# Studies of some organonitrogen groups in molybdenum and tungsten complexes

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# STUDIES OF SOME ORGANONITROGEN GROUPS IN MOLYBDENUM AND TUNGSTEN COMPLEXES.

by

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A thesis submitted to the University of Durham
for the degree of Master of Science.

February, 1977.

To my Husband.

# MEMORANDUM.

The work described in this thesis was carried out in the University of Durham between October, 1975, and September, 1976. It has not been submitted for any other degree and is the original work of the author except where acknowledged by reference. Part of this work was presented at the Climax Second International Conference on the Chemistry and Uses of Molybdenum, Oxford, September, 1976, and is published as a paper in the Proceedings of the Climax Second International Conference on the Chemistry and Uses of Molybdenum, 1976. A copy of the paper is appended.

## ACKNOWLEDGEMENTS.

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B.K.Gaylani,
Durham,1977.

# SUMMARY.

The amidino-group has the potential to act as a uni-dentate, bidentate or a bridging group, and in addition the potential to chelate either through $\sigma$, $\sigma$ or $\sigma,\pi$ or $\pi$ attachment. New amidino-complexes of molybdenum and tungsten are described. Structures of the complexes and the nature of the bonding of the amidino-group to the metal are discussed and mechanisms proposed for the various reactions.

Lithioamidines and $H_2NC(Me)NH$ react with $[(\eta^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo,W) to produce yellow carbamoyl-type complexes $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(R')C(R)NR']$, (I; R = H, R′ =Ph; R =Me, R′=H,Ph, p-tolyl; R =Ph, R′= Me) supposedly by nucleophilic attack at a carbonyl group, whereas reactions of parent N, N′- disubstituted amidines appear to centre at the metal to produce $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]$, (II, R =H,R′=Ph; R =Me, R′=Ph,p-tolyl; R = Ph, R′=Me). No reaction occurred when the above compounds were reacted with neutral ligands such as $PPh_3$ or hex-2-ene.

Decarbonylation of (I) to yield (II) is achieved thermally or photolytically in small yields. I.r. data provides support for the generation of metal-tricarbonyl intermediates of the type $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\{R'NC(R)N(Me)R'\}]^+I^-$ in the photolytic reactions undertaken in the presence of MeI.

Reactions of lithioamidines with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ yielded (II), whereas parent amidines gave a non-carbonyl compound $[(\eta^5\text{-}C_5H_5MoO\{R'NC(R)NR'\}]$ and a monocarbonyl complex which may be of the type $[(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)\{R'NC(R)NR'\}]$. The lithioderivative of 2-aminopyridine reacted with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ to yield a yellowish carbamoyl-type complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC_5H_4N]$, while its neutral derivative gave traces of a dicarbonyl complex. Some exploratory reactions are also described.

# CONTENTS

Page

CHAPTER 1 Introduction

1.1. General Considerations. 1

1.2. The 18-electron Rule. 2

1.3. Infrared Spectra. 3

1.4. Metal Cyclopentadienyls. 5

1.5. π-Cyclopentadienyl Metal Carbonyls and Related Compounds. 8

1.6. Organonitrogen Derivatives. 10

References. 13

CHAPTER 2 A Survey of $\eta^5$-Cyclopentadienyltricarbonylmolybdenum and tungsten Complexes.

2.1. Routes into $\eta^5$-cyclopentadienylmolybdenum- and tungsten. 15

a) $\eta^5$-cyclopentadienyltricarbonylmolybdenum and tungsten dimer. 15

b) $\eta^5$-cyclopentadienyltricarbonylmolybdenum and tungsten hydride. 17

c) Halogen Derivatives. 17

2.2. a) $\eta^1$- and $\eta^3$- Alkyl and Acyl Derivatives. 19

b) Carbamoyl Derivatives. 26

2.3. Nitrogen Derivatives. 29

a) Nitrosyl Derivatives. 29

b) Methyleneamino Derivatives. 31

c) Aza allyl/allene Derivatives. 34

d) Amidine Derivatives. 37

2.4. B, Al, Tl Derivatives. 39

2.5. Si, Ge, Sn, Pb Derivatives. 41

Page

2.6. a) P Derivatives. 46

b) As, Sb Derivatives. 50

2.7. S, Se, Te Derivatives. 52

2.8. Ionic Derivatives. 55

2.9. Transition-Metal Derivatives. 56

2.10. Li, Na, K, Mg Derivatives. 58

References. 61

CHAPTER 3 Experimental Work.

3.1. General Aspects. 69

3.2. Reactions of $[\eta^5CpM(CO)_3Cl]$ (M = Mo,W) with Amidine. 70

3.3. Reactions of $[\eta^5CpM(CO)_3Cl]$ (M = Mo,W) with Lithioamidines. 81

3.4. Decarbonylation Reactions. 93

3.5. Miscellaneous Reactions. 95

References. 101

CHAPTER 4 Results and Discussion.

4.1. Reactions Using Amidines. 102

4.2. Reactions With Lithioamidines. 107

4.3. Decarbonylation Studies. 113

4.4. Additional Reactions. 115

References. 117

# CHAPTER 1

# INTRODUCTION.

## 1.1 General Considerations.

The ability of carbon monoxide to bond to transition metals in low oxidation states relies on the simultaneous $\sigma$-donation of the lone pair of electrons from the weakly donating carbon monoxide and the back donation from non-bonding metal d-orbitals to the antibonding $\pi$-orbitals of the carbon monoxide molecule. This 'synergic effect' prevents excessive build up of electron density on the metal and results in a metal-carbon bond order greater than one. Replacement of a carbonyl group by another ligand results in competition between the new and remaining ligands for the bonding potentialities of the metal. Thus the stability to disproportionation of the complex will depend upon the relative $\sigma$- and $\pi$-bonding capabilities of the ligands concerned. Displacement of a carbonyl group in a binary metal carbonyl (i.e. the metal formally in zero oxidation state) by a ligand with no $\pi$-acceptor properties (e.g. organic amines or ammonia) will strengthen the remaining metal-carbon bonds via increased $d\pi-\pi^*$bonding (i.e. more electron density available and less competition), but only up to a certain point, e.g.[1] $Cr(CO)_6 + liq.NH_3 \xrightarrow{120^o} Cr(CO)_3(NH_3)_3 + 3CO$

Further substitution past the $M(CO)_3L_3$ stage is not possible since the remaining groups are not able to dissipate the further charge build-up which would be caused.[2] If the ligand L, however, had $\pi$-acceptor properties (e.g. NO, $N^-$,$C_2H_4$), then dissipation of excessive electronic charge would not be the sole responsibility of the carbonyl groups and it may be possible to effect further replacement of CO from an $M(CO)_3L_3$ complex.

Interest has recently been focused on those complexes which contain a nitrogen atom and which are able to reduce the electron density on the metal. This has led to the developments in the chemistry of unsaturated organonitrogen ligands in which a 'sinergic effect' may also operate.

## 1.2 The 18-electron Rule.

One of the most useful and generally applicable concepts in the chemistry of the metal carbonyls and their derivatives is the "18-electron rule", which may also be known as the "effective atomic number" or "rare gas" rule. That is, the central metal atom accepts a number of additional electrons from its surrounding ligands so that it achieves a formally closed shell, or "noble" gas configuration. This simple rule has been very successful in predicting the stoichiometry of complexes that the few compounds which do not conform to the rule are still considered as "exceptions".

The inert-gas formalism can be applied whatever types of ligands are involved, but many compounds can be regarded in at least two ways for this electron counting procedure. For example, the compound $Fe(CO)_4I_2$ may be considered to be composed of (i) $Fe^0$ (8-electrons), two $I^\bullet$ radicals (2x1 electrons) and four carbonyl groups (4x2 electrons), or (ii) $Fe^{+II}$ (6 electrons), two $I^-$ anions (2x2 electrons) and the four carbonyl groups (4x2 electrons). In either case there is no net charge on the complex, and the total number of electrons is 18. The apparent difference in formal oxidation state of the metal atom has little real meaning in most cases in which strong metal-ligand bonding exists, although according to the definition of oxidation state, the iodine anion acts as a two-electron donor. The assignment of oxidation states to the metal is often only for the purpose of "electron counting".

Polynuclear, but particularly binuclear species, are common among the metal carbonyls and their derivatives. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$, exemplifies the simplest type of compound, in which the two halves of the molecule are joined only by a metal-metal bond, but in others, e.g. $Co_2(CO)_8$, bonding also involves bridging carbonyl groups. Bidentate ligands, which are more normally encountered in a chelating capacity, are also known to act as bridges, e.g. ethylenediamine (en) in $[M(CO)_4en]$, M = Cr, Mo,W[3] and $[(CO)_3M(en)_3M(CO)_3]$ , M = Cr[4], Mo[5]. In some cases, both ligand bridges and a metal-metal bond are required to satisfy the inert gas rule. For example, a group of compounds of composition $[Fe(CO)_3SR]_2$[6] are diamagnetic, but an electron count gives a total of only 17-electrons per iron atom. The postulated metal-metal bond to complete the electron shell and account for the diamagnetism, has been verified by X-ray studies.[7]

In the compounds $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NHR'\}]$ to be discussed in Chapters 3 and 4, the amidino ligand acts as a three electron donor to the metal (3-electrons), Mo(6-electrons), cyclopentadienyl ring (5-electrons), and 2 carbonyl groups (2x2 = 4-electrons); thus these complexes obey the 18-electron rule.

## 1.3 Infrared Spectra.

Infrared spectroscopy has proved one of the most useful tools in studies of transition metal carbonyls and their derivatives. The carbonyl stretching frequencies of metal carbonyl compounds are found between about 2150 and 1650 $cm^{-1}$, a region normally free of any other absorptions, and a study of the high resolution spectrum of a compound in this area can often be very informative.

The symmetry properties of a carbonyl complex determine the number and type of infrared active vibrational modes which are expected for the carbonyl groups, and the arrangement of the groups in a complex can often be deduced from the absorption pattern.[8] The method has certain limitations, however, notably that the ligands are usually regarded as points when considering the overall symmetry of the molecule and splitting of bands is sometimes observed, caused by the local symmetry of the ligand and lowering of the symmetry through crystal packing in the solid. Accidental coincidence of bands is also observed.

The CO stretching frequencies are a reflection of the bonding capabilities of other ligands present in a complex, since they reflect the

C–O bond order. Strongly electronegative groups such as halide ions or perfluoroalkyl and perfluoroacyl groups inductively withdraw charge from the metal, reducing its back-donating ability and resulting in an increased C–O bond order, reflected in the CO stretching frequencies which are higher than in the parent carbonyl complexes.[9] Conversely, ligands such as amines, with no $\pi$-acceptor properties donate charge to the metal resulting in carbonyl frequencies which are much lower than those of the parent carbonyl.

There have been numerous comparisons of the relative $\sigma$-donor and $\pi$-acceptor abilities of different ligands,[8,10] using carbonyl frequencies themselves and the application of semi-qualitative force constant calculations have verified the qualitative conclusions and yielded some new ones.[8,10] The donor-acceptor properties of ligands are not constant, but vary with the nature of the central atom and its environment. In general, unsaturated nitrogen-containing ligands are thought to possess small acceptor abilities; pyridine, in the disubstituted complexes $[M(CO)_4(py)_2]$(M = Cr,Mo,W) does accept electrons, but in the $[M(CO)_5py]$ complexes, the 5 carbonyl groups accept all the electron density and pyridine is purely a donor.[3] A comparison of the force constant-bond order relationship for $[(dien)Mo(CO)_3]$ (dien = diethylene triamine) and (acetonitrile)$_3$Mo(CO)$_3$ suggests that the carbon-nitrogen multiple bond has a small, but real ability to accept electrons from the metal.[8]

However, there is some discussion in the literature as to the reliability of carbonyl frequency shifts as a measure of the $\pi$-bonding abilities of ligands. Angelici[11] has studied the CO stretching frequencies of a number of substituted complexes, as a function of the pKa values of the ligands. He assumed that the aqueous pKa values of the ligands are a relative measure of the ability of L to donate $\sigma$-bonding electrons to the metal, and by comparing non $\pi$-bonding ligands (e.g. amines) and $\pi$-bonding ligands (pyridine and phosphines) he concluded that the carbonyl frequency shifts could be explained in terms of σ-bonding only, and could not be rationalised in terms of π-bonding between metal and pyridine or phosphine. In view of the large amount of data which suggests that phosphines and pyridines do π-bond to the metal, Angelici questions the relationship between π-bonding ability of ligands and the CO frequencies of their metal carbonyl complexes.

## 1.4 Metal Cyclopentadienyls.

A new field of organometallic chemistry was introduced in 1951 by the discovery of ferrocene. This independent discovery by Kealy and Pauson,[12] and Miller et al,[13] stimulated intensive research in the field of cyclopentadienylmetal chemistry and led to the synthesis of several hundred of compounds, which had been reviewed on many occasions.[14-19] Two general approaches have been applied to the synthesis of cyclopentadienylmetal compounds:[17] direct formation of cyclopentadienyl-metal bonds; and transformation of cyclopentadienyl-metal compounds to other related compounds.

### Bonding.

Figure 1.1 depicts the features of the bond between the transition metal and the cyclopentadienyl ring in the π-cyclopentadienyl derivatives.[18] In order to understand this type of bonding, it is first necessary to consider the molecular orbitals of the symmetrical, planar, pentagonal $C_5H_5$ ring. These can be divided into the following three types:

a) A bonding orbital - this orbital has no nodes, and, in the $C_5H_5^-$ anion, contains an electron pair.

b) $E_1$ bonding orbitals - these orbitals represent a degenerate pair. Each orbital has a single node. The two nodes in the two orbitals of this degenerate pair are perpendicular, i.e. they form $90^o$ angles with one another. In the $C_5H_5^-$ anion, each of the two degenerate $E_1$ bonding orbitals contains an electron pair.

c) $E_2$ antibonding orbitals - these orbitals, like the $E_1$ bonding orbitals, represent a degenerate pair. Each $E_2$ orbital has two perpendicular nodes.

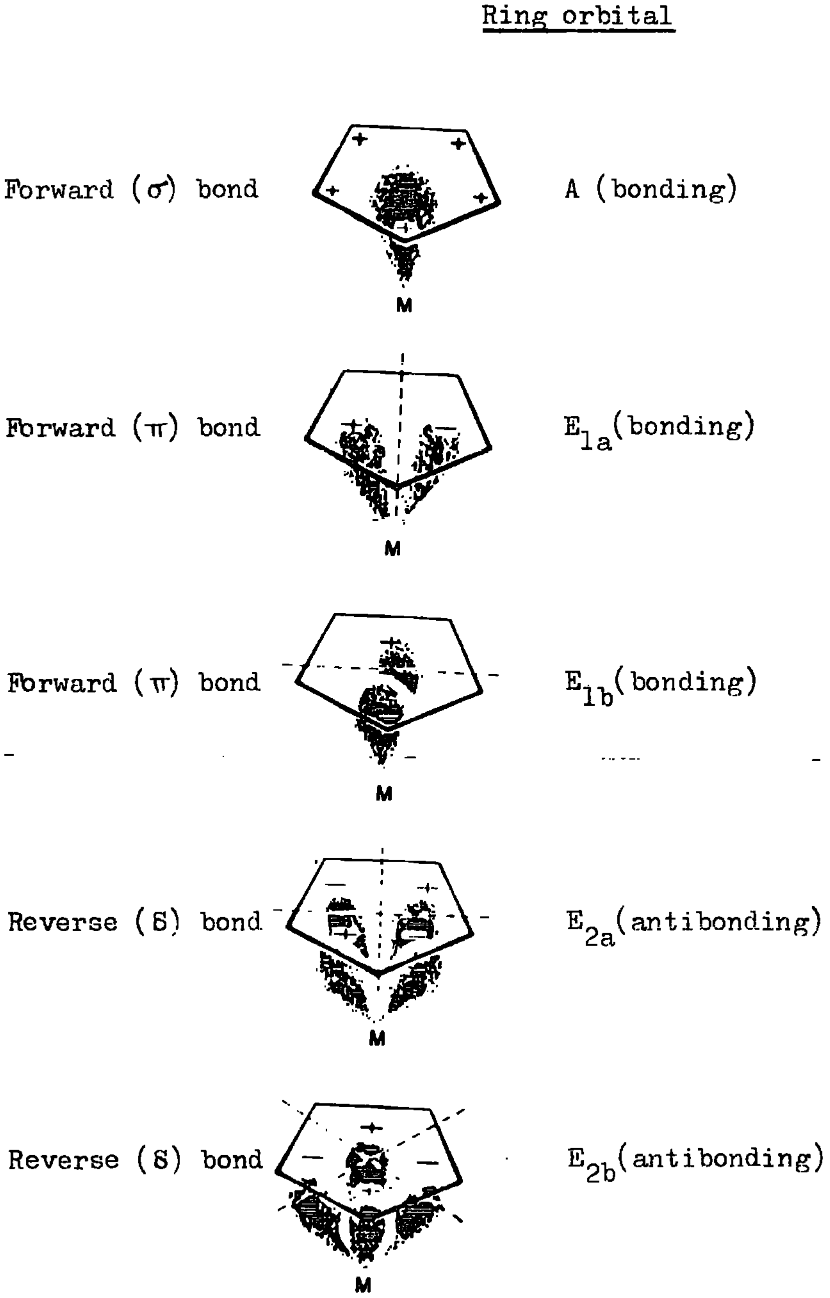


Figure 1.1 The components of the metal –π cyclopentadienyl bond.

The two pairs of perpendicular nodes in the two orbitals of this degenerate pair form 45° angles with one another. In the $C_5H_5^-$ anion, neither of the two degenerate $E_2$ antibonding orbitals contains an electron pair.

The $C_5H_5^-$ anion in the π-cyclopentadienyl metal derivatives may be regarded as a tridentate ligand, i.e. a ligand that donates three electron pairs to the metal atom. The filled (A) bonding orbital of the $C_5H_5^-$ ring can donate its electron pair to the metal atom by forming a σ-bond with a metal hybrid orbital. The pair of orthogonal filled $E_1$ bonding orbitals of $C_5H_5^-$ ring can donate their two electron pairs to the metal atom by forming a pair of orthogonal π-bonds with appropriate metal orbitals. The $C_5H_5^-$ ring thus donates its three electron pairs to the metal atom by means of a metal-ring triple bond composed of one σ-bond and two orthogonal π-bonds similar to the carbon-carbon triple bond in acetylene and its derivatives. Furthermore, the metal-ring triple bond in π-cyclopentadienyl metal derivatives with only one σ-bond and two orthogonal π-bonds uses different metal orbitals than the three σ-bonds between metal atoms and either of three monodentate ligands such as carbonyl groups or a nondelocalized tridentate ligand such as diethylenetriamine. The differences in the metal orbitals involved in the forward bonding mean that in the hexacovalent derivative $Cr(CO)_6$ the σ-bonding involves the use of S, Px, Py, Pz, $dz^2$, and $dx^2-y^2$ metal orbitals, whereas in the similarly formal hexacovalent derivatives $C_5H_5Mn(CO)_3$ and $(C_5H_5)_2Fe$ the forward bonding uses the S, Px, Py, Pz, dxz and dyz metal orbitals assuming that the $C_5H_5$-M axis is considered to be the z-axis.

The retrodative bonding that occurs in the bonding of metal carbonyls, also occurs in the π-cyclopentadienylmetal derivatives, but to a lesser extent than in the metal carbonyls. The retrodative bonding in π-cyclopentadienylmetal derivatives involves partial back donation of the electron pair in a binodal metal orbital not involved in the forward bonding (generally the $dx^2-y^2$ and dxy orbitals) to the empty binodal ligand $E_2$ orbitals. Since these reverse metal-ligand bonds in $\pi$-cyclopentadienylmetal compounds have two perpendicular nodal planes, this type of back bonding in $\pi$-cyclopentadienylmetal derivatives may be regarded as retrodative $\delta$-bonding. This contrasts with the reverse metal-ligand bonds in metal carbonyls, which have but one nodal plane and, therefore, represent retrodative $\pi$-bonding.

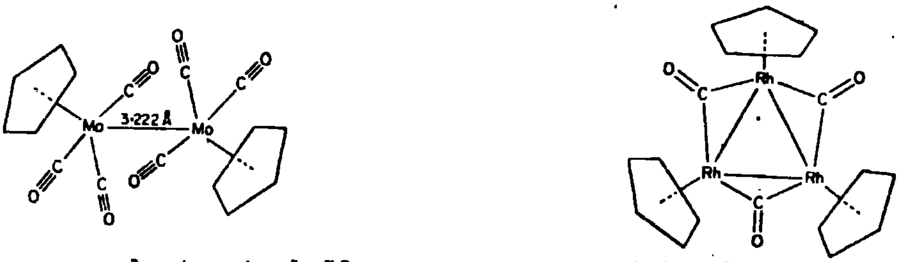
## 1.5 $\eta^5$Cyclopentadienyl Metal Carbonyls and related Compounds.

Since the first preparation by Wilkinson[20] of the binuclear cyclopentadienyl carbonyl compounds of molybdenum and tungsten, a large number of different cyclopentadienyl metal carbonyl compounds have been described. The structures of some are illustrated in Figure 1.2. With very few exceptions these compounds obey the 18-electron rule.[21] The simplest derivatives of the elements Cr, Fe and Ni are binuclear and held together either by metal-metal bonds or by bridging carbonyl groups and metal-metal bonds, whereas the two halves of the molecule $[\pi\text{-}C_5H_5Os(CO)_2]_2$ are held together purely by a 2-electron metal-metal bond; no evidence for any carbonyl bridged isomer has been obtained in the latter case.[21] The ruthenium complex is intermediate in character and an equilibrium between bridged and unbridged forms has been observed in solution from studies of the infrared spectrum in the carbonyl stretching region. Thus the tendency to form structures involving bridging carbonyl groups seems to fall off in order 1st>2nd>3rd transition series. These trends may be due to the increase in the size of the metal atoms with increase in atomic number. The metal-metal distance may become too large for a CO ligand to bridge.

Similar complexes containing bridging nitrosyl, isocyanide, phosphine, and hydride ligands, are known. A number of $\pi$-cyclopentadienyl metal complexes are known which contain clusters of three or more metal atoms, held together by metal-metal bonds and sometimes by bridging ligands as well. Of particular interest is the nickel complex, in which the two carbonyl groups

Mononuclear complex

Binuclear - with bridging CO groups



Binuclear - only terminal CO groups

Trinuclear - bridging CO groups

Trinuclear - triply bridging CO groups

Binuclear - bridging nitrosyl

Figure 1.2 Some π-cyclopentadienyl carbonyl and nitrosyl complexes.

each bridge all three metal atoms.

$\eta^5$-cyclopentadienyl metal carbonyls are usually rather stable thermally, and in the solid state most resist oxidation by oxygen at room temperature. They can often be reduced by sodium amalgam to yield $\eta^5$-cyclopentadienyl carbonyl anions. This reduction may proceed either by loss of carbon monoxide, e.g. $\eta^5\text{-}C_5H_5V(CO)_4 \xrightarrow[THF]{Na/Hg} (Na^+)_2[\eta^5\text{-}C_5H_5V(CO)_3]^{2-}$ + CO or by cleavage of a metal-metal bond, e.g.

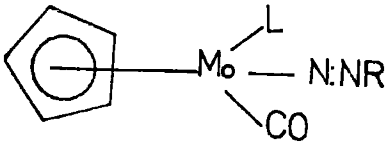
$$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2 \xrightarrow[THF]{Na/Hg} 2[\eta^5\text{-}C_5H_5Fe(CO)_2]^- Na^+$$

$$[\eta^5\text{-}C_5H_5Mo(CO)_3]_2 \xrightarrow[THF]{Na/Hg} 2[\eta^5\text{-}C_5H_5Mo(CO)_3]^- Na^+$$

## 1.6. Organonitrogen Derivatives.

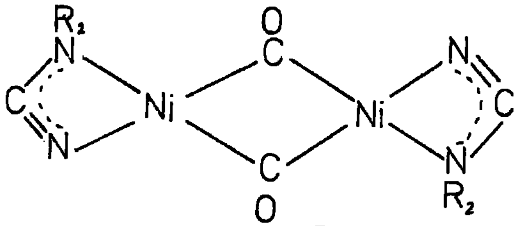
The importance of organonitrogen groups in transition metal chemistry has been recognised for many years, particularly in the field of homogeneous catalysis where organonitrogen-metal intermediates are postulated.[22,23] More recently, interest has been focused on the versatility of the bonding in unsaturated organonitrogen groups, especially those containing carbon-nitrogen and nitrogen-nitrogen multiple bonded systems, the reactions of which, in the presence of transition metal carbonyl complexes have recently been reviewed.[22] The versatility of organonitrogen groups in bonding to low valent transition metals is illustrated in Figure 1.3. The various bonding modes possible for the amidino-group will be discussed later in the context of the work described.

Figure 1.3 Some Organonitrogen Complexes.

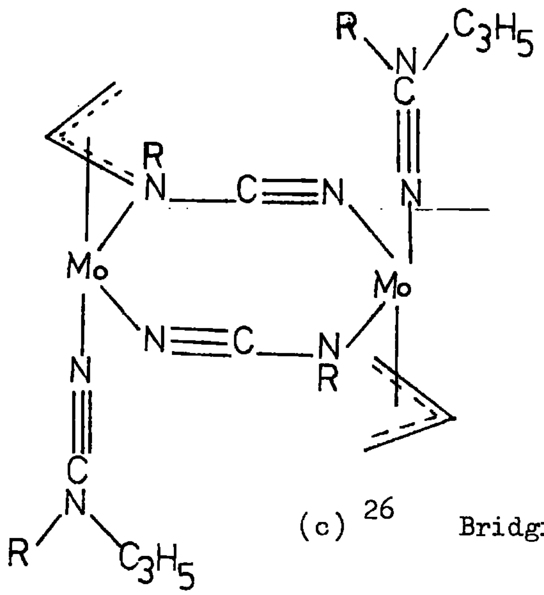


(a) [24]

Terminal

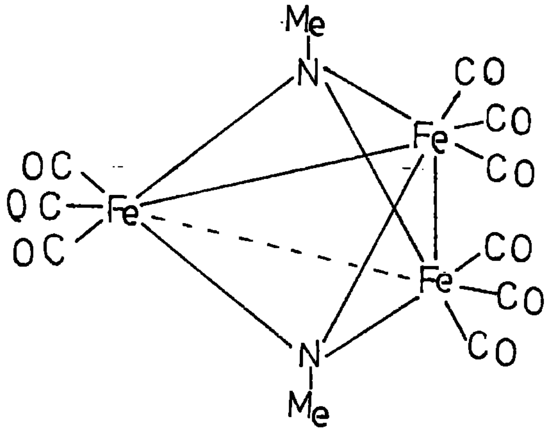


(b) [25]

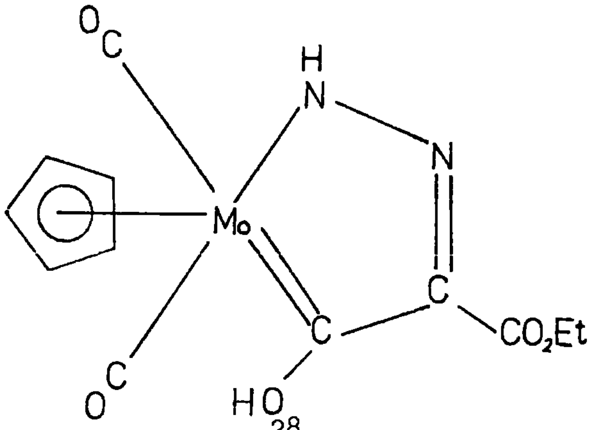


(c) [26]

Bridging

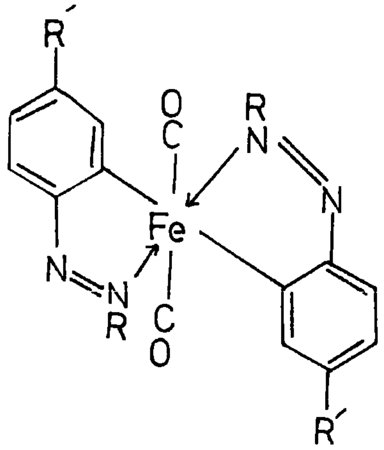


(d) [27]



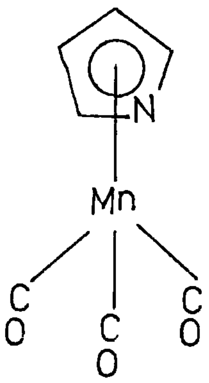
(e) [28]

Cyclic



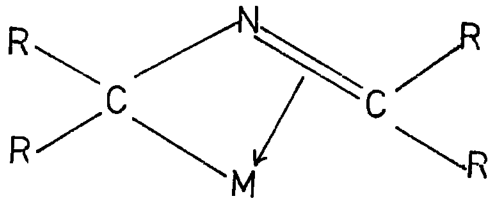
(f) [29]

Ortho-Metallated



(g) [30]

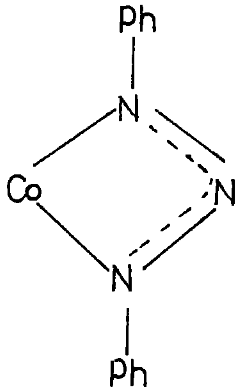
π- bonded heterocyclic



$M = \eta^5\text{-}C_5H_5Mo(CO)_2$

(h) [31]

σ - π bonded



(i) [32]

σ , σ attachment.

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# CHAPTER 2

## A Survey of $\eta^5$-Cyclopentadienyltricarbonylmolybdenum and - tungsten Complexes.

In this Chapter the wide variety of $\eta^5$-cyclopentadienylmolybdenum and - tungsten complexes are reviewed. Derivatives are known with substituent groups from most groups of the Periodic Table, and except for those derivatives which have wide synthetic use, the complexes are discussed in the context of the Periodic Group of the atom attached to the metal. All complexes appear to obey the 18-electron rule. Consequently the ligands attached to molybdenum or tungsten, in addition to the $\eta^5$-cyclopentadienyl group, provide a total of seven electrons to the bonding. Thus derivatives are of the general type $[\eta^5\text{-}C_5H_5M(CO)_xL_{3-x}X]$, where L is a neutral two-electron donor molecule such as a phosphine or nitrogen base, and X is a one-electron donor such as a halogen, pseudo-halogen, etc. or another metal fragment. $\eta^5$-Cyclopentadienylmolybdenum and - tungsten complexes of the types given above are usually rather thermally stable, and in the solid state commonly resist oxidation under normal conditions. The complexes have traditionally been popular in organometallic chemistry for studies involving the formation of bonds between a transition metal and some other element.

## 2.1 Routes into $\eta^5$-Cyclopentadienylmolybdenum and - tungsten Chemistry.

Such routes inevitably involve the $\eta^5$-cyclopentadienyltricarbonyl dimers and their carbonylate anions, hydrido-, and halo-derivatives as starting materials, all of which are most conveniently prepared from the hexacarbonyls, $M(CO)_6$ (M = Mo,W). Each of these types of complexes will be discussed below separately before the other derivatives which are classified according to the nature of the atom coordinated to the metal.

### a) $[\eta^5\text{-}CpM(CO)_3]_2$ (M = Mo,W) *

These air stable, moderately soluble, purple red complexes were first prepared by Wilkinson[1] in a vapour phase reaction of cyclopentadiene with metal carbonyls at elevated temperatures (Mo, 240°, yield 30%; W ~250°). Wilson and Shoemaker[2] suggested a nonlinear structure with a metal-metal bond

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* Cp is used throughout the thesis as an abbreviation for the $\eta^5$-cyclopentadienyl group.

and with six terminal carbonyl groups, as shown in Figure 1.

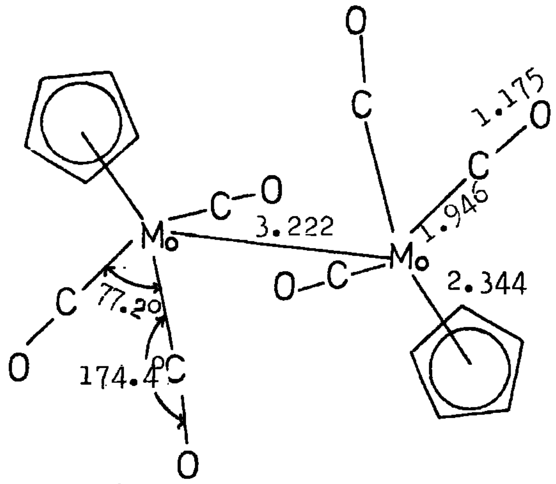


Figure 1 Structure of $[(\eta^5\text{-CpMo(CO)}_3]_2$ .

Reduction of $[\text{CpM(CO)}_3]_2$ (M = Mo,W) by Na/K alloy in THF at room temperature provides a rapid and clean method for the production of $[\text{CpM(CO)}_3]^-$,[3] precipitated as [CpCo] $[\text{CpM(CO)}_3]$ and $\text{Hg}[\text{CpM(CO)}_3]_2$, whereas oxidative metal-metal bond cleavage results from photolysis in the presence of halogen containing compounds.[4]

$$[\text{CpM(CO)}_3]_2 \xrightarrow[\text{CCl}_4,\ 25^\circ]{\text{photolysis}} 2[\text{CpM(CO)}_3\text{Cl}]$$

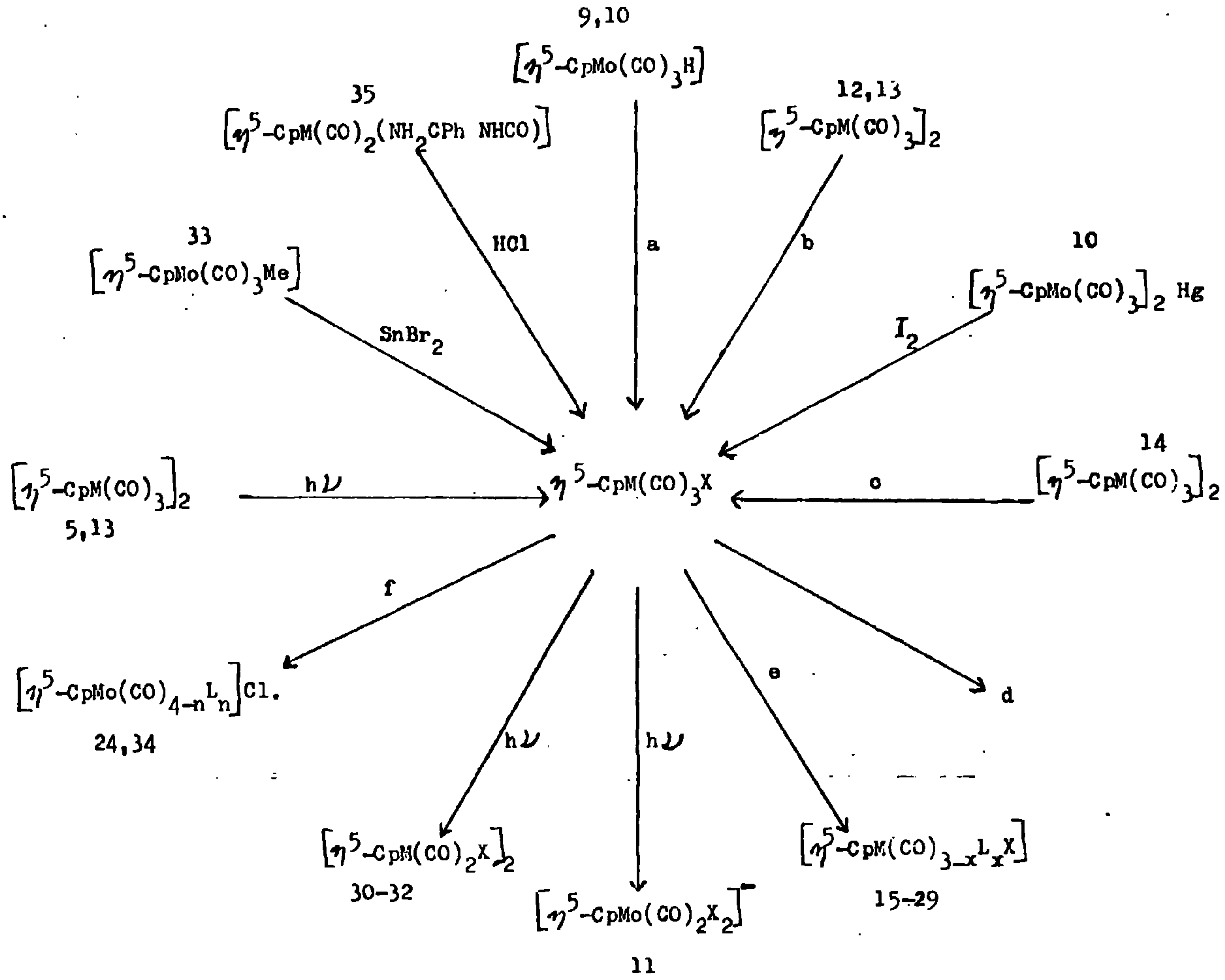
The simultaneous photolysis of $[\text{CpM(CO)}_3]_2$ with dimers of the type $[\text{M}'_2(\text{CO})_{10}]$ (M′= Mn,Re) yields $[(\text{CO})_5\text{M}'\text{M(CO)}_3\text{Cp}]$[5] in good yield, which on photolysis at 366nm in $\text{CCl}_4$ produces $[\text{CpM(CO)}_3\text{Cl}]$. In the presence of phosphines and phosphites the photolysis of the molybdenum dimer causes the substitution of two carbonyl groups to form complexes of the type[6] $[\text{CpMo(CO)}_2\text{L}]_2$ $[\text{L} = \text{PPh}_3, \text{P(OCH}_2)_3\text{CMe}, \text{P(OR)}_3\ (\text{R} = \text{Et, Me, Pr}^i, \text{Bu}^n]$.[7] Interestingly the photolysis of $[\text{Cp(CO)}_3\text{MoGe(C}_2\text{H}_3)\text{Me}_2]$ produced a new $\eta^5$-cyclopentadienylcarbonyl complex $[\eta^5\text{-CpMo(CO)}_2]_2$, albeit in small yield, in addition to $[\eta^5\text{-CpMo(CO)}_3]_2$. The tetracarbonyl dimer was formulated with a Mo≡Mo triple bond to conform with the 18-electron rule.[8]

### b) $[CpM(CO)_3H]$ (M = Mo,W).

The hexacarbonyls react with metalcyclopentdienides, M′Cp (M′= Li, Na, K), in dimethylformamide at 130° to give $[CpM(CO)_3]M'$ (M = Mo,W)[9] which are converted to oxygen sensitive $[CpM(CO)_3H]$ by treatment with acids, usually acetic acid.[3] Purification by vacuum sublimation yields a bright yellow molybdenum derivative (m.p.50-2°), and a pale yellow tungsten derivative (m.p. 66-7°).[3] $[CpMo(CO)_3H]$ loses hydrogen on heating or exposure to air[10] and forms $[CpMo(CO)_3]_2$. $[CpW(CO)_3H]$ is much more thermally stable but is also more light-sensitive than $[CpMo(CO)_3H]$.[3]

### c) Halogen derivatives.

The orange-red (X = Cl) and red (X = Br,I) halide complexes $[CpM(CO)_3X]$ were prepared by Piper and Wilkinson starting from $[CpM(CO)_3H]$.[9,10] They were also prepared from cleavage of the metal-metal bond of $[CpM(CO)_3]_2$ by photolysis or heating in halogenated solvents.[11-14] A variety of ligands (L) of the type $R_3P$, $R_3As$, etc. react with $[CpM(CO)_3X]$ by replacement of one, two or all three carbonyl groups to form complexes of the type $[CpM(CO)_2LX]$, $[CpM(CO)L_2X]$,[15-27] and $[CpML_3X]$.[28,29] A rather novel reaction, which involves the elimination of a phosphine rather than carbon monoxide as is usual,[30,31] involves the photolysis of $[CpM(CO)_2LX]$ (M = Mo,W; L = $P(OPh_3)$, $PPh_3$, $P(C_6H_{11})_3$; X = I,Cl; L = CO) which yields $[CpM(CO)_2X]_2$. Here the halide probably acts as a three electron bridging group, and is a particularly unusual product to form since halogen bridges are commonly cleaved by phosphines,[32] etc. Some reported preparations and reactions of halide derivatives are summerized in Scheme 2.1.



SCHEME 2.1. The Preparation and Some Reactions of $[CpM(CO)_3X]$ (M = Mo,W; X = Cl,Br,I) Complexes.

a) Reaction for X = Cl, $CCl_4$, I, MeI, Br,N - bromosuccinimide.

b) Ph CO CH : CHI, $I_2$

c) With Sn $X_2$ (X = F,Cl,Br,I)

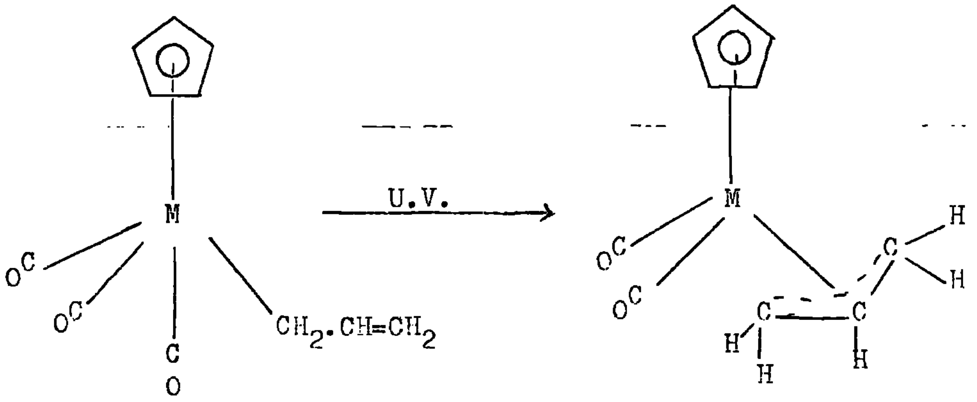
d) A wide variety of cyclopentadienyl molybdenum and tungsten carbonyl complexes.

e) L = phosphines and phosphites.

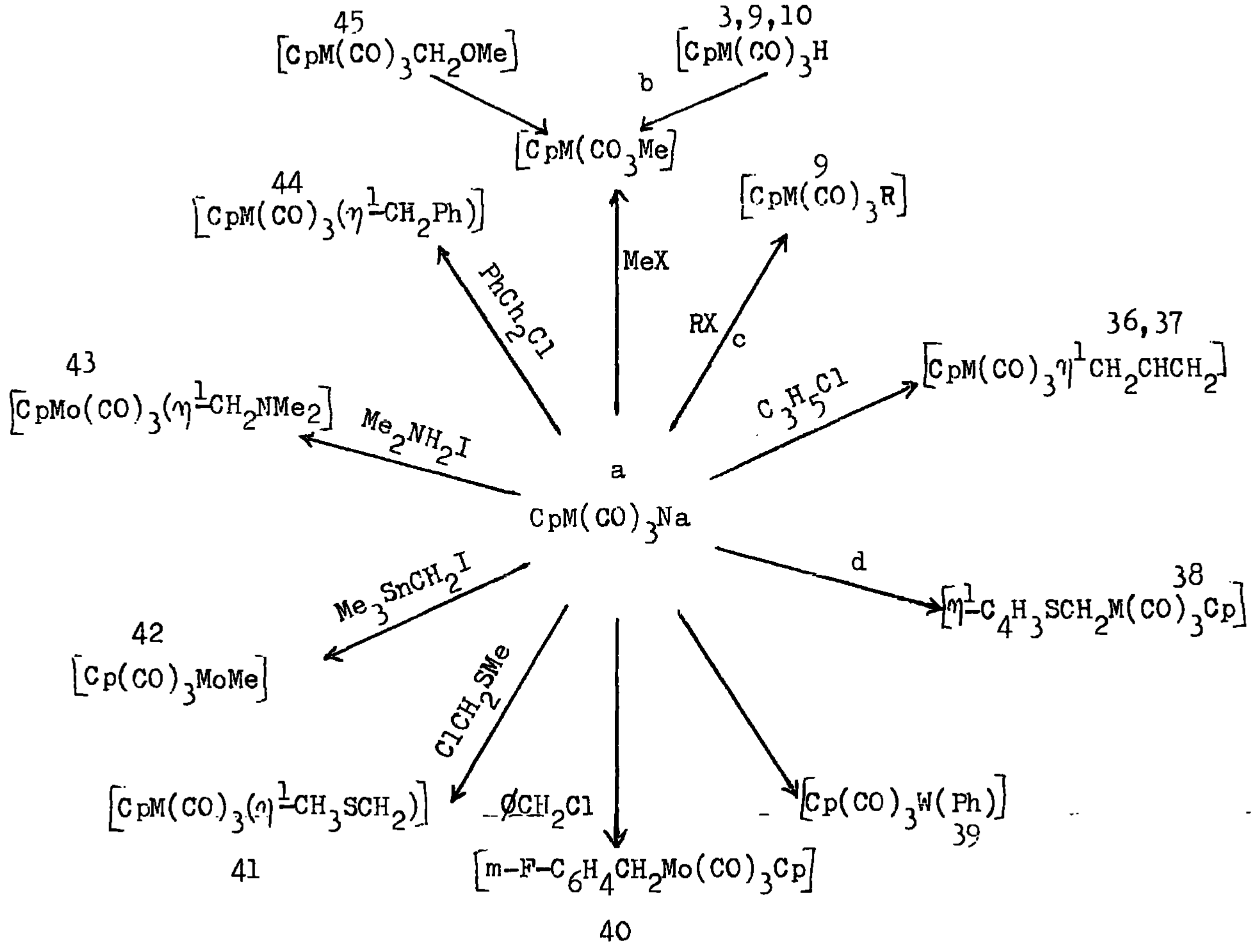
f) L = $NH_3$, $N_2H_4$, $NH_2R$, $PEt_3$; $L_2$ = Diphos.

## 2.2 a) $\eta^1$ and $\eta^3$-Alkyl Derivatives.

Alkyl and aryl complexes of cyclopentadienyl molybdenum and tungsten carbonyl were first prepared by Piper and Wilkinson,[9] whose paper in 1956 is regarded as one of the classic papers in transition metal organometallic chemistry. These complexes are mostly prepared starting from $[CpM(CO)_3]Na$ (M = Mo,W) with alkyl or aryl halides, as illustrated in Schemes 2.2 and 2.3. Some known σ-alkyl derivatives are listed in Table 2.1, together with some physical properties. Decarbonylation of $[\eta^5CpM(CO)_3\eta^1-R]$ complexes, where R is allyl or related group to form π-derivatives $[\eta^5CpM(CO)_2\eta^3-R]$ can be achieved thermally or by irradiation with U.V. light.



(M = Mo,W)



SCHEME 2.2 Some Preparations of σ-Alkyl Derivatives.

a) M = Mo,W.

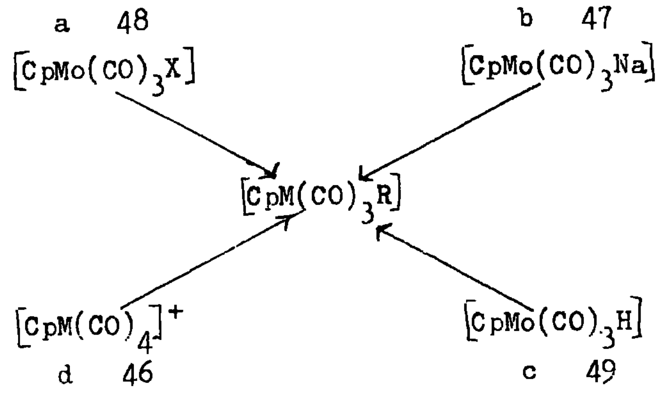
b) With $CH_2N_2$.

c) R = Et, $C_3H_7$.

d) With 2- Chloromethylthiophene or 3- Bromomethylthiophene.

Table 2.1 Some Properties of $\sigma$-Alkyl Compounds.

| Complex | Colour | m.p. | $\nu$(CO),cm$^{-1}$ |
|---|---|---|---|
| $\eta^5$-CpMo(CO)$_3$Me | yellow | 124° | 2020(VS),1937(VS) |
| $\eta^5$-CpMo(CO)$_3$Et | yellow | 77.5–8.5 | 2016(VS),1932(VS) |
| $\eta^5$-CpMo(CO)$_3$Pr-iso | yellow | 29–30° | 2010(VS),1930(VS) |
| CpW(CO)$_3$Me | lemon yellow | 144.7–5.3 | 2020(VS),1930(VS),1740(W) |
| CpW(CO)$_3$Et | yellow | 93–3.5 | 2020(VS),1920(VS) |
| CpMo(CO)$_3$$\eta^1$-CH$_2$CHCH$_2$ | pale yellow oil | | 2021(VS),1911(VS),1856(VS) |
| CpMo(CO)$_2$$\eta^3$-C$_3$H$_5$ | lemon yellow | ~134 | 1961(VS),1886(S),1871(VS) |
| Cp(CO)$_3$Mo$\eta^1$-CH$_3$SCH$_2$ | yellow | 66–67° | 2029(S),1952,1943(VS) |
| Cp(CO)$_2$Mo$\eta^3$-CH$_3$SCH$_2$ | yellow-orange | 65–67° | 1922(S),1838(S) |
| Cp(CO)$_3$Mo$\eta^1$-CH$_2$Ph | yellow | 87–88° | |
| Cp(CO)$_2$Mo$\eta^3$-PhCH$_2$ | red | 83–85° | |
| m-FC$_6$H$_4$CH$_2$Mo(CO)$_3$Cp | yellow | 102–104° | 2017(S),1937(VS) |
| $\eta^1$-2-C$_4$H$_3$SCH$_2$Mo(CO)$_3$Cp | yellow | m.p. 63°–87° for $\eta^1$-complexes 102–127°c for $\eta^3$-complexes | 2027(S),1944(S),1940(S) |
| $\eta^1$-3-C$_4$H$_3$SCH$_2$Mo(CO)$_3$Cp | yellow | | 2025(S),1945(S),1935(S) |
| $\eta^3$-2-C$_4$H$_3$SCH$_2$Mo(CO)$_2$Cp | red-orange | | 1967(S),1963(Sh,1895(S)1882(m) |
| $\eta^3$-3-C$_4$H$_3$SCH$_2$Mo(CO)$_2$Cp | red-orange | | 1970(S),1897(S),1884(m) |
| $\eta^1$-2-C$_4$H$_3$SCH$_2$W(CO)$_3$Cp | yellow | | 2024(S),1934(Sh),1930(S) |
| $\eta^1$-3-C$_4$H$_3$SCH$_2$W(CO)$_3$Cp | yellow | | 2010(S),1941(S),1928(S) |
| CpMo(CO)$_3$($\eta^1$-Me$_2$NCH$_2$) | pale yellow | | 2037(m),1969(S),1953(m) |
| CpW(CO)$_3$($\eta^1$-Me$_2$NCH$_2$) | yellow | | 2045(S),1961(VS),1945(S) |
| CpMo(CO)$_2$($\eta^2$-Me$_2$NCH$_2$) | yellow | | 1936(S),1844(S) |



SCHEME 2.3 <u>Some Preparations of Fluoroalkyl Derivatives.</u>

a) $CpMo(CO)_3X$ (X = halide) with silver perfluorocarboxylates

$R = R_FCO_2$; $R_F = CF_3$, $C_2F_5$, $n\text{-}C_3F_7$.

b) with $C_3F_7COCl$. $R = COC_3F_7$.

c) with $C_2F_4$. $R = CF_2CF_2H$.

d) with $C_6F_5Li$. $R = COC_6F_5$. Mo = Mo,W.

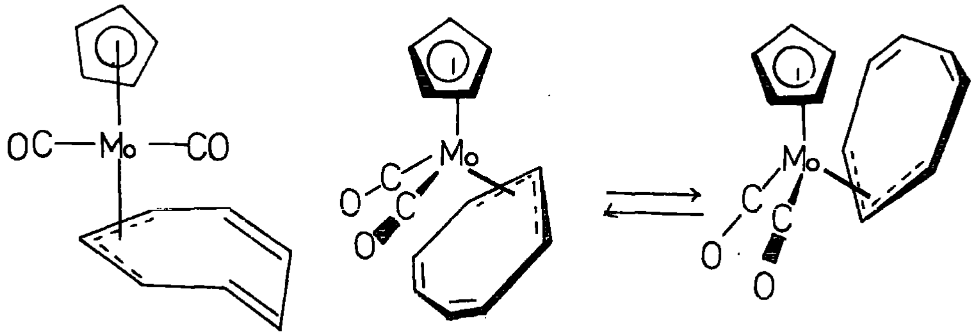
σ-Alkyl complexes on reaction with phosphines etc. may undergo carbonyl insertion reactions to give the corresponding acyl complexes $[\eta^5\text{-}CpM(CO)_2L(COR)]$[27,50-57], and it was found that the rate constant for cleavage of the metal-carbon bond in $[\eta^5\text{-}CpM(CO)_3R]$ complexes decreases in the following order $Me > CH_2Ph > Et$.[58] These and other reported insertion reactions are given in Table 2.2. The alkyl ligand groups may be of a wide variety of different groups, and have various substituents as illustrated by the following complexes of the type $[\eta^5\text{-}CpM(CO)_3CH_2X]$. (X = $C_6H_4Cl\text{-}p$, $C_6H_5$, $C_6H_4OCH_3\text{-}p$, CN,CL,[50] $CH_2\text{-}CH = CMe_2$,[60] $C_6H_4(m\text{-}F)$,[40] COPh,[61] Cl,[45] Br,[62] OMe, I,[63] $NC_5H_4$,[64] MeOCO,[65] EtOCO,[65] $CO_2H$,[66] $CONH_2$,[66] $C_6H_4Me\text{-}p$,[67] $C_6H_3(3,5\text{-}i\text{-}Pr)_2$).[67]

Table 2.2 **Reactions of $[\eta^5\text{-}CpMo(CO)_3R]$ with Neutral Ligands.**

| R | L | reaction conditions | Products | Ref. |
|---|---|---|---|---|
| Me | $CNC_6H_{11}$ | benzene, R.T. | $CpMo(CO)_2(CNC_6H_{11})(COMe)$ | 50 |
| $CH_2Ph$ | $CNC_6H_{11}$ | benzene, R.T. | $CpMo(CO)_2(CNC_6H_{11})COCH_2Ph$ | 50 |
|  |  |  | $CpMo(CO)_3(CNC_6H_{11})CH_2Ph$ | 50 |
| $CH_2C_6H_4PX$ | $CNC_6H_{11}$ | benzene, R.T. | $CpMo(CO)_3[C\{CH_2C_6H_4X\text{-}\underline{p}\}{=}NC_6H_{11}]$ | 50 |
| Me, Ph | $Me_3CNC$ | MeCN, R.T. | $CpMo(CO)_2\{Me_3CNC(COR)\}$ | 27 |
| $PhCH_2$,Et<br>$NC(CH_2)_3$ | KCN | MeOH | $K[CpMo(CO)_2(CN)(COR)]$ | 51 |
| Me | $Ph_3As$ | acetonitrile | $CpMo(COCH_3)(CO)_2AsPh_3$ | 52 |
| Me | $[(Me_3Si)_2CH]_2Sn$ |  | $Cp(CO)_3Mo\text{-}Sn[(Me_3Si)_2CH]_2Me$ | 53 |
| Me | $[(Ph)_2PC{\equiv}CPh]$ | MeCN, 25° | $CpMo(CO)_2(COMe)L$ | 54 |
| $CH_2Ph$ | $[(Ph)_2PC{\equiv}CPh]$ | MeCN, 25° | $CpMo(CO)_2(COCH_2Ph)L$ | 54 |
| Me,Et | $PR'_3$, $P(OR')_3$ |  | $CpMo(CO)_2(PR'_3)(COR)$ | 55 |
|  |  |  | $CpMo(CO)_2\ P(OR'_3)\ (COR)$ | 55 |
| Me,Et,$CH_2Ph$ | $SO_2$ |  | $CpMo(CO)_3R.\ SO_2$ | 55 |
| $CH_2Ph$ | phosphines or phosphites | acetonitrile | $PhCH_2.COMe(CO)_2(L)Cp$ | 56 |
| $C_3H_5$ | phosphines or phosphites | acetonitrile | $C_3H_5COMo(CO)_2(L)Cp$ | 56 |
| $C_4H_7$ | $PPh_3$ | acetonitrile | $CH_3.CH \overset{c}{=} CH.CH_2(OMe(CO)_2Cp$ $(PPh_3)$ | 56 |
| Me | $PPh_3$ | THF, 65° | $CpMo(CO)_2[(Ph)_3P(COCH_3)]$ | 57 |
| Et | CO |  | $EtCOMo(CO)_3Cp$ | 59 |

## Some interesting $\pi$-allyl complexes.

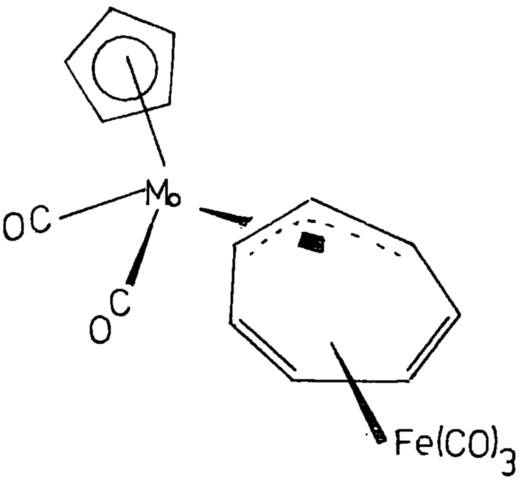
Treatment of $[\eta^3\text{-}C_7H_7Mo(CO)_2I]$ with $C_5H_5Na$ in THF gave an orange crystalline volatile complex $[\eta^5\text{-}CpMo(CO)_2\eta^3\text{-}C_7H_7]$.[68,69] The most probable structure for this complex is that in Figure 2(i)



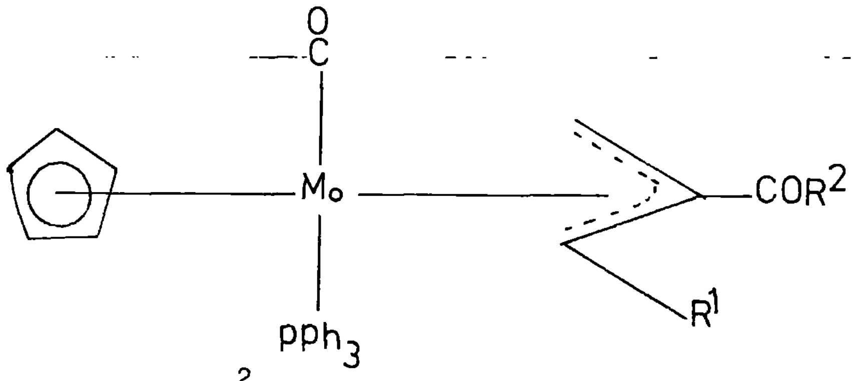
(i) (ii) (iii)

Figure 2 Structures of $[\eta^5\text{-}C_5H_5Mo(CO)_2\eta^3\text{-}C_7H_7]$

In this structure the molybdenum atom receives three electrons from the $\pi$-cycloheptatrienyl ring, five electrons from $\eta^5$-cyclopentadienyl ring and four electrons from the two carbonyl groups giving it the desired inert gas configuration.[70,71] Spectroscopic study of the complex and the similarity of its i.r. spectrum to that of the $\pi$-allyl derivatives strongly suggests an equilibrium between structures (ii) and (iii) shown in Figure 2.[72] Red crystals of a related complex $[\eta^5\text{-}CpMo(CO)_2(C_7H_7Fe(CO)_3]$ were obtained from photochemical reaction of $[\eta^5\text{-}CpMo(CO)_2(\eta^3\text{-}C_7H_7)]$ with $[Fe(CO)_5]$ and/or $Fe_2(CO)_9$.[73] The heterodinuclear complex has a structure in which the $[\eta^5\text{-}CpMo(CO)_2]$ group lies over one face of the $(C_7H_7)$ ring and interacts with a sequence of three carbon atoms (a $\pi$-allyl-type complex), while $Fe(CO)_3$ lies over the other face and interacts with a butadiene-like sequence of four carbon atoms.[73]



An unusual preparative route to $\eta^3$-allyl derivatives is illustrated by the reaction of $[\eta^5\text{-CpMo(CO)}_2(\text{PPh}_3)\text{CH(R)C} : \text{CR}^1]$ with $R^2H(R^2 = \text{MeO,PhS,EtO,Me}_2\text{CO})$[74] to form the following derivative:



$R^1$ = H, Me, Ph;  $R^2$ = MeO, PhS, EtO, $Me_2CO$

Another interesting reaction involves homoallyl bromides which react with $[\text{CpMo(CO)}_3]^-$ to yield anti- and syn- forms of the products given below.[75]

$\eta^5\text{-CpMo(CO)}_3^- + \text{Br(CH}_2)_2\text{-CH = CH-R} \xrightarrow{\text{THF}} \eta^5\text{-CpMo(CO)}_2\pi\text{-C}_4\text{H}_6\text{R}$ (R = H,Me)

$\eta^5\text{-CpMo(CO)}_3^- + \text{Br(CH}_2)_2\text{ CH = CH-R + PPh}_3 \xrightarrow{\text{THF}} \eta^5\text{-CpMo(CO)}_2(\text{PPh}_3)(\text{CO})(\text{CH}_2)_2$
$\text{-CH = CH-R} + \eta^5\text{-CpMo(CO)}_2\text{-}\pi\text{C}_4\text{H}_7\text{R}$

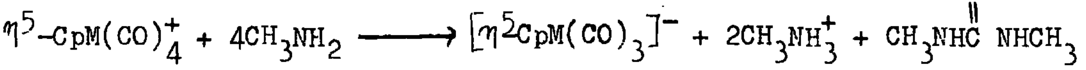
b) Carbamoyl Derivatives.

The carboxamido complexes were prepared by Jetz and Angelici from primary and secondary alkylamines according to the equations.[76]

$$\eta^5\text{-CpM(CO)}_4^+ + 2R_2NH \longrightarrow \eta^5\text{-CpM(CO)}_3(CONR_2) + R_2NH_2^+$$

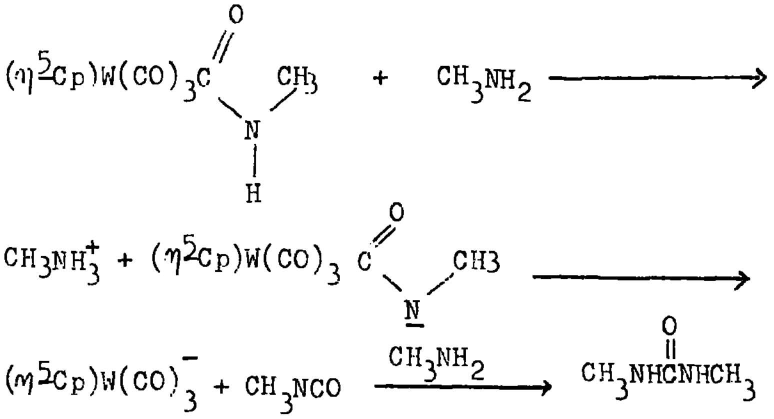
$$\eta^5\text{-CpM(CO)}_4^+ + 2RNH_2 \longrightarrow \eta^5\text{-CpM(CO)}_3(CONHR) + RNH_3^+$$

(M = Mo,W), and it was indicated by their $^1$H.n.m.r. spectra that the two methyl groups were non-equivalent, presumably caused by restricted rotation around the C-N bond of the carboxamido group. In contrast to the stable complexes [$\eta^5$-C$_5$H$_5$W(CO)$_3$CONHR] (R = Me,CMe$_3$), the molybdenum analogues were too unstable to isolate in pure form and readily decomposed to [$\eta^5$-C$_5$H$_5$Mo(CO)$_3$]$_2$.[76] The use of an excess of the primary amine may lead to the formation of 1,3- dialkylureas and [$\eta^5$-CpW(CO)$_3$]$^-$ according to the equation.[76]



$$\eta^5\text{-CpM(CO)}_4^+ + 4CH_3NH_2 \longrightarrow [\eta^5\text{-CpM(CO)}_3]^- + 2CH_3NH_3^+ + CH_3NH\overset{O}{\overset{\|}{C}}\,NHCH_3$$

It was shown that the reaction proceeded by initial formation of the carboxamido complex, which reacted with excess amine to generate CH$_3$NCO as an intermediate. Further reaction with the amine rapidly yielded 1,3 - dimethylurea



An interesting reaction is that of [$\eta^5$-CpW(CO)$_3$H] with CH$_3$NCO to produce the carboxamido complex.[76] $(\eta^5\text{-Cp})W(CO_3H + CH_3NCO \xrightleftharpoons{Et_3N} \eta^5\text{-CpW(CO)}_3C(O)NHCH_3$ which formally appears to be an insertion of CH$_3$NCO into the W-H bond, but mechanistically it almost certainly proceeds by nucleophylic attack of

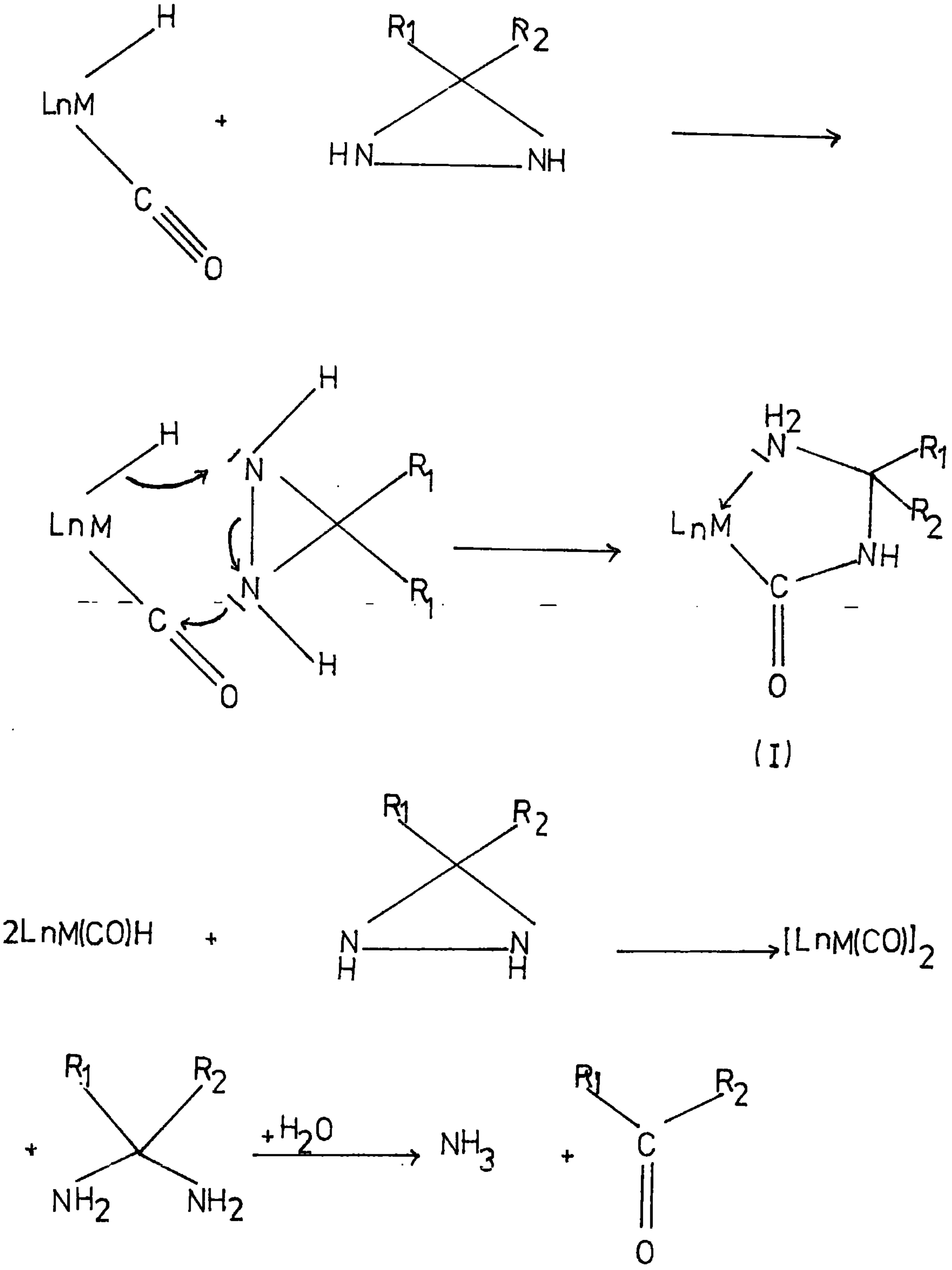
$[\eta^5\text{-CpW(CO)}_3]^-$ on the isocyanate.

Some spectroscopic data on carbamoyl complexes are given in Table 2.3 for comparative purposes in connection with the experiment work reported later in this thesis.

Table 2.3 Infrared Data for Carbamoyl Complexes.

| Complex | Solvent | $\nu$(CO), cm$^{-1}$ |
|---|---|---|
| $\eta^5\text{-CpW(CO)}_3\text{CONHCH}_3$ | $CCl_4$ | 2018S, 1928VS, 1597m |
| $\eta^5\text{-CpW(CO)}_3\text{CONHC(CH}_3)_3$ | Hexane | 2016S, 1930VS, 1627m |
| $\eta^5\text{-CpW(CO)}_3\text{CON(CH}_3)_2$ | Hexane | 2016S, 1928VS, 1576m |
| $\eta^5\text{-CpW(CO)}_3\text{CON(CH}_2)_5$ | Heptane | 2015S, 1930VS, 1926SSh, 1571m |
| $\eta^5\text{-CpMo(CO)}_3\text{CONHCH}_3$ | $CCl_4$ | 2020S, 1935VS, 1614m |
| $\eta^5\text{-CpMo(CO)}_3\text{CON(CH}_3)_2$ | Hexane | 2019S, 1941VS, 1934S, 1594m |
| $\eta^5\text{-Cp Mo(CO)}_3\text{CON(CH}_2)_5$ | Heptane | 2018S, 1937VS, 1931SSh, 1590m |
| $\eta^5\text{-CpMo(CO)}_2\text{CONHR}_1\text{R}_2\text{NH}_2$ |  | 1933S, 1807VS, 1533S |
| $\eta^5\text{-CpW(CO)}_2\text{CONHR}_1\text{R}_2\text{NH}_2$ |  | 1937VS, 1782S, 1798VS, 1529S |

More recently the reaction of metal carbonyl hydride $[\eta^5\text{-CpM(CO)}_3\text{H}]$ (M = Mo, W) with pentamethylenediaziridine provided a new route to cyclic carbamoyl complexes as indicated below.[35]



(I)

M = Mo,W

Ln = $(CO)_2$ $(C_5H_5)$

$R_1$, $R_2$ = pentamethylene.

When the carbamoyl complexes (I) (M = Mo,W) were heated with [$HCONH_2$], they gave [$\eta^5$-Cp(CO)$_2$MN : CRR$^1$] (RR$^1$ = pentamethylene; M = Mo,W), whereas treatment of (I) with HCl gave [$\eta^5$-CpM(CO)$_3$Cl].[35]

## 2.3. Nitrogen Derivatives.

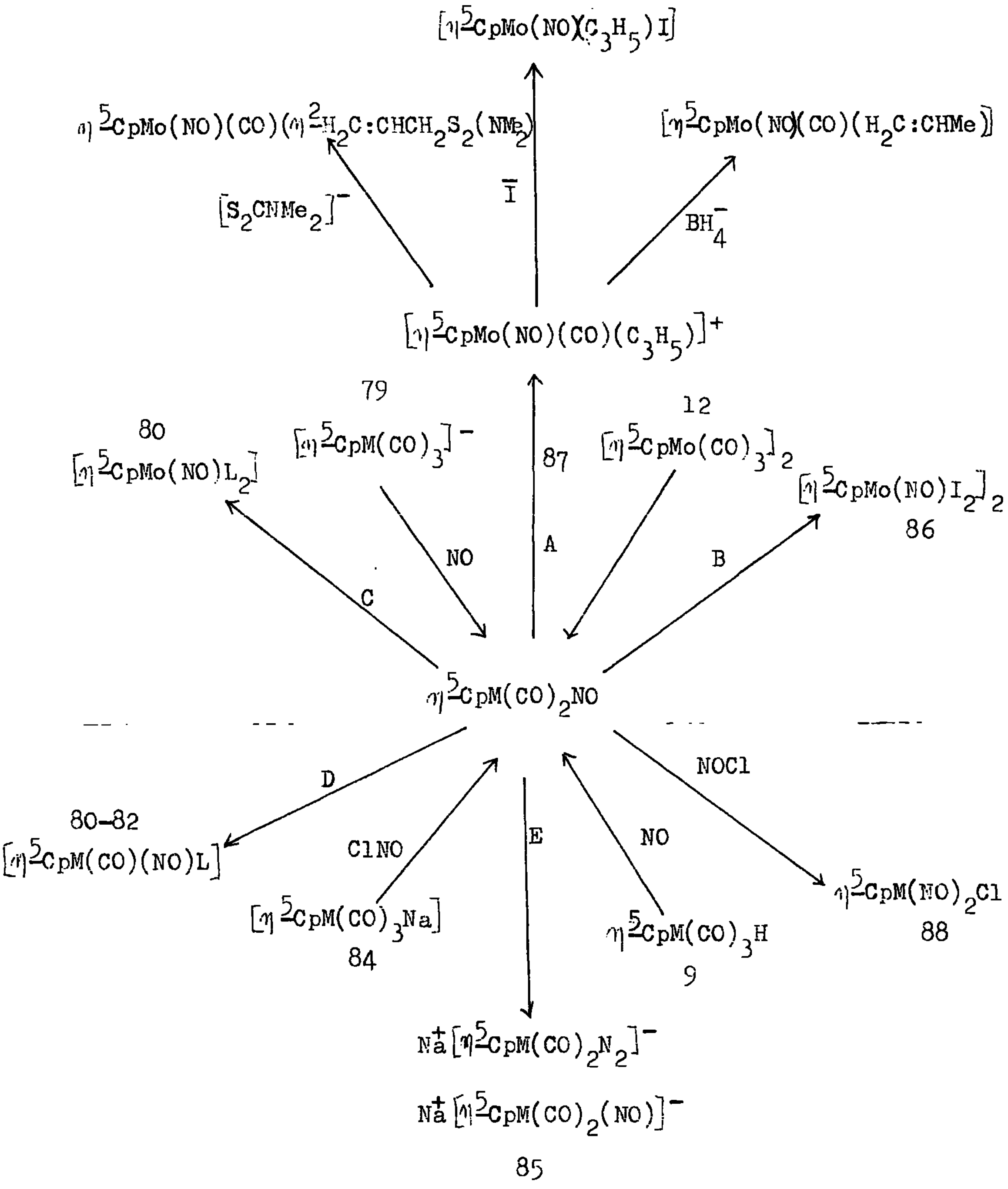
### Introduction

Few complexes have been reported in which the nitrogen group, $NR_2$ or amines and related compounds bonds to molybdenum or tungsten in cyclopentadienyl carbonyl complexes. [($\eta^5$-$C_5H_5$)Mo(CO)$_2$NMe$_2$]$_2$ has been prepared using $Me_3SiNMe_2$,[77] and [($\eta^5$-$C_5H_5$)Mo(CO)$_2$(HN : CBu$^t$Ph)Cl] in the reaction between [($\eta^5$-$C_5H_5$)Mo(CO)$_3$Cl] and $Me_3$SiN : CBu$^t$Ph,[78] but others are rare. The inability of the $NR_2$ groups to form stable complexes with the majority of transition metals has been rationalised in terms of the incompatibility of a "hard-base" with a "soft-acid".

An important purpose of this section is to place the work on amidino-complexes of molybdenum and tungsten, to be described in the following chapter, in perspective with studies made on other organonitrogen ligand systems. Other ligand systems discussed will be the nitrosyl group (NO), the methyleneamino group (N : $CR_2$), the aza allyl/allene group ($R_2$C NC$R_2$), and the amidine group (RN : C(R$'$) NR). All these groups act as three electron donor ligands to the metal atom. The preparation, properties and some reactions of these ligand complexes will be discussed in addition to their structures and bondings.

### (a) Nitrosyl Derivatives.

The orange nitrosyl complex [$\eta^5$-CpM(CO)$_2$NO], first prepared by Fischer[79] in 1955 from the direct reaction of the carbonylate anion [$\eta^5$-CpMo(CO)$_3$]$^-$ with nitric oxide is readily converted into the mono-substituted products [$\eta^5$-CpM(CO)(NO)L] by refluxing with phosphorus III compounds in suitable solvents.[80-82] In these products the metal atom is pseudo tetrahedrally surrounded by four different substituents. Irradiation,



Scheme 2.4 Some of the Preparations and Reactions of $[\eta^2\text{-}CpM(CO)_2(NO)]$ (M=Mo,W).

A - with $C_3H_5Br$ and Ag $PF_6$

B - with $CH_2Cl_2$, $I_2$

C - with L = $PPh_3$, $(Ph)_2PCH_2\ CH_2\ P\ (Ph)_2$.

D - with L = $[P(CH_3)_2\ C_6H_5]$, $[P(OCH_3)_3]$, $[PPh_3]$.

E - with $NaN(Si)_2\ (CH_3)_6$

however, produces further substitution and the disubstituted products $[\eta^5\text{-CpMo(NO)L}_2]$ are formed.[80] Some additional preparations and reactions of $[\eta^5\text{-CpM(CO)}_2\text{NO}]$ are given in Scheme 2.4. An interesting nitrosyl-type complex is formed in the reaction between $(\text{CH}_3)_2\text{C(NO)Br}$ and $\text{NaMo(CO)}_3\text{Cp}$. X-ray crystallography showed that the $(\text{CH}_3)_2\text{CNO}$ group in the purple complex $[(\text{CH}_3)_2\text{C(NO)Mo(CO)}_2\text{Cp}]$[83] bonds to the metal through three atoms,[84] carbon, nitrogen and oxygen.

### (b) Methyleneamino Derivatives.

The type of complex formed in the reactions of methyleneamino-derivatives with transition metal complexes are considerably influenced by the substituents on the methyleneamino-group.[89] The reaction of $\text{Ph}_2\text{C : NLi}$ or $\text{Ph}_2\text{C : NSiMe}_3$ with $[\eta^5\text{-CpM(CO)}_3\text{X}]$ (M = Mo,W; X = Cl,Br,I) produce the complexes $[\eta^5\text{-CpM(CO)}_2\text{N : CPh}_2]$[90] and $[\eta^5\text{-CpM(CO)N : CPh}_2]_2$[91] (M = Mo,brown; M = W, blue), whereas the reaction of $\text{Ph}_2\text{C : NLi}$ with $[\eta^5\text{-CpM(CO)}_3\text{Cl}]$ in the presence of added substrates such as $\text{Ph}_2\text{CO}$, $\text{Me}_2\text{CO}$, PhCN, PhNCO, $\text{PhNH}_2$, and *trans* - PhCH = CHPh, yields a blue form of $[\eta^5\text{-CpM(CO)}_2\text{N : CPh}_2]$ (M = Mo,W).[89,92] In both types of complexes the $\text{N : CR}_2$ group acts as a 3-electron donor replacing both the halogen and acarbonyl group from the starting complex $[\eta^5\text{-C}_5\text{H}_5\text{M(CO)}_3\text{Cl}]$. It is believed that the different derivatives arising from the presence of different substituents may be entirely due to steric rather than electronic factors.[93] The spectral features of the two forms of $[\eta^5\text{-CpMo(CO)}_2\text{NCPh}_2]$ are entirely different as shown in Table 2.4, but the same formulations have been assigned on the basis of the analytical and mass spectral data.[89] It is apparent that the blue material from the preparative route involving $\text{Ph}_2\text{C : NLi}$ has a close similarity with those of other $[\eta^5\text{-CpMo(CO)}_2\text{N : CR}_2]$ complexes whereas the brown material is distinctly different with no known methyleneamino analogues.[92]

Table 2.4 I.r. Spectroscopic Data for Methyleneamino-Carbonyl Complexes.

| Complexes | $\nu$(CO), $\text{cm}^{-1}$ |
|---|---|
| $[\eta^5\text{-CpMo(CO)}_2\text{N:CPh}_2]$ † | 1955VW,Sh, 1920S, 1856S, 1802ms |
| $[\eta^5\text{-CpMo(CO)}_2\text{N:CPh}_2]$ † | 1964S, 1949S, 1879S, 1874S |
| $[\eta^5\text{-CpW(CO)}_2\text{N:CPh}_2]$ † | 1956S, 1940S, 1869S, 1863S |
| $[\eta^5\text{-CpW(CO)N:CPh}_2]_2$ † | 1936S, 1847S, 1930S, 1836S |
| $[\eta^5\text{-CpMo(CO)N:CPh}_2]_2$ † | 1860S, 1826W,Sh |
| $[\eta^5\text{-CpMo(CO)}_2\text{N:CBu}^t{}_2]$ † | 1968S, 1884S, 1949S, 1851S |
| $[\eta^5\text{-CpW(CO)}_2\text{N:CBu}^t_2]$ † | 1946Sh, 1862Sh, 1929S, 1833S |
| $[\eta^5\text{-CpMo(CO)}_2\text{N:CBu}^t\text{Ph}]$ * | 1942VS, 1855VS, 1825W |
| $[\eta^5\text{-CpW(CO)}_2\text{N:CBu}^t\text{Ph}]$ * | 1931VS, 1836VS, 1810W,Sh |
| $[\eta^5\text{-CpMo(CO)}_2\text{N:C(}p\text{-tolyl)}_2]$ * | 1949S, 1855S |
| $[\eta^5\text{-CpW(CO)}_2\text{N:C(}p\text{-tolyl)}_2]$ * | 1938S, 1838S |

† : nujol mull, * KBr disc.

Blue complexes of the type $[\eta^5\text{-CpM(CO)}_2\text{N:CR}_2]$ (M = Mo,W; R = $\text{Bu}^t$, p-tolyl) were produced from the reaction of $[\eta^5\text{-CpM(CO)}_3\text{Cl}]$ with $\text{R}_2\text{C:N SiMe}_3$ or $\text{R}_2\text{C:NLi}$.[94,95] The reactions of $[\eta^5\text{-CpM(CO)}_3\text{Cl}]$ (M = Mo,W) with $\text{PhBu}^t\text{C:NLi}$, and the reaction of $[\eta^5\text{-CpW(CO)}_3\text{Cl}]$ with $\text{PhBu}^t\text{C:NSiMe}_3$ produced complexes of the type $[\eta^5\text{-CpM(CO)}_2\text{N:CBu}^t\text{Ph}]$, thus closely resembling the reactions with $\text{Bu}^t{}_2\text{C:NLi}$ and $\text{Bu}_2\text{C:NSiMe}_3$.[93] Reactions of complexes of the type $[\eta^5\text{-CpM(CO)}_2\text{N:CR}_2]$ again depend on the substituent group.[93] Diphenylmethyleneamino-derivatives of the type $[\eta^5\text{-CpM(CO)}_2\text{N:CPh}_2]$ (M = Mo,W) readily dimerise,[89] with loss of carbon monoxide to the complexes $[\eta^5\text{-CpM(CO)N:CPh}_2]_2$, but attempts to dimerise the t-butyl, p-tolyl, and phenyl-t-butyl derivatives were unsuccessful.[93-95] For R = Ph,[91] p-tolyl[95] no reaction occurred with $\text{PPh}_3$ under forcing conditions over many days, but when R = $\text{Bu}^t$, reactions occurred forming $[\eta^5\text{-CpM(CO)(PPh}_3)_2\text{H}]$[94] and $[\text{PPh}_3\text{Bu}^t][\eta^5\text{-CpMCl}_4]$ in monoglyme and $\text{CCl}_4$ solvents respectively. With iodine, diphenyl derivatives produced $[\eta^5\text{-Cp}_3\text{M}_3\text{I}_3\text{O}_4]$ complexes,[91] whereas t-butyl and Ph-Bu$^t$ complexes gave $[\eta^5\text{-CpM(CO)I}_2\text{NCR}_2]$ and $[\eta^5\text{-CpM(CO)}_2\text{I}_2\text{N:CBu}^t\text{Ph}$.[93,94] In contrast to all other methyleneamino complexes, $[\eta^5\text{-CpM(CO)}_2\text{N:CPhBu}^t]$ with $\text{PPh}_3$ forms a substitution product $[\eta^5\text{-CpMo(CO)(PPh}_3)\text{N:CPhBu}^t]$.[93]

It is interesting that the complex $[\eta^5\text{-CpM(CO)}_2\text{NCBu}^t{}_2]$ in solution undergoes reversible i.r. and $^1$Hn.m.r. spectral changes with change in temperature which is due to rotational changes about the metal-nitrogen bond as shown in Figure 3.[94] Conformation (a) is adopted in the solid state.

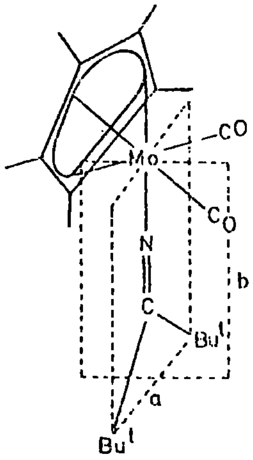


Figure 3 Structure of $[\eta^5\text{-CpMo(CO)}_2\text{NCBu}^t{}_2]$

It is believed that for all types of R group in $\text{R}_2\text{C:N}$ ligands the M-N-C skeleton is linear as a result of maximum overlap of the nitrogen lone pair (in a p orbital) with suitable metal d orbitals.[96] This was confirmed by the single $^1$Hn.m.r. signal observed at -60° and the preliminary X-ray structural data for $[\eta^5\text{-CpM(CO)}_2\text{ N:CBu}^t{}_2]$.[97]

## (c) Aza allyl/allene Derivatives.

The aza-allyl/allene complexes are the products of an unusual reaction between $[\eta^5\text{-CpM(CO)}_3\text{Cl}]$ (M = Mo,W) and a lithioketimine $[\text{LiN:CR}_2]$ (R = Ph,*p*-tolyl) in 1 : 2 molar ratio.[91,95] The products $[\eta^5\text{-CpM(CO)}_2\text{R}_2\ \text{CNCR}_2]$ are stable for several months in air at room temperature and are unreactive to neutral ligands such as phosphines in refluxing chloroform or toluene.[91] It is interesting to note that whereas the complex $[\eta^5\text{-CpM(CO)}_2\text{Ph}_2\text{CNCPh}_2]$ is golden brown in the solid state, its solution in polar organic solvents is intensely purple even when dilute.[91] Several bonding modes of the ligand may be envisaged as shown in Figure 4, but variable temperature studies on $[\eta^5\text{-CpM(CO)}_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ between -20 and +70° showed that the bonding of the aza-allyl group to the metal to be of the $\sigma-\pi$ type.[99] Epimerisation occurs at the higher temperature through processes of rotation and interchange of $\sigma-\pi$ bonding as shown in Figures 5 and 6.[99]

Linear or bent aza-allyl form
(A)

$\sigma-\pi$ Form
(B)

Aza-allene ligand
(C)

Aziridino-form
(D)

(E)

(F)

Figure 4 Possible structures for $(\pi\text{-C}_5\text{H}_5)\text{M(CO)}_2(\text{R}_2\text{CNCR}_2)$.

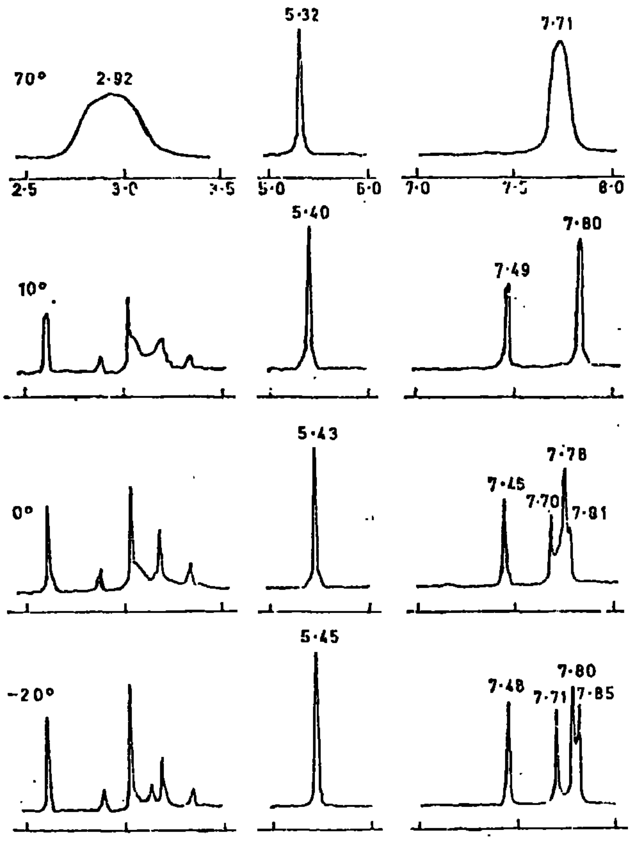


Figure 5 $^1$H n.m.r. spectra for $[(\eta^5\text{-}C_5H_5)W(CO)_2\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}]$ in $CS_2$

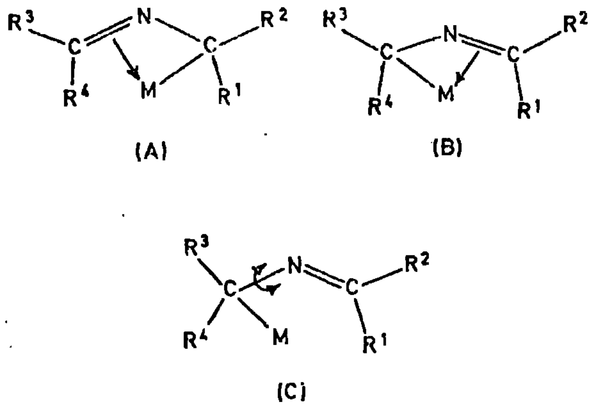
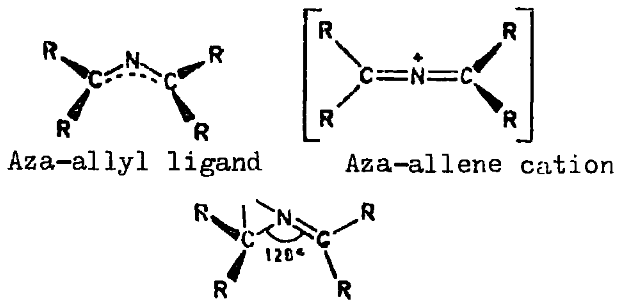


Figure 6 Interchange and rotation of $\sigma$ - $\pi$ bonding in $[(\eta^5\text{-}C_5H_5)W(CO)_2$ $\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}]$



Aza-allyl ligand    Aza-allene cation

Figure 7 Aza-allene group in $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}]$

For $[\eta^5\text{-CpM(CO)}_2(\underline{p}\text{-tolyl})_2\text{CNC}(\underline{p}\text{-tolyl})_2]$, two forms exist in the solid state[95] (form A and B), for M = Mo is form A, and for M = W, form B results. Form A has an aza-allene group rather than aza-allyl group as shown in Figure 7 and the planes of the $-\text{CR}_2$ group are perpendicular.[95] The two C-N bond lengths correspond essentially to a single and a double with $\widehat{\text{CNC}} = 128^\circ$, whereas the Mo-C and Mo-N bond lengths are slightly less than accepted single-bond lengths indicating extensive back donation into the ligand anti-bonding orbitals.[95]

Table 2.5 Infrared Spectroscopic Data for Aza-allyl/allene Complexes.

| Complex | Form | $\nu$(CO),(Cm$^{-1}$) |
|---|---|---|
| $[\eta^5\text{-CpMo(CO)}_2(\text{Ph}_2\text{CNCPh}_2)]$ | nujol mull | 1927S, 1845S |
| | $\text{CHCl}_3$ Soln. | 1934S, 1842S |
| $[\eta^5\text{-CpW(CO)}_2(\text{Ph}_2\text{CNCPh}_2)]$ | nujol mull | 1918S, 1835S |
| | $\text{CHCl}_3$ soln. | 1933S, 1835S |
| $[\eta^5\text{-CpMo(CO)}_2\{(\underline{p}\text{-tolyl})_2\text{CNC}(\underline{p}\text{-tolyl})_2\}]$ | KBr | 1936S, 1821S |
| | $\text{CS}_2$ soln. | 1938S, 1844S |
| | hexane soln. | 1949S, 1856S, br |
| $[\eta^5\text{-CpW(CO)}_2\{(\underline{p}\text{-tolyl})_2\text{CNC}(\underline{p}\text{-tolyl})_2\}]$<br>Form A | KBr | 1934S, 1815S |
| | $\text{CS}_2$ soln. | 1932S, 1838S |
| | hexane sol. | 1944S, 1850S, br |
| $[\eta^5\text{-CpW(CO)}_2\{(\underline{p}\text{-tolyl})_2\text{CNC}(\underline{p}\text{-tolyl})_2\}]$<br>Form B | KBr | 1931S, 1830S |
| | $\text{CS}_2$ soln. | 1932S, 1838S |
| | hexane soln. | 1944S, 1850S, br |
| $[\eta^5\text{-CpMo(CO)}_2\{(\underline{p}\text{-tolyl})(\underline{p}\text{-MeOC}_6\text{H}_4)\text{CNC}(\underline{p}\text{-tolyl})(\underline{p}\text{-MeOC}_6\text{H}_4)\}]$ | KBr disc | 1930S, 1831S |
| $[\eta^5\text{-CpMo(CO)}_2\{(\underline{p}\text{-tolyl})(\text{Ph})\text{CNC}(\text{Ph})(\underline{p}\text{-tolyl})\}]$ | KBr | 1924S, 1841S |
| $[\eta^5\text{-CpMo(CO)}_2\{(\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{CNC}(\text{p-CF}_3\text{C}_6\text{H}_4)_2\}]$ | KBr | 1962S, 1883S[a]<br>1954S, 1857S |
| $[\eta^5\text{-CpW(CO)}_2\{(\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{CNC}(\text{p-CF}_3\text{C}_6\text{H}_4)_2\}]$ | KBr | 1963S, 1880S[a]<br>1954S, 1866S |

[a] Two isomers exist in the solid state

### (d) Amidino-Derivatives.

The amidino group $[R^1NC(R)NR^1]$ is another potential three atom delocalised π-ligand and efforts have been made to attach it to molybdenum for purposes of comparison with the isoelectronic π-allyl and carboxylato-groups.[89] In an attempt to produce an amidine derivative $Mo(CO)_6$ was heated with RNHC(Ph) : NR(R = Ph,*p*-tolyl), but the products were red, air stable crystalline solids containing only the deprotonated ligands attached to the metal. Analytical and spectral data indicated the general formulation $[Mo_2\{R'NC(R)NR'\}_4]$[89] which has a cupric acetate type structure with four bridging amidino groups. The central skeleton, that which is left after deleting the phenyl groups (Figure 8), has essentially D4h symmetry. For the molecule as a whole this symmetry is degraded to $C_2$ by the fact that all of the phenyl groups are rotationally oriented so as to be neither parallel nor perpendicular to the $\overline{NCNMoMo}$ plane.[100]

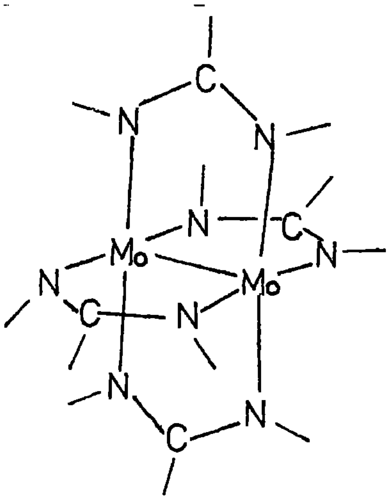


Figure 8 Structure of tetrakis(N,N$^1$-diphenylbenzamidinato)-dimolybdenum.

The complex was found to be resistant to attack by carbon monoxide (even under very high pressure), pyridine and $PPh_3$,[89] reflects the weak tendency for coordination in the *trans*-position to a strong metal-metal multiple bond. The novel complexes $[\eta^5\text{-}CpMo(CO)_2\{R'NC(Ph)NR'\}]$ (M = Mo,W; R$'$= H,Ph,*p*-tolyl) were isolated as air sensitive golden yellow solids from the reaction of lithioamidines with $[\eta^5\text{-}CpM(CO)_3Cl]$ (M = Mo,W) in ether at temperatures

Table 2.6 Infrared and $^1$Hn.m.r. spectroscopic data for $[(\pi\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]$ (II; M = Mo or W) complexes

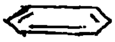
| Complex | Form | $\nu$(CO)str.frequencies/cm$^{-1}$ | $^1$HN.m.r.($\tau$)* |
|---|---|---|---|
| $[(\pi\text{-}C_5H_5)Mo(CO)_2\{PhNC(Ph)NPh\}]$ | $CCl_4$ | 1970VS, 1890VS | 3.5(3), † 4.7(1) |
| | Mull | 1950VS, 1864Sh, 1852VS | |
| $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(\underline{p}\text{-tolyl})NC(Ph)N(\underline{p}\text{-tolyl})\}]$ | $(CH_2Cl)_2$ | 1956VS, 1868VS | ca.3.0(13),†4.62(5),<br>7.67(6) |
| $[(\pi\text{-}C_5H_5)Mo(CO)_2(HNC(Ph)NH\}]$ (a) | $CH_2Cl_2$ | 1962VS, 1874VS | |
| (a) | Mull | 1968sh, 1955VS, 1875VS,1860sh | |
| (b) | Mull | 1958VS, 1853sh, 1833VS | |
| $[(\pi\text{-}C_5H_5)W(CO)_2\{PhNC(Ph)NPh\}]$ | Mull | 1935VS, 1840VS | |
| | $(CH_2Cl)_2$ | 1965VS, 1877VS | |
| $[(\pi\text{-}C_5H_5)W(CO)_2\{(\underline{p}\text{-tolyl})NC(Ph)N(\underline{p}\text{-tolyl})\}]$ | $(CH_2Cl)_2$ | 1949VS, 1852VS | ca.3.0(13),†4.48(5),<br>7.67(6) |
| $[(\pi\text{-}C_5H_5)W(CO)_2\{HNC(Ph)NH\}]$ (a) | $CH_2Cl_2$ | 1945VS, 1858VS | |
| (b) | Nujol | 1941VS, 1839sh, 1820VS | |

* In $CS_2$ solution. † Multiplet.

between 0 and 25° C.[101] That the amidino group acts as a strong three-electron-donor was indicated by the lack of reaction of the amidino-complexes with (PPh$_3$) and (CO) even under forcing conditions,[89] and was confirmed by spectroscopic data (i.r. and $^1$Hn.m.r.) given in Table 2.6.

The structure of amidino complexes will be discussed in detail in Chapter 4. Other complexes with metal-nitrogen bonds which are not discussed individually are listed in Table 2.7.

Table 2.7 Some additional metal ( M = Mo,W) - nitrogen complexes reported in the literature.

| | Ref. |
|---|---|
| $\eta^5$-CpMo(CO)$_2$N(HCMePh) = CH - N  | 102 |
| $\eta^5$-Cp(CO)$_2$ $\overline{\mathrm{Mo\ :\ N.\ N\ R.C\ (CO_2Et).\ C}}$. OH (R = H,Me) | 103 |
| $\eta^5$-CpMo(CO)$_2$ N = NCH$_2$SiMe$_3$ | 104 |
| $\eta^5$-CpMo(CO)$_2$NN(P-CH$_3$OC$_6$H$_4$) | 105 |
| $\eta^5$-CpMo(CO)$_2$(N$_2$Ar) | 106 |
| $\eta^5$-CpMo(CO)$_2$(C$_6$H$_4$N$_2$Ph) | 107 |
| $\eta^5$-CpMo(CO)$_2$[Me$_2$C:C:NMe$_2$] | 108 |
| $\eta^5$-CpMo(CO)$_3$(CH$_2$NCO) | 109 |
| $\eta^5$-CpMo(CO)$_2$N$_2$R(R = Ph,p-tolyl,P-CH$_3$OC$_6$H$_4$,P-O$_2$NC$_6$H$_4$,1-C$_{14}$H$_7$O$_2$N$_2$) | 110 |
| $\eta^5$-CpMo(CO)$_3$N$_3$F$_2$C$_3$ | 111 |
| $\eta^5$-Cp $\overline{\mathrm{W(CO)_2COCH_2CH_2NH_2}}$ | 112 |

## 2.4 B, Al, Tl Derivatives.

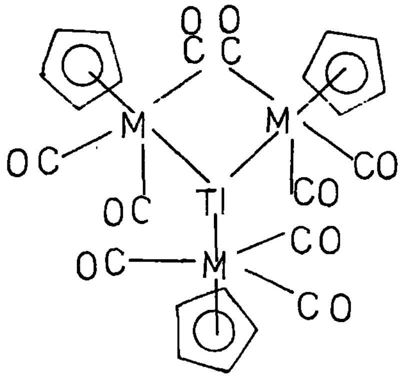
The synthesis of a new class of 'reactive mixed metal' complexes containing a metal-metal bond between aluminium and a Group (VI) transition metal was first reported by Kroll and McVicker in 1971.[113]

$$R_2Al\text{-}R' + \underset{I}{H\text{-}Mo(C_5H_5)(CO)_2L} \longrightarrow \underset{II}{R_2Al\text{-}Mo(C_5H_5)(CO)_2L} + R'H$$

(R = alkyl; R′= alkyl or H; L = CO, $MePPh_2$, $PPh_3$).

The protolysis reaction, which is also observed with the tungsten analogue, proceeds readily at ambient temperature with the following order of reactivity: $Bu^i{}_2AlH > AlEt_3 > AlMe_3$.[113] When complexes (II) reacts with stoichiometric amounts of weak organic acids (phenol, acetylacetone), a fast quantitative cleavage of the aluminium - molybdenum bond takes place, indicating that the reactivity of the mixed metal-metal bond is greater than that of the Al-C bond towards protolytic attack.[113] Both cis- and trans-isomers of complexes (II) are possible, by analogy with the hydrides (I) (L = phosphine), and $^1$Hn.m.r. study indicated that exchange between the two isomeric forms takes place.[113]

Thallium (I) derivatives were prepared by metathetical reactions of $Na[M(CO)_3Cp]$ (M = Mo,W) and thallium (I) nitrate or sulphate in water.[114] The yellow products $Tl[M(CO)_3Cp]$ were sufficiently stable to be stored under an atmosphere of argon without decomposition for a few days at room temperature.[114] In THF, $[Co_2(CO)_8]$ undergoes oxidative addition with $Tl[W(CO)_3Cp]$ to form the mixed-metal complex $Tl[(Co(CO)_4]_2[W(CO)_3Cp]$.[114] The thallium (III ) derivatives $Tl[M(CO)_3Cp]_3$ (M = Mo,W) were isolated as very dark red crystals from the reaction of thallium (III) chloride and $Na[M(CO)_3Cp]$ in THF.[114] They were also prepared by King from the reaction between hexacarbonylmolybdenum and thallium (I) cyclopentadienide, and structure (III) was suggested.[115]



III

Another Tl complex was prepared according to the following equation.[116]

$Me_3Tl + HMo-\eta^5\text{-}Cp(CO)_3 \longrightarrow Me_2Tl[Mo\eta^5\text{-}Cp(CO)_3] + CH_4$ .

Boron halides $X_2BCl$ ( X = Ph,Cl) react with $Na[M(CO)_3\eta^5\text{-}Cp]$ (M = Mo,W) to yield the metal-boron compounds $[X_2B\text{-}M(CO)_3\eta^5\text{-}Cp]$.[45]

$X_2BCl + NaM(CO)_3Cp \longrightarrow X_2B\text{-}M(CO)_3Cp + NaCl$ (M = Mo,W; X = Ph,Cl)

Their thermal stability increases in the series Cr, Mo, W and X = Cl,$C_6H_5$. The dichlorides form 1 : 1 adducts with triethylamine, e.g. $(C_2H_5)_3N.Cl_2B\text{-}M(CO)_3(\eta^5\text{-}Cp)$.

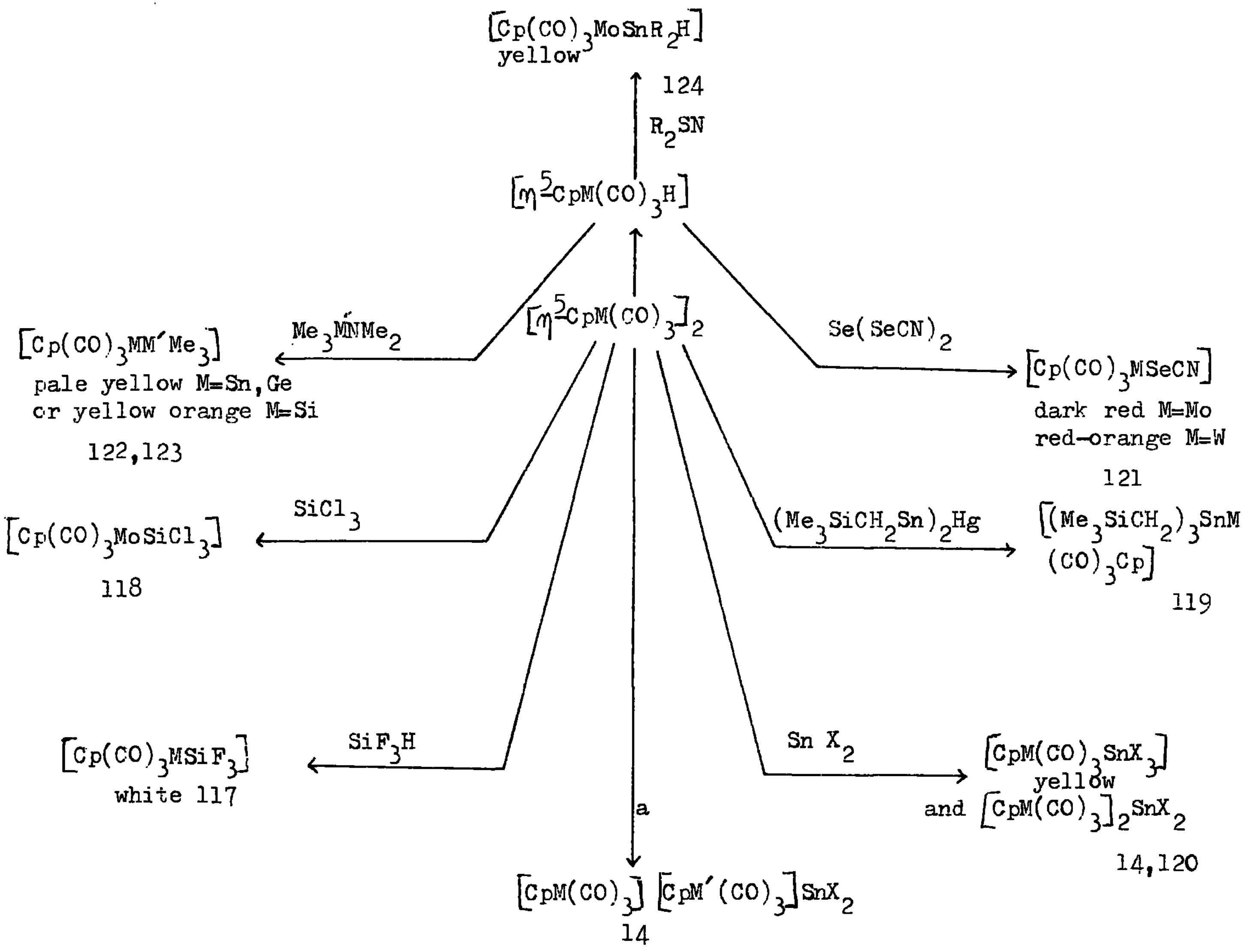
Table 2.8 Properties of some TI and B Derivatives.

| Compound | Colour | m.p. | $\nu$ (CO),Cm$^{-1}$ |
|---|---|---|---|
| $TL[Mo(CO)_3(Cp)]$ | yellow | 230 dec. | 1932VS, 1840S, 1812VS$^a$ |
| $TL[W(CO)_3(Cp)]$ | yellow | 275 dec. | 1925VS, 1836S, 1803VS$^a$ |
| $TL[Mo(CO)_3(Cp)]_3$ | deep red | 225-30 dec. | |
| $TL[W(CO)_3(Cp)]_3$ | red | 275-85 dec | |
| $TL[Co(CO)_4]_2[W(CO)_3(Cp)]$ | deep red | 74-76 | |
| $Ph_2BMo(CO)_3Cp$ | brown | 85 | 2058, 1961, 1901 |
| $Ph_2BW(CO)_3Cp$ | dark brown | 168 | 1984, 1945, 1865 |
| $Cl_2BMo(CO)_3Cp$ | dark brown | 45-50 | 2049, 1984, 1949 |
| $Cl_2BW(CO)_3Cp$ | brown | 75-78 | 1984, 1949, 1923 |

a) in THF

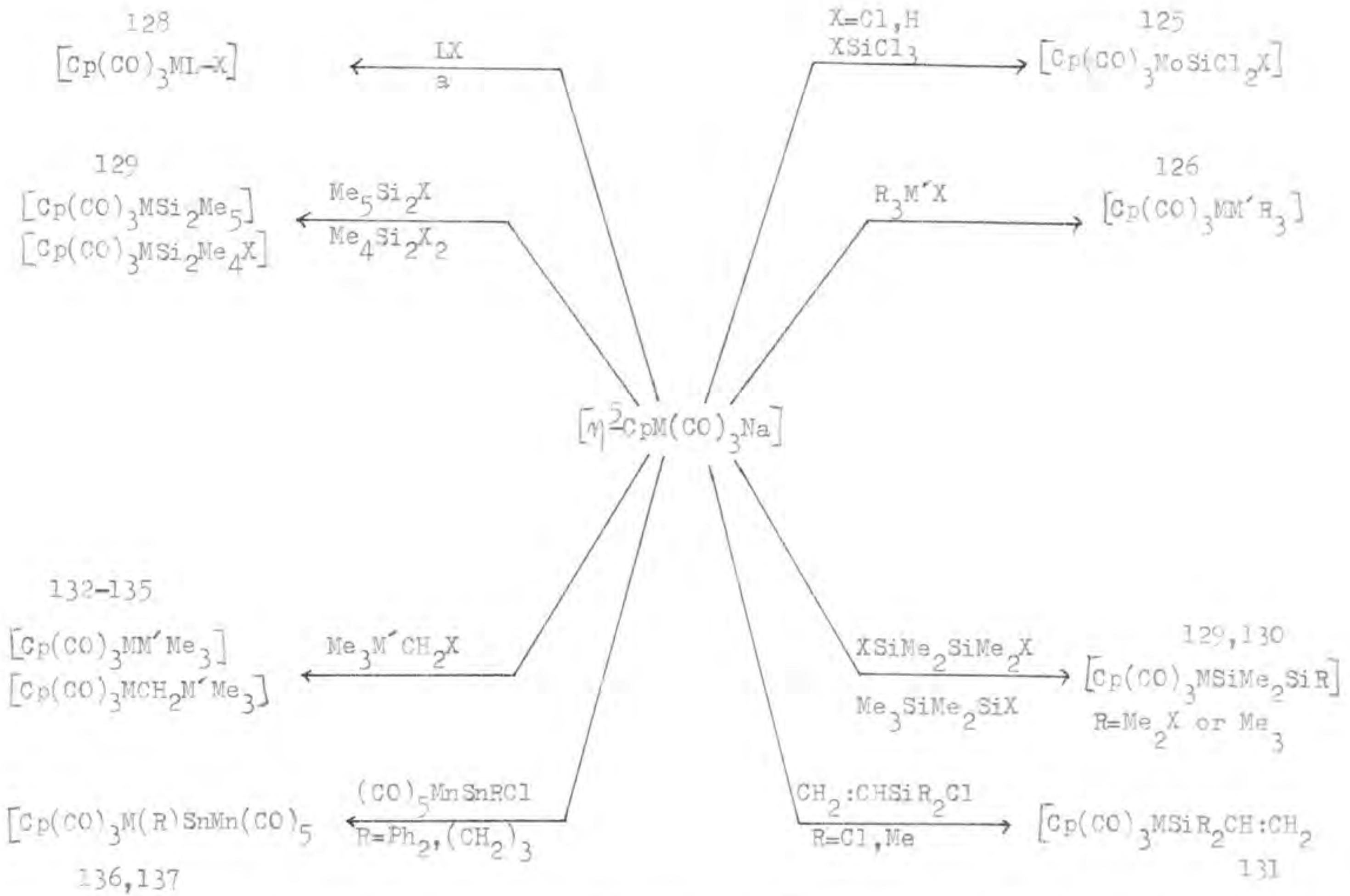
## 2.5 Si, Ge, Sn, Pb Derivatives.

These complexes were prepared mainly from $[\eta^5\text{-}CpM(CO)_3]_2$,[14,117-120] $[\eta^5\text{-}CpM(CO)_3H]$[121-124] or $[\eta^5\text{-}CpM(CO)_3]Na$[126-138] ( M = Mo,W). Some of these preparations are summarised in Schemes 2.5 and 2.6. Cyclopentadienyl molybdenum and tungsten carbonyl complexes containing Si, Ge, Sn, Pb undergo either metal-metal or metal-non metal bond cleavage in their reactions, as discussed below.



Scheme 2.5 Some Preparations and Properties of Si, Ge, Sn, Pb Derivatives. (M = Mo,W; X = halide; M' =Si,Ge,Sn,Pb).

a) With $[CpM'(CO)_3SnX_3]$; M,M' = Mo,W.



Scheme 2.6 Preparations of some Si, Ge, Sn, Pb Derivatives. (M = Mo,W; M′= Si,Ge,Sn,Pb; X = halide)

a) LX = $Me_3SiBr$, $HMeSiCl_2$ , $CH_3SiCl_3$, $HSiCl_3$, $SiCl_4$, $SiBr_4$.

Sn derivatives tend to undergo Sn–C rather than Sn–M cleavage, in contrast to Si and Ge analogues for which M–M′ bond cleavage is more common.[138]

(i) Reactions resulting in the cleavage of the metal–metal bond:[139,140]

Most of the reactions of this type are summarised in the following equations:[138]

$$R_3EMo(CO)_3Cp + X_2 \longrightarrow R_3EL + L_3M(CO)_2Cp \quad \text{—— eq(1)}$$

R = Me; E = Sn; M = Mo; $X_2$ = $Cl_2$; solvent = $C_5H_{12}$

Table 2.9 Properties of Some Si, Ge, Sn, Pb Complexes.

| Complex | Colour | m.p. | $\nu$(CO), $cm^{-1}$ | Ref. |
|---|---|---|---|---|
| $Cp(CO)_3MoSnCl_3$ | yellow | 164 | 2060S, 1996Sh, 1972s | 120 |
| $Cp(CO)_3WSnCl_3$ | yellow | 187 | 2042s, 1972Sh, 1950s, 1924Sh | 120 |
| $Cp(CO)_3MoSiCl_3$ |  | 149-151 | 2041, 1976, 1959 | 118 |
| $Cp(CO)_3MoSeCN$ | dark red | 105 dec | 2050, 1979, 1962 | 121 |
| $Cp(CO)_3WSeCN$ | red–orange | 131-133 dec | 2046, 1967, 1948 | 121 |
| $Cp(CO)_3MoGePPh_3$ | pale green | 219-222 dec | 2008, 1925, 1918 | 126 |
| $Cp(CO)_3MoSnMe_3$ | pale yellow | 97-98 | 1997, 1922, 1895 | 126 |
| $Cp(CO)_3MoSnMe_2Cl$ | pale yellow | 89-90 | 2013, 1947, 1913 | 126 |
| $Cp(CO)_3MoSnPh_3$ | pale green | 211-214 | 2004, 1934, 1909 | 126 |
| $Cp(CO)_3MoPbMe_3$ | pale orange | 93-95 | 1992, 1921, 1895 | 126 |
| $Cp(CO)_3MoPbPh_3$ | yellow | 200 dec | 2002, 1934, 1910 | 126 |
| $Cp(CO)_3WGePh_3$ | pale yellow | 240 dec | 2004, 1930, 1911 | 126 |
| $Cp(CO)_3WSnMe_3$ | pale yellow | 119-120 | 1994, 1915, 1891 | 126 |
| $Cp(CO)_3WSnPh_3$ | pale green | 227-228 | 2014, 1927, 1902 | 126 |
| $Cp(CO)_3WPbPh_3$ | yellow | 214-215 dec | 1999, 1927, 1907 | 126 |
| $[Cp(CO)_3Mo]_2SnMe_2$ | yellow | 156-159 dec | 2004,1988,1937,1925,1910,1894 | 126 |

R = Me, Ph; M = Mo,W; E = Sn: $X_2 = I_2$; solvent = $CHCl_3$

$\eta^5\text{-}CpM(CO)_3SiR_2CH : CH_2 + HX \longrightarrow \eta^5\text{-}Cp(CO)_3MH + XSiR_2CH : CH_2$[131] —— eq(2)

X = halogen, $CF_3CO_2, CCl_3CO_2$; R = $CH_3$,Cl .

$\eta^5\text{-}Cp(CO)_3MEMe_3 + Me_3P = CH_2 \longrightarrow \underset{I}{[\eta^5\text{-}Cp(CO)_3Mo][Me_3P\text{-}CH_2\text{-}EMe_3]}$[141]

$I + Me_3P = CH_2 \rightleftharpoons Me_3\ P = CH\text{-}EMe_3 + [Me_4P][\eta^5\text{-}Cp(CO)_3M]$[141] —— eq(3)

M = Mo,W; E = Si,Sn

$\eta^5\text{-}CpMo(CO)_3GeR_3 + HCl \longrightarrow \eta^5\text{-}CpMo(CO)_3H + R_3GeCl$[142] —— eq(4)

(ii) Reactions resulting in the cleavage of metal-non-metal bond:

(a) The reactions of chlorosilicon and chlorogermanium transition metal complexes with $AgBF_4$, produce in high yield the corresponding fluoro derivatives according to the equation:[143]

$LnM\text{-}M^1Cl_mR_{3-m} + mAgBF_4 \longrightarrow LnM\text{-}M^1FmR_{3-m} + mAgCl + mBF_3$ —— eq(5)

[Ln = $\eta^5\text{-}Cp(CO)_3$; M = Mo or W; $M^1$ =Si,Ge; $X_mR_{3-m}$= $Y_3$[143] $Ph_2Y$,[144] $[Y_2CH{=}CH_2]$,[145] $Me_2Y$, $MeY_2$[146] where Y = Cl,F].

The later reaction proceeds rapidly in either coordinating or aromatic solvents and the fluoro derivatives are produced in high yield.[143] The infrared spectra in the carbonyl stretching region are relatively insensitive to the substitution of chlorine by fluorine, and the π-accepting ability of the group (IV) ligand has increased only slightly.[143] When the reaction shown in equation (5) was attempted with transition metal-tin compounds, the product isolated was ionic, i.e. $[\eta^5\text{-}CpMo(CO)_3Sn(Ph)_2]BF_4$.[143] Cleavage of Si-H bond was achieved by the reaction of $CCl_4$ or $CBr_4$ with complexes of the type $[\eta^5\text{-}CpM(CO)_3SiX_3]$ ($X_3$ = $HMe_2$, HMeCl, $HCl_2$; M = Mo,W) to produce the halogenated complexes $[\eta^5\text{-}Cp(CO)_3MSiY_3]$( Y = $Me_2Cl$, $Me_2Br$, $MeCl_2$,$Cl_3$).[125]

In a series of Cl/F and H/F exchange processes, the complexes $[HCl_2SiM(CO)_3Cp]$ and $[HMeClSiM(CO)_3Cp]$ (M = Mo,W) were converted to $[F_3SiM(CO)_3Cp]$ and $[F_2MeSiM(CO)_3Cp]$ respectively.[146]

(b) Reactions which lead to cleavage of group (IVB) metal-carbon bonds are:

The reactions of HCl or HBr with systems containing Sn-M′ bonds resulted in partial or complete replacement of the organic groups bound to Sn.

$R_3SnM(CO)_3Cp + HCl \longrightarrow R_{3-x}Cl_xSnM(CO)_3Cp$ [138,147] —— eq(6) [Re = Me, Ph; M = Mo,W; solvent = $CCl_4$, diethyl ether, $CH_2Cl_2$, pentane].

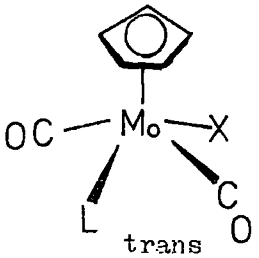
Other reactions involving group (IV) - carbon bond cleavage are summarised in the following equations:

$\eta^5\text{-}CpMo(CO)_3GePh_2F + PF_5 \xrightarrow{benzene} \eta^5\text{-}CpMo(CO)_3GePhF_2 \longrightarrow \eta^5\text{-}CpMo(CO)_3GeF_3.$ [143]

$\eta^5\text{-}Cp(CO)_3M - SiF_2(CH{=}CH_2) + AgBF_4 \longrightarrow \eta^5\text{-}Cp(CO)_3M\text{-}SiF_3.$ [144]

## 2.6 a) Phosphine and Phosphite Derivatives.

Phosphorus ligands have the ability to substitute one or two carbonyl groups from cyclopentadienyl molybdenum and tungsten tricarbonyl[15-29,56,57,148-150] complexes to form complexes of the type $[\eta^5\text{-}CpM(CO)_{3-n}L_nX]$ (L = wide variety of phosphines and phosphites; X = hydrides, halides, alkyl and acyl groups). $PPh_3$, however, react with $[(NC)_2C = C(Cl)Mo(CO)_3Cp]$ with complete replacement of all three carbonyl groups to form $[\eta^5\text{-}CpMo(PPh_3)_2\{C = C(CN)_2\}Cl]$.[29] Of several factors which determine the degree of substitution, steric features appear to dominate,[24] e.g. the main difference between the behaviour of the ligands ($PPh_3$) and (Diphos)(only the latter forms disubstituted products) is likely to be steric in nature. It is known that compounds having the general formula $[\eta^5\text{-}CpMo(CO)_{3-n}L_nX]$ may be formally considered to be seven coordinate complexes of molybdenum with the cyclopentadienyl ring occupying three coordination positions.[15] The idealised lowest-energy configuration of such compounds would involve the four remaining ligands located approximately at the corners of a square such that a structure similar to a square pyramid would result. The possibility of the existence of two geometric isomers arises from this square pyramidal geometry.[15]



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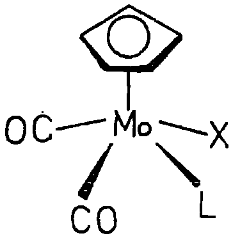
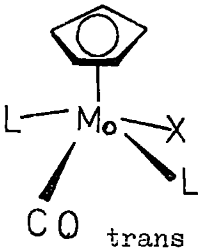


cis



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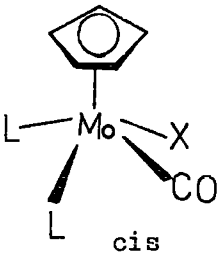
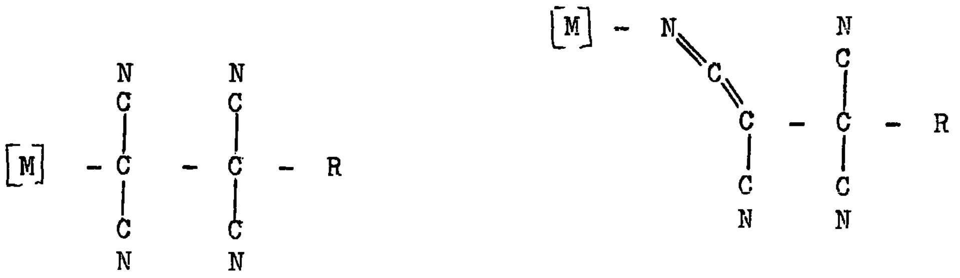


cis

$^1$Hn.m.r. study has shown that for the complexes where X = acyl group, only the trans isomers occur in solution[151], while cis- trans interconversion occurs in analogous alkyl, halide and hydride complexes.[151,152] The relative proportions of these isomers depend markedly on the nature of L and X.[152]

The ligands [L = $P(OR)_3$ (R =Me,Et; i$C_3H_7$; n-$C_4H_9$),$P(OCH_2)_3CCH_3$; $P(OC_3H_5)_3$; $P(OC_3H_5)_2(C_6H_5)$; $P(OC_3H_5)(C_6H_5)_2$] were observed to effect disproportionation of $[\eta^5\text{-}CpMo(CO)_3]_2$ in benzene at room temperature to yield ionic $[\eta^5\text{-}CpMo(CO)_2L_2]^+$ $[\eta^5\text{-}CpMo(CO)_3]^-$, prior to the formation of neutral $[\eta^5\text{-}CpMo(CO)_2L]_2$ or neutral $[\eta^5\text{-}CpMo(CO)_2L\ L']$.[153] $[\eta^5\text{-}CpMo(CO)_2LCOMe]$ (L = $PPh_3$, $P(OPh)_3$)are thermally decarbonylated in variety of solvents to the corresponding methyl derivatives $[\eta^5\text{-}CpMo(CO)_2LMe]$[154] which reacts with tetracyanoethylene to give the insertion products $[\eta^5\text{-}CpMo(CO)_2(L)C(CN)_2C(CN)_2Me]$ and $[\eta^5\text{-}CpMo(CO)_2LN : C : C\ (CN)C(CN)_2Me]$ in 10-40% yield.[155]

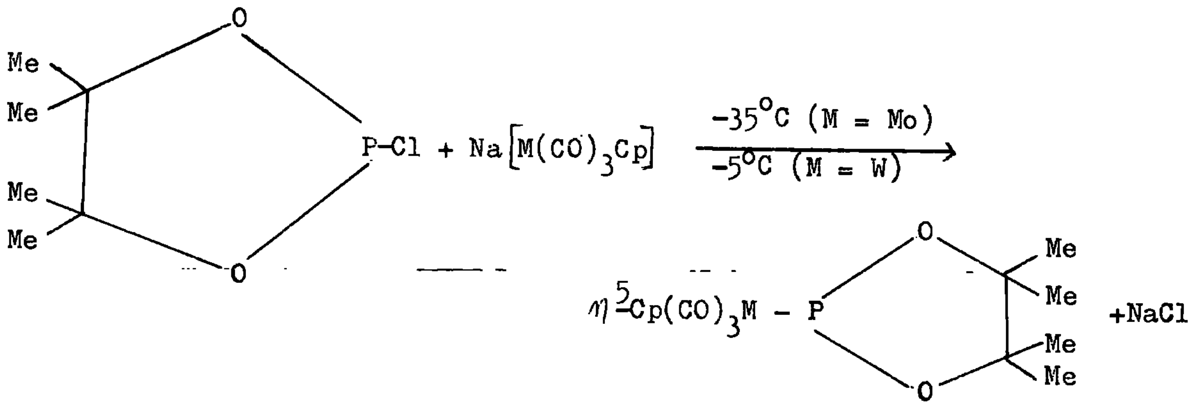
Cyanoalkyl complex isomerise to the keteniminato complex in solution.[155]



metal cyanoalkyl　　　　　metal keteniminate

$[M] = \eta^5Cp(Mo(CO)_2L.$

Transition metal - substituted dioxaphospholanes were prepared according to the equation.[156]



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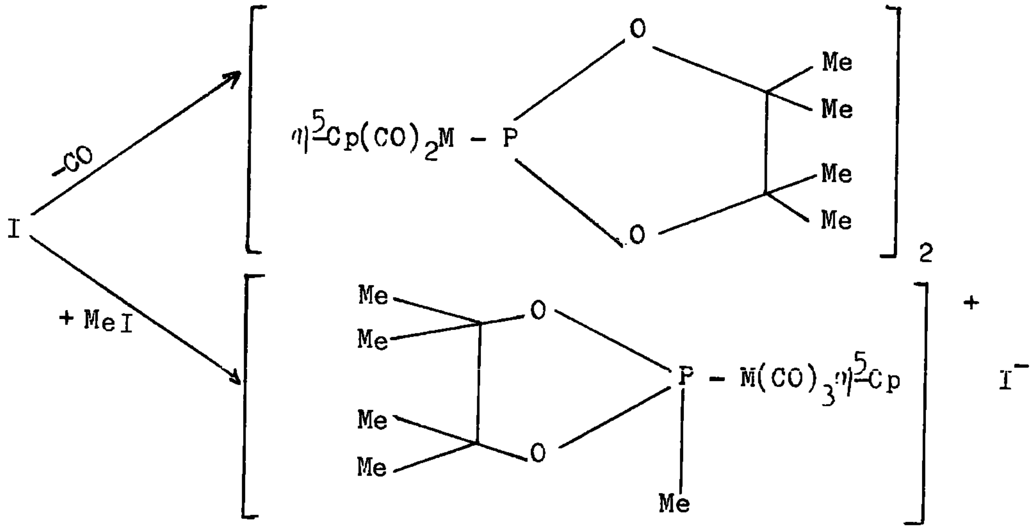
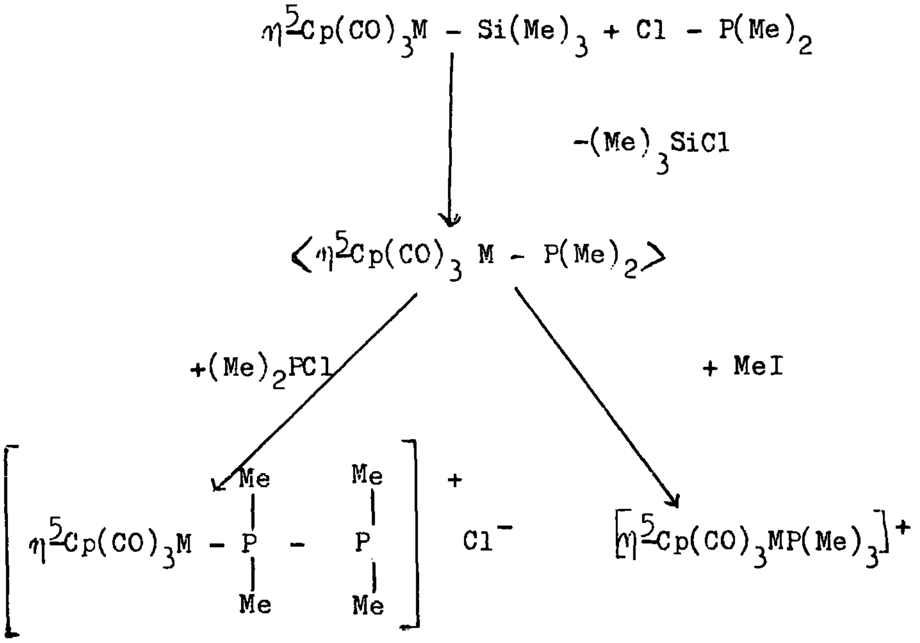
As a consequence of the basicity of the VB element this species can be readily converted to bridged dinuclear or cationic mononuclear complexes



A phosphino derivative was formed from the reaction:[156]



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(M = Mo,W)

Table 2.10 Some [$\eta^5$CpM(CO)$_2$LX] (M = Mo,W) Complexes.

| L | X |
|---|---|
| $PPh_3$ | H[56], Cl[24], I[24], $PhCH_2CO$[56], EtCO[148], MeCO[148], $C_6F_5CO$[57], $(CF_3)_2CO$[21], $C_4H_7CO$[56], Me[57]<br>$PhCH_2$[56], $C_3H_5CO$[56]. |
| $P(\eta\text{-}C_4H_9)_3$ | H[20]. |
| $PPhBu^n_2$ | Cl[19]. |
| $PBu^n_3$ | Cl[19], I[23], $PhCH_2CO$[56], EtCO[148], MeCO[148]. |
| $PEt_3$ | I[24]. |
| $P(cyclohexyl)_3$ | I[24]. |
| $P(NMe_2)_3$ | I[23]. |
| $P(OMe)_3$ | H[19], Cl[19], Br[19], I[19], EtCO[148], MeCO[148], Me[19]. |
| $P(OPh)_3$ | H[19], Cl[19], I[24], $PhCH_2CO$[56], EtCO[148], MeCO[148], Me[127], $PhCH_2$[127], Et[127], $CF_3CO_2$[127], $Me_3Sn$[127],<br>$C_3H_5$[127]. |
| $P(OEt)_3$ | I[23], EtCO[148], MeCO[148]. |
| $P(OMe)_3CR$ | H[20], Cl[15], Br[15], I[15], $PhCH_2CO$[56], EtCO[148], MeCO[148]. |

(R = Me,Et,Pr)

## b) As and Sb Derivatives.

An interesting complex (i) is formed when [$\eta^5$-CpMo(CO)$_3$I] is heated with [Me$_2$As(CH$_2$)$_3$Cl] in benzene for 12h. at the reflux temperature. The product obtained as purple prisms undergoes cyclisation when reduced with a three fold excess of sodium amalgam in THF giving (ii), as air-stable yellow needles, as shown in Figure 9. Trityl fluoroborate abstracts hydrogen this product to give the cationic species (iii), which was indicated by the high frequency of i.r. the $\nu$(CO) stretching vibrations (20 15m, 1930S; Nujol), approximately 80cm$^{-1}$ to higher frequencies than those found in the neutral starting material, complex (ii).[157] Reaction of (iii) with a methanol solution of KCN did not lead to addition to the coordinated double bond, but resulted in displacement of the alkene giving (iv) in small yield together with extensive decomposition. As and Sb compounds normally act as 3 electron donors in their derivatives and substitute carbonyl groups but occasionally As and Sb(V) derivatives result as in the complex [Br$_2$Me$_2$SbM(CO)$_3$Cp].[161] Additional preparations and properties of complexes containing As and Sb are given in Table 2.11.

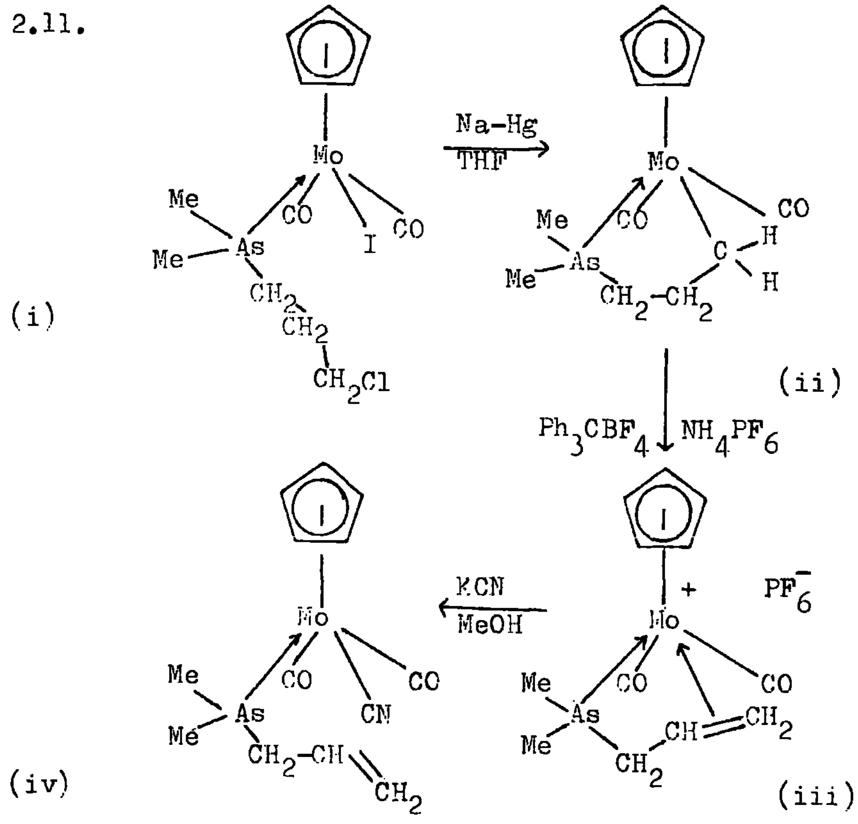


Figure 9 $^{5}$-CpMo(CO)$_2$I Me$_2$AsC$_3$H$_6$Cl and complexes derived from it.

Table 2.11 Infrared Data for Some As and Sb Derivatives.

| Complex | Form | $\nu$(CO), $cm^{-1}$ | Ref. |
|---|---|---|---|
| $[\eta^5\text{-CpMo(CO)}_2(\text{AsPh}_3)\text{Cl}]$ [a] | $CHCl_3$ | 1975, 1886 | 24 |
| $[\eta^5\text{-CpMo(CO)}(\text{AsPh}_3)_2\text{Cl}]$ [a] | $CHCl_3$ | 1791 | 24 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{SbPh}_3)\text{Cl}]$ [a] | $CHCl_3$ | 1974, 1884 | 24 |
| $[\eta^5\text{-CpMo(CO)}(\text{SbPh}_3)_2\text{Cl}]$ [a] | $CHCl_3$ | 1796 | 24 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{AsMePh}_2)\text{I}]$ [a] | $CCl_4$ | 1968, 1882 | 24 |
| $[\eta^5\text{-CpMo(CO)}(\text{AsMePh}_2)_2\text{I}]$ [a] | $CCl_4$ | 1807 | 24 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{AsPh}_3)\text{I}]$ [a] | $CHCl_3$ | 1966, 1883 | 24 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{SbPh}_3)\text{I}]$ [a] | $CHCl_3$ | 1964, 1880 | 24 |
| $[\eta^5\text{-CpMo(CO)}(\text{SbPh}_3)_2\text{I}]$ [a] | $CCl_4$ | 1812 | 24 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{AsPh}_3)\text{Br}]$ [a] | $CHCl_3$ | 1978VS, 1890VS | 25 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{SbPh}_3)\text{Br}]$ [a] | $CHCl_3$ | 1980VS, 1889VS | 25 |
| $[\eta^5\text{-CpW(CO)}_2(\text{AsPh}_3)\text{Cl}]$ [a] | $CHCl_3$ | 1962VS, 1870VS | 25 |
| $[\eta^5\text{-CpW(CO)}_2(\text{SbPh}_3)\text{Cl}]$ [a] | $CHCl_3$ | 1965VS, 1870VS | 25 |
| $[\eta^5\text{-CpM(CO)}_3\text{SbBr}_2]$ [b] | | | 158 |
| $[\eta^5\text{-CpMAsMe}_2(\text{CO})_3]$ [c] | | | 159 |
| $[\eta^5\text{-CpMo(COCH}_3)(\text{CO})_2\text{AsPh}_3]$ [d] | $CHCl_3$ | 1940S, 1860VS, 1600m | 160 |
| $[\eta^5\text{-CpM(CO)}_3\text{SbMe}_2\text{Br}_2]$ [e] | | | 161 |
| $[\eta^5\text{-CpMo(CO)}_3\text{As}(\text{C}_6\text{F}_5)_2]$ [f] | tetrachloroethylene | 2026S, 1966S, 1942S. | 162 |
| $[\eta^5\text{-CpMo}\{\text{As}(\text{CF}_3)_2\}(\text{CO})_3]$ [g] | $CS_2$ | 2040VS, 1974VS, 1956VS | 163 |

a) Prepared by U.V. irradiation of $[\eta^5\text{-CpM(CO)}_3\text{X}]$ (M = Mo,W; X= Cl,Br,I) with $AsPh_3$, $SbPh_3$ and $AsMePh_2$.

b) Prepared from $[\eta^5\text{-CpM(CO)}_3]$ Na with $SbBr_3$.

c) Prepared from $[\eta^5\text{-CpM(CO)}_3]$ Na with $Me_2AsCl$.

d) Prepared from $[\eta^5\text{-CpMo(CO)}_3\text{CH}_3]$ with $AsPh_3$.

e) Prepared from $[\eta^5\text{-CpM(CO)}_3\text{SbMe}_2]$ with $Br_2$.

f) Prepared from $[\eta^5\text{-CpMo(CO)}_3]^-$ with $[(C_6F_5)_2AsCl]$ or from $[\eta^5\text{-CpMo(CO)}_3]_2$ with $[(C_6F_5)_2\ As]_2$.

g) Prepared from $[\eta^5\text{-CpMo(CO)}_3]_2$ with $(CF_3)_4As_2$.

## 2.7 S, Se, Te Derivatives.

Known cyclopentadienyl molybdenum and tungsten carbonyl complexes[164,165] containing Se and Te groups are few in number compared with sulphur derivatives. $[\eta^5\text{-CpW(CO)}_3\text{Cl}]$[166] and $[\eta^5\text{-CpMo(CO)}_3]_2$[167] were used as starting materials for the preparation of dithiocarbamate complexes $[\eta^5\text{-CpM(CO)}_2\text{S}_2\text{CNR}_2]$ $[\text{M} = \text{Mo,W};\ \text{R} = \text{Me,Et,NR}_2(\text{R}_2\text{=Me}_2\text{,Et}_2\text{,C}_5\text{H}_{10})]$[168], in which the group is chelated to the metal through two sulphur atoms, as shown in Figure 10.

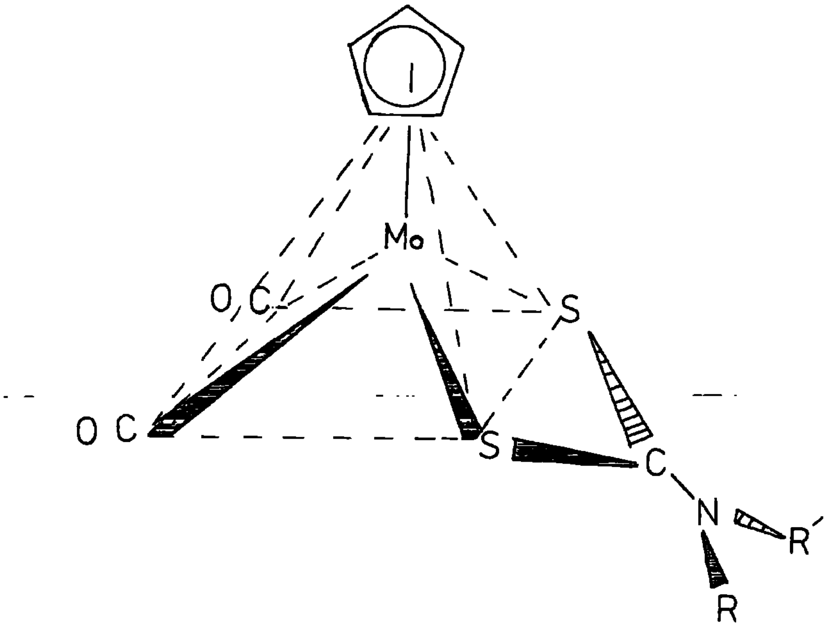
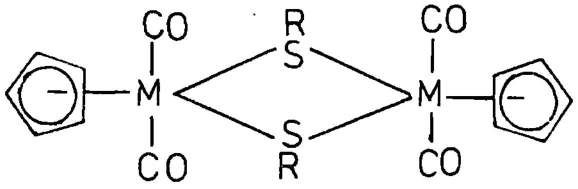


Figure 10 The structure of $[\eta^5\text{-CpM(CO)}_2\text{S}_2\text{CNR}_2]$ complex.

Red-brown crystals of $[\eta^5\text{-CpMo(CO)}_2\text{CSNMe}_2]$ were obtained from the reaction of $\text{ClCSNMe}_2$ with $[\eta^5\text{-CpMo(CO)}_3]^-$ or $[\eta^5\text{-CpMo(CO)}_2\text{PPh}_3]^-$; the bidentate thiocarboxamido group bonds through C and S atoms.[169] Interestingly the coordinated sulphur atoms can be readily alkylated using $[\text{Me}_3\text{O}]\text{BF}_4$[169] according to:

$$\eta^5\text{-CpMo(CO)}_2\text{CSNMe}_2 + [\text{Me}_3\text{O}]^+ \longrightarrow [\eta^5\text{-CpMo(CO)}_2\text{C(SMe)NMe}_2]^+.$$

The reaction between dimethyl disulphide and the cyclopentadienyl tricarbonylhydride of molybdenum and tungsten has been reported by Treichel and Morris[170] to yield the binuclear complexes (I; M = Mo,W). On the basis of additional experimental evidence this result was confirmed for the molybdenum compound, but found that the tungsten compound is better represented by the mononuclear structure (II; M = W).[171] Each of the complexes (I) and (II) undergo $CS_2$ insertion producing the stable alkyl trithiocarbonate complexes (III).[171]



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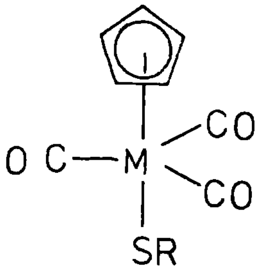
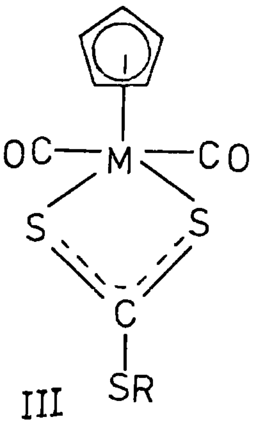


II



III

$[\eta^5\text{-}CpW(CO)_3(SR)]$ (R = Me,p-tolyl) were also prepared from the reaction of $[\eta^5\text{-}CpW(CO)_3I]$ with RSK.[172] However, it was not possible to prepare and isolate a pure sample of the p-tolyl complex because of its rapid conversion to the binuclear sulphur-bridged compound upon loss of carbon-monoxide in solution at room temperature. Moreover, this binuclear sulphur-bridged compound reacted with carbon monoxide in THF when heated at reflux temperature to form the mononuclear species $[\eta^5\text{-}CpM(CO)_3(P\text{-}CH_3C_6H_4S)]$.[172] Interestingly the dinuclear metal carbonyl complex with a single methylthio bridge $[M\text{-}S(CH_3)\text{-}M']$ $\{M = Cp(CO)_3Mo, Cp(CO)_3W, M' = Cr(CO)_5, W(CO)_5, Mn(CO)_2Cp\}$ can be prepared (a) from the free organometallic Lewis bases $M - SCH_3$ and the metal carbonyl unit M′, and (b) from the methylthiostannane derivatives $(CH_3)_3Sn\text{-}SCH_3\text{-}M'$ and the halides M-Cl. They are deeply coloured, crystalline and mostly air stable.[173]

An additional route to sulphur-containing derivatives involves insertion of sulphur dioxide; for example, $SO_2$ insertion was achieved for $[\eta^5\text{-}CpMo(CO)_3R]$ (R = Me,Et,$CH_2Ph$) and $[\eta^5\text{-}CpMo(CO)_2(PPh_3)Me]$ to afford the golden or yellow crystalline products $[\eta^5\text{-}CpMo(CO)_3SO_2R]$.[55]

Table 2.12 Infrared Data for Sulphur Derivatives.

| Complex | $\nu$ (CO), $cm^{-1}$ | Ref. |
|---|---|---|
| $[\eta^5\text{-CpMo(CO)}_2\text{SCH}_3]_2$ | 1965S, 1947S, 1877S, 1869S, 1852m [a] | 170 |
| | 1967VS, 1948S, 1940(Sh), 1879S, 1862(Sh) [a] | 172 |
| | 1852(Sh) [a] | |
| $[\eta^5\text{-CpW(CO)}_2\text{SCH}_3]_2$ | 2034S, 1948S [b] | 172 |
| | 1955VS, 1930(Sh), 1861S, 1852(Sh) [b] | 172 |
| $[\eta^5\text{-CpW(CO)}_3(\text{CH}_3\text{S})]$ | 2030VS, 1943VS [b] | 172 |
| $[\eta^5\text{-CpW(CO)}_3(\text{P-CH}_3\text{C}_6\text{H}_4\text{S})]$ | 2033VS, 1948VS [b] | 172 |
| $[\eta^5\text{-CpW(CO)}_2(\text{P-CH}_3\text{C}_6\text{H}_4\text{S})]_2$ | 1893m, 1848S [b] | 172 |
| $[\eta^5\text{-CpMo(CO)}_3(\text{P-CH}_3\text{C}_6\text{H}_4\text{S})]$ | 2040VS, 1959VS [b] | 172 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{P-CH}_3\text{C}_6\text{H}_4\text{S}]_2$ | 1964Sh, 1954VS, 1873VS [b] | 172 |
| $[\eta^5\text{-CpMo(CO)}_3\text{SO}_2\text{CH}_3]$ | 2058VS, 1975VS [c] | 55 |
| $[\eta^5\text{-CpMo(CO)}_3\text{SO}_2\text{C}_2\text{H}_5]$ | 2056VS, 1985VS [c] | 55 |
| $[\eta^5\text{-CpMo(CO)}_3\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5]$ | 2056VS, 1996VS, 1973VS [c] | 55 |
| $[\eta^5\text{-CpMo(CO)}_2(\text{PPh}_3)\text{SO}_2\text{CH}_3]$ | 1982m, 1901VS [c] | 55 |

a) Cyclohexane solution.

b) $CCl_4$ solution.

c) $CHCl_3$ solution.

## 2.8 Ionic Derivatives.

The cationic complexes can be considered to be disubstituted derivatives of the yellow, air stable carbonyl cations $[\eta^5\text{-CpM(CO)}_4]^+$ (M = Mo,W),[24] which were prepared by treatment of $[\text{CpM(CO)}_3\text{Cl}]$ with $\text{AlCl}_3$ at 60-70° and 240 atm. CO pressure in $C_6H_6$, and then isolated as the hexafluorophosphate salts.[174] This cation can be assumed to have a structure in which the carbonyl groups are disposed in a local $C_{4\nu}$ symmetry.[24] Hence, it is possible that cations of the type $[\eta^5\text{-CpMo(CO)}_2L_2]^+$ where L = unidentate ligand could exist in two isomeric forms in which cis and trans carbonyl groups have been displaced.[24] Ionic complexes of the types $[\eta^5\text{-CpM(CO)}_3L]X$[34,175] and $[\eta^5\text{-CpM(CO)}_2L_2]X$[24,176] have been prepared according to the equation:

$$\eta^5\text{-CpM(CO)}_3\ X + L \longrightarrow [\eta^5\text{-CpM(CO)}_{3-n}L_x]X$$

(M = Mo,W; n = 0,1; x = 1,2; X = halogen; L = phosphines, phosphites, alkyls, ammonia derivatives). The cation $[\eta^5\text{-CpMo(CO)}_2(\text{PPh}_3)_2]^+$ however, could not be prepared under normal conditions, but it could be prepared provided the reaction was carried out in the presence of $\text{AlCl}_3$, when yellow crystals of $[\eta^5\text{-CpMo(CO)}_2(\text{PPh}_3)_2]\ \text{AlCl}_4$ separated.[24] Furthermore, yellow $[\text{CpMo(CO)}_2(\text{Diphos})]$ $[\text{CpMo(CO)}_3]$ complexes were formed by the unsymmetrical cleavage of the metal-metal bond of $[\eta^5\text{-CpMo(CO)}_3]_2$ upon reaction with chelating ditertiary phosphines in hydrocarbon solvents.[176] The yellow complexes $[\eta^5\text{-CpM(CO)}_2L_2]X$ are considered as intermediates in formation of neutral complexes. In general the cationic complexes undergo nucleophilic reactions, e.g. $NH_3$ adds to $[\eta^5\text{-CpMo(CO)}_3C_2H_4]^+$ to give $[\eta^5\text{-CpMo(CO)}_3\text{CH}_2\text{CH}_2]_2\ \text{NH}_2^+$.[177]

$[\eta^5\text{-CpM(CO)}_3R]$ complexes $[M = \text{Mo,W};\ R = \text{Me,Et,(CH}_2)_3\text{Br,PhCH}_2\text{,NC(CH}_2)_3]$ react with KCN in methanol to afford the corresponding cyano(acyl) metallates $K[\eta^5\text{-CpM(CO)}_2(\text{CN})(\text{COR})]$.[51,179,180] Moreover, the reaction of $[\eta^5\text{-CpMo(CO)}_3(\text{CH}_2)_3\text{Br}]$ with KCN yielded the <u>cis</u>- and trans-complexes $K[\eta^5\text{-CpMo(CO)}_2(\text{CN})(\text{CH}_2)_3\text{CN})]$.[180] Anionic complexes undergo electrophilic reactions i.e. $[\eta^5\text{-CpMo(CO)}_2\ (\text{CNMe})]^-$ undergoes chemical reactions via halide displacement from $CH_2ClCN, Me_3GeBr, Me_3SnCl, Ph_3PbI$ in THF to form the neutral complexes $[\eta^5\text{-}CpMo(CO)_2(CNMe)R]$ $[R = CH_2CN, GeMe_3, SnMe_3, PbPh_3]$.[180] Another example for electrophilic reactions of the anion complexes $[\eta^5\text{-}CpMo(CO)_2(CNCH_3)]^-$ and $[\eta^5\text{-}CpMo(CO)_2L]^-$ (L = phosphines and phosphites) with acetic acid form the hydride derivatives $[\eta^5\text{-}CpMo(CO)_2(CNCH_3)H]$ and $[\eta^5\text{-}CpMo(CO)_2LH]$ respectively.[180,17]

### 2.9 Transition Metal Derivatives.

The complex $Hg[\eta^5\text{-}CpM(CO)_3]_2$ (M = Mo,W) prepared from the anion $[\eta^5\text{-}CpM(CO)_3]^-$ and $Hg(CN)_2$,[3] undergoes metal-exchange reaction with excess zinc and cadmium metals in a polar solvent such as THF to form the analogue complexes $Zn[\eta^5\text{-}CpM(CO)_3]_2$ and $Cd[\eta^5\text{-}CpM(CO)_3]_2$.[181] The spectra and properties of these complexes are consistent with structures involving linear arrangements of three metal atoms linked by non-polar, covalent metal-to-metal bonds.[181,182]

Phosphine and phosphite ligands $[L = PPh_3, P(OMe)_3, P(OPh)_3]$ substitute one carbonyl group from $Hg[\eta^5\text{-}Cp\,M(CO)_3]_2$ and $[\eta^5\text{-}CpM(CO)_3HgX]$ (M = Mo,W; X = Cl,Br,I) [the latter complex was prepared by exchange reaction between $[\eta^5\text{-}CpM(CO)_3]_2Hg$ and $HgX_2$[183] or between $[\eta^5\text{-}CpMo(CO)_3MgBr]$ and $HgCl_2$[184]] to form the substituted complex $[\eta^5\text{-}CpM(CO)_2L]_2Hg$ and $[\eta^5\text{-}CpM(CO)_2LHgX]$ respectively.[185]

$[C_6F_5HgMo(CO)_3\eta^5\text{-}Cp]$ was prepared in good yield from the reaction of $C_6F_5HgBr$ with $Na[\eta^5\text{-}CpMo(CO)_3]$ in THF.[186] Attempts to prepare $[C_6F_5HgW(CO)_3\eta^5\text{-}Cp]$ by the above method gave $Hg[W(CO)_3\eta^5\text{-}Cp]_2$ and $Hg(C_6F_5)_2$.[186] Redistribution occurs very rapidly with mercuric bromide at room temperature.[186]

$$C_6F_5HgMo(CO)_3\eta^5\text{-}Cp + HgBr_2 \longrightarrow C_6F_5HgBr + BrHgMo(CO)_3\eta^5\text{-}Cp$$

and substitution reactions occur with $PPh_3$, $P(OPh)_3$, in ethanol at reflux to give the new compounds $[\eta^5\text{-}CpMo(CO)_2(PPh_3)C_6F_5]$ and $[\eta^5\text{-}CpMo(CO)_2\{P(OPh)_3\}C_6F_5]$ in good yield.[186] Mercury derivatives are in general yellow crystals, air stable and moderately soluble in polar solvents.

$[Ph_3PAu\text{-}W(CO)_3\eta^5\text{-}Cp]$ in which the phosphorus, gold and tungsten atoms are collinear was prepared by the reaction between $[\eta^5\text{-}CpW(CO)_3]Na$ and $[Ph_3PAuCl]$ in THF solution,[187] but it has been found more convenient to use the reaction between the hydride $[\eta^5\text{-CpM(CO)}_3\text{H}]$ with the metal-halide.[187] The products $[\eta^5\text{-Cp(CO)}_3\text{M-ER}]$ $[\text{M} = \text{Mo,W};\ \text{E} = \text{Au,Cu};\ \text{R} = \text{PPh}_3, \text{P(Cyclohexyl)}_3, \text{P(OPh)}_3$ (o-triars)], are diamagnetic and are non-electrolytes in nitrobenzene.[187] Yellow crystals of the type $[\{\eta^5\text{-CpM(CO)}_3\text{Ag}\}_n]$, $[\{\eta^5\text{-CpMo(CO)}_3\text{Cu}.\tfrac{1}{2}\text{OH}_2.\tfrac{1}{2}\text{NH}_3\}_n]$, or $[\{\eta^5\text{-CpW(CO)}_3\text{CuOH}_2\}_n]$ were prepared by the reaction of a solution of Na$[\eta^5\text{-CpM(CO)}_3]$ (M = Mo,W) in bis (2-methoxyethyl) ether and water with $\text{AgNO}_3$ in water or with CuCl in 5% aqueous ammonia.[188] The salts $[\text{Me}_4\text{N}]$ $[\text{Ag}\{\text{M(CO)}_3\ \eta^5\text{-Cp}\}_2]$ and $[\text{Me}_4\text{N}]$ $[\text{Cu}\{\text{M(CO)}_3\text{Cp}\}_2]$ were prepared by the reaction of solid CuCl or aqueous $\text{AgNO}_3$ with Na$[\eta^5\text{-CpM(CO)}_3]$ (M = Mo,W) in bis (2-methoxyethyl) ether-water, and the salt $[\text{Me}_4\text{N}]$ $[\text{Ag}\{\text{Mo(CO)}_3\text{Cp}\}\ \{\text{W(CO)}_3\text{Cp}\}]$ was prepared from solid $[\{\eta^5\text{-CpMo(CO)}_3\text{Ag}\}_n]$ and an aqueous bis (2-methoxyethyl) ether solution of Na$[\text{W(CO)}_3\text{Cp}]$.[188] The covalent compounds are very light and air sensitive but the $[\text{Me}_4\text{N}]$ $[\text{M}'\{\text{M(CO)}_3(\text{Cp})\}_2]$ salts (M = Mo,W; M′= Cu.Ag) are more resistant to oxidation. The salts are insoluble in non-polar solvents, and their solutions in THF or pyridine have high conductivities.[188] Similarity between the i.r. spectra of the $[\text{Ag}\{\text{M(CO)}_3(\text{Cp})\}_2]^-$ salts and their neutral $[\{\eta^5\text{-CpM(CO)}_3\}_2\text{Hg}]$ analogues imply that the two series are isostructural with linear M-Ag-M or M-Hg-M systems.[188]

Three novel compounds containing Pt-Mo and Pd-Mo bonds were prepared according to the equations:[189]

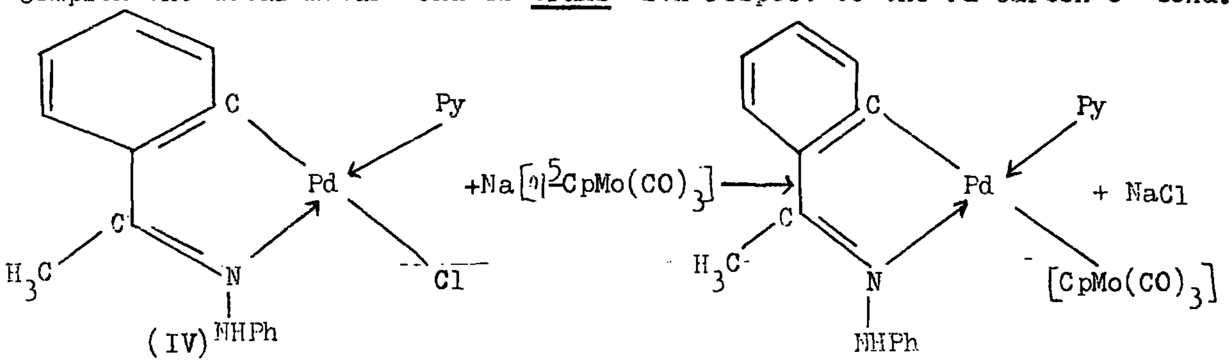
$$2\ \underline{\text{trans}}\text{-PtPy}_2\text{Cl}_2 + 3\text{Na}[\eta^5\text{-CpMo(CO)}_3] \longrightarrow 3\text{NaCl} + \underset{\text{(I)}}{\underline{\text{trans}}\text{-PtPy}_2\text{Cl}[\eta^5\text{-CpMo(CO)}_3]} + \underset{\text{(II)}}{\underline{\text{trans}}\text{-PtPy}_2[\eta^5\text{-CpMo(CO)}_3]_2}.$$

$$\underline{\text{trans}}\text{-PdPy}_2\text{Cl}_2 + 2\text{Na}[\eta^5\text{-CpMo(CO)}_3] \longrightarrow 2\text{NaCl} + \underset{\text{(III)}}{\underline{\text{trans}}\text{-PdPy}_2[\eta^5\text{-CpMo(CO)}_3]_2}$$

Complexes (II) and (III) have the same crystal structure, as was shown by their X-ray powder photographs. The platinum compounds are stable in air but decompose slowly in THF, while the palladium compound decomposes slowly in air and very rapidly in solution.[189]

It is noteworthy that the carbonyl stretching frequencies of the two trans - $PtPy_2Cl[\eta^5\text{-CpMo(CO)}_3]$ and trans-$PtPy_2[\eta^5\text{-CpMo(CO)}_3]_2$ in solution are very similar. The three bands are comparable with those reported by Haines, Nyholm and Stiddard[187] for $[\eta^5\text{-Cp(CO)}_3\text{Mo-AuL}]$, and the insensitivity to the nature of the groups attached to the metal is consistent with the soft character of the $Pt^{II}$ centre.

Another Pd-Mo complex was formed from the reaction of the chelated palladium compound (IV) with $[\eta^5\text{-CpMo(CO)}_3]^-$ in THF/pentane solution at -10°C. In this complex the metal-metal bond is trans with respect to the Pd-carbon-σ-bond.[190]



(IV)

$[\eta^5\text{-CpM(CO)}_3]\text{Na}$ (M = Mo,W) react with $[\text{Mn(CO)}_5\text{X}]$ (X = Cl,Br) in THF solution to give the new metal-metal, red complexes $[\eta^5\text{-Cp(CO)}_3\text{MoMn(CO)}_5]$.[191] Similarly the reaction of $[\eta^5\text{-CpNa}]$ with $\text{Mo(CO)}_6$ in THF gave after addition of $[\text{ReCl(CO)}_5]$, yellow-orange $[\eta^5\text{-Cp(CO)}_3\text{MRe(CO)}_5]$ (M = Mo,W).[191] The same products were obtained either by continuous or flash photolysis of degassed isooctane solutions of $[\eta^5\text{-CpM(CO)}_3]_2$ (M = Mo,W) and $M'_2\text{(CO)}_{10}$ (M' = Mn,Re).[5]

$$\text{CpM}_2\text{(CO)}_6 + M'_2\text{(CO)}_{10} \xrightarrow[\text{benzene}]{h\nu} \text{CpM(CO)}_3 - M'\text{(CO)}_5.$$

The reaction of the sodium salt of tricarbonylcyclopentadienylmolybdenum with tricarbonylcyclopentadienyltungsteniodide gave:

$$\eta^5\text{-CpMo(CO)}_3\text{Na} + \eta^5\text{-CpW(CO)}_3\text{I} \longrightarrow \text{NaI} + \eta^5\text{-Cp(CO)}_3\text{Mo.W(CO)}_3\text{Cp}.$$

It is believed that this was the first carbonyl complex with a metal-metal bond between different transition metals.[192]

## 2.10 Li,Na,K,Mg Derivatives.

$[\eta^5\text{-CpM(CO)}_3]M'$ (M = Mo,W; M' = Li,Na,K) complexes were prepared from the reaction of the hexacarbonyls $M(CO)_6$ (M = Mo,W) with the metal cyclopentadienide (M′Cp) (M′= Li,Na,K) in dimethylformamide at 130°.[3,9] Molybdenum carbonyl derivatives of magnesium were prepared by many routes.[193,194] The most general method is the reductive cleavage of the $\eta^5$-cyclopentadienylmolybdenumtricarbonyl dimer or halide with a dilute magnesium amalgam in the presence of a Lewis base (B).[196] The product complexes $B_4Mg[\eta^5\text{-}CpMo(CO)_3]_2$ (B = $C_4H_8O$, $C_5H_5N$) can be isolated as crystalline solids but they are extremely sensitive to air. Upon air exposure the complexes are rapidly oxidized to MgO and the corresponding dimeric carbonyl complexes.[195] Some of the properties of $B_4Mg[\eta^5\text{-}CpMo(CO)_3]_2$ complexes are given in Table 2.13.

Burlitch and co-workers have determined the crystal structure of $[(Py)_4Mg(Mo(CO)_3Cp)_2]$.[196] The molecule exhibits essentially octahedral coordination about the magnesium atom, with the equatorial positions occupied by the four pyridine molecules and the axial positions are filled by the two $(Mo(CO)_3Cp)$ groups. Each $(Mo(CO)_3Cp)$ group is bonded to the central magnesium atom via the oxygen atom of a single carbonyl group, as shown in Figure 11.

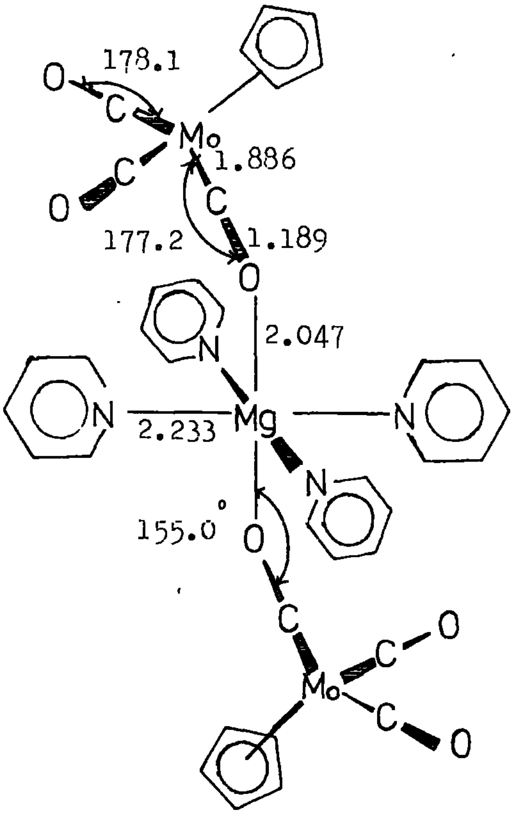


Figure 11 A portion of the structure of $[\eta^5\text{-}CpMo(CO)_3]_2Mg(C_5H_5N)_4$.

Table 2.13 Properties of Some Mg Derivatives.

| Compound. | Colour | $\nu$(CO), cm$^{-1}$ | |
|---|---|---|---|
| | | Nujol mull | Benzene Soln. |
| $(C_4H_8O)_4Mg[Mo(CO)_3Cp]_2$ | off-white | 1908VS | 1925VS |
| | | 1810VS | 1825VS |
| | | 1674VS | 1668VS |
| $(C_5H_5N)_4Mg[Mo(CO)_3Cp]_2$ | light green | 1918VS | 1922VS |
| | | 1826VS | 1825VS |
| | | 1659VS | 1665VS |
| $(C_4H_8O)_4Mg[Mo(CO)_2(PMePh_2)Cp]_2$ | yellow | 1802VS | 1800S |
| | | 1627VS | 1732VS |
| | | | 1617VS |
| $(C_4H_8O)_4Mg[Mo(CO)_2(P(C_4H_9)_3)Cp]_2$ | clear yellow | 1788VS, br | 1791VS |
| | | 1604VS, br | 1737VS |
| | | | 1702S |
| | | | 1687S |
| | | | 1624S |
| | | | 1592VS |

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# CHAPTER 3

# EXPERIMENTAL WORK.

This chapter describes the preparation and properties of some new amidino derivatives of molybdenum and tungsten. Lithioamidines and $H_2NC(Me)NH$ react with $[(\eta^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo,W) to produce yellow carbamoyl-type complexes $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(R')C(R)NR']$, (I; R = H, R′= Ph; R = Me, R′= H, Ph, *p*-tolyl; R = Ph, R′= Me) whereas reactions of parent N, N′-disubstituted amidines give orange complexes of the type $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]$, (II: R = H, R′= Ph; R = Me, R′= Ph, *p*-tolyl; R = Ph, R′= Me). (II) were also produced, in small yields, from thermal or photolytical decarbonylation of (I).

## 3.1 General Aspects:

N, N′- Dimethylbenzamidine,[1] and NN′ - di-*p*-tolyl acetamidine[2] were synthesised by standard methods, and N,N′-diphenylacetamidine, NN′-diphenylformamdine, acetamidine hydrochloride, 2-Aminopyridine, NN′-Dicyclohexylcarbodiimide, triphenylphosphine and 2-hexene were obtained commercially. The free benzamidine was obtained from the hydrochloride hydrate by a standard method.[3] N-Butyl-lithium, *Ca.* 1.5 and 2.13 M in hexane, was used as supplied commercially without purification. Complexes $[(\eta^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo,W),[4] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)]$,[5] $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$[5] and $Fe_2(CO)_9$[5] were prepared by standard methods.

**Solvents:** Solvents were degassed ($10^{-1}$mmHg) before use and stored under nitrogen. Hydrocarbon solvents and di-ethyl ether were dried over sodium wire, and monoglyme was freshly distilled, under nitrogen from $LiAlH_4$. All solvents were transferred by syringe against a counter flow of nitrogen, and reactions were performed with rigorous exclusion of air.

**Nitrogen supply:** 'White spot' nitrogen direct from the storage tank was used, and a constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler.

Spectra: Infrared spectra in the range 4000 - 250 $cm^{-1}$ were recorded on a Perkin-Elmer 457 instrument. Spectra of solid samples were recorded in the form of nujol mulls between KBr plates or as pressed KBr discs. Solution spectra were recorded using a solution cell with KBr windows (separation 0.1mm.) which was filled using a syringe. Nuclear magnetic resonance spectra were recorded using a Varian A56/60D spectrometer fitted with a variable temperature controller, operating at 60 MHZ/sec. Samples were normally in $CDCl_3$ or $CS_2$ solution. The internal reference standard was tetramethylsilane. Sample tubes were filled by syringe against a counter-current of nitrogen. Mass spectra were recorded on a A.E.I. MS9 mass spectrometer at 70 eV and an accelerating potential of 8KV, with a source temperature between $80^o$ and $220^o$ (depending on the sample) and electromagnetic scanning. Compounds were introduced by direct insertion into the ion source.

Analysis: — Carbon, hydrogen and nitrogen contents of the complex were determined with a Perkin-Elmer 240 Elemental Analyser, and molybdenum and tungsten contents by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrophotometer. Combustion methods of analysis have not proved entirely reliable for the complexes reported here and elsewhere even though the author was confident that pure samples were used. Consequently identification has been based on both elemental analyses and spectroscopic data.

## 3.2 Reactions of $[(\eta^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo,W) with Amidines:

3.2.1 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with [PhNHC(Me)NPh] . - This reaction was performed on several occasions under different conditions (temperature, molar ratio).

$[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) and [PhNHC(Me)NPh] (0.75g, 3.57mmol) were dissolved in toluene (35ml), and the mixture stirred at 50 - $55^o$ for 9.5h. During this period a colour change from orange to orange-brown took place and a white precipitate separated. At the end of the reaction, monitored using the 2060 $cm^{-1}$ i.r. absorption of the carbonyl chloride, filtration yielded an orange filtrate. The filtrate was reduced in volume ($20^{o}$, in vacuo) and on cooling to $-20^{o}$ yielded orange crystals of $[(\eta^{5}\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ , which were recrystallised from diethyl ether (30ml) (yield : 0.44g, 57%).

The white precipitate was extracted with chloroform/hexane mixture (5 : 1), which was reduced to a small bulk, and cooled to $-20^{o}$ when white crystals separated out. This compound was identified as $[PhNHC(Me)NHPh]^{+}Cl^{-}$ by elemental analysis, mass spectrometry and comparing the i.r. spectrum with that of an authentic sample.

Properties of $[(\eta^{5}\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ : The orange crystals melted with decomposition at 138 - $141^{o}$ and were both thermally and air stable at room temperature, but solutions were susceptible to aerial oxidation. It decomposed when stirred in toluene under nitrogen at $60^{o}$ for 1h. giving a brown precipitate of a non-carbonyl material. It was very soluble in chloroform and dichloromethane, soluble in diethyl ether and toluene, moderately soluble in acetone, and insoluble in hexane.

Analysis: Found C, 59.11; H, 3.82; N, 6.36; Mo, 20.66. $C_{21}H_{18}MoN_2O_2$ requires C, 59.16; H, 4.25; N, 6.56; Mo, 22.50%.

Infrared spectrum (KBr disc): Two very strong carbonyl absorptions were observed at 1953(VS),1850(VS). The full spectrum is: 1953(VS), 1850(VS), 1828(Sh), 1594(M), 1578(W), 1498(M-S), 1450(W), 1427(M-S), 1370(M-W), 1477(Sh), 1299(W), 1272(M-W), 1229(M), 1178(M-W), 1159(W), 1082(W), 1068(VW), 1059(VW), 1035(W), 1014(W), 854(W), 841(W), 818(M), 772(M-W), 753(M), 699(M), 547(M-W), 524(M-W), 502(W), 483(W),455(M-W), 429(W) $cm^{-1}$. $\nu$(CO) (toluene) : 1980(Sh), 1953(S), 1859(S) $cm^{-1}$.

$^{1}$Hn.m.r. spectrum ($CDCl_3$, - $50^{o}$): Multiplet signal at 2.41$\tau$(centre of multiplet) typical of phenyl groups, and singlets at 3.87$\tau$, 7.61$\tau$ due to $(\eta^{5}\text{-}C_5H_5)$ and Me protons respectively.

| Temperature | $C(CH_3)$ | $\eta^5\text{-}C_5H_5$ | $2(C_6H_5)$ |
|---|---|---|---|
| -30° | 7.61 $\tau$ | 3.87 $\tau$ | 2.37 $\tau$ |
| -10° | 7.67 $\tau$ | 4.00 $\tau$ | 2.55 $\tau$ |
| 0° | 7.75 $\tau$ | 4.00 $\tau$ | 2.52 $\tau$ |
| 20° | 7.78 $\tau$ | 4.05 $\tau$ | 2.61 $\tau$ |

Mass spectrum : (direct insertion probe at source temperature). The spectrum obtained showed the parent ion and breakdown pattern associated with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ . The major molybdenum containing ions observed are listed in Table 111.1.

3.2.2 Reactions of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $[PhNHC(Me)NPh]$. - $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.50g, 1.36mmol) and $[PhNHC(Me)NPh]$ (0.57g., 2.71mmol) were dissolved in toluene (35ml), and the mixture stirred at 70 -80° for 17.5h. The procedure described previously was followed and orange crystals of $[(\eta^5\text{-}C_5H_5)W(CO)_2\{PhNC(Me)NPh\}]$ (m.p. 143 - 144°) were obtained by crystallisation of the crude product from diethyl ether.

Properties of $[(\eta^5\text{-}C_5H_5)W(CO)_2\{PhNC(Me)NPh\}]$ : The orange crystals were stable in air at room temperature, but in solution decomposition occurred fairly rapidly. They were insoluble in cyclohexane and carbon tetrachloride, very soluble in dichloromethane, chloroform, diethylether and toluene.

Analysis: Found C, 49.23; H, 3.58; N, 5.45; W, 36.84. $C_{21}H_{18}WN_2O_2$ requires C, 49.05; H, 3.53; N, 5.44; W, 35.75%.

Infrared spectrum (KBr disc): 1927(VS), 1812(VS), 1600(M), 1584(W), 1499(M-S), 1451(W), 1426(M-S), 1372(M-W), 1318(VW), 1300(W), 1278(W), 1230(M), 1180(W), 1160(W), 1118(VW), 1083(W), 1071(VW), 1036(M-W), 1016(M-W), 816(VW), 845(VW), 824(M), 773(W), 755(M), 700(M), 549(W), 526(M-W), 465(M-W) $cm^{-1}$. $\nu$(CO) (toluene): 1942(S), 1842(S) $cm^{-1}$.

Table **III.1** Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)M(CO)_2\{PhNC(Me)NPh\}]$ (M = Mo,W).

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | Fragment lost |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me):NPh\}]^+$ | 428 | | | 15.5 | $[(\eta^5\text{-}C_5H_5)W(CO)_2\{PhNC(Me):Nph\}]^+$ | 514 | | |
| | | 373 | CO | | | | 459 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)\{PhNC(Me):NPh\}]^+$ | 400 | | | 5.22 | $[(\eta^5\text{-}C_5H_5)W(CO)\{PhNC(Me):NPh\}]^+$ | 486 | | |
| | | 345 | CO | | | | 431 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo\{PhNC(Me):NPh\}]^+$ | 372 | | | 100 | $[(\eta^5\text{-}C_5H_5)W\{PhNC(Me):NPh\}]^+$ | 458 | | |
| | | 294 | MeCN | | | | 376 | MeCN |
| $[(\eta^5\text{-}C_5H_5)Mo\{(Ph)_2N\}]^+$ | 331 | | | 17.7 | $[(\eta^5\text{-}C_5H_5)W\{(Ph_2)N\}]^+$ | 417 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{PhN\}]^+$ | 254 | | | 11.1 | $[(\eta^5\text{-}C_5H_5)W\{PhN\}]^+$ | 340 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(Ph)]^+$ | 240 | | | 7.7 | $[(\eta^5\text{-}C_5H_5)W(Ph)]^+$ | 326 | | |
| $[PhNC(Me) : NPh]^+$ | 210 | | | | $[PhNC(Me) : NPh]^+$ | 210 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me):NPh\}]^{++}$ | 214 | | | | $[(\eta^5\text{-}C_5H_5)W(CO)_2\{PhNC(Me):NPh\}]^{++}$ | 257 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)\{PhNC(Me):NPh\}]^{++}$ | 200 | | | | $[(\eta^5\text{-}C_5H_5)W(CO)\{PhNC(Me):NPh\}]^{++}$ | 243 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{PhNC(Me):NPh\}]^{++}$ | 186 | | | | $[(\eta^5\text{-}C_5H_5)W\{PhNC(Me):NPh\}]^{++}$ | 229 | | |

3.2.3 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $[($*p*-tolyl$)NHC(Me)N($*p*-tolyl$)]$. - $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) and $[($*p*-tolyl$)NHC(Me)N($*p*-tolyl$)]$ (0.85g, 3.56mmol) were dissolved in toluene (35ml) and heated at $50 - 60^\circ$ for 5h. during which time reaction occurred precipitating white $[($*p*-tolyl$)NHC(Me)NH($*p*-tolyl$)]^+Cl^-$. The reaction mixture was filtered and the procedure described previously was followed. Orange cystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{($*p*-tolyl$)NC(Me)N($*p*-tolyl$)\}]$ were obtained by crystallisation of the crude product from diethyl ether (30ml).

Properties of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{($*p*-tolyl$)NC(Me)N($*p*-tolyl$)\}]$ : Stability and solubility were similar to those described for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\{PhNC(Me)NPh\}]$. It melted with decomposition at $152 - 154^\circ$.

Analysis: Found C, 60.88; H, 4.98; N, 5.53; Mo, 15.11. $C_{23}H_{22}MoN_2O_2$ requires C, 60.79; H, 4.88; N, 6.16; Mo, 21.11%.

Infrared spectrum (KBr disc): Two strong C-O stretching vibrations were observed at 1942 and 1842. The full spectrum is: 1942(S), 1842(S), 1820(Sh) 1648(W), 1578(W), 1510(M-S), 1500(Sh), 1480(M), 1425(M-S), 1370(M-W), 1320(W), 1295(W), 1272(M-W), 1230(M), 1116(M-W), 1022(M-W), 1012(M-W), 813(M), 530(W), 522(M), 442(W) $\text{cm}^{-1}$. $\nu$(CO) (toluene): 1951(S), 1857(S) $\text{cm}^{-1}$.

$^1$Hn.m.r. spectrum: The complex was dissolved in $CDCl_3$ on warming, but some insoluble decomposition material was produced. Decomposition arose either by reaction of the complex with $CDCl_3$ or by exposure to air. The spectrum consists of a multiplet at $2.58\tau$ (centre of multiplet) (8H), and singlets at $3.96\tau$ (5H), $7.30\tau$ (6H), $7.79\tau$ (3H). The signals are due to $2(C_6H_4)$, $[(\eta^5\text{-}C_5H_5)$, 2(Me) and Me protons respectively. No splitting of the Me and 2Me signals were observed at $-87^\circ$.

Mass spectrum (direct insertion probe at source temperature): The spectrum obtained showed the parent ion and breakdown pattern associated with

$[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{(\underline{p}\text{-tolyl})NC(Me)N(\underline{p}\text{-tolyl})\}]$. The major molybdenum containing ions observed are listed in Table III.2.

Identification of the white precipitate:

1) The white precipitate was recrystalised from chloroform/hexane mixture (5 : 1) into well-formed crystals of $[(\underline{p}\text{-tolyl})NHC(Me)NH(\underline{p}\text{-tolyl})]^+ Cl^-$, which were insoluble in distilled water and acetone, but very soluble in chloroform [m/e 238 ($p^+$). Found C, 70.22; H, 6.78; N, 10.54. $C_{16}H_{19}N_2Cl$ requires C, 69.93; H, 6.91; N, 10.19% .

2) Sublimation: A white sublimate of $[(\underline{p}\text{-tolyl})NH_2C(Me)N(\underline{p}\text{-tolyl})]Cl$ was yielded as a result of purification of the white precipitate by sublimation. [Found C, 70.29; H, 6.74; N, 9.84. $C_{16}H_{19}N_2Cl$ requires C, 69.93; H, 6.91; N, 10.19%].

3) Direct preparation of $[(\underline{p}\text{-tolyl})NH_2C(Me)N(\underline{p}\text{-tolyl})]Cl$ for comparative purposes: $[(\underline{p}\text{-tolyl})NHC(Me)N(\underline{p}\text{-tolyl})]$ (0.50g) was dissolved in methanol (5ml), and HCl (dil.) (2ml) was added to the reaction mixture by a syringe. Shaking the reaction flask for a few minutes and allowing the mixture to settle for 30 minutes followed by pumping the solvent to dryness yielded a white powder [Found C, 69.51; H, 6.55; N, 9.72; Cl, 13.38. Found for the white precipitate C, 70.22; H, 6.78; N, 10.54%].

3.2.4 Reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $[(\underline{p}\text{-tolyl})NHC(Me)N(\underline{p}\text{-tolyl})]$. - $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.50g, 1.36mmol) and $[(\underline{p}\text{-tolyl})NHC(Me)N(\underline{p}\text{-tolyl})]$ (0.65g, 2.71mmol) were stirred in toluene (35ml) at 80 - 90° for 10h. The reaction mixture was filtered and the procedure outlined for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ followed. Orange crystals m.p. (decomp.) 158° of $[(\eta^5\text{-}C_5H_5)W(CO)_2\{(\underline{p}\text{-tolyl})NC(Me)N(\underline{p}\text{-tolyl})\}]$ were obtained by crystallisation of the crude product from diethyl ether (25ml).

Analysis for $[(\eta^5\text{-}C_5H_5)W(CO)2\{(\underline{p}\text{-tolyl})NC(Me)N(\underline{p}\text{-tolyl})\}]$ : Found C, 50.71; H, 3.75; N, 5.18. $C_{23}H_{22}WN_2O_2$ requires C, 50.93; H, 4.08; N, 5.16%.

Table III.2 Mass Spectral Data for $[(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\{(\text{p-tolyl})\text{NC(Me)N}(\text{p-tolyl})\}]$ (M = Mo,W)

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | Fragment lost |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 456 | 401 | CO | 17.46 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 542 | 487 | CO |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 428 | 350 | CO | 1.20 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 514 | 459 | CO |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 400 | 322 | ($\underline{p}$-tolyl) CN | 100 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{+}$ | 486 | 407 | ($\underline{p}$-tolyl) CN |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{(\underline{p}\text{-tolyl})_2\text{N}\}]^{+}$ | 359 | | | 8.33 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{(\underline{p}\text{-tolyl})_2\text{N}\}]^{+}$ | 445 | | |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{(\underline{p}\text{-tolyl})\text{N}\}]^{+}$ | 268 | | | 7.73 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{(\underline{p}\text{-tolyl})\text{N}\}]^{+}$ | 354 | | |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\underline{p}\text{-tolyl})]^{+}$ | 254 | | | 2.38 | $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\underline{p}\text{-tolyl})]^{+}$ | 340 | | |
| $[(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})]^{+}$ | 238 | | | | $[(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})]^{+}$ | 238 | | |
| | | | | | $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{++}$ | 271 | | |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{++}$ | 200 | | | | $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})^{++}$ | 257 | | |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{(\underline{p}\text{-tolyl})_2\text{N}\}]^{++}$ | 179.5 | | | | $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{(\underline{p}\text{-tolyl})\text{NC(Me)}:\text{N}(\underline{p}\text{-tolyl})\}]^{++}$ | 243 | | |

Infrared spectrum (KBr disc): 1920(VS), 1822(VS), 1648(M-W), 1615(M-W), 1578(W), 1510(M-S), 1496(W), 1488(W), 1422(M), 1389(W), 1370(M-W), 1319(M-W), 1295(W), 1273(W), 1230(M), 1183(W), 1118(M-W), 1012(M-W), 858(W), 820(W), 810(M), 713(W), 528(M), 465(W), 443(W), cm$^{-1}$. $\nu$(CO) (toluene): 1939(S), 1838(S) cm$^{-1}$.

$^{1}$Hn.m.r. spectrum (CDCl$_3$, 30°): The spectrum consists of a multiplet with four signals at $2.34\tau$, $2.47\tau$, $2.57\tau$, $2.71\tau$ due to 2($C_6H_4$) protons, and singlets at $3.82\tau$, $7.22\tau$, $7.76\tau$ due to ($\eta^5$-$C_5H_5$), 2(Me), and Me protons respectively. No splitting of the 2(Me) and Me protons was observed at-70°.

3.2.5 Reaction of [($\eta^5$-$C_5H_5$)Mo(CO)$_3$Cl] with [MeNHC(Ph)NMe)]. - [($\eta^5$-$C_5H_5$)Mo(CO)$_3$Cl] (0.50g, 1.78mmol) and [MeNHC(Ph)NMe] (0.53g, 3.57mmol) were stirred in toluene (40ml) at 60-65°. The solution turned orange-brown with deposition of a white precipitate [{MeNHC(Ph)NHMe} Cl], and the reaction was shown to be complete by i.r. spectroscopy after 1.15h. The solution was filtered, and on removal of the solvent (20°, in vacuo) gave a viscous material which was extracted with diethyl ether (25ml) and yielded orange crystals of [($\eta^5$-$C_5H_5$)Mo(CO)$_2${MeNC(Ph)NMe}] (m.p. 125-126°).

Analysis for [($\eta^5$-$C_5H_5$)Mo(CO)$_2${MeNC(Ph)NMe}] : Found C, 53.65; H, 4.23; N, 7.09; Mo, 26.53. $C_{16}H_{16}MoN_2O_2$ requires C, 52.74; H, 4.42; N, 7.68; Mo, 26.33%.

Infrared Spectrum (KBr disc): 1941(VS), 1853(VS), 1828(S), 1583(W), 1522(M), 1489(W), 1448(W), 1402(M), 1252(M-W), 1168(W), 1116(W), 1081(W), 1055(W), 1039(W), 1028(W), 933(W), 813(M), 782(M), 712(M), 551(W), 520(M-W), 488(W), 462(M-W) cm$^{-1}$. $\nu$(CO) (toluene): 1948(VS), 1918(W), 1854(VS); (CS$_2$): 1951(VS), 1858(VS) cm$^{-1}$.

$^{1}$Hn.m.r. Spectrum: The spectrum in CDCL$_3$ colution at 11° consists of two sharp singlets at $6.58\tau$ (6H) and $3.89\tau$ (5H) due to (2Me) and ($\eta^5$-$C_5H_5$) protons respectively. A multiplet due to the phenyl group, centred at $2.28\tau$ and $2.06\tau$ was also observed.

Mass Spectrum (direct insertion probe at source temperature): The parent ion, corresponding to $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{MeNC(Ph)NMe\}]^+$ and ions formed in the expected breakdown of this, were all observed. The major peaks in the spectrum are listed in Table III.3.

3.2.6 Reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $[MeNHC(Ph)NMe]$. The above procedure was followed using $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.50g, 1.36mmol) and $[MeNHC(Ph)NMe]$ (0.40g, 2.71mmol) in toluene (35ml), and the reaction mixture was heated at 80-90° for 2.15h. Orange crystals of $[(\eta^5\text{-}C_5H_5)W(CO)_2\{MeNC(Ph)NMe\}]$ (m.p. 132-133°) were obtained by crystallisation of the crude product from diethyl ether (25ml).

Analysis for $[(\eta^5\text{-}C_5H_5)W(CO)_2\{MeNC(Ph)NMe\}]$: Found C, 42.38; H, 3.12; N, 6.05; W, 43.10. $C_{16}H_{16}WN_2O_2$ requires C, 42.49; H, 3.56; N, 6.19; W, 40.65%.

Infrared spectrum(KBr disc): 1923(VS), 1900(Sh), 1832(VS), 1795(W), 1789(W), 1655(M), 1583(W), 1520(M), 1489(W), 1448(W), 1425(W), 1403(M), 1260(M-W), 1168(W), 1114(W), 1082(W), 1058(W), 1040(W), 1028(M-W), 1011(W), 935(W), 822(M), 783(M), 740(W), 714(M), 532(M-W), 516(W), 485(W), 472(M-W) $cm^{-1}$.

$\nu$(CO) (toluene): 1932(S), 1832(S) $cm^{-1}$.

$^1$Hn.m.r. spectrum:($CDCl_3$)

| Temperature | $C_6H_5$ | $(\eta^5\text{-}C_5H_5)$ | 2(Me) |
|---|---|---|---|
| 10° | $2.15^{\dagger}\tau$ | $3.73\,\tau$ | $6.49\,\tau$ |
| -80° | $1.99^{\dagger}\tau$ | $3.60\,\tau$ | $6.39\,\tau$ |

† multiplet

Table III.3 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)M(CO)_2\{MeNC(Ph)NMe\}]$ (M = Mo,W).

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | Fragment lost |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{MeNC(Ph):NMe\}]^+$ | 366 | | | 24.36 | $[(\eta^5\text{-}C_5H_5)W(CO)_2\{(MeNC(Ph):NMe\}]^+$ | 452 | | |
| | | 312 | CO | | | | 397 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)\{MeNC(Ph):NMe\}]^+$ | 338 | | | 5.13 | $[(\eta^5\text{-}C_5H_5)(CO)\{MeNC(Ph):NMe\}]^+$ | 424 | | |
| | | 284 | CO | | | | 369 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo\{MeNC(Ph):NMe\}]^+$ | 310 | | | 100 | $[(\eta^5\text{-}C_5H_5)W\{MeNC(Ph):NMe\}]^+$ | 396 | | |
| | | 254 | NMe | | | | 340 | NMe |
| $[(\eta^5\text{-}C_5H_5)Mo\{MeNCPh\}]^+$ | 281 | | | 46.15 | $[(\eta^5\text{-}C_5H_5)W\{MeNCPh\}]^+$ | 367 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CPh)]^+$ | 252 | | | 25.64 | $[(\eta^5\text{-}C_5H_5)W(CPh)]^+$ | 338 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(Ph)]^+$ | 240 | | | 16.66 | $[(\eta^5\text{-}C_5H_5)W(Ph)]^+$ | 326 | | |
| $[(\eta^5\text{-}C_5H_5)Mo]^+$ | 163 | | | 35.89 | $[(\eta^5\text{-}C_5H_5)W]^+$ | 249 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{MeNC(Ph):NMe\}]^{++}$ | 183 | | | | $[(\eta^5\text{-}C_5H_5)W(CO)_2\{MeNC(Ph):NMe\}]^{++}$ | 226 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)\{MeNC(Ph):NMe\}]^{++}$ | 169 | | | | $[(\eta^5\text{-}C_5H_5)W(CO)\{MeNC(Ph):NMe\}]^{++}$ | 212 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{MeNC(Ph)NMe\}]^{++}$ | 155 | | | | $[(\eta^5\text{-}C_5H_5)W\{MeNC(Ph):NMe\}]^{++}$ | 198 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{MeNCPh\}]^{++}$ | 140.5 | | | | $[(\eta^5\text{-}C_5H_5)W(CPh)]^{++}$ | 159 | | |
| | | | | | $[(\eta^5\text{-}C_5H_5)W(Ph)]^{++}$ | 163 | | |

3.2.7 Reaction of [$(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$] with [PhNHC(H)NPh]. - [$(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$] (0.50g, 1.78mmol) and [PhNHC(H)NPh] (0.70g, 3.57mmol) were stirred in toluene (40ml) under nitrogen at 60-70°. A darkening in colour occurred gradually, and was accompanied by separation of a white precipitate [identified as {PhNHC(H)NHPh}Cl. Found C, 66.69; H, 4.45; N, 11.02. $C_{13}H_{13}N_2Cl$ requires C, 66.76; H, 5.60; N, 11.97%]. The reaction was shown by spectrophotometry to be complete after 17h. Filtration of the mixture and evaporation of the filtrate, gave an orange powder, which was recrystallised from diethyl ether (30ml) to give orange crystals of [$(\eta^5\text{-}C_5H_5)Mo(CO)_2$ {PhNC(H)NPh}] (m.p. 158 - 160°).

Analysis for [$(\eta^5\text{-}C_5H_5)Mo(CO)_2$ {PhNC(H)NPh}]*: Found C, 58.94; H, 4.05; N, 4.44; Mo, 33.95. $C_{20}H_{16}MoN_2O_2$ requires C, 58.26; H, 3.91; N, 6.79; Mo, 23.27%.

Infrared spectrum (KBr disc): 1950(S), 1870(S), 1830(Sh), 1602(M), 1540(M-S), 1515(M), 1498(M), 1292(W), 1277(M-S), 1250(W), 1236(M-W), 1183(M-W), 1161(M), 1087(W), 1070(W), 1038(M-W), 1020(M-W), 1012(W), 1004(W), 980(W), 962(W), 932(M-W), 896(W), 860(W), 849(W), 840(W), 835(W), 820(M-S), 760(M-S), 695(M-S), 560(W), 547(M-W), 539(M), 511(W), 481(W), 455(M) cm$^{-1}$. $\nu$(CO) (toluene): 1963(S), 1872(S) cm$^{-1}$.

$^1$Hn.m.r. spectrum: ($CS_2$)

| Temperature | $2(C_6H_5)$ | $(\eta^5\text{-}C_5H_5)$ | (CH) |
|---|---|---|---|
| 20° | 2.45τ (10) † | 3.89τ (5) | 3.99τ (1) |
| -10° | 2.41τ (10) † | 3.84τ (5) | 3.97τ (1) |

† multiplet

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* The formulation of this complex as [$(\eta^5\text{-}C_5H_5)Mo(CO)_2$ {PhNC(H)NPh}] is based on spectroscopic and other data, and on comparisons with related derivatives. Since these analytical data were obtained on a pure sample, the poor agreement between the experimentally determined Mo and N contents and the theoretical contents can not be adequately explained. Data obtained for different samples generally corresponded poorly with theoretical values.

Table III.4 Mass Spectral Data for $[(\eta^5-C_5H_5)Mo(CO)_2\{PhNC(H)NPh\}]$.

| Ion | m/e | m* | Fragment lost |
|---|---|---|---|
| $[(\eta^5-C_5H_5)Mo(CO)_2\{PhNC(H)NPh\}]^+$ | 414 | | |
| | | 359 | CO |
| $[(\eta^5-C_5H_5)Mo(CO)\{PhNC(H)NPh\}]^+$ | 386 | | |
| | | 332 | CO |
| $[(\eta^5-C_5H_5)Mo\{PhNC(H)NPh\}]^+$ | 358 | | |
| | | 306 | HCN |
| $[(\eta^5-C_5H_5)Mo\{(Ph)_2N\}]^+$ | 331 | | |
| $[(\eta^5-C_5H_5)Mo(PhN)]^+$ | 254 | | |
| $[(\eta^5-C_5H_5)Mo(CO)\{PhNC(H)NPh\}]^{++}$ | 193 | | |
| $[(\eta^5-C_5H_5)Mo\{PhNC(H)NPh\}]^{++}$ | 179 | | |
| $[(\eta^5-C_5H_5)Mo\{(Ph)_2N\}]^{++}$ | 165.5 | | |
| $[(\eta^5-C_5H_5)Mo(PhN)]^{++}$ | 127 | | |

## 3.3 Reactions of $[(\eta^5-C_5H_5)M(CO)_3Cl]$ (M = Mo,W) with Lithioamidines.

**3.3.1 Reaction of $[(\eta^5-C_5H_5)Mo(CO)_3Cl]$ with LiN(Ph)C(Me)N(Ph).** - A suspension of LiN(Ph)C(Me)N(Ph) was prepared by the addition of n-butyl-lithium in hexane (1.2ml, 1.5M) to [(PhNHC(Me)N(Ph)] (0.37g, 1.78mmol) in diethyl ether (50ml) previously cooled to the liquid nitrogen temperature (-196°), the mixture then being allowed to warm slowly to ambient temperature. After stirring for 20 minutes the solution was added to a frozen solution of $[(\eta^5-C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) in ether (40ml), then the mixture allowed to warm slowly to ambient temperature. The solution turned yellow-orange with deposition of a white solid. The reaction was shown to be complete by i.r. spectroscopy after 1.15h. at room temperature. Filteration of the mixture and evaporation of the filterate, gave a yellow powder. Recrystallisation from chloroform/hexane mixtures yielded yellow crystals of $[(\eta^5-C_5H_5)Mo(CO)_2CON(Ph)C(Me)N(Ph)]$.

Properties of $[(\eta^5-C_5H_5)Mo(CO)_2CON(Ph)C(Me)N(Ph)]$ .- The yellow crystals melted with decomposition at (166°). They were stable in air at room temperature, but in solution decomposition occurred. They were very soluble in chloroform and dichloromethane, moderately soluble in toluene, sparingly soluble in diethyl ether, and insoluble in hexane.

Analysis: Found C, 56.46; H, 5.27; N, 6.05; Mo, 18.29. $C_{22}H_{18}MoN_2O_3$ requires C, 58.15; H, 3.99; N, 6.16; Mo, 21.11%.

Infrared spectrum (KBr disc): Two strong carbonyl absorptions at 1950(VS), 1862(VS) due to the two terminal carbonyl groups, and a carbamoyl absorption at 1620(M-S) were observed. The full spectrum is: 1950(VS), 1862(VS), 1620(M-S), 1595(W), 1492(M), 1454(W), 1418(M), 1378(W), 1271(M), 1212(W), 1179(W), 1080(W), 1068(W), 1042(M-W), 1015(W), 960(M), 918(M-W), 852(W), 838(W), 818(M-W), 800(M-W), 782(W), 758(M), 719(W), 703(M), 648(M-W), 615(W), 591(VW), 563(W), 537(M-W), 518(M-W), 481(VW), 447(W) $cm^{-1}$. $\nu$(CO) (toluene): 1960(S), 1878(S); $(CHCl_3)$: 1963(VS), 1879(S) $cm^{-1}$.

$^1$Hn.m.r. spectrum: $(CDCl_3$, 20°): The spectrum consists of a multiplet centred at 2.18$\tau$ (10H), and singlets at 4.13$\tau$ (5H) and 7.70 $\tau$ (3H).

Mass spectrum: A parent peak, corresponding to $[(\eta^5-C_5H_5)Mo(CO)_2CON(Ph)C(Me)N(Ph)]^+$, was observed at (m/e 456). The breakdown pattern consisted of successive loss of carbonyl groups followed by loss of MeCN. The observed metal-containing ions are listed in Table III.5.

3.3.2 Reaction of $[(\eta^5-C_5H_5)W(CO)_3Cl]$ with LiN(Ph)C(Me)N(Ph). - A suspension of LiN(Ph)C(Me)N(Ph) was formed from [PhNHC(Me)NPh] (0.28g, 1.36mmol) and $Bu^nLi$ in hexane (0.90ml, 1.5M), in ether (50ml) by mixing at (-196°), allowing the mixture to warm, then stirring the mixture of the white precipitate at ambient temperature for 30 minutes. Addition of this mixture to a frozen solution of $[(\eta^5-C_5H_5)W(CO)_3Cl]$ (0.50g, 1.36mmol) in ether (40ml) and stirring for 3h. at ambient temperature gave a yellow-brown solution and a fine white

Table III.5 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(Ph)C(Me)NPh]$ (M = Mo,W) Complexes.

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | % of base peak |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)C(Me)NPh]^+$ | 456 | | | 0.41 | $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(Ph)C(Me)NPh]^+$ | 542 | | 1.61 |
| | | 401 | CO | | | | 487 | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(Ph)C(Me)NPh]^+$ | 428 | | | 16.43 | $[(\eta^5\text{-}C_5H_5)W(CO)_2N(Ph)C(Me)NPh]^+$ | 514 | | 22.58 |
| | | 373 | CO | | | | 459 | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(Ph)C(Me)NPh]^+$ | 400 | | | 1.43 | $[(\eta^5\text{-}C_5H_5)W(CO)N(Ph)C(Me)NPh]^+$ | 486 | | 6.45 |
| | | 345 | CO | | | | 431 | |
| $[(\eta^5\text{-}C_5H_5)Mo\{N(Ph)C(Me)NPh\}]^+$ | 372 | | | 100 | $[(\eta^5\text{-}C_5H_5)W\{N(Ph)C(Me)NPh\}]^+$ | 458 | | 100 |
| | | 294 | MeCN | | | | 379 | |
| $[(\eta^5\text{-}C_5H_5)Mo\{(Ph)_2N\}]^+$ | 331 | | | 17.14 | $[(\eta^5\text{-}C_5H_5)W\{(Ph)_2N\}]^+$ | 417 | | 17.74 |
| $[(\eta^5\text{-}C_5H_5)Mo\{(Ph)N\}]^+$ | 254 | | | 16.43 | $[(\eta^5\text{-}C_5H_5)W\{(Ph)N\}]^+$ | 340 | | 6.45 |
| $[(\eta^5\text{-}C_5H_5)Mo(Ph)]^+$ | 240 | | | 7.86 | $[(\eta^5\text{-}C_5H_5)W(Ph)]^+$ | 326 | | 4.84 |
| $[(\eta^5\text{-}C_5H_5)Mo\{N(Ph)C(Me)NPh\}]^{++}$ | 186 | | | | $[(\eta^5\text{-}C_5H_5)W(CO)N(Ph)C(Me)NPh]^{++}$ | 243 | | |
| | | | | | $[(\eta^5\text{-}C_5H_5)W\{N(Ph)C(Me)NPh\}]^{++}$ | 229 | | |
| | | | | | $[(\eta^5\text{-}C_5H_5)W\{(Ph)_2N\}]^{++}$ | 208.5 | | |

precipitate. Filtration of the mixture and evaporation of the filtrate (20°, in vacuo), gave a yellow powder. Yellow crystals of [($\eta^5$-$C_5H_5$)W(CO)$_2$CON(Ph)C(Me)NPh (m.p. 184-185°C decomp.) were obtained by crystallisation of the crude product from chloroform/hexane mixtures.

Analysis for [($\eta^5$-$C_5H_5$)W(CO)$_2$CON(Ph)C(Me)NPh] : Found C, 46.17; H, 4.72; N, 5.73. $C_{22}H_{18}WN_2O_3$ requires C, 48.72; H, 3.34; N, 5.16%.

Infrared spectrum (KBr disc): Two strong carbonyl absorptions were observed at 1940(VS), 1850(S) due to the two terminal carbonyl groups. A medium-strong absorption assigned to the carbamoyl group occurred at 1619(M). The full spectrum is: 1940(VS), 1850(S), 1619(M), 1596(M), 1493(M), 1426(M-W), 1380(W), 1275(M), 1081(W), 1042(W), 958(M-W), 826(W), 805(M-W), 785(W), 760(M), 720(W), 707(M), 651(W), 617(W), 590(W), 568(W), 537(W), 517(W) $cm^{-1}$. $\nu$(CO) ($CHCl_3$): 1948(VS), 1853(VS) $cm^{-1}$.

$^1$Hn.m.r. spectrum ($CDCl_3$): An attempt was made to record the $^1$Hn.m.r. spectrum of this material, but the sample decomposed rapidly at room temperature. Attempts to produce a solution of the complex in $CDCl_3$ at low temperature (0°) also failed.

3.3.3 Reaction of [($\eta^5$-$C_5H_5$)Mo(CO)$_3$Cl] with LiN(p-tolyl)C(Me)N(p-tolyl). - The lithioamidine suspension prepared by the method previously described from [(p-tolyl)NHC(Me)N(p-tolyl)] (0.42g, 1.78mmol) and Bu$^n$Li(1.2ml, 1.5M in hexane) in ether (50ml) was mixed at liquid nitrogen temperature with a solution of [($\eta^5$-$C_5H_5$)Mo(CO)$_3$Cl] (0.50g, 1.78mmol) in ether (40ml), the mixture then being allowed to warm slowly to ambient temperature. The reaction was shown by i.r. spectroscopy to be virtually complete after 1.10h. at room temperature. Following the procedure described previously, yellow crystals of [($\eta^5$-$C_5H_5$)Mo(CO)$_2$CON(p-tolyl)C(Me)N(p-tolyl)] (m.p. 158-159°) were obtained by crystallisation of the crude product from dichloromethane/hexane mixtures (0.20 g, 37.16% yield).

Analysis for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]$ :

Found C, 57.40; H, 3.41; N, 5.34; Mo, 14.39. $C_{24}H_{22}MoN_2O_3$ requires C, 59.75; H, 4.59; N, 5.80; Mo, 19.89%.

Infrared spectrum (KBr disc): 1952(VS), 1865(S), 1630(S), 1578(W), 1512(M-S), 1425(M), 1378(W), 1311(W), 1271(M), 1216(M-W), 1180(W), 1115(M-W), 1032(W), 1016(W), 960(W), 935(W), 872(W), 836(W), 810(M), 783(M-W), 758(M), 728(M-W), 713(W), 622(M-W), 582(M-W), 538(W), 521(M-W), 501(W), 480(W), 443(W) $cm^{-1}$.

$\nu$(CO) ($CHCl_3$): 1961(VS), 1873(S), 1627(Sh), 1608(M) $cm^{-1}$.

$^1$Hn.m.r. spectrum ($CDCl_3$):

| Temperature | $C(CH_3)$ | $2(CH_3)$ | $(\eta^5\text{-}C_5H_5)$ | $2(C_6H_4)$ |
|---|---|---|---|---|
| + 20 | 7.80 τ (3) | 7.20 τ (6) | 4.22 τ (5) | 2.24 τ (8) |
| - 30 | 7.73 τ (3) | 7.14 τ (6) | 4.13 τ (5) | 2.17 τ (8) |
| - 49 | 7.72 τ (3) | 7.14 τ (6) | 4.12 τ (5) | 2.17 τ (8) |
| + 20 | 7.77 τ (3) | 7.16 τ (6) | 4.20 τ (5) | 2.24 τ (8) |

Table III.6 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]$.

| Ion | m/e | m* | Fragment lost |
|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]^+$ | 484 | 429 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(p\text{-tolyl})C(Me)N(p\text{-tolyl})]^+$ | 456 | 401 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(p\text{-tolyl})C(Me)N(p\text{-tolyl})]^+$ | 428 | 373 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo\{N(p\text{-tolyl})C(Me)N(p\text{-tolyl})\}]^+$ | 400 | 322 | MeCN |
| $[(\eta^5\text{-}C_5H_5)Mo\{(p\text{-tolyl})_2N\}]^+$ | 359 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{(p\text{-tolyl})N\}]^+$ | 268 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(p\text{-tolyl})]^+$ | 254 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(p\text{-tolyl})C(Me)N(p\text{-tolyl})]^{++}$ | 214 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{N(p\text{-tolyl})C(Me)N(p\text{-tolyl})\}]^{++}$ | 200 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{(p\text{-tolyl})_2N\}]^{++}$ | 179.5 | | |

3.3.4 Reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with LiN(p-tolyl)C(Me)N(p-tolyl) . - This reaction was attempted several times under varying conditions (solvent, temperature, molar ratio). The lithio-reagent formed from [(p-tolyl)NHC(Me)N(p-tolyl)] (0.65g, 2.71mmol) and $Bu^nLi$ (1.27ml, 2.13M in hexane) in ether solution (50ml) was added to a frozen solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.50g, 1.36mmol) in ether (40ml). The mixture was stirred at room temperature for 3h. when a colour change from orange to deep yellow occurred and a precipitate separated. Filtration of the mixture followed by evaporation of the filtrate (20°C, in vacuo), gave a viscous material. Attempts to obtain crystals of the complex from many different solvent mixtures failed, the same yellow-brown viscous material being recovered on each occasion. The i.r. spectrum showed similarities with those of the other amidino-metal complexes described previously as $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(R^1)C(R)NR^1]$ complexes. $\nu$(CO) (KBr disc): 1944(VS), 1853(S); ($CHCl_3$): 1952(VS), 1861(S) $cm^{-1}$.

Mass spectrum: Even after many attempts no tungsten containing ions could be observed.

The same reaction was attempted with molar-ratio 1 : 1, but the starting material $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ was recovered after a period of 3.30h. of stirring at room temperature.

3.3.5 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with LiN(Me)C(Ph)N(Me). The lithium compound prepared from [(Me)NHC(Ph)N(Me)] (0.26g, 1.78mmol) and $Bu^nLi$(1.2ml, 1.5M in hexane) in ether (50ml) was added to a frozen solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) also in ether (40ml) and the mixture was stirred for 2h. at room temperature. At the end of the reaction, as indicated by i.r. spectroscopy, the solvent was removed (20°, in vacuo), and the residue extracted with dichloromethane/hexane mixtures (5 : 1). Fractional crystallisation techniques enabled yellow crystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Me)C(Ph)NMe]$ (m.p.174-175°) to be isolated.

Analytical data for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Me)C(Ph)NMe]$ : Found, C,51.76; H, 3.41; N, 6.91; Mo, 24.79. $C_{17}H_{16}MoN_2O_3$ requires C, 52.04; H, 4.11; N, 7.13; Mo, 24.45%.

Infrared spectrum $\nu$(CO) (nujol): 1949(S), 1861(Sh), 1853(VS); (KBr disc): 1950(VS), 1862(S), 1612(M), 1600(M), 1542(M-W), 1502(M-W, 1450(W), 1428(W), 1395(W), 1242(M), 1200(W), 1060(M-W), 1017(M-W), 930(Sh), 917(Sh), 882(M-W), 860(W), 832(W), 819(M-W), 781(M-W), 718(M), 700(Sh), 628(W), 615(W), 600(W), 548(M-W), 519(W), 502(W), 463(M-W), 403(W) $cm^{-1}$. $\nu$ (CO) ($CHCl_3$): 1963(VS), 1877(S) $cm^{-1}$.

$^1$Hn.m.r. spectrum ($CDCl_3$,0°): The spectrum showed a multiplet for the phenyl group at (1.97 $\tau$, 2.36 $\tau$) (5H), and singlets at 4.1 $\tau$ (5H), 6.29 $\tau$ (3H), 6.71 $\tau$ (3H) due to $(\eta^5\text{-}C_5H_5)$, (N-Me), and (N-Me) protons respectively.

3.3.6 Reactions of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with LiN(Me)C(Ph)N(Me). - This reaction was performed on several occasions under different conditions (solvent, temperature, molar ratio). The amidine (0.20g, 1.36mmol) was converted into the lithio-derivative as described previously, and transferred to a flask containing a frozen mixture of carbonyl chloride (0.50g, 1.36mmol) in ether (40ml). The resulting mixture was allowed to warm to room temperature and then stirred for 3h. During this period a colour change from light orange to deep yellow took place and some precipitation occurred. At the end of the reaction, as indicated by the consumption of all the carbonyl chloride (as monitored by i.r. spectroscopy), the solvent was removed in vacuo (20°; $10^{-1}$mmHg) and the residue extracted with a chloroform/hexane mixtures (5 : 1). Several attempts at fractional crystallisation of the product from this and different solvent mixtures gave only a yellow-brown powder. Analytical data proved unreliable, but the complex $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(Me)C(Ph)NMe]$ was characterised by mass spectrometry, and only by comparison of spectroscopic data with those of the NN-diphenyl acetamidine complexes. $\nu$(CO)(KBr disc): 1946(S), 1852(S); ($CHCl_3$): 1953(S), 1864(S) $cm^{-1}$.

Table III.6 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(Me)C(Ph)NMe]$ (M = Mo,W).

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | Fragment lost |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Me)C(Ph)NMe]^+$ | 394 | | | 5.98 | $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(Me)C(Ph)NMe]^+$ | 480 | | |
| | | 339 | CO | | | | 425 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(Me)C(Ph)NMe]^+$ | 366 | | | 19.66 | $[(\eta^5\text{-}C_5H_5)W(CO)_2N(Me)C(Ph)NMe]^+$ | 452 | | |
| | | 312 | CO | | | | 397 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(Me)C(Ph)NMe]^+$ | 338 | | | 5.13 | $[(\eta^5\text{-}C_5H_5)W(CO)N(Me)C(Ph)NMe]^+$ | 424 | | |
| | | 284 | CO | | | | 369 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo\{NMeC(Ph)NMe\}]^+$ | 310 | | | 100 | $[(\eta^5\text{-}C_5H_5)W\{NMeC(Ph)NMe\}]^+$ | 396 | | |
| | | 254 | NMe | | | | 340 | NMe |
| $[(\eta^5\text{-}C_5H_5)Mo\{MeNC(Ph)\}]^+$ | 281 | | | 34.12 | $[(\eta^5\text{-}C_5H_5)W\{NMeC(Ph)\}]^+$ | 367 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{C(Ph)\}]^+$ | 252 | | | 22.22 | $[(\eta^5\text{-}C_5H_5)W\{C(Ph)\}]^+$ | 338 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(Ph)]^+$ | 240 | | | 15.81 | $[(\eta^5\text{-}C_5H_5)W]^+$ | 249 | | |
| $[(\eta^5\text{-}C_5H_5)Mo]^+$ | 163 | | | 39.32 | | | | |

3.3.7 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $LiN(Ph)C(H)N(Ph)$.– The lithio reagent prepared from the amidine (0.35g, 1.78mmol) in ether (50ml) was added to a frozen solution of the carbonyl chloride (0.50g, 1.78mmol) also in ether (40ml) and the mixture, after warming to room temperature, was stirred for 3.3h. An i.r. spectrum of the reaction solution at this stage showed some remaining carbonyl chloride, therefore another portion (1.78mmol) of the lithioamidine solution was added by a syringe, and the reaction mixture was stirred for an additional 3h. at room temperature. At the end of the reaction, as indicated by i.r. spectroscopy, the mixture was filtered and the solvent removed from the filtrate (20°, $10^{-1}$mmHg). The residue was extracted with a chloroform/hexane mixtures (5 : 1), and a yellow powder separated after cooling the mixture to -20°. All attempts to purify the product from traces of [PhNHCHNPh] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ failed, but the presence of the complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)C(H)NPh]$ was shown by mass spectrometry and by comparison of spectroscopic data with those of the other amidino-complexes. $\nu$(CO)(KBr disc): 1956(S),1869(S); ($CHCl_3$): 1969(VS), 1886(S) $cm^{-1}$. $^m/e$ ($P^+$)442.

Table III.7 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)CHNPh]$.

| Ion | m/e | m* | Fragment lost |
|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)C(H)NPh]^+$ | 442 | | |
| | | 387 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(Ph)C(H)NPh]^+$ | 414 | | |
| | | 359 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(Ph)C(H)NPh]^+$ | 386 | | |
| | | 332 | CO |
| $[(\eta^5\text{-}C_5H_5)Mo\{NPhC(H)NPh\}]^+$ | 358 | | |
| | | 306 | HCN |
| $[(\eta^5\text{-}C_5H_5)Mo\{(Ph)_2N\}]^+$ | 331 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(Ph)C(H)NPh]^{++}$ | 207 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{NPhC(H)NPh\}]^{++}$ | 179 | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{(Ph)_2N\}]^{++}$ | 165.5 | | |

3.3.8 Attempted reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $LiN(Ph)C(H)NPh$. - The lithioamidine suspension prepared from a frozen solution of $[PhNHC(H)NPh]$ (0.25g, 1.26mmol) and Bu$^n$Li (0.84ml, 1.5M in hexane) in ether (50ml) was added to a frozen solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.47g, 1.26mmol) also in ether (40ml) at -196°. The resulting mixture after warming to room temperature and heating to 80-90° for 15.5h. failed to show by i.r. spectroscopy that reaction had occurred, and work-up of the solution caused the starting complex to be recovered.

3.3.9 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $LiNHC(Me)NH$. - A solution of n-butyl-lithium in hexane (2.37ml, 1.5M, 3.56mmol) was added by syringe to a suspension of $[H_2NC(Me)NH_2]Cl$ (0.17g, 1.78mmol) in monoglyme (50ml) at room temperature. An immediate reaction occurred and the mixture became very clear. Addition of this mixture to a frozen solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) in ether (40ml), and stirring at room temperature for 1.15h. gave a yellow-orange solution and a fine light coloured precipitate. Evaporation of the filtrate (in vacuo, 20°) gave a yellow powder. Yellow crystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$ were obtained by crystallisation of the crude product from chloroform/hexane mixtures at (-20°).

Properties of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$ : The yellow crystals melted at 155° - 156° and were both thermally and air stable at room temperature, but solutions were susceptible to aerial oxidation. It was very soluble in chloroform, moderately soluble in toluene, but insoluble in dichloromethane, diethyl ether and hexane.

Analysis: Found C, 37.51; H, 3.96; N, 9.69; Mo, 30.69. $C_{10}H_{10}MoN_2O_3$ requires C, 39.75; H, 3.33; N, 9.26; Mo, 31.75%.

Infrared spectrum (KBr disc): 1953(S), 1928(Sh), 1853(S), 1630(M-W), 1550(M-S), 1428(M-W), 1270(W), 1230(W), 1202(W), 1093(M), 1068(W), 1010(W), 998(W), 835(W), 822(M), 540(M-W), 530(W), 512(W), 490(M-W), 448(M-W) cm$^{-1}$. $\nu$(CO)

($CHCl_3$): 1968(S), 1879(S) $cm^{-1}$.

3.3.10 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $NH_2C(Me)NH$. - A solution of n-butyl lithium (2.37ml, 1.5M, 3.56mmol) in hexane was added by syringe to a suspension of $[H_2NC(Me)NH_2]Cl$ (0.34g, 3.56mmol) in monoglyme at room temperature. The resulting mixture was stirred for 2h. at room temperature before it was added to a solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) also in monoglyme at room temperature. The original deep orange colour of the solution gradually became yellow and the reaction was shown to be complete by i.r. spectroscopy after 2h. at room temperature. Filtration of the mixture and evaporation of the filtrate gave a yellow powder. Recrystallisation of the residue from dichloromethane/hexane mixtures (5 : 1) yielded yellow crystals identified by i.r. spectroscopy, mass spectrometry, and analytical data as $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$ m/e 304 ($P^+$).

3.3.11 Reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $NH_2C(Me)NH$. - A solution of $[NH_2C(Me)NH]$ was formed from $[NH_2C(Me)NH_2]Cl$ (0.34g, 3.56mmol) and $Bu^nLi$ (2.37ml, 1.5M, 3.56mmol) in monoglyme (75ml) by mixing at room temperature, then stirring the mixture at ambient temperature for 2h. Addition of this mixture to a solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ (0.66g, 1.78mmol) in monoglyme (40ml) at room temperature, and stirring for 4h. gave a yellow-orange solution and a white precipitate. At the end of the reaction, as indicated by the consumption of all the carbonyl chloride as monitored by i.r. spectroscopy, the solvent was removed in vacuo (20°; $10^{-1}$mmHg), and the residue extracted with a dichloromethane/hexane mixtures (5 : 1). Fractional crystallisation techniques enabled yellow crystals of $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(H)C(Me)NH]$ [m.p.(decomp.)188°] to be isolated. Found C, 27.84; H, 2.67; N, 7.39. $C_{10}H_{10}WN_2O_3$ requires C, 30.79; H, 2.58; N, 7.17%. I.r. $\nu$ (CO) (KBr): 1949(S), 1819(S), 1791(Sh), 1627(M-W), 1558(M-S), 1428(M-W) 1388(W), 1358(W), 1269(W), 1211(M), 1069(M), 1060(W), 1020(W), 1010(W), 1001(W), 852(W), 843(W), 821(M), 686(M-W), 637(W), 620(W), 602(W), 540(M-W), 517(M-W), 491(W), 456(M-W) $cm^{-1}$. ($CHCl_3$): 1950(VS), 1859(S) $cm^{-1}$.

Table III.8 Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(H)C(Me)NH]$ (M = Mo,W).

| Ion | m/e | m* | Fragment lost | % of base peak | Ion | m/e | m* | % of base peak |
|---|---|---|---|---|---|---|---|---|
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]^+$ | 304 | | | 16.66 | $[(\eta^5\text{-}C_5H_5)W(CO)_2CON(H)C(Me)NH]^+$ | 389 | | 17.77 |
| | | 251 | CO | | | | 335 | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(H)C(Me)NH]^+$ | 276 | | | 34.76 | $[(\eta^5\text{-}C_5H_5)W(CO)_2N(H)C(Me)NH]^+$ | 361 | | 28.88 |
| | | 223 | CO | | | | 307 | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(H)C(Me)NH]^+$ | 248 | | | 20.00 | $[(\eta^5\text{-}C_5H_5)W(CO)N(H)C(Me)NH]^+$ | 333 | | 27.77 |
| | | 195 | CO | | | | 279 | |
| $[(\eta^5\text{-}C_5H_5)Mo\{NHC(Me)NH\}]^+$ | 220 | | | 100 | $[(\eta^5\text{-}C_5H_5)W\{NHC(Me)NH\}]^+$ | 305 | | 100 |
| | | 145 | (Me)CN | | | | 229 | |
| $[(\eta^5\text{-}C_5H_5)Mo\{NH_2\}]^+$ | 179 | | | 57.14 | $[(\eta^5\text{-}C_5H_5)W\{NH_2\}]^+$ | 264 | | 74.22 |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_2N(H)C(Me)NH]^{++}$ | 138 | | | | $[(\eta^5\text{-}C_5H_5)W\{NHC(Me)NH\}]^{++}$ | 152.5 | | |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)N(H)C(Me)NH]^{++}$ | 124 | | | | | | | |
| $[(\eta^5\text{-}C_5H_5)Mo\{NHC(Me)NH\}]^{++}$ | 110 | | | | | | | |

## 3.4 Decarbonylation reactions:

3.4.1 U.v. irradiation of $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_2CON(Ph)C(Me)N(Ph)}]$. - A solution of the complex in toluene contained in a silica flask was irradiated with 300 watt Hg lamp. The original yellow colour of the solution gradually became orange, and the reaction was allowed to continue for 16 minutes. After pumping the reaction mixture to dryness ($20^{\circ}$, $10^{-1}$mm Hg), an i.r. spectroscopic examination of the residue showed the presence of a new carbonyl containing species with an absorption at 2060 $cm^{-1}$. The complex was believed to be of the type $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_3\{NPhC(Me)NPh\}}]$ and to be the intermediate in the decarbonylation reaction. In an attempt to obtain the decarbonylated complex, the intermediate complex was dissolved in toluene and exposed to u.v. light for an additional 40 minutes, after which decomposition to non-carbonyl material occurred.

In an attempt to stabilise the intermediate complex $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_3\{NPhC(Me)NPh\}}]$, subsequent reactions were attempted in the presence of MeI.

3.4.2 U.v.irradiation of $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_2CON(Ph)C(Me)NPh}]$ with MeI. - MeI (0.10ml) was added by a syringe to a solution of $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_2CON(Ph)C(Me)NPh}]$ in toluene, and the resulting mixture was irradiated with a 300 watt Hg lamp. The solution darkened from yellow to orange as the reaction proceeded, and the reaction was allowed to continue for 12 minutes. Filtration of the reaction mixture and evaporation of the filtrate *in vacuo* gave a product in small yield believed to be $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_3\{NPhC(Me)NMePh\}}]$ I. The nature of the complex is based solely upon the presence of $\nu$(CO) stretching vibration above 2000 $cm^{-1}$ which is consistent only with the occurrence of a terminal tricarbonyl unit in the complex.

3.4.3 Thermal decarbonylation of $[(\eta^5\text{-}C_5H_5)\mathrm{Mo(CO)_2CON(Ph)C(Me)NPh}]$ - The complex was dissolved in toluene, and MeI (0.30ml) was added by a syringe to the mixture. No reaction was observed after stirring the reaction mixture for 3 days at room temperature. Heating to $70^{\circ}$ caused reaction to occur and was complete, as indicated by i.r. spectroscopy, after 10h. During which time the original yellow colour of the solution gradually became dark orange. An i.r. spectrum of the solution indicated a new absorption at 2048 $cm^{-1}$. The product could not be isolated in a pure form because of its small quantity.

3.4.4 U.v. irradiation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]$ with MeI. - MeI (0.10ml) was added to a solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]$ in toluene (40ml). Irradiation of the resulting mixture with a 300 watt Hg lamp for 23 minutes followed by filteration of the solution gave an orange filterate. A viscous material was obtained after evaporation of the filt rate (in vacuo, 20°). Extraction of the viscous material with diethyl ether (30ml), followed by concentration of the resultant solution (in vacuo, 20°), and cooling to -20° yielded three types of complexes in small quantities, identified by i.r. spectroscopy/mass spectrometry as $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})NC(Me)N(p\text{-tolyl})\}]$ m/e 456($P^+$), $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\{N(p\text{-tolyl})C(Me)NMe(p\text{-tolyl})\}]I$, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]I$ m/e 374 ($P^+$).
The nature of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\{N(p\text{-tolyl})C(Me)NMe(p\text{-tolyl})\}]I$ is based on the mass spectrum of its thermolysis products, and upon the presence of a $\nu(CO)$ stretching vibration at 2048 $cm^{-1}$.

3.4.5 U.v. irradiation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$. - In an attempt to decarbonylate the yellow complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$, it was dissolved in toluene and heated with stirring at 80°, but no reaction was observed after a period of 12h. The solution was transferred to a silica tube and irradiated with a 300 watt Hg lamp. The original yellow colour of the solution gradually became orange and after 0.53h. the solution was filtered. An i.r. spectrum of the residue indicated some residual starting material $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(H)C(Me)NH]$, and new carbonyl absorptions due to a complex identified by mass spectrometry as $[(\eta^5\text{-}C_5H_5)_2(Mo)_2(CO)_3\{NHC(Me)NH\}_2]$ m/e 518 ($P^+$). The filterate was evaporated (invacuo, 20°), and the residue was extracted with diethyl ether (30ml). Concentration of the resultant solution (in vacuo, 20°) and cooling to -20° enabled crystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ to be isolated. The second set of material isolated in small yield from ether solution were brown crystals. Sufficient material was obtained only for a mass spectrum which gave $Mo_2$ isotopic patterns at m/e 518 and 434 corresponding to $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3\{NHC(Me)NH\}_2]^+$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2\{NHC(Me)NH\}_2]^+$ respectively.

## 3.5 Miscellaneous reactions:

3.5.1 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ with PhNHC(Me)NPh. - $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (0.50g, 1.02mmol) in toluene solution (35ml) was sitrred with PhNHC(Me)NPh (0.43g, 2.03mmol) and the mixture heated to the reflux temperature of 13.5h. At the end of the reaction as monitored by i.r. spectroscopy, the solvent was removed (in vacuo, 20°) and the residue extracted with diethyl ether (30ml). Fractional crystallisation techniques enabled orange crystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ to be isolated (in low yield). m/e ($P^+$) 428.

3.5.2 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with Li-2-aminopyridine. - A solution of $[LiNHC_5H_4N]$ was prepared by the addition of $Bu^nLi$ (1.67ml, 2.13M in hexane) to $[NH_2C_5H_4N]$ (0.34g, 3.56mmol) in ether (50ml) at -196°, the mixture then being allowed to warm slowly to room temperature. After stirring for 30 minutes the solution was added to a frozen solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) also in ether (40ml) and the resulting mixture was allowed to warm slowly to room temperature. The original orange colour of the solution turned dark brown in colour after 15minutes, and the reaction was shown to be complete by i.r. spectroscopy after 3.15h. at room temperature. The solution was evaporated (in vacuo, 20°), and the residue was extracted with chloroform/hexane mixtures (5 : 1). Concentration of the resultant solution (20°, in vacuo) and cooling to -20° yielded brown viscous material, which on recrystallisation from diethyl ether gave yellowish powder of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC_5H_4N]$.

Found: C, 44.67; H, 2.19; N, 12.84. $C_{13}H_{10}MoN_2O_3$ requires C, 46.17; H, 2.98; N, 8.28%.

The major metal containing ions observed are: m/e 340 $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC_5H_4N]^+$, 312 $[(\eta^5\text{-}C_5H_5)Mo(CO)_2NHC_5H_4N]^+$, 284 $[(\eta^5\text{-}C_5H_5)Mo(CO)NHC_5H_4N]^+$, 256 $[(\eta^5\text{-}C_5H_5)Mo NHC_5H_4N]^+$.

I.r. $\nu$(CO)(KBr) 1959(VS), 1873(S), 1619(M-W); ($CH_2Cl_2$) 1964(VS), 1881(S), 1617(M-S) $cm^{-1}$.

Properties of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC_5H_4N]$ : The yellowish powder was stable in air at room temperature, but solutions were susceptible to aerial oxidation. It was insoluble in hexane, but soluble in chloroform, dichloromethane, and diethyl ether. Even after several crystallisations, attempts to obtain crystals of the complex failed, the same yellowish powder being recovered on each occasion.

3.5.3 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with 2-aminopyridine. - $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) and $[NH_2C_5H_4N]$ (0.34g, 3.56mmol) were stirred in toluene (35ml) at 70-90°. A darkening in colour, accompanied by separation of a precipitate took place, and the reaction was shown spectrophotometrically to be complete after 7h. The solution was evaporated (in vacuo, 20°), and an i.r. spectrum of the brown residue indicated traces of a dicarbonyl complex $\nu$ (CO) (KBr) 1952(VS), 1841(S) $cm^{-1}$. Even after many attempts to obtain its mass spectrum, no molybdenum containing ions could be detected.

3.5.4 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ with LiNPhC(Me)NPh. - A solution of LiNPhC(Me)NPh was prepared by dissolving [H N(Ph)C(Me)N(Ph)] (0.14g, 0.67mmol) in monoglyme (50ml), cooling to liquid nitrogen temperature and adding $Bu^nLi$ (0.45ml, 1.5M in hexane) by syringe. The solution was stirred at room temperature for 30 minutes, before it was added to a solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ (0.35g, 0.67mmol) in monoglyme (40ml) at -196°. After stirring at room temperature for 5h. during which time the progress of the reaction was very slow, the temperature was raised to 70-80° for 2h. At the end of the reaction, as indicated by the consumption of the reactant complex (shown by i.r. spectroscopic monitoring of the $\nu$(CO) stretching region), filtration yielded an orange solution which was evaporated to dryness (in vacuo, 20°). Extraction with diethyl ether (40ml), followed by concentration of the resultant solution (20°, in vacuo) and cooling to -20° yielded orange crystals of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$, m/e ($P^+$) 428.

3.5.5 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ with PhNHC(Me)NPh. - The amidine (0.41g, 1.94mmol) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ (0.50g, 0.97mmol) in toluene (35ml) were heated with reflux at 80 -130° for $14\frac{1}{2}$hr. The colour of the solution became progressively brown and a brown precipitate slowly separated. The reaction mixture was filtered from a brown non-carbonyl material which was identified by mass spectrometry as $[(\eta^5\text{-}Cp)MoO\{PhNC(Me)NPh\}]$, m/e ($P^+$) 388. When this experiment was repeated, heating at 80-90° for 38h., the i.r. spectrum of the product showed a single carbonyl stretching frequency at 1800 cm$^{-1}$, may be due to a monocarbonyl complex of the type $[(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)\{PhNC(Me)NPh\}]$.

3.5.6 Attempted reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $[C_6H_{11}NCNC_6H_{11}]$. - $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.56g, 2.00mmol) was dissolved in toluene (20ml), and a suspension of $[C_6H_{11}NCNC_6H_{11}]$ (0.41g, 2.00mmol) in toluene (25ml) added by syringe at room temperature. After heating the reaction mixture to 80-100° for 5h., during which time the progress of the reaction was very slow, the temperature was raised to reflux temperature for 2h. After the consumption of the reactant complex (shown by i.r. spectroscopic monitoring of the $\nu$(CO) stretching region), the solution was filtered leaving a brown non-carbonyl precipitate. Concentration of the filtrate (20°, in vacuo) and cooling to -20° yielded $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, and an unidentified brown non-carbonyl material which was soluble in chloroform.

3.5.7 Attempted reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)]$ with $[C_6H_{11}NCNC_6H_{11}]$. - A solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)]$ (0.47g, 1.79mmol) in toluene (25ml) was added to a suspension of $[C_6H_{11}NCNC_6H_{11}]$ (0.37g, 1.79mmol) in toluene (25ml). The original yellow colour of the solution turned light green after 2h. heating at 80 - 100°, and gradually became blackish after an additional period of 2h. An i.r. spectrum of the reaction solution at this stage showed some remaining starting material, hence the solution was heated at 80 - 110° for an additional 14h. The solution was filtered from a beige non-carbonyl organic precipitate which was insoluble in toluene, diethyl ether, hexane, and sparingly soluble in dichloromethane, but very soluble in chloroform. Concentration of the filt rate (20°, in vacuo) and cooling to -20° yielded residual unreacted starting material $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)]$.

3.5.8 Attempted reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})NC(Me)N(p\text{-tolyl})\}]$ with $PPh_3$. - A small quantity of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})NC(Me)N(p\text{-tolyl})\}]$ (0.04g, 0.09mmol) was ground with $[PPh_3]$ (0.02g, 0.09mmol), and the mixture was placed in a small flask (25ml). The flask was evacuated ($10^{-1}$mmHg) and the solid heated at 100-150°, but no reaction was observed during a period of 6.75h.

3.5.9 Attempted reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)C(Me)NPh]$ with hex-2-ene. - A small quantity of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CON(Ph)C(Me)NPh]$ was dissolved in toluene (30ml), and hex-2-ene (0.50ml) was added by syringe. The resulting mixture was heated at 50-60° for 1.5h. but since the progress of the reaction was very slow, the temperature was raised to 95-100° (reflux). The original yellow colour of the solution gradually became olive-green in colour and after 1.5h. the solution was filtered. The residue was a non-carbonyl decomposition material, olive-green in colour which was insoluble in chloroform. An i.r. spectrum of the yellow filt rate indicated some residual starting material.

3.5.10 Attempted reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $[NHC(Ph)NH_2]$. - A clear solution of $[NHC(Ph)NH_2]$ was formed from $[C_6H_5C(NH)NH_2.HCl.H_2O]$ (0.62g, 3.57mmol) and $Bu^nLi$ (3.35ml, 2.13M in hexane) in monoglyme (80ml) by mixing at room temperature. The resulting mixture was stirred for 1h. at room temperature before it was added to a solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) also in monoglyme (40ml) at room temperature. A colour change from dark orange to red occurred after heating the reaction mixture at 60-70°. Only formation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ occurred over 1h.

3.5.11 Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ with $[NHC(Ph)NH_2]$. - Benzamidine (0.43g, 0.36mmol) prepared from benzamidinum chloride monohydrate, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) were dissolved in toluene (35ml) and the mixture heated at 60 - 70° for 1.15h. At the end of the reaction, monitored using the 2060 $cm^{-1}$ i.r. absorption of the carbonyl chloride, filtration yielded an orange-red solution. Concentration of the filtrate and cooling to -20°, yielded the dimer $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and two types of yellow complexes in very low yield. The yellow products were recrystallised from diethyl ether, and fractional crystallisation techniques enabled them to separate. The first complex was identified by mass spectrometry as $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5\{NH_2C(Ph)NH\}]$, m/e ($P^+$) 580, while the second material had a monomolybdenum pattern and was identified as $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{HNC(Ph)NH\}]$, m/e 383. The highest fragmentation pattern, however, arose from $(P\text{-}2CO)^+$. These products were isolated in very low yield, so their identification was based solely on their mass spectra.

3.5.12 Attempted reaction of $[Fe_2(CO)_9]$ with $[PhC(Cl)NPh]$. - A suspension of $[Fe_2(CO)_9]$ (0.50g, 1.37mmol) and $[PhC(Cl)NPh]$ (0.59g, 2.75mmol) in monoglyme (45ml) was heated at 60-70° for 11h., during which time a colour change from yellow-orange to brown took place and a brown precipitate separated. After heating for additional 12h. at 70 - 80°, the solution was filtered leaving a light brown residue identified by mass spectrometry as $Ph\underset{\overset{\|}{O}}{C}-NHPh$ m/e ($P^+$) 197. The filtrate was evaporated (20°, in vacuo) to yield the residual starting material $[Ph(Cl)CNPh]$.

3.5.13 Attempted reaction of $[Fe_2(CO)_9]$ with $[PhNHC(Me)NPh]Cl$. - $[PhNHC(Me)NPh]Cl$ (0.95g, 3.85mmol) [formed from passing HCl gas through a solution of $[PhNHC(Me)NPh]$ in chloroform], partly dissolved and partly suspended in toluene (55ml) was stirred with $[Fe_2(CO)_9]$ (0.70g, 1.92mmol). The resulting mixture was heated for 30 minutes at 50-70° when a colour change from light orange to clear red took place and precipitation occurred. The reaction mixture was heated at 80° for 3h. during which time the progress of the reaction was very slow, the temperature was raised to 90-95°. A colour change from red to pale yellow occurred after 1h. with separation of brownish viscous precipitate. The i.r. spectrum of the solution at this stage indicated large quantity of residual starting material $[Fe_2(CO)_9]$, refluxing for 30h. led only to eventual decomposition.

3.5.14 Attempted reaction of $[NHC(Me)NH_2]$ with $[(\eta^5-C_5H_5)Mo(CO)_3Cl]$. - In an attempt to produce $[NHC(Me)NH_2]$, $[NHC(Me)NH_2]$ Cl (0.34g, 3.56mmol) was reacted with metal sodium in monoglyme (50ml). The mixture was heated to 70 - 80° for 1.15h. before it was added to a solution of $[(\eta^5-C_5H_5)Mo(CO)_3Cl]$ (0.50g, 1.78mmol) also in monoglyme (40ml) at room temperature. The reaction mixture was heated for 4h. at 70 - 80°, then the solvent was evaporated (20°, in vacuo). An i.r. spectrum of the residue indicated some residual starting material $[(\eta^5-C_5H_5)Mo(CO)_3Cl]$ but large quantities of $[(\eta^5-C_5H_5)Mo(CO)_3]_2$.

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# CHAPTER 4

# RESULTS AND DISCUSSION.

## 4.1 Reactions using amidines. -

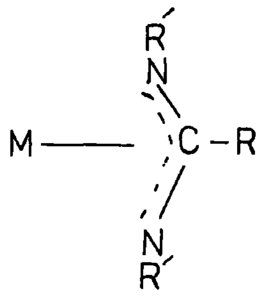
The chlorides, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (M = Mo,W), react with amidines $[R'NC(R)NHR'$; R = H,R' = Ph; R = Me, R' = Ph, p-tolyl; R = Ph, R' = Me$]$ in toluene solution at 50 - 70° (M = Mo), 70 - 90° (M = W) to form orange complexes of the type $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]$, which are soluble in polar organic solvents, but insoluble in non-polar solvents. The liberated HCl is trapped by part of sample of the amidine used, so consequently complete reaction occurs only after the addition of two molar equivalents of the amidine to one of the carbonyl chloride. The amidinum chloride $[R'NHC(R)NHR']^+ Cl^-$ separates from toluene solution and is more readily removed from this solvent than from many other solvents in which the reaction is performed. Recrystallisation of the white powder for analytical purposes, is achieved using chloroform/hexane mixtures. Interestingly acetamidine, $[H_2NC(Me)NH]$ yields a yellow tricarbonyl complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC(Me)NH]$ whereas $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ was produced in low yield from the reaction of N, N', diphenylacetamidine with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. The orange products were recrystallised from diethyl ether as well formed crystals, which analysed correctly for dicarbonyl complexes. The products proved unreactive to neutral ligands such as triphenyl phosphine even after 6.75h. heating at 100 - 150° in the absence of a solvent. They were both thermally and air stable at room temperature, melting between 125 - 160° some with decomposition, but solutions were susceptible to aerial oxidation. However, when $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(Me)NPh\}]$ was heated in toluene under nitrogen at 60° for 1h., it decomposed to a brown non-carbonyl material, which was not identified.

Neutral amidines themselves are potential bidentate ligands as demonstrated by Hieber,[1] and efforts have been made to attach them to molybdenum for purposes of comparison with the isoelectronic $\pi$-allyl and carboxylato groups. Inglis[2] attempted the reaction of $[RNHC(Ph)NR$; R = Ph, p-tolyl$]$ with $M(CO)_6$ (M = Mo,Cr) which led to loss of hydrogen and formation of the crystalline product $M_2[RNC(Ph)NR]_4$ with the cupric acetate type of structure.[3] On the other hand, N-arylamidines react with palladium (11) chloride to give grey-green $[Pd(Am-H)Cl]_n$ with 6-membered ortho-metallated ring systems.[4]

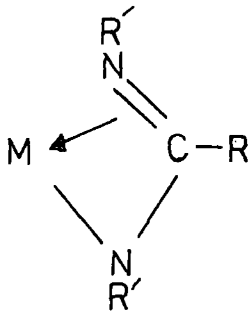
In the mass spectrum, each of the orange complexes ,prepared as part of the present study,produced a parent ion distribution pattern corresponding to $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]^+$, and ions corresponding to loss of one and two carbonyl groups. Fragmentation occurred subsequently by loss of the RCN group, a pattern observed also for aza allyl/allene complexes.[5] The highest fragmentation pattern arose from $(P-2CO)^+$ ions. Further spectroscopic data (i.r. and $^1$Hn.m.r., given in Chapter 3) confirm that these are dicarbonyl complexes in which the amidino group is acting as a 3-electron donor ligand. Only two strong $\nu$(CO) stretching frequencies positioned below 2000 cm$^{-1}$ are observed, the higher frequency band being at (~ 1950 - 1960 cm$^{-1}$) and the lower band at (~ 1850 - 1870 cm$^{-1}$); both absorptions are close to the $\nu$ (CO) absorptions for aza allyl/allene complexes. Loss of hydrogen from the ligand is confirmed by the formation of $[R'NHC(R)NHR']Cl$ salts in the reactions, and the absence of $\nu$(NH) and corresponding $^1$Hn.m.r. signals. Fully delocalised, symmetrical $\pi$-allyl ligands chelate metals with the metal placed above the skeletal plane of the group,[6] whereas bidentate carboxylato-groups chelate metals through $\sigma$, $\sigma$ attachment, as in $[Ru(OCOR')(CHNR)(CO)(PPh_3)_2]$[7] (R = *p*-tolyl); R' = Me, Et, Ph), with the metal lying in the plane of chelating carboxylato groups.[8] Other iso-electronic groups intermediate between the two extremes represented by the allyl and carboxylato-groups, are aza allyl/allene, amidino, and triazino ligands. The aza allyl/allene group is a bidentate ligand , and its bonding to the metal is believed to be of the $\sigma$, $\pi$ type,[9] whereas the triazenyl group is either monodentate or bidentate as shown by Robinson and Uttley,[10] but Knoth[11] suggested bidentate structure only, either bridging or chelating through $\sigma$ , $\sigma$ attachment. Finally, amidino groups are known to act as monodentate 1-electron donor in $[\{MeNC(Ph)N(Me)\}$ M'

$(Me)_3]$ ($M' = Si,Sn$),[12] and to bridge between metals in $Mo_2\{PhNC(Ph)NPh\}_4$,[2] or to chelate through σ, σ- attachment in $[Pd\{$p-tolylNC(Me)Nptolyl$\}_2]$.[13]

The amidino-group may fulfil its 3-electron donor role by bonding through either (i) one nitrogen atom, or (ii) more than one skeletal atom; the latter is preferred, however, for two reasons. In the first place, complexes of the type $[\eta^5\text{-}CpM(CO)_2NRR']$ (M = Mo,W) are not known and attempts to prepare them have failed.[14] Secondly, the orange amidino-complexes are found to have carbonyl stretching frequencies at positions close to those of the 2-aza-allyl complexes. Bonding through one nitrogen atom would cause the two nitrogen substituents to be distinguishable by $^1$Hn.m.r. techniques, particularly at low temperatures, but no differences were observed experimentally. Three possible modes of attachment are feasible for such a group; structure (A) has a delocalised, pseudo-π-allylic arrangement, (B) has localised σ, π-bonding in which a M-N σ- bond is supported by alkene-type bonding through the C=N double bond, as in aza allyl/allene complexes, (C) has the chelate ring completed by lone pair donation from the second nitrogen atom, as found in the triazene complex $[\eta^5\text{-}CpMo(CO)_2N_3(Ph)_2]$, and (D) has a σ, σ- attached delocalised group with the metal lying in the NCN plane. The latter type of attachment is adopted in bidentate triazino and carboxylato complexes.



(A)



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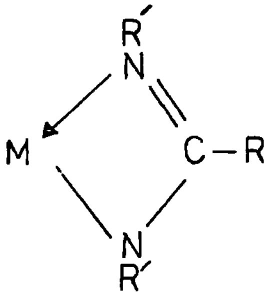

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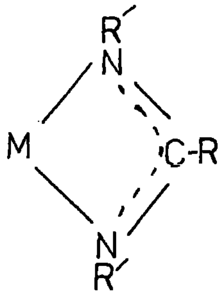
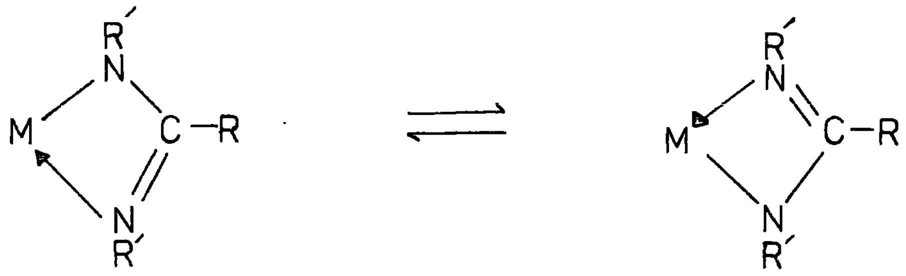


(D)

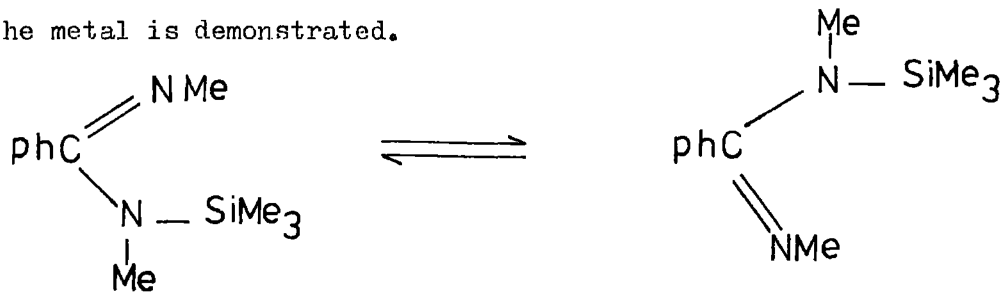
Structure (D) is preferred on several accounts; it is adopted in the complexes $[\mathrm{Pd}\{$*p*-tolylNC(Me)N-*p*-tolyl$\}_2]$[13], $[\mathrm{TaCl_2(Me)}\{\mathrm{C_6H_{11}NC(Me)NC_6H_{11}}\}_2]$[15], $[\mathrm{TaCl_3}\{$*i*-$\mathrm{C_3H_7NC(Me)N}$-*i*-$\mathrm{C_3H_7}\}_2]$[16], although one amidino-group in the last complex adopts a mode intermediate between structure (C) and (D). $\sigma$- bonding through nitrogen is generally preferred to $\pi$-bonding via a $\rangle$C : N-system, and is particularly illustrated by the above palladium complex for which, in the context of the large variety of known palladium complexes, all four structures are feasible. Certainly no absorption in the 1600 $\mathrm{cm^{-1}}$ region of the i.r. spectrum can be assigned readily to a $\nu$(NCN) stretching frequency, and indeed, the NCN stretching frequencies appear to be moved to lower energies to regions complicated by absorptions arising from substituent groups.

Variable temperature $^1$Hn.m.r. data are more consistent with either structures (A) and (D), and spectra for the complexes $[\eta^5\text{-CpMo(CO)}_2\{\text{R}'\text{NC(R)NR}'\}]$ (R = H, R$'$= Ph; R = Me, R$'$= Ph, *p*-tolyl; R = Ph, R$'$= Me) remained little changed in $\mathrm{CDCl_3}$ down to the freezing point of the solution. The complex $[(\eta^5\text{-Cp})\text{Mo(CO)}_2\{$(*p*-tolyl)NC(Me)N(*p*-tolyl)$\}]$ have one signal at 7.30 $\tau$ due to the two methyl groups of the (*p*-tolyl) group indicating that the two methyl groups are equivalent, and no splitting of this signal was observed at -87°. This is in contrast to the aza-allyl complex $[(\eta^5\text{-Cp})\text{M(CO)}_2\{$(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2\}]$[17] which have four signals of equal intensity due to the methyl protons, indicating that all four methyl groups are non-equivalent at low temperature, but at 70° these signals coalesce to a broader signal of the four original signals indicating that all four methyl groups are equivalent on the $^1$Hn.m.r. time scale. Similarly, the triazene complex $[\mathrm{R_2N_3RhC_8H_{12}}]$[11] has equivalent terminal nitrogen atoms (triaza-$\pi$-allyl structure), but at lower temperature the terminal nitrogen atoms become non-equivalent, possibly due to stabilization of $\sigma$, $\pi$ form at low temperatures.

Thus for the present amidino complexes the environments of both nitrogen substituents remain identical throughout the temperature range. The possibility of rapid interchange between structures based on (B) and (C), as shown below cannot be entirely eliminated, although such process can normally be slowed down sufficiently at -80° for individual substituent groups in different environments to be detected.



A related process has been observed for the interchange of nitrogen atoms of the monodentate amidino-complexes $[\{MeN:C(Ph)NMe\}M'(Me)_3]$ (M' = Si or Sn),[18] and the triazino derivative $[Pt(PPh_3)_2Cl(\underline{p}\text{-tolylNNN-}\underline{p}\text{-tolyl})]$[19] as detected by $^1$Hn.m.r. studies. Although in the solid state, attachment of only one nitrogen to the metal is demonstrated.



For the present complexes structure (D) is most consistent with all the spectroscopic data, and with the known bonding behaviour of chelating nitrogen ligands, and is preferred.

## 4.2 Reactions with lithioamidines. -

$[(\eta^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo,W) react smoothly with lithioamidines $[LiN(R')C(R)NR']$ (R = Me, R′= Ph, *p*-tolyl; R = Ph, R′= Me; R = H, R′= Ph; R = Me, R′= H) and the neutral acetamidine $[NHC(Me)NH_2]$between 0 and 20° in ethers to form yellow complexes of composition $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\{R'NC(R)NR'\}]$. They were very soluble in chloroform and dichloromethane, moderately soluble in toluene, sparingly soluble in diethyl ether, but insoluble in hexane. Solutions of the complexes were susceptible to aerial oxidation, but solids were air stable. No reaction could be achieved between the complexes and neutral ligands such as hex-2-ene in toluene at 100°.

In the mass spectrometer parent ions are detected only at low source temperatures, and then the ion current transmitted by the parent ion is low compared with that transmitted by the $[P\text{-}CO]^+$ and $[P\text{-}3CO]^+$ ions. The i.r. spectra exhibit two very strong absorptions in the 1870 - 1970 $cm^{-1}$ region, assigned to terminal $\nu(CO)$ stretching frequencies with the higher frequency absorption having a higher intensity than the lower absorption, and a medium intensity absorption at *Ca.* 1610 - 1630 $cm^{-1}$. The intensity and position of the last absorption is consistent with previous observations on carbamoyl carbonyl groups $[MC(O)N]$ , as shown in Table 4.1 . Further i.r. data on carbamoyl complexes are given in Chapter 2, Table 2.3.

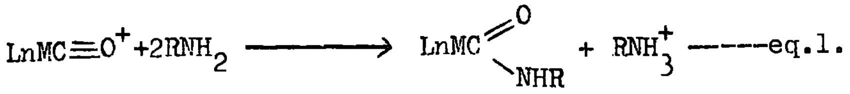
Although the carbamoyl functional groups have been known in organic chemistry for over a century, only in the past 13 years have inorganic analogues been reported. The first known carbamoyl complex $[R_2NCOFe(CO)_2(\eta^5\text{-}C_5H_5)]$ was prepared by King,[20,21] as an unstable, orange, volatile solid from the reaction of $R_2NCOCl$ (R = Me, Et) with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$. In recent years many more transition metal complexes containing the carbamoyl

Table 4.1 Infrared Absorptions, $\nu$(CO) for Some Carbamoyl Complexes.

| Complex | Solvent | $\nu$ (CO)Stretching Frequencies, cm$^{-1}$ | | Ref. |
|---|---|---|---|---|
| | | Terminal | Carbamoyl | |
| $\eta^5$-Cp(CO)$_2$FeCON(Et)$_2$ | Halocarbon oil mulls | 1942, 1964, 2004, 2017 | 1534 | 20 |
| [Mn(CO)$_4${CO.NHC(Ph):NH}] | CHCl$_3$ | 2090(m-S),1992(S,br),1954(S). | 1615(S) | 22 |
| [Mn(CO)$_4${CO.N(Ph).C(Me):N(Ph)}] | cyclohexane | 2085(m),2004(S),1986(VS),1972(VS) | 1694(m) | 22 |
| [Mn(CO)$_4${CO.N(p-tolyl).C(Me).N(p-tolyl)}] | cyclohexane | 2081(W),1997(m),1984(VS),1969(S) | 1674(m) | 22 |
| [Mn(CO)$_4${CO.N(Ph).C(Ph):N(Ph)}] | cyclohexane | 2083(S),2004(S),1988(VS),1974(VS) | 1698(S) | 22 |
| [Mn(CO)$_4${CO.N(p-tolyl).C(Ph):N(p-tolyl)}] | cyclohexane | 2083(S),2002(S),1987(VS),1972(VS) | 1695(m) | 22 |
| $C_5H_{10}$NCOCo(CO)$_3$(PPh$_3$) | THF | 2050(m),1983(VS),1952(VS) | 1591(m) | 23 |
| (n-$C_3H_7$)$_2$NCOCo(CO)$_3$(PPh$_3$) | THF | 2050(m),1983(VS),1949(VS) | 1598(m) | 23 |
| Li[Me$_2$NCONi(CO)$_3$] | ether | 2057,1978(S),1958(m) | 1560 | 24 |
| $\eta^5$-CpFe(CO)$_2$[CONHC(Me)$_3$] | hexane | 2022(S),1959(VS) | 1633(m) | 25 |
| $\eta^5$-CpFe(CO)[CNC(Me)$_3$][CONHC(Me)$_3$] | hexane | 2109(m),2071(W)(Sh),1939(S) | 1609(m) | 25 |
| $\eta^5$-CpRu(CO)$_2$(CONHCH$_3$) | methyl-cyclohexane | 2030(S),1969(S) | 1631(m) | 26 |
| $\eta^5$-CpRu(CO)$_2$[CONHCH(Me)$_2$] | cyclohexane | 2026(S),1965(S) | 1628(m) | 26 |
| $\eta^5$-CpRu(CO)$_2$[CONH(CH$_2$)$_3$CH$_3$] | cyclohexane | 2026(S),1965(S) | 1626(m) | 26 |
| $\eta^5$-CpRu(CO)$_2$(CONHC$_6$H$_{11}$) | methyl-cyclohexane | 2024(S),1964(S) | 1621(m) | 26 |

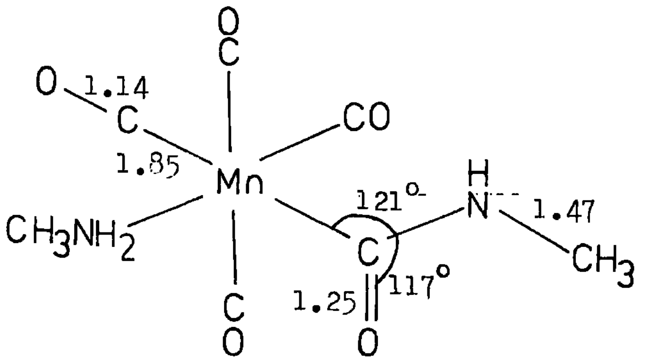
| Complex | Solvent | $\nu$(CO)Stretching Frequencies, $cm^{-1}$ | | Ref. |
|---|---|---|---|---|
| | | Terminal | Carbamoyl | |
| $Re(CO)_4(NH_2Me)(CONHMe)$ | KBr | 2092(m),1990(S),1965(S),1919(S) | 1512(m) | 27 |
| $\eta^5$-$CpFe(CO)_2(CONH_2)$ | $CH_2Cl_2$ | 2015(S),1963(S) | 1593(m) | 28 |
| $\eta^5$-$CpFe(CO)_2(CONHMe)$ | methyl cyclohexane | 2015(S), 1972(S) | 1625(m) | 28 |
| $\eta^5$-$CpFe(CO)_2(CONHCH_2CH_3)$ | methyl cyclohexane | 2015(S), 1968(S) | 1622(m) | 28 |
| $\eta^5$-$CpFe(CO)_2[CONHCH(Me)_2]$ | methyl cyclohexane | 2015(S), 1965(S) | 1620(m) | 28 |
| $\eta^5$-$CpFe(CO)_2[CONH(CH_2)_3Me]$ | methyl cyclohexane | 2019(S), 1968(S) | 1622(m) | 28 |
| $\eta^5$-$CpFe(CO)_2[CON(Me)_2]$ | $CH_2Cl_2$ | 2015(S), 1960(S) | 1612(m) | 28 |
| $\eta^5$-$CpFe(CO)_2(CONC_4H_8)$ | heptane | 2023(S), 1967(S) | 1566(m) | 28 |
| $\eta^5$-$CpFe(CO)_2(CONC_5H_{10})$ | cyclohexane | 2020(S), 1968(S) | 1560(m) | 28 |
| $\eta^5$-$CpFe(CO)(PPh_3)(CONHMe)$ | $CH_2Cl_2$ | 1915(S) | 1558(m) | 28 |
| $\eta^5$-$CpFe(CO)(PPh_3)(CONHCH_2CH_3)$ | $CH_2Cl_2$ | 1911(S) | 1560(m) | 28 |
| $\eta^5$-$CpFe(CO)(PPh_3)[CONHCH(Me)_2]$ | cyclohexane | 1924(S) | 1585(m) | 28 |
| $Mn(CO)_4(CONHCMe)(NH_2Me)$ | $CHCl_3$ | 2075(W), 1983(S),1930(m) | 1605(VW) | 30 |
| | KBr | 2071(m),1995(S,br),1964(S),<br>1893(S) | 1610(W)<br>1540(m) | 30 |

ligand, $-C(O)NRR'$, have been prepared[20-30] and reviewed.[31,32] With few exceptions cationic metal carbonyl complexes react with primary and secondary alkylamines to form carboxamido complexes according to eq.1.



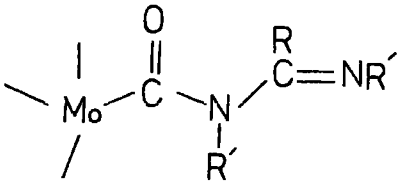
$$LnMC{\equiv}O^{+} + 2RNH_2 \longrightarrow LnMC{\overset{\displaystyle O}{\underset{\displaystyle NHR}{\lessgtr}}} + RNH_3^{+} \text{ -----eq.1.}$$

Such reactions have been found for complexes of Ru,[26] Re,[27] Fe,[28,29] Mn,[30] Mo,[33] and W.[33] This reaction represents by far the most general method of preparing carbamoyl complexes,[32] and is presumed to proceed by nucleophilic attack of the amine at the carbon atom of a terminal carbonyl group with loss of a proton to another amine molecule to give $RNH_3^+$.[26,28,31] cis-$Mn(CO)_4(NH_2Me)(CONHMe)$ was shown by X-ray crystallography to have the following structure:[34]

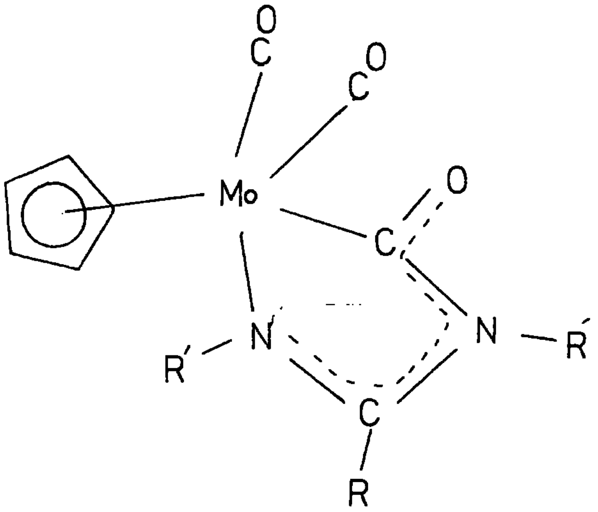


Behrens and co-workers[35] had previously suggested this structure for [cis-$Re(CO)_4(NH_3)(CONH_2)$] and [cis-$Re(CO)_4(NH_2Me)(CONHMe)$] which were prepared from $Re(CO)_5Cl$ and $NH_3$ or $CH_3NH_2$.

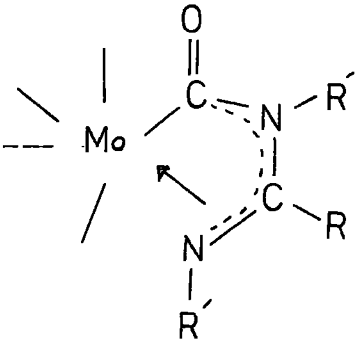
Some possible bonding modes for the present complexes are given in the Figure (p.111).Structure (E) has a conventional carbamoyl group but the metal remains a 16-electron system, so this structure can be easily eliminated on the basis of i.r. data and on failing to conform to the 18-electron rule, usually followed by these types of complexes. Structures (F) and (G) have 3-electron donor groups forming 5-membered rings, the difference arising from the possibility of either the nitrogen lone pair of electrons or the π-electrons



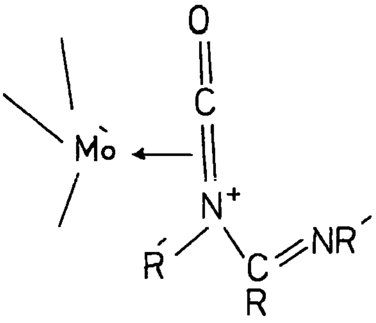
(E)



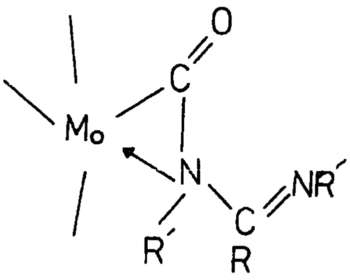
(F)



(G)



(H)



(I)

of the C-N bond providing the second attachment to the metal. Otherwise they are both basically carbamoyl derivatives. Bonding as an aza-keten group $[R'R''N^{+}=C=O]$ ($R''$ = $R'N{:}CR$),(H) and (I) may occur, structure (H) and (I) representing the two extremes of alkene-type attachment. Structures involving rings containing oxygen as well as two nitrogen atoms are dismissed on the basis of the 1600 - 1700 $cm^{-1}$ absorptions.

Related complexes of manganese of the type $[Mn(CO)_4CON(R')C(R)NR']$[22] have been prepared, and as for these complexes structure (F) is preferred on the basis of a 5-membered metallocyclic ring rather than a 3-membered ring, and on the stereochemistry of the chelate group. In (G) the MoC(O)N and NCN planes are non-coincidental and against extensive delocalisation of the ligand group favoured by i.r. data. The three membered ring structure (I) may be expected to have an associated ligand absorption in the carbonyl stretching region higher than normal carbamoyl complexes and close to those of related acyl complexes because of the involvement of the nitrogen lone pair in bonding with the metal. Indeed acyl $\nu$(CO) absorptions for complexes of the type $[(\eta^5\text{-}C_5H_5)Mo(CO)_2LCOR]$ ($R = CH_3, C_2H_5$; $L = Ph_nPMe_{3-n}$ or $Ph_nPEt_{3-n}$; $n = 1,2$)[36] occur in the region 1635 - 1642 $cm^{-1}$, very close to the region (1610 - 1630) for the present complexes. However, since no second absorption in the latter region, assignable to the $\nu$(CN) stretching frequency of the free imino-group is detected, structure (F) is the favoured structure.

Two types of nitrogen substituents are expected for a complex with structure (F), and for the N, N'-dimethyl-benzamidino-complex, two methyl $^1$Hn.m.r. signals are indeed detected at 6.29 $\tau$ and 6.71 $\tau$ (0°). However, when the nitrogen substituents are p-tolyl groups, no observable difference in the p-methyl groups is detectable and a single resonance is observed at 7.20 $\tau$ (20°) [7.14 $\tau$ at -49°]. Similar behaviour was noticed for the corresponding manganese complexes $[Mn(CO)_4CON(p\text{-tolyl})C(R)N(p\text{-tolyl})]$ (R = Me, Ph),[22] therefore, the conclusion must now be that the methyl protons of p-tolyl groups are insensitive to the differences, both electronic and steric, between the two nitrogen atoms of the carbamidino-complexes.

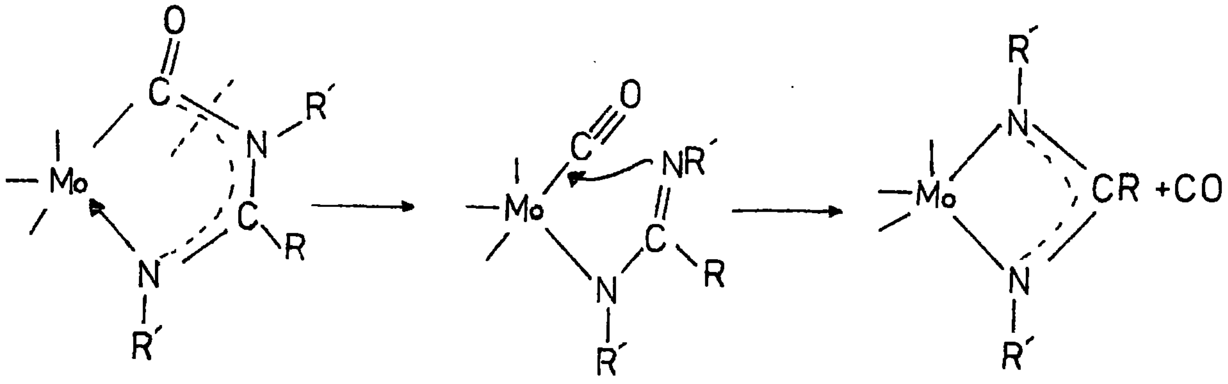
Lithioamidines and acetamidine produce carbamoyl-type complexes whereas N, N′-disubstituted amidines lead to carbon monoxide displacement. Thus the nucleophilicity of the nitrogen atoms appear critical in determining the course of the reactions. The highly nucleophilic lithio-derivatives prefer to attack thecarbon of a coordinated carbonyl group to form carbamoyl complexes, whereas the less nucleophilic parent amidines appear to attack the metal directly to eliminate amidinium chloride and displace carbon monoxide. Interestingly, the amidines with hydrogen attached to nitrogen, which have intermediate nucleophilicity also attack the carbon monoxide preferentially. Steric factors do not appear to be of importance in controlling the course of the reactions. N, N′-disubstituted amidines and their lithio-derivatives are both large molecules, and most probably oligomeric in the solvents used, whereas acetamidine is comparatively small. Yet the expected reagents of greatest and least bulk undergo comparable reactions.

### 4.3 Decarbonylation studies. -

Yellow carbamoyl-type complexes are decarbonylated in toluene solution using u.v. irradiation, or heating at 70° to yield an orange solution from which $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]$ complexes were isolated in small quantity. Much decomposition occurs, and the decarbonylation route provides an inefficient, low yield means of obtaining the orange complexes.

Attempted decarbonylations of carbamoyl complexes $(M\text{-}C(O)NR_2)$ are known to produce cleavage of the $\text{-}C(O)\text{-}N$ bond to generate a terminal carbonyl group with elimination of the $R_2N$ group. Thus for the carbamidino complexes cleavage of the $\text{-}C(O)\text{-}N$ bond will generate the complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_3N(R')C(R)NR']$ having a unidentate amidino-group. The free nitrogen atom may then attack the metal centre and displace a carbonyl group. The final product is identical to the product expected from an acyl-type decarbonylation reaction although the mechanism will be different. Interestingly the corresponding manganese derivatives $[Mn(CO)_4\{CO.N(R').C(R):NR'\}]$[22] furnished the first examples of carbamoyl complexes which decarbonylate with the formation of metal-nitrogen bonds. The action of heat, or u.v. irradiation in cyclohexane on the carbamoyl complexes $[Mn(CO)_4\{CO.N(R').C(R):NR'\}]$ causes decarbonylation to occur giving $[Mn(CO)_4\{R'N.C(R):NR'\}]$ derivatives which have symmetrical delocalised amidino-$\pi$-system but it has not been established whether or not the attachment of the group to the metal is similar to that of $\pi$-$C_3H_5Mn(CO)_4$.

In the present derivatives, the nitrogen group is not lost from the complex but remains attached to the metal through the second nitrogen atom. Subsequent attack at the metal by the free nitrogen will result in displacement of carbon monoxide and generation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]$ complexes, as shown below:



(i) yellow

(ii) intermediate

(iii) orange

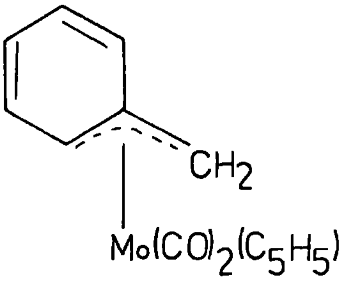
In order to test the validity of this proposed mechanism, attempts were made to isolate $[(\eta^5\text{-}C_5H_5)Mo(CO)_3N(R')C(R)NR']$ type complexes by irradiating the carbamoyl-type complexes in the presence of methyl iodide. Reaction of the free nitrogen with MeI would thus prevent further attack at the metal centre and displacement of carbon monoxide.

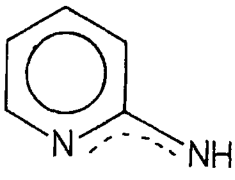
$\eta^5\text{-}C_5H_5\,Mo(CO)_2CON(R')C(R)NR' + MeI \xrightarrow{u.v} [\eta^5\text{-}C_5H_5Mo(CO)_3N(R')C(R)N(Me)R]I$

Indeed an absorption above 2000cm$^{-1}$, for example at 2048 for the N,N'-di p-tolylacetamidino derivative, was detected which is consistent only with the occurrence of a terminal tricarbonyl unit in the complex, although efforts to obtain pure samples of the solid products failed. Thus good evidence exists for the detection of an intermediate-type complex in the decarbonylation reaction. Interestingly, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]I$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ have been detected in addition to $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]$. Acetamidine, unlike N, N'-disubstituted amidines, yield the yellow tricarbonyl complex, but attempted decarbonylation of this complex yields only $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and a dimolybdenum complex, identified by mass spectrometry as $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3\{NHC(Me)NH\}_2]$.

## 4.4 Additional Reactions. -

A new type of amidine is 2-amino pyridine, which can be considered as a derivative of benzyl by replacement of two carbon atoms with two nitrogen atoms. It is known that the benzyl group attaches the metal atom through an allylic sequence of three carbon atoms, one of which is the exocyclic methylene carbon atom, as in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_6H_5CH_2)]$.[37,38]





Reactions between 2-aminopyridine and the carbonyl chloride were attempted in order to achieve insertion of -N=C=N group into Mo-C bond to obtain amidino-complexes.

The lithioderivative of 2-aminopyridine reacts with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ in ether at 0°to yield a yellowish carbamoyl complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CONHC_5H_4N]$, whereas the reaction of parent 2-aminopyridine with the carbonyl chloride in toluene at 70-90° gave traces of a dicarbonyl complex $\nu(CO)(KBr)$ 1952(VS), 1841(S) cm$^{-1}$. No molybdenum containing ions could be detected in its mass spectrum. Attempts to obtain substituted products by reaction of lithioamidines with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ yielded $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]$, while parent amidine react with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ to give the non-carbonyl complex $[(\eta^5\text{-}C_5H_5)MoO\{R'NC(R)NR'\}]$. A new absorption in the i.r. spectrum at 1800 cm$^{-1}$ was also detected which may be due to a monocarbonyl complex of the type $[CpMo(CO)(PPh_3)\{R'NC(R)NR'\}]$. In an attempt to achieve insertion reaction to obtain amidino-complexes, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3X]$ (X = Me,Cl) was reacted with dicyclohexylcarbodiimide in refluxing toluene, but even after prolonged periods of time the only products obtained were $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and a non-carbonyl decomposition material. Attempted reactions of $[Fe_2(CO)_9]$ with $[PhC(Cl)NPh]$ or $[PhNHC(Me)NPh]Cl$ in toluene also failed.

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# Three-Skeletal Atom Organonitrogen Derivatives of Molybdenum

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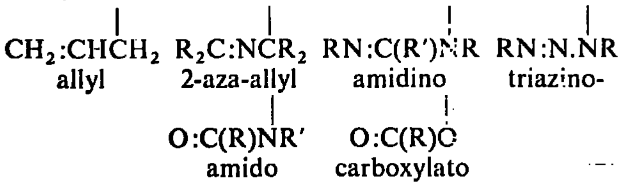
Amidino-complexes of two types are reported. Lithioamidines and $H_2NC(Ph)NH$ react with $[(\eta^5\text{–}C_5H_5)Mo(CO)_3Cl]$ to produce yellow carbamoyl-type complexes $[(\eta^5\text{–}C_5H_5)Mo(CO)_2CON(R')C(R)NR']$, (I; R=H, R′=Ph; R=Me, R′=H, Ph, *p*-tolyl; R=Ph, R′=Me) supposedly by nucleophilic attack at a carbonyl group, whereas reactions of parent N, N′-disubstituted amidines appear to centre at the metal to produce $[(\eta^5\text{–}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]$, (II; R=H, R′=Ph; R=Me, R′=Ph, *p*-tolyl; R=Ph, R′=Me). Decarbonylation of (I) to yield (II) is achieved thermally or photolytically in small yields. I.r. data provide support for the generation of metal-tricarbonyl intermediates of the type $[\eta^5\text{–}C_5H_5)Mo(CO)_3\{R'NC(R)N(Me)R'\}]^+I^-$ in the photolytic reactions undertaken in the presence of MeI. Reactions of lithio-amidines with $[(\eta^5\text{–}C_5H_5)Mo(CO)_2(PPh_3)Cl]$ gave (II), whereas no comparable reaction was achieved using the parent amidines. Structures of the complexes are discussed, and mechanisms proposed for various reactions. References are made to the related tungsten complexes.

THE iso-electronic relationship between allyl and carboxylate groups is a factor often overlooked because of the widely different properties of the two series of derivatives. These differences are illustrated by the different structures of their complexes. Allyl groups chelate metals with the metal placed above the skeletal plane of the group,[1] whereas the metal lies in the plane of chelating carboxylato-groups.[2] Interesting structural and bonding possibilities occur for the other iso-electronic groups intermediate between these extremes represented by the allyl and carboxylato-groups, and here attention is directed to the amidino-group which is one of several iso-electronic groups in the series shown below:



$CH_2{:}CHCH_2$ allyl, $R_2C{:}NCR_2$ 2-aza-allyl, $RN{:}C(R')NR$ amidino, $RN{:}N.NR$ triazino-, $O{:}C(R)NR'$ amido, $O{:}C(R)O$ carboxylato

The amidino-group has the potential to act as a unidentate, bidentate or a bridging group, and in addition the potential to chelate either through $\sigma$, $\sigma$ or $\sigma$, $\pi$ or $\pi$ attachment exists. Thus the amidino-group represents an intermediate group between allyl and carboxylato-groups, which may adopt properties very similar to one of these groups or alternatively adopt a set of properties intermediate between those of the two groups. Amidino-groups are known to bridge between metals in $[Mo_2\{PhNC(Ph)NPh\}_4]$,[3] and to chelate through $\sigma$, $\sigma$-attachment in $[Pd\{p\text{-tolylNC}(CH_3)N\text{-}p\text{-tolyl}\}_2]$,[4] and in both types of complexes the NCN skeletal $\pi$-systems are fully delocalised. Ortho-metallation reactions of N-arylamidines have been achieved using palladium(II) chloride,[5] and illustrate an addition chelate bonding type for amidines which needs to be considered also.

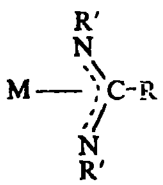
Some reactions of amidines and lithioamidines with $[\eta^5\text{-}C_5H_5Mo(CO)_3Cl]$ are reported here and the two series of complexes formed are compared one with the other. Some structural data are presented and the possible structures of the complexes discussed, and compared with corresponding allyl and carboxylato-complexes.

## RESULTS AND DISCUSSION

*Reactions Using Amidines.* – The chloride, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$, reacts with amidines $[R'NC(R)NHR'$; R = H, R′ = Ph; R = Me; R′ = Ph, *p*-tolyl; R = Ph, R′ = Me] in toluene solution at 50–80 ° to form orange complexes of the type $[\eta^5\text{-}C_5H_5Mo(CO)_2\{R'NC(R)NR'\}]$. The liberated HCl is trapped by part of the sample of the amidine, so consequently a 2:1 molar ratio of amidine/carbonyl chloride is used for optimum formation of the product. The amidinium chloride separates from toluene solution and is more readily removed from this solvent than from many other solvents in which the reaction is achieved. Interestingly benzamidine, $H_2NC(Ph)NH$, yields a yellow tricarbonyl complex $[\eta^5C_5H_5)Mo(CO)_2CONHC(Ph)NH]$ (see section B), whereas $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{PhNC(CH_3)NPh\}]$ was produced in low yield from the reaction of N, N′-diphenylacetamidine with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. The orange products were recrystallised from diethyl ether as well-formed crystals, which analysed correctly for dicarbonyl complexes. The solids were both thermally and air stable at room temperature, melting between 125–160 ° some with decomposition, but solutions were susceptible to aerial oxidation.

In the mass spectrum each of the complexes produced a parent ion distribution pattern for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{R'NC(R)NR'\}]^+$, and ions corresponding to loss of one and two carbonyl groups. Subsequent fragmentation occurred by loss of the RCN group. All complexes are characterised by two strong $\nu(CO)$ stretching frequencies positioned below 2000 $cm^{-1}$, the higher frequency band (~1950–1960 $cm^{-1}$) having a higher intensity than the lower band (~1850–1870 $cm^{-1}$). These low frequencies, together with the other spectroscopic data given in Table 1, support the conclusion that the complexes are dicarbonyl complexes in which the amidino-group is acting as a 3-electron donor ligand. Loss of hydrogen from the ligand is confirmed by the formation of $[R'NHC(R)NHR']Cl$ salts in the reactions, and the absence of $\nu(NH)$ and corresponding $^1H$ n.m.r. signals.

The amidino-group may fulfil its 3-electron donor role by bonding through either (*a*) one nitrogen atom, or (*b*) more than one skeletal atom. Since $[\eta^5\text{-}C_5H_5Mo(CO)_2NRR']$ complexes are not known and attempts to prepare them have failed,[6] the latter bonding type is preferred. Indeed bonding through one nitrogen atom would cause the two nitrogen substituents to be distinguishable by $^1H$ n.m.r. techniques, particularly at low temperatures, but no differences were observed experimentally. That the group acts as a strongly $\sigma$-donating group is reflected in the low $\nu(CO)$ stretching frequencies, and their positions, close to those found for the 2-aza-allyl and related complexes, points to attachment as a bidentate amidino-group. Three possible modes of attachment are feasible for such a group; structure (1) has a delocalised, pseudo-$\pi$-allylic arrangement, (2) has localised $\sigma$, $\pi$-bonding in which a M-N $\sigma$-bond is supported by alkene-type bonding through the C=N double bond, (3) has the chelate ring completed by lone pair donation from the second nitrogen atom, and (4) has a σ, σ-attached delocalised group with the metal lying in the NCN plane. Structure (4) is preferred on several accounts; it is adopted in the complexes $[Pd\{p\text{-tolyl NC(CH_3)N-}p\text{-tolyl}\}_2]$[4], $[TaCl_2Me\{C_6H_{11}NCMeNC_6H_{11}\}_2]$[7], $[TaCl_3\{Pr^iNCMeNPr^i\}_2]$,[8] although it must be pointed out that one amidino-group in the last complex adopts a mode intermediate between structures (3) and (4). σ-Bonding through nitrogen is generally preferred to π-bonding *via* a >C:N-system, and is particularly illustrated by the above palladium complex for which, in the context of the large variety of known palladium complexes, all four structures are feasible. Certainly no absorption in the 1600 cm$^{-1}$ region of the i.r. spectrum can be assigned readily to a ν(NCN) stretching frequency, and indeed the NCN stretching frequencies appear to be moved to lower energies to regions complicated by absorptions arising from substituent groups.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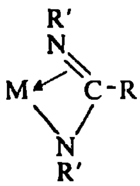
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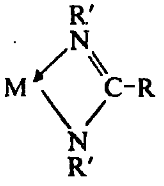
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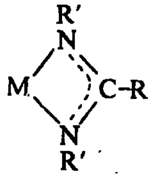
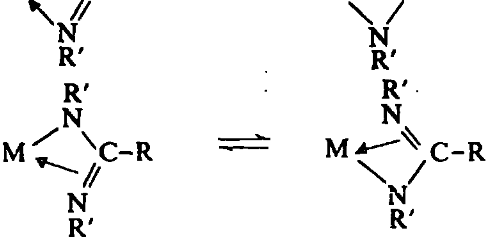
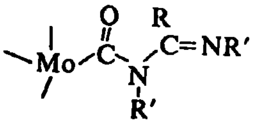

(4)

Variable temperature $^1$H n.m.r. data are more consistent with either structures (1) and (4) ,and spectra for the complexes $[\eta^5\text{-}C_5H_5Mo(CO)_2\{R'NC(R)NR'\}]$ (R=H, R'=Ph; R=Me, R'=Ph, *p*-tolyl; R=Ph, R'=Me) (Table 1) remained little changed in $CDCl_3$ down to the freezing point of the solution. Thus throughout the temperature range the environments of both nitrogen substituents remain identical. The possibility of rapid interchange between structures based on (2) and (3), as shown below, can not be entirely eliminated, although such processes can normally be slowed down sufficiently at −80 ° for individual substituent groups in different environments to be detected. A related process has been observed for the interchange of nitrogen atoms of the mono-dentate amidino-complexes $[Pt(PPh_3)_2Cl(p\text{-tolyl NN-N-}p\text{-tolyl})]$, a process readily detected by $^1$H n.m.r. measurements,[9] although in the solid state attachment of only one nitrogen to the metal is demonstrated by the *X*-ray crystal structure of the closely related triazenido complex, $[Pt(PPh_3)_2Cl(p\text{-tolyl NNN-}p\text{-tolyl})]$.[9] For the present complexes structure (4) is most consistent with all the spectroscopic data, and with the known bonding behaviour of chelating nitrogen ligands, and is preferred. The ligand is strictly comparable with bidentate carboxylato-groups, but comparable derivatives are not known. The complexes $[\eta^5\text{-}C_5H_5Mo(CO)_3(OCOR)]$[10] contain a unidentate 1-electron donor carboxylate-group, which, with bridged attachment, is the preferred mode of bonding to low valent metals.



*Reactions with Lithioamidines.* – $[\eta^5\text{-}C_5H_5Mo(CO)_3Cl]$ reacts smoothly with lithioamidines, LiN(R')C(R)NR', between 0 and 20 ° in ethers to form yellow complexes of composition $[\eta^5\text{-}C_5H_5)Mo(CO)_3\{R'NC(R)NR'\}]$, stable to air in the solid state, but susceptible to aerial oxidation in solution. In the mass spectrometer parent ions are detected only at low source temperatures, and then the ion current transmitted by the parent ion is low compared with that transmitted by the $[P\text{-}CO]^+$ and $[P\text{-}3CO]^+$ ions. Indeed the parent ion may not be observed except under optimum conditions. That the three carbonyl groups in the complexes are not all terminal groups is demonstrated by the i.r. spectra (Table 2) which exhibit two very strong absorptions in the 1870–1970 cm$^{-1}$ region assigned to terminal ν(CO) stretching frequencies, and a medium intensity absorption at *ca.* 1610–1630 cm$^{-1}$. The last absorption occurs in the region associated with carbamoyl carbonyl groups [MC(O)N], and because of the low position of the two terminal carbonyl groups, bidentate attachment of a carbamoyl group appears likely. Although structure (5) can thus be easily eliminated on the basis of i.r. data and on failing to conform to the 18-electron rule, usually followed by these types of complexes, several structural possibilities exist for bidentate attachment (Structures 6–9).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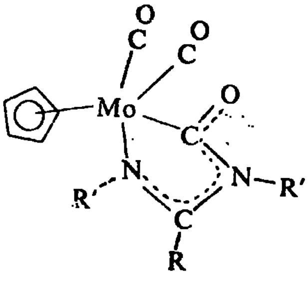
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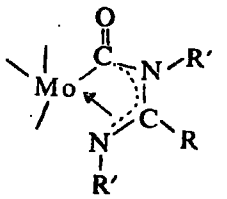
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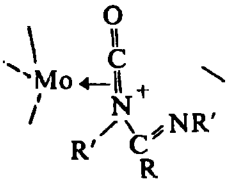
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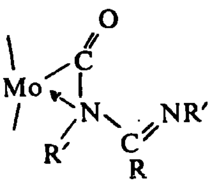

(9)

Structures (6) and (7) have 3-electron donor groups forming 5-membered rings, the difference arising from the possibility of either the nitrogen lone pair of electrons or the π-electrons of the C-N bond providing the second attachment to the metal. Otherwise they are both basically carbamoyl derivatives. Bonding as an aza-keten group $[R'R''N^+{=}C{=}O(R''{=}R'N{:}CR)$, (8) and (9)] may occur, structures (8) and (9) representing the two extremes of alkene-type attachment. Structures involving rings containing oxygen as well

TABLE 1

Spectroscopic and other data for $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(R)NR'\}]$ (M = Mo, W) complexes

| Complex | Mp/°C[a] | I.r. spectra[b] ν(CO) | | Solvent | $^1H$ n.m.r. spectra and assignments[c] |
|---|---|---|---|---|---|
| $[\eta^5\text{-}C_5H_5Mo(CO)_2\{MeNC(Ph)NMe\}]$ | 125–126 | 1854vs | 1948vs | $CDCl_3$ | 2·06, 2·28(5H) 3·89(5H) 6·58(6H) |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNCHNPh\}]$ | 158–160 | 1872vs | 1963vs | $CS_2$ | 2·60(10H) 3·89(5H) 3·99(1H) |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNC(Me)NPh\}]$ | 138–141 | 1859vs | 1953vs | $CDCl_3$ | 2·61(10H) 4·05(5H) 7·78(3H) |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2\{p\text{-tolylNC(Me)N-}p\text{-tolyl}\}]$ | 152–154 | 1857vs | 1951vs | $CDCl_3$ | 2·50, 2·64(8H) 3·96(5H) 7·3(6H) 7·79(3H) |
| $[\eta^5\text{-}C_5H_5W(CO)_2\{MeNC(Ph)NMe\}]$ | 132–133 | 1832vs | 1932vs | $CDCl_3$ | 2·02, 2·25(5H) 3·73(5H) 6·49(6H) |
| $[\eta^5\text{-}C_5H_5W(CO)_2\{PhNC(CH_3)NPh\}]$ | 143–144 | 1842vs | 1942vs | | |
| $[\eta^5\text{-}C_5H_5W(CO)_2\{p\text{-tolylNC(Me)N-}p\text{-tolyl}\}]$ | ca. 158 | 1838vs | 1939vs | $CDCl_3$ | 2·34, 2·47, 2·57, 2·71(8H) 3·82(5H) 7·22(6H) 7·76(3H) |

[a] Or decomposition temperature. [b] Maxima (ν/cm$^{-1}$) and relative intensities (vs, very strong) of peaks assigned to CO vibrations for the compounds dissolved in toluene. [c] τ values (p.p.m.), relative to tetramethylsilane.

as two nitrogen atoms are dismissed on the basis of the 1600–1700 cm$^{-1}$ absorptions.

Related complexes of manganese of the type $[Mn(CO)_4CON(R')C(R)NR']$[12] have been prepared, and as for these complexes structure (6) is preferred on the basis of a 5-membered metallocyclic ring rather than a 3-membered ring, and on the stereochemistry of the chelate group. In (7) the MoC(O)N and NCN planes are non-coincidental and against extensive delocalisation of the ligand group favoured by i.r. data. The three membered ring structure (9) may be expected to have an associated ligand absorption in the carbonyl stretching region higher than normal carbamoyl complexes and close to those of related acyl complexes because of the involvement of the nitrogen lone pair in bonding with the metal. Indeed acyl ν(CO) absorptions for complexes of the type $[\eta^5\text{-}C_5H_5)Mo(CO)_2LCOR]$ (R = Me, Et, L = $Ph_nPMe_{3-n}$ or $Ph_nPEt_{3-n}$; $n = 1, 2$)[11] occur in the region 1635–1642 cm$^{-1}$, very close to the region (1610–1630) for the present complexes. However, since no second absorption in the latter region, assignable to the ν(CN) stretching frequency of the free imino-group is detected, structure (6) is the favoured structure.

Two types of nitrogen substituents are expected for a complex with structure (6), and for the N, N'-dimethylbenzamidino-complex, two methyl $^1H$ n.m.r. signals are indeed detected. However, when the nitrogen substituents are $p$-tolyl groups, no observable difference in the methyl groups is detectable and a single resonance is observed. As suspected for the corresponding manganese complexes $[Mn(CO)_4CON(p\text{-tolyl})\,NC(R)N(p\text{-tolyl})]$ (R = Me, Ph)[12] the conclusion must now be that the methyl protons of $p$-tolyl groups are insensitive to the differences, both electronic and steric, between the two nitrogen atoms The successful use of $p$-tolyl and other $p$-substituted aryl substituents in structural studies of aza-allyl/allene complexes, but not carbamidino-complexes, demonstrates the limited use of such groups, and the inherent dangers in the interpretation of resultant data.

Lithioamidines and benzamidine produce carbamoyl-type complexes whereas N, N'-disubstituted amidines lead to carbon monoxide displacement. Thus the nucleophilicity of the nitrogen atoms appear critical in determining the course of the reactions. The highly nucleophilic lithio-derivatives prefer to attack the carbon of a co-ordinated carbonyl group to form carbamoyl complexes, whereas the less nucleophilic parent amidines appear to attack the metal directly to eliminate lithium chloride and displace carbon monoxide. Interestingly, the amidines with hydrogen attached to nitrogen, which have intermediate nucleophilicity also attack the carbon monoxide preferentially. Steric factors do not appear to be of importance in controlling the course of the reactions. N, N'-disubstituted amidines and their lithio-derivatives are both large molecules, and most probably oligomeric in the solvents used, whereas benzamidine is comparatively small. Yet the expected reagents of greatest and least bulk undergo comparable reactions.

Some yellow benzamidino-$\eta^5$-cyclopentadienyl molybdenum and -tungsten complexes have been previously reported,[13] and although identified as $[(\eta^5\text{-}C_5H_5)M(CO)_2\{R'NC(Ph)NR'\}]$ complexes on the basis of mass spectral evidence, in the absence of satisfactory elemental analytical data, the complexes exhibit a close resemblance to the presently reported yellow carbamoyl complexes. Indeed in the context of data collated on these carbamoyl-type complexes, the

TABLE 2

Spectroscopic and other data for $[(\eta^5\text{-}C_5H_5)M(CO)_2CON(R')C(R)NR']$ (M = Mo, W) complexes

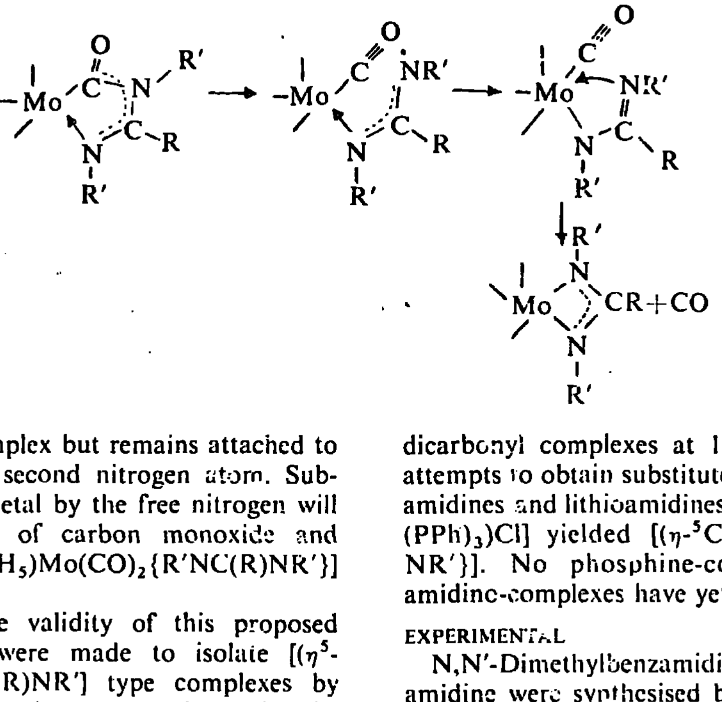
| Complex | Mp/°C[a] | I.r. spectra[b] ν(CO) | | | | $^1H$ n.m.r. spectra and assignments[f] |
|---|---|---|---|---|---|---|
| $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Ph)CHNPh]$ | | 1955vs | 1870vs[c] | | 1628[c] | |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2CONHC(Me)NH]$ | 155–156 | 1968vs | 1879vs[d] | | 1630m[c] | |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Ph)C(Me)NPh]$ | 166 | 1960vs | 1878vs[e] | | 1620m[c] | 2·18(10H)[g] 4·13(5H) 7·70(3H) |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(p\text{-tolyl})C(Me)N(p\text{-tolyl})]$ | 158–159 | 1961vs | 1873vs[d] | | 1630m[c] | 2·24(8H)[g] 4·20(5H) 7·16(6H) 7·76(3H) |
| $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Me)C(Ph)NMe]$ | 174–175 | 1963vs | 1877vs[d] | | 1612m[c] | 1·97, 2·36(5H) 4·10(5H) 6·29(3H) 6·71(3H) |
| $[\eta^5\text{-}C_5H_5W(CO)_2CONHC(Me)NH]$ | 155–156 | 1949vs | 1819vs | 1719sh[c] | 1627m[c] | |
| $[\eta^5\text{-}C_5H_5W(CO)_2CON(Ph)C(Me)NPh]$ | 166 | 1948vs | 1853vs[d] | | 1619m[c] | |

[a] Or decomposition temperature. [b] Maxima (ν/cm$^{-1}$) and relative intensities (vs, very strong; m, medium; sh, shoulder) of peaks assigned to CO vibrations. [c] KBr disc. [d] $CHCl_3$ solution. [e] Toluene solution. [f] τ values (p.p.m., relative to tetramethylsilane, for the compounds in $CDCl_3$ at 20 °C. [g] Multiplet.

previously reported complexes are most satisfactorily reformulated as [$\eta^5$-$C_5H_5M(CO)_2CON(R')C(Ph)NR'$] (M=Mo, W; R'=H, Ph, *p*-tolyl). The parent ions appear not to be observed in the m.s., the highest fragmentation pattern arising from $(P\text{-}CO)^+$ ions. Also the absorption at *ca.* 1630 $cm^{-1}$ in the i.r. spectrum of each complex now appears to be most satisfactorily interpreted as arising from a predominantly carbamoyl-type carbonyl group stretching vibration rather than from one associated predominantly with a NCN-skeleton.

*Decarbonylation Studies.* – Yellow carbamoyl-type complexes are decarbonylated in toluene solution using u.v. irradiation to yield an orange solution from which [$\eta^5$-$C_5H_5Mo(CO)_2\{R'NC(R)NR'\}$] complexes may be isolated in small quantity. Much decomposition occurs, and the decarbonylation route provides an inefficient, low yield means of obtaining the orange complexes. Alternatively the decarbonylation may be achieved thermally, again in low yield, *e.g.* [$\eta^5$-$C_5H_5Mo(CO)_2CON(Ph)C(Me)NPh$] in toluene at 70° for 10 h.

Attempted decarbonylations of carbamoyl complexes, M-C(O)$NR_2$, are known to produce cleavage of the -C(O)-N bond to generate a terminal carbonyl group with elimination of the $R_2N$ group. Thus for the carbamidino complexes cleavage of the -C(O)-N bond will generate the complex [$\eta^5$-$C_5H_5Mo(CO)_3N(R')C(R)NR'$] having a unidentate amidino-group. Unlike other carbamoyl derivatives the nitrogen group is not lost from the complex but remains attached to the metal through the second nitrogen atom. Subsequent attack at the metal by the free nitrogen will result in displacement of carbon monoxide and generation of [($\eta^5$-$C_5H_5$)$Mo(CO)_2\{R'NC(R)NR'\}$] complexes.



In order to test the validity of this proposed mechanism, attempts were made to isolate [($\eta^5$-$C_5H_5$)$Mo(CO)_3N(R')C(R)NR'$] type complexes by irradiating the carbamoyl-type complexes in the presence of methyl iodide. Reaction of the free nitrogen with MeI would thus prevent further attack at the metal centre and displacement of carbon monoxide.

$$\eta^5\text{-}C_5H_5Mo(CO)_2CON(R')C(R)NR' + MeI \xrightarrow{u.v.} [\eta^5\text{-}C_5H_5Mo(CO)_3N(R')C(R)N(Me)R']I.$$

The ionic products would be expected to exhibit in the i.r. spectrum a *facial* tricarbonyl pattern of $\nu$(CO) stretching frequencies with one absorption >2000 $cm^{-1}$; dicarbonyl complexes will have all $\nu$(CO) stretching absorptions to lower frequencies than 2000 $cm^{-1}$. Indeed an absorption above 2000 $cm^{-1}$, for example at 2026 $cm^{-1}$ for the N, N'-diphenylacetamidino-derivative, was detected, although efforts to obtain pure samples of the solid products have so far failed. Thus good evidence exists for the detection of an intermediate-type complex in the decarbonylation reaction. Interestingly, ($\pi$-$C_5H_5Mo(CO)_3I$] and polynuclear molybdenum species have been detected in the products in addition to [($\eta^5$-$C_5H_5$)$Mo(CO)_3]_2$ and [($\eta^5$-$C_5H_5$)$Mo(CO)_2\{R'NC(R)NR'\}$].

For most systems the decarbonylation route to the orange complexes is not used because orange complexes may be obtained directly using amidines. However, benzamidine, unlike N, N'-disubstituted amidines, yields the yellow tricarbonyl complex, but attempted decarbonylation of this complex yields only [$\eta^5$-$C_5H_5Mo(CO)_3]_2$ and a dimolybdenum complex, at present unidentified. No dicarbonyl benzamidino-complex has so far been isolated.

*Reactions using carbodiimides.* Insertion of carbodiimides into metal-carbon and even metal-chlorine bonds is documented and yields amidino-complexes. Attempts to achieve insertion using [($\eta^5$-$C_5H_5$)$Mo(CO)_3X$) (X=Me, Cl) and dicyclohexylcarbodiimide in refluxing toluene over prolonged periods of time yielded decomposition material and traces of [$\eta^5$-$C_5H_5$)$Mo(CO)_3]_2$. No evidence was obtained for formation of other carbonyl containing materials.

*Attempted reactions with $PPh_3$.* Triphenylphosphine failed to substitute for carbon monoxide in the orange dicarbonyl complexes at 130–150° over 6·5 h, and attempts to obtain substituted products by reaction of amidines and lithioamidines with [($\eta^5$-$C_5H_5$)$Mo(CO)_2(PPh_3)Cl$] yielded [($\eta$-$^5C_5H_5$)$Mo(CO)_2\{R'NC(R)NR'\}$]. No phosphine-containing molybdenum-amidine-complexes have yet been characterised.

## EXPERIMENTAL

N,N'-Dimethylbenzamidine and N,N'-di-*p*-tolylacetamidine were synthesised by standard methods, and N,N'-diphenylacetamidine, N,N'-diphenylformamidine, 2-aminopyridine and acetamidine hydrochloride were obtained commercially. n-Butyl-lithium, *ca.* 2·4 M in hexane, was used as supplied commercially without purification. Complexes [($\eta^5$-$C_5H_5$)$M(CO)_3Cl$] (M=Mo,W) were prepared from the hexacarbonyls by standard methods.[15] Hydrocarbon solvents and diethyl ether were dried over extruded sodium, but chloroform was used without purification. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with rigorous exclusion of air.

I.r. spectra in the range 4000–200 cm$^{-1}$ were recorded with a Perkin-Elmer 457 spectrophotometer and $^1$H n.m.r. spectra at 60 MHz with a Varian A56/60D spectrometer. Mass spectra were obtained with an A.E.I. MS 9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures between 80 and 220 °C.

Carbon, hydrogen and nitrogen contents of the complexes were determined with a Perkin-Elmer 240 Elemental Analyser, and molybdenum and tungsten contents by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrophotometer. Combustion methods of analysis have not proved entirely reliable for the complexes reported here and elsewhere[12] even though the authors were confident that pure samples were used. Consequently identification has been based on both elemental analyses and spectroscopic data.

*Reaction of PhNHC(Me) NPh with* $[\eta^5\text{-}C_5H_5Mo(CO)_3Cl]$. The amidine (0·75 g, 3·56 mmol) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ (0·5 g, 1·78 mmol) were dissolved in toluene (35 cm$^3$) and the mixture heated at 50–55 °C for 9·5 h. The colour of the solution became progressively orange-brown and a white precipitate slowly separated. At the end of the reaction, monitored using the 2060 cm$^{-1}$ i.r. absorption of the carbonyl chloride, filtration yielded a white residue which was recrystallised from chloroform/hexane mixtures. The compound was identified as $[PhNHC(Me)NHPh]^+Cl^-$ by elemental analyses, mass spectrometry and comparing the i.r. spectrum with that of an authentic sample. The orange filtrate was reduced in volume *in vacuo*, and on cooling to −10 °C yielded orange crystals of $[\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNC(Me)NPh\}]$, which were recrystallised from diethyl ether.

(Yield 0·44 g, 57%; m.p. 138–141°) (Found: C, 59·1; H, 3·80; Mo, 20·6; N, 4·73. $C_{21}H_{18}MoN_2O_2$ requires C, 59·2; H, 4·25; Mo, 22·5; N, 6·56%.) $^m/_e(P^+)$ 428, $^m/_e(P\text{-}CO)^+$ 400, $^m/_e(P\text{-}2CO)^+$ 372. I.r. [$\nu$(CO), KBr] 1828sh, 1850s, 1953s cm$^{-1}$.

*Reactions of Other Amidines with* $[\eta^5\text{-}C_5H_5)M(CO)_3Cl](M{=}Mo,W)$. – The method described above was used generally to prepare the following complexes as orange crystals. Yields were typically 50–60%.

$[\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNCHNPh\}]$. m.p. 158–160 °C. (Found: C, 58·9; H, 4·05; Mo, 22·7; N, 4·44. $C_{20}H_{16}MoN_2O_2$ requires C, 58·3; H, 3·91; Mo, 23·2; N, 6·79%.) $^m/_e(P^+)$ 414, $^m/_e(P\text{-}CO)^+$ 386, $^m/_e(P\text{-}2CO)^+$ 358. I.r. [$\nu$(CO), KBr] 1870s, 1950s, 1830sh, cm$^{-1}$.

$[\eta^5\text{-}C_5H_5Mo(CO)_2\{MeNC(Ph)NMe\}]$. m.p. 125–6 °C. (Found: C, 53·7; H, 4·23; Mo, 26·5; N, 7·09. $C_{16}H_{16}MoN_2O_2$ requires C, 52·7; H, 4·42; Mo, 26·3; N, 7·68%.) $^m/_e(P^+)$ 366, $^m/_e(P\text{-}CO)^+$ 338, $^m/_e(P\text{-}2CO)$ 310. I.r. [$\nu$(CO), KBr] 1828sh, 1853s, 1941s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5Mo(CO)_2\{(p\text{-}tolyl)NC(CH_3)N(p\text{-}tolyl)\}]$. m.p. 152–4 °C. Found: C, 60·8; H, 4·98; N, 5·53. $C_{23}H_{22}MoN_2O_2$ requires C, 60·8; H, 4·88; N, 6·16%) $^m/_e(P^+)$ 456, $^m/_e(P\text{-}CO)^+$ 428, $^m/_e(P\text{-}2CO)^+$ 400. I.r. [$\nu$(CO), KBr] 1820sh, 1842s, 1942s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5W(CO)_2\{MeNC(Ph)NMe\}]$. m.p. 132–3 °C. (Found: C, 42·4; H, 3·12; N, 6·30; W, 43·1. $C_{16}H_{16}N_2O_2W$ requires C, 42·5; H, 3·56; N, 6·19; W, 40·7%.) $^m/_e(P^+)$ 452; $^m/_e(P\text{-}CO)^+$ 424, $^m/_e(P\text{-}2CO)^+$ 396. I.r. [$\nu$(CO), KBr] 1808sh, 1832s, 1900sh, 1923s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5W(CO)_2\{PhNC(CH_3)NPh\}]$. m.p. 143-4 °C. (Found: C, 49·2; H, 3·58; N, 5·45; W, 36·8. $C_{21}H_{18}N_2O_2W$ requires C, 49·1; H, 3·53; N, 5·44; W, 35·7%.) $^m/_e(P^+)$ 514, $^m/_e(P\text{-}CO)^+$ 486, $^m/_e(P\text{-}2CO)^+$ 458. I.r. [$\nu$(CO), KBr] 1812s, 1927s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5W(CO)_2\{(p\text{-}tolyl)NC(CH_3)N(p\text{-}tolyl)\}]$ m.p. *ca.* 158 °C (decomp). (Found: C, 50·7; H, 3·75; N, 5·18. $C_{23}H_{22}N_2O_2W$ requires C, 50·9; H, 4·08; N, 5·16%.) $^m/_e(P^+)$ 542, $^m/_e(P\text{-}CO)^+$ 514, $^m/_e(P\text{-}2CO)^+$ 486. I.r. [$\nu$(CO), KBr] 1822s, 1920s cm$^{-1}$.

*Reaction of PhN(Li)C(Me)NPh with* $[\eta^5\text{-}C_5H_5Mo(CO)_3Cl]$. – A suspension of the lithio-reagent was formed from the amidine (0·38 g, 1·78 mmol) and Bu$^n$Li (1·2 cm; 1·50M) in ether (50 cm$^3$) by mixing at −196 °C, allowing the mixture to warm, then stirring the mixture at ambient temperature for 1 h. The reagent was added to a frozen solution of $[\eta^5\text{-}C_5H_5Mo(CO)_3Cl]$(0·50 g, 1·78 mmol) in diethyl ether (200 cm$^3$) at −196 °C, and the mixture allowed to warm slowly to ambient temperature. The original deep orange colour of the solution gradually became yellow-orange, and after 1·25 h the solution was evaporated to dryness (*in vacuo*, 20 °C). The product was extracted from the residue with chloroform (50 cm$^3$), and separated from solution by reducing its volume, adding hexane and cooling to −10 °C. Recrystallisation from chloroform-hexane mixtures yielded yellow crystals of $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Ph)C(Me)NPh]$, m.p. 166 °C. (Found: C, 56·5; H, 5·27; Mo, 18·3; N, 6·05. $C_{22}H_{18}MoN_2O_2$ requires C, 58·2; H, 3·99; Mo, 21·1; N, 6·16%.) $^m/_e(P^+)$ 456, $^m/_e(P\text{-}CO)^+$ 428, $^m/_e(P\text{-}2CO)^+$ 400, $^m/_e(P\text{-}3CO)^+$ 372. I.r. [$\nu$(CO), KBr] 1862s, 1950s cm$^{-1}$.

*Reactions of Other Lithio-amidines with* $[\eta^5\text{-}C_5H_5M(CO)_3Cl](M{=}Mo,W)$. – The method described above was used generally to prepare the following complexes as yellow crystals typically in 40% yields.

$[\eta^5\text{-}C_5H_5Mo(CO)_2CONHC(Me)NH]$, m.p. 155–6 °C. (Found: C, 37·5; H, 3·16; Mo, 30·7; N, 9·69. $C_{10}H_{10}MoN_2O_3$ requires C, 39·7; H, 3·33; Mo, 31·7; N, 9·26%.) $^m/_e(P^+)$ 304, $^m/_e(P\text{-}CO)^+$ 276, $^m/_e(P\text{-}2CO)^+$ 248, $^m/_e(P\text{-}3CO)^+$ 220. I.r. [$\nu$(CO), KBr] 1827sh, 1853s, 1928sh, 1953s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Ph)CHNPh]$, $^m/_e(P^+)$ 442, $^m/_e(P\text{-}CO)^+$ 414, $^m/_e(P\text{-}2CO)^+$ 386, $^m/_e(P\text{-}3CO)^+$ 358. I.r. [$\nu$(CO), KBr] 1869s, 1956s; [$CHCl_3$] 1886s, 1969s cm$^{-1}$. Analytically pure samples of this complex could not be obtained; N,N′-diphenylformamidine was the contaminant.

$[\eta^5\text{-}C_5H_5Mo(CO)_2CON(p\text{-}tolyl)C(Me)N(p\text{-}tolyl)]$. (37%; m.p. 158–9 °C.) (Found: C, 57·4; H, 3·41; N, 5·34 $C_{24}H_{22}MoN_2O_3$ requires C, 59·7; H, 4·59; N, 5·80%.) $^m/_e(P^+)$ 484, $^m/_e(P\text{-}CO)^+$ 456, $^m/_e(P\text{-}2CO)^+$ 428, $^m/_e(P\text{-}3CO)^+$ 400. I.r. [$\nu$(CO), KBr] 1865s, 1952s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5Mo(CO)_2CON(Me)C(Ph)NMe]$, m.p. 174–5 °C. (Found: C, 51·8; H, 3·41; Mo, 24·8; N, 6·91. $C_{17}H_{16}MoN_2O_3$ requires C, 52·0; H, 4·11; Mo, 24·5; N, 7·13%.) $^m/_e(P^+)$ 394, $^m/_e(P\text{-}CO)^+$ 336, $^m/_e(P\text{-}2CO)^+$ 338, $^m/_e(P\text{-}3CO)^+$ 310. I.r. [$\nu$(CO), KBr] 1853s, 1851sh, 1949s cm$^{-1}$.

$[\eta^5\text{-}C_5H_5Mo(CO)_2CONHC_5H_4N]$. $^m/_e(P^+)$ 340, $^m/_e(P\text{-}CO)^+$ 312, $^m/_e(P\text{-}2CO)^+$ 284, $^m/_e(P\text{-}3CO)^+$ 256. I.r. [$\nu$(CO), KBr] 1873s, 1959s cm$^{-1}$. Samples of this complex, isolated in small quantity, were shown by elemental analyses to be contaminated by decomposition impurities.

*$[\eta^5\text{-}C_5H_5W(CO)_2CON(Ph)C(Me)NPh]$*. m.p. 184–5 °C. (Found: C, 49·2; H, 4·72; N, 5·73. $C_{22}H_{18}N_2O_3W$ requires C, 48·7; H, 3·34; N, 5·16%.) $^{m}/_{e}(P^{+})$ 542, $^{m}/_{e}(P\text{-}CO)^{+}$ 514, $^{m}/_{e}(P\text{-}2CO)^{+}$ 486, $^{m}/_{e}(P\text{-}3CO)^{+}$ 458. I.r. [$\nu$(CO), KBr] 1850s, 1940s cm$^{-1}$.

*$[\eta^5\text{-}C_5H_5W(CO)_2CONHC(Me)NH]$*. m.p. 188 °C (decomp). (Found: C, 27·84; H, 2·67; N, 7·39. $C_{10}H_{10}N_2O_3W$ requires C, 30·79; H, 2·58; N, 7·17%.) $^{m}/_{e}(P^{+})$ 389, $^{m}/_{e}(P\text{-}CO)^{+}$ 361, $^{m}/_{e}(P\text{-}2CO)^{+}$ 333, $^{m}/_{e}(P\text{-}3CO)^{+}$ 305. I.r. [$\nu$(CO), KBr] 1791sh, 1819s, 1949s cm$^{-1}$.

*$[\eta^5\text{-}C_5H_5W(CO)_2CON(Me)C(Ph)NMe]$*, $^{m}/_{e}(P^{+})$ 480, $^{m}/_{e}(P\text{-}CO)^{+}$ 452, $^{m}/_{e}(P\text{-}2CO)^{+}$ 424, $^{m}/_{e}(P\text{-}3CO)^{+}$ 396. I.r. [$\nu$(CO) KBr] 1851s, 1946s; [$CHCl_3$] 1864s, 1953s.

*Attempted Decarbonylation Reactions of $[\eta^5\text{-}C_5H_5Mo(CO)_2CON(R')C(R)NR']$*. – Samples of the complex (R=Me, R′=Ph), partly dissolved and partly suspended in toluene, were irradiated with a 300 watt Hg 1 amp for periods up to 15 min. Much decomposition to non-carbonyl materials occurred, but the solution slowly developed a pale orange colour. After filtration of the mixture, an i.r. spectroscopic examination of the filtrate showed the presence of a new carbonyl containing species with an absorption at 2026 cm$^{-1}$.

In an attempt to stabilise the new complex, believed to be of the type $[\eta^5\text{-}C_5H_5Mo(CO)_3N(R')C(R)NR']$ and to be the intermediate in the decarbonylation reaction, subsequent reactions were attempted in the presence of MeI. In reactions using $[\eta\text{-}C_5H_5Mo(CO)_2CON(R')C(R)NR']$ (R=Me, R′=Ph, *p*-tolyl) in toluene with exposure times of 15–20 min. infrared spectroscopy and mass spectrometry indicated the formation of $[\eta^5\text{-}C_5H_5Mo(CO)_2\{R'NC(R)NR'\}]$ and $[\eta^5\text{-}C_5H_5Mo(CO)_3I]$ with $[\eta^5\text{-}C_5H_5Mo(CO)_3N(R')C(R)N(Me)R']]$ in small quantities. The nature of the latter complex is based on the mass spectrum of its thermolysis products, and upon the presence of a $\nu$(CO) stretching vibration above 2000 cm$^{-1}$ which is consistent only with the occurrence of a terminal tricarbonyl unit in the complex.

*Reaction of $PhN(Li)C(Me)NPh$ with $[\eta^5\text{-}C_5H_5Mo(CO)_2(PPh_3)Cl]$*. – The lithioreagent prepared from the amidine (0·14 g, 0·67 mmol) and butyl lithium (0·45 cm$^3$, 1·5M) in monoglyme (50 cm$^3$) was added to a solution of $[\eta^5\text{-}C_5H_5Mo(CO)_2(PPh_3)Cl]$ (0·35 g, 0·67 mmol) also in monoglyme (40 cm$^3$). After stirring at room temperature for 5 h during which time the progress of the reaction was very slow, the temperature was raised to 70-80 °C for 2 h. At the end of the reaction, as indicated by the consumption of the reactant complex (shown by i.r. spectroscopic monitoring of the $\nu$(CO) stretching region), filtration yielded an orange solution which was evaporated to dryness. Extraction with diethylether (40 cm$^3$), followed by concentration of the resultant solution (20 °C, *in vacuo*) and cooling to −10 °C yielded orange crystals of $[\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNC(Me)NPh\}]$ $^{m}/_{e}(P^{+})$ 428.

*Attempted Reactions of $C_6H_{11}NCNC_6H_{11}$ with $[\eta^5\text{-}C_5H_5Mo(CO)_3X]$ (X=Cl, Me)*. – Stoichiometric quantities of the carbodiimide and molybdenum complex were heated in toluene at the reflux temperature for periods between 7 and 18 h without detectable formation of amidino-complexes. Much decomposition to non-carbonyl materials occurred; a trace of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ was the only carbonyl product, identified by i.r. and m.s. methods.

*Reaction of $PhNHC(Me)NPh$ with $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$*. – $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ (0·5 g, 1·02 mmol) in toluene (35 cm$^3$) was stirred with {PhNHC(Me)NPh} (0·43 g, 2·03 mmol), and the resulting mixture was heated to reflux temperature for 13·5 h. At the end of the reaction, as indicated by i.r. spectroscopy, the solvent was removed (*in vacuo*, 20 °C) and the residue extracted with diethyl ether (30 cm$^3$). Fractional crystallisation techniques enabled orange crystals of $[(\eta^5\text{-}C_5H_5Mo(CO)_2\{PhNC(Me)NPh\}]$ to be isolated (in low yield. $^{m}/_{e}(P^{+})$ 428.

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