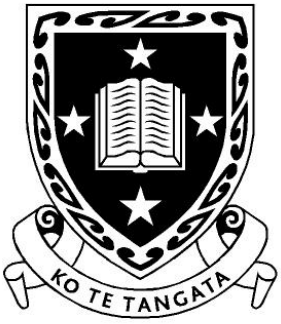
Reactions of Some Cyclomanganated Compounds with *C*-Nitroso Compounds, Allenes, and Ketenimines



THE UNIVERSITY OF
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Te Whare Wānanga o Waikato

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submitted in partial fulfilment
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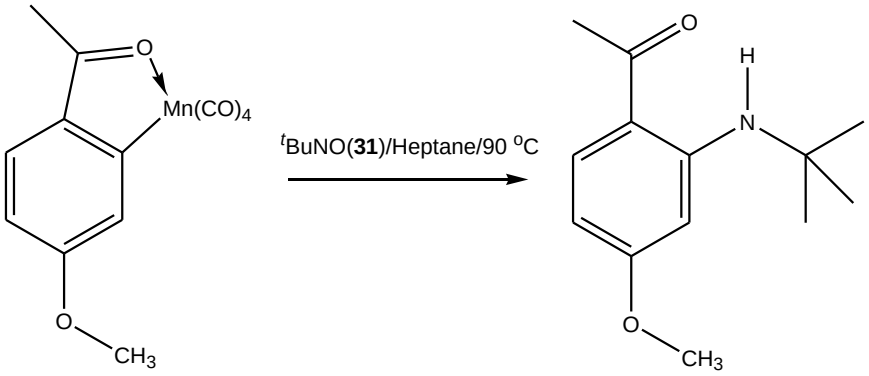
Abstract

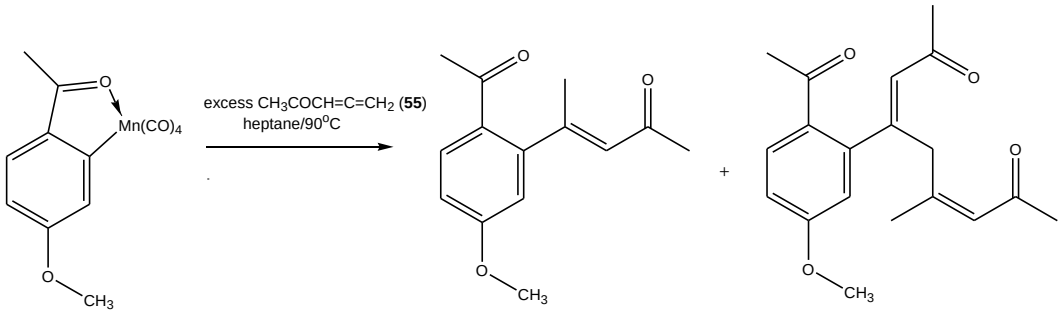
η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (**30**) was reacted with 2-methyl-2-nitrosopropane (**31**) to form 2-acetyl-5-methoxy-*N*-(*tert*-butyl)aniline (**43**) in low yield. Attempts to improve the yield by varying the solvent were unsuccessful.



30 **43**

Substrate **30** was reacted with nitrosodurene and orthomanganated triphenylphosphine sulfide was reacted with 2-methyl-2-nitrosopropane (**31**), however no new compounds were characterised in either case.

Acetylallene (**55**) was reacted with **30**. Electrospray ionisation-mass spectrometry (ESI-MS) provided evidence for the insertion of one and two molecules of **55** into the Mn-C bond of **30** to form the products tentatively identified as **56** and **57**.



30 **56** **57**

The reaction of orthomanganated triphenylphosphine sulfide with acetylallene was attempted but no new compounds were characterised.

In order to extend the study to ketenimines, the synthesis of the diphenylketene *N*-(*p*-tolyl)imine was attempted by the dehydration of *N*-(*p*-tolyl)diphenylacetamide

under a variety of conditions, but it was not isolated in useful quantities. A single preliminary study of the reaction of diphenylketene *N*-(*p*-tolyl)imine with **30** gave an intense green solution, but no products were isolated.

Acknowledgements

I would like to thank my supervisors Brian Nicholson and Lyndsay Main. They have always been kind, courteous and approachable. My thesis would have been impossible without their guidance and support.

I would also like to thank Pat Gread for her help providing me with chemicals, equipment, and also for her help with the ESI-MS, Wendy Jackson for taking me through SOP training and finding chemicals for me in Pat's absence, Amu Upreti whose friendly attitude made CHEM101/102 demonstrating more enjoyable, Jannine Rhodes for training me to use the GC-MS, and Merilyn Manley-Harris for her help with the NMR.

I would like to thank the other students of room C3.04 Carol, Kelly, Bevan, Matthew, Ujams, for making me feel welcome and lending me their glassware (whether they knew it or not), Toshi for being impeccably tidy with our shared workbench, and especially fellow manganese chemists Stephen and Narendra who passed on the secret knowledge of a long lineage of manganese chemists.

Lastly I would like to thank Leo, Maria and Laura for their assistance in proof-reading my thesis. It was a tremendous help, the sheer number of grammatical errors they discovered is testament to that.

Table of Contents

Abbreviations

Ac	Acetyl
acac	acetylacetonate
aq	Aqueous
Bu	*n*-butyl
bp	boiling point
br	broad (FTIR, PLC)
COSY	correlation spectroscopy
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
d	doublet (^{1}H NMR)
δ	chemical shift in ppm
DCM	dichloromethane
DMF	dimethylformamide
EAS	electrophilic aromatic substitution
EPR	electron paramagnetic resonance spectroscopy
ESI	electrospray ionisation
Et	ethyl
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
h	hours or Planck's constant
hν	photochemical conditions (from photon energy (E) = hν)
J	coupling constant in Hz (NMR)
m	meta
m	medium (FTIR, ^{13}C NMR), multiplet (^{1}H NMR)
Me	methyl
MicrOTOF	ESI-MS by Brucker with high resolution TOF detector
min	minutes
mp	melting point
MS	mass spectrometry
m/z	mass to charge ratio (MS)
NMR	nuclear magnetic resonance
o	ortho
p	para
PLC	preparative layer chromatography
ppt	precipitate
q	quartet (^{1}H NMR)
R_f	retention factor (TLC, PLC)
RT	retention time (GC), or room temperature
s	strong (FTIR, PLC, TLC, ^{13}C NMR), singlet (^{1}H NMR)
sh	sharp (FTIR)
^{t}Bu	tertiary butyl
THF	tetrahydrofuran
TLC	thin layer chromatography

TMEDA	tetramethylethylenediamine
TOF	time of flight detector (MS)
Ts	tosyl, *p*-$CH_3C_6H_4SO_2$-
UV	ultraviolet
w	weak (FTIR, PLC, TLC, ^{13}C NMR)
Ph	phenyl
ν	frequency in cm^{-1} (FTIR)

Chapter 1: Literature Review

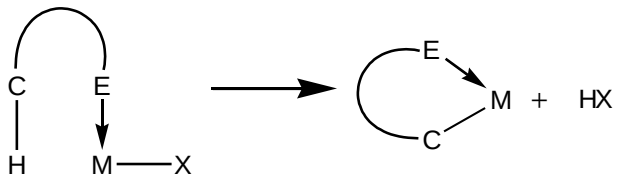
1.1 Introduction

Manganese is a relatively inexpensive common element. It is widely distributed throughout the world and large quantities can be found as manganese nodules on the ocean floor[1]. The majority of manganese mined is used in the steel industry as ferromanganese. Manganese plays an important role in photosynthesis[2]. Manganese carbonyl compounds are common in organomanganese chemistry. This has been attributed to the availability and stability of the common starting materials manganese carbonyl and methylcyclopentadienyl manganese tricarbonyl[3]. Methylcyclopentadienyl manganese tricarbonyl is used commercially as an anti-knocking agent in petrol to replace tetraethyllead[4] and was used as a combustion catalyst in Concord aircraft[5]. A disadvantage to organomanganese chemistry is the cost of the starting materials. The most common starting materials for organomanganese compounds are manganese carbonyl at $(AUS) 312.00 for 10 g, and methylcyclopentadienyl manganese at $(AUS) 287.00 per 50 g compared to manganese metal which is relatively cheap at $(AUS) 90 per kg[6].

1.2 Cyclometalation

1.2.1 Introduction

Cyclometalation is a term that describes a metal reacting with a ligand to form a bidentate intramolecular coordination compound (or cyclometalated compound).



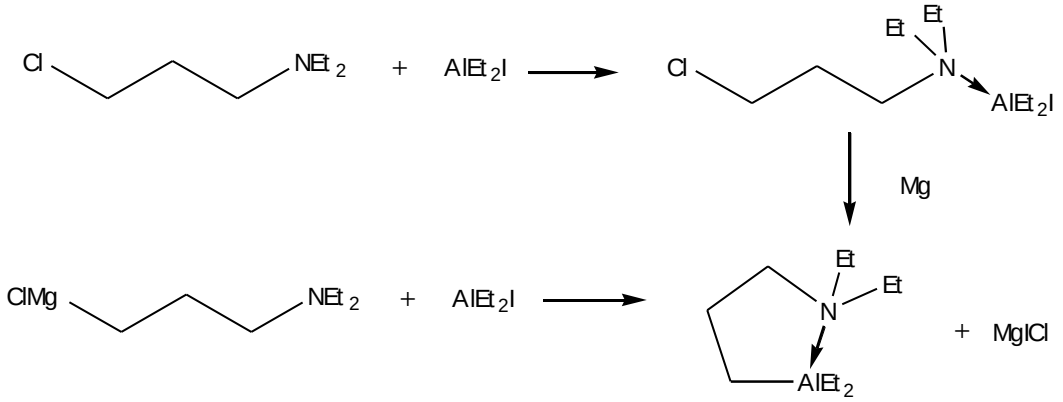
Scheme 1-1: A cyclometalation reaction. E is any atom or bond capable of forming a coordinate bond; M is a metal and X is an appropriate leaving group (from Bruce[7]).

Scheme 1-1 illustrates a general cyclometalation reaction. A relatively unreactive, strong, non-polar C-H bond is replaced by a more reactive polar C-M bond (other atoms i.e. C-F[8] and C-Br[9] have been substituted instead of H and are still considered cyclometalation reactions). The C-M bond will undergo reactions not

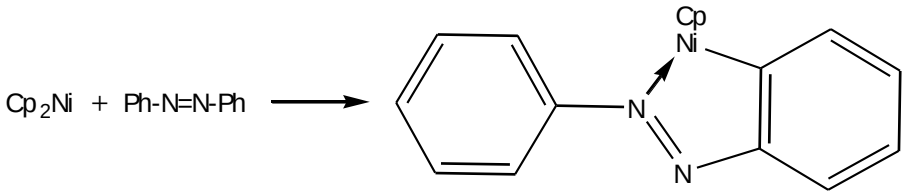
otherwise available to the C-H bond (e.g. insertion reactions). This makes cyclometalation a useful tool in synthetic chemistry.

The term "cyclometalation" is first attributed to Trofimenko when he used "cyclopalladation" to describe the formation of intramolecular coordination compounds of palladium[10].

The first published examples of cyclometalation were aluminium complexes (in 1955)[11]. One example is shown in Scheme 1-2.



Scheme 1-2: One of the first examples of cyclometalation. The scheme shows two different ways in which Bähr and Müller prepared the same cyclometalated compound[11]. This example was originally cited by Omae[12].



Scheme 1-3: The first published cyclometalation reaction of a transition metal[13].

The first example of a cyclometalated transition metal compound was published in 1963[13] (Scheme 1-3).

1.2.2 Cyclometalated Compounds

A large number of reviews have been written on cyclometalated compounds[7, 12, 14-18]. Important features of a cyclometalated compound are shown in Figure 1-1. The donor atom can be any atom with a lone pair of electrons that will form a dative bond with the metal atom. Groups with a donor atom coordinating through a lone pair of electrons are *σ-donors*. Alternatively a compound can coordinate through π bonds; these are called *π-donors*. Nitrogen is the most common donor atom, but O, P, and S are also common. Other donor atoms exist e.g. As[19, 20] and Se[21].

The ring is commonly but not exclusively five-membered. This can be explained by the chelate effect. Smaller ring sizes have a large ring strain and are therefore less stable. Larger ring sizes have smaller entropies of formation because of the degrees of freedom lost for every extra bond that cannot rotate because it is held in a ring. The ring is often unsaturated in cyclometalated compounds frequently sharing the edge of an aromatic ring and the metallocycle may show some degree of aromaticity[22].

Cyclometalated compounds must contain a metal-carbon bond. Often it is a metal-carbon σ-bond, however some definitions[12] include M-C π-bonds.

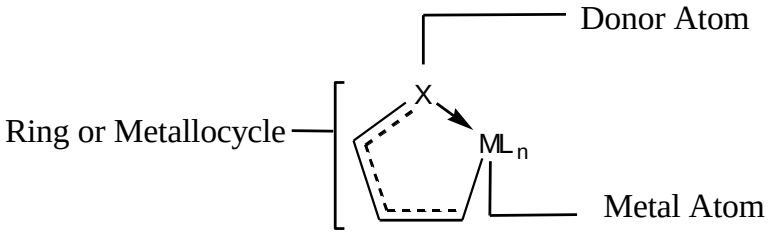


Figure 1-1: Some general features of a cyclometalated compound.

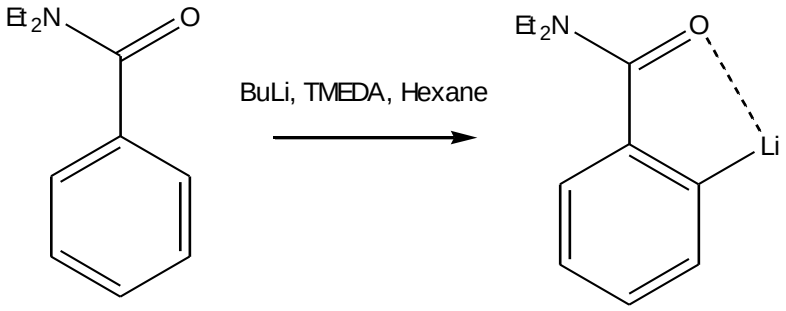
The terms "cyclometalated compounds" and "intramolecular coordination compounds" are often used interchangeably, however the precise definition varies within the literature. For example, Omae did not consider compounds with a non carbon atom in the ring (excluding the metal and donor atom) as "organometallic intramolecular coordination compounds"[12] because they tend to have different properties, but Brown et al.[23] and others[21, 24] have accepted a broader view to include compounds that contain heteroatoms (e.g. a phosphorus) instead of a carbon as a spacer group in the metallocycle.

1.2.3 Orthometalation

"Orthometalation" is the metalation of an aromatic ring *ortho* to a specific functional group and it is a common form of cyclometalation. Orthometalation is not necessarily cyclometalation because a compound can be metalated in the ortho position and not form a cyclometalated ring.

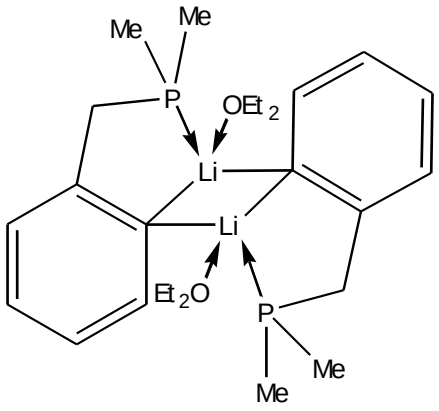
Orthometalation will derivatise a compound in the ortho position exclusively. This is a useful advantage over alternative methods such as electrophilic aromatic substitution (EAS). EAS will derivatise *ortho* and *para* to electron donating groups and halogens (*meta* for electron withdrawing groups excluding halogens). Generally the *para* position is favoured because it has less steric hindrance.

Ortholithiation is one of the most widely used forms of orthometalation. An alkyl lithium reagent such as butyllithium will undergo transmetalation reactions with aromatic compounds. If an aromatic compound contains an appropriate donor group (e.g. ether, amide, amine) the alkyl lithium will transmetalate ortho to that functional group[25] e.g. Scheme 1-4.



Scheme 1-4: An example of ortholithiation. TMEDA = tetramethylethylenediamine. The TMEDA is used to break up the unreactive hexamer that butyllithium forms in hexane.

The ortholithiated compound will react with a large number of electrophiles to give a wide variety of products. X-Ray crystal structures of many ortholithiated compounds show five-membered rings common to cyclometalated compounds. However instead of a metal-carbon σ bond, electron-deficient bonding exists commonly resulting in dimers, e.g. ortholithiated benzyldimethylphosphine[26] (**1**).



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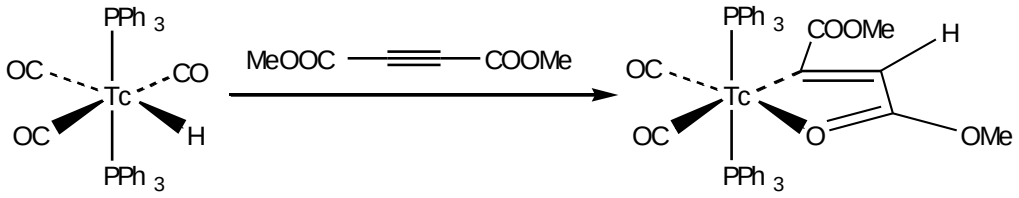
1.2.4 Cyclomanganated Compounds

Broadly speaking, cyclomanganated compounds are cyclic compounds containing manganese. More specifically it is a name given to intramolecular coordination compounds of manganese.

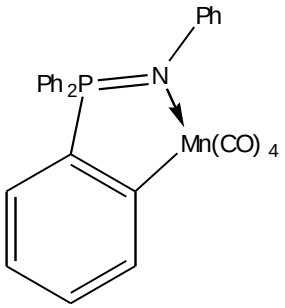
Cyclomanganated compounds are unique because they can be formed from direct cyclometalation reactions with ketones. The first example of direct cyclometalation of a ketone was the orthomanganation of acetophenone[27].

Cyclometalation of a ketone is rare for all other metals except rhenium. Technetium has the potential to undergo direct cyclometalation of ketones, however problems with accessing and handling radioactive technetium compounds has hindered this research. This is not to say cyclotechnetiated compounds have not been made. $HTc(CO)_3(PPh_3)_2$ reacts with $CH_3O_2CC{\equiv}CCO_2CH_3$ to give a cyclotechnetiated compound[28] (Scheme 1-5).



Scheme 1-5: A rare example of a cyclotechnetiated complex.

A review has been published on orthomanganated aryl ketones[29].
Some interesting examples of cyclomanganated compounds exist. A thermochromic compound that changes from yellow to intense purple above 100 °C has been made[24] (**2**). So far it has proved to be the first and only thermochromic manganese molecule. The reason for the thermochromicity is so far unknown. Leeson et al.[24] suggested a thermally accessible excited state may be the cause, stating that the most common reason for thermochromicity, i.e. a change in geometry, was unlikely.



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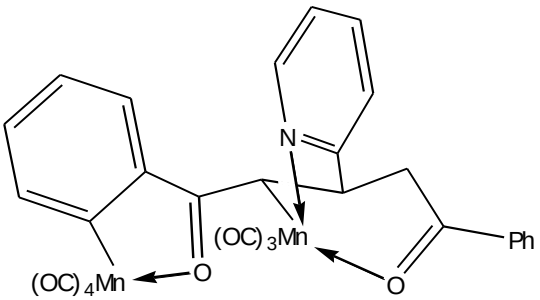

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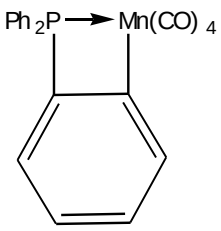

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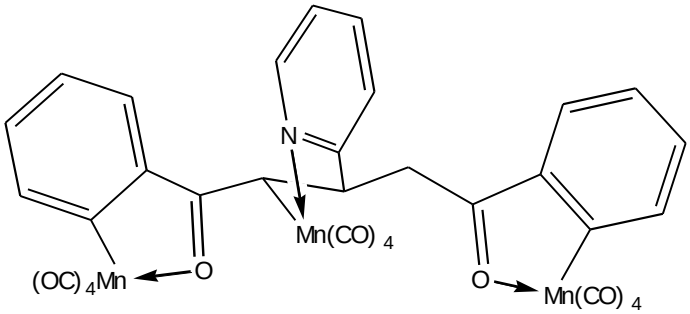
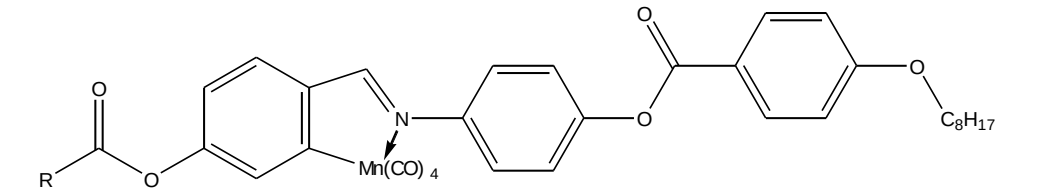


5

Orthomanganated triphenylphosphine (**3**) has been made[30]. This is a rare example of a four-membered cyclomanganated ring.

A number of di- and tri-manganated compounds (**4** and **5**) have been prepared that have both ketone and pyridyl donor groups[31]. These provide rare examples of direct cyclomanganation to a sp^3 hybridised carbon.

Cyclomanganated liquid crystals have been made[32] (**6**). These were the first examples of a simple octahedral liquid crystalline metal complex and the first calamitic (rod-like) manganese liquid crystals. The compounds had nematic phases in the temperature range of 120 to 190 °C.



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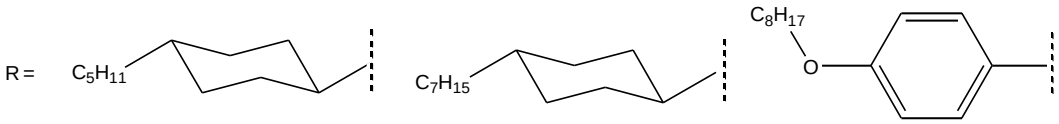
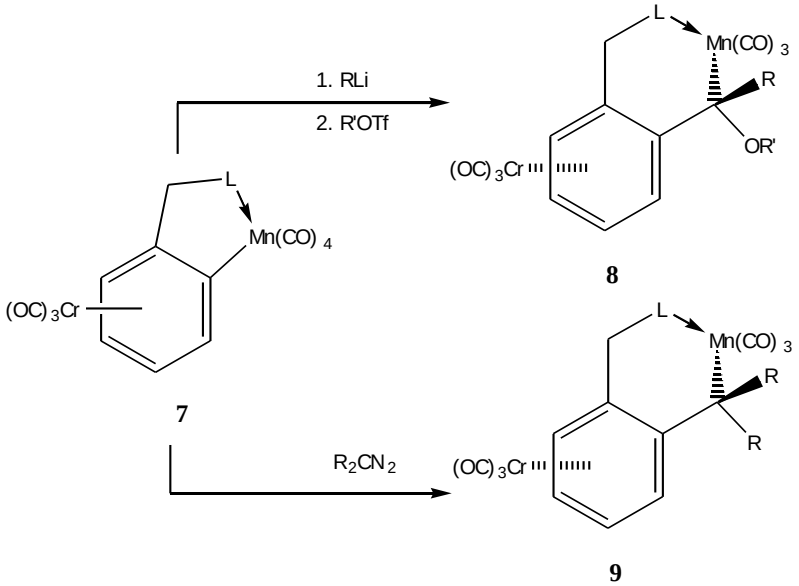


η^6-(Arene)$Cr(CO)_3$ compounds have been orthomanganated[33] (**7**). These are examples of heterobimetallic compounds. On reaction with RLi and R`OTf or R_2N_2 both η^6-(arene)$Cr(CO)_3$ compounds and other orthomanganated compounds have formed metallospiralenes[34] (**8** and **9** respectively, Scheme 1-6).



7 **8** **9**

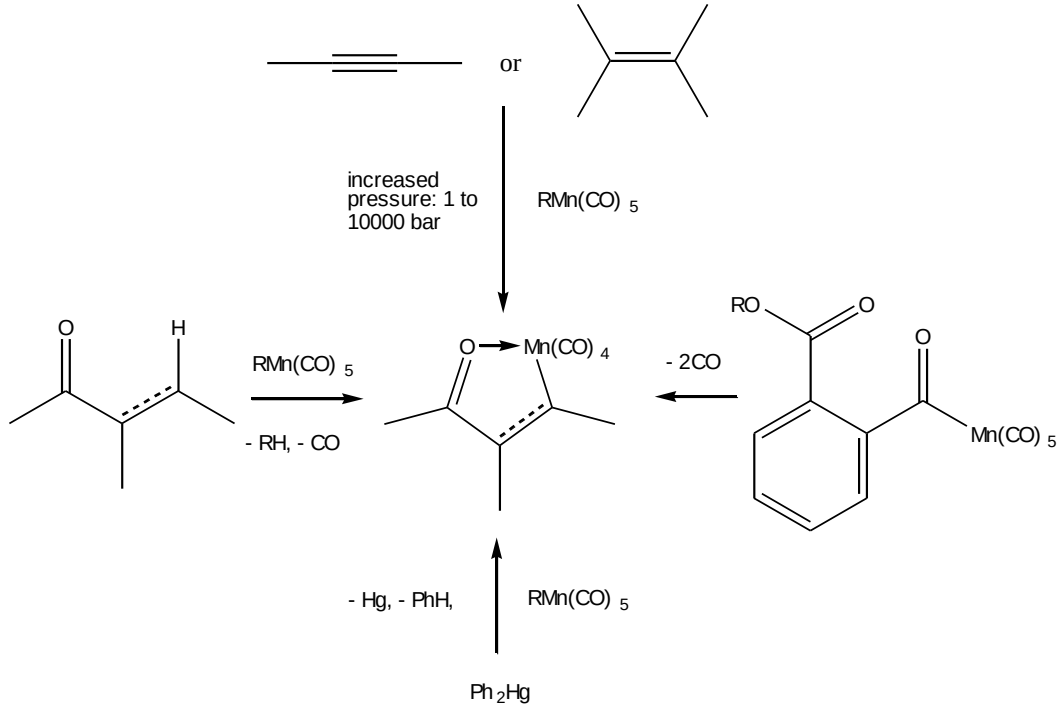
Scheme 1-6: The formation of metallospiralenes by the insertion of carbenes. L is generally an sp^2 hybridized nitrogen, e.g. 7 = orthomanganated 2-phenylpyridine.

These metallospiralenes contain 6-membered cyclomanganated rings of helical geometry. There is interest in metallospiralenes because of their potential use in nonlinear optics[34].

1.3 Synthesis of Cyclomanganated Compounds

1.3.1 Introduction

A large number of cyclomanganated compounds have been made and many of these with excellent yield. Synthesis of cyclomanganated compounds have advantages over other organometallic compounds because of their stability and ease of work-up[29]. Cyclomanganated compounds are often air-stable at room temperature (but should be stored in a freezer when not in use) and can often be isolated by chromatography without decomposing. Reaction progress can be monitored with IR spectroscopy. Examination of the lowest frequency metal-carbonyl band (~1900-2000 cm^{-1}) is common practice in monitoring the decrease of reactant and increase of product concentration. Synthesis and reactions should be done in a dry inert atmosphere because the cyclomanganated compounds will react faster with water and oxygen when in solution or at an elevated temperature. Scheme 1-7 gives an overview of the different methods used to make cyclomanganated compounds.



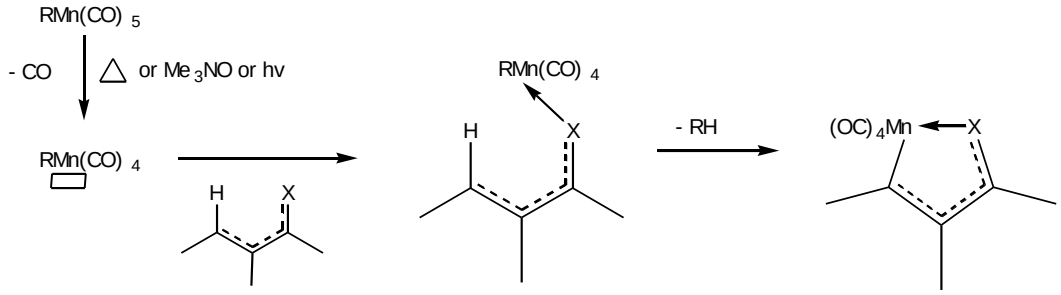
Scheme 1-7: Some methods used to make cyclometalated compounds.

1.3.2 Sequential Insertion of CO and Unsaturated Compound

Alkylpentacarbonylmanganese compounds ($RMn(CO)_5$) will insert carbon monoxide followed by an alkene or alkyne to form a cyclomanganated ketone[35, 36] or enone[37] respectively. The insertion is generally regiospecific with a tendency for the bulkiest and most electron-withdrawing side of asymmetric alkenes or alkynes to be closest to the manganese. Increased pressure (2-10 kbar) is required for reactions with alkenes and for reactions with $PhCH_2Mn(CO)_5$. $CH_3Mn(CO)_5$ and $PhMn(CO)_5$ react with many alkynes at atmospheric pressure. Interesting C-glycosyl cyclomanganated compounds have been made this way from glycosylmanganese pentacarbonyl complexes[38, 39].

1.3.3 Substitution

Alkylpentacarbonylmanganese compounds ($RMn(CO)_5$) can react directly with substrates that have a hydrogen atom on the carbon γ to a donor atom[40]. Scheme 1-4 illustrates how the donor atom might guide the manganese (or any metal) to form a bond with the γ-carbon. Manganese carbonyl compounds such as $RMn(CO)_5$ are believed to lose a carbon monoxide ligand to form a vacant coordination site before reacting. Usually this is facilitated by heating but some manganese carbonyl reactions have been promoted by photochemical decarbonylation[41, 42] or chemical decarbonylation[43]. A donor atom such as oxygen or nitrogen may coordinate to the manganese and guide the Mn-alkyl group to a nearby hydrogen atom as shown in Scheme 1-8. A hydrocarbon is eliminated and a $Mn(CO)_4$ group replaces the hydrogen.



Scheme 1-8: An illustration of how a general cyclomanganation reaction occurs. The donor atom (X) guides the manganese to the hydrogen on the carbon γ to the donor atom. The hydrogen is eliminated as a hydrocarbon and a new Mn-C bond forms.

This substitution reaction is common for manganation on aromatic substrates and rare for saturated substrates. This suggests the reaction is facilitated by the π-

electron system probably by delocalisation of electronic charge in a transition state.

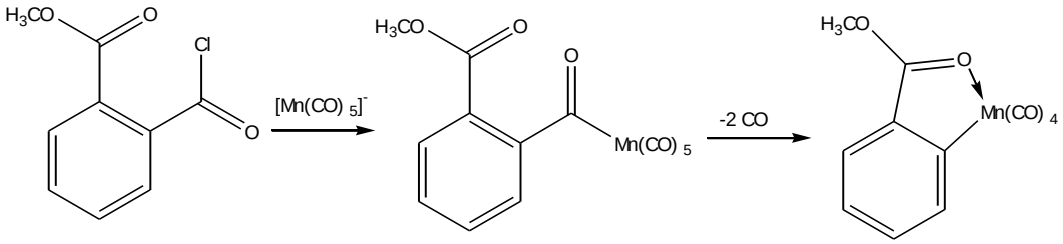
Derivatives of podocarpic acid and dehydroabietic acid have been manganated this way[44-46].

$NaMn(CO)_5$ has been reacted with cyclopalladated complexes such as chloro-2-(phenylazo)phenylpalladium dimer in a transmetalation reaction to form the cyclomanganated analogue[47].

1.3.4 Other Methods of Synthesis

Orthomanganated compounds have been made by reacting alkylmanganesepentacarbonyl compounds with diphenylmercury in refluxing toluene[48].

Orthomanganated aromatic methyl esters have been made by an indirect route. An *ortho*-chloromethanoyl methyl benzoate was reacted with $[Mn(CO)_5]^-$ to form an $R\text{-}COMn(CO)_5$ complex. This loses two CO ligands to form an orthomanganated compound[49] (Scheme 1-9).



Scheme 1-9: The formation of an orthomanganated ester through an indirect route.

1.4 Reactions of Cyclomanganated Compounds

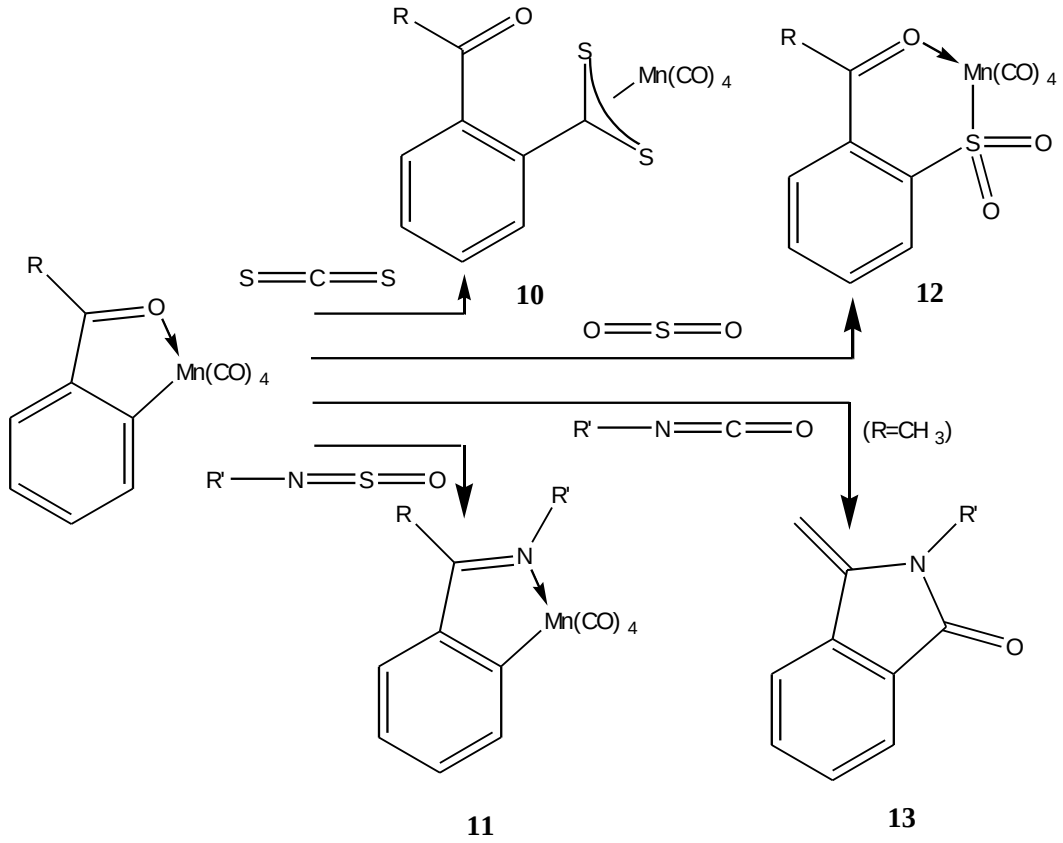
1.4.1 Introduction

Cyclomanganated compounds undergo a large variety of reactions; from very general reactions where most cyclomanganated compounds will react with a compound in the same way to give the same type of product, to unpredictable reactions where multiple products form and the favoured product depends greatly on reaction conditions and reactants. This section will cover some (but not all) reactions that cyclometalated compounds undergo with extra emphasis on reactions involving compounds with ketone donor groups.

1.4.2 Orthomanganated Compounds and Cumulenes

Cumulenes are "hydrocarbons (and by extension, derivatives formed by substitution) having three or more cumulative double bonds"[50]. Some literature[51] include allenes (hydrocarbons with two consecutive double bonds) in its definition of cumulenes. Heterocumulenes are cumulenes where one or more carbon atoms are substituted with heteroatoms[52]. In this thesis cumulenes are defined as a broader definition of any molecule with two or more consecutive double bonds. Cumulenes range from common compounds such as carbon dioxide to highly reactive and exotic compounds such as diazomethane (CH_2N_2) and carbon suboxide (O=C=C=C=O). The cumulenes ketenimines $R_2C=C=N-R$ and allenes ($R_2C=C=CR_2$) are discussed further in later chapters.

Cumulenes have shown an interesting chemistry with orthomanganated compounds. Some typical reactions are seen in Scheme 1-10.



Scheme 1-10: Some typical reactions of cyclomanganated compounds with selected cumulenes.

Orthomanganated aryl ketones generally insert CS_2 into the C-Mn bond to form η^2-dithiocarboxylato-$Mn(CO)_4$ compounds (**10**) whereas other cyclomanganated compounds such as η^2-[(2-diphenylthiophosphinyl)-

phenyl]tetracarbonylmanganese form $(\mu^3\text{-}CS_3)_2Mn_4(CO)_{16}$ as the main product[53, 54].

PhNSO will react with some orthomanganated ketones to form an orthomanganated imine (**11**) with the elimination of SO_2[55, 56].

SO_2 inserts into the C-Mn bond of orthomanganated ketones to form a six-membered metallocycle (**12**). This can be demetallated by oxidation to form sulfinates and sulfonates[57]. *N*,*N*-dimethylbenzamide reacted with SO_2 uniquely forming a complex comprised of two thiosalicylate molecules and two $Mn(CO)_4$ units[58].

Isocyanates have been reacted with orthomanganated acetophenones to form 3-alkylidene phthalimidines[59] (**13**).

Orthomanganated 2-phenylpyridines have been reacted with diazoalkanes to form (allyl)$Mn(CO)_3$ complexes[60]. The diazoalkane possibly does not react with the orthomanganated compound in this case but instead the carbene that the diazoalkane forms.

Each of these cumulenes reacted in different ways. It is reasonable to expect other cumulenes to react with cyclomanganated compounds too.

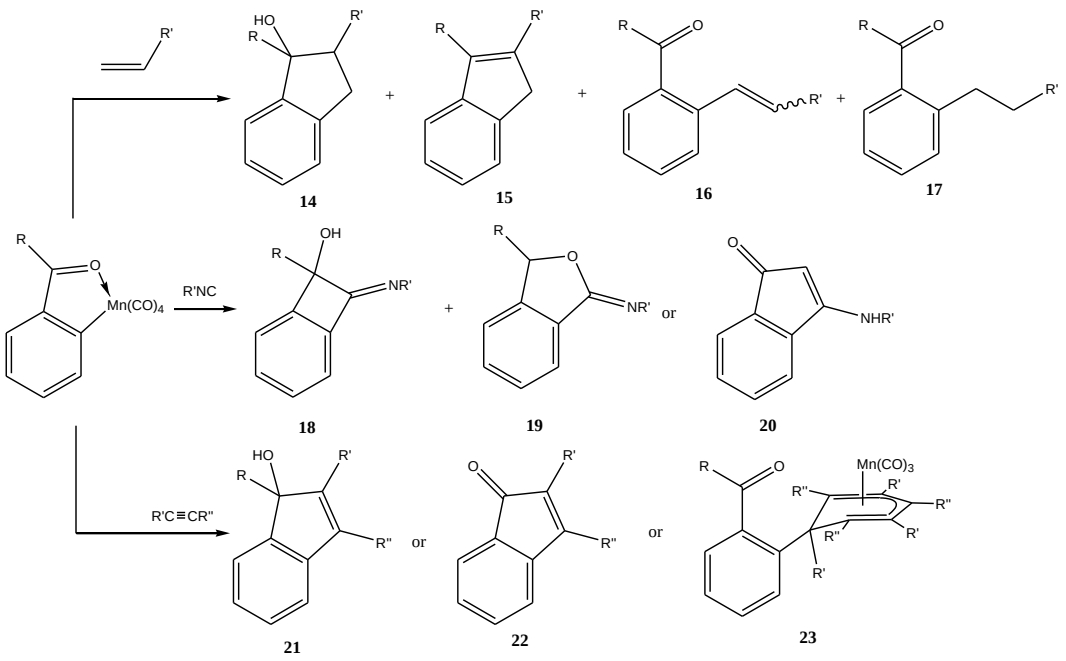
1.4.3 Reactions of Cyclomanganated Compounds with Other Unsaturated Compounds

Scheme 1-11 shows how orthomanganated compounds react with some unsaturated compounds.

Alkenes have been shown to undergo insertion reactions with orthomanganated compounds[61]. This reaction has been promoted by Me_3NO[43, 46, 62] and yields four different types of compounds (**14-17**) (Scheme 1-11). Alternatively the thermally promoted reaction with Li_2PdCl_4 in acetonitrile is more specific giving three different products (**15-17**)[46, 62]. The reaction has also been done in the presence of $NiBr_2(PPh_3)_2$[63]. This is a more specific reaction yielding only one or two products (**14** and **15**).

Orthomanganated acetophenone has given a variety of compounds when reacted with isocyanides[54]. Ethyl isocyanide reacted to form two cyclic imines with a four-membered ring (**18**) or a five-membered oxygen containing heterocycle (**19**), whereas (2-methyl)propyl-2-isocyanide gave an amino-substituted indenone (**20**).

Orthomanganated compounds can insert alkynes into the Mn-C bond to form seven-membered metallocycles[64, 61].



Scheme 1-11: Reactions of orthomanganated compounds with some unsaturated compounds. Each of these reactions has multiple products. The favoured product and the ratio of products depend largely on reactants and reaction conditions.

Orthomanganated ketones insert alkynes to form inden-1-ols (**21**)[43, 65]. Related compounds (certain orthomanganated benzamides, benzoate esters, benzaldehydes) will form indenones (**22**). Novel triple insertion reactions forming η^5-cyclohexadienyl)$Mn(CO)_3$ complexes (**23**) occurred when these related compounds were reacted with acetylene (i.e. where R = R´ = H).

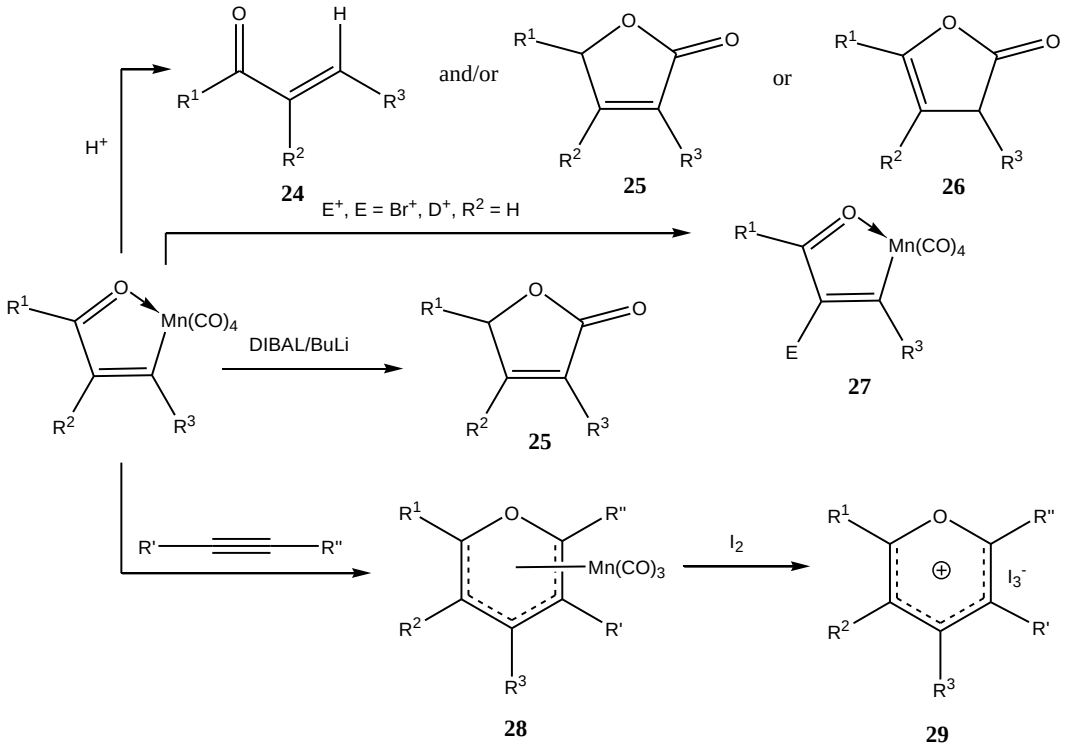
1.4.4 Other Reactions of Orthomanganated Compounds

Orthomanganated aryl ketones and esters refluxed in methanol with $HgCl_2$ yielded orthomercurated compounds in good yields[66]. This transmetalation reaction is useful because it provides a regiospecific synthesis that is unavailable through direct mercuration or via RLi or Grignard reagents.

Orthomanganated arylketones and esters react with ICl to give *ortho*-iodo compounds[67]. Compare this to iodination by conventional electrophilic aromatic substitution where a ketone is *meta*-directing. This provides a useful method for iodination in sterically crowded positions.

1.4.5 Reactions of Other Cyclomanganated Compounds

Scheme 1-12 illustrates some reactions of orthomanganated enones.



Scheme 1-12: Reactions of cyclomanganated enones. Br^+ comes from (*N*-bromo)succinimide and D^+ from DCl(aq) in CH_3CN. DIBAL = diisobutylaluminium hydride.

Under acidic conditions cyclomanganated compounds will demetalate. This occurs either by substitution of manganese with hydrogen to form an enone[36] (**24**) or with the insertion of carbon monoxide to form a five-membered lactone[36] (**25** and **26**). Alternatively cyclomanganated enones can form five-membered lactones on reaction with diisobutylaluminium hydride and butyllithium[36].

One reaction that was used as evidence for the aromaticity of cyclomanganated compounds was the electrophilic substitution seen when a cyclomanganated enone was reacted with DCl or (*N*-bromo)succinimide giving **27**[36].

Cyclomanganated enones insert alkenes[68] and carbon monoxide to give cyclic products or alternatively just an alkene to give acyclic products.

Cyclomanganated chalcones insert alkynes regiospecifically in carbon tetrachloride to form η^5-pyranyltricarbonylmanganese compounds (**28**). These products react with iodine to form pyrylium triiodide salts[69] (**29**).

1.5 Conclusion

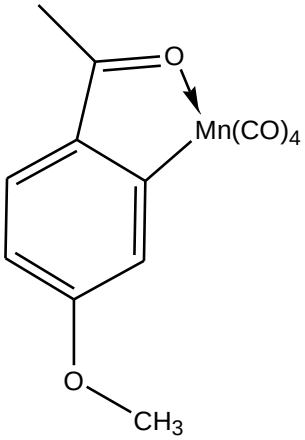
Many of the reactions above are not general for all cyclomanganated compounds but they are included to give an idea of how cyclomanganated compounds react. Derivatisation by cyclomanganated intermediates has proved a useful method in organic synthesis and has the potential to be utilised further in syntheses of new

molecules. It is not without its problems however. Reactions sometimes give small yields or do not work at all with some cyclomanganated compounds. The current knowledge of the chemistry of cyclomanganated compounds is extensive but by no means complete. New and interesting reactions will be discovered with a little bit of luck, but most probably with a lot of time and effort

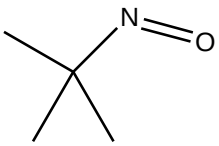
Chapter 2: Insertion Reactions of Cyclomanganated Compounds with *C*-Nitroso Compounds

2.1 Introduction

A preliminary investigation of the reaction of η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (**30**) and 2-methyl-2-nitrosopropane (**31**) was previously undertaken in an undergraduate project by Charlotte Calnan[70]. Preparative layer chromatography (PLC) of the reaction product showed only three main bands indicating a reaction with only a few products. This project was continued here with the aim of identifying the products, to find the optimum conditions for the reaction, and to study other reactions between *C*-nitroso substrates and cyclomanganated compounds.



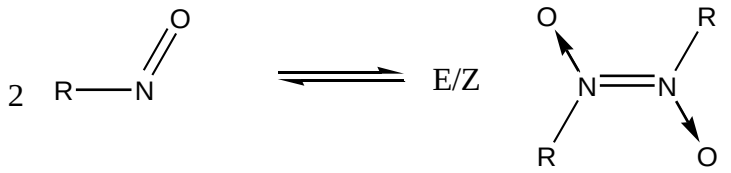
30



31

2.1.1 *C*-Nitroso Compounds

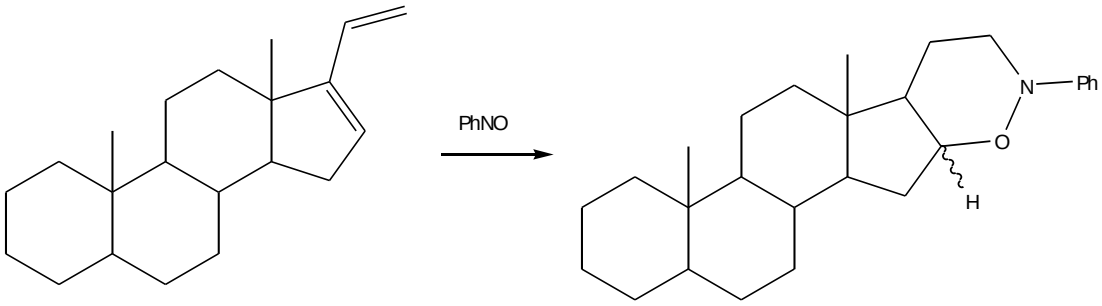
C-nitroso compounds (R-N=O) are generally in a monomer-dimer equilibrium[71] (Scheme 2-1). The dimer (usually colourless or pale yellow) is favoured in the solid state and the monomer (usually blue or green) is favoured in the liquid phase, gas phase, and in solution. Some compounds exist entirely as monomers in all phases such as 2-bromo-2-nitrosopropane, *N*,*N*-dimethyl-4-aminonitrosobenzene, and 4-iodonitrosobenzene. The stability of the monomer compared to the dimer depends largely on the electronic effects on the α-carbon. Electron-withdrawing groups on the α-carbon stabilise the monomer. Aromatic *C*-nitroso compounds tend to favour the monomer more than alkyl-nitroso compounds and this is attributed to resonance stabilisation of the monomer.



Scheme 2-1: The monomer dimer equilibrium of *C*-nitroso compounds.

The *C*-nitroso group is an electrophile[72]. Generally the nitrogen acts as the electrophilic centre, however nucleophilic attack has occurred on the oxygen atom often in the presence of a Lewis acid[73].

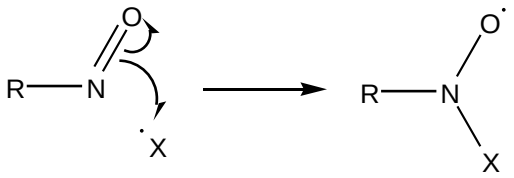
C-Nitroso compounds also act as dienophiles[72] forming 1,4-amino-oxo compounds e.g. Scheme 2-2.



Scheme 2-2: A Diels-Alder reaction with a *C*-nitroso compound as a dienophile (from Skoda-Földes et al.[74]).

Diels-Alder reactions of *C*-nitroso compounds have been used to make biologically active compounds such as cis-zeatin[75] and 5-amino-5,6-dideoxy-DL-hexonic acids[76].

C-Nitroso compounds have been used extensively in electron paramagnetic resonance (EPR) studies as spin-trap reagents[77-80]. They react with (or "trap") short-lived radicals to form nitroxides (Scheme 2-3).

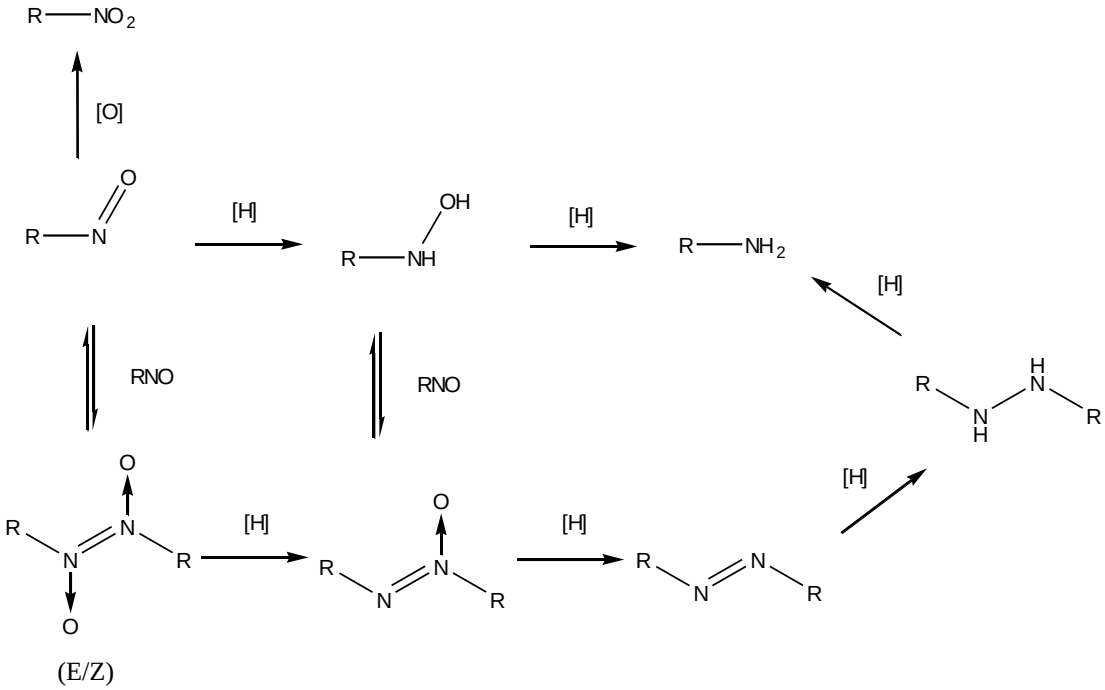


Scheme 2-3: *C*-nitroso compounds react with radicals to form nitroxides.

These nitroxides have a relatively long life and are used to detect radical intermediates that would otherwise not accumulate in high enough concentration to be detected by EPR. Commonly *C*-nitroso compounds will not have any hydrogen atoms on α-carbons. Although those with α-hyydrogens can be made

they will isomerise to the thermodynamically favoured oxime[71] (a polar solvent or a strong acid or base will facilitate this).

The redox properties of *C*-nitroso compounds are important. They can be oxidised to nitro compounds or reduced to hydroxylamines, azoxy, azo, hydrazo compounds or primary amines (Scheme 2-4)[79].

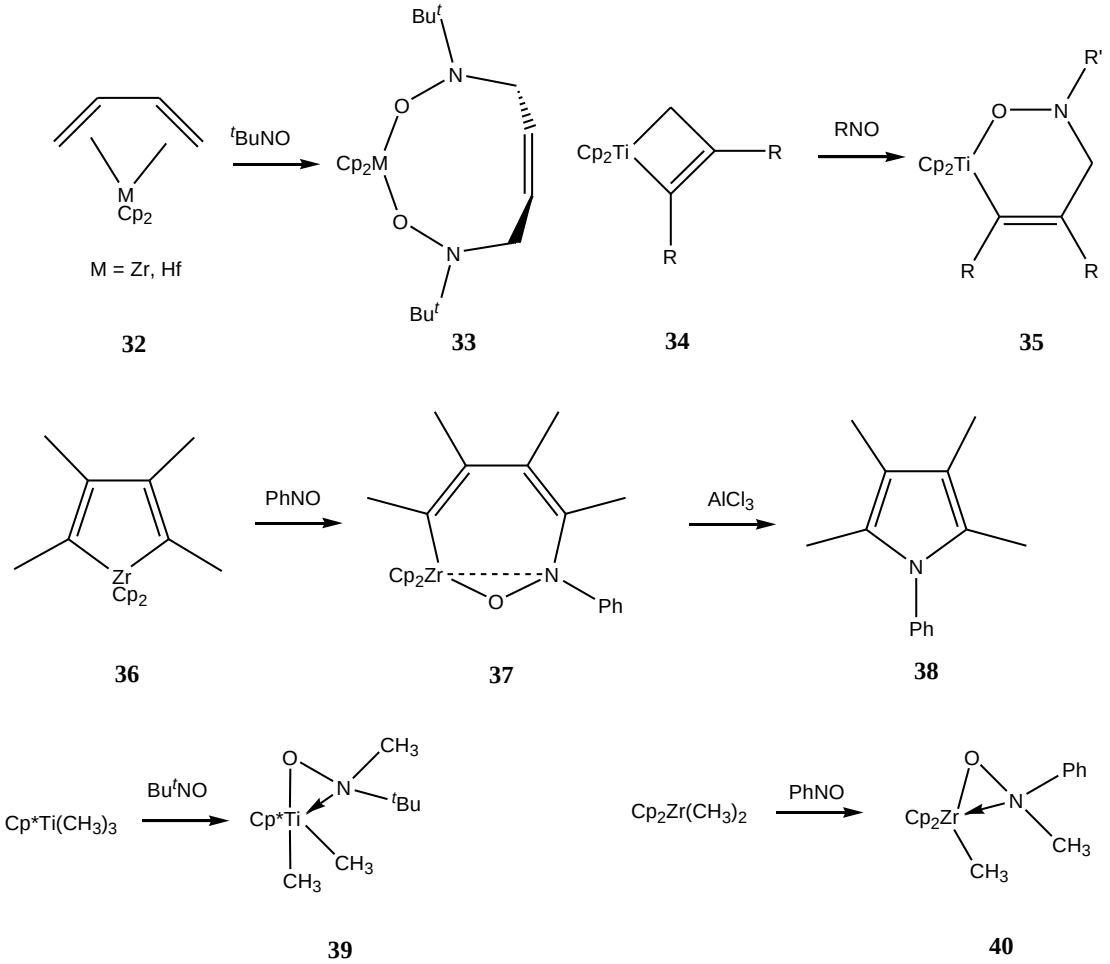


Scheme 2-4: *C*-Nitroso compounds have a wide range of redox products. [O] = oxidation, [H] = reduction.

The biochemistry of *C*-nitroso compounds has been of some interest. Aromatic *C*-nitroso compounds combine with haemoglobin[81, 82] and *C*-nitroso compounds are intermediates in the metabolism of amines[83].

2.1.2 Insertion Reactions Involving *C*-Nitroso Compounds

There are only a few published examples of a *C*-nitroso compound inserting into a metal-carbon bond. All examples located involve Group 4 metals with cyclopentadienyl ligands (Scheme 2-5). The first example was published in 1989[84]. Zirconocene- and hafnocene-butadiene complexes (**32**) insert two molecules of 2-methyl-2-nitrosopropane (**31**) to form a nine-member metallocycle (**33**). In 1994 a variety of *C*-nitroso compounds were reacted with titanacyclobutene complexes[85] (**34**). The *C*-nitroso compounds regiospecifically insert into M-CH_2 bonds to form six-membered metallocycles (**35**). Zirconocycles (**36**) have inserted nitrosobenzene to form a seven-membered metallocycle[86] (**37**). The metallocycle reacts with $AlCl_3$ to form N-phenylpyrroles (**38**). Cp*$TiMe_3$ inserts **31** to form a hydroxylaminato complex[87] (**39**) which is a precursor to an active catalyst in atactic propylene polymerisation. Dimethylzirconocene has been reacted with nitrosobenzene to form a hydroxylaminato complex[88] (**40**).



Scheme 2-5: Selected *C*-nitroso insertion reactions.

2.1.3 *C*-Nitroso Compounds and Cyclomanganated Compounds

As mentioned in Chapter 1, cyclomanganated compounds have undergone insertion reactions with a wide variety of unsaturated compounds. Calnan[70] found **30** reacted with **31** to form a new product that was not characterised. A literature search found that *C*-nitroso compounds have only undergone insertion reactions with group 4 metals. It was suspected that this may be the first *C*-nitroso insertion reaction with a metal of another group. For this reason it was decided the reaction of cyclomanganated compounds and *C*-nitroso compounds warranted further research.

2.2 Experimental

2.2.1 General Method of Reacting *C*-nitroso Compounds with Cyclomanganated Compounds

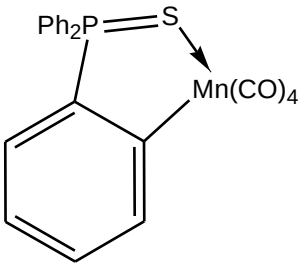
The cyclomanganated compound was transferred to a Schlenk flask with fitted reflux condenser. Three molar excess of the *C*-nitroso compound was added under nitrogen in an appropriate dry and degassed solvent. The reaction flask was heated in an oil bath (90 °C). Reaction progress was monitored by thin layer chromatography (TLC) and Fourier transform infrared spectroscopy (FTIR). When the FTIR metal-carbonyl peaks of the cyclomanganated reactant disappeared or got very small the hot solution was filtered. The filtrate was evaporated to dryness on a vacuum line. The residue was dissolved in dichloromethane and loaded onto a preparative layer chromatography (PLC) plate. TLC of the filtrate with a variety of solvents was used to decide which solvent would give the best separation of products on the PLC plate. After PLC the products of interest were extracted from the PLC plate with dichloromethane and evaporated to dryness on a vacuum line. The precipitate was analysed for products of interest by collecting the dichloromethane-soluble fraction of the precipitate and analysing its FTIR spectrum. If metal-carbonyl peaks were seen in the spectrum the precipitate was analysed further. If metal-carbonyl peaks were not seen it was assumed that the precipitate was not worth analysing. This was because the reactants used in these reactions were fairly non-polar and the products were expected to be a combination of the organic part of the cyclomanganated compound and the *C*-nitroso compound, or an organic manganese compound in which case manganese-carbonyl peaks were likely to be

seen. It is possible that polar groups such as amines or alcohols may be in a product, however this will probably be only a small part of the molecule and will still dissolve in hot non-polar organic solvents such as heptane.

2.2.2 2-Methyl-2-nitrosopropane (31) Reacted with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30)

31 (83 mg, 950 μmol) and **30** (100 mg, 320 μmol) in solvent (15 mL, heptane, acetonitrile, or toluene respectively) were heated in an oil bath (90 °C) for 1-2 h.

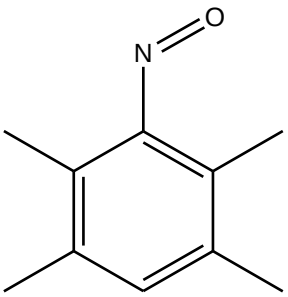
2.2.3 2-Methyl-2-nitrosopropane (31) Reaction with η^2-[(2-Diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (41)



41

31 (83 mg, 950 μmol) and (**41**) (140mg, 300 μmol) in heptane (15 mL) were heated in an oil bath (90 °C) for 1-2 h.

2.2.4 Nitrosodurene (42) Reaction with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in Toluene



42

Nitrosodurene **42** (160 mg, 950 μmol) and **30** (100 mg, 320 μmol) in toluene (15 mL) were heated in an oil bath (90 °C) for 1-2 h.

2.3 Results and Discussion

2.3.1 General Observations

Optimum Temperature

Initial reactions were performed with an increasing temperature gradient. When there was no indication of a reaction the temperature was raised gradually until further reaction commenced. Indication of a reaction was detected by looking for obvious visual changes in the reaction solution, using TLC to detect any new products that form, and using FTIR to detect any new manganese-carbonyl compounds and to monitor the consumption of cyclomanganated reactants. Generally the reactions were slow until the oil bath temperature was 90 °C or above. Oil bath temperature may have reached as high as 105 °C during some reactions but the effect of raising the temperature above 90 °C was not investigated. Generally a brown precipitate[*] began to form when the oil bath reached 90 °C. It may have been formed from the thermal decomposition of the cyclomanganated reactant, or as a by-product of the reaction with the *C*-nitroso compounds.

*Reactions Involving 2-Methyl-2-nitrosopropane (**31**)*

Reaction solutions involving **31** generally turned green shortly after it dissolved in the solvent. The dissociation of the colourless dimer [$(Bu^tNO)_2$] to the blue monomer (Bu^tNO)[89] combined with the yellow colour of cyclomanganated compounds explained this colour change. Further colour changes were seen which varied with solvent and reactants. Excess **31** was conveniently removed during work-up when evaporating the filtrate to dryness on a vacuum line.

The Effect of Light on C-Nitroso Compounds

Nirosoalkanes can form nitroxides in red light[71]. The first reaction (**31** reacted with **30** in heptane) was attempted with and without the reaction flask covered in foil (to stop the exposure of light). The colour change was slower in the absence of light, however with some heating (oil bath at 50 °C) the appearance was essentially the same as for the reaction with light. There was no observed difference in the final products with or without light. Nitroxides may form thermally as well as photochemically[79]. In all reactions involving **31,** evaporation

[*] The brown precipitate is believed to be a form of inorganic manganese because it is insoluble in organic solvents, it is a feasible destination for the manganese that was previously in the manganese carbonyl complexes, and some inorganic manganese compounds are brown e.g. MnO_2.

of the final reaction solution on a vacuum line yielded a blue solution in the muck trap. This indicated that excess **31** was present throughout the whole reaction because the solutions appeared the same after heating with and without light. Further reactions with **31** were done with light. There were no precautions to exclude light from the reactions involving **42** because **42** is more resistant to photolysis than **31**[80].

2.3.2 2-Methyl-2-nitrosopropane (31) Reacted with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in Heptane

Observations

An immediate colour change from yellow to green was observed within a few minutes of mixing the reactants without heating. The solution darkened with time and the solution eventually turned black-red. TLC showed a new pink spot with the same R_f as **30** which faded within a few minutes. When the early green reaction solution was left in a capillary in air for a few minutes it turned red/pink. The darkening of the solution is difficult to explain. It is not uncommon for a minor by-product to be highly coloured. It is possible that the colouring was due to nitroxides (some nitroxides are red[90]). When the red-pink solution was developed on a TLC plate the red colour had the same R_f value as the **30**. The red colour eventually faded leaving the yellow **30** spot. The fading colour could be explained if the red compound was volatile or if it reacted further to form a colourless compound. TLC showed no other new spots besides a weak spot at the baseline.

TLC

TLC (dichloromethane) initially showed two spots R_f = 0.32 (^{t}BuNO), 0.94 (η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese). After heating to 90 °C it showed the formation of new spots R_f = 0.51, 0.70 (w), 0.30 (streak from baseline).

TLC (1:2 EtOAc: hexane) initially gave R_f = 0.54 (^{t}BuNO), 0.73 (η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese) new spots formed at R_f = 0.21 (m), 0.17 (w), 0.09 (s, yellow, streak from baseline)

FTIR

No additional peaks were observed in the metal-carbonyl region of the FTIR spectrum. This indicated that no new metal-carbonyl compounds were formed.

PLC

PLC (dichloromethane) showed three main bands, R_f = 0.29 (a streak from the baseline), 0.53 (br), 0.76, 0.92.

R_f= 0.53

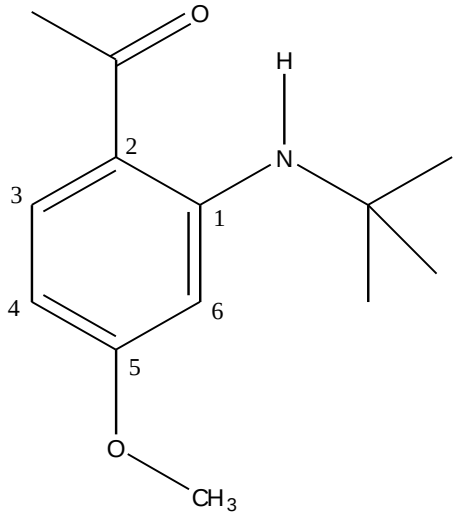
This was assigned as the demetallated **30**, i.e. 4-methoxyacetophenone:
^{1}H NMR: δ = 2.56 (s, 3H), 3.88 (s, 3H), 6.94 (d, J = 8.9 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H) ppm. Generally this was the main product that was isolated in this reaction. The yield was not recorded but it clearly appeared to be in greater quantity than the other products.

R_f = 0.92

^{1}H NMR indicated this fraction was a small amount of grease.

R_f = 0.76

Spectroscopic evidence indicated that this compound was 2-acetyl-5-methoxy-*N*-(*tert*-butyl)aniline (**43**) and this is discussed further below.



43

The R_f = 0.76 fraction fluoresced blue with UV light (254 nm) on a silica plate. Phenyl alkyl ketones generally only fluoresce if they meet any of the following criteria[91]:

(A) If there is a hydrogen-bonding group, e.g. an amine or hydroxyl group in the *ortho* position;

(B) If it is in a hydrogen-bonding solvent and the aromatic ring contains an electron donating group;

(C) If it is in a strongly acidic medium.

The fluorescence process is believed to involve the emission of a protonated excited carbonyl group[91]. Compound **43** fits criterion A because of the secondary amine group in the ortho position.

FTIR (neat oil): ν = 3277 (w, br, N-H), 2965 (m, CH_3), 2928 (m, CH_3), 1678 (w, sh), 1633 (s, C=O), 1585(s, N-H bend), 1258 (s, C-N), 1227(s, C-N) cm^{-1}.

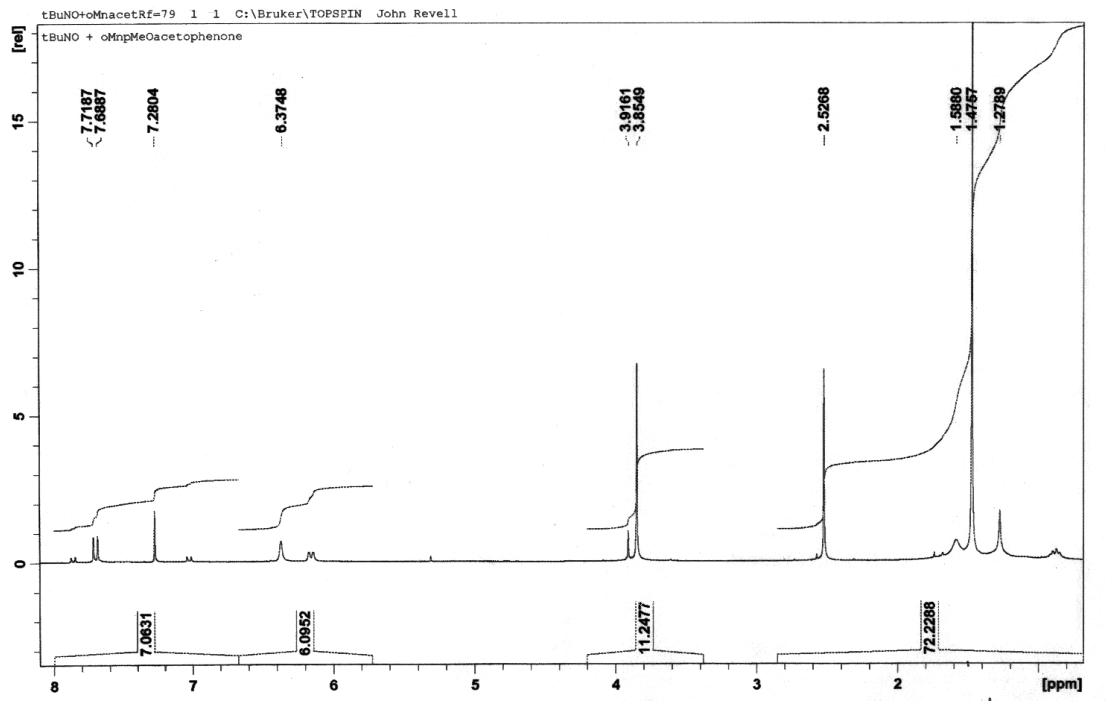


Figure 2-1: The ^{1}H NMR spectrum of the R_f = 0.76 PLC fraction from the reaction of 2-methyl-2-nitrosopropane (31) and η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in heptane.

^{1}H NMR ($CDCl_3$) (Figure 2-1): δ = 1.46 (s, 9H, ^{t}Bu), 2.51 (s, 3H, $COCH_3$), 3.84 (s, 3H, OCH_3), 6.16 (d, J = 8.7 Hz, 1H, br, H-4), 6.38 (s, 1H, br, H-6), 7.69 (d, J = 9.0 Hz, 1H, H-3) ppm; N-H peak not seen (probably because of peak broadening caused by proton exchange with traces of water in the solvent).

The two peaks assigned as methyl groups had similar chemical shifts to those in 4-methoxyacetophenone i.e. 2.51 compared with 2.56 and 3.84 compared with 3.88. This suggests the methyl groups in this molecule are in similar environments to that of 4-methoxyacetophenone and that the compound probably contains a 4-methoxy-acetophenone moiety. Two doublets and one singlet in the aromatic region of the spectrum agrees with a 1,2,4-trisubstituted aromatic ring.

ESI-MS (methanol):

Positive Ion (m/z)

(20 V) 244 (6 %), 222 (100 %), 172 (9 %), 166 (4 %) Da.

(40 V) 222 (43 %), 166 (100 %) Da.

(60 V) 166 (100 %), 148 (44 %) Da.

The peaks m/z = 244 $[M+Na]^+$ and 222 $[M+H]^+$ Da are seen (M = compound **43**). The m/z = 166 Da peak may correspond to an $[M-(CH_3)_2C=CH_2+H]^+$ ion. The β-elimination of the *tert*-butyl group on a protonated **43** molecule would give an ion of this mass. This could possibly be facilitated by collision induced dissociation, and would explain the increase in relative intensity of the m/z = 166 Da peak with higher cone voltage. It is uncommon for fragmentation such as this to be seen at such soft ionising conditions as with a cone voltage of 20V. It may be that the *ortho*-acetyl group may facilitate this reaction by acting as an intramolecular base allowing easier transfer of a *tert*-butyl hydrogen to the nitrogen.

The m/z = 148 Da peak may really be 149 $[M-NHC(CH_3)_3]^+$ Da.

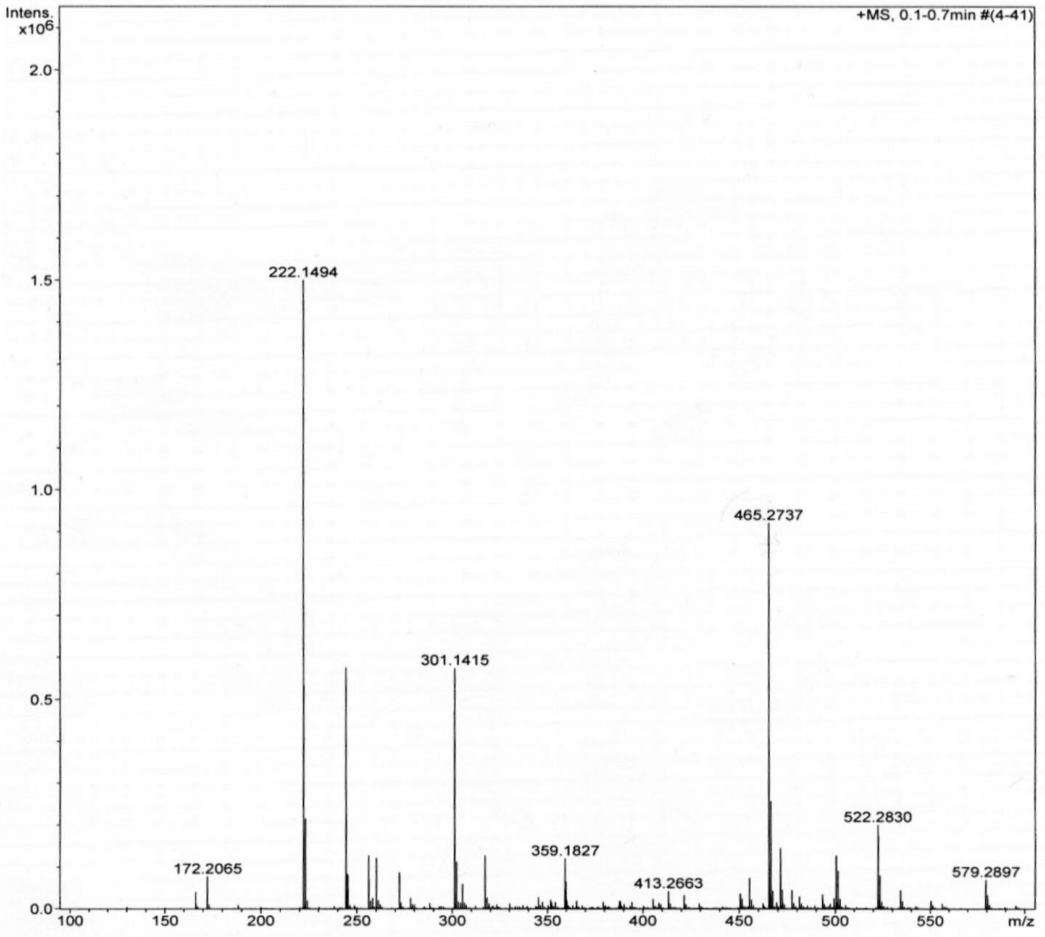
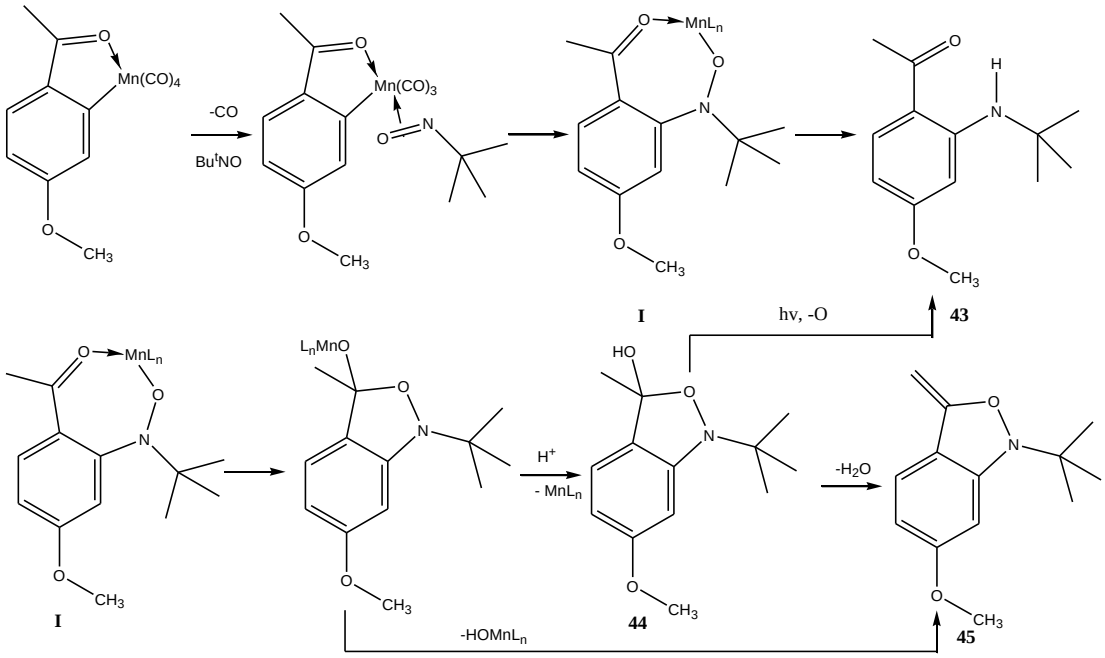


Figure 2-2: The MicrOTOF spectrum of the R_f = 0.76 fraction.

MicrOTOF analysis (Figure 2-2) of the sample gave an empirical formula $C_{13}H_{19}NO_2$ with an $[M+H]^+$ peak at m/z = 222.1494 Da compared with 222.1489 Da (calculated), $[M+Na]^+$ 244.1306 Da compared to 244.1308 Da (calculated), $[2M+Na]^+$ 465.2737 Da compared to 465.2729 Da (calculated). No other formula is consistent with these values. The most likely compound for the R_f = 0.76 is **43**.

*Possible Mechanism of the Formation of **43***

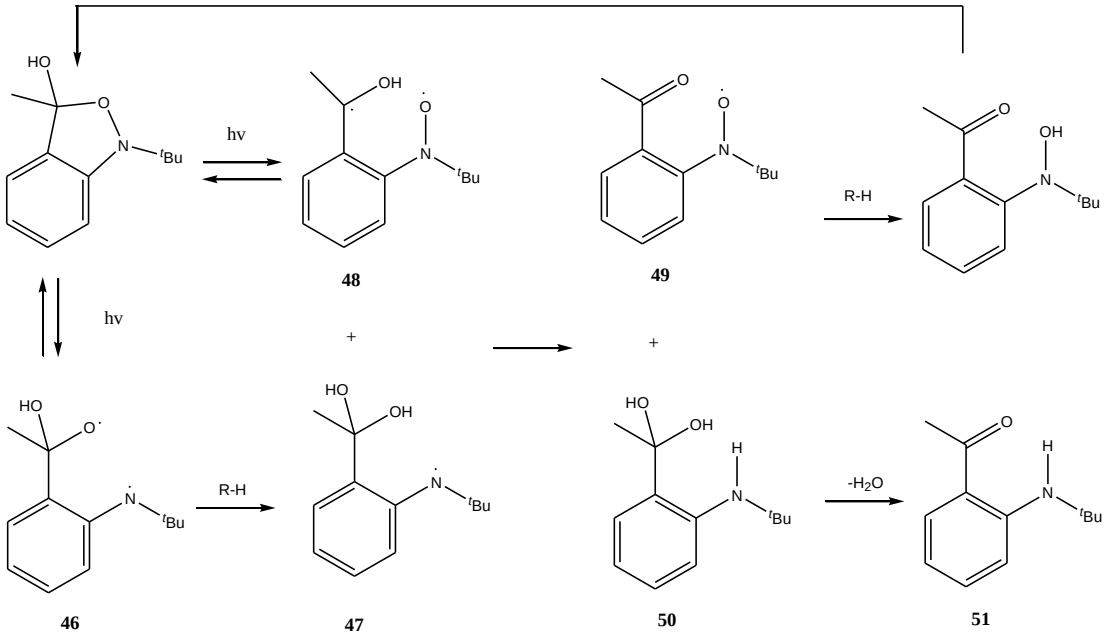
It could be that **43** formed via a hydroxybenzisoxazolidine derivative **44** (see Scheme 2-6) followed by a radical reaction to form 2-acetyl-5-methoxy-*N*-*t*-butylaniline as studied by Srivastava and Falvey[92].



Scheme 2-6: The top of this scheme shows how Bu^{t}NO possibly inserts into the Mn-C bond to form a seven-membered metallocycle intermediate (I) which reacts further to form 43. The bottom of the scheme shows a mechanism that would explain the formation of 43 as well as the formation of a species seen in the GC-MS chromatogram which could possibly be 45.

Srivastava and Falvey's study was mainly focused on the photochemistry of 3-hydroxybenzisoxazolidine derivatives but thermal reactions were not mentioned. The reaction proceeds through a radical mechanism initiated with the scission of either an N-O or a C-O bond to form a diradical (Scheme 2-7). The nitrogen/oxygen diradical (**46**) is believed to extract a hydrogen radical from the solvent to form an anilino radical (**47**). **47** is more persistent than **46** and is believed to receive another hydrogen atom from the carbon/oxygen diradical (**48**) because it will give a hydrogen atom to **47** more efficiently than the solvent. This

reaction gives a nitroxide radical (**49**) that has been detected by EPR, and a molecule (**50**) that loses H_2O to form a 2-acetyl-*N*-*t*-butylaniline (**51**).

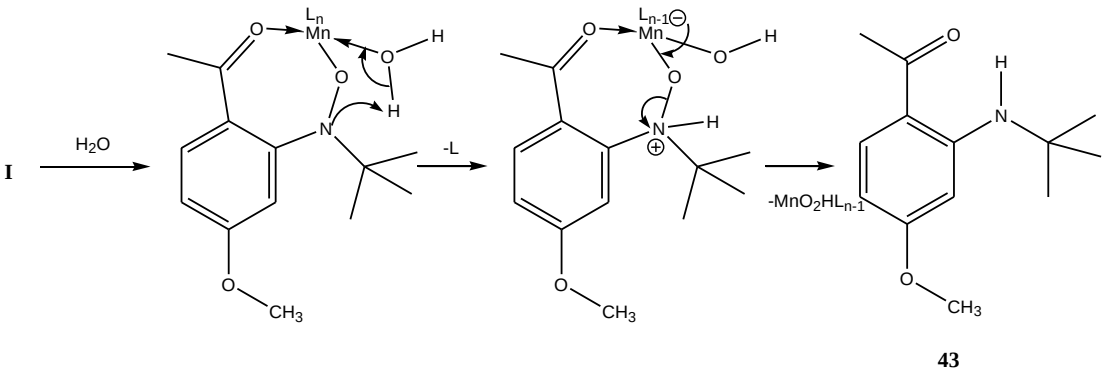


Scheme 2-7: The mechanism proposed by Srivastava and Falvey for the formation of 2-acetyl-*N*-butylanilines (51, bottom right) from 3-hydroxybenzisoxazolidines (top left).

It may be that this reaction occurs thermally as well. The formation of a 3-hydroxybenzisoxazolidine intermediate is reasonable because the insertion of an unsaturated substrate to form a five-membered ring has been seen before with alkenes[46] and alkynes[43, 65]. This mechanism could explain a compound detected by GC-MS (discussed below).

The elimination of water from **44** would give **45** which would give the same molecular ion as the compound seen in the GC-MS.

43 may form without the cyclic intermediate **44** but instead with the oxygen originally belonging to 2-nitroso-2-methylpropane leaving with the manganese (e.g. Scheme 2-8).



Scheme 2-8: A possible mechanism for the formation of 43.

A reaction of an intermediate (**I**, Scheme 2-6) with water might occur. Although care was taken to exclude water (the glassware used was only heated to 100 °C for 2 hours or more), water will still be adsorbed on to the flask at this temperature. Because the reaction was done on a small molar scale and the yield of **43** was small there would be sufficient water to take part in the reaction.

Other methods of forming (2-acetyl)-N-tert-butylanilines

A literature search did not find any published examples of **43**, but other (2-acetyl)-*N*-*tert*-butylanilines were discovered. The method previously used to make (2-acetyl)-*N*-*tert*-butylanilines was the photolysis of 3-hydroxy-2,3-dihydro-2,1-benzisoxazoles or *N*-tert-butyl-3-methylanthranilium ions[92, 93]. The R_f = 0.76 fraction (**43**) showed similarities to a previously characterised 2-acetyl-*N*-*tert*-butylaniline: 2-acetyl-*N*-*tert*-butyl-4-nitroaniline[93]. Both were yellow solids[*], both had similar mass spectrometry fragmentation ($M^{+\bullet}$, $[M\text{-}CH_3]^+$, $[M\text{-}33]^+$,…).

GC-MS of Filtrate

A sample of the reaction filtrate was diluted in dichloromethane and analysed by GC-MS. The chromatogram (Figure 2-3) showed three main peaks at 12.9, 17.3, and 17.5 minutes.

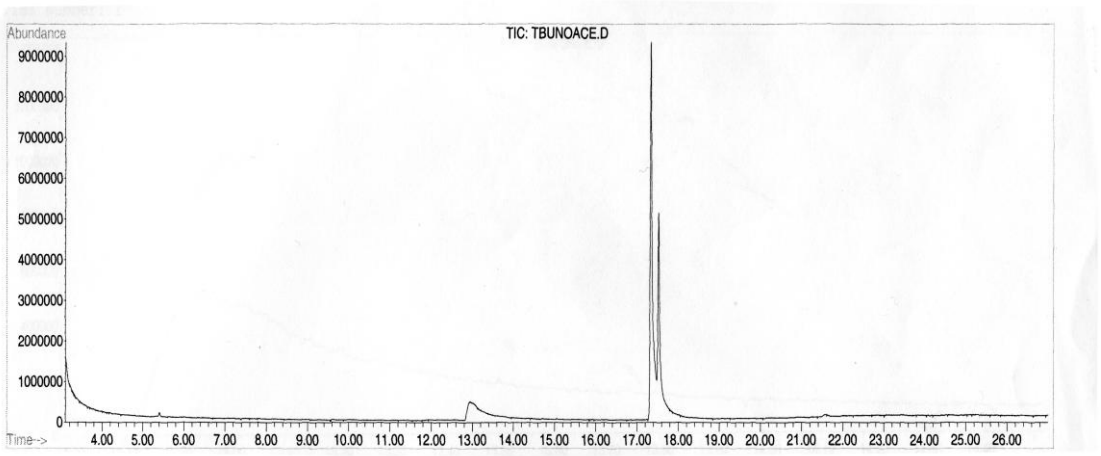


Figure 2-3: The GC-MS chromatogram of the filtrate of the reaction of 2-methyl-2-nitrosopropane (31) and η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in heptane.

Retention Time (RT) = 12.9 Min Fraction

This was assigned as the demetalated product 4-methoxyacetophenone with the mass spectrum m/z = 150 ($M^{+\bullet}$), 135 ($[M\text{-}CH_3]^+$), 107($[M\text{-}COCH_3]^+$) Da. The

[*] **2** was generally isolated as a yellow/orange oil. When the reaction was done on a larger scale a couple of yellow crystals appeared to have formed in the oil.

peaks show some tailing which may mean the solution injected into the GC was too concentrated.

RT = 17.3 Min Fraction

The peak corresponding to 17.3 minutes gave a mass spectrum containing the ions: m/z = 219 ($M^{+\bullet}$), 204 ($[M\text{-}CH_3]^+$), 192 ($[M\text{-}HCN]^{+\bullet}$), 176 ($[M\text{-}CH_3CO]^+$), 163 ($[M\text{-}(CH_3)_2C{=}CH_2)]^{+\bullet}$), 162 ($[M\text{-}C(CH_3)_3]^+$), 149 ($[M\text{-}(CH_3)_2CCH_2N]^+$, 135 ($[M\text{-}C_5H_{10}N]^+$, 107 ($[M\text{-}C_6H_{10}NO]^+$), 57 ($(CH_3)_3C^+$) Da.

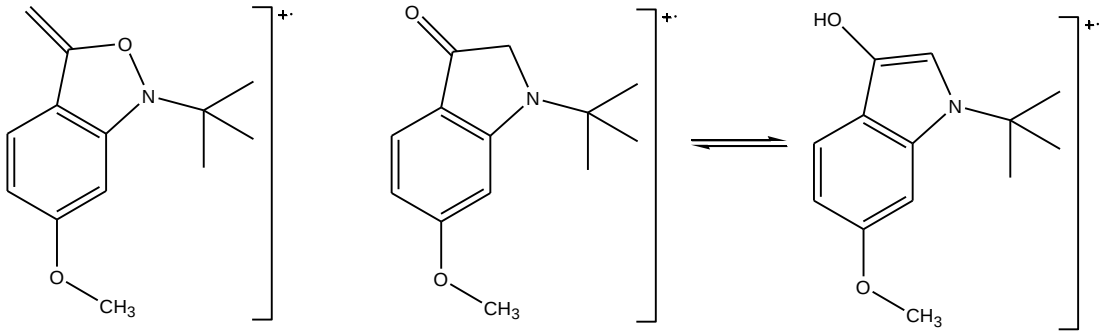
The structure of this compound is not known, however possible structures are discussed below.

RT = 17.5 Min Fraction

m/z = 221 ($M^{+\bullet}$), 206 ($[M\text{-}CH_3]^+$), 188, 164 ($[M\text{-}C(CH_3)_3]^+$), 150 (4-methoxy-acetophenone$^{+\bullet}$), 135, 107, 92, 77, 57 $[(CH)_3C^+]$ Da.

The mass spectrum of the peak 17.3 minutes was closely related to the 17.5 minute one. It should be noted the chromatogram shows overlap between the two species so ions seen in both mass spectra may belong solely to the compound with the shorter retention time. The similar retention time indicates a similar molecular mass. If the molecular ions were assigned correctly there were two compounds of molecular mass 219 and 221 respectively. This may correspond to the difference of a double bond or a ring between molecules. The m/z = 221 Da and RT = 17.5 compound probably corresponds to the same molecule isolated at R_f = 0.76, i.e. **43**.

The 219 molecule was more difficult to assign because the compound has not been isolated. If the $M^{+\bullet}$ = 219 is similar to the 221 molecule it is likely to be a cyclic product. There was no position in molecule **43** to put another π-bond in order to get a compound of molecular weight of 219 that would be stable. The formation of five-membered rings from cyclomanganated compounds is common and a number of products are possible, e.g. **45**, **52**, and **53** were likely products. This product was not isolated through PLC although it is possible it decomposed on the silica during PLC, this being one possible explanation for the streaking on the PLC plate.



45 **52** **53**

GC-MS of the reaction filtrate revealed only three species in the chromatogram. Two of these peaks 4-methoxyacetophenone and **43** have been identified and the third seems to be a compound closely related to **43**. The fact that there were only a few products (volatile enough to be analysed by GC but involatile enough not to be removed on the vacuum line) was an indication that this was a potentially useful reaction.

This reaction had the advantage that it was simple with a small number of steps, the product of interest (**43**) was adequately isolated, and no methods of synthesis of **43** have been published. The reaction has some disadvantages. The yield of **43** was only 1-5%; this could possibly improve with further adjustment of reaction conditions. However the starting orthomanganated compounds are expensive and the synthesis is probably uneconomical to do on a large scale compared to other methods.

2.3.3 2-Methyl-2-nitrosopropane (31) Reacted with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in Acetonitrile

The solution began to go cloudy when the oil bath reached 90 °C (acetonitrile, b.p. = 81.6 °C[94], began to reflux when the oil bath reached 93 °C) but no significant amounts of brown solid formed. The blue green colour slowly faded during reflux with a slight brown colour forming with time. Filtration of the final cloudy solution yielded a solution that was also cloudy.

TLC

TLC (dichloromethane) gave spots initially at R_f = 0.36 (Bu^{t}NO, w), 0.46 (4-methoxyacetophenone, m)*, 0.92 (**30**). New spots formed at R_f = 0.00 (s, brown), 0.63 (w), and the R_f = 0.46 peak grew broader with time.

FTIR

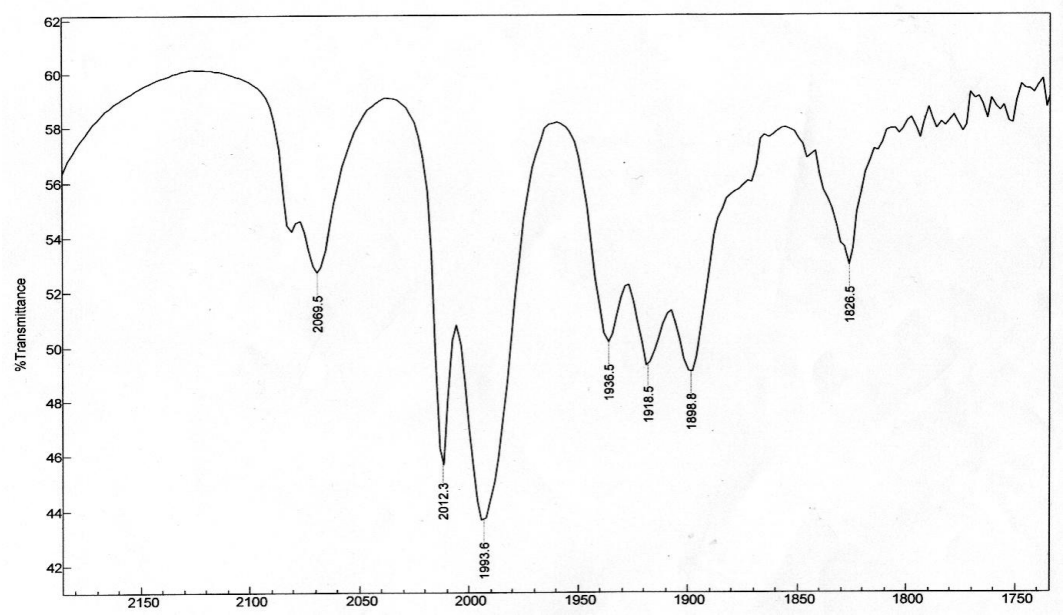


Figure 2-4: New metal-carbonyl peaks seen at 2012, 1918, and 1897 cm^{-1} along with the peaks of η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (30) (2080, 1994, and 1937 cm^{-1}).

New peaks in the metal-carbonyl region (2012 (sh), 1919, 1899 cm^{-1}) appeared after approximately 30 minutes refluxing. These peaks disappeared before the original **30** peaks (2070, 1994, 1937 cm^{-1}, Figure 2-4) disappeared. These new peaks could correspond to **30** with CO ligand(s) substituted with CH_3CN. **30** has previously had one CO ligand substituted with *t*-butylisocyanide[54], which had FTIR peaks attributed to CO at 2016, 1955, 1915 cm^{-1}. The 2012 and 1919 cm^{-1} peaks fit well with the 2016, 1915 cm^{-1}, however no peaks around 1955 cm^{-1} were seen in this spectrum.

PLC

PLC (dichloromethane) gave four fractions (R_f = 0.00 (brown), 0.76 (4-methoxyacetophenone), 0.82 (thin), 0.99 (yellow, thin, grease and **30**). The R_f = 0.00 and 0.99 bands were ignored as they were unlikely to be of interest. The R_f =

* The 4-methoxyacetophenone comes from the batch of **30** used in this experiment. It was used as a precursor to **30** and was not completely removed during workup. Although its presence was not ideal it is a common by-product to reactions involving **30** so it would be present in the reaction anyway and the 4-methoxyacetophenone makes up only a small fraction of this batch of **30.**

0.76 band was analysed by NMR (see section 2.3.2 *Fraction R_f = 0.53* for NMR data on 4-methoxyacetophenone). A barely perceptible quantity of the 0.82 fraction was isolated and was not analysed further. The position of the 0.82 fraction relative to 4-methoxyacetophenone was approximately where **43** would come. It did not fluoresce under UV light though.

2.3.4 2-Methyl-2-nitrosopropane (31) Reacted with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in Toluene

TLC

TLC (1:2 Ethyl acetate: hexane) initially gave two spots R_f = 0.55 (**31**), 0.73 (**30**). New spots formed at R_f = 0.49 (m, with a weak streak tailing it to the baseline), R_f = 0.27 (m, yellow, distinguishable from the base line).

TLC (dichloromethane) initially gave two spots 0.36 (**31**), 0.91 (**30**). New spots appeared at R_f = 0.10 (yellow and red streak from base line), 0.53 (s), 0.63 (m),

FTIR

No new metal-carbonyl peaks were seen in the FTIR spectrum. Toluene does absorb strongly around 1950 cm^{-1}. Any new peaks below about 2000 cm^{-1} would be obscured.

PLC

PLC (2:1 X4: ethyl acetate) gave seven bands R_f = 0.00 (s, brown, inorganic manganese and other polar compounds), 0.22 (w), 0.48 (m), 0.62 (m), 0.70 (w), 0.83 (m), 0.87 (w).

2.3.5 2-Methyl-2-nitrosopropane (31) Reaction with η^2-[(2-Diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (41) in Heptane

TLC

Initial TLC (1:4 EtOAc: hexane) gave three spots R_f = 0.40 (w, 2-nitroso-2-methylpropane), 0.46 (triphenylphosphine sulfide, an impurity from **41**, 0.67 (**41**). New spots formed at R_f = 0.00, 0.11.

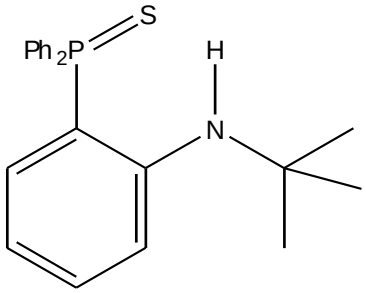
PLC

PLC (1:2 ethyl acetate: X4) gave one large streak under the UV lamp (254 nm), however a fluorescent band could be distinguished from the streak at R_f = 0.52 (s,

fluoresces purple with UV light (254 and 312 nm)). Other coloured bands could be seen at R_f = 0.00 (s, brown) and 0.95 (thin, **41**).

R_f = 0.52

^{1}H NMR ($CDCl_3$) gave a spectrum of poor quality. The fact that it fluoresced suggests a triphenylphosphine sulfide equivalent of **43**, i.e. **54,** but NMR spectra suggests yields are too low for this method of preparation to be useful.



54

Composition of the Streak Fraction (triphenylphosphine sulfide)

A portion of the streak between R_f = 0.54 and 0.84 was extracted and gave a white solid that was assigned as demetallated **41**, i.e. triphenylphosphine sulfide.

^{1}H NMR: δ = 7.45 (d, 6H, *o*-H), 7.52 (t, 3H, *p*-H), 7.73 (q, 6H, *m*-H) ppm, lit[95] 7.4, 7.5, 7.7 ppm.

^{13}C NMR (proton decoupled): δ = 128.9 (d), 131.9 (d), 132.7 (d) ppm (quaternary carbon not detected), lit[96]: 128.5 (*m*-C, d, J = 12.7 Hz), 131.8 (*p*-C, d, J = 2.8 Hz), 132.1 (*o*-C, d, J = 10.6 Hz), 133.0 (C-1, d, J = 85 Hz) ppm.

2.3.6 Nitrosodurene (42) Reacted with η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) in Toluene

This reaction was done twice, the first time with limited exposure to the atmosphere[*], and the second time with standard Schlenk techniques. Both reactions gave similar observations however the products were separated with different eluents. The first reaction had dichloromethane as an eluent, the second 1:1 ethyl acetate: X4. The reaction that may have been contaminated with air is included because a fraction extracted from it gave an interesting ^{1}H NMR spectrum.

[*] The nitrogen inlet was off for part of the reaction. This is reason to believe some oxygen (and to a lesser extent water) would have contaminated the reaction mixture.

42 would not dissolve at room temperature but dissolved at a higher temperature. The solution gradually turned a deep dark red possibly due to the formation of nitroxides.

TLC

TLC (dichloromethane) initially gave two spots R_f = 0.57 (**42**), 0.82 (**30**). TLC of the final filtrate gave spots at R_f = 0.00 (s, red), 0.18 (s), 0.43 (s, br), 0.57 (s), 0.63 (m, thin), 0.74 (m, thin), 0.82 (s, thin), 0.89 (s, thin). The red product in the base line was interesting and appears to be insoluble in dichloromethane so the TLC and PLC were repeated in other solvents.

TLC (1:1 ethyl acetate: hexane) of the filtrate split the red colour into two bands R_f = 0.40 (s, purple), 0.76 (s, orange).

PLC

PLC (dichloromethane) gave a brown base line with a purple streak to R_f = 0.01, a band at R_f = 0.21, and three poorly resolved bands at R_f = 0.70, 0.86, 0.98 (red).

R_f = 0.72

The red streak at R_f = 0.72 was extracted as a red oil. ^{1}H NMR of the red oil gave a reasonably clean spectrum (Figure 2-5). δ = 7.94 (d, 2H), 6.94 (d, 2H), 3.86 (s, 4.6H), 2.66 (s, 4.1H), 2.25 (s, 5.5H), 2.08 (s, 5.6H) ppm.

^{13}C NMR: 133.98 (w), 130.86 (s), 128.30 (w), 122.51 (w), 118.42 (w), 114.06 (s), 55.81 (m), 30.05 (w), 26.64 (m), 20.55 (m), 19.07 (w), 13.36 (w).

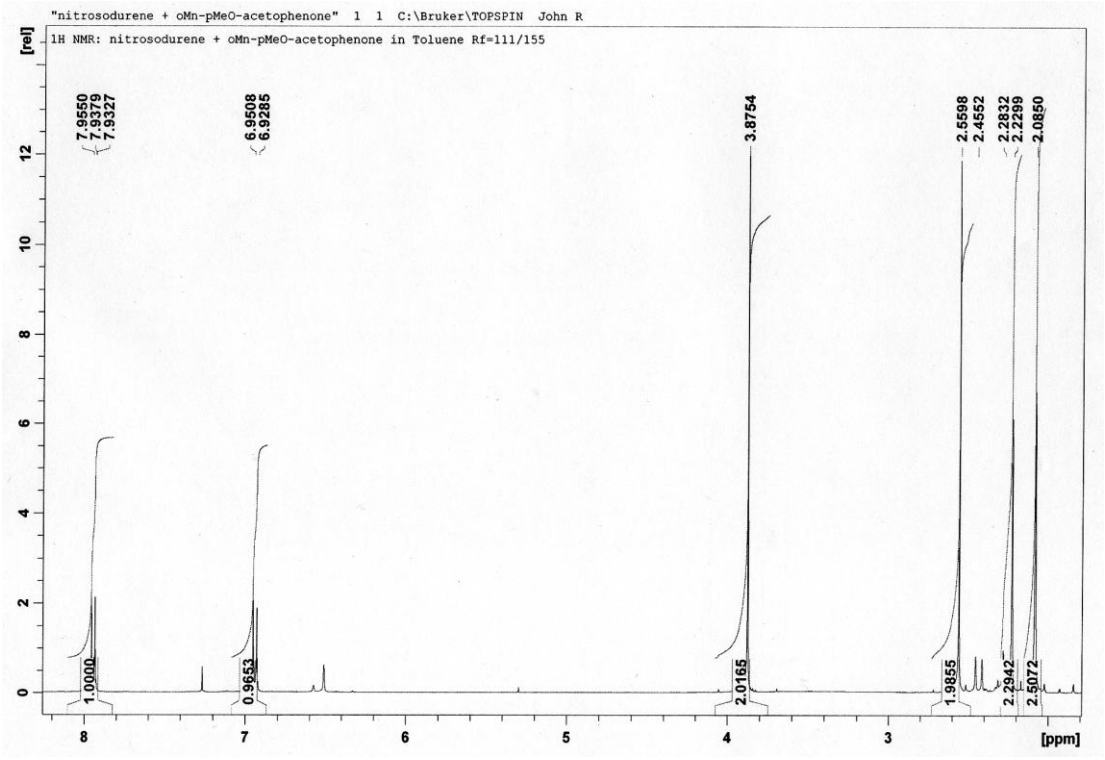


Figure 2-5: ^{1}H NMR spectrum of red R_f = 0.72 fraction.

The spectrum could be interpreted as of a mixture of 4-methoxyacetophenone and another molecule probably with a durene moiety. If so, the durene moiety was not **42** (^{1}H NMR δ = 2.30 (s, 6H), 2.34 (s, 6H), 7.13 (s, 1H)). Although the chemical shifts match 4-methoxyacetophenone very well the integrals do not. In this spectrum the integral was 1:1:2:2 compared to the predicted 2:2 (aromatic, 2H each) to 3 (methoxy, 3H) to 3 (methyl, 3H).

ESI-MS (methanol):

Positive Ion (m/z)

(20 V) 307 (100 %), 184 (30 %), 173 (33 %), 162 (35 %), 150 (46 %) Da.

(60 V) 307 (100 %), 162 (15 %), 150 (33 %), 135 (16 %) Da.

The m/z = 173 ($[M+Na]^+$), 150 ($M^{+\bullet}$), and 135 ($[M-CH_3]^+$) Da peaks support the presence of 4-methoxyacetophenone. There was possibly a molecule of mass 161 present because of peaks m/z = 162 $[M+H]^+$, 184 $[M+Na]^+$ Da.

PLC (1:1 ethyl acetate: X4) gave a multicoloured band (yellow, orange and red colours) from R_f = 0.74 to 0.98 and a purple band at R_f = 0.60, and a brown band at R_f = 0.00. Under UV light (254 nm) only one streak was seen on the PLC plate. The large number of bands is an indication that yield for any product was likely to be small and analysis of each band would be tedious and is unlikely to give useful amounts of product. For this reason only the coloured bands were examined.

R_f = 0.74-0.98

ESI-MS (methanol):

Positive Ion (m/z)

(20 V) 461 (9 %), 322 (13 %), 308 (46 %), 297 (29 %), 294 (18 %), 185 (7 %), 163 (34 %), 151 (100 %) Da.

(40 V) 308 (50 %), 297 (54 %), 294 (23 %), 163 (45 %), 151 (100 %) Da.

This fraction possibly contains **42** which is suggested by the peaks 163 $M^{+\bullet}$. A compound of mass 162 is also possible, with the peaks 163 $[M+H]^+$ and 185 $[M+Na]^+$ Da. 4-Methoxyacetophenone may also be in this fraction suggested by the 151 $[M+H]^+$ ion.

R_f = 0.60

The ^{1}H NMR spectrum was of poor quality. The sample appeared to contain multiple compounds. A relatively strong peak at 7.27 ppm ($CHCl_3$) provided evidence that the sample was dilute. Peaks corresponding to 4-methoxyacetophenone were seen. A large multiplet was seen at 2.25 ppm and further unidentified peaks were seen in the aromatic region.

2.4 Conclusion

The compound 2-acetyl-5-methoxy-*N*-(*tert*-butyl)aniline (**43**) can be made in small yields from reacting **30** with **31**. Evidence for the formation of a compound with two fewer hydrogen atoms than **43** can be seen by GC-MS analysis. Small yields of new products and large yields of the demetallated cyclomanganated compounds make this reaction inefficient. Further changes of reaction conditions may improve yields. Activation of cyclomanganated compounds by UV light or Me_3NO may not be appropriate because *C*-nitroso compounds are likely to be oxidised to nitroxides and NO under UV light and Me_3NO would probably oxidise the *C*-nitroso compounds to nitro compounds. Further changes in solvent and reactants would be appropriate.

Chapter 3: Insertion Reactions of Acetylallene with Cyclomanganated Compounds

3.1 Introduction

Allenes (1,2-dienes) are hydrocarbons with two consecutive double bonds. They are named after the parent molecule allene ($H_2C=C=CH_2$, also known by its IUPAC name, propadiene). A number of reviews have been written on allenes[51, 97-100]. Allenes are relatively rare in nature with an estimate of 150 allenic or cumulenic natural products known as of 2004[101]. The first discovered allenic natural product was mycomycin[102], an antibiotic of fungal origin (Figure 3-1).

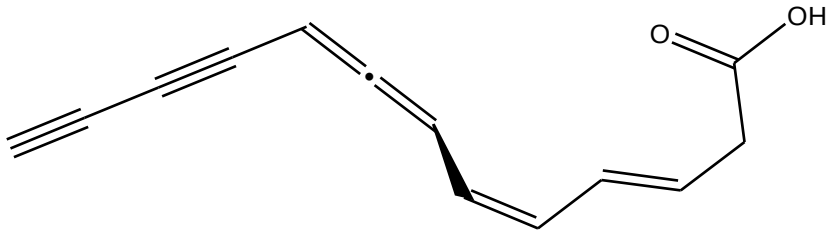


Figure 3-1: Mycomycin, an allenic antibiotic. The allenic bond causes the molecule to be chiral; mycomycin is in the R configuration.

There has been some interest in the use of allenes as pharmaceuticals, due to allenic compounds having useful biological activity such as enzyme inhibition[103], cytotoxicity[104], and antiviral properties[105].

3.1.1 Structure

The two adjacent π-bonds in allenes are orthogonal. With the allenic bond along the z axis, the central sp hybridised carbon uses its $2p_x$ orbital to form a π-bond with the p orbital on an adjacent sp^2 hybridised carbon and its $2p_y$ orbital to form a π-bond with the p orbital on the other adjacent sp^2 hybridised carbon. This is illustrated in Figure 3-2. A consequence of the orthogonality is that allenes are chiral when each end of the allene is bonded to two different groups, this is called "axial chirality"[106]. The configuration of a chiral allene is designated R or S based on the Cahn-Ingold-Prelog priority rules[51]. Figure 3-2 explains how allenes are assigned R or S.

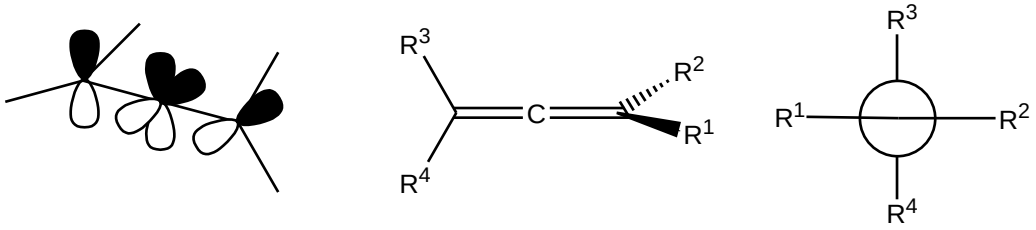


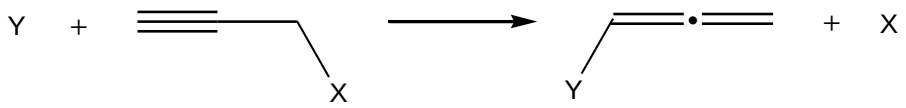
Figure 3-2: The p orbitals used to make the two orthogonal π-bonds (left). On the right is a Newman projection of an allene (centre). An allene is assigned R if the priority of groups is in the order $R^1 > R^2$, $R^4 > R^3$, and S if $R^1 > R^2$, $R^3 > R^4$. It does not matter which end the allene is viewed from.

3.1.2 Allene Chemistry Compared to Alkenes

Allene chemistry is closer to that of alkenes than 1,3-dienes because the two π-bonds are orthogonal. However allenes will isomerise to the generally more stable 1,3-diene if possible (i.e. if the chemical structure can form a 1,3-diene and if the rearrangement mechanism is kinetically viable). Reactions that allene and alkenes have in common include [2+2] cycloadditions[107], Diels-Alder [4+2] cycloadditions (as dienophiles[108, 109] or if conjugated with a double bond it may act as a diene[110]), free radical addition[111], nucleophilic addition[112], electrophilic addition [113], oxidation reactions (e.g. with ozone[114] or permanganate[115]), and hydrogenation[116]. Allenes can oligimerise thermally by [2+2] cycloadditions yielding a variety of dimers, trimers, tetramers, and pentamers[117].

3.1.3 Allene-acetylene Isomerisation

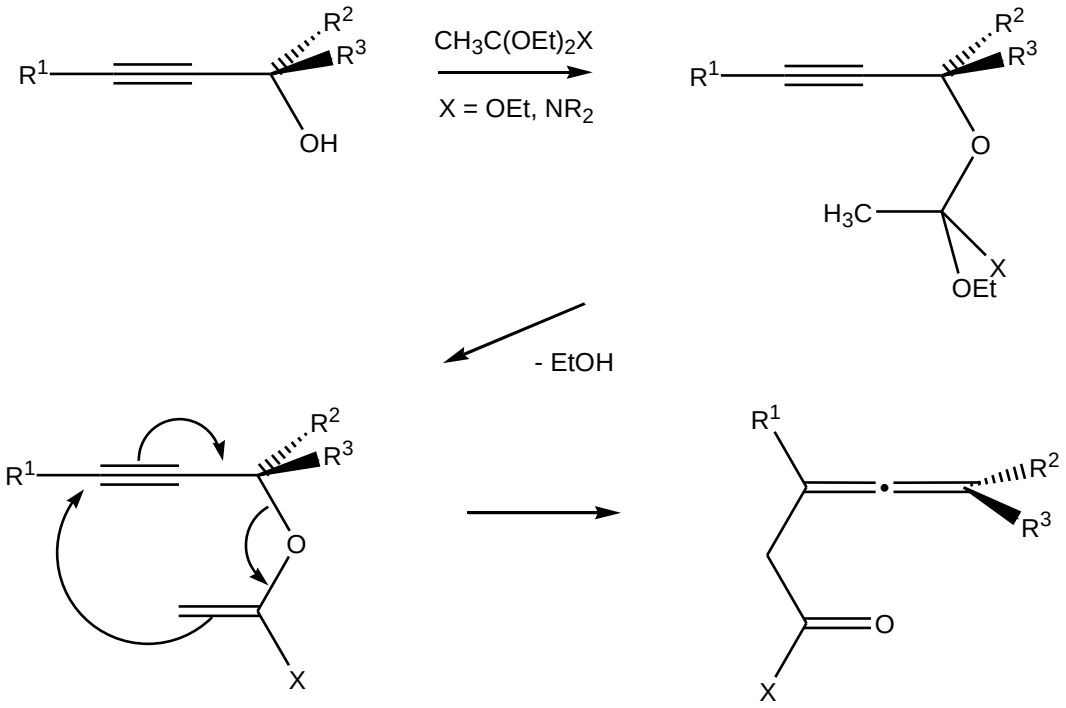
Allenes can undergo rearrangement reactions with alkynes, particularly with propargyl ($HC{\equiv}CCR_2$-) compounds[51, 99] (e.g. the propargyl rearrangement, Scheme 3-1).



Scheme 3-1: The propargyl rearrangement.

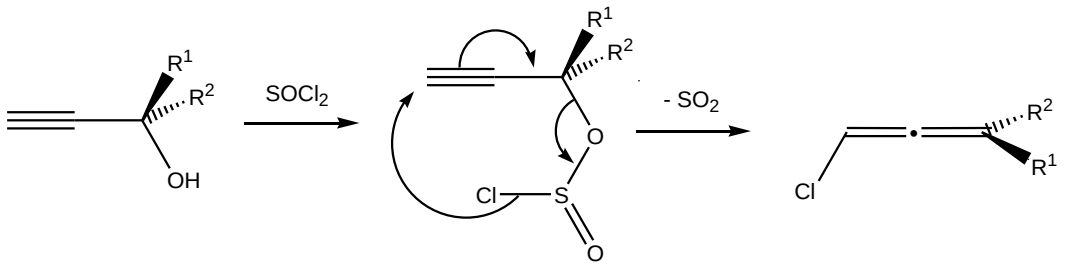
Propargyl alcohols are commonly used in the preparation of allenes. Chiral propargyl alcohols ($HC{\equiv}CCR^1R^2(OH)$, where $R^1 \neq R^2 \neq OH \neq C{\equiv}CH$) can be used to form allenes through rearrangement reactions while maintaining stereochemical purity. Propargyl alcohols have been reacted with $CH_3C(OEt)_3$ and

$CH_3C(NR_2)(OEt)_2$ to form an ether that undergoes a Claisen rearrangement to give β-allenic esters[118] and amides[119] (Scheme 3-2).



Scheme 3-2: Propargyl alcohols can form allenes by a Claisen rearrangement.

In a similar way propargyl alcohols can react with $SOCl_2$ to form chloroallenes, once again through an ether intermediate[120] (Scheme 3-3).

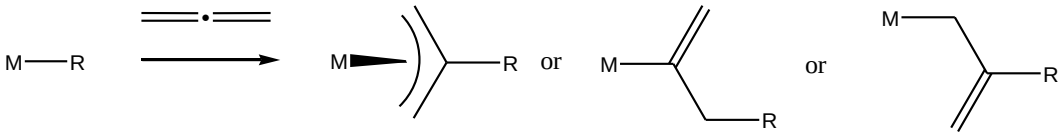


Scheme 3-3: Propargyl alcohols can be converted to chloroallenes with thionyl chloride.

Along with alkynes forming allenes, the reverse is also common. Where compounds of the type $HC{\equiv}CCHR^1R^2$ (R^1 = alkyl group, R^2 = H or alkyl group) will isomerise to form allenes ($H_2C{=}C{=}CR^1R^2$), allenes of the type $H_2C{=}C{=}CHR$ will isomerise to form alkynes of the type $CH_3C{\equiv}CR$[99]. This isomerisation generally requires increased temperature and a catalyst such as a strong base.

3.1.4 Insertion Reactions of Allenes

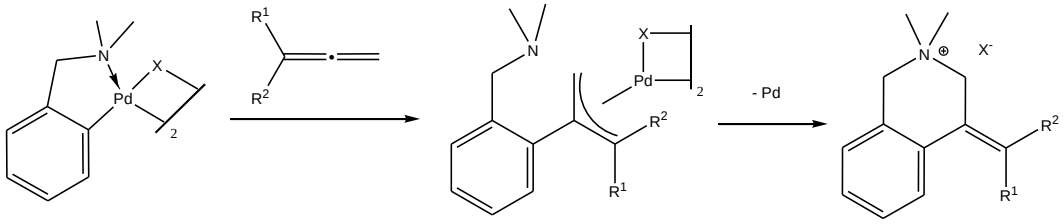
The most common insertion reaction of allenes involves the formation of η^3-allyl complexes. Other possible insertion products include η^1-vinyl and η^1-allyl complexes (Scheme 3-4).



Scheme 3-4: The insertion reactions of allenes commonly yield η^3-allyl complexes (left product), and sometimes η^1-vinyl complexes (middle product) or η^1-allyl complexes (right product).

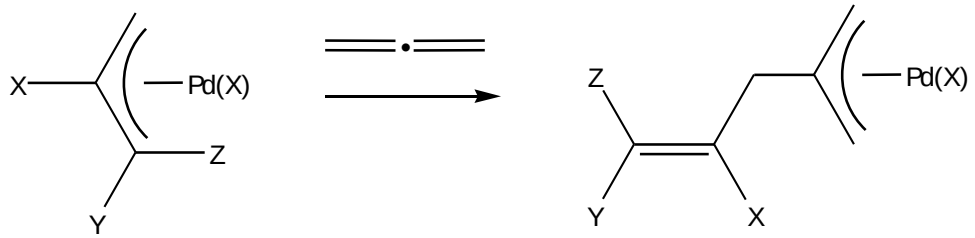
The type of insertion can be affected by the ligands on the metal centre. $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) tend to form allylic complexes when reacted with allenes whereas $MHCl(PPh_3)_3$ tends to form vinyl complexes[121]. Bidentate palladium complexes generally insert allenes to form η^3-allyl complexes but terpyridine complexes will insert allenes to form η^1-allyl complexes in order to maintain terdentate coordination[122].

Insertion reactions of allenes into a Pd-C bond to form allylic complexes are particularly common. One use of such η^3-allylic complexes is that they can be reacted further to form heterocyclic quaternary ammonium compounds that have biological activity[123] (Scheme 3-5).



Scheme 3-5: The insertion of allene into a cyclopalladated compound.

η^3-Allyl palladium complexes themselves can insert allene to form new η^3-allyl complexes[124] (Scheme 3-6).



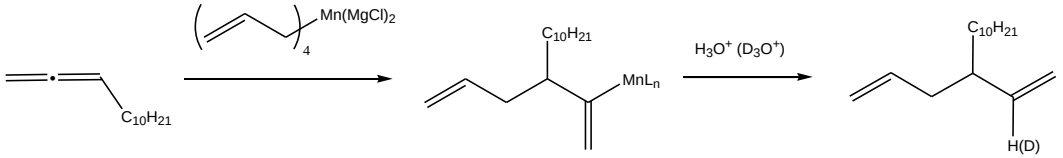
Scheme 3-6: the insertion of allene into an allylic bond to form a new allylic bond. X = Cl, acac, hexafluoro acac; acac = acetylacetonate.

Other metals that have undergone insertion reactions with allenes include Pt[125], Hf[126], and Zr[127], Rh[128].

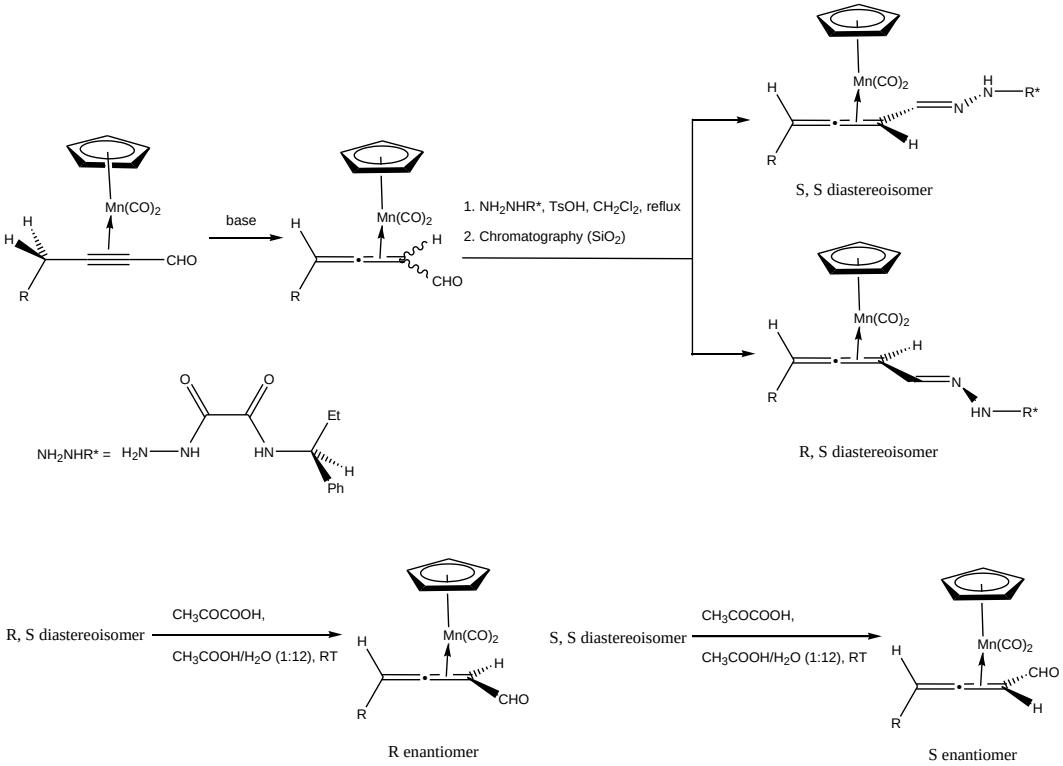
3.1.5 Previous Reactions of Allenes with Manganese

[5+2] Cycloaddition of 1,1-disubstituted allenes to a manganese-coordinated cyclohexadienyl group has been performed[129]. One, two and three allenic molecules have added to the cyclohexadienyl group. $(\eta^5\text{-}C_6H_7)Mn(CO)_3$ is converted to the reactive $(\eta^5\text{-}C_6H_7)Mn(CO)_2(THF)$ photochemically. The THF ligand is readily substituted by an allene and from there the complex undergoes stepwise metal-mediated cycloaddition.

Tetraallylmanganate has been used to allylate allenes to give 1,5-dienes (Scheme 3-7).



Scheme 3-7: The allylation of allene by $Mn(CH_2CH{=}CH_2)_4(MgCl)_2$.



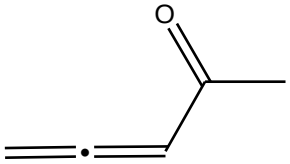
Scheme 3-8: The chromatographic separation of allenic diastereoisomers can be enhanced by coordination to organomanganese.

Manganese has been coordinated to chiral allenes in order to increase the asymmetry in order to separate the enantiomers more effectively[130]. The allene-

manganese complex is attached to a chiral compound such as (S)-(−)-5-(α-phenylethyl)semioxamazide. This yields diastereoisomers that can be separated by chromatography and are separated more efficiently than the corresponding diastereoisomers of the uncoordinated allene (Scheme 3-8).

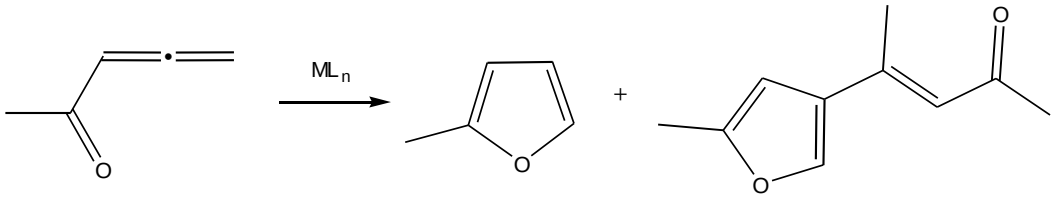
3.1.6 Allenes and Cyclomanganated Compounds

As mentioned in section 1.4.2, a variety of cumulenes have undergone insertion reactions with cyclomanganated compounds. The chemistry of allenes is closely related to both alkenes and alkynes, both of which have undergone insertion reactions with cyclomanganated compounds. Because the related compounds undergo insertion reactions with cyclomanganated compounds it is likely allenes will too.



55

In this project acetylallene (**55,** also known as penta-3,4-dien-2-one) was chosen as a compound to react with cyclomanganated compounds because it is made by a relatively simple method using widely available starting materials (the preparation is outlined in section 5.3.2). **55** has undergone cyclisation with some transition metals (Cu, Ag, Rh, Ru, Pd) at room temperature to form 2-methylfuran[131] and has dimerised to form another furan in the presence of a palladium catalyst (Scheme 3-9). Without a catalyst, thermal cyclisation of **55** to form 2-methylfuran requires greater temperature (above 433 °C[132]).



55

Scheme 3-9: The transition-metal (M) catalysed cyclisation of 55 to form 2-methylfuran (centre). When M = Pd, 55 can dimerise to another furan (right).

3.2 Experimental

3.2.1 The Reaction of Acetylallene (55) and η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30)

55 (~80 mg, 85 μL, ~1 mmol) and **30** (100 mg, 320 μmol) were stirred in dry degassed heptane (15 mL) under a nitrogen atmosphere. The solution was heated (90 °C oil bath) until any new metal-carbonyl peaks in the spectrum reached a maximum intensity. If no new peaks in the FTIR spectrum were seen, or if the new peaks vanished the solution was removed from heat when the initial metal carbonyl peaks (ν = 2082, 1995, and 1943 cm^{-1}) were very small (~ 1 h). The hot solution was filtered and the precipitate was washed with heptane (3 × 2 mL). The washings and filtrate were combined and the solvent was removed on a vacuum line. The yellow residue obtained was dissolved in dichloromethane (2 mL), and the components separated by preparative scale layer chromatography (PLC). The precipitate was dissolved in dichloromethane, filtered, and the products separated by PLC.

3.2.2 Acetylallene (55) reacted with η^2-[(2-Diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (41)

The reaction was done in the same way as that between **55** and **30** and on the same molar scale.

3.3 Results and Discussion

3.3.1 The Reaction of Acetylallene (55) and η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30)

TLC

Initial TLC gave peaks at R_f = (dichloromethane) 0.67 (m, acetylallene), 0.86 (s, yellow, **30**); (1:3 ethyl acetate: hexane) 0.70 (s, yellow, **30**), 0.80 (m, acetylallene). New spots formed at R_f = (dichloromethane) 0.12 (yellow/brown streak from baseline), 0.33 (s, yellow, 4-methoxyacetophenone), 0.44 (w); (1:3 ethyl acetate: hexane) 0.23 (s, yellow/brown streak from baseline), 0.28 (s, yellow), 0.50 (s, 4-methoxyacetophenone).

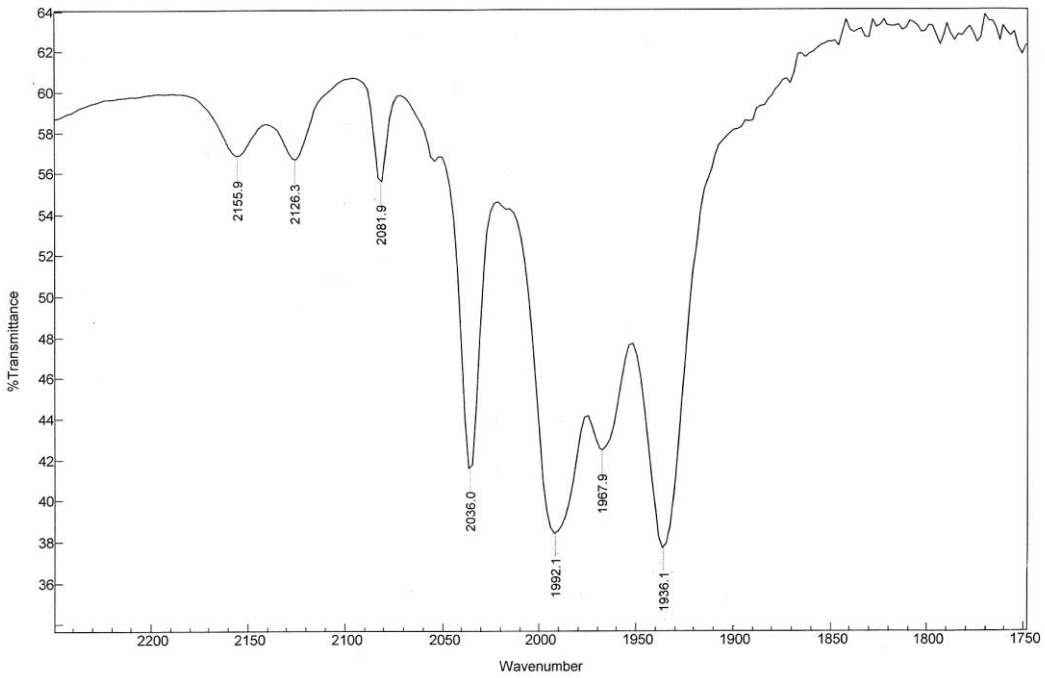


Figure 3-3: The FTIR spectrum of the reaction solution prior to workup. The 2036, 1968, and 1936 cm^{-1} peaks correspond to an unidentified product.

Infrared spectroscopy (heptane) of the reaction solution showed the formation of peaks in the metal-carbonyl region of the spectrum (2036, 1968 cm^{-1}, Figure 3-3). The reaction flask was removed from heat when these new peaks appeared to reach a maximum intensity. The new peaks were probably due to a small amount of a new manganese carbonyl compound (possibly with a $Mn(CO)_3$ moiety). The 1936 cm^{-1} peak appears to be new as well. **30** has a peak in this region of the spectrum (1943 cm^{-1}) but usually with a smaller intensity than the 1990 cm^{-1} peak.

Filtrate

PLC

PLC (1:1 Ethyl acetate: X4) gave one large streak when viewed under UV light (254 nm). Five coloured bands could be seen: R_f = 0.00 (brown, fluoresced green under 312 nm light), 0.61 (pale yellow, fluoresced orange under 312 nm light), 0.74 (pale yellow, fluoresced blue/green under 312 nm light), 0.89 (yellow, fluoresced green under 312 nm light), 0.95 (yellow).

R_f =0.61

The ESI-MS (methanol) spectrum was complex but the major peaks include

Positive Ion (m/z)

(20 V) 353 (100 %), 337 (75 %), 271 (100 %), 255 (86 %), 151 (71 %) Da.
(60 V) 352 (28 %), 337 (100 %), 255 (50 %), 215 (45 %), 165 (26 %) Da.
Negative Ion (m/z)
(-20 V) 255 (51 %), 231 (34 %), 212 (33%), 163 (61 %), 151 (100 %), 127 (33 %) Da.
(-60 V) 212 (35 %), 126 (100 %) Da.
Some of these major peaks are common to other fractions. This was expected because streaking was observed on the PLC plate. The m/z = 337 and 255 Da in the positive ion spectra and the 231 in the negative ion spectrum are common to the fraction with an R_f of 0.74 and are discussed with that fraction. 4-Methoxyacetophenone may have been in the fraction detected as m/z = 151 $[M+H]^+$ Da. Peaks possibly corresponding to compound **55** could be seen i.e. 165 $[2M+H]^+$ Da in the positive ion mode and 163 $[2M-H]^-$ Da in the negative ion mode. Alternatively these peaks could correspond to a dimer of **55** such as the one shown in section 3.1.6.

R_f =0.74
ESI-MS (Figure 3-4)

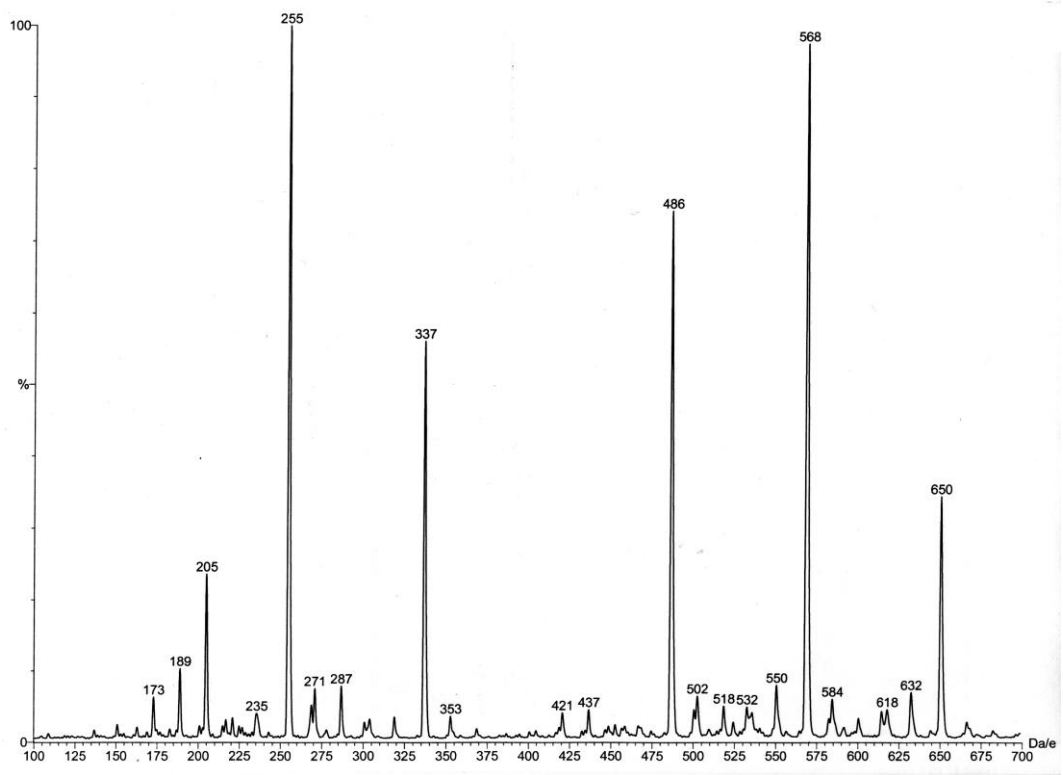


Figure 3-4: The ESI-MS spectrum (positive ion, 20 V) of the R_f = 0.74 fraction. The peaks are assigned 650 $[2M´+Na]^+$, 568 $[M+M´+Na]^+$, 486 $[2M+Na]^+$, 337$[M´+Na]^+$, 255 $[M+Na]^+$ Da. where M = insertion product, M´ = double insertion product.

Positive Ion (m/z)

(20 V) 651 (35 %), 569 (90 %), 487 (71 %), 337 (56 %), 255 (100 %) Da.

(60 V) 337 (100 %), 255 (48 %) Da.

(90 V) 337 (100 %) Da.

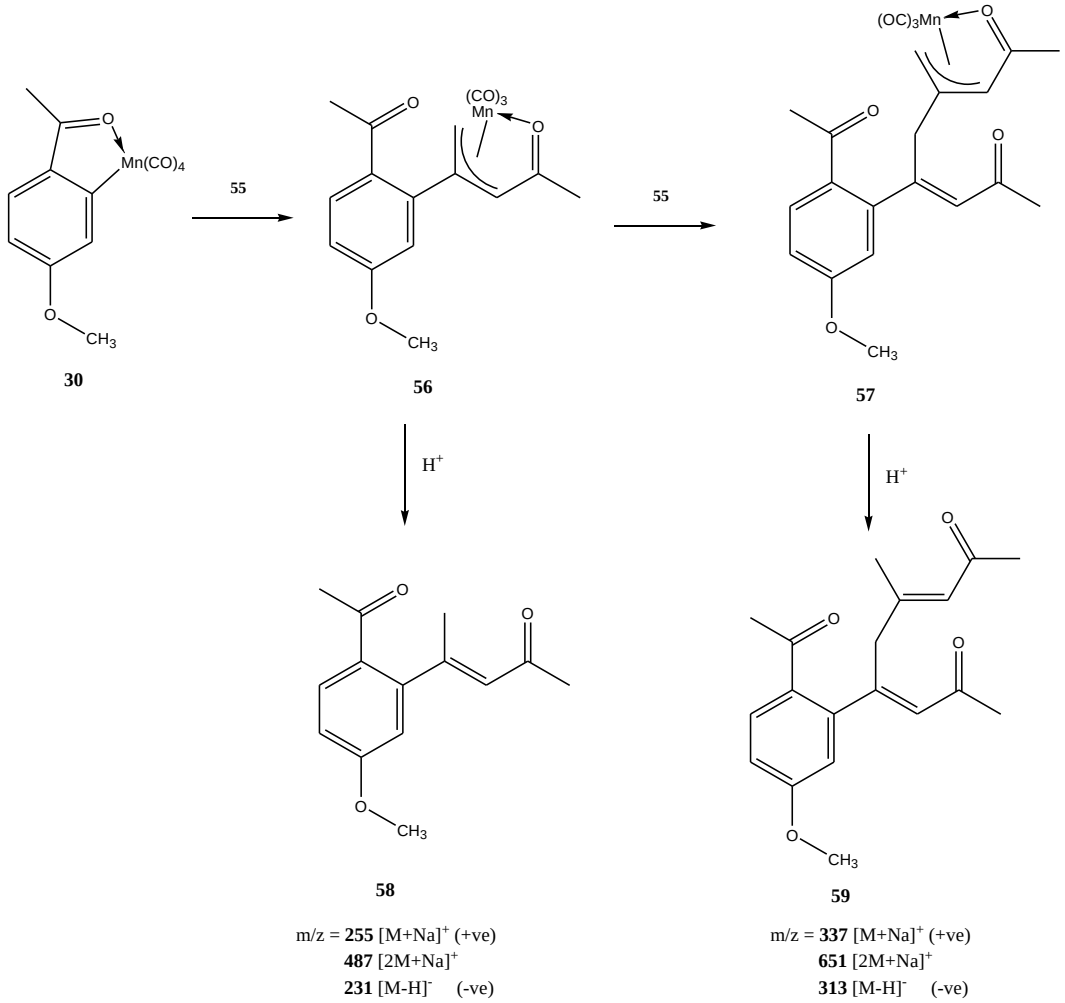
Negative Ion (NaOMe, m/z)

(-20 V) 371 (70 %), 369 (57 %), 313 (39 %), 231 (100 %) Da.

(-50 V) 313 (23 %), 284 (94 %), 216 (72 %), 213 (100 %), 198 (68 %) Da.

(-80 V) 201 (100 %), 197 (82 %) Da.

This spectrum is evidence for demetallated single and double insertion products such as **58** and **59** as illustrated in Scheme 3-10.



Scheme 3-10: The single and double insertion of acetylallene (55) into 30 followed by demetallation explains peaks seen in the ESI-MS spectra.

*ESI-MS evidence for **58***

ESI-MS peaks that suggest a compound of mass = 232 e.g. **58** or an isomer of **58** are given below.

Positive Ion (m/z)

487 $[2M+Na]^+$, 255 $[M+Na]^+$ Da.

Negative Ion (m/z, NaOMe)

231 $[M-H]^-$, 216 $[M-CH_3]$, 213 $[M-H_3O]^-$, 201 $[M-CH_3O]$ Da.

*ESI-MS evidence for **59***

ESI-MS peaks that suggest a compound of mass = 314 Da e.g. **59** or an isomer of **59** are given below.

Positive Ion (m/z)

651 $[2M+Na]^+$, 337 $[M+Na]^+$ Da.

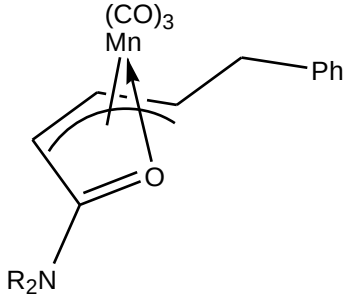
Negative Ion (m/z, NaOMe)

313 $[M-H]^-$ Da.

The m/z = 337 Da ion is particularly stable. This is illustrated by its strong intensity even with a cone voltage of 90 V. A sodium adduct of a compound such as **59** would be particularly stable because the multiple carbonyl groups allow terdentate coordination.

The peak at m/z = 569 [**58** + **59** + Na]$^+$ Da also suggests the formation of **58** and **59** or other isomers.

Scheme 3-10 shows a possible pathway to the formation of compounds **58** and **59**. η^3-Allyl metal-complexes are likely intermediates because they are common products in allene insertion reactions. η^3-Allyl $Mn(CO)_3$-complexes similar to the intermediates in Scheme 3-10 (**56** and **57**) have been seen before[133] (e.g. **60**). An η^3-allyl $Mn(CO)_3$ with intramolecular coordination to a carbonyl group has been formed by an insertion reaction of a cyclomanganated indole with ethyne[134]. The η^3-allyl $Mn(CO)_3$ compound formed by the cyclomanganated indole was different to this case because the carbonyl group was γ to the allylic group and not α.



60

Examples of multiple allene insertions have been published. $Co_2(CO)_8$ has inserted 2, 3, 4, and more units of 3-methyl-1,2-butadiene[135]. $HRh(PPh_3)_4$

undergoes quadruple insertion reactions with excess arylallenes[128]. [(π-Allyl)NiOCOCF$_3$]$_2$ polymerises allenes by many consecutive insertions[136].

R_f = 0.89

ESI-MS (methanol):

Positive Ion (m/z)

(20 V) 323 (100 %), 205 (49 %), 173 (76 %) Da.

(50 V) 337 (38 %), 173 (13 %), 102 (100 %) Da.

(90 V) 337 (52 %), 255 (70 %), 155(100 %) Da.

Negative Ion (m/z)

(-20 V, NaOMe) 370 (97 %), 368 (100 %), 286 (55 %) Da.

(-40 V, NaOMe) 368 (50 %), 286 (52 %), 284 (100 %), 258 (48 %), 211 (49 %), 203 (60 %), 126 (64 %) Da.

This fraction probably included 4-methoxyacetophenone with the ions m/z = 173 $[M+Na]^+$, 203 $[M+Na+MeOH]^+$, 323 $[2M+Na]^+$ Da.

An insertion product i.e. **56** (m/z = 370 $[M-H]^-$ Da) and a compound similar to **56** with one more double bond or ring (m/z = 368 $[M-H]^-$ Da) may be compounds in this fraction. The 286 and 284 Da ions could correspond to the loss of 3 CO molecules from the 370 and 368 Da ions. The fraction contains peaks common to 0.74 i.e. m/z = 337 [**59**+Na]$^+$, 255 [**58**+Na]$^+$ Da.

R_f = 0.95

ESI-MS:

Positive Ion (m/z)

(20 V) 351 (37 %), 337 (42 %), 187 (100 %), 173 (59 %) Da.

(40 V) 690 (13 %), 578 (15 %), 413 (23 %), 337 (46 %), 301 (91 %), 187 (100 %), 173 (35 %) Da.

(60 V) 413 (65 %), 337 (39 %), 301 (100 %) Da.

Negative Ion (m/z)

(-20 V) 371 (100 %) Da.

(-40 V) 371 (24 %), 315 (4 %), 287 (82 %), 259 (100 %), 231 (16 %), 203 (23 %), 175 (10 %) Da.

(-60 V) 540 (4 %), 371 (5 %), 203 (33 %), 148 (100 %), 117 (13 %) Da.

Once again a peak, possibly due to an insertion product was seen at m/z =371 Da. At increased absolute cone voltage, peaks were seen that correspond to [M–

2CO+H]$^-$ (315 Da) and [M–3CO+H]$^{\bullet-}$ (287 Da). However it is more likely that the latter two peaks corresponds to **30** i.e. 315 [M-H]$^-$, 287 [M-CO-H]$^-$ Da. Other peaks corresponding to **30** include m/z = 259 [M-2CO-H]$^-$, 231 [M-3CO-H]$^-$, 203 [M-4CO-H]$^-$ Da. The positive ion spectra were not very clean and only the most intense peaks were listed. The presence of acetylallene was suggested by the 187 [2M+Na]$^+$ and 351 [4M+Na]$^+$ Da peaks. The presence of 4-methoxyacetophenone is suggested by the 173 [M+Na]$^+$ and 301 [2M+H]$^+$ Da peaks. The presence of **59** or an isomer of **59** is suggested by the 337 [M+Na]$^+$ Da ion.

MicrOTOF was used to get an accurate mass of the main negative ion which was found to be 370.9092 Da. This was compared to the mass of **56** calculated to be 370.0249 Da. No empirical formula was found that matched this mass. This was evidence that the m/z = 371 Da peak was not due to an insertion product.

Precipitate

The light yellow/brown precipitate was soluble in dichloromethane and turned brown when dissolved. The IR spectrum gave peaks in the metal carbonyl region ν (dichloromethane) = 2023 (w), 1986 (w), 1925 (m, br) cm^{-1} (Figure 3-5). ν (KBr disc) = 2019 (vw), 1919 (w) cm^{-1} (Figure 3-6).

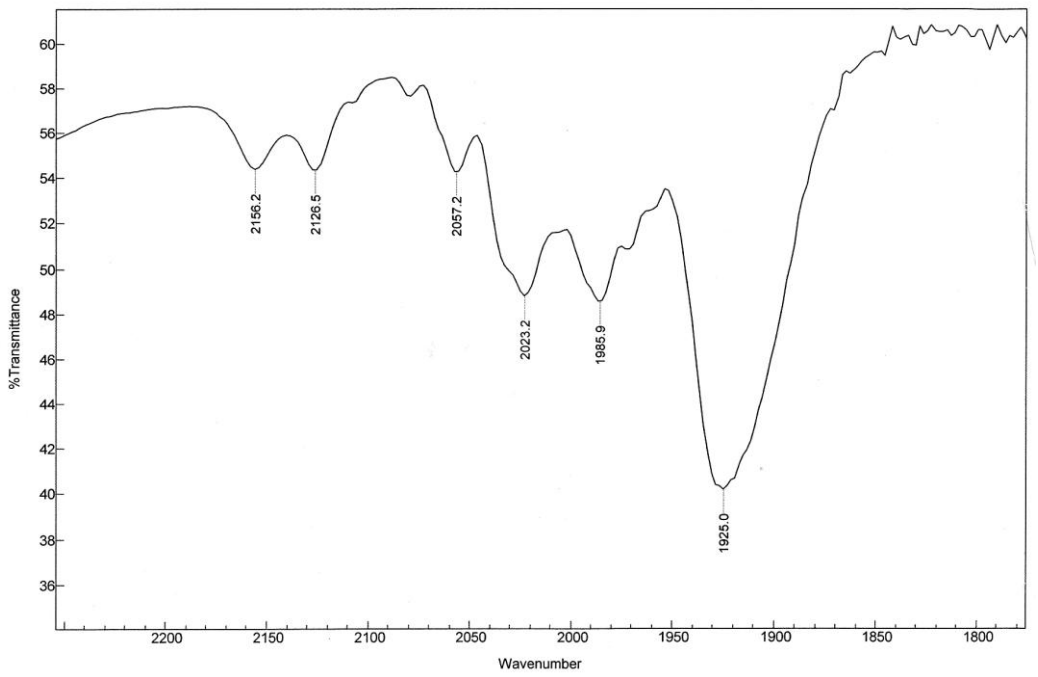


Figure 3-5: The FTIR spectrum (dichloromethane) of the precipitate formed in the reaction of 30 with acetylallene. Peaks at 2156 and 2127 belong to the solvent dichloromethane

These spectra are from two different batches of the same experiment. This and the different matrices may account for the batch in dichloromethane having an extra peak at 1986 cm^{-1}. Both spectra show two peaks at 2020 and 1920 cm^{-1}. This pattern of two peaks with the lower frequency peak more intense than the higher could be seen with compounds containing a *fac*-$M(CO)_3$ moiety[137].

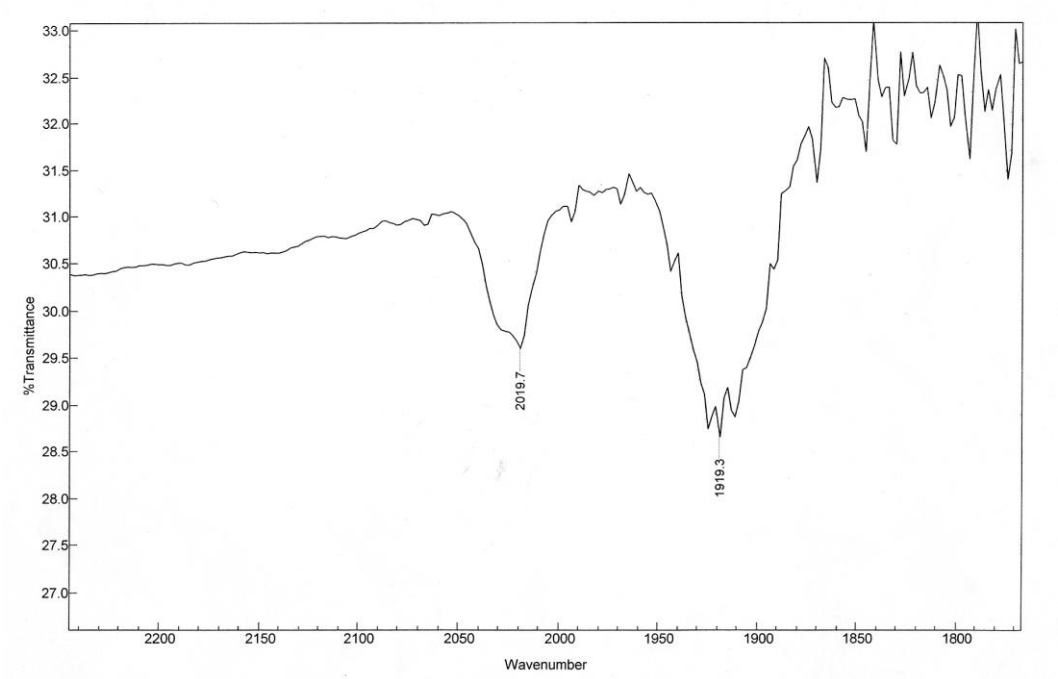


Figure 3-6: The FTIR (KBr disc) spectrum of the precipitate formed in the reaction of 30 with acetylallene.

A *fac*-$Mn(CO)_3$ moiety will give three peaks in the IR spectrum (2A` + A``) or two peaks (A_1 + E) if the molecule is of C_{3V} symmetry or if two of the peaks are coincidentally degenerate[138].

The precipitate may have contained an allene group. Cumulenes absorb strongly around 2000 cm^{-1} (acetylallene (neat): ν (C=C=C) = 1933, 1950 cm^{-1}). The fact that the precipitate was insoluble in hot heptane (80 °C) and that its components have low R_f values in dichloromethane (0.55 is the highest) suggests that the compounds are polar, perhaps containing hydrogen bonding groups such as hydroxyl groups.

The ESI-MS (methanol) of the precipitate was complex, however the main peaks included:

Positive Ion (m/z)

(20 V) 301 (76 %), 269 (33 %), 219 (52 %), 206 (48 %) Da.

(40 V) 301 (46 %), 269 (100 %), 237 (61 %), 219 (41 %), 187 (46 %) Da.

Negative Ion (m/z)

(-20 V) 400 (86 %), 398 (80 %), 370 (53 %), 365 (100 %), 356 (71 %), 319 (79 %), 181 (83 %) Da.

(-40 V) 400 (71 %), 398 (69 %), 370 (86 %), 349 (66 %), 317 (63 %), 315 (67 %), 287 (100 %), 181 (65 %) Da.

Negative Ion (m/z, NaOMe)

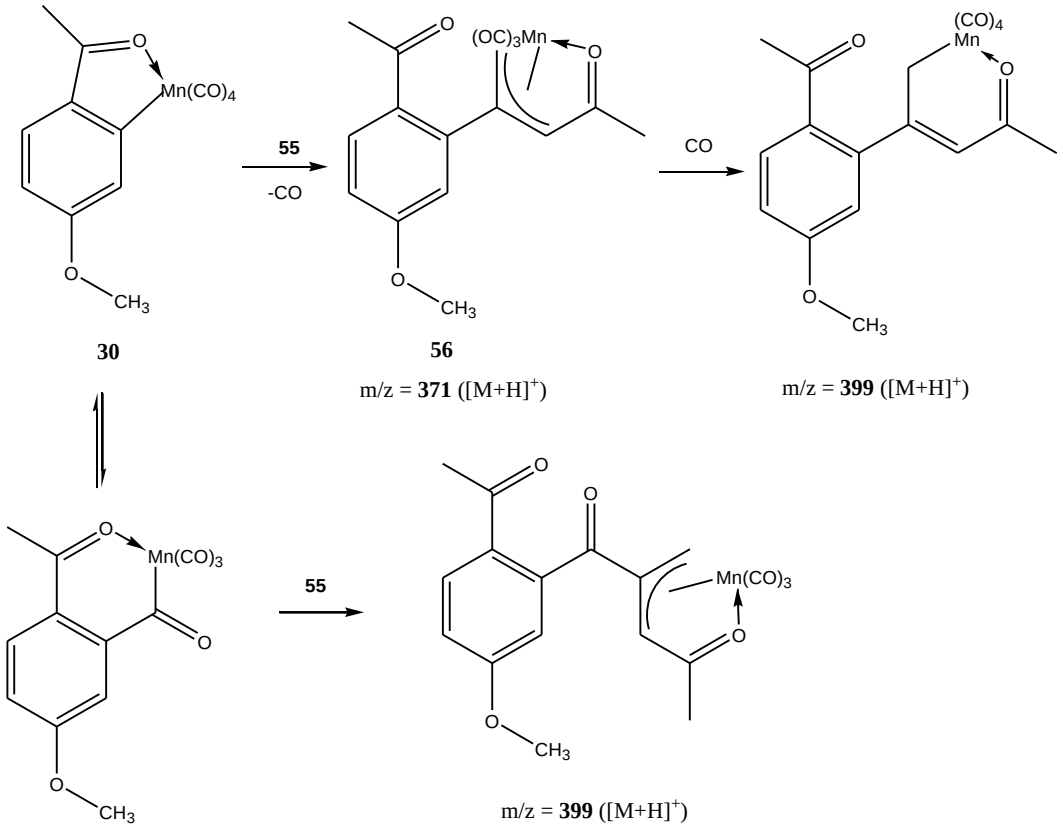
(-20 V) 371 (100 %), 351 (19 %), 181 (44 %) Da.

(-40 V) 371 (38 %), 287 (78 %), 259 (100 %), 181 (56 %) Da.

Dimers and trimers of **55** may be present with peaks such as 301 $[M+Na+MeOH]^+$, 269 $[M+Na]^+$ Da where M is a trimer of **55**, and the peaks 219 $[M+Na+MeOH]^+$, 187 $[M+Na]^+$ Da where M is a dimer of **55**.

The m/z = 181 Da peak was possibly due to the presence of 4-methoxyacetophenone $[M+CH_3O]^-$.

In the negative ion mode the 371 Da peak (as discussed in previous sections) may have belonged to an insertion product such as **56**. If this is the case the m/z = 287 Da peak would correspond to the loss of three CO molecules from the m/z = 371 ion. There is also an ion (m/z = 259 Da) that may correspond to the loss of four CO molecules from the 371 ion but it is unlikely a $Mn(CO)_3$ compound such as **56** would lose more than three CO molecules. The m/z = 398 Da ion may belong to an $Mn(CO)_4$ version of **56** with an η^1-allyl instead of η^3-allyl coordination or alternatively an $Mn(CO)_3$ compound where a CO molecule has been inserted somehow. The m/z = 400 Da ion could be a hydrogenated version of the m/z = 398 Da ion.



Scheme 3-11: Some reactions to explain the 399 ion in the mass spectrum.

The precipitate of one batch was dissolved in dichloromethane and eluted through a 5 mm silica column to remove any paramagnetic inorganic manganese. The solvent was dried and the residue analysed by ^{1}H and ^{13}C NMR ($CDCl_3$). The NMR spectra suggested impurity and contamination with grease.

PLC

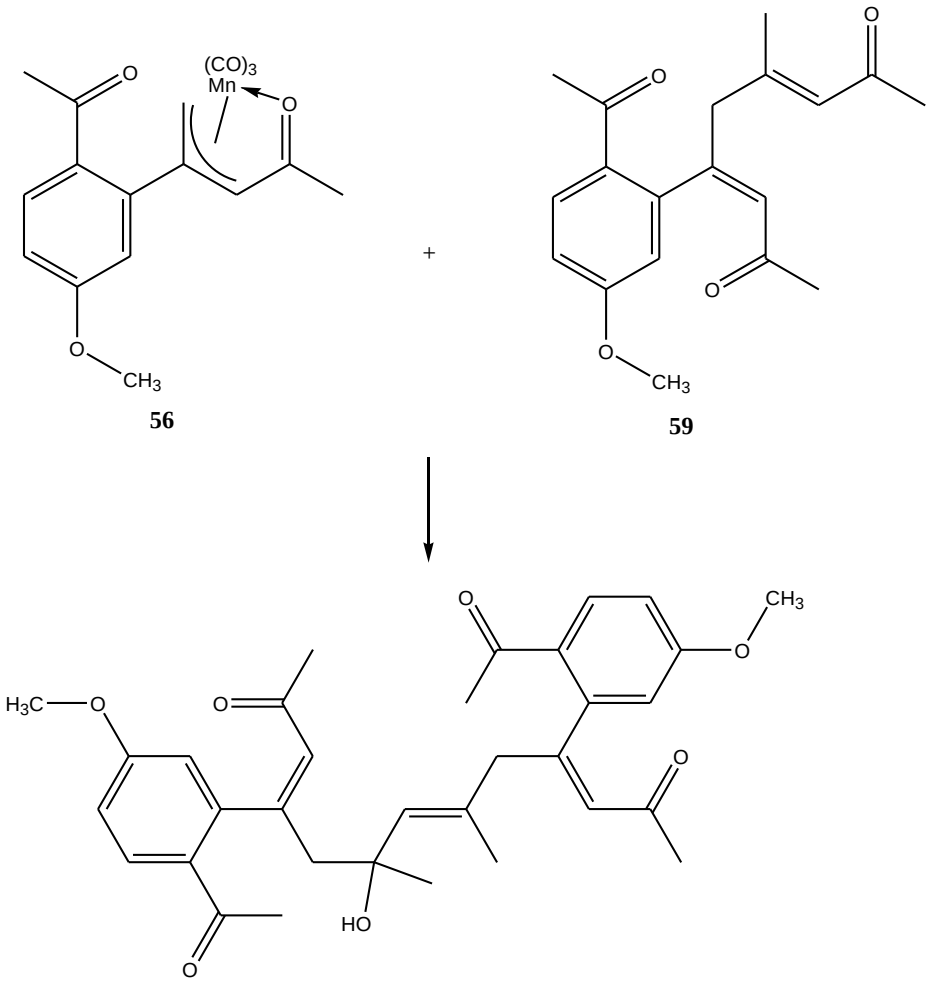
PLC (dichloromethane) gave two thin yellow bands at R_f = 0.48, 0.55 and a streak up to R_f = 0.33. The baseline was brown with a yellow outline.

R_f = 0.33

ESI-MS (methanol):

Positive Ion (m/z)

(20 V) 547 (22 %), 524 (22 %), 502 (24 %), 381 (23 %), 254 (26 %), 214 (25 %), 172 (26 %), 101 (100 %) Da.The m/z = 547 Da peak may belong to an ion $[2M+3M'+H]^+$. An ion of this mass could be formed by the coupling of a single insertion product with a double insertion product as illustrated in Scheme 3-12.

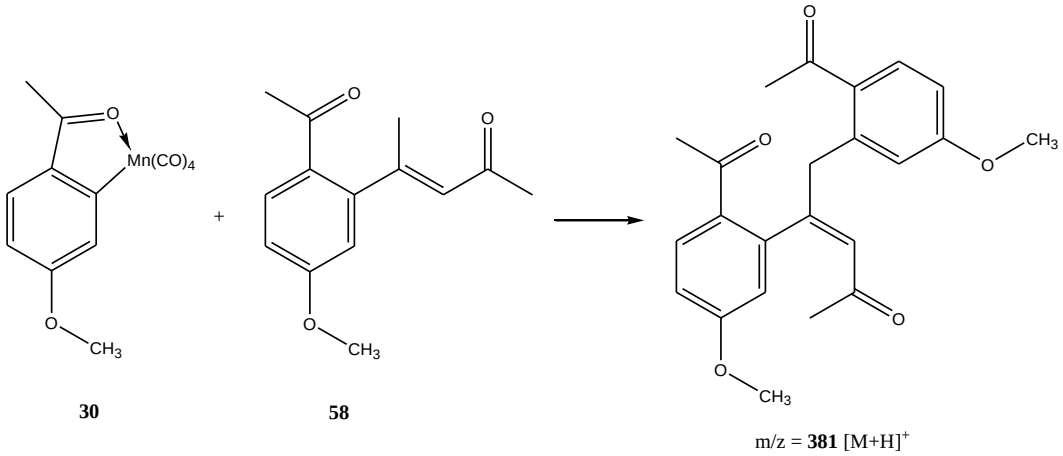


56 **59**

m/z = **547** $[M+H]^+$

Scheme 3-12: A reaction that would give the m/z = 547 Da ion.

The m/z = 381 Da peak may be a $[2M+M'-H]^+$ ion, where M is 4-methoxyacetophenone and M′ is **55**. This could possibly be formed by the reaction of a single insertion product with **30** as shown in Scheme 3-13.



30 **58**

m/z = **381** $[M+H]^+$

Scheme 3-13: A reaction that would give the m/z = 381 Da ion.

The presence of a m/z = 502 $[M+H]^+$ and 524 $[M+Na]^+$ Da peaks suggest the presence of a compound with a mass of 501 Da.

FTIR (dichloromethane): 2018 (w, sh), 1937 (w, br) cm^{-1}.

This was similar to the spectra of compounds with a $Mn(CO)_3$ moiety; however in this spectrum the 1937 cm^{-1} peak was two thirds the intensity of the 2018 cm^{-1} peak, whereas in $Mn(CO)_3$ compounds with an A_1 + E (i.e. with two peaks) arrangement the E peak (the broad peak of lower frequency) is normally more intense than the A_1 peak. $Mn(CO)_2$-containing compounds generally have two peaks of similar intensity, however the intensity of the 1937 cm^{-1} peak was still too small. As mentioned with the IR spectrum of the bulk precipitate, the peaks may have belonged to a cumulenic compound most likely an allene but not **55** (ν (C=C=C), (dichloromethane) = 1959, 1929 cm^{-1}).

R_f = 0.48

ESI-MS (methanol):

Positive Ion (m/z)

(40 V) 524 (100 %), 502 (34 %), 387 (36 %), 368 (43 %), 323 (35 %), 304 (54 %), 279 (81 %), 256 (12 %) Da.

Negative Ion (m/z)

(-20 V) 536 (62 %), 315 (100 %), 254 (48 %) Da.

(-40 V) 403 (8 %), 338 (13 %), 324 (16 %), 254 (24 %), 143 (73 %), 126 (100 %) Da.

Like the 0.33 fraction a compound with a mass of about 501 Da may have been present with peaks at 502 $[M+H]^+$ and 524 $[M+Na]^+$ Da. The negative ion peak m/z = 315 $[M-H]^-$ Da suggests **30** may have been present.

R_f = 0.55

ESI-MS (methanol):

Positive Ion (m/z)

(40 V) 368 (28 %), 305 (40 %), 301 (49 %), 279 (100 %) Da.

Negative Ion (m/z)

(-20 V) 316 (26 %), 88 (100 %) Da.

(-40 V) 325 (25 %), 280 (31 %), 254 (64 %), 144 (43 %), 126 (88 %), 61 (100 %) Da.

The m/z = 301 and 279 Da ions may correspond to ions containing three units of compound **55** i.e. $[3M+MeOH+Na]^+$ and $[3M+MeOH+H]^+$.

3.3.2 Acetylallene (55) reacted with η2-[(2-Diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (41)

This was done on the same molar scale as the reaction of **30** with **55** and yielded very similar results in terms of observations including the formation of a precipitate and a number of yellow PLC bands in the filtrate.
PLC (1:1 EtOAc: X4) gave five coloured bands: 0.00 (brown, fluoresced green), 0.51 (faint yellow), 0.72 (yellow), 0.85 (faint yellow), 0.96 (faint yellow).
Further analysis of these fractions was aborted because of issues with purity of the reagents.

3.4 Conclusion

ESI-MS gives evidence for the single and double insertion of **55** with **30**. FTIR spectroscopy detected peaks that may correspond to $Mn(CO)_3$-complexes, possibly metallated precursors (**56** and **57**) to the compounds detected in the ESI-MS. Plausible structures were assigned to ions detected in the ESI mass spectra for most fractions of the reaction of **30** with **55**. Generally the yield of the products was low, making characterisation through other techniques difficult. The detection of insertion products may make this reaction worthy of further attention. Perhaps repeating the experiment with different allenes or different solvents would be useful.

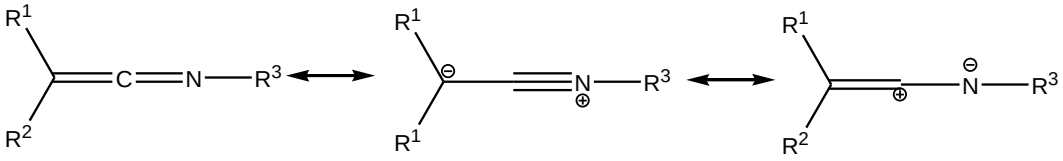
Chapter 4: The Synthesis of Diphenylketene *N*-(*p*-Tolyl)imine (62)

4.1 Introduction

Ketenimines ($R_2C=C=NR$, also known as ketene imines) are heteroallenes. They have two consecutive double bonds like an allene but one of the outer allene carbon atoms is substituted with a nitrogen atom. Some reviews have been written on ketenimines[99, 139]. Ketenimines are used as substrates in heterocyclic chemistry[140]. The parent molecule ketenimine ($H_2C=C=NH$) has been detected in interstellar clouds[141].

4.1.1 The Structure of Ketenimines

Ketenimines can be chiral if the groups on the end carbon are different, however the barrier to inversion of the nitrogen is generally low and therefore racemisation readily occurs at room temperature. Some cannot be chiral as the C=N-R bond angle is 180 ° e.g. $(Me_2OS)_2C=C=NMe$ is not chiral because the C=N-R bond angle is 180 °[99]. This geometry can be explained by examining the resonance structures of ketenimines[99] (Scheme 4-1). Electron-withdrawing groups on the sp^2 hybridised (R^1 and R^2) allenic carbon and or electron-donating groups on the nitrogen (R^3) stabilise the sp-hybridised cationic nitrogen resonance form. The consequence of this is a C=N-R bond angle of >120 ° and a shorter C=N bond than the average imine bond.



Scheme 4-1: Resonance forms of ketenimines.

4.1.2 Reactions of Ketenimines

Ketenimines can be quite unstable and polymerise readily (e.g. small trialkylketenimines). Triarylketenimines are relatively stable and are more commonly used because they are synthesised more easily.

Like allenes, ketenimines have a similar chemistry to alkenes. The heteroatom differentiates the ketenimine from normal allenes by polarising the allene. As

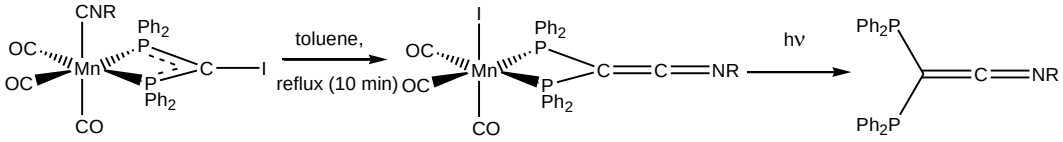
illustrated in Scheme 4-1, the middle allenic carbon is electrophilic, and nucleophilic attack invariably occurs there[99]. Ketenimines will react with water to form amides[142] and have been used as dehydration agents (i.e. have formed anhydrides when reacted with dicarboxylic acids[143]).

Ketenimines have undergo a large variety of cycloaddition reactions and like nucleophilic addition, this is generally across the carbon-carbon double bond[139].

4.1.3 Organometallic Chemistry Involving Ketenimines

There are very few examples of insertion reactions of ketenimines in the literature. Diphenylketene *N*-(*p*-tolyl)imine has inserted into the niobium-hydrogen bond of $Cp_2NbH(CO)$[144].

Some organometallic compounds form ketenimines when reacted with isocyanides. The compound *fac*-$[Mn(CO)_3(CNR)\{(PPh_3)_2CI\}]$ rearranges to form a complex containing a ketenimine functional group (Scheme 4-2)

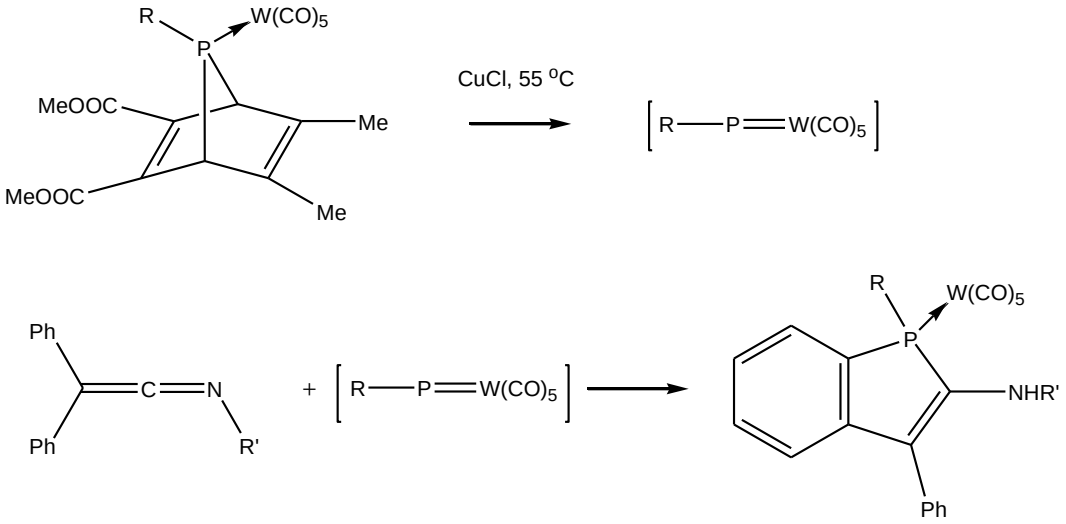


Scheme 4-2: The formation of ketenimines by the rearrangement of *fac*-$[Mn(CO)_3(CNR)\{(PPh_2)_2CI\}]$.

Other metals that have formed ketenimine complexes on the reaction with isocyanides include palladium[145] and ruthenium[146].

2-Aminophosphindoles have been synthesised from the reaction of ketenimines with transient phosphinidene tungsten complexes $[RP=W(CO)_5]$ formed from a 7-phosphanorbornadiene precursor[147] (Scheme 4-3).

A tungsten carbene complex (pentacarbonylbenzylidenetungsten) has undergone a metathesis-like reaction with a triaryl ketenimine to form an imine and an allenic tungsten carbene complex[148].



Scheme 4-3: Ketenimines react with phosphinidene complexes to form 2-aminophosphindoles.

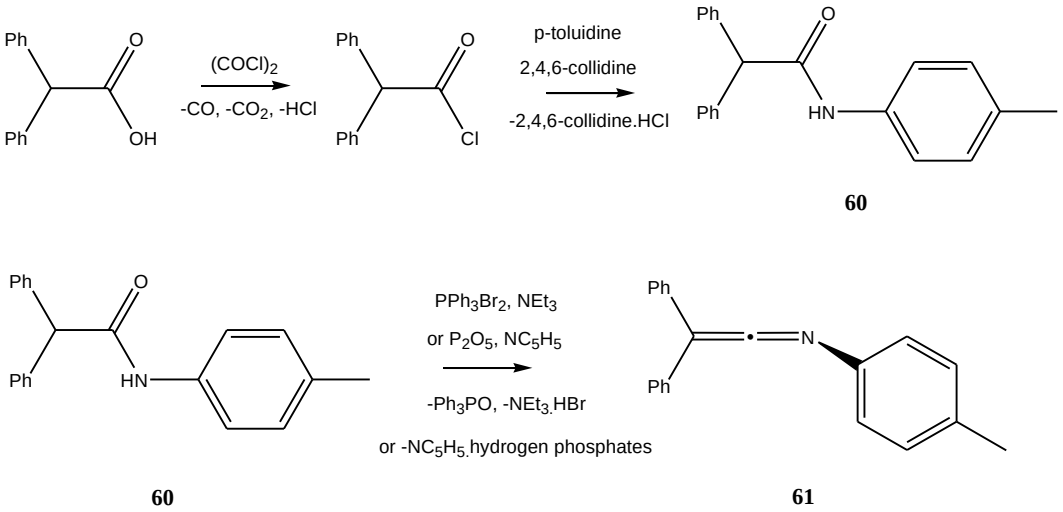
4.1.4 Cyclomanganated Compounds and Ketenimines

Due to the similarities in chemistry between alkenes and ketenimines it is possible that ketenimines may undergo insertion reactions with cyclomanganated compounds in a similar way to alkenes. The high reactivity of ketenimines suggests that it is likely that a reaction will occur. The role of the ketenimine nitrogen in the reaction (if it does occur) would be interesting. Would the nitrogen take an active role in insertion reaction? Or will it just be a spectator and maintain its imine functionality?

4.2 Experimental

4.2.1 Introduction

The synthesis of the ketenimine diphenylketene *N*-(*p*-tolyl)imine (**62**) by the dehydration of the amide *N*-(*p*-tolyl)diphenylacetamide (**61**) was attempted by two different methods (see section 5.3.4 for the preparation of **61**). Dehydration was attempted with triphenylphosphine dibromide and triethylamine. It was then attempted with phosphorus pentoxide, as illustrated in Scheme 4-4.



Scheme 4-4: The synthesis of diphenylketene *N*-(*p*-tolyl)imine (62) by the dehydration of *N*-(*p*-tolyl)diphenylacetamide (61).

4.2.2 Synthesis of Diphenylketene *N*-(*p*-Tolyl)imine (62) by the Dehydration of *N*-(*p*-Tolyl)diphenylacetamide (61) with Ph_3PBr_2/NEt_3

The synthesis of **62** was a scaled down version of a translated published method[149]. The preparation was repeated multiple times based on the following method:

Bromine (260 mg, 83 µL, 1.6 mmol) was added dropwise to triphenylphosphine (430 mg, 1.6 mmol) in dichloromethane (10 mL). Dry triethylamine (excess, 820 mg, 1.2 mL, 8 mmol) in CH_2Cl_2 (5 mL) was added dropwise. **61** (500 mg, 1.6 mmol) in dichloromethane (10 mL) was added dropwise. The solution was refluxed for 1 h. The solvent was evaporated and the remaining oil was digested in hexane until just boiling. The solution was then filtered and the filtrate evaporated to dryness on a rotary evaporator.

Different variations of this method were used because of unsuccessful outcomes and poor yields. These variations included:

1 Adding the bromine and triethylamine as neat liquids and adding them as diluted dichloromethane solutions (bromine: 0.6 mol L^{-1} standardised solution; triethylamine: 1.2 mL in 5 mL dichloromethane).

2 Performing the reaction exposed to the atmosphere (but with $CaCl_2$ drying tube) and doing the reaction under a dry nitrogen atmosphere.

3 Adding the reactants at room temperature and adding them to ice-cold solution (cooled with an ice-bath).

4. Using reagents merely stored in a desiccator and using reagents dried in high vacuum (0.1 mm Hg) before storing in the desiccator.

4.2.3 Synthesis of Diphenylketene *N*-(*p*-Tolyl)imine (62) by the Dehydration of *N*-(*p*-Tolyl)diphenylacetamide (61) with P_2O_5

This preparation was done by the same method as that which was published by Stevens and Singhal[142] with some adaption described below.

61 (1 g, 3.3 mmol) in pyridine (30 mL) was added to phosphorus pentoxide (2.5 g) and alumina (5.0 g) in pyridine (20 mL). The stirred solution was refluxed for 7 h. The solution was filtered. The solid residue was crushed and heated in pyridine (20 mL) until just boiling. The solution was then filtered. The combined filtrates were evaporated, and the residue was collected.

4.2.4 The Reaction of Diphenylketene *N*-(*p*-Tolyl)imine (62) with η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (30)

Heptane (15 mL) was added to a 50 mL Schlenk flask containing **62** (37 mg, 130 μmol, as an oil) and **30** (33 mg, 100 μmol). The solution was refluxed under nitrogen atmosphere until the solution turned dark brown. The solution was evaporated to dryness on a vacuum line. The residue was dissolved in dichloromethane (10 mL) and filtered.

4.3 Results and Discussion

4.3.1 The Synthesis of Diphenylketene *N*-(*p*-Tolyl)imine (62) by the Dehydration of *N*-(*p*-Tolyl)diphenylacetamide (61) with Ph_3PBr_2/NEt_3

The synthesis of **62** was occasionally successful, however only in very low yields (~ 10 mg, and not fully characterised). When it was successful it was isolated as a yellow oil (FTIR (neat): ν (C=C=N) =1996 cm^{-1}) which crystalised with the addition of methanol (approximately 1 mL) and gentle warming of the flask with the palm of the hand.

62 is a yellow solid (mp: 83-83.5 °C) with a strong cumulenic absorption in the IR spectrum (2000 cm^{-1})[150]. The colour and IR spectrum were used to indicate a successful synthesis of **62**. This synthetic method was compared to that of acetylallene from acetylacetone (**58**) by Ph_3PBr_2/NEt_3[151] (as outlined in section 5.3.1 and 5.3.2). The method specifies the use of an ice bath, nitrogen atmosphere,

and the dilution of reagents. These conditions were always used after reading the method but still **62** could not be made reproducibly. One major difference between the two methods was that the acetylallene synthesis was a two-step method. In the first step acetylacetone was reacted with Ph_3PBr_2 to make 2-bromopent-2-en-4-one which was isolated as a pure compound. In the second step NEt_3 was reacted with the 2-bromopent-2-en-4-one to form acetylallene. For the ketenimine the NEt_3 is added before the amide is even added.
Hegarty et al.[152] have also made ketenimines using the Ph_3PBr_2/NEt_3 method. The difference between their method and this method was in the workup after refluxing the reagents together for 1 h in dichloromethane. Instead of extracting the ketenimine in hexane the ketenimine was adsorbed on to silica gel, dried and eluted through a silica column with carbon tetrachloride. This is a low temperature alternative to heating until boiling in hexane. In fact the literature method that was used by Bestman et al.[149] only specified digestion in petroleum spirits not the temperature of the digest. It could be that it was not supposed to be heated as much as it was in this instant and high temperature (up to 69 °C) caused the ketenimine to react further. FTIR spectroscopy was attempted to detect the level of ketenimine during the reaction but precipitation of Ph_3PBr_2 inside the FTIR solution cell made this impractical.

4.3.2 Synthesis of Diphenylketene *N*-(*p*-Tolyl)imine (62) by the Dehydration of *N*-(*p*-Tolyl)diphenylacetamide (61) with P_2O_5

This reaction was only performed once. The only hint of a successful reaction was on crushing up the solid residue[*]. The inside of the residue was yellow. Upon further work up of the reaction only a white solid was isolated with no cumulene peak in the FTIR spectrum.

4.3.3 The Reaction of Diphenylketene *N*-(*p*-Tolyl)imine (62) with η^2-(5-methoxy-2-acetylphenyl)tetracarbonylmanganese (30)

TLC (dichloromethane) of the solution prior to filtering gave six separate spots, R_f = 0.0 (brown), 0.34, 0.41, 0.72, 0.83, 0.93. The final filtered solution was a very dark green colour. There were a large number of products in the final solution. This would suggest that further research into this reaction would involve analysis

[*]The solid residue consisted of white, hard, pebble shaped solids, and approximately 5 mm in length. It was largely made up of alumina and phosphorus pentoxide.

of small amounts of many products. However it would be interesting to discover what compounds cause the dark green colour. It should be noted that the reaction was performed on a very small scale and **62** was not fully characterised, and its purity was unknown.

4.4 Conclusion

No conclusions can be drawn from this single reaction of **30** with **62** because the purity of **62** was unknown. An intensely green compound formed and a number of compounds were seen in the TLC but it is not known if it is from a reaction between **30** and **62** or from another compound within the ketenimine oil.
If this topic were to be extended, the reaction of cyclomanganated compounds with ketenes ($R_2C=C=O$) may be a convenient supplementary topic. The reason for the convenience is that ketenes can be reacted with triphenylphosphinalkylimines to give ketenimines in good yields[153].
Diphenylketene may be a good reactant for a preliminary investigation because it can be synthesised by a relatively simple process in good yield[154].

Chapter 5: Materials and Methods

5.1 Purification of Solvents and Reagents

The solvents and liquid reagents were purified dried as listed in table 5-1.

liquid	Method of Purification	Drying Agent
acetone	none	
acetonitrile	distillation	CaH_2
acetylacetone	distillation	Type 3A molecular sieve
bromine	none	
dichloromethane	SPS	
dimethylformamide (DMF)	none	
diethyl ether	SPS	
ethanol (100 %)	none	
ethyl acetate	none	
heptane	distillation	CaH_2
hexane	SPS	
pyridine	distillation	KOH
tetrahydrofuran (THF)	SPS	
toluene	SPS	
triethylamine	distillation	KOH
water	distillation	
X4	none	

Table 5-1: The methods used to purify and dry the solvents

All distillations were done under nitrogen. The solvents labelled “SPS” in Table 5-1 were obtained from a PureSolv solvent purification system model PS-SD-5 (SPS). The SPS gives dry deoxygenated solvents suitable for water- and oxygen-sensitive chemistry.

Some reagents required recrystallisation; these are listed in table 5-2. All solids were stored in desiccators except for the organomanganese compounds and 2-methyl-2-nitrosopropane, which were stored at -20 °C. Liquid reagents and solvents were stored in tightly stoppered bottles. 2-Bromopent-2-en-4-one and acetylallene were stored at -20 °C. Diethyl ether, THF, and sometimes other solvents were used straight from the SPS.

Compound	Recrystallisation Solvent
triphenylphosphine	100 % ethanol (N_2 atmosphere)
η^2-(5-methoxy-2-acetylphenyl) tetracarbonylmanganese (**30**)	Hexane
N-(*p*-tolyl)diphenylacetamide	acetone/water
p-toluidine	100 % ethanol

Table 5-2: The solvents used for recrystallisation of some reagents.

5.2 The Handling of Organomanganese Reagents

No special precautions were taken when handling organomanganese compounds at room temperature. Established Schlenk techniques were used. Glassware was dried in an oven (101 °C) at least two hours before use. All solvents were dried as specified in section 5.1 and degassed by exposing the solvent to low pressures to induce boiling multiple times.

5.3 The Preparation of Reagents

5.3.1 Preparation of 2-Bromopent-2-en-4-one

2-Bromopent-2-en-4-one was prepared by the method outlined by Buono[151] but on the scale given below.

The reaction was carried out in a three-neck round-bottom flask with condenser under a nitrogen atmosphere. The reaction solution was kept under 10 ºC using an icebath until it was to be refluxed. Bromine (64 g, 20.5 mL, 400 mmol) in dichloromethane (40 mL) was added dropwise to a stirred solution of triphenylphosphine (105 g, 400 mmol) in dichloromethane (300 mL). Acetylacetone (40 g, 41 mL, 400 mmol) in dichloromethane (40 mL) was added dropwise over 10 min. The solution was refluxed for 4-5 h. The cooled mixture was then evaporated to 200 mL. Triphenylphosphine oxide was precipitated by the addition of ether (~40 mL). The solution was suction filtered and the precipitate was washed (2 × 80 mL ether). The filtrate is filtered again and washed again to remove any more triphenylphosphine oxide precipitate. The filtrate and washings were distilled under vacuum (b.p. 47-48 °C/8 torr, 54-55 °C/15 torr). Yield: 36.6 g (56 %).

FTIR: 1698 (s). 1600 (vs) cm^{-1}

5.3.2 Preparation of Acetylallene (58)

Acetylallene was prepared by the method outlined by Buono[151] but on the scale given below. An updated version of this method is reported by Buono and Constantieux[155]. The new method is optimised and does not include isolating the intermediate 2-bromopent-2-en-4-one.

Triethylamine (22 g, 31 mL, 220 mmol) in ether (20 mL) was added dropwise to a stirred solution of E/Z-2-bromopent-2-en-4-one (36 g, 220 mmol) in anhydrous ether (150 mL). The mixture was stirred for 4 h. The $Et_3N.HBr$ precipitate was removed by suction filter and the precipitate was washed with ether (2 × 40 mL). The combined filtrate and washings were washed with 5 % $HCl_{(aq)}$ solution until all triethylamine had been removed as checked by washing the ether solution finally with water (40 mL) and testing the pH with litmus paper. The ether solution was then dried with magnesium sulphate. The ether was evaporated on a rotary evaporator and the residual product was vacuum distilled in a 10 cm Vigreux column to give a colourless liquid. The pressure was kept between 60 and 80 torr and the fraction collected was between 49 and 59 °C (lit.[151] b.p. 62 °C/80 torr, 49 °C/60 torr). Yield: 5.5g (30 %).

FTIR (neat): 1956 (s), 1933 (s), 1682 (vs, br), 859 (vs, br) cm^{-1}, lit[151]. 1960-1930, 1690-1650, 840 cm^{-1}

^1H NMR ($CDCl_3$, 300 MHz): δ^* = 1.98 (d, 3H, J = 2.9Hz), 5.02 (dd, 2H, J= 2.1, 6.5 Hz), 5.48 (dt, 1H) ppm. lit.[155]: (500 MHz, $CDCl_3$) 2.26, (s, 3H), 5.25 (d, 2H, J = 6.5 Hz), 5.77 (t, 1H, 6.4 Hz) ppm.

The difference in multiplicity of the peaks was unexpected. ^1H-^1H correlation spectroscopy (COSY) was used to identify the cause of the extra multiplicity (Figure 5-1). The spectrum showed long-range six-bond coupling between the protons on C-1 and those on C-5 (Figure 5-2) i.e. the cross-peak at 5.02 by 1.98 ppm indicates C-1-C-5 coupling. The cross-peaks at 5.48 by 5.02 and 5.48 by 1.98 ppm show the expected coupling between C-1 and C-3, and C-3 and C-5. The coupling still did not match the expected multiplicity of the peaks i.e. C-1 a doublet of triplets, C-3 a triplet of quartets, and C-5 a doublet of quartets. This is

* The differences in chemical shifts were likely to be due to the difference in calibration of spectrometers.

probably because the multiplets are not fully resolved i.e. the quartets on C-3 and C-5 appear to be doublets and the triplets on C-1 appear to be singlets.

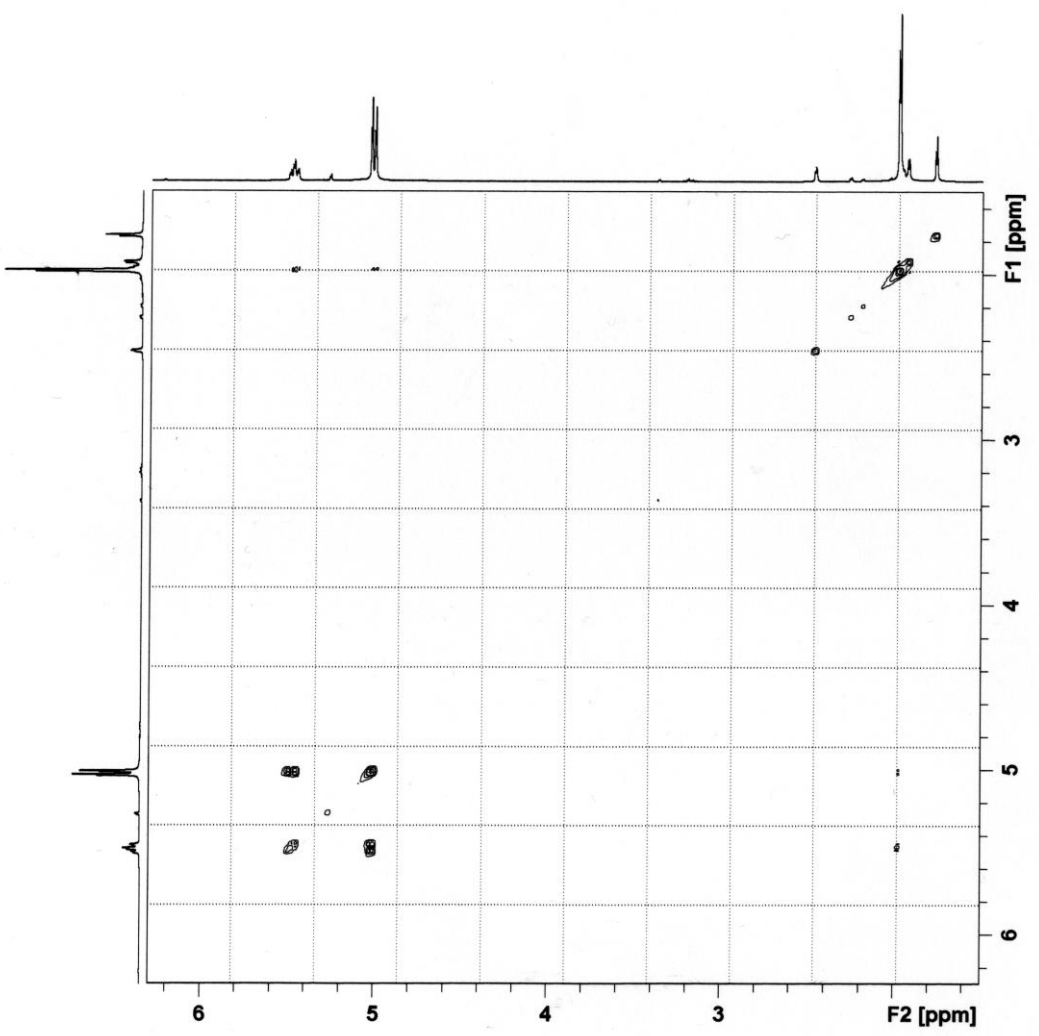
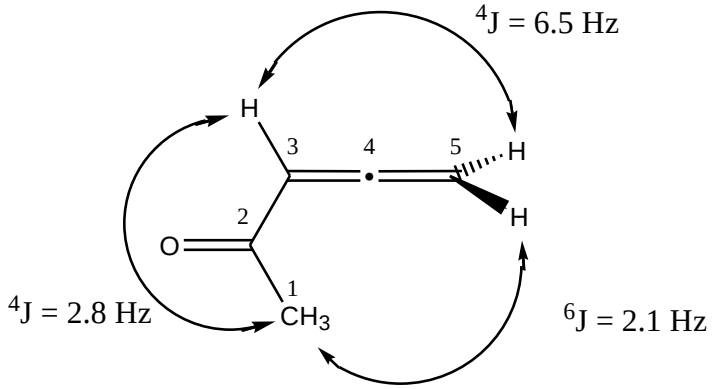


Figure 5-1: The ^{1}H-^{1}H COSY NMR spectrum of acetylallene (55).



55

Figure 5-2: The atom numbering system for acetylallene (55) showing the ^{1}H-^{1}H coupling.

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5.3.3 Preparation of Diphenylacetyl Chloride

Diphenylacetyl chloride was synthesised by the following method described by Main[156].

Diphenylacetic acid (1 g, 4.7 mmol) and a few drops dimethylformamide were dissolved in dichloromethane (15 mL) in a dry round bottom flask fitted with a condenser and anhydrous calcium chloride filled drying tube. Excess oxalyl chloride (1.2 g, 0.8 mL, 9.4 mmol) in dichloromethane (10 mL) was added slowly to the stirred diphenylacetic acid solution. The solution was left for 15 min after the bubbling stopped. The solvent was evaporated on a rotary evaporator to give an oil which was used without further purification. **Note: carbon monoxide is formed during this reaction and it should therefore be done in a fumehood.**

5.3.4 Preparation of *N*-(*p*-Tolyl)diphenylacetamide (61)

N-(*p*-Tolyl)diphenylacetamide was prepared by the method published by Stevens and French[150], with the exception that the diphenylacetyl chloride was made by the method in section 5.3.3.

Diphenylacetyl chloride (1 g, 4.3 mmol) in ether (10 mL) was mixed with an ether (10 mL) solution of *p*-toluidine (510 mg, 4.7 mmol) and an ether (20 mL) solution of 2,4,6-collidine (600 mg, 0.65 mL 4.9 mmol) and the solution was stirred for 1 h and left overnight. The solution was filtered and the precipitate was washed well with ether (3 × 5 mL), heated until boiling in ethyl acetate (20 mL), and filtered. The filtrate was evaporated to dryness then recrystallised in an acetone/water solution. Yield: 75 %.

mp: 180 °C (lit.[150] 179.5-185.5 °C)

FTIR: 3300 (m), 1660 (s), 1607 (s), 814 (m), 695 (m) cm^{-1}

5.3.5 Preparation of Benzylpentacarbonylmanganese

Benzylpentacarbonylmanganese ($PhCH_2Mn(CO)_5$) was synthesised as illustrated by Main and Nicholson[29], with an adjustment made to the method. The method is the same up to adding a THF solution of $Na[Mn(CO)_5]$ to benzyl bromide and stirring for 10 minutes. From there, instead of using a silica column to clean the crude solution of benzylpentacarbonylmanganese, the solution was evaporated to dryness and the residue dissolved in hexane and filtered. The hexane was evaporated and the remaining benzylpentacarbonylmanganese was sublimed onto a cold finger.

FTIR (heptane): 2107 (m), 2010 (vs, br), 1993 (s) cm^{-1} (lit[29]. 2105 (s), 2010 (vs, br), 1990 (s) cm^{-1}).

5.3.6 Preparation of η^2-(5-Methoxy-2-acetylphenyl)tetracarbonylmanganese (30) and η^2-[(2-Diphenylthiophosphinyl)phenyl]tetracarbonylmanganese (44)

Both cyclomanganated compounds were made based on the method by Depree et al.[21] describing the synthesis of **44**. The synthesis of **30** was done by substituting triphenylphosphine sulfide with 4-methoxyacetophenone using the same molar quantity. When the reaction was complete, the hot solution was filtered and the product was allowed to crystalise in the freezer overnight.

FTIR (**30**, heptane): 2082 (m), 1995 (vs), 1943 (s) cm^{-1} (lit.[40] (cyclohexane) 2082 (m), 1997 (vs), 1944 (m)).

FTIR (**44**, heptane): 2072 (m), 1992 (vs), 1983 (s), 1941 (s) cm^{-1} (lit.[21] (KBr disk) 2072 (m), 1993 (vs), 1978 (vs), 1933 (vs)).

5.4 Instrumentation

5.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

All FTIR analysis was performed on a Digilab Scimitar FTS 2000 series spectrometer using Varian Resolutions software version 4.1.0.101. Solutions were analysed in an IR cell between two potassium bromide windows. Neat liquids were analysed as a thin film with potassium bromide windows. Solid samples were finely ground and compacted into a potassium bromide disc.

5.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR analysis was performed on either a Bruker Avance DRX 300 or a Bruker Avance DRX 400 spectrometer using Topspin software version 1.3. All chemical shifts were reported in ppm relative to tetramethylsilane.

5.4.3 Electrospray Ionisation-Mass Spectrometry (ESI-MS)

ESI-MS was carried out on a VG Platform II spectrometer using MassLynx software version 2.0.

High-resolution ESI-MS analysis was done on a Bruker Daltonics MicrOTOF spectrometer with DataAnalysis software version 3.3.

Samples were generally run as methanol solutions in concentrations of approximately 1 mg mL^{-1}. Mass to charge ratios of ions are given in the units Da (Daltons) but more correctly the units are Da e^{-1} where e is the elementary charge i.e. the charge of a single proton, 1.60×10^{-19} coulombs.

5.4.4 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS analysis was performed on a Hewlett Packard HP6890 GC with an HP5973 mass selective detector using HP enhanced ChemStation 61701AA version A.03.00 software. The sample was injected as a dichloromethane or heptane solution of approximately 1 mg mL^{-1} concentration. The capillary column temperature was programmed to rise steadily from 50 to 300 °C in 27 minutes. The detector was run in total ion mode.

5.5 Chromatography

5.5.1 Thin Layer Chromatography (TLC)

All TLC was performed on 70×15 mm TLC strips made of silica gel 60 F_{254} deposited on aluminium sheets. A UV lamp using 254 nm and 312 nm wavelength light was used to view the fractions.

5.5.2 Preparative Layer Chromatography (PLC)

PLC plates were made by depositing a layer (approximately 2 mm thick) of silica gel 60 PF/water slurry on to 200×200 mm glass plates. The plates were dried in an oven (101 °C) for at least 12 hours, and removed approximately 18 hours before use for atmospheric equilibration. As with TLC the different fractions were viewed with the assistance of a UV lamp employing light of 254 nm and 312 nm wavelength.

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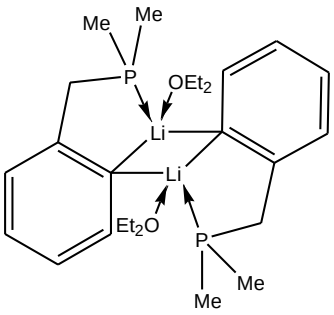
Appendix: List of Compounds



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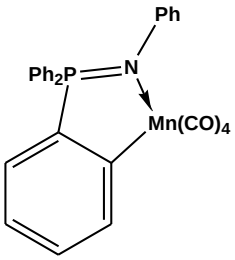

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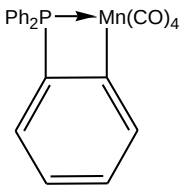

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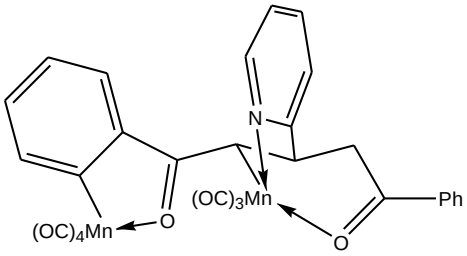

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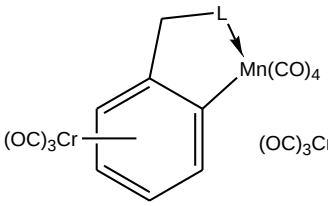

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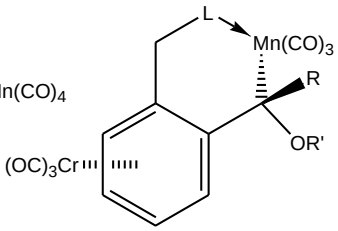

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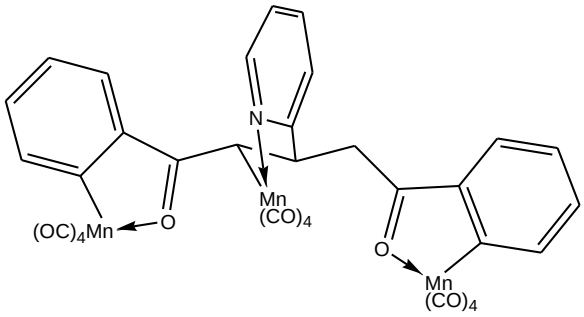

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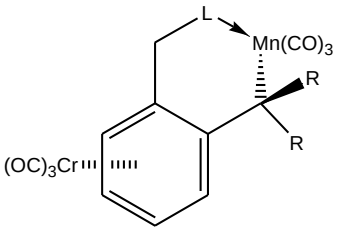

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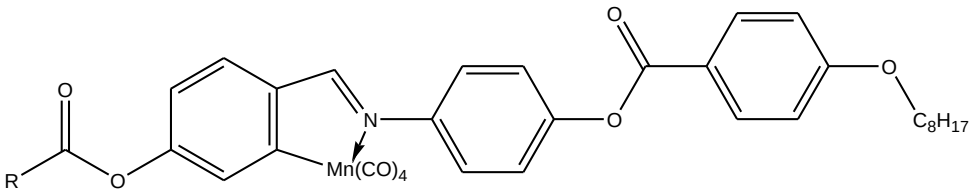

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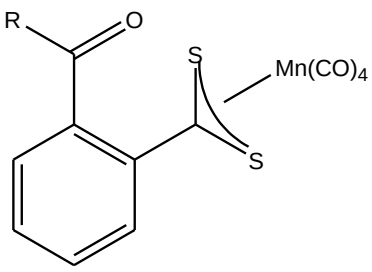

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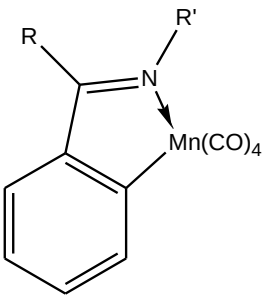

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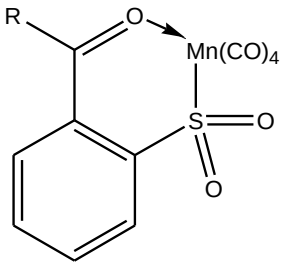

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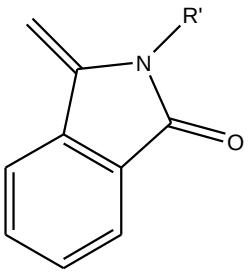

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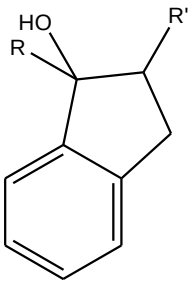

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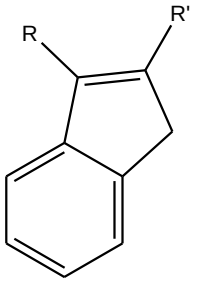

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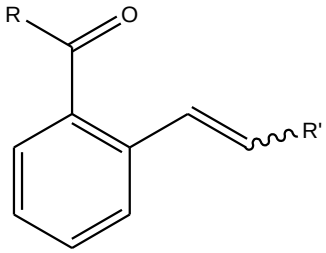

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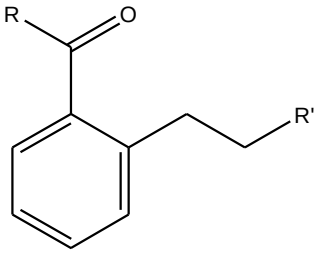

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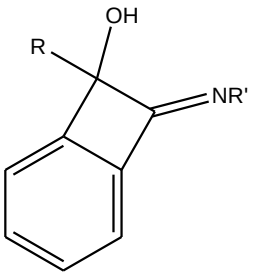

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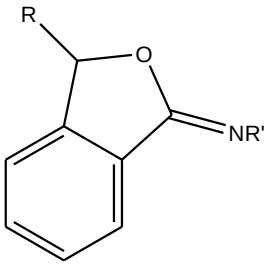

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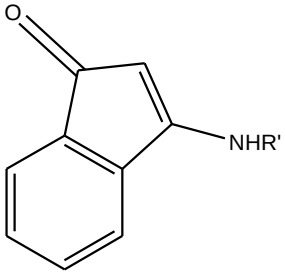

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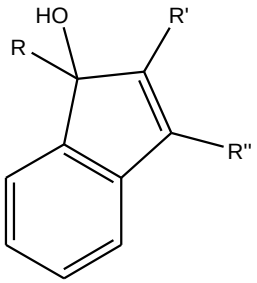

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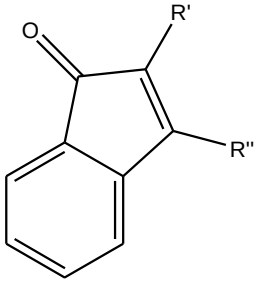

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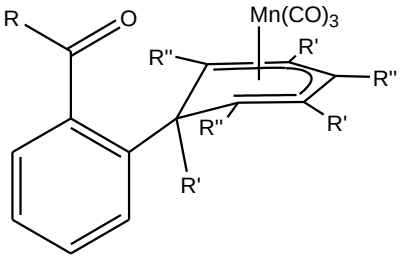

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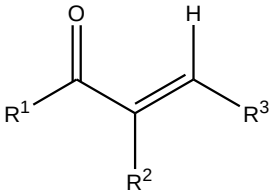

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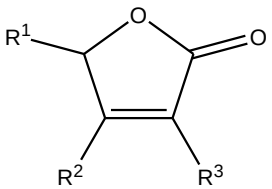

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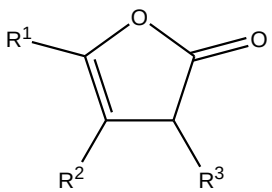

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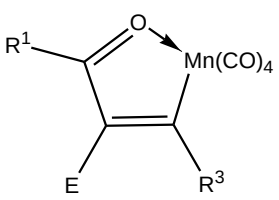

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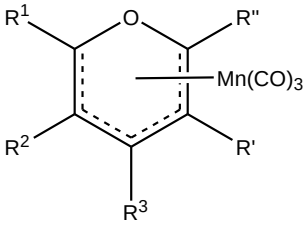

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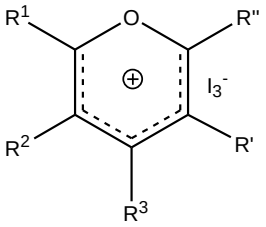

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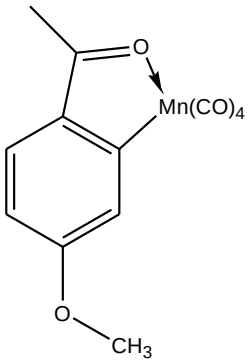

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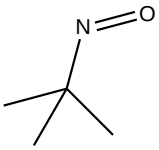

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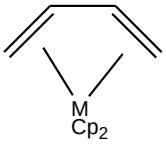

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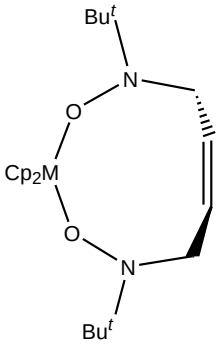

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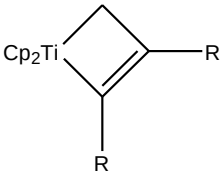

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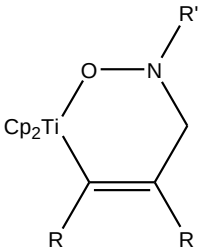

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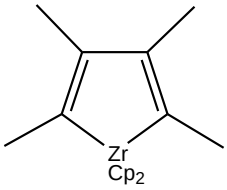

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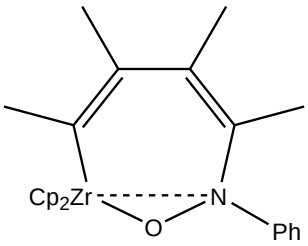

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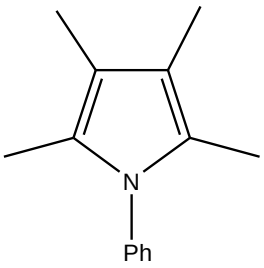

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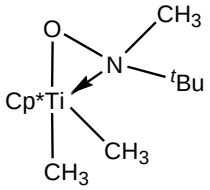

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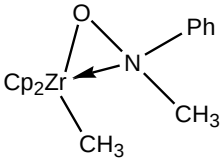

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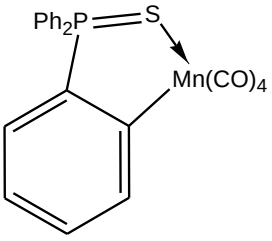

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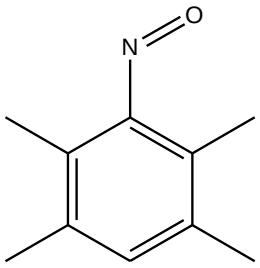

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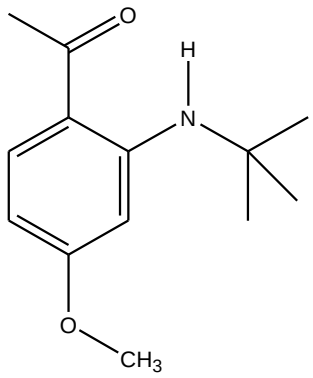

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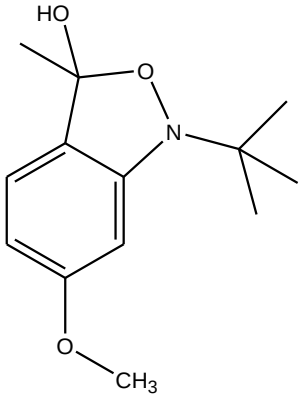

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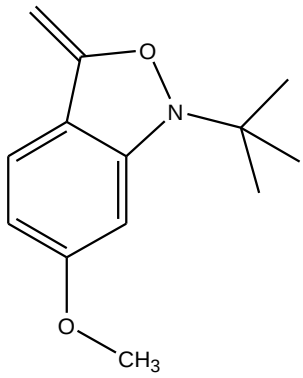

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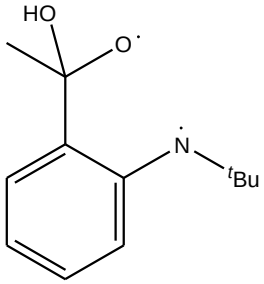

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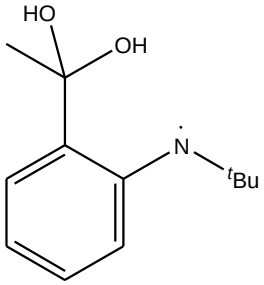

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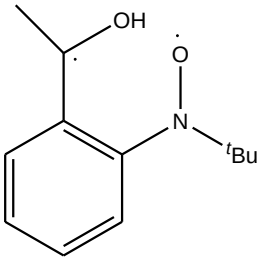

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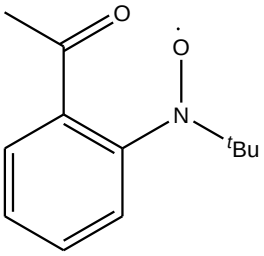

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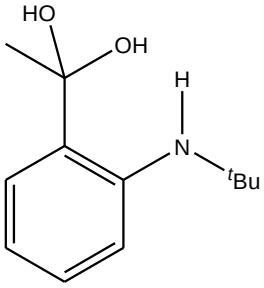

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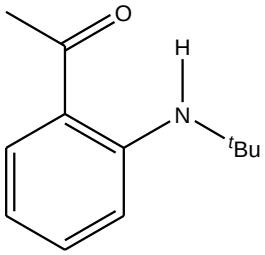

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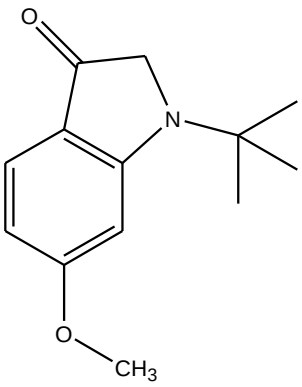

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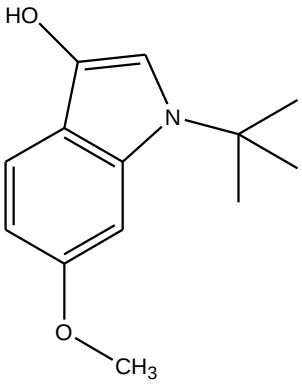

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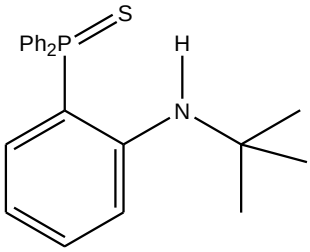

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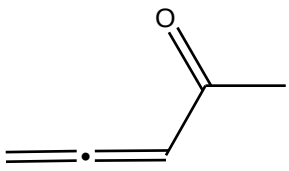

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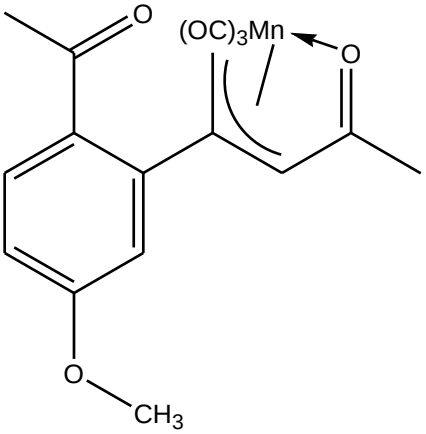

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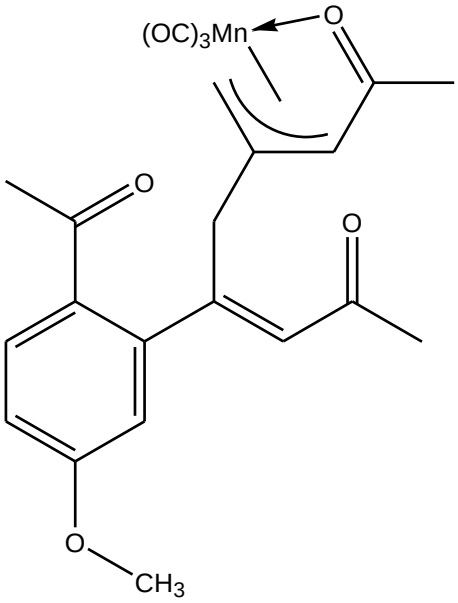

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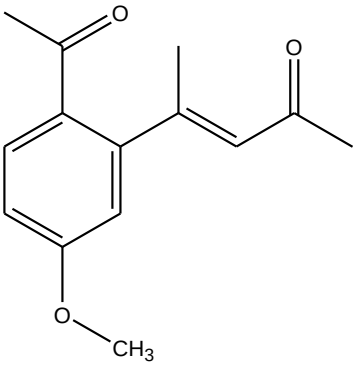

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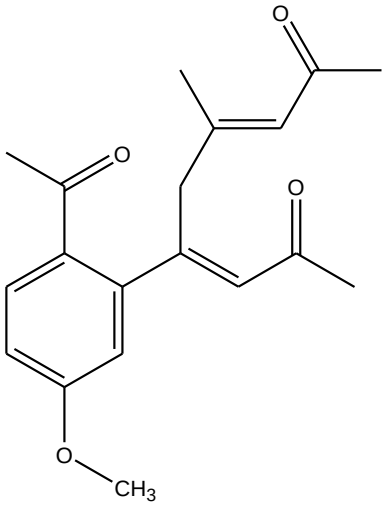

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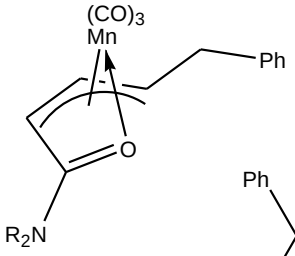

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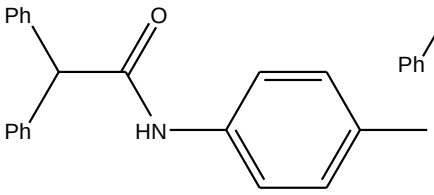

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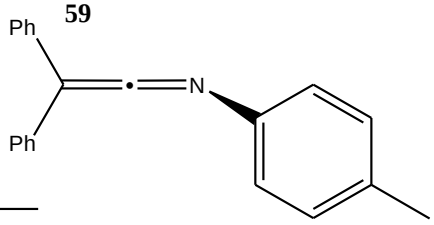

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