Reactions of Cyclomanganated Compounds

The University of Waikato
Te Whare Wananga o Waikato

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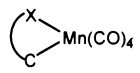
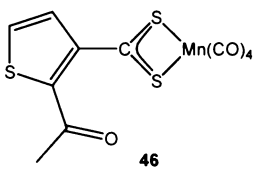
Abstract

This thesis describes novel reactions of cyclomanganated compounds of the general form shown below. The ligand is bonded by a metal-carbon σ-bond, with X acting as a donor atom to form the chelate ring. The organic ligands were derived from aryl and heteroaryl ketones, chalcones, dienones and azabutadienes.



general form of cyclomanganated compounds

A preliminary investigation has previously been undertaken into the reaction of carbon disulfide with some orthomanganated aryl ketones. In the present study these reactions were further investigated, with the isolation of new η^2-S,S-dithiocarboxylate complexes, e.g. **46**. In other cases the reaction of carbon disulfide with cyclomanganated compounds afforded the novel Mn_4 species **50** in low yield.



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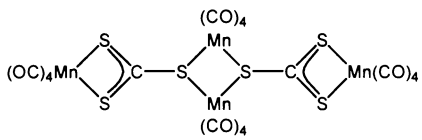

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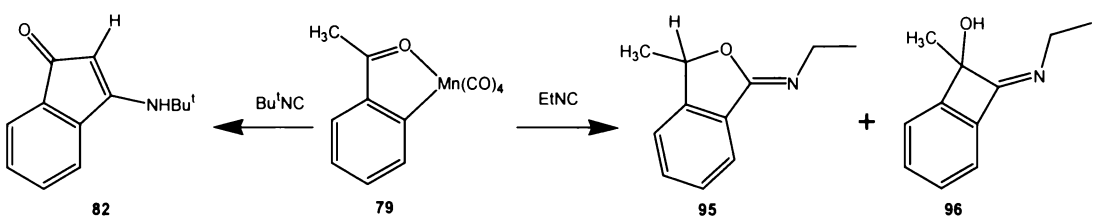
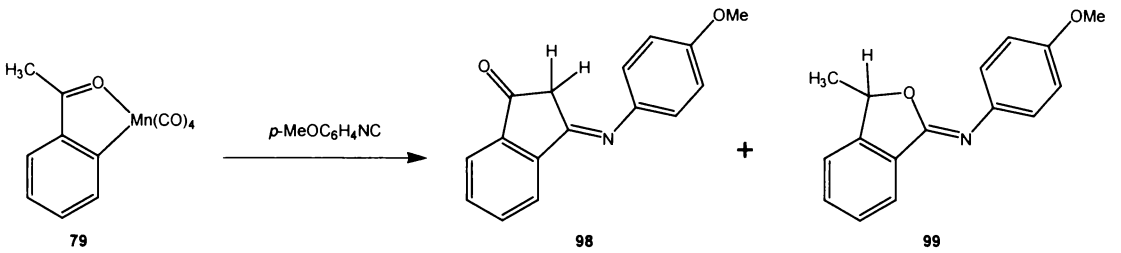
The reactions of orthomanganated acetyl-aryl compounds with organic isocyanides (C≡NR) afforded a number of novel compounds. For example η^2-(2-acetylphenyl)-tetracarbonylmanganese (**79**) afforded four different types of products depending on the isocyanide; *tert*-butyl isocyanide produced **82**, ethyl isocyanide produced **95** and **96**, and 4-methoxyphenyl isocyanide produced **98** and **99**.



82 **79** **95** **96**

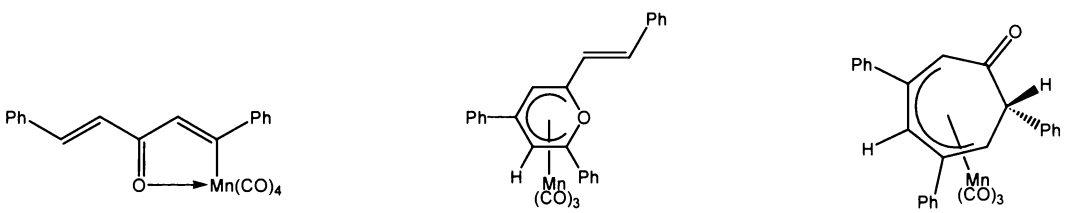


79 98 99

With orthomanganated 2-acetylthiophene, CNBu^t gave the quinone species **88** and **89**, which showed high antifungal and antitumor activity.

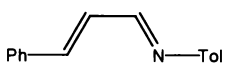
88 89

Cyclomanganated dienones (e.g. **127**) were previously known to react with alkynes to give either (η^5-pyranyl)Mn(CO)$_3$ (e.g. **130**) or (η^5-oxocycloheptadienyl)Mn(CO)$_3$ (e.g. **129**) products. The factors influencing which product is formed were more systematically investigated and a deuterium-labelling experiment was used to probe the 1,2-phenyl shift that occurs for the (η^5-oxocycloheptadienyl)Mn(CO)$_3$ products.

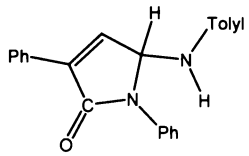


127 130 129

A preliminary investigation of the reactions of 4-phenyl-1-(4-tolyl)-1-azabuta-1,3-diene (TAD) with PhCH$_2$Mn(CO)$_5$ and unsaturated substrates including phenyl acetylene, methyl acrylate, PhNCO, Bu^{t}NC and carbon disulfide is also described. A number of novel compounds were produced, including **169** from the reaction involving PhNCO.

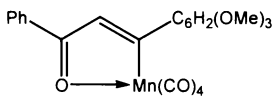


TAD



169

In contrast η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese with allyl isothiocyanate gave simply 2-allyl-4-methoxyacetophenone by allylation of the orthomanganated starting compound. Allyl bromide behaved similarly. However, allyl bromide and ethyl bromide when reacted with the cyclomanganated chalcone **54** gave furanone products (e.g. **190** and **191**). An oxidative addition and reductive elimination mechanism was proposed to explain this reaction.



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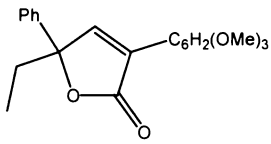

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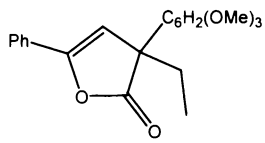

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Among others, the crystal structures of **50**, **89** and **130** were determined.

Acknowledgments

First and foremost I would like to thank my supervisors, Prof. Brian Nicholson and Assoc. Prof. Lyndsay Main, for their support, guidance, and for giving me the room to explore. Both Brian and Lyndsay were free with their counsel, and were active in fostering my interest in all areas of chemistry. The assistance of Dr. Michèle Prinsep, Assoc. Prof. Alistair Wilkins and Assoc. Prof. Bill Henderson was greatly appreciated, for their help with biological testing, GC/MS and experimental techniques.

My gratitude also goes to all the members of the Chemistry Department of the University of Waikato. A special mention is deserved for Wendy Jackson and Pat Gread, the two technicians without whom no research could ever be undertaken. Their tireless efforts to keep the ESMS in working order, and to help solve the other problems of the research students, ensured that research did indeed get done, and normally with a smile.

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I would like to dedicate this thesis to my lovely wife.

This is for you Louise.

All numbered compounds prepared in this study appear in a fold-out section at the rear of this thesis.

Note on Nomenclature

For convenience and brevity, throughout this thesis cyclomanganated compounds containing oxygen, sulfur, selenium, and nitrogen donor atoms are named using a η^2 naming convention to specify that both the aryl carbon and donor atom concerned are coordinated. Strictly speaking this should be specified with a η^2-(C,O) nomenclature, or more correctly using the κ notation. For example, η^2-(acetylphenyl)tetracarbonyl-manganese (**79**) should be written 2-acetyl-κO-phenyl-κC^1-tetra(carbonyl-κC)manganese(I).

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M	metal atom	Tol	4-tolyl
TM	transition metal atom	Xy	2,6-xylyl
R	organic substituent	Mes	2,4,6-mesityl
L	ligand	Cp	cyclopentadienyl
X	halogen	Cp*	pentamethylcyclopentadienyl
Me	methyl	dppe	1,2-*bis*(diphenylphosphino)ethane
Et	ethyl	dmpe	1,2-*bis*(dimethylphosphino)ethane
Pr^{i}	*iso*-propyl	CNR	isocyanide
Bu	butyl	DMAD	dimethyl acetylenedicarboxylate
Bu^{t}	*tert*-butyl	THF	tetrahydrofuran
Cy	cyclohexyl	DMSO	dimethylsulfoxide
Ar	aryl substituent	Ether	diethyl ether
Ph	phenyl		

ESMS	electrospray mass spectroscopy
IR	infra-red spectroscopy
GC/MS	gas chromatography coupled mass spectroscopy
NMR	nuclear magnetic resonance
DEPT	distortionless enhancement by polarisation tranfer
COSY	correlation spectroscopy
HSQC	heteronuclear single quantum correlation
HMBC	heteronuclear multiple bond correlation
PLC	preparative layer chromatography
tlc	thin layer chromatography

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

Chapter 1. Introduction

1.1. Cyclomanganated Complexes.

A cyclometalated complex is formed when a ligand coordinates to a metal centre to form a stable, predominantly five-membered ring (**1** in Figure 1-1). The ligand is bonded to the metal by a M-C σ-bond, with L acting as a donor group, and Y acting as a linker to obtain the five-membered ring. In most cases there is some degree of unsaturation between the carbon atom (C) and the donor group (L). The donor group can be one of many groups containing a heteroatom such as N, O, P, S, etc.

Figure 1-1 General structure of cyclomanganated (**1**) and orthomanganated (**2**) complexes. (L = donor group, Y = linker group).

In the more specific case of an orthometalated complex the carbon to which the metal is bonded is part of an aryl ring system, with the donor group L attached to the *ortho*-site of the aryl ring (**2** in Figure 1-1).

A cyclomanganated complex is normally prepared by reacting an organic precursor with a reactive manganese carbonyl complex such as $MeMn(CO)_5$ or $PhCH_2Mn(CO)_5$. Other indirect routes are also available.

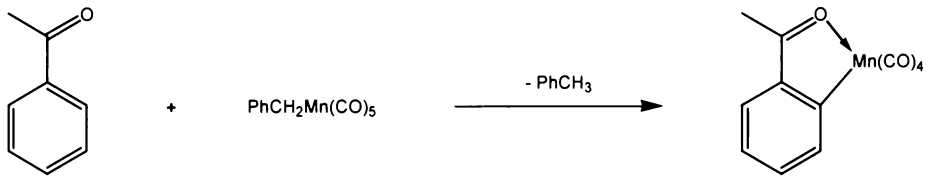
The preparation of orthomanganated acetophenone is shown in Scheme 1-1. The first orthomanganated aromatic ketones to be routinely prepared were reported in 1975 by Kaesz's group[1,2,3,4].

[1] R. J. McKinney, R. Hoxmeier, H. D. Kaesz, *J. Amer. Chem. Soc.*, **97** (1975) 3059

[2] R. J. McKinney, H. D. Kaesz, *J. Amer. Chem. Soc.*, **97** (1975) 3066

[3] R. J. McKinney, G. Firestein, H. D. Kaesz, *Inorg. Chem.*, **14** (1975) 2057

[4] C. B. Knobler, S. S. Crawford, H. D. Kaesz, *Inorg. Chem.*, **14** (1975) 2062



Scheme 1-1 Preparation of orthomanganated acetophenone.

It is the heteroatom of the coordinating group that directs the manganese to attach to the carbon, forming the heterometalocyclic ring. In the case of orthomanganated complexes, the coordinating group directs the manganese to the carbon *ortho* to the functional group. This effect is seen in the orthomanganation of 3-methoxyacetophenone, where the dominant product is formed through the manganese attaching in the more sterically crowded 2-position[3]. The methoxy group appears to further direct the manganese, possibly through lone-pair coordination prior to insertion[5].

Orthomanganated complexes with a range of functional groups with oxygen[3], nitrogen[6,7], sulphur, selenium or phosphorus donor atoms have been prepared, including aldehydes[8], ketones[9], esters, thioethers[10], imines[11], imidazoles[12] and benzamides[8]. A range of triphenylphosphine chalcogenides[13] and triphenylphosphite[14] have also been orthomanganated. Some examples are shown in Figure 1-2 (see reference 5 for a complete list of the earlier examples).

[5] L. Main, B. K. Nicholson, *Adv. Met.-Org. Chem.*, **3** (1994) 1

[6] M. B. Dinger, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **565** (1998) 125

[7] M. A. Leeson, B. K. Nicholson, M. R. Olsen, *J. Organomet. Chem.*, **579** (1999) 243

[8] N. P. Robinson, L. Main, B. K. Nicholson, *J Organomet. Chem.*, **349** (1988) 209

[9] J. M. Cooney, L. H. P. Gommans, L. Main, B. K. Nicholson, *J Organomet. Chem.*, **349** (1988) 197

[10] R. L. Bennett, M. I. Bruce, I. Matsuda, R. J. Doedens, R. G. Little, J. T. Veal, *J. Organomet. Chem.*, **67** (1974) C72

[11] C. Morton, D. J. Duncalf, J. P. Rourke, *J. Organomet. Chem.*, **530** (1997) 19

[12] A. Suárez, J. M. Vila, M. T. Pereira, E. Gayoso, M. Gayoso, *J. Organomet. Chem.*, **335** (1987) 359

[13] G. J. Depree, N. D. Childerhouse, B. K. Nicholson, *J. Organomet. Chem.*, **533** (1997) 143

[14] W. J. Grigsby, L. Main, B. K. Nicholson, *Organometallics*, **12** (1993) 397

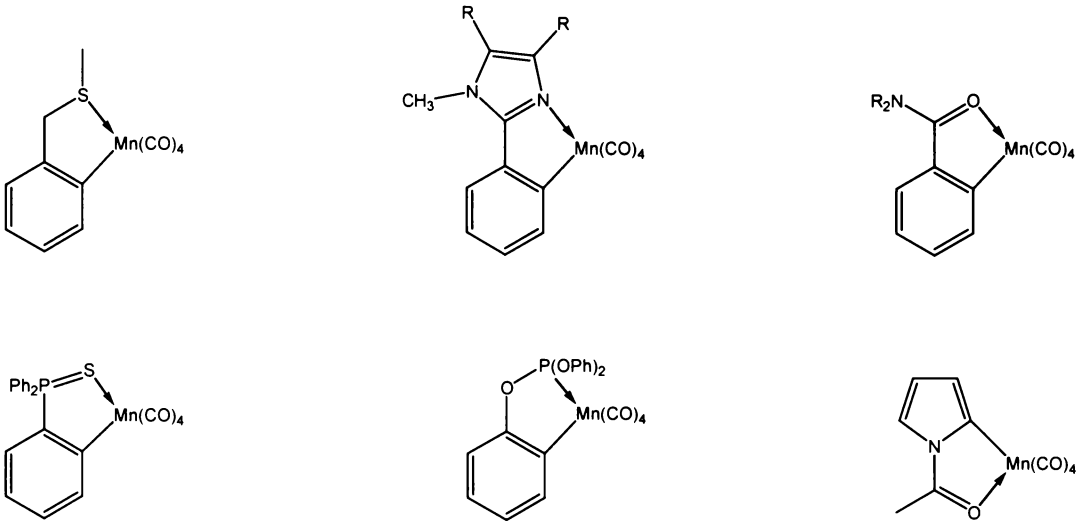
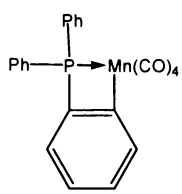


Figure 1-2 The structures of selected orthomanganated complexes.

Cyclomanganated and orthomanganated complexes form predominantly five-membered metalocyclic rings, with no examples known for the direct formation of a six-membered ring metalocyclic ring. A four-membered metalocyclic ring exists for the orthomanganation of triphenylphosphine[1] (**3**), but this is the only directly prepared orthomanganated complex known to directly form a metalocyclic ring other than five-membered.



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The formation of such an orthometalated complex is not unique to manganese, as orthopalladated complexes are commonly prepared, and there are also examples of other metals that form orthometalated complexes[15,16,17]. The characteristic that has raised interest in orthomanganated complexes is the ease with which orthomanganated

[15] M. I. Bruce, B. L. Goodall, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1975) 1651

[16] M. I. Bruce, R. C. F. Gardner, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1976) 81

[17] J. Cámpora, E. Gutiérrez, A. Monge, P. Palma, M. L. Poveda, C. Ruíz, E. Carmona, *Organometallics*, **13** (1994) 1728

complexes can be formed with ketone functional groups, without the necessity of prior activation of the *ortho* site.

The accessibility of orthomanganated aryl ketones has led to considerable investigation into the reactions of these compounds with unsaturated substrates. The idea of such research is to explore the possibility of using orthomanganated aryl ketones in synthetic chemistry. A review was undertaken in the mid-1990's focusing on this aspect of the chemistry[5]. Since that time further studies have continued to explore the synthetic potential of orthomanganated aryl ketones through reactions with a range of unsaturated complexes[18,19], and the research has broadened into reactions involving cyclomanganated non-aromatic ketones[20,21] and other orthomanganated precursors[22]. However, though research has continued, there are a number of unsaturated substrates which still remain unexplored.

1.1.1. Reactions of orthomanganated complexes.

The reactions between orthomanganated complexes and unsaturated substrates can be promoted by either thermal or chemical (oxidative decarbonylative) activation. The most common method is thermal activation, though Adams[23] and Liebeskind[24] have both had success with oxidative decarbonylative activation either in preparing cyclomanganated complexes or reacting orthomanganated complexes with alkynes.

Liebeskind has reacted orthomanganated acetophenones with a range of alkynes in the presence of trimethylamine *N*-oxide (Me_3NO) with acetonitrile as the solvent. The Me_3NO removes one carbonyl from the orthomanganated acetophenone, allowing the precoordination of the alkyne to the complex prior to insertion (see Scheme 1-2). The intermediate undergoes cyclisation and elimination of the metal centre to afford functionalised 1-methylinden-1-ols in very good yields. Similar products are also

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[18] J. M. Cooney, C. V. Depree, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **515** (1996) 109

[19] J. M. Cooney, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **516** (1996) 191

[20] W. Tully, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **503** (1995) 75

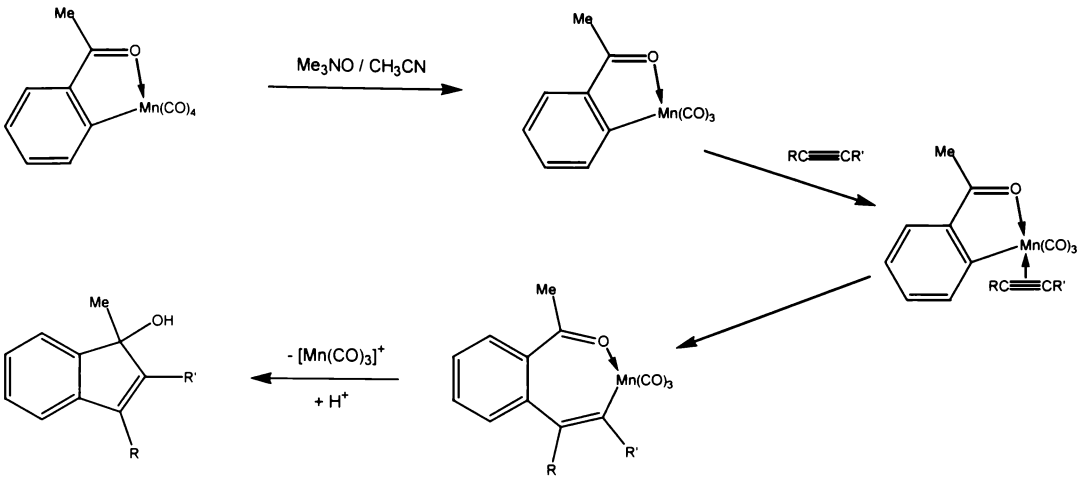
[21] W. Tully, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **507** (1996) 103

[22] G. J. Depree, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **551** (1998) 281

[23] R. D. Adams, M. Huang, *Organometallics*, **14** (1995) 506

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

accessible by thermal activation of the same reactants[25].



Scheme 1-2 Chemically activated reaction of acetophenone and alkynes.

Thermal activation has been the predominant approach for the reaction of an orthomanganated complex with an unsaturated substrate. Quite a range of substrates have been investigated, including alkenes, alkynes, isocyanates[26], sulfur dioxide[27] and PhNSO[19]. All (except PhNSO) initially react by inserting into the Mn-C bond, with many undergoing further reaction to give synthetically interesting products.

The production of an indenyl core is routine, with the preparations of substituted indanols[28], indenols, indenones, indenes[29] and indenyl hydrazines[6] possible. The method has also been extended to the addition of DMAD to cyclomanganated N-acetylindole[30]. This reaction forms a tricyclic carbinolamine **4** which is related to the core of the mitomycin class of antibiotics (**5**).

[25] N. P. Robinson, L. Main, B. K. Nickolson, *J. Organomet. Chem.*, **364** (1989) C37

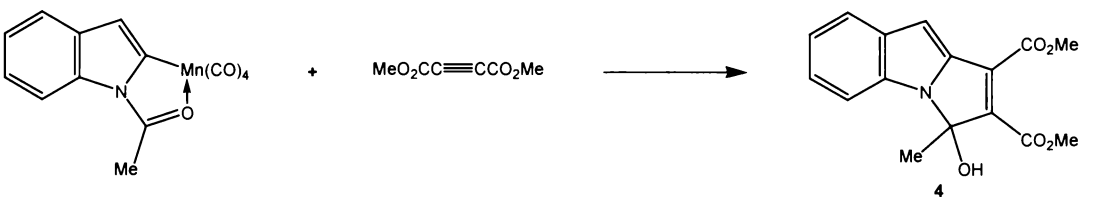
[26] L. S. Liebeskind, S. A. Johnson, J. S. McCallum, *Tetrahedron Lett.*, **31** (1990) 4379

[27] C. V. Depree, L. Main, B. K. Nicholson, K. Roberts, *J. Organomet. Chem.*, **517** (1996) 201

[28] W. J. Grigsby, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **540** (1997) 185

[29] L. H. P. Gommans, L. Main, B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, (1987) 761

[30] N. P. Robinson, Ph.D. Thesis, University of Waikato, (1989)



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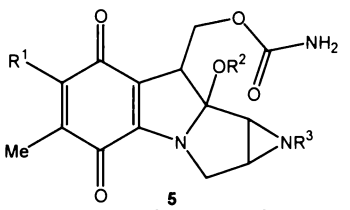

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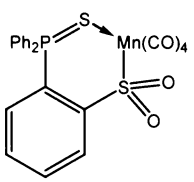
$R^1 = OCH_3, NH_2$; $R^2 = CH_3$, H; R^3 = H, CH_3

The unsaturated substrate SO_2 has been reacted with a range of orthomanganated complexes. Orthomanganated triphenylphosphine chalcogenides[22] and aryl ketones[18] undergo insertion of the SO_2 into the Mn-C bond, affording the S-sulfinato products **6** and **7** respectively. In some cases the aryl ketone products were not able to be isolated in a pure form, with the products evolving CO to give the di-manganese product **8**.



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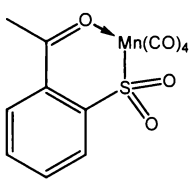

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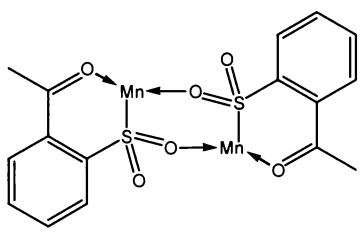

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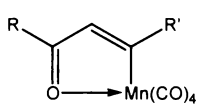
1.1.2. Reactions of cyclomanganated non-aromatic ketones.

Of more interest to the present study are the reactions of cyclomanganated enones (**9**) and dienones (**10**). Both have been shown to have interesting chemistry with unsaturated substrates.



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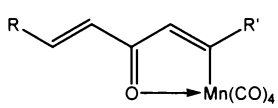

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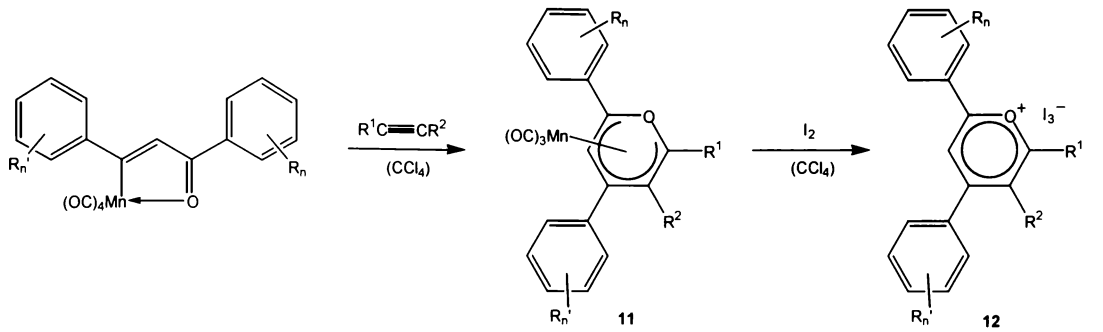
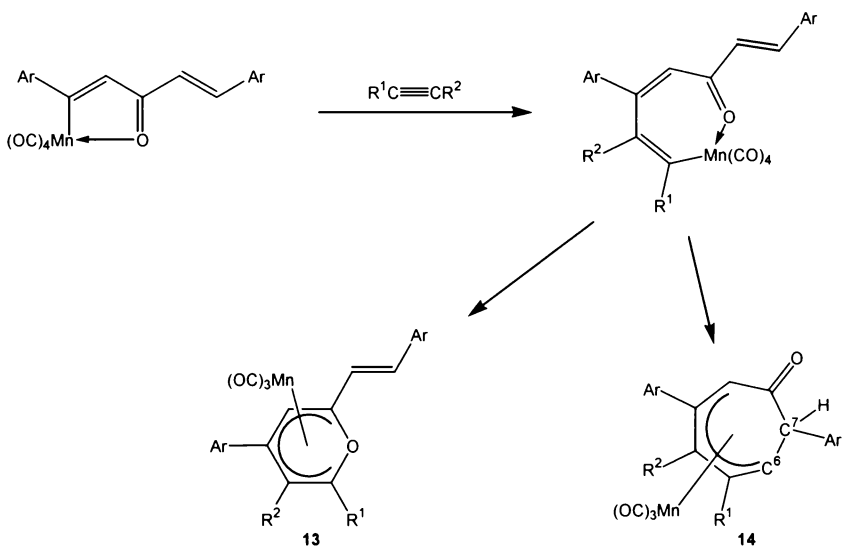
The reaction of cyclomanganated enones with alkynes leads to the production of substituted (η^5-pyranyl)$Mn(CO)_3$ complexes (**11**), which can then be converted into pyrylium triiodide salts (**12**) by addition of excess I_2[21].



However, if cyclomanganated dienones are reacted with alkynes in the same manner, then either of two products is formed, to the exclusion of the other product[31].

The first product is analogous to the substituted pyranyl complex formed above (**13**), but the second product is a (η^5-oxocycloheptadienyl)$Mn(CO)_3$ complex (**14**). The seven-membered ring appears to be formed by cyclisation of the inserted alkyne with the second alkene bond of the carbon chain rather than with the ketone oxygen (Scheme 1-3).



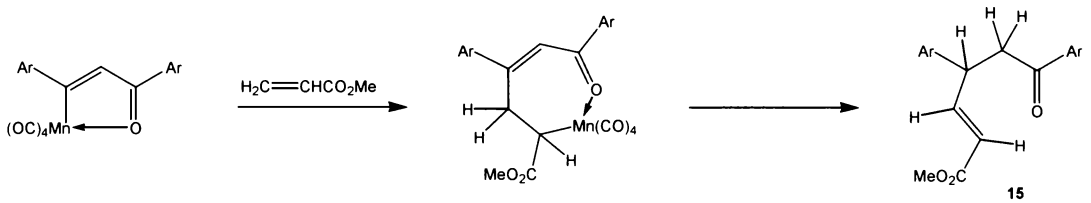
Scheme 1-3 The pyranyl (**13**) and oxocycloheptadienyl (**14**) products from the reaction of orthomanganated dienones and alkynes.

This reaction was of interest for two reasons. Firstly, it was not determined what factors were directing the production of the two products. And secondly, in the

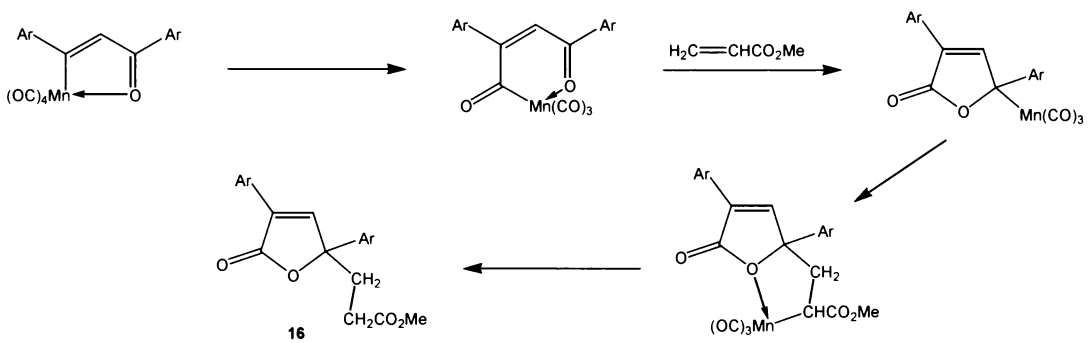
[31] W. Tully, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **633** (2001) 162

oxocycloheptadienyl products, one of the original phenyl groups from the original dienone had undergone a shift from C^6 to C^7. Two mechanisms were proposed, but further investigation was required to determine which was the correct mechanism, and a more thorough investigation was required to determine the factors involved in determining whether the pyranyl or oxocycloheptadienyl complexes were produced. A more detailed investigation of this system is reported in Chapter 4.

When cyclomanganated enones and alkenes such as methyl acrylate and methyl vinyl ketone are thermally reacted, the solvent affects what the final products will be[20]. When reacted in carbon tetrachloride, the only product formed is the insertion and demetalation product **15** in excellent yield.



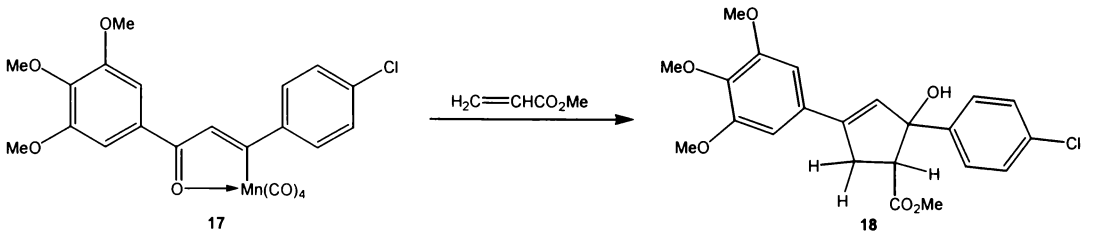
However, when the reaction is conducted in acetonitrile, then the expected insertion product is only produced in low yield (if at all), with a second product (**16**) being formed in good yields. The second product is apparently formed through the insertion of a carbonyl ligand into the Mn-C bond of the original cyclomanganated complex prior to attack of the alkene (see Scheme 1-4). The inserted carbonyl undergoes cyclisation forming a furanyl, with the alkene then inserting into the Mn-$C_{furanyl}$ bond to form **16**.



Scheme 1-4 The reaction of cyclomanganated enones with alkenes in acetonitrile, forming furan products.

This reaction is of interest as a route to substituted furan compounds.

One other product was isolated from the reaction of **17** with methyl acrylate in acetonitrile, that being the cyclopentenol compound **18**.



17 18

1.2. Other Orthometalated Compounds.

1.2.1. Orthopalladated complexes.

Palladium is another metal which has been the focus of considerable research with regards orthometalation. This has predominantly been because palladium is an excellent catalyst for a number of C-C and C-heteroatom bond forming reactions. Recently it has been found that orthopalladated complexes are amongst the most active of these catalysts.

A number of reviews on orthopalladated complexes have been published[32,33], with emphasis on their use as catalysts in a number of bond forming reactions (Heck, Suzuki, Buchwald-Hartwig amination etc.).

Orthopalladated complexes are similar to orthomanganated complexes in the coordination of the chelating ligand, with PR_2, NR, NR_2 and SR groups as the typical donors (L in Figure 1-3). However, orthopalladated complexes differ from orthomanganated complexes in their ability to form "pincer" complexes (**19**), and their tendency to form dimeric complexes depending on the nature of the other ligands (**20**).

[32] J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.*, (2001) 1917

[33] R. B. Bedford, *Chem. Commun.* (2003) 1787

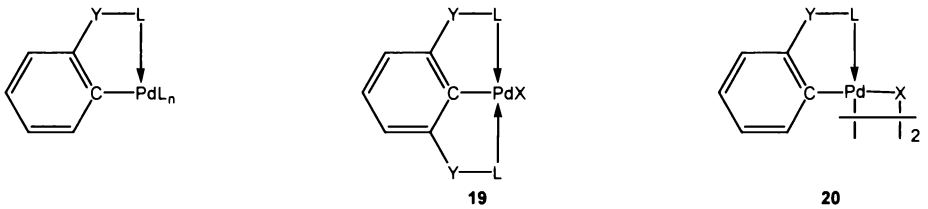


Figure 1-3 General structures of orthopalladated complexes. (L = donor, Y = linker, X = monodentate anionic ligand).

A wide range of orthopalladated complexes have been used in catalytic systems, a selection of which are shown in Figure 1-4. Often the same precatalyst can be used in different systems.

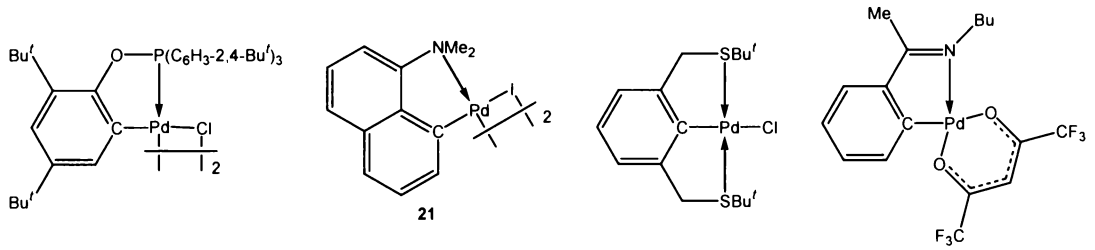
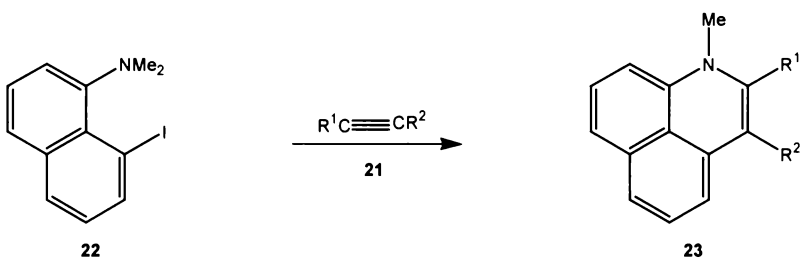


Figure 1-4 A selection of cyclopalladated catalysts.

An example of a catalytic process for which an orthopalladated precatalyst has been used is the hetero-annulation of (dimethylamino)iodonaphthalenes (**22**) to form quinolines (**23**) (Scheme 1-5).

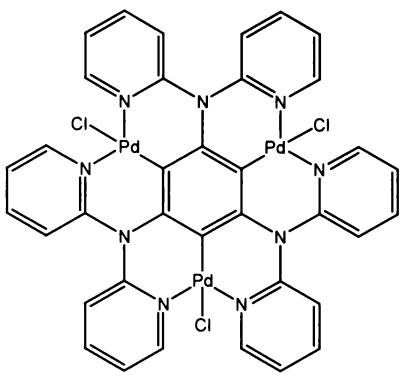


Scheme 1-5 Catalytic preparation of quinolines using the palladium catalyst **21**.

There are also many studies on stoichiometric reactions of cyclopalladated compounds. These reactions are mostly outside the scope of the present study. Relevant examples are discussed in the introduction to Chapter 3. There are also a number of reviews on the

subject[34,35].

There has been some interest into the multiple palladation of benzene rings shown in the last decade. A number of complexes have been prepared where a single benzene ring has been doubly cyclopalladated, but until very recently there was no example of a triply cyclopalladated complex. The triply cyclopalladated complex **24** was prepared by the reaction of 1,3,5-tris(di-2-pyridylamino)benzene and palladium chloride[36].



24

A number of orthomanganated complexes have been prepared which contain a single benzene that has been doubly orthomanganated[37], but there are no known examples of a triply orthomanganated complex equivalent to **24**.

1.2.2. Orthoruthenium complex.

An orthoruthenium complex (**25**) prepared directly from acetophenone and the labile dihydrogen dihydride ruthenium complex $Ru(H_2)H_2(PPh_3)_3$ in high yield[38] has been published since the start of the present study. No investigation has been conducted as to the reactivity of the orthoruthenated complex.

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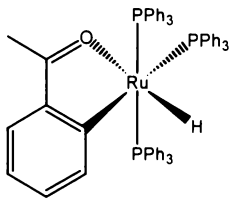
[34] A. D. Ryabov, *Synthesis*, (1985) 233

[35] J. Spencer, M. Pfeffer, *Adv. Metal-Organic Chem.*, (1998) 103

[36] C. J. Sumby, P. J. Steel, *Organometallics*, **22** (2003) 2358

[37] N. P. Robinson, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **430** (1992) 79

[38] R. F. R. Jazzar, M. F. Mahon, M. K. Whittlesey, *Organometallics*, **20** (2001) 3745



25

1.3. Prelibation

Cyclomanganated complexes have been the subject of considerable research, including their reactions with a number of unsaturated substrates. However, there are still a number of other unsaturated substrates whose reactions with cyclomanganated compounds are yet to be explored. The present study investigates the reactions of some of these substrates.

Chapter 2 continues on from a preliminary investigation into the insertion of carbon disulfide into orthomanganated ketones. The present study determines the optimum conditions for the reaction, and fully characterises the previous product and additional products generated. The insertion of carbon disulfide into other orthomanganated compounds, and into cyclomanganated non-aromatic ketones is also explored, leading to the characterisation of a dimeric Mn_4 species.

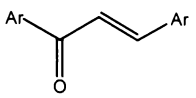
Chapter 3 explores the reactions of isocyanides (mainly *tert*-butyl isocyanide) with orthomanganated compounds. The triple C≡N-R bond is related to the R-C≡C-R bond of acetylenes, so similar insertion/cyclisation reactions were expected.

Chapter 4 investigates the reaction of cyclomanganated dienones with alkynes to determine why two different products can be produced from the same reaction with only slight alteration of the starting substrates. A mechanistic study was also conducted utilising deuterium labelling in an effort to explain a 1,2-phenyl shift that occurs in the production of one of the products.

Chapter 5 explores the cyclomanganation of azabutadiene compounds. Azabutadienes (**27**) are the imine equivalent of enones (**28**), and had not been explored with regards cyclometalation prior to this study[39]. Cyclomanganated azabutadienes may prove to have

[39] Concurrent with the present study, cyclopalladated azabutadienes have been reported (S. Tenreiro, G. Alberdi, J. Martínez, M. lópez-Torres, J. M. Ortigueira, M. T. Pereira, J. M. Vila, *Inorg. Chim. Acta*, **342**

interesting chemistry with regards to their reactions with unsaturated substrates, similar to the reactions of cyclomanganated enones.



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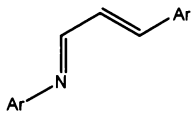


27

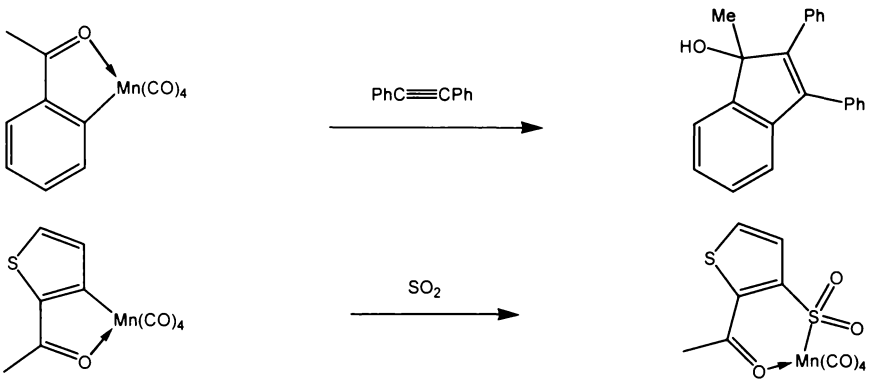
Chapter 6 investigates the reactions of a range of orthomanganated and cyclomanganated compounds with another unsaturated substrate, allyl isothiocyanate. Due to the combination of two different sites of reactivity (the isothiocyanate group (S=C=N-) and the double bond of the allyl group (CH_2=CH-)), allyl isothiocyanate was expected to give some interesting chemistry.

(2003) 145), but have not been further investigated with regards to their reactions with unsaturated substrates.

Chapter 2. The Reaction of Carbon Disulfide with Cyclomanganated Compounds

2.1. Introduction

In the past two decades interest has been shown in the coupling of *ortho*-functionalised cyclomanganated complexes with simple unsaturated molecules (alkenes, alkynes, isocyanides and sulfur dioxide). Examples include the insertion of alkynes into orthomanganated aryl ketones forming inden-1-ols[40] and the insertion of sulfur dioxide into orthomanganated aryl ketones forming aryl sulfonates[41] (Scheme 2-1).



Scheme 2-1 Insertion of alkynes and SO_2 into orthomanganated aryl ketones.

One heterocumulene that has not been explored in detail with regards orthomanganated complexes is carbon disulfide. This small unsaturated molecule has long been known to insert into a variety of metal-element bonds, including M-C(sp^2), with reactions between copper mercaptides and carbon disulfide found to produce trithiocarbonates as early as 1931[42].

Carbon disulfide has the same valence electron configuration and is isostructural with carbon dioxide, but is one of the more reactive heterocumulenes. It is more reactive than carbon dioxide due to a higher electrophilicity of the carbon atom and increased polarity

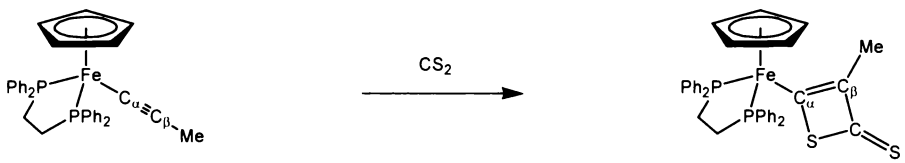
[40] N. P.Robinson, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **364** (1989) C37

[41] J. M. Cooney, C. V. Depree, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **515** (1996) 109

[42] W. E. Duncan, E. Ott, E. E. Reid, *Ind. Eng. Chem.*, **23** (1931) 381

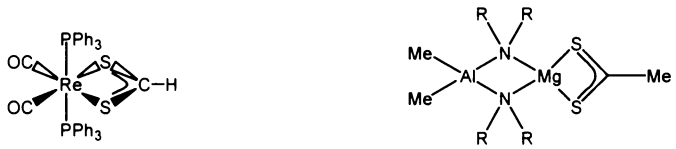
of the C=S bond[43]. These effects arise due to sulfur forming weaker π-interactions with the carbon, and as a result carbon disulfide is a better σ-donor and π-acceptor than carbon dioxide[44].

The electrophilic nature of carbon disulfide is evident in the reaction of Cp(dppe)FeC≡CMe (**28**). The alkynyl β-carbon has increased electron density caused by backbonding from the filled metal orbitals, and reacts with the electrophilic carbon disulfide carbon to form the 2 + 2 cycloaddition complex **29**.



28 **29**

Carbon disulfide has quite an extensive insertion chemistry, with insertion into M-H and M-C(sp^3) bonds well known for a range of complexes. The resulting products are generally isolated as stable bidentate dithioformate or dithiocarboxylate complexes respectively. Examples include the reaction of carbon disulfide with $Re(CO)_3(PPh_3)_2(H)$[45] and $[Me_2Al(\mu\text{-}NR_2)_2MgMe]$[46] forming **30** and **31** respectively. The reaction of carbon disulfide with $HTc(CO)_3(PPh_3)_2$ forms the expected dithioformate complex, which remains bidentate even when heated in the presence of a potential ligand such as carbon monoxide[47].



30 **31**

[43] E. B. Brouwer, P. Legzdins, S. J. Rettig, K. J. Ross, *Organometallics*, **12** (1993) 4234

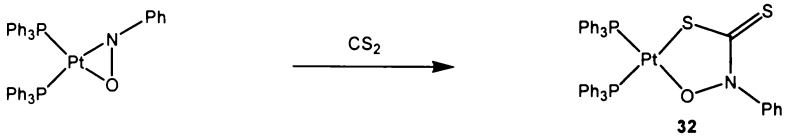
[44] K. K. Pandey, *Coord. Chem. Rev.*, **140** (1995) 37

[45] V. G. Albano, P. L. Bellon, G. Ciani, *J. Organometal. Chem.*, **31** (1971) 75

[46] C-C. Chang, J-H. Chen, B. Srinivas, M. Y. Chiang, G-H. Lee, S-M. Peng, *Organometallics.*, **16** (1997) 4980

[47] J. Cook, A. Davison, W. M. Davis, A. G. Jones, *Organometallics*, **14** (1995) 650

Although consistently encountered, the bidentate η^2-S_2C complex is not exclusively formed. The platinum species $PtX(SC(S)H)(PR_3)_2$[48] is one of few examples of a η^1-SC(S) complex formed by the insertion of carbon disulfide. Insertion into the Pt-N bond of $Pt(PhNO)(PPh_3)_2$ is a rare example where insertion occurs to form a bidentate complex (**32**) in which coordination to one of the original chelating atoms is retained[49].



32

Carbon disulfide insertion is not limited to M-H or M-C(sp^3) bonds. Other common insertions involve the M-C(aryl), M-N, M-O, M-P, and M-S bonds; e.g. $Cp^*Mo(NO)(\eta^2$-$S_2CAryl)(Aryl)$[50], $Ti(\eta^2$-$S_2CNR_2)_4$[51], $Ni(\eta^2$-$S_2COMe)_2$[52], $[RuH(CO)(\eta^2$-$S_2CPCy_3)(PCy_3)_2]$[53], and $CpMo(CO)_2(\eta^2$-$S_2CSR)$[54]. $[Pt(PPh_3)_2(\eta^2$-$S_2CF)]HF_2$[55] is one of the rare examples of a product from insertion into a M-X bond.

There are believed to be two mechanisms for the insertion of carbon disulfide into a M-X bond; either direct attack by the electrophilic carbon of carbon disulfide on a metal-bound nucleophile or coordination of carbon disulfide to the metal centre, prior to insertion.

An example of attack on a metal-bound nucleophile is the insertion of carbon disulfide into the Re-O bond of $(OC)_3Re(PMe_3)_2OMe$[56]. The reaction occurs rapidly at low temperatures (-40°C) affording a η^1-S_2COMe ligand in the final product. Kinetic experiments determined that the reaction occurred by attack of the electrophile directly at

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[48] A. Palazzi, L. Busetto, M. Graziani, *J. Organometal. Chem.*, **30** (1971) 273

[49] S. Cenini, F. Porta, M. Pizzotti, C. Crotti, *J. Chem. Soc. Dalton Trans.*, (1985) 163

[50] E. B. Brouwer, P. Legzdins, S. J. Rettig, K. J. Ross, *Organometallics.*, **12** (1993) 4234

[51] D. C. Bradley, M. H. Gitlitz, *J. Chem. Soc. (A)*, (1969) 1152

[52] N. Nehmé, S. J. Teichner, *Bull. Soc. Chim. Fr.*, (1960) 659

[53] T. R. Grafney, J. A. Ibers, *Inorg. Chem.*, **21** (1982) 2062

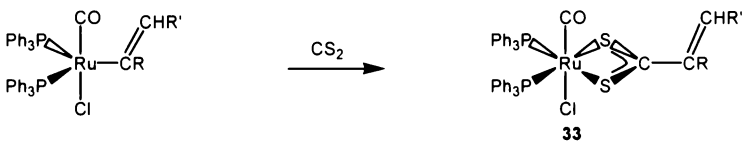
[54] I. S. Butler, A. E. Fenster, *J. Organometal. Chem.*, **66** (1974) 161

[55] J. A. Evans, M. J. Hacker, R. D. W. Kemmit, D. R. Russell, J. Stocks, *Chem. Commun.*, (1972) 72

[56] R. D. Simpson, R. G. Bergman, *Angew. Chem. Int. Ed. Engl.*, **31** (1992) 220

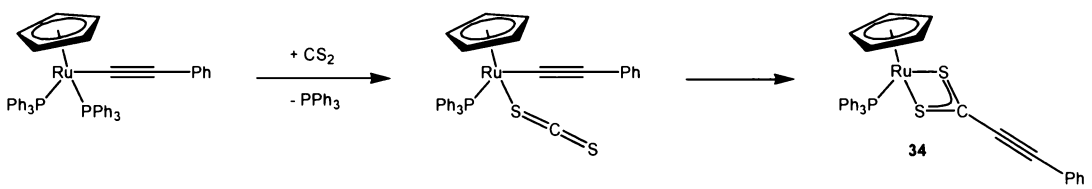
the oxygen atom of the alkoxido ligand. The low temperature (-40°C *cf.* 140-150°C[57,58]) indicates that an available coordination site is not necessary for the reaction to occur.
The reaction of the corresponding aryloxido-Re complex with carbon disulfide does not appear to progress by electrophilic attack. A higher temperature (100°C) is necessary for a reaction to occur, indicating a site of unsaturated coordination is required.

The coordinatively unsaturated complex $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ undergoes a reaction with carbon disulfide by initial coordination of the carbon disulfide prior to insertion. The insertion affords the coordinatively saturated complex **33**[59].



33

The coordinatively saturated complex $CpRu(C{\equiv}CPh)(PPh_3)_2$ appears to insert carbon disulfide due to the labile nature of the PPh_3 ligands. Dissociation of one of the ligands allows coordination of the carbon disulfide, with further reaction affording the insertion product **34**[60].



34

A mechanistic study of the related complex $CpRu(SR)(PPh_3)_2$ supports the requirement of a coordinatively unsaturated site for insertion[61]. It was shown that the rate of insertion was increased with increasing carbon disulfide concentration, but inhibited by the addition of free PPh_3. In the presence of carbon monoxide and carbon disulfide the product formed is $CpRu(SR)(PPh_3)(CO)$, which will not insert carbon disulfide without activation by UV

[57] E. Lindner, R. Grimmer, H. Weber, *J. Organometal. Chem.*, **23** (1970) 209

[58] E. Lindner, R. Grimmer, *J. Organometal. Chem.*, **25** (1970) 493

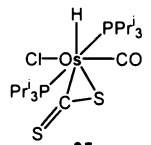
[59] H. Loumrhari, J. Ros, R. Yáñez, *J. Organometal. Chem.*, **408** (1991) 233

[60] M. I. Bruce, M. J. Liddell, M. R. Snow, E. R. T. Tiekink, *J. Organometal. Chem.*, **352** (1988) 199

radiation.

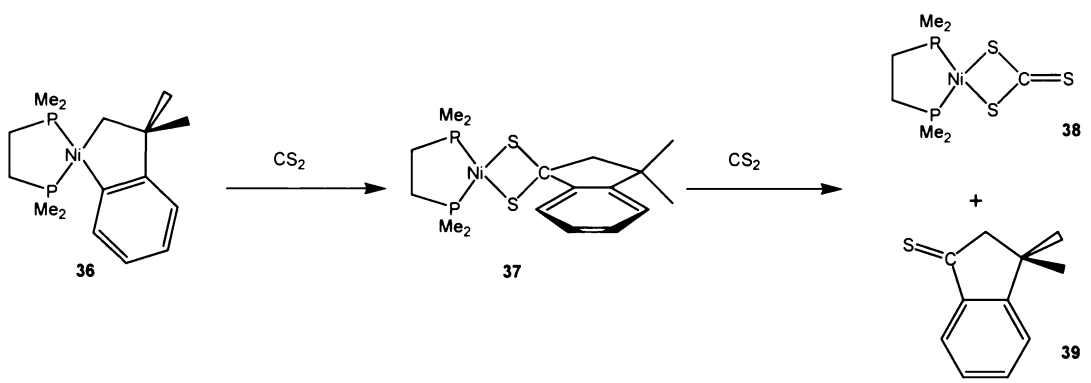
The analogous complex CpRu(SR)(dppe) is unable to form a coordinatively unsaturated site, as the bidentate dppe ligand will not take a monodentate coordination. Therefore no insertion of carbon disulfide was observed.

Further evidence for this mechanism is given by H. Werner *et al.*[62] who have isolated the 1:1 adduct **35** formed by reaction of carbon disulfide and $OsHCl(CO)(PPr^{i}_{3})_2$.



35

The nickel complex **36** is one of the few orthometalated complexes to undergo insertion of carbon disulfide[63]. It forms the *gem*-dithiolate complex **37** by insertion of carbon disulfide into the original nickelocycle. The *gem*-dithiolate has a bonding structure common to carbon disulfide insertion products. Reaction with further carbon disulfide results in the Ni(II) trithiocarbonate complex **38** and the thioketone **39**.



36 **37** **38** **39**

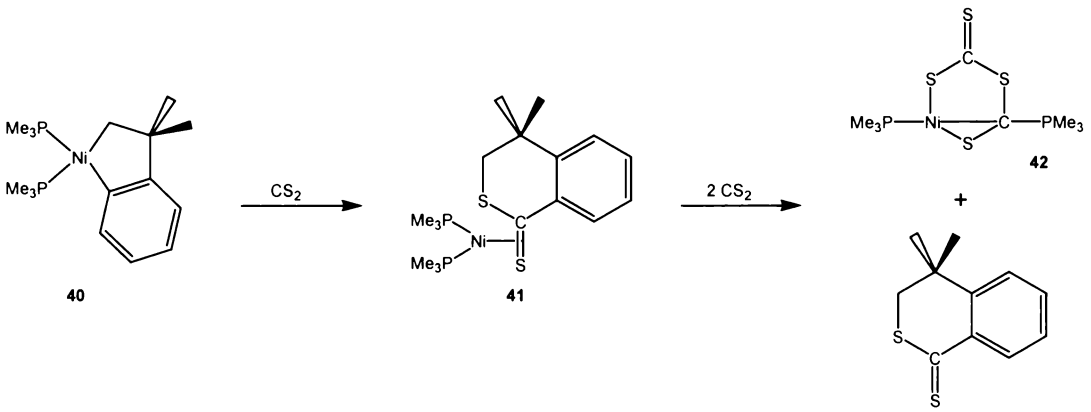
If **40** (where the bidentate phosphorus ligand is replaced by two monodentate ligands) is

[61] A. Shaver, P-Y. Plouffe, P. Bird, E. Livingstone, *Inorg. Chem.*, **29** (1990) 1826

[62] H. Werner, M. A. Tena, N. Mahr, K. Peters, H-G. von Schnering, *Chem. Ber.*, **128** (1995) 41

[63] J. Cámpoar, E. Gutiérrez, A. Monge, P. Palma, M. L. Poveda, C. Ruiz, E. Carmona, *Organometallics.*, **13** (1994) 1728

reacted with one equivalent of carbon disulfide, the insertion product is the novel dithiolactone complex **41**. This complex has a different binding mode to other carbon disulfide insertion products, and incorporates one sulfur into the thiolactone ring. Reaction with a further two equivalents of carbon disulfide leads to displacement of the dithiolactone, and insertion of two carbon disulfide molecules into one of the Ni-P bonds, with head-to-tail dimerisation to form the heterometalocycle **42**.



40 41 42

2.2. Aims of the Current Research

The objective of the present section of work was to determine how extensively carbon disulfide would insert into orthomanganated complexes. It has been found that the rate of the insertion of carbon disulfide into Re-C bonds follows the order Ph>>Me>CH_2Ph>>CF_3[64]. This is in agreement with the mechanisms discussed earlier, and the electrophilic nature of carbon disulfide. The more electron density on the metal bound carbon, the more reactive the complex is towards insertion.

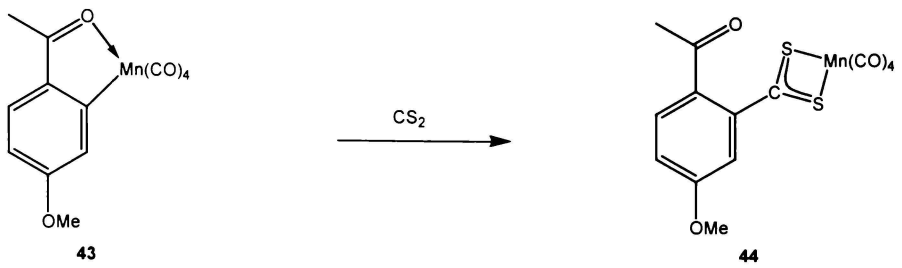
Orthomanganated ketones were chosen as orthometalated ketones are largely only routinely available with Mn/Re complexes. Manganese was attractive as it offers a higher reactivity than the rhenium analogues.

The present work builds on a preliminary study by M. Hagyard[65] which had shown that the orthomanganated aryl ketone **43** did insert carbon disulfide to give the bidentate

[64] A. Wojcicki, *Adv. Organometal. Chem.*, **12** (1974) 31

[65] M. Hagyard, *Some reactions of orthomanganated aryl ketones with CS_2*, Dissertation, University of Waikato, (1998)

dithio-carboxylate complex **44**.



43 **44**

Though the product **44** was isolated and an X-ray crystal structure obtained, full characterisation and development of the process was not undertaken[65].

Analysis of the crystal structure of **44** showed that the carbon disulfide had inserted into the Mn-aryl bond, with the manganese no longer coordinated to the ketone oxygen. The manganese coordinates equivalently to both sulfur atoms (η^2-S_2C), forming a four-membered metalocycle. The plane of the ring is perpendicular to the plane of the aryl ring, indicating no conjugation from the dithiocarboxylate to the aryl ring. An ORTEP perspective view is shown in Figure 2-1.

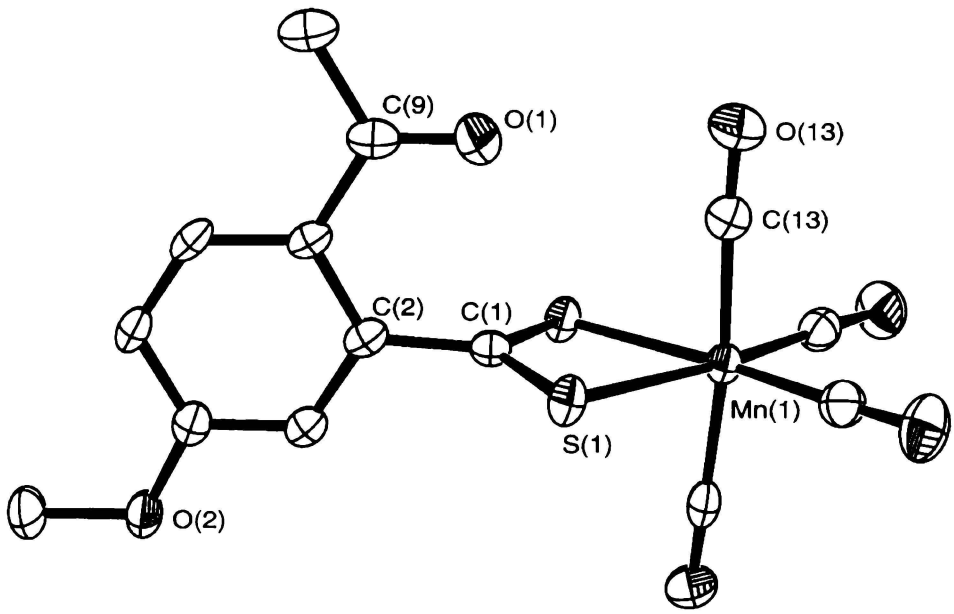


Figure 2-1 ORTEP perspective view of the previously prepared dithiocarboxylate complex **44**.

The underlying purpose of this study was to further explore the insertion of carbon

disulfide into a range of cyclomanganated complexes, the goal being to determine how general the insertion reaction is, and to gauge the limits of its application. The original reaction was revisited with the view to identifying optimum conditions for the reaction and to enable full characterisation of the original product.

2.3. Results and Discussion

2.3.1. Optimisation of reaction conditions

The earlier reaction was repeated under different conditions in order to determine the optimum conditions for the reaction, and to maximise the yield of **44**.

The carbon disulfide used for the reactions had been purified by trap-to-trap distillation on a vacuum line. The general procedure involved taking a sample of **43**, transferring it to an ampoule with excess carbon disulfide, and sealing the ampoule under vacuum. Ampoules were heated to various temperatures for periods of 8-48 hours. At the conclusion of the reaction time, the ampoule was opened and the reaction mixture was concentrated under vacuum. The concentrated CS_2 solution was then cooled to -20°C overnight in an effort to encourage crystallisation of the product. When this method was unsuccessful, further work-up was conducted as described in the Section 2.4.

The optimum temperature was found to be 85°C, with temperatures above this leading to decomposition, while temperatures below 80°C were insufficient to initiate a reaction. A reaction time of 24 hours was shown to be the most convenient, with longer times leading to decomposition. The optimum yield obtained for **44** was 55%.

All subsequent reactions involving alternative orthomanganated and cyclomanganated precursors were undertaken using the standard conditions (85°C, 24 hours).

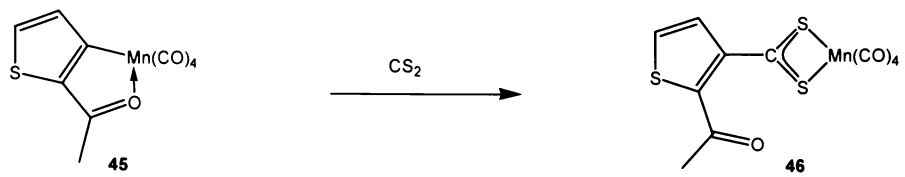
2.3.2. Insertion of carbon disulfide into orthomanganated ketones

When η^2-(2-acetylthien-3-yl)$Mn(CO)_4$ (**45**) was heated with carbon disulfide, a dark orange solution was obtained. Cooling the concentrated solution did not afford any crystals, therefore other methods were explored for the work-up of the reaction mixture.

^1H NMR of the reaction mixture indicated that a reaction had occurred. Initially chromatography was trialled as a method of purifying the reaction mixture, but the ^1H

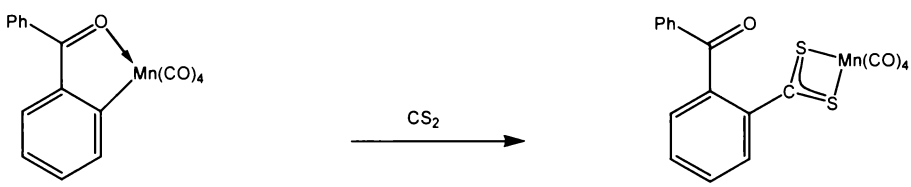
NMR spectrum showed that the product was decomposing on the silica plate.

The reaction was repeated, and the solvent was removed under vacuum. The residue was recrystallised from dichloromethane/petroleum spirits as yellow/orange rods. This product was characterised as **46** (80% yield) by IR, ESMS, ^{1}H and ^{13}C NMR spectroscopy.



45 46

The heating of η^2-(2-benzoylphenyl)$Mn(CO)_4$ (**47**) with carbon disulfide lead to a dark red/brown solution. No crystals were formed from the cooling of the concentrated solution. ^{1}H NMR of the reaction solution indicated that a reaction had occurred, therefore a recrystallisation from dichloromethane/petroleum spirits was attempted. No crystals were produced, so the solvent was removed under vacuum, and the residue was chromatographed (alumina column, 1:1 ether/petroleum spirits). The first fraction to elute off the column was collected, and the solvent removed to afford a dark red/brown oil which failed to crystallise. The oil was identified as **48** (67% yield) by IR, ESMS, ^{1}H and ^{13}C NMR spectroscopy.



47 48

Spectroscopic and mass spectrometric characterisation

IR Spectra

The carbonyl region of the IR spectrum for each of the insertion products shows the standard $2a_1$+e pattern of a pseudo-C_{2v} $L_2Mn(CO)_4$ complex, with broadening or splitting of the central band showing the true lower symmetry. In each case the pattern is shifted to a higher frequency than that of the original orthomanganated complexes by 5-10 cm^{-1}, indicating an increase in the bond order of the carbonyl ligands. The dithiocarboxylate retains more of the negative charge localised on it than does the original O,C-bonded

ligand. This decreases the electron density on the manganese centre, and thereby reduces the π-back donation to the carbonyl ligands, leading to the observed increase in C≡O bond order.

The IR signals for each complex before and after insertion of carbon disulfide are shown in Table 2-1.

Table 2-1 IR signals of orthomanganated complexes and resulting insertion products.

Substrate	IR Signals (cm^{-1})			Product	IR Signals (cm^{-1})		
	a_1	e	a_1		a_1	e	a_1
43 η^2-(C,O)	2083	1996	1944	**44** η^2-(S,S)	2093	2016, 2002	1963
45 η^2-(C,O)	2088	2002	1953	**46** η^2-(S,S)	2093	2016	1966
47 η^2-(C,O)	2083	1997	1948	**48** η^2-S,S)	2093	2019, 2007	1964

The similarity of the IR signals confirms that **46** and **48** have a similar structure to that determined for **44.**

ESMS Spectra

The carbon disulfide insertion product from *p*-methoxyacetophenone, **44**, was analysed in negative ion mode as a MeOH solution, with NaOMe added to aid chemical ionisation[66].

At low cone voltages (-10 V), the dominant peak was assigned as the methoxide adduct, $[M+OMe]^-$, shown in Figure 2-2. Other lesser peaks were assigned as being generated from the loss of one carbonyl ligand from this adduct, affording $[M-CO+OMe]^-$, and from the abstraction of a proton from the parent molecule, with the loss of a carbonyl, leading to a peak assigned as $[M-CO-H]^-$.

[66] W. Henderson, J. S. McIndoe, B. K. Nicholson, P. J. Dyson, *J. Chem. Soc., Dalton Trans.*, (1998) 519

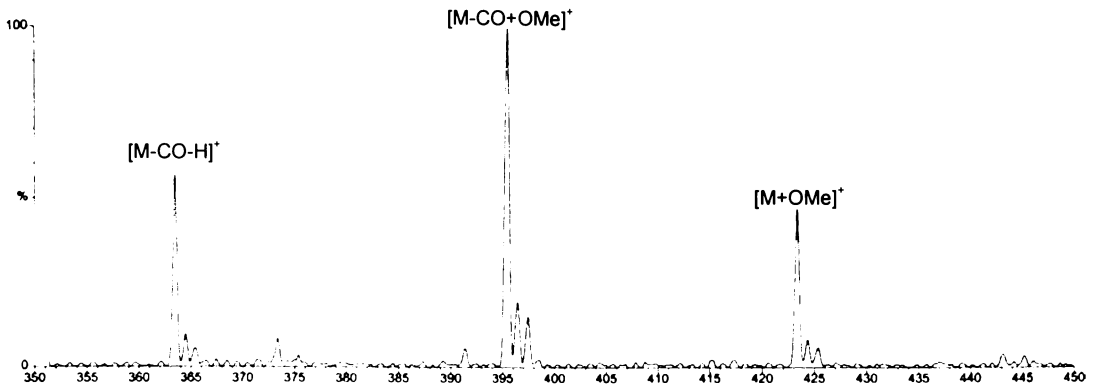


Figure 2-2: ESMS spectrum of **44** analysed as a MeOH/NaOMe solution, cone voltage -10 V.

A very weak $[M-H]^-$ peak could sometimes be observed in the spectrum of **44**, but was never more than ~5% in intensity. This contrasts with the original orthomanganated *p*-methoxyacetophenone, **43**, which shows a strong $[M-H]^-$ (and $[M-CO-H]^-$) peak and relatively weak $[M+OMe]^-$ (and $[M-CO+OMe]^-$) peak[66]. In **43** the abstraction of a proton is stabilised by the coordination of the keto-oxygen to the manganese centre (Figure 2-3). The low intensity of the proton abstraction peaks ($[M-H]^-$ and $[M-CO-H]^-$) in **44** support the loss of coordination of the keto-oxygen to the manganese centre.

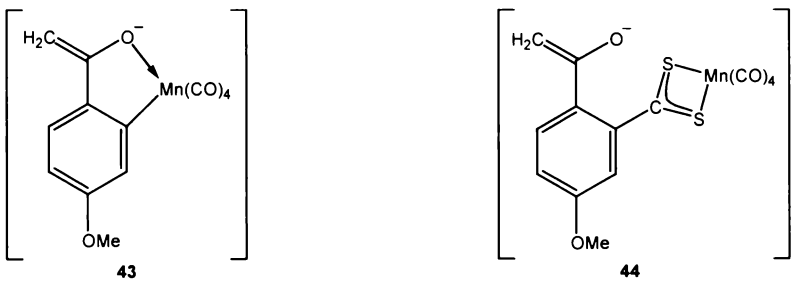


Figure 2-3 Proposed structures of the $[M-H]^-$ ions of **43** and **44**.

The loss of more than one carbonyl group was not observed. The use of higher cone voltages leads to the formation of a peak assigned as $[M+L-CO]^-$, where L is the dithiocarboxylate ligand. The loss of one CO ligand from the parent molecule apparently allows the coordination of any free dithiocarboxylate ligand via η^1-S coordination, as depicted in Figure 2-4. At higher cone voltages (typically 30 V) this peak dominates the spectrum.

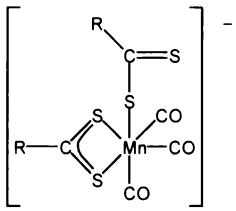


Figure 2-4 Assumed structure of $[M+L-CO]^-$ ion.

The ESMS signals described above were also common to **46**, with similar observed relative intensities (Figure 2-5). The benzophenone product **48** showed no peaks assigned to $[M-CO-H]^-$, indicating that there were no abstractable protons. The complex did show similar $[M+OMe]^-$ peaks with similar relative intensities.

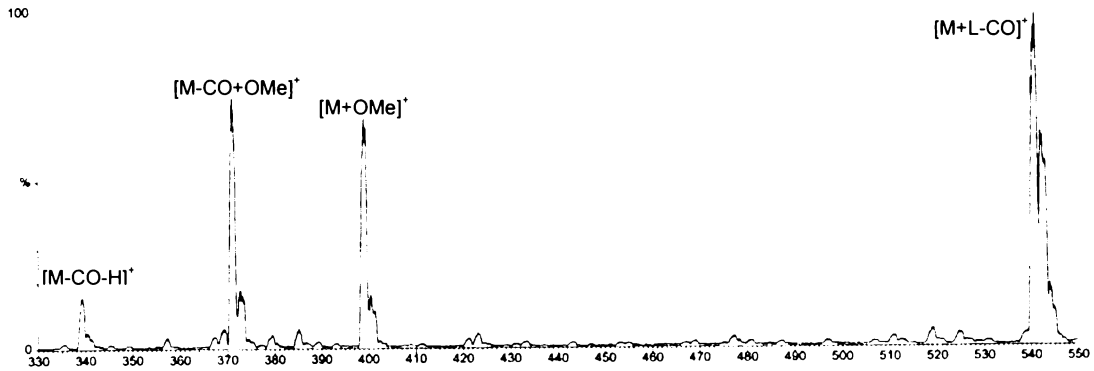


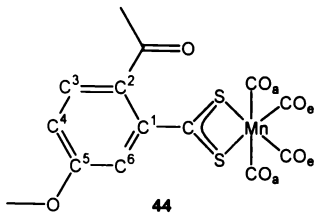
Figure 2-5 ESMS spectrum of **46** analysed as a MeOH/NaOMe solution, cone voltage -20 V.

Full assignment of the peaks seen in each ESMS spectrum are given for each complex in Section 2.5.

NMR Spectra

^1H, ^{13}C, HSQC and HMBC NMR spectroscopy experiments allowed complete assignment of the ligand structure of **44**, with the notable exception of the dithiocarbonato carbon.

The ^1H NMR spectrum showed five signals; two singlets corresponding to three protons each (the methyl signals), and three signals in the aromatic region each corresponding to one proton each. The methyl signals were at 2.59 ppm from the acetyl group, and 3.92 ppm from the methoxy group. The 1,2,5-substitution of the benzene ring meant that there were two adjacent protons (H^3 and H^4), with H6 being four bonds from H^4. Thus H^3 and H^6 both give doublets in the ^1H NMR spectrum, with ^3J and ^4J coupling respectively. H^4 is a doublet of doublets with both ^3J and ^4J coupling to the other protons.



44

The ^{13}C NMR spectrum shows nine signals, corresponding to two methyl groups, six aromatic signals and a ketone. HSQC shows direct H-C correlations, and was used to identify the carbon signals of C^3, C^4 and C^6 in association with the ^1H spectrum.

The HMBC spectrum shows long range (two and three bond) H-C correlations.

H3 correlated to the ketone ^{13}C signal (199.2 ppm), indicating that the acetyl group was attached at C^2. The methyl ^1H signal at 2.59 ppm correlated to the ketone and the aromatic signal at 129.6 ppm (C^2). Thus the acetyl group was confirmed to be attached to C^2.

H3 also correlated to the ^{13}C signals at 149.2 and 161.9 ppm, belonging to either C^1 or C^5. H^4 cannot correlate to C^1 (as this would be four bonds), but correlated to the signal at 161.9 ppm, indicating that this is due to C^5. The methyl ^1H signal at 3.92 ppm also correlated to 161.9 ppm, confirming that the methoxy group was attached to C^5.

Thus the dithiocarboxy group was attached to C1.

Though the signals due to the coordinated carbonyls and the dithiocarbonato carbons were not detected, they are expected in the range 210-230 ppm.

The ^1H and ^{13}C spectra of **46** and **48** were consistent with insertion having occurred in the same manner, though full NMR experiments were not undertaken.

The aryl region of the ^1H NMR spectrum (6.5-8.5 ppm) indicated insertion had occurred by an upfield shift (~0.4-0.7 ppm) of the protons adjacent to the site of insertion. The presence of manganese attached to a benzene ring also has the effect of spreading the range of observed proton signals. This is seen in benzophenone where the signals range

from 7.51-7.84 ppm compared to orthomanganated benzophenone (**47**) (7.21-8.23 ppm). The change in the range and position of the signals for **44** and **46** are fully consistent with the insertion of carbon disulfide into the aryl C-Mn bond.

^{13}C NMR spectroscopy also supported the insertion of carbon disulfide, showing a ~10 ppm downfield shift at C(1) (where insertion had occurred). The downfield shift of ~5 ppm observed for the ketone carbon signal is due to higher electron density on the oxygen atom as it is no longer coordinated to the manganese centre. This also causes a downfield shift for the attached methyl carbon.

Full assignments (where possible) are given in the Experimental Section.

2.3.3. Reaction of carbon disulfide with other cyclomanganated complexes, and with $Mn_2(CO)_{10}$.

Orthomanganated complexes with non-oxygen donor atoms were also reacted with CS_2 to determine if a seven-membered metalocycle could be formed. It was hoped that nitrogen or sulfur donor atoms would retain their original coordination to the manganese with the inserted carbon disulfide only coordinating through one sulfur atom, as depicted in Figure 2-6.

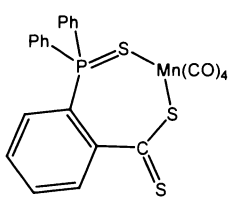
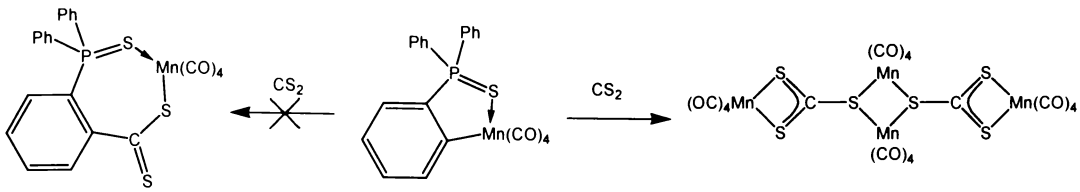


Figure 2-6 Proposed seven-membered ring formed by insertion of CS_2.

Reaction of orthomanganated triphenylphosphine sulfide (49) with CS_2.

When **49** was heated with CS_2, no sign of a product with a seven-membered ring was identified, with the cyclomanganated complex **49** not undergoing insertion of carbon disulfide under the same conditions as the orthomanganated aryl ketones. Instead another product was isolated in low yield. Spectroscopic data (IR, ESMS and NMR) did not give a clear picture as to the nature of the product. Therefore an X-ray crystal structure determination was undertaken. The structure showed that the complex was the dimer (μ_3-$CS_3)_2Mn_4(CO)_{16}$, **50**.



49 50

X-ray crystal structure of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, 50.

Crystals of **50** were grown from dichloromethane/diethyl ether at -20°C. The crystal was shown to be triclinic, with the space group P-1. There is only one molecule in the unit cell, lying on an inversion centre. Crystal and refinement details are given in a table in Section 2.5.2. An ORTEP perspective view is shown in Figure 2-7, along with the atom labelling scheme. Selected bond lengths and angles are listed in Table 2-2. The CIF file can be found on the CD inside the back cover.

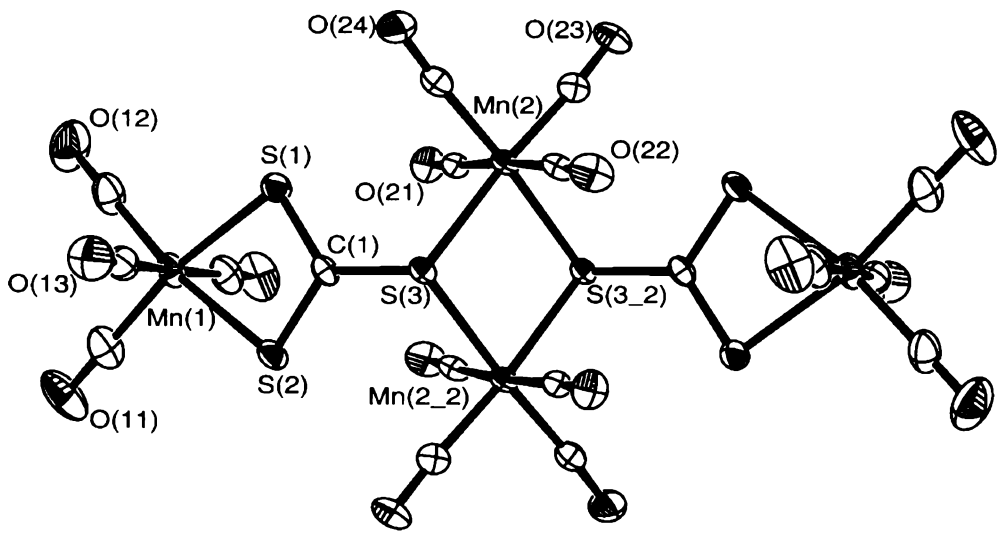


Figure 2-7 ORTEP perspective view of **50**, showing atom labelling scheme.

Table 2-2 Selected bond lengths (Å) and angles (°) of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **50**.

Bond	Length	Bonds	Angle
Mn(1)-S(1)	2.3866(11)	S(1)-Mn(1)-S(2)	73.18(3)
Mn(1)-S(2)	2.3971(13)	Mn(1)-S(1)-C(1)	86.14(10)
S(1)-C(1)	1.691(3)	Mn(1)-S(2)-C(1)	85.89(10)
S(2)-C(1)	1.699(3)	S(1)-C(1)-S(2)	114.52(16)
S(3)-C(1)	1.763(3)	S(1)-C(1)-S(3)	122.84(16)
Mn(2)-S(3)	2.4035(13)	S(2)-C(1)-S(3)	122.53(16)
Mn(2)-S(3')	2.4067(11)	C(1)-S(3)-Mn(2)	112.89(9)

C(1)-S(3)-Mn(2')	112.24(10)
S(3)-Mn(2)-S(3')	79.82(3)
Mn(2)-S(3)-Mn(2')	100.18(3)

The overall structure is two trithiocarbonate anions with two bridging and two terminal $Mn(CO)_4$ moieties. Each $Mn(CO)_4$ moiety is octahedral, with *cis* co-ordination to two sulfur atoms. The thiocarbonate anions and terminal $Mn(CO)_4$ moieties form two parallel planes. The dihedral angle between the planes defined by Mn(2)-S(3)-Mn(2') and S(3)-C(1)-S(1)-S(2) is 52.2°. The interplanar angle is shown graphically in Figure 2-8.

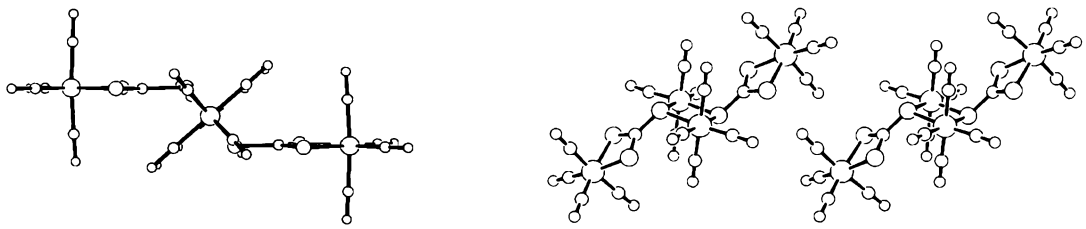


Figure 2-8 Perspective view of **50** showing the interplanar angle, with a stereo view showing the stereochemistry of the molecule.

The S(1)-Mn(1)-S(2) bite angle to the terminal manganese is constrained to 73.18° by the bidentate trithiocarbonate (**i** in Figure 2-9), but in the bridging case (S(3)-Mn(2)-S(3')) where there are no such confines it is still 79.81° (**ii** in Figure 2-9), considerably less than the preferred 90° for a perfect octahedral coordination. The axial carbonyl groups of Mn(2) and Mn(2') do not appear to influence the angle, with the carbonyl oxygens being 3.48 Å apart, with the carbonyls being slightly angled in towards each other.

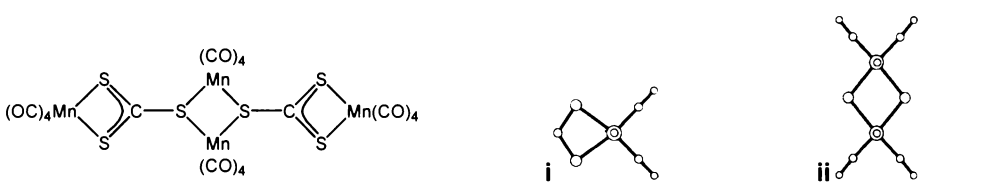


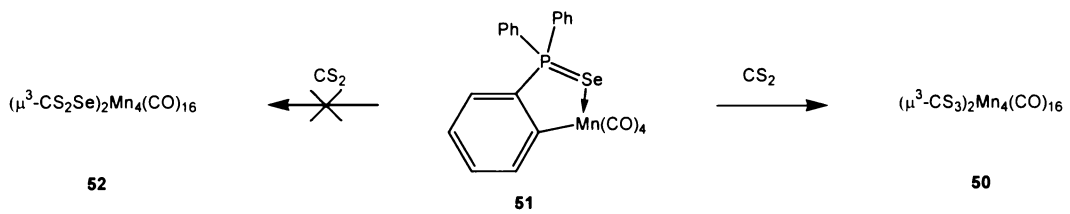
Figure 2-9 Structure of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **50**, showing the bite angles (**i** and **ii**) of the terminal and bridging $Mn(CO)_4$ groups.

Further reactions exploring the preparation of the dimer 50.

Of interest in the formation of the trithiocarbonate ligand was the origin of the third sulfur atom. It was thought that the source could be the Ph_3PS, which has been used as a source

of sulfur in reactions[67]. ^{31}P NMR of the reaction mixture showed the presence of Ph_3PS and **49**, but no Ph_3P as would be expected if the Ph_3PS was the source of the sulfur. Carbon disulfide can undergo sulfur elimination in the presence of a suitable acceptor[44] such as Ph_3P, which has been used to abstract sulfur from carbon disulfide[54]. This could explain the observations from the NMR spectrum.

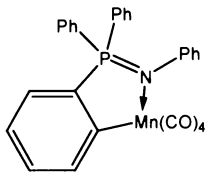
To see if the Ph_3PS was the initial source of the sulfur, carbon disulfide was reacted with **51**, the selenium analogue of **49**. It was expected that the analogous complex containing a dithioselenocarbonate ligand (**52**) would be formed, with Ph_3PSe acting as a selenium donor. The presence of either Ph_3P or Ph_3PS would confirm the reaction path. However, by ^{31}P NMR of the reaction mixture it was determined that only Ph_3PSe and **51** were present. ESMS of the product also confirmed that **52** had not been formed, with only **50** present. This indicated that the carbon disulfide was acting as the direct source of the third sulfur.



52 **51** **50**

The reaction of the cyclomanganated phosphorimine **53** with carbon disulfide also produced the Mn_4 species **50**. ^{31}P NMR of the reaction mixture showed starting material as expected, but no Ph_3P=NPh, instead indicating the presence of Ph_3PS. This was confirmed using ESMS by signals corresponding to $[nPh_3PS+Na]^+$ (n=1,2,3). (The formation of such adducts is not uncommon, with the same signals occurring for the reaction mixture of **49** and carbon disulfide, and for Ph_3PS when run alone under the same conditions as above).

[67] H. Su, Y. Xie, P. Gao, H. Lu, Y. Xiong, Y. Qian, *Chem. Let.*, **29** (1990) 1662



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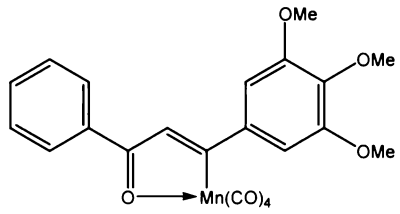


54

The complex **50** was also formed when there were no Ph_3P ligands present, as seen in the reaction of the cyclomanganated chalcone **54** and carbon disulfide. This further confirms that the carbon disulfide is acting as the direct source of the third sulfur atom. The reaction of **54** with CS_2 produced a large number of other products which could not be isolated by chromatography or recrystallisation. These products were all found in low yield.

The yields of the Mn_4 compound **50** from all of the previous reactions were low (~1%), so that insufficient sample could be isolated for elemental analysis. To determine if **50** could be produced by a more direct route, and in greater yields, a sample of $Mn_2(CO)_{10}$ was reacted with carbon disulfide. The reaction produced a gas, presumably carbon monoxide, and a much higher yield of **50**, 39%. This method proves to be a much simpler and more direct route to the trithiocarbonato complex.

The rhenium analogue to **50** has been prepared under similar conditions by reaction between $CF_3Re(CO)_5$ and carbon disulfide[68]. The crystal structure showed the rhenium analogue to be isomorphous with **50.**

Other complexes containing a trithiocarbonate ligand have also been prepared, by the reactions of anionic transition metal complexes with CS_2[69]. $[M(CO)_5]^-$ (M = Mn, Re), $[Fe(CO)_2Cp]^-$ and $[Mo(CO)_3Cp]^-$ as the sodium salts have been reacted with CS_2 forming trithiocarbonate ligands.

$[N(PPh_3)_2][Mn(CO)_4CS_3]$ (**55**) has been prepared in high yield by the reaction of $[N(PPh_3)_2][Mn(CO)_5]$ with CS_2 in tetrahydrofuran[70]. Reaction of **55** with MeI formed a

[68] G. Thiele, G. Liehr, E. Lindner, *J. Organometal. Chem.*, **70** (1974) 427

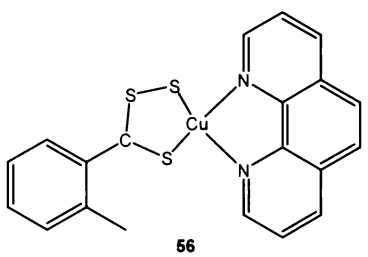
[69] J. Hunt, S. A. R. Knox, V. Oliphant, *J. Organometal. Chem.*, **80** (1974) C50

[70] I. B. Benson, J. Hunt, S. A. R. Knox, V. Oliphant, *J. Chem. Soc. Dalton Trans.*, (1978) 1240

η^2-S_2CMe complex, while reaction with $M(CO)_5Br$ (M = Mn, Re) led to the formation of $(OC)_4Mn(S_2CS)M(CO)_5$ (M = Mn, Re), the monomeric form of the dimeric **50**.

Again in these reactions it appears that CS_2 acts as the source of the third sulfur atom for the trithiocarbonate.

These are not the only types of reaction where CS_2 is acting as a source of sulfur. The reaction of CS_2 with Cu-aryl complexes has lead to the formation of perthio (**56**) complexes[71].



56

Spectroscopic and mass spectrometric characterisation of $(\mu_3$-$CS_3)_2Mn_4(CO)_{16}$, 50.

IR Spectrum

The IR spectrum of **50** showed five peaks, at 2091(s), 2049(m), 2009(vs, br), 1979(m), 1965(m) cm^{-1}. This compares with the six peaks observed for the Re analogue. The broad strong peak at 2009 cm^{-1} likely hides a second peak in the same region.

ESMS Spectra

A MeCN solution of **50** was analysed in negative ion mode. At low cone voltages (-10 V) the main peak was $[M\text{-}Mn(CO)_4]^-$ observed at *m/z* 717. Successive CO ligands were lost as the cone voltage was increased, giving peaks assigned to $[M\text{-}Mn(CO)_4\text{-}nCO]^-$ where $n=1\rightarrow9$. $[M\text{-}Mn(CO)_4\text{-}3CO]^-$ was shown to be a stable ion, as a considerably higher voltage was required to achieve the $n\geq4$ ions. $[M\text{-}Mn(CO)_4\text{-}3CO]^-$ corresponds to the loss of one carbonyl from each $Mn(CO)_4$ moiety, affording $Mn(CO)_3$ moieties.

A MeOH solution of **50** with NaOMe added to aid chemical ionisation was analysed in negative ion mode in an attempt to see the $[M+OMe]^-$ ion. This ion wasn't observed,

however at a cone voltage of −10 V peaks were seen at *m/z* 501 and *m/z* 275, corresponding to $[M\text{-}Mn(CO)_4\text{-}CS_3\text{+}CO\text{+}OMe]^-$ and $[Mn(CO)_4\text{+}CS_3]^-$ respectively, in addition to the base peak at *m/z* 717 of $[M\text{-}Mn(CO)_4]^-$. As the cone voltage was increased the loss of nCO (n = 1→3) was observed in all cases. $[Mn(CO)_4\text{+}CS_3\text{-}CO]^-$ remained the dominant peak at higher cone voltages, with n = 2 and n = 3 only minor peaks.

2.4. Conclusion

The reaction of carbon disulfide with orthomanganated ketones is an effective method of producing aromatic compounds with a dithiocarboxylate functional group *ortho* to a keto functional group. This reaction may have applications in preparing these unusual *o*-keto-dithiocarboxylates from aromatic ketones.

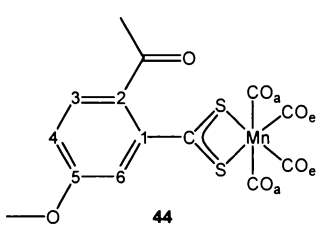
2.5. Experimental

General method for reacting cyclomanganated complexes with CS_2.

The cyclomanganated complex was transferred to an ampoule, which was then attached to a vacuum line. Using standard vacuum line procedures, approximately 10 ml of degassed carbon disulfide was transferred to the ampoule, which was then sealed under vacuum. The ampoule was transferred to a Carius tube, and heated to 85°C for 24 hours. The ampoule was allowed to cool, opened and the reaction mixture transferred under nitrogen to a round bottom flask for further work-up if required.

*Reaction of (2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**43**) with CS_2.*

43 (133 mg, 0.420 mmol) was reacted via the standard method. The reaction mixture was concentrated by removal of approximately half the CS_2 under vacuum, and stored at -20°C for 72 hours. Crystals of **44** (91 mg, 55% yield) were obtained from the reaction mixture as orange blocks.



44

m.p. = 116°C M_r = 392.3 $C_{14}H_9MnO_6S_2$

[71] A. Camus, N. Marsich, A. M. Manotti Lanfredi, F. Ugozzoli, *Inorg. Chim. Acta*, **175** (1990) 193

Elemental Analysis : Calculated C 42.86 H 2.31

Experimental C 44.19 H 2.28

IR: (CH_2Cl_2) ν(C≡O) 2093(m), 2016(vs), 2002(vs), 1963(s) cm^{-1}

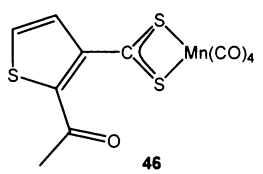
ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 589 (28%, $[2M-Mn(CO)_5]^-$), 423 (33%, $[M+OMe]^-$), 395 (100%, $[M+OMe-CO]^-$), 363 (48%, $[M-CO-H]^-$)

^1H NMR: ($CDCl_3$) δ 2.59 (3H, s, $COCH_3$), 3.92 (3H, s, OCH_3), 6.95 (1H, d, $^4J_{H-H}$ = 2.07 Hz, H6), 7.02 (1H, dd, $^3J_{H-H}$ = 8.50 Hz, $^4J_{H-H}$ = 2.16 Hz, H4), 7.59 (1H, d, $^3J_{H-H}$ = 8.56 Hz, H3)

^{13}C NMR: ($CDCl_3$) δ 29.6 (CH_3CO), 56.2 (CH_3O), 113.0 (C6), 116.1 (C4), 129.6 (C2), 131.2 (C3), 149.2 (C1), 161.9 (C5), 199.2 (CH_3CO)

*Reaction of (2-acetylthiophien-3-yl)tetracarbonylmanganese (**45**) with CS_2.*

45 (112 mg, 0.384 mmol) was reacted by the standard method. Solvent was removed from the reaction mixture, and the residue recrystallised from dichloromethane/petroleum spirits at -20°C overnight to give yellow/orange rods of **46** (114 mg, 80% yield).



46

m.p. = 108°C M_r = 368.3 $C_{11}H_5MnO_5S_3$

Elemental Analysis : Calculated C 35.87 H 1.37

Experimental C 36.14 H 1.35

IR: (CH_2Cl_2) ν(C≡O) 2093(m), 2016(vs, br), 1966(s) cm^{-1}.

ESMS: (MeOH/NaOMe, cone -10 V) *m/z* 541 (100%, $[2M-Mn(CO)_5]^-$), 399 (68%, $[M+OMe]^-$), 371 (74%, $[M+OMe-CO]^-$), 339 (16%, $[M-CO-H]^-$)

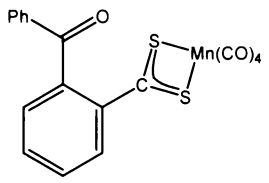
^1H NMR: ($CDCl_3$) δ 2.66 (3H, s, $COCH_3$), 7.24 (1H, d, $^3J_{H-H}$ = 4.99 Hz, Ar-H), 7.45 (1H, d, $^3J_{H-H}$ = 4.99 Hz, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 30.0 ($COCH_3$), 128.4 (Ar-H), 129.8 (Ar-H), 140.0 (Ar), 150.4 (Ar), 191.4 ($COCH_3$)

*Reaction of (2-benzoylphenyl)tetracarbonylmanganese (**47**) with CS_2.*

47 (190 mg, 0.546 mmol) was reacted via the standard method. Solvent was removed from the reaction mixture under vacuum, and the residue chromatographed (alumina column, 1:1 ether/petroleum spirits). The product was eluted in the first fraction, with the solvent

removed under vacuum to give **48** as a dark oil which did not crystallise (156 mg, 67% yield).



48

M_r = 368.3 $C_{11}H_5MnO_5S_3$

IR: (CH_2Cl_2) ν(C≡O) 2093(m), 2019(vs), 2007(vs), 1964(s) cm^{-1}.

ESMS: (MeOH/NaOMe, cone -10 V) *m/z* 653 (78%, $[2M-Mn(CO)_5]^-$), 455 (40%, $[M+OMe]^-$), 427 (100%, $[M+OMe-CO]^-$), 258 (23%, $[M-Mn(CO)_4]^-$)

^1H NMR: ($CDCl_3$) δ 7.86-7.43 (m, Ar-H).

^{13}C NMR: ($CDCl_3$) δ 126.0 (Ar-H), 128.4 (Ar-H), 128.7 (Ar-H), 129.1 (Ar-H), 129.7 (Ar-H), 132.1 (Ar-H), 133.7 (Ar-H), 136.9 (Ar), 137.2 (Ar), 145.4 (Ar), 196.9 ($C'OCH_3$)

*Reaction of ((2-diphenylthiophosphinyl)phenyl)tetracarbonylmanganese (**49**) with CS_2.*

49 (125 mg, 0.312 mmol) was reacted via the standard method. The presence of starting material and free ligand in the reaction mixture was ascertained prior to carbon disulfide removal by ^{31}P NMR and ESMS respectively. Excess carbon disulfide was removed under vacuum, with the residue being dissolved in dichloromethane and then filtered. The filtrate was recrystallised from dichloromethane/diethyl ether at -20°C, giving small yellow/orange block crystals of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **50**, in low yield (1.2 mg, <1%).

*Reaction of ((2-diphenylselenophosphinyl)phenyl)tetracarbonylmanganese (**51**) with CS_2.*

51 (102 mg, 0.202 mmol) was reacted via the standard method. ^{31}P NMR of the reaction solution showed the presence of **26** and Ph_3PSe. Excess CS_2 was removed under vacuum, and the residue chromatographed (PLC, 1:1 diethyl ether/petroleum spirits) to afford a low yield of **50** (~1 mg, <1%). The production of **50** was confirmed by ESMS analysis. No other products were isolated.

*Reaction of ((N-phenyl-2-diphenyliminophosphinyl)phenyl)tetracarbonyl-manganese (**53**) and CS_2.*

53 (100 mg, 0.192 mmol) was reacted via the standard method. ^{31}P NMR of the reaction

solution showed peaks at 44.3, 44.1 and 4.3 ppm. These represent **26**, Ph_3PS and Ph_3PNPh respectively. The presence of Ph_3PS was confirmed by ESMS. Solvent was removed under vacuum, and the residue chromatographed (PLC, ether) to afford a low yield of **50** (~1mg, <1% yield). The production of **50** was confirmed by ESMS analysis. No other products were isolated.

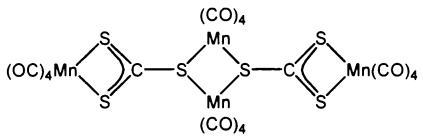
*Reaction of the orthomanganated chalcone **54** with CS_2.*

54 (95.4 mg, 0.206 mmol) was reacted via the standard method. Excess solvent was removed under vacuum, and a separation of the residue was attempted using chromatography. It was not possible to isolate any products from the residue due to extreme trailing of the compounds on the alumina column and silica PLC plates trialled. Analysis of the reaction mixture by ESMS indicated the presence of **50**.

Reaction of $Mn_2(CO)_{10}$ with CS_2.

$Mn_2(CO)_{10}$ (517 mg, 1.33 mmol) was reacted via the standard method, at the higher temperature of 110°C. The unopened ampoule was stored at -20°C for 48 hrs, at which time the ampoule was opened and the reaction mixture was filtered giving crude crystals of the product. These crystals were chromatographed (PLC plate, 1:1 dichloromethane/petroleum spirits) and the second band removed to afford **50** (217 mg, 39% yield). The product was confirmed using ESMS and IR analyses.

*Characterisation of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **50**.*



50

m.p. = dec. >115°C M_r = 884.3 $C_{18}Mn_4O_{16}S_6$

Elemental Analysis : Calculated C 24.45 H 0.0

Experimental C 23.51 H 0.0

IR: (KBr) ν(C≡O) 2091(s), 2049(m), 2009(s, br), 1979(m), 1965(m) cm^{-1}

(CH_2Cl_2) ν(C≡O) 2092(s), 2037(s), 2015(m, br), 2006(m, br), 1986(m), 1966(m) cm^{-1}

ESMS: (MeCN, cone -10 V) *m/z* 717 (100%, $[M\text{-}Mn(CO)_4]^-$), 689 (27%, $[M\text{-}Mn(CO)_4\text{-}CO]^-$), 661 (8%, $[M\text{-}Mn(CO)_4\text{-}2CO]^-$)

ESMS: (MeOH/NaOMe, cone -10 V) *m/z* 717 (100%, $[M\text{-}Mn(CO)_4]^-$), 689 (42%, $[M\text{-}Mn(CO)_4\text{-}CO]^-$), 661 (15%, $[M\text{-}Mn(CO)_4\text{-}2CO]^-$), 633 (8%, $[M\text{-}Mn(CO)_4$-

3CO]$^-$), 501 (65%, [M-Mn(CO)$_4$-CS$_3$+CO+OMe]$^-$), 473 (21%, [M-Mn(CO)$_4$-CS$_3$+OMe]$^-$), 445 (9%, [M-Mn(CO)$_4$-CS$_3$+OMe-CO]$^-$), 275 (18%, [Mn(CO)$_4$+CS$_3$]$^-$), 247 (45%, [Mn(CO)$_4$+CS$_3$-CO]$^-$)

2.5.1. Crystal data and structure refinement parameters for 50.

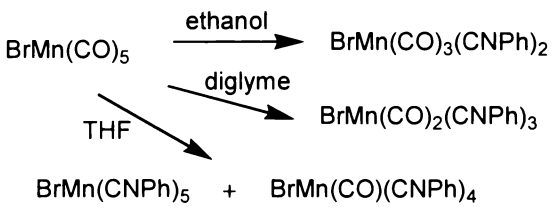
Empirical formula	$C_{18}Mn_4O_{16}S_6$	
Formula weight	884.32	
Temperature	168 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.010(3) Å	α = 83.401(6)°
	b = 8.410(4) Å	β = 80.037(12)°.
	c = 13.674(6) Å	γ = 74.207(13)°
Volume	762.1(5) $Å^3$	
Z	1	
Density (calculated)	1.927 g/cm^3	
Absorption coefficient	2.099 mm^{-1}	
F(000)	432	
Crystal size	0.05 x 0.16 x 0.26 mm	
Theta range for data collection	2.52 to 26.44°.	
Index ranges	-8<=h<=4, -10<=k<=10, -17<=l<=16	
Reflections collected	9435	
Independent reflections	3015 [R(int) = 0.0333]	
Completeness to theta = 26.41°	96.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3015 / 0 / 199	
Goodness-of-fit on F^2	0.952	
Tmin/Tmax	0.795 and 1.000	
Final R indices [I>2sigma(I)]	R_1 = 0.0309, wR_2 = 0.0664	
R indices (all data)	R_1 = 0.0484, wR_2 = 0.0702	
Largest diff. peak and hole	0.634 and -0.502 $e.Å^{-3}$	

Chapter 3. Reactions of Isocyanides with Cyclomanganated Compounds.

3.1. Introduction

Isocyanides (CNR) are isolobal with carbon monoxide (CO), and have a similar bonding mode when coordinating to a metal centre; isocyanides are better σ-donors and poorer π-acceptors[72] (aryl isocyanides are better π-acceptors than alkyl isocyanides[73]). Evidence for the stronger σ-bonding is often seen in the higher oxidation state of the metal centre of homoleptic CNR complexes compared to the CO equivalents.

The substitution of CO ligands by CNR ligands is relatively easy. In some cases the number of CO ligands replaced can be controlled by varying the solvents, molar ratios or the reaction temperature. The series $BrMn(CO)_{5-n}(CNPh)_n$ (n = 2-5) has been prepared by varying the reaction temperature and solvents[74].



The ability to replace CO ligands with CNR ligands, coupled with the slight differences in the bonding modes allows the CNR ligand to be utilised in changing the electronic properties of the metal centre. Changing the character of the R-group of the CNR ligand alters the electronic effect exerted by the ligand, for example a *p*-nitrophenyl R-group will decrease the electron density on the metal centre, while a *t*-butyl group will increase it. The CNR group has the advantage over phosphine alternatives (PMe_3, $P(OMe)_3$) of imparting less steric influence due to lower steric bulk. If steric bulk is a desired influence more bulky isocyanides such as $(2,6\text{-}Pr^i{}_2C_6H_3)NC$ or $(c\text{-}C_6H_{11})_3CNC$ can be used[75].

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[72] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, in *Advanced Inorganic Chemistry*, John Wiley & Sons, inc., New York, 6th edn., (1999) 246

[73] E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.*, **22** (1983) 209

[74] K. K. Joshi, P. L. Pauson, W. H. Stubbs, *J. Organomet. Chem.*, **1** (1963) 51

[75] P. P. M. de Lange, H.-W. Frühauf, M. J. A. Kraakman, M. van Wijnkoop, M. Kranenburg, A. H. J. P.

The use of CNR ligands to alter the electronic nature of a metal centre has the drawback that the CNR group can be susceptible to insertion reactions. This is not always an undesired occurrence, as isocyanides have been used to study the insertion of CO into M-H bonds. The formimidines formed are more thermodynamically stable than the formyl analogues, and have allowed the isolation of the individual reduction steps from the reaction of zirconium hydrides with isocyanides[73].

Isocyanide insertions into M-C bonds are more facile compared to carbonyl insertions[73], and the more stable iminoacyl products have not been observed to undergo reverse migration of CNR.

Isocyanides have an extensive insertion chemistry, with examples known for insertion into M-H[76,77], M-C, M-N[78] and M-O[79], using different forms of activation (photo-chemical, thermal, chemical). Of the insertions into the various M-C bonds (M = Ti[80], Zr[81], V, Ta[80], Mo[82], W[81], Mn, Re[80], Fe[83,84], Ru[85], Co[86], Ni, Pd[87,88,89], Pt), there are few examples where CNR insertion occurs into a cyclometalated complex, and only one example known for insertion into orthometalated complexes.

Groot, K. Vrieze, J. Fraanje, Y. Wang, M. Numan, *Organometallics*, **12** (1993) 417

[76] R. D. Adams, N. M. Golembeski, *J. Am. Chem. Soc.*, **101** (1979) 2579

[77] D. F. Christian, H. C. Clark, R. F. Stepaniak, *J. Organomet. Chem.*, **112** (1976) 209

[78] L. S. Hegedus, O. P. Anderson, K. Zetterberg, G. Allen, K. Siirala-Hansen, D. J. Olsen, A. B. Packard, *Inorg. Chem.*, **16** (1977) 1887

[79] B. K. Panda, S. Chattopadhyay, K. Ghosh, A. Chakravorty, *Organometallics*, **21** (2002) 273

[80] E. Klei, J. H. Telgen, J. H. Teuben, *J. Organomet. Chem.*, **209** (1981) 297

[81] K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1981) 2088

[82] R. D. Adams, D. F. Chodosh, *J. Am. Chem. Soc.*, **99** (1977) 6544

[83] G. Bellachioma, G. Cardaci, P. Zanazzi, *Inorg. Chem.*, **26** (1987) 84

[84] K. Aoki, Y. Yamamoto, *Inorg. Chem.*, **15** (1976) 48

[85] W. R. Roper, G. E. Taylor, J. M. Waters, L. J. Wright, *J. Organomet. Chem.*, **157** (1978) C27

[86] H. Yamazaki, K. Aoki, Y. Yamamoto, Y. Wakatsuki, *J. Am. Chem. Soc.*, **97** (1975) 3546

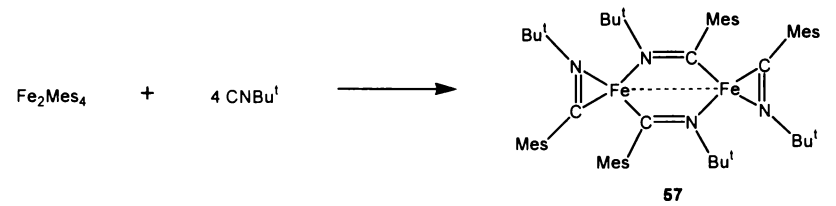
[87] G. R. Owen, R. Vilar, A. J. P. White, D. J. Williams, *Organometallics*, **21** (2002) 4799

[88] J. Vicente, J-A. Abad, E. Martínez-Viviente, *Organometallics*, **21** (2002) 4454

[89] J. Vicente, J-A. Abad, A. D. Frankland, J. López-Serrano, *Organometallics*, **21** (2002) 272

Both single and multiple CNR insertions into M-C bonds are common. Multiple insertions occur readily, especially in complexes with a nucleophilic centre[90]. An alkyl isocyanide tends to insert step-wise, with isolation of the mono-, bis-, tris-, etc. insertion products possible. By comparison, an aryl isocyanide tends towards concerted insertion, with the multiple insertion product the only product able to be isolated.

An unusual example of multiple single insertions is observed for the iron complex Fe_2Mes_4 which undergoes four insertions of a Bu^tNC into each of the four mesityl ligands to form the homoleptic iminoacyl complex **57**[91].



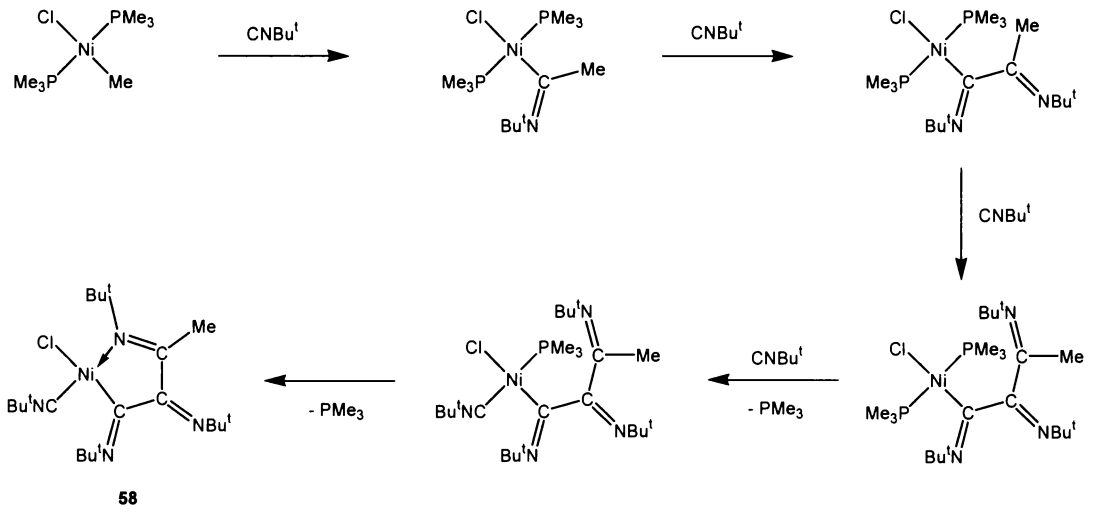
57

A multiple insertion into a single M-C bond is observed in the reaction of Bu^tNC with the nickel complexes *trans*-[Ni(R)Cl(PMe_3)$_2$] (R = Me, CH_2SiMe_3, $CH_2C_6H_4$-*o*-Me)[92]. The reaction was determined to occur by step-wise insertion of the isocyanide forming mono-, bis- and tris-insertion products before attack by a fourth Bu^tNC (and subsequent removal of both PMe_3 ligands) resulted in the final product **58**.

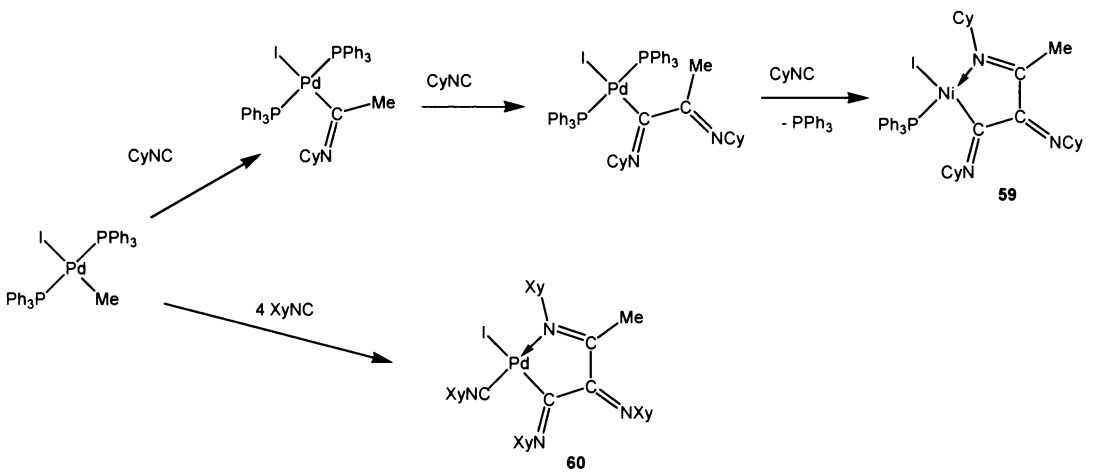
[90] E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.*, **22** (1983) 209

[91] A. Klose, E. Solari, R. Ferguson, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Organometallics*, **12** (1993) 2414

[92] E. Carmona, J. M. Marín, P. Palma, M. L. Poveda, *J. Organomet. Chem.*, **377** (1989) 157



The step-wise insertion of alkyl isocyanides into the Pd-CH_3 bond has also been reported[93], with isolation of the mono-, bis- and tris-insertion products. The reaction of a Pd-CH_3 complex with 3 mole equivalents of CyNC forms the tris-insertion product **59**, which forms the metalocycle by loss of the phosphine ligand. However, the same Pd-CH_3 complex reacted spontaneously with the aryl isocyanide 2,6-XyNC to form the equivalent product **60**, regardless of the molar ratio used in the reaction[94].



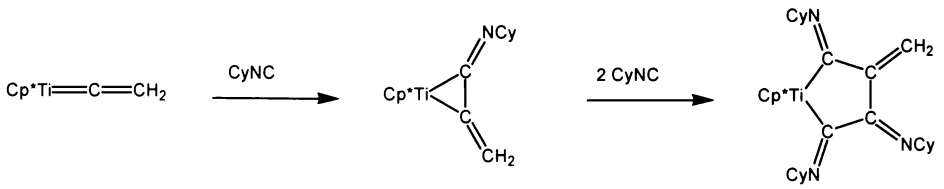
Isocyanides have also been shown to insert successively into the carbene bond of $[Cp_2^*Ti{=}C{=}CH_2]$[95]. The first isocyanide inserts into the carbene bond forming a three-

[93] Y. Yamamoto, H. Yamazaki, *Inorg. Chem.*, **13** (1974) 438

[94] Y. Yamamoto, T. Tanase, K. Yanai, T. Asano, K. Kobayashi, *J. Organomet. Chem.*, **456** (1993) 287

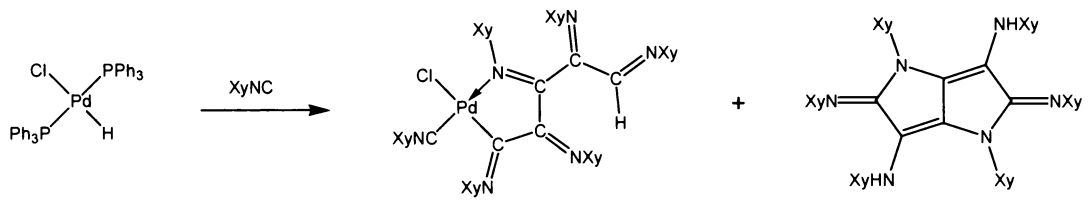
[95] C. Santamaría, R. Beckhaus, D. Haase, R. Koch, W. Saak, I. Strauss, *Organometallics*, **20** (2001) 1354

membered metalocycle, with a second inserting into the remaining original Ti-C bond. A third isocyanide inserts into either of the new Ti-C bonds to form the final product, the five-membered metalocycle **61**.



61

The insertion of one, two and three isocyanide groups is not uncommon in organometallic complexes; however there is one example found where five isocyanides have inserted into a Pd-H bond[96]. The chain of inserted isocyanides bends so that the third imino-nitrogen can coordinate to the Pd centre, with a sixth isocyanide replacing the remaining phosphine ligand to afford **62** as the main product. The purely organic product **63** was also isolated.



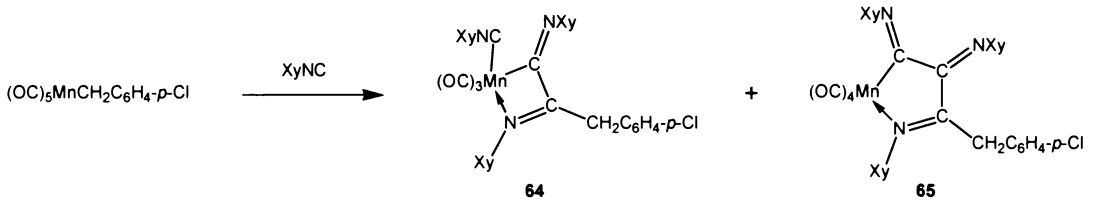
62 **63**

Specific to manganese there are a number of cases of multiple insertion. XyNC inserts into $(OC)_5MnCH_2C_6H_4$-*p*-Cl to give the bis- and tris-insertion products **64** and **65** which have a four- or five-membered metalocyclic ring respectively[97]. Similar products were formed when *p*-TolNC was substituted as the isocyanide[98].

[96] T. Tanase, T. Ohizumi, K. Kobayashi, Y. Yamamoto, *Organometallics*, **15** (1996) 3404

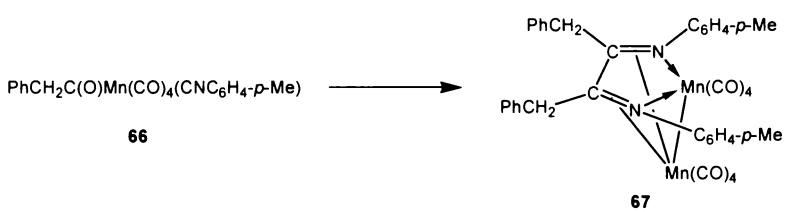
[97] T. M. Becker, J. J. Alexander, J. A. Krause Bauer, J. L. Nauss, F. C. Wireko, *Organometallics*, **18** (1999) 5594

[98] P. L. Motz, J. J. Alexander, D. M. Ho, *Organometallics*, **8** (1989) 2589



Earlier it was mentioned that the alkyl and aryl isocyanides have different reactivity, with the alkyl isocyanides undergoing step-wise insertion compared to the concerted insertion seen for the aryl isocyanides. Alkyl and aryl isocyanides also react differently in manganese systems.

When $PhCH_2Mn(CO)_5$ was reacted with CNR (R = alkyl) in THF, the product was $PhCH_2C(O)Mn(CO)_4(CNR)$, due to the insertion of a carbonyl ligand. The complex can be thermally decarbonylated to afford the mono-substituted product $PhCH_2Mn(CO)_4(CNR)$[99]. However, when the equivalent aryl isocyanide-substituted complex **66** was thermally decarbonylated, the product was the diazabutadiene complex **67**[100]. A trapping study showed that the product was likely due to decarbonylation of the acyl group followed by rapid preferential insertion of the coordinated isocyanide ligand before a radical coupling of two such complexes. This indicates that aryl isocyanides more readily insert into Mn-benzyl bonds than alkyl isocyanides.



There is also an example of a chemically activated reaction between a coordinated isocyanide and dimethyl acetylenedicarboxylate (DMAD)[23]. One of the carbonyl ligands is oxidatively removed initiating the reaction. The product **68** has two five-membered manganocycles, one involving coordination to the nitrogen atom, the other to one of the carboxylate groups.

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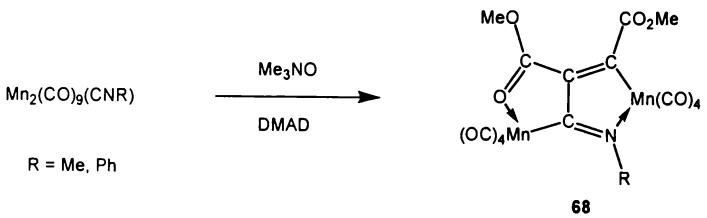
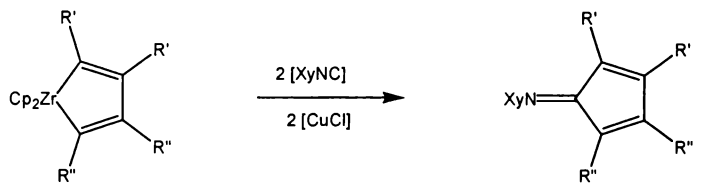
[99] D. W. Kuty, J. J. Alexander, *Inorg. Chem.*, **17** (1978) 1489

[100] P. L. Motz, J. P. Williams, J. J. Alexander, D. M. Ho, J. S. Ricci, W. T. Miller, *Organometallics*, **8** (1989) 1523



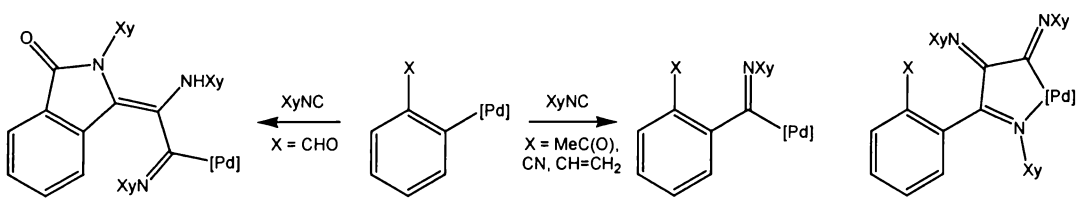
68

One example of insertion into a cyclometalated complex is the insertion of 2,6-XyNC into the Zr-C bond of the zirconacyclopentadiene complex **69**, which is followed by a demetalation and cyclisation to form the final product, an iminocyclopentadiene (**70**).



69 70

Recently there has been reported the reaction of *ortho*-substituted arylpalladium complexes with isocyanides, forming the aryliminopalladium complexes **71**, **72**, and the cyclisation product **73**[101,102]. The cyclised product has been formed by the attack of the nucleophilic imino nitrogen on the electrophilic carbonyl carbon. Products like **73** are of interest as they can be converted into isoindolinones, which have potential pharmacological activity.



73 71 72

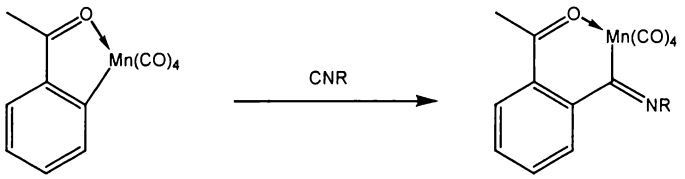
3.2. Aim of the Present Study

There has been no record found where an orthometalated or orthomanganated complex has reacted with an isocyanide. It was expected as the basis of the present study that an

[101] J. Vicente, J. A. Abad, E. Martínez-Viviente, P. G. Jones, *Organometallics*, **21** (2002) 4454

[102] J. Vicente, J. A. Abad, E. Martínez-Viviente, P. G. Jones, *Organometallics*, **22** (2003) 1967

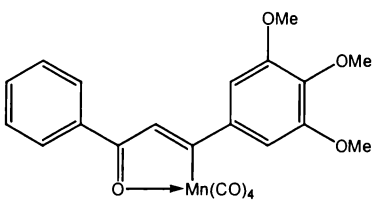
isocyanide would react with an orthomanganated complex to initially form an iminoacyl complex, with a six-membered metalocyclic ring, with the possibility of the product undergoing subsequent reactions.



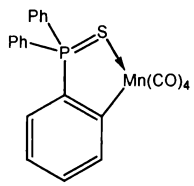
The reactions of a number of isocyanides were explored, including aromatic and aliphatic isocyanides of differing steric bulk. Also the addition of various metal complexes was explored in an effort to increase product yields.

3.3. Results and Discussion

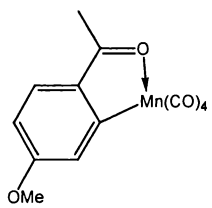
Orthomanganated chalcone (**54**), triphenylphosphine sulfide (**49**) and *p*-methoxyacetophenone (**43**) were chosen as three examples of orthomanganated complexes to react with Bu^{t}NC. Both **49** and **43** reacted differently with carbon disulfide, and therefore it was expected they might react differently with the isocyanide. Also **54** has been shown to have a unique chemistry for reactions with unsaturated molecules[103], and was therefore included in the initial investigation.



54



49



43

The reaction of **54** and Bu^{t}NC in refluxing heptane did not afford any dominant products. An inseparable mixture of multiple products was produced, with some of the products not being chromatographically stable. These products could not be isolated by solvent extraction of the residue, nor by recrystallisation, so this substrate was abandoned.

The second reaction to be investigated involved the reaction of **49** with Bu^{t}NC in a 1:8

[103] W. Tully, B. K. Nicholson, L. Main, *J. Organomet. Chem.*, **503** (1995) 75

ratio in refluxing heptane. The sequential substitution of three coordinated carbonyls by three isocyanides was observed by monitoring the carbonyl region of the IR spectrum (Figure 3-1) over the course of the reaction.

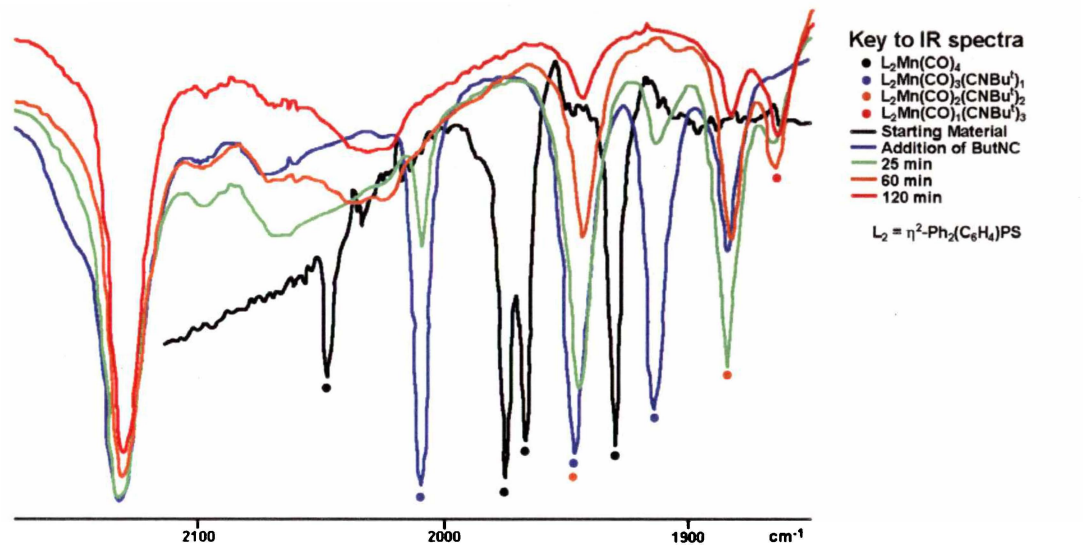


Figure 3-1 Monitoring the reaction of **49** and Bu^tNC using IR spectroscopy shows the substitution of up to three carbonyls over a 120 minute reaction time (Bu^tNC was added to the reaction mixture after heating to reflux in heptane).

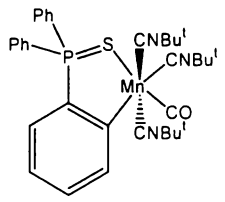
The first carbonyl substitutes as soon as the isocyanide is added, with a further second and third substitution occurring over two hours. There was no evidence for a fourth substitution, with increased reaction time and/or temperature leading to the organic ligand being lost with the formation of $[Mn(CNBu^t)_6]^+$ and $[Mn(CO)(CNBu^t)_5]^+$ species (as detected by ESMS of the reaction mixture).

Orange rosettes were obtained from the cooled reaction mixture, and were analysed by IR, ESMS and NMR to determine the nature of the product.

The IR spectrum of the orange rosettes showed only one carbonyl stretching vibration (1885 cm^{-1}), indicating that there was only one carbonyl coordinated to the manganese centre. There was also a broad peak at 2040 cm^{-1} which may indicate the presence of coordinated isocyanide ligands.

^1H, ^{13}C and ^{31}P NMR analysis of the orange rosettes confirmed the structure as the

trisubstituted product **74**.



74

The ^{1}H NMR showed only two signals for three Bu^t groups, with integration showing that the peak at 1.05 ppm was due to two Bu^t groups, and the peak at 1.46 ppm due to one group. As two isocyanide groups are in the same chemical environment, this implies that two of the isocyanides occupy the axial position, while the third occupies one of the equatorial positions around the octahedral manganese centre. The remaining aromatic protons formed a broad multiplet.

The ^{13}C NMR spectrum confirmed that two of the Bu^t groups were in the same environment, showing only four signals for the three Bu^t groups.

The ^{31}P NMR spectrum showed a single peak at 64.4 ppm. The signal for triphenylphosphine sulfide comes at 43 ppm, while the signal for orthomanganated triphenylphosphine sulfide comes at 67 ppm. The downfield shift is due to the forming of a heterocycle including the phosphorus atom. The peak at 64.4 ppm in **74** indicates that there is still a cyclised product with a five-membered ring. The shift from 67 ppm to 64.4 ppm is due to the substitution of the three carbonyl ligands by the isocyanide ligands.

The ESMS spectra showed a dominant peak at *m/z* 625, assigned as $[M]^+$, which confirmed the molecular mass of the complex was that of the trisubstituted product **74**. A second minor peak at *m/z* 514 was assigned as $[M\text{-}CNBu^t\text{-}CO]^+$, due to the loss of a coordinated carbonyl and a coordinated isocyanide ligand.

A third peak in the spectrum at *m/z* 709 was of interest, as this correlated with a $[M+CNBu^t+H]^+$ species. This species may be due to the insertion of a coordinated isocyanide into the Mn-C bond under ESMS conditions, with the vacant coordination site being filled by any available free isocyanide. The NMR spectra indicate that there are three isocyanide groups in two different environments, so it could be envisioned that two

isocyanides were in the axial coordination sites, while the third was inserted into the Mn-C bond. The ESMS peak at *m/z* 625 would in this case be due to $[M\text{-}CO]^+$. Therefore to rule out the possibility of this being the product an X-ray crystal structure determination of **74** was undertaken.

The rosettes were recrystallised by vapour diffusion (ether/pentane) at -20°C to afford X-ray crystallographic quality crystals. The crystal structure is discussed in section 3.3.7.

3.3.1. Reaction of Bu^{t}NC with orthomanganated acetyl-aryl compounds.

Reaction of Bu^{t}NC with orthomanganated *p*-methoxyacetophenone (43).

The orthomanganated complex **43** was reacted in a 1:8 ratio with Bu^{t}NC in heptane under reflux. The reaction conditions were analogous to those used for the reaction of **49**. The carbonyl region of the IR spectrum was used to monitor the reaction. At temperatures above 80°C the single substitution of a carbonyl ligand by an isocyanide was observed, and the peaks due to this product (2016, 1955, and 1915 cm^{-1}) became the dominant peaks in the spectrum. The reaction was continued for 2 hours, with the mono-substituted product providing the dominant peaks throughout.

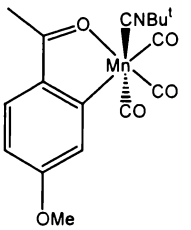
The reaction mixture failed to produce crystals, therefore the reaction was worked up by chromatography, affording a number of products.

The main product isolated was the single substitution product **75**. IR, ESMS and NMR spectroscopy were all consistent with the substitution of one carbonyl ligand.

The IR spectrum of **75** showed three peaks at 2016, 1955 and 1915 cm^{-1}, corresponding to a $Mn(CO)_3$ moiety. The ESMS spectrum of **75** run as a MeOH solution in negative ion mode gave two peaks assigned as $[M\text{-}H]^-$ and $[M\text{-}Bu^tNC\text{-}H]^-$ at *m/z* 370 and 287 respectively, indicating the molecular mass of 371 amu. This corresponds to the mono-substituted product.

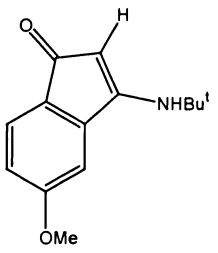
The ^1H NMR spectrum showed the three aromatic protons, the methoxy group, the acetyl group, and one Bu^t group from the coordinated isocyanide.

An X-ray crystal structure determination was undertaken to further confirm the structure of **75**, and to rule out the possibility that the isocyanide had inserted into the Mn-$C_{(aryl)}$ bond. X-ray crystallographic quality crystals where obtained by recrystallisation from warm petroleum spirits. The crystal structure determination is discussed in Section 3.3.7.

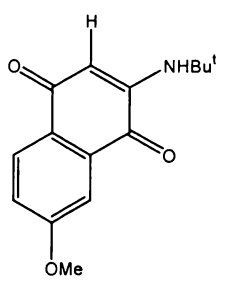


75

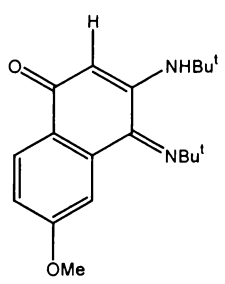
Three further compounds (**76**, **77** and **78**) were isolated from the reaction mixture of **43** with Bu^{t}NC, and the IR spectra of each indicated that there was no manganese carbonyl associated with the compounds. The compounds were able to be identified by the use of ESMS, GCMS and NMR, with 2D-NMR experiments being used to determine the structures of the bicyclic compounds. There was no trace of any di- or tri-substituted versions of **75** detected.



76



77



78

When analysed by ESMS in a MeCN solution at positive cone voltages, **76** gave strong peaks due to the forming of protonated ion species, with a signal at *m/z* 463 (assigned as $[2M+H]^+$) affording the dominant peak. This gave the molecular mass of the compound as being 231 amu, which is equivalent to the loss of the $Mn(CO)_4$ moiety from **43**, with the addition of a Bu^{t}NC group and the further loss of a proton.

GCMS of **76** confirmed the molecular mass by the detection of an $[M]^+$ species at *m/z* 231.

The ^{1}H NMR spectrum of **76** showed two methyl singlets, three aromatic protons, and two other signals, one of which was a broadened peak at 5.13 ppm. The ^{13}C NMR spectrum showed twelve signals, of which (using a DEPT135 experiment) two were assigned as methyl and four as CH, with three of the latter in the aromatic region.

An HSQC experiment was used to determine which protons were connected to which carbons, as an HSQC experiment shows single-bond correlations between carbons and protons. Table 3-1 shows the connectivity as indicated by the HSQC spectrum. By integration of the ^{1}H NMR spectrum it was possible to determine the number of protons associated with each signal, and therefore to identify the *tert*-butyl and methoxy signals.

Table 3-1 HSQC NMR correlations for 3-*tert*-butylamino-5-methoxy-inden-1-one (**76**).

Integration	^{1}H δ (ppm)	^{13}C δ (ppm)	Functional group
9H	1.49	29.2	*tert*-butyl
3H	3.87	56.1	methoxy
1H	5.05	95.3	-
1H	6.66	105.6	aromatic
1H	6.76	111.7	aromatic
1H	7.41	122.1	aromatic

A COSY spectrum was acquired of **76** to determine H-H correlations, while an HMBC spectrum was acquired to determine long range (two- and three-bond) H-C correlations.

The methoxy proton at 3.87 ppm correlated to an aromatic ^{13}C signal at 162.6 ppm, indicating that this is C^{6}, the aromatic ring carbon to which the methoxy group is attached.

The three proton signals at 6.66, 6.76, and 7.41 ppm all correlate to C^{6}, confirming that these are the aromatic protons. From the COSY spectrum it was possible to determine that the proton signals at 6.66, 6.76 and 7.41 are due to H^{4}, H^{7} and H^{8} respectively. The HMBC spectrum was used to confirm these assignments.

The HMBC experiment used a mixing time of 0.6 msec which favours the expression of three-bond correlations for aromatic protons. This is why H^{5} and H^{8} show weak correlations to the adjacent C^{6} and C^{7} respectively, and why H^{7} shows no two-bond correlations.

The remaining carbon signals from the aromatic ring could be identified from the HMBC correlations. The signal at 127.6 ppm must be due to C^9, as there is a correlation from H^6, and C^4 is not within the three-bond range of HMBC correlations. The remaining carbon, C^4, has a signal at 142.5 ppm, as there is a correlation from H^8. The correlations for all the protons are shown in Figure 3-2.

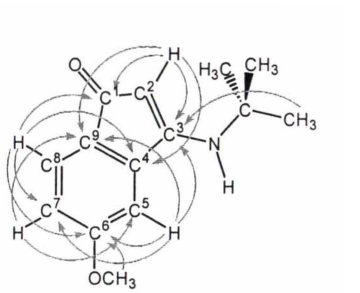


Figure 3-2 HMBC correlations of **76**.

H5 and H8 correlate to signals at 160.0 and 194.0 ppm respectively. These are not part of the aromatic ring system, but are part of the adjoining ring. The signal at 194.0 ppm is indicative of a ketone group, while the signal at 160.0 ppm is further downfield than would be expected for an amine carbon, indicating the presence of the double bond in the second ring system.

The final two signals are C^2 and the attached proton. H^2 correlates to the four carbon signals due to C^1, C^3, C^4 and C^9, confirming the second ring structure. The signal for H^2 is at 5.05 ppm, which is in the region expected for a methylene proton, while C^2 comes at 95.3 ppm, again in the region expected for a methylene carbon.

C^3 was confirmed as having the NHBu^t group attached, as the protons on the Bu^t group showed a weak correlation to C^3 (with the four bond correlation being observed due to the 9 protons in the Bu^t group). The broad peak at 5.13 ppm is due to the NH proton.

Table 3-2 shows full NMR assignments for **76**.

Table 3-2 Full NMR assignments for 3-*tert*-butylamino-5-methoxy-inden-1-one (**76**).

Proton δ (ppm)		Carbon δ (ppm)			
1.49	Bu^t	29.2	$C(CH_3)_3$	122.1	C8
3.87	OMe	53.3	$C(CH_3)_3$	127.6	C9
5.05	H2	56.1	OMe	142.5	C4
5.13	NH	95.3	C2	160.0	C3
6.66	C5	105.6	C5	162.6	C6
6.76	C7	111.7	C7	194.0	C1
7.41	C8				

Compound **76** was recrystallised from chloroform to give yellow rod-like crystals suitable for X-ray crystallography. This was undertaken to confirm the structure of the compound, and the crystal structure determination is discussed in Section 3.3.7.

The products **77** and **78** were identified similarly to **76**. Though **77** gave a very weak ESMS spectrum, the molecular masses of each were obtained from the GCMS spectra. The molecular mass of **77** (259 amu) corresponds to the loss of the $Mn(CO)_4$ moiety and a proton, with the addition of an isocyanide and a carbonyl ligand. The molecular mass of **78** (314 amu) corresponds to the same as **77**, but with the addition of two isocyanides and no carbonyl ligands.

The ^1H NMR of **77** showed signals similar to those seen for **76**, except that the signals due to the single protons (e.g. the aromatic proton etc.) were shifted downfield. The ^{13}C NMR showed similar peaks, but with two carbonyl peaks at 183.0 and 183.1 ppm compared to the one peak in **76**. This confirmed the extra carbonyl ligand included in the molecule that had been indicated by the molecular mass.

The use of 2D-NMR techniques again enabled the characterisation of the aryl ring, and the determination that one each of the two carbonyl groups were attached separately to the aryl ring. The proton signal at 5.92 ppm was determined as not being due to a proton on the aryl ring, and from its correlations it was possible to characterise the second ring fused to the original aryl ring system.

A similar process was used to characterise **78**. The ^1H and ^{13}C NMR of **78** showed the extra signals due to the incorporation of a second isocyanide ligand into the molecule. 2D-

NMR allowed the characterisation of the aryl ring.

The correlations for both **77** and **78** are shown in Figure 3-3, with the full NMR assignments given in Table 3-3.

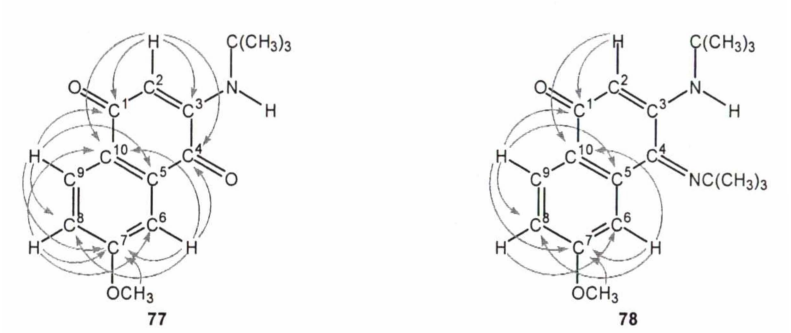


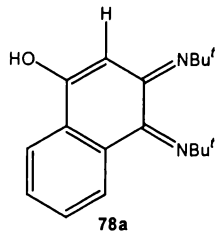
Figure 3-3 HMBC correlations of **77** and **78**.

Table 3-3 Full NMR assignment for 2-*tert*-butylamino-7-methoxy-[1,4]naphthoquinone (**77**) and 3-*tert*-butylamino-4-*tert*-butylimino-6-methoxy-4*H*-naphthalen-1-one (**78**).

	Proton δ (ppm)			Carbon δ (ppm)	
	77	**78**		**77**	**78**
Bu^t	1.47	1.43, 1.54	$C(CH_3)$	28.7	28.7, 31.2
NH	5.88	6.74	$C(CH_3)$	51.9	51.2, 57.0
H2	5.92	5.74	C1	183.1	182.5
H6	7.51	7.24	C2	102.9	98.4
H8	7.21	7.04	C3	146.1	124.9
H9	8.05	8.10	C4	183.0	154.4
OMe	3.94	3.90	C5	132.5	131.4
			C6	110.6	116.4
			C7	162.9	160.1
			C8	120.9	114.8
			C9	128.6	128.4
			C10	127.2	149.8
			OCH_3	56.1	55.6

The HMBC spectrum of **78** did not allow full characterisation of the second fused ring through correlations. However, no other sensible structure can be assigned from the data. With the molecular mass indicating a double bond in the fused ring, the only other structure that could be proposed is that of **78a**. This structure does not correspond to the NMR data, as the proton on the second ring would be further upfield compared to the

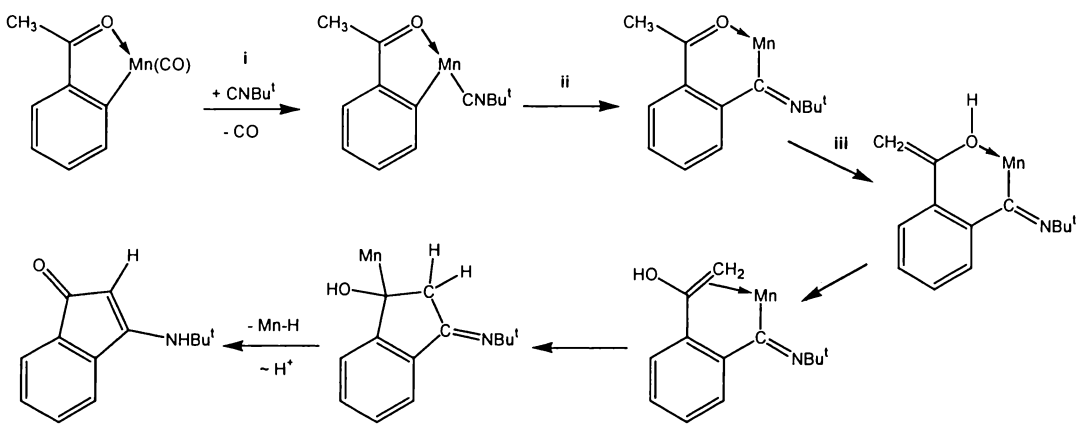
proton in **78**. The proton in **78** is shifted downfield by the adjacent amine group.



78a

Mechanism for the insertion of Bu^{t}NC into orthomanganated complexes.

The products **76**, **77** and **78** appear to be formed by the insertion of one or more ligands into the Mn-$C_{(aryl)}$ bond of **43**, followed by a cyclisation step which eliminates the manganese plus a proton. A reaction mechanism is proposed in Scheme 3-1; for clarity the mechanism is shown for the single insertion product **76**, with no functionalisation of the benzene ring.



Scheme 3-1 Proposed mechanism for the reaction of Bu^{t}NC and cyclomanganated acetophenones. The functionalisation of the aryl ring and additional ligands are omitted for clarity.

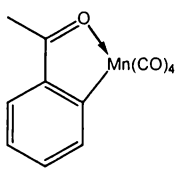
The initial step (**i**) of the reaction involves the forming of the mono-substituted intermediate **75** via thermally activated substitution. The insertion of a coordinated ligand (e.g. the isocyanide in the formation of **76**) into the Mn-C bond of the orthomanganated ligand is promoted by another isocyanide interacting with the complex (step **ii**). At this stage multiple insertions can take place. The product **77** can be formed either by the initial insertion of a carbonyl ligand, followed by an isocyanide ligand, or by the hydrolysis of **78**. The product **78** is formed by the insertion of two isocyanide ligands.

The intermediate formed is unstable, and rapidly undergoes further reaction (step **iii**). The intermediates in the reaction are proposals, as none could be isolated. The final steps in the mechanism involve the loss of the manganese centre (possibly by β-elimination with the adjacent alcohol proton) and a proton transfer to the nitrogen forming the amine group.

Though the production of **77** can be achieved by insertion of a carbonyl then a isocyanide ligand, it appears less likely than the alternative route of hydrolysis of **78** during workup as CNR insertions are more facile than CO insertions.

Further reactions of Bu^{t}NC with orthomanganated complexes.

Various orthomanganated complexes were reacted with Bu^{t}NC to determine the generality of the reaction, including orthomanganated acetophenone (**79**), 3-methoxyacetophenone (**80**), 2-acetylthiophene (**45**) and 1-acetylindole (**81**).



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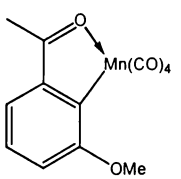

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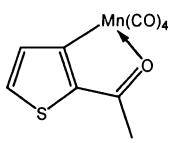

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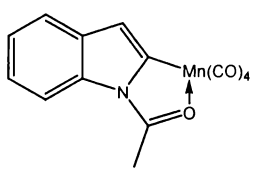


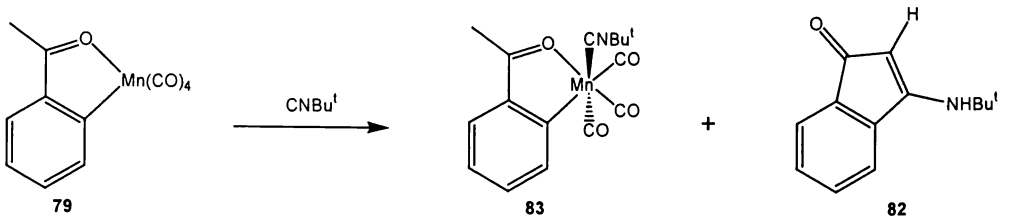
81

Reaction of Bu^{t}NC with other orthomanganated acetophenones.

Other acetophenone derivatives formed the organic products corresponding to those obtained in the *p*-methoxyacetophenone case, with varying ratios of the indenone and naphthyl products. These organic products were identified by ESMS, GCMS and NMR spectroscopy by comparison to the data collected for the products from the reaction of **43** and Bu^{t}NC.

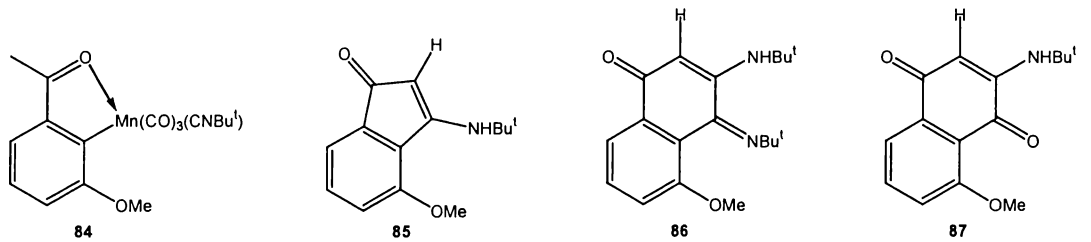
The acetophenone complex **79** did not produce any of the naphthyl compounds, but produced a higher yield of the indenone **82** (22%) compared to the yield from **43** (13%). The mono-substituted orthomanganated complex **83** was also isolated from the reaction mixture.

The products were identified in a similar manner to those from the reaction of **43** with Bu^{t}NC, using IR, ESMS, GCMS and NMR spectroscopy.



When the 6-methoxy derivative **80** was reacted with Bu^{t}NC in refluxing heptane for 2 hours, the major product was the monosubstituted product **84** (51% yield), with the indenone (**85**) and 1,4-naphthoquinone imine (**86**) products only in minor yield (16% and 4% respectively). The reaction was repeated under the same conditions but for 6 hours reaction time. The longer reaction time led to a higher production of the indenone **85** (22%), and also gave a high yield of the naphthoquinone **87** (25%). There was no significant yield of the 1,4-naphthoquinone imine or monosubstituted products isolated.

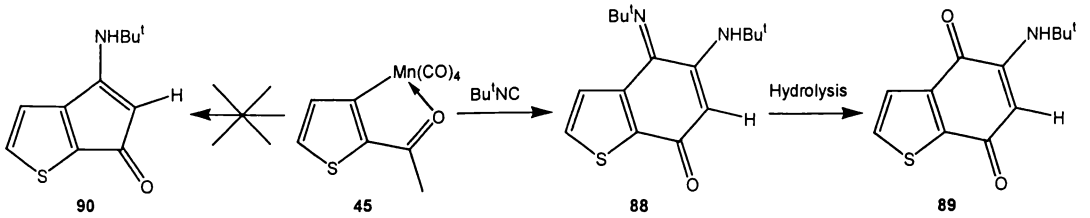
Again the products were identified in a similar manner to those from the reaction of **43** with Bu^{t}NC, using IR, ESMS, GCMS and NMR spectroscopy.



Reaction of Bu^{t}NC with orthomanganated 2-acetylthiophene (45).

The orthomanganated 2-acetylthiophene (**45**) reacted to form two major products, assigned the structures **88** (yield 26%) and **89** (yield 5%). The remaining product mixture was inseparable and of undetermined nature. It may have also contained unreacted starting material, but this was not possible to clarify by spectral analysis of the mixture.

ESMS, GCMS and 2D-NMR were used to assign **88** and **89**, with a crystal structure obtained for **89**, allowing confirmation of the structural assignments. The crystal structure is discussed in Section 3.3.7. There was no evidence for a product similar to **90** from the insertion of a single isocyanide (compared to **76**, **82** and **85** from the acetophenones).



The ESMS of both **88** and **89** showed dominant peaks due to sodium adducts $[nM+Na]^+$ where n = 1, 2, 3 (and in the case of **88** the n = 4 adduct was also observed). The product **89** was run as a MeCN solution (compared to MeOH for **88**), and showed a dominant signal for $[M+H]^+$, but showed no other proton adducts, just the sodium adducts. The observation of a signal due to $[4M+Na]^+$ is rarely seen, as there appears to be insufficient room around the sodium cation to allow all four molecules of **88** to coordinate. It is suggested that two or three molecules of **88** coordinate to the sodium cation, with the remaining one or two molecules hydrogen bonding to the coordinated molecules through interactions with the ketone functional group (see Figure 3-4).

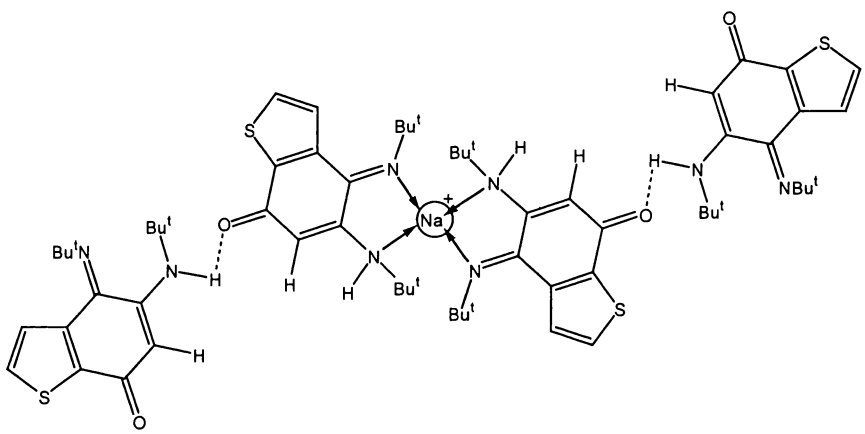


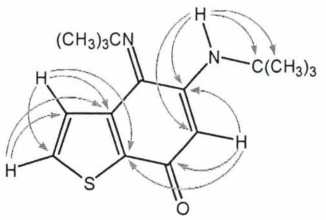
Figure 3-4 Coordination and hydrogen bonding involved in the forming of the $[4M+Na]^+$ sodium adduct of **88** observed in the ESMS spectrum.

The GCMS spectra of both **88** and **89** confirmed the molecular masses of the products, indicating that they were similar to **77** and **78**, i.e. double insertion products.

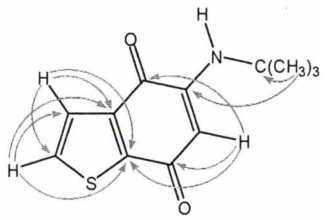
The ^{1}H NMR spectrum of **88** showed the presence of two NBu^t groups with signals at 1.42 and 1.55 ppm. By comparison to **78** it could be determined that the signal at 1.42 ppm was due to a NBu^t group where the nitrogen is an amine, while an imine nitrogen gives the signal at 1.55 ppm. This was confirmed by an HMBC NMR experiment that showed a correlation between the amine proton (7.24 ppm) and the attached Bu^t protons (1.42 ppm).

The amine proton in **88** is shifted downfield compared to that in **89** (7.24 ppm *cf* 5.90 ppm). This is likely to be due to hydrogen bonding to the adjacent imine group. The stronger hydrogen bonding effect is likely to be what causes the large number of molecules involved in the forming of the sodium adducts discussed above, and why the forming of such adducts does not apply to **89**.

Further analysis of the HMBC spectrum showed the two fused rings, but did not allow a determination between the two thiophene protons (and attached carbons) or between the two carbons involved in the fusing of the two ring systems.



88



89

The ^{1}H NMR spectrum of **89** showed only one NBu^{t} group, while the ^{13}C NMR showed two carbonyl signals at 178.0 and 179.0 ppm, indicating that one imine had been hydrolysed to a carbonyl. Again HMBC showed the formation of a fused ring system, but did not allow the determination between the thiophene protons (and attached carbons) or between the two carbons involved in the fusing of the ring system, or between the two carbonyl groups.

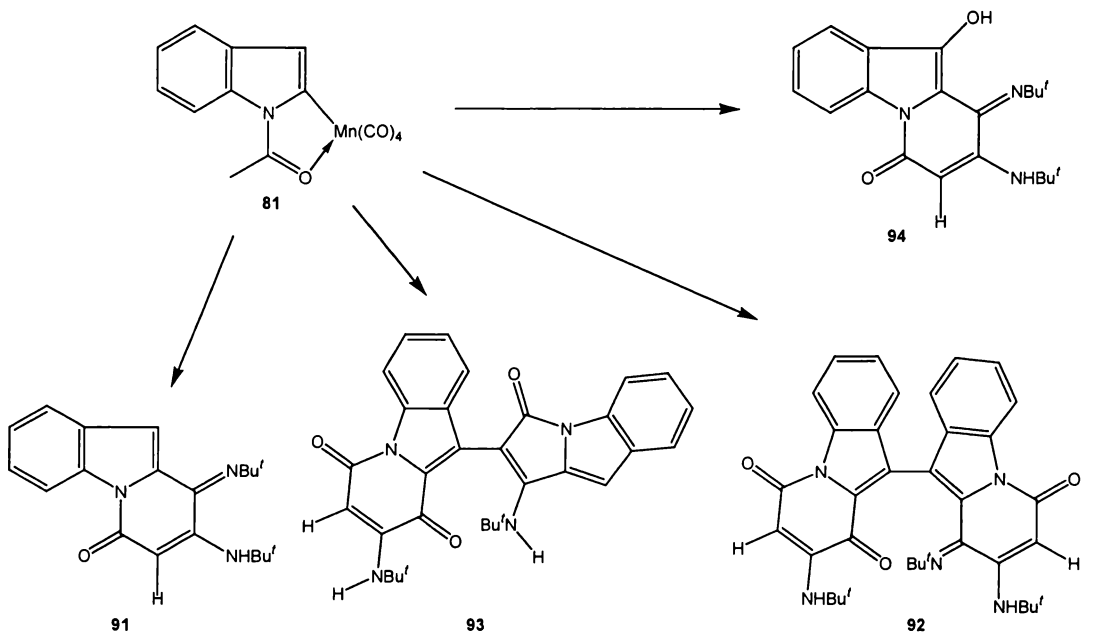
A literature search showed that benzo[*b*]thiophenone derivatives similar to **88** exhibit antibiotic properties[104]. With this in mind more **89** was prepared by hydrolysing a sample of **88** using dilute HCl and THF (forming **89** in a quantitative yield). Samples of both compounds were sent to the University of Canterbury for assay in all systems; antitumour, antimicrobial and antiviral. The results of the tests are discussed later in Section 3.3.4.

Reaction of Bu^{t}NC with orthomanganated 1-acetylindole (81).

The reaction of orthomanganated 1-acetylindole (**81**) with Bu^{t}NC in toluene at reflux afforded a range of products: **91** (yield 19%), **92** (yield 15%), **93** (yield 44%) and **94** (yield

[104] J. Valderrama, A. Fournet, C. Valderrama, S. Bastias, C. Austudillo, A. Rojas de Arias, A. Inchausti, G. Yaluff, *Chemical and Pharmaceutical Bulletin*, **47** (1999) 1221

17%). The product **91** and **94** could be identified by ESMS, GCMS and NMR spectroscopy by comparison with the previous compounds, however the structures of **92** and **93** could not be fully characterised by these techniques. The structures speculatively assigned **92** and **93** are based on the available spectral data. Suitable crystals could not be grown to allow any X-ray crystal structure determinations.



The ESMS of **91** when run as a MeOH solution at positive cone voltages showed the series of proton and sodium adducts $[nM+H]^+$ (n = 1, 2) and $[nM+Na]^+$ (n = 2, 3, 4, and 5). Similar to **88** it appears that **91** is a good ligand towards the sodium cation, seen in the high number of molecules making up the n = 4 and 5 adducts. And again the effect is likely due to hydrogen bonding.

The ESMS results indicated a molecular mass of 323 amu, which was confirmed using GCMS by a molecular ion at *m/z* 323.

The ^{1}H NMR spectrum of **91** shows two NBu^t groups, similar to those seen for **88**, and again by comparison to previous data it can be determined that the more upfield signal at 1.44 ppm is from an NBu^t group where the nitrogen is an amine. This was confirmed from the HMBC spectrum which showed the correlation from the amine proton to the Bu^t group.

By comparison of the NMR spectra of the other products from the reactions of orthomanganated complexes and Bu^{t}NC, it was determined that a similar fused ring system had been produced. HMBC did not allow full characterisation of the structure, but the NMR signals correlated to the structure of **91**.

The ESMS of **94** showed the proton adducts $[nM+H]^+$ (n = 1, 2) and adducts formed with protonated *tert*-butyl amine $[nM+Bu^tNH_3]^+$ (n = 1, 2, and 3). The free amine is likely to be an impurity in the batch of isocyanide used in the reaction. The amine is difficult to remove, and the small traces remaining appear to be sufficient to produce the adducts in the ESMS spectrum.

The ESMS spectrum indicated a molecular mass of 339 amu, which was confirmed using GCMS by a molecular ion of *m/z* 339. This did not correspond to any of the previous products formed by the reaction of orthomanganated complexes with Bu^{t}NC. The molecular ion for **94** is 16 amu higher than for **91**, indicating the incorporation of oxygen atom into the molecule.

The ^{1}H NMR showed the four expected aromatic signals from the benzene ring. Two NBu^t groups were evident, one showing a signal corresponding to an amine nitrogen (this assignment was confirmed in the HMBC spectrum by the correlations shown by the amine proton). The other nitrogen is an imine, as this makes chemical sense. The proton on C^2 gave a signal at 5.51 ppm (again confirmed in the HMBC spectrum by correlation to the adjacent carbon).

The two differences to note between the ^{1}H NMR spectra of **91** and **94** are the position of the amine signal, and the absence of the signal for the proton on C^6, which appears to be replaced by a broad peak at 5.07 ppm. Both effects are inter-related.

The proton at C^6 appears to have been replaced by a hydroxyl group, which undergoes hydrogen bonding to the adjacent imine group (causing the downfield shift in the signal). The upfield shift of the amine signal in **94** *c.f.* **91** is due to less hydrogen bonding to the adjacent imine group, as the imine group is preferentially bonding to the hydroxyl group. Hydrogen bonding by the hydroxyl group to the imine (Figure 3-5) appears to cause an

upfield shift in the protons of the NBu^t group from approximately 1.6 ppm to the 1.32 ppm observed.

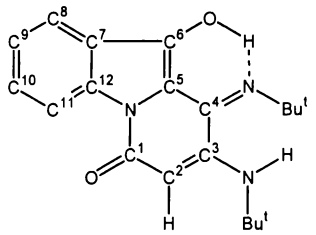


Figure 3-5 H-bonding of the hydroxyl group (dotted line).

The chemistry involved in the formation of **94** remains undetermined, though unusual manganese related chemistry has been observed for indoles in the past[105].

The ESMS of **92** when run as an MeCN solution at positive cone voltages showed the proton adducts $[M+H]^+$ and $[2M+H]^+$, giving a molecular mass of 589 amu. From this molecular mass a molecular formula of $C_{36}H_{39}N_5O_3$ was calculated, allowing a calculation of the yield. The molecular mass could not be confirmed by GCMS as the large mass of **92** was not conducive to analysis by this method.

The ^{1}H NMR spectrum supported the molecular formula as it indicated the presence of two indole units and three NBu^t groups. Two of the NBu^t have amine nitrogens as the proton signals are close to the 1.4 ppm expected for an amine NBu^t group. The other NBu^t proton signal is at 0.86 ppm, considerably upfield from the expected region for the signal. It is unclear why this upfield shift has occurred, or what the nitrogen is present as.

The observation to note from the ^{1}H NMR is the absence of any signal corresponding to the protons on C^6. This implies that the two indole units are linked through the C^6 carbons.

The ^{13}C NMR show three carbonyl signals at 161.4, 164.2 and 172.6 ppm, confirming that there are at least three oxygen atoms in the molecular formula.

Through analysis of the 2D-NMR spectra it appeared that one of the indole units contained

[105] G. J. Depree, Ph.D. Thesis, University of Waikato (1995)

a six-membered ring formed by the insertion and cyclisation of two isocyanide groups, while the other indole unit contained the equivalent six-membered ring with hydrolysis of the imine group to afford a carbonyl. This structure (shown in Figure 3-6) does not reasonably explain the upfield shift of the Bu^t protons on the imine group, and could not be fully characterised by 2D-NMR.

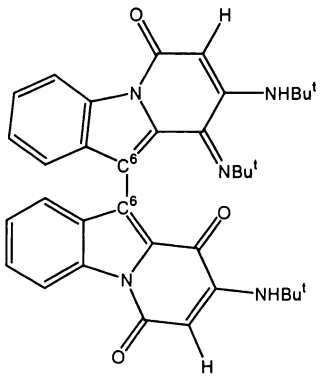


Figure 3-6 Proposed structure of **92**.

The ESMS of **93** showed a number of different positive ion adducts being formed; $[nM+H]^+$ (n = 1, 2), $[nM+Na]^+$ (n = 2, 3), $[nM+Bu^tNH_3]^+$ (n = 1, 2 and 3). These all indicated a molecular mass of 506 amu, corresponding to two indole units with the insertion of one isocyanide into each and the addition of a carbonyl ligand.

Again GCMS could not be used to confirm the molecular mass as the size of the molecule is not conducive to GC analysis.

The ^{1}H NMR spectrum showed the presence of two NBu^t groups, along with the two indole groups. Two signals that were missing from the spectrum were one proton signal each associated with C^2 and C^6. From the HMBC spectrum it was determined that one signal was lost from each unit of the indole, indicating that the two units were linked between the C^2 carbon of one indole and the C^6 carbon of the second indole unit.

Through the HMBC spectrum it was determined that one indole had a fused six-membered ring attached, formed due to the insertion and cyclisation of two isocyanides with subsequent hydrolysis. The other indole had a five-membered ring due to the insertion of one isocyanide. Full characterisation of the structure could not be achieved through 2D-

NMR, with a speculative structure proposed in Figure 3-7.

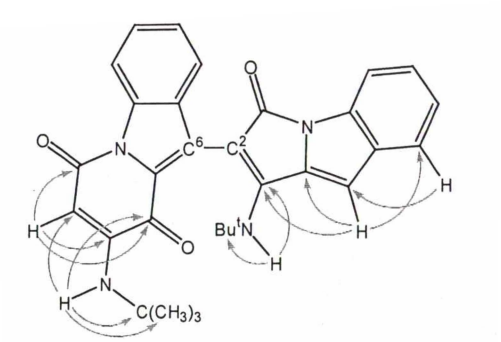


Figure 3-7 HMBC correlations and proposed structure of **93**.

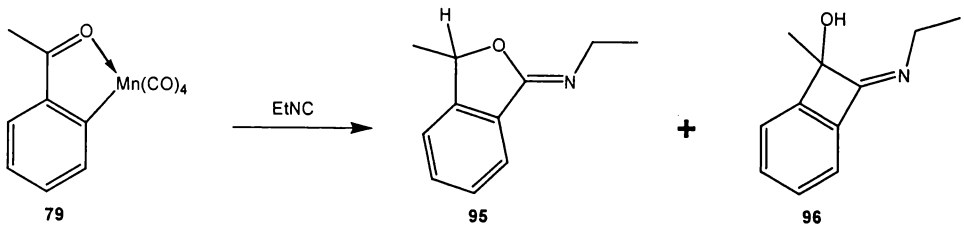
It is not clearly understood what is occurring in the reactions to form **92-94**, but it appears that the initial reaction follows the same mechanism as for the previous $CNBu^t$ reactions. The products also show that the formation of a six-membered ring appears to be favoured when the ring is being formed adjacent to a five-membered ring, as in the thiophene and indole complexes.

3.3.2. Reactions of EtNC with orthomanganated acetyl-aryl compounds.

Reaction of EtNC with orthomanganated acetophenone (79).

So far only Bu^tNC had been reacted with orthomanganated complexes. Ethyl isocyanide (EtNC) and *p*-methoxyphenyl isocyanide were reacted with **79** to determine whether other isocyanides reacted similarly to Bu^tNC to form the indenone and naphthyl products, with different functional groups on the amine and imine.

Due to the volatile nature of EtNC, the reaction between it and **79** was undertaken in a sealed ampoule. A deoxygenated heptane solution of the reactants was sealed in the ampoule and heated to 95°C for 24 hours in a Carius tube. The reaction mixture was worked up by chromatography, producing three fractions, the second and third of which were collected to afford ethyl-(3-methyl-3*H*-isobenzofuran-1-ylidene)-amine (**95**, 23% yield) and 8-ethylimino-7-methyl-bicyclo[4.2.0]octa-1(6),2,4-trien-7-ol (**96**, 17% yield). The first fraction was a mixture of the orthomanganated starting material and a mono-substituted product. There was no evidence of any indenone or naphthyl products.



79 95 96

The products **95** and **96** were characterised by ESMS, GCMS and NMR spectroscopy techniques. ESMS and GCMS were used to determine the molecular mass of the products, which was confirmed as 175 amu in both cases. This mass corresponded to the loss of the $Mn(CO)_4$ moiety from **79**, with the addition of the isocyanide and a proton, which affords the proposed molecular formula $C_{11}H_{13}NO$.

The coupling and intensity of the peaks in the ^1H NMR spectrum of **95** indicated the presence of four aromatic protons, an ethyl group, a methyl group, and a proton adjacent to the methyl group. The ethyl group shows a triplet at 1.29 ppm (integrating as three protons) and a quartet at 3.55 ppm (two protons). The methyl gave a doublet at 1.59 ppm, indicating the presence of a single proton on the adjacent carbon. This was the quartet signal at 5.56 ppm (which integrated as a single proton).

The ^{13}C NMR spectrum showed 11 signals, corresponding to the molecular formula. An HSQC experiment was used to determine the H-C connectivity within the molecule.

From a COSY and HMBC experiment it was possible to characterise the four aromatic protons of the aryl ring. From the COSY spectrum it was possible to determine that the aromatic signals at 7.83 and 7.30 ppm were the protons on C^3 and C^6. The COSY correlations are shown in Figure 3-8.

From the HMBC correlations of the aromatic protons it could be determined which carbon signals were due to the aryl ring carbons. The protons on C^3 and C^6 also correlated to two other carbon signals at 80.0 and 159.5 ppm. The HMBC correlations are shown in Figure 3-8.

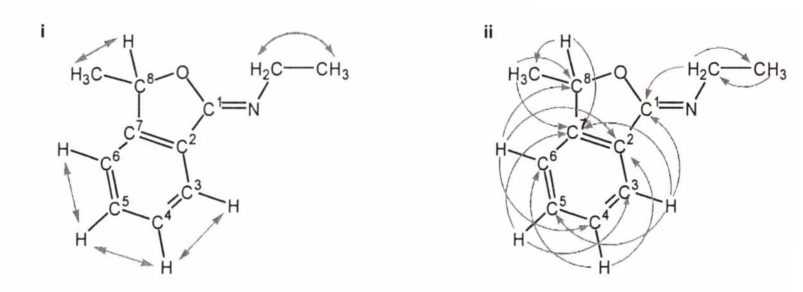


Figure 3-8 COSY (**i**) and HMBC (**ii**) correlations of **95**.

The proton signal at 7.83 ppm correlated to the imine carbon at 159.5 ppm, indicating that this proton was H^3. It was known that the carbon signal at 159.5 ppm was due to the imine carbon as the CH_2 protons of the ethyl group correlated to this carbon signal also.

The proton signal at 7.30 ppm (H^6) correlated to the carbon signal at 80.0 ppm. This was also shown (by HSQC) to be the carbon to which the proton signal at 5.56 ppm was attached. This proton (H^8) also correlated in the COSY spectrum to the methyl protons at 1.59 ppm, as the methyl carbon is attached to C^8. This is why H^8 is seen as a quartet in the ^1H NMR spectrum, and why the methyl protons give a doublet by coupling to H^8.

The methyl protons (at 1.59 ppm) confirm the connectivity by the correlations in the HMBC spectrum. The methyl protons correlate to C^8 and to the aryl ring carbon C^7.

There is no correlation from the methyl protons or H^8 to the imine carbon (159.5 ppm) to indicate the cyclic nature of the second fused ring. However for the structure to match the molecular mass (or proposed formula) there must be the incorporation of an oxygen atom into the molecule. Putting the oxygen as a cyclic ether between the imine and C^8 accounts for the extra mass required, and makes chemical sense of the NMR spectra. The signal for C^8 is too far downfield for a tertiary carbon, and requires the attachment of a heteroatom to effect the downfield shift required. The incorporation of an oxygen atom also accounts for the downfield shift of H^8.

The ^1H NMR spectrum of **96** showed the same ethyl group attached to an imine by the triplet and quartet at 1.32 and 3.61 ppm respectively. Also observed were the four aromatic protons, a methyl singlet, and a broad peak at 2.03 ppm.

Using the COSY spectrum it was possible to determine that the aromatic signals at 7.41 and 7.83 ppm were due to the protons on C^2 and C^5. The HMBC spectrum allowed the determination of which carbon signals were due to the aromatic carbons, and showed that the carbons giving signals at 90.5 and 158.3 ppm were directly attached to the aryl ring. The COSY correlations and the HMBC correlations are shown in Figure 3-9.

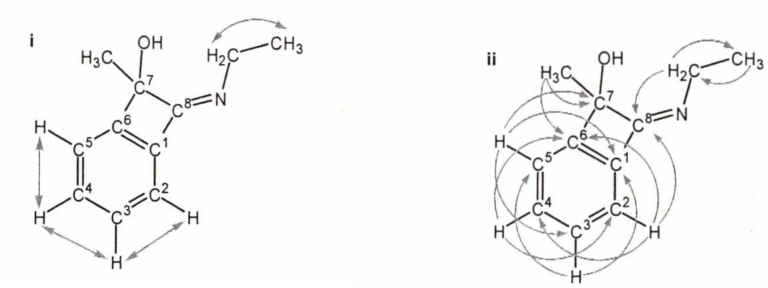


Figure 3-9 COSY (**i**) and HMBC (**ii**) correlations of **96**.

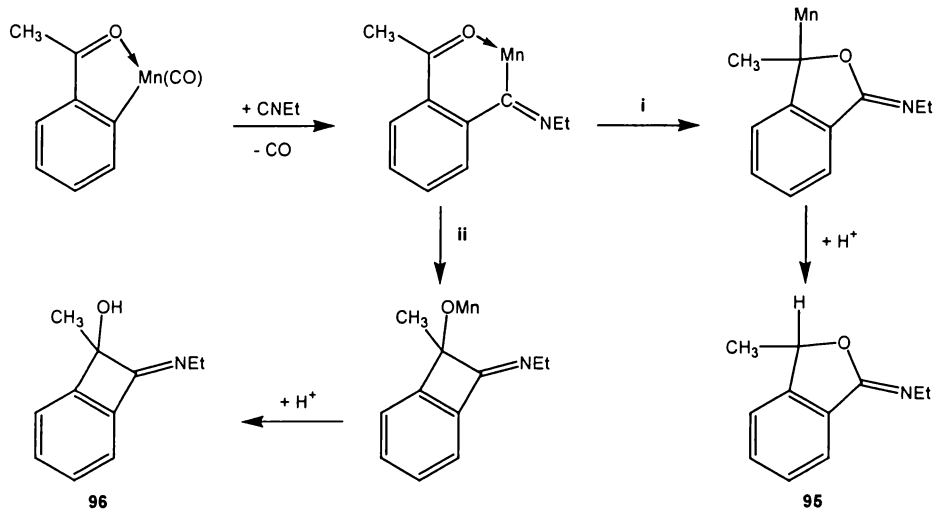
Using the HMBC spectrum it was determined that the signal at 7.83 ppm correlated to the imine carbon at 158.3 ppm, indicating that this was H^2. The signal at 158.3 ppm was confirmed as the imine carbon by a correlation from the ethyl CH_2 protons in the HMBC spectrum.

H5 (7.41 ppm) correlated to the carbon signal at 90.5 ppm, indicating that this was C^7 attached to C^6. The methyl protons also correlated to the signal at 90.5 ppm indicating that the methyl group was attached to C^7.

The broad signal in the proton spectrum at 2.03 ppm is from a hydroxyl group attached to C^7. This causes a downfield shift in C^7. There were no correlations linking C^7 to the imine carbon, but this linkage is required to make chemical sense with regards the NMR spectra and the proposed molecular formula. The downfield shift of C^7 is too large to be solely caused by the hydroxyl group, and is enhanced by the forming of the four-membered ring system by the linkage from C^7 to the imine carbon C^8.

It is not clear what chemistry is occurring in the formation of **95** and **96**, or why the products are so different from the products formed by reaction with Bu^{t}NC. A mechanism is proposed in Scheme 3-2 to account for the two products formed. Once inserted, the EtNC appears to react with either the oxygen (route **i**) or the carbon (route **ii**) of the ketone

functionality to form respectively the fused five- and four-membered ring products. Electronically, the oxygen is a nucleophile, while the carbon is an electrophile, so the EtNC appears to be reacting as both an electrophile and a nucleophile in the same reaction.



Scheme 3-2 Proposed mechanisms for the formation of **95** and **96**.

*Solvent effects on the reaction of EtNC with orthomanganated acetophenone (**79**).* The reaction of **79** with EtNC was repeated in toluene to determine if the yields of the products could be increased, or if the product ratios could be altered.

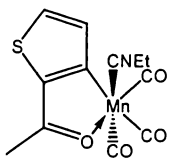
When the reaction was worked-up, it was found that the same products were formed, but that the yields were slightly altered. The production of the furan product **95** was favoured, with the yield increasing from 23% from heptane to 36% from the toluene reaction. The production of **96** remained similar, 17% from the heptane reaction with 13% produced from the toluene reaction.

Using toluene as the reaction solvent appears to increase the yield of organic products by increasing the yield of the furan product **95**.

Reaction of EtNC with orthomanganated 2-acetylthiophene (45).

Initially **45** was reacted with EtNC in toluene for 24 hours in a sealed ampoule, similarly to the above reaction. Toluene was used as the reaction solvent as this had been shown to be the optimum solvent for the reaction of **45** with Bu^{t}NC (see Section 3.3.5). Work-up of the reaction mixture by chromatography afforded an inseparable mixture of many products.

It was thought that the reaction conditions could be too severe. Therefore the reaction was repeated but only at 90°C for 2 hours. Work-up of the reaction mixture by chromatography (PLC plate, 1:1 dichloromethane/petroleum spirits) afforded two products in similar yield. The first product to be eluted was unreacted starting material, while the second product was the mono-substituted product **97** which was identified by IR, ESMS and NMR spectroscopy.



97

The IR spectrum showed 3 peaks at 2010, 1913 and 1893 cm^{-1}, which corresponds to a $Mn(CO)_3$ moiety. The molecular mass of **97** was confirmed using ESMS, with the observation of a peak at *m/z* 318 assigned as $[M-H]^-$.

The ^1H NMR showed five proton signals, corresponding to an ethyl group, an acetyl group and two aromatic protons. The ethyl group is attached to the nitrogen of the original isocyanide, as indicated by the downfield shift of the methylene protons.

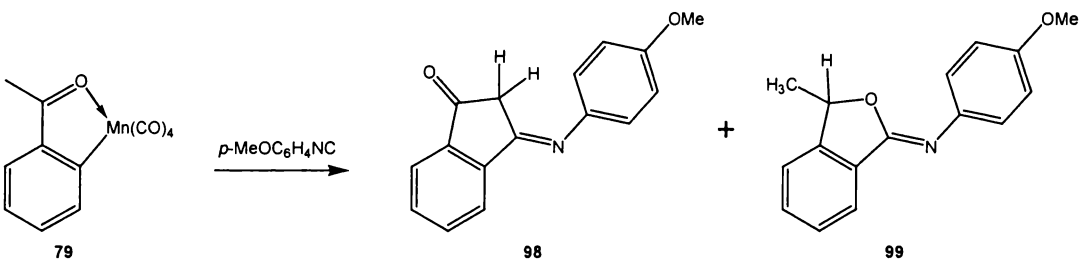
The ^{13}C NMR spectrum shows the carbon signals associated with the organic ligand, with three further signals for the carbonyl ligands, and three for the isocyanide ligand. A carbon signal at 229.1 ppm is likely to be due to the carbon of the isocyanide coordinated to the manganese centre. This signal is too far downfield to be due to a coordinated carbonyl.

It appears that though the mono-substituted product is formed, it does not continue to react in a clean process. The different reactivity of EtNC compared to Bu^{t}NC leads to the production of multiple products if the reaction is forced to continue past the mono-substituted product.

3.3.3. Reaction of *p*-methoxyphenyl isocyanide with orthomanganated acetophenone (79).

The aromatic isocyanide *p*-methoxyphenyl isocyanide was reacted with **79** in heptane at reflux for two hours. This reaction produced two main products, which were isolated by

chromatography (PLC plate, 1:1 petroleum spirits/ether) as oils: 3-(4-methoxyphenyl)imino-indan-1-one (**98**, 12% yield) and (4-methoxyphenyl)-(3-methyl-3*H*-isobenzofuran-1-ylidene)-amine (**99**, 36% yield). The separation was not clean in either case, with both oils containing *p*-methoxyphenyl isocyanide as there was considerable tailing on the plate. No better solvent combination or stationary phase was identified. The yield of the respective products was calculated by integration of the signals in the ^{1}H NMR spectrum.

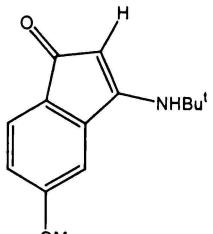


79 98 99

The furan product **99** was identified in a similar manner to the furan product **95** identified above from the reaction of **79** with EtNC. ESMS and GCMS confirmed the molecular mass as 253 amu, and 2D-NMR confirmed the connectivity of the compound.

The indanone product **98** was identified in a similar manner. The GCMS spectrum of **98** showed a molecular ion of 251 amu, which indicated a product similar to the indenone products seen for the reaction of the acetophenone derivatives **43**, **79** and **80**.

The ^{1}H NMR spectrum however showed two signals at 5.02 and 5.05 ppm, rather than a single peak as would be expected for the indenone product. The HSQC spectrum showed that both protons were attached to the carbon with a signal at 86.9 ppm. This indicated that the product was the indanone **98**, as opposed to an analogue of the indenone **77**. The two protons of the indanone ring are in slightly different chemical environments as shown by the two signals in the spectrum, compared to one singlet expected if they were in the same environment. A molecular model of **98** did not indicate any reason for the two protons to be in a different environment, other than the *p*-methoxy group being rotated slightly out of the plane of the aryl ring.



77

To confirm the structure of **98**, a full 2D-NMR characterisation was undertaken. The correlations are shown in Figure 3-10. No correlation was seen to link the inserted isocyanide group to the acetyl group, but this link between C2 and C3 is required to make chemical sense of the structure.

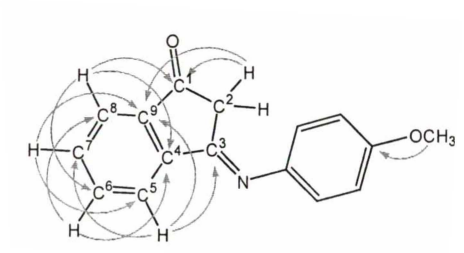


Figure 3-10 HMBC correlations of **98**.

As with the EtNC reaction, the furan was the main product, but in this case there was no trace of a bicyclooctatrienol type product detected. This may be due to the greater steric bulk of the phenyl ring (compared to the ethyl group) inhibiting the formation of the four-membered ring.

Of interest was the production of the indanone, compared to an indenone for the previous reactions. The computer modelling program Macromodel was used to determine which of the indanone/indenone tautomeric forms was more thermodynamically favoured, and whether the more stable tautomer was influenced by the substituent on the nitrogen.

Calculation of the structures of the indanone **98** and its tautomer **98a** showed that the indanone was favoured (193.05 kJ/mol and 219.72 kJ/mol respectively), while calculation of the structures of the indenone **76** and its tautomer **100** showed that the indenone was favoured (190.04 kJ/mol and 222.22 kJ/mol respectively). This explains why the indenone was formed in the reaction with Bu^{t}NC compared to the indanone when *p*-methoxyphenyl

isocyanide was used.

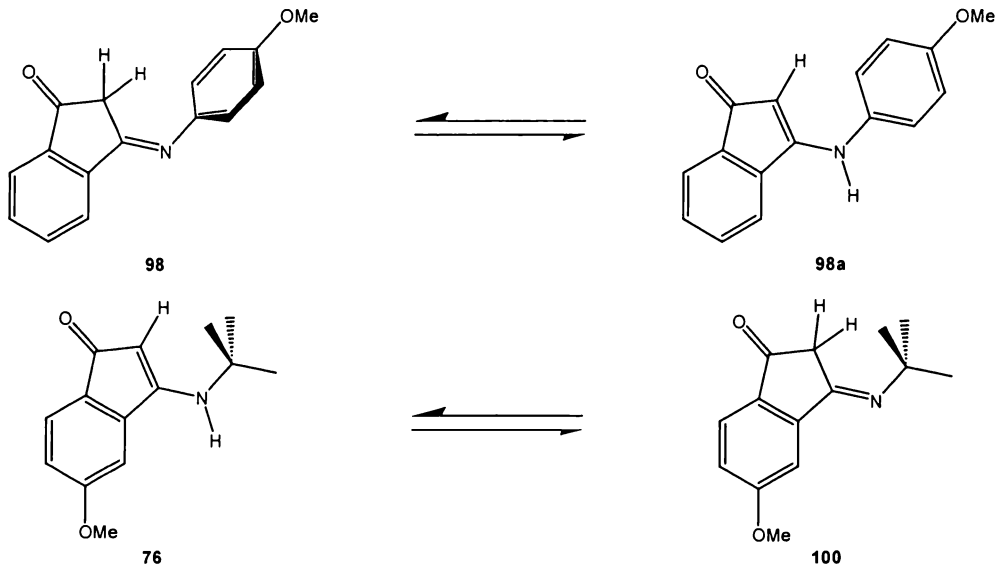


Figure 3-11 Structures of the two tautomers of **98** and **76**, with the most favoured tautomer shown to the left.

Macromodel calculated the structure of the indenone **76** as having the same structure as that shown in the crystal structure determination (Section 3.3.7), with the *t*-butyl group in the plane of the molecule (Figure 3-11 above). The calculated structure of the indanone **98** showed the *p*-methoxyphenyl group to be in the plane of the molecule, but rotated at 90°, inhibiting any conjugation between the phenyl ring and the imine functional group (Figure 3-11 above). With both groups being in the plane of the molecule, the different steric effects of the *t*-butyl or aryl group may be influencing the stable form, indenone *cf* indanone.

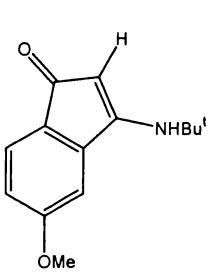
Solvent effects on the reaction of p-*methoxyphenyl isocyanide with orthomanganated acetophenone (**79**).*

The above reaction was repeated using toluene as the solvent to determine if the yields of the products could be increased, or if the product ratios could be altered.

Work-up of the reaction mixture afforded the same two products, but in different yields to those of the original reaction. The indanone **98** was produced in 21% yield, nearly twice the yield when the reaction is conducted in heptane (13%). The production of **99** was slightly lower from the toluene reaction, 25% compared to 33% from the heptane reaction.

3.3.4. Bioassay of isocyanide reaction products.

The organic products **76**, **78**, **88**, **89**, **91** and **94** were assayed for antitumour, antimicrobial and antiviral activity at the University of Canterbury, using the standard suite of assays at a dose rate of 2 mg/ml. Further information on the testing methods can be obtained from Gill Ellis of the Chemistry Department, University of Canterbury. These compounds were chosen as related compounds have been shown to have antibiotic and antitumour activity[106].



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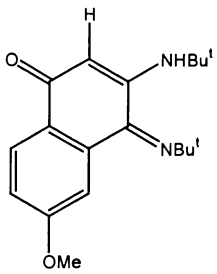

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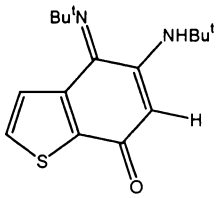

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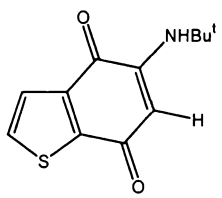

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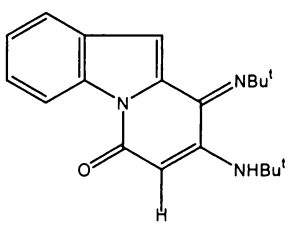

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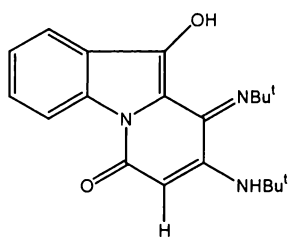

94

Compounds **76**, **78**, **91** and **94** showed little activity. The most promising compounds were **88** and **89** which were shown to have broad spectrum antifungal activity, and a stronger effect on the *B. subtilis* bacteria than the other compounds tested. The full test results are presented in Table 3-4.

[106] N. G. Clark, *Pesticide Science*, **16** (1985) 23

Table 3-4 Tablulated biological testing results. The highlighted areas refer to the minimum inhibitory concentration.

	Compound	76	78	90	93	88											89
Antitumour	P388	> 12500	> 12500	> 12500	> 12500	4032											2094
	PConc	1	1	1	1	1											1
Antimicrobial	E coli																
	B sub		1		1	5											8
	P aer																
	C alb					3	5	1	0	0	12	12	10	1			
	T ment					8	13	8	2	0	13	^	^	^	^	0	
	C res					6	12	5	*	0	16	8	4~	0			
	AConc	1	1	1	1	1	1	1	1	1	1	1	1	1	0.1	0.1	
	AVol	40	40	40	40	40	40	20	10	5	40	20	10	5	40	20	
Antiviral	HSV	ND	?	ND	ND	?					?						
	HCyt	ND	2+	ND	ND	+					4+						
	PV1	ND	?	ND	ND	?					?						
	PCyt	ND	2+	ND	ND	+					4+						
	VVol	40	40	40	40	40					40						
	VConc	1	1	1	1	1					1						

~ growth retard only
^ redo too active
* slight inhibition

Summary of the biological assays.

For the antimicrobial assays, a "lawn" of bacteria or fungi was prepared on a petri dish.

The sample was applied to a 6 mm diameter disk of filter paper, and the filter paper placed on top of the "lawn" and incubated. If the samples showed any antimicrobial activity, there was a zone of inhibition outside the disk. This zone was measured in millimetres, and was recorded for each bacteria or fungi. A blank in the column indicates no inhibition.

The six organisms tested were:

Bacteria - *Escherichia coli.* (G-ve)
Bacillus subtilis. (G+ve)
Pseudomonas aeruginosa. (G-ve)

Fungi - *Candida albicans.*
Trichophyton mentagrophytes.
Cladosporium resinae.

B. Subtilis and *T. mentagrophytes* are the most sensitive organisms.

For the antiviral assay, the samples are similarly pipetted onto 6 mm disks of filter paper. The disks are placed directly onto BSC-1 cells (African Green Monkey kidney) that are infected with either the Herpes simplex type 1 virus or polio virus type 1, and then incubated. The assays are then viewed, and the zones of antiviral inhibition or cytotoxicity are measured. A + indicates a zone of 1-2 mm (25% zone), 2+ 2-4 mm (50% zone), 4+ the whole well (100% zone). Where cytotoxicity is present, it is not possible to determine whether there is antiviral activity, therefore a ? appears in the antiviral column.

The antitumour assay is a more sensitive assay for cytoxicity than the antiviral assay (approximately 100 times more sensitive). The sample is incubated with P388 (Murine Leukaemia) cells, and the concentration required to reduce the cell growth by 50% is determined by comparison with control samples. The result is expressed as an IC_{50} in ng/ml, the lower the number, the more active the compound. A result of >12500 indicates that the compound is very inactive, requiring an undetermined concentration greater than 12.5 mg/ml to inhibit the cell growth.

Both **88** and **89** showed cytotoxicity against the BSC-1 cells used in the antiviral assay, but as cytotoxicity masks any antiviral activity, it was not possible to determine if any antiviral activity was present. It should be noted that in the case of **89** the cytotoxicity was a strong effect, killing all cells in the test.

The antitumour assays showed **88** and **89** to be active against the P388 (Murine Leukaemia) used in the assay. The results are expressed as an IC_{50} in ng/ml. The results for **88** and **89** showed a concentration of 4032 and 2094 ng/ml respectively were sufficient to reduce the P388 cell growth by 50%. This is a notable response, though not high. This result is likely to be linked to the cytotoxicity of the compounds towards the BSC-1 cells used in the antiviral assay. The cytotoxicity implies that the compounds will kill a number of cell types, with the effect not restricted to cancer cells.

The antifungal activity was the most promising of all the results, indicating that both **88** and **89** were broad spectrum antifungal agents. Both compounds showed strong antifungal activity, with large inhibition zones.

As a compound can have a strong inhibitory response, but a low diffusion rate, the area of inhibition may not directly relate to the effectiveness of a compound as an antifungal agent. Therefore further testing was undertaken on **88** and **89** to determine the minimum inhibitory dosage required for a response.

The minimum inhibitory dosages for **88** were 20-40 μg for *Candida albicans*, and 5-10 μg for *Trichophyton mentagrophytes* and *Cladosporium resinae*. The minimum inhibitory dosages for **89** were considerably lower, being 5-10 μg for *Cladosporium resinae*, 4-5 μg for *Candida albicans*, and 2-4 μg for *Trichophyton mentagrophytes*.

These are very low values, however the high cytotoxicity may affect any ability to use these in practice. The compounds are likely to kill surrounding tissue as well as any fungi that they are targeted at.

On average the hydrolysed product **89** showed a higher activity in all systems. This may imply that having two bulky groups on the fused ring system lowers the activity, or that having a quinone structure increases the activity.

3.3.5. Investigation into alternative reaction conditions.

Solvent effects on the reaction of orthomanganated 2-acetylthiophene (45) with Bu^{t}NC.

Due to the positive results of the assays, the optimum reaction conditions needed to be

explored for the production of **88** and **89**.

The reaction was repeated using either toluene or dioxane as the solvent in place of heptane, and the reaction time was increased to six hours. Toluene and dioxane were chosen as solvents as both have a boiling point above 80°C, and both have different characteristics to heptane. Toluene is an aromatic solvent, whereas dioxane is a coordinating solvent. The reaction time was increased as in the initial reaction there were a number of other products detected by tlc which were not able to be identified. It was thought that some of these may have been intermediates in the reaction, including the mono-substitution product.

Both reaction solutions were similarly heated to reflux for 6 hours, then the solvent was removed under vacuum and the residue chromatographed using a Chromatotron (eluted with 1:1 ether/petroleum spirits). Both solvents showed a marked increase in the yield of **88** with toluene the better solvent with the yield of 77% compared to 65% in dioxane. In both reactions there was only a minor trace (<1%) of **89** observed as a thin orange band eluting from the Chromatotron.

The effect of photochemical activation on the reaction of orthomanganated 2-acetylthiophene (45) with Bu^{t}NC.

The reaction of orthomanganated aryl-acetyl complexes with Bu^{t}NC has been proven to proceed if thermally activated. It was thought that the reactions may also be able to be conducted using photochemical activation, by use of a Hg UV lamp. The UV wavelengths are suitable for the decarbonylation of orthomanganated complexes, theoretically allowing the formation of the mono-substitution products and further reaction to form the final products described previously.

A toluene solution of **45** and Bu^{t}NC was transferred to a 20 ml Schlenk flask under nitrogen, and placed in front of a Hg UV lamp. The reaction mixture was irradiated at room temperature for one hour. The solvent was then removed under vacuum, and the residue worked-up by chromatography (PLC plate, 2:3 ether/petroleum spirits). The numerous products could not be properly isolated, with the plate affording three fractions, all containing multiple products. Further chromatography did not afford better separation.

There appeared to be none of the expected products formed, and no other products could be isolated.

Reaction of orthomanganated 4-methoxyacetophenone (43) with Bu^{t}NC in the presence of added metal complexes.

In an effort to increase the yields from the reactions of the orthomanganated acetophenone derivatives and Bu^{t}NC, the use of metal complexes as catalysts was explored. Anhydrous $CoCl_2$ and a $(Bu^tNC)_2NiBr_2$ complex were tested as possible catalysts in reactions of **43** with Bu^{t}NC.

$CoCl_2$ has been used to catalyse the substitution of carbonyl ligands by isocyanide ligands on group 6 complexes[107]. The cobalt complex $(XyNC)_4CoBr_2$ has also been used to catalyse the insertion of XyNC into 2-bromoacetophenone[108]. By using $CoCl_2$ in the present reactions it was though that milder conditions would be required for the initial isocyanide substitution and for the insertion of the substituted isocyanide into the Mn-C bond. In this way it was thought that the yields of the respective products may be increased.

The nickel complex dippeNi(2,6-XyNC)$_2$ (dippe = *bis*(diisopropylphosphino)ethane) has been used for the catalytic insertion of 2,6-XyNC into diphenylene[109]. With regards orthomanganated complexes, the nickel complex $(PPh_3)_2NiBr_2$ has been used as a catalyst for the insertion of alkenes into manganated complexes[28]. Due to its previous success in manganese systems, the latter nickel complex was considered for testing as a catalyst for the isocyanide system. If the catalytic process involved the insertion of an isocyanide that was coordinated to the Ni, it was thought that the best results would be achieved by preparing the equivalent catalyst with Bu^{t}NC ligands, $(Bu^tNC)_2NiBr_2$.

The effect of adding $CoCl_2$.

Anhydrous $CoCl_2$ was added to a THF solution of **43** and Bu^{t}NC in a 1:1 molar ratio with the orthomanganated compound, and heated to reflux for six hours. The main product from the reaction was the mono-substituted complex **75**, which was detected by IR spectroscopy and ESMS. The products from the reaction were not able to be separated to allow further characterisation.

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[107] M. O. Albers, N. J. Coville, T. V. Ashworth, E. Singleton, *J. Organomet. Chem.*, **199** (1980) 55

[108] K. Sugano, T. Tanase, K. Kobayashi, Y. Yamamoto, *Chem. Lett.*, **6** (1991) 921

[109] B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *Organometallics*, **18** (1999) 4040

Work-up of the reaction mixture produced no indenone or naphthyl compounds. This may have been due to the temperature of refluxing THF not being high enough to induce a reaction, but shows that $CoCl_2$ is ineffective at these temperatures.

Preparation of the Ni complex.

The preparation of $(Bu^tNC)_2NiI_2$ has been described in the literature[110]. $NiBr_2$ was substituted for NiI_2 due to availability, and for continuity from the previous study.

The anhydrous $NiBr_2$ was stirred with excess Bu^tNC in a THF solution for 3 hours. The reaction was conducted under a nitrogen atmosphere to ensure the absence of moisture from the reaction vessel.

At the conclusion of the reaction, the solvent and excess Bu^tNC were removed under vacuum, and the residue was recrystallised from dichloromethane/petroleum spirits. Dark red/brown crystals formed when the solution was cooled to -20°C. Care was required to eliminate any moisture from the solvents, as any moisture reacted with the Ni complex to form a pale green precipitate.

The sensitivity of the complex precluded characterisation of the product, as it would start to decompose as soon as it was exposed to air. As soon as the complex was dissolved in an NMR solvent it again started to decompose, and no solvent could be found suitable for ESMS analysis.

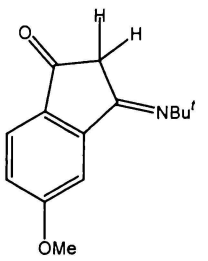
However, it is expected that the complex formed was indeed the $(Bu^tNC)_2NiBr_2$ product desired.

The effect of adding the $(Bu^tNC)_2NiBr_2$ complex.

The $(Bu^tNC)_2NiBr_2$ complex was added to a heptane solution of **43** and Bu^tNC in a 1:1 molar ratio with the orthomanganated compound, and then heated to reflux for two hours. Work-up of the reaction solution produced no trace of the indenone or naphthyl products, but instead produced a 40% yield of 5-methoxy-3-*tert*-butyliminoindan-1-one (**100**) as a pale oil. This was characterised by ESMS, GCMS and NMR, with 2D-NMR experiments being used to confirm the indanone ring structure. The remaining products isolated were

[110] S. Otsuka, A. Nakamura, Y. Tatsuno, *J. Amer. Chem. Soc.*, **91** (1969) 6994

the mono-substituted product **75** and 4-methoxyacetophenone from the demetalation of the starting material.



100

The ESMS showed a peak assigned as $[M+H]^+$, giving the molecular mass as 231 amu. The GCMS however showed a molecular ion at *m/z* 232. This result does not correlate to the ESMS assignment, nor does it with the NMR data that follows. It is not understood why this peak is observed.

The ^{1}H NMR spectrum shows the three aromatic protons, the methoxy group and the Bu^t group. There are two peaks at 4.74 and 4.81 ppm for the methylene protons, similar to the two peaks observed for **98** (Figure 3-10, page 75), the indanone product from the reaction of **43** with *p*-methoxyphenyl isocyanide. From the HSQC spectrum it can be seen that both protons are attached to the same carbon, that giving the signal at 83.3 ppm.

The aromatic ring and the substituents on it could be identified using the correlations in the HMBC spectrum. These correlations are shown in Figure 3-12.

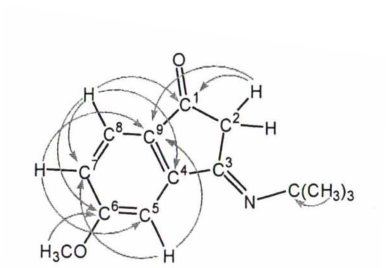


Figure 3-12 HMBC correlations of **100**.

The proton on C^8 (H^8) correlated to the carbonyl carbon (C^1) at 155.5 ppm, indicating that this is attached to C^9. The two protons at 4.74 and 4.81 ppm both correlate to the C^1 and to C^9, indicating these are the protons on C^2. The bond C^2-C^3 is required to make chemical

sense of the structure, and to accommodate the large downfield shift of C^2. A methylene carbon adjacent to a carbonyl will not be moved so far downfield, thus requiring the forming of the ring system (which influences a downfield shift) which places C^2 adjacent to an imine group, which causes a further downfield shift, giving the final chemical shift of 83.3 ppm.

The addition of the Ni catalyst has increased the yield from the reaction, but it has also influenced the product formed. From the reaction of orthomanganated acetophenone (**79**) with *p*-methoxyphenyl isocyanide the indanone product was also formed, but this was shown through the computer modelling program Macromodel[111] to be the thermodynamically more stable tautomer (Section 3.3.3). Similar calculations were conducted on the two tautomers **76** and **100**. The indenone **76** was shown to have a lower calculated energy (190.04 $kJmol^{-1}$) than the indanone **100** (222.22 $kJmol^{-1}$).

The Ni appears to change the reaction path, causing the less favoured indanone to be isolated. This may occur due to a transmetalation of the manganese and nickel at some stage during the reaction. A nickel complex formed by transmetalation may react by a path different from the original manganese reaction. It is not clear how the reaction path is altered, as the original reaction path is not clearly understood.

In situ use of $NiBr_2$.

Due to the unstable nature of the $NiBr_2(CNBu^t)_2$ complex, and the fact that it could not be properly characterised, its *in situ* preparation as a catalyst was investigated.

The *in situ* reaction was first conducted in dioxane, as this is a solvent with similar coordinating properties to THF, but with a higher boiling point. The idea was that the $NiBr_2(CNBu^t)_2$ complex would be formed *in situ*, and would then be available to react with the orthomanganated compound to form the indanone product.

This reaction produced the indanone product **100**, but in a lower yield (15%) compared to the original reaction (40%). The main products from the reaction were **75** and 4-methoxyacetophenone.

[111] Macromodel Interactive Modeling System Ver. 7.0, Schrödinger Inc, Columbia University, USA, (1999)

The *in situ* reaction was repeated with heptane as the solvent, as the original reaction was conducted in heptane. Though the $NiBr_2(CNBu^t)_2$ was very insoluble in heptane, the original reaction progressed with a high yield. It was therefore thought that the poor solubility of $NiBr_2$ might not be a hindrance to the reaction. However, the second *in situ* reaction in heptane produced a yield of **100** (16%) similar to that of the dioxane reaction, but neither were as high as the original reaction using the preformed $NiBr_2(CNBu^t)_2$ complex.

*Attempted acid catalysed conversion of the indanone **100** to the indenone **76**.*
A sample of **100** (~10 mg) was dissolved in deutero-methanol and transferred to an NMR tube with the organic acid 4-amino-toluene-3-sulfonic acid (~2 mg). The ^1H NMR spectrum of the sample was collected immediately after the addition of the organic acid, and then monitored for 20 days.

The addition of the organic acid did not catalyse the conversion of the indanone (**100**) to the indenone form (**76**), instead degrading the compound and affording a number of peaks from an unidentified degradation product. These included a triplet at 1.19 ppm, a quartet at 3.50 ppm and a broad signal at 4.84 ppm.

3.3.6. Investigating the use of 5-*tert*-butylamino-4-*tert*-butylimino-4*H*-benzo[*b*]thiophen-7-one (88) as a metal ligand.

The ESMS spectrum indicated that **88** could be a good ligand, as seen by the observation of the $[4M+Na]^+$ adduct.

A brief search of the literature produced examples of complexes formed by coordination of a bidentate nitrogen ligand (**101** and **102**)[112,113]. The ligand coordination sites are similar to the amine and imine sites of thiophenone **88**. It was thought that a coordination complex similar to **103** could be produced by reacting **88** with a suitable metal precursor. There was also found a complex formed by the coordination of a N,O-ligand (**104**)[114].

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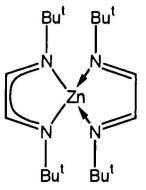
[112] E. Rijnberg, B. Richter, K.-H. Thiele, J. Baersma, N. Veldman, A. L. Spek, G. van Koten, *Inorg. Chem.*, **37** (1998) 56

[113] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.*, **123** (2001) 2213

[114] K. S. Min, T. Weyhermüller, K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, (2003) 1126



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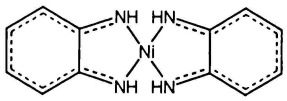

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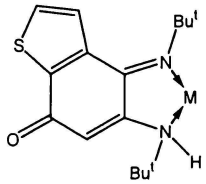

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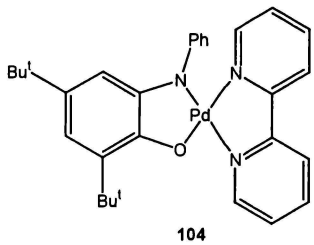


104

*Reaction of **88** with zinc acetate.*

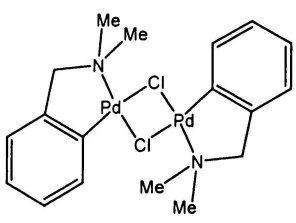
Zinc was the metal initially chosen to test the formation of a complex similar to **101**. Zinc acetate was added stoichiometrically to an ethanol solution of **88**, and stirred at room temperature overnight. The reaction was undertaken open to the atmosphere, with no attempt made to exclude either oxygen or moisture.

ESMS of the reaction mixture showed no evidence for a new metal complex being formed with **88** acting as a ligand on the zinc metal. It was thought that the amine proton may have needed to be removed to allow the formation of the complex. Therefore a trace of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added as a proton sponge. After stirring for a further night the reaction mixture showed no change, with no evidence by ESMS of a reaction occurring.

All of **88** was recovered unchanged from the reaction mixture by chromatography (PLC plate, ether).

*Reaction of **88** with di-μ-chloro-bis-(N,N-dimethylbenzylamine)palladium(II) (**105**).*

105 was dissolved in dichloromethane, and to this solution was added **88** in a stoichiometric ratio. The solution was stirred overnight at room temperature, open to the atmosphere. ESMS of the reaction mixture at this time showed the dominant species to be **105** and **88**, with no evidence for a reaction between the two.



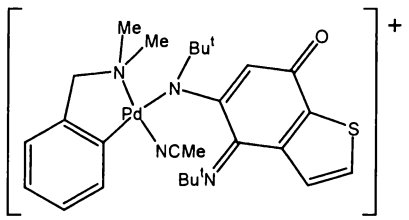
105

Therefore a trace of DBU was added to the reaction mixture to act as a proton sponge, deprotonating the amine group, and encouraging the coordination to the Pd centre. The

reaction was stirred for a further night.

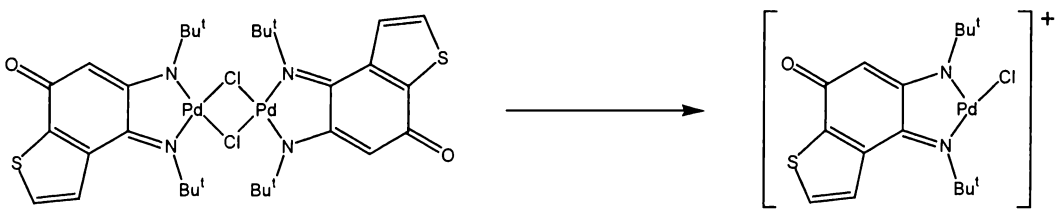
ESMS of the reaction mixture after stirring overnight indicated the formation of two species containing the Pd centre and a deprotonated **88** ligand, as indicated by the appearance of two weak series of peaks in the spectrum.

One series of peaks forming an isotope pattern (with the most intense peak at 572 amu) was assigned as being due to the complex **106**. The *m/z* of the peak indicated that a MeCN ligand was included, implying that the thiophenone ligand was monodentate, rather than bidentate as intended.



106

The second series of peaks formed an isotope pattern (with the most intense peak at 433 amu) that was assigned to the monomer **107**, formed by the dissociation of the dimer **108** in solution under ESMS conditions. In **108** the thiophenone ligand is bidentate as intended.



108 **107**

The weak nature of the peaks in the ESMS spectrum indicates that neither product was formed in a large yield. The dominant peaks of the spectrum were from the unreacted ligand **88**. Neither product could be isolated by chromatography, solvent extraction or recrystallisation.

3.3.7. X-ray crystal structure determinations.

X-ray crystal structure of [η^2-(diphenylthiophosphinyl)phenyl]carbonyl-tri(*tert*-butylisocyanide)manganese, 74.

The orange crystals were shown to be monoclinic, of space group $P2_1$, with two molecules in the unit cell. Crystal and structure refinement data are given in a table in Section 3.5.5, while the CIF files can be found on the CD inside the back cover. An ORTEP perspective view is shown in Figure 3-13.

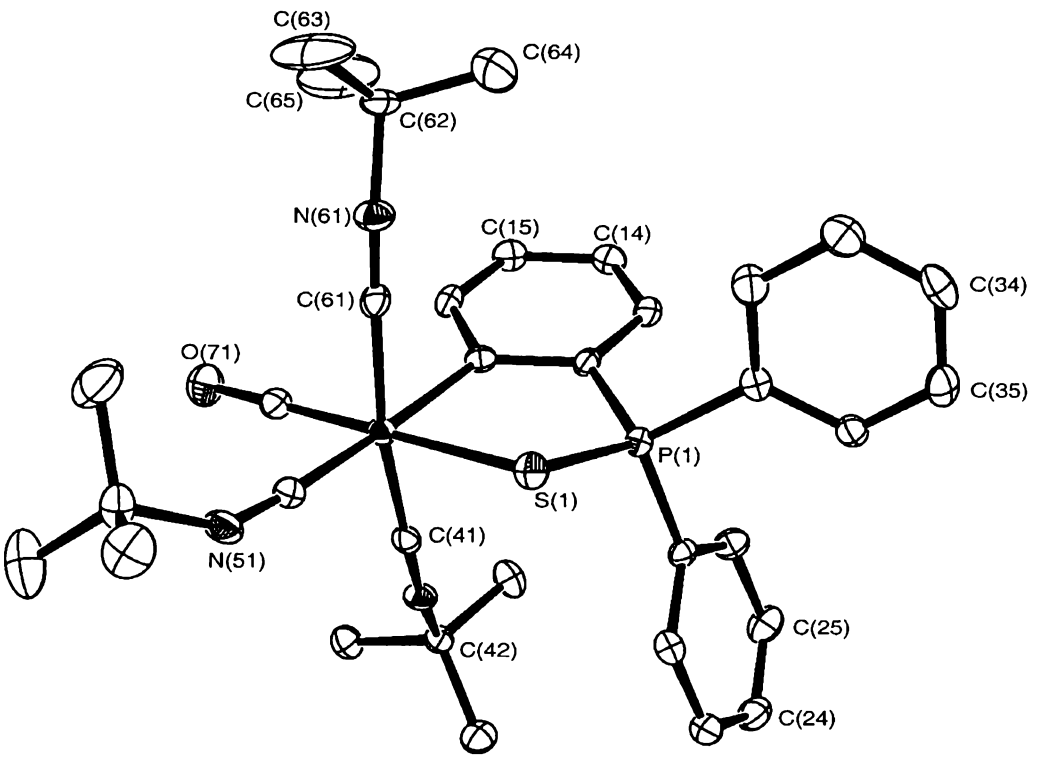


Figure 3-13 ORTEP perspective view of **74**.

The crystal structure shows an octahedrally coordinated manganese centre with *mer*-$Mn(CNBu^t)_3$, a bidentate triphenylphosphine sulfide ligand, and a CO ligand. The lone carbonyl coordinates opposite the sulfur.

In the original $Mn(CO)_4$ complex **49**, the axial CO associations have the longest bond lengths, while the CO equatorially coordinated opposite the sulfur (e_s) shows the shortest bond length. This implies that the e_s coordination is the strongest, thus the other carbonyls are substituted first. The Mn-C bond length for the e_s carbonyl in **49** is 1.784(3) Å

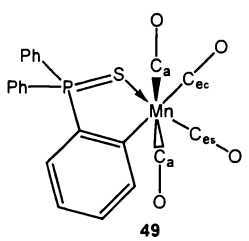
compared to 1.748(6) Å in **74**. The coordination of the e_s carbonyl is strengthened by the coordinated isocyanide ligands, as these increased the electron density on the manganese due to their being stronger σ-donors than the carbonyls they replace. The increased Mn-C bond order is mirrored by the decrease in the C≡O bond order of the e_s carbonyl, with the bond length increasing from 1.146(3) Å in **49** to 1.176(7) Å in **74**.

The e_s carbonyl coordination is also stronger in **74** than in η^2-$Ph_2P(S)C_6H_4Mn(CO)_2[P(OMe)_3]_2$ **109** (where the $P(OMe)_3$ ligands are axially coordinated). The Mn-$C_{(es)}$ bond length in **74** is 1.748(6) Å compared to 1.766(5) Å in **109**.

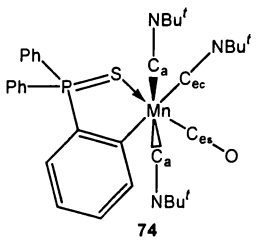
Table 3-5 Selected bond lengths (Å) of the *ortho*manganated complexes **49**, **74**, and **109**.

Bond	*ortho*manganated complex		
	49	**74**	**109**
Mn-S	2.410(1)	2.465(2)	2.413(1)
S=P	1.996(1)	1.989(2)	1.993(2)
Mn-$C_{(aryl)}$	2.081(2)	2.080(5)	2.078(4)
Mn-$X_{(a)}$	1.836(2)[a]	1.898(5)[a]	2.227(1)[b]
Mn-$X_{(a)}$	1.846(2)[a]	1.906(4)[a]	2.228(1)[b]
Mn-$C_{(es)}$	1.784(3)	1.748(6)	1.766(5)
Mn-$C_{(ec)}$	1.825(3)	1.870(6)	1.782(5)
$X_{(a)}$-Y	1.133(3)[a,c]	1.158(6)[a,d]	-
$X_{(a)}$-Y	1.137(3)[a,c]	1.175(5)[a,d]	-
$C_{(es)}$-O	1.146(3)	1.176(7)	1.155(6)
$C_{(ec)}$-Y	1.140(3)[c]	1.174(7)[d]	1.167(5)[c]

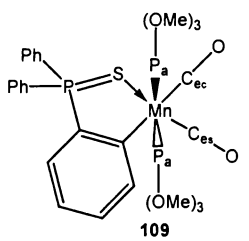
The X atom represents: [a] carbon atom, [b] phosphorus atom; the Y atom represents: [c] oxygen atom, [d] nitrogen atom.



49



74



109

For the three complexes the Mn-$C_{(aryl)}$ bond lengths remain constant at 2.080 Å. The Mn-S and S=P bonds do show differences between the three complexes.

The Mn-S coordination is weakest in **74**, seen in the longer bond length (2.465(2) Å compared to 2.410(1) and 2.413(1) Å). A higher electron density on the Mn means that

less contribution is required from the lone pair electrons on the sulfur, therefore increasing the bond length. This also leads to a slightly decreased P=S bond length of 1.989(2) Å (compared to 1.996(1) and 1.993(2) Å).

In **74** the Mn-C bond length to the isocyanide ligands is longer than for the analogous carbonyl ligands in **49**, but follows a similar trend; axial bonds are longer than the equatorial. The two axial Mn-C bond lengths in **74** are 1.898(5) and 1.906(4) Å compared to 1.870(6) Å for the equatorial.

Table 3-6 Selected bond angles (°) of complex **74**.

Bond	Angle	Bond	Angle
C(11)-Mn(1)-S(1)	88.74(15)	P(1)-S(1)-Mn(1)	96.85(7)
C(51)-Mn(1)-S(1)	88.87(18)	C(12)-P(1)-S(1)	109.74(17)
C(71)-Mn(1)-C(51)	87.3(3)	C(71)-Mn(1)-C(11)	94.9(2)
C(61)-Mn(1)-C(41)	166.0(2)	O(71)-C(71)-Mn(1)	177.8(5)
C(41)-N(41)-C(42)	163.2(5)	N(41)-C(41)-Mn(1)	173.3(5)
C(51)-N(51)-C(52)	146.6(5)	N(51)-C(51)-Mn(1)	175.2(5)
C(61)-N(61)-C(62)	160.6(5)	N(61)-C(61)-Mn(1)	174.2(4)

The two axial isocyanide ligands both arc towards the Mn-$C_{(aryl)}$ bond. The same arc effect is seen to a lesser extent for the carbonyl ligands in complex **49**. The equatorial isocyanide arcs out of the plane defined by Mn(1)-C(32)-C(31)-P(1). Both of these characteristics are shown in the Figure 3-14.

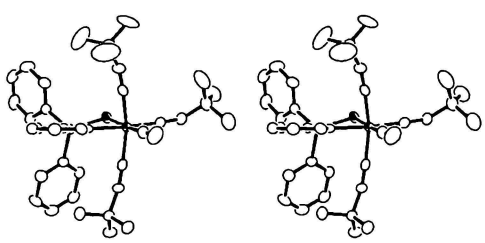


Figure 3-14 Stereo view of **74** showing arcing of isocyanide ligands.

The equatorially coordinated isocyanide shows a large deviation from 180° in the C≡N-C bond angle. This is likely to be due to unequal back-donation from the manganese to one of the two degenerate π^* orbitals of the isocyanide ligand. The manganese has two axial isocyanide ligands which are good σ-donors but weak π-acceptors, which leads to the

axial p-orbital of the manganese containing an increased electron density. This electron density is donated to the equatorial isocyanide π^*-orbital causing the bent shape. The effect is increased by the equatorial carbonyl ligand which is a weaker σ-donor and stronger π-acceptor compared to the isocyanide ligands, therefore increasing the electron density of the axial manganese P-orbital.

X-ray crystal structure of [η^2-5-methoxy-2-acetylphenyl]tricarbonyl-*tert*-butylisocyanidemanganese, 75.

The dark yellow crystals were shown to be monoclinic, of space group $P2_1/n$, with four molecules in the unit cell. Crystal and structure refinement data are given in a table in Section 3.5.5, while the CIF files can be found on the CD inside the back cover. An ORTEP perspective view showing the atom labelling scheme is given in Figure 3-15.

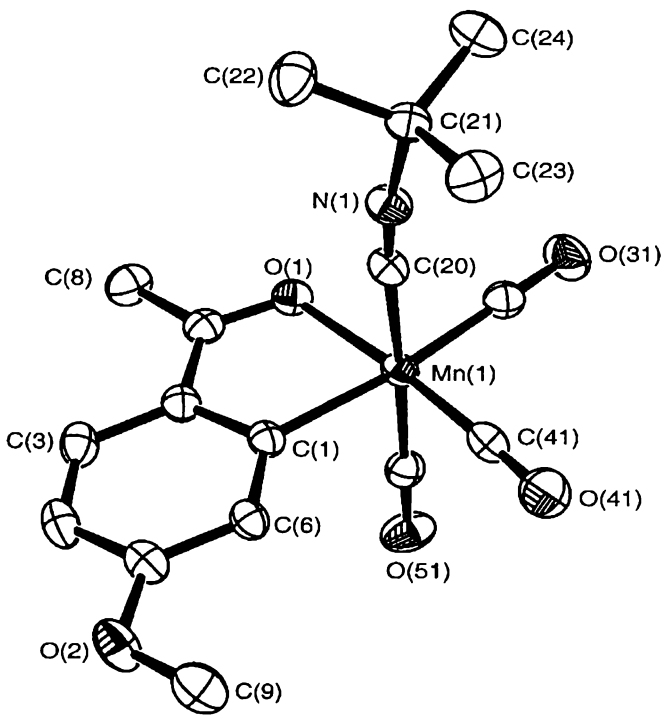


Figure 3-15 ORTEP perspective view of **75**, showing the atom labelling scheme.

The crystal structure shows an octahedrally coordinated manganese atom with a bidentate *p*-methoxyacetophenonyl ligand, two carbonyl ligands in the equatorial sites, and the remaining carbonyl and isocyanide in the axial sites. All angles between adjacent ligands are approximately 90° with the exception of the bidentate ligand angle which is

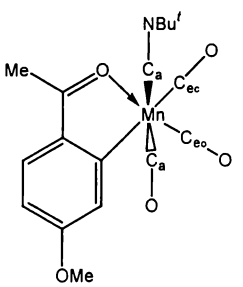
constrained at 79.7°.

Analysis of the crystal structures of orthomanganated acetophenone[4] (**79**) and 1-phenylpropan-2-one[115] (**110**) show that the axial carbonyl coordinations are weaker than the equatorial equivalents (the same as the trend seen for orthomanganated triphenylphosphine sulfide complexes discussed previously). It is expected that in the formation of **75**, the axial carbonyl is thermally removed allowing coordination of the isocyanide ligand. By comparison with **79** and **110**, this substitution appears to strengthen the coordination of the remaining axial carbonyl (CO_a) and the equatorial carbonyl opposite the aryl carbon (CO_{ec}), seen in a shortening of the Mn-C bond lengths (see Table 3-7).

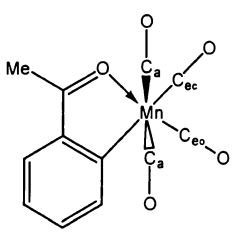
Table 3-7 Selected bond lengths of the *ortho*manganated complexes **75**, **79** and **110**.

Bond	*ortho*manganated complex		
	75	**79**	**110**
Mn-O	2.067(1)	2.055(2)	2.065
O=C	1.256(2)	1.244(3)	1.247
Mn-$C_{(aryl)}$	2.037(2)	2.042(2)	2.073
Mn-$C_{(a)}$	1.948(2)	1.857(3)	1.861
Mn-$C_{(a)}$	1.821(2)	1.856(3)	1.861
Mn-$C_{(eo)}$	1.787(2)	1.786(3)	1.740
Mn-$C_{(ec)}$	1.838(2)	1.849(3)	1.848
$C_{(a)}$-X	1.152(2)[a]	1.132(3)[b]	1.126[b]
$C_{(a)}$-O	1.143(2)	1.126(3)	1.124
$C_{(eo)}$-O	1.153(2)	1.150(3)	1.188
$C_{(ec)}$-O	1.145(2)	1.130(3)	1.131

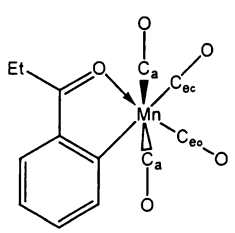
The X atom represents: [a] nitrogen atom, [b] oxygen atom.



75



79



110

[4] C. B. Knobler, S. S. Crawford, H. D. Kaesz, *Inorg. Chem.*, **14** (1975) 2062

[115] H.-J. Haupt, G. Lohmann, U. Florke, *Z. Anorg. Allg. Chem.*, **526** (1985) 103

This strengthening of the carbonyl coordination is analogous to that seen in the triphenylphosphine complex **74** discussed earlier. The isocyanide donates electron density to the manganese centre, increasing back-bonding to the carbonyl ligands.

The isocyanide ligand is not as strongly coordinated to the manganese as in the tri-substituted triphenylphosphine sulfide complex **74**. In **74** the Mn-C bond length to the axial isocyanide ligands was ~1.90 Å, compared to 1.948(2) Å in **75**. The isocyanide ligand in **75** also accepts less back-donation from the p-orbital of the manganese into the π^*-orbital. This is observed in the shorter C≡N bond length (1.1516(19) Å compared to ~1.17 Å for the axial isocyanides in **74**). The C≡N-C bond angle of 171.1° is close to 180°, indicating that the back-bonding occurs symmetrically, compared to that observed in **74**.

Table 3-8 Selected bond lengths (Å) and angles (°) of complex **75**.

Bond	Length	Bond	Angle
Mn(1)-C(1)	2.0365(14)	C(1)-Mn(1)-O(1)	79.69(5)
Mn(1)-O(1)	2.0669(10)	C(41)-Mn(1)-C(1)	94.68(6)
Mn(1)-C(20)	1.9483(15)	C(41)-Mn(1)-C(31)	94.29(7)
Mn(1)-C(31)	1.8380(15)	C(31)-Mn(1)-O(1)	91.35(5)
Mn(1)-C(41)	1.7870(15)	C(7)- O(1) -Mn(1)	115.49(9)
Mn(1)-C(51)	1.8212(15)	C(51)-Mn(1)-C(20)	174.45(6)
O(1)-C(7)	1.2557(18)	O(31)-C(31)-Mn(1)	179.44(14)
C(20)-N(1)	1.1516(19)	O(41)-C(41)-Mn(1)	178.30(13)
O(31)-C(31)	1.1445(19)	O(51)-C(51)-Mn(1)	176.91(13)
O(41)-C(41)	1.1534(19)	Mn(1)-C(20)-N(1)	174.83(13)
O(51)-C(51)	1.1429(18)	C(20)- N(1) -C(21)	171.73(14)

X-ray crystal structure of 5-methoxy-3-*tert*-butylaminoinden-1-one, 76.

The E statistics did not conclusively indicate whether the structure should be solved in the centrosymmetric space group Pnma or the non-centrosymmetric space group $Pna2_1$ ($|E^2-1| = 0.827$ compared to 0.968 for centrosymmetric; 0.736 for non-centrosymmetric). All attempts to solve the structure in Pnma gave no sensible results, in contrast with $Pna2_1$ where the refinement was well-behaved with direct convergence and no sign of correlation between the two independent molecules. Therefore the structure was solved and refined in $Pna2_1$, with two independent molecules in the unit cell. The final $Pna2_1$ structure showed

no mirror planes in the unit cell packing diagrams.

The absolute structure of **76** could not be determined from the Flack parameter. There was no atom of sufficient weight to give confidence in the Flack calculation. The structure was solved, and then inverted and resolved, with the Flack parameters for the two solutions being 1.1(13) and -0.2(1.4) (standard deviations in parentheses).

The unit cell contains four asymmetric units, each containing two independent molecules. Crystal and structure refinement data are given in a table in Section 3.5.5, while the CIF files can be found on the CD inside the back cover. Figure 3-16 shows an ORTEP perspective view of the two independent molecules and the labelling scheme.

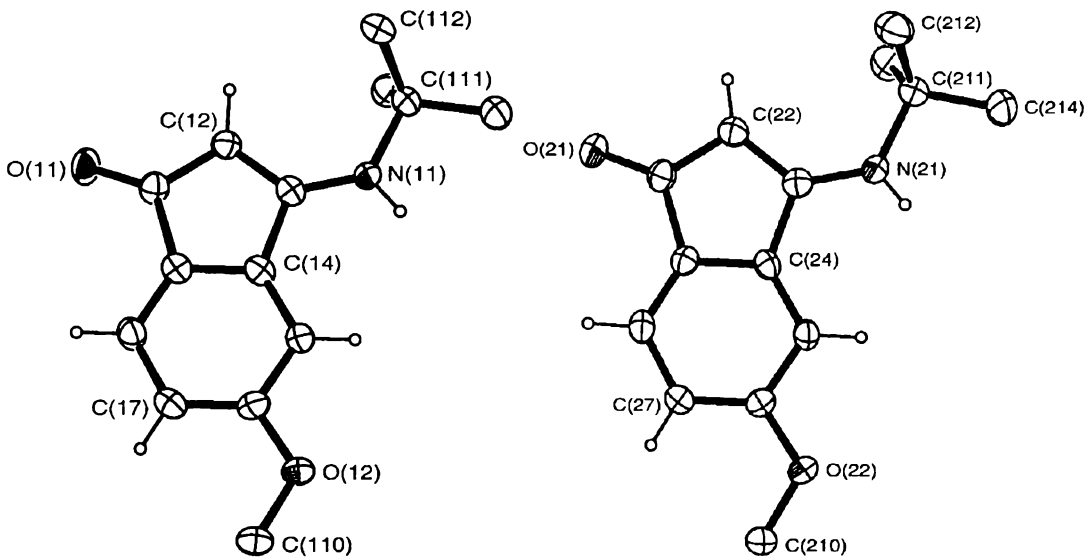


Figure 3-16 ORTEP perspective view of **76**, the second molecule has been rotated to allow for easier comparison.

When viewed down the b axis of the unit cell the molecules form staggered layers, with molecules aligned down the b axis (Figure 3-17). A stereo view is also given in Figure 3-17 to show the ruffled sheet-like layering.

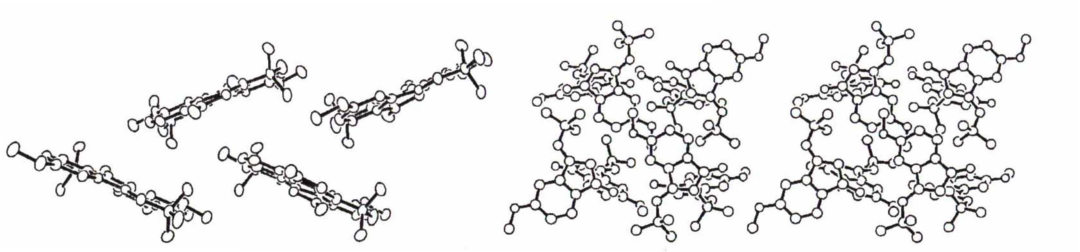


Figure 3-17 View down the b axis of **76**, with a stereo view to show the stacking.

Analysis of the bond lengths and angles of the two independent molecules show that there are no major differences in the two molecules outside what would be expected for two molecules of the same structure in different crystal structure environments. Selected bond lengths and angles are shown in Table 3-9.

Table 3-9 Selected bond lengths and angles of compound **76**.

Bond	Length	Bond	Length
O(11)-C(11)	1.240(3)	O(21)-C(21)	1.236(3)
C(11)-C(12)	1.436(3)	C(21)-C(22)	1.445(3)
C(12)-C(13)	1.388(3)	C(22)-C(23)	1.392(3)
N(11)-C(13)	1.338(3)	N(21)-C(23)	1.335(3)
N(11)-C(111)	1.489(3)	N(21)-C(211)	1.492(3)
C(14)-C(15)	1.376(3)	C(24)-C(25)	1.378(3)
C(15)-C(16)	1.415(3)	C(25)-C(26)	1.415(3)
C(16)-C(17)	1.386(3)	C(26)-C(27)	1.392(3)
C(17)-C(18)	1.406(3)	C(27)-C(28)	1.410(3)
C(18)-C(19)	1.379(3)	C(28)-C(29)	1.369(3)
C(14)-C(19)	1.401(3)	C(24)-C(29)	1.404(3)
O(12)-C(16)	1.374(3)	O(22)-C(26)	1.377(3)
O(12)-C(110)	1.429(3)	O(22)-C(210)	1.427(3)
C(13)-C(14)	1.506(3)	C(21)-C(29)	1.498(3)
C(11)-C(19)	1.503(3)	C(23)-C(24)	1.503(3)

Bond	Angle	Bond	Angle
O(11)-C(11)-C(12)	128.7(2)	O(21)-C(21)-C(22)	128.5(2)
C(11)-C(12)-C(13)	109.7(2)	C(21)-C(22)-C(23)	109.5(2)
N(11)-C(13)-C(12)	131.8(2)	N(21)-C(23)-C(22)	131.0(2)
N(11)-C(13)-C(14)	120.0(2)	N(21)-C(23)-C(24)	120.8(2)

C(13)-N(11)-C(111)	126.1(2)	C(23)-N(21)-C(211)	126.7(2)

The bond lengths around the aromatic rings show that there is incomplete delocalisation of the π-electrons, with alternating longer and shorter bond lengths as in the resonance form shown in Figure 3-18.

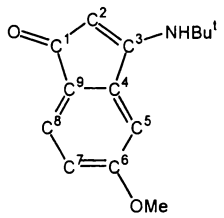


Figure 3-18 Resonance form of **76** showing long and short bonds around the aryl ring.

There is evidence for conjugation from the ketone through to the amino group, as the bond lengths through the intervening atoms deviate from double and single bonds. The bond length of C(2)-C(3) is longer than the classical double bond (1.39 Å compared to 1.34 Å). The C(3)-N(1) bond is shorter than expected for a single bond at 1.34 Å compared to 1.47 Å. The bond angle C(3)-N(1)-C(11) is 126° which deviates from 108° which would be expected for an amine functionality. The bulk of the butyl group may increase the angle, but is not able to rotate to a less sterically crowded position due to the conjugation of the nitrogen with the ring.

There is also evidence for donation from the lone pair electrons on the methoxy oxygen to the indene ring system, as indicated by the decreased C(6)-O(2) bond length (1.38 Å compared to 1.43 Å).

All of the above observations are consistent with the planarity of the molecule.

X-ray crystal structure of 5-*tert*-butylaminobenzo[*b*]thiophen-4,7-dione, 89.

The dark red crystals were shown to be orthorhombic, of space group Pbca, with eight molecules in the unit cell. Crystal and structure refinement data are given in a table in Section 3.5.5, while the CIF files can be found on the CD inside the back cover. An ORTEP perspective view showing the atom labelling scheme is given in Figure 3-19.

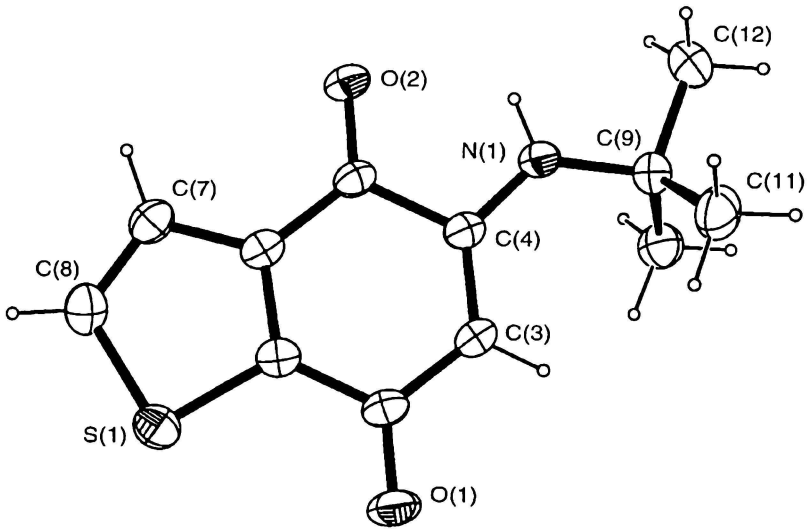


Figure 3-19 ORTEP perspective view of **89** showing the atom labelling scheme.

The crystal data was of a quality that allowed the proton positions to be determined in the penultimate difference map, and these were freely refined with isotropic temperature factors.

Though **89** is a planar molecule, this planarity does not result in π-stacking within the crystal structure. Instead the molecules are staggered within the unit cell. A stereo view of the packing within the unit cell is shown in Figure 3-20. There were no remarkable inter-atomic interactions.

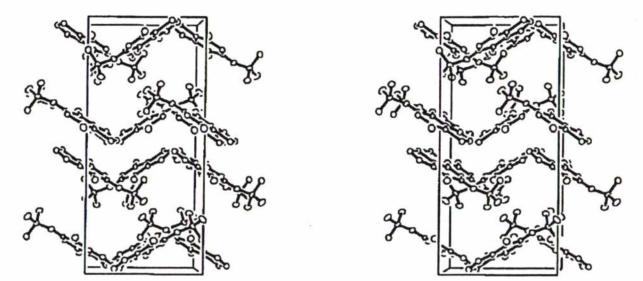
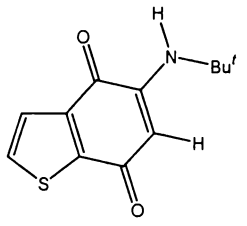


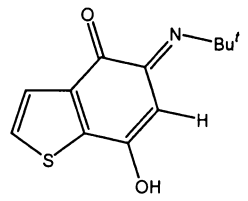
Figure 3-20 Stereo view of **89** showing the packing within the unit cell.

With the planarity of **89**, there is the possibility of having the alternate isomer **89a**, where the nitrogen is part of an imine group, the oxygen O(1) is an alcohol, and there is a C=C double bond between C(2) and C(3). However, due to the bond distances, and the fact that the protons positions were refined, the true structure was determined to be that of **89**. The bond lengths and angles of the thiophene and quinone functionalities are in agreement

with previously determined structures[116]. Table 3-10 shows selected bond lengths and angles for **89**.



89



89a

Table 3-10 Selected bond lengths and angles for compound **89**.

Bond	Length	Bond	Angle
S(1)-C(1)	1.7081(17)	C(8)-S(1)-C(1)	91.33(9)
S(1)-C(8)	1.715(2)	S(1)-C(1)-C(6)	111.61(13)
C(8)-C(7)	1.355(3)	C(1)-C(6)-C(7)	112.59(16)
C(7)-C(6)	1.418(2)	C(6)-C(7)-C(8)	111.75(17)
C(6)-C(1)	1.374(2)	C(7)-C(8)-S(1)	112.72(16)
C(1)-C(2)	1.473(2)	C(6)-C(1)-C(2)	123.82(16)
C(2)-C(3)	1.438(2)	C(1)-C(2)-C(3)	116.47(14)
C(3)-C(4)	1.368(2)	C(2)-C(3)-C(4)	122.45(16)
C(4)-C(5)	1.524(2)	C(3)-C(4)-C(5)	120.44(15)
C(5)-C(6)	1.455(2)	C(4)-C(5)-C(6)	117.08(13)
O(1)-C(2)	1.2419(19)	C(5)-C(6)-C(1)	119.65(15)
O(2)-C(5)	1.2210(19)	O(1)-C(2)-C(3)	123.12(17)
N(1)-C(4)	1.341(2)	O(2)-C(5)-C(4)	119.55(16)
N(1)-C(9)	1.475(2)	N(1)-C(4)-C(3)	128.26(16)
N(1)-H(1)	0.85(2)	C(4)-N(1)-C(9)	130.70(15)

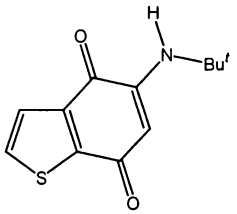
The thiophene part of the molecule is as expected, with the bond lengths and angles supporting the thiophene structure.

In the quinone part of the molecule, the C(4)-N(1) distance is shorter than the C(9)-N(1) distance due to conjugation of the lone-pair electrons on the nitrogen with the π-bond of C(3)-C(4). This π-electron overlap is what causes the trigonal planar coordination of the nitrogen. There is further conjugation from the double bond through to the carbonyl group

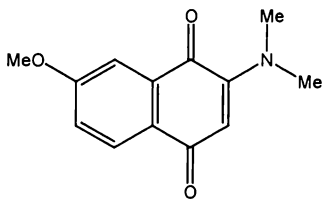
[116] A. Gitterio, R. Sebastiano, A. Maronati, F. Viola, A. Farina, *Tetrahedron*, **52** (1996) 13227

of O(1), seen in the shorter C(2)-C(3) distance of 1.438(2) Å compared to the other single bonds of the quinone. By contrast, there is no conjugation with the other carbonyl group, as the C(4)-C(5) bond is the longest C-C bond in the ring system.

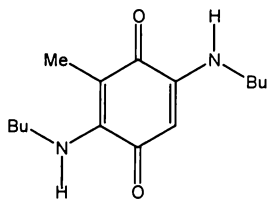
This difference in the conjugation around a quinone ring is as expected when there is an amine substituent. The structures of both **111**[117] and **112**[118] show a similar longer C-C bond to the adjacent carbonyl carbon, with a shorter C-C bond to the opposite carbonyl (1.509 and 1.523 Å compared to 1.423 and 1.404 Å respectively). Both structures also show the conjugation with the nitrogen lone-pair electrons, and are both planar molecules.



89



111



112

In **89** the secondary amine group is angled towards the carbonyl group, as seen by the C(3)-C(4)-N(1) angle of 128.26(16)°. This may be due to the bulk of the *t*-butyl group on the amine, as the H···H distance from the *t*-butyl group to the proton on C(3) is only 2.250 Å. However, the effect may also be due to intermolecular hydrogen bonding between the amine proton and the carbonyl group. This is supported by the short H-O distance of 2.152 Å, and by the orientation of the carbonyl group. The carbonyl of O(2) is angled towards the amine, as seen by the O(2)-C(5)-C(4) angle of 119.55(16)°, compared to 123.37(15)° for the other angle (O(2)-C(5)-C(6)).

The characteristics of **89** above are mirrored in **112**. In both cases in **112** the amine is angled towards the carbonyl group, and the carbonyl towards the amine, seen by angles of less than 117° in each case. The effect is strongest for the amine adjacent to the methyl substituent, due to the extra steric bulk.

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[117] A. C. Donguetto, C. A. Santos, D. S. Raslan, N. G. Fernandes, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, **55** (1999) 639

[118] M. Chakraborty, D. B. McConville, Y. Niu, A. Tessier, W. J. Youngs, *J. Org. Chem.*, **63** (1998) 7563

3.3.8. Spectroscopic and mass spectrometric characterisation.

ESMS spectra

The tri-substituted triphenylphosphine sulfide complex **74** was run as an acetonitrile solution at a cone voltage of +20 V. Under these conditions the dominant peak was due to the oxidation of the parent molecule to afford the $[M]^+$ ion. A minor peak was also observed due to the loss of a carbonyl and Bu^tNC ligand from the parent ion.

The parent ion is easily oxidised because of the increased electron density on the manganese centre from the three coordinating $CNBu^t$ ligands.

The mono-substituted complex **75** did not afford a spectrum under the same conditions. Instead **75** was run as a methanol solution at a cone voltage of -20 V. These conditions produced a $[M-H]^-$ peak due to the abstraction of a proton from the parent molecule, presumably from the acetyl group. A minor peak was also observed due to the additional loss of the coordinated Bu^tNC ligand.

The organic products from all the reactions in this chapter were run either as a methanol or acetonitrile solution at a cone voltage of +20 V. Under these conditions proton and/or sodium adducts were formed, affording series of peaks assigned as $[nM+H]^+$ (where n = 1, 2, 3, 4) or $[nM+Na]^+$ (where n = 1, 2, 3, 4) (Figure 3-21). In the case of **91** $[nM+Na]^+$ adducts were also formed where n = 5. The other case of note was **94** where peaks were assigned as the adducts $[nM+Bu^tNH_3]^+$ (where n = 1, 2, 3).

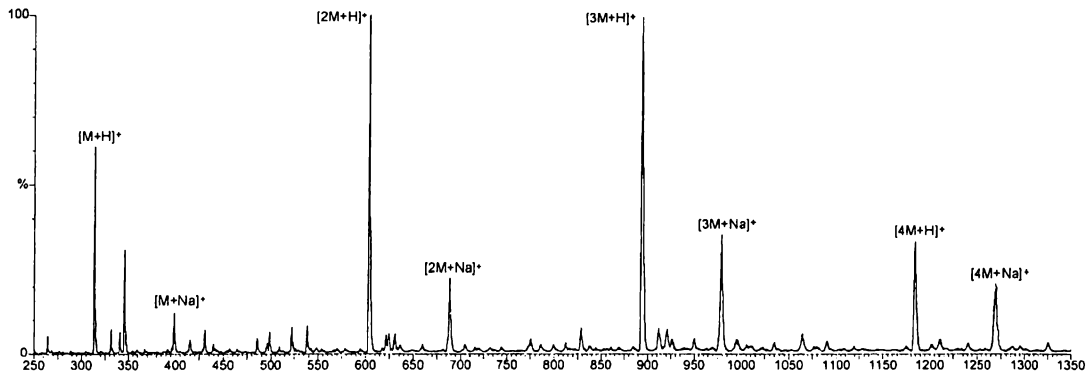


Figure 3-21 ESMS spectrum of **88** showing the series of $[nM+H]^+$ and $[nM+Na]^+$ adducts.

GCMS spectra

All of the organic compounds (except **92**, **93**, and **96**) were analysed by GCMS.

The indenone **76** showed a major peak for the molecular ion M^{+}, as well as for $M\text{-}15^{+}$ formed by the loss of a CH_3 unit (probably from the methoxy groups). The dominant peak was due to $M\text{-}56^{+}$, formed by the loss of the *tert*-butyl group as $(CH_3)_2C{=}CH_2$ from the molecular ion.

The indanone **100** and the other indenone and the naphthoquinone compounds **77** and **87** also showed similar peaks, though the molecular ion and $M\text{-}15^{+}$ peaks were stronger for the naphthoquinones than in the indenone compounds. The indenone and naphthoquinone compounds from **80**, those being **85** and **87** gave M^{+} as the dominant ion.

The imino-1,4-naphthoquinone imine **78** showed major peaks for M^{+} and $M\text{-}15^{+}$, with the dominant peak being due to $M\text{-}71^{+}$. This peak is formed by the lose of one *tert* butyl group (as above) as well as a methyl group from M^{+}. The other major peak of note was due to $M\text{-}113^{+}$, which is formed from the loss of one *tert*-butyl group as $(CH_3)_2C{=}CH_2$ and a second as $(CH_3)_3C^{-}$ from the parent molecule. The iminobenzothiophenone **88** and the iminopyridoindolone **91** also gave similar peaks, though the $M\text{-}113^{+}$ peak of **91** was not as strong as for the other two compounds.

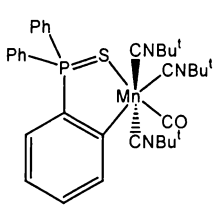
The hydroxy-substituted iminopyridoindolone **94** showed the M^{+} ion, but did not show the $M\text{-}15^{+}$ ion as with the spectra of the preceding compounds. The other major peaks were due to $M\text{-}56^{+}$, $M\text{-}71^{+}$ and $M\text{-}112^{+}$. This final peak was the dominant peak in the spectrum, and was due to the loss of both *tert* butyl groups as $(CH_3)_2C{=}CH_2$ from the M^{+} ion.

The organic products from isocyanides other than $Bu^{t}NC$ gave spectra with the major peaks being due to the M^{+} and $M\text{-}15^{+}$ ions. In all cases the dominant peak was due to M^{+} ion. For the indanone **98** there was also a major peak due to $M\text{-}31^{+}$.

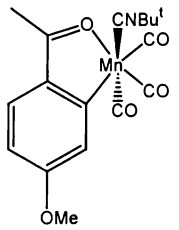
NMR Spectra

The tri- and mono-substituted orthomanganated complexes **74**, **75**, and **83** all showed spectra similar to the parent orthomanganated complexes, with variations limited to those

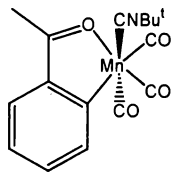
atoms in close proximity to the manganese.



74



75



83

The proton spectra of the tri-substituted complex **74** shows that the equatorial and axial Bu^{t}NC are in different environments, with the signals for the axial CNBu^t protons appearing at 1.46 ppm, while the equatorial protons are further upfield at 1.05 ppm.

The ^{31}P NMR spectrum shows a upfield shift of 3 ppm to 64.4 ppm. The high downfield value (compared to 44.1 ppm for Ph_3PS) shows that the complex is still orthomanganated.

It was not possible to obtain clear ^{13}C NMR spectra as **74** decomposes too quickly in a solvent matrix, forming paramagnetic Mn(II) species that cause broadening of the spectral peaks.

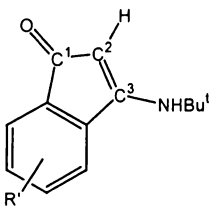
In the ^{1}H NMR spectra of **75** and **83** the substitution of a carbonyl ligand by the CNBu^t gives rise to an additional peak in the spectra at 1.24 and 1.22 ppm respectively, but has little effect on the other proton signals.

In the ^{13}C spectra of **75** and **83**, the substitution of a carbonyl ligand is apparent in the downfield shifts of the ketone carbon and carbonyl ligands, due to the increased electron density on the manganese centre. The ketone carbon was shifted by ~13 ppm, while the carbonyls are shifted 3-5 ppm.

The organic products can be grouped according to the nature of the additional ring formed in the reaction. The following tables show the key signals in the ^{1}H and ^{13}C NMR spectra for the different groups.

Table 3-11 Selected ^{1}H and ^{13}C NMR signals for the organic products formed with an additional five membered ring.

	R'	R''	C^2-H	Bu^t	N-H	C^1	C^2	C^3
82	H		5.08	1.50	5.37	193.9	94.5	161.7
85	3-MeO		4.92	1.47	5.34	193.3	92.1	164.5
76	4-MeO		5.05	1.49	5.13	194.0	95.3	160.0
100	4-MeO	NBu^t	4.74 4.81	1.46	-	179.9	83.3	155.5
99	H	NC_6H_4-4-OMe	5.02 5.05	-	-	155.6	86.9	153.1



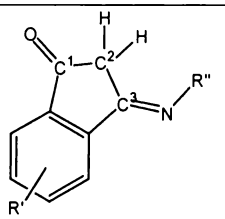
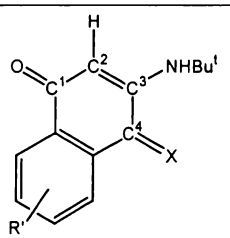
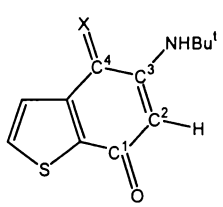
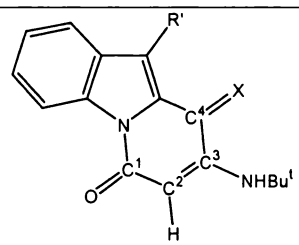


Table 3-12 Selected ^{1}H and ^{13}C NMR signals for the organic products formed with an additional six membered ring.

	R'	X	C^2-H	N-H	Bu^t	X-H	C^1	C^2	C^4
87	3-MeO	O	5.94	6.16	1.45	-	180.9	101.2	182.2
77	4-MeO	O	5.92	5.88	1.47	-	183.1	102.9	183.0
78	4-MeO	NBu^t	5.74	6.74	1.43	1.54	182.5	98.4	154.4
89		O	5.76	5.90	1.45	-	177.7	100.3	178.8
38		NBu^t	5.71	7.24	1.42	1.55	178.6	97.4	152.7
91	H	NBu^t	5.51	7.05	1.44	1.60	163.4	91.4	141.2
94	OH	NBu^t	5.74	5.65	1.46	1.32	183.5	97.1	152.2







In the ^{1}H NMR spectrum, the disappearance of the acetyl signal, and the appearance of the signal due to C^2-H shows that the additional ring has been formed. The C^2-H signal for the five membered ring is generally 0.8 ppm further upfield of the same signal for the six membered ring. The appearance of the broad N-H peak is a further indicator, though this may be lost in the baseline and therefore should not be relied on. Also, in the case of the indole and thiophene compounds, the N-H peak can fall over a large range depending on whether the compound is hydrolysed and what other substituents are on the parent ring

system.

The difference between the five membered ring and the hydrolysed six membered ring may alternatively be determined by observation of the ^{13}C NMR spectrum. For the five membered ring the signals due to C^1 and C^3 are ~190 and ~160 ppm respectively, compared to both being ~180 ppm in the hydrolysed six-membered ring products.

Table 3-13 Selected ^1H and ^{13}C NMR signals for the organic furan products.

	R'	C*-*H*	*CH*$_3$	C*	C=N
96	Et	5.56	1.59	80.0	159.5
98	C_6H_4-4-OMe	5.68	1.65	81.0	158.1

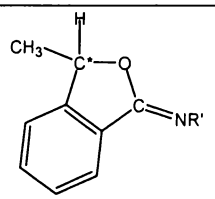
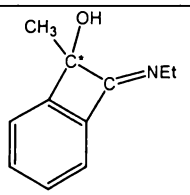


Table 3-14 Selected ^1H and ^{13}C NMR signals for the bicyclooctatrienol product.

	OH	*CH*$_3$	C*	C=N
47	2.03	1.35	90.5	158.3



The furan and bicyclooctatrienol complexes above can be distinguished from the five and six membered ring compounds by the presence of the C*-CH_3 methyl peak at ~1.5 ppm. The two different products can be further distinguished as the furan C*-CH_3 signal is a doublet (with the C*-H giving a quartet), while in the bicyclooctatrienol the C*-H signal is absent, replaced by a broad OH signal at 2 ppm.

3.4. Conclusion

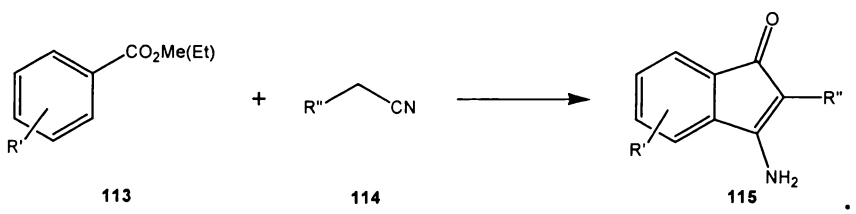
The products formed by the reactions of Bu^{t}NC and orthomanganated acetyl-aryl compounds are unique compounds, with only one reference found in the literature with

regards to the preparation of one of the compounds prepared in this study[119].

The preparation found was for 3-aminoinden-1-ones related to **76**. The method involved the reaction of 1,3-indanones with $COCl_2$ in the presence of $Me_2NCONMe_2$ to afford the 3-chloroinden-1-one. This product was converted to the 3-aminoinden-1-one by reaction with the desired primary amine. The preparation of **76** by this manner afforded a yield of 48%, considerably higher than from the present study.

Though the other compounds prepared in this study appear unique, related aminoindenone and hydroxyquinone compounds have previously been prepared[120].

Kayaleh *et al* developed a preparation of 2-substituted-3-aminoinden-1-ones (**115**) by the reaction of acetonitriles (**114**) with aryl esters (**113**), with yields generally around 50% when the acetonitrile had an aryl substituent (e.g. R = aryl). These products all had a substituent at the 2-position, generally an aryl group. The related product with a proton at the 2-position could not be prepared. The other difference to note is that the products have primary amines compared to the secondary amines of the products prepared in the present study.

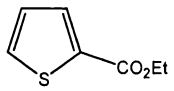


113 **114** **115**

Kayaleh *et al* also tried to extend the preparation to the use of five-membered aromatic systems such as ethyl thiophen-2-carboxylate (**116**) with no success. The results from the present study suggest that there is too much strain involved in the forming of the two fused five-membered rings. From the results of the present study, the forming of a product having a fused five- and six-membered ring system appears to be favoured over the forming of a product consisting of two fused five-membered rings.

[119] H. Moehrle, H. J. Novak, *Chem. -Ztg.*, **106** (1982) 19

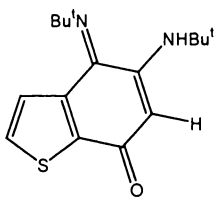
[120] N. E. Kayaleh, R. C. Gupta, F. Johnson, *J. Org. Chem.*, **65** (2000) 4515



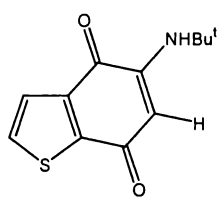
116

A selective synthesis of hydroxynaphthoquinones and hydroxythienoquinones was developed from the reaction of aromatic β-keto esters with oxalyl chloride in the presence of aluminium trichloride[121]. The resulting quinones are analogous to those produced in the present study, with the exception of having a hydroxyl group in the 3-position of the quinone, compared to a secondary amine. The final hydroxyquinones were generally produced in high yields (>70%).

The biological activity of the products from the reaction of orthomanganated 2-acetylthiophene and Bu^{t}NC (**88** and **89**) require further investigation. The use of other thiophene derivatives with substituents in the 4- and 5-positions may lead to a more selective cytotoxicity, allowing the use of the compounds for antifungal applications, and possibly allowing for anti-tumour applications.



88



89

3.5. Experimental

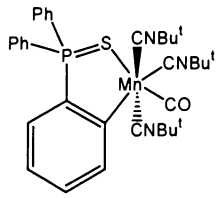
3.5.1. Reactions of Bu^{t}NC with orthomanganated complexes.

*Reaction of [η^2-(diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (**49**) with Bu^{t}NC.*

49 (212 mg, 0.46 mmol) and Bu^{t}NC (500 μl, 4.4 mmol) were heated under reflux in heptane (20 ml) for 2 hours. Large orange rosettes of **74** (115 mg, 40%) were obtained from the reaction mixture after cooling to -20°C overnight. A quantity of insoluble material was also observed on the inside of the reaction vessel, which was shown by ESMS analysis to largely contain $[Mn(CNBu^t)_5(CO)]^+$ and $[Mn(CNBu^t)_6]^+$ species. X-ray

[121] G. Sartori, F. Bigi, G. Canali, R. Maggi, G. Casnati, X. Tao, *J. Org. Chem.*, **58** (1993) 840

crystallographic quality crystals of **74** were obtained by vapour diffusion (ether/pentane).



74

m.p. = 108-110°C M_r = 625.7 $C_{34}H_{41}MnN_3OPS$

IR : (petroleum spirits) ν(C≡O) 1885(m) cm^{-1}; ν(C≡N) 2040(w, br) cm^{-1}

ESMS : (MeCN, cone +20 V) *m/z* 709 (21%, $[M+CNBu^t+H]^+$), 625 (100%, $[M]^+$), 514 (15%, $[M-CNBu^t-CO]^+$)

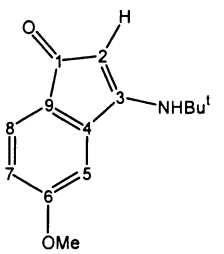
^{1}H NMR : ($CDCl_3$) δ 1.05 (18H, s, $Bu^t_{(a)}$), 1.46 (9H, s, $Bu^t_{(e)}$), 6.75-8.30 (14H, m, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 31.5 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 51.6 ($C(CH_3)_3$), 56.1 ($C(CH_3)_3$), 119.6-183.3 (Ar/Ar-H)

^{31}P NMR : ($CDCl_3$) δ 64.4

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**43**) with Bu^tNC.*

43 (118 mg, 0.37 mmol) and Bu^tNC (500 µl, 4.4 mmol) were reacted in heptane (20 ml) at reflux for 2 hours. Chromatography (PLC, ether) gave two fractions, the second of which was collected to afford **76** (11 mg, 13%) which was recrystallised from chloroform as yellow rod-like crystals. The first fraction required further chromatography (PLC, dichloromethane) to afford three main fractions, **75** (35 mg, 26%) (which was recrystallised as dark yellow crystals from warm petroleum spirits), **77** (14 mg, 15%) as a dark orange oil, and **78** (5 mg, 4%) as a dark orange solid.



76

m.p. = 166°C M_r = 231.3 $C_{14}H_{17}NO_2$

Elemental analysis : Calculated - C 72.70 H 7.41 N 6.06

Experimental - C 70.67 H 7.15 N 5.94

High Resolution Mass Spectroscopy : Calculated : 231.1259

Experimental :231.1266

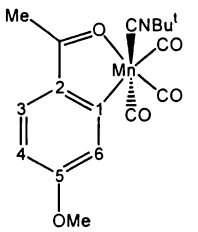
IR : (CH_2Cl_2) ν(C=O) 1705 cm^{-1-}

ESMS : (MeCN, cone +20 V), *m/z* 232 (53%, $[M+H]^+$), 463 (100%, $[2M+H]^+$), 694 (5%, $[3M+H]^+$), 717 (4%, $[3M+Na]^+$)

GCMS : (70 eV) *m/z* 231 (M^+, 33%), 216 (24), 175 (100), 57 (15), 41 (17)

^{1}H NMR : ($CDCl_3$) δ 1.49 (9H, s, Bu^t), 3.87 (3H, s, OMe), 5.05 (1H, s, H2), 5.13 (1H, s, NH), 6.66 (1H, d, $^4J_{HH}$ = 1.9 Hz, H5), 6.76 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.9 Hz, H7), 7.41 (1H, d, $^3J_{HH}$ = 7.9 Hz, H8)

^{13}C NMR : ($CDCl_3$) δ 29.2 ($C(CH_3)_3$), 53.3 ($C(CH_3)_3$), 56.1 (OMe), 95.3 (C2), 105.6 (C5), 111.7 (C7), 122.1 (C8), 127.6 (C9), 142.5 (C4), 160.0 (C3), 162.6 (C6), 194.0 (C1)



75

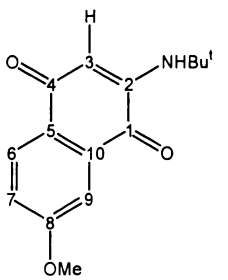
m.p. = 54°C M_r = 371.3 $C_{17}H_{18}MnNO_5$

IR : (CH_2Cl_2) ν(C≡O) 2016(s), 1955(s), 1915(m) cm^{-1}, ν(C≡N) 2153 cm^{-1}

ESMS : (MeOH, cone -20 V) *m/z* 370 (100%, $[M-H]^-$), 287 (76%, $[M-CNBu^t-H]^-$)

^{1}H NMR : ($CDCl_3$) δ 1.24 (9H, s, $CNBu^t$), 2.53 (3H, s, $COCH_3$), 3.97 (3H, s, OCH_3), 6.60 (1H, dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.3 Hz, H4), 7.70 (1H, d, $^4J_{HH}$ = 2.2 Hz, H6), 7.76 (1H, d, $^3J_{HH}$ = 8.6 Hz, H3).

^{13}C NMR : ($CDCl_3$) δ 24.3 ($COCH_3$), 30.7 ($CNC(CH_3)_3$), 55.7 (OCH_3), 57.4 ($CNC(CH_3)_3$), 110.8 (C4), 123.2 (C6), 132.8 (C3), 138.9 (C2), 162.7 (C5), 163.1 ($CNC(CH_3)_3$), 208.2 (C1), 211.3 ($COCH_3$), 216.5 (MnCO), 216.6 (MnCO), 226.3 (MnCO)



77

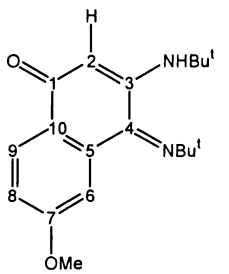
m.p. = 94°C M_r = 259.3 $C_{15}H_{17}NO_3$

IR : (CH_2Cl_2) ν(C=O) 1676 cm^{-1}

GCMS : (70 eV) *m/z* 259 (M^+, 53%), 244 (82), 203 (100), 176 (80), 160 (25), 135 (35), 57 (41)

^1H NMR : ($CDCl_3$) δ 1.47 (9H, s, Bu^t), 3.94 (3H, s, OMe), 5.88 (1H, s, NH), 5.92 (1H, s, H3), 7.21 (1H, dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.6 Hz, H7), 7.51 (1H, d, $^4J_{HH}$ = 2.7 Hz, H9), 8.05 (1H, d, $^3J_{HH}$ = 8.6 Hz, H6)

^{13}C NMR : ($CDCl_3$) δ 28.7 ($C(CH_3)_3$), 51.9 ($C(CH_3)_3$), 56.1 (OCH_3), 102.9 (C3), 110.6 (C9), 120.9 (C7), 127.2 (C5), 128.6 (C6), 132.5 (C10), 146.1 (C2), 162.9 (C8), 183.0 (C1), 183.1 (C4)



78

m.p. = 96°C M_r = 314.4 $C_{19}H_{26}N_2O_2$

IR : (CH_2Cl_2) ν(C=O) 1677 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 965 (7%, $[3M+Na]^+$), 629 (94%, $[2M+H]^+$), 315 (100%, $[M+H]^+$)

GCMS : (70 eV) *m/z* 314 (M^+, 15%), 299 (4), 257 (10), 243 (100), 228 (22), 215 (25), 201 (50), 175 (35), 160 (35), 57 (96)

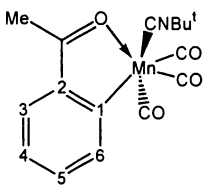
^1H NMR : ($CDCl_3$) δ 1.43 (9H, s, $NHBu^t$), 1.54 (9H, s, NBu^t), 3.90 (OCH_3), 5.74 (1H, s, H2), 6.74 (1H, s, NH), 7.04 (1H, dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.3 Hz, H8), 7.24 (1H, d, $^4J_{HH}$ = 2.3 Hz, H6), 8.10 (1H, d, $^3J_{HH}$ = 8.6 Hz, H9)

^{13}C NMR : ($CDCl_3$) δ 28.7 ($NHC(CH_3)_3$), 31.2 ($NC(CH_3)_3$), 51.2 ($NHC(CH_3)_3$), 55.6 (OCH_3), 57.0 ($NC(CH_3)_3$), 98.4 (C2), 114.8 (C8), 116.4 (C6), 124.9 (C3), 128.4 (C9), 131.4 (C10), 149.8 (C5), 154.4 (C4), 160.1 (C7), 182.5 (C1)

*Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (**79**) with Bu^tNC.*

79 (106 mg, 0.37 mmol) and Bu^tNC (300 µl, 2.7 mmol) were reacted in heptane (20 ml) under reflux for 2 hours. Chromatography (PLC, ether) gave two fractions, the first being **83** (48 mg, 45%), isolated as a dark yellow solid, the second **82** (15 mg, 22%), was

recrystallised from dichloromethane/petroleum spirits as yellow crystals.

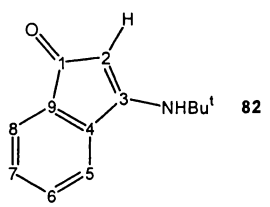


83

M_r = 341.2 $C_{16}H_{16}MnNO_4$

^{1}H NMR : ($CDCl_3$) δ 1.22 (9H, s, Bu^t), 2.61 (3H, s, $COCH_3$), 7.09 (1H, t, $^3J_{HH}$ = 7.4 Hz, H4), 7.35 (1H, t, $^3J_{HH}$ = 7.2 Hz, H5), 7.82 (1H, d, $^3J_{HH}$ = 7.6 Hz, H3), 8.21 (1H, d, $^3J_{HH}$ = 7.3 Hz, H6)

^{13}C NMR : ($CDCl_3$) δ 24.7 ($COCH_3$), 30.7 ($CNC(CH_3)_3$), 57.4 ($CNC(CH_3)_3$), 122.7 (C4), 131.0 (C3), 132.6 (C5), 141.1 (C6), 145.3 (C2), 162.4 ($CNC(CH_3)_3$), 204.1 (C1), 214.6 ($COCH_3$), 216.2 (MnCO), 216.5 (MnCO), 226.3 (MnCO)



82

m.p. = 141°C M_r = 201.3 $C_{13}H_{15}NO$

Elemental analysis : Calculated - C 77.58 H 7.51 N 6.96

Experimental - C 76.87 H 7.36 N 7.02

IR : (CH_2Cl_2) ν(C=O) 1673 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 202 (25%, $[M+H]^+$), 224 (28%, $[M+Na]^+$), 403 (12%, $[2M+H]^+$), 425 (73%, $[2M+Na]^+$), 626 (100%, $[3M+Na]^+$)

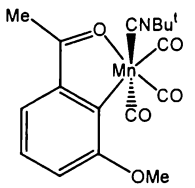
GCMS : (70 eV) *m/z* 201 (M^+, 40%), 186 (20), 145 (100), 117 (27), 101 (30), 89 (39), 75 (24), 57 (40)

^{1}H NMR : ($CDCl_3$) δ 1.50 (9H, s, NBu^t), 5.08 (1H, s, H2), 5.37 (1H, s, NH), 7.12 (1H, dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.9 Hz, H5), 7.34 (1H, td, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 1.7 Hz, H6), 7.37 (1H, td, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.6 Hz, H7), 7.48 (1H, dd, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 2.3 Hz, H8)

^{13}C NMR : ($CDCl_3$) δ 29.3 ($NHC(CH_3)_3$), 53.5 ($NHC(CH_3)_3$), 94.5 (C2), 116.0 (C5), 120.8 (C8), 130.6 (C6), 130.6 (C7), 135.2 (C9), 139.8 (C4), 161.7 (C3), 193.9 (C1)

*Reaction of η^2-(2-acetyl-6-methoxyphenyl)tetracarbonylmanganese (**80**) with Bu^tNC.*

80 (62 mg, 0.20 mmol) and Bu^tNC (250 µl, 2.2 mmol) were reacted in heptane (10 ml) under reflux for 2 hours. Chromatography (PLC, 1:1 petroleum spirits/ethyl acetate) gave four fractions. The first contained traces of unreacted starting material while the second fraction contained the mono-substituted complex **84**. The third was collected to afford **85** (7 mg, 16%) which was recrystallised from chloroform as orange crystals. The fourth fraction was collected to afford a small yield of **86** (2 mg, 4%) as dark yellow crystals.



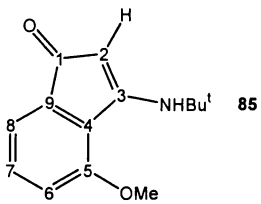
84

$M_r = 371.3$ $C_{17}H_{18}MnNO_5$

IR : (CH_2Cl_2) ν(C≡O) 2013(s), 1938(s), 1913(m) cm^{-1}, ν(C≡N) 2164 cm^{-1}

ESMS : (MeOH/NaOMe, cone -20 V) *m/z* 403 (29%, $[M+OMe]^-$, 370 (100%, $[M-H]^-$), 287 (71%, $[M-CNBu^t-H]^-$)

^{1}H NMR : ($CDCl_3$) δ 1.20 (9H, s, $CNBu^t$), 2.59 (3H, s, $COCH_3$), 3.88 (3H, s, OCH_3), 6.86 (1H, d, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.10 (1H, t, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.49 (1H, d, $^3J_{HH}$ = 7.7 Hz, Ar-H).



85

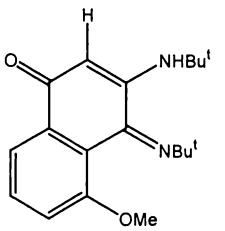
$M_r = 231.2$ $C_{14}H_{17}NO_2$

IR : (CH_2Cl_2) ν(C=O) 1668 cm^{-1}.

GCMS : (70 eV) *m/z* 231 (M^+, 100%), 216 (21), 189 (35), 175 (75), 146 (38)

^{1}H NMR : ($CDCl_3$) δ 1.47 (9H, s, Bu^t), 3.96 (3H, s, OMe), 4.92 (1H, s, H2), 5.34 (1H, s, NH), 6.94 (1H, d, $^3J_{HH}$ = 8.4 Hz, H6), 7.16 (1H, d, $^3J_{HH}$ = 7.0 Hz, H8), 7.33 (1H, d, $^3J_{HH}$ = 7.7 Hz, H7)

^{13}C NMR : ($CDCl_3$) δ 29.2 ($CNC(\mathit{C}H_3)_3$), 53.1 ($CN\mathit{C}(CH_3)_3$), 56.2 (OCH_3), 92.1 (C2), 114.4 (C8), 115.2 (C6), 124.1 (C4), 132.4 (C7), 137.9 (C9), 153.4 (C5), 164.5 (C3), 193.3 (C1)



86

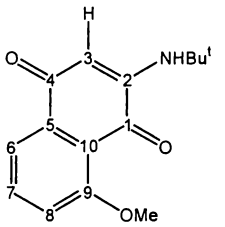
$M_r = 259.3$ $C_{15}H_{17}NO_3$

GCMS : (70 eV) *m/z* 314 (M^+, 55%), 259 (22), 243 (75), 228 (19), 201 (100), , 57 (10)

^{1}H NMR : ($CDCl_3$) δ 1.26 (9H, s, NHBu^t), 1.40 (9H, s, NBu^t), 3.87 (OCH_3), 5.63 (1H, s, H2), 6.30 (1H, s, NH), 6.91 (2H, m, Ar-H), 7.44 (1H, m, Ar-H)

*Six hour reaction of η^2-(2-acetyl-6-methoxyphenyl)Mn(CO)$_4$ (**80**) and Bu^{t}NC.*

80 (51 mg, 0.17 mmol) and Bu^{t}NC (250 µl, 2.2 mmol) were reacted in heptane (10 ml) under reflux for 6 hours. Chromatography (PLC, 1:1 petroleum spirits/ethyl acetate) gave four fractions. The first and second were mixtures of the starting material and the mono-substituted complex. The third was collected and recrystallised from ethyl acetate to afford **87** as orange plate-like crystals (10 mg, 25%). The fourth fraction was collected to afford **85** (8 mg, 22%).



87

m.p. = 119°C $M_r = 259.3$ $C_{15}H_{17}NO_3$

High Resolution Mass Spectroscopy : Calculated : 259.1208

Experimental : 259.1210

IR : (CH_2Cl_2) ν(C=O) 1670 cm^{-1}

GCMS : (70 eV) *m/z* 259 (M^+, 100%), 244 (92), 226 (17), 203 (31), 186 (16), 57 (8)

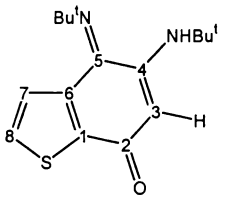
^{1}H NMR : ($CDCl_3$) δ 1.45 (9H, s, Bu^t), 4.02 (3H, s, OMe), 5.94 (1H, s, H3), 6.16 (1H, s, NH), 7.19 (1H, d, $^3J_{HH}$ = 8.5 Hz, , H8), 7.68 (1H, t, $^3J_{HH}$ = 8.0 Hz, H7), 7.81 (1H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.9 Hz, H6)

^{13}C NMR : ($CDCl_3$) δ 28.4 (C(CH_3)$_3$), 51.7 (C(CH_3)$_3$), 56.4 (OMe), 101.2 (C3), 115.8 (C8), 119.0 (C6), 128.9 (C10), 136.0 (C7), 136.3 (C5), 147.0 (C2), 160.1 (C9),

180.9 (C4), 182.2 (C1)

*Reaction of η^2-(2-acetylthiophenyl)Mn(CO)$_4$ (**45**) and Bu^{t}NC in heptane.*

45 (107 mg, 0.37 mmol) and Bu^{t}NC (300 µl, 0.27 mmol) were reacted in heptane (20 ml) under reflux for 2 hours. Chromatography (PLC, 1:4 petroleum spirits/ether) gave three fractions, the first of which afforded multiple inseparable products. The second was collected to afford **88** (27 mg, 26%) as an orange oil. The third fraction afforded **89** (4 mg, 5%) as a red solid.



88

M_r = 290.4 $C_{16}H_{22}N_2OS$

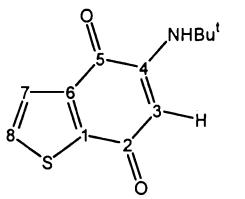
IR : (CH_2Cl_2) ν(C=O) 1666(m) cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 313 (60%, $[M+Na]^+$), 603 (100%, $[2M+Na]^+$), 893 (100%, $[3M+Na]^+$), 1183 (30%, $[4M+Na]^+$)

GCMS : (70 eV) *m/z* 290 (M^+, 38%), 275 (7), 233 (18), 219 (100), 204 (17), 191 (24), 177 (33), 136 (17), 57 (31), 41 (32)

^{1}H NMR : ($CDCl_3$) δ 1.42 (9H, s, NHBu^t), 1.55 (9H, s, NBu^t), 5.71 (1H, s, H3), 7.24 (1H, s, NH), 7.41 (1H, d, $^3J_{HH}$ = 5.2 Hz, H8), 7.59 (1H, d, $^3J_{HH}$ = 5.2 Hz, H7)

^{13}C NMR : ($CDCl_3$) δ 28.8 (NHC(CH_3)$_3$), 30.6 (NC(CH_3)$_3$), 51.6 (NHC(CH_3)$_3$), 56.1 (NC(CH_3)$_3$), 97.4 (C3), 127.6 (C8), 130.8 (C7), 131.7 (C1), 144.8 (C4), 147.6 (C6), 152.7 (C5), 178.6 (C2)



89

m.p. = 58°C M_r = 235.3 $C_{12}H_{13}NO_2S$

Elemental analysis : Calculated - C 61.25 H 5.57 N 5.95

Experimental - C 58.81 H 5.48 N 5.69

IR : (CH_2Cl_2) ν(C=O) 1677(m) cm^{-1}

ESMS : (MeCN, cone +20 V) *m/z* 236 (100%, $[M+H]^+$), 471 (44%, $[2M+H]^+$), 493

(41%, $[2M+Na]^+$), 728 (24%, $[3M+Na]^+$)

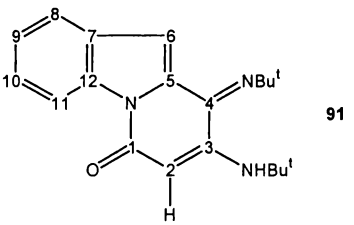
GCMS : (70 eV) *m/z* 235 (M^+, 80%), 220 (69), 179 (100), 152 (51), 111 (22), 57 (52), 41 (55)

^{1}H NMR : ($CDCl_3$) δ 1.45 (9H, s, Bu^t), 5.76 (1H, s, H3), 5.90 (1H, s, NH), 7.46 (1H, d, $^3J_{HH}$ = 5.0 Hz, H8), 7.49 (1H, d, $^3J_{HH}$ = 5.0 Hz, H7)

^{13}C NMR : ($CDCl_3$) δ 28.3 ($C(CH_3)_3$), 52.0 ($C(CH_3)_3$), 100.3 (C3), 125.8 (C7), 130.0 (C8), 137.3 (C6), 145.5 (C4), 148.3 (C1), 177.7 (C2), 178.7 (C5)

*Reaction of η^2-(1-acetylindolyl)tetracarbonylmanganese (**81**) with Bu^tNC.*

81 (89 mg, 0.27 mmol) and Bu^tNC (500 µl, 4.4 mmol) were reacted in toluene (15 ml) under reflux for 2 hours. Chromatography (PLC, 1:1 ethyl acetate/petroleum spirits) gave four main fractions from which were collected; **91** (17 mg, 19%) which was recrystallised by vapour diffusion (dichloromethane/petroleum spirits) as orange plates, **92** (12 mg, 15%) as a dark yellow oil, **93** (30 mg, 42%) which was recrystallised from dichloromethane /petroleum spirits as dark red micro-crystals, and **94** (16 mg, 17%) which was recrystallised from ethyl acetate/petroleum spirits as fine yellow needles.



91

m.p. = >350°C M_r = 323.4 $C_{20}H_{25}N_3O$

High Resolution Mass Spectroscopy : Calculated : 323.1998

Experimental : 323.1991

IR : (CH_2Cl_2) ν(C=O) 1660 cm^{-1}

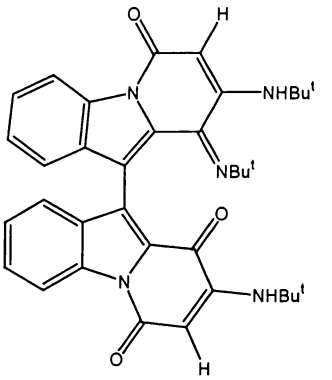
ESMS : (MeOH, cone +20 V) *m/z* 324 (100%, $[M+H]^+$), 647 (36%, $[2M+H]^+$), 669 (34%, $[2M+Na]^+$), 992 (44%, $[3M+Na]^+$), 1315 (62%, $[4M+Na]^+$), 1638 (35%, $[5M+Na]^+$)

GCMS : (70 eV) *m/z* 323 (M^+, 36%), 308 (18), 266 (20), 252 (100), 237 (23), 143 (17), 57(28), 41 (29)

^{1}H NMR : ($CDCl_3$) δ 1.44 (9H, s, $NHC(CH_3)_3$), 1.60 (9H, s, $NC(CH_3)_3$), 5.51 (1H, s, H2), 7.05 (1H s, NH), 7.24 (1H, td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, H10), 7.25 (1H, s, H6), 7.44 (1H, td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, H9), 7.63 (1H, d, $^3J_{HH}$ = 7.9

Hz, H11), 8.63 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 0.7 Hz, H8)

^{13}C NMR : ($CDCl_3$) δ 28.9 ($NHC(\mathit{C}H_3)_3$), 29.0 ($NC(\mathit{C}H_3)_3$), 51.2 ($NH\mathit{C}(CH_3)_3$), 55.8 ($N\mathit{C}(CH_3)_3$), 91.4 (C2), 117.4 (C10), 118.0 (C8), 122.1 (C11), 123.6 (C6), 127.0 (C3), 128.0 (C12), 128.2 (C9), 135.9 (C7), 141.2 (C4), 150.1 (C5), 163.4 (C1)



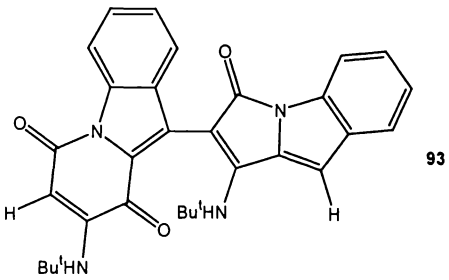
92

	M_r = 589.7		$C_{36}H_{39}N_5O_3$	
Elemental analysis :	Calculated -	C 73.32	H 6.67	N 11.88
	Experimental -	C 71.34	H 7.12	N 10.37

ESMS : (MeCN, cone +40 V) *m/z* 590 (100%, $[M+H]^+$), 1179 (18%, $[2M+H]^+$)

^{1}H NMR : ($CDCl_3$) δ 0.89 (9H, s, $NC(CH_3)_3$), 1.45 (9H, s, $NHC(C\mathit{H}_3)_3$), 1.49 (9H, s, $NHC(C\mathit{H}_3)_3$), 5.49 (1H, s, CH=C), 5.74 (1H, s, CH=C), 5.88 (1H, s, NH), 6.18 (1H, s, NH), 7.21 (1H, t, $^3J_{HH}$ = 7.4 Hz, Ar-H), 7.25 (1H, d, $^3J_{HH}$ = 7.5 Hz, Ar-H), 7.26 (1H, t, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.45 (1H, t, $^3J_{HH}$ = 6.9 Hz, Ar-H), 7.46 (1H, d, $^3J_{HH}$ = 7.0 Hz, Ar-H), 7.59 (1H, t, $^3J_{HH}$ = 7.8 Hz, Ar-H), 8.59 (1H, d, $^3J_{HH}$ = 8.4 Hz, Ar-H), 8.62 (1H, d, $^3J_{HH}$ = 8.4 Hz, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 28.4 ($NHC(\mathit{C}H_3)_3$), 28.9 ($NHC(\mathit{C}H_3)_3$), 29.1 ($NC(\mathit{C}H_3)_3$), 51.6 ($NH\mathit{C}(CH_3)_3$), 51.7 ($NH\mathit{C}(CH_3)_3$), 58.8 ($N\mathit{C}(CH_3)_3$), 90.3 (*C*H=C), 95.7 (*C*H=C), 115.4 (Ar), 116.8 (Ar-H), 117.3 (Ar-H), 121.0 (Ar-H), 123.2 (Ar-H), 124.2 (Ar-H), 127.0 (Ar-H), 127.4, 127.8, 131.1 (Ar-H), 137.0, 145.6, 146.4, 155.6, 161.6, 164.2 (C=O), 172.6 (C=O)



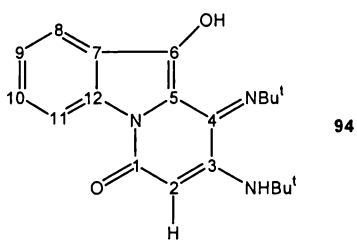
93

M_r = 506.6 $C_{31}H_{30}N_4O_3$

ESMS : (MeOH, cone +20 V) *m/z* 507 (98%, $[M+H]^+$), 580 (100%, $[M+NBu^tH_3]^+$), 1013 (21%, $[2M+H]^+$), 1035 (32%, $[2M+Na]^+$), 1086 (59%, $[2M+NBu^tH_3]^+$), 1541 (24%, $[3M+Na]^+$), 1592 (19%, $[3M+NBu^tH_3]^+$)

^{1}H NMR : ($CDCl_3$) δ 1.46 (9H, s, NHC(CH_3)$_3$), 1.61 (9H, s, NHC(CH_3)$_3$), 5.01 (1H, s, NH), 5.74 (1H, s, CH=C), 5.98 (1H, s, NH), 6.94 (1H, s, CH=C), 7.16 (1H, t, $^3J_{HH}$ = 7.6 Hz, Ar-H), 7.30 (1H, t, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.38 (1H, t, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.57 (1H, d, $^3J_{HH}$ = 7.8 Hz, Ar-H), 7.58 (1H, t, $^3J_{HH}$ = 7.4 Hz, Ar-H), 7.82 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar-H), 7.94 (1H, d, $^3J_{HH}$ = 8.1 Hz, Ar-H), 8.62 (1H, d, $^3J_{HH}$ = 8.4 Hz, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 28.7 (NHC(CH_3)$_3$), 30.0 (NHC(CH_3)$_3$), 51.9 (NH*C*(CH_3)$_3$), 53.9 (NH*C*(CH_3)$_3$), 96.2 (*C*H=C), 111.9 (Ar-H), 113.1 (Ar-H), 117.4 (Ar-H), 122.8 (Ar-H), 122.9 (Ar-H), 124.2 (Ar-H), 124.6 (Ar-H), 128.1 (Ar-H), 131.4 (Ar-H), 132.5, 133.0, 134.4, 138.1, 146.9, 151.7, 162.0 (C=O), 163.7 (C=O), 171.8 (C=O)



94

m.p. = >350°C M_r = 339.4 $C_{20}H_{25}N_3O_2$

ESMS : (MeOH, cone +20 V) *m/z* 340 (100%, $[M+H]^+$), 413 (53%, $[M+NBu^tH_3]^+$), 679 (91%, $[2M+H]^+$), 752 (69%, $[2M+NBu^tH_3]^+$), 1091 (67%, $[3M+NBu^tH_3]^+$)

GCMS : (70 eV) *m/z* 339 (M^+, 20%), 283 (28), 268 (20), 227 (100), 57 (27)

^{1}H NMR : ($CDCl_3$) δ 1.32 (9H, s, NC(CH_3)$_3$), 1.46 (9H, s, NHC(CH_3)$_3$), 5.07 (1H, s, OH), 5.65 (1H, s, NH), 5.74 (1H, s, H2), 7.22 (1H, td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ =

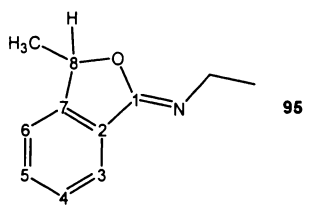
0.8 Hz, H10), 7.63 (1H, td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, H9), 7.74 (1H, dd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 0.6 Hz, H11), 8.60 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.6 Hz, H8)

^{13}C NMR : ($CDCl_3$) δ 28.8 ($NHC(CH_3)_3$), 30.9 ($NC(CH_3)_3$), 52.0 ($NHC(CH_3)_3$), 58.0 ($NC(CH_3)_3$), 97.1 (C2), 118.0 (C8), 123.9 (C12), 124.4 (C11), 124.9 (C10), 131.2 (C6), 130.5 (C3), 137.1 (C9), 147.0 (C7), 152.2 (C4), 160.2 (C5), 185.3 (C1)

3.5.2. Reactions with other isocyanides.

*Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (**79**) with EtNC.*

79 (116 mg, 0.40 mmol) and EtNC (300 µl of 15% solution in $EtNH_2$) were transferred to an ampoule with heptane (10 ml), and sealed under vacuum. The ampoule was placed in a Carius tube, and heated to 95°C for 24 hours. The ampoule was allowed to cool, then opened and the reaction mixture transferred to a round bottom flask. The solvent was taken off under vacuum, and the residue chromatographed (PLC, ether) to afford three fractions. The first was a mixture of the starting material and the mono-substitution product, as evidenced by the IR spectrum. The two compounds could not be separated. The second and third were collected as pale oils to afford **95** (17 mg, 23% yield) and **96** (12 mg, 17% yield).



95

M_r = 175.2 $C_{11}H_{13}NO$

High Resolution Mass Spectroscopy : Calculated : 175.0997

Experimental : 175.0996

IR : (CH_2Cl_2) ν(C≡O) 1763 cm^{-1}

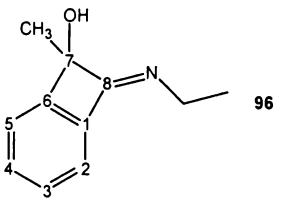
ESMS : (MeOH, cone +20 V) *m/z* 176 (100%, $[M+H]^+$)

GCMS : (70 eV) *m/z* 175 (M^+, 30%), 160 (100), 131 (37), 103 (24), 77 (18), 57 (7)

^{1}H NMR : ($CDCl_3$) δ 1.29 (3H, t, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 1.59 (3H, d, $^3J_{HH}$ = 6.6 Hz, C8-CH_3), 3.55 (2H, q, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 5.56 (1H, q, $^3J_{HH}$ = 6.5 Hz, H8), 7.30 (1H, d, $^3J_{HH}$ = 7.4 Hz, H6), 7.41 (1H, t, $^3J_{HH}$ = 7.1 Hz, H4), 7.49

(1H, t, $^3J_{HH}$ = 7.4 Hz, H5), 7.83 (1H, d, $^3J_{HH}$ = 7.5 Hz, H3)

^{13}C NMR : ($CDCl_3$) δ 16.3 (CH_2CH_3), 21.6 (C8-CH_3), 42.0 (CH_2CH_3), 80.0 (C8), 121.3 (C6), 123.6 (C3), 128.8 (C4), 130.8 (C2), 131.5 (C5), 148.1 (C7), 159.5 (C1)



96

M_r = 175.2 $C_{11}H_{13}NO$

IR : (CH_2Cl_2) ν(C≡O) 1771 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 198 (100%, $[M+Na]^+$)

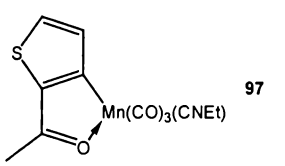
GCMS : (70 eV) *m/z* 175 (M^+, 66%), 160 (100), 146 (9), 132 (34), 103 (9), 77 (8)

^{1}H NMR : ($CDCl_3$) δ 1.32 (3H, t, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 1.35 (3H, s, C7-CH_3), 2.03 (1H, s, OH), 3.61 (2H, qd, $^3J_{HH}$ = 6.5 Hz, $^2J_{HH}$ = 2.5 Hz, CH_2CH_3), 7.41 (1H, m, H5), 7.48 (1H, m, H3), 7.53 (1H, m, H4), 7.83 (1H, dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.0 Hz, H2)

^{13}C NMR : ($CDCl_3$) δ 16.3 (CH_2CH_3), 21.9 (C7-CH_3), 42.3 (CH_2CH_3), 90.5 (C7), 122.8 (C5), 123.5 (C2), 129.5 (C3), 131.5 (C1), 131.7 (C4), 147.6 (C6), 158.3 (C8)

*Reaction of η^2-(2-acetylthiophenyl)tetracarbonylmanganese (**45**) with EtNC.*

45 (101 mg, 0.34 mmol) and EtNC (300 μl of 15% solution in $EtNH_2$) were transferred to an ampoule with toluene (10 ml), and sealed under vacuum. The ampoule was placed in a Carius tube, and heated to 95°C for 2 hours. The ampoule was allowed to cool, then opened and the solvent was taken off under vacuum. The residue was chromatographed (PLC, ether) to afford two fractions. The first contained the starting material (**45**) and from the second was isolated the mono-substitution product **97** (21 mg, 19% yield).



97

M_r = 319.2 $C_{12}H_{10}NO_4MnS$

IR : (CH_2Cl_2) ν(C≡O) 2010(s), 1913(s, br), 1893(s, br) cm^{-1}

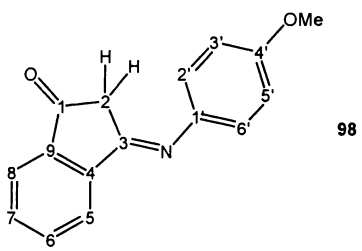
ESMS : (MeOH/NaOMe, cone +20 V) *m/z* 318 (100%, $[M-H]^-$)

^{1}H NMR : ($CDCl_3$) δ 1.13 (3H, t, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 2.58 (3H, s, $COCH_3$), 2.77 (2H, m, CH_2CH_3), 7.77 (1H, d, $^3J_{HH}$ = 5.3 Hz, Ar-H), 7.48 (1H, d, $^3J_{HH}$ = 5.3 Hz, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 16.3 (CH_2CH_3), 21.9 (C7-CH_3), 42.3 (CH_2CH_3), 90.5 (C7), 122.8 (C5), 123.5 (C2), 129.5 (C3), 131.5 (C1), 131.7 (C4), 147.6 (C6), 158.3 (C8)

*Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (**79**) with p-methoxyphenyl isocyanide.*

79 (104 mg, 0.36 mmol) and p-methoxyphenyl isocyanide (400 mg, 3.0 mmol) were reacted in heptane (15 ml) at reflux for 2 hours. The solvent was removed under vacuum, and the residue chromatographed (PLC, 1:1 ether/petroleum spirits) to afford four fractions, the second and third of which were collected to give **98** (11 mg, 12% yield) and **99** (33 mg, 36% yield). The fourth fraction was unreacted p-methoxyphenyl isocyanide.



98

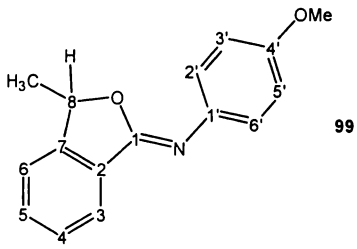
M_r = 251.3 $C_{16}H_{13}NO_2$

IR : (CH_2Cl_2) ν(C≡O) 1696 cm^{-1}

GCMS : (70 eV) *m/z* 251 (M^+, 100%), 236 (34), 220 (42), 208 (21), 130 (11)

^{1}H NMR : ($CDCl_3$) δ 3.86 (3H, s, OCH_3), 5.02 (1H, d, $^3J_{HH}$ = 2.8 Hz, H2), 5.05 (1H, d, $^3J_{HH}$ = 2.8 Hz, H2), 6.96 (2H, d, $^3J_{HH}$ = 8.9 Hz, H3'/5'), 7.48 (2H, d, $^3J_{HH}$ = 8.9 Hz, H2'/6'), 7.56 (1H, t, $^3J_{HH}$ = 7.4 Hz, H6), 7.60 (1H, t, $^3J_{HH}$ = 6.9 Hz, H7), 7.67 (1H, d, $^3J_{HH}$ = 7.5 Hz, H8), 7.99 (1H, d, $^3J_{HH}$ = 7.3 Hz, H5)

^{13}C NMR : ($CDCl_3$) δ 55.8 (OCH_3), 86.9 (C2), 114.3 (C3'/5'), 120.6 (C8), 123.8 (C5), 126.1 (C2'/6'), 130.5 (C6), 131.5 (C4), 132.2 (C7), 136.3 (C9), 138.9 (C1'), 153.1 (C3), 155.6 (C1), 157.4 (C4')



99

$M_r = 253.3$ $C_{16}H_{15}NO_2$

IR : (CH_2Cl_2) ν(C≡O) 1679 cm^{-1}

ESMS : (MeCN, cone +20 V) *m/z* 254 (100%, $[M+H]^+$)

GCMS : (70 eV) *m/z* 253 (M^+, 71%), 238 (100), 167 (7), 131 (16), 103 (12), 77 (8)

^{1}H NMR : ($CDCl_3$) δ 1.65 (3H, d, $^3J_{HH}$ = 5.8 Hz, C8-CH_3), 3.84 (3H, s, OCH_3), 5.68 (1H, q, $^3J_{HH}$ = 5.8 Hz, H8), 6.93 (2H, d, $^3J_{HH}$ = 7.7 Hz, H3'/5'), 7.37 (1H, d, $^3J_{HH}$ = 7.0 Hz, H6), 7.41 (2H, d, $^3J_{HH}$ = 7.8 Hz, H2'/6'), 7.51 (1H, t, $^3J_{HH}$ = 7.0 Hz, H4), 7.56 (1H, t, $^3J_{HH}$ = 6.8 Hz, H5), 7.97 (1H, d, $^3J_{HH}$ = 6.7 Hz, H3)

^{13}C NMR : ($CDCl_3$) δ 21.5 (C8-*C*H_3), 55.8 (OCH_3), 81.0 (C8), 114.3 (C3'/5'), 121.3 (C6), 124.2 (C3), 125.4 (C2'/6'), 129.2 (C4), 131.4 (C2), 132.0 (C5), 140.0 (C1'), 148.0 C7), 156.7(C4'), 158.1 (C1)

*Reaction of η²-(2-acetylphenyl)tetracarbonylmanganese (**79**) with p-methoxyphenyl isocyanide in toluene.*

79 (102 mg, 0.36 mmol) and p-methoxyphenyl isocyanide (400 mg, 3.0 mmol) were reacted in toluene (20 ml) under reflux for 2 hours. The solvent was removed under vacuum, and the residue chromatographed (PLC, 1:1 ether/petroleum spirits) to afford four fractions, the second and third of which were collected to give **98** (19 mg, 21% yield) and **99** (22 mg, 25% yield). The fourth fraction was unreacted p-methoxyphenyl isocyanide.

3.5.3. Alternative reaction conditions.

Solvent effects on the reaction of η²-(2-acetylthiophenyl)tetracarbonyl-manganese (45) with Bu^{t}NC.

*Reaction of η²-(2-acetylthiophenyl)tetracarbonylmanganese (**45**) with Bu^{t}NC in toluene.*

45 (51 mg, 0.18 mmol) and Bu^{t}NC (150 μl, 0.13 mmol) were reacted in toluene (10 ml) under reflux for 6 hours. Chromatography (Chromatotron, 1:1 ether/petroleum spirits) gave two fractions, the second of which was collected to afford **88** (33 mg, 65% yield) as an orange oil.

*Reaction of η^2-(2-acetylthiophenyl)tetracarbonylmanganese (**45**) with Bu^tNC in dioxane.*

45 (50 mg, 0.17 mmol) and Bu^tNC (150 µl, 0.13 mmol) were reacted in dioxane (10 ml) under reflux for 6 hours. Chromatography (Chromatotron, 1:1 ether/petroleum spirits) gave two fractions, the second of which was collected to afford **88** (39 mg, 77% yield) as an orange oil.

*Hydrolysis of 5-tert-butylamino-4-tert-butylimino-4H-benzo[b]thiophen-7-one (**88**).*

88 (17 mg, 0.06 mmol) was dissolved in THF (10 ml) and transferred to a 50 ml round bottom flask with dilute HCl (10 ml). The solution was stirred for 2 hours before the product was extracted with ether (2 x 5 ml), then washed with water (2 x 5 ml), and dried over magnesium sulfate. The ether solution was filtered and the solvent was removed under vacuum to afford a quantitative yield of 5-*tert*-butylamino-benzo[*b*]thiophene-4,7-dione (**89**) as a red solid, identified by NMR spectroscopy.

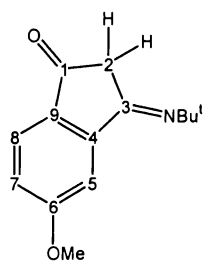
The addition of metal complexes to the reactions of orthomanganated acetyl-aryl complexes with isocyanides.

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**43**) with Bu^tNC in tetrahydrofuran with $CoCl_2$ as a catalyst.*

43 (110 mg, 0.35 mmol), Bu^tNC (500 µl, 4.4 mmol) and anhydrous $CoCl_2$ (54 mg, 0.42 mmol) were reacted in THF (15 ml) under reflux for 6 hours. Chromatography (PLC, ether) gave three fractions, none of which contained any of the indenone or naphthyl products.

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**43**) with Bu^tNC in heptane with $NiBr_2(CNBu^t)_2$ as a catalyst.*

43 (51 mg, 0.17 mmol), Bu^tNC (250 µl, 2.2 mmol) and $[NiBr_2(CNBu^t)_2]$ (67 mg, 0.17 mmol) were reacted in heptane (10 ml) under reflux for 2 hours. Chromatography (PLC, 1:1 ethyl acetate/petroleum spirits) gave three fractions, of which the first was collected to afford **100** (15 mg, 40% yield) as pale oil.



100

$M_r = 231.3$ $C_{14}H_{17}NO_2$

IR : (CH_2Cl_2) ν(C=O) 1776 cm^{-1}.

ESMS : (MeCN, cone +20 V), *m/z* 232 (100%, $[M+H]^+$)

GCMS : (70 eV) *m/z* 232 (14%), 217 (5), 176 (100), 57 (35)

^{1}H NMR : ($CDCl_3$) δ 1.46 (9H, s, Bu^t), 3.90 (3H, S, OMe), 4.74 (1H, d, $^3J_{HH}$ = 2.6 Hz, H2), 4.81 (1H, d, $^3J_{HH}$ = 2.6 Hz, H2), 7.08 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.4 Hz, H7), 7.25 (1H, d, $^4J_{HH}$ = 2.3 Hz, H5), 7.48 (1H, d, $^3J_{HH}$ = 8.5 Hz, H8)

^{13}C NMR : ($CDCl_3$) δ 30.7 ($C(CH_3)_3$), 51.6 ($C(CH_3)_3$), 56.2 (OMe), 83.3 (C2), 105.4 (C5), 121.0 (C7), 121.5 (C8), 128.6 (C9), 132.1 (C4), 155.5 (C3), 161.8 (C6), 179.9 (C1)

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**43**) with Bu^tNC in dioxane with $NiBr_2$ as a catalyst.*

43 (101 mg, 0.32 mmol), Bu^tNC (300 μl, 2.7 mmol) and $NiBr_2$ (73 mg, 0.33 mmol) were reacted in dioxane (20 ml) under reflux for 2 hours. Chromatography (PLC, 1:1 ether/petroleum spirits) gave three fractions, from the second of which was isolated **100** (11 mg, 15% yield) as pale oil. The other two fractions were determined by IR spectroscopy to be unreacted starting material and the mono-substituted product **75**.

3.5.4. Preparation of Isocyanides and the $[NiBr_2(CNBu^t)_2]$ catalyst.

Preparation of isocyanides

A variation of the phase transfer catalysis method reported by Gokel *et al*[122] was used to prepare both the ethyl and *tert*-butyl isocyanides.

Preparation of Ethyl Isocyanide, EtNC.

To a 2 litre 3-neck round bottom flask containing a large magnetic stirrer bar was attached a 500 ml pressure-regulating funnel and an efficient water condenser. Atop the condenser was a second condenser, containing an acetone slush bath. This second condenser is required due to the very low boiling point of ethyl amine (~18°C). The third opening was stoppered.

The round bottom flask was charged with distilled water (300 ml), with NaOH (300 g) being added in small portions with stirring. The solution was then allowed to cool to

[122] G. W. Gokel, R. P. Widera, W. P. Weber, *Organic Syntheses*, **55** (1976) 96

approximately 30°C. The funnel was charged with bromoform (100 ml), $[Et_4N]OH$ solution (10 ml of 25% in H_2O), chlorobenzene (200 ml) and finally ethyl amine (200 ml). The organic solution from the funnel was added drop-wise to the vigorously stirred solution in the round-bottom flask over a period of 2 hours, with care not to induce vigorous reflux of the solution. The solution was then stirred for a further 2 hours after complete addition of the organic solution.

The reaction mixture was then diluted with approximately 800 ml of ice water, and the organic layer collected. The aqueous layer was washed with chlorobenzene (2 x 100 ml), which was then added to the organic layer. The organic layer was then washed with distilled water (100 ml) and a NaCl solution (100 ml of 5% in H_2O), then dried over $MgSO_4$. The resulting organic solution was distilled under a nitrogen atmosphere to afford an 15% solution of EtNC in $EtNH_2$ (78-81°C, ~35 ml). The purity was determined by NMR spectroscopy.

Preparation of tert-Butyl Isocyanide.

The apparatus for the preparation of *tert*-butyl isocyanide was the same as for the preparation of ethyl isocyanide, except that the acetone slush bath condenser was not necessary and was not used.

The round-bottom flask was charged with distilled water (150 ml), with NaOH (150 g) added in small portions with stirring. The funnel was charged with chloroform (40 ml), dichloromethane (150 ml), benzyltrimethylamine bromide (1.5 g) and *tert*-butyl amine (100 ml). This organic solution was added drop-wise to the round-bottom flask over a 30 minute period, with the aqueous solution warmed to ~45°C to initiate the reaction. The solution was stirred for a further 3 hours after the complete addition of the organic solution. After this time the reaction mixture was diluted with ice water (400 ml), and the organic layer collected. The aqueous layer was extracted with 50 ml of dichloromethane which was added to the organic layer. The organic combined layer was washed with distilled water (50 ml), then NaCl solution (50 ml of 5% in H_2O), then dried over $MgSO_4$. This dried organic layer was then filtered and distilled under a nitrogen atmosphere affording pure Bu^tNC (91-92°C, ~30 ml) as determined by NMR spectroscopy.

Preparation of $[NiBr_2(CNBu^t)_2]$ catalyst.

Anhydrous $NiBr_2$ (0.66 g, 3.0 mmol) and Bu^tNC (2.0 ml, 18 mmol) were stirred in THF

(30 ml) under a N_2 atmosphere for 3 hours. The solvent was removed under vacuum, and the residue recrystallised from dichloromethane/petroleum spirits to afford red/brown rosettes. All attempts to characterise the complex formed were unsuccessful.

3.5.5. Crystal Data and Structural Refinement Tables

Crystal data and structure refinement for 74.

Empirical formula	$C_{34}H_{41}MnN_3OPS$
Formula weight	625.67
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 12.5276(8) Å
	b = 9.7128(6) Å β = 104.068(1)°
	c = 14.2264(9) Å
Volume	1679.12(18) $Å^3$
Z	2
Density (calculated)	1.237 g/cm^3
Absorption coefficient	0.532 mm^{-1}
F(000)	660
Theta range for data collection	1.48 to 25.40°.
Index ranges	-15<=h<=14, -11<=k<=8, 0<=l<=17
Reflections collected	9088
Independent reflections	4877 [R(int) = 0.0464]
Completeness to theta = 25.40°	99.1 %
Tmin/Tmax	0.711 and 0.971
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4877 / 1 / 379
Goodness-of-fit on F^2	1.098
Final R indices [I>2sigma(I)]	R_1 = 0.0459, wR_2 = 0.0954
R indices (all data)	R_1 = 0.0669, wR_2 = 0.1168
Largest diff. peak and hole	0.390 and -0.284 $e.Å^{-3}$

Crystal data and structure refinement for 75.

Empirical formula	$C_{17}H_{18}MnNO_5$
Formula weight	323.22
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.2361(1) Å
	b = 9.3014(1) Å β = 100.549(1)°
	c = 16.9957(1) Å
Volume	1746.22(3) $Å^3$
Z	4
Density (calculated)	1.229 g/cm^3
Absorption coefficient	0.770 mm^{-1}
F(000)	672
Crystal size	0.40 x 0.28 x 0.34 mm^3
Theta range for data collection	2.02 to 25.75°.
Index ranges	-13<=h<=13, 0<=k<=11, 0<=l<=20
Reflections collected	9945
Independent reflections	3334 [R(int) = 0.0153]
Completeness to theta = 25.75°	99.5 %
Tmin/Tmax	0.709 and 0.852
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3334 / 0 / 222
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R_1 = 0.0239, wR_2 = 0.0652
R indices (all data)	R_1 = 0.0273, wR_2 = 0.0669
Largest diff. peak and hole	0.263 and -0.231 $e.Å^{-3}$

Crystal data and structure refinement for 76.

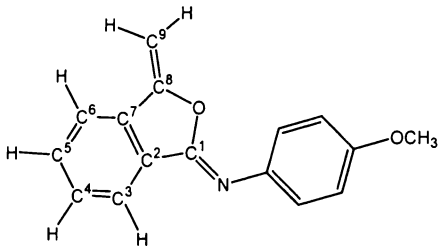
Empirical formula	$C_{14}H_{17}NO_2$
Formula weight	231.29
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 19.2656(5) Å
	b = 13.6243(4) Å
	c = 9.6785(3) Å
Volume	2540.42(13) $Å^3$
Z	8
Density (calculated)	1.209 g/cm^3
Absorption coefficient	0.081 mm^{-1}
F(000)	992
Theta range for data collection	1.83 to 26.31°.
Index ranges	0<=h<=24, 0<=k<=16, -12<=l<=8
Reflections collected	15034
Independent reflections	4250 [R(int) = 0.0291]
Completeness to theta = 26.31°	99.7 %
Tmin/Tmax	0.903 and 1.000
Absolute structure parameter (Flack)	1.1(13)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4250 / 1 / 323
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R_1 = 0.0516, wR_2 = 0.1269
R indices (all data)	R_1 = 0.0580, wR_2 = 0.1340
Largest diff. peak and hole	0.549 and -0.263 $e.Å^{-3}$

Crystal data and structure refinement for 89.

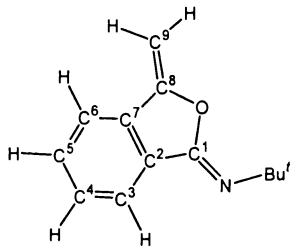
Empirical formula	$C_{12}H_{13}NO_2S$
Formula weight	235.29
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 9.5947(2) Å
	b = 11.9564(3) Å
	c = 21.4407(4) Å
Volume	2459.64(9) $Å^3$
Z	8
Density (calculated)	1.271 g/cm^3
Absorption coefficient	0.248 mm^{-1}
F(000)	992
Crystal size	0.36 x 0.30 x 0.20 mm^3
Theta range for data collection	1.90 to 25.34°.
Index ranges	-11<=h<=11, -7<=k<=14, -25<=l<=25
Reflections collected	12470
Independent reflections	2261 [R(int) = 0.0268]
Completeness to theta = 25.34°	100.0 %
Absorption correction	Empirical
Tmin/Tmax	0.846 and 0.970
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2261 / 0 / 198
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R_1 = 0.0338, wR_2 = 0.0780
R indices (all data)	R_1 = 0.0460, wR_2 = 0.0849
Extinction coefficient	0.0027(5)
Largest diff. peak and hole	0.214 and -0.193 $e.Å^{-3}$

3.5.6. Erratum

The structures **98** and **100** have been incorrectly assigned. The true structures are shown below.



98



100

The corrected structures show the oxygen in the heterocyclic ring, rather than as the ketones. The positioning of the oxygen explains why there was no correlation from the CH_2 protons to the imine side of the ring (see discussion on pages 71 and 80).

The corrected structures also accommodate the difference between the chemical shifts of the two CH_2 protons on C^9. The two protons are in different environments, which would lead to the larger shifts observed.

Errata:Wade Mace: PhD thesis, "Reactions of Cyclomanganated Compounds", UW 2003

With reference to section 3.5.6 Erratum (page 128 of thesis) the following corrections to the erratum were made after the thesis was submitted and catalogued:

Structure 100

The structure 100 on p.82 and 120 is incorrect as indicated in the Erratum on p.128 – but the replacement structure 100 given on p.128, though otherwise correct, lacks the required MeO group on the C atom labelled 4.

The structure labelled 100 on page 74 is however correct in the context referred to; it is not the same compound referred to as 100 on pages 81-2 and 120 and it should not be "corrected" to the structure labelled 100 in the erratum on page 128. The original thesis numbering was incorrect in this sense. It may be best to label it 76a on p.74 (and on p 73 in the text) - as was done for 98/98a tautomers.

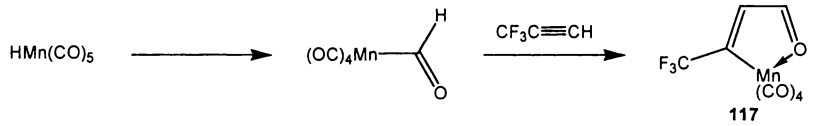
Structure 98

The correction for structure 98 in the erratum (p.128) should be made on the incorrect structures 98 given on p.72 and p.118.

Chapter 4. The Reaction of Alkynes with Cyclomanganated Compounds.

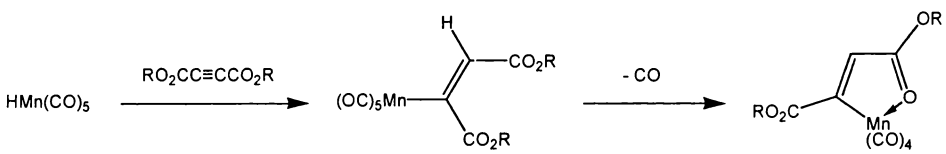
4.1. Introduction

The preparation of one of the first reported cyclomanganated enones was from the reaction of $HMn(CO)_5$ with 3,3,3-trifluoropropyne, giving **117** as the product in good yield[123]. It is thought that a formyl group is initially formed by the insertion of CO into the Mn-H bond, followed by insertion of the alkyne group to form the acyl-coordinated manganocycle.



117

This work was extended to a range of $RMn(CO)_5$/alkyne combinations. The low temperature reaction of $HMn(CO)_5$ and $RO_2CC{\equiv}CCO_2R$ (R = H, Me) in a coordinating solvent resulted in the insertion of the alkyne into the Mn-H bond[124]. This product (**118**) is thermally converted to the cyclomanganated product (**119**) by loss of a CO ligand and coordination through the ester/acid carbonyl oxygen.



118 **119**

The reaction of $RMn(CO)_5$ (R = Me, Ph) and any alkyne under the same conditions resulted in the initial insertion of a carbonyl into the Mn-C bond, followed by insertion of the alkyne to form a cyclomanganated complex analogous to **117** above[125,126]. The high pressure (2-10 kbar) reaction of $RMn(CO)_5$ (R = Me, Ph) and alkynes resulted in the same products[127,128].

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[123] D. A. Harbourne, F. G. A. Stone, *J. Chem. Soc. (A)*, (1968) 1765

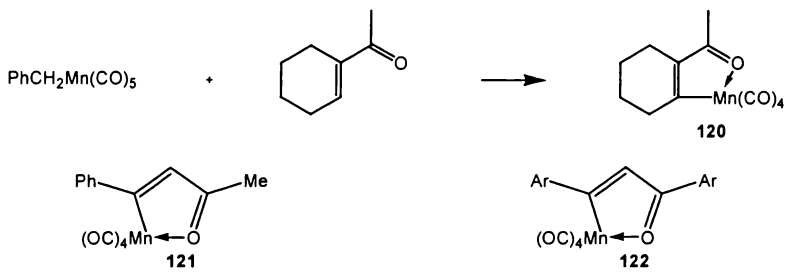
[124] B. L. Booth, R. G. Hargreaves, *J. Chem. Soc. (A)*, (1969) 2766

[125] B. L. Booth, R. G. Hargreaves, *J. Chem. Soc. (A)*, (1970) 308

[126] W. D. Bannister, B. L. Booth, R. N. Haszeldine, P. L. Loader, *J. Chem. Soc. (A)*, (1971) 930

[127] P. DeShong, D. R. Sidler, G. A. Slough, *Tetrahedron Lett.*, **28** (1987) 2233

The first direct cyclomanganation of an enone was reported by Cabral[129]. $PhCH_2Mn(CO)_5$ and 1-acetylcyclohexene were heated in heptane to afford a good yield of **120**. Robinson[130] applied the same process in the cyclomanganation of 4-phenylbut-3-en-1-one, and Tully[20] has cyclomanganated several 1,3-substituted prop-2-en-1-ones forming **121** and **122** respectively.



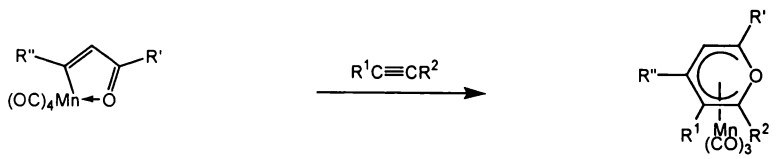
In the reaction of the 1,3-diarylprop-2-en-1-ones, two products can be formed, with manganation occurring either at the β-carbon (**123**) or *o*-aryl carbon (**124**) sites. The site of manganation can be directed by altering the substituents on either aryl ring[20], e.g. 1-phenyl-3-(4-trifluoromethylphenyl)prop-2-en-1-one reacts at the β-carbon, whereas 1-(6-methoxyphenyl)-3-(2-trifluoromethylphenyl)prop-2-en-1-one gave the *o*-aryl product.

Tully[21] described a reaction whereby cyclomanganated enones **125** reacted with alkynes to form coordinated pyranyl complexes **126**. This type of product is not unexpected, as the analogous pyranyl products were obtained in low yield from the reaction of $RMn(CO)_5$ with excess alkyne[125].

[128] P. DeShong, D. R. Sidler, P. J. Rydczynski, G. A. Slough, A. L. Rheingold, *J. Am. Chem. Soc.*, **110** (1988) 2575

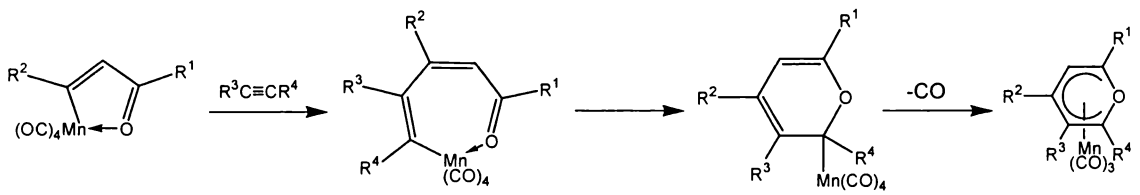
[129] A. W. Cabral, *Ph.D. Thesis*, University of California, Los Angeles, (1981)

[130] N. P. Robinson, *Ph.D. Thesis*, University of Waikato, Hamilton, (1989)



125 126

This was confirmed as a general route to pyranyl complexes by the reaction of various alkynes and cyclomanganated diarylpropenones. With unsymmetrical alkynes it was found that the bulkier end group was adjacent to the oxygen on the pyranyl ring. A mechanism was proposed[125] (Scheme 4-1) with the initial step being coordination of the alkyne to the manganese centre. The alkyne inserts into the Mn-C bond with the bulky group adjacent to the manganese due to the steric effects of the group R^2. Cyclisation occurs at the oxygen atom, affording the final pyranyl product.



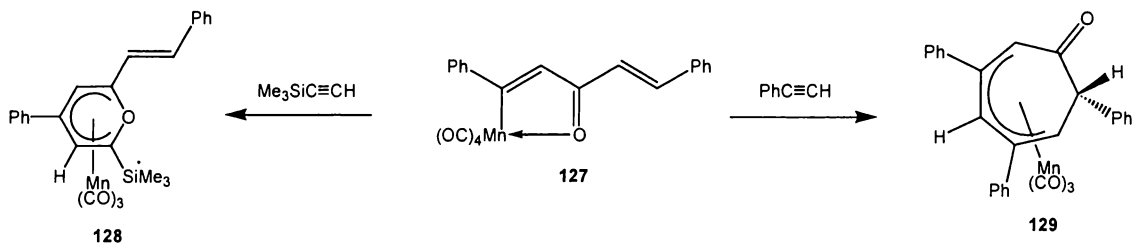
Scheme 4-1 Proposed mechanism for the insertion of acetylenes into cyclomanganated enones, forming pyranyl complexes[125].

A one pot synthesis of the pyranyl complex was also undertaken using 1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one, phenylacetylene and $PhCH_2Mn(CO)_5$. This achieved a higher yield of the pyranyl complex compared to the step-wise preparation via the cyclomanganated enone (52% *cf.* 48%).

When the same reactions were conducted using cyclomanganated diarylpentadienones[131], the products formed depended on the diarylpentadienone and the alkyne used in the reaction (Scheme 4.2). Cyclomanganated diphenylpentadienone **127** reacts with trimethylsilyl acetylene to form the pyranyl **128**, in a reaction similar to that seen for the diarylpropenones. However, when **127** reacted with phenyl acetylene under the same conditions, the product formed was [1-oxo-3,5,7-triphenylcycloheptadienyl-

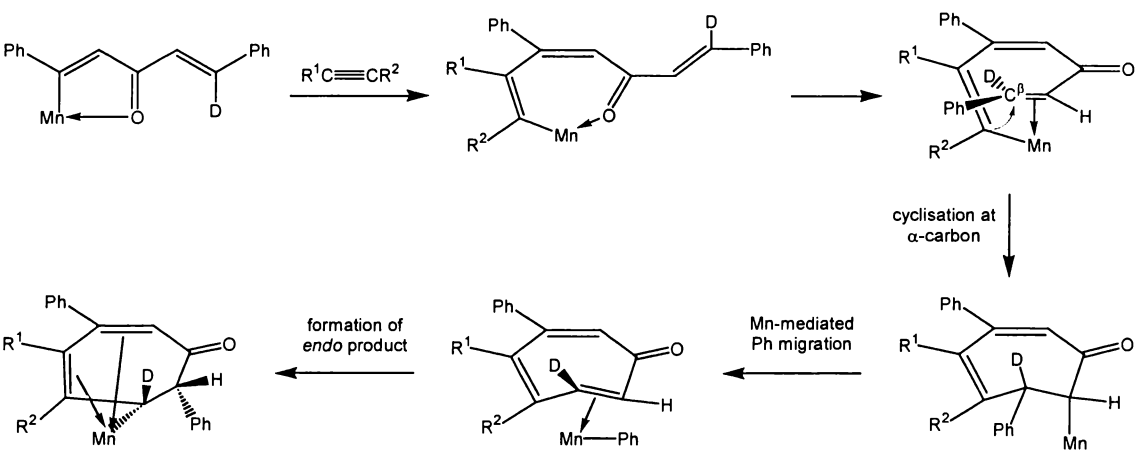
[131] W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633** (2001) 162

η^5]tricarbonylmanganese with the Ph group in the *endo* position (**129**).

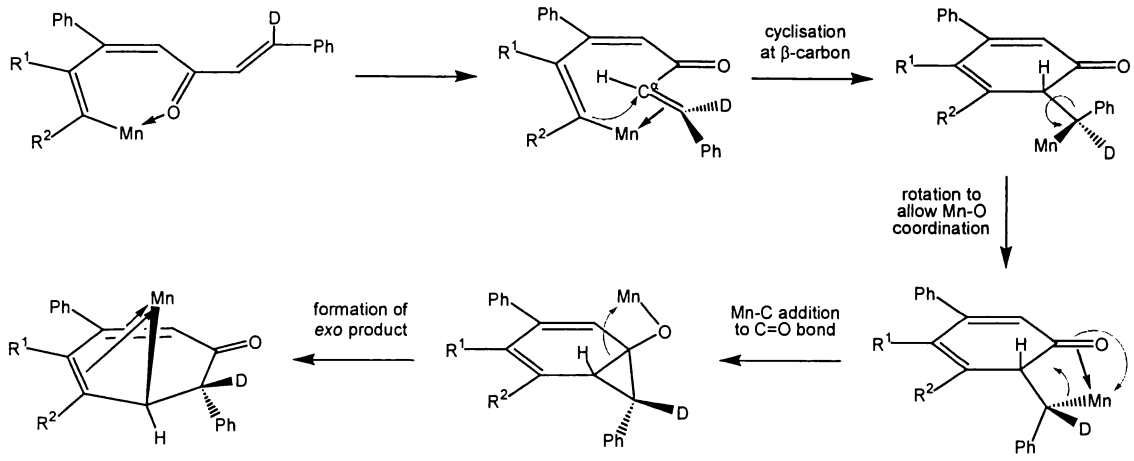


Scheme 4-2 Production of pyranyl or oxocycloheptadienyl complexes from cyclomanganated dienones depends on the acetylene used.

Two mechanisms were considered[131] for the formation of **129** (Scheme 4-3 and Scheme 4-4), one involving ring closure at the β-carbon, with a subsequent metal-mediated phenyl migration, the other involving ring closure at the α-carbon with a rearrangement of the carbon backbone to afford the final product. The second mechanism was rejected as the final stereochemistry would be *exo*, and no extra steps were envisaged which could allow for an *endo* product.



Scheme 4-3 Proposed mechanism for formation of oxocycloheptadienyl by Mn-mediated phenyl transfer.

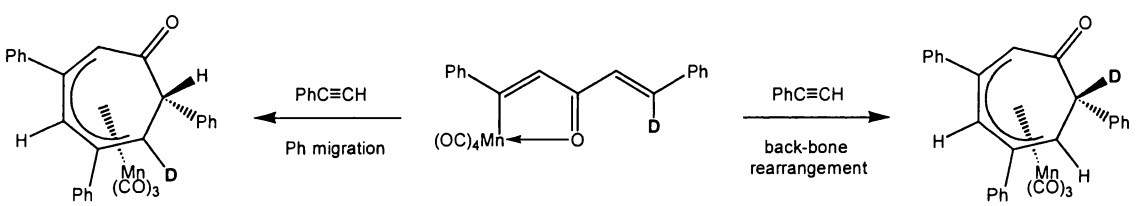


Scheme 4-4 Proposed mechanism for formation of oxocycloheptadienyl by carbon back-bone rearrangement.

4.2. Aim of Present Study

From the previous study[131] it was unclear why the two different products (pyranyl and oxocycloheptadienyl complexes) were formed, and what factors were influencing their production. The first goal of the present study was to determine these factors. The second goal of the present study was to clarify the mechanism for the production of the oxocycloheptadienyl product, including the *endo* stereochemistry of the migrating Ph group.

To determine by what pathway the reaction was proceeding, cyclomanganated 5-deutero-labelled diphenylpentadienone was reacted with phenylacetylene. The position of the deutero-labelled carbon in the final product would indicate whether the reaction occurred by phenyl migration or backbone rearrangement. If a phenyl migration was occurring the phenyl group would be on the carbon adjacent to the deutero-labelled carbon, whereas rearrangement of the carbon backbone would result in the labelled carbon also having the phenyl group attached.



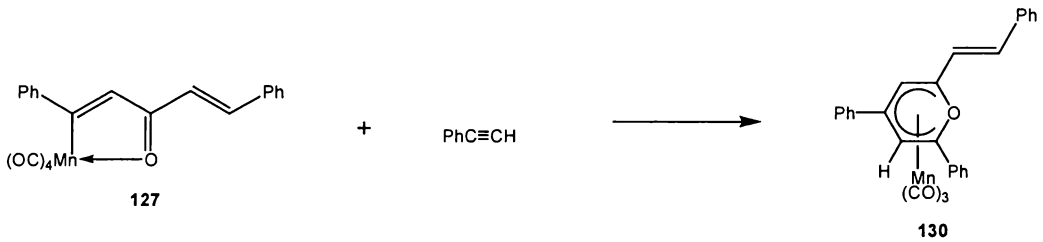
4.3. Results and Discussion

4.3.1. Factors that influence which product is formed.

During the previous research[131] a key observation was made of the IR spectrum while monitoring the synthesis of **129**. The presence of peaks corresponding to a pyranyl complex was observed in the early stages of the reaction, but they soon disappeared as the reaction progressed.

This suggested that the pyranyl complex was an intermediate in the route to the formation of the oxocycloheptadienyl products. Hence in the current study the reaction was repeated under milder conditions in an attempt to exclusively form and isolate the pyranyl product.

Thus a solution of phenylacetylene and **127** was stirred in CCl_4 at ambient temperature (rather than under reflux), and was completely converted to the pyranyl product (**130**) in approximately 8 hours. Only minor traces of the oxocycloheptadienyl complex were detected in the IR spectrum of the reaction mixture. Work-up of the reaction mixture gave **130** in 27% yield with no oxocycloheptadienyl product isolated.



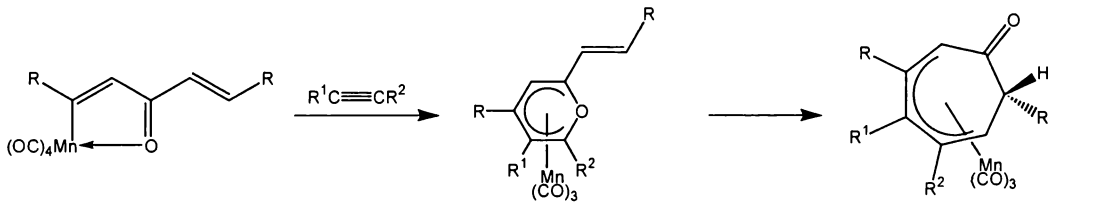
127 **130**

The pyranyl product was fully characterised by IR, ESMS and NMR. The structure of **130** was further confirmed by X-ray crystal structure analysis (discussed in Section 4.3.3).

To confirm that the pyranyl complex was being converted to the oxocycloheptadienyl complex, a sample of **130** was heated in heptane to reflux. Monitoring of the reaction by IR spectroscopy showed that after approximately 1 hr all traces of **130** had disappeared, being replaced by signals corresponding to **129**. NMR analysis of the final separated product confirmed that **129** was produced.

Previously, various cyclomanganated diarylpentadienones and alkynes have been reacted

forming either the pyranyl or oxocycloheptadienyl product[131]. To assess the generality of the substrate-to-pyranyl-to-oxocycloheptadienyl pathway a selection of these reactions were repeated under different conditions. The reaction conditions were altered in an attempt to isolate the other of the two products; milder conditions were used to prepare the pyranyl complexes, while more forcing conditions were utilised to form the oxocycloheptadienyl complexes. In all but one case the alternative product was isolated from the product mixture. The products were identified by comparison of IR, ESMS and NMR data with the previously prepared compounds. The table below shows the products formed and the conditions required.



127 R = Ph
131 R = 2-$CF_3C_6H_4$

130 R = Ph, R^1 = H, R^2 = Ph
132 R = Ph, R^1, R^2 = Ph
128 R = Ph, R^1 = H, R^2 = $SiMe_3$
135 R = 2-$CF_3C_6H_4$, R^1 = H, R^2 = Ph
137 R = 2-$CF_3C_6H_4$, R^1, R^2 = Ph
139 R = 2-$CF_3C_6H_4$, R^1 = H, R^2 = $SiMe_3$

129 R = Ph, R^1 = H, R^2 = Ph
133 R = Ph, R^1, R^2 = Ph
134 R = Ph, R^1 = H, R^2 = $SiMe_3$
136 R = 2-$CF_3C_6H_4$, R^1 = H, R^2 = Ph
138 R = 2-$CF_3C_6H_4$, R^1, R^2 = Ph
140 R = 2-$CF_3C_6H_4$, R^1 = H, R^2 = $SiMe_3$

Table 4-1 Acetylene/cyclomanganated diarylpentadienone reaction pairs, showing products formed and conditions required.

Substrates		Pyranyl			Oxocycloheptadienyl		
		Prod.	Conditions	Yield	Prod.	Conditions	Yield
127	Phenylacetylene	**130**	8 hours, RT	27%	**129**	24 hours, 65°C	13%
					129[a]	24 hours, 85°C[a]	66%
127	Diphenylacetylene	**132**	4 days, 30°C	-	**133**	4 days, 30°C	29%
127	Trimethylsilylacetylene	**128**	24 hours, 95°C	29%	**134**	24 hours, 95°C	29%
		128[a]	4 hours, 85°C[a]	79%			
131	Phenylacetylene	**135**	24 hours, 95°C	17%	**136**	24 hours, 95°C	52%
		135[a]	4 hours, 85°C[a]	70%			
131	Diphenylacetylene	**137**	2 days, 30°C	9%	**138**	2 days, 30°C	13%
					138[a]	24 hours, 85°C[a]	35%
131	Trimethylsilylacetylene	**139**	7 days, 95°C	36%	**140**	7 days, 95°C	20%
		139[a]	4 hours, 85°C[a]	96%			

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

[131] W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633** (2001) 162

In all but one case both the pyranyl and oxocycloheptadienyl products were isolated, showing that the key factors controlling the product yielded are the temperature and reaction time. The exception is the reaction between **127** and diphenylacetylene. Monitoring of the reaction by IR spectroscopy showed that the pyranyl was formed, but that it was never a dominant product, rather in this case conditions required to progress to the oxocycloheptadienyl product were the same as those needed to form the pyranyl.

By contrast, trimethylsilylacetylene requires more forcing reaction conditions to form the oxocycloheptadienyl product. In neither reaction involving trimethylsilylacetylene could the product be completely converted to the oxocycloheptadienyl complex. More forcing conditions than those applied led to progressively more degradation of the reaction mixture.

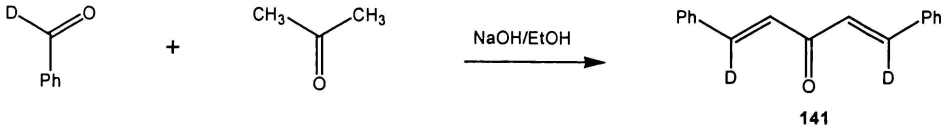
Steric factors are likely to be behind the high energy barrier for the reactions involving trimethylsilylacetylene. After initial insertion of the acetylene, the bulky trimethylsilyl group will be on the terminal carbon, and will hinder any cyclisation to the sp^2 carbons of the ethenyl side chain (refer to Scheme 4-1, page 133), preferring to cyclise to the sterically unhindered ketone oxygen.

In the original mechanism[131] it was proposed that after the insertion of the acetylene, the reaction progressed down either of two paths, forming the pyranyl or oxocycloheptadienyl products. The results from this study suggest that the pyranyl product is formed initially, with further reaction forming the oxocycloheptadienyl product. Mechanistically this implies that either the formation of the pyranyl is reversible, or that the reaction progresses from the pyranyl to the oxocycloheptadienyl by an as yet undetermined pathway.

4.3.2. Investigation into the formation of the η^5-oxocycloheptadienyl complexes.

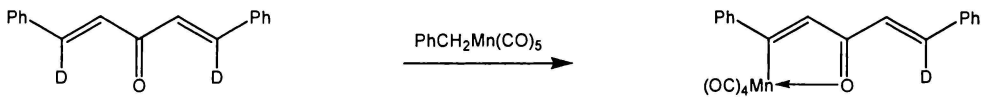
The deuterium labelled precursor, 1,5-^{2}H,^{2}H-1,5-diphenylpenta-1,4-dien-3-one (**141**), was prepared from D-benzaldehyde and acetone using base catalysis. The compound was recrystallised from ethyl acetate, and the position of the deuterium labels confirmed by comparison of the ^{1}H NMR spectrum with the non-deuterated compound.

[131] W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633** (2001) 162



141

Cyclomanganation of **141** to produce **142** was achieved using the standard method of refluxing in petroleum spirits, and recrystallisation from the same. Again ^{1}H NMR spectroscopy was used to confirm the product.



141 **142**

Reaction of the cyclomanganated complex **142** with phenylacetylene resulted in the expected oxocycloheptadienyl complex **143**. This was purified by chromatography and analysed by ^{1}H and ^{13}C NMR spectroscopy to confirm its structure.

Comparison of the ^{1}H NMR spectra of the original (non-labelled) complex (**129**) with the deuterium labelled complex (**143**) showed that one of the ring proton signals was absent (indicated by *), indicating this was the deuterated site (Figure 4-1).

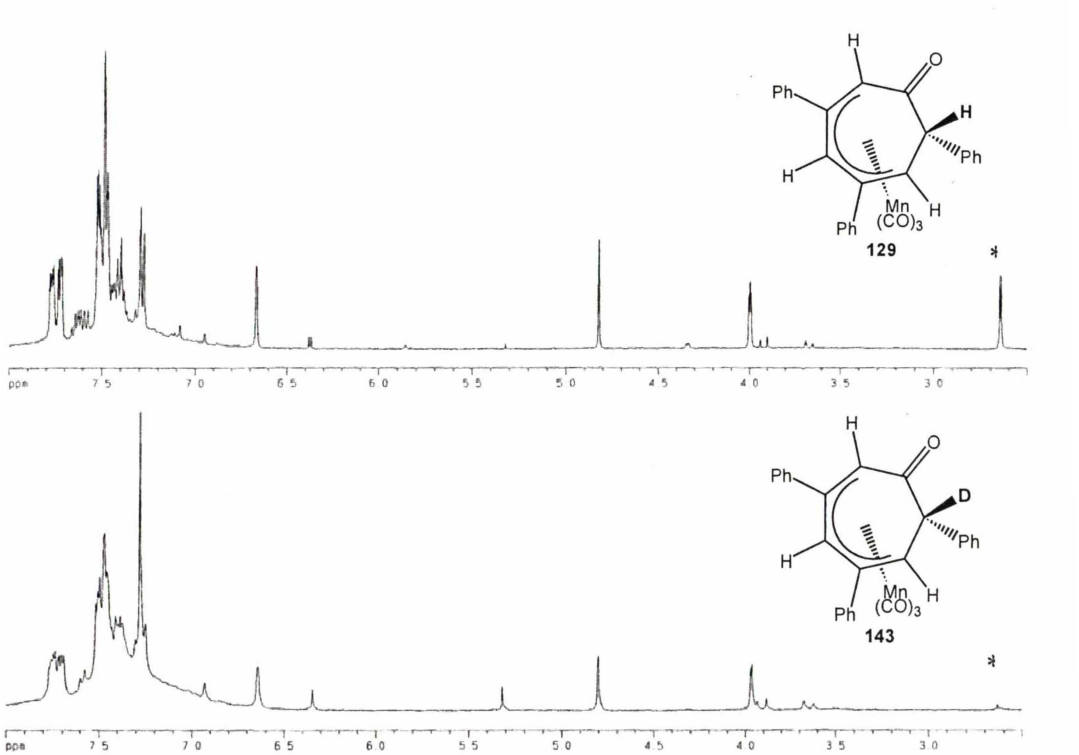


Figure 4-1 ^{1}H NMR of **129** and **143**, the non-labelled and labelled η^{5}-oxocycloheptadienyl complexes.

From the ^{1}H NMR spectrum it was not unambiguous as to which carbon the deuterium was attached. Therefore a detailed analysis of the structure of **129** was undertaken using 2D-NMR to fully characterise the complex, and ensure correct assignment of the deuterated carbon position. This is discussed in Section 4.3.4.

Position of the deuterium in 143.

The ^{1}H NMR of the **143** shows a signal missing at 2.64 ppm. From the 2D-NMR characterisation of **129** (Section 4.3.4) it was determined that this was the due to the proton on the carbon at position 7 of the oxocycloheptadienyl ring. This positioning of the deuterium corresponded to the mechanism (Scheme 4-4, page 131) involving rearrangement of the carbon back-bone, as the deuterium is attached to the same carbon as the phenyl group. However, the product in the proposed mechanism has *exo* stereochemistry, while the true product has *endo* stereochemistry.

No mechanism could be envisaged to account for the stereochemistry of the final product.

4.3.3. X-ray crystal structure of the pyranyl complex 130.

Dark-red elongated crystals were obtained from dichloromethane/petroleum spirits at -20°C. The crystals were shown to be monoclinic, of space group $P2_1/c$, with four molecules in the unit cell. An ORTEP perspective view is given in Figure 4-2 showing the atom labelling scheme. Selected bonds and angles are listed in Table 4-2. Crystal and structure refinement data are given in a table in Section 4.4.1, while the CIF files can be found on the CD inside the back cover.

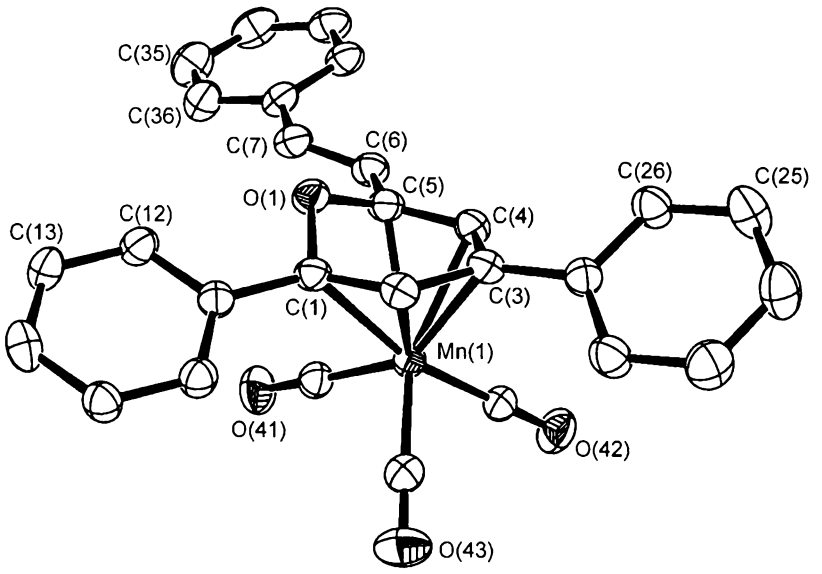


Figure 4-2 ORTEP perspective view of **130** showing atom labelling scheme.

Table 4-2 Selected bond lengths (Å) and angles (°) of **130** (estimated standard deviations in parentheses).

Bond	Length	Bond	Angle
Mn(1)-C(1)	2.189(3)	O(1)-C(1)-C(2)	117.5(3)
Mn(1)-C(2)	2.127(3)	C(1)-C(2)-C(3)	118.5(3)
Mn(1)-C(3)	2.131(3)	C(2)-C(3)-C(4)	114.3(3)
Mn(1)-C(4)	2.177(3)	C(3)-C(4)-C(5)	121.2(3)
Mn(1)-C(5)	2.401(3)	C(4)-C(5)-O(1)	119.2(3)
Mn(1)-C(41)	1.810(3)	C(1)-O(1)-C(5)	107.1(2)
Mn(1)-C(42)	1.814(3)	C(5)-C(6)-C(7)	123.8(3)
Mn(1)-C(43)	1.811(3)	C(6)-C(7)-C(31)	125.7(3)
O(1)-C(1)	1.428(3)	Mn(1)-C(41)-O(41)	177.4(3)
C(1)-C(2)	1.408(4)	Mn(1)-C(42)-O(42)	177.8(3)
C(2)-C(3)	1.416(4)	Mn(1)-C(43)-O(43)	178.4(3)
C(3)-C(4)	1.438(4)		
C(4)-C(5)	1.392(4)		
C(5)-O(1)	1.387(4)		
C(1)-C(11)	1.470(4)		
C(3)-C(21)	1.480(4)		
C(5)-C(6)	1.454(4)		
C(6)-C(7)	1.334(5)		
C(7)-C(31)	1.472(4)		

The structure of **130** consists of a $Mn(CO)_3$ "piano stool" moiety coordinating to a 2,4,6-substituted η^5-pyranyl ring. The oxygen of the pyranyl ring is lifted out of the plane of the ring at a dihedral angle of 42.9(2)°, shown in the stereo view in Figure 4-3.

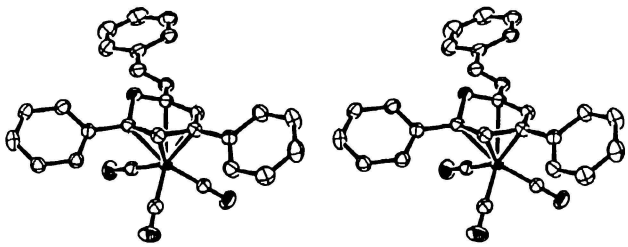


Figure 4-3 Stereo view of **130** showing non-planarity of the oxygen and pyranyl ring substituents.

The second stereo view (Figure 4-4) shows the packing of the molecules in the unit cell. The molecules form layers with the molecules alternating in arrangement within the layer. The layers stack within the crystal lattice, as shown in the unit cell in Figure 4-4. There appears to be interaction between the phenyl rings of adjacent molecules.

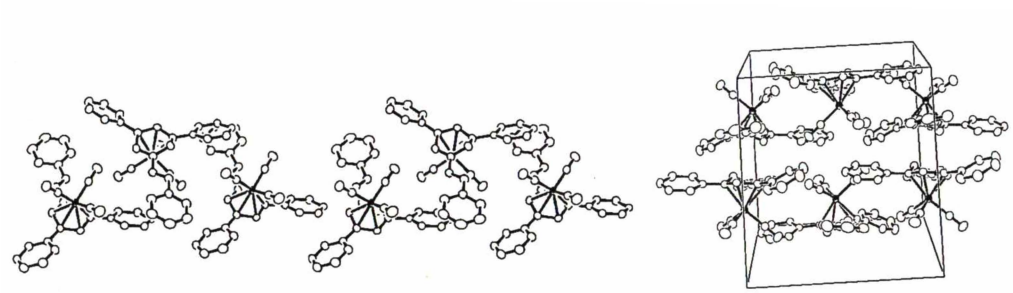


Figure 4-4 Stereo view and view of the unit cell packing of **130**.

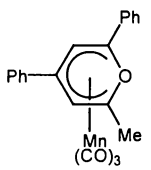
The bond lengths around the ring system are not equal, with C(3)-C(4) being the longest, and C(4)-C(5) being the shortest. The lengths do not correspond to a dominant resonance form as the lengths do not progressively alternate between long and short around the ring. The bond lengths also show that the oxygen atom in the pyranyl ring has a shorter bond length to C(5) compared to C(1) (see Table 4-2).

There appears to be little conjugation between the π-bonds of the pyranyl ring and the substituent groups. Though the bonds between the pyranyl ring and the phenyl groups are shorter than expected for a sp^2-sp^2 single bond, they are not significantly shorter. The phenyl groups are not co-planar with the pyranyl ring, being at an angle of 36° or 26° to

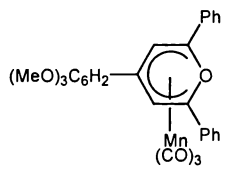
the plane, which hinders any π-electron interaction.

Though the ethenyl group [C(6)-C(7)-C(31)] is not co-planar with the ring system, the smaller angle of 14° does allow for more π-electron interaction. This interaction is still not strong, as the bond length of 1.334(5) Å for C(6)-C(7) corresponds to a C=C double bond with little conjugation.

The bond lengths of the ring carbons to the manganese show that the manganese is closer to C(2) and C(3), and has a noticeably longer bond length to C(5) (2.127(3) and 2.131(3) Å compared to 2.401(3) Å). This positions the $Mn(CO)_3$ moiety in a non-symmetric coordination relative to the pyranyl ring, and this was thought to be influenced by the substituents on the pyranyl ring. Having a non-phenyl group as the 2- or 6-substituent may affect the manganese coordination, causing the manganese to be positioned closer to the side of the ring system opposite to the non-phenyl group. A crystal structure has been reported for **144**[132], with a methyl group in the 6-position, but no crystal structures for other similar pyranyl complexes were found. Therefore complex **145** was prepared and a crystal structure obtained to determine whether the observation was due to the effect of a non-phenyl group (the characterisation of **145** is discussed in section 4.3.5).



144



145

The structure of **144** showed a similar positioning of the $Mn(CO)_3$ moiety away from the non-phenyl substituent. The positioning was not as extreme as that seen in **130**, with a Mn-(C5) bond length of 2.280(9) Å compared to 2.401(3) Å in **130**. The Mn-C bonds to C(3) and C(4) are still the shorter bonds. The two phenyl rings are at an angle of 19° and 25° to the plane of the pyranyl ring, with the connecting C-C bonds longer than the corresponding bonds in **130** (1.498 Å and 1.485 Å compared to 1.470(4) Å and 1.480(4) Å in **130**).

[132] W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **507** (1996) 103

The crystal structure of **145** has two independent molecules. Both show a central positioning of the $Mn(CO)_3$ moiety, with the shortest Mn-C bonds being to C(2) and C(4) in both molecules (compared to C(3) and C(4) in **130** and **144** respectively). Of the phenyl rings, two are at a similar angle to the plane of the pyranyl ring when compared to **130** and **144**, being ~36° and ~19°. The third phenyl ring is nearly co-planar with the pyranyl ring, approximately 3°. The C-C bonds from the pyranyl ring to the phenyl groups are all very similar (1.475-1.488 Å), indicating no increased conjugation when the phenyl ring is co-planar with the pyranyl ring system.

From the structures of **130**, **144**, and **145** it can be seen that having a non-aromatic substituent on the pyranyl ring in position 2 or 6 leads to the $Mn(CO)_3$ moiety being positioned closer to the opposite side of the pyranyl ring. This appears not to be influenced by π-bonding interactions between the substituent phenyl rings and the pyranyl ring.

4.3.4. Spectroscopic and mass spectrometric characterisation.

2D-NMR analysis of [η^5-1-oxo-3,5,7-triphenylcycloheptadienyl]Mn(CO)$_3$ (129).
The chemical shifts that were of interest for the deuterium-labelling experiment arise from the protons on C^6 and C^7, adjacent to the ketone group, as these are the sites involved in the phenyl migration. A ^{1}H NMR spectrum does not provide sufficient information to be confident of the chemical shift assignments, therefore four NMR experiments were run on a sample of **129**, acquiring ^{1}H, ^{13}C, HSQC and HMBC spectra. From these spectra, full assignment could be achieved.

The ^{1}H spectrum showed signals due to protons around the oxocycloheptadienyl ring at 2.64, 3.99, 4.82 and 6.66 ppm, with the signals due to the phenyl protons giving a multiplet at 7.36-7.76 ppm. The ^{13}C spectra gave the chemical shifts of each carbon atom in the complex. From the HSQC spectrum (which shows single bond proton-to-carbon correlations) it was possible to ascertain the protonated carbons in the oxocycloheptadienyl ring. The HMBC spectrum gave long range (two (^2J) and three (^3J) bond) proton-to-carbon correlations. The mixing time of 0.6 msec favoured the expression of three bond correlations for aromatic protons.

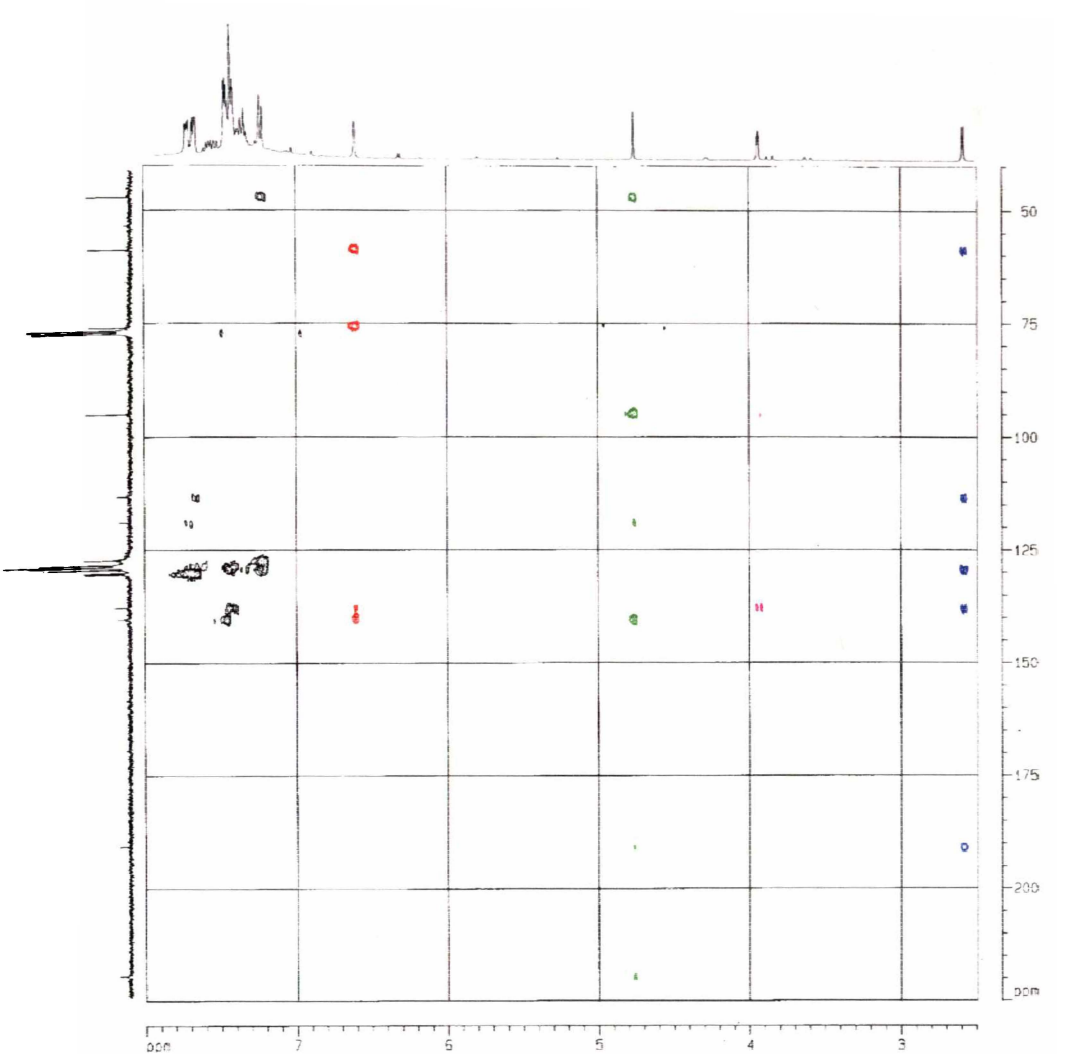


Figure 4-5 HMBC NMR spectrum of **129** with projected ^{1}H and ^{13}C NMR spectra.

The structure of [1-oxo-3,5,7-triphenylcycloheptadienyl-η^5]$Mn(CO)_3$ below (Figure 4-6) shows the correlations from the HMBC spectrum. Of interest is the correlation from the ring proton (4.81 ppm) to the carbonyls coordinated to the manganese. This phenomenon was looked at further, and is discussed in Section 4.3.5.

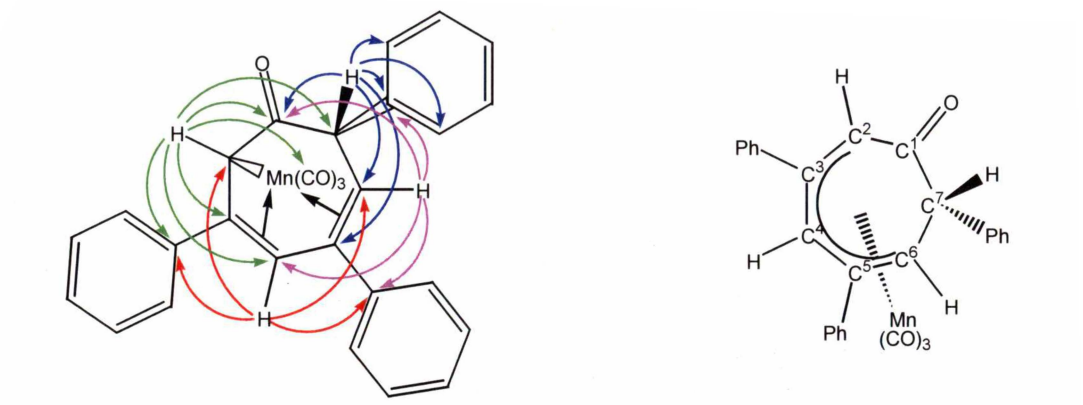


Figure 4-6 Structure of **129**, showing HMBC correlations and labelling scheme.

Using the spectra, full assignment of the oxocycloheptadienyl ring was achieved, with assignments shown in Table 4-3.

Table 4-3 Full NMR assignments for [1-oxo-3,5,7-triphenylcycloheptadienyl-η^5]$Mn(CO)_3$.

Proton δ (ppm)		Carbon δ (ppm)			
4.81	H2	191.4	C1	47.5	C7
6.66	H4	76.3	C2	127.8-130.9	Ar-H
3.99	H6	119.5	C3	140.9	*i-Ar*-C3
2.64	H7	95.5	C4	138.3	*i-Ar*-C5
7.39-7.76	Ar-H	113.8	C5	138.3	*i-Ar*-C7
		59.2	C6	220.2	Mn(CO)

IR Spectra

For both the pyranyl and oxocycloheptadienyl complexes, the carbonyl region of the IR spectrum showed three peaks, corresponding to the a_1 + e modes of a "piano stool", ideally C_{3v} $Mn(CO)_3$ fragment. The symmetry is less than C_{3v}, so the e mode splits and with the a_1 mode affords the three peaks observed in the spectrum.

The peaks due to the pyranyl complexes have lower frequencies than those of the corresponding oxocycloheptadienyl complexes. This indicates that there is stronger electron donation from the d-orbitals of the manganese to the π*-orbitals of carbonyls in the case of the pyranyl complexes compared to the oxocycloheptadienyl complexes, which suggests that the pyranyl ring is a better donor towards the manganese centre than is the oxocycloheptadienyl ring.

Table 4-4 IR ν(C≡O) peaks of the η^5-pyranyl and η^5-oxocycloheptadienyl complexes.

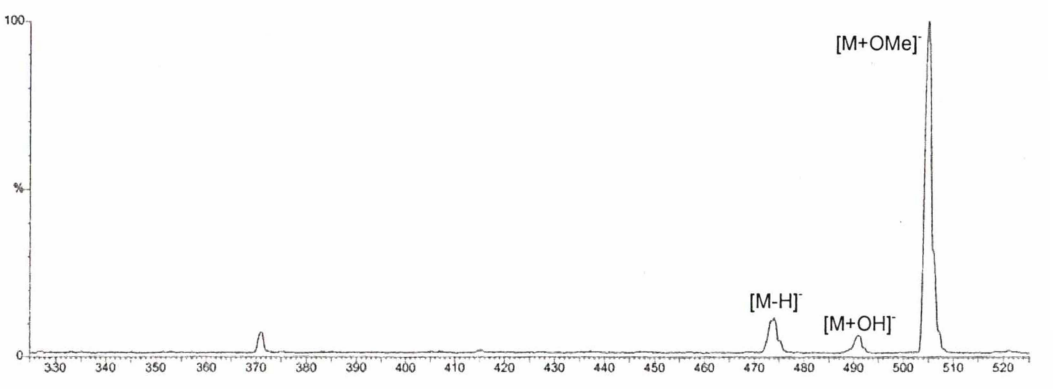
Substrate	Prod	Pyranyl (cm^{-1})			Prod	Oxocycloheptadienyl (cm^{-1})		
127 Phenylacetylene	**130**	2015	1956	1934	**129**	2033	1974	1959
127 Diphenylacetylene	**132**	2017	1957	1934	**133**	2028	1969	1948
127 Trimethylsilylacetylene	**128**[a]	2008	1942	1930	**134**	2031	1974	1947
131 Phenylacetylene	**135**[a]	2016	1955	1934	**136**	2033	1973	1960
131 Diphenylacetylene	**137**	2020	1962	1935	**138**[a]	2028	1967	1952
131 Trimethylsilylacetylene	**139**[a]	2013	1948	1930	**140**	2030	1972	1949

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

ESMS Spectra

When the (η^5-pyranyl)$Mn(CO)_3$ complexes were analysed as MeOH solutions (with NaOMe added to aid chemical ionisation[133]) the dominant peaks were due to $[M+OMe]^-$ species, with minor contributions from $[M-H]^-$ species. The opposite was true for the (η^5-oxocycloheptadienyl)$Mn(CO)_3$ complexes, with the $[M-H]^-$ species dominating. This difference in peak intensity allows a distinction between the pyranyl and oxocycloheptadienyl complexes, as any reaction pair (e.g. **130** and **129**) have the same mass.

Often a third minor peak was observed due to a $[M+OH]^-$ species. The free hydroxide likely originates from the preparation of the NaOMe, by adding sodium metal to undried methanol.



[133] W. Henderson, B. K. Nicholson, L. J. McCaffrey, *Polyhedron*, **17** (1998) 4291

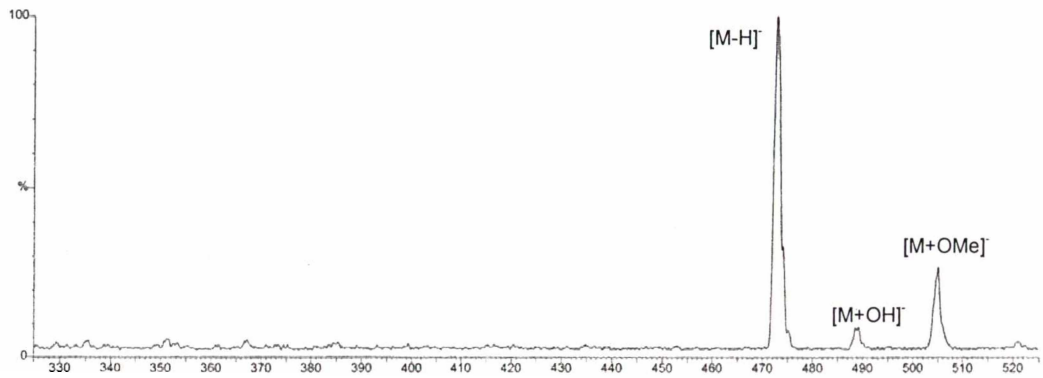


Figure 4-7 ESMS spectra of [4,6-diphenyl-2-(2-phenylethenyl)pyranyl-η^5]$Mn(CO)_3$ (**130**) and [1-oxo-3,5,7-triphenylcycloheptadienyl-η^5]$Mn(CO)_3$ (**129**) run in MeOH/NaOMe.

The only exceptions to the above observations were due to the pyranyl and oxocycloheptadienyl complexes containing a trimethylsilyl group, when desilylation occurred, affording peaks assigned as $[M\text{-}SiMe_3]^-$ and $[M\text{-}SiMe_3\text{+}H\text{+}OMe]^-$ for both types of complexes. Here, the organic ligand was probably being desilylated by nucleophilic attack of the methoxide. Similar desilylations occur with allyl groups where there is also resonance stabilisation of the carbanion[134].

The parent ion for both the pyranyl and oxocycloheptadienyl complexes could be observed by analysing the sample as an acidified (formic acid) MeCN solution in positive ion mode, giving peaks assigned as $[M+H]^+$ and $[2M+H]^+$.

[134] C. Eaborn, R. W. Bott, *Organometallic Compounds of the Group IV Elements*, ed. A. G. MacDiarmid, Marcel Dekker Inc, New York, 1968, vol. 1 (part 1), pp 395

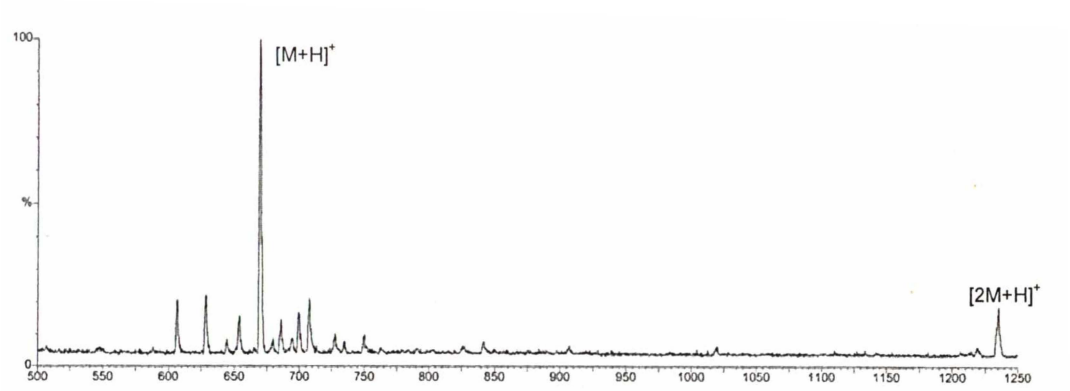


Figure 4-8 ESMS spectra of **140**; MeOH/NaOMe cone –20 V, MeCN (formic acid) cone +20 V.

When ESMS were collected as a MeOH solution in positive ion mode, the dominant peaks in the spectra of both the pyranyl and oxocycloheptadienyl complexes were due to $[M-Mn(CO)_3]^+$, where the organic ligand had been oxidised to the pyryllium or tropanonium ion respectively.

NMR Spectra

The NMR spectra were assigned using 2D-NMR techniques.

The ^1H chemical shifts around the pyranyl ring range from 4.6-5.7. This is consistent with a η^5-group. A trimethylsilyl substituent has the effect of lowering the chemical shifts of both of the ring protons compared to a phenyl substituent.

Table 4-5 ^1H NMR shifts of the protons around the η^5-pyranyl ring.

substrates			ppm	
		Prod	H^2	H^4
127	Phenylacetylene	**130**	5.06	5.72
127	Trimethylsilylacetylene	**128**[a]	4.75	5.21
131	Phenylacetylene	**135**[a]	4.88	5.38
131	Diphenylacetylene	**137**	4.93	
131	Trimethylsilylacetylene	**139**[a]	4.62	4.85

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

The chemical shift for a carbon in the pyranyl ring system ranges from 81.2 - 104.7 ppm. Changing the substituents has only a minor effect on the chemical shifts of the individual carbons.

Table 4-6 ^{13}C NMR shifts of the carbons around the η^5-pyranyl ring.

substrates		Prod	ppm C^1	C^2	C^3	C^4	C^5
127	Phenylacetylene	**130**	101.1	82.4	97.2	81.2	94.6
127	Trimethylsilylacetylene	**128**[a]	104.4	82.0	99.3	91.0	88.0
131	Phenylacetylene	**135**[a]	100.2	86.2	~94.7	83.3	~94.7
131	Diphenylacetylene	**137**	104.7	82.1	102.9	84.4	104.2
131	Trimethylsilylacetylene	**139**[a]	102.4	86.6	97.4	94.5	88.7

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

The chemical shifts for the protons around the oxocycloheptadienyl ring fall over a wider range due to the inclusion of the sp^3 carbon and the ketone group. H^7 is attached to the sp^3 carbon, but is shifted downfield by the adjacent ketone group to ~2.8 ppm. H^2 and H^6 are attached to the sp^2 carbons, which would put them both at ~3.9 ppm, except that H^2 is shifted further downfield by the adjacent ketone group.

H^4 is also attached to a sp^2 carbon, but is shifted considerably downfield compared to H^2 and H^6. This is likely due to the extra shielding afforded by the two adjacent phenyl rings and a stronger ring current towards the centre of the η^5 system. When one of the adjacent groups is replaced by a trimethylsilyl group the shielding is reduced as observed in an upfield shift of H^6.

Table 4-7 ^1H NMR shifts of the protons around the η^5-oxocycloheptadienyl ring.

substrates		Prod	ppm H^2	H^4	H^6	H^7
127	Phenylacetylene	**129**	4.81	6.66	3.99	2.64
127	Diphenylacetylene	**133**	4.67		3.91	2.82
127	Trimethylsilylacetylene	**134**	4.83	6.01	3.44	2.52
131	Phenylacetylene	**136**	4.61	6.40	4.04	2.94
131	Diphenylacetylene	**138***	4.41		3.95	3.27
131	Trimethylsilylacetylene	**140**	4.68	5.75	3.50	2.88

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

Due to the sp^3 carbon and the ketone group, the carbon chemical shifts of oxocycloheptadienyl complexes also fall over a wider range (41.6-191.4 ppm). Changing the substituents around the ring has little effect on the shifts observed for individual

carbons.

Table 4-8 ^{13}C NMR shifts of the carbons around the η^5-oxocycloheptadienyl ring.

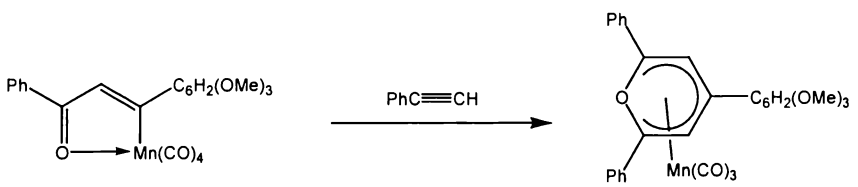
substrates		Prod	ppm C^1	C^2	C^3	C^4	C^5	C^6	C^7
127	Phenylacetylene	**129**	191.4	76.3	119.5	95.5	113.8	59.2	47.5
127	Diphenylacetylene	**133**	191.4	79.7	121.9	114.2	116.4	63.8	47.3
127	Trimethylsilylacetylene	**134**	188.5	76.3	122.7	99.1	106.4	67.6	48.6
131	Phenylacetylene	**136**	187.8	77.0	120.9	97.8	112.0	61.0	41.8
131	Diphenylacetylene	**138**	188.2	76.2	<125.6	<125.6	<125.6	66.5	41.6
131	Trimethylsilylacetylene	**140**	184.8	77.3	124.1	102.0	104.1	70.7	43.2

[a] Data from W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **633**, (2001), 162.

4.3.5. Supplementary information

Preparation and X-ray crystal structure of 145.

The orthomanganated chalcone **54** was reacted with phenylacetylene in refluxing petroleum spirits to afford the pyranyl complex **145** (62% yield). The product was purified by chromatography (PLC, 1:1 petroleum spirits/ether), and analysed by IR, ESMS, and NMR to confirm the structure of the product prior to a crystal structure analysis being undertaken.



54 **145**

The IR spectrum of **145** showed three bands in the carbonyl region (2013, 1949, and 1931 cm^{-1}) which are indicative of a $Mn(CO)_3$ moiety coordinated to a pyranyl ring system. The IR spectrum compared well with literature values for similar pyranyl complexes[132] which afford peaks at ~2013, ~1950 and ~1933 cm^{-1}.

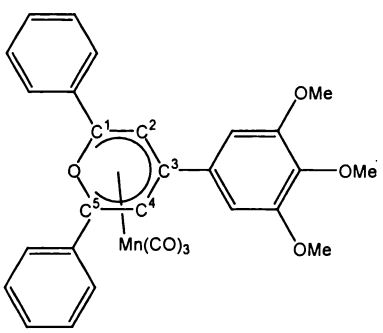
When run as a MeOH solution at positive cone voltages, the ESMS of **145** gave a dominant peak for the pyranyl ligand, formed by the dissociation of the $Mn(CO)_3$ moiety

[132] W. Tully, L. Main, B. K. Nicholson, *J. Organometal. Chem.*, **507** (1996) 103

from the complex, affording a peak assigned as $[M\text{-}Mn(CO)_3]^+$. A series of peaks assigned as $[nM+Na]^+$ (n = 1-3) were also seen, presumably due to the coordination of a sodium ion to the methoxy groups on the second aryl ring, as it is difficult to envisage how three molecules of **145** could coordinate to the sodium if coordinating by the pyranyl ring oxygen.

The ESMS spectrum of **145** when run as a MeOH solution at negative cone voltages (with NaOMe added to aid chemical ionisation) showed only the peak assigned as $[M+OMe]^-$.

The ^1H NMR of **145** showed two methyl signals, one proton signal at 5.57 ppm, and the remaining aromatic protons. The two methyl proton signals and the aromatic signals are consistent with the structure of **145**, comparing to the literature values. By further comparison to the literature values, it can be shown that the remaining proton signal (5.57 ppm) was due to the two ring protons on C^2 and C^4. The related compound **146** shows peaks for the ring protons at 5.52 and 5.56 ppm. The symmetry of **145** leads to the two protons being in the same chemical environment, and therefore they give only the single signal.



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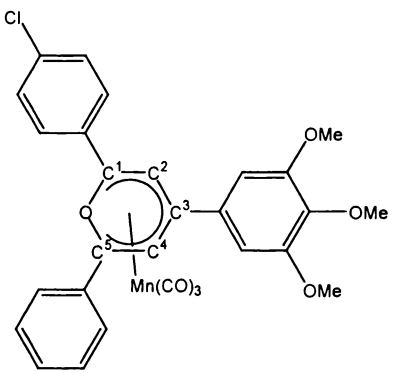


146

The ^{13}C NMR spectrum shows only 14 signals, again due to the symmetry of the molecule. The two phenyl rings attached to C^1 and C^5 give only 4 ^{13}C signals between them, the pyranyl ring only three signals ($C^1 = C^5$, $C^2 = C^4$) and the remaining 6 signals from the remaining aryl group. The signals due to the pyranyl ring system match those in the literature for **146**, with minor differences due to the 4-chlorophenyl group in **146**.

An HMBC spectrum was collected for **145** to compare to the HMBC spectrum of **130**.

Again a correlation was seen between the ring protons and the carbonyls coordinated to the manganese centre.

Once the structure of **145** had been confirmed as the expected structure, crystals were grown for X-ray crystal structure determination. Vapour diffusion from dichloromethane/petroleum spirits produced dark orange crystals.

*X-ray crystal structure of **145**.*

The crystals were triclinic, of space group P-1, with four molecules in the unit cell. An ORTEP perspective view is given in Figure 4-9 showing the atom labelling scheme. Selected bond lengths and angles are listed in Table 4-9. The CIF file is on the CD inside the back cover.

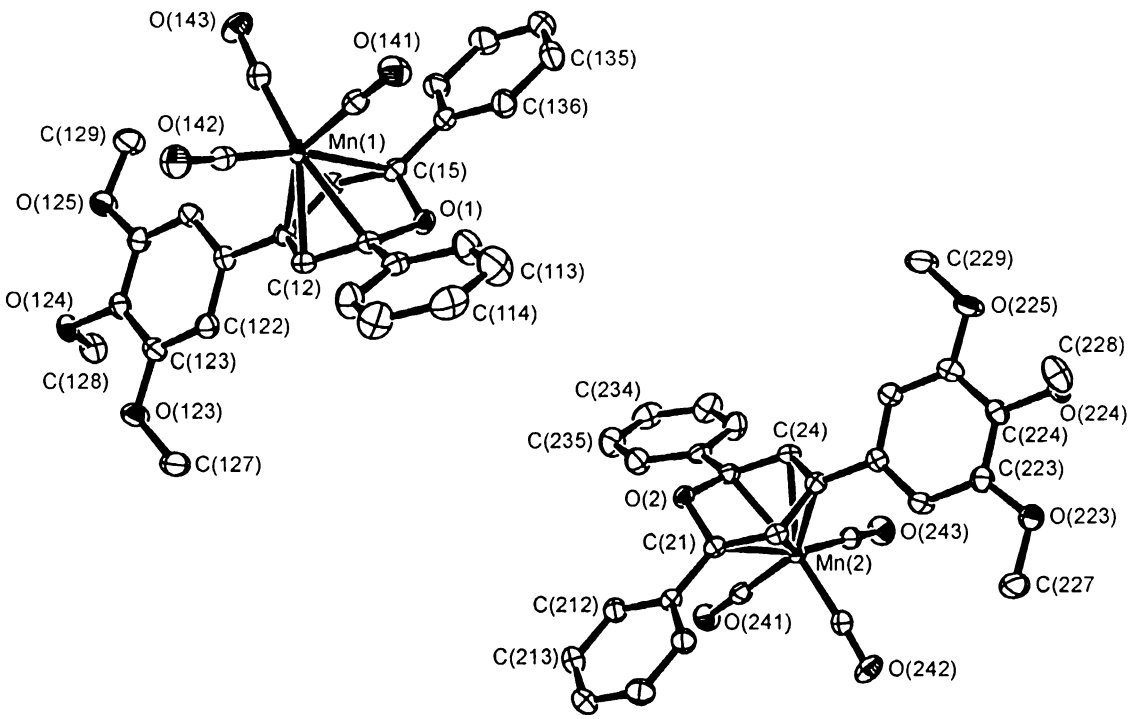


Figure 4-9 ORTEP perspective view of **145** (with solvent molecules and hydrogen atoms omitted for clarity).

Table 4-9 Selected bond length (Å) and angles (°) for **145** (estimated standard deviations in parentheses).

Molecule 1		Molecule 2	
Bond	Length	Bond	Length
Mn(1)-C(11)	2.2247(17)	Mn(2)-C(21)	2.2577(17)
Mn(1)-C(12)	2.1449(17)	Mn(2)-C(22)	2.1371(17)
Mn(1)-C(13)	2.1583(17)	Mn(2)-C(23)	2.1580(17)
Mn(1)-C(14)	2.1308(17)	Mn(2)-C(24)	2.1429(17)
Mn(1)-C(15)	2.2346(17)	Mn(2)-C(25)	2.2052(17)
Mn(1)-C(141)	1.8056(19)	Mn(2)-C(241)	1.8075(19)
Mn(1)-C(142)	1.8216(19)	Mn(2)-C(242)	1.8118(18)
Mn(1)-C(143)	1.8117(18)	Mn(2)-C(243)	1.8145(19)
O(1)-C(11)	1.423(2)	O(2)-C(21)	1.414(2)
C(11)-C(12)	1.397(2)	C(21)-C(22)	1.396(2)
C(12)-C(13)	1.433(2)	C(22)-C(23)	1.431(2)
C(13)-C(14)	1.427(2)	C(23)-C(24)	1.426(2)
C(14)-C(15)	1.398(2)	C(24)-C(25)	1.400(2)
O(1)-C(15)	1.418(2)	O(2)-C(25)	1.424(2)
C(11)-C(111)	1.481(2)	C(21)-C(211)	1.475(2)
C(13)-C(121)	1.488(2)	C(23)-C(221)	1.486(2)
C(15)-C(131)	1.475(2)	C(25)-C(231)	1.477(2)
Bond	Angle	Bond	Angle
C(11)-O(1)-C(15)	105.44(12)	C(21)-O(2)-C(25)	105.17(12)
O(1)-C(11)-C(12)	117.50(15)	O(2)-C(21)-C(22)	117.69(15)
C(11)-C(12)-C(13)	119.10(16)	C(21)-C(22)-C(23)	119.84(16)
C(12)-C(13)-C(14)	114.82(15)	C(22)-C(23)-C(24)	114.82(15)
C(13)-C(14)-C(15)	119.77(16)	C(23)-C(24)-C(25)	118.86(16)
C(14)-C(15)-O(1)	117.46(15)	C(24)-C(25)-O(2)	117.17(15)
O(141)-C(141)-Mn(1)	178.26(15)	O(241)-C(241)-Mn(2)	178.60(16)
O(142)-C(142)-Mn(1)	177.15(17)	O(242)-C(242)-Mn(2)	177.46(16)
O(143)-C(143)-Mn(1)	176.83(16)	O(243)-C(243)-Mn(2)	176.93(16)

The two molecules of the unit cell effectively have the same structure, with the majority of the bond lengths and angles within the estimated standard deviation for the measurements. The two differences to note are the coordination of the $Mn(CO)_3$ to the pyranyl ring, and the interplanar angle between the pyranyl ring and the trimethoxyphenyl group.

The $Mn(CO)_3$ moiety in one molecule coordinates symmetrically to the pyranyl ring,

while in the other independent molecule the $Mn(CO)_3$ moiety is slightly closer to one side of the pyranyl ring than the other. The orientation away from the symmetrical point is small (as shown in Table 4-9) and is likely due to the packing forces within the crystal structure, as both molecules are chemically the same. In both cases the coordination of the $Mn(CO)_3$ moiety is considerably more central than in the cases of **130** and **144** discussed earlier. Due to the similarity between the two molecules, further discussion applies to both molecules in the unit cell.

The structure of **145** shows a puckered pyranyl ring, with the oxygen elevated out of the plane described by the five pyranyl carbons (C(11), C(12), C(13), C(14), C(15)) at a dihedral angle of approximately 49°. The $Mn(CO)_3$ moiety coordinates symmetrically to the lower side of the pyranyl ring, away from the oxygen atom. There is a large interplanar angle between the pyranyl ring and the trimethoxyphenyl ring (approximately 35°) for both asymmetric molecules, however in one molecule the trimethoxyphenyl ring is rotated to the left, in the other molecule to the right.

When viewed down the a axis of the unit cell it can be seen that a "column"-like structure is formed with alternating independent molecules. The molecules are linked by stacking of the trimethoxyphenyl rings, which requires the large interplanar angles seen for the trimethoxyphenyl rings with regards to the pyranyl rings. This interaction is shown in the stereo view depicted in Figure 4-10.

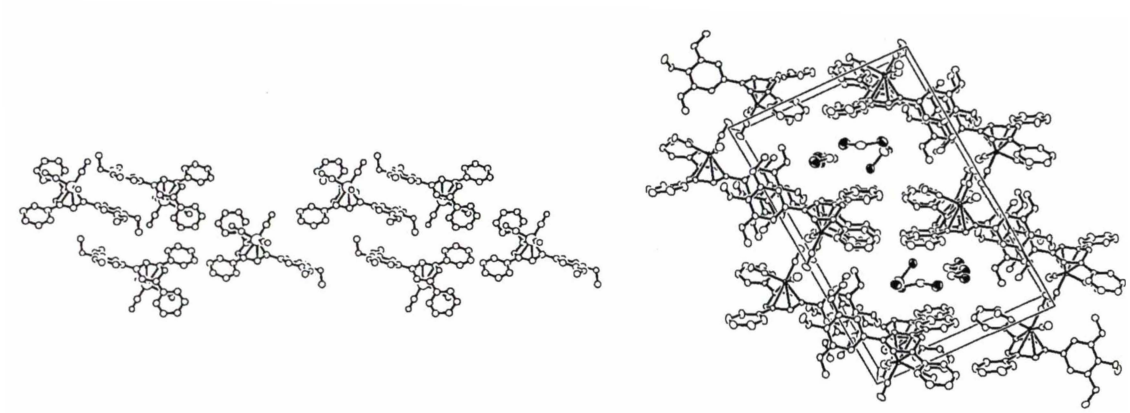


Figure 4-10 Stereo view and view of the unit cell packing of **145**.

The "columns" are arranged so that in one plane the phenyl rings of one "column" match up with the phenyl rings of the adjoining "column" (across the page, as depicted in Figure

4-10). There is no overlap between the phenyl rings of the adjoining "columns" (as shown in the stereo view). In another plane, perpendicular to that mentioned for the phenyl interaction, the "columns" are linked by interaction between the $Mn(CO)_3$ moieties. These two interactions lead to a channel running down the a axis, allowing the incorporation of solvent molecules (dichloromethane).

HMBC correlations of the pyranyl ring system.

The HMBC NMR spectrum of both of the pyranyl complexes **130** and **145** showed a correlation from one of the ring protons to a carbon of the carbonyls coordinated to the manganese centre. No mention of a correlation from a proton to a coordinated carbonyl was found in the literature.

It was unclear whether the phenomenon is limited to (η^5-pyranyl)$Mn(CO)_3$ complexes, or whether other η^5- or η^6-$LMn(CO)_3$ systems would show similar correlations. Therefore a previously prepared sample of $[\eta^6\text{-}C_6H_6Mn(CO)_3]BF_4$ (**147**) was analysed by NMR.

The ^1H NMR showed all the protons giving a singlet at 6.94 ppm, with no further peaks other than a peak at 2.11 ppm due to the residual protons of the D_6-acetone solvent, indicating a pure sample of **147**. The carbon spectrum was similarly clean, showing only two peaks at 102.0 and 215.4 ppm (excluding the solvent peaks at 29.4 and 206.1 ppm).

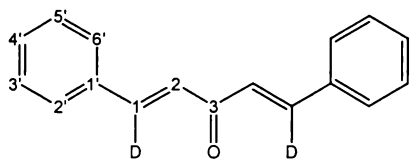
The HMBC spectrum of **147** showed the expected correlation of the aryl protons to the adjacent carbons of the aryl ring, but also showed a second correlation to the carbonyls on the manganese centre. This indicates that the correlation is common for the (η^5-pyranyl)$Mn(CO)_3$ and $[\eta^6\text{-}C_6H_6Mn(CO)_3]^+$ complexes. It suggests that the correlation is common for any compound in which the $Mn(CO)_3$ moiety has the carbonyls within the three bond range of a proton, as required for a correlation in the HMBC spectrum.

4.4. Experimental

*Preparation of 1,5-^2H,^2H-1,5-diphenylpenta-1,4-dien-3-one (**141**).*

To a 50 ml round bottom flask was added ethanol (100%, drum grade) (10 ml) and a solution of sodium hydroxide (2.0 g in 15 ml of distilled water). The resulting solution was cooled in ice, then transferred to a cold water bath and stirred with a large magnetic stirrer bar. A mixture of acetone (0.36 ml, 4.9 mmol) and d-benzaldehyde (1.0 ml, 9.8

mmol) was added drop-wise. The solution was stirred for a further hour. The resulting solution was filtered through a #2 sintered glass crucible by aid of a Büchner funnel. The residue was washed with distilled water until the filtrate was neutral to litmus paper. The residue was transferred to a round bottom flask and dried under vacuum for a number of hours. This crude product was recrystallised from hot ethyl acetate to afford pale lemon needle crystals of **141** (840 mg, 73% yield). Integration of the ^{1}H NMR of the product showed C1 was 99% deuterated.



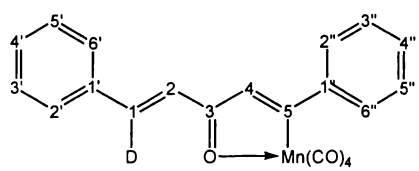
141

^{1}H NMR: ($CDCl_3$) δ 7.11 (2H, s, C2), 7.44 (6H, m, C3′/C4′/C5′), 7.65 (4H, m, C2′/C6′)

^{13}C NMR: ($CDCl_3$) δ 125.7 (C2), 128.7 (C2′/C6′), 129.3 (C3′/C5′), 130.9 (C4′), 143.3 (C1), 189.3 (C3)

*Cyclomanganation of **141**.*

141 (503 mg, 2.14 mmol) and $PhCH_2Mn(CO)_5$ (663 mg, 2.32 mmol) were transferred to a Schlenk flask containing petroleum spirits (30 ml). The solution was heated under reflux until such time as the reaction was deemed complete, as determined by the disappearance of the 2108 cm^{-1} peak due to $PhCH_2Mn(CO)_5$. After approximately 5 hours the reaction was stopped, and the solvent removed under vacuum. The residue was chromatographed (alumina column, 1:8 dichloromethane/petroleum spirits) to afford the product, **142** (390 mg, 46% yield).



142

General method for reacting cyclomanganated complexes with acetylenes.

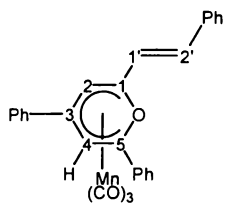
A 1:3 ratio of the cyclomanganated diaryldienone[135] and the acetylene were transferred to a 100 ml Schlenk flask with the reaction solvent, and stirred under a nitrogen atmosphere for the required time. An oil bath with thermostated heating coil was used for reactions

[135] The preparation of cyclomanganated diaryldienones can be found in the Chapter 7.3.2.

requiring a constant temperature, with the exception of reactions at reflux, which were heated directly. At the end of the reaction time, the solvent was removed under vacuum, and the residue was purified by chromatography. Pyranyl complexes were recrystallised from saturated dichloromethane and petroleum spirits by cooling to -20°C. Oxocycloheptadienyl complexes were recrystallised by vapour diffusion with ethyl acetate and petroleum spirits.

*Preparation of [4,6-diphenyl-2-(2-phenylethenyl)pyranyl-η^5]tricarbonylmanganese (**130**).*

[(1-Phenyl-2-(3-phenylprop-2-en-1-oyl))ethenyl]tetracarbonylmanganese **127** (155 mg, 0.39mmol) and phenylacetylene (155 µl, 0.98 mmol) were stirred in carbon tetrachloride (20 ml) for 28 hours. The residue was chromatographed (alumina column, 1:8 dichloromethane/petroleum spirits). The red band was collected, the solvent removed under vacuum, and the product recrystallised to give large elongated dark red crystals of **130** (49.8 mg, 27% yield).



130

M_r = 474.4 $C_{28}H_{19}MnO_4$

Elemental analysis : Calculated - C 70.89 H 4.04

Experimental -C 70.94 H 4.10

IR: (CCl_4) ν(C≡O) 2015(vs), 1956(s), 1934(s) cm^{-1}

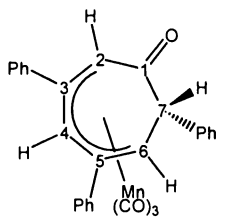
ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 505 (100%, $[M+OMe]^-$), 491 (5%, $[M+OH]^-$), 473 (12%, $[M-H]^-$); (MeOH, cone +20 V) *m/z* 335 (100%, $[M-Mn(CO)_3]^+$), 333 (76%, $[M-Mn(CO)_3-2H]^+$)

^{1}H NMR: ($CDCl_3$) δ 5.06 (1H, s, H2), 5.72 (1H, s, H4), 6.32 (1H, d, $^3J_{HH}$ = 15.6 Hz, H1′), 7.11 (1H, d, $^3J_{HH}$ = 15.6 Hz, H2′), 7.56-7.31 (13H, m, Ar-H), 7.91 (2H, d, $^3J_{HH}$ = 7.6 Hz, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 81.2 (C4) , 82.4 (C2), 94.6 (C5), 97.2 (C3), 101.1 (C1), 123.4 (Ar-H), 123.8 (C1′(C=*C*H)), 127.0 (Ar-H), 127.4 (Ar-H), 128.4 (Ar-H), 128.7 (Ar-H), 129.0 (Ar-H), 129.2 (Ar-H), 129.6 (Ar-H), 130.0 (C2′(*C*H =C)), 136.5 (Ar), 136.5 (Ar), 137.1 (Ar), 222.2 (MnC≡O)

*Preparation of [1-oxo-3,5,7-triphenylcycloheptadienyl-η^5]tricarbonylmanganese (**129**).*

[(1-Phenyl-2-(3-phenylprop-2-en-1-oyl))ethenyl]tetracarbonylmanganese **127** (115 mg, 0.288 mmol) and phenylacetylene (100 µl, 0.91 mmol) were refluxed in carbon tetrachloride (20 ml) for 24 hours. The residue was chromatographed (PLC, 1:4 ether/petroleum spirits). The yellow/orange band was eluted and the solvent removed to provide a pure product, **129** (as determined by NMR) (18 mg, 13% yield). The product was identified as **129** by comparison with literature values[131].



129

M_r = 474.4 $C_{28}H_{19}MnO_4$

IR: (heptane) ν(C≡O) 2033(vs), 1974(m), 1959(m) cm^{-1}

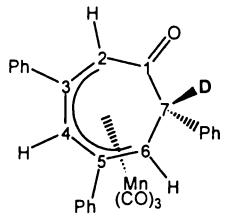
ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 505 (31%, $[M+MeO]^-$), 491 (7%, $[M+OH]^-$), 473 (100%, $[M-H]^-$); (MeOH, cone +20 V) *m/z* 335 (100%, $[M-Mn(CO)_3]^+$)

^{1}H NMR: ($CDCl_3$) δ 2.64 (1H, d, $^3J_{HH}$ = 3.5 Hz, H7), 3.99 (1H, d, $^3J_{HH}$ = 3.4 Hz, H6), 4.81 (1H, s, H2), 6.66 (1H, s, H4), 7.28-7.78 (15H, m, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 47.5 (C7), 59.2 (C6), 76.3 (C2), 95.5 (C4), 113.8 (C5), 119.5 (C3), 127.8 (Ar-H), 128.7 (Ar-H), 129.2 (Ar-H), 129.2 (Ar-H), 129.3 (Ar-H), 129.4 (Ar-H), 129.9 (Ar-H), 130.7 (Ar-H), 130.9 (Ar-H), 138.3 (C5-*i*-Ar), 138.3 (C7-*i*-Ar), 140.9 (C3-*i*-Ar), 191.4 (C1), 220.2 (MnC=O)

*Preparation of [7-deutero-1-oxo-3,5,7-triphenylcycloheptadienyl-η^5]tricarbonylmanganese (**143**).*

142 (184 mg, 0.46 mmol) and phenylacetylene (180 µl, 1.64 mmol) were refluxed in carbon tetrachloride (30 ml) for 24 hours. The residue was chromatographed (alumina column, 1:1 dichloromethane/petroleum spirits). The yellow/orange band was collected and the solvent removed to provide a pure product, **143** (as determined by NMR) (21.8 mg, 10% yield).

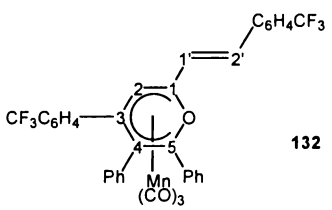


143

^{1}H NMR: ($CDCl_3$) δ 3.97 (1H, d, $^3J_{HH}$ = 3.4 Hz, H6), 4.80 (1H, s, H2), 6.64 (1H, s, H4), 7.28-7.78 (15H, m, Ar-H)

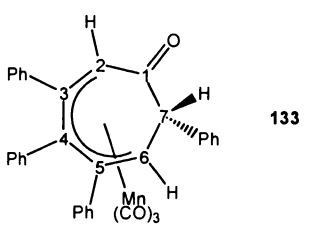
*Reaction of **127** with diphenylacetylene, 4 days at 30°C in heptane.*

[(1-Phenyl-2-(3-phenylprop-2-en-1-oyl))ethenyl]tetracarbonylmanganese **127** (104 mg, 0.26 mmol) and diphenylacetylene (143 mg, 0.80 mmol) were stirred in heptane (20 ml) at 30°C for 4 days. Monitoring of the reaction by IR spectroscopy showed minor peaks appearing at 2017, 1957, 1934 cm^{-1} which correspond to the pyranyl product **132**. The dominant peaks in the spectrum were due to **133**. The solvent was removed, and the residue chromatographed (alumina column, 1:3 ether/petroleum spirits). The yellow/orange band was collected to afford **133** (42 mg, 29% yield). No pyranyl product could be isolated.



132

IR: (heptane) ν(C≡O) 2017(vs), 1957(s), 1934(s) cm^{-1}



133

M_r = 550.5 $C_{34}H_{23}MnO_4$

IR: (CH_2Cl_2) ν(C≡O) 2028(vs), 1969(s), 1948(s) cm^{-1}

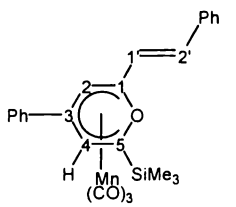
ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 581 (10%, [M+OMe]$^-$), 567 (9%, [M+OH]$^-$), 549 (100%, [M-H]$^-$)

^{1}H NMR: ($CDCl_3$) δ 2.82 (1H, d, $^3J_{HH}$ = 3.6 Hz, H7), 3.44 (1H, d, $^3J_{HH}$ = 3.6 Hz, H6), 4.67 (1H, s, H2), 6.86-7.31 (20H, m, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 47.3 (C7), 63.8 (C6), 79.7 (C2), 114.7 (C4), 116.4 (C5), 121.9 (C3), 127.6-152.5 (Ar-H, Ar), 191.4 (C1), 220.8 (MnC≡O)

*Reaction of **127** with trimethylsilylacetylene, 24 hours refluxing heptane.*

[(1-Phenyl-2-(3-phenylprop-2-en-1-oyl))ethenyl]tetracarbonylmanganese **127** (21 mg, 52 μmol) and trimethylsilylacetylene (25 μl, 177 μmol) were refluxed in heptane (10 ml) for 24 hours. The residue was chromatographed (PLC, 2:3 ethyl acetate/petroleum spirits) affording two bands. The first band was identified as **128** (7 mg, 29% yield) by comparison with literature IR data[131]. The second band was collected to afford **134** (7 mg, 29%), a yellow oil.

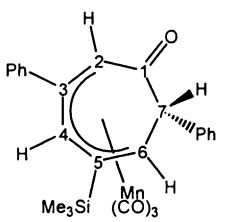


128

M_r = 470.5 $C_{25}H_{23}MnO_4Si$

IR: (CH_2Cl_2) ν(C≡O) 2017(vs), 1933(s, br) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 396 (10%, $[M-SiMe_3]^-$)



134

M_r = 470.5 $C_{25}H_{23}MnO_4Si$

IR: (petroleum spirits) ν(C≡O) 2031(vs), 1974(s), 1947(s) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 469 (79%, $[M-H]^-$), 397 (100%, $[M-SiMe_3]^-$)

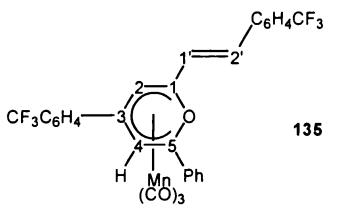
^{1}H NMR: ($CDCl_3$) δ 0.39 (9H, s, SiCH_3), 2.52 (1H, d, $^3J_{HH}$ = 3.4 Hz, H7), 3.44 (1H, d, $^3J_{HH}$ = 2.0 Hz, H6), 4.83 (1H, s, H2), 6.01 (1H, s, H4), 7.61-7.14 (10H, m, Ar-*H*)

^{13}C NMR: ($CDCl_3$) δ -1.2 ($Si(CH_3)_3$, 48.6 (C7), 67.6 (C6), 76.3 (C2), 99.1 (C4), 106.4 (C5), 122.7 (C3), 127.7 (Ar-H), 129.1 (Ar-H), 129.2 (Ar-H), 129.2 (Ar-H), 129.8 (Ar-H), 130.4 (Ar-H), 138.2 (Ar), 140.8 (Ar), 188.5 (C1), 220.5

(MnC=O)

*Reaction of **131** with phenylacetylene, 24 hours refluxing heptane.*

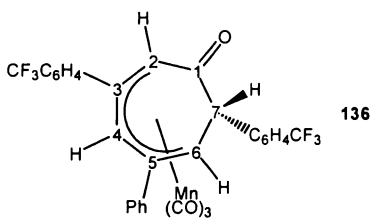
[(1-(2-Trifluoromethylphenyl)-2-(3-(2-trifluoromethylphenyl)prop-2-en-1-oyl))-ethenyl]tetracarbonylmanganese **131** (53 mg, 99 μmol) and phenylacetylene (35 μl, 0.32 mmol) were refluxed in heptane (10 ml) for 24 hours. The residue was chromatographed (PLC, 1:3 ether/petroleum spirits) to afford two fractions. The first fraction was identified as **135** (10 mg, 17% yield) by comparison with literature IR ν(C≡O) data[131]. The second fraction was collected to afford **136** (32 mg, 52% yield), a yellow oil, which was crystallised by vapour diffusion for elemental analysis.



135

M_r = 610.4 $C_{30}H_{17}F_6MnO_4$

IR: (heptane) ν(C≡O) 2014(vs), 1935(s, br) cm^{-1}



136

M_r = 610.4 $C_{30}H_{17}F_6MnO_4$

Elemental analysis : Calculated - C 59.03 H 2.81

Experimental -C 59.25 H 2.65

IR: (heptane) ν(C≡O) 2033(vs), 1973(s), 1960(s) cm^{-1}

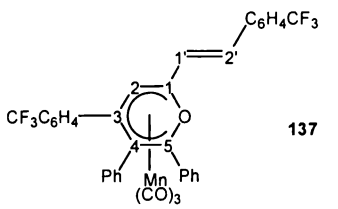
ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 641 (100%, $[M+OMe]^-$), 627 (26%, $[M+OH]^-$), 609 (10%, $[M-H]^-$)

^1H NMR: ($CDCl_3$) δ 2.94 (1H, d, $^3J_{HH}$ = 2.9 Hz, H7), 4.04 (1H, s, H6), 4.61 (1H, s, H2), 6.40 (1H, s, H4), 7.41-7.85 (13H, m, Ar-*H*)

^{13}C NMR: ($CDCl_3$) δ 41.8 (C7), 61.0 (C6), 77.0 (C2), 97.8 (C4), 112.0 (C5), 120.9 (C3), 125.5-138.9 (Ar-H, Ar-CF_3, Ar), 187.8 (C1), 219.7 (MnC=O)

*Preparation of [1-oxo-4,5-diphenyl-3,7-(2-trifluoromethylphenyl)cycloheptadienyl-η^5]-tricarbonylmanganese (**138**).*

[(1-(2-Trifluoromethylphenyl)-2-(3-(2-trifluoromethylphenyl)prop-2-en-1-oyl))ethenyl]-tetracarbonylmanganese **131** (100 mg, 0.186 mmol) and diphenylacetylene (108 mg, 0.606 mmol) were stirred in heptane (20 ml) at 30°C for 48 hours. The residue was chromatographed (PLC, 1:3 ethyl acetate/petroleum spirits) to afford four fractions. The first two fraction contained unreacted starting material. The fourth fraction was collected to afford **137** (17 mg, 13% yield), a yellow oil. The third band was identified as **138** (12 mg, 9% yield) by comparison with literature IR ν(C≡O) data[131].



137

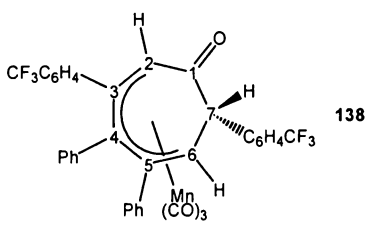
M_r = 686.5 $C_{36}H_{21}F_6MnO_4$

IR: (heptane) ν(C≡O) 2020(vs), 1962(s), 1935(s) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 717 (100%, $[M+OMe]^-$), 703 (28%, $[M+OH]^-$), 585 (47%, $[M-H]^-$)

^1H NMR: ($CDCl_3$) δ 4.93 (1H, s, H2), 6.29 (1H, d, $^3J_{HH}$ = 15.4 Hz, H2'), 7.00-7.74 (18H, m, Ar-H/H1'), 8.22 (1H, d, $^3J_{HH}$ = 7.6 Hz, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 82.1 (C2), 84.4 (C4), 102.9 (C3), 104.2 (C5), 104.7 (C1), 123.2-138.9 (Ar-H, Ar), 220.6 (MnC=O)



138

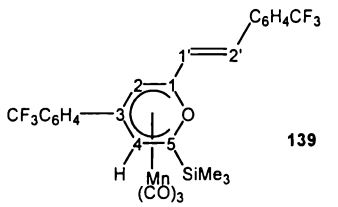
M_r = 686.5 $C_{36}H_{21}F_6MnO_4$

IR: (heptane) ν(C≡O) 2030(vs), 1972 (s), 1952(s) cm^{-1}

*Reaction of **131** and trimethylsilylacetylene, 7 days refluxing heptane.*

[(1-(2-Trifluoromethylphenyl)-2-(3-(2-trifluoromethylphenyl)prop-2-en-1-oyl))-ethenyl]-tetracarbonylmanganese **131** (171 mg, 0.32 mmol) and trimethylsilylacetylene (150 μl, 1.1

mmol) were refluxed in heptane (20 ml) for 7 days. The residue was chromatographed (PLC, 1:1 dichloromethane/petroleum) affording three bands. The first contained unreacted starting material. The second band identified as **139** (69 mg, 36% yield) by comparison with literature IR ν(C≡O) data[131]. The third fraction was collected to afford **140** (39 mg, 20% yield), a yellow oil, which was crystallised by vapour diffusion for elemental analysis.

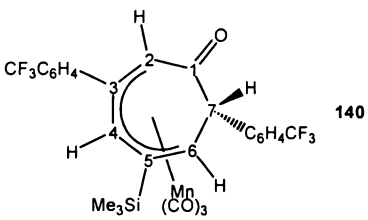


139

M_r = 606.5 $C_{27}H_{21}F_6MnO_4Si$

IR: (petroleum spirits) ν(C≡0) 2017(vs), 1958(s), 1936(s) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 637 (32%, $[M+OMe]^-$), 565 (100%, $[M+H-SiMe_3+OMe]^-$), 533 (6%, $[M-SiMe_3]^-$)



140

M_r = 606.5 $C_{27}H_{21}F_6MnO_4Si$

Elemental analysis : Calculated - C 53.47 H 3.49

Experimental -C 53.78 H 3.41

IR: (petroleum spirits) ν(C≡0) 2030(vs), 1972(s), 1949(s) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 565 (100%, $[M+H-SiMe_3+OMe]^-$), 551 (8%, $[M+H-SiMe_3+OH]^-$), 533 (28%, $[M-SiMe_3]^-$); (MeCN/formic) *m/z* 1235 (8% $[2M+Na]^+$), 1213 (15%, $[2M+H]^+$), 607 (100%, $[M+H]^+$)

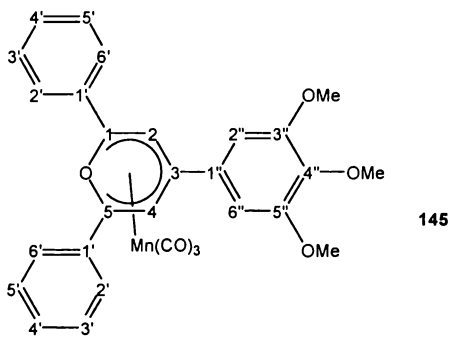
^{1}H NMR: ($CDCl_3$) δ 0.35 (9H, s, $SiMe_3$), 2.88(1H, d, $^3J_{HH}$ = 2.9 Hz, H7), 3.50 (1H, s, H6), 4.68 (1H, s, H2), 5.75 (1H, s, H4), 7.41-7.79 (8H, m, Ar-H)

^{13}C NMR: ($CDCl_3$) δ -1.6 ($SiMe_3$), 43.2 (C7), 70.7, (C6), 77.3 (C2), 102.0 (C4), 104.1 (C5), 122.2 (d, $^2J_{CF}$ = 14.1 Hz, *Ar*-CF_3), 124.1 (C3), 125.4 (q, $^1J_{CF}$ = 5.6 Hz, CF_3), 125.8 (d, $^2J_{CF}$ = 13.3 Hz, *Ar*-CF_3), 126.9 (q, $^1J_{CF}$ = 5.3 Hz, CF_3), 127.2 (Ar-H), 129.6 (Ar-H), 131.0 (Ar-H), 132.4 (Ar-H), 132.6 (Ar-H), 136.4 (Ar),

138.8 (Ar), 184.8 (C1), 219.7 (MnC=O)

*Preparation of [2,6-diphenyl-4-(3,4,5-trimethoxyphenyl)pyranyl-η^5]tricarbonylmanganese **145**.*

Orthomanganated 1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**31**) (103 mg, 0.222 mmol) and phenylacetylene (100 µl, 0.909 mmol) were transferred to a Schlenk flask with dioxane (15 ml) and heated to reflux for 2 hours. The solvent was removed under vacuum, and the residue chromatographed (PLC plate, 1:1 petroleum spirits/ether) to afford three fractions. The first two were minor fractions containing phenylacetylene and another unidentified product. The third, major, fraction contained **145**, which was collected as an orange solid (75 mg, 62% yield). The product was recrystallised by vapour diffusion with dichloromethane/petroleum spirits to afford dark orange crystals.



145

M_r = 538.4 $C_{29}H_{23}MnO_7$

Elemental analysis : Calculated - C 64.69 H 4.31

Experimental -C 65.23 H 4.47

IR: (petroleum spirits) ν(C≡0) 2013(vs), 1949(s), 1931(s) cm^{-1}

ESMS: (MeOH/NaOMe, cone -20 V) *m/z* 569 (100%, $[M+OMe]^-$)

ESMS: (MeOH, cone +20 V) *m/z* 399 (100%, $[M-Mn(CO)_3]^+$), 539 (22%, $[M+H]^+$), 561 (48%, $[M+Na]^+$), 1099 (73%, $[2M+Na]^+$), 1637 (8%, $[3M+Na]^+$)

^{1}H NMR: ($CDCl_3$) δ 3.98 (3H, s, OMe), 4.02 (6H, s, OMe), 5.57 (2H, s, H2/H4), 7.16 (2H, s, C2″/C6″), 7.36 (1H, t, $^3J_{HH}$ = 7.1 Hz, C4′), 7.45 (2H, t, $^3J_{HH}$ = 7.6 Hz, C3′/C5′), 7.52 (2H, d, $^3J_{HH}$ = 7.8 Hz, C2′/C6′)

^{13}C NMR: ($CDCl_3$) δ 56.4 (OCH_3), 61.1 (OCH_3), 81.5 (C2/C4), 94.9 (C1/C5), 98.5 (C3), 104.9 (C2″/C6″), 123.3 (C2′/C6′), 128.3 (C4′), 128.9 (C3′/C5′), 132.7 (C1″), 135.7 C1′), 138.7 (C4″), 153.8 (C3″/C5″), 221.9 ($Mn(CO)_3$)

4.4.1. Crystal data and structure refinement tables

Crystal data and structure refinement of 130.

Empirical formula	$C_{28}H_{19}MnO_4$
Formula weight	474.37
Temperature	168 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.165(4) Å
	b = 12.397(4) Å β = 109.912(4)°
	c = 13.581(4) Å
Volume	2242.3(12) $Å^3$
Z	4
Density (calculated)	1.405 g/cm^3
Absorption coefficient	0.621 mm^{-1}
F(000)	976
Theta range for data collection	2.24 to 26.41°
Index ranges	-17<=h<=17, -9<=k<=15, -16<=l<=16
Reflections collected	28951
Independent reflections	4552 [R(int) = 0.0332]
Completeness to theta = 26.41°	98.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4552 / 0 / 374
Goodness-of-fit on F^2	1.137
Tmin/Tmax	0.863 and 1.000
Final R indices [I>2sigma(I)]	R_1 = 0.0464, wR_2 = 0.1240
R indices (all data)	R_1 = 0.0584, wR_2 = 0.1305
Largest diff. peak and hole	1.090 and -0.333 $e.Å^{-3}$

Crystal data and structure refinement of 145.

Empirical formula	$C_{30.5}H_{26}Cl_3MnO_7$ ($C_{29}H_{23}MnO_7.1½CH_2Cl_2$)	
Formula weight	665.80	
Temperature	200 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2119(2) Å	α = 94.638(1)°
	b = 14.5024(3) Å	β = 100.469(1)°
	c = 22.7430(3) Å	γ = 93.699(1)°
Volume	2968.24(1) $Å^3$	
Z	4	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	0.761 mm^{-1}	
F(000)	1364	
Crystal size	0.30 x 0.24 x 0.38 mm^3	
Theta range for data collection	0.91 to 25.39°.	
Index ranges	-11<=h<=10, -17<=k<=17, 0<=l<=27	
Reflections collected	26577	
Independent reflections	10816 [R(int) = 0.0176]	
Completeness to theta = 25.39°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10816 / 0 / 956	
Goodness-of-fit on F^2	1.043	
Tmin/Tmax	0.811 and 0.918	
Final R indices [I>2sigma(I)]	R_1 = 0.0296, wR_2 = 0.0743	
R indices (all data)	R_1 = 0.0402, wR_2 = 0.0799	
Largest diff. peak and hole	0.260 and -0.273 e. $Å^{-3}$	

Chapter 5. Reactions of Azabutadienes with Unsaturated Molecules.

5.1. Introduction

The 1-azabuta-1,3-diene (AD) family of compounds can act as ligands by coordination through the two π-bonds and/or the electron lone pair on the nitrogen, offering a range of coordination modes to transition metals (TM). A selection of metal coordination modes is shown in Figure 5-1. Mode F shows the coordination of the deprotonated 1-azabuta-1,3-dienyl ([AD-H]) that is of most interest to the present study.

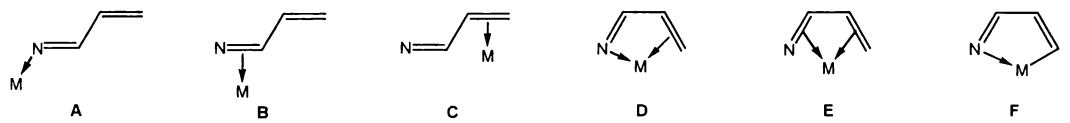


Figure 5-1 Mono and bidentate coordination of AD ligands (A, B, C, D and E) and of [AD-H] (F).

For such a wide range of possible coordination modes there appears to be a narrow range to the TM complexes that have previously been prepared. The literature indicates that AD and [AD-H] ligands are limited to Ta, Cr, Mo, Mn, Fe, Ru, Co, Ni and Pt complexes. There has been little research into the reactivity of these complexes (with regards to synthetic chemistry), and only one preliminary investigation into the preparation of cyclomanganated complexes has previously been undertaken.

The first azabutadiene complexes were the iron carbonyl species reported in 1967[136]. The $Fe(AD)(CO)_3$ complexes were prepared by thermal or photochemical reaction of either $Fe_2(CO)_9$ or $Fe(CO)_5$ and the desired AD ligand, and resulted in the bidentate coordination mode E via coordination of the four π-electrons of the two unsaturated bonds.

The $(OC)_3Fe(AD)$ complexes have been shown to efficiently transfer the $Fe(CO)_3$ moiety to cyclohexa-1,3-dienes[137]. Further research has led to the development of a catalytic

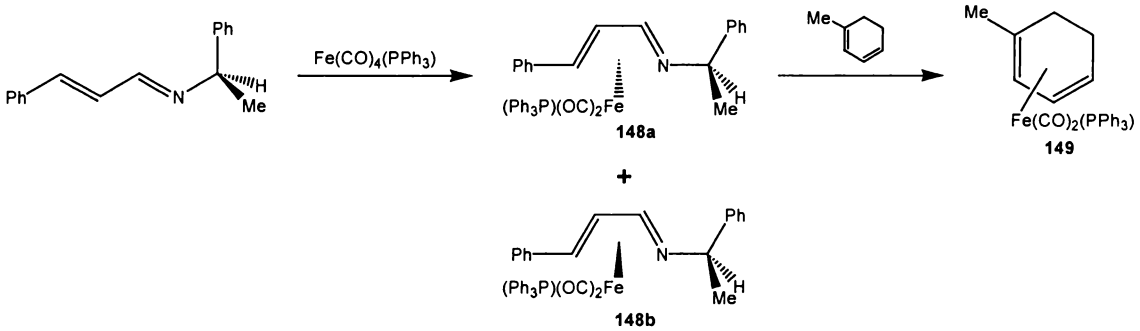
[136] S. Otsuka, T. Yoshida, A. Nakamura, *Inorg. Chem.*, **6** (1967) 20

[137] H-J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P. G. Jones, *Eur. J. Inorg. Chem.* (1998) 993

process for generating Fe(η^4-cyclohexa-1,3-diene)$(CO)_3$ from $Fe_2(CO)_9$[138]. Catalytic amounts of AD have enabled both of the $Fe(CO)_3$ fragments of $Fe_2(CO)_9$ to be utilised, allowing quantitative complexation with cyclohexa-1,3-diene.

A further development of this chemistry was the preparation of optically pure $Fe(AD)L_3$ complexes ($L_3 = (CO)_2(PPh_3)$)[139]. These complexes were further used to transfer the FeL_3 moiety to cyclohexa-1,3-dienes, generating optically pure complexes.

$Fe(CO)_4(PPh_3)$ and 4-phenyl-(1'R)-(1'-phenylethyl)-1-azabuta-1,3-diene when subjected to UV radiation produced two diastereoisomers (**148a** and **148b**). Pure **148a** could be obtained by column chromatography. The reaction of this complex with 1-methylcyclohexa-1,3-dienes gave optically active Fe(η^4-1-methylcyclohexa-1,3-diene)$(CO)_2(Ph_3P)$ **149**. When **149** is prepared by other methods a mixture of optical isomers is produced that cannot be effectively separated by chromatography.

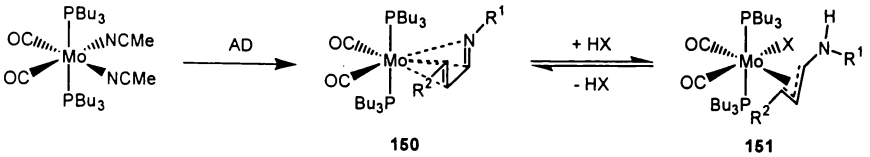


Molybdenum forms complexes with similar coordination to that seen in the $Fe(AD)(CO)_3$ complexes above. Substitution of the acetonitrile ligands of $Mo(PBu_3)_2(CO)_2(CH_3CN)_2$ with AD leads to the production of **150**[140]. The complex can be reversibly protonated at the nitrogen, leading to the production of complex **151**.

[138] H-J. Knölker, E. Baum, P. Gonser, G. Rohde, H. Röttele, *Organometallics*, **17** (1998) 3916

[139] L. A. P. Kane-Maguire, S. G. Pyne, A. F. H. Siu, B. W. Skelton, A. H. White, *Aust. J. Chem.*, **49** (1996) 673

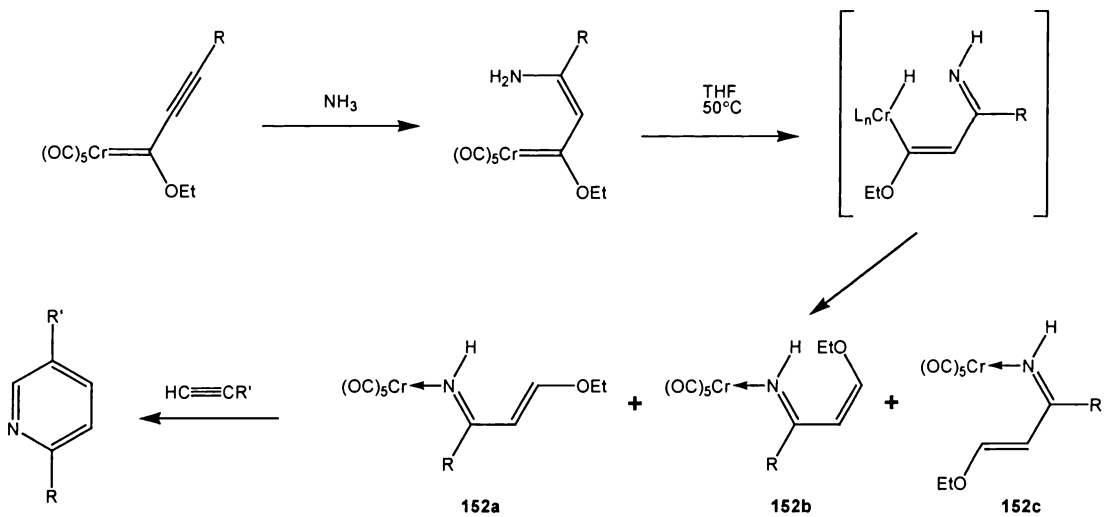
[140] F. Hohmann, H. T. Dieck, K. D. Franz, K. A. O. Starzewski, *J. Organomet. Chem.*, **55** (1973) 321



150 151

Not all TM-AD and TM-[AD-H] complexes are produced by direct reaction of a TM complex and the AD ligand. The following chromium and cobalt complexes were produced by reaction of pre-coordinated precursors to form the ligand complex.

The Cr-AD complex isomers **152a**, **152b** and **152c** were prepared from the alkynyl carbene by reaction with ammonia[141]. Three different isomers where formed depending on the R-group involved, but in each case the coordination was through the lone pair of electrons on the nitrogen. The Cr-AD complexes could be further reacted with acetylenes to form 2,5-disubstituted pyridines.

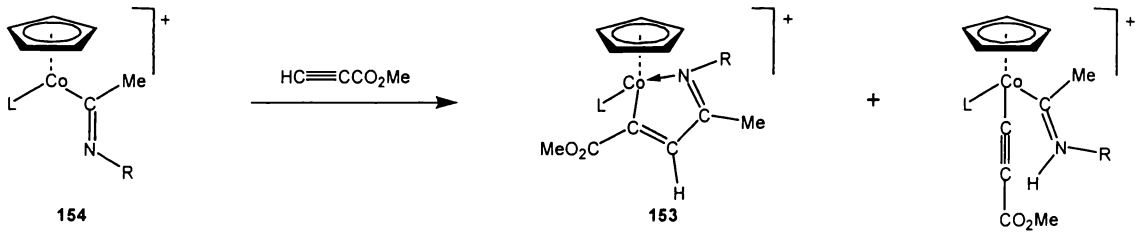


152a 152b 152c

A Co-AD complex (**153**) with η^2-C,N coordination of the [AD-H] ligand was obtained from the reaction of **154** with $HC{\equiv}CCO_2Me$[142]. The reaction is general for a range of HC≡CR, though the nature of the terminal R-group affects the rate of reaction: CH_2OH, CH_2OMe, $(CH_2)_2OH$ > H, Me > Ph, *n*Bu.

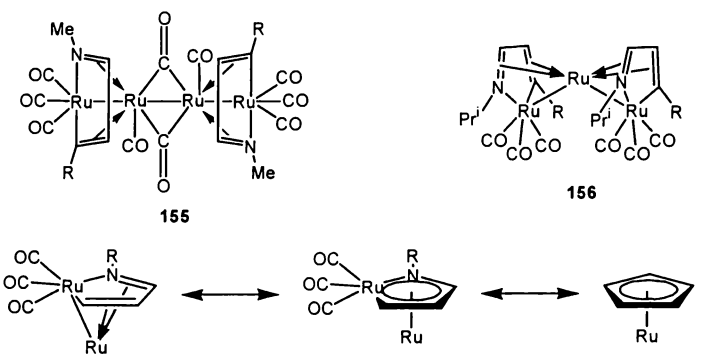
[141] M. Duetsch, F. Stein, F. Funke, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.*, **126** (1993) 2535

[142] H. Werner, L. Xiaolan, K. Peters, H. G. von Schnering, *Chem. Ber.*, **130** (1997) 565



Of more interest to the present study is the formation and reactions of complexes with the deprotonated version of the azabutadiene, namely TM-[AD-H] complexes similar to **153**.

The thermal reaction of $Ru_3(CO)_{12}$ with AD has generated a number of different products[143,144,145,146]. The first to be isolated was the linear cluster $[AD\text{-}H]_2Ru_4(CO)_{10}$ (**155**). The terminal $[AD\text{-}H]Ru(CO)_3$ fragments are isolobal with the cyclopentadienyl ligand. The Ru_3 complex **156**, equivalent to $RuCp_2$, has also been isolated.



The similarity between cyclopentadienyl and the $[AD\text{-}H]Ru(CO)_3$ fragment has allowed the preparation of a range of heteronuclear [AD-H] species. The reaction of **155** with oxidising reagents such as I_2, Br_2 and CCl_4, followed by treatment with CO, led to the production of mononuclear $[AD\text{-}H]RuX(CO)_3$ complexes. Further reaction with anionic $M(CO)_n^-$ species can generate a range of heteronuclear species with, $[AD\text{-}H]Ru(CO)_3$ acting as a cyclopentadienyl ligand.

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[143] L. H. Polm, W. P. Mul, C. J. Elsevier, K. Vrieze, M. J. N. Christophersen, C. H. Stam, *Organometallics*, 7 (1988) 423

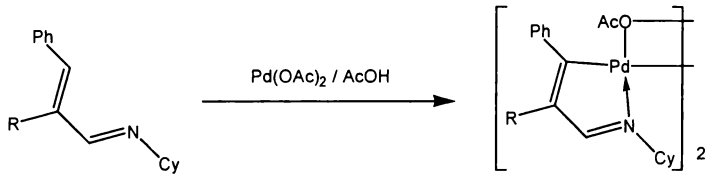
[144] W. P. Mul, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, *Inorg. Chem.*, **30** (1991) 4152

[145] C. J. Elsevier, W. P. Mul, K. Vrieze, *Inorg. Chim. Acta*, **198** (1992) 689

[146] W. Imhof, *J. Chem. Soc., Dalton Trans.*, (1996) 1429

The [AD-H] ligand in this case is acting as a spectator, allowing the preparation of the heteronuclear species, but no reactions have been undertaken involving the [AD-H] ligand in this case.

Very recently dinuclear Pd-[AD-H] (**157**) complexes have been prepared by the treatment of the AD ligands with $Pd(OAc)_2$[147]. The dinuclear complexes could be converted to the mononuclear complexes by reaction with Tl(acac), $Tl(C_5H_5)$ or triphenylphosphine, but no further reactions of the ligand complex have yet been reported.

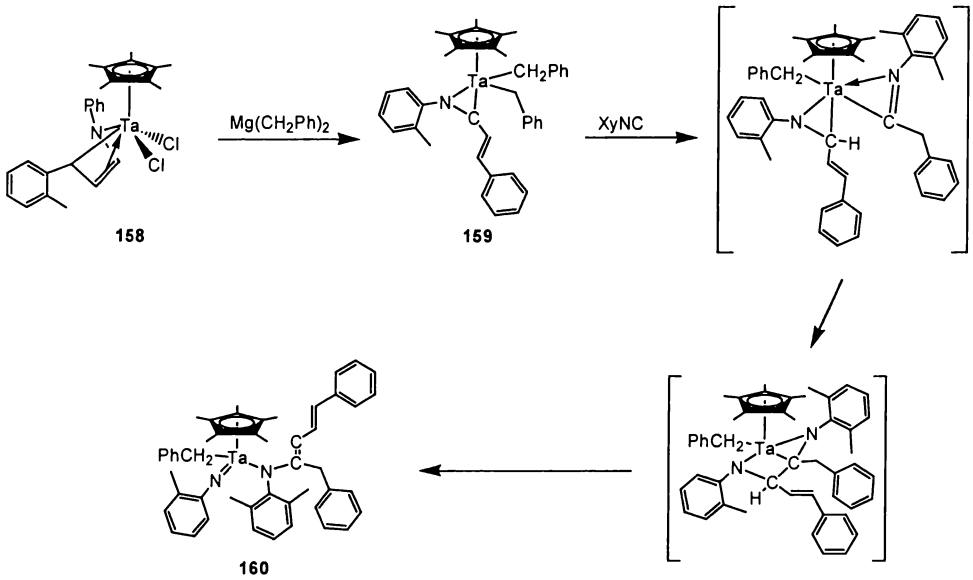


157

Few reactions of coordinated AD ligands have been reported. One that has been observed for a Ta-AD complex involves a reaction with 2,6-xylyl isocyanide (CNXy). The Ta complex **158** was prepared from $[TaCl_2Cp^*]_2$. Treatment of **158** with $Mg(CH_2Ph)_2$ resulted in the coordination mode changing from η^4 to η^2, affording **159**[148]. Further reaction with the CNXy led to the production of complex **160** possessing an amido and imido ligand. The carbon chain is cleaved from the coordinated azabutadiene, to be attached to the isocyanide. The proposed mechanism is shown in Scheme 5-1.

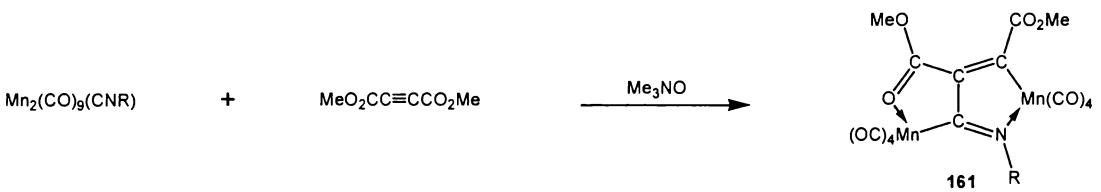
[147] S. Tenreiro, G. Alberdi, J. Martínez, M. López-Torres, J. M. Ortigueira, M. T. Pereira, J. M. Vila, *Inorg. Chim. Acta*, **342** (2003) 145

[148] K. Mashima, Y. Matsuo, S. Nakahara, K. Tani, *J. Organomet. Chem.*, **593** (2000) 69



Scheme 5-1 Proposed mechanism for the reaction of a coordinated [AD-H] ligand with CNR.

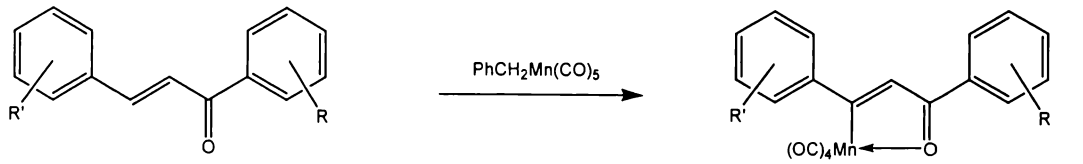
Only one cyclomanganated azabutadiene has been reported in the literature, that being the dimanganese complex **161**[23]. This was not prepared from direct reaction with a AD compound, but by oxidative activation (Me_3NO) of $Mn_2(CO)_9(CNR)$ in the presence of $MeO_2CC{\equiv}CCO_2Me$.



5.2. Aim of Present Study

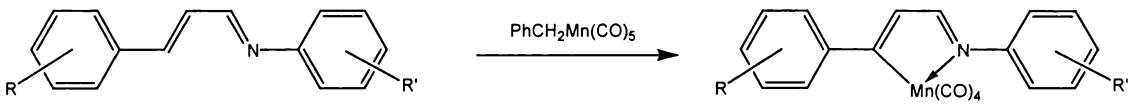
The aim of the present study was to directly prepare cyclomanganated azabutadienes by the method developed for the cyclomanganation of chalcones[20]. The azabutadiene compounds were initially of interest because of their similarity to the chalcone compounds used to make cyclomanganated complexes of the general form **162**. These cyclomanganated chalcones undergo insertion reactions with various unsaturated compounds (e.g. alkenes[20], alkynes[21], and alkyl halides[149]) to form a range of novel compounds.

[149] Chapter 6 of this thesis



162

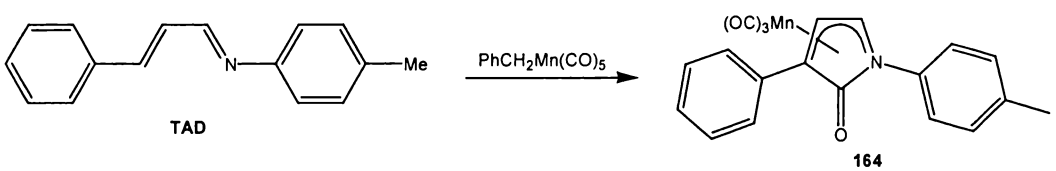
It was envisioned in the present study that azabutadienes could similarly be cyclomanganated to form the analogous cyclomanganated complex **163**, and that further reactions with unsaturated compounds would lead to further novel chemistry.



163

5.3. Results and Discussion

A preliminary investigation had been undertaken to determine if cyclomanganated azabutadienes could be prepared directly. The azabutadiene 4-phenyl-1-(4-tolyl)-1-azabuta-1,3-diene (TAD) was reacted with $PhCH_2Mn(CO)_5$. From the results of the study it could not be ascertained what reactions were occurring, or whether the cyclomanganated complex was being formed. The only compound isolated was complex **164**, for which a crystal structure was obtained (an ORTEP perspective view is shown in Figure 5-2). No supporting data were obtained[150].



164

[150] Unpublished data, Daniel Van Der Pas, undergraduate project, University of Waikato, (2002)

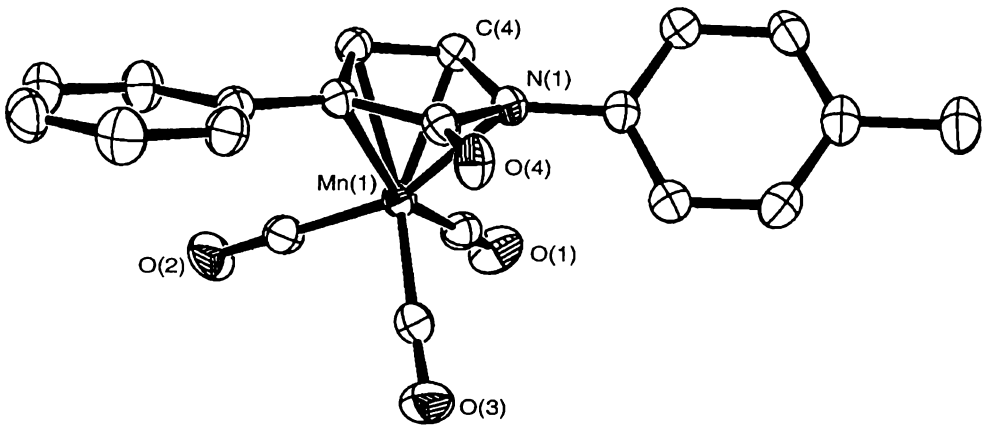


Figure 5-2 ORTEP perspective view of **164**.

Clearly this is an interesting reaction which merited further study.

The reactions in the initial investigation were conducted under more forcing conditions than generally applied for the preparation of cyclomanganated complexes. In the previous study the reactants were heated in refluxing petroleum spirits for 6 hours, whereas under standard conditions the reactants are heated for only as long as the precursors are still detectable by IR spectroscopy, generally 2 hours. The much longer reaction time may have led to the cyclomanganated complex (**163**) undergoing further reaction to afford the isolated product **164**. Therefore the reaction was repeated under milder conditions to determine if **163** could be isolated.

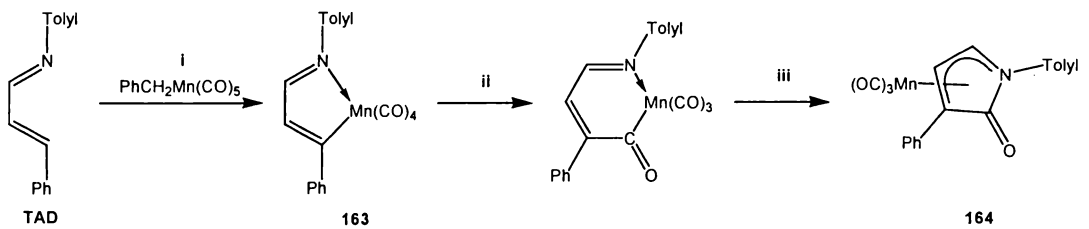
Reaction of 4-phenyl-1-(4-tolyl)-1-azabuta-1,3-diene (TAD) with $PhCH_2Mn(CO)_5$.

To determine if the cyclomanganated complex **163** could be isolated, the reaction was repeated in heptane using an oil bath to slowly raise the temperature of the reaction mixture over a number of hours. IR spectroscopy was used to monitor the reaction, using the distinctive peaks observed for the $Mn(CO)_3$ and $Mn(CO)_4$ moieties.

No reaction was observed until the temperature of the oil bath reacted 70°C, at which time a peak at 2034 cm^{-1} appeared, accompanied by a small feature on the baseline at 2076 cm^{-1}. The first peak is indicative of the $Mn(CO)_3$ moiety, comparing to 2028-32 cm^{-1} seen for (diaryloxocycloheptadienyl)$Mn(CO)_3$ complexes[31]. The minor feature is indicative of the

$Mn(CO)_4$ moiety, comparing to 2079-84 cm^{-1} seen for cyclomanganated chalcones **162**[151].

As the reaction continued, the 2034 cm^{-1} peak became more dominant, while the 2076 cm^{-1} peak was never more than a minor feature. It was not possible to isolate the product affording the peak at 2076 cm^{-1} (which is presumably the cyclomanganated $Mn(CO)_4$ complex **163**), with **164** being isolated as the only product. The IR spectra indicate that the cyclomanganated complex **163** is an intermediate, being formed initially, but then rapidly converted to **164** (Scheme 5-2). It is thought that after the formation of **163** (step **i**), one of the coordinated carbonyls inserts into the Mn-C bond of **163** (step **ii**), with the complex undergoing subsequent cyclisation (step **iii**). The remaining $Mn(CO)_3$ moiety then moves into a position to coordinate to the pyrrolone ring to afford the final product **164**.



Scheme 5-2 Proposed route for the production of **164**, showing the proposed reactive intermediate **163**.

In order to fully characterise the product, the reaction was repeated in refluxing petroleum spirits, and after a reaction time of 6 hours a yield of 35% was obtained for **164**. The IR spectrum of the reaction mixture indicated that even after this time there was unreacted starting material, but longer reaction times were not used due to increasing degradation of the $PhCH_2Mn(CO)_5$ and the product **164**.

Spectroscopic and mass spectrometric characterisation

The IR spectrum of **164** showed three peaks at 2034, 1962 and 1945 cm^{-1}, indicative of a $Mn(CO)_3$ moiety coordinating to a planar, 5 electron donor ring system. The peaks are very similar to those observed for the (η^5-oxocycloheptadienyl)$Mn(CO)_3$ complexes discussed in Chapter 4.

ESMS analysis required that the sample be run as a MeOH solution with NaOMe added to

[151] W. Tully, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **503** (1995) 75

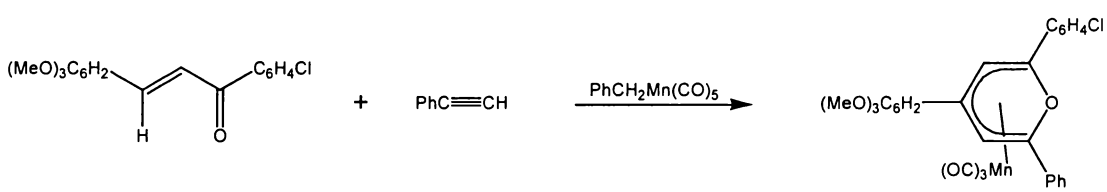
facilitate chemical ionisation. As there are no easily abstractable protons, the negative ion spectrum was dominated by a peak assigned to the formation of $[M+OMe]^-$ (*m/z* 418), with small contributions from $[M-H]^-$ and $[2M+OMe]^-$ species.

The NMR spectra further confirmed the structure of **164**, with 2D-NMR allowing full assignment of the complex. The protons on the pyrrolone ring gave doublets at 5.98 and 6.23 ppm.

Further reactions of TAD.

As the cyclomanganated intermediate **163** could not be isolated, it was not possible to do step-wise reactions with unsaturated substrates as has been done with other cyclomanganated complexes in the past. However, "one-pot" reactions have been looked into for some cyclomanganated systems, and this method has been shown to be effective.

An example of the "one-pot" method is the reaction of acetylenes with chalcones[152] (Scheme 5-3), where equivalent yields were obtained for the product via both the direct ("one-pot") method, and the indirect method (where the cyclomanganated complex was isolated before further reaction). It should be noted that there were no competing insertion reactions involved in that system.



Scheme 5-3 "One-pot" synthesis of (η^5-pyranyl)$Mn(CO)_3$ complexes[152].

As the "one-pot" method had been proven successful for the insertion of acetylenes, the analogous reaction was conducted for the azabutadiene TAD.

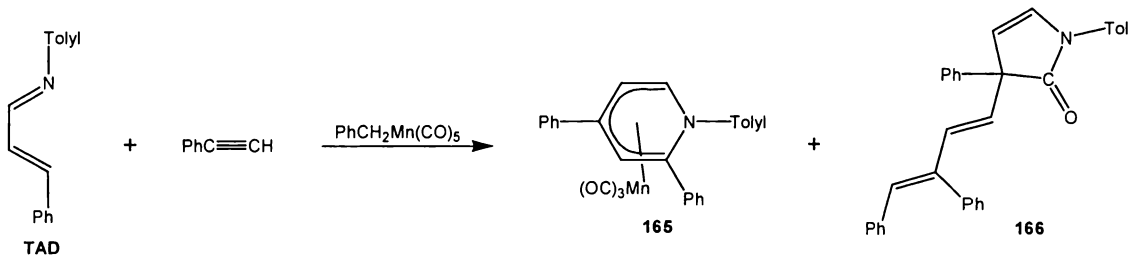
Reaction of TAD with $PhCH_2Mn(CO)_5$ and PhC≡CH.

An approximate 1:3:1 mixture of TAD, PhC≡CH and $PhCH_2Mn(CO)_5$ was heated in

[152] W. Tully, Ph.D. thesis, University of Waikato, (1994)

petroleum spirits. An IR spectrum taken as soon as the mixture had reached reflux indicated that a reaction was occurring, with peaks appearing at 2025, 1965 and 1946 cm^{-1}. This pattern of peaks is indicative of a $Mn(CO)_3$ group, and the peak at 2025 cm^{-1} is ~10 cm^{-1} lower than the corresponding peak for **164**, indicating that a new product was being formed.

As the reaction continued, no other peaks were apparent, indicating only one manganese-containing product. Work-up of the reaction mixture afforded two products, **165** (87%) and the tentatively assigned structure **166** (10%).



Spectroscopic and mass spectrometric characterisation.

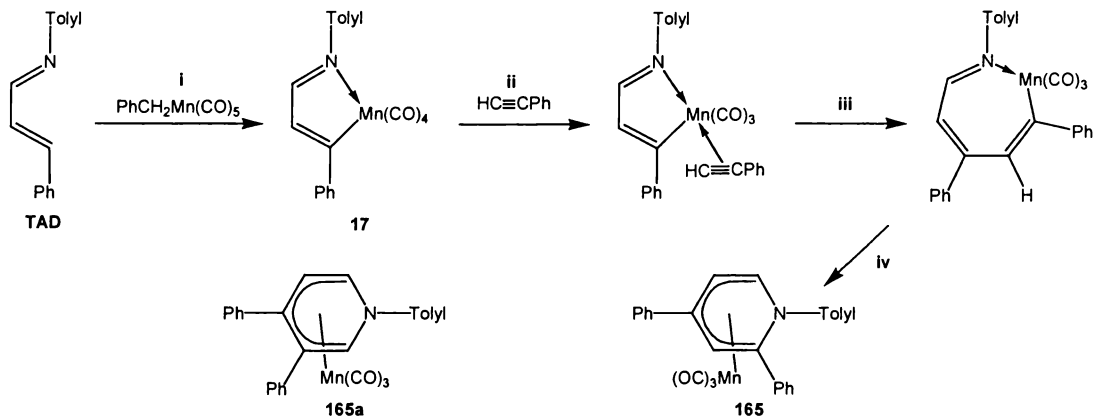
The IR spectrum of **165** showed three ν(C≡O) signals (2025, 1965 and 1946 cm^{-1}), indicating a $Mn(CO)_3$ moiety, but with less electron donation to the $Mn(CO)_3$ from the ligand than in the case of **164**. The peaks are similar to those observed for the (η^5-pyranyl)$Mn(CO)_3$ complexes discussed in Chapter 4. The peak at 2025 cm^{-1} is slightly higher in frequency than the equivalent peak of the (η^5-pyranyl)$Mn(CO)_3$ complexes, which is likely due to the difference in the electronegativities of the oxygen and the nitrogen. The nitrogen withdraws less electron density from the ring system compared to the oxygen.

The ESMS spectrum of **165** when run in MeOH (with NaOMe added to aid chemical ionisation) showed a negative ion spectrum dominated by a peak assigned as $[M+OMe]^-$, with a minor peak of $[M-H]^-$. This corresponded to a molecular mass of 461 amu, which is consistent with a combination of [TAD-H], $Mn(CO)_3$ and PhCCH fragments.

The ^1H NMR spectrum showed 14 proton signals in the aromatic region (6.58 - 7.70 ppm) confirming that a phenyl acetylene had been incorporated into the molecule. Three further

proton signals were observed at 5.01, 5.52 and 6.29 ppm. Analysis of the 2D-NMR spectra showed that the structure was consistent with **165**, where the phenyl acetylene had been inserted into the Mn-C bond of the proposed intermediate **163**, with subsequent cyclisation.

Scheme 5-4 shows the proposed reaction mechanism for the production of **165**. In step **ii** the phenyl acetylene coordinates to the manganese by displacing a carbonyl. The acetylene inserts into the Mn-C bond of the intermediate (step **iii**) with the more sterically bulky phenyl group towards the manganese. Step **iv** involves the cyclisation of the inserted acetylene, with the $Mn(CO)_3$ moiety moving to coordinate the π-electrons of the ring system.



Scheme 5-4 Proposed reaction mechanism for the forming of **165**.

This isomer of **165** was confirmed in the NMR experiments, as the proton from the phenyl acetylene correlates to one of the protonated carbons of the original TAD. If the alternate isomer **165a** were produced, this correlation would not be seen, as this would be further than the four bond distance for HMBC correlations.

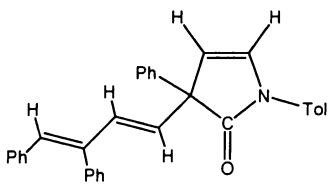
The product **165** is the N-analogue of the pyranyl complexes formed from the reaction of cyclomanganated chalcones and acetylenes. It is therefore evident that the cyclomanganated complex **163** is initially formed, with PhC≡CH preferentially inserting into the Mn-C bond.

For the by-product **166**, it was determined by IR spectroscopy that there was no

manganese carbonyl moiety present due to an absence of peaks in the 2000 cm^{-1} region of the spectrum. A peak was observed at 1676 cm^{-1}, indicating either a carbonyl or imine group was present.

The ESMS of **166** was run in MeOH (with NaOMe), and showed a dominant $[M-H]^-$ peak, with a minor peak assigned $[2M-H]^-$. This is consistent with a molecular mass of 453 amu, which corresponds to the addition of two PhC≡CH and one CO group to the TAD.

The ^1H NMR spectrum showed 19 aromatic protons and a methyl group, confirming the incorporation of two PhC≡CH groups and the original TAD. The ^1H NMR also showed five other proton signals at 3.34, 3.40, 3.75, 5.33 and 6.42 ppm. The coupling constants of the latter two signals (7.2 and 7.5 Hz respectively) indicated that these were the protons positioned α and β to the nitrogen of the original TAD, while the coupling between the signals at 3.34 and 3.75 ppm (13.2 Hz) was indicative of the protons of an alkene in a *trans* configuration. There was long range (4 bond) coupling seen between the signals at 3.34/3.40 ppm, and 3.75/6.42 ppm. From the above information it was possible to tentatively propose the following structure for **166**, but the structure could not be confirmed by further NMR experiments, nor could a crystal be grown suitable for crystal structure analysis. The ^1H and ^{13}C NMR signals are given in the experimental section of this chapter.



166

Approximately 10% of the time the competitive insertion of a carbonyl appears to be successful, with an intermediate similar to **164** being formed that then undergoes further reaction with two acetylene groups. It is unclear what occurs at this stage to generate the final product (**166**), though a phenyl migration or rearrangement of the inserted acetylene groups is required.

It has been shown in Chapter 6 of this study that the chalcone equivalent of **164** reacts

with alkyl halides by oxidative addition and reductive elimination to form substituted furanone compounds. It is possible that a similar reaction is occurring in the forming of **166**.

Reaction of TAD with PhC≡CH and $PhCH_2Mn(CO)_5$ in a CO atmosphere.

The dominance of **165** in the product ratio (~9:1) shows that PhC≡CH undergoes more facile insertion into the cyclomanganated TAD system. However, in the reaction the only source of carbon monoxide was from the manganese reagent, compared to the PhC≡CH which was present in a three-fold excess. The low availability of carbon monoxide may be limiting the production of **166**. The reaction was therefore repeated under a CO atmosphere to determine whether the presence of free CO would affect the product ratios in favour of **166**.

The reaction was repeated under the same conditions as for the previous reaction, with the exception of a CO atmosphere being used. Work-up of the resulting reaction mixture afforded the same two products in approximately the same yields (**165** (89%) and **166** (9%)), showing no significant difference in the product ratios due to the CO atmosphere.

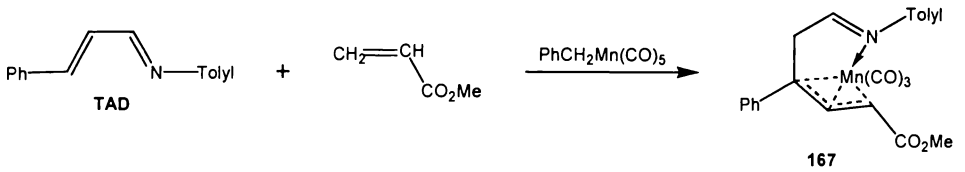
As an acetylene was successful in inserting into the presumed cyclomanganated intermediate, a number of other unsaturated compounds were trialled to determine the scope of azabutadiene chemistry for these types of reactions. The unsaturated molecules chosen were CH_2=$CHCO_2Me$, PhNCO, Bu^tNC and CS_2.

Reaction of TAD with $PhCH_2Mn(CO)_5$ and CH_2=$CHCO_2Me$.

An approximate 1:5:1 mixture of TAD, CH_2=$CHCO_2Me$ and $PhCH_2Mn(CO)_2$ was heated at reflux in petroleum spirits for two hours. The main product was characterised as **167** (39% yield), isolated by chromatography along with small quantities of the unreacted starting materials.

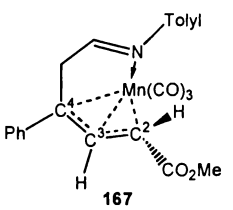
The two peaks in the ν(C≡O) region of the IR spectrum (at 2017 and 1933 cm^{-1}) of **167** indicate the presence of a $Mn(CO)_3$ moiety. The broadening of the second peak is due to lower symmetry in the molecule. Two broad peaks at 1734 and 1699 cm^{-1} indicate the presence of CO_2Me and C=N functional groups respectively. The peak for the ester ν(C=O) has been shifted to a higher frequency compared to CH_2=$CHCO_2Me$, indicating

that there is no longer conjugation between the carbonyl and adjacent C=C bond, as the adjacent allyl group has been delocalised to afford a η^3-coordination to the manganese centre.



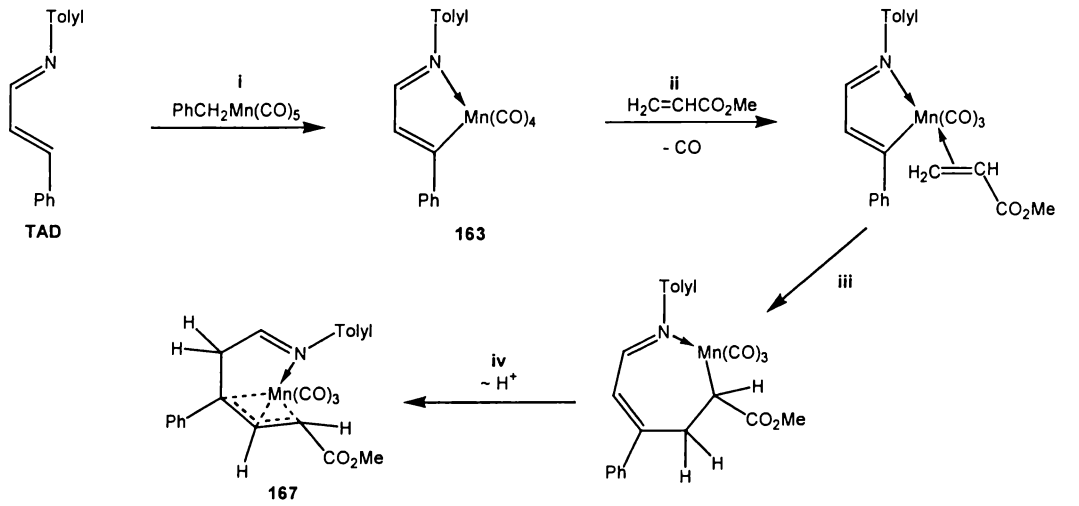
ESMS spectroscopy indicated a molecular mass of 445 amu, corresponding to the addition of CH_2=$CHCO_2Me$ and $Mn(CO)_3$ to the deprotonated TAD. An ESMS spectrum of **167** when run as a MeOH solution gave weak peaks for $[M+Na]^+$ and $[2M+Na]^+$. The major peak was assigned as $[M-Mn(CO)_3+2H]^+$ at *m/z* 308. It appears that the complex is demetalated under electrospray conditions, with the demetalated ligand picking up protons from the solvent to afford the dominant ion. The presence of both a C=N and CO_2Me functional group appears to be sufficient to enable the protonation.

2D-NMR allowed full characterisation of the ligand structure. The coupling constants of the two protons on C^2 and C^3 (H^2 and H^3 respectively) indicate a distorted *trans* arrangement of the carbon backbone to allow coordination of the manganese centre.



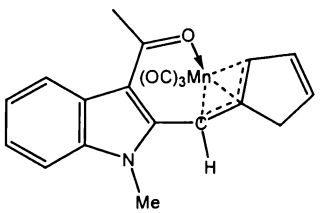
A possible route to **167** (Scheme 5-5) involves the loss of one CO ligand from the cyclomanganated intermediate (**163**) to allow coordination of CH_2=$CHCO_2Me$ (step **ii**). After insertion of CH_2=$CHCO_2Me$ (step **iii**), the organic ligand undergoes a proton migration (step **iv**), with the $Mn(CO)_3$ moiety shifting to coordinate by a η^3-allylic coordination to the newly formed azaheptadienyl. The $Mn(CO)_3$ maintains coordination to the lone pair electrons on the nitrogen. The $Mn(CO)_3$ moiety could also coordinate to the ester oxygen lone pairs, though this is less likely due to conformational strain, and the ν(C=O) for the ester has not been moved to a lower frequency as would be expected for a

coordinating C=O group.



Scheme 5-5 Proposed mechanism for the forming of **167**.

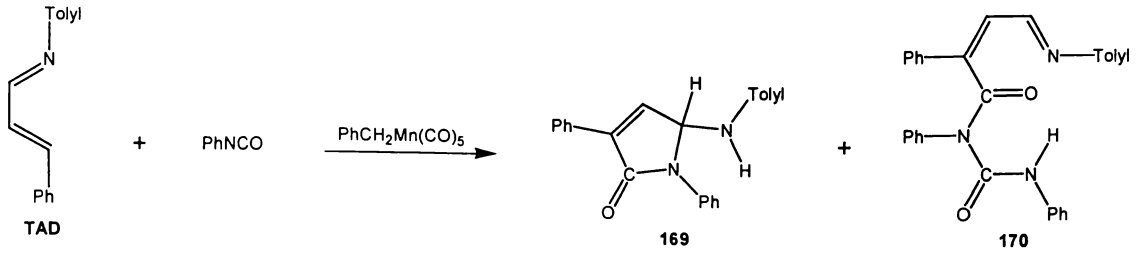
The structure of **167** is unique. The closest analogue comes from the reaction of orthomanganated 1-methyl-3-acetylindole with ethyne which produced the complex (**168**) possessing a similar η^3-allylic coordination to a $Mn(CO)_3$ centre[153]. In this case the remaining coordination was filled by the electron pair from a carbonyl oxygen.



Reaction of TAD with $PhCH_2Mn(CO)_5$ and PhNCO.

TAD and PhNCO were reacted with $PhCH_2Mn(CO)_5$ in a 1:3:1 ratio in petroleum spirits. IR indicated that the reaction was initiated at a temperature of 80°C, with the reaction temperature maintained at 85°C for two hours. Chromatography of the reaction mixture afforded two products in equal yield (30%), **169** and an unidentified product **170**.

[153] G. J. Depree, Ph.D. thesis, University of Waikato, (1995)



Spectroscopic and mass spectrometric characterisation.

An ESMS spectrum was obtained for a MeCN solution of **169**, and gave a dominant peak for $[M+H]^+$ at *m/z* 341, with additional peaks due to $[2M+H]^+$ and $[nM+Na]^+$ (n = 1, 2, 3). These peaks indicated a molecular mass of 340 amu which corresponds to the addition of PhNCO to the original TAD.

The IR spectrum of **169** showed a peak at 1715 cm^{-1}, indicating the presence of a C=O group. The ν(C=O) is pushed to a higher frequency by the five-membered ring.

The ^1H NMR spectrum of **169** showed 14 aromatic protons and the methyl group, with three additional signals. The two additional signals at 6.05 and 7.30 ppm were determined to be the protons around the central ring system, while the broad signal at 3.90 ppm was assigned to the amine attached to the ring.

The protons at 6.05 and 7.30 ppm do not show strong coupling, indicating that the dihedral angle between them is distorted towards 90° by the sp^3 character of C^5 (see Figure 5-3, page 190). Only the signal at 7.30 ppm is resolved as a doublet, as the amine proton is not rapidly exchanging, and couples to the proton on C^5, broadening the signal at 6.05 ppm. This coupling is further shown in the COSY NMR spectrum by a weak correlation between the amine proton and the signal at 6.05 ppm.

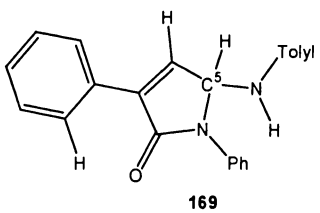


Figure 5-3 Structure of **169** showing sp^3 carbon (C^5).

2D-NMR allowed partial assignment of the structure of **169**. The ring proton at 7.30 ppm correlates to ^{13}C signals at 137.9, 131.0 and 168.2 ppm. The latter is the ring carbonyl C^2 (which shows no further correlations as there are no further protons within the three bond range of HMBC correlations). The proton on the phenyl ring adjacent to the carbonyl group also correlates to the signal at 137.9 ppm, indicating that this is C3 as depicted in Figure 5-4. The carbon signal at 131.0 ppm is due to the phenyl carbon attached to the central ring.

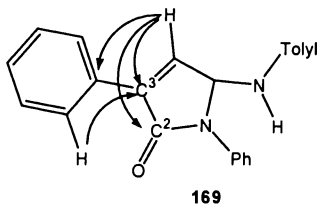
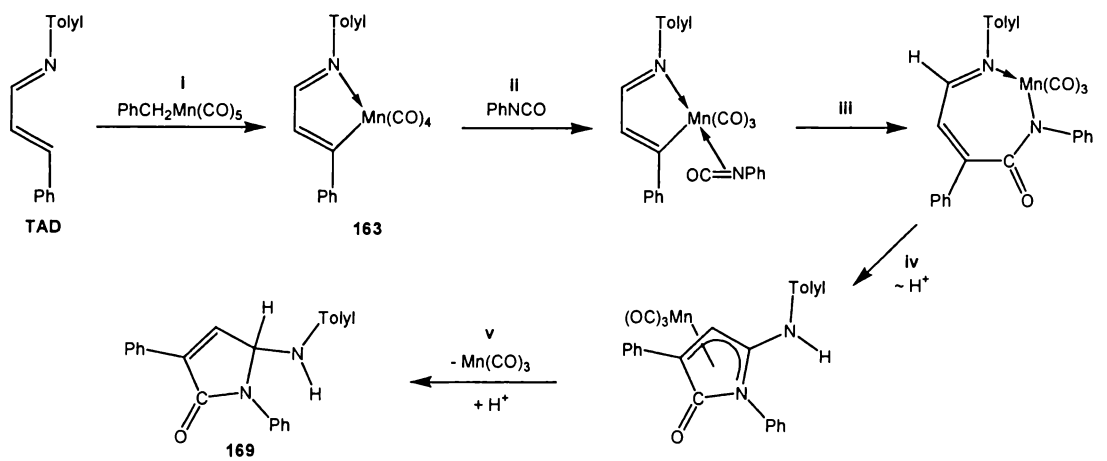


Figure 5-4 Structure of **169** showing selected HMBC correlations.

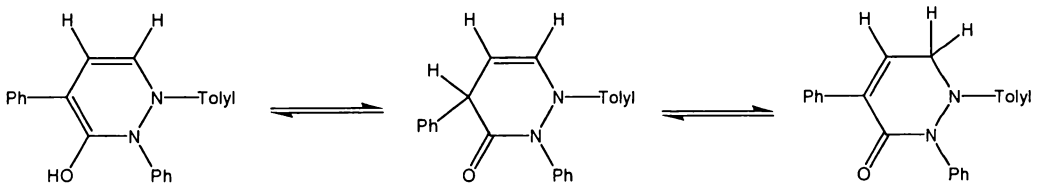
It appears that **169** is formed by the insertion of PhNCO into the intermediate **163** (step **iii**), followed by a cyclisation to form the five-membered ring. The PhNCO inserts so that the more bulky phenyl group is adjacent to the manganese due to steric pressure. The ring closure is initiated by attack of the nucleophilic amine nitrogen on the imine α-carbon (step **iv**). The final product is then formed by loss of the manganese centre and protonation occurring during workup.



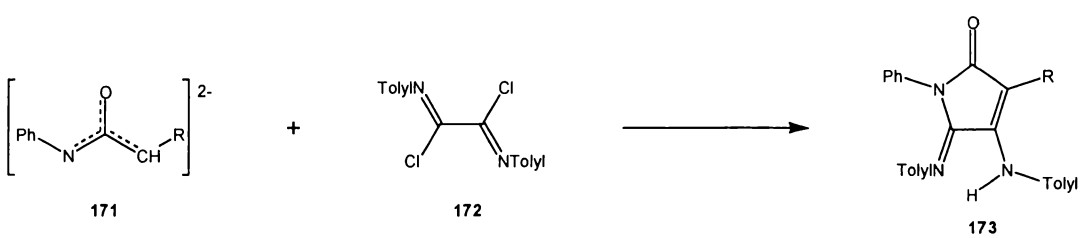
Scheme 5-6 Proposed mechanism for the forming of **169**.

In the other products thus far produced by the reactions of unsaturated substrates with

TAD, the cyclisation has occurred through the original nitrogen of the TAD, whereas in this case the cyclisation occurred through the imine carbon. The alternative products **169a**, **169b** and **169c** produced by cyclisation through the TAD nitrogen were ruled out in this case. **169a** does not have a carbonyl or imine group (as required from the IR spectrum). The other two compounds (**169b** and **169c**) do have a carbonyl group, but the NMR spectra do not agree with the two structures. Neither compound has a group which would afford the broadened peak seen in the ^{1}H spectrum. In **169b** there would be strong coupling between the two protons on the sp^2 carbons, while in **169c** there would be strong coupling between the protons on the sp^3 carbon. Neither of these couplings are evident in the ^{1}H NMR spectrum.



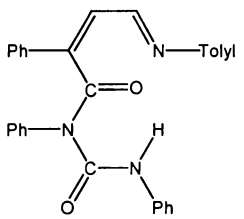
A compound similar to **169** has been prepared by the reaction of the dianion **171** and the diimine **172**[154]. The product (**173**) shows the same core structure as **169**, with an additional amine substituent on the ring system. The other difference is the imine adjacent to the ring nitrogen, where in **169** this is an amine functional group. However, the preparation of **173** shows that **169** is not an unprecedented structure.



For the other product, **170**, the ESMS gave a major peak assigned as $[M+Na]^+$ at *m/z* 482, with a secondary peak for $[2M+Na]^+$. This indicated a molecular mass of 459 amu, which corresponds to the addition of two PhNCO molecules to one TAD molecule. The IR spectrum showed three signals in the range expected for C=O and C=N groups, those

being 1718, 1703 and 1676 cm^{-1}. These indicate that the original imine from the TAD remains intact, and that imine and/or carbonyl groups remain from each of the inserted PhNCO groups.

A structure is proposed in Figure 5-5 that accounts for the observations seen in the ESMS and IR spectra, but the structure could not be confirmed by NMR. The data collected is presented in the experimental section of this chapter.

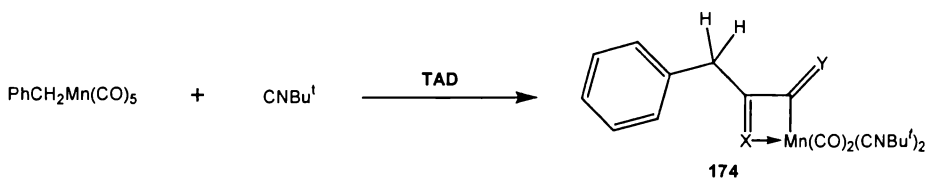


170

Figure 5-5 Proposed structure for **170**.

Reaction of $PhCH_2Mn(CO)_5$ with *tert*-butyl isocyanide in the presence of TAD.

TAD, Bu^tNC and $PhCH_2Mn(CO)_5$ were reacted in a 1:7:1 ratio in refluxing petroleum spirits for 2 hours. One pure product was isolated from the reaction mixture by chromatography, as well as a fraction containing a mixture of $[Mn(CNBu^t)_6]^+$ and $[Mn(CO)(CNBu^t)_5]^+$ species. The product isolated (**174**, 10%) was shown to contain no TAD, but to be the product of a reaction between $PhCH_2Mn(CO)_5$ and Bu^tNC. The TAD was recovered from the reaction mixture unaltered. Spectroscopic techniques could not determine which of two isomers were produced (Scheme 5-7).



174

Scheme 5-7 Proposed product **174** from the reaction of $PhCH_2Mn(CO)_5$ and Bu^tNC, where X and Y = O or NBu^t.

It appears that the Bu^tNC preferentially reacts with the $PhCH_2Mn(CO)_5$ before the [TAD-

[154] P. Lannger, J. Wuckelt, M. Döring, R. Beckert, *Eur. J. Org. Chem.*, (1998) 1467

H]$Mn(CO)_4$ intermediate **163** can be formed. The substitution of one or more CO ligands by Bu^tNC initiates the insertion of either a CO or Bu^tNC ligand into the Mn-C bond of the benzyl group. This leaves a vacant site allowing another Bu^tNC ligand to become coordinated. The steric strain around the Mn centre is released by the insertion of a second ligand into the newly formed Mn-C bond. The free coordination site is filled by coordination to the heteroatom of the originally inserted ligand, producing the final product.

The reaction of alkyl isocyanides with *p*-X-$C_6H_4CH_2Mn(CO)_5$ (X = H, Cl, OMe)[99] has previously been explored. Under the reaction conditions (room temperature with reactants in a 1:1 ratio) the preferential insertion of a coordinated carbonyl was observed. The acyl products *p*-X-$C_6H_4CH_2C(O)Mn(CO)_4(CNR)$ (R = cyclohexyl, *t*-butyl, butyl; X = H, Cl, OMe) were produced by the insertion of a coordinated carbonyl, with an isocyanide filling the vacant coordination site on the manganese.

The conditions used in the present study are more forcing, with the reaction being conducted in refluxing petroleum spirits with an excess of the isocyanide in the reaction mixture (approximate ratio 1:7). These conditions are more suited to the preparation of manganese complexes with multiple substitution of the coordinated carbonyls by alkyl isocyanides. The insertion of a carbonyl and an isocyanide can be envisaged as there is an excess of a bulky isocyanide driving the insertion of coordinated ligands into the Mn-C bond of the benzyl ligand. It is likely that the first ligand to be inserted is the carbonyl, following the trend of the previous study, and that as the reaction progresses, the substitution to form more isocyanide ligands leads to the insertion of one such ligand. This would afford **174** where X = O and Y = NBu^t (see Scheme 5-7 or Figure 5-6).

Previous research[155,98] into the reaction of *p*-X-$C_6H_4CH_2Mn(CO)_5$ (X = H, Cl, OMe) with aromatic isocyanides has produced products equivalent to **174** from the successive insertion of two isocyanide ligands (compared to the insertion of a CO and Bu^tNC as seen in the present case).

[155] P. L. Motz, J. P. Williams, J. J. Alexander, D. M. Ho, J. S. Ricci, W. T. Miller, *Organometallics*, **8** (1989) 1523

Spectroscopic and mass spectrometric characterisation.

The IR spectrum of **174** shows the Bu^{t}NC ligands ν(C≡N) as a broad peak at 2135 cm^{-1}, while the two CO ligands give two peaks in the ν(C≡O) range at 1990 and 1939 cm^{-1}. The two peaks for the carbonyl ligands indicates that there are two ligands attached to the manganese in a *cis* configuration. The imine and ketone give signals at 1713 and 1679 cm^{-1}.

An ESMS spectrum was obtained from a MeOH solution of **174**, affording a peak assigned as $[M+H]^+$ at *m/z* 480, which is consistent with the molecular mass of **174** being 479 amu. The basicity of the imine appears to be sufficient for the complex to be partially protonated in MeOH to form the ion observed.

The ^{1}H NMR spectrum of **174** showed three aromatic signals, three Bu^t signals, and two protons at 3.83 and 4.27 ppm coupling to each other. The Bu^t signals indicate that there are two Bu^{t}NC ligands on the manganese centre in a *cis* configuration. The third Bu^t signal is from an isocyanide that has been incorporated into the organic ligand.

The two protons on C^3 (see Figure 5-6) do not give a singlet due to the lack of a mirror plane in the molecule. The lack of symmetry in the molecule causes the two protons to be in different environments, therefore giving different signals in the ^{1}H NMR spectrum, and allowing them to couple to each other forming the two doublets observed[156].

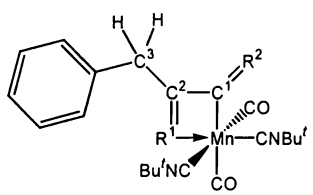
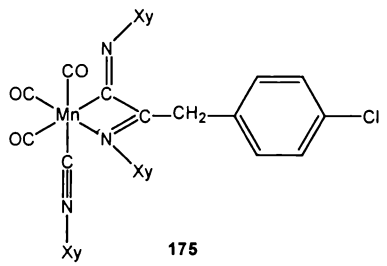


Figure 5-6 Structure of **174** showing chiral manganese centre (R^1, R^2 = O, NBu^t).

2D-NMR was used to partially assign the structure of **174**, but the functional groups on C^1 and C^2 could not be confirmed unambiguously. Compound **175** has been prepared

[156] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd Ed., VCH, Weinheim, Germany, (1993)

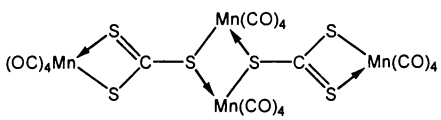
previously[157], and gives a ^{13}C NMR signal at 187.9 ppm for C^1, close to the 186.2 ppm observed for **174**. This supports the initial insertion of a carbonyl ligand. Compound **175** gives a signal at 179.1 ppm for C^2, compared to 194.8 ppm observed in **174**. This difference is due to the carbon in **175** being an imine compared to a carbonyl in **174**, as a coordinated carbonyl will be shifted further downfield.



175

Reaction of $PhCH_2Mn(CO)_5$ and CS_2 in the presence of TAD.

TAD and $PhCH_2Mn(CO)_5$ were sealed in an ampoule with CS_2 (5 ml) and heated in a Carius tube for 48 hours. Crystals of **50** were obtained from the cooled reaction mixture (2 mg, 3% yield). Work-up of the remaining CS_2 solution afforded a range of minor compounds that were poorly resolved by chromatography. No pure compounds could be isolated.



50

The complex **50** is the same as obtained from the reaction of $Mn_2(CO)_{10}$ and CS_2 under the same conditions, as discussed in Chapter 2. It appears that the $PhCH_2Mn(CO)_5$ reacts with the CS_2 before reacting with the TAD to form the intermediate **163**. Therefore no major product is observed for a reaction between TAD and CS_2.

The crystals were confirmed as being **50** by IR and ESMS by comparison to the data in Chapter 2.

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[157] T. M. Becker, J. J. Alexander, J. A. Krause Bauer, J. L. Nauss, F. C. Wireko, *Organometallics*, **18** (1999) 5594

5.4. Conclusion

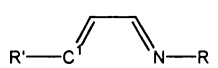
TAD has a varied chemistry in reactions involving $PhCH_2Mn(CO)_5$ and unsaturated molecules.

In the absence of any unsaturated molecules, the cyclomanganated intermediate assumed to be formed (**163**) is more reactive towards CO insertion than any cyclomanganated complex yet studied, and immediately forms the pyrrolonyl complex **164**.

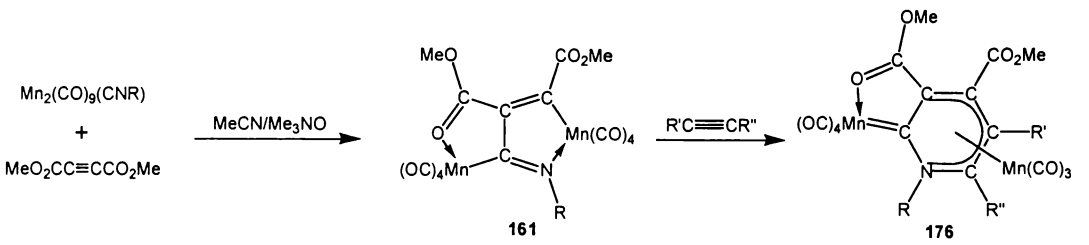
This increased reactivity of the intermediate towards CO does not prohibit the insertion of a number of other unsaturated molecules into the Mn-C bond. PhC≡CH, PhNCO and CH_2=$CHCO_2Me$ all successfully insert into the Mn-C bond of the proposed intermediate **163**. In the case of PhC≡CH there is competitive insertion between PhC≡CH and the CO ligands, with PhC≡CH dominating in a 9:1 ratio. In the other three cases the unsaturated molecule exclusively inserts into the Mn-C bond of the intermediate.

Care does need to be taken in not choosing an unsaturated molecule that is too reactive. $CNBu^t$ and CS_2 proved too reactive, with both reacting with the $PhCH_2Mn(CO)_5$ before the intermediate can be formed, inhibiting any reaction between TAD and either $CNBu^t$ or CS_2.

Future Study



It is expected that altering the electronic nature of C^1 of the azabutadiene may enable the isolation of the cyclomanganated intermediate. The cyclomanganated azabutadiene **161** has been produced by the oxidatively activated reaction of $Mn_2(CO)_9(CNR)$ and $MeO_2CC{\equiv}CCO_2Me$. **161** appears to be stabilised by the electron-withdrawing ester group on C^1, allowing isolation of the complex. The complex can be further reacted with alkynes to form **176**, showing that though the cyclomanganated complex is stabilised by the electron-withdrawing group, this stabilisation does not inhibit further reactions occurring.

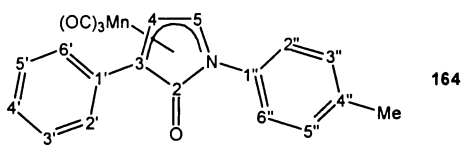


It is proposed that using an azabutadiene where the aryl group on C^1 has an electron-withdrawing effect would lead to the isolation of cyclomanganated intermediate. The isolation of this intermediate would allow a wider range of unsaturated compounds to be reacted with the azabutadiene.

5.5. Experimental

Reaction of TAD with $PhCH_2Mn(CO)_5$ in petroleum spirits.

A solution of TAD (51 mg, 0.23 mmol) and $PhCH_2Mn(CO)_5$ (80 mg, 0.28 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux for 6.5 hours. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and chromatographed (PLC 1:1 petroleum spirits/ether) to afford three fractions. The first fractions contained unreacted TAD and $PhCH_2Mn(CO)_5$, while the third fraction was collected to afford **164** (32 mg, 35% yield) which was recrystallised as yellow needles from a cooled ether solution.



164

m.p. = 143°C M_r = 387.3 $C_{20}H_{14}MnNO_4$

Elemental analysis : Calc. C 62.03 H 3.64 N 3.62

Expt. C 63.36 H 3.66 N 3.82

IR : (heptane) ν(C≡O) 2034(s), 1962(m), 1945(m) cm^{-1}

ESMS : (MeOH/NaOMe, cone -20 V) *m/z* 386 (4%, $[M-H]^-$), 418 (100%, $[M+OMe]^-$), 805 (12%, $[2M+OMe]^-$)

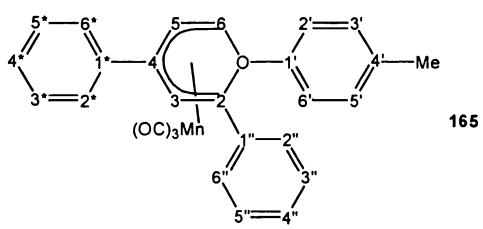
^1H NMR : ($CDCl_3$) δ 2.41 (3H, s, CH_3), 5.98 (1H, d, $^3J_{HH}$ = 2.4 Hz, H4), 6.23 (1H, d, $^3J_{HH}$ = 2.4 Hz, H5), 7.27 (4H, m, H2"/H3"/H5"/H6"), 7.31 (1H, t, $^3J_{HH}$ = 7.4 Hz, H4'), 7.42 (2H, t, $^3J_{HH}$ = 7.6 Hz, H3'/H5'), 7.92 (2H, d, $^3J_{HH}$ = 7.5

Hz, H2'/H6')

^{13}C NMR : ($CDCl_3$) δ 21.4 (CH_3), 71.2 (C3), 78.9 (C5), 83.1 (C4), 126.2 (C2'/C6'), 126.5 (C2"/C6"), 127.8 (C4'), 129.1 (C3'/C5'), 130.5 (C3"/C5"), 132.2 (C1'), 132.5 (C1"), 140.1 (C4"), 152.4 (C2), 221.5 ($Mn(CO)_3$)

Reaction of TAD and PhC≡CH with $PhCH_2Mn(CO)_5$.

A solution of TAD (52 mg, 0.23 mmol), PhC≡CH (75 μL, 0.68 mmol) and $PhCH_2Mn(CO)_5$ (87 mg, 0.30 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux, and the reaction stopped after three hours due to increasing degradation products. The solvent was removed under vacuum, and the residue chromatographed (PLC, 1:1 petroleum spirits/ether) to give three fractions. The first was the main fraction, and was collected to afford **165** (94 mg, 87% yield) which was recrystallised by vapour diffusion (ether/petroleum spirits) as a cream powder. The second fraction was a mixture of minor products including unreacted TAD, and no attempt was made to purify this fraction. The third fraction contained **166** (11 mg, 10% yield), which recrystallised as orange rosettes by vapour diffusion (dichloromethane/petroleum spirits).



165

m.p. = 176°C M_r = 461.4 $C_{27}H_{20}MnNO_3$

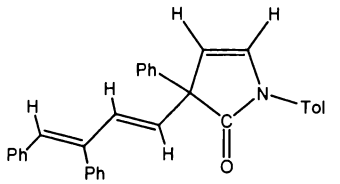
IR : (Petroleum spirits) ν(C≡O) 2025(s), 1965(m), 1946(m) cm^{-1}

ESMS : (MeOH/NaOMe, cone -20 V) *m/z* 460 (27%, $[M-H]^-$), 492 (100%, $[M+OMe]^-$)

^{1}H NMR : ($CDCl_3$) δ 2.22 (3H, s, CH_3), 5.01 (1H, d, $^3J_{HH}$ = 4.2 Hz, H6), 5.52 (1H, d, $^3J_{HH}$ = 4.2 Hz, H5), 6.29 (1H, s, H3), 6.58 (2H, d, $^3J_{HH}$ = 7.8 Hz, H2'/H6'), 6.92 (2H, d, $^3J_{HH}$ = 8.5 Hz, H3'/H5'), 7.30 (1H t, $^3J_{HH}$ = 7.3 Hz, H4"), 7.34-7.45 (5H, m, Ar-H), 7.58 (2H, d, $^3J_{HH}$ = 8.4 Hz, H2"/H6"), 7.70 (2H, d, $^3J_{HH}$ = 6.8 Hz, H2*/H6*)

^{13}C NMR : ($CDCl_3$) δ 20.8 (CH_3), 66.0 (C6), 82.0 (C2), 88.6 (C3), 91.7 (C5), 102.3 (C4), 115.4 (C2'/C6'), 123.9 (C2"/C6"), 127.2 (C2*/C6*), 127.9 (C4"),

128.9 (Ar-H), 129.3 (C3'/C5'), 129.4 (Ar-H), 130.3 (C1'), 136.9 (C1*), 138.1 (C1"), 153.1 (C4'), 221.7 ($Mn(CO)_3$)



166

m.p. = 209°C M_r = 453.6 $C_{33}H_{27}NO$

Elemental analysis : Calc. C 87.39 H 6.00 N 3.09

Expt. C 85.80 H 6.15 N 3.10

IR : (dichloromethane) ν(C=O) 1676 cm^{-1}

ESMS : (MeOH/NaOMe, cone -20 V) *m/z* 452 (100%, $[M-H]^-$), 905 (27%, $[2M-H]^-$)

^1H NMR : ($CDCl_3$) δ 2.21 (3H, s, CH_3), 3.34 (1H, dd, $^3J_{HH}$ = 13.2 Hz, $^4J_{HH}$ = 3.5 Hz, CH), 3.40 (1H, d, $^4J_{HH}$ = 3.6 Hz, CH), 3.75 (1H, d, $^3J_{HH}$ = 13.1 Hz, CH), 5.33 (1H, d, $^3J_{HH}$ = 7.2 Hz, CH), 6.42 (1H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 3.7 Hz, CH), 6.70-7.24 (19H, m, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 21.1 (CH_3), 45.9 (CH), 52.0 (CH), 56.3 (CH), 113.0 (CH), 124.9-129.8 (Ar-H), 132.0 (CH), 132.2 (Ar), 136.6 (Ar), 139.7 (Ar), 140.5 (Ar), 142.3 (Ar), 163.1 (C=O)

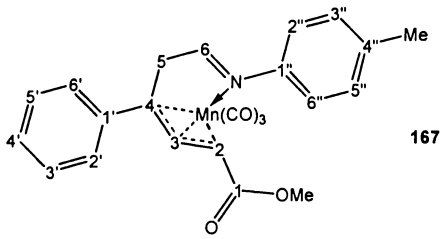
Reaction of TAD and PhC≡CH with $PhCH_2Mn(CO)_5$ under a CO atmosphere.

A solution of TAD (54 mg, 0.24 mmol), phenyl acetylene (75 μL, 0.68 mmol) and $PhCH_2Mn(CO)_5$ (86 mg, 0.30 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The flask was then flushed with CO before the reaction mixture was heated to reflux under a positive CO atmosphere for 3 hours. The solvent was removed under vacuum, and the residue chromatographed (PLC, 1:1 petroleum spirits/dichloromethane) to give four fractions. The first and third were minor fractions containing unreacted $PhCH_2Mn(CO)_5$ and TAD respectively. The second and fourth fractions afforded **165** (103 mg, 89% yield) and **166** (12 mg, 9%) respectively.

Reaction of TAD and CH_2=$CHCO_2Me$ with $PhCH_2Mn(CO)_5$.

A solution of TAD (53 mg, 0.24 mmol), CH_2=$CHCO_2Me$ (115 μL, 1.2 mmol) and $PhCH_2Mn(CO)_5$ (79 mg, 0.28 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux for 2 hours before the

solvent was removed under vacuum. The residue was chromatographed (PLC, 1:1 ethyl acetate/petroleum spirits) giving three fractions. The first and last were minor fractions containing a mixture of products (no further purification was attempted on these fractions). The second fraction contained the main product **167** (28 mg, 39% yield), recrystallised as a yellow powder by vapour diffusion (benzene/hexane).



167

m.p. = 148°C M_r = 445.4 $C_{23}H_{20}MnNO_3$

Elemental analysis : Calc. C 62.03 H 4.53 N 3.15

Expt. C 63.35 H 4.73 N 3.27

IR : (CH_2Cl_2) ν(C≡O) 2017(s), 1933(m, br) cm^{-1}, ν(C=O) 1734 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 308 (100%, $[M\text{-}Mn(CO)_3+2H]^+$), 468 (17%, $[M+Na]^+$), 913 (11%, $[2M+Na]^+$)

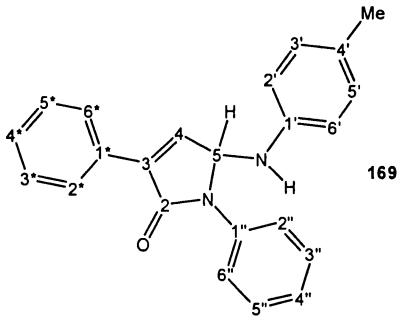
^{1}H NMR : ($CDCl_3$) δ 2.23 (1H, d, $^3J_{HH}$ = 11.8 Hz, H2), 2.40 (3H, s, Me), 3.33 (1H, d, $^3J_{HH}$ = 22.3 Hz, H5), 3.72 (1H, d, $^3J_{HH}$ = 22.2 Hz, H5), 3.83 (3H, s, OMe), 6.43 (1H, d, $^3J_{HH}$ = 11.7 Hz, H3), 7.04 (2H, d, $^3J_{HH}$ = 8.1 Hz, H2"/H6"), 7.22 (2H, d, $^3J_{HH}$ = 8.1 Hz, H3"/H5"), 7.23 (1H, m, H4'), 7.39 (2H, m, H3'/H5'), 7.53 (1H, S, H6), 7.66 (2H, m, H2'/H6')

^{13}C NMR : ($CDCl_3$) δ 21.1 (Me), 44.7 (C5), 51.6 (OMe), 59.9 (C2), 90.5 (C4), 102.2 (C3), 120.7 (C2"/C6"), 126.5 (C2'/C6'), 126.5 (C4'), 128.7 (C3'/C5'), 129.9 (C3"/C5"), 137.6 (C4"), 145.7 (C1'), 150.6 (C1"), 174.7 (C1), 176.4 (C6)

Reaction of TAD and PhNCO with $PhCH_2Mn(CO)_5$.

A solution of TAD (53 mg, 0.24 mmol), PhNCO (80 μL, 0.74 mmol) and $PhCH_2Mn(CO)_5$ (71 mg, 0.25 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux for 2 hours before the solvent was removed under vacuum. The residue was chromatographed (PLC, 1:4 ethyl acetate/petroleum spirits) to give four fractions, the first two of which were minor fractions containing unreacted TAD and $PhCH_2Mn(CO)_5$. The third fraction was collected to afford **170** (24

mg, 30% yield) as a yellow solid. The fourth fraction afforded **169** (33 mg, 30% yield) as a dark yellow solid.



169

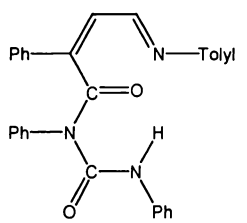
M_r = 340.4 $C_{23}H_{20}N_2O$

IR : (dichloromethane) ν(C=O) 1715(br) cm^{-1}

ESMS : (MeCN, cone +20 V) *m/z* 341 (100%, $[M+H]^+$), 363 (45%, $[M+Na]^+$), 681 (43%, $[2M+H]^+$), 703 (20%, $[2M+Na]^+$), 1043 (8%, $[3M+Na]^+$)

^{1}H NMR : ($CDCl_3$) δ 2.27 (3H, s, CH_3), 3.90 (1H, s, NH), 6.05 (1H, s, H5), 6.67 (2H, d, $^3J_{HH}$ = 8.4 Hz, H2'/H6'), 7.01 (2H, d, $^3J_{HH}$ = 8.3 Hz, H3'/H5'), 7.22 (1H, t, $^3J_{HH}$ = 7.4 Hz, H4"), 7.30 (1H, d, $^3J_{HH}$ =2.0 Hz, H4), 7.39 (2H, m, H3"/H5"), 7.43 (2H, m, H3*/H5*), 7.46 (1H, m, H4*), 7.58 (2H, d, $^3J_{HH}$ = 7.6 Hz, H2"/H6"), 7.95 (2H, d, $^3J_{HH}$ = 6.3 Hz, H2*/H6*)

^{13}C NMR : ($CDCl_3$) δ 20.8 (CH_3), 70.9 (C5), 115.9 (C2'/C6'), 123.4 (C2"/C6"), 125.8 (C4"), 127.9 (C2*/C6*), 128.9 (C3*/C5*), 129.4 (C3"/C5"), 129.5 (C4*), 129.7 (C1'), 130.3 (C3'/C5'), 131.0 (C1*), 136.8 (C1"), 137.9 (C3), 138.2 (C4), 142.5 (C4'), 168.2 (C2)



170

m.p. = 192°C M_r = 459.5 $C_{30}H_{25}N_3O_2$

IR : (heptane) ν(C=O) ν(C=N) 1718, 1703, 1676 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 482 (100%, $[M+Na]^+$), 941 (36%, $[2M+Na]^+$)

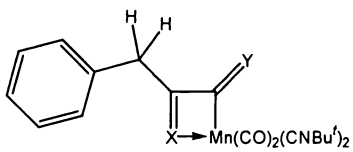
^{1}H NMR : ($CDCl_3$) δ 2.35 (3H, s, CH_3), 6.07 (CH), 6.78-7.82 (Ar-H), 8.96 (NH)

^{13}C NMR : ($CDCl_3$) δ 21.5 (CH_3), 67.6 (CH), 120.2-140.4 (Ar-H, Ar), 153.8 (C=N),

154.6 (C=O), 168.0 (C=O)

Reaction of $CNBu^t$ with $PhCH_2Mn(CO)_5$ in the presence of TAD.

A solution of TAD (52 mg, 0.24 mmol), $CNBu^t$ (200 μL, 1.8 mmol) and $PhCH_2Mn(CO)_5$ (88 mg, 0.31 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux for 2 hours before the solvent was removed under vacuum. The residue was chromatographed (PLC, 1:1 petroleum spirits/dichloromethane) to give three fractions. The first fraction was unreacted TAD, while the second was collected to afford **174** (15 mg, 10% yield) recrystallised as yellow crystals from hexane. ESMS determined that the third fraction contained a mixture of $[Mn(CNBu^t)_6]^+$ and $[Mn(CNBu^t)_5(CO)]^+$ species, and was not analysed further.



174

X = O, NBu^t; Y = NBu^t, O

m.p. = 96°C M_r = 479.5 $C_{25}H_{34}MnN_3O_3$

IR : (heptane) ν(C≡N) 2135 cm^{-1}, ν(C≡O) 1990(m), 1939(m) cm^{-1}, ν(C=O) 1713, 1679 cm^{-1}

ESMS : (MeOH, cone +20 V) *m/z* 480 (100%, $[M+H]^+$)

^{1}H NMR : ($CDCl_3$) δ 1.31 (9H, s, Bu^t), 1.39 (9H, s, Bu^t), 1.46 (9H, s, Bu^t), 3.83 (1H, d, $^2J_{HH}$ = 14.1 Hz, H3), 4.27 (1H, d, $^2J_{HH}$ = 14.1 Hz, H3), 7.17 (2H, m, H3'/H5'), 7.18 (1H, m, H4'), 7.23 (2H, m, H2'/H6')

^{13}C NMR : ($CDCl_3$) δ 29.9 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 31.0 ($C(CH_3)_3$), 32.7 (C3), 56.4 ($C(CH_3)_3$), 56.9 ($C(CH_3)_3$), 59.6 ($C(CH_3)_3$), 125.7 (C4'), 128.3 (C3'/C5'), 128.7 (C2'/C6'), 138.9 (C1'), 186.2 (C1), 194.8 (C2), 217 221.5 224.4 (Mn-CO, Mn-$CNBu^t$)

Reaction of TAD and CS_2 with $PhCH_2Mn(CO)_5$.

$PhCH_2Mn(CO)_5$ (81 mg, 0.284 mmol), TAD (54 mg, 0.243 mmol) and CS_2 (5 ml) were transferred to an ampoule and sealed under vacuum. The ampoule was heated to 85°C in a Carius tube for 48 hours. Small yellow crystals of **50** (2 mg, 3% yield) crystallised out of the cooled reaction mixture. The crystals were identified by ESMS and IR. For characterisation of **50** refer to the experimental section of chapter 2. A tlc of the remaining reaction mixture showed a multitude of products. Excess carbon disulfide was removed

under vacuum, and the residue chromatographed (PLC, 1:1 petroleum spirits/ether). No major products could be isolated from the mixture.

Chapter 6. Further Reactions of Cyclomanganated Complexes.

6.1. Introduction

This section of work was designed to continue on from Chapter 2 as an initial survey of the reactions of orthomanganated complexes with organo isothiocyanates (RNCS) and carbodiimides $(RN)_2C$. Both classes of compounds have a less extensive insertion chemistry than carbon disulfide.

The few examples of organo isothiocyanate insertions that were found in the literature involve insertion into Mg-C[158], Ta/Nb-H, Os-S[159], Ni-C, Pd-C[160], Tc-H, Re-C and Re-N[161] bonds. Most of these reactions are proposed to occur via initial coordination of the isothiocyanate group to the metal centre, with insertion occurring to afford a coordinated bidentate ligand, similar to the reactions observed for carbon disulfide.

$Cp_2M(L)H$ (M = Nb, Ta; L = CO, PMe_2Ph) readily inserts RNCS into the M-H bond forming a heterometalocycle with coordination to the N and S atoms[162]. This is analogous to the coordination observed for the insertion of CS_2 into the M-H bonds, as described in Chapter 2.

Under anhydrous conditions $[Re(CO)_2(PPh_3)_2(\eta^2\text{-}OCHNC_6H_4\text{-}p\text{-}Me)]$ reacts in a similar manner with insertion of PhNCS into the Re-N bond to form a thioureido complex[163], with analogous N,S-coordination. The initial step in the reaction is believed to involve the isothiocyanate coordinating via a σ-bond, forming the intermediate **176**. The nitrogen of

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[158] C-C. Chang, J-H. Chen, B. Srinivas, M. Y. Chiang, G-H. Lee, S-M. Peng, *Organometallics*, **16** (1997) 4980

[159] H. Werner, M. A. Tena, N. Mahr, K. Peters, H.-G. von Schnering, *Chem. Ber.*, **128** (1995) 41

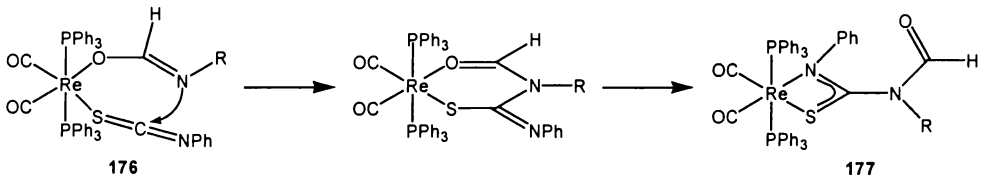
[160] J. Vicente, J-A. Abad, R. Bergs, M. C. Ramirez de Arellano, E. Martínez-Viviente, P. G. Jones, *Organometallics*, **19** (2000) 5597

[161] R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Castellato, R. Graziani, *J. Chem. Soc., Dalton Trans.*, (1988) 899

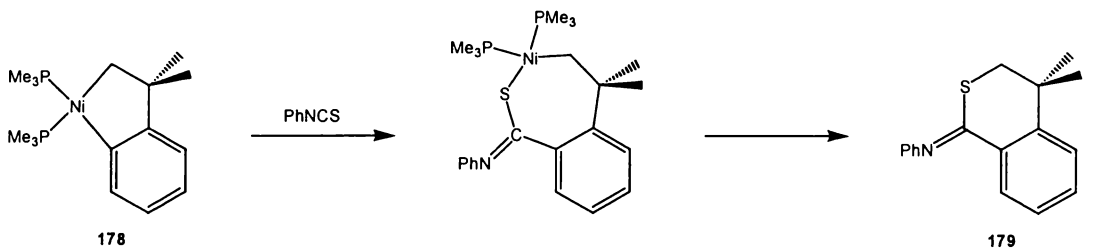
[162] J.-F. Leboeif, J.-C. Leblanc, C. Moïse, *J. Organometallic Chem.*, **335** (1987) 331

[163] R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Castellato, R. Graziani, A. Hussein, *J. Chem. Soc., Dalton Trans.*, (1988) 1853

the original ligand attacks the electrophilic carbon of the isothiocyanate forming the thioureido complex, which then rearranges to afford the η^2-N,S complex **177**.



Though few were found, one example of a reaction between a metalocycle and an isothiocyanate was the insertion of phenyl isothiocyanate into the Ni-aryl bond of the orthonickelated complex $(Me_3P)_2Ni(CH_2CMe_2C_6H_4)$ (**178**)[17]. The initial product formed was an unstable 7-membered metalocycle that rearranged to afford a cyclic imine thioether (**179**).



Organo isothiocyanates appear to be less reactive towards insertion compared to the equivalent reactions of carbon disulfide, and this may explain why there are so few reactions in the literature. The reactions of isothiocyanates are generally slower and requiring of more forcing conditions, producing markedly lower yields[164,158]. Comparing the insertion of methyl isothiocyanate and carbon disulfide into the Tc-H bond of $HTc(CO)_3(PPh_3)_2$, methyl isothiocyanate requires a longer reaction time (24 hours *vs* 1.5 hours) and produces a lower yield (45% vs. 72%) than does carbon disulfide[165].

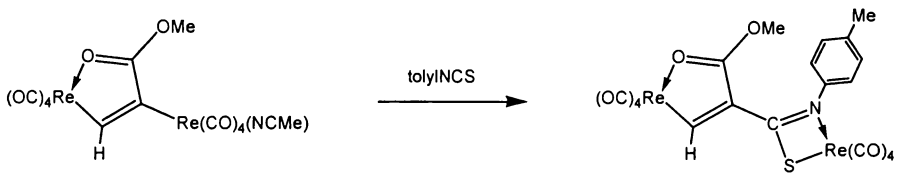
There is one example where an aryl isothiocyanate inserts into the M-C bond of a group 7 complex, that being the Re-C bond of the reactive complex $Re(CO)_4$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_4(NCMe)$ (**180**)[166]. Complex **180** is more reactive than the

[164] J. Zhongsheng, *J. Organomet. Chem.*, **447** (1993) 227

[165] J. Cook, A. Davison, W. M. Davis, A. G. Jones, *Organometallics*, **14** (1995) 650

[166] R. D. Adams, L. Chen, W. Wu, *Organometallics*, **12** (1993) 3812

$Re(CO)_5$ equivalent, and is prepared by reacting $Re(CO)_4$[*trans*-μ-HC=C(CO_2Me)]$Re(CO)_5$ with Me_3NO in a MeCN solution. The MeCN ligand is easily dissociated leaving a vacant coordination site for the isothiocyanate to then occupy, allowing the reaction to continue. When **180** is reacted with *p*-tolyl isothiocyanate in refluxing dichloromethane, the isothiocyanate inserts to form the η^2-N,S complex **181**.



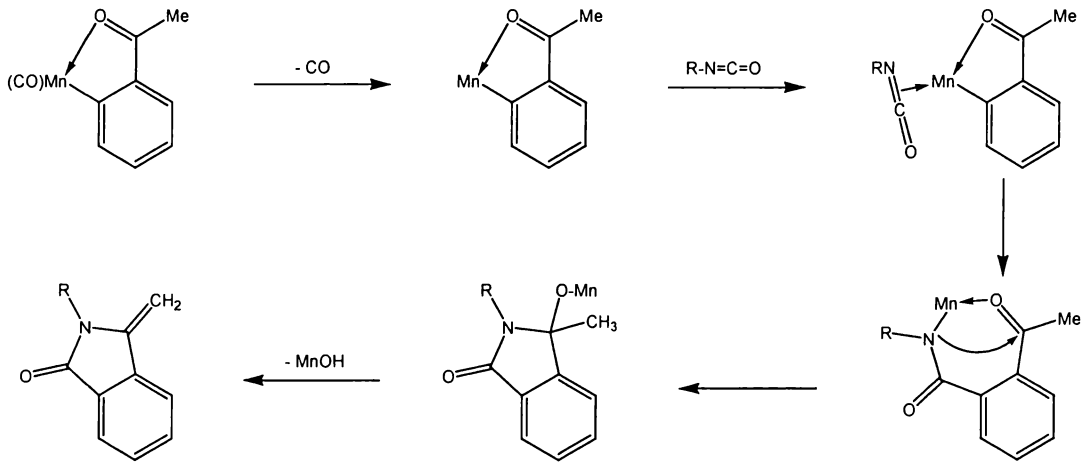
180 **181**

This form of chemical activation using Me_3NO is less aggressive and more selective than thermal or photochemical activation[167]. Although it has been used with orthomanganated substrates[168], this technique was not used in this study, thermal activation being the favoured technique.

Orthomanganated aromatic complexes have been reacted with organo isocyanates in dioxane to produce 3-alkylidene phthalimidine in good yields[26]. The reaction is initiated via thermal dissociation of a carbonyl ligand, allowing coordination of the isocyanate. After insertion, the nitrogen attacks the ketone carbonyl causing cyclisation and subsequent loss of "LMnOH" to afford the final product (Scheme 6-1).

[167] T.-Y. Luh, *Coord. Chem. Rev.*, **60** (1984) 255

[168] L. S. Liebeskind, J. R. Gasdaska, J. S. McCallum, *J. Org. Chem.*, **54** (1989) 699



Scheme 6-1 Insertion of isocyanates into an orthomanganated complex forming a 3-alkylidene phthalimidine. Additional carbonyls have been removed for clarity.

It was anticipated that isothiocyanates would react similarly with orthomanganated complexes under the same conditions.

There has been some research conducted on the reactions of carbodiimides with transition metal complexes, but the research has not been extensive, and has been largely limited to the early transition metals (e.g. Ti[169,170], Zr[171], Nb[172] and Ta[173]) and the hydrides of Mn[174], Ru[175] and Os[176].

One example is the insertion of *p*-tolylcarbodiimide into $[Cp_2M(L)H]$ (M = Nb, Ta; L = CO, PMe_2Ph) to give $Cp_2M(\eta^3\text{-}N(Ar)CH{=}NAr)$ (Ar = *p*-tolyl)[162] (**182**).

[169] L. A. Koterwas, J. C. Fettinger, L. R. Sita, *Organometallics*, **18** (1999) 4183

[170] O. Meth-Cohn, D. Thorpe, H. J. Twichett, *J. Chem. Soc. C*, (1970) 132

[171] E. Hey-Hawkins, F. Lindenberg, *Z. Naturforsch., B: Chem. Sci.*, **48** (1993) 951

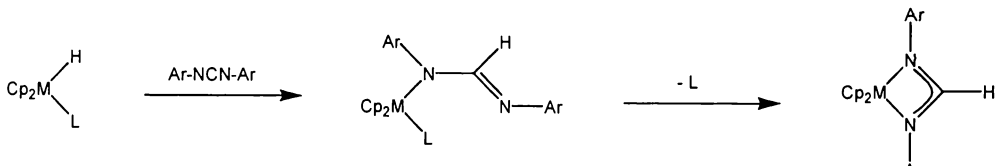
[172] M. K. T. Tin, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.*, **38** (1999) 998

[173] J. Wilkins, *J. Organomet. Chem.*, **80** (1974) 349

[174] F. J. Garcia Alonso, M. Garcia Sanz, V. Riera, *J. Organomet. Chem.*, **421** (1991) C12

[175] A. D. Harris, S. D. Robinson, A. Sahajpal, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1981) 1327

[176] M. A. Esteruelas, A. M. Lopez, *J. Organomet. Chem.*, (1997) 495 and 545



182

Carbodiimides are less reactive than isothiocyanates and it was uncertain whether a reaction would occur.

6.2. Results and Discussion

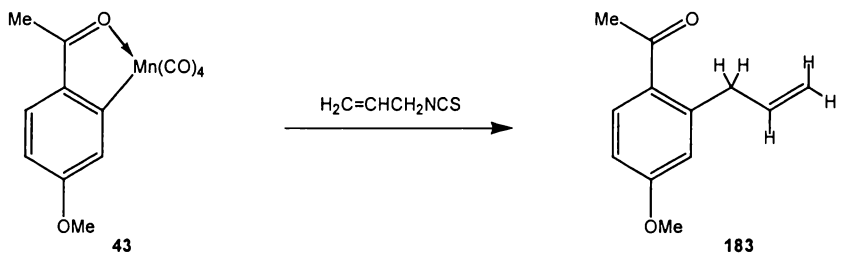
6.2.1. Reactions of orthomanganated compounds with isothiocyanates.

Phenyl isothiocyanate and allyl isothiocyanate were reacted with orthomanganated *p*-methoxyacetophenone (**43**) to determine if the isothiocyanate group underwent a similar insertion to that of carbon disulfide (Chapter 2.3.1). Allyl isothiocyanate was included in the preliminary investigation as the unsaturated carbon-carbon bond offered another site of reaction.

Phenyl isothiocyanate was initially reacted with **43** using the method described by Liebeskind *et al*[26] for the reaction of isocyanates with orthomanganated aromatic ketones (dioxane, 90°C, 3 hours). It was expected that analogous 3-methylidene phthalimidines would be produced, as the thiocarbonyl would be hydrolysed during work-up.

This was not the case, with the main reaction being slow demetalation of the orthomanganated starting material. Alternative reaction conditions were explored, including refluxing in heptane, and the use of Li_2PdCl_4 in MeCN both at ambient and refluxing temperatures. Similar results were observed, with no indication of a reaction between **43** and phenyl isothiocyanate.

In contrast, allyl isothiocyanate did react with **43** in dioxane at 90°C over 3 hours, but did not give the expected 3-methylidene phthalimidine. Instead 2-allyl-4-methoxyacetophenone (**183**) was produced (40% yield) as identified by NMR spectroscopy. The IR ν(C=O) vibration (1679 cm^{-1}) corresponded with acetophenone, with ESMS confirming the molecular weight.

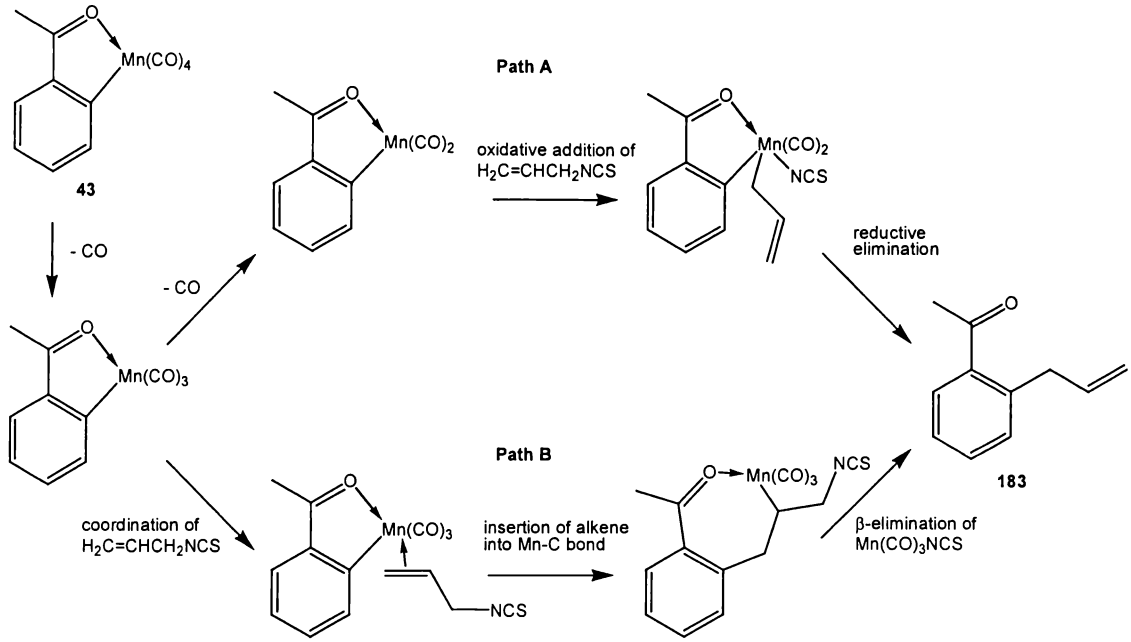


43 183

The reaction was repeated in MeCN with Li_2PdCl_4 added as a catalyst. It has been found that the products from the reaction of alkenes with orthomanganated complexes can be influenced by conducting the reaction in the presence of Pd(II). In the present study it was of interest whether the introduction of Pd(II) would promote the insertion of the isothiocyanate, or would increase the yield of the previous product (**183**).

A solution of **43** and allyl isothiocyanate in MeCN (with Li_2PdCl_4) was stirred overnight at ambient temperatures. The reaction afforded the same product as when the reaction was conducted in dioxane, but a lower yield was obtained. All further reactions were conducted by stirring the reactants in dioxane at 90°C for 3 hours. Due to the interfering peaks associated with dioxane, the reactions could not be monitored by IR spectroscopy. However, tlc of the reaction mixture showed that in most cases after 3 hours there was no orthomanganated starting material remaining.

The reaction between **43** and allyl isothiocyanate can be proposed to progress via either an oxidative addition/reductive elimination reaction (Path A in Scheme 6-2), or initial insertion of the allyl group into the Mn-C bond followed by β-elimination (Path B in Scheme 6-2).



Scheme 6-2 Two possible reaction mechanism for the formation of 2-allyl-4-methoxyacetophenone (the methoxy group is not shown for clarity).

6.2.2. Reactions of orthomanganated compounds with allyl substrates.

The product formed in the above reaction (**183**) suggests that the isothiocyanate group is acting as a pseudohalide, in a reaction similar to the Heck allyl halide coupling reactions[177]. This is not altogether unexpected, as the isothiocyanate group has previously been reported to behave as a pseudohalide[178]. To confirm this, the reactions of **43** with allyl bromide and allyl iodide were investigated.

The yields of **183** from the respective reactions were 57% for allyl bromide and 71% for allyl iodide, indicating that the isothiocyanate group is acting as a pseudohalide. By comparison, the yield from the reaction with allyl isothiocyanate was 40% under the same conditions, implying that the isothiocyanate group is not as efficient in this reaction. This may favour the oxidative addition pathway A, as the ease of oxidative addition will be R-NCS < R-Br < R-I, due to the difference in the bond energies of the R-X and Mn-X bonds. In another experiment, allyl alcohol was reacted with **43** as the hydroxyl group favours β-elimination over oxidative addition. Under the same reaction conditions the yield of **183**

[177] R. F. Heck, *J. Amer. Chem. Soc.*, **90** (1968) 5531

[178] M. F. Lappert, B. Prokai, *Adv. Organometallic Chem.*, **5** (1967) 225

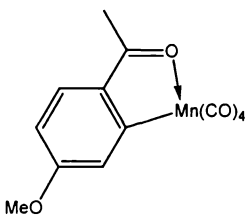
was 42%, comparable to the isothiocyanate.

As a final test, ethyl bromide and benzyl bromide were reacted with **43**, as neither of these can undergo the insertion reaction which is the initial step in the β-elimination pathway B. If either substrate is to react, it can only be by the oxidative addition/reductive elimination pathway A.

No reaction was observed other than the demetalation of the orthomanganated starting material. This result indicates that Path B is the favoured pathway, with the initial insertion of the allyl group the key step in the mechanism. This also explains why there was no evidence for a similar *ortho*-substituted product from the reaction of **43** with phenyl isothiocyanate.

Allyl bromide was chosen to test the generality of the reaction with other cyclomanganated substrates. The reactions were undertaken in dioxane, with the reaction mixtures heated to reflux for 3 hours.

Orthomanganated 2-acetylthiophene (**45**), *N*-(4-tolyl)-4-methoxybenzylimine (**184**) and triphenylphosphine sulfide (**49**) all gave the same type of *ortho*-substituted product as seen in the reaction of **43**, where the allyl group replaces the $Mn(CO)_4$ group. The reaction conditions and yields are shown in Table 6-1. The notable exception was the cyclomanganated chalcone **54**.



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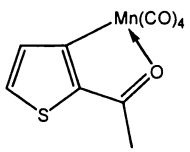
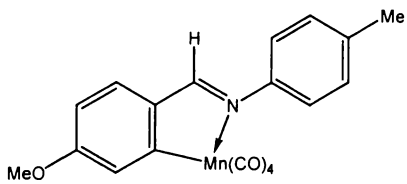


45



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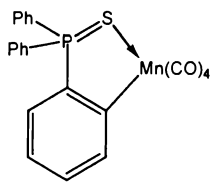

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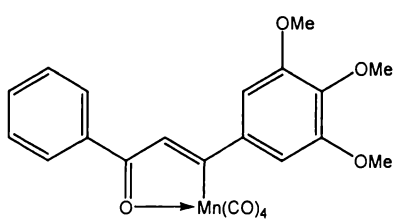
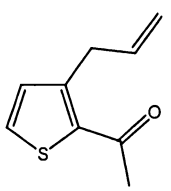


54

Table 6-1 Reaction conditions and yields for the reactions of η^2-(2-acetyl-5-methoxyphenyl)$Mn(CO)_4$.

Substrate	R-X	Reaction conditions	Product	Yield
43	AllylNCS	Li_2PdCl_4, MeCN, 3 hours reflux	**183**	9%
43	AllylNCS	Dioxane, 90°C, 3 hours	**183**	40%
43	AllylBr	Dioxane, 90°C, 3 hours	**183**	57%
43	AllylI	Dioxane, 90°C, 3 hours	**183**	71%
43	AllylOH	Dioxane, 90°C, 3 hours	**183**	42%
43	EthylBr	Dioxane, 90°C, 3 hours	-	0%
43	BenzylBr	Dioxane, 90°C, 3 hours	-	0%
45	AllylBr	Dioxane, 90°C, 3 hours	**185**	80%
184	AllylBr	Dioxane, 90°C, 3 hours	**186**	97%
49	AllylBr	Dioxane, 90°C, 3 hours	**187**	13%
54	AllylBr	Dioxane, 90°C, 3 hours	**188**	13%
			189	16%
54	EthylBr	Dioxane, 90°C, 3 hours	**190**	5%
			191	8%

Product **185** has previously been prepared by L. Gommans[179] from the reaction of **45** with allyl alcohol in MeCN with Li_2PdCl_4 as a catalyst. The yield obtained was 55% compared to a yield of 80% from the present study.



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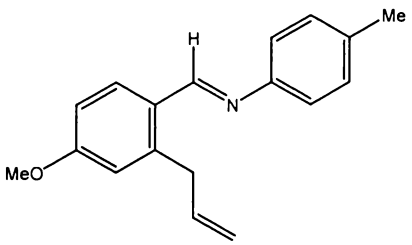

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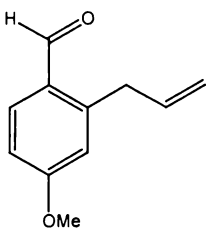


192

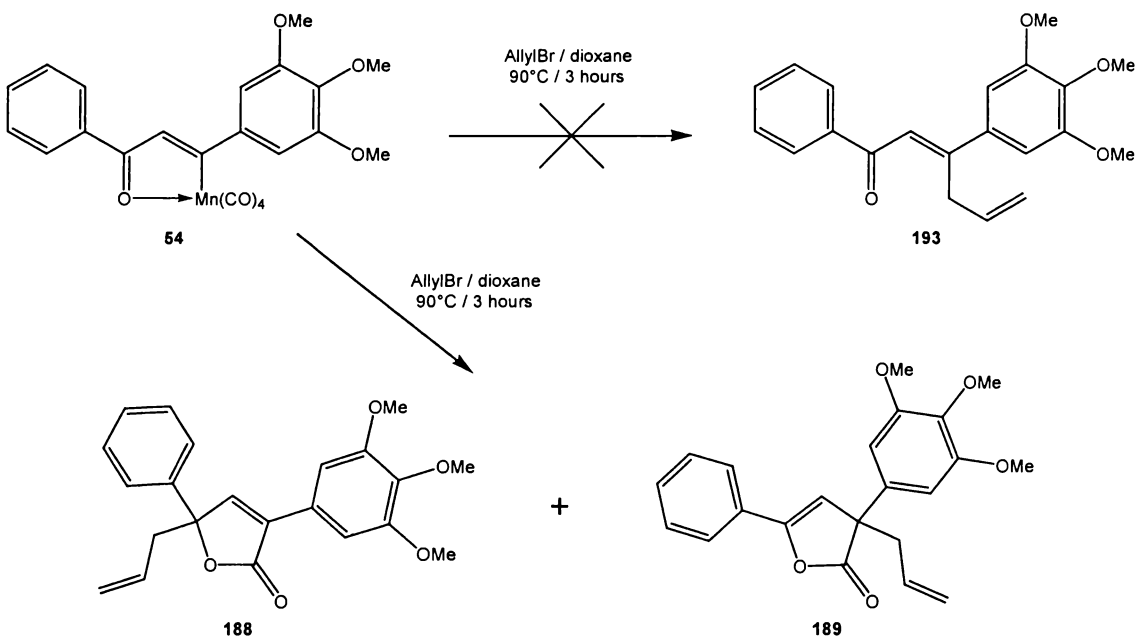
It was noticed during the work-up of the reaction of **184** and allyl bromide that if the reaction was purified by chromatography (PLC plate), appreciable quantities of 2-allyl-4-methoxybenzaldehyde (**192**) were isolated. The reaction of **184** and allyl bromide was repeated. Workup of the repeated reaction involved the removal of the reaction solvent under reduced pressure, and extraction of the residue with ethyl acetate to afford **186** (97%).

[179] L. Gommans, Ph.D. Thesis, University of Waikato, (1992)

A sample of **186** was hydrolysed in a solution of THF and dilute HCl to afford a sufficient quantity of **192** for characterisation.

6.2.3. Reactions of cyclomanganated compounds with organic halides.

When the cyclomanganated chalcone **54** was reacted with allyl bromide under the same conditions as the orthomanganated complexes, IR spectroscopy indicated the product formed was not the expected allyl coupling product **193** (Scheme 6-3). The expected region for the ν(C=O) band of a conjugated ketone (as found in **193**) is below 1700 cm^{-1}. The ν(C=O) bands for both **188** and **189** were above 1700 cm^{-1}, being 1760 and 1796 cm^{-1} respectively. ESMS of both compounds showed their mass to be 28 amu higher than would be expected for **193**, indicating that a carbonyl group had also been incorporated into the molecule.

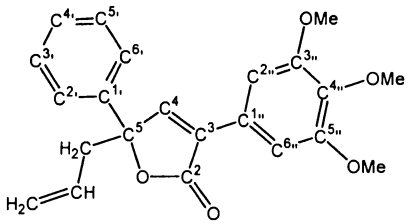


Scheme 6-3 The reaction of **54** and allyl bromide showing the expected product **193**, and those prepared (**188** and **189**).

The ν(C=O) bands of **188** and **189** are consistent with a furanone and isofuranone respectively. To confirm the structure of each compound, a 2D-NMR investigation was undertaken.

The ^{1}H NMR spectrum of **188** showed 12 proton environments, while the ^{13}C NMR spectrum showed 17 environments. The 12 proton environments were consistent with compound **193**, however an extra ^{13}C signal confirmed that an extra carbon had been introduced into the compound.

The HSQC spectrum (which shows single bond proton-to-carbon correlations) was used to identify which protons were attached to which carbons, while the HMBC spectrum gave long range (two (^{2}J) and three (^{3}J) bond) proton-to-carbon correlations, allowing a determination of the structure of **188**.



The protons $H^{2''}$and $H^{6''}$ were identified as the signal at 7.15 ppm, an aromatic singlet integrating as two protons. From the HMBC spectrum it could be determined that C^{3} and $C^{1''}$ gave signals at 125.5 and 130.6 ppm, as the other correlations seen by $H^{6''}$ were due to the other carbons in the aryl ring.

The only other proton signal that could correlate to C^{3} is H^{4}, which gives a peak at 7.69 ppm. H4 also correlated to C^{2} (170.8 ppm), C^{5} (87.8 ppm), $C^{1'}$ (139.5 ppm) and the first carbon of the allyl group (44.7 ppm). The assignment of these carbon signals could be confirmed by the correlation of other protons to each carbon, e.g. H3′ correlates to a carbon signal at 139.5 ppm, confirming this as $C^{1'}$ (as this is the only signal within the three bond range of the HMBC correlations). The only carbon whose assignment could not be confirmed by correlation from another proton is C^{2}, 170.8 ppm. This is because no other proton is within the three-bond range of HMBC correlations, therefore confirming the assignment.

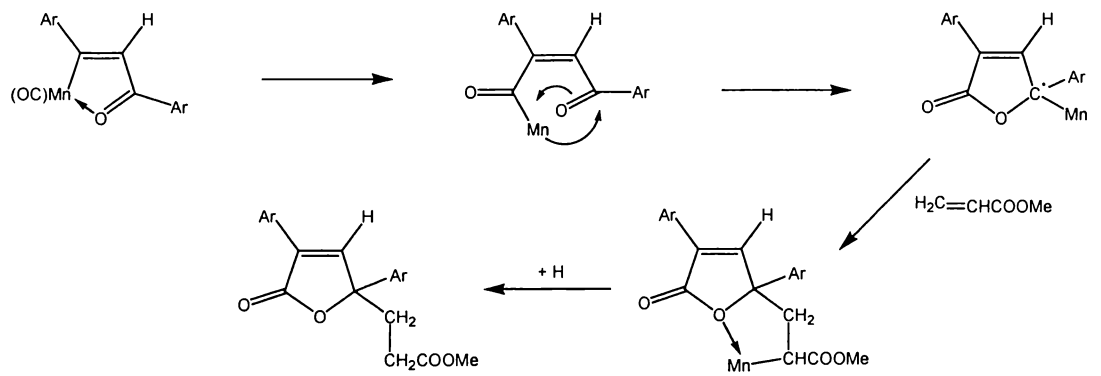
The full NMR assignment of **188** is listed in the experimental section.

The 2D-NMR analysis of **188** confirmed the product as a tri-substituted furanone, and by

comparison of the IR spectrum and values for ^{1}H and ^{13}C NMR, **189** was confirmed as the isofuranone.

The production of a furanone from a cyclomanganated precursor is not unique, as such a compound has previously been reported from the acidic demetalation of cyclomanganated enones[180]. A stirred acetonitrile solution of a cyclomanganated enone treated with aqueous HCl yielded a furanone product with a core structure similar to **188**. DeShong *et al* found that increasing the CO pressure (and therefore CO concentration) increased the ratio of furanone to enone produced.

More recently substituted furanones similar to **188** have been prepared from the reaction of alkene-manganated chalcones with the activated alkenes methyl acrylate and methyl vinyl ketone[20]. The reactions were undertaken in the coordinating solvent MeCN, at reflux. A mechanism was proposed, depicted in Scheme 6-4, involving the migratory insertion of a coordinated carbonyl, followed by cyclisation to form the furanyl ring. At this stage the alkene inserted into the Mn-furanyl bond, always attaching at the carbon adjacent to the ring oxygen (C*), implying that the manganese is bound to this carbon. The final step involved demetalation with H^{+} during work-up to give the final product.



Scheme 6-4 Mechanism proposed by Tully *et al* for the formation of furanones by coupling of alkene-manganated chalcones with methyl acrylate. Additional carbonyl ligands are omitted for clarity.

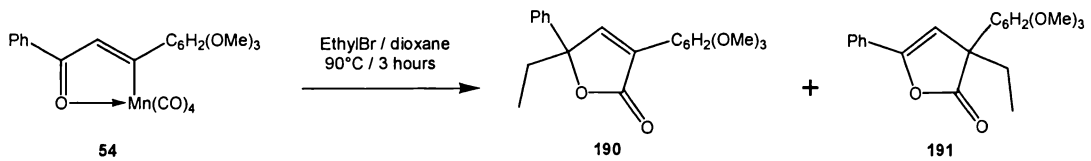
The formation of the furanyl is caused by the initial insertion of a carbonyl ligand into the Mn-C bond, followed by cyclisation. Tully *et al* suggested that the insertion of the

[180] P. DeShong, D. R. Sidler, P. J. Rybczynski, G. A. Slough, A. L. Rheingold, *J. Amer. Chem. Soc.*, **110**

carbonyl ligand may be induced by a donor solvent molecule. This is supported by the present study, as dioxane is also a donor solvent.

It was initially thought that the reaction proceeded via the mechanism proposed by Tully *et al*, but with β-elimination being the terminating step. It was unclear why β-elimination would not have occurred in the Tully reactions (affording unsaturated substituents), yet apparently had in the present study. The possibility that the reaction was progressing by another mechanism was explored by reacting ethyl bromide with **54**. Ethyl bromide does not have a suitable function group to undergo insertion into a Mn-C bond, so therefore any reaction would indicate a different mechanism.

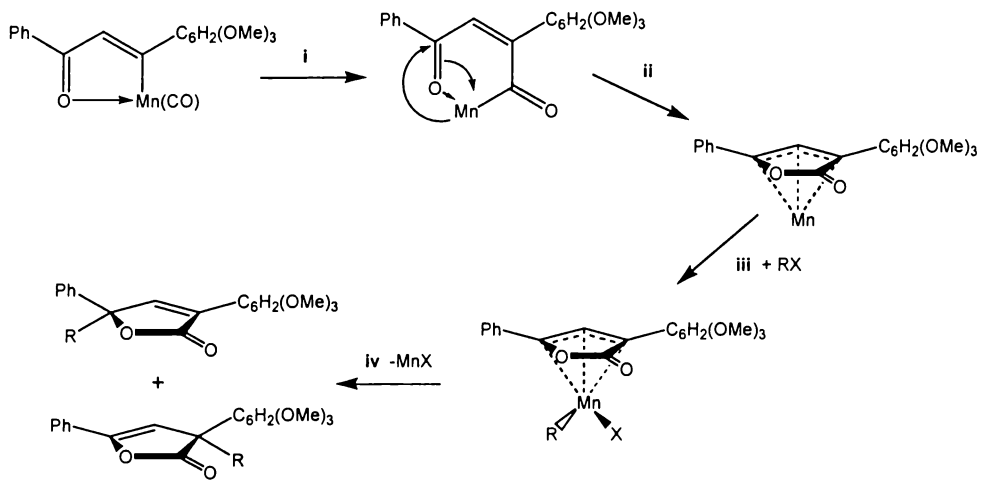
The reaction between ethyl bromide and **54** afforded the ethyl substituted furanone/isofuranone pair **190** and **191**, products analogous to those observed from allyl bromide.



54 **190** **191**

The proposed mechanism for the reaction of alkyl halides with cyclomanganated enones is depicted in Scheme 6-5. The furanyl intermediate is produced by the same process as described by Tully *et al* (steps **i** and **ii**), but the reaction of the furanyl intermediate with the substrate (alkyl halide) occurs by oxidative addition of the alkyl halide to the manganese centre (step **iii**). The final products are formed by reductive elimination (step **iv**).

(1988) 2575



Scheme 6-5 Mechanism for the reaction of alkyl halides with η^2-[1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-on-3-yl]$Mn(CO)_4$ (**54**); additional carbonyls are not shown for clarity.

Attempted reactions with carbodiimides

Dicyclohexylcarbodiimide was reacted with orthomanganated 4-methoxyacetophenone (**43**) by heating in heptane. Monitoring the reaction by IR showed that even at reflux the manganated starting material was not reacting with the carbodiimide, as observed by the unchanging peaks in the spectrum.

The reaction was allowed to continue for 2 hours at reflux before being worked-up. Chromatography of the reaction residue afforded **43** and 4-methoxyacetophenone, with no trace of the carbodiimide. It is thought that the carbodiimide polymerised, as there was an appreciable amount of insoluble material in the reaction vessel after the residue had been transferred to the chromatography plate with dichloromethane.

6.2.4. Spectroscopic and mass spectrometric characterisation

IR Spectra

In the products of the reactions of allyl-X with the orthomanganated precursors, the carbonyl oxygen is no longer coordinated to the manganese, and therefore the ν(C=O) shifts to a higher frequency by ~20 cm^{-1}, to values expected for a free aryl ketone.

However, for the furanone products from **54**, a higher frequency was found for ν(C=O) because of the incorporation into the furanone ring. The frequency depends on the position

of the double bond[181]; for the furanone the band is at ~1750 cm^{-1}, while for the isofuranone it occurs at ~1800 cm^{-1}.

Table 6-2 IR carbonyl bands for the organic products of the reaction of cyclomanganated complexes with alkyl halides.

	Compound	ν(C=O) cm^{-1}
183	2-allyl-4-methoxyacetophenone	1679
185	2-acetyl-3-allylthiophene	1664
186	*N*-(4-tolyl)-2-allyl-4-methoxybenzylimine	1623
192	2-allyl-4-methoxybenzaldehyde	1687
188	5-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone	1760
189	3-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone	1796
190	5-ethyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone	1757
191	3-ethyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone	1795

ESMS spectra

All of the compounds form sodium adducts in the ESMS when run in MeOH at a cone voltage of +20 V. These adducts gave peaks assigned as $[M_n+Na]^+$ (where n = 1-3), with n = 1 affording the dominant peak. The sodium adduct is a commonly seen peak under these conditions, as there is residual sodium from previous users always in the instrument.

In the case of *N*-(4-tolyl)-2-allyl-4-methoxybenzylimine the dominant peak was due to $[M+H]^+$. This is likely due to the more basic nature of the iminyl nitrogen compared to the carbonyl oxygen.

GCMS spectra

The GCMS spectrum of **183** showed a small molecular ion peak ($M^{\bullet+}$, 2%), but the dominant peak at *m/z* 175 was due to M-15$]^+$. This peak is due to the loss of $CH_3^{\bullet}$ either from the acetyl group (a common peak observed for aromatic ketones) or from the methoxy group (commonly seen for aryl methyl ethers). The further loss of CO from what was either group is also commonly observed, and leads to the peak at *m/z* 147.

A peak is also observed at *m/z* 160. This is generated from the molecular ion by the

[181] E. Pretsch, J. Siebl, W. Simon, T. Clerc in *Tables of spectral data for structure determination of organic compounds*, ed W. Fresenius, J. F. K. Huber, E. Pungor, G. A. Rechnitz, W. Simon, Th. S. West, Springer-Verlag, Berlin Heidelberg, 2nd edn., (1989), pp I140

elimination of formaldehyde from the methoxy group. The spectrum of **183** is shown in Figure 6-1.

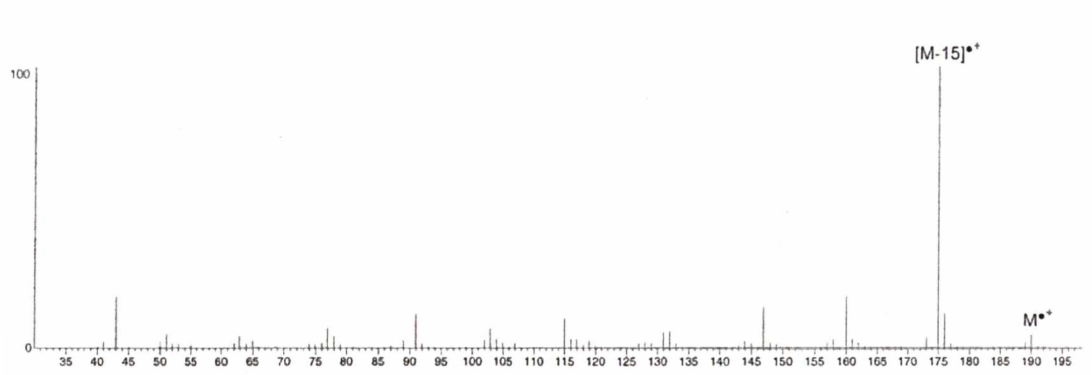


Figure 6-1 GCMS spectrum of **183** with molecular ion and dominant peak labelled.

The thiophene product **185** and the aryl imine product **186** both gave a similarly weak molecular ion and a dominant M-15$^+$ peak, again due to the loss of CH_3 from the acetyl group and methoxy group respectively.

The aldehyde group of 2-allyl-4-methoxybenzaldehyde (**192**) afforded a major peak observed for M-1$^+$, from the loss of the aldehyde H forming a benzoyl ion. The loss of a methyl radical from the methoxy group of the M-1$^+$ ion gave the dominant peak at *m/z* 161. The other peak of note was *m/z* 148, due to the decarbonylation of the benzoyl ion. Due to the weak nature of the molecular ion, the M-1$^+$ peak was used for the high resolution mass spectrometric characterisation of the molecule.

The furanones gave spectra showing a strong molecular ion, and dominant peaks due to loss of alkyl or α-substituents, and peaks from two successive decarbonylations[181]. For the allyl iso/furanone compounds **189** and **188** the peaks due to decarbonylation were very weak, with the spectra dominated by M-allyl$^+$.

Spectra of the ethyl iso/furanone compounds **191** and **190** are also dominated by peaks due to the loss of the alkyl substituent, namely M-ethyl$^+$. However, decarbonylation is more apparent; the ethyl furanone (**190**) has a major peak assigned as M-2CO-ethyl$^+$ while the ethyl isofuranone (**191**) has a major peak for M-CO-Ph$^+$ (as the α-substituent is the phenyl ring).

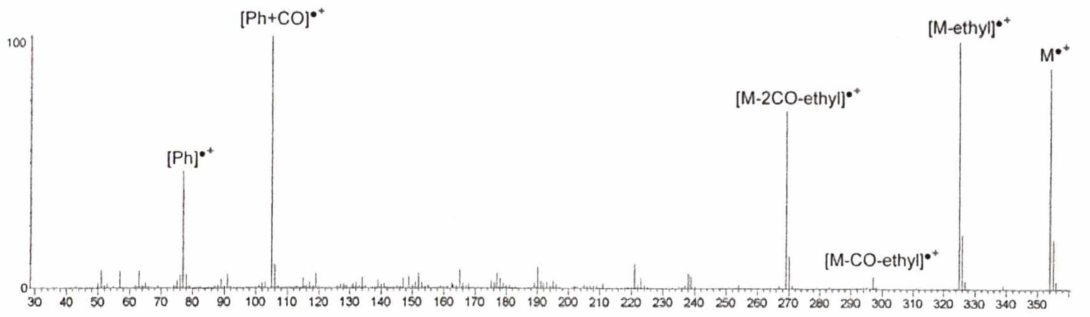


Figure 6-2 GCMS spectrum of **190** with molecular ion and major peaks labelled.

NMR spectra

The ^{1}H NMR spectra of the orthomanganated reaction products show that the manganese has been replaced by the allyl group. This is seen in the aromatic protons, specifically the proton adjacent to the site of reaction, where the peak has been shifted upfield by ~0.8 ppm from that observed for the original orthomanganated complex.

By analysis of the ^{1}H NMR spectra it was confirmed that the organic fragment had been attached as an allyl group and not the alternative methyl vinyl group. The allyl group gives rise to three signals that integrate as 2H, 1H and 2H, where the methyl vinyl group would give peaks integrating as 3H, 1H, and 1H.

The ^{1}H NMR peaks from the allyl functional groups of the allyl products are shown in Table 6-3. It can be seen that with the exception of **188** and **189**, all compounds show similar spectra, with little deviation in the chemical shifts of the allyl peaks.

Table 6-3 ^{1}H NMR of the allyl functional group for the organic products of the reaction of cyclomanganated complexes with allyl bromide.

		ppm		
	Compounds	-C*H*$_2$-	-C*H*=	=C*H*$_2$
183	2-allyl-4-methoxyacetophenone	3.70	5.97	5.01, 5.01
185	2-acetyl-3-allylthiophene	3.82	6.02	5.09, 5.10
186	N-tolyl-2-allyl-4-methoxybenzylimine	3.71	6.06	5.05, 5.14
22	2-allyl-4-methoxybenzaldehyde	3.82	6.04	5.04, 5.12
187	2-allylphenyl-diphenylphosphine sulfide	3.66	5.76	4.96, 4.99
188	5-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone	2.90, 2.99	5.70	5.17, 5.18
189	3-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone	2.89	5.68	5.13, 5.19

Using *N*-(4-tolyl)-2-allyl-4-methoxybenzylimine **186** as an example, it can be seen that the two protons on the methylene carbon of the allyl group are equivalent. They give a single signal split by ^3J coupling to the adjacent methenyl proton, and weak ^4J coupling to the terminal protons of the allyl group (**i** of Figure 6-3). The terminal protons give two signals, the *trans* at a slightly lower chemical shift than the *cis*. Both signals are split by ^3J coupling to the methenyl proton, which allows discrimination between them on the basis of the *cis* vs. *trans* coupling constants (*cis* generally being 7-11 Hz, *trans* 12-18 Hz). The two terminal protons also couple to each other affording the fine splitting of ~2 Hz (**ii** of Figure 6-3). The methenyl proton shows a single signal with complex splitting due to coupling to the surrounding *trans*, *cis* and *geminal* protons (**iii** of Figure 6-3).

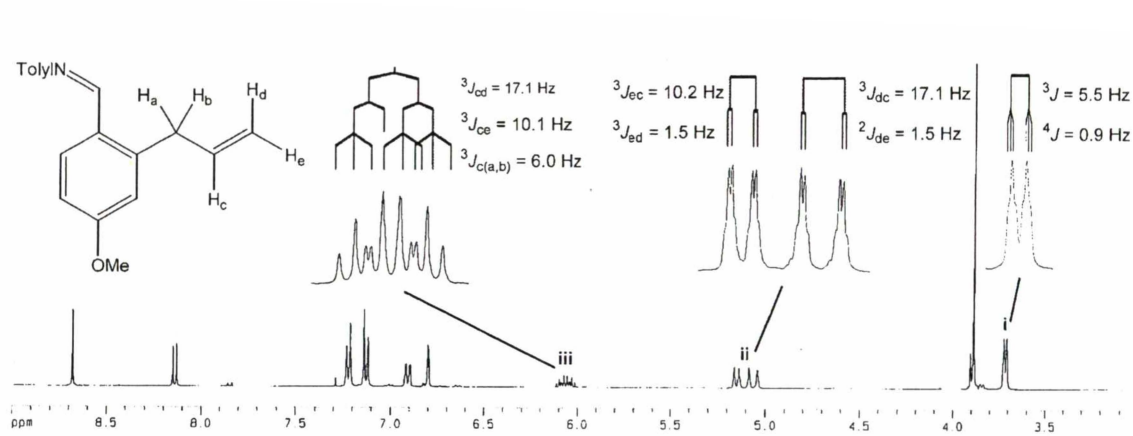


Figure 6-3 ^{1}H NMR spectrum of **186** with insets showing enlargements of the allyl protons peaks to show couplings.

The allyl groups of **188** and **189** give the equivalent signals to those of the aryl products, with the methylene protons shifted upfield by ~0.8 ppm. The main difference is that the allyl group is attached to a chiral centre, which causes the two methylene protons to become inequivalent[156]. The inequivalence afforded two signals which are coupled to each other and to the adjacent methenyl proton (**i** of Figure 6-4).

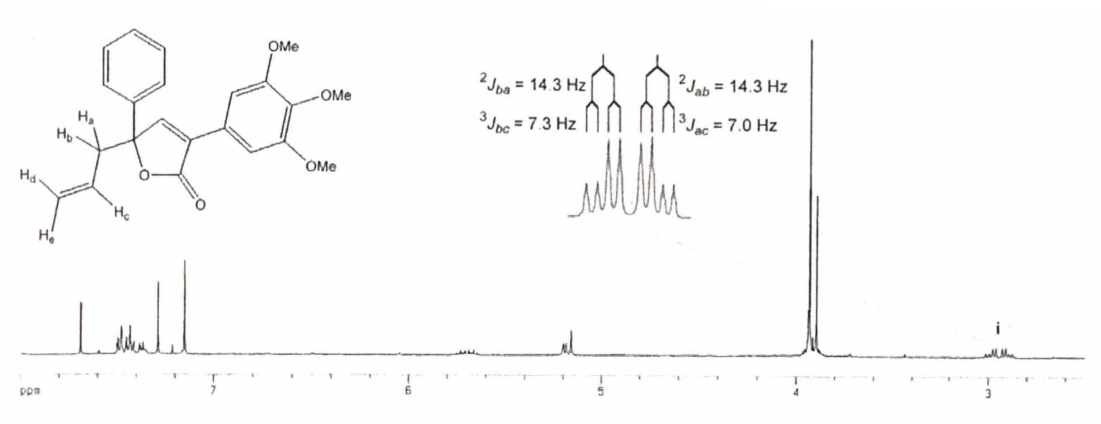


Figure 6-4 ^{1}H NMR spectrum of **188** with insets showing enlargements of the allyl methylene proton peaks to show couplings.

The carbon signals associated with the allyl groups of products show equivalent signals, with the furanone causing a slight change in the chemical shifts. The furanone ring appears to have an equal affect on the chemical shifts with the position of attachment having little influence.

Table 6-4 ^{13}C NMR of the allyl functional group for the organic products of the reaction of cyclomanganated complexes with allyl bromide.

		ppm		
	Compound	-CH_2-	-CH=	=CH_2
183	2-allyl-4-methoxyacetophenone	38.9	137.7	116.0
185	2-acetyl-3-allylthiophene	34.8	136.3	116.5
186	N-tolyl-2-allyl-4-methoxybenzylimine	37.5	137.3	116.7
22	2-allyl-4-methoxybenzaldehyde	36.8	136.7	116.6
187	2-allylphenyl-diphenylphosphine sulfide	38.6	133.6	116.7
188	5-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone	44.7	130.9	120.8
189	3-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone	44.0	130.0	119.9

6.3. Conclusion

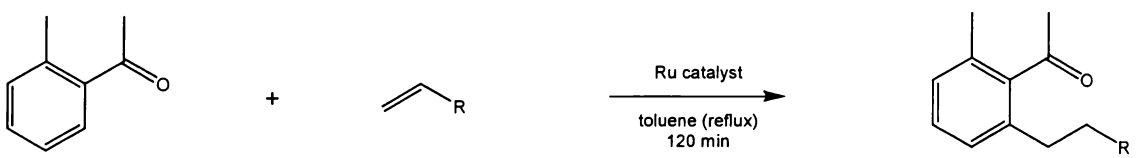
The reaction of orthomanganated aryl ketones with allyl halides is not unique in the forming of *ortho*-allylated aryl ketones. Both the Heck reaction and the Murai reactions can also be employed to afford *ortho*-substituted aryl ketones.

The Heck reaction can be used to prepare allyl-substituted aryl compounds by the reaction

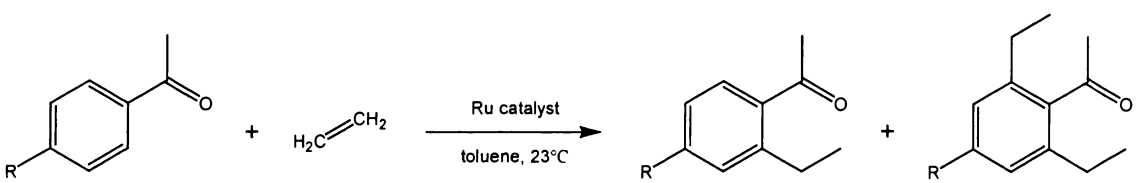
of arylpalladium complexes with allylic chlorides[182].

The aryl-palladium complexes are generated from aryl-tin, -lead or commonly -mercuric compounds, hence limiting the application of the reaction to those aryl complexes that can generate the original aryl-metal compounds. The allyl-aromatic compound can also be isomerised to the methyl vinyl structure if the reaction conditions are not maintained at their optimum[183].

The Murai reaction uses a ruthenium catalyst to activate the *ortho* C-H bond of an aryl ketone[184,39]. Substituted terminal alkenes can be reacted with aryl ketones in the presence of the catalyst, resulting in the insertion of the alkene into the C-H. The reaction forms a *ortho*-alkylated aryl ketone, with functionalisation of the *ortho*-substituent determined by the starting alkene.



Though the reaction can proceed with very high yields (>90%), the catalytic nature of the reaction can lead to difficulties. In the example above, the second *ortho* site was protected by a methyl group, but if this is not the case mixtures of the 2-monosubstituted and 2,6-disubstituted products can be produced[185].



[182] R. F. Heck, *Organotransition metal chemistry, a mechanistic approach*, Academic Press, New York, 1974, pp 108

[183] R. F. Heck, *J. Amer. Chem. Soc.*, **90** (1968) 5518

[184] S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature*, **366** (1993) 529

[185] S. Busch, W. Leitner, *Adv. Synth. Catal.*, **343** (2000) 192

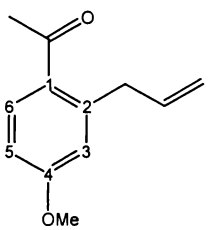
What makes the method described in this study appealing is the ability to use unactivated precursors compared to the Heck reaction, and of achieving mono-allylation without excessive care in the reaction conditions, as can be required by the Murai reaction. The method is a relatively efficient (57 - 97%) and simple way to achieve *ortho*-allylated aryl ketones.

6.4. Experimental

Reactions of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ and allyl isothiocyanate.

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and allyl isothiocyanate in dioxane (90°C).*

43 (50 mg, 0.16 mmol) and allyl isothiocyanate (66 µl, 0.67 mmol) were transferred to a 50 ml round bottom flask with dioxane (10 ml) under nitrogen. The solution was heated to 90°C for 3 hours, at which stage the solvent was removed under vacuum. The residue was chromatographed (PLC plate, 1:2 ether/petroleum spirits) to afford two bands. The most mobile fraction was collected to afford 2-allyl-4-methoxyacetophenone (**183**, 12 mg, 40%) as a yellow oil. The second fraction contained 4-methoxyacetophenone from demetalation of the starting material. An appreciable amount of immobile material remained at the origin of the PLC plate.



183

M_r = 190.2 $C_{12}H_{14}O_2$

High Resolution Mass Spectroscopy : Calculated : 190.0994

Experimental : 190.0996

IR: (CH_2Cl_2) ν(C=O) 1679 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 593 (27%, $[3M+Na]^+$), 403 (100%, $[2M+Na]^+$), 213 (7%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 190 (M^+, 2%), 175 (100), 160 (23), 147 (20), 91 (11), 43 (18)

^{1}H NMR: ($CDCl_3$) δ 2.52 (3H, s, CH_3CO), 3.70 (2H, d, $^3J_{HH}$ = 6.0 Hz, $CH_2CH=CH_2$), 3.83 (3H, s, CH_3O), 5.01 (1H, d, $^3J_{HH}$ = 15.4 Hz, $CH_2CH=CH_2$), 5.01 (1H, d, $^3J_{HH}$ = 11.2 Hz, $CH_2CH=CH_2$), 5.97 (1H, td, $^3J_{HH}$ = 16.6 Hz, $^3J_{HH}$ = 6.7 Hz,

$CH_2CH{=}CH_2$), 6.76 (1H, d, $^3J_{HH}$ = 9.6 Hz, H5), 6.77 (1H, s, H3), 7.71 (1H, d, $^3J_{HH}$ = 8.3 Hz, H6)

^{13}C NMR: ($CDCl_3$) δ 29.6 (CH_3CO), 38.9 ($CH_2CH{=}CH_2$), 55.7 (CH_3O), 111.2 (C3), 116.0 ($CH_2CH{=}CH_2$), 117.1 (C5), 130.4 (C2), 132.7 (C6), 137.7 ($CH_2CH{=}CH_2$), 144.0 (C1), 200.0 (CH_3CO)

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and allyl isothiocyanate in MeCN with Li_2PdCl_4.*

$PdCl_2$ (28 mg, 0.16 mmol) and LiCl (28 mg, 0.66 mmol) were transferred to a Schlenk flask under nitrogen and stirred in MeCN (5 ml) for 3 hours, until the palladium had become soluble. **43** (50.6 mg, 0.16 mmol) and allyl isothiocyanate (66 µl, 0.67 mmol) were transferred to the reaction vessel with further MeCN (2 ml), and the mixture stirred at ambient temperature overnight. Care was taken to exclude water from the reaction vessel. Solvent was removed under vacuum, and the residue extracted with ether. A large quantity of insoluble material remained in the vessel after extraction with ether. The ether extract was filtered and chromatographed (PLC plate, 1:2 ethyl acetate/petroleum spirits) to afford two fractions, similar to the previous reaction. The more mobile fraction was collected, giving 2-allyl-4-methoxyacetophenone (**183**, 2.6 mg, 8.5%) as a yellow oil.

6.4.1. Reactions of cyclomanganated complexes with allyl substrates.

General reaction of cyclomanganated complexes with allyl substrates.

A 1:3 ratio of the cyclomanganated complex (ca 50 mg) and allyl halide or allyl alcohol was transferred to a Schlenk flask with dioxane (10 ml). The Schlenk flask was heated to 90°C (oil bath) until the reaction was complete (as determined by IR spectroscopy), generally 2-3 hours. The reaction was conducted under a nitrogen atmosphere. The solvent was removed under vacuum, and the residue was purified by chromatography (PLC plate, 1:1 ether/petroleum spirits).

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and allyl bromide.*

43 (55 mg, 0.17 mmol) and allyl bromide (65 µl, 0.75 mmol) reacted in dioxane for 3 hours. Chromatography gave three fractions, the more mobile of which was collected, affording 2-allyl-4-methoxyacetophenone (**183**, 19 mg, 57%) as a pale yellow oil. The remaining fractions were 4-methoxyacetophenone and a minor quantity (<1%) of unreacted **43**.

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and allyl iodide.*

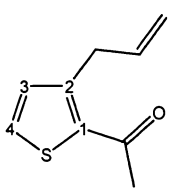
43 (53 mg, 0.17 mmol) and allyl iodide (80 µl, 0.87 mmol) were reacted in dioxane for 2 hours. Chromatography gave two fractions, the first of which was collected to afford 2-allyl-4-methoxyacetophenone (**183**, 22 mg, 71% yield) as a yellow oil. The remaining fraction was 4-methoxyacetophenone.

*Reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and allyl alcohol.*

43 (54 mg, 0.17 mmol) and allyl alcohol (35 µl, 0.51 mmol) were reacted in dioxane for 3 hours. Chromatography gave three fractions, the first of which was collected to afford 2-allyl-4-methoxyacetophenone (**183**, 14 mg, 42% yield) as a yellow oil. The remaining fractions were 4-methoxyacetophenone and a minor quantity (<1%) of unreacted **43**.

*Reaction of η^2-(2-acetylthiophene)Mn(CO)$_4$ (**45**) and allyl bromide.*

45 (51 mg, 0.17 mmol) and allyl bromide (45 µl, 0.52 mmol) were reacted in dioxane for 2 hours. Chromatography gave two fractions, the less mobile of which was collected, affording 2-acetyl-3-allylthiophene (**185**, 23 mg, 80% yield) as an oil. **185** was identified by comparison of the IR and NMR data with literature values[179]. The other fraction was 2-acetylthiophene, produced from the de-metalation **45**.



185

Mr = 166.2 $C_9H_{10}OS$

IR: (CH_2Cl_2) ν(C=O) 1664 cm^{-1}.

ESMS: (MeOH, cone +20 V) (*m/z* 355, 10%) $[2M+Na]^+$, (189, 100%) $[M+Na]^+$.

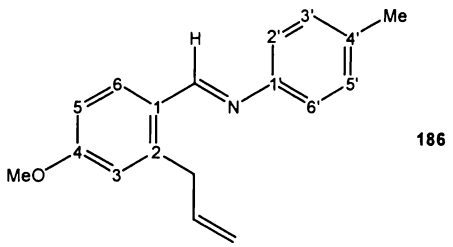
GCMS: (70 eV) *m/z* 166 (M^+, 5%), 151 (100), 133 (7), 123 (19), 45 (26), 43 (24).

^{1}H NMR: ($CDCl_3$) δ 2.57 (3H, s, $COCH_3$), 3.82 (2H, d, $^3J_{HH}$ = 6.5 Hz, -C*H*$_2$CH=CH$_2$), 5.09 (H, dd, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 1.4 Hz, -CH$_2$CH=C*H*$_2$), 5.10 (H, dd, $^3J_{HH}$ = 15.6 Hz, $^2J_{HH}$ = 1.6 Hz, -CH$_2$CH=C*H*$_2$), 6.02 (H, ddt, $^3J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.6 Hz, -CH$_2$C*H*=CH$_2$), 7.04 (H, d, $^3J_{HH}$ = 4.9 Hz, CH), 7.45 (H, d, $^3J_{HH}$ = 4.9 Hz, CH).

^{13}C NMR: ($CDCl_3$) δ 30.0 (CO*C*H$_3$), 34.8 (-*C*H$_2$CH=CH$_2$), 116.5 (-CH$_2$CH=*C*H$_2$), 124.6 (C), 129.1 (C), 130.2 (CH), 131.9 (CH), 136.3 (-CH$_2$*C*H=CH$_2$), 191.4(*C*OCH$_3$).

*Reaction of η^2-(N-(4-tolyl)-5-methoxy-2-benziminyl)Mn(CO)$_4$ (**184**) and allyl bromide.*

184 (91 mg, 0.23 mmol) and allyl bromide (100 µl, 1.2 mmol) were reacted in dioxane for 2 hours. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting oil was extracted with ethyl acetate, and dried under vacuum to afford *N*-(4-tolyl)-2-allyl-4-methoxybenzylimine (**186**, 60 mg, 97% yield) as an orange oil.



186

M_r = 265.4 $C_{18}H_{19}NO$

IR: (CH_2Cl_2) ν(C=N) 1623 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 818 (12%, $[3M+Na]^+$), 553 (31%, $[2M+Na]^+$), 288 (14%, $[M+Na]^+$), 266 (100%, $[M+H]^+$)

GCMS: (70 eV) *m/z* 265 (M^+, 9%), 250 (100), 207 (17), 91 (5), 65 (5)

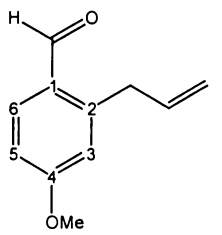
^{1}H NMR: ($CDCl_3$) δ 3.71 (2H, dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 0.9 Hz, -C*H*$_2$CH=CH$_2$), 5.05 (1H, dt, $^3J_{HH}$ = 17.1 Hz, $^2J_{HH}$ = 1.5 Hz, -CH$_2$CH=C*H*$_2$), 5.14 (1H, dt, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.5 Hz, -CH$_2$CH=C*H*$_2$), 6.06 (1H, ddt, $^3J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 6.0 Hz, -CH$_2$C*H*=CH$_2$), 6.79 (1H, d, $^4J_{HH}$ = 2.4 Hz, H3), 6.90 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.5 Hz, H5), 7.13 (2H, d, $^3J_{HH}$ = 8.2 Hz, H2′/H6′), 7.22 (2H, d, $^3J_{HH}$ = 8.0 Hz, H3′/H5′), 8.14 (1H, d, $^3J_{HH}$ = 8.7 Hz, H6), 8.68 (1H, s, HC=N)

^{13}C NMR: ($CDCl_3$) δ 21.3 (tolyl-CH_3), 37.5 (-*C*H$_2$CH=CH$_2$), 55.7 (OCH_3), 112.8 (C5), 115.9 (C3), 116.7 (-CH$_2$CH=*C*H$_2$), 121.2 (C2′/C6′), 127.6 (C2), 130.1 (C3′/C5′), 130.3 (C6), 135.6 (C4′), 137.3 (-CH$_2$*C*H=CH$_2$), 142.5 (C1), 150.7 (C1′), 157.9 (HC=N), 162.2 (C4)

Hydrolysis of N-tolyl-2-allyl-4-methoxybenzylimine.

N-(4-tolyl)-2-allyl-4-methoxybenzylimine (**186**, 21 mg, 0.080 mmol) was transferred to a 50 ml round bottom flask with THF (10 ml). Dilute HCl (0.1 M, 10 ml) was added, and the mixture stirred for 2 hours, at which time the hydrolysed product was extracted with ether. The ether solution was dried over magnesium sulfate, filtered and evaporated to

dryness to afford a quantitative yield of 2-allyl-4-methoxybenzylaldehyde (**193**) as a pale oil.



192

M_r = 176.2 $C_{11}H_{12}O_2$

High Resolution Mass Spectroscopy : Calculated : 175.0759 [M-H]

Experimental : 175.0757 [M-H]

IR: (CH_2Cl_2) ν(C=O) 1687 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 375 (64%, $[2M+Na]^+$), 199 (100%, $[M+Na]^+$), 177 (16%, $[M+H]^+$)

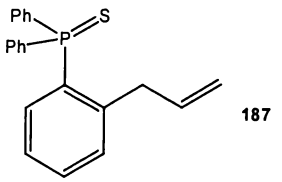
GCMS: (70 eV) *m/z* 177 (M^+, 10%), 176 (78), 161 (100), 148 (59), 144 (43), 115 (31), 91 (27), 77 (31)

^{1}H NMR: ($CDCl_3$) δ 3.82 (2H, dd, $^3J_{HH}$ = 6.3 Hz, -C*H*$_2$CH=CH$_2$), 5.04 (1H, dt, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 1.7 Hz, -CH$_2$CH=C*H*$_2$), 5.12 (1H, dt, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.5 Hz, -CH$_2$CH=C*H*$_2$), 6.04 (1H, ddt, $^3J_{HH}$ = 16.8 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 6.3 Hz, -CH$_2$C*H*=CH$_2$), 6.80 (1H, d, $^4J_{HH}$ = 2.4 Hz, H3), 6.89 (1H, dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.5 Hz, H5), 7.83 (1H, d, $^3J_{HH}$ = 8.6 Hz, H6), 10.12 (1H, s, HC=O)

^{13}C NMR: ($CDCl_3$) δ 36.8 (-*C*H$_2$CH=CH$_2$), 55.5 (OCH_3), 112.0 (C5), 116.4 (C3), 116.6 (-CH$_2$CH=*C*H$_2$), 129.9 (C2), 134.6 (C6), 136.7 (-CH$_2$*C*H=CH$_2$), 145.0 (C1), 157.6 (C4), 190.9 (HC=O)

*Reaction of η^2-(triphenylphosphine sulphide)Mn(CO)$_4$ (**49**) and allyl bromide.*

49 (51 mg, 0.11 mmol) and allyl bromide (50 μl, 0.58 mmol) were reacted in dioxane for 2 hours. Chromatography was ineffective at isolating the product **187** (13%) from the reaction mixture which contained the starting material (**49**, 11%) and triphenylphosphine sulfide (76%) produced by de-metalation of **49**. The yield of the compounds in the reaction mixture was calculated from integration of the peaks in the ^{31}P NMR spectrum. The ^{1}H and ^{13}C NMR signals were assigned by eliminating those peaks known to be from **49** and triphenylphosphine sulfide.



187

M_r = 334.4 $C_{21}H_{19}PS$

ESMS: (MeOH, cone +20 V) *m/z* 1025 (5%, $[3M+Na]^+$), 691 (67%, $[2M+Na]^+$), 357 (100%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 334 (M^+, 100%), 319 (86), 301 (41), 287 (13), 243 (19), 225 (24), 183 (37), 91 (19)

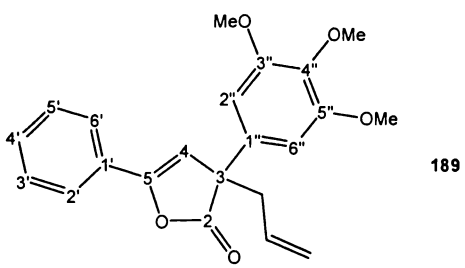
^{1}H NMR: ($CDCl_3$) δ 3.66 (2H, d, $^3J_{HH}$ = 6.5 Hz, -C*H*$_2$CH=CH$_2$), 4.96 (H, s, -CH$_2$CH=C*H*$_2$), 4.99 (H, s, -CH$_2$CH=C*H*$_2$), 5.76 (H, m, -CH$_2$C*H*=CH$_2$), 7.46-7.78 (14H, m, Ar-H)

^{13}C NMR: ($CDCl_3$) δ 38.6 (-*C*H$_2$CH=CH$_2$), 116.7 (-CH$_2$CH=*C*H$_2$), 133.6 (-CH$_2$-*C*H=CH$_2$), 123.1-144.5 (Ar, Ar-H)

^{31}P NMR: ($CDCl_3$) δ 42.85

*Reaction of orthomanganated chalcone (**54**) and allyl bromide.*

54 (55 mg, 0.12 mmol) and allyl bromide (55 μl, 0.64 mmol) reacted in dioxane for 2 hours. Chromatography afforded two main fractions, the first collected to afford 3-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone (**189**) (7 mg, 16 % yield), and the second affording 5-allyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone (**188**) (6 mg, 13% yield), both as pale yellow oils. A quantity of immobile material remained at the origin of the plate, and could not be eluted.



189

M_r = 366.4 $C_{22}H_{22}O_5$

High Resolution Mass Spectroscopy : Calculated : 366.1467

Experimental : 366.1482

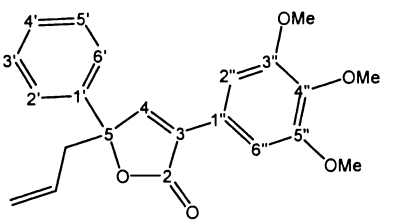
IR: (CH_2Cl_2) ν(C≡O) 1796 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 1121 (6%, $[3M+Na]^+$), 755 (34%, $[2M+Na]^+$), 389 (100%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 366 (M^+, 11%), 325 (100), 105 (86), 77(21).

^{1}H NMR: ($CDCl_3$) δ 2.89 (1H, m, -C*H*$_2$CH=CH$_2$), 3.85 (3H, s, *p*-OCH$_3$), 3.90 (6H, s, *m*-OCH$_3$), 5.13 (1H, d, $^3J_{HH}$ = 10.1 Hz, -CH$_2$CH=C*H*$_2$), 5.19 (1H, d, $^3J_{HH}$ = 17.1 Hz, -CH$_2$CH=C*H*$_2$), 5.68 (1H, m, -CH$_2$C*H*=CH$_2$), 6.12 (1H, s, H4), 6.76 (2H, s, H2″/H6″), 7.45 (3H, m, H3′/H4′/H5′), 7.70 (2H, dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 2.5 Hz, H2′/H6′).

^{13}C NMR: ($CDCl_3$) δ 44.0 (-*C*H$_2$CH=CH$_2$), 57.0 (C3), 56.4 *m*-OCH$_3$), 60.9 (*p*-OCH$_3$), 104.1 (C2″/C6″), 105.4 (C4), 119.9 (-CH$_2$CH=*C*H$_2$), 125.1 (C2′/C6′), 128.2 (C1′), 128.8 (C3′/C5′), 130.0 (-CH$_2$*C*H=CH$_2$), 131.9 (C4′), 134.5 (C1″), 136.9 (C4″), 152.3 (C5), 153.4 (C3″/C5″), 178.1 (C2)



188

M_r = 366.4 $C_{22}H_{22}O_5$

High Resolution Mass Spectroscopy : Calculated : 366.1467

Experimental : 366.1484

IR: (CH_2Cl_2) ν(C≡O) 1759 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 1121 (32%, $[3M+Na]^+$), 755 (94%, $[2M+Na]^+$), 389 (100%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 366 (M^+, 10%), 325 (100), 105 (86), 77(22)

^{1}H NMR: ($CDCl_3$) δ 2.90 (1H, dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.0 Hz, -C*H*$_2$CH=CH$_2$), 2.99 (1H, dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.3 Hz, -C*H*$_2$CH=CH$_2$), 3.90 (3H, s, *p*-OCH$_3$), 3.93 (6H, s, *m*-OCH$_3$), 5.17 (1H, d, $^3J_{HH}$ = 10.8 Hz, -CH$_2$CH=C*H*$_2$), 5.18 (1H, dd, $^3J_{HH}$ = 17.1 Hz, $^2J_{HH}$ = 1.4 Hz, -CH$_2$CH=C*H*$_2$), 5.70 (1H, ddt, $^3J_{HH}$ = 16.6 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 7.2 Hz, - CH$_2$C*H*=CH$_2$), 7.15 (2H, s, H2″/H6″), 7.36 (1H, tt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.6 Hz, H4′), 7.43 (2H, td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz, H3′/H5′), 7.49 (2H, dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.6 Hz, H2′/H6′), 7.69 (1H, s, H4)

^{13}C NMR: ($CDCl_3$) δ 44.7 (-CH_2CH=CH_2), 56.7 (*m*-OCH_3), 61.3 (*p*-OCH_3), 87.8 (C5), 105.0 (C2″/C6″), 120.8 (-CH_2CH=CH_2), 125.5 (C3), 125.5 (C2′/C6′), 128.6 (C4'), 129.2 (C3′/C5′), 130.6 (C1″), 130.9 (-CH_2CH=CH_2), 139.4 (C4″), 139.5 (C1′), 149.8 (C4), 153.7 (C3″/C5″), 170.8 (C2)

6.4.2. Reactions of cyclomanganated complexes with organic halides.

The following reactions were also undertaken using the general method described in Section 6.4.1.

*Attempted reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and benzyl bromide.*

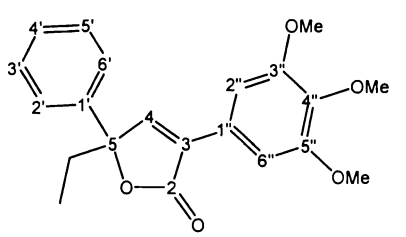
43 (51 mg, 0.16 mmol) and benzyl bromide (60 μl, 0.50 mmol) were reacted in dioxane for 4 hours. Chromatography showed the only products to be 4-methoxyacetophenone (from the demetalation of **43**) and benzyl bromide.

*Attempted reaction of η^2-(2-acetyl-5-methoxyphenyl)Mn(CO)$_4$ (**43**) and ethyl iodide.*

43 (51 mg, 0.16 mmol), and ethyl iodide (40 μl, 0.50 mmol) were reacted in dioxane for 2 hours. Chromatography showed the only products to be 4-methoxyacetophenone (from the demetalation of **43**) and ethyl iodide.

*Reaction of orthomanganated chalcone (**54**) and ethyl iodide.*

54 (101 mg, 0.22 mmol) and ethyl iodide (80 μl, 0.99 mmol) were reacted in dioxane for 2 hours. Chromatography afforded two main fractions, the first of which was collected to afford 3-ethyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)isofuranone (**191**) (6 mg, 8% yield), and the second afforded 5-ethyl-5-phenyl-3-(3,4,5-trimethoxyphenyl)furanone (**190**) (4 mg, 5% yield), both as pale yellow oils. A large quantity of material remained at the origin of the plate, and could not be eluted.



190

M_r = 354.4 $C_{21}H_{22}O_5$

High Resolution Mass Spectroscopy : Calculated : 354.1467

Experimental : 354.1474

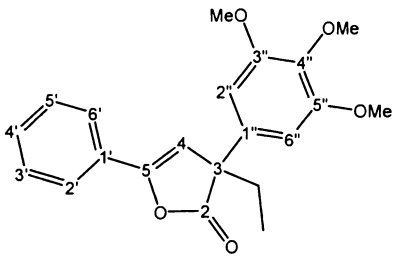
IR: (CH_2Cl_2) ν(C≡O) 1795 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 1085 (10%, $[3M+Na]^+$), 731 (32%, $[2M+Na]^+$), 377 (100%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 354 (M^+, 26%), 325 (100), 249 (22), 105 (100), 77(48)

^1H NMR: ($CDCl_3$) δ 0.98 (3H, t, $^3J_{HH}$ = 7.4 Hz, $-CH_2CH_3$), 2.15 (1H, m, $-CH_2CH_3$), 2.23 (1H, m, $-CH_2CH_3$), 3.86 (3H, s, *p*-OCH_3), 3.90 (6H, s, *o*-OCH_3), 6.11 (1H, s, H4), 6.77 (2H, s, H2"/H6"), 7.46 (2H, m, H3'/H5'), 7.48 (1H, m, H4'), 7.72 (2H, dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.8 Hz, H2'/H6').

^{13}C NMR: ($CDCl_3$) δ 9.8 ($-CH_2CH_3$), 33, ($-CH_2CH_3$), 58.0 (C3), 56.7 (*m*-OCH_3), 61.2 (*p*-OCH_3), 104.4 (C2"/C6"), 105.8 (C4), 125.4 (C2'/C6'), 127.4 (C1'), 129.1 (C3'/C5'), 130.2 (C4'), 134.9 (C1"), 138.2 (C4"), 152.8 (C5), 153.7 (C3"/C5"), 179.0 (C2)



191

M_r = 354.4 $C_{21}H_{22}O_5$

IR: (CH_2Cl_2) ν(C≡O) 1759 cm^{-1}

ESMS: (MeOH, cone +20 V) *m/z* 1085 (9%, $[3M+Na]^+$) 731 (40%, $[2M+Na]^+$), 377 (100%, $[M+Na]^+$)

GCMS: (70 eV) *m/z* 354 (M^+, 87%), 325 (98), 269 (71), 105 (100), 77(45)

^1H NMR: ($CDCl_3$) δ 0.97 (3H, t, $^3J_{HH}$ = 7.4 Hz, $-CH_2CH_3$), 2.14 (1H, m, $-CH_2CH_3$), 2.29 (1H, m, $-CH_2CH_3$), 3.89 (3H, s, *p*-OCH_3), 3.93 (6H, s, *m*-OCH_3), 7.16 (2H, s, H2"/H6"), 7.36-7.49 (5H, m, H2'-H6'), 7.67 (1H, s, H4)

^{13}C NMR: ($CDCl_3$) δ 8.5 ($-CH_2CH_3$), 33.5 ($-CH_2CH_3$), 56.7 (*m*-OCH_3), 61.3 (*p*-OCH_3), 89.0 (C5), 105.0 (C2"/C6"), 125.2 (C3), 125.5 (C2'/C6'), 128.5 (C4'), 129.2 (C3'/C5'), 130.1 (C1"), 139.6 (C4"), 139.7 (C1'), 150.5 (C4), 153.4 (C3"/C5"), 171.4 (C2)

Chapter 7. General Experimental Procedures and Preparation of Precursors.

7.1. General Experimental Techniques

Many of the compounds used or prepared in this study are oxygen or moisture sensitive, requiring that reactions be carried out under an inert atmosphere of oxygen-free nitrogen. Standard Schlenk line techniques were used for the handling and reaction of such compounds[186].

Silicone oil baths in combination with a thermostatted heating coil were used for reactions requiring constant temperatures, while reactions at reflux were heated directly with a heating mantle or thermostated heating block.

Melting point determinations were undertaken on a Reichert Thermovar apparatus, and are uncorrected.

Carbon, hydrogen and nitrogen analyses were performed at University of Otago at the Campbell Microanalytical Laboratory.

7.1.1. Chromatography

Preparative layer chromatography (PLC) plates were prepared by mixing silica gel (Merck Kieselgel $60PF_{254}$) with twice its weight of distilled water. The resulting slurry was spread onto 20 x 20 cm glass plates to a depth of 1-1.5 mm and allowed to air dry prior to activation at 110°C. The mixture to be separated was applied as a CH_2Cl_2 solution by pipette as a thin line near the base of the plate. The plates were developed in tanks containing the required solvent mixture. Colourless bands were identified using UV light. Bands to be collected were removed from the plates and the products eluted from the silica with either CH_2Cl_2 or Et_2O.

Column chromatography was used for large scale separations or when alumina was required. Packing material, either Merck Kieselgel 60 or BDH alumina oxide (Brockman

[186] D. F. Shriver, M. A. Drezdzon, *The manipulation of air-sensitive compounds*, 2nd Ed., John Wiley & Sons, New York, (1986)

Grade, activity II), was slowly poured into a column with the required solvent. The column was previously fitted with a cotton wool plug below a 5 mm layer of acid washed sand. The suspension was allowed to settle overnight before use. Mixtures to be chromatographed were added as solutions, and allowed to run into the column before developing. Where mixtures were insoluble in the chromatography solvent, said mixtures were dissolved in CH_2Cl_2 and absorbed onto 2-4 g of the packing material. CH_2Cl_2 was removed under vacuum, with the absorbed material transferred to the column and developed. Bands were collected according to colour.

7.1.2. Chemicals

Unless stated below, chemicals were used as received.

Solvents were generally purified prior to use, to remove oxygen and water, by distillation over a drying agent under a nitrogen atmosphere (Table 7-1).

Table 7-1 Purification of general solvents.

Solvent	Purification (in nitrogen atmosphere)
Acetone	Distilled from $KMnO_4$
Acetonitrile	Distilled from CaH_2
Benzene	Distilled from sodium
Carbon tetrachloride	Distilled from $KMnO_4$
Diethyl ether	Distilled from sodium/benzophenone
Dichloromethane	Distilled from CaH_2
Dioxane	Distilled from sodium/benzophenone
Heptane	Distilled from CaH_2
Petroleum Spirits (60-80° fraction)	Distilled from CaH_2
Tetrahydrofuran	Distilled from sodium/benzophenone
Toluene	Distilled from sodium

Carbon disulfide was used as received, with oxygen removed by successive freeze/evacuate/thaw cycles on a vacuum line.

Anhydrous $CoCl_2$, $NiBr_2$, and $CuCl_2$ were prepared by drying the appropriate hydrate under vacuum at 120°C. The anhydrides were prepared fresh each time they were required. Anhydrous LiCl was stored at 110°C.

Benzyl bromide, acetophenone and aniline were freshly distilled.

7.2. Instrumental Techniques

7.2.1. Infrared Spectroscopy

Infrared spectroscopy was carried out on a Bio-Rad Digilab Division FTS-40 FTIR, using Bio-Rad Win-IR Ver. 4.4 software. Solution spectra were obtained using a solution cell with 0.1 mm path length and KBr windows.

Observations were made of the carbonyl stretching region of metal carbonyls (1800-2400 cm^{-1}). Chemical information can be obtained from the number, pattern, intensity and position of the peaks in this region. The subtraction facility was utilised to obtain spectra free of solvent and atmospheric absorbances.

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

7.2.2. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy was performed using either a Bruker Avance DRX 300 or Avance DRX 400 spectrometer using XWIN-NMR software V. 3.0 or V. 3.1 respectively. Deuterated chloroform, acetone and dimethylsulfoxide solvents were used, with ^{1}H and ^{13}C spectra referenced to TMS (Me_4Si) and ^{31}P spectra referenced to 85% H_3PO_4.

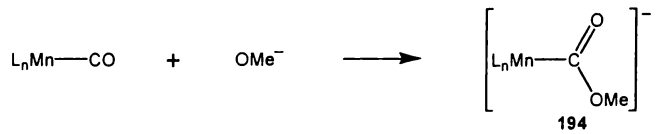
7.2.3. Mass spectroscopy

Electrospray mass spectra were obtained on a Fisons Instruments VG Platform II using MassLynx V. 2.0 software. Analyses were conducted over a range of cone voltages in both positive and negative modes. A range of solvents and ionisation agents were used as required, with two standard methods predominating. Using acetonitrile as the mobile phase, approximately 1 mg of the compound was dissolved in 0.5 ml of the mobile phase, then immediately injected into the machine. The second method used methanol as the mobile phase solvent, and prior to injection, a few drops of a methanol solution of NaOMe were added to the sample, as an ionisation aid[187].

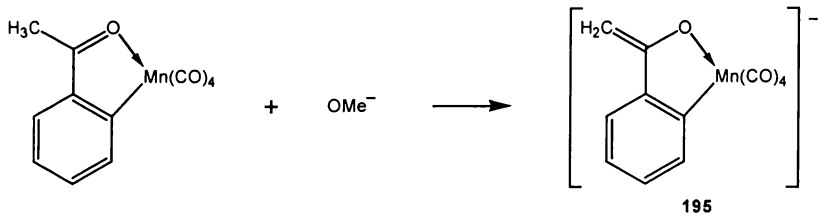
The introduction of OMe^- ions to a metal carbonyl can lead to the formation of a

[187] W. Henderson, J. S. McIndoe, B. K. Nicholson, P. J. Dyson, *J. Chem. Soc., Dalton Trans.*, (1998) 519

coordinated methyl formate ion (**194** in Scheme 7-1), giving peaks assigned as $[M+OMe]^-$ (where M is the molecular mass of the product). Where there is an available proton, as is the case with a coordinated acetyl-aryl ligand, the OMe^- ion can abstract the proton, giving peaks assigned as $[M-H]^-$, forming in this case an enol (**195** in Scheme 7-2).



Scheme 7-1 Formation of formate anion by addition of OMe^-.



Scheme 7-2 Formation of enolate anion by addition of OMe^-.

The methanol solution of NaOMe was prepared by the addition of a small sample of sodium metal to drum grade methanol.

In instances where compounds were insoluble in the mobile phase, the compound was dissolved in a few drops of CH_2Cl_2 before addition of the mobile phase.

Volatile, thermally stable compounds were also analysed by coupled gas chromatography/mass spectroscopy (GC/MS). Electron impact mass spectra were collected on a Hewlett-Packard 5970 mass selective detector coupled to a HP 5890A gas chromatograph. Spectra were processed and analysed using HP Enhanced Chemstation 61701AA V. A.03.00 software.

Compounds were dissolved in either CH_2Cl_2 or ether for direct injection analysis by GC/MS.

High resolution mass spectroscopy samples were run at the Mass Spectrometry Unit at Hortresearch in Palmerston North on a VG-70S Double focussing Magnetic Sector Mass

Spectrometer (VG Micromass UK). High Resolution spectra were obtained on standard EI Mode (+) at 5000RP with PFK calibrant being used for accurate mass calibration and measurement. 1 μl of sample in methanol was desorbed from heated solids probe into EI source. Standard 8 kV and 70 eV was used. Accurate mass data was formulated using VG-Opus Elemental Program for formulation and PPM error calculations.

7.2.4. X-ray crystallography

Generally preliminary investigations were undertaken by precession photography using nickel-filtered Cu-Kα X-ray radiation. This gave an indication of crystal quality, and allowed the determination of space group and unit cell dimensions.

If full crystal structure determination was required, intensity data sets were collected by Auckland University or Canterbury University, both of which are equipped with a Siemens SMART CCD diffractometer. Structure solution and refinement was carried out using the SHELX program[188], running under the WINGX[189] suite of programs.

Complete tables of bond lengths, bond angles, final position parameters and thermal parameters are presented on a CD (inside back cover) in the form of the CIF files. The program Mercury[190] can be used to view the structures.

7.3. Preparation of Reaction Precursors

Most of the preparations in this section were found in the literature. In general the published method was altered for reasons of convenience or scale. Those preparations that are not referenced are original syntheses based on similar preparations in the literature. The purity of all compounds were confirmed using NMR spectroscopy.

Benzylpentacarbonylmanganese[191]

An amalgam of mercury (5 ml) and sodium (approximately 0.7 g) was prepared in a Schlenk flask (100 ml) under nitrogen. To the Schlenk flask was added THF (60 ml) followed by $Mn_2(CO)_{10}$ (2.0 g, 5.1 mmol), and the solution was stirred vigorously for 2

[188] SHELX-97, G. M. Sheldrick, University of Goettingen. Germany, (1997) (Release 97-2)

[189] WinGX – Version 1.64.05, L. J. Farrugia, Department of Chemistry, University of Glasgow; L. J. Farrugia, *J. Appl. Cryst.*, **32** (1999) 837

[190] Mercury Version 1.1, available from www.ccdc.cam.ac.uk/mercury/

[191] M. I. Bruce, M. J. Liddell, G. N. Pain, *Inorg. Synth.*, **26** (1989) 172

hours. The pale grey/green solution was decanted under nitrogen into a second Schlenk flask containing benzyl bromide (1.1 ml). The solution was stirred for a further 10 minutes, then run through a short silica column, and washed through with THF (2x10 ml). The solvent was removed from the pale yellow solution under reduced pressure. The resulting yellow oil was sublimed onto a cold finger (0.5 mm Hg, 50°C), affording pale yellow crystals of $PhCH_2Mn(CO)_5$ (2.3 g, 78%, ν(C≡O) (dichloromethane) 2108(m), 2011(vs, br), 1990(s, br) cm^{-1}).

7.3.1. Preparation of orthomanganated precursors

General method for preparation of orthomanganated precursors

A 1:1 ratio of the organic compound to be orthomanganated and $PhCH_2Mn(CO)_5$ was transferred to a Schlenk flask containing the reaction solvent (heptane unless stated) and refluxed under nitrogen. The progress of the reaction was monitored by observation of the carbonyl region of the infrared spectrum, and the reaction was deemed complete with the disappearance of the 2108 cm^{-1} peak (of $PhCH_2Mn(CO)_5$). The hot reaction mixture was filtered through filter paper into a round bottomed flask and cooled to -20°C overnight to afford crystals of the product. These crystals were then dried under vacuum, and stored at -20°C until required.

The IR spectra of compounds that have previously been prepared were compared to literature values. Purity was confirmed by NMR spectroscopy.

*η^2- (5-methoxy-2-acetylphenyl)tetracarbonylmanganese (**43**)*[192]

4-Methoxyacetophenone (104 mg, 0.690 mmol) and $PhCH_2Mn(CO)_5$ (199 mg, 0.696 mmol) were reacted in heptane (20 ml). The reaction mixture afforded pale yellow crystals of η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (174 mg, 80%, ν(C≡O) (petroleum spirits) 2083(m), 1996(vs, br), 1944(s) cm^{-1}).

*η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**45**)*[192]

2-Acetylthiophene (285 μml, 2.64 mmol) and $PhCH_2Mn(CO)_5$ (756 mg, 2.64 mmol) were reacted in heptane (20 ml). The reaction mixture afforded orange crystals of η^2- (2-acetylthien-3-yl)tetracarbonylmanganese (584 mg, 76%, ν(C≡O) (petroleum spirits)

[192] J. M. Cooney, L. H. P. Gommans, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **349** (1988) 197

2088(m), 2002(vs, br), 1953(s) cm^{-1}).

*η^2-(2-benzoylphenyl)tetracarbonylmanganese (**47**)*[3]

Benzophenone (217 mg, 1.19 mmol) and $PhCH_2Mn(CO)_5$ (325 mg, 1.14 mmol) were reacted in heptane (20 ml). The reaction mixture afforded yellow crystals of η^2-(2-benzoylphenyl)tetracarbonylmanganese (347 mg, 88%, ν(C≡O) (petroleum spirits) 2082(m), 1997(vs, br), 1948(s) cm^{-1}).

*η^2-[(2-diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (**49**)*[13]

Triphenylphosphine sulfide (519 mg, 1.76 mmol) and $PhCH_2Mn(CO)_5$ (502 mg, 1.76 mmol) were reacted in heptane (20 ml). The reaction mixture afforded yellow crystals of η^2-[(2-diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (636 mg, 90%, ν(C≡O) (petroleum spirits) 2073(m), 1992(vs, br), 1983(vs, br), 1948(s) cm^{-1}).

*η^2-[(2-diphenylselenophosphinyl)phenyl]tetracarbonylmanganese (**51**)*[13]

Triphenylphosphine selenide (841 mg, 2.46 mmol) and $PhCH_2Mn(CO)_5$ (703 mg, 2.46 mmol) were reacted in heptane (20 ml). The reaction mixture afforded yellow crystals of η^2-[(2-diphenylselenophosphinyl)phenyl]tetracarbonylmanganese (158 mg, 13%, ν(C≡O) (petroleum spirits) 2067(m), 1986(vs, br), 1975(s, br), 1930(s) cm^{-1}).

*η^2-[(N-phenyl-2-diphenylphosphinylimine)phenyl]tetracarbonyl-manganese (**53**)*[193]

Triphenylphosphine phenylimine (253 mg, 0.717 mmol) and $PhCH_2Mn(CO)_5$ (202 mg, 0.715 mmol) were reacted in heptane (20 ml). The reaction mixture afforded bright yellow crystals of η^2-[(N-phenyl-2-diphenylphosphinylimine)phenyl]-tetracarbonylmanganese (307 mg, 83%, ν(C≡O) (dichloromethane) 2069(m), 1979(vs, br), 1921(s) cm^{-1}).

*η^2-(N-(4-tolyl)-4-methoxybenzylimine)tetracarbonylmanganese (**186**)*

N-(4-Tolyl)-4-methoxybenzylimine (419 mg, 1.86 mmol) and $PhCH_2Mn(CO)_5$ (529 mg, 1.85 mmol) were reacted in heptane (20 ml). The reaction mixture afforded η^2-(*N*-(4-tolyl)-4-methoxybenzylimine)tetracarbonylmanganese (402 mg, 55%) as yellow needle-like crystals.

IR : ν(C≡O) (petroleum spirits) 2075(m), 1988(vs, br), 1945(s) cm^{-1}

ESMS : (MeOH/NaOMe, cone -20 V) *m/z* 422 (100%, $[M+OMe]^-$), 394 (18%, $[M-CO+OMe]^-$), 366 (22%, $[M-2CO+OMe]^-$)

[193] M. A. Leeson, B. K. Nicholson, M. R. Olsen, *J. Organomet. Chem.*, **579** (1999) 243

^{1}H NMR : ($CDCl_3$) δ 2.41 (3H, s, CH_3CO), 3.95 (3H, s, OCH_3), 6.70 (1H, dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.3 Hz, Ar-H), 7.09 (2H, d, $^3J_{HH}$ = 8.2 Hz, Ar-H), 7.23 (2H, d, $^3J_{HH}$ = 8.0 Hz, Ar -H), 7.58 (1H, d, $^4J_{HH}$ = 2.3 Hz, Ar-H), 7.61 (1H, d, $^3J_{HH}$ = 8.4 Hz, Ar-H), 8.20 (1H, s, HC=N)

^{13}C NMR : ($CDCl_3$) δ 21.1 (CH_3CO), 55.3 (CH_3O), 110.6 (Ar-H), 121.8 (Ar-H), 125.5 (Ar-H), 129.8 (Ar-H), 131.7 (Ar-H), 137.0 (Ar), 141.9 (Ar), 151.5 (Ar), 161.8 (Ar), 174.5 (HC=N), 187.4 (Ar), 213.6 (Mn(CO)), 213.9 (Mn(CO)), 220.4 (Mn(CO))

*η^2-(N-Acetyl-2-indolyl)tetracarbonylmanganese (**81**)*[194]

N-Acetylindole (230 µl, 2.00 mmol) and $PhCH_2Mn(CO)_5$ (590 mg, 2.06 mmol) were reacted in heptane (20 ml). The reaction mixture afforded yellow crystals of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (333 mg, 51%, ν(C≡O) (dichloromethane) 2088(m), 2001 (vs, br), 1945(s) cm^{-1}).

All other orthomanganated complexes were archived samples, with NMR being used to confirm purity.

7.3.2. Preparation of cyclomanganated precursors.

General method for preparation of cyclomanganated precursors

The method for preparing the following cyclomanganated enones is analogous to the method for preparing orthomanganated complexes, but with two exceptions. Petroleum spirits was used as the reaction solvent, and the work-up of the reaction mixture was modified.

At the end of the reaction, the solvent was removed under vacuum, the residue re-dissolved in dichloromethane and absorbed onto ~4 g of alumina (Brookman grade, activity II). The absorbed alumina was loaded onto the top of an alumina column, and the product eluted as an orange band with 1:8 dichloromethane/petroleum spirits. The chromatographically pure product was then recrystallised from warm petroleum spirits.

*η^2-[1-Phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-on-3-yl]tetra-carbonylmanganese (**54**)*[20]

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[194] N. P. Robinson, L. Main, B. K. Nicholson, *J. Organomet. Chem.*, **349** (1988) 209

1-Phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one (202 mg, 0.677 mmol) and $PhCH_2Mn(CO)_5$ (199 mg, 0.694 mmol) were reacted in petroleum spirits (20 ml). Workup of the reaction mixture afforded orange crystals of η^2-[1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-on-3-yl]tetracarbonylmanganese (236 mg, 75%, ν(C≡O) (chloroform) 2083 (m), 1997(vs, br), 1942(s)).

*η^2-[[1-Phenyl-2((E)-3-phenylprop-2-en-1-oyl]ethenyl]tetracarbonyl-manganese (**127**)*[31]

(E,E)-1,5-Diphenylpenta-1,4-dien-3-one (238 mg, 1.01 mmol) and $PhCH_2Mn(CO)_5$ (308 mg, 1.08 mmol) were reacted in petroleum spirits (20 ml). Workup of the reaction mixture afforded dark orange crystals of η^2-[[1-phenyl-2((E)-3-phenylprop-2-en-1-oyl]ethenyl]tetracarbonylmanganese (332 mg, 82%, ν(C≡O) (carbon tetrachloride) 2082 (m), 1998 (vs, br), 1950 (s)).

*η^2-[[1-(4-Trifluoromethylphenyl)-2((E)-3-(4-trifluoromethylphenyl)prop-2-en-1-oyl]ethenyl]tetracarbonylmanganese (**131**)*[31]

(E,E)-1,5-Di(trifluoromethylphenyl)penta-1,4-dien-3-one (517.6 mg, 1.376 mmol) and $PhCH_2Mn(CO)_5$ (447.9 mg, 1.565 mmol) were reacted in petroleum spirits (20 ml). Workup of the reaction mixture afforded dark orange crystals of η^2-(C,O)-[[1-(4-trifluoromethylphenyl)-2((E)-3-(4-trifluoromethylphenyl)prop-2-en-1-oyl]ethenyl]-tetracarbonylmanganese (673.4 mg, 91%, ν(C≡O) (petroleum spirits) 2089 (m), 2016 (vs), 1997 (vs), 1960 (s)).

7.3.3. Preparation of organic precursors

Preparation of triphenylphosphine sulphide[195]

Triphenylphosphine (2.39 g, 9.1 mmol) and sulfur (323 mg, 10.1 mmol) were placed in a Schlenk flask (100 ml) containing methanol (40 ml). Sufficient dichloromethane was added to dissolve the triphenylphosphine. The mixture was sonicated for approximately 5 hours, with the reaction progress monitored by ^{31}P NMR spectroscopy to determine when the reaction was complete. The solvent was removed under vacuum, and the product was recrystallised from dichloromethane/petroleum spirits at -20°C affording clear needles of triphenylphosphine sulphide (2.54 g, 95%, ^{31}P NMR ($CDCl_3$) δ 44.0 *cf* 43.3 from literature[153]).

[195] S. Alley, Ph.D. Thesis, University of Waikato, (2001)

Preparation of triphenylphosphine phenylimine[196]

Hydrochloric acid (2 ml) was added to distilled water (10 ml) in an ice cooled 100 ml round bottom flask. Phenyl hydrazine (750 mg) was added drop-wise with stirring over a 5 minute period, while the temperature was maintained at 0°C. Diethyl ether (6 ml) was added prior to the drop-wise addition of $NaNO_2$ solution (900 mg in 2.5 ml of distilled water). The resulting solution was steam distilled, and the first 15 ml of distillate was collected. The ether layer was collected, with the water layer washed with further ether (5 ml). The organic fractions were combined and dried over $CaCl_2$, resulting in a ethereal solution of PhN_3. An ethereal solution of triphenylphosphine (1.96 g) was added, producing yellow crystals of triphenylphosphine phenylimine (440 mg, 17%, ^{31}P NMR ($CDCl_3$) δ 3.4) on standing. These crystals were washed with ether (2 x 7 ml) to remove excess triphenylphosphine.

N-(4-tolyl)-4-methoxybenzylimine

Anisaldehyde (2 ml, 16.5 mmol) and *p*-toluidine (1.826 g, 17.04 mmol) were refluxed for three days in toluene (100 ml) using a Dean-Stark apparatus. Solvent was removed under reduced pressure, and the residue was recrystallised from dichloromethane/ petroleum spirits. The product was filtered and washed, affording pale cream crystals of N-tolyl-4-methoxybenzylimine (1.079 g, 29%, m.p. = 91°C).

^1H NMR : ($CDCl_3$) δ 2.40 (3H, s, Ar-CH_3), 3.90 (3H, s, OCH_3), 7.01 (2H, dd, $^3J_{H\text{-}H}$ = 6.99 Hz, $^4J_{H\text{-}H}$ = 2.00 Hz, Ar-H), 7.15 (2H, dd, $^3J_{H\text{-}H}$ = 6.43 Hz, $^4J_{H\text{-}H}$ = 1.89 Hz, Ar-H), 7.22 (2H, d, $^3J_{H\text{-}H}$ = 8.08 Hz, Ar-H), 7.88 (2H, td, $^3J_{HH}$ = 8.75 Hz, $^4J_{H\text{-}H}$ = 1.98 Hz, Ar-H),8.43 (1H, s, HC=N).

^{13}C NMR : ($CDCl_3$) δ 21.4 (Ar-*C*H_3), 55.8 (OCH_3), 114.5 (Ar-H), 121.2 (Ar-H), 129.7 (Ar), 130.1 (Ar-H), 130.8 (Ar-H), 135.7 (Ar), 150.1 (Ar), 159.4 (HC=N), 162.5 (Ar).

Standard preparation of diarylpentadienones and diarylpropenones

The diarylpentadienones and diarylpropenone were prepared using a standard base-catalysed condensation of aryl aldehydes and ketones[31].

Ethanol (10 ml) and a solution of NaOH (2 g in 5 ml of distilled water) were added to an ice-cooled 50 ml round bottom flask. The flask was transferred to a water bath (~15°C)

[196] A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993, pp 404

and stirred while a solution of acetone and the benzaldehyde was added drop-wise over 5 minutes. The reaction was stirred for a further hour. At this time the solution was filtered, and the residue washed with distilled water until neutral to litmus. The crude product was dried under vacuum, and recrystallised from hot ethyl acetate affording yellow crystals. The purity of the compounds prepared was confirmed by NMR spectroscopy.

Preparation of (E,E)-1,5-diphenylpenta-1,4-dien-3-one

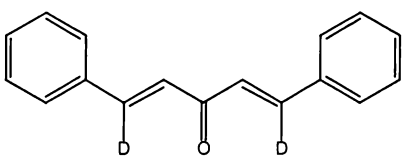
A mixture of acetone (0.6 ml, 8.2 mmol) and benzaldehyde (1.6 ml, 15.7 mmol) was added dropwise to the ethanolic NaOH solution over a period of 5 minutes. Filtering and recrystallisation of the reaction mixture afforded (E,E)-1,5-diphenylpenta-1,4-dien-3-one (443 mg, 58%, m.p. = 112°C) as bright yellow crystals.

^{1}H NMR : ($CDCl_3$) δ 7.11 (2H, d, $^3J_{HH}$ = 15.95 Hz, CH=C), 7.44 (6H, m, Ar-H), 7.64 (4H, m, Ar-H), 7.77 (2H, d, $^3J_{HH}$ = 15.94 Hz, C=CH)

^{13}C NMR : ($CDCl_3$) δ 125.5 (*C*H=C), 128.5 (Ar-H), 129.0 (Ar-H), 134.9 (Ar), 143.4 (C=*C*H), 189.0 (C=O)

Preparation of d,d-1,5-(E,E)-1,5-diphenylpenta-1,4-dien-3-one ***(141)***

A mixture of acetone (0.36 ml, 4.9 mmol) and d-benzaldehyde (1 ml, 9.8 mmol) was added dropwise to the ethanolic NaOH solution over a period of 5 minutes. Filtering and recrystallisation of the reaction mixture afforded d,d-1,5-(E,E)-1,5-diphenylpenta-1,4-dien-3-one (839 mg, 73%,) as bright yellow crystals.



^{1}H NMR : ($CDCl_3$) δ 7.11 (2H, s, C=CH), 7.44 (6H, m, Ar-H), 7.65 (4H, M, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 125.7 (C=CH), 128.7 (Ar-H), 129.3 (Ar-H), 130.9 (Ar-H), 135.1 (Ar), 143.3 (CD=C), 189.3 (C=O)

From an HMBC NMR experiment it was confirmed that the β-carbon of the ketone group was deuterated. The aryl protons (at 7.65 ppm) do not correlate to the protonated allyl carbon (at 125.7 ppm), indicating that it is more than three bonds distant, and therefore the α-carbon of the ketone group.

Preparation of (E,E)-1,5-di(2-trifluoromethylphenyl)penta-1,4-dien-3-one

A mixture of acetone (0.5 ml, 6.8 mmol) and 2-trifluoromethylbenzaldehyde (1.8 ml, 13.6 mmol) was added dropwise to the ethanolic NaOH solution over a period of 5 minutes. Filtering and recrystallisation of the reaction mixture afforded (E,E)-1,5-di(2-trifluoromethylphenyl)penta-1,4-dien-3-one (2.31 g, 92 %, m.p. = 131°C) as yellow crystals.

^{1}H NMR : ($CDCl_3$) δ 7.05 (2H, d, $^3J_{HH}$ = 15.8 Hz, C=CH), 7.55 (2H, t, $^3J_{HH}$ = 7.7 Hz, Ar-H), 7.65 (2H, t, $^3J_{HH}$ = 7.6 Hz, Ar-H), 7.76 (2H, d, $^3J_{HH}$ = 8.4 Hz, Ar-H), 7.83 (2H, d, $^3J_{HH}$ = 7.7 Hz, Ar-H), 8.12 (2H, d, $^3J_{HH}$ = 15.8 Hz, CH=C)

^{13}C NMR : ($CDCl_3$) δ 123.0 (CF_3), 125.7 (Ar), 126.6 (Ar-H), 128.3 (Ar-H), 129.2 (C=CH), 130.4 (Ar-H), 132.5 (Ar-H), 134.1 (Ar), 139.6 (CH=C), 188.6 (C=O)

Preparation of 1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one

In a reaction analogous to the production of diarylpentadienones, a mixture of acetophenone (0.3 ml, 2.57 mmol) and 3,4,5-trimethoxybenzaldehyde (402.5 mg, 2.05 mmol) was added dropwise to the ethanolic NaOH solution over a period of 5 minutes. Filtering and recrystallisation of the reaction mixture afforded 1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one (383.5 mg, 63%) as pale yellow crystals.

^{1}H NMR : ($CDCl_3$) δ 3.93 (3H, s, OMe), 3.95 (6H, s, OMe), 6.90 (2H, s, Ar-H), 7.43 (1H, d, $^3J_{HH}$ = 15.6 Hz, C=CH), 7.54 (2H, t, $^3J_{HH}$ = 7.6 Hz, Ar-H), 7.62 (1H, t, $^3J_{HH}$ = 7.3 Hz, Ar-H), 7.75 (1H, d, $^3J_{HH}$ = 15.7 Hz, CH=C), 8.04 (2H, d, $^3J_{HH}$ = 8.1 Hz, Ar-H)

^{13}C NMR : ($CDCl_3$) δ 56.3 (OCH_3), 61.1 (OCH_3), 105.8 (Ar-H), 121.6 (C-H), 128.6 (Ar-H), 128.7 (Ar-H), 130.4 (Ar), 132.* (C-H), 138.4 (Ar), 145.1 (C-H), 153.6 (Ar), 190.7 (C=O)

Phenyl isothiocyanate[197]

Diphenylthiourea (50.3 g, 221 mmol) was refluxed in conc. hydrochloric acid (200 ml) for 1 hour. The oily product was distilled over, and diluted with an equal quantity of distilled water. The product was extracted with diethyl ether (200 ml), and the organic fraction was washed with $NaHCO_3$ solution, and dried over $CaCl_2$ before the solvent was removed under reduced pressure. The resulting oil was distilled under a nitrogen atmosphere, with

[197] A. I. Vogel, *Practical Organic Chemistry*, 5 Ed., revised by B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, Langman Singapore Publishers Pte Ltd, Singapore, (1996), pp. 966-967

the fraction at 208-210°C (lit. 217-220°C) collected to afford phenyl isothiocyanate (10.2 g, 34%) as a colourless oil.