Studies of some organo-nitrogen three-electron ligands in transition metal carbonyl complexes

Keable, H. R.

Keable, H. R. (1972) *Studies of some organo-nitrogen three-electron ligands in transition metal carbonyl complexes*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8670/

STUDIES OF SOME ORGANO-NITROGEN THREE-ELECTRON LIGANDS IN TRANSITION METAL CARBONYL COMPLEXES.

by

H.R. Keable, B.Sc.

A thesis submitted to the University of Durham
for the degree of Doctor of Philosophy

August 1972

To My Mother and Father.

'Implacable? It is the truth. Truth is implacable.

But the nature and meaning of this truth is not.'

JOHN FOWLES

'The Magus' (1968)

CONTENTS

Page

Acknowledgements i

Memorandum ii

Abstract iii

Notes on Nomenclature v

CHAPTER 1 Introduction 1

CHAPTER 2 Reactions of R_2N- Systems with π-$C_5H_5Mo(CO)_3Cl$.

A: Experimental 9

B: Discussion 15

CHAPTER 3 Synthetic Routes to Ketimino and Aza-allyl/allene Derivatives of Molybdenum and Tungsten.

A: Experimental 24

B: Discussion 50

CHAPTER 4 Properties and Reactions of Molybdenum and Tungsten Ketimino Complexes.

A: Experimental 56

B: Discussion 59

CHAPTER 5 A Survey of Allyl and Related Transition Metal Complexes.

A: Introduction 68

B: Allyl Metal Complexes 68

C: Allene Metal Complexes 80

D: Ketenimine Metal Complexes 85

E: Amidino Metal Complexes 87

F: N.M.R. Spectral Studies of Allyl Complexes 89

Page

CHAPTER 6 Aza-allyl/allene Derivatives of Molybdenum and Tungsten.

A: Aza-allyl/allene Complexes 104

B: Complexes of the type π-$C_5H_5M(CO)_2[R_2CNCR_2]$-(R_2CO), (M = Mo,W; R = p-tolyl) 117

CHAPTER 7 Nuclear Magnetic Resonance Studies of Aza-allyl/allene Complexes. 121

CHAPTER 8 Reaction of Manganese Pentacarbonyl Bromide with Di-p-tolylketimino-lithium.

A: Experimental 141

B: Discussion 144

APPENDIX 1 Preliminary Reactions of $[R_2CNCR_2](Li)$ Systems with π-$C_5H_5M(CO)_3Cl$ (M = Mo, W).

A: Introduction 153

B: Experimental 154

C: Discussion 158

APPENDIX 2 Experimental Details and Starting Materials. 159

APPENDIX 3 Instrumentation 161

APPENDIX 4 Analytical Methods 163

APPENDIX 5 Calculation of Activation Energies from NMR Spectral Data. 164

REFERENCES 166

ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to Dr M. Kilner, under whose supervision this research was carried out, for his continual advice and encouragement.

My thanks are also due to Dr H.M.M. Shearer and Mr J.D. Sowerby of this department, for details of the X-ray crystal structure of one of the compounds described in this thesis, and to Dr D.T. Clark and Mr D. Briggs, also of this department, for running and interpreting the X-ray photoelectron spectra discussed.

I also wish to thank Jane Spencer for checking the original manuscript, and Diane Rothery for valuable technical assistance during the course of the work.

Finally, I am indebted to the Science Research Council for a maintenance grant.

H.R. Keable
Durham 1972

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1969 and July 1972. It has not been submitted for any other degree and is the original work of the author except when acknowledged by reference.

Part of the work in this thesis has formed the subject matter of the following publications:

(i) σ-π Interaction in Aza-allyl Complexes. ^{1}H Nuclear Magnetic Resonance Studies of π-$C_5H_5M(CO)_2[(p\text{-}CH_3C_6H_4)_2CNC(p\text{-}CH_3C_6H_4)_2]$ (M = Mo, W).
by H.R. Keable and M. Kilner. Chem. Comm., 1971, 349.

(ii) Methyleneamine Derivatives of Molybdenum and Tungsten Carbonyl Complexes.
by H.R. Keable and M. Kilner. Abstr. 5th Internat. Conf. on Organomet. Chem., Moscow 1971, 545.

(iii) Fluxional Behaviour of Aza-allyl Complexes.
by H.R. Keable and M. Kilner. Abstr. Autumn Meeting, Chemical Society, York, 1971, B16.

(iv) Organo-nitrogen Groups in Metal Carbonyl Complexes. Part IV. Isomeric forms of Aza-allyl-Allene Complexes of Molybdenum and Tungsten. by H.R. Keable and M. Kilner. J. Chem. Soc. Dalton Trans., 1972, 153.

(v) Organo-nitrogen Groups in Metal Carbonyl Complexes. Part V. Fluxional Behaviour of Aza-allyl Complexes.
by H.R. Keable and M., Kilner. J. Chem. Soc. Dalton Trans., in the press.

ABSTRACT

The work to be described is a continuation of the study of organonitrogen-transition metal complexes with particular reference to ketimino and related derivatives. Earlier work by colleagues has shown that the nature of the product formed from the reaction of π-$C_5H_5M(CO)_3Cl$,[I] ($M = Mo,W$), with lithio-ketimines, $R_2C{:}NLi$, depends on the group R. Thus for R = Ph, the product is the aza-allyl/allene derivative π-$C_5H_5M(CO)_2[Ph_2CNCPh_2]$ and for R = Bu^t, the ketimino complex π-$C_5H_5M(CO)_2NCBu^t{}_2$ is formed.

Reaction of [I] with (p-tolyl)$_2$C:NLi, however, produced three types of complex, π-$C_5H_5M(CO)_2NC$(p-tolyl)$_2$[II], π-$C_5H_5M(CO)_2$[(p-tolyl)$_2$CNC-(p-tolyl)$_2$] [III], and π-$C_5H_5M(CO)_2$[(p-tolyl)$_2$CNC(p-tolyl)$_2$](p-tolyl)$_2$C:O [IV]. Two forms of [III], (M = W) were isolated in the solid state but a common species was formed in solution. [IV]also gave the same solution species together with the free ketone. A mechanism for the formation of the complexes and the biproducts (p-tolyl)$_2$C:O, NCO^- and CN^- is proposed. All complexes failed to undergo substitution reactions with PPh_3 and reaction of iodine with [II] caused total decomposition of the complex. Dimerisation of [II] to [π-$C_5H_5M(CO)NC$(p-tolyl)$_2$]$_2$could be achieved for M = W, but not for M = Mo.

Reaction of [I] with $R_2C{:}NLi$ in the presence of $R_2C{:}O$ (R = Ph, p-tolyl) resulted in formation of the complexes π-$C_5H_5M(CO)_2NCR_2$ to the exclusion of the aza-allyl/allene complexes, which are formed in the absence of $R_2C{:}O$. The possible role of the ketone in the reaction is discussed.

Variable temperature ^{1}H n.m.r. studies on [III] showed the molecules to be fluxional, the observed temperature dependance being consistent with the occurrence of two distinct averaging processes within the aza-allyl/allene ligand. Further structural information was obtained from the ^{1}H n.m.r. spectra of the compounds π-$C_5H_5Mo(CO)_2[(R'C_6H_4)$-$(R''C_6H_4)CNC(R'C_6H_4)(R''C_6H_4)]$ (R' = p-OMe, H; R'' = p-Me) which showed that at low temperatures, certain orientations of the CR_2 groups with respect to the rest of the ligand are preferred. Kinetic measurements made from the ^{19}F n.m.r. spectra of the compounds π-$C_5H_5M(CO)_2[(p\text{-}CF_3C_6H_4)_2$-$CNC(p\text{-}CF_3C_6H_4)_2]$ (M = Mo,W) gave values of E_a for the lower temperature process of 11.6 and 6.8 Kcal/mole respectively.

Preliminary attempts to synthesise aza-allyl/allene complexes by reacting [I] with the preformed ligand system $[R_2CNCR_2][Li]$ are described.

Reactions of [I] with the amino derivatives R_2NLi and R_2NSiMe_3 were attempted in order to synthesise complexes of the type π-$C_5H_5M(CO)_2NR_2$ and to compare them with the parallel series of ketimino derivatives π-$C_5H_5M(CO)_2NCR_2$. No products were obtained using R_2NLi, but with R_2NSiMe_3 a new nitrogen-bridged, dinuclear molybdenum complex is thought to have been obtained.

Attempts to attach the $(p\text{-tolyl})_2$ C:N- group to manganese resulted only in complexes containing the neutral ketimine, $(p\text{-tolyl})_2C{:}NH$, and possibly the species $[(p\text{-tolyl})_2C{:}NH_2]^+$.

NOTES ON NOMENCLATURE

The Chemical Society have requested the name 'methyleneamine' be used for the (unknown) compound $CH_2:NH$ and that derivatives be named accordingly. Hence compounds containing the units $R_2C:N-$ are known as di-alkyl or di-aryl- methyleneamino- derivatives depending on the nature of the group R.

In this thesis, however, the older, but rather more clearer term 'ketimino' will be used, for this group, partly for the sake of brevity and partly because such terminology clearly distinguishes 'imino' from 'amino' derivatives.

Throughout this work the nomenclature of the organonitrogen group $[R_2CNCR_2]$ has been based on structurally related carbo-groups. The term 'Aza-allyl' refers to the group when the R_2C planes are planar (cf. the isoelectronic allyl group, $R_2CC(H)CR_2$), and the term aza-allene to the group when the R_2C planes are perpendicular. The latter group is formally derived from $[R_2C{=}\overset{+}{N}{=}CR_2]$, the dialkylideneammonium ion, which is isoelectronic and isostructural with allenes, $R_2C{=}C{=}CR_2$. Where general reference is made to the class of compounds containing the R_2CNCR_2 group the term aza-allyl/allene will be used and this does not imply the ligand is in a particular form. Where it is obvious that the bonding mode of the ligand within a compound is being discussed, the appropriate term will be used.

CHAPTER 1

INTRODUCTION

A. General Considerations.

The scope and extent of transition metal carbonyl chemistry has increased dramatically over the past decade, resulting in, amongst other things, improved industrial processes and a better, if not yet complete, understanding of some naturally occurring processes. The thermal stability of many organometallic complexes has undoubtedly been significant in many of the advances that have been made. This stability can be traced back to the so-called 'synergic' effect, operative in the bonding of metals with carbonyl and π-bonded organo- groups and refers to the simultaneous σ-donation of the lone pair, or π-electrons, from, for example, the carbon of a carbonyl group or π-bond of the ethylene molecule respectively, together with back donation from non-bonding metal d-orbitals to antibonding π-orbitals of the ligand. Each process has the effect of mutually increasing the other and for carbonyls results in a metal-carbon bond order of greater than one and also a stronger bond than would be possible by combining the separate effects of σ- and π-bonding. Such a synergic effect prevents excessive charge build-up on the metal and thus allows the carbonyl group to stabilise the metal in low oxidation states. Replacement of a carbonyl group by another ligand will result in competition for metal electron density between the new and remaining ligands and the outcome will depend upon the relative σ- and π-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 π-acceptor properties (e.g. organic amines or ammonia) will strengthen the remaining metal-carbon bonds via increased $d_\pi \rightarrow \pi^*$ bonding (i.e. less competition), but only up to a certain point, e.g.[1]

$$Cr(CO)_6 + \text{liq. } NH_3 \xrightarrow{120^\circ} Cr(CO)_3(NH_3)_3 + 3CO$$

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. If the ligand L, however, had π-acceptor properties (eg. NO, CN^-, 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.

B. 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.[2,3] 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.[2] In this respect, the ketimino-group has proved very versatile indeed, both in the reactions it undergoes and the bonding modes it adopts. The neutral ligand $R_2C{:}NH$ reacts as a normal nitrogen base, σ-bonding through the nitrogen lone pair as a 2-electron donor, as in compounds of the type $[Mn(CO)_3(Ph_2C{=}NH)_2Br]$.[4] Backbonding is also possible from filled metal d-orbitals into π^* orbitals on the ligand, but the MNC system will be necessarily bent, due to sp^2 hybridisation at nitrogen (Fig. I.1(a)).

As an anionic ligand we have the possibility of donation of 1 or 3 electrons, depending on the involvement of the nitrogen lone pair in the bonding. For maximum orbital overlap it is thought that the MNC skeleton should be linear. In this situation nitrogen would be sp hybridised and the lone pair in a pure p orbital - of the correct symmetry to overlap with metal d-orbitals - bonding would then involve electron donation via σ and $p_\pi \rightarrow d_\pi$ bonding and back donation via $d_\pi \rightarrow p_\pi*$ bonding (Fig. I.2). If the MNC skeleton were bent then σ donation and $d_\pi \rightarrow p_\pi*$ back donation would still be possible, but the lone pair would now occupy an orbital which in the limit would approximate to sp^2. Although Ebsworth[5] has calculated overlap integrals for nitrogen bonded to silicon and concluded that substantial $p \rightarrow d$ π bonding from a nitrogen lone pair to vacant silicon d-orbitals is possible in a non-linear system (Fig. I.1(b), it is not expected to be as extensive as in a linear system. There is also the increased possibility in non-linear systems that the lone pair will donate to a second metal atom forming nitrogen-bridged dinuclear species. The possibility of lateral overlap, as in olefin complexes, of the C=N π-system with suitable metal orbitals also exists.

Studies carried out so far on ketimino-derivatives of molybdenum and tungsten suggest that in mononuclear complexes the ligand assumes a near linear MNC skeleton.[6] A crystal structure of the complex π-$C_5H_5Mo(CO)_2NCBu^t_2$ shows an MNC of 172° (the small deviation from linearity is thought to be due to crystal packing[6a]). The M-N bond length of 1.87Å is considerably shorter than the accepted single bond length of 2.32 Å [7] indicating considerable M-N multiple bonding. A dinuclear complex of formula $[\pi\text{-}C_5H_5M(CO)NCPh_2]_2$ (M = Mo,W) containing bridging $Ph_2C{:}N\langle$ groups has also been prepared[8].

Ketimino complexes are not the sole products obtained in reactions of $R_2C{:}N-$ systems with transition metal derivatives. With π-$C_5H_5M(CO)_3Cl$ (M=Mo,W) under certain conditions, 2-aza-allyl complexes are formed of formula π-$C_5H_5M(CO)_2(R_2CNCR_2)$[9], containing an organonitrogen group acting as a three electron ligand. The aza-allyl group (R_2CNCR_2) is formed by 'condensation' of two $R_2C{=}N-$ units, the extra nitrogen atom appearing as cyanate ion together with the carbonyl group lost.

A more detailed study of this type of complex was of interest, in order to obtain information on the bonding mode adopted by the ligand. The possibilities are shown in Fig. I.3. The symmetric π-aza-allyl group (Fig. I.3(a)) may be linear or bent depending on the extent to which the nitrogen lone pair is utilised in the bonding, i.e. sp or sp^2 hybridisation at the nitrogen respectively. In both cases empty metal σ- and π-orbitals have the correct symmetry for overlap with ligand orbitals. For a bent skeleton we would have a situation directly comparable to the iso-electronic π-allyl group (the bonding of π-allyl groups to transition metals is discussed more fully in Chapter 5). A linear CNC system with the lone pair in a p-orbital would create a more favourable situation for participation of the lone pair in the bonding. For the σ-π form (Fig. I.3(b)), the extreme structure shown would have a metal-carbon σ-bond and lateral overlap of suitable metal d-orbitals with the C=N π-system. A bent skeleton would be more likely here due to the steric requirements of this particular bonding situation. In both these structures (Fig. I.3(a) and (b)) all R groups would be coplanar. Bonding of the aza-allene ligand (Fig. I.3(c)) would be expected to be of the mono-olefin type through one of the double bonds, (as is found in many of the known π-allene complexes), with the unco-ordinated group bent away from the metal,[10] (Fig I.3(e)). Alternatively, the bonding may be as represented in Fig. I.3(f) involving σ-bonding of the carbon to the metal and bonding to nitrogen through the lone pair of electrons. This represents an extreme situation in which carbon-nitrogen bonding is reduced to a bond order of 1. R groups in this situation would be in perpendicular planes. The aziridino structure (Fig. I.3(d)) has not been reported in transition metal systems, although it is well known attached to main group elements.[11] The absence of an i.r. absorption band in the 850-900 cm^{-1}. region, which has been used as diagnostic of the aziridine ring system[12] suggests that this mode of bonding is not adopted. The synthetic routes to the type of complexes mentioned so far have been discussed elsewhere.[6b] The two methods which were found to be successful, and which were used to prepare the complexes discussed in this thesis are:

a) $M(CO)_nX + R_2C{:}NLi \rightarrow$

b) $M(CO)_nX + R_2C{:}N\text{-}SiMe_3 \rightarrow$

The types of products obtained depend on the group R and the reaction conditions used.

In view of the successful synthesis of a number of ketimino derivatives of molybdenum and tungsten[8,13,14] and with regard to the remarks made earlier concerning the substitution of carbonyl groups by ligands with and without π-acceptor properties, it was of interest to investigate the possibilities of synthesising a parallel series of complexes containing the amino ligand, R_2N- which has no π-acceptor properties, but is still able to act as 1- or 3-electron donor. Carbonyl complexes with terminal amino groups are well established but not numerous because of the tendency of nitrogen to use the lone pair electrons to bond to a second metal atom forming nitrogen-bridged species. e.g. Reaction of hydrazine with the phosphine-substituted rhenium complexes, cis-$[Re(CO)_4LBr]$ and trans-$[Re(CO)_3L_2Br]$ (L = Me_2PPh) gave $[Re(CO)_3L(N_2)(NH_2)]$ and $[Re(CO)_2L_2(N_2)(NH_2)]$ respectively. σ-N-pyrrolyl complexes e.g. π-$C_5H_5Fe(CO)_2$(σ-N-pyrrolyl) have been isolated as intermediates in the formation of the corresponding π-complexes e.g. π-C_5H_5Fe(π-pyrrolyl), although in this case, nitrogen is part of a π-system and therefore has π-acceptor properties. A series of binary metal-amides has been prepared by Bradley et al., including $Ti(NR_2)_4$ and $Nb(NR_2)_4$[15], $Cr(NR_2)_3$[16] and more recently $Cr(NEt_2)_4$[17] and $Mo(NR_2)_4$, (R = Me,Et).[18] The general preparative route was from the appropriate metal halide and lithium di-alkylamide derivatives. The compounds contain the metal in a high oxidation state, hence charge build-up at the metal is not likely to be excessive. In the complexes, π-$C_5H_5Mo(CO)_xNR_2$ we planned to study, the metal would formally be in the +2 oxidation state and points of interest would be whether the $-NR_2$ group acts as a 1- or 3-electron donor (ie. formation of tri- or di- carbonyl species) and the effect on the carbonyl frequencies compared with the $-N{=}CR_2$ group.

Chapter 2 of this thesis describes attempts to prepare amino derivatives of molybdenum and tungsten carbonyls and the conclusions which may be drawn in the light of the above remarks. Other chapters describe the structural and spectroscopic studies undertaken to determine the bonding mode(s) adopted by the aza-allyl/allene ligand in its complexes with molybdenum and tungsten and preliminary attempts to synthesise similar complexes using the preformed ligand groups (R_2CNCR_2).

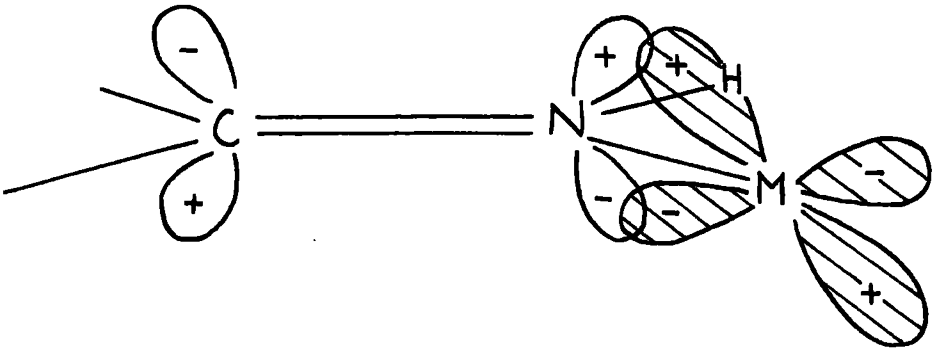


Fig. I.1(a) $d\pi$-π^* bonding involving a neutral methyleneamino-ligand

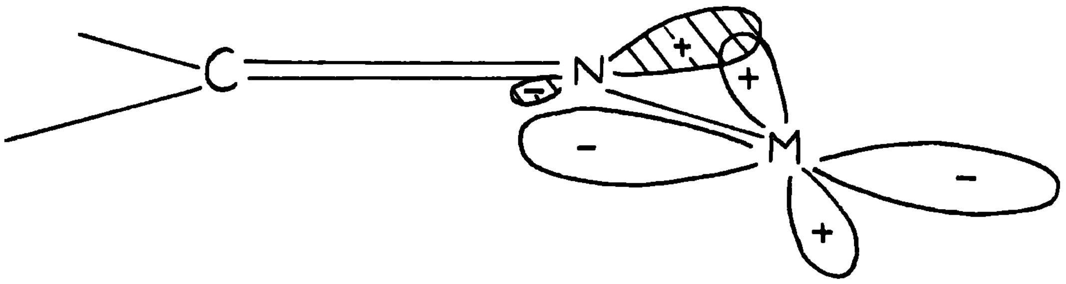


Fig. I.1(b) π-bonding involving a bent C=N-M skeleton

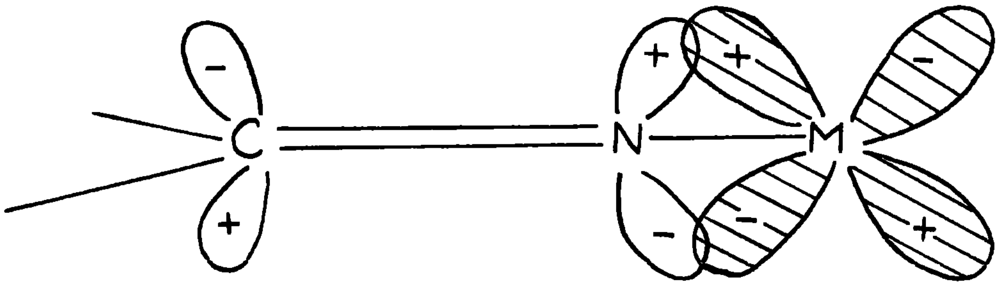


Fig.I.2(a) $d\pi$-π^* bonding involving linear C=N-M skeleton

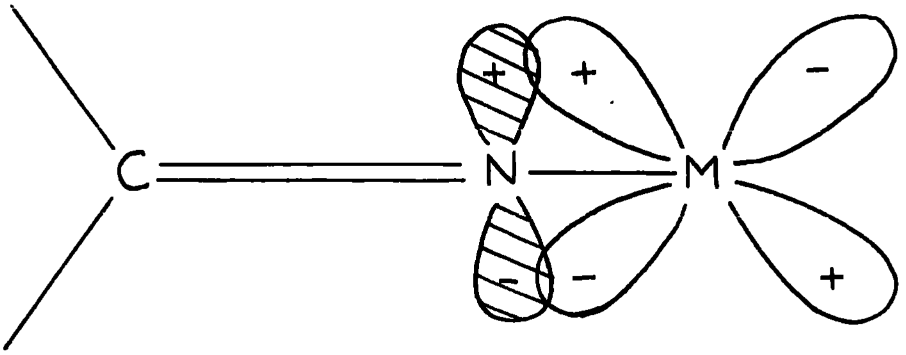
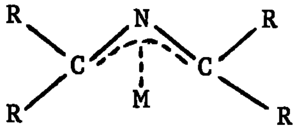
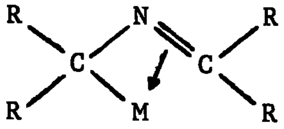


Fig. I.2(b) $p\pi$-$d\pi$ bonding involving a linear C=N-M skeleton



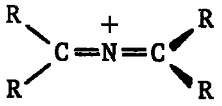
Linear or bent
aza-allyl form

(A)



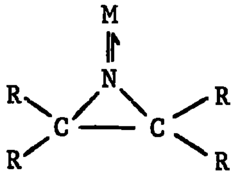
σ-π Form

(B)



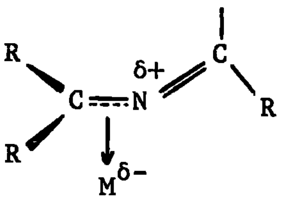
Aza-allene ligand

(C)

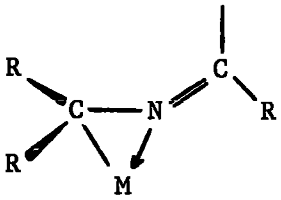


Aziridino-form

(D)



(E)



(F)

Fig. I-3 Possible structures for $(\pi\text{-}C_5H_5)M(CO)_2(R_2CNCR_2)$

CHAPTER 2

REACTIONS OF R_2N- SYSTEMS WITH $\pi-C_5H_5Mo(CO)_3Cl$

The synthetic routes used in the attempts to obtain amino derivatives of the type π-$C_5H_5Mo(CO)_2NR_2$ were those found to be successful in the preparation of corresponding ketimino derivatives, i.e. metathetical reactions using N-lithio- or N-trimethylsilylamines and π-cyclopentadienyl molybdenum tri-carbonyl chloride, π-$C_5H_5Mo(CO)_3Cl$.

A. Experimental

1. Reaction of $LiNMe_2$ with π-$C_5H_5Mo(CO)_3Cl$.

This reaction was attempted several times under varying conditions.

a) Me_2NH (0.16g., 3.5 mmole) was condensed into a 2-necked flask cooled to liquid nitrogen temperature (-196°) and ether (10 ml.), followed by ^nBuLi (3.5 mmole) in pentane (1.8 ml.), added. The mixture was allowed to warm to room temperature, during which time reaction occurred slowly, precipitating white $LiNMe_2$. After stirring for 15 min., the flask was cooled again to liquid nitrogen temperature and an ethereal solution of π-$C_5H_5Mo(CO)_3Cl$ (1.0g., 3.5 mmole, 50 ml.) added by syringe. The reaction mixture was allowed to attain room temperature and stirred for 24 hr. during which time the orange-red colour darkened considerably.

An i.r. spectrum of the reaction solution at this stage showed some remaining starting material and large quantities of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (by comparison with authentic i.r. spectra). There was however a new weak-medium absorption at 1855 cm^{-1}. The reaction mixture was filtered and the solvent removed in vacuo. π-$C_5H_5Mo(CO)_3Cl$ and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ are almost insoluble in hexane hence the residue was extracted with hexane (2 x 20 ml.) and filtered giving a red-brown solution and a red-purple residue, which was shown by i.r. spectroscopy to be a mixture of starting material and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. The hexane solution was cooled to -20°, but the only solid which could be obtained was a non-carbonyl decomposition product.

b) In the previous reaction, the $LiNMe_2$ had been used as a suspension in ether; the reactivity may be improved by keeping it in solution. Using the same quantities and procedure as above, a solution of $LiNMe_2$ in ether (65 ml) was prepared. After cooling to liquid nitrogen temperature the solution of π-$C_5H_5Mo(CO)_3Cl$ in ether (50 ml) was added by syringe and the mixture allowed to reach room temperature. The i.r. spectrum of the reaction solution after 6 hrs. showed almost complete conversion to the dimer, $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. The new carbonyl band at 1855 $cm.^{-1}$ observed in the previous reaction was detectable but very weak - a similar work-up procedure did not produce any new product.

c) To a suspension of $LiNMe_2$, prepared as in a), in ether (20 ml.) was added π-$C_5H_5Mo(CO)_3Cl$ (1.0g, 1:1 molar ratio) as a solid, through a transfer tube, at room temperature. The solution became dark red and most of the solid dissolved. An i.r. spectrum of the reaction solution after 15 min. showed that reaction had progressed significantly. Strong new carbonyl absorptions were apparent at 1955 $cm.^{-1}$ and 1860 $cm.^{-1}$ and only a small amount of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ had been formed. The mixture was filtered after about 30 min. leaving a pinkish residue which contained unreacted π-$C_5H_5Mo(CO)_3Cl$(identified by i.r. spectroscopy) and also gave a positive test for chloride ion ($AgNO_3$ test). The solvent was pumped off the filtrate and the residue extracted with hexane, but again only decomposition material could be obtained from this solution.

2. Reaction of Me_3SiNMe_2 with π-$C_5H_5Mo(CO)_3Cl$.

This reaction was performed on several occasions under different conditions (solvent, temperature etc.) and the same product was obtained from all reactions, in varying yields. The following procedure is that which optimised the yield of the required product.

π-$C_5H_5Mo(CO)_3Cl$ (1.0 g., 3.5 mmole) was dissolved in toluene (60 ml.) and a solution of Me_3SiNMe_2 (0.42g., 3.5 mmole), (prepared according to the method of Stober, Michael and Speier[19]), in toluene (40 ml.) added by syringe at room temperature. Heating the reaction mixture to 50° caused reaction to occur and was complete, as determined by i.r. spectroscopy, after 3hr. Filtration of the dark red solution followed by reduction of the volume of solvent (10^{-1} mm. Hg, 20°) and cooling to 0°, produced a dark red precipitate (I) (0.60 g.). Attempts to obtain crystals of the complex from many different solvents failed, the same red powder being recovered on each occasion (except with chloroform - see below).

Properties: The red powder melted with decomposition at 128-130° in a sealed tube, and was stable in air for several days, but in solution decomposition occurred fairly rapidly. It was very sparingly soluble in hexane, moderately soluble in ether, monoglyme, benzene and toluene. Reaction occurred in chloroform solution to regenerate the starting material π-$C_5H_5Mo(CO)_3Cl$ (identified by i.r. spectroscopy).

Analyses: C, H and N analyses were performed on several occasions on different samples. The range of results obtained was C, 36.10 - 36.70, (average 36.50); H, 3.85 - 4.20, (average 4.05); N, 3.40 - 5.40% (average 4.50%). Nitrogen determined by the Kjeldhal method gave 5.2%.

Molecular Weight: 425 by cryoscopy in benzene.

Infra-red Spectrum (KBr disc): Two strong carbonyl absorptions were observed at 1950, 1862 cm^{-1}. A medium-strong band which occurred at 3199 cm^{-1} may be assigned to ν_{N-H} or ν_{C-H} of the C_5H_5 ring. The full spectrum is: 3199 ms, 3082 m, 3020 w, 2925 m, 1950 s, 1862 s, 1465 m, 1432 m, 1418 m, 1406 m, 1356 w, 1262 w, 1208 w, 1124 m, 1059 m, 1047 m, 1023 m 1016 m, 1002 w, 906 m, 859 w, 847 w, 838 w, 818 ms, 599 w, 549 m, 513 m, 500 w, 478 m, 438 m, 429 m cm^{-1}.

^1H n.m.r. spectrum: In deuterobenzene solution a singlet at 5.12 τ due to π-C_5H_5 protons and 4 peaks of equal intensity at 7.66, 7.76, 8.16, 8.26 τ due to N-methyl protons were observed. Integration ratio of π-C_5H_5: N-Me groups was 5:6. In monoglyme solution however a very different spectrum was obtained. The π-C_5H_5 singlet was shifted downfield to 4.49 τ (5) while only two N-methyl signals were observed at 7.37, 7.47 τ (6).

Mass Spectrum (direct insertion probe at low temperature): Mo_2 containing species appeared at m/e 466, 450, 422, 394, 358. Mononuclear molybdenum containing ions were observed at m/e 299, 228, 243, 198 (w.r.t ^{98}Mo). Possible assignments are given in the discussion section.

3. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with Ph_3Sn-NMe_2

Ph_3SnNMe_2 (1.38 g., 3.5 mmoles), (prepared according to the method of Lappert and Jones[20]) was dissolved in ether (50 ml.) and a solution of π-$C_5H_5Mo(CO)_3Cl$ (1.0 g., 3.5 mmoles) in ether (70 ml.) added dropwise over 30 min. at room temperature. The mixture was stirred overnight, the colour changing from dark red-brown to a definite dark red. The i.r. spectrum at this point showed little carbonyl chloride remaining and new bands were evident at 1995, 1960, 1930, 1905, 1855 cm^{-1}.

The filtered solution was reduced to about 2/3 volume and cooled to 0°, when a dark-red powder separated out (0.1g). This was filtered off, recrystallised from toluene, and shown by melting point and i.r. spectroscopy to be identical with (I), the product from the reaction with Me_3SiNMe_2. Further reduction in volume of the mother liquor and cooling caused pale yellow crystals of π-$C_5H_5Mo(CO)_3SnPh_3$ (II) to separate (0.4g.) m.pt. 212-214°.

Analysis: Found, C, 52.20; H, 3.40%. $C_{26}H_{20}MoSnO_3$ requires C, 52.10; H, 3.35%.

Infra-red Spectrum (Nujol): ν_{CO} at 1986 s, 1917 s, 1905 s, 1891 sh.cm^{-1}.

^1H n.m.r. spectrum (Acetone): Signals at 4.41τ (5) and 2.53τ (15), (centre of multiplet), due to π-C_5H_5 and Ph protons respectively.

Mass Spectrum (direct insertion probe at source temperature): The parent ion $[\pi\text{-}C_5H_5Mo(CO)_3SnPh_3]^+$ was observed at m/e 596, the isotopic distribution pattern corresponding to that computed for $C_{26}H_{20}MoSnO_3$. The major peaks in the spectrum are listed in Table II.1.

4. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with Ph_2NLi.

A solution of Ph_2NLi was prepared by adding ^nBuLi (3.5 mmoles) in hexane (1.9 ml.) to Ph_2NH (0.59 g., 3.5 mmoles) in ether (50 ml.), at liquid nitrogen temperature. Warming to room temperature produced a clear, pale yellow solution, which was subsequently cooled in a CO_2/acetone slush bath. A solution of π-$C_5H_5Mo(CO)_3Cl$ (1.0g., 3.5 mmoles) in toluene (70 ml.) was added dropwise over 30 min. After 2 hr. at ambient temperature the i.r. spectrum of the reaction solution showed the absence of starting material and new carbonyl bands at 1960, 1860 cm^{-1}., together with a small amount of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. The solution was filtered from a

TABLE II.1

Mass Spectral Data for π-$C_5H_5Mo(CO)_3SnPh_3$

Ion	m/e[a]	m^*	fragment lost
[π-$C_5H_5Mo(CO)_3SnPh_3]^+$	596		
		542	CO
[π-$C_5H_5Mo(CO)_2SnPh_3]^+$	568		
		462	$(CO)_2$
[π-$C_5H_5MoSnPh_3]^+$	512		
$[SnPh_3]^+$	351		
[π-$C_5H_5MoPh_2]^+$	317		
[π-$C_5H_5MoPh]^+$	240		
$[SnPh]^+$	197		
[π-$C_5H_5Sn]^+$	185		
[π-$C_5H_5Mo]^+$	163		

a) refers to most abundant isotope or isotope combination i.e. ^{98}Mo, ^{120}Sn, ^{216}(Mo-Sn).

whitish solid, (which gave a positive chloride ion test), reduced to small bulk (0.1 mm. Hg; 20°) and hexane (15 ml.) added. The only materials which could be obtained from this solution were $[\pi\text{-}C_5H_5Mo(CO)_3]_2$, identified by i.r. spectroscopy, and decomposition products.

5. Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl + Ph_2NSiMe_3$.

Ph_2NSiMe_3 (0.86g., 3.5 mmoles), (prepared by reaction of $LiNPh_2$ with Me_3SiCl), and $\pi\text{-}C_5H_5Mo(CO)_3Cl$ (1.0 g., 3.5 mmoles) were dissolved in monoglyme (80 ml.) and heated to reflux temperature. No reaction was apparent over a period of 2 days except for formation of some $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. This, together with the starting complex,were recovered from solution.

6. Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with Ph(Me)NLi.

This reaction was performed in an entirely analogous manner to the reaction with Ph_2NLi. New carbonyl bands were observed at 1960, 1860 $cm.^{-1}$, and rather more $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ was formed. This was the only species which could be obtained from the reaction.

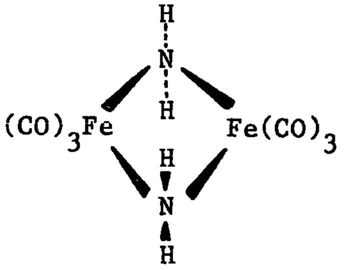
7. Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl + Ph(Me)NSiMe_3$.

No reaction was apparent in refluxing monoglyme over a period of 3 days. A mixture of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ was recovered from solution.

Discussion.

Although no products could be isolated from the majority of the reactions described, reaction did occur under the conditions used, new carbonyl species being detected in solution, but decomposing during the work-up procedure. Reaction of Me_3SiNMe_2 with π-$C_5H_5Mo(CO)_3Cl$, however, did produce a new compound (I). Analytical and spectroscopic data are not self-consistent with any one formulation, but on the basis of the available data, I is tentatively thought to be the dinuclear nitrogen-bridged species $[\pi\text{-}C_5H_5Mo(CO)_xNMe_2]_2$ where x is 1 or 2. Evidence for a dinuclear formulation comes from a) Molecular weight measurements, (obtained 425, theoretical 466 for $[\pi\text{-}C_5H_5Mo(CO)NMe_2]_2$), which although slightly low, is rather too large a value for any conceivable mononuclear species, and b) Mass spectrometric studies. Several patterns corresponding to Mo_2 species were observed, including a possible parent peak at m/e 466 (referred to $^{192}(Mo_2)$, the most abundant peak), corresponding to the formulation $[\pi\text{-}C_5H_5Mo(CO)NMe_2]_2^+$. No indication of the tetracarbonyl species $[\pi\text{-}C_5H_5Mo(CO)_2NMe_2]_2^+$ (at m/e 522) could be found. Other molybdenum containing ions and possible assignments are listed in Table II.2. No metastable peaks were observed.

Looking at the sequence of ions in Table II.2, it is a little surprising to see that systematic loss of carbonyl groups does not occur as has been observed for most metal carbonyl species including many molybdenum-organonitrogen species.[8,13,14] The amino-bridged derivatives of iron[21] and chromium[22] given below, exhibit systematic loss of CO and NO groups respectively before the amino bridges are cleaved. A more closely analogous and significant example however is the NMe_2 bridged chromium complex, $[\pi\text{-}C_5H_5Cr(NO)NMe_2]_2$ which does not apparently show systematic loss of NO groups.[23] Unfortunately no further information is given as to the observed breakdown.



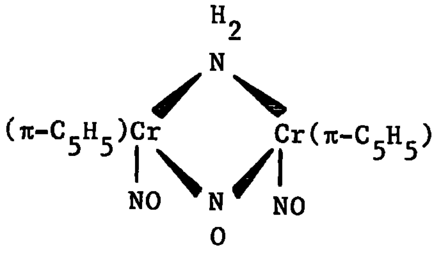


TABLE II.2

Mass Spectral Data for complex I.

m/e	Ion	Fragment lost
466	$[(C_5H_5)_2Mo_2(CO)_2(NMe_2)_2]^+$	Me + H
450	$[(C_5H_5)_2Mo_2(CO)_2(NMe_2)(NMe) -H]^+$	NMe_2
422	$[(C_5H_5)_2Mo_2(CO)_2(NMe_2)]^+$	CO
394	$[(C_5H_5)_2Mo_2(CO)(NMe_2)]^+$	C_2H_4
	or $[(C_5H_5)_2Mo_2(CO)_2(NH_2)]^+$	
299	$[(C_5H_5)_2Mo(CO)(NMe_2)-H]^+$	
243	$[(C_5H_5)_2MoMe]^+$	
228	$[(C_5H_5)_2Mo]^+$	
198	$[Mo(CO)_2NMe_2]^+$	

For complex I, the bridges are broken while at least one, and possibly both carbonyl groups remain attached. At this point rearrangement must occur resulting in both cyclopentadienyl groups becoming bound to the same metal atom. Similar transfer of C_5H_5 groups is observed in the chromium complexes mentioned above.[22,23]

This information suggests, possibly, that NMe_2 bridges are relatively weak compared with NH_2 and ketimino bridges where loss of CO before the bridging units is also observed.[8] This view may be further substantiated by the reaction of I with chloroform, in which bridge-breaking and disproportionation occurs to regenerate the starting material, π-$C_5H_5Mo(CO)_3Cl$.

The analytical data required for $[\pi\text{-}C_5H_5Mo(CO)_xNMe_2]_2$ is, for x = 1, C, 412; H, 4.75; N, 6.0%; for x = 2, C, 41.4; H, 4.2; N, 5.35%. The data obtained does not fit either of these formulations at all well, the carbon figure being particularly low. At first the product was thought to be impure, even after 'recrystallisation' since crystals other than microcrystals could never be obtained, but the consistency of the analytical results, particularly the determined carbon content on samples from different preparations tends not to support this view. Similar difficulties were experienced in the analysis of the complex π-$C_5H_5Mo(CO)_2(Ph_2CNCPh_2)$, which gave a carbon figure consistently ca. 5% low.[4] The identity of this compound however was proved conclusively by other methods. It is not possible therefore to base any conclusions on the available analytical data.

Assuming for the moment a formulation of the type $[\pi\text{-}C_5H_5Mo(CO)_xNMe_2]_2$; as well as the possibility of cis- and trans- isomers, the $(Mo\text{-}N)_2$ ring may be planar or puckered. A number of organometallic complexes containing various bridging units have been the subject of X-ray diffraction studies, and the observations are that cyclic $(MX)_2$ fragments with metal-metal bonds are planar when the ligands around the metal atom occupy 4 or 6 co-ordination sites with the metal-metal bond assigned to an additional 5th or 7th position.[24] For example, trans-[π-$C_5H_5Cr(NO)SPh]_2$,[25] [π-$C_5H_5Fe(CO)_2]_2$[26] and $[EtSFe(NO)_2]_2$[27] have essentially planar rings, while $[(p\text{-tolyl})_2C{:}NFe(CO)_3]_2$,[28] $[Ph_2PCo(\pi\text{-}C_5H_5)]_2$[29] and $[EtSFe(CO)_3]_2$[30] have substantially puckered rings, which has been rationalised by the concept of 'bent' metal-metal bonds associated with octahedral co-ordination sites on metal atoms.[24] For complex I, however, for x = 1, a double metal-metal bond would be required for the inert gas rule to hold, or for x = 2, no metal-metal bond would be required, hence the above generalisation is of little predictive use on this occasion. The infrared and ^1H n.m.r. spectra though consistent with the proposed formulation do not show whether the ring is planar or puckered. The closely analogous complex, $[\pi\text{-}C_5H_5Cr(NO)NMe_2]_2$ has been shown by X-ray diffraction to exist as cis- and trans- isomers, (Fig. II.1), both of which have planar $(Cr\text{-}N)_2$ rings, in accordance with the above generalisation,[24] with the π-C_5H_5 rings symmetrically placed with respect to a plane perpendicular to the $(Cr\text{-}N)_2$ plane and containing the Cr-Cr axis.

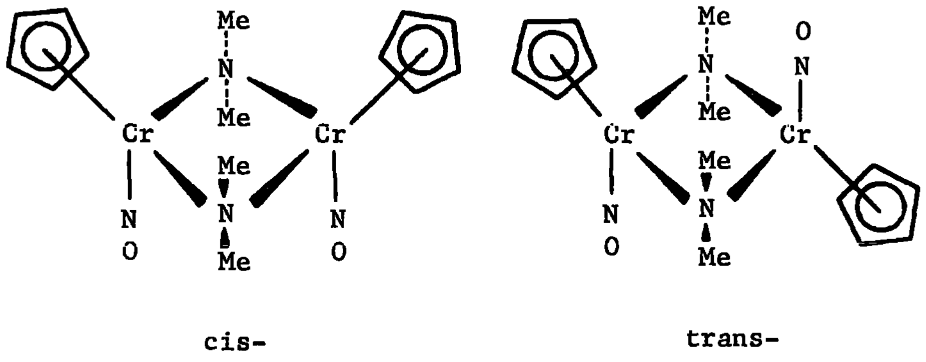
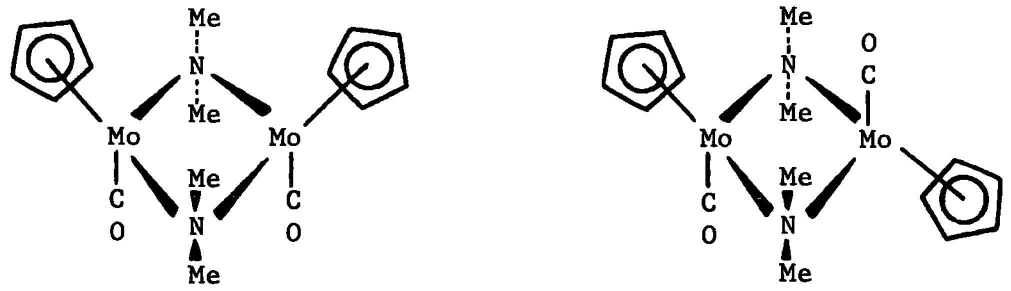


Fig. II.1

Thus in the ^{1}H n.m.r. spectrum, the trans-isomer shows a single N-Me signal, at 6.79 τ, while the cis- isomer has 2 N-Me signals, at 6.45 and 7.26 τ, as expected.

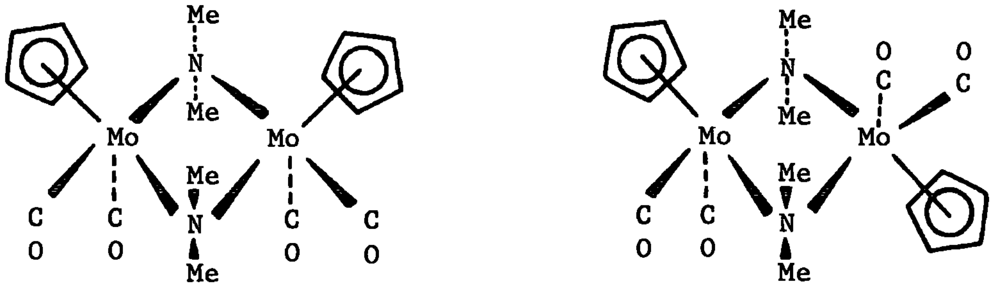
Eight possible structures for complex I are shown in Fig. II.2, obtained by taking cis- and trans- isomers with planar or puckered $(Mo-N)_2$ rings for x (no. of carbonyl groups) = 1 or 2. Considering first of all the ^{1}H n.m.r. spectrum obtained in monoglyme solution, two N-Me signals were observed at 7.37, 7.47 τ, of equal intensity, and a single, sharp π-C_5H_5 signal at 4.49 τ, the integration indicating a π-C_5H_5:NMe_2 ratio of 1:1. No change was observed on cooling to -40°. This information eliminates structures b) and d) in Fig. II.2, for which only one N-Me signal would be expected. Structures f) and h) (Fig. II.2) may also be ruled out since the π-C_5H_5 groups are not symmetrically placed with respect to the bridging units; thus two signals should result, yet only one is observed. For all other structures, however, the signals observed would be expected owing to a plane of symmetry perpendicular to the N-N axis. This poses a problem in the interpretation of the spectrum obtained in deuterobenzene solution, where a single, sharp π-C_5H_5 signal at 5.12 τ is observed, together with 4 N-Me signals of equal intensity at 7.66, 7.76, 8.16, 8.26 τ, again, the integration indicating a π-C_5H_5:NMe_2 ratio of 1:1. No single isomer as shown in Fig. II.2 could be responsible for all four N-Me signals and a mixture of isomers is unlikely due to the presence of only one π-C_5H_5 signal, which would tend to indicate a single species unless there is accidental degeneracy. It would appear therefore that the solvating benzene molecules are able to distort the molecule in some way, thus lowering the symmetry. A possible distortion process would be one in which the π-C_5H_5 rings were displaced

Fig. II.2



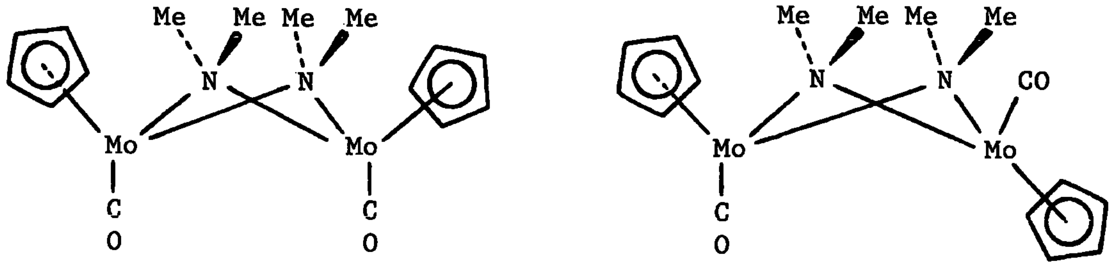
a) x = 1, planar ring, cis-

b) x = 1, planar ring, trans-



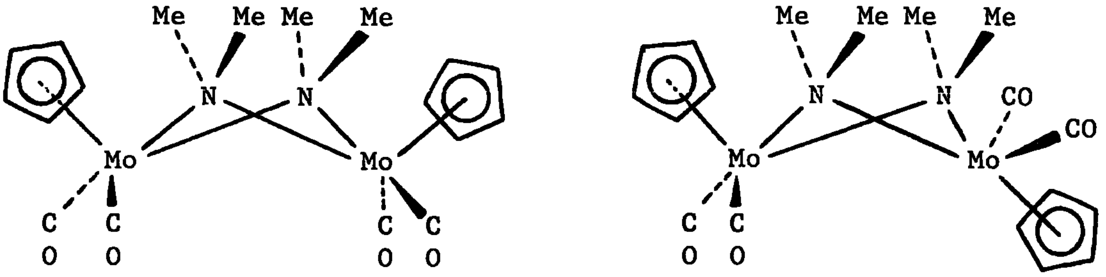
c) x = 2, planar ring, cis-

d) x = 2, planar ring, trans-



e) x = 1, puckered ring, cis-

f) x = 1, puckered ring, trans-



g) x = 2, puckered ring, cis-

h) x = 2, puckered ring, trans-an equal amount in the same direction off the metal-metal axis, thus removing the mirror plane perpendicular to the N-N axis. This would serve to remove the equivalence of the N-Me groups while retaining that of the π-C_5H_5 groups (in the cis- positions). Also significant are the large shifts shown by the signals on changing from monoglyme to benzene. If benzene molecules are becoming closely associated with the molecule in some way then one might expect the ring current of the aromatic system to affect the shielding of the neighbouring groups causing aizeable up- or downfield shifts, depending on the relative orientations of benzene and the groups concerned.

Reverting back to the monoglyme spectra, we are left with all four cis-isomers as possible structures on the basis of n.m.r. evidence. The infrared spectrum in monoglyme solution however shows only two strong carbonyl absorptions (1959, 1865 cm^{-1}.) which would tend not to favour structures c) or g) (Fig. II.2) for which more than two carbonyl bands would be predicted. Hence we may tentatively predict that the structure of I is a) or e) (Fig. II.2), although some of the data, especially the analytical data, are clearly inconsistent with this formulation and will have to be re-examined before a more definite structure can be assigned.

Since the reaction of Me_3SnNMe_2 with π-$C_5H_5M(CO)_3H$, (M = Mo, W), gave the product π-$C_5H_5M(CO)_3SnMe_3$,[31] use of the carbonyl chloride instead of the hydride may lead to a greater chance of attachment of the $-NMe_2$ fragment to the metal in preference to the tin-containing moiety. Hence in view of the non-reactivity of Ph_2N-$SiMe_3$ and $Ph(Me)N$-$SiMe_3$ with π-$C_5H_5Mo(CO)_3Cl$, the weaker Sn-N bond and also the high heat of formation of R_3Sn-X (X = halogen), the reaction of Ph_3Sn-NMe_2 with π-$C_5H_5Mo(CO)_3Cl$ was attempted first of all to see if the same product to that obtained from the analogous reaction with Me_3Si-NMe_2 would be formed.

Reaction did indeed occur under milder conditions than with $Me_3Si-NMe_2$ and although a small amount of complex I was formed, the major product was the molybdenum-tin complex $\pi-C_5H_5Mo(CO)_3SnPh_3$;[32] hence this route was not pursued further.

In the reaction of $LiNMe_2$ with $\pi-C_5H_5Mo(CO)_3Cl$, the carbonyl frequencies observed in solution are very similar to those observed in the corresponding reaction using $Me_3Si-NMe_2$, however the failure to isolate a product from the former reaction, due to its instability in solution suggests that it is a different compound. A similar parallel in carbonyl frequencies is evident in the ketimino derivatives $\pi-C_5H_5W(CO)_2NCPh_2$ and $[\pi-C_5H_5W(CO)NCPh_2]_2$,[8] hence a possibility may be that the species in solution is the compound we were hoping to prepare, i.e. the monomeric derivative $\pi-C_5H_5Mo(CO)_2NMe_2$, and is unstable in solution because the metal is unable to dissipate the excess charge build-up successfully, so the molecule subsequently falls apart.

We may conclude therefore that the $-NR_2$ ligand does not show a strong tendency to bond as a terminal three-electron ligand to metals in low oxidation states, possibly because of a lack of suitable π-acceptor orbitals to allow back-donation to occur, but follows, in preference, the more well-established tendency to use the lone pair of electrons on nitrogen to bond to a second metal atom.

CHAPTER 3

SYNTHETIC ROUTES TO KETIMINO AND AZA-ALLYL/ALLENE DERIVATIVES OF MOLYBDENUM AND TUNGSTEN

This chapter describes the synthetic methods used in the preparation of p-tolyl and other aryl ketimino and aza-allyl/allene complexes of molybdenum and tungsten. The initial aims of the work were to use the para-methyl protons on the tolyl group as ^1H n.m.r. probes in an n.m.r. study of the aza-allyl complexes (see Chapter 6) to obtain information on the bonding mode adopted by the ligand. From the results of this study it became apparent that it would be necessary to prepare other aza-allyl complexes with suitable n.m.r. probes in para- positions to obtain a fuller picture of the bonding.

A. Experimental

1) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $(p\text{-tolyl})_2C{:}NLi$, starting at low temperature.

A solution of $(p\text{-tolyl})_2$ C:NLi was prepared by the addition of n-butyl-lithium (4.3 mmole) in hexane (1.9 ml.) to $(p\text{-tolyl})_2C{:}NH$ (0.90g., 4.3 mmole) in diethyl ether (40 ml.) at -78°, the mixture then being allowed to warm slowly to room temperature. After stirring for 15 min. the solution was added to a frozen solution (-196°) of π-$C_5H_5Mo(CO)_3Cl$ (1.21g., 4.3 mmole) in ether (70 ml.) which was then allowed to warm slowly to room temperature. The solution turned a greenish-brown with deposition of a whitish solid and slow evolution of gas. The reaction was shown to be complete by i.r. spectroscopy after 20hr. at room temperature. The reaction mixture was filtered leaving a white-brown residue which contained Cl^-. The filtrate was evaporated to dryness and the oily residue extracted with hexane (5 x 10 ml.). Filtration gave a green solution, and a red powder, which was shown to be the dimer $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.11g., 10%) by i.r. spectroscopy. On cooling the

Table III.1

Mass Spectral Data for π-$C_5H_5M(CO)_2N{:}C(p\text{-tolyl})_2$, (M = Mo,W).

Ion	M = Mo			M = W		
	m/e	m*	Fragment lost	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5M(CO)_2NC(p\text{-tolyl})_2]^+$	427			513		
		372	CO		458	CO
$[\pi\text{-}C_5H_5M(CO)NC(p\text{-tolyl})_2]^+$	399			485		
		345	CO		431	CO
$[\pi\text{-}C_5H_5MNC(p\text{-tolyl})_2]^+$	371			457		
					253	(p-tolyl)CN
$[\pi\text{-}C_5H_5M(p\text{-tolyl})]^+$	254			340		
$[\pi\text{-}C_5H_5M(CO)_2NC(p\text{-tolyl})_2]^{2+}$	-			256.5		
$[\pi\text{-}C_5H_5MNC(p\text{-tolyl})_2]^{2+}$	-			228.5		

solution to 0°, deep blue crystals of π-$C_5H_5Mo(CO)_2N{:}C$(p-tolyl)$_2$ separated and were recrystallised from a hexane/monoglyme mixture. (Yield, 0.64g., 35%), m.pt. 113° (decomp.).

Properties: The dark blue crystals were air-stable for several weeks, but solutions in organic solvents decomposed rapidly in air giving brown non-carbonyl decomposition products. Solubility in aliphatic hydrocarbons was limited, but the complex was readily soluble in most other organic solvents.

Analysis: Found, C, 62.15; H, 4.30; N, 3.60%. $C_{22}H_{19}MoNO_2$ requires C, 62.20; H, 4.45; N, 3.30%.

Molecular Weight: 421 by osmometryin chloroform, (Th. 425).

Infrared Spectrum: ν_{CO}(KBr), 1949s, 1955s cm^{-1}. ν_{CO}(CS_2), 1965s, 1883s cm^{-1}.

^1H n.m.r. Spectrum ($CDCl_3$): multiplet signal at 2.70(8)τ and singlets at 4.13(5)τ , 7.57(6)τ due to aromatic, π-C_5H_5 and Me protons respectively.

Mass Spectrum: (direct insertion probe at source temperature). The isotopic distribution pattern observed for the parent ion [π-$C_5H_5Mo(CO)_2N{:}C$(p-tolyl)$_2$]$^+$ corresponded to that computed for $C_{22}H_{19}MoNO_2$. The major molybdenum containing ions observed are listed in Table III.1.

2) Reaction of π-$C_5H_5W(CO)_3Cl$ with (p-tolyl)$_2C{:}NLi$, starting at low temperature.

The corresponding reaction using π-$C_5H_5W(CO)_3Cl$ gave a rather more purple reaction solution when allowed to warm to room temperature and a similar work-up procedure gave two complexes on fractional crystallisation at 0°.

a) π-$C_5H_5W(CO)_2N{:}C$(p-tolyl)$_2$, (Yield; 0.12g., 12%), m.pt. 180-182° (decomp.).

Properties: As for the molybdenum complex.

Analysis: Found, C, 51.80; H, 3.65; N, 2.85%. $C_{22}H_{19}NO_2W$ requires C, 51.45; H, 3.75; N, 2.75%.

Molecular Weight: 519 by osmometry in benzene, (Th. 513).

Infrared Spectrum: ν_{CO}(KBr), 1938s, 1838s cm^{-1}. ν_{CO}(CS_2), 1948s, 1866s cm^{-1}.

^1H n.m.r. Spectrum ($CDCl_3$): multiplet signal at 2.82(8) τ, and singlets at 4.09(5) τ, 7.59(6) τ due to aromatic, π-C_5H_5 and Me protons respectively.

Mass Spectrum: (direct insertion probe at source temperature). For the parent ion [π-$C_5H_5W(CO)_2N{:}C$(p-tolyl)$_2$]$^+$ the isotopic distribution pattern corresponded to that computed for $C_{22}H_{19}WNO_2$. The major peaks in the spectrum are listed in Table III.1

b) π-$C_5H_5W(CO)_2$[(p-tolyl)$_2$CNC(p-tolyl)$_2$] (Yield, 0.41g., 31%). This complex is described more fully in a following section.

3) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with (p-tolyl)$_2$C:NLi, starting at room temperature.

A solution of (p-tolyl)$_2$C:NLi (4.3 mmole) in ether (40 ml.) was prepared as above and to it was added dropwise a solution of π-$C_5H_5Mo(CO)_3Cl$ (0.61g., 2.15 mmole) at room temperature. The solution became purple almost immediately and i.r. spectroscopy showed that a different product to the one described above was being formed; the reaction being complete in 2hr. The reaction mixture was filtered leaving a grey-white residue which contained NCO^-, Cl^- and also CN^-. The filtrate was evaporated to yield an oil (0.1 mm. Hg, 20°), which was extracted with a hexane/monoglyme mixture (6 x 10 ml.) and filtered. Fractional crystallisation at 0° gave two products;

a) π-$C_5H_5Mo(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$ (yield, 0.72g., 53%), m.pt. 190-191°.

Properties: The dark purple crystals were stable in air for many months; solutions were also air-stable for short periods. All common organic solvents readily dissolved the crystals (hexane to a lesser extent) forming very intense deep purple solutions.

Analysis: Found, C, 72.40; H, 5.35; N, 2.20%. $C_{37}H_{33}MoNO_2$ requires C, 71.75; H, 5.40; N, 2.25%.

Molecular Weight: 615 by osmometry in benzene, (Th. 619).

Infrared Spectrum: ν_{CO}(KBr), 1936s, 1821s cm^{-1}. ν_{CO}(CS_2), 1938s, 1844s cm^{-1}.

^{1}H n.m.r. Spectrum (CS_2): solutions showed a number of signals in the regions expected for aromatic, π-cyclopentadienyl and methyl protons, which varied in number, intensity and position, with changes in temperature. These changes are discussed more fully in Chapter 7, but data obtained at -20° are presented in Table III.2.

Mass Spectrum: (direct insertion probe at source temperature). The parent ion, $[\pi\text{-}C_5H_5Mo(CO)_2(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$ had an isotopic distribution pattern corresponding to that computed for $C_{37}H_{33}MoNO_2$. The major molybdenum containing ions are listed in Table III.3. Other significant peaks corresponding to organic fragments were $[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$ (m/e 402), $[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})]^+$ (m/e 311), $[(\underline{p}\text{-tolyl})_2CNH]^+$ (m/e 209), $[(\underline{p}\text{-tolyl})_2CN]^+$ (m/e 208), $[(\underline{p}\text{-tolyl})_2C]^+$ (m/e 194), $[\underline{p}\text{-tolylCN}]^+$ (m/e 117), $[\underline{p}\text{-tolyl}]^+$ (m/e 91).

Table III.2

^1H n.m.r. spectral data for some aza-allyl and related complexes, at -20° in CS_2 solution.

Complex	$\tau(C_6H_4)^a$	$\tau(C_5H_5)$	$\tau(Me)$
$\pi\text{-}C_5H_5Mo(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$	2.92(16)	5.54(5)	7.49(3), 7.73(3), 7.82(3), 7.86(3).
$\pi\text{-}C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]\text{-}(\underline{p}\text{-tolyl})_2CO$	2.82(24)	5.50(5)	7.49(3), 7.13(3), 7.82(3), 7.86(3), 7.58(6)
$\pi\text{-}C_5H_5W(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$	2.92(16)	5.45(5)	7.48(3), 7.71(3) 7.81(3), 7.85(3)
$\pi\text{-}C_5H_5W(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]\text{-}(\underline{p}\text{-tolyl})_2CO$	2.82(24)	5.41(5)	7.48(3), 7.71(3) 7.81(3), 7.85(3), 7.58(6)

[a] Centre of multiplet.

Table III.3

Mass Spectral data for π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$ and the ketone derivative.

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$	621		
		566	CO
$[\pi\text{-}C_5H_5Mo(CO)(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$	593		
		538	CO
$[\pi\text{-}C_5H_5Mo(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$	565		
$[\pi\text{-}C_5H_5Mo(\underline{p}\text{-tolyl})]^+$	254		
$[\pi\text{-}C_5H_5Mo(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^{2+}$	282.5		

b) π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2](p\text{-tolyl})_2C{:}O$, (Yield, < 1%), m.pt. 120-121°, as deep purple crystals.

Properties: Stability and solubility were similar to those described for π-$C_5H_5Mo(CO)_2(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$.

Analysis: Found, C, 75.25; H, 5.70; N, 1.80%. $C_{52}H_{47}MoNO_3$ requires C, 75.20; H, 5.65; N, 1.70%.

Molecular Weight: 340 by cryoscopy in cyclohexane, (Th. 829 - see Chapter 6).

Infrared Spectrum: $\nu_{C\equiv O}$(KBr), 1919s, 1832s cm.$^{-1}$; $\nu_{C=O}$(KBr); 1645 m cm.$^{-1}$; $\nu_{C\equiv O}(CS_2)$, 1938s, 1844s cm.$^{-1}$; $\nu_{C=O}(CS_2)$, 1660 m cm.$^{-1}$

^{1}H n.m.r. Spectrum: Similar changes to those observed for π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$ with temperature were apparent. Data obtained at -20° are given in Table III.2.

Mass Spectrum: (direct insertion probe at low temperature. A parent peak could not be observed. The highest molybdenum containing ion corresponded to $[\pi$-$C_5H_5Mo(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]^+$, the rest of the spectrum being very similar to that obtained for this complex (see Table III.3).

4) Reaction of π-$C_5H_5W(CO)_3Cl$ with $(p\text{-tolyl})_2C{:}NLi$, starting at room temperature.

This reaction was performed in an similar manner to the previous reaction. Fractional crystallisation at 0° led to analogous products.

a) π-$C_5H_5W(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$, (Form B - see Chapter 6), (Yield, 0.59g., 44%), m.pt. 128-132° (darkens at 80°).

Properties: as for the molybdenum complex.

Analysis: Found, C, 63.00; H, 4.75; N, 1.90%. $C_{37}H_{33}NO_2W$ requires C, 62.80; H, 4.70; N, 2.00%.

Molecular Weight: 726 by osmometry in benzene (Th. 707).

Infrared Spectrum: ν_{CO}(KBr), 1931s, 1830s cm.$^{-1}$ ν_{CO}(CS_2), 1932s, 1838s cm.$^{-1}$

^{1}H n.m.r. Spectrum: A similar temperature dependant spectrum to that observed for the corresponding molybdenum complex was obtained. Data at -20^o are presented in Table III.2.

Mass Spectrum: (direct insertion probe at source temperature). The parent ion [π-$C_5H_5W(CO)_2$(p-tolyl)$_2$CNC(p-tolyl)$_2$]$^+$ had an isotopic distribution pattern corresponding to that computed for $C_{37}H_{33}NO_2W$. The major metal containing ions are listed in Table III.4. Peaks corresponding to the organic fragment [(p-tolyl)$_2$CNC(p-tolyl)$_2$]$^+$ (m/e 402) and ions resulting from its breakdown were also observed.

Table III.4

Mass Spectral Data for π-$C_5H_5W(CO)_2$[(p-tolyl)$_2$CNC(p-tolyl)$_2$] and the ketone derivative.

Ion	m/e	m*	fragment lost
[π-$C_5H_5W(CO)_2$(p-tolyl)$_2$CNC(p-tolyl)$_2$]$^+$	707	652	CO
[π-$C_5H_5W(CO)$(p-tolyl)$_2$CNC(p-tolyl)$_2$]$^+$	679	625	CO
[π-C_5H_5W(p-tolyl)$_2$CNC(p-tolyl)$_2$]$^+$	651		
[π-C_5H_5W(p-tolyl)$_2$CNC(p-tolyl$_2$)]$^{2+}$	325.5		

b) π-$C_5H_5W(CO)_2$[(p-tolyl)$_2$CNC(p-tolyl)$_2$](p-tolyl)$_2$CO, (Yield, < 1%), m.pt. 139-140^o.

Analysis: Found, C, 68.05; H, 5.05; N, 1.65%. $C_{52}H_{47}No_3W$ requires C, 68.00; H, 5.10; N, 1.55%.

Molecular Weight: 464 by osmometry in chloroform, (Th. 917 - see Chapter 6).

Infrared Spectrum: $\nu_{C=O}$(KBr), 1917s, 1830s cm.$^{-1}$; $\nu_{C=O}$(KBr), 1645m cm.$^{-1}$, $\nu_{C=O}$(CS_2), 1932s, 1838s cm.$^{-1}$; $\nu_{C=O}$(CS_2), 1660m cm^{-1}.

^{1}H n.m.r. Spectrum: Similar changes with temperature to those observed for π-$C_5H_5W(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$were apparent. Data obtained at -20^o are presented in Table III.2.

Mass Spectrum: (direct insertion probe at low temperature). A parent ion could not be observed. The highest metal containing fragment appeared at m/e 707 corresponding to $[\pi\text{-}C_5H_5W(CO)_2(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]^+$. The major ions observed are listed in Table III.4.

5) Reaction of π-$C_5H_5M(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$, (M = Mo,W) with Triphenylphospine (1:1 molar ratio).

The complex and triphenylphosphine were dissolved in a hexane/ monoglyme mixture (ca. 1:1). No reaction was observed during a period of 24 hr. under reflux and starting materials were recovered unchanged.

6) Action of heat on π-$C_5H_5M(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2](p\text{-tolyl})_2$ C:O), (M = Mo,W).

A small quantity (ca. 20mg.) of complex was placed in a narrow glass tube (5 mm. in diameter) sealed at one end. The tube was evacuated and the solid heated to ca. 110^o for 30 min. White crystals formed on the cooler parts of the tube and were shown to be di-$\underline{p}$-tolyl ketone by i.r. and mass spectrometry. The dark purple residue was shown by i.r. spectroscopy to be π-$C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$, (M = Mo,W).

7) Reaction of π-$C_5H_5M(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$,(M = Mo, W) with (p-tolyl)$_2$C:O.

The complex and a large excess of the ketone (ca. 1:10 molar ratio) were dissolved in a hexane/monoglyme mixture. Crystallisation at 0° yielded unchanged (p-tolyl)$_2$C:O and dark purple crystals, m.pt. 120-121° (M = Mo); 139-140°(M = W), identified by i.r. spectroscopy as π-$C_5H_5M(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2](p\text{-tolyl})_2C{:}O$.

8) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with (p-tolyl)$_2$C:NSiMe$_3$.

π-$C_5H_5Mo(CO)_3Cl$ (0.56g., 2mmole) and (p-tolyl)$_2$C:NSiMe$_3$ (0.56g., 2mmole) were dissolved in monoglyme (20ml.) and heated at reflux temperature for 1½ hr. when reaction was shown to be complete, by i.r. spectrescopy. New carbonyl bands were observed at 1958, 1871 cm^{-1}. The green-brown solution was filtered, reduced in volume (0.1 mm.Hg, 20°) and hexane (20ml.) added. Crystallisation at 0° produced dark-blue crystals of the monomeric species π-$C_5H_5Mo(CO)_2N{:}C(p\text{-tolyl})_2$, identified by i.r. and mass spectrometry. This was the only product obtained from the reaction and has already been described (Section 1).

9) Reaction of π-$C_5H_5W(CO)_3Cl$ with (p-tolyl)$_2$C:NSiMe$_3$.

π-$C_5H_5W(CO)_3Cl$ (0.74g., 2 mmole) and (p-tolyl)$_2$C:NSiMe$_3$ (0.56g., 2mmole) were dissolved in monoglyme (20 ml.) and heated at reflux temperature for 3 hr. when reaction was shown to be complete, by i.r. spectroscopy. New carbonyl bands were observed at 1946, 1860 cm.$^{-1}$ The dark-green solution was filtered, reduced in volume (0.1 mm.Hg, 20°) and hexane (25 ml.) added. Crystallisation at 0° gave dark-blue crystals of the monomeric species π-$C_5H_5W(CO)_2N{:}C(p\text{-tolyl})_2$, identified by i.r. and mass spectrometry. This was the only product obtained from the reaction and has already been described (section 2).

Other aza-allyl/allene complexes of molybdenum and tungsten, prepared specifically for the n.m.r. study to be described in Chapter 7, were obtained by using the conditions favouring their formation, i.e. reaction of π-$C_5H_5M(CO)_3Cl$ with the appropriate lithio-ketimine at room temperature, and although small amounts of other species (probably ketimino derivatives) were observed, by i.r. spectroscopy, in the reaction solution, no attempt was made to isolate them, except in the reaction of π-$C_5H_5W(CO)_3Cl$ with $(\underline{p}\text{-}CF_3C_6H_4)_2C{:}NLi$ when the two products were obtained in comparable yield.

All reactions were carried out in an analogous manner to reactions 3) and 4) described above differing only in the preparation of the lithio-ketimine solutions, which previously had been prepared from the ketimine and n-butyllithium. The following method was devised for the preparation of lithio-ketimine solutions from readily available starting materials, utilising the method of metal-halogen exchange.[33]

Typically, an aryl bromide ($R''Br$) (4mmole) was dissolved in ether (50 ml.) and cooled in liquid nitrogen (ca. - 100°). A solution of ^nBuLi (4 mmole) in hexane (1.25 ml.) was added by syringe and the solution warmed to room temperature with stirring. Change of colour indicated reaction to be occurring, and the solution was stirred for 30 min. to ensure complete equilibration (for aryl bromides and n-butyllithium the equilibrium position favours almost complete formation of the aryl-lithium compound)[33]. The solution was cooled again in liquid nitrogen (ca. - 100°) and a solution of an aryl nitrile (R'CN) (4mmole) in ether (5-10 ml.) was added by syringe. An orange or red colour developed rapidly indicating formation of the lithio-ketimine; the solution was warmed to room temperature and stirred for ca. 20 min. Reaction with π-$C_5H_5M(CO)_3Cl$ (2mmole) and the initial workup procedure are as described in sections 3) and 4) above.

Crystallisation at 0^{o} from hexane or hexane/monoglyme mixtures gave the following products of the type π-$C_5H_5M(CO)_2(R'R''CNCR'R'')$:

a) R' = p-$MeOC_6H_4$-, R" = p-MeC_6H_4-, M = Mo: m.pt. 86-88^{o}.

Properties: the dark purple crystals were stable in air for many months though solutions were rather less air-stable decomposing slowly in a matter of days. Solubility in hexane was slight, though most other common organic solvents readily dissolved the crystals giving very intense purple solutions.

Analysis: Found, C, 68.35; H, 4.90; N, 2.20%. $C_{37}H_{33}MoNO_4$ requires C, 68.10; H, 5.10; N, 2.15%.

Infrared Spectrum: ν_{CO} (KBr), 1930s, 1831s cm^{-1}.

^{1}H n.m.r. Spectrum: A number of signals which changed in number, position and intensity with variation in temperature were observed (see Chapter 7). Data obtained at -40^{o} are presented in Table III.5.

Mass Spectrum: (direct insertion probe at source temperature). The parent ion $[\pi\text{-}C_5H_5Mo(CO)_2\{(p\text{-}MeC_6H_4)(p\text{-}MeOC_6H_4)CNC(p\text{-}MeC_6H_4)(p\text{-}MeOC_6H_4)\}]^+$ had an isotopic distribution pattern corresponding to that computed for $C_{37}H_{33}MoNO_4$. The major ions observed are listed in Table III.6.

b) R' = C_6H_5, R" = p-MeC_6H_4, M = Mo, m.pt. 183-184^{o}.

Properties: As for the previous complex.

Analysis: Found, C, 71.40; H, 4.95; N, 2.25%. $C_{35}H_{29}MoNO_2$ requires C, 71.00; H, 4.90; N, 2.35%.

Infrared Spectrum: ν_{CO}(KBr), 1924s, 1841s $cm.^{-1}$

^{1}H n.m.r. Spectrum: The full temperature dependant spectrum is discussed in Chapter 7. Data obtained at -40^{o} are presented in Table III.5.

Table III.5

^{1}H[a] and ^{19}F[b] n.m.r. data for some aza-allyl/allene complexes.

Complex	Temp.	τ(aromatic)[c]	τ(C_5H_5)	τ(MeO)	τ(Me)	ppm.(CF_3)
π-$C_5H_5Mo(CO)_2[(p\text{-}MeOC_6H_4)(p\text{-}MeC_6H_4)CNC\text{-}(p\text{-}MeOC_6H_4)(p\text{-}MeC_6H_4)]$	-40°	2.90	5.39,5.48 5.51	6.11,6.27 6.40,6.45	7.46,7.70 7.79,7.86	
π-$C_5H_5Mo(CO)_2[(p\text{-}MeC_6H_4)(C_6H_5)CNC\text{-}(p\text{-}MeC_6H_4)(C_6H_5)]$	-40°	2.85	5.46,5.49, 5.55,5.58		7.52,7.75 7.84,7.88	
π-$C_5H_5Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$	-20°		5.32(5)[d]			62.23(3),62.79(3), 62.90(3),63.44(3)
π-$C_5H_5W(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$	-35°		5.40(5)[e]			62.58(3),63.06(3), 63.21(3),63.76(3)

[a] CS_2 solution. [b] Toluene solution, p.p.m.values rel. to $CFCl_3$. [c] Centre of multiplet. [d] 20°. [e] -5°.

Table III.6

Mass Spectral data for π-$C_5H_5Mo(CO)_2(R'R''CNCR'R'')$ (R' = p-$MeOC_6H_4$, R'' = p-MeC_6H_4).

Ion	m/e	m *	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2R'R''CNCR'R'')]^+$	653		
		598	CO
$[\pi\text{-}C_5H_5Mo(CO)(R'R''CNCR'R'')]^+$	625		
		571	CO
$[\pi\text{-}C_5H_5Mo(R'R''CNCR'R'')]^+$	597		
$[\pi\text{-}C_5H_5MoR']^+$	270		
$[\pi\text{-}C_5H_5Mo(R'R''CNCR'R'')]^{2+}$	298.5		
$[R'R''CNCR'R'']^+$	434		

Mass Spectrum: (direct insertion probe at source temperature). The isotopic distribution pattern observed for the parent ion, $[\pi\text{-}C_5H_5Mo(CO)_2\{(\underline{p}\text{-}MeC_6H_4)(C_6H_5)CNC(C_6H_5)(\underline{p}\text{-}MeC_6H_4)\}]^+$ corresponded to that computed for $C_{35}H_{29}MoNO_2$. The major ions are listed in Table III.7.

Table III.7

Mass Spectral Data for $\pi\text{-}C_5H_5Mo(CO)_2(R'R''CNCR'R'')$ $R' = C_6H_5$, $R'' = \text{p-}MeC_6H_4$.

Ion	m/e	m*	fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2(R'R''CNCR'R'')]^+$	593	538	CO
$[\pi\text{-}C_5H_5Mo(CO)(R'R''CNCR'R'')]^+$	565	511	CO
$[\pi\text{-}C_5H_5Mo(R'R''CNCR'R'')]^+$	537		
$[\pi\text{-}C_5H_5Mo(R'R''CNCR'R'')]^{2+}$	268.5		
$[R'R''CNCR'R'']^+$	374		

c) $R' = R'' = \underline{p}\text{-}CF_3C_6H_4$, M = Mo; m.pt. 163-164°.

Properties: the blue-black, air-stable, microcrystalline solid was very soluble in all common organic solvents giving bluish-purple solutions which were also fairly air-stable.

Analysis: Found, C, 52.90; H, 2.50; N, 1.70; F, 26.80%. $C_{37}H_{21}F_{12}MoNO_2$ requires C, 53.20; H, 2.50; N, 1.70; F, 27.30%.

Molecular Weight: 825 by osmometry in benzene, (Th. 835).

Infrared Spectrum: ν_{CO}(KBr), 1962s, 1954s, 1883s, 1857s cm.$^{-1}$, ν_{CO}(hexane), 1965s, 1877s cm.$^{-1}$ The four bands in the KBr spectrum are thought to arise from the presence of isomers in the solid state (see Chapter 6).

^{1}H and ^{19}F n.m.r. Spectra: temperature dependant spectra were observed which are discussed more fully in Chapter 7. Data obtained at -20° are presented in Table III.5.

Mass Spectrum: (direct insertion probe at source temperature). The parent ion, $[\pi\text{-}C_5H_5Mo(CO)_2\ (\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2\ ]^+$ had an isotopic distribution pattern corresponding to that computed for $C_{37}H_{21}F_{12}MoNO_2$. The parent ion in this case appears to have a choice of breakdown pathways, either loss of a fluorine atom followed by loss of two carbonyl groups or stepwise loss of the carbonyl groups followed by loss of a fluorine atom. The major ions observed are listed in Table III.8.

d) R' = R" = $\underline{p}$-FC_6H_4, M = Mo, m.pt. 164-165°.

Properties: Stability and solubility are similar to other aza-allyl/allene complexes described.

Analysis: Found, C, 62.40; H, 3.30; N, 2.45; F, 12.50%.

$C_{33}H_{21}F_4MoNO_2$ requires C, 62.30; H, 3.30; N, 2.20; F, 12.00%.

Infrared Spectrum: ν_{CO}(KBr), 1936s, 1847s cm.$^{-1}$

^{1}H and ^{19}F n.m.r. Spectra: The ^{1}H n.m.r. spectrum showed a multiplet for the aromatic (16) and a singlet for the π-C_5H_5(5) protons in the expected regions. The ^{19}F n.m.r. spectrum showed a number of signals which varied in a manner different from the variations noted for the other aza-allyl/allene complexes. Data obtained at single temperatures are not particularly meaningful and are therefore not given at this stage. A fuller discussion of the behaviour in the full temperature range studied will be given in Chapter 7.

Mass Spectrum:(direct insertion probe at source temperature). The parent ion $[\pi\text{-}C_5H_5Mo(CO)_2\ (\underline{p}\text{-}FC_6H_4)_2CNC(\underline{p}\text{-}FC_6H_4)_2\ ]^+$ had an isotopic distribution pattern corresponding to that computed for $C_{33}H_{21}F_4MoNO_2$. In this case

Table III.8

Mass Spectral Data for $\pi\text{-}C_5H_5Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2\{(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2\}]^+$	837	782	CO
$[\pi\text{-}C_5H_5Mo(CO)_2\{(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)\text{-}(\underline{p}\text{-}CF_2C_6H_4)\}]^+$	818		
$[\pi\text{-}C_5H_5Mo(CO)\{(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2\}]^+$	809		
		754	CO
$[\pi\text{-}C_5H_5Mo\{(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2\}]^+$	781		
$[\pi\text{-}C_5H_5Mo\{(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)\text{-}(\underline{p}\text{-}CF_2C_6H_4)\}]^+$	762		
$[(\underline{p}\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2]^+$	618		

loss of a fluorine atom from the parent ion was not observed. The major ions are listed in Table III.9.

The reaction between π-$C_5H_5W(CO)_3Cl$ and ($\underline{p}$-$CF_3C_6H_4)_2C$:NLi produced two products in significant yield.

i) π-$C_5H_5W(CO)_2[(\underline{p}$-$CF_3C_6H_4)_2CNC(\underline{p}$-$CF_3C_6H_4)_2]$, (yield, 0.41g., 22%), m.pt. 153-154^o.

Properties: as for the other aza-allyl/allene complexes.

Analysis: Found, C, 48.00; H, 2.50; N, 1.50%. $C_{37}H_{21}F_{12}NO_2W$ requires C, 48.10; H, 2.30; N, 1.50%.

Infrared Spectrum: ν_{CO}(KBr), 1963s, 1954s, 1880s, 1866s cm.$^{-1}$, ν_{CO}(Hexane), 1961s, 1873s cm^{-1}. Again the four bands in the KBr spectrum are thought to arise from the presence of isomers in the solid state (see Chapter 6).

^{1}H and ^{19}F n.m.r. Spectra: temperature dependant spectra were observed which are discussed more fully in Chapter 7. Data obtained at -35^o are presented in Table III.5.

Mass Spectrum: (direct insertion probe at source temperature). A similar breakdown to the molybdenum analogue was observed in that the parent ion initially lost either a fluorine atom or carbonyl group. The major ions observed are listed in Table III.10.

ii) π-$C_5H_5W(CO)_2N$:$C(\underline{p}$-$CF_3C_6H_4)_2$, (yield, 0.56g., 45%), m.pt. 146-150^o (decomp.).

Properties: the air-stable, microcrystalline, dark-green solid was soluble in all common organic solvents giving green solutions which were air-stable for short periods only.

Table III.9

Mass Spectral Data for $\pi\text{-}C_5H_5Mo(CO)_2[(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2]$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2\{(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2\}]^+$	637		
		582	CO
$[\pi\text{-}C_5H_5Mo(CO)\{(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2\}]^+$	609		
		555	CO
$[\pi\text{-}C_5H_5Mo\{(p\text{-}FC_6H_4)_2CN\dot{C}(p\text{-}FC_6H_4)_2\}]^+$	581		
$[\pi\text{-}C_5H_5Mo\{(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2\}]^{2+}$	290.5		
$[\pi\text{-}C_5H_5Mo(p\text{-}FC_6H_4)]^+$	258		
$[(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2]^+$	418		

Table III.10

Mass Spectral Data for $\pi\text{-}C_5H_5W(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$.

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5W(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]^+$	923		
$[\pi\text{-}C_5H_5W(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)\text{-}(p\text{-}CF_2C_6H_4)\}]^+$	904		
		869	CO
$[\pi\text{-}C_5H_5W(CO)\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]^+$	895		
		840	CO
$[\pi\text{-}C_5H_5W\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]^+$	867		
		796	2CO
		829	F
$[\pi\text{-}C_5H_5W\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)(p\text{-}CF_2C_6H_4)\}]$	848		
		742	C_5H_5
$[W\ (p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]^+$	802		
$[\pi\text{-}C_5H_5W(CO)_2NC(p\text{-}CF_3C_6H_4)_2]^+$	621		
		566	CO
$[\pi\text{-}C_5H_5W(CO)NC(p\text{-}CF_3C_6H_4)_2]^+$	593		
		538	CO
$[\pi\text{-}C_5H_5WNC(p\text{-}CF_3C_6H_4)_2]^+$	565		
		274	$(p\text{-}CF_3C_6H_4)CN$
$[\pi\text{-}C_5H_5W(p\text{-}CF_3C_6H_4)\ ]^+$	394		

The last four ions correspond to the parent and breakdown ions of the ketimino derivative and are more likely to be due to impurity (the two complexes were difficult to separate by fractional crystallisation) rather than fragmentation products.

Analysis: Found, C, 42.30; H, 2.25; N, 2.25%. $C_{22}H_{13}F_6NO_2W$ requires C, 42.50; H, 2.10; N, 2.25%.

Infrared Spectrum: ν_{CO}(KBr), 1956s, 1869s, cm.$^{-1}$, ν_{CO}(Hexane), 1975s, 1898s cm^{-1}.

^1H and ^{19}F n.m.r. Spectra: (toluene solution). In the ^1H n.m.r. spectrum a single π-C_5H_5 signal was observed at 4.69τ. The ^{19}F n.m.r. spectrum showed a single $-CF_3$ signal 62.9 ppm upfield from $CFCl_3$.

Mass Spectrum: (direct insertion probe at source temperature). The parent ion $[\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-}CF_3C_6H_4)_2]^+$ had an isotopic distribution pattern corresponding to that computed for $C_{22}H_{13}F_6NO_2W$. The major ions observed are listed in Table III.11.

10) Reaction of π-$C_5H_5W(CO)_3Cl$ with Ph_2C:NLi in the presence of Ph_2C:O.

Ph_2C:NH (0.645g., 3.5 mmole) and Ph_2C:O (0.64g., 3.5 mmole) were dissolved in ether (40 ml.) and cooled in liquid nitrogen (ca. -100°). ^{n}BuLi (3.5 mmole) in hexane (1.25 ml.) was added by syringe. A dark-red colour developed immediately but on warming to room temperature the colour lightened and after stirring for ca. 20 min. at room temperature, the solution was pale yellow. A solution of π-$C_5H_5W(CO)_3Cl$ (1.33g., 3.5 mmole) in ether (70 ml.) was added dropwise at room temperature. Initially the solution turned purple, but after 5-10 min. a greenish tinge began to develop which became more prominent as reaction progressed. The i.r. spectrum of the solution after 24 hr. at room temperature indicated little residual starting material and new, strong carbonyl absorptions at 1960, 1873 cm^{-1}. A weak band was also observed at 1850 cm.$^{-1}$, and a medium band at 1670 cm.$^{-1}$ The reaction solution was filtered from a grey-white residue, which contained Cl^- and very small amounts of NCO^- and CN^-, and the solvent

Table III.11

Mass Spectral Data for π-$C_5H_5W(CO)_2NC(p\text{-}CF_3C_6H_4)_2$.

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-}CF_3C_6H_4)_2]^+$	621		
$[\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-}CF_3C_6H_4)(\underline{p}\text{-}CF_2C_6H_4)]^+$	602		
		566	CO
$[\pi\text{-}C_5H_5W(CO)NC(\underline{p}\text{-}CF_3C_6H_4)_2]^+$	593		
		538	CO
$[\pi\text{-}C_5H_5WNC(\underline{p}\text{-}CF_3C_6H_4)_2]^+$	565		
$[\pi\text{-}C_5H_5W(\underline{p}\text{-}CF_3C_6H_4)]^+$	394		
		355	HF
$[\pi\text{-}C_5H_5W(\underline{p}\text{-}CF_2C_6H_3)]^+$	374		
$[\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-}CF_3C_6H_4)_2]^{2+}$	310.5		

removed in vacuo. The residue was extracted with hexane (8 x 10 ml.) and filtered through a ½" column of coarse alumina. The resulting dark-green solution was reduced to small bulk, (0.1 mm.Hg, 20°), and cooled to 0° when dark blue crystals separated out. These were filtered off, washed with hexane and pumped dry.(Yield 0.34g.), m.pt. 110-112°. This complex was identified by mass spectroscopic and analytical data as the mononuclear ketimino complex $\pi\text{-}C_5H_5W(CO)_2NCPh_2$, previously obtained from the reaction of $\pi\text{-}C_5H_5W(CO)_3Cl$ with $Ph_2C{:}NSiMe_3$[8]. The only inconsistent set of data obtained was the solid state i.r. spectrum, which now showed four strong carbonyl absorptions at 1956, 1940, 1869, 1863 $cm.^{-1}$, instead of the two bands (1942s, 1873s $cm.^{-1}$) previously reported. This has been shown, however, to be due to lack of resolution in the 2000-1600 $cm.^{-1}$ region on the spectrophotometer used at that time. The four bands may be due to conformational isomers of the type observed for the analogous complex $\pi\text{-}C_5H_5Mo(CO)_2N{:}C^tBu_2$[13], (see Chapter 4), or to solid state effects.

11) Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with $Ph_2C{:}NLi$ in the presence of $Ph_2C{:}O$.

This reaction was carried out in an analogous manner to the previous reaction. The resulting dark-green hexane solution on cooling to 0° gave dark-blue crystals, which were filtered off, washed with hexane and pumped dry (yield, 0.64g.), m.pt. 104-106°. [This complex is believed to be $\pi\text{-}C_5H_5Mo(CO)_2NCPh_2$, previously reported as a brown powder obtained on one occasion from the reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with $Ph_2C{:}NSiMe_3$[8]. Although the analytical and spectroscopic data obtained at that time were consistent with the proposed formulation, the i.r. and n.m.r. data in particular were unusual (see Chapter 4 for a fuller discussion) and bore no resemblance to the tungsten analogue nor to the corresponding p-tolyl compounds (molybdenum and tungsten) described earlier. The complex obtained from the reaction just described, however, closely resembles these latter three complexes in both physical appearance and spectroscopic properties (given below). Consequently this new complex is thought to be π-$C_5H_5Mo(CO)_2NCPh_2$, which thus questions the identity of the complex originally thought to have this formulation. Alternative structures are suggested in Chapter 4.]

Properties: the air-stable, dark-blue crystals were moderately soluble in hexane and very soluble in most other common organic solvents giving intense, dark-green air-sensitive solutions.

Analysis: Found, C, 60.35; H, 4.15; N, 3.80%. $C_{20}H_{15}MoNO_2$ requires C, 60.50; H, 3.80; N, 3.55%.

Infrared Spectrum: ν_{CO}(KBr), 1964s, 1949s, 1879s, 1874s cm.$^{-1}$, ν_{CO}(hexane), 1974s, 1897s cm^{-1}. The four carbonyl stretching frequencies in the solid state may be due to conformational isomers of the type found in the analogous t-butyl complex π-$C_5H_5Mo(CO)_2NC^tBu_2$,[13] (see Chapter 4), or to solid state effects.

^{1}H n.m.r. Spectrum: (CS_2 solution). A multiplet signal at 2.71τ (10) and a singlet at 4.22τ (5) due to phenyl and π-C_5H_5 protons respectively were observed.

Mass Spectrum: (direct insertion probe at source temperature). The isotopic distribution pattern observed for the parent ion, $[\pi$-$C_5H_5Mo(CO)_2NCPh_2]^+$ corresponded to that computed for $C_{20}H_{15}MoNO_2$. The major ions observed in the spectrum are listed in Table III.12.

12) Reaction of π-$C_5H_5W(CO)_3Cl$ with Ph_2C:NLi in the presence of (p-tolyl)$_2C$:O.

This reaction was performed in exactly the same manner as the previous

Table III.12

Mass Spectral Data for π-$C_5H_5Mo(CO)_2NCPh_2$.

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2NCPh_2]^+$	399		
		344	CO
$[\pi\text{-}C_5H_5Mo(CO)NCPh_2]^+$	371		
		317	CO
$[\pi\text{-}C_5H_5MoNCPh_2]^+$	343		
		168	PhCN
$[\pi\text{-}C_5H_5MoPh]^+$	240		
$[\pi\text{-}C_5H_5Mo]^+$	163		
$[\pi\text{-}C_5H_5Mo(CO)_2NCPh_2]^{2+}$	199.5		
$[\pi\text{-}C_5H_5MoNCPh_2]^{2+}$	171.5		

reactions. Dark-blue crystals of π-$C_5H_5W(CO)_2NCPh_2$ were obtained, m.pt. 110-112°, identified by i.r. and mass spectroscopy. There was no evidence for the presence of π-$C_5H_5W(CO)_2NC$(p-tolyl)$_2$.

13) Reaction of π-$C_5H_5W(CO)_3Cl$ with (p-tolyl)$_2$C:NLi in the presence of $Ph_2C:O$.

A similar reaction to those described immediately above took place. Cooling the resulting dark-green hexane solution to 0° produced dark-blue crystals, m.pt. 180-182° (decomp.), identified by i.r. and mass spectroscopy as π-$C_5H_5W(CO)_2NC$(p-tolyl)$_2$. No evidence was found for the presence of π-$C_5H_5W(CO)_2NCPh_2$.

B. Discussion.

The reactions described above involving (p-tolyl)$_2$C:NLi clearly indicate that introduction of a methyl group into the para- position of an aromatic ring produces a delicate balance between the formation of ketimino- and aza-allyl/allene complexes, i.e. π-$C_5H_5M(CO)_2NCR_2$ or π-$C_5H_5M(CO)_2(R_2CNCR_2)$. A controlling factor is initial reaction temperature. Observations made from the large number of reactions performed show that in general, the lower the initial reaction temperature, the greater the proportion of ketimino-complex formed. With the other ketimines used in the past, the balance has been rather more heavily weighted towards one or the other. Reaction of $Ph_2C:NLi$ with π-$C_5H_5M(CO)_3Cl$ (M = Mo,W) gave only the aza-allyl/allene derivatives, under all conditions tried[8], while the corresponding reaction using $^tBu_2C:NLi$ produced the ketimino derivatives as the sole products,[13] although there is the more likely possibility that this may be a result of the steric requirements of the ^{t}Bu groups, rather than an electronic effect.

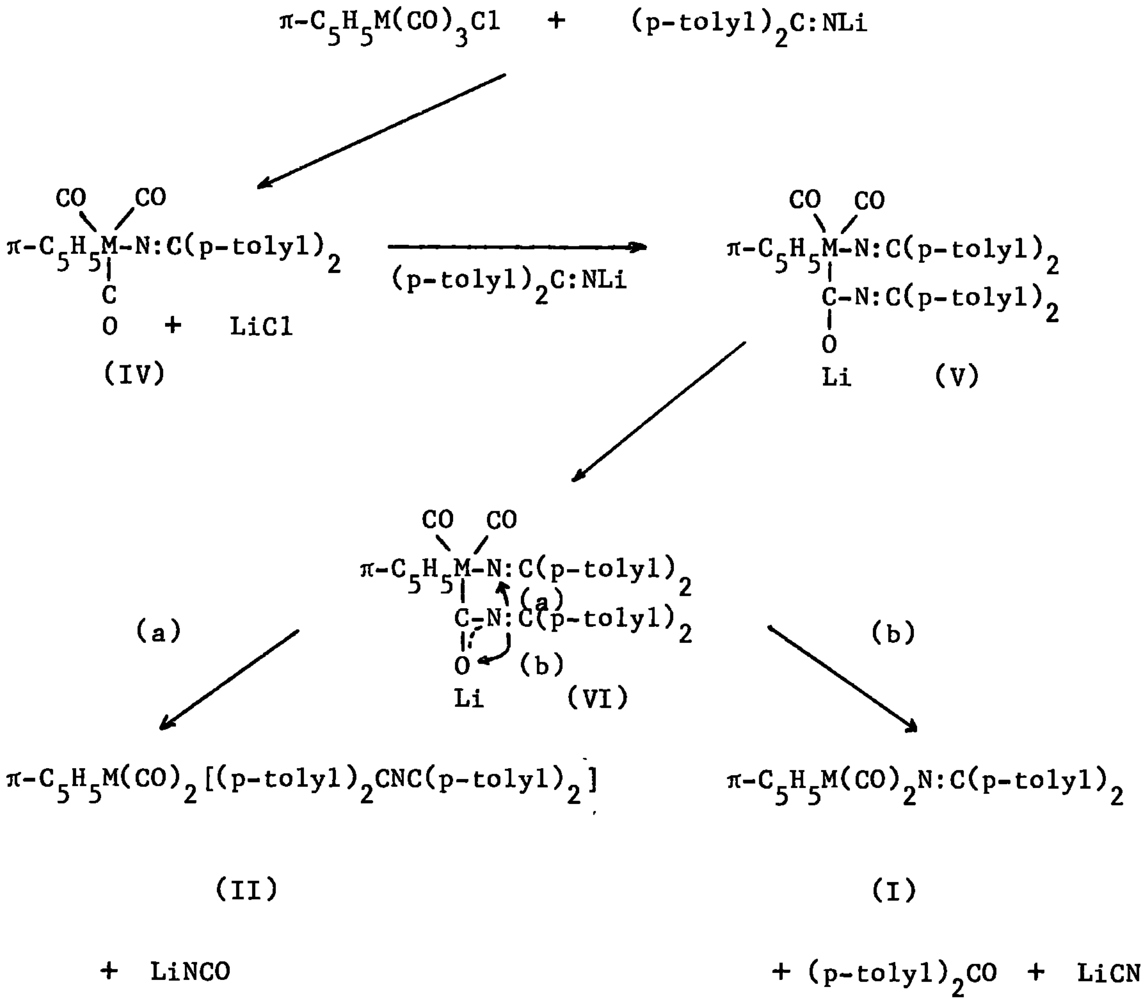
The analogous reaction of the mixed ketimino ligand, $Ph(^tBu)C{:}NLi$, also gave only the ketimino derivative, and one might have thought that this ligand would have rather less stringent steric requirements than the di-t-butyl ligand, as in an aza-allyl/allene complex the ^tBu groups could be able to take up positions remote from groups likely to interfere.* This suggests that electronic factors may be important in the latter reaction.

The reaction of $(\underline{p}\text{-tolyl})_2C{:}NLi$, as well as producing the ketimino and aza-allyl/allene derivatives, gave a type of complex not produced in reactions involving the other ketimines used, and is formulated as $\pi\text{-}C_5H_5M(CO)_2\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}(\underline{p}\text{-tolyl})_2C{:}O$ (M = Mo,W) i.e. an aza-allyl/allene derivative apparently having a ketone molecule co-ordinated to the metal in some way (see Chapter 6). This type of complex could not be obtained for the other aza-allyl/allene complexes prepared, and di-p-tolyl ketone could not be replaced by a different ketone (e.g. Ph_2CO). The ketone is formed during the reaction, its presence as a hydrolysis product in the ketimine used having been eliminated by use of a ketiminolithium solution prepared from p-tolyl-lithium and p-tolunitrile, which still resulted in formation of the complex. Atmospheric hydrolysis is unlikely as reactions were performed with rigorous exclusion of oxygen and moisture. The mechanism of the formation of the aza-allyl ligand itself is not yet clear. It is almost certain to take place at the metal, as one of the carbonyl groups is lost as NCO^- and also possibly as CN^-. If initial co-ordination of one ketimine unit occurs with elimination of Cl^-(IV) (see Scheme) then attack of a further ketimine unit at a carbonyl carbon atom may be envisaged. Similar attack of $LiNR_2$ molecules at metal carbonyl groups is well established and is a route to carbamoyl complexes.[34] Breakdown of the C=N system of (V), resulting in formation of a carbene

---

* Construction of a reasonable model suggests that this type of complex would be sterically possible though this does not imply that the transition states leading to its formation would also be sterically feasible.

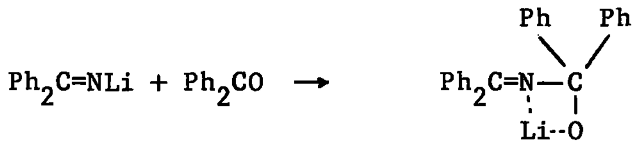
Scheme


π-C5H5M(CO)3Cl + (p-tolyl)2C:NLi
CO CO
π-C5H5M-N:C(p-tolyl)2
C
O + LiCl
(IV)
(p-tolyl)2C:NLi
CO CO
π-C5H5M-N:C(p-tolyl)2
C-N:C(p-tolyl)2
O
Li (V)
CO CO
π-C5H5M-N:C(p-tolyl)2
(a)
C-N:C(p-tolyl)2
O (b)
Li (VI)
(a)
(b)
π-C5H5M(CO)2[(p-tolyl)2CNC(p-tolyl)2]
(II)
+ LiNCO
π-C5H5M(CO)2N:C(p-tolyl)2
(I)
+ (p-tolyl)2CO + LiCN

intermediate, may then occur followed by attack of this carbene moiety (VI) at the nitrogen of the other co-ordinated ketimine unit, forming (II) and eliminating the cyanate ion. Alternatively the carbene may attack the oxygen of the carbonyl group, resulting in formation of the ketone, complex (I), and the cyanide ion - all observed products. It would be of interest to perform the reaction in the presence of a carbene trap (e.g. cyclohexene) to see if a cyclopropyl adduct could be isolated and also to react the ketimino derivatives, π-$C_5H_5M(CO)_2NCR_2$ with say R_2CN_2 in the hope that R_2C: would be released and attack the nitrogen atom giving an aza-allyl complex. This may enable such complexes with R groups other than aryl (hitherto unknown) to be prepared.

Unlike the diphenyl derivative,[8] reaction of ($\underline{p}$-tolyl)$_2$C:NSiMe$_3$ with π-$C_5H_5M(CO)_3Cl$ (M = Mo,W) gave only the mononuclear ketimino derivatives, π-$C_5H_5M(CO)_2NC$($\underline{p}$-tolyl)$_2$. No evidence for a dinuclear species of the type [π-$C_5H_5Mo(CO)N{:}CR_2]_2$, as found in the diphenyl system, was obtained, again showing the delicate nature of the balance between the factors influencing the type of product formed.

An investigation of the reactions of $Ph_2C{:}NLi$ with π-$C_5H_5M(CO)_3Cl$ (M = Mo,W) in the presence of 1 molar equivalent of a ketone was prompted by observations made on the reaction between ($\underline{p}$-tolyl)$_2$C:NLi with π-$C_5H_5W(CO)_3Cl$ (2:1 ratio) plus a molar equivalent of (p-tolyl)$_2$CO, at room temperature. This was done in an effort to prepare sufficient of the aza-allyl 'ketone' complex for further study since only a small quantity was usually obtained from the 'straight' 2:1 reaction. A significant amount of the required complex was indeed obtained, but the major product was the ketimino derivative, π-$C_5H_5W(CO)_2NC$($\underline{p}$-tolyl)$_2$, and although small quantities of this complex are detected spectroscopically during reaction without ketone present initially, under these conditions, it would seem possible that the ketone may be directly involved. To substantiate this, the reaction of $Ph_2C{:}NLi$, π-$C_5H_5W(CO)_3Cl$ and Ph_2CO (1:1:1 ratio) was attempted, since the ketimino derivative was never observed in the 'straight 2:1' reaction. The reaction was performed as in the experimental section and the ketimino derivative, π-$C_5H_5W(CO)_2NCPh_2$ was the only product isolated. This would seem to be fairly conclusive evidence for the involvement of $Ph_2C{:}O$ in the reaction. Another significant point is the loss of colour from the $Ph_2C{:}NLi$ solution on warming to room temperature suggesting a reaction was taking place. The i.r. spectrum of the reaction mixture at this point showed the ketone carbonyl absorption (at 1670 cm^{-1}.) to have almost disappeared. A possible reaction is shown below:



VII

i.e. addition across the carbonyl group, involving nucleophilic attack at the carbonyl carbon atom, a process quite common in organic chemistry. The purple colouration observed right at the beginning of the reaction will presumably be due to a small amount of unreacted $Ph_2C{:}NLi$ which would react in the normal way with π-$C_5H_5M(CO)_3Cl$ to give the aza-allyl complex. Reaction of species (VII) with π-$C_5H_5M(CO)_3Cl$ could possibly involve initial co-ordination through the oxygen and through the C=N π-system, with elimination of LiCl, forming a 5-membered ring system.

A rearrangement process would follow whereby the Ph_2CO is displaced (indicated by the re-appearance of the absorption at 1670 $cm.^{-1}$ during the reaction), together with a carbonyl group, leaving the ketimino derivative. Reactions involving the mixtures $Ph_2C{:}NLi$ + $(p\text{-tolyl})_2CO$ and $(p\text{-tolyl})_2C{:}NLi$ + Ph_2CO led only to the ketimino derivatives corresponding to the ketimine used indicating that no sort of 'scrambling' process occurred. The importance of this particular reaction is that it allows ketimino derivatives to be prepared, which could previously have been obtained only by reaction with $R_2C{:}NSiMe_3$, by a route using readily available starting materials ($R_2C{:}NLi$ can be prepared from (RBr + ^{n}BuLi) + R-CN) and as the sole products, thus eliminating difficult separation techniques. Also there is scope for extending the method from ketones to other molecules containing multiple bonds e.g. nitriles, in which the chances of stabilising a possible cyclic intermediate may be improved. In this respect further studies on this type of system may be worthwhile.

CHAPTER 4

PROPERTIES AND REACTIONS OF MOLYBDENUM AND TUNGSTEN KETIMINO COMPLEXES

This Chapter describes the reactions and structural characteristics of the ketimino derivatives obtained from the reactions described in Chapter 3 in terms of a comparison with those studied previously, e.g. π-$C_5H_5M(CO)_2NCR_1R_2$ (M = Mo,W) ($R_1 = R_2$ = Ph, ^tBu; R_1 = Ph, R_2 = ^tBu).

A. Experimental

1. Action of heat on π-$C_5H_5Mo(CO)_2NCPh_2$ in monoglyme solution.

The dark-blue complex (0.4g. lmmole) was dissolved in monoglyme (15 ml.), giving a dark-green solution, and heated to 80°. No reaction was detected by i.r. spectroscopy over a period of 24 hr., though the colour was now a distinct green-brown, indicating some decomposition. The solvent was removed *in vacuo* and a mass spectrum of the oily residue showed only peaks corresponding to the starting material, no evidence for a dinuclear species was obtained.

2. Action of heat on π-$C_5H_5Mo(CO)_2NC(p\text{-tolyl})_2$ in monoglyme solution.

The complex (0.21g., 0.5 mmole) was dissolved in monoglyme (10 ml.) and heated to 80°. No reaction was detected by i.r. spectroscopy over 24 hr., though some decomposition occurred. The solvent was removed *in vacuo* and a mass spectrum of the residue showed only peaks corresponding to the starting material, no evidence for any dinuclear species being obtained.

3. Action of heat on π-$C_5H_5W(CO)_2NC(p\text{-tolyl})_2$ in monoglyme solution.

The dark-blue complex (0.1g. 0.2 mmole) was dissolved in monoglyme (8 ml.), giving a dark-green solution, and heated at 80° for 4 hrs. during which time the colour changed to orange-red. The i.r. spectrum showed that the original carbonyl bands (at 1947, 1860 $cm.^{-1}$) had been replaced by two new bands at slightly lower frequencies (1934, 1852 $cm.^{-1}$). Addition of hexane (5 ml.) and cooling to 0° gave a very small quantity of a red powder. The supernatant liquid was syringed off and the powder pumped dry. The quantity isolated was sufficient only to allow an infrared and mass spectrum to be obtained, but these, together with the similarity to the corresponding reaction of the diphenyl monomer, indicated that the material was the dinuclear material $[\pi\text{-}C_5H_5W(CO)NC(\underline{p}\text{-tolyl})_2]_2$.

Infrared Spectrum: (Nujol), ν_{CO} 1930s, 1836s cm.$^{-1}$

Mass Spectrum: (direct insertion probe at source temperature). The parent ion $[(\pi\text{-}C_5H_5)_2W_2(CO)_2\{NC(\underline{p}\text{-tolyl})_2\}_2]^+$ had an isotopic distribution pattern corresponding with that computed for $C_{42}H_{38}N_2O_2W$. The major peaks in the spectrum are listed in Table IV.1.

4. Reaction of $\pi\text{-}C_5H_5Mo(CO)_2NC(p\text{-tolyl})_2$ with Triphenylphosphine (1:1 molar ratio).

The complex (0.09g.) was dissolved in hexane (45 ml.) and triphenylphosphine (0.0555g.) in hexane (15 ml.) was added. No reaction occurred on stirring at room temperature. Refluxing led only to eventual decomposition.

5. Reaction of $\pi\text{-}C_5H_5Mo(CO)_2NC(p\text{-tolyl})_2$ with iodine.

The complex (0.425g., 1 mmole) was dissolved in monoglyme (30 ml.) and a solution of iodine (0.25 g., 2 mmole) in monoglyme (15 ml.) added. Gas evolution occurred at room temperature and a yellow white solid was deposited which was shown to be non-carbonyl decomposition material.

6. Reaction of $\pi\text{-}C_5H_5Mo(CO)_2NCPh_2$ with iodine.

Addition of a solution of iodine (.097 g., 0.38 mmole) in monoglyme (10 ml.) to $\pi\text{-}C_5H_5Mo(CO)_2NCPh_2$ (0.102g., 0.25 mmole) also in monoglyme (10 ml.) at room temperature over a period of 15 min. caused a change in colour of the solution from green to dark red. After 1 hr. the solvent was removed in vacuo and the residue extracted with methylene chloride

TableIV.1

Mass Spectral Data for $(\pi\text{-}C_5H_5W(CO)NC(p\text{-tolyl})_2]_2$.

Ion	m/e	m*	Fragment lost
$[(\pi\text{-}C_5H_5)_2W_2(CO)_2\{(NC(\underline{p}\text{-tolyl})_2\}_2]^+$	970		
		915	CO
$[(\pi\text{-}C_5H_5)_2W_2(CO)\{NC(\underline{p}\text{-tolyl})_2\}_2]^+$	942		
		886	CO
$[(\pi\text{-}C_5H_5)_2W_2\{NC(\underline{p}\text{-tolyl})_2\}_2]^+$	914		
		696	$(\underline{p}\text{-tolyl})CN$
$[(\pi\text{-}C_5H_5)_2W_2(\underline{p}\text{-tolyl})\{NC(\underline{p}\text{-tolyl})_2\}]^+$	797		
		580	$(\underline{p}\text{-tolyl})CN$
$[(\pi\text{-}C_5H_5)_2W_2(\underline{p}\text{-tolyl})_2]^+$	680		

(10 ml.). Addition of hexane (5 ml.) and cooling to 0^{o} caused a dark-green powder (purple when mulled) to separate, which was identified by i.r. spectroscopy as $Mo_3(\pi\text{-}C_5H_5)_3I_3O_4$.[4,8]

B. Discussion

As one might expect, the di-p-tolylketimino derivatives in their properties and reactions show greater similarity to the diphenyl than the di-t-butyl analogues. The only difference is the reaction with iodine, where rapid decomposition occurs with the di-p-tolyl derivative instead of formation of a complex of the type $Mo(\pi\text{-}C_5H_5)_3I_3O_4$, and indicates a lower resistance to oxidation. Di-t-butyl- and phenyl(t-butyl)- derivatives both react with iodine giving substitution products of the type $\pi\text{-}C_5H_5M(CO)(I_2)NCR'R''$ (M = Mo, W; R' = ^{t}Bu, R" = ^{t}Bu,Ph).[13,14]

The introduction of a para- methyl group into the aromatic ring enabled more detailed information regarding the bonding mode of the ligand to be obtained from ^{1}H n.m.r. spectra. A single methyl absorption only was observed, there being no indication of line broadening on cooling to -40^{o}. This strongly suggests a linear M-N-C skeleton, which is also indicated by the ^{19}F n.m.r. spectrum for the complex $\pi\text{-}C_5H_5W(CO)_2NC(p\text{-}CF_3C_6H_4)_2$. Correspondingly larger shifts are generally observed in fluorine spectra, hence any small structural change to which the environment of para-methyl protons may not be sufficiently sensitive should manifest itself in the ^{19}F n.m.r. spectrum. However, only one signal was observed throughout the range -50 to $+40^{o}$.

A virtually linear M-N-C skeleton has been shown by X-ray diffraction for $\pi\text{-}C_5H_5Mo(CO)_2NC^{t}Bu_2$,[6a] although a model indicated that this may be due to the steric requirements of the ligand and not solely to electronic effects. For aryl ketimino-derivatives, steric requirements are less stringent, hence it is probable that the proposed linearity could be a result of electronic factors, i.e. maximum overlap of the nitrogen lone pair (in a p-orbital) with suitable metal d-orbitals and the subsequent increase in d_π-π^* back donation (the 'synergic' effect).

A significant degree of back-bonding in these ketimino- complexes is also indicated from the X-ray photoelectron spectra[35] (or ESCA*). Data obtained are given in Table IV.2. Changes in binding energy of core electrons tend to reflect changes in electron density at that particular atom - a decrease in binding energy implies an increase in electron density. The figures for the N(1s) binding energies indicate that electron density on the nitrogen atom of a ketimine is very little changed on replacing the hydrogen by a transition metal, suggesting that either the lone pair is not involved in bonding, or that the π-donor and π-acceptor tendencies of the ligand are effectively balanced. Considerable metal-nitrogen multiple bonding is indicated from the X-ray crystal structure of π-$C_5H_5Mo(CO)_2NCBu^t{}_2$,[6a] where a metal-nitrogen distance of 1.87Å was found, (c.f. the Mo-N single bond length of 2.32Å found in $Mo(CO)_3$-$[H_2N(CH_2)_2NH(CH_2)_2NH_2]$[7]). This extensive π-bonding was originally thought to involve mainly donation of the lone pair from the p-orbital on nitrogen to the metal, back-donation into π^* orbitals of the C=N system being relatively unimportant since $\nu_{C=N}$ was not appreciably lowered,[13] as one might expect if back donation were significant. The ν_{CO} were very low for terminal carbonyl groups suggesting that the R_2C=N- ligand was a poor π-acceptor (or vice versa, a strong $\sigma + \pi$ donor).

It has been shown, however, that for ketimino groups bound linearly to the main group metals[36a] (e.g. Be, B, Al, Si, Ga), where $d_\pi \rightarrow \pi^*$

---

* ESCA = Electron Spectroscopy for Chemical Analysis.

Table IV.2

X-ray Photoelectron Spectral Data for some Ketimino derivatives of Molybdenum and Tungsten.[35]

Complex	C(1s)	N(1s)	Mo($3d_{5/2}$)	W($4f_{7/2}$)	F(1s)
$\pi\text{-}C_5H_5Mo(CO)_2NC(\underline{p}\text{-tolyl})_2$	285.0	398.4	229.0	-	-
$\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-tolyl})_2$	285.0	398.8	-	31.6	-
$\pi\text{-}C_5H_5W(CO)_2NC(\underline{p}\text{-}CF_3C_6H_4)_2$	286.1	399.8	-	32.3	690.8
$(\underline{p}\text{-tolyl})_2C{:}NH$	285.0	398.7	-	-	-
$(\underline{p}\text{-}CF_3C_6H_4)_2C{:}NH$	286.3	400.1	-	-	690.8

NOTES:

1. Carbon C(1s) binding energies are taken from the centroid of relatively broad peaks. Under these conditions the Au($4f_{7/2}$)peak has a binding energy of 84 eV. All lines were calibrated to this value.

2. The underlined values are used as internal reference peaks to correct for charging effects. Binding energies are correct to ± 0.3eV. F(1s) = 690.8 eV for $PhCF_3$ was run as a thin film on gold where charging effects are negligible. Similarly C(1s) = 285.0 for the carbon centroid from $PhCH_3$ was run on gold. From these two standards the calculated C(1s) binding energy from the CF_3-C_6H_4group would be ca. 286.3 which is in satisfactory agreement with the found 286.1 (C(1s) from the CF_3 groups was always at 293.8 eV).

back-donation is not possible, $\nu_{C=N}$ is significantly increased, sometimes by as much as 150-200 cm.$^{-1}$ for compounds of beryllium and boron. Observations on these systems also show[36b] that as the metal becomes heavier, the increase in frequency is smaller, e.g. gallium and indium complexes containing linear, terminally bound ketimino groups show increases in $\nu_{C=N}$ of ca. 60 and 35 cm.$^{-1}$ respectively. Consequently, small, but significant increases might be expected to occur in transition metal complexes for a purely forward donation processes which would also tend to decrease electron density on nitrogen. It is necessary therefore to invoke a $d_{\pi} \rightarrow \pi^*$ process for such complexes in order to balance π-donation, thus retaining $\nu_{C=N}$ in its 'free' ketimine position and balancing the nitrogen→metal electron drift. For the di-p-tolyl derivatives, $\nu_{C=N}$ could not be confidently assigned due to the presence of aromatic ring vibrations in the 1500-1600 cm.$^{-1}$ region, although it is likely to be between 1570 and 1590 cm.$^{-1}$ ($\nu_{C=N}$ for (p-tolyl)$_2$C:NH is at 1597 cm.$^{-1}$).

Replacement of the p-Me group in π-$C_5H_5W(CO)_2NC$(p-tolyl)$_2$ for a p-CF_3 group causes a significant reduction of electron density at nitrogen and on the metal, as one would expect considering the powerful electron-withdrawing properties of -CF_3 groups, with a consequent increase in the observed carbonyl infrared frequencies (1956, 1869cm.$^{-1}$ compared with 1938, 1838 cm.$^{-1}$ for π-$C_5H_5W(CO)_2NC$(p-tolyl)$_2$).

The mononuclear derivative π-$C_5H_5Mo(CO)_2NCPh_2$ has been reported previously,[8] but was only isolated on one occasion, as a brown powder, from the reaction of π-$C_5H_5Mo(CO)_3Cl$ with $Me_3SiNCPh_2$ in monoglyme at reflux temperature, the main product being the dinuclear species $[\pi$-$C_5H_5Mo(CO)\ NCPh_2]_2$. In this respect the reaction of π-$C_5H_5Mo(CO)_3Cl$

with Ph_2C:NLi in the presence of Ph_2C:O was of particular interest since by comparison with the corresponding tungsten reaction the mononuclear ketimino-derivative should be formed. The dark-blue crystalline material (II) isolated from the reaction gave analytical and spectroscopic data consistent with the formulation expected as well as correlating well with the other derivatives of the series. The data, however, were very different in many respects from that obtained on the brown powder, (III). The two sets of data obtained, together with those of the tungsten complex π-$C_5H_5W(CO)_2NCPh_2$ (for comparison purposes) are presented in Table IV.3. The most dramatic differences are in the i.r. and ^1H n.m.r. spectra. For complex III the lowest carbonyl frequency (1802 cm.$^{-1}$) was originally thought to be due to an impurity as the intensity tended to vary somewhat between samples. The two π-C_5H_5 signals at much higher field than normally found for complexes of this type (typically 4.0 - 4.4τ) cannot be satisfactorily explained by the proposed formulation.

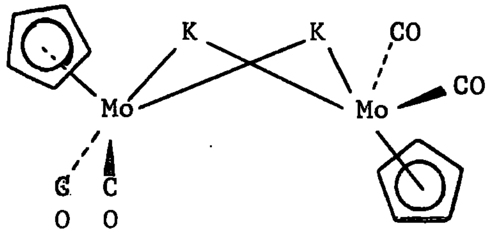
It is now thought therefore that this material is not the mononuclear derivative, π-$C_5H_5Mo(CO)_2NCPh_2$, but could possibly be the dinuclear species $[\pi$-$C_5H_5Mo(CO)_2NCPh_2]_2$, formed as an intermediate in the reaction producing $[\pi$-$C_5H_5Mo(CO)NCPh_2]_2$, (IV), presumably the more stable product. The analytical data for the species $[\pi$-$C_5H_5Mo(CO)_2NCPh_2]_n$ would be the same for all values of n, but to explain the spectroscopic data a structure with the $(Mo - N)_2$ ring puckered and the π-C_5H_5 rings adopting trans- positions (Fig. IV.1) would have to be adopted.

Such a structure would give rise to two π-C_5H_5 signals (a cis-isomer, or structures with planar $(Mo-N)_2$ ring systems would give only one signal c.f. Chapter 2), and also would possess C_s symmetry, for which one would predict four carbonyl absorptions (2A' + 2A"). Of these, from dipole moment considerations, one would expect three strong and one weak absorption.

Table IV.3

Analytical and Spectroscopic Data obtained for the Diphenyl Ketimino Complexes

Complex	Analytical Data						Spectroscopic Data			
	C%		H%		N%		I.r.	^1H n.m.r.		Mass
	Found	Reqd	Found	Reqd	Found	Reqd	ν_{CO}cm.$^{-1}$	τ Ph	τ C_5H_5	
'π-$C_5H_5Mo(CO)_2NCPh_2$' Brown Powder	60.6	60.5	4.45	3.8	-	3.55	1920s1856s 1802ms.	2.48(10)	5.05,5.11 (5)	Consistent with mononuclear formulation
'π-$C_5H_5Mo(CO)_2NCPh_2$'	60.35	60.5	4.15	3.8	3.8	3.55	1964s,1949s, 1879s,1874s.	2.71(10)	4.22(5)	"
π-$C_5H_5W(CO)_2NCPh_2$	49.2	49.4	3.15	3.25	2.9	2.9	1956s,1940s, 1869s,1863s.	2.63(10)	4.02(5)	"



(K = $Ph_2C{=}N$)

Fig. IV.1

The three strong bands are certainly observed (1920, 1856, 1802 cm.$^{-1}$), and there is a weak shoulder at ca. 1955 cm^{-1}. The mass spectrum, however, shows no peaks attributable to Mo_2 species, hence the assumption would have to be that the first event to occur in the mass spectrometer would be bridge cleavage resulting in formation of the monomeric ion $[\pi\text{-}C_5H_5Mo(CO)_2NCPh_2]^+$, originally thought to be the parent. This type of behaviour is unusual for molecules of this type, where systematic loss of carbonyl and other terminal groups is usually observed before the bridging unit splits up.[21,23,23a]

The ready conversion of III to IV by heat is easily explainable, as all that is involved is loss of two carbonyl groups and the adoption of a planar ring system giving the observed single infrared carbonyl absorption and $\pi\text{-}C_5H_5$ signal in the ^1H n.m.r; rather than a dimerisation process as first thought. In fact the true monomer (II) (and the di-p-tolyl analogue) could not be dimerised by heating to give species resembling III or IV. In order to fully solve this problem a further quantity of complex III would have to be prepared, but so far it has not been possible to repeat the exact reaction conditions necessary to allow its formation and subsequent isolation. Use of a derivative of the type $Me_3SnN{:}CPh_2$ (instead of $Me_3SiN{:}CPh_2$) may prove useful as one would hope milder reaction conditions could be used thereby reducing the amount of complex IV formed.

The complex π-$C_5H_5W(CO)_2N{:}C$(p-tolyl)$_2$ on heating in solution gave the dinuclear complex [π-$C_5H_5W(CO)N{:}C$(p-tolyl)$_2$]$_2$ which resembled the diphenyl analogue very closely.[6b,8] At present the difference in tendency to dimerise between the molybdenum and tungsten monomeric species is not understood.

In the solid state, the mononuclear complexes π-$C_5H_5M(CO)_2NCPh_2$ (M = Mo,W), displayed four strong carbonyl absorptions, instead of the two expected and which were observed in solution. This could be due to solid state crystal effects or, perhaps more likely, to conformational isomers of the type observed in the corresponding di-t-butyl complex π-$C_5H_5Mo(CO)_2N{:}CBu^t{}_2$ (V).[13,37]

On cooling hexane solutions of V, the carbonyl absorptions shift to lower frequencies, as do the Bu^t and π-C_5H_5 signals in the ^1H n.m.r. These changes are consistent with conformational changes about the Mo-N bond (Fig. IV.2), the low temperature and solid state forms probably being IV.2(a) the more sterically favoured form. The cylindrical symmetry of the d-orbitals involved in dπ-pπ bonding allows rotation about the Mo-N bond[38] (in the same way as postulated for the carbene group) and the high temperature form may be conformer IV.2(b) or the form with free rotation.

If similar conformational changes occur within the diphenyl analogues, the rotation process must be very much more rapid as no change is observed in the ^1H n.m.r. π-C_5H_5 signal on cooling to -60°, implying that the energy

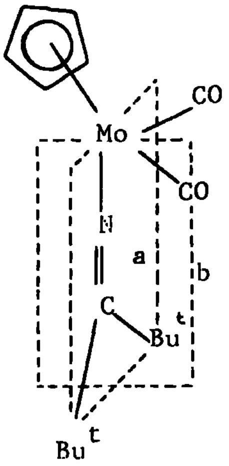


Fig. IV.2

difference between the two forms is very small, hence crystallisation results in approximately equal amounts of each conformer in the solid state, as is observed. The X-ray photoelectron spectrum of the solids shows only single nitrogen 1s and metal $3d_{5/2}$ (Mo) or $4f_{7/2}$(W)peaks,[35] in keeping with the small changes proposed.

CHAPTER 5

A SURVEY OF ALLYL AND RELATED TRANSITION METAL COMPLEXES.

A. Introduction

The purpose of this chapter is to place the work on 2-aza-allyl/allene complexes of molybdenum and tungsten, to be described in the following two chapters, in perspective with studies made on other, related ligand systems. By far the most common of these is the allyl ligand, C_3H_5, which can act as a one (σ-allyl) or three (π-allyl) electron donor. Other ligand systems discussed will be the allene group $R_2C{=}C{=}CR_2$, the ketenimine group, $R_2C{=}C{=}NR$, and the amidine group, $RN{=}C(R){-}NR$. The emphasis will be placed on structural and spectroscopic studies relating to the bonding mode(s) adopted by the ligands in their complexes and particularly for allyl derivatives, on the fluxional behaviour as detected by n.m.r. spectroscopy. Preparations and properties therefore will be mentioned only briefly as the preparative routes used have not so far been found to be applicable to the synthesis of 2-aza-allyl/allene complexes. Also, the properties of these latter compounds have not yet been fully investigated.

B. Allyl Metal Complexes

Several reviews on the subject have been published.[39-44]

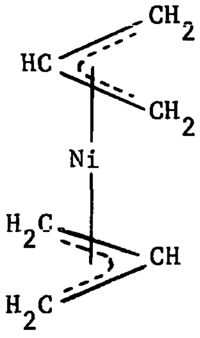
1. Synthesis.

The general synthetic routes available are as follows:

a) From allyl Grignard reagents

Pure π-allyl complexes are conveniently prepared by treatment of suitable metal salts with allyl Grignard reagents,[45,46] such as allyl magnesium bromide, e.g.

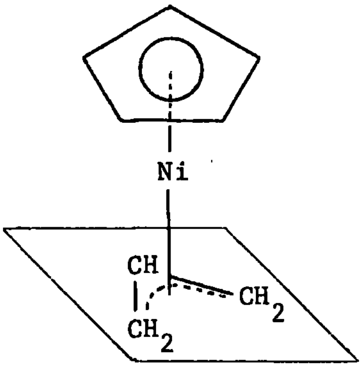
$$2C_3H_5MgBr + NiCl_2 \xrightarrow[-10^{o}]{\text{ether}}$$



Mixed π-allyl complexes may also be prepared by this route[47]

e.g.

$$(\pi\text{-}C_5H_5)_2Ni \quad + \quad C_3H_5MgBr \longrightarrow$$



b) <u>From allyl halides and allyl alcohols</u>.

Allyl halides react with a variety of anionic metal complexes to form π-allyl-metal bonds. These reactions are thought to proceed via a σ-allyl intermediate which, in some cases, may have to be decomposed by heat or u.v. irradiation in order to obtain the desired π-allyl derivative. Usually, however, the σ-allyl complex is very unstable, decomposing at low temperatures to yield the π-allyl complex alone, e.g.

$$\begin{tikzcd}
Na^+Mn(CO)_5^- + ClCH_2CH{=}CH_2 \arrow[r] & (CO)_5Mn\text{-}\sigma\text{-}C_3H_5 \arrow[d, "\text{u.v. or } 80^\circ\ {}^{48}"] \\
 & Mn(CO)_4(\pi\text{-}C_3H_5)
\end{tikzcd}$$

$$\begin{tikzcd}
Na^+[\pi\text{-}C_5H_5Mo(CO)_3]^- + ClCH_2CH{=}CH_2 \arrow[r] & \pi\text{-}C_5H_5Mo(CO)_3(\sigma\text{-}C_3H_5) \arrow[d, "\text{u.v.}\ {}^{49}"] \\
 & \pi\text{-}C_5H_5Mo(CO)_2(\pi\text{-}C_3H_5)
\end{tikzcd}$$

$$\begin{tikzcd}
Na^+[Co(CO)_4]^- + BrCH_2CH{=}CH_2 \arrow[r] & {[\sigma\text{-}C_3H_5Co(CO)_4] + Br^-} \arrow[d, "-CO\ {}^{50}"] \\
 & \pi\text{-}C_3H_5Co(CO)_3
\end{tikzcd}$$

$$XCH_2CH{=}CH_2 + Na_2PdCl_4 \xrightarrow[50^\circ,X{=}OH,Cl]{50\%HAc^{51}} [\pi\text{-}C_3H_5PdCl]_2$$

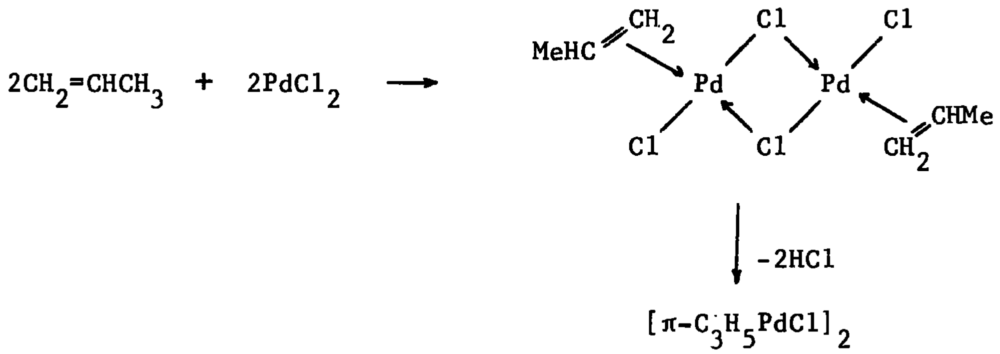
Allyl halides and alcohols will also react directly with metal compounds, e.g.[52,53]

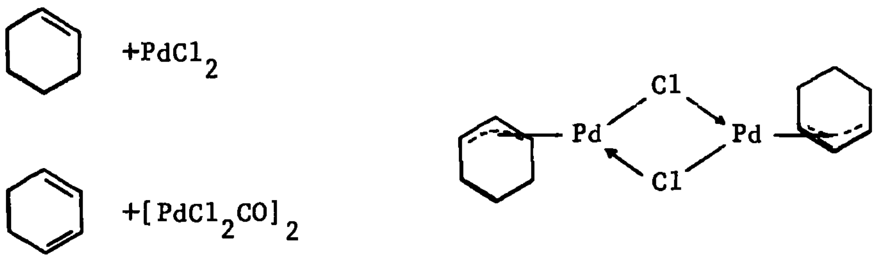
$$XCH_2CH{=}CH_2 + Fe_2(CO)_9 \xrightarrow[X=Cl,Br]{} \pi\text{-}C_3H_5Fe(CO)_3X$$

$$XCH_2CH{=}CH_2 + Ni(CO)_4 \xrightarrow[X=Br,I]{C_6H_6,80^o} [\pi\text{-}C_3H_5NiX]_2$$

c) <u>Reactions of Olefins and Allenes with Metal Salts</u>

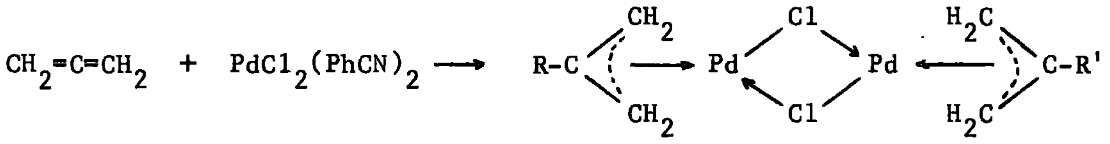
i) The formation of π-allyl complexes from a mono-olefin probably proceeds via the prior formation of an unstable metal-olefin complex, followed by loss of a hydrogen atom. The reaction may be compared with that of allyl halides which lose the halogen, e.g.[54,55]





With dienes (the latter reaction), the formation of the π-allyl type ligand requires the <u>addition</u> to the diene of another group. Thus, in the above equation a hydrogen atom has been acquired, by cyclohexa-1,3-diene, presumably from the solvent.

ii) Treatment of some palladous salts with allenes affords π-allylic complexes, depending on the stoichiometry of the reaction, and on the nature of the solvent.[56,57] R and R' may be Cl or $-C(CH_2Cl)=CH_2$.

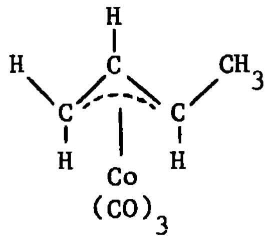


d) Addition of Transition Metal Hydrides to Dienes

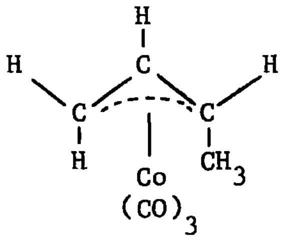
Treatment of conjugated dienes with a transition metal hydride can yield substituted π-allyl complexes, e.g.[58]

$$HCo(CO)_4 + CH_2=CH-CH=CH_2 \longrightarrow \pi\text{-}C_4H_7Co(CO)_3$$

The complex was isolated in two isomeric forms (syn and anti-) depending on the position of the methyl substituent on the terminal carbon atom i.e.



syn-



anti-

For certain metal hydrides, σ-allyl complexes may be isolated.[40]

$$\pi\text{-}C_5H_5Fe(CO)_2H + CH_2=CH-CH=CH_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}CH_2CH=CHCH_3)$$

e) Recent, potentially useful, methods

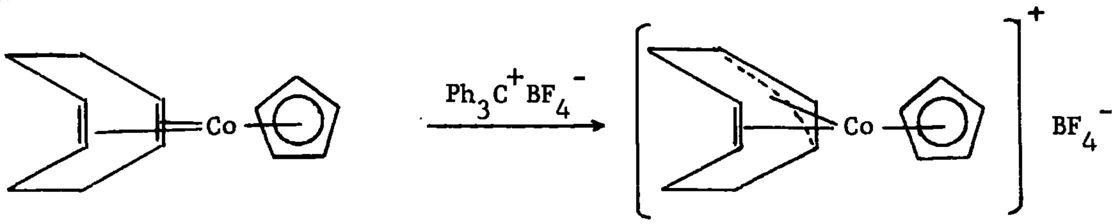
i) Allylation using Allyl Mercury Halides.[59]

$$C_3H_5HgCl + 2Na_2PdCl_4 \xrightarrow{MeOH} (\pi\text{-}C_3H_5PdCl)_2$$

Reaction occurs immediately at room temperature in quantitative yields and would appear to have some general applicability.

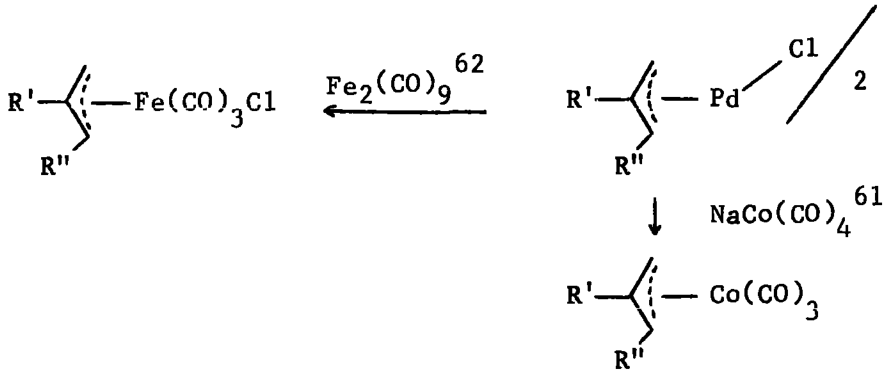
ii) Hydride Abstraction.

Treatment of several stable diene transition metal complexes with trityl tetra-fluoroborate results in hydride abstraction from a carbon atom, α to a co-ordinated olefin, and formation of a cationic π-allylic species. e.g.[60]



iii) Allyl Ligand Exchange Reactions.

Exchange of π-allylic ligands from readily prepared π-allylic palladium(II) chlorides to other transition metals provides a potentially useful route for synthesising hitherto difficultly obtainable substituted π-allylic complexes, e.g.



2. Structure and Bonding

X-ray crystallographic studies have shown that in most π-allyl-metal systems a 'sandwich' structure is adopted, i.e. the metal lies below the plane formed by the three carbons of the π-allyl group. e.g. for the dimeric palladium complex $[\pi\text{-}C_3H_5PdCl]_2$[63] the overall structure is that given in Fig. V.1.

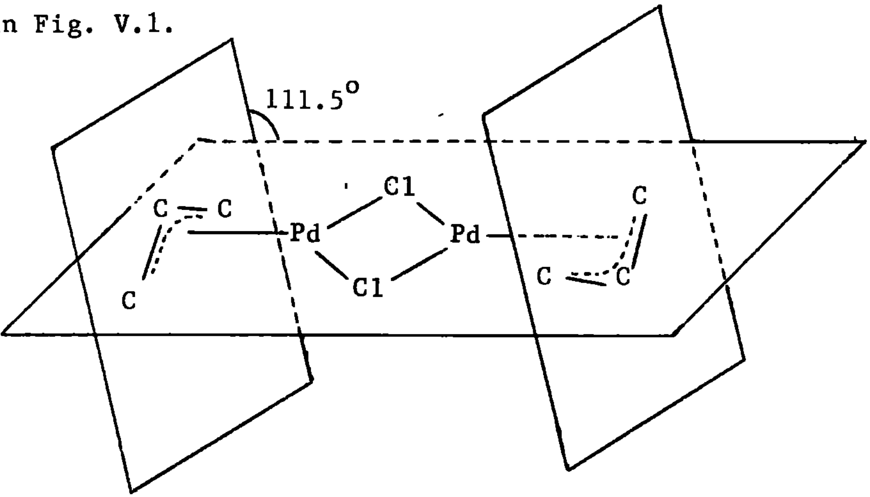


Fig. V.1.

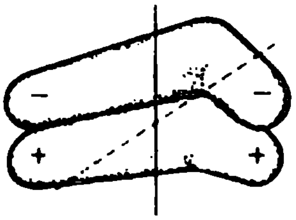
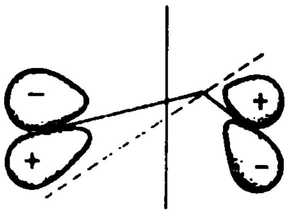
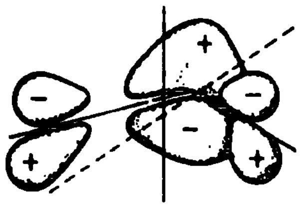
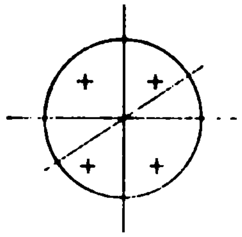
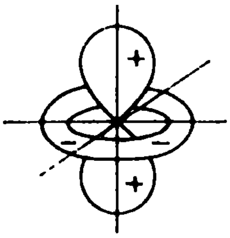
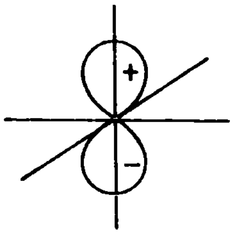
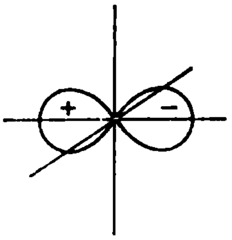
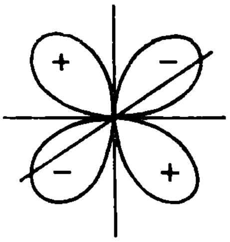
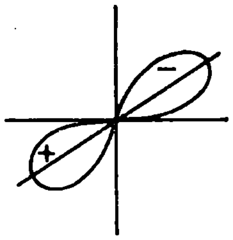
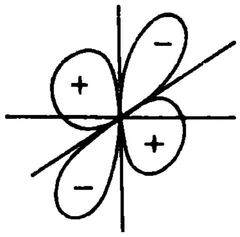
The plane of the three π-allyl carbons intersects the $(Pd\text{-}Cl)_2$ plane at an angle of 111.5±0.9°, with the central carbon tipped away from the palladium. All three Pd-C distances are essentially equal (2.11 Å) as are the two C-C distances of the π-allyl group (av. 1.37 Å). A low temperature X-ray crystallographic study locates approximately the hydrogens of the allyl groups, which are found to lie (within experimental error) in the plane of the allyl carbons.[63b]

For the symmetrical π-allyl-metal system (i.e. terminal carbon atoms equidistant from the metal, as above,) the simplest description of the bonding is one which is somewhat analogous to the π-ethylene-metal system.[41] The three carbons of the π-allyl group form an isoceles triangle and in this configuration the three pπ-orbitals form three molecular orbitals which are represented in Fig. V.2.

The local symmetry of the $\pi\text{-}C_3H_5M$ system is C_s, which is very low, hence symmetry arguments alone are of little assistance in determining

Fig. V.2

Representations of the π-allyl molecular orbitals Ψ_1, Ψ_2, and Ψ_3 and, beneath them, are the metal orbitals with which they are most likely to interact to give substantial metal-allyl bonding. The metal lies along the vertical axis, below the C_3-plane.

$\psi_1 = \frac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3)$	$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$	$\psi_3 = \frac{1}{2}(\phi_1 - \sqrt{2}\phi_2 + \phi_3)$
		
  	 	 

which ligand and metal orbitals may interact since, as shown in Table V.1, there are a very large number of possible combinations.

Table V.1[41]

Classification of ligand and metal orbitals of the π-C_3H_5M system according to the symmetry group C_s.

Symmetry	Metal Orbitals	Ligand Orbitals
A'	s, p_y,p_z, $d_{x^2-y^2}$, d_{z^2}, d_{yz}	Ψ_1, Ψ_3
A"	p_x, d_{xy}, d_{xz}	Ψ_2

In order to distinguish from amongst the above symmetry-allowed combinations those which are likely to produce strong metal-ligand bonding, one must resort to overlap and energy considerations. Regarding overlap, the combinations most likely to result in significant metal-ligand interaction are represented pictorially in Fig. V.2. A rough estimate of the relative energies of metal and ligand orbitals, based on the ionisation potentials of the allyl radical and palladium metal, suggest that the strongest bonding situation is likely to arise from the interaction between the Ψ_1, and Ψ_2 orbitals and metal orbitals.[40] In other words, the allyl group may be considered to bond to the metal by a σ-bond and a π-bond in a pictorially somewhat similar way to that proposed for the π-ethylene-metal system.[41]

A type of metal-allyl bonding perhaps best described as asymmetric-π has been observed for certain complexes, both in solution (by n.m.r. spectroscopy - to be described later) and in the solid state. The formulation of (π-allyl)Pd(Ph_3P)Cl, shown in Fig. V.3 has recently been confirmed by X-ray diffraction.[64]

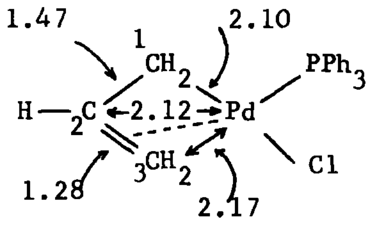


Fig. V.3.

These distances clearly indicate considerable localisation of the allylic carbon-carbon bonding, resulting in an essentially full double bond trans- to the phosphorus. Furthermore, the equivalent isotopic temperature factors are much larger for C_2 and C_3 suggesting that they are more loosely bound to the palladium than is C_1, in keeping with the observed Pd-C interatomic distances.[64]

3. Properties.

The properties of π-allyl complexes are many and varied, depending not only on the metal, but also to a large extent on the other ligands present in the molecule. Some π-allyl complexes exhibit versatile catalytic properties, which have been reviewed.[42,45]

A selection of known π-allyl complexes together with physical characteristics is presented in Table V.2. Some comments on the stability, and reactions with donor ligands, are given below.

Table V.2

π-Allyl Metal Complexes

	Colour	M.pt. or b.pt/mm.Hg	References
π-allyl carbonyls			
π-allylMn$(CO)_4$	Pale yellow	52-53.5°	48,50b
(π-allyl$)_2$Fe$(CO)_2$	Yellow-orange	57-58°d.	65
π-allylCo$(CO)_3$	Orange	-33°(39.15mm)	50a,66,67
π-allyl halides			
[(π-allyl$)_2$RhCl$]_2$	Yellow-orange	-	68
[π-allylNiBr$]_2$	Red	93.95°d.	47
[π-allylNiI$]_2$	Dark-red	118-120d.	53
[π-allylPdX$]_2$ where X = Cl,Br,I.	Deep-yellow to yellow	114-200°	69,70,71,72, 54,5173,74
[π-allyl(PtCl$]_2$	Orange	-	75
π-allyl-π-cyclopentadienyls			
π-allyl(Ti(π-$C_5H_5)_2$	-	-	76
π-allylNi-π-C_5H_5	Red	40°/0.05mm.	53,50b
π-allylPd-π-C_5H_5	Dark Red	64°	70,72,77,78
π-allylPt-π-C_5H_5	Lemon-yellow	63-64°	72
π-allyl carbonyl halides			
π-allylFe$(CO)_3$X where X = Cl, Br, I.	Yellow brown -dark brown	85-89°	52,80
π-allylNi(CO)Cl	Orange	-	81,82
π-allylNi(PR_3)Cl	Orange	-	82,83
π-allyl-π-cyclopentadienyl-carbonyls			
π-allylMo-π-$C_5H_5(CO)_2$	Yellow	134°d.	49
π-allylW-π-$C_5H_5(CO)_2$	Yellow	-	84
π-allylFe-π-C_5H_5(CO)	Yellow	65°d.	85
π-allyl-π-cyclopentadienyl halides			
π-allylCo-π-C_5H_5I	Dark Red	95.5-97°	86
π-allylCo-π-C_5H_5Br	Red	96-98°	86

a) Stability

The thermal stability of π-allyl complexes varies from the very stable complexes of palladium (often to above 200°), to the very unstable tris(π-allyl) complexes of chromium and iron. Most are oxidised by atmospheric oxygen, especially in solution, usually fairly slowly, but bis-(π-allyl)nickel is spontaneously inflammable in air.[45]

Many π-allylic complexes are unaffected by water, (including bis-(π-allyl)nickel), but others hydrolyse even at room temperature.[87,54]

$$[(\pi\text{-1-methallyl})Fe(CO)_3] + BF_4^- \xrightarrow{H_2O} CH_3CH_2COCH_3 + CO$$
$$+ \text{ iron hydroxides etc.}$$

$$[\pi\text{-}C_3H_5PdCl]_2 \xrightarrow[2Hr.]{H_2O} CH_2{=}CHCHO + CH_2{=}CHCH_3 + Pd + 2HCl.$$

b) Reactions with Donor Ligands

The resistance of π-allylic groups to displacement or partial displacement by other ligands, such as tertiary phosphines, carbon monoxide, olefins etc. varies widely. Some of the possible reactions are discussed below.

i) Under a pressure of carbon monoxide, the π-allyl group may be partially displaced from $(\pi\text{-}C_3H_5)Mn(CO)_4$ leaving a σ-allyl derivative.[40]

$$(\pi\text{-}C_3H_5)Mn(CO)_4 \underset{u.v.}{\overset{CO}{\rightleftharpoons}} (\sigma\text{-}C_3H_5)Mn(CO)_5$$

ii) Studies of n.m.r. spectra of some π-allyl palladium complexes in dimethyl sulphoxide solution suggest that the π-allyl system is partially displaced from the metal and a σ-allyl complex formed.[73] The 'σ-allyl complexes' have not been isolated from solution since removal of the solvent leads to the reformation of the π-allyl complex.

iii) With (π-allyl)Co(CO)$_3$, the π-allyl group is not displaced on treatment with triphenylphosphine, a carbonyl group being preferentially displaced.[66]

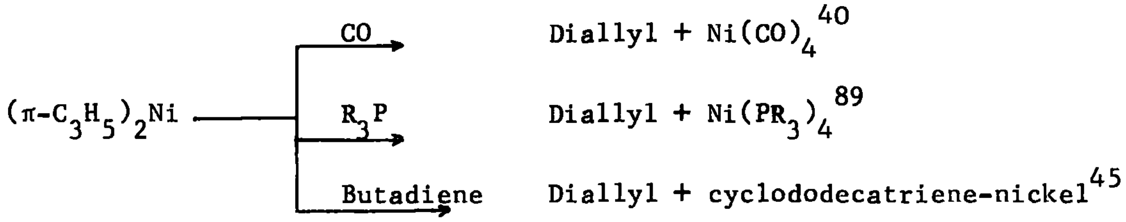
$$\pi\text{-}C_3H_5Co(CO)_3 + Ph_3P \longrightarrow \pi\text{-}C_3H_5Co(CO)_2(Ph_3P)$$

Similarly the π-allyl system in [π-allylNiCl]$_2$ is not displaced by triphenylphosphine; instead symmetrical cleavage of the (Ni-Cl)$_2$ bridge occurs.[82]

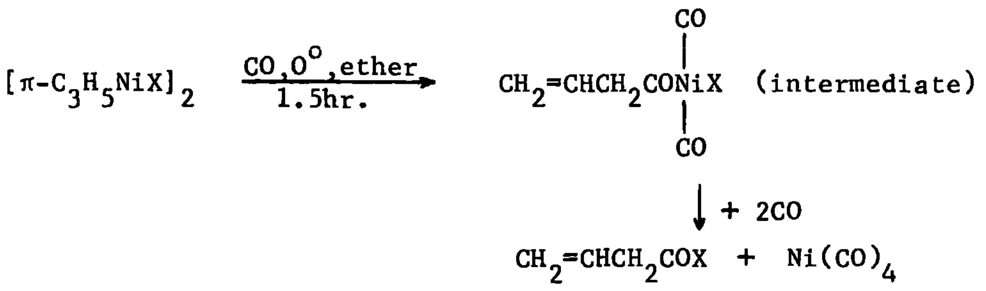
$$[\pi\text{-}C_3H_5NiCl]_2 + 2Ph_3P \longrightarrow 2(\pi\text{-}C_3H_5)Ni(Ph_3P)Cl$$

Similar bridge splitting reactions have been observed for analogous palladium complexes.[88]

iv) In contrast, bis(π-allyl)nickel(II) is very reactive and readily loses both π-allyl groups, even when treated with olefins.



v) The reaction of bis(π-allyl)nickel halide dimers with carbon monoxide is rather more complex than the reaction with triphenylphosphine, the π-allyl system being displaced.[90] The following reaction sequence has been suggested by Heck.[91]

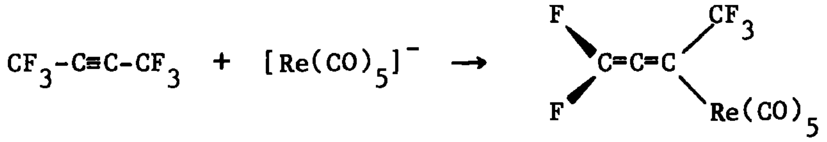


$$[\pi\text{-}C_3H_5NiX]_2 \xrightarrow[1.5hr.]{CO,0^{o},ether} CH_2{=}CHCH_2CO\overset{CO}{\underset{CO}{Ni}}X \text{ (intermediate)} \xrightarrow{+\,2CO} CH_2{=}CHCH_2COX + Ni(CO)_4$$

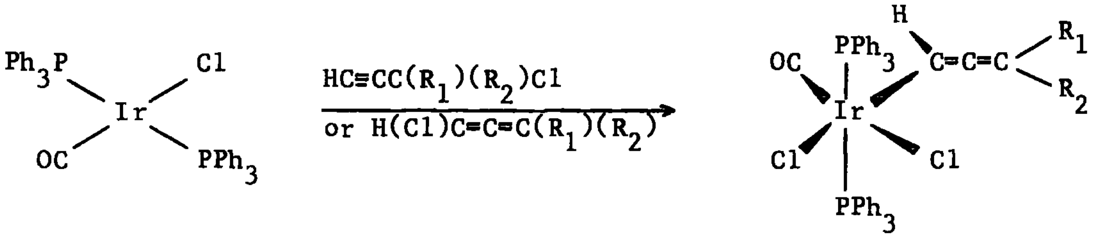
C. Allene Metal Complexes.

The interest in allene derivatives of transition metals appears to have developed comparatively recently, consequently, although well-established they are by no means as numerous as π-allyl complexes.

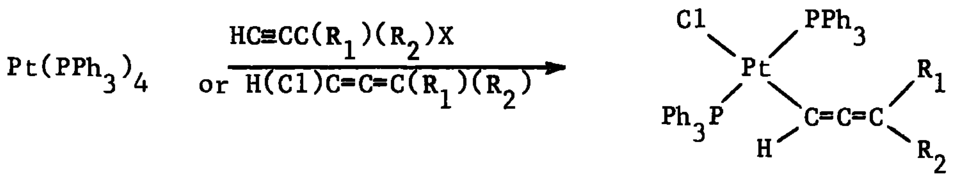
Relatively few complexes containing an allenyl group σ-bonded to a metal have been prepared. The first to be reported, as such, in the literature is a perfluoroallenylrhenium carbonyl,[92] prepared from hexafluorobut-2-yne and the anion $[Re(CO)_5]^-$. i.e.



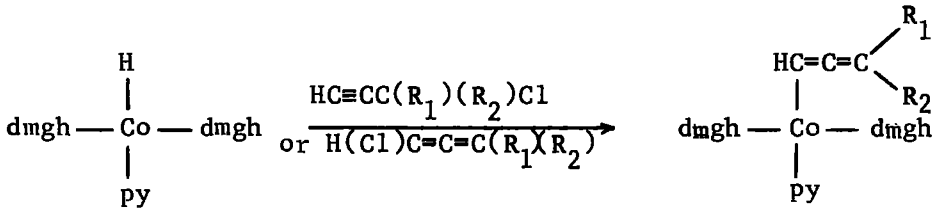
The n.m.r. and i.r. spectra are consistent with the proposed formulation, the allenic asymmetric stretching vibration being observed at 1992 $cm.^{-1}$ More recently,[93] other σ-allenyl complexes have been prepared, mainly of iridium, cobalt and platinum, the reactions being classed as oxidative additions,[93b] of which a selection is given below.



R_1	R_2	(93b)
H	H	
H	CH_3	
CH_3	CH_3	



R_1	R_2	X	
H	H	Br	(93b)
H	H	Cl	(93c)
H	CH_3	Cl	(93b,93c)
CH_3	CH_3	Cl	(93b)



R_1	R_2	
H	H	(93a,93b)
CH_3	CH_3	(93b)

dmgh = monoanion of; py = pyridine
dimethylglyoxine

I.r. and ^1H n.m.r. data support the allenyl structure. Weak bonds (strong in the Raman ^{93b}) are observed in the 1910-1920 cm.$^{-1}$ region, attributable to $\nu_{C=C=C}$, and the chemical shifts of protons directly attached to the allene unit are clearly in the olefin, rather than acetylene or allyl regions.[93]

Reaction of the sodium salt, $Na^+[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with prop-2-ynyl bromide gave a yellow, crystalline complex of formula $\pi\text{-}C_5H_5Fe(CO)_2(C_3H_3)$ which was originally formulated, (wrongly),[93a] as $\pi\text{-}C_5H_5Fe(CO)_2CH_2.C{\equiv}CH$.[94] The true formulation was later shown[95] to be the rearranged product $\pi\text{-}C_5H_5Fe(CO)_2C{\equiv}C\text{-}CH_3$, isomerisation occuring during chromatography using a silica gel or acid-washed alumina column. A further product was also obtained from the same reaction, as an amber liquid, prior to chromatography and to this was assigned the structure $\pi\text{-}C_5H_5Fe(CO)_2CH_2.C{\equiv}CH$. Johnson et. al.[93a] however, are of the opinion, mainly from n.m.r. spectral evidence, that the correct structure should be $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CH_2$, i.e. a σ-allenyl complex.

The original intention[94] of this reaction was to produce a σ-bonded species of the type $\pi\text{-}C_5H_5Fe(CO)_2CH_2.C{\equiv}CH$ in the hope that protonation would lead to formation of a π-allene species (protonation of metal- σ-allyl complexes has been shown to lead to π-olefin derivatives[49,85]) and, in fact, protonation of what is now thought to be[95] $\pi\text{-}C_5H_5Fe(CO)_2C{\equiv}C\text{-}CH_3$ with anhydrous HCl, followed by precipitation with $HSbCl_6$, produced a salt for which spectroscopic and analytical evidence indicated the formulation $[\pi\text{-}C_5H_5Fe(CO)_2(CH_2{=}C{=}CH_2)]^+$.[94] This same cation has also been reported as being prepared from reaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with allene and aluminium chloride.[96]

More stable π-bonded allene complexes of platinum and rhodium have been prepared recently. Allene reacts immediately with $Pt(Ph_3P)_4$ in benzene[10b] depositing white crystals of the complex $Pt(Ph_3P)_2(CH_2{=}C{=}CH_2)$. This same complex has also been prepared according to,[97]

$$cis\text{-}[Pt(Ph_3P)_2Cl_2] \xrightarrow[\text{autoclave, 70-80°}\ \text{95\% EtOH}]{N_2H_4.H_2O\text{,allene}} Pt(Ph_3P)_2(CH_2{=}C{=}CH_2)$$

The complex is air stable, but allene can be displaced from solution at room temperature by treatment with excess PPh_3. When allene is bubbled throgh a dichloromethane solution of $Rh(PPh_3)_3Cl$, yellow crystals of the complex $Rh(PPh_3)_2(CH_2{=}C{=}CH_2)Cl$, $^1/2CH_2Cl_2$ are deposited.[10b]

A number of substituted allene derivatives have been prepared by Vrieze et. al.[98] using the ligands tetramethyl allene (TMA) and 1,1-dimethyl allene (1,1-DMA). e.g.

$$[(\pi\text{-}C_2H_4)PtCl_2]_2 \ + \ 2\ TMA \longrightarrow [(TMA)PtCl_2]_2$$

$$[(\pi\text{-}C_2H_4)PtCl_2]_2 + 2\ 1,1\text{-DMA} \longrightarrow [(1,1\text{-DMA})PtCl_2]_2$$

$$(\pi\text{-}C_2H_4)_2Rh(acac) + 2\ TMA \longrightarrow (TMA)_2Rh(acac)$$

These dimeric species react with pyridines forming monomeric derivatives of the type (allene)$PtCl_2(NC_5H_5)$. TMA also reacts with $Fe_2(CO)_9$ to give the complex $Fe(CO)_4$(TMA).[99]

N.m.r. studies of the above complexes are consistent with two extremes of structure, Fig. V.4(a) (allene perpendicular to the co-ordinating plane)and Fig. V.4(b) (allene in the co-ordinating plane).

Thus, $Pt(PPh_3)_2$ $(CH_2{=}C{=}CH_2)$ is thought to have a structure similar to that shown in Fig. V.4(b),[97,10b] and recently confirmed by an X-ray crystallographic study,[99a] whereas in $Fe(CO)_4$(TMA)[99] the TMA ligand is thought to be π-bonded as in Fig. V.4(a) and in fact oscillate rapidly between the two orthogonal π-systems, as indicated by collapse of the three methyl signals (integration ratio 1:1:2), observed in the low temperature(-60°)n.m.r. spectrum, to a single line at 30°. A similar process is inferred for the platinum complexes $[(TMA)PtCl_2]_2$ and $(TMA)PtCl_2(NC_5H_5)$[98] which show a similar temperature dependence of their n.m.r. spectra.

For the complex $[(1,1\text{-DMA})PtCl_2]_2$,[98] the $C{=}CH_2$ end of the allene is thought to be involved in the bonding to platinum since ^{195}Pt-H coupling is observed and not ^{195}Pt-CH_3 coupling. Even at low temperatures (-70°) the $C{=}CH_2$ protons are equivalent and it is thought that rotation about the Pt-allene bond may occur.[98]

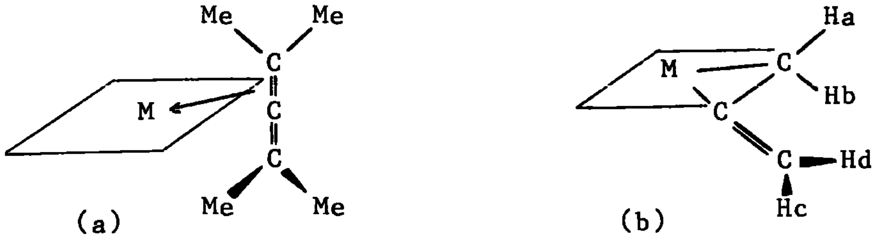


Fig. V.4

The available X-ray crystallographic data on π-allene complexes suggests that the majority adopt the type of structure shown in Fig. V.4(a).[10a,100] E.g. the crystal structure of the complex (acac)Rh(TMA)$_2$,[10a] (acac = acetylacetonato) shows that the TMA ligands are functioning as π-bonded mono-olefins, hence each co-ordinating double bond is approximately perpendicular to the co-ordinating plane and each allene group acts as a unidentate ligand. Also, the distance of the metal ion to the centre of the olefinic bond is less than either M-C distance. Thus a description of the bonding may be made in terms of the Chatt-Dewar scheme,[101] i.e. σ-donation from the ligand to the metal and back donation from filled metal d-orbitals into π^* orbitals on the ligand.

Upon co-ordination to a metal ion, the $\nu_{C=C}$ of olefins generally shows a shift to lower wavenumbers, consistent with the 'synergic' effect proposed, and in some cases a lengthening of the bond occurs.[10a] For the rhodium complex above, the co-ordinated double bond shows an increase in length while the unco-ordinated bond stays close to the free ligand value. Also, on complexation, the C-C-C skeleton is no longer linear, but shows a $C\hat{C}C$ of ca. 150°. The flow of electron density into ligand π^* orbitals, which reduces the π-bonded order, will introduce more s character into the skeletal bonding causing a change in hybridisation at the central carbon from sp to something between sp and sp^2; hence the observed deviation from linearity.

No temperature dependant n.m.r. spectrum was observed for (TMA)$_2$Rh(acac),[98] indicating a statically bonded allene group in solution. This is thought to be due,at least in part, to stronger Rh-allene bonding, as indicated by the longer co-ordinated double bond, which shows stronger π-backbonding than in [(TMA)PtCl$_2$]$_2$.2CCl$_4$[10a] where the co-ordinated and unco-ordinated C-C bond lengths are essentially equal.

D. Ketenimine Metal Derivatives

The Ketenimine group, $R_2C{=}C{=}NR$, is quite rare in transition metal chemistry and very few derivatives are known. In view of the ready protonation of σ-allyl derivatives to give π-olefin complexes, attempts were made[102] to protonate the related 1-cyanoalkyl complexes of the type $\pi\text{-}C_5H_5Fe(CO)_2CH(R)CN$ (R=H,Me). Reaction with dry HCl gave the cationic ketenimine derivatives $[\pi\text{-}C_5H_5Fe(CO)_2(RCH{=}C{=}NH)]^+$, to which the structure below (Fig. V.5) was assigned.

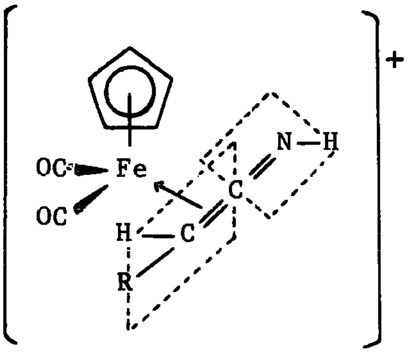
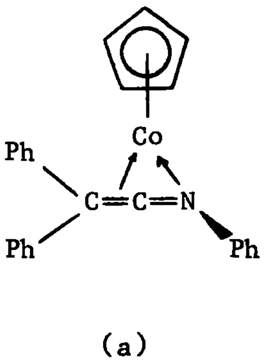


Fig. V.5

The presence of an i.r. absorption attributable to $\nu_{C=N}$ suggested that bonding took place through the C=C rather than the C=N. Exo and endo isomers are indicated by two ν_{NH} and two δ_{NH} deformation modes in the i.r. spectrum, together with two N-H signals in the ^1H n.m.r. spectrum.

Reaction of the preformed ketenimine ligands $Ph_2C{=}C{=}NR$ (R=Ph,Me) with $Fe_3(CO)_{12}$ and $\pi\text{-}C_5H_5Co(CO)_2$ gave the complexes $Fe_2(CO)_6(Ph_2C{=}C{=}NR)$ (R=Ph,Me) and $\pi\text{-}C_5H_5Co(CO)_2(Ph_2C{=}C{=}NR)$, (R=Ph) respectively.[103] For the cobalt complex, spectroscopic evidence suggests bonding involves the C=C system and the nitrogen lone pair. The structure shown in Fig. V.6(a) is tentatively postulated.



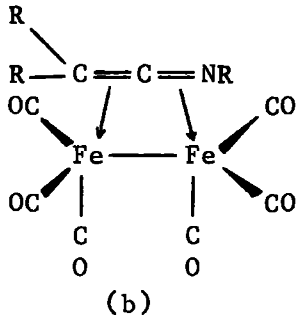


Fig. V.6

I.r. and ^1H n.m.r. data are consistent with the structure shown in Fig. V.6(b), suggested for the iron derivative, in which bonding involves both the C=C and C=N systems. No stretching mode attributable to either of these units is apparent in the i.r. spectrum. However, an X-ray crystal structure of the complex where R=Me,[104] showed that the organo-nitrogen group bridged as a 1-aza-allyl ligand as shown in Fig. V.7

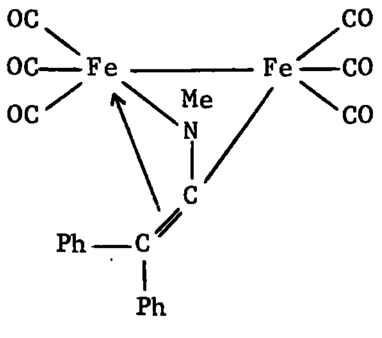


Fig. V.7

Insertion of tetracyanoethylene into metal-alkyl and metal-hydride bonds has been found to give ketenimino-derivatives bonded only through the nitrogen.[105,106] Reaction between π-$C_5H_5Fe(CO)_2CH_2Ph$ and $(NC)_2C{=}C(CN)_2$ in CH_2Cl_2 solution at room temperature gives as the major product a complex formulated as in Fig. V.8.[105]

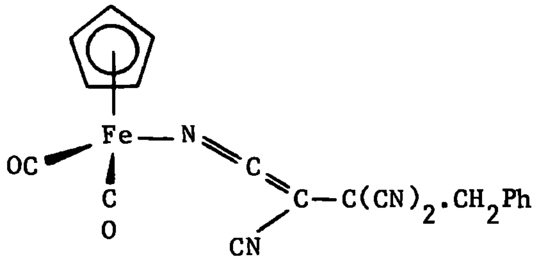


Fig. V.8

I.r. absorptions at 2151 and 1296 cm.$^{-1}$ have been assigned to asymmetric and symmetric stretches, respectively, of the N=C=C system. A crystal structure of the iridium complex,[106] (Fig. V.9), $Ir(CO)[C_2(CN)_4](PPh_3)_2N{=}C{=}C(CN)CH(CN)_2$ showed the Ir-NC_2 skeleton to be only slightly bent at nitrogen ($Ir\hat{N}C_2$ = 162°)

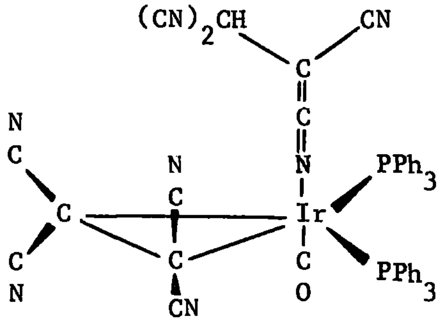


Fig. V.9

E. Amidine Metal Derivatives.

Our studies concerning the nature of the bonding in aza-allyl complexes,[107,108] have stimulated interest in the possibility of further organonitrogen analogues of the π-allyl group. In this respect amidino-groups, [RNC(R')NR"], are potential 3-electron donors. In addition to the normal modes of attachment detected for the π-allyl group, further modes may be possible for the amidino-group because of the presence of lone pairs of electrons on the nitrogen atoms.

Amidino complexes have been synthesised using either the neutral amidines, [RNC(R')NHR"] or their lithio-derivatives. Reaction of RNC(Ph)NRLi, (R = Ph, p-tolyl) with π-$C_5H_5M(CO)_3Cl$, (M = Mo,W) gave golden-yellow, air sensitive complexes formulated as π-$C_5H_5M(CO)_2$[RNC(Ph)NR] on the basis of analytical and spectroscopic evidence.[109] ^{1}H n.m.r. studies in the temperature range -40° to +50° for the complex with R = p-tolyl suggest that the amidino- group is bound symmetrically to the metal, possibly as in π-allyl complexes, as only a single methyl signal is observed.

In contrast, $Mn(CO)_5Br$ reacts with R"CN(R')NR"Li to give the complexes $(CO)_4\overline{MnC(O).N(R'').C(R'):N}R''$ formulated as a cyclic carbamoyl derivative,[110] (Fig.V.10(a)).

(a) (b)

R'	R"
Ph	Ph
Ph	p-tolyl
Me	Ph
Ph	H

R'	R"
Ph	Ph
Ph	p-tolyl

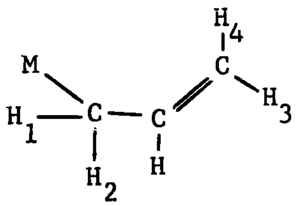
Fig. V.10

Four terminal carbonyl absorptions are observed, together with a medium band ca. 1700 cm.$^{-1}$ attributed to $\nu_{C=O}$ of the ketonic carbonyl group. The action of heat, or u.v. irradiation in cyclohexane on this complex causes decarbonylation to occur giving the 1,3-diaza-allyl derivative shown in Fig. V.10(b).[110] The carbonyl stretching frequencies closely resemble those of π-$C_3H_5Mn(CO)_4$,[48] and a similar delocalised π-system is indicated from the n.m.r. spectrum of the complex for which R" = p-tolyl, since only one methyl signal is observed throughout the temperature range -50° to +40°.

Reaction of the neutral amidines with metal carbonyls leads to loss of hydrogen and formation of complexes of the amidino group. $Mo(CO)_6$ forms the red crystalline product $Mo_2[RNC(Ph)NR]_4$, (R = Ph, p-tolyl)[109] which may have the cupric acetate type of structure.[111] The analogous reaction with $Cr(CO)_6$ gives the corresponding product $Cr_2[RNC(Ph)NR]_4$, (R = Ph, p-tolyl) and also a derivative formulated as $(PhR_2CN_2H)Cr(CO)_3$ (R = Ph, p-tolyl), in which the $-Cr(CO)_3$ moiety may be π-bonded to one of the aromatic rings.[112]

F. N.m.r. Studies of 'dynamic' allyl systems.

It has been observed that the ^1H n.m.r. spectra of allylic-metal complexes fall into essentially three categories. The σ-bonded allyls give the spectra to be expected from their written formulation (shown below)



i.e. protons 1 and 2 are magnetically equivalent while protons 3 and 4 are not.

Similarly most π-allyl groups, e.g. π-$C_3H_5Mn(CO)_4$,[50b] show spectra corresponding to an AM_2X_2 system, (Fig. V.11(a)) i.e. equivalent syn-protons (H_2) and equivalent anti- protons (H_3). In fact a detailed high resolution analysis of the spectrum of π-$C_3H_5Mn(CO)_4$ shows that there is long range coupling between the protons, (H_2-H_3) and the actual spectrum is more complicated than that shown in Fig. V.11(a).[41] The third class of spectra suggest that the allyl group has equivalent terminal hydrogens i.e. they have a spectrum such as that shown in Fig. V.11(b), which is typical of an AX_4 system and is considered to be diagnostic of the so-called dynamic allyl. Upon sufficient cooling, a spectrum of a static, rigidly bound π-allyl is often observed. Much speculation and discussion has arisen concerning the interconversions which are responsible for the coalescence of the static π-allyl resonance to give the more simple spectrum of a dynamic allyl on raising the temperature.

The transition from an AM_2X_2 type of spectrum to an AX_4 type implies the occurrence of syn-anti exchange, i.e. H_2 and H_3 (Fig. V.11(a)) become equivalent. Two mechanisms by which this could occur have been proposed. By far the most popular amongst workers in the field[113-117] is a reversible interconversion of the allyl group from the π-allyl ground state to a short-lived σ-intermediate (Fig. V.12) in which rotation about the C-C single bond can occur before reversion to the π-allyl ground state.

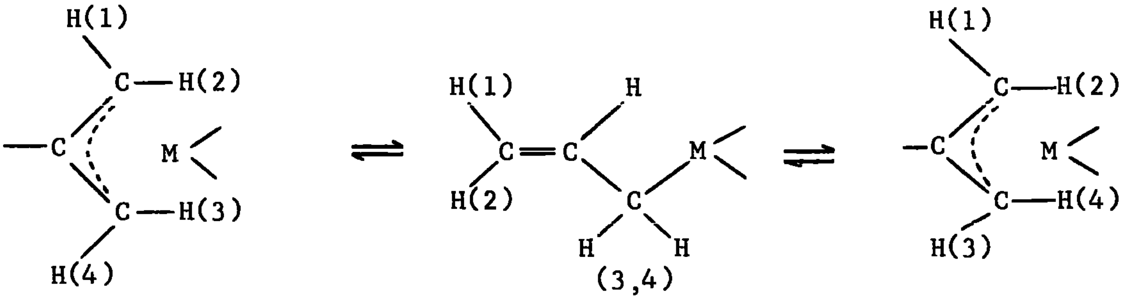
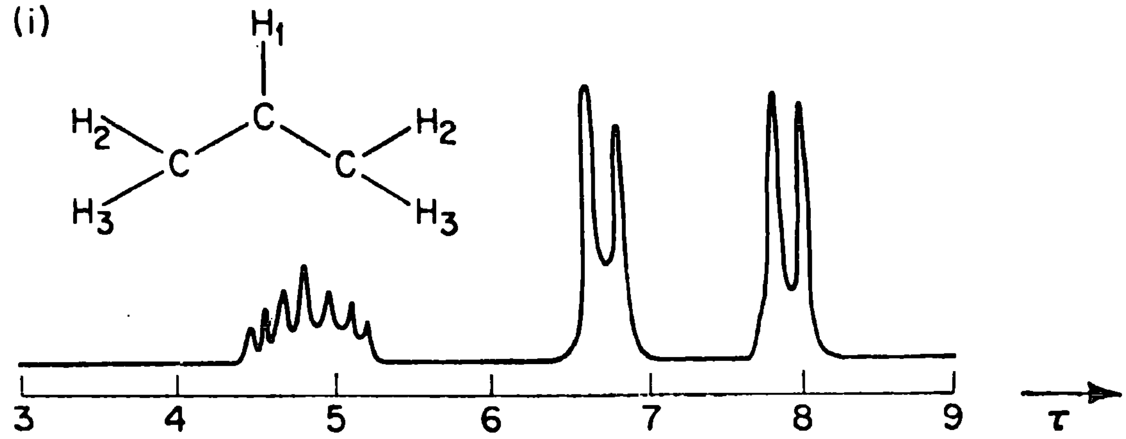


Fig. V.12

Interconversion of protons (3) and (4) via a σ-intermediate.



Assignment	H_1	H_2	H_3
Range of reported chemical shifts	3·5–6	5–7·6	6–9
Typical values	4·8	6·1	7·4
Relative areas	1	2	2

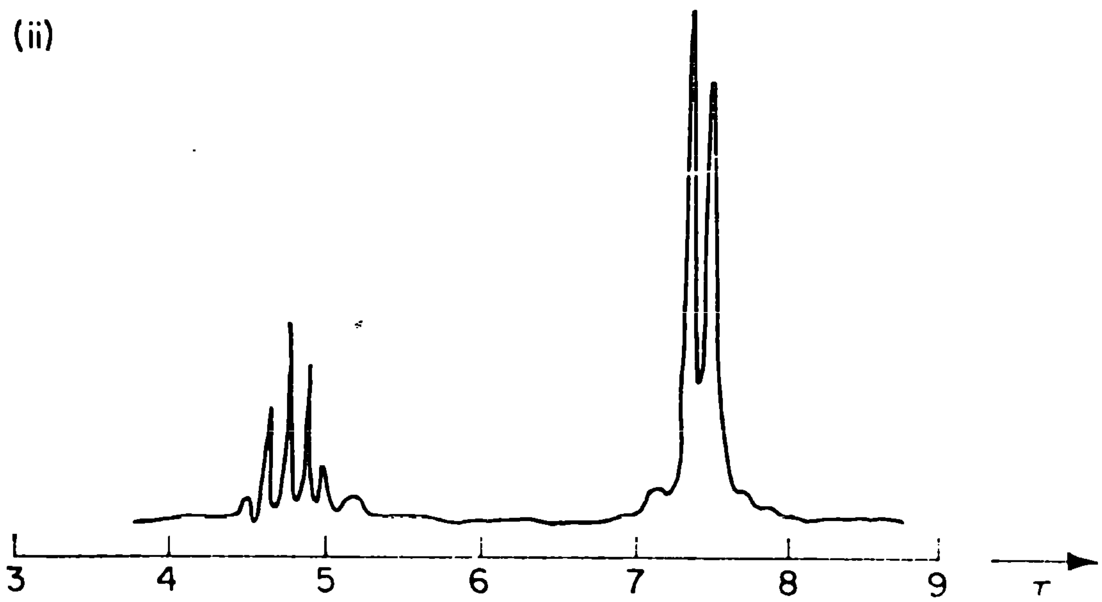


Fig. V.11

i) A typical ^{1}H n.m.r. spectrum of a π-allyl AM_2X_2group.

ii) ^{1}H n.m.r. spectrum of $Zr(C_3H_5)_4$ at -20°; an AX_4 system.

A good example of this process is provided by the rhodium(III) complex $(Ph_3As)_2Rh(\pi\text{-2-methallyl})Cl_2$[113] which changes from an AM_2X_2 spectrum at 15° to an AX_4 spectrum at 60°. Also, the rhodium-methyl group spin-spin coupling (^{103}Rh, $I={}^1/2$) is retained throughout the temperature range, indicating an intramolecular process. Vrieze et. al,[118] have called this mechanism the 'π-σ' reaction.

Beconsall et. al.[119,120,42] have proposed, from their studies on certain isoleptic* π-allyl complexes, e.g. $M(\pi\text{-}C_3H_5)_4$, (M = Th,Zr, Hf), and $Pd(\pi\text{-}C_3H_5)_2$, that syn-anti exchange is caused by rotation of the $-CH_2$ groups about the C-C bonds while the allyl group remains π-bonded to the metal. The spectrum of $Zr(\pi\text{-}C_3H_5)_4$ at -66° is a typical AM_2X_2 type consisting of two CH_2 doublets and a nine-line multiplet due to the central proton. At -20° a single CH_2 doublet is observed and the central proton resonance is simplified to a quintet. Evidence for the rotation mechanism comes from a) the chemical shift of the central proton remains unaltered on the change from AM_2X_2 to AX_4; b) the chemical shift of the AX_4-CH_2 doublet is midway between the chemical shifts of two AM_2X_2 doublets, and c) the single coupling constant in the AX_4 spectrum is the average of the two coupling constants in the AM_2X_2 spectrum. Similar behaviour is observed for $Th(\pi\text{-}C_3H_5)_4$ although the $AM_2X_2 \rightarrow AX_4$ transition occurs at much higher temperatures. In contrast, $Hf(\pi\text{-}C_3H_5)_4$ shows an AX_4 spectrum even at low temperatures, no indication of line broadening being observed at -72°.

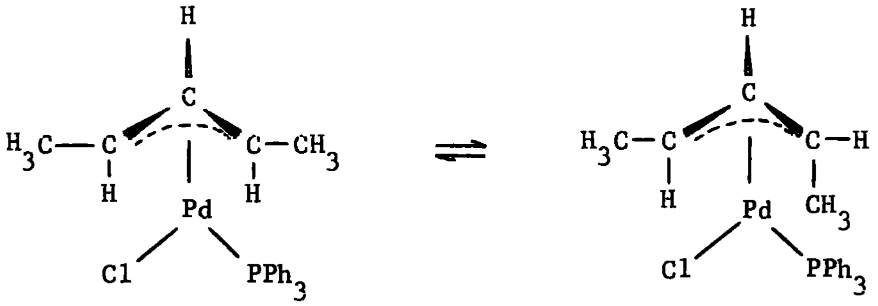
The theoretical basis for this hindered rotation mechanism[42] is that the C═C bonds, which are already weakened by interaction with the metal, become further loosened at higher temperatures, thus allowing relatively easy rotation around the C-C bonds. Activation energies for the process

---

* The term isoleptic indicates that all ligands attached to the central metal atom are identical in constitution.

have been measured and are about 10 Kcal/mole [$Zr(\pi\text{-}C_3H_5)_4$] and 15 Kcal/mole [$Th(\pi\text{-}C_3H_5)_4$]. For these latter compounds, if it is assumed that four allyl anions are bonded to the central metal (in the +4 oxidation state), then no filled metal d-orbitals are available for back-donation to the ligand, hence the bonding will depend entirely on any additional metal-ligand charge transfer as in olefin-metal complexes the donor capabilities of the allyl anion being, at most, of minor importance. Hence the ease of the transition π-allyl → 'dynamic' allyl could therefore be due to the absence of sufficiently strong back-donation. Significantly, allyl compounds of main group elements (which also have no d-electrons for back-donation), e.g. allyl Grignard reagents,[121] and di-allylmagnesium,[42] show AX_4 type spectra at all temperatures, lending support to the theory.

Strong critiscism of this mechanism has come from Vrieze et.al.[118] who, as well as doubting such a rotation from a theoretical point of view, put forward experimental evidence which suggests that C═C bond rotation is virtually impossible because of steric effects, viz. the syn-anti exchange observed in the methyl substituted compounds:



It would seem a little unwise, however, to extend observations made in palladium chemistry to the somewhat non-analogous complexes which occur in zirconium and thorium chemistry, although Beconsall et.al,[120] while admitting that experimental results obtained for Zr(π-$C_3H_5)_4$ and Th(π-$C_3H_5)_4$ can be adequately explained in terms of a σ-intermediate or C$\overset{=}{-}$C bond rotation, reject the former on account of its failure to explain the temperature dependance of the n.m.r. spectrum of Pd(π-$C_3H_5)_2$. The spectrum of this complex can be analysed as two superimposed AM_2X_2 spectra with different intensities (approximately 3:1 at low temperature). Conformational isomers of the type shown in Fig. V.13 are proposed to explain this. In each of these static structures the two

Fig. V.13

allylic ligands occupy equivalent positions, and each is expected to give an AM_2X_2 spectrum. On increasing the temperature to ca. 70°, both forms show broadening of the resonances. This has been attributed to syn-anti exchange via the onset of internal rotation of the CH_2 groups rather than a σ-intermediate, since the latter process would effect an interchange of structures Fig. V.13(a) and (b) at four times the rate of syn-anti exchange (the latter exchange occurring at only one end of one allyl group in each (a) ⟶ (b) interconversion). The observed spectra show that on the contrary, syn-anti exchange is the more rapid process.

It was pointed out, however, by Davison and Rode,[122] that the line broadening could be explained by an acceleration of an equilibrium between forms (a) and (b) (Fig. V.13), rather than syn-anti exchange*. Such conformational equilibria are now thought to exist for several π-allyl complexes, where isomers differing in the orientation of the π-allyl group with respect to the rest of the molecule are postulated; e.g. Rh(π-allyl)$_3$,[124] π-$C_5H_5Mo(CO)_2$(π-C_3H_5),[122] π-$C_3H_5Fe(CO)_2I$,[125] and $W(CO)_4$(π-C_3H_5)X, (X = Br,I).[126] The n.m.r. spectra of these compounds show two distinct AM_2X_2 systems at low or room temperature which coalesce to a single AM_2X_2 system at higher temperatures no syn-anti exchange being apparent. The mechanism usually put forward to account for these observations is a rotation of the whole π-allyl group about the metal-allyl axis.

A further process not involving syn-anti- exchange is apparent in the complexes (π-allyl)PdCl(amine) and (π-2-methallyl)PdCl(amine) where amine = (S)-α-phenylethylamine.[127] At room temperature an ABCDX type spectrum is observed, (the four terminal protons of allyl group are magnetically non-equivalent due to the inherent asymmetry of the molecule), showing a complex resonance for the syn-protons and two resonances for the anti-protons. Above 30° broadening of the anti- signals occurs and coalescence (π-allyl complex) takes place at 70°. No broadening of the syn-proton signals is observed in this temperature range. No mechanism discussed, so far, can adequately explain these results, hence it was postulated that rotation through 180° of the allyl moiety about the C_1 - C_3 axis took place, which would effectively be a 'flip' movement passing through a transition state in which the allyl skeleton and the palladium atom are coplanar,[127,128] as shown in Fig. V.14. Such a

---

* Later work by Beconsall and O'Brien[123] indicated that both these processes were occurring on increase in temperature.

process accounts for the spectral variations observed, as the position of the syn- protons is largely unchanged throughout the movement due to the geometry of the allyl group.

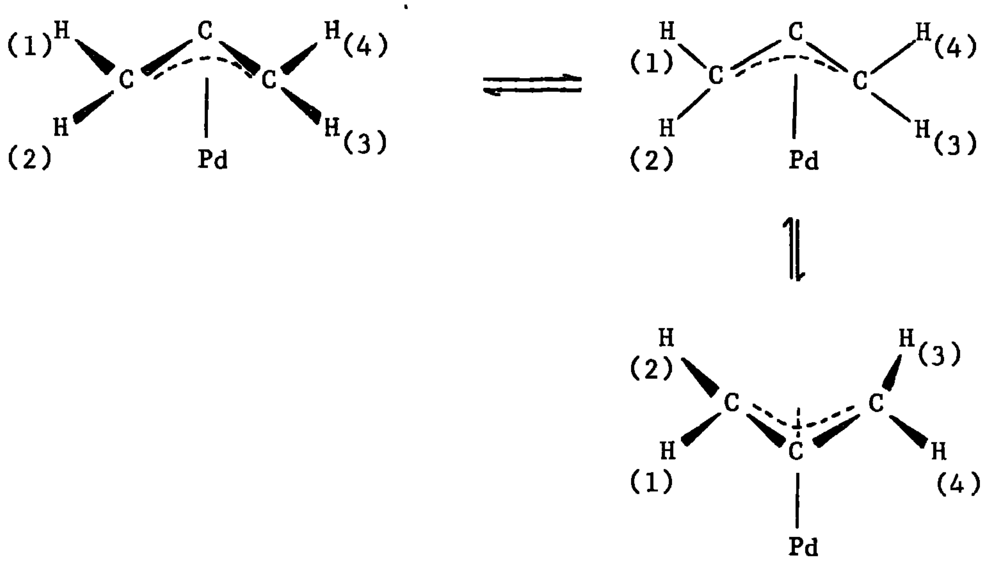


Fig. V.14

It has been pointed out[129] that in the coplanar intermediate the molecular orbitals of the ligand can still overlap with metal orbitals, thereby decreasing the activation energy of the process. A similar mechanism has also been considered by other workers for similar compounds, but the evidence there was inconclusive.[130]

Many research groups have devoted their attention to the n.m.r. study of palladium-π-allyl systems of the general type (π-allyl)Pd(L)X, where L is a basic ligand (phosphines, arsines, amines, dimethylsulphoxide etc.) and X is usually chloride. The dimeric species $[(\pi\text{-allyl})PdCl]_2$ does not show a temperature dependant spectrum,but the AM_2X_2 type expected for a static, symmetrical, π-bonded allyl group.[117] Reaction of this compound however with basic ligands (L) causes cleavage of the chlorine bridges and formation of the monomeric species (π-allyl)Pd(L)Cl, which show spectra characteristic of dynamic allyls.[117,44] In the absence of exchange processes (i.e. in general the low temperature limiting spectrum) all four terminal allylic protons will have a different chemical shift since the molecule no longer has a plane of symmetry perpendicular to the Pd-Cl-L and allyl planes[131] (Fig. V.15), (the dimer, $[(\pi\text{-allyl})PdCl]_2$ has a plane of symmetry perpendicular to the $[Pd\text{-}Cl]_2$ plane, hence the AM_2X_2 type spectrum). Thus, the spectrum in the absence of exchange processes is expected to be of the AGMPX type.

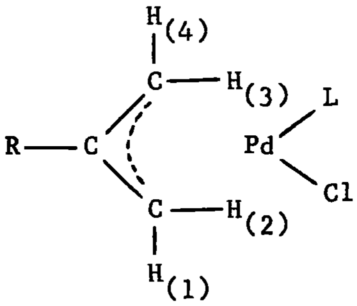


Fig. V.15

Two distinct averaging processes are generally observed, a) syn-syn together with anti-anti exchange, i.e. H(1) with H(4) and H(2) with H(3), which effectively is a left→right interchange of the allyl grouping with respect to the Pd(L)Cl unit, and b) syn-anti exchange i.e. H(1) with H(2) and H(3) with H(4). The predominant process, or the process which occurs first (i.e. at the lower temperature) depends on a number of factors,[131] namely the ligand L, the ligand/metal ratio* and also in some cases[132] on the substituent, R, on the central carbon atom (Fig. V.15). Most studies have been carried out with 2-methallyl complexes (i.e. $R=CH_3$) because of the greater stability and a simpler n.m.r. spectrum. For the complexes (π-1-methallyl)Pd(L)-Cl,($L=Ph_3P,Ph_3As$), on increasing the temperature from the point at which the limiting spectrum was observed (ca. -80°), (L/Pd ratios > 1), left→right interchange was observed between -70° and -40°, the rate in the case of Ph_3As being proportional to the concentration of free arsine.[133,134] Between 10° and 80° with larger L/Pd ratios syn-anti exchange was observed, again the rate being proportional to the concentration of free arsine.

For L/Pd ratios <1 and for $L = Ph_3P$ at temperatures slightly above -80°, coalescence of protons in sites (3) and (4) (Fig. V.15) was observed while signals due to H(1) and H(2) remained sharp. No exchange of phosphine was evident as the phosphorus coupling to H(1) and H(2) remained unchanged.[131] At higher temperatures (-20° to +25°) syn-anti exchange was observed at both ends of the allyl group, again without exchange of phosphine, and with no broadening of the dimer signals.[135] Further increases in temperature caused coalescence of all monomer signals and also collapse of the dimer resonances. These latter reactions were the only ones observed for $L = Ph_3As$ (L/Pd $\nless$1).[134]

Left-right interchange of π-allyl groups is considered to involve a rotation of the group in its own plane through 180° together with simultaneous ligand exchange[133,135] as shown in Fig. V.16.

---

* The reaction between $[(\pi\text{-allyl})PdCl]_2$ and basic ligands is an equilibrium of the type:

$[(\pi\text{-allyl})PdCl]_2 + 2L \rightleftharpoons 2(\pi\text{-allyl})Pd(L)Cl$ which is usually far over to the right. A ligand/metal ratio greater than one (L/Pd >1) implies excess L and hence little dimer present in solution. For L/Pd <1, the opposite is implied.

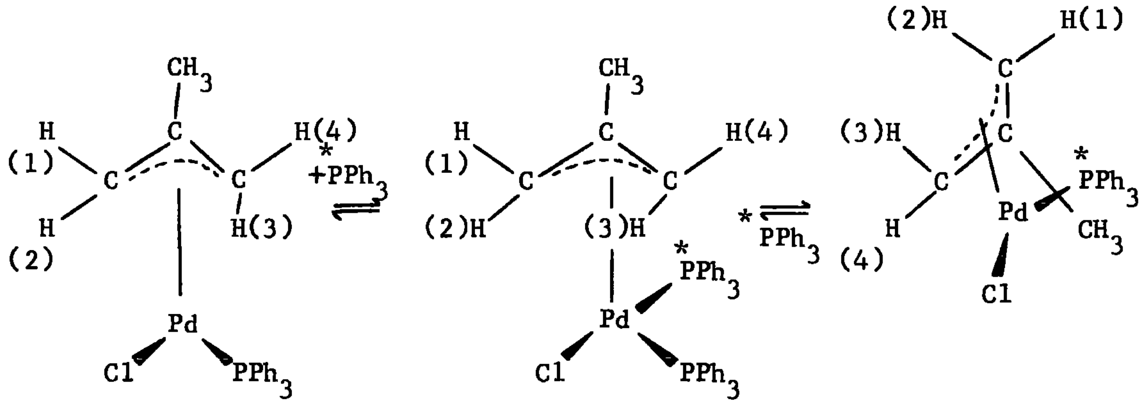


Fig. V.16

Although consistent with the observations, the mechanism has been criticised by Powell and Shaw,[44] who point out that ligand substitution processes alone are sufficient to explain the observed exchange processes without postulating π-rotation.

The mechanism by which syn-anti exchange occurs for L/Pd > 1 is thought to be via a σ-intermediate initiated by ligand exchange[114,134] as shown in Fig. V.17. With L/Pd < 1, i.e. in the presence of the dimer

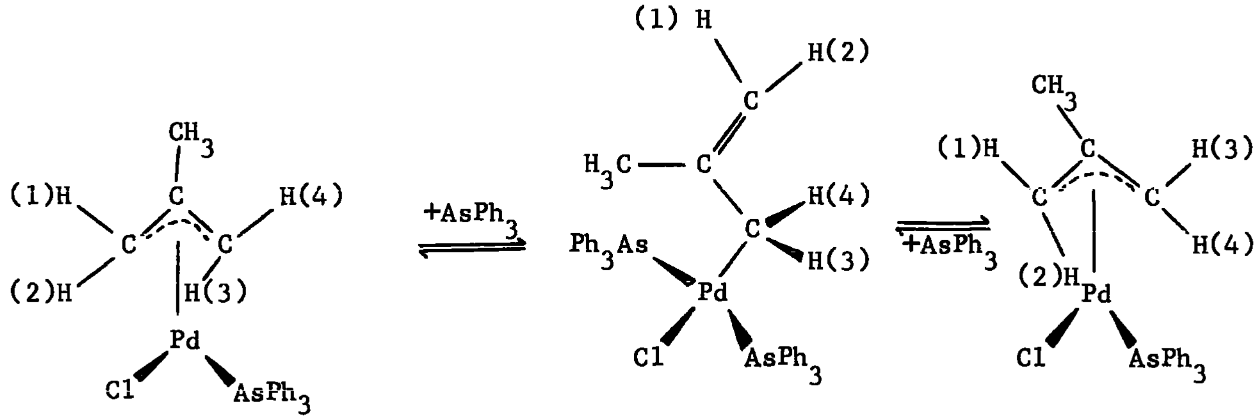


Fig. V.17

Interchange of protons (3) and (4) via a ligand induced σ-intermediate (protons (1) and (2) may exchange by the same mechanism).

[(π-2-methallyl)PdCl]$_2$, syn-anti exchange is thought to go via an intermediate involving the dimer since the rate is dependant on the concentration of the latter.[114] (Fig. V.18). Other dimeric species, e.g. 1,5-cyclooctadiene-rhodium chloride dimer,[136] have also been found to catalyse syn-anti exchange.

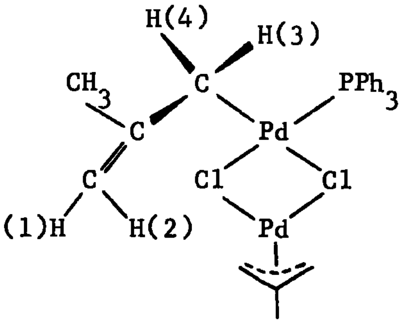


Fig. V.18

A σ-intermediate causing interchange of protons (3) and (4) involving [(π-2-methallyl)PdCl]$_2$.

Fairly conclusive proof that a σ-intermediate is involved in this particular process has been obtained by van Leeuwen et. al.[132,137] from their studies of complexes where L = PMe_2Ph. The free ligand has a plane of symmetry, but once it is attached to the metal, the plane is destroyed and thus the methyl groups will be non-equivalent in the n.m.r. spectrum and will remain so irrespective of any rotation of the phosphine. However, when by some mechanism, the allyl plane interconverts with its mirror image (the MLCl plane being the mirror plane), the complex does have a plane of symmetry in a certain time scale, hence the two methyl groups become equivalent in the same time scale. For the complex π-$C_3H_5PdCl(PMe_2Ph)$, (Fig. V.19), the n.m.r. spectrum at -20^o shows

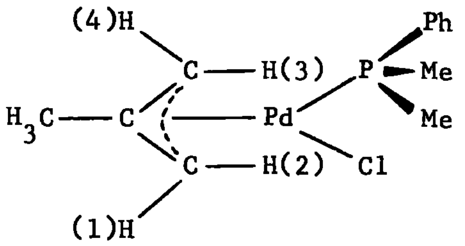


Fig. V.19

separate signals for all four terminal protons and also for the methyl groups. Warming to 20^o causes an exchange between H(3) and H(4) while the H(1) and H(2) signals remain sharp. Simultaneously with this process the methyl groups on phosphorus become equivalent. Ligand exchange is ruled out since coupling of phosphorus to H(2) is retained, even above 20^o. These observations are compatible only with exchange taking place via a σ-intermediate.[137]

The preferential coalescence of protons (3) and (4) before protons (1) and (2) has been rationalised in terms of asymmetry of the palladium-allyl bond.[114,131,134] X-ray crystallographic data obtained on the complex (π-2-methallyl)PdCl(Ph$_3$P)[138] prompted Powell and Shaw[114] to suggest that the structure lay somewhere between a symmetrical π-2-methallyl and a σ-π type similar to that shown in Fig. V.3., though this has been criticised by Vrieze et. al.[131] and by Cotton[117] who suggests that since the C-C bonds of the allyl skeleton are equal to within three standard deviations of the reported error, the bonding is still essentially π-allylic in nature, but the small degree of asymmetry present is best described as a small perturbation of the molecular orbital description of an unperturbed (π-allyl)M unit, caused by the presence of two different ligands (Cl and PPh$_3$), in the molecule.

Alternatively, the 'trans effect' may be invoked to explain the n.m.r. and structural observations.[139] Strictly speaking, the 'trans effect',[140] only denotes the ability of ligands to labilise the metal-ligand bond trans to it towards substitution. Although no substitution occurs during a π-σ rearrangement, a breaking and making of bonds is implied, which is an analogous situation. In the complex (π-2-methallyl)Pd(Ph_3P)Cl, as PPh_3 has a higher 'trans-effect' than Cl^-, one would expect the Pd-C bond trans- to PPh_3 to be preferentially broken resulting in interchange of protons (3) and (4), before (1) and (2), (Fig. V.15) as is observed.[131] As mentioned previously, this exchange process requires the presence of the dimer $[(\pi\text{-2-methallyl})PdCl]_2$, i.e. it is an intermolecular process, suggesting that perhaps the bonding in the allyl group is only weakly influenced by the difference in 'trans effect' between PPh_3 and Cl^-. For the complex (π-2-methallyl)Pd(OAc)(PPh_3), the difference in 'trans effect' between PPh_3 and OAc^- is greater and exchange of protons (3) and (4), while (1) and (2) (Fig. V.15) remain sharp, is found to occur by an intra-molecular process,[139] indicating perhaps that the 'trans effect' does play a significant role in this mechanism. Further support is gained by studies made on the systems (π-allyl)PdCl(amine). Amines and chloride ion have similar trans- effects hence no π-σ reactions of this type would be expected until high temperatures are reached, which is indeed observed.[130]

A 'trans effect' theory also rules out the C$\overset{...}{=}$C internal rotation mechanism proposed by Beconsall et. al.[119,120] for these particular systems. Assuming the structure in Fig. V.15, if CH_2 rotation were operative, one would expect averaging of protons(1) and (2) before protons (3) and (4) since the Pd-carbon bond trans to L(= PPh_3) would be weaker. This is not the case, as protons (3) and (4) are observed to coalesce first, (the assignment of particular signals in the spectrum to positions in Fig. V.15 is determined from a consideration of chemical shifts and coupling constants[114]).

In conclusion it would appear reasonable to accept the probability that more than one averaging mechanism operates in π-allylic systems, (particularly with regard to the syn-anti exchange process) rather than to extend results obtained on particular systems to cover the whole field, as has been attempted. A rather more balanced view is put forward by Cotton,[117] who although stating that equilibria involving transient σ-allylic species are primarily responsible for the processes observed in allyl-palladium systems, willingly accepts that the internal π-rotation mechanism proposed by Beconsall et. al.[119,120] may well be operative in the widely differing systems to which he refers.

CHAPTER 6

AZA-ALLYL/ALLENE DERIVATIVES OF MOLYBDENUM AND TUNGSTEN

This chapter describes the solid state properties of the aza-allyl/allene derivatives π-$C_5H_5M(CO)_2[R'R''CNCR'R'']$, (M = Mo,W) where R' and R'' are various aryl groups but in particular p-tolyl, and also the related derivatives π-$C_5H_5M(CO)_2[R_2CNCR_2](R_2C{:}O)$, (M = Mo,W; R = p-tolyl). In the main, attention is devoted to the mode of bonding adopted between the aza-allyl/allene ligand and the metal, and is discussed in terms of the spectroscopic and crystallographic data[6a] obtained.

A. Aza-allyl/allene Complexes.

Optimum yields of aza-allyl/allene derivatives were obtained by dropwise addition of the appropriate lithio-ketimine solution to π-$C_5H_5M(CO)_3Cl$, (M = Mo,W). All but two of the complexes described in Chapter 3 were dark purple crystalline solids. π-$C_5H_5Mo(CO)_2$[(p-tolyl)(Ph)-CNC(p-tolyl)(Ph)] was a more red-brown colour although intensely purple solutions in organic solvents were obtained. π-$C_5H_5Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2\text{-}CNC(p\text{-}CF_3C_6H_4)_2]$ was a dark-blue-black microcrystalline solid giving blue-purple solutions.

The aza-allyl/allene ligand is thought to act as a three-electron donor, thus fulfilling the inert gas rule, on the basis of a) the failure to add a further neutral 2-electron donor such as triphenylphosphine, even addition of a further CO molecule under conditions of high temperature and pressure could not be effected,[112] and b) the low carbonyl frequencies, indicating dissipation of high charge build-up on the metal. In fact the carbonyl frequencies of the aza-allyl/allene complexes so far prepared correlate well with the electronic properties of the para-substitutents on the R groups as indicated by their Hammett σ-constants[141] (see Table VI.1).

Table VI.1

Correlation of ν_{CO} for the complexes π-$C_5H_5Mo(CO)_2[(p\text{-}XC_6H_4)\text{-}CNC(p\text{-}XC_6H_4)_2]$ with the Hammett σ constant of the para-substituent X.

X	σ	ν_{CO} cm.$^{-1}$
CF_3	+ 0.54	1958, 1870
F	+ 0.062	1937, 1846
H	0.000	1927, 1845
CH_3	- 0.17	1936, 1836

The high frequency absorption of the p-tolyl complex is anomalously high, but the low frequency bands correlate very well. X-ray photoelectron spectra of the two extremes in this series i.e. the p-$CH_3C_6H_4$ and p-$CF_3C_6H_4$ compounds show that for the latter, electron density on the nitrogen and on the metal are significantly reduced,[35] in keeping with the observed change in carbonyl frequencies.

The Hammett σ constants of para-substituents (σ_p) on aromatic rings have also been related to the chemical shifts of π-C_5H_5 groups attached to metals. Knox et, al.[142] have studied a series of compounds of formula π-$C_5H_5Fe(CO)_2$(p-XC_6H_4) where X ranges from CN (σ_p = + 0.63) to MeO (σ_p = -0.27). A good linear relation between σ_p and $\tau_{C_5H_5}$ was obtained, (as the electron donating ability of X increases, so $\tau_{C_5H_5}$ increases), although a range of only 0.07 ppm was reported. Owing to the difficulties in attaining reproducible conditions (i.e. solvent, temperature and concentration of both solute and standard, particularly the latter two) for a series of spectra and in view of the small differences one could expect, a systematic study of this type on our series of aza-allyl complexes was not attempted.

Considering now the complexes where R' = R" = p-tolyl, (M = Mo,W) two isomers are thought to exist in the solid state (forms A and B). The product of the reaction for M = Mo, is form A, and for M = W, form B can be obtained exclusively, providing a co-ordinating solvent (e.g. ether or monoglyme) is used in the crystallisation process. If hexane only is used then a mixture of isomers is usually obtained. Form A in a pure state for tungsten is very difficult to obtain. Small quantities result by allowing a hexane solution of the complex to stand for a week or more, followed by a slow crystallisation process. The function of the co-ordinating solvent in the crystallisation of form B is not clear, unless it serves to 'hold' the aza-allyl/allene ligand in a certain orientation until the moment of crystallisation, when lattice forces take over. Although solvent of crystallisation has been observed in form B (n.m.r. studies) for some samples, it is by no means essential to its existence as many samples uncontaminated by solvent have been obtained.

Evidence for the presence of isomers arises from the solid-state (KBr disc) i.r. spectra, which are sufficiently different to allow crystalline modifications to be ruled out. The major differences are shown in Fig. VI.1. The low frequency carbonyl stretching mode is shifted 15 $cm.^{-1}$ to lower frequency and quite a different absorption pattern is apparent between $700-750cm.^{-1}$, the aromatic C-H out-of-plane bending region. Solution spectra show that both isomers form a common species in solution as only two carbonyl absorptions are observed. In solvents other than aliphatic hydrocarbons, these absorptions correspond to those for the solid state form B (M = W), as does the $700-750\ cm.^{-1}$ region (CS_2 solution). No evidence has been found for this form in the solid state for M = Mo. The apparent difference between the molybdenum and tungsten systems is unlikely to be due to steric factors as the effective sizes of the two metals are very similar, due to the lanthanide contraction. However, it would be unwise to speculate too much on the question of factors influencing the formation of either isomer A or B until the precise nature of the two forms has been determined.

Possible bonding modes of the $[R_2CNCR_2]$ ligand to transition metals have been discussed in Chapter 1 and the crystal structure of π-$C_5H_5Mo(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$, (V), (Fig. VI.2),[6a] shows that in form A, the ligand adopts the aza-allene bonding mode, the CR_2 groups

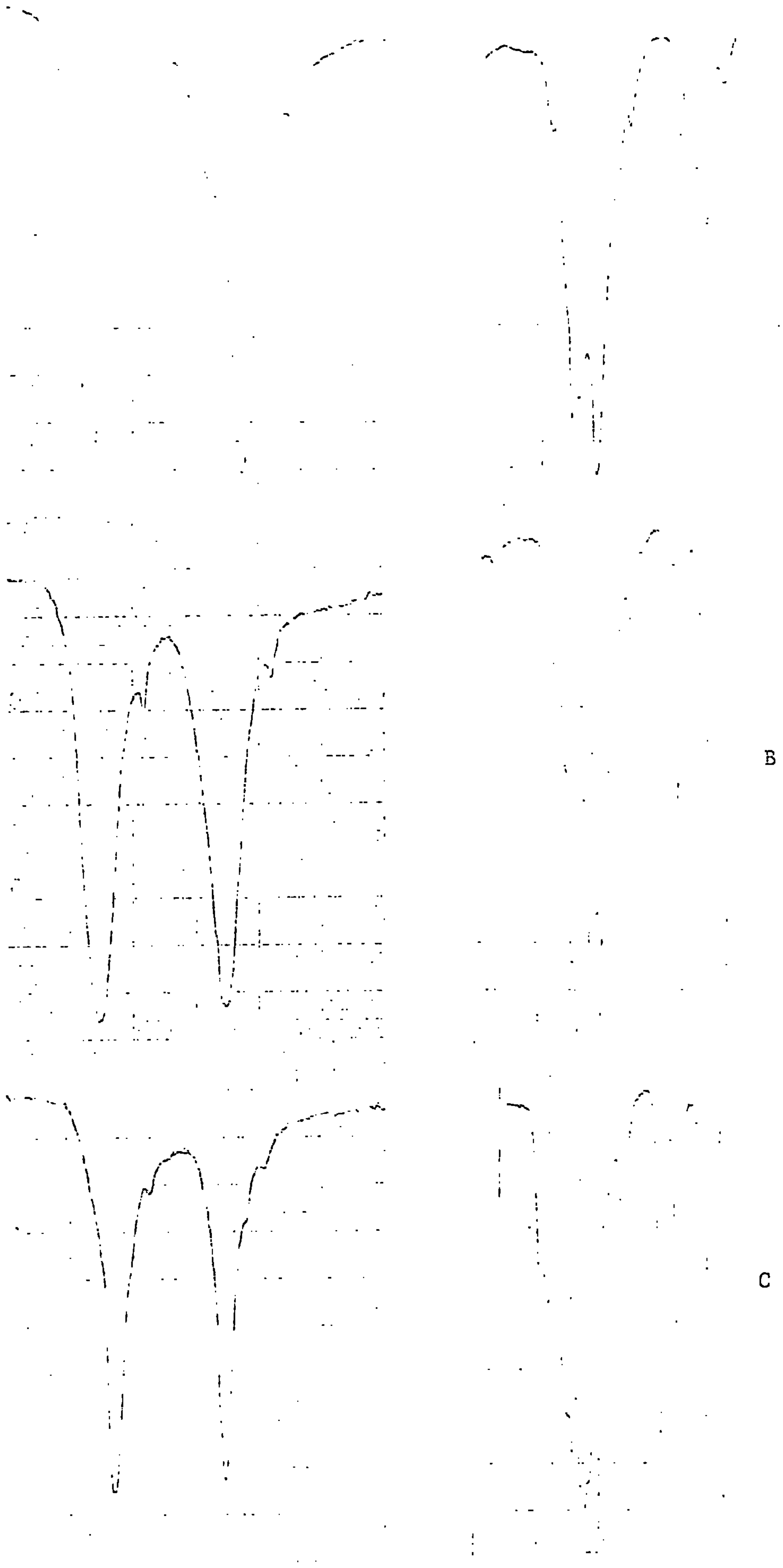
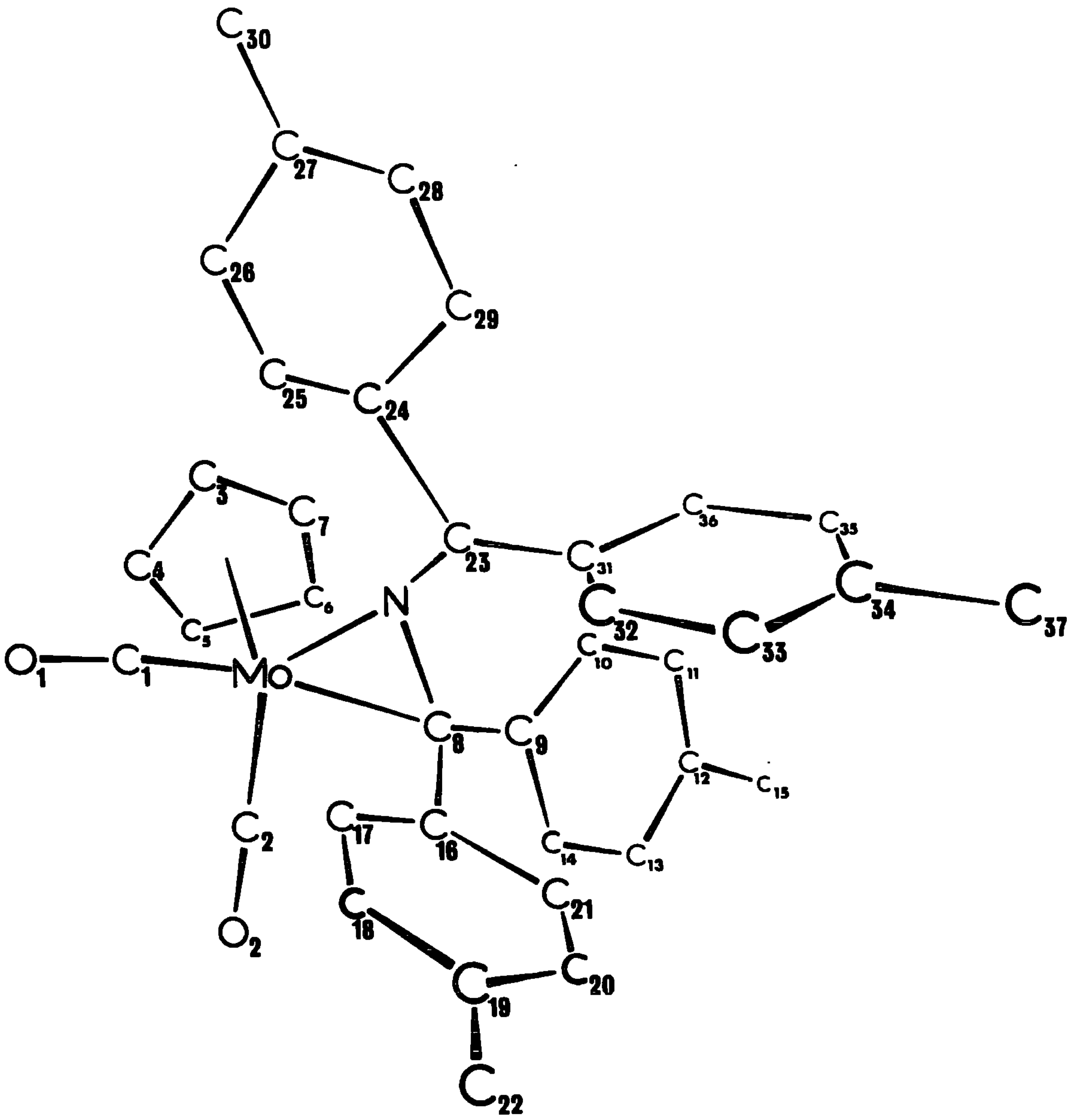


Fig. VI.1

I.r. Data for π-$C_5H_5W(CO)_2[R_2CNCR_2]$ (forms A and B) and π-$C_5H_5W(CO)_2[R_2CNCR_2]$ (R_2CO), (C).



$(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-}tolyl)_2CNC(p\text{-}tolyl)_2]$

Numbering of the Atoms

Fig. VI.2

being in essentially perpendicular planes. The exact angle is 83^{o}, the deviation from orthogonality probably being due to the steric requirements of the bulky p-tolyl groups. Other important bond distances and angles are given in Table VI.2. The co-ordinated C-N bond (1.43 Å) is equal to that expected for a C-N single bond,[143a] and the unco-ordinated bond (1.30Å) slightly longer than the accepted C=N distance of 1.27Å.[143b] The $\widehat{CNC}$ of 128^{o} implies an essentially sp^{2}-hybridised nitrogen in the complex. Some degree of sp^{3} hybridisation of the co-ordinated carbon is also apparent.

Single bond lengths for Mo-N(sp^{2}) and Mo-C(sp^{3}) are given as 2.29 and 2.39Å respectively,[7] hence a greater degree of bond shortening (0.20Å for the Mo-N bond as against 0.13Å for the Mo-C bond) is apparent for the Mo-N bond. Two extreme bonding modes of the aza-allene ligand may be envisaged, as shown in Fig. VI.3.

(a) (b)

Fig. VI.3

The first (Fig. VI.3(a)), involves transfer of an electron to the metal leaving a positively charged ligand which is isoelectronic with the allenes; bonding is explained in terms of the ligand acting as a 2-electron donor through one of the double bonds to the negative metal, in a manner similar to olefins. The second type, (Fig. VI.3(b)) would

Table VI.2

Interatomic distances and bond angles for the complex π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$.[6a]

Bond	Distance (Å)	Bonds	angle
Mo—N	2.09	$C_8\widehat{N}C_{23}$	128°
Mo—C_8	2.26	$C_{24}\widehat{C_{23}}C_{31}$	115°
Mo—π-C_5H_5	2.03	$Mo\widehat{C_8}N$	64°
ring (centroid)		$Mo\widehat{N}C_8$	78°
Mo—C_1	1.91	$C_9\widehat{C_8}C_{16}$	119°
Mo—C_2	1.89	$C_8\widehat{Mo}N$	38°
C_1—O_1	1.20		
C_2—O_2	1.20		
N—C_8	1.43		
N—C_{23}	1.30		
C_8— aromatic ring (av)	1.52		
C_{23}— aromatic ring (av)	1.50		

imply bonding of the aza-allene radical, $R_2C{=}N{-}\dot{C}R_2$, via a metal-carbon σ-bond and σ-donation of the nitrogen lone pair, resulting in formation of an essentially σ-bonded 3-membered ring. The observed molecular geometry and interatomic distances are not inconsistent with either of these two formulations, although the electronic distribution in the complex might be expected to be significantly different for each type. Consider first of all,that likely to arise were the complex bonded as in Fig. VI(a).

Bonding here would be similar to that found in allene complexes of transition metals (see Chapter 5) involving σ-donation and $d\pi{\rightarrow}\pi^*$ back donation. This latter process does not appear to have a great effect on the bond lengths of the co-ordinated and unco-ordinated C-C bonds. In the complex $[PtCl_2(Me_2C{=}C{=}CMe_2)]_2$, the C-C bonds are slightly longer than the free ligand values but are still essentially equal,while for $Rh(acac)(Me_2C{=}C{=}CMe_2)_2$ the co-ordinated and unco-ordinated C-C bonds are 1.33 and 1.37 Å respectively.[10a] Considerable asymmetry in the metal-allene bonding is apparent for these complexes as indicated by unequal metal-carbon bond lengths, the metal-central-carbon distance being ca. 0.15 Å shorter. To account for this it has been suggested[10a] that as well as back-bonding from filled metal d-orbitals into the π^* orbitals of the co-ordinated C=C system, such donation into the orthogonal π^* orbitals on the central carbon of the unco-ordinated C=C bond is also possible. A similar process would be possible for the aza-allene complex (V), which may account for the preferential shortening of the Mo-N bond.

The metal-carbon distances in allene complexes are on average slightly longer than a single bond, e.g. the Rh-C (central) and Rh-C (terminal) distances in $Rh(acac)(Me_2C{=}C{=}CMe_2)_2$ are 2.03 and 2.18 Å respectively as against an Rh-C(sp^3) distance of 2.05Å,[144] and in this complex, back-bonding is thought to be strong enough to prevent rotation of the allene group about the Rh-allene bond[98] (see Chapter 5). This data suggests that for this type of bonding in the aza-allene complex, back-donation must play a very significant role since the Mo-N and Mo-C bond lengths are rather less than single bonds and the co-ordinated C-N bond has the single-bond value of 1.43Å. This is not too difficult to rationalise as we are considering the aza-allene ligand to be positively charged prior to co-ordination. One would expect such a ligand to be a poor σ-donor and a very strong π-acceptor, which in this respect is very similar to tetra-cyano ethylene (TCNE). This molecule is regarded as one of the strongest π-acceptors known,[145] owing to the strong electron-withdrawing nature of the CN group. Bonding in its complexes is visualised as almost a 'pure' π-bond, i.e. very little σ-donation from the double bond.[146] The C-C bond length in $Pt(PPh_3)_2(TCNE)$ is lengthened by 0.21Å to 1.52Å, almost a C-C single bond, but the Pt-C bonds (2.10Å) are still slightly longer than the Pt-C single bond length (2.02Å for CH_3-Pt in $(CH_3)_3Pt(C_3H_7CO.CH.CO.C_3H_7)$.[147] As a consequence of this, more extensive back-donation would be likely for $R_2C{=}\overset{+}{N}{=}CR_2$ than for the isoelectronic allenes, and indeed, this is implied to an equal, if not greater extent than in TCNE complexes, (and also than in the corresponding ketimino complexes - see Chapter 4), by the relevant observed bond lengths. This results in a flow of electron density towards the ligand which is likely to more than balance initial transfer of an electron to the metal prior to co-ordination since the co-ordinated C-N bond is reduced to a bond order of one. The smaller angle at nitrogen in (V) (128^o), compared with $C\hat{C}C$ of $140-150^o$ in allene complexes, is also consistent with stronger back donation (see Chapter 5), although the steric requirements of the ligand may be responsible for part of the contraction. One may predict, therefore, for this type of aza-allene bonding, a fairly high electron density on nitrogen and low electron density on molybdenum.

On the other hand, the second bonding extreme (Fig. VI.3(b)) is predominantly a donation process of the nitrogen lone pair to the metal, together with a metal-carbon σ-bond. The more effective molybdenum-nitrogen bonding would take place when the nitrogen lone pair occupies an orbital approaching sp^2 hybridisation, since in this situation most of the electron density would be directed towards the metal. This would imply a $C\hat{N}C$ similar to that observed, together with Mo-N and Mo-C single bond distances. The observed distances are in fact rather shorter than single bonds, implying a degree of back donation. This may occur for the Mo-N bond by $d\pi$-π^* donation into π^* orbitals of the unco-ordinated C=N system as mentioned in the previous case, but in the structure shown in Fig. VI.3(b), there would be no π^* orbitals available for back donation on the co-ordinated carbon atom. A less extreme structure than that shown, in which some π character is given to the co-ordinated C-N bond, must therefore be invoked if the observed structural parameters are to be meaningful. The net result, however,is still likely to be one in which a build-up of electron density on the metal occurs, at the expense of the nitrogen.

The pertinent spectroscopic data available for complex V would suggest that the structure in Fig. VI.3(b) is the main contributor to the bonding. The X-ray photoelectron spectrum[35] (Table VI.3) gives the nitrogen (1s) binding energy as 400.0 eV, 1.3 eV greater than in π-$C_5H_5Mo(CO)_2N$:C(p-tolyl)$_2$, and 1.2 eV greater than in (p-tolyl)$_2$C=NCHPh$_2$,

Table VI.3[a]

X-ray Photoelectron Spectroscopic Data for Aza-allyl/allene- and Ketimino-Complexes of Molybdenum and Tungsten.

Compound	Binding Energies (eV)				
	C 1s	N 1s	Mo 3d(5/2)	W 4f(7/2)	F 1s
π-$C_5H_5Mo(CO)_2NC(p\text{-tolyl})_2$	285.0	398.4	229.0	-	-
π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$	285.0	400.0	228.4	-	-
π-$C_5H_5Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$	286.1	401.0	229.3	-	690.8
π-$C_5H_5W(CO)_2NC(p\text{-tolyl})_2$	285.0	398.8	-	31.6	-
π-$C_5H_5W(CO)_2NC(p\text{-}CF_3C_6H_4)_2$	286.1	399.8	-	32.3	690.8
π-$C_5H_5W(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$ (B)	285.0	400.1	-	31.0	-
π-$C_5H_5W(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$(A+B)	285.0	400.1	-	31.2	-
$(p\text{-tolyl})_2C{=}N\text{-}CHPh_2$	285.0	398.8	-	-	-

[a] The same footnotes as for Table IV.2 apply.

which may be taken as a reasonable model for the free ligand. Such increases indicate a considerable relative reduction of electron density at nitrogen.[35] A somewhat less relative increase is observed in the metal electron density, which is consistent with the lower carbonyl frequencies of the aza-allene complex, and also the large upfield shift of the π-C_5H_5 ^1H n.m.r. signal (ca. 1.4 τ).* These three sets of data clearly suggest that bonding of the aza-allene group to molybdenum involves a greater degree of electron donation from ligand to metal, than is apparent in the analogous ketimino complexes, rather than the predominantly metal-ligand back-donation process implied by the structure shown in Fig. VI.3(a) and is therefore strong evidence for the direct involvement of the nitrogen lone pair in the bonding.

The X-ray structure of isomer B (M = W) (VI) has not yet been completed, but on the basis of n.m.r. data (see Chapter 7) and the resemblance of Form B to the solution species we would tentatively suggest that the R_2CNCR_2 ligand adopts an aza-allylic arrangement in this form as opposed to the aza-allene structure found for Form A. Whether or not the bonding in the solid state is of the symmetric or asymmetric (σ-π) π-aza-allyl type (Fig. I.2) cannot be stated with any certainty, although some degree of asymmetry in the bonding is indicated in solution from the n.m.r. studies, which would also suggest a bent rather than a linear skeleton.[107] For the former arrangement the nitrogen lone pair is unlikely to be involved in the bonding as it would occupy

---

* Although this data was observed in solution and it is not always wise to apply such data to solid-state structures, we are of the opinion that it is meaningful to do so in this case. On the basis of i.r. evidence the solution form of V is thought to be very similar to the solid-state form B. The ESCA data given in Table VI.3 indicate that forms A and B have identical electron distributions, indicating that if Form A could exist as such in solution, the π-C_5H_5 ^1H n.m.r. signal would be in a similar position to that found for Form B.

an sp^2 orbital directed away from the metal. Symmetrical bonding would then be analogous to that found in corresponding π-allyl complexes. Asymmetric bonding, which in the extreme situation would be the σ-π type, would involve a metal-carbon σ bond and interaction between the metal and the C=N π-system.

Whatever the structure, however, the ESCA data indicates that the electron distribution in both Form A and B are essentially the same, since a mixture gave a spectrum with only single molybdenum and nitrogen peaks, though this is not considered surprising in view of the small structural changes involved.[35]

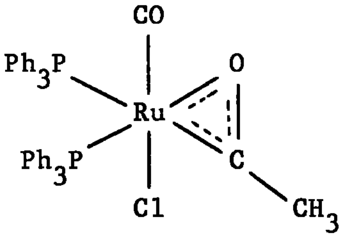
Similar isomeric forms are thought to occur for the complexes $\pi\text{-}C_5H_5M(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(\underline{p}\text{-}CF_3C_6H_4)_2]$ (M = Mo,W). Four carbonyl bands of approximately equal intensity are observed in the solid-state i.r. spectrum, while only two bands are seen in solution. The two forms cannot be separated by fractional crystallisation, the same isomer ratio (ca. 1:1) being found for all samples obtained. Quite why some aza-allyl/allene derivatives and not others should crystallise in isomeric forms is not clear, but the balance between formation of one or the other (or both) would appear to be very delicate indeed.

B. Complexes of the type $\pi\text{-}C_5H_5M(CO)_2(R_2CNCR_2)(R_2C{:}O)$(M = Mo,W;R = p-tolyl)

Reaction of $\pi\text{-}C_5H_5M(CO)_3Cl$, (M = Mo,W) with $Ph_2C{:}NLi$ produced only the aza-allyl/allene derivatives $\pi\text{-}C_5H_5M(CO)_2(Ph_2CNCPh_2)$, no other carbonyl products being detected.[8] In contrast, the reaction with $(\underline{p}\text{-tolyl})_2C{:}NLi$ gave three carbonyl products; $\pi\text{-}C_5H_5M(CO)_2NC(\underline{p}\text{-tolyl})_2$, $\pi\text{-}C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2]$ (VII), and $\pi\text{-}C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2](\underline{p}\text{-tolyl})_2C{:}O$ (VIII). The three products have sufficiently different solubilities to allow fractional crystallisation, from hexane/monoglyme (or ether) mixtures, to be employed as a method of separation. Complex (VIII) is the final material to be obtained from the mother liquor, not unexpectedly since in solution dissociation to (VII) and free ketone occurs (see later). Consequently complex (VIII) will crystallise only when the ketone is in large excess, i.e. when the bulk of (VII) has already been removed from solution, and the volume of solution has been reduced drastically.

The ketone complexes, isolated for both molybdenum and tungsten, were dark-purple, air-stable crystals, identical in physical appearance to the aza-allyl/allene complexes. The melting points are sharp, however, indicating an actual complex rather than just a mixture of complex(VII) and free ketone. This view is further supported by solid-state i.r. (Fig. VI.1) and ^{1}H n.m.r. evidence. The metal-carbonyl stretching frequencies are significantly different from those of the corresponding aza-allyl/allene complexes and also $\nu_{C=O}$ at 1645 cm.$^{-1}$ for the ketone is slightly lowered from the free ketone value (1660 cm.$^{-1}$), indicating weak co-ordination to the metal.[148] The spectrum in the 700-750 cm.$^{-1}$ region, when the ketone absorptions (measured for the free ketone) are subtracted, is identical to that observed for complex (VII), Form B. As Form B for M = Mo could not be isolated, (VIII) is unlikely to be a mixture. In the ^{1}H n.m.r. spectrum, integration of the para-methyl signals arising from the ketone suggests a precise 1:1 complex, which is confirmed by analytical data.

The nature of the metal-ketone interaction can be determined with any certainty only by X-ray diffraction, but the most likely bonding situation would be donation of one of the lone pairs on the oxygen to the metal. A lateral interaction of metal orbitals and the C=O π-system as well as being unlikely on steric grounds, might also be expected to result in a larger decrease of $\nu_{C=O}$ than is, in fact, observed. In the recently reported compound shown below[149] (prepared from $Ru(PPh_3)_3(CO)HCl$ and CH_3CHO), the 'carbonyl' stretching frequency is lowered to 1505 $cm.^{-1}$



On heating solid (VIII) in vacuo to 110°, white crystals were deposited on the cooler parts of the apparatus and were identified by i.r. and mass spectroscopy as di-p-tolyl ketone. The residues for both the molybdenum and tungsten complexes were shown by i.r. spectroscopy to be the corresponding complexes (VII) (Form A). Heating Form B in the solid state did not produce Form A. It would seem that the disruption of the lattice necessary to release the ketone from (VIII) allows the complex to reform preferentially as Form A, presumably the thermodynamically more stable form.

In solution (VIII) dissociates according to:

$$\pi\text{-}C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2](\underline{p}\text{-tolyl})_2C{:}O$$
$$\rightleftharpoons$$
$$\pi\text{-}C_5H_5M(CO)_2[(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2] + (\underline{p}\text{-tolyl})_2C{:}O$$

the presence of an equilibrium is indicated by the following factors.

i) The mixing of equimolar solutions of (VII) and the ketone followed by a process of crystallisation results in recovery of (VII) with no (VIII) whereas if a large excess of ketone is used, (VIII) alone can be crystallised from the solution. ii) Molecular weight measurements indicate the presence of two species in solution as approximately half the expected value is obtained. The value for the molybdenum complex (by cryoscopy in cyclohexane) is a little low (found, 340; expected value 829), but a more accurate determination (osmometry in benzene), for the tungsten complex gave confirmation (found 464; expected value 917). iii) I.r. solution spectra of (VIII) are identical to (VII) when peaks due to free ketone are subtracted. $\nu_{C=O}$ corresponds to the free ketone value. iv) The ^1H n.m.r. spectrum in CS_2 solution shows the same variable temperature behaviour as (VII) for the aza-allyl p-methyl groups[107] and the position of the methyl resonance arising from the ketone corresponds exactly to the free ketone position, measured under similar conditions.

The factors allowing formation of this type of complex must depend critically upon the nature of the para-substituents on the aromatic rings, since the combination described is the only one which could be isolated.

CHAPTER 7

NUCLEAR MAGNETIC RESONANCE STUDIES OF AZA-ALLYL/ALLENE COMPLEXES

This chapter describes structural studies of aza-allyl/allene complexes performed in solution using n.m.r. spectroscopy. The original derivatives of this type, π-$C_5H_5M(CO)_2[Ph_2CNCPh_2]$,^{8} were not amenable to this type of study as there are no suitable n.m.r. probes within the molecule. Since complexes with aryl substituents only can be synthesised, we chose, first of all, to study the related p-tolyl complex in order to use the p-Me groups as n.m.r. probes. The structure of the complex π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$ 'Form A', in the solid state has been discussed in Chapter 6. The results to be presented here, however, suggest that in solution a significantly different structure is adopted and is in fact more akin to the solid state Form B.

On the question of a linear or bent skeleton for the ligand in solution (as a rigid molecule- see later), a linear arrangement can be eliminated with some confidence solely on electronic and steric considerations, without recourse to spectral evidence. If the group acts as an π-aza-allene moiety, the skeleton will be necessarily bent as a direct consequence of the bonding (see Chapter 6). In the π-aza-allyl arrangement, where all R groups would be essentially coplanar, any realistic bonding situation would involve all three skeletal atoms. For both types of aza-allyl bonding involving a linear skeleton, symmetric π and asymmetric $\pi(\sigma\text{-}\dot{\pi})$, (Fig. VII.1) it is

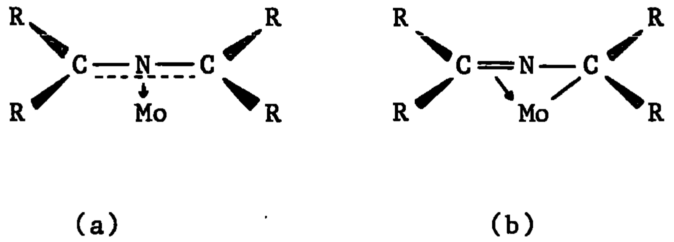


Fig. VII.1

difficult to envisage, particularly in the latter, how effective bonding involving both terminal carbon atoms may occur, since the distances involved would be too great for efficient orbital overlap, a view which is shared by Cotton et. al.[117] (In addition, symmetrically π-bonded aza-allyl groups involving linear or bent skeletons can also be eliminated on n.m.r. spectral evidence - see later).

Variable-temperature studies between -20^o and $+70^o$ showed the molecules to be fluxional.[107,150] Typical spectra obtained for the p-Me protons of the molybdenum complex are shown in Fig. VII.2. At low temperature, there are four signals of equal intensity due to p-Me protons, indicating that four non-equivalent environments are adopted. Warming to ca. 10^o causes two signals (7.71 and 7.85 τ) to broaden, whilst the other two remain fairly sharp, before coalescing to a signal which is superimposed on the signal at 7.80 τ. Thus two signals, of intensity ratio 1:3, apparently result. At 70^o, these signals coalesce to a broader time averaged resonance at the mean (7.71 τ) of the four original signals* indicating that all four methyl groups become equivalent on the n.m.r. time scale. All these changes are completely reversible.

A number of explanations for the occurrence of four methyl signals at low temperature (i.e. in the rigid structure) may be discounted immediately in view of the observed temperature dependance and other spectral details (Table III. 2). Isomers of the type found in the

---

* Using CS_2 as solvent, 70^o cannot be safely attained (b.pt. of CS_2 = 46^o), hence the spectrum at 70^o was obtained in benzene solution. However, the spectrum at 40^o in CS_2 (Fig. VII.2) shows this process to be occurring.

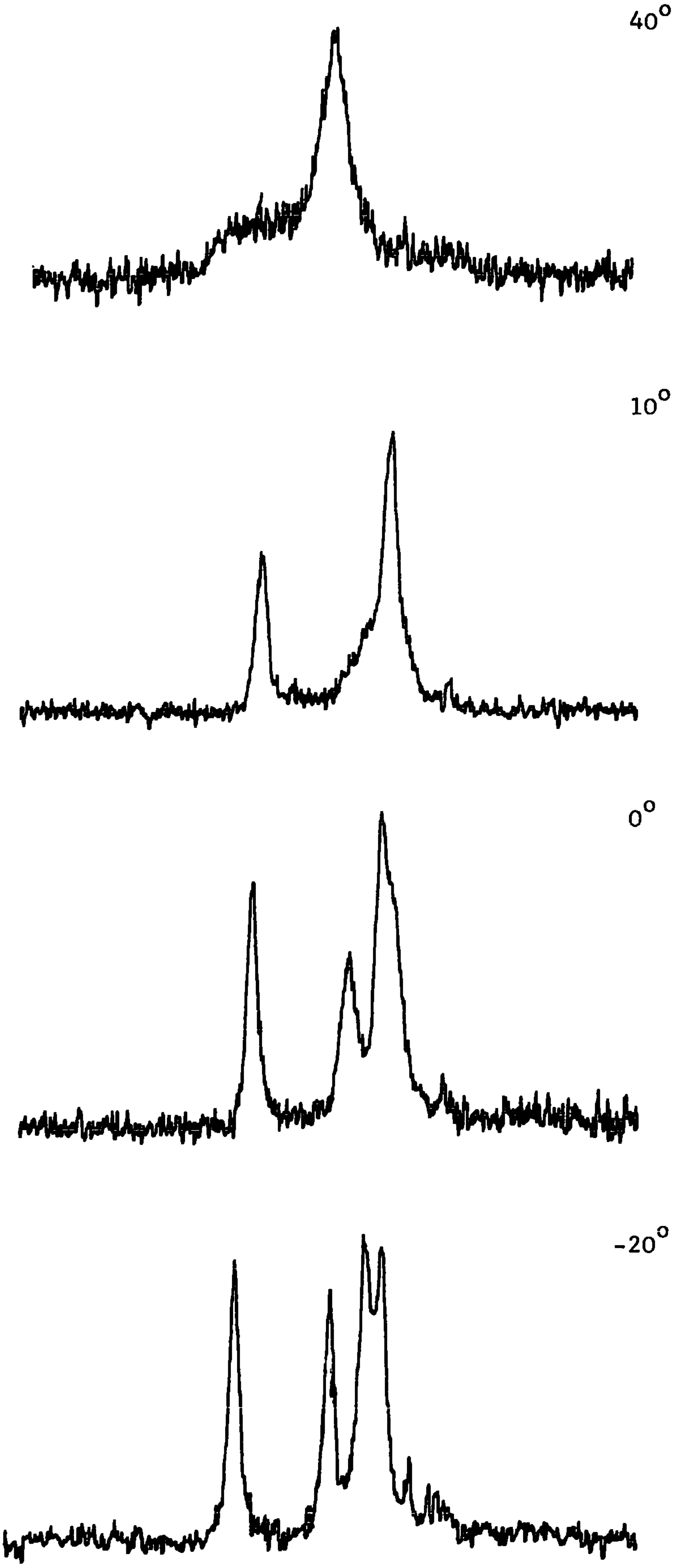


Fig. VII.2

p-Me ^{1}H n.m.r. signals for π-$C_5H_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$

in CS_2 solution.

analogous complex, π-$C_5H_5Mo(CO)_2\pi$-C_3H_5,[122] (Fig. VII.3), where two superimposed AM_2X_2 spectra are observed in the ^1H n.m.r. spectrum

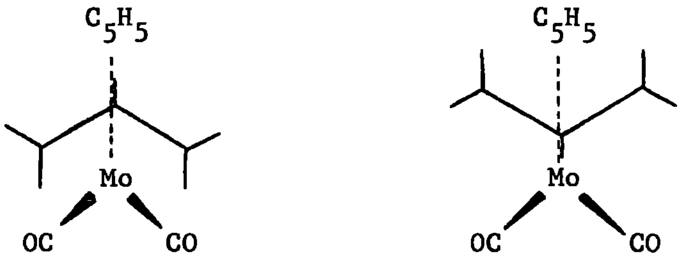


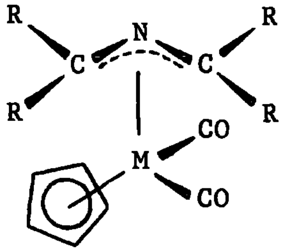
Fig. VII.3

together with four carbonyl absorptions in the i.r. spectrum, are not possible. In this situation the ligand would be bound as a symmetrical π-aza-allyl group for which two signals (one for the 'syn-' groups and one for the 'anti-' groups *) for each isomer are expected. No plausible mechanism is available, however, to explain why one pair of signals should coalesce before the other, which would have to be the case to be consistent with the observations. The presence of only two carbonyl absorptions in solution and the single π-C_5H_5 signal in the ^1H n.m.r. (two would be expected) are also inconsistent with this possibility.

---

* 'syn' and 'anti' when discussing π-allyl groups refer to the position of the substituents on the terminal carbons with respect to the group on the central carbon. For the π-aza-allyl ligand no such group is present, but the position of substituents may be referred to the lone pair on nitrogen (bent skeleton) which may be considered as occupying a similar position.

A symmetrically bound π-aza-allyl group, but orientated with respect to the rest of the molecule as shown in Fig. VII.4,



(R = p-tolyl)

Fig. VII.4

would also give rise to four p-Me signals as a rigid structure, but again there is no likely mechanism whereby the observed temperature dependance may be fulfilled.

Cis-trans isomers (with respect to the carbonyl groups) may be eliminated on steric considerations as well as on spectral evidence.

Two rigid structures are possible which could show fluxional behaviour compatible with that observed.

i) An aza-allene structure bound in an asymmetric fashion to the rest of the molecule (as observed in the crystal structure of π-$C_5H_5Mo(CO)_2$-[(p-tolyl)$_2$CNC(p-tolyl)$_2$],^{6a} (Fig. VI. 2) shown in Fig. VII.5(a).

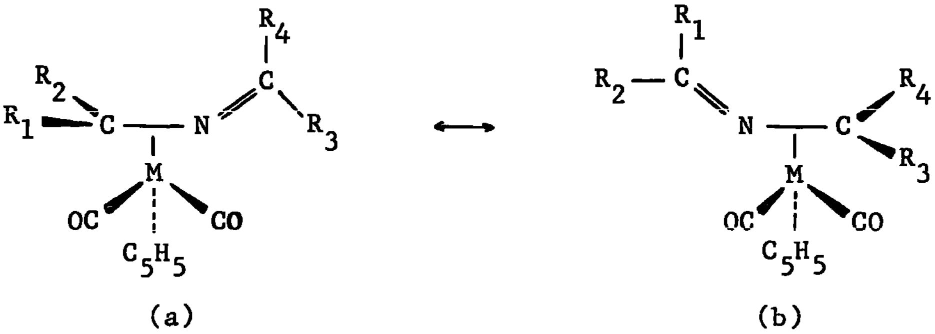


Fig. VII.5

As a rigid structure, four p-Me signals would result as R_1 and R_2 are in different environments. Coalescence of R_1 and R_2 (but not R_3 and R_4) could occur by rotation about the metal-ligand axis. Complete collapse of all four signals is possible via the ligand-metal interaction alternating between two orthogonal π-molecular orbitals of the aza-allene system, together with the rotation process. Similar temperature dependant spectra are observed and similar mechanisms have been invoked for the allene complexes $Fe(CO)_4(Me_2C{=}C{=}CMe_2)$,[99] $[PtCl_2(Me_2C{=}C{=}CMe_2)]_2$[98] and also for π-olefin complexes such as $\pi\text{-}C_5H_5Rh(\pi\text{-}C_2H_4)_2$[151,152] and (Acac)PtCl(π-olefin).[153]

ii) An asymmetric π- (or σ-π) aza-allyl grouping bound with respect to the rest of the molecule as in Fig. VII.6(a) (this structure representing an extreme) would exhibit four p-Me signals as a result

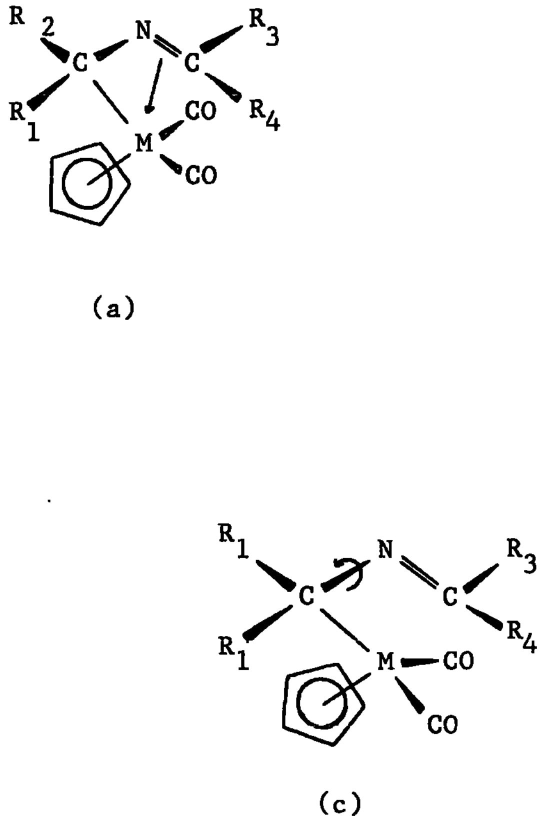


Fig. VII.6

of the asymmetry of the ligand. Coalescing of signals at ca. + 10° is interpreted as detachment of the C=N π-system from the metal and rotation of the $N=CR_2$ unit about the C-N single bond, thus causing R_1 and R_2 (Fig. VII.6(c)) to be equivalent. This in fact would be analogous to the 'π-σ' reaction thought to occur in many stereochemically non-rigid π-allyl complexes, particularly those of palladium (see Chapter 5).[118] At higher temperatures, interchange of σ-π bonding (Fig. VII.6(a) and (b)) is postulated, together with the rotation process, producing four equivalent groups.

On balance, the latter mechanism is preferred. From steric considerations, based upon models constructed from the crystallographic data of the molybdenum complex, the rotational processes proposed for both mechanisms are possible as the planes containing the aromatic rings can be twisted to any suitable angle to minimise steric interactions, although these are likely to be greater in the former case. It has been mentioned already that some metal-allene complexes exhibit rotational movements about the metal-allene axis. However, these complexes are the type which can be considered to occupy only a single co-ordination position, i.e. are bonded at right angles to the co-ordination plane. Allene and some olefin complexes which occupy two co-ordination positions, i.e. are bonded in the co-ordination plane, have been found not to show fluxional behaviour. E.g. $(PPh_3)_2Pt(allene)$[10b] and $(PPh_3)_2Pt(CF_2 = CF_2)$[154] both show temperature invariant n.m.r. spectra.*

---

* For $(PPh_3)_2Pt(allene)$ the allene protons on the co-ordinated carbon atom are equivalent in the static structure due to a mirror plane bisecting the HCH angle. No evidence was obtained for alternation between the two orthogonal C=C π-systems.

The bonding in these complexes is thought to involve essentially a σ-bonded, three-membered ring system as evidenced by n.m.r.[10b,154] and crystallographic data.[99a] For the fluoro-olefin complex, the geminal F, F coupling constant is of the order observed in saturated fluorocarbon systems (ca. 200 Hz), and for the allene complex, the protons on the co-ordinated carbon are well towards the aliphatic region. The co-ordinated allene C-C bond length (1.48 Å) is approaching the value normally associated with a C-C single bond (1.54 Å). This is in direct contrast with the platinum-allene complexes in which the allene is perpendicular to the co-ordinating plane. The skeletal C-C bond lengths are approximately equal (1.36 Å) in $[PtCl_2(Me_2C{=}C{=}CMe_2)]_2$,[10a] and in $[PtCl_2(H_2C{=}C{=}CMe_2)]_2$, where the $H_2C{=}C-$ unit is bonded to the metal,[98] the chemical shift of the $H_2C{=}$ protonsis little changed from that found in the free ligand. Consequently,it is reasonable to suggest that $d\pi$-π^* back-donation is considerably more extensive in complexes where these ligands are bonded in the co-ordination plane, resulting in a stronger metal-ligand interaction, and it is this which is thought to be responsible for the absence of rotational phenomena on the n.m.r. time scale[154,10a] in such complexes. For our aza-allyl/allene complexes, π-$C_5H_5M(CO)_2[R_2CNCR_2]$ (M = Mo, W; R = p-tolyl), if the metal-ligand rotation mechanism, (i),is invoked to explain the n.m.r. results, i.e. an aza-allene form at low temperature, the co-ordination about the metal system is best described as a '3-4' arrangement as shown in Fig. VII.7, with the π-C_5H_5 ring occupying three co-ordination sites,

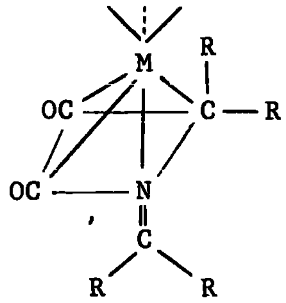


Fig. VII.7

the carbonyl groups one site each, and the aza-allene ligand two sites. This is confirmed by the X-ray crystal structure of the molybdenum complex, which also indicates that the metal-ligand interaction is very strong, by the short Mo-C and Mo-N bond lengths.[6a] Whether this is due to extensive back-donation or predominantly σ-donation processes has been discussed in Chapter 6, but the net result of either would be an essentially σ-bonded, three-membered ring system. A comparison with the allene and olefin complexes just discussed, therefore, suggests that a metal-ligand rotation process is unlikely in this system.

Thus, having decided in favour of a rotation mechanism within the ligand to account for the n.m.r. observations, we must consider the type of rotation involved. Although it has been described above in terms of the 'π-σ' reaction,[118] there is also the possibility of $\mathrm{C}\overset{\curvearrowleft}{=}\mathrm{C}$ bond rotation as proposed by Beconsall and O'Brien for $Zr(allyl)_4$ and $Th(allyl)_4$,[120] though this is thought to be improbable on theoretical and steric grounds (see Chapter 5). Such a rotation would involve the N=C bond in Fig. VII.6(a) (and also in any other structure intermediate between a symmetric π and σ-π form), as it would be more weakly bound to the metal, thus resulting in coalescence of the methyl signals arising from R_3 and R_4, not R_1 and R_2. For π-allyl complexes the problem of 'which mechanism' is easily overcome since the position of a hydrogen in the allyl moiety can be directly related to its chemical shift hence by observing which pair coalesce, one may infer the rotation mechanism by which it is occurring. Unfortunately, the chemical shifts of the p-Me groups in the aza-allyl/allene ligand give little information as to which R group gives rise to which signal, except to say that one might expect the p-Me protons on R groups attached to the carbon of the C-N bond having a greater degree of double bond character, to absorb at lower field. From Fig. VII.2, the low temperature spectrum shows that one R group (at 7.48 τ) is in a significantly different environment from the other three. Observations made on the model constructed from the crystallographic data, together with a degree of intuition suggest that this group is R_4 (Fig. VII.6(a)). Therefore the signals which coalesce correspond to the groups R_1 and R_2, hence the rotation mechanism involved must be the 'π-σ' reaction. (Assuming this mechanism these assignments, and others can be made with a greater degree of certainty - see later).

Confirmation of the higher temperature average process proposed i.e. interchange of σ-π bonding (Fig. VII.6(a) and (b)) has been obtained by studying the variable temperature ^1H n.m.r. spectrum of π-$C_5H_5Mo(CO)_2[R'R''CNCR'R'']$ (R' = p-$MeOC_6H_4$; R" = p-MeC_6H_4) for which the n.m.r. probes are a methoxy and a methyl group at each end of the ligand. At higher temperatures two broad time-averaged signals are observed, one arising from the methoxy and one from the methyl groups. The low temperature (limiting) spectrum is shown in Fig. VII.8, the methoxy resonances being to lower field. Four distinct signals are observed for both types of proton, the integration indicating six of each. At low temperatures all four possible orientations of the aza-allyl ligand are therefore frozen out. Thus, each end of the ligand must become free from the metal at some stage to allow the rotational process to occur at each end, i.e. we have interchange of σ-π bonding as postulated.

An additional point of interest to note from Fig. VII.8 is that the signals within each group are not all of equal intensity. This implies that at low temperatures, certain orientations of the CR_2 unit with respect to the rest of the molecule are preferred, and allows assignment of each of the four signals to a particular R group on the ligand to be made. The four possible orientations of the ligand are shown in Fig. VII.9.

Construction of suitable models shows that the para-substituents do not interact sterically with the π-$C_5H_5Mo(CO)_2$- part of the molecule during the rotational process. Any possible steric interaction between the ligand and the π-$C_5H_5Mo(CO)_2$- moiety would involve the aromatic rings. The models do show, however, that during rotation significant interaction is possible between the p-MeO substituents at each end of the ligand. Thus, the structure most likely to be adopted in the absence of rotation is the one in which the p-MeO groups are furthest away, both from each other and from the p-Me groups (Fig. VII.9(I)). The ^1H n.m.r. results indicate that rotation of the $-N{=}CR_2$ unit causes signals due to R groups on C(2) (Fig. VII.9) to coalesce, and these are peaks 2 and 4, 6 and 8 in Fig.VII.8. On the basis of this data and the relative intensities of the signals, assignment of each signal to a substituent at a particular position on the ligand can be made. We therefore assign peaks 3 and 5 (Fig. VII.8) to R' and R" respectively on C(1) (Fig. VII.9(I)), peaks 2 and 6 (Fig. VII.8) to R' and R" respectively on C(2) (Fig. VII.9(I)). Hence peaks 1 and 4 (Fig. VII.8) refer to R' on C(1) and C(2) respectively (Fig. VII.9(IV)) and peaks 7 and 8 (Fig. VII.8) to R" on C(1) and C(2) respectively (Fig. VII.9(IV)). The signals arising from the substituents in the various positions in the structures of Fig. VII.9 are indicated by numbers in parentheses referring to signals in Fig. VII.8. This substantiates the intuitive assignments made earlier.

If these assignments, based upon steric arguments are correct, then by putting R' = C_6H_5 in Fig. VII.9, i.e. replacing the p-MeO substituents by H, the most favourable structure at low temperature would be Fig. VII.9(IV), with the p-Me groups furthest away from each other, minimising any steric interaction between them. Thus, we would expect the new intensity pattern of the methyl resonances at low temperature to

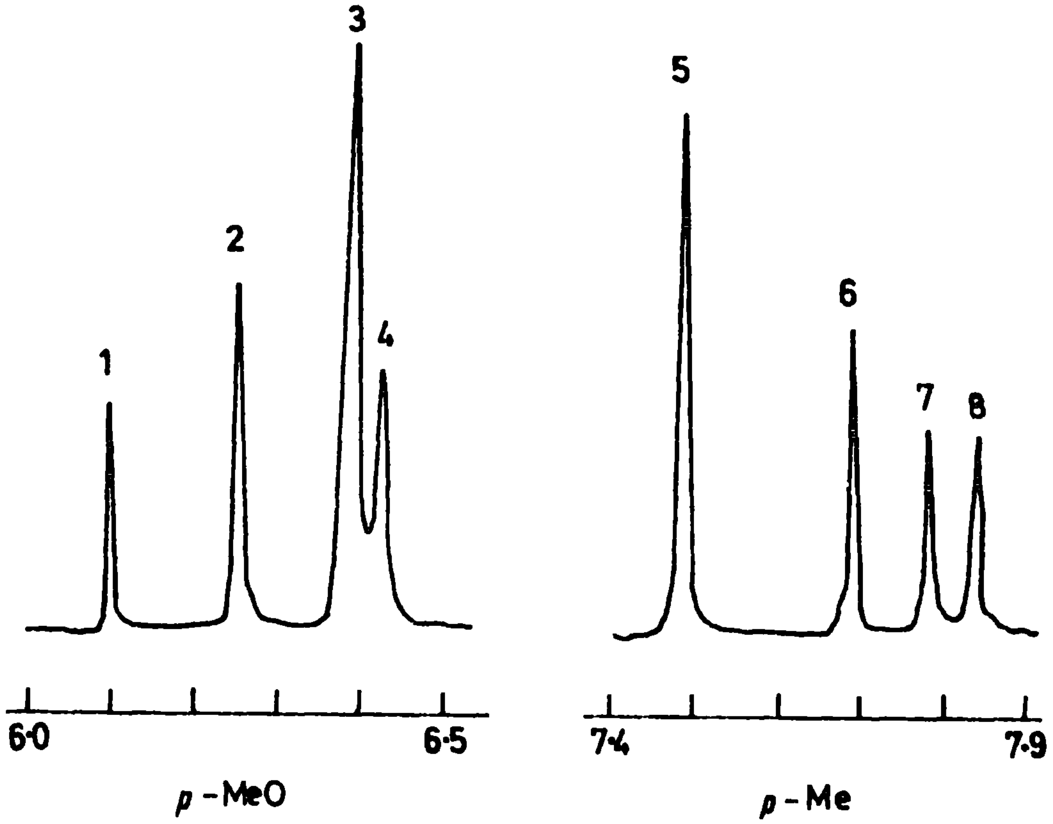


Fig. VII.8

^{1}H n.m.r. spectrum for π-$C_5H_5Mo(CO)_2$[R'R"CNCR'R"] in CS_2 at -40°, (R' = *p*-$MeOC_6H_4$, R" = *p*-MeC_6H_4)

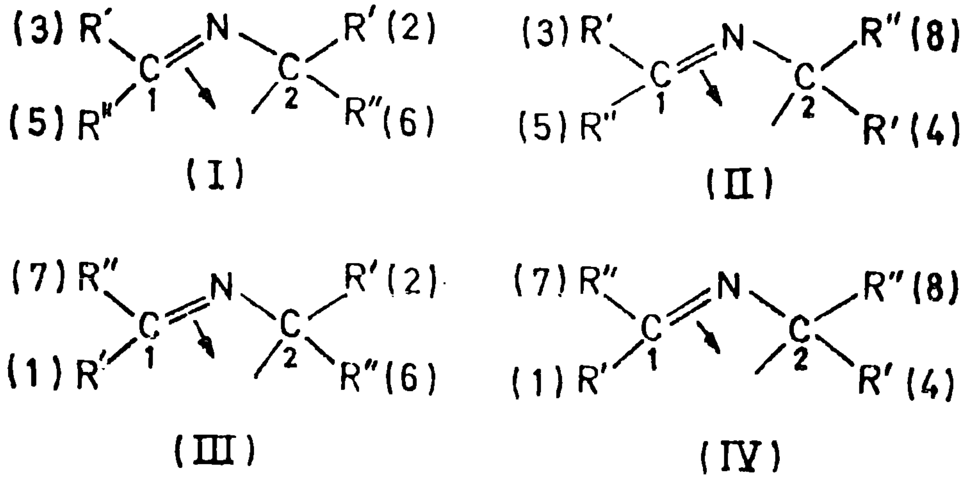


Fig. VII.9

R' = *p*-$MeOC_6H_4$, R" = *p*-MeC_6H_4

be qualitatively very similar to the pattern observed for the p-MeO resonances in Fig. VII.8. If there is no steric interaction between the p-Me groups, then four peaks of equal intensity should result. The spectrum obtained at -40^o for R' = C_6H_5 and R" = p-MeC_6H_4 is shown in Fig. VII.10, and indeed, the intensity pattern of the methyl signals is in excellent agreement with the predictions.

The ^1H n.m.r. results have been interpreted on the basis of an asymmetric π (σ-π) type of bonding mode for the aza-allyl ligand, and the first coalescence of signals arising from detachment of the C=N π system from the metal and rotation of the $-N=CR_2$ unit about the C-N single bond. The strength of the interaction between the metal and what would effectively be a lateral C=N system will be reflected in the activation energy for rotation, consequently attempts have been made to determine the kinetics of the process.

Inspection of the spectra of all the complexes described shows that a) the separation between the coalescing peaks is too small (ca. 8 Hz) to allow accurate measurements to be made, and b) the presence of a third p-Me signal between the two made measurements impossible. Introduction of CF_3 groups into the para- positions of all four R groups however solved both problems. The separation at low temperature between the coalescing signals increased, as expected, to ca. 30 Hz. and fortuitously neither of the remaining CF_3 signals interfered. Relevant spectral details are shown in Fig. VII.11. A similar temperature dependance to that already described for the p-tolyl derivative is observed, indicating that we are considering the same rotational process. Activation energies were calculated by two independant methods, the peak separation method of Gutowsky[155] and the intensity ratio method described by Rogers and Woodbrey[156] (see Appendix 5). Good agreement between the methods was obtained and the results are summarised in Table VII.1.

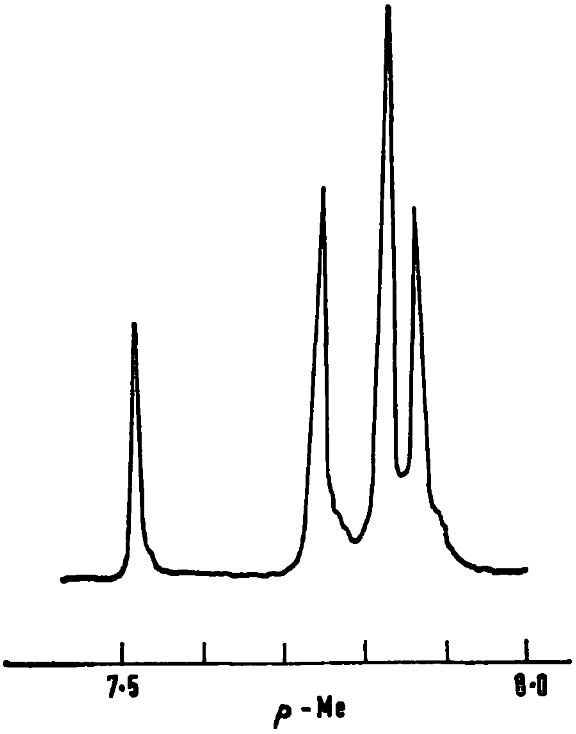


Fig.VII.10

^{1}H n.m.r. spectrum for π-$C_5H_5Mo(CO)_2[R'R''CNCR'R'']$ in CS_2 at -40°, ($R' = C_6H_5$, $R'' =$ p-MeC_6H_4)

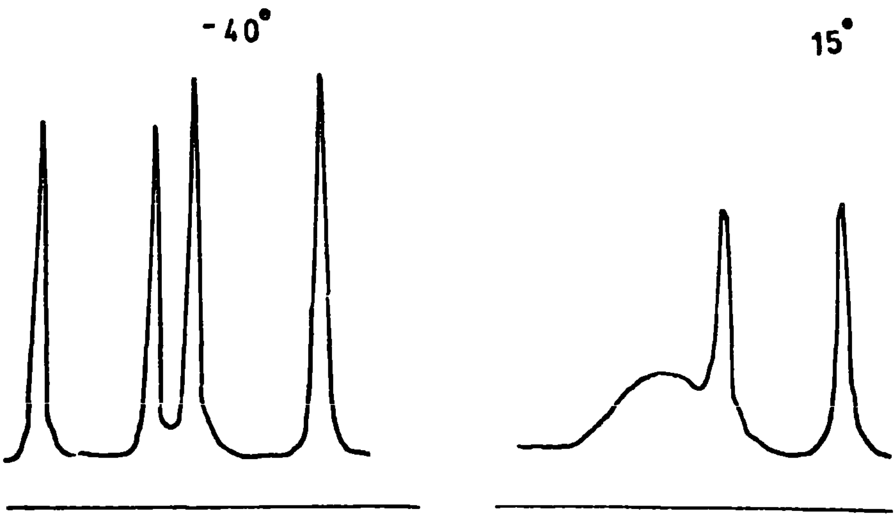


Fig. VII.11

^{19}F n.m.r. spectrum for π-$C_5H_5Mo(CO)_2[($p-$CF_3C_6H_4)_2CNC$-[p-$CF_3C_6H_4)_2]$ in toluene.

Table VII.1

Activation Parameters for π-$C_5H_5M(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$.

M = Mo: $Ea = 11.6 \pm 1.2$ Kcal/mole
$\log_{10}A = 10.8 \pm 1.0$

M = W: $Ea = 6.8 \pm 0.5$ Kcal/mole
$\log_{10}A = 7.2 \pm 0.4$

Comparable activation energy values for similar processes in related π-allyl systems are in the range 7-20 Kcal/mole.[113] The values for the aza-derivatives are consistent with the contention that the activation energy results predominantly from metal-ligand interaction, rather than from steric inhibition of rotation. If the latter were operative, then similar activation energies would be expected for the molybdenum and tungsten compounds, owing to the similarity in size of the two central atoms - covalent radii have been estimated as 1.61 Å for molybdenum[157,158] and 1.58 Å for tungsten[158] - resulting in similar molecular dimensions. It would appear therefore that the interaction between the metal and the C=N π-system is considerably stronger for molybdenum. Unfortunately no appropriate bond energy data are available for molybdenum or tungsten-nitrogen bonds, but the order observed is in notable contrast to the observed trend for metal-carbonyl bond energies, i.e. W - CO > Mo - CO.[159]

The temperature dependant n.m.r. spectrum of the complex π-$C_5H_5Mo(CO)_2[(p\text{-}FC_6H_4)_2CNC(p\text{-}FC_6H_4)_2]$ is unique amongst those of all aza-allyl/allene complexes studied so far. Since we are dealing with a system where fluorine is directly attached to the aromatic nucleus, the additional complexity of ^{1}H - ^{19}F coupling is introduced, resulting in 9-line multiplets for each ^{19}F resonance. Consequently, it was difficult to decide whether some of the temperature dependant phenomena observed could be interpreted in terms of line-broadening and subsequent coalescence, or merely accidental overlap of sharp peaks. Proton decoupled measurements (made by PCMU at Harwell) over a limited temperature range (+20° → -50°) resulted in singlet resonances for the ^{19}F nuclei, allowing a correct interpretation to be made.

At temperatures above 20°, similar behaviour to other aza-allyl/allene complexes was observed. Thus, at 70° and above, a single, time-averaged signal was apparent at 50.05 p.p.m. downfield from C_6F_6, which on cooling to 20° gave two sets of resonances, of equal intensity,at 54.4 and 45.7 p.p.m. (downfield from C_6F_6). The ^{1}H decoupled spectrum showed that the lower field set consisted of two sharp signals of equal intensity separated by 38.5 Hz., while the higher field set was a single,sharp signal. Further cooling caused this signal to separate into two, equally intense, sharp components. The separation increased with decreasing temperature and was ca. 35 Hz at -90°. The effect of cooling on the lower field set of resonances was the unusual feature. The separation decreased gradually with no increase in line width (in fact the lower field signal sharpened somewhat) until between -40 and -50° the two were coincident. Lowering the temperature further caused the separation to increase (38 Hz at -90°), the signal which had previously been to higher field, now being to lower field. The decoupled spectra obtained are represented pictorially in Fig. VII.12 and data giving the

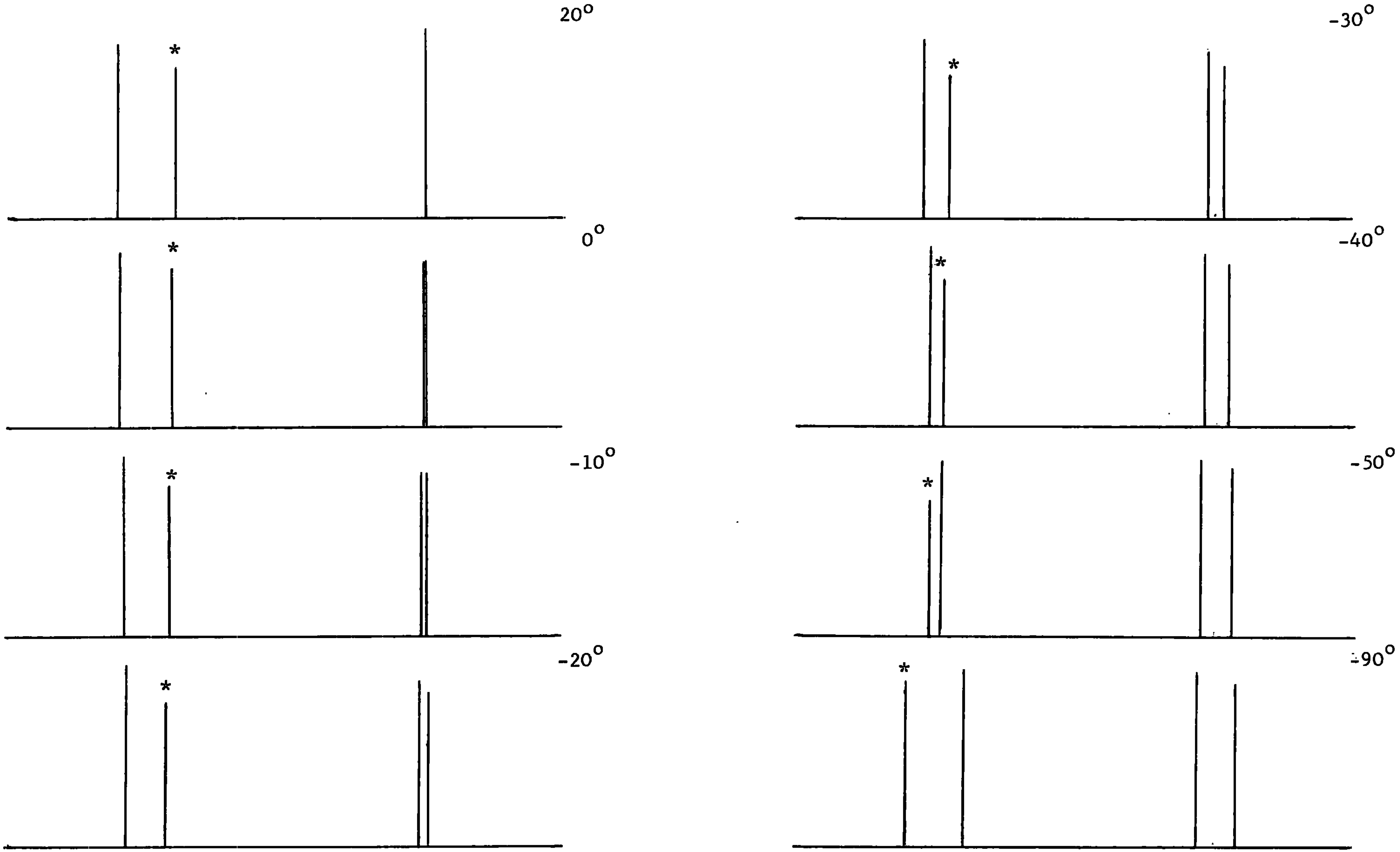


Fig. VII.12

Pictorial representation of ^{19}F n.m.r. spectra obtained for a $C_5H_5Mo(CO)_1[(\underline{p}\text{-}FC_6H_4)_2CNC(\underline{p}\text{-}FC_6H_4)_2]$ in toluene

Table VII.2

^{19}F n.m.r. spectral data for π-$C_5H_5Mo(CO)_2[(p$-$FC_6H_4)_2CNC(p$-$FC_6H_4)_2]$

Temperature	Separation of low and high field sets (Hz)	Separation within sets(Hz)	
		Low field	High field
+ 20°	813.0	38.5	0.0
0°	813.5	34.0	0.5
- 10°	814.5	28.5	8.0
- 20°	812.5	23.5	13.0
- 30°	812.0	15.5	15.5
- 40°	810.0	7.5	19.5
- 50°	809.0	- 7.0	25.5
- 90° [a]	810.0	-38.0	36.0

[a] ^1H coupled spectrum at 56.4MHz.

separation between the centroids of each set of resonances together with the separation within the set, as a function of temperature,are given in Table VII.2. Line broadening is not observed for any signal below 20°.

Above 20°, the observations are consistent with the mechanism postulated for the other aza-allyl/allene complexes, i.e. interchange of σ-π bonding together with rotation of the $-N=CR_2$ unit about the C-N single bond. At 20° the former process ceases and the spectrum (Fig. VII.12) is consistent with either a structure in which the latter rotation process is sufficiently rapid to give rise to sharp signals, or a statically bonded aza-allene structure in which the two R groups attached to the co-ordinated carbon are equivalent.

The latter is preferred as the absence of line broadening below 20° implies that we are not observing dynamic equilibria of any type. Consequently the spectral data must be interpreted in terms of a series of statically bonded structures which differ slightly in their bonding to the metal. A possible transition is from an aza-allene structure at room temperature to an aza-allyl structure at low temperatures, which is, in effect, a rotation of the $-N=CR_2$ unit about the C-N bond, through 90° and corresponds to a change from one structural extreme to the other. As well as being consistent with the data, such a gradual transformation would appear to be theoretically possible as effective metal-ligand bonding can apparently take place at all intermediate structures, via a varying combination of contributions from the nitrogen lone pair and C=N π-system.

In view of the lack of comparable structural changes reported in the literature it is difficult to state whether the above postulate is realistic, except to say that it is consistent with the observations. Why also, only this complex should exhibit this type of behaviour is not understood at this time, although it is the only derivative, studied in detail, which has a single (small) atom as *para*-substituent.

CHAPTER 8

REACTION OF MANGANESE PENTACARBONYL BROMIDE WITH DI-p-TOLYLKETIMINO-LITHIUM.

This chapter describes the reaction of (p-tolyl)$_2$C:NLi with Mn(CO)$_5$Br and the possible structures of the products obtained.

A. Experimental.

1. Reaction of (p-tolyl)$_2$C:NLi with Mn(CO)$_5$Br(2:1 molar ratio).

A solution of (p-tolyl)$_2$C:NLi (4.2 mmole) in ether (50 ml.) was prepared as described in Chapter 3 and stirred at room temperature for 15 min. A solution of Mn(CO)$_5$Br (0.575g., 2.1 mmole) in ether/monoglyme (80 ml., 1:1 mixture) was added dropwise at room temperature over 30 min. during which time a white precipitate formed and the solution turned orange-red. The i.r. spectrum of the reaction solution at this point showed new carbonyl absorptions at 2020, 1960,1920 cm.$^{-1}$ together with some remaining starting material. The reaction was shown to be virtually complete after 5 hr. at room temperature. Filtration gave a whitish residue (which contained Br$^-$) and a golden-yellow solution. The volume of solvent was reduced *in vacuo* and the solution filtered through a $\frac{1}{2}$" column of coarse alumina to remove any remaining LiBr. Further reduction of the volume of solvent (0.1 mm. Hg, 20^o) followed by addition of hexane (20 ml.) and fractional crystallisation at 0^o gave two complexes (IX and X).

i) Complex IX, formulated as Mn(CO)$_4$(C$_{15}$H$_{16}$N).

Properties: The light-yellow crystals were air-stable and melted without decomposition at 163-164^o. Solubility in hydrocarbon solvents was limited, but ether and monoglyme dissolved them readily giving yellow solutions which were rather less air and thermally stable. Reaction occurred with CHCl$_3$ or CCl$_4$ giving Mn(CO)$_5$Cl, (detected by i.r. spectroscopy).

Table VIII.1

Mass Spectral Data for $Mn(CO)_4(C_{15}H_{16}N)$.

Ion	m/e	m^*	Fragment lost
$[Mn(CO)_4(C_{15}H_{16}N)]^+$	377		
			CO
$[Mn(CO)_3(C_{15}H_{16}N)]^+$	349		
		295	CO
$[Mn(CO)_2(C_{15}H_{16}N)]^+$	321		
		267	CO
$[Mn(CO)(C_{15}H_{16}N)]^+$	293		
		239	CO
$[Mn(C_{15}H_{16}N)]^+$	265		
$[Mn(C_{15}H_{15}N)]^+$	264		

Analysis: found, C, 60.50; H, 4.10; N, 3.60; Mn, 14.40%.

$C_{19}H_{16}MnNO_4$ requires C, 60.50; H, 4.25; N, 3.70; Mn, 14.55%.

Infrared Spectrum: ν_{CO}(KBr), 2061s, 1982s, 1963s, 1946s, 1927s, 1896s, 1890sh, 1874w cm.$^{-1}$ ν_{CO}(monoglyme), 2055s, 1957vs (broad), 1917s cm.$^{-1}$ ν_{N-H}(KBr), 3384m, 3307m cm.$^{-1}$ No band could be assigned to $\nu_{C=N}$.

^{1}H n.m.r. Spectrum: (monoglyme solution). Owing to fairly rapid decomposition at the operating temperature (40°) of the spectrometer, the spectrum was difficult to obtain. However, signals were observed at 7.82(6)τ and 2.75(8)τ (multiplet) due to p-Me and aromatic protons, typical of a p-MeC_6H_4- unit.

Mass Spectrum: (direct insertion probe at source temperature). A parent peak, corresponding to $Mn(CO)_4(C_{15}H_{16}N)$, was observed at m/e 377. The breakdown pattern consisted of successive loss of carbonyl groups followed by loss of the organic fragment (m/e 210). The observed metal-containing ions are listed in Table VIII.1.

ii) Complex X, formulated as $Mn(CO)_3[$(p-tolyl)$_2C:NH)]Br$.

Properties: the orange-brown crystalline solid was air-stable and melted without decomposition at 139-140°. It was slightly soluble in hexane and readily soluble in ether, monoglyme, chloroform, toluene etc. giving orange air-sensitive solutions.

Analysis: found, C, 61.80; H, 4.85; N, 4.30; Br, 12.20%.

$C_{33}H_{30}BrMnO_3$ requires C, 62.1; H, 4.70; N, 4.40; Br, 12.55%.

Infrared Spectrum: (KBr), ν_{CO} 2025s, 1947s, 1920s cm.$^{-1}$ $\nu_{C=N}$ 1594 cm.$^{-1}$ ν_{N-H} 3252 cm.$^{-1}$

^{1}H n.m.r. Spectrum: ($CHCl_3$ solution). Signals at 7.62(6) τ and 0.12 τ (1) due to p-Me and NH protons respectively were observed. Absorptions due to aromatic protons were detected under the CH resonance of $CHCl_3$.

Mass Spectrum: (direct insertion probe at source temperature). Even after many attempts no manganese containing ions could be observed.

2. Reaction of (p-tolyl)$_2$C:NLi with $Mn(CO)_5Br$ (1:1 molar ratio).

This reaction was performed in a manner analogous to that described above. After the addition of $Mn(CO)_5Br$, the solution was much redder than before, and the i.r. spectrum showed that reaction was proceeding differently. A strong,new band was apparent at 2000 cm.$^{-1}$ with weaker bands at 1960, 1940 and 1915 cm.$^{-1}$ Reaction was complete after 19 hr. when the solution was separated by filtration from a yellow-white residue which contained Br^-. The golden-yellow filtrate was reduced in volume (0.1 mm. Hg, 20^o) and fractional crystallisation at 0^o gave two products, X described above, and $Mn_2(CO)_{10}$, identified by i.r. spectroscopy. No evidence was obtained for the formation of complex IX.

B. Discussion.

The purpose of these reactions was to prepare ketimino and/or aza-allyl/allene complexes of manganese. Such derivatives are known[4,160] but are not too well characterised and are less stable than molybdenum and tungsten derivatives, especially in solution. Reaction of $Mn(CO)_5Cl$ with $Ph_2C{:}NLi$ gave two products,[4] one of which was uncharacterised and the other formulated on the available evidence as $Mn(CO)_{4-5}NCPh_2$; while the reaction of $Mn(CO)_5Br$ with $Ph_2C{:}NSiMe_3$ gave only $Mn(CO)_3(Ph_2C{:}NH)Br$, the source of hydrogen introduced into the ligand presumably being the solvent. The preformed aza-allyl ligand $Ph_2C{:}N\text{-}C(Cl)Ph_2$ reacted with $Mn(CO)_5Br$ giving $Mn(CO)_4Ph_2CNCPh_2$.[160] No evidence was ever obtained for the formation of aza-allyl/allene derivatives from the 'condensation' of two $Ph_2C{:}N\div$ units. A greater chance of success in obtaining this latter type of reaction was anticipated by use of (p-tolyl)$_2$C:NLi due to the increased nucleophilic character over $Ph_2C{:}NLi$, a factor which may be important as the mechanism is thought to involve nucleophilic attack at a carbon of a carbonyl group (Chapter 3). If complexes of the type $Mn(CO)_{4-5}NC$(p-tolyl)$_2$ only were formed, however, the p-Me groups would be useful in a ^1H n.m.r. structural study.

The '2:1' reaction was attempted first of all and two unexpected products were obtained (IX) and (X). (X) was easily identifiable as $Mn(CO)_3$[(p-tolyl)$_2$C:NH]Br by the normal methods and also by the great similarity in i.r. spectra to the analogous complex $Mn(CO)_3(Ph_2C{:}NH)Br$.[4] Three strong carbonyl absorptions were observed, at slightly lower frequency than the diphenyl compound, in keeping with the increased electron-donating capacity of the p-tolyl group. This is consistent with the three carbonyl groups being in mutually cis-positions giving the complex C_s symmetry, for which three strong bonds (2A' + A") are predicted.[161] The N-H stretching frequency is lowered by some 25 cm.$^{-1}$ from the free ligand value (3275 cm.$^{-1}$), indicating some electron withdrawal from nitrogen via the σ-bond, upon co-ordination, while $\nu_{C=N}$ is little changed from the free ligand value (1597 cm.$^{-1}$), which is fairly typical of other transition metal-diphenyl-ketimine complexes[160] and also of adducts of the latter with main group metals.[162] The source of hydrogen into the ligand is assumed to be the solvent.

Table VIII.2

ν_{N-H} for some Transitional-Metal Ketimine Complexes.

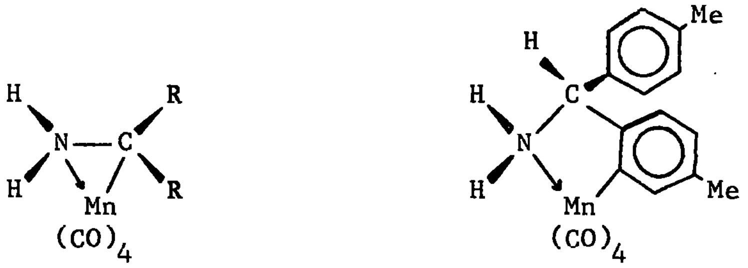
Complex	ν_{N-H}(cm.$^{-1}$)	Ref.
$Ph_2C:NH$	3260	4
$(Ph_2C:NH)_2CoCl_2$	3279	160
$(Ph_2C:NH)_2NiCl_2$	3175	160
$(Ph_2C:NH)(PPh_3)CoCl_2$	3279	160
$CuCl_2.(Ph_2C:NH)_2$	3281	163
$CuCl_2.(Ph_2C:NH)$	3200	163
$Mn(CO)_3(Ph_2C:NH)_2Cl$	3215	4
$Mn(CO)_3(Ph_2C:NH)_2Br$	3215	4
$Mo(CO)_3(Ph_2C:NH)_3$	3279	164
($\underline{p}$-tolyl)$_2$C:NH	3275	This work
Mn(CO)$_3$[($\underline{p}$-tolyl)$_2$C:NH]$_2$Br	3250	This work

Complex IX proved rather more difficult to characterise and, in fact, a definite structure still cannot be assigned with any degree of certainty. The available data were originally thought to be consistent with the formulation $[Mn(CO)_4K_H]_2$ [K_H = (p-tolyl)$_2$C:NH] i.e. a dinuclear species, probably analogous to $Mn_2(CO)_{10}$ with one CO group on each manganese replaced (asymmetrically) by a K_H unit, which would give rise to the large number of carbonyl absorptions in the solid state and the two ν_{N-H} bands observed. Analytical data were acceptable and the mass spectrum, although very difficult to count, gave a parent about m/e 376, which corresponded to $Mn(CO)_4K_H$, followed by successive loss of four carbonyl groups, hence the assumption was that the first event to occur in the mass spectrometer was cleavage of the metal-metal bond.

A closer and more careful examination of the available data, however, suggested that such a structure was unlikely. A re-counting of the mass spectrum showed the parent to be in fact at m/e 377. Loss of four carbonyl groups in succession followed giving $[Mn(C_{15}H_{16}N)]^+$(m/e 265) which readily lost a proton to give a much more intense peak at m/e 264 corresponding to $[MnK_H]^+$. Also it is unusual that no dinuclear manganese containing ions are observed since loss of carbonyl groups is generally observed before metal-metal bond cleavage takes place,[23a] thus the mass spectrum would suggest a mononuclear formulation.

The i.r. spectrum shows no band in the 1580-1610 cm.$^{-1}$ region, where $\nu_{C=N}$ would be expected, which would be very unusual for a structure in which the ketimine is σ-bonded through the nitrogen lone pair (see earlier remarks). Two N-H stretching bands are observed but they are considerably higher (3384, 3307, cm.$^{-1}$) than the values normally found in ketimine complexes (see Table VIII.2) and are further into the region associated with the symmetrical and asymmetrical N-H stretches in primary amines. In fact they are in almost identical positions to the two ν_{N-H} bands in the compound (p-tolyl)$_2$CHNH$_2$. This would indicate the presence of a -NH$_2$ unit in the molecule, implying abstraction of two protons from the solvent.

Thus, all this data, taken together, strongly suggest a formula of the type $Mn(CO)_4(C_{15}H_{14}NH_2)$. The mononuclear formulation could not, unfortunately, be confirmed by molecular weight measurements due to the low solubility of the complex, but, as such, would require the organonitrogen ligand to act as a three-electron donor if the inert gas rule were to be satisfied. There would appear to be two possible basic structures (Fig. VIII.1).



(a) (b)

Fig. VIII.1

The ortho-metallated structure (Fig. VIII.1(b) appears attractive, at first sight, as formation of a 5-membered ring would be sterically more favourable than a 3-membered ring. A number of similar ortho-metallated compounds are known[165] including two of manganese prepared from $Mn_2(CO)_{10}$ and $Ph_2C{=}NR$ (R = Ph, Me) of formula $Mn(CO)_4RN{:}CPh.C_6H_4$.[65]

Bonding of the organonitrogen group to the metal is thought to involve chelation via the nitrogen lone pair and a metal-carbon σ- bond with little involvement of the C=N system, which is confirmed by spectroscopic and structural data on the complex $Mn(CO)_4PhN:CH.C_6H_4$.[166]

Such a structure, however, is unlikely on a number of grounds. Firstly, the n.m.r. spectrum is essentially that of a single, 'unpeturbed' p-tolyl group. For the type of structure shown in Fig. VIII.1(b), two methyl signals would be expected together with a much more complex pattern in the aromatic region as is observed with the examples given above. Also, no signal is apparent for the single C-H proton. Secondly, the occurrence of 6 strong and 1 weak carbonyl absorptions in the infrared spectrum (KBr) cannot be explained (four bands would be expected, 2A' + 2A", as the complex would have C_s symmetry,[167])and furthermore, cis-trans and conformational isomers cannot be invoked as the ligand must always occupy two, mutually cis- positions in an essentially octahedral environment.

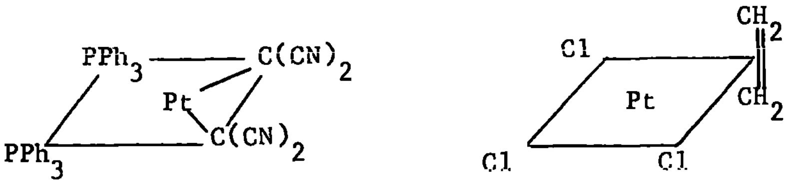
Fig. VIII.1(a) has no such drawbacks, being consistent with all the available data, and is thus tentatively postulated as the structure of complex IX. The n.m.r. data is as expected (no NH signals were observed due to the poor signal-to-noise ratio of the instrument, made necessary by the low solubility of the complex; also NH resonances are generally broad due to the effect of the electrical quadrupole moment of the nitrogen nucleus,) and although the single structure shown cannot explain more than four carbonyl absorptions, a larger number can arise if one assumes the possibility of conformational isomers of the type shown in Fig. VIII.2 i.e. structures based on octahedral and trigonal bipyramidal arrangements where the organonitrogen ligand is considered to occupy two

(a) (b)

Fig. VIII.2

and one co-ordination site(s) respectively. Both forms would have C_s symmetry[167] and would give rise to a different set of four carbonyl absorptions. A mixture of such isomers in the crystal therefore could explain the observations. In solution rapid rotation may occur about the ligand-metal axis in a manner similar to that proposed for olefin complexes,[168,153] resulting in collapse of the carbonyl absorptions to an 'average' set of four bands as is observed (the broad peak at 1957 cm.$^{-1}$ may well be two unresolved bands.)

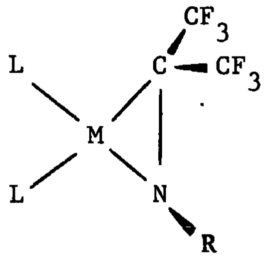
Structures shown in Fig. VIII.2 occur individually in allene complexes (see Chapter 5) and in olefin complexes, particularly those of platinum. For the complex $(PPh_3)_2Pt[(CN)_2CC(CN)_2]$,[146] the olefin lies in the square co-ordination plane (Fig. VIII.3(a)) and in $K[PtCl_3(C_2H_4)]$, ethylene is perpendicular to the co-ordination plane (Fig. VIII.3(b)).



(a) (b)

Fig. VIII.3

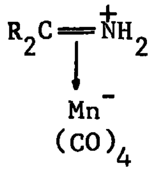
A number of complexes of nickel(0) and platinum(0) containing ketimines laterally bonded to the metal are known,[169] of the type shown in Fig. VIII.4. The complexes are thought to have an essentially σ-bonded 3-membered ring system as the $\nu_{C=N}$ mode of the free ligand disappears upon complexation. A similar structure is likely for complex IX as there is no band in the i.r. spectrum readily assignable to $\nu_{C=N}$. Two types of bonding, however, can lead to an apparently σ-bonded structure in Fig. VIII.4



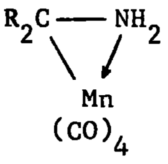
a) M = Ni, L = PPh_3, R = H
b) M = Ni, L = PPh_3, R = Me
c) M = Ni, L = PPh_2Me, R = Me
d) M = Pt, L = PPh_3, R = H
e) M = Pt, L = PPh_3, R = Me

Fig. VIII.4

(similar to those described in Chapter 6 for aza-allene complexes). One may consider prior transfer of an electron from ligand to metal with formation of the species $(\underline{p}\text{-tolyl})_2C = \overset{+}{N}H_2$, which would then function as a 2-electron ligand via the C=N π-system, with $d_\pi \rightarrow \pi^*$ back donation likely to be the most important process (Fig. VIII.5(a).



(a)



(b)

Fig. VIII.5

Alternatively, one may consider the ligand to act as a 3-electron donor via σ-donation of the nitrogen lone pair and a metal carbon σ-bond (Fig. VIII.5(b)) i.e. primarily an electron donating process from ligand to metal.

Data which may solve this structural problem, ESCA and X-ray crystallographic, are not available, unfortunately, at the present time, but it is hoped that such studies may take place in the near future.

The 1:1 molar ratio reaction (attempted due to the failure to obtain an aza-allyl/allene type of product from the 2:1 reaction) gave no evidence for the formation of complex IX, the only products being X and $Mn_2(CO)_{10}$. The reason for this is not understood, except to say that the reaction which takes place to form IX occurs only in the presence of excess ligand.

On the basis of this, and other studies,[4,160] it would seem reasonable to suggest that manganese does not show the same tendency as molybdenum and tungsten to form complexes with 3-electron organo-nitrogen ligands. Steric factors are unlikely to account for this as the manganese residues used are rather less crowded. Consequently one must assume a degree of incompatibility between the electronic properties of the $Mn(CO)_4$ and ligand units.

APPENDICES

Appendix 1

Preliminary Reactions of $[R_2CNCR_2](Li)$ Systems with π-$C_5H_5M(CO)_3Cl$ (M = Mo,W).

A. Introduction.

Although quite a number of aza-allyl/allene complexes π-$C_5H_5M(CO)_2[R_2CNCR_2]$, have been recently prepared, the possible range of such complexes is severely limited, mainly by the synthetic route which, at present, has to be adopted, i.e. via lithio-ketimines. Only di-aryl ketimines have so far been found to undergo this reaction and the only metal complexes which do so are π-$C_5H_5M(CO)_3Cl$ (M = Mo,W). Consequently it would be desirable to devise a synthetic route of possible general applicability. Such a route could involve reaction of a preformed ligand derivative, $[R_2CNCR_2]X$ with appropriate metal complexes, where the restrictions on R and the metal are likely to be less. Some measure of success was obtained from the reaction of $Mn(CO)_5Br$ with $Ph_2C{=}N{-}C(Cl)Ph_2$, (i.e. X = Cl), which gave the derivative $Mn(CO)_4[Ph_2CNCPh_2]$,[160] although no reaction was detected in the corresponding reaction with $Na^+[Mn(CO)_5]^-$. Use of the Grignard derivative, $Ph_2C{=}N{-}C(MgCl)Ph_2$ did not produce the desired products with any of the metal complexes used, hence ligand derivatives of the type $R_2CNCR_2(X)$ where X = Cl or -MgCl do not appear to be suitable systems. Many of the successful syntheses in this particular sphere of organonitrogen-transition metal chemistry have used organo-lithium compounds, particularly lithio-ketimines.[8,13,14] Consequently, the report that 2-aza-allyl lithium compounds underwent cyclo-addition reactions with unsaturated hydrocarbons[170] and other unsaturated multiple bonded functional groups[171] was of interest.

The lithio- compounds used are shown in Fig. A1.1 (a) and (b), and were prepared by the action of $LiN[CH(CH_3)_2]_2$ on $Ph_2C{:}NCH_3$ and $Ph(H)C{:}NCH_2Ph$ respectively at -60°, though whether they have the structure shown in Fig. A1.1 is not certain. Such compounds however could well lead to the type of compound desired as the number of suitable metal complexes for reaction is fairly large and also the substituents on carbon could be easily varied as N-substituted ketimines are fairly straightforward to prepare.

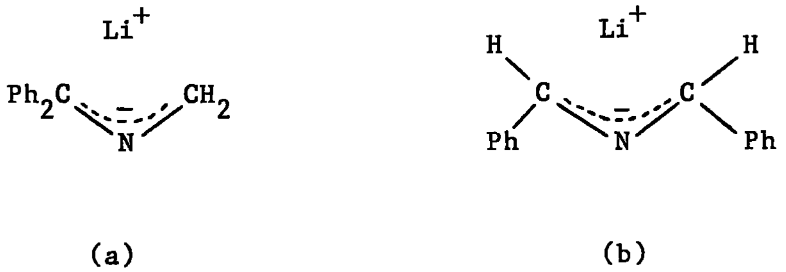


Fig. A1.1

We chose therefore to study initially, ligands from which complexes similar to those already prepared by the indirect route should result, i.e. with aryl groups as substituents, from reaction with π-$C_5H_5M(CO)_3Cl$ (M = Mo,W). Later work involved replacement of one aryl group at each end of the ligand by hydrogen.

B. Experimental.

1. Starting materials.

The ketimines $R_2C{:}N\text{-}C(H)R_2$ were prepared by the standard method of condensing the appropriate carbonyl compound and amine in the absence of a solvent. For phenyl substituents these derivatives were readily available, but for the p-tolyl compounds, the amines (p-tolyl)CH_2NH_2 and (p-tolyl)$_2CHNH_2$ had to be prepared by reducing (p-tolyl)C≡N and (p-tolyl)$_2C{=}NH$ with $NaBH_4/AlCl_3$/diglyme[173] and $NaBH_4$/MeOH respectively. More vigorous conditions were required for condensation of ketones than for the aldehydes (i.e. higher temperatures and conc.HCl as catalyst). The desired product was obtained by extracting the reaction mixture with hot absolute ethanol, filtration and cooling. A second re-crystallisation from hot ethanol was usually performed.

Reaction of the ketimines with both $LiN[CH(CH_3)_2]_2$ (prepared from $HN[CH(CH_3)_2]_2$ and ^nBuLi) and ^nBuLi, at low temperatures was performed and identical reactions apparently took place, hence in preparations of the 2-aza-allyllithium solutions, ^nBuLi was used directly as the metallating reagent.

2. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $(Ph_2CNCPh_2)(Li)$.

A solution of $(Ph_2CNCPh_2)(Li)$ was prepared by dissolving $Ph_2C{=}NCHPh_2$ (0.62g., 1.75 mmole) in ether (50 ml.), cooling to liquid nitrogen temperature and syringing in ^nBuLi (1.75 mmole) in hexane (0.65 ml.) A pale green colouration formed initially which only intensified slightly up to ca. 0°, but above this temperature a very intense dark green-brown colour developed quite rapidly. The solution was stirred at room temperature for ca. 15 min. when π-$C_5H_5Mo(CO)_3Cl$ (0.50g., 1.75 mmole) in ether (40 ml.) was added dropwise over 15 min. No immediate reaction was apparent, but overnight the reaction solution had turned a cherry-red colour and the i.r. spectrum showed that the only carbonyl product formed was the dimer $[\pi$-$C_5H_5Mo(CO)_3]_2$. Mixing the solution at low temperature (ca. -100°) and allowing to warm up to room temperature had no effect on the course of the reaction.

3. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with [(p-tolyl)$_2$CNCPh$_2$] (Li).

A solution of [(p-tolyl)$_2$CNCPh$_2$](Li) (1.75 mmoles) was prepared in an analogous manner to the preparation of (Ph_2CNCPh_2)(Li) described above, and a similarly coloured solution was obtained at room temperature. Dropwise addition of π-$C_5H_5Mo(CO)_3Cl$ (0.50g., 1.75 mmole) in ether (40 ml.) at room temperature resulted in complete conversion to the dimer, [π-$C_5H_5Mo(CO)_3$]$_2$ within 3hr. Again, mixing of the solutions at low temperature had no effect on the course of the reaction.

4. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with [Ph_2CNC(p-tolyl)$_2$](Li)

This reaction was carried out in a similar manner to those described above. [π-$C_5H_5Mo(CO)_3$]$_2$ was the only carbonyl product formed during the reaction.

5. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with [(p-tolyl)(H)CNC(H)(p-tolyl)](Li)

(p-tolyl)(H)C:NCH$_2$(p-tolyl) (0.40g., 1.75 mmole) was dissolved in ether (40 ml.) and cooled to liquid nitrogen temperatures. ^{n}BuLi (1.75 mmole) in hexane (0.65 ml.) was added by syringe and a pale lilac colour developed, which intensified on warming to room temperature and became redder. After stirring for ca. 20 min. a solution of π-$C_5H_5Mo(CO)_3Cl$ (0.50g., 1.75 mmole) in ether (40 ml.) was added dropwise at room temperature. No initial reaction was apparent, but the i.r. spectrum of the reaction solution after 2hr. showed that the starting material had been converted almost entirely to the dimer [π-$C_5H_5Mo(CO)_3$]$_2$, together with a weak, new band at 1857 cm.$^{-1}$ It was decided at this point to repeat the reaction starting, this time, at low temperature. Thus, the solution of (p-tolyl)(H)CNC(H)(p-tolyl)(Li), prepared as above, was cooled to liquid nitrogen temperature and the solution of π-$C_5H_5Mo(CO)_3Cl$ in ether syringed in. The flask was allowed to warm up to room temperature and the i.r. spectrum of the reaction solution after ca. 2hr. showed that the new band at 1857 cm.$^{-1}$ was considerably stronger, although large quantities of $[\pi$-$C_5H_5Mo(CO)_3]_2$ had again been formed. Little starting material remained, hence the solution was filtered and the solvent removed *in vacuo*, from the filtrate. This residue was extracted with hexane (4 x 10 ml.) giving a deep-red solution. The i.r. spectrum of this solution showed a little residual π-$C_5H_5Mo(CO)_3Cl$ and $[\pi$-$C_5H_5Mo(CO)_3]_2$, strong carbonyl absorptions at 1960, 1864cm^{-1} and two weak bands at 2045, 2030 cm.$^{-1}$ Cooling to 0^o caused crystallisation of the former materials which were filtered off. No solid could be obtained from the remaining solution, so the solvent was removed in *vacuo* to yield a thick, dark-red oil. The i.r. spectrum, on a thin film, showed strong carbonyl bands at 1947, 1850 cm.$^{-1}$ and weak bands at 2035, 2015cm.$^{-1}$ The oil was thought to be impure, however, since dissolving the oil in hexane, cooling, filtering and removing the solvent again *in vacuo* gave resultant oils with differing relative intensities of the carbonyl absorptions. A mixture of products therefore seemed likely. The rest of the i.r. spectrum showed some bands which are fairly characteristic of aza-allyl/allene complexes containing *p*-tolyl groups, hence the desired product may well have been present in the oil.

6. Reaction of π-$C_5H_5W(CO)_3Cl$ with [(p-tolyl)(H)CNC(H)(p-tolyl)](Li)

This reaction was performed in an entirely analogous manner to the low temperature reaction described immediately above, and a similar dark-red oil was obtained which had strong carbonyl absorptions at 1935, 1837 cm.$^{-1}$, and weak bands at 2035, 2020 cm.$^{-1}$, indicating that similar products had been formed.

C. Discussion

The failure of the tetra-aryl ligands to react even under cold conditions is likely to be due to steric factors since the bulky phenyl groups would make close approach of the metal and the reactive CNC part of the ligand very difficult, particularly for a bent skeleton. Consequently, if the lithium abstracts the chlorine from the π-$C_5H_5Mo(CO)_3Cl$, dimerisation is likely to occur before reaction with the ligand. This is borne out to some extent by the fact that the lesser substituted ligand [(p-tolyl)(H)CNC(H)(p-tolyl](Li) does react at low temperature. In this case, the aromatic groups can adopt orientations remote from the metal prior to co-ordination thus allowing sufficiently close approach to enable reaction to occur. It seemed likely from the i.r. spectra of the oils that the desired product was being formed, although more studies regarding reaction conditions and separation methods are necessary if pure products are to be obtained.

Providing attention is paid, therefore, to the steric requirements of both ligand and metal systems, it would appear from these reactions that this method is potentially a useful synthetic route to aza-allyl/allene complexes, hence further work in this area could be worthwhile.

Appendix 2

Experimental Details and Starting Materials

All the reactions described were carried out in an atmosphere of pure dry nitrogen in two-necked flasks. Air sensitive materials were handled in a glove box, or if in solution, were transferred from one vessel to another by syringe against a counter current of nitrogen.

Nitrogen supply.

'White Spot' nitrogen direct from the cylinder was dried by passage through two traps maintained at -196°, through a tower at 400° containing copper wire to remove traces of oxygen and delivered to a multiple outlet system. A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler.

Glove Box.

The nitrogen atmosphere in the Glove Box was purified by continuously recycling it through two traps at -196°, through two towers at 400° containing copper wire and back to the box. Cylinder nitrogen was used, after passage through this system, to flush out the transfer tube. All external tubing was of copper where possible, and the gloves used were made of 'Butasol' rubber. An oxygen level of less than 50 p.p.m. was maintained by this system.

Solvents.

Solvents were degassed on the vacuum line before use and stored under nitrogen. Hydrocarbon solvents and di-ethyl ether were dried over sodium wire. Chloroform was dried over molecular sieve and monoglyme freshly distilled, under nitrogen from $LiAlH_4$.

Starting Materials.

The transition metal derivatives used as starting materials are readily available by methods described in the literature i.e. π-$C_5H_5M(CO)_3Cl$ (M = Mo,W);[174] $Mn(CO)_5Br$.[175] All the ligands used were prepared according to literature methods or the preparation is described in the text.

Appendix 3

Instrumentation

Infrared 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 0.1 mm.) which was filled by syringe.

Nuclear Magnetic Resonance Spectra.

Nuclear magnetic resonance spectra were recorded using a Varian A56/60D spectrometer fitted with a variable temperature controller, operating at 60 MHz/sec. (^1H) or 56.4 MHz/sec. (^{19}F). Samples were normally in CS_2 or toluene solution. The internal reference standards were tetramethylsilane (^1H) or a $CFCl_3/C_6F_6$ mixture (^{19}F). Temperature calibration for the kinetic measurements was by use of the standard Varian methanol sample. Sample tubes were filled by syringe against a counter-current of nitrogen and where necessary, sealed under nitrogen.

Mass Spectra

Mass Spectra were recorded on a A.E.I. MS9 mass spectrometer at 70 eV and an accelerating potential of 8 kV, 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. Isotopic distribution patterns were computed using a programme kindly supplied to us by Dr E.H. Brooks.

X-ray Photoelectron Spectra

X-ray photoelectron spectra were measured on an AEI ES100 electron spectrometer. Samples were studied in powder form (pressed on to Scotch tape backing or as pressed discs, when sufficient quantities were available), using $MgK\alpha_{1,2}$ radiation. Deconvolutions of overlapping peaks were carried out with a Dupont 310 curve resolver. All levels were calibrated with respect to $Au(4f_{7/2})$ 84 eV. binding energy.

Molecular Weights by Osmometry

Molecular weights were measured using a 'Mechrolab Osmometer' in $CHCl_3$ or benzene solution using either analytical grade biphenyl or triphenylphosphine as standard solute.

Appendix 4

Analytical Methods

Carbon, Hydrogen and Nitrogen

Carbon, Hydrogen and Nitrogen were determined with a Perkin-Elmer 240 Elemental Analyser; nitrogen was also determined by the Kjeldhal method.

Halogens.

Analyses for fluorine and bromine content were carried out by the departmental microanalyst by conventional potassium-fusion and titration methods.

Manganese.

Manganese was estimated by Atomic Absorption Spectrophotometry using a Perkin-Elmer 403 instrument.

Appendix 5

Calculation of Activation Energies from N.M.R. Spectral Data.

Activation energies, E_a, for the low temperature averaging process described in Chapter 7 were obtained from measurements of the rate of internal rotation ($1/2\tau$) at a series of temperatures by fitting the data to the Arrhenius equation:

$$\log_{10}(1/2\,\tau) = \log_{10}A - E_a/2.303RT.$$

Values of E_a, and the frequency factor, $\log_{10}A$, were derived from linear plots of $\log_{10}(1/2\,\tau)$vs. $10^3/2.303RT$ by the method of least squares. Values of τ at individual temperatures were obtained by two independant methods. That described by Rogers and Woodbrey[156] relates τ to the ratio (r) of maximum to central minimum v-mode intensities of the coalescing doublet by the equation:

$$dv = \pm\ 1/\pi\surd 2.\ [r \pm (r^2-r)^{1/2}]^{1/2} \text{ for } \pi\surd 2\,\tau\,dv > 1$$

where dv is the chemical shift difference (Hz) between the two signals, and the effect of overlap of the components of the doublet is negligible, in the absence of rotational averaging. The method developed by Gutowsky and Holm[155] relates τ to the separation (Hz) between the components of the coalescing doublet at various temperatures, by the equation:

$$dv_e = (1 - 2/\tau^2 dv^2)^{1/2}.\ dv \text{ for } \tau\,dv > \surd 2$$

where dv is as above and the same conditions as to overlap apply. dv_e Is the experimentally observed separation.

A major drawback of this latter method becomes apparent when the value of dv is not constant with respect to temperature, i.e. the separation in the absence of rotation increases with decreasing temperature with no further decrease in line width.[176] This has the effect of increasing the range in which the rate appears to be changing and results in correspondingly smaller values of the activation energy. Such a problem was encountered in our measurements and the initial calculations showed large discrepancies between the two methods, owing to the value of dv being taken at too low a temperature. However, use of the value of dv obtained from the temperature at which no further line narrowing was apparent, gave results from the two methods which agreed within experimental error. The limits of E_a and $\log_{10}A$ were calculated for 90% confidence using conventional statistical methods.[177]

REFERENCES

References

1. H. Behrens and N. Harder, Chem. Ber., 1964, 97, 433.

2. A. Rosenthal and I. Wender, 'Organic Syntheses via Metal Carbonyls' (I Wender and P. Pino, eds.), Vol. 1, pp. 405-466. Wiley 1968 and references therein.

3. H. Brintzinger, J. Amer. Chem. Soc., 1966, 88, 4307.

4. K. Farmery, Ph.D. Thesis, Univ. of Durham, 1968.

5. E.A.V. Ebsworth, Chem. Comm., 1966, 530.

6a. H.M.M. Shearer and J.D. Sowerby, personal communication;

b. C. Midcalf, Ph.D. thesis, Univ. of Durham, 1971.

7. F.A. Cotton and R.M. Wing, Inorg. Chem., 1965, 4, 314.

8. K. Farmery, M. Kilner and C. Midcalf, J. Chem. Soc. (A), 1970, 2279.

9. K. Farmery and M. Kilner, J. Organometallic. Chem., 1969, 16, P51.

10a. T.G. Hewitt and J.J. De Boer, J. Chem. Soc. (A), 1971, 817;

b. J.A. Osborne, Chem. Comm., 1968, 1231.

11. N.S. Nametkin, V.N. Perchenko and L.G. Batalova, Dokl. Akad. Nauk S.S.S.R., 1964, 158, 660.

12. T.B. Jackson and J.O. Edwards, Inorg. Chem., 1962, 1, 398.

13. M. Kilner and C. Midcalf, J. Chem. Soc. (A), 1971, 292.

14. M. Kilner and J.N. Pinkney, J. Chem. Soc. (A), 1971, 2887.

15. D.C. Bradley and I.M. Thomas, J. Chem. Soc., 1960, 3857.

16. E.C. Alyea, J.S. Basi, D.C. Bradley and M.H. Chisholm, Chem. Comm., 1968, 495.

17. J.S. Basi, D.C. Bradley and M.H. Chisholm, J. Chem. Soc. (A), 1971, 1433.

18. D.C. Bradley and M.H. Chisholm, J. Chem. Soc. (A), 1971, 2741.

19. M.R. Stober, K.W. Michael and J.L. Speier, J. Org. Chem., 1967, 32, 2742.

20. K. Jones and M.F. Lappert, Proc. Chem. Soc., 1962, 358; J. Chem. Soc., 1965, 1944.

21. L.E. Dahl, W.R. Costello and R.B. King, J. Amer. Chem. Soc., 1968, 90, 5422.

22. N. Flitcroft, J. Organometallic Chem., 1968, 15, 254.

23. F.J. Preston and R.I. Reed, Chem. Comm., 1966, 51.

23a. M.I. Bruce, Adv. in Organometallic Chem., 1968, 6, 273.

24. M.A. Bush and G.A. Sim, J. Chem. Soc. (A), 1970, 611.

25. A.T. McPhail and G.A. Sim, J. Chem. Soc. (A), 1968, 1858.

26. O.S. Mills, Acta Cryst., 1958, 11, 620.

27. J.T. Thomas, J.H. Robertson and E.G. Cox, Acta Cryst., 1958, 11, 599.

28. D. Bright and O.S. Mills, Chem. Comm., 1967, 245.

29. J.M. Coleman and L.F. Dahl, J. Amer. Chem. Soc., 1967, 89, 542.

30. L.F. Dahl and C.H. Wei, Inorg. Chem., 1963, 2, 328.

31. D.J. Cardin, S.A. Keppie, B.M. Kingston and M.F. Lappert, Inorg. Nucl. Chem. Lett., 1968, 4, 365.

32. H.R.H. Patil and W.A.G. Graham, Inorg. Chem., 1966, 5, 1401.

33. G.E. Coates, M.L.H. Green and K. Wade, 'Organometallic Compounds', Vol. 1, (3rd. Edn), Methuen,London (1967), p.14-16.

34. S. Fukuoka, M. Ryang, and S. Tsutsumi, J. Org. Chem., 1968, 33, 2973; E.O. Fischer and H.J. Kollmeier, Angew. Chem. Int. Edn., 1970, 9, 309.

35. D. Briggs and D.T. Clark, personal communication.

36a. R. Snaith, C. Summerford, K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1970, 2635.

b. J.B. Farmer and K. Wade, personal communication.

37. M. Kilner and C. Midcalf, Chem. Comm., 1970, 552.

38. M.L.H. Green in 'Organometallic Compounds' by G.E. Coates, M.L.H. Green and K. Wade, Vol. 2 'The Transition Elements', 3rd. Edn., Methuen, London (1968), p.219.

39. R.G. Guy and B.L. Shaw, Adv. Inorg. Chem. Radiochem., 1962, 4, 78.

40. M.L.H. Green and P.L.I. Nagy, Adv. Organometallic Chem., 1964, 2, 325.

41. Reference 38 p.39-64.

42. G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, Angew. Chem. Int. Edn., 1966, 5, 151.

43. M.I. Lobach, B.D. Babitskii and V.A. Kormer, Russ. Chem. Rev., 1967, 476.

44. J. Powell, MTP International Review of Science, Inorg. Chem. Series 1, Vol. 6, Butterworths, 1972, p.273.

45. G. Wilke, Angew. Chem. Int. Edn.,1963, 2, 105.

46. G. Wilke and B. Bogdanovic, Angew. Chem., 1961, 73, 756.

47. E.O. Fischer and G. Burger, Z. Naturforsch., 1961, 16b, 77.

48. H.D. Kaesz, R.B. King and F.G.A. Stone, Z. Naturforsch., 1960, 15b, 682.

49. M. Cousins and M.L.H. Green, J. Chem. Soc., 1963, 889.

50a. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 1960, 82, 750;

b. W.R. McClellan, H.H. Hochn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc., 1961, 83, 1601.

51. J. Smidt and W. Hafner, Angew. Chem., 1959, 71, 284.

52. H.D. Murdoch and E. Weiss, Helv. Chim. Acta, 1962, 45, 1927.

53. E.O. Fischer and G. Burger, Chem. Ber., 1961, 94, 2409.

54. R. Huttel, J. Kratzer and M. Bechter, Chem. Ber., 1961, 94, 766; and Ref. 39.

55. E.O. Fischer and H. Werner, Chem. Ber., 1962, 95, 695.

56. R.G. Schultz, Tetrahedron, 1964, 20, 2809.

57. M.S. Lupin and B.L. Shaw, Tetrahedron Letters, 1964, 883.

58. D.W. Moore, H.B. Jonassen, T.B. Joyner and A.J. Bertrand, Chem. Ind. (London), 1960, 1304.

59. A.N. Nesmeyanov, A.Z. Rubezhov, S.P. Gubin, A.S. Ivanov and L.I. Voronchikhina, Bull. Acad. Science U.S.S.R., (Div. Chem. Science), 1972, 2249 (English Edn.).

60. J. Lewis and A.W. Parkins, J. Chem. Soc. (A), 1967, 1150.

61. R.F. Heck, J. Amer. Chem. Soc., 1968, 90, 317.

62. A.N. Nesmeyanov, S.P. Gubin and A.Z. Rubezhov, J. Organometallic Chem., 1969, 16, 163.

63a. W.E. Oberhansli and L.F. Dahl, J. Organometallic Chem., 1965, 3, 43; J.M. Rowe, Proc. Chem. Soc., 1962, 66.

b. A.E. Smith, Acta Cryst., 1965, 18, 331.

64. A.E. Smith, Acta Cryst., 1969, A25, 5161.

65. A.N. Nesmeyanov and I.I. Kritskaya, J. Organometallic Chem., 1968, 14, 387.

66. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 1960, 82, 4438.

67. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 1961, 83, 1097.

68. J. Powell and B.L. Shaw, Chem. Comm., 1966, 236.

69. I.I. Moiseev, E.A. Federovskaya and Y.K. Syrkin, Russ. J. Inorg. Chem. (Eng.), 1959, 4, 1218.

70. H.P. Fritz, Chem. Ber., 1961, 94, 1217.

71. H.C. Dehm and J.C.W. Chien, J. Amer. Chem. Soc., 1960, 82, 4429.

72. B.L. Shaw and N. Sheppard, Chem. Ind., 1961, 517.

73. H.C. Dehm and J.C.W. Chien, Chem. Ind., 1961, 745.

74. R. Hüttel, J. Kratzer and M. Bechter, Angew. Chem., 1959, 75, 456.

75. R.J. Goodfellow and L.M. Venanzi, J. Chem. Soc. (A), 1966, 784;
G. Paiaro and A. Musco, Tetrahedron Letters, 1965, 21, 1583.

76. H.A. Martin and F. Jellinek, Angew. Chem., 1964, 76, 274;
J. Organometallic Chem., 1966, 6, 293.

77. R. Reimschneider, Monatsch. Chem., 1961, 92, 777.

78. B.L. Shaw, Proc. Chem. Soc., 1960, 247.

79. D.W. McBride, R.L. Pruett, E. Pitcher and F.G.A. Stone, J. Amer. Chem. Soc., 1962, 84, 497.

80. R.A. Plowman and F.G.A. Stone, Z. Naturforsch., 1962, 17b, 575.

81. G.P. Chiusoli, Chim. Ind. (Milan), 1959, 41, 504.

82. R.F. Heck, J.C.W. Chien and D.S. Breslow, Chem. Ind., 1961, 986.

83. D. Walter and G. Wilke, Angew. Chem., 1966, 78, 941.

84. M.L.H. Green and A.N. Stear, J. Organometallic Chem., 1963, 1, 230.

85. M.L.H. Green and P.L.I. Nagy, J. Chem. Soc., 1963, 189.

86. R.F. Heck, J. Org. Chem., 1963, 28, 604.

87. G.F. Emerson and R. Pettit, J. Amer. Chem. Soc., 1962, 84, 4591.

88. S.D. Robinson and B.L. Shaw, J. Chem. Soc., 1963, 4806.

89. G.N. Schrauzer, Adv. Organometallic Chem., 1964, 2, 1.

90. E.O. Fischer, H.P. Kögler and P. Kuzel, Chem. Ber., 1960, 93, 3006.

91. R.F. Heck, J. Amer. Chem. Soc., 1963, 85, 2013.

92. M. Green, N. Mayne and F.G.A. Stone, Chem. Comm., 1966, 755.

93a. M.D. Johnson and C. Mayle, Chem. Comm., 1969, 192.

b. J.P. Collman, J.N. Cawse and J.W. Kang, Inorg. Chem., 1969, 8, 2574.

c. B.E. Mann, B.L. Shaw and N.I. Tucker, J. Chem. Soc. (A), 1971, 2667.

94. J.K.P. Ariyaratne and M.L.H. Green, J. Organometallic Chem., 1963, 1, 90.

95. P.W. Jolly and R. Pettit, J. Organometallic Chem., 1968, 12, 491.

96. E.O. Fischer and K. Fichtel, Chem. Ber., 1962, 95, 2063.

97. S. Otsuka, A. Nakamura and K. Tari, J. Organometallic Chem., 1968, 14, P.30.

98. K. Vrieze, H.C. Volger and A.P. Praat, J. Organometallic Chem., 1970, 21, 467.

99. R. Ben-Shoshar and R. Pettit, J. Amer. Chem. Soc., 1967, 89, 2231.

99a. M. Kadonaga, N. Yasuoka and N. Kasai, Chem. Comm., 1971, 1597.

100. T. Kasiwagi, N. Yasuoka, N. Kasai and M. Kukudo, Chem. Comm., 1969, 317; P. Racanelli, G. Pantini, A. Immirzi, G. Allegra and L. Porri, Chem. Comm., 1969, 361.

101. M.J.S. Dewar, Bull. Soc. Chim. France, 1951, 18, C71; J. Chatt, J. Chem. Soc. 1953, 2939.

102. J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., 1963, 2976.

103. S. Otsuka, A. Nakanura and T. Yoshida, J. Organometallic Chem., 1967, 7, 339.

104. K. Ogawa, A. Torii, H. Kobayashi-Tamwa, T. Watanabé, T. Yoshida and S. Otsuka, Chem. Comm., 1971, 991.

105. S.R. Su, J.A. Hanna and A. Wojcicki, J. Organometallic Chem., 1970, 21, P.21.

106. J.S. Rieci, J.A. Ibers, M.S. Fraser and W.H. Baddley, J. Amer. Chem. Soc., 1970, 92, 3489.

107. H.R. Keable and M. Kilner, Chem. Comm., 1971, 349.

108. H.R. Keable and M. Kilner, J. Chem. Soc., Dalton Trans., 1972, 153.

109. T. Inglis and M. Kilner, Abstr. Autumn Meeting Chem. Soc. York., 1971, B15.

110. T. Inglis, M. Kilner and T. Reynoldson, Chem. Comm., 1972, 774.

111. D. Lawton and R. Mason, J. Amer. Chem. Soc., 1965, 87, 921.

112. T. Inglis and M. Kilner, personal communication.

113. K. Vrieze and H.C. Volger, J. Organometallic Chem., 1967, 9, 537.

114. J. Powell and B.L. Shaw, J. Chem. Soc. (A), 1967, 1839.

115. G.L. Statton and K.C. Ramey, J. Amer. Chem. Soc., 1966, 88, 1327, 4387.

116. P. Corradini, G. Maglio, A. Musco and G. Paiaro, Chem. Comm., 1966, 618.

117. F.A. Cotton, J.W. Faller and A. Musco, Inorg. Chem., 1967, 6, 179.

118. K. Vrieze, H.C. Volger and P.W.N.M. van Leeuwen, Inorg. Chim. Acta Rev., 1969, 3, 109.

119. J.K. Beconsall and S.O'Brien, Chem. Comm., 1966, 302.

120. J.K. Beconsall, B.E. Job and S.O'Brien, J. Chem. Soc. (A), 1967, 423.

121. J.E. Nordlander and J.D. Roberts, J. Amer. Chem. Soc., 1959, 81, 1769.

122. A. Davison and W.C. Rode, Inorg. Chem., 1967, 6, 2124.

123. J.K. Beconsall and S.O'Brien, J. Organometallic Chem., 1967, 9, P.27.

124. J.K. Beconsall and S.O'Brien, Chem. Comm. 1966, 720.

125. J.D. Cotton, D. Doddrell, R.L. Heazlewood and W. Kitching, Aust. J. Chem., 1969, 22, 1785.

126. C.E. Holloway, J.D. Kelly and M.H.B. Stiddard, J. Chem. Soc.(A), 1969, 931.

127. P. Ganis, G. Maglio, A. Musco and A.L. Segre, Inorg. Chim. Acta, 1969, 3, 266.

128. F. De Candia, G. Maglio, A. Musco and G. Paiaro, Inorg. Chim. Acta, 1968, 2, 233.

129. S.F.A. Kettle and R. Mason, J. Organometallic Chem., 1966, 5, 573.

130. J.W. Faller, M.J. Incorvia, M.E. Thomsen, J. Amer. Chem. Soc., 1969, 91, 518.

131. K. Vrieze, C. Maclean, P. Cossee and C.W. Hilbers, Rec. Trav. Chim., 1966, 85, 1077.

132. P.W.N.M. van Leeuwen, A.P. Praat and M. van Diepen, J. Organometallic Chem., 1971, 29, 433.

133. K. Vrieze, P. Cossee, C. Maclean and C.W. Hilbers, J. Organometallic Chem., 1966, 6, 672.

134. K. Vrieze, P. Cossee, C.W. Hilbers and A.P. Praat, Rec. Trav. Chim., 1967, 86, 769.

135. K. Vrieze, P. Cossee, A.P. Praat and C.W. Hilbers, J. Organometallic Chem., 1968, 11, 353.

136. P.W.N.M. van Leeuwen, K. Vrieze and A.P. Praat, J. Organometallic Chem., 1969, 20, 219.

137. P.W.N.M. van Leeuwen and A.P. Praat, Chem. Comm., 1970, 365.

138. R. Mason and D.R. Russell, Chem. Comm., 1966, 26.

139. P.W.N.M. van Leeuwen and A.P. Praat, J. Organometallic Chem., 1970, 21, 501.

140. F. Basolo and R.G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, 1967.

141. J.D. Roberts and M.C. Caserio, 'Basic Principles of Organic Chemistry', Benjamin, New York, 1964, p.954.

142. E.S. Bolton, G.R. Knox and C.G. Robertson, Chem. Comm., 1969, 664.

143a. G. Avitabile, P. Ganis and M. Nemiroff, Acta Cryst., B, 1971, 725.

b. I.N. Levine, J. Chem. Phys., 1963, 38, 2326.

144. A.C. Skapski and P.G.H. Troughton, Chem. Comm., 1969, 666.

145. R.E. Merrifield and W.D. Phillips, J. Amer. Chem. Soc., 1958, 80, 2778.

146. C. Panattoni, G. Bombieri, U. Belluco and W.H. Baddley, J. Amer. Chem. Soc., 1968, 90, 798.

147. A.G. Swallow and M.R. Truter, Proc. Roy. Soc. London, 1960, A254, 205.

148. W. Hieber and F. Stanner, Chem. Ber., 1970, 103, 2836.

149. R.R. Hitch, S.K. Gondal, C.T. Sears, Chem. Comm., 1971, 777.

150. H.R. Keable and M. Kilner, J. Chem. Soc., (Dalton Trans.), 1972, 1535.

151. R. Cramer, J. Amer. Chem. Soc., 1964, 86, 217.

152. R. Cramer, J. Amer. Chem. Soc., 1967, 89, 5377.

153. C.E. Holloway, G. Hulley, B.F.G. Johnson and J. Lewis, J. Chem. Soc. (A), 1969, 53.

154. M. Green, R.B.L. Osborn, A.J. Rest and F.G.A. Stone, Chem. Comm., 1966, 502.

155. H.S. Gutowsky and C.H. Holm, J. Chem. Phys., 1956, 25, 1228.

156. M.T. Rogers and J.C. Woodbrey, J. Phys. Chem., 1962, 66, 540.

157. M.A. Bush and P. Woodward, J. Chem. Soc. (A), 1968, 1221.

158. V.A. Senior, Y.A. Chapovskii, V.T. Struchkov and A.N. Nesmeyanov, Chem. Comm., 1968, 666.

159. R.B. King, Organometallic Chem. Rev., B, 1968, 4, 35.

160. C.A. Payling, Ph.D. Thesis, University of Durham, 1969.

161. M. Kilner, Ph.D. Thesis, University of Nottingham, 1963.

162. K. Wade, J.R. Jennings, I. Pattison and B.K. Wyatt, J. Chem. Soc. (A), 1967, 1608.

163. A. Misona, T. Osa and S. Koda, Bull. Chem. Soc. Japan, 1968, 41, 373.

164. K. Farmery and M. Kilner, unpublished work.

165. M.M. Bagga, W.T. Flannigan, G.R. Knox and P.L. Pauson, J. Chem. Soc. (C), 1969, 1534.

166. M.I. Bruce, B.L. Goodall, M.Z. Iqbal, F.G.A. Stone, R.J. Doedens and R.G. Little,Chem. Comm., 1971, 1595.

167. W. Hieber, G. Faulhaber and F. Theubert, Z. Anorg. Chem., 1962, 314, 125.

168. B.F.G. Johnson, C.E. Holloway, G. Hulley and J. Lewis, Chem. Comm., 1967, 1143.

169. J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. (A), 1970, 3161.

170. T. Kaufmann, H. Berg and E. Köppelmann, Angew. Chem. Int., 1970, 9, 380.

171. T. Kauffmann, H. Berg, E. Ludorff and A. Woltermann, Angew. Chem. Int., 1970, 9, 960.

172. 'The Chemistry of the Carbon-Nitrogen Double Bond', ed. S. Patai, Interscience, New York, 1970.

173. H.C. Brown and B.C. Sabba Rao, J. Amer. Chem. Soc., 1956, 78, 2582.

174. T.S. Piper and G. Wilkinson, J. Inorg. and Nucl. Chem., 1956, 3, 104.

175. E.W. Abel and G. Wilkinson, J. Chem. Soc., 1959, 1501.

176. J.D. Roberts, Chem. Brit., 1966, 2, 529; R. Craner, J.B. Kline and J.D. Roberts, J. Amer. Chem. Soc., 1969, 91, 2519.

177. J.F. Kenney and E.S. Keeping, 'Mathematics of Statistics', part 2, 2nd Edn., D. Van Nostrand Co. Inc., New York, 1951.