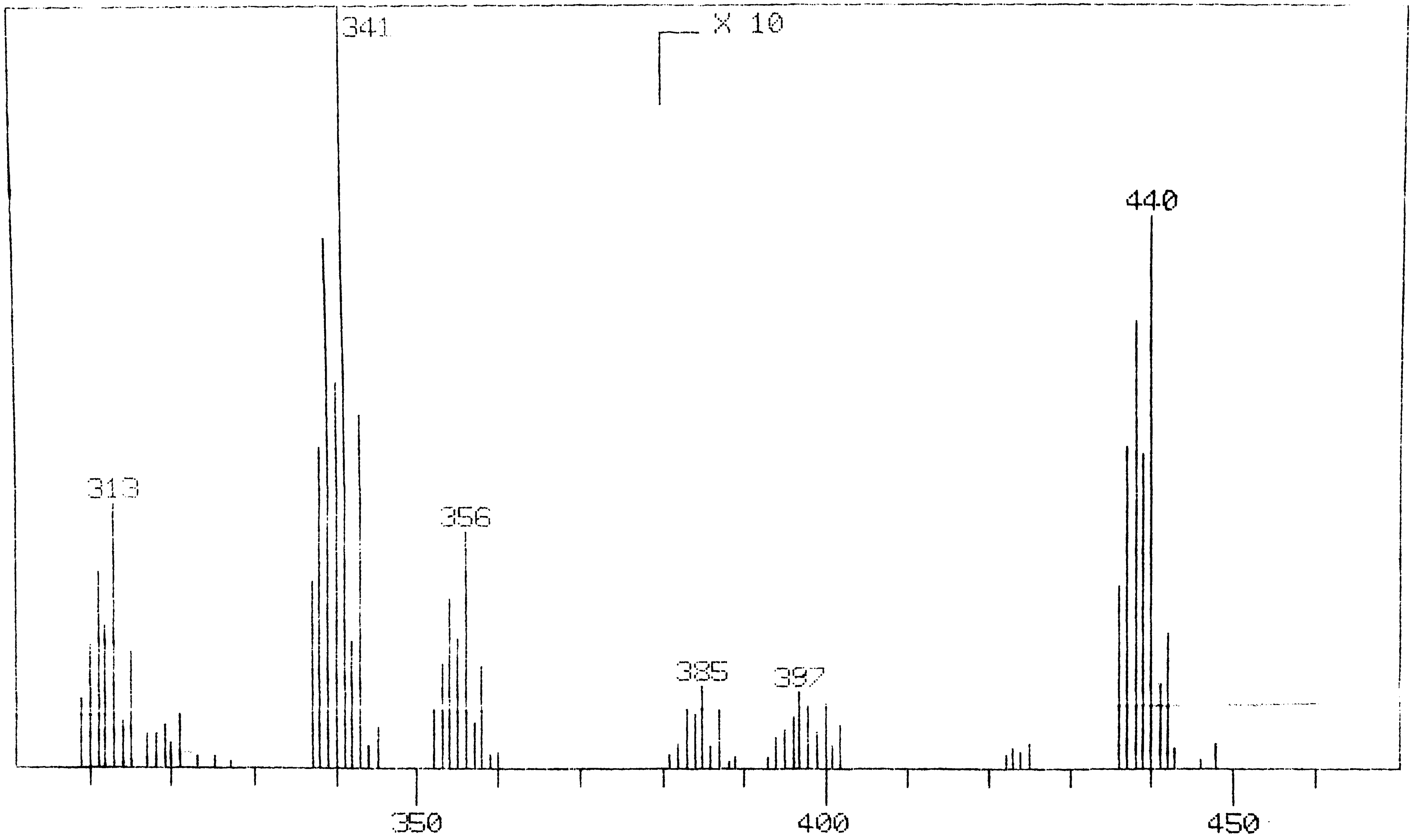


Figure 5.1 Mass spectrum of chloro-(2-acetylphenyl)mercury(II)

and bis-(2-acetylphenyl)mercury(II)

201.07 (s, CO), 149.96 (s, Hg-C), 141.24 (s, 1-C), 138.32 (d, #), 133.89 (d, #), 131.68 (d, #), 128.69 (d, #), (methyl ketone quartet obscured by d^6-acetone septet); # carbons not assigned.

Mass spectrum see figure 5.1.

5.2.15 Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) with mercury(II) chloride in methanol.

η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2; 0.217 g, 0.686 mmol) and mercury(II) chloride (0.186 g, 0.686 mmol) were dissolved in dry methanol (15 ml). This solution was degassed by evacuation, purged with N_2 and stirred at room temperature. After 150 minutes no reaction had occurred as adjudged by t.l.c. The solution was then gently refluxed for 90 minutes during which time a white solid started to precipitate. After refluxing for a further 90 minutes the mixture was cooled and filtered. The fine white needles of product were washed with methanol (3 X 5 ml), and air dried to yield chloro-(2-acetyl-5-methoxyphenyl)-mercury(II) (**57** ;0.20 g, 76 %), m.p. 223-224°C, pure by sharpness of melting point and mass spectroscopy. However a ^{1}H-NMR spectrum of the product gave broad lumps indicative of some paramagnetic impurity, probably traces of Mn^{2+}. A pure sample was obtained by washing the material through a short column of silica (with CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) δ 7.78 (d, J = 8.6 Hz, 1H, H-3), 7.57 (d, J = 2.4 Hz, 1H, H-5), 6.66 (dd, J = 8.6 Hz, J = 2.4 Hz, 1H, H-4), 3.95 (s, 3H, OCH_3), 2.53 (s, 3H, $COCH_3$); Mass spectrum see figure 5.2.

5.2.16 Attempted methylation of the η^2-(2-acetyl-5-methoxyphenyl)-tetracarbonylmanganese (2) with iodomethane and palladium(II) acetate

η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2; 0.100 g, 0.316 mmol), palladium(II) acetate (0.071 g, 0.316 mmol) and excess methyl iodide (0.5 ml) were dissolved in dry acetonitrile. The solution was refluxed for 2 hours whereupon it was filtered [to remove Pd(0)] and run through a plug of silica gel. The excess methyl iodide

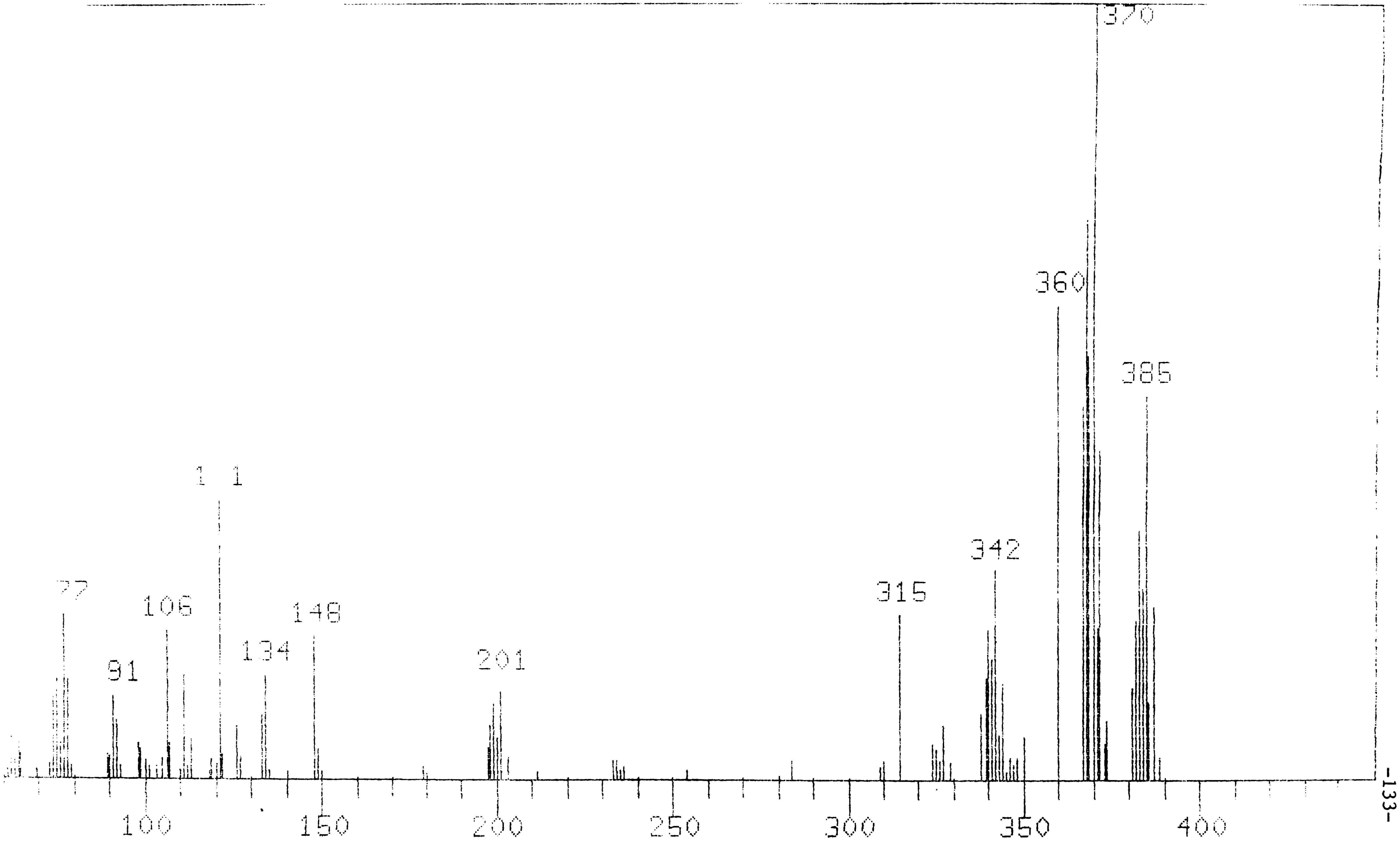


Figure 5.2 Mass spectrum of **chloro-(2-acetyl-5-methoxyphenyl)mercury(II)**

and the solvent were removed under vacuum and the residual oil chromatographed (p.l.c., 1:9 ether/petroleum spirit). The band at R_f 0.85 was unreacted manganated ketone (2, 0.010 g, 10 %), whereas the other band at R_f 0.6 was 4'-methoxyacetophenone (0.034 g, 72 %, pure by ^{1}H-NMR). No trace of any methylated product was found.

5.3 Discussion

5.3.1 Coupling of orthomanganated ketones with a variety of alkenes promoted by palladium(II)

The coupling of η^{2-}(2-acetylphenyl)tetracarbonylmanganese (1) with methyl acrylate in the presence of Li_2PdCl_4 results in the formation of methyl E-3-(2-acetylphenyl)-acrylate (**38**) in 75% yield. Similarly, coupling of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (2) with excess styrene in methanol affords E-1-(2-acetyl-5-methoxyphenyl)-2-phenylethene (**39**) in 29% yield. A large quantity of the metallated ketone (2; 73%), palladium metal and a lump of what we took to be polystyrene was recovered from this latter reaction. The coupling of methyl acrylate with η^2-(2-acetyl-4, 5, 6-trimethoxyphenyl)tetracarbonylmanganese (4) with methyl acrylate was unsuccessful, with the parent acetophenone of (4) being produced in 81% yield. There were no traces of any coupled products which was surprising especially since the coupling of the manganated ketone (1) with methyl acrylate proceeded smoothly and in good yield. Possibly the coupling of the manganated ketone (4) with methyl acrylate is inhibited by the steric effects of the methoxy and acetyl substituents ortho to the aryl site being vinylated. The coupling of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**10**) with methyl acrylate proceeded smoothly and gave methyl E-3-(2-acetyl-3-thienyl)acrylate (**40**) in 63% yield.

The coupling of these manganated ketones [(1), (2) and (**10**)] with methyl acrylate and styrene can be explained by making a direct analogy with the mechanism of coupling (as proposed by Heck) of organomercurials with alkenes (refer to scheme 5.2). The only difference in the mechanism would be that the co-ordinatively unsaturated fragment [ClMn(CO)$_4$], would be eliminated in the first transmetallation step.

Having demonstrated the method for a small number of orthomanganated arenes our efforts were directed to the coupling of a wide variety of alkenes with the metallated thiophene (**10**).

All of the coupled products formed by reaction of the manganated thiophene (**10**) with the variety of alkenes promoted by palladium(II) are summarised in table 5.1.

The coupling of (**10**) with Li_2PdCl_4 and methyl vinyl ketone in methanol gives 4-(2-acetyl-3-thienyl)-butan-2-one (**41**) in quantitative yield. No trace of the expected unsaturated derivative was observed. Similarly, the major product from the coupling of (**10**) with propenal (acrolein) is the dimethyl acetal (**43**) of the saturated aldehyde, 3-(2-acetyl-3-thienyl)-propanal (85%). Presumably, the saturated aldehyde [3-(2-acetyl-3-thienyl)propanal] undergoes an acid-catalysed reaction with methanol to form the dimethylacetal (**43**). Both of these products (**41**) and (**43**) are unexpected especially since the couplings of acrolein and methyl vinyl ketone with chlorophenylpalladium (II) (generated from diphenylmercury (II) with $LiPdCl_3$ in acetonitrile) is known to produce the expected coupled products cinnamaldehyde (60%) and benzalacetone (64%) respectively.[1]

If it is assumed that our coupling reactions (of (**10**) with methyl vinyl ketone and acrolein) proceed in a manner similiar to that illustrated in scheme 5.2, it is possible that the σ-Pd-carbon bond [in (v)] (equation 5.7) is cleaved by the HCl generated in the reaction, thus giving rise to saturation in the side chain.

Table 5.1 Products obtained from the coupling of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (10) with alkenes promoted by palladium(**II**) in methanol

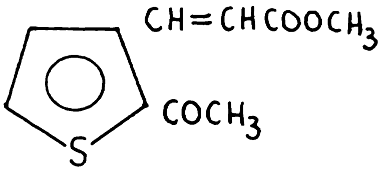
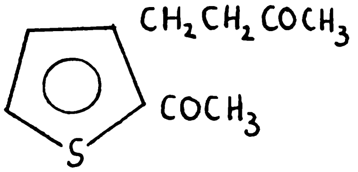
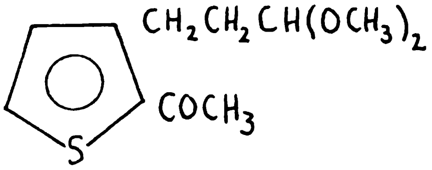
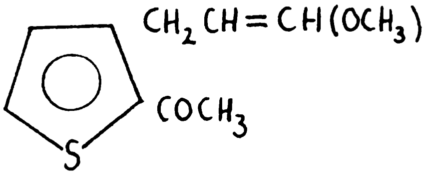
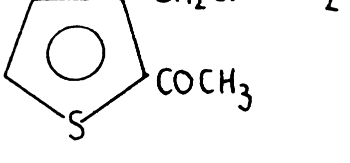
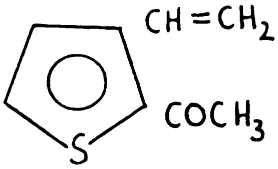
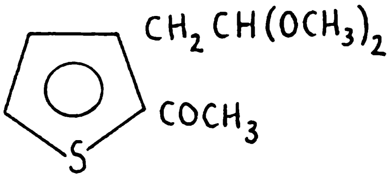
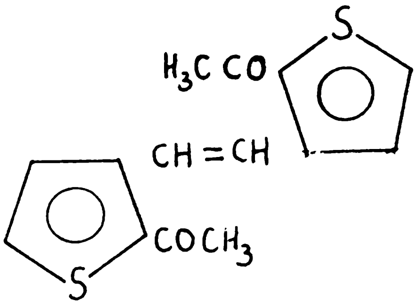
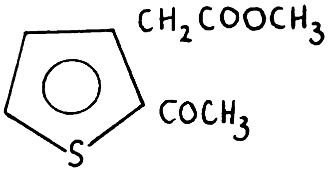
Alkene	Product(s)	Yield
$H_2C=CHCOOCH_3$		63%
$H_2C=CHCOCH_3$		97%
$H_2C=CHCHO$		85%
		5%
$H_2C=CHCH_2OH$		55%

Table 5.1 (cont.)

Alkene	Product(s)	Yield
$H_2C=CHOCOCH_3$		55%
		25%
		10%
$H_2C=CHC\equiv N$		29%

$$\mathrm{ArCH_2CH(PdX)(COR)} \xrightarrow{\mathrm{HCl}} \mathrm{ArCH_2CH_2COR} \ + \ \mathrm{ClPdX}$$

(v)

equation 5.7

The coupling of (**10**) with allyl alcohol affords 2-acetyl-3-prop-2-enylthiophene (**44**) in 55% yield. Some unreacted manganated ketone (10; 35%) was also recovered. Clearly, there are big differences between this coupling reaction with allyl alcohol and Heck's mercury one (refer to scheme 5.3). The main difference is that Heck observed three products from the coupling of chlorophenylpalladium(II) with allyl alcohol [3-phenylpropanal (35%), 3-phenylpropene (12%) and 3-phenylprop-2-en-1-ol (4%)].[4] However, it should be pointed out that Heck performed his coupling reactions in the presence of excess dicyclohexylethylamine. This amine supposedly prevents the conversion of allyl alcohol to allyl chloride by removing HCl. The significance of this is that the allyl chloride can be coupled with organomercurials to form allyl benzenes.[4,5] It is therefore possible that under our reaction conditions allyl alcohol is converted into allyl chloride which then couples with the metallated thiophene (**10**) to form allyl thiophene. We have not yet attempted a reaction in the presence of an amine base to see if this had any effect.

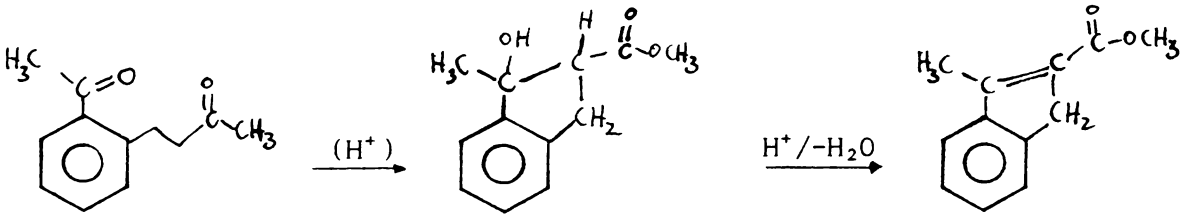
Three products are observed from the coupling of vinyl acetate with the manganated thiophene (10). 2-Acetyl-3-vinylthiophene (**45**; 58%) is the major product with two other compounds, 2-acetyl-3-(2-(2-acetylthienyl)-vinyl)-thiophene (**46**; 10%) and the dimethylacetal of 2-(2-acetyl-3-thienyl)-ethanal (**47**; 25%) being formed in lesser quantities.

These products can be explained by consideration of the mechanism as proposed by Heck for the coupling of vinyl acetate with chlorophenylpalladium(II) (scheme 5.4). The most noticeable feature of our coupling reaction as compared with Heck's are the different types of products and the yields. For example, in Heck's work (solvent acetic acid, $CuCl_2$ added as reoxidant) he observed only 3% of styrene. We observe 58% of the comparable product 2-acetyl-3-vinylthiophene. Also no thiophene equivalent of phenylacetaldehyde enol acetate is found in our reaction while in Heck's it is formed in 30% yield. As was found in the coupling of (**10**) with propenal the aldehyde that is produced in this coupling reaction [2-(2-acetyl-3-thienyl)ethanal] is also converted into its dimethylacetal (**47**).

The coupling of (**10**) with acrylonitrile was less successful, with the ester methyl 2-(2-acetyl-3-thienyl)acetate (**48**) being formed in 29% yield. This was the only major product observed in this reaction. We can offer no feasible mechanism which can explain the formation of this product.

Attempts to couple some alkenes with other manganated aryl ketones were less successful. For example, the coupling of acrylonitrile and vinyl acetate with η^2-(2-acetylphenyl)tetracarbonylmanganese (**1**) by the standard method was unsuccessful. In both cases between 80-85% of the manganated ketone (**1**) was recovered. Similarly, attempts to couple methyl acrylate with η^2-(3-acetylindol-2-yl)-tetracarbonylmanganese (**14**) was unsuccessful, over 90% of the manganated indole being recovered. More research into the experimental conditions, such as different solvents, addition of a reoxidant for Pd(0) such as Cu(II), higher reaction temperatures, etc. is needed for these reactions.

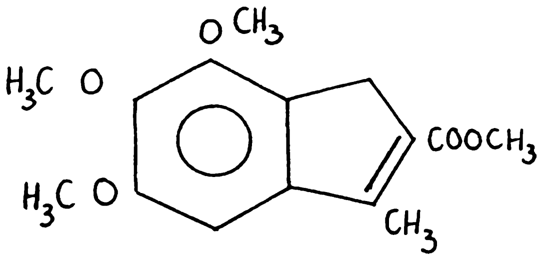
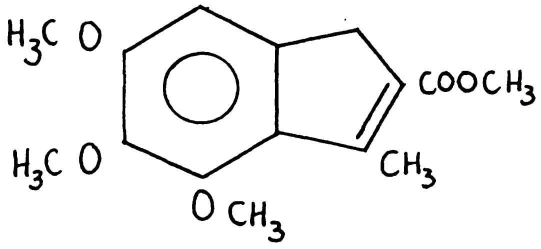
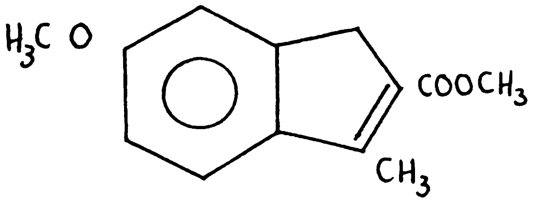
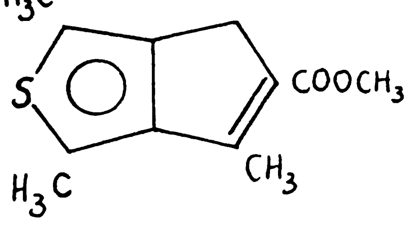
As mentioned earlier the coupling of η^2-(2-acetyl-4, 5, 6-trimethoxyphenyl)tetracarbonylmanganese (**4**) with methyl acrylate in methanol was unsuccessful. Further attempts were made to couple (**4**) with methyl acrylate in acetonitrile under more forcing conditions. Unexpectedly, however, the major product was the indene (**53**), formed in 89 % yield. By a similar procedure the corresponding carbomethoxy indenes from the tetracarbonylmanganese compounds **2**, **3**, and **11** were prepared. That is, we have prepared methyl 3-methyl-4,5,6-trimethoxyindene-2-carboxylate (**49**; 66 %), methyl 3-methyl-6-methoxyindene-2-carboxylate (**51**; 76 %) and methyl 2,5,6-trimethyl-3H-cyclopenta-[c]-thiophene-4-carboxylate (**54**; 34 %). These products may be formed by acid catalysed aldol condensation and elimination (scheme 5.7), but the possibility that the cyclisation is somehow catalysed by palladium cannot be discounted.



scheme 5.7

The yields of the indenes vary from modest to excellent (refer to table 5.2). The lowest yield is obtained when two five membered rings are fused together to form methyl 2,5,6-trimethyl-3H-cyclopenta-[c]-thiophene-4-carboxylate (**54**). This is perhaps not too surprising as such fusing would be expected to be a difficult process. The uncyclised product (**55**) is the major product in this reaction. More interestingly, it is found that the reaction is not inhibited by steric factors, which we felt might be the explanation for the failure of the attempted coupling of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)-tetracarbonylmanganese (**4**) with methyl acrylate in methanol rather

Table 5.2 Indenes prepared by reaction of orthomanganated ketones with methyl acrylate and palladium(II) in acetonitrile

	Yield
	89%
	66%
	76%
	34%

than acetonitrile. Reactions in the latter are carried out at a higher temperature, however.

One major drawback to all of the coupling reactions is that they use stoichiometric quantities of palladium(II) which is an expensive transition metal. As previously discussed the palladium(II) is reduced to palladium metal during the coupling process. This makes the recycling of palladium a very convenient and easy process. The palladium metal could be collected by filtration and converted back into $Pd(OAc)_2$, $Pd(Cl)_2$ or $Pd(Cl)_2(CH_3CN)_2$ by a number of simple laboratory procedures.[13]

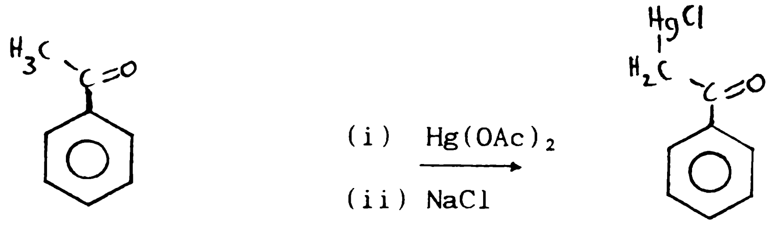
Finally, we are investigating the possibility of using catalytic quantities of $PdCl_2/CuCl_2$ for our coupling reactions. The idea being that the Pd(0) formed during the coupling reactions might be oxidised back to Pd(II) by Cu(II), a recycling such as occurs in the Wacker process[14] (oxidation of ethylene to acetaldehyde promoted by catalytic quantities of $PdCl_2/CuCl_2$).

5.3.2 Mercuration of orthomanganated acetophenones

Like palladium(II), mercury(II) is capable of transmetallating a number of organo-complexes of metals such as tin, lead, lithium, magnesium, zinc and palladium, and similar reactions are known for organoboron compounds. However to the best of our knowledge transmetallation of organomanganese compounds by mercury(II) has not yet been reported.

Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (1) with mercury(II) acetate in dichloromethane was not a very clean reaction. After stirring the reaction mixture for ten days at room temperature less than 30 % [recrystallised product] of chloro-(2-acetylphenyl)-mercury(II) (**56**) was obtained. Mercuration with mercury(II) chloride was more successful. That is, the manganated ketone (2) was mercurated with mercury(II) chloride in refluxing methanol to afford chloro-

(2-acetyl-5-methoxyphenyl)mercury(II) (57) in 76 % yield. The ease with which we obtained pure chloro-(2-acetyl-5-methoxyphenyl)-mercury(II) (57) suggests that this procedure could be a useful general synthesis of 2′-mercurated acetophenones. By contrast, direct mercuration of acetophenone is reported to yield the 2-mercurated product (vi) (equation 5.8).[15]



(vi)

equation 5.8

Furthermore, chlorophenylmercury(II) derivatives are known to undergo a vast array of synthetically useful transformations.[16] Apart from the alkene coupling reactions already dicussed in some detail some of the more important ones are dimerisation reactions (equation 5.9)[16,17] and carbonylation reactions (equation 5.10).[18]

$$2\ ArHgX + Cu \xrightarrow[PdCl_2,\ 115\ ^\circ C]{pyridine} Ar\text{-}Ar + Hg + CuX_2$$

equation 5.9

$$ArHgCl \xrightarrow[70\ ^\circ C,\ THF,\ 24\ hours]{LiCl,\ 800\ p.s.i.\ CO,\ 0.5\ \%\ [Rh(CO)_2Cl]_2} Ar(CO)Ar$$

equation 5.10

The accessibility of ortho-mercurated acetophenones through transmetallation of orthomanganated acetophenones has synthetic potential, therefore, for introducing orthosubstituents not available through reaction of the orthomanganated acetophenones themselves. In addition, there is likely to be similiar value with other donor aryl groups, e.g. esters, for which direct mercuration occurs meta rather than ortho,[16] unlike the orthomanganation-mercuration route.

The crystal structure of chloro-(2-acetylphenyl)mercury(II) (**56**) was carried out with the main interest being centred on the mercury to carbonyl oxygen interaction.

5.3.3 X-ray crystal structure of chloro-(2-acetylphenyl)mercury(II) (**56**)

Colourless long needles were obtained by slow recrystallisation from chloroform. Premininary precession photography (Cu-K_α, λ = 1.5418 Å) indicated orthorhombic symmetry with systematic absences appropriate for the space group $P2_12_12_1$. Intensity data were obtained on a Nicolet XRD P3 four circle diffractometer with monochromated Mo-K_α radiation.

Crystal data C_8H_7ClHgO, M = 355.10, orthorhombic, space group $P2_12_12_1$ (No 19), a 5.346(1) , b 10.543(3) , c 14.743(2) Å, U 831.02 Å^3, Z = 4, F(000) = 892, μ(Mo-K_α) = 187.64 cm^{-1}.

Intensity data were collected at -150°C in the range 5°< 2θ < 55° using a θ-2θ scan technique. A total of 1140 unique data were collected and after correction for Lorentz, polarisation and absorption effects the 1023 data for which $I > 2\sigma(I)$ were used in all calculations.

Solution and refinement The position of the mercury atom was found by Patterson methods. Subsequent difference electron density maps revealed all of the missing non-hydrogen atoms. The model was refined using full-matrix, least-squares refinement with the mercury and chlorine atoms being assigned anisotropic temperature factors. The hydrogen atoms were included in their calculated positions with each different type of hydrogen assigned separate isotropic temperature factors. The refinememt converged with $R = 0.0442$ and $R_w = 0.0534$ where $w = [\sigma^2(F) + 0.008F_o{}^2]^{-1}$ with no parameter shifting more than 0.6σ in the final cycle of least squares refinement. The final difference map was featureless apart from a ripple of electron density around the mercury atom (ca. 3.5 e Å^3).

Plan and side elevations (along with a numbering scheme) of the molecule can be seen in figure 5.3.

Bond angles and bond lengths appear in table 5.3 .The atomic positions of all atoms, the thermal parameters for all non-hydrogen atoms and the positions and thermal parameters of the hydrogen atoms appear in appendix IV.

5.3.4 Discussion of the structure

A literature survey including a computer search of Cambridge crystallography files, led us to believe this is the first reported crystal structure of a chlorophenylmercury(II) compound. The main point of interest was to see if there was any appreciable interaction between the ketone oxygen and the mercury atom. The mercury to oxygen distance of 2.712 (10) Å is somewhat shorter than the sums of the Van der Waals radii of these atoms (mercury 1.50-1.73 Å, oxygen 1.40 Å),[19] indicative of weak interaction. This bonding distance is considerably longer than that observed for covalent mercury to oxygen bonds (2.01-2.16 Å).[19] The near linearity of the C(1)-Hg-Cl linkage also indicates that any interaction is weak, with a genuinely 2 co-ordinate Hg atom. There is a recent review available discussing Hg-O bonded and non-bonded distances.[19] All of the other acetophenone bond lengths and bond angles are in close agreement with those reported for the crystal structure of acetophenone[20] and require no comment.

5.4 Miscellaneous reactions

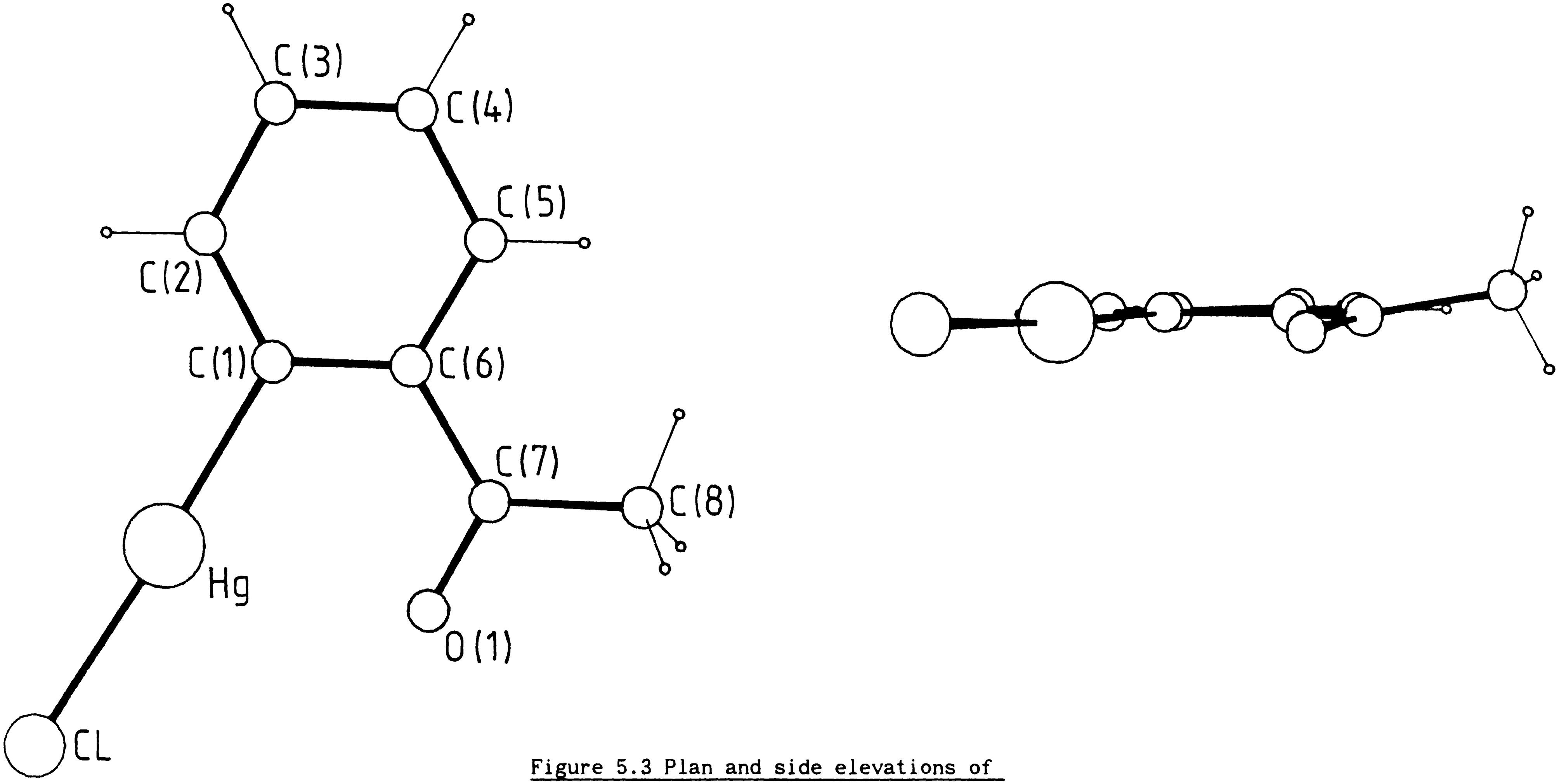


Figure 5.3 Plan and side elevations of

chloro-(2-acetylphenyl)mercury(II)

Table 5.3 Bond angles (°) and bond lengths (Å) of chloro-2-acetylphenylmercury (II)

Bond lengths

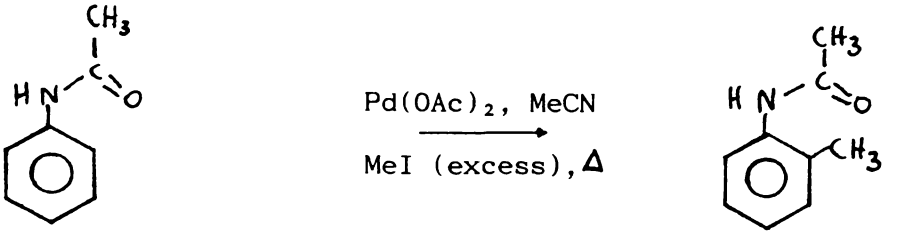
C(1)	-Hg	2.066 (11)
Hg	-Cl	2.323 (3)
C(6)	-C(7)	1.517 (19)
C(7)	-C(8)	1.533 (19)
C(7)	-O(1)	1.204 (17)
Hg	····O(1)	2.712 (10)

Bond angles

C(1) -Hg -Cl	175.9 (4)

All aromatic C-C bonds 1.39 Å as expected, and all other bond angles did not differ significantly from 120 °

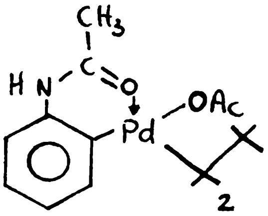
A very interesting reaction is known in which acetanilides are orthoalkylated by the action of iodomethane and palladium acetate (equation 5.11).[21]



(81%)

equation 5.11

Iodoethane and 3-iodopropene reacted similarly. This is believed to proceed through the methylation of the following orthopalladiated intermediate.[21]



We have attempted to react the orthomanganated acetophenone (2) with palladium(II) acetate and excess methyl iodide, under reflux in acetonitrile, but the reaction was unsuccessful with no methylation being observed. The only product which was found was 4'-methoxyacetophenone (72 %) the origin of which is not clear.

References

(1) R. F. Heck,

J. Am. Chem. Soc., 90, 5518, 1968.

(2) A. D. Ryabov,

Synthesis, 235, 1985.

(3) S. Kamiyama, T. Kimura, A. Kasahara, T. Izumi and M. Maemura,

Bull. Chem. Soc. Jpn., 52, 142, 1979.

(4) R. F. Heck,

J. Am. Chem. Soc., 90, 5526, 1968.

(5) R. F. Heck,

J. Am. Chem. Soc., 90, 5531, 1968.

(6) R. F. Heck,

J. Am. Chem. Soc., 90, 5535, 1968.

(7) R. F. Heck,

Organometal. Chem. Syn., 1, 455, 1972.

(8) R. C. Larock, S. Varaprath, H. H. Lau and C. A. Fellows,

J. Am. Chem. Soc., 106, 5274, 1984.

(9) M. Somei, T. Hasegawa and C. Kaneko,

Heterocycles, 20, 1983, 1983.

(10) M. E. Volpin, L. G. Nolkova, I. Y. Levitin, N. N. Boronina,

A. M. Yurkevich,

J. Chem. Soc., Chem. Commun., 849, 1971.

(11) R. F. Heck,

Org. Reactions, 27, 345, 1980.

(12) S. Danno, I. Moritani and Y. Fujiwara,

Tetrahedron, 25, 4819, 1969.

(13) R. F. Heck,

"Palladium reagents in Organic Synthesis",

Academic Press, London, 1985.

(14) J. Tsuji,

"Organic Synthesis with Palladium Compounds",

Springer-Verlag, Berlin, 1980, p. 6.

(15) R. C. Larock,
"*Organomercury Compounds in Organic Synthesis*",
Springer-Verlag, Berlin, 1985, p. 28.

(16) R. C. Larock,
"*Organomercury Compounds in Organic Synthesis*,
Springer-Verlag, Berlin, 1985.

(17) R. A. Kretchmer and R. Glowinski,
J. Org. Chem., **41**, 2661, **1976**.
R. C. Larock and J. C. Bernhardt,
J. Org. Chem., **42**, 1680, **1977**.

(18) R. C. Larock and S. S. Hershberger,
J. Org. Chem., **45**, 3840, **1980**.

(19) J. L. Wardell, in
"*Comprehensive Organometallic Chemistry*",
ed. G. Wilkinson, F. G. A. Stone, E. W. Abel,
Pergamon Press, Oxford, **1982**, Vol 2, p. 906.

(20) Y. Tanimoto, H. Kobayashi, S. Nagakura and Y. Saito,
Acta Crystallogr., Sect. B, **29**, 1822, **1973**.

(21) S. J. Tremont and H. Ur Rahman,
J. Am. Chem. Soc., **106**, 5759, **1984**.

CHAPTER SIX

Crystal structures of the isoelectronic molecules η^6-$(C_{18}H_{24})Mn(CO)_3$ where M = Cr, Mn^+

6.1 Introduction

There is a very extensive literature on the preparation, structures, spectroscopic properties and use in syntheses of arene $Cr(CO)_3$ complexes,[1-5] and to a lesser extent, on the isoelectronic arene $Mn(CO)_3^+$ complexes.[6,7,8] Interest in the structures of (η^6-arene)$M(CO)_3$ complexes relates partly to assessing the factors which determine the orientation of the $M(CO)_3$ group relative to the arene, especially for substituted arenes.[1] This work is of importance since the orientation of the tripod can direct regioselective electrophilic and nucleophilic attack at the arene.[9] Experimental and theoretical analyses confirm two ideal cases.[1,3,9] The first has the $M(CO)_3$ group orientated so that the CO ligands lie across the mid-points of the C-C bonds, and is observed for unsubstituted or hexa-substituted arenes. The second has the CO ligands projected onto carbon atoms of the ring and is normally adopted by mono or 1,3,5 species with electron releasing substituents.

We are interested in complexes of the arene docecahydrotriphenylene, $C_{12}H_{18}$, (58). This is a hexa-substituted benzene ring with each carbon atom electronically equivalent, but the overall symmetry is only three-fold. There is long standing interest in molecules with saturated rings fused to an arene ring,[10] with some unresolved debate as to whether there is partial double-bond localisation induced, i.e. whether there is a predominance of either of the resonance forms (i) or (ii) (figure 6.1).

For a $M(CO)_3$ fragment there are three vacant orbitals *trans* to each carbonyl which are directed towards the regions of a co-ordinated ring where the electron density is the greatest,[1] so that any bond-localisation in the arene ring should be reflected in the orientational preferences of a co-ordinated $M(CO)_3$. Thus a dominance of form (i) in the free ligand should lead to conformation (iii) in the complex, and similarly for (ii) and (iv) (figure 6.1).

We have prepared and structurally characterised the neutral $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ and the two crystalline modifications of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3^+]BF_4^-$ (see experimental). As far as we are aware there is no previous report of a structural characterisation of an $[(arene)Mn(CO)_3]^+$ derivative. The structural features of the isoelectronic pair of $(arene)M(CO)_3$ complexes where M= Cr, Mn^+, have been compared.

6.2 Experimental

The ligand dodecahydrotriphenylene, (58), was prepared from cyclohexanone by a literature procedure.[11]

6.2.1 Preparation of triaminetricarbonylchromium

This was prepared by the method of Rausch et al.[12]

Potassium hydroxide (3.90 g, 0.069 mol) was dissolved in 60 ml of 95% ethanol. This solution was then poured into a 100 ml pressure vessel containing chromium hexacarbonyl (2.25 g, 0.01 moles). The pressure vessel was evacuated and placed in a steam bath for 300 minutes. After this time the vessel was cooled in an ice-bath and the solution poured through a stream of nitrogen into a large excess of nitrogen-saturated, concentrated aqueous ammonia.

The flask containing the ammoniacal solution was then evacuated twice, purged with nitrogen, tightly stoppered and stirred overnight. After twelve hours the solution containing a bright-yellow precipitate was filtered through a glass frit to afford $Cr(NH_3)_3(CO)_3$ (1.40 g, 75%).

6.2.2 Preparation of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ (59)

$Cr(NH_3)_3(CO)_3$ (0.20 g, 1.07 mmol) and $C_{18}H_{24}$ (0.25g, 1.04 mmol) in dioxane (15 ml) were refluxed under a flow of nitrogen for four hours. After cooling in ice, the solution was filtered through a glass frit, and the dioxane was removed under vacuum. The yellow residue was dissolved in CH_2Cl_2 and chromatographed on a silica column, eluting with hexane:CH_2Cl_2 (4:1). The yellow band on evaporation yielded flakey yellow crystals of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ (59; 0.23 g, 59%); Well developed crystals were obtained from hexane at -20°C, m.p. 175-178°C. Infrared spectrum; ν(CO) (CH_2Cl_2) 1942, 1857 ; (Nujol) 1950, 1932, 1847, 1850 cm^{-1}, (all strong). ^{1}H-NMR ($CDCl_3$) δ 2.57 (m, α-H), 1.76 (m, β-H); ^{13}C-NMR ($CDCl_3$) δ 235.21 (s, CO), 107.25 (s, aryl-C), 26.05 (t, α-C), 22.02 (t, β-C).

6.2.3 X-ray structure of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ (59)

A yellow block-shaped crystal 0.18 X 0.19 X 0.20 mm was obtained from hexane. Preliminary precession photography defined the space group as $P2_1/a$. Intensity data were obtained on a Nicolet XRD P3 diffractometer using monochromated Mo-K_α X-rays.

Crystal data: $C_{21}H_{24}CrO_3$, M 376.42, monoclinic, space group $P2_1/a$, a 19.484 (2), b 9.855 (2), c 20.951 (5) A, 113.44 (2), U 3630 A^3. D_c 1.375 g cm^{-1} for Z = 8. F(000)=1583, μ(Mo-K_α) 5.9 cm^{-1}, T = 23°C. Intensity data in the range $3° < 2\theta < 43°$ were collected using a θ-2θ scan technique. Absorption corrections were applied (max, min transmission factors 0.87, 0.80 respectively). A total of 3717 unique reflections were collected and those 3135 for which $I > 2\sigma(I)$ were used in all calculations.

The positions of the two unique chromium atoms were located by Patterson methods, and all other non-hydrogen atoms were found routinely in subsequent difference maps. In the final cycles of full-matrix least-squares refinement the chromium and methylene carbon atoms were assigned anisotropic temperature factors, other atoms were treated isotropically, and hydrogen atoms were included in their calculated positions with a common isotropic temperature factor. The refinement converged at R = 0.0531, R_w = 0.0610 where w = $[\sigma^2(F)$ +

$0.0008F^2]^{-1}$ with no parameter shifting more than 0.1 times its e.s.d in the final cycle. The highest peak in a final difference map was <0.4 e A^{-3}. Bond angles and bond lengths appear in Table 6.1. The final positional and thermal parameters appear in Appendix V. Figure 6.2 shows (with a numbering scheme) a plan view of one independent molecule. Figure 6.3 illustrates a stereoview of the unit cell while figure 6.4 shows stereoviews of the two independent molecules in the asymmetric unit.

6.2.4 Preparation of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+ BF_4^-$ (60)

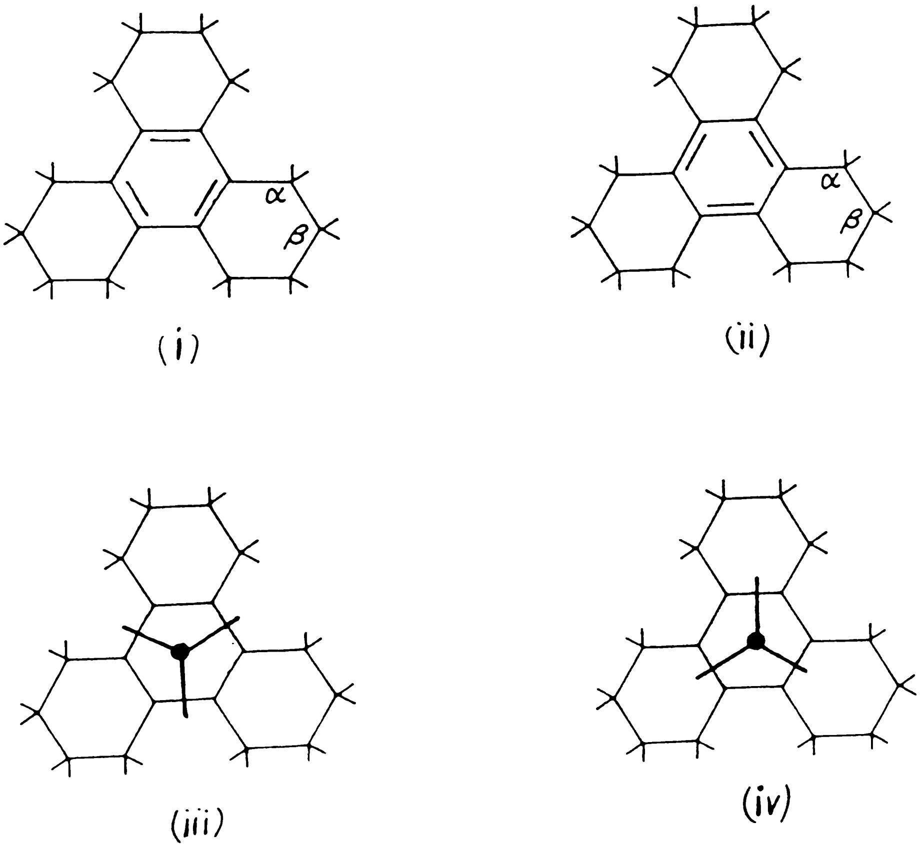
This was prepared by the method of Munro and Pauson.[6] Bromopentacarbonylmanganese (1.0 g, 3.6 mmol) and dodecahydrotriphenylene (1.0 g, 4.2 mmol) were heated with finely-crushed aluminium trichloride (1.0 g, 7.5 mmol) in 1,3-dichlorobenzene (20 ml) for 4 hours at 100°C. The solution was cooled in ice and extracted with ice-water (3 X 6 ml). The aqueous extract was shaken vigorously with carbon tetrachloride (10 ml) which was then separated and discarded. An excess of aqueous HBF_4 (40%) was added dropwise to the stirred aqueous solution. Filtration gave the pale yellow product, (0.87 g, 52% based on $BrMn(CO)_5$). Recrystallisation from acetone/ether (4:1) gave two crystal forms; orthorhombic needles and trigonal thick plates. Infrared spectrum;ν(CO) (CH_2Cl_2) 2050 (vs), 1988 (vs); (Nujol, needles) 2047 (vs), 1986 (sh), 1972 (s); (Nujol, plates) 2050 (vs), 1980 (s).

^{1}H-NMR ($CDCl_3$) 2.73 (m, α-H), 1.87 (m, β-H); ^{13}C-NMR (d^6-acetone) 218.6 (s, CO), 114.6 (s, aryl-C), 26.5 (t, α-C), 21.5 (t, β-C).

6.2.5 Crystal structure of the orthorhombic modification of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ (60)

Yellow, needle-shaped crystals were obtained from acetone/diethyl ether solution. Preliminary precession photography indicated orthorhombic symmetry with systematic absences appropriate for space

Figure 6.1



(i) (ii)

(iii) (iv)

Table 6.1 Bond angles and bond lengths for (η^6-$C_{18}H_{24}$)Cr(CO)$_3$ (59)

Bond Lengths (Å).

Cr(1) ---C(11)	2.230(5)	C(14) ---C(155)	1.533(8)
Cr(1) ---C(12)	2.239(5)	C(15) ---C(16)	1.423(7)
Cr(1) ---C(13)	2.231(6)	C(15) ---C(152)	1.539(6)
Cr(1) ---C(14)	2.228(6)	C(16) ---C(115)	1.521(7)
Cr(1) ---C(15)	2.213(5)	C(112)---C(113)	1.48(1)
Cr(1) ---C(16)	2.231(5)	C(113)---C(114)	1.25(1)
Cr(1) ---C(17)	1.821(6)	C(114)---C(115)	1.49(1)
Cr(1) ---C(18)	1.812(6)	C(132)---C(133)	1.469(8)
Cr(1) ---C(19)	1.825(7)	C(133)---C(134)	1.33(1)
C(11) ---C(12)	1.435(7)	C(134)---C(135)	1.51(1)
C(11) ---C(16)	1.409(6)	C(152)---C(153)	1.48(1)
C(11) ---C(112)	1.513(7)	C(153)---C(154)	1.23(1)
C(12) ---C(13)	1.402(7)	C(154)---C(155)	1.473(9)
C(12) ---C(135)	1.514(6)	C(17) ---O(17)	1.153(8)
C(13) ---C(14)	1.442(6)	C(18) ---O(18)	1.162(8)
C(13) ---C(132)	1.502(7)	C(19) ---O(19)	1.150(8)
C(14) ---C(15)	1.392(7)		
Cr(2) ---C(21)	2.229(4)	C(24) ---C(255)	1.532(7)
Cr(2) ---C(22)	2.228(4)	C(25) ---C(26)	1.429(7)
Cr(2) ---C(23)	2.228(5)	C(25) ---C(252)	1.522(7)
Cr(2) ---C(24)	2.220(5)	C(26) ---C(215)	1.503(9)
Cr(2) ---C(25)	2.241(5)	C(212)---C(213)	1.53(1)
Cr(2) ---C(26)	2.222(5)	C(213)---C(214)	1.467(9)
Cr(2) ---C(27)	1.821(7)	C(214)---C(215)	1.513(9)
Cr(2) ---C(28)	1.817(7)	C(232)---C(233)	1.496(9)
Cr(2) ---C(29)	1.834(7)	C(233)---C(234)	1.39(1)
C(21) ---C(22)	1.426(9)	C(234)---C(235)	1.49(1)
C(21) ---C(26)	1.403(7)	C(252)---C(253)	1.50(1)
C(21) ---C(212)	1.540(8)	C(253)---C(254)	1.46(1)
C(22) ---C(23)	1.408(7)	C(254)---C(255)	1.502(9)
C(22) ---C(235)	1.520(7)	C(27) ---O(27)	1.162(8)
C(23) ---C(24)	1.431(7)	C(28) ---O(28)	1.142(8)
C(23) ---C(232)	1.509(9)	C(29) ---O(29)	1.142(9)
C(24) ---C(25)	1.367(8)		

Table 6.1 continued

C(21) -Cr(2) -C(22)	37.3(2)
C(21) -Cr(2) -C(23)	66.9(2)
C(21) -Cr(2) -C(24)	78.3(2)
C(21) -Cr(2) -C(25)	66.1(2)
C(21) -Cr(2) -C(26)	36.8(2)
C(21) -Cr(2) -C(27)	114.0(2)
C(21) -Cr(2) -C(28)	92.6(2)
C(21) -Cr(2) -C(29)	157.1(3)
C(22) -Cr(2) -C(23)	36.9(2)
C(22) -Cr(2) -C(24)	66.6(2)
C(22) -Cr(2) -C(25)	78.1(2)
C(22) -Cr(2) -C(26)	67.0(2)
C(22) -Cr(2) -C(27)	151.0(2)
C(22) -Cr(2) -C(28)	88.6(2)
C(22) -Cr(2) -C(29)	120.2(3)
C(23) -Cr(2) -C(24)	37.5(2)
C(23) -Cr(2) -C(25)	66.1(2)
C(23) -Cr(2) -C(26)	79.3(2)
C(23) -Cr(2) -C(27)	158.5(2)
C(23) -Cr(2) -C(28)	112.4(3)
C(23) -Cr(2) -C(29)	91.0(2)
C(24) -Cr(2) -C(25)	35.7(2)
C(24) -Cr(2) -C(26)	66.3(2)
C(24) -Cr(2) -C(27)	121.0(2)
C(24) -Cr(2) -C(28)	149.7(3)
C(24) -Cr(2) -C(29)	87.8(2)
C(25) -Cr(2) -C(26)	37.3(2)
C(25) -Cr(2) -C(27)	94.1(3)
C(25) -Cr(2) -C(28)	157.9(3)
C(25) -Cr(2) -C(29)	111.5(2)
C(26) -Cr(2) -C(27)	89.8(2)
C(26) -Cr(2) -C(28)	120.9(3)
C(26) -Cr(2) -C(29)	148.5(2)
C(27) -Cr(2) -C(28)	89.1(3)
C(27) -Cr(2) -C(29)	88.7(3)
C(28) -Cr(2) -C(29)	90.5(3)
Cr(2) -C(21) -C(22)	71.3(3)
Cr(2) -C(21) -C(26)	71.4(3)
Cr(2) -C(21) -C(212)	132.1(4)
C(22) -C(21) -C(26)	120.3(5)
C(22) -C(21) -C(212)	118.6(5)
C(26) -C(21) -C(212)	121.0(5)
Cr(2) -C(22) -C(21)	71.4(3)
Cr(2) -C(22) -C(23)	71.6(3)
Cr(2) -C(22) -C(235)	130.7(4)
C(21) -C(22) -C(23)	120.0(5)
C(21) -C(22) -C(235)	119.5(5)
C(23) -C(22) -C(235)	120.4(5)
Cr(2) -C(23) -C(22)	71.5(3)
Cr(2) -C(23) -C(24)	70.9(3)
Cr(2) -C(23) -C(232)	129.6(3)
C(22) -C(23) -C(24)	118.6(5)
C(22) -C(23) -C(232)	120.4(5)
C(24) -C(23) -C(232)	121.0(4)
Cr(2) -C(24) -C(23)	71.6(3)
Cr(2) -C(24) -C(25)	73.0(3)
Cr(2) -C(24) -C(255)	129.3(3)
C(23) -C(24) -C(25)	121.3(4)
C(23) -C(24) -C(255)	117.8(5)
C(25) -C(24) -C(255)	120.9(4)
Cr(2) -C(25) -C(24)	71.3(3)
Cr(2) -C(25) -C(26)	70.6(3)
Cr(2) -C(25) -C(252)	131.2(3)
C(24) -C(25) -C(26)	120.7(5)
C(24) -C(25) -C(252)	122.1(5)
C(26) -C(25) -C(252)	117.2(5)
Cr(2) -C(26) -C(21)	71.9(3)
Cr(2) -C(26) -C(25)	72.0(3)
Cr(2) -C(26) -C(215)	128.4(3)
C(21) -C(26) -C(25)	118.9(5)
C(21) -C(26) -C(215)	120.9(5)
C(25) -C(26) -C(215)	120.2(4)
C(21) -C(212)-C(213)	113.0(5)
C(212)-C(213)-C(214)	111.2(5)
C(213)-C(214)-C(215)	111.6(6)
C(26) -C(215)-C(214)	113.7(5)
C(23) -C(232)-C(233)	113.4(6)
C(232)-C(233)-C(234)	116.3(7)
C(233)-C(234)-C(235)	114.4(8)
C(22) -C(235)-C(234)	114.3(5)
C(25) -C(252)-C(253)	113.9(6)
C(252)-C(253)-C(254)	113.5(6)
C(253)-C(254)-C(255)	112.9(5)
C(24) -C(255)-C(254)	112.8(6)
Cr(2) -C(27) -O(27)	178.1(6)
Cr(2) -C(28) -O(28)	178.8(5)
Cr(2) -C(29) -O(29)	176.1(6)

Table 6.1 continued.

Bond Angles (degrees).

C(11) -Cr(1) -C(12)	37.5(2)
C(11) -Cr(1) -C(13)	66.9(2)
C(11) -Cr(1) -C(14)	78.9(2)
C(11) -Cr(1) -C(15)	66.8(2)
C(11) -Cr(1) -C(16)	36.8(2)
C(11) -Cr(1) -C(17)	115.5(2)
C(11) -Cr(1) -C(18)	155.3(2)
C(11) -Cr(1) -C(19)	91.7(2)
C(12) -Cr(1) -C(13)	36.6(2)
C(12) -Cr(1) -C(14)	66.7(2)
C(12) -Cr(1) -C(15)	78.8(2)
C(12) -Cr(1) -C(16)	66.9(2)
C(12) -Cr(1) -C(17)	152.8(2)
C(12) -Cr(1) -C(18)	118.0(2)
C(12) -Cr(1) -C(19)	90.1(2)
C(13) -Cr(1) -C(14)	37.7(2)
C(13) -Cr(1) -C(15)	67.0(2)
C(13) -Cr(1) -C(16)	79.2(2)
C(13) -Cr(1) -C(17)	156.7(2)
C(13) -Cr(1) -C(18)	90.1(3)
C(13) -Cr(1) -C(19)	114.9(2)
C(14) -Cr(1) -C(15)	36.5(2)
C(14) -Cr(1) -C(16)	66.7(2)
C(14) -Cr(1) -C(17)	119.0(2)
C(14) -Cr(1) -C(18)	88.2(3)
C(14) -Cr(1) -C(19)	152.5(2)
C(15) -Cr(1) -C(16)	37.4(2)
C(15) -Cr(1) -C(17)	92.1(2)
C(15) -Cr(1) -C(18)	113.5(2)
C(15) -Cr(1) -C(19)	156.3(2)
C(16) -Cr(1) -C(17)	90.4(2)
C(16) -Cr(1) -C(18)	150.8(2)
C(16) -Cr(1) -C(19)	119.0(2)
C(17) -Cr(1) -C(18)	89.2(3)
C(17) -Cr(1) -C(19)	88.4(3)
C(18) -Cr(1) -C(19)	90.2(3)
Cr(1) -C(11) -C(12)	71.6(3)
Cr(1) -C(11) -C(16)	71.6(3)
Cr(1) -C(11) -C(112)	129.8(4)
C(12) -C(11) -C(16)	119.9(4)
C(12) -C(11) -C(112)	118.9(4)
C(16) -C(11) -C(112)	121.2(4)
Cr(1) -C(12) -C(11)	70.9(3)
Cr(1) -C(12) -C(13)	71.4(3)
Cr(1) -C(12) -C(135)	131.3(4)
C(11) -C(12) -C(13)	120.1(4)
C(11) -C(12) -C(135)	118.8(4)
C(13) -C(12) -C(135)	121.0(4)
Cr(1) -C(13) -C(12)	72.0(3)
Cr(1) -C(13) -C(14)	71.0(3)
Cr(1) -C(13) -C(132)	130.5(4)
C(12) -C(13) -C(14)	119.5(4)
C(12) -C(13) -C(132)	121.3(4)
C(14) -C(13) -C(132)	119.1(4)
Cr(1) -C(14) -C(13)	71.2(3)
Cr(1) -C(14) -C(15)	71.2(3)
Cr(1) -C(14) -C(155)	129.3(4)
C(13) -C(14) -C(15)	119.9(4)
C(13) -C(14) -C(155)	118.8(4)
C(15) -C(14) -C(155)	121.3(4)
Cr(1) -C(15) -C(14)	72.3(3)
Cr(1) -C(15) -C(16)	72.0(3)
Cr(1) -C(15) -C(152)	131.4(4)
C(14) -C(15) -C(16)	121.0(4)
C(14) -C(15) -C(152)	120.4(4)
C(16) -C(15) -C(152)	118.5(4)
Cr(1) -C(16) -C(11)	71.6(3)
Cr(1) -C(16) -C(15)	70.6(3)
Cr(1) -C(16) -C(115)	129.6(4)
C(11) -C(16) -C(15)	119.5(4)
C(11) -C(16) -C(115)	121.3(4)
C(15) -C(16) -C(115)	119.3(4)
C(11) -C(112)-C(113)	112.1(5)
C(112)-C(113)-C(114)	128.3(8)
C(113)-C(114)-C(115)	123.1(7)
C(16) -C(115)-C(114)	113.8(5)
C(13) -C(132)-C(133)	115.5(5)
C(132)-C(133)-C(134)	116.7(7)
C(133)-C(134)-C(135)	122.5(7)
C(12) -C(135)-C(134)	110.6(5)
C(15) -C(152)-C(153)	113.0(5)
C(152)-C(153)-C(154)	125.9(8)
C(153)-C(154)-C(155)	126.1(9)
C(14) -C(155)-C(154)	112.8(6)
Cr(1) -C(17) -O(17)	179.6(4)
Cr(1) -C(18) -O(18)	177.2(7)
Cr(1) -C(19) -O(19)	178.4(6)

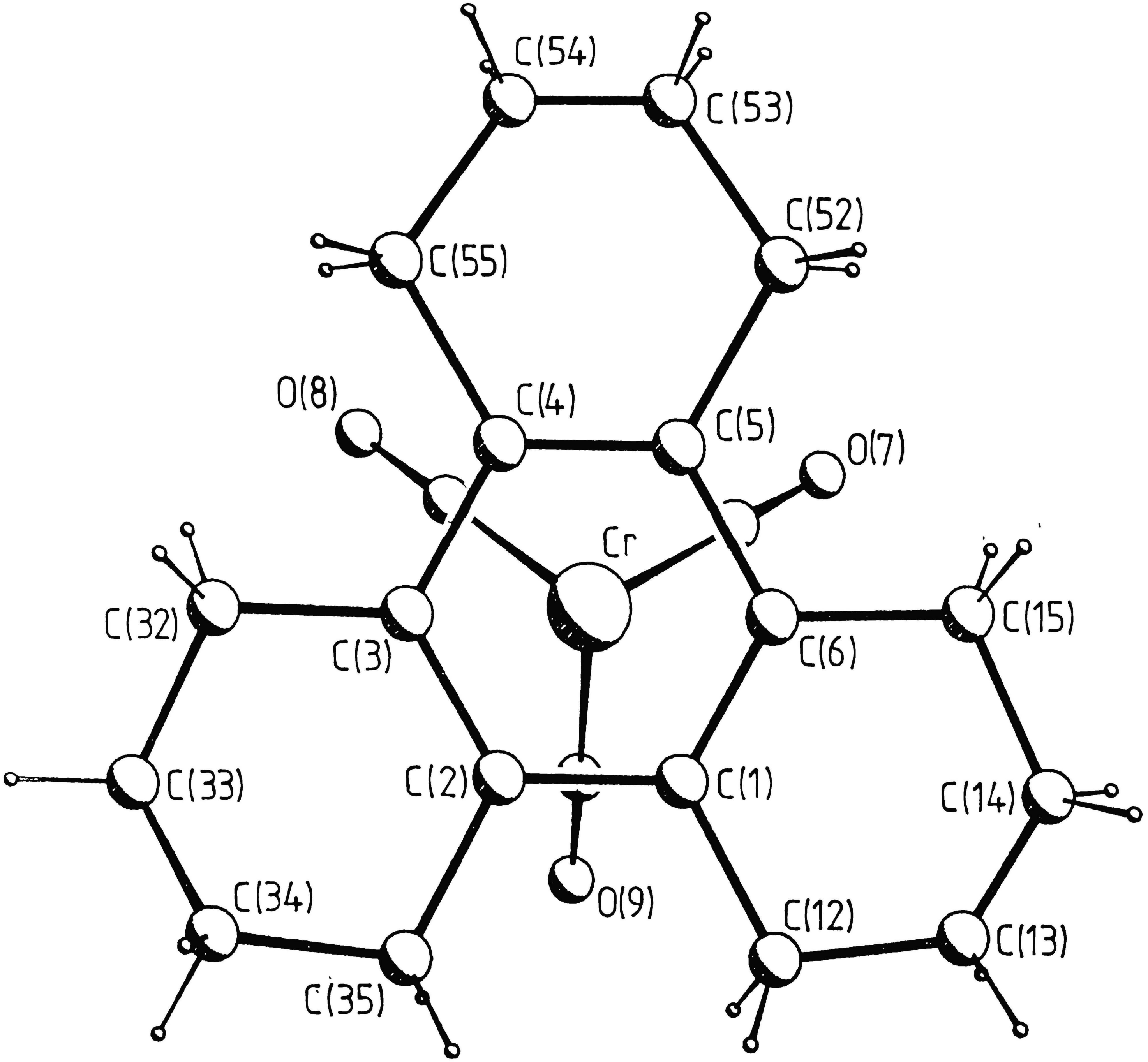


Figure 6.2 Plan view of one independent molecule of (η^6-$C_{18}H_{24}$)$Cr(CO)_3$

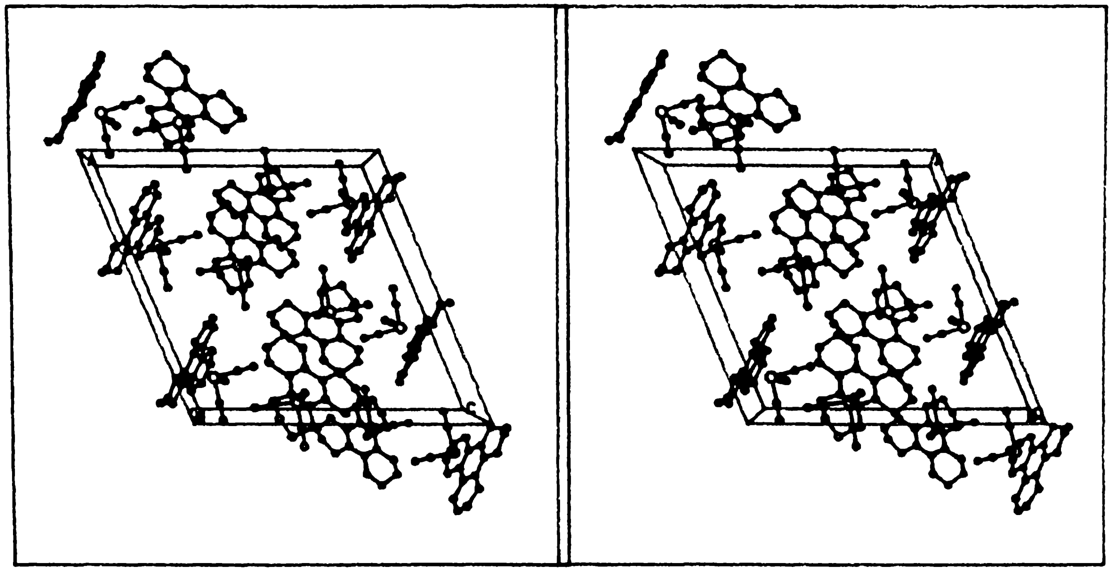
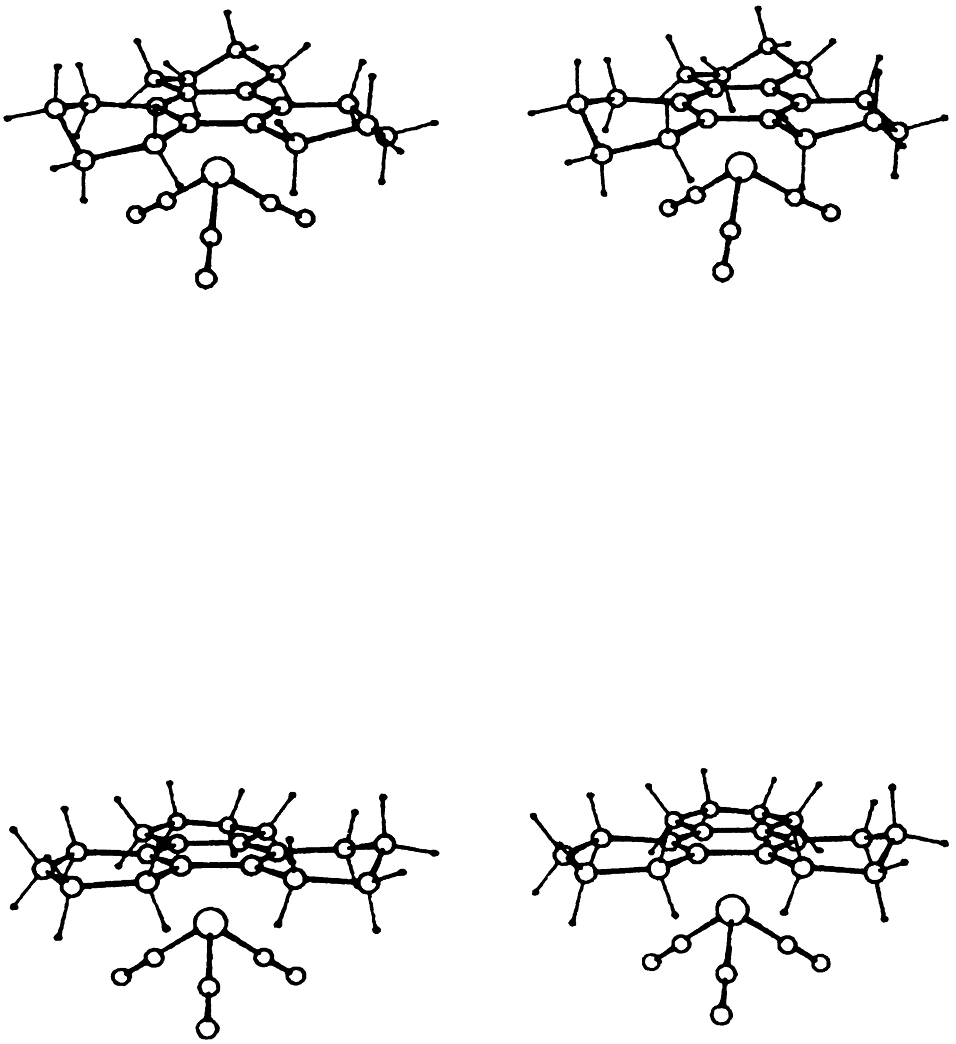


Figure 6.3 Stereoview of the unit cell of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$

Figure 6.4 Stereoview of the two independent molecules of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ (59)



group $P2_12_12_1$. Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer with monochromated Mo-K_α radiation, using a crystal of dimensions 0.26 X 0.18 X 0.16 mm.

Crystal data. $C_{21}H_{24}BF_4MnO_3$, M = 466.17, orthorhombic, space group $P2_12_12_1$ (No. 19), a 9.950 (2), b 10.398 (2), c 20.412 (3) A, U 2112 A^3. D_c 1.47 g cm^{-3} for Z = 4. F(000) = 960, μ(Mo-K_α) 6.2 cm^{-1}.

Intensity data were collected in the range $3° < 2\theta < 43°$ using a θ-2θ scan technique. A total of 1925 unique data were collected, and after correction for Lorentz, polarisation and absorption effects, the 1516 data for which $I > 3\sigma(I)$ were used in all calculations.

Solution and refinement. The structure was solved by Patterson methods and all non-hydrogen atoms were located by standard difference map techniques. In the final cycles of full-matrix, least-squares refinement, all non-hydrogen atoms, except the arene carbon atoms, were assigned anisotropic temperature factors and hydrogen atoms were included in calculated positions (d(C-H) 0.98 Å) with a common isotropic temperature factor. The refinement converged at R = 0.0551, R_w = 0.0580 where $w = [\sigma^2(F_0) + 0.0008F_0^2]^{-1}$, with no parameter shifting by more than 0.1σ in the final cycle. The high values for the thermal parameters of the fluorine atoms, and some residual electron density (ca. 0.7 e A^{-3}) indicated a partially disordered BF_4^- ion, but no attempts were made to compensate for this in the refinement. Bond angles and bond lengths appear in Table 6.2. A view of the cation normal to the arene plane is given in figure 6.5. The final positional and thermal parameters for all atoms appear in Appendix VI.

6.2.6 Crystal structure of the trigonal modification of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ (60)

Yellow triangular plates were obtained on recrystallisation from acetone/ether 4:1 (together with orthorhombic needles). Preliminary precession photography indicated trigonal symmetry. Intensity data were collected as for (59).

Table 6.2 Bond lengths and bond angles for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+ BF_4^-$ (60) (orthorhombic)

Bond lengths:

Mn	---C(1)	2.206 (7)	C(5)	---C(152)	1.504 (13)
Mn	---C(2)	2.212 (7)	C(6)	---C(155)	1.530 (13)
Mn	---C(3)	2.198 (7)	C(112)	---C(113)	1.500 (15)
Mn	---C(4)	2.229 (8)	C(113)	---C(114)	1.503 (15)
Mn	---C(5)	2.230 (8)	C(114)	---C(115)	1.461 (14)
Mn	---C(6)	2.195 (8)	C(132)	---C(133)	1.528 (16)
Mn	---C(31)	1.791 (12)	C(133)	---C(134)	1.450 (18)
Mn	---C(32)	1.809 (8)	C(134)	---C(135)	1.554 (17)
Mn	---C(33)	1.786 (11)	C(152)	---C(153)	1.520 (20)
C(1)	---C(2)	1.393 (10)	C(153)	---C(154)	1.322 (24)
C(1)	---C(6)	1.420 (11)	C(154)	---C(155)	1.495 (19)
C(1)	---C(112)	1.528 (11)	C(31)	---O(31)	1.149 (16)
C(2)	---C(3)	1.432 (10)	C(32)	---O(32)	1.149 (10)
C(2)	---C(115)	1.542 (12)	C(33)	---O(33)	1.148 (14)
C(3)	---C(4)	1.385 (11)	B	---F(1)	1.303 (16)
C(3)	---C(132)	1.518 (11)	B	---F(2)	1.440 (18)
C(4)	---C(5)	1.460 (11)	B	---F(3)	1.312 (15)
C(4)	---C(135)	1.518 (12)	B	---F(4)	1.253 (13)
C(5)	---C(6)	1.403 (11)	Mn	---Ring centroid	1.70

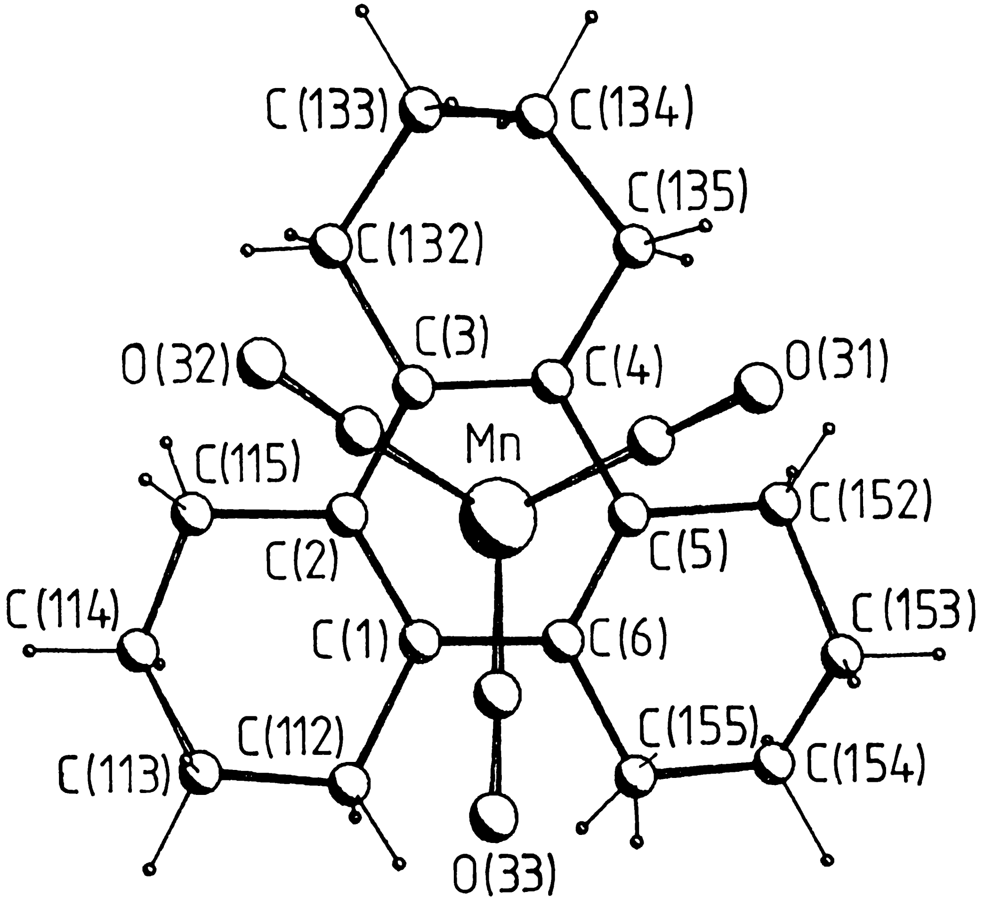


Figure 6.5 Plan view of the orthorhombic form of

$[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ (60)

Crystal Data: $C_{21}H_{24}BF_4MnO_3$, M = 466.17, trigonal, space group P3 or $P\bar{3}$ (see below), a 10.762 (2), c 20.679 (5) A, U 2074 A^3, D_c = 1.47 g cm^{-1} for Z = 4. F(000) = 960, $\mu(Mo\text{-}K_\alpha)$ 6.34 cm^{-1}, T = -130°C. A total of 7072 reflections were collected in the range $0°<2\theta<70°$ using a θ-2θ scan technique.

The solution of the structure was complicated by space group ambiguity and by disorder. The intensity data showed no systematic absences, and was solved initially in the non-centrosymmetric space group P3. This gave the positions of the four $(C_{18}H_{24})Mn$ fragments and the four BF_4^- ions, all lying on the three-fold axes, and these refined sensibly. A difference map showed two orientations for the unique carbonyl ligands on each cation, and these were included with half-occupancy in the final refinement. A full-matrix least-squares refinement with anisotropic temperature factors for the Mn, B, F and carbonyl C and O atoms, other atoms anisotropic, and with hydrogen atoms in calculated positions, converged at R = 0.0895, R_w = 0.1050 for 318 parameters and the 4693 unique reflections with $I>4\sigma(I)$, where $w = [\sigma^2(F) + 0.0008(F)^2]^{-1}$. Convergence was slow, there was significant correlation, and the final positional parameters could be divided into two sets related by a center of symmetry, so refinement was attempted in the centrosymmetric space group $P\bar{3}$. With the equivalent model for two independent formula units in the cell, refinement of the 165 parameters against the 4258 unique reflections with $I>4\sigma(I)$ converged with R = 0.1258, R_w = 0.1465, with $w = [\sigma^2(F) + 0.00015(F)^2]^{-1}$. For refinement in either space group there were several peaks in the range 1-2 e $Å^{-3}$ in the final difference map. We cannot be sure of the space group but in keeping with Marsh's recent recommendation[13] we shall assume the centrosymmetric space group $P\bar{3}$, with two independent $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ in the unit cell, while recognising that the disorder problems mean that bond parameters are not very reliable. Table 6.3 contains the full list of bond angles and bond lengths. The final positional and thermal parameters of all atoms appear in Appendix VII. Figure 6.6 illustrates a plan view of one independent cation.

6.3 Results and Discussion

The complex $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ was readily synthesised by reaction of $Cr(NH_3)_3(CO)_3$ and the ligand in refluxing dioxane. The chemical and spectroscopic properties were as expected by comparison with other (arene)$Cr(CO)_3$ compounds.[2]

The preparation of the complex (**60**) was straightforward, good yields being obtained according to equation 6.1:

$$C_{18}H_{24} + (CO)_5MnBr + AlCl_3 \longrightarrow [(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+ + AlCl_3Br^- + 2CO$$

equation 6.1

The complex was isolated as air-stable yellow crystals with BF_4^- as counter-ion. In solution the complex (**60**) exhibited the expected[6] two ν(CO) bands in the infrared spectrum. The ^{1}H-NMR showed two poorly resolved multiplets corresponding to the CH_2 groups α and β to the aromatic ring.

The crystal structure of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$, (**59**), consists of two independent molecules in the asymmetric unit which differ only in the conformations of the cyclohexene rings. The cyclohexene rings are expected to adopt 'half-boat' conformations, however in one molecule, pseudo 'half-boat' conformations are observed (see figure 6.4). The β-carbons have high thermal motion, therefore the flattened cyclohexene rings are an artifact arising from the averaging of two disordered half-boat conformations. Both independent molecules of (**59**) have the chromium atom centrally situated above the planar aromatic ring (see Figure 6.2).

Table 6.3 Bond angles and bond lengths for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+ BF_4^-$ **(60)** (trigonal form)

Bond Lengths (Å).

Mn(1) ---C(11)	2.200(5)
Mn(1) ---C(12)	2.177(5)
Mn(1) ---C(1A)	1.85(1)
Mn(1) ---C(1B)	1.82(1)
C(11) ---C(12)	1.425(8)
C(11) ---C(16)	1.521(8)
C(12) ---C(13)	1.489(8)
C(13) ---C(14)	1.54(1)
C(14) ---C(15)	1.54(1)
C(15) ---C(16)	1.550(9)
C(1A) ---O(1A)	1.12(2)
C(1A) ---C(1B)	1.70(2)
C(1B) ---O(1B)	1.18(2)
O(1B) ---O(2B)	1.47(2)
Mn(2) ---C(21)	2.239(6)
Mn(2) ---C(22)	2.235(5)
Mn(2) ---C(2A)	1.78(1)
Mn(2) ---C(2B)	1.75(2)
C(21) ---C(22)	1.414(8)
C(21) ---C(26)	1.516(8)
C(22) ---C(23)	1.524(8)
C(23) ---C(24)	1.520(9)
C(24) ---C(25)	1.520(9)
C(25) ---C(26)	1.519(9)
C(2A) ---O(2A)	1.16(2)
C(2A) ---C(2B)	1.14(2)
C(2A) ---O(2B)	1.86(2)
O(2A) ---C(2B)	1.91(2)
C(2B) ---O(2B)	1.18(2)
B(1) ---F(11)	1.37(1)
B(1) ---F(12)	1.398(5)
B(2) ---F(21)	1.42(2)
B(2) ---F(22)	1.390(6)

Bond Angles (degrees).

C(11) -Mn(1) -C(12)	38.0(2)
C(11) -Mn(1) -C(1A)	123.1(5)
C(11) -Mn(1) -C(1B)	88.2(4)
C(12) -Mn(1) -C(1A)	160.9(4)
C(12) -Mn(1) -C(1B)	115.9(4)
C(1A) -Mn(1) -C(1B)	55.2(6)
Mn(1) -C(11) -C(12)	70.1(3)
Mn(1) -C(11) -C(16)	132.2(4)
C(12) -C(11) -C(16)	120.2(5)
Mn(1) -C(12) -C(11)	71.9(3)
Mn(1) -C(12) -C(13)	132.4(4)
C(11) -C(12) -C(13)	123.0(5)
C(12) -C(13) -C(14)	113.1(5)
C(13) -C(14) -C(15)	108.0(6)
C(14) -C(15) -C(16)	109.5(6)
C(11) -C(16) -C(15)	112.0(5)
Mn(1) -C(1A) -O(1A)	176(1)
Mn(1) -C(1A) -C(1B)	61.6(6)
O(1A) -C(1A) -C(1B)	121(1)
Mn(1) -C(1B) -C(1A)	63.2(6)
Mn(1) -C(1B) -O(1B)	178(2)
C(1A) -C(1B) -O(1B)	117(1)
C(1B) -O(1B) -O(2B)	127(1)
C(21) -Mn(2) -C(22)	36.8(2)
C(21) -Mn(2) -C(2A)	90.2(4)
C(21) -Mn(2) -C(2B)	92.9(6)
C(22) -Mn(2) -C(2A)	95.9(5)
C(22) -Mn(2) -C(2B)	118.6(6)
C(2A) -Mn(2) -C(2B)	37.5(7)
Mn(2) -C(21) -C(22)	71.4(3)
Mn(2) -C(21) -C(26)	132.9(4)
C(22) -C(21) -C(26)	121.6(5)
Mn(2) -C(22) -C(21)	71.7(3)
Mn(2) -C(22) -C(23)	130.9(4)
C(21) -C(22) -C(23)	120.5(5)
C(22) -C(23) -C(24)	114.0(5)
C(23) -C(24) -C(25)	109.8(5)
C(24) -C(25) -C(26)	110.8(5)
C(21) -C(26) -C(25)	113.4(5)
Mn(2) -C(2A) -O(2A)	177(1)
Mn(2) -C(2A) -C(2B)	69(1)
Mn(2) -C(2A) -O(2B)	106.1(8)
O(2A) -C(2A) -C(2B)	112(2)
O(2A) -C(2A) -O(2B)	75(1)
C(2B) -C(2A) -O(2B)	37(1)
C(2A) -O(2A) -C(2B)	33.5(9)
Mn(2) -C(2B) -C(2A)	72(1)
Mn(2) -C(2B) -O(2A)	107(1)
Mn(2) -C(2B) -O(2B)	167(2)
C(2A) -C(2B) -O(2A)	34.3(9)
C(2A) -C(2B) -O(2B)	107(2)
O(2A) -C(2B) -O(2B)	73(1)
O(1B) -O(2B) -C(2A)	142(1)
O(1B) -O(2B) -C(2B)	132(1)
F(11) -B(1) -F(12)	110.4(4)
F(21) -B(2) -F(22)	109.2(5)

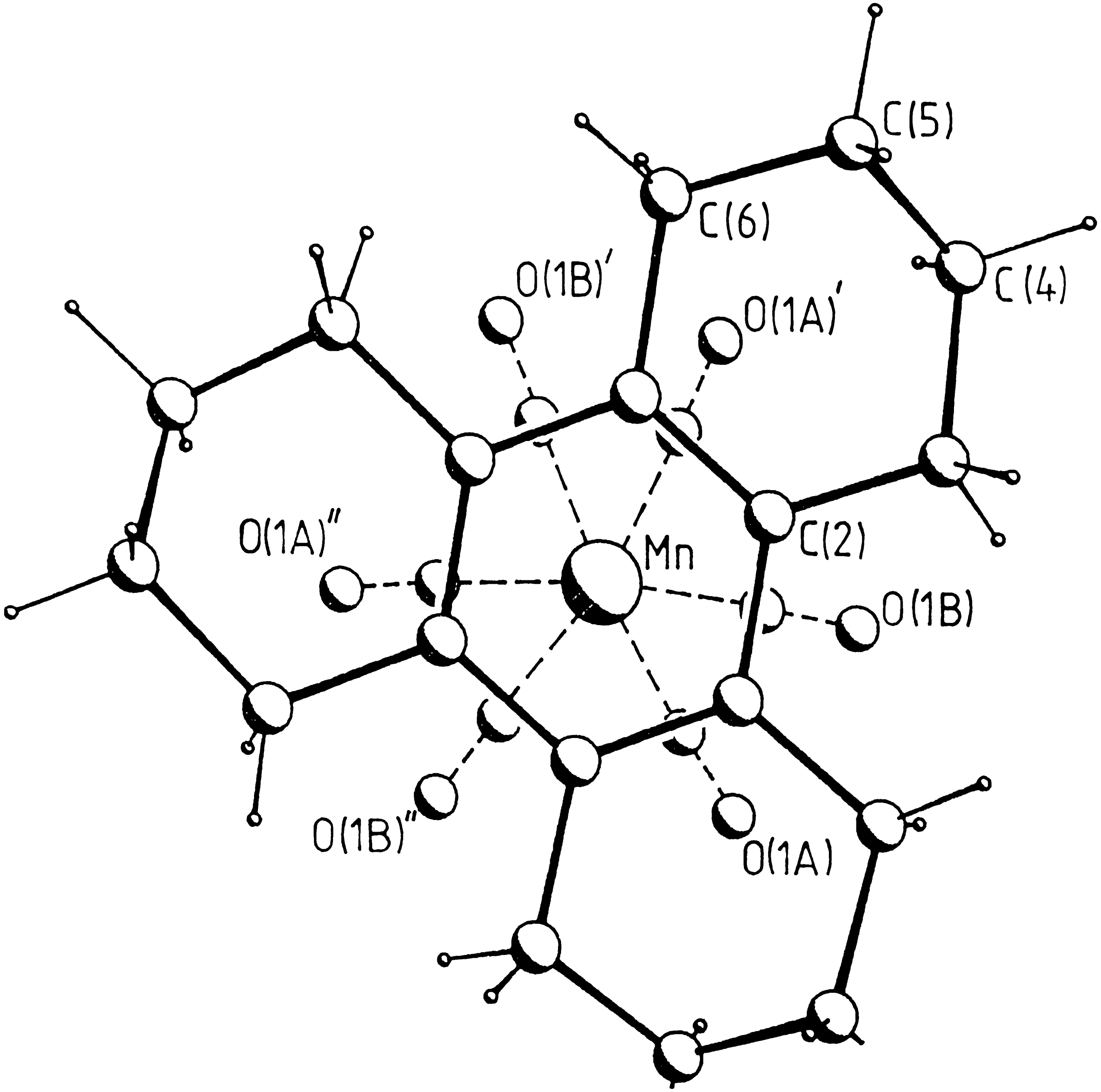


Figure 6.6 Plan view of the trigonal form of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ BF_4^- (60)

Crystals of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ (**60**; orthorhombic) contain discrete cations and anions. The cations have essentially C_3 symmetry with the planar ring sitting above the $Mn(CO)_3$ fragment (figure 6.5).

The M---Ring centroid distance for structures (**59**) and (**60**) (orthorhombic) are surprisingly similar, 1.72 and 1.70 Å respectively. This suggests a difference in the bonding radii of Cr(0) and Mn(I) of ca. 0.02 Å, which is less than that found, for example, for $Cr(CO)_3(dien)$[14] and $Mn(CO)_3(NH_3)_3$[15] where a difference of 0.05-0.09 Å is found for the M-C and M-N bonds. It is interesting that the increased nuclear charge on going from the Cr complex (**59**) to the Mn complex (**60**; orthorhombic) affects the M-C(ring) and M-CO distances nearly equally, since the increased charge on the metal might have been expected to enhance the bonding to the π-donor arene ligand to a greater extent than to CO, where the π-acceptor interaction is more important.

The most interesting feature of the structures for the two independent molecules of (**59**) and the orthorhombic modification of (**60**) is that the carbonyl groups are projected onto the unbridged C-C bonds of the planar arene, corresponding to orientation (iii) (see Figure 6.2). This is true for all three species despite the fact that they are in different crystal environments, and hence subject to different crystal packing interactions so this may indicate a genuine preference for this configuration.

There is clear evidence for bond localisation in the arene ring in both $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$, (**59**) and the orthorhombic form of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+BF_4^-$ (**60**). For both structures the unbridged aromatic C-C bonds are longer than the non-bridged set (see Table 6.4). This is consistent with higher π-electron density in the C-C bonds towards which the acceptor orbitals of the $M(CO)_3$ groups are directed but whether this is caused by the $M(CO)_3$ group or directs it is not clear.

We have deliberately not discussed the second crystalline modification of (60) in detail since the structure could not be precisely determined because of disorder problems and space group ambiguity (see experimental). Nevertheless the main features are clear. The structure consists of two independent pairs (in space group $P\bar{3}$) of discrete ions, $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ and BF_4^-, stacked alternately on the crystallographic three-fold axes. While the BF_4^- and the $(C_{18}H_{24})Mn$ fragment refined cleanly, there was some difficulty in defining the CO ligands of the cation. This arose because of disorder, with apparently equal numbers of cations with conformations (iii) and (iv) in the crystal. Poor refinement of CO ligands with half-occupancy, and residual electron density in the final difference map in regions associated with the CO groups suggested that there is little barrier to rotation of the $Mn(CO)_3$ group with respect to the arene ring, so that in this crystal there is no preference for either of the idealised configurations. The low accuracy of the structure precludes detailed discussion of bond lengths. However the average Mn-C(ring) and Mn-CO distances are essentially the same as in the orthorhombic form (see table 6.4). The variations in the lengths of the C-C bonds of the arene rings in the two cations are much less than in the other ordered crystalline form or in the chromium analogue, consistent with the conclusion that we are observing an average of the two conformations (iii) and (iv).

We can conclude from these structural studies that the aromaticity of the free ligand is not perturbed by bond localisation (induced by the fused alicyclic rings) sufficiently to strongly direct the orientation of the metal fragment. There may be a slight preference for the form in which the CO ligands eclipse the unbridged C-C bonds of the arene group, but the origin of this, if real, is not clear. The fact that the magnitude of the bond alternation in the arene group of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ is similar to that in higher symmetry arene complexes[16] suggests the fused cyclohexene rings have little influence on the π-electron distribution in the arene ring. The complete disorder of the $Mn(CO)_3$ tripod in the trigonal crystals clearly indicates minimal intramolecular energy differences for the conformational pair (iii) and (iv).

TABLE 6.4

Average Bond Lengths in $[(\eta^6\text{-}C_{18}H_{24})M(CO)_3]$

	M = Cr(0)		M = Mn(I)	
	Molecule 1	Molecule 2	Trigonal[a]	Orthorhombic
M-C(arene)	2.230(5)	2.229(5)	2.21	2.212(7)
C(arene)-C(arene)				
- bridged	1.399(8)	1.395(8)	1.42	1.393(10)
- unbridged	1.434(8)	1.430(8)	1.43	1.437(10)
M - CO	1.821(6)	1.822(6)	1.80	1.80(1)
C - O	1.157(7)	1.153(7)	1.15	1.15(1)
C(arene)-C_α	1.520(6)	1.522(7)	1.51	1.52(1)
C_α - C_β	1.48(1)	1.50(1)	1.53	1.51(1)
C_β - C_β[b]	1.26(1)	1.44(1)	1.53	1.43(1)

(a) Averaged over both cations; accuracy diminished by disorder.

(b) Shortened by excessive thermal motion.

References

(1) E. L. Muetterties, J. R. Bleeke, E. J. Wucherer and T. A. Albright,

Chem. Rev., **82**, 499, 1982.

(2) R. Davis and L. A. P. Kane-Maquire, in

"Comprehensive Organometallic Chemistry",

ed. G. Wilkinson, F. G. A. Stone, E. W. Abel,

Pergamon Press, Oxford, **1982**, Ch. 26.

(3) T. A. Albright,

Acc. Chem. Res., **15**, 149, **1982**.

(4) R. D. Rogers, J. L. Atwood, T. A. Albright, W. A. Lee and M. D. Rausch,

Organometallics, **3**, 263, **1984**.

(5) R. C. Cambie, G. R. Clark, A. C. Gourdie, P. S. Rutledge and P. D. Woodgate,

J. Organomet. Chem., **297**, 177, **1985**.

(6) G. A. M. Munro and P. L. Pauson,

Z. Anorg. Allgem. Chem., **458**, 211, **1979**.

(7) G. A. M. Munro and P. L. Pauson,

Israel J. Chem., **15**, 258, **1977**.

(8) Y. K. Chung, P. G. Williard and D. A. Sweigart,

Organometallics, **1**, 1053, **1982**.

(9) T. A. Albright and B. K. Carpenter,

Inorg. Chem., **19**, 3092, **1980**.

T. A. Albright, P. Hofmann and R. Hoffmann,

J. Am. Chem. Soc., **99**, 7546, **1977**.

(10) Y. Apeloig and D. Arad,

J. Am. Chem. Soc., **108**, 3241, **1986**.

(11) C. Mannich,

Chem. Ber., **40**, 153, **1907**.

P. Rollin,

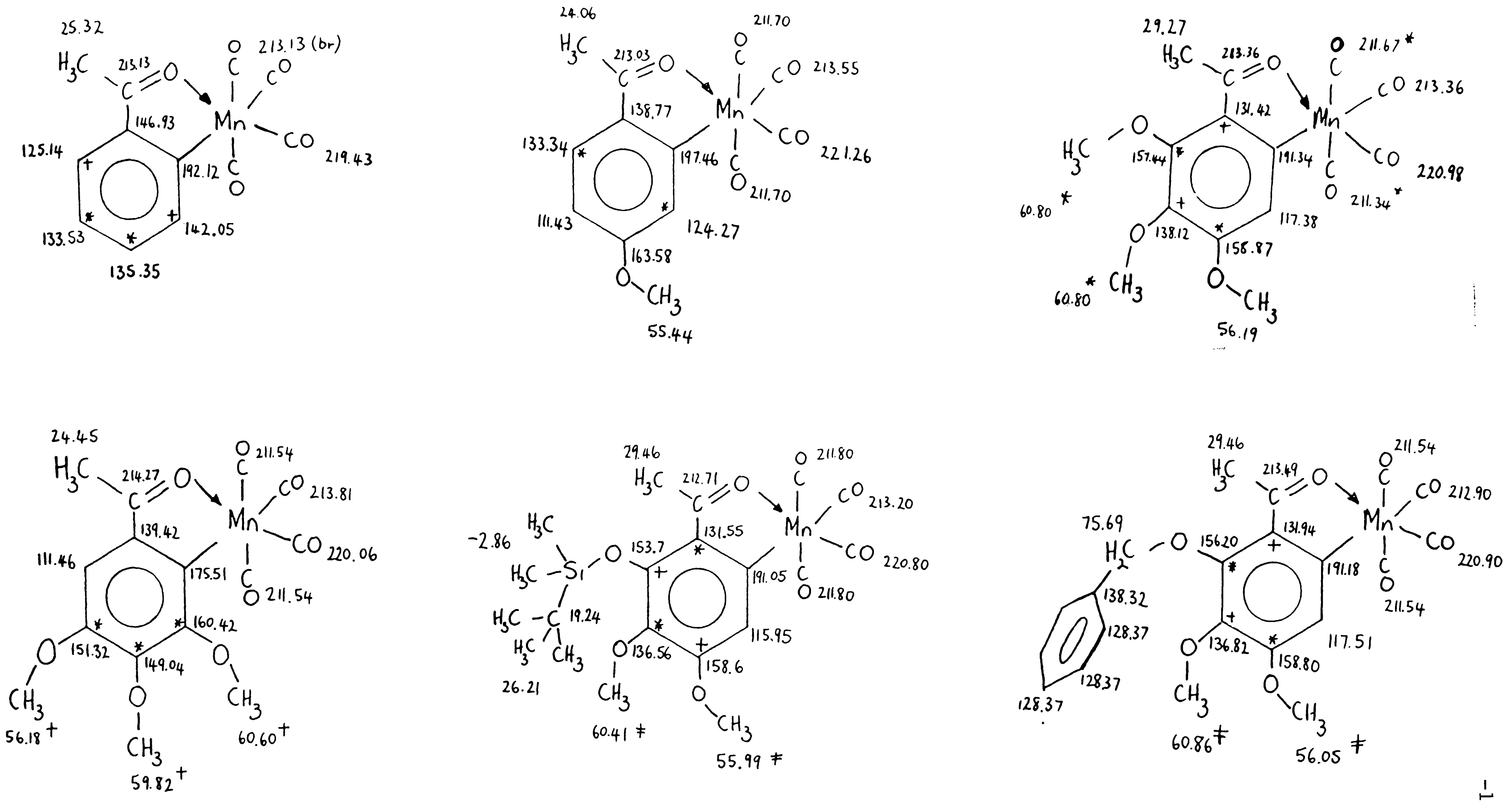
Bull. Chem. Soc. France, 1509, **1973**.

(12) M. D. Rausch, G. A. Moser, E. J. Zaiko and A. L. Lipman, *J. Organomet. Chem.*, **23**, 185, **1970**.

(13) F. A Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851, **1966**.

(14) M. Herberhold, F. Wehrmann, D. Neugebauer and G. Huttner, *J. Organomet. Chem.*. **152**, 329, **1978**.

(15) B. Rees and P. Coppens, *Acta Cryst.*, **B29**, 2516, **1973**.

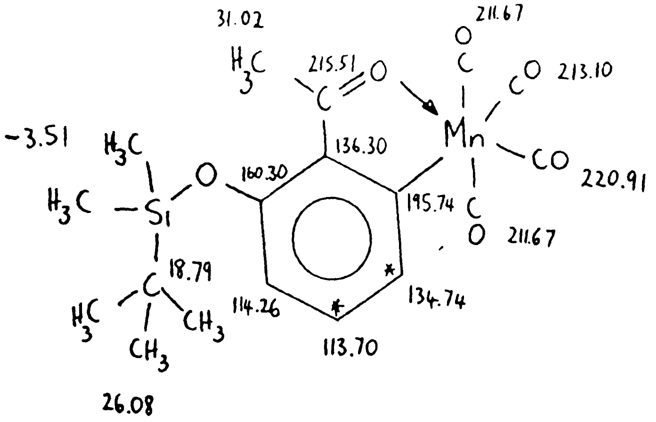


Appendix I

^{1}H-NMR and ^{13}C-NMR chemical shift assignments for all orthomanganated ketones prepared in this study

signal not observed

+, *, # assignments interchangeable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H_3C
Si
O
160.30
31.02
H_3C
215.51
C
O
136.30
Mn
O
C
211.67
CO
213.10
CO
220.91
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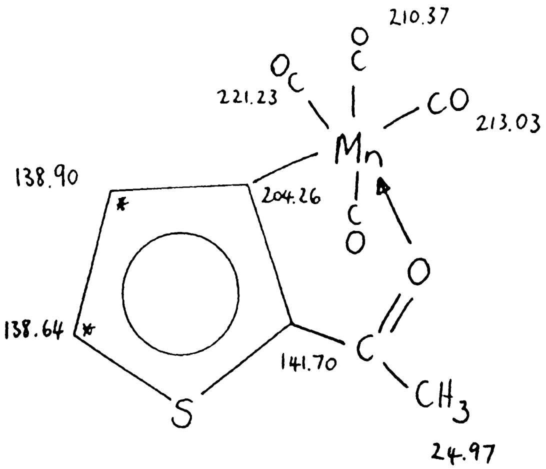
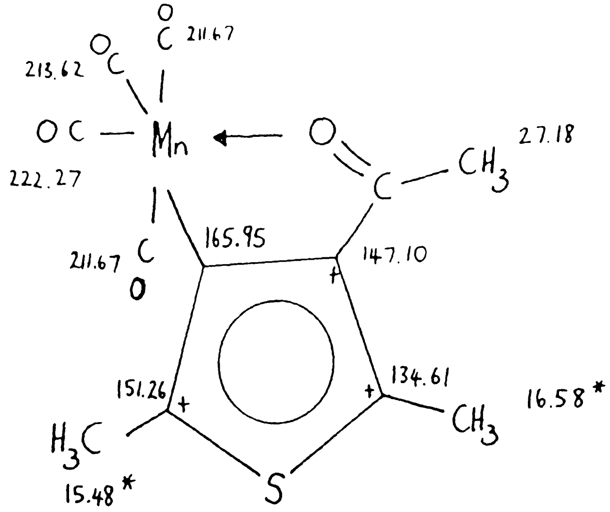
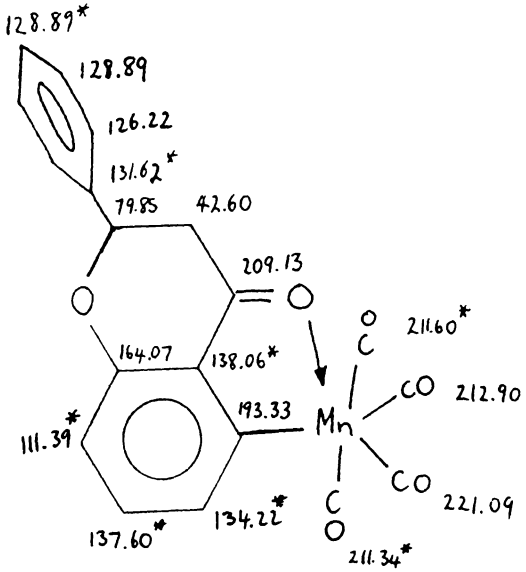
CH_3
CH_3
26.08


210.37
O
C
OC
221.23
Mn
CO
213.03
138.90
204.26
C
O
138.64
O
C
141.70
CH_3
S
24.97


O
C
211.67
OC
213.62
OC
Mn
222.27
O
C
CH_3
27.18
C
O
211.67
165.95
147.10
151.26
134.61
H_3C
15.48 *
CH_3
16.58 *
S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42.60
209.13
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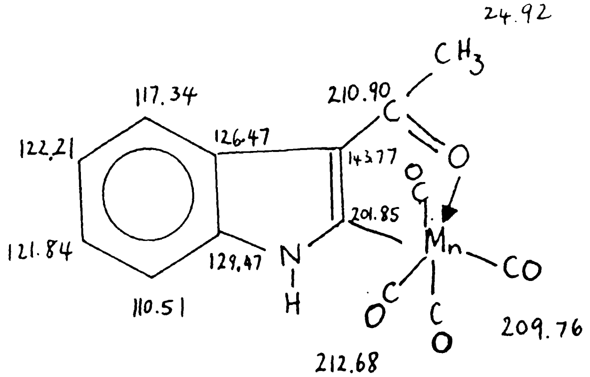
CO
212.90
193.33
Mn
111.39*
CO
221.09
C
O
211.34*
137.60*
134.22*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CH_3
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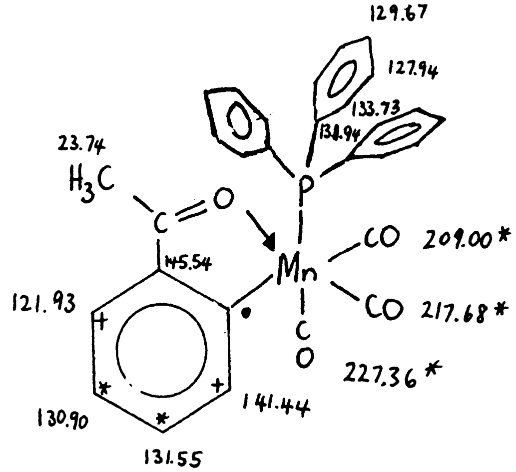
N
H
129.47
Mn
CO
110.51
OC
C
O
212.68
209.76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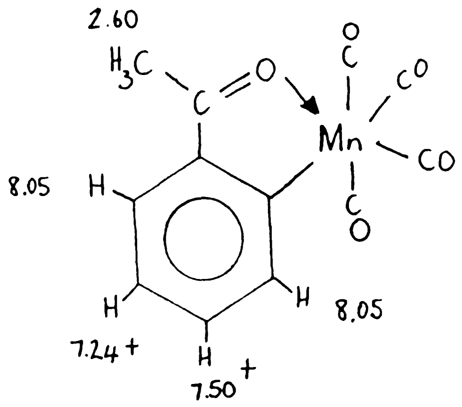
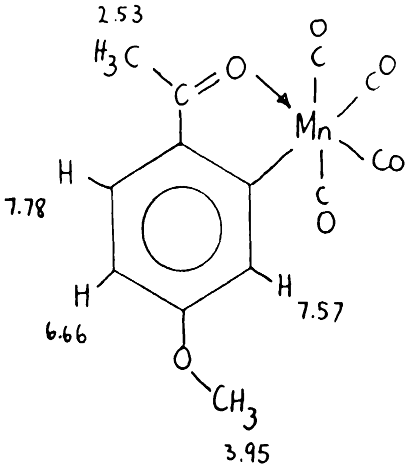
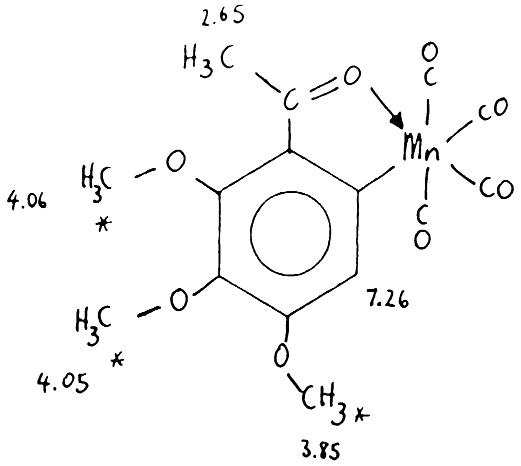
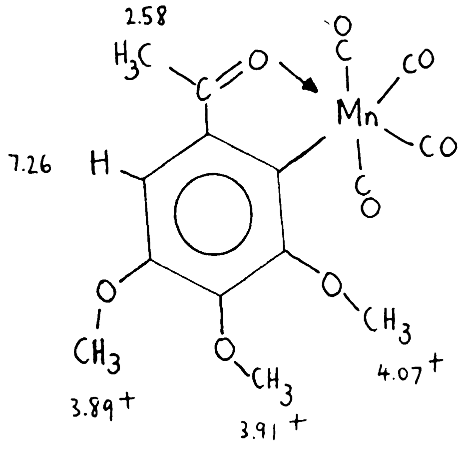
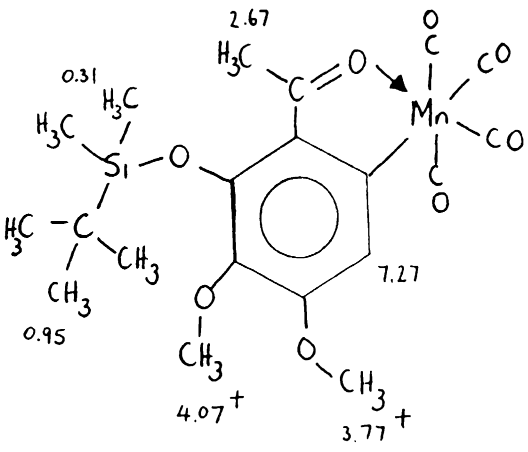
133.73
134.94
P
23.74
H_3C
C
O
145.54
Mn
CO
209.00*
121.93
CO
217.68*
C
O
227.36*
141.44
130.90
131.55

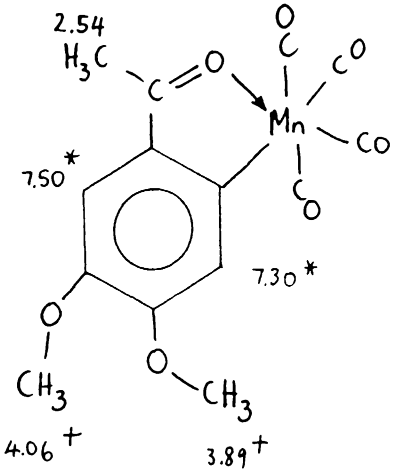

2.60
H3C
C=O
Mn
CO
8.05 H
H 8.05
7.24+ H
H 7.50+

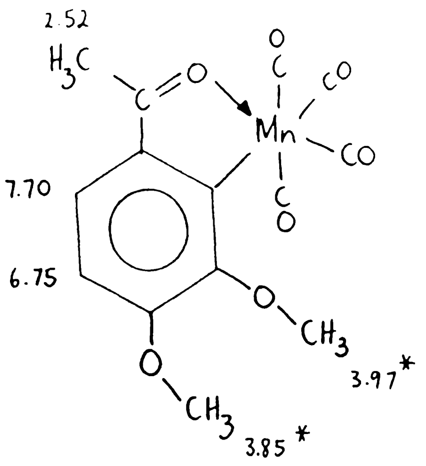

2.53
H3C
C=O
Mn
CO
7.78 H
H 7.57
6.66 H
O—CH3
3.95

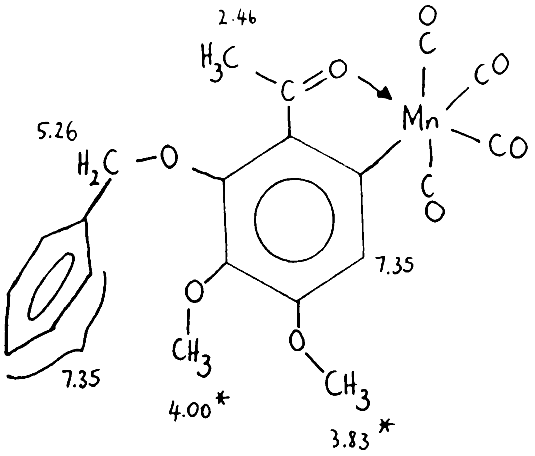

2.65
H3C
C=O
Mn
CO
4.06 H3C—O *
H3C—O
4.05 *
7.26
O—CH3*
3.85

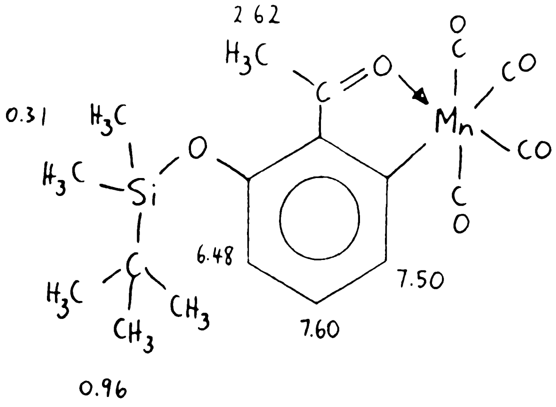

2.58
H3C
C=O
Mn
CO
7.26 H
O—CH3
3.89+
O—CH3
3.91+
O—CH3
4.07+

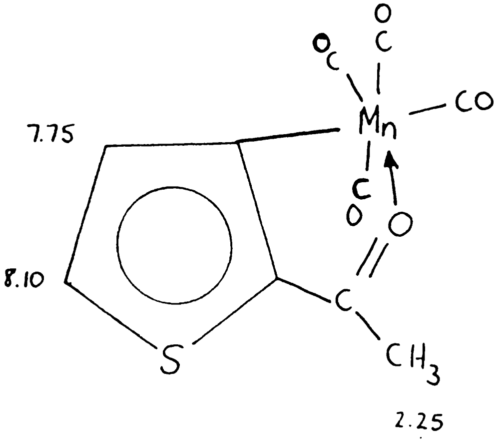

2.67
H3C
C=O
Mn
CO
0.31
H3C
H3C
Si—O
H3C—C—CH3
CH3
0.95
7.27
O—CH3
4.07+
O—CH3
3.77+

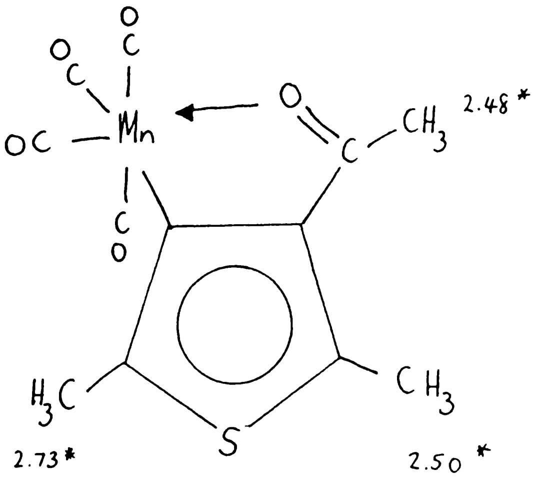

2.54
H3C
C=O
Mn
CO
7.50*
7.30*
O—CH3
4.06+
O—CH3
3.89+

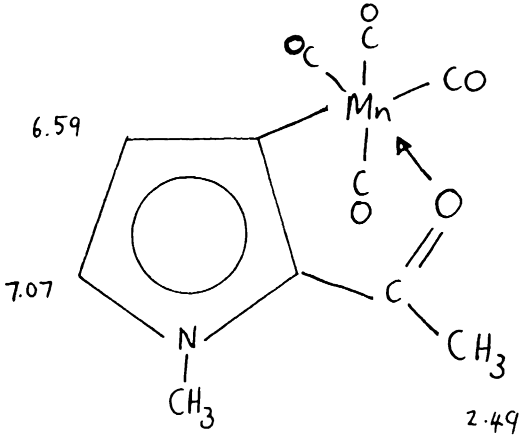

2.52
H3C
C=O
Mn
CO
CO
CO
CO
7.70
6.75
O–CH3
3.97*
O–CH3
3.85*

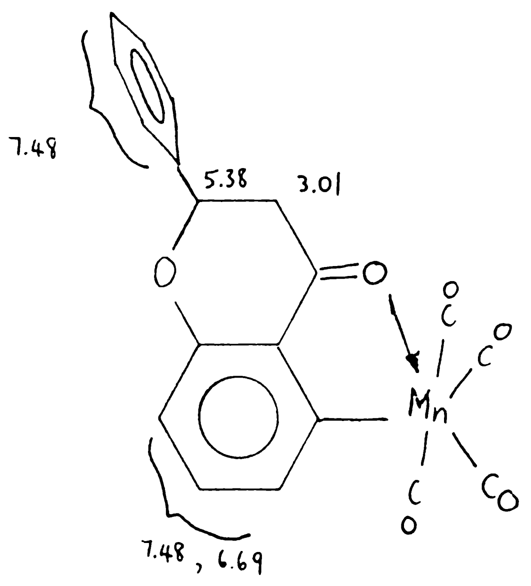

2.46
H3C
C=O
Mn
CO
CO
CO
CO
5.26
H2C
O
7.35
7.35
O
CH3
4.00*
O
CH3
3.83*

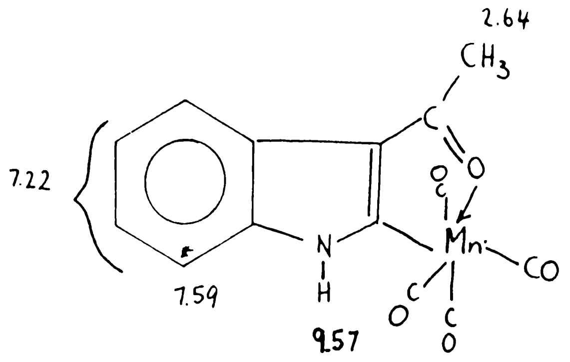

2.62
H3C
C=O
Mn
CO
CO
CO
CO
0.31
H3C
H3C
Si
O
C
H3C
CH3
CH3
0.96
6.48
7.60
7.50

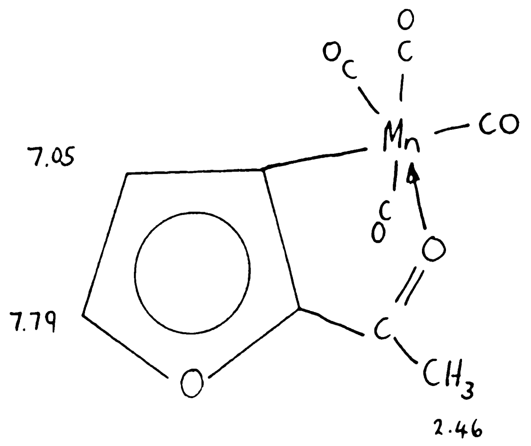

OC
CO
Mn
CO
CO
7.75
8.10
S
O
C
CH3
2.25


OC
CO
OC
Mn
CO
O
C
CH3
2.48*
H3C
S
CH3
2.73*
2.50*


OC
CO
Mn
CO
CO
6.59
7.07
N
CH3
O
C
CH3
2.49


7.48
5.38
3.01
O
O
Mn
OC
CO
CO
CO
7.48 , 6.69


2.64
CH3
7.22
C
O
OC
Mn
CO
N
H
OC
CO
7.59
9.57


OC
CO
Mn
CO
7.05
OC
O
7.79
O
C
CH3
2.46

Appendix II

Thermal and positional parameters for η^2-(3-acetyl-2,5-dimethylthien-4-yl tetracarbonylmanganese (11)

Final positional parameters

ATOM	X/A	Y/B	Z/C	ATOM	X/A	Y/B	Z/C
Mn	0.1604(2)	0.2289(1)	0.5687(1)	O(4)	0.363(1)	0.3814(9)	0.6032(6)
S	0.0994(3)	0.1159(2)	0.7847(1)	C(5)	-0.031(1)	0.0767(8)	0.5978(6)
C(1)	0.300(1)	0.1365(9)	0.5676(6)	O(5)	0.0113(9)	0.1259(6)	0.5497(4)
O(1)	0.387(1)	0.0813(9)	0.5691(5)	C(6)	0.028(1)	0.0988(7)	0.6633(5)
C(2)	0.173(1)	0.257(1)	0.4790(7)	C(7)	0.006(1)	0.0577(8)	0.7248(6)
O(2)	0.184(1)	0.2746(8)	0.4233(5)	C(8)	0.175(1)	0.1962(8)	0.7270(6)
C(3)	0.022(1)	0.3175(8)	0.5877(6)	C(9)	0.129(1)	0.1778(7)	0.6644(5)
O(3)	-0.059(1)	0.3731(7)	0.6002(6)	C(10)	-0.2099(7)	0.0034(5)	0.5672(3)
C(4)	0.285(1)	0.3208(9)	0.5884(7)	C(11)	-0.085(1)	-0.027(1)	0.7452(7)
C(12)	0.280(1)	0.2659(9)	0.7525(7)				

Thermal parameters

ATOM	U11	U22	U33	U23	U13	U12
Mn	0.0290(3)	0.0292(3)	0.0183(3)	-0.0012(1)	0.0010(1)	-0.0035(1)
S	0.0399(4)	0.0414(4)	0.0250(4)	0.0063(2)	-0.0026(2)	0.0044(3)
C(1)	0.0365(6)					
O(1)	0.051(1)	0.067(2)	0.052(2)	0.000(1)	-0.002(1)	0.014(1)
C(2)	0.0402(6)					
O(2)	0.073(2)	0.064(2)	0.027(1)	0.0092(9)	0.006(1)	0.006(1)
C(3)	0.0343(5)					
O(3)	0.057(1)	0.045(1)	0.056(1)	-0.004(1)	0.001(1)	0.007(1)
C(4)	0.0408(6)					
O(4)	0.068(2)	0.066(2)	0.053(1)	-0.011(1)	0.009(1)	-0.038(1)
C(5)	0.0311(5)					
O(5)	0.0349(9)	0.0404(9)	0.0232(8)	-0.0078(7)	0.0006(7)	-0.0049(7)
C(6)	0.0275(5)					
C(7)	0.0326(5)					
C(8)	0.0291(5)					
C(9)	0.0263(4)					
C(10)	0.0397(6)					
C(11)	0.0450(7)					
C(12)	0.0356(6)					

Final positional and thermal parameters of calculated hydrogen atoms

ATOM	X/A	Y/B	Z/C	U11
H(1)	-0.2141(3)	0.0114(2)	0.6195(2)	0.100
H(2)	-0.1099(3)	-0.0627(2)	0.5842(2)	0.100
H(3)	-0.1783(3)	0.0225(2)	0.5414(2)	0.100
H(4)	-0.0674(3)	-0.0224(2)	0.7936(2)	0.071
H(5)	-0.0478(3)	-0.0873(2)	0.7280(2)	0.071
H(6)	-0.1843(3)	-0.0225(2)	0.7363(2)	0.071
H(7)	0.2545(3)	0.2799(2)	0.7998(1)	0.063
H(8)	0.2782(3)	0.3256(2)	0.7269(1)	0.063
H(9)	0.3729(3)	0.2378(2)	0.7515(1)	0.063

Appendix III

Thermal and positional parameters for (36)

Thermal parameters

ATOM	U11	U22	U33	U23	U13	U12
C(1)	0.0368(8)					
C(2)	0.0282(7)					
C(3)	0.0250(7)					
C(4)	0.0284(7)					
C(5)	0.0286(7)					
C(6)	0.0266(7)					
C(7)	0.0259(7)					
C(8)	0.0254(7)					
N	0.0292(6)					
C(9)	0.029(2)	0.061(3)	0.030(2)	0.011(2)	0.001(2)	-0.007(2)
C(10)	0.0391(9)					
O(1)	0.021(1)	0.039(1)	0.033(1)	-0.003(1)	0.0131(9)	0.001(1)
O(2)	0.040(1)	0.050(2)	0.032(1)	0.012(1)	0.018(1)	-0.010(1)
O(3)	0.023(1)	0.039(1)	0.035(1)	0.002(1)	0.016(1)	-0.003(1)
O(4)	0.025(1)	0.039(1)	0.024(1)	0.007(1)	0.0045(9)	-0.002(1)
O(5)	0.025(1)	0.037(1)	0.028(1)	0.003(1)	0.010(1)	-0.006(1)

Final positional parameters

ATOM	X/A	Y/B	Z/C	ATOM	X/A	Y/B	Z/C
C(1)	0.6517(4)	0.6113(6)	0.9714(2)	N	0.3875(3)	0.5903(4)	0.7451(2)
C(2)	0.6011(3)	0.4902(5)	0.8869(2)	C(9)	-0.0254(4)	0.3154(7)	0.5735(2)
C(3)	0.4750(3)	0.3429(5)	0.8561(2)	C(10)	0.0547(4)	-0.1621(6)	0.6866(2)
C(4)	0.4617(3)	0.1710(5)	0.8939(2)	O(1)	0.7218(2)	0.3975(4)	0.8949(1)
C(5)	0.3180(3)	0.0649(5)	0.8463(2)	O(2)	0.2987(3)	-0.0869(4)	0.8810(1)
C(6)	0.1952(3)	0.1442(5)	0.7565(2)	O(3)	0.0620(2)	0.0466(4)	0.7179(1)
C(7)	0.2118(3)	0.3153(5)	0.7179(2)	O(4)	0.1157(2)	0.4080(4)	0.6378(1)
C(8)	0.3538(3)	0.4214(5)	0.7700(2)	O(5)	0.5330(2)	0.6455(4)	0.8110(1)

Final positional and thermal parameters of calculated hydrogen atoms

ATOM	X/A	Y/B	Z/C	U11
H(1)	0.5670(4)	0.6781(6)	0.9660(2)	0.027
H(2)	0.7222(4)	0.7204(6)	0.9808(2)	0.027
H(3)	0.6999(4)	0.5139(6)	1.0231(2)	0.027
H(4)	-0.0811(4)	0.4044(7)	0.5193(2)	0.058
H(5)	-0.0809(4)	0.3005(7)	0.6004(2)	0.058
H(6)	-0.0099(4)	0.1755(7)	0.5568(2)	0.058
H(7)	-0.0445(4)	-0.2192(6)	0.6604(2)	0.062
H(8)	0.1278(4)	-0.2510(6)	0.7376(2)	0.062
H(9)	0.0751(4)	-0.1604(6)	0.6404(2)	0.062
H(10)	0.5458(3)	0.1172(5)	0.9521(2)	0.025

Appendix IV

Thermal and positional parameters for chloro-(2-acetylphenyl)mercury(II)

Thermal parameters

ATOM	U11	U22	U33	U23	U13	U12
Hg	0.0227(4)	0.0141(4)	0.0168(4)	0.0020(1)	0.0014(3)	0.0005(3)
Cl	0.033(2)	0.014(1)	0.021(2)	0.001(1)	0.003(2)	0.007(2)
C(1)	0.013(2)					
C(2)	0.014(2)					
C(3)	0.023(3)					
C(4)	0.023(3)					
C(5)	0.023(3)					
C(6)	0.019(3)					
C(7)	0.019(3)					
C(8)	0.027(3)					
O(1)	0.028(2)					

Final positional and thermal parameters of calculated hydrogen atoms

ATOM	X/A	Y/B	Z/C
H(1)	1.302(2)	-0.086(1)	1.0296(8)
H(2)	1.311(3)	-0.310(1)	1.0586(9)
H(3)	1.011(3)	-0.396(1)	1.1594(9)
H(4)	0.703(3)	-0.265(1)	1.2272(9)
H(5)	0.385(3)	-0.156(1)	1.295(1)
H(6)	0.325(3)	-0.008(1)	1.283(1)
H(7)	0.571(3)	-0.052(1)	1.337(1)

Final positional parameters

ATOM	X/A	Y/B	Z/C	ATOM	X/A	Y/B	Z/C
Hg	0.9955(1)	0.1462(1)	1.0820(1)	C(4)	1.011(3)	-0.305(1)	1.1467(9)
Cl	1.0111(7)	0.3620(3)	1.0507(2)	C(5)	0.826(3)	-0.229(1)	1.1854(9)
C(1)	1.008(3)	-0.045(1)	1.1127(8)	C(6)	0.827(3)	-0.098(1)	1.1666(8)
C(2)	1.180(2)	-0.124(1)	1.0711(8)	C(7)	0.625(3)	-0.018(1)	1.211(1)
C(3)	1.186(3)	-0.255(1)	1.0864(9)	C(8)	0.459(3)	-0.072(1)	1.286(1)
O(1)	0.600(2)	0.092(1)	1.1907(7)				

Appendix V

Thermal parameters for $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$

ATOM	U11	U22	U33	U23	U13	U12
Cr(1)	0.0404(5)	0.0324(5)	0.0378(5)	0.0001(4)	0.0188(4)	-0.0008(4)
C(11)	0.040(1)					
C(12)	0.038(1)					
C(13)	0.039(1)					
C(14)	0.039(1)					
C(15)	0.039(1)					
C(16)	0.041(1)					
C(112)	0.071(4)	0.038(3)	0.077(4)	0.016(3)	0.038(3)	0.013(3)
C(113)	0.20(1)	0.053(6)	0.19(1)	-0.050(7)	-0.026(9)	0.051(7)
C(114)	0.128(8)	0.056(5)	0.164(9)	-0.054(6)	0.010(7)	0.016(5)
C(115)	0.069(4)	0.042(4)	0.063(4)	-0.010(3)	0.029(3)	-0.018(3)
C(132)	0.072(4)	0.050(4)	0.051(3)	-0.013(3)	0.026(3)	-0.015(3)
C(133)	0.073(5)	0.103(7)	0.122(7)	-0.054(6)	0.000(5)	-0.004(5)
C(134)	0.145(8)	0.092(7)	0.097(6)	-0.020(6)	-0.070(6)	-0.011(7)
C(135)	0.059(4)	0.069(4)	0.044(3)	0.010(3)	0.005(3)	-0.001(4)
C(152)	0.043(3)	0.075(5)	0.051(3)	0.007(3)	0.004(3)	0.008(3)
C(153)	0.082(6)	0.089(7)	0.16(1)	0.011(7)	-0.039(6)	0.012(5)
C(154)	0.20(1)	0.122(9)	0.097(7)	-0.027(6)	-0.041(7)	0.123(9)
C(155)	0.074(4)	0.050(4)	0.058(4)	0.006(3)	0.029(3)	0.029(3)
C(17)	0.068(4)	0.056(4)	0.046(4)	-0.002(3)	0.022(3)	-0.014(3)
C(18)	0.077(4)	0.047(4)	0.058(4)	0.000(3)	0.045(3)	-0.002(3)
C(19)	0.050(4)	0.067(4)	0.065(4)	0.011(3)	0.030(3)	0.008(3)
O(17)	0.117(4)	0.114(4)	0.048(3)	-0.018(3)	0.033(3)	-0.027(3)
O(18)	0.159(5)	0.040(3)	0.115(4)	0.006(3)	0.100(4)	-0.006(3)
O(19)	0.062(3)	0.130(5)	0.123(4)	0.032(4)	0.050(3)	0.026(3)
Cr(2)	0.0426(5)	0.0372(5)	0.0423(5)	-0.0054(4)	0.0165(4)	-0.0044(4)
C(21)	0.045(1)					
C(22)	0.042(1)					
C(23)	0.040(1)					
C(24)	0.037(1)					
C(25)	0.040(1)					
C(26)	0.039(1)					
C(212)	0.053(4)	0.069(4)	0.071(4)	0.003(3)	0.025(3)	0.027(3)
C(213)	0.071(4)	0.101(6)	0.094(5)	-0.005(5)	0.034(4)	0.032(4)
C(214)	0.071(4)	0.098(6)	0.077(5)	-0.022(4)	0.039(4)	0.007(4)
C(215)	0.050(3)	0.060(4)	0.056(3)	-0.010(3)	0.030(3)	-0.007(3)
C(232)	0.058(4)	0.073(4)	0.055(3)	-0.004(3)	0.035(3)	0.006(3)
C(233)	0.138(7)	0.151(9)	0.085(5)	0.041(6)	0.082(5)	0.049(7)
C(234)	0.123(7)	0.120(7)	0.098(6)	0.054(6)	0.071(5)	0.035(6)
C(235)	0.078(4)	0.060(4)	0.044(3)	0.016(3)	0.017(3)	0.019(4)
C(252)	0.070(4)	0.046(4)	0.048(3)	0.010(3)	0.015(3)	0.000(3)
C(253)	0.118(6)	0.083(6)	0.081(5)	0.043(4)	0.038(5)	0.040(5)
C(254)	0.087(5)	0.099(6)	0.089(5)	0.038(5)	0.022(4)	0.053(5)
C(255)	0.051(3)	0.058(4)	0.052(3)	-0.005(3)	0.012(3)	0.019(3)
C(27)	0.059(4)	0.071(4)	0.057(4)	-0.012(4)	0.027(3)	-0.015(3)
C(28)	0.104(6)	0.043(4)	0.070(4)	-0.010(4)	0.020(4)	-0.012(4)
C(29)	0.067(4)	0.067(4)	0.068(4)	-0.021(3)	0.032(3)	-0.022(4)
O(27)	0.114(4)	0.129(5)	0.056(3)	-0.037(3)	0.036(3)	-0.034(4)
O(28)	0.209(7)	0.043(3)	0.123(5)	0.009(3)	0.037(5)	-0.004(4)
O(29)	0.047(3)	0.127(5)	0.136(4)	-0.038(4)	0.041(3)	-0.029(3)

Final positional parameters for $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$

ATOM	x	y	z
Cr(1)	0.1590(1)	0.7191(1)	0.1243(1)
C(11)	0.1668(3)	0.8912(5)	0.0573(2)
C(12)	0.1377(3)	0.7753(5)	0.0126(2)
C(13)	0.1765(3)	0.6517(5)	0.0286(2)
C(14)	0.2465(3)	0.6428(5)	0.0894(2)
C(15)	0.2742(3)	0.7557(5)	0.1325(2)
C(16)	0.2352(3)	0.8816(5)	0.1167(2)
C(112)	0.1234(3)	1.0230(6)	0.0388(3)
C(113)	0.1604(6)	1.1317(8)	0.0904(6)
C(114)	0.2221(5)	1.1282(8)	0.1419(5)
C(115)	0.2679(3)	1.0029(6)	0.1647(3)
C(132)	0.1477(3)	0.5291(6)	-0.0176(3)
C(133)	0.0731(4)	0.5434(9)	-0.0747(4)
C(134)	0.0527(5)	0.6674(9)	-0.0999(5)
C(135)	0.0655(3)	0.7900(6)	-0.0524(3)
C(152)	0.3502(3)	0.7492(6)	0.1961(3)
C(153)	0.3836(5)	0.6120(9)	0.2079(6)
C(154)	0.3566(6)	0.511(1)	0.1715(5)
C(155)	0.2885(3)	0.5071(6)	0.1057(3)
C(17)	0.1849(3)	0.7587(6)	0.2175(3)
C(18)	0.1422(3)	0.5450(6)	0.1422(3)
C(19)	0.0626(3)	0.7626(6)	0.1085(3)
O(17)	0.2017(3)	0.7833(5)	0.2766(2)
O(18)	0.1333(3)	0.4316(4)	0.1523(3)
O(19)	0.0014(3)	0.7894(6)	0.0969(3)
Cr(2)	0.0910(1	0.1496(1)	0.3762(1)
C(21)	0.2106(3)	0.1913(5)	0.4446(3)
C(22)	0.1682(3)	0.1956(5)	0.4873(2)
C(23)	0.1056(3)	0.2817(5)	0.4686(2)
C(24)	0.0862(3)	0.3643(5)	0.4067(2)
C(25)	0.1275(3)	0.3614(5)	0.3664(2)
C(26)	0.1898(3)	0.2714(5)	0.3834(2)
C(212)	0.2809(3)	0.1013(7)	0.4686(3)
C(213)	0.3302(4)	0.1300(8)	0.4282(4)
C(214)	0.2852(3)	0.1450(7)	0.3521(3)
C(215)	0.2327(3)	0.2651(6)	0.3369(3)
C(232)	0.0605(3)	0.2872(6)	0.5135(3)
C(233)	0.0986(5)	0.221(1)	0.5843(4)
C(234)	0.1357(5)	0.1004(9)	0.5854(4)
C(235)	0.1922(3)	0.1093(6)	0.5538(3)
C(252)	0.1098(3)	0.4528(6)	0.3021(3)
C(253)	0.0525(4)	0.5595(8)	0.2948(4)
C(254)	-0.0084(4)	0.5118(8)	0.3134(4)
C(255)	0.0184(3)	0.4583(6)	0.3877(3)
C(27)	0.0745(3)	0.1039(7)	0.2855(3)
C(28)	0.1002(4)	-0.0296(7)	0.3991(3)
C(29)	-0.0102(4)	0.1406(7)	0.3520(3)
O(27)	0.0633(3)	0.0784(6)	0.2271(2)
O(28)	0.1070(4)	-0.1415(5)	0.4146(3)
O(29)	-0.0733(3)	0.1430(6)	0.3371(3)

Final positional and thermal parameters
of calculated hydrogen atoms for [(η^6-$C_{18}H_{24}$)Cr(CO)$_3$]

ATOM	X/A	Y/B	Z/C	U11
H(121)	0.0733(3)	1.0071(6)	0.0376(3)	0.082
H(122)	0.1193(3)	1.0526(6)	-0.0081(3)	0.082
H(123)	0.1249(6)	1.1526(8)	0.1118(6)	0.082
H(124)	0.1636(6)	1.2089(8)	0.0617(6)	0.082
H(125)	0.2536(5)	1.1936(8)	0.1305(5)	0.082
H(126)	0.2137(5)	1.1603(8)	0.1831(5)	0.082
H(127)	0.3179(3)	1.0213(6)	0.1661(3)	0.082
H(128)	0.2719(3)	0.9798(6)	0.2124(3)	0.082
H(131)	0.1459(3)	0.4536(6)	0.0126(3)	0.082
H(132)	0.1830(3)	0.5074(6)	-0.0393(3)	0.082
H(133)	0.0363(4)	0.5136(9)	-0.0562(4)	0.082
H(134)	0.0707(4)	0.4838(9)	-0.1136(4)	0.082
H(135)	0.0807(5)	0.6855(9)	-0.1293(5)	0.082
H(136)	-0.0010(5)	0.6641(9)	-0.1298(5)	0.082
H(137)	0.0236(3)	0.7970(6)	-0.0377(3)	0.082
H(138)	0.0680(3)	0.8724(6)	-0.0780(3)	0.082
H(141)	0.3433(3)	0.7775(6)	0.2387(3)	0.082
H(142)	0.3849(3)	0.8115(6)	0.1874(3)	0.082
H(143)	0.3901(5)	0.5878(9)	0.2561(6)	0.082
H(144)	0.4328(5)	0.6227(9)	0.2060(6)	0.082
H(145)	0.3963(6)	0.473(1)	0.1591(5)	0.082
H(146)	0.3459(6)	0.448(1)	0.2033(5)	0.082
H(147)	0.3031(3)	0.4852(6)	0.0666(3)	0.082
H(148)	0.2545(3)	0.4370(6)	0.1093(3)	0.082
H(221)	0.2651(3)	0.0062(7)	0.4611(3)	0.082
H(222)	0.3103(3)	0.1171(7)	0.5191(3)	0.082
H(223)	0.3653(4)	0.0547(8)	0.4355(4)	0.082
H(224)	0.3582(4)	0.2140(8)	0.4463(4)	0.082
H(225)	0.3187(3)	0.1583(7)	0.3276(3)	0.082
H(226)	0.2556(3)	0.0624(7)	0.3344(3)	0.082
H(227)	0.1968(3)	0.2598(6)	0.2875(3)	0.082
H(228)	0.2623(3)	0.3483(6)	0.3439(3)	0.082
H(231)	0.0128(3)	0.2410(6)	0.4880(3)	0.082
H(232)	0.0511(3)	0.3825(6)	0.5210(3)	0.082
H(233)	0.0606(5)	0.203(1)	0.6031(4)	0.082
H(234)	0.1354(5)	0.286(1)	0.6153(4)	0.082
H(235)	0.1612(5)	0.0711(9)	0.6347(4)	0.082
H(236)	0.0985(5)	0.0323(9)	0.5588(4)	0.082
H(237)	0.2379(3)	0.1487(6)	0.5893(3)	0.082
H(238)	0.2027(3)	0.0174(6)	0.5421(3)	0.082
H(241)	0.0910(3)	0.3958(6)	0.2597(3)	0.082
H(242)	0.1561(3)	0.4976(6)	0.3058(3)	0.082
H(243)	0.0315(4)	0.5913(8)	0.2457(4)	0.082
H(244)	0.0773(4)	0.6350(8)	0.3263(4)	0.082
H(245)	-0.0431(4)	0.5870(8)	0.3080(4)	0.082
H(246)	-0.0346(4)	0.4384(8)	0.2808(4)	0.082
H(247)	0.0319(3)	0.5357(6)	0.4202(3)	0.082
H(248)	-0.0221(3)	0.4069(6)	0.3931(3)	0.082

Appendix VI

Thermal parameters for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+\ BF_4^-$ (orthorhombic)

ATOM	U11	U22	U33	U23	U13	U12
MN	0.0415(5)	0.0498(6)	0.0357(5)	-0.0033(7)	0.0057(5)	-0.0031(8)
C1	0.041(2)					
C2	0.040(2)					
C3	0.043(2)					
C4	0.049(2)					
C5	0.049(2)					
C6	0.047(2)					
C112	0.075(6)	0.044(5)	0.088(7)	-0.003(5)	0.014(5)	-0.006(5)
C113	0.13(1)	0.052(5)	0.085(7)	0.000(5)	0.029(7)	0.013(7)
C114	0.083(7)	0.072(7)	0.088(7)	-0.004(6)	0.012(6)	0.031(6)
C115	0.050(5)	0.078(7)	0.061(6)	0.001(5)	0.004(5)	0.012(5)
C132	0.044(5)	0.076(6)	0.067(6)	0.013(5)	0.008(4)	-0.016(4)
C133	0.085(8)	0.12(1)	0.081(8)	0.026(7)	-0.010(7)	-0.052(8)
C134	0.12(1)	0.058(6)	0.097(8)	0.005(6)	0.020(8)	-0.037(7)
C135	0.095(7)	0.049(5)	0.087(7)	0.011(5)	0.000(7)	-0.001(6)
C152	0.048(6)	0.087(7)	0.102(8)	0.006(7)	0.000(6)	0.018(5)
C153	0.06(1)	0.12(1)	0.29(2)	-0.03(1)	0.05(1)	0.03(1)
C154	0.042(7)	0.15(1)	0.30(2)	0.05(2)	0.02(1)	0.010(9)
C155	0.050(6)	0.078(7)	0.102(8)	-0.004(6)	0.002(6)	-0.020(5)
C31	0.095(9)	0.104(9)	0.064(7)	-0.021(7)	-0.001(6)	0.007(7)
C32	0.057(5)	0.083(6)	0.040(4)	0.008(6)	0.005(4)	-0.007(7)
C33	0.070(7)	0.074(6)	0.055(6)	0.007(5)	0.015(5)	-0.012(5)
031	0.23(1)	0.093(7)	0.107(7)	-0.051(6)	0.005(7)	0.057(7)
032	0.057(4)	0.165(7)	0.073(4)	-0.005(7)	-0.016(3)	-0.012(6)
033	0.129(7)	0.137(7)	0.080(5)	0.034(5)	0.027(5)	-0.042(6)
B1	0.099(8)	0.065(7)	0.065(6)	-0.018(5)	0.029(7)	-0.037(8)
F1	0.42(2)	0.096(6)	0.19(1)	-0.001(6)	0.15(1)	-0.052(9)
F2	0.147(7)	0.28(2)	0.22(1)	0.01(1)	-0.001(8)	0.05(1)
F3	0.23(1)	0.143(6)	0.096(5)	0.024(5)	0.061(6)	0.105(7)
F4	0.28(1)	0.156(7)	0.052(3)	-0.001(4)	0.051(5)	-0.031(8)

Final positional parameters for $(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3^+ BF_4^-$ (orthorhombic)

ATOM	x	y	z	ATOM	x	y	z
MN	0.3003(1)	0.5096(1)	0.5642(1)	C(152)	0.570(1)	0.363(1)	0.6364(6)
C(1)	0.3470(8)	0.6654(7)	0.6340(4)	C(153)	0.690(2)	0.428(2)	0.605(1)
C(2)	0.2227(7)	0.6136(7)	0.6509(3)	C(154)	0.711(2)	0.550(2)	0.619(1)
C(3)	0.2071(7)	0.4779(7)	0.6605(3)	C(155)	0.597(1)	0.643(1)	0.6132(6)
C(4)	0.3187(8)	0.3986(7)	0.6572(4)	C(31)	0.345(1)	0.370(1)	0.5178(5)
C(5)	0.4502(8)	0.4507(7)	0.6397(4)	C(32)	0.1324(8)	0.511(1)	0.5302(4)
C(6)	0.4603(9)	0.5833(7)	0.6280(4)	C(33)	0.357(1)	0.613(1)	0.5001(5)
C(112)	0.362(1)	0.8096(8)	0.6213(5)	O(31)	0.379(1)	0.2794(8)	0.4901(5)
C(113)	0.230(1)	0.8748(9)	0.6097(5)	O(32)	0.0232(6)	0.508(1)	0.5119(3)
C(114)	0.131(1)	0.840(1)	0.6626(5)	O(33)	0.391(1)	0.6841(9)	0.4603(4)
C(115)	0.1003(9)	0.7022(9)	0.6616(5)	B	0.200(2)	0.470(1)	0.3335(6)
C(132)	0.0693(8)	0.4246(9)	0.6773(5)	F(1)	0.234(2)	0.5870(9)	0.3183(5)
C(133)	0.064(1)	0.280(1)	0.6660(6)	F(2)	0.074(1)	0.479(2)	0.2991(6)
C(134)	0.174(1)	0.217(1)	0.6999(6)	F(3)	0.255(1)	0.3783(9)	0.2981(4)
C(135)	0.313(1)	0.2555(8)	0.6716(5)	F(4)	0.168(1)	0.4445(8)	0.3915(3)

Hydrogen atom parameters for $(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3^+ BF_4^-$ (orthorhombic)

ATOM	X/A	Y/B	Z/C	U11
H1	0.419(1)	0.8218(8)	0.5826(5)	0.113(8)
H2	0.405(1)	0.8491(8)	0.6595(5)	0.113(8)
H3	0.243(1)	0.9681(9)	0.6098(5)	0.113(8)
H4	0.194(1)	0.8480(9)	0.5670(5)	0.113(8)
H5	0.048(1)	0.888(1)	0.6559(5)	0.113(8)
H6	0.170(1)	0.862(1)	0.7053(5)	0.113(8)
H7	0.0590(9)	0.6795(9)	0.7037(5)	0.113(8)
H8	0.0361(9)	0.6863(9)	0.6262(5)	0.113(8)
H9	0.0500(8)	0.4423(9)	0.7235(5)	0.113(8)
H10	0.0016(8)	0.4667(9)	0.6498(5)	0.113(8)
H11	0.071(1)	0.262(1)	0.6189(6)	0.113(8)
H12	-0.022(1)	0.246(1)	0.6824(6)	0.113(8)
H13	0.171(1)	0.241(1)	0.7463(6)	0.113(8)
H14	0.163(1)	0.123(1)	0.6958(6)	0.113(8)
H15	0.328(1)	0.2079(8)	0.6309(5)	0.113(8)
H16	0.383(1)	0.2337(8)	0.7035(5)	0.113(8)
H17	0.592(1)	0.334(1)	0.6809(6)	0.113(8)
H18	0.546(1)	0.288(1)	0.6096(6)	0.113(8)
H19	0.685(2)	0.416(2)	0.557(1)	0.113(8)
H20	0.770(2)	0.382(2)	0.622(1)	0.113(8)
H21	0.748(2)	0.557(2)	0.664(1)	0.113(8)
H22	0.779(2)	0.579(2)	0.587(1)	0.113(8)
H23	0.613(1)	0.713(1)	0.6447(6)	0.113(8)
H24	0.595(1)	0.679(1)	0.5687(6)	0.113(8)

Appendix VII

Thermal parameters for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+[BF_4]^-$ (trigonal)

ATOM	U11	U22	U33	U23	U13	U12
Mn(1)	0.0192(5)	0.0192(5)	0.0167(7)	0.0000(0)	0.0000(0)	0.0096(2)
C(11)	0.0158(9)					
C(12)	0.017(1)					
C(13)	0.023(1)					
C(14)	0.031(1)					
C(15)	0.032(1)					
C(16)	0.021(1)					
C(1A)	0.034(7)	0.034(7)	0.014(4)	-0.006(5)	-0.010(5)	0.023(6)
O(1A)	0.074(9)	0.067(8)	0.015(4)	-0.008(5)	-0.001(5)	0.057(7)
C(1B)	0.045(8)	0.023(6)	0.009(4)	-0.007(4)	0.018(5)	0.004(6)
O(1B)	0.10(1)	0.029(6)	0.037(6)	-0.009(5)	-0.009(7)	0.008(7)
Mn(2)	0.0180(5)	0.0180(5)	0.0092(6)	0.0000(0)	0.0000(0)	0.0090(2)
C(21)	0.018(1)					
C(22)	0.017(1)					
C(23)	0.020(1)					
C(24)	0.025(1)					
C(25)	0.023(1)					
C(26)	0.022(1)					
C(3A)	0.030(7)	0.033(7)	0.011(4)	0.003(5)	0.008(4)	0.014(6)
O(3A)	0.043(6)	0.057(7)	0.029(5)	-0.006(5)	0.007(5)	0.031(6)
C(3B)	0.06(1)	0.043(9)	0.021(6)	0.002(6)	0.019(7)	0.028(9)
O(3B)	0.07(1)	0.052(7)	0.035(6)	-0.018(5)	-0.022(6)	0.036(7)
B(1)	0.027(3)	0.027(3)	0.007(4)	0.000(0)	0.000(0)	0.014(2)
F(11)	0.051(3)	0.051(3)	0.016(3)	0.000(0)	0.000(0)	0.025(2)
F(12)	0.027(2)	0.021(2)	0.046(2)	0.000(2)	0.005(2)	0.013(2)
B(2)	0.020(3)	0.020(3)	0.033(6)	0.000(0)	0.000(0)	0.010(2)
F(21)	0.055(3)	0.055(3)	0.028(4)	0.000(0)	0.000(0)	0.010(2)
F(22)	0.023(2)	0.026(2)	0.038(2)	-0.002(2)	0.000(2)	0.012(2)

Final positional parameters for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+[BF_4]^-$ (trigonal)

ATOM	x	y	z
Mn(1)	0.6667(0)	0.3333(0)	0.3204(1)
C(11)	0.5225(6)	0.2168(6)	0.4014(2)
C(12)	0.5489(6)	0.3604(6)	0.3995(2)
C(13)	0.4320(7)	0.3962(7)	0.4010(3)
C(14)	0.2841(8)	0.2682(8)	0.3839(3)
C(15)	0.2613(8)	0.1390(8)	0.4250(3)
C(16)	0.3694(6)	0.0915(7)	0.4036(3)
C(1A)	0.748(2)	0.254(2)	0.2680(5)
O(1A)	0.803(2)	0.209(2)	0.2379(4)
C(1B)	0.566(2)	0.173(1)	0.2712(5)
O(1B)	0.500(2)	0.071(1)	0.2388(6)
Mn(2)	0.3333(0)	0.6667(0)	0.1833(1)
C(21)	0.3033(6)	0.7806(6)	0.0995(3)
C(22)	0.1889(6)	0.6371(6)	0.1000(3)
C(23)	0.0338(6)	0.6044(6)	0.0982(3)
C(24)	0.0160(7)	0.7330(7)	0.1131(3)
C(25)	0.1245(7)	0.8624(7)	0.0746(3)
C(26)	0.2767(6)	0.9060(7)	0.0947(3)
C(3A)	0.260(2)	-0.256(2)	0.2364(5)
O(3A)	0.208(1)	-0.207(1)	0.2693(5)
C(3B)	0.381(2)	-0.189(2)	0.2358(7)
O(3B)	0.412(2)	-0.079(1)	0.2605(6)
B(1)	0.6667(0)	0.3333(0)	0.5702(5)
F(11)	0.6667(0)	0.3333(0)	0.6365(3)
F(12)	0.7098(4)	0.2389(4)	0.5466(2)
B(2)	0.3333(0)	0.6667(0)	0.9313(6)
F(21)	0.3333(0)	0.6667(0)	0.8626(4)
F(22)	0.4711(4)	0.7609(4)	0.9534(2)

Final positional and thermal parameters of calculated hydrogen atoms $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+[BF_4]^-$ (trigonal)

ATOM	X/A	Y/B	Z/C	U11
H(131)	0.4274(7)	0.4332(7)	0.4490(3)	0.031
H(132)	0.4564(7)	0.4808(7)	0.3665(3)	0.031
H(141)	0.2799(8)	0.2423(8)	0.3332(3)	0.031
H(142)	0.2014(8)	0.2940(8)	0.3947(3)	0.031
H(151)	0.2785(8)	0.1696(8)	0.4753(3)	0.031
H(152)	0.1531(8)	0.0512(8)	0.4184(3)	0.031
H(161)	0.3393(6)	0.0434(7)	0.3562(3)	0.031
H(162)	0.3650(6)	0.0134(7)	0.4377(3)	0.031
H(231)	-0.0084(6)	0.5662(6)	0.0504(3)	0.031
H(232)	-0.0271(6)	0.5214(6)	0.1332(3)	0.031
H(241)	0.0339(7)	0.7571(7)	0.1641(3)	0.031
H(242)	-0.0913(7)	0.7085(7)	0.1006(3)	0.031
H(251)	0.1114(7)	0.8353(7)	0.0238(3)	0.031
H(252)	0.1059(7)	0.9509(7)	0.0828(3)	0.031
H(261)	0.2965(6)	0.9567(7)	0.1416(3)	0.031
H(262)	0.3502(6)	0.9819(7)	0.0598(3)	0.031

Appendix VIII

General Experimental Section

All air sensitive reactions and recrystallisations were performed under an atmosphere of dry N_2 using standard Schlenk techniques.

THF and ether were dried by distillation from sodium/benzophenone under N_2. Hexane was dried by distillation from CaH_2 under N_2. Petroleum spirit was of A.R. quality and of boiling point range 60-80°C. Heptane was dried over $CaCl_2$ or $MgSO_4$.

Deuterium oxide (Riedel-de Haen > 99.7 D % atom) and deuterioacetic acid (Fison > 99.5 D % atom), manganese carbonyl, chromium hexacarbonyl (Pressure Chemical Co.) and aluminium chloride (B.D.H) were used as received. Deactivated neutral alumina (activity III - 6 % H_2O; activity V) was prepared by adding the appropriate quantity of water to alumina and shaking the mixture until it was homogeneous.

NMR spectra were recorded in $CDCl_3$, d^6-DMSO or d^6-acetone as solvent. ^1H-NMR were recorded on Joel C-60 HL instrument (operating in the external lock mode), Joel FX-90 Q or Bruker AC-200 instruments. All ^1H-NMR chemical shifts are recorded in p.p.m. and are referenced downfield from TMS. The ^{13}C-NMR spectra were recorded on a Joel FX 90 Q multinuclear instrument operating at 22.49 MHz in the ^{13}C observation channel and at 89.55 MHz in the proton decoupling channel. ^{13}C-^1H decoupled spectra using INEPT and SEFT pulse sequences were recorded to assign s, d, t and q signals. The central septet peak for d^6-DMSO was taken as being 40.38 p.p.m. downfield from TMS, while the central peak of $CDCl_3$ was taken as being 77.06 p.p.m. downfield from TMS. ^{13}C-NMR chemical shifts were directly referenced downfield from TMS in d^6-acetone as solvent.

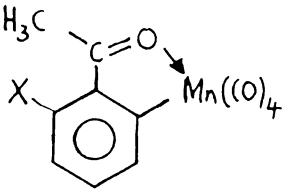
The infrared spectra were recorded on a Perkin-Elmer 180 B instrument either as nujol mulls or by using a solution cell (KBr windows).

Mass spectra were recorded by Mr A.L. Brennan at the Ruakura Agricultural Research Centre on a Varian MAT CH5 instrument.

Thin layer chromatography (t.l.c) and preparative layer chromatography (p.l.c) were carried out on Merck silica gel 60 $F_{254 + 366}$ coated glass plates. Melting points were carried out on a Reichert Thermopan melting point instrument and are uncorrected.

Elemental analyses were obtained from the Microanalytical Laboratory, Chemistry Department, University of Otago.

Appendix IX List of Compounds by Numbers



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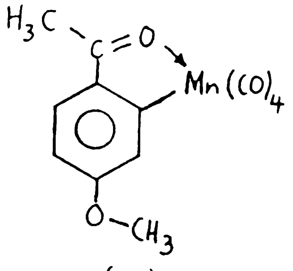

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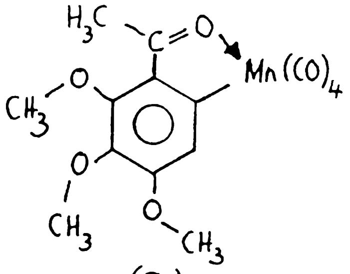

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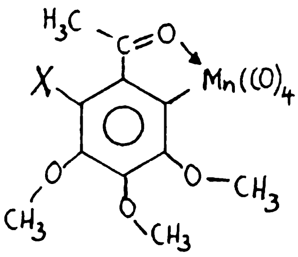

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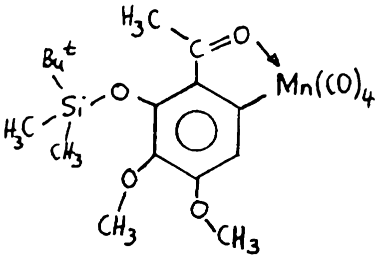

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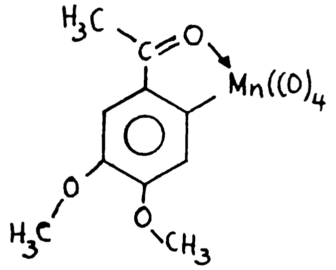

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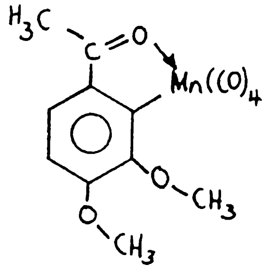

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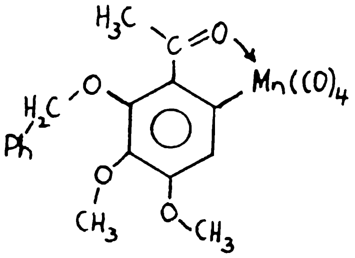

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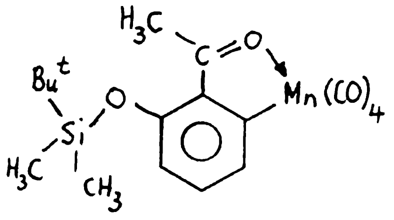

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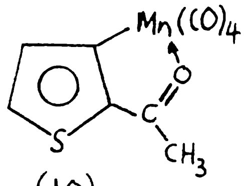

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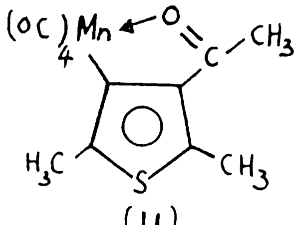

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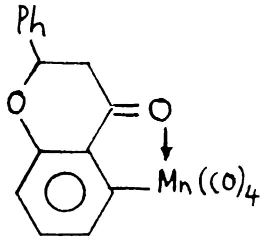

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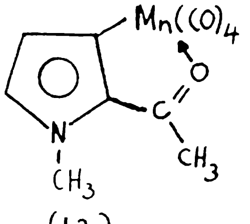

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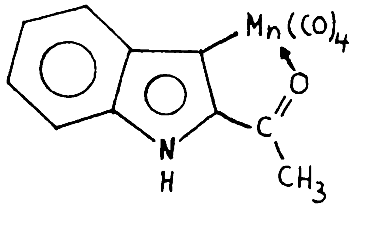

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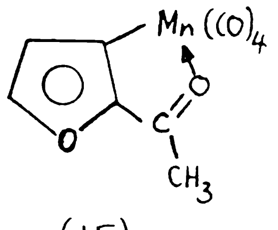

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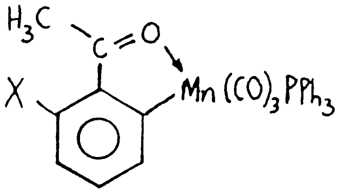

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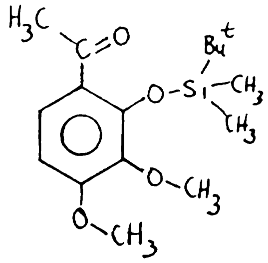

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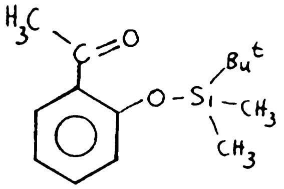

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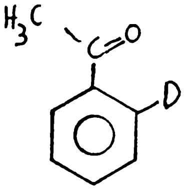

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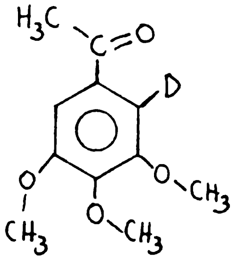

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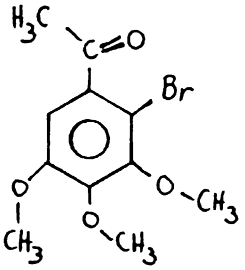

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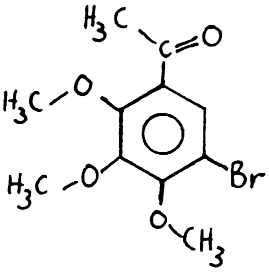

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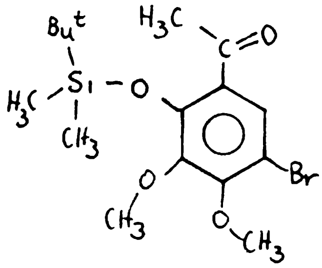

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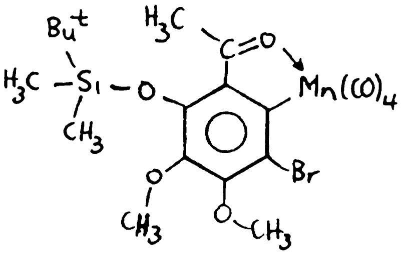

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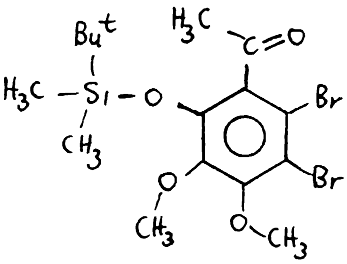

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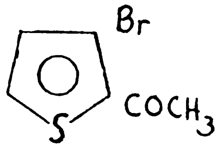

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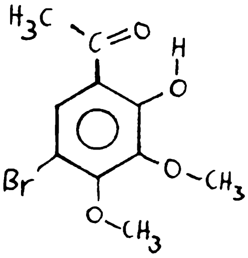

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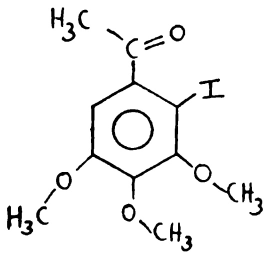

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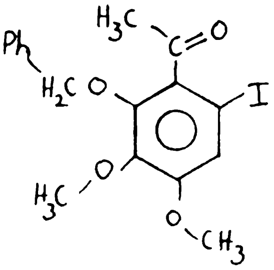

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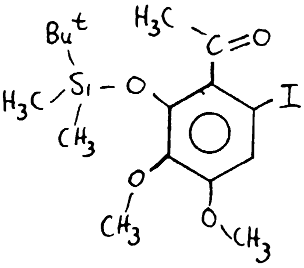

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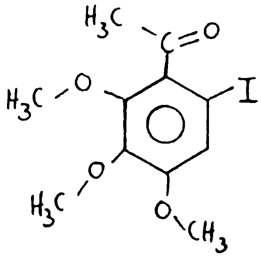

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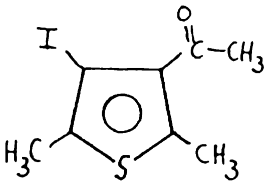

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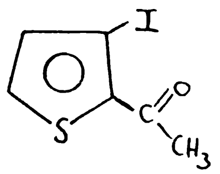

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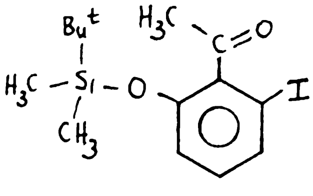

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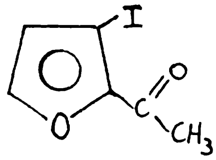

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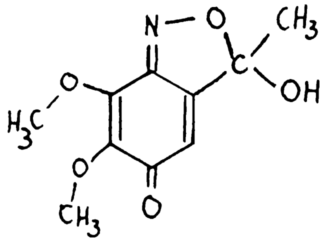

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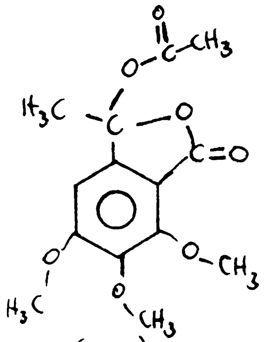

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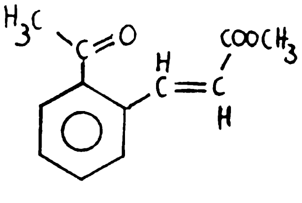

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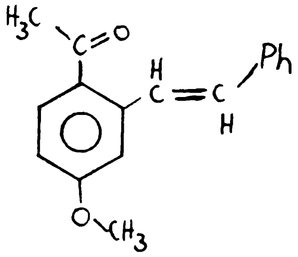

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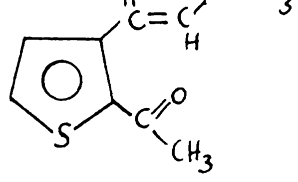

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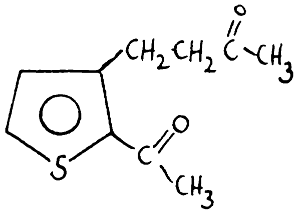

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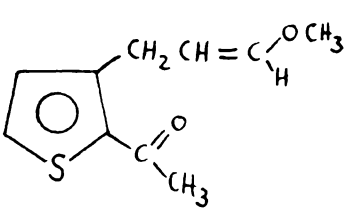

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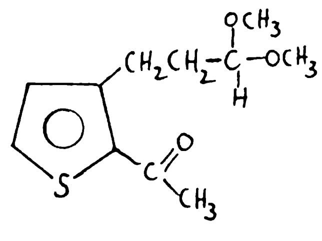

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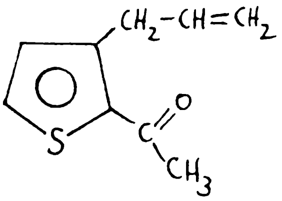

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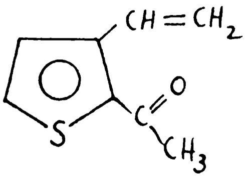

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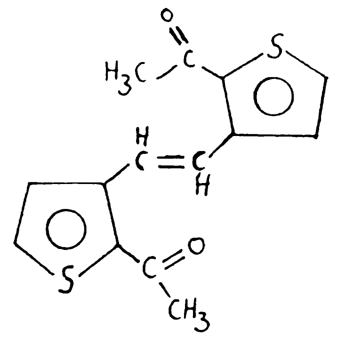

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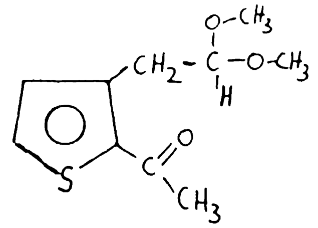

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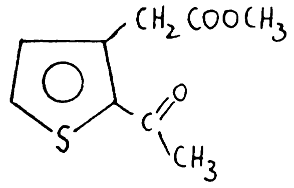

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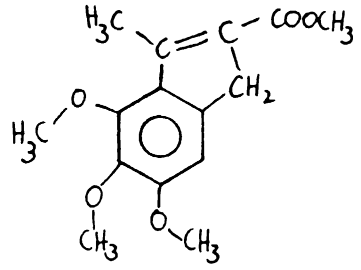

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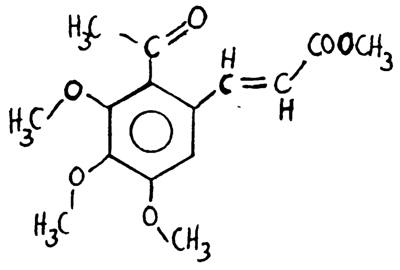

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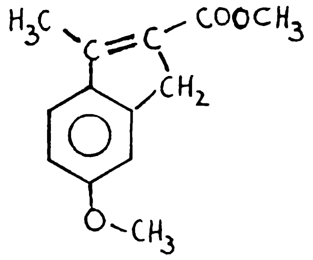

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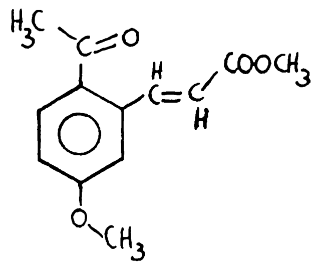

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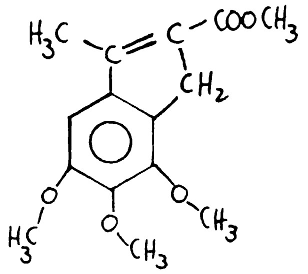

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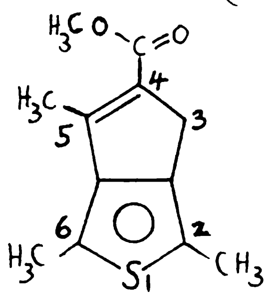

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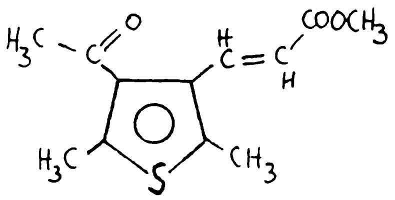

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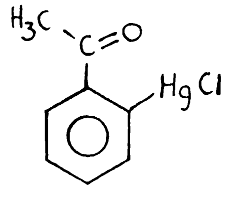

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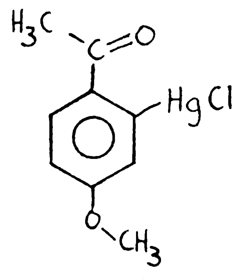

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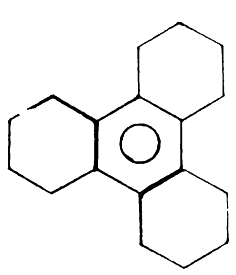

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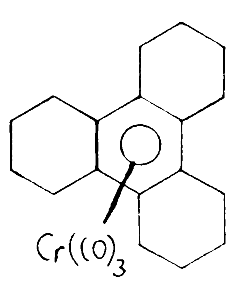
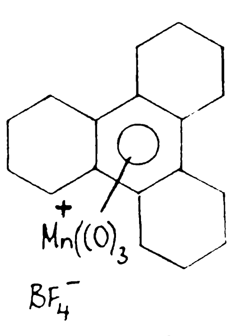


(59)



(60)