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Synthesis and Reactions of Some Orthomanganated Complexes



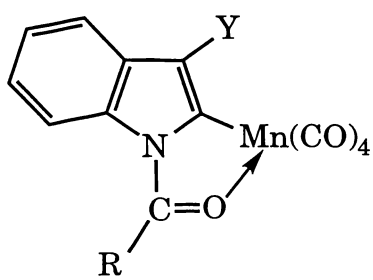
A thesis submitted in partial fulfilment
of the requirements for the Degree of
Doctor of Philosophy in Chemistry
at the University of Waikato
by

Gary John Depree

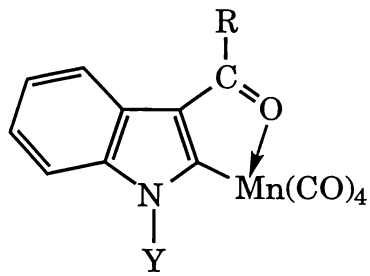
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Abstract

New orthomanganated indoles of the types shown in Figure 1 have been prepared, including two new examples of orthomanganated aldehydes which are relatively rare. The first crystal structure determination of an orthomanganated aldehyde was carried out on η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese **(11)**.



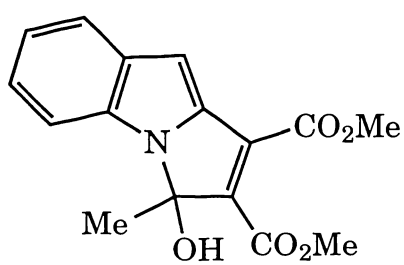
Y=H, CHO
R=CH_3, $C(CH_3)CH_2$



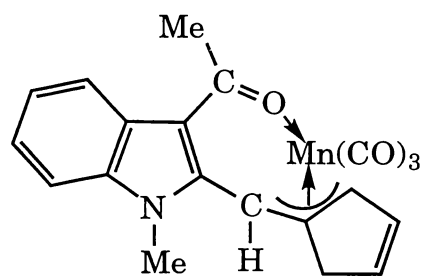
Y=H, CH_3
R=H, CH_3
(11) R=H, Y=CH_3

Figure 1

Solvent effects on the thermally induced coupling reactions of η^2-(2-acetylphenyl)tetracarbonylmanganese **(9)** and η^2-(1-acetyl-2-indolyl)-tetracarbonylmanganese **(4)** with a range of alkynes were shown to influence the course of reaction markedly but unpredictably. Of special interest was the reactions of **(4)** with dimethyl acetylenedicarboxylate which afforded the tricyclic carbinolamine **(17)** (Figure 2). Reactions of other orthomanganated indole derivatives with various alkynes are also reported. For example, a complex **(21)** (Figure 2) arising from the triple-insertion of ethyne was characterised by a single X-ray crystal structure determination, as a η^3-allyl species that could be converted to a η^5-C_5H_5 complex on heating.



(17)



(21)

Figure 2

A new class of orthomanganated compound (Figure 3) has been prepared from the reaction of $PhCH_2Mn(CO)_5$ with triphenylphosphine chalcogens (Figure 3). These are the first reported examples of orthometalated tertiary phosphine chalcogenide metal complexes. Single crystal X-ray structure determinations of the examples with X=S **(31)** and Se **(32)** were determined.

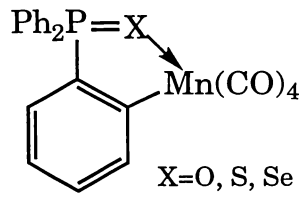
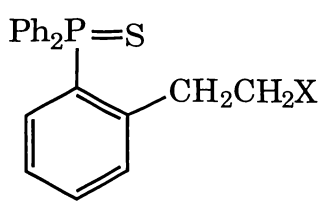


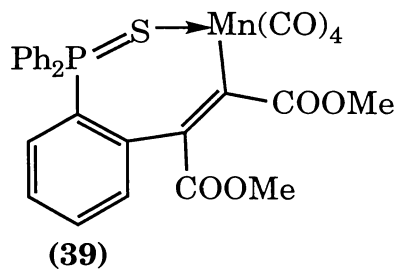
Figure 3

Cis-$PhCH_2Mn(CO)_4PPh_3$ **(34)** and $[Mn(CO)_4(\mu\text{-}SeCH_2Ph)]_2$ **(33)** were also isolated from the orthomanganation reaction of $Ph_3P{=}Se$, with the latter being identified by a crystal structure determination.

The thermally induced coupling reactions of orthomanganated $Ph_3P{=}S$ **(31)** with the alkenes methyl vinyl ketone, methyl acrylate and acrylonitrile gave mainly arylalkane products (Figure 4) in moderate yields.

Similar alkyne-coupling reactions of orthomanganated $Ph_3P{=}S$ **(31)** were explored. Reaction with dimethyl acetylenedicarboxylate yielded **(39)** (whose crystal structure is reported) (Figure 4), and a doubly inserted alkyne complex was tentatively identified.





(39)

Figure 4

However, the insertion of alkynes into the Mn-C_{aryl} bond of **(31)** was not general, as methyl propiolate was the only other alkyne to undergo insertion.

Sulfur dioxide inserts efficiently into the Mn-C_{aryl} bond of orthomanganated $Ph_3P{=}S$ **(31)** and $Ph_3P{=}Se$ **(32)**, to give the corresponding S-sulfinato complexes which contain novel metallocyclic rings (Figure 5).

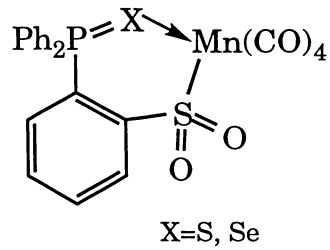


Figure 5

The X-ray crystal structure of the example with X=Se **(45)** was determined: it has a six-membered metallocycle ring incorporating five different elements. Reactions of other cyclomanganated species with SO_2 were found to be less straightforward. Preliminary investigations into the reactions Ph-N=S=O and Ph-N=C=O with orthomanganated $Ph_3P{=}S$ are also described.

The crystal structure of the phosphite substituted complex **(40)** (Figure 6) was determined, and its reactivity towards SO_2 and an alkyne was compared with that of the unsubstituted precursor.

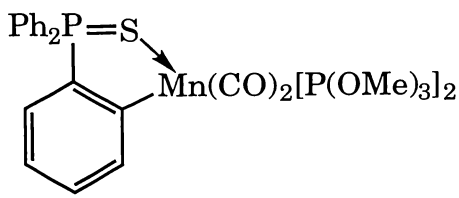


Figure 6

Acknowledgements

I would like to thank my supervisors Assoc. Prof. L. Main and Prof. B. K. Nicholson for their guidance and encouragement throughout the course of this investigation. Their unique sense of humour (including the infamous rainbow reaction incident) always seemed to make life in the lab more interesting, not to mention the many occasions outside of the lab which also made graduate life enjoyable.

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To my parents who have given me every opportunity possible and for their continual support throughout the years, a big thankyou.

Thanks to fellow members of what has become a rather elite wine club, whose trade mark appears to be the ownership of empty wine racks, for the many distractions provided, which temporarily dulled the pain of writing up, and who can forget Jim.

To the New Zealand Vice Chancellors Committee and the William Georgetti Trust for their generous financial support over the last three years.

Finally a special thanks to Karyn for your continual support and tolerance over the last six months. Despite it being stretched to the limit on a few occasions, you were always there (including all the last minute proof reading), for which I think you definitely deserve another trip overseas as payment.

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

Note on Nomenclature

For convenience and brevity, throughout this thesis orthomanganated compounds containing carbonyl oxygen donor atoms are named using a η^2 naming convention to specify that both the aryl carbon and the oxygen atom concerned are coordinated. Strictly speaking this should be specified with a η^2-(C,O) nomenclature, or more correctly using the κ notation. So for example, η^2-(2-acetylphenyl)tetracarbonylmanganese **(9)** should be 2-acetyl-κO-phenyl-κC^1-tetra(carbonyl-κC)manganese(I).

Contents

Abstract ii
Acknowledgements v
Contents viii
List of Tables ivx
Abbreviations xvii

Chapter One: Introduction: Cyclometalation 1
1.1 Definition 1
1.2 History 3
1.3 Chelate Ring Size 4
1.4 Donor Atoms 5
1.4.1 Nitrogen 5
1.4.2 Phosphorus 6
1.4.3 Arsenic 7
1.4.4 Oxygen 8
1.4.5 Sulphur 10
1.5 Oxygen-Coordinated Orthomanganated Complexes 10
1.6 Reactions of Oxygen-Coordinated Manganese Complexes 12
1.7 Outline of Present Study 12

Chapter Two: Orthofunctionalisation of Substituted Indoles via Manganation 21
2.1 Introduction 21
2.2 Discussion of Results 23
2.2.1 General 23
2.2.2 Orthomanganation of Heteroaromatic Ketones and *N*-Acyl Heteroaromatics 23
2.2.3 Orthomanganation of Heteroaromatic Aldehydes 30
2.3 Properties of Orthomanganated Complexes 33
2.3.1 General 33
2.3.2 Infrared Spectra 34
2.3.3 ^{13}C NMR Spectroscopy 36
2.4 X-Ray Crystal Structure of η^2-(1-Methyl-3-formyl-2-indolyl)-tetracarbonylmanganese **(11)** 38

2.4.1 Results of Preliminary Studies 38
2.4.2 Data Collection 38
2.4.3 Solution and Refinement 39
2.4.4 Discussion of the Structure 40
2.5 Experimental Section 45
2.5.1 Preparation of Starting Materials 45
2.5.2 Preparation of Orthomanganated Complexes 48
2.5.3 Unsuccessful Orthomanganations 52

Chapter Three: Coupling Reactions of Orthomanganated Aromatic and Heteroaromatic Compounds with Alkynes 55

3.1 Introduction 55
3.1.1 Coupling of Alkynes with Cyclopalladiated Complexes 56
3.1.2 Coupling of Alkynes with Cyclometalated Manganese Carbonyls 57
3.2 Discussion of Results 61
3.2.1 Solvent Effects on Thermally Induced Alkyne-Coupling Reactions 61
3.2.2 Coupling Reactions of Orthomanganated 1-Acetylindole and DMAD 65
3.2.3 Alkyne-Coupling Reactions of Various Orthomanganated Complexes 70
3.2.4 Alkyne-Coupling Reactions of Orthomanganated Aldehyde Complexes 77
3.2.5 Attempted Intramolecular Coupling Reactions of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonylmanganese 77
3.2.6 Reaction of Ethyne with $PhCH_2Mn(CO)_5$ 79
3.3 X-Ray Crystal Structure of **(21)** 81
3.3.1 Results of Preliminary Studies 81
3.3.2 Data Collection 81
3.3.3 Solution and Refinement 82
3.3.4 Discussion of the Structure 86
3.4 Experimental Section 89
3.4.1 Preparation of Starting Materials 89
3.4.2 General Procedures for Thermally Induced Coupling Reactions of Alkynes with Orthomanganated Compounds 90

3.4.3 Solvent Effects on Thermally Induced Alkyne-Coupling Reactions 91
3.4.4 General Procedures for Oxidatively Induced Coupling Reactions of Alkynes with Orthomanganated Compounds 99
3.4.5 Coupling Reactions of Orthomanganated 1-Acetylindole with Various Alkynes 99
3.4.6 Alkyne-Coupling Reactions of Various Orthomanganated Complexes 104
3.4.7 Alkyne-Coupling Reactions of Orthomanganated Aldehydes 108
3.4.8 Attempted Reactions of η^2-(1-(2-Methylprop-2-enoyl)-indolyl)tetracarbonylmanganese 109
3.4.9 Reaction of Ethyne with Benzylpentacarbonyl-manganese 110

Chapter Four: Orthofunctionalisation of Triphenyl-phosphine Chalcogens via Manganation 116

4.1 Introduction: Tertiary Phosphine Chalcogenide Metal Complexes 116
4.2 Discussion of Results 119
4.3 Properties of Orthomanganated Triphenylphosphine Chalcogenide Complexes 124
4.3.1 General 124
4.3.2 Infrared Spectra 124
4.3.3 ^{13}C NMR Spectroscopy 126
4.3.4 ^{31}P NMR Spectroscopy 127
4.4 X-Ray Crystal Structure of η^2-(C,S)-[(2-diphenylthio-phosphinyl)phenyl]tetracarbonylmanganese **(31)** 128
4.4.1 Results of Preliminary Studies 128
4.4.2 Data Collection 129
4.4.3 Solution and Refinement 129
4.4.4 Discussion of the Structure 130
4.5 X-Ray Crystal Structure of η^2-(C,Se)-[(2-diphenylseleno-phosphinyl)phenyl]tetracarbonylmanganese **(32)** 135
4.5.1 Results of Preliminary Studies 135
4.5.2 Data Collection 135
4.5.3 Solution and Refinement 136
4.5.4 Discussion of the Structure 140

4.6 X-Ray Crystal Structure of bis[(benzylseleno)tetracarbonyl-manganese] **(33)** 142
4.6.1 Results of Preliminary Studies 142
4.6.2 Data Collection 142
4.6.3 Solution and Refinement 143
4.6.4 Discussion of the Structure 146
4.7 Experimental Section 147
4.7.1 Preparation of Starting Materials 147
4.7.2 Orthomanganation of Triphenylphosphine Chalcogens 149

Chapter Five: Coupling Reactions of Orthomanganated Triphenylphosphine Sulfide with Alkenes and Alkynes 154

5.1 Introduction: Coupling Reactions of Orthomanganated Complexes with Alkenes 154
5.2 Reactions of Orthomanganated Triphenylphosphine Sulfide **(31)** with Alkenes 159
5.2.1 Palladium-Promoted Coupling Reactions with Alkenes 159
5.2.2 Thermally Induced Coupling Reactions with Alkenes in the absence of Palladium 162
5.3 Reactions of Orthomanganated Triphenylphosphine Sulfide **(31)** with Alkynes 168
5.4 X-Ray Crystal Structure of **(39)** 175
5.4.1 Results of Preliminary Studies 175
5.4.2 Data Collection 175
5.4.3 Solution and Refinement 176
5.4.4 Discussion of the Structure 177
5.5 X-Ray Crystal Structure of *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis(trimethylphosphite)-manganese **(40)** 183
5.5.1 Results of Preliminary Studies 183
5.5.2 Data Collection 183
5.5.3 Solution and Refinement 184
5.5.4 Discussion of the Structure 185
5.6 Experimental Section 190
5.6.1 Starting Materials 190

5.6.2 Attempted Li_2PdCl_4 Promoted Coupling Reactions of Alkenes with Orthomanganated Triphenylphosphine Sulfide 191
5.6.3 General Procedures for Thermally Induced Coupling Reactions of Alkenes and Alkynes with Orthomanganated Triphenylphosphine Sulfide 192
5.6.4 Thermally Induced Coupling Reactions of Alkenes with Orthomanganated Triphenylphosphine Sulfide 192
5.6.5 Thermally Induced Coupling Reactions of Alkynes with Orthomanganated Triphenylphosphine Sulfide 197
5.6.6 Unsuccessful Coupling Reactions 200

Chapter Six: Reactions of Orthomanganated Compounds with Sulfur Dioxide 204

6.1 Introduction 204
6.2 Discussion of Results 209
6.2.1 Reactions of Orthomanganated Triphenylphosphine Chalocogenides with SO_2 209
6.2.2 Reactions of Trimethylphosphite-Substituted Orthomanganated Complexes with SO_2 216
6.2.3 Attempted Insertion of SO_2 into **(39)** 221
6.2.4 Reaction of PhNSO with Orthomanganated Triphenylphosphine sulfide 222
6.2.5 Reaction of PhNCO with Orthomanganated Triphenylphosphine sulfide 223
6.3 X-Ray Crystal Structure of η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]tetracarbonylmanganese **(45)** 226
6.3.1 Results of Preliminary Studies 226
6.3.2 Data Collection 226
6.3.3 Solution and Refinement 227
6.3.4 Discussion of the Structure 228
6.4 Experimental Section 236
6.4.1 Starting Materials 236
6.4.2 Sulfur Dioxide Insertion Reactions of Orthomanganated Triphenylphosphine Chalcogenides 236
6.4.3 Attempted Sulfur Dioxide Insertion Reactions of **(18)**, **(39)** and **(40)** 239

6.4.4 Reaction of Orthomanganated Triphenylphosphine sulfide with PhNSO 240

6.4.5 Reaction of Orthomanganated Triphenylphosphine sulfide with PhNCO 241

Appendices:

Appendix I General Experimental 244

Appendix II Thermal and Positional Parameters for η^2-(1-Methyl-3-formyl-2-indolyl)tetracarbonyl-manganese **(11)** 248

Appendix III Thermal and Positional Parameters for **(21)** 255

Appendix IV Thermal and Positional Parameters for η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetracarbonyl-manganese **(31)** 258

Appendix V Thermal and Positional Parameters for η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetracarbonyl-manganese **(32)** 261

Appendix VI Thermal and Positional Parameters for bis[(benzylseleno)tetracarbonylmanganese] **(33)** 264

Appendix VII Thermal and Positional Parameters for **(39)** 266

Appendix VIII Thermal and Positional Parameters for *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonyl-bis(trimethylphosphite)manganese **(40)** 271

Appendix IX Thermal and Positional Parameters for η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]-tetracarbonylmanganese **(45)** 276

Appendix X Infrared Stretching Frequencies υ(C=O) of Substituted Indoles and their Corresponding Orthomanganated Complexes 279

Appendix XI List Of Compounds By Numbers and NMR Numbering Schemes 280

List of Tables

2.1 Orthometalated Compounds Prepared in this Study 24

2.2 Infrared Stretching Frequencies υ(C=O) of Various Aldehydes and their Yield in Orthomanganation 31

2.3 Selected ^{13}C NMR Chemical Shifts of Various Orthomanganated Complexes and their Corresponding Free Ligand 37

2.4 Bond Lengths (Å) for η^2-(1-methyl-3-formyl-2-indolyl)tetra-carbonylmanganese **(11)** 42

2.5 Bond Angles (°) for η^2-(1-methyl-3-formyl-2-indolyl)tetra-carbonylmanganese **(11)** 43

3.1 Yield (%) of Indenols and Tricyclic Carbinolamines from Thermally Induced Coupling Reactions 62

3.2 Yield (%) of Indenols and Tricyclic Carbinolamines from Oxidatively Induced Coupling Reactions 67

3.3 Metal-Carbonyl Vibrational Spectra (υ(C≡O) cm^{-1}) of Substituted Orthomanganated Complexes 69

3.4 Bond Lengths (Å) for **(21)** 84

3.5 Bond Angles (°) for **(21)** 84

3.6 Bond Length (Å) and Angle Data (°) for π-Allyl Groups of Selected Complexes 88

4.1 Products obtained from the Orthometalation Reaction of Triphenylphosphine Chalcogenides with $PhCH_2Mn(CO)_5$ 120

4.2 M-C≡O Infrared Stretching Frequencies of Orthomanganated Chalcogenides 125

4.3 Infrared Stretching Frequencies of υ(P=X) 125

4.4 Selected ^{13}C NMR Chemical Shifts of Orthomanganated Chalcogenides and their Corresponding Free Ligand 126

4.5 ^{31}P NMR Chemical Shifts of Orthomanganated Chalcogenides and their Corresponding Free Ligand 127

4.6 Bond Lengths (Å) for η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]tetracarbonylmanganese **(31)** 132

4.7 Bond Angles (°) for η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]tetracarbonylmanganese **(31)** 133

4.8 Bond Lengths (Å) for η^2-(C,Se)-[(2-diphenylselenophosphinyl)-phenyl]tetracarbonylmanganese **(32)** 138

4.9 Bond Angles (°) for η^2-(C,Se)-[(2-diphenylselenophosphinyl)-phenyl]tetracarbonylmanganese **(32)** 139

4.10 Selected Bond Lengths and Angles of Complexes **(32)** and **(31)** 140

4.11 Bond Lengths (Å) for Bis[(benzylseleno)tetracarbonyl-manganese] **(33)** 145

4.12 Bond Angles (°) for Bis[(benzylseleno)tetracarbonyl-manganese] **(33)** 145

5.1 Yields (%) of Products from the Thermally Induced Coupling Reaction of Orthomanganated 3-Acetylthiophene with Methyl Acrylate 157

5.2 Yields (%) of Products from Thermally Induced Coupling Reactions of Orthomanganated $Ph_3P{=}S$ **(31)** with Methyl Vinyl Ketone in a Range of Solvents 162

5.3 Yields (%) of Products from Thermally Induced Coupling Reactions of Orthomanganated $Ph_3P{=}S$ **(31)** with a Range of Alkenes in Acetonitrile and Methanol 163

5.4 ^{31}P NMR Chemical Shifts of Complexes **(31)**, **(39)**, and **(42)** 172

5.5 M-C≡O Infrared Stretching Frequencies of Complexes **(31)**, **(39)**, and **(42)** 173

5.6 Bond Lengths (Å) for **(39)** 179

5.7 Bond Angles (°) for **(39)** 180

5.8 Selected Bond Lengths (Å) and Angles (°) of **(39)** and Related Compounds 182

5.9 Bond Lengths (Å) for *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis(trimethylphosphite)-manganese **(40)** 187

5.10 Bond Angles (°) for *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]dicarbonylbis(trimethylphosphite)manganese **(40)** 188

5.11 Selected Bond Lengths (Å) and Angles (°) of Complexes **(40)** and **(31)** 189

6.1 Assignment of ESMS Spectra of Complexes **(44)** and **(45)** 212

6.2 Assignment of the ESMS Spectrum of the Crude Reaction Mixture Obtained from the Reaction of **(30)** with SO_2 212

6.3 M-C≡O Infrared Stretching Frequencies of S-Sulfinate Complexes Derived From Orthomanganated Chalcogenides 214

6.4 ^{31}P NMR Chemical Shifts of S-Sulfinate Complexes and Related Compounds 215

6.5 Bond Lengths (Å) for η^2-(S,Se)-[(2-diphenylselenophoshinyl)-phenylsulfonyl]tetracarbonylmanganese **(45)** 231

6.6 Bond Angles (°) for η^2-(S,Se)-[(2-diphenylselenophoshinyl)-phenylsulfonyl]tetracarbonylmanganese **(45)** 232

6.7 Selected Bond Lengths (Å) and Angles (°) of **(45)** and Related Compounds 234

Abbreviations

br	-	broad
Bu^t	-	tertiary-butyl
DMAD	-	dimethyl acetylenedicarboxylate
1D	-	one-dimensional
2D	-	two-dimensional
δ	-	chemical shift (ppm)
d	-	doublet
DMSO	-	dimethyl sulfoxide
EIMS	-	electron impact mass spectroscopy
ESMS	-	electrospray mass spectroscopy
FABMS	-	fast atom bombardment mass spectroscopy
GCMS	-	gas chromatography mass spectroscopy
IR	-	infrared
J	-	coupling constant (Hz)
m	-	medium
m	-	multiplet
M^+	-	molecular ion
Me	-	methyl
MS	-	mass spectrum/spectroscopy
NMR	-	nuclear magnetic resonance
NOE	-	nuclear Overhauser effect
^nPr	-	n-propyl
Ph	-	phenyl
p.l.c	-	preparative layer chromatography
q	-	quartet
s	-	strong
s	-	singlet
t	-	triplet
THF	-	tetrahydrofuran
t.l.c.	-	thin layer chromatography
TMANO	-	trimethylamine-N-oxide
υ	-	stretching frequency (IR)
vs	-	very strong
w	-	weak

Chapter One

Introduction: Cyclometalation

Cyclometalated complexes have attracted considerable attention from researchers as is evident from the several comprehensive reviews now available [1-5]. These complexes have become an important, rapidly expanding area of organometallic chemistry because of their successful use in catalysis [6], organic synthesis [7], asymmetric synthesis [8] and photochemistry [9]. They also mimic some key intermediates in catalytic transformations [10] and have shown promise as potential biologically active materials [11,12] and constituents of ordered mesophases [13,14].

1.1 Definition

Cyclometalated complexes are defined by Omae [1] as organometallic intramolecular-coordination compounds with a metal-carbon σ bond of the configuration shown in Figure 1.1, where Y the coordinating atom or group can be bound to the metal via σ- or π-coordination depending on the nature of Y.

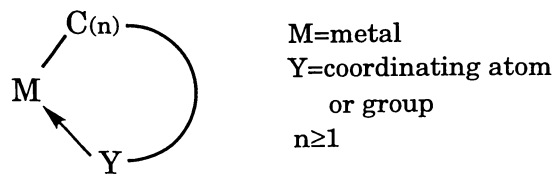
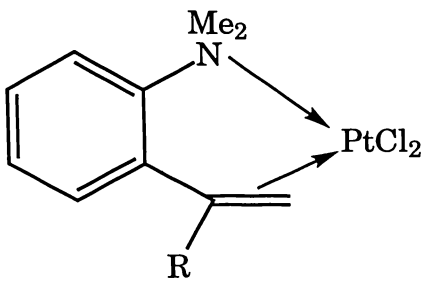


Figure 1.1

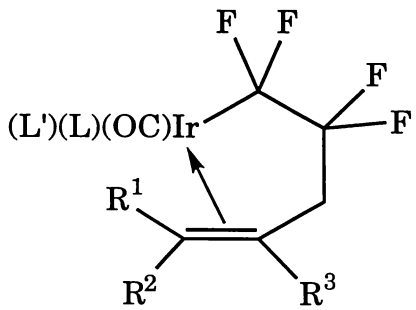
π-Coordinated cyclometalated compounds mainly have vinylene, π-allyl, cyclopentadienyl, or aryl as the coordinating group Y, whereas σ-coordinated cyclometalated compounds have N, P, As, or Sb from Group 15, O or S from Group 16, and Cl, Br or I from Group 17 as the

coordinating group Y. Of these N, P, As, O and S are more prevalent than the other elements. The M-C bond can also be σ- or π-bonded and illustrative examples are given in Figure 1.2. Cyclometalated compounds involving π-coordination are considered outside the scope of this review and will be considered no further.



R=H, Me

[15]



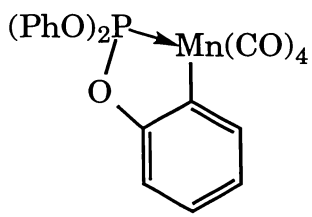
R^1-R^3=H, Me

L, L'=PPh_3, $AsPh_3$, CO

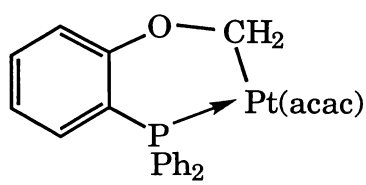
[16]

Figure 1.2

Strictly speaking Omae's [1] definition is inadequate as it specifically excludes compounds which contain a non-carbon atom in the metallocyclic ring. There are numerous examples of such compounds in the literature which must be recognised as being cyclometalated compounds in the true sense of the term as many of these compounds are of importance to cyclometalation chemistry. Examples include:



[17]



[18]

It is therefore appropriate to extend Omae's definition to include such compounds. Compounds of this type feature almost exclusively in Chapters Two and Four.

1.2 History

The first examples of cyclometalated complexes were reported by Bähr and Müller [19-21] in 1955 (Figure 1.3). Some bicyclic beryllïum analogues were also reported.

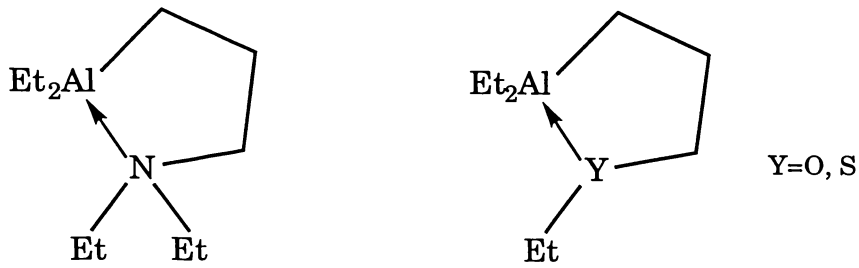
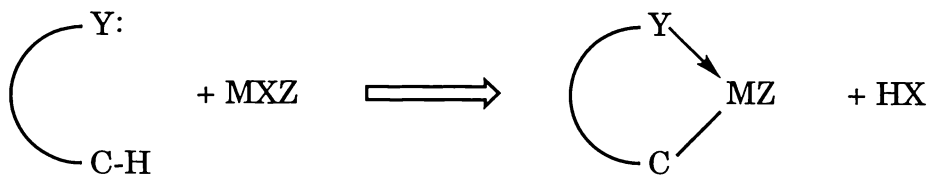


Figure 1.3

The term "cyclometalation" was introduced by Trofimenko [22] in 1973 to describe the ring formation reaction of cyclometalated compounds (Equation 1.1).

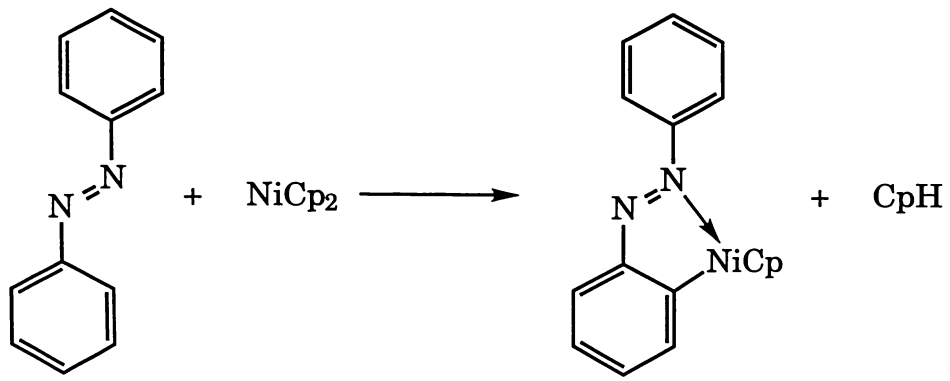


Equation 1.1

The key features of this reaction type are the donor atom directing the formation of the metal-carbon bond, and the elimination of a neutral species as a product.

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

Based on this definition the azobenzene complex of nickel reported by Keiman and Dubeck [23] in 1963 can be identified as the first example of orthometalation (Equation 1.2), followed closely by the report from Cope and Seikman [24] of an analogous complex of palladium in 1965.



Equation 1.2

1.3 Chelate Ring Size

The chelate rings of cyclometalated complexes generally contain three- to eight-members, with the five-membered ring being by far the most common [10,25]. It is believed that this ring size is most stable because of favourable geometry and entropy considerations [25a]. X-ray crystallography studies have shown the five-membered ring configuration has closest to the ideal geometry (bond angles and bond lengths) of all the possible ring sizes. X-ray crystal structure studies have also shown that there is considerable ring strain associated with three- and four-membered rings [26] as is illustrated by the example given in Figure 1.4.

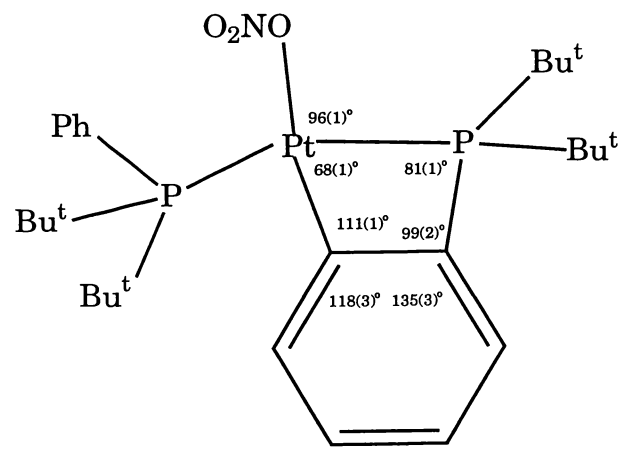


Figure 1.4

This preference for the formation of five-membered metallocyclic rings is illustrated by the reactions of $C_6H_5(CH_2)_nNMe_2$ where n=0, 1, 2 or 3 with $PdCl_2$. Orthometalation of the benzylamine occurs only when n=1 (i.e. to give formation of a five-membered ring), while the other amines which would form four-, six-, or seven-membered rings on orthometalation give only the complexes $[C_6H_5(CH_2)_nNMe_2]_2PdCl_2$ [25]. Similarly *o*-methyl-*N*,*N*-dimethylbenzylamine, which could in theory close at either the *ortho*-carbon giving a five-membered ring or at the methyl carbon giving a six-membered ring, is found to form only the five-membered palladocyclic ring structure despite the methyl carbon being more reactive towards palladium compounds [27].

Cyclometalated complexes having sulfur or phosphorus as the donor atom have shown an increasing tendency to form three- or four-membered rings compared to corresponding complexes having oxygen or nitrogen donor atoms. Omae suggests this is due to the larger size of the atoms involved and the possibility of d-orbital participation in the bonding with the metal, giving rise to small chelate rings with less strain [1].

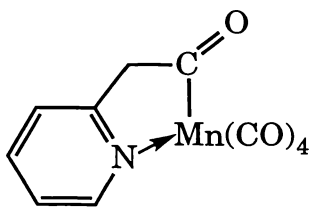
1.4 Donor Atoms

To highlight the diversity of cyclometalated compounds reported, a brief overview of the main donor atoms involved in σ-coordination will be presented.

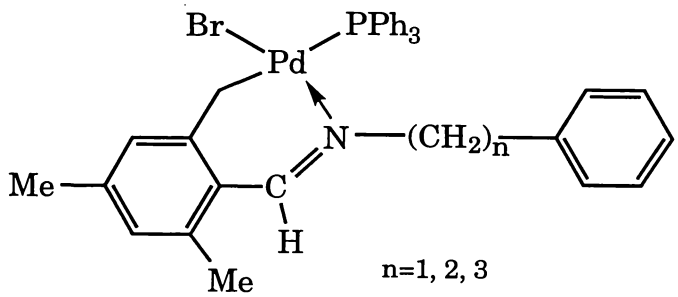
1.4.1 Nitrogen

Cyclometalation reactions are perhaps best developed for N-donor substrates with Pd(II), as is evident from the large number of articles and reviews reported in the literature [29,30]. Cyclometalated compounds with a nitrogen donor can be divided into ten distinct groups: azobenzenes, benzylamines, tolylamines, benzoylamines, ferrocenylmethylamines, benzylideneamines, heteroaromatic compounds, phenyldiazenes, alkylamines and imines. The diversity of metals that coordinate to *N*-donor ligands is also large, examples

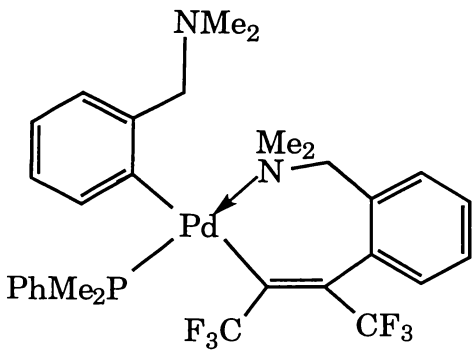
reported in the literature include Li [31], Al [20], Ti [29], Cr [30], W [30], Fe [30], Mo [30], Mn [32], Re [29,32], Ru [29], Os [29], Rh [29], Ir [30], Ni [23], Pd [24], Pt [24], Cu [1], Au [29] and Hg[1]. Almost all of these complexes have a five-membered ring (Figure 1.4) for reasons previously mentioned. However, there are a few examples of nitrogen-containing complexes having six- or seven-membered rings (Figure 1.5) and a very few compounds having three- or four-membered metallocyclic rings have been reported.



[1]



[33]



[34]

Figure 1.5

1.4.2 Phosphorus

As phosphorus belongs to the same group as nitrogen it is not unexpected that many organometallic intramolecular coordinated compounds which are direct analogues of their nitrogen counterparts have been reported. Phosphorus donor ligands include aryl phosphites, phenylphosphines, benzylphosphines, *ortho*-tolylphosphines, 1-naphthylphosphines, 2-alkoxyphenylphosphines, and propylphosphines

while cyclometalated complexes are known for Mn [35], Ru [36], Rh [1], Ir [1], Pt [1], Pd [4], Ni [1], Fe [36], Au [36], Re [35], and Os [1]. These complexes form four-, five-, six-, seven-, and eight-membered cyclometalated rings (Figure 1.6), although the larger ones are not formed directly.

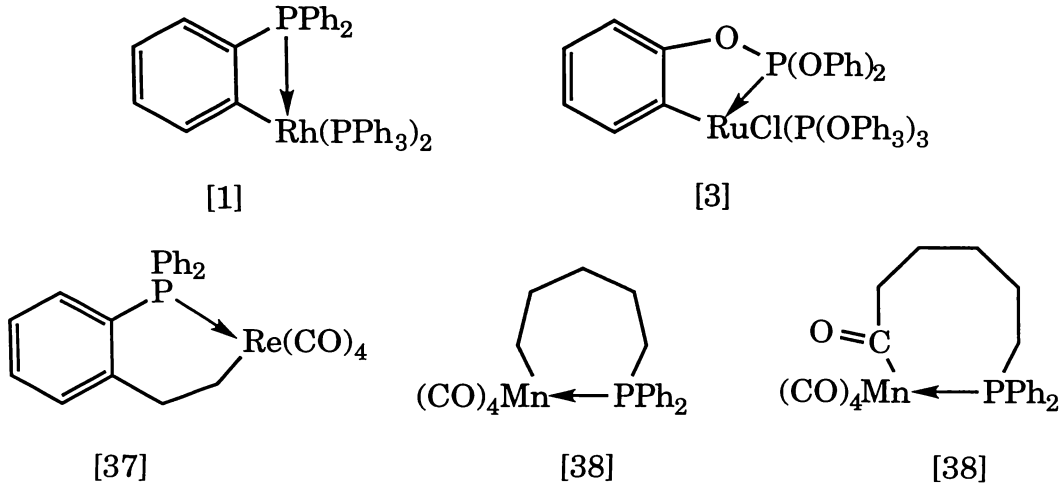
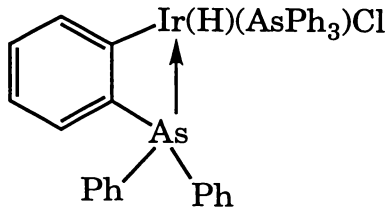


Figure 1.6

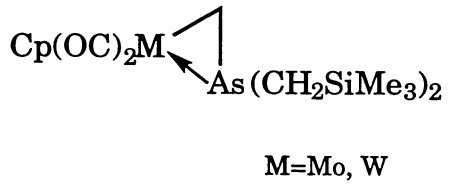
Although the stability of cyclometalated rings in these compounds decreases in the order five > six > four [1], a relatively large number of four-membered ring compounds have been reported, as previously discussed.

1.4.3 Arsenic

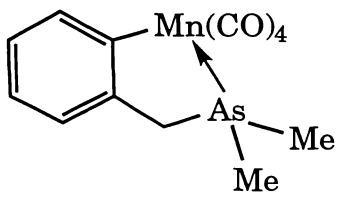
There are relatively few examples of organometallic intramolecular σ-coordinated compounds containing an arsenic donor ligand [39]. Arsenic donor ligands include benzylarsine, phenylarsine, tolylarsine, naphthylarsine and propylarsine incorporated into complexes of Mn, Mo, Pd, Pt and Ir. These cyclometalated compounds form three- [41], four- [40], five- [42] and six-membered ring compounds [1] (Figure 1.7) with five-membered ring structures similar to those of corresponding phosphine compounds being preferred.



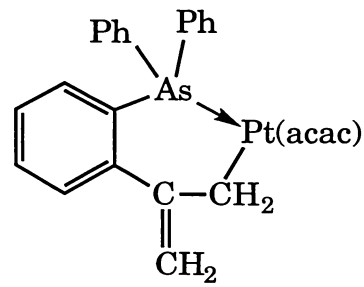
[40]



[41]



[42]



[1]

Figure 1.7

1.4.4 Oxygen

In cyclometalated compounds containing an oxygen donor atom, the ligand groups are in most instances carbonyl groups or, in a few cases, alkoxy groups. The carbonyl series comprise principally ketones, amides, esters, and more rarely, aldehydes. There are also a few examples of nitro [43], hydroxy [44], phosphoryl [45], nitrato [46] and sulphinyl [47] groups as ligands (Figure 1.8).

Cyclometalated complexes have been reported for Mo [51], Fe [49], Sn [52], Os [53], Pd [54], Pt [55], W [56], Ti [57], Mn [50], Sb [57], Rh [58], Ir [58], Ru [59], Re [50] and Hg [1]. Intramolecular coordination compounds have also been reported for the non-metals Se and Te [61]. The vast majority of these complexes contain a five-membered ring, however there are several reports of compounds containing four- [48] or six-membered [60] rings (Figure 1.9).

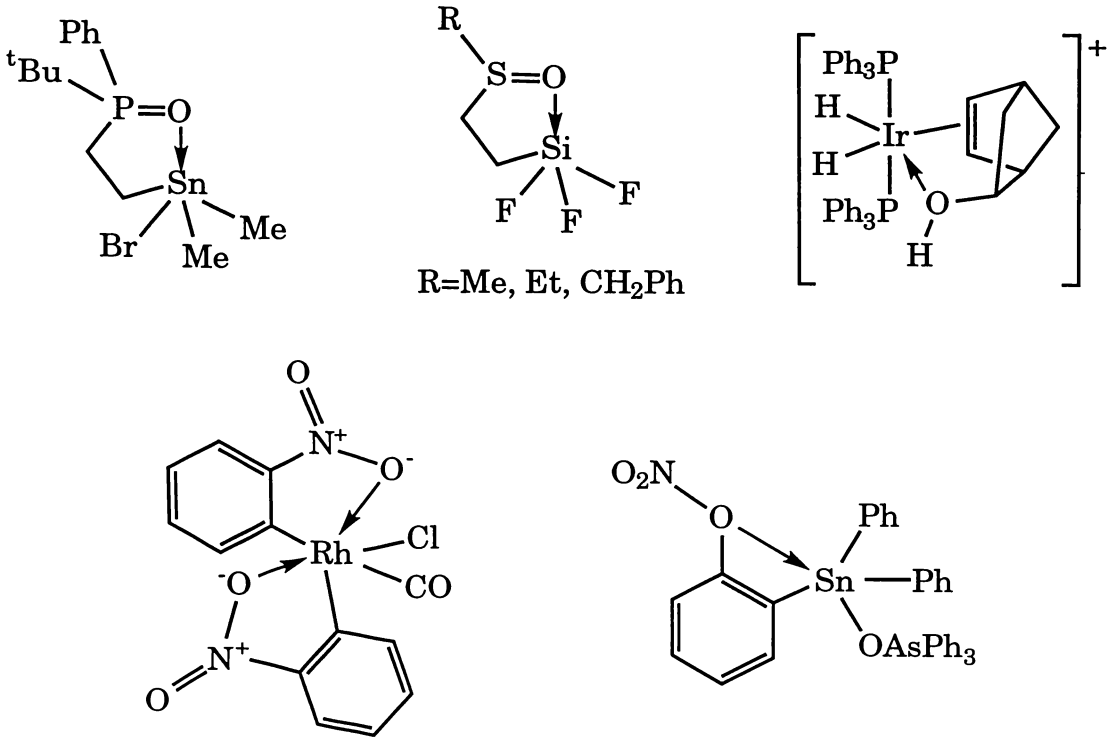


Figure 1.8

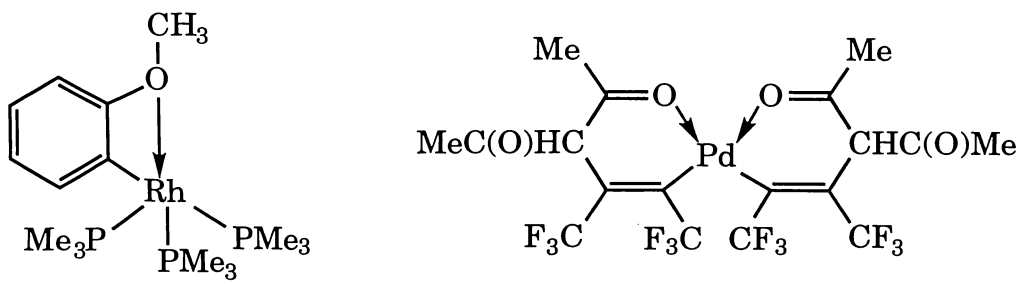


Figure 1.9

As oxygen donor compounds are particularly relevant to this thesis specific examples are discussed in more detail in Section 1.5.

1.4.5 Sulfur

A number of cyclometalated compounds containing sulfur-donor ligands have been reported [1]. Examples include alkane thioethers, alkene thioethers, benzyl thioethers and thiobenzophenone ligands forming cyclometalated complexes with Al [1], Be [62], Fe [63], Mn [64], Re [65], Pd [2], Pt [4], W [1], Mo [1] and Rh [65]. These cyclometalated complexes incorporate three-, four-, five- and six-membered rings, with the five-membered ring configuration being most prevalent (Figure 1.10).

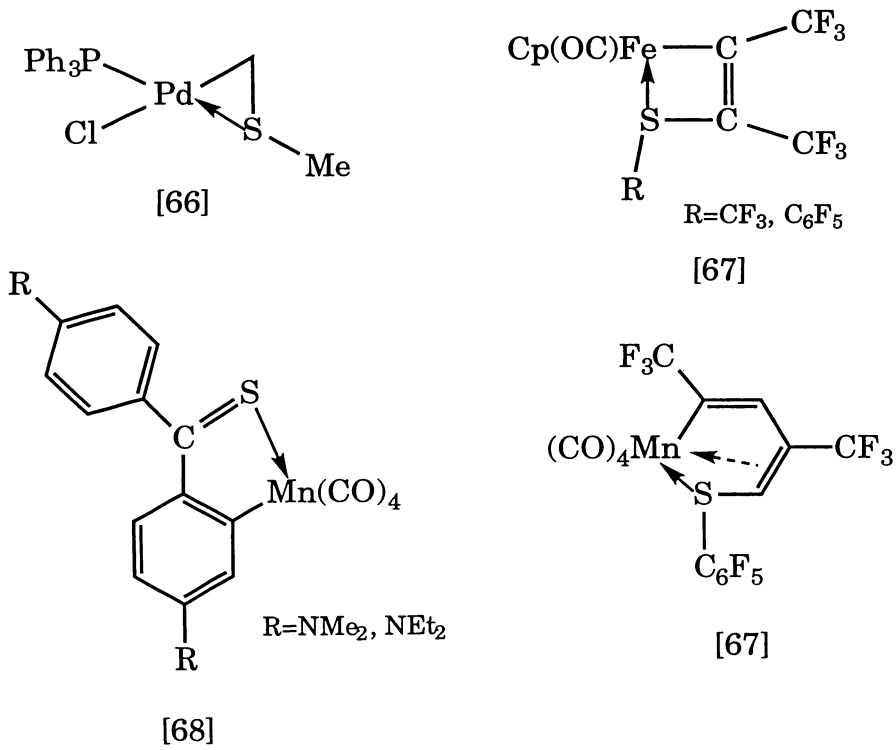
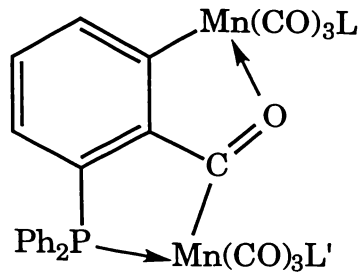


Figure 1.10

1.5 Oxygen-Coordinated Orthomanganated Complexes

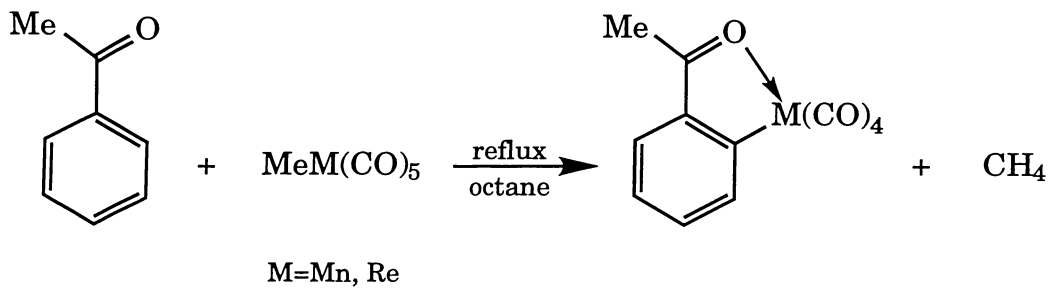
The discovery of secondary metalated products from the thermolysis of methyltetracarbonyltriphenylphosphinemanganese(I) [69,70] (Figure 1.11) led Kaesz's group into the area of direct metalation of aromatic ketones.



(i)L=CO, L'=PPh_3
(ii)L=PPh_3, L'=CO
(iii)L=PPh_3, L'=PPh_3

Figure 1.11

These reactions were distinctive in that they gave rise to the first reports of *ortho*-substitution by a transition metal of an aromatic system in which an oxygen functionality directs the metalation [71] (Equation 1.3).



M=Mn, Re

Equation 1.3

The use of benzylpentacarbonylmanganese as the metalating agent rather than methylpentacarbonylmanganese which was originally used by Kaesz's group has now become standard. The former requires less forcing reaction conditions, giving rise to fewer decomposition products and in most cases studied resulted in a higher yield of the cyclometalated product.

The scope of this reaction has been extended to include other substrates such as quinones [72], heteroaromatic ketones [73], aromatic aldehydes [74], aromatic esters [75], benzylamines [82], benzamides [74] and derivatives of podocarpic acid [83].

To date, only manganese, rhenium (which is an expensive manganese substitute) and a small number of ruthenium orthometalated keto-donor compounds have been reported [78,79], while other metals that react routinely with nitrogen, phosphorus or sulfur donor ligands are not

known to form orthometalated complexes [22,80]. The reason for the distinctive behaviour of manganese towards aromatic ketones is still not clear.

Little has been deduced about the mechanism of orthomanganation because of a paucity of data available. The evidence that is available [73,74] is consistent with an oxidative addition/reductive elimination type mechanism, but this is still at best only speculative.

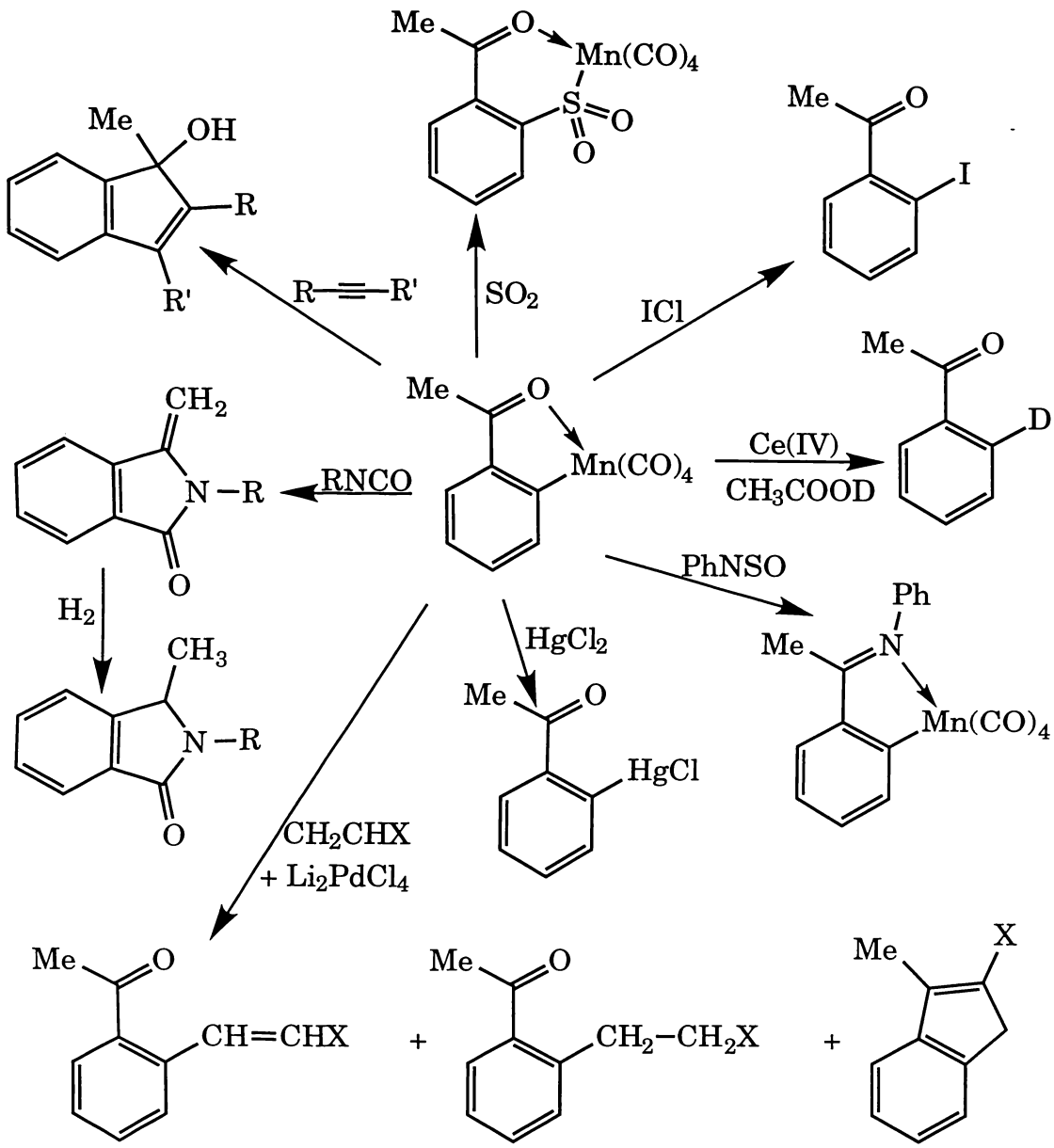
1.6 Reactions of Oxygen-Coordinated Manganese Complexes

Orthomanganated compounds are of particular interest to the organic chemist because of their synthetic potential to functionalise the *ortho* position of carbonyl containing aryl compounds (particularly aromatic ketones) in which the carbonyl function is *meta*-directing and deactivating with respect to electrophilic substitution. These reactions have been recently reviewed [81] and their synthetic diversity is illustrated in Scheme 1.1. It should be noted that not all of the reactions shown are general to other orthomanganated compounds. While much chemistry has been discovered, there is still a need to investigate the generality of such reactions with different substrates and to study the effects of different reaction conditions in an effort to optimise the yield of synthetically useful products.

1.7 Outline of the Present Study

The focus of this thesis is on the preparation of various orthomanganated compounds (Chapters Two and Four) and the study of their reactivity towards a variety of compounds to assess their synthetic potential (Chapters Three, Five and Six).

In Chapter Two the preparation of a range of orthomanganated compounds including orthomanganated *N*-acyl heteroaromatics, heteroaromatic ketones, and heteroaromatic aldehydes, specifically



Scheme 1.1 Some Synthetic Applications of Orthomanganated Ketones

derived from substituted indoles is described. These orthomanganated complexes were prepared primarily for subsequent reactivity studies.

In Chapter Three an investigation into the solvent effects of thermally and oxidatively induced alkyne-coupling reactions of orthomanganated 1-acetylindole and orthomanganated acetophenone with a variety of alkynes is reported. The reactivity of several other orthomanganated substituted-indoles is also investigated.

In Chapter Four a range of novel orthomanganated compounds derived from triphenylphosphine chalcogens which is a new type of substrate is reported. The general properties of these compounds are discussed and compared to previously prepared orthomanganated compounds.

In Chapter Five the reactivity of orthomanganated triphenylphosphine sulfide towards a number of alkenes and alkynes is investigated.

Finally in Chapter Six the insertion of sulfur dioxide into the Mn-aryl carbon bond of the orthomanganated triphenylphosphine chalcogenide series is investigated. The reactivity of sulfur dioxide towards a couple of trimethylphosphite substituted orthomanganated compounds is also described, along with preliminary studies on the reactivity of orthomanganated $Ph_3P{=}S$ towards the cumulenes Ph-N=S=O and Ph-N=C=O.

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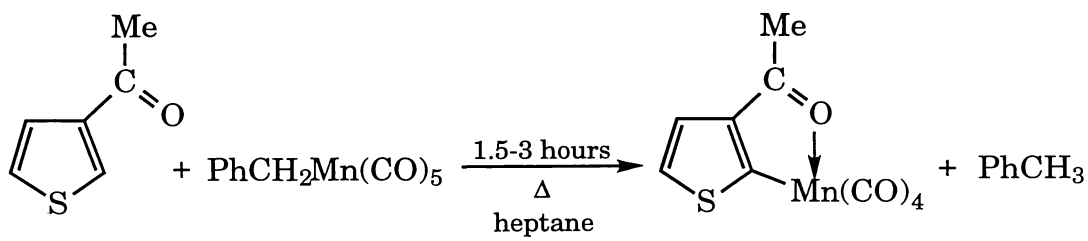
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Chapter Two

Orthofunctionalisation of Substituted Indoles via Manganation

2.1 Introduction

The orthomanganation of a wide range of simple aromatic and heteroaromatic ketones has been well established [1-11]. The reactions proceed smoothly using $PhCH_2Mn(CO)_5$ in refluxing heptane (e.g. Equation 2.1) under an inert atmosphere of nitrogen to give the orthomanganated product, generally in high yield.



Equation 2.1

Extension to other oxygen-donor substrates is not straightforward. There are relatively few examples of orthomanganated esters [6,10], amides and aldehydes [11] compared to orthomanganated ketones.

To date only three orthomanganated indoles have been prepared; these are the orthomanganated heteroaromatic ketone 3-acetylindole [8] and the orthomanganated *N*-acyl compounds 1-acetyl- and 1-benzoyl-indole [11] (Figure 2.1).

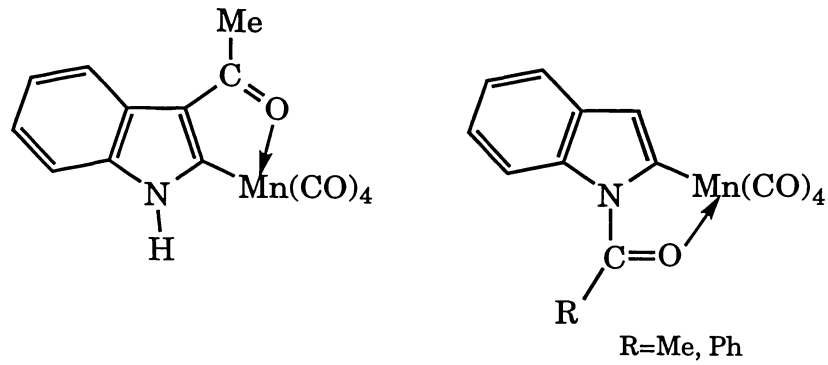


Figure 2.1

A unique feature of the latter is the inclusion of a nitrogen atom in the five-membered metallocyclic ring. As a result, these orthomanganated complexes have the potential to form unusual heterocyclic ring assemblies via coupling reactions already established for other orthomanganated compounds. This has been illustrated by the preparation of dimethyl 1-methyl-1-hydroxypyrrolo-[1,2a]indole-2,3-dicarboxylate (Figure 2.2) from the coupling reaction of orthomanganated 1-acetylindole and dimethyl acetylenedicarboxylate, albeit in low yield (17%) [12].

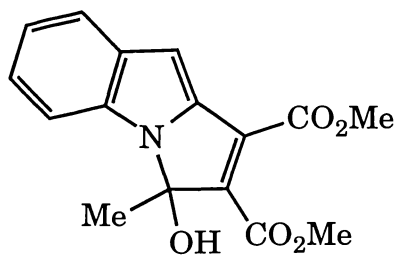


Figure 2.2

With a view to exploring in more detail the alkyne-coupling reactions of orthomanganated indoles to assess reactivity patterns and to optimise synthetic methods, a number of orthomanganated indole complexes including some aldehyde derivatives have been prepared.

2.2 Discussion of Results

2.2.1 General

The yields and work-up procedures for the orthomanganated compounds prepared in this study are given in Table 2.1. Experimental conditions, melting points, elemental analysis data and spectral data are given in Section 2.4.

2.2.2 Orthomanganation of Heteroaromatic Ketones and *N*-Acyl Heteroaromatics

Following the standard procedure employed for preparing orthomanganated ketones, 1-acetylindole **(1)**, 1-(2-methylprop-2-enoyl)indole **(2)**, 1-acetylindole-3-carboxaldehyde, 3-acetylindole, and 1-methyl-3-acetylindole **(3)** were treated with benzylpentacarbonyl-manganese to yield compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)** respectively.

The orthomanganation of 1-acetylindole, 3-acetylindole, and the aromatic ketone acetophenone gave high yields consistent with those previously reported, while that of orthomanganated 1-methyl-3-acetylindole **(8)** was also high. In contrast, the yields obtained of orthomanganated 1-(2-methylprop-2-enoyl)indole **(5)** and especially orthomanganated 1-acetylindole-3-carboxaldehyde **(6)** were low.

The substrate 1-(2-methylprop-2-enoyl)indole was interesting, as it contained two possible sites where cyclomanganation (Figure 2.3) could occur. The first product would arise from attack at the C-2 position of the indole nucleus resulting in the formation of a five-membered metallocyclic ring, with the inclusion of nitrogen, as observed in the orthomanganation of the corresponding *N*-acyl compounds 1-acetylindole **(4)** and 1-benzoylindole. The second site of attack would involve metalation at the terminal alkene carbon (position 3') giving rise to the formation of a cyclomanganated α,β-unsaturated ketone. A number of these non-aromatic complexes have been synthesised in good yields via the direct manganation of α,β-unsaturated ketones [3,12-14].

Table 2.1 Orthometalated Compounds Prepared in this Study

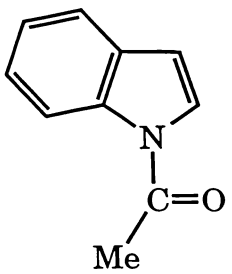
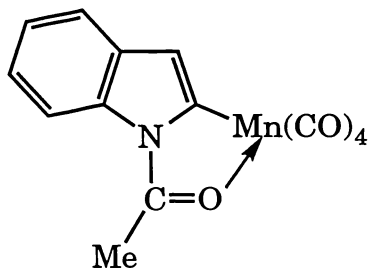
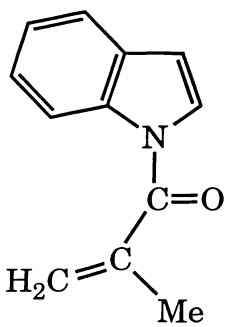
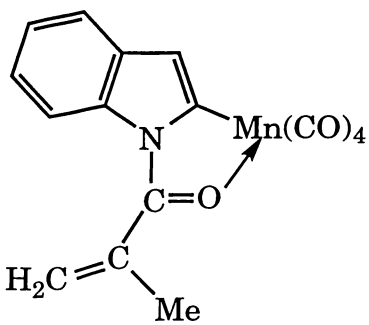
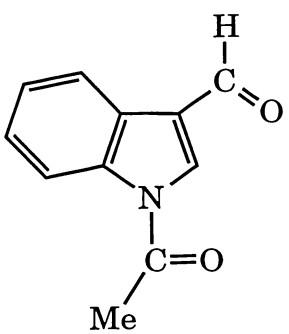
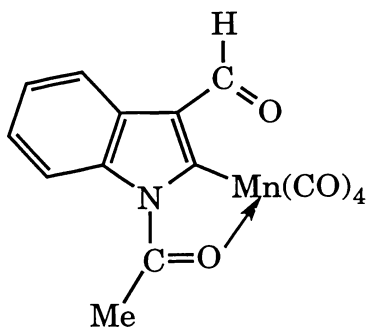
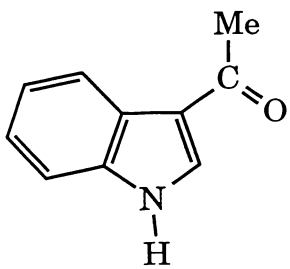
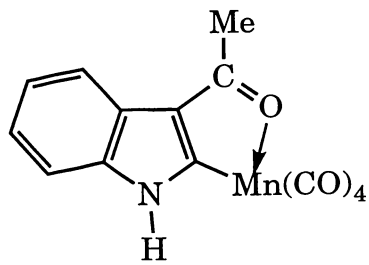
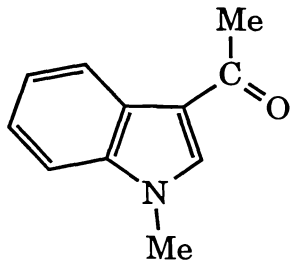
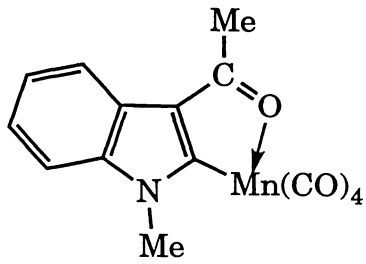
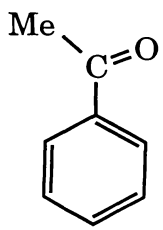
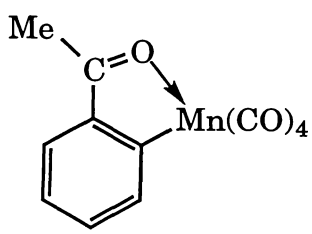
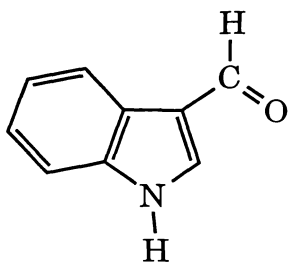
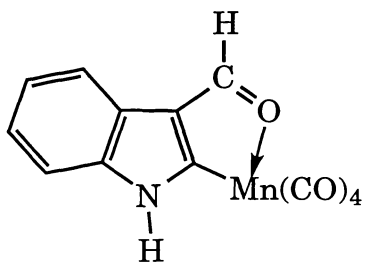
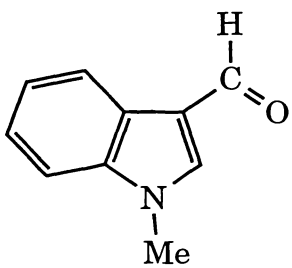
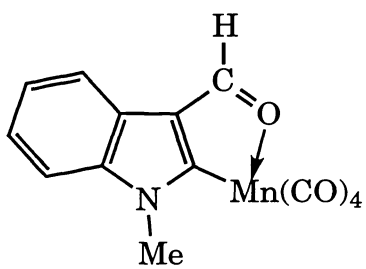
Substrate	Product	Yield	Method of Purification
 (1)	 (4)	69%	A
 (2)	 (5)	29%	B
	 (6)	7%	C
	 (7)	81%	B

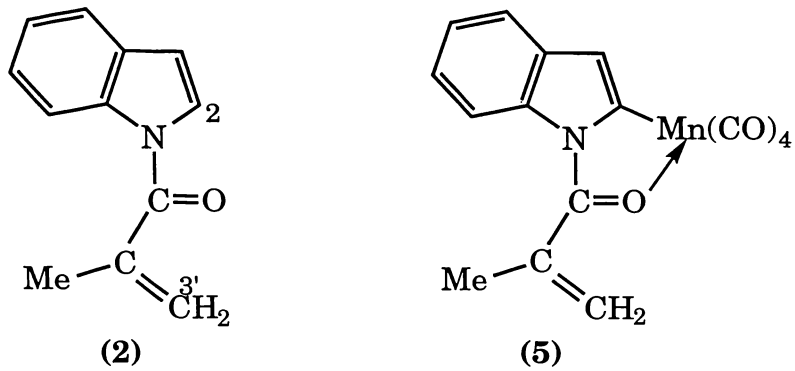
Table 2.1 continued

Substrate	Product	Yield	Method of Purification
 (3)	 (8)	84%	B
	 (9)	91%	B
	 (10)	17%	B
	 (11)	68%	B

A=P.l.c. 1:4 v/v dichloromethane/petroleum spirit

B=P.l.c. 1:9 v/v ether/petroleum spirit

C=P.l.c. 2:3 v/v ethyl acetate/petroleum spirit



(2) **(5)**

Figure 2.3

However, an IR spectrum of the crude reaction mixture indicated only one orthomanganated compound. This was separated from some unreacted ketone and $Mn_2(CO)_{10}$ by p.l.c. Both ^{13}C and ^{1}H NMR spectroscopy clearly showed that manganation had occured at the C-2 position of the indole nucleus to give **(5)** (position 1). The NMR spectra showed that the signal arising from H-3 had undergone a change in multiplicity from a doublet to a singlet, and the signal arising from C-2 had undergone a downfield chemical shift of approximately 45 ppm and now appeared as a singlet carbon, as is consistent with manganation at the C-2 position of the indole nucleus. The formation of only one cyclometalated complex probably reflects the relative reactivities of the different C-H bonds in the substrate.

All previous reactions involving the direct cyclomanganation of α,β-unsaturated ketones have been carried out on substrates where the β-carbon of the substrate has been mono-substituted (Figure 2.4). The substituted group in these substrates was normally a phenyl or substituted aryl ring. This suggests that β-substitution with these groups may make the β-H more reactive electronically, and the failure of **(2)** to undergo cyclomanganation at the alkene carbon may therefore reflect the absence of substitution at the β-carbon.

Perhaps a more obscure reason or contributing factor for the failure of manganation to occur at the terminal alkene carbon is related to the observation that if a cyclic compound is in equilibrium with an open chain derivative it appears to be the almost invariable rule that alkyl

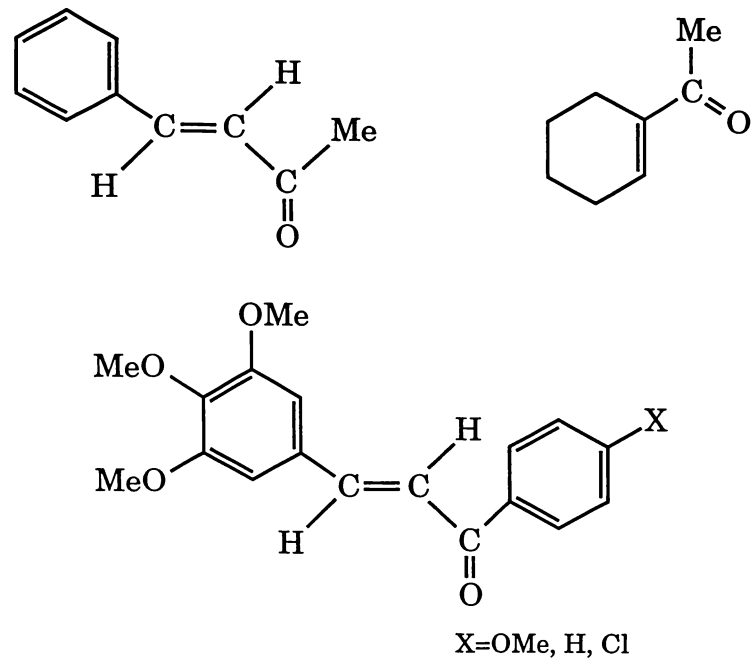


Figure 2.4

substitution favours the ring form [15]. This has been rationalised in terms of the Thorpe-Ingold effect for three- and four-membered rings, while the proposals of Allinger and Zalkow are generally utilised to rationalise similar trends in five- and six-membered rings. Allinger and Zalkow [16] suggest the enthalpy of ring-closure is more favourable for alkyl-substituted *n*-hexanes because of the increased number of *gauche* interactions in the open chain compared with the cyclic product. The entropy of ring closure is also more favourable, as branching reduces the rotational entropy of the open chain form significantly more than that of the ring, which has built in restrictions to internal rotation. An example of this effect is illustrated in the orthomanganation of isopropyl and methyl benzoate [10]. The isopropyl ester would be expected to be more effective at promoting ring closure (i.e. undergoing orthomanganation) than its methyl analogue due to its increased alkyl substitution. This is reflected in orthomanganation which gave the orthomanganated isopropyl benzoate in good yield, while only a trace of the corresponding methyl analogue was obtained. A similar effect may therefore be occurring in the present case, where the presence of β-substituents in previously prepared cyclomanganated α,β-unsaturated

ketones may be more effective at promoting ring closure in a similar way to alkyl substitution than the unsubstituted β-carbon in **(2)**.

A pure sample of **(5)** could not be obtained as the resulting impure orange oil failed to crystallise and was susceptible to demetalation. Even immediately after purification by chromatography (p.l.c.), ^{1}H and ^{13}C NMR showed the presence of a little of the demetalated compound 1-(2-methylprop-2-enoyl)indole **(2)**.

1-Acetylindole-3-carboxaldehyde was another interesting candidate for orthomanganation as it contains two different carbonyl oxygen donor groups. As a result, there is the possibility of three orthomanganated products depending on whether the coordinated donor group is the ketone carbonyl, the aldehyde carbonyl or both.

However, it soon became obvious that this substrate was less than ideal for the orthomanganation reaction. Longer reaction times of ~9 hours had to be employed, and in contrast to previous orthomanganations the reaction solution never went yellow but instead remained brown in colour throughout. Only one manganated product was detected and it was isolated in very low yield. IR spectroscopy revealed that the compound was a tetracarbonyl species, ruling out the possibility of the tricarbonyl manganese species which would have resulted if both donor groups were coordinated. To determine which carbonyl group had become coordinated to the manganese, the ^{13}C chemical shifts of the respective carbonyls in the orthomanganated complex were compared to those of the free ligand. Comparison of these chemical shifts is generally a good indicator as to whether or not coordination has occurred, as this results in a significant ^{13}C downfield chemical shift of the organic carbonyl signal by ~10-21 ppm [17]. However, in this case comparison of the size of the ^{13}C downfield chemical shift of the respective organic carbonyl signals going from the free ligand to the cyclomanganated complex led at first to ambiguity in interpretation, as both the acyl carbonyl and the aldehyde carbonyl were consistent with the expected downfield chemical shifts (12.3 and 4.7 ppm respectively) of a coordinated carbonyl oxygen (see Section 2.3.3). This is illustrated by comparison with the related compounds from 1-acetylindole **(4)** (9.8 ppm) and 1-methylindole-3-carboxaldehyde **(11)** (4.3 ppm).

This led to the comparison of the IR stretching frequencies of the respective carbonyl groups. Generally coordination results in the lowering of the C=O stretching frequency by ~100-150 cm^{-1} compared to that of the free ligand [17]. Examination of the respective frequencies clearly showed that the manganese had become coordinated to the *N*-acyl carbonyl group as its stretching frequency had been lowered by ~153 cm^{-1}, while that of the aldehyde carbonyl had only been lowered by ~30 cm^{-1}. The observed downfield chemical shift of the aldehyde carbonyl carbon may be the result of the carbonyl group being shifted out of the plane of the ring due to the insertion of the bulky $Mn(CO)_4$ fragment into the sterically congested site.

The yield of **(6)** was only 7%, presumably because of steric congestion inhibiting the formation of the Mn-C bond. This has some precedence. For example, 1,3-diacetylbenzene afforded the orthomanganated products shown in Figure 2.5 [12].

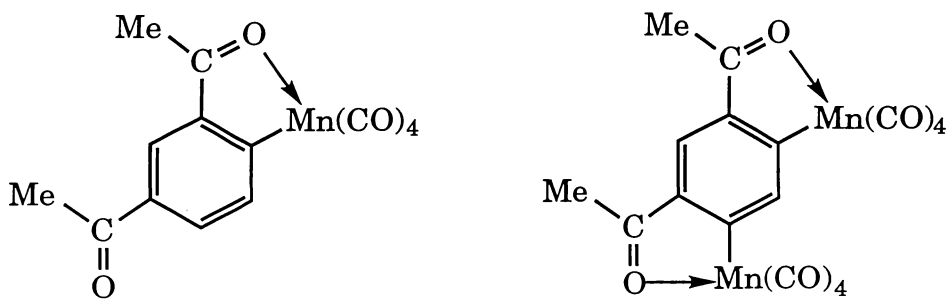


Figure 2.5

There was no sign of the isomeric mono- and di-metalated products which would have resulted from attack of the manganese at the sterically congested C-2 position. Similarly, attempts to orthomanganate 1,3,5,-triacetylbenzene were unsuccessful [18].

The indole derivative 1,3-diacetylindole **(12)** failed to yield the corresponding orthometalated complex, indicating, that the presence of the extra methyl group compared to 1-acetylindole-3-carboxaldehyde is critical to the outcome of the reaction. Orthomanganated 1-acetylindole-3-carboxaldehyde appears to be the only example of an orthomanganated complex in which manganation occurs between two possible donor carbonyls.

All of the orthomanganated 1-acylindole complexes prepared in this study **(4, 5, 6)** also contained another possible site of cyclomanganation at the C-7 position in the six-membered ring of the indole nucleus. Attack at this position would give rise to a six-membered metallocyclic ring. However, this type of product was never detected which may reflect the relative stability of a five-membered metallocyclic ring over that of a six-membered ring.

Orthomanganated compounds **(4)** and **(7)** which have been prepared previously, were synthesised in this study primarily to compare their reactivity towards alkynes with other orthomanganated ketones (see Chapter 3), and to complete their full characterisation, including updating of their NMR assignments. There was a major discrepancy between the melting point of orthomanganated 1-acetylindole obtained in this study which decomposed at 148 °C compared to the literature value of 112 °C. The former value would appear to be a more accurate representation of the melting point of orthomanganated 1-acetylindole as it was determined on several different occasions using several different batches of the orthomanaganated complex. The large difference may suggest that a different crystalline form was obtained in the earlier study.

2.2.3 Orthomanganation of Heteroaromatic Aldehydes

Examples of orthomanganated aldehydes are relatively rare. They include some substituted orthomanganated benzaldehydes [11], orthomanganated thiophenecarboxaldehydes [12] and orthomanganated diterpenoid-derived aldehydes [19]. It is generally accepted that this is caused by the poorer donor ability of the aldehyde carbonyl compared to that of the ketone carbonyl group. This is also reflected in the significantly lower yields of the orthomanganated aldehyde complexes obtained compared to those of orthomanganated ketones, and in the formation of **(6)** where the manganese is coordinated to the *N*-acyl carbonyl group and not to the aldehyde group.

From a study [11] on the orthomanganation of a series of benzaldehydes an interesting result emerged. Cyclomanganation of benzaldehydes

carrying electron-donating substituents such as -OMe or -NMe_2 in the *para* position were achieved in reasonable yields. However, the parent aldehyde benzaldehyde was unreactive under the same conditions. The reason for this is not totally clear as the mechanism of cyclomanganation reactions has not yet been established, but it is thought to reflect in part the poorer donor ability of the aldehyde carbonyl group in benzaldehyde.

Electron-donating substituents would enhance the donor strength of the aldehyde oxygen atom [3,20] as is evident from the lowering of the C=O stretching frequencies (Table 2.2). This would favour complexation of the donor O atom to $PhCH_2Mn(CO)_5$ and would result in the metalation step occurring within a complex in which there is increased electron density on the manganese, which at least for an oxidative-addition mechanism, may provide activation.

Table 2.2 Infrared Stretching Frequencies υ(C=O) of Various Aldehydes and their Yield in Orthomanganation

Aldehyde	υ(C=O) cm^{-1}	Yield (%)
benzaldehyde	1700	0
3,4,5-trimethoxybenzaldehyde [11]	1690	6
p-methoxybenzaldehyde [11]	1685	33
p-dimethylaminobenzaldehyde [11]	1660	77
2-thiophenecarboxaldehyde [12]	1675	11
3-thiophenecarboxaldehyde [12]	1685	20
indole-3-carboxaldehyde	1634	17
1-methylindole-3-carboxaldehyde	1642	68

However, an ambiguity arises as the donor ability of the C=O group may not be the important factor since the presence of electron-donating substituents on the aromatic ring may also enhance the reactivity of the ring to attack by the metal. Despite this uncertainty these results showed a useful empirical guide which predicts that substrates for orthomanganation should have υ(C=O) < 1700 cm^{-1}.

Woodgate's group reported an indirect route to the previously inaccessible orthomanganated benzaldehyde complex [21]. This involved orthomanganating benzoyltrimethylsilane which contains a relatively low υ(C=O) of ~1620 cm^{-1}, followed by the subsequent conversion of the acylsilane complex to the orthomanganated benzaldehyde via flouride-catalysed desilyation in good yield.

Comparison of the υ(C=O)'s of indole-3-carboxaldehyde (υ(C=O) 1634 cm^{-1}) and 1-methylindole-3-carboxaldehyde (υ(C=O) 1642 cm^{-1}) indicated that these substrates were suitable candidates for orthomanganation. Reaction of indole-3-carboxaldehyde and 1-methylindole-3-carboxaldehyde with $PhCH_2Mn(CO)_5$ afforded the corresponding orthomanganated aldehyde complexes **(10)** and **(11)** in low and good yields respectively (Table 2.1). The crystal structure of **(11)** was determined by X-ray methods and full discussion of the structure is deferred to Section 2.4.

There appears to be no obvious reason for the large difference in the yields of the different orthomanganated aldehyde complexes **(10)** and **(11)**. From comparison of the carbonyl stretches in the benzaldehyde series (Table 2.2) with the yield of the corresponding orthomanganated complexes, there appears to be a trend that the lower the υ(C=O) stretch, the higher the yield of product. However at best this correlation is only tentative and is not observed for the indole-3-carboxaldehydes.

Another contributing factor which must be considered, is the presence of a protic function in the substrate. It is assumed that the presence of these functions interferes with orthomanganation [4] as is illustrated by the failure of benzoic acid (υ(C=O) 1695 cm^{-1}) to undergo orthomanganation. The failure of benzamide to undergo orthomanganation, unlike the *N*,*N*-dialkylated benzamides [12] also suggests that even weakly acidic protic groups prevent reaction, although the basicity arising from the presence of a lone pair on the N of benzamide may also be a contributing factor for this example. In the attempted orthomanganation of 2-acetylpyrrole the presence of the N-H bond complicates the reaction, whereas for 2-acetyl-*N*-methylpyrrole the normal manganation product was observed [4]. In contrast, this effect was not observed in the orthomanganation of 3-acetylindole which

proceeded in high yield. The presence of an N-H bond in indole-3-carboxaldehyde therefore cannot be used to explain the low yield of the orthomanganated complex as there is unlikely to be any significant N-H acidity difference between the aldehyde and ketone derivatives.

The use of υ(C=O) in rationalising results should be treated with caution. This is because strictly speaking the requirement that υ(C=O) < 1700 cm^{-1} is useful only within a single group, such as the benzaldehyde series. Direct comparisons between aldehyde groups on different aromatic cores cannot be made because of the impure nature of the C=O stretch arising from υ(C=O) coupling to C=C (aromatic) vibrations. As a result, the cross-over point between no reaction and the formation of an orthomanganated product in different classes of aldehydes may be different from that of the benzaldehyde series.

If we try to extend this rule to other classes of compounds such as the *N*-acyl heteroaromatics, 1-acetyl indole (υ(C=O) 1707 cm^{-1}) and 1-acetylpyrrole (υ(C=O) 1722 cm^{-1}) [12], it is immediately clear they contravene the rule as they both give rise to orthomanganated products in good yield. The comparison of the structurally similar compounds, acetophenone (υ(C=O) 1695 cm^{-1}) and benzaldehyde, also illustrates the invalidity of the prediction, as the yield of orthomanganated acetophenone is essentially quantitative despite υ(C=O) being very close to the proposed point of no reaction.

2.3 Properties of Orthomanganated Complexes

2.3.1 General

The orthomanganated complexes prepared in this study were all easily handled. They are mostly yellow to orange crystalline solids with sharp melting points, with the exception of **(5)** which yielded an orange oil. They are generally air stable and can be stored in a refrigerator (-20 °C) for extended periods without any appreciable decomposition. The

orthomanganated compounds dissolve readily in all organic solvents, which means there are no constraints for spectroscopy and reactivity studies.

2.3.2 Infrared Spectra

All of the orthomanganated complexes prepared in this study exhibited three characteristic absorptions in the metal carbonyl region. There was usually a medium intensity band around 2090 cm^{-1}, an intense band around 2010 cm^{-1} , and a strong band around 1945 cm^{-1}. For a *cis*-$L_2M(CO)_4$ molecule four bands are predicted in the υ(CO) region of the spectrum. However, the two intense bands expected around 2000 cm^{-1} are accidentally degenerate and not resolved. As the high-energy band of this pattern is well resolved from those of the metalating agent benzylpentacarbonylmanganese and from the by-product decacarbonyldimanganese, the progress of reaction may be followed spectroscopically.

Coordination of manganese to the oxygen atom of the carbonyl group of both the heteroaromatic ketones and the *N*-acyl compounds resulted in the lowering of υ(C=O) by ~120-150 cm^{-1}, which is consistent with previously reported examples [17]. In contrast, the aldehyde carbonyls υ(C=O) were only lowered by ~80 cm^{-1} upon coordination. However, comparison with other orthomanganated aldehydes for which shifts range from ~72-144 cm^{-1} [12] shows that these shifts are also consistent.

The orthomanganated *N*-acyl complexes show metal carbonyl IR bands approximately 10-15 cm^{-1} higher than those of simple aromatic ketones. This has been attributed in the past to the presence of the electronegative nitrogen atom in the metallocyclic ring [11]. It was proposed that the inductive effect of the nitrogen led to the reduction of electron density on the carbonyl group available for donation to the manganese. This would result in less electron density on the manganese available for back bonding to the π^* of the metal carbonyls, resulting in the observed increase in υ(C≡O). However, examination of the metal carbonyl IR bands of the orthomanganated heteroaromatic ketones and aldehydes, which contain their respective functional groups in the 3-position of the indole nucleus, also reveals that these bands are also 10-15 cm^{-1} higher

than those of simple aromatic ketones and aldehydes respectively, despite the absence of nitrogen in the metallocyclic ring. This suggests that the electronegative nitrogen is drawing electron density away from the C-2 carbon and not the *N*-acyl carbonyl group, which would result in the observed increases in $\upsilon(C\equiv O)$ for reasons already mentioned. It would therefore be expected that this would lead to the formation of a rather short Mn-C bond compared to other orthomanganated complexes. The crystal structures of orthomanganated indole-3-carboxaldehyde (Section 2.4) and orthomanganated 1-acetylindole [11] have been determined, and the Mn-C bond lengths were found to be 2.003 and 2.012 Å respectively, which are the two shortest examples known; for other orthomanganated aromatic compounds the Mn-C distances fall between 2.03 and 2.07 Å [17].

The possibility of resonance effects involving the lone pair of electrons on the nitrogen atom must also be considered. Examination of the bond lengths obtained from the crystal structure of orthomanganated indole-3-carboxaldehyde (Section 2.4) and orthomanganated 1-acetylindole suggests that there is a significant contribution of the resonance structure arising from the delocalisation of the nitrogen lone pair, leading to the localisation of electron density on the carbonyl oxygen atoms (Figure 2.6). In contrast to the inductive effect of nitrogen, this would result in more electron density on the manganese because of the increased donor ability of the carbonyl oxygen which would contribute to a lowering in $\upsilon(C\equiv O)$. It is obvious from the higher $\upsilon(C\equiv O)$'s observed that the -I effect of the nitrogen is greater than that of the +R effect.

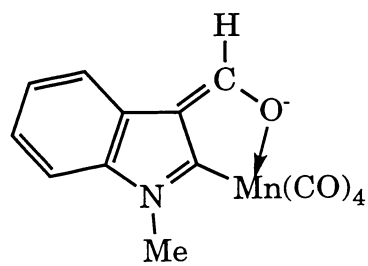


Figure 2.6

Comparison of the metal carbonyl IR bands of the orthomanganated aldehydes with those of the heteroaromatic ketones and *N*-acyl heteroaromatics show there is very little difference between them. This

was unexpected since the aldehyde carbonyl is expected to be a weaker donor, which may have been reflected in higher values of $\upsilon(C\equiv O)$'s. However, it is possible that the inductive effect of the electronegative nitrogen described above may overwhelm any effect arising from differences in donor properties on $\upsilon(C\equiv O)$.

2.3.3 ^{13}C NMR Spectroscopy

Selected chemical shifts are given in Table 2.3. The orthomanganated complexes generally show three broad signals around δ 215 ppm of intensity 1:1:2 which can be assigned to the terminal Mn-CO groups. Based on previous assignments for related compounds, they can be attributed to the manganese-bonded carbonyl ligand opposite the oxygen atom at lowest field, the next lowest from the carbonyl ligand *trans* to the aryl carbon, and the remaining two carbonyl groups *trans* to each other at highest field [8]. It should be noted however, that although this assignment pattern is self consistent over a whole range of compounds, it is based on the assumption that the CO groups with the lowest CO force constant (most back-bonding) give rise to the highest ^{13}C chemical shift. There is no independent confirmation of this assumption.

The signal of the coordinated carbonyl group generally appears in the 180-215 ppm region, having been shifted by 9-12 ppm to lower field on coordination, which is in agreement with shifts in previously studied compounds [17]. However, the cyclomanganated aldehydes **(10)** and **(11)** only exhibit a downfield shift of approximately 4 and 6 ppm respectively. The reason for this is not clear as other orthomanganated aldehydes show the normal shift of ~10 ppm downfield. The heteroaromatic *N*-acyl carbonyl carbons of **(4)**, **(5)** and **(6)** appear around 178-181 ppm, approximately 20 ppm to higher field compared with orthomanganated phenyl ketones. These lower values have been attributed to the nitrogen atom bonded to the carbonyl group [12]. The aryl carbon bonded to the manganese was normally found in the range 170-217 ppm. Coordination of the manganese shifts the signal of the metalated carbon by 47-76 ppm to lower field, and those on either side generally by 9-16 ppm to lower field, with only small shifts for the remaining aryl carbon signals.

Table 2.3 Selected ^{13}C NMR Chemical Shifts of Various Orthomanganated Complexes and their Corresponding Free Ligand

Compound	C=O	C-Mn/ C-H	C≡O
1-acetylindole			
orthomanganated **(4)**	178.4	172.6	220.1, 212.3, 209.8
free ligand **(1)**	168.6	125.0	-
1-(2-methylprop-2-enoyl)indole			
orthomanganated **(5)**	178.6	172.6	220.1, 212.3, 209.8
free ligand **(2)**	169.8	127.2	-
1-acetylindole-3-carboxaldehyde			
orthomanganated **(6)**	180.9[a] 190.7[b]	199.5	218.9, 211.9, 207.9
free ligand	168.6[a] 185.6[b]	135.1	-
indole-3-carboxaldehyde*			
orthomanganated **(10)**	191.6	217.1	220.8, 212.7, 209.4
free ligand	185.3	138.0	-
1-methylindole-3-carboxaldehyde			
orthomanganated **(11)**	188.7	216.5	221.4, 213.2, 209.3
free ligand	184.4	139.2	-
3-acetylindole#			
orthomanganated **(7)**	205.2	214.6	220.2, 212.6, 209.7
free ligand	196.6	138.3	-
1-methyl-3-acetylindole			
orthomanganated **(8)**	200.7	212.1	220.7, 213.3, 209.7
free ligand **(3)**	193.0	135.9	-
acetophenone			
orthomanganated **(9)**	216.6	193.4	221.1, 212.9, 211.5
free ligand	198.2	128.6	-

*NMR spectra recorded in d_6-acetone; # NMR spectra recorded in d_6-DMSO; [a] *N*-acyl carbonyl; [b] Aldehyde carbonyl.

2.4 X-Ray Crystal Structure of η^2-(1-Methyl-3-formyl-2-indolyl)tetracarbonylmanganese (11)

The crystal structure of η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese was determined as no structure of an orthomanganated aldehyde complex has been reported. The crystal structure was also determined to see if there was any structural reason for the unusually small change in the ^{13}C NMR chemical shift observed for the carbonyl carbon upon cyclomanganation.

2.4.1 Results of Preliminary Studies

Orange block-shaped crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated chloroform solution of **(11)** at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated monoclinic symmetry although the space group was not further determined.

2.4.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -114 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{14}H_8O_5MnN$

M_r=325.15

Crystal class=monoclinic; Space group=$P2_1$

a=9.656(2), b=11.966(2), c=23.486(5) Å

β=101.78(3)°

U=2656.5(9) $Å^3$

D_{calc}=1.626 g cm^{-3}

Z=8

F(000)=1312

μ(Mo-K_α)=1.014 mm^{-1}

A total of 7748 reflections were collected in the range $4° \leq 2\theta \leq 57°$ of which 4912 were unique (R_{int}=0.0013). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method. Of these, 4326 had $I \geq 2\sigma(I)$.

2.4.3 Solution and Refinement

The solution and refinement was performed by Associate Professor Geoff Jameson, Massey University because of the complexity involved, arising from the presence of twinning and the translational disorder of one of the two crystallographically independent molecules in the space group $P2_1/a$. This disorder resulted in the constraint of the a-glide plane being dropped to give four crystallographically independent molecules in the asymmetric unit cell in the space group $P2_1$. The structure was solved using SHELXS and refined on F^2 (including $F^2<0$) by means of SHELXL-93.

The refinement converged with R_1=0.0453 (2σ data); R_1=0.0595, wR_2=0.1502, and Goof=1.015 for all data and with no parameter shifting more than 0.7 σ in the final cycle. The chosen polarity of the space group was shown to be correct by a Flack parameter of 0.00(4). The final difference map showed no peaks or troughs greater than 0.523 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 2.4 and 2.5 respectively. Due to the inherent problems in solving this structure the accuracy of bond lengths and angles is uncertain despite the relatively low R value. Comparison between certain bond lengths and angles in the four independent molecules in the asymmetric unit show at first what appear to be significant differences, for example the C(10)-O(10) bond length varies between 1.248(14) and 1.289(14) Å while the bond angle N-C(1)-C(2) varies between 104.8(9) and 109.9(9)°. However, because of the large estimated standard deviations involved these differences are not significant when analysed statistically. Overall, despite the final errors

being uncertain the averaged data appear to be chemically sensible and gives a good representation of the complex, although one must be cautious when making accurate comparisons to other orthomanganated complexes.

Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix II.

The structure of one of the molecules is shown in Figure 2.7.

2.4.4 Discussion of the Structure

The bond lengths and angles mentioned in the following discussion are an average of the respective values in each of the four independent molecules.

The molecule is essentially planar (with the exception of the two axial metal carbonyl ligands), consisting of a aldehyde-substituted indole core with a tetracarbonylmanganese group attached at the C(1)-position. The carbonyl oxygen atom is attached to the manganese atom giving rise to a six-coordinate manganese atom and a five-membered metallocyclic ring.

The strain imposed by joining two five-membered rings together is reflected in the Mn(1)-C(1)-N(1) and C(10)-C(2)-C(3) angles of 141.5(8)° and 136.5(10)° respectively. However, this has no obvious effect on the ease of preparation as the yield is comparable to those of less-strained analogues.

The C(2)-C(10) distance (1.36(2) Å) is shortened by ~0.1 Å with respect to an average sp^2-sp^2 distance of 1.46 Å, while C(1)-C(2) (1.43(2) Å) and C(10)-O(10) (1.267(14) Å) distances are both correspondingly lengthened.

The C(1)-N(1) bond is noticably shorter than the C(8)-N(1) bond (1.34(2) versus 1.41(8) Å) indicating that the C(1)-N(1) bond has more double bond character.

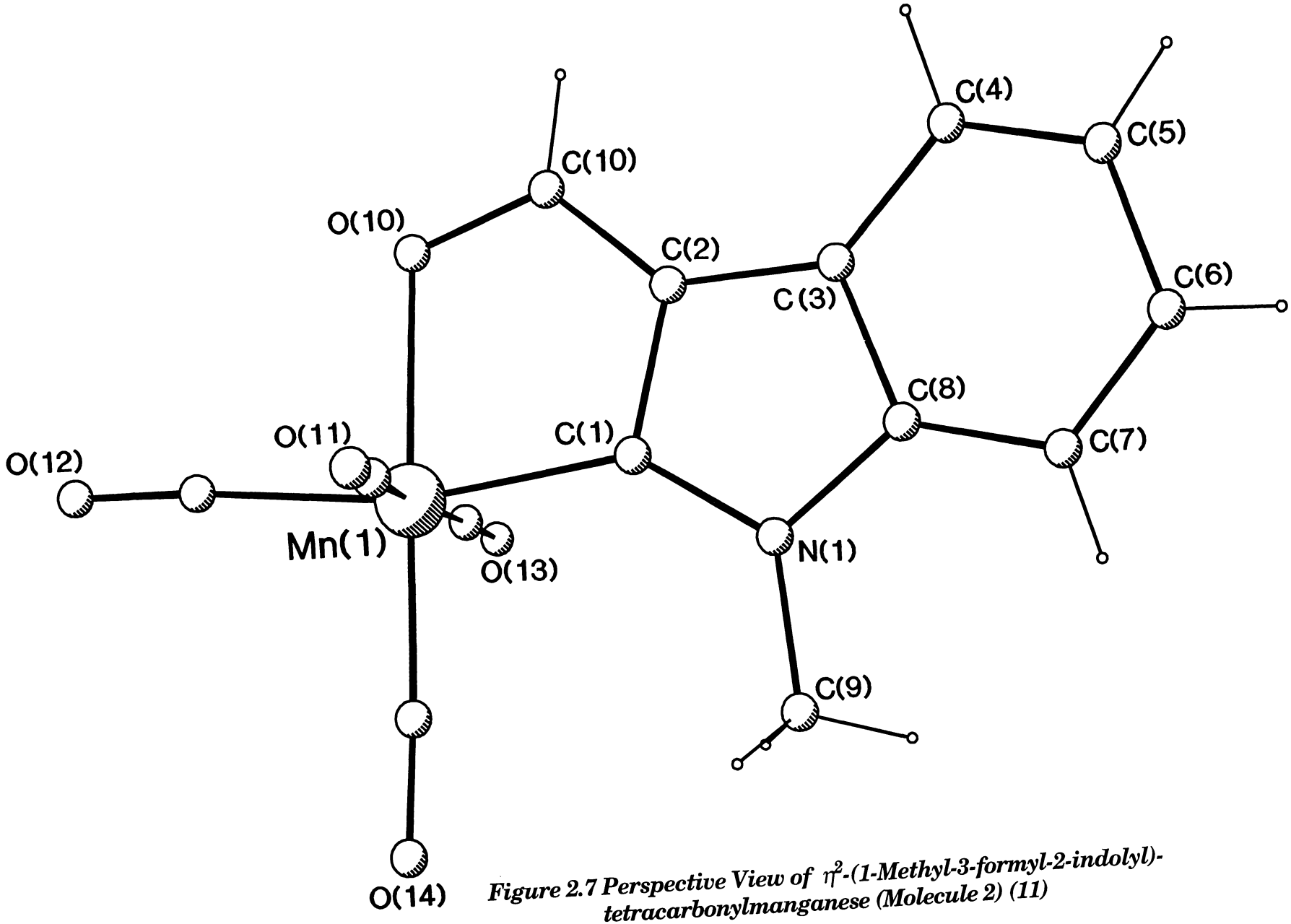


Figure 2.7 Perspective View of η^2-(1-Methyl-3-formyl-2-indolyl)-tetracarbonylmanganese (Molecule 2) (11)

Table 2.4 Bond Lengths (Å) for η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese (11)

Bond	Molecule			
	1	**2**	**3**	**4**
Mn(1)–C(14)	1.774(14)	1.803(13)	1.790(14)	1.773(12)
Mn(1)–C(13)	1.842(12)	1.849(12)	1.872(14)	1.846(12)
Mn(1)–C(12)	1.841(12)	1.87(2)	1.84(2)	1.829(13)
Mn(1)–C(11)	1.883(11)	1.859(11)	1.855(14)	1.877(11)
Mn(1)–C(1)	2.040(11)	1.971(11)	1.983(11)	2.019(12)
Mn(1)–O(10)	2.078(8)	2.076(8)	2.056(8)	2.072(8)
C(1)–N(1)	1.30(2)	1.38(2)	1.34(2)	1.32(2)
C(1)–C(2)	1.42(2)	1.426(14)	1.434(14)	1.44(2)
C(2)–C(10)	1.36(2)	1.36(2)	1.363(14)	1.37(2)
C(2)–C(3)	1.456(14)	1.44(2)	1.42(2)	1.452(14)
C(3)–C(4)	1.38(2)	1.41(2)	1.38(2)	1.40(2)
C(3)–C(8)	1.41(2)	1.43(2)	1.40(2)	1.389(14)
C(4)–C(5)	1.40(2)	1.32(2)	1.38(2)	1.40(2)
C(5)–C(6)	1.38(2)	1.40(2)	1.39(2)	1.38(2)
C(6)–C(7)	1.37(2)	1.38(2)	1.40(2)	1.39(2)
C(7)–C(8)	1.37(2)	1.36(2)	1.39(2)	1.38(2)
C(8)–N(1)	1.42(2)	1.409(14)	1.39(2)	1.407(14)
N(1)–C(9)	1.439(14)	1.441(14)	1.464(13)	1.458(14)
C(10)–O(10)	1.248(14)	1.289(14)	1.284(13)	1.248(14)
C(11)–O(11)	1.121(13)	1.131(13)	1.13(2)	1.118(13)
C(12)–O(12)	1.12(2)	1.10(2)	1.14(2)	1.13(2)
C(13)–O(13)	1.132(14)	1.113(14)	1.11(2)	1.14(2)
C(14)–O(14)	1.16(2)	1.116(14)	1.14(2)	1.165(14)

Table 2.5 Bond Angles (°) for η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese (11)

Angle			Molecule			
			1	**2**	**3**	**4**
C(14)	-Mn(1)	-C(12)	92.7(5)	92.5(6)	92.4(6)	92.1(5)
C(14)	-Mn(1)	-C(13)	89.2(6)	89.6(5)	89.1(6)	89.2(5)
C(12)	-Mn(1)	-C(13)	94.3(5)	94.2(5)	94.9(5)	93.0(5)
C(14)	-Mn(1)	-C(11)	88.7(5)	89.5(5)	88.2(5)	89.8(5)
C(12)	-Mn(1)	-C(11)	91.9(5)	92.4(5)	91.8(5)	94.4(5)
C(13)	-Mn(1)	-C(11)	173.5(6)	173.4(6)	172.9(5)	172.6(6)
C(14)	-Mn(1)	-C(1)	99.2(5)	99.6(5)	99.0(5)	98.3(5)
C(12)	-Mn(1)	-C(1)	168.0(5)	167.7(5)	168.2(5)	169.6(5)
C(13)	-Mn(1)	-C(1)	87.7(5)	88.1(4)	88.3(4)	87.0(5)
C(11)	-Mn(1)	-C(1)	86.6(4)	85.7(5)	85.7(5)	85.8(5)
C(14)	-Mn(1)	-O(10)	177.7(5)	179.4(5)	178.6(5)	178.2(5)
C(12)	-Mn(1)	-O(10)	88.9(4)	88.0(5)	88.1(5)	89.7(4)
C(13)	-Mn(1)	-O(10)	89.0(5)	90.1(4)	89.6(5)	91.4(4)
C(11)	-Mn(1)	-O(10)	92.9(4)	90.8(4)	93.0(4)	89.7(4)
C(1)	-Mn(1)	-O(10)	79.2(4)	80.0(4)	80.5(4)	79.9(4)
N(1)	-C(1)	-C(2)	109.9(9)	105.4(9)	104.8(9)	107.5(10)
N(1)	-C(1)	-Mn(1)	139.7(8)	141.3(8)	143.8(8)	141.1(9)
C(2)	-C(1)	-Mn	110.4(7)	113.3(7)	111.9(7)	111.3(7)
C(10)	-C(2)	-C(1)	116.5(10)	114.3(10)	115.1(9)	114.0(10)
C(10)	-C(2)	-C(3)	136.3(10)	135.2(10)	135.3(10)	139.2(10)
C(1)	-C(2)	-C(3)	107.1(9)	110.4(9)	109.6(9)	106.7(9)
C(4)	-C(3)	-C(8)	118.8(10)	116.1(11)	119.8(11)	120.0(11)
C(4)	-C(3)	-C(2)	136.6(10)	139.1(11)	135.1(10)	133.6(10)

Table 2.5 continued

Angle			Molecule			
			1	2	3	4
C(8)	-C(3)	-C(2)	104.6(9)	104.8(10)	105.0(9)	106.4(9)
C(3)	-C(4)	-C(5)	118.3(11)	121.3(12)	119.2(10)	117.0(10)
C(6)	-C(5)	-C(4)	121.4(12)	121.5(13)	120.1(11)	121.2(11)
C(7)	-C(6)	-C(5)	120.4(13)	120.4(12)	122.7(11)	122.4(12)
C(8)	-C(7)	-C(6)	118.9(12)	118.0(11)	115.1(11)	115.8(11)
C(7)	-C(8)	-N(1)	129.7(11)	129.0(11)	128.8(11)	128.7(10)
C(7)	-C(8)	-C(3)	122.1(11)	122.7(11)	123.0(11)	123.5(10)
N(1)	-C(8)	-C(3)	108.2(10)	108.3(10)	108.1(10)	107.8(9)
C(1)	-N(1)	-C(8)	110.2(9)	111.1(9)	112.3(9)	111.6(9)
C(1)	-N(1)	-C(9)	129.4(11)	126.9(10)	125.4(10)	127.4(10)
C(8)	-N(1)	-C(9)	120.4(11)	123.0(10)	122.3(11)	121.0(9)
O(10)	-C(10)	-C(2)	119.9(10)	120.4(10)	119.5(10)	121.9(10)
C(10)	-O(10)	-Mn	113.9(8)	112.0(7)	113.0(7)	112.8(7)
O(11)	-C(11)	-Mn	174.5(10)	177.2(10)	173.7(9)	177.3(10)
O(12)	-C(12)	-Mn	178.5(11)	176.3(13)	178.2(13)	176.2(12)
O(13)	-C(13)	-Mn	177.8(12)	177.7(12)	178.8(11)	178.3(12)
O(14)	-C(14)	-Mn	177.3(11)	178.8(12)	178.3(12)	178.0(11)

The Mn(1)-C(1) bond (2.003(11) Å) is the shortest yet recorded for an orthomanganated arene. Presumably the effect of the delocalised π-bonding over the metallocyclic ring is enhanced by electron density withdrawal from the C(1) carbon atom by the nitrogen atom. As discussed in Section 2.3.2 this is manifested as a short Mn(1)-C(1) bond.

The variations in C-C bond lengths within the molecule can be understood in terms of contributions from two resonance forms (Figure 2.8) indicating a delocalised π-bonding network over both rings.

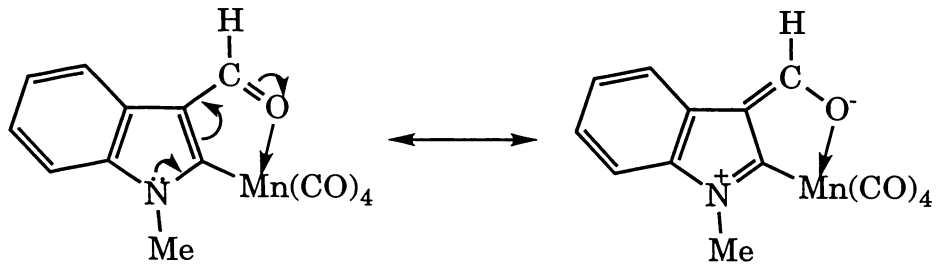


Figure 2.8

Coordination about the manganese atom is essentially octahedral, although the small bite angle of the chelating ligand, as observed in other orthomanganated complexes, gives rise to a C(1)-Mn(1)-O(10) angle of 79.9(4)°, and the out of plane *trans*-CO ligands lean towards the weaker π-acceptor ligands. The shortest Mn-CO bond is in the carbonyl ligand *trans* to the Mn-O bond (1.785(13) Å), that opposite the Mn-C_{aryl} is next shortest (1.845(10) Å), with the two equivalent Mn-CO bonds above and below the plane of the molecule the longest (1.852(12) and 1.869(11) Å). Overall the relative Mn-CO distances and C-Mn-C angles of the $Mn(CO)_4$ group fall into the pattern established for other *ortho*-manganated complexes and the geometry of the metallocycle is fully consistent with other orthomanganated complexes in which there is delocalised π-bonding over the whole ring. There is nothing unusual in the structure which would account for the anomalous carbonyl ^{13}C NMR chemical shift upon manganation.

2.5 Experimental Section

2.5.1 Preparation of Starting Materials

The following commercial materials were used as supplied: 3-acetylindole (Aldrich, 98%), indole-3-carboxaldehyde (Aldrich, 97%), 1-methylindole-3-carboxaldehyde (Aldrich, 97%), 1-acetylindole-3-carboxaldehyde (Aldrich, 97%), and acetophenone (Aldrich, 97%).

Preparation of Benzylpentacarbonylmanganese

$PhCH_2Mn(CO)_5$ was prepared by the standard method of Closson *et al.* [22,23] m.p. 36-37 °C (lit., 37.5-38.5 °C [22]) IR ($CHCl_3$): υ(CO) 2108 (m), 2012 (vs, br), 1993 (s) cm^{-1}.

Preparation of 1-Acetylindole

Method 1

Indole (2.07 g, 17.7 mmol) was dissolved in THF (50 mL) and cooled to 0 °C in an ice bath. n-Butyllithium (11 mL, 1.6 mol L^{-1}, 17.7 mmol) was added dropwise under a constant stream of nitrogen over 30 minutes. Stirring was continued for a further 30 minutes at 0 °C. Acetic anhydride (1.75 mL, 18.50 mmol) was added dropwise over 15 minutes. The solution was allowed to warm to room temperature, and stirred for a further 30 minutes. The reaction mixture was quenched with water (40 mL), extracted with ethyl acetate (3 x 40 mL), followed by drying of the combined extracts ($MgSO_4$) and evaporation under reduced pressure to yield a reddish brown oil. The oil was chromatographed (2:1 CH_2Cl_2/hexane) to give *1-acetylindole* as a colourless oil [**(1)**; 1.45 g, 52%].

Method 2

Indole (2.07 g, 17.7 mmol), potassium carbonate (12.2 g, 88.4 mmol), and acetic anhydride (1.75 mL, 18.5 mmol) were refluxed in acetone (AR, 100 mL) for 24 hours. The solution was filtered and worked up as described in method 1 to give *1-acetylindole* as a colourless oil [**(1)**; 1.38 g, 49%]. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.45 (*d*, ^3J=8.0 Hz, 1H, H-7), 7.59 (*d*, ^3J=7.5 Hz, 1H, H-4), 7.41 (*d*, ^3J=3.7 Hz, 1H, H-2), 7.36 (*m*, 1H, H-6), 7.28 (*m*, 1H, H5), 6.64 (*d*, ^3J=3.7 Hz, 1H, H-3), 2.63 (*s*, 3H, CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 168.6 (*s*, 1-$\underline{C}OCH_3$), 135.5 (*s*, C-7a), 130.4 (*s*, C-3a), 125.2 (*d*, C-5), 125.0 (*d*, C-2), 123.6 (*d*, C-6), 120.8 (*d*, C-4), 116.5 (*d*, C-7), 109.0 (*d*, C-3), 23.8 (*q*, 1-CO$\underline{C}H_3$). GCMS: m/z 159 (M^+).

Preparation of 1-(2-Methylprop-2-enoyl)indole

3-acetylindole (1.00 g, 8.54 mmol), potassium carbonate (5.90 g, 42.7 mmol) and methacrylic anhydride (1.76 mL, 11.1 mmol) were refluxed in acetone (AR, 70 mL) for 40 hours. The solution was filtered then

poured into a separating funnel containing water (50 mL) and ether (40 mL) and further extracted with ether (2 x 20 mL). The ethereal solution was dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure and the residue chromatographed (p.l.c. 1:4 v/v ethyl acetate/petroleum spirit) to give *1-(2-methylprop-2-enoyl)indole* as a colourless oil [**(2)**; 0.56 g, 35%]. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 8.43 (*d*, ^{3}J=8.2 Hz, 1H, H-7), 7.59 (*d*, ^{3}J=7.6 Hz, 1H, H-4), 7.48 (*d*, ^{3}J=3.7 Hz, 1H, H-2), 7.37 (*m*, 1H, H-6), 7.30 (*m*, 1H, H-5), 6.61 (*d*, ^{3}J=3.7 Hz, 1H, H-3), 5.69 (*m*, 1H, 1-COC(CH_3)C$\underline{H}_2$), 5.48 (*m*, 1H, 1-COC(CH_3)C$\underline{H}_2$) 2.17 (*s*, 3H, 1-COC(C$\underline{H}_3$)CH_2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 169.8 (*s*, 1-$\underline{C}$OC(CH_3)CH_2), 140.0 (*s*, 1-CO$\underline{C}$(CH_3)CH_2), 135.8 (*s*, C-7a), 131.2 (*s*, C-3a), 127.2 (*d*, C-2), 125.0 (*d*, C-6), 124.1 (*d*, C-5), 122.1 (*t*, 1-COC(CH_3)$\underline{C}H_2$), 121.0 (*d*, C-4), 116.7 (*d*, C-7), 108.6 (*d*, C-3), 20.1 (q, 1-COC($\underline{C}H_3$)CH_2).

Preparation of 1-Methyl-3-acetylindole

3-Acetylindole (1.00 g, 6.28 mmol), potassium carbonate (4.42 g, 32.0 mmol) and methyl iodide (0.51 mL, 8.19 mmol) were refluxed in acetone (AR, 70 mL) overnight. The solution was filtered and the acetone was removed on the rotary evaporator. The residue was redissolved in ether (40 mL), poured into a separating funnel containing water (50 mL) and further extracted with ether (2 x 20 mL). The ethereal solution was washed with NaOH (2 mol L^{-1}), then H_2O and dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure to give *1-methyl-3-acetylindole* as a creamy brown coloured crystalline solid [**(3)**; 0.90 g, 83%], m.p.=108-109 °C (lit. 108 °C [24]). ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 8.37 (*m*, 1H, H-4), 7.66 (*s*, 1H, H-2), 7.30 (*m*, 3H, H-5, H-6, H-7), 3.81 (*s*, 3H, 1-CH_3), 2.50 (*s*, 3H, 3-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 193.0 (*s*, 3-$\underline{C}OCH_3$), 137.5 (*s*, C-7a), 135.9 (*d*, C-2), 126.2 (*s*, C-3a), 123.3 (*d*, C-5 or C-6), 122.5 (*d*, C-4, C-5 or C-6), 116.8 (*s*, C-3), 109.7 (*d*, C-7), 33.4 (*q*, 1-CH_3), 27.6 (*q*, 3-CO$\underline{C}H_3$). GCMS: m/z 173 (M^+).

Preparation of 1,3-Diacetylindole

3-Acetylindole (1.50 g, 9.42 mmol), potassium carbonate (6.51 g, 47.1 mmol) and acetic anhydride (1.26 mg, 12.3 mmol) were refluxed in acetone (AR, 100 mL) for 24 hours. The solution was filtered then

poured into a separating funnel containing water (40 mL) and further extracted with ether (3 x 40 mL). The ethereal solution was dried over $MgSO_4$. The ether was removed by evaporation under reduced pressure and the solid creamy brown residue chromatographed (CH_2Cl_2) to give *1,3-diacetylindole* [**(12)**; 0.52 g, 28%] as small chunky white crystals, m.p. 138-140 °C. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 8.36 (*m*, 2H, H-4, H-7), 8.07 (*s*, 1H, H-2), 7.41 (*m*, 2H, H-5, H-6), 2.74 (*s*, 3H, 3-$COCH_3$), 2.60 (*s*, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 193.6 (*s*, 3-$\underline{C}OCH_3$), 168.6 (*s*, 1-$\underline{C}OCH_3$), 136.0 (*s*, C-7a), 131.2 (*d*, C-2), 127.2 (*s*, C-3a), 126.2 (*d*, C-5 or C-6), 125.1 (*d*, C-5 or C-6), 122.5 (*d*, C-4), 121.8 (*s*, C-3), 122.5 (*d*, C-7), 27.8 (*q*, 3-CO$\underline{C}H_3$), 24.0 (*q*, 1-CO$\underline{C}H_3$).

2.5.2 Preparation of Orthomanganated Complexes

The standard procedure employed in the orthomanganation of compounds is described for 1-acetylindole.

Orthomanganation of 1-Acetylindole

1-Acetylindole (313 mg, 1.96 mmol) and $PhCH_2Mn(CO)_5$ (630 mg, 2.20 mmol) were dissolved in heptane (AR, 40 mL) and the solution degassed and flushed with nitrogen twice. After refluxing under nitrogen for 90 minutes, the heptane was removed under vacuum. The resultant yellow/brown residue was dissolved in CH_2Cl_2 and chromatographed on silica gel plates with 1:4 v/v CH_2Cl_2/petroleum spirit as the eluant. A broad yellow band of *η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese* [**(4)**; 439 mg, 69%] was collected which recrystallised from petroleum spirit as yellow plates, m.p. dec. 148 °C (lit. 112 °C [11]). IR ($CHCl_3$): υ(CO) 2090(m), 2007(vs, br), 1946(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.52 (*d*, ^{3}J=8.0 Hz, 1H, H-7), 7.42 (*d*, ^{3}J=7.5 Hz, 1H, H-4), 7.26 (*m*, 1H, H-5), 7.12 (*m*, 1H, H-6), 6.84 (*s*, 1H, H-3), 2.79 (*s*, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.1 (*s*, br, C≡O), 212.3 (*s*, br, C≡O), 209.8 (*s*, br, 2xC≡O), 178.4 (*s*, 1-$\underline{C}OCH_3$), 172.6 (*s*, C-2), 137.6 (*s*, C-7a), 137.2 (*s*, C-3a), 124.7 (*d*, C-5), 121.9 (*d*, C-3), 121.3 (*d*, C-6), 118.5 (*d*, C-4), 112.1 (*d*, C-7), 22.8 (*q*, 1-CO$\underline{C}H_3$).

Orthomanganation of 1-(2-Methylprop-2-enoyl)indole

Similarly prepared from $PhCH_2Mn(CO)_5$ (662 mg, 2.31 mmol) and N-methylprop-2-enoyl indole (387 mg, 2.09 mmol) under reflux over 1.5 hours was *η^2-(1-(2-methylprop-2-enoyl)indolyl)tetracarbonylmanganese* [**(5)**; 210 mg, 29%] a yellow oil which failed to crystallise. IR ($CHCl_3$): υ(CO) 2090(m), 2006(vs, br), 1950(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.65 (*d*, ^3J=8.1 Hz, 1H, H-7), 7.41 (*d*, ^3J=7.6 Hz, 1H, H-4), 7.26 (*m*, 1H, H-5), 7.05 (*m*, 1H, H-6), 6.90 (*s*, 1H, H-3), 5.68 (*m*, 1H, 1-COC(CH_3)C$\underline{H}_2$), 5.51 (*m*, 1H, 1-COC(CH_3)C$\underline{H}_2$), 2.16 (*s*, 3H, 1-COC(CH_3)CH_2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.1 (*s*, br, C≡O), 212.3 (*s*, br, C≡O), 209.8 (*s*, br, 2xC≡O), 178.6 (*s*, 1-$\underline{C}$OCCH_2(CH_3)), 172.6 (C-2), 137.7, 137.6, 137.4 (*s*, 1-CO$\underline{C}$$CH_2$($CH_3$), C-7a, C-3a), 124.9 (*d*, C-5), 122.6 (*d*, C-3), 121.5 (*t*, 1-COC$\underline{C}$$H_2$($CH_3$)), 121.1 (*d*, C-6), 118.2 (*d*, C-4), 113.1 (*d*, C-7), 19.7 (*q*, 1-COCCH_2($\underline{C}H_3$)). EIMS: m/z 351 (M^+), 295 $(M-2CO)^+$, 267 $(M-3CO)^+$, 239 $(M-4CO)^+$.

Orthomanganation of 1-Acetylindole-3-Carboxaldehyde

Similarly prepared from $PhCH_2Mn(CO)_5$ (344 mg, 1.20 mmol) and 1-acetylindole-3-carboxaldehyde (199 mg, 1.06 mmol) under reflux over 9 hours was 1-acetyl-κO-3-formylindolyl-κC^2-tetra(carbonyl-κC)manganese(I) [**(6)**; 26 mg, 7%] (κ notation had to be employed in this case to avoid any ambiguity as to which carbonyl oxygen atom was coordinated to the manganese), a fine yellow powder which failed to recrystallise. Anal. Found: M^+, 352.9716; $C_{15}H_8O_6NMn$ calcd.: M, 352.9732. IR ($CHCl_3$): υ(CO) 2098 (m), 2015 (vs, br), 1960 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 10.31 (*s*, 1H, 3-CHO), 8.40 (*d*, ^3J=7.6 Hz, 1H, Ar-H), 7.55 (*d*, ^3J=8.2 Hz, 1H, Ar-H), 7.37 (*m*, 1H, Ar-H), 7.27 (*m*, 1H, Ar-H), 2.91 (*s*, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 218.9 (*s*, br, C≡O), 211.9 (*s*, br, C≡O), 207.9 (*s*, br, 2xC≡O), 199.5 (s, C-2), 190.7 (*d*, 3-CHO), 180.9 (*s*, 1-$\underline{C}$$OCH_3$), 137.4 (*s*), 136.8 (*s*), 132.8 (*s*), 125.9 (*d*, Ar-C), 123.8 (*d*, Ar-C), 121.3 (*d*, Ar-C), 111.9 (*d*, Ar-C), 23.5 (*q*, 1-CO$\underline{C}$$H_3$). EIMS: m/z 353 ($M^+$), 297 $(M-2CO)^+$, 269 $(M-3CO)^+$, 241 $(M-4CO)^+$.

Orthomanganation of 3-Acetylindole

Similarly prepared from $PhCH_2Mn(CO)_5$ (929 mg, 3.25 mmol) and 3-acetylindole (453 mg, 2.85 mmol) under reflux over 2 hours was *η^2-(3-acetyl-2-indolyl)tetracarbonylmanganese* [**(7)**; 749 mg, 81%] which recrystallised from $CHCl_3$/pentane as yellow needles, m.p. dec. 144 °C. Anal. Found: C, 51.97; H, 2.21; N, 4.32; $C_{14}H_8O_5NMn$ calcd.: C, 51.71; H, 2.48; N, 4.31%. IR ($CHCl_3$): υ(CO) 2092(m), 2010(vs, br), 1943(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.47 (*s*, br, 1H, H-1), 7.64 (*d*, ^3J=7.4 Hz, 1H, H-4), 7.41 (*d*, ^3J=8.2 Hz, 1H, H-7), 7.21 (*m*, 2H, H-5, H-6), 2.65 (*s*, 3H, 3-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.2 (*s*, br, C≡O), 212.6 (*s*, br, C≡O), 210.8 (*s*, C-2), 209.7 (*s*, br, 2xC≡O), 201.9 (*s*, 3-$\underline{C}OCH_3$), 143.7 (*s*, C-7a), 129.5 (*s*, C-3), 126.5 (*s*, C-3a), 122.2 (*d*, C-5), 121.9 (*d*, C-6), 117.3 (*d*, C-4), 110.5 (*d*, C-7), 25.0 (q, 3-CO$\underline{C}H_3$).

Orthomanganation of 1-Methyl-3-acetylindole

Similarly prepared from $PhCH_2Mn(CO)_5$ (746 mg, 2.61 mmol) and 1-methyl-3-acetylindole (409 mg, 2.36 mmol) under reflux over 2 hours was *η^2-(1-methyl-3-acetyl-2-indolyl)tetracarbonylmanganese* [**(8)**; 671 mg, 84%] which recrystallised from $CHCl_3$/pentane as yellow blocks, m.p. 142-144 °C. Anal. Found: C, 53.26; H, 2.67; N, 4.14; $C_{15}H_{10}O_5NMn$ calcd.: C, 53.12; H, 2.97; N, 4.13%. IR ($CHCl_3$): υ(CO) 2091 (m), 2010 (vs), 1943 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.60 (*m*, 1H, H-4), 7.35 (*m*, 1H, H-7), 7.23 (*m*, 2H, H-5, H-6), 4.05 (*s*, 3H, 1-CH_3), 2.61 (*s*, 3H, 3-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.7 (*s*, br, C≡O), 213.3 (*s*, br, C≡O), 212.1 (*s*, C-2), 209.7 (*s*, br, 2xC≡O), 200.7 (*s*, 3-$\underline{C}OCH_3$), 144.8 (*s*, C-7a), 127.7 (*s*, C-3), 127.0 (*s*, C-3a), 122.1 (*d*, C-5), 121.5 (*d*, C-6), 117.2 (*d*, C-4), 109.5 (*d*, C-7), 35.7 (*q*, 1-CH_3), 24.8 (*q*, 3-CO$\underline{C}H_3$).

Orthomanganation of Acetophenone

Similarly prepared from $PhCH_2Mn(CO)_5$ (942 mg, 3.29 mmol) and acetophenone (351 mg, 2.93 mmol) under reflux over 1.5 hours was *η^2-(2-acetylphenyl)tetracarbonylmanganese* [**(9)**; 750 mg, 91%] which recrystallised from $CHCl_3$/pentane as yellow blocks, m.p. 114-116 °C (lit.

110-116 [2]). IR ($CHCl_3$): υ(CO) 2083 (m), 1999 (vs, br), 1943 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.11 (*d*, ^3J=7.4 Hz, 1H, H-6), 7.86 (*d*, ^3J=7.8 Hz, 1H, H-3), 7.43 (*t*, ^3J=7.3 Hz, 1H, H-5), 7.19 (*t*, ^3J=7.5 Hz, 1H, H-6), 2.63 (*s*, 3H, 2-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 221.1 (*s*, br, C≡O), 216.6 (*s*, 2-$\underline{C}OCH_3$), 212.9 (*s*, br, C≡O), 211.5 (*s*, br, 2xC≡O), 193.4 (*s*, C-1), 145.4 (*s*, C-2), 141.5 (*d*, C-6), 133.9 (*d*, C-5), 131.7 (*d*, C-3), 123.9 (*d*, C-4), 24.6 (*q*, 2-$CO\underline{C}H_3$).

Orthomanganation of Indole-3-carboxaldehyde

Similarly prepared from $PhCH_2Mn(CO)_5$ (405 mg, 1.42 mmol) and indole-3-carboxaldehyde (188 mg, 1.26 mmol) under reflux over 19 hours was *η^2-(3-formyl-2-indolyl)tetracarbonylmanganese* [**(10)**; 65 mg, 17%] which recrystallised from diethyl ether/pentane as yellow needles, m.p. 148-149 °C. Anal. Found: C, 50.43; H, 1.89; N, 4.55; $C_{13}H_6O_5NMn$ calcd.: C, 50.19; H, 1.94; N, 4.50%. IR ($CHCl_3$): υ(CO) 2094 (m), 2012 (vs, br), 1947 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.66 (*s*, br, 1H, H-1), 9.29 (*s*, 1H, 3-CHO) 7.68 (*m*, 1H, H-4), 7.40 (*m*, 1H, H-7), 7.21 (*m*, 2H, H-5, H-6). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.8 (*s*, br, C≡O), 215.9 (*s*, C-2), 212.7 (*s*, br, C≡O), 209.4 (*s*, br, 2xC≡O), 190.2 (*d*, 3-CHO), 143.8 (*s*, C-7a), 131.8 (*s*, C-3), 126.3 (*s*, C-3a), 122.8 (*d*, C-5 or C-6), 122.6 (*d*, C-5 or C-6), 117.9 (*d*, C-4), 110.6 (*d*, C-7).

Orthomanganation of 1-Methylindole-3-carboxaldehyde

Similarly prepared from $PhCH_2Mn(CO)_5$ (413 mg, 1.44 mmol) and 1-methylindole-3-carboxaldehyde (206 mg, 1.26 mmol) under reflux over 75 minutes was *η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese* [**(11)**; 277 mg, 68%] which recrystallised from $CHCl_3$/pentane as orange blocks, m.p. 118-120 °C. Anal. Found: C, 51.82; H, 2.09; N, 4.36; $C_{14}H_8O_5NMn$ calcd.: C, 51.71; H, 2.48; N, 4.31%. IR ($CHCl_3$): υ(CO) 2093 (m), 2012 (vs, br), 1947 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.19 (*s*, 1H, 3-CHO), 7.65 (*m*, 1H, H-4), 7.34 (*m*, 1H, H-7), 7.24 (*m*, 2H, H-5, H-6), 4.08 (*s*, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 221.4 (*s*, br, C≡O), 216.5 (*s*, C-2), 213.2 (*s*, br, C≡O), 209.3 (*s*, br, 2xC≡O), 188.7 (*d*, 3-CHO), 144.9 (*s*, C-7a), 130.1 (*s*, C-3), 127.0 (*s*, C-3a), 122.7 (*d*, C-5 or C-6), 122.3 (*d*, C-5 or C-6), 117.6 (*d*, C-4), 109.6 (*d*, C-7), 35.7 (*q*, 1-CH_3).

2.5.3 Unsuccessful Orthomanganations

1,3-Diacetylindole

$PhCH_2Mn(CO)_5$ (354 mg, 1.24 mmol) and 1,3-diacetylindole (201 mg, 1.00 mmol) were refluxed in heptane for 3 hours. T.l.c. indicated no major products. IR showed the presence of possible cyclometalated products. The residue was chromatographed (p.l.c. 1:4 dichloromethane/petroleum spirit) to give η^2-(3-acetyl-2-indolyl)tetracarbonylmanganese [**(7)**; 14 mg, 4%], and three minor bands (each ~5 mg) which were not identified.

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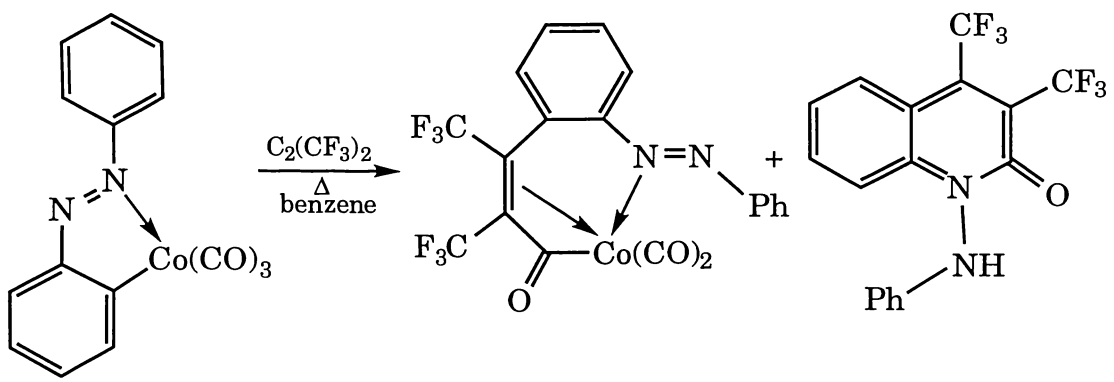
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Chapter Three

Coupling Reactions of Orthomanganated Aromatic and Heteroaromatic Compounds with Alkynes

3.1 Introduction

Insertion reactions of organometallic complexes with alkynes have been well studied. Examples include reactions of complexes of Ru [1], Rh [2], Co [3], Pd [4] (Equation 3.1), Mn, Mo [5] and W [5]. The formation of new carbon-carbon bonds has always been an important theme for synthetic organic chemistry, and coupling of alkynes adds another important element to the synthetic potential of organometallic complexes, with the preservation of functionality in the form of a double bond.



Equation 3.1

A recent review by Schore [6] summarises the reactions of organometallic complexes with alkynes in cycloaddition processes, resulting in the formation of cyclic and heterocyclic compounds, and illustrates the enormity of the field.

3.1.1 Coupling of Alkynes with Cyclopalladiated Complexes

Coupling reactions of palladium(II) cyclometalated complexes and alkynes have been extensively studied and have provided many synthetically useful reactions [7-10]. These involve insertion into the palladium-carbon σ-bond prior to the formation of an organic product. Often the alkyne-inserted metallocyclic intermediate can be isolated and subsequently converted to the organic product. A representative example [8,11] is shown in Figure 3.1.

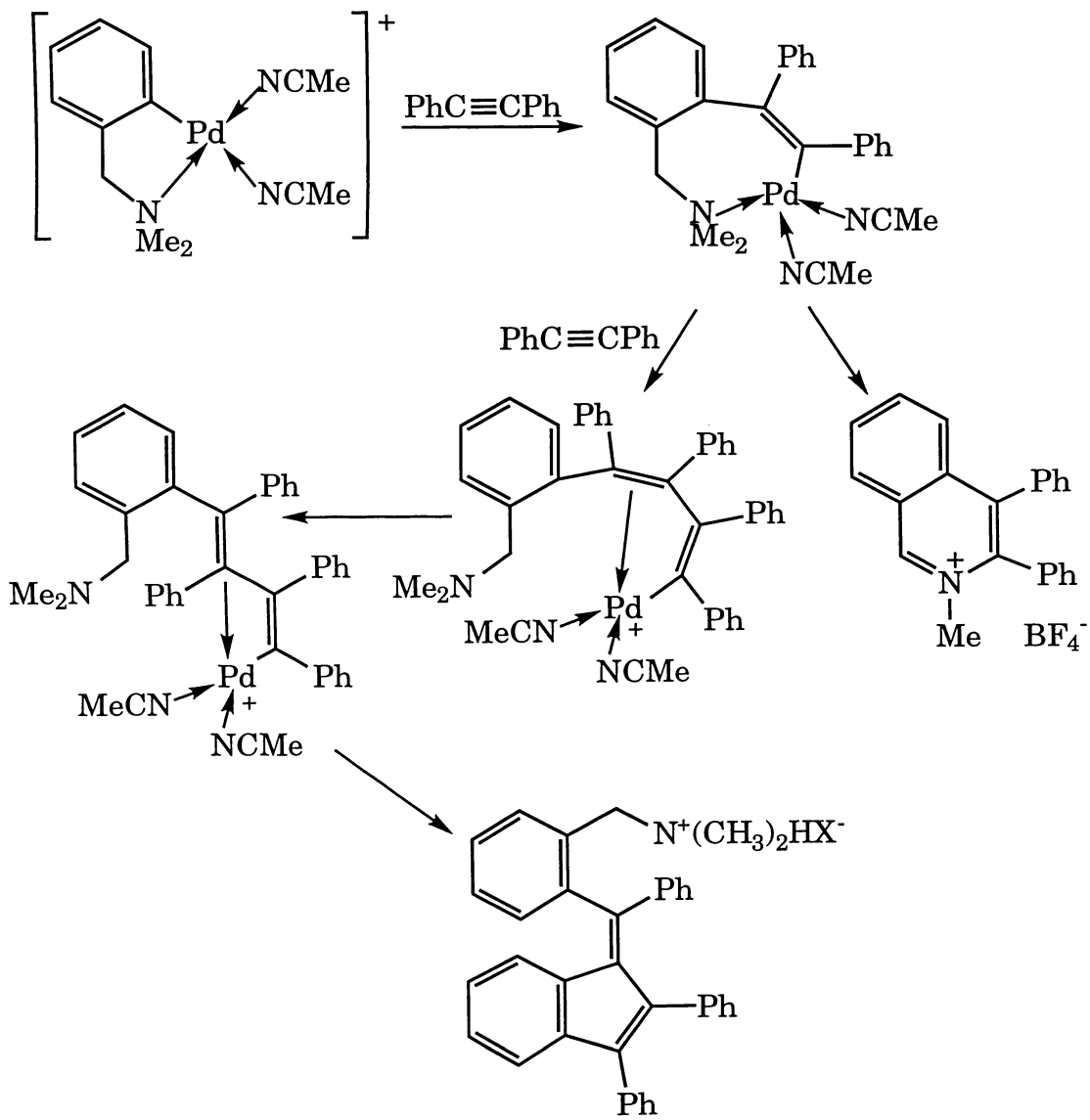


Figure 3.1

These coupling reactions show a high degree of regioselectivity with unsymmetrical alkynes and therefore offer potentially important routes in the synthesis of heterocyclic compounds. Stepwise double insertion of alkynes has been observed, but appears to be limited to the alkynes diphenylacetylene, dimethyl acetylenedicarboxylate [11] and 1-phenylprop-1-yne [11a]. Electrophilic orthopalladiation occurs for a wide variety of substituted aromatic compounds. However the inability of palladium to undergo electrophilic orthopalladiation of aromatic ketones has clearly left a conspicuous gap in the range of organic substrates studied. It was therefore considered to be worth investigating orthomanganated complexes since cyclometalated ketones are available in this system.

3.1.2 Coupling of Alkynes with Cyclometalated Manganese Carbonyls

Booth's group reported [12-14] that reaction of $RMn(CO)_5$ (R=H. Me, Ph) with alkynes formed metallocyclic products (Figure 3.2, first step). More recently, DeShong [15-17] extended this reaction by reducing the metallocycles with hydride to yield butenolides (Figure 3.2).

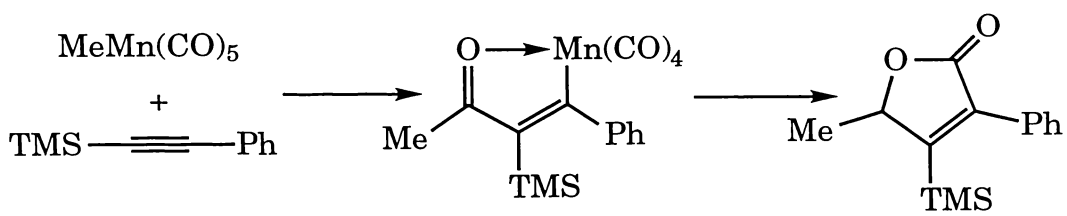
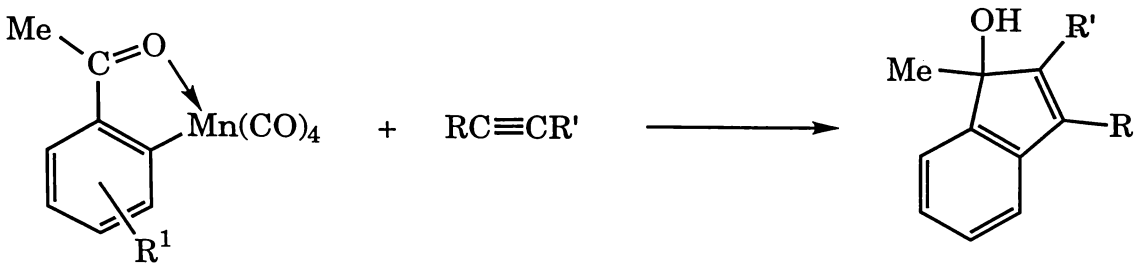


Figure 3.2

However, the use of cyclometalated aryl manganese carbonyls in this area was not investigated until recently, when two groups independently reported that high yields of substituted inden-1-ols could be obtained from the reactions of alkynes with orthomanganated ketones (Equation 3.2). Both groups reported similar results with an extensive range of alkynes, although a different method of activation of the orthomanganated complex was employed by each group. Liebeskind's group [18] used trimethylamine-N-oxide (TMANO) to activate the orthomanganated complex by oxidative decarbonylation at ambient

temperature while the Waikato group [19] used a thermally induced method.



R^1=H, F, Cl, CF_3

Equation 3.2

Of particular interest was the report by Robinson [20] of the tricyclic carbinolamine shown in Figure 3.3 from the reaction of orthomanganated 1-acetylindole and dimethyl acetylenedicarboxylate (DMAD), as this product contains the core of the mitomycin class of antibiotics [21] which are used in the treatment of brain tumours. This reaction giving the tricyclic carbinolamine was isolated in low yield and has been investigated in more detail in the present study (Section 3.2.2).

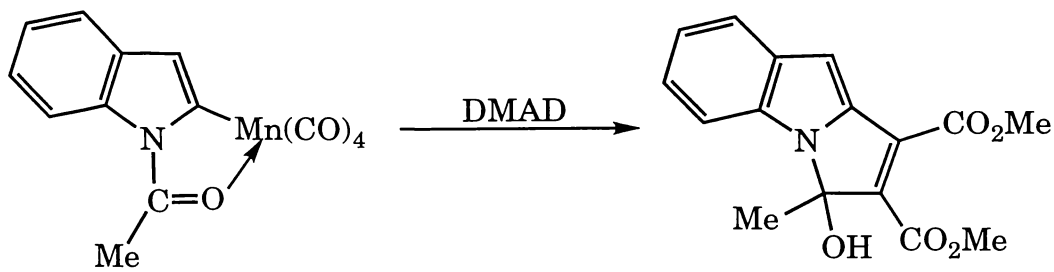
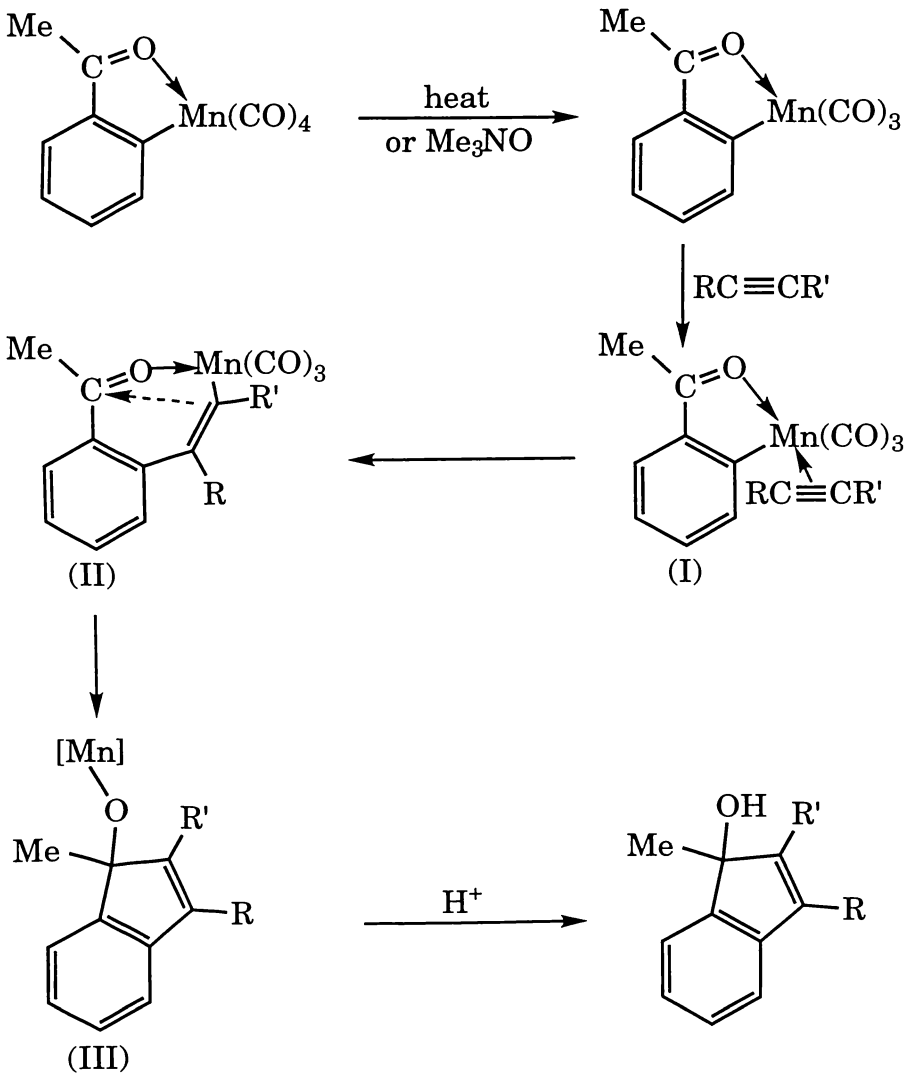


Figure 3.3

Robinson also reported [19] the formation of indanones from the reactions of alkynes with orthomanganated benzamide, benzoate and various substituted aldehydes. The scope of reaction has now been extended to include a large variety of substituted orthomanganated aromatic ketones [22], various derivatives of podocarpic acid [23-25] and a range of cyclomanganated enones [26]. A high degree of regiospecificity for unsymmetrical alkynes is exhibited by all these coupling reactions and will be discussed in more detail in Section 3.2.1.

The currently accepted mechanism [27] for alkyne-coupling and indenol formation is shown in Scheme 3.1. The first step involves the loss of CO via oxidative decarbonylation with TMANO or thermally induced dissociation to create a vacant coordination site enabling the alkyne to become η^2-coordinated (I). This is followed by a regiospecific migration of the aryl carbon to the nearest alkyne carbon resulting in the possible formation of a seven-membered metallocyclic ring (II). An intramolecular addition of C-Mn across C=O gives rise to an alkoxide species (III) which subsequently undergoes hydrolysis to form the indenol.



Scheme 3.1

None of the intermediates (I, II or III) have been isolated, but there is good evidence supporting the proposed intermediates in this mechanism from the isolation of compounds such as that shown in Figure 3.4, which was obtained when orthomanganated triphenylphosphite was reacted with diphenylacetylene [28]. More compounds of this type are discussed in Chapter Five.

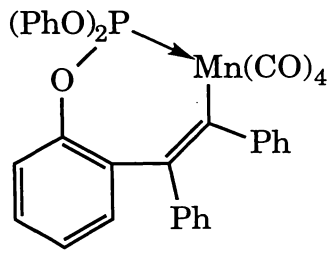
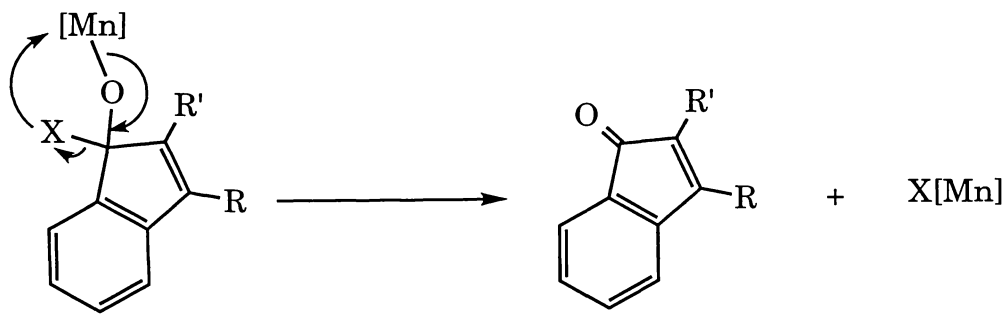


Figure 3.4

This mechanism can also be extended to explain the formation of indenones by replacing the final protonolysis with the elimination of X[Mn] as shown in Scheme 3.2.



Scheme 3.2

As previously stated most of the cyclopenta-annulation reactions are specific, with few by-products. Multiple insertion of alkynes into orthomanganated compounds is not as common as for orthopalladiated compounds, but there have been a few reports [20,29,30] of the isolation, albeit in low yields, of η^5-cyclohexadienyl type complexes (Figure 3.5) which are thought to arise from the insertion of three alkyne fragments into the Mn-C bond with subsequent cyclisation.

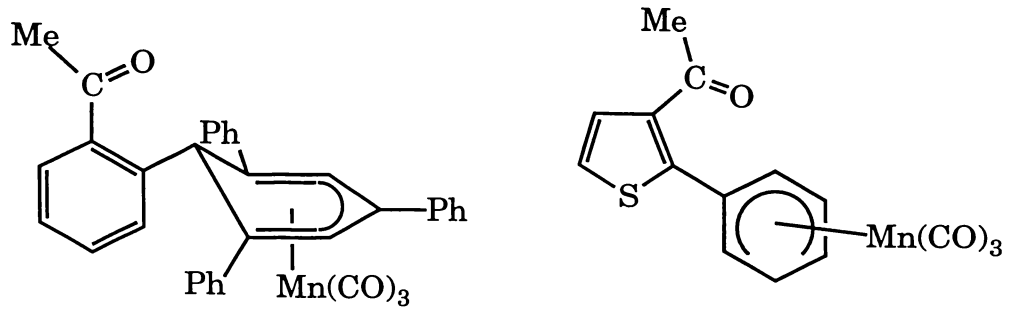


Figure 3.5

There are several instances of the isolation of tricarbonyl or tetracarbonyl compounds in very low yields which have been tentatively assigned as products resulting from the double insertion of an alkyne [31]. However at present, none of these compounds has been fully characterised.

3.2 Results and Discussion

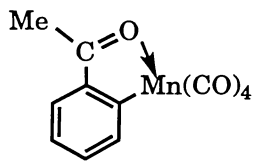
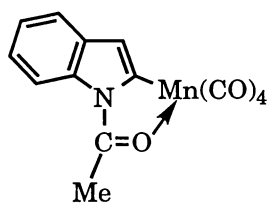
In contrast to the previously studied alkyne-coupling reactions with orthomanganated complexes in the benzene series [18,19], those in the orthomanganated indole series were less straightforward. Coupled products were generally formed in low yields, if at all. Some reactions resulted in the formation of several minor species which caused problems in the isolation of "major" products by chromatography. The overall recovery of organic material was also generally low. As a result, the synthetic potential of these orthomanganated complexes appears to be very limited.

3.2.1 Solvent Effects on Thermally Induced Alkyne-Coupling Reactions

It has been shown that the solvent choice for these reactions is critical. For example [19], the thermally induced reaction of orthomanganated acetophenone and diphenylacetylene was a lot faster and gave greater yields of the indenol in benzene than in methanol (98% versus 51%). To gain some insight into the use of suitable solvents for future reactions,

an extensive preliminary investigation into the effect of using different solvents on the yields of indenols was undertaken on the previously studied orthomanganated compounds of 1-acetylindole and acetophenone with a variety of alkynes. Results are given in Table 3.1.

Table 3.1 Yield (%) of Indenols and Tricyclic Carbinolamines from Thermally Induced Coupling Reactions

	Reaction Solvent				Compd.
	C_6H_6	Pet. spirit	CH_3CN	CCl_4	
Reactions of  **(9)** **with:**					
Diphenylacetylene	94	90	78	57	**(13)**
2-Hexyne	50	60	38	37	**(14)***
DMAD	67	54	91	87	**(15)**
Reactions of  **(4)** **with:**					
Diphenylacetylene	61	64	22	0	**(16)**
2-Hexyne	0	0	0	0	
DMAD	1	15	18	14	**(17)**

* **(14)** consisted of a mixture of both regioisomers **(14a)** and **(14b)**.

The coupling reaction of orthomanganated 1-acetylindole **(4)** was also carried out in THF without success. The results illustrate the importance of solvent choice to the yield of indenol product. However, no obvious useful trends are apparent. The choice of solvent is clearly

dependent on both the alkyne and orthomanganated compound being used. Even more ominous, is the comparison between the reactivity of the two orthomanganated complexes which suggests that the indole system may be less than ideal for future coupling reactions. The reason for the apparent lack of reactivity of orthomanganated 1-acetylindole toward DMAD and 2-hexyne, which are known to be fairly reactive alkynes towards other orthomanganated complexes [19, 29] is not obvious.

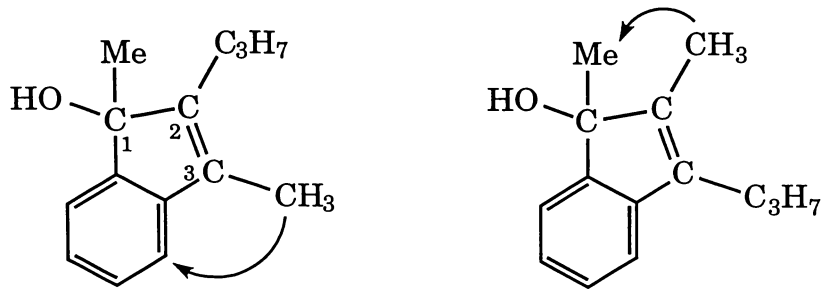
The solvent of choice for new reactions appeared to be petroleum spirit because even though it did not always give the highest yield of the corresponding indenol it seemed to be the best indicator of whether the reaction was going to work or not.

Coupling reactions carried out in acetonitrile were generally faster than those carried out in the other solvents. This is consistent with kinetic studies with Pd [4] and Mn [13] complexes, which have shown that the alkyne insertion into the metal-carbon bond is the rate determining step and that this rate of insertion is very solvent dependent [13], being faster in polar solvents than in non-polar solvents.

Two major differences were apparent when comparing these results to those of Robinson. The first was the formation of the indenol **(15)** from the reaction of orthomanganated acetophenone and DMAD in good to excellent yields, contrary to a report by Robinson [20] (mentioned in a subsequent review [27]) that this indenol was not formed for no obvious reason. The second involved the reactions of orthomanganated acetophenone with 2-hexyne. Robinson [20] observed the formation of the regioisomer with the bulkier n-C_3H_7 group in the 2-position. However, in the present study a mixture of both regioisomers was obtained in all of the solvents used (Figure 3.6).

Differential NOE experiments showed that the major regioisomer was **(14a)**, where the bulkier n-C_3H_7 group is located in the 2-position, as irradiation of the singlet signal at 1.98 ppm arising from the terminal methyl group of 2-hexyne of the major isomer led to an NOE enhancement of the neighbouring aromatic proton assigned as H-3' at 7.10 ppm. Similarly, **(14b)** was identified by irradiation of the corresponding methyl singlet in the minor regioisomer at 1.89 ppm

which led to an NOE enhancement of the methyl group bonded to the C-1 atom of the indenol ring at 1.47 ppm. Integration of the respective methyl signals showed that **(14a)** dominated **(14b)** by a 3:1 ratio in acetonitrile and a 2:1 ratio in the other solvents used. Both regioisomers were also observed in the coupling reaction between 2-hexyne and orthomanganated 1-(4-methoxyphenyl)-2-phenyl-1-butanone carried out in benzene [29].



(14a) **(14b)**

Figure 3.6

Previously studied thermally- and TMANO-induced reactions also gave rise to the regioisomer with the bulkier alkyne substituent in the 2-position of the inden-1-ol ring. Steric effects were found to control the regiochemistry of these reactions and this is consistent with other systems in which the bulkier substituent of the alkyne is inserted adjacent to the metal [12,15-17]. This sterically biased insertion is probably a direct result of the alkyne coordinating to the manganese intermediate in such a way that the bulkier substituent points away from the aryl ring as shown in Figure 3.7.

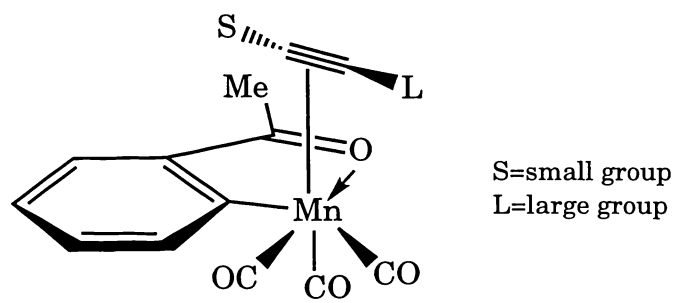


Figure 3.7

The pre-insertion intermediate requires a coplanar alignment of the alkyne C≡C bond with that of the Mn-C σ-bond to meet orbital overlap requirements [32]. Steric interactions would be reduced if the bulkier alkyne substituent is positioned over the metal carbonyl group and not the aromatic ring.

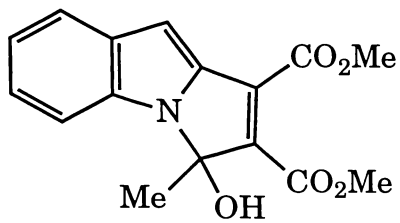
From the range of alkynes investigated (apart from the acetylenic esters of the type $RC{\equiv}CCO_2Et$), the only exception to the regiospecific insertion of an alkyne into the Mn-C bond has been the coupling reaction of orthomanganated acetophenone with 1-hexyne, which gave rise to a mixture of both regioisomers, that with the bulkier n-C_4H_9 group in the 2-position dominating by a 7:1 ratio [18]. In contrast, the reactions of the acetylenic esters $RC{\equiv}CCO_2Et$ with orthomanganated acetophenone resulted in the formation of indenols with the ester group being incorporated at the 2-position regardless of the steric bulk of the R group, suggesting that steric effects were not controlling the regiochemistry of these reactions [18]. It has been proposed that this may arise from the presence of a possible electronic directing effect manifested by the highly polarised nature of the electron-deficient alkynes or alternatively, the ester group may act as a directing ligand by prior coordination of the carbonyl oxygen to the manganese atom.

In the case of 2-hexyne, the steric restrictions associated with the bulk of the respective substituent groups are very similar, so the formation of the regioisomer with the bulky group in the 3-position is not unexpected.

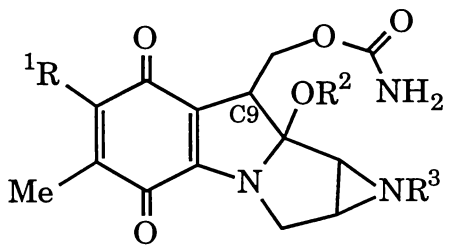
3.2.2 Coupling Reactions of Orthomanganated 1-Acetylindole and DMAD

A central difficulty in the mitomycin synthesis is the formation of the heterocyclic skeleton. As a result, only one total synthesis of mitomycin exists [33]. The formation of the tricyclic carbinolamine **(17)** via the thermally induced reaction between orthomanganated 1-acetylindole and DMAD, albeit in low yield, is of particular interest because of its structural similarity to the heterocyclic skeleton of the mitomycin class of antibiotics (Figure 3.8). The synthetic versatility of the attached

carboxylate groups makes this a potential starting material for the preparation of new mitomycin analogues. In an attempt to find reaction conditions to maximise the yield of **(17)** the TMANO-induced and palladium-promoted reactions of orthomanganated 1-acetylindole with DMAD were investigated.



(17)



	R^1	R^2	R^3	C9 Config.
Mitomycin A	OCH_3	CH_3	H	β
Mitomycin B	OCH_3	H	CH_3	α
Mitomycin C	NH_2	CH_3	H	β

Figure 3.8

Decarbonylative activation of a yellow solution of orthomanganated 1-acetylindole by treatment with anhydrous TMANO for about 15 minutes at ambient temperature resulted in the yellow solution intensifying slightly in colour. This contrasts with the treatment of other orthomanganated complexes with TMANO which resulted in a distinctive colour change from yellow to orange/red within five minutes of its addition [18,29]. On addition of alkyne to the resulting yellow solution a slow reaction generally occurred over 8-24 hours, although reactions carried out in acetonitrile were generally a lot faster (~3 hours). Over the course of this time a colour change to a pale yellow or brown colour was normally observed. The results from these coupling reactions are given in Table 3.2.

Table 3.2 Yield (%) of Indenols and Tricyclic Carbinolamines from Oxidatively Induced Coupling Reactions

Alkyne	Reaction Solvent				Compd.
	C_6H_6	Pet. spirit	CH_3CN	CCl_4	
Diphenylacetylene	30	-	61	-	**(16)**
2-Hexyne	0	-	0	-	
DMAD	61	50	61	33	**(17)**

The reaction was also carried out in methanol and yielded the tricyclic carbinolamine **(17)** in a yield of 18%. Despite there being solubility problems of TMANO in all of the solvents except acetonitrile and methanol, the reaction of orthomanganated 1-acetylindole with DMAD gave **(17)** in consistently higher yields than those obtained when the reactions were promoted thermally. As a result, the corresponding coupling reactions of the alkynes diphenylacetylene and 2-hexyne were also investigated. However, the yield of the tricyclic carbinolamine formed from diphenylacetylene was considerably lower compared to that of the thermally promoted reactions, and the reaction of orthomanganated 1-acetylindole with 2-hexyne again failed to yield the corresponding coupled product. Similarly to the thermally promoted reactions, there are no obvious trends between solvent properties and the yield of indenol obtained.

As indenyl compounds have been synthesised from the coupling reaction of palladium complexes and alkynes [34], and given that Pd(II) reportedly [35-38] transmetalates at the Mn-C σ-bond, the coupling reaction of DMAD with orthomanganated 1-acetylindole in the presence of Pd(II) in refluxing acetonitrile was investigated. The Pd(II)-mediated coupling reaction did not give a clean reaction in comparison to those either thermally or oxidatively induced, with the desired tricyclic carbinolamine product obtained in poor yield (5%). Similar results were reported in the attempted Pd(II)-mediated alkyne-coupling reactions with orthomanganated 1-(4-methoxyphenyl)-2-phenyl-1-butanone [29].

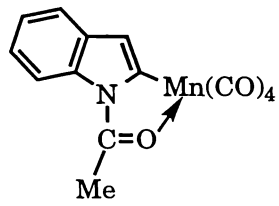
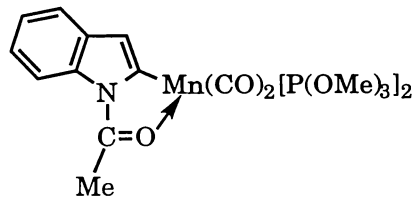
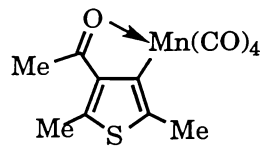
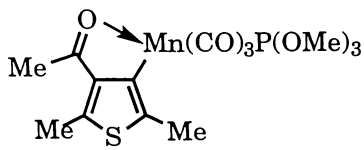
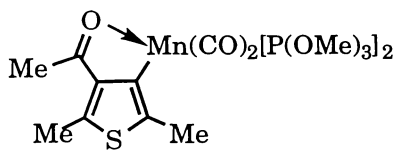
Recent studies by Cooney [37] have shown that changing the reactivity of the metal centre by substituting carbonyl ligands for stronger Lewis bases favours the formation of cyclised products in alkene-coupling reactions with orthomanganated complexes. It was also evident that for palladium-promoted and thermally induced alkene-coupling reactions there is steady progression towards increased yield of the cyclised product as the extent of substitution of CO by trimethylphosphite increases (in palladium-promoted alkene-coupling reactions of orthomanganated ketones, current experimental results suggest that the cyclised products are derived from the orthomanganated substrate and not the corresponding palladium transmetalated complex).

These results have been rationalised by considering the electron density distribution within the orthomanganated phosphite derivative. Tertiary phosphites are much stronger Lewis bases than CO but they are generally poorer π-acceptors. Substituting CO ligands by ligands with less back-accepting ability means that the remaining CO groups must accept $d\pi$ electrons from the manganese to a greater extent to prevent the accumulation of negative charge on the metal atom. This increase in the M-C bond order causes a corresponding decrease in the C-O bond order, which in turn causes a drop in the CO vibrational frequency (Table 3.3).

The nett effect of replacing a CO with a better σ-donor is that it effectively increases the amount of electron density on the manganese atom which in turn leads to more electron density about the aryl carbon giving it more anionic character. Presumably the same holds true for the metal-bonded alkyl/alkene carbon following insertion of the alkene or alkyne into the metal aryl carbon bond. Increased electron density at the metal-bonded alkyl/alkene carbon could then promote cyclisation across the acyl carbonyl atom, which may be particularly susceptible to nucleophilic attack due to donation of electron density from the carbonyl oxygen to the metal atom.

The bis-trimethylphosphite derivative of orthomanganated 1-acetylindole was prepared in high yield (91%) by the reaction of the orthomanganated complex **(4)** with trimethylphosphite in refluxing heptane. The progress of reaction was monitored by IR spectroscopy and after 5 hours, the reaction appeared complete.

Table 3.3 Metal-Carbonyl Vibrational Spectra υ(C≡O) cm^{-1} of Substituted Orthomanganated Complexes

Orthomanganated Complex	υ(C≡O) cm^{-1}		
 (4)	2090,	2007,	1946
 (18)	1948,	1868	
	2081,	1997,	1935
	2018,	1939,	1897
	1937,	1854	

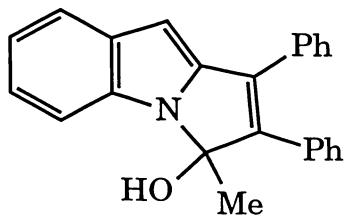
The coupling reaction of the orthomanganated trimethylphosphite derivative **(18)** with DMAD in refluxing petroleum spirit failed. After 30 hours t.l.c. showed the presence of the orthomanganated triphenylphosphite complex **(18)**. Similarly no reaction was observed when the reaction was repeated in refluxing acetonitrile, even after the addition of TMANO. The lack of reactivity displayed by this complex could be caused by one or a combination of the following factors. Firstly, the substitution of two carbonyl ligands by two bulkier

trimethylphosphite ligands may sterically prevent the insertion of the alkyne DMAD into the Mn-C_{aryl} bond. Secondly, the observed increase in the M-C bond order of the two remaining metal carbonyls of **(18)**, which is reflected in the corresponding decrease in the C-O bond order shown by IR spectroscopy, may prevent the liberation of a CO ligand to obtain coordinative-unsaturation prior to alkyne insertion. However, neither of these factors appeared to be a problem in the coupling reactions of the trimethylphosphite derivatives of orthomanganated 2-acetylthiophene with methyl acrylate, despite the *bis*-substituted derivative containing lower $\upsilon(C\equiv O)$'s than the corresponding indole derivative **(18)** (Table 3.3).

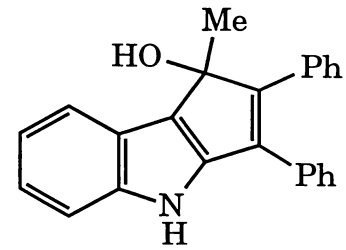
Since the initial discovery of the tricyclic carbinolamine **(17)** from the thermally induced reaction of orthomanganated 1-acetylindole with DMAD in benzene [20], a major drawback for its use in subsequent investigations to synthesize possible mitomycin analogues has been the low yield in which it was obtained. However, the results from this study have clearly shown that if TMANO-induced reaction conditions are employed, the reaction of orthomanganated 1-acetylindole with DMAD carried out in acetonitrile or benzene leads to the formation of **(17)** in good yield. As a result, the use of this compound as a starting material in the synthesis of mitomycin analogues may now be justified.

3.2.3 Alkyne-Coupling Reactions of Various Orthomanganated Complexes

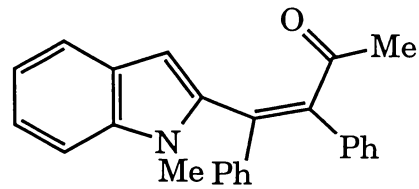
The coupling reaction of diphenylacetylene and orthomanganated 3-acetylindole **(7)** in refluxing petroleum spirit failed to yield the expected indenol product **(19)** (Figure 3.9). Instead the identical tricyclic carbinolamine product **(16)** formed in the coupling reaction of orthomanganated 1-acetylindole **(4)** and diphenylacetylene was obtained in low yield (18%) (Figure 3.9). The batch of orthomanganated 3-acetylindole **(7)** was immediately checked by NMR which confirmed its identity and the reaction was repeated with an identical result. The transfer of the acetyl group was totally unexpected and is unprecedented in alkyne-coupling reactions with orthomanganated complexes.



(16)



(19)

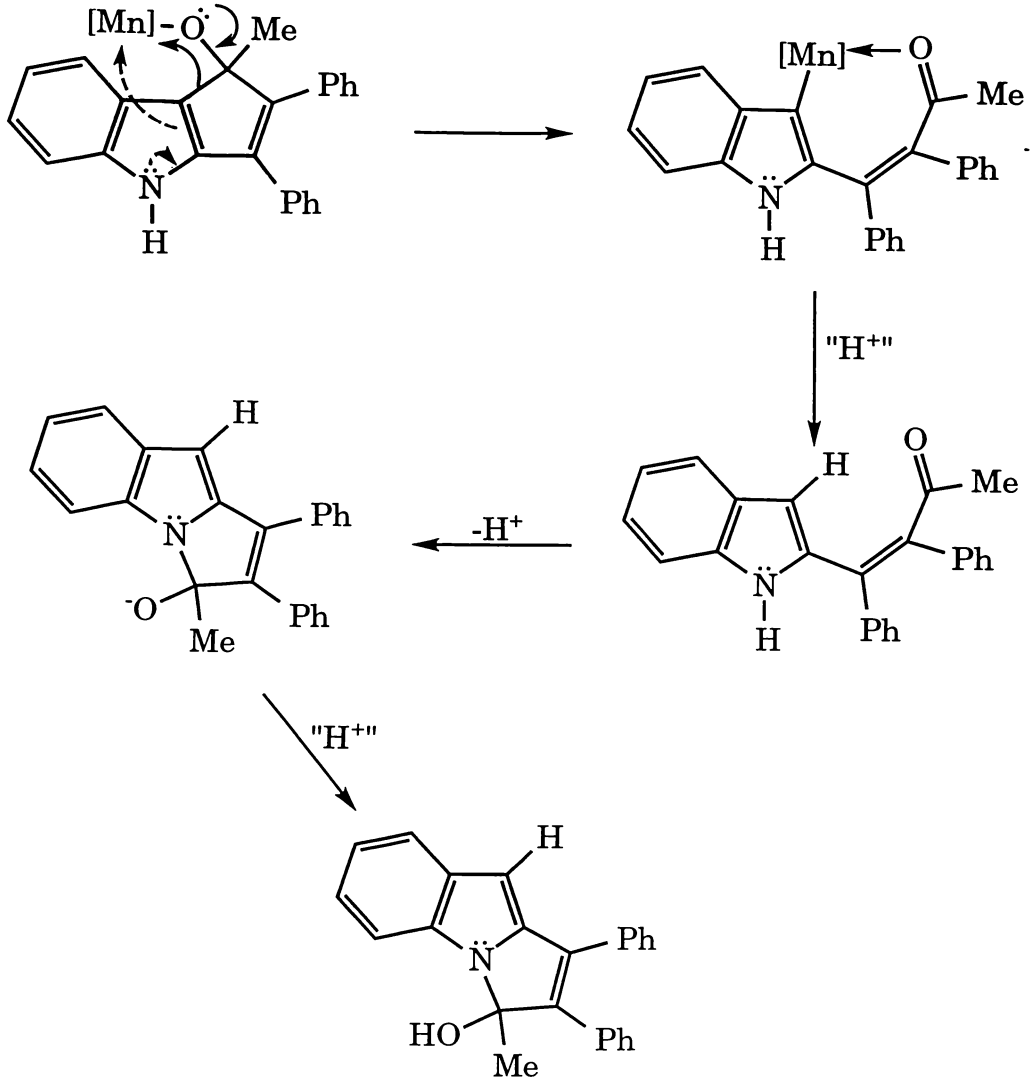


(20)

Figure 3.9

Similarly, the coupling reaction of orthomanganated 1-methyl-3-acetylindole **(8)** with diphenylacetylene also failed to yield the expected tricyclic indenol type product. The 3-acetyl group was again cleaved giving rise to the formation of **(20)** in 43% yield (Figure 3.9) (the stereochemistry of the alkene function was not determined) as subsequent cyclisation is obviously prevented by the inability of nitrogen to undergo reaction due to the methyl group bonded to it. The singlet arising from one proton at 6.68 ppm in the ^{1}H NMR spectrum and the appearance of a doublet carbon at 106.7 ppm clearly show that the acetyl group has been transfered as these signals are indicative of a proton being attached to the C-3 position of the indole nucleus. The singlet arising from H-3 in the proton spectrum at ~6.6 ppm is also characteristic of all the tricyclic carbinolamines formed from orthomanganated 1-acetylindole **(4)** where substitution of the 2-position has occurred. An identical result was obtained when this reaction was repeated using TMANO with **(20)** being isolated in 53% yield.

A possible mechanism for this rearrangement is outlined in Scheme 3.3.

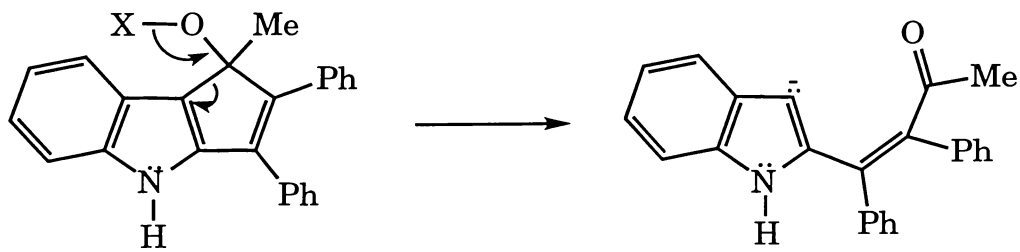


Scheme 3.3

It is assumed that the alkyne becomes inserted into the Mn-C_{aryl} bond and the resulting intermediate undergoes an intramolecular addition of C-Mn across C=O to yield an alkoxide species as is consistent with the previously proposed mechanism. However, instead of the alkoxide species undergoing hydrolysis to yield the expected indenol, donation of the lone pair of electrons on the indole nitrogen (see dotted arrows in first structure) may facilitate the formation of the new Mn-C bond which would give rise to a seven-membered metallocyclic intermediate. Protonolysis of this intermediate possibly from adventitious water would induce demetalation and the resulting intermediate would then undergo cyclisation. In the case of the coupling reaction of orthomanganated 1-

methyl-3-acetylindole **(8)** with diphenylacetylene, the reaction cannot proceed any further once demetalation of the manganese group has occurred as the cyclisation step is no longer possible.

Compounds **(16)** and **(20)** could also be envisaged as forming from the manganese alkoxide species or the expected indenol product itself via the transfer of electron density from the O-[Mn] or possibly the O-H bond to the C-O bond resulting in the cleavage of the acetyl group and the formation of a carbanion (Scheme 3.4). However, there is no obvious reason why this process would occur, as it has not been observed in any of the other many systems now studied. The formation of the indole carbanion would also be highly unfavoured as the negative charge could not be delocalised successfully without disrupting the aromaticity of the neighbouring ring.



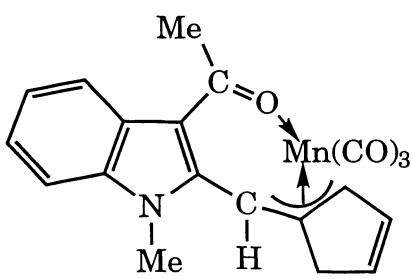
X=H, [Mn]

Scheme 3.4

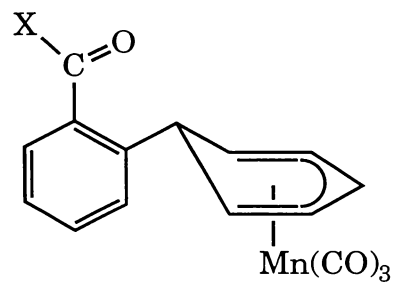
This type of reaction was not found to be general for other alkynes. Attempts at coupling (induced either thermally or oxidatively) orthomanganated 3-acetylindole **(7)** with DMAD and 2-hexyne were unsuccessful with no coupled products being isolated. Similarly, the coupling reaction of orthomanganated 1-methyl-3-acetylindole **(8)** and DMAD did not yield any coupled product, with only some orthomanganated and demetalated material obtained. However, the reaction of orthomanganated 1-methyl-3-acetylindole **(8)** and phenylacetylene gave several minor bands by p.l.c. which GCMS indicated to include three of the four possible diastereoisomers of the corresponding alkyne-inserted product, although none were isolated.

The attempted thermal coupling reaction of 2-methyl-3-butyn-2-ol with orthomanganated 1-acetylindole **(4)** in refluxing petroleum spirit gave no coupled product and resulted in the demetalation of **(4)**. An identical result was obtained when 2-butyne-1,4-diol was used, although in this case there was also a solubility problem with the alkyne. It has been reasoned that the lack of reactivity of alkynols with orthomanganated complexes is due to the presence of the alcohol group, a protic function which may cause the degradation of the orthometalated complex [20]. However, this is probably only one contributing factor to their apparent lack of reactivity, as coupling reactions of orthomanganated complexes with alkenes and alkynes have been successfully carried out in methanol. To date there has only been one example involving an alkynol coupling with an orthomanganated ketone. The thermal coupling of 3-butyn-1-ol with orthomanganated 1-(4-methoxyphenyl)-2-phenyl-1-butanone in refluxing benzene yielded both diastereoisomeric inden-1-ol products in good yield [29] (a combined yield of 65%).

The thermally induced coupling reaction of orthomanganated 1-methyl-3-acetylindole **(8)** with ethyne was not a clean reaction. A tricarbonyl complex was isolated in low yield as orange crystals and was identified by a crystal structure determination as **(21)** (17%) as full assignment by NMR was not possible. The instability of the complex in solution over time was the apparent reason for shimming problems. Full discussion of the structure is deferred to Section 3.3.



(21)



X=NMe_2, OMe

Figure 3.10

The tricarbonyl complex **(21)** presumably arises from the successive insertion of three ethyne units into the Mn-C bond with subsequent rearrangement. This complex contrasts markedly with previously reported examples [20] in which the triple insertion of ethyne has occurred, as they gave η^5-hexadienyl tricarbonyl complexes of the type shown in Figure 3.10.

The complex **(21)** is also unusual as it has formed a η^3-allyl type complex when it has a potential η^5-cyclopentadienyl type ligand which would be thermodynamically more stable. A similar structure has been reported involving a Mo complex forming a η^3-allyl type complex with a potential η^5-cyclopentadienyl type ligand (Figure 3.11), although in this case geometric constraints presumably prevent the formation the η^5-cyclopentadienyl ligand [39].

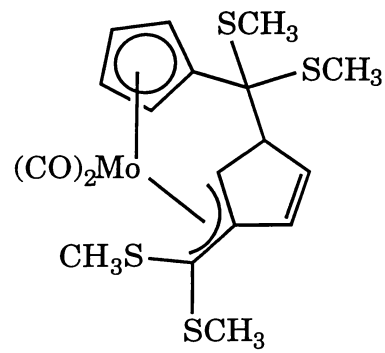
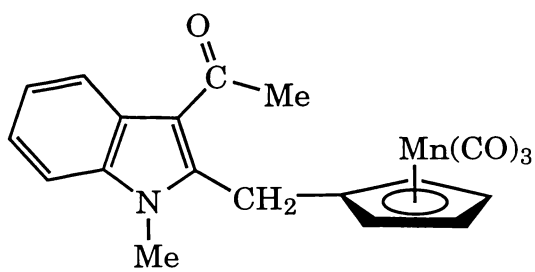


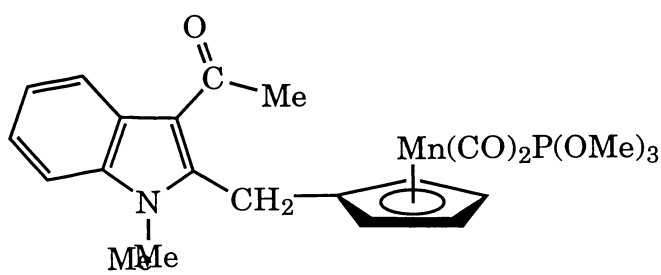
Figure 3.11

To assess the stability of complex **(21)** its reactivity was examined. Refluxing **(21)** in heptane resulted in the formation of 1-methyl-3-acetyl-2-indolylmethylcyclopentadienyltricarbonylmanganese **(22)** containing η^5-cyclopentadienyl (Figure 3.12) ligand in fair yield (52%). This complex was initially identified by the comparison of IR and NMR spectra with that of the complex methylcyclopentadienyl manganesetricarbonyl and by the appearance of a triplet carbon in the ^{13}C NMR spectrum of **(22)**. The ^{13}C NMR spectrum of **(22)** showed signals at 100.9, 84.4 and 81.2 which appear to be characteristic of a mono-substituted cyclopentadienyl ligand when compared to the methylcyclopentadienyl manganesetricarbonyl complex (102.2, 82.4 and 82.0 ppm). Similarly, comparison of the metal carbonyl IR bands of **(22)** with those of the methylcyclopentadienyl manganesetricarbonyl

complex shows a close match (2021 (s), 1937 (vs, br) cf. 2020 (s), 1936 (vs, br)). The ^1H NMR spectrum showed two triplets each arising from two protons at 4.87 and 4.57 ppm which is consistent for this type of cyclopentadienyl ligand as it contains an A_2B_2 type system. Treatment of **(21)** with $P(OMe)_3$ in refluxing heptane also resulted in the formation of an η^5-cyclopentadienyl type ligand complex, along with the substitution of one metal carbonyl by $P(OMe)_3$ **(23)** (Figure 3.12) in 50% yield. This complex was also identified by the characteristic signals in the carbon spectrum arising from the cyclopentadienyl ligand (although due to the poor quality of the proton spectrum obtained, the splitting of the two signals arising from the cyclopentadienyl protons was not observed). The composition of structures **(22)** and **(23)** were also confirmed by accurate mass measurements which corresponded to the molecular formulas of the respective complexes. The low yields of complexes **(22)** and **(23)** obtained are probably the direct result of the small size scale of the reactions employed. The amount of **(21)** used in each reaction was only 46 and 20 mg respectively.



(22)



(23)

Figure 3.12

3.2.4 Alkyne-Coupling Reactions of Orthomanganated Aldehyde Complexes

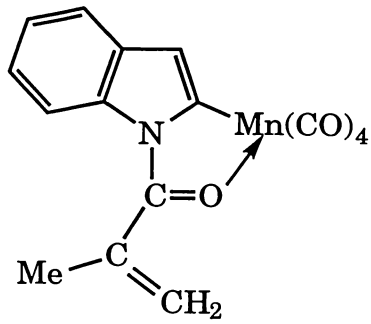
As mentioned in the introduction, the coupling reaction of orthomanganated aldehydes with alkynes led to the formation of indanones. To date only two successful reactions have been reported, those of orthomanganated *p*-dimethylaminobenzaldehyde with diphenylacetylene or ethyne which gave rise to the corresponding indanones in yields of 46% and 20% respectively [19].

The coupling reaction of diphenylacetylene with orthomanganated 1-methyl-indole-3-carboxaldehyde **(11)** was carried out in refluxing petroleum spirit for 7 hours. As was common for many of the coupling reactions of orthomanganated indoles with alkynes, the reaction was not clean. After p.l.c. several minor bands (< 5 mg) were extracted but none of the products were identified.

Reactions with other alkynes were not attempted because diphenylacetylene appeared to be the most reactive alkyne towards orthomanganated indoles, consistently giving the highest yields in thermally induced coupling reactions. In addition, only moderately low yields of the indanone were obtained with the substituted benzaldehyde, and as this type of aromatic system appears to be more favourable for alkyne-coupling than that of the orthomanganated substituted indoles further reaction attempts would appear to be futile.

3.2.5 Attempted Intramolecular Coupling Reactions of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonylmanganese

The orthomanganated complex **(5)** is interesting as it contains a terminal alkene which appears to be suitably placed to undergo a potential intramolecular cyclisation via an alkene insertion reaction (Figure 3.13). Reactions of this type with orthomanganated complexes have never been investigated.



(5)

Figure 3.13

Background to the coupling chemistry between alkenes and orthomanganated complexes will be discussed in more detail in the introduction to Chapter Five. Briefly, these coupling reactions can be carried out either thermally in the absence of palladium, or in the presence of Pd(II) which is solubilised as Li_2PdCl_4. Palladium-catalysed reactions are carried out in either refluxing acetonitrile or methanol at ambient temperature.

The thermally induced intramolecular alkene-coupling reaction was carried out in refluxing heptane. However, after 22 hours, t.l.c. showed that complete demetalation had occurred with no sign of any other product. Identical results were obtained when **(5)** was refluxed in acetonitrile and carbon tetrachloride.

An oxidatively induced reaction was attempted by treating orthomanganated 1-(2-methylprop-2-enoyl)indole with TMANO in acetonitrile at ambient temperature, but this also resulted in the demetalation of **(5)**.

The Pd(II)-promoted reaction was then attempted in refluxing acetonitrile, which also resulted in the formation of 1-(2-methylprop-2-enoyl)indole **(2)** (37%).

The failure of orthomanganated 1-(2-methylprop-2-enoyl)indole **(5)** to undergo intramolecular cyclisation may be due to the unfavourable geometry required. In the coupling reactions of alkynes and alkenes [37] in the absence of palladium, experimental evidence suggests that the

manganese remains coordinated to the oxygen atom of the carbonyl group because of the isolation of complexes of the type shown in Figure 3.4, and the apparent lack of formation of arylalkene type products in alkene-coupling reactions, although a recent review has cast uncertainty on this interpretation (see Section 5.2.2). However, assuming that manganese remains coordinated to the oxygen atom, this would then make it difficult for the approach of the terminal alkene carbon to the Mn-C_{aryl} bond and its subsequent insertion. In the case of the palladium-promoted alkene-coupling reactions, the currently accepted mechanism [37] involves in part the transmetalation of manganese for palladium. In the transmetalated palladium complex the palladium would not be bound to the carbonyl donor group because of its low affinity for oxygen. However, despite the absence of this constraint the failure to detect any coupled product suggests that the geometry required for the insertion of the alkene into the Pd-C_{aryl} bond still cannot be obtained.

3.2.6 Reaction of Ethyne with $PhCH_2Mn(CO)_5$

While carrying out a coupling reaction between orthomanganated 1-methyl-3-acetylindole **(8)** and ethyne, a routine orthomanganation of 3-acetylindole was carried out concurrently on the same Schlenk line. Upon workup of the orthomanganated complex **(7)** an extra band (p.l.c.) was observed which had not been seen in any of its previous preparations. The band was extracted to yield an orange solid in low yield. IR spectroscopy of the metal carbonyl region revealed a pattern characteristic of a $Mn(CO)_3$ species. Good quality NMR spectra could not be obtained because of the apparent instability of the product or products in solution. Samples could not be shimmed because of the presence of paramagnetic species, even after passing the solution through a short column of silica or florisil. However, the ^{13}C NMR spectra obtained did suggest that more than one product was present. It was thought that these products may have arisen from the reaction of $PhCH_2Mn(CO)_5$ with residual ethyne in the Schlenk line and this was confirmed by a deliberate reaction, with the isolation of the same orange solid, again in low yield. The reaction of $Mn_2(CO)_{10}$ and ethyne in refluxing heptane was also investigated to show beyond a reasonable doubt that the ethyne was reacting with $PhCH_2Mn(CO)_5$ and not

$Mn_2(CO)_{10}$. The reaction between ethyne and $Mn_2(CO)_{10}$ performed in an autoclave is known to yield the product in Figure 3.14 [40]. However, no reaction was observed.

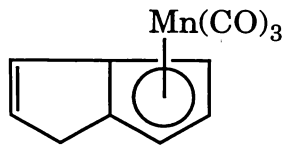
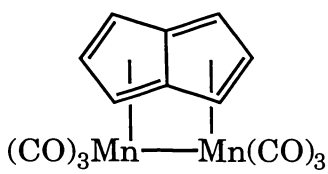


Figure 3.14

Isolation of one of these products contained in the orange solid was unsuccessful. However, an EIMS spectrum confirmed the presence of three tricarbonyl species containing molecular ions of 380, 332 and 242 mass units, with the peaks arising from the last of these components being the most intense in the spectrum.

The tricarbonyl species with a molecular mass of 380 was assigned as the pentalene type complex **(24)** (Figure 3.15). This was based solely on mass spectral evidence as the fragment peaks due to the successive cleavage of six carbonyl groups and two manganese atoms are consistent with the fragmentation pattern of the isoelectronic iron complex [41] also shown in Figure 3.15.



(24)

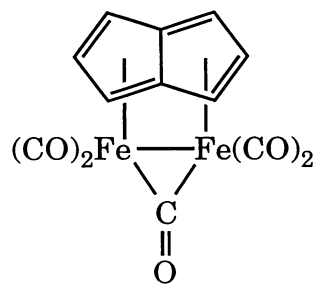
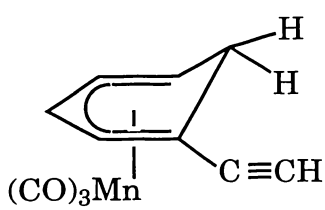
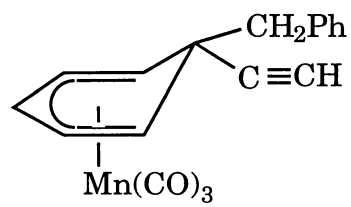


Figure 3.15



(26)



(25)

Figure 3.16

The two remaining compounds each had fragmentation consistent with the loss of an -$Mn(CO)_3$ moiety. The remaining organic fragments had masses consistent with the ligands shown in Figure 3.16. However, the absence of NMR data meant definitive characterisation was not possible.

3.3 X-Ray Crystal Structure of (21)

The crystal structure of **(21)** was determined to characterise the product from the reaction between orthomanganated 1-methyl-3-acetylindole and ethyne. The structure was of interest as conventional spectroscopy indicated that multiple insertion of the alkyne had occurred, yielding a product different from that observed for other orthomanganated complexes.

3.3.1 Results of Preliminary Studies

Orange-plate crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated ether solution of **(21)** at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated monoclinic symmetry, space group $P2_1/c$. The full data set was collected in the non-standard setting of $P2_1/n$ to provide a better β angle.

3.3.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -143 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{20}H_{16}O_4MnN$

M_r=389.28

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

a=12.109(2), b=8.443(2), c=17.227(3) Å

β=97.66(3)°

U=1745.6(6) $Å^3$

D_{calc}=1.481 g cm^{-3}

Z=4

F(000)=800

μ(Mo-K_α)=0.781 mm^{-1}

A total of 3473 reflections were collected in the range $4° \leq 2\theta \leq 57°$ of which 3075 were unique (R_{int}=0.0604). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method ($T_{max,min}$ 0.790 and 0.618 respectively). Of these, 2251 had $I \geq 2\sigma(I)$.

3.3.3 Solution and Refinement

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

The refinement converged with R_1=0.0594 (2σ data); R_1=0.0889, wR_2=0.1568, and Goof=1.056 for all data, where $w=[\sigma^2(F_o)^2+(0.0921P)^2]^{-1}$ with $P=1/3[F_o^2+2F_c^2]$. No parameter shifted more than 0.001 σ in the final cycle. The final difference map showed no peaks or troughs greater than 0.968 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 3.4 and 3.5 respectively.

Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix III.

The structure is shown in Figure 3.17 and illustrates the atom labelling scheme.

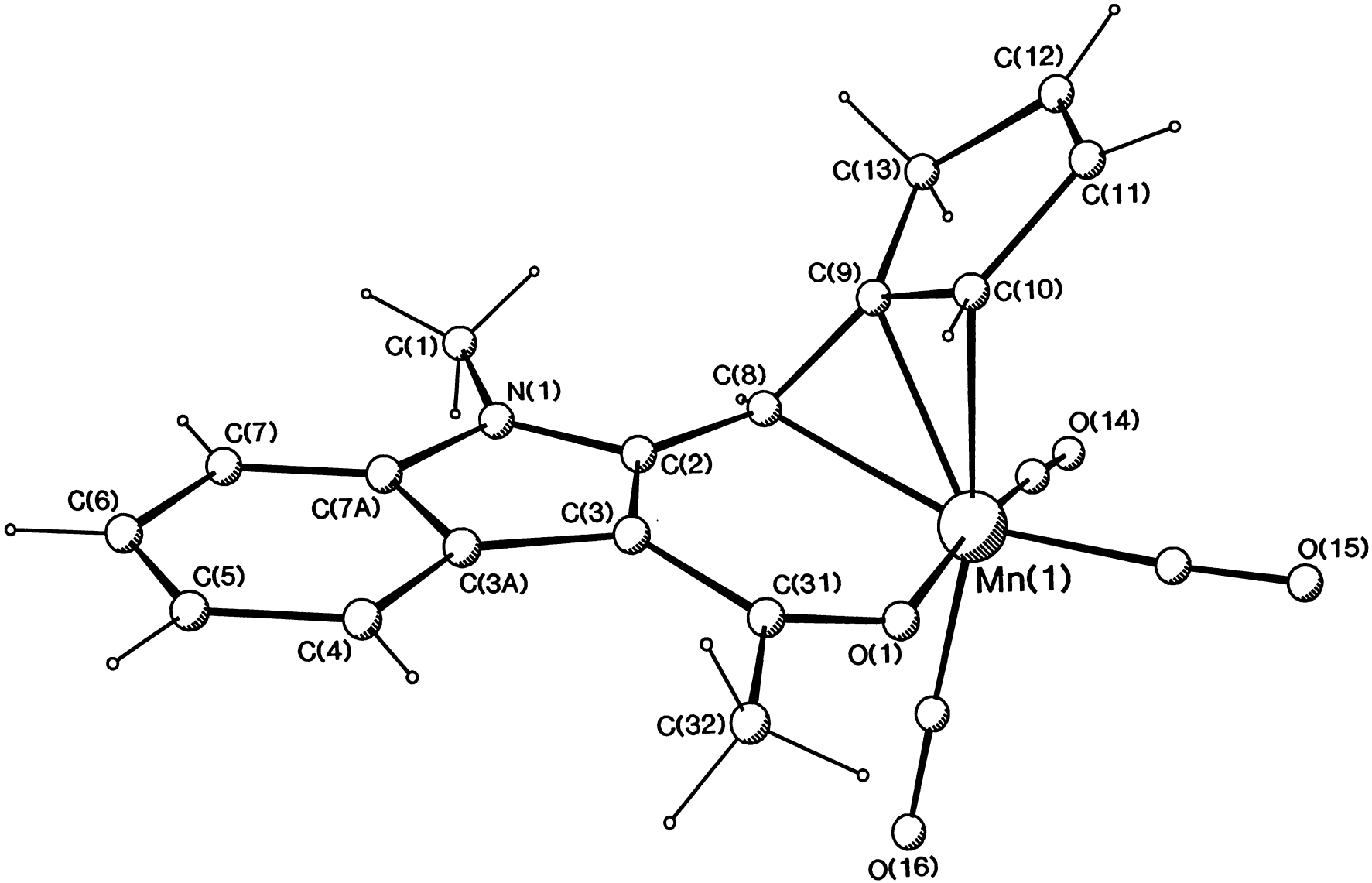


Figure 3.17 Perspective View of (21)

Table 3.4 Bond Lengths (Å) for (21)

Mn(1)–C(14)	1.780(4)	C(3A)–C(4)	1.405(6)
Mn(1)–C(16)	1.804(5)	C(4)–C(5)	1.380(6)
Mn(1)–C(15)	1.821(5)	C(5)–C(6)	1.387(7)
Mn(1)–C(11)	2.052(3)	C(6)–C(7)	1.398(6)
Mn(1)–C(8)	2.145(4)	C(7)–C(7A)	1.389(6)
Mn(1)–C(9)	2.155(4)	C(8)–C(9)	1.442(6)
Mn(1)–C(10)	2.280(5)	C(9)–C(10)	1.376(6)
N(1)–C(2)	1.362(5)	C(9)–C(13)	1.520(6)
N(1)–C(7A)	1.413(5)	C(10)–C(11)	1.461(6)
N(1)–C(1)	1.452(5)	C(11)–C(12)	1.336(7)
O(1)–C(31)	1.260(5)	C(12)–C(13)	1.491(7)
C(2)–C(3)	1.415(6)	C(14)–O(14)	1.156(5)
C(2)–C(8)	1.463(6)	C(15)–O(15)	1.143(5)
C(3)–C(31)	1.413(6)	C(16)–O(16)	1.151(5)
C(3)–C(3A)	1.455(6)	C(31)–C(32)	1.508(6)
C(3A)–C(7A)	1.404(6)		

Table 3.5 Bond Angles (Å) for (21)

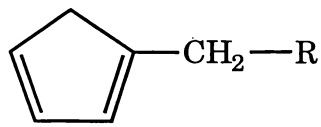
C(14)	-Mn(1)	-C(16)	87.2(2)	C(7A)	-C(3A)	-C(4)	117.7(4)
C(14)	-Mn(1)	-C(15)	87.6(2)	C(7A)	-C(3A)	-C(3)	106.3(4)
C(16)	-Mn(1)	-C(15)	96.3(2)	C(4)	-C(3A)	-C(3)	135.9(4)
C(14)	-Mn(1)	-O(1)	172.8(2)	C(5)	-C(4)	-C(3A)	119.3(4)
C(16)	-Mn(1)	-O(1)	85.7(2)	C(4)	-C(5)	-C(6)	121.9(4)
C(15)	-Mn(1)	-O(1)	90.3(2)	C(5)	-C(6)	-C(7)	120.5(4)
C(14)	-Mn(1)	-C(8)	93.5(2)	C(7A)	-C(7)	-C(6)	117.0(4)
C(16)	-Mn(1)	-C(8)	102.2(2)	C(7)	-C(7A)	-C(3A)	123.6(4)

Table 3.5 continued

C(15)	-Mn(1)	-C(8)	161.4(2)	C(7)	-C(7A)	-N(1)	128.1(4)
O(1)	-Mn(1)	-C(8)	90.7(2)	C(3A)	-C(7A)	-N(1)	108.4(4)
C(14)	-Mn(1)	-C(9)	87.5(2)	C(9)	-C(8)	-C(2)	122.2(4)
C(16)	-Mn(1)	-C(9)	140.6(2)	C(9)	-C(8)	-Mn(1)	70.8(2)
C(15)	-Mn(1)	-C(9)	122.5(2)	C(2)	-C(8)	-Mn(1)	114.9(3)
O(1)	-Mn(1)	-C(9)	99.5(14)	C(10)	-C(9)	-C(8)	128.4(4)
C(8)	-Mn(1)	-C(9)	39.2(2)	C(10)	-C(9)	-C(13)	107.4(4)
C(14)	-Mn(1)	-C(10)	105.8(2)	C(8)	-C(9)	-C(13)	123.8(4)
C(16)	-Mn(1)	-C(10)	164.5(2)	C(10)	-C(9)	-Mn(1)	76.9(3)
C(15)	-Mn(1)	-C(10)	91.9(2)	C(8)	-C(9)	-Mn(1)	70.1(2)
O(1)	-Mn(1)	-C(10)	81.2(2)	C(13)	-C(9)	-Mn(1)	123.7(3)
C(8)	-Mn(1)	-C(10)	69.9(2)	C(9)	-C(10)	-C(11)	109.5(4)
C(9)	-Mn(1)	-C(10)	36.0(2)	C(9)	-C(10)	-Mn(1)	67.0(3)
C(2)	-N(1)	-C(7A)	109.3(3)	C(11)	-C(10)	-Mn(1)	124.9(3)
C(2)	-N(1)	-C(1)	127.0(4)	C(12)	-C(11)	-C(10)	109.5(4)
C(7A)	-N(1)	-C(1)	123.6(3)	C(11)	-C(12)	-C(13)	110.0(4)
C(31)	O(1)	-Mn(1)	132.8(3)	C(12)	-C(13)	-C(9)	103.6(4)
N(1)	-C(2)	-C(3)	108.9(4)	O(14)	-C(14)	-Mn(1)	176.9(4)
N(1)	-C(2)	-C(8)	119.5(4)	O(15)	-C(15)	-Mn(1)	174.5(4)
C(3)	-C(2)	-C(8)	131.6(4)	O(16)	-C(16)	-Mn(1)	179.1(4)
C(31)	-C(3)	-C(2)	123.9(4)	O(1)	-C(31)	-C(3)	123.8(4)
C(31)	-C(3)	-C(3A)	128.2(4)	O(1)	-C(31)	-C(32)	116.1(4)
C(2)	-C(3)	-C(3A)	107.0(4)	C(3)	-C(31)	-C(32)	120.2(4)

3.3.4 Discussion of the Structure

On solving the structure it was apparent that the alkyne coupled product was the result of a triple insertion of ethyne into the Mn-C_{aryl} bond of **(8)**, which presumably underwent a subsequent rearrangement to yield a formally deprotonated cyclopentadiene methylene group (Figure 3.18) bonded to the C(2) position of the original substituted indole core.



R=1-methyl-3-acetylindole

Figure 3.18

Coordination of the $Mn(CO)_3$ group to the complex ligand is made up with two electrons from coordination of the oxygen of the acetyl group, and three electrons from an allyl portion of the ligand, involving one of the C=C bonds of the cyclopentadiene group and the exocyclic carbon, C(8).

The bond lengths of the allylic system show that it is not symmetrical as both the C-C (C(8)-C(9) 1.442(6) and C(9)-C(10) 1.376(6) Å) and the Mn-terminal carbon bond lengths (Mn(1)-C(8) 2.145(4) and Mn(1)-C(10) 2.280(5) Å) of the allyl group are not identical, which may be the result of the allyl complex being substituted in such a way that it cannot obtain the ideal orientation for bonding. The central carbon-manganese distance Mn(1)-C(9) is 2.155(4) Å. The perpendicular distance from Mn(1) to the plane of the allyl group is 1.63(1) Å.

The C(9)-C(10) distance is short suggesting that the dominant resonance structure for the allyl group is A rather than B in Figure 3.19.

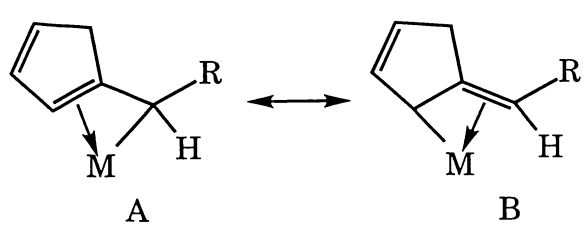


Figure 3.19

The C(8)-Mn-C(10) and C(8)-C(9)-C(10) angles of 69.9(2) and 128.4(4)° are comparable to other typical π-allyl systems [42] suggesting that despite the allyl complex being part of a five membered-ring there is little strain. In contrast compounds having strained π-allyl systems such as π-$(CH_3)_4C_4$(σ-C_5H_5)Ni(π-C_5H_5) [43] or $R_3C_4OCo(CO)_3$ (R=C_6H_5 or CH_3) [44] have a C-C-C angle of 89°.

The dihedral angle between the plane defined by Mn(1) and the terminal carbon atoms (C(8) and C(10)) and the plane defined by the three-carbon skeleton (C(8), C(9) and (10)) of the allyl group is 115.8(3)°, which is in accord with other allyl-containing complexes in which the two planes were not perpendicular to each other. For example, angles of 105.5° and 110.3° were found in the complexes (2-CH_3-π-C_3H_4)$_2$Ni and [(π-C_3H_5)$_2$RhCl]$_2$ [45].

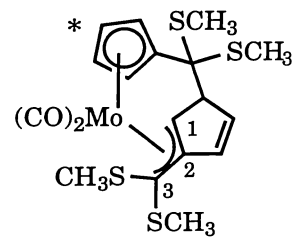
Similarly, it is also generally found in such complexes that the allyl plane is not perpendicular to the coordination plane of the metal, with the central carbon being tipped away from the metal atom [42]. In the present case, the dihedral angle between the allyl C_3 plane and the equatorial plane defined by Mn(1), C(15) and C(16) is 121.5(4)°.

Overall the deprotonated cyclopentadiene methylene group is essentially planar with no atom deviating more than 0.06(2) Å from the calculated plane. There is a dihedral angle of 6.6(7)° between the allyl C_3 plane and the plane defined by the six atoms of the deprotonated cyclopentadiene methylene group.

Previously reported examples of manganese complexes [46,47] containing a π-allyl group, incorporate an isolated three-carbon system which was essentially symmetrical (Table 3.6). The only example similar to the present case appears to be the Mo complex [41] shown in Figure 3.11 in which the π-allyl system also deviates from symmetrical bonding (Table 3.6).

Table 3.6 Bond Length (Å) and Angle Data (°) for π-Allyl Groups of Selected Complexes

	$(\eta^3\text{-}C_3H_5)Mn(CO)_2(P(OMe)_3)_2$	$(\eta^3\text{-}C_3H_5)Mn(CO)_3(CNMe)$	$(C_{16}H_{20}S_4)Mo(CO)_2$*
M-C(1)	2.223(17)	2.211(1)	2.30(1)
M-C(2)	2.114(15)	2.114(1)	2.27(1)
M-C(3)	2.229(13)	2.214(1)	2.41(1)
C(1)-C(2)	1.38(2)	1.448(2)	1.44(2)
C(2)-C(3)	1.40(2)	1.371(2)	1.39(2)
C(1)-M-C(3)	67.0(6)	68.4(4)	-
C(1)-C(2)-C(3)	124.5(15)	124.5(9)	-



The C(3)-C(31) distance of **(21)** (1.413 (6) Å) is shortened by ~0.05 Å with respect to an average sp^2-sp^2 distance of 1.46 Å, while C(2)-C(3) (1.415 (6) Å) and C(31)-O(1) (1.260 (5) Å) distances are both correspondingly lengthened.

The C(2)-N(1) bond is noticeably shorter than the C(7A)-N(1) bond (1.362 (5) versus 1.413 (5) Å) indicating that the C(1)-N bond has more double bond character.

These variations of bond lengths within the molecule can be understood in terms of contributions from two resonance forms (Figure 3.20) indicating a delocalised π-bonding network similar to that observed in the orthomanganated aldehyde **(11)**.

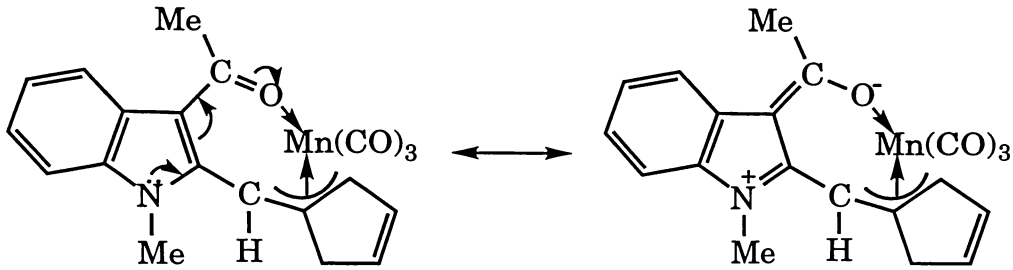


Figure 3.20

The indole nucleus is planar although the dihedral angle between this plane and the metallocyclic ring defined by Mn(1), O(1), C(31), C(3), C(2), and C(8) of 12° shows that this half of the structure is presumably being pushed down as a result of crystal packing forces.

Overall the relative Mn-CO distances and C-Mn-C angles of the $Mn(CO)_3$ group fall into the ranges normally found in manganese carbonyl derivatives.

3.4 Experimental Section

3.4.1 Starting Materials

The following commercial materials were used as supplied: dimethyl acetylenedicarboxylate (Aldrich, 99%), diphenylacetylene (Aldrich, 99%), 2-hexyne (Aldrich, 99%), 2-butyne-1,4-diol (Aldrich, 97%), 2-methyl-3-butyn-2-ol (Aldrich, 98%), trimethylphosphite (Aldrich, 97%), palladium chloride (Aldrich, 99%), lithium chloride (BDH, 99%) was oven dried before use, and acetylene (NZ Industrial Gases).

Phenylacetylene (BDH) was distilled under nitrogen at ambient pressure, b.p. 143-145 °C (lit. 142-144 °C [48]).

Preparation of η^2-(1-acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)-manganese

η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese [**(4)**; 203 mg, 0.623 mmol], and trimethylphosphite (0.37 mL, 3.14 mmol) were added to nitrogen saturated heptane. The solution was refluxed for 5 hours and the heptane was removed under vacuum. The yellow residue was chromatographed (p.l.c. 1:2 ethyl acetate/hexane) to give *η^2-(1-acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)manganese* [**(18)**; 294 mg, 91%] as a yellow solid which recrystallised from CH_2Cl_2/pentane as yellow blocks, m.p. 133-134 °C. Anal. Found: C, 41.93; H, 4.99; N, 2.66; $C_{18}H_{26}O_9MnNP_2$ calcd.: C, 41.79; H, 5.07; N, 2.71%. IR ($CHCl_3$): υ(CO) 1948(s), 1869(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.46 (*d*, J=8.0 Hz, 1H, H-7), 7.30 (*d*, J=7.7 Hz, 1H, H-4), 7.16 (*m*, 1H, H-5), 6.95 (*m*, 1H, H-6), 6.83 (*t*, $^4J_{PH}$=4.1 Hz, 1H, H-3), 3.54 (*t*, $^3J_{PH}$=5.3 Hz, 18H, $P(OCH_3)_3$), 2.71 (*s*, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 228.5 (*s*, $^2J_{PC}$=33.8 Hz, br, C≡O), 220.0 (*s*, $^2J_{PC}$=27.9 Hz, br, C≡O), 188.1 (*s*, $^2J_{PC}$=36.4 Hz, C-2), 176.4 (*s*, 1-$\underline{C}OCH_3$), 138.0 (*s*, C-7a), 137.0 (*s*, C-3a), 123.6 (*d*, C-5), 120.7 (*d*, $^3J_{PC}$=5.5 Hz, C-3), 118.9 (*d*, C-6), 117.0 (*d*, C-4), 111.6 (*d*, C-7), 51.7 (*q*, $P(OCH_3)_3$), 22.6 (*q*, 1-CO$\underline{C}H_3$). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 179.0. ESMS: m/z 518 $(M+H)^+$.

3.4.2 General Procedures for Thermally Promoted Coupling Reactions of Alkynes with Orthomanganated Compounds

The orthomanganated compound (~100 mg) and alkyne (1.2-2.2 mol equivalent) were dissolved in AR solvent (20 mL), the solution was degassed and flushed with nitrogen several times. The mixture was refluxed under nitrogen for 2 hours to several days, with the extent of reaction being monitored by t.l.c. and IR. At the completion of reaction the solvent was removed under vacuum and the remaining residue chromatographed on a p.l.c. silica gel plate (200 x 200 x 2 mm) using the appropriate eluant. Only major bands were extracted, with minor bands not generally being pursued; products are reported in order of increasing polarity.

3.4.3 Solvent Effects on Thermally Induced Alkyne-Coupling Reactions

Reactions of η^2-(2-Acetylphenyl)tetracarbonylmanganese with Diphenylacetylene

(a) In Benzene

The orthomanganated ketone [**(9)**; 105 mg, 0.367 mmol] and diphenylacetylene (96 mg, 0.538 mmol) were refluxed in benzene for 8 hours. The residue was chromatographed (p.l.c. 2:3 CH_2Cl_2/petroleum spirit) to give 1-methyl-2,3-diphenylinden-1-ol [**(13)**; 103 mg, 94%] as a yellowish oil which crystallised from CH_2Cl_2/petroleum spirit as white chunky crystals, m.p. 143-144 °C (lit. 143-144 °C [18]). ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.44-7.21 (*m*, 14H, Ar-H), 2.32 (*s*, br, 1H, 1-OH), 1.59 (*s*, 3H, -CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 149.7 (*s*), 147.1 (*s*), 142.2 (*s*), 138.7 (*s*), 134.8 (*s*), 134.7 (*s*), 129.5 (*d*, 2xAr-C), 129.3 (*d*, 2xAr-C), 128.6 (*d*, 2xAr-C), 128.5 (*d*), 128.0 (*d*, 2xAr-C), 127.6 (*d*), 127.3 (*d*), 126.6 (*d*), 121.9 (*d*), 120.8 (*d*), 83.3 (*s*), 24.1 (*q*). GCMS: m/z 262 (M^+).

(b) In Petroleum Spirit

The orthomanganated ketone [**(9)**; 104 mg, 0.362 mmol] and diphenylacetylene (96 mg, 0.538 mmol) were refluxed in petroleum spirit for 7 hours. The residue was chromatographed (p.l.c. 2:3 CH_2Cl_2/petroleum spirit) to give 1-methyl-2,3-diphenylinden-1-ol [**(13)**; 97 mg, 90%].

(c) In Acetonitrile

The orthomanganated ketone [**(9)**; 105 mg, 0.367 mmol] and diphenylacetylene (95 mg, 0.531 mmol) were refluxed in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 2:3 CH_2Cl_2/petroleum spirit) to give 1-methyl-2,3-diphenylinden-1-ol [**(13)**; 85 mg, 78%].

(d) In Carbon Tetrachloride

The orthomanganated ketone [**(9)**; 107 mg, 0.374 mmol] and diphenylacetylene (96 mg, 0.539 mmol) were refluxed in carbon

tetrachloride for 3 hours. The residue was chromatographed (p.l.c. 2:3 CH_2Cl_2/petroleum spirit) to give 1-methyl-2,3-diphenylinden-1-ol [**(13)**; 64 mg, 57%].

Reactions of η^2-(2-Acetylphenyl)tetracarbonylmanganese with 2-Hexyne

(a) In Benzene

The orthomanganated ketone [**(9)**; 111 mg, 0.387 mmol] and 2-hexyne (0.031 mL, 0.276 mmol) were refluxed in benzene for 22 hours. The residue was chromatographed (p.l.c. 1:1 CH_2Cl_2/petroleum spirit) to give a band consisting of both regioisomers; 1,3-dimethyl-2-n-propylinden-1-ol and 1,2-dimethyl-3-n-propylinden-1-ol which could not be separated, as a white solid which recrystallised from CH_2Cl_2/petroleum spirit as small white chunky crystals. Integration of the proton methyl singlets showed that the ratio of 1,3-dimethyl-2-propylinden-1-ol to 1,2-dimethyl-3-propylinden-1-ol was approximately 2:1.

1,3-dimethyl-2-propylinden-1-ol [**(14a)**; 19 mg, 34%]: ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.37 (*d*, 1H, ^{3}J=7.6 Hz, Ar-H), 7.26 (*m*, 1H, Ar-H), 7.14 (*m*, 2H, Ar-H), 2.34 (*m*, 2H, 2-C$\underline{H}_2$CH$_2$CH$_3$), 1.98 (*s*, 3H, 3-CH$_3$), 1.59 (*m*, 2H, 2-CH$_2$C$\underline{H}_2$CH$_3$), 1.51 (*s*, 3H, 1-CH$_3$), 1.00 (*t*, 3H, ^{3}J=7.4 Hz, 2-CH$_2$CH$_2$C$\underline{H}_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 149.2 (*s*), 147.8 (*s*), 143.8 (*s*), 132.3 (*s*), 128.3 (*d*, Ar-C), 125.4 (*d*, Ar-C), 121.1 (*d*, Ar-C), 118.4 (*d*, Ar-C), 82.6 (*s*, C-1), 27.0 (*t*, 2-$\underline{C}$H$_2$CH$_2$CH$_3$), 23.4 (*q*, 1-CH$_3$), 22.8 (*t*, 2-CH$_2\underline{C}$H$_2$CH$_3$), 14.7 (*q*, 2-CH$_2$CH$_2\underline{C}$H$_3$), 10.4 (*q*, 3-CH$_3$). GCMS: m/z 202 (M^+).

1,2-dimethyl-3-propylinden-1-ol [**(14b)**; 9 mg, 17%]: ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.40 (*d*, 1H, ^{3}J=7.5 Hz, Ar-H), 7.25 (*m*, 1H, Ar-H), 7.14 (*m*, 2H, Ar-H), 2.34 (*m*, 2H, 3-C$\underline{H}_2$CH$_2$CH$_3$), 1.89 (*s*, 3H, 2-CH$_3$), 1.59 (*m*, 2H, 3-CH$_2$C$\underline{H}_2$CH$_3$), 1.47 (*s*, 3H, 1-CH$_3$), 0.94 (*t*, 3H, ^{3}J=7.4 Hz, 3-CH$_2$CH$_2$C$\underline{H}_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 149.5 (*s*), 144.4 (*s*), 143.2 (*s*), 135.3 (*s*), 128.2 (*d*, Ar-C), 125.1 (*d*, Ar-C), 121.4 (*d*, Ar-C), 118.7 (*d*, Ar-C), 81.9 (*s*, C-1), 27.0 (*t*, 3-$\underline{C}$H$_2$CH$_2$CH$_3$), 23.1 (*q*, 1-CH$_3$), 21.6 (*t*, 3-CH$_2\underline{C}$H$_2$CH$_3$), 14.1 (*q*, 3-CH$_2$CH$_2\underline{C}$H$_3$), 9.0 (*q*, 2-CH$_3$). GCMS: m/z 202 (M^+).

(b) In Petroleum Spirit

The orthomanganated ketone [**(9)**; 103 mg, 0.361 mmol] and 2-hexyne (0.070 mL, 0.621 mmol) were refluxed in petroleum spirit for 5 hours. The residue was chromatographed (p.l.c. 1:1 CH_2Cl_2/petroleum spirit) to give a mixture of both regioisomers consisting of 1,3-dimethyl-2-propylinden-1-ol [**(14a)**; 33 mg, 45%] and 1,2-dimethyl-3-propylinden-1-ol [**(14b)**; 11 mg, 15%] (integration of the proton methyl singlets showed the ratio of 1,3-dimethyl-2-propylinden-1-ol to 1,2-dimethyl-3-propylinden-1-ol was approximately 3:1).

(c) In Acetonitrile

The orthomanganated ketone [**(9)**; 107 mg, 0.373 mmol] and 2-hexyne (0.030 mL, 0.267 mmol) were refluxed in acetonitrile (60-80) for 3.5 hours. The residue was chromatographed (p.l.c. 1:1 CH_2Cl_2/petroleum spirit) to give a mixture of both regioisomers consisting of 1,3-dimethyl-2-propylinden-1-ol [**(14a)**; 14 mg, 25%] and 1,2-dimethyl-3-propylinden-1-ol [**(14b)**; 7 mg, 13%] (integration of the proton methyl singlets showed the ratio of 1,3-dimethyl-2-propylinden-1-ol to 1,2-dimethyl-3-propylinden-1-ol was approximately 2:1).

(d) In Carbon Tetrachloride

The orthomanganated ketone [**(9)**; 108 mg, 0.378 mmol] and 2-hexyne (0.031 mL, 0.276 mmol) were refluxed in carbon tetrachloride (60-80) for 7 hours. The residue was chromatographed (p.l.c. 1:1 CH_2Cl_2/petroleum spirit) to give a mixture of both regioisomers consisting of 1,3-dimethyl-2-propylinden-1-ol [**(14a)**; 14 mg, 24%] and 1,2-dimethyl-3-propylinden-1-ol [**(14b)**; 7 mg, 12%] (integration of the proton methyl singlets showed the ratio of 1,3-dimethyl-2-propylinden-1-ol to 1,2-dimethyl-3-propylinden-1-ol was approximately 2:1).

Reactions of η^2-(2-Acetylphenyl)tetracarbonylmanganese with Dimethyl Acetylenedicarboxylate

(a) In Benzene

The orthomanganated ketone [**(9)**; 105 mg, 0.368 mmol] and dimethyl acetylenedicarboxylate (97 mg, 0.684 mmol) were refluxed in benzene for

4.5 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate [**(15)**; 64 mg, 67%] as a colourless oil. Anal. Found: M^+, 262.0840; $C_{14}H_{14}O_5$ calcd.: M, 262.0841. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.48-7.26 (*m*, 4H, Ar-H), 3.92 (*s*, 3H, $-OCH_3$), 3.84 (*s*, 3H, $-OCH_3$), 3.92 (*s*, br, 1H, H-1), 1.69 (*s*, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 165.0 (*s*, C=O), 164.9 (*s*, C=O), 149.3 (*s*), 141.4 (*s*), 140.3 (*s*), 136.3 (*s*), 129.6 (*d*), 129.1 (*d*), 123.1 (*d*), 122.6 (*d*), 82.0 (*s*, C-1), 52.5 (*q*, $-OCH_3$), 52.2 (*q*, $-OCH_3$), 24.8 (*q*, 1-CH_3).

(b) In Petroleum Spirit

The orthomanganated ketone [**(9)**; 304 mg, 1.063 mmol] and dimethyl acetylenedicarboxylate (216 mg, 1.519 mmol) were refluxed in petroleum spirit for 24 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

η^2-(2-acetylphenyl)tetracarbonylmanganese [**(9)**; 35 mg, 11%]
dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate [**(15)**; 151 mg, 54%]

(c) In Acetonitrile

The orthomanganated ketone [**(9)**; 104 mg, 0.363 mmol] and dimethyl acetylenedicarboxylate (74 mg, 0.519 mmol) were refluxed in acetonitrile for 1 hour. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate [**(15)**; 87 mg, 91%].

(d) In Carbon Tetrachloride

The orthomanganated ketone [**(9)**; 103 mg, 0.360 mmol] and dimethyl acetylenedicarboxylate (75 mg, 0.530 mmol) were refluxed in carbon tetrachloride for 3 hours. The residue was chromatographed (p.l.c. 1:1 CH_2Cl_2/petroleum spirit) to give dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate [**(15)**; 82 mg, 87%].

Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese with Diphenylacetylene

(a) In Benzene

The orthomanganated complex [**(4)**; 105 mg, 0.322 mmol] and diphenylacetylene (82 mg, 0.459 mmol) were refluxed in benzene for 4 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 66 mg, 61%] as an off white solid which recrystallised from CH_2Cl_2/pentane as creamy chunky crystals m.p. 183-184 °C. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.62 (*d*, J=7.9 Hz, 1H, H-4'), 7.57 (*d*, J=8.0 Hz, 1H, H-7'), 7.50 (*m*, 4H, Ar-H), 7.35 (*m*, 6H, Ar-H), 7.22 (*m*, 1H, H-6'), 7.11 (*m*, 1H, H-5'), 6.41 (*s*, 1H, H-3'), 2.78 (*s*, br, 1H, 1-OH), 1.82 (*s*, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 145.3 (*s*), 143.3 (*s*), 133.7 (*s*), 133.3 (*s*), 133.2 (*s*), 132.9 (*s*), 131.5 (*s*), 129.3 (*d*), 129.0 (*d*), 128.6 (*d*), 128.5 (*d*), 128.4 (*d*), 128.3 (*s*), 128.1 (*d*), 122.6 (*d*, C-6'), 121.9 (*d*, C-4'), 119.9 (*d*, C-5'), 110.1 (*d*, C-7'), 95.3 (*d*, C-3'), 91.6 (*s*, C-1), 23.8 (*q*, 1-CH_3).

The parent compound 1-acetylindole (7 mg, 13%).

(b) In Petroleum Spirit

The orthomanganated complex [**(4)**; 106 mg, 0.325 mmol] and diphenylacetylene (86 mg, 0.480 mmol) were refluxed in petroleum spirit for 5 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 70 mg, 64%].
The parent compound 1-acetylindole (5 mg, 10%).

(c) In Acetonitrile

The orthomanganated complex [**(4)**; 103 mg, 0.317 mmol] and diphenylacetylene (95 mg, 0.532 mmol) were refluxed in acetonitrile for 5 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 23 mg, 22%].
The parent compound 1-acetylindole (32 mg, 62%).

(d) In Carbon Tetrachloride

The orthomanganated complex [**(4)**; 104 mg, 0.319 mmol] and diphenylacetylene (79 mg, 0.442 mmol) were refluxed in carbon tetrachloride for 4 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give the parent compound 1-acetylindole (13 mg, 25%).

Attempted Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese with 2-Hexyne

(a) In Benzene

The orthomanganated complex [**(4)**; 103 mg, 0.317 mmol] and 2-hexyne (0.053 mL, 0.475 mmol) were refluxed in benzene for 22 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

Unreacted η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (7 mg, 7%).
The parent compound 1-acetylindole (23 mg, 45%).

(b) In Petroleum Spirit

The orthomanganated complex [**(4)**; 106 mg, 0.325 mmol] and 2-hexyne (0.051 mL, 0.450 mmol) were refluxed in petroleum spirit for 23 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

Unreacted η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (8 mg, 8%).
The parent compound 1-acetylindole (16 mg, 31%).

(c) In Acetonitrile

The orthomanganated complex [**(4)**; 102 mg, 0.315 mmol] and 2-hexyne (0.051 mL, 0.450 mmol) were refluxed in acetonitrile for 2.5 hours. The

residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

Unreacted η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (8 mg, 8%).
The parent compound 1-acetylindole (41 mg, 81%).

(d) In Carbon Tetrachloride

The orthomanganated complex [**(4)**; 108 mg, 0.332 mmol] and 2-hexyne (0.053 mL, 0.475 mmol) were refluxed in carbon tetrachloride for 22 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

Unreacted η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (5 mg, 5%).
The parent compound 1-acetylindole (22 mg, 42%).

Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese with Dimethyl Acetylenedicarboxylate

(a) In Benzene

The orthomanganated complex [**(4)**; 104 mg, 0.320 mmol] and dimethyl acetylenedicarboxylate (74 mg, 0.518 mmol) were refluxed in benzene for 24 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give 14 minor bands one of which was dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 1 mg, 1%].

(b) In Petroleum Spirit

The orthomanganated complex [**(4)**; 81 mg, 0.250 mmol] and dimethyl acetylenedicarboxylate (60 mg, 0.421 mmol) were refluxed in petroleum spirit for 5 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (11 mg, 27%).

Dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 12 mg, 15%] as a yellow oil which crystallised from CH_2Cl_2/petroleum

spirit as yellow needles, m.p. 98-99 °C (lit. 97.5-99.5. [20]). ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.63 (*d*, J=8.0 Hz, 1H, H-4'), 7.53 (*d*, J=8.2 Hz, 1H, H-7'), 7.26 (*t*, J=8.2, 1H, H-6'), 7.11 (*t*, J=8.0, 1H, H-5'), 6.60 (*s*, 1H, H-3'), 3.92 (*s*, 3H, -$COOCH_3$), 3.87 (*s*, 3H, -$COOCH_3$), 3.44 (*s*, 1H, 1-OH), 1.95 (*s*, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 163.0 (*s*, -$\underline{C}OOCH_3$), 162.9 (*s*, -$\underline{C}OOCH_3$), 140.6 (*s*, C-2), 137.0 (*s*, C-3), 134.4 (*s*, C-7a'), 132.9 (*s*, C-3a'), 132.6 (*s*, C-2'), 124.4 (*d*, C-6'), 122.9 (*d*, C-4'), 120.6 (*d*, C-5'), 110.6 (*d*, C-7'), 99.8 (*d*, C-3'), 90.2 (*s*, C-1), 52.9 (*q*, -COO$\underline{C}H_3$), 52.6 (*q*, -COO$\underline{C}H_3$), 24.1 (*q*, 1-CH_3).

(c) In Acetonitrile

The orthomanganated complex [**(4)**; 102 mg, 0.314 mmol] and dimethyl acetylenedicarboxylate (83 mg, 0.584 mmol) were refluxed in acetonitrile for 2.5 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (2 mg, 4%).
Dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 17 mg, 18%].

(d) In Carbon Tetrachloride

The orthomanganated complex [**(4)**; 105 mg, 0.322 mmol] and dimethyl acetylenedicarboxylate (67 mg, 0.473 mmol) were refluxed in carbon tetrachloride for 2.5 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (7 mg, 14%).
Dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 14 mg, 14%].

(e) In Tetrahydrofuran

The orthomanganated complex [**(4)**; 106 mg, 0.326 mmol] and dimethyl acetylenedicarboxylate (65 mg, 0.455 mmol) were refluxed in tetrahydrofuran for 3 hours. T.l.c. showed no major organic products so the reaction was abandoned.

3.4.4 General Procedures for Oxidatively Induced Coupling Reactions of Alkynes with Orthomanganated Compounds

The orthomanganated compound (~100 mg) and alkyne (1.2-1.6 mol equivalent) was dissolved in AR solvent (20 mL), the solution degassed and flushed with nitrogen several times. Trimethylamine-N-oxide (TMANO) (~1.4 mole equivalent) was then added and the solution stirred for 15-20 minutes, resulting in a more intense yellow colour change. The alkyne was then added and the mixture stirred at ambient temperature from between 3 to 24 hours. If any orthomanganated compound still remained after 24 hours the solution was refluxed for approximately 40 minutes, by which time t.l.c. showed the reaction was complete. The solvent was removed under vacuum and the remaining residue chromatographed on a p.l.c. silica gel plate (200 x 200 mm) using ethyl acetate/petroleum spirit. Only major bands were extracted, minor bands were generally not pursued; products are reported in order of increasing polarity.

3.4.5 Coupling Reactions of Orthomanganated 1-Acetylindole with Various Alkynes

Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese and Diphenylacetylene with Trimethylamine-N-Oxide

(a) In Benzene

The orthomanganated complex [**(4)**; 103 mg, 0.316 mmol], TMANO (37 mg, 0.490 mmol) and diphenylacetylene (87 mg, 0.485 mmol) were stirred at ambient temperature in benzene for 24 hours then refluxed for 40 minutes. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 32 mg, 30%].
The parent compound 1-acetylindole (31 mg, 62%).

(b) In Acetonitrile

The orthomanganated complex [**(4)**; 103 mg, 0.318 mmol], TMANO (37 mg, 0.486 mmol) and diphenylacetylene (89 mg, 0.497 mmol) were stirred at ambient temperature in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 8 mg, 7%].
The parent compound 1-acetylindole (40 mg, 80%).

Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese and 2-Hexyne with Trimethylamine-N-Oxide

(a) In Benzene

The orthomanganated complex [**(4)**; 103 mg, 0.317 mmol], TMANO (36 mg, 0.483 mmol) and 2-hexyne (0.055 mL, 0.489 mmol) were stirred at ambient temperature in benzene for 24 hours then refluxed for 40 minutes. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give the parent compound 1-acetylindole (26 mg, 52%).

(b) In Acetonitrile

The orthomanganated complex [**(4)**; 106 mg, 0.326 mmol], TMANO (38 mg, 0.500 mmol) and 2-hexyne (0.055 mL, 0.489 mmol) were stirred at ambient temperature in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give the parent compound 1-acetylindole (42 mg, 81%).

Reactions of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese and Dimethyl Acetylenedicarboxylate with Trimethylamine-N-Oxide

(a) In Benzene

The orthomanganated complex [**(4)**; 107 mg, 0.328 mmol], TMANO (36 mg, 0.483 mmol) and dimethyl acetylenedicarboxylate (0.057 mL, 0.464 mmol) were stirred at ambient temperature in benzene for 22 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (12 mg, 22%).
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 60 mg, 61%].

(b) In Petroleum Spirit

The orthomanganated complex [**(4)**; 106 mg, 0.327 mmol], TMANO (34 mg, 0.449 mmol) and dimethyl acetylenedicarboxylate (0.057 mL, 0.464 mmol) were stirred at ambient temperature in petroleum spirit for 24 hours then refluxed for 40 minutes. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (5 mg, 9%).
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 49 mg, 50%].

(c) In Acetonitrile

The orthomanganated complex [**(4)**; 110 mg, 0.337 mmol], TMANO (37 mg, 0.486 mmol) and dimethyl acetylenedicarboxylate (0.058 mL, 0.471 mmol) were stirred at ambient temperature in acetonitrile for 8 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (8 mg, 15%).
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 62 mg, 61%].

(d) In Carbon Tetrachloride

The orthomanganated complex [**(4)**; 106 mg, 0.325 mmol], TMANO (35 mg, 0.470 mmol) and dimethyl acetylenedicarboxylate (0.057 mL, 0.464 mmol) were stirred at ambient temperature in carbon tetrachloride for 24 hours then refluxed for 40 minutes. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (10 mg, 20%).
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 32 mg, 33%].

(e) In Methanol

The orthomanganated complex [**(4)**; 108 mg, 0.332 mmol], TMANO (38 mg, 0.503 mmol) and dimethyl acetylenedicarboxylate (71 mg, 0.496 mmol) were stirred at ambient temperature in methanol for 24 hours then refluxed for 40 minutes. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole (23 mg, 43%).
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 18 mg, 18%].

Reaction of η^2-(1-Acetyl-2-Indolyl)tetracarbonylmanganese with Li_2PdCl_4 and Dimethyl Acetylenedicarboxylate in Refluxing Acetonitrile

$PdCl_2$ (61 mg, 0.343 mmol) and LiCl (61 mg, 1.44 mmol) were stirred in dry acetonitrile (15 mL) for 2 hours to solubilise the $PdCl_2$ as Li_2PdCl_4. The orthomanganated complex [**(4)**; 108 mg, 0.332 mmol] and dimethyl acetylenedicarboxylate (0.057 mL, 0.464 mmol) were added and the mixture refluxed for 20 hours. Upon reaction the solution turned black with the precipitation of palladium metal. The mixture was filtered to remove metal, the filtrate passed through a short silica column and the solvent evaporated under reduced pressure. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give:

The parent compound 1-acetylindole [**(1)**; 7 mg, 13%].
1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate [**(17)**; 6 mg, 5%].

Reactions of η^2-(1-Acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)-manganese with Dimethyl Acetylenedicarboxylate

(a) In Petroleum Spirit

The orthomanganated complex [**(18)**; 169 mg, 0.327 mmol] and dimethyl acetylenedicarboxylate (80 mg, 0.562 mmol) were refluxed in petroleum spirit for 30 hours. T.l.c. only showed the presence of the orthomanganated ketone so the reaction was abandoned.

(b) In Acetonitrile

The orthomanganated complex [**(18)**; 134 mg, 0.258 mmol] and dimethyl acetylenedicarboxylate (60 mg, 0.417 mmol) were refluxed in acetonitrile for 28 hours. T.l.c. only showed the presence of the orthomanganated ketone so the reaction solution was left to cool and treated with TMANO (25 mg, 0.33 mmol). The solution was stirred for 3 hours, again t.l.c. only indicated the presence of orthomanganated starting material so the reaction was abandoned.

(c) In Acetonitrile with TMANO

The orthomanganated complex [**(18)**; 94 mg, 0.182 mmol], TMANO (21 mg, 0.282 mmol) and dimethyl acetylenedicarboxylate (42 mg, 0.296 mmol) were stirred at ambient temperature in acetonitrile for 27 hours. The residue was chromatographed (p.l.c. 1:2 hexane/ethyl acetate) to give:

Unreacted η^2-(1-acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)-manganese [**(18)**; 81 mg, 87%].
The parent compound 1-acetylindole [**(1)**; 2 mg, 8%].

Reaction of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese with 2-Butyne-1,4-diol in Petroleum Spirit

The orthomanganated complex [**(4)**; 107 mg, 0.328 mmol] and 2-butyne-1,4-diol (53 mg, 0.614 mmol) were refluxed in petroleum spirit for 2 hours. T.l.c. indicated that demetalation had occurred. The alkyne also appeared to be insoluble in refluxing petroleum spirit. Attempts at finding a hydrocarbon solvent in which 2-butyne-1,4-diol was soluble were unsuccessful so the reaction was abandoned.

Reaction of η^2-(1-Acetyl-2-indolyl)tetracarbonylmanganese with 2-Methyl-3-butyn-2-ol in Petroleum Spirit

The orthomanganated complex [**(4)**; 106 mg, 0.326 mmol] and 2-methyl-3-butyn-2-ol (0.047 mL, 0.485 mmol) were refluxed in petroleum spirit for

8 hours. T.l.c. indicated that demetalation had occurred so the reaction was not pursued.

3.4.6 Alkyne-Coupling Reactions of Various Orthomanganated Complexes

Reaction of η^2-(3-Acetyl-2-indolyl)tetracarbonylmanganese with Diphenylacetylene in Petroleum Spirit

The orthomanganated ketone [**(7)**; 104 mg, 0.320 mmol] and diphenylacetylene (82 mg, 0.462 mmol) were refluxed in petroleum spirit for 7 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give 1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole [**(16)**; 20 mg, 18%].

Reaction of η^2-(3-Acetyl-2-indolyl)tetracarbonylmanganese with Dimethyl Acetylenedicarboxylate in Petroleum Spirit

The orthomanganated ketone [**(7)**; 105 mg, 0.322 mmol] and dimethyl acetylenedicarboxylate (0.055 mL, 0.447 mmol) were refluxed in petroleum spirit for 26 hours. T.l.c. showed the presence of unreacted starting material and no other major organic products, so the reaction was abandoned.

Reaction of η^2-(3-Acetyl-2-indolyl)tetracarbonylmanganese with 2-Hexyne in Petroleum Spirit

The orthomanganated ketone [**(7)**; 105 mg, 0.322 mmol] and 2-hexyne (0.051 mL, 0.454 mmol) were refluxed in petroleum spirit for 6 hours. T.l.c. showed no major organic products so the reaction was abandoned.

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese with Diphenylacetylene in Petroleum Spirit

The orthomanganated ketone [**(8)**; 103 mg, 0.303 mmol] and diphenylacetylene (82 mg, 0.461 mmol) were refluxed in petroleum spirit for 24 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give 4-(1-methyl-2-indolyl)-3,4-diphenyl-but-3-en-2-one [**(20)**; 46 mg, 43%] which recrystallised from $CHCl_3$/pentane as chunky yellow crystals, m.p. 160-162 °C. Anal. Found: M^+, 351.1620; $C_{25}H_{21}NO$ calcd.: M, 351.1623. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.63 (*d*, J=7.8 Hz, 1H, H-4'), 7.25-6.99 (*m*, 13H, Ar-H), 6.68 (*s*, 1H, H-3'), 3.34 (*s*, 3H, 1'-CH_3), 2.09 (*s*, 3H, 2'-C(Ph)C(Ph)COC$\underline{H}_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 205.2 (*s*, 2'-C(Ph)C(Ph)$\underline{C}OCH_3$), 146.0 (*s*), 139.2 (*s*), 138.6 (*s*), 138.2 (*s*), 137.4 (*s*), 135.1 (*s*), 130.5 (*d*, Ar-C), 130.2 (*d*, Ar-C), 128.6 (*d*, Ar-C), 128.3 (*d*, Ar-C), 128.0 (*d*, Ar-C), 127.8 (*s*), 122.7 (*d*, Ar-C), 121.1 (*d*, C-4'), 119.9 (*d*, Ar-C), 109.5 (*d*, Ar-C), 106.7 (*d*, C-3'), 31.1 (*q*, 2'-C(Ph)C(Ph)CO$\underline{C}H_3$), 30.8 (*q*, 1'-CH_3). GCMS: m/z 351 (M^+).

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese and Diphenylacetylene with Trimethylamine-N-Oxide in Acetonitrile

The orthomanganated ketone [**(8)**; 102 mg, 0.302 mmol], TMANO (35 mg, 0.462 mmol) and diphenylacetylene (77 mg, 0.434 mmol) were stirred at ambient temperature in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 1:1 ethyl acetate/petroleum spirit) to give:

4-(1-methyl-2-indolyl)-3,4-diphenyl-but-3-en-2-one [**(20)**; 57 mg, 53%].
The parent ketone 1-methyl-3-acetylindole (9 mg, 18%).

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese with Dimethyl Acetylenedicarboxylate in Petroleum Spirit

The orthomanganated ketone [**(8)**; 100 mg, 0.296 mmol] and dimethyl acetylenedicarboxylate (0.055 mL, 0.448 mmol) were refluxed in petroleum spirit for 24 hours. The residue was chromatographed (p.l.c. 40% dichloromethane/petroleum spirit) to give:

Unreacted η^2-(1-methyl-3-acetyl-2-indolyl)tetracarbonylmanganese (26 mg, 26%).
The parent ketone 1-methyl-3-acetylindole (12 mg, 23%).

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese and Dimethyl Acetylenedicarboxylate with Trimethylamine-N-Oxide in Acetonitrile

The orthomanganated ketone [**(8)**; 104 mg, 0.308 mmol], TMANO (35 mg, 0.469 mmol) and dimethyl acetylenedicarboxylate (0.057 mL, 0.464 mmol) were stirred at ambient temperature in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 1:1 ethyl acetate/petroleum spirit) to give several minor bands that were not identified.

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese with Phenylacetylene in Petroleum Spirit

The orthomanganated ketone [**(8)**; 101 mg, 0.297 mmol] and phenyl acetylene (0.049 mL, 0.446 mmol) were refluxed in petroleum spirit for 24 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give:

The parent ketone 1-methyl-3-acetyl indole (12 mg, 23%).

No other major organic products were isolated however, GCMS on two minor bands indicated the presence of three of the following compounds:

E 4-(1-methyl-2-indolyl)-4-phenyl-but-3-en-2-one
Z 4-(1-methyl-2-indolyl)-4-phenyl-but-3-en-2-one
E 4-(1-methyl-2-indolyl)-3-phenyl-but-3-en-2-one
Z 4-(1-methyl-2-indolyl)-3-phenyl-but-3-en-2-one

GCMS: m/z 275 (M^+).

Reaction of η^2-(1-Methyl-3-acetyl-2-indolyl)tetracarbonylmanganese with Acetylene in Petroleum Spirit

The orthomanganated ketone [**(8)**; 200 mg, 0.303 mmol] and acetylene were refluxed in petroleum spirit for 6 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give **(21)** (39 mg, 17%) which recrystallised from chloroform/pentane as chunky orange crystals, m.p. 135-137 °C. IR ($CHCl_3$): υ(CO) 2013 (s), 1932 (s, br), 1899 (s, br) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.65 (*d*, J=7.3 Hz, 1H, H-4), 7.37 (*d*, J=7.5 Hz, 1H, H-7) 7.30 (*m*, 2H, H-5, H-6), 6.77 (*d*, J=4.8 Hz, 1H), 6.15 (*d*, J=4.8 Hz, 1H), 5.11 (*s*, 1H), 4.06 (*s*, 3H), 3.59 (*d*, J=22.5 Hz, 1H), 3.41 (*s*, 1H), 3.20 (*d*, J=22.5 Hz, 1H), 2.56 (*s*, 3H). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 223.2 (*s*), 222.7 (*s*), 221.8 (*s*), 194.3 (*s*), 153.8 (*s*), 137.4 (*s*), 136.4 (*d*), 128.5 (*d*), 125.8 (*s*), 123.0 (*d*), 122.8 (*d*), 120.0 (*d*), 110.0 (*d*), 95.7 (*d*), 48.6 (*t*), 43.2 (*d*), 30.4 (*q*), 29.9 (*q*). This compound was identified by a single X-ray crystal structure.

Reaction of (21) in Heptane under Reflux

Complex **(21)** (46 mg, 0.117 mmol) was refluxed in heptane (15 mL) for 24 hours. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give 1-methyl-3-acetyl-2-indolylmethyl-cyclopentadienyltricarbonylmanganese [**(22)**; 24 mg, 52%] as an opaque oil. Anal. Found: MH^+, 390.0543; $C_{20}H_{17}O_4NMn$ calcd.: MH, 390.0538. IR ($CHCl_3$): υ(CO) 2021 (s), 1937 (vs, br). ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.92 (*m*, 1H, H-4'), 7.40 (*m*, 1H, H-7') 7.30 (*m*, 2H, H-5', H-6'), 4.87 (*t*, J=2.1 Hz, 2H, H-3, H-6 or H-4, H-5), 4.57 (*t*, J=2.1 Hz, 2H, H-3, H-6 or H-4, H-5), 4.24 (*s*, 2H, H-1), 3.83 (*s*, 3H, 1'-CH_3), 2.73 (*s*, 3H, 3'-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 224.9 (*s*, M-C≡O), 194.3 (*s* , 3'-$\underline{C}OCH_3$), 145.1 (*s*, C-2'), 136.8 (*s*, C-7a'), 125.9 (*s*, C-3a'), 122.7 (*d*, C-5' or C-6'), 122.4 (*d*, C-5' or C-6'), 120.8 (*d*, C-4'), 114.1 (*s*, C-3'), 110.2 (*d*, C-7'), 100.9 (*s*, C-2), 84.4 (*d*, C-3, C-6 or C-4, C-5), 81.2 (*d*, C-3, C-6 or C-4, C-5), 31.9 (*q*, -CH_3), 30.0 (*q*, -CH_3), 24.4 (*t*, C-1). ESMS: m/z 407 $(M+NH_4)^+$, 390 $(M+H)^+$.

Reaction of (21) and Trimethylphosphite in Heptane under Reflux

Complex **(21)** (20 mg, 0.051 mmol) and trimethylphosphite (50 mL, 0.424 mmol) were refluxed in heptane (10 mL) for 4.5 hours. The residue was chromatographed (p.l.c. 3:7 ethyl acetate/petroleum spirit) to give 1-methyl-3-acetyl-2-indolylmethylcyclopentadienyldicarbonyltrimethylphosphitemanganese [**(23)**; 12 mg, 50%] as a yellow oil. Anal. Found: M^+, 485.0807; $C_{22}H_{25}O_6NPMn$ calcd.: M, 485.0800. IR ($CHCl_3$): υ(CO) 1946 (s), 1877 (s). ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.93 (*m*, 1H, H-4'), 7.36 (*m*, 1H, H-7') 7.30 (*m*, 2H, H-5', H-6'), 4.65 (*m*, 2H, H-3, H-6 or H-4, H-5), 4.34 (*m*, 2H, H-3, H-6 or H-4, H-5), 4.27 (*s*, 2H, H-1), 3.86 (*s*, 3H, 1'-CH_3), 3.60 (*d*, $^3J_{PH}$=11.6 Hz, 9H, -$P(OCH_3)_3$), 2.71 (*s*, 3H, 3'-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 230.0 (*s*, M-C≡O), 229.5 (*s*, M-C≡O), 194.2 (*s*, 3'-$\underline{C}OCH_3$), 146.2 (*s*, C-2'), 136.8 (*s*, C-7a'), 126.1 (*s*, C-3a'), 122.4 (*d*, C-5' or C-6'), 122.2 (*d*, C-5' or C-6'), 120.8 (*d*, C-4'), 113.8 (*s*, C-3'), 110.1 (*d*, C-7'), 98.9 (*s*, C-2), 82.2 (*d*, C-3, C-6 or C-4, C-5), 80.6 (*d*, C-3, C-6 or C-4, C-5), 51.6 (*q*, -$P(OCH_3)_3$), 31.8 (*q*, -CH_3), 30.4 (*q*, -CH_3), 24.7 (*t*, C-1). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 209.9. ESMS: m/z 486 $(M+H)^+$.

3.4.7 Alkyne-Coupling Reactions of Orthomanganated Aldehydes

Reaction of η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese with Diphenylacetylene in Petroleum Spirit

The orthomanganated aldehyde [**(11)**; 101 mg, 0.310 mmol] and diphenylacetylene (79 mg, 0.444 mmol) were refluxed in petroleum spirit for 7 hours. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give several minor bands that were not identified.

3.4.8 Attempted Reactions of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonylmanganese

(a) Reaction of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonyl-manganese in Refluxing Heptane

The orthomanganated complex [**(5)**; 50 mg, 0.154 mmol] was refluxed in heptane (15 mL) for 22 hours. T.l.c. showed that demetalation had occurred hence the reaction was not pursued.

(b) Reaction of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonyl-manganese in Refluxing Acetonitrile

The orthomanganated complex [**(5)**; 51 mg, 0.144 mmol] was refluxed in acetonitrile (15 mL) for 20 hours. T.l.c. showed that demetalation had occurred hence the reaction was not pursued.

(c) Reaction of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonyl-manganese in Refluxing Carbon Tetrachloride

The orthomanganated complex [**(5)**; 97 mg, 0.277 mmol] was refluxed in carbon tetrachloride (15 mL) for 7 hours. T.l.c. showed that demetalation had occurred hence the reaction was not pursued. The residue was chromatographed (p.l.c. 1:4 ethyl acetate/petroleum spirit) to give the demetalated product 1-(2-methylprop-2-enoyl)indole [**(2)**; 25 mg, 49%].

(d) Reaction of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonyl-manganese with Trimethylamine-N-Oxide

The orthomanganated complex [**(5)**; 86 mg, 0.245 mmol] and TMANO (28 mg, 0.369 mmol) were stirred at ambient temperature in acetonitrile for 3 hours. The residue was chromatographed (p.l.c. 1:9 ethyl acetate/petroleum spirit) to give:

Unreacted η^2-(1-(2-methylprop-2-enoyl)indolyl)tetracarbonylmanganese [**(5)**; 7 mg, 9%].
The parent compound 1-(2-methylprop-2-enoyl)indole [**(2)**; 33 mg, 73%].

(e) Reaction of η^2-(1-(2-Methylprop-2-enoyl)indolyl)tetracarbonylmanganese with Li_2PdCl_4 in Refluxing Acetonitrile

$PdCl_2$ (55 mg, 0.310 mmol) and LiCl (55 mg, 1.30 mmol) were stirred in dry acetonitrile (15 mL) for 2 hours to solubilise the $PdCl_2$ as Li_2PdCl_4. The orthomanganated complex [**(5)**; 103 mg, 0.293 mmol] was added and the mixture refluxed for 17 hours. Upon reaction the solution turned black with the precipitation of palladium metal. The mixture was filtered to remove metal, the filtrate passed through a short silica column and the solvent evaporated under reduced pressure. The residue was chromatographed (p.l.c. 1:9 ethyl acetate/petroleum spirit) to give the demetalated product 1-(2-methylprop-2-enoyl)indole [**(2)**; 20 mg, 37%].

3.4.9 Reaction of Ethyne with Benzylpentacarbonylmanganese

Reaction of Benzylpentacarbonylmanganese with Ethyne in Petroleum Spirit

Benzylpentacarbonylmanganese (305 mg, 1.07 mmol) and a continuous stream of ethyne were refluxed in petroleum spirit (50 mL) for 90 minutes. The residue was chromatographed (p.l.c. 1:9 diethyl ether/petroleum spirit) to give an orange solid (39 mg) which from EIMS was tentatively assigned as a mixture of:

Pentalene-hexacarbonyldimanganese **(24)** EIMS: m/z 380 (M^+), 352 $(M\text{-}CO)^+$, 324 $(M\text{-}2CO)^+$, 296 $(M\text{-}3CO)^+$, 268 $(M\text{-}4CO)^+$, 240 $(M\text{-}5CO)^+$, 212 $(M\text{-}6CO)^+$, 157 $(M\text{-}6CO\text{-}Mn)^+$, 212 $(M\text{-}6CO\text{-}2Mn)^+$.

(25) EIMS: m/z 332 (M^+), 276 $(M\text{-}2CO)^+$, 248 $(M\text{-}3CO)^+$, 212 $(M\text{-}3CO\text{-}Mn)^+$.

(26) EIMS: m/z 242 (M^+), 214 $(M\text{-}CO)^+$, 186 $(M\text{-}2CO)^+$, 158 $(M\text{-}3CO)^+$, 103 $(M\text{-}3CO\text{-}Mn)^+$.

Reaction of Manganese Carbonyl with Ethyne in Heptane

Manganese carbonyl (401 mg, 1.03 mmol) and a continuous stream of acetylene were refluxed in heptane (50 mL) for 7 hours. T.l.c. and IR just showed the presence of starting material so the reaction was abandoned.

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Chapter Four

Orthofunctionalisation of Triphenylphosphine Chalcogens via Manganation

4.1 Introduction: Tertiary Phosphine Chalcogenide Metal Complexes

Since the first reports of the tertiary phosphine chalcogenide metal complexes $PdCl_2L_2$ (L=Ph_3PS, Ph_3PSe) and $SnCl_4(Ph_3PSe)_2$ by Bannister and Cotton [1] in 1960, numerous examples containing these ligands have been reported.

A recent review [2] describes the coordination chemistry of the $R_3P{=}X$ ligands (X=O, S, Se) and related chelating ligands. These ligands exhibit a number of different bonding modes to metals, such as unidentate, bridging bidentate, chelating bidentate, chelating tridentate, chelating bridging tridentate, and chelating bridging tetradentate depending on the number of donor atoms contained within the ligand. As a result, a number of novel bonding, structural and spectroscopic properties have been observed for some of these complexes. Examples include the formation of cage compounds by a tripod ligand $(Ph_2P(S))_3CH$ [3], the presence of a six-membered Cu-S ring in $(Cu(Me_3PS)Cl)_3$ [4], an unusual feature of Cu(I) chemistry, and the occurrence of monomer and dimer moieties of $NbSCl_3^-(Ph_3PS)$ in the same unit cell [5,6].

The diversity of metals investigated is large and they can be divided into three groups depending on the attention they have received. The first group has been extensively studied and consists of Cr, Mo, W, Pd, Pt, Cu, Cd, and Hg. They are followed by Nb, Ta, Fe, Co, Rh, Ir, Ni, Zn, B and Sn which comprise the next group which has been moderately well

studied. The final group which includes Ti, Zr, V, Mn, Ru, Al, Tl, Pb, Sb, Bi and Te has been poorly studied and this is illustrated by there being only one reported tertiary phosphine chalcogenide metal complex of manganese (Figure 4.1).

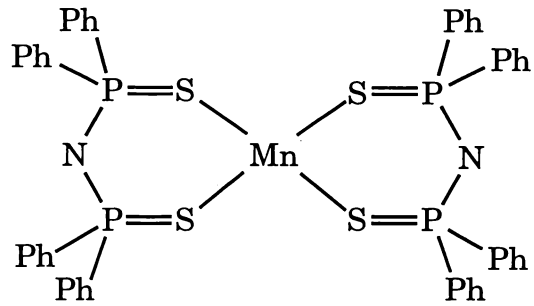


Figure 4.1

To date there have been no reports of cyclometalated complexes of triphenylphosphine chalcogenide ligands. Metal complexes that have been reported involve the triphenylphosphine chalcogenide ligand binding to the metal in a unidentate fashion (Figure 4.2) via a coordinate covalent bond from the X atom to the metal, although in some cases bridging by S or Se has been identified [2].

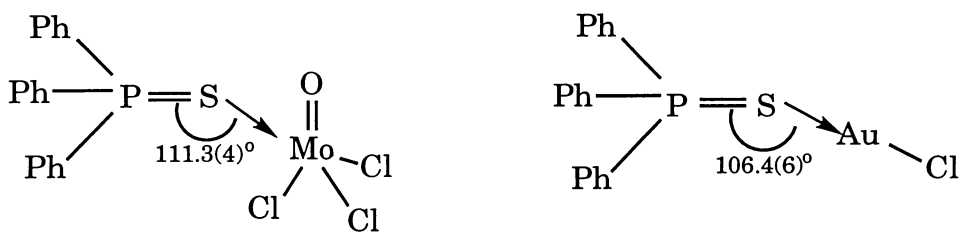
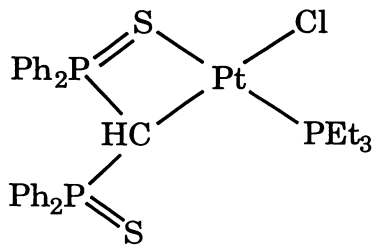
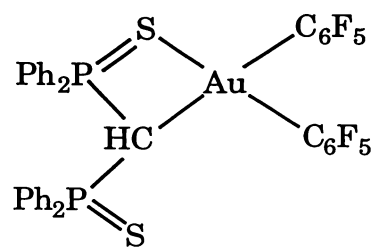


Figure 4.2

The only known examples of cyclometalated tertiary phosphine chalcogenide complexes appear to be derived from the ditertiary anionic ligand $(Ph_2PS)_2CH^-$, in which the metal atom becomes coordinated via the methine carbon atom and a sulfur atom forming a four-membered metallocyclic ring (Figure 4.3).



[9]



[10]

Figure 4.3

The Pt(II) containing cyclometalated complex is also interesting, as ^{31}P NMR studies have shown that the Pt-S bond is sufficiently labile to allow dynamic solution interchange with the other sulfur. In contrast to the common simple exchange of coordination sites in a "dangling" ligand, this process is unusual as it essentially involves a "bimolecular" reaction controlled by a pivotal motion about a strong metal-ligand bond.

Triphenylphosphine chalcogens are of primary interest to this thesis for two reasons. Firstly, they satisfy the requirements for an orthometalation substrate, which are; the presence of a suitable coordinating/donor atom, and the possibility of formation of a five-membered metallocyclic ring by M-C bond formation at the *ortho* site. Secondly, they are related to ligands such as triphenylphosphite which readily undergoes orthometalation [11] (Figure 4.4) with $PhCH_2Mn(CO)_5$ in good yield (60%).

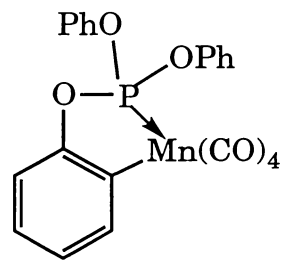


Figure 4.4

The successful orthomanganation of triphenylphosphine oxide would yield an orthomanganated complex containing a metallocyclic ring with an identical make-up of atom types compared to the corresponding

metallocyclic ring of the orthomanganated triphenylphosphite complex. The only difference between the respective rings would be the reversal of position of the oxygen and phosphorus atoms.

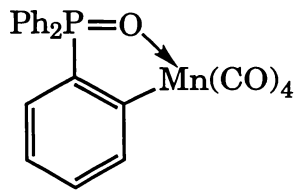
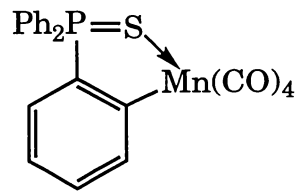
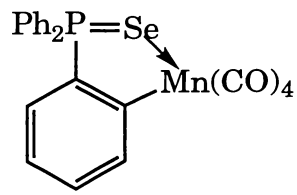
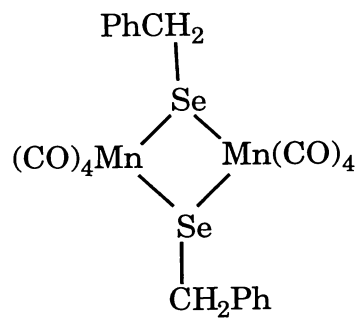
An investigation into the reaction of $Ph_3P{=}X$ (X=O, S, Se) with $PhCH_2Mn(CO)_5$ therefore creates an opportunity to establish the first orthometalated tertiary phosphine chalcogenide metal complexes.

4.2 Discussion of Results

Reaction of $Ph_3P{=}O$ **(27)**, $Ph_3P{=}S$ **(28)**, and $Ph_3P{=}Se$ **(29)** with $PhCH_2Mn(CO)_5$ yielded the corresponding orthomanganated compounds **(30)**, **(31)**, and **(32)** in fair to excellent yield (Table 4.1). The orthomanganation of $Ph_3P{=}S$ was carried out in refluxing heptane, while that of $Ph_3P{=}Se$ was carried out under more gentle reaction conditions in refluxing petroleum spirit because of the failure to induce a clean reaction in heptane. The orthometalation of $Ph_3P{=}O$ was carried out in both refluxing heptane [**(30)**; 33%] and petroleum spirit [**(30)**; 41%], with reaction in the latter resulting in a slightly higher yield of the cyclomanganated product. The tellurium analogue was not prepared, as a method for the preparation of $Ph_3P{=}Te$ is yet to be found [12].

The orthometalated complexes were separated by p.l.c. or column chromatography to give orthomanganated $Ph_3P{=}S$ **(31)** or $Ph_3P{=}Se$ **(32)** as yellow crystalline solids that are readily handled, while orthomanganated $Ph_3P{=}O$ **(30)** was isolated as an orange oil which failed to crystallise. These complexes appear to be the first examples of orthometalated tertiary phosphine chalcogenide complexes, and orthomanganated $Ph_3P{=}Se$ **(32)** is the first known example of an orthomanganated complex containing a selenium donor atom coordinated to manganese. The orthomanganated chalcogenides also contain metallocyclic rings that are unique compared to other orthomanganated complexes, so the crystal structures of orthomanganated $Ph_3P{=}S$ **(31)** and $Ph_3P{=}Se$ **(32)** were determined by X-ray methods for complete characterisation. Full discussion of the structures is deferred to Sections 4.4 and 4.5.

Table 4.1 Products obtained from the Orthometalation Reaction of Triphenylphosphine Chalcogenides with $PhCH_2Mn(CO)_5$

Substrate	Products	Yield	Method of Purification
$Ph_3P{=}O$ **(27)**	 **(30)**	41%	A
$Ph_3P{=}S$ **(28)**	 **(31)**	90%	B
$Ph_3P{=}Se$ **(29)**	 **(32)**	22%	B
	 **(33)**	14%	B
	$PhCH_2Mn(CO)_4PPh_3$ **(34)**	16%	B

A=P.l.c. 1:3 v/v ethyl acetate/petroleum spirit

B=P.l.c. 2:3 v/v dichloromethane/petroleum spirit

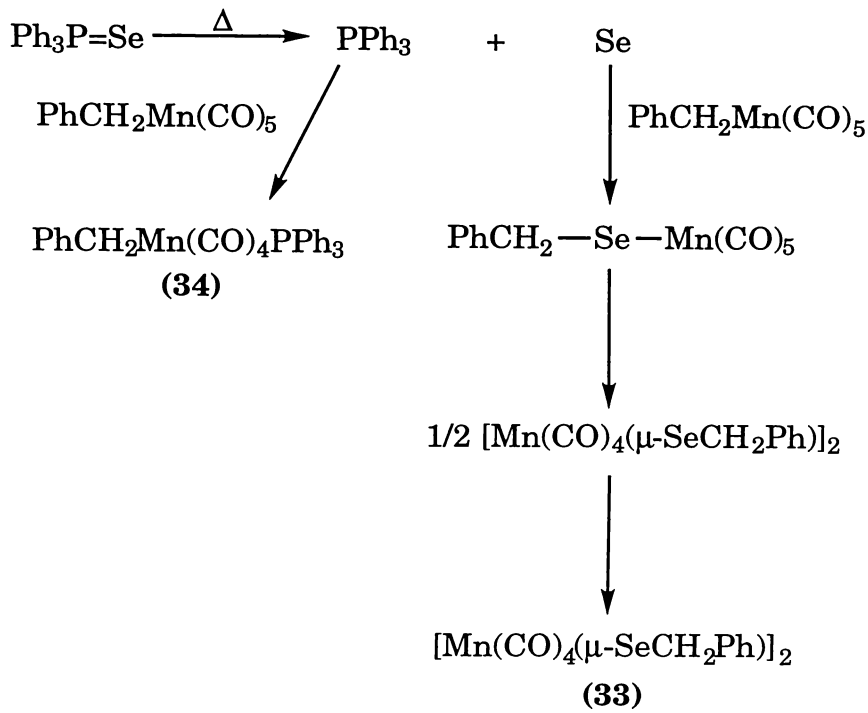
In addition to the formation of the orthomanganated Ph_3P=Se **(32)**, two other products containing $Mn(CO)_4$ fragments were isolated from the reaction of Ph_3P=Se with $PhCH_2Mn(CO)_5$. These compounds were identified as *bis*[(benzylseleno)tetracarbonylmanganese] **(33)**, a red crystalline solid, and *cis*-benzyltetracarbonyltriphenylphosphine-manganese **(34)**, a colourless crystalline solid (Table 4.1). The crystal structure of **(33)** was determined and is discussed in Section 4.6.

A number of analogous $Mn_2Y_2(CO)_8$ (Y=PR_2, AsR_2, SR, SeR) type complexes have been reported [13]. Of particular relevance are the dinuclear complexes $[Mn(CO)_4(\mu\text{-TeR})]_2$ (R=Me, Et, Pr^i, CH_2SiMe_3 and $Si(SiMe_3)_3$) formed from the reaction of $BrMn(CO)_5$ with LiTeR in THF [14]. The formation of these complexes is thought to arise via a $RTeMn(CO)_5$ intermediate, which was never detected, before the subsequent loss of CO. However, evidence for the formation of such intermediates exists in the isolation of the tellurium-inserted *mer-trans*-$RTeMn(CO)_3(PEt_3)_2$ (R=Me, CH_2Ph) type complexes obtained from the reaction of $TePEt_3$ and $RMn(CO)_5$ with an excess of PEt_3 in refluxing toluene, in which the phosphine ligands probably prevent the formation of the corresponding dimer compound. Presumably, formation of **(33)** occurs via the corresponding $RSeMn(CO)_5$ intermediate formed from the insertion of Se into the Mn-C bond of $PhCH_2Mn(CO)_5$.

There have been some examples of the direct insertion of chalcogens into transition metal-carbon bonds [15] where it was found that the rate of insertion depends on the chalcogen and decreases in the order S > Se > Te. In an attempt to isolate **(33)** in higher yield, $PhCH_2Mn(CO)_5$ was reacted with powdered selenium in refluxing heptane. However, this resulted in the decomposition of $PhCH_2Mn(CO)_5$ with no trace of the dinuclear complex being detected.

This suggests that Ph_3P=Se is acting as a source of soluble selenium, as the insolubility of powdered selenium in heptane was obvious. It is also consistent with the results observed in the attempted insertion of tellurium metal into the Mn-C bond of $RMn(CO)_5$ (R=Me, CH_2Ph), which resulted in the decomposition of $RMn(CO)_5$ [14]. However, the use of soluble tellurium in the form of $TePEt_3$ resulted in the formation of the tellurium-inserted product, *mer-trans*-$RTeMn(CO)_3(PEt_3)_2$.

The proposed reaction scheme for the formation of **(33)** and **(34)** is shown in Scheme 4.1.



Scheme 4.1

Thermolysis of $Ph_3P{=}Se$ results in the cleavage of the P=Se bond yielding soluble selenium and PPh_3. Insertion of selenium into the Mn-C bond of $PhCH_2Mn(CO)_5$ presumably results in the formation of an intermediate manganese pentacarbonyl species which undergoes subsequent ligand dissociation of CO and dimerises to form **(33)**. The formation of **(34)** simply arises from a ligand substitution of CO by Ph_3P, a well-known reaction.

To rationalise the wide variation in the yields of orthomanganated chalcogenides obtained and the formation of compounds **(33)** and **(34)**, the chemical stability of the respective triphenylphosphine chalcogens, i.e. the relative strengths of the P=X bond (X=O, S, Se) and the donor ability of the X atom involved must be considered.

The traditional picture of the P=X bond is that it consists of a σ and a π-bond (p_π-d_π) between P and X, although the presence of the π-bond is not completely accepted [16]. Bond dissociation energies, infrared force constant calculations and semi-empirical molecular orbital calculations imply the strength of the P=X bond decreases in the order $R_3P{=}O$ > $R_3P{=}S$ > $R_3P{=}Se$ [17].

Considering the relative electronegativities of the potential donor atoms involved, the donor ability of the X atom is expected to be in the order Se > S > O, reflecting the increasing electronegativity of the respective atoms (although the electronegativity of selenium is only slightly lower than that of sulfur). Hard/Soft Acid/Base Theory also predicts that the M-X bond strength will be in the same order due to manganese(I) being a relatively soft Lewis acid.

By considering these factors, the low yield of orthomanganated $Ph_3P{=}Se$ obtained, despite selenium being theoretically the best donor atom is clearly caused by the instability of $Ph_3P{=}Se$ due to the weakness of the P=X bond. The cleavage of the P=Se bond obviously led to the formation of the by-products $[Mn(CO)_4(\mu\text{-}SeCH_2Ph)]_2$ **(33)** and $PhCH_2Mn(CO)_4PPh_3$ **(34)**. The absence of formation of $PhCH_2Mn(CO)_4PPh_3$ and the corresponding sulfur-inserted dinuclear complex, suggests that bond stability considerations of P=X are no longer important and that the donor ability of the X atom will play a more important role in determining the product yields of the remaining two orthomanganated triphenylphosphine chalcogenide complexes. Presumably, reaction of $Ph_3P{=}S$ with $PhCH_2Mn(CO)_5$ results in the highest yield of the corresponding orthomanganated complex as it possesses the optimum balance between P=X bond stability and the donor ability of the X atom, while the lower yield of orthomanganated $Ph_3P{=}O$ presumably reflects the poorer donor ability of the oxygen atom in $Ph_3P{=}O$.

4.3 Properties of Orthomanganated Triphenylphosphine Chalcogenide Complexes

4.3.1 General

Complexes **(30)**, **(31)** and **(32)** are generally air stable and can be stored in a refrigerator (4 °C) for extended periods without any appreciable decomposition. The orthomanganated complexes dissolve readily in all organic solvents, which means there are no constraints for spectroscopy and reactivity studies.

4.3.2 Infrared Spectra

Orthomanganated complexes **(31)** and **(32)** exhibited four characteristic absorptions in the metal carbonyl region (see Section 2.3.2) while **(30)** displayed only three as the middle two are accidentally degenerate.

As for other orthomanganated complexes, the high energy bands of this pattern are well resolved from those of the metalating agent $PhCH_2Mn(CO)_5$ and from the by-product $Mn_2(CO)_{10}$, so the progress of reaction may be followed spectroscopically.

The IR bands of the metal carbonyls for the orthomanganated chalcogenides are given in Table 4.2. Comparison of these bands reveals a downward trend within the series, which presumably reflects the electronegativity (and hence donor ability) of the donor atom coordinated to the manganese. Moving down the series, the electronegativity of the donor atom decreases, which would result in the manganese atom possessing more electron density available for back bonding to the carbonyl π^* orbital. This would lead to the weakening of the C≡O bond and the observed decrease in frequency in the metal carbonyl IR region.

Table 4.2 M-C≡O Infrared Stretching Frequencies of Orthomanganated Chalcogenides

Orthomanganated Complex	υ(C≡O) (cm^{-1})
X=O **(30)**	2080(m), 1991(vs, br), 1935(s)
X=S **(31)**	2072(m), 1993(vs, br), 1978(vs, br), 1933(s)
X=Se **(32)**	2067(m), 1990(vs), 1973(vs), 1931(s)

The IR bands of υ(P=X) for the respective triphenylphosphine chalcogens and their corresponding orthomanganated chalcogenides are given in Table 4.3.

Table 4.3 Infrared Stretching Frequencies of υ(P=X)

Atom	Free Ligand υ(P=X) (cm^{-1})	Orthomanganated υ(P=X) (cm^{-1})
X=O	1190	1066
X=S	639	606
X=Se	562	549

Coordination of manganese to the oxygen atom of Ph_3P=O resulted in the lowering of υ(P=O) by 124 cm^{-1}, the magnitude of which is comparable to those experienced by orthomanganated ketones upon manganation, although the difference is at the lower end of the range. Manganation of Ph_3P=S resulted in the lowering of υ(P=S) by 33 cm^{-1}, and is consistent with the shifts observed in other metalated Ph_3P=S complexes which generally lie in the 33 to 107 cm^{-1} [2] range. The observed decrease in υ(P=Se) upon manganation is only 13 cm^{-1}, which presumably reflects the low sensitivity of the heavier selenium to coordination. In contrast to previously prepared orthomanganated ketones and amides, the use of υ(P=X) to establish whether or not orthomanganation has occurred would appear to be only useful in the Ph_3P=O case, due to the small changes involved upon coordination of manganese to the remaining two ligands.

4.3.2 ^{13}C NMR Spectroscopy

Selected chemical shifts are given in Table 4.4. The orthomanganated complexes generally show three broad signals around δ 215 ppm of intensity 1:1:2 going from lower to higher field, which can be assigned to the terminal Mn-CO groups. The middle Mn-CO signal which has been tentatively assigned as the metal carbonyl *trans* to the aryl carbon (Section 2.3.2), experienced a splitting arising from a ^{3}J coupling to the phosphorus atom which ranged from approximately 10-18 Hz. The crystal structures of orthomanganated Ph_3P=S **(31)** and Ph_3P=Se **(32)** (Figures 4.5 and 4.8) show that there is a W-type configuration between the phosphorus atom and the coupled carbonyl carbon, which is similar to that in systems where long range coupling through conjugation has been observed. This may explain why coupling is only observed between phosphorus and one metal carbonyl carbon atom and provides further support to the initial assignment of the respective metal carbonyls, which was based on the reasoning that CO groups with the lowest CO force constant (most back-bonding) give rise to the highest ^{13}C chemical shift [18].

Table 4.4 Selected ^{13}C NMR Chemical Shifts of Orthomanganated Chalcogenides and their Corresponding Free Ligand

Compound	C-Mn/C-H	C≡O
Orthomanganated Ph_3P=O **(30)**	180.9	221.3, 213.7, 213.0
Ph_3P=O **(27)**	132.1	-
Orthomanganated Ph_3P=S **(31)**	179.7	219.9, 215.3, 214.6
Ph_3P=S **(28)**	132.3	-
Orthomanganated Ph_3P=Se **(32)**	180.0	220.5, 216.0, 215.0
Ph_3P=Se **(29)**	132.7	-

The aryl carbon bonded to the manganese was found around 180 ppm. Coordination of the manganese shifts the signal of the metalated carbon by ~50 ppm to lower field, and those on either side generally by ~10 ppm to lower field (with the exception of orthomanganated triphenylphosphine oxide which showed a shift of only 4.3 ppm

downfield for the metalated carbon neighbour C-1), with only small shifts for the remaining aryl carbon signals. Overall these differences are consistent with previously studied systems.

Comparison of the metal carbonyl chemical shifts within the series shows no apparent trend despite the observed trend in the IR bands of the metal carbonyls which reflected the decrease in electronegativity down the series. This is probably due to the poorer sensitivity of ^{13}C NMR spectroscopy compared to IR spectroscopy.

4.3.3 ^{31}P NMR Spectroscopy

^{31}P NMR has been established as a method for distinguishing between the free ligand and metalated phosphine or phosphite ligands [19,20] where the phosphorus atom is coordinated to the metal. Coordination of the ligand generally results in the significant movement (Δ) of the phosphorus resonance downfield compared to that of the free ligand. Garrou has shown that incorporation of phosphorus into a chelate ring makes an additional contribution to the chemical shift compared with non-chelated ligands [19]. This quantity has been treated quantitatively and is known as Δ_R. From the large number of complexes containing a five-membered chelate ring it appears that the phosphorus resonance is deshielded by approximately a further 21-33 ppm compared to similar non-chelated ligands.

Table 4.5 ^{31}P NMR Chemical Shifts of Orthomanganated Chalcogenides and their Corresponding Free Ligand

Compound	Free Ligand	Metalated Ligand
triphenylphosphine oxide	29.0	64.4
triphenylphosphine sulfide	43.3	66.6
triphenylphosphine selenide	35.2	52.2

Comparison of the ^{31}P chemical shifts for the orthometalated- and free-ligands given in Table 4.5, clearly shows a significant shift downfield in

accord with previous results. Therefore, ^{31}P NMR is a good indicator of whether or not orthometalation has occurred.

These compounds are different from those previously studied as the phosphorus atom is not coordinated to the manganese. There appears to be no ^{31}P NMR data available on metal complexes in which the triphenylphosphine chalcogenide ligand is bound in a unidentate fashion. One may assume that the contribution to the ^{31}P chemical shift arising from the coordination of manganese would be small compared to that of chelated phosphine complexes, as the electronic properties of the phosphorus atom of the former would be effected to a significantly lesser degree, due to the phosphorus atom being indirectly bound to the metal. As a result, Δ may be approximated to Δ_R. The values of Δ_R (17-35.4) roughly fall in the range of those observed for previously studied compounds, thus giving support to this initial assumption.

As is common with phosphorus NMR, there is no obvious explanation for the trend in chemical shifts down both the free ligand and orthomanganated series [17].

4.4 X-Ray Crystal Structure of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetra-carbonylmanganese (31)

The crystal structure of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-tetracarbonylmanganese **(31)** was determined to fully characterise the reaction product between $Ph_3P{=}S$ **(28)** and $PhCH_2Mn(CO)_5$.

4.4.1 Results of Preliminary Studies

Yellow block-shaped crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated chloroform solution of **(31)** at -20 °C. Preliminary precession photography (Cu-Kα, λ=1.5418 Å) indicated monoclinic symmetry, with systematic absences defining space group $P2_1/c$.

4.4.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -143 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{22}H_{14}O_4MnPS$

M_r=460.30

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

a=9.689(2), b=12.183(1), c=16.861(2) Å

β=91.19(1)°

U=1989.9(5) $Å^3$

D_{calc}=1.536 g cm^{-3}

Z=4

F(000)=936

μ(Mo-K_α)=0.875 mm^{-1}

A total of 3700 reflections were collected in the range $4° \leq 2\theta \leq 50°$ of which 3496 were unique (R_{int}=0.0211). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method ($T_{max,min}$ 0.692 and 0.574 respectively). Of these, 2908 had $I \geq 2\sigma(I)$.

4.4.3 Solution and Refinement

The heavy atom positions (all 29 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R_1=0.0301 (2σ data); R_1=0.0419, wR_2=0.0708, and Goof=1.041 for all data, where

$w=[\sigma^2(F_o)^2+(0.0322P)^2+1.11P]^{-1}$ with $P=1/3[F_o^2+2F_c^2]$. No parameter shifted more than 0.001 σ in the final cycle. The final difference map showed no peaks or troughs greater than 0.338 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 4.6 and 4.7 respectively. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix IV.

A perspective view of the structure is shown in Figure 4.5 and illustrates the atom labelling scheme.

4.4.4 Discussion of the Structure

The molecule consists of a triphenylphosphine sulfide ligand bound to a tetracarbonylmanganese group in a chelating fashion via a Mn-S bond and a Mn-C bond to the *ortho*-position of one of the phenyl rings, giving rise to a six-coordinate manganese atom in a distorted octahedral arrangement.

The unique Mn-S-P-C-C five-membered metallocyclic ring is essentially planar with no atom deviating more than 0.090(1) Å away from the calculated plane. Comparison of bond angles indicates that the sulfur containing metallocyclic ring is less strained than the corresponding ring of other orthomanganated complexes, such as orthomanganated acetophenone. This is particularly evident in the angles at C(12) and C(11), which approach closely to their ideal trigonal values in the present complex. This is made possible mainly by the acceptance by the S atom of a smaller bond angle (Mn(1)-S(1)-P(1)=99.64(3)°) than that at the O atom in orthomanganated acetophenone (116.5(2)°) [21].

There is an almost ideal octahedral value of 89.60(6)° for the C(12)-Mn(1)-S(1) angle compared to the corresponding angle of other cyclomanganated structures, which range from ~78-80°. For example, a

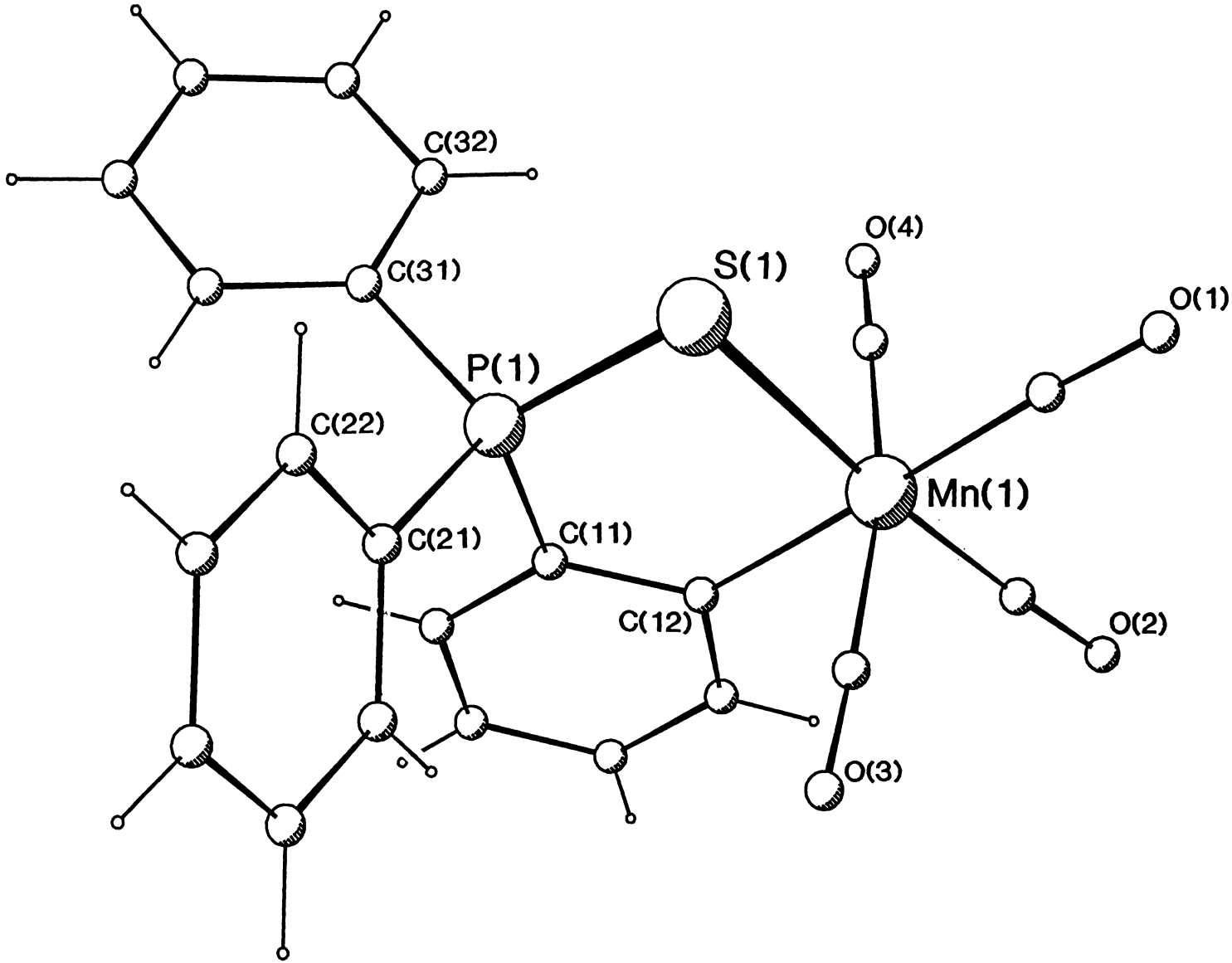


Figure 4.5 Perspective View of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-tetracarbonylmanganese (31)

Table 4.6 Bond Lengths (Å) for η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]tetracarbonylmanganese (31)

Mn(1)–C(2)	1.784(3)	C(12)–C(13)	1.405(3)
Mn(1)–C(1)	1.825(3)	C(13)–C(14)	1.379(4)
Mn(1)–C(4)	1.836(2)	C(14)–C(15)	1.382(4)
Mn(1)–C(3)	1.846(2)	C(15)–C(16)	1.372(3)
Mn(1)–C(12)	2.081(2)	C(21)–C(26)	1.386(3)
Mn(1)–S(1)	2.410(1)	C(21)–C(22)	1.387(3)
P(1)–C(11)	1.782(2)	C(22)–C(23)	1.383(3)
P(1)–C(31)	1.799(2)	C(23)–C(24)	1.378(4)
P(1)–C(21)	1.807(2)	C(24)–C(25)	1.371(4)
P(1)–S(1)	1.996(1)	C(25)–C(26)	1.383(3)
C(1)–O(1)	1.140(3)	C(31)–C(36)	1.378(3)
C(2)–O(2)	1.146(3)	C(31)–C(32)	1.397(3)
C(3)–O(3)	1.137(3)	C(32)–C(33)	1.375(3)
C(4)–O(4)	1.133(3)	C(33)–C(34)	1.376(4)
C(11)–C(12)	1.399(3)	C(34)–C(35)	1.378(4)
C(11)–C(16)	1.402(3)	C(35)–C(36)	1.389(3)

Table 4.7 Bond Angles (Å) for η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]tetracarbonylmanganese (31)

C(2)	-Mn(1)	-C(1)	90.0(1)	C(12)	-C(11)	-C(16)	123.6(2)
C(2)	-Mn(1)	-C(4)	89.6(1)	C(12)	-C(11)	-P(1)	119.1(2)
C(1)	-Mn(1)	-C(4)	96.6(1)	C(16)	-C(11)	-P(1)	117.3(2)
C(2)	-Mn(1)	-C(3)	93.1(1)	C(11)	-C(12)	-C(13)	114.1(2)
C(1)	-Mn(1)	-C(3)	95.1(1)	C(11)	-C(12)	-Mn(1)	122.1(2)
C(4)	-Mn(1)	-C(3)	168.0(1)	C(13)	-C(12)	-Mn(1)	123.8(2)
C(2)	-Mn(1)	-C(12)	93.3(1)	C(14)	-C(13)	-C(12)	122.9(2)
C(1)	-Mn(1)	-C(12)	175.6(1)	C(13)	-C(14)	-C(15)	121.1(2)
C(4)	-Mn(1)	-C(12)	86.27(9)	C(16)	-C(15)	-C(14)	118.6(2)
C(3)	-Mn(1)	-C(12)	81.96(9)	C(15)	-C(16)	-C(11)	119.7(2)
C(2)	-Mn(1)	-S(1)	175.27(8)	C(26)	-C(21)	-C(22)	119.8(2)
C(1)	-Mn(1)	-S(1)	87.28(8)	C(26)	-C(21)	-P(1)	120.4(2)
C(4)	-Mn(1)	-S(1)	86.81(8)	C(22)	-C(21)	-P(1)	119.7(2)
C(3)	-Mn(1)	-S(1)	91.00(8)	C(23)	-C(22)	-C(21)	119.7(2)
C(12)	-Mn(1)	-S(1)	89.60(6)	C(24)	-C(23)	-C(22)	120.1(2)
C(11)	-P(1)	-C(31)	107.9(1)	C(25)	-C(24)	-C(23)	120.2(2)
C(11)	-P(1)	-C(21)	108.5(1)	C(24)	-C(25)	-C(26)	120.4(2)
C(31)	-P(1)	-C(21)	107.5(1)	C(25)	-C(26)	-C(21)	119.7(2)
C(11)	-P(1)	-S(1)	108.42(8)	C(36)	-C(31)	-C(32)	119.5(2)
C(31)	-P(1)	-S(1)	112.07(7)	C(36)	-C(31)	-P(1)	123.6(2)
C(21)	-P(1)	-S(1)	112.33(8)	C(32)	-C(31)	-P(1)	116.7(2)
P(1)	-S(1)	-Mn(1)	99.64(3)	C(33)	-C(32)	-C(31)	119.8(2)
O(1)	-C(1)	-Mn(1)	177.1(2)	C(32)	-C(33)	-C(34)	120.7(2)
O(2)	-C(2)	-Mn(1)	177.2(2)	C(33)	-C(34)	-C(35)	119.8(2)
O(3)	-C(3)	-Mn(1)	175.8(2)	C(34)	-C(35)	-C(36)	120.1(2)
O(4)	-C(4)	-Mn(1)	177.3(2)	C(31)	-C(36)	-C(35)	120.1(2)

chelate bite angle of 79.4(1)° was found in orthomanganated acetophenone. The sulfur-containing metallocyclic ring of the complex shown in Figure 4.6 [22] was also found to be less strained with a chelate bite angle of the organosulfur ligand of 82.9(2)°.

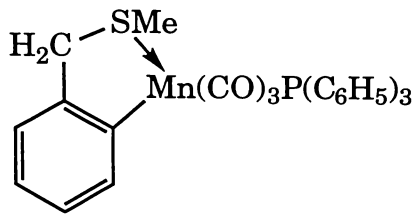


Figure 4.6

The P(1)-S(1) distance is lengthened significantly on coordination to the manganese, 1.996(1) Å (compared to 1.959 Å in free $Ph_3P{=}S$ [7]). This may simply arise from the donation of electron density from the sulfur atom to the manganese atom. The Mn(1)-S(1) distance (2.410(1) Å) is comparable to the corresponding distance in the complex $Mn[(SPPh_2)_2N](CO)_4$ (2.420(2) Å) (Figure 4.7) [23]. None of the remaining bonds in the metallocyclic ring deviate from expected values, so there is no need to invoke delocalised π-interaction to explain the geometry.

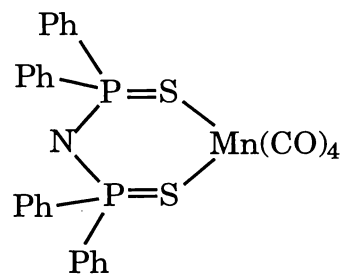


Figure 4.7

The only major distortion from octahedral coordination about the manganese atom is the out-of-plane *trans*-CO ligands leaning towards the weaker π-acceptor ligands as expected. The shortest Mn-CO bond is to the carbonyl ligand *trans* to the Mn-S bond (1.784(3) Å), that opposite the $Mn\text{-}C_{aryl}$ is next shortest (1.825(3) Å), with the two axial Mn-CO

bonds the longest (1.836(2) and 1.846(2) Å). Overall, the relative Mn-CO distances and C-Mn-C angles of the $Mn(CO)_4$ group fall into the pattern established for other orthomanganated complexes.

Other distances and angles within the complex are normal and require no further comment.

4.5 X-Ray Crystal Structure of η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetra-carbonylmanganese (32)

The crystal structure of η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]-tetracarbonylmanganese **(32)** was determined to compare with that of the corresponding orthomanganated triphenylphosphine sulfide complex **(31)**.

4.5.1 Results of Preliminary Studies

Yellow rectangular block-shaped crystals were obtained by recrystallisation from chloroform/petroleum spirit (1:1) at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated that the complex was isomorphous with **(31)**.

4.5.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -143 °C with monochromated Cu-K_α radiation (λ=1.5418 Å).

Crystal Data

Formula=$C_{22}H_{14}O_4MnPSe$

M_r=507.20

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

a=9.653(2), b=12.293(2), c=16.990(3) Å

β=90.45(3)°

U=2016.0(6) $Å^3$

D_{calc}=1.671 g cm^{-3}

Z=4

F(000)=1008

$\mu(Cu\text{-}K_\alpha)$=8.369 mm^{-1}

A total of 2877 reflections were collected in the range 4°≤2θ≤110° of which 2534 were unique (R_{int}=0.0496). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method ($T_{max,min}$ 0.745 and 0.431 respectively). Of these, 2141 had I≥2σ(I).

4.5.3 Solution and Refinement

The heavy atom positions (all 29 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R_1=0.0368 (2σ data); R_1=0.0436, wR_2=0.1067, and Goof=1.081 for all data, where $w=[\sigma^2(Fo)^2+(0.0695P)^2]^{-1}$ with $P=1/3[Fo^2+2Fc^2]$. No parameter shifted more than 0.001 σ in the final cycle. The final difference map showed no peaks or troughs greater than 0.883 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 4.8 and 4.9 respectively. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix V.

A perspective view of the structure is shown in Figure 4.8 and illustrates the atom labelling scheme.

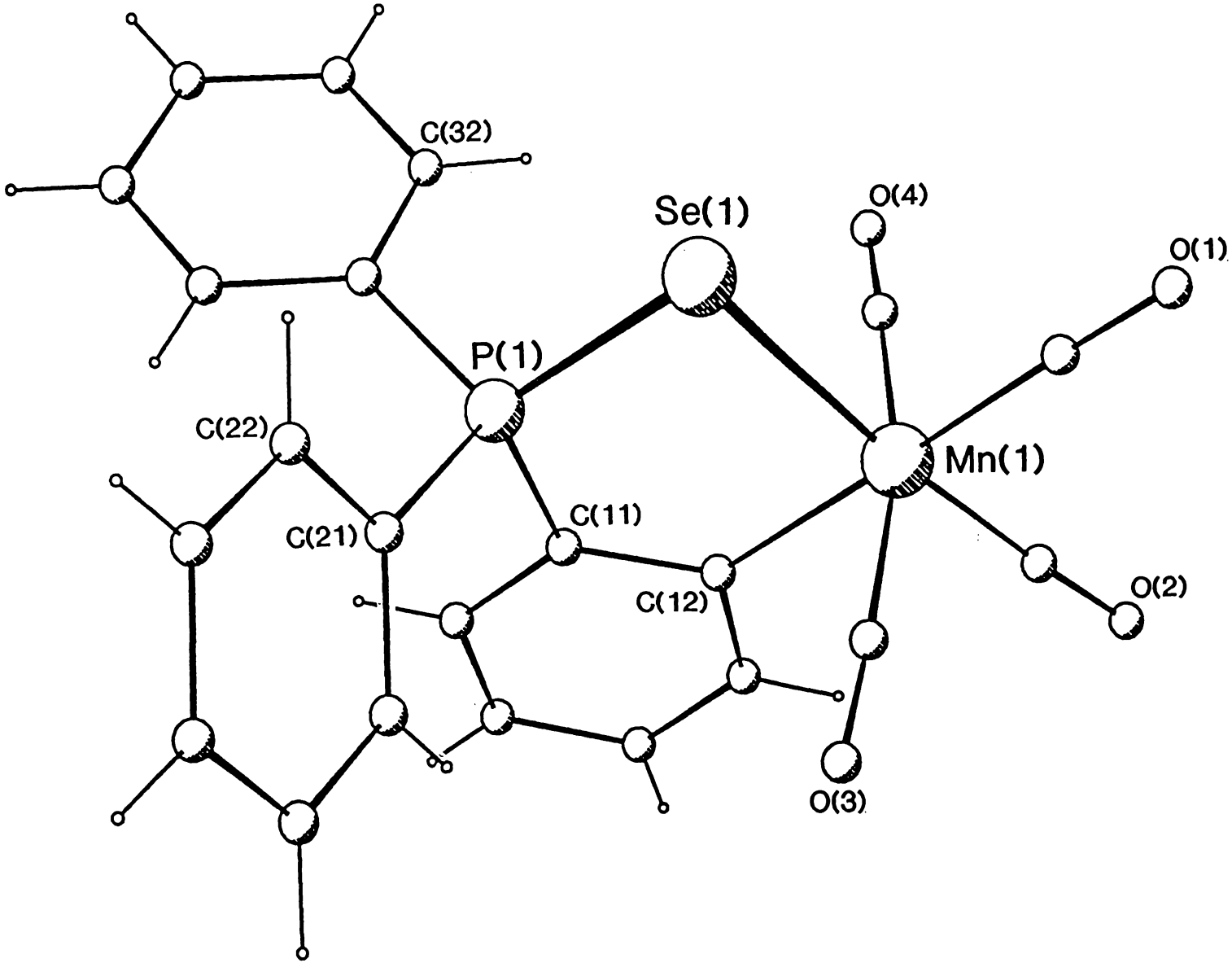


Figure 4.8 Perspective View of η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]-tetracarbonylmanganese (32)

Table 4.8 Bond Lengths (Å) for η^2-(C,Se)-[(2-diphenylselenophosphinyl)-phenyl]tetracarbonylmanganese (32)

Mn(1)–C(2)	1.784(6)	C(16)–C(15)	1.369(7)
Mn(1)–C(1)	1.822(6)	C(15)–C(14)	1.391(7)
Mn(1)–C(3)	1.843(5)	C(14)–C(13)	1.379(7)
Mn(1)–C(4)	1.846(6)	C(13)–C(12)	1.403(7)
Mn(1)–C(12)	2.096(5)	C(21)–C(22)	1.393(7)
Mn(1)–Se(1)	2.514(1)	C(21)–C(26)	1.393(7)
Se(1)-P(1)	2.154(1)	C(22)–C(23)	1.373(7)
P(1)–C(11)	1.796(5)	C(23)–C(24)	1.374(8)
P(1)–C(31)	1.804(5)	C(24)–C(25)	1.383(8)
P(1)–C(21)	1.811(5)	C(25)–C(26)	1.384(7)
C(2)–O(2)	1.144(6)	C(31)–C(36)	1.392(6)
C(4)–O(4)	1.122(6)	C(31)–C(32)	1.394(7)
C(1)–O(1)	1.152(6)	C(35)–C(36)	1.370(7)
C(3)–O(3)	1.144(6)	C(35)–C(34)	1.388(7)
C(11)–C(16)	1.401(7)	C(34)–C(33)	1.375(7)
C(11)–C(12)	1.410(6)	C(33)–C(32)	1.379(7)

Table 4.9 Bond Angles (Å) for η^2-(C,Se)-[(2-diphenylselenophosphinyl)-phenyl]tetracarbonylmanganese (32)

C(2)	-Mn(1)	-C(1)	89.5(2)	C(16)	-C(11)	-C(12)	123.6(4)
C(2)	-Mn(1)	-C(3)	93.6(2)	C(16)	-C(11)	-P(1)	116.0(3)
C(1)	-Mn(1)	-C(3)	95.4(2)	C(12)	-C(11)	-P(1)	120.4(4)
C(2)	-Mn(1)	-C(4)	90.3(2)	C(15)	-C(16)	-C(11)	119.6(4)
C(1)	-Mn(1)	-C(4)	97.4(2)	C(16)	-C(15)	-C(14)	119.4(5)
C(3)	-Mn(1)	-C(4)	166.6(2)	C(13)	-C(14)	-C(15)	119.8(5)
C(2)	-Mn(1)	-C(12)	93.3(2)	C(14)	-C(13)	-C(12)	124.1(5)
C(1)	-Mn(1)	-C(12)	176.1(2)	C(13)	-C(12)	-C(11)	113.5(4)
C(3)	-Mn(1)	-C(12)	81.7(2)	C(13)	-C(12)	-Mn(1)	123.1(3)
C(4)	-Mn(1)	-C(12)	85.3(2)	C(11)	-C(12)	-Mn(1)	123.4(4)
C(2)	-Mn(1)	-Se(1)	174.5(2)	C(22)	-C(21)	-C(26)	119.9(4)
C(1)	-Mn(1)	-Se(1)	86.4(2)	C(22)	-C(21)	-P(1)	119.5(4)
C(3)	-Mn(1)	-Se(1)	90.5(2)	C(26)	-C(21)	-P(1)	120.6(4)
C(4)	-Mn(1)	-Se(1)	86.4(2)	C(23)	-C(22)	-C(21)	119.5(5)
C(12)	-Mn(1)	-Se(1)	90.8(1)	C(22)	-C(23)	-C(24)	121.2(5)
P(1)	-Se(1)	-Mn(1)	96.09(4)	C(23)	-C(24)	-C(25)	119.5(5)
C(11)	-P(1)	-C(31)	107.6(2)	C(24)	-C(25)	-C(26)	120.5(5)
C(11)	-P(1)	-C(21)	109.0(2)	C(25)	-C(26)	-C(21)	119.5(5)
C(31)	-P(1)	-C(21)	107.9(2)	C(36)	-C(31)	-C(32)	118.5(4)
C(11)	-P(1)	-Se(1)	108.2(2)	C(36)	-C(31)	-P(1)	124.0(4)
C(31)	-P(1)	-Se(1)	112.2(2)	C(32)	-C(31)	-P(1)	117.4(3)
C(21)	-P(1)	-Se(1)	111.9(2)	C(35)	-C(36)	-C(31)	121.0(5)
O(2)	-C(2)	-Mn(1)	177.0(5)	C(36)	-C(35)	-C(34)	119.8(5)
O(4)	-C(4)	-Mn(1)	178.4(5)	C(33)	-C(34)	-C(35)	120.0(5)
O(1)	-C(1)	-Mn(1)	177.5(5)	C(34)	-C(33)	-C(32)	120.3(5)
O(3)	-C(3)	-Mn(1)	176.4(5)	C(33)	-C(32)	-C(31)	120.4(4)

4.5.4 Discussion of the Structure

The molecule is isostructural with the sulfide complex **(31)**, consisting of a triphenylphosphine selenide ligand bound to a tetracarbonylmanganese group in a chelating fashion via a Mn-Se bond and a Mn-C bond to the *ortho*-position of one of the phenyl rings, giving rise to a six-coordinate manganese atom in a distorted octahedral arrangement and a unique Mn-Se-P-C-C five-membered metallocyclic ring. This crystal structure analysis has thus provided confirmation of the proposed structure of this complex and establishes it as the first structurally documented example of an orthomanganated species with a selenium donor ligand.

Selected bond parameters of orthomanganated complexes **(32)** and **(31)** are provided in Table 4.10 for comparison.

Table 4.10 Selected Bond Lengths and Angles of Complexes (32) and (31)

Bond (Å)/Angle(°)	**Orthomanganated Ph_3P=Se (32)**	**Orthomanganated Ph_3P=S (31)**
X(1)-P(1)	2.154(1)	1.996(1)
Mn(1)-X(1)	2.514(1)	2.410(1)
Mn(1)-C(12)	2.096(5)	2.081(2)
C(11)-C(12)	1.410(6)	1.399(3)
P(1)-C(11)	1.796(5)	1.782(2)
P(1)-X(1)-Mn(1)	96.09(4)	99.64(3)
C(12)-Mn(1)-X(1)	90.8(1)	89.60(6)
C(11)-C(12)-Mn(1)	123.4(4)	122.1(2)
C(12)-C(11)-P(1)	120.4(4)	119.1(2)
C(11)-P(1)-X(1)	108.2(2)	108.42(8)
C(3)-Mn(1)-C(4)	166.6(2)	168.04(10)

Overall, the inclusion of the larger selenium atom into the metallocyclic ring has effectively expanded the ring compared to the sulfur-containing metallocyclic ring. The only exception is the P(1)-X(1)-Mn(1) angle which is significantly smaller (3.66(4)°) than the corresponding angle in the sulfur complex. This presumably reflects the larger size of selenium. As with orthomanganated $Ph_3P{=}S$ **(31)**, the metallocyclic ring is also essentially planar with no atom deviating more than 0.089(1) Å from the calculated plane. The P(1)-Se(1) distance is lengthened upon coordination to manganese relative to the corresponding distance in $Ph_3P{=}Se$ (2.106 Å) [2]. Despite the lack of well-defined benchmark bondlengths for comparison, the longer Mn-Se(1) distances in **(32)** compared with those in bis[(benzylseleno)tetracarbonylmanganese] **(33)** (2.481(2) and 2.493(2) Å), despite a lower coordination number at Se suggests the Mn-Se bond is not multiple. Again, none of the remaining bonds in the metallocyclic ring deviate from their expected values indicating the absence of any delocalised π-bonding over the ring.

The ability of the selenium and sulfur atoms to adopt significantly lower P(1)-X(1)-Mn(1) angles than those in previously studied orthomanganated complexes containing oxygen and nitrogen donor atoms is a distinguishing feature of these compounds. This results in the metallocyclic ring being less strained, which is reflected in the almost ideal angles attained at C(11), C(12) and the bite angle of the chelating ligand.

The Mn(1)-C(12) distances in both **(31)** and **(32)** are longer than any other corresponding distances recorded in orthomanganated complexes, which range from 2.00 to 2.07 Å. This may be the result of the better donor ability of the sulfur and selenium atoms compared to that of oxygen, which would presumably lead to increased electron density at the manganese and the observed lengthening of the Mn(1)-C(12) bond, and/or the absence of π-delocalised bonding over the metallocyclic ring. The fact that the Mn(1)-C(12) bond is longer in **(32)** than **(31)** may reflect the slight difference in electronegativity between the two donor atoms.

4.6 X-Ray Crystal Structure of Bis[(benzylseleno)tetracarbonylmanganese] (33)

The crystal structure of bis[(benzylseleno)tetracarbonylmanganese] **(33)** was determined to fully characterise the second reaction product from $Ph_3P{=}Se$ **(29)** and $PhCH_2Mn(CO)_5$.

4.6.1 Results of Preliminary Studies

Red block-shaped crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated chloroform solution of **(33)** at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated triclinic symmetry, $P\bar{1}$ was assumed and was confirmed by the successful refinement.

4.6.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -143 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{11}H_7O_4MnSe$

M_r=337.07

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

a=6.377(1), b=9.448(2), c=10.358(2) Å

α=85.11(3)°, β=85.50(3)°, γ=72.55(3)°

U=592.3(2) $Å^3$

D_{calc}=1.890 g cm^{-3}

Z=2

F(000)=328

μ(Mo-K_α)=4.184 mm^{-1}

A total of 2433 reflections were collected in the range $4°\leq 2\theta \leq 50°$ of which 2085 were unique (R_{int}=0.1412). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method ($T_{max,min}$ 1.000 and 0.484 respectively). Of these, 1638 had $I \geq 2\sigma(I)$.

4.6.3 Solution and Refinement

The heavy atom positions (all 17 non-hydrogen atoms of the unique half of the molecule) were located by the TREF option of SHELXS-86. The phenyl ring was disordered across two sites, so was refined as two half-rings with isotropic temperature factors. In the final cycle of full-matrix least-squares refinement all other non-hydrogen atoms were assigned anisotropic temperature factors. The hydrogen atoms bonded to the phenyl ring were included in calculated positions with temperature factors 1.2 times the U's of the carbon atoms they were bonded, while the remaining methylene hydrogen atoms were also included in calculated positions.

The refinement converged with R_1=0.0499 (2σ data); R_1=0.0714, wR_2=0.1351, and Goof=1.071 for all data, where $w=[\sigma^2(Fo)^2+(0.0792P)^2]^{-1}$ with $P=1/3[Fo^2+2Fc^2]$. No parameter shifted more than 0.001 σ in the final cycle. The final difference map showed no peaks or troughs greater than 1.370 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 4.11 and 4.12 respectively.

Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix VI.

A perspective view of the structure of only one of the two orientations of the dissordered C_6H_5 ring is shown in Figure 4.9 and illustrates the atom labelling scheme.

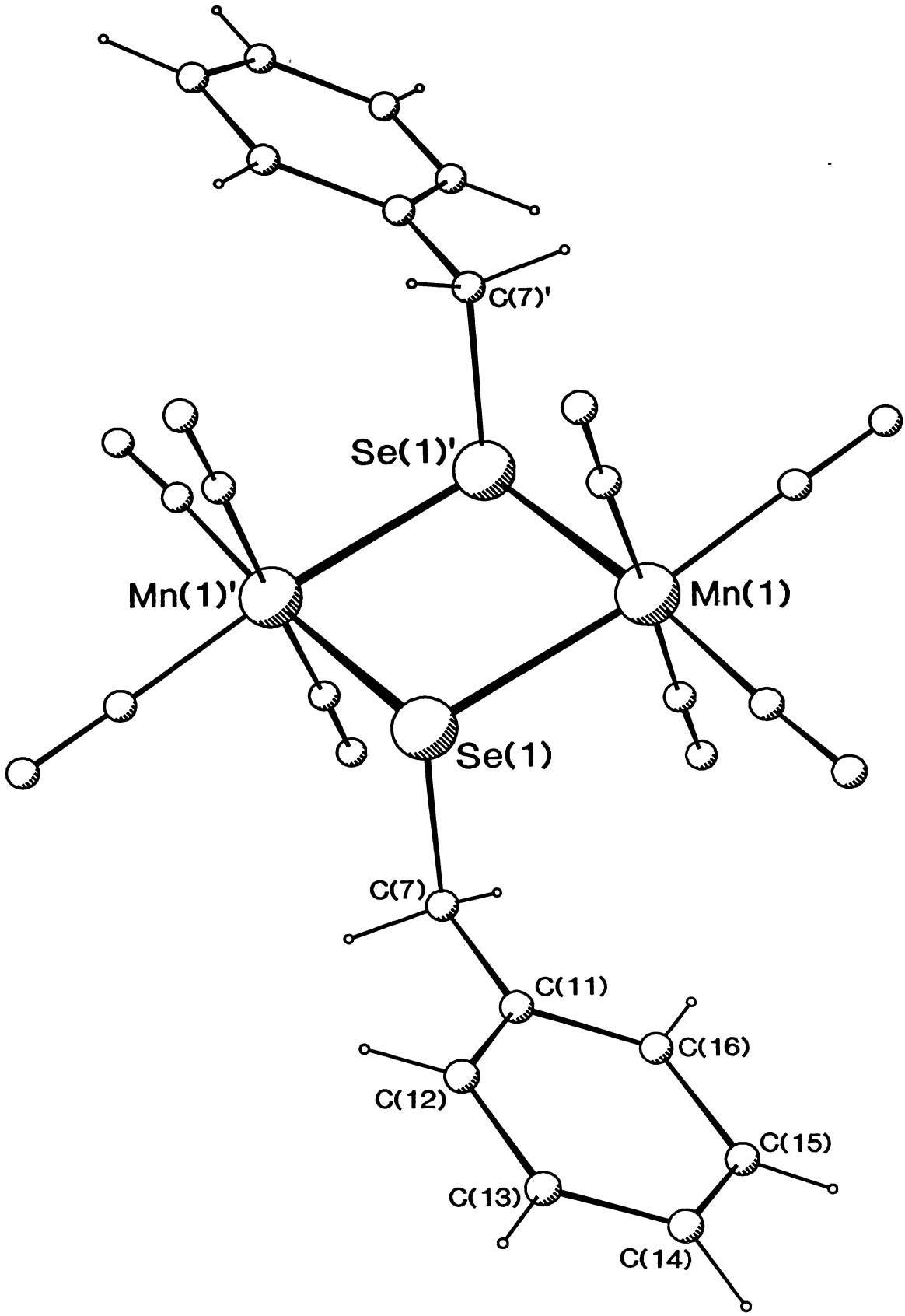


Figure 4.9 Perspective View of bis[(benzylseleno)-tetracarbonylmanganese] (33)

Table 4.11 Bond Lengths (Å) for Bis[(benzylseleno)-tetracarbonylmanganese)] (33)

Se(1)–C(7)	1.982(7)	C(7)–C(11)	1.50(2)
Se(1)–Mn(1)	2.481(2)	C(11)–C(12)	1.39(2)
Se(1)–Mn(1)'	2.493(2)	C(11)–C(16)	1.45(2)
Mn(1)–C(1)	1.812(7)	C(12)–C(13)	1.36(2)
Mn(1)–C(3)	1.827(7)	C(13)–C(14)	1.41(3)
Mn(1)–C(2)	1.853(8)	C(14)–C(15)	1.37(2)
Mn(1)–C(4)	1.854(7)	C(15)–C(16)	1.40(2)
Mn(1)–Se(1)'	2.493(2)	C(11A)–C(12A)	1.38(2)
O(1)–C(1)	1.132(8)	C(11A)–C(16A)	1.39(2)
O(2)–C(2)	1.133(8)	C(12A)–C(13A)	1.42(2)
O(3)–C(3)	1.130(8)	C(13A)–C(14A)	1.39(2)
O(4)–C(4)	1.128(8)	C(14A)–C(15A)	1.43(2)
C(7)–C(11A)	1.49(2)	C(15A)–C(16A)	1.36(2)

Table 4.12 Bond Angles (Å) for Bis((benzylseleno)-tetracarbonylmanganese) (33)

C(7)	-Se(1)	-Mn(1)	109.7(2)	O(3)	-C(3)	-Mn(1)	177.5(6)
C(7)	-Se(1)	-Mn(1)'	104.8(2)	O(4)	-C(4)	-Mn(1)	177.9(6)
Mn(1)	-Se(1)	-Mn(1)'	97.81(4)	C(11A)	-C(7)	-Se(1)	115.9(6)
C(1)	-Mn(1)	-C(3)	91.8(3)	C(11)	-C(7)	-Se(1)	107.1(6)
C(1)	-Mn(1)	-C(2)	90.9(3)	C(12)	-C(11)	-C(16)	117.7(13)
C(3)	-Mn(1)	-C(2)	91.9(3)	C(12)	-C(11)	-C(7)	127.9(13)
C(1)	-Mn(1)	-C(4)	90.9(3)	C(16)	-C(11)	-C(7)	114.2(13)
C(3)	-Mn(1)	-C(4)	89.3(3)	C(13)	-C(12)	-C(11)	122(2)
C(2)	-Mn(1)	-C(4)	177.8(3)	C(12)	-C(13)	-C(14)	118(2)

Table 4.12 continued

C(1)	-Mn(1)	-Se(1)	174.2(3)	C(15)	-C(14)	-C(13)	125(2)
C(3)	-Mn(1)	-Se(1)	93.3(2)	C(14)	-C(15)	-C(16)	115(2)
C(2)	-Mn(1)	-Se(1)	91.6(2)	C(15)	-C(16)	-C(11)	123(2)
C(4)	-Mn(1)	-Se(1)	86.4(2)	C(12A)	-C(11A)	-C(16A)	118.0(13)
C(1)	-Mn(1)	-Se(1)'	92.8(2)	C(12A)	-C(11A)	-C(7)	115.2(13)
C(3)	-Mn(1)	-Se(1)'	175.3(2)	C(16A)	-C(11A)	-C(7)	126.8(12)
C(2)	-Mn(1)	-Se(1)'	86.8(2)	C(11A)	-C(12A)	-C(13A)	124.0(14)
C(4)	-Mn(1)	-Se(1)'	91.9(2)	C(14A)	-C(13A)	-C(12A)	115(2)
Se(1)	-Mn(1)	-Se(1)'	82.19(4)	C(13A)	-C(14A)	-C(15A)	123(2)
O(1)	-C(1)	-Mn(1)	177.5(6)	C(16A)	-C(15A)	-C(14A)	118(2)
O(2)	-C(2)	-Mn(1)	178.7(6)	C(15A)	-C(16A)	-C(11A)	122(2)

4.6.4 Discussion of the Structure

The molecule consists of a two $Mn(CO)_4$ groups bridged by two $C_6H_5CH_2Se$ ligands giving rise to two six-coordinate manganese atoms and a planar $[MnSe]_2$ unit with an exact crystallographic centre of symmetry at the centre of the $[MnSe]_2$ rhombus. It is therefore a new member of the quite extensive $Mn_2X_2(CO)_8$ (X=Cl, Br, I, PR_2 (R=Me, Ph), $AsPh_2$, SR (R=Me, Et, Bu, Ph, Tol), $SeCF_3$, TePh, N_2Ph, and $NSOF_2$) class of molecule [13].

The two Mn-Se bond lengths (2.493(2) and 2.481(2) Å) are just crystallographically different and are comparable to the Mn-Se bond lengths observed in bis[(fluoromethylseleno)tetracarbonylmanganese] (2.505(6) and 2.490(6) Å) [24]. This suggests that the Mn-Se bonds are insensitive to changes to the organic substituent on the selenium atom. More detailed discussion is not warranted because of the relatively poor quality of data for bis[(fluoromethylseleno)tetracarbonylmanganese] (R_1=0.115).

Coordination about the manganese atom is essentially octahedral, apart from the Se(1)-Mn(1)-Se(1)' angle of 82.19(4)° which is similar to the corresponding angle observed in bis[(fluoromethylseleno)tetracarbonylmanganese] (83.1(3)°). In contrast to orthomanganated complexes, where the out-of-plane *trans*-CO ligands lean towards the weaker π-acceptor ligand, the C(2)-Mn(1)-C(4) angle is essentially linear (177.8(3)°). A similar angle of 177.4(14)° was also observed in bis[(fluoromethylseleno)tetracarbonylmanganese]. It appears that pronounced leaning of the axial metal carbonyls only occurs in complexes where one of the atoms bound to the manganese atom is a Group 14 element. For example, in the complex $[CpSnFe(CO)_4]_2$ an angle of 163.6(2)° is observed, compared to the corresponding angle in the SO_2 inserted complex **(45)** (Section 6.3), where the chelating ligand is bound via sulfur and selenium atoms, an almost linear angle of 176.6(11)° is observed.

The Mn-C and C-O bond lengths in $[Mn(CO)_4(\mu\text{-}SeCH_2Ph)]_2$ fall within the ranges found in manganese carbonyl derivatives. The shortest Mn-CO bonds are to the equatorial carbonyl ligands *trans* to the Mn-Se bonds (1.812(7) and 1.827(7) Å) with the two equivalent Mn-CO bonds above and below the plane of the molecule the longest (1.853(8) and 1.854(7) Å).

4.7 Experimental Section

4.7.1 Preparation of Starting Materials

Preparation of Triphenylphosphine Oxide

Triphenylphosphine (5.00 g, 0.019 mol) was dissolved in acetone (AR, 40 mL) and hydrogen peroxide (5.25 mL, 10%, 0.019 mol) was added dropwise with stirring over 10 minutes. The acetone was removed by evaporation under reduced pressure. The remaining residue was dissolved in benzene (AR, 30 mL) and poured into a separating funnel where it was washed with saturated ferrous ammonium sulphate (2 x 20 mL) then H_2O (1 x 20 mL). The benzene was removed under vacuum and the resulting oil crystallised from absolute ethanol to give *triphenylphosphine oxide* [**(27)**; 4.29 g, 81%] as small white crystals, m.p. 151-153 °C (lit. 152-153 °C [25]). IR (KBr disk): υ(P=O) 1190(s) cm^{-1}.

^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.68-7.61 (*m*, 6H, Ar-H), 7.52-7.40 (*m*, 9H, Ar-H). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 132.8 (*s*, $^{1}J_{PC}$=102.4 Hz, C-1), 132.1 (*d*, $^{2}J_{PC}$=9.9 Hz, C-2, C-6), 132.0 (*d*, $^{4}J_{PC}$=1.7 Hz, C-4), 128.5 (*d*, $^{3}J_{PC}$=12.1 Hz, C-3, C-5). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 29.0.

Preparation of Triphenylphosphine Sulfide

Triphenylphosphine (5.03 g, 0.019 mol) and sulfur (0.71 g, 0.022 mol) were refluxed in toluene (AR, 80 mL) for 3 hours. The toluene was removed by evaporation under reduced pressure to yield a creamy crystalline solid which was recrystallised from CH_2Cl_2/petroleum spirit to give *triphenylphosphine sulfide* [**(28)**; 4.37 g, 77%] as colourless needles, m.p. 162-164 °C (lit. 162-164 °C [25]). IR (KBr disk): υ(P=S) 639(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.76-7.69 (*m*, 6H, Ar-H), 7.52-7.41 (*m*, 9H, Ar-H). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 133.0 (*s*, $^{1}J_{PC}$=85.0 Hz, C-1), 132.3 (*d*, $^{2}J_{PC}$=10.7 Hz, C-2, C-6), 131.6 (*d*, $^{4}J_{PC}$=2.6 Hz, C-4), 128.6 (*d*, $^{3}J_{PC}$=12.3 Hz, C-3, C-5). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 43.3.

Preparation of Triphenylphosphine Selenide

Triphenylphosphine (5.01 g, 0.019 mol) and selenium (1.61 g, 0.020 mol) were refluxed in toluene (AR, 80 mL) for 3 hours. The solution was filtered and the toluene was removed by evaporation under reduced pressure to yield a creamy crystalline solid which was recrystallised from CH_2Cl_2/petroleum spirit to give *triphenylphosphine selenide* [**(29)**; 4.37 g, 77%] as small colourless chunky crystals, m.p. 186-188 °C (lit. 187-188 °C [25]). IR (KBr disk): υ(P=Se) 562(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.76-7.69 (*m*, 6H, Ar-H), 7.50-7.41 (*m*, 9H, Ar-H). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 132.7 (*d*, $^{2}J_{PC}$=10.8 Hz, C-2, C-6), 131.8 (*s*, $^{1}J_{PC}$=76.7 Hz, C-1), 131.6 (*d*, $^{4}J_{PC}$=2.1 Hz, C-4), 128.6 (*d*, $^{3}J_{PC}$=12.3 Hz, C-3, C-5). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 35.2.

4.7.2 Orthomanganation of Triphenylphosphine Chalcogens

Orthomanganation of Triphenylphosphine Oxide

(a) In Petroleum Spirit

Triphenylphosphine oxide (174 mg, 0.623 mmol) and $PhCH_2Mn(CO)_5$ (187 mg, 0.653 mmol) were dissolved in petroleum spirit (AR, 40 mL) and the solution degassed and flushed with nitrogen twice. After refluxing under nitrogen for 6 hours, the petroleum spirit was removed under vacuum. The resultant yellow/brown residue was dissolved in CH_2Cl_2 and chromatographed on silica gel plates with 1:3 v/v ethyl acetate/petroleum spirit as the eluant. A broad yellow/orange band of *η^2-(C,O)-[(2-diphenylphosphinyl)phenyl]tetracarbonylmanganese* [**(30)**; 114 mg, 41%] was collected as an orange oil which failed to crystallise. IR ($CHCl_3$): υ(CO) 2080(m), 1991(vs, br), 1935(s) cm^{-1}; (KBr disk): υ(P=O) 1066(m) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.02 (*m*, 1H, H-6), 7.72-7.35 (*m*, 10H, H-2', H-3', H-4', H-5', H-6'), 7.24 (*m*, 1H, H-5), 7.15 (*m*, 2H, H-3, H-4). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 221.3 (*s*, br, C≡O), 213.7 (*s*, $^3J_{PC}$=9.6 Hz, C≡O), 213.0 (*s*, br, 2xC≡O), 180.9 (*s*, $^2J_{PC}$=24.0 Hz, C-1), 142.1 (*d*, $^3J_{PC}$=16.2 Hz, C-6), 137.1 (*s*, $^1J_{PC}$=120.5 Hz, C-2), 133.0 (*d*, $^4J_{PC}$=1.9 Hz, C-4'), 132.0 (*d*, $^2J_{PC}$=10.6 Hz, C-2', C-6'), 131.4 (*d*, $^4J_{PC}$=2.7 Hz, C-5), 130.2 (*s*, $^1J_{PC}$=100.6 Hz, C-1'), 129.8 (*d*, $^2J_{PC}$=20.5 Hz, C-3), 129.0 (*d*, $^3J_{PC}$=12.1 Hz, C-3', C-5'), 123.9 (*d*, $^3J_{PC}$=13.2 Hz, C-4). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 64.4.

(b) In Heptane

Similarly prepared from $PhCH_2Mn(CO)_5$ (202 mg, 0.707 mmol) and triphenylphosphine oxide (171 mg, 0.615 mmol) under reflux in heptane over 80 minutes was *η^2-(C,O)-[(2-diphenylphosphinyl)phenyl]tetracarbonylmanganese* [**(30)**; 90 mg, 33%].

Orthomanganation of Triphenylphosphine Sulfide

Similarly prepared from $PhCH_2Mn(CO)_5$ (426 mg, 1.49 mmol) and triphenylphosphine sulfide (397 mg, 1.35 mmol) under reflux over 1.5 hours was *η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetracarbonylmanganese* [**(31)**; 557 mg, 90%] which recrystallised from

CH_2Cl_2/pentane (vapour diffusion) as yellow blocks, m.p. 163 °C. Anal. Found: C, 57.86; H, 2.73; $C_{22}H_{14}O_4MnPS$ calcd.: C, 57.40; H 3.07%. IR ($CHCl_3$): υ(CO) 2072(m), 1993(vs, br), 1978(vs, br), 1933(s) cm^{-1}; (KBr disk): υ(P=S) 606(m) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.07 (*m*, 1H, H-6), 7.61 (*m*, Ar-H), 7.48 (*m*, Ar-H), 7.27 (*m*, 1H, H-5), 7.08 (*m*, 2H, H-3, H-4). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 219.9 (*s*, br, C≡O), 215.3 (*s*, $^3J_{PC}$=17.5 Hz, C≡O), 214.6 (*s*, br, 2xC≡O), 179.7(*s*, $^2J_{PC}$=38.9 Hz, C-1), 144.4 (*d*, $^3J_{PC}$=19.9 Hz, C-6), 141.6 (*s*, $^1J_{PC}$=106.7 Hz, C-2), 132.8 (*d*, $^4J_{PC}$=2.3 Hz, C-4'), 132.6 (*d*, $^2J_{PC}$=10.7 Hz, C-2', C-6'), 131.4 (*d*, $^2J_{PC}$=19.6 Hz, C-3), 130.5 (*d*, $^4J_{PC}$=3.0 Hz, C-5), 130.2 (*s*, $^1J_{PC}$=78.6 Hz, C-1'), 129.0 (*d*, $^3J_{PC}$=12.5 Hz, C-3', C-5'), 123.2 (*d*, $^3J_{PC}$=12.8 Hz, C-4). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 66.6.

Orthomanganation of Triphenylphosphine Selenide

Following the standard procedure triphenylphosphine selenide (402 mg, 1.18 mmol) was treated with $PhCH_2Mn(CO)_5$ (383 mg, 1.34 mmol) and refluxed in petroleum spirit over 4 hours. The residue was chromatographed to give:

Bis[(benzylseleno)tetracarbonylmanganese] [**(33)**; 56 mg, 14%] which crystallised from CH_2Cl_2/pentane to yield red block-shaped crystals, m.p. dec. 150 °C. Anal. Found C, 39.37; H, 1.96; $C_{22}H_{14}O_8Mn_2Se_2$ calcd.: C, 39.20; H 2.09%. IR ($CHCl_3$): υ(CO) 2062(m), 2006(vs), 1996(vs), 1967(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.26 (*m*, 10H, Ar-H), 3.84 (*s*, 2H, CH_2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 139.0 (*s*, C-1), 128.9 (*d*, (C-2, C-6) or (C-3, C-5)), 128.8 (*d*, (C-2, C-6) or (C-3, C-5)), 127.7 (*d*, C-4). EIMS: m/z 676 (M^+), 564 $(M-4CO)^+$, 508 $(M-6CO)^+$, 452 $(M-8CO)^+$, 361 $(M-8CO-CH_2C_6H_5)^+$, 91 $(M-8CO-CH_2C_6H_5-2Mn-2Se)^+$.

cis-Benzyltetracarbonyltriphenylphosphinemanganese [**(34)**; 98 mg, 16%] which crystallised from $CHCl_3$/petroleum spirit to yield colourless plates, m.p. 156 °C (lit. 155 °C [26]. IR: ($CHCl_3$) υ(CO) 2053(m), 1966(vs), 1937(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.57-7.46 (*m*, 15H, Ar-H), 7.06 (*m*, 2H, Ar-H), 6.95 (*m*, 2H, Ar-H), 6.88 (*m*, 1H, Ar-H), 1.71 (*d*, $^3J_{PH}$=5.8 Hz, 2H, CH_2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 61.1. ESMS: m/z 562 $(M+H+CH_3CN)^+$, 521 $(M+H)^+$, 470 $(M+CH_3CN-CH_2C_6H_5)^+$, 429

$(M\text{-}CH_2C_6H_5)^+$. EIMS: m/z 429 $(M\text{-}CH_2C_6H_5)^+$, 401 $(M\text{-}CH_2C_6H_5\text{-}CO)^+$, 373 $(M\text{-}CH_2C_6H_5\text{-}2CO)^+$, 345 $(M\text{-}CH_2C_6H_5\text{-}3CO)^+$, 317 $(M\text{-}CH_2C_6H_5\text{-}4CO)^+$, 318 $(Ph_3PMn+H)^+$, 262 $(Ph_3P)^+$.

η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetracarbonylmanganese [**(32)**; 134 mg, 22%] which crystallised from $CHCl_3$/petroleum spirit to yield yellow block shaped crystals, m.p. 165-167 °C. Anal Found: C, 52.32; H, 2.62; $C_{22}H_{14}O_4MnPSe$ calcd.: C, 52.10; H 2.78%. IR ($CHCl_3$): υ(CO) 2067(m), 1990(vs), 1973(vs), 1931(s) cm^{-1}; (KBr disk): υ(P=Se) 549(m) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.15 (*m*, 1H, H6), 7.63 (*m*, Ar-H), 7.49 (*m*, Ar-H), 7.26 (*m*, 1H, H-5), 7.06 (*m*, 2H, H-3, H-4). ^{13}C NMR (75 47 MHz) ($CDCl_3$): δ 220.5 (*s*, br, C≡O), 216.0 (*s*, $^3J_{PC}$=15.8 Hz, C≡O), 215.0 (*s*, br, 2xC≡O), 180.0 (*s*, $^2J_{PC}$=43.1 Hz, C-1), 145.4 (*d*, $^3J_{PC}$=21.2 Hz, C-6), 141.7 (*s*, $^1J_{PC}$=99.4 Hz, C-2), 132.8 (*d*, $^2J_{PC}$=10.8 Hz, C-2', C-6'), 132.8 (*d*, C-4'), 132.0 (*d*, $^2J_{PC}$=18.7 Hz, C-3), 130.1 (*d*, $^4J_{PC}$=3.4 Hz, C-5), 129.2 (*s*, $^1J_{PC}$=71.0 Hz, C-1'), 129.0 (*d*, $^3J_{PC}$=12.3 Hz, C-3', C-5'), 123.0 (*d*, $^3J_{PC}$=12.1 Hz, C-4). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 52.2. EIMS: m/e 508 (M^+), 424 $(M\text{-}3CO)^+$, 396 $(M\text{-}4CO)^+$, 342 $(Ph_3PSe+H)^+$, 262 $(Ph_3P)^+$.

The parent chalcogen triphenylphosphine selenide [**(29)**; 97 mg, 25%].

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Chapter Five

Coupling Reactions of Orthomanganated Triphenyl-phosphine Sulfide with Alkenes and Alkynes

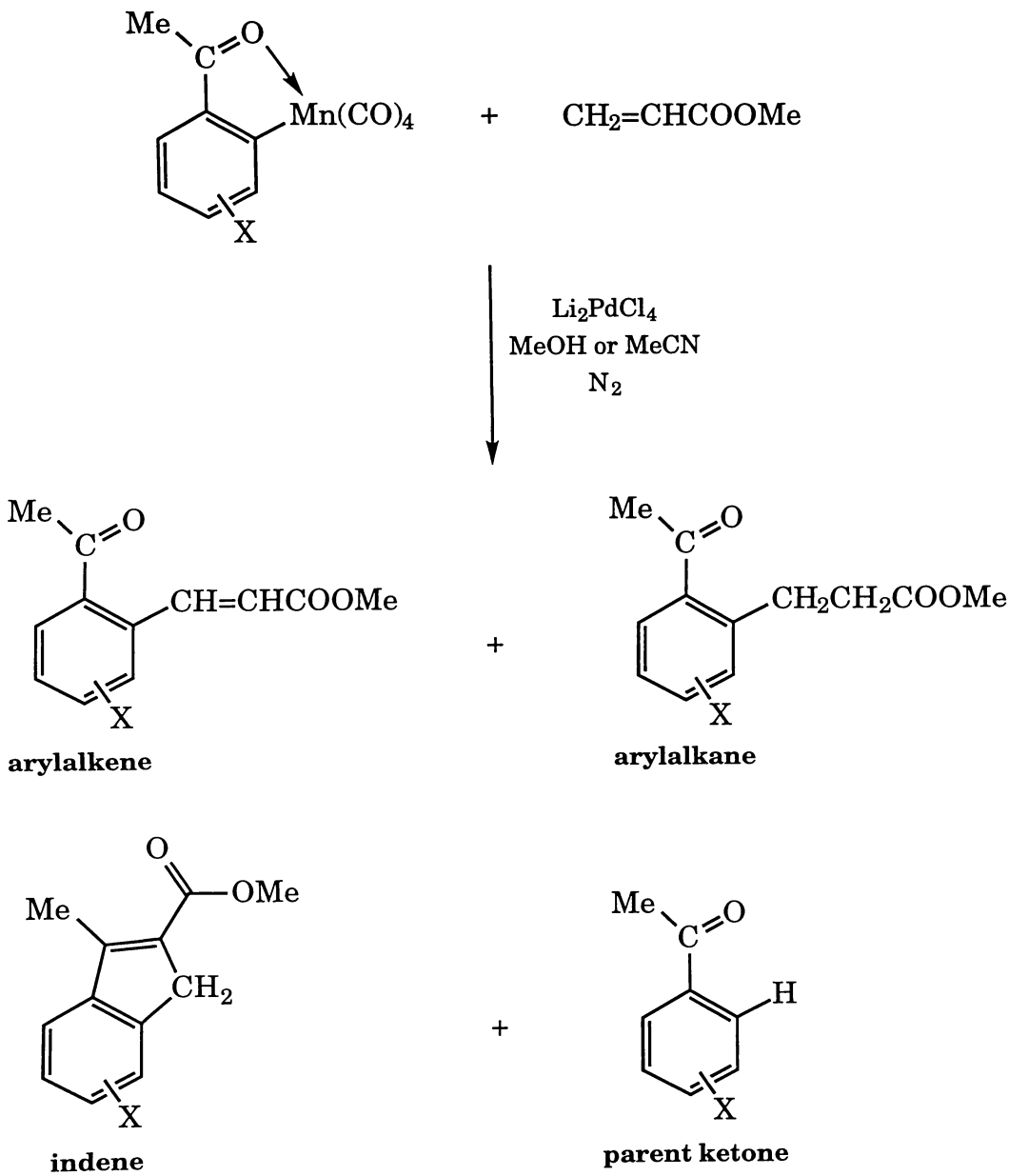
5.1 Introduction: Coupling Reactions of Orthomanganated Complexes with Alkenes

The coupling reactions of alkenes at the metal-activated aryl carbon, which make aryl complexes of Hg, Pd, Sn, Pb, Tl and Li so synthetically useful [1,2], are not applicable to *ortho*-functionalisation of aromatic ketones because of the inability of these metals to orthometalate this type of substrate.

This led to an investigation of the coupling reactions of orthomanganated ketones with alkenes, and from the range of reactions so far studied [3-6], there is sufficient diversity in reactivity to suggest considerable potential for these reactions in organic synthesis.

The coupling of orthomanganated compounds with alkenes was normally carried out in the presence of Pd(II), as in the Heck reactions of aryl-mercury [1,7] and -halo compounds [1,8], in refluxing acetonitrile or methanol at ambient temperature. The coupling reactions normally proceed in excellent yield and produce three main coupling products, arylalkene (the normal Heck product), arylalkane and indene (Equation 5.1). The ratio of these products is dependent on reaction conditions and substrate. For example, indene formation is favoured in refluxing acetonitrile, or by changing the reactivity of the metal centre by

substituting two carbon monoxide ligands by trimethylphosphite ligands. Often a fourth, unwanted minor product is the parent ketone formed by demetalation at the aryl carbon.



Equation 5.1

The formation of arylalkane and indene coupling products were distinguishing features of alkene-coupling with orthomanganated precursors, as the cyclised indene-type product is inaccessible by the

Heck method and the formation of arylalkanes has not been observed in any of Heck's reactions, with one exception. Arylmercury (and aryltin) complexes were reported [9] to give arylalkanes with enones instead of the normal arylalkene products in a Pd(II)-promoted reaction in a two-phase CH_2Cl_2/HCl system incorporating $(n\text{-}Bu)_4NCl$. However, in this case the added acid may be involved in directing coupling to the arylalkane product by acid cleavage of Pd-C.

Not surprisingly, recent studies [5] have shown that alkenes can insert efficiently into the aryl carbon-manganese bond in the absence of palladium, showing that transmetalation by palladium is not a necessary prerequisite to alkene-coupling with orthomanganated complexes. Similarly, this resulted in the isolation of arylalkanes and indenes but, in contrast to the palladium-promoted reactions, the formation of cyclopentanol type products (Figure 5.1) was also detected. The arylalkene was rarely found, and then only in small yields, for reasons which will be discussed later in Section 5.2.2.

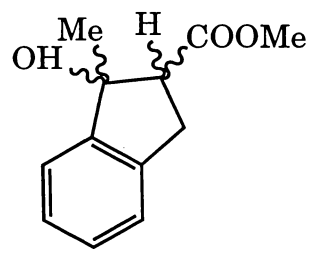


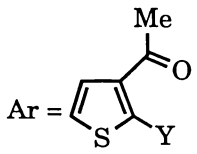
Figure 5.1

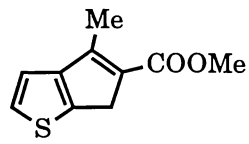
As for the palladium-promoted reactions, solvent choice was critical to the outcome of these thermally promoted reactions. This dependence is illustrated by the coupling reaction of η^2-(3-acetylthien-2-yl)tetracarbonylmanganese with methyl acrylate [5], which was carried out in both refluxing benzene and carbon tetrachloride (Table 5.1).

Generally, reaction in benzene tended to afford either the indene-type product and/or the arylalkane, while carbon tetrachloride as solvent favoured the formation of the indene-type product and/or the cyclopentanols with little arylalkane formation.

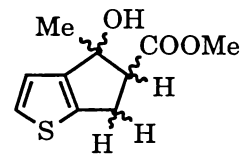
Table 5.1 Yields (%) of Products from the Thermally Promoted Coupling Reaction of Orthomanganated 3-Acetylthiophene with Methyl Acrylate

Product	C_6H_6	CCl_4
Ar-Y, Y=CH_2CH_2COOMe	83	48
Ar-indene	-	trace
Ar-(4S*, 5R*) indanol	-	32
Ar-(4R*, 5R*) indanol	-	5





Ar-indene

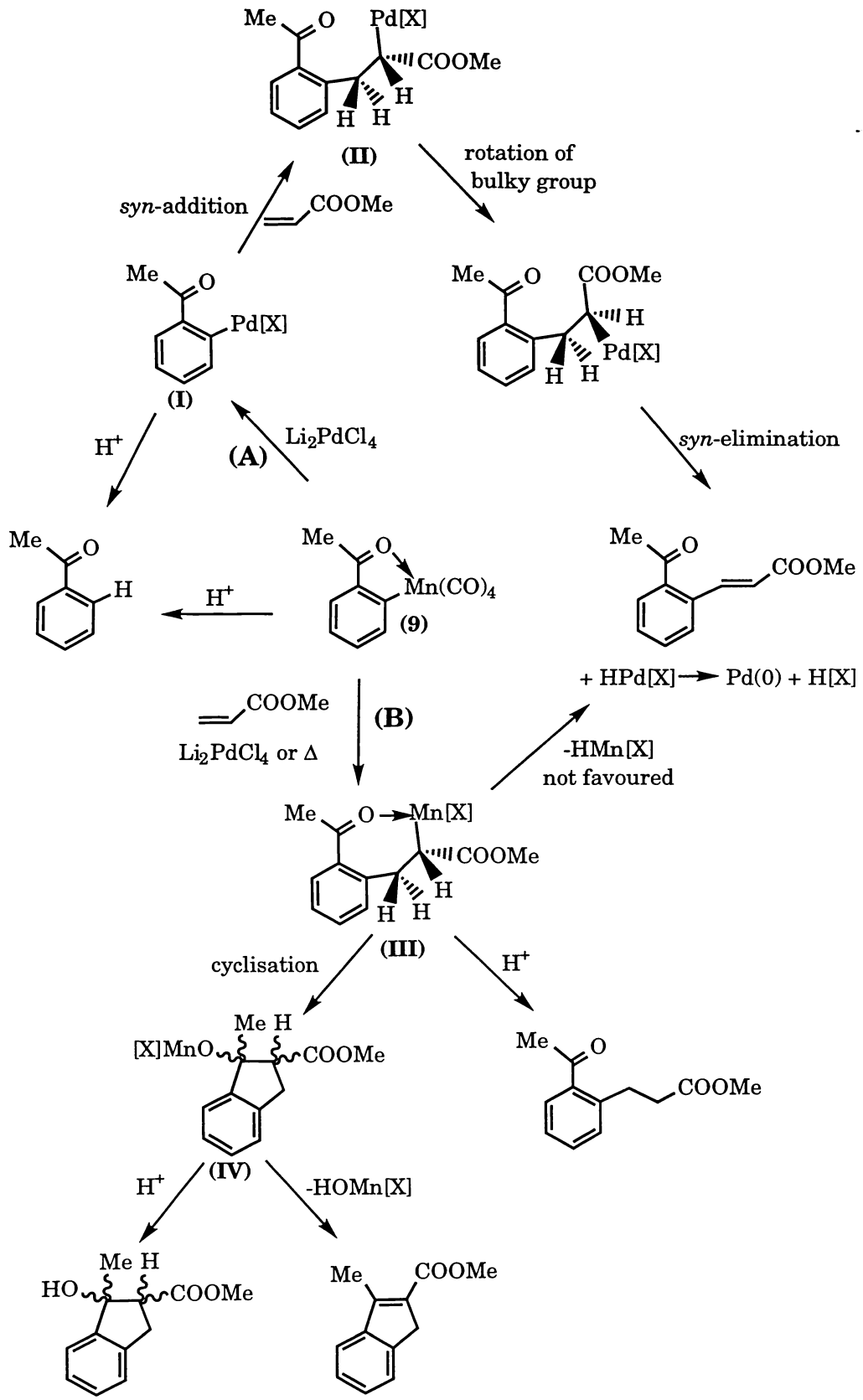


Ar-indanol

The proposed reaction scheme [5] for the formation of these products in thermally and palladium-promoted reactions is shown in Scheme 5.1.

In the presence of palladium the formation of arylalkenes (Route A) is as proposed by Heck for the arylation of alkenes. Addition of the arylpalladium complex to the alkene is *syn* resulting in the formation of (II), followed by rotation of the aryl group and *syn*-elimination of [X]PdH. When R is bulky, the most stable conformation for *syn*-elimination would orientate the bulky aryl ring *trans* to the alkene R group, resulting in the exclusive formation of the E-isomer. For smaller groups both E and Z isomers are formed [10].

The formation of arylalkanes and indenes (Route B) in both types of reaction, is proposed to occur from a common intermediate (III), formed from the insertion of an alkene into the Mn-C_{aryl} bond. Similarly to the thermally promoted reactions of orthomanganated compounds with alkynes, thermally induced decarbonylation presumably affords a coordinatively unsaturated intermediate which allows the alkene to become η^2-coordinated and to undergo insertion into the aryl carbon-manganese bond of **(9)** to form (III). Cleavage of the carbon manganese bond in intermediate (III) as a result of protonolysis would lead to the formation of the arylalkane. A similar reaction on **(9)** and (I) would


Me
O
Pd[X]
COOMe
H
H H
(II)
rotation of
bulky group
syn-addition
COOMe
Me
O
Pd[X]
(I)
Me
O
COOMe
H
Pd[X]
H H
H+
(A)
Li2PdCl4
syn-elimination
Me
O
H
H+
Me
O
Mn(CO)4
(9)
Me
O
COOMe
+ HPd[X] → Pd(0) + H[X]
COOMe
Li2PdCl4 or Δ
(B)
-HMn[X]
not favoured
Me
O
Mn[X]
COOMe
H
H H
(III)
cyclisation
H+
Me H
[X]MnO
COOMe
Me
O
COOMe
H+
(IV)
-HOMn[X]
Me H
HO
COOMe
Me
COOMe

Scheme 5.1

lead to the formation of the parent ketone. Manganese may remain coordinated (Scheme 5.1, (III)) or become recoordinated to the donor ketone carbonyl group, which presumably causes electron withdrawal and increases the susceptibility of the ketone carbonyl to attack by the manganated carbon, leading to the formation of a cyclised intermediate (IV). Elimination of HOMn[X] would then yield the indene. In the thermally promoted reactions in the absence of palladium, cyclopentanol formation can also be envisaged via the same route proposed for indene formation. However, upon cyclisation subsequent protonolysis rather than elimination, as in indene formation would yield the cyclopentanol diastereoisomers.

It should be mentioned that Woodgate's group has successfully used the method employed by Liebeskind, who promoted the coupling of orthomanganated ketones with alkynes using trimethylamine-N-oxide (TMANO), to couple various alkenes with some orthomanganated diterpenoid compounds [11-12].

The background for the coupling reactions of orthomanganated compounds with alkynes has been discussed in some detail in the introduction to Chapter 3 and will not be discussed any further.

All subsequent alkene and alkyne-coupling reactions described in this chapter were limited to the orthomanganated $Ph_3P{=}S$ complex because of the high yield in which it could be prepared compared to the other two members of the series.

5.2 Reactions of Orthomanganated $Ph_3P{=}S$ (31) with Alkenes

5.2.1 Palladium-Promoted Coupling Reactions with Alkenes

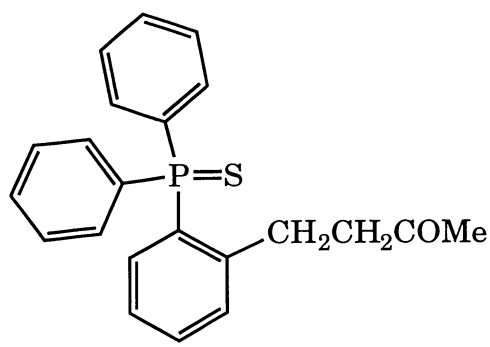
An initial investigation into the coupling of orthomanganated $Ph_3P{=}S$ with alkenes in the presence of Li_2PdCl_4 employed methyl vinyl ketone because previous work has indicated that this olefin and methyl acrylate

consistently gave the highest yields of coupled products [5]. The reaction was carried out in refluxing acetonitrile, and in methanol at ambient temperature.

The palladium-promoted coupling reaction carried out in acetonitrile afforded the demetalated product $Ph_3P{=}S$ **(28)** in low yield (6%) after 17 hours, with no sign of any coupled products being detected. The extremely low recovery of organic material suggests that the precipitation observed during these reactions, which in the past has been attributed to palladium metal [5], may in the present case be the result of the formation of some type of insoluble palladium complex.

Similarly, reaction in methanol resulted only in the formation of $Ph_3P{=}S$ (shown by t.l.c.) after a significantly longer reaction time, so the reaction was abandoned.

In an attempt to establish whether or not the presence of palladium was interfering with the formation of alkene-coupled products, the reaction of orthomanganated $Ph_3P{=}S$ with methyl vinyl ketone in methanol at ambient temperature was carried out concurrently with the palladium reaction. After leaving the reaction for the same amount of time as for the palladium-promoted reaction (~63 hours), the reaction residue was chromatographed to yield orthomanganated $Ph_3P{=}S$ [**(31)**; 41%], $Ph_3P{=}S$ [**(28)**; 13%] and the arylalkane coupled product [**(35)**; 19%] shown in Figure 5.2.



(35)

Figure 5.2

This result suggests that palladium is inhibiting the formation of alkene-coupled products. Because palladium-promoted alkene-coupling reactions with methyl vinyl ketone are known, palladium is not preventing the alkene from reacting, so the palladium is presumably interfering with the orthomanganated substrate.

From the reaction scheme shown in Scheme 5.1, arylalkene formation is expected from an alkanyl-palladium alkene insertion intermediate (I) and arylalkane formation from the alkanyl-manganese intermediate (II). From the absence of any arylalkene product it could be assumed that the corresponding palladium intermediate is not being formed. As previously mentioned, the low recovery of any material from the palladium-promoted reaction carried out in acetonitrile suggests that the formation of some unidentified type of insoluble palladium complex is instead occurring. In support of this argument, the reaction of orthomanganated triphenylphosphite with alkenes in the presence of palladium leads to the formation of various palladium chloride complexes with no coupling products being detected [13].

The formation of such a complex however, does not account for the absence of arylalkane type products. As mentioned in the introduction, the arylalkane is thought to arise from an alkene-inserted manganese intermediate, which should be accessible in both cases, especially in the reaction carried out in methanol where the rate of any transmetalation was considerably slower than that in refluxing acetonitrile as orthomanganated $Ph_3P{=}S$ **(31)** was still present after 60 hours.

The formation of the arylalkane in methanol at ambient temperature in the absence of palladium clearly demonstrates that heat is not required for the formation of the coupled product. So how the palladium prevents the formation of the arylalkane in methanol at ambient temperature is not understood.

Despite the lack of success in palladium-promoted coupling reactions of orthomanganated $Ph_3P{=}S$ with alkenes, the preliminary result from the reaction carried out in the absence of palladium indicates that the corresponding thermally promoted coupling reactions may be more successful.

5.2.2 Thermally Promoted Coupling Reactions with Alkenes in the absence of Palladium

The reaction of orthomanganated $Ph_3P{=}S$ with methyl vinyl ketone was originally attempted in refluxing carbon tetrachloride, as it had been reported [6] that high yields of alkene-coupled products were obtained from the coupling reactions of orthomanganated chalcones with various alkenes in refluxing carbon tetrachloride in the absence of palladium. This afforded the arylalkane 4-[(2-diphenylthiophosphinyl)phenyl]-butan-2-one [**(35)**; 17%] and the demetalated parent compound $Ph_3P{=}S$ [**(28)**; 27%]. To assess the suitability of various solvents for use in subsequent alkene-couplings, the reaction was repeated in refluxing benzene, acetonitrile and methanol. The results are shown in Table 5.2.

Table 5.2 Yields (%) of Products from Thermally Promoted Coupling Reactions of Orthomanganated $Ph_3P{=}S$ (31) with Methyl Vinyl Ketone in a Range of Solvents

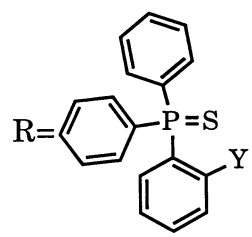
Product	CCl_4	C_6H_6	MeCN	MeOH
arylalkane **(35)**	17	13	61	54
$Ph_3P{=}S$ **(28)**	28	38	12	28

It is obvious from these results that the use of polar solvents such as acetonitrile and methanol favours the formation of the arylalkane. The reaction times for these polar solvents were also generally a lot shorter than those for the remaining solvents. As a result all subsequent reactions were carried out in acetonitrile and methanol.

A summary of all the products identified in subsequent coupling reactions is given in Table 5.3.

Table 5.3 Yields (%) of Products from Thermally Promoted Coupling Reactions of Orthomanganated $Ph_3P{=}S$ (31) with a Range of Alkenes in Acetonitrile and Methanol

Alkene $CH_2{=}CHX$	Products (R-Y)	MeCN (%)	MeOH (%)
X=COMe	Y=H (**28**)	12	28
	Y=CH_2CH_2COMe (**35**)	61	54
X=COOMe	Y=H (**28**)	8	52
	Y=CH_2CH_2COOMe (**36**)	12	31
	Y=$CH_2CH(COMe)COOMe$ (**37**)	58	-
X=CN	Y=H (**28**)	6	48
	Y=CH_2CH_2CN (**38**)	44	34



The solvent choice for this reaction was critical to the yield of arylalkane obtained. The thermally promoted reaction of orthomanganated $Ph_3P{=}S$ with methyl acrylate in methanol afforded the arylalkane methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(36)**; 31%] and $Ph_3P{=}S$ [**(28)**; 52%].

In contrast, when the reaction was carried out in acetonitrile, as well as the formation of the arylalkane [**(36)**; 12%] and $Ph_3P{=}S$ [**(28)**; 8%], a third product was isolated and identified as methyl 2-acetyl-3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(37)**; 58%], the formation of which presumably accounts for the lower yield of the arylalkane in comparison to the reaction carried out in methanol. Cooney reported the formation of a similar product in low yield from the reaction of η^2-(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese with methyl

acrylate in acetonitrile [5]. The formation of this type of compound probably arises from a subsequent insertion of solvent acetonitrile once the alkene is inserted, as there is no sign of acylation at the aryl carbon, indicating such insertion does not occur at the aryl manganese stage. The imine formed upon workup could hydrolyse to the ketone (Scheme 5.2 p.167). Support for this explanation comes from Cooney who repeated the coupling reaction in propionitrile as solvent, and obtained the corresponding propanoyl insertion product [5].

In an attempt to see if other species such as carbon monoxide could be made to insert into the Mn-C bond subsequent to alkene insertion, the reaction was repeated in methanol under a static atmosphere of carbon monoxide. The reaction was carried out in methanol to avoid the competition of solvent insertion. However, after chromatography only the aryl alkane [**(36)**; 30%] and $Ph_3P{=}S$ [**(28)**; 52%] were recovered.

Reaction of orthomanganated $Ph_3P{=}S$ with acrylonitrile in methanol afforded the arylalkane 3-[(2-diphenylthiophosphinyl)phenyl]-propanenitrile [**(38)**; 34%] and $Ph_3P{=}S$ [**(28)**; 48%]. When the reaction was carried out in acetonitrile, the arylalkane [**(38)**; 44%] and $Ph_3P{=}S$ [**(28)**; 6%] were isolated as well as an unidentified colourless crystalline solid (20 mg). ESMS of the compound indicated that it was of molecular mass of 388 which is consistent with the insertion of a molecule of both acrylonitrile and acetonitrile. The only positive NMR assignments were to the triphenylphosphine nucleus with a methylene group attached to the *ortho*-position of one of the phenyl rings, and to a methyl group. The appearance of singlet carbons at 156.4 and 75.0 and a broad singlet in the proton spectrum at 5.00 ppm arising from possibly two protons were unaccounted for. Irradiation of this proton signal led to NOE enhancements of both the methylene and methyl signals. An XH experiment showed that the protons giving rise to the broad singlet at 5.00 ppm were not bonded to carbon, while a long-range HMBC (Heteronuclear multiple-bond coherance) experiment showed that both the methylene carbon and methyl carbon appeared to be coupled to the two unknown carbon singlets. This may suggest that the unknown compound could be some type of cyclised product. However, a plausible structure consistent with all of these observations could not be formulated.

Generally, alkene-coupling reactions with orthomanganated $Ph_3P{=}S$ in refluxing acetonitrile resulted in the larger yield of arylalkane with the exception of methyl acrylate, which led to the formation of the solvent-inserted alkene-coupled product **(37)** as the major product. Reactions carried out in methanol resulted in the formation of greater amounts of the demetalated starting material $Ph_3P{=}S$ **(28)**, which may be attributed to the protic nature of the solvent [14].

The formation of cyclised coupling products is obviously not possible for orthomanganated $Ph_3P{=}S$, however, these results are still consistent with the proposed reaction mechanism. Overall, the higher yield of arylalkanes observed in comparison to previously studied systems is probably a consequence of the inability of the metalated intermediate to undergo the necessary cyclisation reaction required in the formation of indene and cyclopentanol type products.

The absence of arylalkenes is consistent with previously studied alkene-coupling reactions in the absence of palladium, where the arylalkene was rarely detected, and then only in small yields. These observations further support the proposed mechanism where the manganese remains coordinated to the sulfur atom or the ketone oxygen, depending on the substrate used.

The formation of the arylalkene in palladium-promoted reactions is envisaged as arising from the elimination of HPd[X] via β-elimination. An arylalkene could also be formed under thermal conditions in the absence of palladium by the elimination of an HMn[X] species. However, this step is obviously not occurring based on our experimental results. It has been generally accepted [15,16] that β-elimination of metal hydrides for Mn-alkyls is facile based on the instability of $EtMn(CO)_5$. However, a recent review [17] questions this assumption and suggests that the instability of the *n*-alkyl pentacarbonylmanganese complexes (n=2, 3) is due to facile carbonylation rather than β-elimination, since higher *n*-alkyl derivatives (n>5) are all relatively thermally stable. Whether or not β-elimination can occur readily for $RMn(CO)_5$ compounds in the cyclometalated complexes, it is likely to be blocked anyway because the alkyl group is part of a chelate ring if the sulfur atom remains coordinated (as appears to occur with alkynes)

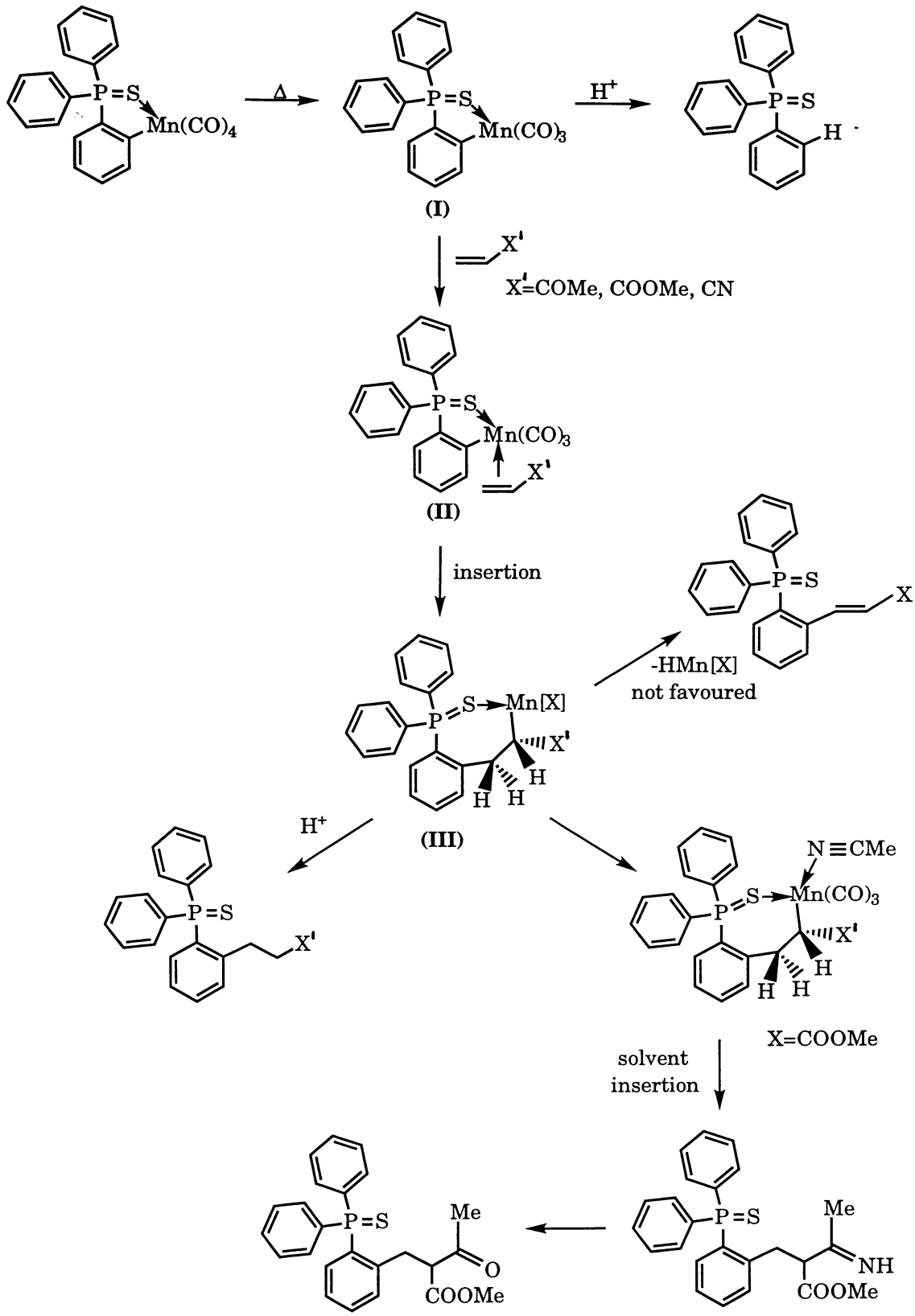
after alkene insertion. Hence, the ring imposes an unfavourable M-C-C-H dihedral angle preventing close approach of H_β to the metal. This would explain why the arylalkene is not formed for the manganese systems.

Scheme 5.2 illustrates the proposed reaction scheme for the formation of arylalkane, nitrile-inserted product and $Ph_3P{=}S$ from orthomanganated $Ph_3P{=}S$ with alkenes in the absence of palladium.

Steric effects were found to control the regiochemistry of these reactions and this is consistent with previous work in which the alkene carbon bonded to the bulkiest substituent was inserted adjacent to the metal. This sterically biased insertion is probably a direct result of the alkene coordinating to the manganese intermediate in such a way that the bulkier substituent points away from the aryl ring prior to insertion as shown in Scheme 5.2. The pre-insertion intermediate (II) presumably requires a co-planar alignment of the alkene C=C bond with that of the Mn-C σ-bond to meet orbital overlap requirements. Steric interactions would be reduced if the bulkier alkene substituent is positioned over the metal carbonyl group and not the aromatic ring.

The proton source required for the formation of both the arylalkane and $Ph_3P{=}S$ is not obvious. Results from this and other studies [5] have indicated that it is clearly not entirely solvent dependent, as both products are detected in both anhydrous protic and aprotic solvents. It may be argued that the proton source arises from some adventitious H_2O present in the solvent. Woodgate's group has reported that reductive [11] cleavage occurs during the course of reaction and not at the quenching stage during workup. This conclusion was based on the absence of deuterium in the arylalkane and parent ketone in a reaction quenched with CD_3CO_2D. They also reported that coupling in CD_3CN as solvent failed to give any deuterium-labelled products, which provides further support that the proton source does not come from the solvent.

The only other remaining source of protons for the reduced products is possibly the excess of alkene. A mechanism involving this is not immediately obvious, although this premise could be investigated by the use of deuterated alkenes.


P=S
Mn(CO)4
Δ
Mn(CO)3
H+
H
(I)
X'
X'=COMe, COOMe, CN
(II)
insertion
Mn[X]
-HMn[X]
not favoured
X
(III)
H+
N≡CMe
X=COOMe
solvent
insertion
Me
O
NH
COOMe

Scheme 5.2

The results from this preliminary study on the coupling reactions of alkenes with the orthomanganated chalcogenide **(31)** indicate that they are useful in preparing *ortho*-substituted phosphines, which is not always easy. Some of these compounds may be useful as heterodifunctional hard/soft ligands as they contain both sulfur and oxygen donor atoms.

Recently ligands of this type, containing two inequivalent donors have received a lot of attention [18-20] as they often lead to a more subtle control of the coordination sphere of the metal centres to which they are bound and to improved catalytic properties over their corresponding monodentate ligands. This arises from the ability of the more weakly bonded atom to be cleaved reversibly, which gives rise to empty coordination sites when needed in the course of the catalytic cycles, without separation of the oxygen donors from the complex fragment. In effect, this allows intramolecular control of coordinative-unsaturation.

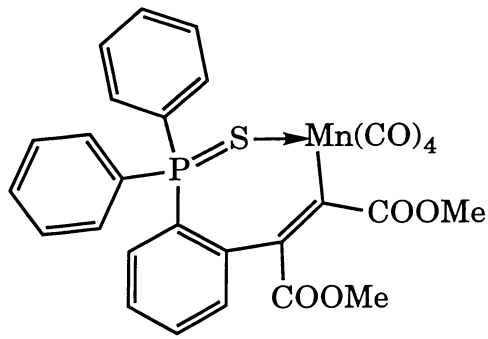
With respect to homogeneous catalysis, hemilabile O-, P-containing ligands have received most attention. Examples include an unusual selectivity-enhancing effect in the nickel-catalysed oligomerisation and polymerisation of ethene, and in the carbonylation and hydrocarbonylation of methanol to oxygen-containing C_2-products such as acetic acid, acetaldehyde, ethanol or ethylidene diacetate [18].

As a result, an investigation into the corresponding alkene-coupling reactions of orthomanganated $Ph_3P{=}Se$ may be warranted, as these would give rise to ligands containing O-, Se-donors if successful.

5.3 Reactions of Orthomanganated $Ph_3P{=}S$ (31) with Alkynes

Reaction of orthomanganated $Ph_3P{=}S$ with DMAD in refluxing benzene for 3.5 hours yielded a yellow oil which afforded a yellow crystalline complex identified as [**(39)**; 57%] (Figure 5.3). This complex is interesting as it is one of only a few examples in which manganese is contained within an apparently stable seven-membered metallocyclic

ring ((**39**) could be stored at -20 °C for extended periods of time without any appreciable decomposition). The metallocyclic ring of **(39)** is also novel compared to similar complexes derived from the photochemically induced reactions of alkynes with orthomanganated triphenylphosphite, as sulfur is incorporated into the ring. Another interesting feature was that in contrast to the characteristic 1:1:2 pattern of signals observed in ^{13}C NMR arising from the metal carbonyls, **(39)** appeared to be the first example where four separate signals arising from each of the metal carbonyls was observed. The crystal structure of **(39)** was determined by X-ray methods and a full discussion of the structure is given in Section 5.4.



(39)

Figure 5.3

In addition to **(39)** crystallising from the yellow oil, an unidentified orange crystalline solid in low yield (5 mg) was also obtained. ESMS of the orange solid indicated that the complex had a molecular mass of 716, based on which the yield obtained was 3%. An IR spectrum showed that manganese was present as a tricarbonyl species. ^{13}C and ^{1}H NMR both showed four signals which were characteristic of methoxy groups. These observations suggest that this product may be the result of a double alkyne insertion. Double alkyne insertions to give nine-membered metallocyclic rings have been established for some cyclopalladiated compounds [21,22]. Recently Grigsby [23] tentatively characterised the complex shown in Figure 5.4, arising from a stepwise double alkyne insertion in the photochemically initiated coupling reaction of orthomanganated triphenylphosphite with DMAD in benzene.

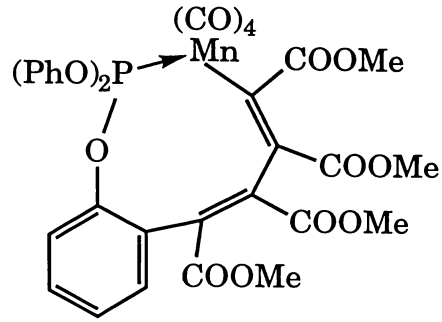


Figure 5.4

The presence of a tricarbonyl species and the fact that multiple insertion of alkynes to give large metallocyclic rings is rare, suggests that in the present case, the nine-membered ring metallocycle which would have resulted from a double alkyne insertion has probably undergone a subsequent rearrangement reaction to yield a product containing a smaller ring size. A possible structure is given in Figure 5.5, which is based on palladium species derived from the double insertion of diphenylacetylene into cyclopalladiated *N*,*N*-dimethylbenzylamine chloro dimers [21,22]. Alternatively, structures involving coordination of one of the C=O groups is also possible.

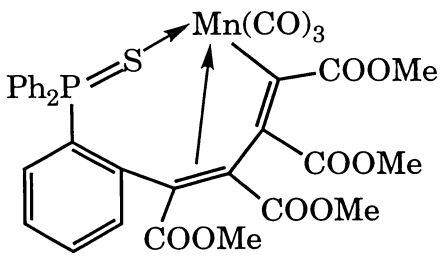
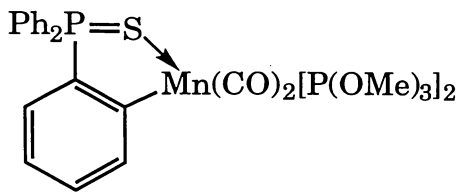


Figure 5.6

In an attempt to increase the yield of this unknown complex so more rigorous spectroscopic studies could be undertaken, the reaction was repeated with excess DMAD. This resulted in only a slight increase in the overall yield to 5%. The reaction was also repeated with excess DMAD for a longer reaction time of 72 hours, but no insertion products were detected after this time so the reaction was abandoned.

Despite numerous recrystallisation attempts, no single crystal suitable for X-ray crystallography studies could be obtained, so complete

characterisation was precluded. It was therefore decided to try to synthesize a trimethylphosphite derivative which might crystallise more successfully. The bis-trimethylphosphite derivative **(40)** (Figure 5.6) of orthomanganated $Ph_3P{=}S$ was prepared in high yield (88%) by the reaction of the orthomanganated complex **(31)** with trimethylphosphite in refluxing heptane. The crystal structure of **(40)** was determined by X-ray methods and full discussion of the structure is in Section 5.5.

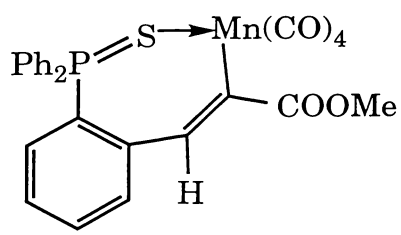


(40)

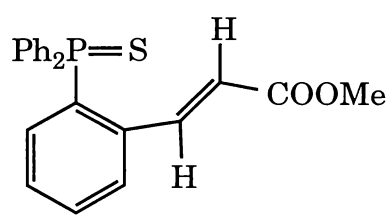
Figure 5.6

Reaction of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis-(trimethylphosphite)manganese **(40)** with DMAD in refluxing benzene yielded the corresponding singly inserted DMAD complex as a yellow crystalline solid in fair yield [**(41)**; 30%] (Figure 5.7). However, no trace of the corresponding doubly inserted DMAD complex was detected, so full characterisation of a complex of this type has still to be achieved.

Reaction of the unsymmetrical alkyne methyl propiolate with orthomanganated $Ph_3P{=}S$ in refluxing benzene for 3.5 hours yielded **(42)** as a yellow oil (41%) and methyl E-3-[(2-diphenylthiophosphinyl)phenyl]-prop-2-enoate [**(43)**; 13%] as a colourless oil (Figure 5.7). The organic product **(43)** presumably arises from the cleavage of the Mn-C bond in **(42)** as a result of protonolysis.



(42)



(43)

Figure 5.7

The sterically biased insertion of methyl propiolate into the Mn-C_{aryl} is consistent with previously studied reactions with orthomanganated aromatic ketones and *N*-acyl complexes discussed in Chapter 3. However, as previously mentioned in Section 3.2.1, reactions of acetylenic esters $RC{\equiv}CCO_2Et$ with various substituted orthomanganated acetophenones resulted in the formation of indenols with the ester group in the 2-position regardless of the steric bulk of the R group [24]. This was thought to be the result of a possible electronic-directing effect manifested by the highly polarised nature of the electron-deficient alkynes or alternatively, the ester group acting as a directing ligand by prior coordination of the carbonyl oxygen to the manganese atom. As a result, an ambiguity arises in interpreting the formation of the methyl propiolate inserted products **(42)** and **(43)** because the resulting complexes, as well as being consistent with a sterically biased insertion, are also consistent with the operation of these electronic or ligand directing effects.

In contrast, reactions of the unsymmetrical alkynes phenylacetylene and trimethylsilylacetylene with orthomanganated triphenylphosphite were not regioselective as both isomers were isolated [23]. However, these reactions were initiated photochemically, so it may be that the reaction mechanisms for the two cases are different.

Comparison of the ^{31}P chemical shifts of **(39)** and **(42)** with that of the orthomanganated precursor **(31)** shows that alkyne insertion, which affords a seven membered ring, results in the movement of the ^{31}P chemical shifts to higher field (Table 5.4).

Table 5.4 ^{31}P NMR Chemical Shifts of Complexes (31), (39), and (42)

Complex	Metalated Ligand	Ring Size	Δ_R
(31)	66.6	5	23.3
(39)	46.0	7	2.7
(42)	45.2	7	1.9

Data on the quantitative treatment of Δ_R for seven-membered rings is limited. In a review by Garrou [25] on the quantification of the chelate ring contribution to the phosphorus chemical shift defined by the term Δ_R, reference to only one example is made, which had a Δ_R of -0.7 ppm. The Δ_R values obtained for the complexes derived from the insertion of alkynes into orthomanganated triphenylphosphite ranged between -4 and 17 ppm. Due to the lack of ^{31}P NMR data for $Ph_3P{=}S$ in nonchelated complexes, the same assumption used in Section 4.3.3 was employed to enable the calculation of an approximate Δ_R value for **(39)** and **(42)**. The resulting Δ_R values appear consistent with previously calculated values, again giving support to this initial assumption.

The insertion of the alkyne DMAD or methyl propiolate into the Mn-C_{aryl} bond of orthomanganated $Ph_3P{=}S$ gave rise to an increase in $\upsilon(C{\equiv}O)$ for the resulting complexes **(39)** and **(42)** (Table 5.5). The increase presumably reflects the electron-withdrawing nature of the inserted alkyne to which the manganese has become bonded, resulting in less electron density being available for backbonding to the carbonyls.

Table 5.5 M-C≡O'Infrared Stretching Frequencies of Complexes (31), (39) and (42)

Complex	$\upsilon(C{\equiv}O)$ (cm^{-1})
(31)	2072(m), 1993(vs, br), 1978(vs, br), 1933(s)
(39)	2081(m), 2001(vs, br), 1959(s)
(42)	2077(m), 1997(vs, br), 1987(vs, br), 1947(s)

The alkyne-coupling reactions of orthomanganated $Ph_3P{=}S$ proved to be less general than those of orthomanganated aryl ketone couplings. Attempts at coupling diphenylacetylene (which previously has reacted with every substrate) with orthomanganated $Ph_3P{=}S$ yielded no coupled products in refluxing benzene, acetonitrile or petroleum spirit. The failure of diphenylacetylene to undergo reaction may be attributed to unfavourable steric effects arising from the bulky nature of the attached phenyl groups. However, the photochemically initiated reaction of diphenylacetylene with orthomanganated triphenylphosphite [23] yielded the corresponding seven-membered metallocyclic ring product,

albeit in low yield (15%), which may reflect slightly more favourable steric effects in the orthomanganated precursor due to the presence of the bridging oxygens.

Other alkynes which have been used routinely in reactions with orthomanganated aromatic ketones, such as trimethylsilylacetylene in benzene or acetylene in petroleum spirit, also resulted only in demetalation of orthomanganated $Ph_3P{=}S$. Alkynols also resulted in the demetalation of **(31)** but, this is not unexpected as there has been only one reported case [26] where an alkynol has coupled with an orthomanganated precursor.

Reaction of orthomanganated $Ph_3P{=}S$ with 2-methyl-1-buten-3-yne posed the intriguing possibility of inserting as an alkyne or alkene. The reaction was carried out in refluxing acetonitrile as this solvent has been observed to favour both alkene- and alkyne-coupling. However, the only major compound detected was $Ph_3P{=}S$ **(28)**.

A most probable sequence for the formation of the alkyne-inserted complexes **(39)** and **(42)** can be proposed based on that discussed in Chapter Three for the formation of indenols from reactions of orthomanganated aromatic ketones with alkynes. A coordinatively unsaturated intermediate generated by the loss of CO would give a 16-electron species. This would allow η^2-coordination of the alkyne, subsequent alkyne insertion into the $Mn\text{-}C_{aryl}$ bond, and base association of CO to give the product. Complexes **(39)** and **(42)** cannot undergo intramolecular rearrangement to yield a cyclised product, so the seven-membered intermediate can be readily isolated. Similar results have been observed with the photochemically initiated reaction of orthomanganated triphenylphosphite with various alkynes [23].

Despite the lack of generality of reaction with other alkynes the complexes **(39)** and **(42)** could be useful for subsequent reactions. For example, the demetalation of these complexes presumably gives an arylalkene product as is indicated by the formation of **(43)**. This provides an alternative route to arylalkenes which are not accessible by the normal Heck reactions involving the palladium-promoted coupling reactions with alkenes (Section 5.2.1). Even though the insertion of a

second alkyne molecule into these complexes did not occur readily, the insertion of other substrates such as cyanides and isocyanides may warrant an investigation. The possible insertion of SO_2 into **(39)** is investigated in the following chapter.

5.4 X-Ray Crystal Structure of (39)

The crystal structure of **(39)** was determined to fully characterise the reaction product between orthomanganated $Ph_3P{=}S$ **(31)** and DMAD. The crystal structure was also determined to see if there was any structural reason for the unusual appearance of four ^{13}C NMR chemical shifts arising from the metal-carbonyls.

5.4.1 Results of Preliminary Studies

Yellow rectangular block-shaped crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated chloroform solution of **(39)** at -20 °C. Preliminary precession photography (Cu-$K\alpha$, λ=1.5418 Å) indicated triclinic symmetry, $P\bar{1}$ was assumed to be the correct space group.

5.4.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -144 °C with monochromated Mo-$K\alpha$ radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{28}H_{20}O_8MnPS.CHCl_3$

M_r=721.78

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

a=10.810(3), b=11.831(4), c=14.347(7) Å

α=67.67(4)°, β=88.47(4)°, γ=87.08(3)°

U=1695(1) $Å^3$

D_{calc}=1.414 g cm^{-3}

Z=2

F(000)=732

μ(Mo-K_α)=0.779 mm^{-1}

A total of 4882 reflections were collected in the range $4° \leq 2\theta \leq 55°$ of which 4379 were unique (R_{int}=0.1359). These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method. Of these, 3306 had $I \geq 2\sigma(I)$.

5.4.3 Solution and Refinement

The heavy atom positions (all 43 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full-matrix least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R_1=0.1234 (2σ data); R_1=0.1391, wR_2=0.3588, and Goof=1.035 for all data, where $w=[\sigma^2(F_o)^2+(0.3030P)^2+1.71P]^{-1}$ with $P=1/3[F_o^2+2F_c^2]$. No parameter shifted more than 0.220 σ in the final cycle. The final difference map showed no peaks or troughs greater than 2.760 e $Å^{-3}$.

The high R_1 values obtained were unexpected as the data set appeared to be good and strong. Despite the high R_{int} value of 0.1359, analysis of the data set $|E^*E-1|$=0.964 (expected 0.968 centrosymmetric and 0.736 non-centrosymmetric) gave no indication that the space group of the crystal was the very unusual P1 rather than $P\bar{1}$. The solvent of crystallisation appeared to have some disorder, however this alone would not explain the high R_1 values obtained. As a result, the poor quality of the refined structure may be arising from some undetectable twinning of the crystal.

Bond lengths and angles are presented in Tables 5.6 and 5.7 respectively.

Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix VII.

A perspective view of the structure is shown in Figure 5.8 and illustrates the atom labelling scheme.

5.4.4 Discussion of the Structure

Poor crystal quality has resulted in less accurate data which precludes the accurate comparison of bond lengths and angles to other complexes. Nevertheless, the crystal structure determination has revealed the atom connectivity.

The molecule consists of a tetracarbonyl manganese group, with the manganese bonded to the sulfur atom of the triphenylphosphine sulfide ligand and to a carbon atom of the inserted acetylene group, which in turn forms a bridge to the *ortho*-carbon of the phenyl group originally bonded to the manganese atom. This gives rise to a six-coordinate manganese atom and a seven-membered metallocyclic ring.

The seven-membered ring has adopted a boat conformation which can be defined by three planes: plane 1 comprising the atoms P(1), C(31), C(32) and C(44) (maximum deviation 0.01(1) Å), plane 2 containing the atoms P(1), S(1), C(41) and C(44) (maximum deviation 0.12(1) Å), and plane 3 defined by the atoms S(1), Mn(1) and C(41). The dihedral angle between planes 1 and 2 is 60.6(9)°, while that between planes 2 and 3 is 36.1(3)°.

In Table 5.8, selected bond distances and angles are tabulated and compared with the corresponding distances and angles reported for the alkyne inserted triphenylphosphite complex (A) shown in Figure 5.9 and the orthomanganated precursor **(31)**.

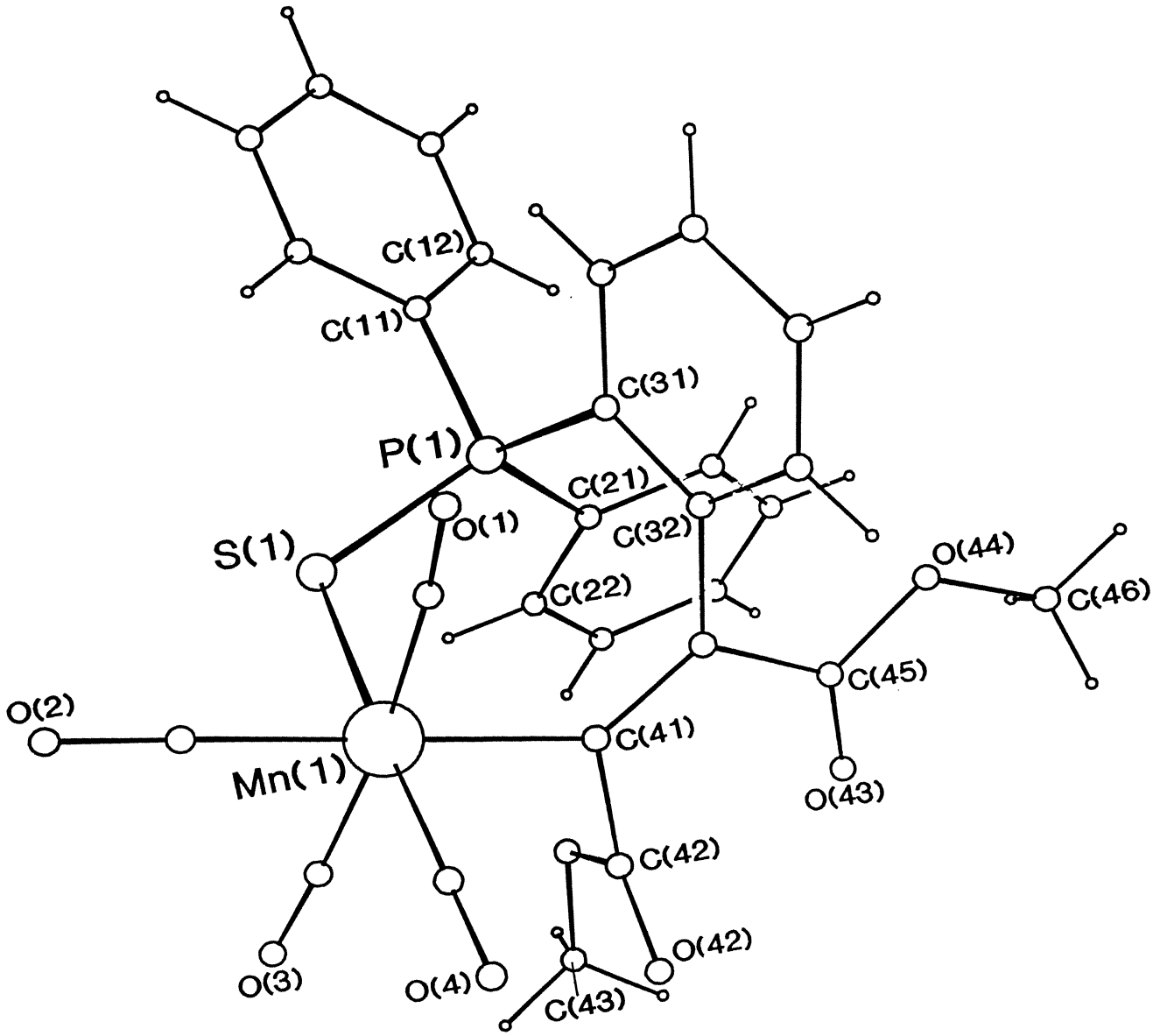


Figure 5.8 Perspective View of Complex (39)

Table 5.6 Bond Lengths (Å) for (39)

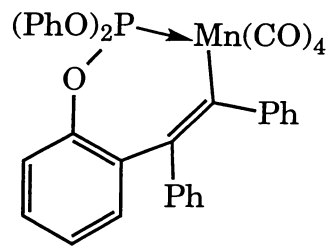
Mn(1)-C(4)	1.806(10)	C(13)-C(14)	1.38(2)
Mn(1)-C(2)	1.818(10)	C(14)-C(15)	1.37(2)
Mn(1)-C(1)	1.877(12)	C(15)-C(16)	1.360(13)
Mn(1)-C(3)	1.897(12)	C(21)-C(22)	1.374(12)
Mn(1)-C(41)	2.080(9)	C(21)-C(26)	1.394(12)
Mn(1)-S(1)	2.400(3)	C(22)-C(23)	1.384(13)
S(1)-P(1)	2.007(3)	C(23)-C(24)	1.36(2)
P(1)-C(21)	1.804(8)	C(24)-C(25)	1.400(14)
P(1)-C(11)	1.805(8)	C(25)-C(26)	1.366(13)
P(1)-C(31)	1.816(9)	C(31)-C(36)	1.393(12)
O(1)-C(1)	1.135(12)	C(31)-C(32)	1.402(12)
O(2)-C(2)	1.154(12)	C(32)-C(33)	1.369(13)
O(3)-C(3)	1.103(12)	C(32)-C(44)	1.505(12)
O(4)-C(4)	1.135(11)	C(33)-C(34)	1.375(13)
O(41)-C(42)	1.355(12)	C(34)-C(35)	1.416(14)
O(41)-C(43)	1.432(11)	C(35)-C(36)	1.356(14)
O(42)-C(42)	1.188(10)	C(41)-C(44)	1.334(13)
O(43)-C(45)	1.197(11)	C(41)-C(42)	1.496(13)
O(44)-C(45)	1.340(11)	C(44)-C(45)	1.505(13)
O(44)-C(46)	1.456(12)	C(99)-Cl(3)	1.75(2)
C(11)-C(12)	1.383(13)	C(99)-Cl(1)	1.743(12)
C(11)-C(16)	1.392(13)	C(99)-Cl(2)	1.708(12)
C(12)-C(13)	1.395(13)		

Table 5.7 Bond Angles (Å) for (39)

C(4)	-Mn(1)	-C(2)	94.5(4)	C(15)	-C(16)	-C(11)	121.0(8)
C(4)	-Mn(1)	-C(1)	89.2(4)	C(22)	-C(21)	-C(26)	120.3(8)
C(2)	-Mn(1)	-C(1)	86.7(5)	C(22)	-C(21)	-P(1)	119.6(6)
C(4)	-Mn(1)	-C(3)	90.7(4)	C(26)	-C(21)	-P(1)	119.9(7)
C(2)	-Mn(1)	-C(3)	85.9(4)	C(21)	-C(22)	-C(23)	120.9(9)
C(1)	-Mn(1)	-C(3)	172.6(4)	C(24)	-C(23)	-C(22)	118.6(9)
C(4)	-Mn(1)	-C(41)	87.0(4)	C(23)	-C(24)	-C(25)	121.1(9)
C(2)	-Mn(1)	-C(41)	177.4(4)	C(26)	-C(25)	-C(24)	120.0(9)
C(1)	-Mn(1)	-C(41)	95.4(4)	C(25)	-C(26)	-C(21)	119.0(9)
C(3)	-Mn(1)	-C(41)	92.0(4)	C(36)	-C(31)	-C(32)	119.8(8)
C(4)	-Mn(1)	-S(1)	177.5(3)	C(36)	-C(31)	-P(1)	119.7(7)
C(2)	-Mn(1)	-S(1)	87.8(3)	C(32)	-C(31)	-P(1)	120.5(6)
C(1)	-Mn(1)	-S(1)	91.9(3)	C(33)	-C(32)	-C(31)	118.9(8)
C(3)	-Mn(1)	-S(1)	88.5(3)	C(33)	-C(32)	-C(44)	120.8(8)
C(41)	-Mn(1)	-S(1)	90.6(2)	C(31)	-C(32)	-C(44)	120.3(8)
P(1)	-S(1)	-Mn(1)	109.40(12)	C(34)	-C(33)	-C(32)	121.7(8)
C(21)	-P(1)	-C(11)	106.6(4)	C(33)	-C(34)	-C(35)	119.1(9)
C(21)	-P(1)	-C(31)	108.0(4)	C(36)	-C(35)	-C(34)	119.6(8)
C(11)	-P(1)	-C(31)	107.1(4)	C(35)	-C(36)	-C(31)	120.8(8)
C(21)	-P(1)	-S(1)	115.1(3)	C(44)	-C(41)	-C(42)	117.7(8)
C(11)	-P(1)	-S(1)	106.5(3)	C(44)	-C(41)	-Mn(1)	131.0(7)
C(31)	-P(1)	-S(1)	113.2(3)	C(42)	-C(41)	-Mn(1)	111.3(6)
C(42)	-O(41)	-C(43)	116.3(7)	O(42)	-C(42)	-O(41)	123.4(8)
C(45)	-O(44)	-C(46)	114.6(7)	O(42)	-C(42)	-C(41)	125.2(9)
O(1)	-C(1)	-Mn(1)	172.6(8)	O(41)	-C(42)	-C(41)	110.5(7)
O(2)	-C(2)	-Mn(1)	179.3(8)	C(41)	-C(44)	-C(32)	124.0(8)
O(3)	-C(3)	-Mn(1)	172.6(9)	C(41)	-C(44)	-C(45)	119.7(8)

Table 5.7 continued

O(4)	-C(4)	-Mn(1)	179.9(5)	C(32)	-C(44)	-C(45)	116.3(7)
C(12)	-C(11)	-C(16)	119.7(8)	O(43)	-C(45)	-O(44)	123.4(8)
C(12)	-C(11)	-P(1)	120.2(7)	O(43)	-C(45)	-C(44)	124.7(8)
C(16)	-C(11)	-P(1)	120.1(7)	O(44)	-C(45)	-C(44)	111.9(7)
C(11)	-C(12)	-C(13)	118.6(9)	Cl(3)	-C(99)	-Cl(1)	108.3(7)
C(14)	-C(13)	-C(12)	120.8(9)	Cl(3)	-C(99)	-Cl(2)	109.0(7)
C(15)	-C(14)	-C(13)	119.9(9)	Cl(1)	-C(99)	-Cl(2)	114.5(8)
C(16)	-C(15)	-C(14)	119.9(9)				



(A)

Figure 5.9

The chelate bite angle of **(39)** (90.6(2)°) is markedly different from that in the alkyne inserted complex (A) (81.3(4)°). This is presumably due to the acceptance of smaller angles by the sulfur atom as observed in the orthomanganated complex **(31)**. The P(1)-S(1)-Mn(1) angle observed in **(39)** is larger than the corresponding angle in the orthomanganated precursor **(31)**, which probably reflects the wider chelate bite angle of a seven-membered chelate ring compared to that of a 5-membered analogue, and possibly the slight opening of the C(31)-P(1)-S(1) in **(39)**.

As observed in the metallocyclic ring of (A), there appears to be little indication of strain except for the C(44)-C(41)-Mn(1) angle 131.0(7)° (cf. 130(1)° in (A)). Non-bonding interactions between the alkyne substituents are presumably responsible for the significant opening of the respective angles.

Table 5.8 Selected Bond Lengths (Å) and Angles (°) of (39) and Related Compounds

	(39)	**(31)**	**(A)**
Mn(1)-S(1)	2.400(3)	2.410(1)	
S(1)-P(1)	2.007(3)	1.996(1)	
Mn(1)-C(41)	2.080(9)	2.081(2)	2.12(2)
C(41)-C(44)	1.334(13)		1.31(2)
Mn(1)-C(1)	1.877(12)	1.846(2)	1.88(2)
Mn(1)-C(2)	1.818(10)	1.825(3)	1.83(2)
Mn(1)-C(3)	1.897(12)	1.836(2)	1.86(2)
Mn(1)-C(4)	1.806(10)	1.784(3)	1.79(2)
C(44)-C(41)-Mn(1)	131.0(7)		131.0(7)
S(1)-Mn(1)-C	90.6(2)	89.60(6)	
P-Mn-C	-	-	130(1)
P(1)-S(1)-Mn(1)	109.40(12)	99.64(3)	
C(31)-P(1)-S(1)	113.2(3)	108.42(8)	

Comparison of the M-CO distances in **(39)** to those of **(31)** shows that the Mn-CO distances of the former have not been significantly lengthened, despite the observed shifts to higher frequencies in the metal-carbonyl region of the IR spectrum. One would have also expected significantly shorter Mn(1)-C(41), Mn(1)-S(1) and longer P(1)-S(1) distances compared to those of **(31)** due to the removal of electron density from manganese by the electron deficient alkyne. However, the similarity of the corresponding values may be the result of the inaccuracy inherent in this structure.

The C(41)-C(44) distance (1.334(13) Å) is consistent with a normal double bond. The carboxylate groups of the inserted alkyne have become orientated in such a way that one is out of the approximate plane of the metallocyclic ring, while the other stays in the plane of the ring. The

relative orientation of the carboxylate groups is presumably responsible for the appearance of all four signals arising from the metal carbonyls in the ^{13}C NMR spectrum. However, despite the similar orientation adopted by the olefinic phenyl groups in complex (A) the ^{13}C NMR spectrum shows the normal 1:1:2 pattern arising from the metal carbonyls.

5.5 X-Ray Crystal Structure of *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-dicarbonylbis(trimethylphosphite)-manganese (40)

The crystal structure of **(40)** was determined as no structure of an orthomanganated complex in which carbonyl ligands have been substituted for stronger Lewis base ligands such as trimethylphosphite has been reported. It was of interest to make a direct comparison between this and the unsubstituted orthomanganated complex **(31)** to see what effect the substitution of CO ligands for stronger Lewis base ligands has on the overall structure of the orthomanganated complex.

5.5.1 Results of Preliminary Studies

Yellow triangular needle shaped crystals were obtained by recrystallisation by vapour diffusion of pentane into a saturated chloroform solution of **(40)** at -20 °C. Preliminary precession photography (Cu-$K\alpha$, λ=1.5418 Å) indicated orthorhombic symmetry, with systematic absences defining space group $P2_12_12_1$.

5.5.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -121 °C with monochromated Mo-$K\alpha$ radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{26}H_{32}O_8MnP_3S$

M_r=652.43

Crystal class=orthorhombic; Space group=$P2_12_12_1$

a=8.709(2), b=16.1543(12), c=20.424(2) Å

U=2873.3(6) $Å^3$

D_{calc}=1.508 g cm^{-3}

Z=4

F(000)=1352

μ(Mo-K_α)=0.746 mm^{-1}

A total of 4298 unique reflections were collected in the range $4°\leq 2\theta \leq 58°$. These were corrected for Lorentz and polarisation effects and for linear absorption by the Ψ scan method ($T_{max,min}$ 0.260 and 0.237 respectively). Of these, 3415 had $I \geq 2\sigma(I)$.

5.5.3 Solution and Refinement

The heavy atom positions (all 39 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R_1=0.0463 (2σ data); R_1=0.0680, wR_2=0.1057, and Goof=1.054 for all data, where $w=[\sigma^2(Fo)^2+(0.0435P)^2+1.71P]^{-1}$ with $P=1/3[Fo^2+2Fc^2]$. No parameter shifted more than 0.009 σ in the final cycle. The final difference map showed no peaks or troughs greater than 0.517 e $Å^{-3}$.

Bond lengths and angles are presented in Tables 5.9 and 5.10 respectively.

Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix VIII.

A perspective view of the structure is shown in Figure 5.10 and illustrates the atom labelling scheme.

5.5.4 Discussion of the Structure

The molecule consists of a triphenylphosphine sulfide ligand bound to a $Mn(CO)_2[P(OMe)_3]_2$ group in a chelating fashion via a Mn-S bond and a Mn-C bond to the *ortho*-position of one of the phenyl rings, giving rise to a six-coordinate manganese atom in an essentially octahedral arrangement. The trimethylphosphite ligands occupy the axial positions with respect to the plane of the metallocyclic ring.

Selected bond lengths and angles of **(40)** and **(31)** are given in Table 5.11.

Overall, the geometry of the two metallocyclic rings is remarkably similar. Both metallocyclic rings are less strained than other orthomanganated complexes containing oxygen and nitrogen donor atoms because of the ability of sulfur to accept a smaller bond angle, which is reflected in the almost ideal value of the chelate bite angle in both complexes. However, the angles C(11)-C(12)-Mn(1) and C(12)-C(11)-P(1) appear to deviate from their ideal trigonal values indicating that the metallocyclic ring of **(40)** may be slightly more strained than the corresponding ring in **(31)**. This is also reflected in the planarity of the metallocyclic ring of **(40)**, in which no atom deviates more than 0.151(2) Å away from the calculated least squares plane, compared to 0.090(2) Å in **(31)**. This may be the result of steric congestion within the molecule arising from the two trimethylphosphite groups, although coordination about the manganese is still essentially octahedral.

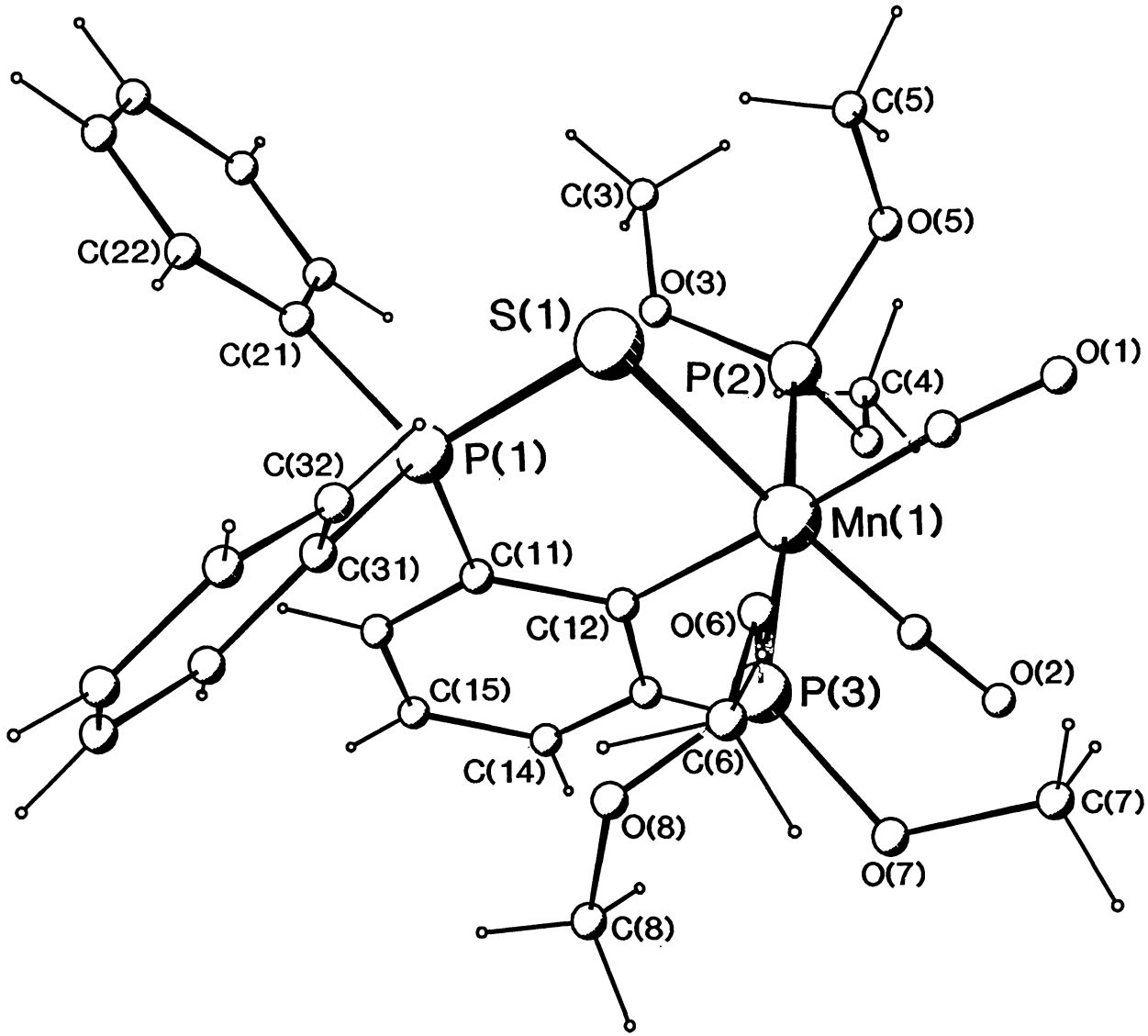


Figure 5.10 Perspective View of trans-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-dicarbonylbis(trimethylphosphite)manganese (40)

Table 5.9 Bond Lengths (Å) for trans-η^2-(C,S)-[(2-diphenylthio-phosphinyl)phenyl]dicarbonylbis(trimethylphosphite)manganese (40)

Mn(1)-C(2)	1.766(5)	C(6)-O(6)	1.443(6)
Mn(1)-C(1)	1.782(5)	C(7)-O(7)	1.438(6)
Mn(1)-C(12)	2.078(4)	C(8)-O(8)	1.435(6)
Mn(1)-P(3)	2.227(1)	C(11)-C(16)	1.400(6)
Mn(1)-P(2)	2.228(1)	C(11)-C(12)	1.422(6)
Mn(1)-S(1)	2.412(1)	C(12)-C(13)	1.422(6)
P(1)-C(11)	1.787(5)	C(13)-C(14)	1.382(7)
P(1)-C(31)	1.810(5)	C(14)-C(15)	1.392(7)
P(1)-C(21)	1.817(5)	C(15)-C(16)	1.369(7)
P(1)-S(1)	1.993(2)	C(21)-C(26)	1.388(7)
P(2)-O(4)	1.590(3)	C(21)-C(22)	1.389(6)
P(2)-O(3)	1.608(3)	C(22)-C(23)	1.384(7)
P(2)-O(5)	1.620(3)	C(23)-C(24)	1.380(7)
P(3)-O(6)	1.593(3)	C(24)-C(25)	1.378(7)
P(3)-O(8)	1.596(3)	C(25)-C(26)	1.382(7)
P(3)-O(7)	1.620(3)	C(31)-C(36)	1.386(7)
C(1)-O(1)	1.167(5)	C(31)-C(32)	1.391(7)
C(2)-O(2)	1.155(6)	C(32)-C(33)	1.382(7)
C(3)-O(3)	1.435(6)	C(33)-C(34)	1.374(8)
C(4)-O(4)	1.426(6)	C(34)-C(35)	1.381(8)
C(5)-O(5)	1.446(6)	C(35)-C(36)	1.393(7)

Table 5.10 Bond Angles (Å) for trans-η^2-(C,S)-[(2-diphenylthio-phosphinyl)phenyl]dicarbonylbis(trimethylphosphite)manganese(40)

C(2)	-Mn(1)	-C(1)	86.9(2)	O(1)	-C(1)	-Mn(1)	174.2(4)
C(2)	-Mn(1)	-C(12)	93.1(2)	O(2)	-C(2)	-Mn(1)	176.1(4)
C(1)	-Mn(1)	-C(12)	177.6(2)	C(3)	-O(3)	-P(2)	125.4(3)
C(2)	-Mn(1)	-P(3)	91.4(2)	C(4)	-O(4)	-P(2)	125.1(4)
C(1)	-Mn(1)	-P(3)	90.0(2)	C(5)	-O(5)	-P(2)	117.2(3)
C(12)	-Mn(1)	-P(3)	92.4(1)	C(6)	-O(6)	-P(3)	121.0(3)
C(2)	-Mn(1)	-P(2)	90.3(2)	C(7)	-O(7)	-P(3)	119.9(3)
C(1)	-Mn(1)	-P(2)	94.0(2)	C(8)	-O(8)	-P(3)	121.9(3)
C(12)	-Mn(1)	-P(2)	83.6(1)	C(16)	-C(11)	-C(12)	123.4(4)
P(3)	-Mn(1)	-P(2)	175.79(6)	C(16)	-C(11)	-P(1)	119.9(4)
C(2)	-Mn(1)	-S(1)	178.4(2)	C(12)	-C(11)	-P(1)	116.7(3)
C(1)	-Mn(1)	-S(1)	91.6(1)	C(11)	-C(12)	-C(13)	113.1(4)
C(12)	-Mn(1)	-S(1)	88.3(1)	C(11)	-C(12)	-Mn(1)	123.5(3)
P(3)	-Mn(1)	-S(1)	89.1(1)	C(13)	-C(12)	-Mn(1)	123.3(3)
P(2)	-Mn(1)	-S(1)	89.3(1)	C(14)	-C(13)	-C(12)	123.4(4)
C(11)	-P(1)	-C(31)	112.7(2)	C(13)	-C(14)	-C(15)	121.0(5)
C(11)	-P(1)	-C(21)	109.9(2)	C(16)	-C(15)	-C(14)	118.4(5)
C(31)	-P(1)	-C(21)	103.8(2)	C(15)	-C(16)	-C(11)	120.6(5)
C(11)	-P(1)	-S(1)	108.4(2)	C(26)	-C(21)	-C(22)	119.2(5)
C(31)	-P(1)	-S(1)	112.6(2)	C(26)	-C(21)	-P(1)	119.3(4)
C(21)	-P(1)	-S(1)	109.4(2)	C(22)	-C(21)	-P(1)	121.2(4)
O(4)	-P(2)	-O(3)	106.0(2)	C(23)	-C(22)	-C(21)	120.5(5)
O(4)	-P(2)	-O(5)	99.6(2)	C(24)	-C(23)	-C(22)	119.5(5)
O(3)	-P(2)	-O(5)	101.6(2)	C(25)	-C(24)	-C(23)	120.5(5)
O(4)	-P(2)	-Mn(1)	111.0(1)	C(24)	-C(25)	-C(26)	120.0(5)
O(3)	-P(2)	-Mn(1)	117.5(1)	C(25)	-C(26)	-C(21)	120.2(5)

Table 5.10 continued

O(5)	-P(2)	-Mn(1)	118.9(1)	C(36)	-C(31)	-C(32)	119.4(5)
O(6)	-P(3)	-O(8)	99.7(2)	C(36)	-C(31)	-P(1)	121.5(4)
O(6)	-P(3)	-O(7)	103.7(2)	C(32)	-C(31)	-P(1)	118.7(4)
O(8)	-P(3)	-O(7)	97.5(2)	C(33)	-C(32)	-C(31)	120.0(5)
O(6)	-P(3)	-Mn(1)	112.6(1)	C(34)	-C(33)	-C(32)	120.5(5)
O(8)	-P(3)	-Mn(1)	121.4(1)	C(33)	-C(34)	-C(35)	120.1(5)
O(7)	-P(3)	-Mn(1)	118.7(1)	C(34)	-C(35)	-C(36)	119.8(5)
P(1)	-S(1)	-Mn(1)	99.59(6)	C(31)	-C(36)	-C(35)	120.1(5)

Table 5.11 Selected Bond Lengths and Angles of Complexes (40) and (31)

Bond (Å)/Angle(°)	**(40)**	**(31)**
S(1)-P(1)	1.993(2)	1.996(1)
Mn(1)-S(1)	2.412(1)	2.410(1)
Mn(1)-C(12)	2.078(4)	2.081(2)
C(11)-C(12)	1.422(6)	1.399(3)
P(1)-C(11)	1.787(5)	1.782(2)
Mn(1)-C(1)	1.782(5)	1.825(3)
Mn(1)-C(2)	1.766(5)	1.784(3)
C(1)-O(1)	1.167(5)	1.140(3)
C(2)-O(2)	1.155(6)	1.146(3)
Mn(1)-P(2)	2.228(1)	
Mn(1)-P(3)	2.227(1)	

Table 5.11 continued

Bond (Å)/Angle(°)	(40)	(31)
P(1)-S(1)-Mn(1)	99.59(6)	99.64(3)
C(12)-Mn(1)-S(1)	88.3(1)	89.60(6)
C(11)-C(12)-Mn(1)	123.5(3)	122.1(2)
C(12)-C(11)-P(1)	116.7(3)	119.1(2)
C(11)-P(1)-S(1)	108.4(2)	108.42(8)
P(2)-Mn(1)-P(3)	175.79(6)	

The metal carbonyl and C-O distances are shorter and longer respectively than the corresponding values in **(31)** (although the trend is barely significant for the Mn(1)-C(2) and C(2)-O(2) distances). This is presumably the result of substituting CO ligands for ligands with less back-accepting ability. This means the remaining carbonyl groups have to accept more dπ-electron density to prevent the accumulation of negative charge on manganese which leads to the observed differences. This is in agreement with the observed decrease in the stretching frequencies of metal carbonyls of substituted complexes.

5.6 Experimental Section

5.6.1 Starting Materials

The following commercial materials were used as supplied: methyl vinyl ketone (Aldrich, 99%), methyl acrylate (Aldrich, 99%), acrylonitrile (Unilab, 95%), 3-butyn-1-ol (Aldrich, 99%), methyl propiolate (Aldrich, 99%), 2-methyl-1-buten-3-yne (Aldrich, 99%), and trimethylsilylacetylene (Aldrich, 98%).

Preparation of trans-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-dicarbonylbis(trimethylphosphite)manganese

Orthomanganated triphenylphosphine sulfide [**(31)**; 201 mg, 0.436 mmol], and trimethylphosphite (0.26 mL, 2.20 mmol) were added to nitrogen-saturated heptane. The solution was refluxed for 5 hours and the heptane was removed under vacuum. The yellow residue was chromatographed (p.l.c., 1:2 ethyl acetate/hexane) to give *trans-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis(trimethylphosphite)-manganese* [**(40)**; 250 mg, 88%] as a yellow solid which recrystallised from CH_2Cl_2/pentane as yellow needles, m.p. 149-150 °C. Anal. Found: C, 47.96; H, 5.22%; $C_{26}H_{32}O_8MnP_3S$ calcd.: C, 47.86; H 4.94%. IR ($CHCl_3$): υ(CO) 1933(s), 1855(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.45 (*m*, 1H, H-6), 7.76-7.63 (*m*, Ar-H), 7.52-7.37 (*m*, Ar-H), 7.10 (*m*, 1H, H-3), 7.03 (*m*, 1H, H-5), 6.89 (*m*, 1H, H-4), 3.33 (*t*, $^3J_{PH}$=4.8 Hz, 18H, $P(OCH_3)_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 226.7 (*s*, $^2J_{PC}$=36.0 Hz, C≡O), 221.8 (*s*, unresolved J_{PC}, C≡O), 195.5 (*s*, $^2J_{PC}$=48.5 Hz, $^2J_{PC}$=33.2 Hz, C-1), 145.7 (*d*, $^3J_{PC}$=21.9 Hz, C-6), 140.4 (*s*, $^1J_{PC}$=107.8 Hz, C-2), 133.3 (*s*, $^1J_{PC}$=77.5 Hz, C-1'), 132.3 (*d*, $^2J_{PC}$=10.1 Hz, C-2', C-6'), 131.3 (*d*, $^4J_{PC}$=2.4 Hz, C-4'), 130.9 (*d*, $^2J_{PC}$=20.9 Hz, C-3), 128.2 (*d*, $^3J_{PC}$=12.0 Hz, C-3', C-5'), 127.5 (*d*, C-5), 120.8 (*d*, $^3J_{PC}$=12.7 Hz, C-4), 51.5 (*q*, -$P(OCH_3)_3$). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 177.7, 69.6. ESMS: m/z 694 $(M+H+CH_3CN)^+$, 653 $(M+H)^+$.

5.6.2 Attempted Li_2PdCl_4 Promoted Coupling Reactions of Alkenes with Orthomanganated Triphenylphosphine Sulfide

Reaction of Orthomanganated Triphenylphosphine Sulfide with Li_2PdCl_4 and Methyl Vinyl Ketone in Refluxing Acetonitrile

$PdCl_2$ (77 mg, 0.435 mmol) and LiCl (77 mg, 1.81 mmol) were stirred in dry acetonitrile (20 mL) for 2 hours to solubilise the $PdCl_2$ as Li_2PdCl_4. The orthomanganated chalcogenide [**(31)**; 200 mg, 0.433 mmol] and methyl vinyl ketone (0.050 mL, 0.601 mmol) were added and the mixture refluxed for 17 hours. Upon reaction the solution turned black with the precipitation of palladium metal. The mixture was filtered to remove

metal, the filtrate passed through a short silica column and the solvent evaporated under reduced pressure. The residue was chromatographed (p.l.c., CH_2Cl_2) to give $Ph_3P{=}S$ [**(28)**; 8 mg, 6%].

Reaction of Orthomanganated Triphenylphosphine Sulfide with Li_2PdCl_4 and Methyl Vinyl Ketone in Methanol at Ambient Temperature

Similarly $PdCl_2$ (39 mg, 0.220 mmol) and LiCl (40 mg, 0.934 mmol) were stirred in dry methanol (20 mL) and treated with the orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and methyl vinyl ketone (0.025 mL, 0.300 mmol). The mixture was stirred at ambient temperature for 60 hours, by which time t.l.c. showed the presence of the orthomanganated compound and $Ph_3P{=}S$. The mixture was refluxed for 3 hours. T.l.c. showed no major organic products except $Ph_3P{=}S$ so the reaction was abandoned.

5.6.3 General Procedures for Thermally Promoted Coupling Reactions of Alkenes and Alkynes with Orthomanganated Triphenylphosphine Sulfide

The orthomanganated chalcogenide (~0.22 mmol) and alkene/alkyne (~1.4 mmol equivalent) were dissolved in AR solvent (20 mL), the solution was degassed and flushed with nitrogen several times. The mixture was refluxed under nitrogen for periods ranging from two hours to several days, with the extent of reaction being monitored by t.l.c.. At the completion of reaction the solvent was removed under vacuum and the residue chromatographed on a silica gel plate (200 x 200 mm) using the appropriate eluant. Only major bands were extracted. Products are reported in order of increasing polarity.

5.6.4 Thermally Promoted Coupling Reactions of Alkenes with Orthomanganated Triphenylphosphine Sulfide

Reactions of Orthomanganated Triphenylphosphine Sulfide with Methyl Vinyl Ketone

(a) In Acetonitrile

The orthomanganated chalcogenide [**(31)**; 100 mg, 0.218 mmol] and methyl vinyl ketone (0.025 mL, 0.300 mmol) were refluxed in acetonitrile for 2 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 8 mg, 12%].

4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one [**(35)**; 48 mg, 61%] as a colourless oil which crystallised from $CHCl_3$/pentane as chunky colourless crystals, m.p. 126-127 °C. Anal. Found: C, 72.15; H, 5.63; $C_{22}H_{21}OPS$ calcd.: C, 72.51; H, 5.81%. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.77 (*m*, 4H, Ar-H), 7.48 (*m*, 7H, Ar-H), 7.30 (*m*, 1H, Ar-H), 7.10 (*m*, 1H, H-5'), 6.92 (*m*, 1H, H-6'), 3.03 (*t*, ^3J=7.8 Hz, 2H, H-4), 2.73 (*t*, ^3J=7.8 Hz, 2H, H-3), 2.02 (*s*, 3H, H-1). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 208.1 (*s*, C-2), 145.9 (*s*, $^2J_{PC}$ =9.1 Hz, C-2'), 133.1 (*d*, $^2J_{PC}$ =12.0 Hz, C-6'), 132.8 (*s*, $^1J_{PC}$ =84.3 Hz, C-1''), 132.3 (*d*, $^2J_{PC}$ =10.6 Hz, C-2'', C-6''), 132.0 (*d*, $^4J_{PC}$ =2.1 Hz, C-4'), 131.9 (*s*, $^1J_{PC}$ =85.0 Hz, C-1'), 131.7 (*d*, $^4J_{PC}$ =1.9 Hz, C-4''), 131.6 (*d*, $^3J_{PC}$ =10.2 Hz, C-3'), 128.7 (*d*, $^3J_{PC}$ =12.5 Hz, C-3'', C-5''), 125.9 (*d*, $^3J_{PC}$ =12.7 Hz, C-5'), 45.2 (*t*, C-3), 29.8 (*q*, C-1), 28.6 (*t*, $^3J_{PC}$ =6.2 Hz, C-4). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.1. GCMS: m/z 364 (M^+).

(b) In Methanol

The orthomanganated chalcogenide [**(31)**; 100 mg, 0.218 mmol] and methyl vinyl ketone (0.025 mL, 0.300 mmol) were refluxed in methanol for 5.5 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 18 mg, 28%].
4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one [**(35)**; 43 mg, 54%].

(c) In Carbon Tetrachloride

The orthomanganated chalcogenide [**(31)**; 111 mg, 0.241 mmol] and methyl vinyl ketone (0.028 mL, 0.338 mmol) were refluxed in carbon

tetrachloride for 24 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 20 mg, 28%].
4-[(2-Diphenylthiophosphinyl)phenyl]butan-2-one [**(35)**; 15 mg, 17%].

(d) In Benzene

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and methyl vinyl ketone (0.025 mL, 0.300 mmol) were refluxed in carbon tetrachloride for 72 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 25 mg, 38%].
4-[(2-Diphenylthiophosphinyl)phenyl]butan-2-one [**(35)**; 10 mg, 13%].

Reactions of Orthomanganated Triphenylphosphine Sulfide with Methyl Acrylate

(a) In Acetonitrile

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and methyl acrylate (0.040 mL, 0.444 mmol) were refluxed in acetonitrile for 3 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 5 mg, 8%].

Methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(36)**; 10 mg, 12%] as a colourless oil which crystallised from ether/pentane as chunky colourless crystals, m.p. 98-99 °C. Anal. Found: C, 68.86; H, 5.78; $C_{22}H_{21}O_2PS$ calcd.: C, 68.93; H, 5.56%.^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.78 (*m*, 4H, Ar-H), 7.48 (*m*, 7H, Ar-H), 7.34 (*m*, 1H, Ar-H), 7.12 (*m*, 1H, H-5'), 6.93 (*m*, 1H, H-6'), 3.60 (*s*, 3H, 1-OCH_3), 3.13 (*t*, ^{3}J=7.8 Hz, 2H, H-3), 2.58 (*t*, ^{3}J=7.8 Hz, 2H, H-2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 173.3 (*s*, C-1), 145.3 (*s*, $^2J_{PC}$ =9.5 Hz, C-2'), 133.1 (*d*, $^2J_{PC}$ =12.0 Hz, C-6'), 132.8 (*s*, $^1J_{PC}$ =84.1 Hz, C-1''), 132.4 (*d*, $^2J_{PC}$ =10.6 Hz, C-2'', C-6''), 132.0 (*d*, $^4J_{PC}$ =2.2 Hz, C-4'), 132.1 (*s*, $^1J_{PC}$ =85.1 Hz, C-1'), 131.7 (*d*, $^4J_{PC}$ =2.1 Hz, C-4''), 131.3 (*d*, $^3J_{PC}$ =10.0 Hz, C-3'), 128.6 (*d*, $^3J_{PC}$ =12.5 Hz, C-3'', C-

5''), 126.0 (*d*, $^3J_{PC}$ =12.4 Hz, C-5'), 51.6 (*q*, 1-OCH_3), 35.1 (*t*, C-2), 29.3 (*t*, $^3J_{PC}$ =5.9 Hz, C-3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.0.

Methyl 2-acetyl-3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(37)**; 54 mg, 58%] as a colourless oil which crystallised from ether/pentane as chunky colourless crystals, m.p. 117-119 °C. Anal. Found: M^+, 422.1101; $C_{24}H_{23}O_3PS$ calcd.: M, 422.1106. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.75 (*m*, 4H, Ar-H), 7.45 (*m*, 7H, Ar-H), 7.29 (*m*, 1H, Ar-H), 7.12 (*m*, 1H, H-5'), 6.90 (*m*, 1H, H-6'), 4.35 (*m*, 1H, H-2), 3.63 (*s*, 3H, 1-OCH_3), 3.42 (*m*, 1H, H-3), 3.18 (*m*, 1H, H-3), 2.14 (*s*, 3H, 2-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 202.9 (*s*, 2-$\underline{C}OCH_3$), 169.6 (*s*, C-1), 142.9 (*s*, $^2J_{PC}$ =9.0 Hz, C-2'), 133.5 (*d*, $^2J_{PC}$ =11.8 Hz, C-6'), 132.5 (*s*, $^1J_{PC}$ =84.1 Hz, C-1' or C-1'' or C-1'''), 132.5 (*s*, $^1J_{PC}$ =84.5 Hz, C-1' or C-1'' or C-1'''), 132.4 -131.8 (*d*, C-2'', C-2''', C-3', C-4', C-6'', C-6'''), 132.1 (*s*, $^1J_{PC}$ =84.2 Hz, C-1' or C-1'' or C-1'''), 128.8 (*d*, $^3J_{PC}$ =12.6 Hz, C-3'', C-5'' or C-3''', C-5'''), 128.7 (*d*, $^3J_{PC}$ =12.3 Hz, C-3'', C-5'' or C-3''', C-5'''), 126.6 (*d*, $^3J_{PC}$ =12.5 Hz, C-5'), 60 (*d*, C-2), 52.3 (*q*, 1-OCH_3), 32.2 (*t*, $^3J_{PC}$ =5.8 Hz, C-3), 30.2 (*q*, 2-$CO\underline{C}H_3$). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.9.

(b) In Methanol

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and methyl acrylate (0.028 mL, 0.311 mmol) were refluxed in methanol for 3.5 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 33 mg, 52%].
Methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(36)**; 26 mg, 31%].

(c) In Methanol under Carbon Monoxide

The orthomanganated chalcogenide [**(31)**; 105 mg, 0.228 mmol] and methyl acrylate (0.028 mL, 0.311 mmol) were refluxed in methanol under a static CO atmosphere for 3.5 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 35 mg, 52%].
Methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate [**(36)**; 26 mg, 30%].

Reactions of Orthomanganated Triphenylphosphine Sulfide with Acrylonitrile

(a) In Acetonitrile

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.220 mmol] and acrylonitrile (0.020 mL, 0.304 mmol) were refluxed in acetonitrile for 2 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(31)**; 4 mg, 6%].

3-[(2-Diphenylthiophosphinyl)phenyl]propanenitrile [**(38)**; 34 mg, 44%] as a colourless oil which crystallised from $CHCl_3$/pentane as colourless plates, m.p. 150-151 °C. Anal. Found: M^+, 347.0892; $C_{21}H_{18}NPS$ calcd.: M, 347.0898. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.75 (*m*, 4H, Ar-H), 7.51 (*m*, 8H, Ar-H), 7.18 (*m*, 1H, H-5'), 6.90 (*m*, 1H, H-6'), 3.13 (*t*, ^3J=7.3 Hz, 2H, H-3), 2.72 (*t*, ^3J=7.3 Hz, 2H, H-2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 142.5 (*s*, $^2J_{PC}$ =9.2 Hz, C-2'), 133.3 (*d*, $^2J_{PC}$ =11.7 Hz, C-6'), 132.4 (*s*, $^1J_{PC}$ =84.4 Hz, C-1'), 132.3 (*s*, $^1J_{PC}$ =84.6 Hz, C-1''), 132.3 (*d*, $^2J_{PC}$ =10.6 Hz, C-2'', C-6''), 132.2 (*d*, $^3J_{PC}$ =10.4 Hz, C-3'), 132.0 (*d*, C-4'), 132.0 (*d*, $^4J_{PC}$ =2.2 Hz, C-4''), 128.8 (*d*, $^3J_{PC}$ =12.6 Hz, C-3'', C-5''), 127.0 (*d*, $^3J_{PC}$ =12.5 Hz, C-5'), 119 (*s*, C-1), 29.9 (*t*, $^3J_{PC}$ =6.1 Hz, C-3), 18.6 (*t*, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.8.

An unidentified colourless oil which crystallised from ether/pentane as chunky white crystals, m.p. 203-206 °C. Anal. Found: C, 69.73; H, 5.17; N, 6.90%. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.80 (*m*, 4H, Ar-H), 7.68 (*m*, 1H, Ar-H), 7.50 (*m*, 7H, Ar-H), 7.13 (*m*, 1H, H-5'), 6.84 (*m*, 1H, H-6'), 5.01 (*s*, br, 2H), 3.52 (*s*, 2H), 2.03 (*s*, 3H). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 156.4 (*s*), 143.6 (*s*, $^2J_{PC}$ =9.4 Hz, C-2'), 132.3 (*d*, $^2J_{PC}$ =10.7 Hz, C-2'', C-6''), 132.0 (*d*, $^4J_{PC}$ =2.4 Hz, C-4''), 132.0 (*d*, C-4'), 131.5(*s*, $^1J_{PC}$ =84.7 Hz, C-1''), 131.4 (*s*, $^1J_{PC}$ =85.2 Hz, C-1'), 130.1 (*d*, $^3J_{PC}$ =9.9 Hz, C-3'), 128.9 (*d*, $^3J_{PC}$ =12.6 Hz, C-3'', C-5''), 126.5 (*d*, $^3J_{PC}$ =12.4 Hz, C-5'), 75.0 (*s*), 32.3 (*t*), 20.6 (*q*). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.4. ESMS: m/z 406 $(M+NH_4)^+$, 389 $(M+H)^+$.

(b) In Methanol

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and acrylonitrile (0.020 mL, 0.304 mmol) were refluxed in methanol for 2 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 31 mg, 48%].
3-[(2-Diphenylthiophosphinyl)phenyl]propanenitrile [**(38)**; 26 mg, 34%].

5.6.5 Thermally Promoted Coupling Reactions of Alkynes with Orthomanganated Triphenylphosphine Sulfide

Reaction of Orthomanganated Triphenylphosphine Sulfide with Dimethyl Acetylenedicarboxylate in Benzene

(a) Standard Conditions

The orthomanganated chalcogenide [**(31)**; 109 mg, 0.237 mmol] and dimethyl acetylenedicarboxylate (0.044 mL, 0.358 mmol) were refluxed in benzene for 3.5 hours. The residue was chromatographed (p.l.c., 1:4 petroleum spirit/ethyl acetate) to give:

Triphenylphosphine sulfide [**(28)**; 12 mg, 17%].

A yellow oil which consisted of (by integration of proton methoxy singlets):

94% E-1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]-tetracarbonylmanganese [**(39)**; 81 mg, 57%] which crystallised from $CHCl_3$/pentane as chunky yellow crystals, m.p. 164-167 °C. Anal. Found: C, 55.92; H, 3.06; $C_{28}H_{20}O_8PSMn$ calcd.: C, 55.82; H, 3.35%. IR ($CHCl_3$): υ(CO) 2081(m), 2001(vs, br), 1959(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.85-7.26 (*m*, 13H, Ar-H), 7.05 (*m*, 1H, Ar-H), 3.58 (*s*, 3H, 1-OCH_3), 3.42 (*s*, 3H, 4-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 215.6 (*s*, br, C≡O), 212.8 (*s*, br, $^3J_{PC}$ =6.5 Hz, C≡O), 211.5 (*s*, br, C≡O), 210.3 (*s*, br, C≡O), 191.3 (*s*, C-2), 179.7 (*s*, C-1), 162.0 (*s*, C-4), 146.3 (*s*, $^2J_{PC}$ =7.6 Hz, C-2'), 135.1 (*s*, C-3), 135.0 (*d*, J_{PC} =10.6 Hz), 133.3 (*d*, J_{PC} =9.4 Hz), 132.8 (*d*), 132.5 (*d*), 132.4 (*d*), 132.3 (*d*), 131.8 (*d*, J_{PC} =11.1 Hz), 129.0 (*d*, J_{PC} =12.1 Hz), 128.3 (*d*, J_{PC} =13.7 Hz), 127.9 (*s*, $^1J_{PC}$ =84.1 Hz), 127.8 (*s*, $^1J_{PC}$ =85.5

Hz), 127.6 (*d*, J_{PC} =12.8 Hz), 127.0 (*s*, $^1J_{PC}$ =86.1 Hz), 51.5 (*q*, 4-OCH_3), 50.0 (*q*, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 46.0. ESMS: m/z 620 $(M+NH_4)^+$, 603 $(M+H)^+$.

6% of an unidentified orange crystalline solid (5 mg, 3% based on a molecular mass of 716) which also crystallised from $CHCl_3$/pentane as small orange rosettes. IR ($CHCl_3$): υ(CO) 2027(s), 1942(s), 1918(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.83-7.16 (*m*, 14H, Ar-H), 4.00 (*s*, 3H, -OCH_3), 3.80 (*s*, 3H, -OCH_3), 3.52 (*s*, 3H, -OCH_3), 3.16 (*s*, 3H, -OCH_3). ESMS: m/z 775 $(M+NH_4+CH_3CN)^+$, 734 $(M+NH_4)^+$, 717 $(M+H)^+$.

(b) Excess Dimethyl Acetylenedicarboxylate

The orthomanganated chalcogenide [**(31)**; 200 mg, 0.434 mmol] and dimethyl acetylenedicarboxylate (0.112 mL, 0.911 mmol) were refluxed in benzene for 16 hours. The residue was chromatographed (p.l.c., 1:4 petroleum spirit/ethyl acetate) to give:

Triphenylphosphine sulfide [**(28)**; 27 mg, 21%].

E-1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]tetra-carbonylmanganese **(39)** (138 mg, 53%).

Unidentified orange solid (15 mg, 5%).

(Yields based upon integration of proton methoxy singlets).

(c) Excess Dimethyl Acetylenedicarboxylate and a Longer Reaction Time

The orthomanganated chalcogenide [**(31)**; 0.090 mL, 0.240 mmol] and dimethyl acetylenedicarboxylate (0.090 mL, 0.732 mmol) were refluxed in benzene for 72 hours. T.l.c. showed no major products except $Ph_3P=S$ **(28)** so the reaction was abandoned (IR showed no sign of the desired products).

Reaction of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis-(trimethylphosphite)manganese with Dimethyl Acetylenedicarboxylate in Benzene

The orthomanganated chalcogenide [**(40)**; 112 mg, 0.172 mmol] and dimethyl acetylenedicarboxylate (0.056 mL, 0.416 mmol) were refluxed in benzene for 3 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 6 mg, 10%].

Unreacted starting material [**(31)**; 11 mg, 9%].

E-1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]-dicarbonylbis(trimethylphosphite)manganese [**(41)**; 41 mg, 30%] which crystallised from $CHCl_3$/pentane as chunky yellow crystals, m.p. 179-182 °C. IR ($CHCl_3$): υ(CO) 1950(s), 1870(s). ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.70-7.10 (*m*, 4H, Ar-H), 3.64 (*m*, 18H, $P(OCH_3)_3$), 3.42 (*s*, 3H, $-COOCH_3$), 3.19 (*s*, 3H, $-COOCH_3$). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 176.5, 175.7, 42.9. ESMS: m/z 812 $(M+NH_4)^+$, 795 $(M+H)^+$.

Reaction of Orthomanganated Triphenylphosphine Sulfide with Methyl Propiolate in Benzene

The orthomanganated chalcogenide [**(31)**; 102 mg, 0.222 mmol] and methyl propiolate (0.030 mL, 0.337 mmol) were refluxed in benzene for 3.5 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 7 mg, 11%].

Z-1-methoxycarbonyl-2-[(2-diphenylthiophosphinyl)phenyl]tetracarbonyl-manganese [**(42)**; 49 mg, 41%] as a yellow oil. IR ($CHCl_3$): υ(CO) 2077(m), 1997(vs, br), 1989(vs, br), 1947(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.72-7.48 (*m*, 12H, Ar-H), 7.37 (*s*, 1H, H-3), 7.22 (*m*, 1H, H-5'), 6.99 (*m*, 1H, H-6'), 3.45 (*s*, 3H, 1-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 217.3 (*s*, br, C≡O), 213.7 (*s*, br, C≡O), 212.7 (*s*, br, 2xC≡O), 179.1 (*s*, C-2),

165.6 (*s*, C-1), 147.1 (*s*, $^2J_{PC}$ =8.1 Hz, C-2'), 142.5 (*d*, C-3), 132.7-131.6 (*d*, C-4', C-6', C-2", C-4", C-6"), 128.9 (*d*, $^3J_{PC}$ =12.2 Hz, C-3", C-5"), 128.8 (*d*, C-3'), 128.3 (*s*, $^1J_{PC}$ =84.8 Hz, C-1"), 126.7 (*d*, $^3J_{PC}$ =12.5 Hz, C-5'), 125.8 (*s*, $^1J_{PC}$ =85.0 Hz, C-1'), 50.7 (*q*, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 45.2. ESMS: m/z 562 $(M+NH_4)^+$, 545 $(M+H)^+$, 517 $(M+H-CO)^+$.

Methyl E-3-[(2-diphenylthiophosphinyl)phenyl]-prop-2-enoate [**(43)**; 11 mg, 13%] as a colourless oil. Anal. Found: M^+, 378.0843; $C_{22}H_{19}O_2PS$ calcd.: M, 378.0843. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.25 (*d*, ^3J =15.7 Hz, 1H, H-3), 7.84 (*m*, 4H, Ar-H), 7.50 (*m*, 8H, Ar-H), 7.30 (*m*, 1H, H-5'), 7.16 (*m*, 1H, H-6'), 6.08 (*d*, ^3J =15.7 Hz, 1H, H-2), 3.64 (*s*, 3H, 1-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 166.4 (*s*, C-1), 143.2 (*d*, $^3J_{PC}$ =7.0 Hz, C-3), 138.4 (*s*, $^2J_{PC}$ =7.4 Hz, C-2'), 133.4 (*s*, $^1J_{PC}$ =82.9 Hz, C-1'), 133.1 (*d*, $^2J_{PC}$ =10.9 Hz, C-6'), 132.5 (*d*, $^2J_{PC}$ =10.6 Hz, C-2", C-6"), 132.1 (*s*, $^1J_{PC}$ =84.8 Hz, C-1"), 132.0 (*d*, $^4J_{PC}$ =2.0 Hz, C-4'), 131.9 (*d*, $^4J_{PC}$ =2.1 Hz, C-4"), 129.1 (*d*, $^3J_{PC}$ =12.3 Hz, C-5'), 128.6 (*d*, $^3J_{PC}$ =12.5 Hz, C-3", C-5"), 128.6 (*d*, C-3'), 120.0 (*d*, C-2), 51.6 (*q*, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.4. GCMS: m/z 378 (M^+), 319 $(M-COOCH_3)^+$.

5.6.6 Unsuccessful Coupling Reactions

Attempted Reactions of Orthomanganated Triphenylphosphine Sulfide with Diphenyl Acetylene

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and diphenyl acetylene (55 mg, 0.306 mmol) were refluxed in benzene for 24 hours. T.l.c. showed no major organic products except the demetalated product **(28)** and unreacted diphenyl acetylene so the reaction was abandoned. Similarly, no products were observed when the reaction was repeated in petroleum spirit for 24 hours, or in acetonitrile for 3 hours.

Attempted Reaction of Orthomanganated Triphenylphosphine Sulfide with 3-Butyn-1-ol in Benzene

The orthomanganated chalcogenide [**(31)**; 105 mg, 0.228 mmol] and 3-butyn-1-ol (0.025 mL mg, 0.330 mmol) were refluxed in benzene for 8

hours. T.l.c. showed no major organic products except the demetalated product **(28)** so the reaction was abandoned.

Attempted Reaction of Orthomanganated Triphenylphosphine Sulfide with 2-Methyl-3-Butyn-2-ol in Benzene

The orthomanganated chalcogenide [**(31)**; 105 mg, 0.228 mmol] and 2-methyl-3-butyn-2-ol (0.044 mL, 0.454 mmol) were refluxed in benzene for 16 hours. T.l.c. showed no major organic products except $Ph_3P{=}S$ **(28)** so the reaction was abandoned.

Attempted Reaction of Orthomanganated Triphenylphosphine Sulfide with Acetylene in Petroleum Spirit (60-80)

The orthomanganated chalcogenide [**(31)**; 180 mg, 0.392 mmol] and a continuous stream of acetylene were refluxed in petroleum spirit (60-80) for 6 hours. T.l.c. showed no major organic products except $Ph_3P{=}S$ **(28)** so the reaction was abandoned.

Attempted Reaction of Orthomanganated Triphenylphosphine Sulfide with Trimethylsilylacetylene in Benzene

The orthomanganated chalcogenide [**(31)**; 101 mg, 0.219 mmol] and trimethylsilylacetylene (0.043 mL, 0.304 mmol) were refluxed in benzene for 8 hours. T.l.c. showed no major organic products except $Ph_3P{=}S$ **(28)** so the reaction was abandoned.

Attempted Reaction of Orthomanganated Triphenylphosphine Sulfide with 2-Methyl-1-buten-3-yne in Acetonitrile

The orthomanganated chalcogenide [**(31)**; 100 mg, 0.217 mmol] and 2-methyl-1-buten-3-yne (0.029 mL, 0.305 mmol) were refluxed in acetonitrile for 2.5 hours. T.l.c. showed no major organic products except $Ph_3P{=}S$ **(28)** so the reaction was abandoned.

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Chapter Six

Reaction of Orthomanganated Compounds with Sulfur Dioxide

6.1 Introduction

The insertion of SO_2 into a variety of M-X bonds is well established. Examples include insertions into metal-carbon σ-bonds, metal-carbon π- (or *polyhapto*) bonds [1], transition metal-Group 14 metal bonds [2], transition metal-transition metal bonds [3], and metal-oxygen bonds [4]. There has also been a report of SO_2 inserting into a M-H bond [5].

Insertion of SO_2 into the metal-carbon bond of coordinatively saturated transition metal alkyls and aryls has been extensively studied and is one of the best understood reactions in organotransition-metal chemistry [6].

In contrast to CO insertion where only an acyl species can be obtained, the products from SO_2 insertion vary depending on the types of linkage formed (Figure 6.1).

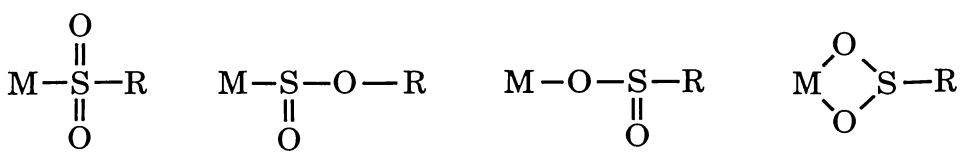
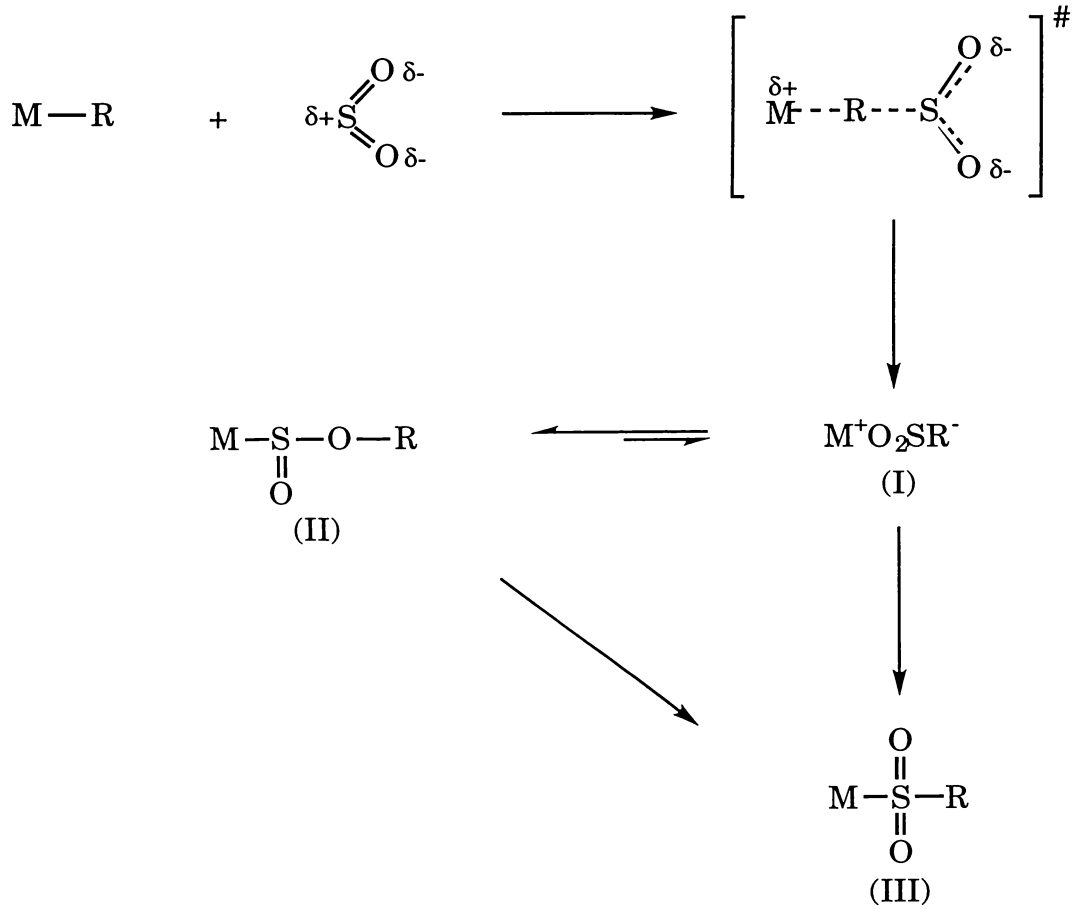


Figure 6.1

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

Wojcicki and Hartman found [7] SO_2 readily inserted into the metal-alkyl bond of $RM(CO)_5$ (M=Mn, R=Me, Et, CH_2Ph; M=Re, R=Me, CH_2Ph) to give the corresponding S-sulfinatopentacarbonyl complexes of Mn and Re in good yields. In contrast, $PhMn(CO)_5$ gave a low yield and only under forcing conditions. Alkyl- and aryl-cyclopentadienyliron dicarbonyl compounds were also found to react with SO_2 to give the corresponding S-sulfinato complexes.

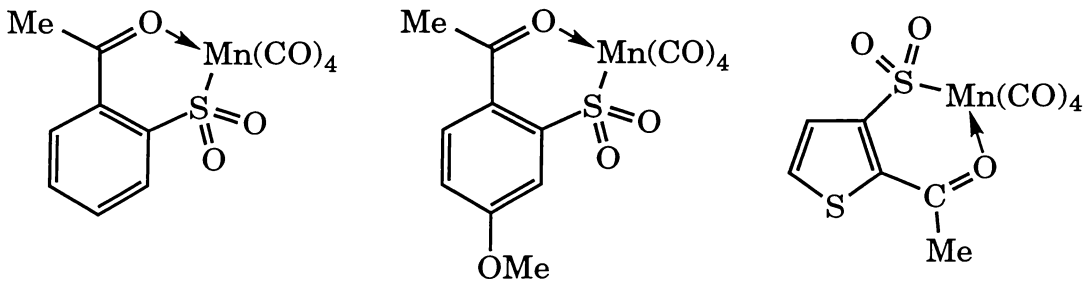
Kinetic studies on the insertion of SO_2 into $RFe(CO)_2Cp$ and other complexes indicates the insertion product is formed by an electrophilic cleavage process, involving backside electrophilic attack of SO_2 at the α-carbon, as shown in Scheme 6.1 [8].



Scheme 6.1

The ion-pair intermediate (I) combines to yield the SO_2-inserted product (III) directly or via an intermediate O-sulfinate (II), which is too unstable to be isolated before isomerising to give the S-bonded sulfinate (III).

The insertion of SO_2 into the Mn-C bonds of orthomanganated complexes has received relatively little attention compared to insertion of other unsaturated species such as alkenes and alkynes. Cooney reported [9] that the reaction of SO_2 with orthomanganated acetophenone, 4'-methoxyacetophenone and 2-acetylthiophene yielded the corresponding S-sulfinate complexes (Figure 6.2) in excellent yield.



(E) (F) (G)

Figure 6.2

The facile insertion of SO_2 into the Mn-C_{aryl} bond of orthomanganated ketones contrasts with the poor reactivity of $PhMn(CO)_5$. The reason for this increased reactivity is presumably the increased electron density at the aryl carbon for the orthomanganated complex as a result of coordination to manganese by the oxygen atom.

A single crystal X-ray structure of (F) revealed that the six-membered metallocyclic ring differs considerably from that of its five-membered precursor. Previously reported crystal structures of orthomanganated complexes containing a five-membered chelate ring have shown that the ring is essentially planar [10]. In contrast, the six-membered chelate ring in (F) shows significant deviation from planarity, presumably as a result of the requirement for the S atom to assume tetrahedral geometry.

As part of an effort to extend the scope of this reaction, recent work by Depree [11] and Dinger [12] has shown that it is less straightforward when applied to other orthomanganated substrates. Depree reported that the insertion of SO_2 into orthomanganated complexes of *N*,*N*-dimethylbenzamide, benzophenone and various methoxy-substituted acetophenones proceeded cleanly in most cases (as shown by IR), but upon attempted crystallisation the S-sulfinate appeared to undergo rearrangement to yield dimeric or other unexpected complexes. An example of a dimeric tricarbonyl species obtained from the reaction of orthomanganated 2',3',4'-trimethoxyacetophenone with SO_2, which was identified by X-ray crystallography is shown in Figure 6.3.

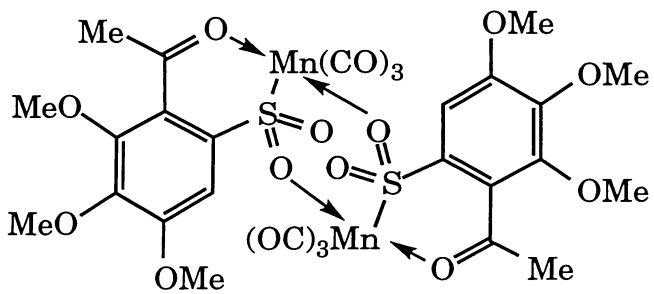


Figure 6.3

The most intriguing SO_2-insertion reaction was that with *N*,*N*-dimethylbenzamide which yielded the totally unexpected insertion product shown in Figure 6.4, identified by X-ray crystallography. The mechanism of formation is still unclear.

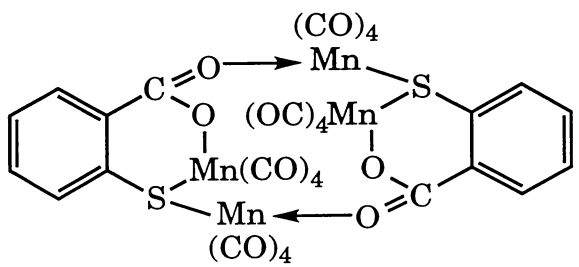


Figure 6.4

Attempted SO_2 insertion into the Mn-C_{aryl} bond of orthomanganated arylhydrazones met with extremely limited success. Dinger reported that SO_2 did not readily insert into these complexes and that the

reactions were not clean. The tentative assignment of the two complexes shown in Figure 6.5 are based solely on the IR spectra of the crude reaction mixtures.

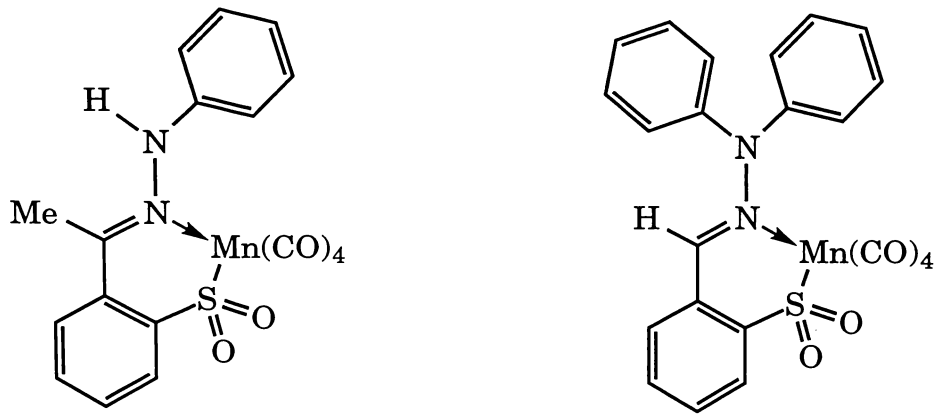
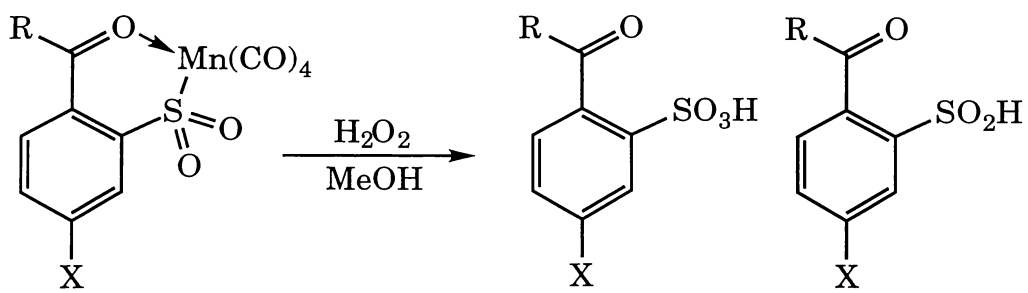


Figure 6.5

A recent investigation [11] has demonstrated the synthetic potential of SO_2-inserted cyclomanganated complexes in the formation of sulfonates (H) and sulfinates (I) via oxidative demetalation (Equation 6.1). Oxidation of these complexes in methanol with iodine and ceric ammonium nitrate appeared to be very selective for the formation of the sulfonate, while oxidation with hydrogen peroxide yielded both the sulfonate and sulfinate. It was found that the reaction conditions could be optimised to favour the formation of either the sulfonate or sulfinate. This was achieved by altering the rate of addition of H_2O_2 and adjusting the temperature at which the reaction was carried out.



(H) (I)

R=Me; X=OMe
R=Ph; X=H

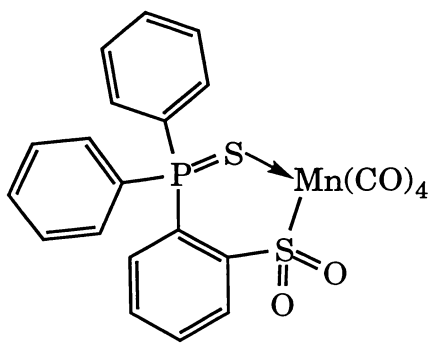
Equation 6.1

Given the variation found for this previous work, it was of interest to investigate the reactions of the orthomanganated chalcogenides with SO_2.

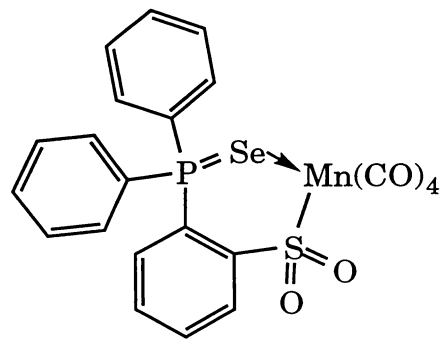
6.2 Results and Discussion

6.2.1 Reactions of Orthomanganated Triphenylphosphine Chalocogenides with SO_2

Orthomanganated triphenylphosphine sulfide **(31)** and selenide **(32)** were each reacted with neat SO_2 at 52 °C for 18 hours. SO_2 was found to insert efficiently and cleanly into the Mn-C_{aryl} bond of orthomanganated Ph_3P=S **(31)** and Ph_3P=Se **(32)** to give the corresponding S-sulfinate complexes **(44)** and **(45)**, incorporating novel six-membered metallocyclic rings in excellent yields (89 and 84% respectively).



(44)



(45)

Figure 6.6

Similarly to previously prepared SO_2-inserted orthomanganated compounds, these complexes were readily identified by the distinctive upward shift in the IR stretches of the metal carbonyls from those in the starting material. This shift is caused by a decrease in electron density on the manganese due to the replacement of the Mn-aryl carbon with an electronegative sulfur atom. A single crystal X-ray structure of **(45)**, which contains five different atoms in the six-membered chelate ring, was determined and is discussed in Section 6.3.

The isolation and purification of complexes **(44)** and **(45)** was straightforward. The reaction residues were dissolved in dichloromethane, filtered to remove any insoluble material and the

solvent removed by evaporation under reduced pressure. The resulting solid residues were recrystallised from dichloromethane/pentane via vapour diffusion (4 °C). Both compounds were readily handled and appeared to be air stable. They could be stored at -20 °C for extended periods without any appreciable decomposition.

However, in solution the insertion reaction appears to be reversible. This was apparent from a ^{13}C NMR spectrum acquired overnight at 27 °C, which indicated reversion of ~10% of the product to the orthomanganated precursor. No such reversion was observed in solution at low temperatures. This concurs with observations made by Cooney, who reported up to 25% reversion to the orthomanganated ketone precursor after 24 hours for the compounds shown in Figure 6.2. This behaviour contrasts with that observed for the majority of other transition metal sulfinates in which elimination of SO_2 was not common. Examples of desulfination appear to be limited to complexes such as $CpFe(CO)_2S(O)_2C_6F_5$ [6], $CpMo(CO)_3S(O)_2CH_2Ph$ [13], and a few complexes of rhodium [14], iridium [15], palladium [16] and platinum [17]. Several of these complexes possess a vacant metal orbital which presumably provides a pathway for the migration of R from $MS(O)_2R$. The absence of a vacant coordination site, or a difficulty in making one available via ligand dissociation, presumably prevents facile desulfination.

The ESMS spectra of compounds **(44)** (Figure 6.7) and **(45)** (Table 6.1) showed clean $(M+H)^+$ peaks together with the typical adduct peak of $(M+NH_4)^+$ (the origins of which are discussed in Appendix I). The formation of the quasi-molecular ion $(M+H-CO+CH_3CN)^+$ was of interest because it was the first time such an ion had been observed in the present study.

In contrast to the reactions above, the insertion of SO_2 into the $Mn-C_{aryl}$ bond of orthomanganated $Ph_3P=O$ **(30)** did not go cleanly. An IR spectrum of the orange oil obtained showed the possible presence of the corresponding S-sulfinate complex and at least one unknown compound. All of the orthomanganated starting material had been

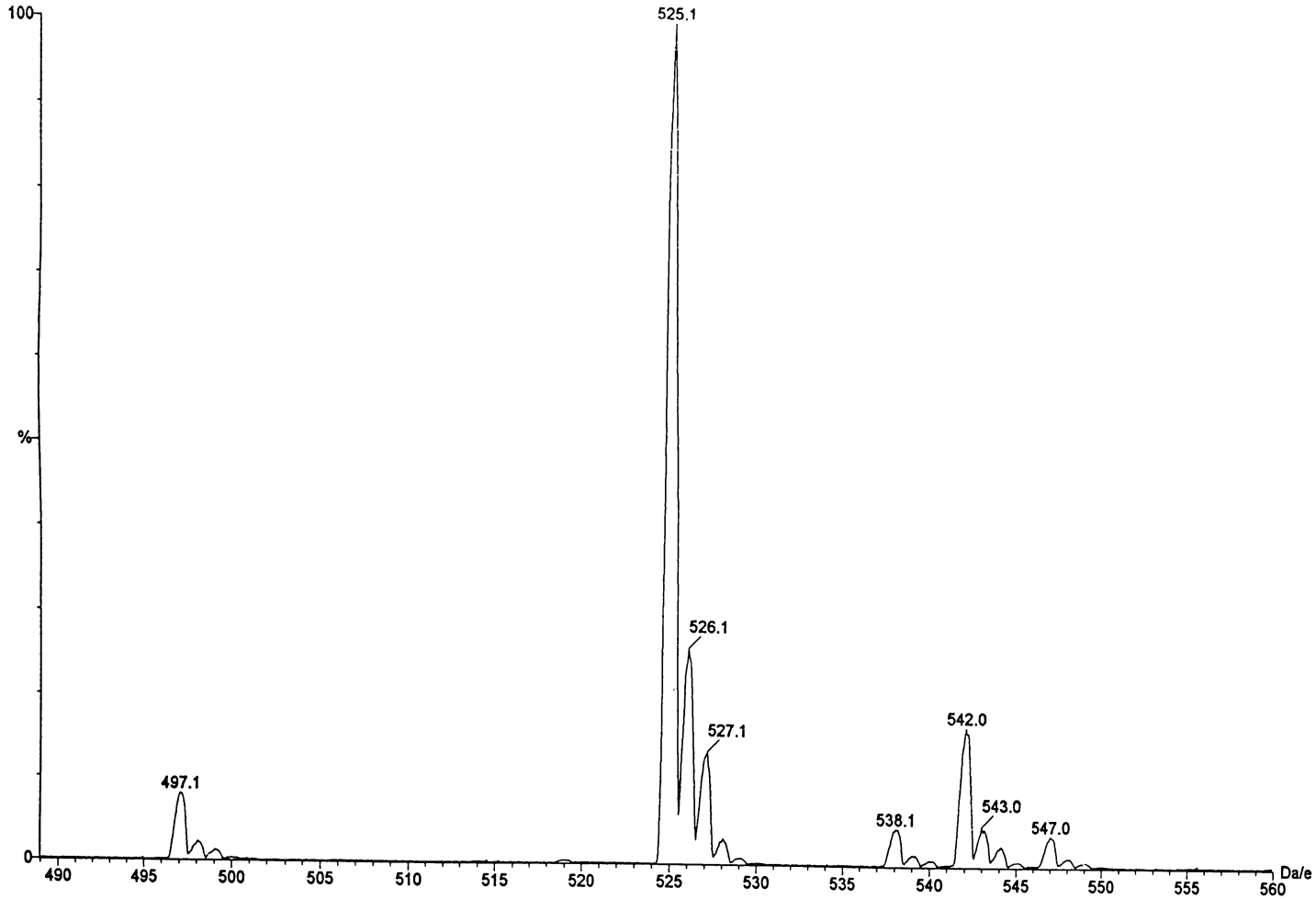


Figure 6.7 ESMS of η^2-(S,S)-[(2-diphenylthiophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (44)

Table 6.1 Assignment of ESMS Spectra of Complexes (44) and (45)

Complex (44) ion (m/z)	Assignment	Complex (45) ion (m/z)
547	$(M+Na)^+$	-
542	$(M+NH_4)^+$	590
538	$(M+H-CO+CH_3CN)^+$	-
525	$(M+H)^+$	573
497	$(M+H-CO)^+$	545
-	$(M+H-4CO+CH_3CN)^+$	502
-	$(M+H-4CO)^+$	461

consumed. The products could not be separated as the oil failed to crystallise and conventional chromatography using silica or alumina (with a range of different solvents) led to the complexes becoming irreversibly bound or decomposing on the plate.

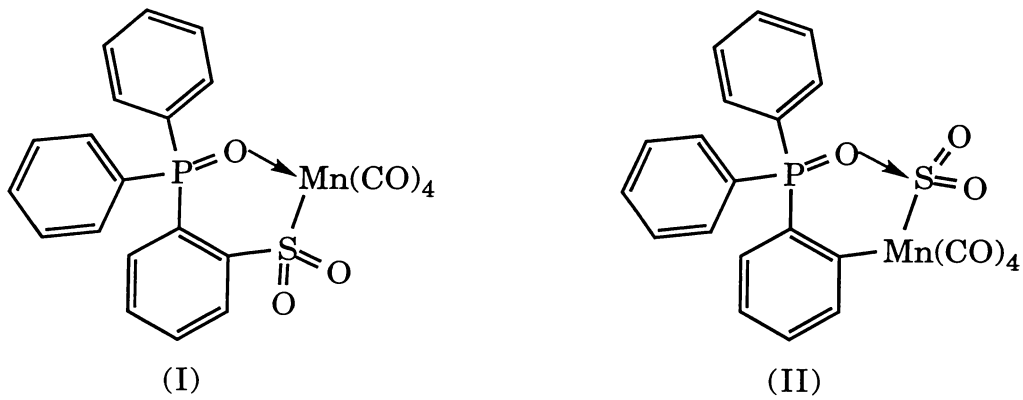
Both ESMS and ^{31}P NMR spectra confirmed the presence of two compounds. ^{31}P NMR showed two signals with chemical shifts of 44.4 and 41.9 ppm while ESMS indicated that the two compounds present possessed molecular masses of 786 and 508 with the peaks arising from the latter being the most intense (Table 6.2).

Table 6.2 Assignment of the ESMS Spectrum of the Crude Reaction Mixture Obtained from the Reaction of (30) with SO_2

Ion (m/z)	Assignment
800	$(M+H-CO+CH_3CN)^+$
787	$(M+H)^+$
759	$(M+H-CO)^+$
557	-
522	$(M'+H-CO+CH_3CN)^+$
509	$(M'+H)^+$
481	$(M'+H-CO)^+$

The peak at 557 mass units did not appear to belong to either of the two products assigned. However, it must be of some significance as it was reproducible and stronger than the three peaks of higher mass.

The peaks corresponding to a molecular mass of 508 are consistent with the formation of the corresponding SO_2-inserted S-sulfinate complex (I) shown in Figure 6.7. However, the possibility of SO_2 inserting into the metal-oxygen bond of **(30)**, giving rise to the product (II) shown in Figure 6.7 must also be considered as the insertion of SO_2 into M-O bonds has been previously observed.



(I) (II)

Figure 6.7

The inability of these compounds to withstand conventional chromatography severely limited attempts to ascertain which of the two possible SO_2-inserted products had formed. ^{13}C NMR spectroscopy would have readily shown which product had formed as the magnitude of chemical shift arising from C-1 would be indicative. However, the apparent presence of paramagnetic species in solution led to major shimming problems and as a result, good quality ^{13}C NMR spectra could not be obtained.

The IR bands of the metal carbonyls of complexes **(44)** and **(45)** along with those which were tentatively assigned as belonging to the SO_2-inserted orthomanganated $Ph_3P{=}O$ complex **(46)** are given in Table 6.3.

Table 6.3 M-C≡O Infrared Stretching Frequencies of S-sulfinate Complexes derived from Orthomanganated Chalocogenides

S-sulphinate complex	υ(C≡O) (cm^{-1})
X=O **(46)**	2109(m), 2044(br, vs), 2036(br, vs), 2010(s)
X=S **(44)**	2101(m), 2031(br, vs), 2013(br, vs), 1986(s)
X=Se **(45)**	2096(m), 2026(br, vs), 2009(br, vs), 1982(s)

Comparison of these bands reveals a downward trend within the series similar to that seen in the orthomanganated precursor series, which presumably reflects the electronegativity (and hence donor ability) of the donor atom coordinated to the manganese. Based on this observation and the fact that all previous reactions of orthomanganated complexes with SO_2 resulted in the insertion of SO_2 into the Mn-C_{aryl} bond, the SO_2-inserted complex with a molecular mass of 508 was tentatively assigned as belonging to the corresponding S-sulfinate complex **(46)** (structure (I) Figure 6.7). The formation of quasi-molecular ions observed for **(46)** (Table 6.2) are consistent with those of the sulfur and selenium analogues (Table 6.1).

The ^{31}P NMR spectrum of the mixture containing **(46)** showed two sharp signals with chemical shifts of 44.4 and 41.9 ppm, with the former being approximately three times larger than the latter. Due to the large difference in intensities between the two signals (assuming the relaxation times of the respective phosphorus nuclei are similar), and IR indicating that **(46)** is the major component, the signal at 44.4 ppm was tentatively assigned to **(46)**.

A tentative assignment of the second complex in the mixture which had an apparent molecular mass of 786 could not be made, as its mass did not correspond to any known type of SO_2-inserted product.

The ^{31}P NMR chemical shifts of the three S-sulfinate complexes along with their corresponding metalated and free ligand values are given in Table 6.4.

Table 6.4 ^{31}P NMR Chemical Shifts of S-sulfinate Complexes and Related Compounds

S-sulphinate complex	δ (ppm)	orthomanganated precursor δ (ppm)	parent δ (ppm)
X=O (**46**)	44.4	64.4	29.0
X=S (**44**)	34.6	66.6	43.3
X=Se (**45**)	15.6	52.2	35.2

Comparison of the ^{31}P chemical shifts of the S-sulfinate complexes **(44)**, **(45)** and **(46)** with those of the corresponding orthomanganated precursors, in each case shows a significant shift to higher field, clearly indicating this to be a reliable method of distinguishing between the two different types of compound.

Studies by Garrou have shown that incorporation of phosphorus into four- and six-membered metallocyclic rings results in the shielding of the phosphorus atom (with a phosphorus atom contained within 4-membered rings generally being shielded more than those in 6-membered rings), compared to that in a non-chelated complex [18]. This is in direct contrast to the observed deshielding of phosphorus atoms contained within a five-membered ring (Section 4.3.3). Results from previous studies on complexes containing a phosphorus atom within a six-membered metallocyclic ring, have shown that the ring contribution term Δ_R to the phosphorus chemical shift varied between ~ -1 and -17 ppm.

Due to the lack of ^{31}P NMR data for $Ph_3P=S$ in nonchelated complexes, the same assumption used initially in Section 4.3.3 and subsequently in Section 5.3 was employed to calculate approximate Δ_R values of the complexes **(44)**, **(45)** and **(46)**. It was therefore assumed that the contribution to the chemical shift arising from the coordination of manganese to the respective ligands would be small, so Δ (which is defined as the change in chemical shift between the metalated ligand and the free ligand) could be approximated to Δ_R. The values of Δ_R for

the S-sulfinate complexes **(44)** and **(45)** are -19.6 and -8.7 ppm respectively, which are consistent with those observed in previous studies, thus supporting the initial assumption.

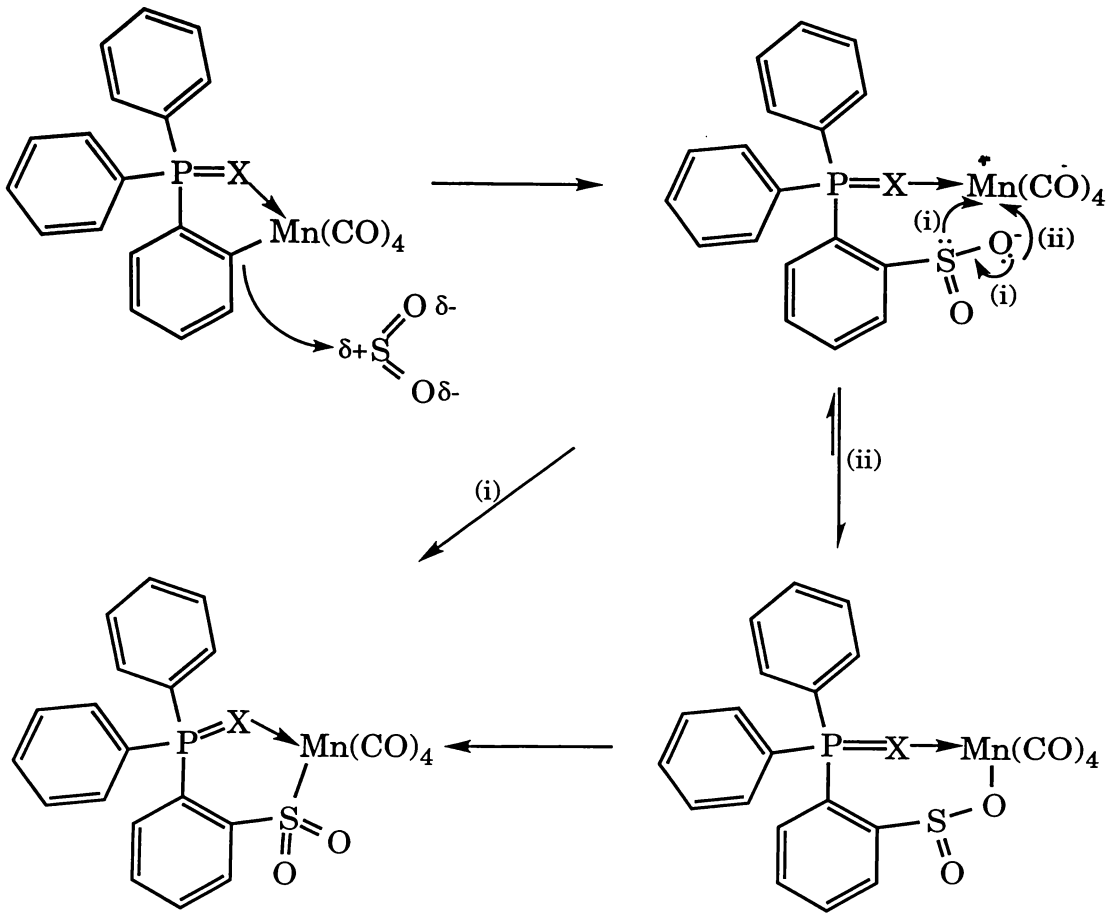
However in contrast, the deshielding of complex **(46)** by 15.4 ppm contradicts the expected shielding and casts doubt on either the validity of the initial assumption (as no firm prediction on the size of the ring that this complex contains can be made based on this Δ_R value) or the tentative assignment of **(46)**.

Overall, the usefulness of all Δ_R values calculated in this study to ascertain the size of the metallocyclic ring present in the various complexes appears to be somewhat limited. With the exception of phosphorus atoms incorporated into five-membered rings, which give rise to distinctive downfield phosphorus chemical shifts of Δ_R ~ 21-35 ppm (the theoretical origin of this unique deshielding effect is unknown), the use of Δ_R values to distinguish between other ring sizes, such as six- and seven-membered rings, is inconclusive because of the overlapping Δ_R ranges observed for each ring size.

As previously mentioned the S-sulfinate product is believed to form by an electrophilic cleavage process, involving backside electrophilic attack of SO_2 at the α-carbon (Scheme 6.1). A similar reaction scheme can also be envisaged for the insertion of SO_2 into the Mn-C_{aryl} bond of the orthomanganated triphenylphosphine chalcogenides (Scheme 6.2).

6.2.2 Reactions of Trimethylphosphite-Substituted Orthomanganated Complexes with SO_2

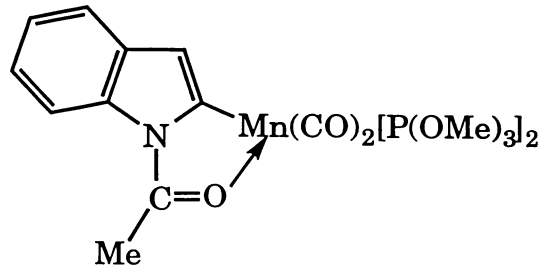
Because of the electrophilic nature of the attacking SO_2, it can be reasoned that replacement of the ligand CO with a stronger base such as trimethylphosphite will increase the electron density on the metal atom, which in turn should result in a greater carbanionic character of the metal-bonded aryl carbon, thus promoting its reaction with SO_2.



Scheme 6.2

This effect has been observed in systems such as $CpFe(CO)(PPh_3)CH_2Ph$, where the rate of SO_2 insertion is rapid in chloroform solution, while the parent $CpFe(CO)_2CH_2Ph$ is inert under comparable conditions [19]. Further examples of this general reactivity pattern include $CpMo(CO)_2(PPh_3)Me$ [13], $CpFe(CO)[P(n\text{-}Bu)_3]Me$ and $CpFe(CO)(PPh_3)Me$ [19] which insert SO_2 much more rapidly than the corresponding complexes, $CpMo(CO)_3Me$ and $CpFe(CO)_2Me$.

Depree reported that the attempted reaction of SO_2 with orthomanganated 1-acetylindole at 55 °C showed no sign of reaction, while at higher temperature (75 °C) all of the orthomanganated starting material was consumed with the formation of an unidentified insoluble white material [11]. It was hoped that the trimethylphosphite substituted derivative **(18)** (Figure 6.8) would facilitate the insertion of SO_2 into the $Mn\text{-}C_{aryl}$ bond of the orthomanganated indole.



(18)

Figure 6.8

In contrast to previously studied orthomanganated substrates, which resulted in a yellow solution upon treatment with neat SO_2, the trimethylphosphite substituted derivative **(18)** resulted in a dark red solution. This could possibly be attributed to the presence of a charge transfer band arising from the electron-rich nature of the substrate involved, because after the ampoule was opened and the SO_2 evaporated an IR spectrum showed that the remaining yellow oil was **(18)**. Alternatively, a rapid insertion-elimination SO_2 reaction may have been facilitated by the stronger Lewis base ligands as observed in the examples previously mentioned. But, by the time the excess SO_2 had evaporated off, the SO_2-inserted product could have reverted back to the orthomanganated precursor, although this seems unlikely.

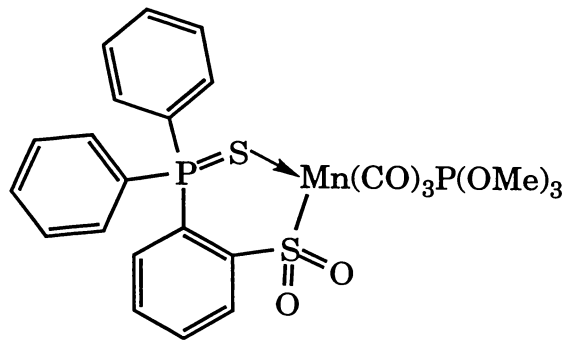
The phosphite-substituted orthomanganated indole **(18)** was reacted with SO_2 at 52 °C for 22 hours. The reaction was worked up as previously described and an IR spectrum of the resultant orange oil showed that the reaction of SO_2 with **(18)** was not clean. It showed the presence of a considerable amount of unreacted starting material **(18)** and a number of other absorptions in the metal carbonyl region. Repeating the reaction with a longer reaction time (72 hours) resulted in major consumption of **(18)**, shown by infrared spectroscopy, and the appearance of the same unidentified absorptions observed above in the metal carbonyl region. Due to chromatographic constraints and the failure of the oil to crystallise, the mixture could not be separated.

ESMS spectra confirmed the presence of a small amount of **(18)** (mass 517) and one other compound with an apparent molecular mass of 657. There was no sign of the desired S-sulfinate complex which would have a molecular mass of 581. Only a poor quality ^{31}P NMR spectrum of the oil could be obtained (probably due to the presence of paramagnetic species), but this did show the presence of three other chemical shifts apart from that of **(18)** at 184.5, 80.1 and 35.0 ppm. All three signals were of similar intensity, with the signal at 80.1 ppm somewhat sharper than the remaining two signals. No tentative assignments of these compounds could be made.

As an alternative way of inducing SO_2 insertion, photochemically induced reactions were investigated. Preliminary work was carried out on a substrate that underwent thermally promoted SO_2 insertion efficiently. Orthomanganated $Ph_3P{=}S$ **(31)** was dissolved in SO_2 and the ampoule was irradiated at 366 nm for 18 hours. This resulted in the complete conversion to the SO_2-inserted S-sulfinato complex **(44)** (87%).

However, when **(18)** was subjected to similar experimental conditions, IR and ESMS spectra indicated that no reaction had occurred, so the reaction was abandoned. Further investigation may be warranted when a more powerful UV source becomes available.

To determine whether or not the trimethylphosphite ligands were complicating the outcome of the SO_2 insertion reaction, the bis(trimethylphosphite) orthomanganated $Ph_3P{=}S$ derivative **(40)** was reacted with SO_2 under thermal conditions. An IR spectrum of the orange oil obtained, indicated the presence of a manganese tricarbonyl species identified by its distinctive pattern along with a couple of other minor absorptions in the metal carbonyl region. The mixture of compounds could not be separated. An ESMS spectrum suggested the possibility of two compounds of molecular masses 434 and 620. The peaks corresponding to a molecular mass of 620 are consistent with the complex shown in Figure 6.9. The subsequent ligand exchange of $P(OMe)_3$ by CO under these conditions is feasible. No tentative assignment could be made for the remaining molecular ion.



(47)

Figure 6.9

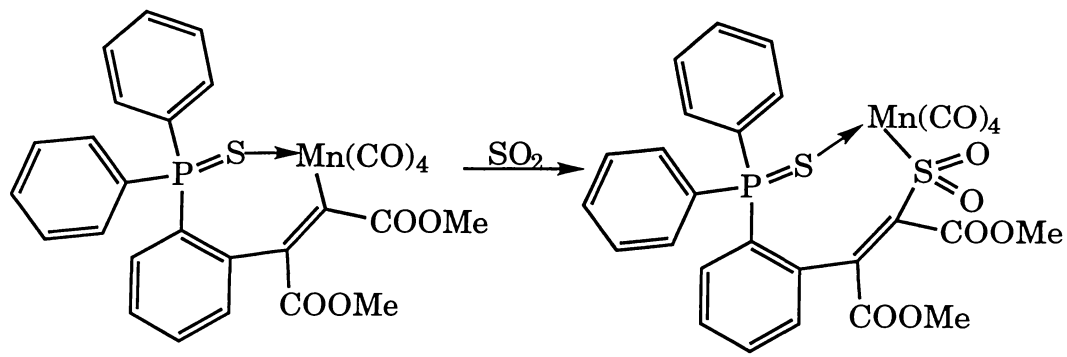
A ^{31}P NMR spectrum revealed that the reaction was not as clean as initially thought. The spectrum showed an intense signal at 72.8 ppm along with several minor signals at 124.7, 43.2, 36.9, 35.3, and 34.3 ppm. Despite the apparent presence of many products, none of the chemical shifts are consistent with the expected chemical shift of a manganese-coordinated $P(OMe)_3$ ligand which is normally found around ~175 ppm. This creates uncertainty about the existence of complex **(47)**.

It should be noted this was only a preliminary investigation using substrates which were synthesised for other areas of work. Mono-substituted tertiary phosphine derivatives were used to facilitate the insertion of SO_2 into M-C bonds in previous work [19,20]. It is therefore possible that the di-substituted *bis*-$P(OMe)_3$ complexes **(18)** and **(40)** do not favour the efficient insertion of SO_2 into the Mn-C_{aryl} because of steric crowding, which is particularly evident from the crystal structure of **(40)** (Section 5.5).

Despite the apparent lack of success in this area, a more detailed study of mono-substituted complexes with phosphine ligands which are known to facilitate SO_2 insertion such as triphenyl- and tributyl-phosphine may still be warranted in an effort to establish an alternative method to insert SO_2 into orthomanganated compounds that do not react under standard conditions.

6.2.3 Attempted insertion of SO_2 into (39)

The multiple insertion of alkynes into the Mn-C_{aryl} bond of several orthomanganated complexes has been reported [20,21]. The reaction of the alkyne-inserted complex **(39)** with SO_2 was investigated to examine the possibility of the stepwise insertion of a second, different type of substrate into the remaining Mn-C bond. This could lead to the formation of complexes of the type shown in Equation 6.2. The possible successive insertion of two different substrates may be potentially useful in organic synthesis.



(39)

Equation 6.2

The reaction of **(39)** with SO_2 was carried out at 52 °C for 24 hours. IR and ESMS of the resultant yellow oil only showed the presence of the starting complex **(39)** confirming that no reaction had occurred. Identical results were observed when the reaction was repeated using longer reaction times (52 °C for 72 hours), higher temperatures (64 °C for 72 hours), and photochemically induced conditions (366 nm for 16 hours).

The failure of **(39)** to undergo the insertion of SO_2 may be rationalised by considering two factors which probably make this complex less than ideal for this reaction.

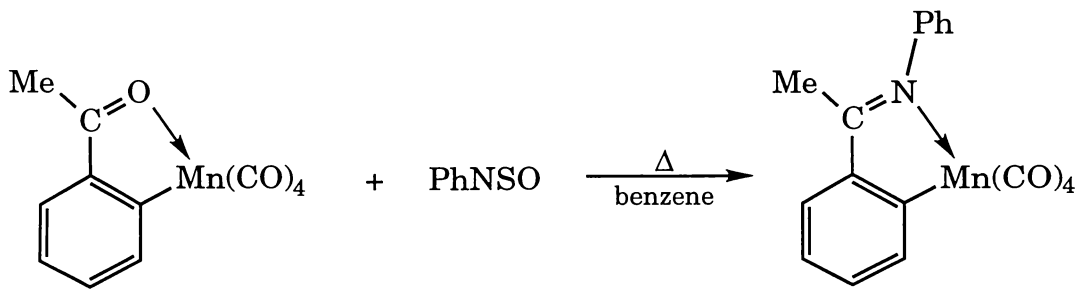
Firstly, the metalated carbon has an electron withdrawing carboxylate group bonded to it. This would presumably lead to the reduced carbanionic character of the carbon atom, which would not favour the electrophilic nature of the SO_2 insertion reaction. However, because of

the lack of general success with the alkyne-coupling reactions of orthomanganated $Ph_3P{=}S$ **(31)**, a suitable substrate to overcome this problem could not be obtained.

Secondly, if the SO_2 were to insert, it would lead to the formation of a presumably unfavourable eight-membered metallocyclic ring. To date, there have been no reports of complexes containing eight-membered metallocyclic rings derived from orthomanganated precursors.

6.2.4 Reaction of PhNSO with Orthomanganated Triphenylphosphine Sulfide (31)

Despite the *N*-sulfinylamine PhNSO being electronically similar to SO_2, it does not appear to react in an analogous manner. Wojcicki showed that PhNSO did not react with $CpFe(CO)_2Me$ at ambient temperature, whereas SO_2 inserted quickly and cleanly [22]. Cooney reported that the reaction of PhNSO with some orthomanganated acetophenones led to the formation of the corresponding orthomanganated imines [9]. An example is given in Equation 6.3.



Equation 6.3

It is thought that the orthomanganated imine is formed as a result of a nucleophilic attack of the nitrogen on the organic carbonyl group followed by rearrangement and elimination of SO_2.

The formation of corresponding orthomanganated imines is obviously not possible for orthomanganated $Ph_3P{=}S$, so the reaction of PhNSO with this substrate was investigated as it may allow the insertion of the *N*-sulfinylamine into the Mn-C_{aryl} bond.

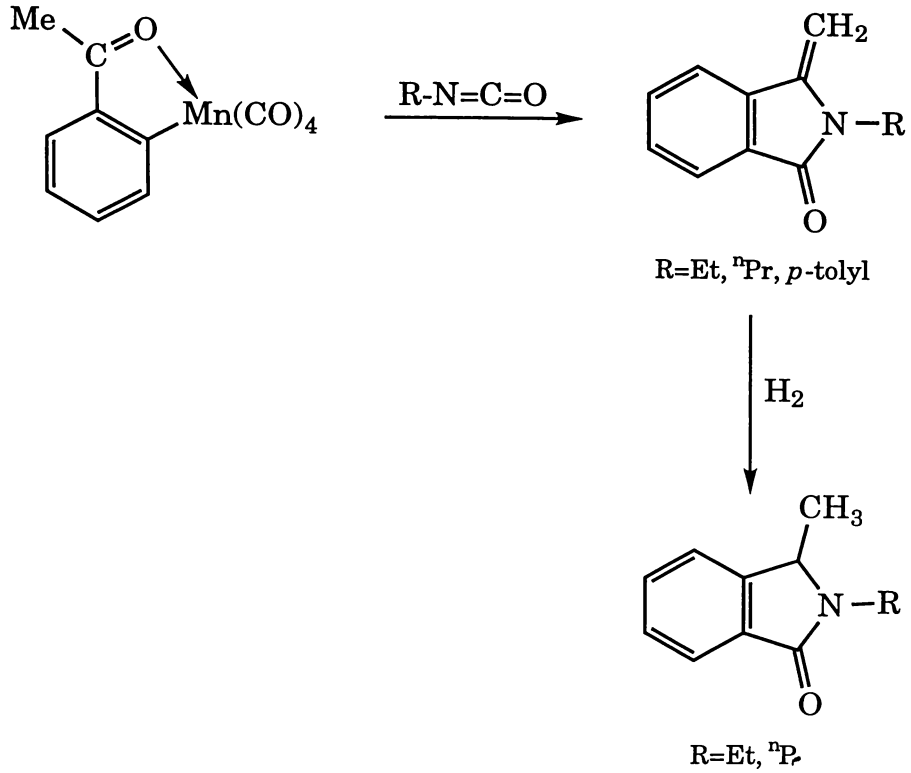
Orthomanganated $Ph_3P{=}S$ with excess PhNSO was refluxed in benzene for 24 hours. By this time an IR spectrum showed all of the orthomanganated starting material had been consumed. However, t.l.c. of the reaction mixture indicated that complete demetalation of **(31)** had occurred. Extensive demetalation was also reported [11] in the attempted reaction of orthomanganated 1-acetylindole with PhNSO in both refluxing acetonitrile and benzene, so the present reaction was abandoned.

6.2.5 Reaction of PhNCO with Orthomanganated Triphenylphosphine Sulfide (31)

Liebeskind's group recently investigated the reaction of orthomanganated acetophenone with organic isocyanates [23]. Insertion of the N=C bond of the isocyanate into the $Mn\text{-}C_{aryl}$ bond gave rise to 3-methylidene phthalimidines in good yields, which incorporate the core unit of a number of isoindole-derived alkaloids. The phthalimidines obtained from R-N=C=O (R=Et, ^{n}Pr) were unstable since phthalimidines bearing an aliphatic substituent on nitrogen readily undergo autoxidation to phthalidimides in air [24], so they were rapidly hydrogenated to give the related stable phthalimidines (Equation 6.4).

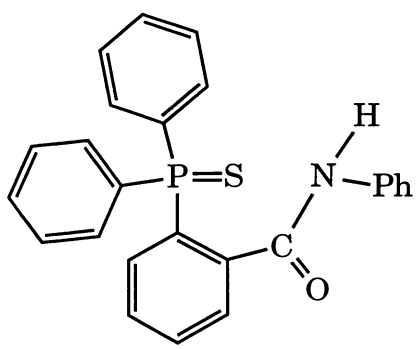
The reaction of *p*-tolyl-N=C=O was extended to other orthomanganated acetophenones containing various substituents (F, Cl, OMe, CF_3). The substituents did not interfere with the reaction, with the corresponding 3-methylidene phthalimidines obtained in moderate to good yields.

It was therefore of interest to see if isocyanates would couple with orthomanganated $Ph_3P{=}S$ **(31)** as there are relatively few reports concerning the reactivity of isocyanates toward transition metal-carbon bonds [25]. Only one preliminary reaction was carried out.



Equation 6.4

Reaction of orthomanganated $Ph_3P{=}S$ with PhNCO in benzene was clean and afforded a white crystalline solid which was tentatively assigned as **(48)** (Figure 6.10) in moderate yield (54 %).

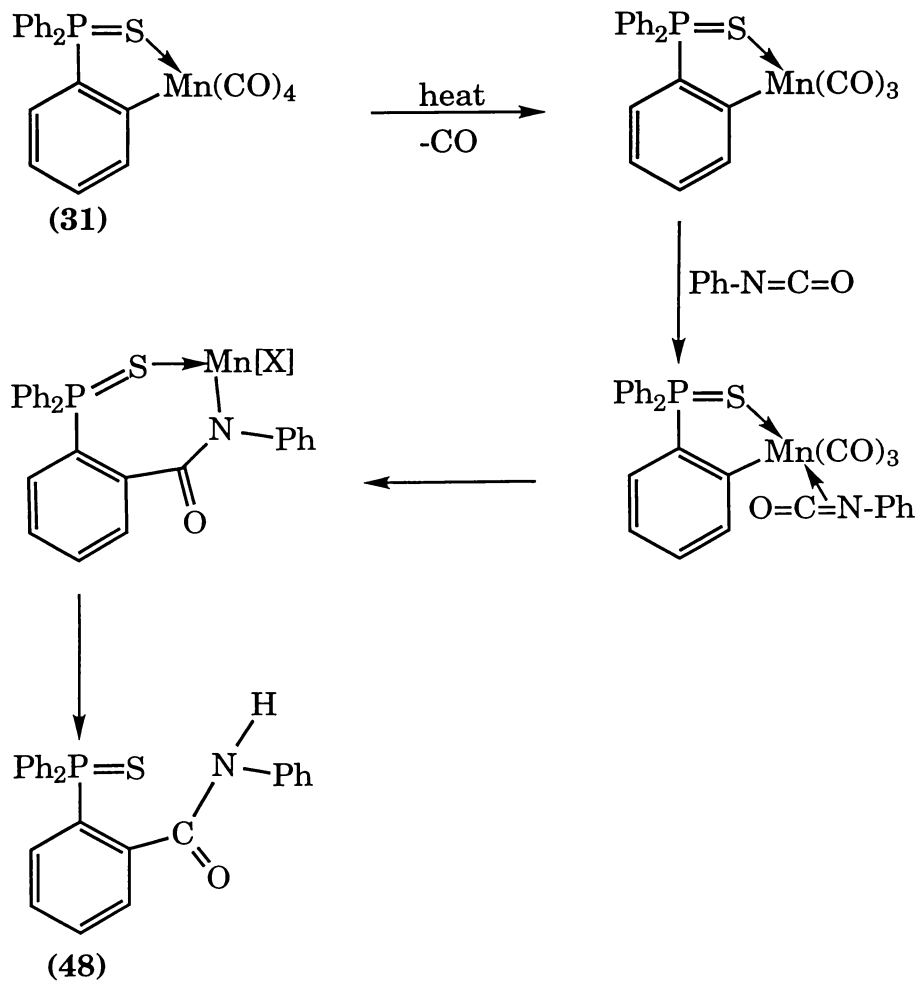


(48)

Figure 6.10

This assignment was based on the following spectroscopic data. An ESMS spectrum indicated the compound had a molecular mass of 413 while an IR spectrum exhibited strong bands at 1642 and 3449 cm^{-1} which are characteristic of υ(C=O) and υ(N-H) stretches of a secondary-amide. NMR spectroscopy showed a broad singlet at 9.78 ppm in the ^{1}H spectrum, while a singlet carbon at 165.9 ppm was observed in a ^{13}C spectrum. Both of these chemical shifts are consistent with the expected chemical shifts of an amide proton and amide carbonyl carbon.

A reasonable mechanism for the formation of **(48)** is shown in Scheme 6.3.



Scheme 6.3

Similarly to the mechanism proposed by Liebeskind's group [24], the first step involves the thermal generation of a coordinatively unsaturated species via loss of CO. This creates a vacant coordination

site which allows the ligation of the isocyanate to the manganese as a prelude to the insertion of the N=C bond into the Mn-C_{aryl} bond. In contrast to the insertion of isocyanates into orthomanganated acetophenones, there is no potential for any cyclisation in the present case. The isocyanate-inserted intermediate presumably undergoes protonolysis resulting in the cleavage of the Mn-N bond and the formation of **(48)**. This preliminary result suggests a more thorough study of organoisocyanate reactions is warranted. Functionalised phosphines are of interest and alternative syntheses of compounds such as **(48)** are not obvious.

6.3 X-Ray Crystal Structure of η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]-tetracarbonylmanganese (45)

The crystal structure of η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenyl-sulfonyl]tetracarbonylmanganese **(45)** was determined to fully characterise the reaction product between orthomanganated Ph_3P=Se **(32)** and SO_2. The structure was of interest as an SO_2 insertion reaction would give rise to a novel metallocyclic ring containing five different atom types.

6.3.1 Results of Preliminary Studies

Yellow plates were obtained by recrystallisation from chloroform/petroleum spirit (1:1) at -20 °C. Preliminary precession photography (Cu-K_α, λ=1.5418 Å) indicated monoclinic symmetry, with systematic absences defining space group $P2_1/c$.

6.3.2 Data Collection

Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer at -143 °C with monochromated Mo-K_α radiation (λ=0.7107 Å).

Crystal Data

Formula=$C_{22}H_{14}O_6MnPSSe$

M_r=571.26

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

a=13.09(3), b=9.163(13), c=18.36(12) Å

β=94.2(3)°

U=2196(16) $Å^3$

D_{calc}=1.728 g cm^{-3}

Z=4

F(000)=1136

μ(Mo-K_α)=2.465 mm^{-1}

A total of 2024 unique reflections were collected in the range $4° \leq 2\theta \leq 45°$. However, poor crystal quality and mosaicity meant the usual Ψ scan correction could not be carried out. Therefore, a semiempirical absorption correction using SHELXA-90 was invoked with maximum and minimum transition factors of 0.83 and 0.28 respectively. A total of 1106 reflections had $I \geq 2\sigma(I)$.

6.3.3 Solution and Refinement

The heavy atom positions (all 32 non-hydrogen atoms) were located by the TREF option of SHELXS-86. In the final cycle of full-matrix least-squares refinement only the non-hydrogen atoms Se, Mn, S, P and O were assigned anisotropic temperature factors. Attempts at making any of the carbons anisotropic resulted in numerous non-positive ellipsoids. The hydrogen atoms were included in their calculated positions with common isotropic temperature factors for each type.

The refinement converged with R_1=0.1003 (2σ data); R_1=0.1801, wR_2=0.2987, and Goof=1.063 for all data, where $w=[\sigma^2(F_o)^2+(0.1081P)^2+76.49P]^{-1}$ with $P=1/3[F_o^2+2F_c^2]$. No parameter shifted more than 0.034 σ in the final cycle. The final difference map showed no peaks or troughs greater than 1.101 e $Å^{-3}$.

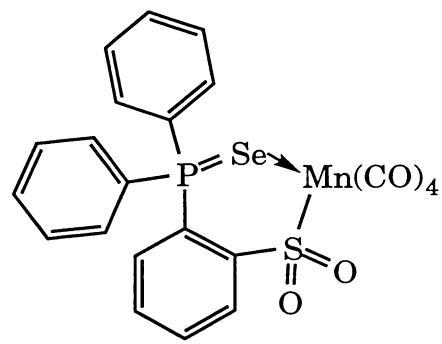
Bond lengths and angles are presented in Tables 6.5 and 6.6 respectively. Tables of final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix IX.

Figures 6.11 and 6.12 shows perspective and side views of **(45)** and illustrates the atom labelling scheme.

6.3.4 Discussion of the Structure

The high R value is the result of poor crystal quality which limits the accuracy of the direct comparison of bond lengths and angles with other structures. However, the structure determination has unequivocally established the atom connectivity in the complex.

Insertion of SO_2 into the Mn-C_{aryl} bond of orthomanganated $Ph_3P{=}Se$ **(32)** has given a novel six-membered metallocyclic ring incorporating five different elements (Figure 6.13). The resulting ligand chelates to the tetracarbonylmanganese group via a Mn-Se and a Mn-S bond.



(45)

Figure 6.13

In contrast to previously reported orthomanganated complexes containing a five-membered chelate ring which are all essentially planar and exhibit remarkably constant geometry, the metallocyclic ring of **(45)** shows considerable deviation from planarity (Figure 6.12). The six-membered ring is highly distorted and has adopted a bent envelope conformation. The ring can be defined by two planes. Plane 1 comprises the atoms Mn(1), Se(1), P(1), and X(1) which is the midpoint

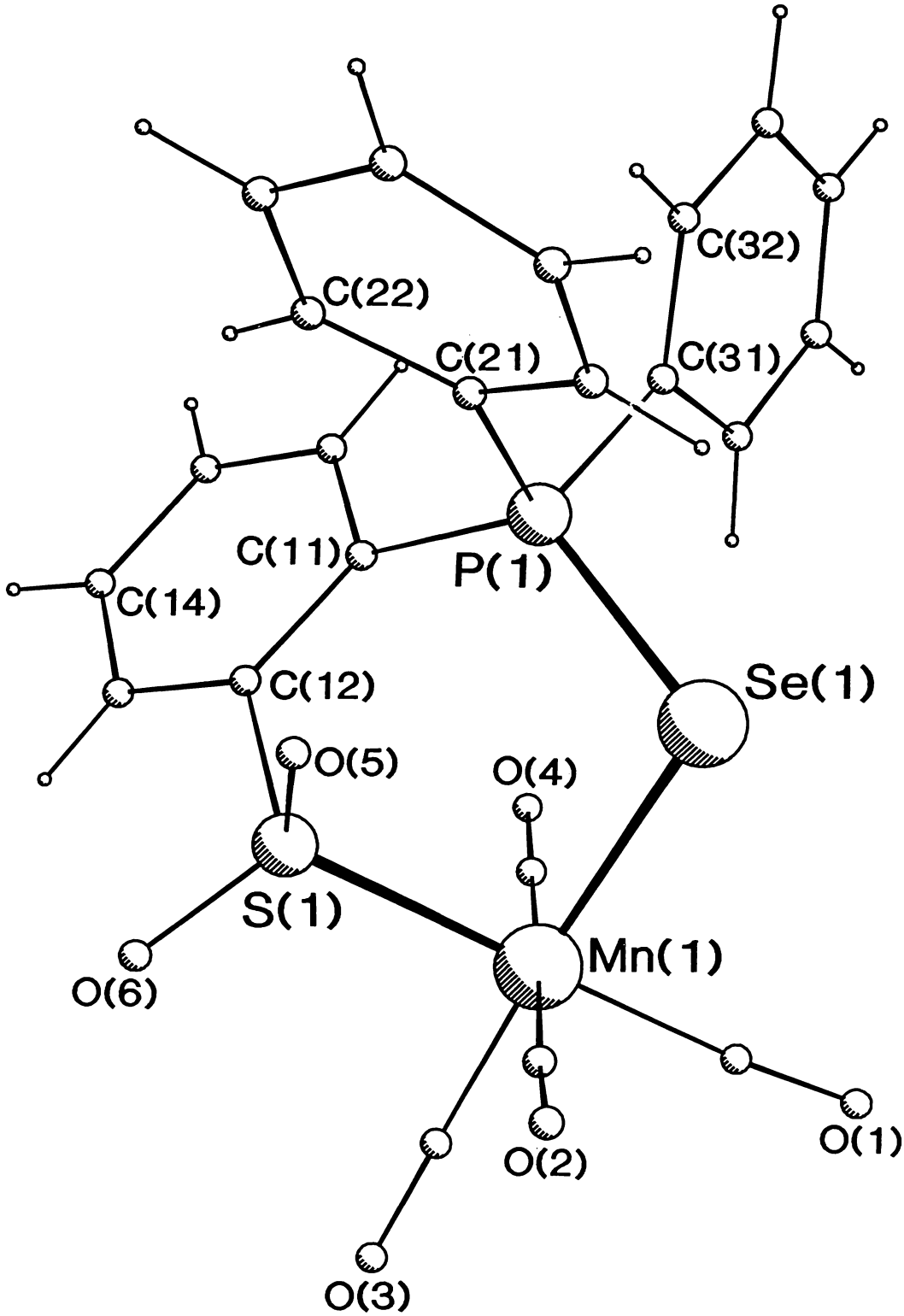


Figure 6.11 Perspective View of η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

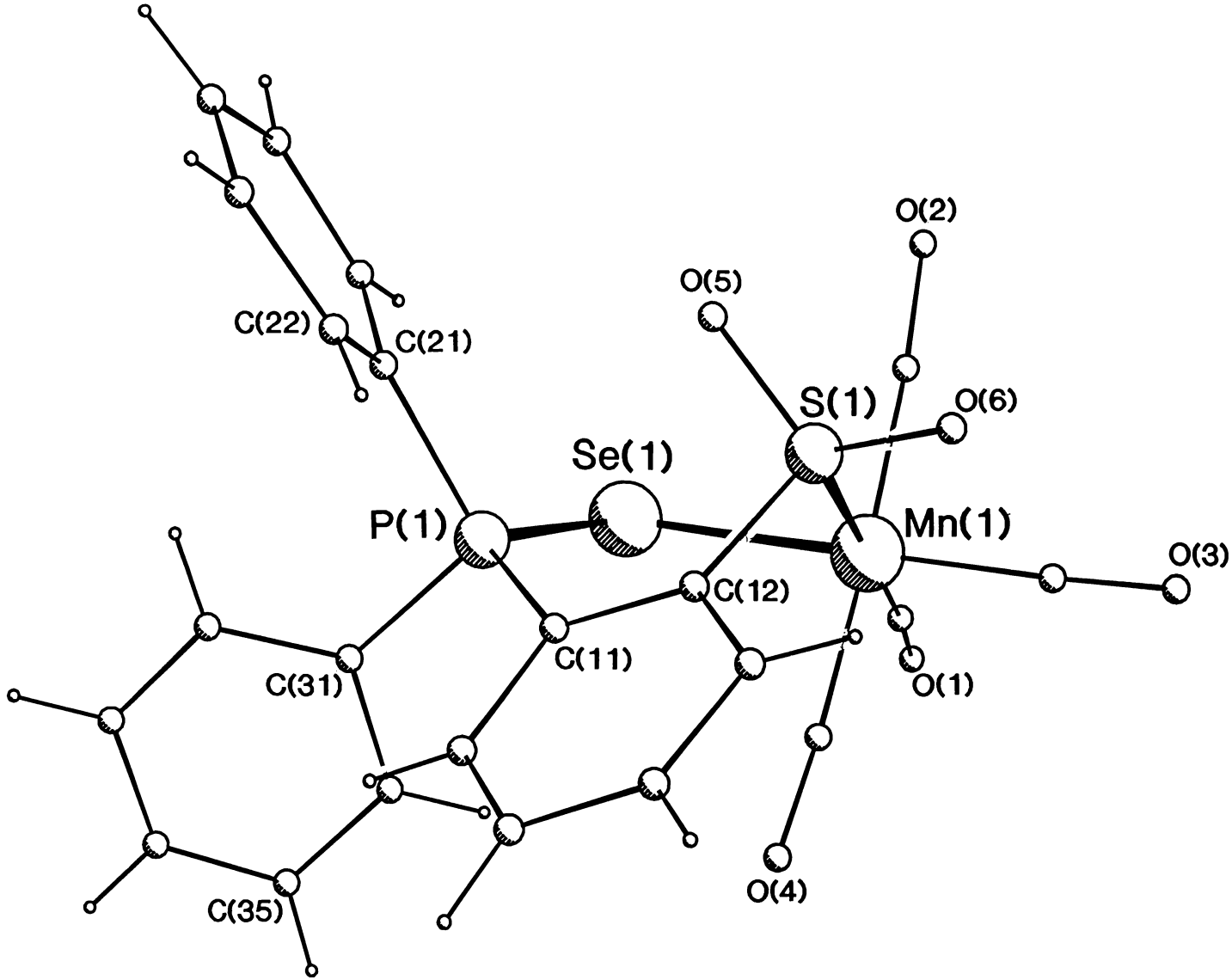


Figure 6.12 Side View of η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

Table 6.5 Bond Lengths (Å) for η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

Se(1)-P(1)	2.185(8)	C(11)-C(16)	1.45(3)
Se(1)-Mn(1)	2.487(7)	C(12)-C(13)	1.38(3)
Mn(1)-C(3)	1.79(4)	C(13)-C(14)	1.38(3)
Mn(1)-C(2)	1.81(2)	C(14)-C(15)	1.38(3)
Mn(1)-C(4)	1.81(2)	C(15)-C(16)	1.37(3)
Mn(1)-C(1)	1.86(3)	C(21)-C(22)	1.35(3)
Mn(1)-S(1)	2.313(8)	C(21)-C(26)	1.36(3)
S(1)-O(6)	1.47(2)	C(22)-C(23)	1.38(3)
S(1)-O(5)	1.48(2)	C(23)-C(24)	1.42(3)
S(1)-C(12)	1.81(2)	C(24)-C(25)	1.34(3)
P(1)-C(31)	1.79(2)	C(25)-C(26)	1.40(3)
P(1)-C(11)	1.80(2)	C(31)-C(32)	1.37(3)
P(1)-C(21)	1.83(2)	C(31)-C(36)	1.42(3)
O(1)-C(1)	1.11(3)	C(32)-C(33)	1.37(3)
O(2)-C(2)	1.23(3)	C(33)-C(34)	1.36(3)
O(3)-C(3)	1.15(3)	C(34)-C(35)	1.34(3)
O(4)-C(4)	1.19(2)	C(35)-C(36)	1.42(3)
C(11)-C(12)	1.40(3)		

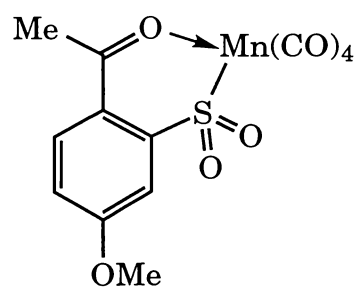
Table 6.6 Bond Angles (°) for η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

P(1)	-Se(1)	-Mn(1)	106.5(3)	O(2)	-C(2)	-Mn(1)	175(2)
C(3)	-Mn(1)	-C(2)	87.9(11)	O(3)	-C(3)	-Mn(1)	177(2)
C(3)	-Mn(1)	-C(4)	94.2(11)	O(4)	-C(4)	-Mn(1)	177(2)
C(2)	-Mn(1)	-C(4)	176.6(11)	C(12)	-C(11)	-C(16)	118(2)
C(3)	-Mn(1)	-C(1)	88.5(12)	C(12)	-C(11)	-P(1)	125(2)
C(2)	-Mn(1)	-C(1)	94.3(10)	C(16)	-C(11)	-P(1)	117(2)
C(4)	-Mn(1)	-C(1)	88.5(10)	C(13)	-C(12)	-C(11)	121(2)
C(3)	-Mn(1)	-S(1)	93.3(9)	C(13)	-C(12)	-S(1)	119(2)
C(2)	-Mn(1)	-S(1)	84.2(8)	C(11)	-C(12)	-S(1)	119(2)
C(4)	-Mn(1)	-S(1)	92.9(7)	C(14)	-C(13)	-C(12)	121(2)
C(1)	-Mn(1)	-S(1)	177.7(9)	C(13)	-C(14)	-C(15)	120(2)
C(3)	-Mn(1)	-Se(1)	176.2(9)	C(16)	-C(15)	-C(14)	121(2)
C(2)	-Mn(1)	-Se(1)	91.7(9)	C(15)	-C(16)	-C(11)	120(2)
C(4)	-Mn(1)	-Se(1)	86.4(8)	C(22)	-C(21)	-C(26)	123(2)
C(1)	-Mn(1)	-Se(1)	87.7(9)	C(22)	-C(21)	-P(1)	121(2)
S(1)	-Mn(1)	-Se(1)	90.5(3)	C(26)	-C(21)	-P(1)	116(2)
O(6)	-S(1)	-O(5)	115.9(10)	C(21)	-C(22)	-C(23)	118(2)
O(6)	-S(1)	-C(12)	103.9(10)	C(22)	-C(23)	-C(24)	121(2)
O(5)	-S(1)	-C(12)	99.9(10)	C(25)	-C(24)	-C(23)	120(2)
O(6)	-S(1)	-Mn(1)	112.7(8)	C(24)	-C(25)	-C(26)	119(2)
O(5)	-S(1)	-Mn(1)	112.2(7)	C(21)	-C(26)	-C(25)	120(2)
C(12)	-S(1)	-Mn(1)	111.0(7)	C(32)	-C(31)	-C(36)	117(2)
C(31)	-P(1)	-C(11)	107.4(10)	C(32)	-C(31)	-P(1)	124(2)
C(31)	-P(1)	-C(21)	104.6(11)	C(36)	-C(31)	-P(1)	119(2)
C(11)	-P(1)	-C(21)	108.4(10)	C(31)	-C(32)	-C(33)	123(2)
C(31)	-P(1)	-Se(1)	104.3(8)	C(34)	-C(33)	-C(32)	119(3)

Table 6.6 continued

C(11)	-P(1)	-Se(1)	116.4(9)	C(35)	-C(34)	-C(33)	123(2)
C(21)	-P(1)	-Se(1)	114.8(7)	C(34)	-C(35)	-C(36)	119(2)
O(1)	-C(1)	-Mn(1)	175(2)	C(35)	-C(36)	-C(31)	119(3)

between the C(11) and C(12) bond (maximum deviation 0.05(3) Å). The sulfur atom lies 1.30(9) Å above this plane, while the atoms C(12) and C(11) are 0.32(13) and 0.25(11) Å above and below the plane respectively. The second plane is defined by the atoms Mn(1), S(1), and C(12), and the dihedral angle between the two planes is 74(2)°. The geometry of the metallocyclic ring, differs considerably from that reported for the SO_2-inserted complex shown in Figure 6.14 [9]. An envelope conformation was observed, in which the manganese atom was folded out of the plane defined by the remaining atoms in the ring. The dihedral angle between the two planes was found to be 50.05(7)°. This significant folding observed in both cases presumably arises from the requirement of the sulfur atom to attain tetrahedral geometry. As a result, there is no possibility that the metallocyclic ring can be viewed as a pseudoaromatic species exhibiting delocalised bonding over a planar ring.



(F)

Figure 6.14

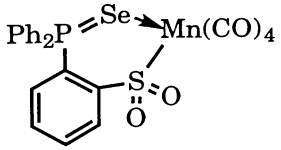
The angle between the axial carbonyls C(2)-Mn(1)-C(4) and corresponding angle in (F) are essentially linear (176.6(11)° and 177.4(1)° respectively). This is in contrast to the pronounced leaning of the axial carbonyls toward the weaker π-acceptor ligands observed in orthomanganated complexes in which the C_{ax}-Mn-C_{ax} angles reported

range from 168-170°. However, this is in agreement with C_{ax}-Mn-C_{ax} angles observed in complexes where the manganese atom is not coordinated to a Group 14 element in which the C_{ax}-Mn-C_{ax} angle also approached 180°.

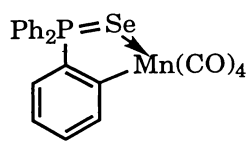
In Table 6.7, the bond distances and angles about the coordination sphere are tabulated and compared with the corresponding distances and angles for orthomanganated Ph_3P=Se **(32)**, and the sulfinate complex obtained from the insertion of SO_2 into orthomanganated *p*-methoxyacetophenone (F).

Table 6.7 Selected Bond Lengths (Å) and Angles (°) of (45) and Related Compounds

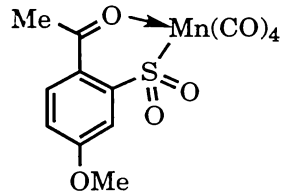
	(45)	**(32)**	**(F)**
Mn(1)-S(1)	2.313(8)		2.270(1)
Mn(1)-Se(1)	2.487(7)	2.514(1)	
Se(1)-P(1)	2.185(8)	2.154(1)	
P(1)-C(11)	1.80(2)	1.796(5)	
C(11)-C(12)	1.40(3)	1.410(6)	1.406(3)
C(12)-S(1)	1.81(2)		1.820(3)
Mn(1)-C(1)	1.86(3)	1.822(6)	1.873(3)
Mn(1)-C(2)	1.81(2)	1.843(5)	1.882(3)
Mn(1)-C(3)	1.79(4)	1.784(6)	1.788(3)
Mn(1)-C(4)	1.81(2)	1.846((6)	1.883(3)
Se(1)-Mn(1)-X (X=S, C)	90.5(3)	90.8(1)	
P(1)-Se(1)-Mn(1)	106.5(3)	96.09(4)	
C(11)-P(1)-Se(1)	116.4(9)	108.2(2)	



(45)



(32)



(F)

The ability of selenium to accept smaller bond angles, as observed in the orthomanganated complex, allows an almost ideal octahedral value for the chelate bite angle of the ligand. The P(1)-Se(1)-Mn(1) bond angle of 106.5(3)° is markedly different from that in the orthomanganated precursor 96.09(4)°. The opening of this angle is presumably the result of the flexibility introduced by the folding of the metallocyclic ring which has enabled selenium to bond at a more normal angle (closer to the expected ideal P(1)-Se(1)-Mn(1) angle of 120°).

Comparison of the Mn(1)-Se(1) distances in complexes **(45)** and **(32)** shows that insertion of SO_2 into the Mn-C_{aryl} bond results in the shortening of this bond. This can be rationalised by the replacement of the sp^2 carbon atom in **(32)** by the more electronegative SO_2 group in **(45)**. This results in the withdrawal of electron density from the manganese, making it a better σ-acceptor from selenium. The withdrawal of electron density from manganese would also make it a poorer π-donor, which is shown by the shift to higher wave numbers in the metal carbonyl region of the infrared spectrum (Section 6.2.1). However, this is not reflected as a corresponding increase in the Mn-CO distances of **(45)**, although this is probably hidden by the inaccuracy inherent in the structure. The structure of (F) revealed a shortening of the Mn-O bond along with longer Mn-CO distances compared to those in the corresponding orthomanganated precursor.

The Mn(1)-S(1) bond is 0.043(8) Å longer than the corresponding distance reported for the S-sulfinate complex (F). Presumably this is due to increased electron withdrawal from manganese to sulfur in complex (F), as a result of coordination to the electronegative oxygen donor atom, compared to the larger, less electronegative selenium atom in **(45)**. Consistent with this idea is the similar Mn(1)-S(1) distance of 2.312(3) Å reported for the six-membered S-sulphinate complex shown in Figure 6.15, in which manganese is also coordinated to a larger, less-electronegative atom.

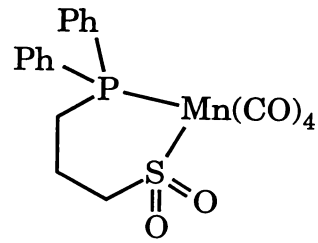


Figure 6.15

The P(1)-Se(1) distance is longer than the corresponding bond in free $Ph_3P{=}Se$ (2.106 Å) [26] and slightly longer than that in **(32)**. The lengthening observed in **(32)** presumably arises from the donation of electron density from the selenium atom to the manganese atom. The same argument also explains the P(1)-Se(1) bond lengthening in **(45)**, which is also compounded by electron withdrawal to manganese due to the effect of the electronegative SO_2 group.

6.4 Experimental Section

6.4.1 Starting Materials

N-sulfinylaniline (PhN=S=O) was prepared by an established literature method [27] and sulfur dioxide (BDH chemicals) was used as supplied.

6.4.2 Sulfur Dioxide Insertion Reactions of Orthomanganated Triphenylphosphine Chalcogenides

Reaction of Orthomanganated Triphenylphosphine Sulfide with Sulfur Dioxide

(a) Thermally

Orthomanganated $Ph_3P{=}S$ [**(31)**; 300 mg, 0.651 mmol] was placed in an ampoule and degassed. Liquid SO_2, which had been degassed by two cycles of freeze-pump-thawing was condensed into the ampoule using standard vacuum line techniques. The ampoule was sealed and placed

in a Carius tube maintained at 52 °C for 18 hours. The ampoule was opened, and after the excess SO_2 had evaporated, the residue was extracted with dichloromethane and filtered. An infrared spectrum showed the complete conversion to the SO_2 insertion product η^2-(S,S)-[(2-diphenylthiophosphinyl)phenylsulfonyl]tetracarbonylmanganese **(44)** by the absence of the peaks at 2072(m), 1993(vs, br), 1978(vs, br), 1933(s) cm^{-1} and the appearance of peaks at higher wave numbers. Vapour diffusion of pentane into a saturated dichloromethane solution of **(44)** gave small yellow chunky crystals (304 mg, 89%), m.p. 119-121 °C. Anal. Found: C, 49.85; H, 2.61; $C_{22}H_{14}O_6S_2MnP$ calcd.: C, 50.39; H 2.69%. IR ($CHCl_3$): υ(CO) 2101(m), 2030(s), 2014(s), 1986(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.40 (*m*, 1H, H-6), 7.78 (*m*, 1H, H-5), 7.63-7.48 (*m*, 10H, Ar-H), 7.39 (*m*, 1H, H-4), 6.90 (*m*, 1H, H-3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 212.6 (*s*, br, C≡O), 212.1 (*s*, br, C≡O), 208.1 (*s*, br, 2xC≡O), 157.2 (*s*, $^2J_{PC}$=8.2 Hz, C-1), 134.0 (*d*, C-5), 133.9 (*d*, C-3), 133.3 (*d*, C-4'), 133.0 (*d*, $^2J_{PC}$=10.7 Hz, C-2', C-6'), 129.7 (*d*, $^3J_{PC}$=12.1 Hz, C-4), 129.0 (*d*, $^3J_{PC}$=13.5 Hz, C-3', C-5'), 127.9 (*s*, $^1J_{PC}$=90.1 Hz, C-1'), 126.1 (*d*, $^3J_{PC}$=8.1 Hz, C-6), 124.2 (*s*, $^1J_{PC}$=80.6 Hz, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 34.6. ESMS: 547 $(M+Na)^+$, 542 $(M+NH_4)^+$, 538 $(M+H-CO+CH_3CN)^+$, 525 $(M+H)^+$, 497 $(M+H-CO)^+$.

(b) Photochemically

Orthomanganated Ph_3P=S [**(31)**; 107 mg, 0.232 mmol] was treated with SO_2 (~10 mL) and placed under a UV lamp (366 nm) for 18 hours at ambient temperature. An infrared spectrum showed the complete conversion to the SO_2 insertion product, η^2-(S,S)-[(2-diphenylthiophosphinyl)phenylsulfonyl]tetracarbonylmanganese [**(44)**; 106 mg, 87%].

Reaction of Orthomanganated Triphenylphosphine Selenide with Sulfur Dioxide

Similarly, orthomanganated Ph_3P=Se [**(32)**; 252 mg, 0.496 mmol] was treated with SO_2 (~10 mL) and left to react for 18 hours at 52 °C. An infrared spectrum showed the complete conversion to the SO_2 insertion product, η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]tetracarbonylmanganese **(45)**. Vapour diffusion of pentane into a saturated

dichloromethane solution of **(45)** gave small yellow chunky crystals (238 mg, 84%), m.p. 133-135 °C. Anal. Found: C, 45,96; H, 2.19%; $C_{22}H_{14}O_6SMnPSe$ calcd.: C, 46.25; H 2.47%. IR ($CHCl_3$): υ(CO) 2096(m), 2026(s), 2009(s), 1982(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.40 (*m*, 1H, H-6), 7.78 (*m*, 1H, H-5), 7.62-7.52 (*m*, 10H, Ar-H), 7.39 (*m*, 1H, H-4), 6.90 (*m*, 1H, H-3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 157.8 (*s*, $^2J_{PC}$=9.1 Hz, C-1), 134.0 (*d*, C-5), 133.5 (*d*, C-3), 133.4 (*d*, $^2J_{PC}$=10.8 Hz, C-2', C-6'), 133.2 (*d*, $^4J_{PC}$=2.6 Hz, C-4'), 129.6 (*d*, $^3J_{PC}$=11.4 Hz, C-4), 129.0 (*d*, $^3J_{PC}$=13.6 Hz, C-3', C-5'), 126.9 (*s*, $^1J_{PC}$=82.0 Hz, C-1'), 126.9 (*d*, $^3J_{PC}$=8.3 Hz, C-6), 123.6 (*s*, $^1J_{PC}$=73.4 Hz, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 15.6. ESMS: 590 $(M+NH_4)^+$, 573 $(M+H)^+$, 545 $(M+H-CO)^+$.

Reaction of Orthomanganated Triphenylphosphine Oxide with Sulfur Dioxide

Orthomanganated $Ph_3P=O$ [**(30)**; 273 mg, 0.614mmol] was treated with SO_2 (~10 mL) and left to react for 18 hours at 52 °C. An orange oil which failed to crystallise was obtained, and was tentatively assigned as consisting of:

η^2-(S,O)-[(2-diphenylphosphinyl)phenylsulfonyl]tetracarbonyl-manganese **(46)**. ESMS: 522 $(M+H-CO+CH_3CN)^+$, 509 $(M+H)^+$, 481 $(M+H-CO)^+$.

An unidentified product. ESMS: 800 $(M+H-CO+CH_3CN)^+$, 787 $(M+H)^+$, 759 $(M+H-CO)^+$.

Combined IR ($CHCl_3$): υ(CO) 2109(m)*, 2044(vs)*, 2036(vs)*, 2010(s)* 1978(s), 1959(vs), 1930(vs) cm^{-1}. Combined ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 44.4*, 41.9.

*Tentatively assigned as belonging to **(46)**.

6.4.3 Attempted Sulfur Dioxide Insertion Reactions of (18), (39) and (40)

Reaction of η^2-(1-acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)-manganese (18) with Sulfur Dioxide

(a) Standard Conditions

η^2-(1-Acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)manganese [**(18)**; 102 mg, 0.197 mmol] was treated with SO_2 (~10 mL) (which resulted in a dark red coloured solution) and left to react for 22 hours at 52 °C. An orange oil which failed to crystallise was obtained consisting of:

Unreacted starting material η^2-(1-acetyl-2-indolyl)dicarbonylbis-(trimethylphosphite)manganese.

An unidentified product(s). IR ($CHCl_3$): υ(CO) 2107(m), 2024(s), 1984(s), 1953(s) 1910(m) cm^{-1}. ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 184.5, 80.1, 35.0. ESMS: 675 $(M+NH_4)^+$, 658 $(M+H)^+$.

(b) Longer Reaction Time

η^2-(1-Acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)manganese [**(18)**; 265 mg, 0.512 mmol] was treated with SO_2 (~10 mL) and left to react for 72 hours at 52 °C. IR and ESMS of the orange oil obtained showed the presence of the same unidentified product(s) and a little unreacted η^2-(1-acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)manganese. The oil failed to crystallise, so the reaction was not pursued.

(c) Photochemically

η^2-(1-Acetyl-2-indolyl)dicarbonylbis(trimethylphosphite)manganese [**(18)**; 100 mg, 0.188 mmol] was treated with SO_2 (~10 mL) and placed under a UV lamp (366 nm) for 24 hours at ambient temperature. IR and ESMS showed that only starting material was present, so the reaction was abandoned.

Reaction of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonyl-bis(trimethylphosphite)manganese (40) with Sulfur Dioxide

η^2-(C,S)-(2-diphenylthiophosphinylphenyl)dicarbonylbis(trimethyl-phosphite)manganese [**(40)**; 202 mg, 0.309 mmol] was treated with SO_2 (~10 mL) and left to react for 22 hours at 52 °C. An orange oil which failed to crystallise was obtained, and was tentatively assigned as consisting of:

η^2-(S,S)-(2-diphenylthiophosphinylphenylsulfonyl)tricarbonyl-trimethylphosphitemanganese **(47)**. ESMS: 621 $(M+H)^+$.

An unidentified product. ESMS: 452 $(M+NH_4)^+$, 435 $(M+H)^+$.

A number of other unidentified products. Combined IR ($CHCl_3$): υ(CO) 2102(w), 2064(w), 2037(s)*, 1982(vs)*, 1952(vs)* cm^{-1}. Combined ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 124.7, 72.8, 43.2, 36.9, 35.3, and 34.3.

*Tentatively assigned as belonging to **(47)**

Attempted Reaction of (39) with Sulfur Dioxide

Following the standard procedure **(39)** [(158 mg, 0.262 mmol) was treated with SO_2 (~10 mL) and left to react for 24 hours at 52 °C. IR and MS showed that the yellow oil obtained was unreacted starting material. Identical results were observed at 52 °C for 96 hours, at 64 °C for 72 hours and under UV irradiation (366 nm) for 16 hours.

6.4.4 Reaction of Orthomanganated Triphenylphosphine Sulfide with PhNSO

A degassed solution of orthomanganated Ph_3P=S [**(31)**; 101 mg, 0.219 mmol] in benzene (15 mL) was treated with PhNSO (43 mg, 0.307 mmol) and refluxed under nitrogen for 24 hours. T.l.c. showed only demetalated starting material, and an infrared spectrum showed only $Mn_2(CO)_{10}$ in the metal carbonyl region, so the reaction was abandoned.

6.4.5 Reaction of Orthomanganated Triphenylphosphine Sulfide with PhNCO

A degassed solution of orthomanganated $Ph_3P{=}S$ [**(31)**; 100 mg, 0.218 mmol] in benzene (15 mL) was treated with PhNCO (35 mL, 0.322 mmol) and refluxed under nitrogen for 3 hours. The residue was chromatographed (p.l.c., CH_2Cl_2) to give:

Triphenylphosphine sulfide [**(28)**; 11 mg, 17%].

A colourless oil which crystallised from chloroform/pentane by vapour diffusion as small white rosettes, m.p. 170-171 °C, which was tentatively assigned as *N*-phenyl-(2-diphenylthiophosphinyl)benzamide [**(48)**; 46 mg, 54%]. IR (KBr disk): υ(N-H) 3449(s), υ(C=O) 1647(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.77 (*s*, br, NH), 7.89 (*m*, Ar-H), 7.61 (*m*, Ar-H), 7.45-7.14 (*m*, Ar-H), 7.39 (*m*, Ar-H). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 43.3. ESMS: 431 $(M+NH_4)^+$, 414 $(M+H)^+$.

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Appendix I

General Experimental

All reactions and recrystallisations in this thesis of air-sensitive compounds were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques.

THF was dried by distillation from sodium/benzophenone under nitrogen. Methanol was dried by an established procedure [1] via distillation from magnesium methylate. Petroleum spirit was of analytical grade and of boiling point range 60-80 °C. All other solvents were of analytical grade stored over 4-A molecular sieves.

All glassware was routinely cleaned in chromic acid, thoroughly rinsed and dried in an air oven.

Thin layer chromatography (t.l.c.) was carried out on Merck Kieselgel $60F_{254}$ silica gel coated (layer thickness 0.2 mm) aluminium sheets. Preparative layer chromatography (p.l.c.) was carried out on Merck Kieselgel $60PF_{254}$ silica gel coated glass plates poured to a thickness of 2 mm. Eluant solvent composition is expressed on a volume per volume (v/v) basis.

Orthomanganated starting materials that had been purified by chromatography (p.l.c.) were generally not recrystallised before their use in subsequent reactions.

Microanalytical samples were normally obtained by diffusion of pentane into a saturated dichloromethane or chloroform solution at -20 °C.

NMR spectra were recorded as $CDCl_3$ solutions unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Brucker AC300 spectrometer. Chemical shifts were referenced internally with TMS

using the following standard references for deuterated chloroform: ^{1}H: 7.25 ppm; ^{13}C: 77.06 ppm. ^{31}P NMR spectra were recorded on a JEOL FX-90Q spectrometer and were externally referenced to 85% H_3PO_4. Chemical shifts are reported in parts per million (ppm) and coupling constants are in Hertz (Hz). Spin multiplicities are indicated by the following symbol convention: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), and *m* (multiplet). Full NMR assignments were made using 2D-COSY [2], XHCORR [3], XHCORRD [3], BIRDTRAP[4], and NOE [5] experiments.

Infrared spectra were recorded in solution cells (KBr windows) with chloroform as solvent or as KBr disks on either a Digilab FTS-45 FTIR or Perkin Elmer 180B spectrometer.

Mass spectra were recorded on either a VG 70-SE mass spectrometer (FABMS, EIMS) at the University of Auckland or a VG Platform II mass spectrometer (ESMS) at the University of Waikato. All ESMS samples were run using 1:1 acetonitrile/water as the solvent.

As ESMS is a relatively new technique a brief introduction to the principles of ESMS will be given (for more detail see [6,7]). ESMS involves spraying the sample as a solution into the source of the mass spectrometer, whereby a complex series of events the analyte is desorbed from the liquid phase to the gas phase by the most gentle ionisation procedure available. There are four main processes involved; the production of charged droplets from the analyte dissolved in a solvent, shrinkage of these charged droplets via solvent evaporation, fission of the droplets which ultimately results in very small droplets of high charge density capable producing gas phase ions (the fundametal principle of all mass spectrometry methods), although the exact mechanism for the final process is not fully understood. Even when the analyte species are not ionic, they can attach other cations to their polar groups and can be desorbed from the droplet as "quasi-molecular ions". Therefore in the analysis of neutral analytes, the parent ion will often appear as the $(M+H)^+$ ion. In some cases other quasi-molecular ions such as $(M+NH_4)^+$ or $(M+H+CH_3CN)^+$ may dominate the spectrum. The desorbtion of NH_4^+ adducts into the gas phase arises from NH_3 produced in the slow hydrolysis of CH_3CN. Advantages ESMS have over

other conventional mass spectroscopy methods include the soft method of ionisation employed which allows minimal fragmentation of the parent species no matter how large of fragile it is, and the speed in which a spectrum can be obtained (~ 3 minutes). Other important features that ESMS offer are:

(1) Remarkable sensitivity in terms of both analyte concentration and sample size.
(2) Intact ions from species containing polar atoms or groups.
(3) The ease with which the strength of ionisation can be varied.
(4) The ease with which the spectrometer can be set to either negative or positive ion modes.

GCMS samples were analysed on a Hewlett Packard 5890 gas chromatograph fitted with a 15 meter HP1 column (0.33 μm film thickness; 0.2 mm internal diameter) using helium carrier (15 p.s.i. head pressure; flow rate 90 mL min^{-1}). A Hewlett Packard 5970 Series Mass Selective Detector linked to a data station provided parent ion mass values. Peak assignments correspond to the most abundant isotopomer, i.e. the most intense peak of the cluster.

For each of the crystal structure determinations, single crystals suitable for X-ray analysis were mounted with grease on a glass fibre. Preliminary precession photography (Cu-K_α radiation) was employed to ascertain the quality of the crystal, possible space groups and unit cell parameters. A Ni filter was used in obtaining zero and first upper-level photographs. Accurate cell parameters and intensity data was collected at the University of Canterbury on a Nicolet XRD P3 four-circle diffractometer using monochromated Mo-K_α radiation (with the exception of **(32)** in which Cu-K_α radiation was used). The structures were solved using SHELXS-86 by direct or Patterson methods, and refined using SHELXL-93.

All melting points were carried out on a Reichert thermopan melting point apparatus and are uncorrected.

Elemental analyses were carried out by the University of Otago Microanalytical Laboratory.

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Appendix II

Thermal and Positional Parameters for η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonyl-manganese (11)

Table AII.1 Final Positional and Equivalent Thermal Parameters for η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese (11)

Atom	X/A	Y/B	Z/C	Ueq
Molecule 1				
Mn(1)	0.1458(2)	0.3591(2)	0.3986(1)	0.023(1)
C(1)	0.0998(12)	0.5240(9)	0.3826(4)	0.022(2)
C(2)	-0.0317(12)	0.5357(9)	0.3432(4)	0.025(2)
C(3)	-0.0539(11)	0.6547(9)	0.3320(4)	0.021(2)
C(4)	-0.1559(13)	0.7210(10)	0.2981(4)	0.026(2)
C(5)	-0.1338(14)	0.8369(10)	0.2984(5)	0.034(3)
C(6)	-0.0164(14)	0.8853(11)	0.3334(5)	0.034(3)
C(7)	0.0844(13)	0.8200(10)	0.3673(5)	0.028(3)
C(8)	0.0663(12)	0.7064(9)	0.3663(4)	0.022(2)
N(1)	0.1542(10)	0.6218(10)	0.3968(4)	0.020(2)
C(9)	0.2822(12)	0.6506(11)	0.4372(5)	0.031(3)
C(10)	-0.1004(12)	0.4393(10)	0.3234(4)	0.030(2)
O(10)	-0.0476(9)	0.3472(7)	0.3407(3)	0.029(2)
C(11)	0.2478(12)	0.3670(9)	0.3384(5)	0.021(2)
O(11)	0.3152(11)	0.3778(7)	0.3052(4)	0.038(2)
C(12)	0.1557(12)	0.2054(10)	0.4003(5)	0.020(3)
O(12)	0.1647(12)	0.1117(10)	0.4012(5)	0.052(3)
C(13)	0.0503(15)	0.3684(10)	0.4588(5)	0.034(3)
O(13)	-0.0046(13)	0.3755(9)	0.4968(5)	0.053(3)
C(14)	0.3078(16)	0.3734(9)	0.4496(5)	0.028(3)
O(14)	0.4162(11)	0.3801(8)	0.4815(4)	0.041(2)

Table AII.1 continued

Atom	X/A	Y/B	Z/C	Ueq
Molecule 2				
Mn(1)	0.6411(2)	0.1409(2)	0.3948(1)	0.025(1)
C(1)	0.5967(11)	-0.0186(9)	0.3802(4)	0.019(2)
C(2)	0.4674(12)	-0.0369(8)	0.3395(4)	0.023(2)
C(3)	0.4450(13)	-0.1549(10)	0.3286(4)	0.026(2)
C(4)	0.3467(13)	-0.2265(11)	0.2936(4)	0.032(2)
C(5)	0.3636(15)	-0.3358(11)	0.2956(5)	0.039(3)
C(6)	0.4815(13)	-0.3854(11)	0.3310(4)	0.034(3)
C(7)	0.5825(13)	-0.3206(9)	0.3660(4)	0.026(2)
C(8)	0.5635(12)	-0.2078(9)	0.3647(4)	0.025(2)
N(1)	0.6508(10)	-0.1241(8)	0.3955(4)	0.018(2)
C(9)	0.7774(12)	-0.1487(10)	0.4379(4)	0.027(2)
C(10)	0.3972(13)	0.0578(10)	0.3194(5)	0.032(2)
O(10)	0.4483(8)	0.1542(7)	0.3369(3)	0.030(2)
C(11)	0.7355(12)	0.1307(10)	0.3335(4)	0.028(2)
O(11)	0.7958(9)	0.1209(8)	0.2973(3)	0.039(2)
C(12)	0.6505(14)	0.2970(15)	0.3955(6)	0.040(4)
O(12)	0.6589(12)	0.3889(10)	0.3989(5)	0.044(3)
C(13)	0.5483(14)	0.1333(9)	0.4562(5)	0.033(3)
O(13)	0.4964(12)	0.1272(12)	0.4943(4)	0.048(2)
C(14)	0.8080(14)	0.1281(11)	0.4454(5)	0.034(3)
O(14)	0.9110(9)	0.1220(8)	0.4771(4)	0.045(2)
Molecule 3				
Mn(1)	0.7460(2)	-0.2353(2)	0.1002(1)	0.023(1)
C(1)	0.7165(11)	-0.3949(9)	0.1170(4)	0.023(2)
C(2)	0.6258(12)	-0.4083(9)	0.1579(4)	0.023(2)
C(3)	0.6132(12)	-0.5239(10)	0.1704(4)	0.024(2)
C(4)	0.5467(12)	-0.5845(9)	0.2071(4)	0.025(2)
C(5)	0.5606(12)	-0.6989(10)	0.2089(4)	0.032(3)
C(6)	0.6418(13)	-0.7524(10)	0.1744(4)	0.029(3)
C(7)	0.7117(13)	-0.6943(10)	0.1367(5)	0.029(3)
C(8)	0.6927(12)	-0.5792(10)	0.1356(4)	0.026(2)
N(1)	0.7499(10)	-0.4993(10)	0.1040(4)	0.021(2)
C(9)	0.8352(12)	-0.5294(10)	0.0615(4)	0.028(2)
C(10)	0.5756(11)	-0.3113(9)	0.1764(4)	0.025(2)

Table AII.1 continued

Atom	X/A	Y/B	Z/C	Ueq
O(10)	0.6114(9)	-0.2175(7)	0.1571(3)	0.030(2)
C(11)	0.9049(15)	-0.2443(9)	0.1597(5)	0.029(3)
O(11)	1.0058(9)	-0.2577(6)	0.1933(3)	0.029(2)
C(12)	0.7582(14)	-0.0818(15)	0.0980(5)	0.040(4)
O(12)	0.7639(10)	0.0135(9)	0.0978(4)	0.040(3)
C(13)	0.5896(16)	-0.2448(9)	0.0384(5)	0.034(3)
O(13)	0.4983(11)	-0.2518(8)	0.0015(4)	0.044(3)
C(14)	0.8598(15)	-0.2521(10)	0.0494(5)	0.032(3)
O(14)	0.9292(12)	-0.2623(9)	0.0160(4)	0.049(3)
		Molecule 4		
Mn(1)	0.2490(2)	0.9786(2)	0.1063(1)	0.025(1)
C(1)	0.2190(12)	0.1427(10)	0.1199(4)	0.026(2)
C(2)	0.1288(12)	0.1589(8)	0.1610(4)	0.024(2)
C(3)	0.1174(12)	0.2788(10)	0.1686(4)	0.022(2)
C(4)	0.0450(12)	0.3454(10)	0.2021(4)	0.026(2)
C(5)	0.0620(13)	0.4613(10)	0.1988(4)	0.028(2)
C(6)	0.1455(13)	0.5075(11)	0.1636(4)	0.032(3)
C(7)	0.2144(13)	0.4428(10)	0.1289(5)	0.029(3)
C(8)	0.1986(11)	0.3285(9)	0.1332(4)	0.020(2)
N(1)	0.2576(11)	0.2428(8)	0.1047(4)	0.023(2)
C(9)	0.3446(12)	0.2686(10)	0.0625(5)	0.028(2)
C(10)	0.0814(12)	0.0616(10)	0.1811(5)	0.030(2)
O(10)	0.1159(9)	0.9681(8)	0.1650(3)	0.033(2)
C(11)	0.3637(12)	0.9922(10)	0.0565(5)	0.027(2)
O(11)	0.4367(10)	0.9987(9)	0.0228(4)	0.047(2)
C(12)	0.2546(11)	0.8261(11)	0.1030(4)	0.020(3)
O(12)	0.2651(13)	0.7322(10)	0.1001(5)	0.047(3)
C(13)	0.0962(14)	0.9879(10)	0.0448(5)	0.033(3)
O(13)	0.0021(12)	0.9964(12)	0.0066(4)	0.051(2)
C(14)	0.4050(12)	0.9895(10)	0.1685(4)	0.028(2)
O(14)	0.5002(9)	0.9989(8)	0.2044(3)	0.042(2)

Table AII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(1-methyl-3-formyl-2-indolyl)tetracarbonyl-manganese (11)

Atom	X/A	Y/B	Z/C	U11
Molecule 1				
H(4)	-0.2273(13)	0.6885(10)	0.2704(4)	0.031
H(5)	-0.2056(14)	0.8764(10)	0.2743(5)	0.041
H(6)	-0.0130(14)	0.9626(11)	0.3302(5)	0.041
H(7)	0.1657(13)	0.8505(10)	0.3901(5)	0.033
H(9C)	0.3357(12)	0.5854(11)	0.4518(5)	0.046
H(9B)	0.2790(12)	0.7113(11)	0.4719(5)	0.046
H(9A)	0.3441(12)	0.7131(11)	0.4319(5)	0.046
H(10A)	-0.1878(12)	0.4444(10)	0.2955(4)	0.036
Molecule 2				
H(4)	0.2730(13)	-0.1940(11)	0.2660(4)	0.039
H(5)	0.2915(15)	-0.3753(11)	0.2715(5)	0.046
H(6)	0.4785(13)	-0.4628(11)	0.3278(4)	0.041
H(7)	0.6638(13)	-0.3512(9)	0.3887(4)	0.031
H(9A)	0.7618(12)	-0.1188(10)	0.4724(4)	0.041
H(9B)	0.8578(12)	-0.1148(10)	0.4266(4)	0.041
H(9C)	0.7912(12)	-0.2281(10)	0.4408(4)	0.041
H(10B)	0.3057(13)	0.0543(10)	0.2941(5)	0.038
Molecule 3				
H(4)	0.4867(12)	-0.5527(9)	0.2281(4)	0.030
H(5)	0.5177(12)	-0.7392(10)	0.2349(4)	0.039
H(6)	0.6445(13)	-0.8299(10)	0.1768(4)	0.035
H(7)	0.7717(13)	-0.7253(10)	0.1146(5)	0.035
H(9A)	0.8688(12)	-0.4631(10)	0.0457(4)	0.041
H(9B)	0.7781(12)	-0.5719(10)	0.0307(4)	0.041
H(9C)	0.9144(12)	-0.5737(10)	0.0802(4)	0.041
H(10C)	0.5170(11)	-0.3137(9)	0.2048(4)	0.031

Table AII.2 continued

Atom	X/A	Y/B	Z/C	U11
Molecule 4				
H(4A)	0.9818(12)	0.3155(10)	0.2250(4)	0.031
H(5A)	0.0155(13)	0.5096(10)	0.2217(4)	0.034
H(6A)	0.1599(13)	0.5870(11)	0.1643(4)	0.038
H(7A)	0.2682(13)	0.4741(10)	0.1026(5)	0.035
H(9A)	0.3760(12)	0.1999(10)	0.0483(5)	0.042
H(9B)	0.4251(12)	0.3114(10)	0.0813(5)	0.042
H(9C)	0.2915(12)	0.3106(10)	0.0305(5)	0.042
H(10D)	0.0195(12)	0.0659(10)	0.2082(5)	0.036

Table AII.3 Thermal Parameters for π^2-(1-methyl-3-formyl-2-indolyl)tetracarbonylmanganese (11)

Atom	U11	U22	U33	U23	U13	U12
Molecule 1						
Mn(1)	0.0234(12)	0.0243(11)	0.0221(9)	0.0001(7)	0.0081(7)	-0.0041(8)
C(11)	0.009(6)	0.028(6)	0.026(5)	0.001(4)	0.002(4)	0.003(4)
O(11)	0.046(6)	0.034(5)	0.036(4)	0.001(3)	0.017(4)	0.003(4)
C(12)	0.014(6)	0.013(6)	0.034(6)	0.002(4)	0.012(5)	0.004(4)
O(12)	0.054(7)	0.035(7)	0.076(7)	-0.011(5)	0.032(6)	-0.003(5)
C(13)	0.030(8)	0.039(7)	0.035(6)	0.000(5)	0.015(6)	-0.009(6)
O(13)	0.067(9)	0.045(6)	0.059(6)	0.003(4)	0.046(6)	0.004(5)
C(14)	0.039(8)	0.020(6)	0.023(5)	-0.003(4)	0.003(5)	0.002(5)
O(14)	0.030(6)	0.043(6)	0.041(5)	-0.002(4)	-0.012(4)	0.006(4)
Molecule 2						
Mn(1)	0.0258(12)	0.0238(11)	0.0251(9)	0.0013(7)	0.0060(7)	0.0004(8)
C(11)	0.035(7)	0.019(5)	0.030(5)	0.002(4)	0.004(5)	0.002(5)
O(11)	0.046(5)	0.043(5)	0.033(4)	0.005(4)	0.017(4)	0.009(4)
C(12)	0.030(9)	0.046(10)	0.048(8)	0.012(6)	0.018(6)	0.010(6)
O(12)	0.043(7)	0.025(7)	0.065(7)	0.012(5)	0.012(5)	-0.004(5)
C(13)	0.045(8)	0.019(5)	0.034(5)	-0.006(4)	0.008(5)	-0.003(6)
O(13)	0.058(6)	0.044(5)	0.053(5)	0.002(4)	0.037(5)	0.005(4)
C(14)	0.041(8)	0.029(6)	0.030(5)	-0.005(5)	0.004(5)	0.004(6)
O(14)	0.028(5)	0.049(6)	0.049(5)	0.005(4)	-0.012(4)	-0.008(5)
Molecule 3						
Mn(1)	0.0218(11)	0.0261(11)	0.0208(8)	-0.0011(7)	0.0053(7)	0.0005(8)
C(11)	0.048(9)	0.019(6)	0.024(5)	-0.003(4)	0.016(6)	0.007(5)
O(11)	0.022(5)	0.032(5)	0.032(4)	-0.003(3)	0.000(4)	0.001(3)
C(12)	0.029(8)	0.070(11)	0.016(5)	0.001(5)	-0.005(5)	0.018(7)
O(12)	0.037(6)	0.027(6)	0.051(5)	0.007(4)	-0.001(4)	-0.001(4)
C(13)	0.061(10)	0.022(6)	0.019(5)	0.007(4)	0.011(6)	0.009(6)
O(13)	0.048(7)	0.042(6)	0.033(5)	0.003(3)	-0.011(5)	0.002(4)
C(14)	0.021(7)	0.034(8)	0.039(6)	-0.004(5)	0.001(5)	0.001(5)
O(14)	0.059(8)	0.049(6)	0.053(6)	0.000(4)	0.043(5)	0.001(5)

Table AII.3 continued

Atom	U11	U22	U33	U23	U13	U12
Molecule 4						
Mn(1)	0.0253(11)	0.0241(11)	0.0250(9)	0.0017(7)	0.0061(7)	-0.0001(8)
C(11)	0.013(5)	0.028(6)	0.036(5)	0.002(5)	-0.004(4)	-0.001(5)
O(11)	0.045(6)	0.052(6)	0.052(5)	-0.003(4)	0.030(5)	0.002(5)
C(12)	0.011(6)	0.017(6)	0.033(6)	0.004(4)	0.007(4)	0.003(4)
O(12)	0.061(8)	0.026(7)	0.054(6)	-0.003(4)	0.010(5)	0.000(5)
C(13)	0.041(7)	0.025(6)	0.035(5)	0.003(5)	0.011(5)	-0.003(6)
O(13)	0.049(6)	0.047(5)	0.046(5)	0.004(4)	-0.013(4)	-0.006(4)
C(14)	0.030(7)	0.032(6)	0.024(5)	-0.002(5)	0.009(5)	0.005(5)
O(14)	0.040(5)	0.049(5)	0.034(4)	-0.003(4)	0.002(4)	-0.002(4)

Appendix III

Thermal and Positional Parameters for (21)

Table AIII.1 Final Positional and Equivalent Thermal Parameters for (21)

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.2072(1)	0.1405(1)	0.6072(1)	0.017(1)
N(1)	0.3436(3)	0.5373(4)	0.4913(2)	0.017(1)
O(1)	0.2331(3)	0.0649(3)	0.4979(2)	0.021(1)
C(1)	0.3538(4)	0.6772(5)	0.5406(3)	0.023(1)
C(2)	0.2918(4)	0.3988(5)	0.5050(2)	0.018(1)
C(3)	0.2962(4)	0.2961(5)	0.4406(2)	0.019(1)
C(3A)	0.3537(4)	0.3807(5)	0.3843(2)	0.019(1)
C(4)	0.3852(4)	0.3477(6)	0.3104(2)	0.022(1)
C(5)	0.4441(4)	0.4598(6)	0.2745(3)	0.025(1)
C(6)	0.4728(4)	0.6050(6)	0.3090(3)	0.025(1)
C(7)	0.4427(4)	0.6424(6)	0.3824(2)	0.021(1)
C(7A)	0.3832(3)	0.5288(5)	0.4178(2)	0.017(1)
C(8)	0.2410(4)	0.3805(5)	0.5769(3)	0.021(1)
C(9)	0.1226(4)	0.3605(5)	0.5760(2)	0.018(1)
C(10)	0.0536(4)	0.2495(5)	0.5362(3)	0.022(1)
C(11)	-0.0566(4)	0.2583(6)	0.5616(3)	0.025(1)
C(12)	-0.0569(4)	0.3713(6)	0.6159(3)	0.027(1)
C(13)	0.0543(4)	0.4498(5)	0.6297(3)	0.024(1)
C(14)	0.1975(4)	0.1879(5)	0.7068(3)	0.022(1)
O(14)	0.1953(3)	0.2143(4)	0.7724(2)	0.031(1)
C(15)	0.1329(4)	-0.0421(5)	0.6221(2)	0.021(1)
O(15)	0.0825(3)	-0.1506(4)	0.6360(2)	0.028(1)
C(16)	0.3450(4)	0.0647(5)	0.6395(2)	0.021(1)
O(16)	0.4324(3)	0.0144(4)	0.6599(2)	0.032(1)
C(31)	0.2671(3)	0.1339(5)	0.4406(2)	0.019(1)
C(32)	0.2792(4)	0.0318(6)	0.3705(3)	0.026(1)

Table AIII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for (21)

Atom	X/A	Y/B	Z/C	U11
H(1A)	0.3592(30)	0.7715(7)	0.5081(4)	0.056(7)
H(1B)	0.4209(17)	0.6686(20)	0.5790(14)	0.056(7)
H(1C)	0.2881(14)	0.6862(24)	0.5680(16)	0.056(7)
H(4)	0.3661(4)	0.2493(6)	0.2854(2)	0.024(5)
H(5)	0.4656(4)	0.4368(6)	0.2246(3)	0.024(5)
H(6)	0.5133(4)	0.6796(6)	0.2826(3)	0.024(5
H(7)	0.4620(4)	0.7411(6)	0.4070(2)	0.024(5)
H(8)	0.2720(44)	0.4443(64)	0.6202(32)	0.040
H(10)	0.0672(43)	0.2065(65)	0.4925(33)	0.040
H(11)	-0.1185(4)	0.1938(6)	0.5424(3)	0.024(5)
H(12)	-0.1188(4)	0.3976(6)	0.6419(3)	0.024(5)
H(13A)	0.0876(4)	0.4397(5)	0.6851(3)	0.023(9)
H(13B)	0.0485(4)	0.5635(5)	0.6156(3)	0.023(9)
H(32A)	0.3578(6)	0.0274(35)	0.3625(13)	0.056(7)
H(32B)	0.2352(24)	0.0770(24)	0.3239(5)	0.056(7)
H(32C)	0.2526(28)	-0.0754(13)	0.3794(9)	0.056(7)

Table AIII.3 Thermal Parameters for (21)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0242(4)	0.0180(4)	0.0096(3)	0.0006(3)	0.0051(2)	-0.0014(3)
N(1)	0.023(2)	0.017(2)	0.011(2)	-0.0008(15)	0.0033(15)	-0.004(2)
O(1)	0.01(2)	0.019(2)	0.0123(15)	0.0008(13)	0.0067(13)	-0.0017(14)
C(1)	0.031(2)	0.021(2)	0.016(2)	-0.003(2)	0.003(2)	-0.001(2)
C(2)	0.020(2)	0.022(2	0.011(2)	0.000(2)	0.002(2)	0.000(2)
C(3)	0.026(2)	0.020(2)	0.011(2)	0.001(2)	0.004(2)	0.001(2)
C(3A)	0.021(2)	0.025(2)	0.011(2)	0.003(2)	0.003(2)	-0.003(2)
C(4)	0.030(2)	0.025(2)	0.012(2)	-0.002(2)	0.006(2)	-0.001(2)
C(5)	0.25(2)	0.038(3)	0.013(2)	0.002(2)	0.008(2)	-0.003(2)
C(6)	0.031(3)	0.027(3)	0.017(2)	0.008(2)	0.006(2)	-0.004(2)
C(7)	0.026(2)	0.021(2)	0.017(2)	0.000(2)	0.007(2)	-0.003(2)
C(7A)	0.019(2)	0.021(2)	0.011(2)	-0.001(2)	0.004(2)	-0.002(2)
C(8)	0.034(3)	0.018(2)	0.012(2)	-0.001(2)	0.006(2)	-0.003(2)
C(9)	0.027(2)	0.015(2)	0.012(2)	0.004(2)	0.006(2)	0.001(2)
C(10)	0.031(3)	0.021(2)	0.014(2)	0.005(2)	0.007(2)	0.002(2)
C(11)	0.026(2)	0.026(2)	0.023(2)	0.008(2)	0.004(2)	-0.001(2)
C(12)	0.029(3)	0.034(3)	0.019(2)	0.008(2)	0.010(2)	0.006(2)
C(13)	0.039(3)	0.021(2)	0.014(2)	0.002(2)	0.010(2)	0.004(2)
C(14)	0.027(2)	0.022(2)	0.016(2)	0.001(2)	0.002(2)	-0.002(2)
O(14)	0.046(2)	0.037(2)	0.013(2)	-0.0032(15)	0.0096(15)	-0.001(2)
C(15)	0.027(2)	0.024(3)	0.013(2)	-0.004(2)	0.003(2)	-0.001(2)
O(15)	0.042(2)	0.023(2)	0.022(2)	-0.0008(15)	0.0107(15)	-0.012(2)
C(16)	0.034(3)	0.021(2)	0.011(2)	-0.001(2)	0.008(2)	-0.003(2)
O(16)	0.029(2)	0.033(2)	0.033(2)	0.008(2)	0.002(2)	0.002(2)
C(31)	0.022(2)	0.022(2)	0.013(2)	-0.003(2)	0.005(2)	-0.003(2)
C(32)	0.040(3)	0.024(2)	0.018(2)	-0.006(2)	0.013(2)	-0.007(2)

Appendix IV

Thermal and Positional Parameters for η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]-tetracarbonylmanganese (31)

Table AIV.1 Final Positional and Equivalent Thermal Parameters for η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (31)

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.2395(1)	0.0913(1)	0.0658(1)	0.017(1)
P(1)	0.4208(1)	0.1198(1)	0.2377(1)	0.015(1)
S(1)	0.4194(1)	0.0122(1)	0.1485(1)	0.021(1)
C(1)	0.2415(2)	-0.0357(2)	0.0083(1)	0.024(1)
C(2)	0.1152(3)	0.1477(2)	-0.0023(2)	0.026(1)
C(3)	0.1065(2)	0.0444(2)	0.1348(1)	0.023(1)
C(4)	0.3774(2)	0.1609(2)	0.0122(1)	0.023(1)
O(1)	0.2369(2)	-0.1145(2)	-0.0280(1)	0.039(1)
O(2)	0.0391(2)	0.1834(2)	-0.0484(1)	0.041(1)
O(3)	0.0244(2)	0.0219(2)	0.1793(1)	0.038(1)
O(4)	0.4602(2)	0.2077(2)	-0.0201(1)	0.039(1)
C(11)	0.3173(2)	0.2346(2)	0.2091(1)	0.016(1)
C(12)	0.2377(2)	0.2288(2)	0.1390(1)	0.017(1)
C(13)	0.1551(2)	0.3217(2)	0.1244(1)	0.024(1)
C(14)	0.1524(2)	0.4106(2)	0.1749(2)	0.027(1)
C(15)	0.2346(2)	0.4138(2)	0.2429(2)	0.024(1)
C(16)	0.3180(2)	0.3255(2)	0.2600(1)	0.021(1)
C(21)	0.3522(2)	0.0623(2)	0.3275(1)	0.018(1)
C(22)	0.4237(3)	-0.0207(2)	0.3669(1)	0.025(1)
C(23)	0.3700(3)	-0.0662(2)	0.4349(2)	0.034(1)
C(24)	0.2451(3)	-0.0304(2)	0.4626(2)	0.034(1)
C(25)	0.1729(3)	0.0500(2)	0.4227(2)	0.031(1)
C(26)	0.2259(2)	0.0972(2)	0.3552(1)	0.024(1)

Table AIV.1 continued

Atom	X/A	Y/B	Z/C	Ueq
C(31)	0.5919(2)	0.1693(2)	0.2609(1)	0.016(1)
C(32)	0.6721(2)	0.2011(2)	0.1970(1)	0.025(1)
C(33)	0.8015(2)	0.2444(2)	0.2107(2)	0.031(1)
C(34)	0.8530(2)	0.2567(2)	0.2869(2)	0.028(1)
C(35)	0.7739(2)	0.2261(2)	0.3502(2)	0.027(1)
C(36)	0.6429(2)	0.1826(2)	0.3372(1)	0.021(1)

Table AIV.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetra-carbonylmanganese (31)

Atom	X/A	Y/B	Z/C	U11
H(13)	0.0986(2)	0.3233(2)	0.0777(1)	0.030(2)
H(14)	0.0930(2)	0.4707(2)	0.1629(2)	0.030(2)
H(15)	0.2335(2)	0.4759(2)	0.2770(2)	0.030(2)
H(16)	0.3760(2)	0.3261(2)	0.3061(1)	0.030(2)
H(22)	0.5092(3)	-0.0462(2)	0.3474(1)	0.030(2)
H(23)	0.4195(3)	-0.1222(2)	0.4625(2)	0.030(2)
H(24)	0.2088(3)	-0.0615(2)	0.5094(2)	0.030(2)
H(25)	0.0859(3)	0.0734(2)	0.4415(2)	0.030(2)
H(26)	0.1759(2)	0.1533(2)	0.3280(1)	0.030(2)
H(32)	0.6374(2)	0.1929(2)	0.1442(1)	0.030(2)
H(33)	0.8559(2)	0.2659(2)	0.1672(2)	0.030(2)
H(34)	0.9427(2)	0.2863(2)	0.2958(2)	0.030(2)
H(35)	0.8091(2)	0.2348(2)	0.4028(2)	0.030(2)
H(36)	0.5884(2)	0.1619(2)	0.3810(1)	0.030(2)

Table AIV.3 Thermal Parameters for η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (31)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0157(2)	0.0212(2)	0.0139(2)	0.0004(1)	-0.0015(1)	-0.0035(1)
P(1)	0.0164(3)	0.0161(3)	0.0134(3)	-0.0013(2)	-0.0015(2)	0.0011(2)
S(1)	0.0241(3)	0.0198(3)	0.0175(3)	-0.0053(2)	-0.0047(2)	0.0049(2)
C(1)	0.0224(12)	0.0333(14)	0.0179(12)	-0.0018(11)	0.0000(10)	-0.0074(11
C(2)	0.0242(13)	0.0312(14)	0.0239(13)	0.0012(11)	-0.0023(11)	-0.0082(11
C(3)	0.0221(12)	0.0204(12)	0.0263(13)	-0.0002(10)	-0.0028(10)	-0.0018(10
C(4)	0.0257(13)	0.0261(13)	0.0174(12)	-0.0019(10)	-0.0032(10)	-0.0028(11
O(1)	0.0447(12)	0.0392(12)	0.0321(11)	-0.0159(9)	0.0057(9)	-0.0121(9)
O(2)	0.0342(11)	0.0505(12)	0.0359(11)	0.0106(10)	-0.0200(9)	-0.0034(9)
O(3)	0.0340(10)	0.0385(11)	0.0431(12)	0.0036(9)	0.0177(9)	-0.0092(9)
O(4)	0.0382(11)	0.0456(12)	0.0325(11)	0.0018(9)	0.0119(9)	-0.0187(9)
C(11)	0.0158(11)	0.0142(11)	0.0192(11)	0.0013(9)	0.0026(9)	0.0003(9)
C(12)	0.0151(11)	0.0192(12)	0.0174(12)	0.0029(9)	0.0034(9)	-0.0025(9)
C(13)	0.0234(12)	0.0250(13)	0.0242(13)	0.0063(10)	-0.0003(10)	0.0031(10
C(14)	0.0234(12)	0.0200(12)	0.0377(15)	0.0060(11)	0.0054(11)	0.0070(10
C(15)	0.0238(12)	0.0165(12)	0.0321(14)	-0.0024(10)	0.0083(10)	-0.0014(10
C(16)	0.0185(11)	0.0208(12)	0.0226(12)	-0.0017(10)	0.0028(9)	-0.0011(10
C(21)	0.0227(12)	0.0181(12)	0.0144(11)	-0.0012(9)	-0.0016(9)	-0.0030(9)
C(22)	0.0288(13)	0.0230(13)	0.0227(12)	0.0019(10)	0.0024(10)	0.0029(10
C(23)	0.047(2)	0.0281(14)	0.0274(14)	0.0089(11)	0.0016(12)	0.0049(12
C(24)	0.047(2)	0.034(2)	0.0213(13)	0.0064(12)	0.0098(12)	-0.0062(13
C(25)	0.0301(14)	0.038(2)	0.0240(13)	-0.0015(12)	0.0086(11)	-0.0035(12
C(26)	0.024112)	0.0275(13)	0.0198(12)	0.0020(10)	-0.0002(9)	0.0006(10
C(31)	0.0161(11)	0.0142(11)	0.0190(11)	-0.0018(9)	-0.0012(9)	0.0014(9)
C(32)	0.0230(12)	0.0321(14)	0.0202(12)	0.0001(11)	-0.0001(10)	-0.0015(11
C(33)	0.0236(13)	0.036(2)	0.0318(14)	0.0033(12)	0.0049(11)	-0.0050(11
C(34)	0.0210(12)	0.0231(13)	0.039(2)	-0.0016(11)	-0.0059(11)	-0.0019(10
C(35)	0.0275(13)	0.0248(13)	0.0274(13)	-0.0059(11)	-0.0091(10)	0.0002(11
C(36)	0.0224(12)	0.0216(12)	0.0190(12)	-0.0048(10)	-0.0012(9)	0.0005(10

Appendix V

Thermal and Positional Parameters for η^2-(C,Se)-[(2-diphenylselenophosphinyl)-phenyl]tetracarbonylmanganese (32)

Table AV.1 Final Positional and Equivalent Thermal Parameters for η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetracarbonylmanganese (32)

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.2368(1)	0.0932(1)	0.0634(1)	0.011(1)
Se(1)	0.4217(1)	0.0013(1)	0.1444(1)	0.013(1)
P(1)	0.4205(1)	0.1172(1)	0.2395(1)	0.009(1)
C(1)	0.2344(5)	-0.0297(5)	0.0034(3)	0.021(1)
C(2)	0.1140(5)	0.1539(5)	-0.0023(3)	0.021(1)
C(3)	0.1031(5)	0.0469(4)	0.1326(3)	0.016(1)
C(4)	0.3794(5)	0.1630(5)	0.0122(3)	0.019(1)
O(1)	0.2278(4)	-0.1078(3)	-0.0339(2)	0.030(1)
O(2)	0.0388(4)	0.1912(3)	-0.0471(2)	0.032(1)
O(3)	0.0220(4)	0.0226(3)	0.1781(2)	0.032(1)
O(4)	0.4658(4)	0.2074(3)	-0.0178(2)	0.031(1)
C(11)	0.3165(4)	0.2313(4)	0.2098(3)	0.009(1)
C(12)	0.2391(5)	0.2278(4)	0.1391(3)	0.011(1)
C(13)	0.1599(5)	0.3218(4)	0.1255(3)	0.016(1)
C(14)	0.1563(5)	0.4098(4)	0.1758(3)	0.020(1)
C(15)	0.2365(5)	0.4093(4)	0.2442(3)	0.018(1)
C(16)	0.3163(5)	0.3203(4)	0.2614(3)	0.014(1)
C(21)	0.3493(5)	0.0595(4)	0.3286(3)	0.011(1)
C(22)	0.4212(5)	-0.0227(4)	0.3678(3)	0.015(1)
C(23)	0.3657(6)	-0.0678(5)	0.4344(3)	0.028(1)
C(24)	0.2400(6)	-0.0338(5)	0.4629(3)	0.027(1)
C(25)	0.1668(6)	0.0460(5)	0.4230(3)	0.023(1)
C(26)	0.2210(5)	0.0937(4)	0.3562(3)	0.016(1)

Table AV.1 continued

Atom	X/A	Y/B	Z/C	Ueq
C(31)	0.5918(5)	0.1674(4)	0.2624(3)	0.010(1)
C(32)	0.6736(5)	0.2008(4)	0.1996(3)	0.017(1)
C(33)	0.8029(5)	0.2449(5)	0.2132(3)	0.022(1)
C(34)	0.8522(5)	0.2566(4)	0.2889(3)	0.020(1)
C(35)	0.7722(5)	0.2233(4)	0.3520(3)	0.019(1)
C(36)	0.6432(5)	0.1803(4)	0.3386(3)	0.015(1)

Table AV.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(C,Se)-[(2-diphenylselenophosphinyl)phenyl]-tetracarbonylmanganese (32)

Atom	X/A	Y/B	Z/C	U11
H(13)	0.1053(5)	0.3249(4)	0.0788(3)	0.019
H(14)	0.0993(5)	0.4706(4)	0.1637(3)	0.024
H(15)	0.2359(5)	0.4702(4)	0.2786(3)	0.022
H(16)	0.3711(5)	0.3188(4)	0.3080(3)	0.016
H(22)	0.5080(5)	-0.0473(4)	0.3487(3)	0.018
H(23)	0.4150(6)	-0.1236(5)	0.4613(3)	0.034
H(24)	0.2038(6)	-0.0649(5)	0.5096(3)	0.033
H(25)	0.0786(6)	0.0681(5)	0.4416(3)	0.027
H(26)	0.1711(5)	0.1493(4)	0.3295(3)	0.019
H(32)	0.6401(5)	0.1931(4)	0.1472(3)	0.021
H(33)	0.8582(5)	0.2674(5)	0.1701(3)	0.027
H(34)	0.9411(5)	0.2875(4)	0.2980(3)	0.024
H(35)	0.8068(5)	0.2303(4)	0.4042(3)	0.023
H(36)	0.5880(5)	0.1591(4)	0.3820(3)	0.018

Table AV.3 Thermal Parameters for η^2-(C,Se)-[(2-diphenylseleno-phosphinyl)phenyl]tetracarbonylmanganese (32)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0060(4)	0.0190(5)	0.0067(4)	0.0011(3)	0.0009(3)	-0.0023(3)
Se(1)	0.0130(3)	0.0146(3)	0.0109(3)	-0.0055(2)	-0.0018(2)	0.0047(2)
P(1)	0.0059(6)	0.0124(7)	0.0073(6)	-0.0004(5)	0.0012(5)	0.0015(5)
C(1)	0.016(3)	0.040(4)	0.009(3)	0.002(3)	0.002(2)	-0.006(3)
C(2)	0.012(3)	0.034(3)	0.017(3)	0.003(3)	-0.002(2)	-0.011(3)
C(3)	0.012(3)	0.018(3)	0.017(3)	0.000(2)	0.005(2)	-0.001(2)
C(4)	0.013(3)	0.035(4)	0.009(3)	0.000(2)	0.002(2)	-0.001(3)
O(1)	0.029(2)	0.037(3)	0.022(2)	-0.018(2)	0.005(2)	-0.008(2)
O(2)	0.022(2)	0.042(3)	0.032(2)	0.011(2)	-0.014(2)	-0.006(2)
O(3)	0.022(2)	0.037(3)	0.036(2)	0.004(2)	0.016(2)	-0.005(2)
O(4)	0.029(2)	0.039(3)	0.025(2)	-0.002(2)	0.016(2)	-0.010(2)
C(11)	0.003(2)	0.014(3)	0.011(2)	0.005(2)	0.004(2)	-0.004(2)
C(12)	0.007(2)	0.015(3)	0.010(2)	0.003(2)	0.007(2)	-0.002(2)
C(13)	0.009(3)	0.020(3)	0.020(3)	0.007(2)	-0.002(2)	0.008(2)
C(14)	0.015(3)	0.015(3)	0.030(3)	0.006(2)	0.008(2)	0.008(2)
C(15)	0.014(3)	0.014(3)	0.027(3)	-0.003(2)	0.013(2)	-0.002(2)
C(16)	0.010(3)	0.017(3)	0.014(3)	0.000(2)	0.004(2)	-0.001(2)
C(21)	0.014(3)	0.013(3)	0.007(2)	-0.002(2)	0.002(2)	0.004(2)
C(22)	0.017(3)	0.010(3)	0.018(3)	0.002(2)	0.004(2)	0.005(2)
C(23)	0.037(4)	0.029(4)	0.019(3)	0.009(3)	0.002(3)	0.013(3)
C(24)	0.036(3)	0.029(3)	0.017(3)	0.004(3)	0.010(3)	-0.005(3)
C(25)	0.020(3)	0.029(3)	0.020(3)	-0.001(3)	0.016(2)	-0.004(3)
C(26)	0.012(3)	0.019(3)	0.016(3)	0.004(2)	0.002(2)	0.001(2)
C(31)	0.011(3)	0.009(3)	0.009(3)	-0.003(2)	0.002(2)	0.004(2)
C(32)	0.016(3)	0.027(3)	0.009(2)	0.002(2)	0.002(2)	-0.005(2)
C(33)	0.011(3)	0.033(3)	0.023(3)	0.001(3)	0.010(2)	0.004(2)
C(34)	0.010(3)	0.015(3)	0.035(3)	-0.003(2)	-0.006(2)	0.004(2)
C(35)	0.018(3)	0.022(3)	0.018(3)	-0.003(2)	-0.008(2)	0.005(2)
C(36)	0.013(3)	0.021(3)	0.010(3)	0.000(2)	0.004(2)	0.001(2)

Appendix VI

Thermal and Positional Parameters for bis[(benzylseleno)tetracarbonylmanganese] (33)

Table AVI.1 Final Positional and Equivalent Thermal Parameters for bis[(benzylseleno)tetracarbonylmanganese] (33)

Atom	X/A	Y/B	Z/C	Ueq
Se(1)	0.1501(1)	0.4944(1)	0.1223(1)	0.020(1)
Mn(1)	0.0993(1)	0.2919(1)	0.0020(1)	0.017(1)
O(1)	0.0241(9)	0.0733(6)	-0.1610(5)	0.040(1)
O(2)	-0.2956(8)	0.2783(6)	0.1719(6)	0.041(1)
O(3)	0.3955(8)	0.0527(6)	0.1628(5)	0.036(1)
O(4)	0.4922(8)	0.3109(6)	-0.1667(5)	0.034(1)
C(1)	0.0573(10)	0.1573(7)	-0.0999(7)	0.024(2)
C(2)	-0.1467(12)	0.2853(8)	0.1073(7)	0.028(2)
C(3)	0.2804(10)	0.1458(7)	0.1038(7)	0.022(1)
C(4)	0.3429(11)	0.3065(7)	-0.1022(6)	0.022(1)
C(7)	0.0036(12)	0.4930(8)	0.2982(6)	0.032(2)
C(11)	0.1660(25)	0.3866(16)	0.3844(13)	0.018(3)
C(12)	0.3559(24)	0.4041(19)	0.4286(15)	0.030(3)
C(13)	0.4783(25)	0.3033(18)	0.5165(15)	0.032(3)
C(14)	0.4072(27)	0.1792(23)	0.5619(18)	0.035(4)
C(15)	0.2212(33)	0.1514(19)	0.5258(17)	0.038(4)
C(16)	0.1034(25)	0.2561(16)	0.4329(14)	0.026(3)
C(11A)	0.0998(23)	0.3603(16)	0.3871(13)	0.017(3)
C(12A)	0.3047(22)	0.3495(16)	0.4288(13)	0.021(3)
C(13A)	0.4147(25)	0.2405(21)	0.5227(16)	0.031(3)
C(14A)	0.3058(29)	0.1366(18)	0.5659(16)	0.029(3)
C(15A)	0.0968(25)	0.1401(16)	0.5226(14)	0.030(3)
C(16A)	0.0003(26)	0.2529(16)	0.4354(14)	0.027(3)

Table AVI.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for bis[(benzylseleno)tetracarbonylmanganese] (33)

Atom	X/A	Y/B	Z/C	U11
H(7A)	-0.0402(12)	0.5938(8)	0.3308(6)	0.038
H(7B)	-0.1299(12)	0.4606(8)	0.2961(6)	0.038
H(12)	0.4018(24)	0.4881(19)	0.3971(15)	0.037
H(13)	0.6080(25)	0.3163(18)	0.5464(15)	0.038
H(14)	0.4949(27)	0.1094(23)	0.6223(18)	0.042
H(15)	0.1760(33)	0.0682(19)	0.5608(17)	0.045
H(16)	-0.0228(25)	0.2405(16)	0.4006(14)	0.032
H(12A)	0.3763(22)	0.4196(16)	0.3921(13)	0.025
H(13A)	0.5519(25)	0.2386(21)	0.5538(16)	0.037
H(14A)	0.3738(29)	0.0592(18)	0.6274(16)	0.035
H(15A)	0.0276(25)	0.0666(16)	0.5535(14)	0.036
H(16A)	-0.1398(26)	0.2582(16)	0.4067(14)	0.033

Table AVI.3 Thermal Parameters for bis[(benzylseleno)tetracarbonylmanganese] (33)

Atom	U11	U22	U33	U23	U13	U12
Se(1)	0.0261(4)	0.0128(4)	0.0207(4)	-0.0024(3)	-0.0059(3)	-0.0056(3)
Mn(1)	0.0217(5)	0.0107(5)	0.0191(5)	-0.0008(4)	-0.0007(4)	-0.0077(4)
O(1)	0.058(3)	0.023(3)	0.044(3)	-0.011(3)	-0.007(3)	-0.019(2)
O(2)	0.030(3)	0.036(3)	0.057(4)	0.000(3)	0.019(3)	-0.014(2)
O(3)	0.040(3)	0.023(3)	0.040(3)	0.007(2)	-0.012(2)	0.000(2)
O(4)	0.032(3)	0.030(3)	0.043(3)	-0.008(2)	0.013(2)	-0.018(2)
C(1)	0.027(3)	0.013(3)	0.033(4)	-0.001(3)	0.003(3)	-0.005(3)
C(2)	0.041(4)	0.015(3)	0.031(4)	-0.008(3)	-0.001(3)	-0.011(3)
C(3)	0.026(3)	0.015(3)	0.026(4)	-0.003(3)	0.003(3)	-0.009(3)
C(4)	0.031(4)	0.016(3)	0.021(3)	-0.004(3)	-0.004(3)	-0.010(3)
C(7)	0.048(4)	0.020(4)	0.017(3)	-0.007(3)	-0.002(3)	0.008(3)

Appendix VII

Thermal and Positional Parameters for (39)

Table AVII.1 Final Positional and Equivalent Thermal Parameters for (39)

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	0.3092(1)	0.3194(1)	0.7595(1)	0.027(1)
S(1)	0.4355(2)	0.4914(2)	0.6783(2)	0.026(1)
P(1)	0.6059(2)	0.4534(2)	0.7377(2)	0.021(1)
O(1)	0.3219(6)	0.3432(8)	0.9603(6)	0.049(2)
O(2)	0.0921(7)	0.4944(7)	0.7263(7)	0.056(2)
O(3)	0.2408(8)	0.3206(7)	0.5582(6)	0.054(2)
O(4)	0.1627(7)	0.1018(7)	0.8569(6)	0.050(2)
O(41)	0.5014(6)	0.1947(6)	0.6161(5)	0.036(2)
O(42)	0.3978(6)	0.0405(6)	0.7270(5)	0.036(2)
O(43)	0.6619(6)	0.0340(6)	0.7728(6)	0.045(2)
O(44)	0.7490(6)	0.0676(6)	0.8989(5)	0.036(2)
C(1)	0.3253(8)	0.3318(9)	0.8852(9)	0.037(2)
C(2)	0.1769(9)	0.4271(9)	0.7390(8)	0.035(2)
C(3)	0.2739(9)	0.3199(8)	0.6305(9)	0.036(2)
C(4)	0.2192(8)	0.1858(9)	0.8192(7)	0.033(2)
C(11)	0.6692(8)	0.5983(8)	0.7208(7)	0.026(2)
C(12)	0.7938(8)	0.6165(9)	0.6993(9)	0.041(3)
C(13)	0.8410(9)	0.7267(9)	0.6932(10)	0.049(3)
C(14)	0.7647(11)	0.8168(9)	0.7060(9)	0.047(3)
C(15)	0.6406(8)	0.7984(8)	0.7252(8)	0.034(2)
C(16)	0.5935(8)	0.6909(8)	0.7325(7)	0.028(2)
C(21)	0.7130(7)	0.3795(7)	0.6779(7)	0.022(2)
C(22)	0.6909(8)	0.3885(8)	0.5814(7)	0.028(2)
C(23)	0.7755(9)	0.3399(9)	0.5311(8)	0.038(2)
C(24)	0.8826(9)	0.2844(10)	0.5787(8)	0.042(3)
C(25)	0.9062(8)	0.2743(9)	0.6771(8)	0.038(2)

Table AVII.1 continued

Atom	X/A	Y/B	Z/C	Ueq
C(26)	0.8222(8)	0.3223(8)	0.7265(7)	0.027(2)
C(31)	0.6056(7)	0.3625(8)	0.8720(7)	0.023(2)
C(32)	0.5818(7)	0.2377(8)	0.9079(7)	0.024(2)
C(33)	0.5820(8)	0.1721(8)	1.0098(7)	0.027(2)
C(34)	0.5988(9)	0.2267(9)	1.0774(8)	0.037(2)
C(35)	0.6197(9)	0.3535(9)	1.0407(7)	0.033(2)
C(36)	0.6237(8)	0.4184(8)	0.9400(7)	0.030(2)
C(41)	0.4623(8)	0.1999(8)	0.7759(7)	0.025(2)
C(42)	0.4542(8)	0.1302(8)	0.7086(7)	0.029(2)
C(43)	0.4921(12)	0.1419(11)	0.5419(9)	0.051(3)
C(44)	0.5610(8)	0.1765(8)	0.8353(7)	0.025(2)
C(45)	0.6601(8)	0.0846(8)	0.8309(7)	0.029(2)
C(46)	0.8501(11)	-0.0171(11)	0.8961(9)	0.053(3)
C(99)	0.1974(10)	0.9198(11)	0.6541(11)	0.047(3)
Cl(1)	0.2307(4)	0.7628(3)	0.6951(3)	0.071(2)
Cl(2)	0.0643(4)	0.9593(5)	0.7035(5)	0.110(2)
Cl(3)	0.1870(6)	0.9789(6)	0.5228(4)	0.111(2)

Table AVII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for (39)

Atom	X/A	Y/B	Z/C	U11
H(12)	0.8461(8)	0.5553(9)	0.6890(9)	0.049
H(13)	0.9267(9)	0.7399(9)	0.6800(10)	0.059
H(14)	0.7979(11)	0.8915(9)	0.7016(9)	0.056
H(15)	0.5877(8)	0.8607(8)	0.7333(8)	0.040
H(16)	0.5076(8)	0.6787(8)	0.7458(7)	0.034
H(22)	0.6166(8)	0.4286(8)	0.5488(7)	0.034
H(23)	0.7594(9)	0.3451(9)	0.4648(8)	0.046
H(24)	0.9422(9)	0.2521(10)	0.5445(8)	0.051
H(25)	0.9806(8)	0.2341(9)	0.7096(8)	0.046
H(26)	0.8381(8)	0.3167(8)	0.7929(7)	0.033
H(33)	0.5701(8)	0.0867(8)	1.0343(7)	0.032
H(34)	0.5965(9)	0.1800(9)	1.1478(8)	0.044
H(35)	0.6308(9)	0.3928(9)	1.0865(7)	0.039
H(36)	0.6390(8)	0.5032(8)	0.9154(7)	0.035
H(43A)	0.5455(57)	0.1844(49)	0.4842(28)	0.077
H(43B)	0.4060(18)	0.1500(64)	0.5196(43)	0.077
H(43C)	0.5184(69)	0.0551(21)	0.5712(20)	0.077
H(46A)	0.8952(45)	0.0173(33)	0.8320(26)	0.080
H(46B)	0.8166(12)	-0.0951(26)	0.9024(59)	0.080
H(46C)	0.9066(40)	-0.0306(56)	0.9520(35)	0.080
H(99)	0.2680(10)	0.9581(11)	0.6731(11)	0.056

Table AVII.3 Thermal Parameters for (39)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0091(8)	0.0243(9)	0.0513(10)	-0.0199(7)	-0.0049(6)	0.0112(6)
S(1)	0.0105(11)	0.0208(12)	0.0486(14)	-0.0157(10)	-0.0085(9)	0.0142(9)
P(1)	0.0101(12)	0.0173(13)	0.0393(14)	-0.0156(10)	-0.0050(9)	0.0126(9)
O(1)	0.026(4)	0.080(6)	0.059(5)	-0.047(4)	0.000(3)	0.012(4)
O(2)	0.023(4)	0.046(5)	0.102(6)	-0.035(4)	-0.007(4)	0.018(4)
O(3)	0.053(5)	0.061(5)	0.053(5)	-0.028(4)	-0.021(4)	0.012(4)
O(4)	0.030(4)	0.047(5)	0.070(5)	-0.018(4)	0.006(4)	-0.011(4)
O(41)	0.037(4)	0.031(4)	0.047(4)	-0.024(3)	0.005(3)	0.003(3)
O(42)	0.033(4)	0.022(4)	0.059(4)	-0.021(3)	-0.010(3)	0.004(3)
O(43)	0.036(4)	0.041(4)	0.077(5)	-0.046(4)	-0.022(4)	0.026(3)
O(44)	0.022(3)	0.036(4)	0.059(4)	-0.029(3)	-0.011(3)	0.027(3)
C(1)	0.008(5)	0.034(6)	0.066(7)	-0.019(5)	0.001(4)	0.005(4)
C(2)	0.013(5)	0.024(5)	0.065(7)	-0.016(5)	-0.004(4)	0.017(4)
C(3)	0.023(5)	0.022(5)	0.061(7)	-0.017(5)	-0.004(5)	0.011(4)
C(4)	0.017(5)	0.037(6)	0.048(6)	-0.022(5)	-0.009(4)	0.014(5)
C(11)	0.019(5)	0.021(5)	0.041(5)	-0.016(4)	-0.010(4)	0.011(4)
C(12)	0.012(5)	0.033(6)	0.090(8)	-0.041(6)	-0.001(5)	0.019(4)
C(13)	0.016(5)	0.036(6)	0.109(9)	-0.044(6)	0.014(5)	-0.003(5)
C(14)	0.052(7)	0.024(6)	0.071(7)	-0.026(5)	0.010(6)	-0.004(5)
C(15)	0.020(5)	0.025(5)	0.064(7)	-0.027(5)	-0.005(4)	0.015(4)
C(16)	0.012(4)	0.025(5)	0.054(6)	-0.022(4)	0.001(4)	0.014(4)
C(21)	0.008(4)	0.017(4)	0.046(5)	-0.021(4)	0.000(4)	0.012(3)
C(22)	0.022(5)	0.022(5)	0.044(6)	-0.018(4)	-0.008(4)	0.013(4)
C(23)	0.027(5)	0.045(6)	0.049(6)	-0.027(5)	0.003(5)	0.014(5)
C(24)	0.023(5)	0.047(6)	0.068(7)	-0.038(6)	0.008(5)	0.017(5)
C(25)	0.013(5)	0.042(6)	0.066(7)	-0.032(5)	-0.008(4)	0.022(4)
C(26)	0.014(5)	0.024(5)	0.051(6)	-0.023(4)	-0.008(4)	0.014(4)
C(31)	0.007(4)	0.022(5)	0.044(5)	-0.019(4)	-0.004(4)	0.016(3)
C(32)	0.010(4)	0.021(5)	0.047(6)	-0.019(4)	-0.005(4)	0.013(3)
C(33)	0.018(5)	0.021(5)	0.043(6)	-0.014(4)	-0.009(4)	0.016(4)
C(34)	0.030(5)	0.036(6)	0.044(6)	-0.017(5)	-0.004(4)	0.014(4)
C(35)	0.032(5)	0.031(6)	0.043(6)	-0.025(5)	-0.007(4)	0.016(4)
C(36)	0.021(5)	0.021(5)	0.051(6)	-0.020(4)	-0.007(4)	0.011(4)
C(41)	0.019(5)	0.017(5)	0.038(5)	-0.009(4)	-0.001(4)	0.003(4)
C(42)	0.015(5)	0.024(5)	0.056(6)	-0.023(5)	-0.011(4)	0.010(4)

Table AVII.3 continued

Atom	U11	U22	U33	U23	U13	U12
C(43)	0.063(8)	0.044(7)	0.059(7)	-0.034(6)	-0.011(6)	0.010(6)
C(44)	0.017(5)	0.019(5)	0.042(5)	-0.014(4)	0.002(4)	0.003(4)
C(45)	0.018(5)	0.019(5)	0.052(6)	-0.016(4)	-0.010(4)	0.012(4)
C(46)	0.037(6)	0.055(7)	0.069(8)	-0.028(6)	-0.016(6)	0.037(5)
C(99)	0.019(6)	0.033(7)	0.101(10)	-0.040(7)	-0.017(6)	0.015(5)
Cl(1)	0.084(3)	0.048(2)	0.094(3)	-0.045(2)	-0.037(2)	0.030(2)
Cl(2)	0.048(2)	0.131(4)	0.211(6)	-0.136(5)	0.025(3)	0.005(3)
Cl(3)	0.109(4)	0.128(5)	0.085(3)	-0.027(3)	-0.025(3)	0.015(3)

Appendix VIII

Thermal and Positional Parameters for *trans*-η^2-(C,S)-[(2-diphenylthiophosphinyl)-phenyl]dicarbonylbis(trimethylphosphite)-manganese (40)

Table AVIII.1 Final Positional and Equivalent Thermal Parameters for trans-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis-(trimethylphosphite)manganese (40)

Atom	X/A	Y/B	Z/C	Ueq
Mn(1)	-0.2782(1)	-0.5147(1)	-0.2033(1)	0.016(1)
P(1)	-0.3848(1)	-0.4791(1)	-0.0469(1)	0.018(1)
P(2)	-0.4416(2)	-0.6193(1)	-0.2175(1)	0.019(1)
P(3)	-0.1132(1)	-0.4131(1)	-0.1814(1)	0.018(1)
S(1)	-0.4653(1)	-0.4469(1)	-0.1346(1)	0.019(1)
C(1)	-0.3432(5)	-0.4598(3)	-0.2737(2)	0.019(1)
C(2)	-0.1442(6)	-0.5636(3)	-0.2554(2)	0.021(1)
C(3)	-0.6698(6)	-0.6999(4)	-0.1541(3)	0.036(1)
C(4)	-0.4221(8)	-0.7775(3)	-0.2557(3)	0.044(2)
C(5)	-0.6918(6)	-0.5424(3)	-0.2543(3)	0.031(1)
C(6)	-0.1056(7)	-0.2505(3)	-0.1665(3)	0.037(1)
C(7)	0.0187(7)	-0.3835(3)	-0.2958(3)	0.034(1)
C(8)	0.0943(6)	-0.4626(3)	-0.0949(3)	0.031(1)
O(1)	-0.3768(4)	-0.4277(2)	-0.3228(2)	0.029(1)
O(2)	-0.0593(4)	-0.5925(2)	-0.2923(2)	0.033(1)
O(3)	-0.5279(4)	-0.6546(2)	-0.1538(2)	0.025(1)
O(4)	-0.3585(4)	-0.6965(2)	-0.2503(2)	0.028(1)
O(5)	-0.5832(4)	-0.6078(2)	-0.2681(2)	0.026(1)
O(6)	-0.1914(4)	-0.3239(2)	-0.1833(2)	0.026(1)
O(7)	0.0369(4)	-0.4026(2)	-0.2274(2)	0.024(1)
O(8)	-0.0277(4)	-0.4072(2)	-0.1124(2)	0.023(1)

Table AVIII.1 continued

Atom	X/A	Y/B	Z/C	Ueq
C(11)	-0.2577(5)	-0.5650(3)	-0.0571(2)	0.019(1)
C(12)	-0.2090(5)	-0.5827(3)	-0.1220(2)	0.017(1)
C(13)	-0.1095(6)	-0.6522(3)	-0.1260(2)	0.023(1)
C(14)	-0.0655(6)	-0.6983(3)	-0.0721(2)	0.026(1)
C(15)	-0.1164(6)	-0.6780(3)	-0.0096(2)	0.028(1)
C(16)	-0.2136(6)	-0.6120(3)	-0.0026(2)	0.024(1)
C(21)	-0.5441(6)	-0.5083(3)	0.0058(2)	0.020(1)
C(22)	-0.6161(6)	-0.4505(3)	0.0457(2)	0.026(1)
C(23)	-0.7493(6)	-0.4707(4)	0.0790(2)	0.033(1)
C(24)	-0.8084(6)	-0.5497(3)	0.0738(3)	0.031(1)
C(25)	-0.7375(6)	-0.6078(3)	0.0347(2)	0.030(1)
C(26)	-0.6049(6)	-0.5875(3)	0.0011(3)	0.028(1)
C(31)	-0.2962(6)	-0.3935(3)	-0.0041(2)	0.022(1)
C(32)	-0.3354(7)	-0.3132(3)	-0.0221(3)	0.033(1)
C(33)	-0.2887(8)	-0.2470(3)	0.0159(3)	0.041(2)
C(34)	-0.1999(7)	-0.2596(3)	0.0706(3)	0.038(1)
C(35)	-0.1552(8)	-0.3387(4)	0.0877(3)	0.040(2)
C(36)	-0.2045(7)	-0.4060(3)	0.0506(3)	0.035(1)

Table AVIII.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for trans-η^2-(C,S)-[(2-diphenylthio-phosphinyl)phenyl]dicarbonylbis(trimethylphosphite)manganese (40)

Atom	X/A	Y/B	Z/C	U11
H(3A)	-0.7421(16)	-0.6740(14)	-0.1236(14)	0.055
H(3B)	-0.6506(9)	-0.7572(7)	-0.1407(18)	0.055
H(3C)	-0.7134(22)	-0.6993(20)	-0.1984(5)	0.055
H(4A)	-0.3517(25)	-0.8130(8)	-0.2805(19)	0.066
H(4B)	-0.5211(25)	-0.7746(5)	-0.2784(19)	0.066
H(4C)	-0.4373(46)	-0.8007(11)	-0.2118(3)	0.066
H(5A)	-0.7844(18)	-0.5505(13)	-0.2808(13)	0.046
H(5B)	-0.6455(16)	-0.4888(4)	-0.2650(17)	0.046
H(5C)	-0.7190(32)	-0.5436(14)	-0.2078(5)	0.046
H(6A)	-0.1608(24)	-0.2015(3)	-0.1821(17)	0.056
H(6B)	-0.0041(19)	-0.2529(12)	-0.1871(16)	0.056
H(6C)	-0.0937(39)	-0.2474(13)	-0.1188(3)	0.056
H(7A)	0.1178(11)	-0.3661(22)	-0.3140(5)	0.052
H(7B)	-0.0560(33)	-0.3386(16)	-0.3008(3)	0.052
H(7C)	-0.0179(41)	-0.4327(8)	-0.3191(4)	0.052
H(8A)	0.0944(26)	-0.4710(17)	-0.0473(3)	0.046
H(8B)	0.1928(7)	-0.4389(11)	-0.1084(16)	0.046
H(8C)	0.0790(23)	-0.5159(8)	-0.1168(14)	0.046
H(13)	-0.0712(6)	-0.6679(3)	-0.1677(2)	0.027
H(14)	0.0006(6)	-0.7446(3)	-0.0779(2)	0.031
H(15)	-0.0845(6)	-0.7093(3)	0.0274(2)	0.033
H(16)	-0.2515(6)	-0.5980(3)	0.0396(2)	0.029
H(22)	-0.5736(6)	-0.3966(3)	0.0501(2)	0.031
H(23)	-0.7996(6)	-0.4305(4)	0.1054(2)	0.040
H(24)	-0.8987(6)	-0.5641(3)	0.0972(3)	0.038
H(25)	-0.7798(6)	-0.6618(3)	0.0308(2)	0.036
H(26)	-0.5553(6)	-0.6279(3)	-0.0252(3)	0.034
H(32)	-0.3942(7)	-0.3038(3)	-0.0606(3)	0.039
H(33)	-0.3183(8)	-0.1924(3)	0.0041(3)	0.049
H(34)	-0.1691(7)	-0.2138(3)	0.0967(3)	0.046
H(35)	-0.0911(8)	-0.3473(4)	0.1247(3)	0.048
H(36)	-0.1752(7)	-0.4605(3)	0.0627(3)	0.042

Table AVIII.3 Thermal Parameters for trans-η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis(trimethylphosphite)manganese (40)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0134(3)	0.0143(3)	0.0191(3)	-0.0007(3)	0.0002(3)	0.0005(3)
P(1)	0.0168(5)	0.0182(5)	0.0184(5)	-0.0017(5)	0.0007(5)	0.0004(5)
P(2)	0.0192(6)	0.0184(5)	0.0196(6)	-0.0015(4)	0.0007(5)	-0.0021(5)
P(3)	0.0154(5)	0.0163(5)	0.0218(6)	0.0004(4)	-0.0002(5)	-0.0006(5)
S(1)	0.0169(5)	0.0207(5)	0.0200(5)	-0.0009(4)	-0.0004(5)	0.0043(5)
C(1)	0.014(2)	0.015(2)	0.028(2)	-0.003(2)	0.003(2)	0.003(2)
C(2)	0.021(2)	0.016(2)	0.025(2)	-0.001(2)	-0.002(2)	0.000(2)
C(3)	0.025(3)	0.047(3)	0.038(3)	0.005(3)	0.000(2)	-0.017(3)
C(4)	0.050(4)	0.025(3)	0.057(4)	-0.013(3)	0.009(3)	-0.006(3)
C(5)	0.024(3)	0.042(3)	0.027(3)	0.001(2)	-0.006(2)	0.002(2)
C(6)	0.037(3)	0.012(2)	0.062(4)	0.000(2)	-0.003(3)	-0.009(2)
C(7)	0.034(3)	0.039(3)	0.030(3)	0.008(2)	0.009(3)	-0.005(3)
C(8)	0.024(3)	0.037(3)	0.031(3)	0.002(2)	-0.006(2)	0.001(2)
O(1)	0.031(2)	0.031(2)	0.025(2)	0.0065(15)	-0.006(2)	0.003(2)
O(2)	0.026(2)	0.030(2)	0.041(2)	-0.009(2)	0.009(2)	0.001(2)
O(3)	0.023(2)	0.029(2)	0.023(2)	0.0016(14)	0.0013(15)	-0.014(2)
O(4)	0.027(2)	0.020(2)	0.038(2)	-0.010(2)	0.003(2)	-0.002(2)
O(5)	0.023(2)	0.033(2)	0.022(2)	-0.0021(14)	-0.0037(15)	-0.006(2)
O(6)	0.021(2)	0.0152(15)	0.042(2)	0.0003(14)	-0.003(2)	-0.0001(14)
O(7)	0.020(2)	0.029(2)	0.022(2)	0.0021(14)	0.0035(14)	-0.003(2)
O(8)	0.024(2)	0.022(2)	0.024(2)	-0.0037(14)	-0.0040(15)	-0.001(2)
C(11)	0.016(2)	0.018(2)	0.022(2)	-0.001(2)	-0.001(2)	0.000(2)
C(12)	0.014(2)	0.015(2)	0.022(2)	-0.002(2)	-0.003(2)	-0.004(2)
C(13)	0.022(2)	0.018(2)	0.028(2)	-0.001(2)	0.003(2)	0.002(2)
C(14)	0.021(2)	0.019(2)	0.037(3)	0.004(2)	-0.002(2)	0.004(2)
C(15)	0.029(3)	0.024(2)	0.030(3)	0.008(2)	-0.003(2)	-0.001(2)
C(16)	0.026(3)	0.028(2)	0.019(2)	0.000(2)	0.000(2)	0.000(2)
C(21)	0.017(2)	0.025(2)	0.018(2)	0.002(2)	0.001(2)	0.000(2)
C(22)	0.029(3)	0.027(2)	0.023(2)	-0.003(2)	0.004(2)	-0.001(2)
C(23)	0.032(3)	0.045(3)	0.024(2)	-0.002(2)	0.010(2)	0.010(3)
C(24)	0.020(3)	0.043(3)	0.030(3)	0.010(2)	0.005(2)	0.000(2)
C(25)	0.025(3)	0.030(3)	0.036(3)	0.003(2)	0.002(2)	-0.003(2)
C(26)	0.027(3)	0.023(2)	0.034(3)	-0.003(2)	0.001(2)	-0.004(2)

Table AVIII.3 continued

Atom	U11	U22	U33	U23	U13	U12
C(31)	0.019(2)	0.026(2)	0.022(2)	-0.007(2)	0.003(2)	-0.004(2)
C(32)	0.035(3)	0.029(3)	0.034(3)	-0.007(2)	-0.005(3)	-0.003(2)
C(33)	0.047(4)	0.022(2)	0.053(4)	-0.006(3)	-0.001(3)	-0.006(3)
C(34)	0.041(3)	0.037(3)	0.037(3)	-0.015(3)	0.007(3)	-0.013(3)
C(35)	0.045(4)	0.046(4)	0.028(3)	-0.009(3)	-0.007(3)	-0.002(3)
C(36)	0.041(3)	0.032(3)	0.031(3)	-0.002(2)	-0.005(3)	0.000(3)

Appendix IX

Thermal and Positional Parameters for η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

Table AIX.1 Final Positional and Equivalent Thermal Parameters for η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]tetracarbonyl-manganese (45)

Atom	X/A	Y/B	Z/C	Ueq
Se(1)	0.2315(2)	0.1478(3)	0.1315(1)	0.037(1)
Mn(1)	0.0747(3)	0.2807(4)	0.1625(2)	0.036(1)
S(1)	0.1696(6)	0.4906(6)	0.1859(3)	0.036(2)
P(1)	0.3327(6)	0.3099(6)	0.0873(3)	0.026(2)
O(1)	-0.0370(15)	0.0037(18)	0.1313(8)	0.054(6)
O(2)	0.1279(14)	0.2174(17)	0.3227(8)	0.048(5)
O(3)	-0.1166(18)	0.4173(21)	0.2022(11)	0.069(6)
O(4)	0.0469(14)	0.3474(17)	0.0025(8)	0.046(5)
O(5)	0.2693(13)	0.4601(16)	0.2258(7)	0.037(5)
O(6)	0.1090(14)	0.6093(17)	0.2154(8)	0.046(5)
C(1)	0.0027(23)	0.1076(29)	0.1456(13)	0.044(7)
C(2)	0.1021(20)	0.2459(23)	0.2588(11)	0.034(6)
C(3)	-0.0421(27)	0.3646(29)	0.1848(13)	0.043(7)
C(4)	0.0549(19)	0.3206(21)	0.0658(11)	0.026(5)
C(11)	0.2750(19)	0.4811(22)	0.0599(10)	0.029(5)
C(12)	0.2130(18)	0.5659(21)	0.1025(10)	0.024(5)
C(13)	0.1756(19)	0.6993(23)	0.0779(11)	0.032(6)
C(14)	0.2029(19)	0.7553(24)	0.0123(11)	0.035(6)
C(15)	0.2626(20)	0.6741(23)	-0.0318(11)	0.036(6)
C(16)	0.2998(19)	0.5400(22)	-0.0098(10)	0.029(5)
C(21)	0.4498(19)	0.3473(22)	0.1445(10)	0.026(5)

Table AIX.1 continued

Atom	X/A	Y/B	Z/C	Ueq
C(22)	0.4944(20)	0.4802(24)	0.1447(11)	0.036(6)
C(23)	0.5885(20)	0.4954(25)	0.1830(11)	0.038(6)
C(24)	0.6339(21)	0.3761(23)	0.2233(11)	0.034(6)
C(25)	0.5829(20)	0.2500(24)	0.2264(11)	0.037(6)
C(26)	0.4895(20)	0.2335(25)	0.1853(11)	0.037(6)
C(31)	0.3759(21)	0.2255(21)	0.0074(10)	0.022(5)
C(32)	0.4769(24)	0.2134(24)	-0.0066(12)	0.037(6)
C(33)	0.5089(22)	0.1563(24)	-0.0701(11)	0.040(6)
C(34)	0.4372(23)	0.1085(24)	-0.1216(12)	0.038(6)
C(35)	0.3368(24)	0.1134(25)	-0.1128(12)	0.042(6)
C(36)	0.3026(23)	0.1688(24)	-0.0465(11)	0.040(6)

Table AIX.2 Final Positional and Thermal Parameters of Calculated Hydrogen Atoms for η^2-(S,Se)-[(2-diphenylselenophosphinyl)-phenylsulfonyl]tetracarbonylmanganese (45)

Atom	X/A	Y/B	Z/C	U11
H(13)	0.1307(19)	0.7529(23)	0.1062(11)	0.038
H(14)	0.1806(19)	0.8501(24)	-0.0026(11)	0.042
H(15)	0.2781(20)	0.7117(23)	-0.0780(11)	0.043
H(16)	0.3417(19)	0.4859(22)	-0.0403(10)	0.035
H(22)	0.4622(20)	0.5603(24)	0.1194(11)	0.043
H(23)	0.6234(20)	0.5863(25)	0.1825(11)	0.046
H(24)	0.6999(21)	0.3862(23)	0.2478(11)	0.041
H(25)	0.6100(20)	0.1724(24)	0.2562(11)	0.044
H(26)	0.4537(20)	0.1433(25)	0.1859(11)	0.045
H(32)	0.5274(24)	0.2461(24)	0.0296(12)	0.044
H(33)	0.5798(22)	0.1503(24)	-0.0779(11)	0.047
H(34)	0.4592(23)	0.0699(24)	-0.1659(12)	0.046
H(35)	0.2887(24)	0.0801(25)	-0.1505(12)	0.050
H(36)	0.2318(23)	0.1681(24)	-0.0382(11)	0.048

Table AIX.3 Thermal Parameters for η^2-(S,Se)-[(2-diphenylseleno-phosphinyl)phenylsulfonyl]tetracarbonylmanganese (45)

Atom	U11	U22	U33	U23	U13	U12
Se(1)	0.042(3)	0.0340(13)	0.0355(13)	0.0024(10)	0.0005(12)	-0.0013(13)
Mn(1)	0.039(4)	0.041(2)	0.028(2)	-0.0017(15)	0.004(2)	-0.005(2)
S(1)	0.045(7)	0.033(3)	0.029(3)	-0.003(2)	0.002(3)	-0.004(3)
P(1)	0.021(6)	0.037(3)	0.022(3)	0.003(2)	0.003(3)	0.001(3)
O(1)	0.063(18)	0.047(11)	0.051(10)	0.005(8)	-0.004(9)	-0.011(10)
O(2)	0.055(17)	0.051(10)	0.038(9)	-0.003(8)	0.010(9)	-0.016(10)
O(3)	0.058(20)	0.056(12)	0.097(14)	0.001(11)	0.028(13)	0.003(12)
O(4)	0.045(17)	0.049(10)	0.041(9)	0.002(7)	-0.007(9)	-0.014(9)
O(5)	0.039(16)	0.041(9)	0.028(7)	0.009(7)	-0.009(8)	0.007(9)
O(6)	0.042(16)	0.048(11)	0.053(9)	-0.006(8)	0.037(9)	-0.007(9)

Appendix X

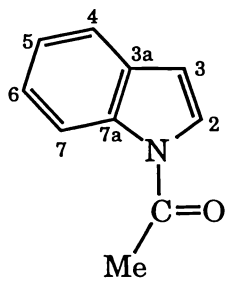
Infrared Stretching Frequencies υ(C=O) of Substituted Indoles and their Corresponding Orthomanganated Complexes

Compound	υ(C=O)
1-acetylindole	
free ligand **(1)**	1707(s)
orthomanganated **(4)**	1588(m), 1565(m)
1-(2-(methylprop-2-enoly)indole	
free ligand **(2)**	1686(s)
orthomanganated **(5)**	1587(m), 1456(m)
1-acetylindole-3-carboxaldehyde	
free ligand	1733(s), 1676(s)[a]
orthomanganated **(6)**	1646(m)[a], 1612(m) 1580(m)
3-acetylindole	
free ligand	1613(s)
orthomanganated **(7)**	1512(m)
1-methyl-3-acetylindole	
free ligand **(3)**	1640(s)
orthomanganated **(8)**	1513(m)
indole-3-carboxaldehyde	
free ligand	1634(s)
orthomanganated **(10)**	1551(m),1540(m)
1-methylindole-3-carboxaldehyde	
free ligand	1642(s)
orthomanganated **(11)**	1545(m)
1,3-diacetylindole	
free ligand **(12)**	1716(s), 1660(s)

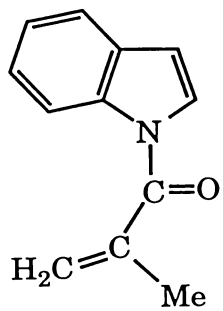
[a]Aldehyde carbonyl

Appendix XI

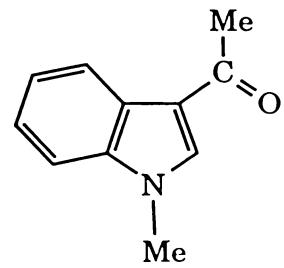
List of Compounds by Numbers and NMR Numbering Schemes



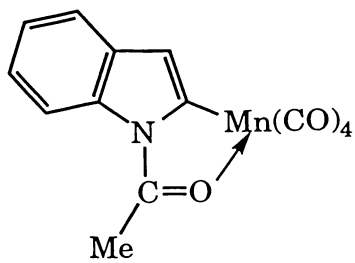
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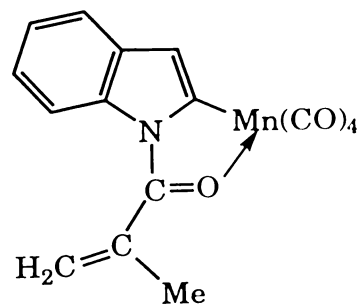
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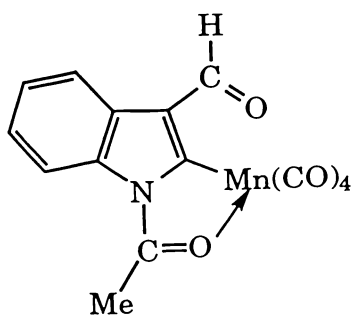
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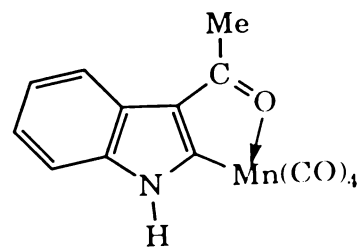
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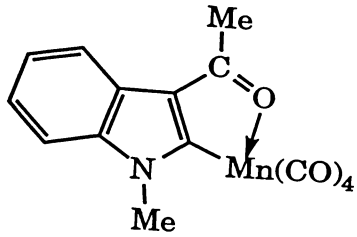
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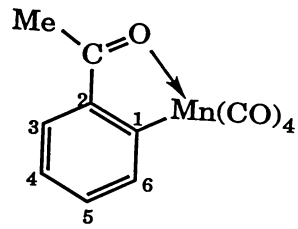
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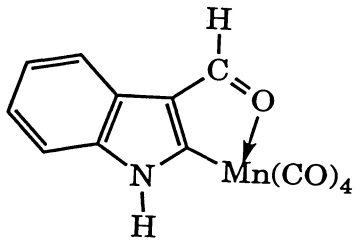
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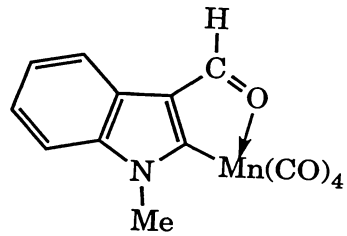
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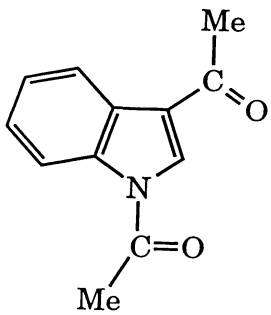
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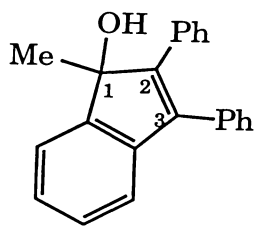
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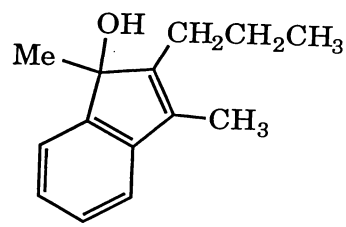
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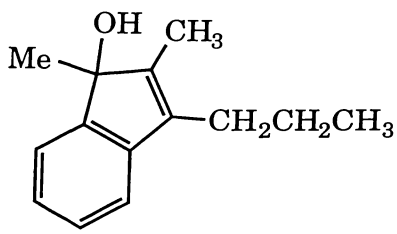
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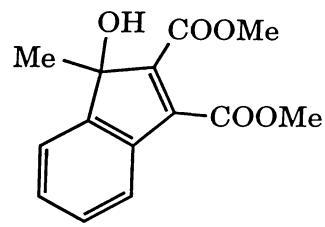
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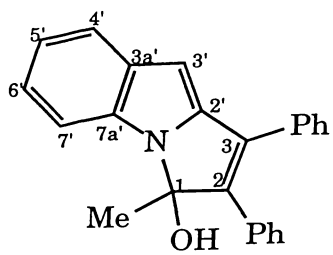
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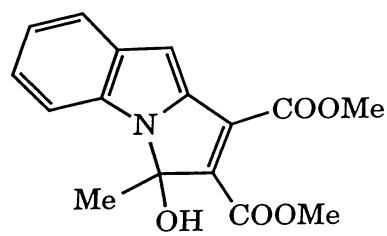
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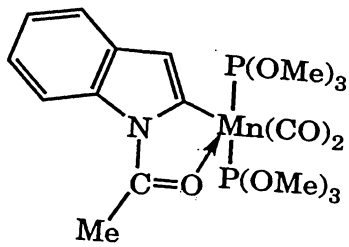
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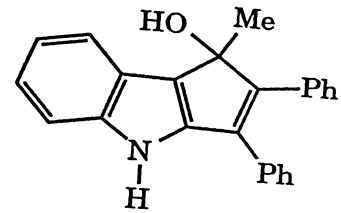
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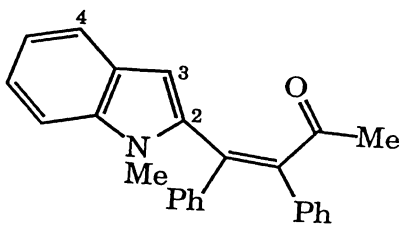
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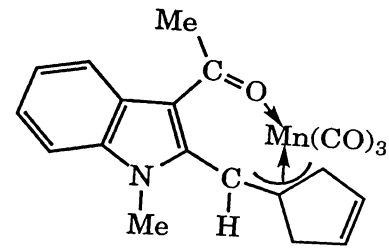
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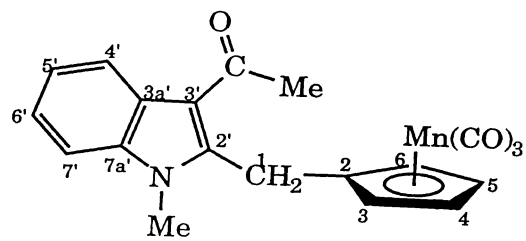
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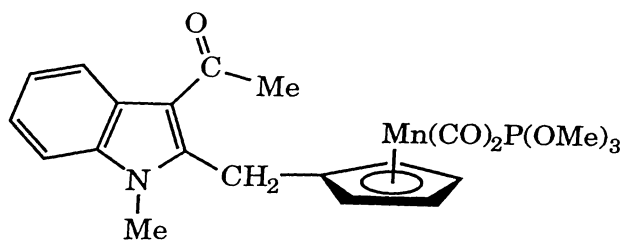
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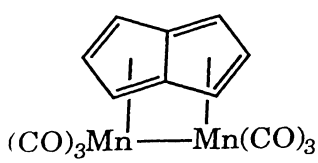
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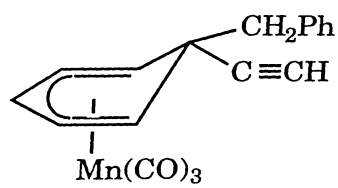
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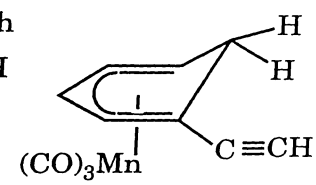
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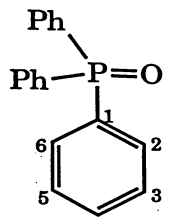
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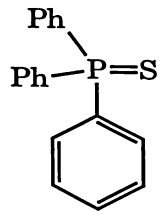
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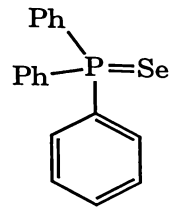
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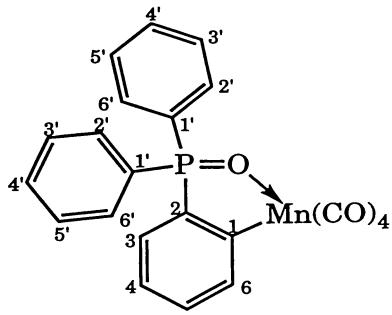
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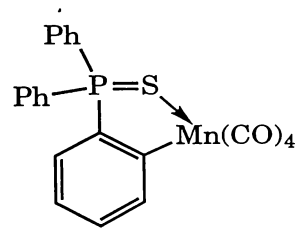
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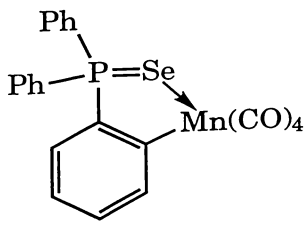
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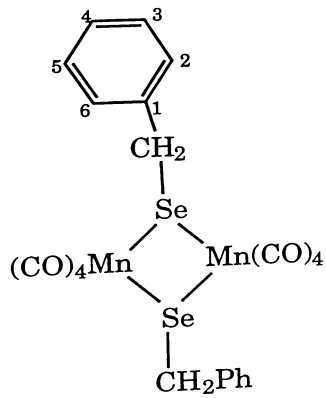
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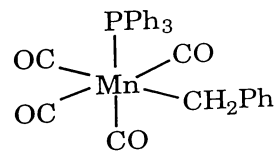
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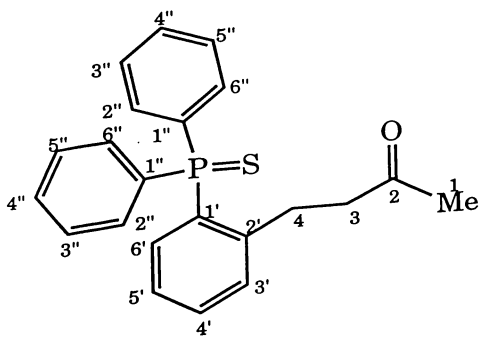
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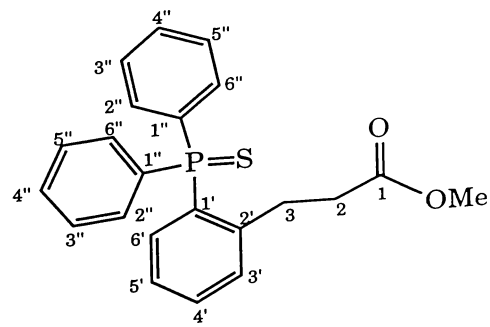
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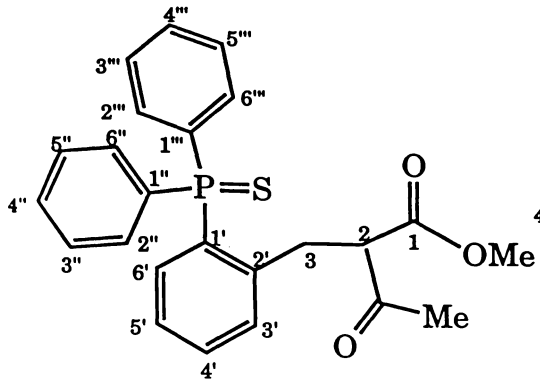
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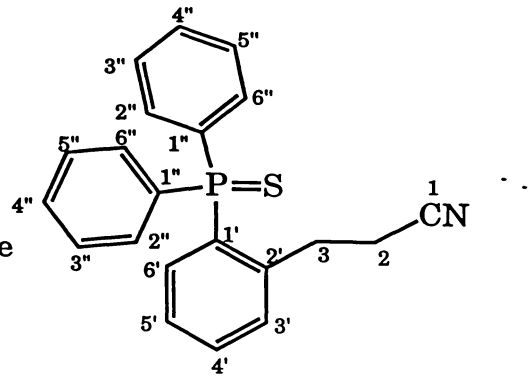
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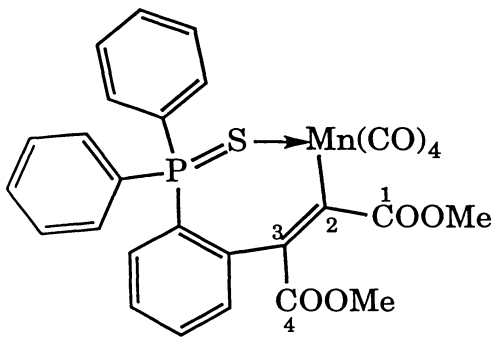
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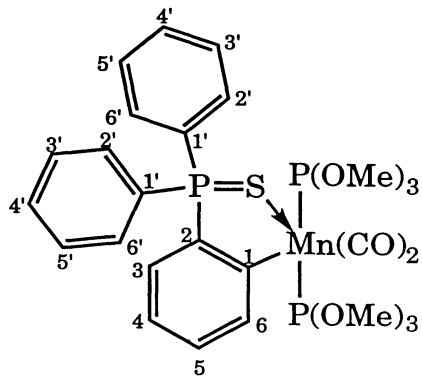
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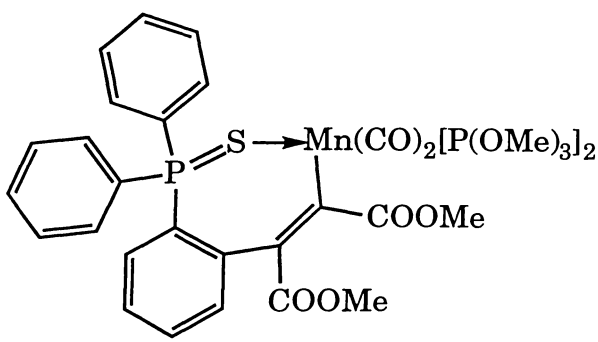
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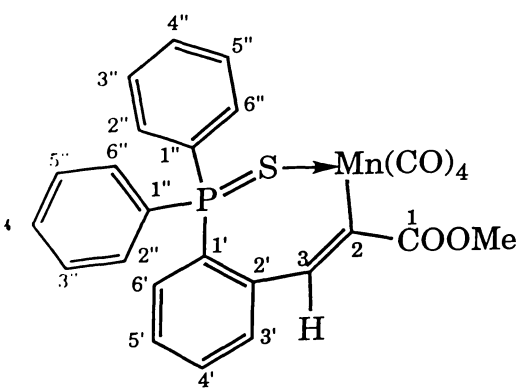
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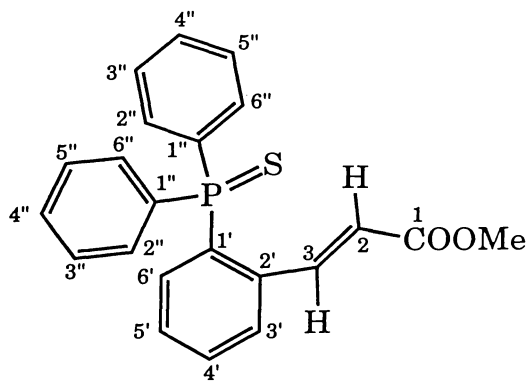
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(41)



(42)



(43)