Preparation and Reactions of Some Orthomanganated Ketones, Amides and Aldehydes

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of the requirements of the Degree of
Doctor of Philosophy in Chemistry
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Nicholas Peter Robinson
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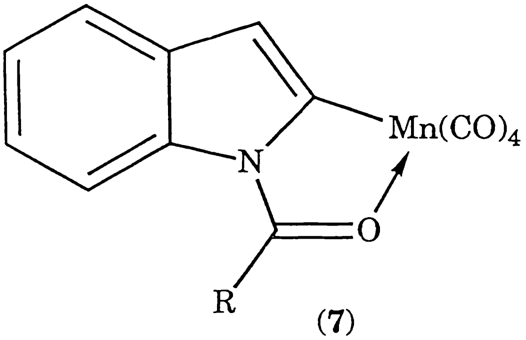
Abstract

η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (**7**, R=CH_3) and η^2-(2-*N,N*-dimethylamidophenyl)tetracarbonylmanganese (**13**), the first examples of orthomanganated amides, have been synthesized by reaction of *N*-acetylindole and *N,N*-dimethylbenzamide respectively with $PhCH_2Mn(CO)_5$. **7** (R=CH_3) was identified by X-ray crystallography. Preparation of the *N*-benzoyl- (**7**, R=Ph) analogue highlights a preference for metalation at the 5-membered indolyl ring, rather than the benzoyl ring. The *N*-benzoylpyrrole analogue of **7**, η^2-(1-benzoyl-2-pyrrolyl)tetracarbonylmanganese (**4**) was also prepared. Orthomanganated *N,N*-dimethylbenzamide (**13**) showed only oxygen donation to manganese, despite the presence of a possible nitrogen donor. *N,N*-diethyl and *N,N*-pyrrolidinyl analogues of **13** behaved similarly.



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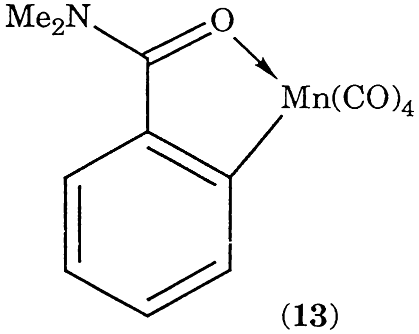


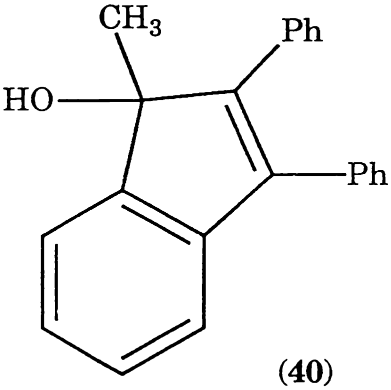
(**13**)

η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (**21**) and its 5-methoxy analogue were prepared similarly and are the first examples of orthomanganated aldehydes. 2-thiophenecarboxaldehyde and 3-thiophenecarboxaldehyde gave analogous 3-metalated and 2-metalated aldehyde products.

Two new dimetalated arenes, η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese (**25**) and η^2,η^2-(2,5-diacetylphenyl)bis-1,4-

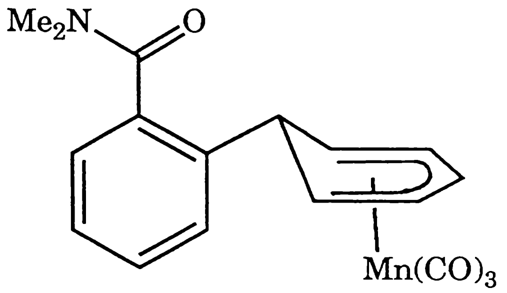
(tetracarbonyl)manganese (**27**), have been identified, in the former case by crystal structure analysis.

The first examples of coupling reactions of orthomanganated carbonyl compounds with alkynes are reported that do not require a palladium(II) catalyst: η^2-(2-acetylphenyl)tetracarbonylmanganese (**39**) was treated with diphenylacetylene to give in good yield 1-methyl-2,3-diphenylinden-1-ol (**40**), the structure of which was determined crystallographically. Acetylene, 4-octyne and bis(trimethylsilyl)-acetylene reacted similarly. For indenols arising from coupling with the unsymmetric alkynes phenylacetylene and trimethylsilylacetylene, the alkyne substituent occupied the 2-position in the final product. A possible mechanism for the couplings is discussed.



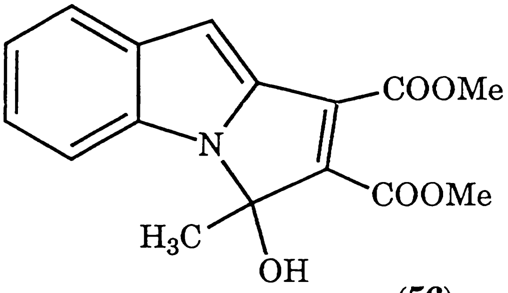
(**40**)

Coupling of diphenylacetylene was effected with three other types of substrate; η^2-(2-*N,N*-dimethylamidophenyl)-tetracarbonylmanganese (**13**) gave 2,3-diphenylindenone, η^2-(2-carboxymethyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**51**) gave 2,3-diphenyl-5-dimethylaminoindenone and η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (**21**) gave rise to 2,3-diphenyl-4,5,6-trimethoxyindenone. Coupling of amide (**13**) with excess acetylene, however, gave a cyclohexadienyl-$Mn(CO)_3$ compound (**50**).



(**50**)

η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (**7**) coupled with dimethyl acetylenedicarboxylate to afford a tricyclic nucleus, that of dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]indole-2,3-dicarboxylate (**56**). The product has potential applications in the synthesis of mitomycin-based anti-tumour agents. Its crystal structure is reported and is of interest as a rare example of a stable carbinolamine. Possible reaction pathways to the variety of product types are considered throughout.



(**56**)

Some preliminary studies into electrophilic substitutions of (arene)$M(CO)_3$ (M= Cr, Mn) complexes were conducted. Despite an apparent lack of success in this area, the experimental procedures are recorded.

Acknowledgements

If I ever get to Madison, or Cambridge, or Southampton, or wherever it was I originally intended to go, the first thing I shall do is pull out a bottle of expensive champagne, pour Linley and myself a large measure, and drink a toast to the following people.

Dr Lyndsay Main, friend and mentor. Here's to New Zealand Sauvignon Blanc, to that tongue in cheek sense of humour and to a wondrous day over at Whiritoa last January.

Dr Brian Nicholson: here's to that dogged Southland decency, to bizarre stories of raising four children, to crystallography and to a blunt wit. Few other people, I suspect, have quite the same grip on chemical and human reality.

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To the University Grants Committee and the William Georgetti Trust for their generous financial support, a big thank you.

Finally, to three people who will probably be sharing this toast, and who matter a great deal: Mum and Dad, and my wife, Linley: friends may be a transient part of one's life, but family will always be there to fall back on.

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Abbreviations

Ac - acetyl
br - broad
Bu - butyl
Cp - η^5-cyclopentadienyl
δ - chemical shift (ppm)
d - doublet
DMSO - dimethyl sulphoxide
Et - ethyl
J - coupling constant (Hz)
m - medium (IR)
m - multiplet (NMR)
Me - methyl
MS - mass spectrum/spectroscopy
NMR - nuclear magnetic resonance
pet. spirit- petroleum spirit (60-80°C)
Ph - phenyl
plc - preparative layer chromatography
Pr^i - iso-propyl
q - quartet
s - strong (IR)
s - singlet (NMR)
sh - shoulder
t - triplet
THF - tetrahydrofuran
tlc - thin layer chromatography
υ - stretching frequency (IR)
vs - very strong
w - weak

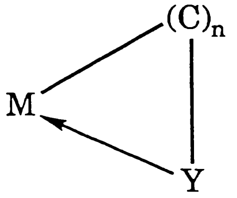
Chapter One

General Aspects of Cyclometalation

1.1 Intramolecular Donor Compounds: Definition

Cyclometalated compounds are organometallic intramolecular-coordination compounds, though the definition of "organometallic" often varies, in some cases excluding carbides and cyanides even though they contain a metal-carbon bond, and in others, including metal hydrides or compounds with coordinated N_2, PH_3 or PF_3, even though they contain no metal-carbon bond.

For our own purposes, the Omae definition [1] is almost adequate, namely, any cyclic compound with a metal-carbon bond of the configuration shown in Figure 1.1.



M = metal

Y = coordinating atom/group

$n \geq 1$

Figure 1.1

The definition (and Omae's review), however, specifically exclude compounds that have a non-carbon atom in the ring, which is unfortunate, as some species of that type feature prominently in Chapter 2 of this thesis. Other compounds that complicate the definition are those in which the metal-carbon bond is a π-bond, such as vinylene or cyclopentadienyl, or compounds where the donor is π-bonded: it is not a simple matter in either case to determine, for example, ring size, nor which is donor and which is the metal-carbon bond.

In the end, the differences are mainly semantic. Our own definition must include those compounds with a heteroatom other than the donor and the metal, not just because of the compounds herein, but because many other compounds of importance to cyclometalation chemistry (such as orthomanganated triphenylphosphites [2]) would also be excluded.

1.2 Cyclometalated Compounds

Probably the first recognition of cyclometalated compounds as a group was by Bähr and Müller [3-5] in 1955, with a report of the compounds shown (Figure 1.2). Some bicyclic beryllium analogues were also described.

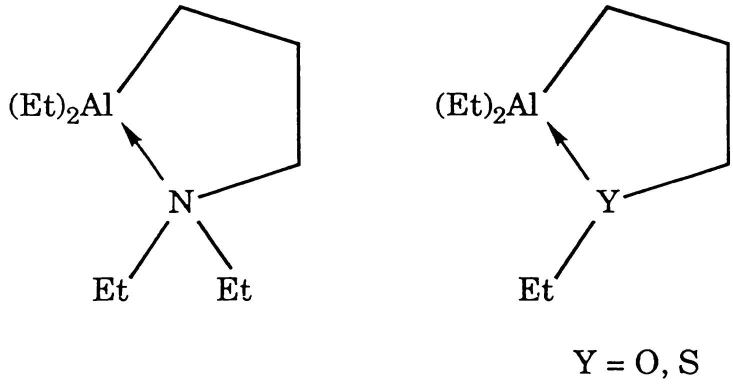


Figure 1.2

Of equal importance historically is the "cyclometalation reaction", although the term seems to date from only 1973 [6]. The conversion in Figure 1.3, reported by Kleiman and Dubeck in 1963 [7], was the first example: key features are the donor atom (nitrogen) directing the formation of the metal-carbon bond, and the elimination of a neutral species (cyclopentadiene) as a product.

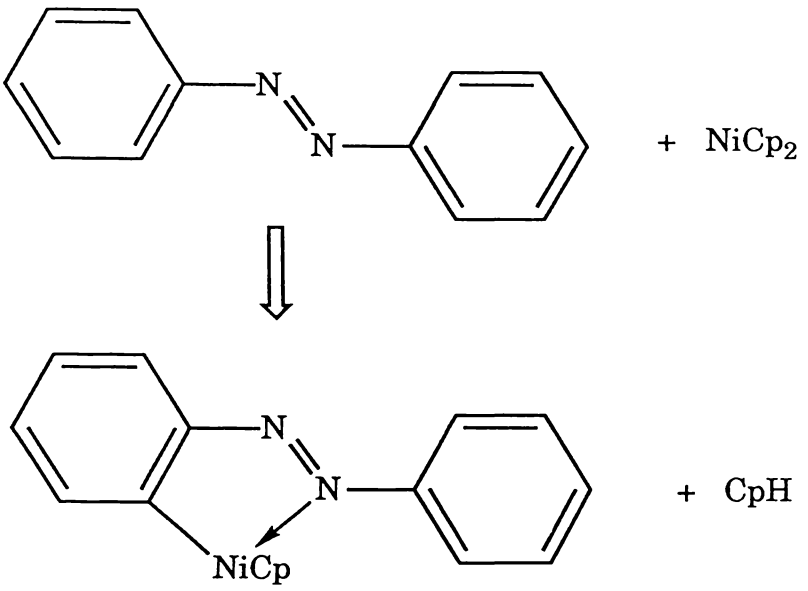


Figure 1.3

The number of cyclometalated compounds obtained from similar reactions since 1963 is enormous, with good general reviews by Omae [1,8], Bruce [9] and Dehand and Pfeffer [10].

The diversity of cyclometalated compounds is also large. Coordinating atoms may be nitrogen, phosphorus, arsenic, oxygen or sulphur, and coordinating groups are mainly vinylene, π-allyl, cyclopentadienyl or aryl. For those compounds with a nitrogen donor, for example, there are no less than ten distinct groups of compounds, each dependent on the nature of the ligand. Most have been known since the 1970s, like benzylamines, benzylideneamines, azobenzenes, alkylamines, imines, etc. Other recent additions (Figure 1.4) [11,12] show the variety that is possible among nitrogen donors.

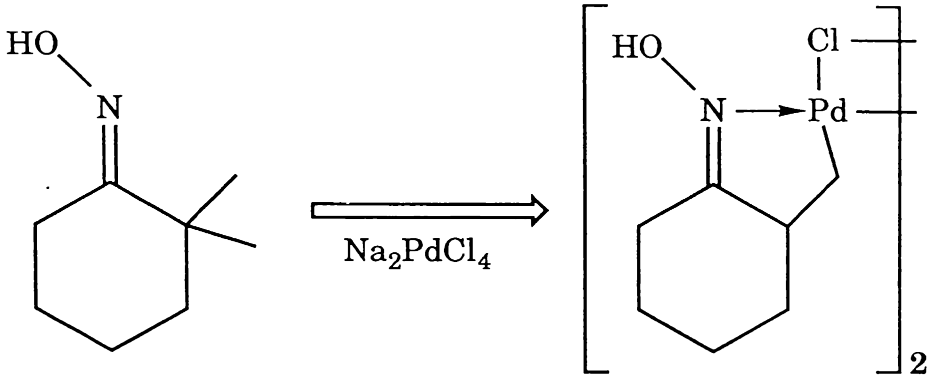
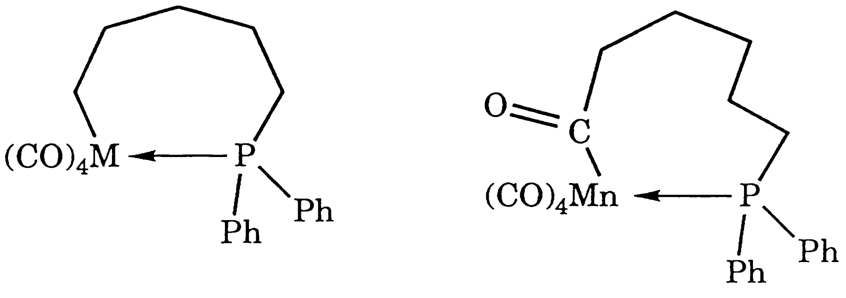


Figure 1.4

The diversity continues into metals: coordination of a benzylamine nitrogen donor has been reported with palladium [13], chromium [14], manganese [14], lithium [15], and gold [16]. Known metals for other donors include mercury [17], aluminium [3], rhodium [18] and iridium [19].

The range of ring sizes is small. Five membered ring products are by far the most stable, but some manganese and rhenium compounds with a phosphorus donor have been reported with ring sizes of seven and eight [20] (Figure 1.5). Ring sizes of three, four and six are also known.



M = Mn, Re

Figure 1.5

It is manganese compounds with an oxygen donor that are of principal relevance to this thesis. Cyclometalation with a manganese reagent was found to proceed smoothly relatively early on [21]: much work was done initially on nitrogen donors, particularly azobenzene ligands in the presence of dimanganese decacarbonyl. Later it was found that the alkyl derivatives, $RMn(CO)_5$, were more effective metalating agents [22].

Oxygen donor groups are well known for carbonyl, alkoxy and aryloxy ligands, though coordination compounds arising from the latter two tend to react readily with a number of reagents. Carbonyl donors have been reported for platinum [23], iron [24], molybdenum [25], ruthenium [26], tungsten [27], tellurium [28], tin [29], manganese [30], palladium [31], osmium [32], titanium [33] and antimony [33]. A sulfinyl ligand has also been reported [34] (Figure 1.6).

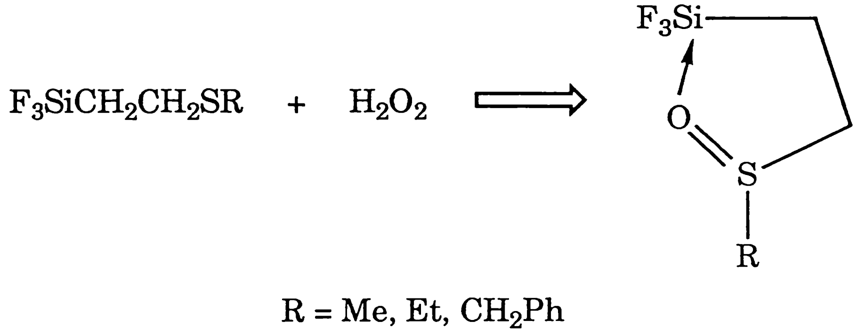
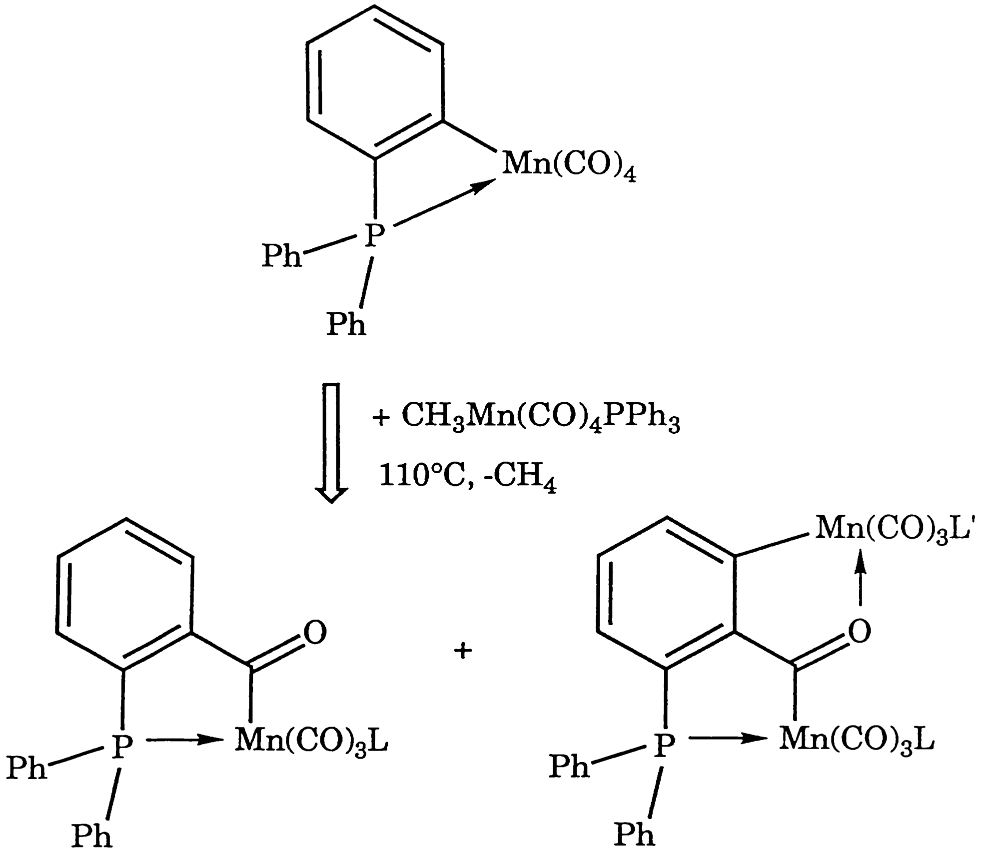


Figure 1.6

Other isolated cases of oxygen coordination are by nitro- [35], hydroxyl- [17], phosphoryl- [36] and nitrato- [37] groups.

Coordination of an ether oxygen to manganese has not been observed. Manganated O-donors thus far have almost exclusively possessed carbonyl ligands. Much of the early work in this area was undertaken by Kaesz et al [30,38] on orthomanganated ketones. These first arose as "secondary metalation products" from the thermolysis of an orthomanganated triphenylphosphine [30,39,40] (Figure 1.7).



(‡) L = CO

(*) L = PPh_3

(i) L = CO, L'= PPh_3

(ii) L = PPh_3, L'= CO

(iii) L = PPh_3, L'= PPh_3

Figure 1.7

The primary metalation products contain only one manganese (‡, *) in the phosphine donor position, and since these could be easily isolated, the secondary products ((i)-(iii)) were presumed to arise from further reaction of ‡ and * with $CH_3Mn(CO)_5$, a fact that was readily confirmed by experiment. When acetophenone was later treated in the same way [38], the reaction proceeded in good yield (ca. 60%).

Considerable momentum developed from those inital results: X-ray crystal structures [39,41,42], kinetic isotope studies [43], comparisons of reactivity [44] and many new compounds were subsequently reported, and have proved a valuable data base for our own studies.

The brief of this thesis, however, was as much the synthetic applications of manganated O-donors as their preparation, and this area seems to have been neglected until relatively recently. The section that follows then, will cover some related synthetic applications thus far reported.

1.3 Synthetic Applications

The role of metals in the activation of carbon centres is already well documented. Numerous texts and reviews are available [45,46], some with a healthy bias towards organic applications [47,48].

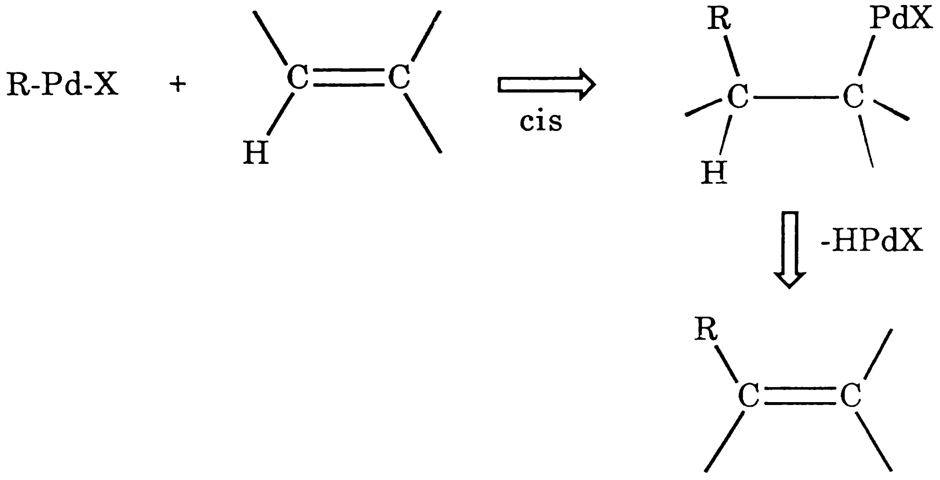


Figure 1.8

The predominance of recent synthetic activity has been with palladium compounds, many of which stem from the reaction in Figure 1.8. Though well known for the functionalization of aromatic compounds, it is restricted by the prerequisite of a carbon already activated by a halo-, amino-, chloromercurio- or other substituent [49].

The palladium attacks the activated position and couplings to alkene can proceed.

Ortho directing donor atoms obviate the need for such activation, and the resulting *o*-pallado-compounds generally participate in smooth coupling [52]. For example, *o*-palladated benzylamines and benzylimines undergo coupling with both styrene and methyl acrylate [56], although coupling of palladated *N*-t-butylbenzylimine with methyl vinyl ketone produces 2-acetylindene (Fig. 1.9). Examples where phosphorus and oxygen are the donor atoms to palladium are also known [50].

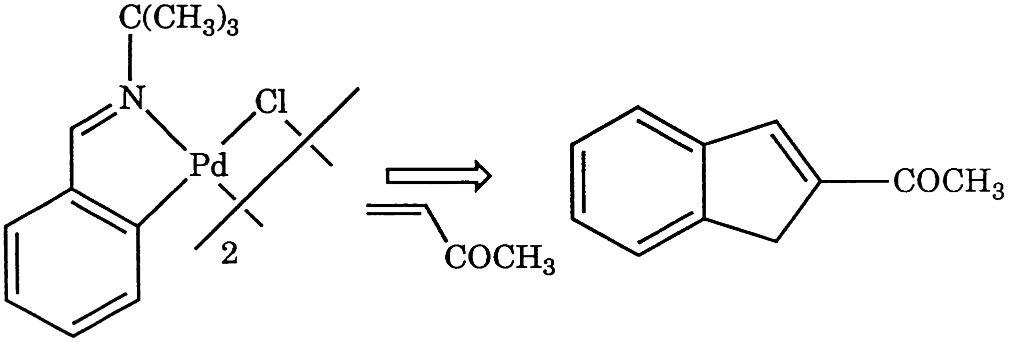


Figure 1.9

Coupling is not restricted to unsaturated groups: Tremont et al [51] have observed that alkylation of orthopalladated acetanilide (in a one pot reaction) gave rise to an ortho methylated product (Figure 1.10). The 2,6-dimethylacetanilide could also be obtained with the use of two moles of palladium acetate and excess methyl iodide.

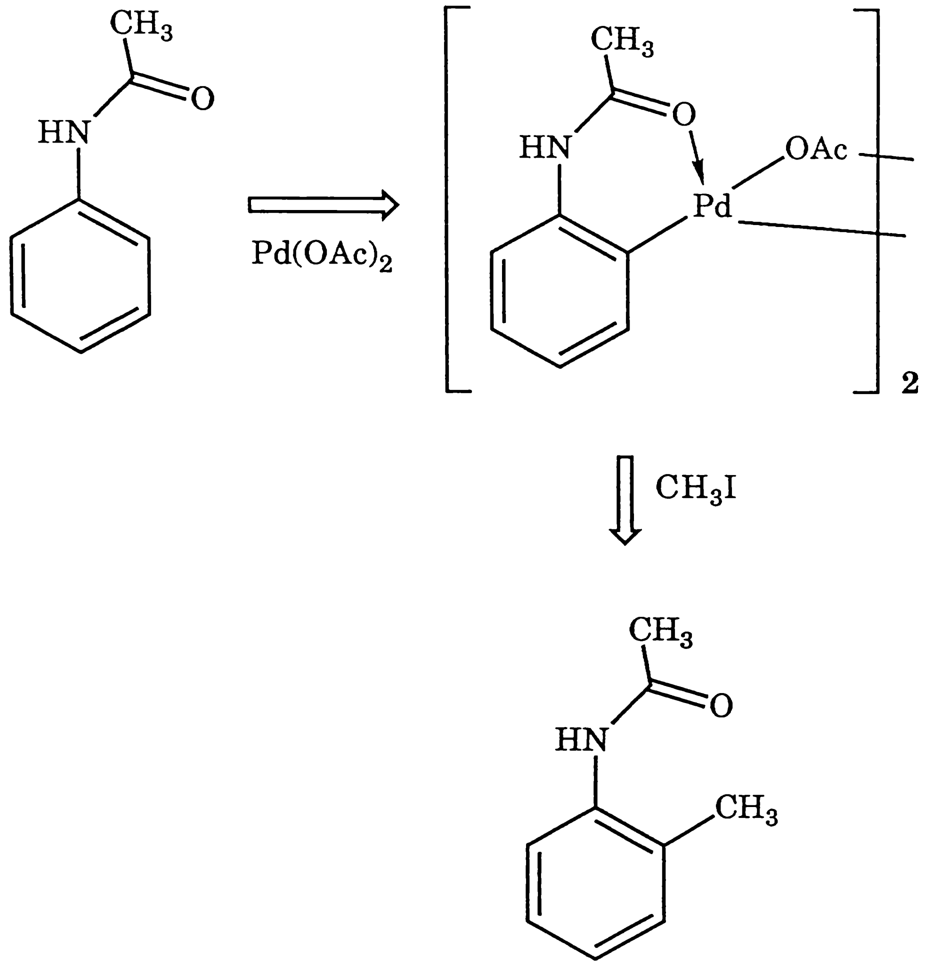


Figure 1.10

Orthomanganated ketones have been functionalized in a similar way [53], although the reactions required the intermediacy of a palladium species to yield the *ortho*-vinyl product. The manganese is not superfluous, as the orthopalladated aromatic ketones are currently not known to exist. The coupled vinyl compound (ca. 8%) was not the major product. Isolated in 76% yield was the cyclized product methyl 3-methyl-6-methoxyindene-2-carboxylate (Figure 1.11).

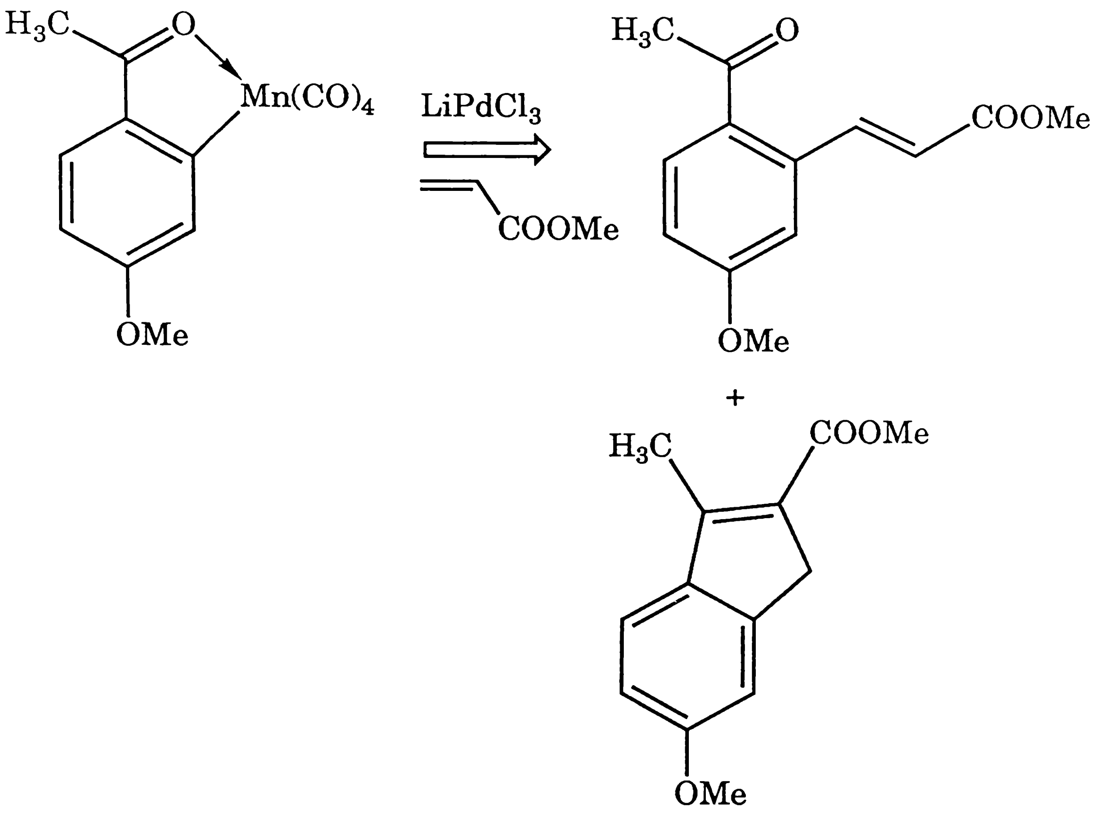


Figure 1.11

No definitive mechanism for the cyclization is currently known. Hegedus et al [53] have observed a similar cyclization: of 2-allylacetanilide in the presence of palladium chloride and benzoquinone, the product of which was *N*-acetyl-2-methylindole (Figure 1.12).

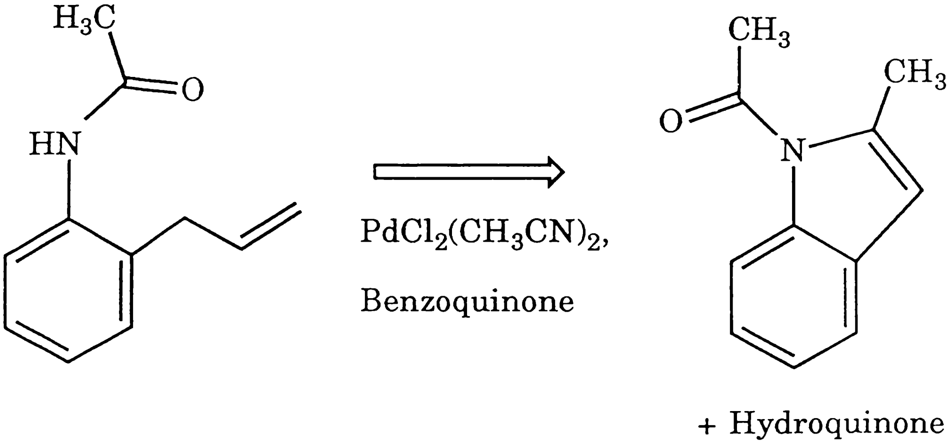


Figure 1.12

Orthodeuteration [54], halogenation [54] and mercuration [55] of orthomanganated ketones have also been reported. The last case is especially versatile as the aryl-mercury(II) products can be used in a wide range of further conversions [57].

Although not obvious from above, the two areas discussed, reactions of cyclopalladated compounds (which dominate the applications of cyclometalated compounds) and reactions of orthomanganated compounds, are very different in size. Our own focus on manganese complexes is due then to the comparative scarcity of applications that seem to exist in that area, a focus that is addressed in Chapter 4.

In the earlier Chapters 2 and 3, some novel orthomanganated compounds are described and an attempt made to address some of the mechanistic problems that currently exist in studies of the orthomanganation reaction.

Described in Chapter 5 are some tentative studies in the quite separate area of attempted electrophilic substitutions of (arene)Cr$(CO)_3$ compounds.

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Chapter Two

Orthomanganation of Pyrroles, Indoles and Benzamides

2.1 Cyclometalated Amides: Introduction

The orthomanganation of aromatic ketones is well established for benzenoid- [1,2] and hetero-arenes [3,4]. Thus, acetophenone, benzophenone, acetylthiophene (Figure 2.1) and numerous others, when treated with an alkylmanganesepentacarbonyl reagent, all yield a product where a manganese-tetracarbonyl group forms a stable σ-bond with the ortho-carbon of the arene and is coordinated to the acetyl oxygen atom of the ketone function.

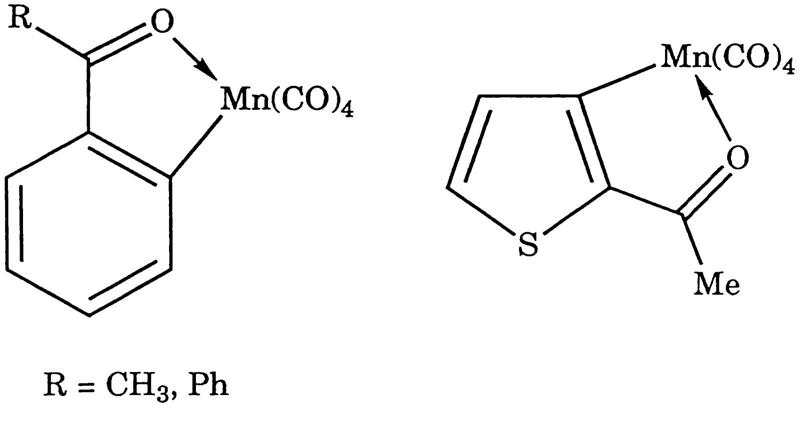


Figure 2.1

Extension to other oxygen-donor aromatic substrates is not straightforward. There are few reports of cyclometalated compounds containing a coordinated alkoxy oxygen ligand [4]. This has been accounted for by the bond between the alkoxy-oxygen and the metal being regarded as "not very strong" [4], giving compounds which are not as stable as those with a carbonyl oxygen donor. Some do exist however: two examples from chromium carbonyl [5] and iron [6] chemistry are shown in Figure 2.2. However, there are no manganese examples.

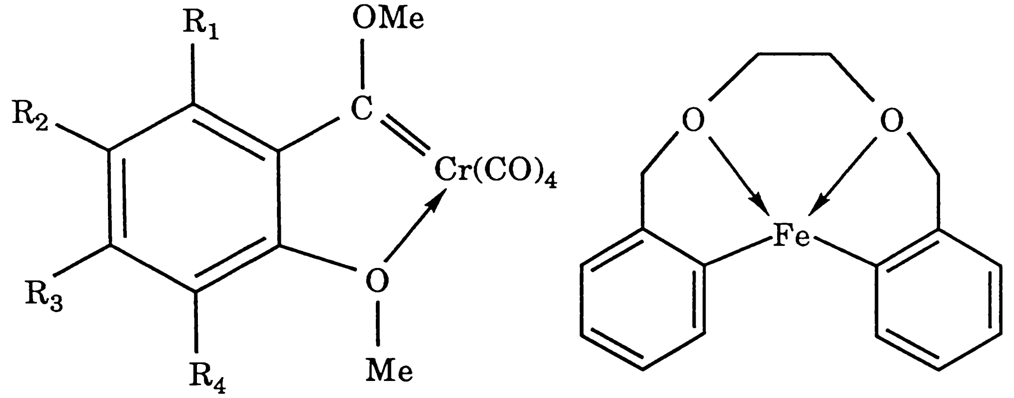


Figure 2.2

There are two possible ways in which an amide ligand can interact with a metal, to form analogues of known orthometalated compounds. Disregarding any nitrogen-metal interaction, the two possibilities are a metallocycle that contains the nitrogen atom, and one that excludes it (Figure 2.3).

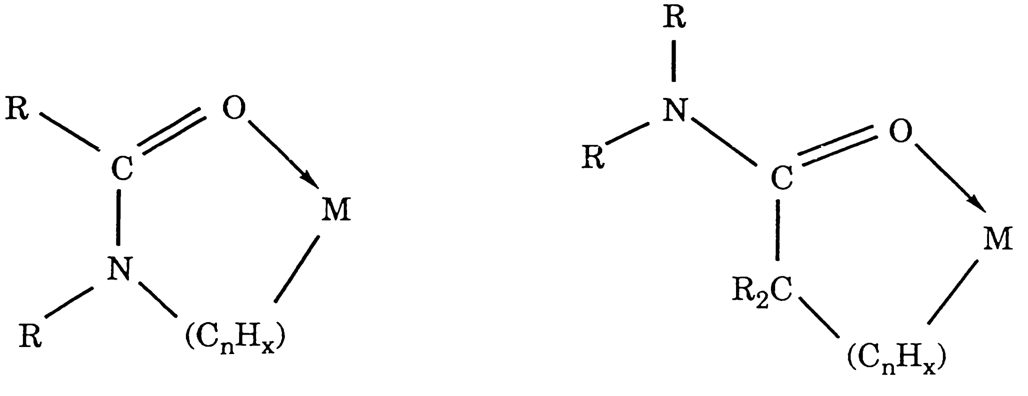


Figure 2.3

Examples related to the former group have been reported by Cowie and Ibers for rhodium [9] (Fig. 2.4(a)), and Roat *et al* for platinum [10] (Fig. 2.4(b)), which show the features common with orthomanganated compounds: a formal M-C σ-bond and a carbonyl oxygen donor. Both structures have key bond lengths comparable to those of the crystal structure discussed later in this chapter.

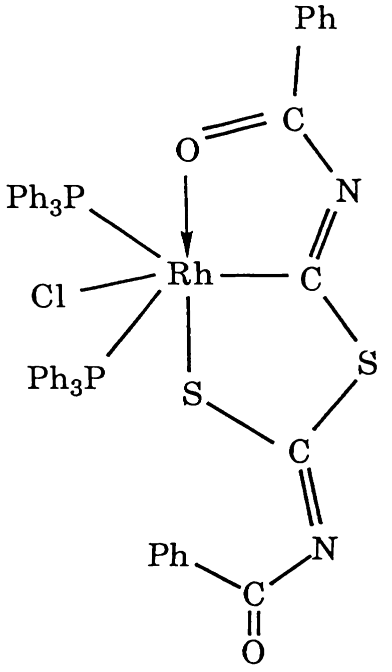


Figure 2.4(a)

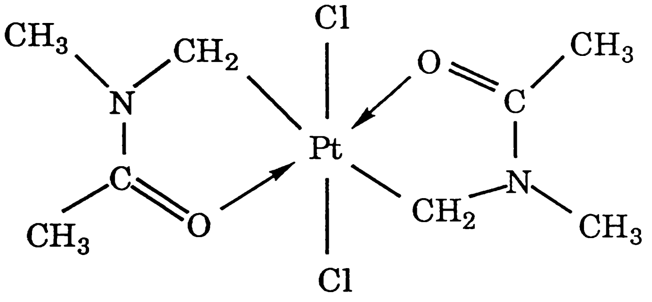


Figure 2.4(b)

Other nitrogen-containing metallocycles bear only a slight resemblance to orthometalated compounds: some do not have a formal M-C σ-bond [11] (Figure 2.5(a)); while others involve carboxylate coordination [12] (Figure 2.5(b)).

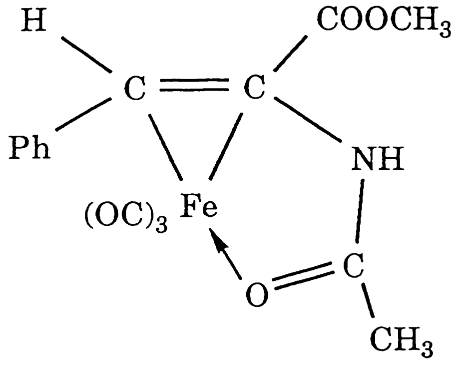


Figure 2.5(a)

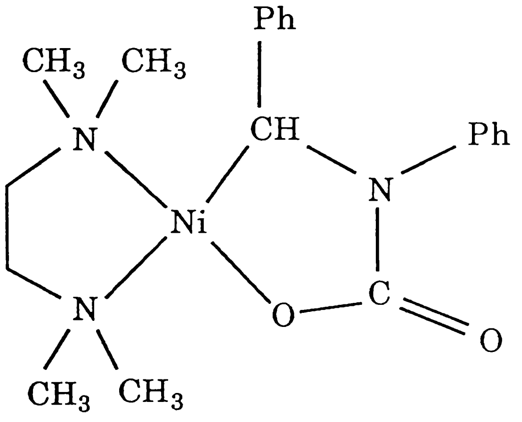
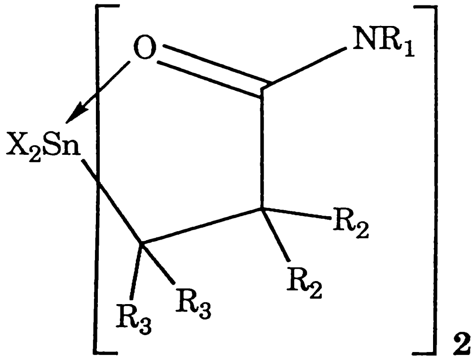


Figure 2.5(b)

The second type shown in Fig. 2.3, cyclometalated amides with the nitrogen atom outside the metallocycle, are known in only a few cases. The examples covered in the comprehensive review by Omae [4] are tin (II) species [14] (Fig. 2.6), notably similar to the aliphatic metalated amides in Figure 2.4(b).



R_1, R_2, R_3 = H, alkyl

Figure 2.6

The tin-oxygen distance is in the range 2.32-2.33 Å, considerably longer than the formal Sn-O σ-bond (2.15-2.20 Å) in compounds such as dimethyl-bis(tropolonato)-tin [16], but only marginally longer than the C=O oxygen donor bond (2.24-2.27 Å) in, for example, bis(pentakis(methoxycarbonyl)-cyclopentadienyl-O,O')tin [17]. The updated Omae review [8] reports that compounds containing carbonyl oxygen donors are limited to "ester carbonyl, keto carbonyl, and, rarely, carboxylic acid carbonyl and aldehyde carbonyl [as a ligand group]...", there being no mention of amides.

In this chapter, the isolation of a number of new cyclomanganated amides (from both groups shown in Fig. 2.3) is reported, and the crystal structure of one of those compounds is described.

2.2 Results and Discussion

2.2.1 Orthomanganation of pyrroles and indoles

By the procedure employed for preparing orthomanganated aromatic ketones, *N*-acetylpyrrole **1** was treated with $PhCH_2Mn(CO)_5$ to give the complex **2**, with the tetracarbonyl manganese group attached to the ligand via Mn-O and Mn-C bonds. For *N*-benzoylpyrrole **3**, two orthomanganation products are possible: the first arising from attack at the C2 of the pyrrole ring, the second from attack at the phenyl ring. Only the first of these was observed, indicating that the pyrrole ring is more reactive than the phenyl ring, despite the fact that **4** contains the strained combination [22] of two five membered rings fused together.

In close parallel, the larger heterocycles, *N*-acetyl- **5** and *N*-benzoylindole **6** gave **7** and **8** respectively. For *N*-benzoylindole **6**, there are three potential sites for metalation: in the five membered ring at C2, the six membered ring at C7 and the phenyl ring (C2'). Attack at only the first of these is observed, which again presumably reflects the relative reactivities of the different C-H bonds in the substrate.

A unique feature of the cyclometalated indole and pyrrole derivatives is the inclusion within the five membered metallocycle of two carbon atoms and one each of Mn, O and N. Comparison with previous orthomanganated species, almost all of which are ketones or esters, reveals that most orthomanganated rings contain three carbon atoms and one each of Mn and O. The pyrroles and indoles therefore have the potential for forming unusual heterocyclic ring assemblies via coupling reactions already established for other orthomanganated compounds. The possibilities will be explored in greater detail in Chapter 4.

2.2.2 Crystal Structure of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (7)

The structure of the orthomanganated *N*-acetylindole **7** was determined by X-ray crystallography in order to compare the novel nitrogen-containing metallocycle ring with the equivalent fragment of cyclometalated ketones. The structure is illustrated in Figure 2.7 and 2.8. The side view (Figure 2.9) shows that the molecule is planar except for the mutually trans CO(11) and CO(14), with no other non-hydrogen atom more then 0.06 Å from the least-squares plane, and fourteen of those seventeen atoms less than 0.02 Å from the least-squares plane.

The $Mn(CO)_4$ group is coordinated to the acetyl oxygen atom and the ortho carbon atom of the five membered ring. The strain imposed by fusing two five-membered rings together is reflected in Mn-C(1)-C(2) and C(9)-N-C(8) angles of 143° and 132° respectively, though that has no obvious effect on ease of preparation: yields are comparable to those of less-strained analogues. A comparison of bond parameters found for **7** with those of *N*-acetyl-3-methylindole [18] shows that metalation has led to the shortening of the N-C(9) bond, and lengthening of the C(9)-O(1), C(1)-N and C(1)-C(2) bonds. Coordination of the acyl oxygen atom to manganese clearly redistributes electron density: to compensate for electron withdrawal away from C(9), the nitrogen atom donates lone pair density to the N-C(9) bond rather than to the arene ring. The result is a longer N-C(1) and shorter N-C(9) in the coordinated arene. Other bond lengths are consistent with delocalised π-bonding over the metallocycle ring, indicating a strong contribution from resonance form **9**. The Mn-C(1) distance of 2.012 Å is the shortest yet recorded for an orthomanganated arene [3,20], indicating substantial π bonding for this bond, while the C=O distance is at the longer end, and the Mn-O at

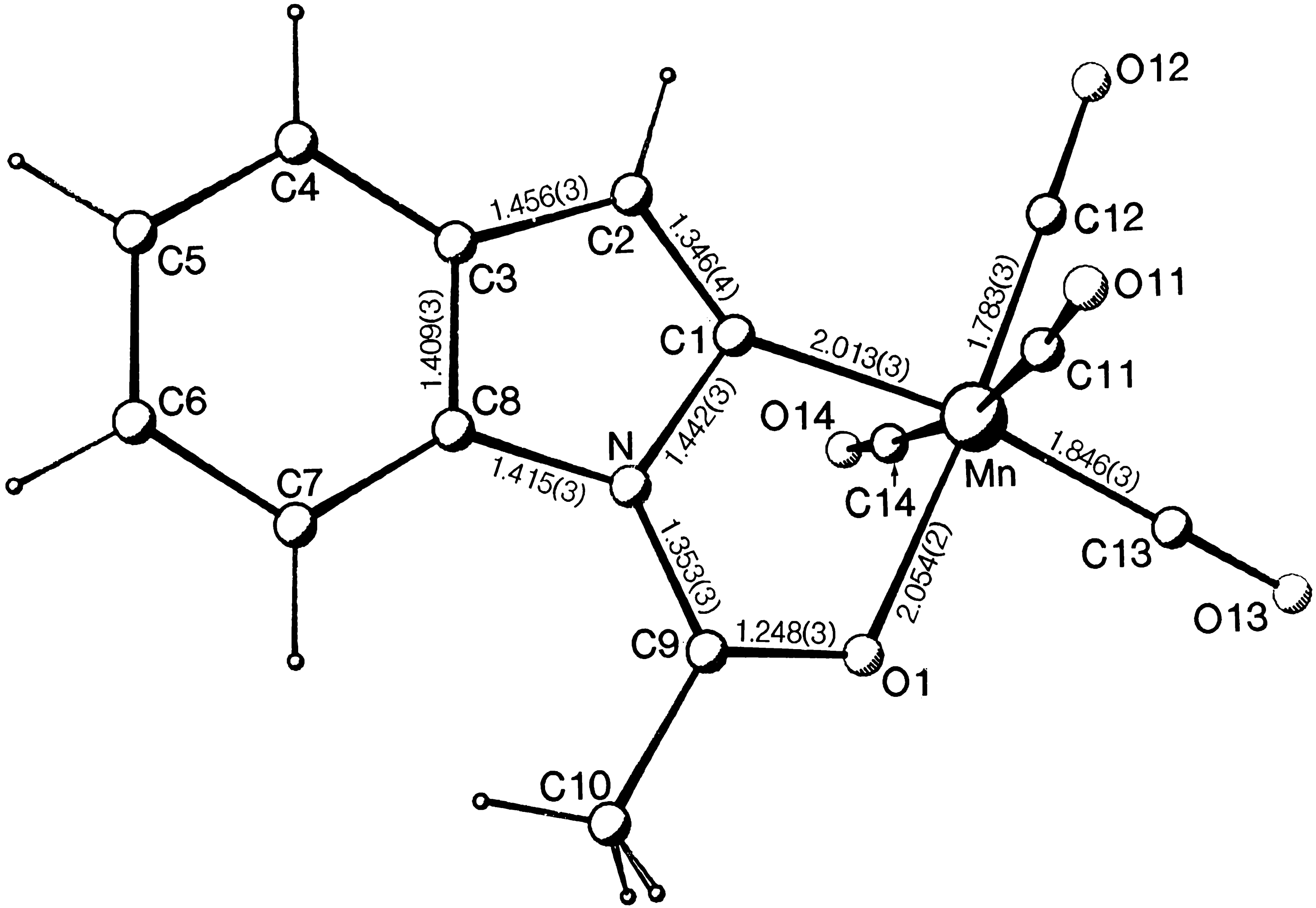


Figure 2.7 Structure and Selected Bond Lengths of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (**7**)

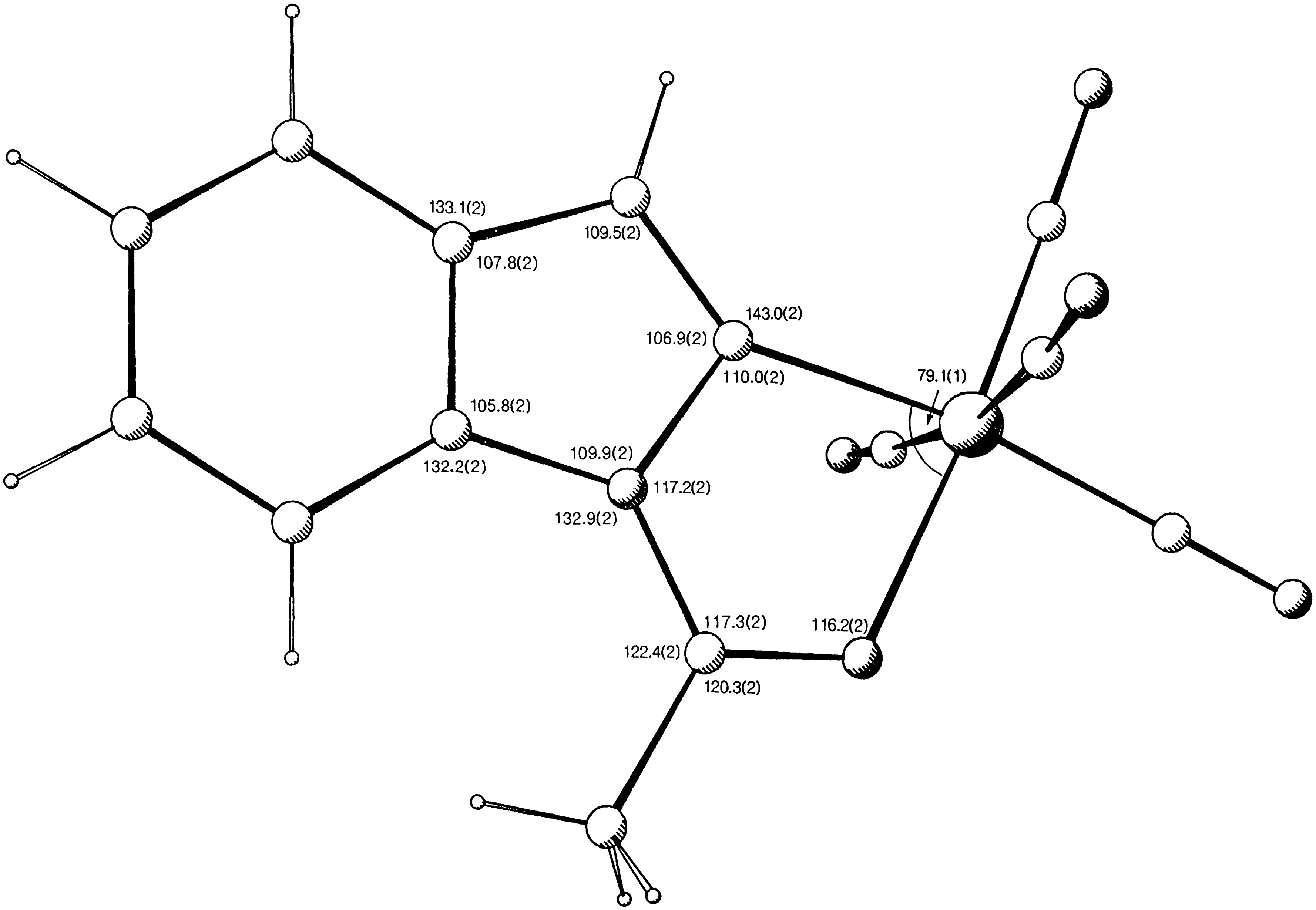


Figure 2.8 Selected Bond Angles of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (**7**)

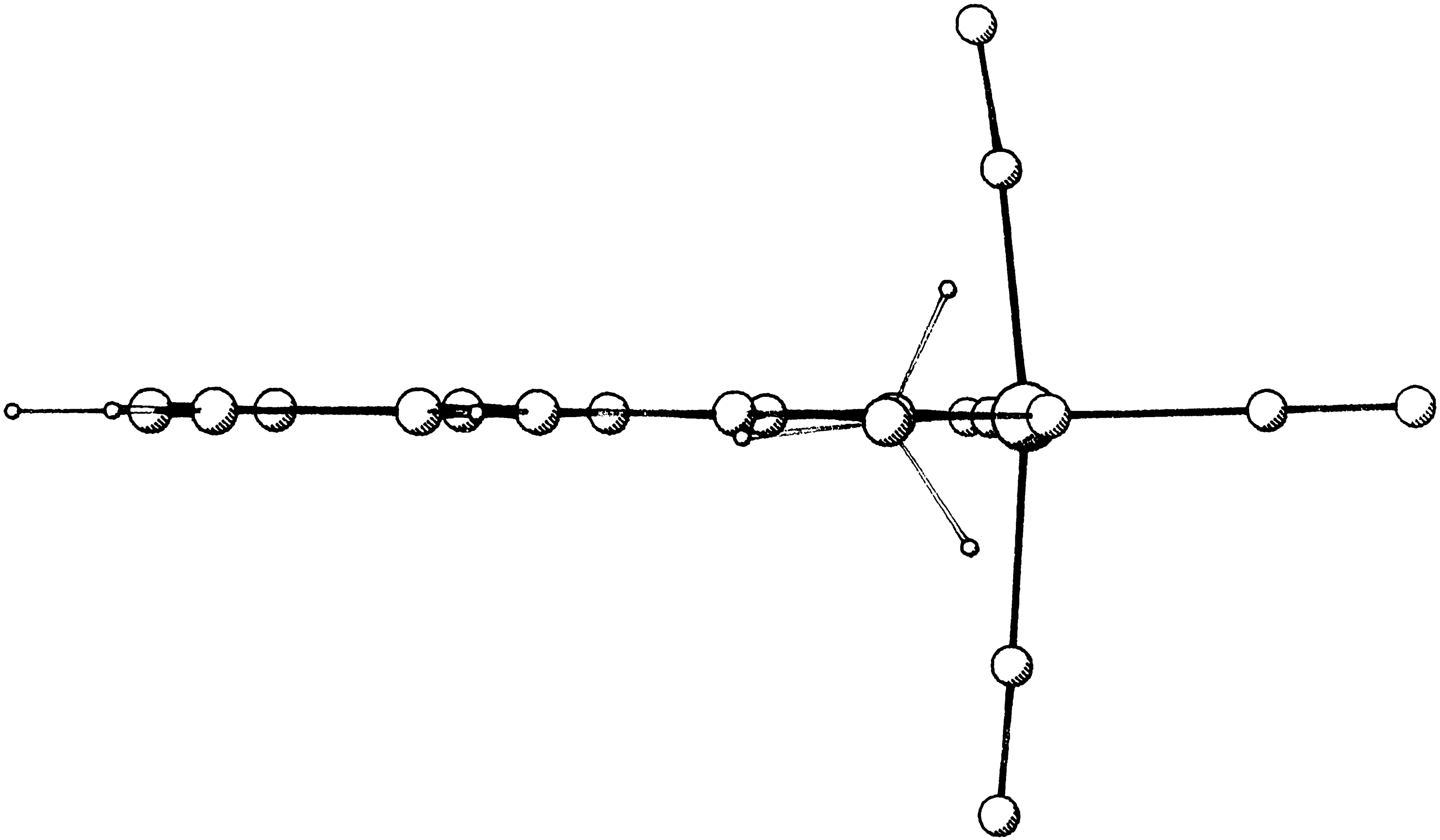


Figure 2.9 Side View of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (**7**) (acetyl CH_3 in foreground).

the shorter end, of respectives ranges found in related molecules. The geometry of the metallocycle of **7** is therefore fully consistent with an enhanced delocalised π bonding interaction arising from the presence of the nitrogen atom in the ring. The other bond parameters of the arene ring are unremarkable, while the relative Mn-(CO) distances and C-Mn-C angles of the $Mn(CO)_4$ group fall into the pattern established for other orthomanganated complexes [3,20]. Selected bond parameters are shown in Figure 2.7.

Table 2.1 Selected Bond Parameters for *N*-acetyl-3-methylindole [18].

Bond Lengths (Å)			
C(1)-C(2)	1.33	C(2)-C(3)	1.43
N-C(1)	1.40	N-C(8)	1.41
N-C(9)	1.38	C(9)-O(1)	1.20

Comparison with the platinum-amide compound (Fig. 2.4(b)) of Roat *et al* [10] reveals similar, but more pronounced, trends to those discussed above. The higher oxidation state of the platinum metal atom results in short Pt-O (2.15 Å) and Pt-C (1.98 Å) bonds, and not unexpectedly, a long C=O bond (1.30 Å).

2.2.3 Orthomanganation of benzamides

Benzamides are another class of compound in which the C=O function is suitably placed for orthomanganation. The parent compound $H_2NCOC_6H_5$ does not give rise to any identifiable organometallic product on treatment with $PhCH_2Mn(CO)_5$ in refluxing heptane. However, the substituted analogues $R_2NCOC_6H_5$ (R=Me (**10**), Et (**11**), $(CH_2)_4$ (**12**)) react straightforwardly to give the orthomanganated derivatives **13-15**. The yield in the case of R=Me is essentially quantitative, while that for R=Et is lower, presumably because of increased crowding adjacent to the C=O group, since the yield is also good for the pyrrolidinyl [R,R=$(CH_2)_4$] example, where the steric constraints are smaller. When R=Pr^i only traces of an analogous complex were detected, and with R=Ph no orthomanganation at all was observed.

For the benzamides, the possibility of different orthomanganation products again arises, since there are now two potential donor atoms: the O of the C=O group and the N of the amide group. Both are suitably positioned to encourage orthomanganation to give either O,C or N,C chelated organic groups, each with a five membered ring. Although the N,C type ring is produced with azobenzenes, imines and amines under similar conditions (e.g. with *N,N*-dimethylbenzylamine [13]), there was no evidence for other than O,C coordination with the benzamides in this study. There is of course considerable lowering of lone pair density on the nitrogen of amides through delocalisation on to the oxygen atom.

It is generally recognised that cyclomanganation of aliphatic ketones is not possible. Explanations for this generally pertain to the lack of reactivity of sp^3 C-H bonds [7], though there are other possible reasons: these will be discussed in some detail in Chapter 3. To confirm the non-reactivity of aliphatic amide substrates, the two amides *N*-acetylpiperidine (**17**) and *N,N*-diethylacetamide (**18**) were each refluxed in heptane with $PhCH_2Mn(CO)_5$, and no cyclometalation was observed. Thus, attack by manganese at an sp^3 carbon is, for the amides, not favoured. In contrast, preparation of the platinum-amide compound (Fig. 2.4(b)) [10] was achieved by the direct reaction of dimethylacetamide with potassium tetrachloroplatinate, the metalation being described as an oxidative addition, a mechanism as yet unproved for manganese cyclometalations.

2.2.4 General Discussion of Properties

Compounds **2**, **4**, **7**, **8** and **13-15** consistently give a pattern of three peaks in the carbonyl region of the infra-red spectrum [1,2], although four are expected for a cis-tetracarbonylmanganese group. The accidental degeneracy of two peaks near 2000 cm^{-1} is observed for almost every orthomanganated oxygen donor compound prepared thus far. One exception where all four absorptions are seen is the orthomanganated product of 1-acetylcyclohexene [7]. For the *N*-acyl complexes **2**, **4**, **7** and **8** all the peaks are shifted to higher frequencies by about 15 cm^{-1} when compared to other orthomanganated species. This results from the presence of the electronegative nitrogen atom in the metallocycle and emphasises the point that these complexes are significantly different from orthomanganated aryl ketones. All the species show two peaks in the 1500-1600 cm^{-1} arising from vibrations associated with the C=O group and the aromatic ring(s), with the lower energy of the two being predominantly from the ketone group, having been shifted about 150 cm^{-1} from the value found for the free ligand (cf. ref. 2).

The ^{1}H NMR data, given in the experimental section, are unremarkable. The ^{13}C NMR data, by comparison with the aryl ketone analogues, contain some differences of note. The benzamide, *N*-acylpyrrole and *N*-acylindole species all show signals arising from the

C=O carbon atom in the region δ 177-180 ppm, which is ca. 20 ppm to higher field than those for phenyl ketones [1]. Similarly, the indole/pyrrole carbon bonded to the manganese atom is observed in the δ 160-175 region, and at ca. δ 185 for the benzamides, whereas values above δ 190 are more usual for previously studied examples. The lower δ values observed for these complexes can be directly attributed to the nitrogen atom bonded to the C=O group (**13-15**), and adjacent to both carbon atoms in question for **2**, **4**, **7** and **8**, since there are similar trends for the free ligands. For all orthomanganated complexes there is a general pattern of the C=O ^{13}C signal shifting from the free ligand value by 10-15 ppm to higher field, while the Mn-C carbon shifts by 40-60 ppm on coordination to the metal. The trends in selected carbon shifts are shown in Table 2.2 (below).

Table 2.2

Selected ^{13}C nmr shifts of orthomanganated amide, free amide ligand and some related compounds.

Compound	C=O	C-Mn	C≡O
N-acetylindole			
orthomanganated (**7**)	178.4	172.5	209.8, 219.3, 220.2
free ligand (**5**)	168.4	125.0	-
N-benzoylindole			
orthomanganated (**8**)	177.5	172.7	209.8, 212.2, 212.4
free ligand (**6**)	162.4	124.2	-
N-acetylpyrrole			
orthomanganated (**2**)	178.9	162.6	210.0, 216.6
free ligand (**1**)	167.4	118.8	-
N-benzoylpyrrole			
orthomanganated (**4**)	177.3	163.3	210.1, 212.4
free ligand (**3**)	167.3	121.0	-
N,N-dimethylbenzamide			
orthomanganated (**13**)	179.7	185.6	212.4
free ligand (**10**)	170.9	126.5	-
N,N-diethylbenzamide			
orthomanganated (**14**)	179.1	185.3	212.5
free ligand (**11**)	169.9	125.2	-
N-benzoylpyrrolidine			
orthomanganated (**15**)	177.2	185.0	212.8
free ligand (**12**)	168.5	126.2	-
Acetophenone			
orthomanganated	213.1	192.1	213.1, 219.4
free ligand	195.7	128.2	-
2-Acetylthiophene			
orthomanganated	208.0	204.3	221.2, 213.0, 210.4
free ligand	190.2	133.4	-

2.3 Experimental

N,*N*-dimethylbenzamide (**10**) was prepared as described by Johnstone and Rose [15]. Benzamide (0.253 g, 2.088 mmol) was added to a suspension of crushed KOH (0.950 g, 16.931 mmol) in DMSO (5 ml), followed by the addition of iodomethane (0.55 ml, 8.815 mmol). The mixture was stirred for 15 minutes. Extraction with CH_2Cl_2, washing with water and drying yielded a colourless oil (0.275 g, 88 %). The amide did not chromatograph on silica particularly well, as was the case for diethylacetamide and acetylpiperidine. The latter two compounds were difficult to locate because they possess weak UV chromophores. Purity was best achieved by vacuum distillation (*N*,*N*-dimethylbenzamide 0.1 mm Hg, 74-80°C; diethylacetamide 0.1 mm Hg, 37°C; acetylpiperidine 0.1 mm Hg, 56°C).

N,*N*-dimethylbenzamide (**10**). ^1H NMR: δ 7.41 (s, 5H, H2-6), 2.99 (s, 6H, NCH_3). ^{13}C NMR: δ 170.9 (C=O), 135.9 (C1), 128.9 (C4), 127.8 (C3,5), 126.5 (C2,6), 38.8, 34.8 (NCH_3).

Preparation of *N*-acetylindole (**5**). Adapted from a procedure reported by Bellamy and Williams [23]. Indole (0.413 g, 3.52 mmol) was dissolved in THF (15 ml) and cooled to 0°C in an ice bath. n-Butyllithium (2.2 ml, 1.6 mol l^{-1}, 3.52 mmol) was added dropwise under a stream of nitrogen over 15 min. Stirring was continued for a further 30 min at 0°C. Acetic anhydride (0.35 ml, 3.71 mmol) was added dropwise during 5 min. The solution was allowed to warm to room temperature, then stirred for a further 30 min. The mixture was poured into water (5 ml), and extraction with ethyl acetate (2 x 30 ml) was followed by drying of the extract ($MgSO_4$) and evaporation under reduced pressure to give a brown oil (0.557 g). The oil was chromatographed with CH_2Cl_2/hexane (1/1) to give a colourless oil (0.398 g, 71 %). Similarly prepared were *N*-benzoylindole, *N*-acetylpyrrole, *N*-benzoylpyrrole, *N*,*N*-diethylbenzamide, *N*-benzoylpyrrolidine, *N*,*N*-diphenylbenzamide, *N*,*N*-diethylacetamide and *N*-acetylpiperidine. All except *N*,*N*-diphenylbenzamide were isolated as liquids after chromatography: purity was therefore confirmed by ^{1}H and ^{13}C NMR spectroscopy (data below).

N-acetylindole (**5**). ^{1}H NMR: δ 8.58 (m, 1H, ArH), 7.35 (m, 4H, ArH, H2), 6.50 (d, J = 3 Hz, 1H, H3), 2.29 (s, 3H, CH_3). ^{13}C NMR: δ 168.4 (C=O), 135.2 (C7a), 130.1 (C3a), 125.0 (C2), 124.7 (C5), 123.3 (C4), 120.5 (C6), 116.1 (C7), 108.6 (C3), 23.4 (CH_3).

N-benzoylindole (**6**). ^{1}H NMR: δ 8.70 (m, 1H, ArH), 7.50 (m, 9H, ArH, H2), 6.61 (d, J = 4 Hz, 1H, H3). ^{13}C NMR: δ 167.1 (C=O), 135.7 (C7a), 132.8 (C1'), 130.3 (C3a), 129.4, 128.3 (C2',3',5',6'), 127.7 (C4'), 124.3 (C2), 121.7 (C5), 120.6 (C4), 119.6 (C6), 111.1 (C7), 102.0 (C3).

N-acetylpyrrole (**1**). ^{1}H NMR: δ 7.40 (d, J = 2 Hz, 2H, H2,5), 6.35 (d, J = 2 Hz, 2H, H3,4), 2.46 (s, 3H, CH_3). ^{13}C NMR: δ 167.4 (C=O), 118.9 (C2,5), 112.8 (C3,4), 21.8 (CH_3).

N-benzoylpyrrole (**3**). ^{1}H NMR: δ 7.54 (m, 5H, H2'-6'), 7.33 (d, J = 2 Hz, 2H, H2,5), 6.35 (d, J = 2 Hz, 2H, H3,4). ^{13}C NMR: δ 167.3 (C=O), 133.0 (C1'), 131.9 (C4'), 129.2, 128.2 (C2',3',5',6'), 121.0 (C2,5), 112.9 (C3,4).

N,*N*-diethylbenzamide (**11**). ^{1}H NMR: δ 7.45 (s, 5H, H2-6), 3.40 (br q, J = 6 Hz, 4H, NCH_2), 1.14 (t, J = 6 Hz, 6H, CH_3). ^{13}C NMR: δ 169.9 (C=O), 136.2 (C1), 127.6 (C4), 127.3 (C3,5), 125.2 (C2,6), 43.8, 38.9 (NCH_2), 12.4 (CH_3).

N-benzoylpyrrolidine (**12**). ^{1}H NMR: δ 7.52 (s, 5H, H2-6), 3.51 (br m, 4H, NCH_2), 1.83 (br m, 4H, β-CH_2). ^{13}C NMR: δ 168.5 (C=O), 136.4 (C1), 128.8 (C4), 127.2 (C3,5), 126.2 (C2,6), 48.5, 45.2 (NCH_2), 25.4, 23.5 (β-CH_2).

N,*N*-diisopropylbenzamide (**16**). ^{1}H NMR: δ 7.50 (s, 5H, H2-6), 3.74 (q, J = 7 Hz, 2H, NCH), 1.35 (d, J = 7 Hz, 12H, CH_3).

N,*N*-diphenylbenzamide (**19**). Recrystallised from ethyl acetate/hexane (3/1) to give colourless rods, m.p. 173-180°C (lit.[21] 180°C).

N,*N*-diethylacetamide (**18**). ^{1}H NMR: δ 3.41 (q, J = 7 Hz, 4H, NCH_2), 2.13 (s, 3H, $COCH_3$), 1.22 (t, J = 6 Hz, 6H, β-CH_3). ^{13}C NMR: δ 172.4 (C=O), 42.2, 39.3 (NCH_2), 20.3 ($COCH_3$), 13.3, 12.2 (β-CH_3).

N-acetylpiperidine (**17**). ^{1}H NMR: δ 3.50 (br s, 4H, H2,6), 2.08 (br s, 3H, CH_3), 1.63 (br s, 6H, H3,4,5). ^{13}C NMR: δ 168.0 (C=O), 46.8, 41.7 (C2,6), 25.7, 24.8 (C3,5), 23.8 (C4), 20.3 (CH_3).

Preparation of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese **7**. A solution of $PhCH_2Mn(CO)_5$ (0.136 g, 0.475 mmol) and *N*-acetylindole (0.081 g, 0.509 mmol) in heptane (25 ml) was refluxed for 4 h. After cooling, the heptane was removed under vacuum and the dissolved (CH_2Cl_2) residue was chromatographed (Harrison Research Co. "Chromatotron", CH_2Cl_2/pet. spirit 1/4 eluent). A yellow solid crystallised from the chromatographed solution (0.105 g, 68 %) and was subsequently recrystallised from petroleum spirit to give yellow plates of **7**, m.p. 112°C (dec.). Found C, 51.76; H, 2.44; N, 4.22 %, $C_{14}H_8NO_5Mn$ calcd: C, 51.71; H, 2.48; N, 4.31, M 325, MS (P^+) 325. IR: 2087 (m), 2003 (vs), 1944 (s), 1586 (m), 1566 (m) cm^{-1}. ^{1}H NMR: δ 7.31 (m, 4H, C_6H_4), 6.83 (s, 1H, H3), 2.74 (s, 3H, CH_3). ^{13}C NMR: δ 220.2, 219.1, 209.8 (CO), 178.4 (C=O), 172.5 (C-Mn), 137.5 (C7a), 137.2 (C3a), 124.6 (C4), 121.8 (C5), 121.2 (C6), 118.5 (C7), 112.1 (C3), 22.6 (CH_3).

Preparation of η^2-(1-acetyl-2-pyrrolyl)tetracarbonylmanganese **2**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.257 g, 0.901 mmol) and *N*-acetylpyrrole (0.098 g, 0.898 mmol) with 5 h reflux was **2** (0.095 g, 36 %), m.p. 102°C. Found C, 43.70; H, 2.12; N, 5.03 %, $C_{10}H_6NO_5Mn$ calcd.: C, 43.66; H, 2.20; N, 5.09 %, M 275, MS (P^+) 275. IR: 2087 (m), 2000 (vs), 1953 (s), 1596 (m), 1550 (m) cm^{-1}. ^1H NMR: δ 7.30, 6.54, 6.44 (br s, 1H each, H2,3 and 4), 2.54 (s, 3H, CH_3). ^{13}C NMR: δ 216.5, 210.0 (CO), 178.9 (C=O), 162.6 (C2), 124.7 (C3), 120.4, 120.7 (C4,5), 19.9 (CH_3).

Preparation of η^2-(1-benzoyl-2-pyrrolyl)tetracarbonylmanganese **4**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.174 g, 0.608 mmol) and *N*-benzoylpyrrole (0.107 g, 0.625 mmol) with 1.5 h reflux was **4** as a non-crystallising oil after chromatography, (0.122 g, 59 %). MS (P^+) 337. IR: 2087 (m), 2000 (vs), 1952 (s), 1586 (m), 1562 (m). ^1H NMR: δ 7.60 (br s, 5H, C_6H_5), 7.76 (m, 1H), 7.46 (m, 1H), 6.56 (s, 1H). ^{13}C NMR: δ 212.4, 210.1 (CO), 177.3 (C=O), 163.3 (C2), 133.2 (C1'), 130.4 (C4'), 129.3, 128.8 (C2',3',5',6'), 125.0 (C3), 122.7, 120.8 (C4,5).

Preparation of η^2-(1-benzoyl-2-indolyl)tetracarbonylmanganese **8**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.130 g, 0.455 mmol) and *N*-benzoylindole (0.118 g, 0.534 mmol) with 5 h reflux was **8** (0.105 g, 59 %) as an oil. MS (P^+ - 2CO) 303. IR: 2087 (m), 1998 (vs), 1952 (s), 1586 (m), 1548 (m). ^1H NMR: δ 7.61 (s, 5H, C_6H_5), 7.30, 6.76 (both m, 2H, C_6H_4), 6.96 (s, 1H, H3). ^{13}C NMR: δ 212.4, 212.2, 209.8 (CO), 177.5 (C=O), 172.7 (C-Mn), 137.9 (C7a), 137.7 (C3a), 132.5 (C1'), 131.7 (C4'), 128.9, 127.8 (C2',3',5',6'), 124.9 (C4), 122.9 (C5), 120.8 (C6), 118.2 (C7), 113.0 (C2).

Preparation of η^2-(2-(*N*,*N*-dimethylamido)phenyl)tetracarbonylmanganese **13**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.160 g, 0.559 mmol) and $C_6H_5CONMe_2$ (0.142 g, 0.952 mmol) with 5 h reflux was **13** (0.176 g, 100 %), m.p. 120-125°C (dec.). Found C, 49.38; H, 3.08; N, 4.37, $C_{13}H_{10}NO_5Mn$ calcd.: C, 49.52; H, 3.20; N, 4.44 %, M 315, MS (P^+) 315. IR: 2076 (m), 1986 (vs), 1924 (s), 1575 (m), 1566 (m). ^1H NMR: δ 8.05, 7.73, 7.27 (all br, 4H, H(ring)), 3.30 (s, 6H, NCH_3). ^{13}C NMR: δ 212.4 (CO), 185.6 (C-Mn), 179.7 (C=O), 141.6 (C2), 138.2 (C6), 130.9 (C3), 128.9, 122.8 (C4,5), 40.4, 39.3 (NCH_3).

Preparation of η^2-(2-(*N*,*N*-diethylamido)phenyl)tetracarbonylmanganese **14**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.116 g, 0.406 mmol) and $C_6H_5CONEt_2$ (0.073 g, 0.412 mmol) with 4 h reflux was **14** (0.047 g, 33 %), m.p. 96-99°C (dec.). Found C, 52.36; H, 4.14; N, 4.08, $C_{15}H_{14}NO_5Mn$ calcd: C, 52.49; H, 4.11; N, 4.08 %; M 343, MS (P^+) 343. IR: 2076 (m), 1986 (vs), 1932 (s), 1573 (m), 1559 (m). ^1H NMR: δ 8.02, 7.60 (all br, 4H, H(ring)), 3.63 (br, 4H, NCH_2), 1.33 (br, 6H, CH_3). ^{13}C NMR: δ 212.5 (CO), 185.3 (C-Mn), 179.1 (C=O), 141.9 (C2), 138.1 (C6), 130.8 (C3), 127.6, 123.0 (C4,5), 44.3 (NCH_2), 13.4 (CH_3).

Preparation of η^2-(2-(pyrrolidinylamido)phenyl)tetracarbonylmanganese **15**. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.135 g, 0.472 mmol) and $C_6H_5CON(CH_2)_4$ (0.097 g, 0.554 mmol) with 5 h reflux was **15**, (0.124 g, 77 %), m.p. 88-93°C (dec.). Found C, 52.74; H, 3.44; N, 4.08, $C_{15}H_{12}NO_5Mn$ calcd.: C, 52.80; H, 3.54; N, 4.10 %, M 341, MS (P^+) 341. IR: 2076 (m), 1986 (vs), 1927 (s), 1574 (m), 1559 (m). ^1H NMR: δ 8.01 (d), 7.74 (d), 7.20 (m) (4H, H(ring)), 3.63 (t, 4H, NCH_2), 1.42 (br s, 4H, CH_2).

^{13}C NMR: δ 212.8 (CO), 185.0 (C-Mn), 177.2 (C=O), 141.6 (C2), 139.0 (C6), 128.0 (C3), 123.0, 123.0 (C4,5), 49.7, 49.2 (NCH_2), 26.9, 23.3 (β-CH_2).

Attempts to orthomanganate *N,N*-diisopropylbenzamide by the same method gave only traces of the expected product, and *N,N*-diphenylbenzamide underwent no orthomanganation.

Crystal structure of η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (7).

Preliminary precession photography showed symmetry no higher than triclinic. Intensity data were collected on an Enraf-Nonius CAD4 automatic four circle diffractometer using monochromated Mo-K_α X-rays.

Crystal data: $C_{14}H_8MnNO_5$, M 325.16, triclinic, space group $P\bar{1}$. a=7.451(1), b=8.963(3), c=10.389(2) Å, α=96.01(2), β=87.27(1), γ=94.99(2)°, U 686.9 Å^3. D_c=1.57 g cm^{-3} for Z=2, F(000) 328, μ(Mo-K_α) 9 cm^{-1}, T 23°C. Intensity data in the range $2<2\theta<52°$ were collected using a θ-2θ scan technique. Minimum and maximum transmission factors of 0.9729 and 0.9991 respectively were applied based on a series of azimuthal scans.

A total of 3114 unique reflections were collected and those 2596 for which $I>2\sigma(I)$ were used in all calculations. The position of the manganese atom was located by Patterson methods, and all other non-hydrogen atoms were found in subsequent difference maps. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were assigned to calculated positions. The refinement converged at R = 0.035, R_w = 0.0414 where $w = [\sigma^2(F) + 0.008F^2]^{-1}$. No parameter shifted by more than 0.11σ in the final cycle and a final difference map revealed no peak or trough of electron density greater than 0.46 e $Å^{-3}$. Calculations were performed using SHELX-76 [19]. Final atom coordinates are given in Appendix I, while the structure is shown in Fig. 2.7.

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Chapter 3

Some Aspects of Orthomanganation Reactivity

At present, little is known about reactivity limitations on the orthomanganation reaction, let alone the mechanism(s) of the reaction. Many reactions occur and many are reported to fail. Some factors that are important as guides to reactivity have started to emerge (e.g. $\upsilon(C=O)$ of donor carbonyl, ring size, presence of acidic protons) but there is insufficient information so far for reliable predictions about reactivity, and little information to define mechanism.

In this chapter are reported successful and unsuccessful attempts at orthometalations on a rather diverse range of substrates, chosen to test some of the reactivity criteria that have been considered in earlier studies, and also to provide some directions in the area of mechanism. The results are grouped together under major headings that describe these reactivity criteria.

3.1 Donor power

3.1.1 Introduction

Suggestions of a qualitative correlation between cyclometalation reaction rate and ketone donor power were initially made by McKinney [1] and later discussed by Cabral [2]. Reference was made to a definitive report by Bellamy and Pace [3], where a correlation is established between carbonyl group oxygen basicity and C=O stretching frequency, for a wide range of compounds. The relevance to cyclometalation reactions is that the basicity of a carbonyl group in a particular compound might be used to describe that oxygen's "donor power".

Bellamy and Pace found that generally, υ(CO) changes smoothly with basicity, and is a good index of bond force constant, k(CO). Cabral and McKinney concluded that υ(CO) therefore correlates with oxygen donor power, and thus was an empirical guide to whether a metalation would occur.

A closer look at Bellamy's report shows that those conclusions need qualification. For example, the results show only a small basicity change across the series acetone, acetophenone, benzophenone, despite the drop in υ(CO) from 1719 cm^{-1} to 1692 cm^{-1} to 1667 cm^{-1}*. Worse, the change is against the direction of an expected increase. Bellamy and Pace maintained that the basicity of the oxygen atom is therefore largely unaltered by conjugation, despite the fact that conjugation does result in a significant decrease in υ(CO). So k(CO), the C=O force constant, does change, but "in such a way that the lone pair electrons of the oxygen atom are essentially undisturbed."

Amides, some of which are important to this project, were also discussed [3]. The nitrogen atom "contributes both of its lone pair electrons to make up the total of four required for the delocalized orbitals." The consequence is a drastic change in charge distribution (of the C=O group) which is reflected in the increased basicity. Thus, the only instance Bellamy found in which conjugation had an influence on basicity was *N*-benzoylpiperidine.

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* The change in υ(CO) is probably due to coupling with C=C vibrations, so υ(CO) will not be proportional to k(CO) across that series.

In sum, there is a good correlation between υ(CO) and basicity. However, no general relationship of this kind is to be expected in conjugated systems, except when comparing closely related compounds. Despite this limitation, it was hoped that the effect of ring substituents on the carbonyl group basicity of aromatic aldehydes could be put to use in obtaining orthomanganated aldehyde products.

Previous accounts of cyclometalated aldehydes are few. Hillhouse reported the reaction [7] of cis,mer-ReH(CO)$_2$(PPh$_3$)$_3$ with carbon suboxide (C_3O_2) to afford the four-membered rhenium metallacycle shown in Figure 3.1. The two metal CO stretches are seen at 1933 and 1859 cm^{-1} and the ring CO stretch at 1516 cm^{-1}, somewhat lower than values commonly observed for other carbonyl oxygen donors (1550-1600 cm^{-1}).

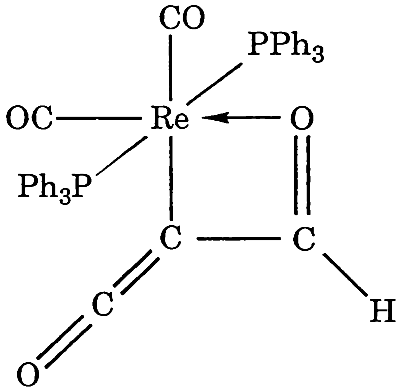

Figure 3.1

3.1.2 Results and Discussion

The results of the donor power study are summarised in Table 3.1, which gives the aldehyde substrates that were subjected to standard orthomanganation reaction conditions, their υ(C=O) stretching frequency and the respective orthomanganation yield from the reaction.

Table 3.1 Infrared stretching frequencies of some aryl carbonyl compounds and their yield in orthomanganation.

	$\upsilon(C=O)$ cm^{-1}	[Reference]	Yield
Acetophenone	1692	[1]	80
Benzaldehyde	1700	[1]	0
3,4,5-trimethoxybenzaldehyde	1690	[1]	6
p-methoxybenzaldehyde	1685	[2]	33
p-dimethylaminobenzaldehyde	1660	[2]	77
2-thiophenecarboxaldehyde	1675	[2]	11
3-thiophenecarboxaldehyde	1685	[2]	20

Table References:
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The large reactivity difference between acetophenone and benzaldehyde was the anomaly that led to study in this area of so-called "donor power". Indeed, if the aromatic systems of acetophenone and benzaldehyde are nearly identical, is it the difference in oxygen donors (in the two substrates) that decides relative reactivity? If so, can the oxygen donor ability of an aldehyde be enhanced by other means (such as the introduction of a substituent on the aromatic ring)?

For benzaldehydes, *para*-substitution by a methoxy or dimethylamino group decreases $\upsilon(CO)$ considerably (to 1685 cm^{-1} and 1660 cm^{-1} respectively) and when each aldehyde was treated with $PhCH_2Mn(CO)_5$, orthomanganation proceeded to give **20** and **21** respectively, in good yield in the latter case. The infra-red stretches of the resulting metalated aldehydes occur at 1588 and 1562 cm^{-1} (*p*-NMe_2) (one vibration due to aromatic ring) and 1581 and 1574 cm^{-1} (*p*-OMe): these are in accord with stretches observed for orthomanganated ketones.

A further route to orthometalated aldehydes involves a heterocyclic ring as the arene. In an aromatic aldehyde, substitution of phenyl by thienyl has a similar effect on υ(CO) to that of *p*-dimethylamino or *p*-methoxy substitution. The resulting C=O stretches are lowered to 1675 cm^{-1} for 2-thiophenecarboxaldehyde and 1685 cm^{-1} for 3-thiophenecarboxaldehyde . This change is obviously significant since when each thiophene aldehyde was treated with $PhCH_2Mn(CO)_5$ (to give **22** and **23**), yields of 11% and 20% respectively were obtained.

As a result of the current study then, υ(CO) is useful within a single group of compounds (we have only considered aromatic aldehydes) as an empirical guide to reactivity towards $RMn(CO)_5$ reagents. This conclusion was possible with the aldehydes because a cross-over point between "no reaction" and "some isolable product" was found, and the "no reaction" case failed for no other apparent reason than its lack of "donor power". Other groups of compounds may yet be shown to follow similar trends.

Comparisons between groups have not been considered because of the impure nature of the C=O stretch. That is, υ(CO) is invariably coupled to C-C(aromatic) vibrations (causing a lowering of υ(CO)). Thus valid comparisons between a number of C=O group stretches can only be made if the surrounding groups are similar or the same. For example, if the cut-off point for "no reaction" in aromatic aldehydes is nominally 1700 cm^{-1}, and we try to extend that value to heterocyclic amides (such as those discussed in Chapter 2), it is immediately clear that *N*-acetylpyrrole (υ(CO) 1722 cm^{-1}) and *N*-acetylindole# (υ(CO) 1710

Compounds in which the nitrogen electrons that would normally donate to the N-C bond are already involved in resonance with the heterocyclic system.

cm^{-1}) contravene the rule, as they both gave rise to orthomanganated products in good yield.

3.2 Ring Size

3.2.1 Introduction

Past reports [22,23] indicate a strong preference for five-membered rings among cyclometalated products. Known six- or seven-membered ring products are almost exclusively palladium metallacycles [22], an example of which is shown in Fig. 3.2.

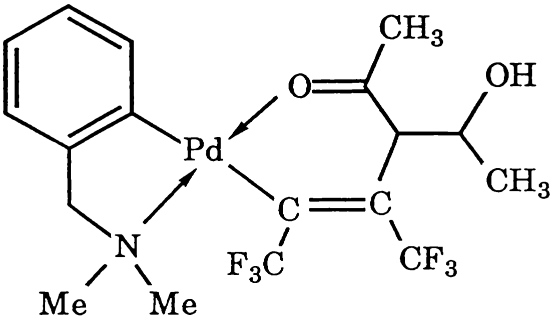
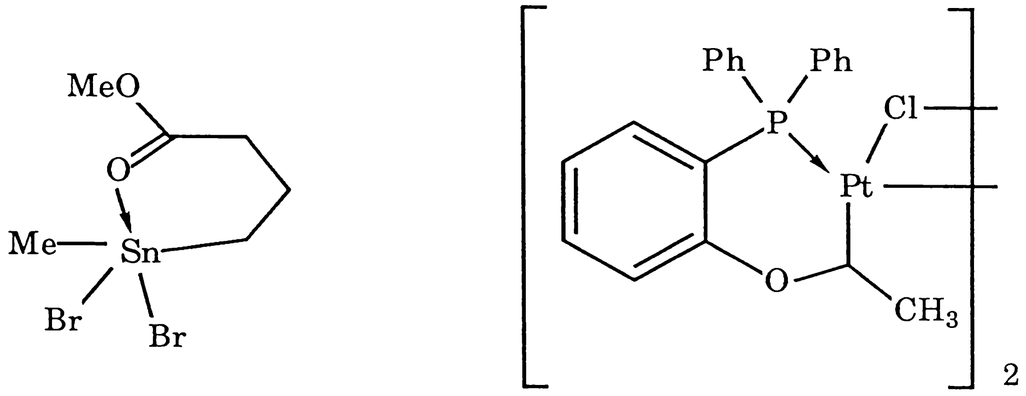


Figure 3.2

Other large rings include a tin compound [22] (Fig. 3.3(a)) and a platinum dimer [30] (Fig. 3.3(b)). Few reports mention attempts to obtain large metallacycle products with other metals.



(a) (b)

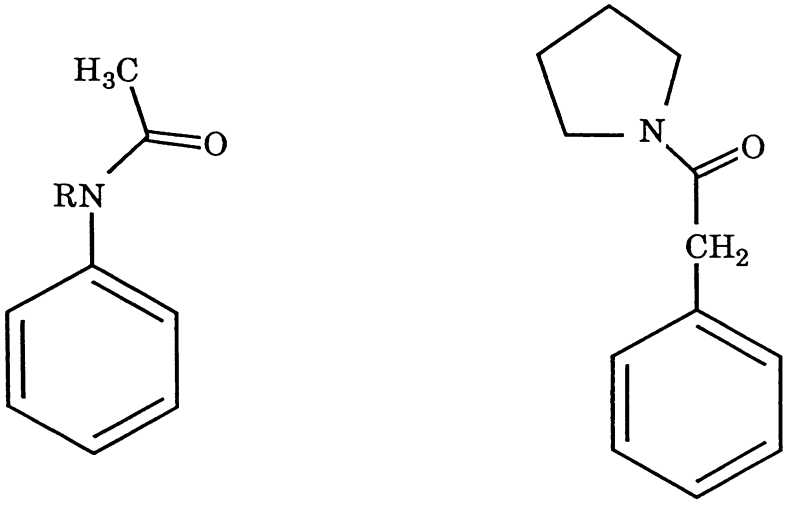
Figure 3.3

3.2.2 Results and Discussion

With regard to the orthomanganation reaction, care is required in the choice of substrate, as displacement of the carbonyl group to a position not conjugated with the aromatic ring results in an increase in ν(CO), thereby decreasing the likelihood of effective oxygen-metal donation.

As described in the introductory section on oxygen donor power, amides have an enhanced oxygen basicity and are therefore likely to be better O-donors than, for example, the ketone counterparts. For that reason, three amides, acetanilide, exalgin (*N*-methylacetanilide) and *N*-(phenylacetyl)pyrrolidine (Fig. 3.4) were each treated with $PhCH_2Mn(CO)_5$, in order to establish the favourability of a six-membered orthomanganated ring.

The first reaction resulted in only $Mn_2(CO)_{10}$ and acetanilide, while the *N*-(phenylacetyl)pyrrolidine and exalgin reactions showed signs of a trace of product in the crude reaction, which could not be isolated after chromatography.



R = H, acetanilide
R = Me, exalgin

N-(phenylacetyl)pyrrolidine

Figure 3.4

Even in the presence of effective O-donors then, the six membered ring appears much less favoured than its five-membered analogue.

3.3 Multiple Metalations

3.3.1 Introduction

All orthomanganated products so far reported in this study have been monometalated. To our knowledge, there have been few reports of multiply metalated single ligands for any metals. Those that have been structurally elucidated cover a range of interactions: η^6,η^6–π-coordinated dimetalated compounds [26], η^6-coordinated metal triads [27], η^3,η^3–π-coordinated (same side) dimetals [26] and σ-coordinated/π-coordinated di- and tri-metallic compounds [28]. The only apparent multiply σ-coordinated compounds are as follows:

(i) the green *p*-divanadocene substituted arene (Figure 3.5) obtained by Kohler *et al* [29] from the reaction of *p*-dilithiobenzene with vanadocene chloride:

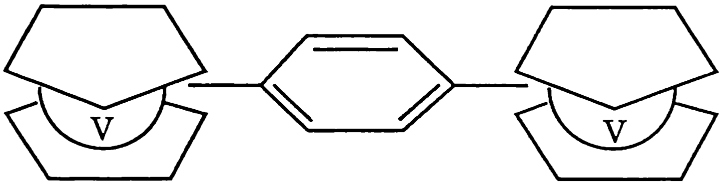


Figure 3.5

(ii) the dimetalated azobenzene product (Figure 3.6) obtained by Bruce *et al* [19]. Azobenzene, by virtue of its two nitrogen donor atoms, coordinates to two manganese tetracarbonyl groups, each of which bonds to a separate ring. The crystal structure has been reported [32].

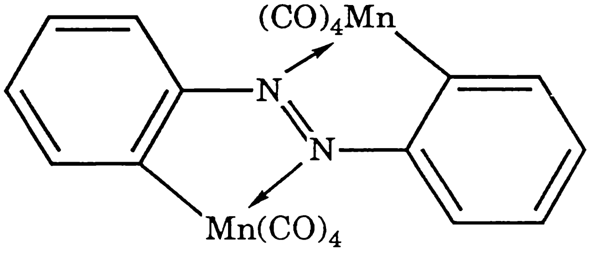
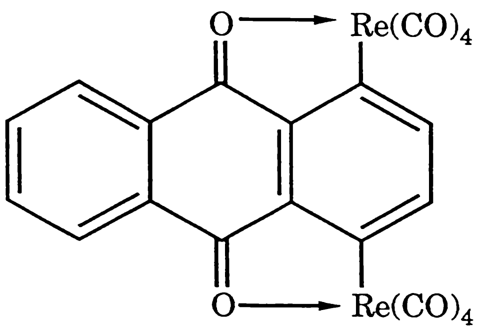


Figure 3.6

(iii) the two dimetalated anthraquinone products obtained by McKinney *et al* [31] from the reaction of methyl rhenium pentacarbonyl with anthraquinone (Figure 3.7). Also, Cabral [2] isolated the two manganese analogues of the compounds below.



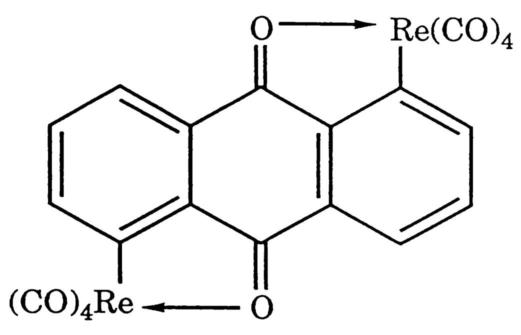


Figure 3.7

Given the scarcity of multiply metalated single rings (only three of the above qualify), it was decided to attempt to orthometalate diacetyl benzenes, in order to substitute one ring with two metal carbonyl functions.

3.3.2 Results and Discussion

1,3-Diacetylbenzene reacted smoothly with $PhCH_2Mn(CO)_5$ under standard orthomanganation conditions to afford two new products: monometalated η^2-(2,4-diacetylphenyl)-tetracarbonylmanganese (**24**) and the dimetalated η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonylmanganese) (**25**). Consumption of available $PhCH_2Mn(CO)_5$ (the limiting reagent) was comparable to other ketones (ca. 75-85%, cf. 80% for acetophenone) and resulted in the formation of approximately double the molar quantity of **24** to **25**. Although possible products of the reaction are four, the isomeric mono- and dimetalated products (Figure 3.8) were not formed.

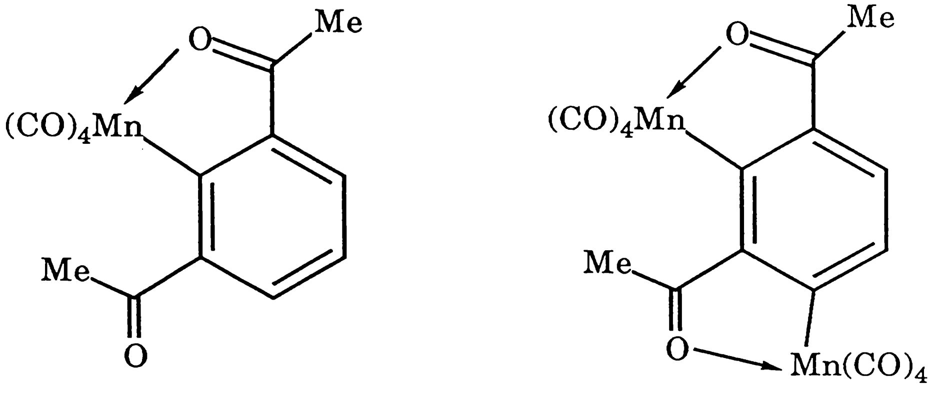


Figure 3.8

Similarly, 1,4-diacetylbenzene was treated with PhCH$_2$Mn(CO)$_5$ to afford the monometalated product (**26**), and the highly coloured dimetalated product, η^2,η^2-(2,5-diacetylphenyl)bis-1,4-(tetracarbonylmanganese) (**27**). Consumption of available PhCH$_2$Mn(CO)$_5$ was usually 60-65%, and again the molar quantity of monometalated **26** was approximately twice that of **27**. The alternative dimetalated product, with two metals *ortho* to each other was not observed (Figure 3.9).

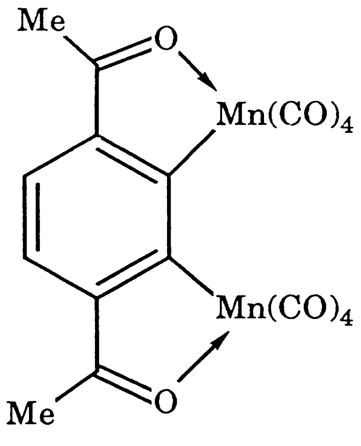


Figure 3.9

3.3.3 Crystal Structure of η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonylmanganese) (25)

The crystal structure of η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonylmanganese) (**25**) was determined. Interest in the structure was twofold:

(i) Are the two metallacycles identical in terms of delocalisation and coordination geometry about the manganese? and

(ii) How does the structure of the arene differ from monometalated compounds reported?

The structure (Figures 3.10 and 3.11) contains two $Mn(CO)_4$ units bonded to the same ring, each in a meta position with respect to the other, and each manganese coordinated to the oxygen atom of only one acetyl group.

In accord with other orthomanganated ketones, the C=O bonds (1.254(5) Å and 1.250(4) Å) suffer considerable lengthening once the oxygen is coordinated, and the C(arene)-C(acetyl) bonds shorten (1.494 Å for acetophenone, 1.450(5) and 1.461(5) Å here). However, there are some differences of note.

The arene bonds that share a metallacycle edge are both considerably longer (1.424(5) and 1.419(5) Å) than the other four arene bonds (C(1)-C(2) 1.398(5), C(2)-C(3) 1.395(5), C(4)-C(5) 1.390(5), C(5)-C(6) 1.391(4)), indicating a contribution from the canonical forms in Figure 3.12.

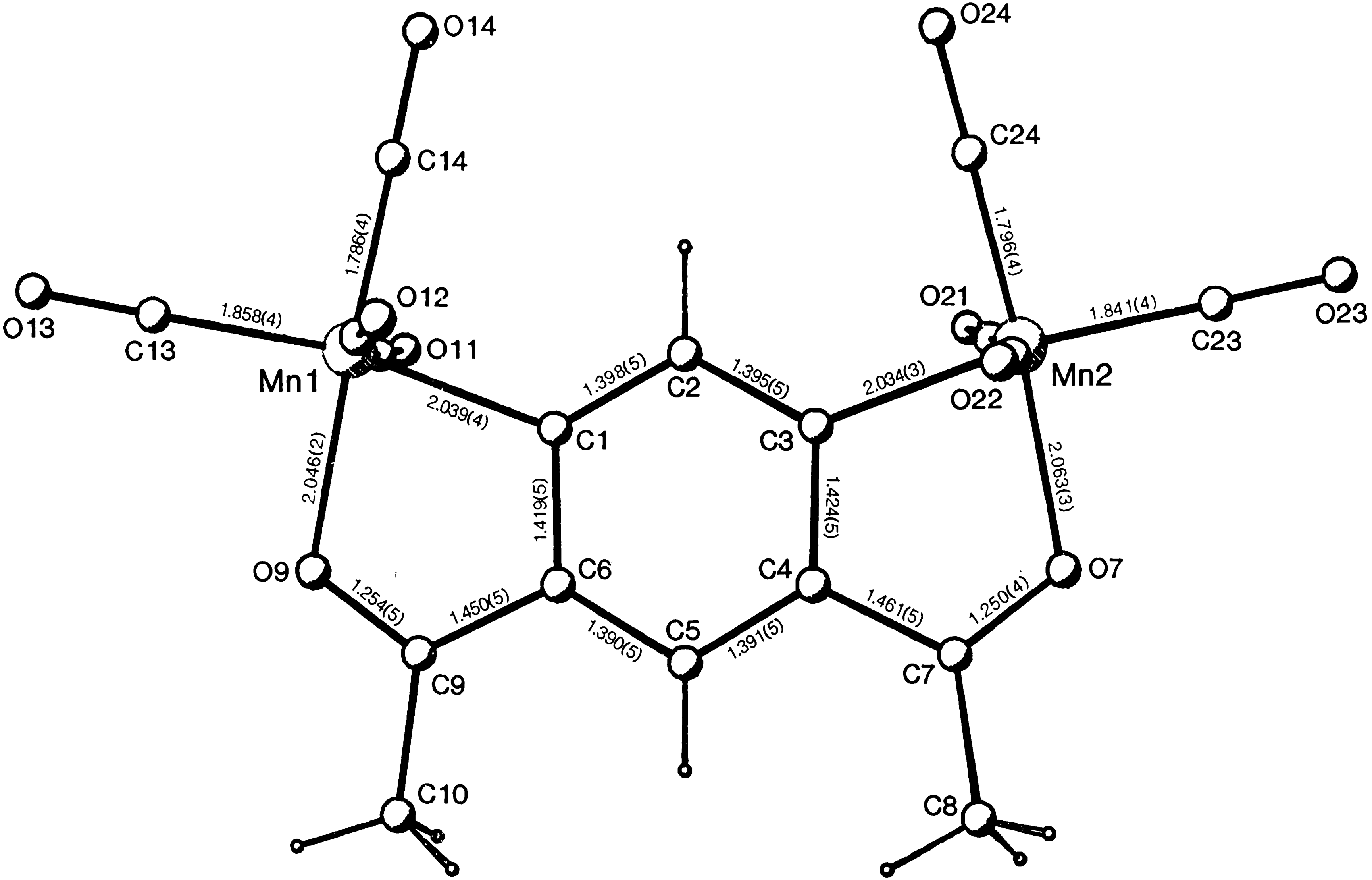


Figure 3.10 Structure and selected Bond Lengths of η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese (**25**).

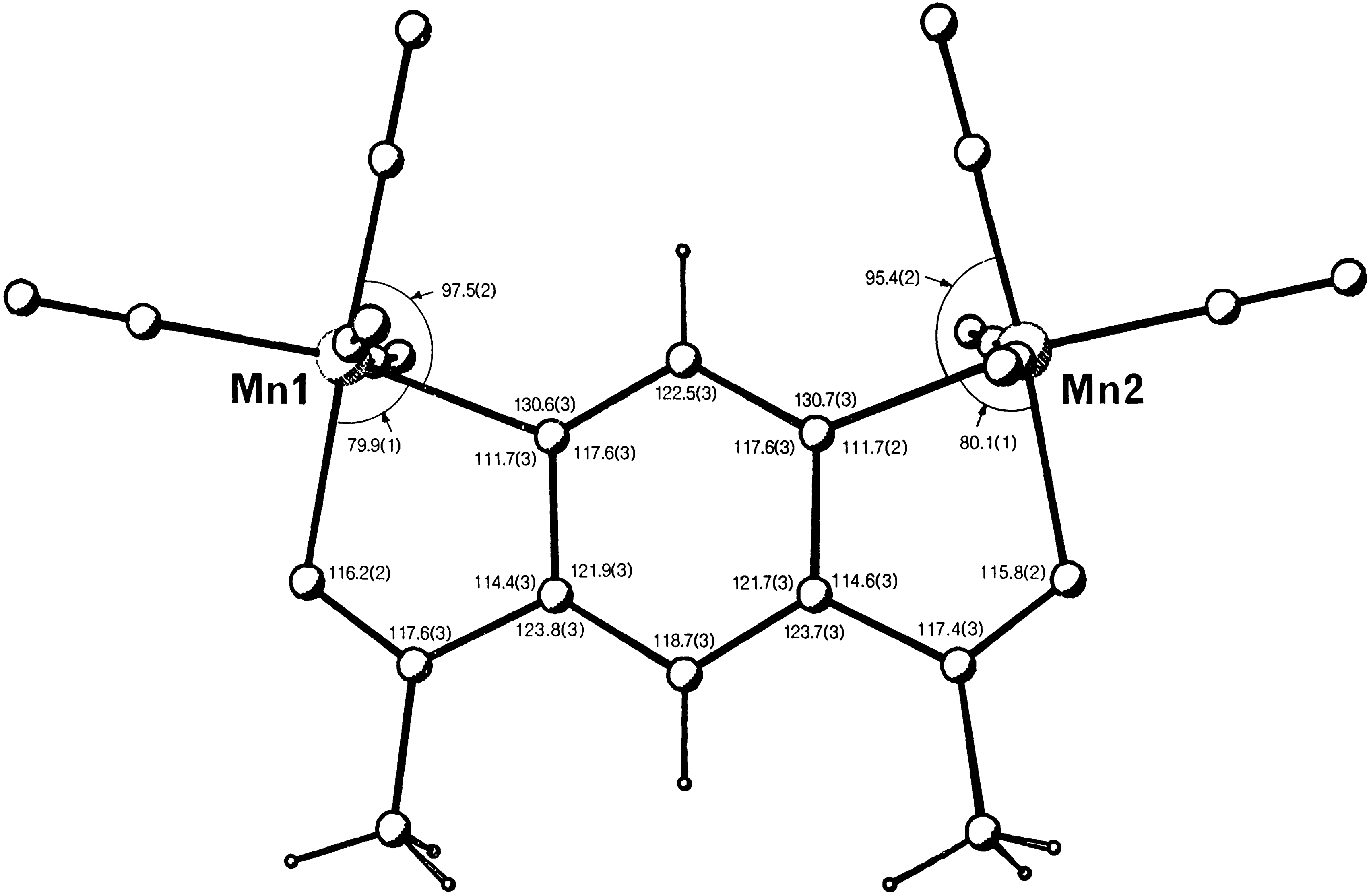


Figure 3.11 Selected bond angles of η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese (**25**).

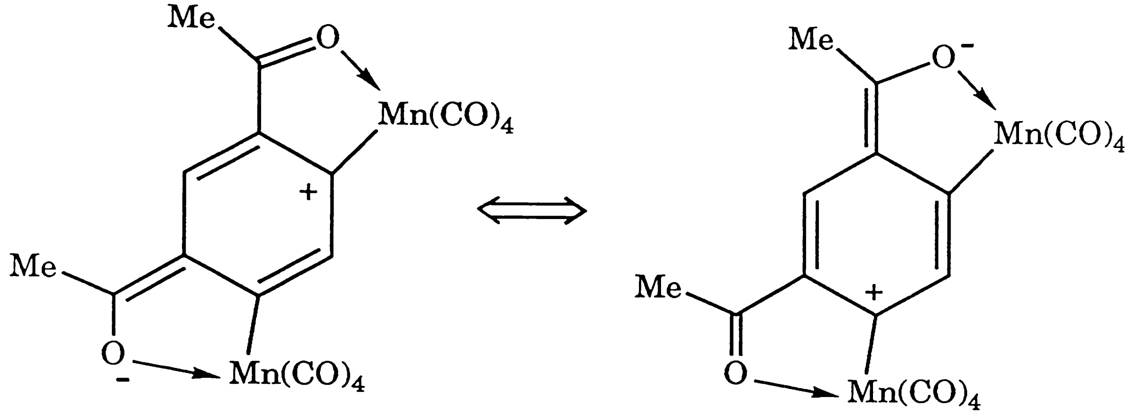
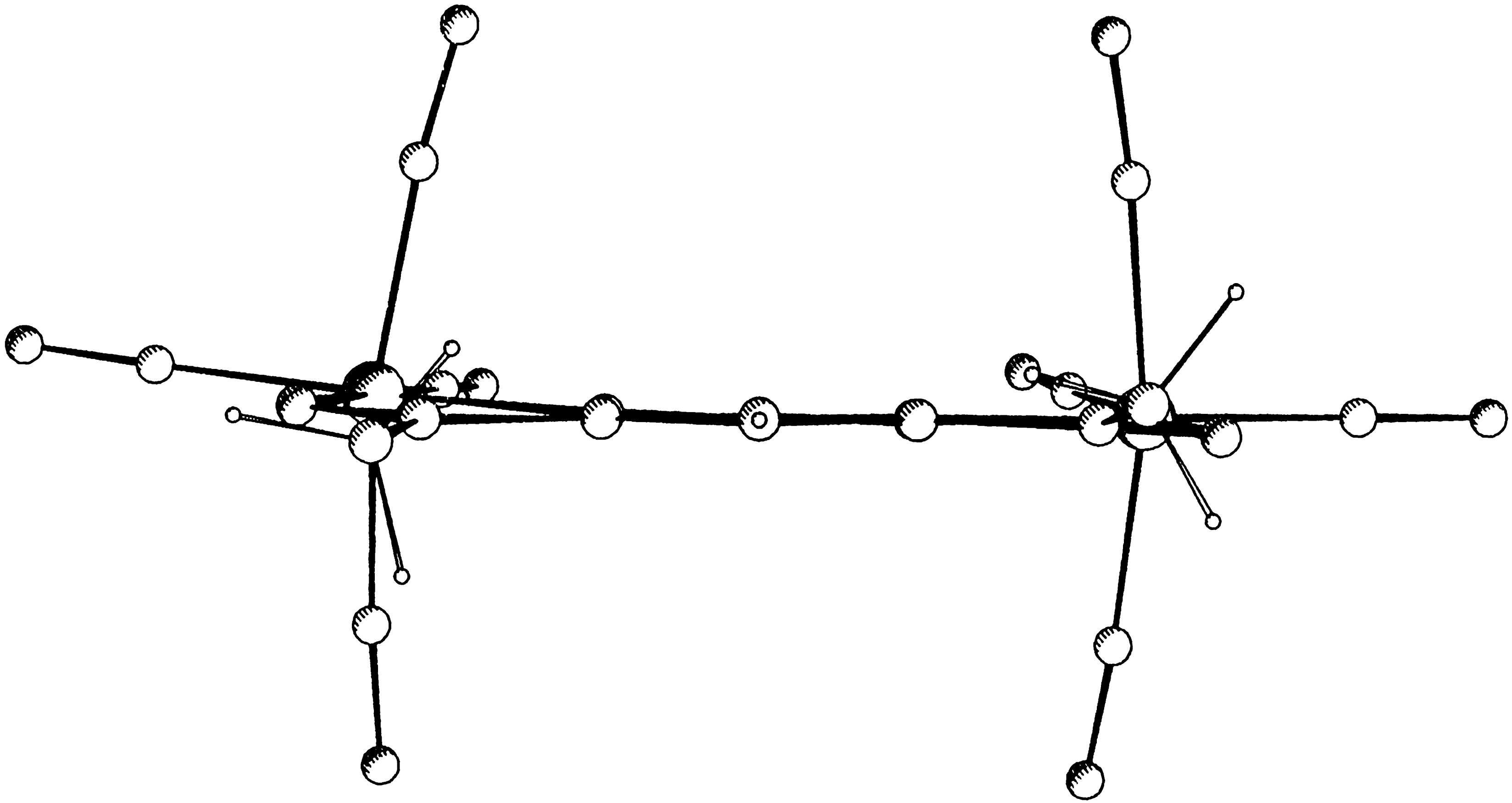


Figure 3.12

Secondly, the two $Mn(CO)_4$ groups have dissimilar Mn-O distances: Mn(1)-O(9) = 2.046(2) Å; Mn(2)-O(7) = 2.063(3) Å). Knobler *et al* [6] have suggested that a shorter Mn-O distance arises from enhanced π-electron donation to the metal [by the coordinated oxygen] followed by flow of metal π-electrons into the π^* antibonding orbitals of the trans CO. The result is a shorter Mn-CO(trans) bond (Mn(1)-C(14) 1.786(4) Å, Mn(2)-C(24) 1.796(4) Å). The effect is less pronounced, but still observable, in the CO trans to the ring carbon (Mn(1)-C(13) 1.858(4) Å, Mn(2)-C(23) 1.841(4) Å), implying π-donation from the ring, consistent with the short Mn-C(ring) distances.

The side view of the structure (Figure 3.13) reveals that one of the $Mn(CO)_4$ units is twisted out of the plane of the aromatic ring. Reports to date show that most $Mn(CO)_4$ metallacycles have, to maximise π-delocalisation, been strictly co-planar with the arene. The least-squares plane through the six arene carbons reveals the extent of puckering of each metallacycle: Mn(1) is vertically displaced from the arene plane by 0.15 Å; Mn(2) is much less vertically displaced at 0.03 Å. The dihedral angle between the aromatic plane and each least-squares

Figure 3.13 Side view of η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese (**25**) (acetyl CH_3s in foreground).



metallacycle plane shows a similar trend: the plane of metallacycle-1 (contains Mn(1)) with the arene is 3.6°, metallacycle-2 forms an angle of only 2.1° with the arene. The torsion angles also support these calculations, in particular, C(5)-C(6)-C(1)-Mn(1) is formally -175.1°: thus the net angle of the Mn(1)-C(1) bond with respect to the arene plane is almost 5°.

Both the dissimilar Mn-O distances and the ring puckering effects described can only be attributed to crystal packing, as there are no obvious electronic or steric reasons for their occurrence.

Despite the twisting of one metallacycle with respect to the arene ligand, both manganese atoms retain near-octahedral geometry. Distortions are observed in the ligand "bite" angle (C(1)-Mn-O(9): 79.9°, C(3)-Mn-O(7): 80.1°) and in the two out of plane carbonyls (with respect to one another and with respect to the equatorial carbonyls): these are bent towards the ring carbon (C(1) and C(3)) in each case, as was observed by Gommans [9], Cooney [16] and Knobler *et al* [6].

In sum, the structure is consistent with the π-delocalised characteristics of previous orthomanganated arenes, but with more pronounced delocalisation away from the arene. Other differences are presumed to arise from crystal packing forces.

3.3.4 Further reactions of monometalated and dimetalated ketones

The isolation of both a monometalated and dimetalated product in the treatment of diacetyl benzenes with $PhCH_2Mn(CO)_5$ gave rise to speculation about the nature of the reaction. It was assumed initially to be stepwise, a feature that was relatively easy to confirm. When the monometalated product (**24**) was treated with an equimolar quantity of $PhCH_2Mn(CO)_5$, the result was **25** in 69% yield (a trace of **24** (7%) was unreacted). A similar route to dimetalated azobenzene has been described by Bruce *et al* [32]. However, the reverse reaction, between 1,3-diacetylbenzene (DAB - free ligand) and dimetalated **25**, was also possible . When equimolar amounts of the two were refluxed together, 31% of **25** remained, while 67% of DAB remained. **24** was produced in 35% yield, which agreed adequately with the 33% DAB consumed, indicating the likelihood of $Mn(CO)_4$ transfer from **25** to DAB, rather than simply from degradation of **25** (which also seemed to occur, given the percentage depletion of **25**).

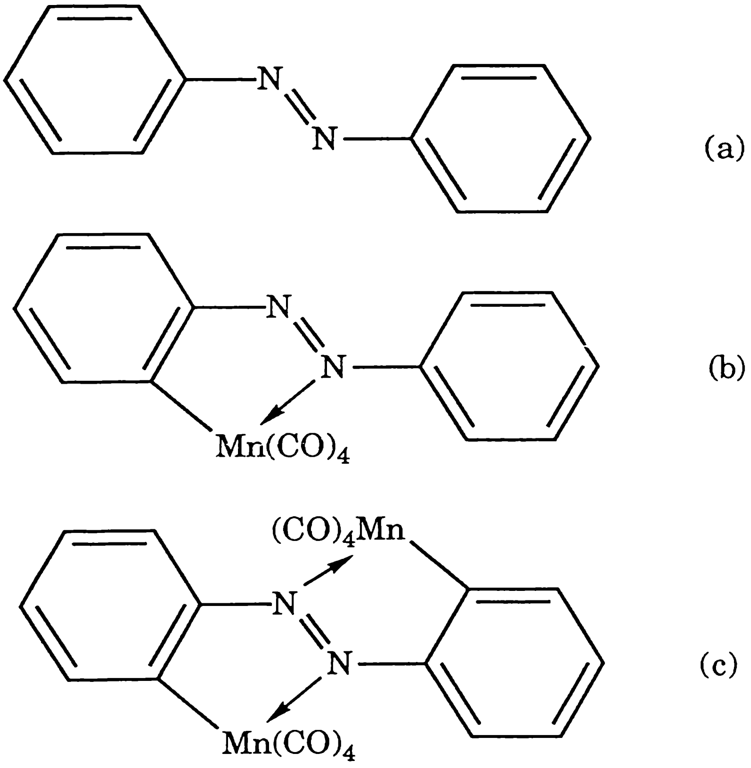


Figure 3.14

The observations of Bruce *et al* [32] were that dimetalated azobenzene (c) (Figure 3.14) was formed even when a 1:1 mixture of starting materials ($PhCH_2Mn(CO)_5$ and azobenzene (a)) was used, leading to a suggestion that once a single $Mn(CO)_4$ is in place, the second phenyl group is activated to further metalation.

When dimetalated azobenzene (c) was treated with an equimolar quantity of azobenzene (free ligand), the monometalated complex (b) was produced in over 60% yield. However, when (c) was treated with azotoluene, only the starting materials were detected after two hours, indicating that extension to other systems is not straightforward.

The reaction between (a) and (c), according to Bruce, is no more than a cyclometalation with a different elimination species, a notion that adequately explains the apparent thermodynamic contradiction in the reaction (which goes each way under nearly identical conditions). On a presumption then that toluene (or other) elimination is the driving force for the reaction, the second metalation step for our reaction would proceed as follows:

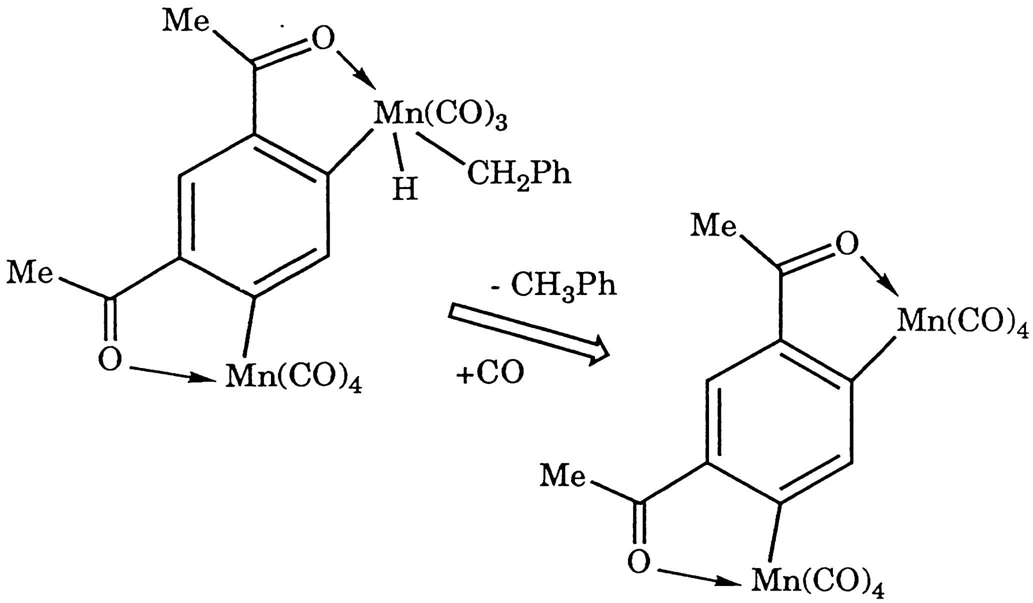


Figure 3.15

On the other hand, for the reverse reaction, a different elimination occurs:

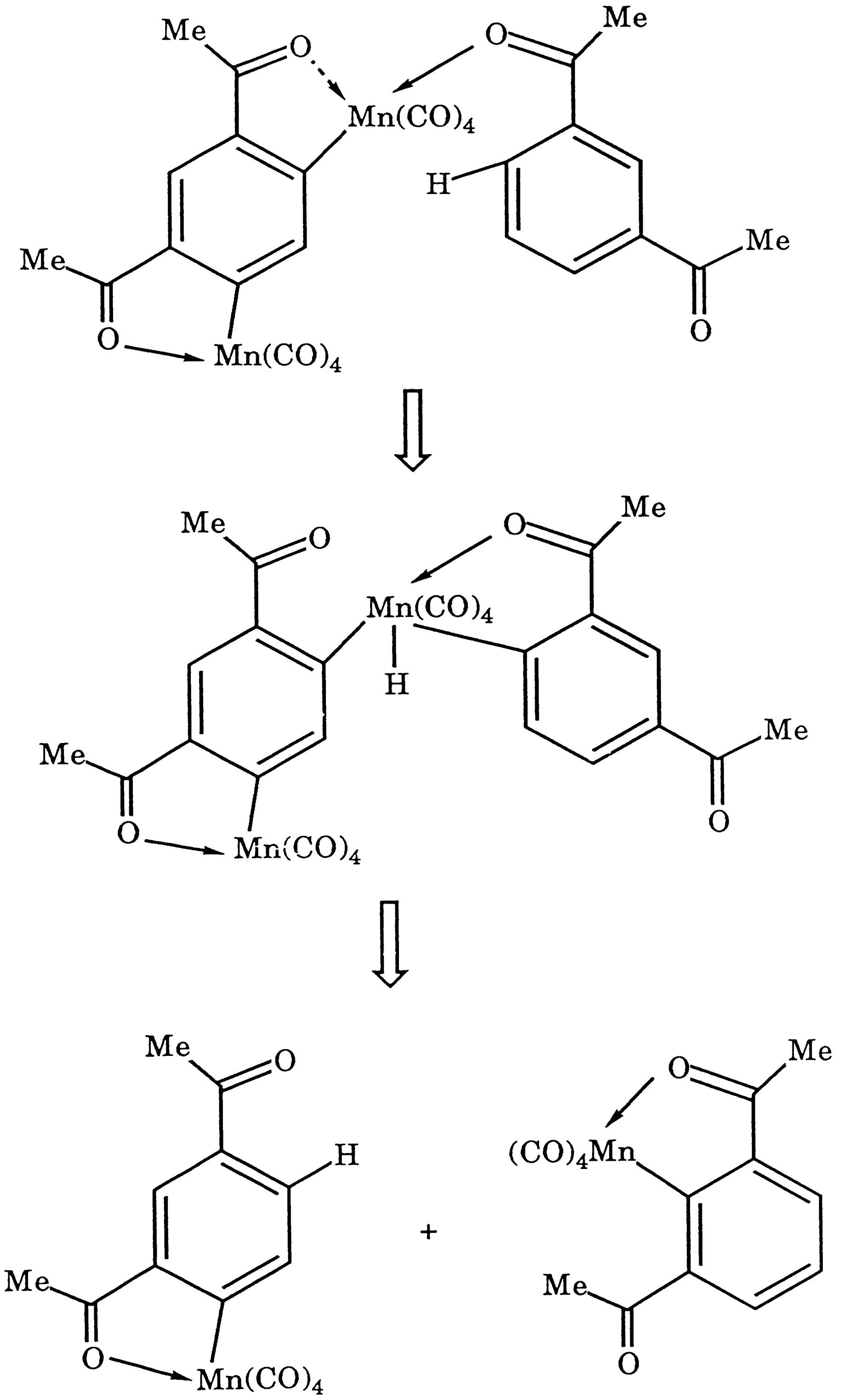


Figure 3.16

3.4 Substituent Effects and the role of electronic effects in reactivity

3.4.1 Introduction

The evidence that manganese has nucleophilic character in cyclometalation reactions has been reported by Bruce *et al* [17]. When substituted azobenzenes were metalated with manganese (I) and palladium (II), metal attack occurred at the electron-poor ring for manganese and at the electron-rich ring for palladium. The alkyl manganese pentacarbonyl reagent was therefore considered to have nucleophilic character. The authors also noted that it was "unlikely that a low valent transition metal complex, such as [$MnMe(CO)_5$], would behave as an electrophile." In question perhaps is whether one nitrogen might be a better donor than the other. The inductive effect of the electron-poor ring, for example, might give donor preference to the furthest nitrogen from it, precluding cyclometalation on the other ring. The authors maintain, however, that the "relative electron donor power of these atoms... should be affected only slightly by the presence of a 3-substituent, and so either nitrogen could coordinate."

3.4.2 Results and Discussion

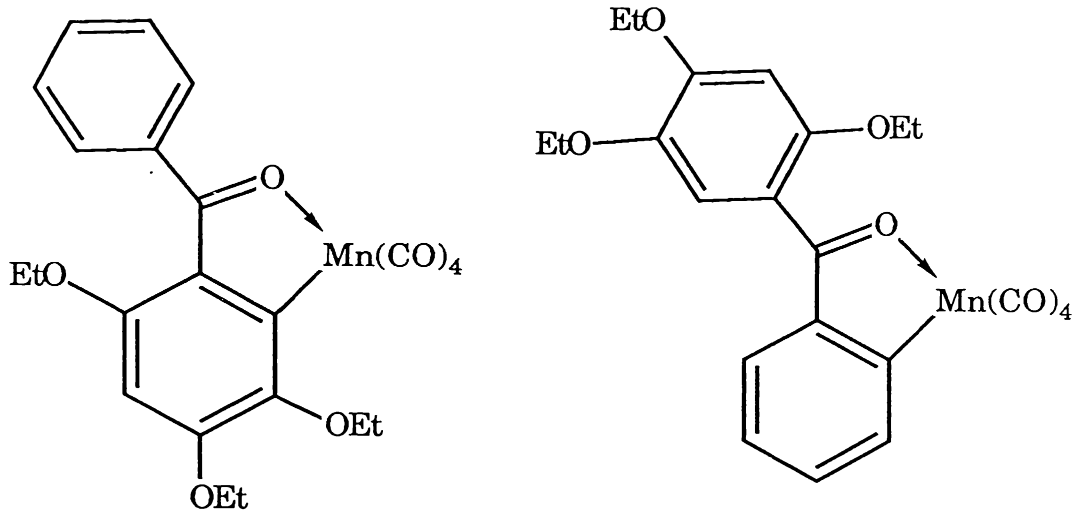
The notion that in the orthomanganation reaction the metal centre might be nucleophilic or electrophilic led to more directed experiments. Substrates in which the ring *ortho*-positions are specifically activated to electrophilic attack (for example, acetophenones with electron donating groups on the ring such as 3-

methoxyacetophenone [9] and 3,4,5-trimethoxyacetophenone [33]) have already been shown to undergo orthomanganation in good yield.

So far untried are ketone substrates in which the position *ortho* to the acyl group is specifically deactivated to electrophilic substitution by a second substituent. In addition, substrates of this type to be tested must have sufficient "donor power" to undergo metalation, otherwise the metalation might not proceed for the wrong reason.

3'-Trifluoromethylacetophenone, a substrate in which the strongly electron-withdrawing -CF_3 group deactivates both positions *ortho* to $COCH_3$ to electrophilic substitution, was treated with $PhCH_2Mn(CO)_5$, and gave the orthomanganated product **28** in 89% yield. Similarly, 4'-trifluoromethylacetophenone gave **29** in 71% yield, though here the -CF_3 group will deactivate the positions *ortho* to $COCH_3$ only relatively weakly. Since the yields here are comparable to each other and to yields obtained when there are electron donating substituents on the ring, the two results tell us little more about the nucleophilic or electrophilic character of the metal centre.

Previous experiments that have been designed to circumvent this uncertainty have been competitive in nature. The reaction of 2,4,5-triethoxybenzophenone [16] with $PhCH_2Mn(CO)_5$ for example (Figure 3.17), yielded the unsubstituted "B" ring isomer as the principle metalation product, despite an expectation that the electron-rich ethoxy substituents might favour "A" ring metalation.



Ratio 1 : 2

Figure 3.17

Steric congestion, a result of the close proximity of two ethoxy groups, was thought to be the reason for the preference. Steric effects must also play a part in the trifluoromethyl acetophenone reactions, as none of the 2-isomer (Fig. 3.18) is detected.

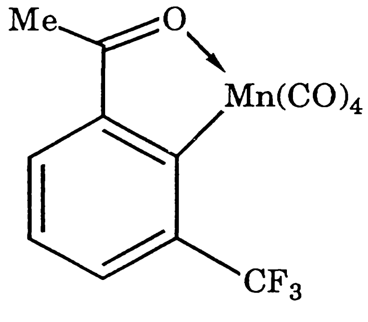


Figure 3.18

A second competition study is that of Bruce *et al* [17], mentioned earlier. Reactions of variously substituted azobenzenes with $MeMn(CO)_5$ resulted in preferential orthomanganation (from 4:1 to 2:1) of the ring carrying the electron-withdrawing (fluoro-) substituents, while azobenzenes with electron-donating substituents displayed a preference for unsubstituted ring metalation (in the case of 3-methylazobenzene, 100% preference!).

In our study, treatment of 3-trifluoromethylbenzophenone with $PhCH_2Mn(CO)_5$ resulted in metalation of both the trifluoromethyl-substituted (A) ring **30** and the unsubstituted (B) ring **31**. The latter product was favoured by a ratio of 2:1. Metalation of 4-trifluoromethylbenzophenone afforded an identical result: the unsubstituted ring metalation isomer **33** was produced in twice the quantity of the CF_3-substituted ring metalation isomer **32**. In each case, the isomer resulting from metal attack at the electron-rich ring is slightly favoured over the electron-poor ring, apparently irrespective of the directive effects of the substituent.

Kinetically speaking, this difference amounts to very little. Electrophilic nitration of a CF_3-substituted ring, by comparison, results in a 100% meta- preference [25].

Conclusions about nucleophilic or electrophilic character, therefore, can only be tentatively made. The benzophenone results indicate, if anything, a metalation preference for the electron-rich ring, but this is offset by the ease of preparation of the trifluoromethylacetophenone metalation products. The ketone reactions are best considered to be quite different from the azobenzene reactions of Bruce *et al*, not only because the conclusions differ, but because the nitrogen donor atom's effect on nucleophilicity or electrophilicity of the metal would seem to be different from that of an oxygen atom.

Further consideration of electronic and mechanistic detail will be given in the discussion at the end of this chapter.

3.5 Acidic Protons

3.5.1 Results and Discussion

It has previously been mooted [9] that the presence of a protic function in the substrate precludes orthomanganation (for example, benzoic acid (υ(C=O) 1695 cm^{-1}) does not undergo orthomanganation), the reasons for which are unknown. As described in Chapter 2, the parent benzamide, $H_2NCOC_6H_5$, did not give rise to any cyclometalated product on treatment with $PhCH_2Mn(CO)_5$, unlike the *N,N*-dialkylated benzamides, so the concept of the "acidic proton" has to include those as weakly acidic as amide protons.

Other related compounds in this study follow a similar trend to the parent benzamide. 5,6,7-Trimethoxyisocarbostyril (**34**) did not undergo any reaction, while the *N*-methylated analogue (**35**) afforded the orthomanganated product **36**. Further confirmation of interference was evident in the reaction of 2-acetylpyrrole (whose ring carbons have been shown [Chapter 2] to be reactive towards a metalating agent); this did not produce any identifiable metalated product on treatment with $PhCH_2Mn(CO)_5$. *N*-Methylation of 2-acetylpyrrole followed by treatment with $PhCH_2Mn(CO)_5$ has previously yielded 1-methyl-2-acetylpyrrol-3-yltetracarbonylmanganese [9].

Our results then, add some weight to Gommans' point [9], that protic functions may cause some kind of degradation of $PhCH_2Mn(CO)_5$ such that $Mn_2(CO)_{10}$ is formed, or that such functions otherwise prohibit formation of the expected product.

3.6 α,β-Unsaturated Carbonyl Substrates

3.6.1 Results and Discussion

Although the three substrates that will be discussed fit into other categories (one aldehyde, one amide, one ketone), they are included together here because of their common α,β-unsaturated C=O functions.

Two of the substrates, cinnamaldehyde and *N,N*-dimethylacrylamide (Figure 3.19), were subjected to orthomanganation conditions and afforded no reaction.

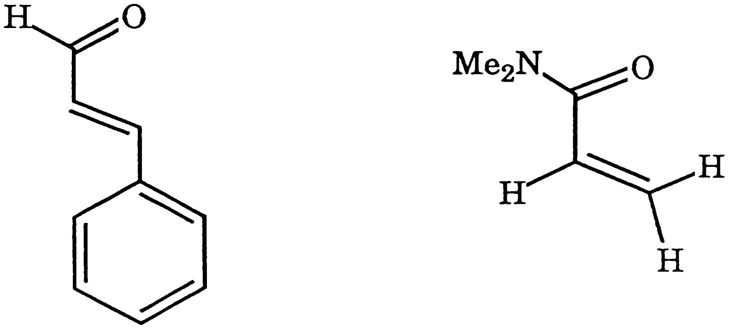


Figure 3.19

A third, trans-4-phenylbut-3-en-2-one, gave rise to an orthomanganated product **37** in 35% yield. This compound has been previously reported by Booth and Hargreaves [35] and more recently by DeShong [36]. Both groups reached the final product by an insertion/addition reaction of phenylacetylene with $MeMn(CO)_5$. A comparison of the approximate costs of each starting material (phenylacetylene versus the phenylbutenone, Aldrich 1989) reveals that it is about fifteen times cheaper to use the butenone as a precursor to **37** than phenylacetylene.

Reports of other non-aromatic cyclomanganese compounds are relatively scarce. Cabral [2] reported an attempt to metalate chalcone, where the β-olefinic site competes with the aromatic sites for manganese. The system proved very reactive, so much so that only one product, which rapidly decomposed to $Mn_2(CO)_{10}$, was recovered after chromatography. Had the conditions been optimised, isolation of an orthomanganated chalcone might well have been achieved, as Booth *et al* [35] have shown it is possible from the addition of phenylacetylene to $PhMn(CO)_5$.

Cabral [2] also reported that 1-acetylcyclohexene reacts with $PhCH_2Mn(CO)_5$ to produce the compound in Figure 3.20 in 61% yield: this is the only α,β-unsaturated orthomanganated product yet obtained by the standard orthomanganation procedure.

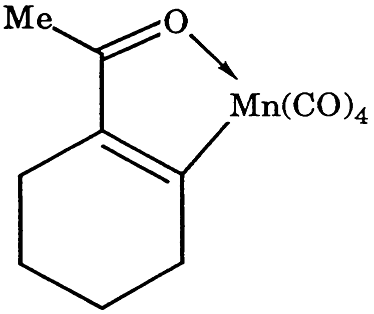


Figure 3.20

The isolation of **37**, in sum, shows that non-aromatic, α,β-unsaturated compounds with a non-cyclic double bond will undergo orthomanganation under normal conditions. In turn, this may allow for greater scope in the synthetic applications of orthomanganated compounds.

3.7 Mechanistic Aspects

3.7.1 Introduction

To conclude the discussion section of this chapter, it is worthwhile to consider how the orthomanganation results in this study fit in with established reactivity patterns for the various types of substrates used (e.g. aldehydes, indoles etc.), and with proposed mechanisms for the orthomanganation reaction.

Below are the principal mechanisms proposed for cyclometalation by an alkyl pentacarbonylmanganese reagent, as reviewed by Gommans [9].

(i) Oxidative addition/reductive elimination (Fig. 3.21): ring carbon and ring hydrogen act as oxidants to give an 18 electron Mn(III) intermediate (†). This was favoured by Jarvinen [10].

(ii) Electrophilic mechanism (Fig. 3.22): no formal oxidative addition, no Mn(III) intermediate, metal attack hinges on electrophilic nature of manganese centre. This was favoured by Hoxmeier [11,12].

(iii) Concerted mechanism (Fig. 3.23): no Mn(III) intermediate, metal attack simultaneous with R-H elimination, no Mn-H bond. This was favoured by Bennett *et al* [4] and Cabral [2].

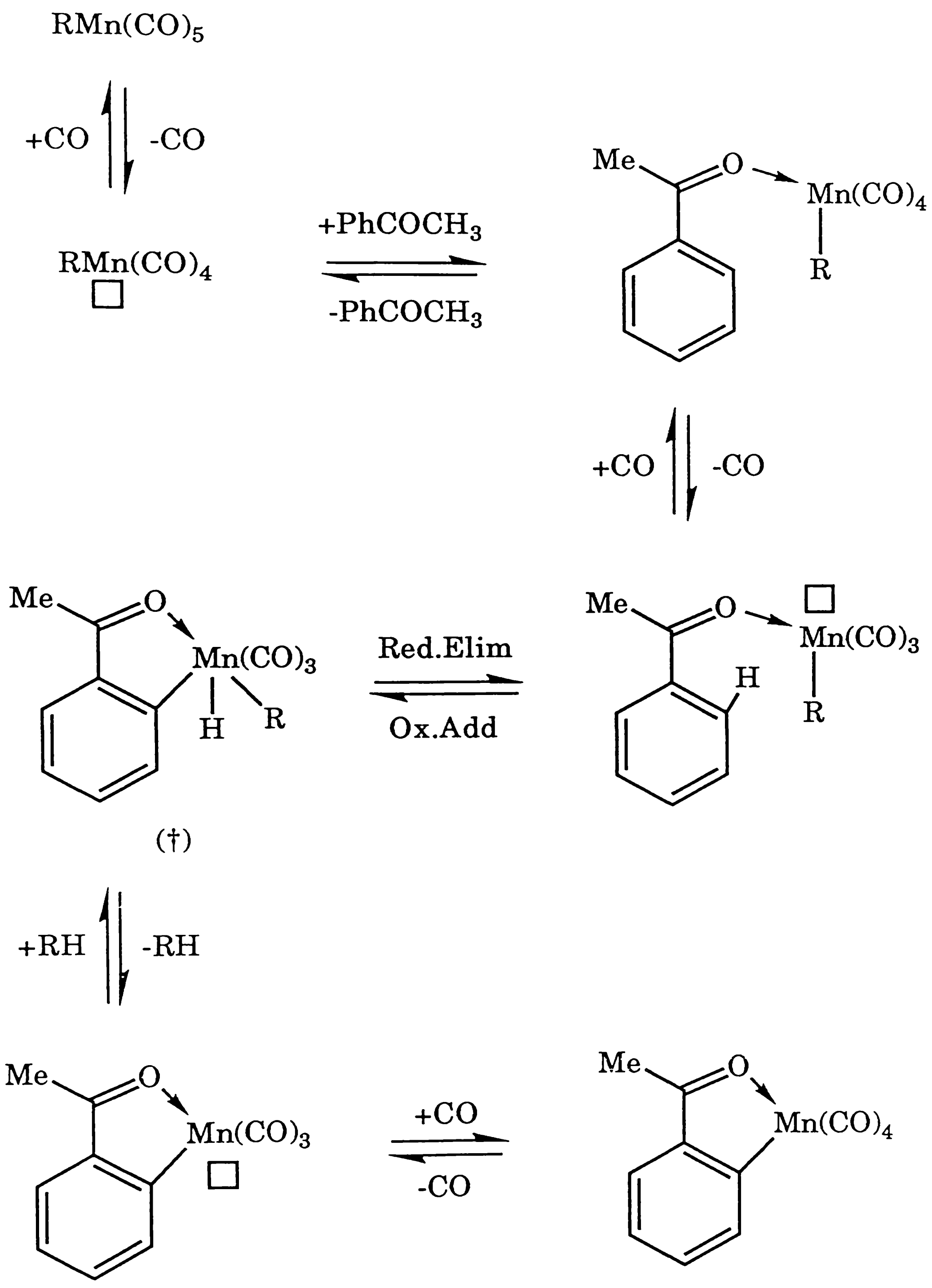

RMn(CO)5
+CO
-CO
RMn(CO)4
+PhCOCH3
-PhCOCH3
Me
O
Mn(CO)4
R
+CO
-CO
Me
O
Mn(CO)3
H
R
(†)
Red.Elim
Ox.Add
Me
O
Mn(CO)3
H
R
+RH
-RH
Me
O
Mn(CO)3
+CO
-CO
Me
O
Mn(CO)4

Figure 3.21

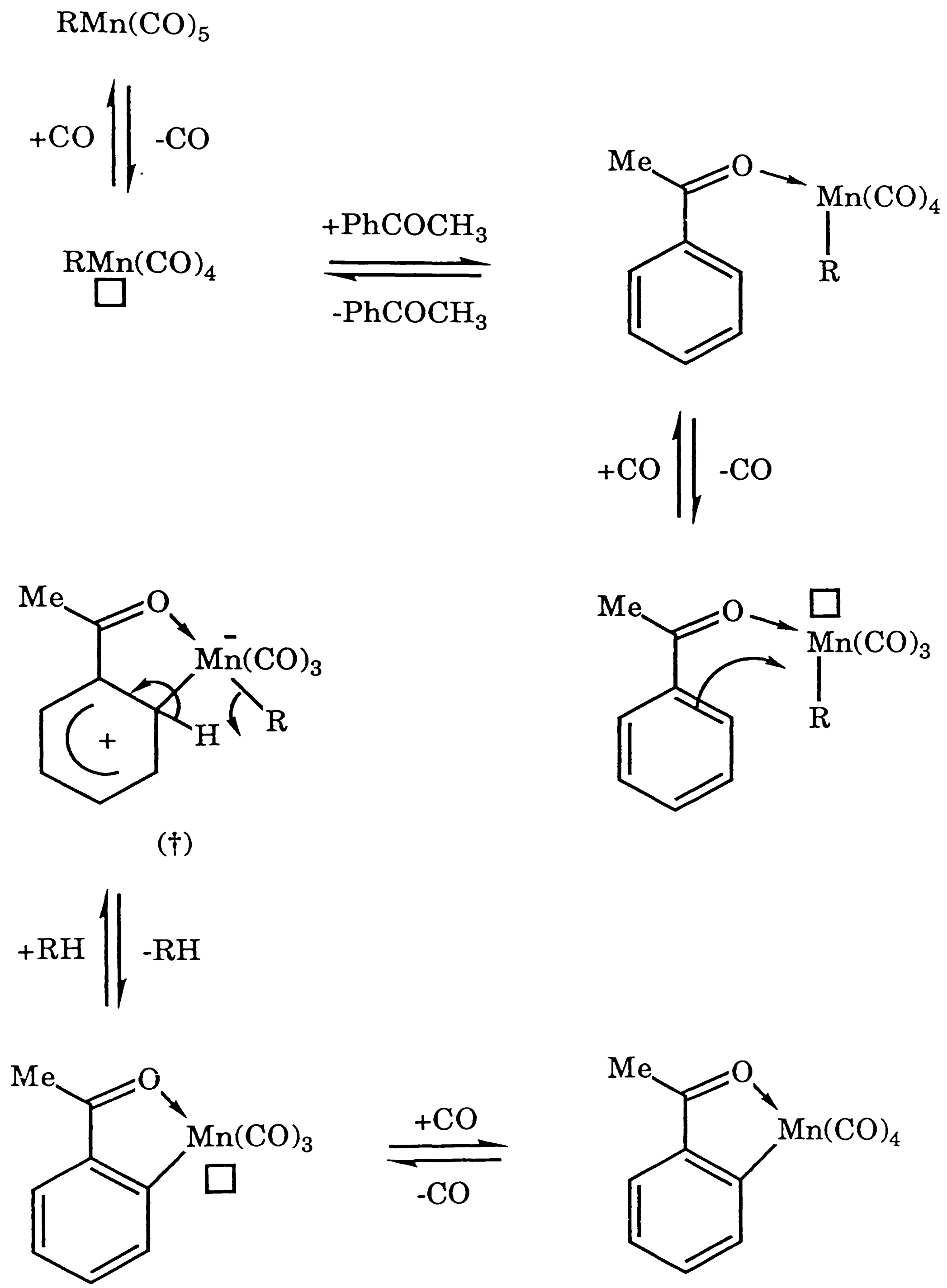

RMn(CO)5
+CO
-CO
RMn(CO)4
+PhCOCH3
-PhCOCH3
Me
O
Mn(CO)4
R
+CO
-CO
Me
O
Mn(CO)3
R
Me
O
Mn(CO)3
H
R
+
(†)
+RH
-RH
Me
O
Mn(CO)3
+CO
-CO
Me
O
Mn(CO)4

Figure 3.22

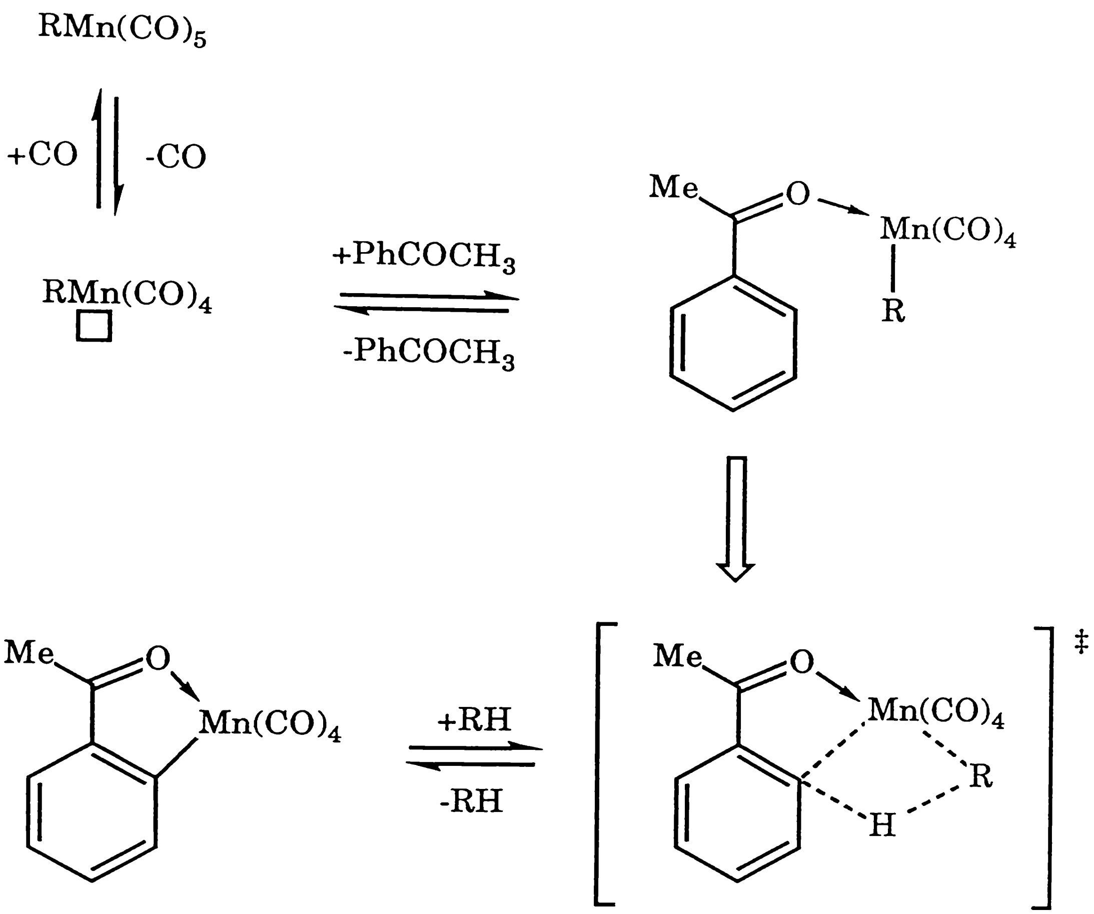


Figure 3.23

Reactivity Patterns of Substrates

The established reactivity patterns of each type of substrate will be discussed separately, then reference made back to the metalation mechanisms to determine if a definite conclusion for each type can be made.

Nitrogen Heterocycles:

Normal reactivity patterns of pyrrole and indole are governed by the π-electron-rich nature of their respective ring systems. Both systems are therefore extremely susceptible to electrophilic attack.

Indole is most reactive towards electrophilic substitution at the 3-position, an observation in accord with total π-electron density measurements and orbital electron calculations [13]. Even when already 3-substituted, electrophilic attack initially produces 3,3-disubstitution, the product of which may rearrange to 2,3-disubstituted indole or further react to produce 2,3,3-trisubstituted indolines.

Electrophilic attack in pyrrole is dominated by 2-substitution, an effect explained by better charge delocalization in the intermediate Figure 3.24(a), compared with the 3-substitution intermediate (b). Under some controlled conditions, however, 3-substitution will occur [13].

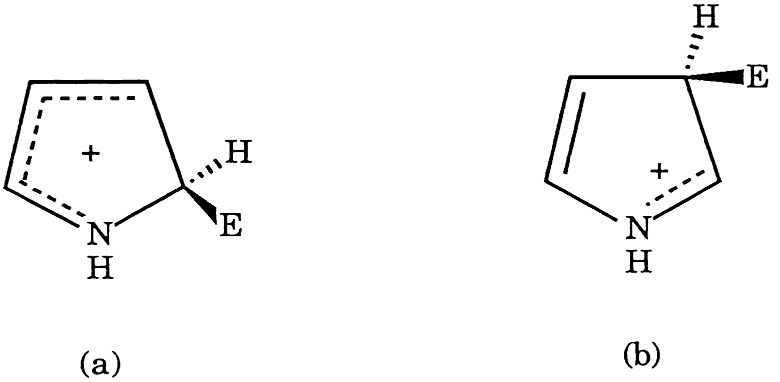


Figure 3.24

Both pyrrole and indole, as a result of their π-electron-rich ring systems, are relatively inert to nucleophilic addition or substitution. Such reactions are rare and promoted only by the presence of electron-withdrawing substituents.

The ring carbons of imidazole are susceptible to electrophilic attack, particularly C5. Far less likely than electrophilic substitution for imidazole is nucleophilic substitution, unless there is a strongly electron-withdrawing group in the ring [14].

Chapter 2 referred to competitive reactions of *N*-benzoylpyrrole and *N*-benzoylindole. For *N*-benzoylpyrrole, it was noted that two orthomanganated products are possible, and that only the pyrrole ring-metalated product was observed, indicating that the pyrrole ring is more "reactive" than the phenyl ring. Similarly, C2 of the indole ring was metalated when *N*-benzoylindole was treated with $PhCH_2Mn(CO)_5$, though two other possibilities, metalation at the phenyl ring and metalation at C7 of the indole ring (to form a six-membered ring), are available.

Thus, the complete preference for the electron-rich ring in both the indole and pyrrole systems is in agreement with an electrophilic attack by manganese.

When *N*-acetylimidazole was treated with $PhCH_2Mn(CO)_5$, no cyclometalated product was isolated, though by comparison with the acetylpyrroles, the carbons of an imidazole heterocycle should be less susceptible to electrophilic attack. The non-reactivity may also be explained, however, in terms of lack of "donor power" (υ(CO) 1762 cm^{-1}, cf. earlier discussion in this chapter).

Benzamides:

Data describing the relative rates of electrophilic substitution at the *ortho*-position of benzamide compared with *N,N*-dialkylbenzamides were not readily available.

The unreactive (anomalous) behaviour of the parent benzamide $H_2NCOC_6H_5$ towards $PhCH_2Mn(CO)_5$ has been described [39].

The observed difference between unsubstituted and *N*-substituted benzamides is unlikely to be due to any difference in activation of the *ortho* site of the substrate, though data indicating the enhanced electron-donating ability of a Me_2NCO group over a H_2NCO group does exist [15].

However, if lack of activation to electrophilic attack, say, is the problem for the parent benzamide, it should be adequately overcome by multiple methoxy-substitution, in such compounds as 5,6,7-trimethoxyisocarbostyril (**34**). As noted earlier, **34** does not afford an orthomanganated product, while metalation of its *N*-methylated analogue results in a good yield of **36**.

Mechanistic conclusions then, can only be muted for the benzamides. No directive effects were studied, as no aryl substituted benzamides were used. Also, no competitive cases were tried, so no preferential metalations were observed.

Aldehydes:

Electrophilic substitution of the parent benzaldehyde is governed by the electron-withdrawing nature of the aldehydic group (-CHO): the 3- and 5-positions are therefore least deactivated by its presence. Electron-withdrawing substituents in the *para-* position will further activate the 3- and 5-positions.

Nucleophilic substitution is most favoured at the 2- and 6-positions, and, conversely to above, electron-donating substituents will cause deactivation of those positions.

Also relevant to this study are 3,4,5-trisubstituted aldehydes: electrophilic attack at the 2- and 6-positions is activated by 3- and 5-position electron donors, while nucleophilic attack is activated only by the aldehyde group.

Table 3.1 described the yields for four benzaldehydes. Immediately evident is the success of electron-donor-substituted aldehydes over benzaldehyde, suggesting a tendency for electrophilic substitution. However, in the two best cases, 4-methoxy- and 4-dimethylamino-benzaldehyde, the 4-substituent does not specifically activate the 2- and 6-positions.

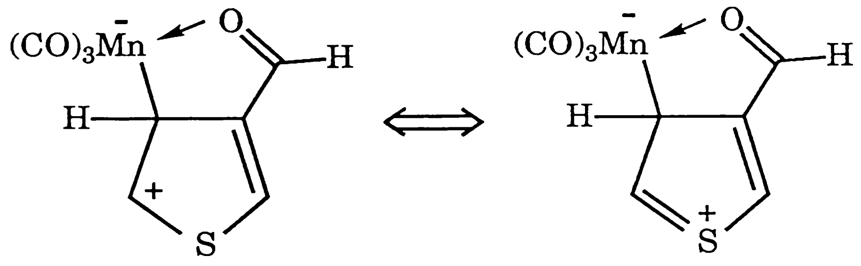
The orientation of electrophilic substitution in thiophenes [34(a)] is directed towards the 2- and 5-position carbons in the ring. For substituents with -I and -R effects (such as an aldehydic or ketonic group) in the 2-position, two competing effects (activation by sulphur of the 5-position, and minimal deactivation by the substituent of the 4-position) result in no dominant preference for all electrophiles (for example, halogenation of thiophene-2-carboxaldehyde leads mainly to the 5-halo isomer; nitration gives the 4- and 5-nitro isomers in a different ratio [34]). When a -I,-R substituent is in the 3-position, the two effects combine to activate only the 5-position.

Reactions with nucleophiles are known [34(b)], but, with strongly basic nucleophiles, often result in 2- or 5- deprotonation or ring opening. Overall, the electron rich nature of the ring makes it more susceptible to electrophilic substitution, with a reactivity comparable to anisole and considerably less than pyrrole.

In this study (again Table 3.1), the electron-rich thiophene ring appears more reactive towards $PhCH_2Mn(CO)_5$ than does benzaldehyde, suggesting electrophilic substitution in the former, but the directing effect of the aldehyde substituent (discussed in the paragraph above) is towards carbons other than those at which metalation occurs.

For 3-thiophenecarboxaldehyde, there is the possibility of 2-metalation or 4-metalation, but only the former is observed. On the basis of an electrophilic mechanism, a rationale for the 2-metalation preference is greater stabilisation of the intermediate for 2- as opposed to 4-substitution, as indicated below:

4-metalation



2-metalation

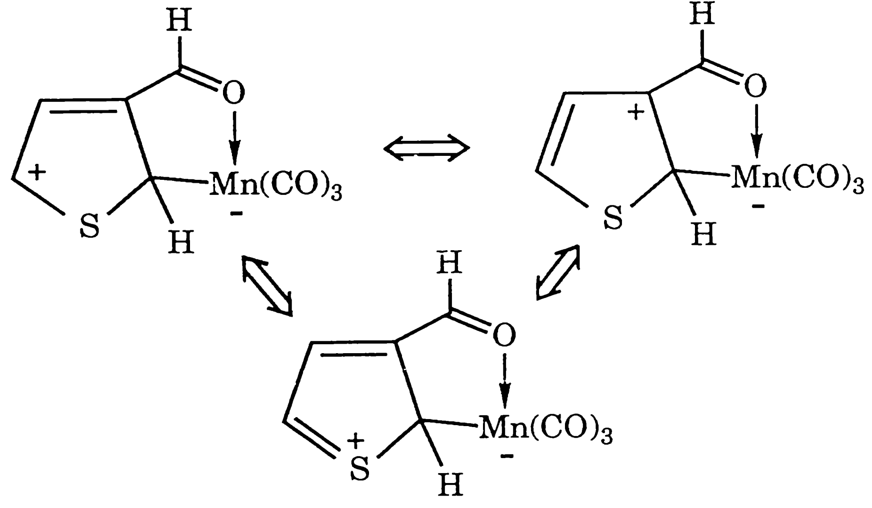


Figure 3.25

3.8 Summary

Our own studies have obviously not been kinetic. They were originally undertaken to define some reactivity boundaries of the orthomanganation reaction, and the results raised questions about mechanistic aspects of the reaction. The mechanistic conclusions that have been reached generally only pertained to whether a reaction proceeded or not, though yields have on occasion been used as a guide.

Considering the range of compounds studied, there are few carbonyl O-donors that have not been given some consideration (with the exception of aroyl halides, for reasons of possible side reactions with the C-X bond). In the future, researchers in this field may at least glean from this chapter an idea of the limitations or complications involved for each group, and their own work may benefit as a result.

3.9 Experimental

The following commercial materials were used as received: *p*-methoxybenzaldehyde (BDH, 98%), *p*-dimethylaminobenzaldehyde (BDH, 99%), 3,4,5-trimethoxybenzaldehyde (Aldrich, 98%), cinnamaldehyde (May and Baker 98%), 2-thiophenecarboxaldehyde (Sigma), 3-thiophenecarboxaldehyde (Sigma, ca. 95%), 5,6,7-trimethoxyisocarbostyril (Alfred Bader Chemicals), 2-acetylpyrrole (Aldrich, 99%), acetanilide, phenylacetyl chloride (BDH, 98%), 3'-trifluoromethylacetophenone (Aldrich, 99%), 4'-trifluoromethylacetophenone (Aldrich, 95%), 3-trifluoromethylbenzophenone (Aldrich, 99%), 4-trifluoromethylbenzophenone (Aldrich, 97%), imidazole (BDH, 99%), 1,3-diacetylbenzene (Aldrich, 99%), 1,4-diacetylbenzene (Aldrich, 98%) and 1,3,5-triacetylbenzene (Aldrich, 98%).

Benzaldehyde was purified by an established procedure [21].

Recrystallisation of trans-4-phenyl-but-3-en-2-one from CH_2Cl_2/Pet. spirit (1/3) gave colourless square plates, m.p. 38-39°C (lit. 39-41°C [37]).

Preparations of the heterocyclic amides and benzamides are described in the experimental section of Chapter 2.

N,N-Dimethylacrylamide, *N*-methyl-5,6,7-trimethoxyisocarbostyril and exalgin were prepared by the method of Johnstone and Rose [20] from acrylamide, 5,6,7-trimethoxyisocarbostyril and acetanilide respectively.

N,N-Dimethylacrylamide, colourless oil, ^{1}H NMR: δ 6.81 (dd, J_{AB} = 16.5 Hz, J_{AC} = 9.7 Hz, 1H, H_A), 6.25 (dd, J_{BC} = 3.0 Hz, J_{BA} = 16.5 Hz, 1H, H_B), 5.72 (dd, J_{BC} = 3.0 Hz, J_{AC} = 9.7 Hz, 1H, H_C), 3.13 (s, 3H, CH_3), 3.00 (s, 3H, CH_3).

N-Methyl-5,6,7-trimethoxyisocarbostyril, yellow solid, m.p. 116-118°C. ^{1}H NMR: δ 7.68 (s, 1H, H8), 7.21 (d, J = 7.5 Hz, 1H, H3), 6.69 (d, J = 7.5 Hz, 1H, H4), 4.00 (s, 9H, 5,6,7-OCH_3), 3.58 (s, 3H, N-CH_3). ^{13}C NMR: δ 161.5 (C=O), 152.9, 147.2, 145.3 (C5,6,7), 130.4, 126.7, 122.0 (C4a,8,8a), 103.7, 100.1 (C3,4), 61.2, 60.7 (5,6-OCH_3), 55.9 (7-OCH_3), 36.8 (N-CH_3).

Exalgin (*N*-methylacetanilide), recrystallised from hot pet. spirit to give colourless needles, m.p. 96.5-97°C (lit. 102-104°C [38]). ^{13}C NMR: δ 170.3 (C=O), 144.5 (C1), 129.6, 127.5, 126.9 (C2-6), 36.9 (N-CH_3), 22.2 (CO$\underline{C}H_3$).

N-(Phenylacetyl)pyrrolidine was prepared by the dropwise addition of pyrrolidine (0.63 ml, 7.56 mmol) to phenylacetyl chloride (1.00 ml, 7.56 mmol) at room temperature over a 5 minute period. The crude mixture was extracted with CH_2Cl_2 (3 x 30 ml), dried ($MgSO_4$) and vacuum distilled (130°C, 0.10 mm Hg) to afford a clear liquid. ^{13}C NMR: δ 172.5 (C=O), 134.1 (C1), 128.1, 127.6 (C2,3,5,6), 125.8 (C4), 46.1, 45.2 (pyrrolidinyl 2- and 5-CH_2), 41.2 ($\underline{C}H_2CO$), 25.2, 23.4 (pyrrolidinyl 3- and 4-CH_2).

N-Acetylimidazole was prepared by the method described for *N*-acetylindole (Chap. 2 Experimental) from imidazole (0.501 g, 7.36 mmol), Bu^{n}Li (4.60 ml, 7.36 mmol) and acetic anhydride (0.69 ml, 7.36 mmol) to afford a yellow solid (0.711 g, 88 %). ^{1}H NMR: δ 8.35 (br s, 1H, H2), 7.63 (br s, 1H, H5), 7.23 (br d, 1H, H4), 2.66 (s, 3H, CH_3) [identical to spectrum in "The Aldrich Library of NMR Spectra", Charles J. Pouchert and John R. Campbell, vol.8, Aldrich Chem. Co. Inc., 1974].

General procedures for orthomanganation reactions are described in Chapter 2 Experimental section. In a typical experiment, $PhCH_2Mn(CO)_5$ (100 mg, 0.350 mmol) was added to heptane (30 ml) that had been degassed under vacuum and flushed with nitrogen several times. The substrate (0.350 mmol) was added, degassing repeated, and the solution was refluxed under nitrogen for 2-5 hours. After cooling, the heptane was removed under vacuum and the residue was chromatographed with CH_2Cl_2/petroleum spirit.

Preparation of η^2-(2-formyl-4-methoxyphenyl)tetracarbonylmanganese (**20**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.127 g, 0.444 mmol) and 4-$MeOC_6H_4CHO$ (0.062 g, 0.455 mmol) with 4.5 hr reflux was **20**, as an oil. MS (P^+) 302. IR: 2083(m), 1996(vs), 1944(s), 1581(m), 1574(m) cm^{-1}. ^1H NMR: δ 9.26 (s, 1H, CHO), 7.85 (d, J = 8.8 Hz, 1H, H(3)), 7.60 (s, 1H, H(6)), 6.72 (d, J = 8.8 Hz, 1H, H(4)), 3.97 (s, 3H, OCH_3). ^{13}C NMR: δ 212.9, 211.3 (CO), 204.0 (C=O), 200.3 (C1), 164.5 (C5), 140.5 (C2), 135.3 (C3), 124.7 (C4), 112.2 (C6), 55.6 (OCH_3).

Preparation of η^2-(2-formyl-4-dimethylaminophenyl)-tetracarbonylmanganese (**21**): above procedure from $PhCH_2Mn(CO)_5$ (0.144 g, 0.503 mmol) and 4-$Me_2NC_6H_4CHO$ (0.083 g, 0.556 mmol) with 5 hr reflux gave **21** (0.122 g, 77%), m.p. 124-128°C. Found: C, 49.92; H, 3.35: N, 4.40 %; $C_{13}H_{10}NO_5Mn$ calcd: C, 49.54; H, 3.20; N, 4.44 %; M 315. MS(P^+) 315. IR: 2079(m), 1991(vs), 1935(s), 1588(m), 1562(m) cm^{-1}. ^1H NMR: δ 8.99 (s, 1H, CHO), 7.70 (d, J = 8.7 Hz, 1H, H(3)), 7.29 (s, 1H, H(6)), 6.46 (dd, J = 8.7, 2.1 Hz, 1H, H(4)), 3.20 (s, 6H, N-CH_3). ^{13}C NMR:

δ 214.1, 213.0, 212.4 (CO), 199.8 (C=O), 196.9 (C1), 153.5 (C5), 135.8 (C2), 134.8 (C3), 121.5 (C4), 108.6 (C6), 40.1 (N-CH_3).

Preparation of η^2-(2-formylthien-3-yl)tetracarbonylmanganese (**22**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.097 g, 0.339 mmol) and 2-thiophenecarboxaldehyde (35 μl, 0.375 mmol) with 3 hrs reflux was **22** (0.010 g, 11 %) as a yellow oil. MS(P^+) 278. IR: 2091(s), 2004(vs), 1955(vs), 1531(m) cm^{-1}. ^1H NMR: δ 9.25 (s, 1H, CHO), 8.16 (d, J = 4.4 Hz, 1H, H4), 7.70 (d, J = 4.4 Hz, 1H, H5). ^{13}C NMR: δ 214.1, 209.9, 206.4 (CO), 193.8 (C=O), 186.5 (C3), 142.5 (C4), 138.8 (C5).

Preparation of η^2-(3-formylthien-2-yl)tetracarbonylmanganese (**23**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.108 g, 0.378 mmol) and thiophene-3-carboxaldehyde (50 μl, 0.571 mmol) with 3 hrs reflux was **23** (0.021 g, 20 %) as a yellow oil. MS(P^+) 278. IR: 2098(m), 2012(s), 1961(s), 1547(m) cm^{-1}. ^1H NMR: δ 9.20 (s, 1H, CHO), 7.60 (d, J = 5.0 Hz, 1H, H4), 7.42 (d, J = 5.0 Hz, 1H, H5). ^{13}C NMR: δ 219.9, 218.2, 213.0 (CO), 209.0 (C2), 195.3 (C=O), 151.2 (C3), 133.5 (C5), 126.3 (C4).

Preparation of η^2-[8-(*N*-methyl-5,6,7-trimethoxyisoquinol-1-onyl)]tetracarbonylmanganese (**36**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.107 g, 0.374 mmol) and *N*-methyl-5,6,7-trimethoxyisocarbostyril (0.101 g, 0.406 mmol) with reflux over 5 hrs was **36** (0.135 g, 87 %) as a light yellow solid. IR: 2079(m), 1990(vs), 1947(s), 1573(w), 1549(w) cm^{-1}. ^1H NMR: δ 6.85 (br s, 1H, H3), 5.28 (br s, 1H, H4), 4.09, 3.96, 3.91 (s, 3H each, 5,6,7-OCH_3), 3.56 (s, 3H, N-CH_3). ^{13}C NMR: δ 220.4, 212.3 (CO), 171.5 (C=O), 162.7, 161.3 (C7,8), 151.2 (C6), 144.8 (C5), 130.1, 129.7 (C4a,8a), 129.4, 104.3 (C3,4), 61.5, 60.7, 60.3 (5,6,7-OCH_3), 36.1 (N-CH_3).

Preparation of η^2-(2-formyl-4,5,6-trimethoxyphenyl)-tetracarbonylmanganese (**38**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.104 g, 0.364 mmol) and 3,4,5-trimethoxybenzaldehyde (0.083 g, 0.423 mmol) with 1.5 hrs reflux was **38** (0.008 g, 6 %) as a yellow oil. ^1H NMR: δ 9.30 (s, 1H, CHO), 7.34 (s, 1H, H3), 4.08 (s, 3H, 4-OCH_3), 3.88 (s, 6H , 5,6-OCH_3).

Preparation of η^2-(1-phenylbut-1-en-3-onyl)tetracarbonyl-manganese (**37**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.089 g, 0.311 mmol) and trans-4-phenyl-but-3-en-2-one (0.050 g, 0.342 mmol) with 5 hrs reflux was **37** (0.034 g, 35 %) as a yellow oil. IR: 2083(m), 1996(vs), 1953(s) cm^{-1}. ^1H NMR: δ 7.38 (s, 5H, H2'-6'), 6.98 (s, 1H, H3), 2.34 (s, 3H, CH_3). ^{13}C NMR: δ 251.3 (C1), 219.3, 210.6 (CO), 214.3 (C=O), 149.5 (C1'), 135.3 (C2), 128.7, 128.4, 125.2 (C2'-6'), 26.4 (CH_3) [identical to spectrum in ref. [36]].

Preparation of η^2-(2-acetyl-4-trifluoromethylphenyl)-tetracarbonylmanganese (**28**): Similarly prepared from $PhCH_2Mn(CO)_5$ (0.107 g, 0.374 mmol) and 3'-trifluoromethylacetophenone (60 µl, 0.394 mmol) with 3 hrs reflux was **28** (0.118 g, 89 %), m.p. 115-125°C (subl.). Found: C, 44.21, H, 1.76, %; $C_{13}H_6F_3MnO_5$ calcd: C, 44.09, H, 1.71 %, M 354. MS(P^+) 354. IR: 2088(s), 2001(vs), 1954(vs), 1602(m), 1590(w) cm^{-1}. ^1H NMR: δ 8.28 (d, J = 8.0 Hz, 1H, H6), 8.06 (s, 1H, H3), 7.62 (d, J = 8.0 Hz, 1H, H5), 2.71 (s, 3H, CH_3). ^{13}C NMR: δ 220.9, 212.7, 210.6 (CO), 216.7 (C=O), 202.2 (C1), 145.4 (C2), 142.0 (C6), 128.8 (C5), 127.2 (q, J = 4 Hz, C3), 127.2 (q, J = 32 Hz, C4), 124.5 (q, J = 273 Hz, CF_3), 24.7 (CH_3).

Preparation of η^2-(2-acetyl-5-trifluoromethylphenyl)-tetracarbonylmanganese (**29**): Similarly prepared from

$PhCH_2Mn(CO)_5$ (0.097 g, 0.339 mmol) and 4'-trifluoromethylacetophenone (0.072 g, 0.383 mmol) with 4 hrs reflux was **29** (0.085 g, 71 %) m.p. 98-100°C. Found: C, 44.02, H, 1.57, %; $C_{13}H_6F_3MnO_5$ calcd: C, 44.09, H, 1.71 %, M 354. MS(P^+) 354. IR: 2089(s), 2002(vs), 1955(vs), 1592(w) cm^{-1}. ^1H NMR: δ 8.30 (s, 1H, H6), 7.91 (d, J = 8.0 Hz, 1H,), 7.37 (d, J = 8.0 Hz, 1H,), 2.64 (s, 3H, CH_3). ^{13}C NMR: δ 220.7, 212.6, 210.6 (CO), 217.1 (C=O), 195.0 (C1), 147.8 (C2), 137.3 (q, J = 4 Hz, C6), 134.2 (q, J = 32 Hz, C5), 131.0 (C3), 124.2 (q, J = 273 Hz, CF_3), 120.9 (q, J = 4 Hz, C4), 24.8 (CH_3).

Orthomanganation of 3-Trifluoromethylbenzophenone: Similarly prepared from $PhCH_2Mn(CO)_5$ (0.099 g, 0.346 mmol) and 3-trifluoromethylbenzophenone (0.099 g, 0.356 mmol) with 5.3 hrs reflux and chromatography were η^2-(2-benzoyl-4-trifluoromethyl-phenyl)tetracarbonylmanganese (**30**) (0.039 g, 19%): IR: 2086(m), 2001(s), 1953(s), 1599(w), 1559(w) cm^{-1}. ^1H NMR: δ 8.35 (d, J = 8.0 Hz, 1H, H6), 8.11 (s, 1H, H3), 7.67, 7.61 (m, 6H, H5, H2'-6'). ^{13}C NMR: δ 221.2, 212.8, 211.0 (CO), 212.1 (C=O), 204.5 (C1), 144.3 (C2), 142.2 (C6), 136.0 (C1'), 133.1 (C4'), 130.1 (C5), 129.2, 128.9 (C2',3',5',6'), 128.4 (q, J = 4 Hz, C3), 127.2 (q, J = 33 Hz, C4), 124.4 (q, J = 273 Hz, CF_3) and η^2-(2-(3-trifluoromethylbenzoyl)phenyl)tetracarbonylmanganese (**31**) (0.117 g, 57 %): IR: 2084(m), 1998(s), 1950(s), 1577(w), 1560(w) cm^{-1}. ^1H NMR: δ 8.22 (d, J = 7.6 Hz, 1H), 7.72 (m, 5H), 7.42 (d, J = 7.3 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H). ^{13}C NMR: δ 221.2, 212.8, 211.0 (CO), 210.5 (C=O), 198.1 (C1), 144.0 (C2), 142.1 (C6), 137.1 (C1'), 134.6, 133.8, 124.0 (C3,4,5), 132.2, 129.2 (C5',6'), 131.8 (q, J = 33 Hz, C3'), 128.9, 126.1 (q, J = 4 Hz, C2',4'), 123.4 (q, J = 273 Hz, CF_3).

Orthomanganation of 4-Trifluoromethylbenzophenone: Similarly prepared from $PhCH_2Mn(CO)_5$ (0.098 g, 0.343 mmol) and 4-

trifluoromethylbenzophenone (0.087 g, 0.348 mmol) with 7 hrs reflux were η^2-(2-benzoyl-5-trifluoromethylphenyl)tetracarbonylmanganese (**32**) and η^2-(2-(4-trifluoromethylbenzoyl)phenyl)tetracarbonylmanganese (**33**) as an inseparable orange oil (0.104 g, 73 %). IR: 2084(m), 1999(s), 1952(s), 1578(w), 1560(w) cm^{-1}. ^{1}H NMR: δ 8.43 (br s), 8.21 (dd, J = 0.9 Hz, J = 7.0 Hz), 8.07, 8.02, 7.98 (br s), 7.87 (dd, J = 0.9 Hz, J = 7.6 Hz), 7.77 (s), 7.67 (t, J = 2.7 Hz), 7.55 (dd, J = 1.8 Hz, J = 7.0 Hz), 7.39 (dd, J = 7.3 Hz, J = 1.5 Hz), 7.16 (td, J = 1.5 Hz, J = 7.4 Hz). ^{13}C NMR: δ 221.1, 212.8, 210.3 (CO[**32**],[**33**]), 212.4 (C=O[**32**]), 211.0 (C=O[**33**]), 198.7 (C1[**33**]), 198.5 (C1[**32**]), 147.0 (C2[**32**]), 144.3 (C2[**33**]), 142.3 (C6[**33**]), 139.6 (C1'[**33**]), 137.6 (q, J = 4 Hz, C6[**32**]), 136.2 (C1'[**32**]), 134.7, 133.9, 124.1 (C3,4,5[**33**]), 134.1 (C4'[**32**]), 129.6 (C2',6'[**33**]), 129.4, 128.9 (C2',3',5',6'[**32**]), 125.6 (q, J = 4 Hz, C3',5'[**33**]), 123.7 (q, J = 273 Hz, CF_3[**32**],[**33**]), 120.7 (q, J = 4 Hz, C4[**32**]).

A number of orthomanganation reactions did not yield any isolable metalated product; details of the attempts are listed below:

N-Acetylimidazole: standard procedure from $PhCH_2Mn(CO)_5$ (0.125 g, 0.437 mmol) and *N*-acetylimidazole (0.048 g, 0.436 mmol) in reflux heptane (20 ml) over 4 hrs; an infrared spectrum showed only $PhCH_2Mn(CO)_5$; chromatography resulted in only $PhCH_2Mn(CO)_5$.

5,6,7-Trimethoxyisocarbostyril (**34**): similar procedure from $PhCH_2Mn(CO)_5$ (0.095 g, 0.332 mmol) and **34** (0.077 g, 0.328 mmol) with reflux over 4 hrs; tlc ($CHCl_3$) showed only the two starting reagents.

Cinnamaldehyde: similarly from $PhCH_2Mn(CO)_5$ (0.106 g, 0.371 mmol) and cinnamaldehyde (0.06 ml, 0.476 mmol) with reflux over 5 hrs; after tlc, infrared and chromatography experiments, no orthomanganated product was isolated.

Benzaldehyde: similarly from $PhCH_2Mn(CO)_5$ (0.064 g, 0.224 mmol) and benzaldehyde (0.04 ml, 0.394 mmol) with reflux over 4 hrs; infrared showed a mixture of $PhCH_2Mn(CO)_5$ and $Mn_2(CO)_{10}$ (ca. 1/2).

Acetanilide: similarly from $PhCH_2Mn(CO)_5$ (0.071 g, 0.248 mmol) and acetanilide (0.040 g, 0.296 mmol) with reflux over 3.3 hrs; infrared showed only $Mn_2(CO)_{10}$.

N-(Phenylacetyl)pyrrolidine: similarly from $PhCH_2Mn(CO)_5$ (0.097 g, 0.339 mmol) and *N*-(2-phenylacetyl)pyrrolidine (0.064 g, 0.338 mmol) with reflux over 4.6 hrs; infrared showed a mixture of $PhCH_2Mn(CO)_5$ and $Mn_2(CO)_{10}$ (ca. 1/2).

N,N-Dimethylacrylamide: similarly from $PhCH_2Mn(CO)_5$ (0.128 g, 0.447 mmol) and *N,N*-dimethylacrylamide (0.045 g, 0.454 mmol) with reflux over 2.5 hrs; tlc at 1 and 2.5 hrs showed only the starting reagents.

2-Acetylpyrrole: similarly from $PhCH_2Mn(CO)_5$ (0.131 g, 0.458 mmol) and 2-acetylpyrrole (0.050 g, 0.458 mmol) with reflux over 17 hrs; tlc and chromatography afforded only $PhCH_2Mn(CO)_5$.

Multiple Metalations

Orthomanganation of 1,3-diacetylbenzene: standard orthomanganation method from 1,3-diacetylbenzene (0.103 g, 0.635 mmol) and $PhCH_2Mn(CO)_5$ (0.156 g, 0.545 mmol) with reflux over 1.5 hrs and chromatography gave η^2-(2,4-diacetylphenyl)tetracarbonylmanganese (**24**) (0.082 g, 46% based on $PhCH_2Mn(CO)_5$) and η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonylmanganese) (**25**) (0.059 g, 44% of available $PhCH_2Mn(CO)_5$).

η^2-(2,4-diacetylphenyl)tetracarbonylmanganese (**24**): yellow solid, m.p. 140-141°C. Found: C, 51.52, H, 2.74 %; $C_{14}H_9MnO_6$; calcd: C, 51.24, H, 2.76 %, M 328.16. MS(P^+) 328. IR: 2085(m), 2000(s), 1951(s), 1693(w), 1591(w) cm^{-1}. ^1H NMR: δ 8.40 (s, 1H, H3), 8.25 (d, J = 7.6 Hz, 1H, H6), 7.91 (d, J = 7.6 Hz, 1H, H5), 2.72 (s, 3H, CH_3). ^{13}C NMR: δ 220.6, 212.4, 210.5 (CO), 217.2 (C=O-Mn), 205.1 (C1), 197.2 (C=O), 145.6 (C2), 141.6 (C6), 133.8 (C4), 131.9 (C5), 129.9 (C3), 26.4 (CH_3), 24.8 (CH_3).

η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonylmanganese) (**25**): yellow solid, m.p. ca. 175 (subl./dec.). Found: C, 43.94, H, 1.58 %; $C_{18}H_8Mn_2O_{10}$; calcd: C, 43.75, H, 1.63 %, M 494.13. MS(P^+) 494. IR: 2085(m), 2076(w), 1999(s), 1952(m), 1548(w) cm^{-1}. ^1H NMR: δ 9.00 (s, 1H, H3), 8.05 (s, 1H, H6), 2.64 (s, 6H, CH_3). ^{13}C NMR: δ 220.5, 212.8, 211.2 (CO), 215.6 (C=O), 207.6 (C1,5), 155.8 (C6), 141.5 (C2,4), 130.9 (C3), 24.0 (CH_3).

Crystal Structure of **25**: A yellow needle of dimensions 0.24 x 0.82 x 0.15 mm was obtained from CH_2Cl_2/pet. spirit (1:4) at 4°C. Preliminary precession photography indicated no symmetry higher than triclinic. Intensity data were collected on a Nicolet P3 four circle diffractometer with monochromated Mo-Kα radiation.

Crystal data: $C_{18}H_8Mn_2O_{10}$, M = 494.13. Space group: $P\bar{1}$ (triclinic), a = 8.774(2), b = 9.782(2), c = 11.898(3). α = 77.25(2)°, β = 82.56(2)°, γ = 85.59(2)°. U = 986.4 Å^3, D_c 1.66 g cm^{-3} for Z = 2. F(000) = 492, μ = 12.8 cm^{-1}.

A total of 3865 reflections in the range $4° < 2\theta < 52°$ were collected at -100°C; after corrections for Lorentz and polarisation effects, 2861 reflections with $I > 3\sigma(I)$ were used in all calculations. Data were also corrected for absorption by a numerical method based on indexed faces and distances: maximum and minimum transmission coefficients were 0.83 and 0.71 respectively. The heavy atom positions were located by both the PATT (two manganese atoms) and TREF (all 30 non-hydrogen atoms) options of SHELXS-86: the TREF solution was used for further development. In the final cycle of full matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. Each type of hydrogen was assigned a separate isotropic temperature factor. The refinement converged with R = 0.0364, R_w = 0.0394 where $w = [\sigma^2(F) + 0.000695F^2]^{-1}$. No parameter shifted by more than 0.14σ in the final cycle. The final difference map showed no peak or trough of electron density greater than 0.55 $eÅ^{-3}$. Final positional parameters, bond lengths and bond angles are in Appendix II.

Orthomanganation of 1,4-diacetylbenzene: standard procedure from 1,4-diacetylbenzene (0.063 g, 0.388 mmol) and $PhCH_2Mn(CO)_5$ (0.107 g, 0.374 mmol) with 3 hrs reflux and chromatography gave η^2-(2,5-diacetylphenyl)tetracarbonylmanganese (**26**) (0.052 g, 42%) and η^2,η^2-(2,5-diacetylphenyl)bis-1,4-(tetracarbonylmanganese) (**27**) (0.020 g, 22%).

η^2-(2,5-diacetylphenyl)tetracarbonylmanganese (**26**): orange solid, m.p. 97-99°C. Found: C, 51.27, H, 2.76 %; $C_{14}H_9MnO_6$; calcd: C, 51.24, H, 2.95 %, M 494.13. IR: 2084(m), 1998(s), 1949(m), 1697(w), 1589(w) cm^{-1}. ^1H NMR: δ 8.56 (d, J = 1.6 Hz, 1H, H6), 7.93 (d, J = 8.0 Hz, 1H, H3), 7.69 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, H4), 2.67 (s, 6H, CH_3). ^{13}C NMR: δ 220.7, 212.5, 210.8 (CO), 217.1 (C=O-Mn), 199.2 (C=O), 194.2 (C1), 148.1 (C2), 140.3 (C6), 139.5 (C5), 131.5 (C3), 123.6 (C4), 27.2 (CH_3), 25.0 (CH_3).

η^2,η^2-(2,5-diacetylphenyl)bis-1,4-(tetracarbonylmanganese) (**27**): red solid, m.p. ca. 120 (subl./dec.). Found: C, 44.55, H, 1.59 %; $C_{18}H_8Mn_2O_{10}$; calcd: C, 43.75, H, 1.63 %, M 494.13. IR: 2080(m), 1999(s), 1947(m), 1579(w) cm^{-1}. ^1H NMR: δ 8.48 (s, 2H, H3,6), 2.77 (s, 6H, CH_3). ^{13}C NMR: δ 221.5, 213.5, 211.3 (CO), 218.7 (C=O), 182.3 (C1,4), 149.4 (C2,5), 143.7 (C3,6), 25.4 (CH_3).

Stepwise and reverse reactions of 1,3-diacetylbenzene.

Stepwise addition: standard procedure from η^2-(2,4-diacetylphenyl)tetracarbonylmanganese (**24**) (0.106 g, 0.323 mmol) and $PhCH_2Mn(CO)_5$ (0.095 g, 0.332 mmol) with reflux over 5 hrs gave **25** (0.110 g, 69 %) and a trace of unreacted **24** (0.007 g, 7 %).

Reverse reaction: standard orthomanganation conditions. **25** (0.049 g, 0.099 mmol) and 1,3-diacetylbenzene (0.019 g, 0.120 mmol) were refluxed in heptane over 2.5 hrs and resulted in **24** (0.014 g, 0.043 mmol produced), 1,3-diacetylbenzene (0.013 g, 0.080 mmol, represents 0.039 mmol reacted) and some unreacted **25** (0.015 g, 31 %).

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Chapter 4

Reactions of Orthomanganated Compounds with Alkynes

4.1 Introduction

Recently published was an excellent review by Schore [1], which gives an idea of the enormity of the field of transition metal interactions with alkynes. The review is not the final word on the subject, but its defined boundaries (most particularly, cycloadditions with the isolation of an organic product) fit well with the theme of this chapter.

The reactions with which Schore deals are transition metal mediated cycloadditions: all cases involve the directed construction of two new carbon-carbon bonds, and isolation of a resulting organic product. A wide range of 3-8 membered rings (and some larger) and a variety of heteroatoms are all described within each ring size group (for example, cyclopentene-ones, -diones, -triones; furans, furanones, etc.). Also included are the cyclotrimerization reactions of alkynes to give benzene derivatives, an area that apparently was "vast" even two decades ago. Some details from the review will be included as needed in later sections.

The literature areas of importance to this chapter are now reviewed.

4.1.1 Preparation of Indenes, Indenols and Indenones

The cycloaddition of an alkyne to a chromium arylalkoxycarbene complex, established by Dötz [6], is a well known method [6] for carrying out the transformation shown below (Figure 4.1).

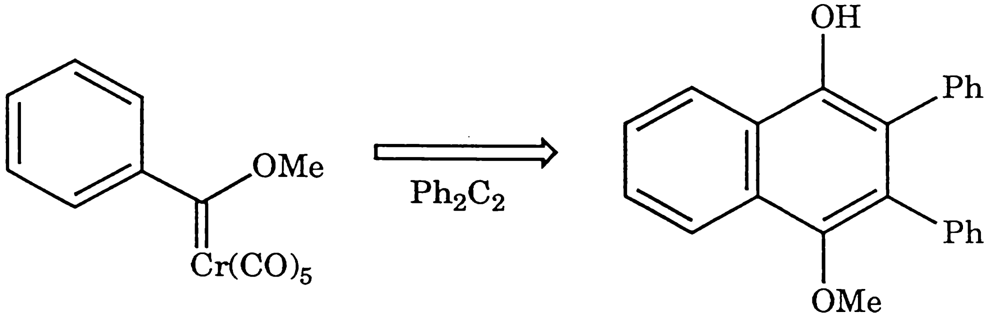


Figure 4.1

The system also provides low yields of indenes, arising from a point in the mechanism before CO insertion occurs (Figure 4.2).

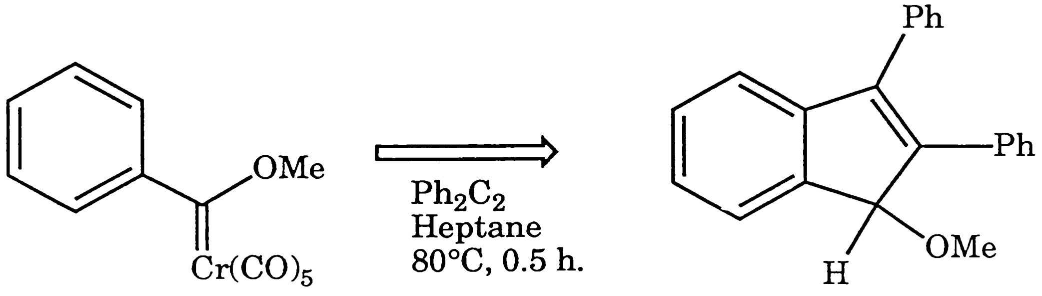


Figure 4.2

Dötz [7] later found systems in which indene formation was the predominant pathway, employing ynamines and ynediamines for that purpose (Figure 4.3).

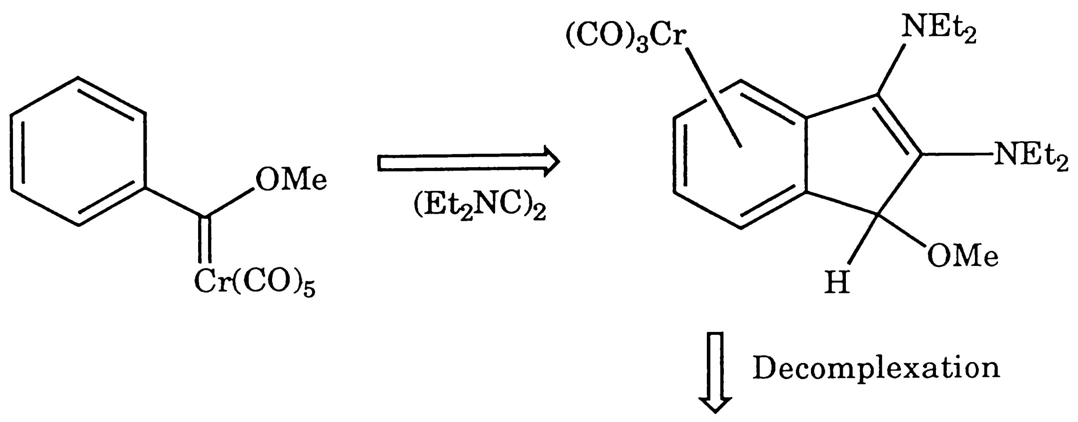


Figure 4.3

A recent variation has been reported by Hoa Tran Huy [8], using a biphenyl biscarbene and diphenylacetylene to produce the corresponding bisindene (Figure 4.4). The hydrogen displaced from the 2-position in the substrate that usually attaches to the carbene carbon has undergone a 1,3-shift in this case, an effect also observed for alkyl groups [10].

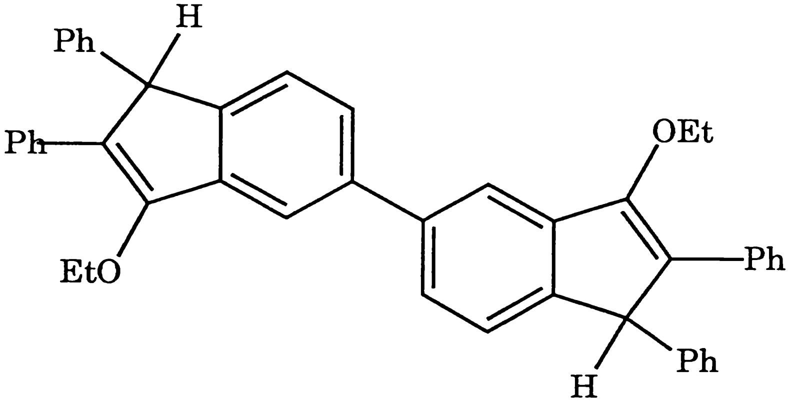


Figure 4.4

In traditional organic preparations, indenols (central to this chapter) have been previously prepared [9] by Grignard synthesis from indenones, a procedure that could be generalised to almost any indenone plus carbon nucleophile.

A brief mention only is given to indenones in Schore's review [1], but a number of related systems are covered in detail. Cyclopentenones from an alkyne-alkene-CO cocyclisation (Figure 4.5) were first reported by Pauson [11] and have been extensively studied.

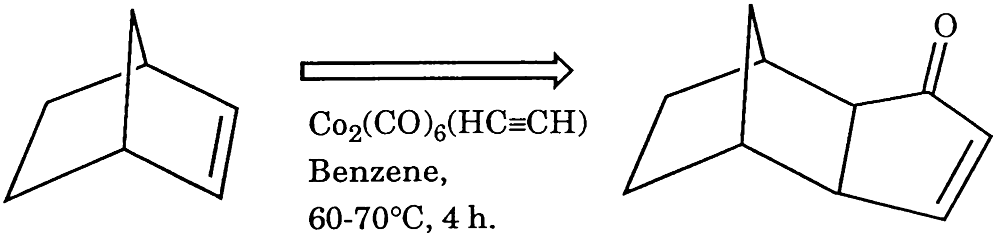


Figure 4.5

Although cycloaddition of two alkynes and CO in the presence of an iron carbonyl [12] (Figure 4.6) or cobalt complex [13] (some rhodium and nickel cases also) are known systems for the isolation of cyclopentadienones, transition metal methodology is only rarely used in the preparation of this type of compound.

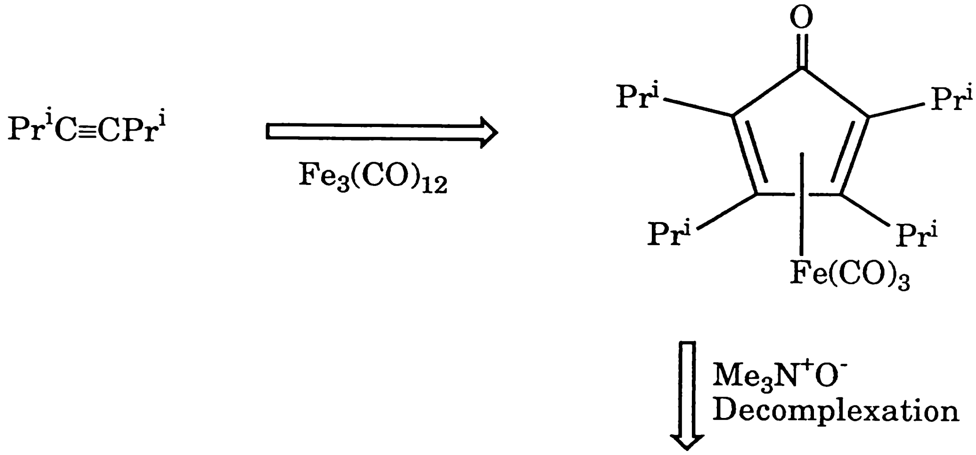


Figure 4.6

A route to an indenone using this type of reaction is through a (possibly metal bound) benzyne intermediate: this was developed by Liebeskind [14] using *o*-diiodobenzene as a benzyne equivalent, in the presence of $Ni(CO)_4$ (Figure 4.7). Regioselectivity with terminal alkynes is excellent, giving the "usual" orientation (shown).

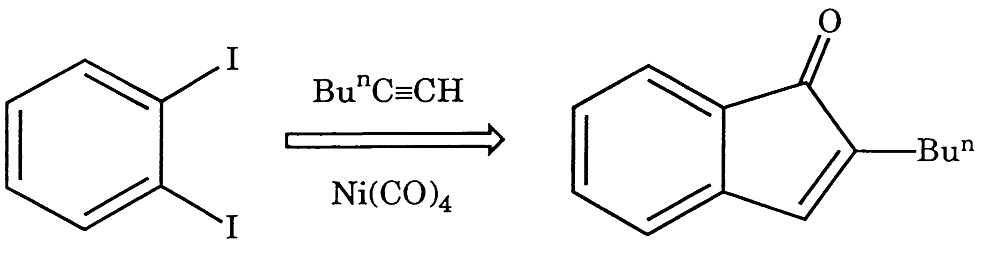


Figure 4.7

A general organic approach to indenones was reported by Floyd and Allen [15], starting from benzaldehyde and ethyl α-

bromoethanoate, and proceeding through five steps to the final product (Figure 4.8).

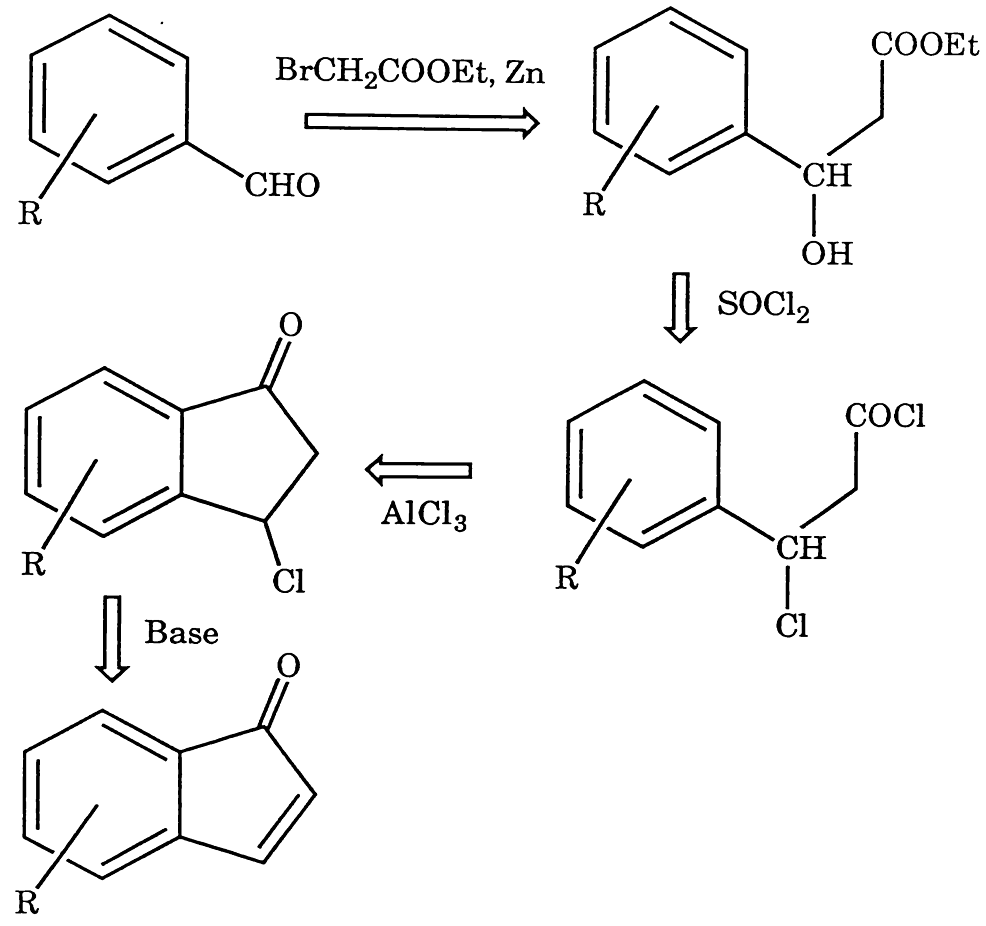


Figure 4.8

4.1.2 Reactions of Cyclometalated Compounds with Alkynes

There are a number of examples from palladium chemistry [2] where alkyne insertion into the palladium-carbon bond results in an organic product. Often, the alkyne inserted intermediate is also isolated. A representative reaction is shown below (Figure 4.9):

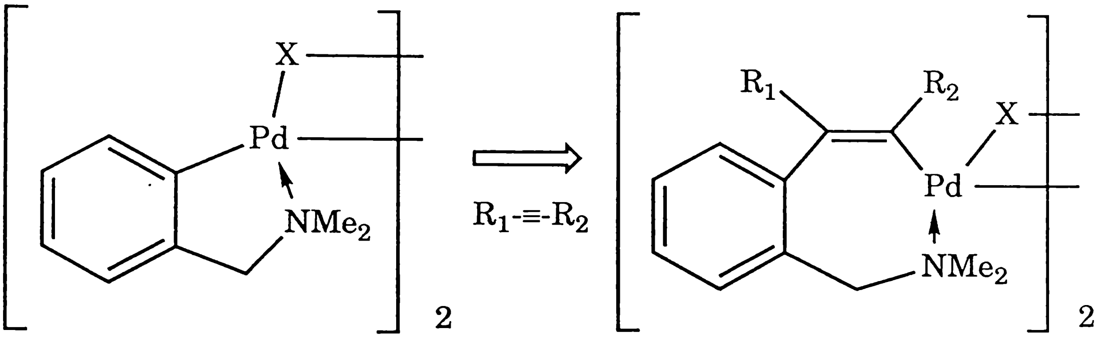


Figure 4.9

Double insertion can also take place, depending on the alkyne substituents. The intermediates shown can duly be converted to a free organic product, most often a tetraalkyl ammonium salt resulting from alkyne attack on the nitrogen atom (or vice versa). A study by Wu *et al* [3] with benzylimines gave similar results, as did the cyclopalladated benzylmethylsulphides [4].

In the presence of phenylacetylene, a cyclometalated azobenzene cobalt complex (Fig. 4.10) has been reported [45] to undergo alkyne insertion, resulting in the tentatively assigned tris(azobenzene)cobalt product shown.

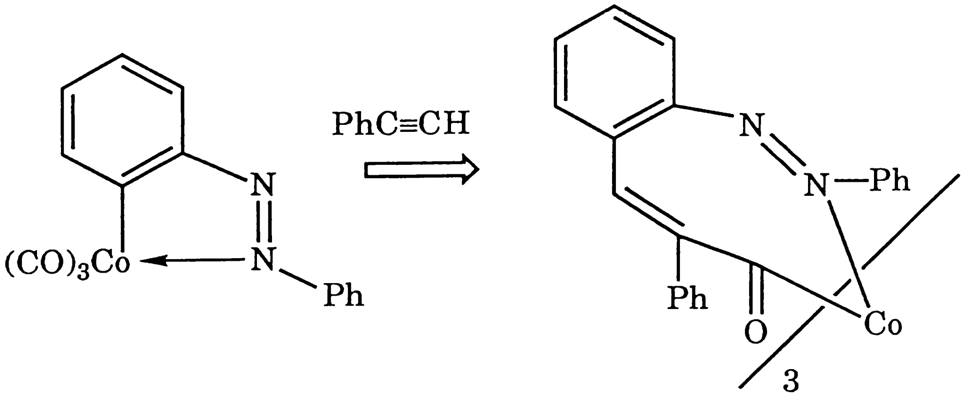


Figure 4.10

4.1.3 Manganese Complexes with Alkynes

A substantial body of work in this area was carried out by Booth *et al* [16] in the early 1970s. Similar reactivity patterns were observed in most cases: a representative reaction for an $RMn(CO)_5$ species with an alkyne is shown in Figure 4.11:

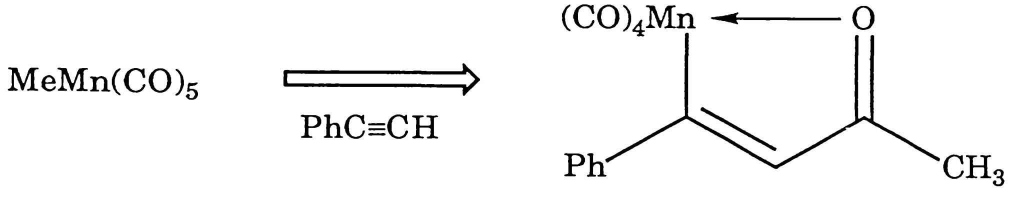
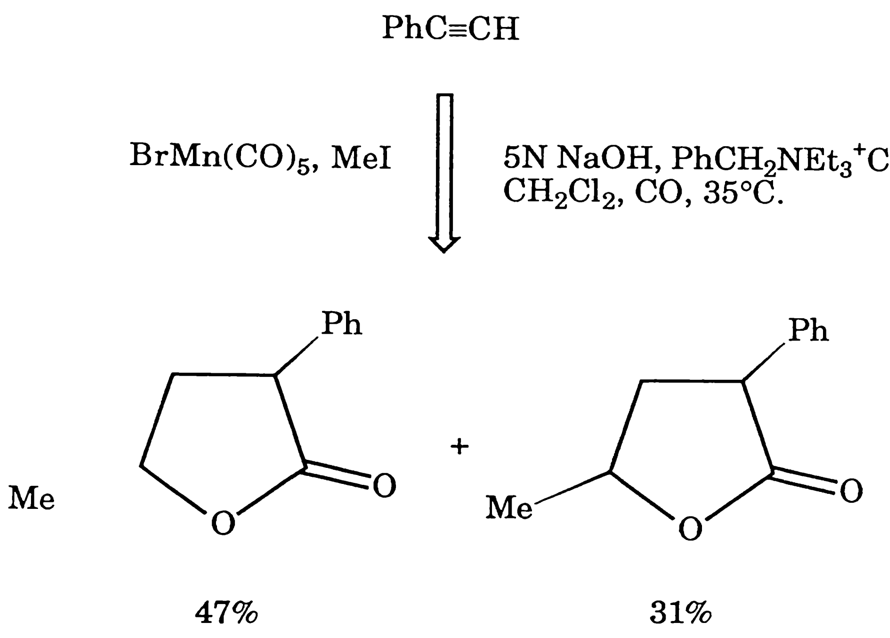


Figure 4.11

Methyl migration to CO was suggested as an early step, concurrent with alkyne addition to give an alkyne donor intermediate, which then rearranged to the product. The bulkier alkyne substituent finishes closer to the manganese, a probable result of less hindered attack on the acetyl group by the terminal alkyne carbon. Similar results were observed for hydridocarbonylmanganese compounds, and a later kinetic study [17] revealed that the reaction rate was very solvent dependent.

Other studies have shown that $[HMn(CO)_4]_3$ will induce a linear dimerization of diphenylacetylene [18], giving rise to the tentatively assigned 1,2,3,4-tetraphenylbutadiene.

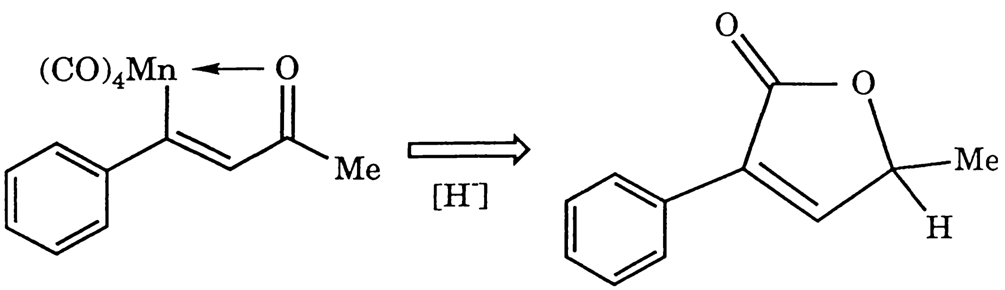
Schore's review [1] contains few examples of the treatment of manganese complexes with alkynes. One interesting case is the isolation of lactones from the procedure below (Figure 4.12):



----- (1)

Figure 4.12

The active species, according to Schore, is either $[Mn_2(CO)_9Br]^-$ or $[Mn(CO)_5]^-$: those species in the presence of MeI may mean, however, that the active agent is $MeMn(CO)_5$. The reaction would then follow the precedent described by DeShong *et al* [19], in which the alkyne manganese adduct (from Fig. 4.11) on treatment with hydride (accompanied by a CO insertion) forms the lactone in Figure 4.13. The difference is reduction of the double bond that results in (1) but not in (2), a result that is difficult to explain using the reagents shown in Fig. 4.12.

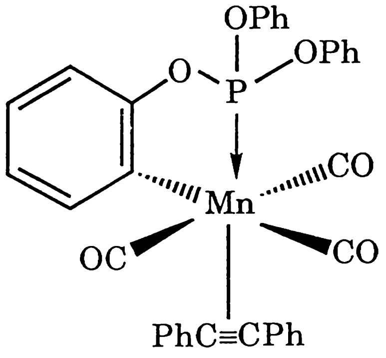


---- (2)

Figure 4.13

DeShong devoted some effort to the isolation of butenolides from the manganacyclic species shown (having prepared the lactone precursor by the alkyne/RMn(CO)$_5$ reaction): treatment with acid results in demetalation and isolation of the protonated ligand, while treatment with hydride is described above. Both are useful strategies for the preparation of highly functionalised carbonyl systems.

In all the manganese systems so far studied, precoordination of the alkyne to form a π-donor intermediate complex is presumed to occur, though no one has yet reported the isolation of such a species or spectroscopic data indicating its presence in any significant concentration. Onaka *et al* [20], however, recently reported the isolation of a colourless crystalline solid which they claimed was (†) (Figure 4.14(a)), the product of treatment of an orthomanganated triphenyl phosphite with diphenylacetylene under photolysis conditions. The assignment was based primarily on ^{13}C nmr evidence, as crystal diffraction data of (†) could not be solved.



(†)

Figure 4.14(a)

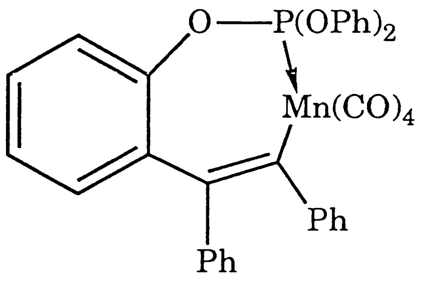


Figure 4.14(b)

Very recent work on the same reaction here at the University of Waikato indicates that the product is instead that of alkyne insertion into the Mn-C(aryl) bond (Fig. 4.14(b)), a notion supported by infra-red data (showing the retention of four CO stretches) and a crystal structure analysis.

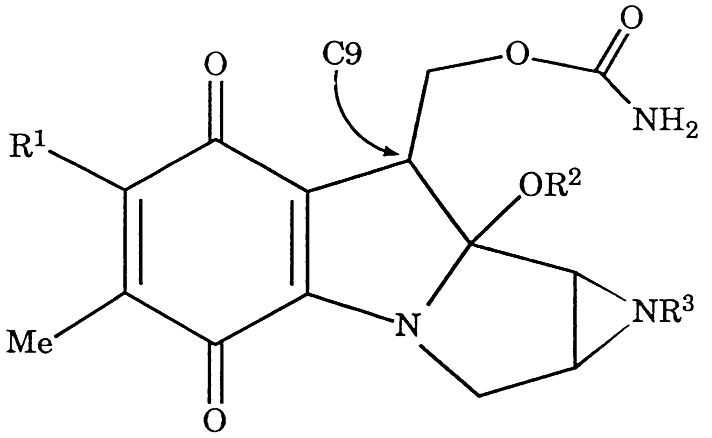
4.1.4 Indoles: synthesis, applications and transition metal interactions

Indoles are a particular area of interest in both this chapter and Chapter 2. It soon became obvious from the literature that they carry the greatest potential for applications in synthesis: as such they are explored here in some detail, along with examples of the use of transition metals in their modification.

Indole can be obtained from the 240-260°C fraction of coal tar [21] and is also found in faeces [22]. Indoles have widely different uses, including perfumes, plant growth regulators, root formation accelerators, antibiotics (isolated from *Streptomyces albus*), or as anti-inflammatory, antipyretic or analgesic agents. Indole is the basis of tryptamine, which occurs in plants, and L-tryptophan, an essential component in human nutrition (not synthesized by the body, casein contains about 1.2%). They form the nucleus of a number of alkaloids such as caracurine-II, found in the bark of *Strychnos toxifera* [23], borreverine, extracted from *Borreria verticillata* [24], C-Calebassin [25] and polyavolensin, an indolosesquiterpenoid from the medicinal plant *Polyathia suaveolens* [26].

More recently, they have received considerable attention because they are the basis of a range of anti-tumour antibiotics called mitomycins (Figure 4.15). It is the area of mitomycins that proved of relevance to the results in this chapter. A central difficulty in the mitomycin synthesis is the formation of the heterocyclic skeleton.

There exists, as a result, only one total synthesis [27], although a number of other meritorious approaches have been reviewed [28-30].



Compound	R^1	R^2	R^3	Confign(C9)
Mitomycin A	OCH_3	CH_3	H	β
Mitomycin B	OCH_3	H	CH_3	α
Mitomycin C	NH_2	CH_3	H	β

Figure 4.15

The field of transition metal/indole interactions is smaller, restricted almost solely to treatments with palladium reagents. Billups *et al* [31] used allyl reagents and palladium acetylacetonate to convert unsubstituted indole to a mixture of 1-, 3- and 1,3-di-allylated products, while Itahara *et al* [32] directed the reaction more effectively by blocking the 1-position with an acetyl or benzoyl substituent. The result was preferential alkenylation at the 3-position (when both the 2- and 3-position were available) and at the 2-position when the 3-position was methyl substituted. Some tricyclic products were also obtained in low yield (Figure 4.16).

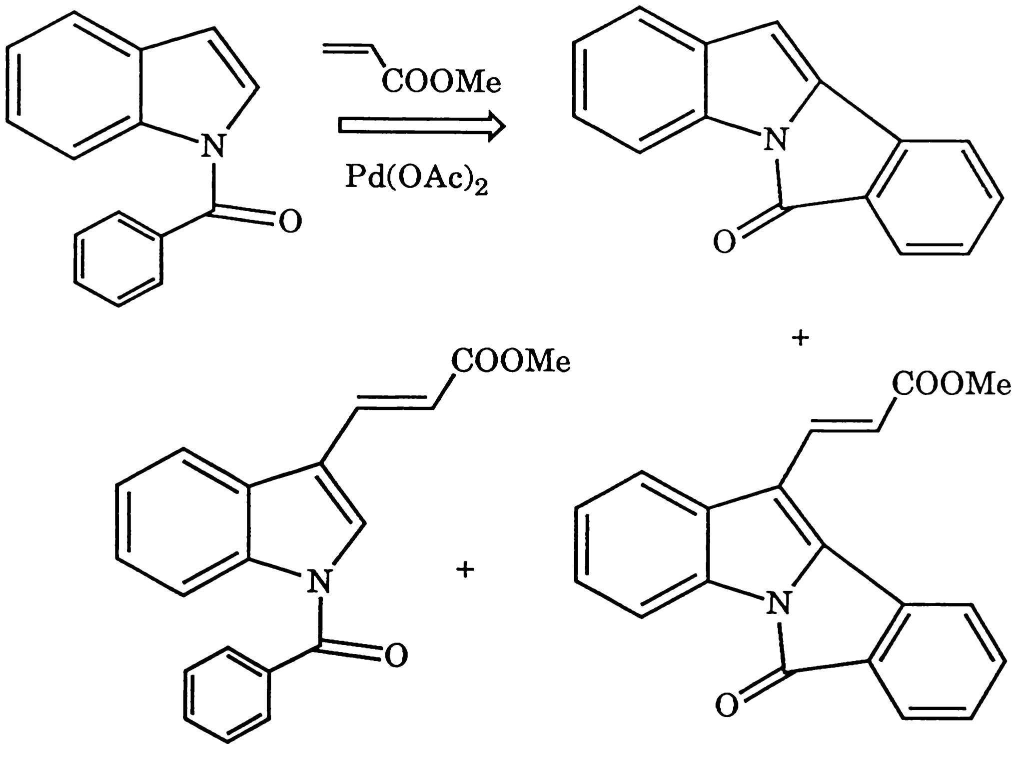


Figure 4.16

The most comprehensive recent review in the indole/transition metal field is by Hegedus [33]. Again, palladium plays a large part, not only in 3-substitutions, but in less accessible 4-substitutions and in a number of rare intramolecular couplings throughout the synthesis of indole alkaloids. Other metal species such as copper and ruthenium salts have been used in the formation of the five-membered pyrrolo ring of indole, and the well known cobalt cyclotrimerization reaction has effected some [2,3-b] fused cyclizations, though the 2,3-bond is single as a consequence. Chromium tricarbonyl systems of indole have introduced functionality at normally unreactive positions, in particular, the 4- or 7-positions, depending on the size of the *N*-substituent.

In sum, the applications of indole systems are sufficiently widespread that organometallic chemists should be able to find many more interesting transformations for use in organic synthesis.

4.2 Results and Discussion

4.2.1 Reactions of cyclometalated ketones with alkynes

η^2-(2-acetylphenyl)tetracarbonylmanganese (**39**) reacted with diphenylacetylene (1 mol) in refluxing benzene over 8 hours to form 1-methyl-2,3-diphenylinden-1-ol (**40**) in 98% yield. 46% of dimanganese decacarbonyl was the only other product isolated. The indenol was identified spectroscopically (^{1}H and ^{13}C NMR), by combustion analysis and by an X-ray crystal structure (see below).

Treatment of η^2-(2-acetylphenyl)tetracarbonylmanganese with diphenylacetylene in refluxing methanol over 18 hours also gave **40** in 51% yield, accompanied by some demetalated acetophenone (22%); in methanol with exclusion of light and 7 hours reflux, 39% of **40** was obtained with 35% demetalated acetophenone and 15% unreacted starting material; while from refluxing heptane (after 4 hours), no **40** could be isolated, although all starting material was consumed.

The absence of an isolable indenol product from the reaction in heptane solvent may be due to solvent polarity. Booth *et al* [17] have observed that the rate of alkyne insertion into an Mn-C bond is very solvent dependent. In benzene and diethyl ether, insertion is much slower than in polar solvents like THF and nitromethane. An advantage of benzene, however, is that it does not promote demetalation during reflux (as methanol does with degradation of the starting material). Light does not appear to play a part in the reaction: had the dark reaction gone on to completion, the yield of **40** would probably have been closer to 51%.

A reasonable sequence for the mechanism (not yet established) can be proposed (Fig. 4.17). Insertion of the alkyne into the Mn-C bond would give the seven-membered ring species (i). Intramolecular addition across the C=O bond ((ii) and (iii)) collapses the seven-membered ring to a five-membered indene ring, and the manganese remains associated with the oxygen in an alkoxide-type intermediate. The alkoxide is readily protonated to generate the indenol (iv).

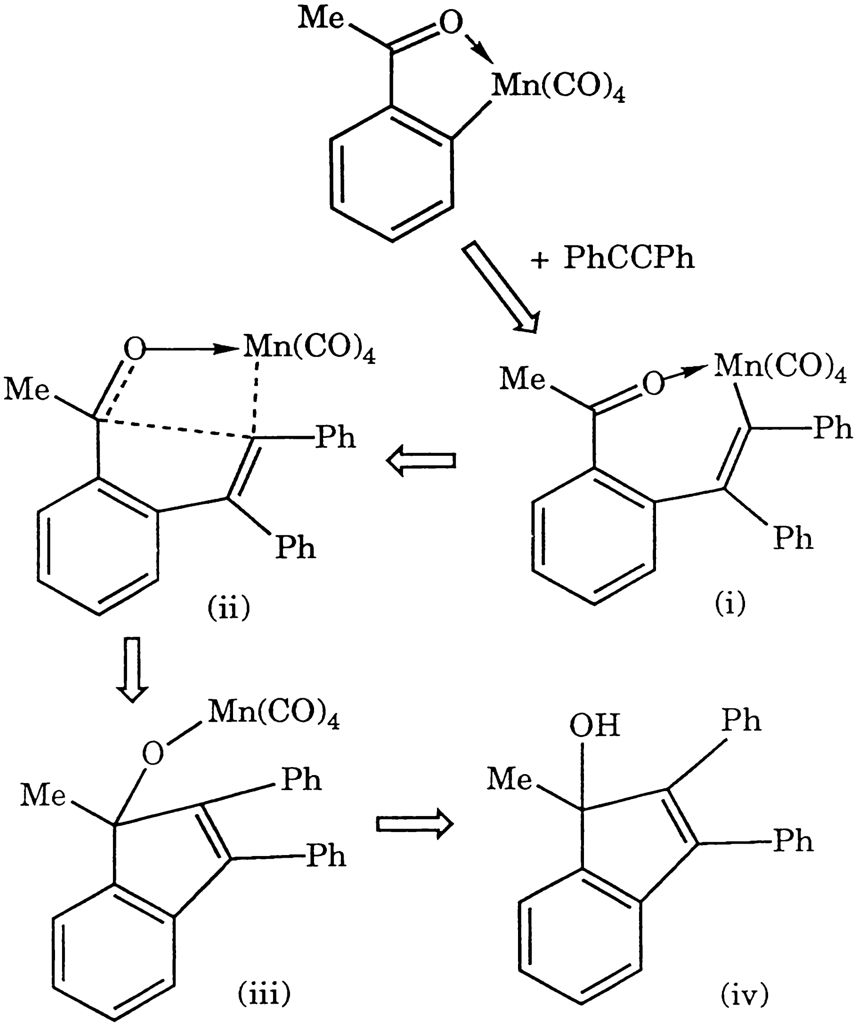


Figure 4.17

Symmetric alkynes were found to be general in their reactivity towards η^2-(2-acetylphenyl)tetracarbonylmanganese (Table 4.1): 4-octyne, ethyne and bistrimethylsilylethyne all gave an indenol product (**42**, **41**, and **43** respectively) though the larger steric constraints of alkyne substituents such as a trimethylsilyl group resulted in a low yield.

Table 4.1 Alkyne couplings with **39** in benzene solvent.

Alkyne	Yield of indenol (%)	Compound
Diphenylacetylene	97	**40**
Acetylene (ethyne)	64	**41**
4-Octyne	51	**42**
Bistrimethylsilylacetylene	8	**43**
Dimethylacetylenedicarboxylate (DMAD)	0	

The mechanism suggests a nucleophilic attack on ketone C=O by the metallo-alkene carbon in (i), which is in agreement with the observed result that DMAD would not undergo coupling with **39** (to afford the dicarboxylate indenol). The strongly electron withdrawing effect of the two carboxymethyl groups probably deactivates such attack in the intermediate (i). Alternatively, the electron deficiency of the triple bond may even prohibit the initial formation of (i).

Under reflux for 18 hours in benzene, diphenylacetylene also adds to η^2-(2-benzoylphenyl)tetracarbonylmanganese to give 1,2,3-triphenylinden-1-ol (**44**) in 85% yield, which indicates another range of available substituents in the indenol product, namely, phenyl substituents in the indenol 1-position.

When η^2-(2-acetylphenyl)tetracarbonylmanganese was treated with an equimolar amount of the unsymmetrical alkyne, phenylacetylene, 43% of indenol **45** resulted. The exclusively generated 2-isomer was identified by NMR and mass spectroscopy, and by combustion analysis: 2-orientation was confirmed by an NMR COSY experiment in which the four bond proton-proton coupling, $J_{H3\text{-}H4}$, was readily observed (Fig. 4.18).

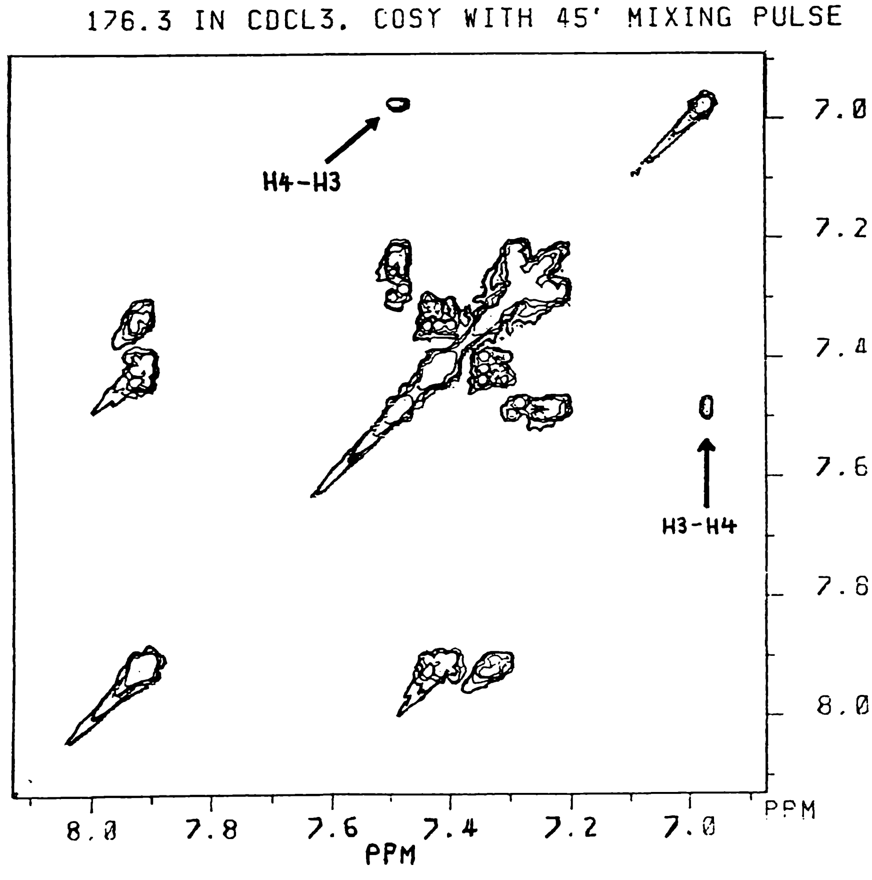
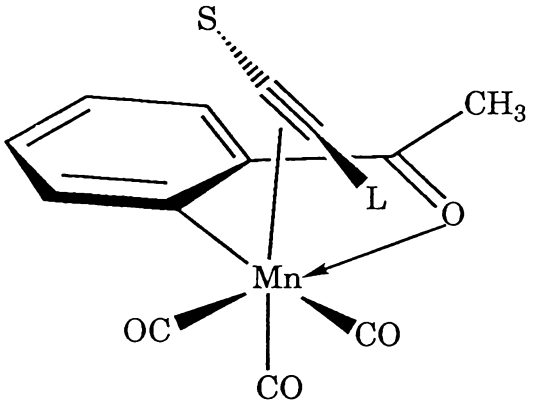


Figure 4.18 COSY NMR: ^1H-^1H correlation of 1-methyl-2-phenylinden-1-ol (**45**) (aromatic region).

A second product, isolated as a yellow oil (3% based on **39**), was identified as **46** based on the following: a molecular ion consistent with the mass of **46** in the mass spectrum, NMR data consistent with related cyclohexadienyl compounds that occur later in this chapter and infra-red data showing three strong vibrations in the CO region. When the experiment was repeated with a threefold molar excess of phenylacetylene, 84% indenol was produced with 14% of the cyclohexadienyl product **46**.

The other possible indenol isomer, 1-methyl-3-phenylinden-1-ol, was not detected. It is presumed that the insertion of phenylacetylene into the Mn-C bond is preceded by a coordination step, where the resulting transient species favours the bulkier phenyl group in a position further from the acetophenone ligand (Figure 4.19). Once alkyne insertion has occurred, the rate of ring closure is competing with the rate of further alkyne insertion; thus the relative rate of each probably decides the quantity of indenol and cyclohexadiene product. In turn, those rates may be reliant on the extent of activation of the C=O bond and, to a degree, the bulk of the alkyne substituents.



S = small group
L = large group

Figure 4.19

Coupling of trimethylsilylacetylene with **39** gave indenol **47** in 82% yield, along with a brown oil which was tentatively assigned a similar cyclohexadienyl structure (on the basis of IR and NMR evidence). Vinylsilanes have been prepared by various methods in the past and have always assumed some importance in organic synthesis, a review of which appeared recently [43]. The silyl indenes can be prepared by only one of four such reported syntheses (substitution of the vinylbromide), as the cyclised aspect of the double bond complicates the other three. Once formed, vinylsilanes can be used in some useful reactions with electrophilic reagents. Both protio- and deuterio-desilylation proceed under acidic conditions at 100°C, while bromination and Friedel Crafts acylation are effected at 25°C or less.

Coupling of 2-hexyne with **39** gave only 1,3-dimethyl-2-*n*-propylinden-1-ol **48** in 32% yield. The unsymmetric 2-position preference observed in all three couplings is in agreement with observations by Booth *et al* [16] and DeShong [19] that were described in the introductory section of this chapter.

In all symmetric and unsymmetric couplings so far, some dimanganese decacarbonyl was detected. The quantity varies between small (18% for acetylene + **39**), and feasibly recyclable (46% for diphenylacetylene + **39**).

The coupled indenol product **40** has previously been prepared by Grignard methods from 2,3-diphenylindenone [9], as have a number of 1-alkyl-2,3-diphenylinden-1-ols. Other alkyl derivatives would be equally easy to prepare by the alkyne coupling method, as Cabral [36] has shown that higher alkyl aryl ketones are readily orthomanganated. A further advantage is the flexibility that the mild reaction conditions of an alkyne coupling offer by comparison with, say, the strongly reducing conditions of Grignard synthesis.

4.2.1.1 Crystal Structure of 1-methyl-2,3-diphenylinden-1-ol (40)

The crystal structure of 1-methyl-2,3-diphenylinden-1-ol (**40**) is described. Primary considerations in the structure were the degree of delocalisation in the five-membered ring, and given the novelty of the product, the three-dimensional geometry of the molecule.

Figures 4.20(a) and (b) depict the structure of **40**, confirming the coupling/cyclisation of diphenylacetylene with **39**. Each phenyl substituent is twisted out of the indene plane (along the C(2)-C(11) and C(3)-C(21) axes) with a dihedral angle of 53°. Variations in the C-C single bond lengths observed for the five-membered indene ring (that is, C(1)-C(2), C(1)-C(9) and C(1)-C(10)) are all in the range 1.530(7)-1.534(7) Å, whereas the other three, C(2)-C(11), C(3)-C(21) and in particular C(3)-C(8), are significantly shorter (1.474(8)-1.495(8) Å) are likely due only to the state of hybridisation of respective pairs of carbons.

The overall structure contains few surprises for the key indene bonds. However, it confirms the reduction of the acyl group to an alcohol, and importantly, the coupling to form two new carbon-carbon bonds.

4.2.2 Reactions of cyclometalated benzamides with alkynes

The reaction of η^2-(2-*N,N*-dimethylamidophenyl)tetracarbonylmanganese (**13**) with diphenylacetylene in refluxing benzene (after 1 hour) gave 2,3-diphenylindenone (**49**) in 56% yield. The mechanism proposed above (Fig. 4.17) can be extended to include this result. Rather

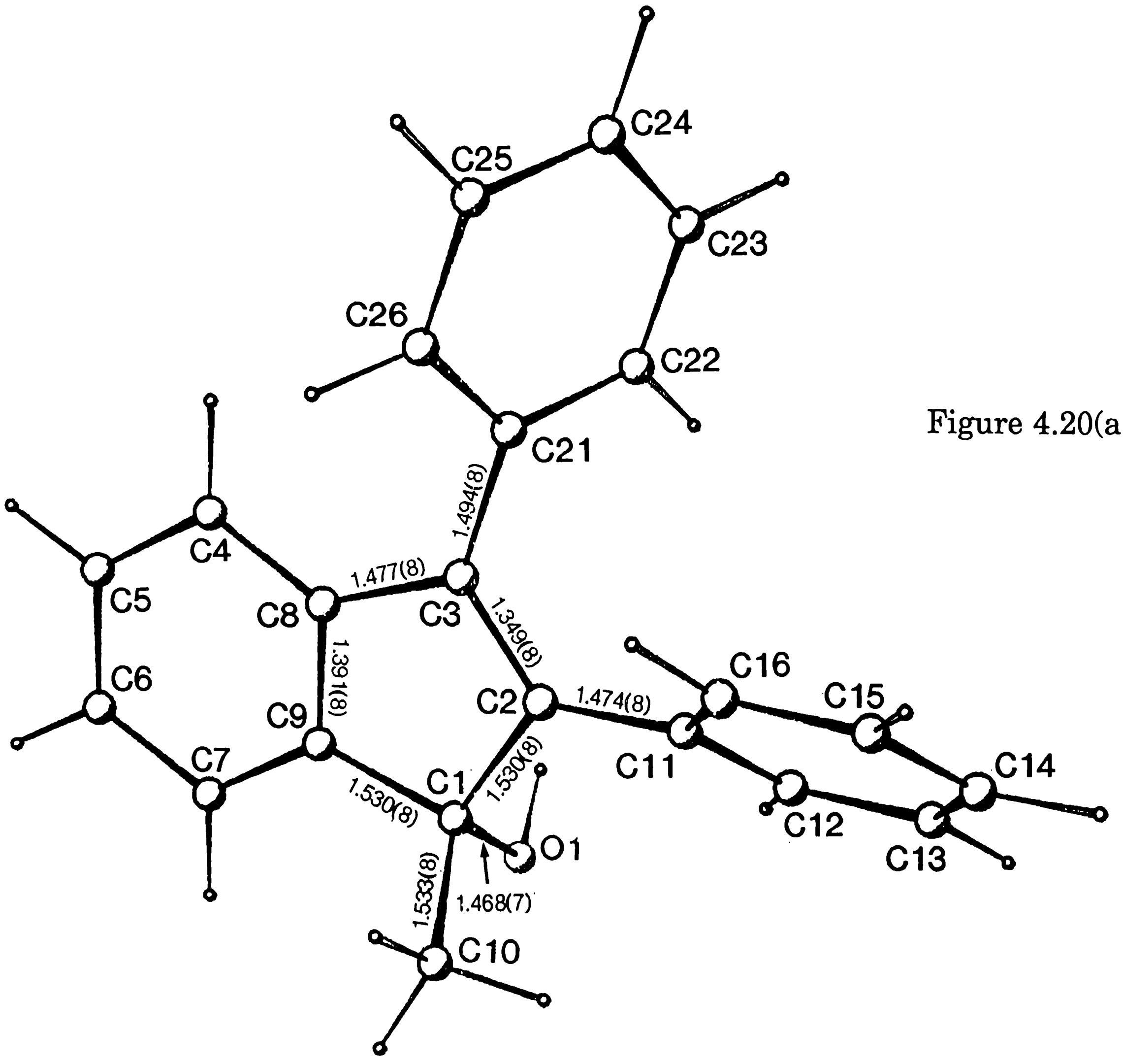


Figure 4.20(a) Structure and Selected Bond Lengths of 1-methyl-2,3-diphenylinden-1-ol (**40**)

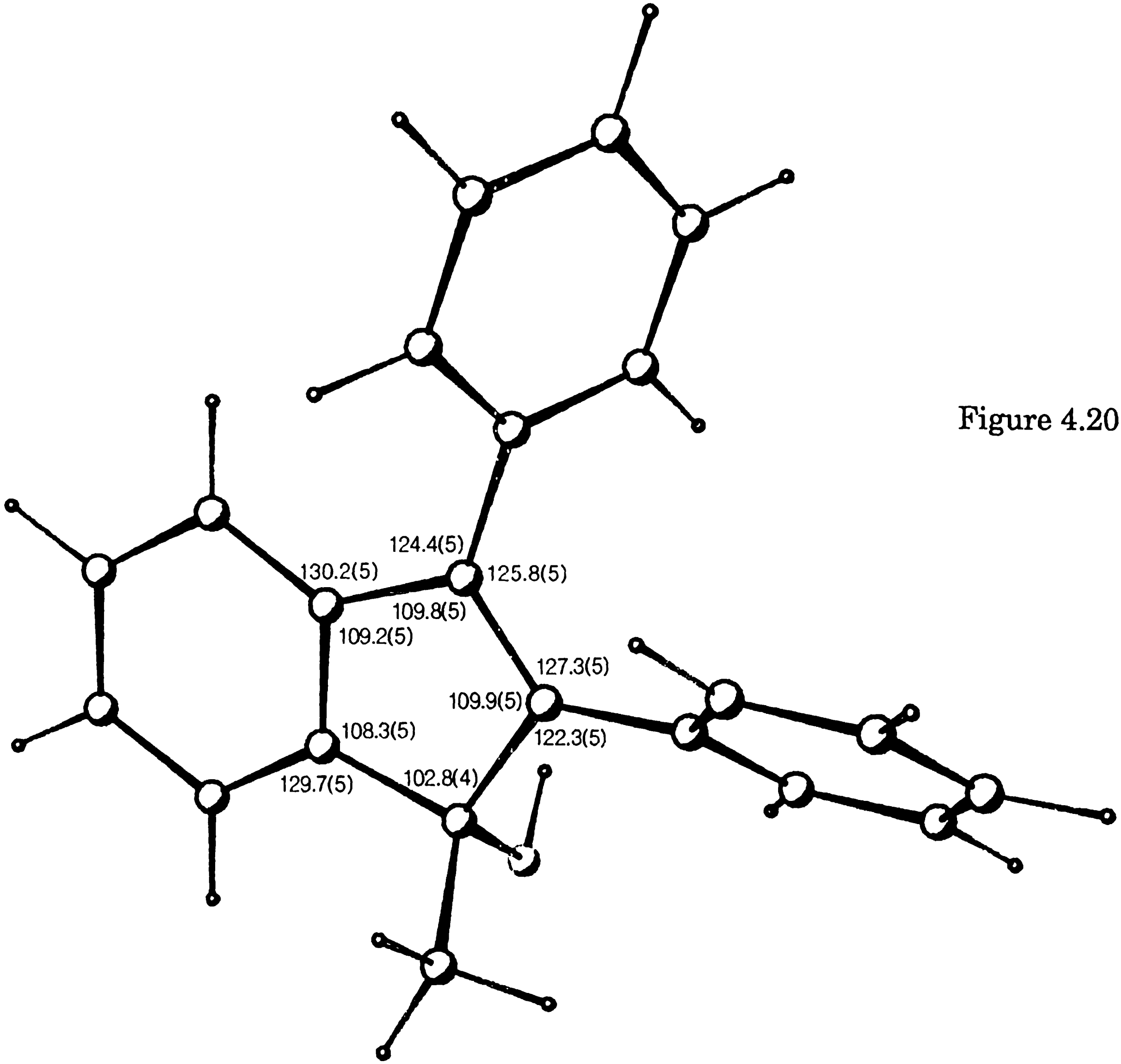


Figure 4.20(b) Selected Bond Angles of 1-methyl-2,3-diphenylinden-1-ol (**40**).

than protonolysis of the manganese-alkoxide intermediate, β-elimination of manganese with NMe_2 could occur to generate the indenone (Fig. 4.21).

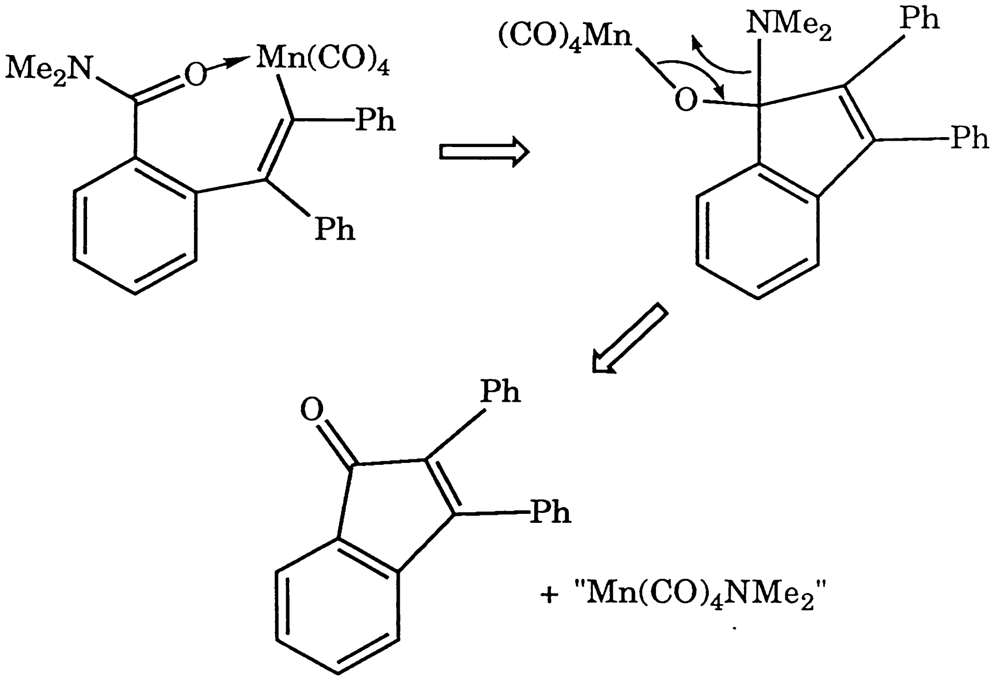
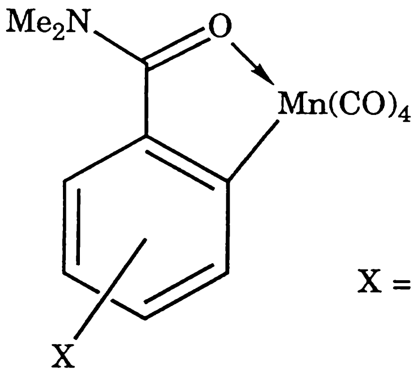


Figure 4.21

Alternatively, but less likely, protonolysis would generate the dimethylaminoinden-1-ol, a species that would be highly susceptible to elimination, in this case of H with NMe_2.

Similar reactions with other *N,N*-dialkylbenzamide substrates were not studied but would be expected to give similar results.

2,3-Diphenylindenone as a product is already widely available and relatively cheap (Aldrich 1989, $US3 per gram), but , as with the indenol products, there is considerable potential for variation in aryl substituents on the starting amide compound. For example, the orthomanganation of aryl substituted N,N-dialkylbenzamide compounds (Figure 4.22) was an area that was not explored in Chapters 2 and 3, but given our current knowledge of the orthomanganation reaction, there are no obvious reasons why the derivatives below cannot be prepared. Coupling with diphenylacetylene should then proceed in the normal way.



X = halogen

Figure 4.22

The orthomanganated benzamide/alkyne couplings proved to be less general than the ketone couplings. When **13** was treated with ethyne, a completely different reaction occurred: the only product isolated was η^6-[1-(2-(N,N-dimethylbenzamido))cyclohexa-2,5-dienyl]tricarbonylmanganese (**50**) in 55% yield. **50** was identified by ^{13}C and ^1H NMR (high field for ^1H and with reference to previously reported compounds [40]), infra-red (three CO peaks compatible with a (cyclohexadienyl)$Mn(CO)_3$ structure) and mass spectroscopy (MI-2CO at 309, molecular weight 365) and by combustion analysis. A possible route to the product is by multiple insertions of ethyne into the Mn-C bond, followed by intramolecular addition of the third inserted ethyne to the first. However, also possible was some sort of a solvolysis reaction with benzene. A repeat of the reaction in toluene solvent indicated that the reaction was with ethyne, rather than the solvent: (**50**) was formed in even higher yield (62%) than in benzene.

The rate of alkyne insertion in the alkyne/cyclometalated amide reaction is much greater than the rate of metallo-alkene attack on C=O, as the only product isolated is from the insertion pathway. On the presumption too that attack on C=O by the initially formed metallo-alkene is nucleophilic, the ethyne/amide result can be explained by the lower susceptibility of R_2N-C=O to nucleophilic attack by comparison with ketone C=O.

The lack of generality of the amide/alkyne couplings is clearly a drawback to their wide use in synthesis. However, further efforts may yet establish that the cyclohexadienyl product is characteristic of the amide/ethyne coupling, and that synthetically more useful alkyne substituents may couple effectively to give the corresponding indenone products.

4.2.3 Reactions of cyclometalated esters with alkynes

The elimination of the dimethylamino group in the reaction of **13** with diphenylacetylene indicated that were the substrate to include a better leaving group, the reaction might proceed in higher yield. Despite the limited number of orthomanganated substrates available, esters were candidates by virtue of the alkoxy leaving group.

Thus when ester **51** was treated with diphenylacetylene in refluxing benzene, 100% of the highly coloured indenone **52** was formed.

Similarly to the amide reactions, when **51** was treated with ethyne, the result was **53** in 36% yield. Again, this limits the synthetic versatility of the ester/alkyne couplings, but the diphenylacetylene coupling result shows that where cyclisation and elimination occurs, it can do so in excellent yield.

4.2.4 Reactions of cyclometalated aldehydes with alkynes

The results with other substrates suggest that the expected product of an orthomanganated aldehyde/alkyne coupling would be an indenol. However, when **21** was treated with diphenylacetylene in refluxing benzene, the only detected product was **54** in 49% yield.

Again, the basic mechanism outlined in Fig. 4.17 can be employed to explain the production of an indenone. After alkyne attack on C=O, the manganese remains associated with the oxygen, generating the intermediate in Fig. 4.23. β-Hydride elimination may then occur, a process that is well known for many transition metals and has been observed for transition metal alkoxides [41,42,44].

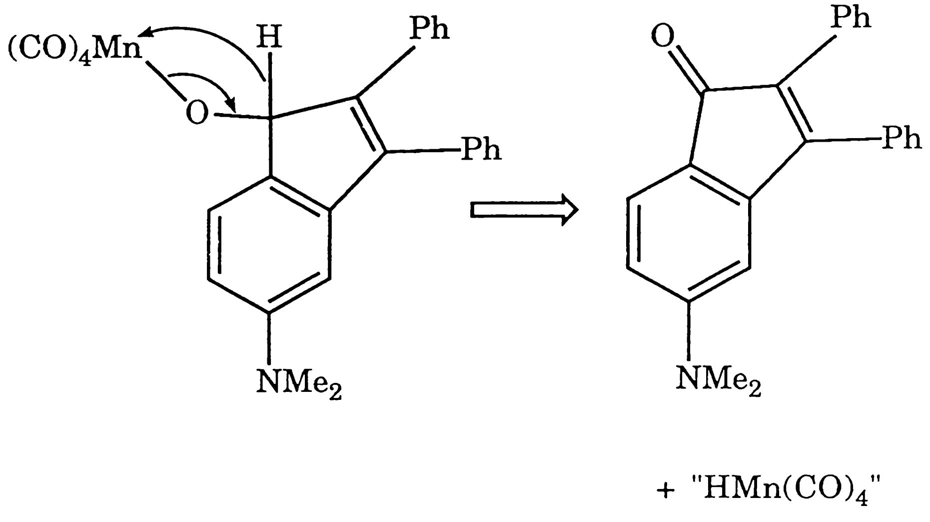


Figure 4.23

The hydride acceptor in this scheme is manganese, the final product of which might be the complex $HMn(CO)_5$. Detection of this unstable species was considered most practicable under nitrogen in a sealed NMR tube. The tube was heated for two days at 60°C, and at no time did any signals appear that could be assigned to an indenol or to an $HMn(CO)_5$ product, despite having a sound reference δ value for the hydridic $HMn(CO)_5$ proton [38]. Depletion of the CHO and NMe_2 signals from the metalated arene indicated, however, that the reaction was taking place, a fact later confirmed by isolation of the indenone and $Mn_2(CO)_{10}$.

A possible variation of the scheme in Fig. 4.23 is production of an indenol followed by air oxidation during the work up. The ease of air oxidation was confirmed in a test-tube reaction. Indenone **54** was dissolved in ethanol/water, giving a purple solution, then warmed with a few grains of sodium dithionite to reduce the carbonyl group. The solution became much lighter and an orange solid precipitated. On standing in air, the solution darkened again and the precipitate dissolved.

The alkyne, diphenylacetylene, was also considered as a possible recipient of hydride donation during the reaction, the product from which would be a stilbene (again with adventitious protonation). This might also have explained the 49% yield: if indenol oxidation/hydride donation occurs at a faster rate than the coupling, it will deplete the alkyne starting material by up to half. A gas chromatography experiment performed on the crude reaction mixture, however, showed no sign of a stilbene.

The reaction of **21** with ethyne resulted in the indenone **55**, but in much lower yield (20%) than with diphenylacetylene.

Synthetically speaking, 2,3-diphenyl-5-dimethylaminoindenone is not any more special than the other diphenylindenones. The 2,3-unsubstituted indenone has clear advantages, however, as it has so far not been been prepared by other ethyne couplings described in this chapter.

4.2.5 Reactions of cyclometalated indoles with alkynes

The applications of indoles to synthetic organic chemistry have been described in the introductory section of this chapter. Danishefsky's assessment [29] of the amount of synthetic activity which mitomycins (an indole-based antitumour antibiotic) have inspired as "enormous", is not overstated.

Treatment of **7** with dimethyl acetylenedicarboxylate (DMAD) in refluxing petroleum spirit (60-80°C) (5 hours) gave rise to **56** in 17% yield. 21% of the orthomanganated substrate remained. The structure of **56** was determined by NMR and mass spectroscopy, combustion analysis and by an X-ray crystal structure (see below, Fig. 4.24 and 4.25). Coupling with DMAD in refluxing benzene solvent was tried initially, but the reflux temperature was such that a miriad of different reaction pathways and products resulted. Petroleum spirit (60-80°C) offered a cooler reaction temperature and a better chance of a single reaction pathway. Attempts to improve the yield with excess DMAD in petroleum spirit were not successful.

An attempted coupling reaction of diphenylacetylene with **7** in refluxing benzene resulted in considerable demetalation (35%) of the cyclometalated arene, along with a green oil that appeared from NMR spectroscopic data to be the cyclised product 1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]indole (**58**). Confirmation of the molecular ion mass by GCMS was not obtained (highest mass peak 207), possibly because of the instability of the product.

Of note in this reactive indole system is the success of the DMAD coupling with **7**, where coupling did not proceed with the ketone substrates. The chief advantage of DMAD over simpler alkynes such as diphenylacetylene is the versatility of the groups, once coupled, in opening up the large field of carboxylate derivatisation, while reduction to the primary alcohol opens up a completely different field.

The reaction of **7** with ethyne gave two products, one of which was assigned as **57** (16%) based on NMR (retention of indole nucleus and C=O signals, ^{1}H signals α and β to C=O visible) and mass spectroscopy (molecular ion consistent with formula weight of 185). The other product, a bright red oil, was not identified. Ring opening has resulted in this case from the indolyl nucleus acting as a leaving group (in a similar way to NMe_2 in the production of indenones from orthomanganated amides), but the product remains a single species by the connectivity of indole C2 to the alkenyl function.

The instability of two strained five-membered rings fused together appears a common factor in both the DMAD and ethyne reactions: the low yield observed in the former case, and ring opening in the latter.

Success in the indole/alkyne couplings was only limited. However, a new route to the indole [1,2-a] nucleus has been discovered, and may prove to be useful to researchers in the mitomycin field.

4.2.5.1 Crystal Structure of dimethyl 1-methyl-1-hydroxypyrrolo-[1,2a]indole-2,3-dicarboxylate (56)

The crystal structure of **56** was determined. A crystallographic solution was desirable for reasons of the potential importance to mitomycin chemistry, the scarcity of structures that currently define the pyrrolo[1,2a]indole nucleus and the absence of an unequivocal assignment by other techniques.

The structure, illustrated in Fig. 4.24, confirms the cycloaddition of DMAD to the previously metalated indole, to yield a novel version of the tricyclic nucleus. Side and perspective views are also displayed, in Fig. 4.25. The strain imposed by fusing another five-membered ring onto the five-membered indole ring is seen in the C(11)-N(1)-C(1) and C(5)-C(4)-C(3) angles of 136(1)° and 144(2)°, though the two angles compare closely with the original metalated structure where angles of 132° and 143° respectively are observed. Strain is also apparent in the acute N(1)-C(1)-C(2) angle of 98(1)°, some 11° short of normal tetrahedral geometry.

Bond lengths show some interesting variations, although the differences (for example, C(2)-C(13) is 1.52(2) Å in length, whereas C(3)-C(15) is 1.47(2) Å) are within two standard deviations, and may not therefore be real.

Comparison with a related structure (Fig. 4.26) described by Ferguson *et al* [34] reveals a similar C(3)-C(15) distance (1.48 Å), though the electrons from the C(2) substituent (-NMe_2) here appear able to undergo considerable delocalisation, the C(2)-N bond being 1.36 Å in length.

In addition, the C(11)-N(1)-C(1) and C(5)-C(4)-C(3) angles of 136° and 143° in the Ferguson structure are nearly identical to those in **56**, indicating a similar degree of strain in the pyrrolo ring.

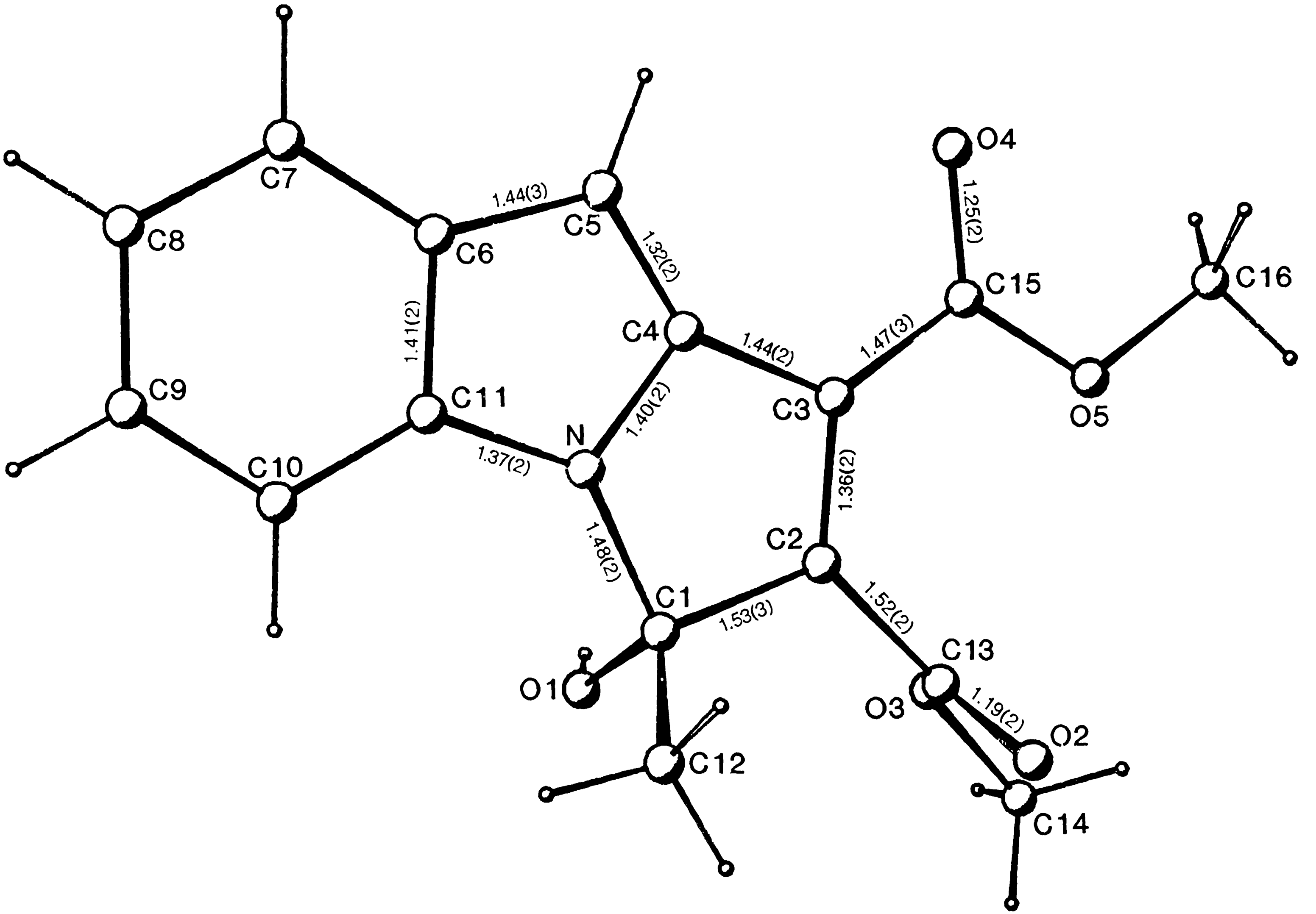


Figure 4.24(a) Structure and Selected Bond Lengths of dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]indole-2,3-dicarboxylate (**56**).

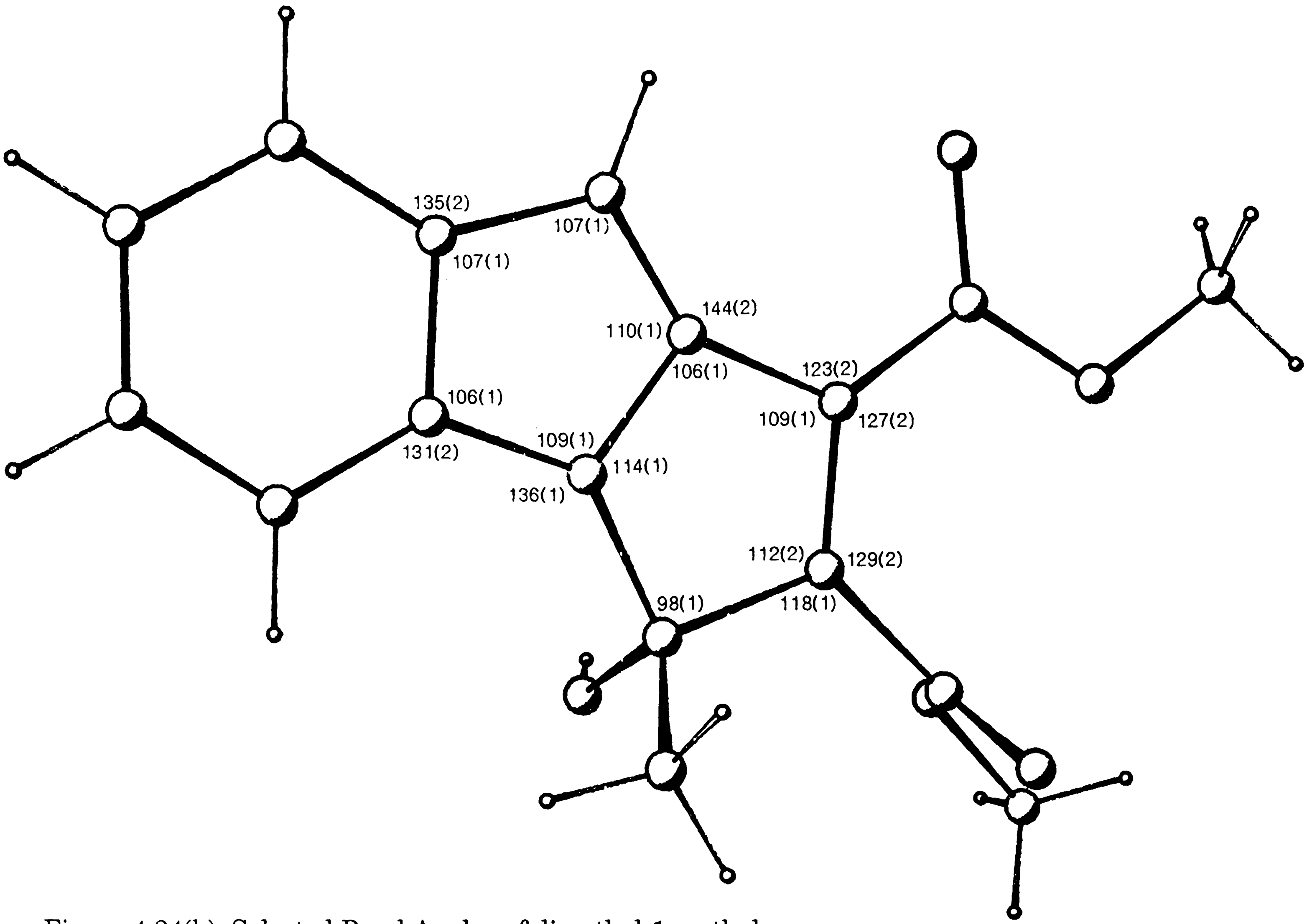


Figure 4.24(b) Selected Bond Angles of dimethyl 1-methyl-1-hydroxy-pyrrolo-[1,2a]indole-2,3-dicarboxylate (**56**).

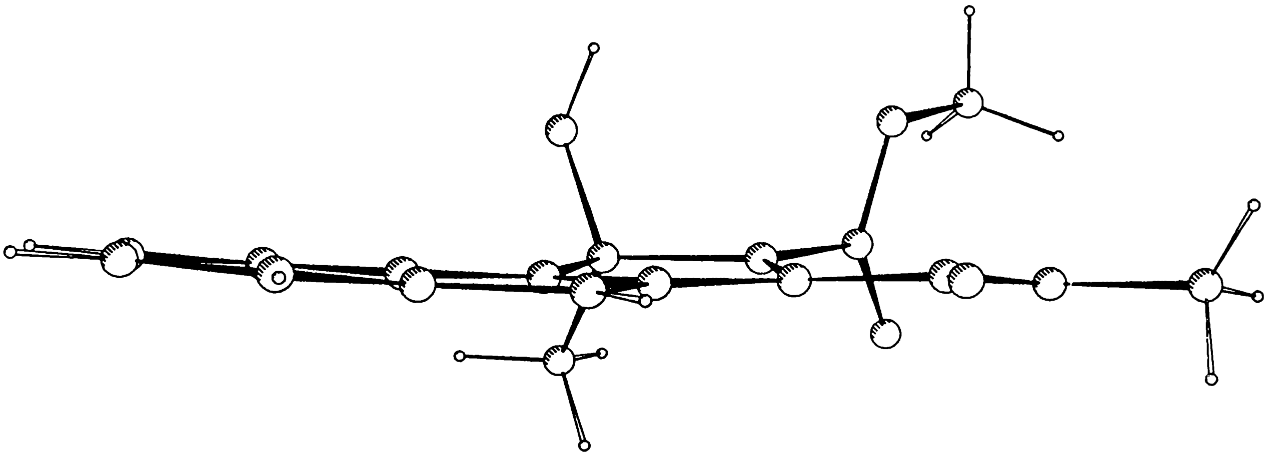
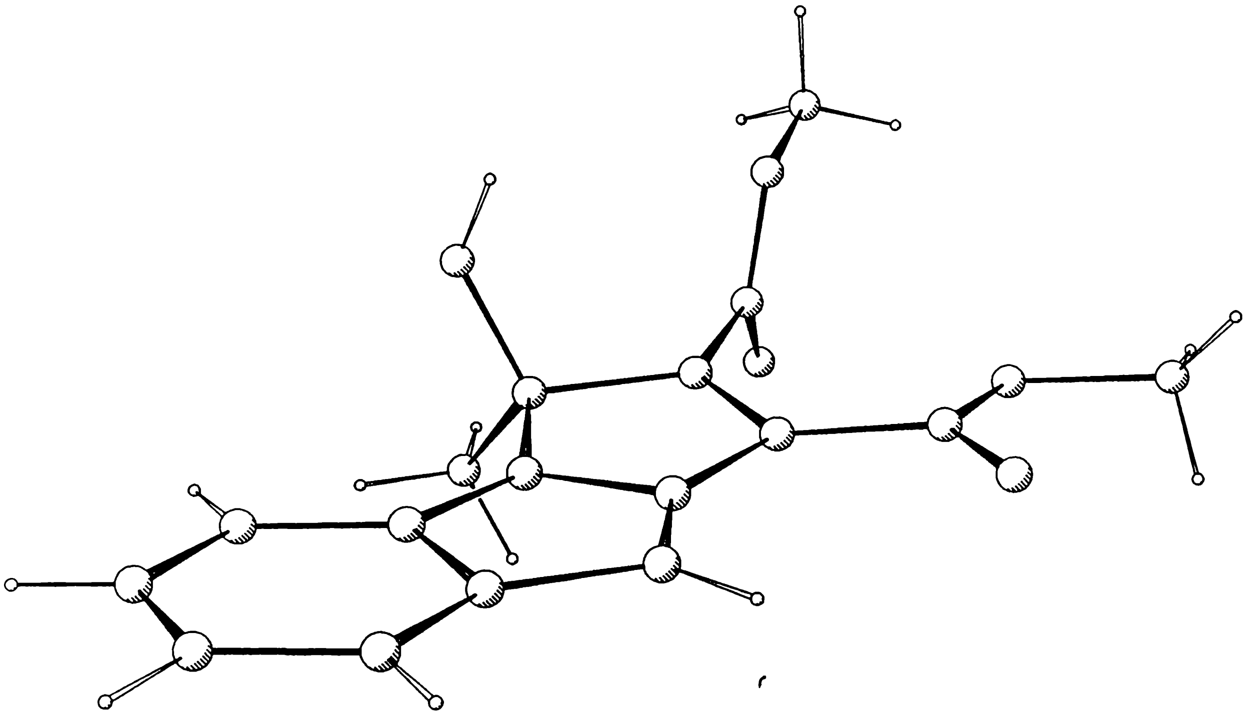


Figure 4.25 Side and perspective views of dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]indole-2,3-dicarboxylate (**56**).



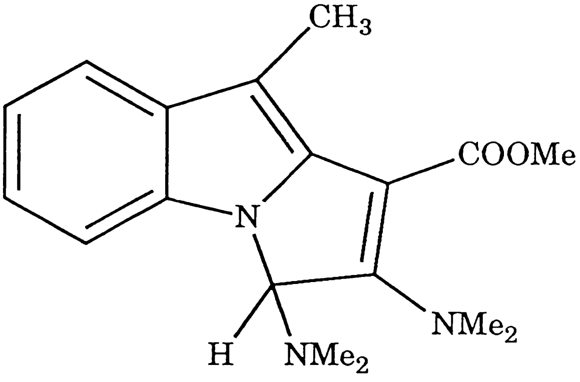


Figure 4.26

Lastly of note is a slight puckering of the pyrrolo (carboxy substituted) ring (hereafter referred to as the "A" ring) with respect to the indolyl nucleus, an effect that was noticably absent in the structure of the metalated starting material, but present in the Ferguson structure (described there as an envelope conformation with the equivalent of C(3) at the "flap"). The reason offered for the puckering was crowding between the -COOMe and neighbouring $-NMe_2$ groups. The resulting angle between the phenyl and "A" ring planes was a significant 12.5°. A second related structure (Fig. 4.27) by Gruska and White [35] reveals an angle between the same two planes of only 4.3°, but there is potential for greater electron delocalisation between each neighbouring ring in this structure, an effect confirmed by the bond distances.

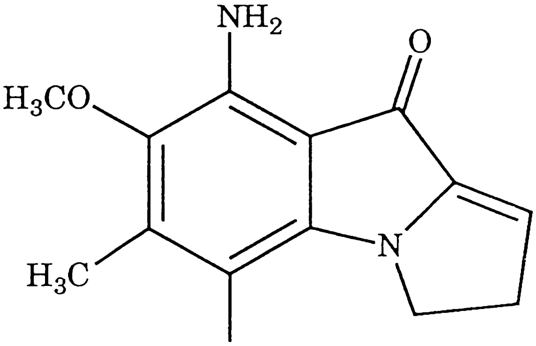


Figure 4.27

Least-squares planes calculations of the extent of puckering in compound **56** revealed an angle of 6° between the "A" ring and the indolyl nucleus. Also, carbons (1), (2) and (3) were displaced out of the indolyl plane by 0.17, 0.26 and 0.12Å respectively. A possible reason, as with the Ferguson structure, is the crowding of neighbouring -COOMe groups.

The complete structure is consistent, therefore, with a certain amount of strain arising from the two five-membered rings fused together, with other features arising from the steric interactions of adjacent COOMe groups.

4.2.6 Addendum

At the latter stages of writing, a report appeared by Liebeskind *et al* [37] that mirrored many of the results in this chapter. In particular, the reactions of cyclometalated ketones with alkynes gave rise to indenols in the same way as described in Section 4.2.1 of this chapter. However, there are also differences throughout, and these are noted below.

The solvent used for all couplings was acetonitrile, but when used alone with the two reagents, it did not effect any reaction. The authors found it necessary to use trimethylamine-*N*-oxide to achieve "decarbonylative activation" of **39** before coupling would proceed. A large number of alkynes (for example, 3-hexyne, cyclohexylacetylene, ethyl 2-butynoate, ethyl cyclohexylethynoate) were then observed to undergo coupling, although ethyne is absent for unstated reasons.

Liebeskind's results for unsymmetrical alkynes showed the same regioselectivity as for indenol **45**, the result of a "sterically biased insertion" into the Mn-C bond. The exceptions to the steric preference were the electron deficient alkynyl esters: in each case where COOEt was an alkyne substituent (adjacent to the triple bond), it occupied the 2-position in the indenol product, even when the other alkyne substituent was a cyclohexyl group. It is possible then for the ester alkynes that insertion is electronically directed, or that the ester acts as a directing ligand in the alkyne-inserted intermediate.

In the light of Liebeskind's results, and of our own current knowledge of orthomanganated arenes, it is fair to say that the only aryl substituents that would restrict generality of the alkyne/metalated ketone coupling scheme are those that prohibit orthomanganation, such as $-NO_2$, -OH, -COOH or $-NH_2$.

Considerable flexibility is therefore available, particularly for substituents in the 4, 5, 6 or 7 indenol positions. Protecting groups in these positions would allow for further synthetic steps, an area that has not been explored in this study, but that could prove fruitful in future work.

4.3 Experimental

The following commercial materials were used as received: 4-octyne (Aldrich, 99%), 2-hexyne (Aldrich, 99%), diphenylacetylene (Sigma), acetylene (ethyne) (NZ Industrial Gases), trimethylsilylacetylene (Petrarch Systems), bis(trimethylsilyl)acetylene (Petrarch Systems), and dimethyl acetylenedicarboxylate (Aldrich, 99%).

Phenylacetylene (BDH) was distilled under nitrogen at ambient pressure, middle fraction 145-147°C (lit. [46] 142-144°C).

Coupling reactions were carried out using Schlenk techniques. The standard approach was to flush the benzene solvent with nitrogen gas, degas the solvent under vacuum, then add both reagents. The mixture was degassed a final time, then refluxed under nitrogen. In cases where the alkyne reagent was acetylene, the reagent gas was gently bubbled through the reaction mixture with a Pasteur pipette while reflux was occurring. To avoid solvent loss, an efficient condenser was employed and a low flow of gas maintained (ca. one bubble per second). Reactions were monitored by tlc (chloroform eluent), in most cases checking for the presence of unreacted orthomanganated arene. After completion of the reaction, benzene was removed under vacuum and the dissolved (CH_2Cl_2) residue filtered through a short column of alumina or silica. The evaporated extract was separated either on a chromatotron or plc plate (CH_2Cl_2/pet. spirit (60-80°C) or EtOAc/pet. spirit (60-80°C) eluent).

Preparation of 1-methyl-2,3-diphenylinden-1-ol (**40**): η^2-(2-acetylphenyl) tetracarbonylmanganese (0.104 g, 0.364 mmol) and diphenylacetylene (0.067 g, 0.376 mmol) were refluxed in benzene over 8 h to give $Mn_2(CO)_{10}$ (0.026 g, 46% based on 1) and 1-methyl-2,3-diphenylinden-1-ol (0.107 g, 98%), m.p. 145-146°C (lit. 143°C [9]). Found: C, 88.34, H, 6.08 %; $C_{22}H_{18}O$ calcd: C, 88.56, H, 6.08, %, M 298.39. MS(P^+) 298. ^{1}H NMR: δ 7.35 (m, 4H, H4-7), 7.20 (br s, 10H, H2'-6',2"-6"), 2.39 (br s, 1H, OH), 1.51 (s, 3H, CH_3). ^{13}C NMR: δ 149.6 (C7a), 147.0 (C2), 142.1 (C3a), 138.6 (C3), 134.8, 134.7 (C1',1"), 129.4, 129.3, 128.5, 127.9 (C2',3',5',6',2",3",5",6"), 128.4, 126.6 (C6,7), 127.5, 127.2 (C4',4"), 121.8, 120.7 (C4,5), 83.3 (C1), 24.0 (CH_3).

Same reaction in methanol solvent: similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.099 g, 0.346 mmol) and diphenylacetylene (0.067 g, 0.376 mmol) refluxed in methanol (15 ml) over 18 h gave $Mn_2(CO)_{10}$ (0.041 g, 76%), acetophenone (0.009 g, 22%) and 1-methyl-2,3-diphenylinden-1-ol (0.053 g, 51%). A repeated preparation with the exclusion of light and refluxing in methanol (40 ml) over 7 h gave the indenol (0.045 g, 39%), acetophenone (0.016 g, 35%) and some unreacted starting material (0.017 g, 15%).

Preparation of 1-methylinden-1-ol (**41**): similarly, η^2-(2-acetylphenyl) tetracarbonylmanganese (0.103 g, 0.360 mmol) and acetylene (continuous flow) were refluxed in benzene over 18 h to give $Mn_2(CO)_{10}$ (0.010 g, 18%) and 1-methylinden-1-ol (0.034 g, 64%) as thin white needles, m.p. 93-96°C (subl.). Found: C, 81.44, H, 7.10 %; $C_{10}H_{10}O$, calcd: C, 82.16, H, 6.89 %, M 146.19, MS(P^+) 146. ^1H NMR: δ 7.41 (m, 4H, H4-7), 6.65 (d, J = 5.6 Hz, 1H, H2), 6.32 (d, J = 5.6 Hz, 1H, H3), 2.10 (br s, 1H, OH), 1.61 (s, 3H, CH_3). ^{13}C NMR: δ 149.4 (C7a), 143.0 (C2), 141.2 (C3a), 130.1 (C3), 128.4, 126.4 (C6,7), 121.6, 121.5 (C4,5), 82.3 (C1), 23.7 (CH_3).

Preparation of 1-methyl-2,3-di-n-propylinden-1-ol (**42**): similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.111 g, 0.388 mmol) and 4-octyne (60 μl, 0.409 mmol) refluxed in benzene over 18 h gave $Mn_2(CO)_{10}$ (0.009 g, 15%) and 1-methyl-2,3-di-n-propylinden-1-ol (0.046 g, 51%) as colourless square plates, m.p. 79.5-81°C. Found: C, 83.31, H, 9.61 %; $C_{16}H_{22}O$ calcd: C, 83.43, H, 9.63 %, M 230.35. MS(P^+) 230. ^1H NMR: δ 7.18 (m, 4H, H4-7), 2.42 (t, J = 6.4 Hz, 2H, H1' or 1''), 2.33 (t, J = 7.3 Hz, 2H, H1' or 1''), 1.58 (m, 4H, H2',2''), 1.54 (s, 3H, CH_3), 1.00 (t, J = 7.3 Hz, 3H, 3' or 3''-CH_3), 0.98 (t, J = 7.3 Hz, 3H, 3' or 3''-CH_3). ^{13}C NMR: δ 149.6 (C7a), 148.0 (C2), 143.0 (C3a), 136.5 (C3), 128.0, 125.1 (C6,7), 121.2, 118.8 (C4,5), 82.5 (C1), 27.4, 27.2 (C1',1''), 23.6 (1-CH_3), 22.8, 21.7 (C2',2''), 14.7, 14.3 (C3',3'').

Preparation of 1-methyl-2,3-bis(trimethylsilyl)inden-1-ol (**43**): similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.108 g, 0.378 mmol) and bis(trimethylsilyl)acetylene (0.068 g, 0.399 mmol) refluxed in benzene over 64 h gave $Mn_2(CO)_{10}$ and some starting metalated arene as an inseparable mixture (0.030 g) and 1-methyl-2,3-bis(trimethylsilyl)inden-1-ol (0.008 g, 9%) as white granules, m.p. 125-128°C. $C_{16}H_{26}OSi_2$ M 290.56. MS(P^+) 290. ^{1}H NMR: δ 7.35 (m, 4H, H4-7), 2.61 (s, 1H, OH), 1.60 (s, 3H, 1-CH_3), 0.41 (s, 9H, Si-CH_3), 0.38 (s, 9H, Si-CH_3).

Preparation of 1,2,3-triphenylinden-1-ol (**44**): similarly, η^2-(2-benzoylphenyl) tetracarbonylmanganese (0.122 g, 0.350 mmol) and diphenylacetylene (0.065 g, 0.365 mmol) refluxed in benzene over 18 h gave $Mn_2(CO)_{10}$ (0.010 g, 18%) and 1,2,3-triphenylinden-1-ol (0.107 g, 85%) as a colourless oil. ^{1}H NMR: δ 7.90 (m, 19H). ^{13}C NMR: δ 150.9 (C7a), 147.6 (C2), 142.7 (C3a), 141.7 (C1'), 140.5 (C3), 134.8 (C1''), 133.9 (C1'''), 129.5, 129.2, 128.7, 128.4, 127.8, 127.0 (C2'-6',2''-6'',2'''-6'''), 127.2, 125.1 (C6,7), 123.2, 121.0 (C4,5), 87.0 (C1).

Preparation of 1-methyl-2-phenylinden-1-ol (**45**): similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.090 g, 0.315 mmol) and phenylacetylene (0.104 ml, 0.947 mmol) refluxed in benzene over 3.5 h gave **46** as a yellow/brown oil (0.027 g, 14% based on Mn reagent) and 1-methyl-2-phenylinden-1-ol (0.059 g, 84%) as a white solid, m.p. 123-125°C (lit. 123-125°C [37]). Found: C, 86.49, H, 6.24 %; $C_{16}H_{14}O$ calcd: C, 86.45, H, 6.35 %, M 222.29. MS(P^+) 222. ^{1}H NMR: δ 7.91 (dd, J = 7.30 Hz, J = 1.30 Hz, 2H), 7.48 (dq, J = 7.16 Hz, J = 0.92 Hz, 1H, H4), 7.41 (tm, J = 7.45 Hz, 2H, H3',5'), 7.32 (tt, J = 7.35 Hz, J = 1.30 Hz, 1H, H4'), 7.25 (m, 3H, H5,6,7), 1.93 (s, 1H, OH), 1.67 (s, 3H, CH_3). ^{13}C NMR: δ 151.3, 151.1 (C2,7a), 140.5 (C3a), 134.1 (C1'), 128.6, 126.3 (C6,7), 128.5 (C3',5'), 127.8 (C4'), 126.8 (C2',6'), 125.6 (C3), 121.6, 121.4 (C4,5), 83.1 (C1), 24.6 (CH_3). η^6-[1-(2-acetylphenyl)-2,4,6-triphenylcyclohexa-2,5-dienyl]tricarbonylmanganese (**46**): M($C_{35}H_{25}MnO_4$) 564, MS(P^+) 564. IR: 2015(s), 1978(w), 1952(s), 1939(br, s). ^1H NMR δ: 7.33, 7.18 (br s, ca. 19H), 6.41 (br s), 6.16 (br d, J=5.4 Hz), 5.74 (br d, J=8.1 Hz), 5.32 (br s), 2.28 (br s, 1H, H1'), 2.03 (br s, 3H, CH_3). ^{13}C NMR δ: 224.0 (CO), 176.5 (C=O), 141.3, 140.3, 138.0, 137.8, 135.7 (C1,2,1'',1''',1''''), 130.6, 130.3, 127.2, 118.8 (C3,4,5,6), 128.9, 128.0, 127.9, 127.7 (C2''-6'',2'''-6''',2''''-6''''), 99.1 (C3',5'), 82.1, 73.2 (C2',4',6'), 21.1 (CH_3).

Preparation of 1-methyl-2-trimethylsilylinden-1-ol (**47**): similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.110 g, 0.386 mmol) and trimethylsilylacetylene (200 μl, 1.415 mmol) refluxed in benzene over 2 h gave 1-methyl-2-trimethylsilylinden-1-ol (0.069 g, 82%) as colourless square plates, m.p. 104.5-105°C (lit. 103-105°C [37]). Found: C, 71.50, H, 8.44 %; $C_{13}H_{18}OSi$ calcd: C, 71.50, H, 8.31 %, M 218.37. MS(P^+) 218. ^1H NMR: δ 7.08 (m, 4H, H4-7), 6.71 (br s, 1H, H3), 1.47 (s, 3H, 1-CH_3), 0.17 (s, 9H, Si-CH_3). ^{13}C NMR: δ 157.2 (C2), 152.9 (C7a), 141.6 (C3a), 139.9 (C3), 128.3, 126.4 (C6,7), 121.6, 121.1 (C4,5), 86.9 (C1), 25.0 (1-CH_3), -0.44 (Si-CH_3); and an unidentified yellow oil (0.024 g) with the following spectral characteristics: IR: 2014(vs), 1946(s), 1932(s), 1657(w), 1640(w). ^1H NMR: δ 7.35 (m, 4H), 4.80 (m, 2H), 4.29 (br s, 1H), 2.18 (s, 3H), 0.39 (s, 9H), 0.31 (s, 9H), 0.22 (s, 9H), 0.06 (s, ca. 6H). ^{13}C NMR: δ 187.7 (s), 146.2 (s), 143.5 (s), 128.4 (d), 126.5 (d), 125.1 (d), 122.9 (d), 118.5 (d), 103.1 (s), 93.9 (d), 60.1 (s), 29.8 (d), 14.0 (q), 2.28, 2.02, 0.91, 0.20, -0.25, -0.64 (all q).

Preparation of 1,3-dimethyl-2-n-propylinden-1-ol (**48**): similarly, η^2-(2-acetylphenyl)tetracarbonylmanganese (0.114 g, 0.399 mmol) and 2-hexyne (50 μl, 0.445 mmol) refluxed in benzene over 18 h gave $Mn_2(CO)_{10}$ (0.020 g, 32%) and 1,3-dimethyl-2-n-propylinden-1-ol (0.026 g, 32%) as a white oily solid. ^1H NMR: δ 7.17 (m, 4H, H4-7), 2.31 (t, J = 7.3 Hz, 2H, 1'-CH_2), 1.94 (s, 3H, 3-CH_3), 1.62 (m, 2H, 2'-CH_2), 1.45 (s, 3H, 1-CH_3), 0.98 (t, J = 7.0 Hz, 3H, 3'-CH_3). ^{13}C NMR: δ 149.6 (C7a), 147.9 (C2), 143.9 (C3a), 132.3 (C3), 128.3, 125.5 (C6,7), 121.1, 118.4 (C4,5), 82.6 (C1), 27.1 (C1'), 23.5 (1-CH_3), 22.6 (C2'), 14.5 (3'-CH_3), 10.2 (3-CH_3).

Preparation of 2,3-diphenylindenone (**49**): similarly, η^2-(2-N,N-dimethylamidophenyl)tetracarbonylmanganese (0.108 g, 0.343 mmol) and diphenylacetylene (0.062 g, 0.348 mmol) refluxed in benzene over 1 h gave $Mn_2(CO)_{10}$ (0.012 g, 22%) and 2,3-diphenylindenone (0.054 g, 56%) as red needles, m.p. 152-156°C (lit. 153-154°C [39]). Found: C, 89.61, H, 5.01 %; $C_{21}H_{14}O$ calcd: C, 89.33, H, 5.00 %, M 282.34. MS(P^+) 282. ^1H NMR: δ 7.59 (d, J = 12.5 Hz, 1H, H4 or 7), 7.40 (s, 5H, ArH), 7.26 (s, 5H, ArH), 7.07 (d, J = 12.5, 1H, H4 or 7). ^{13}C NMR: δ 196.4 (C=O), 155.3 (C3), 145.3 (C7a), 133.4 (C5), 132.8, 132.4 (C2,3a), 130.8, 130.8 (C1',1''), 130.0, 128.8, 128.5, 128.1 (C2',3', 5',6',2'',3'',5'',6''), 129.3, 128.9 (C4',4''), 127.7, 122.9, 121.3 (C4,6,7).

Preparation of η^6-[1-(2-*N,N*-dimethylamidophenyl)cyclohexa-2,5-dienyl] tricarbonylmanganese (**50**): similarly, η^2-(2-*N,N*-dimethylamidophenyl) tetracarbonylmanganese (0.110 g, 0.349 mmol) and acetylene (continuous flow) refluxed in benzene over 2 h gave η^6-[1-(2-dimethylamidophenyl) cyclohexadienyl]tricarbonylmanganese (0.070 g, 55%) as yellow needles, m.p. 61-65°C (dec.). Found: C, 58.90, H, 4.36, N, 3.80 %; $C_{18}H_{16}MnNO_4$ calcd: C, 59.19, H, 4.42, N, 3.83 %, M 365.27. MS(P^+-2CO) 309. IR: 2017(s), 1930(s), 1640(m) [40]. ^1H NMR: δ 7.27 (td, J = 7.6 Hz, J = 1.4 Hz, 1H, H4' or 5'), 7.18 (td, J = 7.5 Hz, J = 1.3 Hz, 1H, H4' or 5'), 7.08 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H, H3' or 6'), 7.05 (dd, J = 7.5, J = 1.4 Hz, 1H, H3' or 6'), 5.75 (tt, J = 5.3 Hz, J = 1.3 Hz, 1H, H4), 4.97 (br t, J = 5.5 Hz, 2H, H3,5), 3.91 (t, J = 5.9 Hz, 1H, H1), 3.38 (br t, J = 6.3 Hz, 2H, H2,6), 3.18 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3). ^{13}C NMR: δ 222.6 (CO), 171.1 (C=O), 142.9 (C2'), 133.7 (C1'), 128.8, 126.9, 126.6, 125.6 (C3'-6'), 96.5 (C3,5), 79.2 (C4), 57.1 (C2,6), 38.7 (NCH_3), 36.5 (C1), 34.5 (NCH_3).

Preparation of 2,3-diphenyl-4,5,6-trimethoxyindenone (**52**): similarly, η^2-(2-methylcarboxy-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (0.098 g, 0.250 mmol) and diphenylacetylene (0.048 g, 0.269 mmol) refluxed in benzene over 1 h gave $Mn_2(CO)_{10}$ (0.002 g, 5%) and 2,3-diphenyl-4,5,6-trimethoxyindenone (0.098 g, 100%) as a maroon solid, m.p. 124-126°C. Found: C, 77.39, H, 5.57 %; $C_{24}H_{20}O_4$ calcd: C, 77.40, H, 5.41 %, M 372.42. MS(P^+) 372. ^1H NMR: δ 7.34 (s, 5H, ArH), 7.16 (s, 5H, ArH), 7.08 (s, 1H, H7), 3.89 (s, 6H, 4,5-OCH_3), 3.29 (s, 3H, 6-OCH_3). ^{13}C NMR: δ 195.3 (C=O), 156.2 (C5), 154.3 (C3), 149.3, 147.7 (C4,6), 134.6 (C7a), 132.3 (C3a), 130.9 (C1''), 129.8, 128.4, 127.8 (C2',3',5',6',2'',3'',5'',6''), 128.9 (C1'), 127.2 (C4,4'), 126.2 (C2), 105.0 (C7), 61.0 (4,5-OCH_3), 56.5 (6-OCH_3).

Preparation of η^6-[1-(2-carboxymethyl-4,5,6-trimethoxyphenyl)-cyclohexadienyl]tricarbonylmanganese (**53**): similarly, η^2-(2-carboxymethyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (0.110 g, 0.280 mmol) and acetylene refluxed over 7 h in benzene gave $Mn_2(CO)_{10}$ (0.004 g, 9%) and **53** (0.045 g, 36%) as a yellow oil. M 442.31. MS(P^+-2CO) 386. ^1H NMR: δ 6.70 (s, 1H, H2'), 5.74 (t, J = 4.7 Hz, 1H, H4), 4.87 (t, J = 6.1 Hz, 2H, H3,5), 4.44 (t, J = 5.56 Hz, 1H, H1), 4.07 (t, J = 7.9 Hz, 2H, H2,6), 3.91, 3.82, 3.53 (each s, 3H, 6H, 3H, -OCH_3). ^{13}C NMR: δ 222.1 (CO), 169.6 (C=O), 152.6 (C5'), 151.8 (C6'), 144.6 (C4'), 131.6 (C2'), 129.4, 127.5, 126.9 (?), 126.2 (C1'), 107.8 (C3'), 96.7 (C3,5), 79.2 (C4), 60.6, 60.5 (5',6'-OCH_3), 58.7 (C2,6), 55.9 (4'-OCH_3), 52.2 (COO<u>Me</u>), 34.9 (C1).

Preparation of 2,3-diphenyl-5-dimethylaminoindenone (**54**): similarly, η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (0.181 g, 0.574 mmol) and diphenylacetylene (0.103 g, 0.578 mmol) refluxed in benzene over 9 h gave $Mn_2(CO)_{10}$ (0.032 g, 36%) and **54** (0.086 g, 46%) as a maroon solid, m.p. 213-218°C. Found: C, 84.99, H, 5.58, N, 4.38%; $C_{23}H_{19}NO$ calcd: C, 84.89, H, 5.88, N, 4.30%, M 325.40. MS(P^+) 325. ^1H NMR: δ 7.39 (s, 5H, ArH), 7.26 (s, 5H, ArH), 6.45 (br d, J = 12 Hz, 1H, H6), 3.04 (s, 6H, NCH_3). ^{13}C NMR: δ 194.7 (C=O), 154.3 (C5), 152.0 (C3), 148.2 (C3a), 134.3, 133.3 (C1',1''), 131.4 (C2), 130.0, 128.7, 127.8, 127.4 (C2'-6',2''-6''), 125.2 (C7), 117.9 (C7a), 108.2 (C6), 106.5 (C4), 40.4 (NCH_3).

Preparation of 5-dimethylaminoindenone (**55**): similarly, η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (0.138 g, 0.438 mmol) and acetylene (continuous flow) refluxed in benzene (40 ml) over 3.5 h gave $Mn_2(CO)_{10}$ (0.004 g, 6%) and **55** (0.015 g, 20%) as a red oil. ^1H NMR: δ 7.73 (d, J = 8.9 Hz, 1H, H7), 7.34 (d, J = 5.7 Hz, 1H, H2), 6.43 (d, J = 2.3 Hz, 1H, H4), 6.26 (dd, J = 8.8 Hz, J = 2.9 Hz, 1H, H6), 5.84 (d, J = 5.8 Hz, 1H, H3), 3.06 (s, 6H, NCH_3).

Preparation of dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]indole-2,3-dicarboxylate (**56**): similarly, η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (0.077 g, 0.237 mmol) and dimethyl acetylenedicarboxylate (30 μl, 0.244 mmol) refluxed in pet. spirit (60-80°C) over 5 h gave $Mn_2(CO)_{10}$ (0.015 g, 41%), η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (0.016 g, 21%) and **56** (0.012 g, 17%) as yellow needles, m.p. 97.5-99.5°C. Found: C, 63.59, H, 5.03, N, 4.93%; $C_{16}H_{15}NO_5$ calcd: C, 63.78, H, 5.02, N, 4.65%, M 301.30. MS(P^+) 301. ^{1}H NMR: δ 7.58 (m, 2H, ArH), 7.17 (m, 2H, ArH), 6.59 (s, 1H, H4), 3.91, 3.86 (each s, 3H, COOMe), 1.95 (s, 3H, CH_3). ^{13}C NMR: δ 162.9 (C=O), 140.7 (C2), 137.0 (C8a), 134.5 (C3a), 132.9, 132.5 (C3,4a), 124.4 (C6), 122.8 (C5), 120.6 (C7), 110.6 (C8), 99.8 (C4), 90.2 (C1), 52.8, 52.5 (COOMe), 24.0 (CH_3).

Preparation of 1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole (**58**): similarly, η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (0.171 g, 0.527 mmol) and diphenylacetylene (0.101 g, 0.569 mmol) refluxed in benzene over 1 h gave $Mn_2(CO)_{10}$ (0.034 g, 41%), *N*-acetylindole (0.030 g, 35%), diphenylacetylene (0.038 g, 38% of starting diphenylacetylene) and **58** (0.019 g, 11%) as a green oil. M 337.42. MS(P^{+-}) 207. ^{1}H NMR: δ 7.29 (m, 14H, ArH), 6.36 (s, 1H, H4), 2.66 (br s, 1H, OH), 1.79 (s, 3H, CH_3). ^{13}C NMR: δ 145.5, 143.3 (C2,3), 133.1 (C3a), 131.2, 129.3, 128.9, 128.6, 128.4, 128.0, 127.8, 127.4, 126.8, 125.8, (C8a,4a,1'-6',1"-6"), 122.5 (C6), 121.8 (C5), 119.8 (C7), 110.1 (C8), 95.2 (C4), 91.5 (C1), 23.8 (CH_3).

Preparation of 2-(but-1-en-3-onyl)indole (**57**): similarly, η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese (0.139 g, 0.427 mmol) and acetylene (continuous flow) refuxed in benzene (40 ml) over 2 h gave $Mn_2(CO)_{10}$ (0.003 g, 5%), **57** (0.013 g, 16%) as a yellow oil: M 185.23, MS(P^+) 185. ^{1}H NMR: δ 7.22 (m, 4H, H4-7), 6.80 (s, 1H, H3), 6.76 (d, J = 12.3 Hz, 1H, H1'), 6.12 (d, J = 12.6 Hz, 1H, H2'), 2.35 (s, 3H, CH_3). ^{13}C NMR: δ 199.4 (C=O), 137.4 (C7a), 134.4 (C2), 133.9 (C1'), 128.1 (C3a), 125.3, 121.5, 120.3, 120.1 (C4,5,6,2'), 112.4, 112.3 (C3,7), 31.7 (CH_3), and an unidentified red oil (0.017 g) with the following spectral characterisitics: MS(P^+) 401; other major peaks: 374, 358, 330, 229, 117. ^{1}H NMR: δ 8.44 (d, J = 9.1 Hz), 7.90 (m), 7.29 (m), 6.69 (d, J = 9.9 Hz), 5.97 (d, J = 9.9 Hz), 3.32 (t, J = 5.4 Hz), 2.79 (s), 2.60 (s), 2.50 (m). ^{13}C

NMR: δ 136.2 (s), 130.3 (d), 125.1, 124.0, 123.7, 123.4, 121.8, 121.3, 120.8, 120.2, 119.5, 119.2 (all d), 116.5, 114.7, 111.5, 109.1, 59.0, 36.8, 27.5, 26.1, 23.9, 20.2.

Crystal Structure of 1-methyl-2,3-diphenylinden-1-ol (40)

Crystals of 1-methyl-2,3-diphenylinden-1-ol were grown from hot petroleum spirit (60-80°C). A colourless square plate showed tetragonal symmetry from preliminary precession photography. Intensity data were collected of a rectangular plate of dimensions 0.64 x 0.34 x 0.10 mm on an Enraf-Nonius CAD4 automatic four-circle diffractometer using monochromated Mo-Kα X-rays.

Data: $C_{22}H_{18}O$, M 298.39, tetragonal, space group $P4_2/n$. a=11.831(2), b=11.831(2), c=24.076(8) Å. U 3369.7 Å^3, D_c=1.15 g cm^{-3} for Z=8. F(000) 1264, μ(Mo-Kα) 0.75 cm^{-1}, T= -100°C. Intensity data in the range $4<2\theta<45°$ were collected using a θ-2θ scan technique.

A total of 2204 unique reflections were collected and those 1198 for which $I>2\sigma(I)$ were used in all calculations. The positions of all heavy atoms were located using the TREF (direct methods) option of SHELXS-86. In the final cycle of full-matrix least-squares refinement, the "fixed" non-hydrogen atoms (C(1-9) and O(1), those held in more rigid positions) were treated isotropically because of the limited number of reflections, and the "dangling" carbons (C(11-16) and C(21-26)) were assigned anisotropic temperature factors. The hydroxyl hydrogen atom was discernible as the strongest unassigned peak of electron density in the penultimate difference map and was included in the final refinement with fixed parameters. All other hydrogen atoms were assigned to calculated positions. The refinement converged at R=0.073, R_w=0.073 where $w=[\sigma^2(F) + 0.000668F^2]^{-1}$. No parameter shifted by more than 0.04σ in the final cycle and the residual electron density was 0.36 $eÅ^{-3}$. Thermal parameters, final positions, bond distances and angles are in Appendix III.

Crystal Structure of dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]indole-2,3-dicarboxylate (56)

Crystals of **56** were grown by liquid diffusion (CH_2Cl_2/pet. spirit (60-80°C), ca. 1/4)) at 4°C. X-ray photography of a yellow plate of dimensions 0.20 x 0.16 x 0.08 mm indicated monoclinic symmetry and intensity data were collected on an Enraf-Nonius CAD4 four-circle diffractometer using monochromated Mo-Kα X-rays.

Crystal data: $C_{16}H_{15}NO_5$, M 301.30, monoclinic, space group $P2_1/c$. a=11.40(1), b=6.674(5), c=19.96(2), β=108.59(8)°. U 1439(2) $Å^3$, D_c= 1.35 for Z=4, F(000) 632, μ(Mo-Kα) = 0.97 cm^{-1}, T= -135°C. Intensity data in the range $4<2\theta<45°$ were collected using a θ-2θ scan technique.

A total of 1873 unique reflections were collected, but because of the small crystal size, only 482 with $I>3\sigma(I)$ were available for further calculations. The heavy atom positions were located by the TREF option of SHELXS-86.

In the final cycle of full-matrix least-squares refinement, all non-hydrogen atoms were treated isotropically because of the low number of data collected. As with the diphenylindenol structure, the hydroxyl hydrogen atom was located as the strongest remaining peak in the penultimate difference map, then included in the final refinement with fixed parameters. All other hydrogen atoms were assigned to calculated positions. The refinement converged at $R=0.076$, $R_w=0.072$, where $w = [\sigma^2(F) + 0.00104F^2]^{-1}$. No parameter shifted by more than 0.10σ in the final cycle, and the difference map showed no peak or trough greater than 0.39 eÅ^{-3}. Atom coordinates, bond lengths and angles and other structural information are in Appendix IV.

Gas chromatography (for detection of reduced products): Experiments were carried out on a Pye 104 machine, containing a 2 metre 10% SE 30 column. Diphenylacetylene, trans-stilbene and 2,3-diphenyl-5-dimethylaminoindenone standards of 2 mg ml^{-1} in benzene were injected in 1 µl quantities. A temperature programme of 40-250°C at 10°C per minute was sufficient to observe reproducible retention times for diphenylacetylene and trans-stilbene, but no indenone was ever eluted. Injection of the crude reaction mixture resulted in only one peak being observed, which was judged compatible with diphenylacetylene (retention time 13.0 minutes, elution temperature 230°C).

NMR experiment for reduction products: η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (0.021 g, 0.066 mmol) and diphenylacetylene (0.011 g, 0.063 mmol) were degassed under vacuum in an NMR tube. Hexadeuteriobenzene (ca. 1 ml) was distilled into the tube using a liquid nitrogen trap, and the tube was sealed. The tube was heated at 60°C for a total of 46 hours, recording spectra at 1 hour intervals for hours 1-5, then at hours 18, 20, 25 and 45. The progress of the reaction was evident by the depletion of the metalated arene NMe_2 and CHO signals and the concurrent appearance of a new NMe_2 signal. After 46 hours, the spectra were no longer changing: the temperature was therefore increased to 70°C for 4 hours, with no significant change, then to 80°C for a further 5 hours, again with no change. At no time were there any signals that might be attributed to an indenol or an $HMn(CO)_5$ product. To check that the reaction had proceeded with normal coupling, the tube was opened and the products separated to give $Mn_2(CO)_{10}$ (0.0066 g, 64%), 2,3-diphenyl-5-dimethylaminoindenone (0.0125 g, 61%), some unreacted η^2-(2-formyl-5-dimethylaminophenyl)tetracarbonylmanganese (0.0020 g, 10%) and unreacted diphenylacetylene (0.0010 g, 9%).

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Chapter 5

Reactions of some (arene)M(CO)$_3$ Complexes

The following work is only exploratory in nature. As often happens in projects of this type, various peripheral areas of research are concurrently pursued, to increase the chances of discovery of an interesting set of reactions in any one area. If unsuccessful, those peripheral areas are often omitted or forgotten in the final report, and researchers that follow can find no clear statement describing the general line of investigation, or sometimes, experimental procedures. The following set of experiments, although not a rigorous study of (arene)tricarbonyl metal species, showed no promising signs of products. It has nevertheless been included as a guideline to any in future who follow the line of electrophilic substitutions of these species and who might benefit from a description of the pitfalls.

Reactions of some (arene)Cr(CO)$_3$ Complexes

5.1 Introduction

Since the discovery of bis(benzene)chromium in 1955, and the subsequent preparation of [(benzene)Cr(CO)$_3$] [1] (also known as benchrotrene), much has been written about the π-arene chemistry of chromium. The range of (η^6-arene)Cr(CO)$_3$ compounds that have been synthesized is large and includes a wide variety of substituents on the arene [2], such as halide, hydroxy, trialkylstannyl, trialkylsilyl, amino, acetyl, alkoxy and carboxyalkyl groups: all of which were obtained by heating Cr(CO)$_6$ with the arene.

Electron donating groups on the ring, such as dimethylamino, promote the reaction, and electron withdrawing groups retard it. Arenes with strongly electron withdrawing groups (CHO, COOH or NO_2) generally require such forcing conditions that isolation of the π-arene complex is not observed. Despite its extensive use, the mechanism of the direct $Cr(CO)_6$/arene reaction has not yet been established.

Moser and Rausch [3] have reported that some arenes, such as styrene, do not react with $Cr(CO)_6$ under standard conditions. Rather, they require the more reactive trisammine complex $(NH_3)_3Cr(CO)_3$ to furnish (styrene)tricarbonylchromium. The route also provides access to sterically crowded (arene)tricarbonylchomium complexes such as (t-butylbenzene)$Cr(CO)_3$ (50% yield, cf. reported yield of 5% by $Cr(CO)_6$ method), products such as (iodobenzene)$Cr(CO)_3$ that have only been previously obtained via lithiation of (benzene)$Cr(CO)_3$ and other rarities such as (thiophene)$Cr(CO)_3$.

The arene ligand is η^6-bonding, a six electron donor that occupies three coordination sites. The net effect of the $Cr(CO)_3$ moiety is electron withdrawing with respect to the free ligand, and the chemistry of (arene)tricarbonylchromium complexes strongly reflects this in several important ways [4]:

(i) enhanced acidity of ring protons and substituent group protons;
(ii) enhanced susceptibility to nucleophilic substitution; and
(iii) steric hindrance of the $Cr(CO)_3$ face of the arene.

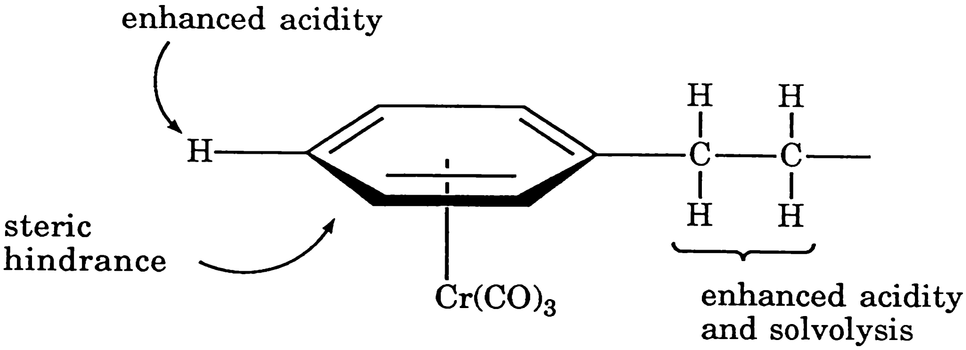

Figure 5.1

As a result, the applications of nucleophilic substitution to synthesis have been extensively studied and reviewed [1,4,5]. It was, however, the possibilities of reactions with mild (non-oxidising) electrophiles that were to be the basis of this study.

Several authors mention the scarcity of products that have arisen from such reactions. Clearly, electron withdrawal from the arene to chromium (an effect considered similar in magnitude to the effect of a nitro group [4]) accounts for the reduced reactivity with electrophiles. According to Collman and Hegedus [4] only Friedel Crafts acylation is viable, furnishing a different isomeric ratio for (toluene)$Cr(CO)_3$ from that with the free ligand, toluene. Other sources [2] confirm the technical problems inherent in reacting an easily oxidised substrate with a strongly oxidising electrophilic reagent. The instability towards strong acids compounds the problem, prohibiting the nitration and sulphonation reactions.

Apart from Friedel Crafts acylation, the only electrophilic reaction that has shown any success is the mercuration of (benzene)$Cr(CO)_3$, reported by Magomedov *et al* [6]. When (benzene)$Cr(CO)_3$ (I) and mercuric acetate were reacted in refluxing ethanol (Figure 5.2), mercuration proceeded to give (‡), which was converted to the chloromercury derivative by the addition of $CaCl_2$. Because the mercuration was seen to occur with "ease", it was concluded that the electron density of the ring in (I) was "raised relative to benzene", which contradicts much of the available evidence on the ring electron density*. The reagent for mercuration, mercuric acetate, at least has the advantage of being non-oxidising with respect to Cr(0).

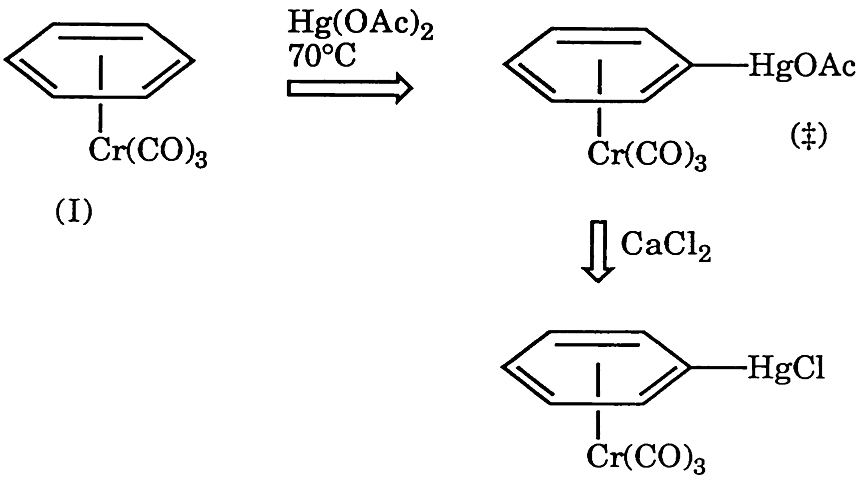

Figure 5.2

Mercurations have been extensively studied as an arene substitution reaction. The mechanism is well known: it follows a typical electrophilic aromatic substitution, and the mercurinium σ-complex (Figure 5.3) has been detected by NMR spectroscopy [7]. A number of reviews [8,9,10] cover aromatic mercurations in some depth.

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* pKa and pKb data [4] of species such as (benzoic acid)chromium tricarbonyl and (aniline)chromium tricarbonyl support the notion that the bound arene has a lower electron density than the free arene. Infra-red data of (benzene)chromium tricarbonyl [4] indicate an increased electron density on the metal by comparison with chromium hexacarbonyl.

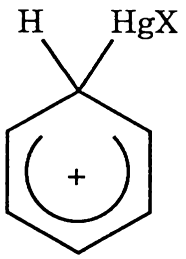

Figure 5.3

A problem in free arene mercurations is the lack of selectivity: many are prone to form isomeric mixtures, or mixtures of mono-, di- and trimercurated products [15,16].

If the electron density in the ring was reduced, as it is in (benzene)$Cr(CO)_3$, the preferred site(s) of substitution might be different and the possibility exists that the reaction might become more selective than in previous studies [15,16]. It was hoped in this study then, that greater selectivity might be achieved in the mercuration of (arene)$Cr(CO)_3$ than is currently observed in free arenes.

5.2 Results and Discussion

5.2.1 (Arene)$Cr(CO)_3$ Preparation and Reactions

A number of variations on the original method of preparation [1-3] were tried in an effort to optimise the yield of (arene)$Cr(CO)_3$ product. The preparation of $(NH_3)_3Cr(CO)_3$ as an alternative [3] to $Cr(CO)_6$ was found to be technically messy and often resulted in an impure $(NH_3)_3Cr(CO)_3$ product. When obtained in reasonable purity, however, its use as a reagent was generally superior to the direct reaction of the arene with $Cr(CO)_6$. Davis and Kane-Maguire reported [2] that the specific use of coordinating solvents, such as THF or di-n-butylether, or specific mixtures of the two, furnish better yields of (arene)Cr$(CO)_3$ for most arenes. A 10/1 THF/di-n-butylether mixture was thereafter adopted as a standard approach, although yields of (arene)Cr$(CO)_3$ did not exceed 25% at any time.

The reaction of (benzene)Cr$(CO)_3$ with mercuric acetate in refluxing ethanol, reported by Magomedov [6] and described in the introduction, provided the impetus for most of the (arene)Cr$(CO)_3$ work. It was originally hoped that (arene)Cr$(CO)_3$ complexes that were more activated to electrophilic attack than (benzene)Cr$(CO)_3$, such as (toluene)Cr$(CO)_3$, would be more susceptible to substitution by mercuric acetate, and might therefore afford routes to less accessible ring substitution positions.

After several attempts at the Magomedov experiment were unsuccessful, some effort was still directed at mercuric acetate substitution of the more activated species, such as the toluene, veratrole and durene analogues of (benzene)Cr$(CO)_3$.

Under conditions of stirring at 70°C with mercuric acetate in ethanol, none of the above underwent the mercuration reaction. Facile degradation of the starting material to the arene and Cr^{3+} was a particular problem for the less stable species, such as (veratrole)Cr$(CO)_3$, but in most other cases, unreacted (arene)Cr$(CO)_3$ was recovered as the only product. Higher temperature experiments were tried for the sturdier substrates, such as (toluene)Cr$(CO)_3$ with mercuric acetate in refluxing ethanol, but afforded the same result.

Mercuric trifluoroacetate has been described as a more effective mercurating agent than mercuric acetate, especially in trifluoroacetic acid solvent [8]. Compared with mercuration in acetic acid, mercuric trifluoroacetate in trifluoroacetic acid reacts faster by a factor of 69×10^4 (benzene substrate), and does not suffer the disadvantages of the former medium [9], such as competitive mercuration of the solvent, or isomerisation of products. Attempts to use this combination in the presence of (veratrole)$Cr(CO)_3$, (durene)$Cr(CO)_3$ and (toluene)$Cr(CO)_3$ at room temperature resulted in either decomplexation of the arene or recovery of the (arene)$Cr(CO)_3$ starting material. Similar efforts using mercuric trifluoroacetate in ethanol were no more successful.

Other assorted attempts to obtain a mercurated (arene)$Cr(CO)_3$ product involved lithiation of (arene)$Cr(CO)_3$ in THF followed by quenching with $HgCl_2$: this resulted in recovery of the starting reagent only.

5.2.2 [(Arene)Mn(CO)$_3$]$^+$ Preparation and Reactions

An avenue of research that was only briefly studied, but that could prove fruitful in the future, was reaction of electrophiles with hydrido adducts of [(arene)$Mn(CO)_3$]$^+$ species.

A number of [(arene)$Mn(CO)_3$]$^+$ salts were prepared by a standard procedure [12] in which the arene was added to a stirred solution of $BrMn(CO)_5$ and $AlCl_3$ in 1,2-dichlorobenzene and heated at 90-100°C. Yields were generally good, ranging from 17% for [(diphenylmethane) $Mn(CO)_3$]$^+PF_6^-$ to 66% for [(hexamethylbenzene)-$Mn(CO)_3$]$^+$ PF_6^-.

As it was highly unlikely that the manganese cationic species would be susceptible to electrophilic attack, attempted substitutions were carried out on the reduced form of these complexes (below).

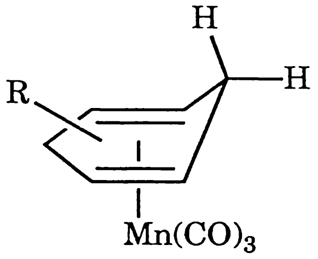

Figure 5.5

The (cyclohexadienyl)Mn(CO)$_3$ preparations were, however, not without their problems. The method used by Pauson *et al* [13] was to treat [(arene)Mn(CO)$_3$]$^+$ with lithium aluminium hydride or sodium borohydride (typical crude yields of 85%), a procedure that we were unable to reproduce as effectively. An alternative treatment was found to be with lithium triethylborohydride ("Super-Hydride^{TM}"), which in one case ([(toluene)Mn(CO)$_3$]$^+$) gave rise to 62% reduced product.

Treatment of the reduced durene analogue with mercuric acetate resulted in the starting material only, while the reaction of a mixture of isomeric reduced [(toluene)Mn(CO)$_3$]$^+$ (Figure 5.6) with bromine afforded demetalation and the recovery of BrMn(CO)$_5$.

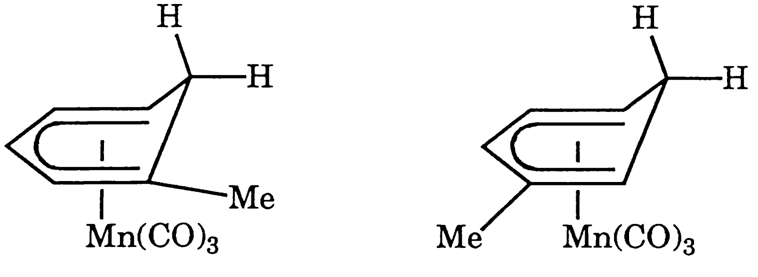

Figure 5.6

One final experiment was an attempted Friedel-Crafts acylation of [(benzene)Mn(CO)$_3$]$^+$, which afforded only the starting material.

5.3 Experimental

The following commercial starting materials were used as received: chromium hexacarbonyl (Pressure Chemicals), mercuric acetate (May and Baker, 96%), mercuric chloride, mercuric oxide (red, BDH, 99%), 1,2,4,5-tetramethylbenzene (durene) (Aldrich), benzene (BDH, AR), toluene (BDH, AR), 1,2-dimethoxybenzene (veratrole) (BDH), phenyl methyl ether (anisole) (BDH, 95%), di-n-butyl ether and hexamethylbenzene (Aldrich).

Preparation of $(NH_3)_3Cr(CO)_3$: standard procedure [2,14] from $Cr(CO)_6$ (2.25 g, 10.2 mmol), KOH (3.93 g, 70.0 mmol), ammonia (conc., 60 ml, ca. 960 mmol) and ethanol (60 ml) gave 0.50 g $(NH_3)_3Cr(CO)_3$ (26% yield).

Preparation of mercuric trifluoroacetate: mercuric oxide (7.29 g, 33.6 mmol) was added to trifluoroacetic acid (20 ml, 268 mmol) at room temperature with stirring. The mixture was cooled to 0°C in an ice bath, upon which mercuric trifluoroacetate crystallised (6.01 g, 42%) as a white solid, m.p. (sealed capillary) 168°C (subl.) (lit. [17] 171-173°C).

(Arene)$Cr(CO)_3$ Preparations

Preparation of (veratrole)$Cr(CO)_3$: chromium hexacarbonyl (0.800 g, 3.64 mmol) was added to a solution of veratrole (0.46 ml, 3.63 mmol), THF (30 ml) and di-n-butyl ether (3 ml) and refluxed under nitrogen for 72 h. After cooling, the solvents were removed under vacuum and the residue purified by column chromatography to give an oily yellow solid (0.188 g, 19%). IR: 1968(s), 1895(s sh), 1890(s).

Preparation of (anisole)Cr(CO)$_3$: similarly, chromium hexacarbonyl (0.800 g, 3.64 mmol) and anisole (0.40 ml, 3.68 mmol) in THF/di-n-butyl ether were refluxed under nitrogen for 41 h to give a yellow solid (0.195 g, 22%), m.p. (sealed capillary) 79-80°C (lit. [2] 83-84°C). IR: 1972(s), 1895(s), 1890(s sh), 1869(w sh).

Preparation of (toluene)Cr(CO)$_3$: similarly, chromium hexacarbonyl (0.800 g, 3.64 mmol) and toluene (0.50 ml, 4.71 mmol) in THF/di-n-butyl ether when refluxed under nitrogen for 23 h gave (toluene)Cr(CO)$_3$ (0.202 g, 24%) as a yellow solid, m.p. (sealed capillary) 77-78°C (lit. [2] 80-81°C). IR: 1976(s), 1908(s), 1899(sh).

Preparation of (benzene)Cr(CO)$_3$: similarly, chromium hexacarbonyl (0.800 g, 3.64 mmol) and toluene (0.50 ml, 5.75 mmol) in THF/di-n-butyl ether, when refluxed under nitrogen for 24 h gave (benzene)Cr(CO)$_3$ (0.133 g, 17%) as a yellow solid, m.p. (sealed capillary) 156-157°C (lit. [2] 162-163°C). IR: 1981(s), 1914(s), 1905(sh).

Preparation of (durene)Cr(CO)$_3$: similarly, chromium hexacarbonyl (0.800 g, 3.64 mmol) and durene (0.50 ml, 4.71 mmol) in THF/di-n-butyl ether when refluxed under nitrogen for 18 h gave (durene)Cr(CO)$_3$ (0.241 g, 24%) as a yellow solid, m.p. (sealed capillary) 93-94°C. IR: 1966(s), 1895(br, s).

Attempted Mercurations

(Benzene)Cr(CO)$_3$/mercuric acetate: mercuric acetate (0.242 g, 0.76 mmol) was dissolved in ethanol (10 ml) and degassed. The solution was added to (benzene)Cr(CO)$_3$ (0.133 g, 0.62 mmol) and stirred at 70°C under nitrogen for 21 h. Tlc ($CHCl_3$) showed only the presence of (benzene)Cr(CO)$_3$.

(Toluene)Cr(CO)$_3$/mercuric acetate: similarly, (toluene)Cr(CO)$_3$ (0.120 g, 0.526 mmol) and mercuric acetate (0.243 g, 0.762 mmol) were refluxed in ethanol for 21 h. Plc resulted in only (toluene)Cr(CO)$_3$ (0.027 g, 22%).

(Veratrole)Cr(CO)$_3$/mercuric acetate: (veratrole)Cr(CO)$_3$ (0.210 g, 0.766 mmol) and mercuric acetate (0.340 g, 1.067 mmol) were refluxed in ethanol (20 ml) for 17 h. Plc resulted in the recovery of veratrole only (0.061 g, 58%).

(Durene)Cr(CO)$_3$/mercuric acetate: similarly, (durene)Cr(CO)$_3$ (0.241 g, 0.892 mmol) and mercuric acetate (0.313 g, 0.982 mmol) were refluxed in ethanol (15 ml) over 17 h. Some mercury metal was observed in the resulting green solution, due probably to the oxidation of Cr^0 to Cr^{3+} and concurrent reduction of Hg^{2+}. Tlc and plc showed only the presence of (durene)Cr(CO)$_3$.

(Veratrole)Cr(CO)$_3$/mercuric trifluoroacetate: mercuric trifluoroacetate (0.293 g, 0.686 mmol) was dissolved in trifluoroacetic acid (5 ml). The solution was degassed and added to (veratrole)Cr(CO)$_3$ (0.188 g, 0.686 mmol), resulting in a bright red solution. The mixture was stirred at 25°C under nitrogen over 2.3 h. Column chromatography (initial eluent CH_2Cl_2/pet. spirit (60-80°C) 3/2, then 100% CH_2Cl_2, then 100% ether) gave rise to only the starting arene, veratrole (0.065 g, 70%).

(Toluene)Cr(CO)$_3$/mercuric trifluoroacetate: similarly, (toluene)Cr(CO)$_3$ (0.050 g, 0.219 mmol) and mercuric trifluoroacetate (0.155 g, 0.363 mmol) were stirred in ethanol (10 ml) at 25°C for 16 h. Tlc ($CHCl_3$) showed only the presence of mercuric trifluoroacetate.

(Durene)Cr(CO)$_3$/mercuric trifluoroacetate: similarly, (durene)Cr(CO)$_3$ (0.070 g, 0.259 mmol) and mercuric trifluoroacetate (0.150 g, 0.352 mmol) were stirred in trifluoroacetic acid (10 ml) at 25°C over 2 h, and gave a bright orange solution. Tlc (CHCl$_3$) showed only the starting reagent (durene)Cr(CO)$_3$. Extraction with CHCl$_3$, washing with NaHCO$_3$ solution, drying and evaporation gave a yellow solid that was identified by NMR and tlc as (durene)Cr(CO)$_3$.

(Benzene)Cr(CO)$_3$/lithiation/mercuration: (benzene)Cr(CO)$_3$ (0.124 g, 0.579 mmol) was dissolved in THF (10 ml) and cooled to -78°C. n-BuLi (0.360 ml, 0.576 mmol) was added from a syringe over 0.5 h. The solution was warmed to 25°C and stirred for a further 0.5 h. Mercuric chloride (0.157 g, 0.579 mmol) was added over 0.25 h, and the mixture stirred for 2 h. Plc of the evaporated residue gave only (benzene)Cr(CO)$_3$ (0.042 g, 34%).

(Durene)Cr(CO)$_3$/lithiation/mercuration: similarly, using (durene)Cr(CO)$_3$ (0.048 g, 0.178 mmol), n-buLi (0.111 ml, 0.178 mmol) and mercuric acetate (0.057 g, 0.178 mmol). Tlc (CHCl$_3$) showed only (durene)Cr(CO)$_3$.

In summary, these attempted mercurations were characterised by recovery of unreacted (arene)Cr(CO)$_3$ or, in the case of veratrole by the free arene itself. The reason for reactant deficiency on workup is not apparent. Significant amounts of other organic products were not detected by chromatography.

[(Arene)Mn(CO)$_3$]$^+$ Preparations

Two representative examples are as follows. Preparation of [(toluene)Mn(CO)$_3$]$^+$PF$_6^-$: the standard procedure [12] using BrMn(CO)$_5$ (0.317 g, 1.15 mmol), AlCl$_3$ (0.314 g, 2.35 mmol) and toluene (2.00 ml, 18.8 mmol) in 1,2-dichlorobenzene (10 ml) gave a yellow powder (0.212 g, 49%), m.p. 200-202°C (dec.).

Preparation of $[(\text{durene})\text{Mn(CO)}_3]^+\text{PF}_6^-$: similarly from BrMn(CO)_5 (0.628 g, 2.28 mmol), AlCl_3 (0.686 g, 5.14 mmol) and durene (1.000 g, 7.45 mmol) in 1,2-dichlorobenzene (10 ml) gave a yellow powder (0.594 g, 62%), m.p. 233-237°C (dec.).

Also prepared were $[(\text{benzene})\text{Mn(CO)}_3]^+\text{PF}_6^-$, m.p. 201-203°C (dec.) and $[(\text{hexamethylbenzene})\text{Mn(CO)}_3]^+\text{PF}_6^-$, m.p. 237-238°C (dec.).

Reduction of $[(\text{durene})\text{Mn(CO)}_3]^+\text{PF}_6^-$: $[(\text{durene})\text{Mn(CO)}_3]^+\text{PF}_6^-$ (0.100 g, 0.239 mmol) was dissolved in THF (10 ml). "Super-Hydride" (lithium triethyl borohydride) (0.239 ml, 0.239 mmol) was added by syringe over 5 minutes and stirring continued for 10 minutes. Remaining unreacted "Super-Hydride" was destroyed by the addition of butanol (1 ml) and the solvents then removed under vacuum. Plc gave a yellow oil (0.041 g, 62%) which had the following spectral characteristics: ^{1}H NMR: δ 5.43 (br s, 1H), 4.61 (br s, 1H), 2.50 (s, 3H), 1.96 (s, 3H), 1.84 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H) cf. ref. [12,13].

Reduction of $[(\text{toluene})\text{Mn(CO)}_3]^+\text{PF}_6^-$: similar procedure from $[(\text{toluene})\text{Mn(CO)}_3]^+\text{PF}_6^-$ (0.070 g, 0.186 mmol) and Superhydride (0.186 ml, 0.186 mmol) in THF (10 ml). The mixture was stirred for 15 minutes then worked up in the same fashion. Plc gave a yellow oil (0.026 g, 60%) with spectral characteristics indicating a mixture of *meta* and *ortho* reduced isomers (ratio of ca. 1/1.4): ^{1}H NMR: δ 5.76 (m), 4.80 (t, J = 5.8 Hz), 4.57 (d, J = 4.5 Hz), 2.83 (m), 2.56 (m), 2.15 (m), 1.84 (s, 3H), 1.59 (s, 3H) cf. ref. [12,13].

Bromination of reduced [(toluene)Mn(CO)$_3$]$^+$PF$_6^-$: above isomeric mixture (0.005 g, 0.021 mmol) was dissolved in CCl$_4$. A solution of 4% Br$_2$ in CCl$_4$ (0.5 ml, 0.388 mmol Br$_2$) was added and the mixture stirred at 25°C under nitrogen over 72 h. The solvent was removed under vacuum and the residue chromatographed (plc) to yield only BrMn(CO)$_5$ (0.010 g, 93%), identified by IR (2134(w), 2052(br s), 2001(s), 1979(w)) and MS (274/272 M(P$^+$)).

Attempted Friedel Crafts Acylation of [(benzene)Mn(CO)$_3$]$^+$PF$_6^-$: [(benzene)Mn(CO)$_3$]$^+$PF$_6$- (0.100 g, 0.276 mmol) was added to a solution of AlCl$_3$ (0.090 g, 0.670 mmol) and acetyl chloride (0.050 ml, 0.703 mmol) in dichloromethane (20 ml). The mixture was stirred for 17 h, then extracted with water (2 x 5 ml). HPF$_6$ was added to the water extract, resulting in a yellow powder (0.064 g, 64%) which was identified by ^{1}H NMR as [(benzene)Mn(CO)$_3$]$^+$PF$_6^-$. A later effort in acetyl chloride solvent was no more successful.

Attempted mercuration of reduced [(durene)Mn(CO)$_3$]$^+$ compound: A degassed solution of mercuric acetate (0.038 g, 0.119 mmol) in ethanol (8 ml) was added to (2,3,5,6-tetramethylcyclohexa-2,5-dienyl)tricarbonylmanganese (0.023 g, 0.084 mmol) and stirred under nitrogen. Tlc (CHCl$_3$) and plc after 3.5 h indicated the presence of only the reduced starting reagent.

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Appendices

Table A1.1 Final positional parameters for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese

ATOM	X/A	Y/B	Z/C
Mn(1)	0.2092(1)	0.3185(1)	0.1692(1)
C(1)	0.2653(3)	0.1299(3)	0.2433(2)
C(2)	0.3241(3)	-0.0073(3)	0.2118(2)
C(3)	0.3248(3)	-0.0865(2)	0.3264(2)
C(4)	0.3743(3)	-0.2276(3)	0.3476(3)
C(5)	0.3612(3)	-0.2702(3)	0.4716(3)
C(6)	0.3001(3)	-0.1748(3)	0.5744(3)
C(7)	0.2497(3)	-0.0330(3)	0.5574(2)
C(8)	0.2630(3)	0.0093(2)	0.4325(2)
N	0.2254(2)	0.1428(2)	0.3810(2)
C(9)	0.1636(3)	0.2733(2)	0.4353(2)
O(1)	0.1424(2)	0.3713(2)	0.3617(2)
C(10)	0.1233(3)	0.3022(3)	0.5762(2)
C(11)	-0.0147(4)	0.2158(3)	0.1351(2)
O(11)	-0.1420(3)	0.1453(3)	0.1075(2)
C(12)	0.2730(4)	0.2588(3)	0.0056(3)
O(12)	0.3142(4)	0.2179(3)	-0.0996(2)
C(13)	0.1417(4)	0.5018(3)	0.1313(3)
O(13)	0.1000(4)	0.6144(2)	0.1079(2)
C(14)	0.4480(4)	0.3893(3)	0.1958(3)
O(14)	0.5947(3)	0.4273(3)	0.2060(3)

Table A1.2. Bond Lengths for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese

Mn(1) ---C(1)	2.012(2)
Mn(1) ---O(1)	2.054(2)
Mn(1) ---C(11)	1.865(3)
Mn(1) ---C(12)	1.783(3)
Mn(1) ---C(13)	1.846(3)
Mn(1) ---C(14)	1.860(3)
C(1) ---N(1)	1.443(3)
C(1) ---C(2)	1.345(3)
C(2) ---C(3)	1.449(3)
C(3) ---C(4)	1.389(3)
C(3) ---C(8)	1.410(3)
C(4) ---C(5)	1.379(4)
C(5) ---C(6)	1.381(4)
C(6) ---C(7)	1.387(3)
C(7) ---C(8)	1.386(3)
C(8) ---N(1)	1.416(3)
N(1) ---C(9)	1.353(3)
C(9) ---O(1)	1.249(3)
C(9) ---C(10)	1.481(3)
C(11) ---O(11)	1.125(3)
C(12) ---O(12)	1.152(3)
C(13) ---O(13)	1.135(3)
C(14) ---O(14)	1.124(4)

Table A1.3 continued. Bond Angles (°) for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese

C(1)	-Mn(1)	-O(1)	79.2(1)	C(2)	-C(3)	-C(8)	107.7(2)
C(1)	-Mn(1)	-C(11)	85.1(1)	C(4)	-C(3)	-C(8)	119.1(2)
C(1)	-Mn(1)	-C(12)	96.2(1)	C(3)	-C(4)	-C(5)	119.1(2)
C(1)	-Mn(1)	-C(13)	169.6(1)	C(4)	-C(5)	-C(6)	120.9(2)
C(1)	-Mn(1)	-C(14)	87.1(1)	C(5)	-C(6)	-C(7)	121.7(2)
O(1)	-Mn(1)	-C(11)	93.4(1)	C(6)	-C(7)	-C(8)	117.1(2)
O(1)	-Mn(1)	-C(12)	175.4(1)	C(3)	-C(8)	-C(7)	122.0(2)
O(1)	-Mn(1)	-C(13)	90.4(1)	C(3)	-C(8)	-N(1)	105.8(2)
O(1)	-Mn(1)	-C(14)	90.9(1)	C(7)	-C(8)	-N(1)	132.2(2)
C(11)	-Mn(1)	-C(12)	86.5(1)	C(1)	-N(1)	-C(8)	109.9(2)
C(11)	-Mn(1)	-C(13)	94.5(1)	C(1)	-N(1)	-C(9)	117.2(2)
C(11)	-Mn(1)	-C(14)	170.3(1)	C(8)	-N(1)	-C(9)	132.9(2)
C(12)	-Mn(1)	-C(13)	94.1(1)	N(1)	-C(9)	-O(1)	117.3(2)
C(12)	-Mn(1)	-C(14)	88.5(1)	N(1)	-C(9)	-C(10)	122.4(2)
C(13)	-Mn(1)	-C(14)	94.2(1)	O(1)	-C(9)	-C(10)	120.3(2)
Mn(1)	-C(1)	-C(2)	143.4(2)	Mn(1)	-O(1)	-C(9)	116.2(1)
Mn(1)	-C(1)	-N(1)	110.1(1)	Mn(1)	-C(11)	-O(11)	174.0(3)
C(2)	-C(1)	-N(1)	106.5(2)	Mn(1)	-C(12)	-O(12)	178.9(3)
C(1)	-C(2)	-C(3)	110.1(2)	Mn(1)	-C(13)	-O(13)	179.90(0)
C(2)	-C(3)	-C(4)	133.2(2)	Mn(1)	-C(14)	-O(14)	176.2(3)

Table A1.4 Thermal parameters for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese

ATOM	U11	U22	U33	U23	U13	U12
Mn(1)	0.0529(3)	0.0368(2)	0.0388(2)	0.0093(1)	-0.0021(2)	0.0125(2)
C(1)	0.044(1)	0.037(1)	0.033(1)	0.0049(9)	0.0002(9)	0.008(1)
C(2)	0.052(1)	0.038(1)	0.036(1)	0.003(1)	0.001(1)	0.011(1)
C(3)	0.035(1)	0.032(1)	0.043(1)	0.0054(9)	-0.0031(9)	0.0035(9)
C(4)	0.043(1)	0.031(1)	0.059(2)	0.006(1)	-0.003(1)	0.006(1)
C(5)	0.042(1)	0.037(1)	0.067(2)	0.020(1)	-0.007(1)	0.004(1)
C(6)	0.043(1)	0.051(1)	0.052(1)	0.024(1)	-0.004(1)	0.003(1)
C(7)	0.038(1)	0.045(1)	0.043(1)	0.010(1)	-0.001(1)	0.004(1)
C(8)	0.030(1)	0.031(1)	0.039(1)	0.0070(9)	-0.0032(8)	0.0023(8)
N	0.0357(9)	0.0311(9)	0.0317(9)	0.0047(7)	-0.0018(7)	0.0061(7)
C(9)	0.032(1)	0.035(1)	0.040(1)	0.0003(9)	-0.0041(9)	0.0037(9)
O(1)	0.055(1)	0.0346(9)	0.0430(9)	0.0028(7)	-0.0036(7)	0.0159(8)
C(10)	0.047(1)	0.047(1)	0.038(1)	-0.003(1)	-0.002(1)	0.010(1)
C(11)	0.065(2)	0.055(2)	0.038(1)	0.007(1)	0.000(1)	0.013(1)
O(11)	0.071(2)	0.103(2)	0.065(1)	0.005(1)	-0.014(1)	-0.017(1)
C(12)	0.071(2)	0.051(2)	0.052(2)	0.016(1)	0.006(1)	0.013(1)
O(12)	0.127(2)	0.096(2)	0.051(1)	0.010(1)	0.027(1)	0.028(2)
C(13)	0.071(2)	0.049(2)	0.049(1)	0.005(1)	-0.019(1)	0.012(1)
O(13)	0.136(2)	0.045(1)	0.087(2)	0.010(1)	-0.052(2)	0.026(1)
C(14)	0.064(2)	0.043(1)	0.068(2)	0.021(1)	0.000(1)	0.015(1)
O(14)	0.059(1)	0.067(2)	0.130(2)	0.029(1)	-0.012(1)	0.002(1)

Table A1.5. Final positional and thermal parameters of calculated hydrogen atoms for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese

ATOM	X/A	Y/B	Z/C	U11
H(2)	0.3608(3)	-0.0479(3)	0.1242(2)	0.055
H(4)	0.4179(3)	-0.2959(3)	0.2752(3)	0.055
H(5)	0.3954(3)	-0.3697(3)	0.4872(3)	0.055
H(6)	0.2924(3)	-0.2080(3)	0.6615(3)	0.055
H(7)	0.2066(3)	0.0344(3)	0.6306(2)	0.055
H(101)	0.1543(3)	0.2164(3)	0.6194(2)	0.080
H(102)	-0.0046(3)	0.3174(3)	0.5937(2)	0.080
H(103)	0.1969(3)	0.3929(3)	0.6091(2)	0.080

Table A2.1 Final positional and equivalent thermal parameters for η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese

ATOM	X/A	Y/B	Z/C	Ueq
Mn(1)	0.3318(1)	0.3047(1)	0.1115(0)	0.020
Mn(2)	0.2353(1)	0.1536(1)	0.6543(0)	0.019
C(1)	0.2740(4)	0.3299(4)	0.2776(3)	0.022
C(2)	0.2721(4)	0.2323(4)	0.3830(3)	0.021
C(3)	0.2401(4)	0.2710(4)	0.4900(3)	0.018
C(4)	0.2081(4)	0.4161(4)	0.4893(3)	0.020
C(5)	0.2071(4)	0.5164(4)	0.3863(3)	0.020
C(6)	0.2384(4)	0.4728(4)	0.2818(3)	0.020
C(7)	0.1752(4)	0.4489(4)	0.6043(3)	0.022
O(7)	0.1699(3)	0.3482(3)	0.6899(2)	0.023
C(8)	0.1548(5)	0.5948(4)	0.6244(3)	0.026
C(9)	0.2401(4)	0.5672(4)	0.1690(3)	0.022
O(9)	0.2800(3)	0.5162(3)	0.0812(2)	0.024
C(10)	0.1921(5)	0.7197(4)	0.1522(4)	0.031
C(11)	0.1274(5)	0.2698(5)	0.1103(4)	0.039
O(11)	0.0033(4)	0.2399(5)	0.1159(4)	0.072
C(12)	0.5312(4)	0.3228(4)	0.1431(3)	0.026
O(12)	0.6487(3)	0.3237(4)	0.1711(2)	0.042
C(13)	0.3874(4)	0.3181(4)	-0.0465(3)	0.025
O(13)	0.4239(4)	0.3250(3)	-0.1428(2)	0.041
C(14)	0.3713(4)	0.1192(4)	0.1447(3)	0.027
O(14)	0.3972(4)	-0.0004(3)	0.1654(3)	0.050
C(21)	0.0386(5)	0.1118(4)	0.6356(3)	0.028
O(21)	-0.0769(4)	0.0822(4)	0.6178(3)	0.050
C(22)	0.4395(4)	0.2042(4)	0.6414(3)	0.022
O(22)	0.5624(3)	0.2366(3)	0.6255(3)	0.037
C(23)	0.2224(5)	0.0737(4)	0.8104(3)	0.030

O(23)	0.2148(4)	0.0221(4)	0.9073(3)	0.052
C(24)	0.3049(4)	-0.0066(4)	0.6109(3)	0.029
O(24)	0.3524(4)	-0.1071(3)	0.5818(3)	0.042

Table A2.2 Final positional and thermal parameters of calculated hydrogen atoms for η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese

ATOM	X/A	Y/B	Z/C	U11
H(2)	0.2940(4)	0.1328(4)	0.3817(3)	0.027
H(5)	0.1848(4)	0.6158(4)	0.3875(3)	0.027
H(81)	0.1777(5)	0.6628(4)	0.5512(3)	0.108
H(82)	0.2315(5)	0.5988(4)	0.6765(3)	0.108
H(83)	0.0521(5)	0.6175(4)	0.6609(3)	0.108
H(101)	0.2454(5)	0.7586(4)	0.2046(4)	0.108
H(102)	0.0807(5)	0.7280(4)	0.1740(4)	0.108
H(103)	0.2176(5)	0.7715(4)	0.0723(4)	0.108

Table A2.3 Thermal parameters

for η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese

ATOM	U11	U22	U33	U23	U13	U12
Mn(1)	0.0224(3)	0.0231(3)	0.0157(3)	-0.0054(2)	-0.0015(2)	-0.0031(2)
Mn(2)	0.0229(3)	0.0198(3)	0.0148(3)	-0.0021(2)	-0.0011(2)	-0.0046(2)
C(1)	0.020(2)	0.025(2)	0.021(2)	-0.007(2)	0.000(1)	-0.006(1)
C(2)	0.022(2)	0.021(2)	0.020(2)	-0.004(1)	-0.003(1)	-0.002(1)
C(3)	0.016(2)	0.022(2)	0.017(2)	-0.003(1)	0.000(1)	-0.005(1)
C(4)	0.022(2)	0.021(2)	0.017(2)	-0.006(1)	-0.001(1)	-0.004(1)
C(5)	0.021(2)	0.017(2)	0.022(2)	-0.004(1)	-0.003(1)	-0.002(1)
C(6)	0.019(2)	0.022(2)	0.019(2)	-0.003(1)	-0.001(1)	-0.003(1)
C(7)	0.015(2)	0.025(2)	0.027(2)	-0.009(2)	-0.003(1)	-0.003(1)
O(7)	0.027(1)	0.022(1)	0.017(1)	-0.002(1)	-0.001(1)	-0.002(1)
C(8)	0.034(2)	0.022(2)	0.025(2)	-0.010(2)	-0.002(2)	0.001(2)
C(9)	0.018(2)	0.024(2)	0.025(2)	-0.006(2)	0.001(1)	-0.004(1)
O(9)	0.031(1)	0.024(1)	0.016(1)	-0.002(1)	0.002(1)	-0.002(1)
C(10)	0.038(2)	0.024(2)	0.028(2)	-0.001(2)	0.002(2)	0.000(2)
C(11)	0.037(3)	0.043(3)	0.041(3)	-0.019(2)	-0.002(2)	-0.002(2)
O(11)	0.032(2)	0.104(3)	0.093(3)	-0.049(3)	0.000(2)	-0.019(2)
C(12)	0.029(2)	0.030(2)	0.016(2)	-0.001(2)	0.000(2)	-0.004(2)
O(12)	0.031(2)	0.066(2)	0.028(2)	-0.004(2)	-0.008(1)	-0.012(2)
C(13)	0.025(2)	0.027(2)	0.026(2)	-0.009(2)	-0.003(2)	-0.004(2)
O(13)	0.049(2)	0.057(2)	0.019(2)	-0.015(1)	0.002(1)	-0.011(2)
C(14)	0.031(2)	0.031(2)	0.020(2)	-0.005(2)	-0.004(2)	-0.003(2)
O(14)	0.067(2)	0.029(2)	0.055(2)	-0.007(2)	-0.016(2)	0.001(2)
C(21)	0.032(2)	0.023(2)	0.030(2)	-0.006(2)	-0.002(2)	-0.004(2)
O(21)	0.030(2)	0.059(2)	0.068(2)	-0.023(2)	-0.008(2)	-0.014(2)
C(22)	0.029(2)	0.023(2)	0.015(2)	-0.004(1)	-0.001(1)	0.001(2)
O(22)	0.027(2)	0.049(2)	0.038(2)	-0.014(1)	0.002(1)	-0.011(1)

C(23)	0.035(2)	0.028(2)	0.026(2)	-0.004(2)	-0.002(2)	-0.002(2)
O(23)	0.076(3)	0.054(2)	0.023(2)	0.006(2)	-0.006(2)	-0.015(2)
C(24)	0.029(2)	0.028(2)	0.029(2)	0.000(2)	-0.004(2)	-0.008(2)
O(24)	0.057(2)	0.026(2)	0.044(2)	-0.013(1)	-0.004(2)	0.002(1)

Table A2.4. Bond Lengths and Angles

for η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese

Bond Lengths (Å).

Mn(1) ---C(1)	2.039(4)
Mn(1) ---O(9)	2.046(2)
Mn(1) ---C(11)	1.854(5)
Mn(1) ---C(12)	1.865(4)
Mn(1) ---C(13)	1.858(4)
Mn(1) ---C(14)	1.786(4)
Mn(2) ---C(3)	2.034(3)
Mn(2) ---O(7)	2.063(2)
Mn(2) ---C(21)	1.856(4)
Mn(2) ---C(22)	1.873(4)
Mn(2) ---C(23)	1.842(4)
Mn(2) ---C(24)	1.796(4)
C(1) ---C(2)	1.398(5)
C(1) ---C(6)	1.419(5)
C(2) ---C(3)	1.396(5)
C(3) ---C(4)	1.424(5)
C(4) ---C(5)	1.391(5)
C(4) ---C(7)	1.461(5)
C(5) ---C(6)	1.390(5)
C(6) ---C(9)	1.451(5)
C(7) ---O(7)	1.250(4)
C(7) ---C(8)	1.492(5)
C(9) ---O(9)	1.254(4)
C(9) ---C(10)	1.495(5)
C(11) ---O(11)	1.139(5)
C(12) ---O(12)	1.125(5)

C(13) ---O(13)	1.138(4)
C(14) ---O(14)	1.152(5)
C(21) ---O(21)	1.133(5)
C(22) ---O(22)	1.129(4)
C(23) ---O(23)	1.147(5)
C(24) ---O(24)	1.145(5)

Bond Angles (°)

for η^2,η^2-(2,4-diacetylphenyl)bis-1,5-(tetracarbonyl)manganese

C(1)	-Mn(1)	-O(9)	79.9(1)
C(1)	-Mn(1)	-C(11)	87.4(2)
C(1)	-Mn(1)	-C(12)	83.3(1)
C(1)	-Mn(1)	-C(13)	169.2(2)
C(1)	-Mn(1)	-C(14)	97.5(2)
O(9)	-Mn(1)	-C(11)	90.8(2)
O(9)	-Mn(1)	-C(12)	93.6(1)
O(9)	-Mn(1)	-C(13)	89.7(1)
O(9)	-Mn(1)	-C(14)	177.2(1)
C(11)	-Mn(1)	-C(12)	168.9(2)
C(11)	-Mn(1)	-C(13)	95.7(2)
C(11)	-Mn(1)	-C(14)	88.0(2)
C(12)	-Mn(1)	-C(13)	94.5(2)
C(12)	-Mn(1)	-C(14)	87.2(2)
C(13)	-Mn(1)	-C(14)	92.9(2)
C(3)	-Mn(2)	-O(7)	80.1(1)
C(3)	-Mn(2)	-C(21)	85.5(2)
C(3)	-Mn(2)	-C(22)	84.0(1)
C(3)	-Mn(2)	-C(23)	170.9(2)
C(3)	-Mn(2)	-C(24)	95.1(2)
O(7)	-Mn(2)	-C(21)	94.9(1)
O(7)	-Mn(2)	-C(22)	87.3(1)
O(7)	-Mn(2)	-C(23)	90.8(1)
O(7)	-Mn(2)	-C(24)	174.1(1)
C(21)	-Mn(2)	-C(22)	168.7(2)
C(21)	-Mn(2)	-C(23)	95.6(2)
C(21)	-Mn(2)	-C(24)	88.1(2)
C(22)	-Mn(2)	-C(23)	95.4(2)

C(22)	-Mn(2)	-C(24)	88.8(2)
C(23)	-Mn(2)	-C(24)	93.9(2)
Mn(1)	-C(1)	-C(2)	130.6(3)
Mn(1)	-C(1)	-C(6)	111.7(2)
C(2)	-C(1)	-C(6)	117.6(3)
C(1)	-C(2)	-C(3)	122.5(3)
Mn(2)	-C(3)	-C(2)	130.7(3)
Mn(2)	-C(3)	-C(4)	111.7(2)
C(2)	-C(3)	-C(4)	117.6(3)
C(3)	-C(4)	-C(5)	121.7(3)
C(3)	-C(4)	-C(7)	114.6(3)
C(5)	-C(4)	-C(7)	123.7(3)
C(4)	-C(5)	-C(6)	118.7(3)
C(1)	-C(6)	-C(5)	121.9(3)
C(1)	-C(6)	-C(9)	114.4(3)
C(5)	-C(6)	-C(9)	123.8(3)
C(4)	-C(7)	-O(7)	117.4(3)
C(4)	-C(7)	-C(8)	123.6(3)
O(7)	-C(7)	-C(8)	118.9(3)
Mn(2)	-O(7)	-C(7)	115.8(2)
C(6)	-C(9)	-O(9)	117.6(3)
C(6)	-C(9)	-C(10)	123.7(3)
O(9)	-C(9)	-C(10)	118.7(3)
Mn(1)	-O(9)	-C(9)	116.2(2)
Mn(1)	-C(11)	-O(11)	174.9(5)
Mn(1)	-C(12)	-O(12)	173.4(3)
Mn(2)	-C(21)	-O(21)	175.2(4)
Mn(2)	-C(22)	-O(22)	175.3(3)
Mn(2)	-C(23)	-O(23)	179.0(4)
Mn(2)	-C(24)	-O(24)	178.3(3)

Table A3.1 Final positional and equivalent thermal parameters for 1-methyl-2,3-diphenylinden-1-ol.

ATOM	X/A	Y/B	Z/C	Ueq/U11
O(1)	0.0878(3)	0.2446(4)	0.2428(1)	0.040(1)
C(1)	-0.0289(5)	0.2627(5)	0.2603(2)	0.036(2)
C(2)	-0.0357(5)	0.3126(5)	0.3183(2)	0.037(2)
C(3)	-0.0869(5)	0.4137(5)	0.3165(2)	0.035(2)
C(4)	-0.1734(5)	0.5353(5)	0.2373(2)	0.041(2)
C(5)	-0.1941(5)	0.5368(5)	0.1800(2)	0.049(2)
C(6)	-0.1593(5)	0.4491(5)	0.1465(3)	0.056(2)
C(7)	-0.1035(5)	0.3555(5)	0.1689(3)	0.050(2)
C(8)	-0.1187(4)	0.4404(5)	0.2591(2)	0.037(2)
C(9)	-0.0844(5)	0.3534(5)	0.2248(2)	0.038(2)
C(10)	-0.0875(5)	0.1484(5)	0.2552(3)	0.050
C(11)	-0.0035(5)	0.2483(5)	0.3678(3)	0.048
C(12)	0.1024(7)	0.2012(6)	0.3734(3)	0.078
C(13)	0.130(1)	0.1381(8)	0.4205(4)	0.113
C(14)	0.053(1)	0.1245(8)	0.4622(4)	0.106
C(15)	-0.0509(9)	0.1689(8)	0.4564(4)	0.103
C(16)	-0.0806(7)	0.2328(6)	0.4107(3)	0.078
C(21)	-0.1081(5)	0.4889(4)	0.3648(3)	0.041
C(22)	-0.0201(6)	0.5197(5)	0.4003(3)	0.049
C(23)	-0.0390(7)	0.5886(6)	0.4456(3)	0.066
C(24)	-0.1483(8)	0.6270(6)	0.4563(3)	0.066
C(25)	-0.2360(7)	0.5974(6)	0.4208(3)	0.065
C(26)	-0.2160(5)	0.5300(5)	0.3748(3)	0.052

Table A3.2 Final positional and thermal parameters of calculated hydrogen atoms for 1-methyl-2,3-diphenylinden-1-ol.

ATOM	X/A	Y/B	Z/C	U11
H(1)	0.133(5)	0.320(5)	0.249(3)	0.086
H(4)	-0.1986(5)	0.6044(5)	0.2634(2)	0.086
H(5)	-0.2376(5)	0.6074(5)	0.1619(2)	0.086
H(6)	-0.1753(5)	0.4526(5)	0.1027(3)	0.086
H(7)	-0.0764(5)	0.2871(5)	0.1429(3)	0.086
H(101)	-0.1744(5)	0.1616(5)	0.2662(3)	0.060
H(102)	-0.0477(5)	0.0961(5)	0.2860(3)	0.060
H(103)	-0.0830(5)	0.1074(5)	0.2155(3)	0.060
H(12)	0.1643(7)	0.2131(6)	0.3414(3)	0.110
H(13)	0.212(1)	0.1000(8)	0.4239(4)	0.110
H(14)	0.075(1)	0.0790(8)	0.4992(4)	0.110
H(15)	-0.1127(9)	0.1543(8)	0.4882(4)	0.110
H(16)	-0.1630(7)	0.2704(6)	0.4083(3)	0.110
H(22)	0.0638(6)	0.4892(5)	0.3922(3)	0.110
H(23)	0.0296(7)	0.6124(6)	0.4723(3)	0.110
H(24)	-0.1646(8)	0.6792(6)	0.4918(3)	0.110
H(25)	-0.3200(7)	0.6272(6)	0.4291(3)	0.110
H(26)	-0.2839(5)	0.5095(5)	0.3471(3)	0.110

Table A3.3 Thermal parameters for 1-methyl-2,3-diphenylinden-1-ol.

ATOM	U11	U22	U33	U23	U13	U12
O(1)	0.040(1)					
C(1)	0.036(2)					
C(2)	0.037(2)					
C(3)	0.035(2)					
C(4)	0.041(2)					
C(5)	0.049(2)					
C(6)	0.056(2)					
C(7)	0.050(2)					
C(8)	0.037(2)					
C(9)	0.038(2)					
C(10)	0.037(4)	0.030(4)	0.082(5)	-0.005(4)	0.000(4)	-0.009(3)
C(11)	0.051(5)	0.027(3)	0.066(5)	0.000(4)	-0.010(4)	0.000(3)
C(12)	0.090(6)	0.086(6)	0.059(5)	-0.023(5)	-0.027(5)	0.050(5)
C(13)	0.17(1)	0.086(7)	0.084(7)	-0.035(7)	-0.063(8)	0.077(7)
C(14)	0.18(1)	0.056(6)	0.078(7)	0.009(6)	-0.074(9)	-0.018(7)
C(15)	0.116(9)	0.105(8)	0.089(7)	0.047(6)	-0.035(7)	-0.060(7)
C(16)	0.070(6)	0.075(6)	0.088(6)	0.033(5)	-0.008(5)	-0.016(4)
C(21)	0.041(4)	0.025(3)	0.058(4)	0.004(3)	-0.002(4)	-0.001(3)
C(22)	0.059(5)	0.036(4)	0.051(4)	0.002(4)	-0.012(4)	0.000(4)
C(23)	0.095(7)	0.045(5)	0.057(5)	0.001(4)	-0.015(5)	0.002(5)
C(24)	0.103(7)	0.052(5)	0.044(5)	-0.003(4)	0.010(5)	0.011(5)
C(25)	0.073(6)	0.057(5)	0.066(5)	-0.006(4)	0.013(5)	0.011(4)
C(26)	0.058(5)	0.042(4)	0.057(4)	-0.006(4)	0.011(4)	0.008(4)

Table A4.1 Final positional and equivalent thermal parameters for dimethyl 1-methyl-1-hydroxy-pyrrolo[1,2a]indole-2,3-dicarboxylate.

ATOM	X/A	Y/B	Z/C	Ueq/U11
N(1)	0.534(1)	0.281(2)	-0.1043(7)	0.020(4)
C(1)	0.412(2)	0.243(3)	-0.158(1)	0.030(6)
C(2)	0.338(1)	0.216(3)	-0.1067(8)	0.016(5)
C(3)	0.408(2)	0.242(3)	-0.0377(9)	0.020(5)
C(4)	0.535(1)	0.270(3)	-0.0343(9)	0.020(5)
C(5)	0.649(1)	0.290(3)	0.0093(8)	0.009(5)
C(6)	0.729(1)	0.310(3)	-0.0333(8)	0.016(5)
C(7)	0.855(2)	0.317(4)	-0.019(1)	0.034(6)
C(8)	0.908(2)	0.325(3)	-0.0747(9)	0.024(5)
C(9)	0.829(2)	0.322(3)	-0.144(1)	0.029(6)
C(10)	0.703(2)	0.312(3)	-0.160(1)	0.033(6)
C(11)	0.654(2)	0.300(3)	-0.1047(8)	0.020(5)
C(12)	0.368(2)	0.407(3)	-0.210(1)	0.036(6)
C(13)	0.200(2)	0.174(3)	-0.1377(9)	0.023(5)
C(14)	0.049(2)	-0.073(4)	-0.172(1)	0.045(7)
C(15)	0.368(2)	0.210(3)	0.0249(9)	0.016(5)
C(16)	0.211(2)	0.178(4)	0.0744(9)	0.029(6)
O(1)	0.420(1)	0.062(2)	-0.1917(6)	0.031(4)
O(2)	0.127(1)	0.305(2)	-0.1587(6)	0.038(4)
O(3)	0.177(1)	-0.019(2)	-0.1397(6)	0.022(3)
O(4)	0.448(1)	0.215(2)	0.0850(6)	0.022(4)
O(5)	0.249(1)	0.201(2)	0.0116(6)	0.023(3)

Table A4.2 Final positional and thermal parameters of calculated hydrogen atoms for dimethyl 1-methyl-1-hydroxy-pyrrolo[1,2a]indole-2,3-dicarboxylate

ATOM	X/A	Y/B	Z/C	U11
H(5)	0.674(1)	0.290(3)	0.0611(8)	0.047
H(7)	0.910(2)	0.317(4)	0.030(1)	0.047
H(8)	0.998(2)	0.333(3)	-0.0644(9)	0.047
H(9)	0.865(2)	0.326(3)	-0.183(1)	0.047
H(10)	0.649(2)	0.313(3)	-0.210(1)	0.047
H(121)	0.373(2)	0.527(3)	-0.181(1)	0.011
H(122)	0.284(2)	0.393(3)	-0.243(1)	0.011
H(123)	0.426(2)	0.420(3)	-0.238(1)	0.011
H(141)	0.058(2)	-0.219(4)	-0.174(1)	0.011
H(142)	0.012(2)	-0.022(4)	-0.220(1)	0.011
H(143)	-0.004(2)	-0.039(4)	-0.144(1)	0.011
H(161)	0.120(2)	0.181(4)	0.0539(9)	0.011
H(162)	0.240(2)	0.303(4)	0.0998(9)	0.011
H(163)	0.235(2)	0.065(4)	0.1072(9)	0.011
H(1)	0.422(0)	-0.063(0)	-0.174(0)	0.020

Table A4.3. Bond Lengths and Angles for dimethyl 1-methyl-1-hydroxy-pyrrolo[1,2a]indole-2,3-dicarboxylate.

Bond Lengths (Å)

N(1) ---C(1)	1.48(2)
N(1) ---C(4)	1.40(2)
N(1) ---C(11)	1.37(2)
C(1) ---C(2)	1.53(2)
C(1) ---C(12)	1.49(2)
C(1) ---O(1)	1.40(2)
C(2) ---C(3)	1.36(2)
C(2) ---C(13)	1.52(2)
C(3) ---C(4)	1.44(2)
C(3) ---C(15)	1.47(2)
C(4) ---C(5)	1.32(2)
C(5) ---C(6)	1.44(2)
C(6) ---C(7)	1.38(2)
C(6) ---C(11)	1.41(2)
C(7) ---C(8)	1.42(2)
C(8) ---C(9)	1.39(2)
C(9) ---C(10)	1.37(2)
C(10) ---C(11)	1.39(2)
C(13) ---O(2)	1.19(2)
C(13) ---O(3)	1.31(2)
C(14) ---O(3)	1.44(2)
C(15) ---O(4)	1.25(2)
C(15) ---O(5)	1.30(2)
C(16) ---O(5)	1.46(2)

Bond Angles (°) for dimethyl 1-methyl-1-hydroxy-pyrrolo[1,2a]indole-2,3-dicarboxylate.

C(1)	-N(1)	-C(4)	114(1)
C(1)	-N(1)	-C(11)	136(2)
C(4)	-N(1)	-C(11)	108(1)
N(1)	-C(1)	-C(2)	98(1)
N(1)	-C(1)	-C(12)	114(2)
N(1)	-C(1)	-O(1)	107(2)
C(2)	-C(1)	-C(12)	115(2)
C(2)	-C(1)	-O(1)	110(2)
C(12)	-C(1)	-O(1)	110(2)
C(1)	-C(2)	-C(3)	112(2)
C(1)	-C(2)	-C(13)	118(1)
C(3)	-C(2)	-C(13)	129(2)
C(2)	-C(3)	-C(4)	108(2)
C(2)	-C(3)	-C(15)	126(2)
C(4)	-C(3)	-C(15)	123(2)
N(1)	-C(4)	-C(3)	106(1)
N(1)	-C(4)	-C(5)	110(1)
C(3)	-C(4)	-C(5)	143(2)
C(4)	-C(5)	-C(6)	107(2)
C(5)	-C(6)	-C(7)	134(2)
C(5)	-C(6)	-C(11)	107(1)
C(7)	-C(6)	-C(11)	117(2)
C(6)	-C(7)	-C(8)	121(2)
C(7)	-C(8)	-C(9)	118(2)
C(8)	-C(9)	-C(10)	122(2)
C(9)	-C(10)	-C(11)	117(2)
N(1)	-C(11)	-C(6)	106(1)
N(1)	-C(11)	-C(10)	131(2)

C(6)	-C(11)	-C(10)	122(2)
C(2)	-C(13)	-O(2)	121(2)
C(2)	-C(13)	-O(3)	111(2)
O(2)	-C(13)	-O(3)	127(2)
C(3)	-C(15)	-O(4)	119(2)
C(3)	-C(15)	-O(5)	114(2)
O(4)	-C(15)	-O(5)	125(2)
C(13)	-O(3)	-C(14)	114(2)
C(15)	-O(5)	-C(16)	114(1)

Appendix V

General Experimental Procedures

All air sensitive reactions and recrystallisations were performed under an atmosphere of dry nitrogen using Schlenk techniques.

THF was dried by distillation from sodium/benzophenone under nitrogen. Heptane was dried by distillation from CaH_2 under nitrogen.

All NMR spectra were recorded in $CDCl_3$ solvent. ^1H NMR spectra were recorded on either a JEOL C-60HL (external lock mode) or JEOL FX-90Q instrument. ^1H chemical shifts are reported in p.p.m and referenced downfield from TMS. ^{13}C NMR spectra were recorded on the JEOL FX-90Q instrument. Chemical shifts are reported in p.p.m with reference to the central peak of $CDCl_3$ (77.06 ppm). ^{13}C assignment ambiguities were resolved by selective decoupling or with standard INEPT pulse techniques. The COSY ^1H-^1H correlation experiment was performed on a Bruker AM400 instrument.

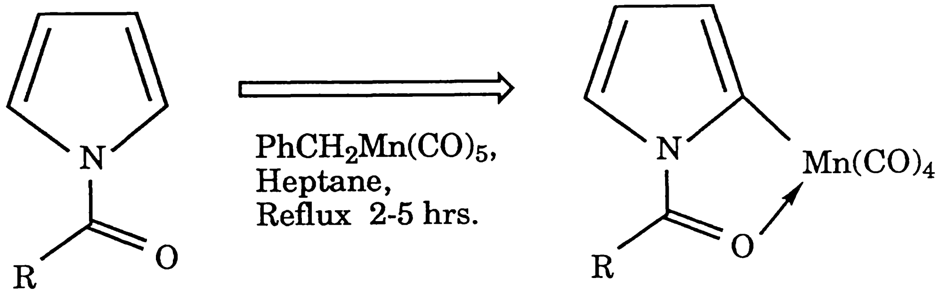
Infra-red data were recorded on a Perkin Elmer 180B instrument or 1600 series FTIR instrument, either in a solution cell (KBr windows, CH_2Cl_2 or pet. spirit solvent) or as a fused KBr disc.

Mass spectra were recorded on a Varian MAT CH5 instrument at Ruakura Agricultural Research Centre.

Thin layer chromatography (tlc) was carried out on Merck Kieselgel $60F_{254}$ silica gel backed by aluminium sheets (layer thickness 0.2 mm). Preparative layer chromatography (plc) was

Appendix VI List of Compounds by Numbers

Preparation of *N*-acylpyrrole-Mn(CO)$_4$ compounds



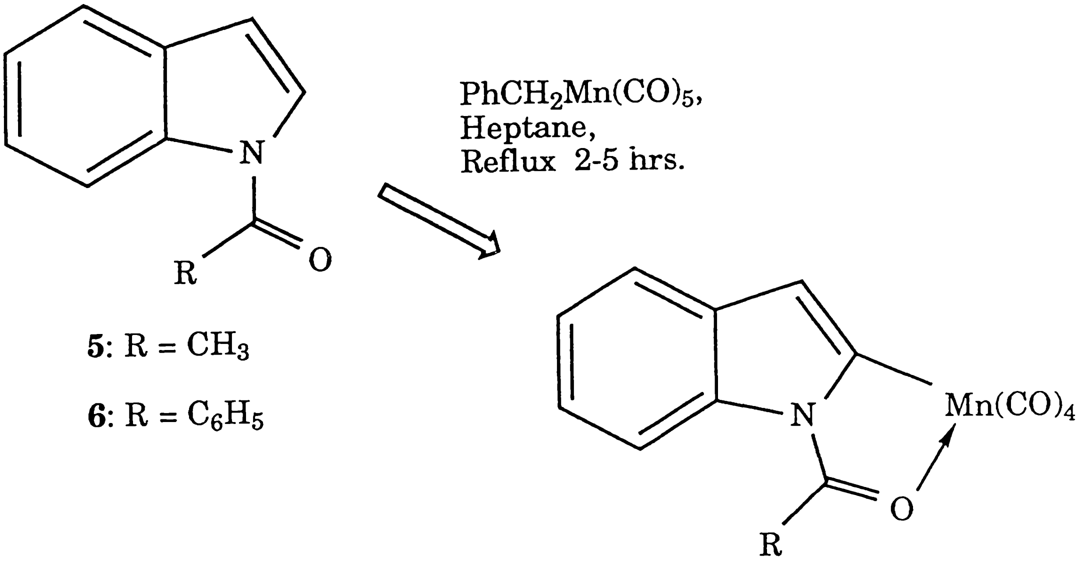
1: R = CH_3

3: R = C_6H_5

2: R = CH_3

4: R = C_6H_5

Preparation of *N*-acylindole-Mn(CO)$_4$ compounds



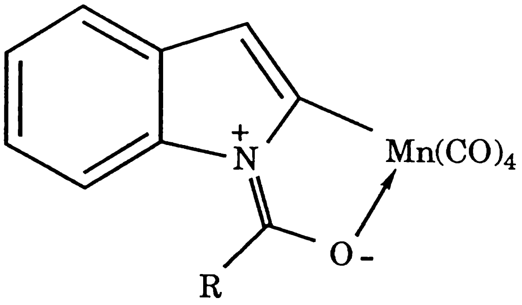
5: R = CH_3

6: R = C_6H_5

7: R = CH_3

8: R = C_6H_5

Alternative resonance form of **7**



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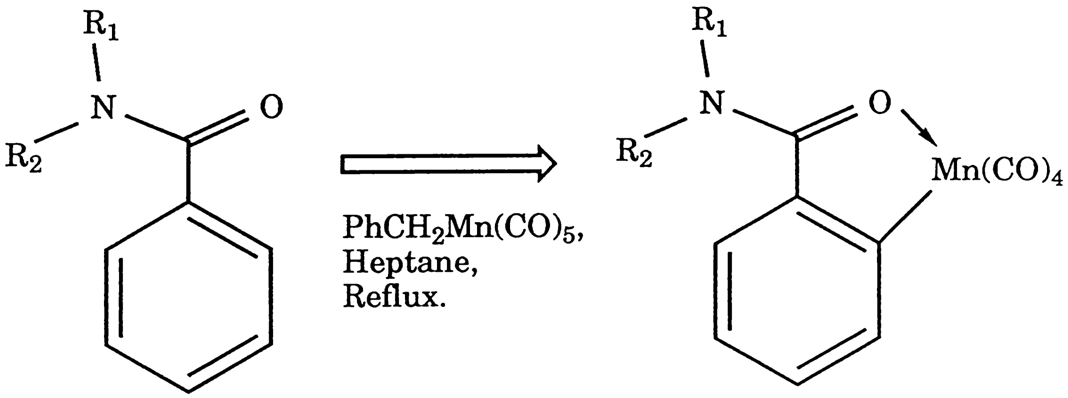
Preparation of benzamide-$Mn(CO)_4$ compounds



10: $R_1 = R_2 = CH_3$

11: $R_1 = R_2 = CH_2CH_3$

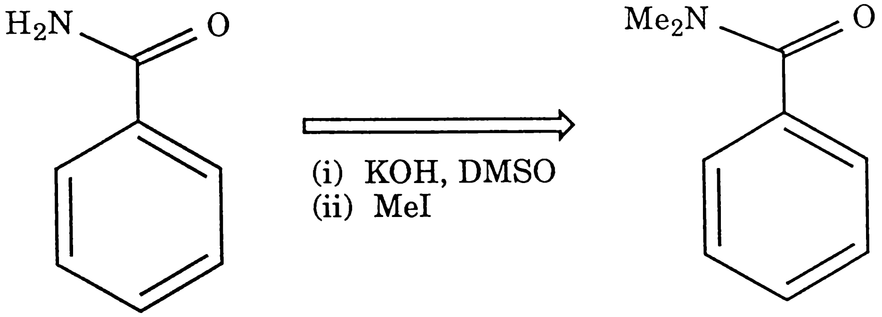
12: $R_1,R_2 = (CH_2)_4$

13: $R_1 = R_2 = CH_3$

14: $R_1 = R_2 = CH_2CH_3$

15: $R_1,R_2 = (CH_2)_4$

Preparation of *N,N*-dimethylbenzamide



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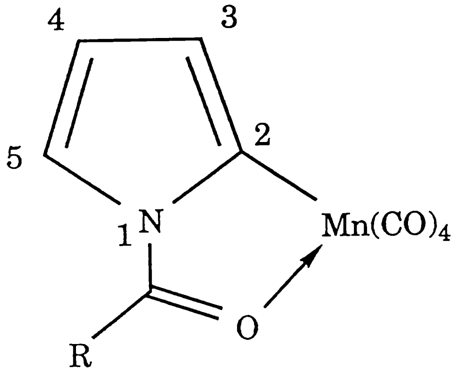
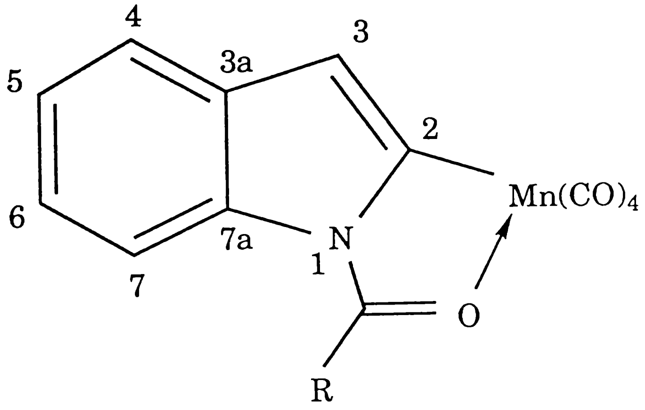
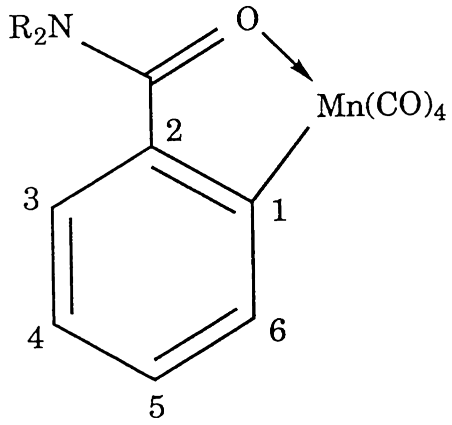
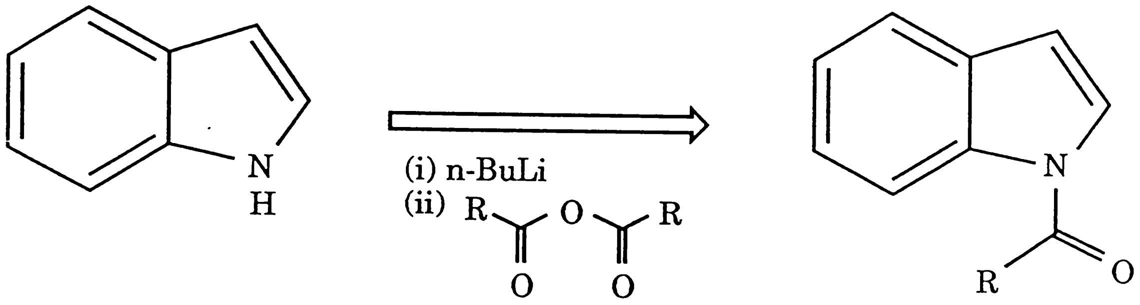
^{13}C NMR Labelling System







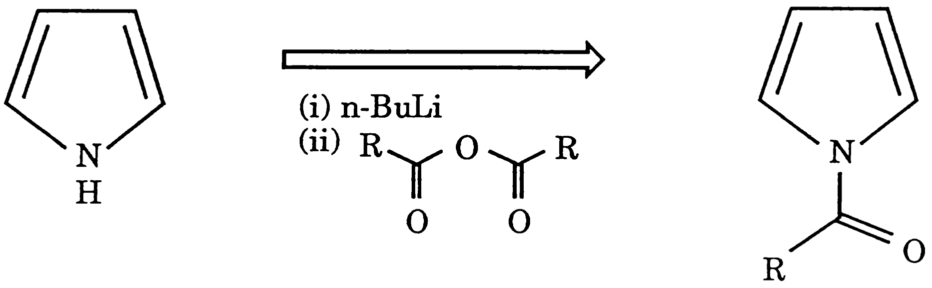
Preparation of acylated indoles



5: R = CH_3

6: R = C_6H_5

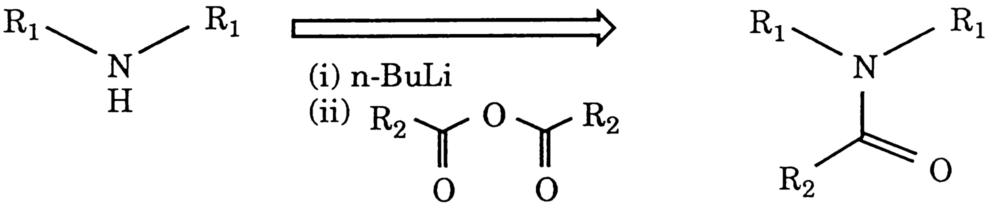
Preparation of acylated pyrroles



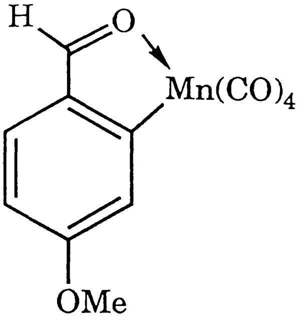
1: R = CH_3

3: R = C_6H_5

Preparation of alkylated amides



	18	**11**	**12**	**17**	**16**	**19**
R_1:	Et	Et	$(CH_2)_4$	$(CH_2)_5$	Pr^i	Ph
R_2:	CH_3	Ph	Ph	CH_3	Ph	Ph



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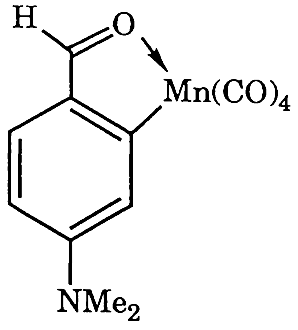

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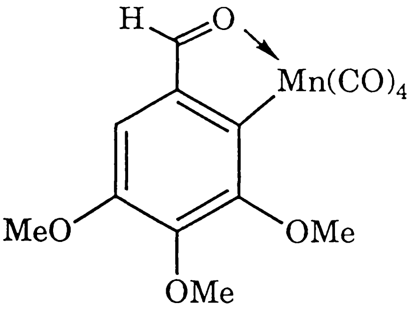

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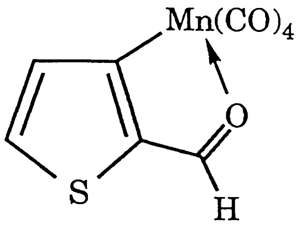

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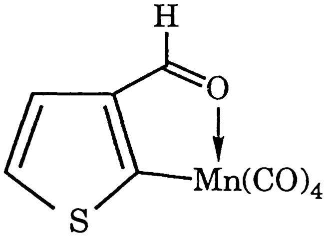

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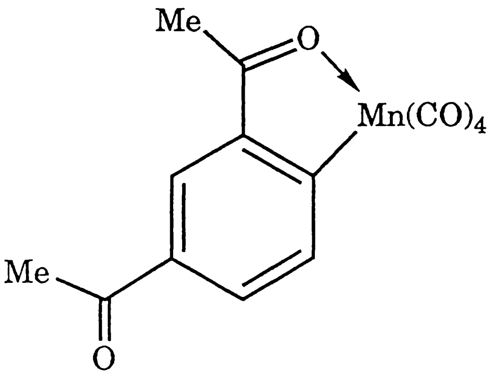

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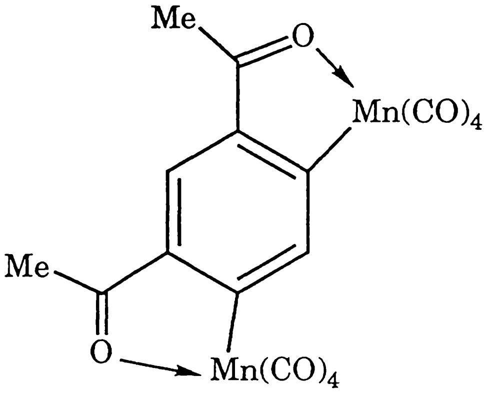

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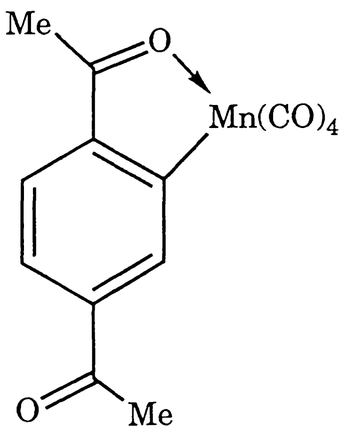

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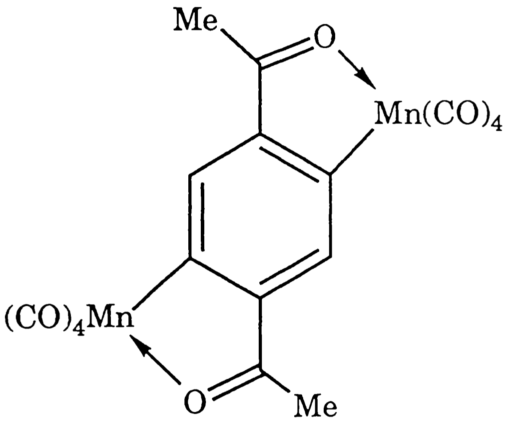

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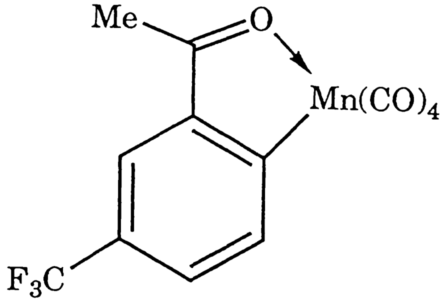

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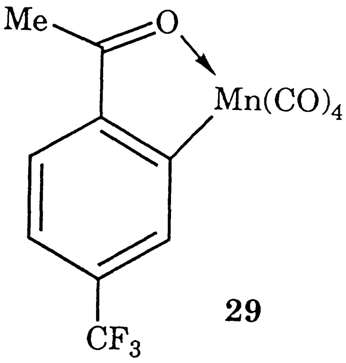

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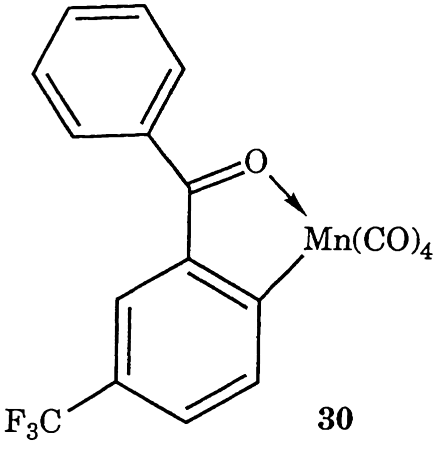

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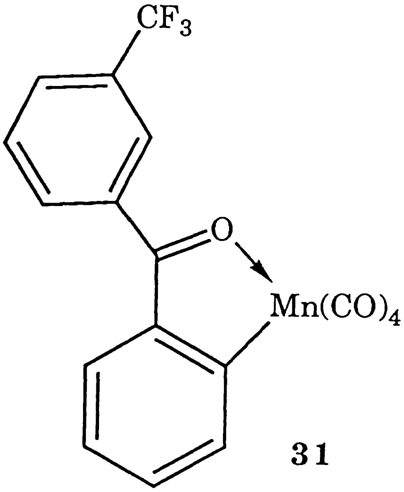
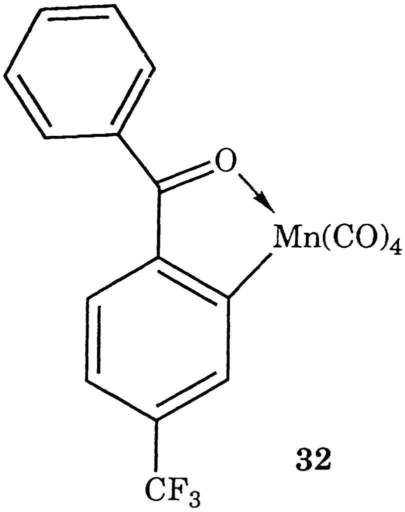


31

Ratio 1 : 2



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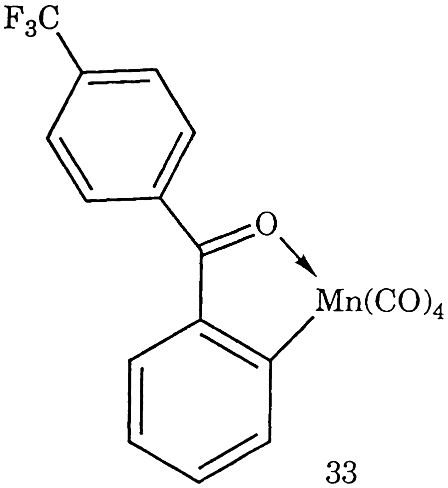

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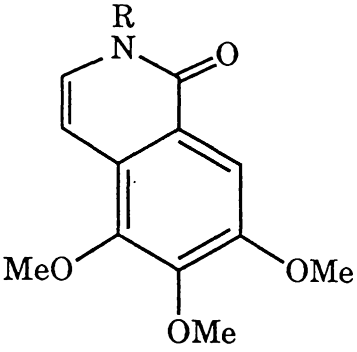
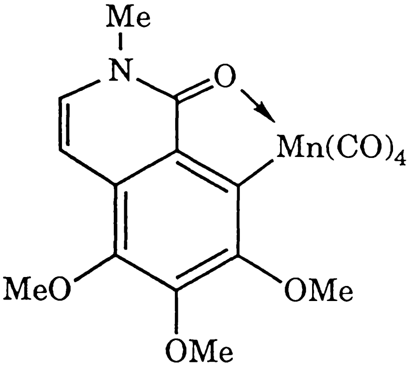
Ratio 1 2



R=H **34**
R=Me **35**



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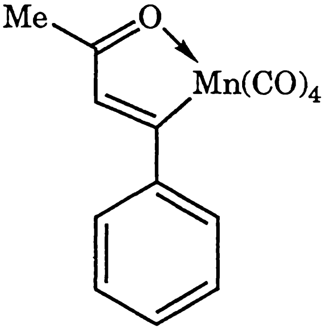

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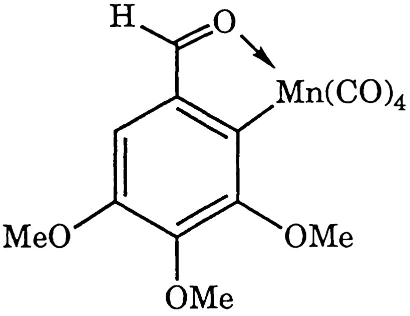

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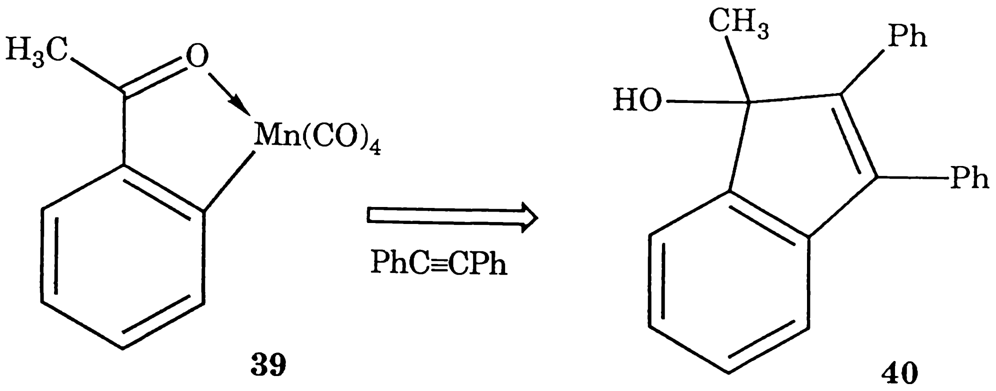
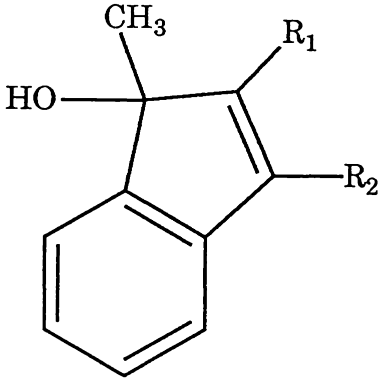


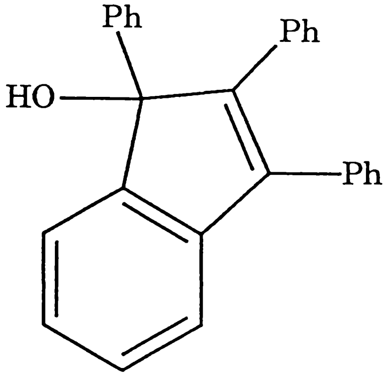
39 **40**



45 R_1 = Ph, R_2 = H

47 R_1 = Si$(CH_3)_3$, R_2 = H

48 R_1 = nC_3H_7, R_2 = CH_3



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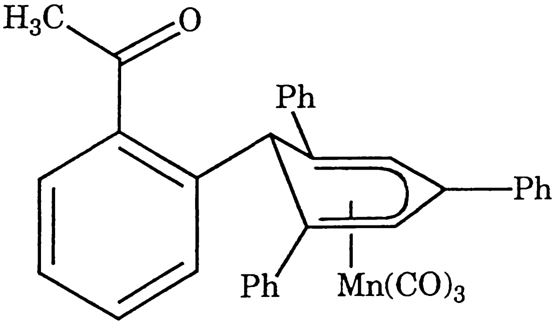

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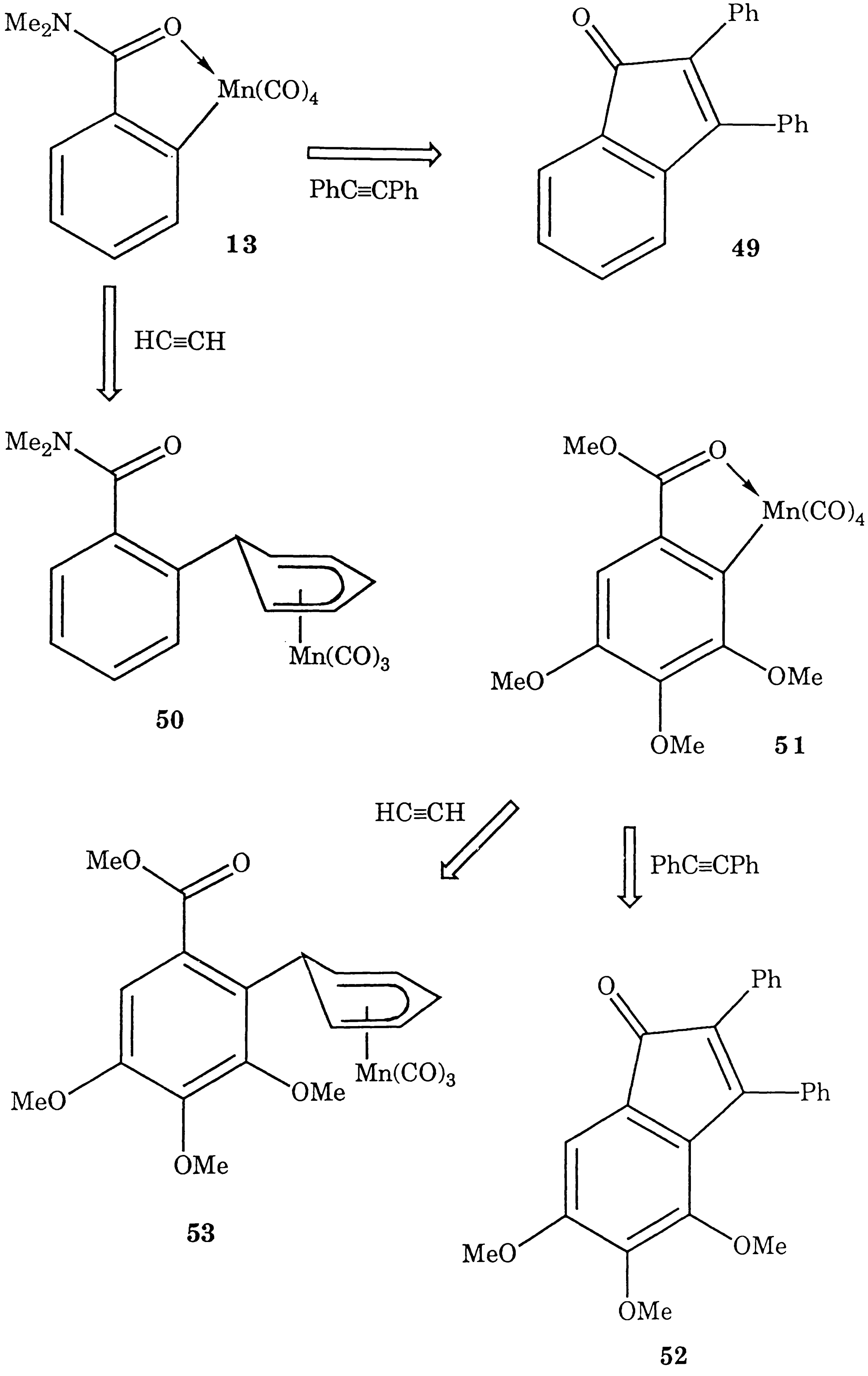
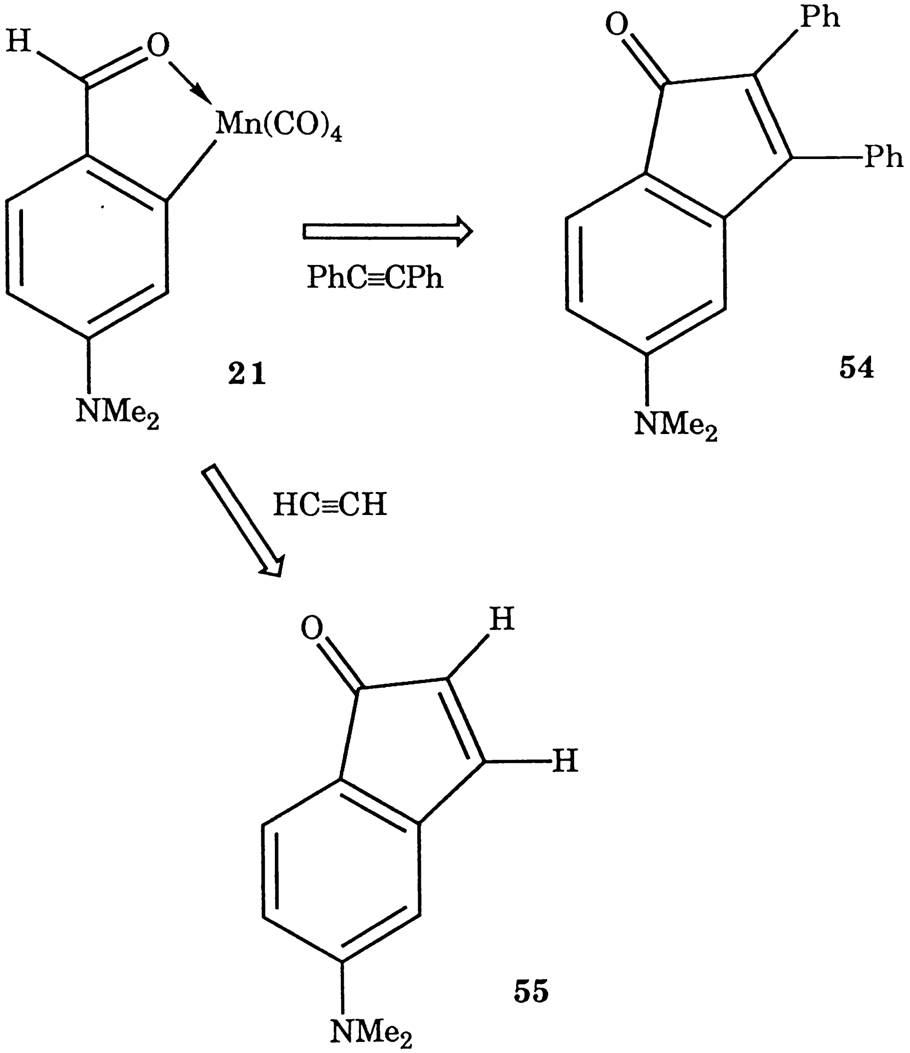
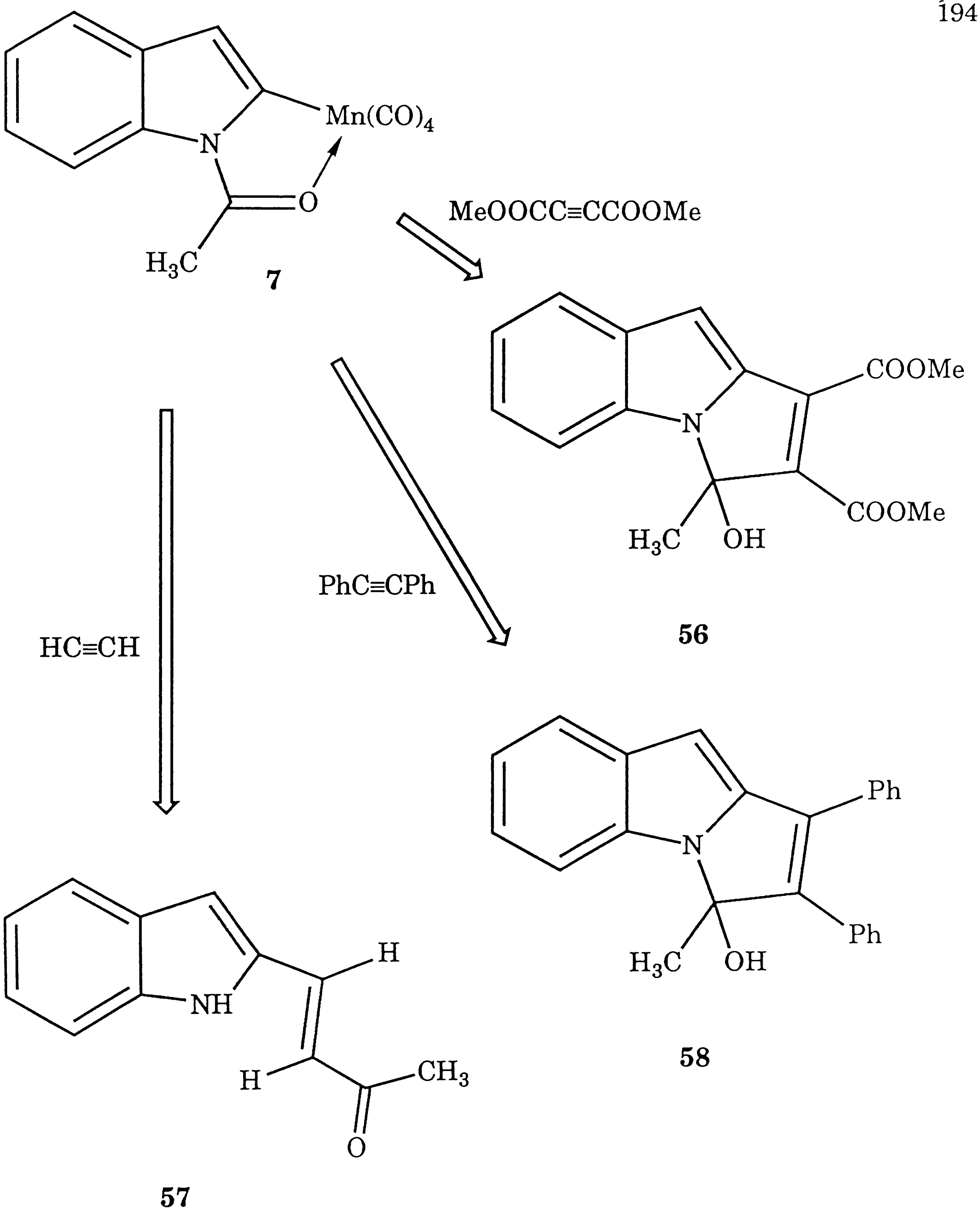

Me$_2$N
O
Mn(CO)$_4$
13
PhC≡CPh
O
Ph
Ph
49
HC≡CH
Me$_2$N
O
Mn(CO)$_3$
50
MeO
O
Mn(CO)$_4$
MeO
OMe
OMe
51
HC≡CH
PhC≡CPh
MeO
O
MeO
OMe
OMe
Mn(CO)$_3$
53
O
Ph
Ph
MeO
OMe
OMe
52


H
O
Mn(CO)4
NMe2
21
PhC≡CPh
O
Ph
Ph
NMe2
54
HC≡CH
O
H
H
NMe2
55


Mn(CO)$_4$
N
O
H$_3$C
7
MeOOCC≡CCOOMe
COOMe
N
COOMe
H$_3$C
OH
56
PhC≡CPh
HC≡CH
Ph
N
Ph
H$_3$C
OH
58
H
NH
H
CH$_3$
O
57