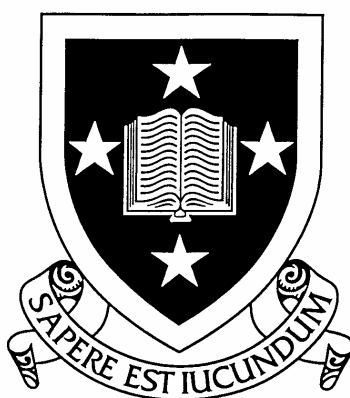


Preparation and Reactions of Orthomanganated Arylhydrazones and Related Compounds



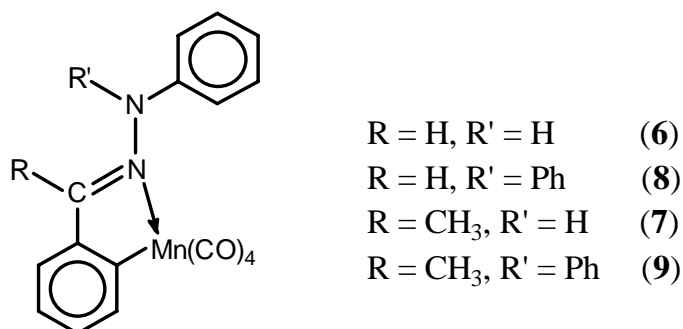
*A thesis submitted in partial fulfilment
of the requirements of the Degree of
Master of Science in Chemistry
at the University of Waikato*

by

Maarten Dinger
1995

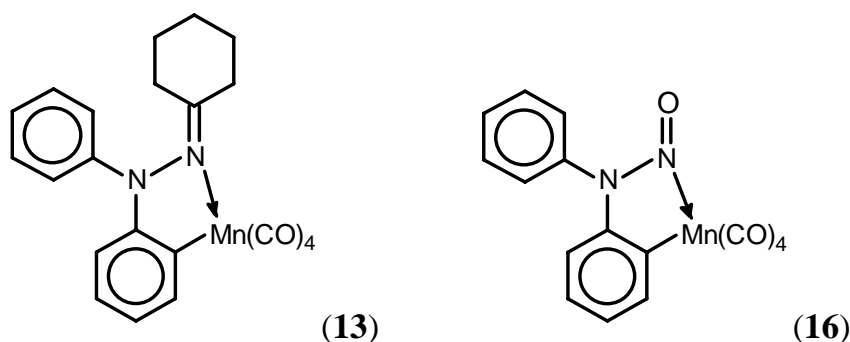
Abstract

The following orthomanganated derivatives of phenyl- and diphenylhydrazones of benzaldehyde and acetophenone have been prepared in good yield, by reaction of the hydrazones with $\text{PhCH}_2\text{Mn}(\text{CO})_5$:



The X-Ray crystal structure of (7) was determined.

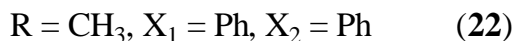
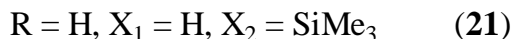
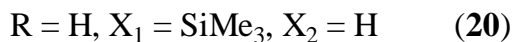
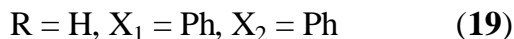
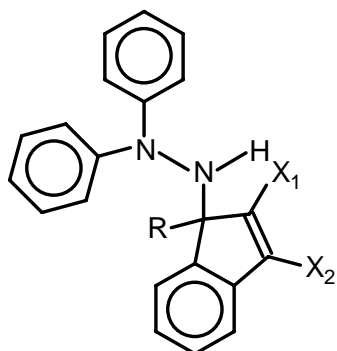
Similarly synthesised was the orthomanganated adduct of cyclohexanone diphenylhydrazone (13), the first example of an orthomanganated compound containing a N-N single bond in the metallocyclic ring. Diphenylnitrosamine also successfully reacted with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ to give a good yield of (16), the first example of an orthometalated aryl nitrosamine. Both (13) and (16) were fully characterised by X-Ray crystal structure analysis.



Attempted manganations of related systems, phenylhydrazine, cyclohexanone phenylhydrazone, N-acetyl-N-phenylhydrazine and 6-(4-chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone, were unsuccessful.

Thermal reactions of (8) with diphenylacetylene and trimethylsilylacetylene gave reasonable yields of the expected indene derivatives (19) and (20)/(21)

respectively. Compound (**9**) reacted similarly to give (**22**) and (**23**) for the same alkynes. For these alkynes at least, both of these systems showed reactivity comparable to orthomanganated aryl ketones



With dimethyl acetylenedicarboxylate (DMAD) multiple products were formed in yields insufficient for characterisation.

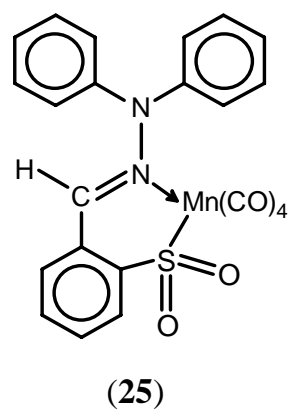
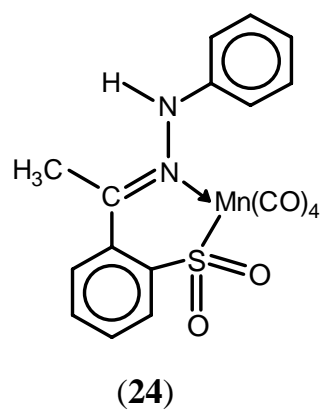
The primary hydrazones (**6**) and (**7**), did not yield corresponding indene products with alkynes.

Reactions of (**13**) with diphenylacetylene and phenylacetylene were found to be very rapid, and produced an unstable tricarbonyl species that was not characterised.

Orthomanganated diphenylnitrosamine (**16**) was reacted with DMAD. The reaction was slow, and no compounds were fully characterised, although a doubly-inserted product is suspected.

For comparison, orthomanganated azobenzene was also reacted with DMAD and phenylacetylene. This proved to be the most unreactive of all systems tested.

Reactions of (**7**) and (**8**) with SO_2 produced what has tentatively been assigned as the SO_2 inserted products (**24**) and (**25**) on the basis of IR data, by analogy with the products previously reported for orthomanganated aryl ketones. Compound (**16**) did not give an inserted product where the metal was retained, with only diphenylhydrazine, the starting material, and an unknown insoluble grey powder collected.

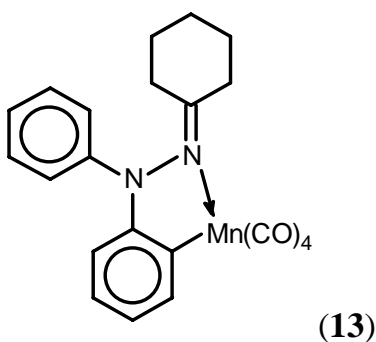


All numbered compounds appear in the fold-out section at the rear of this thesis.

Note on Nomenclature

For convenience and brevity, throughout this thesis orthomanganated compounds are named using an η^2 naming convention to specify that both the aryl carbon and nitrogen (or oxygen) are coordinated. Strictly, this should be specified using an η^2 -(C,N) nomenclature or, more correctly, using the κ notation reviewed by Sloan and Busch (*Inorg. Chem.*, **1978**, 17, 2043).

For example η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonyl-manganese (**13**) could be more correctly named 2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino- κN^2)tetra(carbonyl- κC)(phenyl- κC^1)manganese(I).



Acknowledgments

I would like to thank both my supervisors, Professor Brian Nicholson and Associate Professor Lyndsay Main, who have been most supportive and inspirational throughout the research presented herein.

Further thanks must go out to Dr. Ralph Thomson for tuition and help concerning the mighty JOEL NMR spectrometer, Wendy Jackson for running ESMS and fixing KBr solution cells (which, from time to time, inadvertently broke through no fault of my own) etc., Jannine Sims for FTIR tuition, and again Brian Nicholson for much needed ‘help’ in solving crystal structures. Also thanks to the technician staff who occasionally helped to keep the lab tidy, despite my co-workers efforts to the contrary.

Big thanks also must go out to the following all-round “good-guys”. Mr. Gary Depree, for always keeping the N₂(l) topped up throughout the year and explaining that if sufficient tap grease is used, a “product” yield can be obtained from any reaction; Warreen Tulley, for showing me how to identify the aforementioned “products” using NMR spectroscopy; Janine Cooney, for providing a “reasonably good” model thesis; Metro, for making sure that my research material was always “organised”; and finally Mr. Craig Depree who, despite his stunning successes, remained modest enough to not fully take the spotlight of my own research. He must also be acknowledged for providing a great deal of additional entertainment, although the quality of this was often somewhat dubious.

En eindelijk, moet ik natuurlijk ook “de familie” bedanken. Dus bedankt moeder en vader voor al de steun en aanmoediging die ik heb gehad over de laatste vier jaren voor mijn universiteit’s gedoe. Ook wil ik mijn broer Marcel nog bedanken voor het helpen financieren van de computer waarmee dit *geweldige* boek is geschreven.

Hoe vind je het?!

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Abbreviations

br	-	broad
Bu ^t	-	tertiary butyl
δ	-	chemical shift (ppm)
Cp	-	cyclopentadienyl (η^5 -C ₅ H ₅)
DMAD	-	dimethylacetylenedicarboxylate
<i>d</i>	-	doublet (NMR)
IR	-	infrared
J	-	coupling constant in Hz (NMR)
m	-	medium (IR)
<i>m</i>	-	multiplet (NMR)
Me	-	methyl
ESMS	-	electrospray mass spectrometry
NMR	-	nuclear magnetic resonance
Ph	-	Phenyl
p.l.c.	-	preparative layer chromatography
<i>q</i>	-	quartet (NMR)
s	-	strong (IR)
<i>s</i>	-	singlet (NMR)
<i>t</i>	-	triplet (NMR)
THF	-	tetrahydrofuran
t.l.c.	-	thin layer chromatography
v	-	stretching frequency (IR)
vs	-	very strong (IR)
w	-	weak (IR)

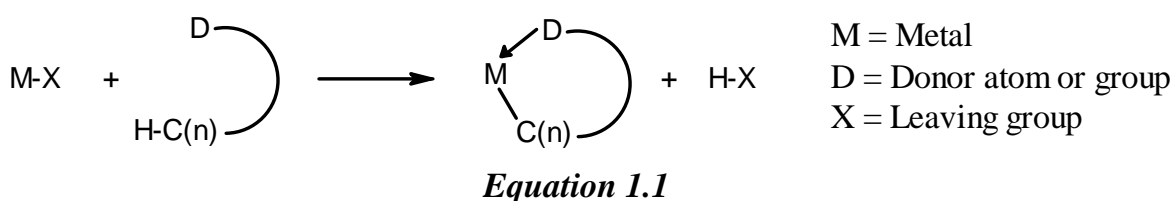
Chapter One

Introduction

1.1 Cyclometalation

1.1.1 General

“Cyclometalation” is defined as a reaction type where a new metal-carbon bond is formed to give, by intramolecular coordination, a chelate ring which consequently includes the metal. Classically this is achieved by the substitution of a hydrogen, but the definition can be extended to include any other atom or group, Equation 1.1.



The leaving group, X, is generally an alkyl species or halogen atom. It has been widely accepted that both carbon and non-carbon atoms can form part of the metallocycle, and the compound still be considered “cyclometalated”. Although the donating atom or group, D, can be either π -coordinating or σ -coordinating, this chapter will deal only with the latter, since this is most relevant to the work of this thesis. Known donor atoms include N, P, As, Sb, O, S, Cl, Br, and I, with those of N, P, As, O and S being by far the most common. A number of reviews of cyclometalations involving these atoms have been published^{2, 3, 4}. The term “orthometalation” applies if the metalation takes place on an aromatic ring in a position *ortho* to the donor substituent.

If no d-orbitals are available (e.g. O- and N-donor), the ring is almost always five-membered if there is a choice, although three-, four-, six-, and seven-

membered systems are also found. The reason for this is that the five-membered configuration has the highest possible stability compared with the alternatives, because it is the closest to the ideal geometry of the constituent atoms and are favoured by entropy considerations³.

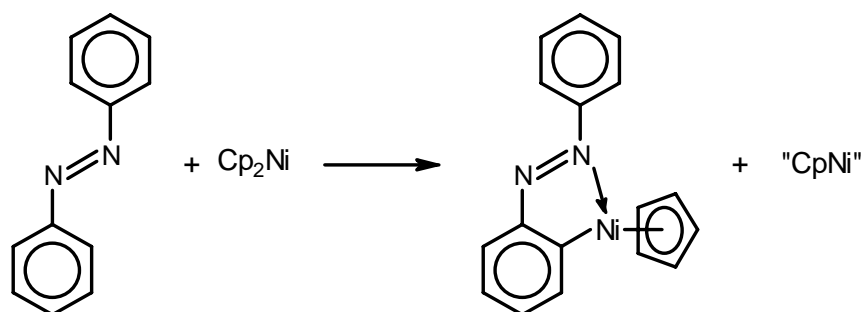
A summary of the various donor atoms follows, restricting the discussion to transition metals, with an emphasis on palladium and manganese.

1.2.1 Donor Atoms

1.2.1.1 N-Donor Complexes

A large number of metallocyclic compounds have been prepared with a wide range of transition metals that involve N-donor ligands.

The first example of orthometalation reported for a transition metal, was for an N-donor system, namely the reaction product of nickelocene and azobenzene⁵, Equation 1.2.



Equation 1.2

Similar complexes were prepared by Cope and Siekman which provided further examples with azobenzene, involving palladium(II) and platinum(II) chlorides, to give $[\text{C}_6\text{H}_5\text{-}\overline{\text{N}=\text{N}-\text{C}_6\text{H}_4}\text{PdCl}]_2$, and $[\text{C}_6\text{H}_5\text{-}\overline{\text{N}=\text{N}-\text{C}_6\text{H}_4}\text{PtCl}]_2$ respectively⁶. Also involving an azobenzene was the orthometalation of $\text{C}_6\text{F}_5\text{N}=\text{NC}_6\text{F}_5$ using $\text{MeMn}(\text{CO})_5$ to give $\text{C}_6\text{F}_5\text{-}\overline{\text{N}=\text{N}-\text{C}_6\text{F}_4}\text{Mn}(\text{CO})_4$, which provides an example of metallation by fluoride abstraction, rather than the usual $\text{C}_{\text{aryl}}\text{-H}$ substitution⁷.

Examples of both six- and seven-membered rings are known for N-donor compounds, the majority for Pd. Two examples of six-membered metallocycles are shown in Figure 1.1^{8,9}.

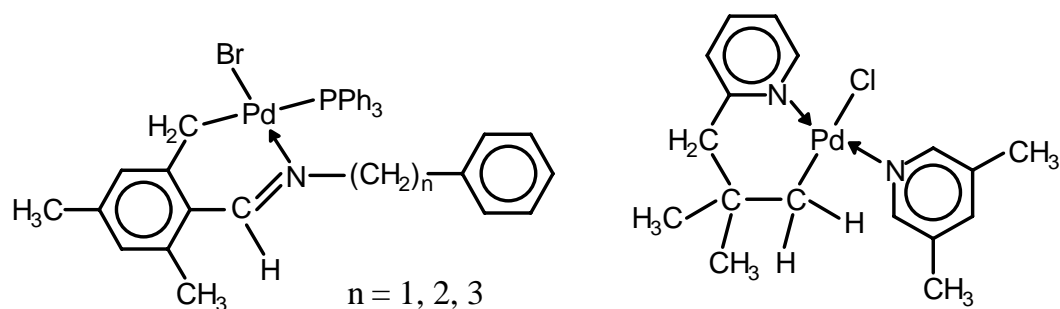


Figure 1.1

A seven-membered ring, fused with two five-membered metallocycles is shown in Figure 1.2¹⁰.

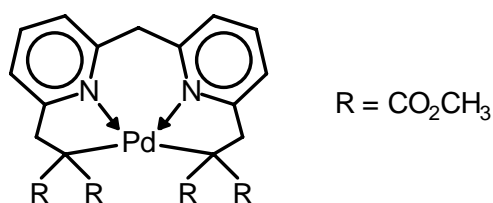


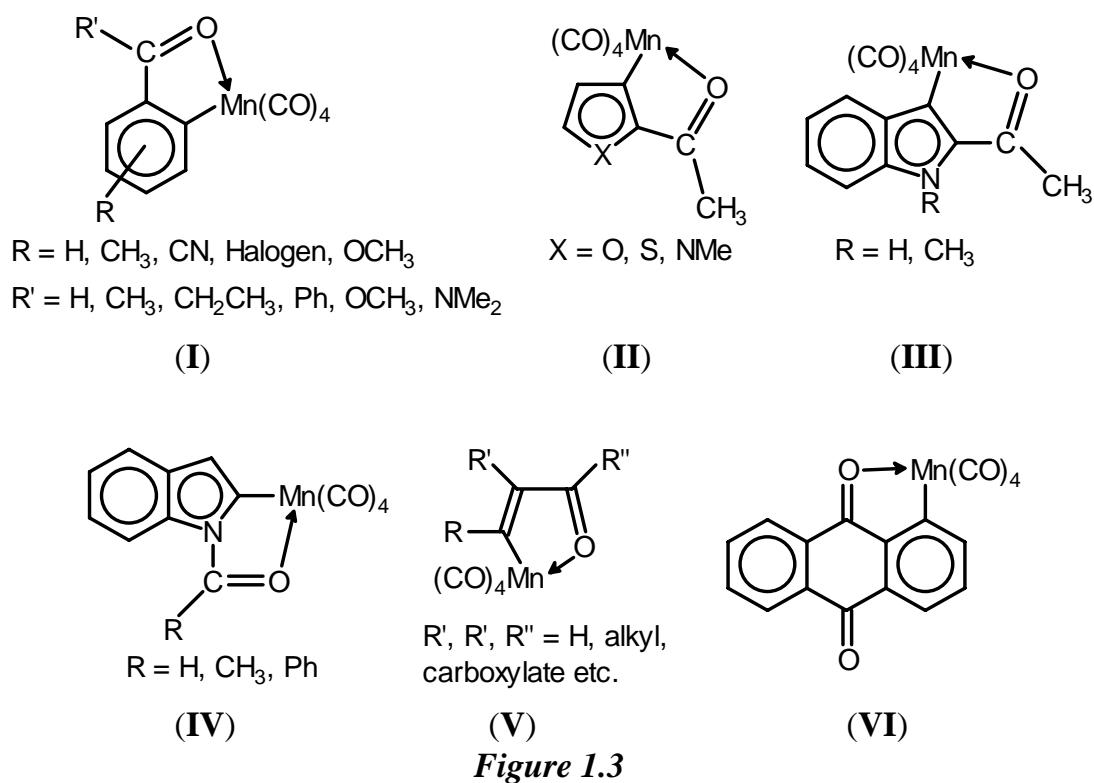
Figure 1.2

A survey of the cyclometalated (five-membered rings) derivatives of various N-donor ligands involving tetracarbonylmanganese, $\text{Mn}(\text{CO})_4$, is given in the introduction to Chapter Two.

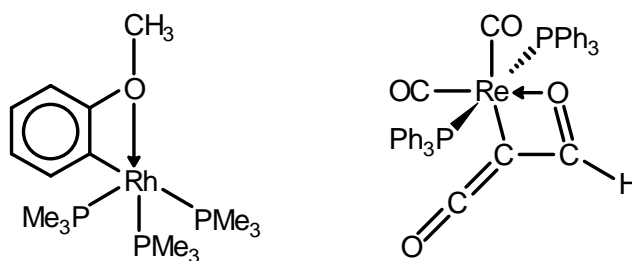
1.2.1.2 O-Donor Complexes

At Waikato a considerable amount of work has been carried out on orthometalated compounds with O-donor substituent(s), with an emphasis on manganese. A recent review by Main and Nicholson gives a good overview¹¹.

The main groups of manganated derivatives include acetophenones, benzaldehydes, benzophenones, benzamides, benzoate esters (**I**); heteroaromatic methyl ketones (**II**) and (**III**); N-acyl heteroaromatics (**IV**); enones (**V**); and quinones (**VI**). Examples from each group are shown in Figure 1.3. Note that this is by no means a complete account.



Although five-membered rings are by far the most common, exceptions are known. Two examples of O-donor complexes with four-membered rings are shown in Figure 1.4^{12, 13}.



The donor atom function is not restricted to carbonyl groups, although these are by far the most common. Examples of organo-nitro, hydroxy, phosphoryl, nitrate or sulfinyl groups as ligands are also found. A nitro example which was characterised by X-Ray crystal structure analysis¹⁴ is shown in Figure 1.5.

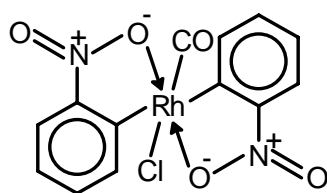


Figure 1.5

1.2.1.3 P-Donor Complexes

Compounds involving a phosphorus atom as the donor atom are relatively common. Phosphorus is in the same group as nitrogen, so it is not surprising many analogous P-donor compounds are formed.

Many four-membered compounds of phosphorus are known (compared to N- and O-donor), despite the overall higher stability of the five-membered ring systems. This is thought to be due to two reasons; the larger size of the P atom, and the possibility of d-orbital interaction in bonding to the metal atom¹⁵. Examples of four-membered ring P-donor complexes (including a manganese example (I)) are shown in Figure 1.6^{16, 17, 18}. An X-Ray crystal structure determination of (III) has shown highly compressed bond angles, as expected.

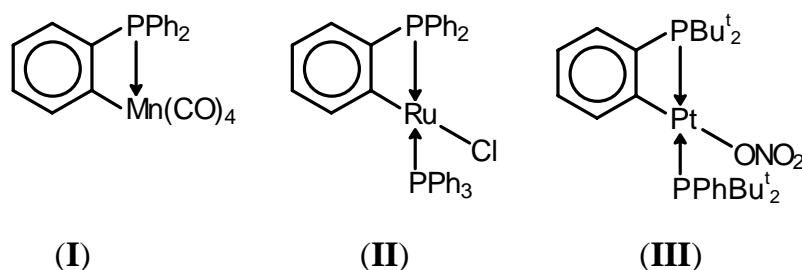


Figure 1.6

A large number of cyclometalated compounds with five-membered rings are also found⁴. Additionally, in contrast to the small ring sizes discussed above, large seven- and eight-membered rings have been reported¹⁹ (Figure 1.7).

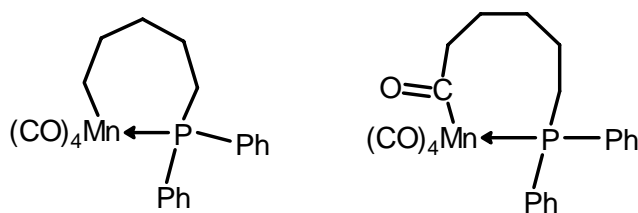


Figure 1.7

1.2.1.4 S-Donor Complexes

Cyclometalated compounds involving sulfur donor atoms are fairly limited. This is probably due to the lower reactivity of S as a donor, when compared to O, N, and P atoms. Examples are mostly five-membered systems, although three- and four-membered rings are known. The increased stability of these smaller, strained, metallocycles is thought to be due to the participation of the sulfur 3d orbitals with bond formation to the metal. Very few manganese compounds have been prepared; examples are shown in Figure 1.8. Pd and Pt chloride analogues of (I) have been reported⁴.

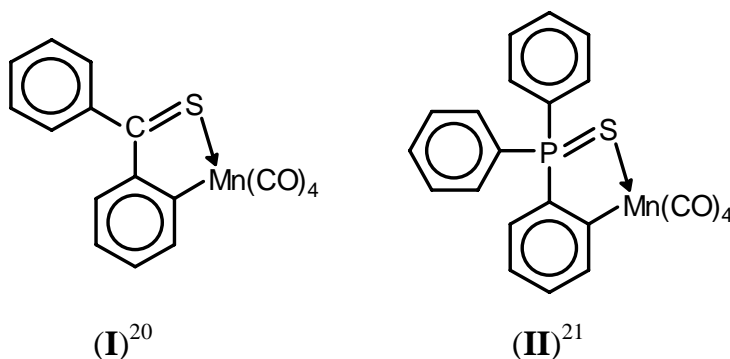


Figure 1.8

1.2.1.5 As-Donor Complexes

Like sulfur, there are a few known arsenic donor compounds. Examples are shown in Figure 1.9^{22, 23}. No manganese derivatives have been prepared to date.

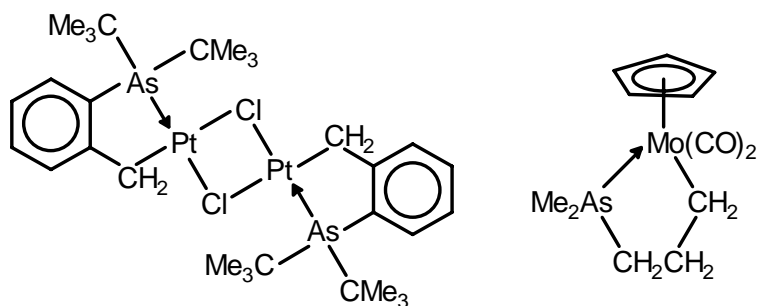
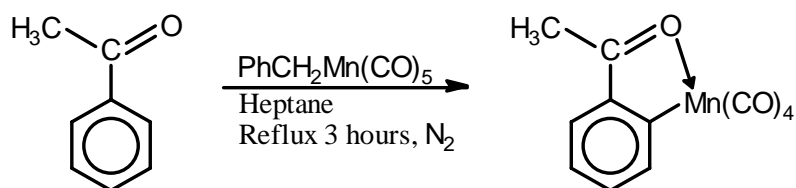


Figure 1.9

1.3.1 Mechanism

Aromatic compounds, providing they have a suitable donor group which is orientated correctly, can be conveniently ortho-functionalised by reacting with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (originally $\text{MeMn}(\text{CO})_5$) generally to give high yields of the orthomanganated product. The scheme and general reaction conditions are shown in Equation 1.3 for acetophenone.

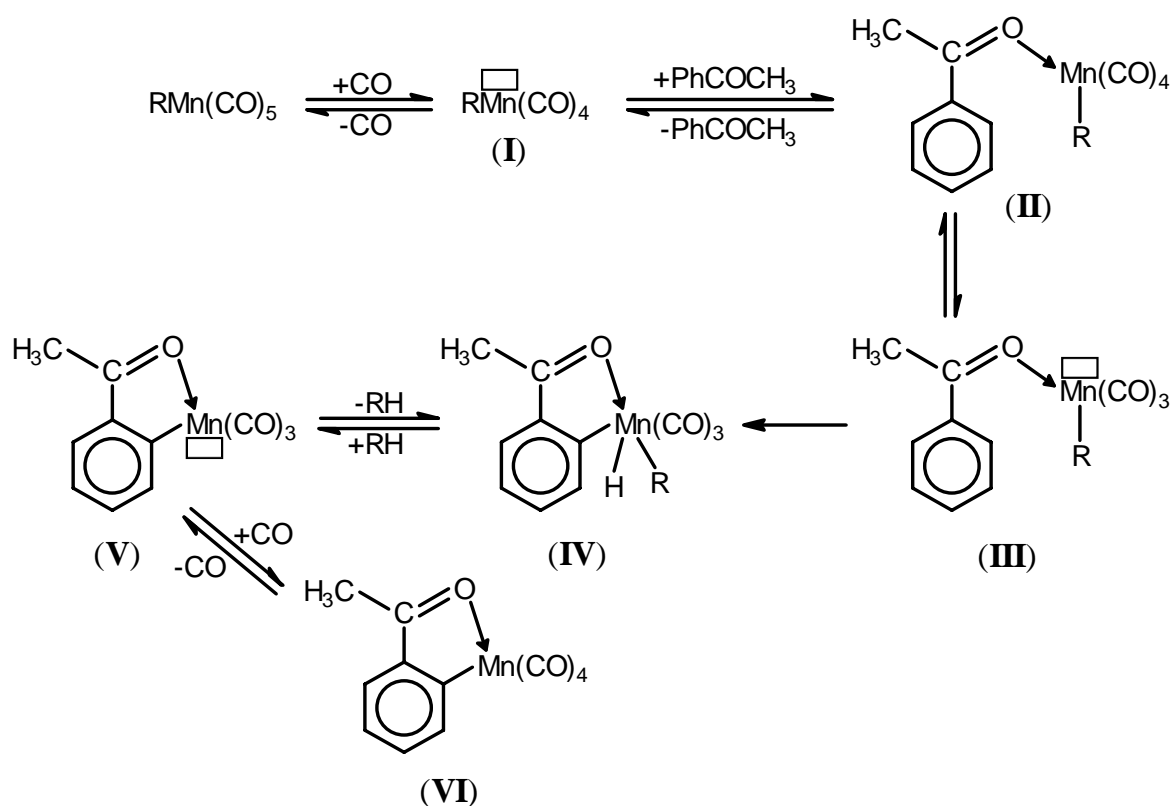


Equation 1.3

Although the definitive mechanism for orthomangantation has not been established, a number of suggestions can be found in the literature including electrophilic²⁴ and concerted²⁵ mechanisms. However the most consistent with experimental evidence is the mechanism (Scheme 1.1) involving oxidative addition/reductive elimination discussed in a recent review²⁶. These have been examined in some detail, including experimental evidence, by Gommans²⁷ and Robinson²⁸.

The oxidative addition/reductive elimination scheme involves base dissociation of CO from $\text{RMn}(\text{CO})_5$ (the manganating reagent) to give the coordinatively unsaturated compound (I), followed by initial donation from the donor atom, to give (II). After a second loss of CO, (III), oxidative addition to this coordinatively unsaturated 16-electron Mn(I) species, gives a Mn(III) 18-electron

intermediate, (IV). This subsequently reductively eliminates the alkane (RH) to give the a tricarbonyl species (V), which associates a CO to give the orthomanganted product (VI).



Scheme 1.1

However, a seven coordinate Mn(III) species (IV) is not very plausible, so a concerted elimination from (III) to (V) is perhaps more likely. The oxygen directs the metalation by initial coordination, and hence only the *ortho* position is functionalised.

The mechanism has been extrapolated to include the orthomanganation of imines, which is suggested to proceed via the same scheme, due to their structural resemblance²⁹.

1.2 Reactions

It has been well-documented that organometallic compounds play an important part in the activation of carbon centres, thus having important applications in organic synthesis³⁰. The majority of work has been carried out using palladium compounds.

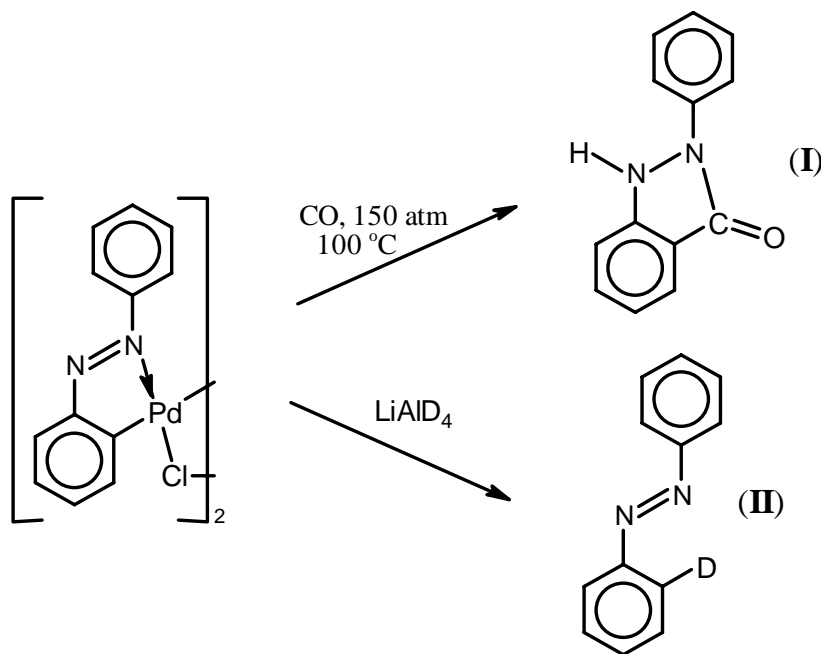
For many orthopalladiated compounds, substitution (or insertion) takes place specifically at the M-C_{aryl} linkage, regardless of the activation and/or directing properties of the donor substituent. Amongst the first orthometalated compounds whose reactivity was investigated were those of the azobenzene system.

Two early reactions of orthopalladiated azobenzene are shown in Equation 1.4. The carbonyl insertion into azobenzene to give indazolone (**I**)³¹, was one of the earliest reactions of cyclometalated compounds. It is also possible to reductively cleave the metal-carbon bond with LiAlD₄ to yield an ortho-deuterated aromatic ring (**II**)³².

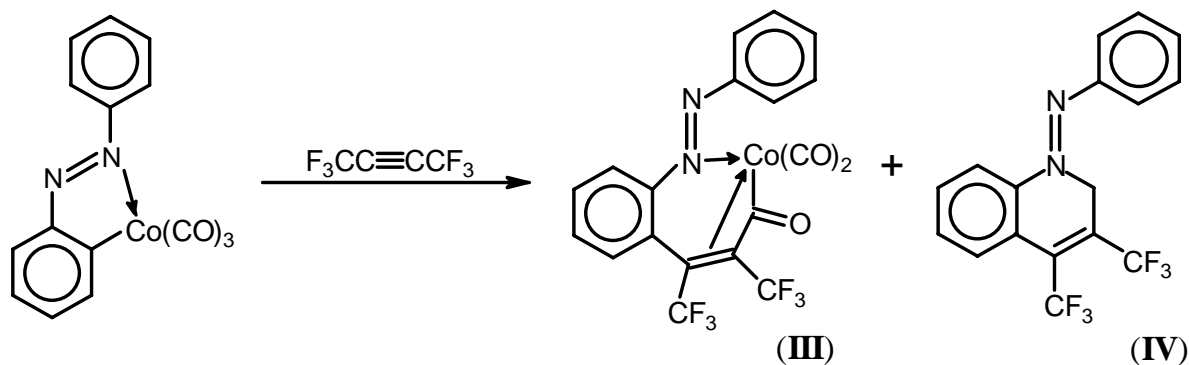
Stone *et al.* obtained a substituted N-anilinoquinoline (**IV**) and a π -acryloyl complex of cobalt (**III**), from the reaction of hexafluorobut-2-yne with orthocobaltated azobenzene (Equation 1.5)³³. A number of other reactions have been carried out using this system by Pauson *et al.*, with phenylacetylene, styrene, methyl acrylate, dimethyl fumarate and acetonitrile³⁴.

Ortho-chloroazobenzene reacts with $\text{C}_6\text{H}_5\text{-}\overline{\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NiCp}}$ to yield 4-4H-phenylcyclopental[c]-cinnoline (**V**) (Equation 1.6)³⁵.

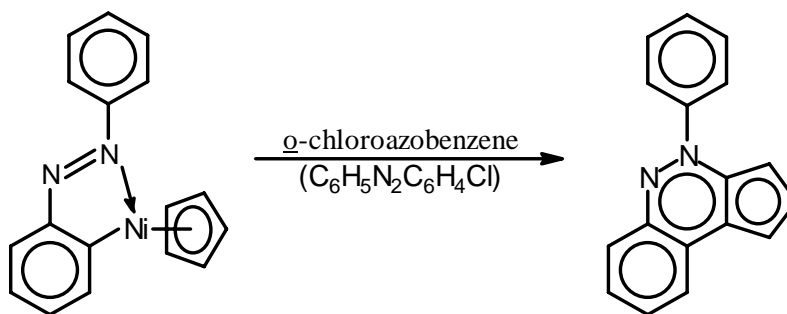
A variety of other reactions with various metalated N-donor compounds beside azobenzene were similarly explored⁴.



Equation 1.4



Equation 1.5



Equation 1.6

Aromatic ketones cannot be orthometalated by these metals, thereby restricting the range of substrates. Kaesz *et al.* first began deliberately metalating aromatic ketones when, as by-products of reactions involving cyclometalated P-donor complexes, orthomanganated O-donor products were collected as secondary di-metalated compounds³⁶. An example is shown in Figure 1.7. Direct metalation of a variety of aryl ketones followed.

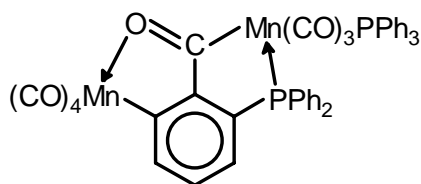
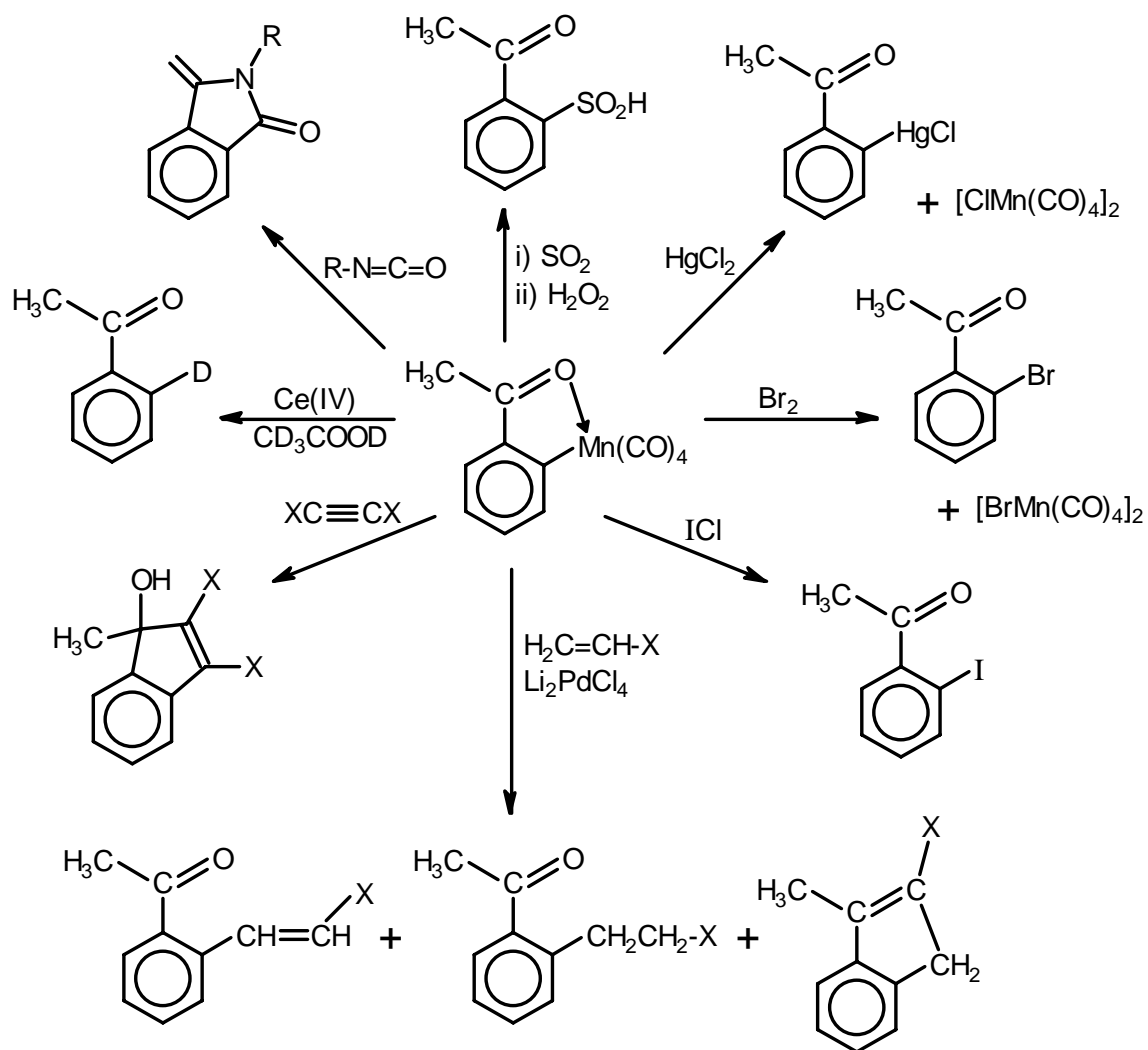


Figure 1.7

Orthomanganated derivatives of aromatic ketones can thus be readily prepared, giving rise to large number of potential synthetically valuable reactions. Some of these are summarised for orthomanganated acetophenone in Scheme 1.2.



Attempts at extending these useful reactions to include N-donor ligands have so far met with only moderate success. Samad carried out reactions of orthomanganated imines with ICl, Br₂, alkenes, alkynes, and mercuric chloride²⁹. Reactions were generally slow and low-yielding.

The aim of the research presented in this thesis was to synthesise new orthomanganated N-donor compounds, and to assess their reactivity towards alkynes or SO₂, thereby determining their synthetic potential.

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Chapter Two

Ortho-Functionalisation of Aromatic Compounds Containing the NN Linkage via Manganation

2.1 Introduction

A large variety of cyclometalated compounds involving various nitrogen donor systems have been prepared. The main classes are summarised as follows, with an emphasis on manganese derivatives:

2.1.1 Aromatic Amines

A number of orthometalated secondary and tertiary amines have been prepared¹. Two manganese examples are shown in Figure 2.1.

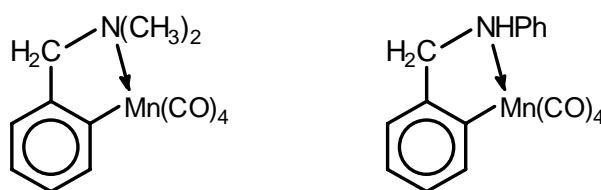


Figure 2.1

The structure of the former has been fully confirmed by X-ray structural determination². Attempts at creating analogues with Fe, Ru or Rh by use of $\text{FeMe}(\text{CO})_2(\text{C}_5\text{H}_5)$, $[\text{RuCl}_2(\text{CO})_3]_2$ and $[\text{RhCl}(\text{CO})_2]_2$ respectively, were unsuccessful¹. However, many Pd^{II} complexes of this type are known, and have been used in synthetically valuable reactions.

2.1.2 Aromatic Imines

Recently Samad³ investigated compounds which incorporated the imine group and orthomanganated a range of compounds (structures **(I)** and **(II)** in Figure 2.2, where R = H, OCH₃), by the well-established modification of the method first developed by Kaesz *et al*⁴.

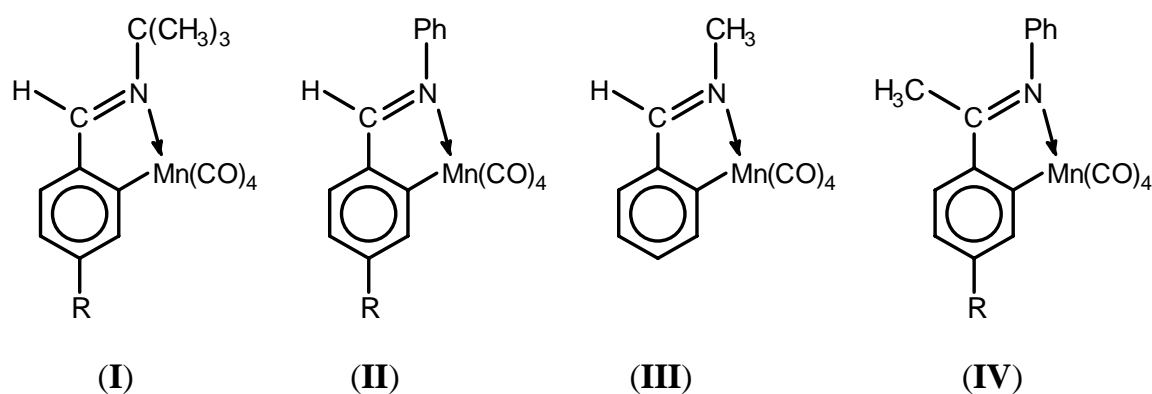


Figure 2.2

In addition, Bruce *et al* prepared and characterised the Mn(CO)₄ adduct of PhCH=NMe⁵, structure **(III)**.

Cooney prepared orthomanganated imines such as **(IV)** (where R = OCH₃, H), by reacting N-thionylaniline (Ph-N=S=O) with orthomanganated acetophenones⁶, the metal centre apparently playing a key role in the conversion to the cyclometalated imine, since the non-metalated acetophenones did not give imines under the same conditions.

2.1.3 Pyridines and Related Aromatic Substrates

An assortment of arylpyridine compounds have been successfully orthomanganated and orthorheniated⁷. Some examples of the manganese derivatives are given below (Figure 2.3):

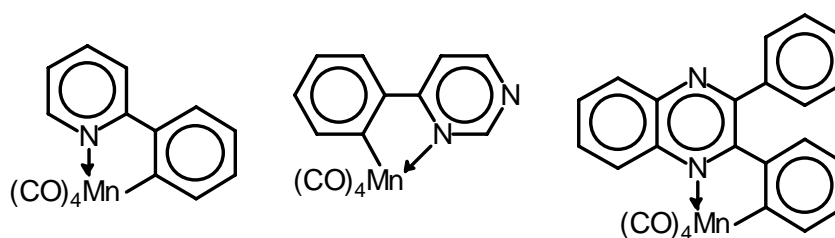


Figure 2.3

2.1.4 Aromatic Hydrazones

Only a limited number of orthomanganated hydrazones are known, although recent attention has been directed to cyclopalladiated derivatives^{8,9}. The only example of a non-cyclic hydrazone that has been metalated to give the $\text{Mn}(\text{CO})_4$ adducts is benzylideneazine^{10,1} (Figure 2.4). The monometalated example (1), has been fully characterised by X-Ray crystal structure determination¹⁰. Preparation of the di-metalated analogue (shown to the right) was also achieved.

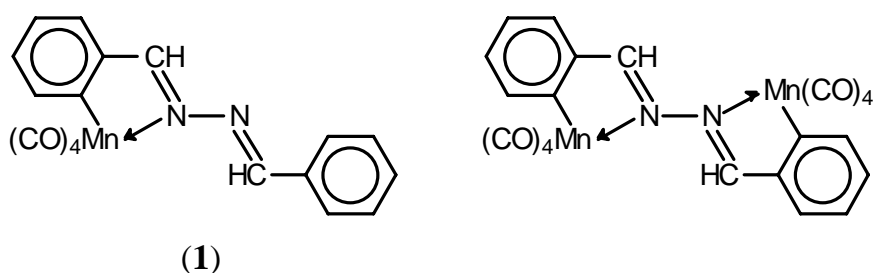


Figure 2.4

In addition 1-phenylpyrazole, which can be regarded as a cyclic hydrazone, has also been manganated⁷ (Figure 2.5). This product is unusual, but not unique, in that it contains two fused five-membered rings.

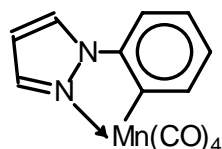


Figure 2.5

2.1.5 Azobenzene

A large variety of metalated derivatives have been prepared of the azobenzene system (Figure 2.6), with various substituents. Both monometalated^{11,12} and dimetalated^{12,13} complexes have been reported. It is without doubt the most thoroughly researched nitrogen-donor system for manganese.

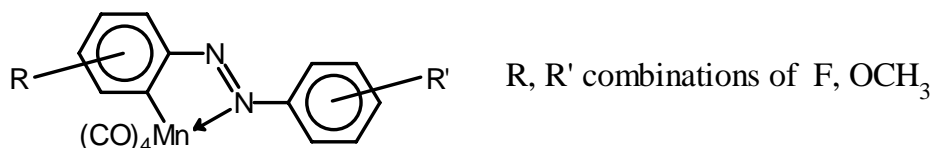


Figure 2.6

In a separate study, manganated derivatives of azobenzene with R, R' = H, OEt, N(CH₃)₂ and OCH₃ substituents have also been prepared¹.

2.1.6 Miscellaneous

N,N-diphenylhydrazine

By reacting PhMn(CO)₅ with azobenzene in refluxing methylcyclohexane for 2 hours, a highly unusual bimetalated tricarbonyl species was apparently isolated¹³, Figure 2.7.

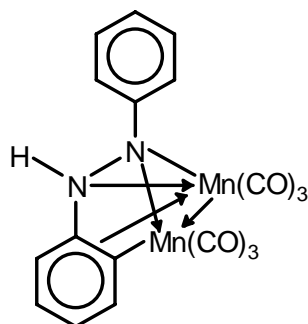


Figure 2.7

The compound is air sensitive, with evidence coming from IR (which shows a strong N-H stretch and six CO absorbances), mass spectrometry and elemental analysis - all of which are fully consistent with the proposed structure. Not surprisingly the yield was low (14%), compared to typical manganation reactions, which generally have very good yields (>70%).

2,5-Diphenyloxazole

The substrate 2,5-diphenyloxazole did not undergo orthometalation when PdCl₂ was used, rather PdCl₂L₂ where L = 2,5-diphenyloxazole⁷ was formed. However, when MeMn(CO)₅ was reacted with the same substrate, the expected orthomanganated product was formed (Figure 2.8).

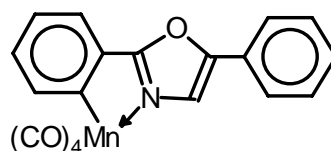


Figure 2.8

2.1.7 Prelibation

From the above summary it is clear that orthomanganated derivatives of nitrogen compounds are readily accessible, but for systems other than azobenzene, there has been little systematic investigation.

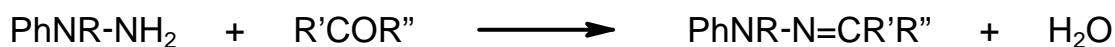
The work described in this chapter is an attempt to expand the chemistry of nitrogen donor ligands, by preparing and characterising a series of new orthomanganated compounds, restricting ourselves entirely to organic molecules containing two nitrogen atoms directly bonded to each other.

Typical chromophores containing the N-N bond will lie between two extremes, R_2N-NR_2 and $R_2C=N-N=CR_2$, where R may be H, alkyl, aryl, or part of a ring system. A full review of organometallic derivatives of this type has been carried out¹⁴, and it was clear that little work had been done on manganese derivatives. The systems investigated in this study include arylhydrazones, arylhydrazines, N,N-diphenylnitrosamine and, for completeness, azobenzene.

2.2 Arylhydrazones

2.2.1 General

Primary and secondary arylhydrazines react with carbonyl compounds (i.e. aldehydes and ketones) to yield arylhydrazones (R = Ph, H):



Equation 2.1

Arylhydrazones are named after the carbonyl compounds from which they are derived (for example PhNH-N=CHPh is referred to as benzaldehyde phenylhydrazone), although in early literature different nomenclature was used. There are three major considerations when dealing with reactions involving hydrazones; these are tautomerism, autoxidation, and geometrical isomerism.

2.2.1.1 Tautomerism

For primary arylhydrazones of aryl carbonyl compounds there exists a possibility of two tautomeric forms (Figure 2.9) - the hydrazone (A) and the azo form (B):

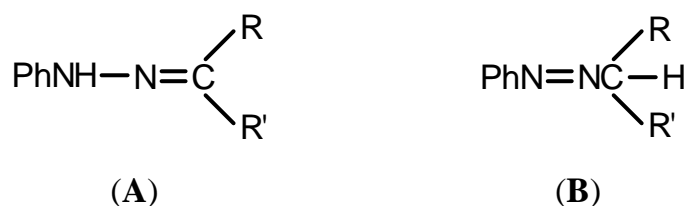


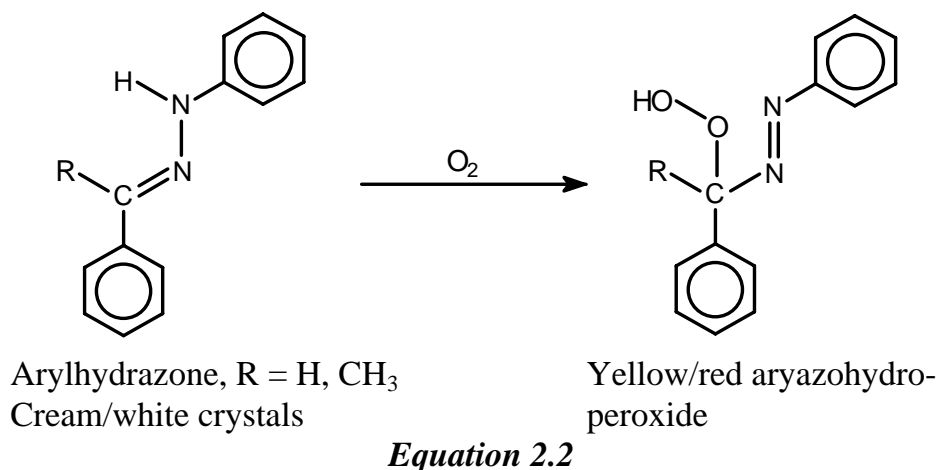
Figure 2.9

The question of hydrazone-azo tautomerism has been the subject of considerable investigation. Kitaev *et al.*¹⁵ claim that the azo tautomer arises only by decomposition of the arylazohydroperoxide (see autoxidation below), and not by direct tautomerism.

The (B) tautomer is generally highly coloured (as is the case for most azo compounds) (*c.f.* (A) which is usually white to pale yellow), which could potentially give rise to confusion interpreting observations of metalation reactions which often themselves yield brightly coloured compounds.

2.2.1.2 Autoxidation

The yellow colouration that develops on standing neutral solutions of arylhydrazones was originally thought to be due to conversion to the azo tautomer, but is now accepted to be due to the autoxidation of the hydrazone (Equation 2.2). The autoxidation product is a peroxide, existing in the azo form.



The process probably proceeds via a radical mechanism¹⁶; and is aided by exposure to light¹⁵. It does not occur in inert atmospheres¹⁵ (such as nitrogen) as expected, and so is not a problem for cyclometalation reactions which, due to their oxygen sensitive nature, are carried out under nitrogen.

All three primary aryl hydrazones prepared for this study (phenylhydrazones of benzaldehyde, acetophenone and cyclohexanone) were observed to decompose to very dark red oils when stored in open vessels under standard laboratory conditions (cyclohexanone phenylhydrazone being the most rapid), presumably oxidising to their respective peroxides.

For storage purposes, primary arylhydrazones should be stored either under nitrogen or alternatively in a freezer, which considerably slows down the rate of colorisation.

Both of the above problems (tautomerism and autoxidation) can be circumvented by using secondary arylhydrazones (i.e. diphenylhydrazones), for which conversion to the azo tautomer and autoxidation to the peroxide is expected to be highly unfavourable. Indeed noticeable decomposition of the diphenylhydrazones prepared for use in this study was not observed.

2.2.1.3 Geometrical Isomersim

There exists a possibility of geometrical (*cis-trans*) isomerism. This *syn-anti* isomerism is induced by exposure to irradiation. NMR spectroscopy can be used to differentiate between the *syn* and *anti* forms, illustrated by the arylhydrazone structures in Figure 2.10, where R = CH₃, H; R' = H, Ph:

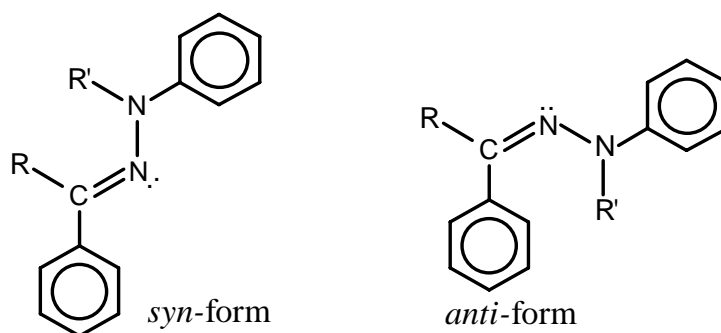


Figure 2.10

In the *syn*-isomer, the anilino group is *cis* to the smaller of the two substituents on the hydrazone carbon. Studies have been carried out on the *syn/anti* distribution for 2,4-dinitrophenylhydrazones of acetaldehyde in various solvents, and the *syn*-isomer has been found to be the dominant form. This is not unexpected since steric crowding in the *syn* form will be considerably less than for the *anti*-isomer.

In this study, both the ¹H NMR and ¹³C NMR for acetophenone phenylhydrazone showed extra peaks (see experimental section), arising presumably from *anti* impurities. Attempts at purifying the hydrazone and isolating the pure *syn*-form proved futile, with small amounts of the *anti*-isomer prevailing. Only the *syn*-isomer is correctly orientated for donation of the nitrogen lone pair onto the metal centre to give what is assumed to be the most stable orthomanganated product. The *anti*-form could, potentially at least, give rise to the compound shown in Figure 2.11.

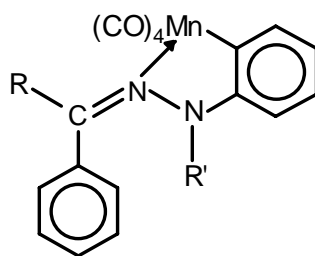
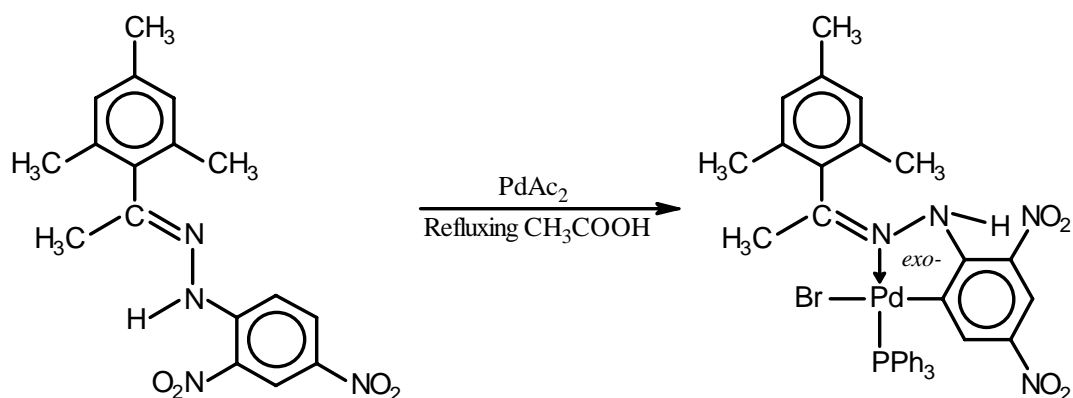


Figure 2.11

Compounds of this type (giving an *exo* ring system) have in fact been detected with cyclopalladiation reactions involving arylhydrazones¹⁷, Equation 2.3. “Drastic conditions” were required (refluxing acetic acid) that decomposed all other hydrazones tested.



Equation 2.3

The infrared stretching band $\nu(\text{C}=\text{N})$ is generally not observed for hydrazones. This is probably due to the compensating action of the amino group making the change of the dipole moment during the vibration near-zero¹⁸.

2.2.2 Orthomanganation of Arylhydrazones

All hydrazones prepared reacted with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ to give the expected cyclometalated derivative in high yield, with the exception of cyclohexanone phenylhydrazone, for which no metalated compounds could be isolated. The cyclometalated products isolated were found to be air stable and easily handled, and could be stored in a refrigerator over long periods of time with no significant decomposition. Details for each case follow.

2.2.2.1 Arylhydrazones of Benzaldehyde and Acetophenone

When metalating the *syn* isomer (the dominant form) of arylhydrazones there exists the possibility of three different cyclomanganated reaction products (Figure 2.12). (A) is expected to be the most favourable product, since the presence of the C=N double bond allows for the formation of a delocalised metallocyclic ring, hence introducing extra stability. Despite the favourable orientation of the lone pair to give a 5-membered ring, (B) is not expected since no delocalised system is available. (C) would give rise to a 4-membered ring, which would lead to a considerably strained metallocycle, with no delocalisation, and is therefore also considered unlikely. Four-membered metallocycles are however known for phosphorous as the donating atom (see Chapter 1). The relative acidities of the *ortho* Ar-H may also be an important factor.

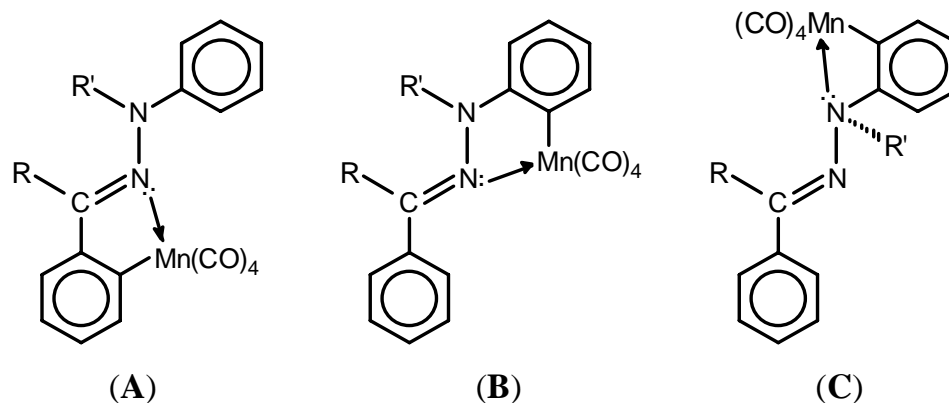


Figure 2.12

When the various arylhydrazones of benzaldehyde and acetophenone were refluxed for a few hours in heptane with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ under an inert atmosphere of nitrogen, the solution was observed to turn orange in the case of the primary (monophenyl) hydrazones and yellow in the case of the secondary (diphenyl) hydrazones. At this stage IR showed the reaction had gone to completion (see later), with the metalating reagent, $\text{PhCH}_2\text{Mn}(\text{CO})_5$, completely consumed. Straightforward workup followed by recrystallisation (with the exception of the product of benzaldehyde phenylhydrazone, which is an oil at ambient temperatures) gave a good yield of the expected orthomanganated adduct. Each was fully characterised by NMR, IR, elemental analysis and in the case of the orthomanganated derivative of acetophenone phenylhydrazone, a single crystal X-ray structure determination.

A complex such as that shown previously in Figure 2.11 above, was not detected at any stage in the reaction procedure. Presumably this is due to the relatively low abundance of the *anti*-isomer and the likely lower stability of the resultant compound. It was therefore concluded that the 'crude' hydrazones produced, without significant purification (i.e. removal of the *anti* impurity), are suitable for cyclometalation reactions.

Isomers of type **(B)** (Figure 2.12), were also not detected during any stage of the reaction procedure.

A summary of the starting reagent hydrazone and subsequent metalated product, along with a physical description, yield and IR data is given in Table 2.1 (overleaf). A related imine prepared by Bruce *et al.*⁵ and Samad³ is also shown, for comparison.

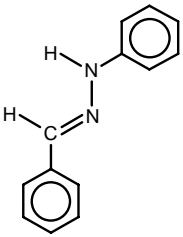
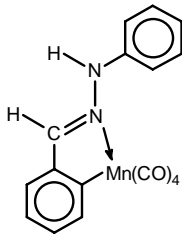
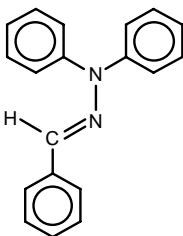
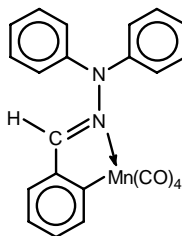
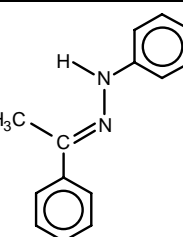
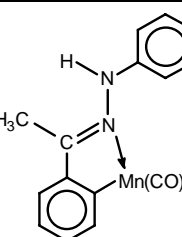
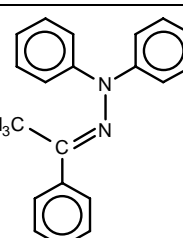
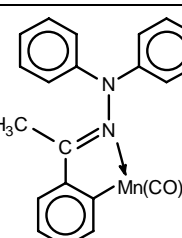
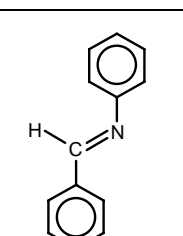
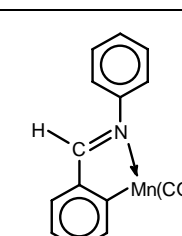
Initially one may be somewhat cautious of the lability of the hydrogen in the N-H group present in the case of the primary phenylhydrazones, which could potentially interact unfavourably with the $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and hence inhibit cyclometalation. However, this was found to not be of great consequence with high yields recorded for all reactions carried out.

Once metalated, the geometry of the hydrazone should be locked in the *syn* conformation, with *syn* to *anti* interconversion no longer a possibility.

Decomposition of the orthomanganated primary arylhydrazones (**6**) and (**7**) via tautomerism/autoxidation was not observed. The most likely explanation for this is that due to the delocalisation of the C=N double bond, the site is less susceptible to substitution and rearrangement reactions.

Interestingly the primary arylhydrazones, (**6**) and (**7**), yielded orange compounds, with the secondary arylhydrazones, (**8**) and (**9**), producing bright yellow solids - both systems would have been expected to be electronically similar. Of relevance

Table 2.1 Summary of Reaction Products of Arylhydrazones of Benzaldehyde and Acetophenone with $\text{PhCH}_2\text{Mn}(\text{CO})_5$

Reagent Hydrazone	Product	Yield and Physical Description of Product	Product IR $\nu(\text{M-CO}) \text{ cm}^{-1}$ (heptane)
 <p>(2)</p>	 <p>(6)</p>	77% Dark orange viscous oil	2077 (m) 1994 (s) 1985 (vs) 1947 (s)
 <p>(3)</p>	 <p>(8)</p>	83% Bright yellow crystals	2074 (m) 1985 (vs) 1950 (s)
 <p>(4)</p>	 <p>(7)</p>	87% Dark orange crystals	2071 (m) 1988 (s) 1980 (vs) 1947 (s)
 <p>(5)</p>	 <p>(9)</p>	86% Bright yellow crystals	2071 (m) 1988 (s) 1980 (vs) 1947 (s)
		86% pale orange crystals	2070 (s) 1982 (s) 1945 (m)

here may be the conformation of the -NHPh or -NPh₂ fragments with respect to the rest of the molecule. Attempts were made to assess the preferred angles using molecular modelling, but unfortunately the current version of the software did not contain data concerning N-N single bonds, and thus the structure could not be solved by this method.

The prediction for the $\nu(\text{CO})$ region of the spectrum for a *cis*-L₂M(CO)₄ group, is four bands. These bands are always well resolved from that of the orthomanganating reagent, benzylpentacarbonylmanganese (PhCH₂Mn(CO)₅), and from the usual reaction by-product, decacarbonyldimanganese (Mn₂(CO)₁₀). This allows the reaction progress to be conveniently followed spectroscopically by periodically monitoring the carbonyl region.

All of the cyclometalated hydrazones shown above, exhibited these four absorptions in the metal carbonyl region (1800 - 2200 cm⁻¹), with the exception of **(8)**. The IR spectra showed a fairly typical orthomanganated metal carbonyl pattern, with the usual medium intensity band at about 2075 cm⁻¹, two very strong absorbances just below 2000 cm⁻¹, and a further strong band around 1940 cm⁻¹. This is somewhat different from the carbonyl IR data for orthomanganated acetophenones, where the usual pattern is only three observed absorbances, with the predicted fourth not generally resolved, purely by coincidence, around 2000 cm⁻¹. This was also the case for **(8)**, and in fact also for the orthometalated aryl imine although the reason for this is not clear, since **(8)** at least, should have a very similar spectrum to **(6)** on electronic grounds. The acetophenone systems both had identical IR $\nu(\text{CO})$ spectra.

Within the substantial range of orthomanganated compounds prepared with various electron donors, no obvious trend has been noted in the positions of the metal carbonyl stretching frequencies⁶.

The ¹³C NMR chemical shifts of the Mn-C and C=N (Table 2.2) for the orthomanganated arylhydrazones of benzaldehyde and acetophenone are entirely consistent with those of the manganated imines prepared by Samad³ (**10**) and Cooney⁶. Clearly the CH₃ moiety in the acetophenone systems **(7)** and **(9)**, has the effect of deshielding the imino carbon, pushing the resonance further downfield.

Table 2.2: Comparison of ^{13}C NMR Data for Compounds With $\text{C}=\text{N}$ as Part of the Metallocycle

Compound	δ (ppm) of $\underline{\text{C}}\text{-Mn}^*$	δ (ppm) of $\underline{\text{C}}=\text{N}^*$
(6)	180.0	170.9
(7)	186.9	180.4
(8)	181.7	173.6
(9)	188.7	182.9
(10) ³	184.3	176.5

* For assignment of NMR spectra, see Appendix I.

2.2.2.1.1 X-Ray Crystal Structure of $\eta^2\text{-2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7)}$

The crystal structure of $\eta^2\text{-2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7)}$ was determined to fully characterise the reaction product of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ with acetophenone phenylhydrazone (4), to examine the absolute geometry of the compound, and for comparison with related systems.

Results of Preliminary Studies

Orange rectangular blocks were obtained by recrystallisation from chloroform. Preliminary precession photography indicated monoclinic symmetry, with systematic absences implying the space group was $\text{P2}_1/\text{c}$, which was later confirmed by successful refinement.

Data Collection

Intensity data were collected on an Nicolet R3 automatic four-circle diffractometer at the University of Canterbury, using a crystal of dimension $0.48 \times 0.46 \times 0.16$ mm, with monochromated $\text{Mo-K}\alpha$ X-rays ($\lambda = 0.71073 \text{ \AA}$).

Crystal Data:Formula: C₁₈H₁₃N₂O₄MnM_r = 376.24

Crystal class = monoclinic

Space group = P2₁/cUnit cell dimensions: a = 10.878(2) Å, b = 8.712(2) Å, c = 17.765(4) Å
β = 93.78(3)°U = 1679.9(6) Å³Density (calculated) = 1.488 g cm⁻³

Z = 4

F(000) = 768

μ(Mo-Kα) = 8.11 cm⁻¹

A total of 2333 reflections in the range $0^\circ < 2\theta < 45^\circ$ was collected at 130(2) K, of which 2197 were unique. These were subsequently corrected for Lorentz effects, polarisation effects, and for linear absorption by a Ψ scan method ($T_{\max, \min} = 0.79, 0.69$).

Solution and Refinement

All non-hydrogen atom positions were located by the TREF direct methods option of SHELXS-86. In the final cycle of the full-matrix least-squares refinement based on F^2 using SHELXL-93, all non-hydrogen atoms were assigned anisotropic temperature factors, with all hydrogen atom positions determined by calculation. The refinement converged with $R_1 = 0.0317$ for 1838 data with $I \geq 2\sigma(I)$, 0.0430 for all data; $wR_2 = 0.0775$, and $GoF = 1.058$.

No parameter shifted by more than 0.000σ in the final cycle, and the final difference map showed no peaks or troughs of electron density greater than $+0.37$ and -0.23 e Å⁻³ respectively.

Selected bond lengths and angles are given in Tables 2.3 and 2.4 (estimated standard deviations in the parentheses). Tables containing complete bond lengths and angles, final positional parameters, thermal parameters and calculated H-atom positions are presented in Appendix II.

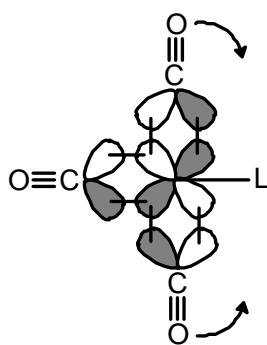
Perspective and side views of the final structure are illustrated in Figure 2.13 and Figure 2.14, along with the atom labelling scheme.

Discussion of the Structure

The structure confirms the expected orthomanganated product (**7**). The metallocycle is analogous to the cyclometalated imine (**14**) structure solved by Cooney⁶ and the orthomanganated hydrazone (**1**) published by Solans and Font-Altaba¹⁰.

As is normal with cyclomanganated compounds, the central metal is co-ordinated in a distorted octahedral arrangement, with the bidentate ligand and two carbonyls in the equatorial plane, the other two carbonyls occupying the remaining axial positions. The main distortion is the C(11)-Mn-N(1) bite angle, which in this case is $78.5(1)^\circ$, so deviating by 11.6° from a regular octahedron. This is due to the geometrical constraint set by the ligand, whose bonds have insufficient flexibility to adopt the 90° angle required for regular octahedral arrangement.

The C(2)-Mn-C(3) angle is not linear at $172.1(1)^\circ$, with the two axial carbonyls bending away from C(4) and toward C(11), as is clearly visible in the side view



of (**7**), Figure 2.14. This observation is well understood. The axial carbonyls compete for electron density with those occupying the equatorial position, as shown in the diagram to the left. However the σ -bonded chelate ligand, L, does not have as significant d-orbital interaction, so the 'right' half (that nearest the chelated ligand) has more electron density available. In order to utilise this, the axial carbonyls tend to

bend towards the extra density, thus maximising $d\pi$ - $p\pi$ overlap.

The metallocycle is essentially planar (with no atom deviating from the least squares plane by more than $0.051(2)$ Å, for N(1)) and is coplanar with the fused phenyl ring. The dihedral angle, with respect to the chelate ring, of the anilino

Figure 2.13: Perspective View of η^2 -2-[1-(N-phenylhydrazono)ethyl]-phenylethyltetraacarbonylmanganese (7)

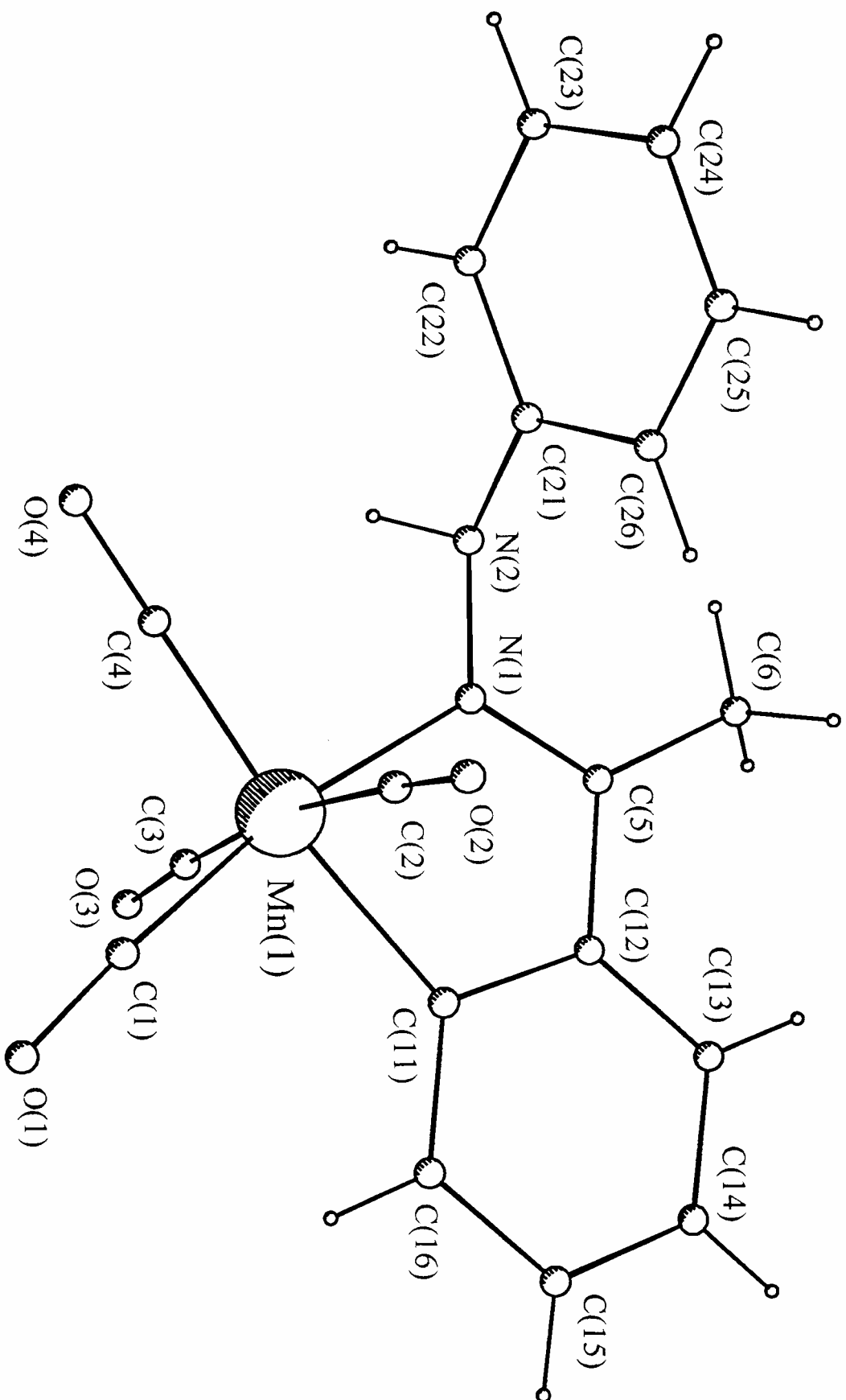


Figure 2.14: Side View of η^2 -2-[1-(N-phenylhydrazono)ethyl]-phenyltetraacarbonylmanganese (7)

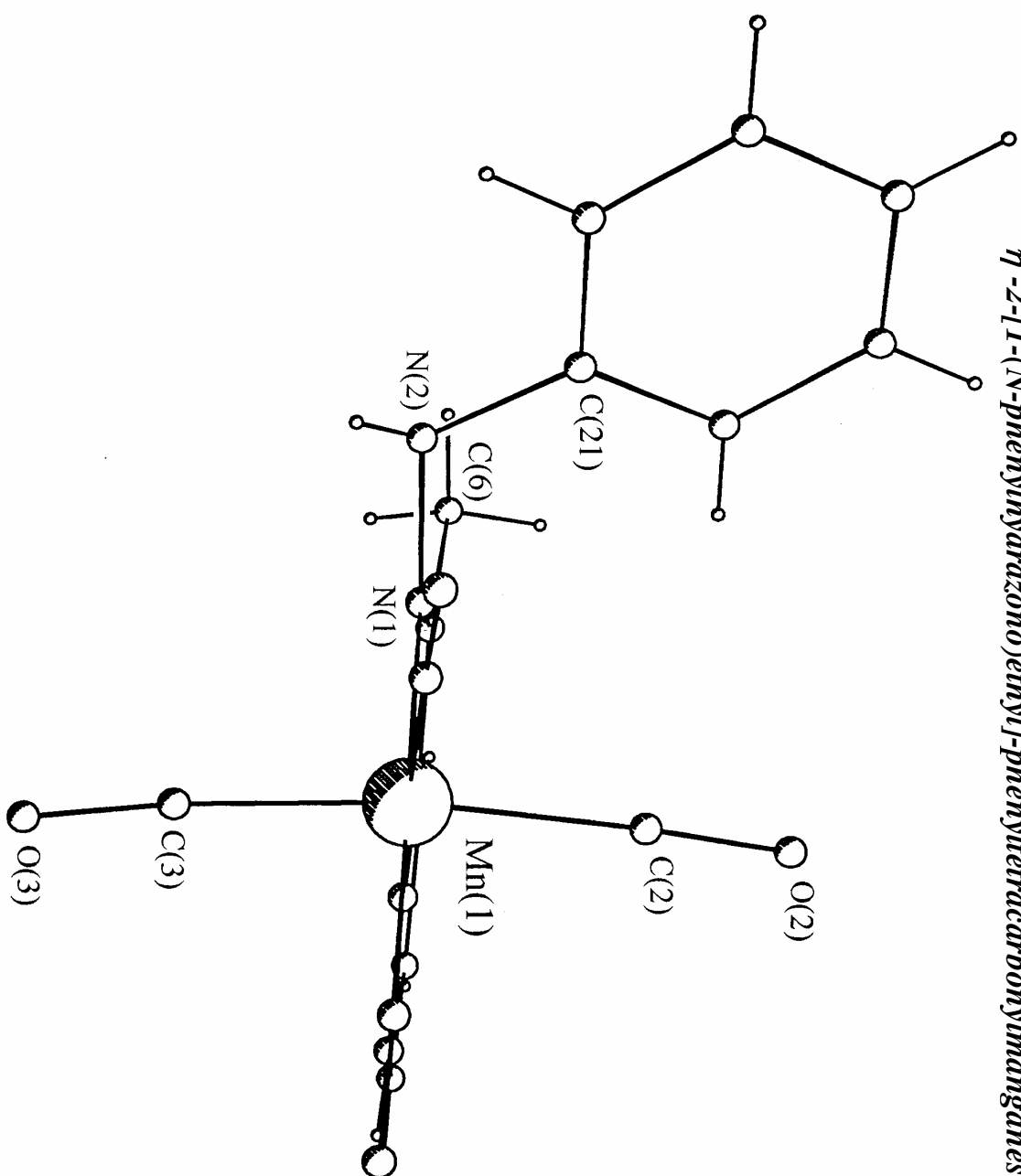


Table 2.3: Selected Bond Lengths for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarboxymanganese (7)

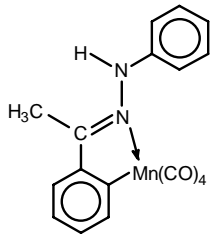
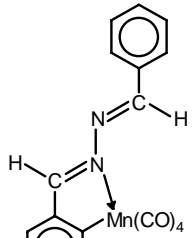
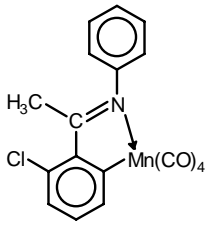
Bond	Length (Å)
Mn(1)-C(1)	1.806(3)
Mn(1)-C(2)	1.881(3)
Mn(1)-C(3)	1.830(3)
Mn(1)-C(4)	1.851(3)
Mn-N(1)	2.053(2)
Mn-C(11)	2.058(3)
C(11)-C(12)	1.416(4)
C(12)-C(5)	1.469(4)
C(5)-N(1)	1.303(4)
N(1)-N(2)	1.427(3)
N(2)-C(21)	1.424(4)

Table 2.4: Bond Angles for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarboxymanganese (7)

Bonds	Angle (degrees)
N(1)-Mn(1)-C(11)	78.45(10)
C(12)-C(11)-Mn(1)	113.2(2)
C(11)-C(12)-C(5)	115.6(2)
C(12)-C(5)-N(1)	113.3(2)
C(5)-N(1)-Mn(1)	119.2(2)
C(5)-N(1)-N(2)	116.4(2)
C(21)-N(2)-N(1)	117.3(2)
C(12)-C(5)-C(6)	122.4(3)
N(1)-C(5)-C(6)	124.3(3)
C(13)-C(12)-C(5)	122.5(3)

group is $76.86(8)^\circ$. This is much larger than the dihedral angle of $21.40(5)^\circ$ for the phenyl ring reported by Cooney for **(14)**. The two phenyl rings are both planar, as expected.

Table 2.5: Comparison of Selected Bond Lengths (\AA) of **(7) With Those of Related Systems**

Bond	 (7)	 (1) ¹⁰	 (14) ⁶
Mn-N(1)	2.053(2)	2.120(5)	2.041(2)
Mn-C(11)	2.058(3)	2.068(5)	2.040(2)
C(11)-C(12)	1.416(4)	1.389(9)	1.422(3)
C(12)-C(5)	1.469(4)	1.446(9)	1.477(3)
C(5)-N(1)	1.303(4)	1.295(8)	1.300(3)
N(1)-N(2)	1.427(3)	1.393(6)	NA

Referring to Table 2.5, it is clear that there are some large differences between the structure of **(7)** and those of the similar compounds, the most notable being the Mn-N bond distance which is considerably shorter in **(7)** than in the closely related compound **(1)**. The reason is not entirely clear, since the metallocycle in **(1)** is very similar to both **(7)** and **(14)**. A possible explanation may lie in the increased delocalisation available for this compound. Clearly **(7)** is much more closely related to **(14)** which has very similar bond lengths (and angles), the distinguishing feature is the Mn-N bond distance which is slightly longer for the hydrazone system, probably resulting from a lowering of electron density about the coordinating nitrogen due to the electronegative pull of the second nitrogen.

2.2.2.3 Arylhydrazones of Cyclohexanone

In a deliberate effort to produce a compound similar to isomer **(B)** in Figure 2.12, cyclohexanone was used instead of the aryl carbonyl compounds. The possible reaction products that could potentially arise are presented in Figure 2.15, where R = H, Ph.

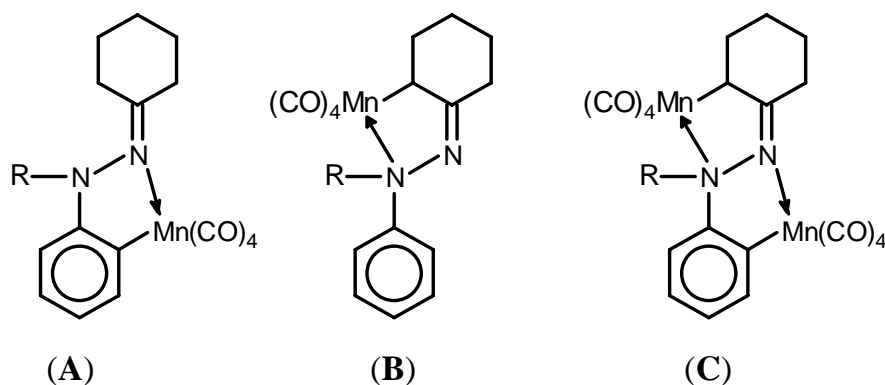


Figure 2.15

However, **(B)** and **(C)** are highly unlikely due to the unreactive nature of sp^3 hybridised carbon atoms toward metalation, making the **(A)** isomer the most favourable and hence likely product.

When cyclohexane diphenylhydrazone (**12**) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ were dissolved in heptane and refluxed for a few hours under nitrogen, the solution was observed to turn deep yellow, clearly indicating a reaction. At completion, standard work-up followed by recrystallisation from petroleum spirit, gave a good yield (94%) of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetra-carbonylmanganese (**13**). The expected isomer **(A)** was the only product detected during the reaction procedure. The yellow product proved to be easily handled and air stable, and was shown by IR, NMR, elemental analysis and X-ray crystal structure to be **(13)**.

The IR spectrum was markedly different from that of the benzaldehyde and acetophenone systems (Table 2.1). The separation between the central two strong absorbances for **(13)** was 14 cm^{-1} (*cf.* the largest separation for the orthomanganated aryl carbonyl hydrazones of 8 cm^{-1} for **(6)**). In addition, the lowest energy absorbance of 1940 cm^{-1} is considerably lower than for the other

metalated hydrazone compounds prepared. The highest energy band at 2073 cm^{-1} is not markedly different from that of other manganated hydrazones.

A comparison of the ^{13}C NMR spectra of (**13**), with those of the previously discussed arylhydrazones (Table 2.1), shows a major difference in the $\text{C}=\text{N}$ moiety, that being a much larger chemical shift [(CDCl_3) 191.7 ppm] in the case of (**13**). This can be attributed to the expected considerable drop in electron density on the coordinated nitrogen, giving rise to significant deshielding of the associated carbon. The chemical shift of the $\text{C}-\text{Mn}$ carbon (160.6 ppm) is also a prominent feature of (**13**), which is considerably lower than those found for the other prepared hydrazones and those reported for the orthomanganated imines and indeed orthomanganated aryl ketones. This is possibly due to the absence of π -delocalisation in (**13**), although this cannot be verified due to the lack of available NMR data on cyclometalated compounds of this type.

When the same reaction was attempted with the primary arylhydrazone (**11**) no metalated product could be isolated, although there was a strong indication that the expected cyclometalation did occur, with the IR spectrum of the crude reaction mixture showing absorbances (amongst numerous others) at $\nu(\text{CO})$ (heptane) 2076, 1993, 1978 and 1938 cm^{-1} , which by comparison with the IR spectra of (**13**) ($\nu(\text{CO})$ (heptane) 1973, 1991, 1977 and 1940 cm^{-1}), suggests an analogous product. Presumably the compound was so air sensitive that it did not survive normal work-up procedures. In addition, the complexity of the carbonyl region of the IR spectrum, indicates the reaction did not proceed cleanly. Only $\text{Mn}_2(\text{CO})_{10}$ and an uncharacterised orange oil that did not contain the manganese carbonyl functionality were isolated after work-up.

2.2.2.3.1 X-Ray Crystal Structure of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonyl manganese (13**)**

The crystal structure of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (**13**) was determined to fully characterise the reaction product of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ and cyclohexanone diphenylhydrazone (**12**). A

crystal structure of a cyclometalated compound of manganese involving a N-N single bond as part of the metallocyclic ring had not been previously reported.

Results of Preliminary Studies

Yellow rectangular blocks of (**13**) were obtained on crystallisation by vapour diffusion of pentane into a saturated diethylether solution of (**13**) at 4 °C.

Preliminary precession photography indicated monoclinic symmetry, and the space group was determined to be either P2/n or Pn, the latter proving correct by successful refinement.

Data Collection

Intensity data were collected on an Enraf-Nonius CAD4 automatic four-circle diffractometer at the University of Auckland, using a crystal of dimensions 0.57 x 0.47 x 0.40 mm, with Mo-K α monochromated X-rays ($\lambda = 0.71069$).

Crystal Data:

Formula C₂₂H₁₉N₂O₄Mn

M_r = 430.33

Crystal class = monoclinic

Space group = Pn

Unit cell dimensions: a = 10.529(2) Å, B = 17.959(3) Å, C = 10.924(2) Å
 $\beta = 94.65(2)^\circ$

U = 2058.8(6) Å³

Density (calculated) = 1.388 g cm⁻³

Z = 4

F(000) = 888

$\mu(\text{Mo-K}\alpha) = 6.71 \text{ cm}^{-1}$

A total of 3897 reflections in the range $1^\circ < \theta < 25^\circ$ was collected at 293(2) K, of which 3816 were unique. These were subsequently corrected for Lorentz effects, polarisation effects, and for linear absorption by a Ψ scan method ($T_{\text{max, min}} = 1.00, 0.96$).

Solution and Refinement

The structure was solved using the TREF direct methods option of SHELXS-86, and the remaining non-hydrogen atoms were located in subsequent difference maps. Full-matrix least-squares refinement was performed on F^2 using SHELXL-93. All non-hydrogen atoms were assigned anisotropic temperature factors in the final cycle, with hydrogen atom positions calculated. The refinement converged with $R_1 = 0.0332$ for 3660 data with $I \geq 2\sigma(I)$ and 0.0356 for all data, $wR_2 = 0.0891$ and $GoF = 1.054$.

No parameter shifted by more than 0.000σ in the final cycle. The final difference map showed residual electron density of no greater than 0.54 and $-0.44 \text{ e } \text{\AA}^{-3}$ respectively.

The Flack x parameter refined to a value of $-0.0042(0.0146)$ indicating the correct polarity had been chosen.

Perspective and side views of the two independent molecules in the crystal are shown in Figures 2.16a/b and 2.17 respectively along with the atom labelling scheme. Selected bond lengths and angles for both independent molecules are presented in Tables 2.6 and 2.7 (estimated standard deviations given in parentheses). Tables of complete bond lengths and angles, final positional parameters, thermal parameters, and calculated H-atom positions are presented in Appendix IV.

Discussion of the Structure

On solving the structure it was immediately evident that the orthomangantion of (**12**) had yielded the expected product, with the cyclometalated ring containing both nitrogen atoms of the hydrazone functionality.

The space group gives rise to two independent molecules in the unit cell, allowing independent determination of each parameter, so that any crystal packing distortions become evident. The molecules are essentially identical, the

Figure 2.16a: Perspective View of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetraacarbonylmanganese (13), 'Molecule 1'

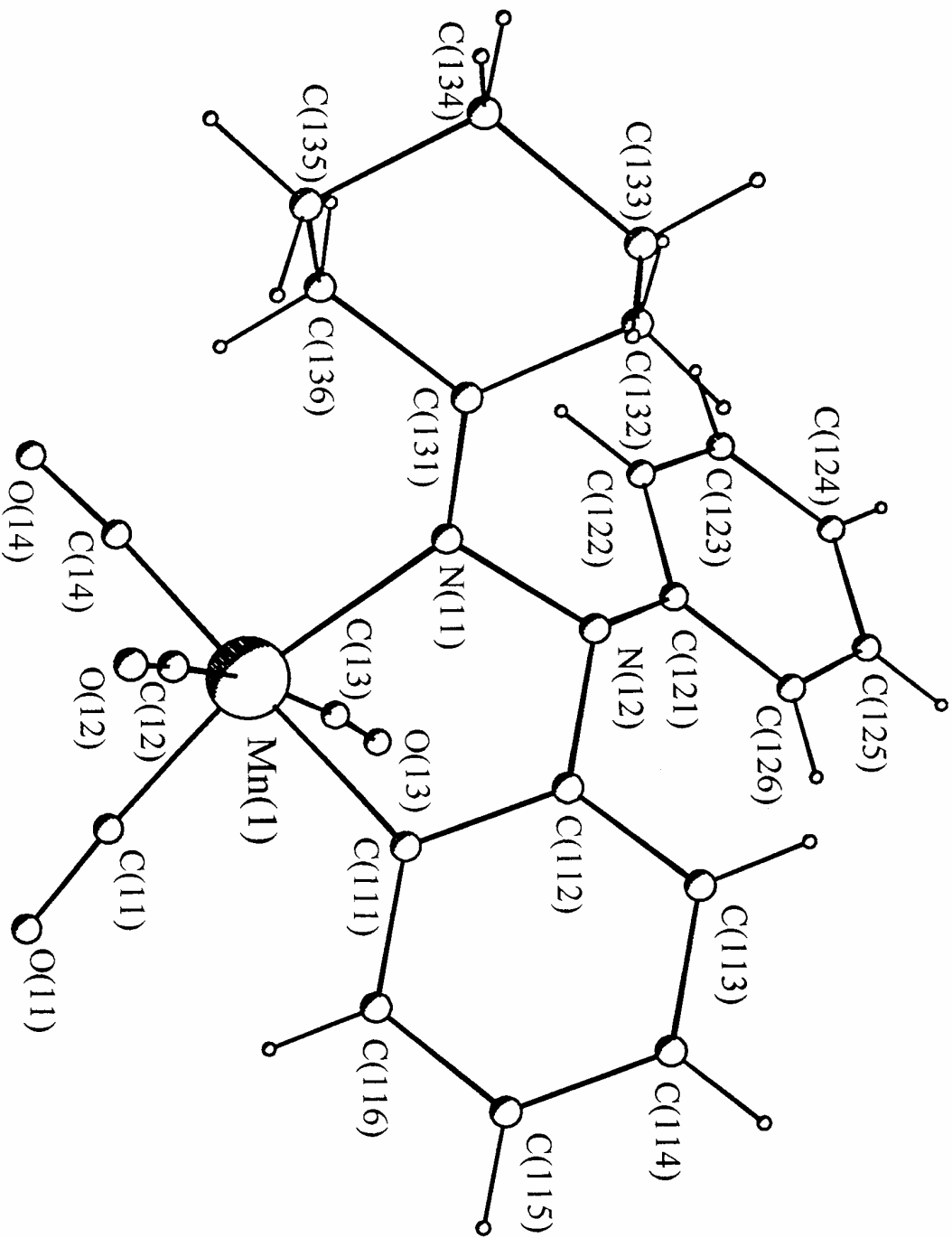


Figure 2.16b: Perspective View of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13), 'Molecule 2'

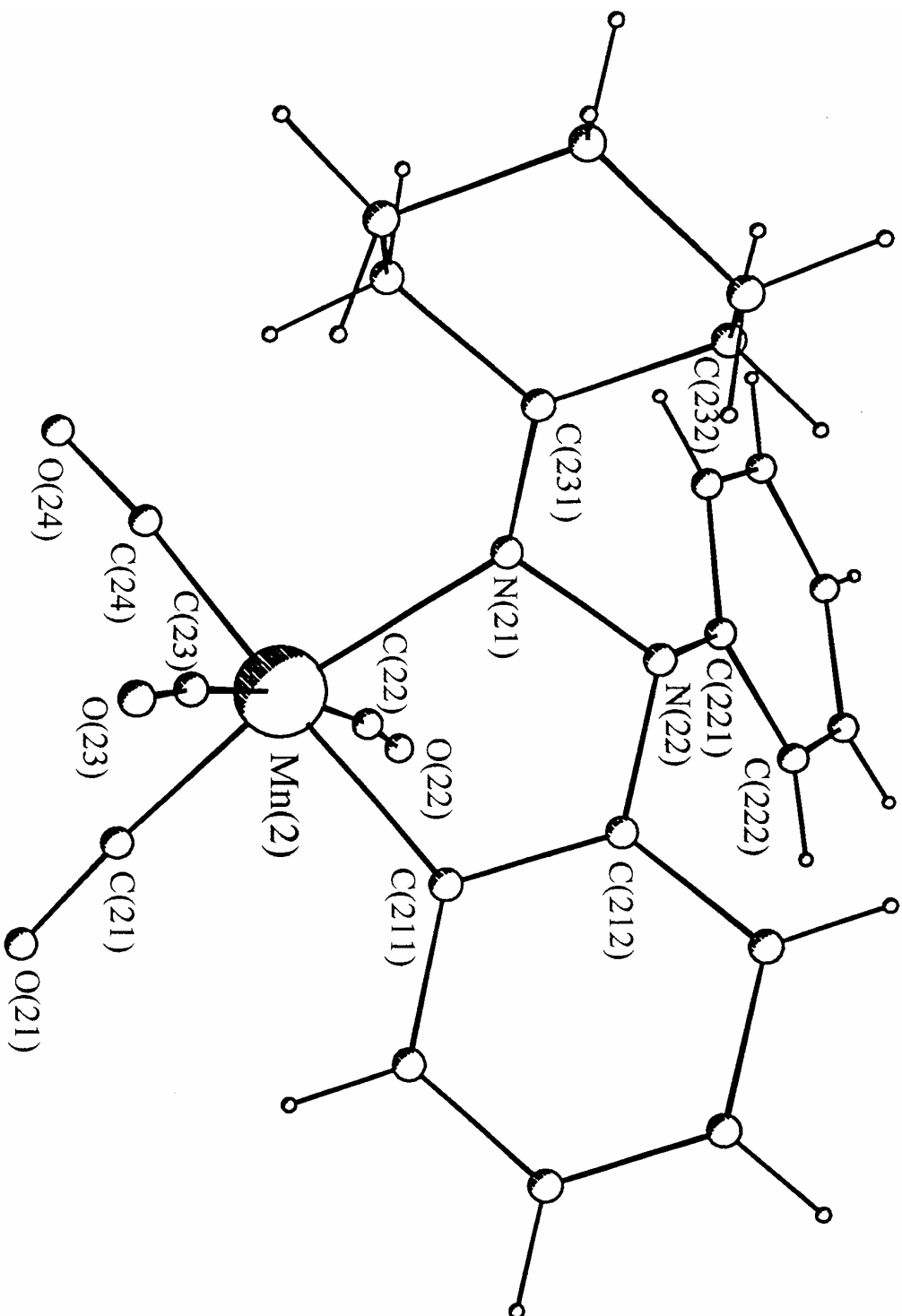


Figure 2.17: Side View of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)-phenyltetracarbonylmanganese (13), 'Molecule 1'

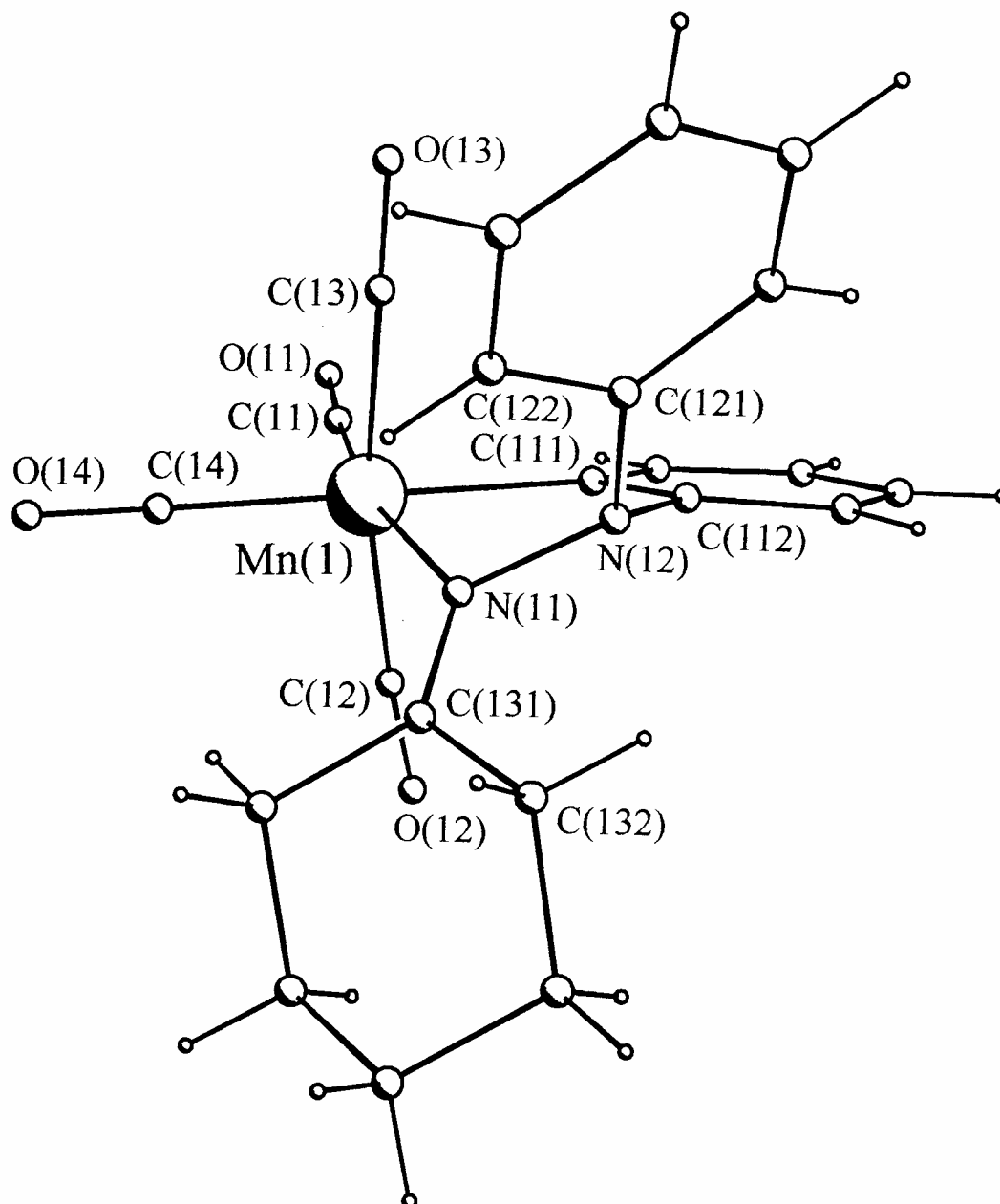


Table 2.6: Selected Bond Lengths for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

Bond	Length (Å) Molecule 1	Length (Å) Molecule 2
Mn(1)-C(11)	1.796(4)	1.798(4)
Mn(1)-C(12)	1.865(4)	1.867(4)
Mn(1)-C(13)	1.863(4)	1.863(4)
Mn(1)-C(14)	1.837(4)	1.842(4)
Mn-N(11)	2.096(3)	2.091(3)
Mn-C(111)	2.055(3)	2.056(4)
C(111)-C(112)	1.391(5)	1.380(6)
C(112)-N(12)	1.429(4)	1.428(5)
N(12)-N(11)	1.437(4)	1.453(4)
N(11)-C(131)	1.278(5)	1.276(5)
N(12)-C(121)	1.416(5)	1.437(5)

Table 2.7: Selected Bond Angles for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenyl hydrazino)phenyltetracarbonylmanganese (13)

Bond	Angle (degrees) Molecule 1	Angle (degrees) Molecule 2
N(11)-Mn(1)-C(111)	77.7(1)	77.4(1)
C(112)-C(111)-Mn(1)	113.0(2)	112.9(3)
C(111)-C(112)-N(12)	117.6(3)	118.1(3)
C(112)-N(12)-N(11)	108.5(3)	113.1(3)
N(12)-N(11)-Mn(1)	110.3(2)	109.7(2)
C(112)-N(12)-C(121)	122.5(3)	118.7(3)
N(12)-N(11)-C(131)	115.0(3)	115.2(3)

major difference being the dihedral angle between the main chelate ring and the second, non-coordinated phenyl ring, which is somewhat smaller for ‘molecule 1’ at $54.1(1)^\circ$, than for ‘molecule 2’ ($70.3(1)^\circ$). This difference is clearly visible when examining Figures 2.16a and 2.16b. The least-squares plane drawn through the cyclohexane ring for ‘molecule 1’ forms a dihedral angle of $80.2(1)^\circ$ with respect to the metallocycle, which is similar to that for ‘molecule 2’, $76.9(2)^\circ$. Bond lengths and angles are essentially the same for both molecules (Tables 2.6 and 2.7), the largest differences being for C(112)-N(12)-N(11) and C(112)-N(12)-C(121), showing these are most susceptible to crystal packing forces. Subsequent discussion is restricted to ‘molecule 1’.

The most notable structural feature is that the metallocycle is not planar, in contrast to the usual case with orthomanganated ketones and imines, but rather is puckered with the N(12) atom pushed above the metallocycle (least-squares plane) by $0.227(2) \text{ \AA}$, and the N(11) atom being $0.244(2) \text{ \AA}$ below. This is not surprising since the non-coordinated nitrogen, N(12), is sp^3 hybridised and so is not compatible with the preferred planar conformation of the sp^2 hybridised N(11) atom (compare with the structure of acetophenone phenylhydrazone where all carbon and nitrogen atoms in the metallocycle are sp^2 hybridised and the expected coplanar conformation is adopted).

As was the case for (7), the manganese atom is coordinated in a somewhat distorted octahedral configuration, the major distortion being the C(111)-Mn-N(11) bite angle of only $77.7(1)^\circ$, and the C(13)-Mn-C(12) angle of $169.6(2)^\circ$ which is substantially non-linear, for reasons discussed earlier for (7).

All four carbonyl substituents deviate slightly from linearity with angles of $176.3(4)^\circ$ and $176.1(4)^\circ$ for the two carbonyl ligands in the equatorial plane, and $175.7(3)^\circ$ and $175.4(4)^\circ$ for the axial carbonyls.

Both phenyl rings are planar, and the cyclohexyl group adopts the typical chair conformation as expected.

Comparing this structure with those species in Table 2.4, we can see that Mn-N bond length is longer (at $2.096(3) \text{ \AA}$) than in both (7) and (14), nearing the length

of the same bond in (1). The Mn-C_{aryl} distance of 2.055(3) Å is virtually identical to that of (7). The N-N bond, which here is part of the cyclometalated ring, at 1.437(4) Å is slightly longer than that of (1) and (7).

2.2.2.4 6-(4-Chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone

The only example of an orthomanganated cyclic hydrazone was given in Figure 2.5. It was of interest to see if the novel hydrazone below (Figure 2.18), could also be cyclometalated in spite of the presence of the alcohol functionality which could potentially react unfavourably with the metalating reagent (PhCH₂Mn(CO)₅).

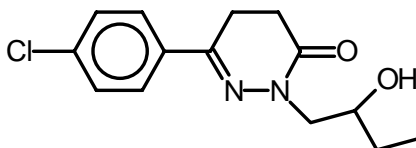


Figure 2.18

Although a reaction was clearly observed to take place, no metalated products could be isolated, presumably due to an unfavourable interaction by the alcohol group.

2.3 N-Nitrosamines

2.3.1 General

Nitrosamines are generally toxic and highly carcinogenic substances that should be handled with care at all times.

N-Nitrosamines can be readily prepared by reacting primary or secondary amines with sodium nitrite, Equation 2.4.



Equation 2.4

The nitrogen-oxygen “double bond” is delocalised over the two nitrogen atoms to give rise to two contributing canonical forms (I) and (II), represented by the resultant ‘overall’ structure (III). This is illustrated below (Figure 2.19) for diphenylnitrosamine (15):

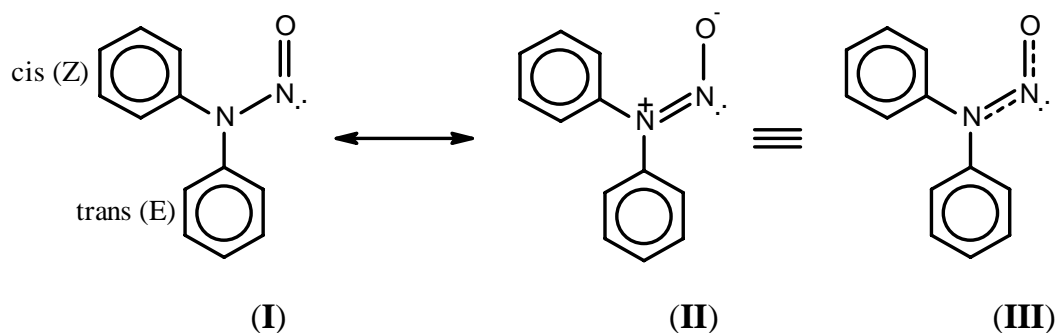


Figure 2.19

Evidence of this delocalisation can be easily observed in the ^{13}C NMR spectra of these compounds which, for the above example, gives 8 separate signals - implying that the two phenyl rings are not in an identical environment which would obviously be the case if the nitrogen-nitrogen bond was truly single. There is restricted rotation about the ‘N-N’ moiety, rendering each phenyl ring distinct. For a given position, the chemical shift of the trans group ($\delta_{(E)}$) is generally larger than the cis ($\delta_{(Z)}$)¹⁹.

2.3.2 Orthomanganation of Diphenylnitrosamine

To further study the reactivity of nitrogen donor groups toward *ortho* substitution to give manganese derivatives, the nitrosamine functionality is of interest due to the partial double bond that exists between the two nitrogen atoms - making them significantly different electronically to isomer (B) (Figure 2.12) of the hydrazone systems.

When diphenylnitrosamine was refluxed in heptane together with $\text{PhCH}_2\text{Mn}(\text{CO})_5$, the solution rapidly turned orange/brown. The reaction was complete after 30 minutes by IR. Standard workup followed by recrystallisation

from petroleum spirit gave a good yield (70%) of η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (**16**).

The compound was eventually fully characterised by IR, mass spectrometry and NMR although the latter was initially inconclusive. Elemental analysis also did not verify or support the proposed structure. The product was subsequently confirmed by single crystal X-ray structure analysis (see below).

The IR spectra of the metal carbonyl region is considerably different from the aryldiazones systems already discussed. The most notable distinctions are both the highest and lowest energy absorbances at 2084 cm⁻¹ and 1970 cm⁻¹ which are both substantially higher in wavenumber than those observed for the hydrazones. The spectra is in fact much more closely matched to the azobenzene system (discussed later), which is entirely in accord with the significant π -delocalisation present in the nitrosamine (and azobenzene) functionality.

2.3.2.1 X-Ray Crystal Structure of η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (16)

The crystal structure of η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese was determined to characterise the reaction product of PhCH₂Mn(CO)₅ and diphenylnitrosamine, since the elemental analysis and ¹³C NMR data (see later), were inconclusive. No crystal structures of any orthometalated compounds derived from nitrosamines have been previously reported.

Results of Preliminary Studies

Orange rosettes were obtained by crystallisation using vapour diffusion of pentane into a saturated dichloromethane solution of (**16**) at 4 °C. A fragment was cleaved from the cluster for analysis.

Preliminary precession photography indicated triclinic symmetry, so the space group was assumed to be P $\bar{1}$ which was confirmed by successful refinement.

Data Collection

Intensity data were collected using a Nicolet R3 automatic four-circle diffractometer at the University of Canterbury, using a crystal of dimensions 0.70 x 0.28 x 0.21 mm, with monochromated X-rays ($\lambda = 0.71073$). The crystal did not diffract well, so the data set and structural analysis are not as precise as usual.

Crystal Data:

Formula $C_{16}H_9N_2O_5Mn \cdot 0.25C_6H_6$ (discussed later)

$M_r = 383.72$

Crystal class = triclinic

Space group = $P\bar{1}$

Unit cell dimensions: $a = 9.677(7) \text{ \AA}$, $b = 11.550(12) \text{ \AA}$, $c = 17.53(3) \text{ \AA}$

$\alpha = 71.45(3)^\circ$, $\beta = 84.49(3)^\circ$, $\gamma = 88.08(3)^\circ$

$U = 1849(4) \text{ \AA}^3$

Density (calculated) = 1.378 g cm^{-3}

$Z = 4$

$F(000) = 778$

$\mu(\text{Mo-K}\alpha) = 7.42 \text{ cm}^{-1}$

A total of 6054 reflections in the range $2^\circ < \theta < 24^\circ$ was collected at 131(2) K, of which 5670 were unique. These were corrected for Lorentz effects, polarisation effects, and for linear absorption by a Ψ scan method ($T_{\text{max, min}} = 0.826, 0.706$). Of these, 2186 had $I > 2\sigma(I)$ and were used in all subsequent calculations.

Solution and Refinement

The structure was solved by using the TREF direct methods option of SHELXS-86. Full-matrix least-squares refinement was performed on F^2 using SHELXL-93. When both independent molecules had been located, residual electron density in the difference maps was apparent. This was modelled as a rigid hexagon of C atoms with site occupancy of 0.5. The identity of this was not clear from the X-Ray data. Non-hydrogen atoms could not be assigned anisotropic temperature factors due to the small number of "observed" data. Hydrogen atom positions were determined by calculation. The refinement converged with $R_1 = 0.119$ for

2186 data with $I \geq 2\sigma(I)$, 0.278 for all data; $wR_2 = 0.364$, and $GoF = 1.058$. These high R factors are attributed to the weak information collected, probably a result of substantial decomposition of the crystal prior to data acquisition.

No parameter shifted by more than 0.007σ in the final cycle. The final difference map showed no peaks or troughs of electron density greater than 0.97 and -0.64 $e \text{ \AA}^{-3}$ respectively.

Perspective and side views of one of the crystallographically independent molecules are shown in Figures 2.20 and 2.21, along with the atom labelling scheme. Selected bond lengths and angles for both the independent molecules are presented in Tables 2.8 and 2.9 (estimated standard deviations given in parentheses).

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

Discussion of the Structure

Notwithstanding the weak data, the structure was solved successfully. During this time it became apparent that the orthomanganation of (**15**) had in fact yielded the desired product, despite the unassignable NMR spectra, implying the latter must contain an inseparable impurity - presumably a result of decomposition.

Due to the poor quality of the data, the calculated bond angles and distances are not particularly precise, precluding definitive comments and detailed comparisons with other compounds. However, the primary reason for determining the structure, to ascertain the reaction product, was realised.

As was the case for the structure of (**12**), the space group ($P\bar{1}$) gives rise to two independent molecules in the unit cell. Bond length and angle data suggests the molecules are virtually identical, excluding dihedral angles.

Figure 2.20: Perspective View of η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyl-tetracarbonylmanganese (16), 'Molecule 1'

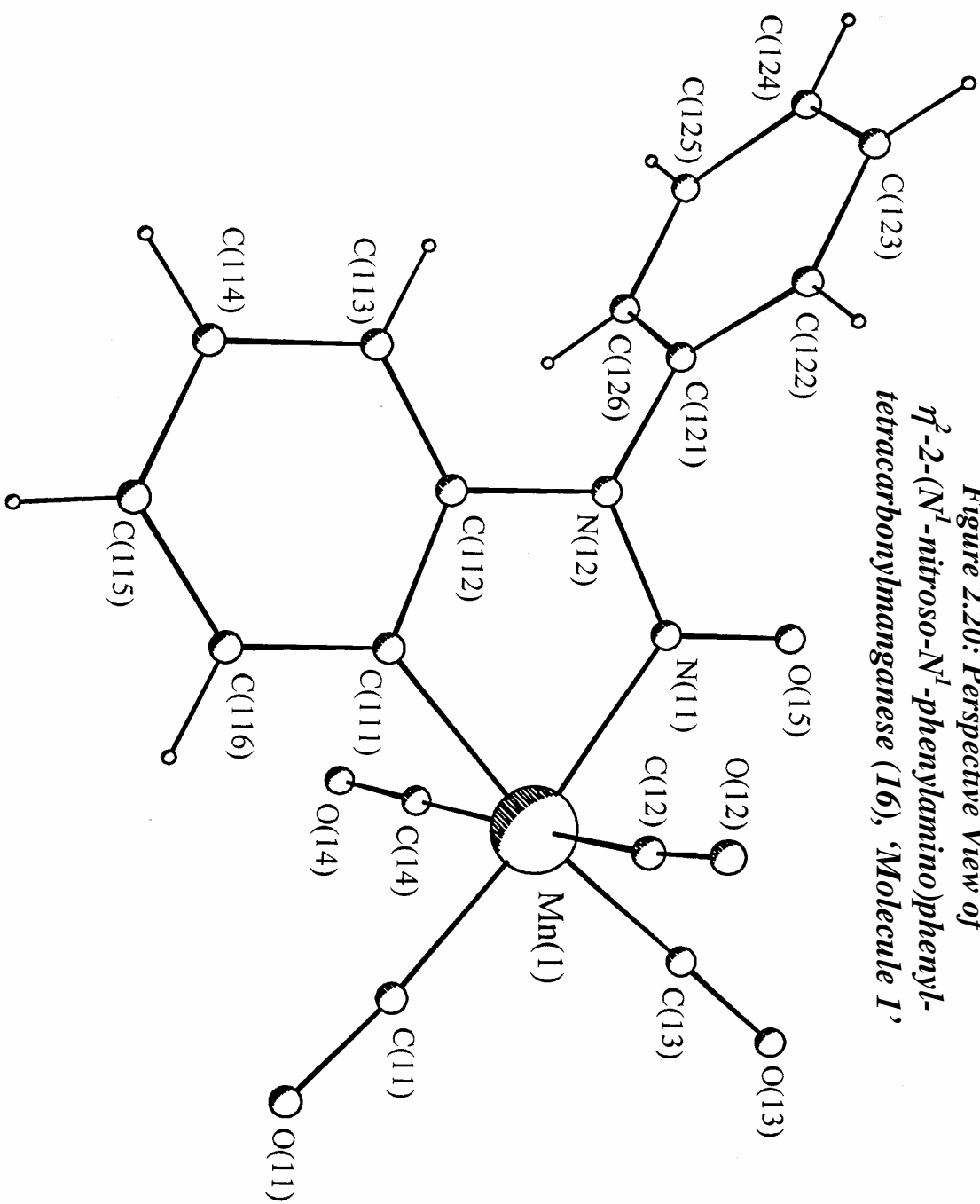


Figure 2.21: Side View of η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarboxylmanganese (16), 'Molecule 1'

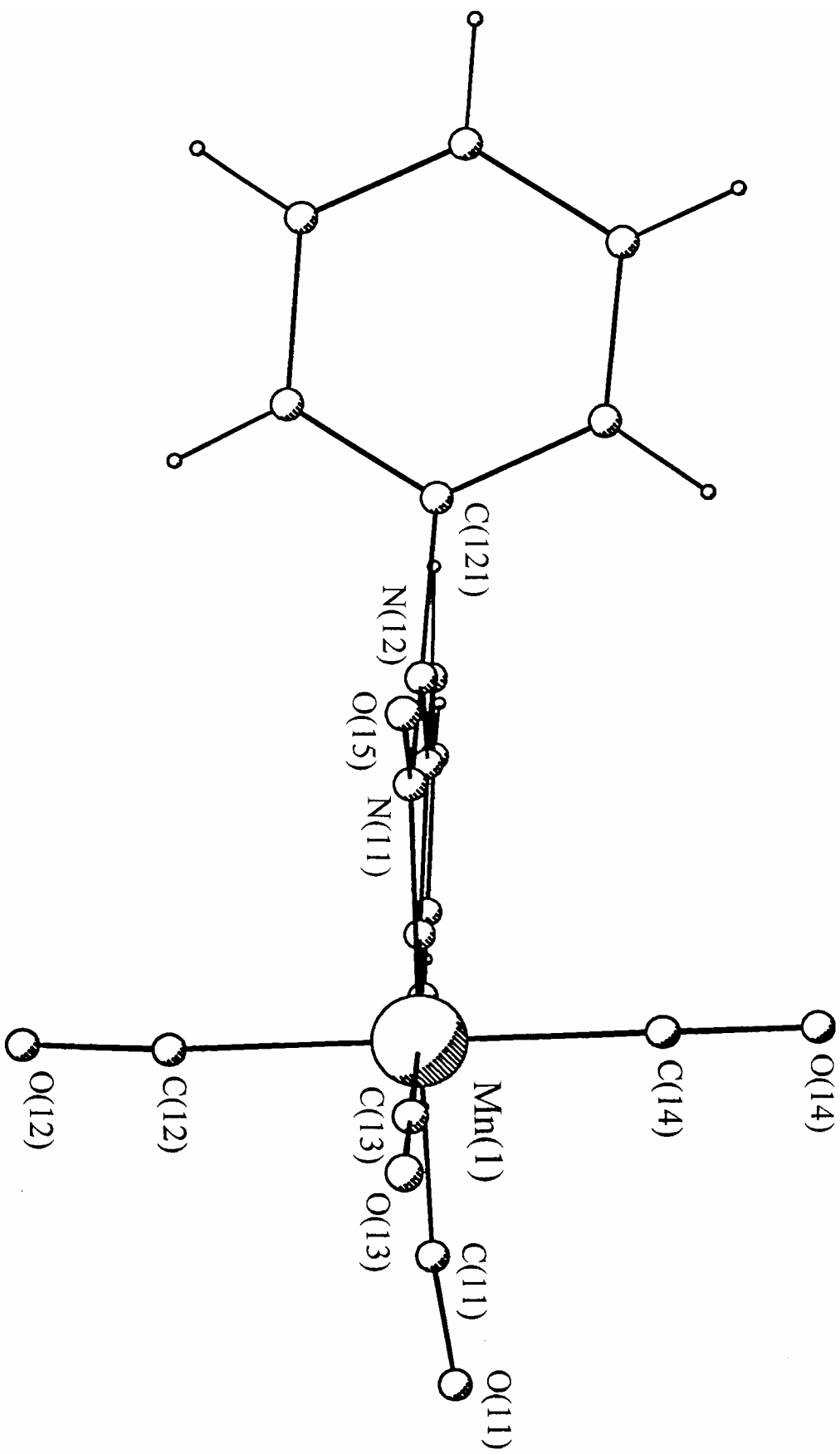


Table 2.8: Bond Lengths (Å) for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarbonylmanganese (16)

Bond	Length (Å) Molecule 1	Length (Å) Molecule 2
Mn(1)-C(11)	1.79(2)	1.77(2)
Mn(1)-C(12)	1.88(2)	1.85(2)
Mn(1)-C(13)	1.83(2)	1.86(2)
Mn(1)-C(14)	1.80(2)	1.82(2)
Mn-N(11)	1.999(14)	1.982(13)
Mn-C(111)	2.02(2)	2.045(14)
C(111)-C(112)	1.40(2)	1.37(2)
C(112)-N(12)	1.45(2)	1.44(2)
N(12)-N(11)	1.32(2)	1.33(2)
N(11)-O(15)	1.22(2)	1.24(2)
N(12)-C(121)	1.42(2)	1.43(2)

Table 2.9: Bond Angles (degrees) for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarbonylmanganese (16)

Bond	Angle (degrees) Molecule 1	Angle (degrees) Molecule 2
N(11)-Mn(1)-C(111)	79.9(6)	79.5(5)
C(112)-C(111)-Mn(1)	112.9(11)	113.2(10)
C(111)-C(112)-N(12)	115.3(14)	115.3(12)
C(112)-N(12)-N(11)	113.9(12)	114.3(12)
N(12)-N(11)-Mn(1)	117.7(10)	117.6(9)
C(112)-N(12)-C(121)	124.5(13)	123.5(12)
N(12)-N(11)-O(15)	116.3(13)	114.4(13)

The most notable structural feature is that the metallocycle is essentially planar, a somewhat unexpected finding since the non-coordinated nitrogen atom, N(12), is formally sp^3 hybridised, which by analogy with the structure of **(13)** should give rise to a puckered ring with the coordinated nitrogen, N(11), lying out of plane of the metallocycle.

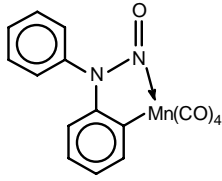
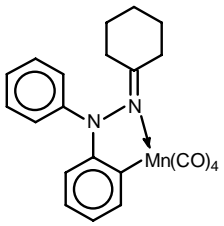
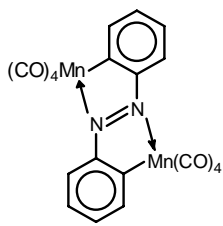
As was the case for **(7)** and **(13)** the manganese atom is coordinated in the usual distorted octahedral configuration, with the most notable distortion being a fairly typical C(111)-Mn-N(11) bite angle of $79.9(6)^\circ$, and the axial carbonyls C(14)-Mn-C(12) angle of $172.1(9)^\circ$.

Both phenyl rings are planar, with the non-metalated ring being virtually perpendicular to the metallocycle with a dihedral angle of $87.0(6)^\circ$ for ‘molecule 1’ and $81.2(5)^\circ$ for ‘molecule 2’.

Comparing this structure with those species in Table 2.5, we can see that Mn-N bond length at $2.00(1) \text{ \AA}$ is considerably shorter than in **(7)**, **(1)** and **(14)**.

A comparison of this structure with other manganese tetracarbonyl compounds containing two nitrogens as part of the metallocycle is given in Table 2.10.

Table 2.10: Comparison of Selected Bond Lengths (\AA) of **(16) With Those of Related Systems**

Bond	 (16)	 (13)	 (17) ¹²
Mn-N(11)	1.999(14)	2.096(3)	2.056(2)
Mn-C(111)	2.02(2)	2.055(3)	2.011(3)
C(111)-C(112)	1.40(2)	1.391(5)	Not given
C(112)-N(12)	1.45(2)	1.429(4)	Not given
N(12)-N(11)	1.32(2)	1.437(4)	1.308(5)

Clearly the Mn-N bond of (**16**) is shorter than that of related compounds. The other feature of note is the N-N bond length, which clearly is very short when compared to the true single bond in (**13**), nearing that of the double bond seen in (**17**). This, in addition to the fact the metallocycle is planar, strongly suggests significant π -delocalisation of electron density in the manganese ring.

After solving the structure, to give the molecule (**16**), residual electron density still remained in the final difference map. This was modelled in the analysis as 0.25 of a benzene ring, although at no stage was benzene involved in the reaction procedure or workup. The C₆ ring obviously belongs to some aromatic co-crystallised species. However, due to the already weak intensity data, the structure of this impurity could not be elucidated fully.

Careful re-examination of the ¹³C NMR spectrum of (**16**), and comparing this to spectra of likely impurities, made it clear that the extra signals were most likely due to either:

- N,N-diphenylhydrazine (Ph₂N-NH₂), which shows ¹³C NMR resonances at (22.49 MHz) (CDCl₃) δ 143.3 (*s*, C-1'), 129.3 (*d*, C-3',5'), 121.1 (*d*, C-4'), 117.9 (*d*, C-2'',6''). These are exactly co-incident with peaks observed in the spectrum of (**16**). Diphenylhydrazine is an intermediate in the synthesis of N,N-diphenylhydrazine from diphenylamine^{20a}.
- Diphenylamine, (Ph₂NH) which shows resonances in the ¹³C NMR spectra at (22.49 MHz) (CDCl₃) δ 143.1 (*s*, C-1'), 129.2 (*d*, C-3',5'), 120.9 (*d*, C-4'), 117.8 (*d*, C-2'',6''). These are also very similar to those observed in the product spectrum, although the correlation is not as close as those for diphenylhydrazine. Diphenylamine is the starting material in the synthesis of diphenylhydrazine, and is therefore a possible decomposition product.

Mass spectrometry showed a parent ion peak at 365 as expected for (**16**) MH⁺. A peak that could be attributed to diphenylhydrazine (M_r = 184.24) was absent from the spectra. However a peak at 170 was present which coincides with diphenylamine MH⁺ (M_r = 170.24). For this reason it was tentatively concluded that (**16**) decomposes to diphenylamine during workup of the product and/or during the NMR data acquisition period.

2.4 Azobenzenes

2.4.1 Orthomanganation of Azobenzene

Although an extensive number of metalated derivatives (including those of tetracarbonylmanganese) of various substituted azobenzenes have been prepared previously, comparatively few reactions of the cyclometalated compounds themselves have been carried out. It was therefore of interest to resurrect this substance, and examine its reactivity toward alkyne insertion (Chapter 3), so comparisons can be drawn between this and other N-donor systems.

One could expect two possible reaction products when dealing with the azobenzene system, monosubstituted (**18**) involving one $\text{Mn}(\text{CO})_4$, or disubstituted (**17**) (Figure 2.22) with two $\text{Mn}(\text{CO})_4$ groups - one on each phenyl ring.

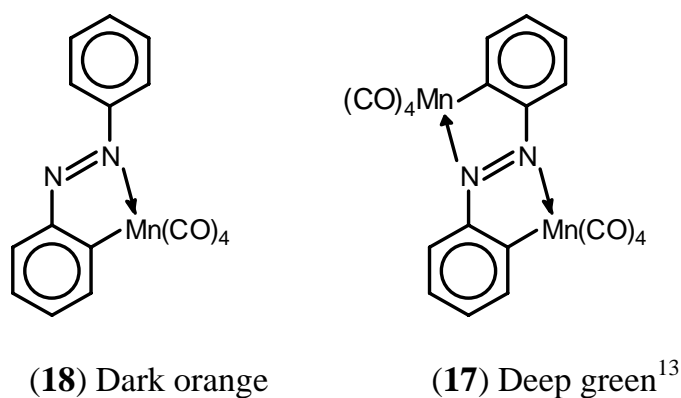


Figure 2.22

Bruce *et al*, reports that even when a 1:1 mixture of reactants (azobenzene and $\text{PhCH}_2\text{Mn}(\text{CO})_5$) is used, the binuclear complex (**17**) could be isolated¹².

In addition it was found that (**17**) reacts with azobenzene to give (**18**) in a greater than 60% yield¹². For this reason, equimolar amounts of starting materials (azobenzene and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in heptane) were refluxed for 2 hours (*cf.* 15 minutes used by Bruce), to maximise the yield of (**18**). During this time the reaction mixture was observed to become almost black in colour. Normal workup

afforded almost exclusively the orthomanganated derivative (**18**), with only trace quantities of (**17**) (characterised by a strong IR band at 2016 cm⁻¹) detected.

Table 2.11: Comparison of ¹³C NMR Data for Compounds With NN in the Metallocycle

Compound	δ (ppm) of <u>C</u> -Mn
(13)	160.6
(16)	156.4
(18)	180.5

Comparing the ¹³C NMR spectra of the metalated systems containing two nitrogen atoms in the metallocycle (Table 2.11), we can see that conjugation and/or the donating power of the coordinating nitrogen play an important role in the net chemical shift of the carbon directly bonded to the metal. The cyclohexanone diphenylhydrazone and diphenylnitrosamine adducts should have considerably less conjugation over the ring, whereas the azobenzene system will have significant delocalisation (all N and C atoms in the metallocycle are sp² hybridised). The ortho-carbon (C-2') of the non-metalated substrates (**13**), (**16**) and (**18**) all have very similar chemical shifts of 120.8, 119.6 and 122.8 ppm respectively.

2.5 Arylhydrazines

2.5.1 Orthomangantion of Arylhydrazines

No published accounts of tetracarbonylmanganane compounds of arylhydrazines are known, so it was of interest to examine the possibility of making metalated derivatives of these species, and determining the potential, if any, of the product(s) in organic synthesis.

The obvious first choice of an arylhydrazine to react with PhCH₂Mn(CO)₅, is phenylhydrazine. The most likely product is depicted in Figure 2.23.

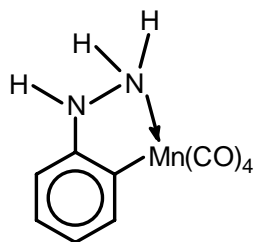


Figure 2.23

In light of the failure to isolate the orthomanganated product of cyclohexanone phenylhydrazone, which has an almost identical metallocycle, it was not surprising to discover that this product could not be isolated by the standard manganation route. An IR spectrum of the crude reaction mixture in CH_2Cl_2 exhibited multiple bands, including $\nu(\text{CO})$ 2082 (w), 2009 (s), 1998 (s) 1939 (m) cm^{-1} , characteristic of the $\text{Mn}(\text{CO})_4$ moiety, indicating that possibly an unstable cyclometalated product had formed.

Another reaction of an arylhydrazine was also attempted, namely N-acetyl-N-phenylhydrazine, which may be expected to afford the structure shown in Figure 2.23.

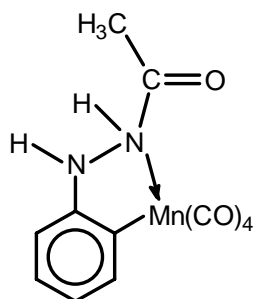


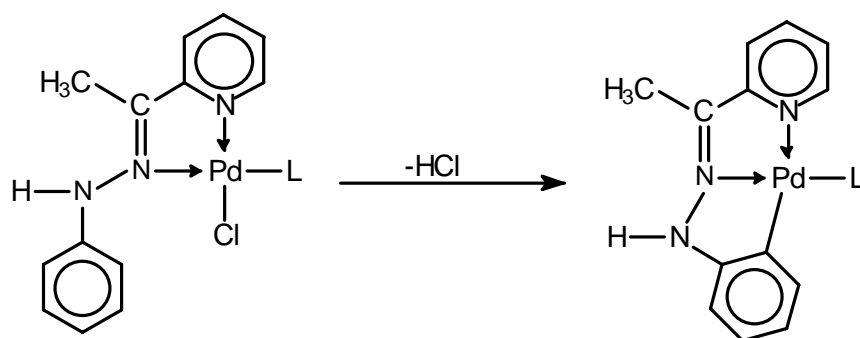
Figure 2.23

This also proved unsuccessful, with no evidence of any metalated product, with the exception of the observation that the reaction mixture became blood red in colour, a dubious indication of a successful cyclomanganation. When exposed to air, the solution instantly became brown suggesting decomposition. The IR spectrum of the carbonyl region revealed only $\text{Mn}_2(\text{CO})_{10}$.

The only example of an orthomanganated compound in the literature that contains the hydrazine functionality is the tricarbonyl species mentioned in the

Introduction (Figure 2.7), an unstable and air sensitive compound containing two $\text{Mn}(\text{CO})_3$ groups. Presumably having the N-H functionality as part of the metallocycle creates highly unstable orthomanganated adducts that to date have been characterised only by IR, although any labile N-H linkage can potentially interfere with the metalation process.

Examples of orthopalladated compounds of 2-acetylpyridine phenylhydrazones containing the N-H group as part of the metallocycle have however been prepared and characterised (including an X-ray crystal structure)⁸. The reaction scheme is shown in Equation 2.5:



Equation 2.5

The product was prepared in high yield and is not reported to have unusually low stability or air sensitivity.

2.6 Experimental Section

General experimental procedures, methods of assignment of NMR spectra, and instrumentation used are given in Appendix I.

2.6.1 Preparation of Benzylpentacarbonylmanganese

This was prepared following the standard method developed by Closson *et al*^{20, 21}.

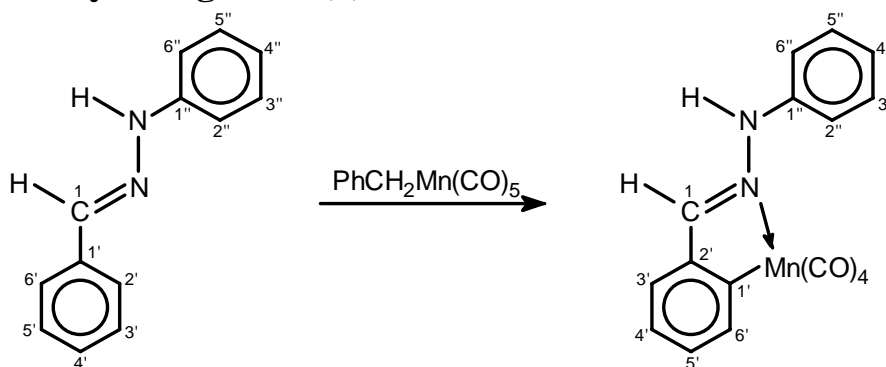
A 1% sodium amalgam was prepared under nitrogen in a 100 ml Schlenk flask by adding, in small portions, sodium metal (0.14 g, 5.83 mmol). When the amalgam cooled, dry deoxygenated THF (100 ml) was added, followed by $\text{Mn}_2(\text{CO})_{10}$ (4.0 g, 10.26 mmol). The mixture was stirred vigorously for 2 hours. The resulting pale green-grey solution of $\text{Na}[\text{Mn}(\text{CO})_5]$ was transferred by decantation to a deoxygenated Schlenk flask containing benzyl bromide (2.40 ml, 3.46 g, 20.0 mmol). A white precipitate formed immediately, and after stirring for 10 minutes the solution was passed through a short column of silica gel (8 x 2.5 cm, 60-120 mesh), washing with THF (2 x 30 ml). The THF was removed using a rotary evaporator, and the residual yellow (or in some cases green) oil was sublimed onto a water-cooled cold finger (1 mm Hg, 50 °C). This yielded crystalline $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (~5.0 g, 85%), m.p. 34-36 °C (lit. 37.5-38.5 °C²¹).

Note: pure $\text{PhCH}_2\text{Mn}(\text{CO})_5$ is white, but the pale yellow product obtained by this route is sufficiently pure for cyclometalation reactions.

IR: (heptane) $\nu(\text{CO})$ 2108 (s), 2009 (vs, br), 1992 (vs) cm^{-1} .

¹H NMR: (90 MHz) (CDCl_3) δ 7.28 (5H, s, C-H aromatic), 2.45 (2H, s, CH_2).

2.6.2 Preparation of η^2 -2-(N-phenylhydrazonomethyl)phenyl-tetracarbonylmanganese (6)



Benzaldehyde Phenylhydrazone

Benzaldehyde (17.6 g, 0.166 mol), phenylhydrazine (18 g, 0.166 mol), and a few drops of glacial acetic acid were added to ethanol (60 ml) and warmed. The resulting solid was filtered, and washed with dilute hydrochloric acid followed by 95% ethanol. The solid was recrystallised from ethanol to yield benzaldehyde phenylhydrazone [(2); 25 g, 77%] as a cream coloured powder of m.p. 155-156 °C (lit. 156 °C²³).

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.68-6.77 (10H, *m*, C-H aromatic), 2.10 (1H, *s*, H-1).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 144.8 (*s*, C-1''), 137.4 (*d*, C-1), 135.4 (*s*, C-1'), 129.3 (*d*, C-3'',5''), 128.6 (*d*, C-2',6'), 128.4 (*d*, C-4'), 126.2 (*d*, C-3',5'), 120.2 (*d*, C-4''), 112.9 (*d*, C-2'',6'').

Orthomanganation of Benzaldehyde Phenylhydrazone

Benzaldehyde diphenylhydrazone (0.189 g, 0.962 mmol) and PhCH₂Mn(CO)₅ (0.295 g, 1.0301 mmol) were added to heptane (AR, 25-30 ml) and degassed (placed under vacuum), and flushed with nitrogen several times. The hydrazone did not dissolve appreciably, until heat was applied. The mixture was refluxed under nitrogen for 2 hours. During this time the solution is observed to become orange tending to deep red at completion. The heptane was removed under vacuum, leaving a viscous black oil. This was dissolved in dichloromethane, and alumina (Brockmann grade II) was added. The solvent was removed under vacuum and the orange powder transferred to an alumina column. Elution was achieved by slowly increasing the polarity of petroleum spirit (b.p. 60-80 °C) using dichloromethane. The first band gathered (from neat petroleum spirit) was

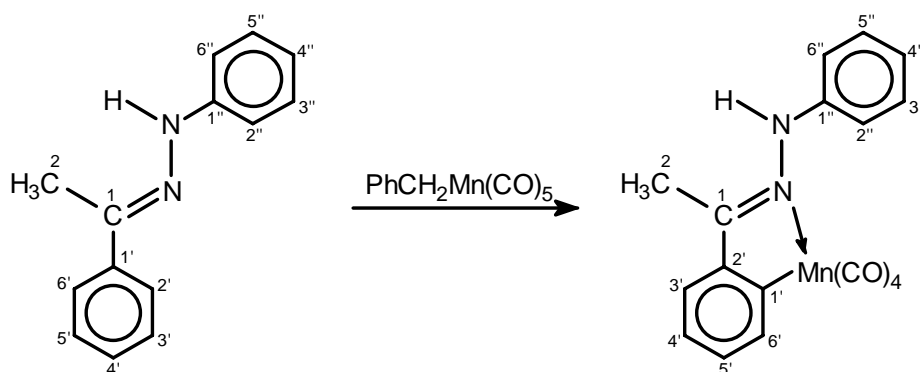
$\text{Mn}_2(\text{CO})_{10}$ (IR: (heptane) $\nu(\text{CO})$ 2046 (s), 1915 (vs), 1984 (s) cm^{-1}). Further elution gave the major deep orange band of η^2 -2-(*N*-phenylhydrazonomethyl)-phenyltetracarbonylmanganese [(6); 0.267 g, 77%], as an oil in standard conditions, which did not crystallise, despite repeated efforts.

IR: (heptane) $\nu(\text{CO})$ 2077 (m), 1994 (s), 1985 (vs), 1947 (s) cm^{-1} .

$^1\text{H NMR}$: (89.55 MHz) (CDCl_3) δ 8.28-6.53 (9H, *m*, C-H aromatic).

$^{13}\text{C NMR}$: (22.49 MHz) (CDCl_3) δ 219.7 (*s*, $\text{C}\equiv\text{O}$), 213.4 (*s*, $\text{C}\equiv\text{O}$), 180.0 (*s*, C-1'), 170.9 (*d*, C-1), 145.0 (*s*, C-1''), 144.1 (*s*, C-2'), 141.2 (*d*, C-6'), 129.6 (*d*, C-3'), 129.2 (*d*, C-3'',5''), 128.6 (*d*, C-5'), 124.5 (*d*, C-4'), 124.0 (*d*, C-4''), 119.2 (*d*, C-2'',6'').

2.6.3 Preparation of η^2 -2-[1-(*N*-phenylhydrazono)ethyl]phenyl-tetracarbonylmanganese (7)



Acetophenone Phenylhydrazone^{20b}

Similarly prepared to (2) above, acetophenone (20 g, 0.167 mol) and phenylhydrazine (18 g, 0.167 mol) were added to 60 ml ethanol containing a few drops of glacial acetic acid. Acetophenone phenylhydrazone [(4); 28 g, 80%] was collected as a cream coloured solid of m.p. 105-106 °C (lit., 106 °C^{20b}).

$^1\text{H NMR}$: (300.13 MHz) (CDCl_3) δ 7.85 (2H, *d*, $^3J_{2',3'}=7.11$ Hz, H-2',6'), 7.43 (2H, *t*, $^3J_{3',4'}=7.16$ Hz, H-3',5'), 7.35 (2H, *t*, $^3J_{3'',4''}=7.16$ Hz, H-3'',5''). 7.26 (2H, *d*, $^3J_{2'',3''}=7.11$ Hz, H-2'',6''), 6.95 (1H, *t*, $^3J_{4'',5''}=7.16$ Hz, H-4''), 6.83 (1H, *t*, $^3J_{4',5'}=7.16$ Hz, H-3',5'), 5.80 (1H, *s*, br, N-H), 2.23 (3H, *s*, H-2). *Anti*-isomer: δ 2.12 (3H, *s*, H-2).

$^{13}\text{C NMR}$: (75.47 MHz) (CDCl_3) δ 145.4 (*s*, C-1''), 141.3 (*s*, C-1), 139.3 (*s*, C-1'), 129.4 (*d*, C-3'',5''), 128.4 (*d*, C-2',6'), 128.0 (*d*, C-4'), 125.6 (*d*, C-3',5'), 120.3 (*d*, C-4''), 113.4 (*d*, C-2'',6''), 11.9 (*s*, C-2). *Anti*-isomer: δ 120.1 (*d*, C-4''), 112.6 (*d*, C-2'',6''), ~15%.

Orthomanganation of Acetophenone Phenylhydrazone

Similarly prepared to (6) above, from $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (0.332 g, 1.160 mmol) and acetophenone phenylhydrazone (0.213 g, 1.013 mmol) added to heptane and refluxed under nitrogen for 2 hours, was η^2 -2-[1-(*N*-phenylhydrazono)ethyl]-phenyltetracarbonylmanganese, (7). The dark orange oil collected was purified by recrystallisation from chloroform, yielding orange rectangular blocks (0.334 g, 87%) of m.p. 76-77 °C.

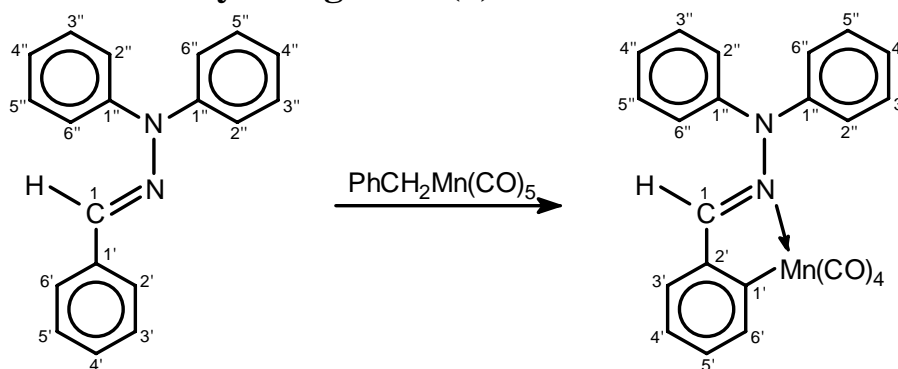
Anal. Found: C, 57.31; H, 3.40; N, 7.39 %; $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_4\text{Mn}$ calc: C, 57.46; H, 3.48; N, 7.45 %.

IR: (heptane) $\nu(\text{CO})$ 2071 (m), 1988 (s), 1980 (vs), 1947 (s) cm^{-1} .

^1H NMR: (300.14 MHz) (CDCl_3) δ 8.01 (1H, *d*, br, H-6'), 7.67 (1H, *d*, br, H-3'), 7.34 (2H, *t*, br, H-3'',5''), 7.25 (2H, *d*, br, H-2'',6''), 7.06 (1H, *t*, br, H-4''), 6.66 (1H, *t*, br, H-5'), 6.05 (1H, *t*, br, H-4'), 5.30 (1H, *s*, br, N-H), 2.53 (3H, *s*, br, H-2).

^{13}C NMR: (75.47 MHz) (CDCl_3) δ 219.5 (*s*, $\text{C}\equiv\text{O}$), 213.5 (*s*, $\text{C}\equiv\text{O}$), 212.7 (*s*, $\text{C}\equiv\text{O}$), 186.9 (*s*, C-1'), 180.4 (*s*, C-1), 145.9 (*s*, C-1''), 144.7 (*s*, C-2'), 141.4 (*d*, C-6'), 131.4 (*d*, C-3'), 129.6 (*d*, C-3'',5''), 129.0 (*d*, C-5'), 123.9 (*d*, C-4'), 122.3 (*d*, C-4''), 114.8 (*d*, C-2'',6''), 15.5 (*q*, C-2).

2.6.4 Preparation of η^2 -2-(*N,N*-diphenylhydrazonomethyl)-phenyltetracarbonylmanganese (8)



Benzaldehyde Diphenylhydrazone

Benzaldehyde (0.35 g, 3.298 mmol) in 10 ml of water was added to a solution containing diphenylhydrazine hydrochloride (0.75 g, 3.398 mmol) and sodium acetate (0.75 g, 9.143 mmol) in 5 ml water (the latter two forming a blue oil). A green/grey solid formed on shaking, which was insoluble in both ethanol and petroleum spirits, but can be recrystallised from dichloromethane, yielding

benzaldehyde diphenylhydrazone [(**3**); 0.58 g, 65%] as a pale green powder of m.p. 114-116 °C.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.66-7.09 (16H, *m*, C-H aromatic), 2.15 (1H, *s*, H-1).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 143.8 (*s*, C-1''), 136.2 (*s*, C-1'), 135.6 (*d*, C-1), 129.8 (*d*, C-3'',5''), 128.6 (*d*, C-2',6'), 128.1 (*d*, C-4'), 126.4 (*d*, C-3',5'), 124.5 (*d*, C-4''), 122.6 (*d*, C-2'',6'').

Orthomanganation of Benzaldehyde Diphenylhydrazone

Similarly prepared to (**6**) above, from PhCH₂Mn(CO)₅ (0.352 g, 1.230 mmol) and benzaldehyde diphenylhydrazone (0.304 g, 1.117 mmol) in heptane and refluxed for 2.5 hours, was η^2 -2-(*N,N*-diphenylhydrazonomethyl)phenyltetracarbonyl- manganese [(**8**); 0.395g, 83%]. During reflux the solution was observed to become increasing yellow in colour, and on removing the solvent a yellow solid remained. Purification was achieved by recrystallisation from chloroform, yielding a bright yellow powder of m.p. 105-106 °C.

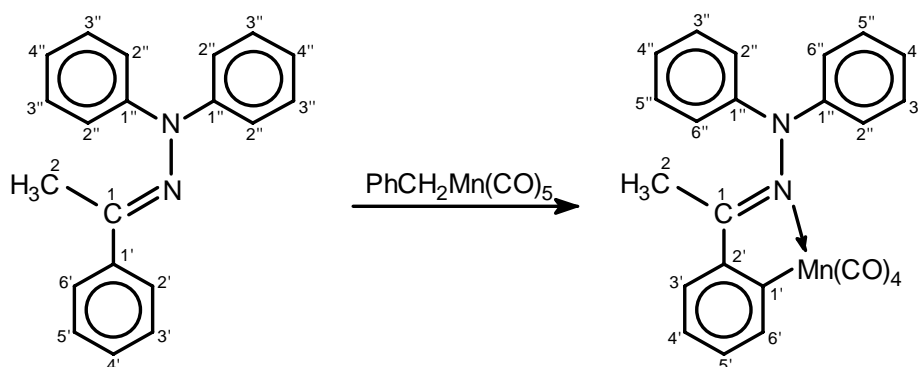
Anal. Found: C, 62.96; H, 3.29; N, 6.34 %; C₂₃H₁₅N₂O₄Mn calc: C, 63.03; H, 3.45; N, 6.39 %.

IR: (heptane) ν(CO) 2074 (*m*), 1985 (*vs*), 1950 (*s*) cm⁻¹.

¹H NMR: (89.55 MHz) (CDCl₃) δ 8.38 (1H, *s*, H-1), 7.98 (1H, *d*, ³J_{6',5'}=5.37Hz, H-6'), 7.56-7.03 (13H, *m*, C-H aromatic).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 220.2 (*s*, C≡O), 213.7 (*s*, C≡O), 211.5 (*s*, C≡O), 181.7 (*s*, C-1'), 173.6 (*d*, C-1), 145.1 (*s*, C-1''), 144.7 (*s*, C-2'), 141.2 (*d*, C-6'), 130.5 (*d*, C-3'), 129.6 (*d*, C-3'',5''), 124.9 (*d*, C-4''), 124.0 (*d*, C-4'), 123.4 (*d*, C-2'',6'').

2.6.5 Preparation of η^2 -2-[1-(N,N-diphenylhydrazono)ethyl]-phenyltetracarbonylmanganese (9)



Acetophenone Diphenylhydrazone

Similarly prepared to (3) above, acetophenone (0.30 g, 2.497 mmol) was added to a diphenylhydrazine hydrochloride (0.75 g, 3.398 mmol)/sodium acetate (0.75 g, 9.143 mmol) solution and shaken. A blue/green oil formed immediately with no precipitation initially. On standing for 2 days, *acetophenone diphenylhydrazone* [(5); 0.435 g, 61%] crystallised as a pale green powder of m.p. 93-94 °C.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.95-7.84 (2H, *m*, C-H aromatic), 7.42-6.95 (13H, *m*, C-H aromatic), 2.08 (3H, *s*, H-2).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 164.3 (*s*, C-1), 148.5 (*s*, C-1''), 138.6 (*s*, C-1'), 129.7 (*d*, C-4'), 129.1 (*d*, C-3'',5''), 128.4 (*d*, C-2',6'), 126.7 (*d*, C-3',5'), 123.1 (*d*, C-4''), 121.9 (*d*, C-), 121.5 (*d*, C-2'',6''), 119.5 (*s*, C-??), 17.8 (*q*, C-2).

Orthomanganation of Acetophenone Diphenylhydrazone

Similarly prepared to (6) above, from PhCH₂Mn(CO)₅ (0.420 g, 1.468 mmol) and acetophenone phenylhydrazone (0.401 g, 1.397 mmol) under reflux in heptane for 2 hours, was η^2 -2-[1-(N,N-diphenylhydrazono)ethyl]phenyltetracarbonylmanganese, (9). After only 15 minutes reflux the solution was observed to turn orange, and it became very dark in colour at completion. Recrystallisation of the major yellow band collected yielded a yellow powder (0.541 g, 86%) of m.p. 88-89 °C.

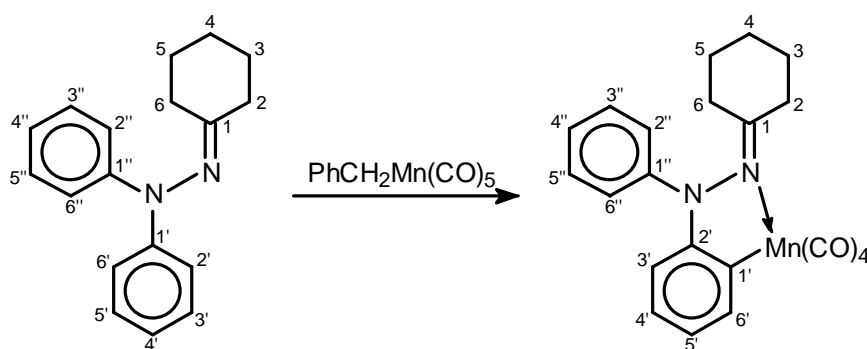
Anal. Found: C, 63.73; H, 3.68; N, 6.17 %; C₂₄H₁₇N₂O₄Mn calc: C, 63.73; H, 3.79; N, 6.19 %.

IR: (heptane) ν(CO) 2071 (*m*), 1988 (*s*), 1980 (*vs*), 1947 (*s*) cm⁻¹.

^1H NMR: (89.55 MHz) (CDCl_3) δ 7.97-7.13 (15H, *m*, C-H aromatic), 2.35 (3H, *s*, H-2).

^{13}C NMR: (22.49 MHz) (CDCl_3) δ 213.5 (*s*, $\text{C}\equiv\text{O}$), 188.7 (*s*, C-1'), 182.9 (*s*, C-1), 145.2 (*s*, C-1'), 143.5 (*s*, C-1''), 141.4 (*d*, C-6'), 131.4 (*d*, C-3'), 129.5 (*d*, C-3'',5''), 123.9 (*d*, C-4'), 123.4 (*d*, C-4''), 120.1 (*d*, C-2'',6''), 17.0 (*q*, C-2).

2.6.6 Preparation of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)



Cyclohexanone Diphenylhydrazone

Similarly prepared to (3) above, cyclohexanone (0.243 g, 2.476 mmol) was added to a solution of diphenylhydrazine hydrochloride (0.502 g, 2.266 mmol) and sodium acetate (0.501 g, 6.095 mmol), and shaken. Although no visible reaction occurred, on standing solid *cyclohexanone diphenylhydrazone* [(12); 0.28 g, 47%] separated. The solid was recrystallised from 95% ethanol to give white crystals of m.p. 72-74 °C.

^1H NMR: (89.55 MHz) (CDCl_3) δ 7.36-6.99 (10H, *m*, C-H aromatic), 2.54-2.26 (*m*, C-H cyclohexyl), 1.70-1.48 (*m*, C-H cyclohexyl).

^{13}C NMR: (22.49 MHz) (CDCl_3) δ 175.6 (*s*, C-1), 148.6 (*s*, C-1',1''), 128.9 (*d*, C-3',5',3'',5''), 122.5 (*d*, C-4',4''), 120.8 (*d*, C-2',6',2'',6''), 35.4 (*t*, C-2), 30.3 (*t*, C-2), 27.2 (*t*, C-4), 25.8 (*t*, C-5), 25.6 (*t*, C-3).

Orthomanganation of Cyclohexanone Diphenylhydrazone

Similarly prepared to (6) above, from $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (0.248 g, 0.938 mmol) and cyclohexanone phenylhydrazone (0.282 g, 0.986 mmol) under reflux in heptane for 2 hours, was η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese [(13); 0.379 g, 94%]. During this time a colour change to a deeper yellow was observed. The product was

recrystallised from petroleum spirit/dichloromethane to yield yellow rectangular blocks of m.p. 110-112 °C.

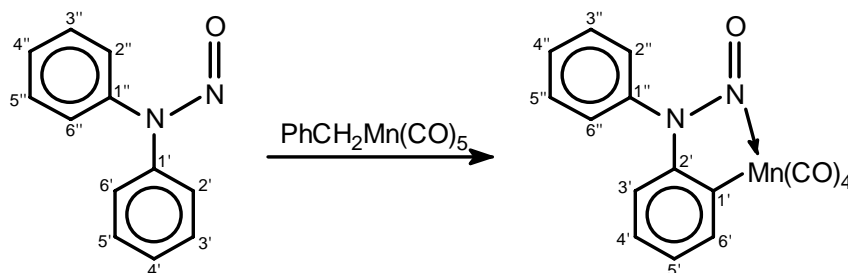
Anal. Found: C, 61.19; H, 4.36; N, 6.40 %; C₂₂H₁₉N₂O₄Mn calc: C, 61.40; H, 4.45; N, 6.51 %.

IR: (heptane) $\nu(\text{CO})$ 2073 (m), 1991 (vs), 1977 (s), 1940 (s) cm⁻¹.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.90-7.82 (1H, *m*, C-H aromatic), 7.23-6.70 (*m*, C-H aromatic), 2.99-2.80 (*m*, C-H cyclohexyl), 1.92-1.43 (*m*, C-H cyclohexyl).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 220.4 (*s*, C≡O), 214.2 (*s*, C≡O), 212.4 (*s*, C≡O), 191.7 (*s*, C-1), 160.6 (*s*, C-1'), 151.3 (*s*, C-2'), 145.0 (*s*, C-1''), 141.7 (*d*, C-6'), 129.2 (*d*, C-3'',5''), 125.8 (*d*, C-4'), 123.8 (*d*, C-5'), 121.9 (*d*, C-4''), 120.4 (*d*, C-3'), 113.6 (*d*, C-2'',6''), 38.8 (*t*, C-6), 32.3 (*t*, C-2), 26.9 (*t*, C-4), 26.4 (*t*, C-5), 24.9 (*t*, C-3).

2.6.7 Preparation of η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyl-tetracarbonylmanganese (16)



Diphenylnitrosamine^{20a}

Nitrosamines are generally toxic and highly carcinogenic substances that should be handled with care at all times.

Pure diphenylamine (17 g, 0.100 mol) was dissolved in warm ethanol (140 ml), and sodium nitrite (8 g, 0.116 mol) was dissolved in water (12 ml). Each solution was cooled in an ice bath, until the temperature reached 5 °C. Concentrated hydrochloric acid (12 ml) was added slowly, with stirring, to the diphenylamine solution, and immediately thereafter, the sodium nitrite solution was poured in (with stirring). A precipitate formed rapidly. The mixture was cooled for 15 minutes, and filtered on a Buchner funnel. The resulting yellow solid was thoroughly washed with water. The crude product was then recrystallised from 95% ethanol/water to yield pale yellow flakes of *diphenylnitrosamine* [(**15**); 15g, 76%] of m.p. 66-67 °C (lit., 68 °C^{20a}).

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.64-7.01 (10H, *m*, C-H aromatic).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 142.4 (*s*, C-1'), 136.7 (*s*, C-1''), 129.6 (*d*, C-3'',5''), 129.3 (*d*, C-4''), 129.2 (*d*, C-3',5'), 127.3 (*d*, C-2'',6''), 126.9 (*d*, C-4'), 119.6 (*d*, C-2',6').

Orthomanganation of Diphenylnitrosamine

Similarly prepared to (6) above, from PhCH₂Mn(CO)₅ (0.303 g, 1.059 mmol) and diphenylnitrosamine (0.201 g, 1.014 mmol) under reflux in heptane for 30 minutes, was *η*²-2-(*N*¹-nitroso-*N*¹-phenylamino)phenyltetracarbonyl manganese [(16); 0.258 g, 70%]. The product was recrystallised from petroleum spirit to yield orange rosettes of m.p. 65-66 °C.

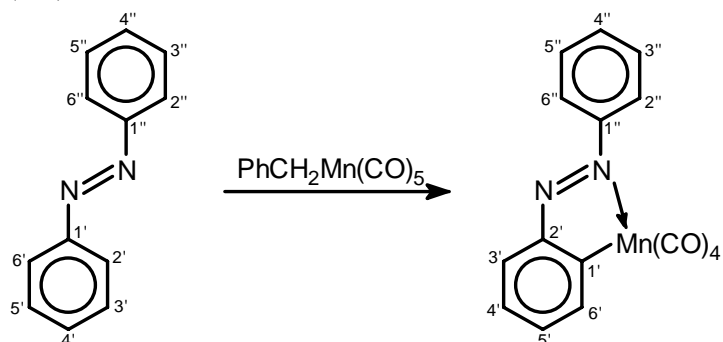
IR: (heptane) ν(CO) 2084 (*m*), 2004 (*s*), 2001 (*vs*), 1970 (*s*) cm⁻¹.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.93 (1H, *d*, ³J_{6',5'}=1.79 Hz, H-6'), 7.86 (1H, *t*, ³J_{4',5'}=1.79 Hz), 7.57-7.51 (3H, *m*, C-H aromatic), 7.28-6.95 (4H, *m*, C-H aromatic).

¹³C NMR: (75.47 MHz) (CDCl₃) δ 219.7 (*s*, C≡O), 211.0 (*s*, C≡O), 210.0 (*s*, C≡O), 156.4 (*s*, C-1'), 147.8 (*s*, C-2'), 141.6 (*d*, C-6'), 135.1 (*s*, C-1''), 130.9 (*d*, C-3'), 130.3 (*d*, C-3'',5''), 127.5 (*d*, C-2'',6''), 127.1 (*d*, C-4'), 124.8 (*d*, C-4''), 114.8 (*d*, C-3'). Diphenylamine impurity peaks at: δ 143.2 (*s*, C-1), 129.4 (*d*, C-3,5), 121.1 (*d*, C-4), 117.9 (*d*, C-2,6).

ESMS: (cone 10, CH₃CN/H₂O) *m/e* 382 (21, M⁺+18, M⁺+H₂O), 366 (20, [MH₂]⁺) 365 (100, [MH]⁺), 336 (13, M⁺-28, M⁺-CO). Diphenylamine impurity: 170 (33, [MH]⁺).

2.6.8 Preparation of η^2 -2-(N-phenylazo)phenyltetracarbonyl manganese (18)



Azobenzene

$^1\text{H NMR}$: (89.55 MHz) (CDCl_3) δ 7.97-7.86 (6H, *m*, C-H aromatic), 7.53-7.41 (4H, *m*, C-H aromatic).

$^{13}\text{C NMR}$: (22.49 MHz) (CDCl_3) δ 152.6 (*s*, C-1',1''), 130.9 (*d*, C-4',4''), 129.0 (*d*, C-3',5',3'',5''), 122.8 (*d*, C-2',6',2'',6'').

Orthomangantation of Azobenzene

Similarly, $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (0.330 g, 1.153 mmol) and azobenzene (0.198 g, 1.087 mmol) were dissolved in heptane and refluxed for 2 hour was η^2 -2-(N-phenylazo)phenyltetracarbonylmanganese [(18); 0.325 g, 85%]. During reflux a colour change from bright orange to black was observed. The product was recrystallised from petroleum spirit to give very dark orange crystals of m.p. 112-113 °C (Lit.²⁴ 112.5-113 °C).

IR: (heptane) $\nu(\text{CO})$ 2080 (*m*), 2001 (*vs*), 1995 (*s*), 1959 (*s*) cm^{-1} . (Lit.²⁴ (CHCl_3) $\nu(\text{CO})$ 2080 (*m*), 2005 (*vs*), 1955 (*s*) cm^{-1}).

$^1\text{H NMR}$: (89.55 MHz) (CDCl_3) δ 8.38-8.08 (4H, *m*, C-H aromatic), 7.53-7.29 (5H, *m*, C-H aromatic).

$^{13}\text{C NMR}$: (22.49 MHz) (CDCl_3) δ 180.5 (*s*, C-1'), 167.0 (*s*, C-2'), 157.4 (*s*, C-1''), 141.1 (*d*, C-6'), 132.5 (*d*, C-), 131.9 (*d*, C-), 130.0 (*d*, C-), 129.0 (*d*, C-3'',5''), 125.3 (*d*, C-), 121.9 (*d*, C-2'',6'').

Orthomanganation reactions were attempted with the following compounds, although no metalated products were isolated. Reaction between starting materials was, however, clearly evident in all cases.

2.6.9 Phenylhydrazine (PhNH-NH₂)

Following established procedures, PhCH₂Mn(CO)₅ (0.153 g, 0.535 mmol) and phenylhydrazine (0.055 g, 0.508 mmol) were dissolved in heptane and refluxed for 2 hours. During this time a colour change from clear to black was observed.

IR of the crude reaction mixture shows (CH₂Cl₂) $\nu(\text{CO})$ 2082 (w), 2054 (w), 2039 (m), 2009 (s), 1998 (s), 1953 (m, br), 1939 (br, m) cm⁻¹, indicating reaction had consumed all PhCH₂Mn(CO)₅, and various products had formed.

Normal workup gave an impure oil (whose constituents were unidentified) and Mn₂(CO)₁₀.

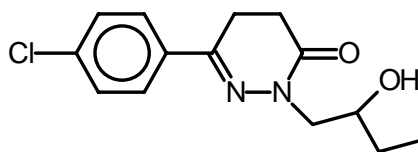
2.6.10 N-acetyl-N-phenylhydrazine (PhNH-NHCOCH₃)

Similarly, PhCH₂Mn(CO)₅ (0.421 g, 1.471 mmol) and N-acetyl-N-phenylhydrazine (0.055 g, 0.508 mmol) were dissolved in heptane and refluxed for 2 hours. During reflux a colour change from cloudy white to blood red was observed. Efforts at solution IR were futile, since the product was apparently so air sensitive that a near instantaneous decomposition to an insoluble brown solid and Mn₂(CO)₁₀ occurred when samples of the solution were removed from the reaction vessel. For this reason an alkyne was added to the reaction mixture directly (see chapter 3), to attempt to identify the product as a derivative.

2.6.11 Cyclohexanone Phenylhydrazone (PhNH-N=Cy)

Similarly, PhCH₂Mn(CO)₅ (0.322 g, 1.125 mmol) and cyclohexanone phenylhydrazone (0.203 g, 1.078 mmol) were dissolved in heptane and reflux initiated. An immediate colour change from pale to deep yellow was observed, tending to bright orange after 10 minutes. After 40 minutes reflux the solution was virtually black in appearance, with a brown solid forming on the sides of the flask. Reaction was complete by IR, after 2 hours. Preliminary TLC revealed greater than 10 compounds were present, so the reaction was abandoned.

IR: Crude reaction mixture, (heptane) $\nu(\text{CO})$ 2076 (m), 2014 (s), 2004 (s), 1993 (s), 1978 (s), 1960 (s), 1938 (s), 1914 (m) cm⁻¹.

2.6.12 6-(4-Chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone

Similarly, $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (0.220 g, 0.768 mmol) and 6-(4-Chlorophenyl)-4,5-dihydro-2-(2-hydroxybutyl)-3(2H)-pyridazinone (0.204 g, 0.732 mmol) were added to heptane and refluxed for 3 hours. During reflux a colour change from cloudy white to clear yellow was observed, with a yellow solid forming on the sides of the reaction vessel. After removing the solvent under vacuum, and supporting the residue on alumina, only 1 band was collected, which by IR was found to be $\text{Mn}_2(\text{CO})_{10}$, together with unreacted $\text{PhCH}_2\text{Mn}(\text{CO})_5$.

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Chapter Three

Coupling Reactions of Orthomanganated Compounds Containing the NN Linkage With Various Alkynes

3.1 Introduction

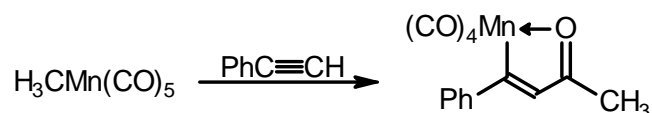
A vast amount of work has been carried out involving transition metal complexes reacting with alkynes, and indeed work is still being actively performed on these potentially very useful reactions.

The most extensively studied alkyne coupling reactions, involving cyclometalated compounds, are those of palladium(II) complexes¹. The reason these systems have had perhaps more attention than others is due to their high reactivity, with alkynes generally inserting readily into the Pd-C bond, thus generating a new C-C linkage.

An overview with an emphasis on manganese systems reacting with alkynes follows.

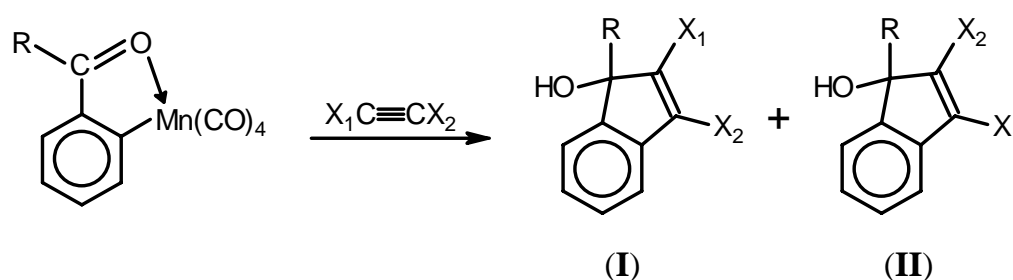
3.1.1 O-donor Ligands

Booth *et al.* investigated the reactions of alkynes with simple manganese alkyls, which subsequently gave cyclometalated enones². A typical reaction is shown below:



Equation 3.1

More recently several groups have studied reactions of alkynes with orthomanganted aryl ketones, in particular enones³, and acetyl thiophenes⁴. In these reactions the metal is generally lost to give a purely organic product (*c.f.* reactions with Pd where the metal is usually retained, Scheme 3.1). The reaction generates a five membered ring (a cyclopenta-annulation), so from acetophenones indenols are produced (Equation 3.2). These form the basis of range of compounds that have a large number of applications in organic synthesis⁵.



Equation 3.2

If an unsymmetrical alkyne is used ($X_1 \neq X_2$) then there are clearly two possible reaction products. The product distribution is nearly always such that if X_1 is the larger substituent, **(I)** will be the dominant isomer. For this reason **(II)** is often not formed to an appreciable extent. This can be explained by the mechanism (discussed later, Scheme 3.1) which involves the precoordination of the alkyne to form a π -donor intermediate complex⁵ (Figure 3.1) before the actual insertion into the Mn-C bond. Such a species has to date not been detected, but on steric grounds it is presumed that in this species the bulkiest group (L) on the coordinated alkyne will be orientated in a position furthest away from the aryl ring system. Hence when subsequent insertion takes place, the larger group will be adjacent to the manganese atom, despite this generally being the more sterically crowded position.

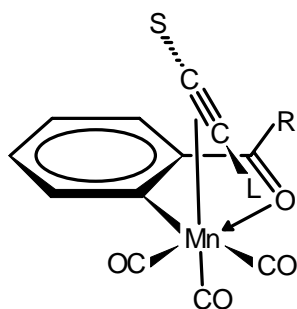
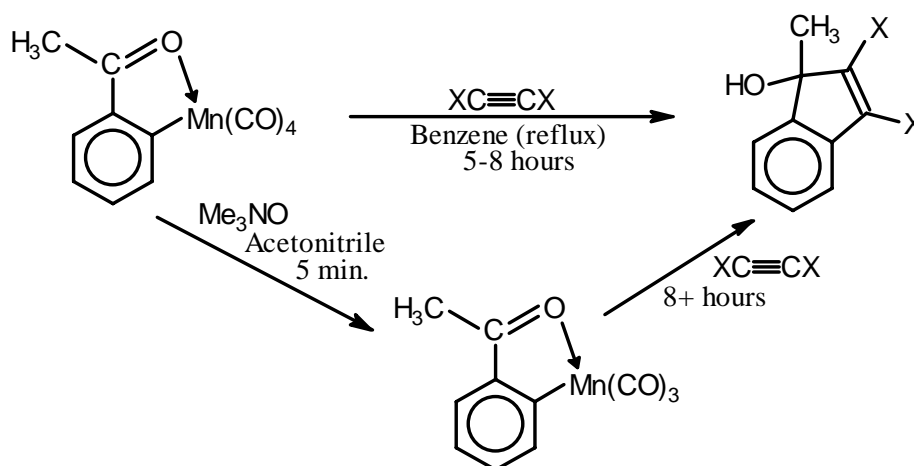


Figure 3.1⁵

Double insertion can also take place to give a seven-membered ring, or triple insertion to give a cyclohexadienyl product such as **(D)** in Figure 3.2. The likelihood of this occurring depends on both the metalated compound and the size of alkyne substituents. The process of a subsequent insertion will compete with the rate of cyclisation. Thus the relative rates of the two decides the final product outcome.

These reactions can be either thermally induced, or Me_3NO can be used to activate the orthomanganated ketone. Both routes produce a reactive 16-electron tricarbonyl species by loss of CO , which facilitates the initial coordination of the alkyne. These two routes to an indenol are shown in Equation 3.3, for the unsymmetrical alkyne phenylacetylene reacting with orthomanganated acetophenone, giving typical conditions and reaction times.

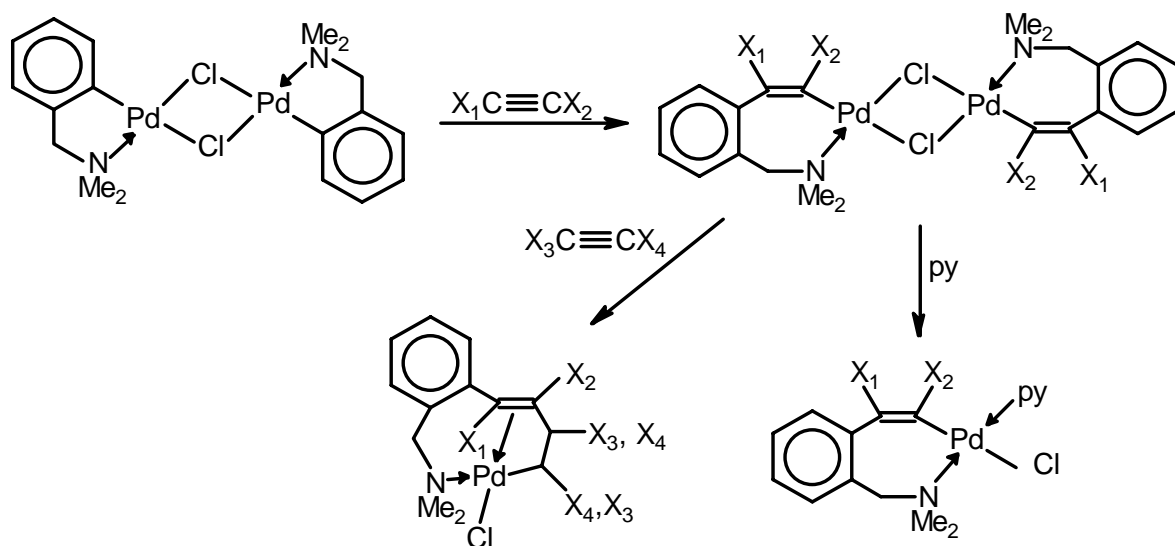


Equation 3.3

3.1.2 N-donor Ligands

Much of what has already been discussed above in the case of O-donor compounds can be extrapolated to include N-donor ligands.

Little work has been carried out on alkyne coupling reactions for the orthomanganated adducts of this important class of compounds, with most research involving palladium derivatives¹. A typical example reaction is shown in Equation 3.4. As mentioned earlier it is usual for the metal to be retained.



Equation 3.4

Samad investigated coupling reactions with alkynes involving orthomanganated imines⁶. Prior to this work, only one reaction involving an alkyne insertion had been carried out⁷. The cyclomanganated imines examined are shown in Figure 2.2 (Chapter 2, Introduction), (I) and (II).

Yields were generally low, and reaction times ranged from 16 to 24 hours. Several products were tentatively identified from both by thermal and Me₃NO assisted reactions. A selection of the compounds isolated from reactions with diphenylacetylene are shown in Figure 3.2.

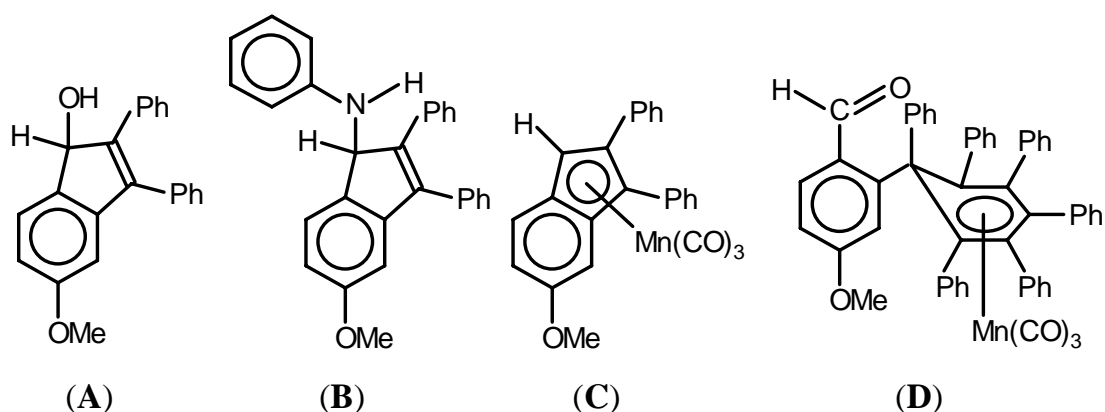
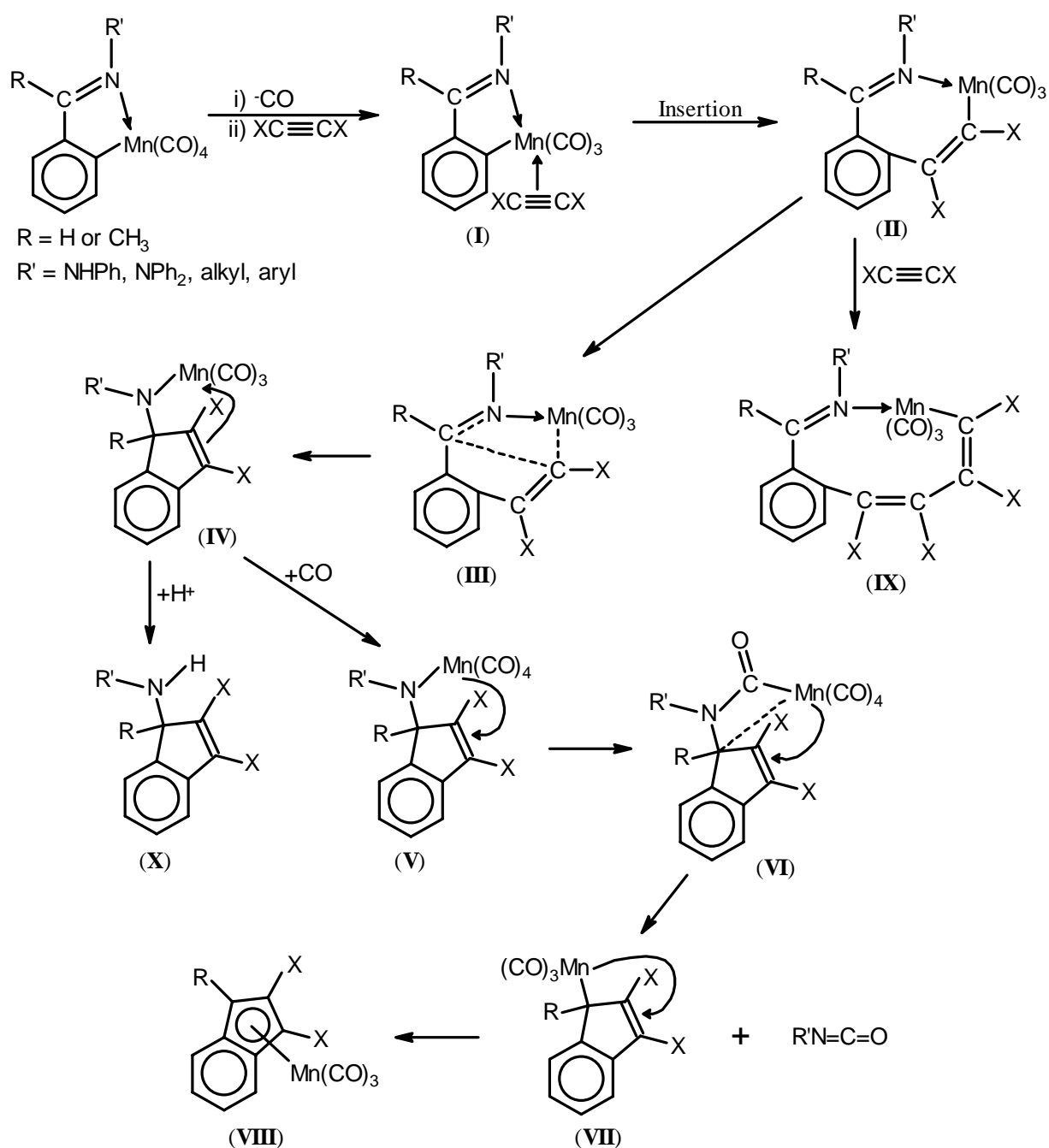


Figure 3.2

The most synthetically useful product is probably (A), since the imine functionality provides a route to give the indenol derivative of benzaldehyde. Unsubstituted aromatic aldehydes generally resist manganation⁵. The yield of

this product was reasonable (39%), and it was thought to be formed by hydrolysis of **(B)** on workup.

Grigsby proposed a reaction mechanism for the insertion process⁷ (Scheme 3.1), which is an extension on that first put forward by Robinson⁵, to help explain the range of products isolated from the imine reactions, and how both doubly inserted products and tricarbonyl species (such as **(C)** in Figure 3.2) can be arrived at.



Scheme 3.1

The initial steps involve coordination of the alkyne (**I**) and subsequent insertion into the Mn-C σ -bond (**II**), intramolecular rearrangement (**III**) and (**IV**), followed by protonation (during workup), to give the purely organic indene derivative (**X**). The alternative pathway from (**IV**), involves base association of CO (**V**), insertion of CO into the Mn-N bond (**VI**), with subsequent loss of R'N=C=O (**VII**), and finally rearrangement to give the tricarbonyl species (**VIII**).

It was the aim of the work described in this chapter to explore the coupling reactions of the new cyclomanganated nitrogen donor systems with a variety of alkynes (including unsymmetrical ones). The hope was that these will include more synthetically viable cyclomanganated N-donor compounds than the imines, which to date had proved to be significantly less reactive than their O-donor counterparts.

3.2 Discussion of Results

3.2.1 Thermally Induced Reactions

Both the relative reaction rates and reaction product(s) varied greatly amongst the systems tested, depending on the alkyne used and the solvent in which the reaction was carried out. The reasons for this are not clear, but the results are consistent with those for aryl ketone systems where similar results have been noted⁵.

3.2.1.1 Orthomanganated Arylhydrazones of Benzaldehyde and Acetophenone

The orthomanganated diphenylhydrazones, (**8**) and (**9**) showed a high degree of reactivity, and produced the expected insertion product in reasonable yield.

When η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (**8**) was refluxed with diphenylacetylene, a rapid colour change to black was

observed. The reaction was complete after only 2 hours. A tricarbonyl species was clearly present as the only significant contributor in the metal carbonyl region of the IR spectrum of the product solution.

Tricarbonyl species $[\text{Mn}(\text{CO})_3]$ can be conveniently identified by their very distinctive IR absorbance pattern. The $\text{Mn}(\text{CO})_3$ moiety can be observed in solution in either of two different environments, **(I)**/**(II)** and **(III)** (Figure 3.3).

Both **(I)** and **(II)** give two strong $\nu(\text{CO})$ peaks in the metal carbonyl region, one of which is broad around $1900\text{--}1970\text{ cm}^{-1}$, the other being sharp and occurring at a higher energy, generally around $2000\text{--}2020\text{ cm}^{-1}$ (*cf.* spectra predicted for $\text{Mn}(\text{CO})_4$ described in Chapter 2). Both of these have been detected in manganoxylation reactions. **(I)** had absorbances at $\nu(\text{CO})$ 2017 (s) and 1930 (s, br)^5 and **(II)** has $\nu(\text{CO})$ 2030 (vs) and $1956\text{ (s, br)}^6\text{ cm}^{-1}$.

The other possibility has quite different geometry at Mn, and is a species such as **(III)**. These have three peaks in the IR spectrum, the highest energy absorbance being sharp, the other two being broad, for example values of $\nu(\text{CO})$ 2005 (vs), 1925 (vs, br) and $1891\text{ (vs, br)}^8\text{ cm}^{-1}$ were recorded for **(III)**. From the IR spectrum it should therefore be possible to differentiate the two possibilities.

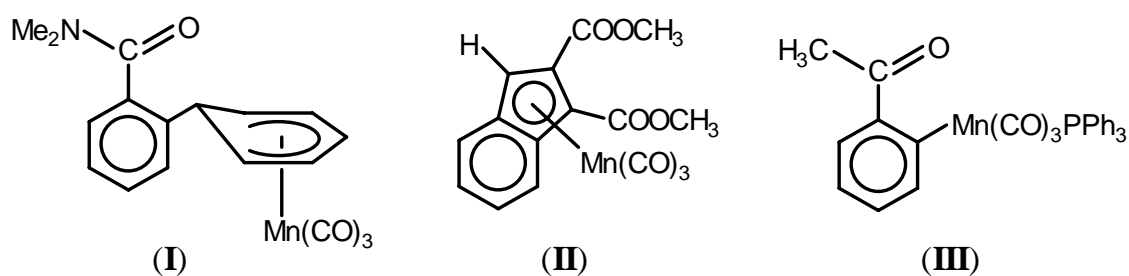
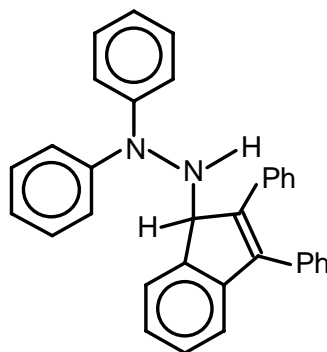


Figure 3.3

In this reaction there were two main absorbances, $\nu(\text{CO})$ 2024 (m) and $1919\text{ (vs, br)}\text{ cm}^{-1}$, which corresponds to a species of type **(I)** or **(II)**, the latter being more likely for diphenylacetylene. However unlike examples in Figure 3.3, the compound detected here was unstable or air sensitive, since attempts at collecting the tricarbonyl species from the reaction proved unfruitful.

However, the compound that was isolated from this reaction was by NMR spectroscopy and elemental analysis strongly indicative of the singly inserted adduct **(19)** (Figure 3.4).

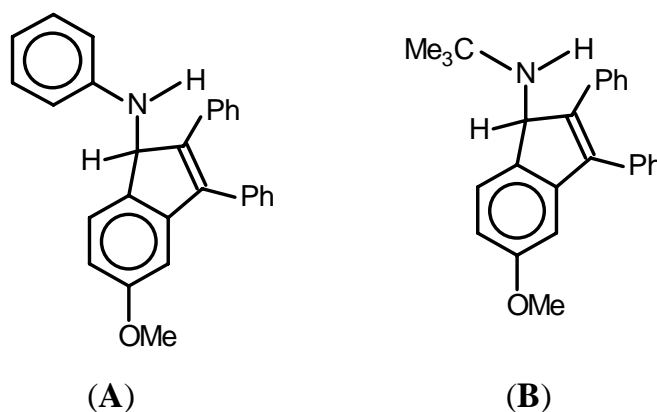


(19)

Figure 3.4

No double insertion product was isolated or detected. This is not unexpected in the case of diphenylacetylene due to the bulky nature of this substrate, and is in line with findings for orthometalated aromatic ketones. Despite this, Samad claims a triple insertion product [(**D**) in Figure 3.2] when orthomanganated N-(4-methoxybenzylidene)-1,1-dimethylethylamine was reacted with diphenylacetylene⁶.

The chemical shift of the indene hydrogen ($\underline{\text{H}}\text{-C-N}$) in the ¹H NMR spectrum of (**19**), 4.48 ppm, is considerably lower than the figures reported for the same hydrogen by Samad for 2,3,-diphenyl-5-methoxy-1-(1-phenylamino)-indene (**A**), 5.74, and 1-(1,1-dimethylethylamino)-5-methoxy-2,3-diphenylindene (**B**), 6.18, (Figure 3.5)⁶, which are expected to be electronically fairly similar.

*Figure 3.5*

When trimethylsilylacetylene was reacted with (**8**), a reasonable yield (54%) of an indene was obtained. Because this involves an unsymmetrical alkyne, two

reaction products are possible (as already discussed in the Introduction). Indeed this was the case for **(8)** with two insertion products **(20)** and **(21)** (characterised by two CH₃ signals in both the ¹H and ¹³C spectra) collected in a 2:1 ratio, which could not be separated using column chromatography (Figure 3.6).

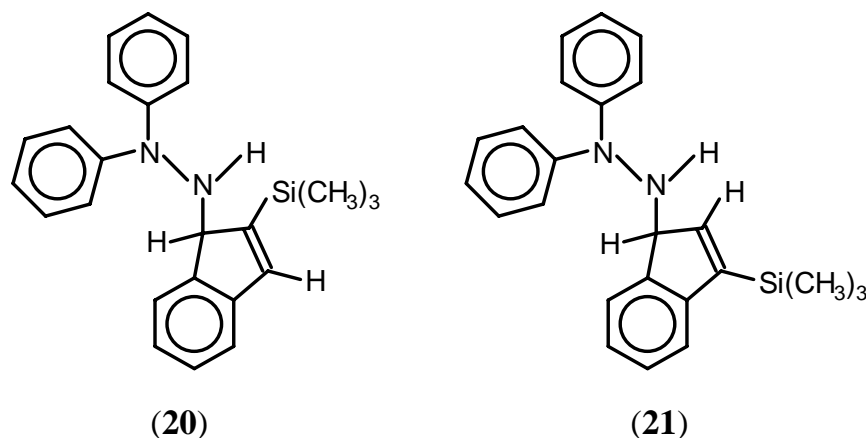


Figure 3.6

Similarly, **(8)** was refluxed in acetonitrile with dimethyl acetylenedicarboxylate (DMAD) and a much faster reaction rate was noted. However, no products could be isolated by chromatography.

When η^2 -2-[1-(N,N-diphenylhydrazono)ethyl]phenyltetracarbonylmanganese **(9)** was refluxed with diphenylacetylene, the rate was very similar to that of **(8)** (complete in 3 hours). In this case no tricarbonyl species was detected.

The product **(22)** was characterised by NMR spectroscopy by analogy with **(19)**, Figure 3.7. When trimethylsilylacetylene was used, similar reactivity (complete in 5 hours) to **(8)** was again noted. However in this case, only one of the two possible isomers was collected, and it was assumed to be **(23)** (Figure 3.7), following the reasons discussed previously.

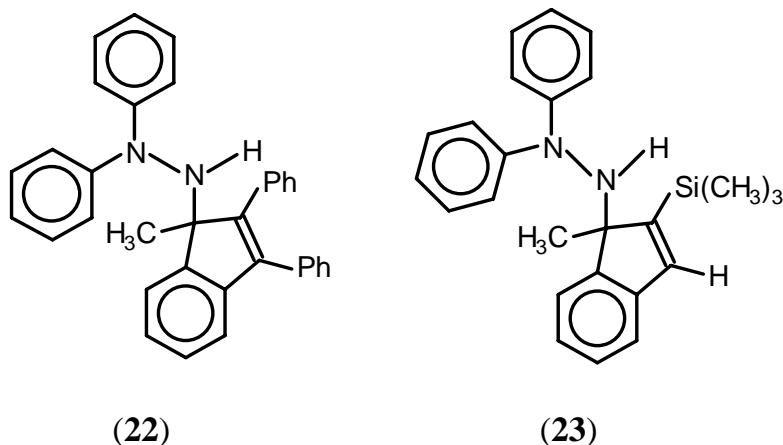


Figure 3.7

Despite the reasonably successful reactions with the secondary arylhydrazones, the reactions of the corresponding primary hydrazones with the same alkynes exhibited extensive decomposition. Relative reaction rates were also significantly slower for these systems.

When η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (**7**) was refluxed in acetonitrile with diphenylacetylene for 6 hours, the dark orange solution became black in colour. The same observation was noted when η^2 -2-(N-phenylhydrazonomethyl)phenyltetracarbonylmanganese (**6**) was used. Neither reaction was straightforward, with multiple products collected in small amounts. There is a strong possibility that the product is initially at least a singly-inserted hydrazine (Figure 3.8, R= H, CH₃), by analogy with the products reported by Samad for similar reactions with orthomanganated aryl imines⁶, and the reaction products for both (**8**) and (**9**).

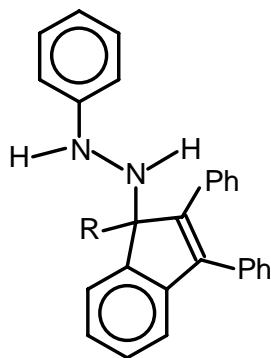


Figure 3.8

However, no such product was isolated. The reason for this is not clear, since we would expect the primary and secondary arylhydrazones to have very similar reactivity, and similar products. A possible cause may be interference from the relatively labile hydrogen associated with the N-H linkage, although this proved to be of no consequence in the metalation of the parent hydrazones.

Table 3.1 shows a summary of reaction rates of all the hydrazone systems tested under thermal conditions with the alkyne used, and the yield of the presumed product, along with whether a tricarbonyl species was detected in the reaction procedure. A comparison with the orthomanganated imines prepared by Samad⁶ is given since these have the same metallocycle. The solvent used in all reactions carried out was acetonitrile (AR). Samad used benzene, and therefore those results are not directly comparable since coupling reactions are often very solvent dependent.

Referring to the table it is clear the reactivity of the primary hydrazones (**6**) and (**7**) is substantially lower than that of the secondary hydrazones (**8**) and (**9**), using the same alkyne substrate. The reason for this is not clear, since electronically the species are very similar. The species prepared by Samad showed slow reaction rates, although this may be due to the solvent.

The reaction rates in each table are grouped broadly into the following four categories, according to the time taken for all reactant to be consumed as measured by IR spectroscopy:

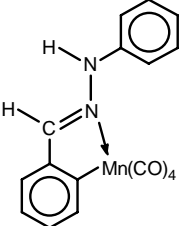
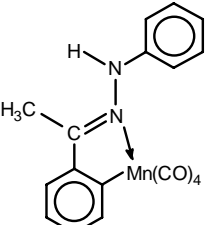
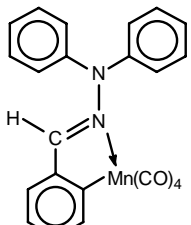
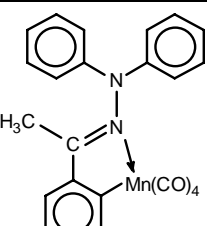
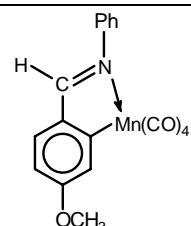
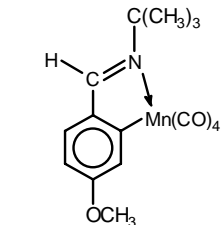
“Very Rapid” \Rightarrow < 1 hour

“Rapid” \Rightarrow 1-5 hours

“Slow” \Rightarrow 6-10 hours

“Very Slow” \Rightarrow >10 hours

Table 3.1: Summary of Thermal Reactions of Alkynes With Compounds Containing C=N as Part of the Metallocycle

Compound	Diphenyl-acetylene (PhC≡CPh)	Dimethyl Acetylene-dicarboxylate (MeO ₂ CC≡CCO ₂ Me)	Trimethyl-silylacetylene (HC≡CSiMe ₃)
 <p>(6)</p>	Slow. No insertion product isolated.	Not Tested.	Not Tested.
 <p>(7)</p>	Slow. No insertion product isolated.	Not Tested.	Not Tested.
 <p>(8)</p>	Rapid. Singly inserted product. Mn(CO) ₃ species detected.	Very Rapid. No insertion product isolated.	Rapid. Mixture of two singly inserted products, 54%.
 <p>(9)</p>	Rapid. Singly inserted product, 42%.	Very Rapid. No insertion product isolated. Mn(CO) ₃ species detected.	Rapid. Singly inserted product, <52%. Mn(CO) ₃ species detected.
 <p>(10)⁶</p>	Very Slow. Singly inserted product, <16%. Mn(CO) ₃ species detected.	Very Slow. Doubly inserted product, 12%. Mn(CO) ₃ species detected.	Not Tested.
	Very Slow. Singly inserted product, 29%. Mn(CO) ₃ species detected.	Very Slow. Single inserted product, 41%. Mn(CO) ₃ species detected.	Not Tested.

3.2.1.2 Orthomanganated Arylhydrazone of Cyclohexanone

When η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (**13**) and diphenylacetylene were refluxed in acetonitrile, a reaction was observed to occur almost immediately, with the solution becoming bright yellow. The reaction was complete (by IR spectroscopy) after only 20 minutes reflux, with the formation of a tricarbonyl species as the sole species exhibiting absorption in the metal carbonyl region: $\nu(\text{CO})$ (CH_3CN) 2003 (m) and 1901 (vs) cm^{-1} . This is markedly different from the IR pattern of the $\text{Mn}(\text{CO})_3$ species recorded for the benzaldehyde diphenylhydrazone system (**8**) ($\nu(\text{CO})$ (CH_3CN) 2024 (m), 1919 (vs) cm^{-1}). On evaporation of the solvent under reduced pressure, the initial residue was a yellow oil. This rapidly became green in colour on further evacuation, implying the solvent must play some role in the reaction process, perhaps stabilising the tricarbonyl species formed. The green oil was found to consist of multiple compounds, none of which contained manganese carbonyl. These were not identified due to low quantities and difficulties with purification. Similar observations were noted when phenylacetylene was used.

The reaction was much slower in petroleum spirit (b.p. 60-80°C), extending the time to 3 hours. No tricarbonyl species were noted with this solvent, giving further evidence of solvent interaction when acetonitrile is used.

The species depicted in Figure 3.9 is suggested as a possible product. Compounds such as this are generally unstable with CH_3CN being a poor coordination species, thus tending to dissociate readily.

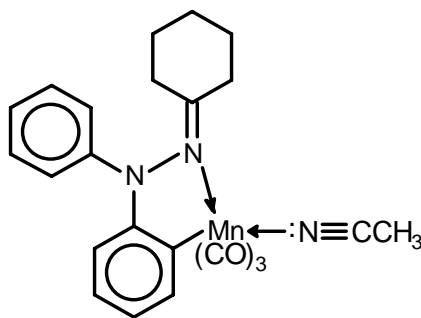


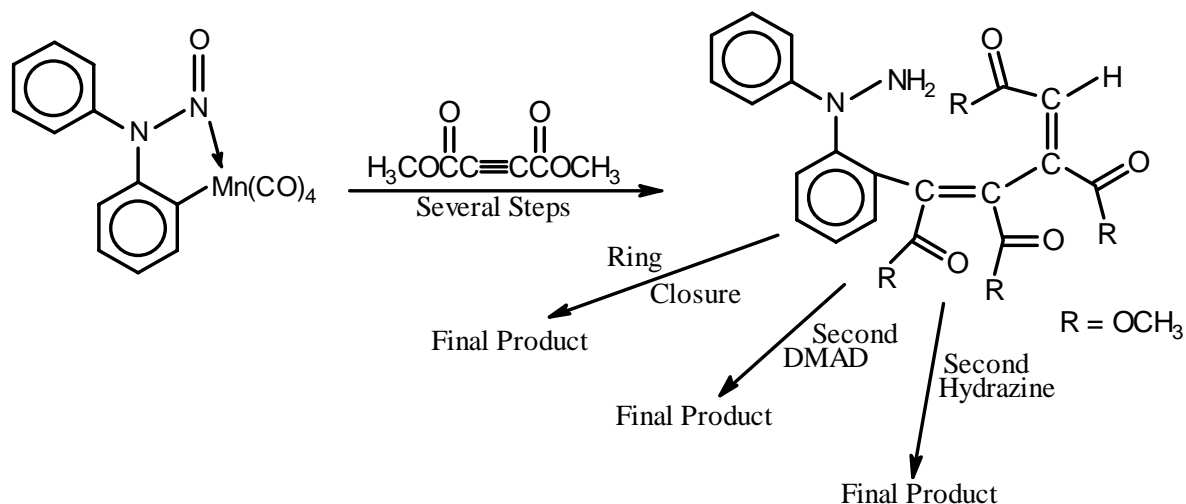
Figure 3.9

3.2.1.3 Orthomanganated Nitrosamine

When η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (**16**) was refluxed in acetonitrile with DMAD a gradual colour change to black was observed. The reaction was much slower than for those systems previously tested, with the reaction complete by IR spectroscopy only after 24 hours. A yellow solid was collected after workup. When greater quantities of both starting material were used, an even longer reaction time, 42 hours, was required before (**16**) was completely consumed. The longer reaction time apparently decomposed the product, with the latter reaction producing multiple compounds.

The product collected from the initial reaction has been subject to full spectroscopic analysis, with results from ¹³C NMR, high-resolution ¹H NMR, and mass spectroscopy. However, the structure has not been determined from this information. From NMR data the compound is apparently a double insertion product (by the presence of four OCH₃ groups), with both *mono*- and *ortho*-disubstituted benzene rings, as would be expected. It appears the OCH₃ groups are in a 3:2:1:2 ratio, implying something somewhat unexpected has occurred. In addition electrospray mass spectroscopy revealed a parent ion of unusually high molecular weight, m/e 855.

We can speculate that complications could arise with the possibility of hydrazine formation (diphenylhydrazine was often a reaction by-product when dealing with this particular cyclomanganated species) which could react either *intra*- or *inter*-molecularly with the carbonyl functionalities present in DMAD (Scheme 3.2). Furthermore dimerisation between other hydrazine groups that may be present is also a possibility, which could explain the very high molecular ion weight in the mass spectra. Presumably for these reasons the structural elucidation of the compound remains elusive.



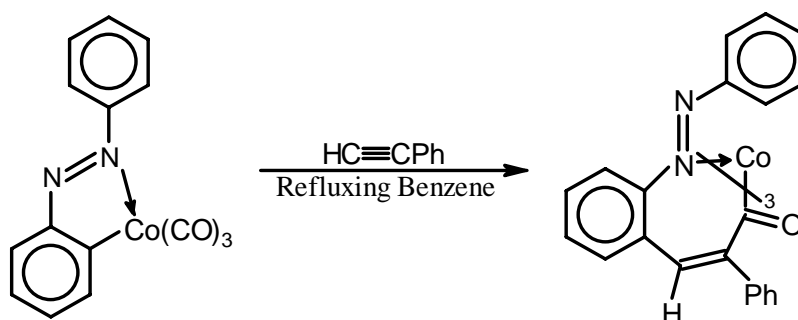
Scheme 3.2

Data from the mass spectrum also shows peaks at m/e 750, which corresponds to a loss of 105. This corresponds to two likely possibilities, loss of PhC=O or loss of $\text{PhN}\equiv\text{N}^+$. The former would have required a carbonyl insertion to have taken place, which is not unreasonable. The loss of 105 is observed in another part of the spectrum also, m/e 576 \Rightarrow 471.

It would be useful to carry out further reactions with different alkynes that do not contain the carbonyl functionality, to shed some light on the species formed using DMAD.

3.2.1.4 Orthomanganated Azobenzene

Pauson *et al.* have carried out coupling reactions of η^2 -2-(N-phenylazo)phenyltricarboxylcobalt with a variety of substrates, including alkynes⁹. An interesting and unusual compound was claimed when the cyclocobalt compound was reacted for 12 hours with phenylacetylene (Equation 3.5). Evidence for the product (a bright blue compound) came entirely from IR spectra (which showed no metal carbonyls) and elemental analysis. If it actually was this species, it would be truly a remarkable example of a stable Co^{III} alkyl complex.



Equation 3.5

No reactions of orthomanganated azobenzene with alkynes have been carried out. Although a manganese analogue of the product shown in Equation 3.1 is highly unlikely, it was of interest to examine the reactivity toward alkyne insertion, and compare this with the other nitrogen donor compounds prepared for this study.

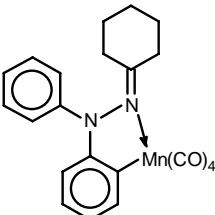
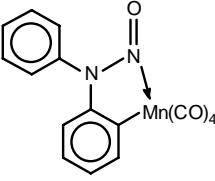
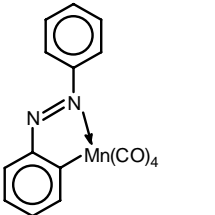
η^2 -2-(N-phenylazo)phenyltetracarbonylmanganese (**18**) and phenylacetylene were refluxed in acetonitrile. No colour change was noted. The reaction was very slow, and reflux had to be maintained for 18 hours before all traces of the $\text{Mn}(\text{CO})_4$ group were absent from the IR spectra. A tricarbonyl species was detected in solution only, with two bands, $\nu(\text{CO})$ (CH_3CN) 2021 (s) and 1997 (vs) cm^{-1} , in the metal carbonyl region. The solvent was removed under vacuum, and on chromatography of the residue, a blue oil was collected, which did not crystallise, and did not contain metal carbonyl stretching bands in the IR spectrum. The compound was observed to decompose to an unknown yellow compound, and these two components could not be separated, making spectroscopic analysis difficult.

Electrospray mass spectroscopy revealed a strong peak at m/e 312, and peak a that corresponds with a loss of CO. This implies a product of the type $[\text{PhN}_2\text{Ph} + \text{CO} + \text{PhC}\equiv\text{C}]^+$. However the exact linkage of this species is uncertain, although it would involve an alkyne insertion into the $\text{Mn}-\text{C}_{\text{aryl}}$ bond, followed by the carbonyl insertion, and perhaps subsequent ring closure. The $\text{C}=\text{O}$ was not observed in the NMR spectrum, although this is not surprising considering the small quantity of the material. Whether this is the same compound that Pauson described is not known, although blue compounds are fairly unusual.

An even slower reaction was observed when DMAD was used, although this reaction was initially carried out in benzene. Refluxing for 24 hours had apparently very little effect, with the tetracarbonylmanganese group still prominent in the IR spectrum. The solvent was consequently changed to acetonitrile (by removing the benzene under vacuum) and reflux recommenced, for a further 10 hours. Only unreacted (**18**) and demetallated azobenzene was collected after workup.

Table 3.2 shows a summary of the thermally induced alkyne coupling reactions of the compounds involving two nitrogens as part of the metallocycle ((**13**), (**16**) and (**18**). Relative reaction rates range from very rapid for (**13**), to practically inert in the case of (**18**).

Table 3.2: Summary of Thermal Reactions of Alkynes With Compounds Containing NN as Part of the Metallocycle

Compound	Diphenyl-acetylene (PhC≡CPh)	Phenyl-acetylene (HC≡CPh)	Dimethyl Acetylene-dicarboxylate (MeO ₂ CC≡CCO ₂ Me)
 <p style="text-align: right;">(13)</p>	Very Rapid. Mn(CO) ₃ species detected.	Very Rapid. Mn(CO) ₃ species detected.	Not Tested.
 <p style="text-align: right;">(16)</p>	Not Tested.	Not Tested.	Very Slow. Doubly inserted product.
 <p style="text-align: right;">(18)</p>	Not Tested.	Very Slow. Mn(CO) ₃ species detected.	Very Slow.

3.2.1.5 N-acetyl-N-phenylhydrazine (PhNH-NHCOCH₃) and PhCH₂Mn(CO)₅

In an effort to characterise the product of the reaction between N-acetyl-N-phenylhydrazine and PhCH₂Mn(CO)₅ (Chapter 2), an *in situ* reaction with the alkyne DMAD was attempted. Only Mn₂(CO)₁₀ and an impure yellow oil were isolated. The latter was not characterised. There were however >3 methyl groups present in the NMR spectra, only one of which was attributable to the starting material (PhNH-NHCOCH₃), indicating an insertion may have taken place.

3.2.2 Me₃NO Assisted Reactions

Only two reactions using trimethylamine oxide to activate the orthometalated starting material were tried, namely (7) with DMAD and (16) with diphenylacetylene. It was evident early on that the Me₃NO did not significantly enhance the reactivity of the cyclometalated compound toward alkyne insertion. Reaction times were long in both cases, often with very little reaction between the orthomanganated systems and the substrate. Consequently reflux was initiated in both cases to promote reaction. Neither produced a “clean” inserted product in a yield sufficiently high for full characterisation. For these reasons further reactions involving Me₃NO were not carried out.

3.2.3 Conclusions

In accord with the findings of Samad for orthomanganated imines, most of the nitrogen-donor systems tested toward alkyne coupling reactions appear not to be of great value in organic synthesis, when compared to those of oxygen-donor systems. Reactions were generally not “clean”, and in most instances reaction rates were slow. In addition, the products obtained by the various systems were unpredictable, and often decomposed on standing, precluding characterisation. Clearly better purification methods and perhaps workup under an inert atmosphere are called for if further investigation into these compounds is to be undertaken.

The only systems that appear to be of some value are those of diphenylhydrazone, which proved to have both rapid reaction rates - comparable to those of aromatic ketones - and straightforward insertion products. However, further investigation with a larger variety of alkynes will be required to assess the generality of alkyne reactivity.

3.3 Experimental Section

The experimental methods used in preparing the orthomanganated adducts (Chapter 2), are essentially unchanged for the work in this chapter, and are given in Appendix I.

Column chromatography was used throughout for workup purposes, despite the significantly lower resolution compared to silica gel preparative layer chromatography. The reason for this is the substantial decomposition observed when the latter was used. Detail is given in Appendix I. For this reason it was often not possible to purify compounds to the level required for structural elucidation.

It should be noted that full NMR assignments of products obtained in this chapter could not be made, either due to lack of purity, decomposition and/or structural complexity. For this reason, assignments are only tentative.

Large excesses of alkyne (1 : 2-3 of orthomanganated compound to alkyne), were used for all reactions, to ensure completion.

After trial reactions involving various solvents (petroleum spirit b.p. 60-80 °C, heptane, benzene, and acetonitrile), it was found that the last produced the fastest reaction times. Petroleum spirit often resulted in no appreciable reaction over 2 days. For this reason acetonitrile was used for the majority of reactions.

All references to “petroleum spirit” refer to petroleum spirit (AR, b.p. 60-80°C).

3.3.1 Thermally Induced Reactions

3.3.1.1 Reaction of η^2 -2-(N-phenylhydrazonomethyl)phenyl-tetracarbonylmanganese (6) with diphenylacetylene

η^2 -2-(N-phenylhydrazonomethyl)phenyltetracarbonylmanganese (6) (0.164 g, 0.453 mmol) and diphenylacetylene (PhC \equiv CPh) (0.157 g, 0.881 mmol) were dissolved in acetonitrile (25 ml), degassed (placed under vacuum) and purged with nitrogen several times. The solution was refluxed under nitrogen, and was complete by IR spectroscopy after 10 hours. During this time a colour change to dark red tending to black was noted. The solvent was removed under vacuum, to leave a dark red oil. The residue was dissolved in dichloromethane, and alumina (Brockmann grade II) was added. The dichloromethane was subsequently removed under vacuum. The resulting powder was transferred to the top of an alumina column (2.5 cm x 8 cm). Separation of products was achieved by slowly increasing the polarity of the eluting solvent (petroleum spirit/dichloromethane). A number of compounds was collected in low yield, none of which were conclusively identified.

3.3.1.2 Reaction of η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyl-tetracarbonylmanganese (7) with diphenylacetylene

Similarly, η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7) (0.152 g, 0.404 mmol), and diphenylacetylene (0.15 g, 0.842 mmol) were dissolved in acetonitrile (25 ml) and refluxed under nitrogen for 6 hours, during which time the solution became black. After normal workup, a range of products was collected, although the quantities and purity were too low to permit characterisation.

3.3.1.3 Reaction of η^2 -2-(N,N-diphenylhydrazonomethyl)phenyl-tetracarbonylmanganese (8) with diphenylacetylene

Similarly, η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (8) (0.251 g, 0.573 mmol), and diphenylacetylene (0.20 g, 1.122 mmol) were dissolved in acetonitrile (25 ml) and refluxed under nitrogen for 2 hours, during

which time the initial bright yellow solution became black. IR revealed no starting material present, but a tricarbonyl species had clearly formed with absorbances at (CH₃CN) $\nu(\text{CO})$ 2024 (m), 1982 (w, br) and 1919 (vs, br) cm⁻¹.

Preliminary t.l.c. revealed 4 reaction products, one of which was unreacted diphenylacetylene.

Elution on an alumina column gave:

Band 1 [Petroleum spirit]: a white solid which contained no metal carbonyls. Identified by NMR as unreacted diphenylacetylene.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.58-7.24 (10H, *m*, C-H aromatic). (Lit.¹⁰ (CDCl₃) δ 7.45 (10H, *m*, C-H aromatic)).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 131.7 (*d*, C-4',4''), 128.4 (*s*, C-3',5',3'',5''), 123.4 (*d*, C-1), 89.5 (*d*, $\text{C}\equiv\text{C}$). These are exactly co-incident with an authentic sample.

Band 2 [30:70 Dichloromethane:petroleum spirit]: an orange oil which contained no metal carbonyls, was collected. It was crystallised from petroleum spirit to yield an orange powder [(**19**), 0.133 g, 53%] of m.p. 132 °C. The structure was tentatively assigned from NMR data and elemental analysis.

Anal. Found: C, 86.96; H, 5.60; N, 6.19; C₃₃H₂₅N₂ calc.: C, 87.16; H, 5.60; N, 6.23 %.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.33-6.91 (24H, *m*, C-H aromatic), 4.48 (1H, *s*, C-1).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 148.0 (*s*), 144.9 (*s*), 144.6 (*s*), 141.4 (*s*), 140.9 (*s*), 134.8 (*s*), 134.0 (*s*), 131.5 (*s*), 129.4 (*d*), 129.1 (*d*), 128.6 (*d*), 128.4 (*d*), 127.7 (*d*), 127.4 (*d*), 126.0 (*d*), 124.8 (*d*), 122.8 (*d*), 121.3 (*d*), 121.1 (*d*), 120.6 (*d*), 117.9 (*d*), 64.2 (*d*).

3.3.1.4 Reaction of η^2 -2-(N,N-diphenylhydrazonomethyl)phenyl-tetracarbonylmanganese (8) with DMAD

Similarly, η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (8) (0.102 g, 0.233 mmol), and dimethyl acetylenedicarboxylate ($\text{CH}_3\text{OOC}\equiv\text{CCOOCCH}_3$) (0.05 g, 0.352 mmol) were dissolved in acetonitrile (28 ml) and refluxed under nitrogen for 1 hour, during which time a colour change from yellow to very dark orange was observed. The product was eluted on a silica column. This apparently induced extensive decomposition.

Two bands were collected:

Band 1 [Petroleum spirit]: a yellow solid which contained no metal carbonyls. Identified by NMR and by the m.p. as diphenylhydrazine (0.0304 g, 72 %), m.p. 34-35 °C (Lit. 35 °C¹¹).

¹³C NMR: (22.49 MHz) (CDCl_3) δ 143.3 (s, C-1), 129.3 (d, C-3,5), 121.1 (d, C-4), 117.9 (d, C-2,6).

Band 2 - 30 : 70 Dichloromethane : petroleum spirit: gave an orange oil which contained no metal carbonyls. The oil did not crystallise and was found to be a mixture of at least 6 compounds (by t.l.c.). The quantities were small and for this reason the individual constituents were not characterised.

3.3.1.5 Reaction of η^2 -2-(N,N-diphenylhydrazonomethyl)phenyl-tetracarbonylmanganese (8) with trimethylsilylacetylene

Similarly, η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (8) (0.102 g, 0.233 mmol), and trimethylsilylacetylene ($\text{HC}\equiv\text{CSi}(\text{CH}_3)_3$) (0.064 g, 0.652 mmol) were dissolved in acetonitrile (25 mls) and refluxed under nitrogen for 4 hours. During this period the solution became bright orange. The residue was supported on alumina, and transferred to a column. Subsequent elution gave:

Band 1 [1 : 10 Dichloromethane : petroleum spirit]: a yellow oil which contained no metal carbonyls. The NMR spectrum strongly suggested a mixture of two

alkyne inserted products (presumably the two expected isomers) in a 2:1 ratio, for which further attempts at separation proved futile. Tentatively characterised as (**20**) and (**21**), (0.065 g, 54 %; both isomers).

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.73-7.08 (15H, *m*, C-H aromatic), 1.62 (1H, *s*, C-1), 1.46 (1H, *s*, C-1), 0.37 (9H, *s*, Si(CH₃)₃), 0.24 (9H, *s*, Si(CH₃)₃).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 143.8 (*s*), 141.2 (*s*), 134.2 (*s*), 133.3 (*s*), 129.9 (*d*), 129.1 (*d*), 127.8 (*s*), 128.1 (*s*), 1 (*s*), 126.7 (*s*), 126.2 (*s*), 124.6 (*d*), 122.6 (*d*), 121.0 (*d*), 29.8 (*d*), 22.8 (*d*), -0.7 (*q*, Si(C₃H₇)₃), -1.17 (*q*, Si(C₃H₇)₃).

Band 1 [3 : 10 Dichloromethane : petroleum spirit then neat dichloromethane]: A small quantity of an orange oil (0.07 g) was collected which could not be crystallised. It was found to constitute of at least 6 compounds by t.l.c., and therefore was not pursued any further.

3.3.1.6 Reaction of η²-2-[1-(N,N-diphenylhydrazono)ethyl]-phenyltetracarbonylmanganese (**9**) with diphenylacetylene

Similarly, η²-2-[1-(N,N-diphenylhydrazono)ethyl]phenyltetracarbonylmanganese (**9**) (0.151 g, 0.334 mmol), and diphenylacetylene (0.091 g, 0.511 mmol) were dissolved in acetonitrile (25 ml) and refluxed under nitrogen for 3 hours, during which time the solution became orange.

Column separation gave:

Band 1 [Petroleum spirit]: a white solid which was identified by NMR as unreacted diphenylacetylene.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.58-7.24 (10H, *m*, C-H aromatic).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 131.7 (*d*, C-4',4''), 128.4 (*s*, C-3',5',3'',5''), 123.4 (*d*, C-1), 89.5 (*d*, C≡C).

Band 2 [30:70 Dichloromethane:petroleum spirit]: an orange oil which contained no metal carbonyls, that was crystallised from petroleum spirit to yield beige crystals of m.p. 127 °C. The structure (**22**) (0.065 g, 42 %) was tentatively assigned from NMR data.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.62-7.11 (24H, *m*, C-H aromatic), 3.06 (3H, *s*, C-1).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 157.7 (*s*), 149.5 (*s*), 137.7 (*s*), 136.0 (*s*), 131.4 (*d*), 130.3 (*d*) 129.9 (*d*), 129.3 (*s*), 128.2 (*d*), 127.6 (*d*), 127.1 (*d*) 126.9 (*d*), 126.5 (*d*), 126.3 (*d*), 125.5 (*d*), 22.76 (*q*, CH₃).

3.3.1.7 Reaction of η²-2-[1-(N,N-diphenylhydrazono)ethyl]-phenyltetracarbonylmanganese (9) with DMAD

Similarly, η²-2-[1-(N,N-diphenylhydrazono)ethyl]phenyltetracarbonylmanganese (9) (0.182 g, 0.402 mmol), and dimethyl acetylenedicarboxylate (CH₃OOCC≡CCOOCH₃) (0.085 g, 0.598 mmol) were added to acetonitrile (25 ml) and refluxed for 1 hour. Only a slight decolorisation to orange was observed. IR clearly indicated the presence of a tricarbonyl species (CH₃CN) ν(CO) 2014 (*vs*), 1924 (*s*, *br*) cm⁻¹, as the only absorption in the metal carbonyl region.

On workup a yellow oil was collected. Subsequent efforts at purification resulted in extensive decomposition with an unknown brown solid forming. No product(s) could be identified.

3.3.1.8 Reaction of η²-2-[1-(N,N-diphenylhydrazono)ethyl]-phenyltetracarbonylmanganese (9) with trimethylsilylacetylene

Similarly, η²-2-[1-(N,N-diphenylhydrazono)ethyl]phenyltetracarbonylmanganese (9) (0.170 g, 0.376 mmol), and trimethylsilylacetylene (0.070 g, 0.708 mmol) were dissolved in acetonitrile and refluxed for 5 hours. During this time, the colour of the solution changed from bright yellow to bright orange/red. A tricarbonyl species was detected in the IR spectrum of the reaction mixture showing absorbances at (CH₃CN) ν(CO) 2003 (*s*), 1905 (*vs*, *br*). The residue was supported on alumina, and transferred to a column. Subsequent elution gave:

Band 1 [1 : 3 Dichloromethane : petroleum spirit]: a yellow oil which contained no metal carbonyls. NMR studies suggest only one insertion product, assigned as

(**23**) (0.072 g, <52 %). Very small quantities of an impurity were clearly present which could not be separated by column chromatography. P.l.c. was attempted, but this completely decomposed the product to at least 6 different compounds.

¹H NMR: (89.55 MHz) (CDCl₃) δ 7.35-6.89 (15H, *m*, C-H aromatic), 2.02 (3H, *s*, C-1), 0.11 (9H, *s*, Si(CH₃)₃).

¹³C NMR: (75.47 MHz) (CDCl₃) δ 168.3 (*s*), 148.7 (*s*), 141.9 (*d*), 139.4 (*s*), 136.9 (*s*), 132.8 (*d*), 129.3 (*d*), 128.7 (*d*), 128.2 (*d*), 127.8 (*d*), 126.4 (*d*), 123.4 (*d*), 121.8 (*d*), 22.6 (*q*, C-1), -1.2 (*q*, Si(CH₃)₃). Impurity resonances: δ 129.4 (*d*), 121.6 (*d*), 117.9 (*d*).

Band 2 [Dichloromethane]: a small quantity of an orange oil (0.04 g) was collected which could not be crystallised. It was found to be at least 6 compounds by t.l.c., and therefore was not characterised.

3.3.1.9 Reaction of η²-2-(N²-cyclohexylidene-N¹-phenylhydrazino)phenyltetracarbonylmanganese (**13**) with diphenylacetylene

Similarly, η²-2-(N²-cyclohexylidene-N¹-phenylhydrazino)phenyltetracarbonyl manganese (**13**) (0.107 g, 0.249 mmol), and diphenylacetylene (0.089 g, 0.499 mmol) were added to acetonitrile (25 ml) and refluxed for 20 minutes. The solution quickly became pale yellow, then within 5 minutes, bright yellow. An IR spectrum was recorded, indicating a tetracarbonyl species was no longer present. The IR data clearly indicated the presence of a tricarbonyl species: (CH₃CN) ν(CO) 2003 (*s*), 1901 (*vs*, *br*) cm⁻¹. On removing the solvent under vacuum the initial yellow/orange oil decomposed rapidly (despite the oxygen free environment), becoming dark muddy green. The residue was supported on alumina and worked up in the usual manner. Subsequent elution gave:

Band 1 [Petroleum spirit (b.p. 60-80 °C)]: a white solid, which was identified from the NMR spectrum as unreacted diphenylacetylene (0.06 g).

Band 2 [1 : 3 Dichloromethane : petroleum spirit]: a bright red oil which contained no metal carbonyls. T.l.c. revealed two compounds. Attempted overnight recrystallisation resulted in extensive decomposition, giving rise to a

brown insoluble solid. T.l.c. showed there were now at least 5 compounds present. For this reason the reaction was abandoned. The transferred alumina still appeared green. This fraction could not be removed, even by very polar solvents.

3.3.1.10 Reaction of η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (**13**) with phenylacetylene

Similarly, η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonyl manganese (**13**) (0.102 g, 0.237 mmol), and phenylacetylene (0.046 g, 0.454 mmol) were added to petroleum spirit (b.p. 60-80 °C) (25 ml) and refluxed for 3 hours. During this time the solution rapidly became darker yellow, then increasingly brown. T.l.c. revealed multiple products, indicating decomposition or possibly air sensitive compounds. For this reason the reaction was discontinued.

The same reaction was carried out in acetonitrile (25 ml) using η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (**13**) (0.101 g, 0.235 mmol), and phenylacetylene (0.046 g, 0.454 mmol). A more rapid reaction was observed, with (**13**) completely consumed in 15 minutes. IR clearly indicated the presence of a tricarbonyl species (CH_3CN) $\nu(\text{CO})$ 2004 (s), 1904 (vs, br) cm^{-1} . After usual workup, two inseparable products were isolated (t.l.c.), as a dark orange oil. Attempts at recrystallisation proved futile, and decomposition, despite freezer temperatures, was extensive after 2 days. For this reason the reaction was eventually abandoned.

3.3.1.11 Reaction of η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyl-tetracarbonylmanganese (**16**) with DMAD

η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarbonylmanganese (**16**) (0.098 g, ~0.3 mmol) and dimethyl acetylenedicarboxylate (0.069 g, 0.488 mmol) were added to acetonitrile (25 ml) and refluxed for 24 hours. During this time the solution became increasingly orange, eventually becoming red/black at completion. After standard workup, a yellow oil was collected, which crystallised

by pentane diffusion into a saturated CH_2Cl_2 solution at 4 °C, to yield (as yet unidentified) very fine yellow needles (0.020 g), of m.p. 145-146 °C.

^1H NMR: (300.13 MHz) (CDCl_3) δ 8.64 (1H, *d*, $^3J_{\text{HH}} = 7.9$ Hz), 7.53 (2H, *tt*, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz), 7.42 (2H, *td*, $^3J_{\text{HH}} = 7.1$ Hz, $^4J_{\text{HH}} = 1.3$ Hz), 7.30 (1H, *td*, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.3$ Hz), 7.10 (1H, *td*, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 1.1$ Hz), 7.00 (2H, *s*), 6.78 (1H, *d*, $^3J_{\text{HH}} = 8.0$ Hz), 3.89 (3H, *s*, OCH_3), 3.88 (3H, *s*, OCH_3), 3.74 (3H, *s*, OCH_3), 3.70 (3H, *s*, OCH_3).

^{13}C NMR: (22.49 MHz) (CDCl_3) δ 166.9 (*s*, $\text{C}=\text{O}$), 166.2 (*s*, $\text{C}=\text{O}$), 163.9 (*s*, $\text{C}=\text{O}$), 162.5 (*s*, $\text{C}=\text{O}$), 146.1 (*s*), 138.0 (*s*), 134.0 (*s*), 132.5 (*d*), 129.8 (*d*), 129.0 (*d*), 128.4 (*d*), 126.6 (*d*), 123.4 (*d*), 122.5 (*d*), 119.9 (*q*), 109.6 (*d*), 93.2 (*t*), 57.0 (*q*, OCH_3), 53.0 (*q*, OCH_3), 52.2 (*q*, OCH_3), 51.7 (*q*, OCH_3).

ESMS: (Cone 10, $\text{CH}_3\text{CN}/\text{H}_2\text{O}$) *m/e* 855 (58, P^+), 576 (100), 559 (53), 471 (72), 366 (50).

The reaction was repeated, using η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyl tetracarbonylmanganese (**16**) (0.201 g, ~0.6 mmol) and dimethyl acetylenedicarboxylate (0.294 g, 2.070 mmol) in acetonitrile (30 ml), to increase product quantity and allow further analysis. The solution was refluxed for 42 hours. Elution gave:

Band 1 [1 : 1 Dichloromethane : petroleum spirit]: a yellow oil, which did not crystallise (0.166 g) and was identified using NMR as a mixture of the same yellow compound isolated from the first attempt together with a new compound which as yet is unidentified. Product separation by recrystallisation was unsuccessful.

Band 2 [Dichloromethane]: a yellow oil (0.044 g), which by NMR constituted of a mixture of compounds, and was therefore not characterised.

3.3.1.12 Reaction of η^2 -2-(N -phenylazo)phenyltetracarbonylmanganese (**18**) with phenylacetylene

Similarly, η^2 -2-(N -phenylazo)phenyltetracarbonylmanganese (**18**) (0.103 g, 0.296 mmol) and phenylacetylene (0.058 g, 0.572 mmol) were added to acetonitrile (25 ml) and refluxed under nitrogen for 18 hours, during which time

no colour change was observed. The IR spectrum clearly indicated the presence of a tricarbonyl species (CH_3CN) $\nu(\text{CO})$ 2021 (s), 1917 (vs, br) cm^{-1} , from the only bands present in the metal carbonyl region. Workup and subsequent elution gave:

Band 1 [1 : 1 Dichloromethane : petroleum spirit]: a yellow oil, that by IR did not contain Mn-CO. The compound crystallised readily, and was identified by NMR as the demetalated starting material, azobenzene (0.025 g, 46%).

$^1\text{H NMR}$: (89.55 MHz) (CDCl_3) δ 7.97-7.86 (5H, *m*, C-H aromatic), 7.53-7.41 (5H, *m*, C-H aromatic).

$^{13}\text{C NMR}$: (22.49 MHz) (CDCl_3) δ 152.6 (*s*, C-1',1''), 130.9 (*d*, C-4',4''), 129.0 (*d*, C-3',3'',5',5''), 122.8 (*d*, C-2',2'',6',6'').

Band 2 - Dichloromethane: a blue oil (0.005 g), which constituted of a mixture of two compounds, blue and yellow. It did not contain the $\text{Mn}(\text{CO})_4$ moiety by IR. Solutions became yellow, on standing.

$^1\text{H NMR}$: (89.55 MHz) (CDCl_3) δ 7.56-7.30 (*m*, C-H aromatic).

$^{13}\text{C NMR}$: (22.49 MHz) (CDCl_3) δ 129 (*m*).

ESMS: (cone 10, CH_3CN) *m/e* 312 (25, M^+), 311 (100, M^+-H), 295 (4, M^+-OH), 283 (5, M^+-CO).

3.3.1.13 Reaction of η^2 -2-(N-phenylazo)phenyltetracarbonylmanganese (**18**) with DMAD

Similarly, η^2 -2-(N-phenylazo)phenyltetracarbonylmanganese (**18**) (0.103 g, 0.296 mmol) and DMAD (0.058 g, 0.572 mmol) were added to benzene (25 ml) and refluxed under nitrogen for 24 hours. No colour change was observed. IR indicated only very little reaction had taken place, with the $\text{Mn}(\text{CO})_4$ pattern still strong in intensity and attributable to the starting material, (**18**). For this reason the solvent was removed under vacuum, and degassed acetonitrile added (25 ml). The resultant solution was refluxed for a further 10 hours. Normal workup produced only unreacted (**18**) and azobenzene.

3.3.1.14 Reaction of N-acetyl-N-phenylhydrazine (PhNH-NHCOCH₃) with PhCH₂Mn(CO)₅ and DMAD

PhCH₂Mn(CO)₅ (0.421 g, 1.471 mmol) and N-acetyl-N-phenylhydrazine (0.055 g, 0.508 mmol) were dissolved in heptane and refluxed for 2 hours. A colour change clearly indicated a reaction had taken place. However the product(s) was too air sensitive to allow characterisation (as previously discussed in Chapter 2). DMAD (0.347 g, 0.244 mmol) was added in attempt to form an isolable derivative. The solution was refluxed for a further 5 hours during which time no colour change was noted. Normal workup gave Mn₂(CO)₁₀ (0.05 g, 19%) and an unknown yellow oil (200 mg), which by t.l.c. was found to contain at least 3 compounds. Efforts at separation by column chromatography and crystallisation were unsuccessful. With p.l.c. decomposition occurred, resulting in at least 12 compounds, all in trace amounts. The reaction was therefore abandoned.

3.3.2 Me₃NO Assisted Reactions

The following reaction were carried out by use of trimethylamine oxide (Me₃NO) as an alternative method of activating the orthomanganated derivative to alkyne substitution.

Approximately 1.4 - 1.5 mole equivalent of Me₃NO was used for each mole of the orthomanganated species.

3.3.2.1 Reaction of η²-2-[1-(N-phenylhydrazono)ethyl]phenyl-tetracarbonylmanganese (7) with diphenylacetylene

Similarly, η²-2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7) (0.175 g, 0.465 mmol) was dissolved in acetonitrile (15 ml). Anhydrous Me₃NO (0.061 g, 0.812 mmol) was added. The colour was observed to change from dark orange to yellow/orange. The tricarbonyl species formed by this reaction showed two absorbances at (CH₃CN) ν(CO) 2022 (s) and 1916 (vs, br) cm⁻¹. After 10 minutes stirring, diphenylacetylene (0.050 g, 0.465 mmol) was added. The solution was left stirring at ambient temperatures for 23 hours. The IR spectrum changed very little during this time. The solution was refluxed for two hours, during which time a colour change from orange to murky yellow was noted.

Standard workup revealed more than 6 bands clearly present on the column. Small quantities and low purity made characterisation of all but $\text{Mn}_2\text{CO}_{10}$ (0.05 g) unsuccessful.

3.3.2.2 Reaction of η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarbonylmanganese (**16**) with DMAD

η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarbonylmanganese (**16**) (0.100 g, ~0.275 mmol) was dissolved in acetonitrile (25 ml) and the solution purged with nitrogen and degassed several times. Anhydrous Me_3NO (0.030 g, 0.399 mmol) was added. After stirring for 10 minutes this was followed by DMAD (0.087 g, 0.609 mmol). The flask was stoppered and solution stirred at ambient temperatures for 24 hours, during which time no colour change occurred. IR revealed little change over time in the metal carbonyl region, indicating reaction progress was poor. For this reason the solution was refluxed for an additional 10 hours, during which time the solution became black. After usual workup the residue was supported on alumina. Subsequent elution produced two yellow oils in small quantities, which could not be crystallised. NMR spectroscopy revealed neither was pure. Efforts at further purification proved to be futile.

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Chapter Four

Insertion Reactions of Orthomanganated Compounds Containing the NN Linkage With SO₂

4.1 Introduction

The insertion of SO₂ into the metal-carbon single bond of transition metal-alkyls and -aryls has been studied extensively, and is a well understood process¹. Although SO₂ insertion can generate four different linkages (Figure 4.1), the product formed, for manganese at least, is generally exclusively the S-sulfinate. For other metals examples of the other linkages have been found¹.

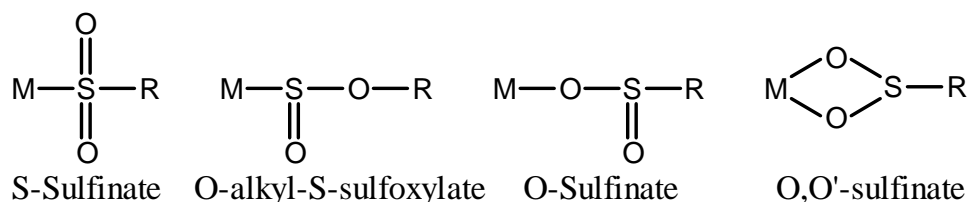


Figure 4.1

Systems closely related to SO₂ include -N=S=O and -N=S=N-, which also insert into the metal-carbon bond of transition metal-alkyl compounds¹, although not in the case of the manganese complexes so far tested².

For the remainder, we will restrict our discussion largely on SO₂ insertion reactions involving manganese compounds.

Wojcicki *et al.* prepared CH₃SO₂Mn(CO)₅ in an 84% yield³, by refluxing CH₃Mn(CO)₅ in liquid SO₂ at -10°C. Similarly prepared in high yields were CH₃CH₂SO₂Mn(CO)₅ and PhCH₂SO₂Mn(CO)₅. PhMn(CO)₅ proved to be considerably less reactive, and even under reasonably forcing conditions, PhSO₂Mn(CO)₅ was collected in only 24% yield. Rhenium analogues were also prepared. The insertion product is thought to be formed via an electrophilic

cleavage process, involving backside electrophilic attack of SO_2 at the α -carbon³.

Cooney recently prepared the SO_2 -inserted adducts from cyclomanganated acetophenone, 4-methoxyacetophenone and 2-acetyl-thiophene, to give complete conversion to (I), (II) and (III) respectively (Figure 4.2)². These were characterised from IR data, and in the case of (II) the NMR spectra and an X-ray crystal structure were also determined. From the latter it was clear that the metallocycle is expanded by forming a sulfinato complex incorporating a six-membered chelate ring.

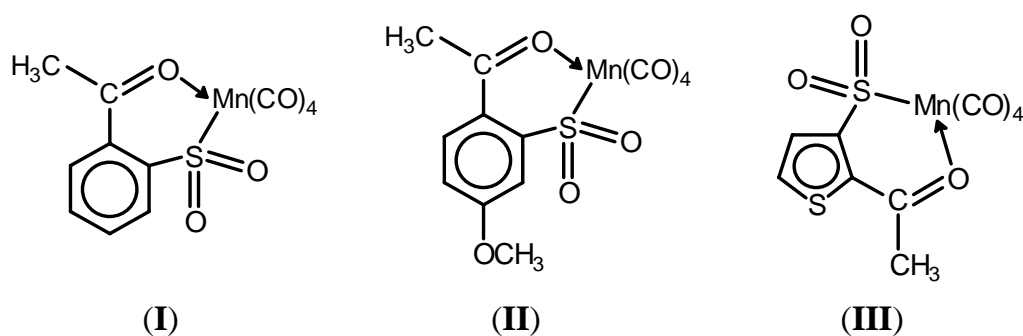


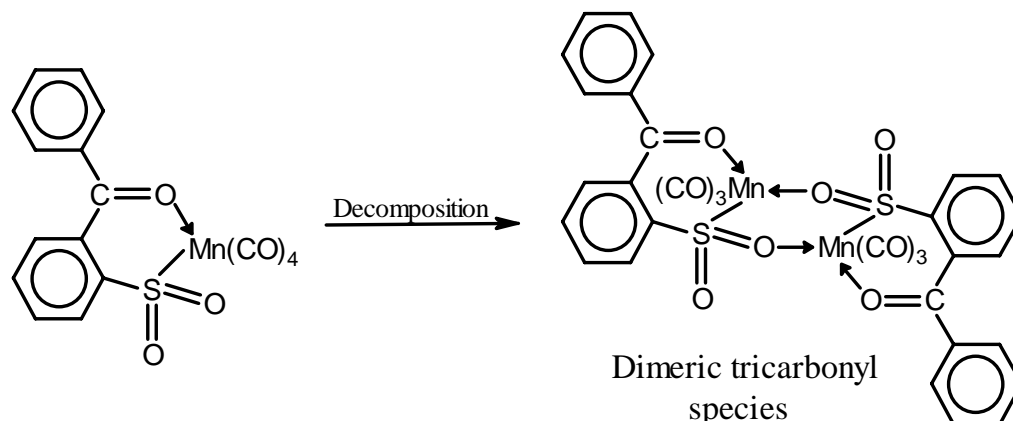
Figure 4.2

The reason for the much increased reactivity of the $\text{Mn-C}_{\text{aryl}}$ bond of cyclomanganated compounds, in contrast to that in PhMn(CO)_5 , is assumed to be due to the increased electron density at the aryl carbon for the cyclomanganated compound as a result of coordination to manganese by the oxygen atom (in this case), which is a π -donor rather than a π -acceptor².

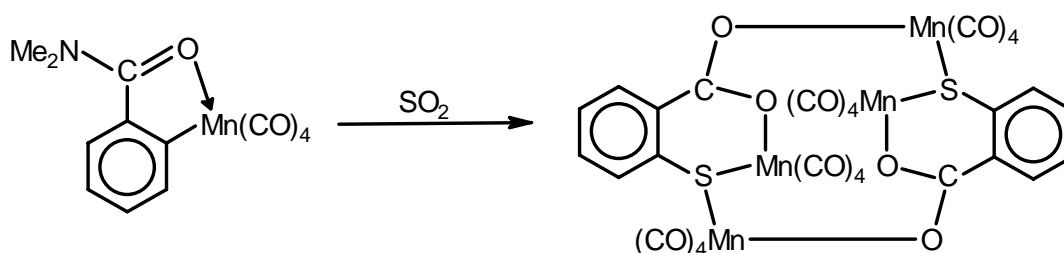
Cooney reported reaction reversibility, with evidence coming from NMR studies, which during an overnight acquisition of an initially pure compound, showed resonances attributable to the orthomanganated precursor. However, the compounds could be stored at low temperatures as solids, or solutions, without significant decomposition occurring.

Depree similarly prepared the SO_2 -inserted derivatives of orthomanganated benzophenone, *N,N*-dimethylbenzamide, and various methoxy substituted acetophenones⁴. In these cases however the reactions appeared to be somewhat less straightforward than those performed by Cooney, despite the similar metallocycles. The SO_2 -inserted products, pure by IR analysis, decomposed

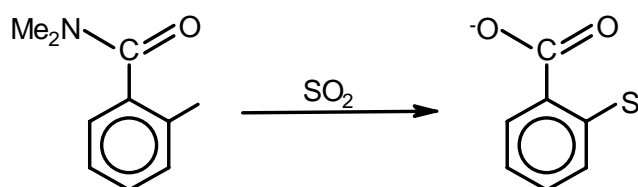
readily to various other compounds. One of these, a tricarbonyl species (Equation 4.1), was characterised by X-Ray crystal structure determination.



When orthomanganated N,N-dimethylbenzamide was treated with SO₂ an unusual tetracarbonylmanganese tetramer was isolated (Equation 4.2)⁴. This was also characterised by an X-Ray crystal structure analysis.

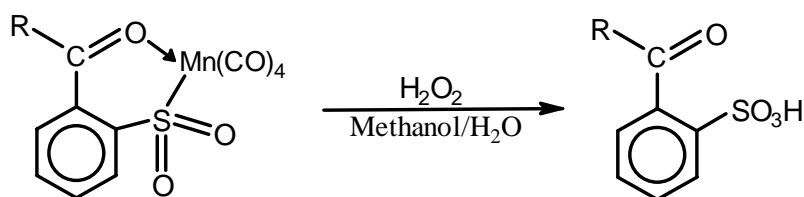


Formation of this species would require the conversion of the starting ligand to one substituted by a sulfide group (Equation 4.3). The mechanism for this is not yet clear.



The synthetic potential of these reactions has been investigated by Depree⁴. It has been found that once the SO₂ insertion has taken place, simple workup using H₂O₂ in methanol at ambient temperatures to demetalate the compound, results in

the SO₃H adduct (Equation 4.4). This provides an extremely mild method of forming a C_{aryl}-S bond specifically *ortho* to the donor substituent.



Equation 4.4

It is aim of the work described in this chapter to extend study of the chemistry of SO₂ with cyclomanganated compounds, already partially established for aromatic ketones, to include nitrogen donors. It was predicted that nitrogen, being less electronegative than oxygen, should increase the electron density of the Mn-C bond, thereby facilitating the electrophilic attack of the SO₂ to a greater extent than in O-donor complexes.

4.2 Discussion of Results

The N-donor compounds tested did not readily insert the SO₂ group into Mn-C_{aryl} σ -bond, certainly not giving complete conversion to the SO₂ inserted product, as demonstrated by Cooney for the orthomanganated aryl ketones². In the cases where an SO₂ inserted product(s) was detected, it was not fully characterised, either because of lack of purity, solubility, and/or stability. Because of the tentative nature of the assignments (see below), this work can only be regarded as exploratory at this stage. A discussion of the individual reactions follows.

4.2.1 η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7)

η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7) was sealed in an ampoule together with liquid SO₂ and heated overnight at 55°C. Although very little colour change occurred, an insoluble yellow precipitate formed, which from the IR spectrum was evidently an SO₂-inserted product. The soluble

fraction was an oil, and also contained what is presumed to be a second insertion product, as detected by IR. Both samples contained the starting material as an impurity. The yellow precipitate was too insoluble to allow characterisation by NMR spectroscopy. The oil was observed to decompose (deinsert) readily to the starting material (7), and for this reason could also not be conclusively characterised. One of these products, probably the oil, is assumed to be the standard SO₂ inserted product (24).

4.2.2 η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (8)

When (8) was treated with SO₂ and heated in a sealed ampoule overnight, only a slight change in colour was observed. As in the previous case, an insoluble precipitate formed, which showed absorbances strongly indicative of an SO₂ inserted product, presumed to be (25), although this is not proven. The soluble fraction, again an oil, was shown by IR spectroscopy to be mainly unreacted starting material, (8).

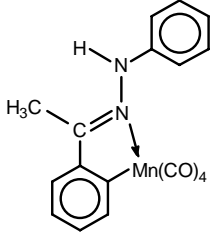
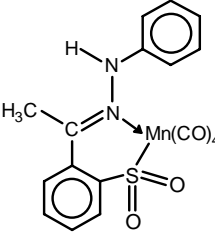
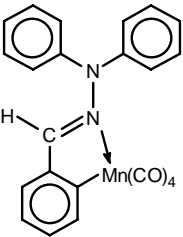
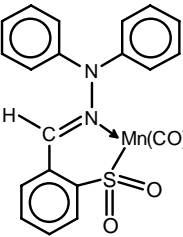
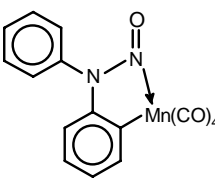
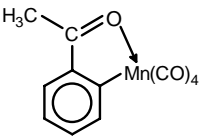
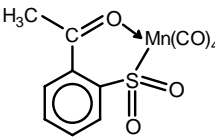
4.2.3 η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (16)

η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (16) was similarly treated with SO₂. The solution noticeably became more orange/yellow. A precipitate formed as above, but was pale grey rather than yellow. IR analysis by a KBr disc of the compound revealed no metal carbonyls. Further spectroscopic analysis could not be carried out due to the highly insoluble nature of this derivative, and therefore it was not characterised. The soluble fraction was identified as N,N-diphenylhydrazine in a >50% yield, together with the starting material (16).

Clearly the reactivity of this system differs markedly from that of the orthometallated hydrazones tested. Since other reducing agents were not used at any stage the SO₂ must play some role in the reduction of diphenylnitrosamine to diphenylhydrazine. However the mechanism for this is not obvious.

Table 4.1 gives a summary of the attempted reactions, showing the starting material, the assumed inserted product, and the absorptions in the carbonyl IR spectra of both the starting material and the product. For (7) two distinct IR

Table 4.1: Summary of Reactions of N-Donor Orthomanganated Compounds With SO₂

Reagent	Assumed Reaction Product	Reagent IR $\nu(\text{M-CO})$ cm^{-1}	Product IR $\nu(\text{M-CO})$ cm^{-1}
 <p>(7)</p>	 <p>(24)</p>	(Heptane) 2071 1988 1980 1947	(CH ₂ Cl ₂) 2101, 2111 2045, 2036 2025, - 1981, 1937
 <p>(8)</p>	 <p>(25)</p>	(KBr) 2074 - 1985 1950	(KBr) 2104 2042 2020 1979
 <p>(16)</p>	No insertion product detected	N/A	N/A
	 <p>(26)</p>	(CH ₂ Cl ₂) 2083 - 1996 1948	(CH ₂ Cl ₂) 2112 2040 2020 1980

patterns were recorded (in the same solvent), indicating two different SO₂ inserted derivatives. Which, if either, of these is (24) is unknown.

The acetophenone species (26) prepared by Cooney² is also presented in the table for comparison.

Depree also found insoluble SO₂-inserted fractions from reactions involving aryl ketones⁴, one of which was the tetramer discussed in the Introduction and shown in Figure 4.3. Therefore unusual species such as these may have formed in the reactions carried out with the N-donors. The products presented in Table 4.1 are only tentatively identified based on IR data.

The IR stretching frequencies of all SO₂-inserted compounds detected were lower than those reported by Cooney². This is in accord with the expected higher electron-density of the N-donor complexes.

4.3 Experimental Section

4.3.1 Reaction of η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7) with SO₂

η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7) (0.203 g, 0.549 mmol) was placed in an glass ampoule, degassed and treated with SO₂ (~10 ml) which had previously been degassed by at least two cycles of freeze-pump-thawing using standard vacuum line techniques. The SO₂ dissolved (7) to give a dark orange solution. The ampoule was sealed, and placed in a Carius tube maintained at 55 °C overnight. Very little colour change had occurred during this time, although a fine yellow precipitate was observed. The ampoule was opened and the SO₂ allowed to evaporate in a fumehood, whereupon the residue was extracted with dichloromethane. The precipitate failed to dissolve to an appreciable extent.

Insoluble Fraction: The yellow powder (0.035 g) was very sparingly soluble in dichloromethane, so a solution IR could be performed. A small quantity of what is assumed to be an SO₂ inserted product was present. However, decomposition

to the starting material (**7**), was also apparent by formation of peaks at 2072, 1980, and 1936 cm^{-1} . The structure (**24**) was tentatively assigned.

IR: (CH_2Cl_2) $\nu(\text{CO})$ 2101 (w), 2072 (w), 2052 (m), 2045 (s), 2025 (m, br), 1981 (vs, br), 1936 (s) cm^{-1} .

Soluble Fraction: gave an orange oil which did not crystallise (0.152 g). The oil was not pure, but IR spectra clearly indicated the presence of an SO_2 inserted product, apparently different from that detected in the insoluble fraction above. Efforts at purification resulted in decomposition, to give the starting material (**7**), whose peaks were also clearly present.

IR: (CH_2Cl_2) $\nu(\text{CO})$ 2111 (m), 2036 (vs, br), 1988 (s), 1976 (s), 1937 (m) cm^{-1} .

4.3.2 Reaction of η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetra carbonylmanganese (**8**) with SO_2

Similarly, η^2 -2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese (**8**) (0.204 g, 0.465 mmol) was placed in an ampoule and treated with SO_2 (~10 ml) and left to react overnight at 55 $^\circ\text{C}$. During this time a colour change from a rich yellow to a pale orange was observed. A yellow precipitate had formed. After the SO_2 was allowed to evaporate, the residue was extracted with dichloromethane. The precipitate did not dissolve appreciably in all solvents tested.

Insoluble fraction: gave a yellow powder (0.020 g). IR spectroscopy of the substance showed the following absorbances: (KBr) $\nu(\text{CO})$ 2104 (w), 2042 (s), 2020 (s), 1979 (s) cm^{-1} , indicating this was an SO_2 inserted product (the starting material has (KBr) $\nu(\text{CO})$ 2070 (s), 1972 (vs, br) and 1950 (vs) cm^{-1}). IR data of a weak solution of the compound in acetonitrile also showed $\nu(\text{CO})$ 2104 (m), 2042 (vs), 2020 (s), 1979 (s) cm^{-1} , giving further support of an SO_2 inserted product, tentatively assigned as (**25**).

Soluble Fraction: Gave a yellow oil which was recrystallised from petroleum spirit/dichloromethane to yield a yellow powder (0.100 g). This was characterised by IR as unreacted/deinserted starting material (**8**).

IR: (CH₃CN) ν (CO) 2070 (s), 1984 (vs), 1938 (s) cm⁻¹.

4.3.3 Reaction of η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (**16**) with SO₂

Similarly, η^2 -2-(N¹-nitroso-N¹-phenylamino)phenyltetracarbonylmanganese (**16**) (0.141 g, ~0.4 mmol) was placed in an ampoule with SO₂ (~10 ml) and left to react for overnight at 60 °C. During this time the colour changed to yellow/orange. A grey precipitate had settled out. After allowing the SO₂ to evaporate, the residue was extracted with dichloromethane.

Insoluble fraction: gave a grey powder (0.076 g), that was insoluble in all solvents tested, including methanol. The IR spectrum of a KBr disc prepared from the compound revealed no metal carbonyls. Due to the extreme insolubility of the product, further characterisation could not be carried out.

Soluble Fraction: Gave a yellow oil comprising of two components. These were successfully separated on an alumina column by slowly increasing the solvent polarity. Two bands were collected.

The first contained no metal carbonyls and was identified from the NMR spectrum as diphenylhydrazine (0.04 g, 53 %).

¹³C NMR: (22.49 MHz) (CDCl₃) δ 143.2 (*s*, C-1), 129.4 (*d*, C-3,5), 121.1 (*d*, C-4), 117.9 (*d*, C-2,6).

The second band gave an orange solid (0.03 g), which was identified using IR spectroscopy as unreacted/deinserted starting material (**16**).

IR: (CH₂Cl₂) ν (CO) 2085 (m), 2001 (vs, br), 1965 (s) cm⁻¹, *cf.* authentic sample of (**16**), (heptane) ν (CO) 2084 (m), 2004 (s), 2001 (vs), 1970 (s) cm⁻¹.

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Appendix I

General Experimental Procedure

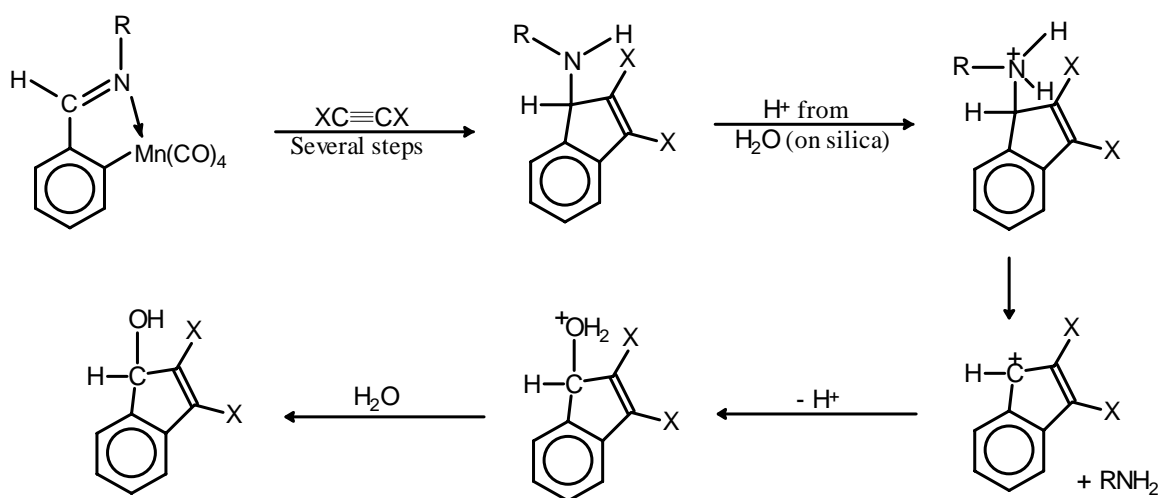
All reactions were carried out under an inert atmosphere of dry nitrogen, using standard established Schlenk techniques. THF was dried by distillation from sodium/benzophenone under nitrogen.

All solvents used for reaction and workup purposes were of analytical grade quality and were stored over 4Å molecular sieves.

All glassware used was cleaned in chromic acid baths and dried in an oven.

Note on Preparative Layer Chromatography (Silica Plate)

The acidic nature of silica gel often causes nitrogen compounds such as those prepared for this study to hydrolyse extensively. Samad observed this process for reactions involving orthomanganated imines (see Chapter 3). The suggested reaction scheme is shown below for an alkyne insertion (Scheme AI.1), but can be extrapolated for other reactions.



The initial insertion product is attacked by H^+ which then rearranges to form a carbocation intermediate, with the elimination of $R-NH_2$. Subsequent nucleophilic attack by H_2O followed by loss of H^+ gives the final product (an indenol), i.e. the same product as would be expected from aromatic ketones.

However, for arylhydrazones it has been found that this process leads to extensive decomposition, with initially formed product(s) often giving rise to more than a dozen when supported on silica. In addition, there always remained a thick baseline, despite the compound having being eluted on an alumina column prior to plating, a further indication of product decomposition. For this reason it was preferable to use alumina (Brockmann grade II) exclusively for experimental workup, both for initial support and subsequent column chromatography, for all reactions. Under these conditions no additional break-down of products was observed. The considerably lower resolution however lead to some compounds not reaching the purity required for conclusive characterisation by NMR and elemental analysis.

Spectroscopic Methods

Nuclear Magnetic Resonance (NMR)

All spectra (1H NMR and ^{13}C NMR) were recorded in $CDCl_3$ solvent, and were generated on either Bruker AC300 or Jeol FX-90Q instruments.

NMR data on arylhydrazones is scarce, and that which is available is almost entirely for 1H NMR only. Unambiguous ^{13}C NMR assignments of hydrazones (and related compounds) therefore had to be made by comparing spectra of starting material and the metalated product (by observing which resonances were shifted upon metalation), by comparison with established spectra of metalated aryl imines and ketones, and comparison of mono-phenyl and di-phenyl hydrazones and also that of aniline. For the latter we assume electron density in the phenyl ring of aniline will be very similar to that of an unsubstituted N-Ph ring on the hydrazone, so the chemical shifts are expected to be roughly the same. We find this assumption is well founded with co-incident resonances occurring within ± 3 ppm.

Often distinguishing the ^{13}C chemical shift of $-\underline{\text{C}}=\text{N}-$ and $\underline{\text{C}}_{\text{aryl}}-\text{Mn}$ is difficult, since the magnitude of their chemical shifts are often interchangeable. For the arylhydrazones of benzaldehyde these are obvious, since the hydrogen in $\text{H}-\underline{\text{C}}=\text{N}-$ creates a “double” intensity signal. However for the the arylhydrazones of acetophenone, both peaks are from quaternary carbons, and look identical in the spectra. However a the peak in both the benzaldehyde and acetophenone systems at ~ 180 ppm have virtually the same chemical shift. These should therefore be the $\underline{\text{C}}_{\text{aryl}}-\text{Mn}$ since the CH_3 moiety will effect this C atom significantly less than the directly bonded $-\text{C}=\text{N}-$.

Infrared

Infrared spectra were recorded on either a Digilab FTS-45 FTIR instrument (resolution 2 cm^{-1}) for final products and reaction monitoring, or a Perkin Elmer 180B FTIR instrument (resolution 4 cm^{-1}) for monitoring reactions only. Solution cells (KBr windows) with heptane, acetonitrile, or dichloromethane solvents, were used.

Other Data

Melting points were determined on a Reichert thermopan melting point machine, and are uncorrected.

Elemental analysis were carried out by the University of Otago Microanalytical Laboratory.

Electrospray mass spectrometry (ESMS), was performed using a VG Platform II instrument, with $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:1) as solvent.

Appendix II

Complete Bond Lengths, Bond Angles, and Thermal and Positional Parameters for η^2 -2-[1-(N-phenyl hydrazono)ethyl]-phenyltetracarboxylmanganese (7)

Table AII.1: Bond Lengths (Å) for η^2 -2-[1-(N-phenylhydrazono)ethyl]-phenyltetracarboxylmanganese (7)

Mn(1)-C(1)	1.806(3)	C(2)-O(2)	1.136(3)
Mn(1)-C(3)	1.830(3)	C(11)-C(16)	1.400(4)
Mn(1)-C(4)	1.851(3)	C(11)-C(12)	1.416(4)
Mn(1)-C(2)	1.881(3)	C(12)-C(13)	1.399(4)
Mn(1)-N(1)	2.053(2)	C(13)-C(14)	1.387(4)
Mn(1)-C(11)	2.058(3)	C(14)-C(15)	1.391(4)
N(1)-C(5)	1.303(4)	C(15)-C(16)	1.389(4)
N(1)-N(2)	1.427(3)	C(21)-C(26)	1.389(4)
N(2)-C(21)	1.424(4)	C(21)-C(22)	1.394(4)
C(5)-C(12)	1.469(4)	C(22)-C(23)	1.379(4)
C(5)-C(6)	1.496(4)	C(23)-C(24)	1.389(4)
C(4)-O(4)	1.147(4)	C(24)-C(25)	1.373(4)
C(1)-O(1)	1.152(3)	C(25)-C(26)	1.395(4)
C(3)-O(3)	1.155(3)		

Table AII.2: Bond Angles (degrees) for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarboxylmanganese (7)

C(1)-Mn(1)-C(3)	87.13(13)	O(4)-C(4)-Mn(1)	179.4(3)
C(1)-Mn(1)-C(4)	95.48(13)	O(1)-C(1)-Mn(1)	175.2(3)
C(3)-Mn(1)-C(4)	95.36(12)	O(3)-C(3)-Mn(1)	175.3(2)
C(1)-Mn(1)-C(2)	88.63(13)	O(2)-C(2)-Mn(1)	177.1(2)
C(3)-Mn(1)-C(2)	172.09(12)	C(16)-C(11)-C(12)	116.5(3)
C(4)-Mn(1)-C(2)	91.69(12)	C(16)-C(11)-Mn(1)	130.3(2)
C(1)-Mn(1)-N(1)	170.13(11)	C(12)-C(11)-Mn(1)	113.2(2)
C(3)-Mn(1)-N(1)	92.17(11)	C(13)-C(12)-C(11)	121.8(3)
C(4)-Mn(1)-N(1)	94.39(11)	C(13)-C(12)-C(5)	122.5(3)
C(2)-Mn(1)-N(1)	90.86(11)	C(11)-C(12)-C(5)	115.6(2)
C(1)-Mn(1)-C(11)	91.68(12)	C(14)-C(13)-C(12)	120.0(3)
C(3)-Mn(1)-C(11)	87.50(11)	C(13)-C(14)-C(15)	119.2(3)
C(4)-Mn(1)-C(11)	172.41(12)	C(16)-C(15)-C(14)	120.7(3)
C(2)-Mn(1)-C(11)	85.94(11)	C(15)-C(16)-C(11)	121.8(3)
N(1)-Mn(1)-C(11)	78.45(10)	C(26)-C(21)-C(22)	119.4(3)
C(5)-N(1)-N(2)	116.4(2)	C(26)-C(21)-N(2)	122.3(3)
C(5)-N(1)-Mn(1)	119.2(2)	C(22)-C(21)-N(2)	118.2(2)
N(2)-N(1)-Mn(1)	124.4(2)	C(23)-C(22)-C(21)	120.5(3)
C(21)-N(2)-N(1)	117.3(2)	C(22)-C(23)-C(24)	120.0(3)
N(1)-C(5)-C(12)	113.3(2)	C(25)-C(24)-C(23)	119.7(3)
N(1)-C(5)-C(6)	124.3(3)	C(24)-C(25)-C(26)	120.9(3)
C(12)-C(5)-C(6)	122.4(3)	C(21)-C(26)-C(25)	119.4(3)

Table AII.3 Final Positional and Equivalent Thermal Parameters for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7)

Atom	X/A	Y/A	Z/A	U(eq)
Mn(1)	0.2777(1)	0.1688(1)	0.5755(1)	0.020(1)
N(1)	0.2886(2)	0.2904(3)	0.4772(1)	0.020(1)
N(2)	0.2643(2)	0.2278(3)	0.4035(1)	0.022(1)
C(5)	0.3174(2)	0.4356(3)	0.4808(2)	0.020(1)
C(6)	0.3200(3)	0.5391(3)	0.4137(2)	0.025(1)
C(4)	0.2154(3)	-0.0063(4)	0.5279(2)	0.024(1)
C(1)	0.2781(3)	0.0915(3)	0.6699(2)	0.025(1)
C(3)	0.4393(3)	0.1100(3)	0.5758(2)	0.022(1)
C(2)	0.1184(3)	0.2452(3)	0.5871(2)	0.025(1)
O(4)	0.1757(2)	-0.1142(3)	0.4983(1)	0.035(1)
O(1)	0.2843(2)	0.0500(3)	0.7315(1)	0.036(1)
O(3)	0.5416(2)	0.0737(2)	0.5813(1)	0.030(1)
O(2)	0.0231(2)	0.2910(3)	0.5974(1)	0.034(1)
C(11)	0.3394(2)	0.3785(3)	0.6156(2)	0.019(1)
C(12)	0.3487(2)	0.4896(3)	0.5580(2)	0.019(1)
C(13)	0.3875(2)	0.6398(3)	0.5740(2)	0.023(1)
C(14)	0.4191(3)	0.6830(3)	0.6479(2)	0.025(1)
C(15)	0.4102(2)	0.5761(3)	0.7054(2)	0.026(1)
C(16)	0.3713(2)	0.4270(3)	0.6894(2)	0.022(1)
C(21)	0.1394(2)	0.2256(3)	0.3738(2)	0.019(1)
C(22)	0.1053(3)	0.1170(3)	0.3187(2)	0.025(1)
C(23)	-0.0117(3)	0.1176(4)	0.2838(2)	0.029(1)
C(24)	-0.0968(3)	0.2269(4)	0.3035(2)	0.028(1)
C(25)	-0.0646(3)	0.3322(3)	0.3589(2)	0.025(1)
C(26)	0.0536(2)	0.3332(3)	0.3945(2)	0.022(1)

Table AII.4 Final Positional and Equivalent Thermal Parameters of Calculated Hydrogen Atoms for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (7)

Atom	U11	U22	U33	U23	U13	U13
Mn(1)	0.0194(3)	0.0217(3)	0.0187(3)	0.0000(2)	0.0032(2)	0.0002(2)
N(1)	0.0163(13)	0.0244(15)	0.0178(13)	-0.0034(10)	0.0017(10)	0.0019(10)
N(2)	0.0233(14)	0.0230(15)	0.0182(13)	-0.0041(11)	0.0016(10)	0.0053(12)
C(5)	0.0114(14)	0.025(2)	0.023(2)	0.0007(13)	0.0047(12)	0.0045(13)
C(6)	0.025(2)	0.028(2)	0.024(2)	0.0017(14)	0.0027(13)	0.0001(14)
C(4)	0.021(2)	0.029(2)	0.024(2)	0.0079(15)	0.0053(13)	0.0038(15)
C(1)	0.022(2)	0.023(2)	0.030(2)	-0.0018(15)	0.0003(14)	-0.0026(13)
C(3)	0.033(2)	0.019(2)	0.0133(15)	0.0002(12)	0.0012(13)	-0.0018(14)
C(2)	0.030(2)	0.027(2)	0.019(2)	-0.0021(14)	-0.0017(14)	-0.007(2)
O(4)	0.0395(13)	0.0275(13)	0.0382(13)	-0.0056(11)	-0.0025(10)	-0.0068(11)
O(1)	0.0426(14)	0.0424(14)	0.0243(13)	0.0063(11)	0.0006(10)	-0.0122(11)
O(3)	0.0234(13)	0.0357(13)	0.0310(12)	0.0012(10)	0.0026(9)	0.0073(10)

O(2)	0.0211(12)	0.0398(14)	0.0418(13)	-0.0091(11)	0.0067(10)	0.0021(10)
C(11)	0.0134(14)	0.024(2)	0.021(2)	-0.0006(13)	0.0056(12)	0.0025(12)
C(12)	0.0128(14)	0.023(2)	0.020(2)	-0.0016(13)	0.0029(12)	0.0047(13)
C(13)	0.0164(15)	0.023(2)	0.030(2)	0.0010(14)	0.0047(12)	0.0023(13)
C(14)	0.022(2)	0.023(2)	0.032(2)	-0.0050(14)	0.0036(13)	0.0010(14)
C(15)	0.020(2)	0.035(2)	0.023(2)	-0.0097(15)	0.0000(13)	0.0006(14)
C(16)	0.018(2)	0.028(2)	0.021(2)	0.0007(14)	0.0033(12)	0.0026(13)
C(21)	0.0171(15)	0.021(2)	0.0181(15)	0.0045(13)	0.0048(12)	-0.0005(13)
C(22)	0.023(2)	0.030(2)	0.025(2)	-0.0055(14)	0.0079(13)	0.0018(14)
C(23)	0.028(2)	0.034(2)	0.026(2)	-0.0089(14)	0.0025(14)	-0.0074(15)
C(24)	0.014(2)	0.035(2)	0.033(2)	0.003(2)	-0.0016(13)	-0.0026(14)
C(25)	0.021(2)	0.024(2)	0.033(2)	0.0034(15)	0.0082(13)	0.0034(14)
C(26)	0.025(2)	0.020(2)	0.0214(15)	-0.0005(13)	0.0023(12)	0.0002(14)

Table AIII.5 Final Positional and Equivalent Thermal Parameters of Calculated Hydrogen Atoms for η^2 -2-[1-(N-phenylhydrazono)ethyl]phenyl-tetracarbonylmanganese (7)

Atom	X/A	Y/B	Z/C	U(eq)
H(2)	0.2907(26)	0.1349(35)	0.4032(16)	0.022(9)
H(61)	0.4002(6)	0.5845(17)	0.4123(6)	0.047(6)
H(62)	0.2595(12)	0.6185(13)	0.4172(6)	0.047(6)
H(63)	0.3019(17)	0.4807(5)	0.3685(2)	0.047(6)
H(13)	0.3921(2)	0.7107(3)	0.5352(2)	0.023(3)
H(14)	0.4460(3)	0.7824(3)	0.6589(2)	0.023(3)
H(15)	0.4305(2)	0.6046(3)	0.7551(2)	0.023(3)
H(16)	0.3664(2)	0.3575(3)	0.7288(2)	0.023(3)
H(22)	0.1620(3)	0.0436(3)	0.3054(2)	0.023(3)
H(23)	-0.0337(3)	0.0448(4)	0.2470(2)	0.023(3)
H(24)	-0.1753(3)	0.2288(4)	0.2794(2)	0.023(3)
H(25)	-0.1223(3)	0.4038(3)	0.3728(2)	0.023(3)
H(26)	0.0748(2)	0.4052(3)	0.4318(2)	0.023(3)

Appendix III

Complete Bond Lengths, Bond Angles, and Thermal and Positional Parameters for Both Independent Molecules of η^2 -2-(N^2 -cyclohexyliden- N^1 -phenylhydrazino)-phenyltetracarbonylmanganese (13)

Table AIII.1: Bond Lengths (Å) for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

Mn(1)-C(11)	1.796(4)	Mn(2)-C(21)	1.798(4)
Mn(1)-C(14)	1.837(4)	Mn(2)-C(24)	1.842(4)
Mn(1)-C(13)	1.863(4)	Mn(2)-C(23)	1.863(4)
Mn(1)-C(12)	1.865(4)	Mn(2)-C(22)	1.867(4)
Mn(1)-C(111)	2.055(3)	Mn(2)-C(211)	2.056(4)
Mn(1)-N(11)	2.096(3)	Mn(2)-N(21)	2.091(3)
N(11)-C(131)	1.278(5)	N(21)-C(231)	1.276(5)
N(11)-N(12)	1.437(4)	N(21)-N(22)	1.453(4)
N(12)-C(121)	1.416(5)	N(22)-C(212)	1.428(5)
N(12)-C(112)	1.429(4)	N(22)-C(221)	1.437(5)
C(11)-O(11)	1.140(5)	C(21)-O(21)	1.130(6)
C(12)-O(12)	1.118(5)	C(22)-O(22)	1.135(5)
C(13)-O(13)	1.115(5)	C(23)-O(23)	1.121(5)
C(14)-O(14)	1.130(5)	C(24)-O(24)	1.133(5)
C(111)-C(116)	1.382(5)	C(211)-C(212)	1.380(6)
C(111)-C(112)	1.391(5)	C(211)-C(216)	1.399(5)
C(112)-C(113)	1.397(5)	C(212)-C(213)	1.386(6)
C(113)-C(114)	1.388(6)	C(213)-C(214)	1.413(8)
C(114)-C(115)	1.372(7)	C(214)-C(215)	1.354(9)
C(115)-C(116)	1.392(6)	C(215)-C(216)	1.370(8)
C(121)-C(122)	1.387(6)	C(221)-C(226)	1.386(5)
C(121)-C(126)	1.397(5)	C(221)-C(222)	1.391(5)
C(122)-C(123)	1.392(6)	C(222)-C(223)	1.387(6)
C(123)-C(124)	1.362(7)	C(223)-C(224)	1.365(7)
C(124)-C(125)	1.370(8)	C(224)-C(225)	1.367(6)
C(125)-C(126)	1.386(7)	C(225)-C(226)	1.393(6)
C(131)-C(136)	1.490(5)	C(231)-C(236)	1.491(5)
C(131)-C(132)	1.508(5)	C(231)-C(232)	1.503(6)
C(132)-C(133)	1.522(6)	C(232)-C(233)	1.521(7)
C(133)-C(134)	1.515(7)	C(233)-C(234)	1.505(9)
C(134)-C(135)	1.513(6)	C(234)-C(235)	1.525(8)
C(135)-C(136)	1.530(6)	C(235)-C(236)	1.520(8)

Table AIII.2: Bond Angles (degrees) for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

C(11)-Mn(1)-C(14)	91.1(2)	C(21)-Mn(2)-C(24)	91.3(2)
C(11)-Mn(1)-C(13)	88.1(2)	C(21)-Mn(2)-C(23)	89.2(2)
C(14)-Mn(1)-C(13)	93.7(2)	C(24)-Mn(2)-C(23)	97.5(2)
C(11)-Mn(1)-C(12)	91.1(2)	C(21)-Mn(2)-C(22)	87.5(2)
C(14)-Mn(1)-C(12)	96.7(2)	C(24)-Mn(2)-C(22)	90.2(2)
C(13)-Mn(1)-C(12)	169.6(2)	C(23)-Mn(2)-C(22)	171.7(2)
C(11)-Mn(1)-C(111)	89.6(2)	C(21)-Mn(2)-C(211)	90.2(2)
C(14)-Mn(1)-C(111)	179.3(2)	C(24)-Mn(2)-C(211)	177.9(2)
C(13)-Mn(1)-C(111)	86.34(14)	C(23)-Mn(2)-C(211)	83.9(2)
C(12)-Mn(1)-C(111)	83.27(14)	C(22)-Mn(2)-C(211)	88.5(2)
C(11)-Mn(1)-N(11)	167.3(2)	C(21)-Mn(2)-N(21)	167.6(2)
C(14)-Mn(1)-N(11)	101.6(2)	C(24)-Mn(2)-N(21)	101.1(2)
C(13)-Mn(1)-N(11)	91.70(14)	C(23)-Mn(2)-N(21)	89.3(2)
C(12)-Mn(1)-N(11)	86.86(13)	C(22)-Mn(2)-N(21)	92.3(2)
C(111)-Mn(1)-N(11)	77.71(12)	C(211)-Mn(2)-N(21)	77.36(14)
C(131)-N(11)-N(12)	115.0(3)	C(231)-N(21)-N(22)	115.2(3)
C(131)-N(11)-Mn(1)	134.1(2)	C(231)-N(21)-Mn(2)	134.2(3)
N(12)-N(11)-Mn(1)	110.3(2)	N(22)-N(21)-Mn(2)	109.7(2)
C(121)-N(12)-C(112)	122.5(3)	C(212)-N(22)-C(221)	118.7(3)
C(121)-N(12)-N(11)	115.5(3)	C(212)-N(22)-N(21)	107.5(3)
C(112)-N(12)-N(11)	108.5(3)	C(221)-N(22)-N(21)	113.1(3)
O(11)-C(11)-Mn(1)	176.3(4)	O(21)-C(21)-Mn(2)	177.2(5)
O(12)-C(12)-Mn(1)	175.7(3)	O(22)-C(22)-Mn(2)	172.7(4)
O(13)-C(13)-Mn(1)	175.4(4)	O(23)-C(23)-Mn(2)	175.7(4)
O(14)-C(14)-Mn(1)	176.1(4)	O(24)-C(24)-Mn(2)	174.3(4)
C(116)-C(111)-C(112)	117.5(3)	C(212)-C(211)-C(216)	116.4(4)
C(116)-C(111)-Mn(1)	129.4(3)	C(212)-C(211)-Mn(2)	112.9(3)
C(112)-C(111)-Mn(1)	113.0(2)	C(216)-C(211)-Mn(2)	130.6(3)
C(111)-C(112)-C(113)	121.4(3)	C(211)-C(212)-C(213)	123.0(4)
C(111)-C(112)-N(12)	117.6(3)	C(211)-C(212)-N(22)	118.1(3)
C(113)-C(112)-N(12)	120.8(3)	C(213)-C(212)-N(22)	118.8(4)
C(114)-C(113)-C(112)	119.4(4)	C(212)-C(213)-C(214)	117.7(5)
C(115)-C(114)-C(113)	119.7(4)	C(215)-C(214)-C(213)	120.4(4)
C(114)-C(115)-C(116)	120.1(4)	C(214)-C(215)-C(216)	120.2(5)
C(111)-C(116)-C(115)	121.7(4)	C(215)-C(216)-C(211)	122.2(5)
C(122)-C(121)-C(126)	117.8(4)	C(226)-C(221)-C(222)	119.0(4)
C(122)-C(121)-N(12)	121.6(3)	C(226)-C(221)-N(22)	120.5(3)
C(126)-C(121)-N(12)	120.4(4)	C(222)-C(221)-N(22)	120.5(3)
C(121)-C(122)-C(123)	120.7(4)	C(223)-C(222)-C(221)	119.4(4)
C(124)-C(123)-C(122)	121.3(5)	C(224)-C(223)-C(222)	121.4(4)
C(123)-C(124)-C(125)	118.3(4)	C(223)-C(224)-C(225)	119.7(4)
C(124)-C(125)-C(126)	122.0(4)	C(224)-C(225)-C(226)	120.2(4)
C(125)-C(126)-C(121)	119.8(4)	C(221)-C(226)-C(225)	120.4(4)
N(11)-C(131)-C(136)	121.1(3)	N(21)-C(231)-C(236)	121.9(3)
N(11)-C(131)-C(132)	124.8(3)	N(21)-C(231)-C(232)	124.9(4)
C(136)-C(131)-C(132)	114.2(3)	C(236)-C(231)-C(232)	113.1(3)
C(131)-C(132)-C(133)	110.9(3)	C(231)-C(232)-C(233)	110.6(4)
C(134)-C(133)-C(132)	111.7(4)	C(234)-C(233)-C(232)	111.6(5)
C(135)-C(134)-C(133)	111.0(4)	C(233)-C(234)-C(235)	111.1(4)
C(134)-C(135)-C(136)	111.1(3)	C(236)-C(235)-C(234)	112.7(4)
C(131)-C(136)-C(135)	111.4(3)	C(231)-C(236)-C(235)	111.2(4)

Table AIII.3 Final Positional and Equivalent Thermal Parameters for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

Atom	X/A	Y/B	Z/C	U(eq)
Mn(1)	0.6901(1)	0.2879(1)	0.3640(1)	0.033(1)
N(11)	0.8262(3)	0.2760(2)	0.2355(3)	0.036(1)
N(12)	0.8331(3)	0.3428(2)	0.1640(3)	0.042(1)
C(11)	0.5557(4)	0.3107(2)	0.4481(3)	0.045(1)
C(12)	0.5966(3)	0.2143(2)	0.2764(3)	0.038(1)
C(13)	0.7702(4)	0.3731(2)	0.4298(3)	0.043(1)
C(14)	0.7560(4)	0.2276(2)	0.4893(4)	0.046(1)
O(11)	0.4691(3)	0.3283(2)	0.4973(3)	0.067(1)
O(12)	0.5397(3)	0.1731(2)	0.2179(3)	0.063(1)
O(13)	0.8108(3)	0.4253(2)	0.4722(3)	0.070(1)
O(14)	0.7902(4)	0.1910(2)	0.5694(3)	0.072(1)
C(111)	0.6182(3)	0.3550(2)	0.2226(3)	0.037(1)
C(112)	0.7071(3)	0.3716(2)	0.1392(3)	0.040(1)
C(113)	0.6725(4)	0.4094(2)	0.0298(4)	0.055(1)
C(114)	0.5487(4)	0.4354(2)	0.0073(4)	0.058(1)
C(115)	0.4607(4)	0.4213(2)	0.0903(4)	0.054(1)
C(116)	0.4953(3)	0.3808(2)	0.1964(4)	0.045(1)
C(121)	0.9395(3)	0.3891(2)	0.1960(3)	0.042(1)
C(122)	1.0439(4)	0.3637(2)	0.2699(4)	0.053(1)
C(123)	1.1515(4)	0.4082(3)	0.2924(5)	0.063(1)
C(124)	1.1588(5)	0.4770(3)	0.2409(5)	0.068(1)
C(125)	1.0549(5)	0.5030(3)	0.1700(5)	0.071(1)
C(126)	0.9450(5)	0.4610(2)	0.1479(4)	0.057(1)
C(131)	0.8900(3)	0.2210(2)	0.1986(3)	0.038(1)
C(132)	0.9691(4)	0.2229(2)	0.0896(4)	0.050(1)
C(133)	0.9337(5)	0.1589(3)	0.0020(4)	0.065(1)
C(134)	0.9399(5)	0.0845(3)	0.0674(5)	0.068(1)
C(135)	0.8556(4)	0.0842(2)	0.1732(4)	0.057(1)
C(136)	0.8908(3)	0.1478(2)	0.2628(3)	0.043(1)
Mn(2)	0.9089(1)	0.8084(1)	0.3054(1)	0.039(1)
N(21)	0.7425(3)	0.7686(2)	0.2100(3)	0.037(1)
N(22)	0.6696(3)	0.8305(2)	0.1552(3)	0.042(1)
C(21)	1.0309(5)	0.8598(3)	0.3937(4)	0.062(1)
C(22)	0.9598(4)	0.8572(2)	0.1666(4)	0.050(1)
C(23)	0.8504(4)	0.7733(2)	0.4512(4)	0.049(1)
C(24)	1.0207(4)	0.7319(2)	0.2811(4)	0.049(1)
O(21)	1.1056(4)	0.8946(3)	0.4472(5)	0.102(2)
O(22)	1.0023(3)	0.8885(3)	0.0895(4)	0.080(1)
O(23)	0.8116(4)	0.7564(2)	0.5396(3)	0.072(1)
O(24)	1.0974(4)	0.6891(2)	0.2678(4)	0.076(1)
C(211)	0.7816(4)	0.8934(2)	0.3261(3)	0.046(1)
C(212)	0.6763(4)	0.8899(2)	0.2425(3)	0.046(1)
C(213)	0.5754(5)	0.9394(3)	0.2424(5)	0.063(1)
C(214)	0.5840(6)	0.9972(3)	0.3305(6)	0.077(2)
C(215)	0.6864(7)	1.0020(3)	0.4135(6)	0.077(2)
C(216)	0.7829(5)	0.9509(2)	0.4126(4)	0.062(1)
C(221)	0.6984(3)	0.8461(2)	0.0314(3)	0.040(1)
C(222)	0.6908(4)	0.9184(2)	-0.0141(4)	0.048(1)

C(223)	0.7177(4)	0.9319(2)	-0.1343(4)	0.054(1)
C(224)	0.7529(4)	0.8757(3)	-0.2087(4)	0.057(1)
C(225)	0.7587(4)	0.8042(2)	-0.1654(4)	0.052(1)
C(226)	0.7317(4)	0.7890(2)	-0.0452(4)	0.047(1)
C(231)	0.6852(4)	0.7059(2)	0.2050(4)	0.044(1)
C(232)	0.5518(4)	0.6934(3)	0.1490(4)	0.058(1)
C(233)	0.4681(5)	0.6626(3)	0.2442(5)	0.069(1)
C(234)	0.5229(6)	0.5923(3)	0.3020(6)	0.083(2)
C(235)	0.6597(6)	0.6044(3)	0.3555(6)	0.083(2)
C(236)	0.7440(4)	0.6377(2)	0.2632(5)	0.059(1)

Table AIII.4 Final Positional and Equivalent Thermal Parameters of Calculated Hydrogen Atoms for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

Atom	X/A	Y/B	Z/C	U(eq)
H(113)	0.7319(4)	0.4171(2)	-0.0274(4)	0.067(3)
H(114)	0.5255(4)	0.4623(2)	-0.0638(4)	0.067(3)
H(115)	0.3777(4)	0.4388(2)	0.0756(4)	0.067(3)
H(116)	0.4342(3)	0.3709(2)	0.2511(4)	0.067(3)
H(122)	1.0420(4)	0.3165(2)	0.3047(4)	0.067(3)
H(123)	1.2199(4)	0.3906(3)	0.3436(5)	0.067(3)
H(124)	1.2324(5)	0.5055(3)	0.2536(5)	0.067(3)
H(125)	1.0583(5)	0.5503(3)	0.1357(5)	0.067(3)
H(126)	0.8752(5)	0.4807(2)	0.1012(4)	0.067(3)
H(13A)	1.0587(4)	0.2194(2)	0.1178(4)	0.070(3)
H(13B)	0.9557(4)	0.2699(2)	0.0467(4)	0.070(3)
H(13C)	0.8481(5)	0.1667(3)	-0.0357(4)	0.070(3)
H(13D)	0.9915(5)	0.1584(3)	-0.0628(4)	0.070(3)
H(13E)	0.9126(5)	0.0454(3)	0.0097(5)	0.070(3)
H(13F)	1.0271(5)	0.0743(3)	0.0981(5)	0.070(3)
H(13G)	0.8647(4)	0.0370(2)	0.2162(4)	0.070(3)
H(13H)	0.7673(4)	0.0893(2)	0.1416(4)	0.070(3)
H(13I)	0.8305(3)	0.1491(2)	0.3254(3)	0.070(3)
H(13J)	0.9749(3)	0.1388(2)	0.3032(3)	0.070(3)
H(213)	0.5044(5)	0.9348(3)	0.1864(5)	0.067(3)
H(214)	0.5189(6)	1.0322(3)	0.3315(6)	0.067(3)
H(215)	0.6912(7)	1.0402(3)	0.4713(6)	0.067(3)
H(216)	0.8516(5)	0.9546(2)	0.4715(4)	0.067(3)
H(222)	0.6679(4)	0.9574(2)	0.0356(4)	0.067(3)
H(223)	0.7116(4)	0.9802(2)	-0.1650(4)	0.067(3)
H(224)	0.7728(4)	0.8860(3)	-0.2883(4)	0.067(3)
H(225)	0.7809(4)	0.7657(2)	-0.2164(4)	0.067(3)
H(226)	0.7359(4)	0.7403(2)	-0.0163(4)	0.067(3)
H(23A)	0.5533(4)	0.6586(3)	0.0812(4)	0.070(3)
H(23B)	0.5166(4)	0.7401(3)	0.1171(4)	0.070(3)
H(23C)	0.4595(5)	0.6997(3)	0.3076(5)	0.070(3)
H(23D)	0.3838(5)	0.6523(3)	0.2053(5)	0.070(3)
H(23E)	0.5212(6)	0.5532(3)	0.2407(6)	0.070(3)
H(23F)	0.4710(6)	0.5765(3)	0.3666(6)	0.070(3)
H(23G)	0.6593(6)	0.6373(3)	0.4259(6)	0.070(3)

H(23H)	0.6952(6)	0.5571(3)	0.3840(6)	0.070(3)
H(23I)	0.8264(4)	0.6502(2)	0.3043(5)	0.070(3)
H(23J)	0.7575(4)	0.6012(2)	0.2001(5)	0.070(3)

Table AIII.5 Thermal Parameters for η^2 -2-(N^2 -cyclohexylidene- N^1 -phenylhydrazino)phenyltetracarbonylmanganese (13)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.0347(2)	0.0337(2)	0.0317(2)	0.0001(2)	0.0039(2)	-0.0023(2)
N(11)	0.0333(13)	0.0358(14)	0.0401(15)	0.0045(12)	0.0071(11)	-0.0009(11)
N(12)	0.0398(14)	0.0390(15)	0.049(2)	0.0108(13)	0.0115(13)	0.0023(12)
C(11)	0.045(2)	0.051(2)	0.038(2)	-0.0059(15)	0.005(2)	-0.010(2)
C(12)	0.037(2)	0.038(2)	0.040(2)	0.0009(14)	0.0049(14)	-0.0004(14)
C(13)	0.046(2)	0.043(2)	0.042(2)	0.000(2)	0.0017(14)	-0.0030(15)
C(14)	0.048(2)	0.050(2)	0.040(2)	0.004(2)	0.000(2)	-0.005(2)
O(11)	0.054(2)	0.087(2)	0.063(2)	-0.021(2)	0.0260(15)	-0.006(2)
O(12)	0.054(2)	0.057(2)	0.075(2)	-0.018(2)	-0.0008(15)	-0.0105(14)
O(13)	0.080(2)	0.052(2)	0.077(2)	-0.022(2)	0.000(2)	-0.017(2)
O(14)	0.089(2)	0.066(2)	0.057(2)	0.023(2)	-0.014(2)	0.000(2)
C(111)	0.042(2)	0.036(2)	0.034(2)	0.0011(13)	0.0042(13)	0.0005(13)
C(112)	0.043(2)	0.038(2)	0.041(2)	0.0061(14)	0.0042(14)	0.0041(14)
C(113)	0.065(2)	0.057(2)	0.043(2)	0.016(2)	0.015(2)	0.007(2)
C(114)	0.066(2)	0.060(2)	0.048(2)	0.014(2)	-0.005(2)	0.012(2)
C(115)	0.051(2)	0.056(2)	0.053(2)	0.005(2)	-0.006(2)	0.012(2)
C(116)	0.041(2)	0.044(2)	0.051(2)	0.001(2)	0.0033(15)	0.0050(14)
C(121)	0.047(2)	0.036(2)	0.047(2)	0.0010(14)	0.0203(15)	0.0010(14)
C(122)	0.045(2)	0.043(2)	0.072(2)	0.002(2)	0.013(2)	-0.001(2)
C(123)	0.046(2)	0.057(2)	0.086(3)	-0.013(2)	0.014(2)	-0.007(2)
C(124)	0.063(3)	0.059(3)	0.086(3)	-0.018(2)	0.030(2)	-0.023(2)
C(125)	0.101(4)	0.043(2)	0.073(3)	-0.002(2)	0.034(3)	-0.024(2)
C(126)	0.071(3)	0.041(2)	0.060(2)	0.008(2)	0.016(2)	-0.004(2)
C(131)	0.0336(15)	0.038(2)	0.042(2)	0.0008(14)	0.0055(13)	-0.0001(13)
C(132)	0.052(2)	0.045(2)	0.055(2)	-0.001(2)	0.022(2)	0.001(2)
C(133)	0.078(3)	0.068(3)	0.051(2)	-0.008(2)	0.026(2)	-0.007(2)
C(134)	0.087(3)	0.051(2)	0.069(3)	-0.016(2)	0.032(2)	-0.007(2)
C(135)	0.068(2)	0.040(2)	0.064(2)	0.000(2)	0.019(2)	-0.004(2)
C(136)	0.047(2)	0.037(2)	0.046(2)	0.0056(14)	0.0092(15)	0.0052(14)
Mn(2)	0.0421(3)	0.0394(2)	0.0359(3)	-0.0004(2)	0.0034(2)	-0.0033(2)
N(21)	0.0378(13)	0.0359(13)	0.0372(14)	0.0029(11)	0.0028(11)	0.0018(11)
N(22)	0.0435(15)	0.0392(14)	0.0431(15)	0.0084(12)	0.0043(12)	0.0071(12)
C(21)	0.061(2)	0.069(3)	0.055(2)	-0.006(2)	-0.004(2)	-0.018(2)
C(22)	0.042(2)	0.055(2)	0.053(2)	0.006(2)	0.007(2)	0.004(2)
C(23)	0.055(2)	0.050(2)	0.040(2)	-0.002(2)	0.001(2)	-0.001(2)
C(24)	0.047(2)	0.056(2)	0.045(2)	0.005(2)	0.001(2)	0.003(2)
O(21)	0.095(3)	0.110(3)	0.097(3)	-0.019(3)	-0.023(2)	-0.045(3)
O(22)	0.064(2)	0.101(3)	0.079(2)	0.040(2)	0.022(2)	-0.007(2)
O(23)	0.093(2)	0.083(2)	0.041(2)	0.008(2)	0.014(2)	-0.009(2)
O(24)	0.067(2)	0.074(2)	0.088(2)	0.010(2)	0.010(2)	0.029(2)

C(211)	0.060(2)	0.038(2)	0.044(2)	0.0029(15)	0.020(2)	0.002(2)
C(212)	0.058(2)	0.036(2)	0.045(2)	0.0083(15)	0.025(2)	0.0045(15)
C(213)	0.068(3)	0.056(2)	0.069(3)	0.021(2)	0.032(2)	0.022(2)
C(214)	0.099(4)	0.040(2)	0.103(4)	0.013(2)	0.068(4)	0.020(2)
C(215)	0.115(4)	0.044(2)	0.080(3)	-0.009(2)	0.058(3)	-0.002(3)
C(216)	0.093(3)	0.042(2)	0.054(2)	-0.009(2)	0.030(2)	-0.007(2)
C(221)	0.0329(15)	0.044(2)	0.043(2)	0.0049(14)	0.0008(13)	0.0011(13)
C(222)	0.050(2)	0.046(2)	0.048(2)	0.005(2)	0.005(2)	0.000(2)
C(223)	0.052(2)	0.056(2)	0.053(2)	0.016(2)	0.000(2)	-0.003(2)
C(224)	0.051(2)	0.077(3)	0.044(2)	0.010(2)	0.005(2)	-0.008(2)
C(225)	0.050(2)	0.060(2)	0.045(2)	-0.003(2)	0.009(2)	-0.002(2)
C(226)	0.046(2)	0.049(2)	0.045(2)	0.001(2)	0.004(2)	0.0024(15)
C(231)	0.047(2)	0.043(2)	0.043(2)	-0.0023(14)	0.004(2)	0.0018(14)
C(232)	0.055(2)	0.058(2)	0.059(2)	0.000(2)	-0.008(2)	-0.011(2)
C(233)	0.058(2)	0.079(3)	0.070(3)	-0.004(2)	0.001(2)	-0.020(2)
C(234)	0.092(4)	0.078(3)	0.078(3)	0.013(3)	-0.002(3)	-0.041(3)
C(235)	0.092(4)	0.067(3)	0.087(4)	0.034(3)	-0.017(3)	-0.027(3)
C(236)	0.062(2)	0.039(2)	0.074(3)	0.000(2)	-0.011(2)	0.002(2)

Appendix IV

Complete Bond Lengths, Bond Angles, and Thermal and Positional Parameters for Both Independent Molecules η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarboxymanganese (16)

Table AIV.1: Bond Lengths (Å) for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)-phenyltetracarboxymanganese (16)

Mn(1)-C(11)	1.79(2)	Mn(2)-C(21)	1.77(2)
Mn(1)-C(14)	1.80(2)	Mn(2)-C(24)	1.82(2)
Mn(1)-C(13)	1.83(2)	Mn(2)-C(23)	1.86(2)
Mn(1)-C(12)	1.88(2)	Mn(2)-C(22)	1.85(2)
Mn(1)-N(11)	1.999(14)	Mn(2)-N(21)	1.982(13)
Mn(1)-C(111)	2.02(2)	Mn(2)-C(211)	2.045(14)
N(11)-O(15)	1.22(2)	N(21)-O(25)	1.24(2)
N(11)-N(12)	1.32(2)	N(21)-N(22)	1.33(2)
N(12)-C(121)	1.42(2)	N(22)-C(221)	1.43(2)
N(12)-C(112)	1.45(2)	N(22)-C(212)	1.44(2)
C(11)-O(11)	1.14(2)	C(21)-O(21)	1.11(2)
C(12)-O(12)	1.11(2)	C(22)-O(22)	1.18(2)
C(13)-O(13)	1.15(2)	C(23)-O(23)	1.13(2)
C(14)-O(14)	1.16(2)	C(24)-O(24)	1.15(2)
C(111)-C(116)	1.37(2)	C(211)-C(212)	1.37(2)
C(111)-C(112)	1.40(2)	C(211)-C(216)	1.39(2)
C(112)-C(113)	1.34(2)	C(212)-C(213)	1.37(2)
C(113)-C(114)	1.40(2)	C(213)-C(214)	1.40(2)
C(114)-C(115)	1.38(2)	C(214)-C(215)	1.35(2)
C(115)-C(116)	1.37(2)	C(215)-C(216)	1.37(2)
C(121)-C(122)	1.34(2)	C(221)-C(222)	1.35(2)
C(121)-C(126)	1.39(2)	C(221)-C(226)	1.40(2)
C(122)-C(123)	1.43(2)	C(222)-C(223)	1.36(2)
C(123)-C(124)	1.35(2)	C(223)-C(224)	1.37(2)
C(124)-C(125)	1.40(2)	C(224)-C(225)	1.39(2)
C(125)-C(126)	1.37(2)	C(225)-C(226)	1.36(2)

Table 2.8: Bond Angles (degrees) for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyltetracarboxymanganese (16)

C(11)-Mn(1)-C(14)	88.1(9)	C(11)-Mn(1)-C(111)	93.8(7)
C(11)-Mn(1)-C(13)	94.6(8)	C(14)-Mn(1)-C(111)	86.8(8)
C(14)-Mn(1)-C(13)	94.9(9)	C(13)-Mn(1)-C(111)	171.6(7)
C(11)-Mn(1)-C(12)	89.1(8)	C(12)-Mn(1)-C(111)	86.0(7)
C(14)-Mn(1)-C(12)	172.1(9)	N(11)-Mn(1)-C(111)	79.9(6)
C(13)-Mn(1)-C(12)	92.7(9)	O(15)-N(11)-N(12)	116.3(13)
C(11)-Mn(1)-N(11)	173.6(7)	O(15)-N(11)-Mn(1)	126.0(11)
C(14)-Mn(1)-N(11)	90.4(8)	N(12)-N(11)-Mn(1)	117.7(10)
C(13)-Mn(1)-N(11)	91.8(7)	N(11)-N(12)-C(121)	121.5(13)
C(12)-Mn(1)-N(11)	91.7(7)	N(11)-N(12)-C(112)	113.9(12)

C(121)-N(12)-C(112)	124.5(13)	C(21)-Mn(2)-C(211)	91.7(7)
O(11)-C(11)-Mn(1)	174(2)	C(24)-Mn(2)-C(211)	172.0(7)
O(12)-C(12)-Mn(1)	176(2)	C(23)-Mn(2)-C(211)	86.2(7)
O(13)-C(13)-Mn(1)	179(2)	C(22)-Mn(2)-C(211)	88.5(6)
O(14)-C(14)-Mn(1)	176(2)	N(21)-Mn(2)-C(211)	79.5(5)
C(116)-C(111)-C(112)	114(2)	O(25)-N(21)-N(22)	114.4(13)
C(116)-C(111)-Mn(1)	133.2(12)	O(25)-N(21)-Mn(2)	127.9(10)
C(112)-C(111)-Mn(1)	112.9(11)	N(22)-N(21)-Mn(2)	117.6(9)
C(113)-C(112)-C(111)	125(2)	N(21)-N(22)-C(221)	121.9(12)
C(113)-C(112)-N(12)	119.6(14)	N(21)-N(22)-C(212)	114.3(12)
C(111)-C(112)-N(12)	115.3(14)	C(221)-N(22)-C(212)	123.5(12)
C(112)-C(113)-C(114)	119(2)	O(21)-C(21)-Mn(2)	177(2)
C(115)-C(114)-C(113)	118(2)	O(22)-C(22)-Mn(2)	175(2)
C(116)-C(115)-C(114)	120(2)	O(23)-C(23)-Mn(2)	176(2)
C(111)-C(116)-C(115)	124(2)	O(24)-C(24)-Mn(2)	177(2)
C(122)-C(121)-C(126)	123(2)	C(212)-C(211)-C(216)	115.1(13)
C(122)-C(121)-N(12)	118(2)	C(212)-C(211)-Mn(2)	113.2(10)
C(126)-C(121)-N(12)	120(2)	C(216)-C(211)-Mn(2)	131.5(11)
C(121)-C(122)-C(123)	118(2)	C(213)-C(212)-C(211)	124.0(14)
C(124)-C(123)-C(122)	119(2)	C(213)-C(212)-N(22)	120.6(13)
C(123)-C(124)-C(125)	122(2)	C(211)-C(212)-N(22)	115.3(12)
C(126)-C(125)-C(124)	118(2)	C(212)-C(213)-C(214)	117.6(14)
C(125)-C(126)-C(121)	120(2)	C(215)-C(214)-C(213)	121(2)
C(21)-Mn(2)-C(24)	96.2(8)	C(214)-C(215)-C(216)	119(2)
C(21)-Mn(2)-C(23)	89.7(9)	C(215)-C(216)-C(211)	123(2)
C(24)-Mn(2)-C(23)	93.6(7)	C(222)-C(221)-C(226)	122(2)
C(21)-Mn(2)-C(22)	88.2(8)	C(222)-C(221)-N(22)	120.5(14)
C(24)-Mn(2)-C(22)	91.9(7)	C(226)-C(221)-N(22)	117.5(14)
C(23)-Mn(2)-C(22)	174.2(7)	C(221)-C(222)-C(223)	119(2)
C(21)-Mn(2)-N(21)	171.2(7)	C(222)-C(223)-C(224)	121(2)
C(24)-Mn(2)-N(21)	92.6(6)	C(223)-C(224)-C(225)	120(2)
C(23)-Mn(2)-N(21)	89.6(7)	C(226)-C(225)-C(224)	120(2)
C(22)-Mn(2)-N(21)	91.6(7)	C(225)-C(226)-C(221)	119(2)

Table AIV.3 Final Positional and Equivalent Thermal Parameters for η^2 -2-(*N*¹-nitroso-*N*¹-phenylamino)phenyltetracarboxylmanganese (16)

Atom	X/A	Y/B	Z/C	U(eq)
Mn(1)	0.3564(3)	0.2243(3)	0.2807(2)	0.035(1)
N(11)	0.3056(15)	0.2243(13)	0.3939(8)	0.035(4)
N(12)	0.2803(13)	0.1180(12)	0.4501(7)	0.026(3)
C(11)	0.3977(18)	0.2063(16)	0.1831(10)	0.036(4)
C(12)	0.5461(23)	0.2097(18)	0.2968(11)	0.043(5)
C(13)	0.3642(21)	0.3910(19)	0.2431(11)	0.047(5)
C(14)	0.1759(24)	0.2164(18)	0.2662(12)	0.050(5)
O(11)	0.4130(13)	0.1912(12)	0.1214(7)	0.049(4)
O(12)	0.6563(13)	0.1982(12)	0.3110(7)	0.046(3)

O(13)	0.3693(14)	0.4959(13)	0.2185(8)	0.057(4)
O(14)	0.0611(14)	0.2043(13)	0.2572(8)	0.055(4)
O(15)	0.2897(15)	0.3145(11)	0.4159(7)	0.053(4)
C(111)	0.3461(16)	0.0424(14)	0.3387(9)	0.026(4)
C(112)	0.3008(17)	0.0142(14)	0.4207(9)	0.026(4)
C(113)	0.2827(16)	-0.0991(14)	0.4724(10)	0.028(4)
C(114)	0.3059(17)	-0.1989(16)	0.4434(10)	0.037(4)
C(115)	0.3502(18)	-0.1753(16)	0.3629(10)	0.038(4)
C(116)	0.3669(16)	-0.0576(14)	0.3133(10)	0.029(4)
C(121)	0.2284(17)	0.1102(14)	0.5302(9)	0.029(4)
C(122)	0.3207(19)	0.1069(15)	0.5830(10)	0.037(4)
C(123)	0.2700(19)	0.0909(16)	0.6648(11)	0.041(4)
C(124)	0.1316(18)	0.0828(15)	0.6857(10)	0.036(4)
C(125)	0.0353(20)	0.0905(16)	0.6292(11)	0.043(5)
C(126)	0.0864(19)	0.1034(16)	0.5515(11)	0.041(5)
Mn(2)	0.2009(3)	0.6713(2)	0.9906(2)	0.026(1)
N(21)	0.2552(13)	0.8371(12)	0.9192(7)	0.023(3)
N(22)	0.2522(12)	0.9262(11)	0.9522(7)	0.025(3)
C(21)	0.1484(21)	0.5337(17)	1.0663(11)	0.042(5)
C(22)	0.3815(20)	0.6347(15)	1.0173(10)	0.033(4)
C(23)	0.0162(17)	0.7103(17)	0.9739(10)	0.035(4)
C(24)	0.2271(18)	0.6072(14)	0.9082(11)	0.031(4)
O(21)	0.1126(14)	0.4498(11)	1.1156(8)	0.047(3)
O(22)	0.4923(15)	0.6058(11)	1.0394(7)	0.052(4)
O(23)	-0.0972(13)	0.7343(12)	0.9681(9)	0.055(4)
O(24)	0.2417(16)	0.5622(13)	0.8580(8)	0.059(4)
O(25)	0.2905(13)	0.8702(10)	0.8455(6)	0.038(3)
C(211)	0.1792(15)	0.7661(13)	1.0717(8)	0.020(3)
C(212)	0.2128(15)	0.8873(13)	1.0378(8)	0.020(3)
C(213)	0.2048(14)	0.9693(13)	1.0797(8)	0.019(3)
C(214)	0.1666(16)	0.9252(14)	1.1627(9)	0.029(4)
C(215)	0.1385(17)	0.8054(14)	1.1999(10)	0.031(4)
C(216)	0.1465(17)	0.7280(15)	1.1546(10)	0.030(4)
C(221)	0.2952(16)	1.0476(13)	0.9068(9)	0.023(3)
C(222)	0.4313(17)	1.0771(15)	0.8933(9)	0.030(4)
C(223)	0.4687(18)	1.1940(15)	0.8508(10)	0.034(4)
C(224)	0.3693(17)	1.2821(15)	0.8249(10)	0.032(4)
C(225)	0.2291(18)	1.2519(16)	0.8406(10)	0.037(4)
C(226)	0.1913(17)	1.1350(14)	0.8816(9)	0.029(4)
C(1)	0.8461(42)	0.4230(32)	0.3303(20)	0.091(7)
C(5)	0.7307(30)	0.4791(34)	0.3570(22)	0.091(7)
C(6)	0.7438(33)	0.5433(32)	0.4109(22)	0.091(7)
C(4)	0.8723(41)	0.5513(32)	0.4381(20)	0.091(7)
C(4)	0.9878(30)	0.4952(34)	0.4114(22)	0.091(7)
C(1)	0.9747(33)	0.4310(32)	0.3575(22)	0.091(7)

Table AIII.4 Final Positional and Equivalent Thermal Parameters of Calculated Hydrogen Atoms for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)phenyl-tetracarbonylmanganese (16)

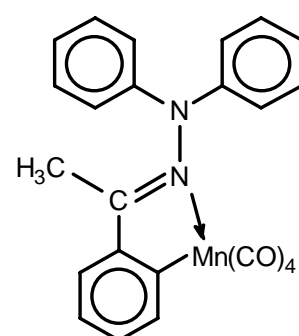
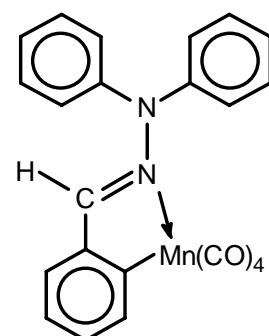
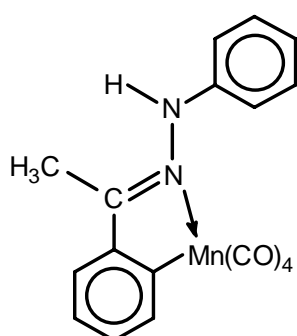
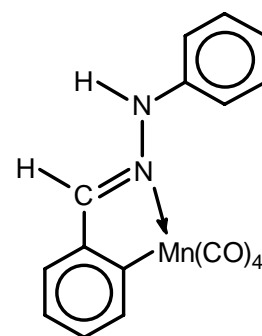
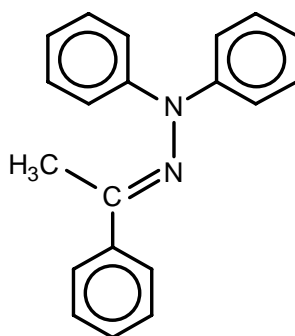
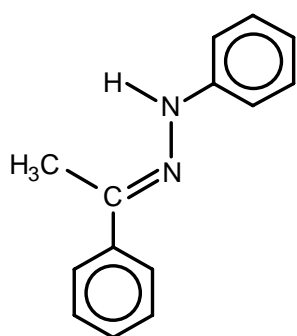
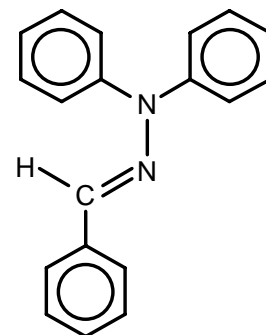
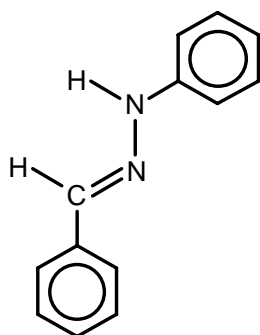
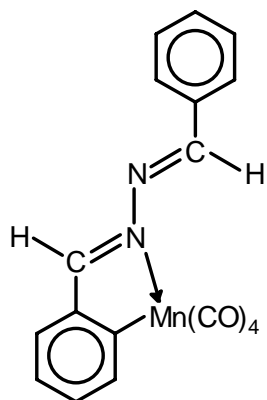
Atom	X/A	Y/B	Z/C	U(eq)
H(113)	0.2546(16)	-0.1117(14)	0.5279(10)	0.038(11)
H(114)	0.2916(17)	-0.2802(16)	0.4783(10)	0.038(11)
H(115)	0.3691(18)	-0.2410(16)	0.3418(10)	0.038(11)
H(116)	0.3947(16)	-0.0444(14)	0.2577(10)	0.038(11)
H(122)	0.4173(19)	0.1150(15)	0.5664(10)	0.038(11)
H(123)	0.3328(19)	0.0861(16)	0.7042(11)	0.038(11)
H(124)	0.0984(18)	0.0714(15)	0.7404(10)	0.038(11)
H(125)	-0.0618(20)	0.0870(16)	0.6444(11)	0.038(11)
H(126)	0.0243(19)	0.1077(16)	0.5119(11)	0.038(11)
H(213)	0.2246(14)	1.0533(13)	1.0532(8)	0.038(11)
H(214)	0.1602(16)	0.9801(14)	1.1934(9)	0.038(11)
H(215)	0.1137(17)	0.7756(14)	1.2565(10)	0.038(11)
H(216)	0.1287(17)	0.6438(15)	1.1813(10)	0.038(11)
H(222)	0.4999(17)	1.0172(15)	0.9133(9)	0.038(11)
H(223)	0.5642(18)	1.2149(15)	0.8388(10)	0.038(11)
H(224)	0.3965(17)	1.3638(15)	0.7962(10)	0.038(11)
H(225)	0.1604(18)	1.3127(16)	0.8227(10)	0.038(11)
H(226)	0.0961(17)	1.1128(14)	0.8931(9)	0.038(11)

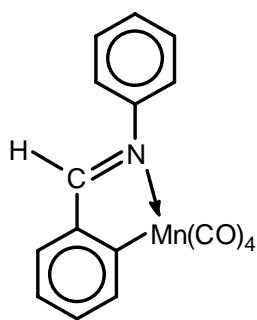
Table AIV.5 Thermal Parameters for η^2 -2-(N^1 -nitroso- N^1 -phenylamino)-phenyltetracarbonylmanganese (16)

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.034(2)	0.044(2)	0.0242(15)	-0.0065(13)	-0.0042(12)	0.0014(13)
N(11)	0.049(10)	0.035(9)	0.026(8)	-0.015(7)	-0.010(7)	0.004(7)
N(12)	0.024(7)	0.032(8)	0.022(7)	-0.010(6)	-0.002(6)	0.005(6)
C(11)	0.032(10)	0.048(12)	0.014(9)	0.008(8)	0.005(8)	-0.008(9)
C(12)	0.050(14)	0.046(12)	0.033(11)	-0.015(9)	0.010(10)	-0.016(10)
C(13)	0.050(13)	0.046(13)	0.032(11)	0.006(9)	-0.009(9)	-0.014(10)
C(14)	0.058(15)	0.040(12)	0.049(13)	-0.010(10)	-0.003(11)	-0.004(11)
O(11)	0.040(8)	0.076(10)	0.027(7)	-0.010(7)	-0.001(6)	-0.002(7)
O(12)	0.020(7)	0.076(10)	0.042(8)	-0.022(7)	-0.003(6)	0.008(7)
O(13)	0.056(10)	0.043(9)	0.069(10)	-0.012(8)	-0.019(8)	0.002(7)
O(14)	0.042(9)	0.062(10)	0.051(9)	-0.005(7)	0.002(7)	-0.010(7)
O(15)	0.090(11)	0.036(8)	0.035(7)	-0.017(6)	0.007(7)	-0.013(7)
Mn(2)	0.027(2)	0.0280(14)	0.0283(14)	-0.0143(11)	-0.0104(12)	0.0059(11)
N(21)	0.022(7)	0.034(8)	0.018(7)	-0.014(6)	-0.007(6)	0.006(6)
N(22)	0.014(7)	0.031(8)	0.031(8)	-0.014(6)	-0.001(6)	-0.001(6)
C(21)	0.060(14)	0.031(11)	0.032(10)	-0.004(9)	-0.012(9)	-0.010(10)
C(22)	0.051(12)	0.030(10)	0.024(9)	-0.014(7)	-0.017(9)	0.010(9)
C(23)	0.014(9)	0.060(13)	0.039(10)	-0.025(9)	-0.018(8)	0.015(9)
C(24)	0.034(10)	0.012(8)	0.049(11)	-0.013(8)	-0.001(8)	0.009(7)
O(21)	0.058(9)	0.033(8)	0.052(9)	-0.014(7)	-0.009(7)	-0.005(7)
O(22)	0.067(10)	0.046(8)	0.039(8)	-0.005(6)	-0.015(7)	0.004(7)
O(23)	0.034(8)	0.055(9)	0.093(11)	-0.047(8)	-0.012(8)	0.011(7)
O(24)	0.087(12)	0.050(9)	0.055(9)	-0.037(7)	-0.010(8)	0.022(8)
O(25)	0.058(9)	0.044(7)	0.013(6)	-0.011(5)	-0.004(6)	0.004(6)

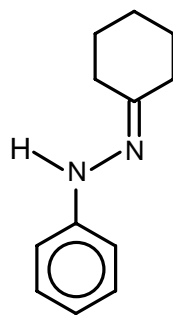
Appendix V

List of Compounds by Number

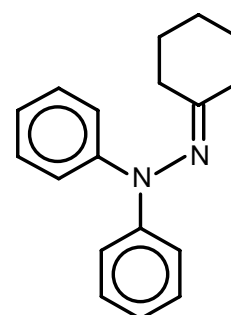




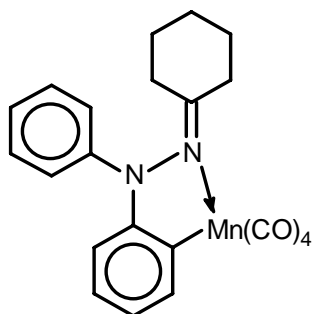
(10)



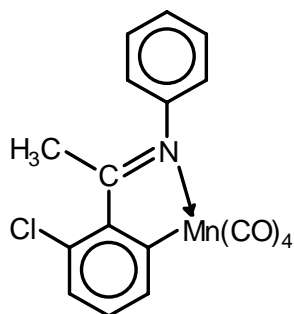
(11)



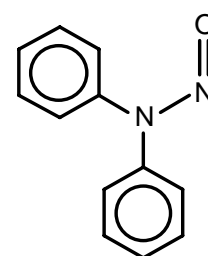
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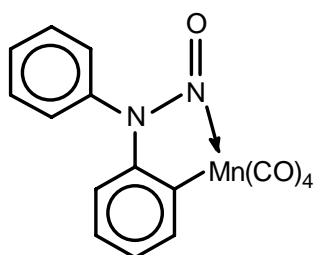
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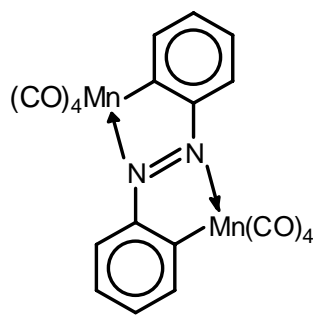
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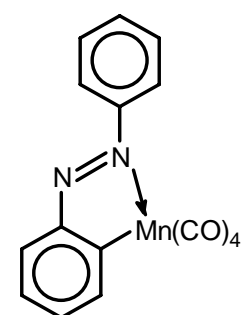
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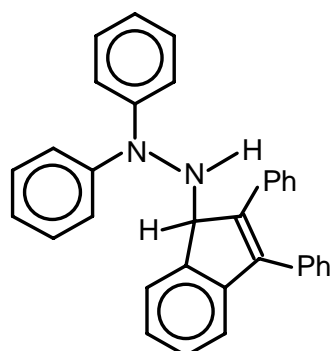
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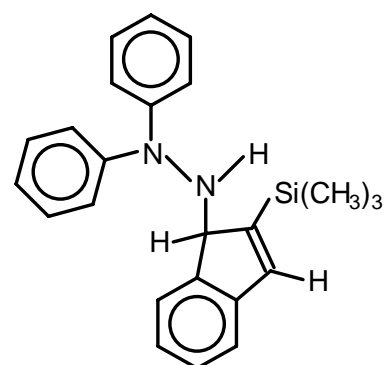
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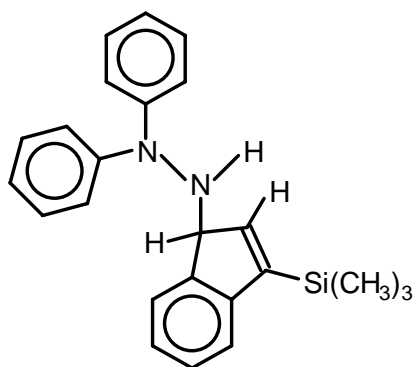
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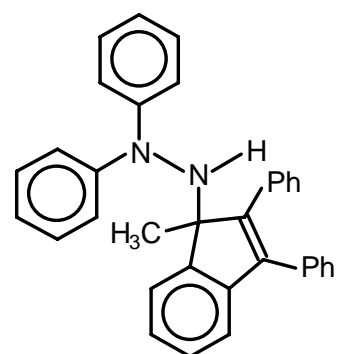
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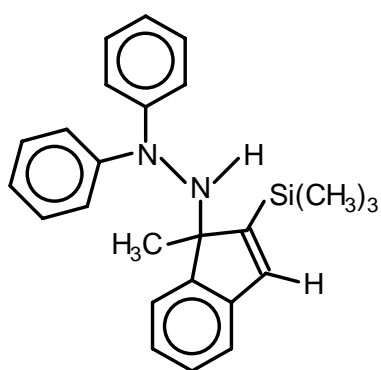
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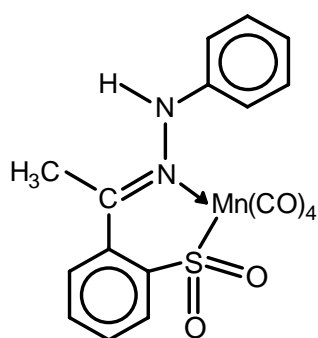
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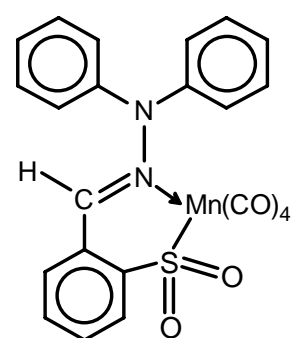
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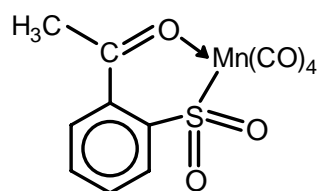
(23)



(24)



(25)



(26)