PHD

Molybdenum mediated carbon-carbon bond formation

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MOLYBDENUM MEDIATED CARBON-CARBON BOND FORMATION

submitted by Colin R. Willis
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SUMMARY

PART I

Chapter one contains a literature survey of some metal assisted carbon-carbon bond forming reactions which are relevant to results described in subsequent sections of Part I.

Investigations into the reaction of cyclic allyl halide and acetate derivatives with dimethylsodiomalonate (dmsm), or sodium pentan-2,4-dionate (Napda), in the presence of catalytic quantities of $Mo(CO)_4bipy$ (bipy = 2,2'-bipyridyl) have shown that allylic couplings can predominate over the expected alkylation reactions. Thus, $\overline{(CH_2)_3CH=CHC}HCH(CO_2Me)_2$ is the major product from molybdenum catalysed $\overline{(CH_2)_3CH=CHC}HOAc$ - dmsm reactions, but the coupled products $[\overline{(CH_2)_nCH=CHCH}]_2$ (n = 3-5) are formed in high yields in analogous reactions between $\overline{(CH_2)_nCH=CHC}HBr$ and Napda, with up to 50% of the total molybdenum content recoverable as $[Mo(\eta^3\text{-}\overline{CHCHCH(CH_2)_n})(CO)_2(bipy)Br]$. Coupling reactions of these and other organic substrates with related molybdenum species are also briefly reported.

PART 2

The chemistry of metal-allyl complexes and the oxidative addition reactions of prop-2-ynylic halides

to transition metal centres are outlined in Chapters Five and Six respectively.

Complexes of stoichiometry $[Mo(C_5H_7O_2)(CO)_2(bipy)X]$ (X = Cl or Br), formed from $[PPh_4][Mo(CO)_3(bipy)X]$ and prop-2-ynyl halides by a methoxycarbonylation reaction, form the subject of Chapter Seven. Chemical and spectroscopic data are in accord with an η^3-oxacyclobutenyl formulation for the $C_5H_7O_2$ ligand in the initial halo-complexes, but on replacement of X by perfluoropropionate, perfluorobutyrate or pyridine, this ligand rearranges to a σ-bonded vinyl ester group, whose structural parameters in $[Mo(C_5H_7O_2)(CO)_2(bipy)(py)][BF_4]$ were determined by X-ray crystallography.

The reaction of $[PPh_4][Mo(CO)_3(bipy)Cl]$ with 1,4-dichlorobut-2-yne in aqueous alcohols ROH (R = Me or Et) gives high yields of $[Mo(\eta^3\text{-}CH_2\overset{\dots}{-}C(CO_2R)\overset{\dots}{-}C{=}CH_2)(CO)_2(bipy)Cl]$, whereas in anhydrous ROH/tetrahydrofuran, $[Mo(\eta^3\text{-}CH_2\overset{\dots}{-}C(CO_2R)\overset{\dots}{-}C(OR)(Me))(CO)_2(bipy)Cl]$ is formed as the major product. Crystal structure determinations reveal that the former complex (R=Me) contains an η^3-bonded <u>trans</u>-butadienyl group, whereas the latter (R = Me) contains an η^3-allyl ligand which can be formally derived from the ligated <u>trans</u>-butadienyl moiety by regio- and stereo- selective addition of ROH

across the non-coordinated double bond. The mechanistic implications of these reactions are presented.

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ABBREVIATIONS

Ac - Acetyl
Asym - Asymmetric
Bipy - $2,2'$-bipyridyl
Bz - Benzyl
Calc - Calculated
Cp - η^5-cyclopentadienyl
Cy - Cyclohexyl
d - Doublet
Diphos - 1,2-Bis(diphenylphosphino)ethane
DMSM - Dimethylsodiomalonate
DMSO - Dimethyl sulphoxide
en - Ethylenediamine
Et - Ethyl
h - hours
HCBD - Hexachlorobutadiene
INEPT - Insensitive Nuclei Enhancement by Polarization Transfer
I.R. - Infrared
kJ - Kilojoule
m (Infrared) - Medium
m (NMR) - Multiplet
Me - Methyl
M.O. - Molecular Orbital
NMR - Nuclear Magnetic Resonance
Nu - Nucleophile
OAc - Acetate

ABBREVIATIONS (CONT'D.)

pda	-	Pentan -2,4-dionate
Ph	-	Phenyl
py	-	Pyridine
q	-	Quartet
qd	-	Quartet of doublets
Rf	-	Retention factor
s (Infrared)	-	Strong
s (NMR)	-	Singlet
Symm	-	Symmetric
t	-	Triplet
THF	-	Tetrahydrofuran
TLC	-	Thin Layer Chromatography
TMS	-	Tetramethylsilane
w	-	Weak

ACKNOWLEDGEMENTS

The author would like to take this opportunity to express his sincere gratitude to Dr. Brian Brisdon and Dr. Dave Brown for their unflagging support and encouragement throughout the project and preparation of this manuscript. Many thanks, also, to the staff and technicians (especially Robert, Annabelle, Sheila, Brenda, Alan and Sue) in the School of Chemistry, without whom much of the work described in this thesis would not have been possible. The author also wishes to express his appreciation to Dr. Mike Drew and A.W. Johans of the University of Reading for the X-ray structural determinations, to the SERC 400 MHz high field NMR service at the University of Warwick and to the University of Bath for the studentship grant. Very special thanks to my sister, Mrs. Irene Robinson for her painstaking efforts in typing the thesis and to Rigby Office Equipment for the generous provision of a typewriter. Last, but not least, sincere thanks to Dave ("that'll never give a spectrum") Wood and Harry ("hand-drawn costs more") Hartell for the miracles performed in their subterranean grotto.

To my family who supported me
and my friends who tolerated me

PART I

Metal-mediated carbon-carbon bond formation: Molybdenum-mediated allylic alkylation, allylic coupling and benzylic coupling

CHAPTER ONE

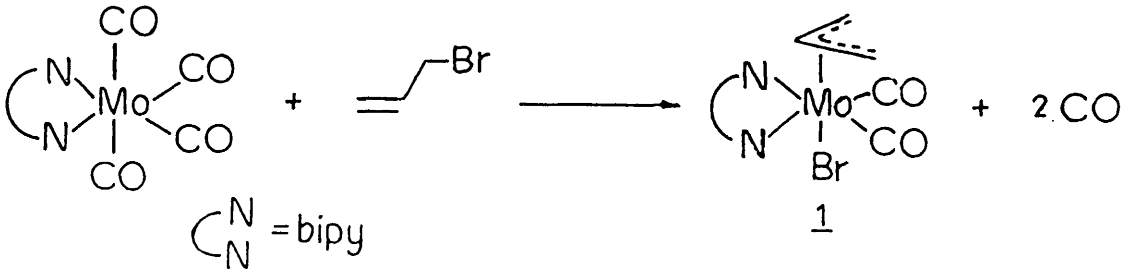
Introduction: Metal-mediated carbon-carbon bond formation

1.1. FOREWORD

The formation of new carbon-carbon bonds is of fundamental importance in organic chemistry. It is important that these new bonds are formed in the appropriate place and provide the required stereochemistry, and over the past three decades, the use of transition metal complexes to achieve stereo-, regio- and chemoselectivity has brought about a renaissance in synthetic organic chemistry[1a]. The "fine-tuning" of a metal complex by subtle changes to its associated ligands, to the reaction medium or to the conditions of the reaction, often has profound effects such that specific catalysts or stoichiometric reagents can be identified for specific systems.[1a,2a,2b]

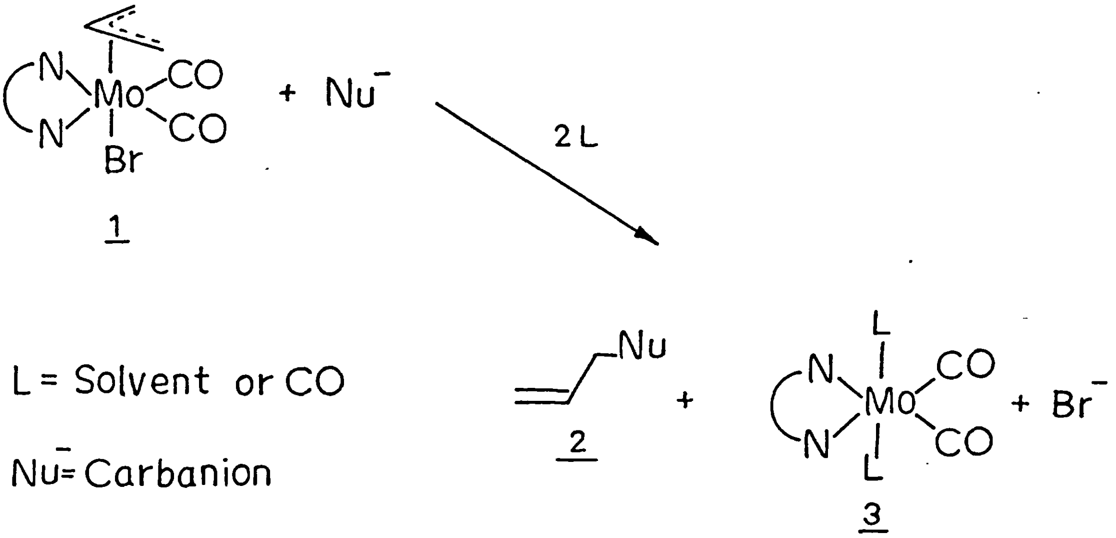
Simplistically, the transition metal centre may be considered to provide a reaction surface that imposes steric and electronic constraints on the reacting species. Important general properties of catalytic moieties include the ability to become coordinatively unsaturated and to reversibly change their formal oxidation states. In view of the subject of this thesis, these properties are well illustrated in Scheme 1.1, which represents the initiation step in a recently reported catalytic allylic alkylation reaction.[3]

Scheme 1.1



The η^3-allyl ligand bound to the intermediate (1) may then react with a carbanion to give the product (2) and regenerate the modified catalyst (3), (Scheme 1.2), which can then re-enter the catalytic cycle.

Scheme 1.2



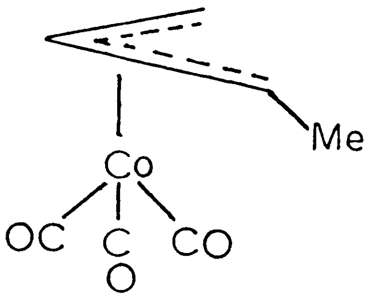
This reaction will be considered in more detail at a later stage in this thesis, the subject of which is primarily concerned with carbon-carbon bond formation arising from the interaction between unsaturated organic compounds such as allyl and propargyl(prop-2-ynyl) halides and molybdenum carbonyl complexes. Thus, the central feature of the author's research described herein is concerned with processes that involve, or may involve η^3-allyl complexes resulting from the oxidative addition of these unsaturated moieties to molybdenum centres.

The oxidative addition of benzyl halides to nickel tetracarbonyl has been reported[2b] and a short account of their behaviour with $Mo(CO)_4$bipy will also be given.

The following introduction outlines the role of the two metals that have dominated π-allyl chemistry in organic synthesis over the past three decades or so: nickel[4] and palladium.[5] More recently, tungsten and molybdenum complexes have been utilized and their contribution to organic synthesis will also be evaluated.

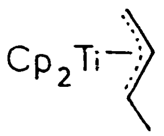
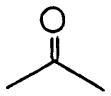
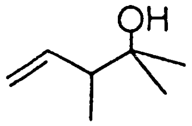
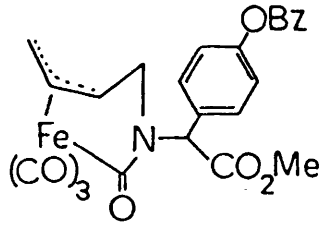
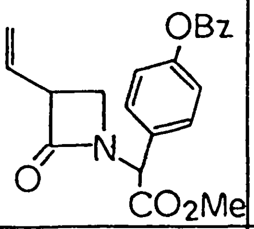
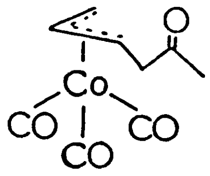
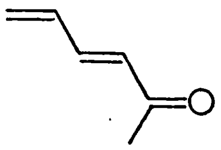
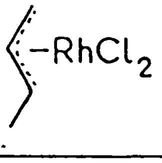
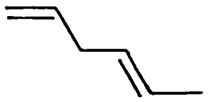
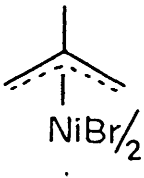
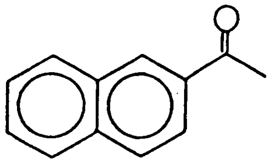
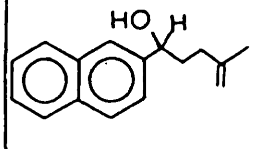
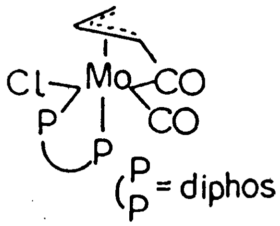
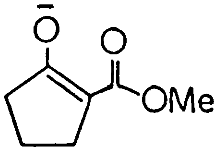
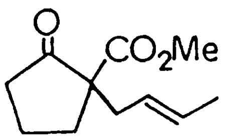
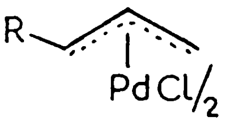
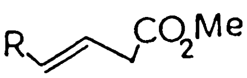
1.2. η^3-ALLYL COMPLEXES IN ORGANIC SYNTHESIS

Transition metal complexes containing a planar three-carbon atom ligand, the η^3-allyl group, were first reported in 1958 with the discovery of $(\eta^3\text{-1-MeC}_3H_4)Co(CO)_3$.[6]



Within the next few years, many more examples were prepared[7a] and their potential as synthetic reagents and reactive intermediates realised. Table 1.1. indicates some of the useful transition metal η^3-allyl complexes that have been used in organic synthesis and the types of reaction they undergo.[3-5,7b-7f]

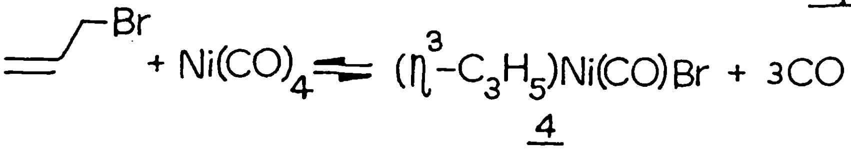
TABLE 1.1. SOME EXAMPLES OF CARBON-CARBON BOND FORMATION REACTIONS VIA TRANSITION METAL ALLYL COMPLEXES

ALLYL-COMPLEX	REACTANT	PRODUCT	REF.
			7b 7c
	Ce^{IV}		7d
	Base		7e
	$CH_2{=}CH_2$		7f
			4
			3
	CO, MeOH		5

1.3. η^3-ALLYL COMPLEXES AS INTERMEDIATES IN NICKEL-MEDIATED CARBON-CARBON BOND FORMATION

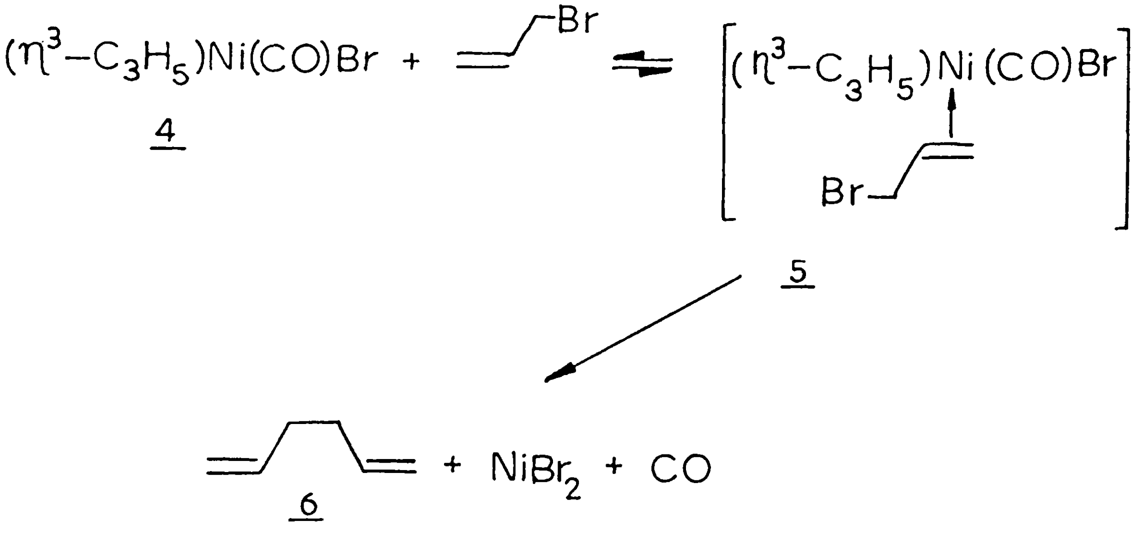
The reaction of nickel tetracarbonyl with allyl halides does not yield a metal-allyl complex but rather coupled organic products as noted over forty years ago by Farbenid.[8] However, the understanding of the mechanism of this reaction is more recent and is largely due to E.J. Corey et al.[9] The first step involves the formation of a nickel η^3-allyl complex (Eq.1.1)

Eq. 1.1

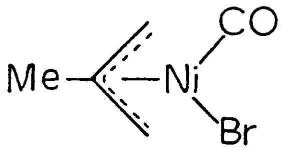


The η^3-allyl complex (4) then reacts with a further molecule of the allyl bromide to form the intermediate (5) which then decomposes to liberate the coupled product (6)(Eq.1.2).

Eq. 1.2



Spectroscopic and other evidence has been provided to support such a mechanism. Thus, complex (7) has been detected by NMR methods[9] and the stable derivative (8) has been studied.[10,11]



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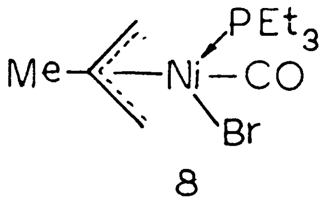

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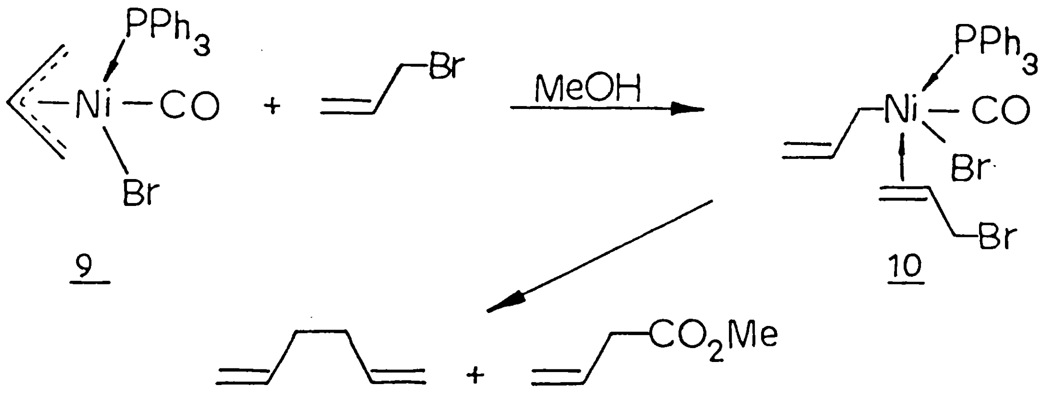
The nature of the bonding of the organic ligands in the intermediate (5) is not completely certain and is probably dependent upon the polarity of the solvent. However, (9) reacts with allyl bromide[12] in methanol to give 1,5-hexadiene and methyl but-3-enoate which is consistent with conversion of the η^3-bonded allyl ligand to an η^1-bonded ligand, followed by either coupling or methoxycarbonylation (Scheme 1.3).

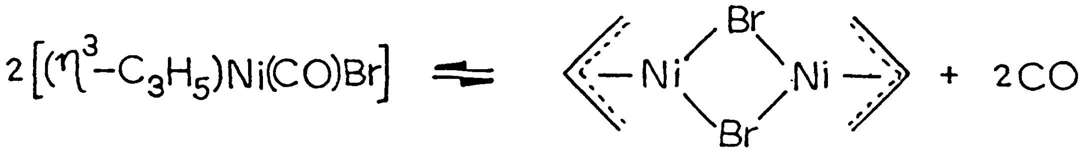
Scheme 1.3



Complex (9) has an 18-electron configuration in which the η^3-allyl ligand can be formally considered as a four-electron donor anion. In order for reaction to take place, its mode of bonding can change to η^1-allyl (which can be formally considered as a two-electron donor anion), and the vacant electron-pair site can then be filled by the two electrons in the π-bond of the attacking allyl bromide moiety, so generating the unstable 18-electron complex (10) which then decomposes to liberate the products.

An alternative mechanism is possible in view of the known reactivity of the intermediate η^3-allyl species (4). This undergoes loss of CO to form the well known dimer $Ni_2Br_2(\eta^3\text{-allyl})_2$[13] (11),(Eq. 1.3), which in turn has been shown to exist in equilibrium with bis(η^3-allyl)nickel (12), (Eq. 1.4).[14,15]

Eq. 1.3



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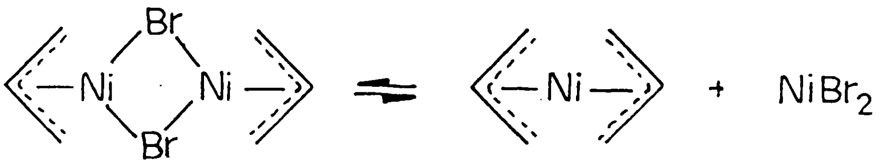
Eq. 1.4



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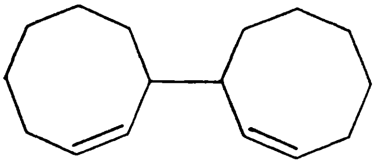
12

Complex (12) is known to react with CO to yield 1,5-hexadiene and nickel tetracarbonyl.[16] However, the reaction between $Ni(CO)_4$ and 3-bromocyclooctene cannot proceed exclusively through a bis(η^3-allyl)nickel intermediate as only 3,3'-bicyclooctenyl (13) is formed whereas the reaction of bis(η^3-cyclooctenyl)nickel with CO gives a 1:1 mixture of (13) and the CO inserted product (14).[9]



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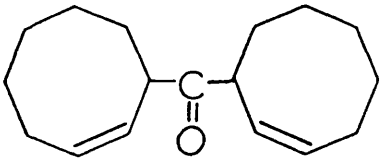

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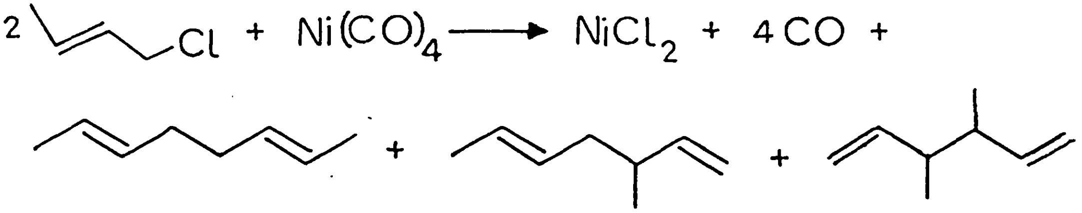
The regioselectivity of the products from nickel assisted coupling reactions is very often non-specific and can be temperature dependent.[13] Crotyl (but-2-enyl) chloride for example reacts with nickel tetracarbonyl at room temperature to produce 2,6-octadiene (15) (58%), 3-methy-1,5-heptadiene (16) (38%) and traces of 3,4-dimethyl-1,5-hexadiene (17) (Eq. 1.5).

Eq. 1.5

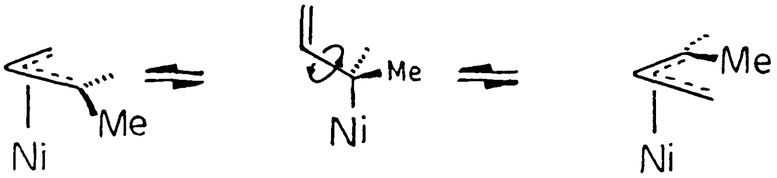


15 16 17

The reaction of bis(η^3-crotyl)nickel with CO gives identical results, but at lower temperatures (-40°C) this reaction yields trans,trans-2,6-octadiene as the major product.

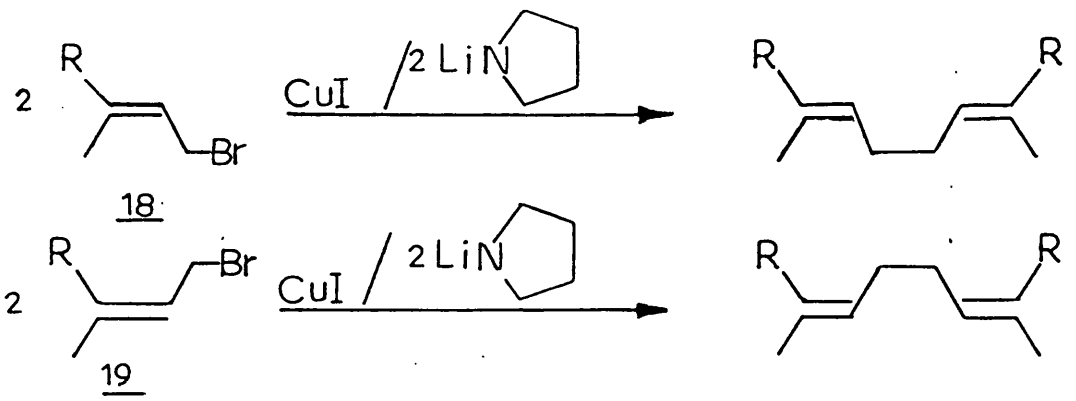
Loss of retention of stereochemistry of cis or trans allyl halides may be explained by a 1,3-rearrangement through an η^1-allyl intermediate[17] (Scheme 1.4.)

Scheme 1.4



Copper-based systems have been used for direct conversion of allylic halides to 1,5-dienes with preservation of stereochemistry.[18,19] Treatment of the bromides (18) and (19) with the complex formed between cuprous iodide and lithium pyrolidide results in the formation of linearly coupled products with retention of stereochemistry (Scheme 1.5).

Scheme 1.5



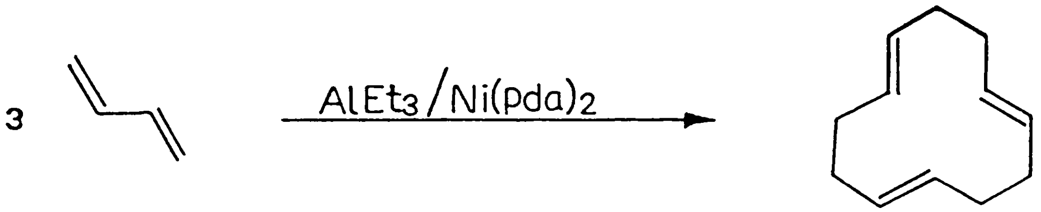
Neither the exact nature of the metallo-intermediate nor the mechanism has been specified, although from the 2:1 ratio of lithium pyrolidide to cuprous iodide used in most of the reactions, the copper complex may have the same stoichiometry as a lithium organocuprate. The same copper system has been used to prepare squalene in a 50% yield from (E,E)-farnesyl bromide.

1.4. NICKEL-MEDIATED CYCLIC OLIGOMERISATION OF CONJUGATED DIENES

Nickel catalysed reductive coupling of conjugated dienes has played an important role in a series of reactions that produce a variety of cyclic oligomers.[20] η^3-Allyl species are believed to be the reactive intermediates responsible for these reactions.

A catalyst prepared from nickel pentan -2,4-dionate (pda) and triethylaluminium will cyclotrimerise 1,3-butadiene to 1,5,9-cyclododecatriene (20) in high yield (Eq.1.6). [21,22] In the presence of phosphorus donor ligands, 1,3-butadiene can be cyclodimerised to any of three products: 1,2-divinylcyclobutane[23] (21), 4-vinylcyclohexene[22] (22), or 1,5-cyclooctadiene[22] (23)(Eq.1.6a.) The product distribution is dependent on the contact time with the catalyst (1,2-divinylcyclobutane catalytically rearranges to 1,5-cyclooctadiene) and the steric and electronic properties of the phosphorus ligand. [24]

Eq. 1.6



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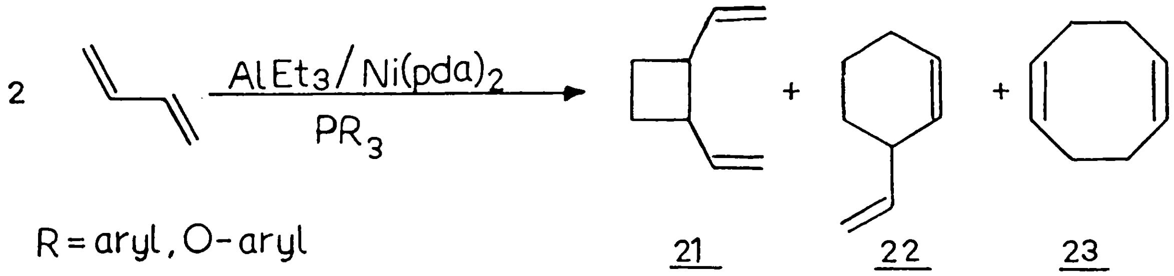
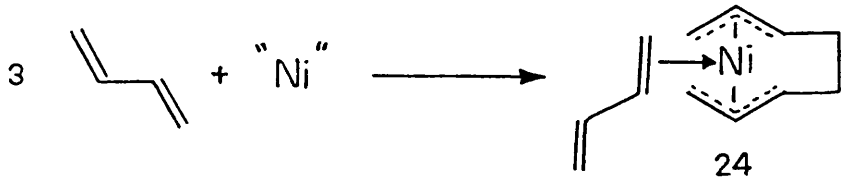
Eq. 1.6a



Any of the three isomers can be obtained in high yield with the correct choice of reaction conditions.

The nickel catalyst which has been termed "naked nickel" owing to it's ability to associate with weakly coordinating ligands such as olefins, is probably a nickel alkyl species.[21] It coordinates with two molecules of 1,3-butadiene, and the ends of the diene units couple to produce a C_8 bis-allyl ligand.[25] A further molecule of 1,3-butadiene is probably coordinated to achieve an 18-electron configuration for nickel (Eq. 1.7).

Eq. 1.7



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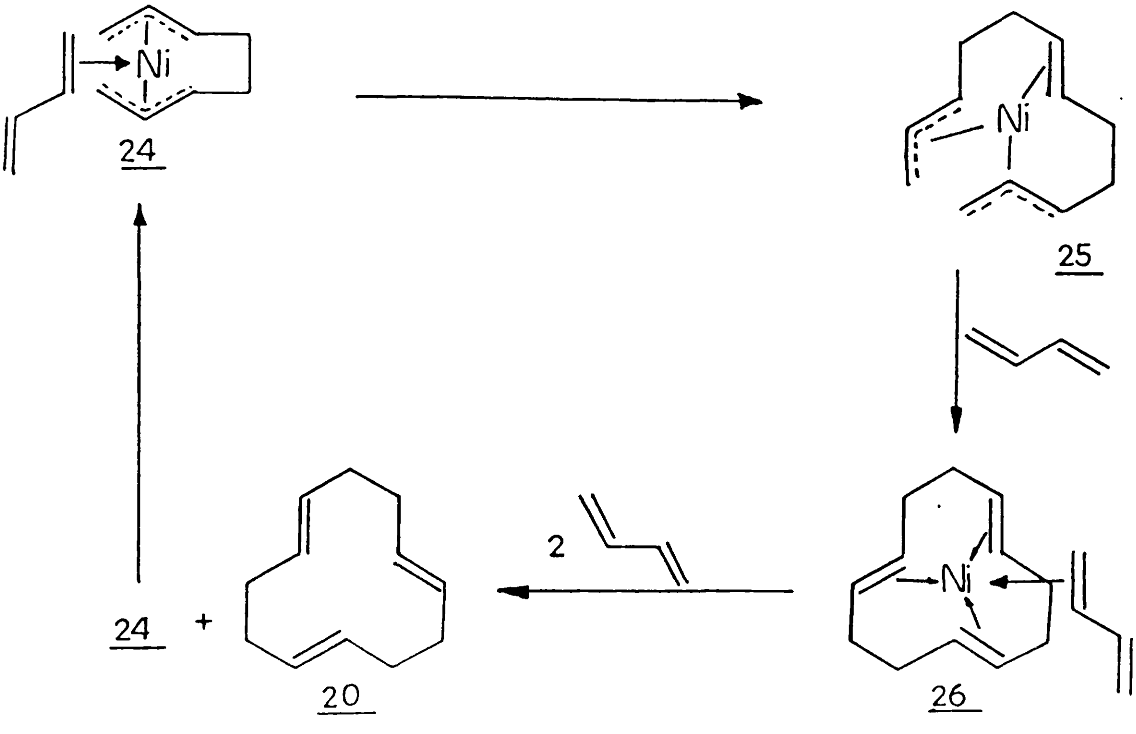
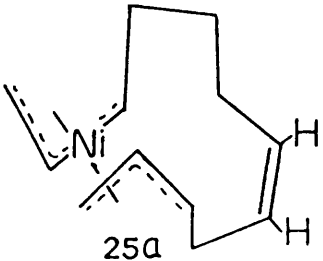
The 1,3-butadiene in complex (24) couples with the bis-allyl moiety to form a linear C_{12} ligand (25)[21,26] and uptake of a further molecule of 1,3-butadiene causes ring closure to 1,5,9-cyclododecatriene (26). Addition of further 1,3-butadiene displaces (20) and regenerates the catalytic cycle (Scheme 1.6).

Scheme 1.6

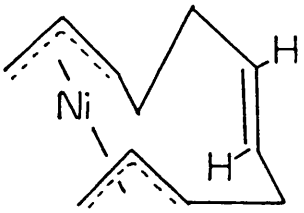


The complex (25) has been implicated by spectral and chemical characterisation.[26] For example, hydrogenation of a solution expected to contain (25) affords n-dodecane in high yield. The species (26) is easier to handle and has been studied in detail.[27]

Of the four possible geometrical isomers of 1,5,9-cyclododecatriene, three are formed. The all-cis isomer does not appear under any conditions. The distribution of the other three isomers is dependent on reaction conditions and can be directed mainly to all-trans-1,5,9-cyclododecatriene by addition of pyridine. It has been suggested that pyridine affects the configuration of the allyl ligand in (24) and (25)[28], and NMR spectroscopy indicates that two configurations of (25) are important,[13] (25a) and (25b).



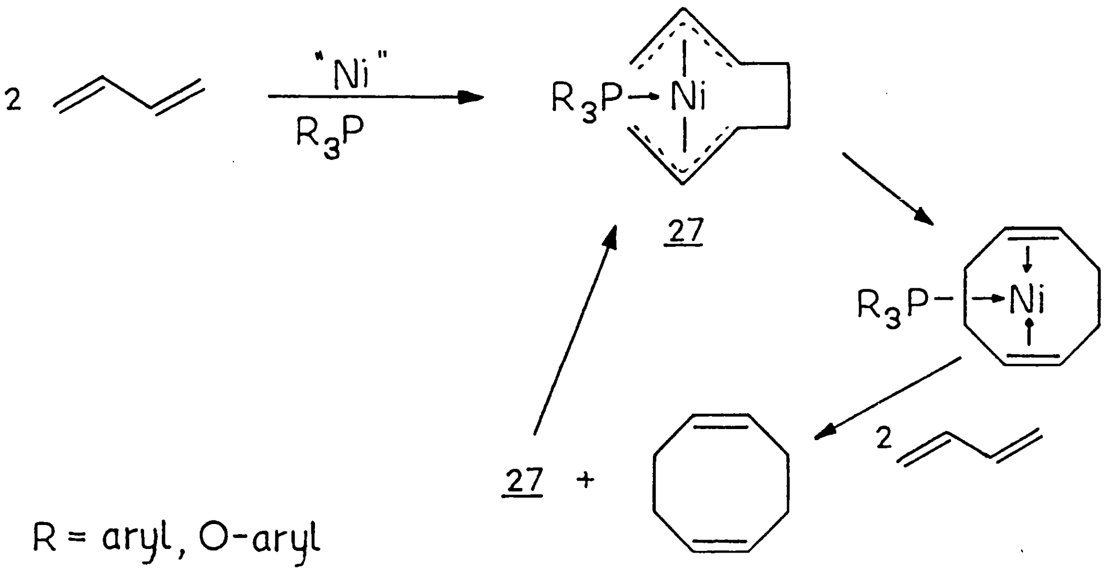
25a



25b

In the presence of phosphines or phosphites, the intermediate (24) is converted to (27), and now the tightly bound phosphorus ligand blocks one coordination site so that no additional diene can coordinate unless the bis-allyl ligand reacts to coordinatively unsaturate the catalyst. Thus, the eight-carbon ligand is converted into 1,5-cyclooctadiene which is displaced from the resulting 16-electron complex by further molecules of 1,3-butadiene to regenerate (27) (Scheme 1.7).[23]

Scheme 1.7



It has been shown from Eq. 1.6a that other C_8H_{12} isomers are also produced.[23] In the presence of triphenylphosphine, 4-vinylcyclohexene is obtained in up to 27% yield, [21] whereas the presence of tri(2-biphenylyl)phosphite gives 1,5-cyclooctadiene yields in excess of 96%.

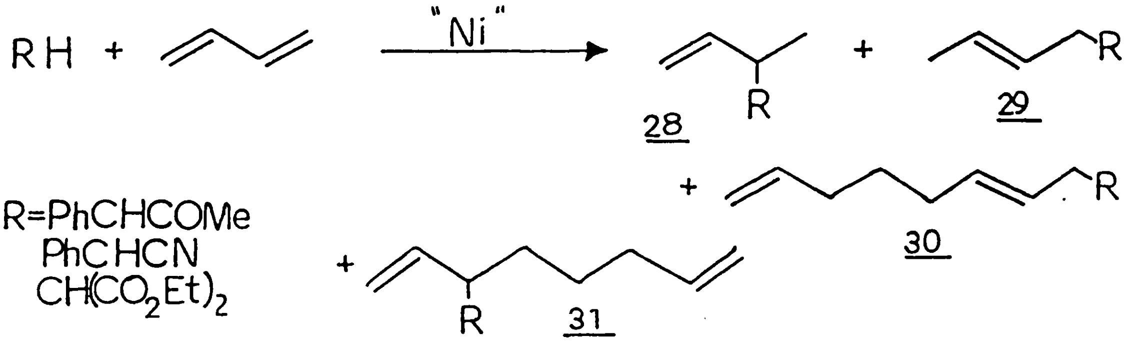
1.5 η^3-ALLYL SPECIES AS REACTIVE INTERMEDIATES IN ALKYLATION REACTIONS OF 1,3-DIENES WITH ACTIVE METHYLENE COMPOUNDS

Nickel and palladium complexes have been used to catalyse the reactions of 1,3-butadiene with alcohols,[29,30] water,[31] amines,[29,30,32] carboxylic acids[29,30,33] and active methylene compounds.[32,24] The products so-formed bear functionalities that may be utilised for further elaboration.

The reaction products from 1,3-butadiene and the active methylene compounds, RH, are shown in Scheme 1.8.[35] The reactions are carried out in the presence of nickel(II) salts, di-isopropoxyphenylphosphine and a co-catalyst such as sodium phenoxide.[36] The role of this co-catalyst[37] is intriguing and still not fully understood.

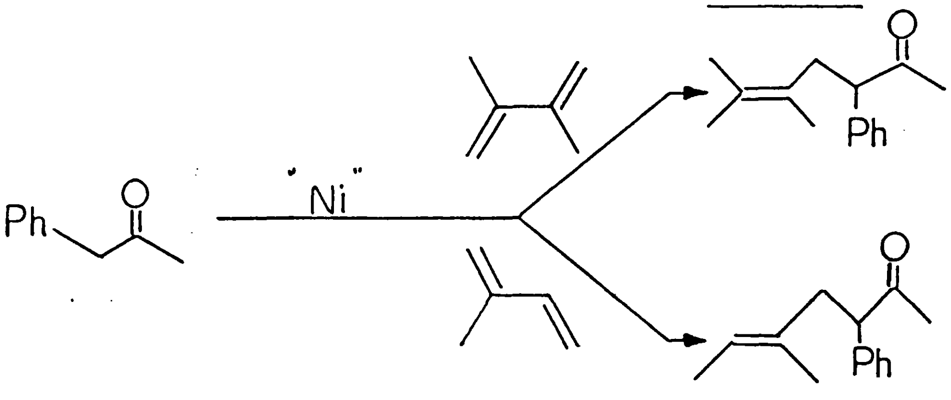
It has been demonstrated that added base assists the reduction of metal species[38] and Ni(O) complexes are thought to be involved in the catalytic cycle.[39] The base would also aid deprotonation of the active methylene compound.

Scheme 8



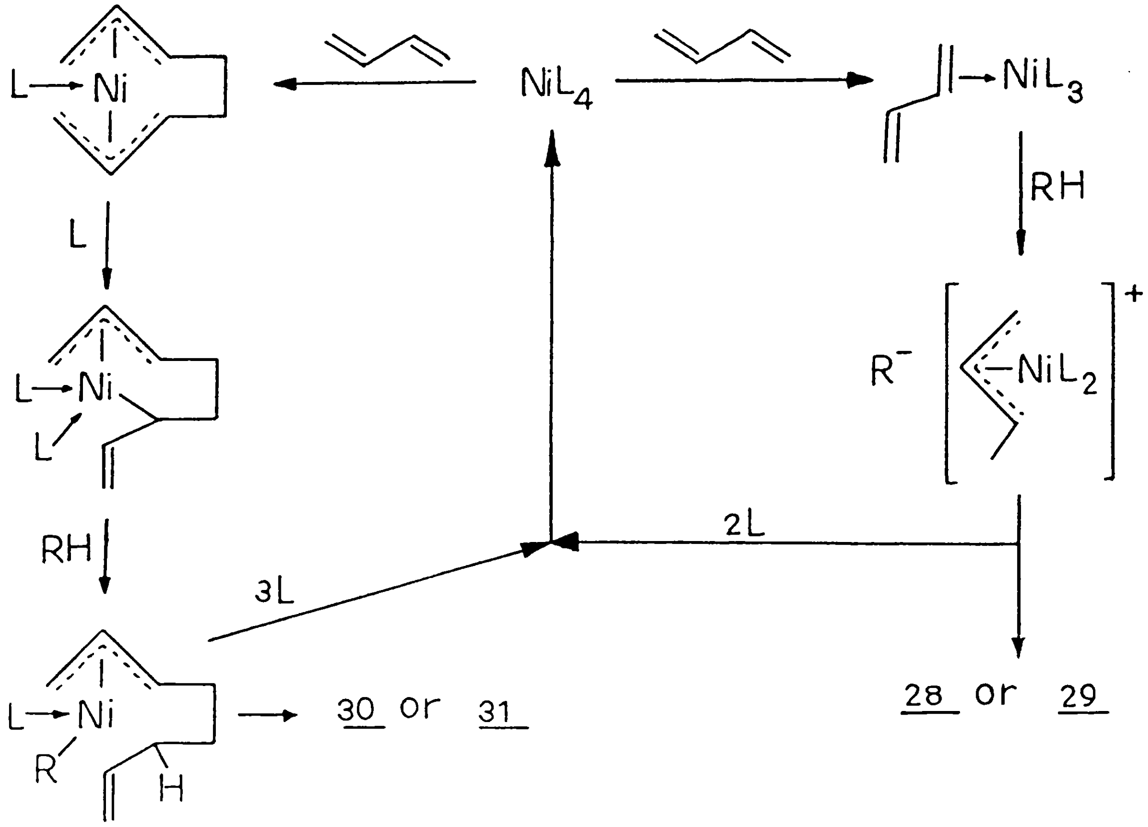
The 2:1 compound (31) is the predominant product of the above reaction and variation in the relative concentrations of the reactive participants can maximise the yield. When substituted dienes are used (isoprene or 2,3-dimethylbutadiene) the 1:1 compound predominates[35] (Scheme 9).

Scheme 9



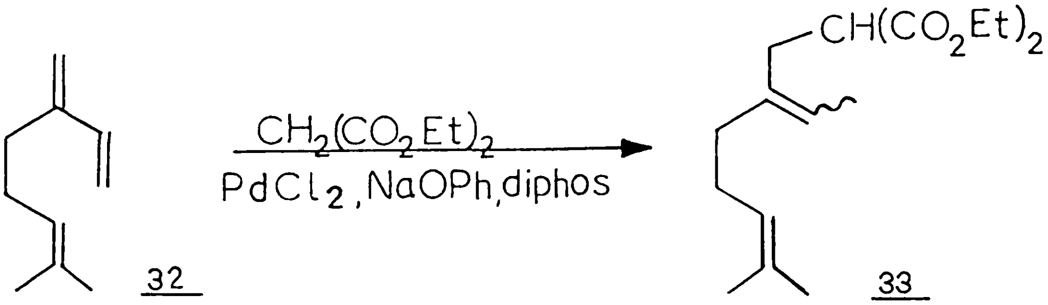
The mechanism by which the 2:1 and 1:1 products are formed is believed to proceed via competing processes involving η^3-allyl and bis(η^3-allyl) moieties. The preformed tetrakis(dialkoxyphenylphosphine)nickel(0) complex resulting from reduction of either nickel(II) halide or nickel(II)(pda)$_2$ can react with the diene by two pathways as shown in Scheme 1.10.

Scheme 1.10



The use of these reactions in natural product chemistry has been explored with emphasis on terpenoid compounds.[40a,40b,41] Myrcene (32) reacts with diethyl malonate in the presence of 1,2-bis(diphenylphosphino)-ethane (diphos) and palladium(II) chloride under basic conditions to give the 1:1 product (33) as a mixture of cis and trans isomers in 52% yield (Eq.1.8), although correct choice of phosphine ligand is necessary to avoid the formation of myrcene dimers.[41]

Eq. 1.8



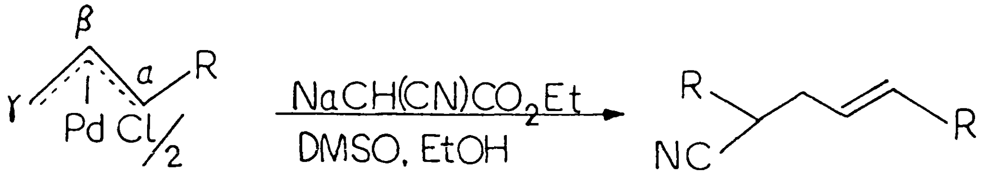
1.6. η^3-ALLYL-PALLADIUM COMPLEXES IN ORGANIC SYNTHESIS

Stoichiometric Reactions

In synthetic terms, η^3-allyl-nickel and palladium complexes are complementary to a degree, since η^3-allyl-nickel complexes tend to react with electron-poor centres (electrophiles) and η^3-allyl-palladium complexes tend to react with electron-rich centres(nucleophiles).[4] Palladium-mediated carbon-carbon bond formation via preformed or transient η^3-allyl-palladium complexes has truely found it's place in synthetic organic chemistry, and a wealth of reactions are known.[5]

Bis(η^3-allyl) palladium chloride reacts with various carbanions including those that are resonance-stabilised, derived from active methylene compounds such as ethyl acetoacetate.[42] However, this direct carbanionic addition to η^3-allyl-palladium dimers fails with any but the unsubstituted parent η^3-allyl complex or with complexes bearing strong electron withdrawing groups such as a carbonyl moiety.[43] Nucelophilic addition to this latter substrate occurs exclusively at the γ-position, thus permitting a regioselective γ-alkylation of α,β-unsaturated carbonyl systems (Eq. 1.9).[44,45,46]

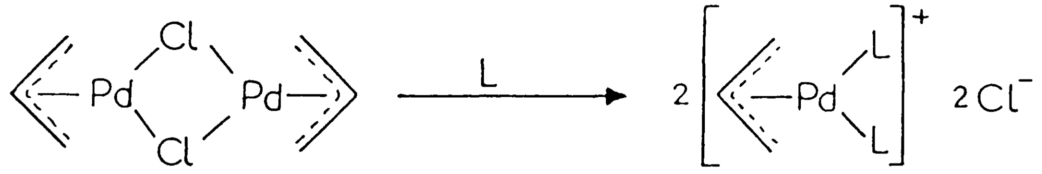
Eq. 1.9



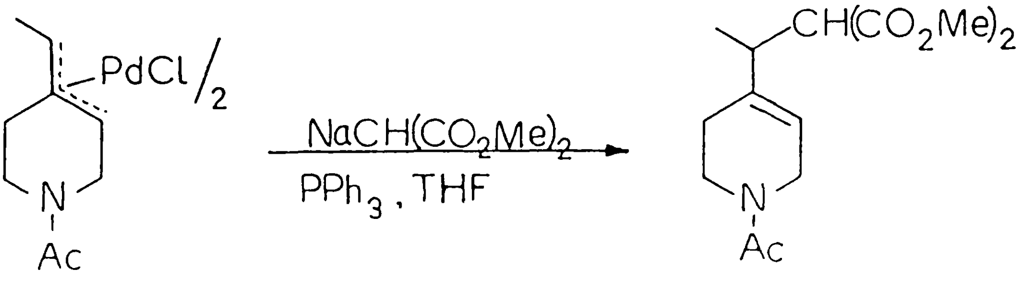
$R = CO_2Et$

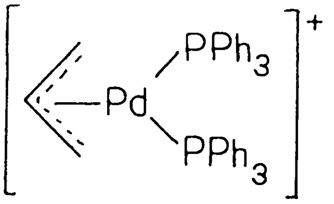
The apparent limited generality of this alkylation methodology is remedied by enhancing the electrophilic character of the η^3-allyl-palladium complex through dissociation of the relatively non-electrophilic η^3-allyl-palladium dimer (Eq.1.10) While coordinating solvents such as dimethyl sulphoxide (DMSO) may serve as ligands,[47,48] activation with phosphines, phosphites or phosphorus triamides in ethereal solution expand the generality of this reaction[49-56b] (Eq.1.11.) Cationic complexes such as (34) are likely intermediates since the optimum stoichiometry for activation is two phosphorus per palladium.[5]

Eq. 1.10



Eq. 1.11

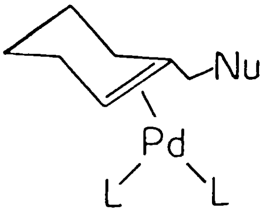




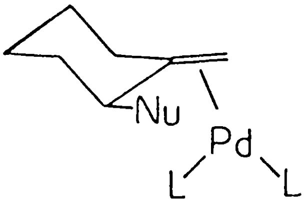
34

The nature of the activating ligand determines the range of nucleophiles which may be utilised. With most resonance-stabilised carbanions, triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (diphos) may be employed. With harder nucleophiles, like those derived from benzenethioacetone or methyl benzenethioacetate, hexamethylphosphoroustriamide is preferred. With even harder nucleophiles such as Grignard reagents, irreversible addition to palladium causes complications.[1b]

With soft carbanions, the regiochemistry of alkylation depends on both the steric environment of the allyl moiety as well as the activating ligand. This dual dependance is understandable in terms of two competing effects - steric approach of the nucleophile favouring attack at the less hindered terminus of the allyl unit, and the relative stability of the initially formed alkene complexes (e.g. 35 and 36), with complexation at the sterically hindered alkene being disfavoured.



35

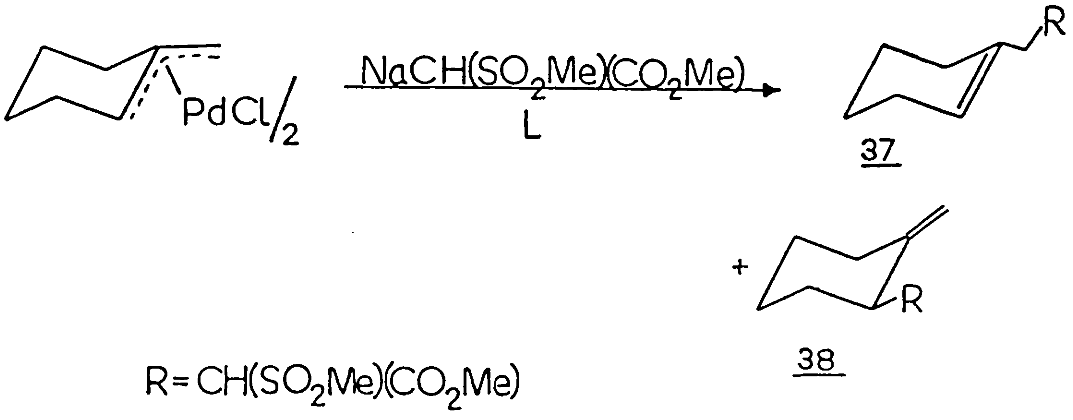


36

In most cases, the first effect is dominant and attack takes place at the less hindered end of the allyl ligand.

However, in the case of six-membered rings, where alkene complexation in complex (35) is highly disfavoured relative to (36),[57] the choice of ligand becomes crucial for determination of regioselectivity. Sterically bulky ligands, e.g. tri-o-tolylphosphine (TOT), which magnify this stability difference, induce increased substitution at the more hindered cyclic position[53,55] (Eq. 1.12).

Eq. 1.12



Ligand, L	Yield (%)	Ratio (37:38)
HMPA	90	100:0
TPP	75	62:38
TOT	79-90	15:85

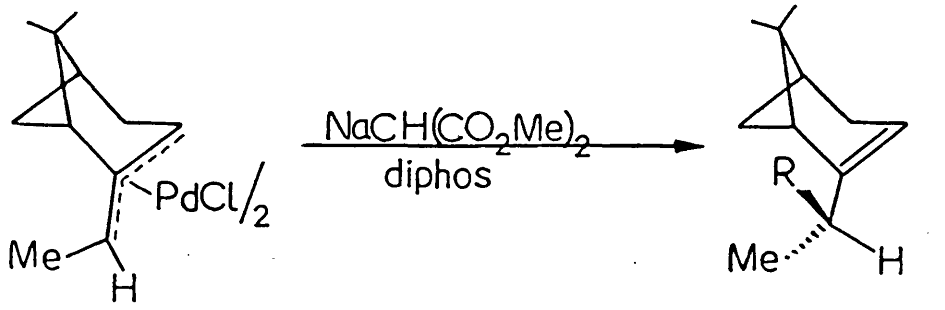
HMPA = Hexamethylphosphoroustriamide

TPP = Triphenylphosphine

TOT = Tri-o-tolylphosphine

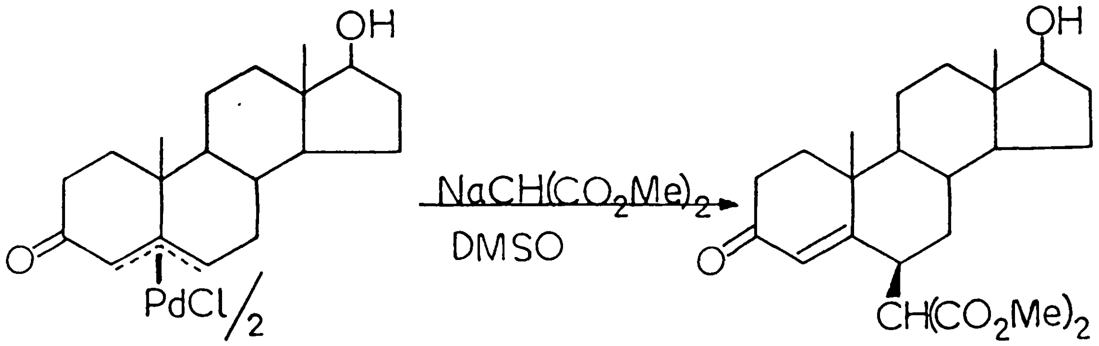
Strong stereochemical control is an important feature of this carbon-carbon bond forming reaction and is dependent on the nucleophile. With soft anions, attack occurs directly at carbon on the face of the allyl unit opposite to palladium (Eq. 1.13 and 1.14)[44,55,58]

Eq. 1.13

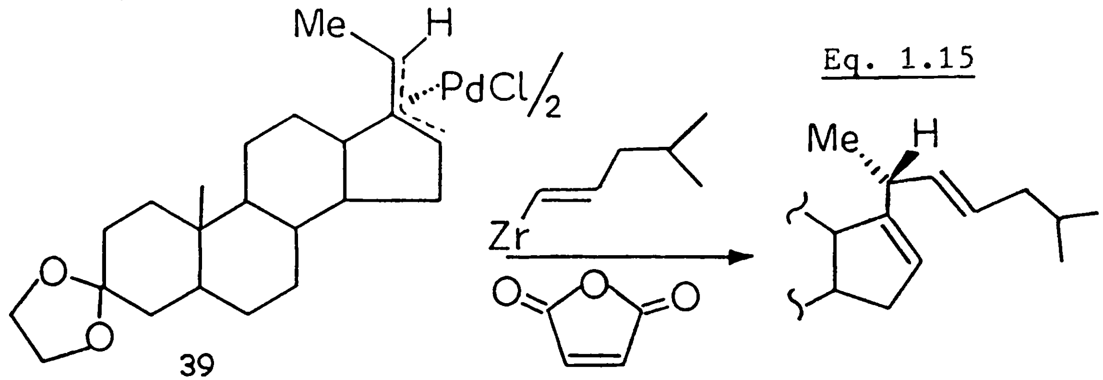


R= $CH(CO_2Me)_2$

Eq. 1.14



Hard anions attack initially at palladium and are subsequently transferred to the allyl ligand from the same side as the palladium atom, i.e. below the "deck", and thus offer complementary stereochemical control. Treatment of the steroid complex (39) with an alkylzirconium species in the presence of maleic anhydride effects a stereospecific alkylation that produces the more common natural 20(R) configuration, opposite to that obtained by alkylation with soft nucleophiles (Eq.1.15)[59]



Eq. 1.15

39

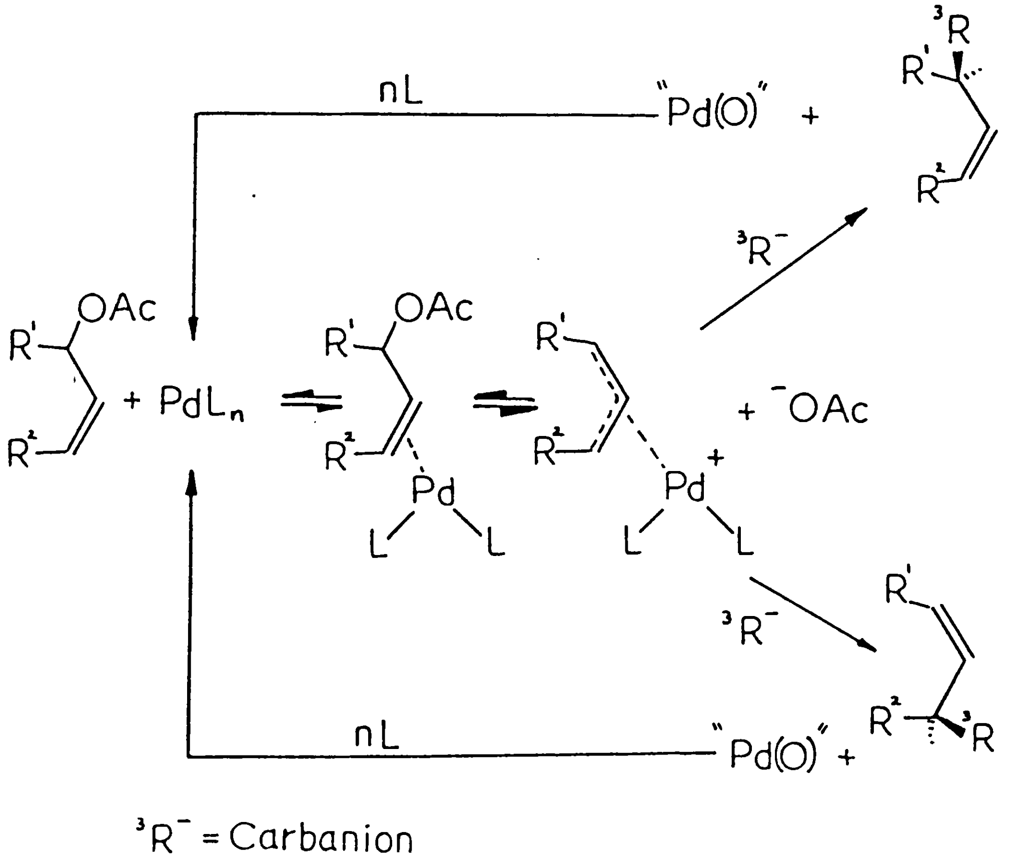
These reactions demonstrate the great regio- and stereoselectivity available from allylic alkylations via η^3-allyl-palladium complexes. While such reactions require stoichiometric amounts of the palladium moieties, ease of recycling of the spent palladium allows such methods to be economically viable for organic synthesis,[1c] although a catalytic process would further enhance the synthetic utility of these reactions.

Catalytic Reactions

Palladium(0) complexes can react with allylically oxidised compounds to afford η^3-allyl-palladium species. These η^3-allyl complexes (generated *in situ*) are then capable of reacting with carbanions in the afforesaid manner and regenerating palladium(0) species for further reaction. Thus, a catalytic cycle is possible (Scheme 1.11).

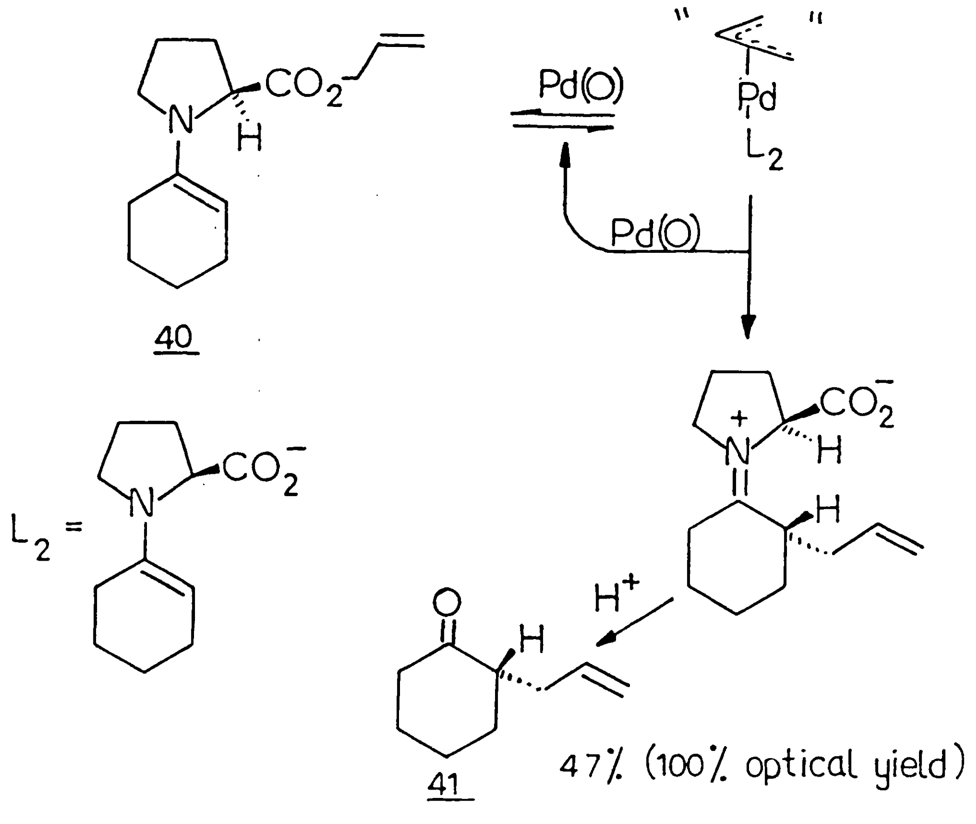
The catalytic cycle begins with an initial activation of the catalyst whereby it becomes coordinatively unsaturated. The high electron density on palladium then initiates disengagement of the leaving group of the allylically oxidised compound to form the η^3-allyl cationic intermediate and the ability to use leaving groups such as acetate,[60-63] sulphones[64] and epoxides[65] allows for considerable versatility. Attack of the carbanion normally takes place on the face of the allyl ligand opposite palladium as with the preformed η^3-allyl complexes. The choice of attack at the two termini of the allyl unit depends on the nature of the nucleophile, the nature of the substitution around the η^3-allyl unit and the nature of the ligands on palladium. Typical catalysts include $Pd(PPh_3)_4$[62] and $Pd(diphos)_2$.[1d]

Scheme 1.11



Recently, much attention has been given to stereoselective synthesis using palladium catalysed allylations,[61,66] the source of the chirality being chiral phosphines,[67] chiral allylic sulphinates[68] and chiral allylic complexes.[69] Very recently,[70] chiral allyl esters under suitable conditions have been used to effect intramolecular allylations in up to 100% optical yield (Scheme 1.12). Enamine (40) reacts with the palladium catalyst to generate the intermediate η^3-allyl complex, and presumably the coordination of the chiral carboxylate leaving group induces a chiral environment about palladium that effects stereospecific allylation. Acid hydrolysis of the reaction mixture affords the chiral ketone (41) in 100% optical yield.

Scheme 1.12

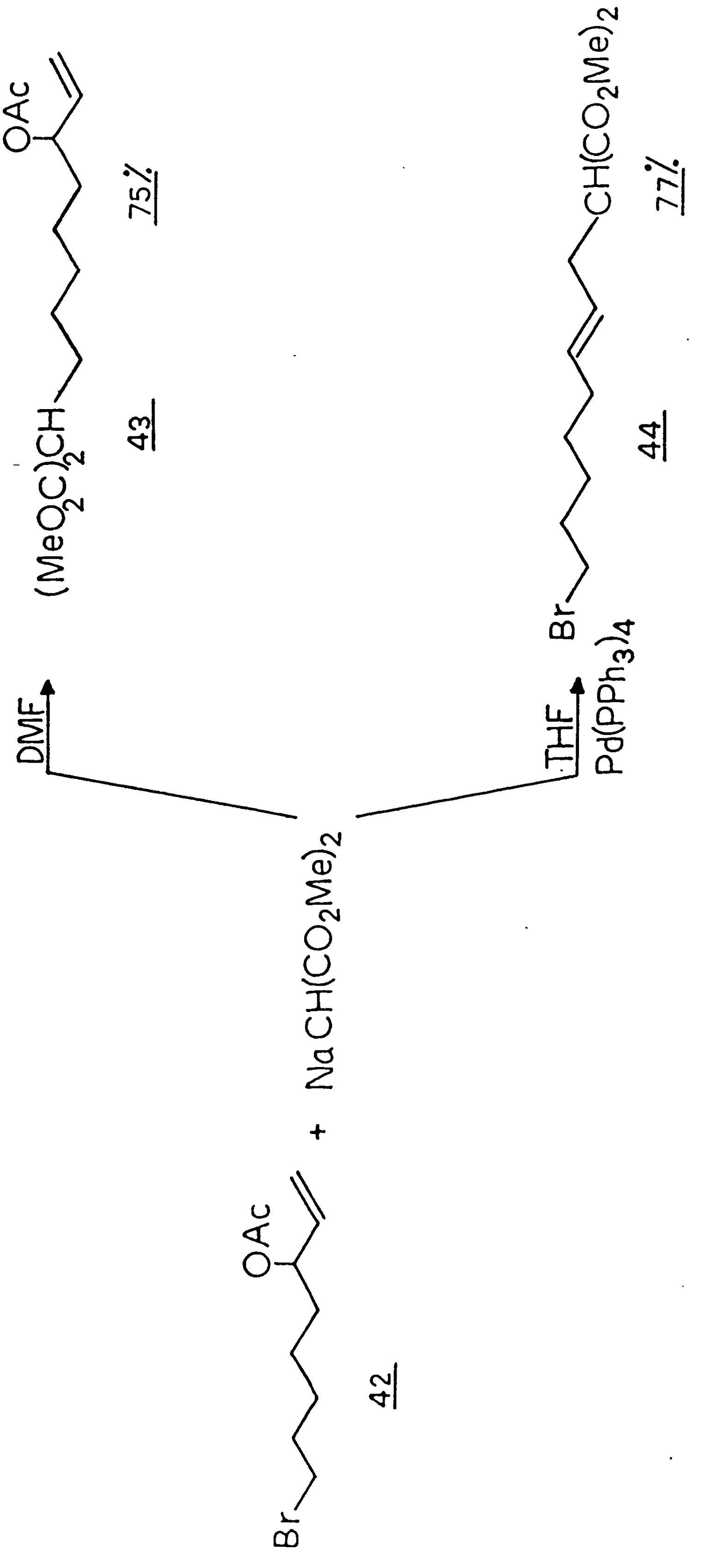


This method represents a significant step forward from previous racemic preparations via allylic carbonates[71] and β-keto-allylcarboxylates.[72]

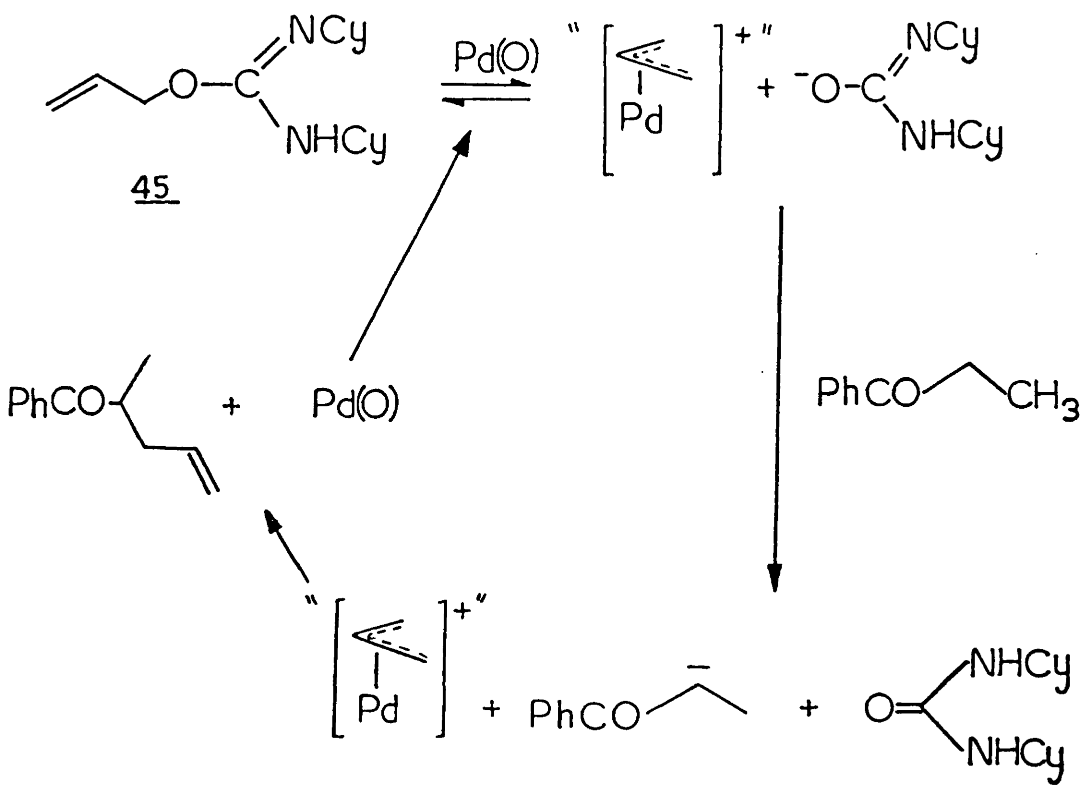
In addition to the regio- and stereoselectivity associated with stoichiometric reactions, the chemoselectivity can be totally altered in catalytic reactions. For example, the bromoacetate (42) exhibits the normal higher reactivity of the alkyl bromide to give the expected alkylated product (43) in DMF (Scheme 1.13). However, the intrinsic reactivity of the alkyl bromide and allyl acetate groups reverses upon the use of a palladium catalyst in THF to give (44) as the major product.[73] No product arising from displacement of bromide is observed.

Metal enolate carbanions tend not to undergo palladium-assisted allylations readily,[61] although several improvements have been made including the change of the palladium catalyst[74] and metal enolates used.[75] The first example of direct α-allylation of a ketone under neutral conditions (i.e. without the necessity to preform the conjugate base) with a palladium(0) catalyst was recently announced[76] and an extension of this method for a variety of ketones and aldehydes has just been published.[77] The method makes use of 2-allyl-1,3-dicyclohexylisourea (45) which on activation with the palladium catalyst, generates a conjugate base capable of deprotonating the α-hydrogen atom of the carbonyl compound (Scheme 1.14).

Scheme 1.13


42
OAc
Br
+
NaCH(CO$_2$Me)$_2$
DMF
THF
Pd(PPh$_3$)$_4$
43
(MeO$_2$C)$_2$CH
OAc
75%
44
Br
CH(CO$_2$Me)$_2$
77%

Scheme 1.14



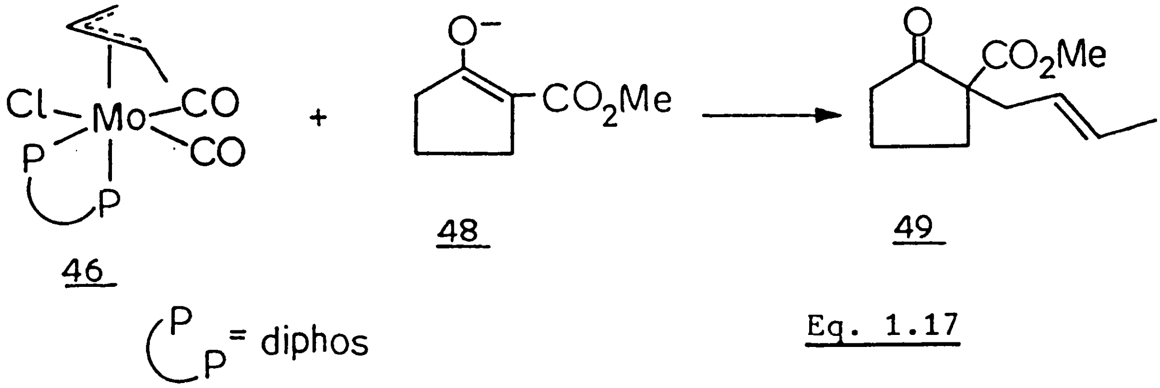
Allylic carbonates have also been shown to be effective allylating reagents under neutral conditions in the presence of transition metal catalysts.[78]

1.7. MOLYBDENUM CATALYSED ALLYLIC ALKYLATION REACTIONS

In view of the information regarding nucleophilic attack on η^3-allyl-molybdenum complexes,[79-82] the high coordination number and the moderate cost of the metal, Trost turned his attention to molybdenum complexes for allylic alkylations about four years ago.[3]

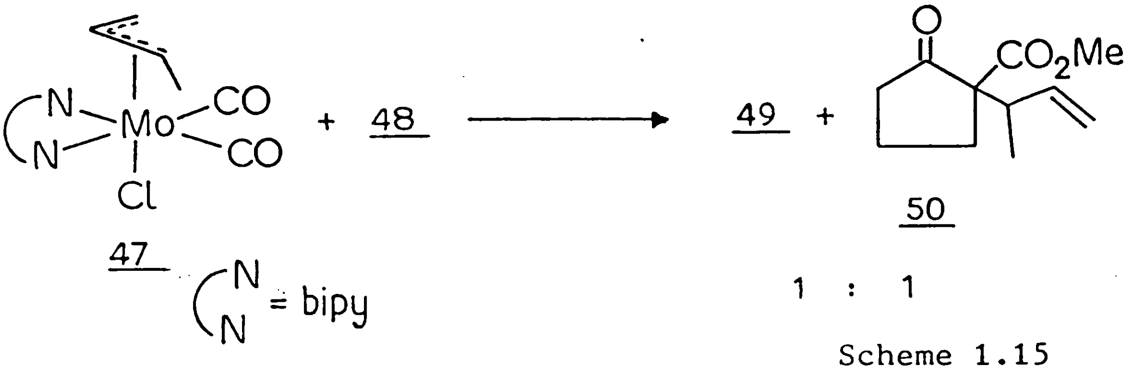
The complexes (46) and (47) react smoothly with the nucleophile (48) in THF to afford (49) and (50) (Eq.1.16 and 1.17).[3] This, together with the knowledge that several molybdenum(0) carbonyl species undergo oxidative addition with allyl halides and acetates to yield η^3-allyl-molybdenum compounds[83,84,85] led to a catalytic process (Scheme 1.15).

Eq. 1.16



46 48 49

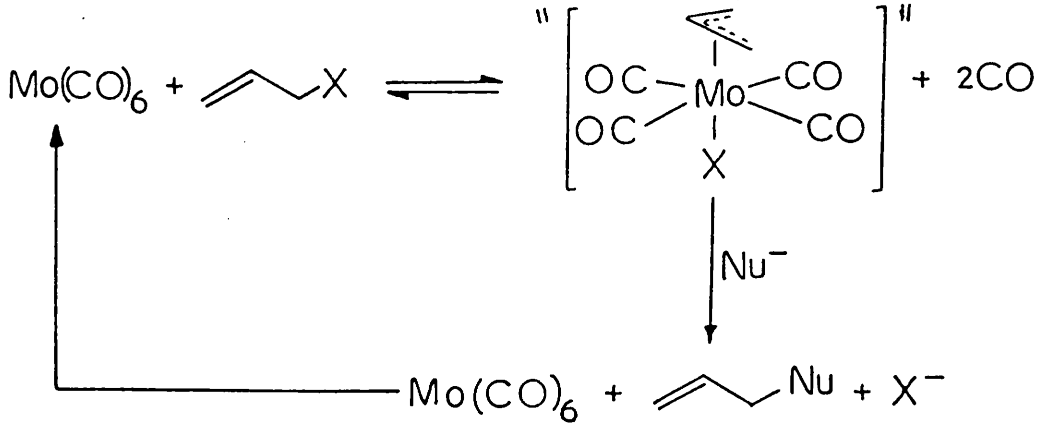
Eq. 1.17



47 50

1 : 1

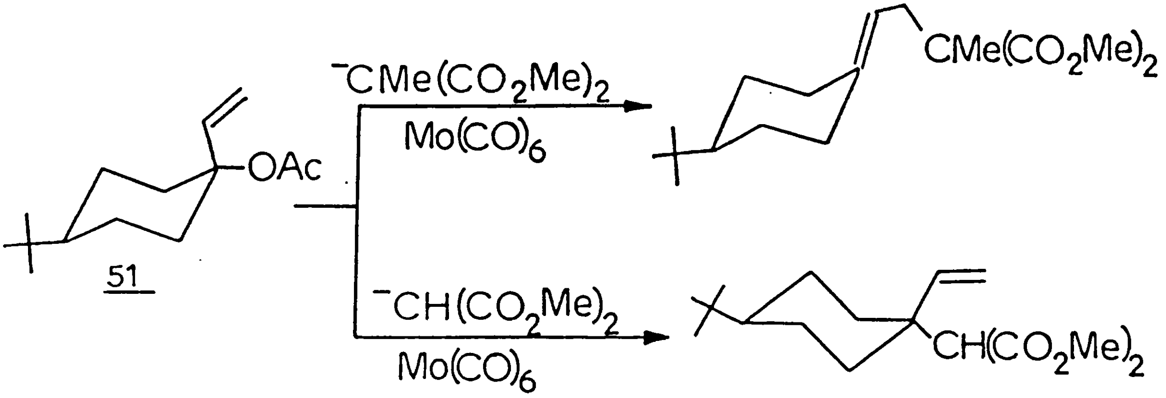
Scheme 1.15



Nu⁻=Nucleophile , X= OAc , Halide

The regioselectivity of the reaction appears to be more sensitive to variation than the palladium based systems. Solvents have a marked effect on the reactions[3] in terms of rate and regioselectivity and the attacking carbanion has been demonstrated to effect the regioselectivity to an unusual degree.[86] For example, the allyl acetate (51) is attacked only at the tertiary position by the dimethyl malonate carbanion and only at the primary position by the dimethyl (methyl malonate) carbanion (Scheme 1.16)

Scheme 1.16



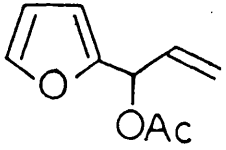
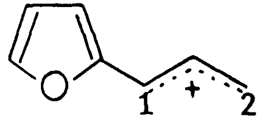
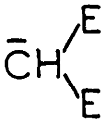
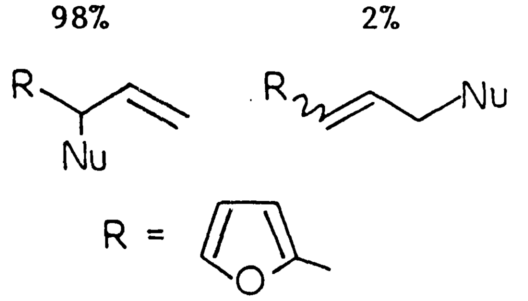
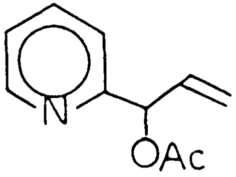
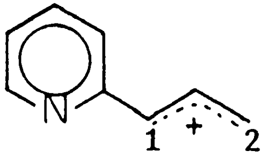
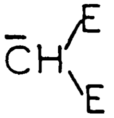
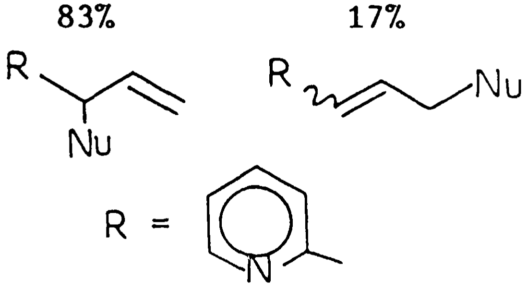
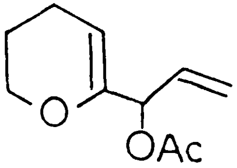
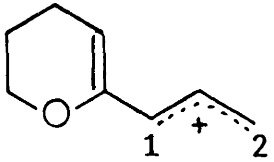
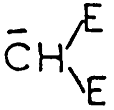
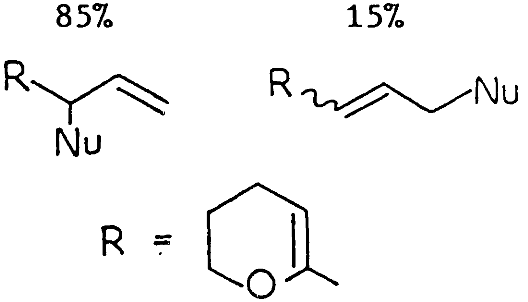
The regioselectivity has been rationalised[3] in terms of the steric demands of the nucleophile, the degree of σ-donation from the ligands in the catalyst, the stability of the molybdenum-olefin intermediate (i.e. as in (35) and (36)) and the charge distribution in the intermediate η^3-allyl complex.[86] Charge distribution has been attributed to the regioselectivity of attack in cationic species,[87,88] although a more recent study[89] has shown that the regioselectivity stems from frontier orbital control (i.e. by the size of the atomic coefficients in the LUMO of the allyl ligand) in both neutral and cationic species. However, electronic asymmetry in the intermediate η^3-allyl complexes will affect the coefficients of the LUMO[89] and thus the source of regioselectivity may be thought of as charge and frontier orbital control.

1.8. TUNGSTEN CATALYSTS

Tungsten catalysts have shown a bias for reaction at the more hindered end of the allyl unit, regardless of the nucleophile.[90] Tungsten is noticeably less reactive than molybdenum or palladium, but it's modest cost and intriguing regiochemical demand permit a level of control not available from previous metal systems.

The regioselectivity of the tungsten catalysts has been rationalised by regarding the intermediate allyl tungsten complexes as allyl cations bound to zero valent metal centres.[91] MO calculations support experimental data with the regioselectivity arising from charge distribution and frontier orbital control (Table 1.2).

TABLE 1.2 **REGIOSELECTIVITY OF ATTACK IN TUNGSTEN CATALYSED ALLYLIC-ALKYLATIONS**

SUBSTRATE	MODEL ALLYL-CATION	NUCLEOPHILE	PRODUCTS
	 $P_1 = 0.342$ $P_2 = 0.258$ $L_1 = -0.623$ $L_2 = 0.474$		
	 $P_1 = 0.428$ $P_2 = 0.314$ $L_1 = 0.656$ $L_2 = -0.525$		
	 $P_1 = 0.351$ $P_2 = 0.267$ $L_1 = -0.621$ $L_2 = 0.474$		

P = CARBON p_z CHARGE L = LUMO COEFFICIENT E = CO_2Me Nu = NUCLEOPHILE

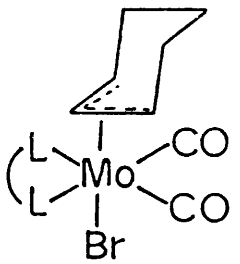
CHAPTER TWO

Molybdenum-mediated allylic alkylation, allylic coupling and benzylic coupling: Results

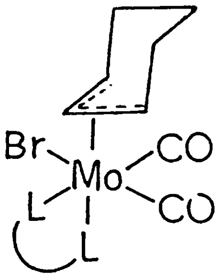
2.1. ALLYLIC COUPLING AND ALKYLATION

In 1975 it was reported[84] that the allyl complexes $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(L_2)X]$ (where L_2=2,2'-bipyridine or di(2-pyridyl)amine; X=Cl or Br) react with sodium pentan-2,4-dionate (Napda) in the presence of added base (pyridine) to form $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(pda)py]$ in high yields. The crystal structure and dynamic behaviour in solution of this product were reported in a subsequent paper.[92] There was no indication in this reaction of attack of the pda anion on the coordinated allyl ligand. However, as described earlier in this thesis (Chapter 1.7), some seven years later Trost et al[3] showed that in the absence of added base, several carbanions are capable of attacking the allyl group on preformed $[Mo(Me\text{-}\eta^3\text{-}C_3H_4)(CO)_2(bipy)Cl]$ so resulting in allylic alkylations. A catalytic procedure employing $Mo(CO)_4$bipy, or an analogue, was subsequently developed for these alkylations.

In order to explore these alternative but complementary reactions further, and to determine whether species such as $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(L_2)X]$ really are formed as intermediates in catalytic cycles employing $Mo(CO)_4L_2$ (where L_2=bipy or diphos), a range of new allylic alkylation reactions have been examined. Initial investigations were centred on preformed pseudooctahedral cis-dicarbonyl complexes of molybdenum containing the η^3-cyclohexenyl ligand. The cis arrangement of the carbonyl groups was established from the number and relative intensities of their stretching frequencies. Low solubilities of the complexes precluded NMR measurements which would differentiate between the two most likely structures (A) or (B),[89] which are found for all but one[93] related molybdenum allyl complexes of this stoichiometry.



A



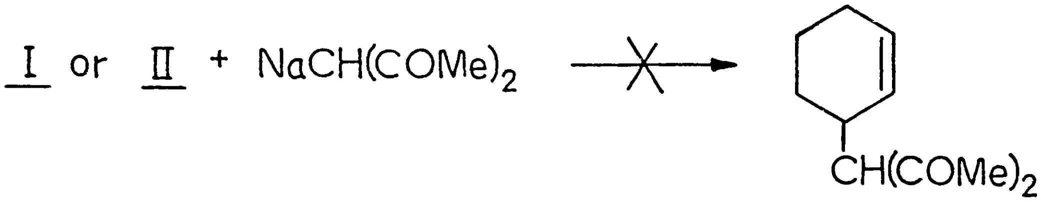
B

Where L⌒L = bipy (I) or diphos (II)

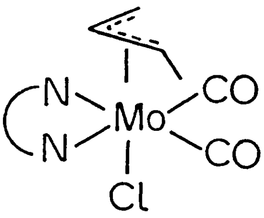
Complexes (I) and (II) were reacted with stoichiometric quantities of Napda in boiling THF, and in contrast to the results obtained by Trost[3] in analogous reactions involving the complexes (IIIa) and (IIIb) with the carbanion (IIIc), the expected product (IV) was not observed. In the event, mainly starting material together with traces of unknown organic decomposition products were recovered (Eq. 2.1).

On reacting (I) with Napda in refluxing toluene, starting materials were again recovered, but a significant proportion (ca 40%) of complex (I) had decomposed and traces of Mo(CO)$_4$bipy, 2,2'-bipyridine and 3,3'-bicyclohexenyl[94] (V) were detected. Formation of (IV) was not observed, and at higher reaction temperatures (boiling n-butyl acetate) complex (I) decomposed yielding Mo(CO)$_4$bipy and free 2,2'-bipyridine as the only isolable products.

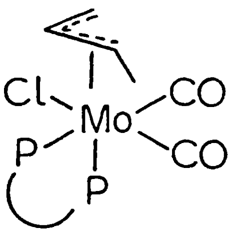
Eq. 2.1



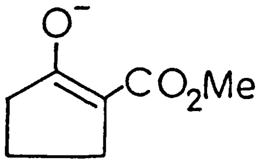
IV



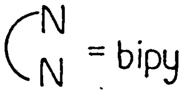
IIIa

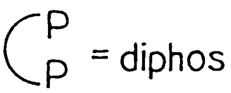


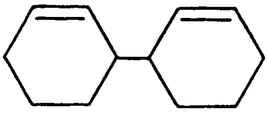
IIIb



IIIc



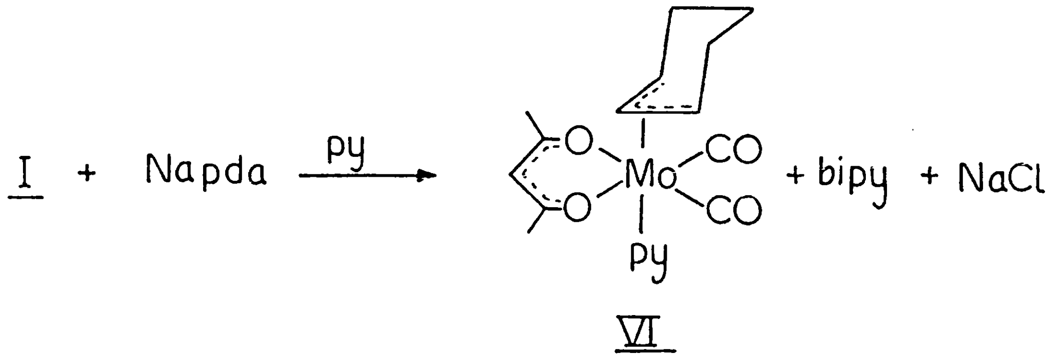




V

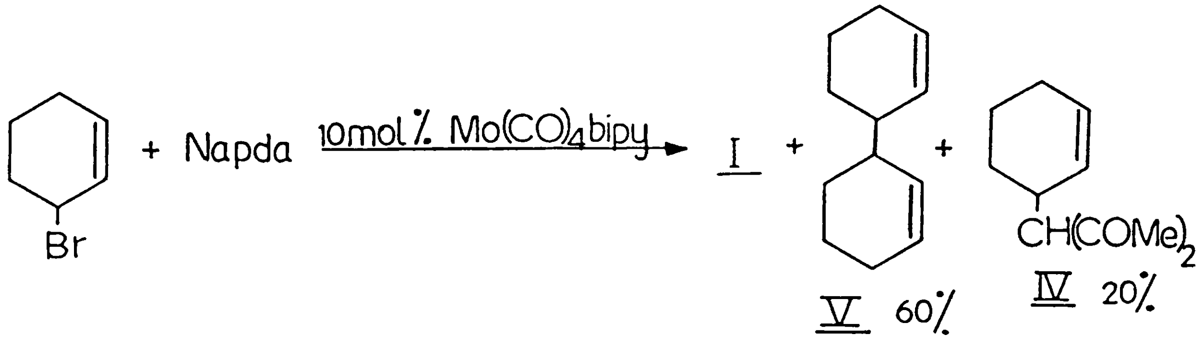
Under only slightly different reaction conditions, it was observed that treatment of (I) with Napda in the presence of pyridine results in ligand exchange with the formation of (VI)[95] in yields of ca 50%, and with no evidence of nucleophilic attack at the allyl moiety[84,95] (Eq. 2.2)

Eq. 2.2



The reaction of 3-bromocyclohexene with Napda in the presence of 10 mol% Mo(CO)$_4$bipy was next investigated. After 0.5 h in boiling toluene, reaction was complete, but the major product (ca 60%) was 3,3'-bicyclohexenyl (V) (Eq. 2.3). Reducing the concentration of the metal complex (5 mol%) had no effect on the rate or direction of the reaction.

Eq. 2.3



In the absence of Mo(CO)$_4$bipy no (V) was formed and only a 16% conversion of 3-bromocyclohexene to (IV) was observed after 0.5 h in refluxing toluene. This is the expected product from an S_N2 or S_N2' process, and a similar yield is also produced as a by-product in the molybdenum catalysed reaction (Eq. 2.3). It may therefore be considered to arise essentially from a non-catalytic process.

^{13}C NMR spectroscopy established the presence of dl and meso forms of the bicyclic product and showed that no significant diastereoselectivity had occurred in the coupling reaction. The only inorganic complex which could be recovered and identified with certainty was complex (I), which had been shown earlier not to undergo nucleophilic attack at the coordinated allyl ligand under similar reaction conditions.

During the work-up of the reaction mixture, an impure solid was also isolated whose infrared spectrum was very similar to that of the aerial oxidation products from $Mo(pda)_3$.[96] However, the possibility that $Mo(pda)_3$ itself was formed in the reaction and was responsible for the coupling reaction was soon dispelled. On reacting 3-bromocyclohexene with Napda in the presence of $Mo(pda)_3$, only a low yield (ca 20%) of (IV) was produced.

A series of investigative reactions were also performed in order to detect possible intermediates produced during the reaction. Interaction of $Mo(CO)_4$bipy with an excess of 3-bromocyclohexene in refluxing toluene gives a complex mixture of organics including 3,3'-bicyclohexenyl (V) and an impure sample of $MoBr_4$bipy.[97] Surprisingly, complex (I) was not produced. Since an excess of 3-bromocyclohexene was used, it was reasoned that any complex (I) formed might be attacked by the excess allyl bromide to give $MoBr_4$bipy and coupled organic products. This, however, was found not to be so since complex

(I) was shown to be unreactive towards excess 3-bromocyclohexene in refluxing toluene.

Finally, the interaction of Napda and $Mo(CO)_4bipy$ in refluxing toluene was investigated, and no reaction was detected under these conditions. Thus, we have no evidence for the formation of a new catalytic species, although Trost has attributed the <u>drop</u> in reactivity of some systems to "new" metal species.[86] For example, in allylic alkylation reactions in which dimethylsodiomalonate is employed as nucleophile, new catalytic moieties such as $[Mo(CO)_5(CHE_2)]^-$ (where $E=-CO_2Me$) have been proposed.[86,98]

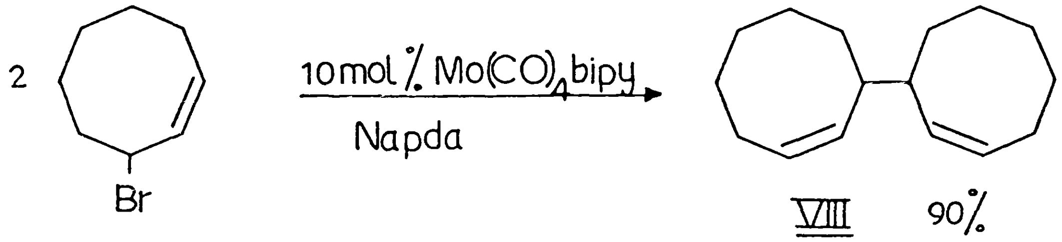
From these experiments, the pda carbanion is shown to play a key role in determining both inorganic and organic products in this molybdenum-mediated allylic coupling reaction, and although the mechanism is still unclear, we tentatively suggest that the metal complex behaves as a halogen transfer agent, facilitating halogen transfer from the allyl bromide to the pda carbanion which is oxidised in the course of the reaction. Although we have no evidence for oxidised species such as $CHBr(COCH_3)$,[99] it is surprising that at the end of the reaction, there appears to be no trace of the pda carbanion except in the substitution reaction product (IV) and the unknown inorganic product whose infrared spectrum appears similar to that of the aerial oxidation product of $Mo(pda)_3$.[96] In most other metal assisted reductive coupling reactions, the oxidised product is a metal species[100] although several examples of organic anions acting as a source of hydride in catalytic cycles are documented.[101]

In order to explore the synthetic utility of this facile coupling reaction, we extended our investigations to other cyclic allyl halides, and found that high yields of 3,3'-bicycloheptenyl[94] (VII) and 3,3'-bicyclooctenyl[94] (VIII) could also be obtained in yields of 61 and 90% respectively.

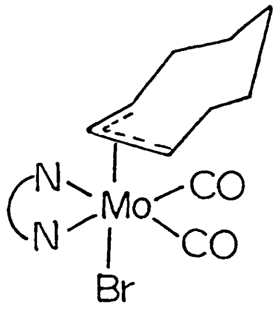
A comparison of integrals of well-resolved, like-^{13}C atoms in the ^{13}C NMR spectra of (VII) and (VIII) indicated that an approximately 1:1 diastereomeric mixture had been obtained in each case. ^{13}C NMR shift values[102] indicate that the double bonds in (VIII) have the Z-configuration.

The only product identified with certainty from the molybdenum-mediated coupling of 3-bromocyclooctene was (VIII)(Eq. 2.4). An impure solid of low solubility was also isolated from the reaction mixture and infrared measurements indicated that it was a cis-dicarbonyl compound. The infrared spectrum differed however from the expected and independently synthesised η^3-cyclooctenyl complex (IX).[95]

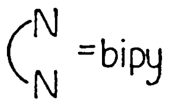
Eq. 2.4



VIII 90%

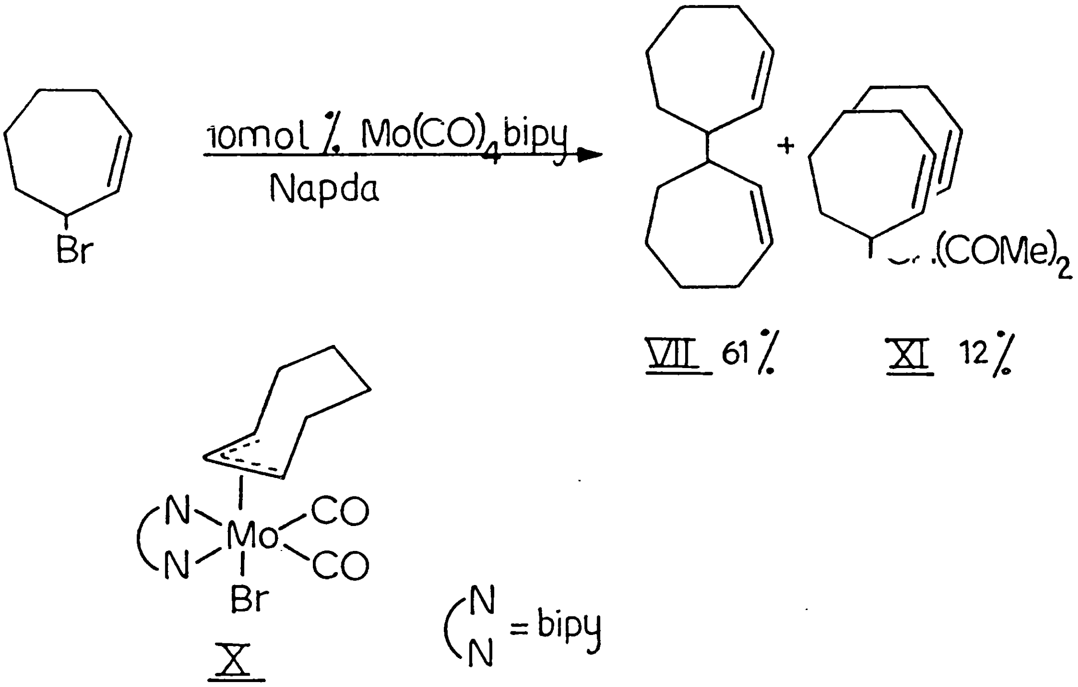


IX



Analysis of the reaction mixture from the molybdenum-mediated coupling of 3-bromocycloheptene showed the reaction to be analogous to that occurring with 3-bromocyclohexene. Thus 3,3'-bicycloheptenyl (VII) was formed in ca 60% and the η^3-cycloheptenyl complex (X) was isolated, although in an impure state. Its identity was confirmed by an independent synthesis.[95] The alkylated product, (XI), was also isolated although in very low yield (ca 12%)(Eq. 2.5). In the absence of $Mo(CO)_4$bipy, 3-bromocycloheptene and Napda react in boiling toluene giving a ca 50% conversion to (XI) in the time taken to give complete reaction in the molybdenum-mediated experiment.

Eq. 2.5



Several other molybdenum complexes were used to effect the coupling of 3-bromocyclohexene in the presence of Napda and these are discussed separately.

$[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH}(\mathrm{C}}\mathrm{H}_2)_3)(\mathrm{CO})_2(\mathrm{bipy})\mathrm{Br}]$

The key role played by the pda carbanion when complex (I) is used to catalyse the allylic coupling of 3-bromocyclohexene became apparent when the reaction was carried out in the absence of this species. Under these conditions, excess 3-bromocyclohexene fails to react with complex (I) and both reactants are recovered unchanged. When the reaction is performed with the addition of one equivalent of Napda, (V) is formed in a 44% yield together with ca 22% of the expected product (IV). Moreover, complex (I) may be recovered (up to 50%) and re-used in subsequent reactions, which makes it an attractive catalyst despite the low yield of coupled product.

$[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH(CH}}{}_2)_3)(\mathrm{CO})_2(\mathrm{pda})(\mathrm{py})]$

The pda complex (VI) also mediates the allylic coupling of 3-bromocyclohexene in the presence of Napda but unlike (I), (VI) is completely consumed during the course of the reaction which affords (V)(30%) and (IV) (23%).

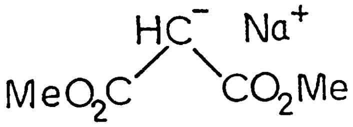
Molybdenum hexacarbonyl, $\mathrm{Mo(CO)_6}$

In contrast to $\mathrm{Mo(CO)_4}$bipy, $\mathrm{Mo(CO)_6}$ is a poor catalyst, and in the presence of Napda it gives only poor yields of (V)(*ca* 24%) from the allylic coupling of 3-bromocyclohexene. The fate of the catalyst is unknown and at the end of the reaction no molybdenum-containing species could be identified with certainty. Again, (IV) is also produced via an apparently non-catalytic pathway.

$\mathrm{Mo(CO)_4}$diphos

This was the only catalyst to give results that paralleled those of Trost.[3,86] 3-Bromocyclohexene reacts with Napda in the presence of $\mathrm{Mo(CO)_4}$diphos (10 mol%) to afford compound (IV) (*ca* 45%) with only a trace of the coupled product (V). The reaction is slow (2 h in refluxing toluene) but definitely catalytic since in the absence of $\mathrm{Mo(CO)_4}$diphos, less than 28% conversion of 3-bromocyclohexene to (IV) occurs.

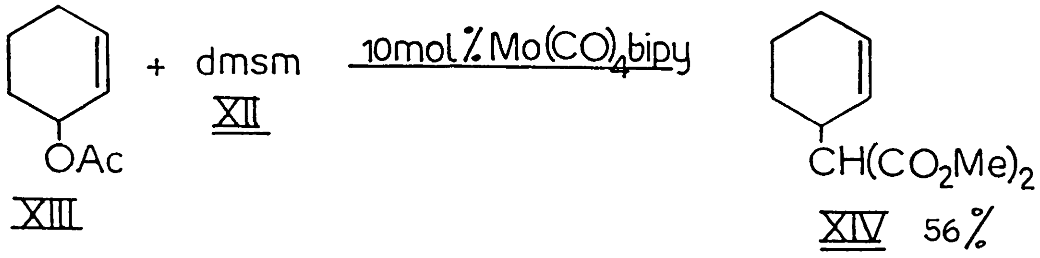
The reaction conditions have also been varied in order to mimic those reported by Trost.[3,86] Thus, allyl acetates have been employed in the presence of a less effective metal complexing carbanion such as that derived from dimethylmalonate (XII).



XII dmsm

3-Acetoxycyclohexene (XIII) reacts with $Mo(CO)_4bipy$ to afford a complex mixture of organic products. However, it was found that (XIII) reacts with dimethylsodiomalonate (dmsm) in the presence of $Mo(CO)_4bipy$ (10 mol%) to afford (XIV) in ca 56% yield (Eq. 2.6). The reaction in refluxing toluene is slow (44 h) but in the absence of $Mo(CO)_4bipy$ only reactant decomposition occurs.

Eq. 2.6



On using Napda in place of dmsm the major product is the bicyclohexenyl (V) (ca 50%), a result which again reflects the critical role of the pda carbanion. Compound (IV) is also produced catalytically as the minor product.

3-Bromocyclohexene is also coupled in the presence of dmsm and $Mo(CO)_4$bipy (10 mol%) which reflects the importance of the anionic leaving group on the allyl substrate in these reactions.

The results of these reactions are summarised in Table 2.1.

TABLE 2.1. PRODUCT FORMATION FROM MOLYBDENUM-MEDIATED ALLYLIC COUPLING AND ALKYLATION REACTIONS

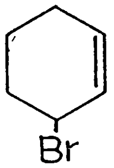
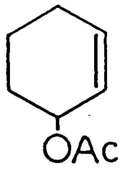
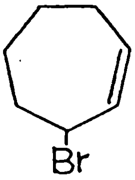
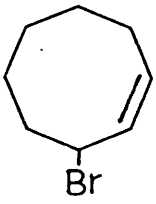
SUBSTRATE	NUCLEOPHILE	CATALYST	ORGANIC PRODUCTS (%)
	pda	(I)	(IV)(22) (V)(44)
		(VI)	(IV)(23) (V)(30)
		$Mo(CO)_4bipy$	(IV)(20) (V)(63)
		$Mo(CO)_6$	(IV)(22) (V)(24)
		$Mo(CO)_4diphos^a$	(IV)(45)
	dmsm	$Mo(CO)_4bipy$	(XIV)(50) (V)(50)
	pda	$Mo(CO)_4bipy^b$	(IV)(23) (V)(52)
	dmsm	$Mo(CO)_4bipy^c$	(XIV)(56)
	pda	$Mo(CO)_4bipy$	(VII)(61) (XI)(12)
	pda	$Mo(CO)_4bipy$	(VIII)(90)

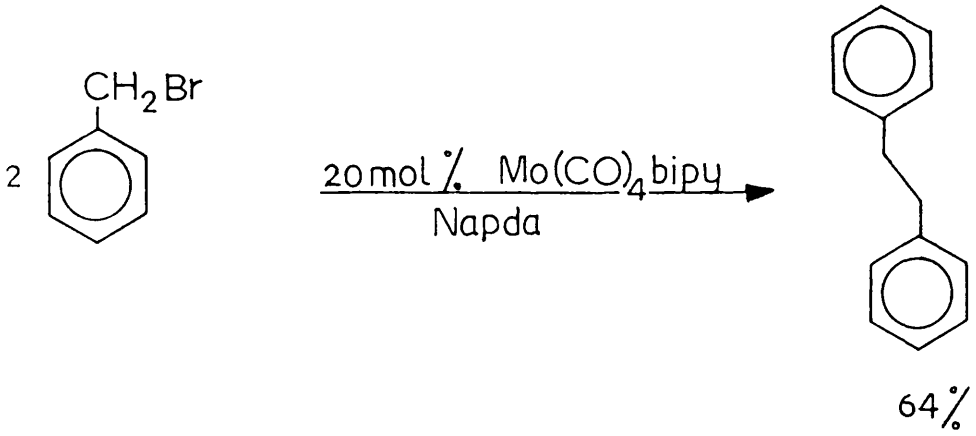
TABLE 2.1. (<u>CONTINUED</u>)

Reactions carried out using equimolar quantities of substrate and nucleophile in refluxing toluene. The reaction time was 0.5 h and 10 mol% of catalyst was employed unless otherwise stated. The alkylation products arise from essentially non-catalytic pathways unless otherwise stated. (a) Reaction time of 2.5 h. A control reaction gave less than 28% (IV). (b) Reaction time of 32 h 20 mol% $Mo(CO)_4bipy$. Compound (IV) was not formed in a control reaction. (c) Reaction time of 44 h. (XIV) was not formed in a control reaction.

2.2 BENZYLIC COUPLING

The benzyl group may be regarded as a pseudoallyl species if the double bonds in the aryl ring are formally localised, and it is known to form η^3-benzyl derivatives of molybdenum.[103] It was therefore of interest to determine whether $Mo(CO)_4bipy$ could be used to effect benzylic coupling in the presence of Napda. Under reaction conditions described above, benzyl bromide was smoothly coupled to afford bibenzyl in a 64% yield (Eq. 2.7).

Eq. 2.7



To determine the effects of electron withdrawing and electron releasing groups on the reaction, and to determine how tolerant the reaction was to substituents on the benzyl substrate,[104] p-nitrobenzyl and p-methoxybenzyl bromide were used under similar conditions. In both cases, considerably reduced yields of the coupled products were obtained.

However, it was later established that benzyl bromide is coupled in the absence of Napda in an identical yield and $MoBr_4$bipy is detected at the end of the reaction by infrared analysis. This observation implies that the molybdenum-mediated coupling of the benzyl compounds investigated is stoichiometric rather than catalytic, and in contrast to allylic reactions, the addition of Napda has no effect on the rate or direction of the reaction, although time has not permitted further study in this area.

CHAPTER THREE

Discussion

3.1. SUMMARY

The experimental observations made on the molybdenum-mediated allylic coupling and alkylation reactions reported in this thesis cannot easily be explained mechanistically. It is apparent that the various products are formed by more than one route, with the predominant pathways being sensitive to the nature of the allyl substituent, the nucleophile and the metal catalyst.

In the presence of $Mo(CO)_4bipy$, allylic coupling occurs almost exclusively when the allylic substrate contains a good leaving group such as bromide and a strong metal-complexing agent such as the pda carbanion is present. Allylic alkylation predominates with this catalyst when the allyl substituent is a relatively poor leaving group such as acetate, and a weaker metal-complexing anion is included in the reaction mixture. Changing the catalyst from $Mo(CO)_4bipy$ to $Mo(CO)_4diphos$ favours alkylation over coupling of allyl halide in the presence of the pda anion.

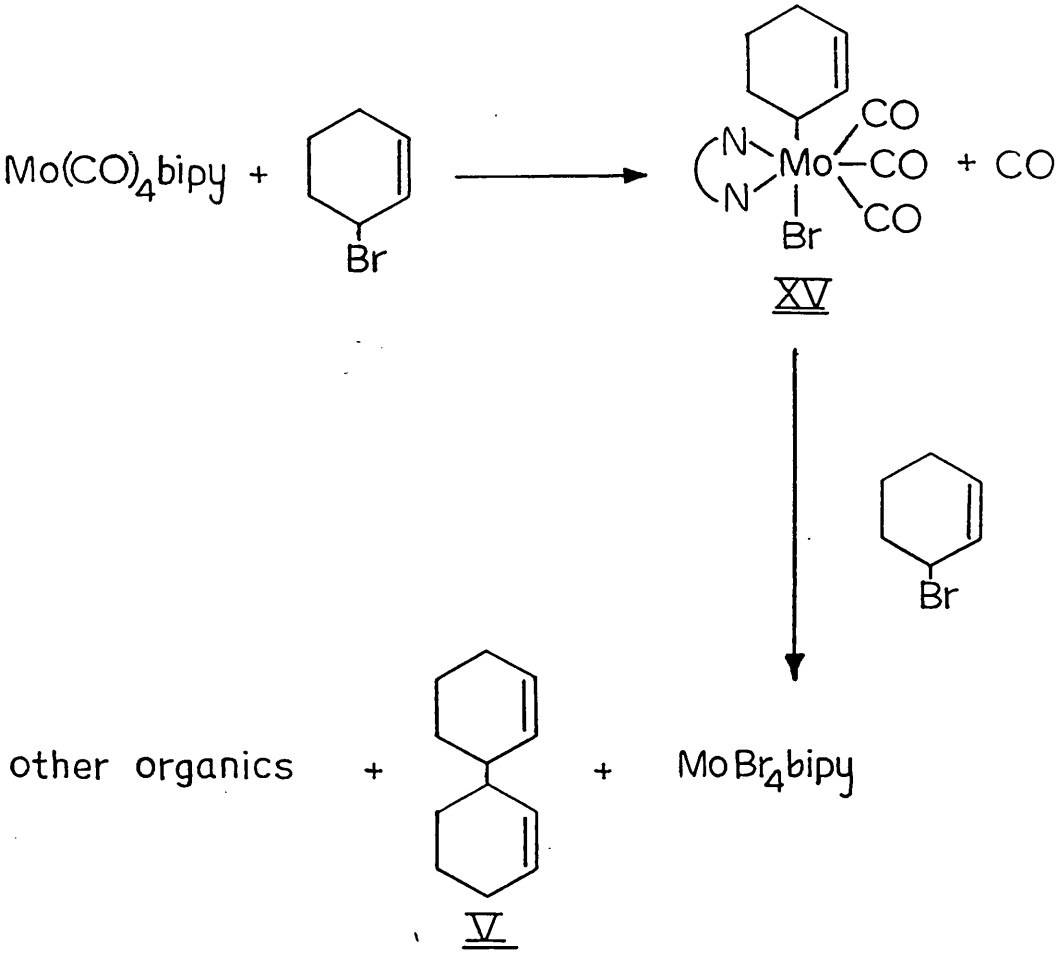
For either reaction, allylic coupling or allylic alkylation, the mechanisms almost certainly involve a redox cycle whereby molybdenum undergoes oxidation and reduction in one or more 1e or 2e processes, thereby generating a catalytic cycle.

3.2. ALLYLIC COUPLING

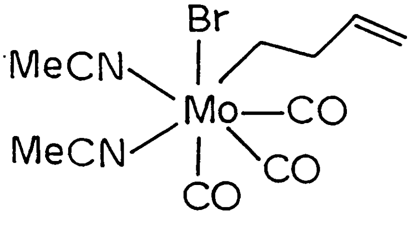
Even though the η^3-allylmolybdenum complex (I) exhibits some catalytic activity towards allylic coupling of 3-bromocyclohexene, it seems unlikely that this complex is the key intermediate responsible for allylic coupling in the $Mo(CO)_4$bipy mediated reaction.

In the absence of the pda anion, excess 3-bromocyclohexene reacts with $Mo(CO)_4$bipy to give $MoBr_4$bipy and a complex mixture of organic products that includes 3,3'-bicyclohexenyl, whereas complex (I) is stable in the presence of excess 3-bromocyclohexene under identical experimental conditions. Therefore, we postulate that the most likely alternative intermediate is an η^1-allyl complex such as (XV) depicted below in Scheme 3.1.

Scheme 3.1



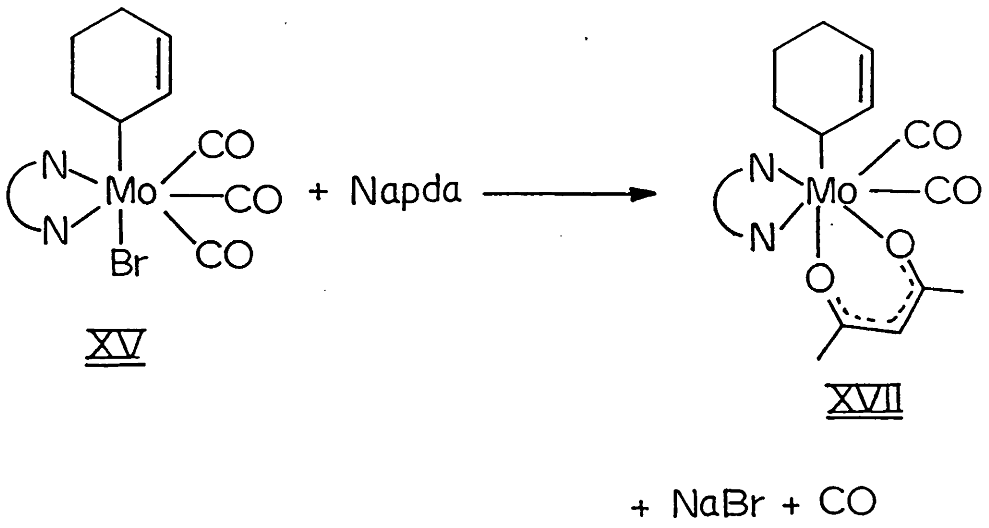
The intermediacy of (XV) could not be established experimentally but indirect support for an η1-bonded intermediate of the type MoBr(CO)$_3$(N-donor)$_2$R is provided by the isolation and characterisation of (XVI).[105]



XVI

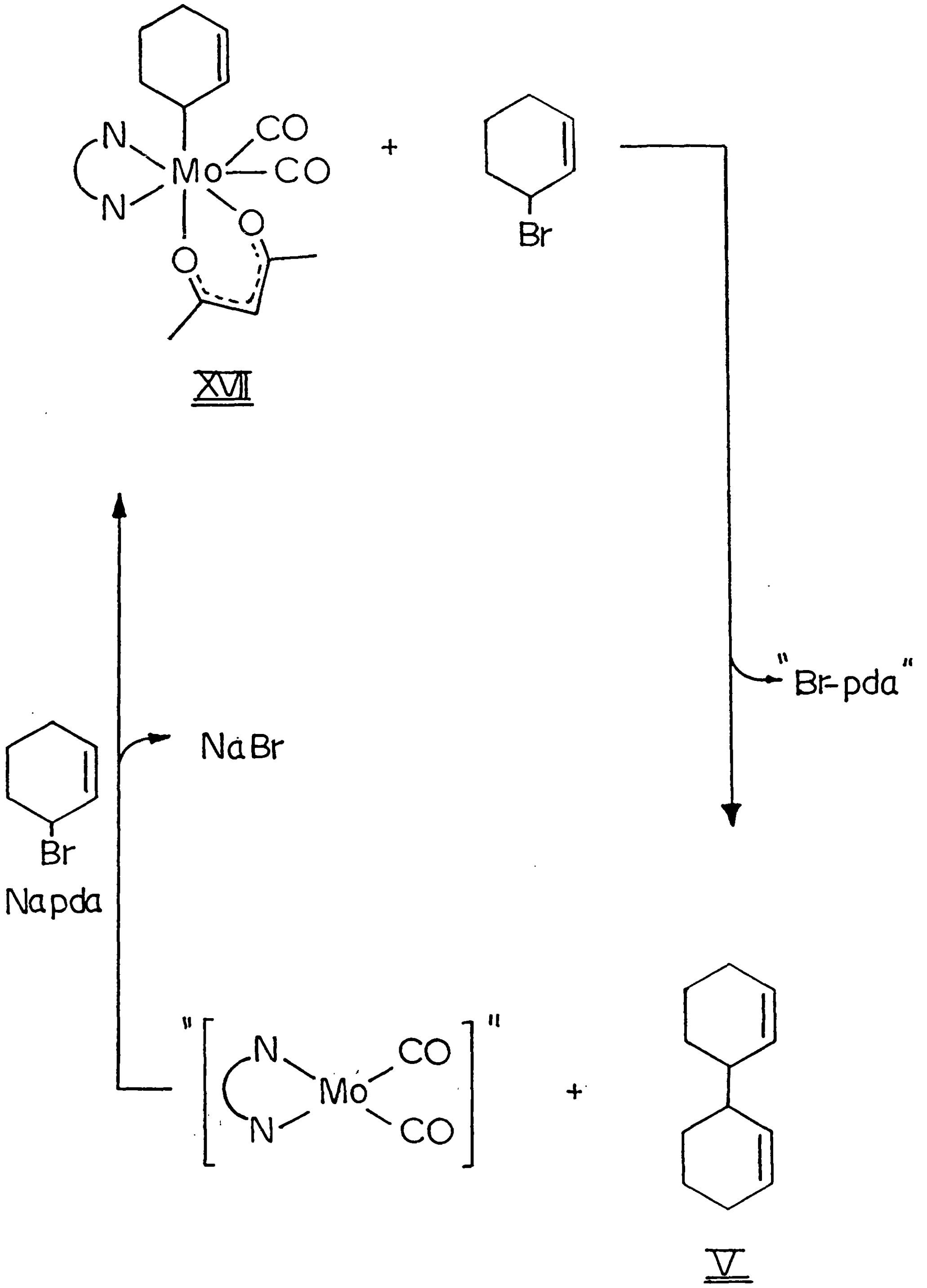
In the presence of a strong metal-complexing anion such as pda, the intermediate (XV) may react with the anion rather than further 3-bromocyclohexene (Scheme 3.1), so forming the type of active intermediate (XVII) responsible for the coupling reaction (Eq. 3.1).

Eq. 3.1



Coupling of the organic moieties by further reaction of 3-bromocyclohexene with (XVII) and subsequent oxidation of the pda anion allows the molybdenum centre to return to a zero oxidation state and re-enter the catalytic cycle. (Scheme 3.2)

Scheme 3.2



It has been established that Napda is consumed in the course of the reaction and apart from the small quantity of pda found in compound (IV) and in the unknown pda-containing complex, its ultimate fate is unknown. The likely oxidation product of the pda anion is 3-bromoacetylacetone (XVIII)

$$CHBr(COMe)_2$$

XVIII

and its thermal instability reported by Tavares _et al_[99] may account for the apparent disappearance of the Napda and our inability to detect any brominated organic compounds.

Since 3-bromocyclohexene does not form an η^3-allyl complex on reaction with $Mo(CO)_4bipy$ in refluxing toluene, nor does complex (I) react further with this organic halide, then it appears unlikely that the proposed initial intermediate (XV) loses CO spontaneously and undergoes an $\eta^1 \longrightarrow \eta^3$ rearrangement to complex (I). This latter complex, which _is_ formed as a by-product in the catalytic reaction may arise via another intermediate, or may be formed from (XV) only under the conditions found in the catalytic cycle.

The proposed mechanism includes an overall two-electron process involving the $Mo(0) \rightleftharpoons Mo(II)$ couple, although it is possible that a further $Mo(II) \rightleftharpoons Mo(IV)$ process occurs in which complex (XV) or (XVII) reacts with two further molecules of 3-bromocyclohexene.

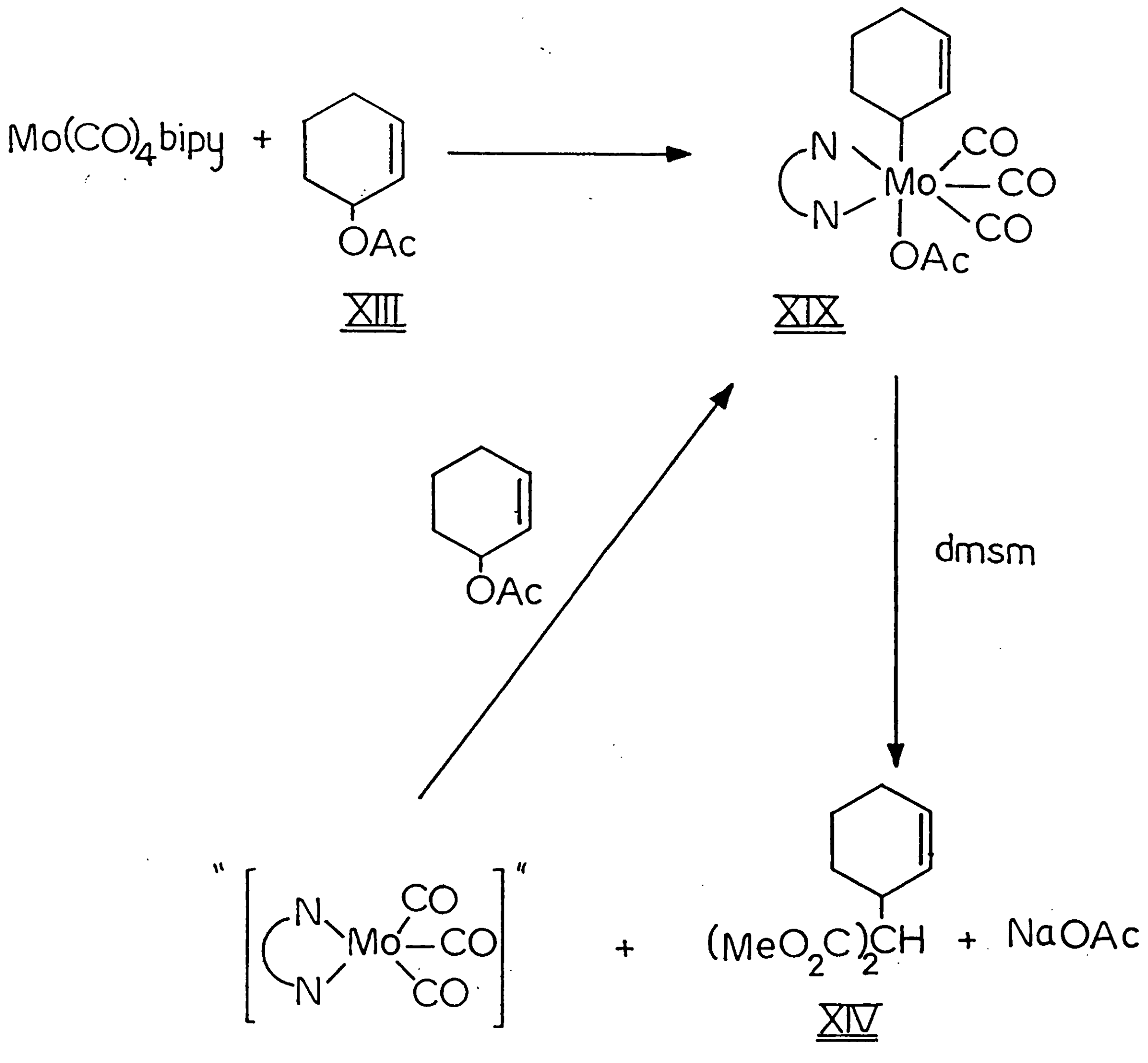
Kochi et al[106] have shown that 17-electron complexes are also common in metal carbonyl chemistry and this cannot be discounted for the reaction under consideration. Oxidative addition of alkyl halides to transition metal centres by a 1-electron process is known[107,108] and certain η^3-allyl-molybdenum complexes are known to undergo electrochemical oxidation to give 17-electron species.[109]

3.3. ALLYLIC ALKYLATION

3-Acetoxycyclohexene and dimethylsodiomalonate react in the presence of $Mo(CO)_4$bipy to afford compound (XIV) in ca 56% yield with no indication of any coupled product (Eq. 2.6). As this reaction is exactly analogous to those described by Trost,[3] we have not pursued this area extensively. However, even in this alternative reaction, the intermediacy of an η^1-allyl species, rather than an η^3-allyl derivative is plausible in terms of the $Mo(0) \rightleftharpoons Mo(II)$ mechanism discussed earlier (Chapter 3.2). Furthermore, it has been reported recently[110] that η^1-allyl complexes are likely key intermediates in some palladium-catalysed allylic alkylations.

The allyl acetate (XIII) may react with $Mo(CO)_4$bipy to produce the η^1-allyl intermediate (XIX) (Scheme 3.3). In the presence of the pda anion, reaction may proceed as in Eq. 3.1 and moderate yields of the coupled product are recovered. In the presence of a weakly coordinating carbanion such as that from dmsm, attack at the η^1-allyl ligand occurs forming (XIV) with regeneration of a Mo(0) species which can re-enter the catalytic cycle (Scheme 3.3).

Scheme 3.3

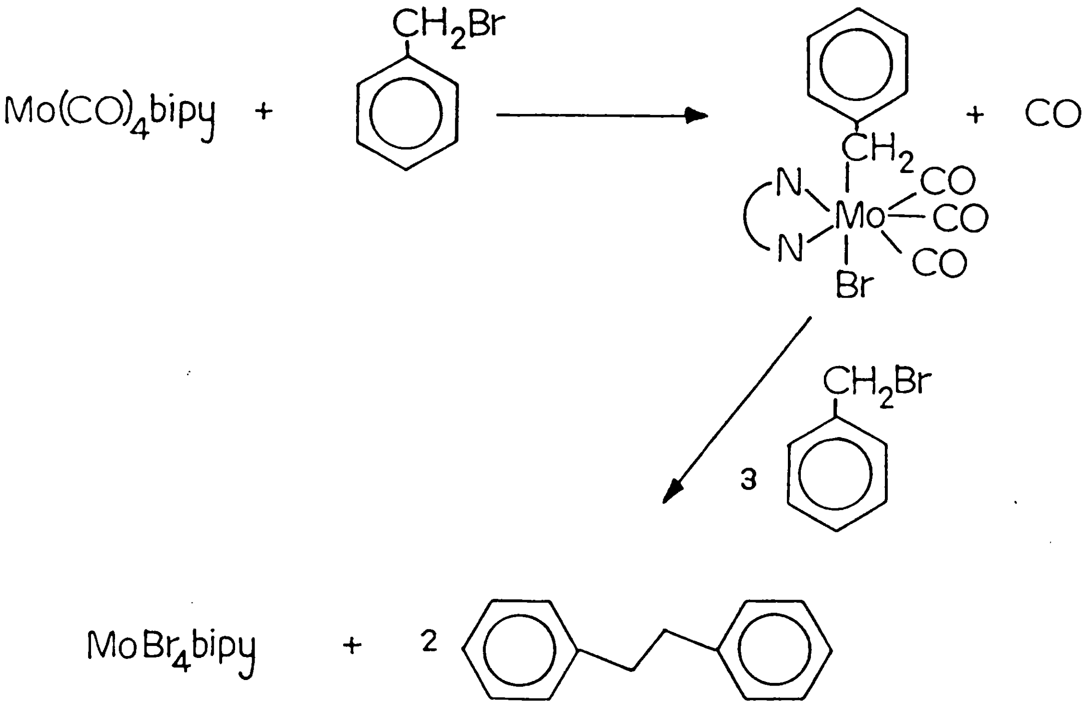


The leaving group on the allyl substrate plays an important role however, since 3-bromocyclohexene reacts with dmsm in the present of $Mo(CO)_4bipy$ to afford the coupled product in <u>ca</u> 50% yield. Compound (XIV) is also produced in similar yield although in the absence of $Mo(CO)_4bipy$, the latter compound is formed in 85% yield.

3.4. BENZYLIC COUPLING

The molybdenum-mediated coupling of benzyl bromide has been demonstrated to take place in the absence of Napda. In contrast to the reaction of 3-bromocyclohexene with $Mo(CO)_4bipy$ in the absence of Napda, the reaction is clean and smooth. The reaction probably occurs via an η^1-benzyl intermediate (Scheme 3.4), and $MoBr_4bipy$ is detected at the end of the reaction. The rate and direction of this reaction appears unaffected by the presence of Napda although time has not permitted a full study

Scheme 3.4



It is worthy of note that bromobenzene failed to couple or alkylate in the presence of $Mo(CO)_4bipy$ and Napda.

CHAPTER FOUR

Experimental

All preparations were performed in an atmosphere of dry nitrogen gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. The starting materials $Mo(CO)_4bipy$, $Mo(CO)_4diphos$, Napda and $\overline{(CH_2)_nCH{=}CHCH}Br$ (where n=3-5) were prepared by literature methods.[111-114] Other chemicals were obtained from commercial sources and used without further purification. Infrared spectra in the region 200-4000 cm^{-1} were recorded on a Perkin-Elmer 597 spectrophotometer as nujol mulls unless otherwise stated. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ solutions unless otherwise stated using JEOL PS 100 and FX90Q FT instruments respectively with TMS as internal standard. Carbon types were identified by the INEPT technique but quoted as if determined by off-resonance decoupling. Thus, δ_c (multiplicity, assignment).

Preparation of $[Mo(\eta^3\text{-}\overline{CHCHCH(CH_2)_n})(CO)_2(bipy)Br]$ Complexes (I),[115] (X) and (IX) Where n=3-5)

A solution of $Mo(CO)_6$ (0.528g, 2.0 mmol) in MeCN (20 ml) was heated under reflux for 24 h. To the cooled reaction mixture was added dropwise with stirring, a solution of the allyl bromide (2.0 mmol) in MeCN (5 ml). The resulting suspension of $[Mo(\eta^3\text{-}\overline{CHCHCH(CH_2)_n})(CO)_2(NCMe)_2Br]$ was stirred at room temperature with bipy(0.312g, 2.0 mmol) dissolved in MeCN (5 ml). The products were isolated in yields of 64, 77 and 44% respectively for n=3,4 and 5 after cooling the reaction mixture in ice

for 0.5 h. Found for (I): C, 46.1; H, 3.80; N, 5.75. Calc. for $C_{18}H_{17}N_2O_2BrMo$: C, 46.1; H, 3.62; N, 5.97% ν(CO): 1920(s) and 1835(s) cm^{-1}
Found for (X): C, 47.2; H, 3.80; N, 5.75.Calc. for $C_{19}H_{19}N_2O_2BrMo$: C, 47.2; H, 3.93; N, 5.80%. ν(CO): 1920(s) and 1835(s) cm^{-1}
Found for (IX): C, 48.2; H, 4.20; N, 5.72.Calc. for $C_{20}H_{21}N_2O_2BrMo$: C, 48.3; H, 4.23; N, 5.63%. ν(CO): 1935(s) and 1850(s) cm^{-1}

Preparation of $[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH(CH}}_2)_3)(\mathrm{CO})_2(\mathrm{diphos})\mathrm{Br}]$ (Complex (II))

A mixture of $[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH(CH}}_2)_3)(\mathrm{CO})_2(\mathrm{NCMe})_2\mathrm{Br}]$ (1.0 g, 2.5 mmol) and diphos (1.0 g, 2.5 mmol) in MeOH (20 ml) was heated under reflux for 0.75 h. The solution was allowed to cool to room temperature whereupon $[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH(CH}}_2)_3)(\mathrm{CO})_2(\mathrm{diphos})\mathrm{Br}]$ crystallised as an orange solid. The product was collected by filtration, washed with a little MeOH and dried *in vacuo*. Yield, 1.34 g, 75%. Found: C, 57.6; H, 4.81.Calc. for $C_{34}H_{33}P_2O_2BrMo$:C, 57.4; H, 4.64%. ν(CO): 1925(s) and 1830(s) cm^{-1}.

Preparation of $[\mathrm{Mo}(\eta^3\text{-}\overline{\mathrm{CHCHCH(CH}}_2)_3)(\mathrm{CO})_2(\mathrm{pda})(\mathrm{py})]$ (Complex (VI))

A mixture of Napda (0.104 g, 0.85 mmol), complex (I) (0.1 g, 0.21 mmol) and pyridine (1.5 ml) was heated in acetone (5 ml) for 15 h during which time the deep red colour of the solution lightened to a pale orange. After cooling, solid NaBr was removed by filtration and the filtrate treated with deaerated water (10 ml). Most of the acetone present in solution was removed in a stream of nitrogen gas and the product allowed to crystallise overnight at 0°C. After filtering, the solid was washed with water and dried in vacuo. Yield, 0.44 g, 50%. Found: C, 52.1; H, 5.20; N, 3.81.Calc. for $C_{18}H_{21}NO_4Mo$: C, 52.6; H, 5.1; N, 3.41%. ν(CO); 1820(s) and 1910(s) cm^{-1}

Molybdenum-Mediated Coupling Reactions of $\overbrace{(CH_2)_nCH=CHCHBr}$ (Where n=3-5)

The general procedure used is illustrated by reference to 3-bromocyclohexene in the presence of Napda and $Mo(CO)_4$bipy. Other reactions were carried out in an analogous manner.

3-Bromocyclohexene (10.1 g, 0.063 mol) was added dropwise to a stirred suspension of $Mo(CO)_4$bipy (5.05 g, 0.014 mol) and Napda (7.66 g, 0.063 mol) in dried, oxygen-free toluene (75 ml). The resulting mixture was stirred and heated under reflux for 0.5 h in an atmosphere of nitrogen gas. After cooling, the reaction mixture was filtered and the solvent removed under reduced pressure. The resulting brown oil was chromatographed on 100-200 mesh florisil using hexane as eluant. The product, 3,3'-bicyclohexenyl[94] (V) was isolated as a colourless, mobile oil. Yield, 3.22 g, 63%. NMR data on a mixture of diastereoisomers, δ (relative intensity, multiplicity, assignment), δ_C, 22.4 (49, t, both C-4s), 25.5 (63, t, both C-5s), 26.1 (39, t, both C-6s), 40.3 (45, d, both C-3s), 127.7 and 128.0 (36, d, C-1s), and 130.5 and 130.7 (28 and 38, d, C-2s).

δ_H, 1.8 (14H, m, CH_2), 5.6 (4H, s, olefinics)

3,3'-Bicycloheptenyl[94] (VII) was isolated as a mixture of diastereoisomers in a 61% yield. NMR data, δ_C, 27.0 (97, t, both C-6s), 28.9, 30.6, 31.2, 31.4 and 31.5 (61, 55, 43, 48, 61, t, C-4s, C-5s and C-7s, not respectively and with one coincidence), 45.6 and 46.0 (42 and 39, d, C-3s), 131.4 and 131.7 (37, d, C-1s), and 136.2 and 136.5 (42 and 45, d, C-2s). δ_H, 2.0(18H, m, CH_2), 5.6(4H,m,olefinics)

(Z)-(Z)-3,3'-Bicyclooctenyl[94] (VIII) was isolated as a mixture of diastereoisomers in a 90% yield. NMR data, δ_C, 26.0 and 26.1 (43 and 54, t, C-5s), 27.0 and 27.4 (69 and 75, t, C-7-8 coincidence for each diastereoisomer), 29.7 and 30.0 (46 and 40, t, C-6s), 34.4 and 34.6 (48 and 31, t, C-4s), 40.9 and 41.3 (38 and 30, d, C-3s), 129.3 and 129.4 (31 and 49, d, C-1s), 133.2 and 134.4 (37 and 47, d, C-2s). δ_H, 2.0 (22H, m, CH_2), 5.5 (4H, m, olefinics).

Preparation of (IV)

3-Bromocyclohexene (1.0 g, 6.2 mmol) was added dropwise to a stirred solution of Napda (0.76 g, 6.2 mmol) in MeOH (25 ml) and the resulting solution was stirred at room temperature for 4 h. The solvent was removed from the pink solution under reduced pressure to afford a suspension of NaBr and product. The product was extracted into a small quantity of diethyl ether and NaBr removed by filtration. The diethyl ether evaporated under reduced pressure and the resulting oil chromatographed on silica gel (Merck PF60$_{254}$) using 6:1hexane/ethyl acetate. Yield, 0.16 g, 14%. Found: C, 73.4; H, 9.14.Calc for $C_{11}H_{16}O_2$: C, 73.3; H, 8.89%. NMR data*,δ_C, 20.8 (t, C-5'), 25.0 (t, C-4'), 26.8 (t, C-6'), 29.6 and 30.0 (q, C-1 and C-5), 35.6 (d, C-3'), 74.8 (d, C-3), 127.3 (d, C-1'), 129.9 (d, C-2') and 203.4 and 203.6 (s, C-2 and C-4).

δ_H, 1.0-2.0 (6H, m, CH_2), 2.15 (6H, s,-$COCH_3$), 3.0 (1H, m, C-3'-H), 3.6 (1H, d, J(HH) 10 Hz, C-3-H, 5.5 (2H, m,olefinics).

* The primed carbon atoms refer to the cyclohexenyl ring.

Product Isolation from the Molybdenum-Mediated Coupling of 3-Bromocyclohexene

3-Bromocyclohexene (3.96 g, 24.6 mmol) was added dropwise to a stirred suspension of Napda (3.0 g, 24.6 mmol) and $Mo(CO)_4bipy$ (2.0 g, 5.5 mmol) in toluene (50 ml) and the resulting mixture heated under reflux for 0.5 h. The brown suspension was cooled, filtered and the solid washed with a little toluene. The solid was then washed separately with water followed by acetone and dried in vacuo. Yield, 1.27 g. I.R. measurements indicated the formation of pure (I) (50% recovery based on Mo). Toluene was removed from the original filtrate under reduced pressure to afford a brown oil contaminated with a brown solid. A small quantity of hexane was added, and the brown solid collected by filtration, washed with a little hexane and dried in vacuo. Yield, 0.13 g. The unknown solid was not identified, but its I.R. spectrum appeared similar to that of the aerial oxidation product of $Mo(pda)_3$.[96] ν, 1560, 1515, 1270, 1020, 950 cm^{-1}. The hexane was removed from the filtrate under reduced pressure and the resulting oil chromatographed on florisil (100-200 mesh) with hexane. The first fraction gave 1.25 g (63%) of 3,3'-bicyclohexenyl. The polarity of the eluant was increased to 6:1 hexane/ethyl acetate, and the following fractions contained mainly (IV) with a little 2,2'-bipyridine. Yield, 0.88 g, 20%.

Product Isolation from the Molybdenum-Mediated Coupling of 3-Bromocycloheptene

3-Bromocycloheptene (4.24 g, 24 mmol) was added dropwise to a stirred suspension of Napda (2.96 g, 24 mmol) and $Mo(CO)_4$bipy(1.94 g,5.3 mmol)in toluene(50ml) and the resulting mixture heated under reflux for 0.5 h. After cooling, the solid was washed with a little toluene and dried *in vacuo*. Yield, 1.2 g. I.R. analysis indicated the presence of complex (X) as the major product. The toluene was evaporated under reduced pressure and the resulting red oil chromatographed on silica gel (Merck $PF60_{254}$) using hexane as eluant. The first fraction afforded 3,3'-bicycloheptenyl. Yield, 1.4 g, 61%. The eluant polarity was increased to 6:1 hexane/ethyl acetate and the subsequent fractions afforded (XI). Yield, 0.56 g, 12%. Found: C, 74.6; H, 9.54.Calc. for $C_{12}H_{18}O_2$:C, 74.2; H, 9.28%. NMR data*, δ_c, 26.4 (t, C-5'), 28.4 (t, C-6'), 30.1 (t, C-7'), 31.0 (t, C-4'), 29.3 and 29.9 (q, C-1 and C-5), 39.7 (d, C-3'), 74.4 (d, C-3). 133.1 and 133.4 (d, C-1'and C-2' *not* respectively), 203.8 (s, C-2 and C-4).

δ_H, 1.5 (8H, m, CH_2), 2.12 and 2.15 (3H, s, CH_3), 3.2 (1H, m, C-3'-H), 3.8 (1H, d J(HH) 10 Hz, C-3-H), 5.5 (2H, m, olefinics)

* The primed carbon atoms refer to the cycloheptenyl ring.

Interaction of 3-Bromocyclohexene with Napda

3-Bromocyclohexene (0.65 g, 4.0 mmol) was added dropwise to a stirred suspension of Napda (0.49 g, 4.0 mmol) in toluene (8 ml) and the resulting mixture heated under reflux for 0.5 h. The suspension was cooled, filtered, washed with a little toluene and the toluene evaporated under reduced pressure. ^{1}H NMR analysis on the resulting oil (0.81 g) indicated *ca* 16% conversion to (IV).

Interaction of Napda with $Mo(CO)_4$bipy

A stirred suspension of Napda (0.067 g, 0.55 mmol) and $Mo(CO)_4$bipy (0.2 g, 0.55 mmol) in toluene (5 ml) was heated under reflux for 0.5 h. The mixture was cooled, filtered and the solid washed with a little toluene and dried *in vacuo*. Yield, 0.25 g. The I.R. spectrum indicated a mixture of starting materials. The solid was washed with water and dried *in vacuo*. Yield, 0.19 g, 95%. I.R. analysis indicated that the solid was pure $Mo(CO)_4$bipy.

Interaction of 3-Bromocyclohexene with $Mo(CO)_4$bipy

3-Bromocyclohexene (0.5 g, 3.1 mmol) was added dropwise to a stirred suspension of $Mo(CO)_4$bipy (0.126 g, 0.35 mmol) in toluene (10 ml) and the resulting mixture heated under reflux for 0.5 h. After cooling, the suspension was filtered, washed with a little toluene and the brown solid dried *in vacuo*. Yield, 0.16 g. Infrared and analytical evidence indicated that the dark solid was impure $MoBr_4$bipy.[97] Theoretical maximum yield, 0.2 g. ν, 1600, 1445, 1315 and 765 cm^{-1}. The toluene was removed from the filtrate under reduced pressure to afford a green oil. Yield, 0.28 g. ^1H NMR analysis indicated the presence of 3,3'-bicyclohexenyl together with a mixture of several other organic components.

Interaction of Napda with Complex (I)

A stirred suspension of complex (I) (0.29 g, 0.6 mmol) and Napda (0.075 g, 0.6 mmol) in toluene (5 ml) was heated under reflux for 0.5 h. After cooling, the mixture was filtered and the solid washed with a little toluene and dried *in vacuo*. Yield, 0.25 g. I.R. analysis indicated that the solid was a mixture of Napda and (I). The solid was washed with water and dried *in vacuo* so yielding 0.18 g, 62%, of pure (I). Addition of hexane (20 ml) to the original filtrate caused precipitation of a brown solid. This was collected by filtration, washed with a little hexane and dried *in vacuo*. Yield, 0.03 g. I.R. analysis indicated a mixture of $Mo(CO)_4$bipy and the unknown solid found in the $Mo(CO)_4$bipy catalysed coupling reaction of 3-bromocyclohexene. Solvents were removed from the filtrate under reduced pressure to afford 0.03 g of an oily solid. ^1H NMR analysis on this sample indicated the presence of free 2,2'-bipyridine together with 3,3'-bicyclohexenyl and other organics, but no (IV) was detected.

Interaction of 3-Bromocyclohexene with Compound (I)

3-Bromocyclohexene (0.31 g, 1.92 mmol) was added dropwise to a stirred suspension of complex (I) (0.2 g, 0.426 mmol) in toluene (15 ml) and the resulting mixture heated under reflux for 0.5 h. The mixture was cooled and the solid collected by filtration, washed with a little toluene and dried *in vacuo*. Yield, 0.18 g, 90%. The I.R. spectrum of the solid was identical to that of complex (I). Toluene was removed under reduced pressure from the filtrate to afford 0.15 g of a brown oil whose ^{1}H NMR spectrum indicated the presence of mainly 3-bromocyclohexene together with some unknown material.

Molybdenum-Mediated Coupling of 3-Bromocyclohexene in the presence of Complex (I)

3-Bromocyclohexene (0.65 g, 4.0 mmol) was added dropwise to a stirred suspension of Napda (0.5g, 4.0 mmol) and Complex (I) (0.42 g, 0.9 mmol) in toluene (25 ml) and the resulting mixture heated under reflux for 0.5 h. After cooling,the mixture was filtered, the solid washed with a little toluene and dried *in vacuo*. Yield, 0.6 g. The I.R. spectrum of this solid indicated that the product was mainly compound (I), which was readily purified by washing with water and drying *in vacuo*. Yield, 0.21 g, 50%. Toluene was removed from the original filtrate under reduced pressure to afford a black gum which was chromatographed on a short-path florisil column (100-200 mesh) using hexane as eluant. The resulting fractions were combined and afforded 0.3 g of a colourless oil which was shown by ^{1}H NMR analysis to be an equimolar mixture of 3,3'-bicyclohexenyl (44%) and (IV) (22%).

Molybdenum-Mediated Coupling of 3-Bromocyclohexene in the Presence of Complex (VI)

3-Bromocyclohexene (0.5 g, 3.11 mmol) was added dropwise to a stirred suspension of Napda (0.38 g, 3.11 mmol) and Complex (VI) (0.515 g, 0.69 mmol) in toluene (15 ml) and the resulting mixture heated under reflux for 0.5 h. After cooling, the mixture was filtered and 40-60 petroleum ether (50 ml) was added to the filtrate to effect precipitation of a black solid. This was removed by filtration and the solvents removed from the filtrate under reduced pressure. The resulting oil was chromatographed on 100-200 mesh florisil using hexane as eluant to afford 0.076 g, 30%, of 3,3'-bicyclohexenyl. The polarity of the eluant was increased to 3:1 hexane/ethyl acetate and the following fractions gave 0.13 g, 23%, of (IV).

$Mo(CO)_4$diphos-Mediated Coupling of 3-Bromocyclohexene

3-Bromocyclohexene (1.98 g, 12.3 mmol) was added dropwise to a stirred suspension of Napda (1.5 g, 12.3 mmol) and $Mo(CO)_4$diphos (1.66 g, 2.73 mmol) in toluene (30 ml) and the resulting mixture heated under reflux for 2.5 h. After cooling, the reaction mixture was filtered and the toluene removed from the filtrate to afford a brown gum. Toluene (20 ml) was added to the gum and the insolubles removed by filtration. Evaporation of the filtrate under reduced pressure and subsequent chromatography (100-200 mesh florisil/5:1/hexane/ethyl acetate) on the resulting oil afforded (IV) as the major product. Yield, 1.0 g, 45%. In the absence of $Mo(CO)_4$diphos, less than 28% conversion of 3-bromocyclohexene to (IV) occurs under otherwise identical conditions.

$Mo(CO)_6$-Mediated Coupling of 3-Bromocyclohexene

3-Bromocyclohexene (0.25 g, 1.55 mmol) was added dropwise to a stirred suspension of Napda (0.189, 1.55 mmol) and $Mo(CO)_6$ (0.09 g, 0.34 mmol) in toluene (15 ml) and the resulting mixture heated under relux for 0.5 h. After cooling, the mixture was filtered and the solvent evaporated under reduced pressure to afford a brown oil. Chromatography (100-200 mesh florisil/hexane) yielded 0.03 g, 24%, of 3,3'-bicyclohexenyl. Increasing the polarity of the eluant to 3:1 hexane/ethyl acetate afforded 0.06 g, 22%, of (IV).

Preparation of Dimethylsodiomalonate (dmsm)(XII)

This salt was prepared by a modification of the literature procedure by Reid and Gomf.[116] To a stirred suspension of sodium shot (1.32 g, 57.0 mmol) in hexane (100 ml) was added dropwise, dimethylmalonate (7.62 g, 58.0 mmol). The resulting mixture was heated under relfux for 20 h, cooled and filtered. The solid was washed thoroughly with hexane followed by diethyl ether and dried *in vacuo*. Yield, 7.1 g, 81%. The anhydrous salt gave satisfactory elemental analysis and I.R. data.

Preparation of (XIV)

3-Bromocyclohexene (0.25 g, 1.55 mmol) was added dropwise to a stirred suspension of dmsm (0.24 g, 1.55 mmol) in toluene (5 ml) and the resulting mixture heated under reflux for 0.5 h. After cooling, the reaction mixture was filtered and the solid NaBr washed with a little toluene and dried *in vacuo*. Yield, 0.16 g, 100%. The filtrate was evaporated under reduced pressure to afford the product (XIV) as a yellow oil. Yield, 0.28 g, 85%. Found: C, 62.1; H, 7.41. Calc. for $C_{11}H_{16}O_4$:C, 62.3; H, 7.55%. NMR data* δ_C, 21.2 (t, C-5'), 25.2 (t, C-4'), 26.9 (t,C-6'), 35.6 (d, C-3'), 52.2 (q, C-1 and C-5), 56.9 (d, C-3), 127.9 (d, C-1') 129.5 (d, C-2'),168.8 (s, C-2 and C-4).

δ_H, 1.8 (6H, m, CH_2), 2.85 (1H, m, C-3'-H), 3.25 (1H, d, J(HH)9 Hz, C-3-H), 3.6 (6H, s,-OCH_3), 5.5 (2H, m, olefinics).

* The primed carbon atoms refer to the cyclohexenyl ring.

Molybdenum-Mediated Coupling of 3-Bromocyclohexene in the Presence of (XII)

3-Bromocyclohexene (1.04 g, 6.46 mmol) was added dropwise to a stirred suspension of dmsm (XII) (1.0 g, 6.46 mmol) and $Mo(CO)_4$bipy (0.52 g, 1.43 mmol) in toluene (20 ml) and the resulting mixture was heated under reflux for 0.5 h. After cooling, the reaction mixture was filtered, the toluene evaporated and the resulting oil chromatographed on 100-200 mesh florisil using hexane as eluant. The first fraction afforded 3,3'-bicyclohexenyl. Yield, 0.26 g, 50%. Following fractions contained (XIV). Yield, 0.68 g, 50%.

In a control experiment, under identical conditions but in the absence of $Mo(CO)_4bipy$, compound (XIV) was obtained in 85% yield.

Interaction of 3-Acetoxycyclohexene with $Mo(CO)_4bipy$

3-Acetoxycyclohexene (0.05 g, 0.34 mmol) was added dropwise to a stirred suspension of $Mo(CO)_4bipy$ (0.49 g, 1.35 mmol) in toluene (10 ml) and the resulting mixture heated under reflux for 32 h. The mixture was cooled and filtered. The filtrate afforded a red oil (0.05 g) that contained a complex mixture of organic products.

Molybdenum-Mediated Coupling of 3-Acetoxycyclohexene in the Presence of Napda

3-Acetoxycyclohexene (0.1 g, 0.71 mmol) was added dropwise to a stirred suspension of Napda (0.087 g, 0.71 mmol) and $Mo(CO)_4bipy$ (0.12 g, 0.33 mmol) in toluene (5 ml) and the resulting mixture heated under reflux for 32 h. After cooling, the mixture was filtered and the toluene evaporated to afford a brown oil which on chromatographic separation (100-200 mesh florisil/hexane) afforded 3,3'-bicyclohexenyl. Yield, 0.03 g, 52%. The eluant polarity was increased to 3:1 hexane/ethyl acetate and the subsequent fractions yielded 0.03 g, ca 23%, of impure (IV). In a control reaction, under identical conditions but in the absence of $Mo(CO)_4bipy$, no reaction took place.

Molybdenum-Mediated Coupling of 3-Acetoxycyclohexene in the Presence of dmsm (XII)

3-Acetoxycyclohexene (0.2 g, 1.43 mmol) was added dropwise to a stirred suspension of dmsm (XII)(0.22 g, 1.43 mmol) and $Mo(CO)_4bipy$ (0.166 g, 0.318 mmol) in toluene (10 ml) and the resulting mixture heated under reflux for 44 h. After cooling, the mixture was filtered and the toluene removed from the filtrate under reduced pressure to afford 0.17 g of a red oil. ^1H NMR analysis indicated the major product to be (XIV), ca 56%. In a control reaction, under identical conditions but in the absence of $Mo(CO)_4bipy$, extensive decomposition of reactants took place.

Molybdenum-Mediated Coupling of p -X-$C_6H_4CH_2Br$ (where X=H,-OCH_3 and -NO_2)

The general procedure used is illustrated by reference to benzyl bromide in the presence of Napda and $Mo(CO)_4bipy$. Other reactions were carried out in an analogous manner.

Benzyl bromide (0.5 g, 2.92 mmol) was added dropwise to a stirred suspension of Napda (0.36 g, 2.92 mmol) and $Mo(CO)_4bipy$ (0.53 g, 1.45 mmol) in toluene (25 ml) and the resulting mixture heated under reflux for 0.5 h.

After cooling, the mixture was filtered and the toluene evaporated under reduced pressure to afford a brown oil. Chromatography [silica gel (Merck 60 PF_{254})(i) hexane, X=H; or (ii) 3:1 hexane/ ethyl acetate, X=$-OCH_3$, $-NO_2$)]afforded bibenzyl.[117] Yield, 0.17 g, 64%.

In the absence of Napda, the yield of bibenzyl remained constant and the solid recovered at the end of the reaction was shown by I.R. analysis to contain $MoBr_4$bipy and other unknown carbonyl-containing species.

4,4'-dinitrobibenzyl: Yield, 0.013 g, 3%. Found: C, 61.5; H, 4.71; N, 10.1. Calc. for $C_{14}H_{12}N_2O_4$: C, 61.8; H, 4.41; N, 10.3%. NMR data, δ_c, 36.9(t, CH_2), 123.8 (d, C-2,2', and C-6,6'), 129.3 (d, C-3,3' and C-5,5'), 148.1 (s, C-4,4') δ_H, 3.08 (4H, s, CH_2), 7.25 (4H, d, J(HH) 9 Hz, C-2, 2'-H and C-6,6'-H), 8.15 (4H, d, J(HH) 9 Hz, C-3,3'-H and C-5,5'-H).

4,4'-dimethoxybibenzyl: Yield, 0.09 g, 25%. Found: C, 7.92; H,7.50. Calc. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.44%. NMR data, δ_c(d_6-DMSO), 37.2 (t, CH_2), 55.1 (q,$-OCH_3$) 113.7 (d, C-3,3' and C-5,5'), 129.3 (d, C-2,2' and C-6,6'), 133.8 (s, C-1,1'), 157.8 (s, C-4,4').

δ_H(d_6-DMSO), 2.8 (4H, s, CH_2), 3.7 (6H, s, $-OCH_3$), 6.75 (6.75 (4H, d, J(HH) 9 Hz, C-2,2'-H and C-6,6'-H), 7.05 (4H, d, J(HH) 9 Hz, C-3,3'-H and C-5,5'-H).

PART 2

η^3- Allyl complexes: Formation of novel molybdenum η^3-allyldicarbonyl complexes *via* molybdenum-mediated alkoxycarbonylation reactions

CHAPTER FIVE

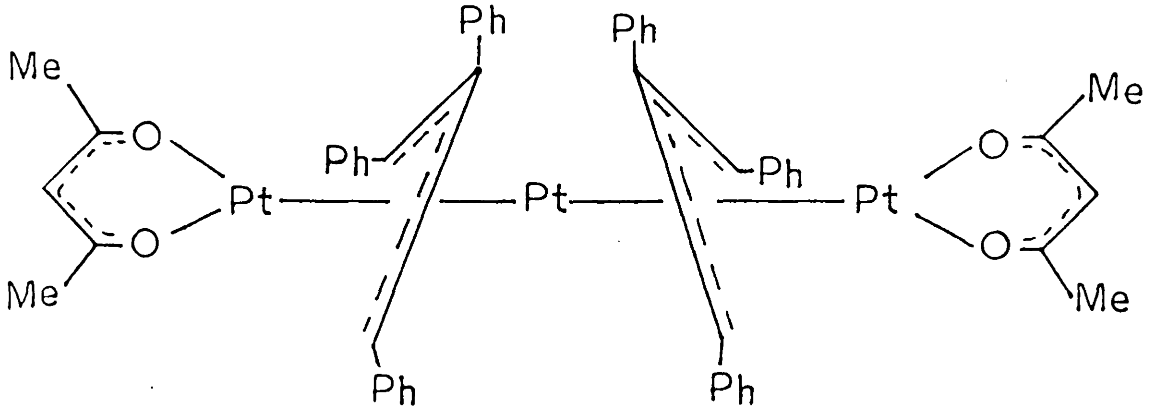
Introduction: η^3-Allyl complexes

5.1. TRANSITION METAL-ALLYL COMPLEXES

Transition metal-allyl compounds are normally classified into three extreme types, which may be differentiated by their mode of allyl to metal bonding.

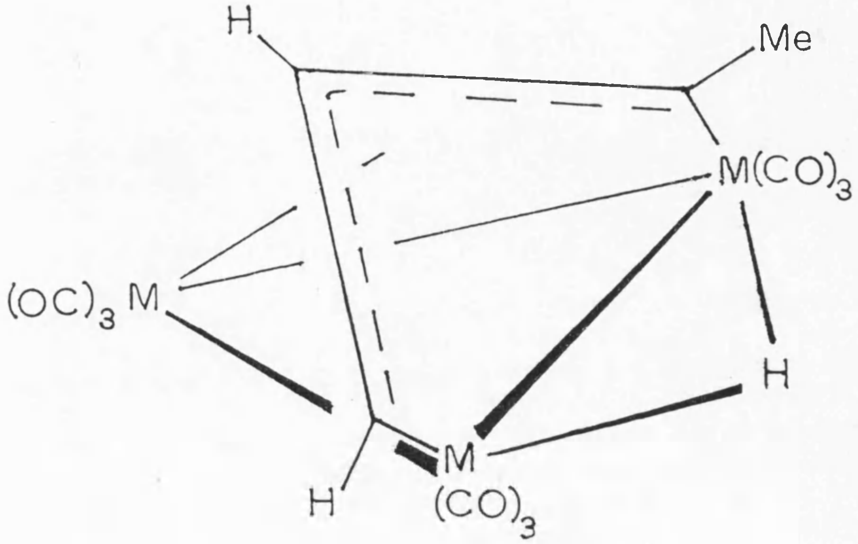
(i) η^1-Allyl: In these compounds, the allyl group acts as a one-electron donor with one terminal carbon atom σ-bonded to the metal atom and a localised double bond between the next two carbon atoms as in $[Mn(\eta^1\text{-}C_3H_5)(CO)_5]$.[118]

(ii) μ-Allyl: These compounds may possess an allyl group that bridges two metal atoms, often being σ-bonded via a terminal carbon to one metal atom and π-bonded via the localised double bond to the other as in $[Pt(\mu\text{-}C_3H_5)pda]_2$[119] (where pda = pentan -2,4-dionate). Alternatively, the allyl group may bridge two metal atoms via its delocalised π-electron cloud as in the platinum complex shown below.[120]



More unusual bridging modes involving allyl ligands are also encountered in other metal-metal bonded complexes[121-123] where π - and σ, π -bonds serve to bridge the metal atoms (Fig. 5.1).

Fig. 5.1. Some Unusual Bridging Modes for Allyl Ligands



M = Ru, Os

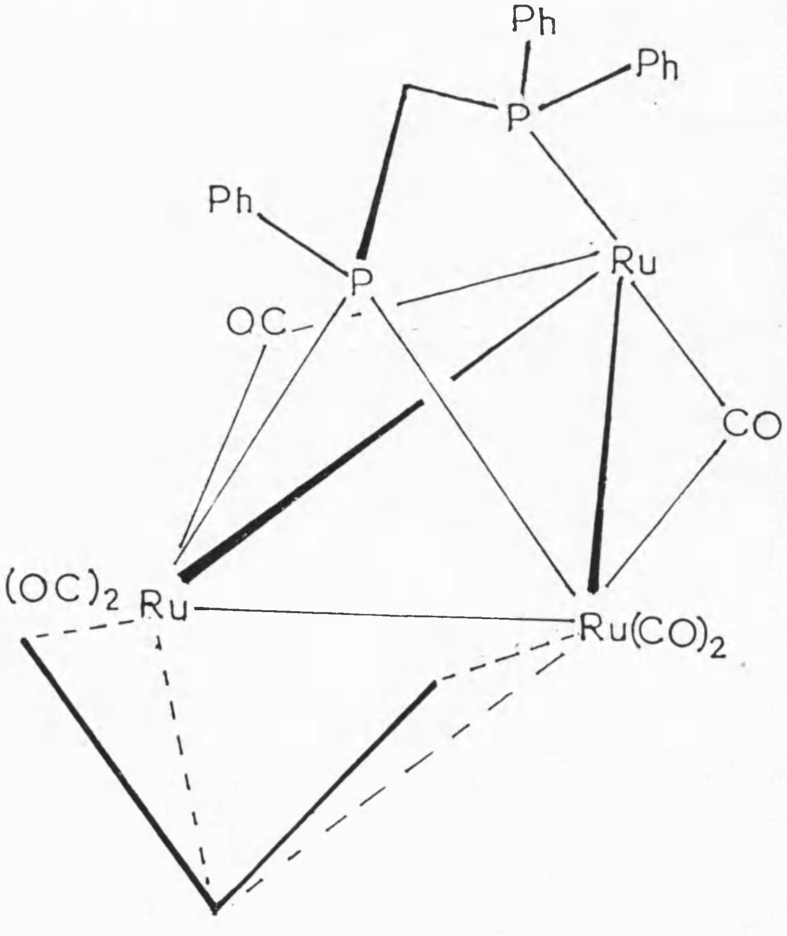
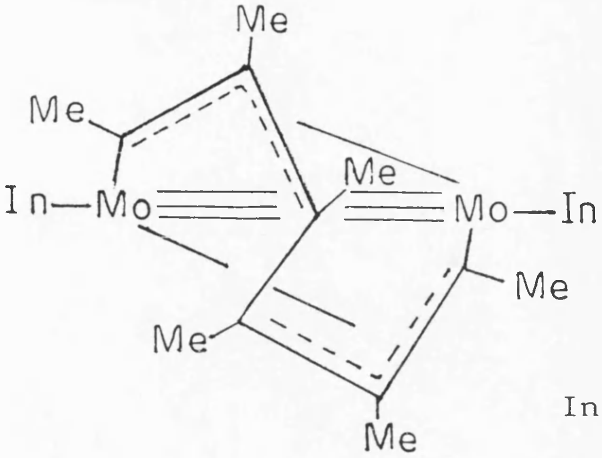


Fig. 5.1 continued



In = η^5-Indenyl

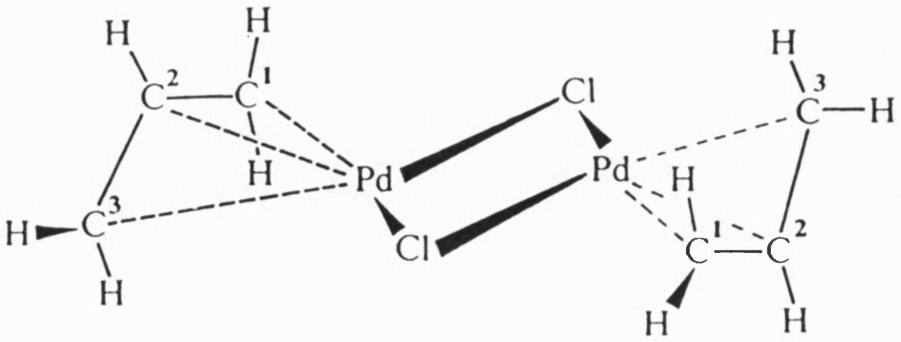
(iii) η^3-Allyl: The bond between the allyl group and the metal atom in η^3-bonded complexes is delocalised and multicentric. All three carbon atoms are involved, although not always equally, and this is often reflected in both the M-C and C-C bond distances, which are very sensitive to both the allyl substituent and to the trans-effect of other ligands in the metal coordination sphere.[124]

For many d-block metals, the mode of bonding of the allyl ligand (η^1/η^3) is dependent upon the electronic requirements of the metal in its aim to achieve a stable 18-electron configuration, but by far the most common, and of particular relevance to the work described in Part 2 of this thesis, are the η^3-allyl transition metal species. Consequently only these will be considered further.

5.2. STRUCTURE AND BONDING IN η^3-ALLYL TRANSITION METAL COMPLEXES

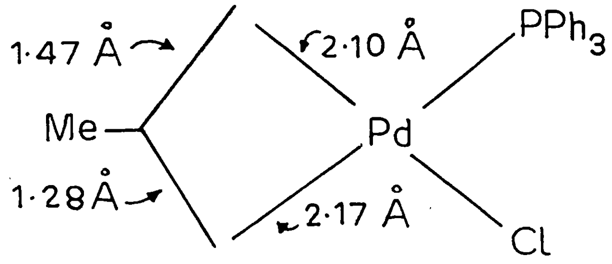
A multicentric mode of bonding in an η^3-allyl complex was first proposed by Smidt and Hafner in 1959.[125] A year later, Heck and Breslow[126] used ^{1}H NMR spectroscopy to show that the allyl group in (η^3-allyl) cobalttricarbonyl was symmetrically bonded to the metal atom, but the palladium dimer $[Pd(\eta^3-C_3H_5)Cl]_2$, was the first η^3-allyl complex to be unequivocally characterised by x-ray diffraction methods.[127-130] The most detailed of these studies[130] showed that the three carbon and five hydrogen atoms of the allyl ligand form a plane orientated at an angle of 111.5° ± 0.9° to the plane containing the $PdCl_2Pd$ unit (Fig. 5.2)

Fig. 5.2. The Orientation of the η^3-Allyl Ligand in $[Pd(\eta^3-C_3H_5)Cl]_2$



The central carbon atom C(2) is tipped away from palladium with a bond distance of 2.108 (9)Å and the terminal carbon atoms C(1) and C(3), are bound essentially equally to the metal at distances of 2.121(7) and 2.132(7)Å respectively. Thus, C(1)-C(2) and C(2)-C(3) are equal to within 0.04 Å, the average bond length being 1.376(15)Å. However, as mentioned earlier, metal π -allyl bonding is very sensitive to steric and/or electronic effects transmitted through the metal atom by additional ligands in the coordination sphere. This is exemplified by $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)Cl]$ [131] which contains a highly asymmetric allyl ligand as shown in Fig. 5.3.

Fig. 5.3. The asymmetric Bonding in $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)Cl$

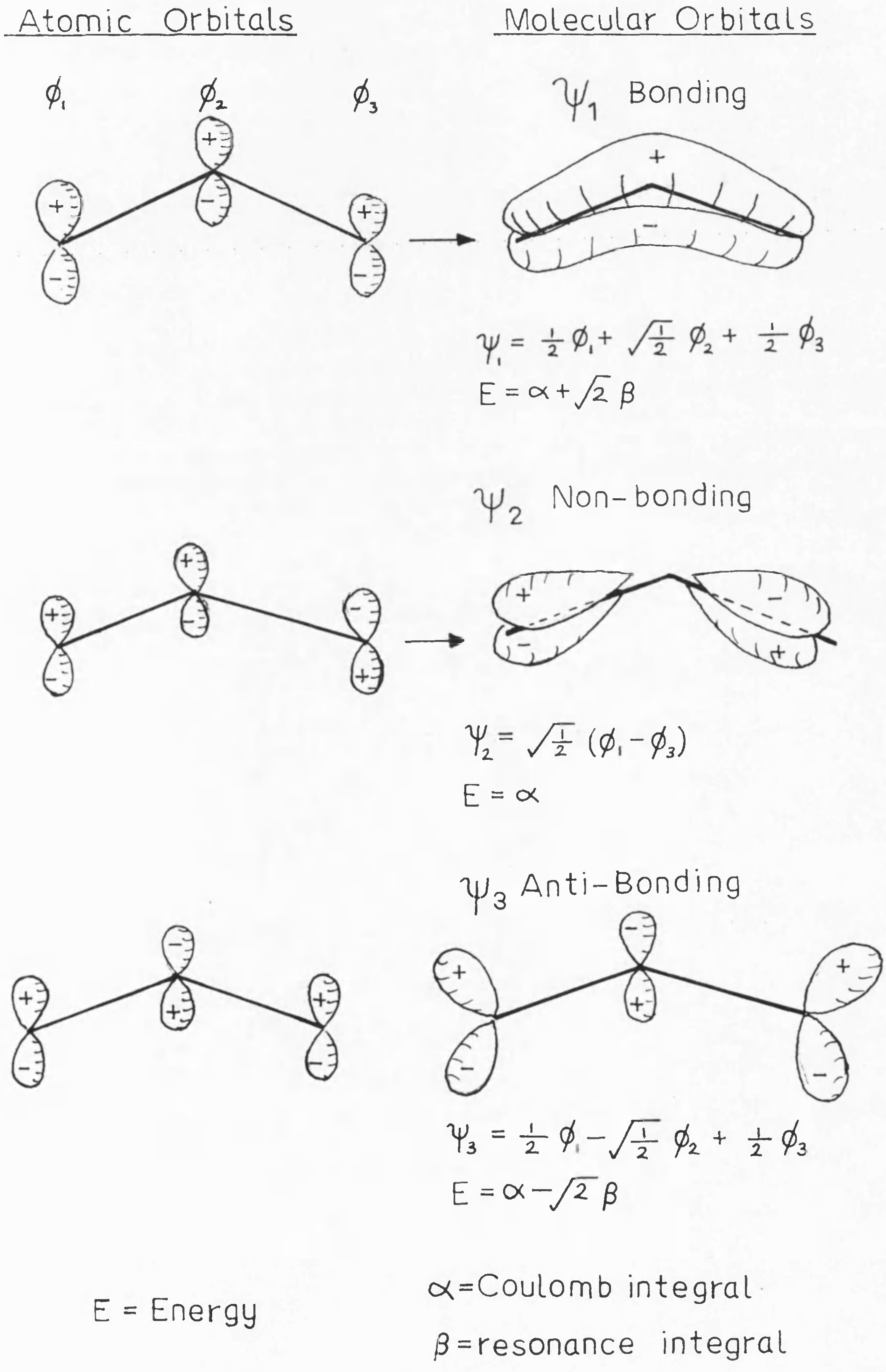


The discovery that the plane of the η^3-allyl ligand was not perpendicular to the usual coordination plane of the molecule was somewhat unexpected, but has since come to be recognised as an inherent structural feature of these compounds. The dihedral or tilt angle χ, is variable but for the majority of η^3-allyl complexes averages at ca 110°, and this feature can be rationalised in terms of the bonding which occurs between the allyl ligand and the metal centre.

BONDING

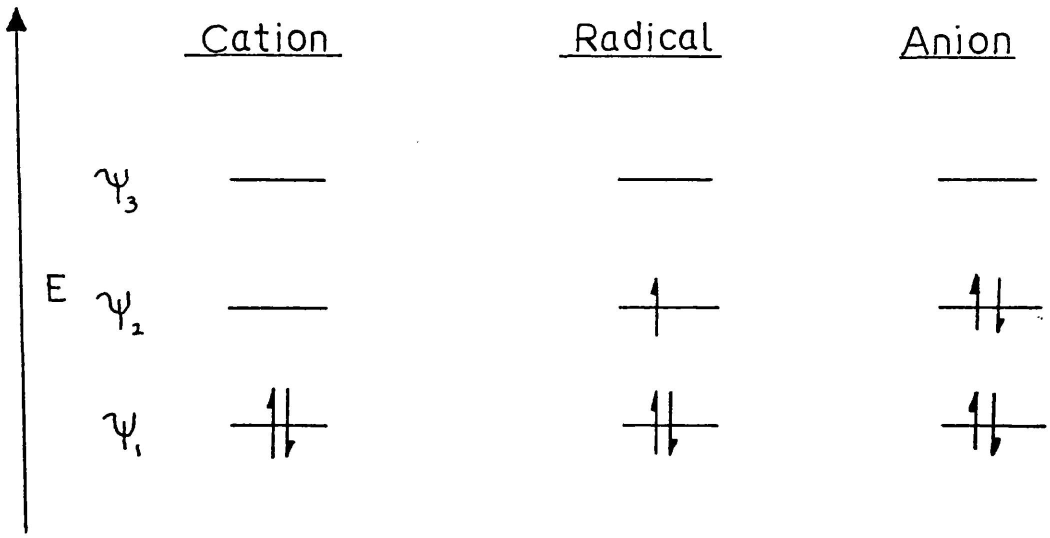
After the σ-bonded framework of the allyl moiety has been constructed, Huckel calculations[132] show that the remaining unused $2p_z$ orbitals of the allyl carbon atoms form three molecular orbitals ψ_1, ψ_2 and ψ_3 (Fig. 5.4) which may interact with appropriate atomic orbitals of the metal atom.

Fig. 5.4. The π-Molecular Orbitals of the Allyl Moiety



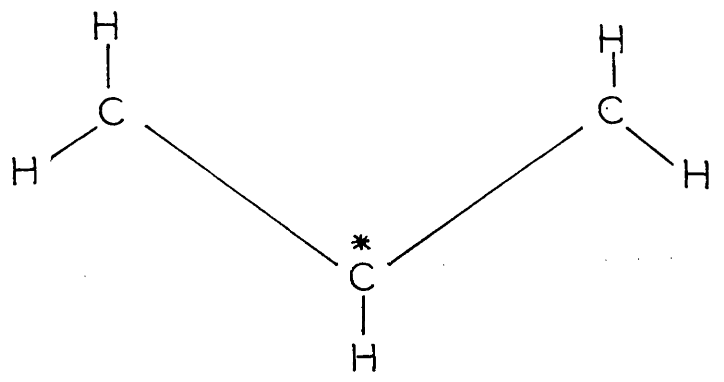
The energies of the allyl cation, radical and anion are similar (to a first approximation) since only non-bonding electrons are involved in deciding the generic outcome, as illustrated in Fig. 5.5.

Fig. 5.5. Electronic Configurations of the Allyl Cation, Radical and Anion



The molecular structure of the free allyl radical, produced by prolysis of 1,5-hexadiene, has been determined very recently by Hargittai et al using electron diffraction methods[133]. The data were consistent with the planar, symmetrical geometry shown in Fig. 5.6.

Fig. 5.6. Molecular Structure of the Allyl Radical

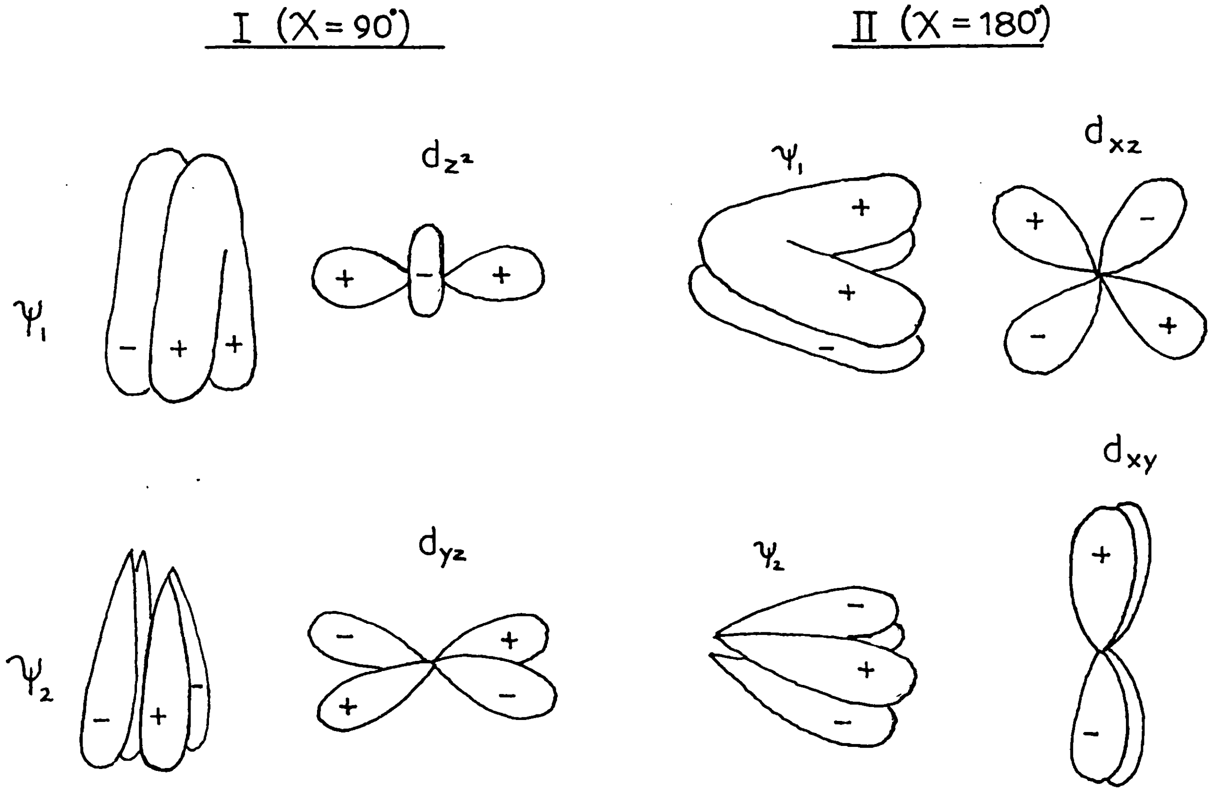


Parameter	Distance (Å), Angle (degrees)
C—C	1·428(13)
C—H	1·069(16)
∠C—C—C	124·6(34)
∠C*—C—H	120·9(34)

Although the η^3-allyl group is normally regarded as a three electron donor ligand, it may on occasions be considered as either a cationic two electron, or anionic four-electron ligand. In order to accommodate this flexibility when electron counting, compensation is made in terms of the formal oxidation state of the metal.

Early theoretical bonding schemes[134] for η^3-allyl-metal systems were based solely on symmetry arguments, with the allyl plane taken to be perpendicular to the coordination plane of the metal. No explanation of the observed tilt ($\chi > 90°$) was made. In 1966, however, Kettle and Mason[135] developed a bonding scheme for $[\mathrm{Pd}(\eta^3\text{-}C_3H_5)\mathrm{Cl}]_2$ which took this structural feature into account. They proposed that the bonding in this system was the result of two distinct overlap mechanisms which differed in the orientation of the bonding interactions of the allyl group with respect to the metal and remaining ligands (Fig. 5.7).

Fig. 5.7. Alternative Orientations for Allyl-Metal Interaction. The Interaction Between Allyl ψ_1 (Top) and ψ_2 (Bottom) Molecular Orbitals are shown for each Orientation

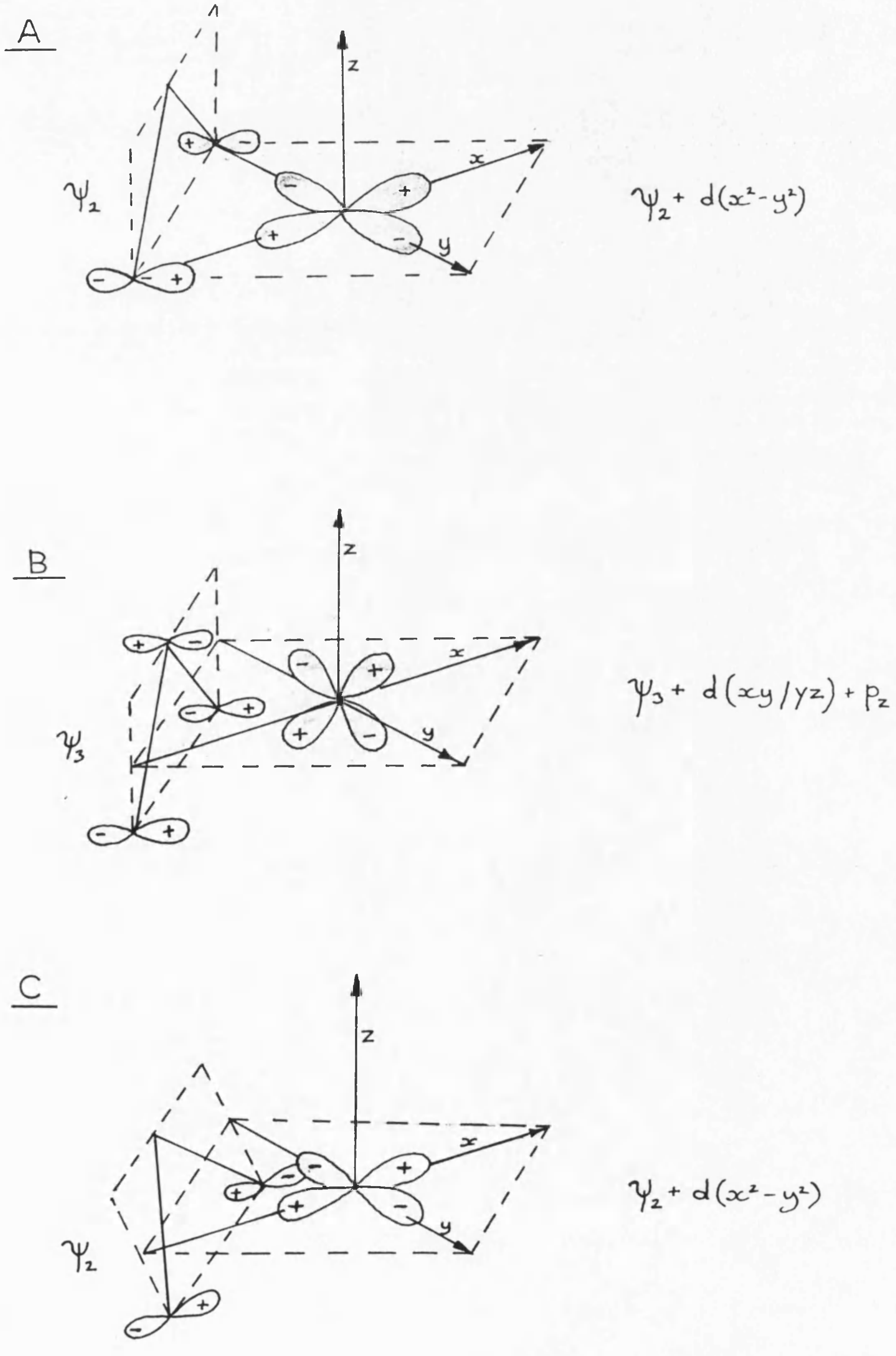


The orientation (I) is such that a line drawn from the palladium atom (z-axis) intersects the allyl plane at $\chi = 90°$. Orientation (II) has the palladium atom co-planar with the allylic ligand. M.O. calculations predicted that a dihedral angle of 114° would maximise the ψ_1, bonding interaction whereas a dihedral angle of 102° would maximise the ψ_2 bonding interaction. Kettle and Mason argued that the ψ_1, molecular orbital of the allyl ligand plays the major role in the palladium-allyl bonding, thus favouring a dihedral angle of ca 114°, which is in close agreement with the experimentally determined value of ca 111°.

However, more recent energy calculations lead to the conclusion that the most important contribution to the allyl-metal bonding comes from the interaction of the ψ_2 molecular orbital of the allyl ligand and the $d_{(x^2-y^2)}$ orbital of the metal[136]. In 1970, Van Leeuwen and Praat developed a modified qualitative bonding scheme which provided a simple explanation for the tilted structure of $[Pd(\eta^3-C_3H_5)Cl]_2$.[136] The most favourable interaction of ψ_2 and $d_{(x^2-y^2)}$ is shown in Fig. 5.8A and has two carbon atoms in the $PdCl_2$ plane. The allyl plane is perpendicular to the xy-plane. The next step is the construction of a configuration suitable for back-donation from filled metal orbitals to the empty ψ_3 orbital. This latter orbital has a nodal plane perpendicular to the allyl plane intersecting the two carbon-carbon bonds (Fig. 5.8B). Maximum overlap of ψ_3 and the palladium orbital (taken as a hybrid of d_{xz}, d_{yz}

and p_z) occurs when the allyl-nodal plane coincides with the metal-nodal plane (xy). This is illustrated in Fig. 5.8B where the two terminal carbon atoms are placed below the xy-plane. However, there is now a considerable decrease in the overlap of the most important bonding interaction (Fig. 5.8A). This is remedied by tilting the allyl plane such that the terminal carbons give a good overlap with $d(x^2-y^2)$ and the nodal (xy) plane still intersects the two nodes of the ψ_3 orbital (Fig. 5.8C). Since the central allyl carbon atom is now closer to the palladium atom than as shown in Fig. 5.8A, the tilting also increases the interaction of ψ_1, with empty metal orbitals.

Fig. 5.8. Van Leeuwen and Praat's Allyl-Metal Bonding Scheme



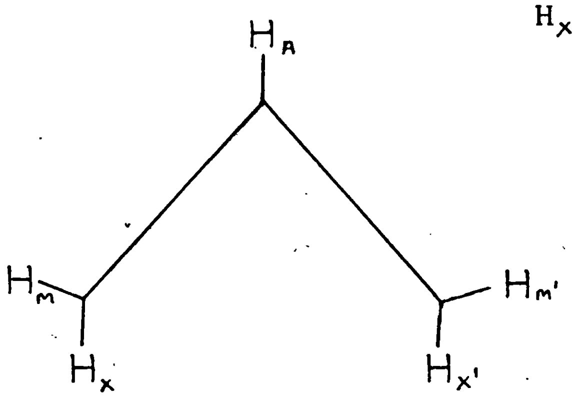
5.3. PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

An η^3-C_3H_5 group may possess up to five magnetically non-equivalent hydrogen atoms in complexes of low symmetry, but an η^3-C_3H_5 group in a symmetrical environment will possess three groups of magnetically distinct hydrogen atoms, H_A, H_M and H_X (Fig. 5.9).

Fig. 5.9 Magnetically Non-Equivalent Hydrogen Atoms of a Symmetrical η^3-C_3H_5 Group

H_M and H_M' = H_{syn}

H_X and H_X' = H_{anti}



Although each proton of the M group and each proton of the X group have the same chemical shift, each of the M protons do not couple equally with each of the X protons and vice versa. The spin system is thus classified as AMM'XX', although this patterm is rarely observed in a ^1H NMR spectrum since J_{MX} , $J_{M'X'}$ and $J_{MX'}$, $J_{M'X}$ are small and often not detected. The majority of published spectral data have therefore been explained in terms of an AM_2X_2 spin system. Fig. 5.10 shows a theoretical line pattern (not to scale) for such a system together with typical values of the ^1H NMR parameters for the η^3-C_3H_5 moiety.

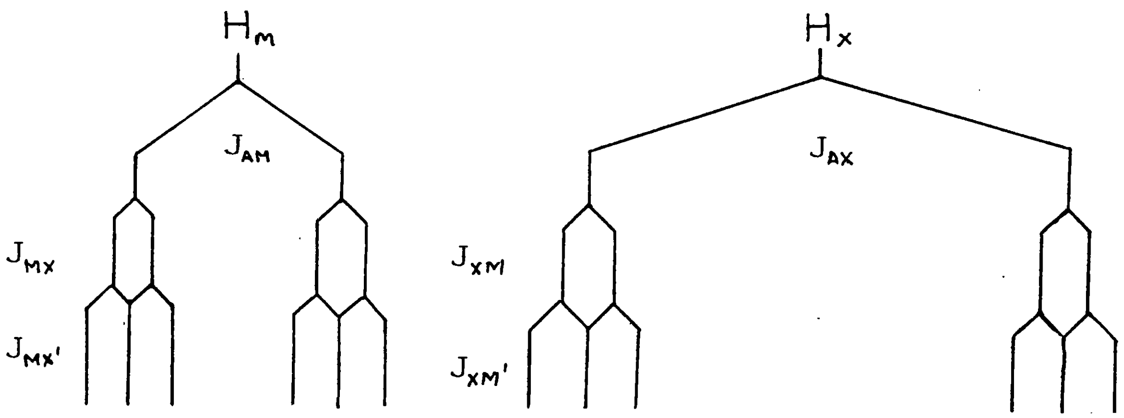
Fig. 5.10 The AM_2X_2 Spin System

	A	M	X
Typical chemical shifts (δ)	6.5–4	5–2.5	4–1
Typical J values (Hz)		7	12
Relative area	1	2	2

The doublet at high field is assigned to the H_x protons on the basis that trans-coupling (J_{AX}) is greater than cis-coupling (J_{AM}). Such an assignment is also in agreement with the structural configuration of the η^3-C_3H_5-metal entity, since H_x protons are subject to the greatest shielding by the metal and consequently resonate at higher field.

Although as previously mentioned, the values of J_{MX}, $J_{M'X'}$ and $J_{MX'}$, $J_{M'X}$ are small, they are not zero, and under high resolution conditions these long-range couplings may be detected. Each line of the two doublets belonging to H_M and H_X may be further split into triplets, caused by the apparent equivalence of J_{MX} and $J_{MX'}$ which are both in the order of 1 Hz[137] (Fig. 5.11)

Fig. 5.11 Fine Splitting of H_M and H_X



According to Karplus,[138] J_{MX} is small because the angle between H_M and H_X is close to 120° (a value consistent with sp^2 hybridisation of the carbon atom) and $J_{MX'}$ is similarly small because it is a long range effect.

Substitution of the H_A proton by another group generally leads to spectral simplification whereas substitution of a terminal proton H_M or H_X leads to more complex spectral patterns, which can be interpreted in terms of syn- or anti-H replacement.[124]

5.4. 13-CARBON NUCLEAR MAGNTIC RESONANCE SPECTROSCOPY

In recent years, the amount of published ^{13}C NMR data for η^3-allyl complexes has increased considerably[139] and ^{13}C chemical shifts of η^3-allyl ligands can be quite characteristic. For unsubstituted derivatives, the terminal carbon atoms have chemical shifts in the range 40-80 p.p.m. and the central carbon resonance is observed at lower field, characteristically in the range 70-120p.p.m. A methyl substituent has a deshielding influence[139-144] and low field shifts compared with the parent η^3-C_3H_5 derivative are commonly observed.

Relatively few $J(^{13}C-^{1}H)$ values have been reported, but they are normally in the range 155-180 Hz [139,141,145-148] A recent study of $J(^{13}C-^{13}C)$ coupling constants[148] for η^3-allyl complexes of zirconium, chromium, molybdenum, tungsten, nickel and platinum has shown that $J(^{13}C-^{13}C)$ lies in the range 40-50 Hz depending on the bonding situation. The variations of $J(^{13}C-^{13}C)$ have been rationalised in terms of the relative weighting of donor and acceptor bonding. This contrasts with values of $J(^{13}C-^{1}H)$ and $J(^{1}H-^{1}H)$ which, in addition to the metal-allyl bonding, are markedly influenced by the deviations of the protons from coplanarity with the allyl carbon skeleton. A direct linear correlation between $J(^{13}C-^{13}C)$ and the corresponding bond lengths in allyl moities has also been demonstrated.[148]

As well as bonding investigations, ^{13}C NMR spectroscopy has also been used to establish the nature of η^3-allyl intermediates, as in the nickel-catalysed transformations of 1,3-dienes[149] discussed earlier in Chapter 1.3 and 1.4 of this thesis.

5.5. FLUXIONAL η^3-ALLYL TRANSITION METAL COMPLEXES

Complexes possessing η^3-allyl ligands are often stereochemically non-rigid or fluxional.[150] This dynamic behaviour may be attributed to one of three common types of rearrangement, namely (i) syn-anti-exchange, (ii) syn-syn, anti-anti-exchange or (iii) interconversion between conformers. These rearrangements may involve either a motion of the η^3-allyl group itself, or the non-rigidity of other parts of the molecule (eg. a pseudorotation).

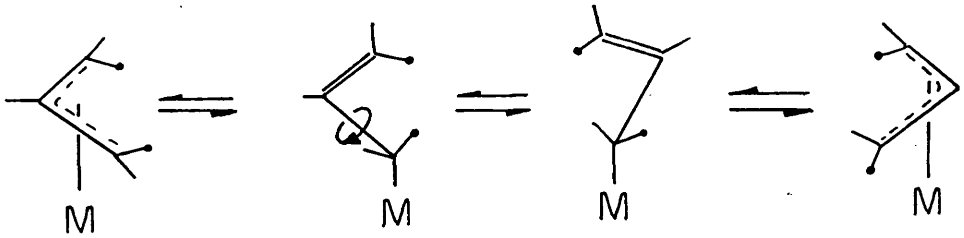
(i) Syn-Anti-Exchange

Some η^3-allyl complexes give misleadingly simple ^{1}H NMR spectra which indicate that all the terminal hydrogens of the allyl ligand are equivalent. The observed spectra are typical of AX_4 spin systems. Many isoleptic η^3-allyl complexes e.g. $M(\eta^3-C_3H_5)_4$ (M=Zr,[151,152] Th[22]) exhibit such spectra at and above room temperature but the spectra become typical of normal AM_2X_2 spin systems at low temperatures.

The equivalence of the terminal protons at ambient temperatures is obviously due to some rapid interchange of syn- and anti- hydrogens and the most widely accepted mechanism[153] involves a rapid $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$

interconversion of the allyl ligand. The syn and anti protons achieve equivalence by a rotation about the carbon-carbon single bond in the short lived η^1-allyl intermediate, followed by reversion to an η^3-allyl complex (Fig. 5.12).

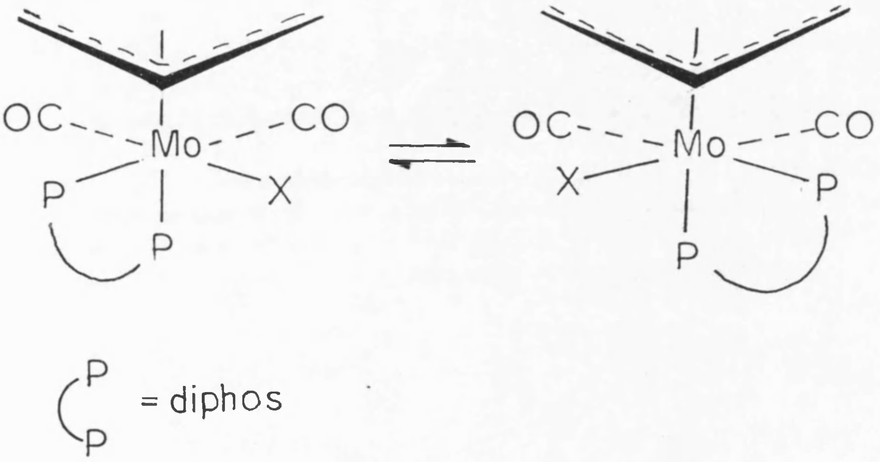
Fig. 5.12 Syn-Anti-Exchange Mechanism



(ii) Syn-Syn-, Anti-Anti- Exchange

This type of exchange is most easily detected for complexes of low symmetry in which the terminal carbon atoms of the η^3-allyl ligand are inequivalent and an AGMPX spin patterm is observed at low temperatures. On raising the temperature, the AGMPX spin pattern simplifies to an AM_2X_2 system, indicating the syn-syn- and anti-anti-protons become equivalent. This may be achieved by a simple rotation of the allyl group about an axis passing through the metal, or alternatively by some pseudorotation by other ligands which by producing a time-averaged ligand environment for the terminal protons, results in the same experimental observation. In many instances, it is impossible to distinguish between the mechanisms, although Faller et al, by using a combination of physical techniques, have deduced that [Mo(η^3-C_3H_5)(CO)$_2$(diphos)X] (X=Cl, Br or I) undergoes a pseudorotation or "trigonal twist" rather than rotation of the allyl ligand (Fig. 5.13).[154]

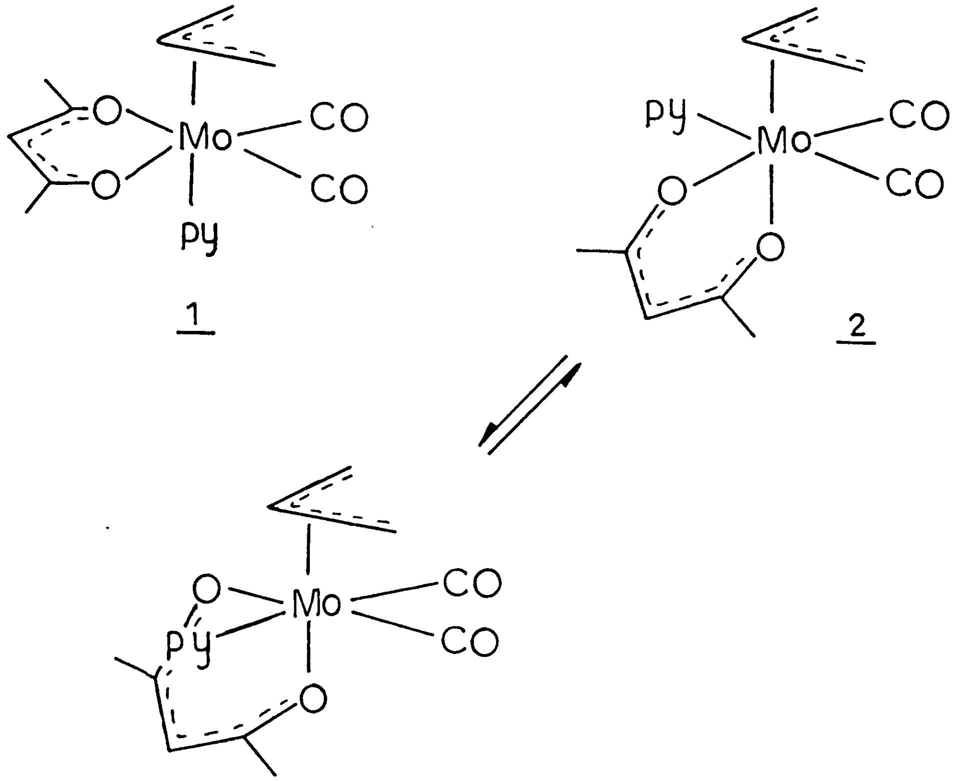
Fig. 5.13 Pseudorotation or "Trigonal Twist"



This process involves the pseudorotation of the triangular face containing the halide and diphos ligands with respect to the face containing the η^3-allyl and carbonyl groups.

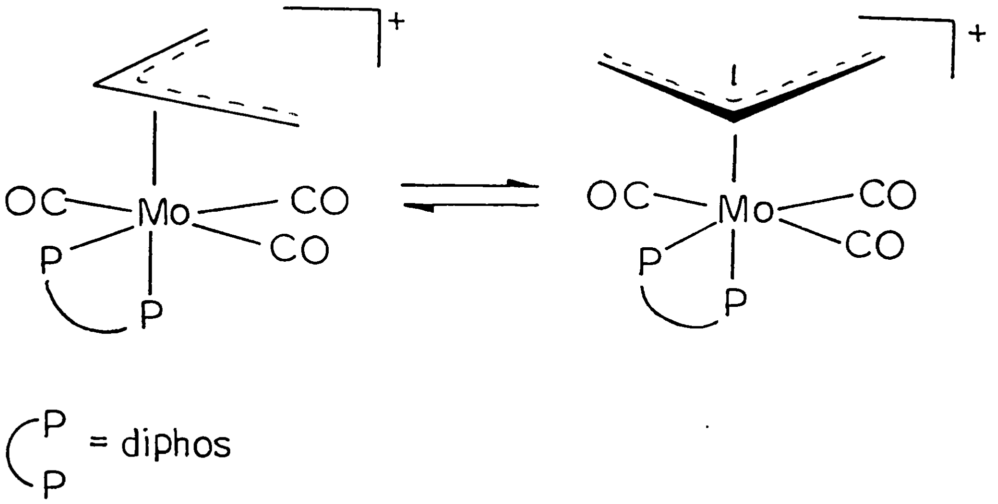
Variable temperature ^1H and ^{13}C NMR spectra have been reported for the related complex [Mo(η^3-C_3H_5)(CO)$_2$(pda)(py)][155], which possesses a similar solid state structure to that of [Mo(η^3-C_3H_5)(CO)$_2$(diphos)Cl], and so contains no plane of symmetry. For this complex however, two isomers ((1) and (2) in Fig. 5.14) were identified in the limiting low temperature ^1H NMR spectrum, giving AM_2X_2 and AGMPX spin patterns respectively. Isomer (1) is temperature invariant whereas isomer (2) undergoes a pseudo-trigonal twist at elevated temperatures with a subsequent change in its ^1H NMR spectrum from AGMPX to AM_2X_2. However, at even higher temperatures, the two AM_2X_2 spin patterns due to (1) and (2) coalesce and give a single AM_2X_2 pattern, indicating a rapid interconversion of the two isomers. This observation led the authors to suggest that a complete rotation of the ligand face formed by the pyridine and pda ligands occurs at elevated temperatures.

Fig. 5.14 The Two Isomers of $[Mo(\eta^3-C_3H_5)(CO)_2(pda)(py)]$ which Co-Exist in Solution at Low Temperatures



Restricted rotation of the η^3-allyl ligand about the allyl-metal bond[156] has been invoked to explain the <u>syn</u>-<u>syn</u>, <u>anti</u>-<u>anti</u> exchange observed in the room temperature ^1H NMR spectrum of $[Mo(\eta^3-C_3H_5)(CO)_3(diphos)][PF_6]$ (Fig. 5.15).

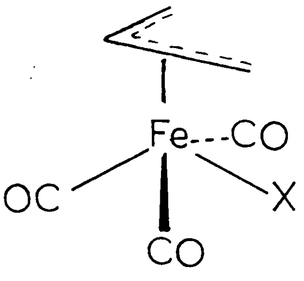
Fig. 5.15 <u>Restricted Rotation of an η^3-Allyl Ligand</u>



(iii) <u>Conformational Isomerism</u>

At room temperature, the ^1H NMR spectrum of $[Fe(\eta^3-C_3H_5)(CO)_3X]$ [157] (X=Cl, Br or I) consists of two overlapping AM_2X_2 spin patterns indicating the presence of two isomers (3) and (4) (Fig. 5.16). (The solid state structure of $[Fe(\eta^3-C_3H_5)(CO)_3X]$ has the configuration (3)[158]).

Fig. 5.16 Two Isomers of $[Fe(\eta^3\text{-}C_3H_5)(CO)_3X]$ (X=Cl, Br or I)



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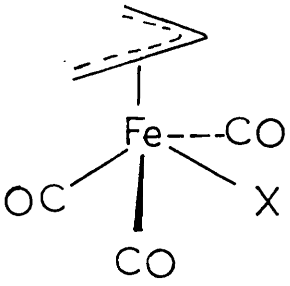

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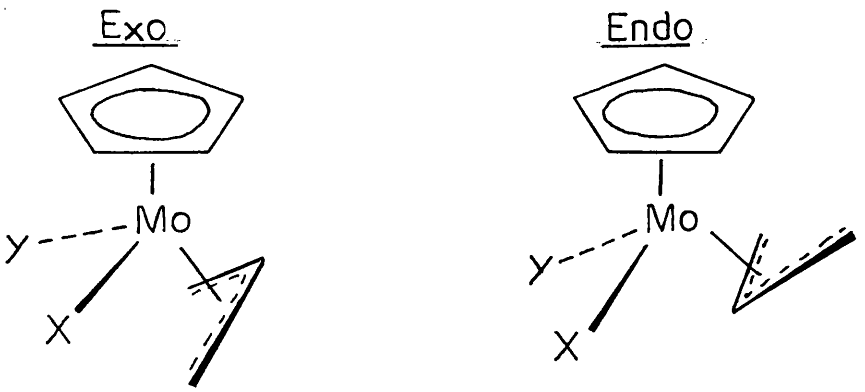
In this instance, the temperature dependence of the interconversion of the isomers cannot be determined due to their decomposition above 25°C, but for other systems including $[Fe(\eta^3\text{-}C_3H_5)_2(CO)_2]$[157] and $[Mo(\eta^3\text{-}C_3H_5)(CO)_2Cp]$[159] the two AM_2X_2 patterns can be observed to coalesce to a single AM_2X_2 pattern at high temperatures indicating rapid interconversion. In both cases, the spectroscopic evidence is consistent with a rotation of the η^3-allyl ligand about the metal-allyl axis.

^{95}Mo NMR spectroscopy has been used by Faller and Whitmore[160] to determine the exo/endo-isomeric ratio in solutions containing the complexes $[Mo(\eta^3\text{-allyl})(X)(Y)Cp]$ (where X=Y=CO, X=NO$^+$ and Y=CO, and X=NO$^+$ and Y=I$^-$) (Fig. 5.17). The ^{95}Mo nucleus in the exo-isomer was found to resonate at higher field than that in the corresponding endo-isomer in all cases examined, which included alkyl and halogeno substituted η^3-allyl moieties.

Fig. 5.17 Exo- and Endo- Isomers of $[Mo(\eta^3-C_3H_5)(X)(Y)Cp]$



The ^{95}Mo chemical shifts for the nitrosyl carbonyl complexes occur in the range -1326 to -1576 p.p.m., at lower field than their dicarbonyl analogues, indicating that the molybdenum nucleus is deshielded to a greater extent upon replacement of a CO ligand with NO^+. This observation can be rationalised by the increased propensity of the nitrosyl ligand for π-back donation compared to the carbonyl group,[161] thus removing electron density from the molybdenum nucleus and thereby causing the observed downfield shift. The nitrosyl iodide complexes have ^{95}Mo chemical shifts at even lower field.

M.O. calculations[162] on structurally idealised molecules of $[Mo(\eta^3-C_3H_5)(CO)_2Cp]$ indicate the energy difference between endo- and exo- forms to be small with a barrier to rotation of the allyl group of ca 190 kJ mol^{-1}. Similar calculations on $[Mo(\eta^3-C_3H_5)(CO)(NO)Cp]$ indicate a barrier to rotation of ca 370 kJ mol^{-1}, with energy minima for the endo- and exo-conformations.

5.6. PSEUDOOCTAHEDRAL η^3-ALLYLDICARBONYL COMPLEXES OF GROUP VI TRANSITION METALS

Numerous η^3-allyl complexes of the Group VI transition metals have been prepared and characterised. These range from the isoleptic complexes such as $Cr(\eta^3-C_3H_5)_3$[22] and $M(\eta^3-C_3H_5)_4$ (M=Mo and W)[22], to those containing several different ligands such as $[M(\eta^3-C_3H_5)(NO)(I)Cp]$ (M=Mo[160] and W[124]). Of particular relevance to the work described in Part 2 of this thesis are the η^3-allyldicarbonyl complexes of general formula $[M(\eta^3\text{-allyl})(CO)_2L_2X]^{n \pm o}$, where L_2=one bidentate or two monodentate ligands and X=halide, pseudohalide or Lewis base. These compounds are readily prepared by one or more of four routes as described below:

(a) Direct allylic oxidation of preformed $M(CO)_4L_2$[83,84] or $M(CO)_5L_2L'$[84] (where M=Mo, L_2=2,2'-bipyridyl, di(2-pyridyl)amine or 1,10-phenanthroline; M=W, L_2=di(2-pyridyl)amine or 1,10-phenanthroline; L'=pyridine) (Eq. 5.1).

Eq. 5.1

$$Mo(CO)_4bipy + C_3H_5Cl \xrightarrow{MeCN} 2CO + [Mo(\eta^3-C_3H_5)(CO)_2(bipy)Cl]$$

(b) Reaction of $M(CO)_6$, (M=Mo or W) and allyl halides or pseudohalides in the presence of N- or O- donor ligands such as diamines,[84] diethers[163] or acetonitrile[84,164,165] (Eq. 5.2).

Eq. 5.2

$$Mo(CO)_6 + C_3H_5Cl \xrightarrow{MeCN} [Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2Cl] + 2CO$$

Displacement of weakly bonded ligands from the resulting complexes, particularly the nitrile species $[M(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2X]$, provides a convenient route to a variety of N- [165-167], P- [168], or As- [169] donor ligand analogues, many of which cannot be prepared directly from $M(CO)_4L_2$ (Eq. 5.3).

Eq. 5.3

$$[Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2Cl] + \text{diphos} \longrightarrow [Mo(\eta^3\text{-}C_3H_5)(CO)_2(\text{diphos})Cl] + 2\,MeCN$$

(c) Bridge-splitting reactions of $[NEt_4][Mo_2(\eta^3\text{-allyl})_2(CO)_4Cl_3]$ [170] with pyridine, 2,2'-bipyridyl or ethylenediamine (Eq. 5.4)

Eq. 5.4

$$[NEt_4][Mo(CO)_5Cl] + 2\text{-}MeC_3H_4Cl \xrightarrow[-\frac{1}{2}NEt_4Cl]{-3CO}$$

$$\tfrac{1}{2}[NEt_4][Mo_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2(CO)_4Cl_3] \xrightarrow{en}$$

$$[Mo(\eta^3\text{-}2\text{-}MeC_3H_4)(CO)_2(en)Cl] + \tfrac{1}{2}NEt_4Cl$$

(d) Reaction of $[M(CO)_3L_2X]^-$ anions (M=Cr, Mo or W) with allyl compounds[84,115,171] (Eq. 5.5)

Eq. 5.5

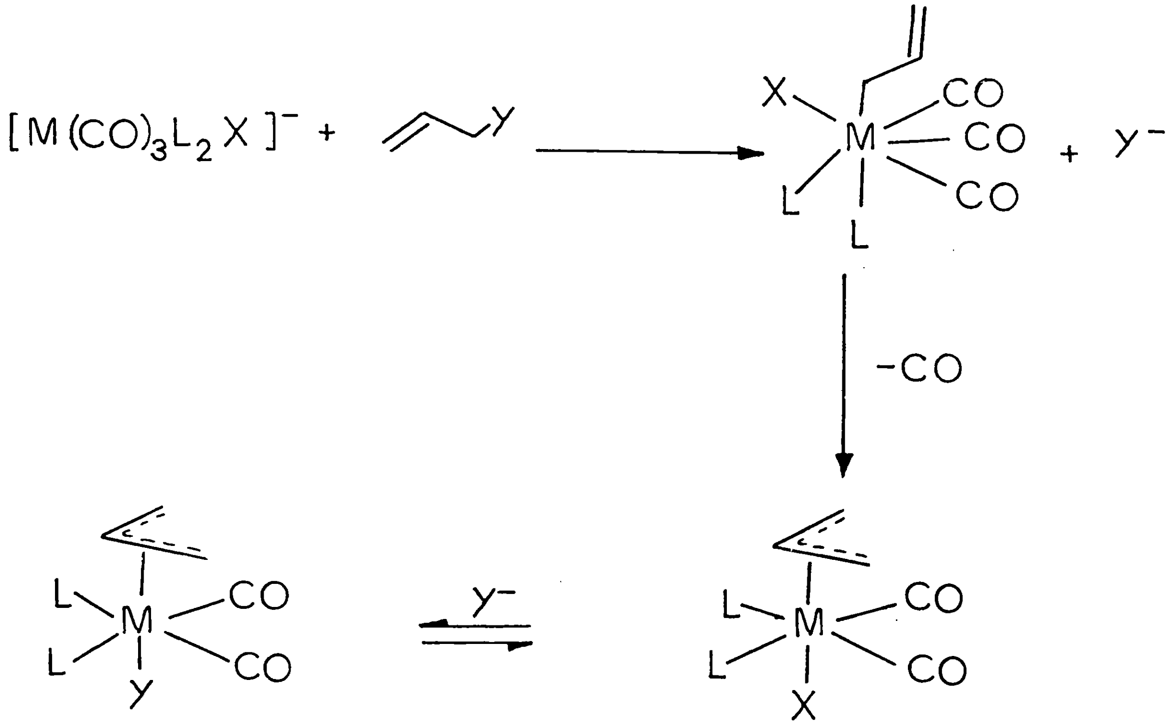
$$W(CO)_4bipy + PPh_4Cl \xrightarrow{-CO}$$

$$[PPh_4][W(CO)_3(bipy)Cl] + C_3H_5Cl \longrightarrow$$

$$[W(\eta^3\text{-}C_3H_5)(CO)_2(bipy)Cl] + PPh_4Cl$$

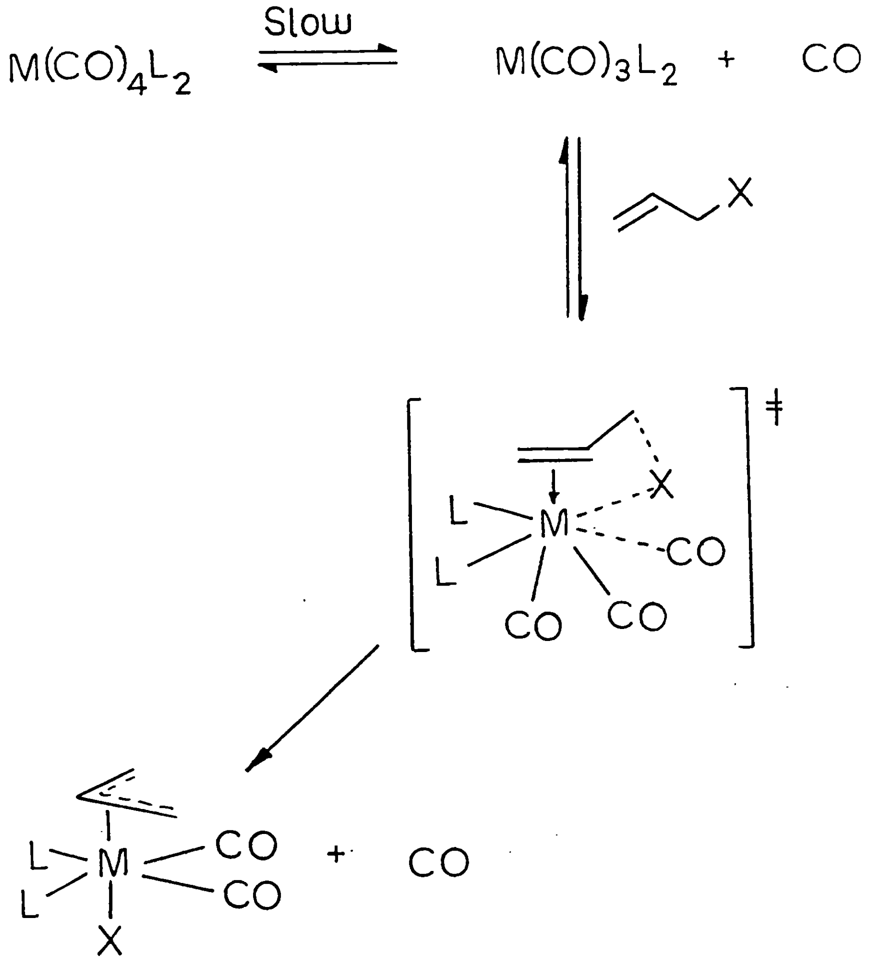
Reaction (d) is especially important as it provides a route to the little known chromium analogues.[171] The very reactive metallate anions $[M(CO)_3L_2X]^-$ probably undergo oxidative addition of allyl compounds via an S_N2 process (Scheme 5.1), followed by a subsequent $\eta^1 \rightarrow \eta^3$ rearrangement with concomitant loss of CO.[115]

Scheme 5.1



Oxidative addition of allyl compounds to the tetracarbonyl complexes $M(CO)_4L_2$ is believed to proceed via an initial rate determining dissociative step, followed by coordination of the allyl compound and elimination of CO to afford the η^3-allyldicarbonyl complex[172] (Scheme 5.2).

Scheme 5.2

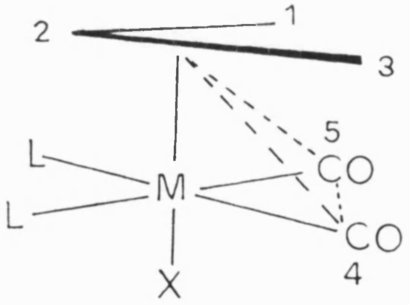


The resulting η^3-allyldicarbonyl complexes are stable to further CO substitution, although the halide X may be replaced readily by other anions such as SCN^-, RCO_2^- or $C_6H_5S^-$ or by neutral donor ligands such as PPh_3, $AsPh_3$ or pyridine[173] in the presence of non-coordinating anions (PF_6^-, BF_4^-) to yield cation species.

Solid State Structures

Crystal structure determinations have been carried out on a large number of compounds of the type $[M(\eta^3\text{-allyl})(CO)_2L_2X]$ [154,155,163,174-179] but most studies have centred on the molybdenum compounds. Notably consistent features in their respective geometries are firstly the pseudooctahedral environment of the metal and secondly the fac-arrangement of the η^3-allyl and cis-dicarbonyl ligands (Fig. 5.18

Fig. 5.18 The Fac-Arrangement of the η^3-Allyl and CO Ligands in $M(\eta^3\text{-allyl})(CO)_2L_2X)$



In all but one case,[93] the crystal structure determinations show that the open face of the allyl ligand points toward the cis-dicarbonyl grouping and recent M.O. calculations[89,180] indicate the rotational preference for the allyl group has its roots in the strong $d_\pi - \pi^*_{co}$ back-bonding to the cis-carbonyl ligands. Table 5.1 list the relevant structural parameters of the $(\eta^3\text{-allyl})(CO)_2$ (where allyl=C_3H_5 or 2-MeC_3H_4) unit in a number of relevant complexes.

TABLE 5.1: THE GEOMETRY OF THE $(\eta^3\text{-ALLYL})M(CO)_2$ UNIT IN DIFFERENT STRUCTURES*

COMPOUND	REF.	STR.≠	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$(\eta^3\text{-}C_3H_5)Mo(CO)_2(dme)(CF_3CO_2)$	163	S	1.45	1.45	114	2.34	2.16	2.34	1.90	79
$(\eta^3\text{-}C_3H_5)W(CO)_2(dme)(CF_3CO_2)$	163	S	1.36	1.36	123	2.29	2.07	2.29	1.84	75
$(\eta^3\text{-}C_3H_5)Mo(CO)_2(bipy)NCS$	175	S	1.46	1.42	116	2.29	2.20	2.35	1.93	78
$(\eta^3\text{-}C_4H_7)Mo(CO)_2(phen)NCS$	176	S	1.45	1.40	117	2.32	2.27	2.35	1.97	83
$[(\eta^3\text{-}C_3H_5)Mo(CO)_2(bipy)py][BF_4]$	174	S	1.37	1.47	111	2.31	2.28	2.29	1.99	78
$(\eta^3\text{-}C_3H_5)W(CO)_2(C_6H_{11}NCH.NCHC_6H_{11})Br$	177	S	1.43	1.43	114	2.33	2.20	2.33	1.99	80
$(\eta^3\text{-}C_4H_7)Mo(CO)_2(C_6H_{11}NCH.NCHC_6H_{11})Cl$	178	S	1.42	1.42	112	2.33	2.27	2.33	1.98	81
$(\eta^3\text{-}C_3H_5)Mo(CO)_2(pda)py$	155	U	1.40	1.37	115	2.30	2.20	2.31	1.95	80
$(\eta^3\text{-}C_3H_5)Mo(CO)_2(salal)py$	179	U	1.37	1.42	115	2.32	2.24	2.34	1.91	79
$(\eta^3\text{-}C_3H_5)Mo(CO)_2(diphos)Cl$	154	U	1.40	1.40	116	2.34	2.22	2.35	1.96	78

* See Fig. 5.18 for numbering sequence. Bond lengths in Å, angles in degrees.

≠ S = Symmetrical, U = Unsymmetrical (see fig. 5.25).

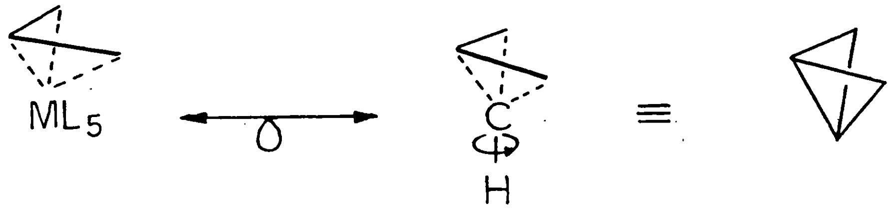
HEADINGS: (1) C(1)-(2); (2) C(2)-(3); (3) C(1)-C(2)-C(3); (4) M-C(1); (5) M-C(2); (6) M-C(3); (7) Mean of M-C(4) & M-C(5)
(8) C(4)-M-C(5)

The Rotational Preference for the η^3-Allyl Ligand

Since in all but one case,[93] the η^3-allyl ligand always orientates its open face toward the two carbonyl ligands, an electronic stabilisation factor for this particular geometry is indicated. M.O. calculations have been carried out for $[Mo(\eta^3-C_3H_5)(CO)_2X_3]$ (where X=Cl or HCN) based on a simple model which assumes perfect octahedral symmetry and an orientation of the planar allyl ligand parallel to the plane containing the two carbonyl and two X ligands.[89]

Consider firstly analysing the problem in terms of the isolobal relationships developed by Hoffmann and co-workers.[181] The d^4ML_5 fragment is isolobal with CH^+. Therefore, the $ML_5(\eta^3-C_3H_5)$ group is isolobal with $(CH^+)(C_3H_5^-)$ or bicyclobutane (Scheme 5.3).

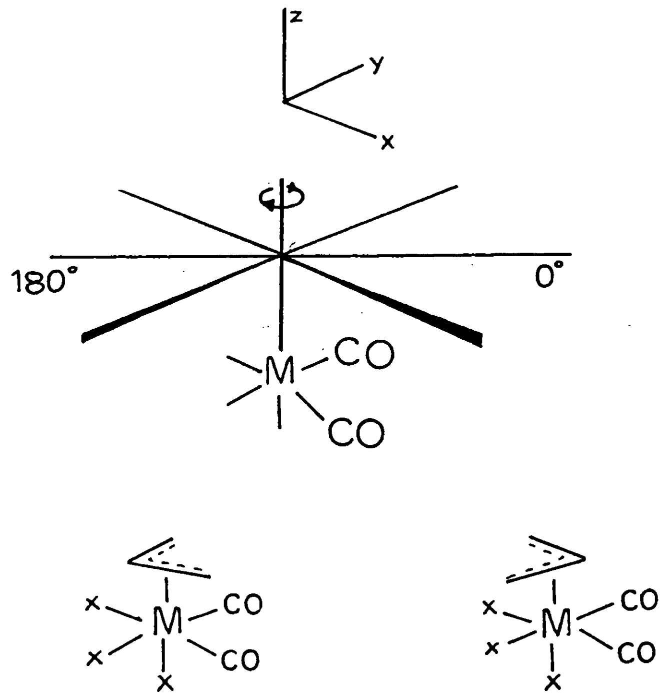
Scheme 5.3



In terms of isolobal reasoning, there should be no appreciable energy barrier to rotation of the C_3H_5 fragment and therefore only a relatively small, second-order effect is expected (and found) to be responsible for the rotational preference of the $\eta^3-C_3H_5$ group in $[Mo(\eta^3-C_3H_5)(CO)_2X_3]$.

Fig. 5.19 shows the $\Theta = 0^\circ$ and $\Theta = 180^\circ$ rotamers. M.O. calculations show that the $\Theta = 0^\circ$ rotamer is more stable by ca 50 kJ mol^{-1} than the rotamer with $\Theta = 180^\circ$ with other rotamers taking intermediate energies. Since $\Theta = 0^\circ$ is the lowest energy conformation and $\Theta = 180^\circ$ the highest, the ensuing discussion will concern only these two extremes.

Fig. 5.19. Rotational Energies for the Rotamers $\Theta = 0^\circ$ and $\Theta = 180^\circ$

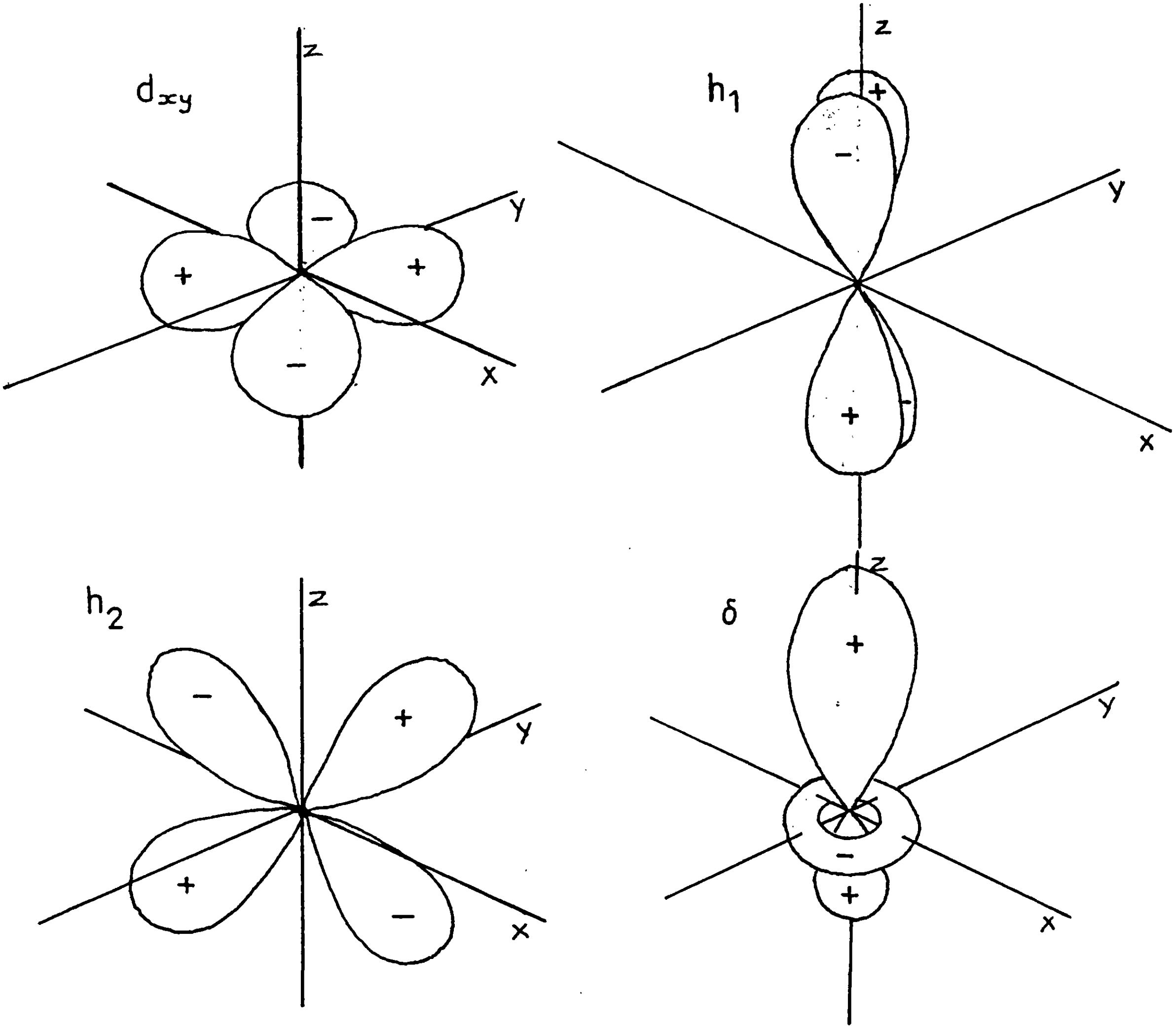


	X	$\Theta = 0^\circ$	$\Theta = 180^\circ$
E=	HCN	0·0	61·4 kJmol^{-1}
E=	Cl	0·0	42·2 kJmol^{-1}

The orbitals of interest are ψ_1, ψ_2 and ψ_3 of the allyl ligand, and the frontier orbitals of the $[\text{Mo(CO)}_2\text{X}_3]$

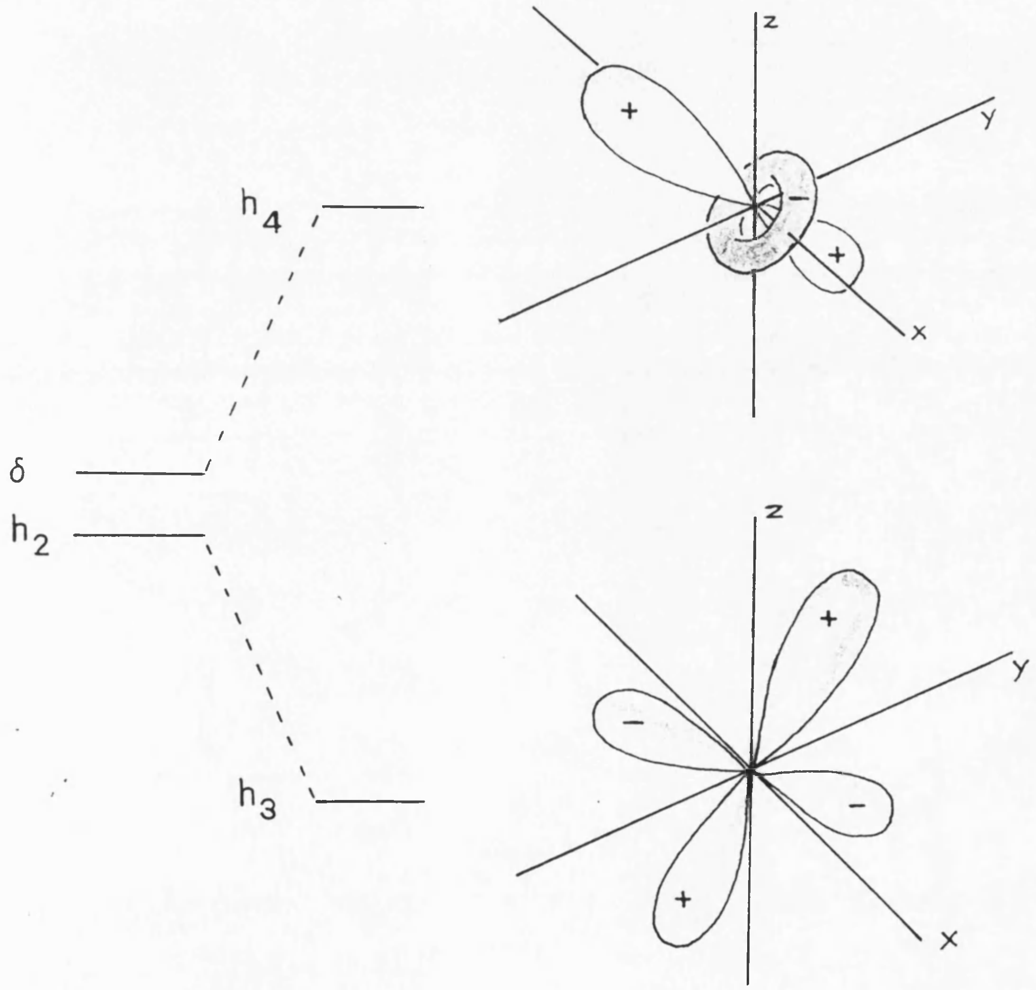
fragment which consist of the d_{xy}, two degenerate hybrids h_1 (xz-yz) and $h_2 \hat{=}$ (xz + yz) and a hybrid, δ , composed mainly of d_z2. The d_{xy} interacts only weakly with the allyl orbitals and hence can be ignored. The $[Mo(CO)_2X_3]$ fragment orbitals are illustrated in Fig. 5.20.

Fig. 5.20. <u>The Fragment Orbitals of $[Mo(CO)_2X_3]$</u>



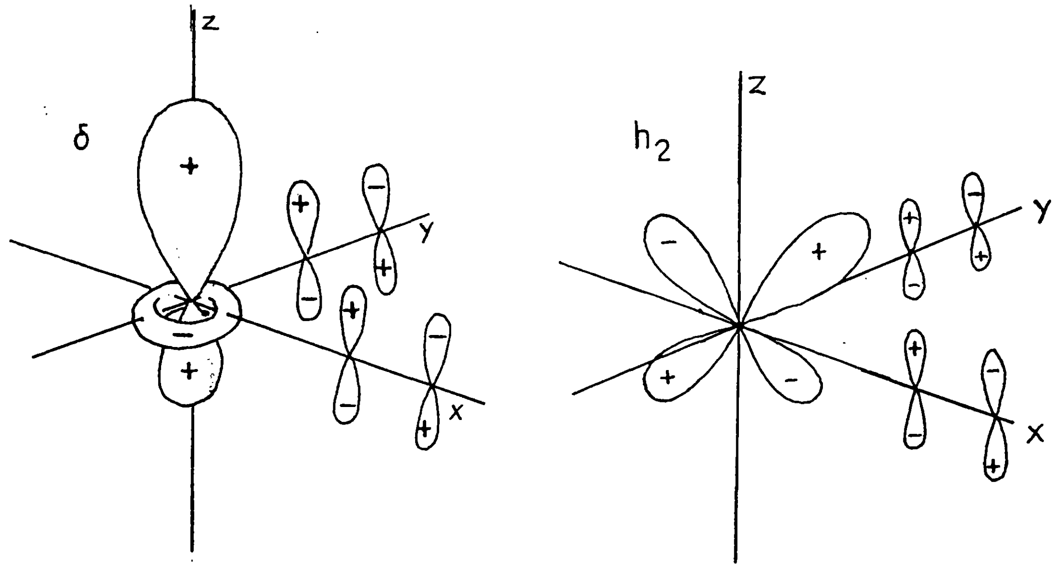
Further mixing of the δ orbital and the h_2 hybrid occurs, resulting in the formation of two new hybrid orbitals, h_3 and h_4 which are tilted toward the allyl central carbon atom in the $\Theta = 0^{\circ}$ orientation (Fig. 5.21).

Fig. 5.21. The Mixing of h_2 and δ



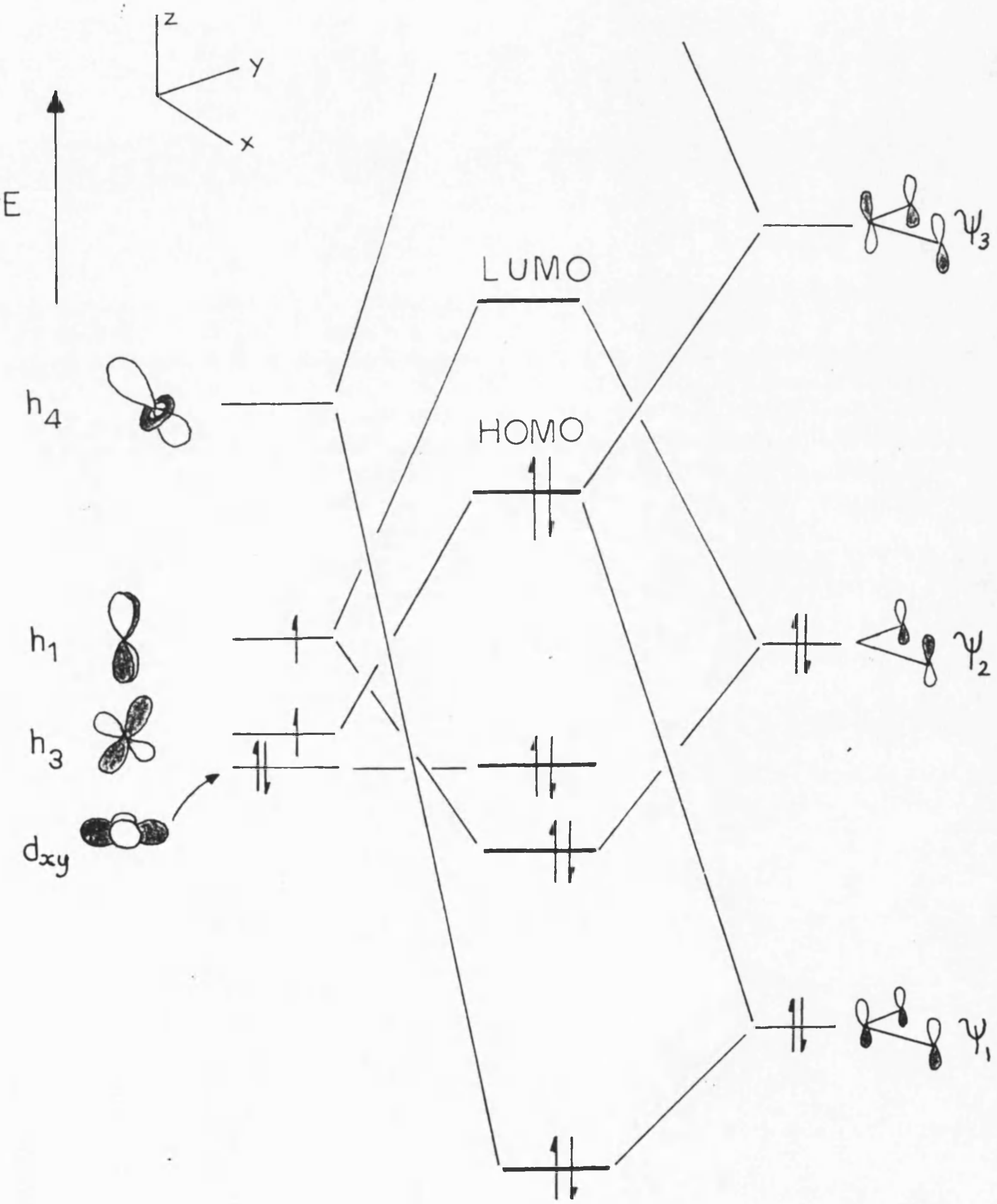
However, since there cannot be direct overlap between the δ -symmetry d_{z^2} and the π - symmetry h_2 orbital, the mixing cannot occur in a first-order fashion. Calculations show these orbitals are mixed via the agency of the π^* orbitals of the two carbonyl groups which have the correct symmetry to back-bond with both the δ and h_2 hybrid orbitals (Fig. 5.22.)

Fig. 5.22. Back-Bonding of δ and h_2 Orbitals with the Carbonyl π^* Orbitals



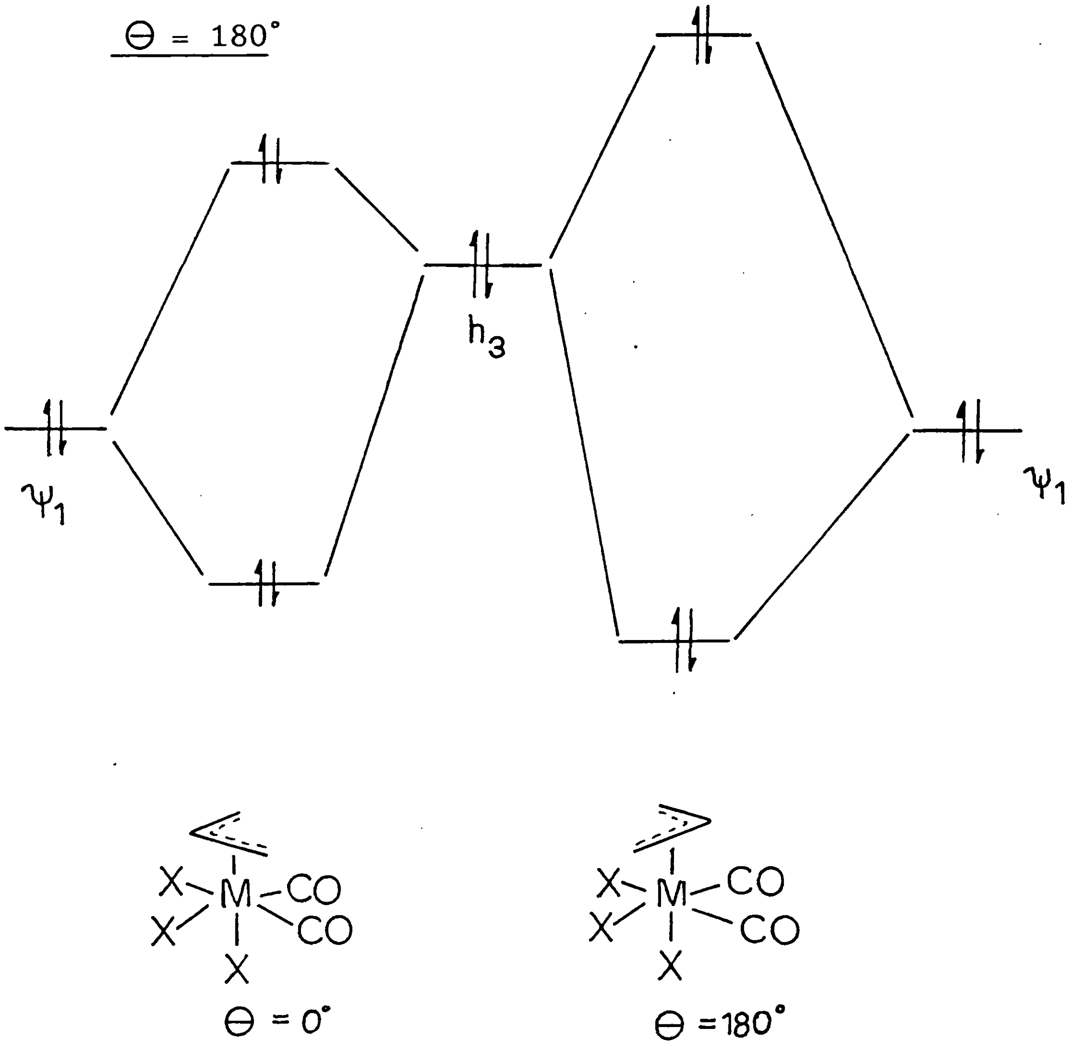
A qualitative M.O. scheme for the interaction of the $[Mo(CO)_2X_3]$ fragment orbitals is shown in Fig. 5.23

Fig. 5.23. Molecular Orbital Energy Level Diagram for the Interaction of η^3-Allyl Orbitals with the Orbitals of a $[Mo(CO)_2X_3]$ Fragment



The rotational preference of $\Theta = 0^\circ$ for the allyl group may now be rationalised as follows: The tilted hybrid h_3 interacts strongly with the filled ψ_1 molecular orbital of the allyl group, and since h_3 is at a higher energy than ψ_1, h_3 is destabilised (i.e. pushed to higher energy) by its interaction with ψ_1. The overlap of ψ_1 and h_3 is greater when the central carbon atom of the allyl group points toward the carbonyl groups (i.e. when $\Theta = 180°$) than when it points away (i.e. when $\Theta = 0°$). Thus, the HOMO of the complex is destabilised to a greater extent with $\Theta = 180°$. The remaining orbitals of the complex show little variation in energy as the allyl group is rotated. Fig. 5.24 illustrates these interactions.

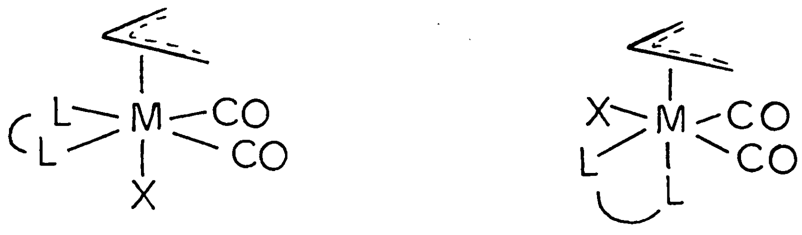
Fig. 5.24. Interaction of ψ_1 and h_3 for $\Theta = 0°$ and $\Theta = 180°$



Symmetrical and Unsymmetrical Structures

Another feature of the η^3-allyldicarbonyl complexes is their ability to adopt a structure with a plane of symmetry ("symmetrical structure") or a structure without a plane of symmetry ("unsymmetrical structure"). In the solid state, the symmetrical structure is by far the more common. The η^3-allyl group occupies the site trans- to the unidentate ligand X, and the donor atoms from the ligand L_2 lie approximately in a plane with the cis- dicarbonyl groups (Fig. 5.25).

Fig. 5.25. Symmetrical and Unsymmetrical Structures for η^3-Allyldicarbonyl Complexes



Symmetrical

Unsymmetrical

Fewer known complexes adopt the unsymmetrical structure in the solid state. Table 5.1 indicates the symmetry of the complexes listed.

Theoretical reasons why these complexes should prefer one of these two ligand distributions have yet to be put forward, but the combination of L_2 and X ligands is certainly significant. It is perhaps noteworthy that the ligands diphos and pda are present in complexes with the low symmetry structure (Table 5.1) and both possess a certain capacity to accept electron density from the metal. Sites which are trans- to the synergically bonded carbonyl ligands will be unfavourable for π-acceptor ligands since competition for electron density at the metal centre would destabilise this arrangement.

Allyl substituents also have a significant effect on the resultant geometry of complexes of this type.[182] The carboxylate complexes $[Mo(\eta^3-C_3H_5)(CO)_2(bipy)O_2CR']$ (where R' = CF_3, C_2F_5 or C_3H_7) have been shown by ^1H NMR to exist in two isomeric forms in solution at room temperature. The relative concentrations of the two isomers is solvent dependent. One isomer has the symmetrical structure and the other is dynamic, but assumes the unsymmetrical structure at low temperature. At elevated temperatures, the two isomers interconvert to give a single dynamic species, indicating a complete pseudorotation of the $(bipy)O_2CR'$ trigonal face. In contrast, the $\eta^3-2-MeC_3H_4$ derivatives adopt the symmetrical structure in solution over the temperature range -90 to +50°C. Molecular models show that the increased size of the $\eta^3-2-MeC_3H_4$ group destabilises the unsymmetrical structure relative to the symmetrical structure, due to steric interactions with the inflexible bipy ligand, and accounts for the formation of a single isomer for these complexes.

Regioselectivity of Nucleophilic Additions to η^3-Allyldicarbonyl Complexes

Carbon nucleophiles are known to attack the terminal carbon atoms of coordinated η^3-allyl ligands in η^3-allyldicarbonyl complexes to afford substituted alkenes (Chapter 1.7).[3] Attack at the central carbon atom would result in the formation of a metallocyclobutane[183] (Eq. 5.6).

Eq. 5.6

This regioselectivity has been shown to be frontier orbital[89] rather than charge controlled.[87,88] In all cases examined, the central carbon atom of the η^3-allyl group is calculated to be positively charged with respect to the terminal carbons.[89] Thus, charge control would always direct an attacking nucleophile to the central carbon atom, a prediction which is not borne out in practice.

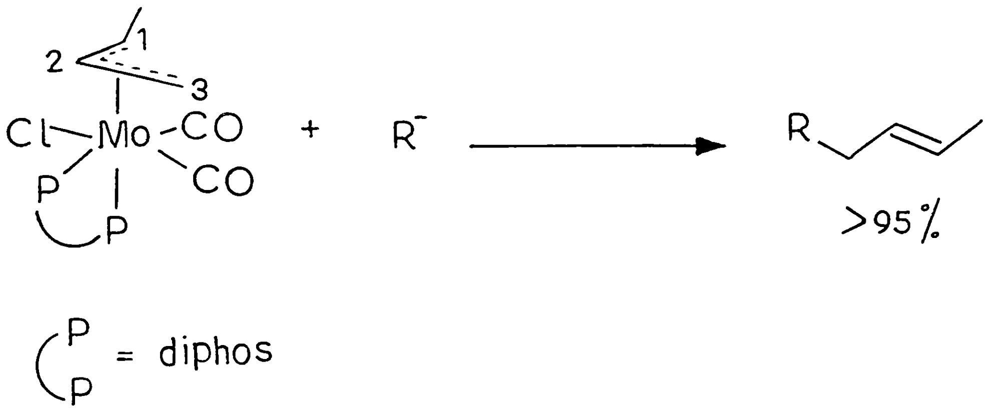
The LUMO of $[Mo(\eta^3\text{-allyl})(CO)_2X_3]$ complexes, which is illustrated in Fig. 5.23, is the anti-bonding combination of ψ_2 and h_1. This is the lowest energy acceptor orbital and it has large "lobes" on the terminal carbon atoms which can accept electron density from an incoming nucleophile.

Thus, frontier orbital control correctly predicts that these complexes will suffer attack at the terminal carbons.[3]

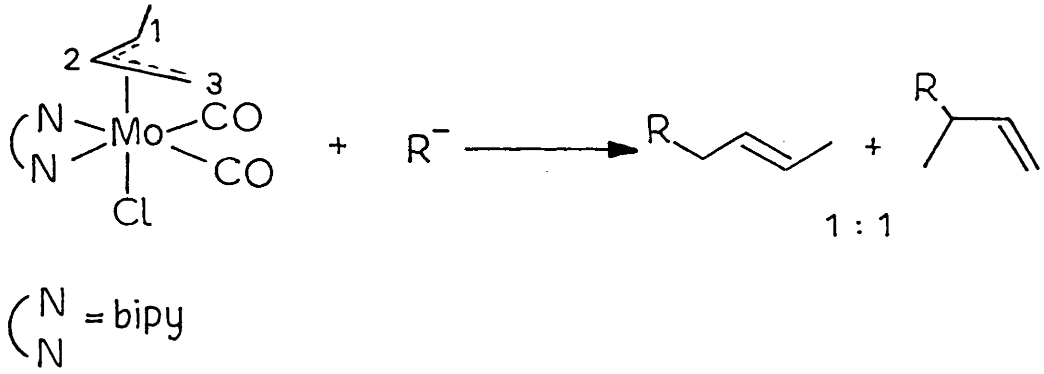
In order for attack to occur at the central carbon atom, the LUMO must possess a large "lobe" at this position in order to accept the incoming nucleophile. This condition is met in the cationic species $[M(\eta^3\text{-allyl})Cp_2]^+$ (M = Mo or W),[89,183] and these give metallocyclobutanes upon reaction with carbon nucleophiles such as Grignard reagents.

It must be recognised that charge distribution can play a role in deciding the regioselectivity of attack at the termini of asymmetrical η^3-allyl ligands (e.g. $\eta^3\text{-1-MeC}_3H_4$). Electronic asymmetry caused either by ligand distribution or a substituent on one termini of the allyl group in question may affect the coefficients of the LUMO and thus render one terminus more susceptible to attack than the other. Consider the nucleophilic attack of the complexes shown below in Eq. 5.7 and 5.8 by a carbon nucleophile, R^-. (These reactions are described earlier in Chapter 1.7). Trost and Lautens[3] reported a 95% regioselectivity for the reaction shown in Eq. 5.7 whereas the reaction shown in Eq. 5.8 demonstrated no regioselectivity. Subsequent M.O. calculations[89] revealed the LUMO coefficients at C_1 and C_3 in $[Mo(\eta^3\text{-1-MeC}_3H_4)(CO)_2(\text{diphos})Cl]$ to be -0.28 and 0.32 respectively whereas the coefficients at C_1 and C_3 in $[Mo(\eta^3\text{-1-MeC}_3H_4)(CO)_2(\text{bipy})Cl]$ have essentially equal magnitudes.

Eq. 5.7



Eq. 5.8



Finally, while frontier orbital control clearly predicts nucleophilic attack at a terminal carbon atom, the LUMO coefficients must not be regarded as the sole arbiter in deciding which particular terminal carbon atom is attacked since the steric bulk of the nucleophile and the substituents on the allyl group may also play a significant role.

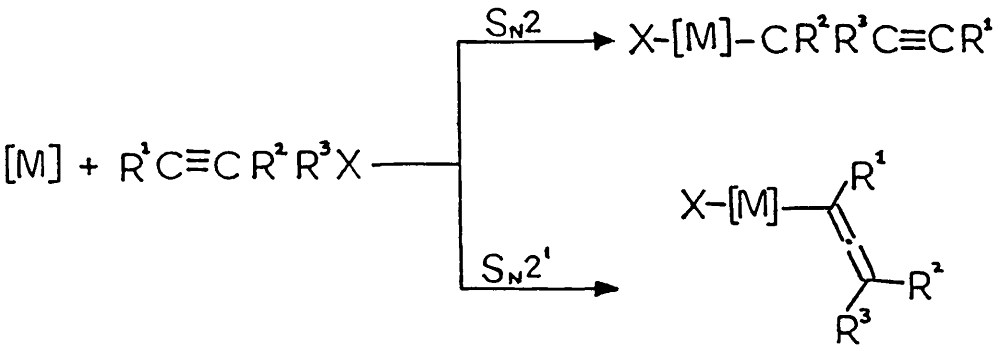
CHAPTER SIX

Oxidative addition of prop-2-ynylic compounds to transition metal centres

6.1 OXIDATIVE ADDITION OF PROP-2-YNYLIC HALIDES TO TRANSITION METAL COMPLEXES

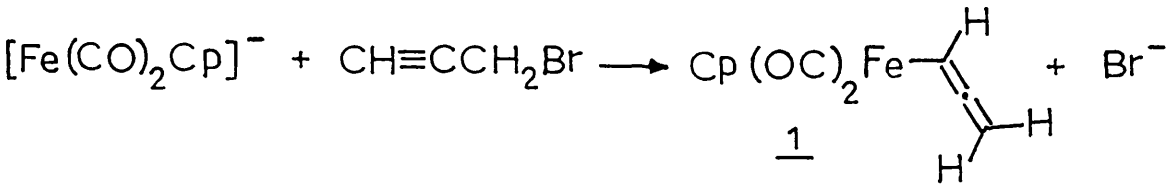
Prop-2-ynylic halides of general formula R^1-C≡C-CR^2R^3X (where R^1, R^2 and R^3 may be combinations of H, alkyl or aryl and X=Cl or Br) are known to undergo oxidative addition reactions with neutral or anionic transition metal complexes by an S_N2[184-187] or S_N2'[188-190] mechanism to give σ-prop-2-ynylic or σ-allenylic complexes respectively (Scheme 6.1).

Scheme 6.1



For example, the $[Fe(CO)_2Cp]^-$ anion reacts with propargyl (prop-2-ynyl) bromide to afford the σ-allenyl complex[188,191] (1) (Eq. 6.1), whereas reaction with 3-phenyl-prop-2-ynyl bromide affords the σ-3-phenyl-prop-2-ynyl complex[191] (2) (Eq. 6.2).

Eq. 6.1



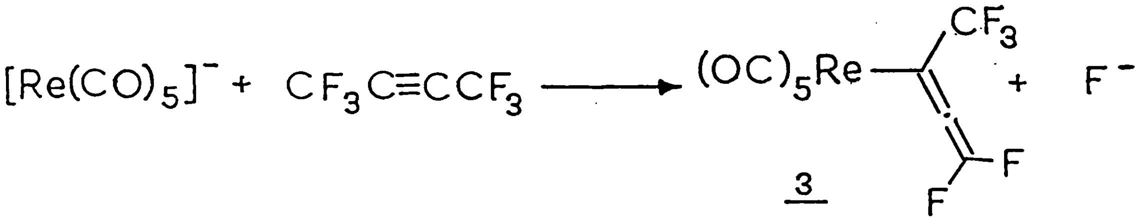
Eq. 6.2

$$[Fe(CO)_2Cp]^- + PhC{\equiv}CCH_2Br \longrightarrow Cp(OC)_2Fe{-}CH_2C{\equiv}CPh + Br^-$$

2

The ambiphilic nature of prop-2-ynylic halides has caused appreciable confusion in the past. In 1966, Green and Stone[192] described the preparation of complex (3) (Eq. 6.3) which was believed to be the first example of a σ-allenyl transition metal complex.

Eq. 6.3

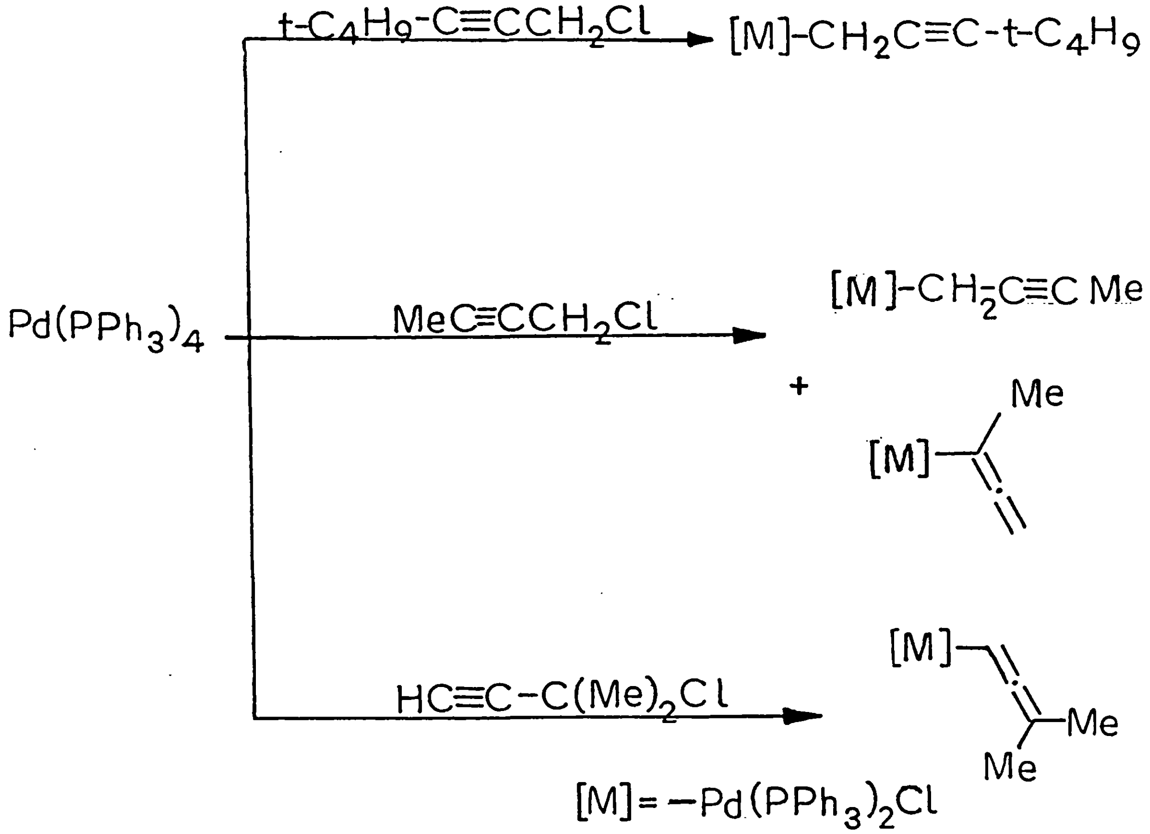


3

The mechanism probably involves η^2-coordination of the electron-deficient alkyne followed by elimination of fluoride, rather than an S_N2' process. However, complex (1) had been prepared two years earlier[193], but incorrectly described as the σ-prop-1-ynyl compound. Furthermore, it had been incorrectly formulated in 1968[194] as the σ-prop-2-ynyl derivative, but its correct structure was recognised in the following year[188].

One key feature that helps determine S_N2 or S_N2' attack appears to be the steric hinderance caused by the R groups (Scheme 6.1) with attack by the metal complex occurring at the less hindered carbon.[189,190] Scheme 6.2 illustrates this point with the trans oxidative addition of substituted prop-2-ynylic chlorides to $Pd(PPh_3)_4$.[190]

Scheme 6.2

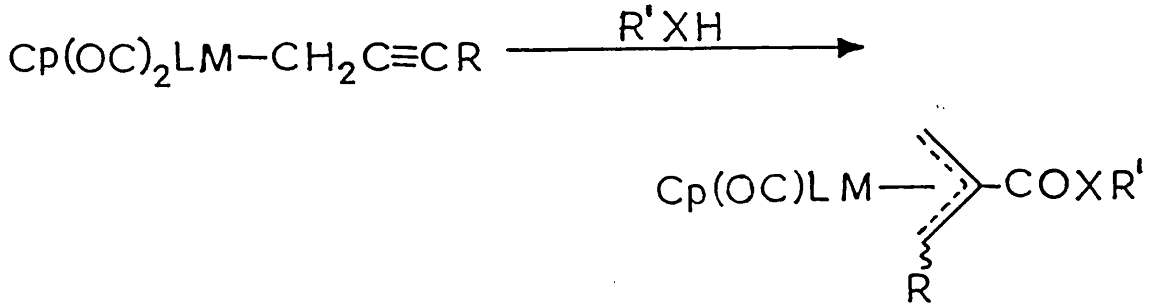


Once formed, transition metal complexes containing such metal-carbon σ- bonds are generally very reactive and frequently act as precursors to novel organometallic compounds, some of which are described below.

6.2 FORMATION OF η^3-ALLYL AND σ-VINYL COMPLEXES BY THE ALKOXYCARBONYLATION OF σ-PROP-2-YNYLIC LIGANDS

Several σ-prop-2-ynylic complexes of molybdenum and tungsten react with alcohols, water or thiols yielding compounds that contain substituted η^3allyl ligands as a result of alkoxy, hydroxy or thioalkoxycarbonylation of the co-ordinated organic ligand[184,185] (Eq. 6.4).

Eq. 6.4

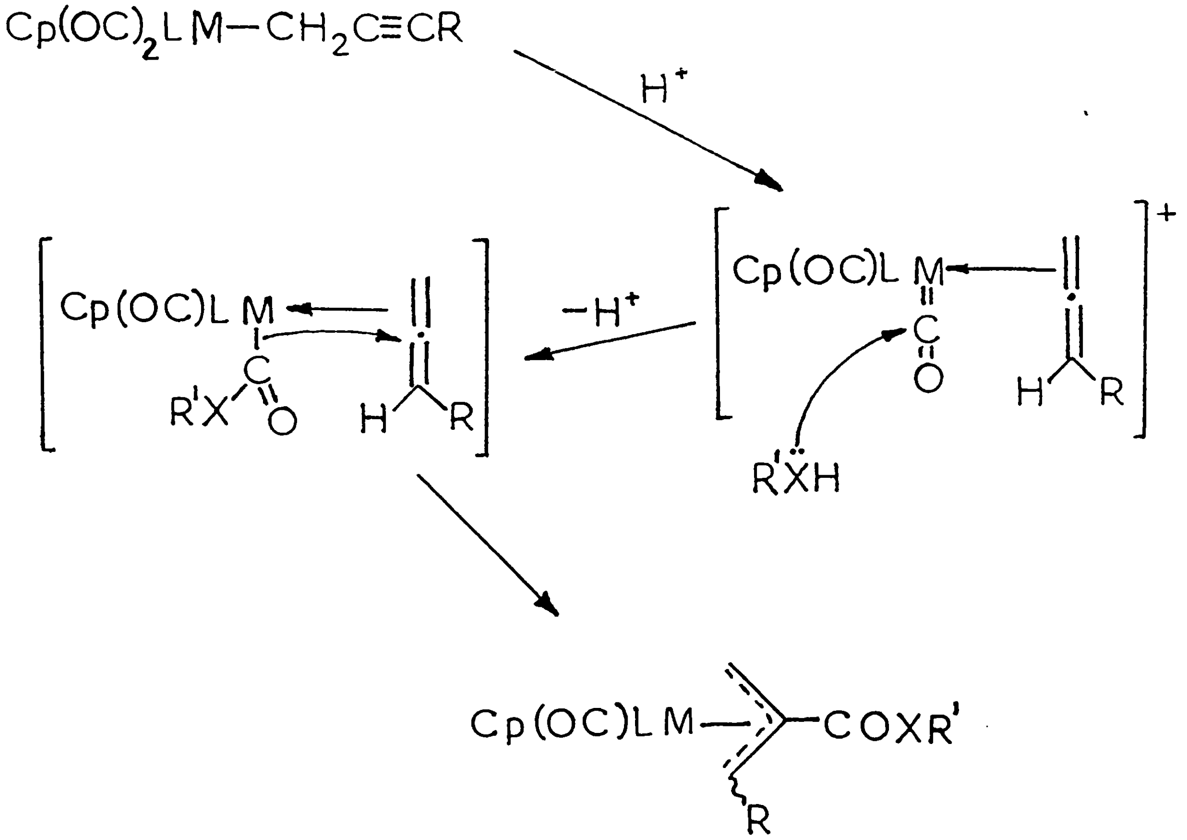


M = Mo,W

X = O,S
R = H, alkyl, aryl
R' = H, alkyl, aryl
L = CO, PPh_3, $P(OPh)_3$, $P(OMe)_3$

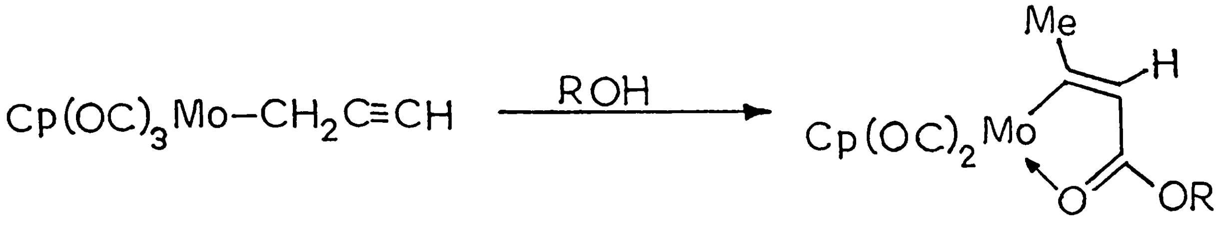
The reactions are sensitive to acid catalysis and a mechanism involving a cationic allene intermediate has been postulated (Scheme 6.3).

Scheme 6.3



The molybdenum complex Cp(OC)$_3$Mo-CH$_2$C≡CH behaves differently however, and only reacts with alcohols to give η^3-allyl compounds if excess propargyl bromide is present.[185] In its absence, the σ-vinyl ester complex (4) is obtained (Eq. 6.5).

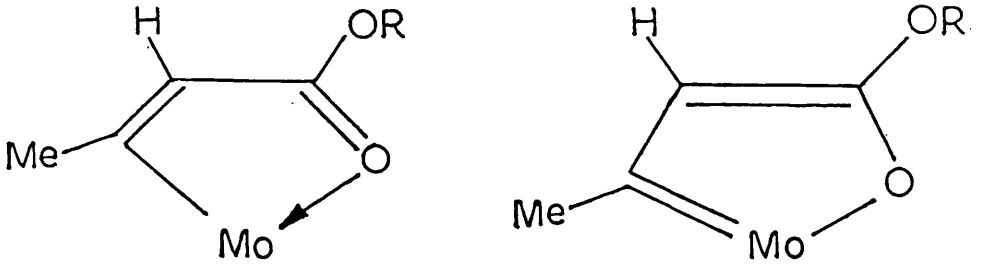
Eq. 6.5



4

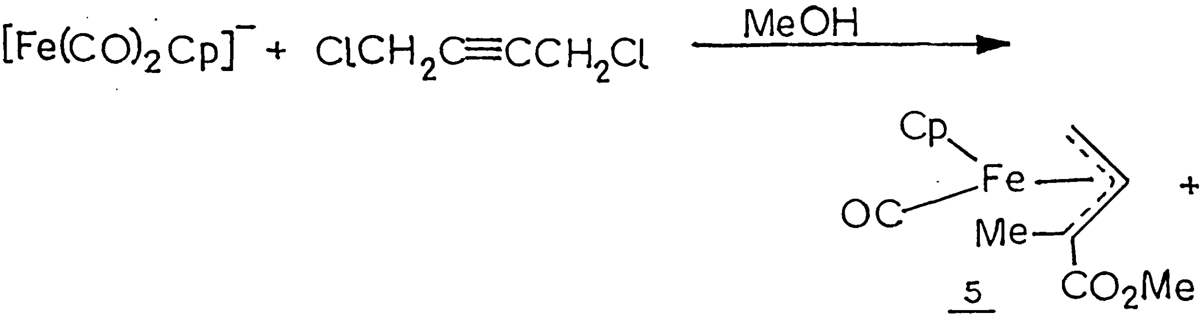
Complex (4) may be represented by two extreme bonding modes as shown in Fig. 6.1, and ^{13}C NMR studies indicate that the carbenoid canonical form is significant[185] in the overall description of the bonding (see Chapter 7.3).

Fig. 6.1 The Two Extreme Bonding Modes of the σ-Vinyl Ester Ligand



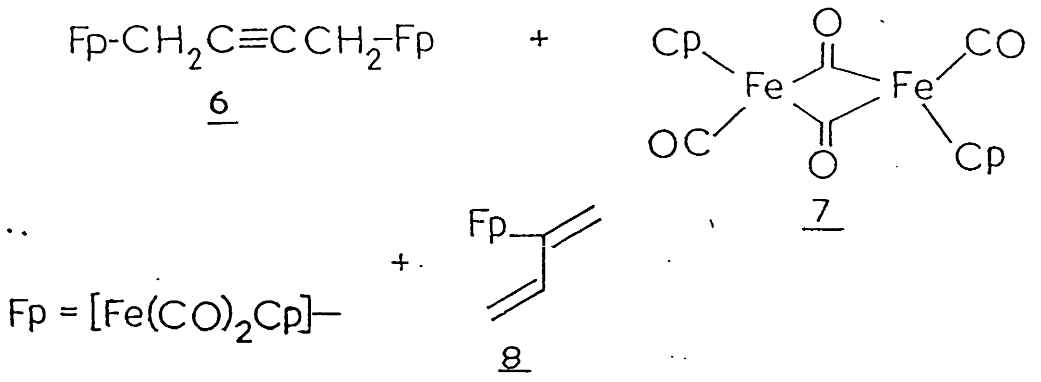
The reactions discussed above were carried out on preformed σ-prop-2-ynylic complexes. Alkoxycarbonylation is also observed when the $[Fe(CO)_2Cp]^-$ anion is reacted with 1,4-dichlorobut-2-yne in the presence of methanol[195] (Eq. 6.6).

Eq. 6.6



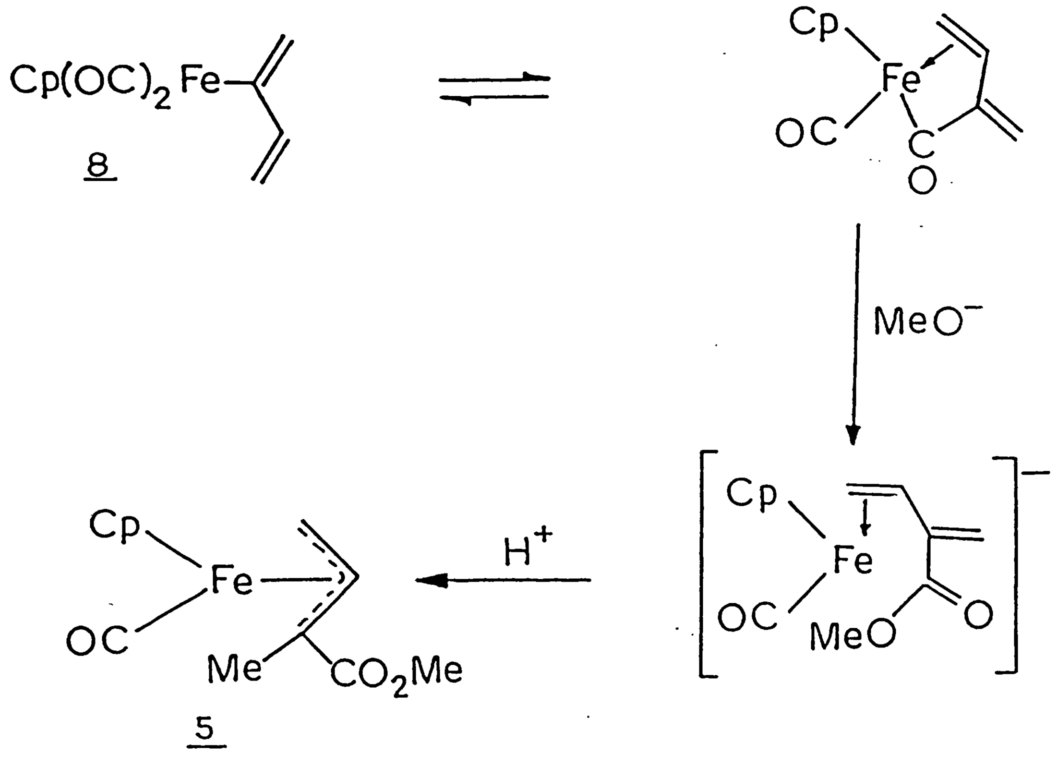
5

Eq. 6.6 Contd.



The alkoxycarbonylated product (5) is obtained in low yield (ca 10%) although it can be improved to ca 40% by employing $PhSO_3$-$CH_2C≡CCH_2$-O_3SPh as substrate. Complexes (6) and (7) are the major products. The η^1-butadienyl complex (8), which is also detected at the end of reaction in low yield, is believed to be an intermediate in the formation of (5) since reaction with $[Fe(CO)_2Cp]^-$/methanol or sodium methoxide affords this complex (Scheme 6.4).

Scheme 6.4



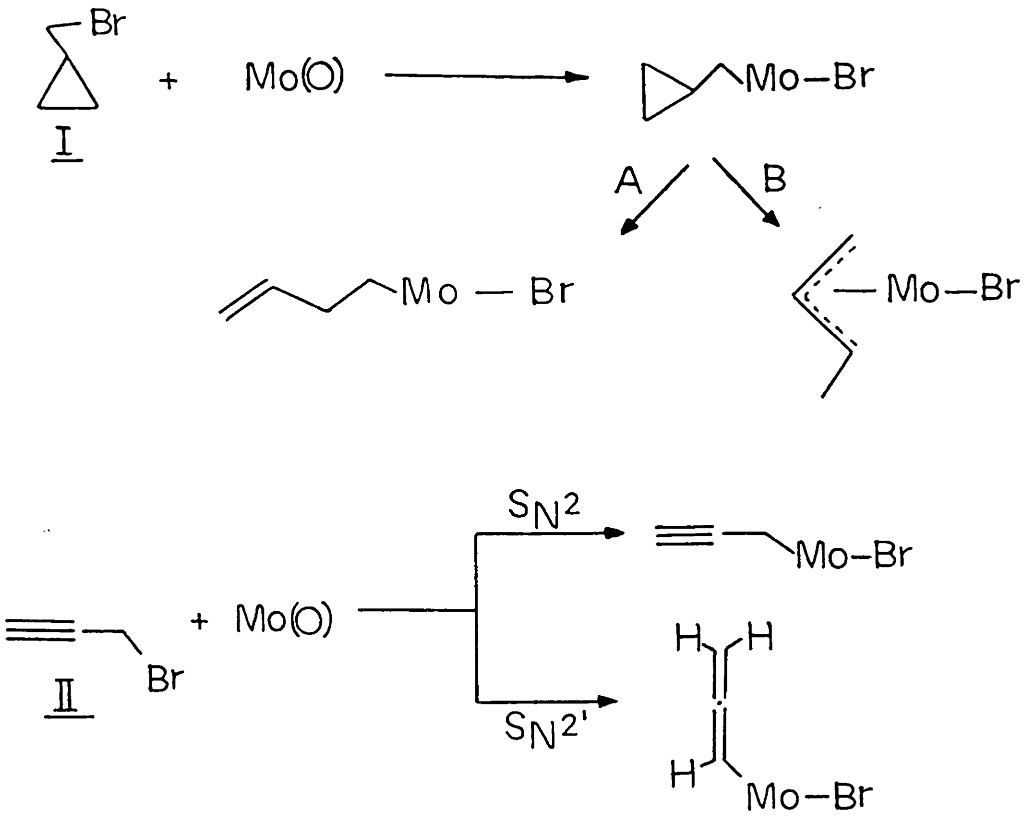
CHAPTER SEVEN

Molybdenum-mediated methoxy carbonylation of propargyl (prop-2-ynyl) halides: Results and discussion

7.1. FOREWORD

In view of the experimental observations made on reactions involving certain allyl and benzyl bromides in the presence of $Mo(CO)_4bipy$ and Napda which resulted in new carbon-carbon bond formations (Chapter 2), other reactive organic halides were reacted with molybdenum species in order to determine whether they would couple or alkylate in a similar fashion, or whether they would yield novel organometallic systems. Thus, bromomethylcyclopropane (I) and propargyl bromide (II) were chosen on the grounds that: (a) they are both potentially capable of oxidative addition to an Mo(0) centre and (b) they possess structural features that might lead to novel complexes (Scheme 7.1).

Scheme 7.1



Reaction pathway (A) in Scheme 7.1 is known for certain cyclopropylmethyl cobaloximes[196] whereas pathway (B) has been shown to occur in reactions of platinum (II) species.[197] The potential ambiphilic nature of propargyl halides has been described in Chapter 6.

Attempts to couple or alkylate bromomethylcyclopropane (I) in the presence of Napda or dmsm using $Mo(CO)_4$bipy or $Mo(CO)_6$ as catalyst in refluxing toluene failed. The reactions afforded complex mixtures and in no case was any compound containing a cyclopropane residue identified. Small quantities of unreacted Napda and $Mo(CO)_4$bipy were often recovered, but reactions involving dmsm resulted in reactant decomposition with dimethyl malonate being the only identifiable product.

On the other hand, propargyl bromide (II) gave more encouraging results in similar reactions. In the presence of one equivalent of Napda and 10 mol% $Mo(CO)_4$bipy, propargyl bromide reacted in boiling toluene to afford a mixture of organic products. ^{1}H NMR spectroscopy revealed traces of the alkylated product 3-(prop-2-ynyl)pentan-1,4-dione[198] in the mixture although an uncatalysed control reaction also gave this compound in low yield (<u>ca</u> 17%). More significantly however, the solid recovered at the end of the catalysed reaction appeared from infrared spectroscopy to contain a <u>cis</u>-dicarbonyl species (ν(CO) 1950, 1865 cm^{-1}). The possibility that propargyl bromide reacts with $Mo(CO)_4$bipy to produce a <u>cis</u>-dicarbonyl organometallic was thus investigated further.

7.2 THE REACTIVITY OF PROPARGYL HALIDES TOWARD THE $[Mo(CO)_3(bipy)X]^-$ ANIONS (WHERE X=Cl or Br)

Although neutral transition metal complexes are known to react with prop-2-ynylic halides[189,190] to afford σ-allenylic or σ-prop-2-ynylic derivatives, attempts to react $Mo(CO)_4bipy$ with just propargyl bromide in refluxing toluene or THF resulted only in decomposition of the propargyl bromide and the formation of intractable mixtures of molybdenum species. When the reaction was performed in refluxing dioxan in the presence of excess propargyl bromide, $Mo(CO)_4bipy$ was oxidised to $MoBr_4bipy$.[97] The addition of propargyl bromide to a solution of the acetonitrile complex $Mo(CO)_3(NCMe)_3$[95] in acetonitrile at room temperature gave a black, intractable tar.

In a further attempt to reduce the severity of the reaction conditions, it was decided to treat the more reactive anion $[Mo(CO)_3(bipy)Br]^-$ [84,115,171] with propargyl bromide. However, no reaction was observed in THF at either -78°C or at room temperature. This is probably a result of the insolubility of $[PPh_4][Mo(CO)_3(bipy)Br]$ (III) in THF over this temperature range as reaction occurred rapidly at -10°C in chloroform, a solvent in which (III) is reasonably soluble. The resulting reaction mixture afforded a red oil which contained a complex mixture of components which could not be identified. Infrared analysis of the oil revealed two CO stretching modes at 1950 and 1865 cm^{-1} as found in the solid residue recovered from the reaction between propargyl bromide and $Mo(CO)_4bipy$ in the presence of Napda. On the premise that these infrared bands belonged to a cis- dicarbonyl complex containing a σ-allenyl , σ-prop-2-ynyl ligand or a derivative thereof, the reaction between propargyl bromide and $[PPh_4][Mo(CO)_3(bipy)Br]$ was performed in methanol at -17°C in the hope that any resulting σ-allenyl or σ-prop-2-ynyl complex would be methoxcarbonylated to afford a stable η^3-allyl derivative.[184,185] This reasoning was justified since when the reaction was carried out in methanol, a light brown solid (IV) precipitated which gave an elemental analysis corresponding to $[Mo(C_5H_7O_2)(CO)_2(bipy)Br]$, the $C_5H_7O_2$ group evidently being formed from a combination of the propargyl moiety with methanol and a CO group (Eq.7.1). The corresponding chloro complex $[Mo(C_5H_7O_2)(CO)_2(bipy)Cl]$(V), was similarly formed in an analogous reaction with propargyl chloride and $[PPh_4][Mo(CO)_3(bipy)Cl]$.

Eq. 7.1

$$[PPh_4][Mo(CO)_3(bipy)X] + HC{\equiv}CCH_2X + MeOH \longrightarrow$$

$$[Mo(C_5H_7O_2)(CO)_2(bipy)X] + PPh_4X$$

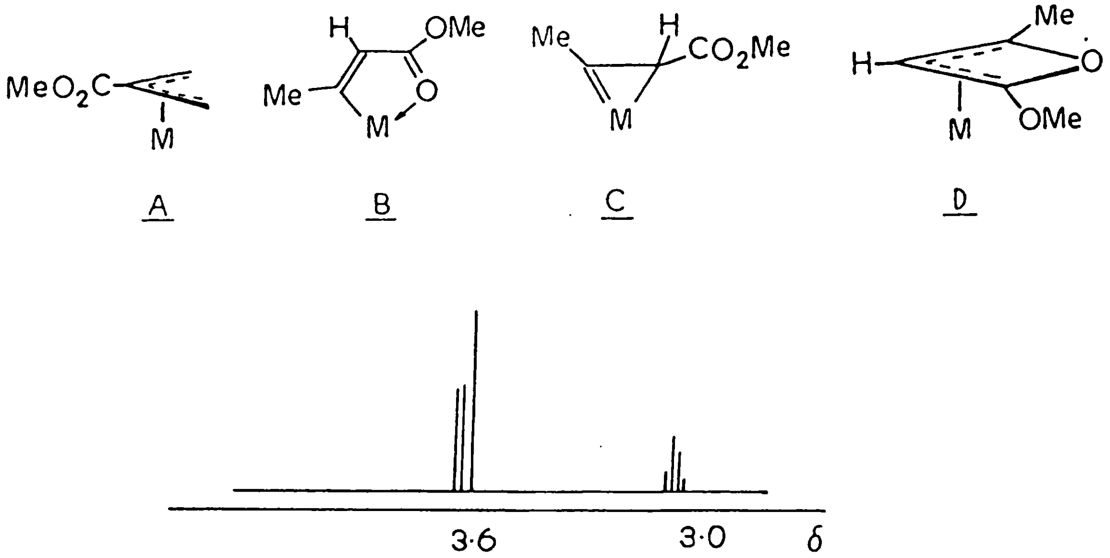
X = Br, IV
X = Cl, V

No analogous product could be obtained under similar conditions in other alcohols ROH(R=Et or $PhCH_2$) or in methane thiol, nor could any organometallic complex be isolated when co-solvents such as chloroform or methylene chloride were used or when the prop-2-ynylic halide contained a bulky substituent. The rate and direction of the reaction were unaffected by the presence of p-toluenesulphonic acid which is known to catalyse the methoxycarbonylation of certain other molybdenum-prop-2-ynylic complexes.[184]

The Structure of Complexes (IV) and (V)

It has been stated earlier (Chapter 6.2) that the propargylic complexes $[Cp(CO)_3M\text{-}CH_2C\equiv CH]$ (M=Mo or W) are methoxycarbonylated in methanol to yield organometallic compounds containing either the η^3-2-$MeO_2CC_3H_4$ ligand (A) or the σ-vinyl ester ligand (B) (Fig. 7.1). Both complexes (IV) and (V) exhibit ν(CO) (and (V) a ν(MoCl)) stretching modes in their infrared spectra which are typical of $[Mo(\eta^3\text{-allyl})(CO)_2(bipy)X]$ [84,85,199,200] but neither complex was very soluble in common NMR solvents. Reasonable ^1H NMR spectra could be recorded however in CD_2Cl_2 and (V) showed $C_5H_7O_2$ resonances at δ 3.65 (doublet), 3.60 (singlet) and 3.05 p.p.m. (quartet) in the approximate intensity 3:3:1 (see Fig. 7.1). Complex (IV) gave a similar spectrum. The ^1H NMR data for the $C_5H_7O_2$ ligand is therefore incompatible with either structural type (A), which requires an entirely different intensity pattern from that observed, or type (B) which requires a vinylic proton signal in the range 5.5-8.0 p.p.m.[185,201,202] Alternative modes of bonding which preserve the 18-electron configuration of the molybdenum atom in (IV) and (V) and are in keeping with the ^1H NMR data are illustrated in (C) and (D) of Fig. 7.1.

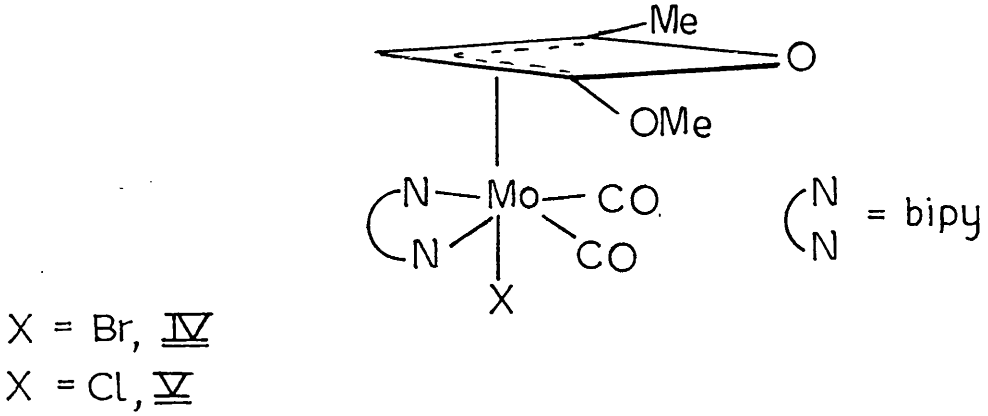
Fig. 7.1 Alternative Modes of Bonding for the $C_5H_7O_2$ Ligand Found in Complexes (IV) and (V) Together with its ^1H NMR Spectrum



The low solubilities of both complexes (IV) and (V) precluded ^{13}C NMR measurements which would readily differentiate between a three-electron η^2-bonded alkylidene species[203] such as (C), and the η^3-oxacyclobutenyl ligand (D). In addition, (C) would exhibit a characteristic ν(C=O) band at *ca* 1730 cm^{-1} [204] in its infrared spectrum. Neither complex (IV) nor (V) exhibit a band characteristic of a free carbonyl group, although a medium intensity band at ca 1650 cm^{-1} is present in the infrared spectra of both complexes. In (D), the electron density is expected to be delocalised via non-bonding electrons on the oxygen atom, and therefore the infrared spectrum of such a ligand may be analogous to heterocyclic compounds such as furans which exhibit moderately intense infrared active bands around 1700 cm^{-1} in their spectra. These bands are believed to originate from either overtones or combination bands of lower frequencies.[205,206]

The normal structure adopted by the hindered allyl complexes of the type $[Mo(\eta^3\text{-allyl})(CO)_2(bipy)X]$ (X=anion) is pseudooctahedral with the allyl group trans to the anion.[89,182] In this configuration, the hydrogen atom on the central carbon of the allyl moiety lies above the plane of the bipy ligand and consequently suffers a high-field shift.[182] The proton signal of intensity 1 at 2.95 ± 0.1 p.p.m. for both (IV) and (V) has the expected chemical shift for the η^3-2-methoxy-4-methyl-1-oxacyclobutenyl ligand in a complex with the stereochemistry shown below in Fig. 7.2. Therefore, based on the limited spectroscopic data available, it seems likely that complexes (IV) and (V) contain the η^3-2-methoxy-4-methyl-1-oxacyclobutenyl ligand (D) shown in Fig. 7.1.

Fig. 7.2. Proposed Structure for Complexes (IV) and (V)



Support for this proposal comes from a previous study in which a σ-oxacyclobutenyl containing product was isolated from the reaction between hexafluoroacetone and $[Cp(OC)_2Fe\text{-}C\equiv CPh]$,[207] and a possible mechanism for the metal carbonyl-mediated formation of an η^3-oxacyclobutenyl ring system was described via a conrotatory ring closure of a σ-vinyl ketone metal species.[208]

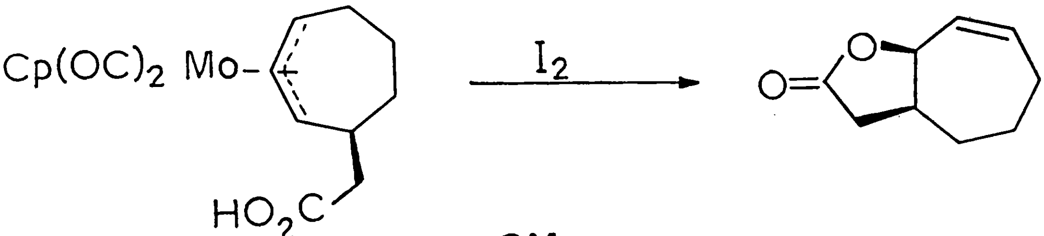
Attempts to confirm these assignments by x-ray crystallography were thwarted by the low solubilities and stabilities of both complexes (IV) and (V) in suitable solvents for recrystallisations. Consequently, confirmatory chemical evidence for the skeletal structure of the $C_5H_7O_2$ ligand was sought from chemical studies while new metallo-derivatives with more tractable physical properties were sought.

7.3. THE REACTIVITY OF COMPLEXES (IV) AND (V)

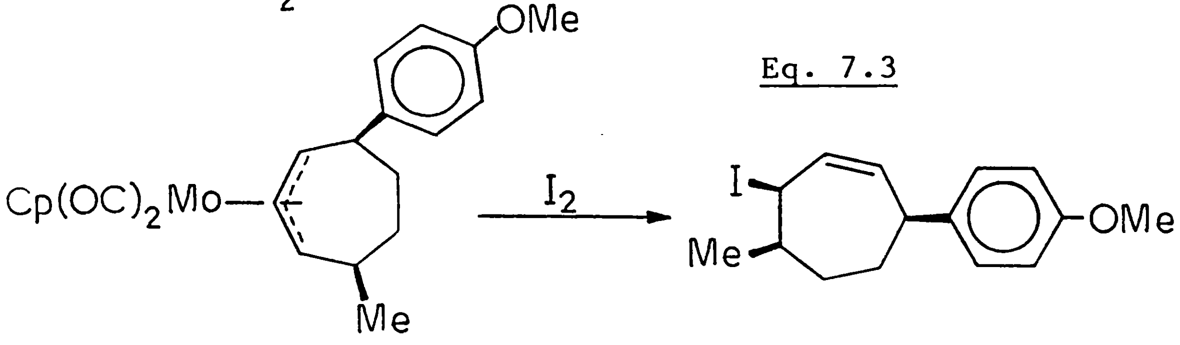
Oxidative Cleavage of the $C_5H_7O_2$ Ligand

The oxidative cleavage of η^3-allyl ligands by iodine to afford either lactones[209,210] (Eq. 7.2) or allyl iodides[210,211] (Eq. 7.3) has been employed recently in natural product synthesis.

Eq. 7.2



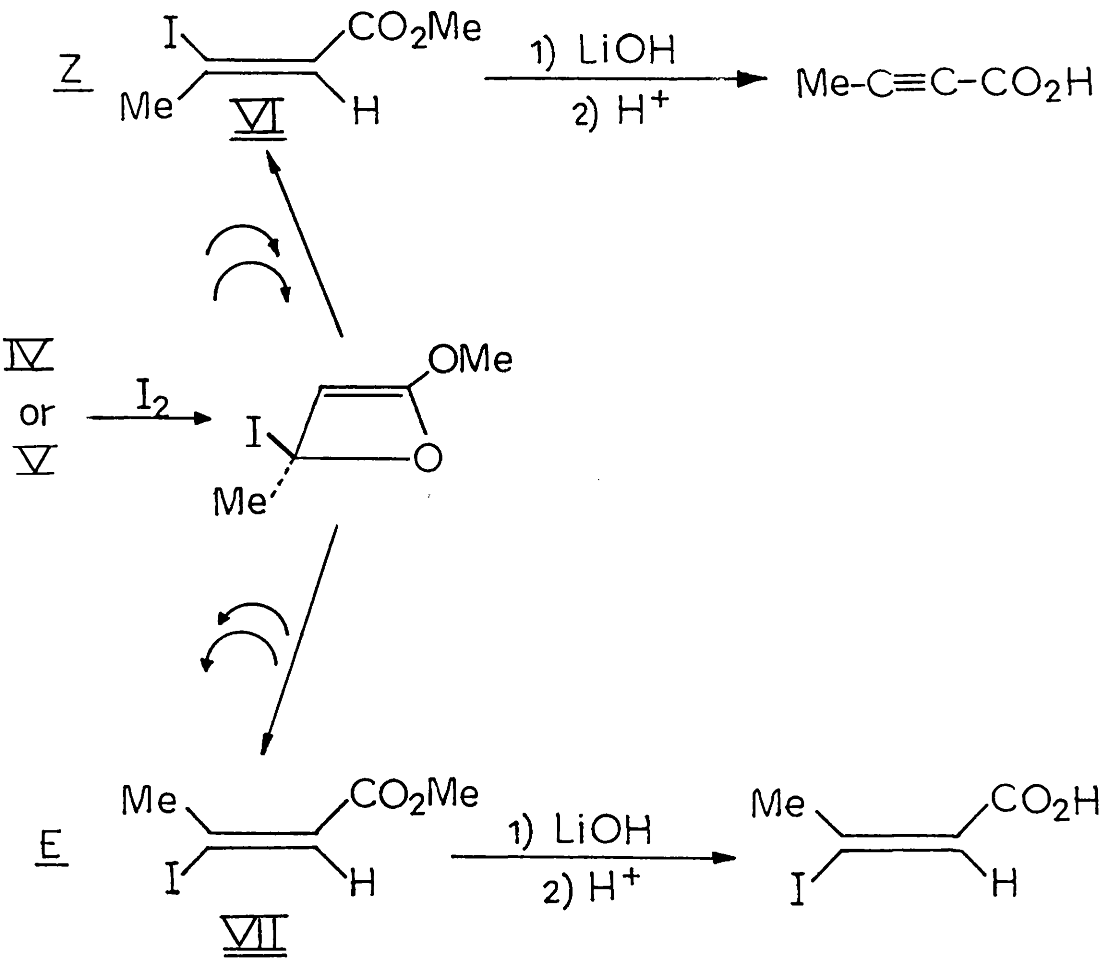
Eq. 7.3



In a similar procedure, both (IV) and (V) suspended in acetonitrile reacted cleanly under mild conditions with an excess of iodine to give two isomeric alkenes, (VI) and (VII) (See Scheme 7.2) which were readily separated by column chromatography. Each isomer gave an elemental analysis corresponding to $C_5H_7IO_2$ and this formula was confirmed by mass spectrometry in which a molecular ion peak at m/z 226 was observed together with fragments at m/z 195 and 167, due to consecutive losses of OMe and CO, and at m/z 99 (base peak) due to loss of an iodine atom from the molecular ion. The presence of the carbomethoxy group was again evident from the fragment at m/z 59. This mass spectral evidence suggested that the two isomers were iodo-derivatives of methyl crotonate or methyl methacrylate. The ^{13}C NMR spectra of isomers (VI) and (VII) were found to correspond closely with the data published for (E)- and (Z)- methyl-3-iodocrotonate respectively,[212] but since neither the source nor the physical constants of the model compounds were given, these assignments were checked as follows. Both isomers reacted completely with LiOH in aqueous THF within four hours. Subsequent acidification of the reaction mixture that contained isomer (VI) afforded tetrolic acid[213] (but-2-ynoic acid), whereas similar treatment of the reaction mixture that contained isomer (VII) gave (E)-3-iodocrotonic[214] acid with no tetrolic acid being detected (Scheme 7.2). Nuclear Overhauser enhancement measurements at 400 MHz indicated that the C-methyl group and the vinylic proton were close to each other in (VI) and distant in (VII). Both these observations place the C-methyl group and the vinylic proton in a syn-relationship in (VI) which is therefore the (Z)-isomer. The foregoing confirms the published assignments of the two iodo-esters and further supports the assignment of an oxacyclobutenyl arrangement for the $C_5H_7O_2$ ligand.

Mechanistically, the formation of the two esters from the oxacyclobutenyl ligand can be regarded as an oxidative cleavage by iodine of the Mo-C bonds giving an iodooxacyclobutene, the two possible conrotatory opening modes of which yield a different geometrical isomer of methyl-3-iodocrotonate (Scheme 7.2).

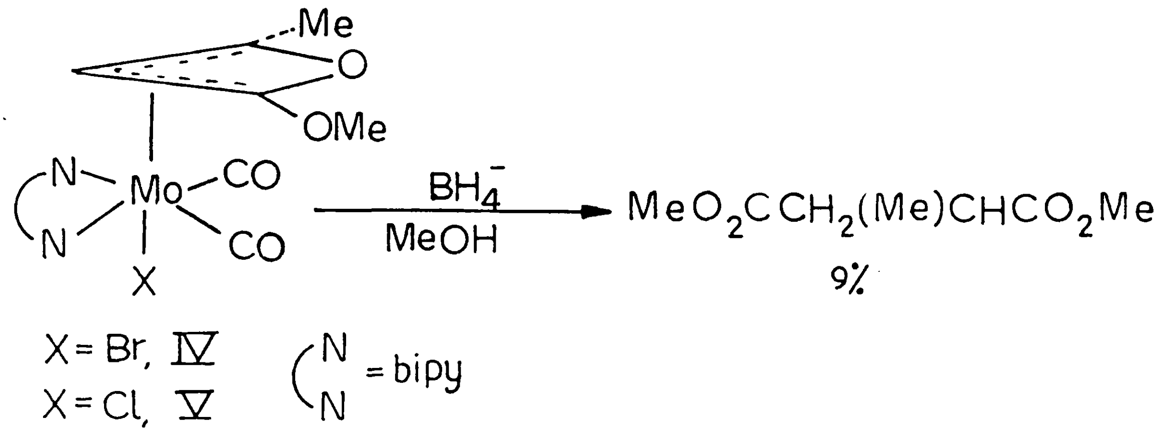
Scheme 7.2



Reductive Cleavage of the $C_5H_7O_2$ Ligand

In contrast to the smooth, oxidative cleavage of the $C_5H_7O_2$ ligand, reductive cleavage using $NaBH_4$[215] in methanol was less effective and gave a complex mixture of organic products. Column chromatography afforded small quantities of dimethyl methylsuccinate (ca 9%). No other organic product could be isolated in a pure state from this reaction and although the mechanism by which dimethyl methylsuccinate is formed is unknown, the carbon skeleton of this compound can be readily derived from the oxacyclobutenyl ligand in (IV) and (V) via hydride attack and CO insertion (Eq. 7.4).

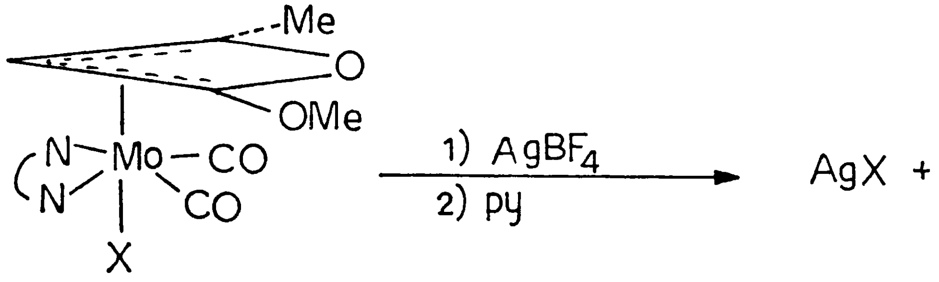
Eq. 7.4



Halide Exchange Reaction with Pyridine

It has been established that the halide anion, X, may be replaced in the complexes $[Mo(\eta^3\text{-allyl})(CO)_2(bipy)X]$ (X=Cl or Br) by neutral ligands such as pyridine,[173] and the cationic complexes so-formed possess greater solubility in polar organic solvents than the parent neutral complexes. Thus, in an attempt to obtain more soluble derivatives of (IV) and (V) for ^{13}C NMR and X-ray crystallographic studies, (IV) or (V) were treated with $AgBF_4$ in acetone followed by pyridine to afford the cationic derivative (VIII) in high yield (ca 90%) (Eq. 7.5).

Eq. 7.5



X = Br, IV
X = Cl, V

$(^N_N$ = bipy

$[Mo(C_5H_7O_2)(CO)_2(bipy)py][BF_4]$
VIII

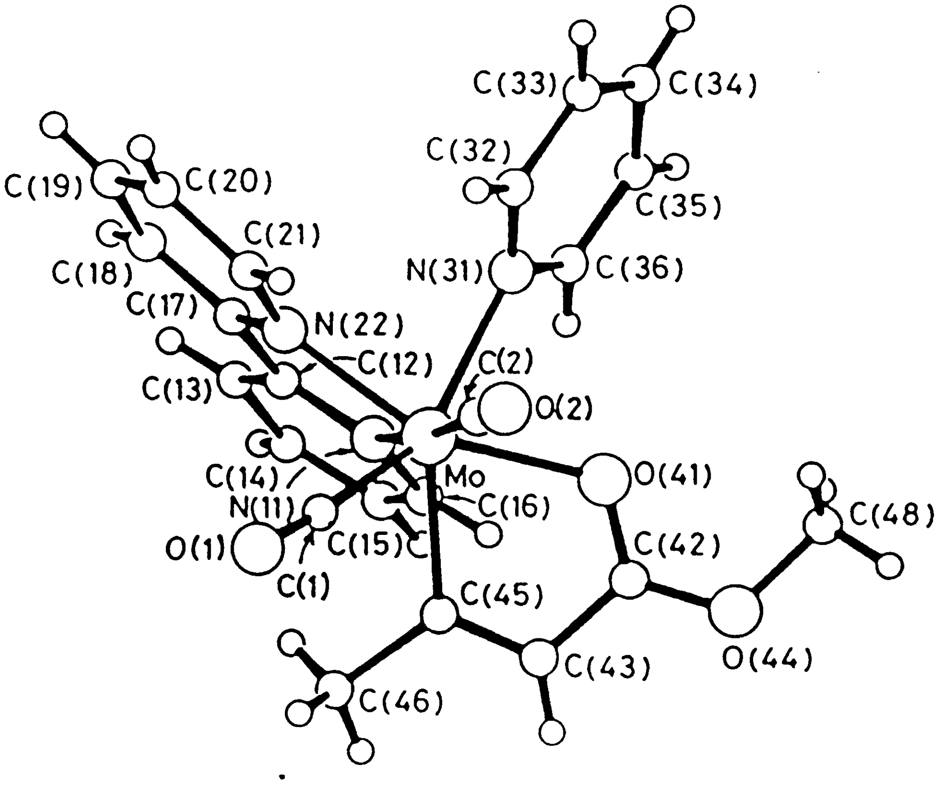
However, although the stoichiometry of the $C_5H_7O_2$ ligand remained the same in (VIII), its mode of bonding had changed from that in (IV) and (V) as evidenced by both infrared and ^1H NMR observations. Of particular significance was the appearance of a coordinated $-CO_2Me$ absorption at ca 1570 cm^{-1} in the infrared spectrum of the coordinated $C_5H_7O_2$ ligand,[185,216] and the change in the ^1H NMR chemical shift of the CH resonance from ca 3.0 p.p.m. in (IV) and (V) to ca 6.4 p.p.m. in (VIII). These latter values are very similar to data reported on the σ-vinyl ketone and σ-vinyl ester complexes of molybdenum and tungsten,[185,201,202] and indicate that a structural rearrangement had occurred on halide abstraction from (IV) and (V). The poor solution stability of complex (VIII) precluded a detailed ^{13}C NMR study, and in order to confirm this structural rearrangement, a single-crystal X-ray diffraction study of complex (VIII) was undertaken.

Discussion of the Structure of Complex (VIII)

For full crystallographic data, the reader is referred to Appendix (I).

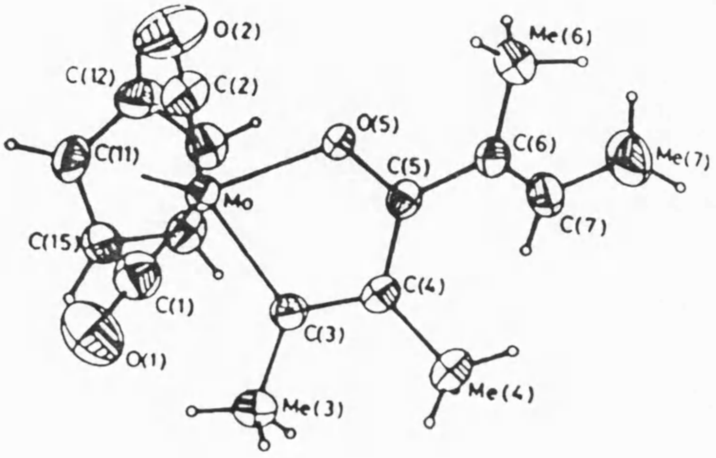
Fig. 7.3 shows the cation together with the atomic numbering scheme. The molybdenum atom is seven-coordinate being bonded to bipy [Mo-N(11) 2.241(7), Mo-N(22) 2.164(7)Å], pyridine [Mo-N(31) 2.275(8)Å] , two carbonyl groups [Mo-C(1) 1.936(10), Mo-C(2) 1.983(11)Å]and to the bidentate $C_5H_7O_2$ ligand. As is apparent from Fig. 7.3, the $C_5H_7O_2$ ligand in complex (VIII) is a chelating σ-vinyl ester moiety, with the metal being bonded to O(41) ((Mo-O(41) 2.164(6)Å)) and C(45) ((Mo-C(45) 2.155(10)Å)). It has been shown to be planar within experimental error.

Fig. 7.3



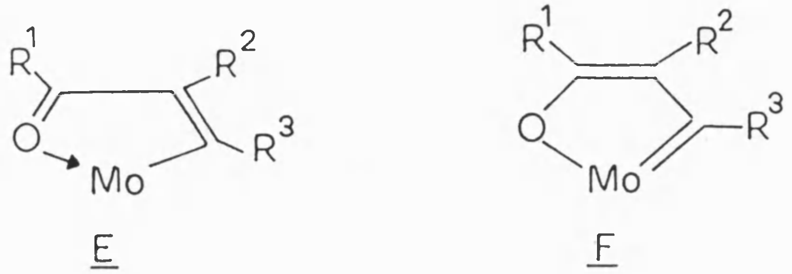
Green et al have recently published the X-ray crystal structure of the molybdenum complex (IX)[217] (Fig. 7.4) which also contains a chelating σ-vinyl ligand.

Fig. 7.4. Crystal Structure of Complex (IX)



As with the σ-vinyl complexes discussed in Chapter 6.2, the organic ligands in complexes (VIII) and (IX) may be considered as intermediate between two extreme cononical forms (E) and (F) as illustrated in Fig. 7.5.

Fig. 7.5. Two Extreme Bonding Modes in Complexes (VIII) and (IX)



R^1= -OMe, R^2 = H, R^3 = Me — VIII

R^2=R^3 = Me, R^1 = —C(Me)=CHMe — IX

The σ-vinyl ketone ligand in (IX) is also planar, reflecting the conjugated nature of the canonical forms (E) and (F). However, consideration of the C-C bond lengths in the ring indicates that canonical form (E) is more significant than (F). Thus, C(4)-C(5) (1.416(4) Å) is longer than C(3)-C(4) (1.380(3) Å), although both these lengths are considerably longer than the C(6)-C(7) distance (1.326(5) Å) which reflects a full C=C double bond. The contribution of canonical form (F) is observed in the C(5)-O(5) distance (1.292(4) Å) that falls between a C-O and C=O bond,[218] and the Mo-C(3) distance (2.142(3) Å) (*cf* Mo-C(sp^2) 2.243(3) Å in [MoCp(P(OMe)$_3$)$_3$(σ-CH=CHBu^t)])[219]. Similarly, the ^{13}C NMR resonance of C(3) is at very low field (261 p.p.m.) indicative of a significant M=C contribution.[139] (cf 129.2 p.p.m. for Mo-C(sp^2) in [MoCp(P(OMe)$_3$)$_3$(σ-CH=CHBu^t)])[219].

The dimensions for the $C_5H_7O_2$ ligand in complex (VIII) are listed in Table 7.1.

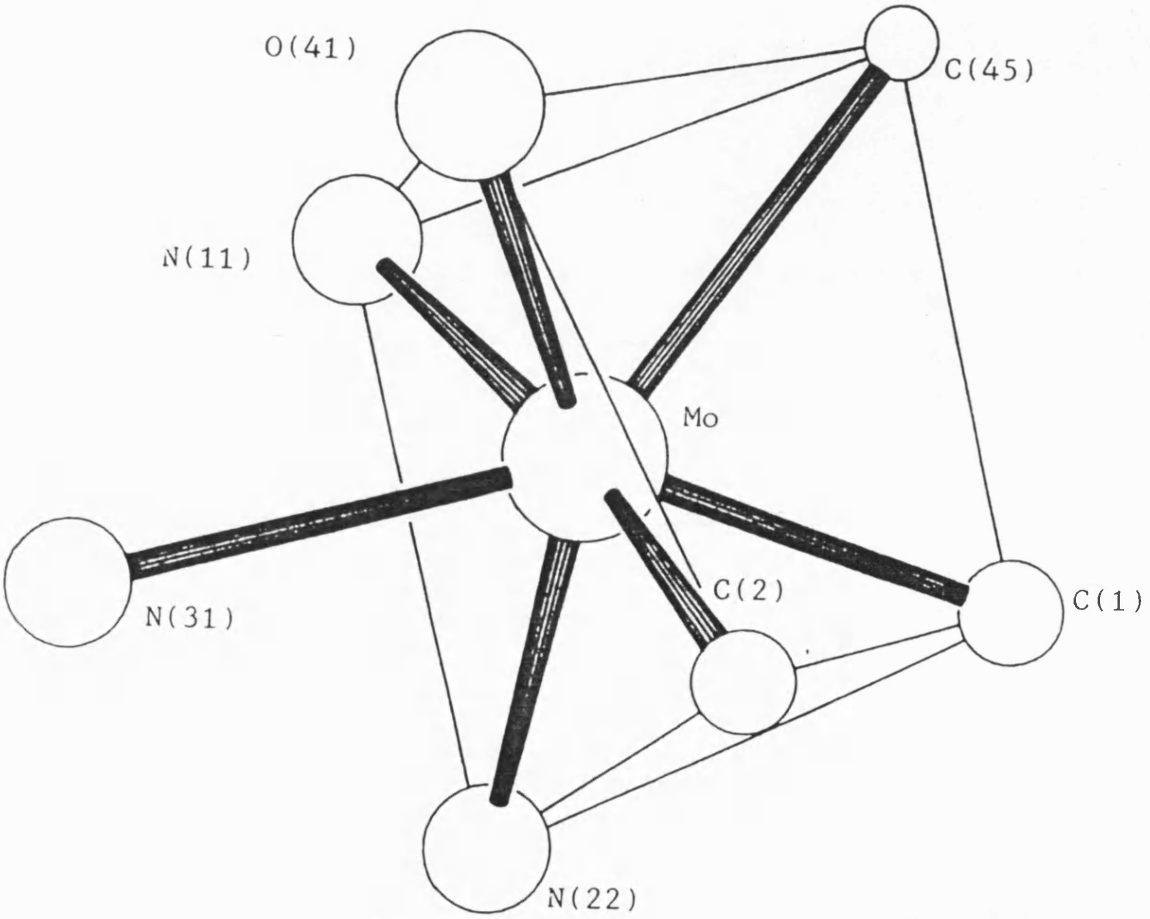
TABLE 7.1 DIMENSIONS FOR THE $C_5H_7O_2$ LIGAND IN COMPLEX (VIII) (DISTANCES IN Å, ANGLES IN DEGREES)

O(41)-C(42)	1.258(12)	Mo-O(41)-C(42)	116.5(5)
C(42)-C(43)	1.388(14)	O(41)-C(42)-C(43)	118.7(8)
C(42)-O(44)	1.329(12)	O(41)-C(42)-O(44)	119.1(8)
C(43)-C(45)	1.329(14)	C(43)-C(42)-O(44)	122.1(9)
O(44)-C(48)	1.399(14)	C(42)-C(43)-C(45)	115.7(9)
C(45)-C(46)	1.533(16)	C(42)-O(44)-C(48)	118.2(8)
		Mo-C(45)-C(43)	115.7(7)
		Mo-C(45)-C(46)	125.5(7)
		C(43)-C(45)-C(46)	118.4(9)

It would appear that the chelating σ-vinyl ester ligand in (VIII) is also best represented by canonical form (E) rather than (F) (Fig. 7.5) from consideration of the C-C bond lengths in the ring system. The C(42)-C(43) (1.388(14)Å) separation is longer than C(43)-C(45) (1.329(14) Å) indicating that the former possesses more C-C bond character than the latter, although C(42)-C(43) is still shorter than the analogous bond in complex (IX), despite the rather large deviation. Again, the contribution from canonical form (F) (Fig. 7.5) to the overall bonding representation is apparent from the C(42)-O(41) distance (1.258(12) Å) and the Mo-C(45) distance (2.155(10) Å). In a recent paper by Bianchini _et al_,[220] the crystal structure of the nickel complex $[(np_3)\overline{\mathrm{NiCH{=}CHC(O}}\mathrm{)OEt}][BPh_4]$ ($np_3{=}N(CH_2CH_2PPh_2)_3$), which also contains a chelating σ-vinyl ester ligand, was described and in contrast to (VIII) and (IX), the organic ligand shows virtually no contribution from cononical form (F) (Fig. 7.5).

The geometry of the seven-coordinate polyhedron around the molybdenum atom in complex (VIII) is highly distorted, no doubt as a result of the steric constraints imposed by the ligands. Using polyhedron analysis,[221] it was found that the geometry is intermediate between a capped trigonal prism and a capped octahedron. In the capped trigonal prism, N(31) is in the capping position, C(2),O(41), N(11) and N(22) occupy the capped face and C(45) and C(1) the remaining edge. This polyhedron is distorted towards a capped octahedron with C(1) in the capping position, N(22), C(45) and C(2) in the capped face and O(41), N(31) and N(11) in the uncapped face. Fig. 7.6. illustrates the primary coordination sphere around the molybdenum atom in complex (VIII).

Fig. 7.6. The Coordination Sphere of Complex (VIII) Showing the Distorted Trigonal Prism

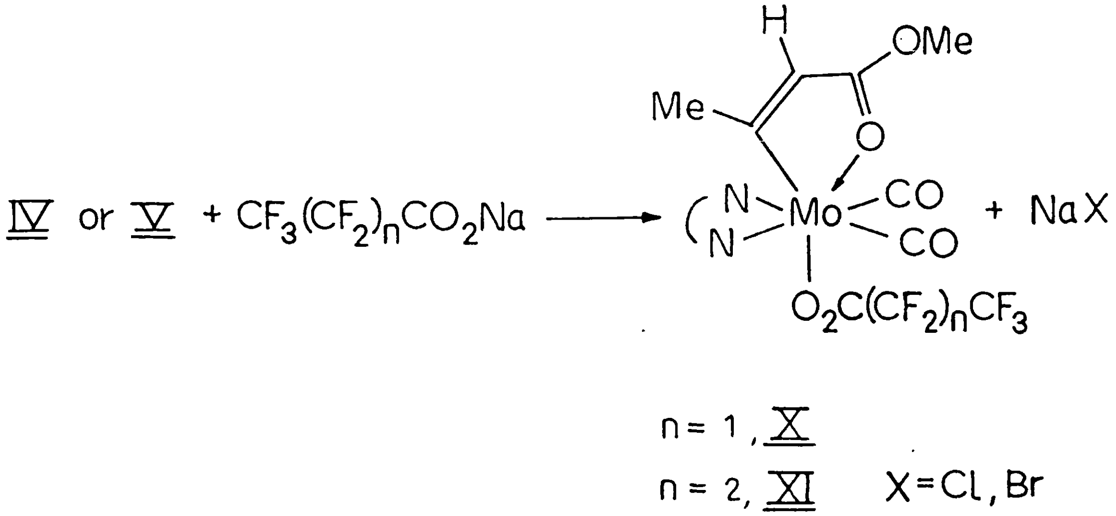


Attempts to convert the chelating σ-vinyl ester ligand into a monodentate vinyl group by treatment with CO or to reform complex (IV) or (V) containing the η^3-oxacyclobutenyl ligand by treating (VIII) with excess halide ions were unsuccessful and resulted instead in reactant decomposition.

Halide Exchange Reaction with $NaO_2C(CF_2)_nCF_3$ (where = 1 or 2)

A halide exchange reaction on the complexes $[Mo(\eta^3\text{-allyl})(CO)_2(bipy)X]$ (where X=Cl or Br) with the anions $CF_3(CF_2)_nCO_2^-$ (where n = 0, 1 or 2)[182] affords perfluorocarboxylate complexes which possess improved solubility in acetone over the parent halogeno compounds. Thus, complexes (IV) and (V) were suspended in acetone and treated with $CF_3(CF_2)_nCO_2Na$ (where n = 1 or 2) to produce moderate yields of the perfluorocarboxylate complexes (X) and (XI) (Eq. 7.6). Although crystallographic data on (X) and (XI) is not available, the similarities in the infrared and ^1H NMR spectra of the $C_5H_7O_2$ ligands in (VIII), (X) and (XI) indicate that this ligand is bonded in a similar way in all three complexes. The asymmetric and symmetric CO_2 stretching modes each occur as single, strong bands separated by ca 235 cm^{-1}, indicative of a monodentate carboxylate ligand[222] as expected for an 18-electron metal atom configuration. Both (X) and (XI) possess greater solution stability than (VIII) which allowed the ^{13}C NMR spectrum of (X) to be recorded. However, despite the higher stability, the solubility of (X) was still insufficient to obtain a signal from the carbon atom σ-bonded to molybdenum.

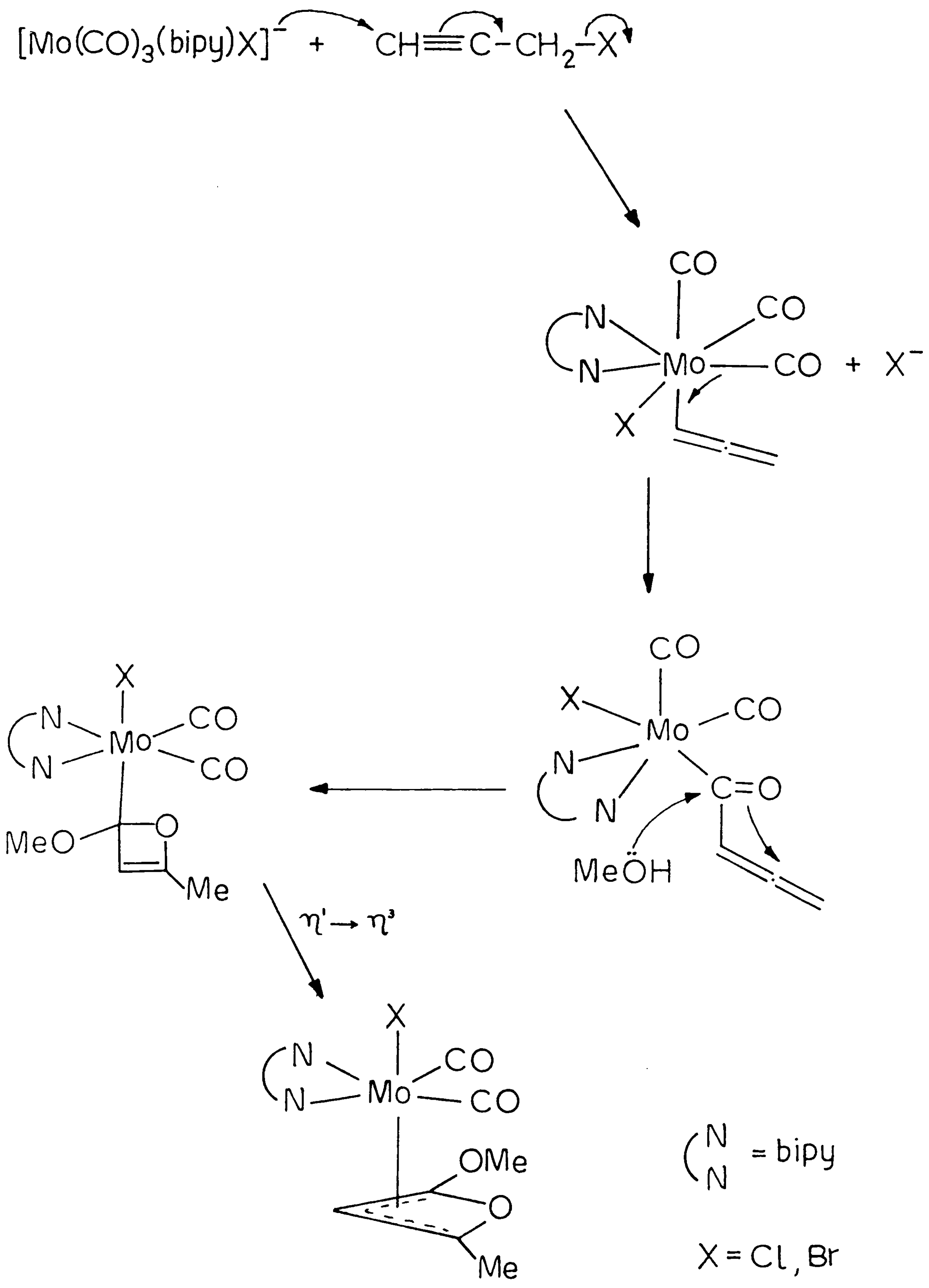
Eq. 7.6.



7.4. MECHANISTIC ASPECTS OF THE FORMATION OF COMPLEXES (IV), (V), (VIII), (X) AND (XI)

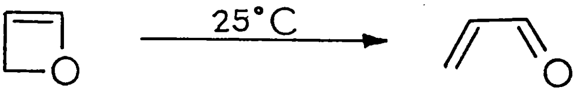
A mechanism for the formation of the η^3-2-methoxy-4-methyl-1-oxacyclobutenyl ligand, as proposed in complexes (IV) and (V), may be rationalised in terms of an S_N2'-type oxidative addition of the propargyl halide (Chapter 6.1) to the $[Mo(CO)_3(bipy)X]^-$ anion (where X = Cl or Br), followed by carbonyl insertion and methanolysis (Scheme 7.3).

Scheme 7.3.


[Mo(CO)3(bipy)X]−
+
CH≡C−CH2−X
CO
N
N
Mo
CO
CO
+ X−
X
CO
X
Mo
CO
N
N
C=O
MeÖH
X
N
N
Mo
CO
CO
MeO
O
Me
η¹ → η³
X
N
N
Mo
CO
CO
OMe
O
Me
N
N
= bipy
X = Cl, Br

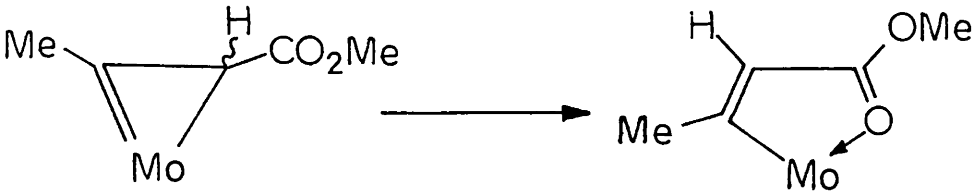
The chelating σ-vinyl ester ligand found in complexes (VIII), (X) and (XI) may be readily derived from the η^3-oxacyclobutenyl ligand via a ring opening process. In this sense, the η^3-oxacyclobutenyl ligand behaves like the "parent" oxete which readily rearranges to acrolein at 25°C[223] (Eq. 7.7).

Eq. 7.7.



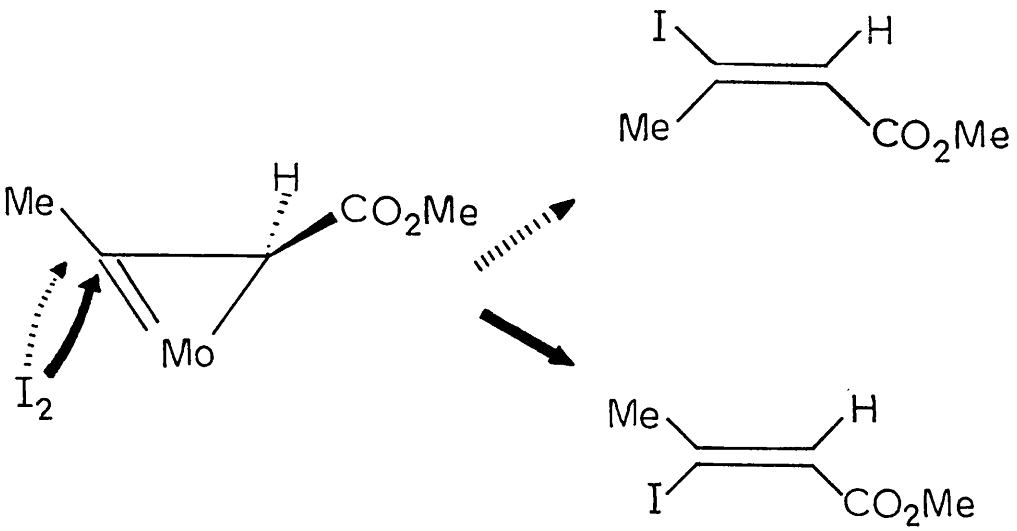
It must be recognised that until the structure of the $C_5H_7O_2$ ligand in (IV) and (V) is established unequivocally, the alternative η^2-alkylidene structure cannot be completely dismissed (Fig. 7.1c). While there is no simple mechanism for the formation of this species from the methoxycarbonylation of a propargyl moiety, the σ-vinyl ester ligand found in (VIII), (X) and (XI) may be readily derived from an η^2-alkylidene species[217] Eq. 7.8.

Eq. 7.4



Finally, the two geometric isomers of methyl-3-iodocrotonate, which are formed when complexes (IV) and (V) are treated with iodine, may also be readily derived from an η^2-alkylidene ligand (Scheme 7.4).

Scheme 7.4.



CHAPTER EIGHT

Molybdenum-mediated methoxy- and ethoxycarbonylation of 1,4-dichlorobut-2-yne: Results and discussion

8.1. FOREWORD

To further investigate the reactivity of $[PPh_4][Mo(CO)_3(bipy)X]$ with prop-2-ynylic halides, the salt $[PPh_4][Mo(CO)_3(bipy)Cl]$ was treated with 1,4-dichlorobut-2-yne in anhydrous methanol in the hope of generating another novel methoxycarbonylated organometallic complex. The reaction mixture precipitated a bright-red microcrystalline solid which was shown by infrared spectroscopy and TLC to contain two *cis*-dicarbonyl complexes. A strong infrared absorption at *ca* 1700 cm^{-1} implied that methoxycarbonylation had occurred in one or both of these complexes. However, it soon became apparent that the relative amounts of the two complexes varied considerably between experiments conducted under apparently identical conditions, and in one case only a single product was found. On the assumption that these inconsistencies were caused by varying traces of water in the solvent, the reaction was carried out in *wet* methanol. This experiment afforded a single product only, whereas a reaction performed in rigorously dried methanol gave a mixture of two products. The second complex was prepared as a single product from the reaction by incorporating dry THF as co-solvent.

Both complexes possessed bonds at *ca* 1700cm^{-1} in their infrared spectra indicating that methoxycarbonylation had indeed occurred in both cases. Analogous reactions could also be performed in ethanol and a reaction mechanism has been postulated in the light of these experimental observations.

8.2 THE REACTIVITY OF $[PPh_4][Mo(CO)_3(bipy)Cl]$ WITH $ClCH_2C\equiv CCH_2Cl$ IN AQUEOUS ALCOHOLS ROH (WHERE R = Me OR Et)

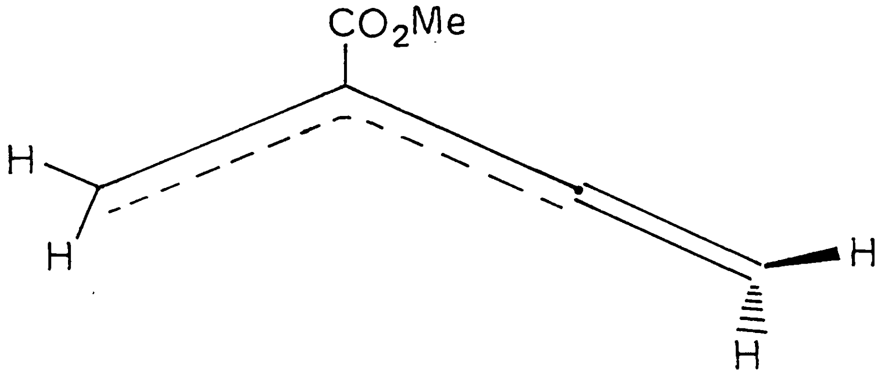
Treatment of a suspension of $[PPh_4][Mo(CO)_3(bipy)Cl]$ in wet methanol with 1,4-dichlorobut-2-yne either at room temperature or at -17°C produced a red, microcrystalline precipitate which was shown by infrared spectroscopy and TLC to be a single complex (XII) containing cis-dicarbonyl ligands (ν(CO) absorptions centred at 1905 and 1980 cm^{-1}). The 1905 cm^{-1} band is split by ca 20 cm^{-1} in samples recorded as nujol mulls but collapses to a single, sharp absorption at 1920 cm^{-1} when spectra were recorded in dichloromethane solutions. ^1H NMR spectroscopy and elemental analysis supported the formula $[Mo(C_6H_7O_2)(CO)_2(bipy)Cl]$, the $(C_6H_7O_2)$ group being evidently formed by the methoxycarbonylation of 1,4-dichlorobut-2-yne. A strong absorption at ca 1700 cm^{-1} in the infrared spectrum of complex (XII) also provided evidence for the presence of an uncoordinated $-CO_2Me$ group.

When the above reaction was performed in wet ethanol, ethoxycarbonylation of 1,4-dichlorobut-2-yne occurred in a similar manner, and the analogous complex (XIII) $[Mo(C_7H_9O_2)(CO)_2(bipy)Cl]$ was obtained in high yield.

The Structure of Complex (XII)

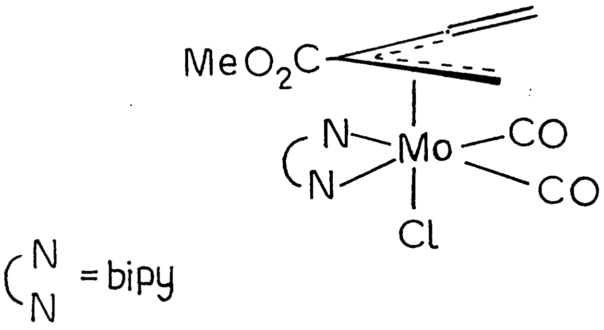
Complex (XII) was only sparingly soluble in common NMR solvents although a satisfactory ^1H NMR spectrum showed $C_6H_7O_2$ resonances at δ 6.28 (doublet), 5.66 (doublet), 3.60 (singlet), 2.82 (singlet) and 1.96 p.p.m. (singlet) in the relative intensities 1:1:1:3:1. These signals are in keeping with an η^3-2-carbomethoxybutadienyl ligand (Fig. 8.1) with the doublets at δ 6.28 and 5.66 p.p.m. (J = 2.1 Hz) belonging to the protons on the uncoordinated $C{=}CH_2$ moiety, and the singlets at δ 3.60 and 1.96 p.p.m. arising from the syn- and anti- protons of the allylic carbon atom respectively.

Fig. 8.1. The η^3-2-Carbomethoxybutadienyl Ligand

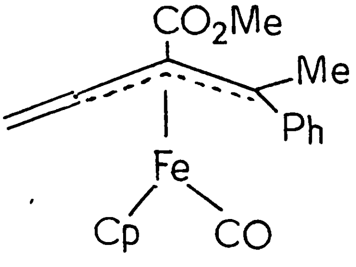


The -OMe protons are found to resonate at rather high field (δ 2.82 p.p.m.), no doubt as a consequence of shielding by the π-electron cloud of the bipy ligand.[182] This observation led to the provisional assignment of the more symmetrical of the two possible structures (see Chapter 5.6, Fig. 5.25) illustrated in Fig. 8.2, which is consistent with the experimental data and yields and expected 18-electron configuration for the molybdenum atom.

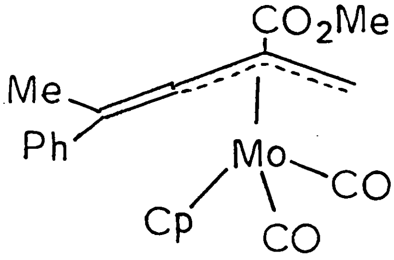
Fig. 8.2. The Provisional Structure of Complex (XII)



While a literature search has not revealed other complexes which possess an η^3-2-carbomethoxybutadienyl ligand, related systems have been reported in complexes (XIV) and (XV).[224]



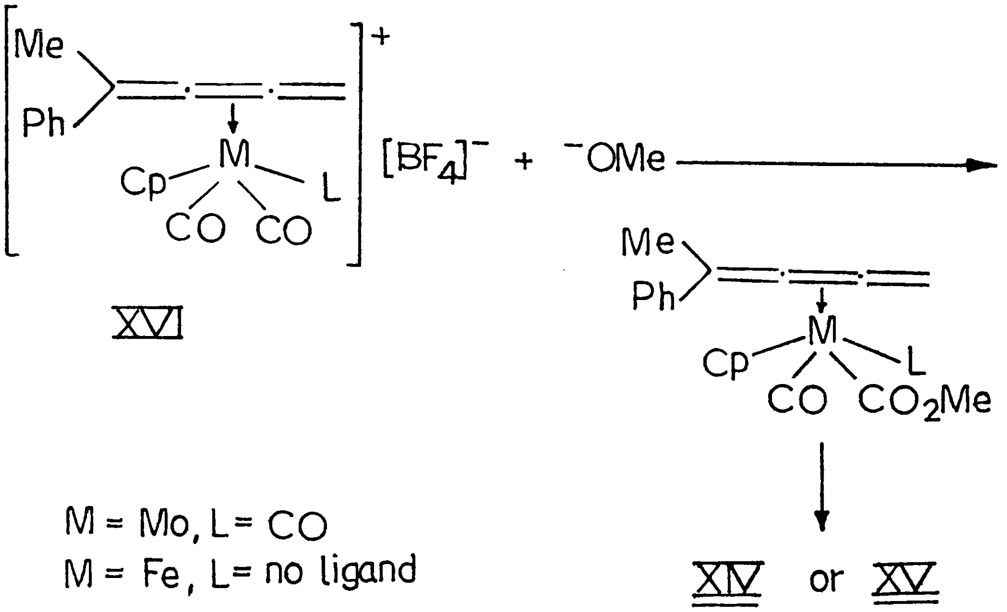
XIV



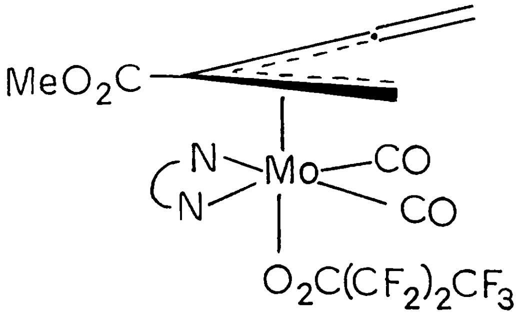
XV

The respective olefinic and allylic protons in (XIV) and (XV) have chemical shifts similar to those found in complex (XII) although the -OMe resonances occur at slightly lower field. These complexes are formed on treating the η^2-butatriene complex (XVI) with sodium methoxide in methanol (Scheme 8.1). Methoxycarbonylation proceeds via the transfer of a metal-bound $-CO_2Me$ group to the coordinated butatriene ligand as shown in Scheme 8.1.

Scheme 8.1



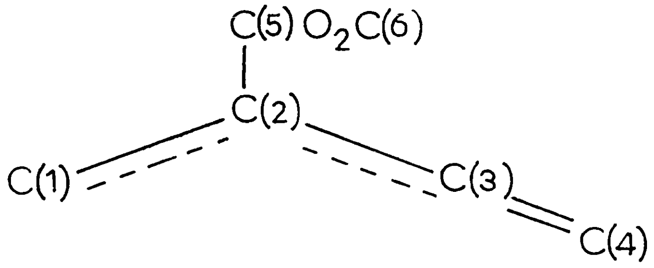
The low solubility of complex (XII) precluded ^{13}C NMR measurements which would have helped confirm the structure of the η^3-2-carbomethoxybutadienyl ligand. However, the corresponding perfluorobutyrate derivative[182] (XVII), prepared by treating complex (XII), with $AgBF_4$ and $NaO_2C(CF_2)_2CF_3$ in acetone, was reasonably soluble in d_6-acetone and gave good ^1H and partial ^{13}C NMR spectra.



XVII

The structure of complex (XVII) is almost certainly that shown above, since 2-methylallyl perfluorocarboxylate complexes are known to adopt this type of symmetrical structure[182] (see Chapter 5.6, Fig. 5.25), and the high field shift of δ 2.80 p.p.m. for the -OMe protons in the ^{1}H NMR spectrum of complex (XVII) is in accordance with this group lying above the π-electron cloud of the bipy ligand. The asymmetric and symmetric $-CO_2-$ stretching modes of the perfluorobutyrate ligand occur at ca 1700 and ca 1460 cm^{-1} respectively in the infrared spectrum of complex (XVII), and the separation of approximately 240 cm^{-1} indicates that the perfluorocarboxylate ligand is monodentate[222] as expected for an 18-electron metal atom configuration (n.b. the $-CO_2-$ asymmetric mode is coincident with the $-CO_2Me$ carbonyl absorption). Of the six carbon atoms in the η^3-2-carbomethoxybutadienyl moiety, only four could be identified with certainty in the ^{13}C NMR spectrum of complex (XVII) (Fig. 8.3). As expected for quaternary carbon atoms, the C(2) and C(3) resonances were of low intensity and were consequently unobserved in the ^{13}C NMR spectrum of complex (XVII).

Fig. 8.3. Proton Decoupled ^{13}C NMR Shift Values for the η^3-2-Carbomethoxybutadienyl Ligand (p.p.m. Relative to TMS)



C(1)	53·4	C(3)	—	C(5)	169·8
C(2)	—	C(4)	106·4	C(6)	51·4

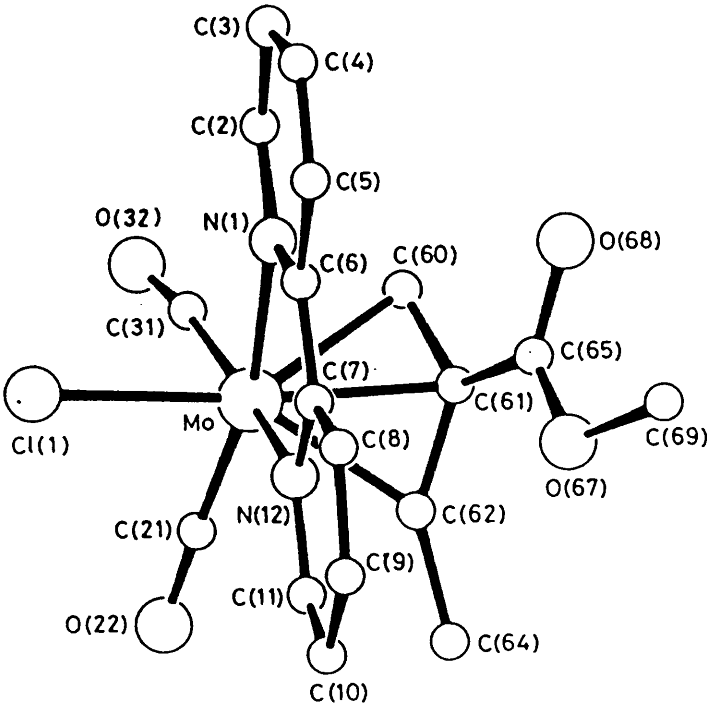
In order to confirm this unusual structure and explore the structural features of the little-known η^3-butadienyl moiety, a single crystal x-ray diffraction study of complex (XII) was undertaken.

Discussion of the Molecular Structure of Complex (XII)

For full crystallographic data, the reader is referred to Appendix (II).

Fig. 8.4 shows the molecular structure of complex (XII). The molybdenum atom occupies pseudooctahedral geometry, being bonded to two carbonyl groups [Mo-C(31) 2.015(34), Mo-C(21) 1.915(37) Å] and a bipy ligand [Mo-N(1) 2.203(20), Mo-N(12) 2.206(26) Å] in the equatorial plane. One axial position is occupied by a chlorine atom [Mo-Cl(1) 2.486(9) Å] and the other by three carbon atoms from the trans-η^3-2-carbomethoxybutadienyl ligand.

Fig. 8.4. The Molecular Structure of Complex (XII)



Of particular interest are the dimensions associated with this unique ligand (Table 8.1)

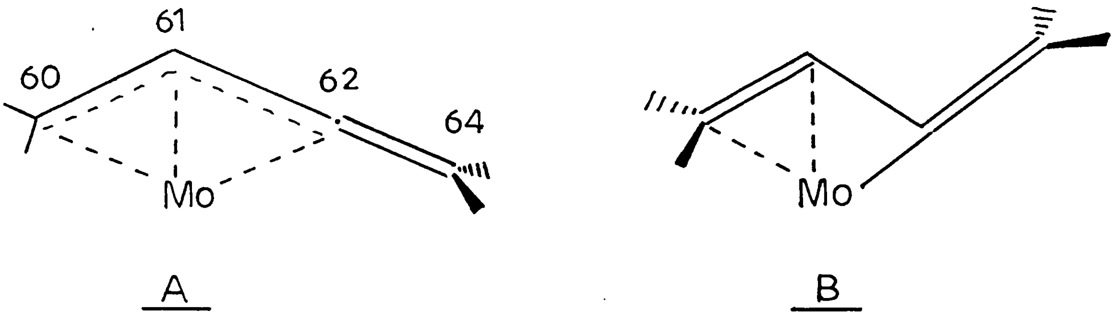
TABLE 8.1. DIMENSIONS FOR THE $C_6H_7O_2$ LIGAND IN COMPLEX (XII) (DISTANCES IN Å, ANGLES IN DEGREES)

Mo-C(60)	2.321(39)	C(60)-C(61)-C(62)	116.2(31)
Mo-C(61)	2.218(34)	C(61)-C(62)-C(64)	148.3(35)
Mo-C(62)	2.224(31)	C(60)-C(61)-C(65)	123.0(33)
C(60)-C(61)	1.442(46)	C(62)-C(61)-C(65)	120.3(32)
C(61)-C(62)	1.41(5)	C(61)-C(65)-O(68)	119.9(33)
C(62)-C(64)	1.45(5)	C(61)-C(65)-O(67)	118.7(30)
C(61)-C(65)	1.463(41)	O(68)-C(65)-O(67)	121.4(30)
C(65)-O(68)	1.268(37)	C(65)-O(67)-C(69)	113.0(29)
C(65)-O(67)	1.298(36)		
O(67)-C(69)	1.496(38)		

The molybdenum atom is bonded to the three carbon atoms C(60), C(61) and C(62) at distances of 2.321(39), 2.218(34) and 2.224(31) Å respectively. The Mo-C(62) distance at 2.224(31) Å is shorter than other reported Mo-terminal allyl carbon distances in analogous complexes[137] (see Chapter 5.6, Table 5.1), and the significant difference in the C(60)-C(61) (1.442(46)Å) and C(61)-C(62)(1.41(5)Å) distances indicates appreciable distortion in the Mo-C(60)-C(61)-C(62) fragment. While the short C(61)-C(62) distance might well be a consequence of the C(61) and C(62) hybridisation states (formerly sp^2 and sp respectively), the overall asymmetry in this fragment, together with the trans-arrangement of the C_4 unit (C(61)-C(62)-C(64) =

148.3(35)°) indicates a distortion from the idealised η^3-allylidene bonding mode (A)(Fig. 8.5) towards the extreme σ,π- bonding mode (B) (Fig. 8.5).

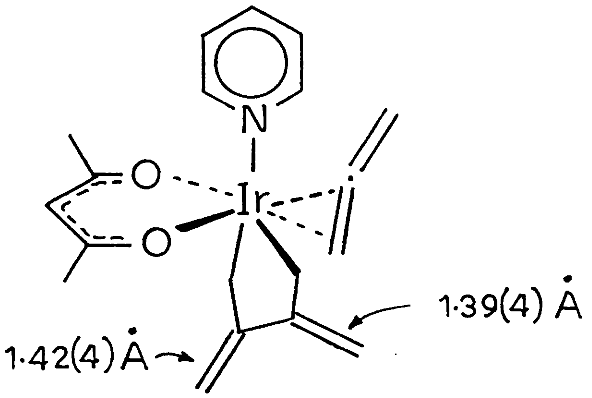
Fig. 8.5. Extreme Bonding Modes for the η^3-Butadienyl Ligand in Complex (XII)



The distortions in the Mo-C(60)-C(61)-C(62) fragment become apparent when the contribution from this bonding mode is considered. Thus, the shortening of C(61)-C(62) and Mo-C(62) can be attributed to the increased σ-character of these bonds while the C(61)-C(62)-C(63) angle of ca 148° reflects the intermediate hybridisation (sp/sp^2) of C(62).

Structural studies have confirmed that the short-long-short C-C bond sequence of free butadiene is frequently reversed in η^4-butadiene complexes[225] as a consequence of the simultaneous donor/acceptor interactions of such ligands.[226] Despite the uncertainties in the C-C bond lengths in complex (XII) which preclude accurate comparisons, it seems likely that the abnormally long uncoordinated carbon-carbon double bond C(62)=C(64)(1.45(5) Å) results from analogous interactions which populate anti-bonding diene orbitals, even though the $C_6H_7O_2$ ligand is η^3-bonded in order that the d^4metal ion achieves an 18-electron configuration.

While the above provides a rationale for the exceptionally long uncoordinated carbon-carbon double bond C(62)=C(64), it is worthy of note that long carbon-carbon double bonds occur in the iridium complex (XVIII)[227]

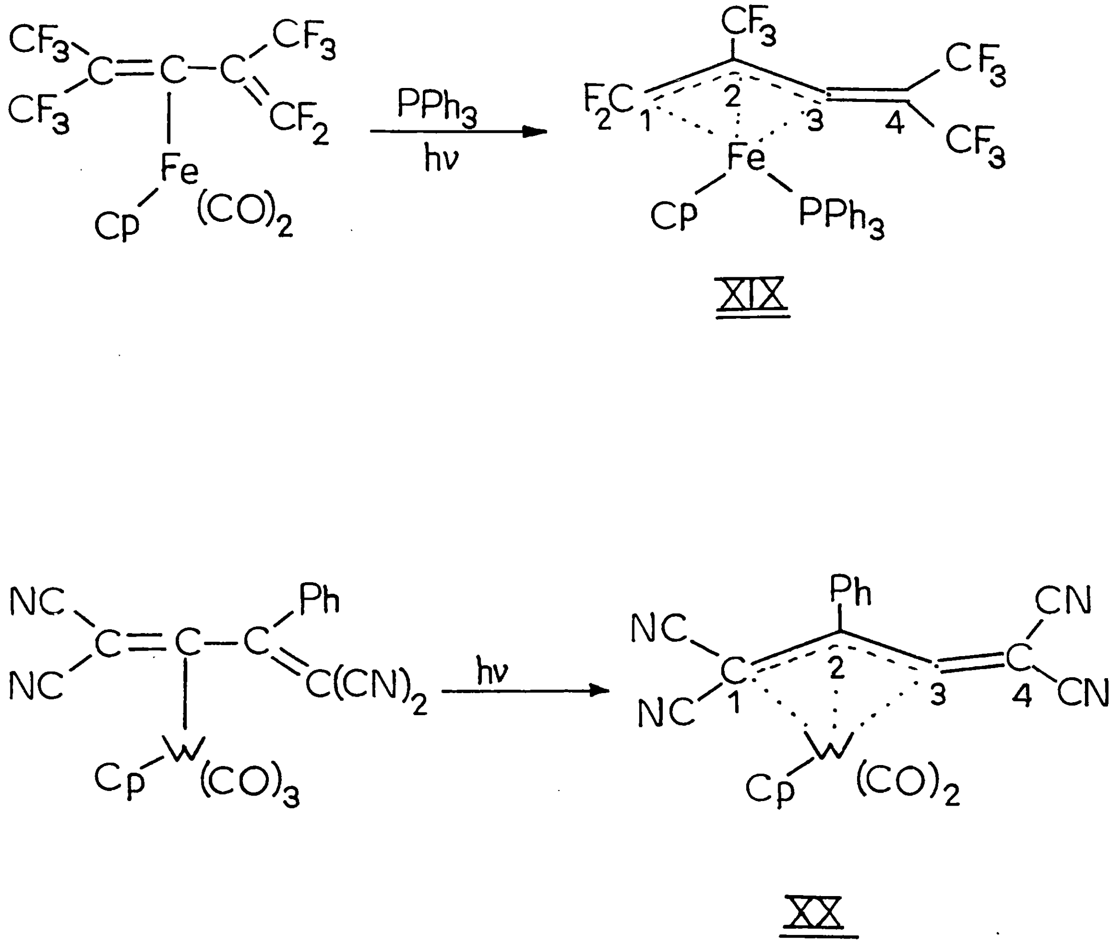


XVIII

The authors make no comment about these dimensions, which is somewhat surprising since the analogous diene fragment in the corresponding 3,4-dimethylenerhodacyclopentane moiety[228] possesses structural parameters similar to gaseous butadiene (C-C=1.464 C=C = 1.337 Å).[229]

A structural survey has revealed only two crystallographic studies on η^3-butadienyl complexes.[230,231] Both complexes (XIX) and (XX) are formed from σ-butadienylic precursors containing highly electron-withdrawing substituents (Scheme 8.2), thus precluding direct comparisons with complex (XII).

Scheme 8.2

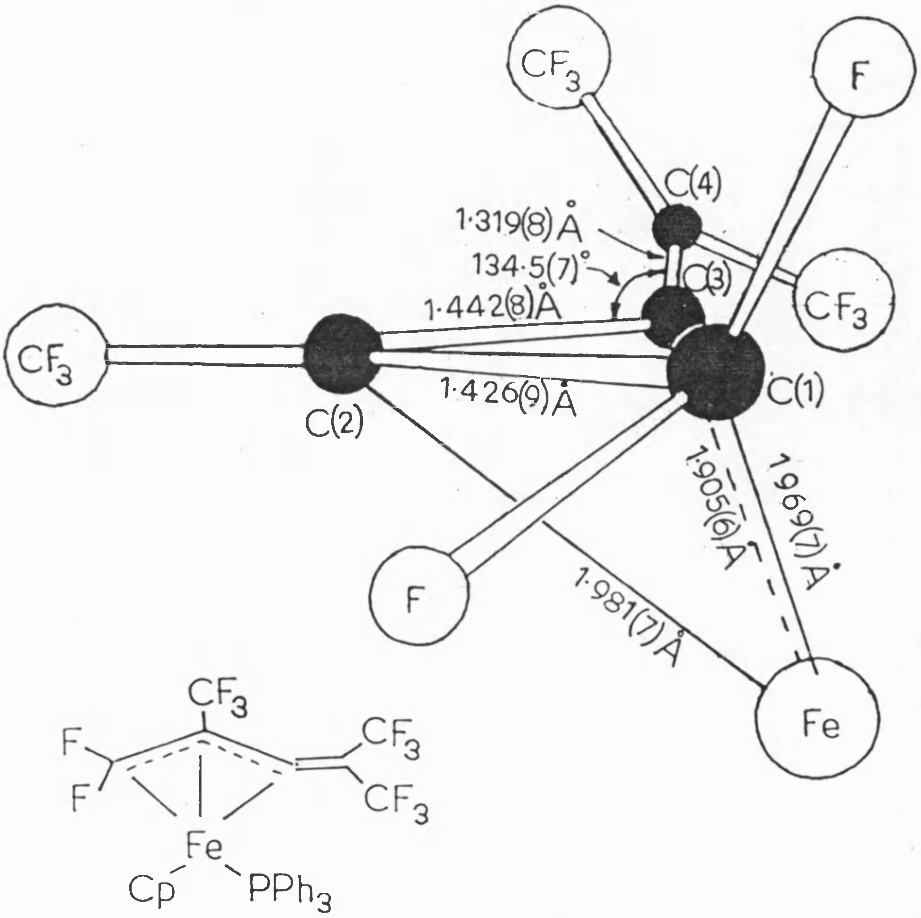


XIX

XX

Fig. 8.6 illustrates the Fe-C_4 fragment of the iron complex (XIX),[230] which has been formulated as an η^3-allylidene complex as shown in the in-lay.

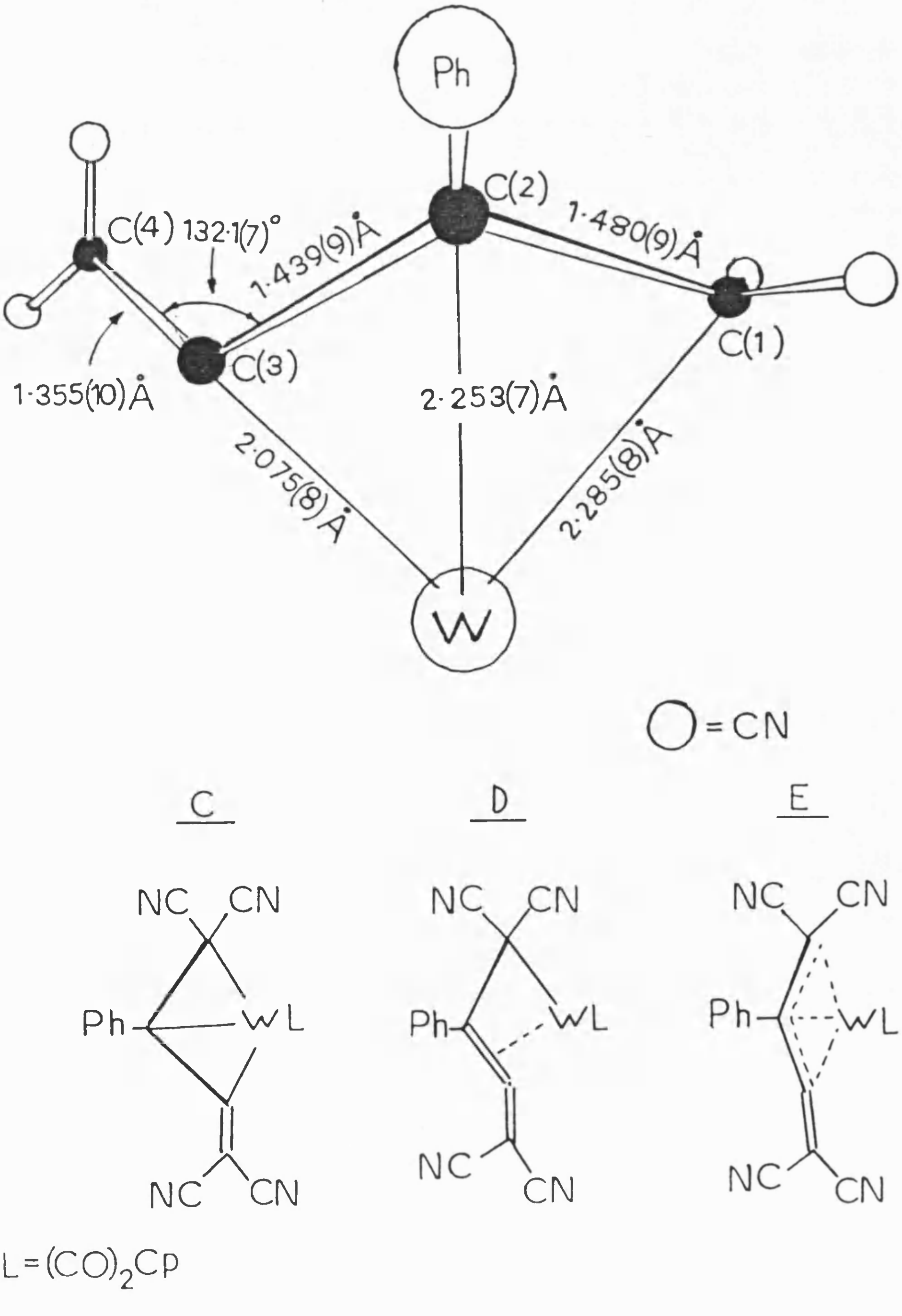
Fig. 8.6. The Structure of the η^3-Butadienyl Ligand in Complex (XIX)



The length of the uncoordinated double bond C(3)=C(4) is 1.319(8) Å and the allylic carbon-carbon bond lengths C(1)-C(2) and C(2)-C(3) are similar at 1.426(9) and 1.442(8)Å respectively. There is however, a pronounced shortening of the Fe-C(3) bond (1.905(6)Å) analogous to that found in complex (XII), and the C(2)-C(3)-C(4) angle of 134.5(7)° is somewhat smaller than would be anticipated for the proposed mode of bonding.

Three bonding modes have been considered for the cyanocarbon ligand found in the tungsten complex (XX).[231] These are illustrated in (C), (D) and (E) of Fig. 8.7, together with the dimensions of the W-C_4 fragment.

Fig. 8.7. The Bonding Descriptions of the Cyanocarbon Ligand in Complex (XX)



The authors believe that the bonding in the W-C_3 fragment of complex (XX) is best related to the methylenetungstabicyclobutane derivative (C). In support of this description are the short W-C bonds, W-C(1) (2.285(8) Å), W-C(2) (2.253(7) Å) and W-C(3) (2.075(8) Å) and the C(1)-C(2)-C(3) bond angle at 104.5(6)°. The allenyl description (D) has also been considered and the structural features supporting this mode of bonding are:

(i) the C(1)-C(2)-C(3)-C(4) sequence, in which separations are consistent with a C-C single bond, a C=C double bond interacting with a tungsten atom, and an uncoordinated C=C double bond,

(ii) the C(2)-C(3)-C(4) angle (132.1(7)°) which is similar to those found in η^2-allene complexes[232-234] and

(iii) the near orthogonality of the two -$C(CN)_2$ fragments (77.9°) which is an expected consequence of the orthogonality of the allene π-orbitals.

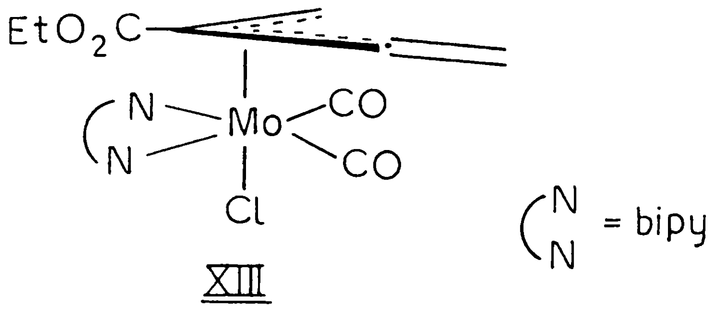
Finally, the authors consider the allylidene formulation (E) consistent with the "similarity" in bond lengths C(1)-C(2) and C(2)-C(3), although the overall geometry of the W-C_3 unit is conspicuous and somewhat unexpected for a multicentric bonding mode.

In summary, it is apparent from the foregoing discussions that a more comprehensive description for the bonding of η^3-butadienyl ligands must await an M.O.-based treatment. However, while it is clear that no single qualitative bonding scheme can be defined, the η^3-butadienyl ligand does behave as a formal 3-electron donor.

The Structure of Complex (XIII)

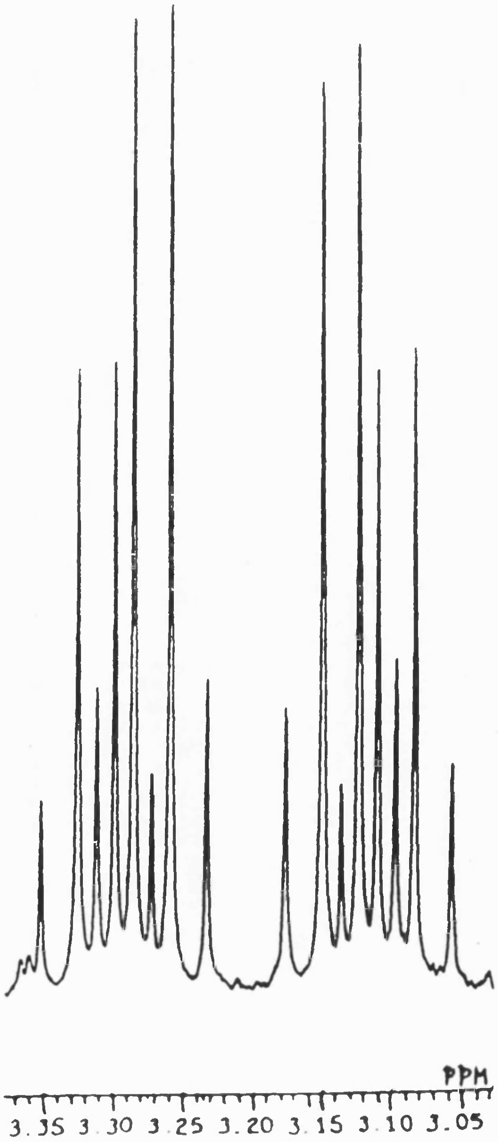
The reaction of [PPh_4][$Mo(CO)_3(bipy)Cl$] with 1,4-dichlorobut-2-yne in wet ethanol either at room temperature or at -17°C affords complex (XIII) as a red, microcrystalline solid. The elemental analysis was consistent with the formula [$Mo(C_7H_9O_2)(CO)_2(bipy)Cl$] and the infrared spectrum of complex (XIII) displayed ν(CO) absorptions at ca 1975 and ca 1905 cm^{-1} together with a ν(C=O) stretching mode at 1690 cm^{-1}. Fig. 8.8. illustrates the structure of complex (XIII) which is expected to be directly analogous to that of complex (XII).

Fig. 8.8. The Proposed Structure of Complex (XIII)



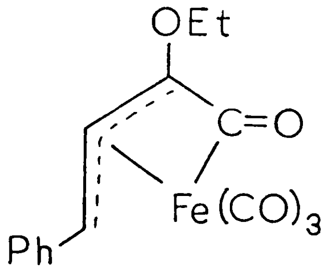
Complex (XIII) displayed improved solubility over complex (XII), and the ^1H NMR spectrum of (XIII) showed $C_7H_9O_2$ resonances which are consistent with an η^3-2-carboethoxybutadienyl ligand. Thus, the uncoordinated $C=CH_2$ protons occur as doublets at δ 6.26 and 5.63 p.p.m. (J=2.0Hz), while the allylic syn- and anti- protons resonate at δ 3.61 and 1.95 p.p.m. respectively. The $-CH_2-$ protons of the ethoxy group, sensing the chirality of the molecule, are magnetically non-equivalent and give rise to a complex spin pattern. Under high resolution at 270 MHz, each proton occurs as a "quartet of doublets" centred at δ 3.28 and 3.11 p.p.m. respectively (Fig. 8.9), the whole conforming to the pattern of intensity expected for an AB system with a $\Delta\nu/J$ of about 4.5.

Fig. 8.9. The ^1H NMR spectrum of the Ethoxy-CH_2- Group in Complex (XIII)



Each "quartet of doublets" arises from the corresponding proton undergoing geminal coupling with its neighbour (J=10.5Hz) and vicinal coupling with the protons of the adjacent $-CH_3$ group (J=7.1Hz). The $-CH_3$ group appears as a triplet at δ 0.65 p.p.m. (J=7.1Hz) since both protons of the $-CH_2-$ group couple equally with the three methyl protons.

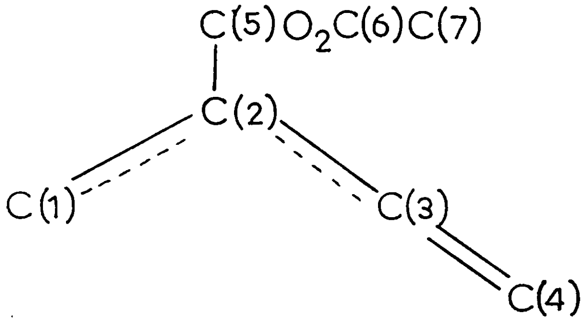
Molecular models have shown that the magnetic non-equivalence of the $-CH_2-$ protons is probably due to a conformational preference of the ethoxy group, imposed by the steric constraints of the bipy ligand. The magnetic non-equivalence of $-CH_2-$ protons in an ethoxy group has also been observed in the iron complex (XXI), with the $-CH_2-$ group appearing as a multiplet at δ 3.89 p.p.m. in its ^1H NMR spectrum.[235]



XXI

Only four of the seven carbon atoms in the η^3-2-carboethoxybutadienyl ligand could be observed in the ^{13}C NMR spectrum of complex (XIII). These are assigned in Fig. 8.10.

Fig. 8.10 Proton Decoupled ^{13}C NMR Shifts Values for the η^3-2-Carboethoxybutadienyl Ligand (p.p.m. Relative to TMS)



C(1)	50·5	C(3)	—	C(5)	—	C(7)	13·8
C(2)	—	C(4)	106·2	C(6)	60·6		

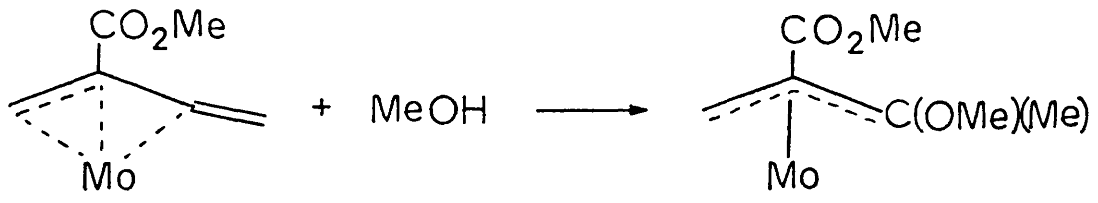
8.3. THE REACTIVITY OF $[PPh_4][Mo(CO)_3(bipy)Cl]$ WITH $ClCH_2C{\equiv}CCH_2Cl$ IN ANHYDROUS ALCOHOLS ROH (WHERE R = Me OR Et) IN THF

Treatment of a suspension of $[PPh_4][Mo(CO)_3(bipy)Cl]$ in anhydrous methanol/THF at room temperature or -17°C afforded a red, microcrystalline solid that was shown by infrared spectroscopy and TLC to contain a single cis-dicarbonyl complex (XXII) (ν(CO) 1875, 1955 cm^{-1}). Elemental analysis gave the formula $[Mo(C_7H_{11}O_3)(CO)_2(bipy)Cl]$, and the strong ν(C=O) stretching mode observed at ca 1700 cm^{-1} in the infrared spectrum revealed the presence of an uncoordinated $-CO_2Me$ group. When the reaction was performed in anhydrous ethanol/THF, the analogous ethoxy complex (XXIII), $[Mo(C_9H_{15}O_3)(CO)_2(bipy)Cl]$ was formed in high yield.

The Structure of Complex (XXII)

It was apparent from elemental analyses that complex (XXII) was a hydromethoxylated derivative of complex (XII). Olefin proton signals were absent from the ^1H NMR spectrum of complex (XXII) and the $C_7H_9O_3$ moiety showed resonances at δ 3.35 (doublet), 3.21 (singlet), 2.88 (singlet), 2.31 (doublet) and 2.30 p.p.m. (singlet) in the relative intensities 1:3:3:1:3, indicative of a hydromethoxylated η^3-2-carbomethoxybutadienyl ligand in which addition of methanol has occurred regiospecifically across the uncoordinated carbon-carbon double bond to afford a terminal -C(OMe)(Me) group (Scheme 8.3).

Scheme 8.3



The signals at δ 3.21 and 2.30 p.p.m. are compatible with the -OMe and -Me substituents respectively, while the remaining signals are consistent with the allylic syn- (δ 3.35 p.p.m.), allylic anti- (δ 2.31 p.p.m.) and $-CO_2Me$ (δ 2.88 p.p.m.) protons.

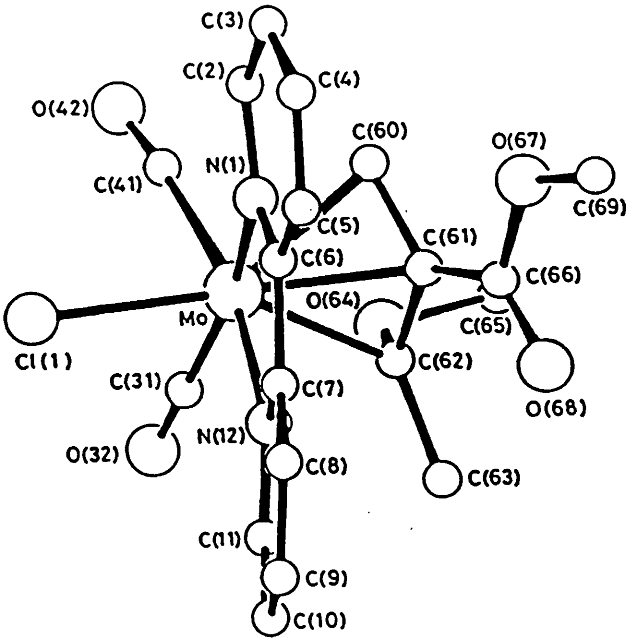
That there are only two signals for the -OMe and -Me groups implies that hydromethoxylation also occurs stereospecifically, affording a single diastereoisomer. The low solubility of complex (XXII) precluded ^{13}C NMR measurements which may have confirmed the regio- and stereospecificity of the hydromethoxylation, and attempts to prepare more soluble derivatives[173,182] (see Chapter 7.3) only resulted in decomposition of the organometallic. A single crystal x-ray diffraction study was therefore undertaken in order to establish the absolute structure of complex (XXII).

Discussion of the Molecular Structure of Complex (XXII)

For full crystallographic data, the reader is referred to Appendix (III).

Fig. 8.11 shows the molecular structure of complex (XXII).

Fig. 8.11 The Molecular Structure of Complex (XXII)



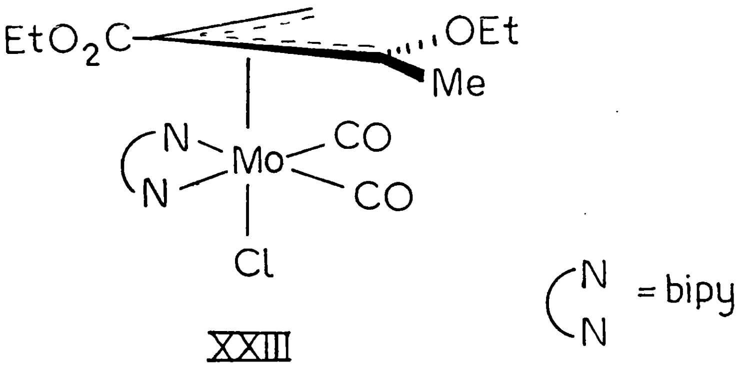
The molybdenum atom occupies pseudooctahedral geometry, being bonded to two carbonyl groups [Mo-C(31)1.922(17) Mo-C(41)2.065(17)Å] and a bipyridyl ligand [Mo-N(1)2.229(12), Mo-N(12)2.232(13)Å] in the equatorial plane. One axial position is occupied by a chlorine atom [Mo-Cl(1)2.482(4)Å] and the other by three carbon atoms of the η^3-$C_7H_{11}O_3$ ligand. The ligand is indeed formally derived from that in complex (XII) by regio- and stereoselective addition of methanol across the -C=CH_2 moiety, so yielding syn-Me and anti-OMe substituents with unexceptional C(61)-C(62)-C(63) and C(61)-C(62)-O(64) bond angles of 123.5(16) and 115.5(1.4)° respectively.[137]

The Mo-C(60)-C(61)-C(62) fragment possesses the geometry associated with a symmetrically bound η^3-allyl ligand (see Chapter 5.6 Table 5.1). Thus, the Mo-C(60) and Mo-C(62) bond lengths are similar at 2.262(19)Å and 2.343(18)A respectively, while the C(60)-C(61) (1.415(26)Å) and C(61)-C(62) (1.409(22)Å) distances are essentially equal. In contrast to the exceptionally long uncoordinated carbon-carbon double bond C(62)-C(64) (1.45(5)Å) in complex (XII), the corresponding C(62)-C(63) (1.465(24)Å) distance in complex (XXII) is characteristic of a Csp^2-Csp^3 interaction,[137, 236] while the conformation of the $-CO_2Me$ substituent is reversed relative to that in complex (XII), in agreement with a mechanism in which hydromethoxylation of the $-C=CH_2$ moiety precedes η^3-bonding of the ligand (see Chapter 8.4). The overall structure of complex (XXII) is therefore typical of a Group (VI) pseudooctahedral η^3-allyl complex[137] and shows no anomalous features.

The Structure of Complex (XXIII)

The reaction of $[PPh_4][Mo(CO)_3(bipy)Cl]$ with 1,4-dichlorobut-2-yne in anhydrous ethanol/THF affords complex (XXIII) which is the hydroethoxylated derivative of complex (XIII). The structure assigned to complex (XXIII) is shown in Fig. 8.12

Fig. 8.12 The Proposed Structure of Complex (XXIII)



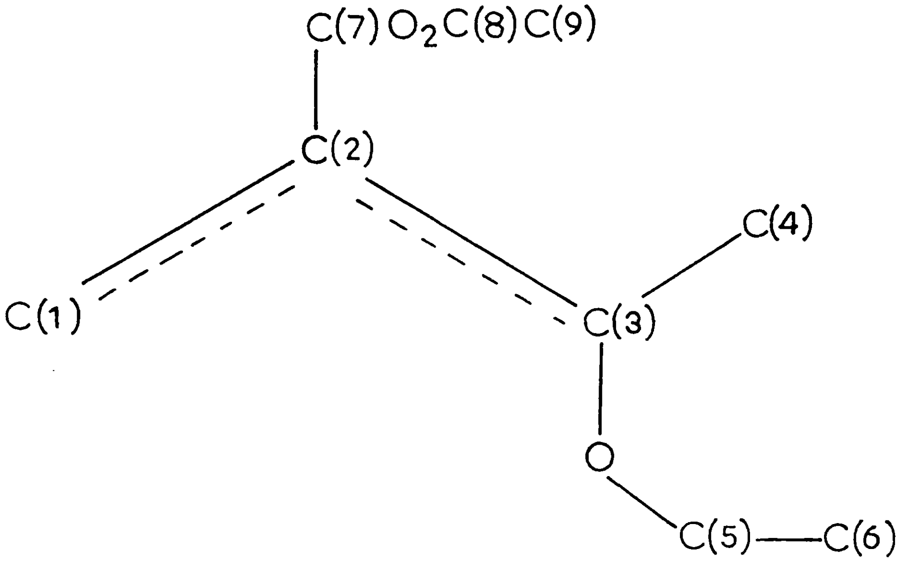
XXIII

A singlet resonance at δ 2.33 p.p.m. in the ^1H NMR spectrum of complex (XXIII) is consistent with the proposed syn-orientation of the terminal -Me group (cf δ 2.30 p.p.m. for syn-Me in complex (XXII)).

Complex (XXIII) was reasonably soluble in CD_2Cl_2 and gave a satisfactory ^{13}C NMR spectrum from which seven of the nine carbon atoms in the η^3-$C_9H_{15}O_3$ ligand could be identified with certainty. Fig. 8.13 illustrates the η^3-$C_9H_{15}O_3$ ligand together with the appropriate ^{13}C NMR assignments.

Fig. 8.13. Proton Decoupled ^{13}C NMR Shift Values for the η^3-$C_9H_{15}O_3$ Ligand in Complex (XXIII)

(p.p.m. Relative to TMS)

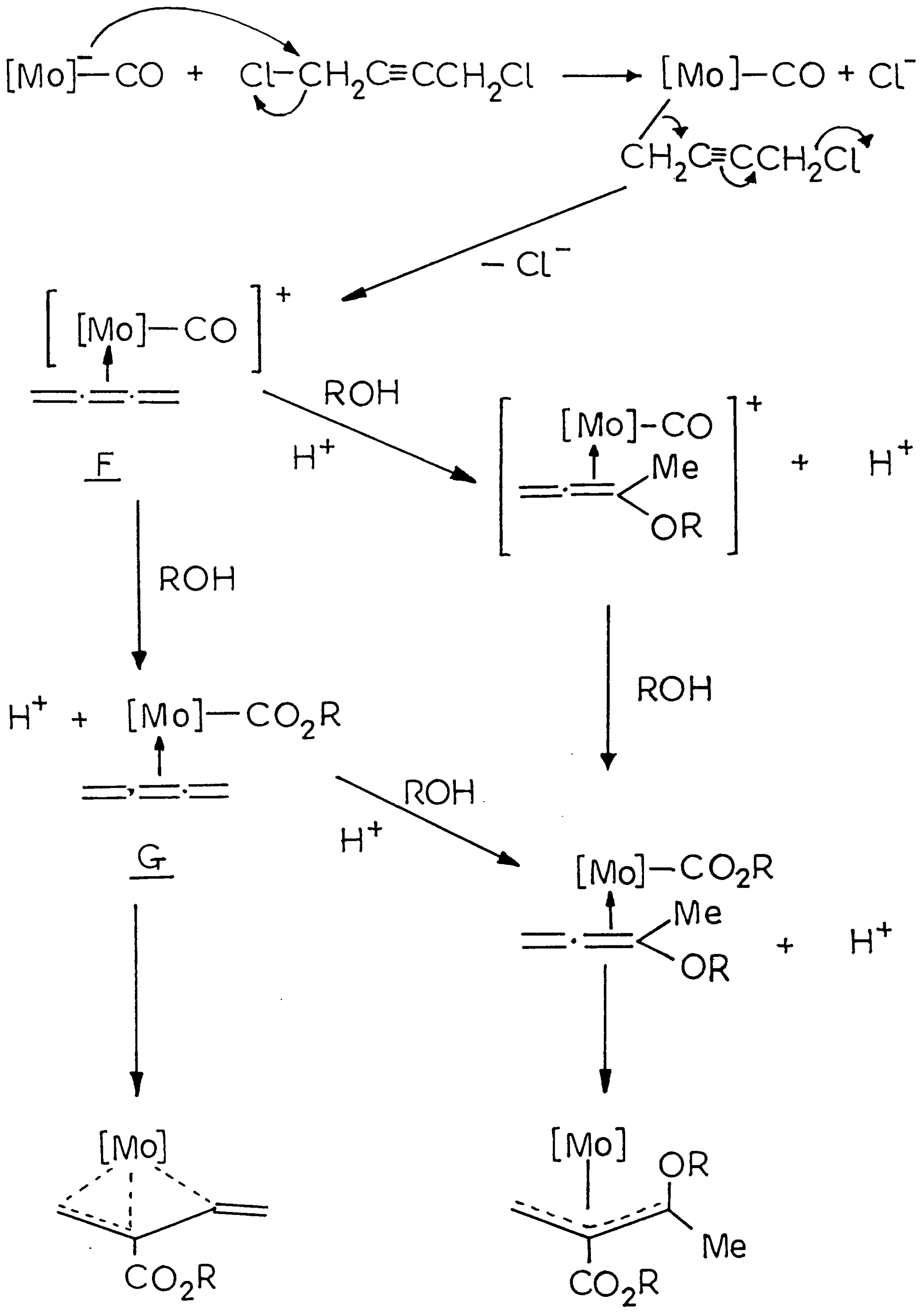


C(1)	48·0	C(4)	21·5	C(7)	170·7
C(2)	——	C(5)	68·4	C(8)	60·0
C(3)	——	C(6)	15·2	C(9)	13·5

8.4. MECHANISTIC ASPECTS OF THE FORMATION OF COMPLEXES (XII), (XIII), (XXII) AND (XXIII)

The formation of complexes (XII), (XIII), (XXII) and (XXIII) would appear at first sight to be directly analogous to the formation of complexes (XIV) and (XV)[224] (Chapter 8.2). Thus, S_N2 oxidative addition of 1,4-dichlorobut-2-yne to the $[Mo(CO)_3(bipy)Cl]^-$ anion and concomitant elimination of a chloride ion forms an intermediate cationic η^2-butatriene complex (F) which may then undergo subsequent alcoholysis to afford the complexes (XII) and (XIII) (Scheme 8.4), while acid catalysed alcoholysis of the η^2-butatriene ligands in (F) and (G) provides a route to the hydroalkoxylated derivatives (XXII) and (XXIII).

Scheme 8.4



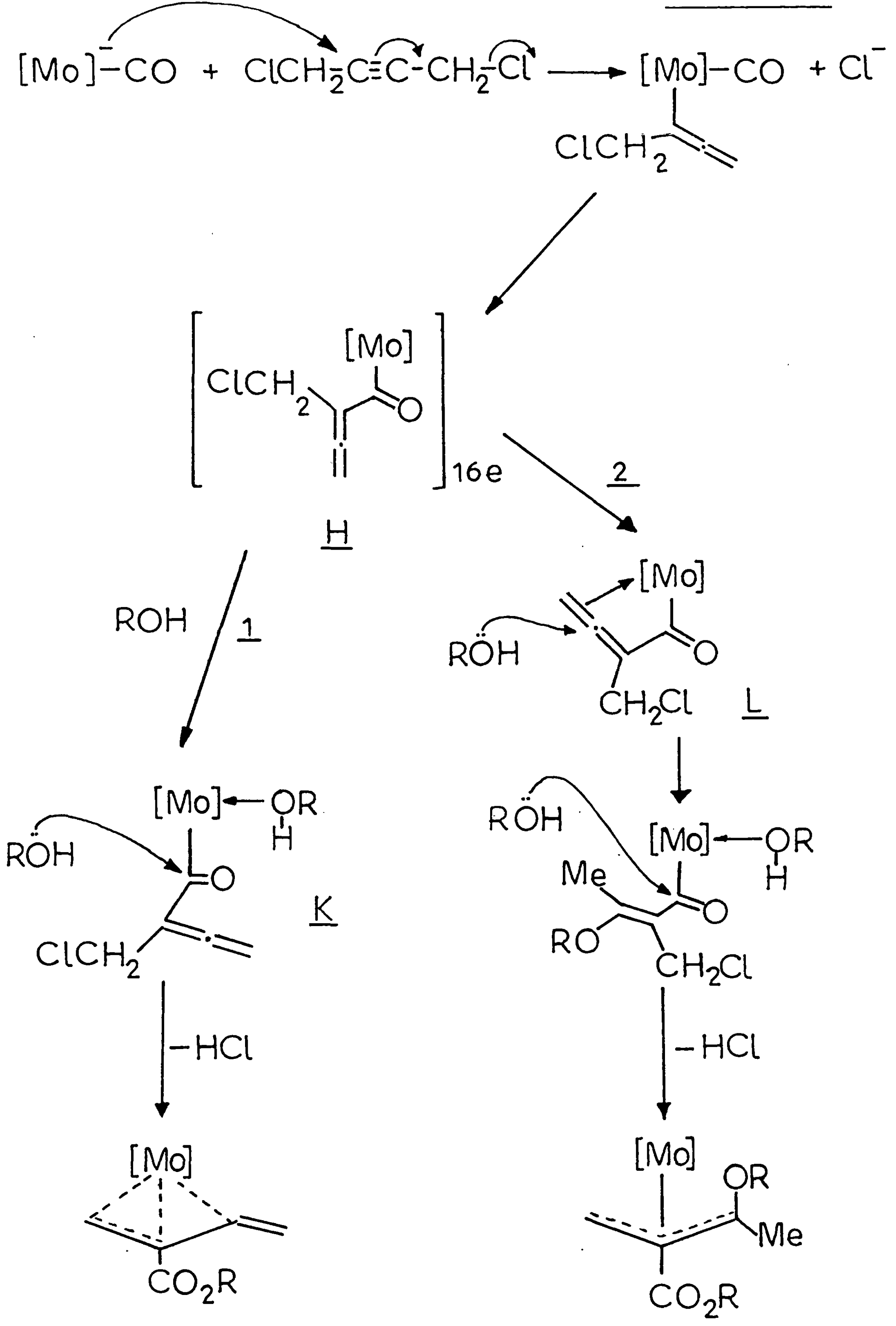
R = Me, XII
R = Et, XIII

R = Me, XXII
R = Et, XXIII

[Mo] = $Mo(CO)_2(bipy)Cl$

Mixtures of (XII)/(XXII) and (XIII)/(XXIII) are indeed obtained when 1,4-dichlorobut-2-yne and $[PPh_4][Mo(CO)_3(bipy)X]$ are reacted in anhydrous methanol and ethanol respectively, in accordance with the above mechanism. However, this mechanism <u>cannot</u> readily provide a rationale for the exclusive formation of complexes (XII) and (XIII) in <u>wet</u> methanol and ethanol respectively, and the exclusive formation of the single hydroalkoxylated derivatives, (XXII) and (XXIII), when the reactions are performed in alcohol/THF mixtures. A mechanism which can however account for these experimental observations is illustrated in Scheme 8.5.

Scheme 8.5



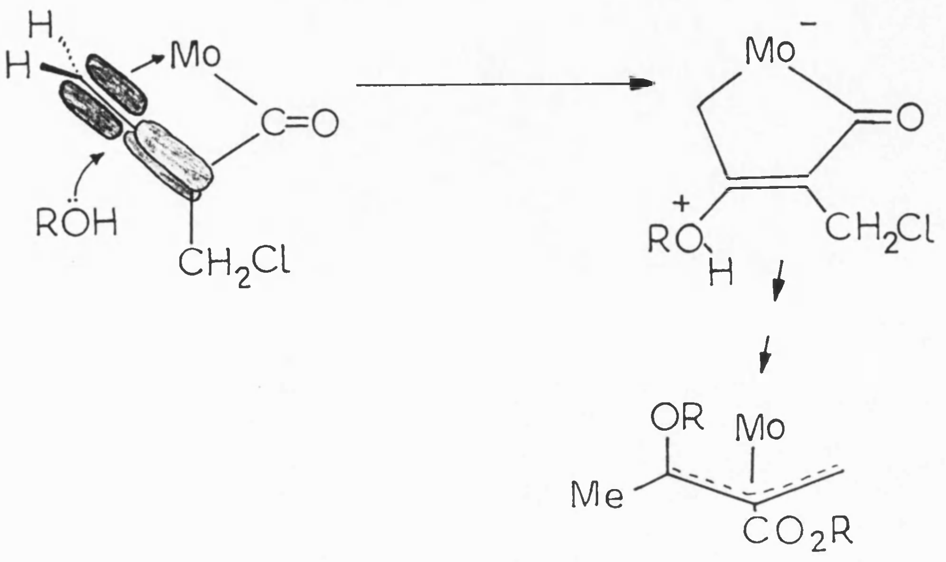
R = Me, XII
R = Et, XIII

R = Me, XXII
R = Et, XXIII

[Mo] = $Mo(CO)_2(bipy)Cl$

Here, S_N2' oxidative addition of 1,4-dichlorobut-2-yne to the $[Mo(CO)_3(bipy)Cl]^-$ anion and subsequent carbonyl insertion[237] affords the reactive 16-electron species (H) which can be stabilised by one of two ways. Firstly, by coordination of a solvent alcohol molecule which leads to pathway (1), or by coordination of the terminal carbon-carbon double bond of the allenylic moiety which leads to pathway (2). In pathway (1), attack by a solvent molecule at the carbonyl moiety in (K) and subsequent loss of HCl results in the formation of the η^3-2-carboalkoxybutadienyl complexes (XII) and (XIII), while in pathway (2), the coordinated olefinic residue in (L) becomes susceptible to regiospecific nucleophilic attack[238] by the solvent, so leading to the hydroalkoxylated derivatives (XXII) and (XXIII). The syn-Me and anti-OMe conformation revealed in the x-ray structure of complex (XXII) (Chapter 8.3) is in accordance with this mechanism (Scheme 8.6)

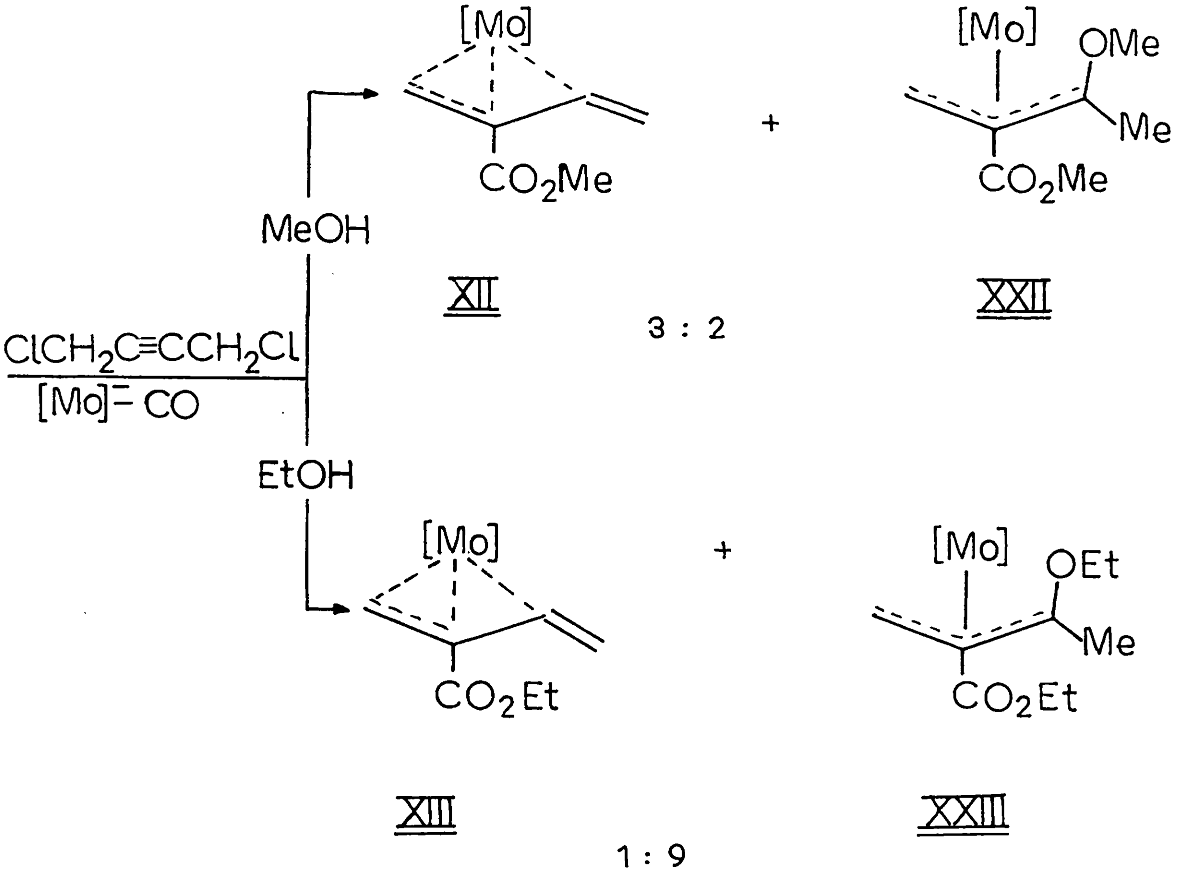
Scheme 8.6



Complexes (XII) and (XIII) react with methanol and ethanol respectively under acidic conditions to afford a mixture of unidentified carbonyl complexes thus excluding them as precursors to the hydroalkoxylated derivatives. X-ray crystallography has revealed that the $-CO_2Me$ in complex (XII) holds a conformation in which a 180° rotation about the C(61)-C(65) bond has occurred relative to that in complex (XXII), in agreement with a mechanism in which hydromethoxylation of the terminal $-C{=}CH_2$ moiety precedes η^3-bonding.

The above mechanism therefore provides a rationale for the experimental observations made on reactions of $[PPh_4][Mo(CO)_3(bipy)Cl]$ with 1,4-dichlorobut-2-yne in neat, anhydrous methanol and ethanol, from which mixtures of complexes (XII)/(XXII) and (XIII)/(XXIII) are obtained respectively. The product distribution is 3:2 and 1:9 respectively (Scheme 8.7), thereby implying that methanol and the $-C{=}CH_2$ residue have a greater affinity for the 16-electron intermediate (H) (Scheme 8.5) than ethanol.

Scheme 8.7



XII XXII XIII XXIII

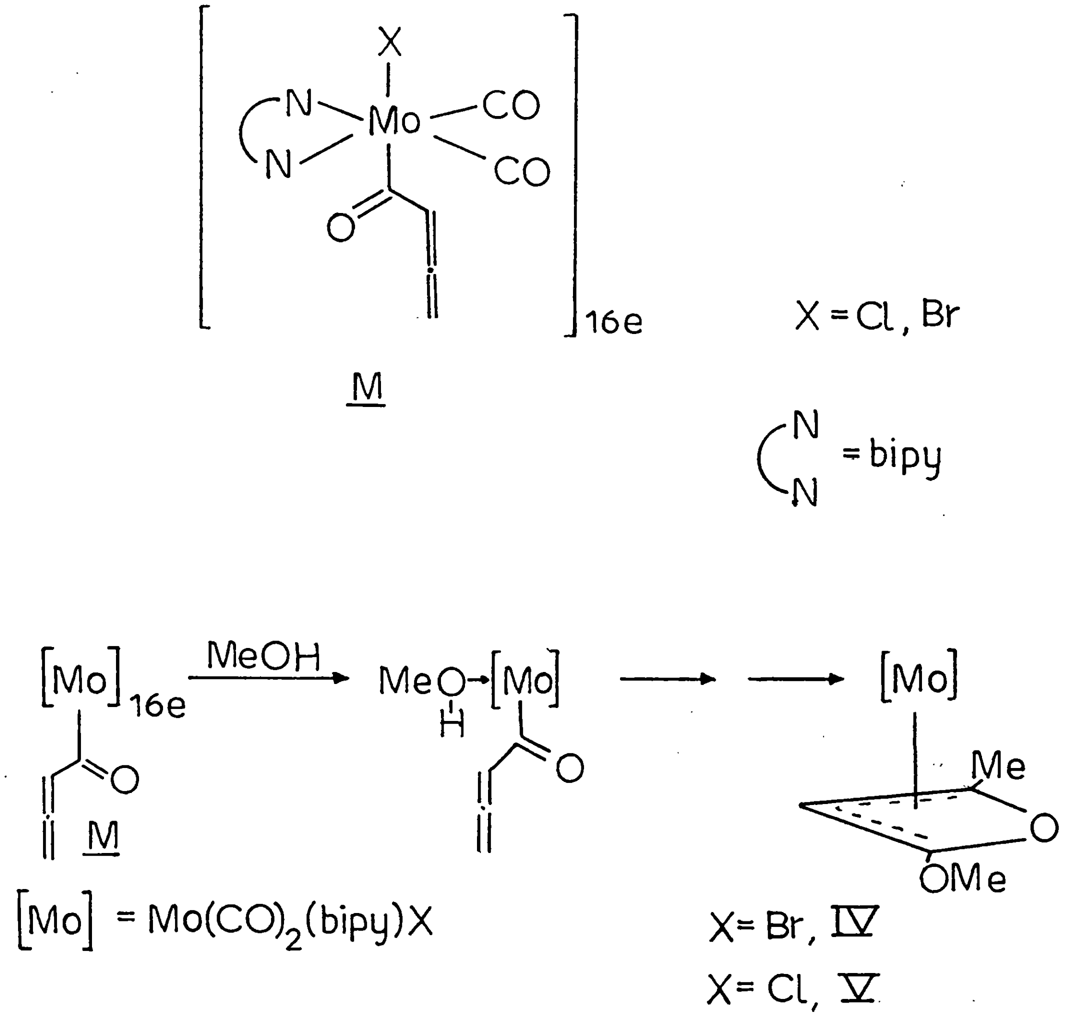
$[Mo] = Mo(CO)_2(bipy)Cl$

However, when the above reaction is carried out in aqueous alcohols, it is postulated that water molecules coordinate preferentially to the 16-electron intermediate, (H)(Scheme 8.5) thus ensuring pathway (1) predominates (Scheme 8.5) and complexes (XII) and (XIII) are formed exclusively. Conversely, in anhydrous alcohol/THF mixtures, the concentration of the alcohol is diminished and (H) is more readily stabilised by the $-C=CH_2$ residue, so promoting pathway (2) (Scheme 8.5) with the formation of the hydroalkoxylated derivatives (XXII) and (XXIII).

In aqueous alcohol/THF mixtures, the η^3-butadienyl complexes (XII) and (XIII) are obtained once again.

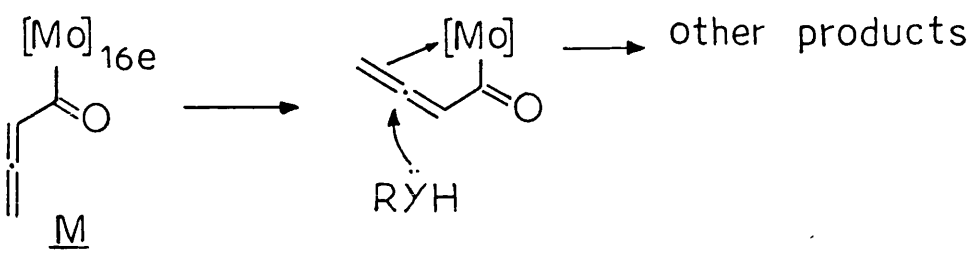
From the aforementioned product distributions of complexes (XII), (XIII), (XXII) and (XXIII) in reactions using neat methanol and ethanol as solvents (see Scheme 8.7), and the proposed role of water in these reactions, it is tempting to specify a hypothetical reactivity series in the order $H_2O > MeOH > -C{=}CH_2 > EtOH$. While this is purely speculative, it is interesting to reflect upon the reaction of $[PPh_4][Mo(CO)_3(bipy)X]$ (where X=Cl or Br) with propargyl chloride or bromide in neat methanol (Chapter 7.2). The η^3-oxacyclobutenyl complexes (IV) and (V) so formed cannot be isolated when the reaction is carried out in the presence of a co-solvent such as methylene chloride, nor can analogous complexes be obtained when the reaction is performed in neat ethanol, benzyl alcohol or methane thiol. An inspection of the proposed mechanism for this reaction which is described and illustrated in Chapter 7.3 and Scheme 7.3, reveals the formation of a 16-electron intermediate (shown below as (M)), which, in the presence of methanol, may solvate and react further to afford the η^3-oxacyclobutenyl complexes (IV) or (V) (Scheme 8.8).

Scheme 8.8



However, when this reaction is carried out in the presence of a co-solvent or in neat ethanol, benzyl alcohol or methanethiol, stabilisation of (M) may proceed by the preferred coordination of the terminal $-C=CH_2$ residue of the allenic moiety, and subsequent nucleophilic attack on the coordinated olefin by ROH or RSH might then lead to other, intractable products (Scheme 8.9).

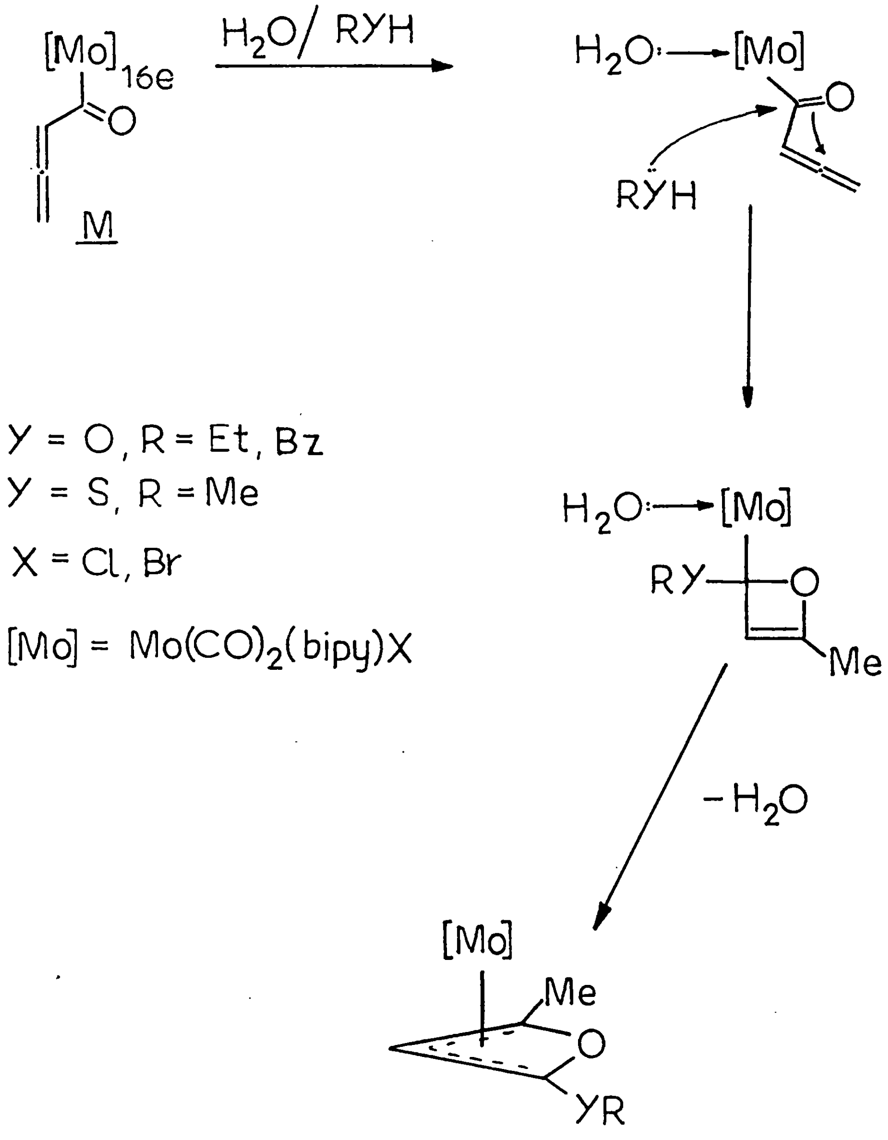
Scheme 8.9



[Mo] = $Mo(CO)_2(bipy)X$ X=Cl,Br Y=O,S

Unfortunately, these experimental observations were only interpreted towards the very end of the research described in this thesis and time has prevented further investigations which could provide more evidence for the proposed mechanisms. Thus, according to the foregoing arguments, the reaction of $[PPh_4][Mo(CO)_3(bipy)X]$ (where X=Cl or Br) in <u>aqueous</u> ethanol, benzyl alcohol or methane thiol should afford the ethoxy, benzyloxy and thiomethoxy analogues of complexes (IV) and (V) respectively by ensuring that "reactive" water molecules coordinate with the intermediate (M) in preference to the $-C{=}CH_2$ residue of the allenic moiety (Scheme 8.10).

Scheme 8.10



Time has also prevented further investigations into the stereospecific hydroalkoxylation reactions of the η^3-butadienyl ligand. While no attempts have been made to induce smooth cleavage of the organic moieties in complexes (XXII) and (XXIII) (see Chapter 7.3), it is anticipated that they could have potential as chiral synthons.

Finally, it is also anticipated that the reactions of $[PPh_4][Mo(CO)_3(bipy)Cl]$ and 1,4-dichlorobut-2-yne are not confined to alcoholic solution, and analogous aminocarbonylation and hydroamination reactions are expected to occur in the presence of primary and secondary amines.[224]

CHAPTER NINE

Experimental

All preparations were performed in an atmosphere of dry nitrogen gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. The starting materials Napda and $Mo(CO)_4$bipy were prepared by literature methods (see Chapter 4). Other chemicals were obtained from commercial sources and used without further purification. Infrared spectra in the region 200-4000 cm^{-1} were recorded on a Perkin-Elmer 597 spectrophotometer as nujol or hexachlorobutadiene (HCBD) mulls unless otherwise stated. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ solutions unless otherwise stated using JEOL PS 100 or FX 270 and FX 90Q FT instruments respectively with TMS as internal standard. Carbon types were identified by the INEPT technique but quoted as if determined by off-resonance decoupling. Thus, δ_C(multiplicity, assignment).

Reactivity of Bromomethylcyclopropane with Napda in the Presence of 10 mol% $Mo(CO)_4$bipy

Bromomethylcyclopropane (0.25 g; 1.85 mmol) was added dropwise to a stirred suspension of Napda (0.226 g, 1.85 mmol) and $Mo(CO)_4$bipy (0.15 g, 0.412 mmol) in toluene (15 ml) and the resulting mixture heated at reflux for 2.5 h. After cooling the suspension was filtered and the resulting solid washed with a little toluene and dried *in vacuo*. Yield, 0.34 g. Infrared analysis of the solid indicated mainly unreacted starting materials. The solvent was removed from the filtrate under reduced pressure to afford 0.01 g of a mixture of organic compounds which could not be identified.

Reactivity of Bromomethylcyclopropane with dimethylsodiomalonate (dmsm) in the Presence of 10 mol % $Mo(CO)_4bipy$

Bromomethylcyclopropane (0.25 g, 1.85 mmol) was added dropwise to a stirred suspension of dmsm (0.28 g, 1.85 mmol) and $Mo(CO)_4bipy$ (0.15 g, 0.412 mmol) in toluene (15 ml) and the resulting mixture heated under reflux for 2.5 h. The reaction mixture was allowed to cool to room temperature, filtered, and the solid washed with a little toluene. The solid rapidly darkened and decomposed to a black tar. The filtrate afforded a pink oil (0.01 g) which was shown by ^1H NMR to contain dimethyl malonate together with other unidentified organic compounds.

Reactivity of Bromomethylcyclopropane with Dimethylsodiomalonate (dmsm) in the Presence of 10 mol % $Mo(CO)_6$

Bromomethylcyclopropane (0.24 g, 1.78 mmol) was added dropwise to a stirred suspension of dmsm (0.27 g, 1.78 mmol) and $Mo(CO)_6$ (0.01 g, 0.379 mmol) in toluene (15 ml) and the resulting mixture heated under reflux for 2.5 h. After cooling to room temperature, the reaction mixture was filtered whereupon the resulting black solid rapidly turned to a black tar. The filtrate afforded minute quantities of an oily residue, which were not investigated further.

Reactivity of Propargyl Bromide with Napda in the Presence of 10 mol % $Mo(CO)_4bipy$

Propargyl bromide (2.5 g, 80% solution in toluene, 16.8 mmol) was added dropwise to a stirred suspension of Napda

(2.05 g, 16.8 mmol) and $Mo(CO)_4$bipy (1.36 g, 3.74 mmol) in toluene (50 ml) and the resulting mixture heated under reflux for 0.5 h. After this time, the reaction mixture was allowed to cool to room temperature, filtered, and the solid washed with a little toluene and dried in vacuo. Yield, 2.73 g. The solid was subsequently washed thoroughly with water and dried in vacuo. Yield, 1.1 g. Infrared analysis revealed the presence of two ν(CO) stretching modes, at ca 1950 and 1865 cm^{-1}, in the product(s).

The toluene was removed from the filtrate under reduced pressure to afford a brown oil (0.13 g). Chromatography (100-200 mesh florisil/5:1 hexane/ethyl acetate) yielded 0.02 g of an impure oil which appeared by ^1H NMR spectroscopy to contain traces of 3-(prop-2-ynyl)pentan-1,4-dione,[198] although this product is formed in ca 17% in a control reaction in the absence of $Mo(CO)_4$bipy.

Interaction of Propargyl Bromide with $Mo(CO)_4$bipy

Toluene as solvent

A stirred suspension of $Mo(CO)_4$bipy (0.5 g, 1.37 mmol) in a toluene solution (15 ml) of propargyl bromide (0.204 g.) 80% solution in toluene, 1.37 mmol) was heated at reflux for 0.5 h and then cooled to room temperature. The mixture was filtered and the solid washed with a little toluene and dried in vacuo. Yield, 0.58 g. Infrared analysis indicated that the product contained $Mo(CO)_4$bipy together with other unknown compounds. The absence of propargyl bromide from a complex

TLC (hexane/silica) of the filtrate indicated that extensive decomposition of propargyl bromide had occurred.

THF as Solvent

The above reaction was performed in THF. The solid product (0.28 g) was shown by infrared spectroscopy to be mainly $Mo(CO)_4bipy$, and TLC (hexane/silica) of the filtrate indicated decomposition of the propargyl bromide.

Interaction of Propargyl Bromide with $Mo(CO)_4bipy$ in Dioxan

Excess propargyl bromide 2.72 g, 80% solution in toluene, 18.28 mmol) was added dropwise to a stirred suspension of $Mo(CO)_4bipy$ (0.5 g, 1.37 mmol) in dioxan (15 ml) and the resulting mixture heated under reflux for 50 min. After cooling to room temperature, the reaction mixture was filtered and solid washed with dioxan and dried in vacuo. Yield, 0.74 g. Infrared analysis indicated that the solid contained $MoBr_4bipy$[97] as the principal constituent. ν, 1600, 1445,1315, 765 cm^{-1}.

Interaction of Propargyl Bromide with $[Mo(CO)_3(NCMe)_3]$

A stirred solution of $Mo(CO)_6$ (1.0g, 3.79 mmol) in MeCN (25 ml) was heated under reflux for 12 h. The resulting yellow solution containing $[Mo(CO)_3(NCMe)_3]$ was allowed to cool to room temperature with stirring, and propargyl bromide (0.415 g, 80% solution in toluene, 2.79 mmol) added dropwise. The mixture rapidly blackened affording a thick intractable tar which was subsequently discarded.

Preparation of $[PPh_4][Mo(CO)_3(bipy)X]$ (where X = Cl or Br)

A stirred suspension of $Mo(CO)_4bipy$ (8.03 g, 22.0 mmol) and PPh_4X (where X = Cl or Br) (22.0 mmol) in 4:1 toluene/MeCN (250 ml) was heated at reflux for 1 h and then cooled to room temperature. The product $[PPh_4][Mo(CO)_3(bipy)X]$ was collected by filtration, washed with 20 ml of cold MeOH and dried in vacuo. Yield, 88%. Satisfactory analyses were obtained, and spectroscopic data correspond well with literature data.[115]

Interaction of Propargyl Bromide with $[PPh_4][Mo(CO)_3(bipy)Br]$ in Chloroform

Propargyl bromide (0.204 g, 80% solution in toluene, 1.37 mmol) was added dropwise to a stirred solution of $[PPh_4][Mo(CO)_3(bipy)Br]$ (0.1 g, 0.132 mmol) in chloroform (20 ml) held at -10°C. The resulting red solution was stirred at this temperature for 5 min. and then at room temperature for a further 0.5 h. The solvent was removed under vacuum and infrared analysis of the resulting red oil (liquid film) revealed the presence of a product with two carbonyl stretching modes. Yield, 0.2 g. ν(CO) ca 1950, 1865 cm^{-1}. Attempts to precipitate a solid from the oil or isolate a definite complex were unsuccessful.

No reaction was observed in THF over the temperature range -78- +24°C.

Interaction of $CH{\equiv}CCH_2X$ with $[PPh_4][Mo(CO)_3(bipy)X]$ (where X=Cl or Br) in Methanol. Preparations of $[Mo(\eta^3-C_5H_7O_2)(CO)_2(bipy)X]$ (X=Cl, (V) or Br, (IV))

Propargyl halide (34.0 mmol) was added dropwise to a stirred suspension of $[PPh_4][Mo(CO)_3(bipy)X]$ (17.0 mmol) in methanol (200 ml) held at -17°C. The mixture was stirred for 0.5 h at this temperature and for a further 0.5 h at ambient temperature. The reaction mixture was filtered and the product washed with a little MeOH and dried *in vacuo*. Yield, 60% for (IV) or (V).

Found for (IV): C, 41.8; H, 3.15; N, 5.9. Calc. for $C_{17}H_{15}BrMoN_2O_4$: C, 41.9; H, 3.1; N, 5.8%.

I.R., 1998(s) and 1930(s) (CO) and 1660(m) cm^{-1}.

NMR data, δ_H (CD_2Cl_2), 2.85 (1H, q, J(HH)2Hz, CH), 3.55 (3H, d, J(HH)2Hz, CMe), 3.60(3H, s, OMe), 7.9-9.0 (8H, m, aromatics).

Found for (V): C, 45.7; H, 3.5; N, 6.5. Calc. for $C_{17}H_{15}ClMoN_2O_4$: C, 46.1; H, 3.4; N, 6.6%.

I.R., 1998(s) and 1930(s) (CO), 1600(m), 260(w) cm^{-1} (Mo-Cl).

NMR data, δ_H (CD_2Cl_2), 3.05 (1H, q, J(HH)2Hz, CH), 3.60 (3H, s, OMe), 3.65 (3H, d, J(HH)2Hz, CMe), 7.9-9.1 (8H, m, aromatics).

When the above reaction was performed in ethanol, benzyl alcohol/dichloromethane or methane thiol, dark red, unstable solutions were obtained from which no pure products could be isolated. Similar results were obtained when the reaction was carried out in methanol/chloroform or methanol/dichloromethane, nor could any product be isolated when but-2-ynyl bromide was used in place of propargyl bromide. In the presence of *ca* 16 mol% *p* toluene sulphonic acid, the rate and direction of the above reaction was unaffected.

Reaction of $[Mo(\eta^3-C_5H_7O_2)(CO)_2(bipy)X]$ (X = Cl, (V) or Br, (IV)) with Iodine

A stirred suspension of complex (IV) or (V) (40 mmol) in MeCN (500 ml) was treated at room temperature with powdered iodine (41 g, 160 mmol). After 40 min. the volume of the solvent was reduced to *ca* 50 ml. Silica gel (60PF-254) was added to the residue and the remainder of the solvent evaporated. The residual mixture was chromatographed using the grade of silica described above and hexane-ethyl acetate (6:1) as eluant, yielding a mixture of two isomers (6.0 g, 66%). This mixture was fractionated using the same chromatographic system. The first component (VII) was (E)-methyl 3-iodocrotonate (1.2 g, 13%). Found for (VII): C, 26.8; H, 3.20; I, 58.0. Calc. for $C_5H_7IO_2$: C, 26.5; H, 3.10; I, 56.2%. I.R., (liquid film): 1720(s), 1615(s), 1175(s) and 1195(s) cm^{-1}. Mass spectrum: m/z 226 (M^+ 5), 195(20), 167(15), 99(100), and 59 (30%); chemical ionisation mode (isobutane): 227(100) and 99 (35%).

NMR data, δ_H (400 MHz) 2.97 (3H, d, J(HH) 1.5 Hz, CMe) 3.68 (3H, s, OMe), and 6.62 (1H, q, J(HH) 1.5 Hz, CH). Irradiation at 6.62 or 2.97 p.p.m. in the nuclear Overhauser enhancement experiment produced no enhancement.

δ_C, 164,2 (s, CO), 131.0 (d, CH), 120.5 (s, CMeI), 51.3 (q, OMe), and 30.9 (q,Me).

An intermediate fraction consisted of a mixture of (E) and (Z) isomers (0.6 g) followed by the second component (VI), (Z)-methyl 3-iodocrotonate (1.8 g, 20%). Found for (VI): C, 25.9; H, 3.24; I, 55.8. Calc. for $C_5H_7IO_2$: C, 26.5; H, 3.10; I, 56.20%. I.R. (liquid film):1725(s), 1625(s), 1170(s) and 1190(s) cm^{-1}. Mass spectrum: m/z 226 (M^+,90), 195(35), 167(30), 99(100) and 59(65%); chemical ionisation mode (isobutane): 227(100) and 99(10).

NMR data, δ_H (400 MHz) 2.73 (3H, d, J(HH) 1.45 Hz, CMe), 3.73 (3H, s, OMe), and 6.28 (1H, q, J(HH) 1.45 Hz, CH).

δ_C 164.2 (s, CO), 125.0 (d, CH), 113.3 (s, CMeI), 51.2 (q, OMe), and 36.3 (q, Me).

Competitive Elimination Reactions of (VI) and (VII)

Each isomer (1.2 g, 5.3 mmol) was disolved in water-THF (1:3, 30 ml) and to each solution was added $LiOH.H_2O$ (0.55 g, 13.0 mmol). The solutions were stirred at ambient temperature for 4 h and then poured into 2M aqueous HCl (50 ml) and extracted once with dichloromethane (50 ml). The dried extracts were evaporated under reduced pressure giving white, crystalline solids in each case. These were identified as tetrolic acid[213] (0.32 g, 71%) from isomer (VI) and (E)-3-iodocrotonic acid[214] (0.8 g, 71%) from isomer (VII).

Reaction of $[Mo(\eta^3-C_5H_7O_2)(CO)_2(bipy)X]$ (X = Cl, (V) or Br,(IV)) with $NaBH_4$

A stirred suspension of complex (IV) or (V) (14 mmol)in

MeOH (250 ml) held at -78°C was treated with $NaBH_4$ (1.07 g, 28 mmol). The mixture was then allowed to warm to room temperature and stirring was continued for a further 0.3 h. Methanol was removed under reduced pressure to leave a gum which was extracted with Et_2O. After filtration and evaporation of the solvent, the crude oil was chromatographed on 63-200 mesh silica gel using 6:1 hexane/ethyl acetate as eluant. Careful fractionation yielded pure dimethylmethylsuccinate[239] (0.16 g, 9%).

Halide Exchange Reaction of $[Mo(\eta^3-C_5H_7O_2)(CO)_2(bipy)X]$ (X = Cl, (V) or Br, (IV)) with Pyridine. Preparation of Complex (VIII)

A stirred suspension of (IV) or (V) (2.0 mmol) in acetone (40 ml) was treated with $AgBF_4$ (0.4 g, 2.0 mmol). After 0.75 h the resulting red solution was filtered and the stirred filtrate treated dropwise with pyridine (1 ml). The mixture was stirred for a further 0.25 h, and then the solvent was evaporated to low bulk under reduced pressure. Dark red crystals of the product (VIII) formed on refrigeration, and were collected by filtration, washed with Et_2O, and dried *in vacuo*. More product was formed by evaporating the filtrate to dryness and recrystallising the residue from acetone. Yield, 1.0 g, 87%. Suitable crystals for X-ray crystallography were obtained by careful crystallisation from acetone. (see Appendix I).

Found for (VIII): C, 46.3; H, 3.6; N, 7.35; Calc. for $C_{22}H_{20}BF_4MoN_3O_4$; C, 46.1; H, 3.5; N, 7.35%.

I.R., 1955(s) and 1860(s)(CO), and 1575(m) cm^{-1} (CO_2Me).

NMR data, δ_H (CD_3NO_2), 2.74 (3H, s, CMe), 4.00 (3H, s, OMe), 6.46 (1H, s, CH) and 7.4-9.0 (13H, m, aromatics).

Attempts to react (VIII) with CO or excess halide ions (PPh_4X, where X = Cl or Br) were unsuccessful and resulted in reactant decomposition.

Halide Exchange Reaction of $[Mo(\eta^3-C_5H_7O_2)(CO)_2(bipy)X]$ (X = Cl, (V) or Br, (IV)) with $CF_3(CF_2)_nCO_2Na$ (n = 1 or 2). Preparation of Complexes (X), (n = 1) and (XI), (n = 2).

A stirred suspension of complex (IV) (0.97 g, 2.0 mmol) in acetone (15 ml) was treated with solid $CF_3(CF_2)_nCO_2Na$ (n = 1 or 2)(4.0 mmol). After 24 h the mixture was filtered, and the filtrate evaporated under reduced pressure leaving a red oil which was recrystallised from water/acetone (5:2) to give a red solid in each case. Yield of (X) and (XI), 44%. Application of the same procedure to complex (V) afforded complexes (X) and (XI) in 22% yield.

Found for (X): C, 42.1; H, 2.45; N, 5.1. Calc. for $C_{20}H_{15}F_5MoN_2O_6$: C, 42.1; H, 2.63; N, 4.9%.

I.R. (HCBD) 1940(s) and 1840(s) (CO), 1675(m) ($-O_2C$ asym), 1560(m) (CO_2Me), and 1435(m) cm^{-1} ($-O_2C$ sym).

NMR data, δ_H (CD_3COCD_3), 2.58 (3H, s, CMe), 3.96 (3H, s, OMe), 6.40 (1H, s, CH), and 7.5-9.0 (8H, m, aromatics).

δ_C (CD_3COCD_3) 248.8 and 243.0 (s, CO), 173.0 (s, $\underline{C}O_2Me$), 155.3, 153.6, 140.0, 126.5, 123.8 (aromatics), 116.5 (d, CH), 53.9 (q, $CO_2\underline{Me}$), and 34.2 (q, $C\underline{Me}$);

Found for (XI): C,40.1; H, 2.35; N, 4.56. Calc. for $C_{21}H_{15}F_7MoN_2O_6$: C, 40.65; H, 2.42; N, 4.52%.

I.R. (HCBD) 1940(s) and 1840(s) (CO), 1690(m)($-O_2C$ asym), 1565(m) (CO_2Me), and 1450 cm^{-1}($-O_2C$ sym);

NMR data, δ_H (CD_3COCD_3), 2.6 (3H, s, CMe), 4.0 (3H, s, OMe), 6.45 (1H, s, CH) and 7.6-9.0 (8H, m, aromatics).

Interaction of 1,4-Dichlorobut-2-yne with $[PPh_4][Mo(CO)_3(bipy)Cl]$ in Aqueous Alcohols, ROH (R = Me or Et). Preparation of Complexes (XII) (R = Me) and (XIII) (R = Et)

1,4-Dichlorobut-2-yne (0.144 g, 1.17 mmol) was added dropwise to a stirred suspension of $[PPh_4][Mo(CO)_3(bipy)Cl]$ (0.82 g, 1.15 mmol) in an alcohol/water mixture (15.5 ml, 15:0.5) held at -17°C or room temperature. The resulting mixture was stirred for 0.5 h (plus a further 0.5 h at ambient temperature for the low temperature method) and the red, microcrystalline product collected by filtration, washed with a little alcohol and dried *in vacuo*. Yield, 70% (XII), 70% (XIII).

ROH = Methanol

Found for (XII): C, 47.15; H, 3.42; N, 6.06; Cl, 7.85%. Calc. for $C_{18}H_{15}ClMoN_2O_4$: C, 47.52; H, 3.30; N, 6.16; Cl, 7.81%.

I.R., 1980(s) and 1905(s) (CO), 1700(m) (CO_2Me), 260(w) cm^{-1} (Mo-Cl). I.R. (CH_2Cl_2), 1990, 1920 cm^{-1} (CO).

NMR data, δ_H (CD_2Cl_2), (270 MHz), 1.96 (1H, s, *anti*-H), 2.82 (3H, s, OMe), 3.60 (1H, s, *syn*-H), 5.66 (1H, d, J(HH) 2.0Hz, $=CH_2$) 6.26 (1H, d, J(HH) 2.0Hz, $=CH_2$), 7.5-8.8 (8H, m, aromatics).

Suitable crystals for X-ray diffraction were grown by careful recrystallisation of (XII) from acetonitrile (see Appendix II).

ROH = Ethanol

Found for (XIII): C, 48.40; H, 3.56; N, 5.95. Calc. for $C_{19}H_{19}ClMoN_2O_5$: C, 46.87; H, 3.91; N, 5.71%.

I.R., 1980(s) and 1900(s) (CO), 1690(m) (CO_2Et), 260(w) cm^{-1} (Mo-Cl);

NMR data, δ_H (CD_2Cl_2), (270 MHz), 0.65 (3H, t, J(HH) 7.1 Hz, Me), 1.95 (1H, s, *anti*-H), 3.11 (1H, qd, J(HH) 7.1, 10.5 Hz, CH_2), 3.28 (1H, qd, J(HH) 7.1, 10.5 Hz, CH_2), 3.61 (1H,s, *syn*-H), 5.63 (1H, d, J(HH) 2.0 Hz, $=CH_2$), 6.26 (1H, d, J(HH) 2.0 Hz, $=CH_2$), 7.5-8.8 (8H, m, aromatics).

δ_C (CD_2Cl_2), 152.7, 152.4, 139.8, 139.2, 126.6, 126.2, 122.6, 122.3 (aromatics), 106.2 (t, $=CH_2$), 60.6 (t, $\overset{\cdots}{-}CH_2$), 50.5 (t, $-CO_2CH_2CH_3$), 13.8 (q, Me)

Interaction of 1,4-Dichlorobut-2-yne with $[PPh_4][Mo(CO)_3(bipy)Cl]$ in THF/Alcohol ROH, (R = Me or Et) Mixtures. Preparation of Complexes (XXII) (R = Me) and (XXIII) (R = Et)

1,4-Dichlorobut-2-yne (0.1 g, 0.813 mmol) was added dropwise to a stirred suspension of $[PPh_4][Mo(CO)_3(bipy)Cl]$

(0.5 g, 0.704 mmol) in an alcohol/THF mixture (20 ml, 1:1) held at -17°C or room temperature. The resulting mixture was stirred for ca 1.5 h after which time the product precipitated as a red solid. It was collected by filtration, washed with a little cold alcohol and dried in vacuo. Yield, 70% (XXII), 55% (XXIII).

ROH = Methanol

Found for (XXII): C, 46.8; H, 3.92; N, 5.76; Cl, 7.09%. Calc. for $C_{19}H_{19}ClMoN_2O_5$: C, 46.87; H, 3.91; N, 5.76; Cl, 7.30%.

I.R., 1955(s) and 1875(s) (CO), 1700(m) (CO_2Me), 260(w) cm^{-1} (Mo-Cl).

NMR data, δ_H, (CD_2Cl_2), (270 MHz), 2.30 (3H, s, CMe), 2.31 (1H, d, J(HH) 3.5 Hz, anti-H),2.88 (3H, s, CO_2Me), 3.20 (3H, s, OMe), 3.34 (1H, d, J(HH) 3.5 Hz, syn-H), 7.6-8.8 (8H, m, aromatics).

Suitable crystals of (XXII) for X-ray diffraction were grown by careful recrystallisation from CH_2Cl_2 (see Appendix III).

ROH = Ethanol

Found for (XXIII): C, 48.4; H, 3.56; N, 5.95. Calc. for $C_{21}H_{23}ClMoN_2O_5$: C, 48.67; H, 3.63; N, 5.98%.

I.R., 1960(s) and 1890(s) (CO), 1690(m) (CO_2Et), 263(w) cm^{-1} (Mo-Cl).

NMR data, δ_H, (CD_2Cl_2), (270 MHz), 0.73 (3H, t, J(HH) 7.0 Hz, $CO_2CH_2\underline{CH_3}$), 1.03 (3H, t, J(HH) 7.0 Hz, $-OCH_2\underline{CH_3}$), 2.33 (3H, s, Me), 3.06 (2H, m, $-\underline{OCH_2}CH_3$, $CO_2\underline{CH_2}CH_3$), 2.33 (1H, d, J(HH) 1.5 Hz, anti-H), 3.36 (1H, d, J(HH) 1.5 Hz, syn-H), 3.48 (1H, qd, J(HH) 7.0, 10.8 Hz, $-O\underline{CH_2}CH_3$), 3.82 (1H, qd, J(HH) 7.0, 9.0 Hz, $CO_2\underline{CH_2}CH_3$), 7.5-8.8 (8H, m, aromatics).

δ_c (CD_2Cl_2), 170.7 (s, $-\underline{C}O_2Et$), 153.6, 153.3, 152.3, 138.9, 126.1, 125.6, 122.3, 122.1 (aromatics), 68.4 (t, $-O\underline{C}H_2CH_3$), 60.0 (t, $=CH_2$), 48.0 (t, $CO_2\underline{CH_2}CH_3$), 21.48 (q, Me), 15.2 (q, $-OCH_2\underline{CH_3}$), 13.5 (q, $CO_2CH_2\underline{CH_3}$).

Interaction of 1,4-Dichlorobut-2-yne with $[PPh_4][Mo(CO)_3(bipy)Cl]$ in Anhydrous Alcohols ROH (R = Me or Et)

1,4-Dichlorobut-2-yne (0.25 g, 2.03 mmol) was added dropwise to a stirred suspension of $[PPh_4][Mo(CO)_3(bipy)Cl]$ (1.44 g, 2.03 mmol) in anhydrous methanol or ethanol (25 ml) held at -17°C or room temperature, and the resulting mixture stirred for 0.5 h (plus a further 0.5 h at ambient temperature for the low temperature method). The red solid was collected by filtration, washed with a little alcohol and dried *in vacuo*. NMR analysis of the products indicated the ratios of (XII):(XXII) and (XIII):(XXIII) to be 3:2 and 1:9 respectively.

TLC: (silica/CH_2Cl_2), Rf complex (XII) 0.53, (XXII) 0.26, (XIII) 0.36, (XXIII) 0.31.

Reaction of Complexes (XII) and (XIII) in Acidified Alcohols ROH (R = Me and Et) respectively

A stirred suspension of complex (XII) or (XIII) (0.7 mmol) in methanol or ethanol respectively (25 ml) held at room temperature was treated with three drops of the corresponding alcohol, previously saturated with HCl gas. The resulting mixture was stirred for 0.5 h, filtered, and the red solid washed with a little alcohol and dried *in vacuo*. Yield, 0.16 g. Infrared analysis indicated a complex mixture of carbonyl-containing species in each case.

I.R., 1940, 1960, 1885, 1850, 1710, 1690 cm^{-1} (CO).

Reaction of Complex (XII) with $CF_3(CF_2)_2CO_2Na$

Preparation of Complex (XVII)

$AgBF_4$ (0.13 g, 0.67 mmol) was added as the solid to a stirred suspension of complex (XII) (0.3 g, 0.66 mmol) in acetone (25 ml) and the resulting mixture stirred for 0.25 h. Sodium perfluorobutyrate (0.28 g, 1.19 mmol) was added as the solid to the flocculant suspension and the mixture stirred for a further 0.25 h. After this time, the suspension was filtered, the acetone removed from the filtrate and the crude orange solid recrystallised from water/acetone. Yield 0.06 g, 14%. Found for (XVII): C, 41.4; H, 2.49; N, 4.40. Calc. for $C_{22}H_{15}F_7MoN_2O_6$: C, 41.8; H, 2.37; N, 4.43%.

I.R., (HCBD) 1980(s) and 1900(s)(CO), 1700(m) (CO_2Me), 1700(m) ($-O_2C$ *asym*), 1460(m) ($-O_2C$ *sym*).

NMR data, δ_H, (CD_3COCD_3), 1.90 (1H, s, *anti*-H), 2.80 (3H, s, CO_2Me), 3.90 (1H, s, *syn*-H), 5.75 (1H, d, J(HH) 1.5 Hz, $=CH_2$), 6.28 (1H, d, J(HH) 1.5 Hz, $=CH_2$), 7.5-9.8 (8H, m, aromatics).

δ_C (CD_3COCD_3), 220.2 (s, CO), 218.6 (s, CO), 174.8 (s, $-O_2C$), 169.8 (s, $-\underline{CO}_2Me$), 154.5, 153.4, 141.0, 127.0, 123.0 (aromatics), 106.4 (t, $=CH_2$), 53.4 (t, $\overset{\cdots}{-}CH_2$), 51.4 (q, OMe).

Application of an analogous procedure to complex (XXII) resulted in decomposition of the organometallic.

APPENDIX I

X-ray data for complex (VIII)

APPENDIX I

Crystal data for $[Mo(C_5H_7O_2)(CO)_2(bipy)(py)][BF_4]$, (VIII):

Suitable crystals of complex (VIII) were obtained by careful crystallization from dry, oxygen free acetone at ca 4°C.

A crystal of approximate size 0.03 x 0.20 x 0.3 mm was mounted on a Stoe Stadi-2 diffractometer and data collected via variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of $(2.0 + \sin\mu/\tan\theta)$. 4170 Independent reflections with $2\theta < 50°$ of which 2623 with $I > 3\sigma(I)$ were used in subsequent refinement. Neither an absorption nor an extinction correction was applied. The structure was determined by heavy atom methods. The BF_4^- ion was disordered and three tetrahedra were observed. These tetrahedra were refined with respective occupancies of 0.5, 0.25, and 0.25. All atoms except for these disordered fluorines and hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometric positions and only their thermal parameters were refined.

Calculations were performed using full-matrix least squares with a weighting scheme $W = 1/[\sigma^2(F) + 0.003F^2]$. Scattering factors were taken from ref. 240. Calculations were performed using SHELX 76[241] on the Amdahl V7A computer at the University of Reading. The final R value was 0.058 (R' = 0.060).

$C_{22}H_{20}BF_4MoN_3O_4$, M = 574.9, monoclinic, space group $P2_1/n$, a = 15.825(11), b = 15.991(11); c = 9.728(8) Å, β = 95.0(1)°, U = 2449.3 $Å^3$, Dm = 1.53(3) gcm^{-3}. Z = 4, Dc = 1.55 g cm^{-3}, F(000) = 1160, Mo-K_α radiation λ = 0.7107 Å, μ = 5.97 cm^{-1}.

MOLECULAR DIMENSIONS IN THE CO-ORDINATION SPHERE OF (VIII)

DISTANCES IN Å, ANGLES IN DEGREES

MO(1)	-	N(11)			2.241(7)
MO(1)	-	N(22)			2.164(7)
MO(1)	-	N(31)			2.275(8)
MO(1)	-	C(1)			1.936(10)
MO(1)	-	C(2)			1.983(11)
MO(1)	-	O(41)			2.164(6)
MO(1)	-	C(45)			2.155(10)
N(11)	-	MO(1)	-	N(22)	72.71(25)
N(11)	-	MO(1)	-	N(31)	84.49(26)
N(22)	-	MO(1)	-	N(31)	80.33(27)
N(11)	-	MO(1)	-	C(1)	109.59(35)
N(22)	-	MO(1)	-	C(1)	76.57(36)
N(31)	-	MO(1)	-	C(1)	147.52(37)
N(11)	-	MO(1)	-	C(2)	173.58(36)
N(22)	-	MO(1)	-	C(2)	103.57(34)
N(31)	-	MO(1)	-	C(2)	89.74(35)
C(1)	-	MO(1)	-	C(2)	74.05(42)
N(11)	-	MO(1)	-	O(41)	102.13(24)
N(22)	-	MO(1)	-	O(41)	155.61(25)
N(31)	-	MO(1)	-	O(41)	75.41(26)
C(1)	-	MO(1)	-	O(41)	126.56(35)
C(2)	-	MO(1)	-	O(41)	79.05(32)
N(11)	-	MO(1)	-	C(45)	80.11(30)
N(22)	-	MO(1)	-	C(45)	127.52(33)

MOLECULAR DIMENSIONS IN THE CO-ORDINATION SPHERE OF (VIII)

(CONT'D.)

N(31) - MO(1) - C(45) 140.85(30)

C(1) - MO(1) - C(45) 71.54(40)

C(2) - MO(1) - C(45) 106.21(39)

O(41) - MO(1) - C(45) 73.04(31)

Dimensions in the C5H7O2 ligand

O(41) - C(42) 1.258(12)

C(42) - C(43) 1.388(14)

C(42) - O(44) 1.329(12)

C(43) - C(45) 1.329(14)

O(44) - C(48) 1.399(14)

C(45) - C(46) 1.533(16)

MO(1) - O(41) - C(42) 116.5(5)

O(41) - C(42) - C(43) 118.7(8)

O(41) - C(42) - O(44) 119.1(8)

C(43) - C(42) - O(44) 122.1(9)

C(42) - C(43) - C(45) 115.7(9)

C(42) - O(44) - C(48) 118.2(8)

MO(1) - C(45) - C(43) 115.7(7)

MO(1) - C(45) - C(46) 125.5(7)

C(43) - C(45) - C(46) 118.4(9)

SUPPLEMENTARY PUBLICATION

REMAINING DIMENSIONS IN (VIII)

N(11)	-	C(12)	1.338(12)
N(11)	-	C(16)	1.339(12)
C(12)	-	C(13)	1.406(13)
C(12)	-	C(17)	1.449(12)
C(13)	-	C(14)	1.385(15)
C(14)	-	C(15)	1.377(18)
C(15)	-	C(16)	1.394(14)
C(17)	-	C(18)	1.393(15)
C(17)	-	N(22)	1.369(11)
C(18)	-	C(19)	1.384(17)
C(19)	-	C(20)	1.366(19)
C(20)	-	C(21)	1.380(15)
C(21)	-	N(22)	1.350(12)
N(31)	-	C(32)	1.332(13)
N(31)	-	C(36)	1.335(12)
C(32)	-	C(33)	1.367(16)
C(33)	-	C(34)	1.368(20)
C(34)	-	C(35)	1.315(20)
C(35)	-	C(36)	1.387(17)
O(1)	-	C(1)	1.166(12)

SUPPLEMENTARY PUBLICATION (CONT'D.)

C(2)	-	O(2)			1.137(13)
MO(1)	-	N(11)	-	C(12)	117.4(5)
MO(1)	-	N(11)	-	C(16)	125.0(6)
C(12)	-	N(11)	-	C(16)	117.5(7)
N(11)	-	C(12)	-	C(13)	121.9(8)
N(11)	-	C(12)	-	C(17)	115.4(7)
C(13)	-	C(12)	-	C(17)	122.7(8)
C(12)	-	C(13)	-	C(14)	119.4(10)
C(13)	-	C(14)	-	C(15)	119.1(9)
C(14)	-	C(15)	-	C(16)	117.8(10)
N(11)	-	C(16)	-	C(15)	124.3(9)
C(12)	-	C(17)	-	C(18)	123.9(8)
C(12)	-	C(17)	-	N(22)	115.4(8)
C(18)	-	C(17)	-	N(22)	120.6(8)
C(17)	-	C(18)	-	C(19)	119.3(10)
C(18)	-	C(19)	-	C(20)	120.1(11)
C(19)	-	C(20)	-	C(21)	118.7(10)
C(20)	-	C(21)	-	N(22)	122.7(9)
MO(1)	-	N(22)	-	C(17)	118.9(5)
MO(1)	-	N(22)	-	C(21)	122.3(5)
C(17)	-	N(22)	-	C(21)	118.6(7)

SUPPLEMENTARY PUBLICATION (CONT'D.)

MO(1)	-	N(31)	-	C(32)	122.1(6)
MO(1)	-	N(31)	-	C(36)	119.7(7)
C(32)	-	N(31)	-	C(36)	117.8(9)
N(31)	-	C(32)	-	C(33)	122.0(10)
C(32)	-	C(33)	-	C(34)	120.1(12)
C(33)	-	C(34)	-	C(35)	117.8(12)
C(34)	-	C(35)	-	C(36)	121.6(11)
N(31)	-	C(36)	-	C(35)	120.7(10)
MO(1)	-	C(1)	-	O(1)	172.9(9)
MO(1)	-	C(2)	-	O(2)	178.6(8)

SUPPLEMENTARY PUBLICATION (CONT'D.)

Anion Dimensions

B(1)	-	F(1)	1.375(21)
B(1)	-	F(2)	1.371(16)
B(1)	-	F(3)	1.355(20)
B(1)	-	F(4)	1.347(19)
B(1)	-	F(11)	1.435(31)
B(1)	-	F(12)	1.387(28)
B(1)	-	F(13)	1.350(40)
B(1)	-	F(21)	1.332(35)
B(1)	-	F(22)	1.370(33)

F(1)	-	B(1)	-	F(2)	123.2(11)
F(1)	-	B(1)	-	F(3)	118.8(12)
F(2)	-	B(1)	-	F(3)	104.1(11)
F(1)	-	B(1)	-	F(4)	103.1(12)
F(2)	-	B(1)	-	F(4)	98.8(11)
F(3)	-	B(1)	-	F(4)	105.7(12)
F(2)	-	B(1)	-	F(11)	104.5(14)
F(4)	-	B(1)	-	F(11)	147.1(15)
F(1)	-	B(1)	-	F(12)	114.0(14)
F(2)	-	B(1)	-	F(12)	120.8(14)
F(11)	-	B(1)	-	F(12)	95.4(17)
F(2)	-	B(1)	-	F(13)	107.0(19)
F(11)	-	B(1)	-	F(13)	117.5(23)
F(12)	-	B(1)	-	F(13)	111.8(20)
F(3)	-	B(1)	-	F(21)	91.4(19)
F(4)	-	B(1)	-	F(21)	134.7(18)
F(3)	-	B(1)	-	F(22)	114.5(17)
F(4)	-	B(1)	-	F(22)	115.2(17)
F(21)	-	B(1)	-	F(22)	93.5(20)

BF_4 anions. F(1), F(2), F(3), F(4), occupancy 0.5, F(2), F(11), F(12), F(13) occupancy 0.25, F(3), F(4), F(21), F(22) occupancy 0.25

HYDROGEN CO-ORDINATES (*10**4) FOR (VIII)

WITH ESTIMATED STANDARD DERIVATIONS IN PARENTHESES

ATOM	X	Y	Z
H(13)	3769(6)	1729(7)	385(12)
H(14)	4697(6)	808(8)	1649(13)
H(15)	4241(7)	154(8)	3619(13)
H(16)	2893(6)	467(7)	4267(10)
H(18)	2923(7)	2679(7)	-503(11)
H(19)	1923(8)	3666(8)	-1372(13)
H(20)	605(8)	3736(7)	-484(12)
H(21)	297(6)	2808(7)	1236(10)
H(32)	833(8)	3436(6)	3728(11)
H(33)	1332(10)	4558(8)	5045(14)
H(34)	2617(10)	4453(9)	6413(14)
H(35)	3315(8)	3210(9)	6480(13)
H(36)	2799(6)	2086(8)	5150(11)
H(43)	1189(6)	-737(7)	4869(11)
H(46)	1735(8)	-187(8)	1701(12)
H(46)	830(8)	-566(8)	1688(12)
H(46)	1581(8)	-975(8)	2576(12)
H(481)	1111(7)	594(9)	8881(11)
H(482)	868(7)	1322(9)	7869(11)
H(483)	1807(7)	1037(9)	8119(11)

ATOMIC CO-ORDINATES (*10**4) FOR (VIII)

WITH ESTIMATED STANDARD DERIVATIONS IN PARENTHESES

ATOM	X	Y	Z
MO(1)	1195(0)	1494(0)	3250(1)
N(11)	2530(4)	1243(4)	2755(7)
C(12)	2798(5)	1625(5)	1649(9)
C(13)	3602(6)	1465(7)	1194(12)
C(14)	4147(6)	917(8)	1933(13)
C(15)	3884(7)	536(8)	3091(13)
C(16)	3073(6)	724(7)	3461(10)
C(17)	2198(5)	2202(6)	950(9)
C(18)	2389(7)	2721(7)	-130(11)
C(19)	1793(8)	3299(8)	-652(13)
C(20)	1017(8)	3340(7)	-135(12)
C(21)	844(6)	2794(7)	903(10)
N(22)	1420(4)	2242(5)	1464(7)
N(31)	1762(4)	2655(5)	4323(8)
C(32)	1349(8)	3381(6)	4300(11)
C(33)	1646(10)	4050(8)	5073(14)
C(34)	2395(10)	3991(9)	5884(14)
C(35)	2799(8)	3271(9)	5909(13)
C(36)	2490(6)	2596(8)	5122(11)

ATOMIC CO-ORDINATES (*10**4) FOR (VIII) (CONT'D.)

O(1)	-119(5)	834(5)	959(8)
C(1)	407(6)	1036(7)	1810(10)
C(2)	49(7)	1850(7)	3698(10)
O(2)	-615(4)	2045(5)	3934(9)
O(41)	1254(4)	1198(4)	5427(6)
C(42)	1207(5)	436(7)	5734(9)
C(43)	1202(6)	-154(7)	4687(11)
O(44)	1178(5)	221(5)	7048(7)
C(45)	1217(5)	151(6)	3419(10)
C(46)	1345(8)	-461(8)	2241(12)
C(48)	1233(7)	855(9)	8043(11)
B(1)	8952(7)	4208(8)	2255(12)
F(1)	9081(10)	3552(11)	1384(16)
F(2)	9427(8)	4331(8)	3486(13)
F(3)	8852(10)	4987(10)	1716(14)
F(4)	8205(9)	4016(10)	2746(16)
F(11)	9385(18)	4678(19)	1273(28)
F(12)	8177(16)	4608(17)	1976(26)
F(13)	8886(23)	3374(24)	2063(43)
F(21)	9357(21)	3955(25)	1184(31)
F(22)	9652(20)	4114(21)	3175(33)

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (VIII)

ANISOTROPIC IN THE FORM EXP(-2*PI*PI*(U11*(ASTAR*H)**2 +....
...U23*BSTAR*CSTAR*K*L + ...))

ISOTROPIC EXP(-8*PI*PI*U*(SIN(THETA)/LAMBDA)**2)

ALL VALUES *1000

ATOM	U11(OR U)	U22	U33	U23	U13	U12
MO(1)	34(0)	54(0)	46(0)	2(0)	6(0)	1(0)
N(11)	38(3)	56(5)	52(4)	6(3)	2(3)	2(3)
C(12)	40(4)	50(5)	63(5)	-4(4)	10(4)	-3(4)
C(13)	45(4)	79(7)	87(7)	5(6)	27(4)	11(5)
C(14)	38(4)	83(8)	106(9)	-3(6)	19(5)	12(5)
C(15)	53(5)	88(8)	94(8)	-5(7)	-1(5)	13(6)
C(16)	50(5)	77(7)	63(6)	5(5)	8(4)	5(5)
C(17)	46(4)	62(6)	58(5)	1(4)	8(4)	-1(4)
C(18)	56(5)	87(8)	68(6)	21(6)	19(5)	2(5)
C(19)	95(9)	93(10)	85(8)	47(7)	28(7)	6(7)
C(20)	88(8)	71(8)	70(7)	22(5)	7(5)	10(5)
C(21)	46(5)	82(7)	59(5)	12(5)	10(4)	13(4)
N(22)	37(3)	61(5)	51(4)	8(3)	5(3)	0(3)
N(31)	49(4)	60(5)	54(4)	0(4)	8(3)	0(3)
C(32)	84(7)	52(7)	71(6)	7(5)	4(5)	-6(5)
C(33)	127(11)	54(7)	85(8)	-5(6)	25(8)	2(7)
C(34)	118(11)	82(9)	77(8)	-16(7)	11(7)	-36(8)

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (VIII) (CONT'D.)

C(35)	68(7)	94(9)	82(8)	-14(7)	0(5)	-23(6)
C(36)	49(5)	85(7)	67(6)	-1(5)	6(4)	1(5)
O(1)	73(4)	90(6)	66(4)	-5(4)	-8(4)	-12(4)
C(1)	58(5)	70(7)	59(6)	0(5)	10(4)	-1(5)
C(2)	68(6)	65(6)	51(5)	13(4)	2(4)	-10(5)
O(2)	17(3)	59(5)	73(5)	4(4)	19(3)	12(3)
O(41)	52(3)	58(4)	47(3)	1(3)	5(2)	1(3)
C(42)	43(4)	68(6)	58(5)	20(5)	8(4)	-2(4)
C(43)	61(6)	55(6)	70(6)	5(5)	14(4)	5(4)
O(44)	71(4)	86(5)	56(4)	12(4)	14(3)	-3(4)
C(45)	42(4)	61(5)	71(6)	1(5)	11(4)	8(4)
C(46)	82(7)	75(8)	80(7)	-9(6)	0(6)	14(6)
C(48)	76(7)	98(9)	59(7)	15(6)	11(5)	2(6)
B(1)	62(2)					
F(1)	85(4)					
F(2)	111(4)					
F(3)	154(5)					
F(4)	155(5)					
F(11)	90(7)					
F(12)	85(7)					
F(13)	119(11)					
F(21)	99(9)					
F(22)	91(9)					

APPENDIX II

X-ray data for complex (XII)

APPENDIX II

Crystal data for $[\mathrm{Mo}(\eta^3\text{-}\mathrm{CH_2}\overset{..}{-}\mathrm{C(CO_2Me)}\overset{..}{-}\mathrm{C{=}CH_2})(\mathrm{CO})_2(\mathrm{bipy})\mathrm{Cl}]$, (XII):

Suitable crystals of complex (XII) were grown from an acetonitrile solution. 881 Independent reflections with $I > 2\sigma(I)$ were measured on a Stoe Stadi-2 diffractometer. The data were of poor quality because the crystals were small and therefore in the refinement only Mo and Cl were refined anisotropically with C, O, N, H isotropic. The final R was 0.084. $C_{18}H_{15}MoN_2O_4Cl$, M = 434.7, orthorhombic, space group P_{cab} (No. 61), Z = 8, a = 12.590(11), b = 13.537(12), c = 20.801(17) Å, U = 3545.2 $Å^3$, F(000) = 1824, D_m = 1.64, D_c = 1.70 gcm^{-3}, μ = 9.06 cm^{-1}, Mo-K_α radiation, λ= 0.7107 A.

MOLECULAR DIMENSIONS IN (XII)

DISTANCES IN Å, ANGLES IN DEGREES

Mo	-	Cl(1)	2.486(9)
Mo	-	C(31)	2.015(34)
Mo	-	C(21)	1.915(37)
Mo	-	N(1)	2.203(29)
Mo	-	N(12)	2.206(26)
Mo	-	C(60)	2.321(39)
Mo	-	C(61)	2.218(34)
Mo	-	C(62)	2.224(31)
C(31)	-	O(32)	1.052(33)
C(21)	-	O(22)	1.168(38)
N(1)	-	C(2)	1.252(35)
N(1)	-	C(6)	1.466(33)
C(2)	-	C(3)	1.403(45)
C(3)	-	C(4)	1.336(47)
C(4)	-	C(5)	1.32(5)
C(5)	-	C(6)	1.416(44)
C(6)	-	C(7)	1.316(39)
N(12)	-	C(7)	1.283(34)
N(12)	-	C(11)	1.289(37)
C(7)	-	C(8)	1.384(45)
C(8)	-	C(9)	1.403(48)
C(9)	-	C(10)	1.354(41)

MOLECULAR DIMENSIONS IN (XII) (CONT'D.)

C(10)	-	C(11)			1.392(44)
C(60)	-	C(61)			1.442(46)
C(61)	-	C(62)			1.41(5)
C(61)	-	C(65)			1.463(41)
C(62)	-	C(64)			1.45(5)
C(65)	-	O(68)			1.268(37)
C(65)	-	O(67)			1.298(36)
O(67)	-	C(69)			1.496(38)
Cl(1)	-	Mo	-	C(31)	36.7(9)
Cl(1)	-	Mo	-	C(21)	85.4(10)
C(31)	-	Mo	-	C(21)	78.5(14)
Cl(1)	-	Mo	-	N(1)	82.2(6)
C(31)	-	Mo	-	N(1)	100.2(10)
C(21)	-	Mo	-	N(1)	167.7(11)
Cl(1)	-	Mo	-	N(12)	84.3(6)
C(31)	-	Mo	-	N(12)	169.4(10)
C(21)	-	Mo	-	N(12)	106.2(13)
N(1)	-	Mo	-	N(12)	73.0(9)
Cl(1)	-	Mo	-	C(60)	146.2(9)
C(31)	-	Mo	-	C(60)	65.7(12)
C(21)	-	Mo	-	C(60)	106.4(14)
N(1)	-	Mo	-	C(60)	83.9(10)
N(12)	-	Mo	-	C(60)	120.5(10)
Cl(1)	-	Mo	-	C(61)	168.2(8)
C(31)	-	Mo	-	C(61)	101.0(13)

MOLECULAR DIMENSIONS IN (XII) (CONT'D.)

C(21)	-	Mo	-	C(61)	104.7(13)
N(1)	-	Mo	-	C(61)	37.6(11)
N(12)	-	Mo	-	C(61)	87.1(10)
C(60)	-	Mo	-	C(61)	37.0(11)
Cl(1)	-	Mo	-	C(62)	147.9(12)
C(31)	-	Mo	-	C(62)	109.4(12)
C(21)	-	Mo	-	C(62)	71.5(13)
N(1)	-	Mo	-	C(62)	120.0(10)
N(12)	-	Mo	-	C(62)	81.2(11)
C(60)	-	Mo	-	C(62)	64.4(14)
C(61)	-	Mo	-	C(62)	37.0(13)
Mo	-	C(31)	-	O(32)	171.3(30)
Mo	-	C(21)	-	O(22)	170.2(32)
Mo	-	N(1)	-	C(2)	127.1(20)
Mo	-	N(1)	-	C(6)	111.8(17)
C(2)	-	N(1)	-	C(6)	120.9(24)
N(1)	-	C(2)	-	C(3)	126.4(33)
C(2)	-	C(3)	-	C(4)	113.5(41)
C(3)	-	C(4)	-	C(5)	124.3(42)
C(4)	-	C(5)	-	C(6)	122.8(41)
N(1)	-	C(6)	-	C(5)	111.9(30)
N(1)	-	C(6)	-	C(7)	118.0(25)
C(5)	-	C(6)	-	C(7)	130.1(32)
Mo	-	N(12)	-	C(7)	118.6(22)
Mo	-	N(12)	-	C(11)	122.5(22)

MOLECULAR DIMENSIONS IN (XII) (CONT'D.)

C(7)	-	N(12)	-	C(11)	118.9(23)
C(6)	-	C(7)	-	N(12)	113.5(29)
C(6)	-	C(7)	-	C(8)	121.4(32)
N(12)	-	C(7)	-	C(8)	120.0(33)
C(7)	-	C(8)	-	C(9)	120.2(36)
C(8)	-	C(9)	-	C(10)	119.4(34)
C(9)	-	C(10)	-	C(11)	113.5(35)
N(12)	-	C(11)	-	C(10)	127.7(33)
Mo	-	C(60)	-	C(61)	57.6(21)
Mo	-	C(61)	-	C(60)	75.4(20)
Mo	-	C(61)	-	C(62)	71.7(20)
C(60)	-	C(61)	-	C(62)	116.2(31)
Mo	-	C(61)	-	C(65)	115.7(22)
C(60)	-	C(61)	-	C(65)	123.0(33)
C(62)	-	C(61)	-	C(65)	120.3(32)
Mo	-	C(62)	-	C(61)	71.3(19)
Mo	-	C(62)	-	C(64)	139.2(31)
C(61)	-	C(62)	-	C(64)	148.3(35)
C(61)	-	C(65)	-	O(68)	119.9(33)
C(61)	-	C(65)	-	O(67)	118.7(30)
O(68)	-	C(65)	-	O(67)	121.4(30)
C(65)	-	O(67)	-	C(69)	113.0(29)

HYDROGEN COORDINATES (*10**4) IN (XII)

ATOM	X	Y	Z
H(2)	4184(26)	1818(23)	624(14)
H(3)	4883(36)	1347(28)	-385(17)
H(4)	4052(35)	53(25)	-879(18)
H(5)	2497(44)	-553(30)	-540(19)
H(8)	1092(35)	-1136(29)	-90(19)
H(9)	-473(27)	-1667(23)	430(15)
H(10)	-991(34)	-897(25)	1380(17)
H(11)	230(28)	246(23)	1806(16)
H(601)	3641(103)	1706(78)	2248(61)
H(602)	4413(107)	1082(102)	1676(87)
H(691)	2205(46)	-2585(28)	1348(17)
H(692)	3397(46)	-2686(28)	1526(17)
H(693)	3042(46)	-1910(28)	1021(17)

ATOMIC CO-ORDINATES (*10**4) FOR COMPLEX (XII) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESIS

ATOM	X	Y	Z
Mo	2208(3)	1478(2)	1522(2)
Cl(1)	1203(11)	2545(8)	758(5)
C(31)	3089(36)	2663(32)	1721(19)
O (32)	3461(26)	3347(25)	1764(13)
C(21)	1398(39)	2082(28)	2180(19)
O(22)	757(30)	2361(24)	2542(16)
N (1)	2993(23)	982(19)	622(11)
C (2)	3842(32)	1340(28)	390(16)
C (3)	4273(43)	1046(35)	-212(22)
C (4)	3752(42)	290(32)	-505(21)
C (5)	2832(57)	-116(37)	-298(24)
C (6)	2387(32)	201(24)	300(16)
N (12)	1222(28)	265(21)	1119(14)
C (7)	1509(36)	-146(30)	589(20)
C (8)	876(46)	-894(39)	287(24)
C(9)	-62(34)	-1177(29)	614(20)

ATOMIC CO-ORDINATES (*10**4) FOR COMPLEX (XII) (CONT'D.)

C (10)	-375(42)	-753(34)	1175(22)
C (11)	357(36)	-26(30)	1421(20)
C (60)	3893(38)	1143(31)	1977(21)
C (61)	3125(39)	338(30)	2037(21)
C (62)	2158(46)	477(29)	2372(19)
C (64)	1400(50)	155(37)	2868(26)
C (65)	3258(38)	-616(33)	1675(19)
O (68)	4118(26)	-740(20)	1358(13)
O (67)	2517(23)	-1279(22)	1701(13)
C (69)	2821(56)	-2272(38)	1408(25)

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (XII)

ANISOTROPIC IN THE FORM EXP(-2*PI*PI*(U11*(ASTAR*H)**2 +....
...U23*BSTAR*CSTAR*K*L + ...))

ISOTROPIC EXP(-8*PI*PI*U*(SIN(THETA)/LAMBDA)**2)

ALL VALUES *1000

ATOM	U11(OR U)	U22	U33	U23	U13	U12
Mo	66(2)	40(1)	44(1)	-1(2)	-4(2)	1(2)
Cl(1)	86(7)	54(4)	59(5)	4(5)	-8(5)	10(6)
C(31)	53(9)					
O(32)	80(8)					
C(21)	59(10)					
O(22)	82(8)					
N(1)	35(5)					
C(2)	53(8)					
C(3)	77(11)					
C(4)	74(11)					
C(5)	95(13)					
C(6)	42(7)					
N(12)	49(7)					
C(7)	47(8)					
C(8)	81(12)					
C(9)	55(9)					

ANTISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (XII)

(CONT'D.)

C(10)	69(10)
C(11)	61(10)
C(60)	65(10)
C(61)	63(10)
C(62)	66(9)
C(64)	89(14)
C(65)	56(10)
O(68)	68(7)
O(67)	70(7)
C(69)	98(13)

STRUCTURE FACTORS FOR (XII)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	2	0	100	112	1	5	1	34	28	0	5	2	184	198	2	3	3	142	159	8	1	4	32	-29
5	2	0	91	-120	2	5	1	69	-80	1	5	2	56	64	3	3	3	190	-208	0	2	4	75	88
6	2	0	24	28	4	5	1	82	-86	2	5	2	130	-159	5	3	3	110	131	1	2	4	63	78
0	4	0	34	-35	6	5	1	100	119	3	5	2	27	-23	6	3	3	48	53	0	3	4	126	124
1	4	0	29	38	12	5	1	35	-24	4	5	2	96	113	7	3	3	76	-95	1	3	4	116	-130
2	4	0	90	103	1	6	1	56	-59	0	6	2	74	-68	8	3	3	32	-57	2	3	4	71	82
4	4	0	167	-215	2	6	1	42	-57	1	7	2	131	-161	2	4	3	84	-100	3	3	4	103	119
6	4	0	63	76	4	6	1	56	77	2	7	2	38	36	5	4	3	84	94	4	3	4	40	-48
0	6	0	39	48	5	6	1	51	77	3	7	2	104	130	6	4	3	57	72	5	3	4	75	-82
1	6	0	82	101	6	6	1	80	-103	4	7	2	53	-77	1	5	3	52	-58	8	3	4	31	42
2	6	0	153	-181	1	7	1	29	37	5	7	2	76	-91	4	5	3	121	123	0	4	4	128	136
3	6	0	68	-73	2	7	1	27	16	1	8	2	39	43	6	5	3	109	-135	1	4	4	85	-94
4	6	0	114	129	3	7	1	55	-65	3	8	2	71	-79	8	5	3	92	110	2	4	4	168	-186
0	8	0	167	203	5	7	1	49	75	4	8	2	32	-38	6	6	3	70	-87	3	4	4	97	108
1	8	0	155	-173	1	8	1	33	-30	0	9	2	168	-177	1	7	3	58	-64	4	4	4	118	138
2	8	0	58	-62	2	8	1	60	-72	1	9	2	34	47	3	7	3	75	85	0	5	4	200	-214
3	8	0	99	113	3	8	1	56	62	2	9	2	70	83	5	7	3	57	-82	1	5	4	29	-27
5	8	0	42	-58	5	8	1	43	-66	3	9	2	34	-42	7	7	3	83	100	2	5	4	78	90
0	10	0	115	-139	2	9	1	45	-46	0	10	2	59	62	9	7	3	55	-68	0	6	4	64	-72
2	10	0	101	122	3	9	1	33	41	2	10	2	79	-57	1	8	3	34	-43	1	6	4	119	-135
0	12	0	39	38	3	9	1	35	55	4	10	2	46	60	2	8	3	59	-70	2	6	4	54	61
1	12	0	51	45	4	10	1	44	-42	0	11	2	71	77	5	8	3	31	-20	3	6	4	85	90
3	12	0	53	-68	6	10	1	34	57	1	11	2	55	67	4	9	3	54	-62	4	6	4	59	-69
5	12	0	36	52	7	10	1	27	16	2	11	2	61	-62	6	9	3	46	48	6	6	4	35	37
0	14	0	33	38	8	10	1	56	-72	3	11	2	60	-62	8	9	3	47	-50	0	7	4	99	102
1	14	0	30	-25	2	11	1	48	57	1	13	2	43	-49	9	9	3	31	35	1	7	4	77	79
2	14	0	44	-49	5	11	1	39	-42	2	13	2	32	-19	10	9	3	41	47	2	7	4	57	-67
3	14	0	35	34	7	11	1	31	43	3	13	2	44	48	2	10	3	36	42	3	7	4	99	-112
4	14	0	39	51	3	12	1	34	-44	0	14	2	34	-36	4	10	3	36	-32	5	7	4	80	98
5	14	0	29	-31	5	12	1	44	60	0	15	2	35	-41	6	11	3	48	-59	1	8	4	102	114
1	16	0	34	-41	5	13	1	29	26	2	15	2	41	51	9	11	3	30	37	2	8	4	55	63
1	2	1	37	-52	6	14	1	30	-38	4	15	2	40	-46	2	12	3	30	-24	3	8	4	48	-55
2	2	1	3[illegible]	41	8	0	2	40	43	2	0	3	111	-117	5	12	3	36	34	4	8	4	35	-40
3	2	1	162	183	2	1	2	210	220	4	0	3	53	53	2	13	3	35	-24	1	9	4	39	-45
5	2	1	94	-121	3	1	2	104	108	6	0	3	59	79	3	13	3	38	28	2	9	4	59	-70
11	2	1	44	48	9	1	2	26	16	10	0	3	45	-46	4	13	3	33	30	4	9	4	50	74
2	3	1	117	136	1	2	2	32	42	2	1	3	98	103	5	13	3	38	-53	0	10	4	102	107
3	3	1	47	62	3	2	2	31	-43	4	1	3	65	-67	6	14	3	30	-33	2	10	4	72	-88
5	3	1	90	-104	6	2	2	31	-39	5	1	3	104	-106	2	0	4	136	157	1	11	4	59	-74
6	3	1	71	-35	0	3	2	85	90	6	1	3	104	122	4	0	4	132	-134	2	11	4	53	64
7	3	1	40	68	1	3	2	194	207	7	1	3	59	69	6	0	4	27	30	3	11	4	38	46
1	4	1	40	43	2	3	2	149	166	8	1	3	99	-114	0	1	4	99	108	4	11	4	49	-66
2	4	1	115	-136	3	3	2	202	-226	9	1	3	49	-60	1	1	4	116	138	1	12	4	43	-52
3	4	1	45	-62	4	3	2	97	-117	10	1	3	44	60	2	1	4	53	-61	3	12	4	47	63
4	4	1	126	-156	5	3	2	112	138	11	1	3	32	55	3	1	4	71	-81	0	14	4	48	-50
5	4	1	69	91	0	4	2	36	30	1	2	3	52	62	4	1	4	103	101	2	14	4	35	36
6	4	1	122	154	1	4	2	31	-25	10	2	3	29	19	5	1	4	87	102	4	14	4	36	-41
6	4	1	52	-76	2	4	2	124	-149	1	3	3	52	53	6	1	4	26	30	0	15	4	41	41

STRUCTURE FACTORS FOR (XII) (CONT'D.)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
2	0	5	185	-210	4	14	5	31	-25	0	9	6	60	69	2	7	7	62	-67	0	7	8	70	-66
4	0	5	119	-128	0	0	6	210	223	1	9	6	42	-42	3	7	7	57	-74	1	7	8	116	-146
6	0	5	157	177	2	0	6	243	-277	0	10	6	65	-70	5	7	7	55	64	3	7	8	106	124
8	0	5	89	-87	4	0	6	200	217	2	10	6	88	105	7	7	7	57	-82	0	8	8	59	-56
10	0	5	80	77	6	0	6	49	-62	4	10	6	63	-78	9	7	7	37	59	1	8	8	42	-47
1	1	5	94	-97	0	1	6	40	-45	2	11	6	42	56	11	7	7	40	-36	3	8	8	40	34
2	1	5	143	158	1	1	6	45	45	1	12	6	51	63	3	8	7	33	20	0	9	8	95	-96
3	1	5	29	28	4	1	6	102	119	3	12	6	36	-51	4	9	7	53	69	1	9	8	45	43
4	1	5	28	39	0	2	6	38	22	0	14	6	64	71	5	9	7	33	-36	2	9	8	79	91
6	1	5	55	-46	1	2	6	47	-59	2	0	7	81	94	6	9	7	49	-62	3	9	8	45	-36
1	2	5	123	131	2	2	6	116	135	6	0	7	66	-86	7	9	7	29	21	4	9	8	47	-68
3	2	5	163	-179	3	2	6	100	108	8	0	7	40	42	8	9	7	31	35	0	11	8	47	56
4	2	5	60	61	4	2	6	80	-85	1	1	7	39	52	6	11	7	33	54	1	11	8	52	61
5	2	5	140	151	5	2	6	62	-80	3	1	7	83	-91	3	12	7	32	-29	2	11	8	39	-49
6	2	5	39	-48	0	3	6	36	36	4	1	7	95	104	5	13	7	35	39	3	11	8	42	-47
7	2	5	102	-115	1	3	6	73	-72	5	1	7	81	78	2	15	7	31	-30	3	12	8	32	-19
8	2	5	36	40	3	3	6	143	168	6	1	7	133	-153	0	0	8	76	-93	1	13	8	48	-66
9	2	5	91	100	5	3	6	66	-82	7	1	7	57	-62	2	0	8	55	57	0	15	8	41	-57
1	3	5	59	-61	8	3	6	29	31	8	1	7	82	90	4	0	8	82	88	2	15	8	39	47
3	3	5	98	113	0	4	6	290	-297	9	1	7	46	52	6	0	8	81	-99	2	0	9	42	-52
4	3	5	61	75	1	4	6	101	114	2	2	7	64	-75	8	0	8	37	-34	4	0	9	92	102
2	4	5	173	-200	2	4	6	104	121	3	2	7	37	36	0	1	8	52	-60	6	0	9	138	-172
3	4	5	59	53	3	4	6	68	-81	4	2	7	44	-44	1	1	8	126	-141	8	0	9	68	75
4	4	5	145	169	4	4	6	34	35	5	2	7	69	-82	2	1	8	128	145	10	0	9	34	-30
5	4	5	81	-86	5	4	6	34	45	7	2	7	33	30	3	1	8	71	88	5	1	9	50	-53
6	4	5	66	-80	6	4	6	80	99	2	3	7	160	-183	4	1	8	122	-137	6	1	9	42	51
8	4	5	96	110	0	5	6	133	-148	3	3	7	94	108	5	1	8	72	-91	8	1	9	45	-56
2	5	5	56	63	1	5	6	37	38	4	3	7	47	59	7	1	8	28	27	1	2	9	49	-57
1	6	5	44	-47	2	5	6	97	111	5	3	7	81	-93	8	1	8	28	19	2	2	9	47	-44
2	6	5	109	129	4	5	6	122	-138	7	3	7	88	107	1	2	8	43	-47	3	2	9	55	66
3	6	5	39	49	11	5	6	31	26	8	3	7	33	41	2	2	8	38	39	5	2	9	74	-81
5	6	5	60	-74	0	6	6	170	183	9	3	7	59	-68	3	2	8	53	64	7	2	9	82	97
6	6	5	62	70	1	6	6	99	109	10	3	7	36	-37	0	3	8	36	-36	9	2	9	53	-62
7	6	5	59	63	2	6	6	85	-100	11	3	7	36	37	1	3	8	163	183	11	2	9	28	27
8	6	5	67	-81	3	6	6	31	-34	2	4	7	37	41	2	3	8	53	60	1	3	9	42	40
9	6	5	56	-70	4	6	6	56	58	3	4	7	63	-69	3	3	8	147	-171	3	3	9	48	-57
2	7	5	35	-39	5	6	6	31	33	6	4	7	45	49	5	3	8	76	89	4	3	9	46	-48
3	7	5	33	33	0	7	6	35	43	8	4	7	39	-39	7	3	8	42	-52	5	3	9	57	72
3	8	5	42	-50	1	7	6	71	79	9	4	7	35	28	2	4	8	30	27	6	3	9	37	38
5	8	5	40	53	3	7	6	44	-56	1	5	7	33	34	4	4	8	42	52	7	3	9	57	-62
2	9	5	35	47	4	7	6	41	-48	2	5	7	54	69	0	5	8	222	250	9	3	9	53	55
4	10	5	54	51	5	7	6	33	37	3	5	7	40	46	1	5	8	43	48	11	3	9	33	-24
5	10	5	31	28	0	8	6	32	15	4	5	7	74	-85	2	5	8	126	-150	2	4	9	67	79
6	10	5	42	-58	1	8	6	92	-108	6	5	7	52	60	6	5	8	30	-39	4	4	9	48	-59
8	10	5	34	53	2	8	6	67	-75	8	5	7	79	-88	8	5	8	32	22	5	4	9	40	37
10	10	5	27	-33	3	8	6	83	98	10	5	7	67	74	10	5	8	31	29	8	4	9	47	-51
3	12	5	46	50	4	8	6	78	95	4	6	7	51	62	2	6	8	38	-46	10	4	9	34	40
5	12	5	36	-42	5	8	6	57	-70	1	7	7	40	50	3	6	8	35	-35	4	5	9	36	55

STRUCTURE FACTORS FOR (XII) (CONT'D.)

H	K	L	FO	FC
6	5	9	62	-83
8	5	9	55	61
10	5	9	34	-45
2	6	9	57	-67
4	6	9	47	49
5	6	9	37	45
6	6	9	29	-32
1	7	9	44	-42
3	7	9	59	62
4	7	9	39	-28
5	7	9	66	-79
6	7	9	37	55
11	7	9	30	29
5	8	9	47	-62
6	8	9	34	-58
7	8	9	40	48
9	8	9	34	-34
2	9	9	34	26
8	9	9	31	-34
4	10	9	47	-54
6	10	9	34	54
8	10	9	34	-28
0	0	10	287	-311
2	0	10	151	180
4	0	10	129	-158
6	0	10	64	74
0	1	10	116	125
3	1	10	42	-44
4	1	10	44	-53
0	2	10	45	44
1	2	10	136	161
2	2	10	34	-37
3	2	10	134	-151
5	2	10	61	79
11	2	10	31	30
0	3	10	59	-53
2	3	10	44	51
5	3	10	57	-72
0	4	10	118	131
1	4	10	93	-102
2	4	10	116	-130
4	4	10	71	86
5	4	10	33	-40
6	4	10	32	-27
1	5	10	52	-57
3	5	10	31	20
6	5	10	28	-24
0	6	10	80	-83
1	6	10	95	-109
2	6	10	65	81
3	6	10	58	67
4	6	10	56	-74
6	6	10	30	29
0	7	10	77	-83
4	7	10	42	36
0	8	10	61	-69
1	8	10	83	94
2	8	10	38	35
3	8	10	66	-77
4	8	10	40	-44
5	8	10	46	58
0	10	10	74	89
2	10	10	65	-81
4	10	10	42	46
6	10	10	32	-37
0	11	10	53	-59
1	12	10	59	-69
0	14	10	45	-51
3	14	10	28	-21
2	0	11	58	72
4	0	11	43	-42
6	0	11	41	57
8	0	11	56	-68
10	0	11	58	59
4	1	11	51	-55
5	1	11	51	-57
6	1	11	39	56
8	1	11	34	-20
11	1	11	29	17
2	2	11	62	-75
3	2	11	71	-85
5	2	11	62	71
7	2	11	69	-81
9	2	11	52	53
11	2	11	33	-35
3	4	11	36	35
4	4	11	77	81
6	4	11	58	-66
7	4	11	39	43
8	4	11	49	56
10	4	11	38	-45
2	5	11	46	-45
3	6	11	39	54
4	6	11	59	-71
6	6	11	65	86
8	6	11	37	-40
9	6	11	39	-40
11	6	11	52	36
5	7	11	35	-39
7	7	11	47	49
9	7	11	38	-20
2	8	11	42	51
3	8	11	38	-55
5	8	11	53	75
7	8	11	42	-53
8	8	11	27	-19
9	8	11	37	36
4	9	11	32	-38
6	9	11	39	52
2	10	11	44	-59
6	10	11	35	-44
2	12	11	28	13
5	12	11	40	-44
0	0	12	51	-66
2	0	12	79	-95
4	0	12	36	51
0	1	12	106	122
1	1	12	86	102
2	1	12	88	-109
3	1	12	64	-68
4	1	12	49	55
5	1	12	45	53
0	2	12	137	-151
3	2	12	47	53
5	2	12	43	-49
1	3	12	119	-142
2	3	12	48	-71
3	3	12	73	97
4	3	12	66	80
7	3	12	33	35
2	4	12	79	95
3	4	12	40	-33
4	4	12	68	-79
0	5	12	115	-117
2	5	12	101	117
4	5	12	70	-84
6	5	12	38	51
4	6	12	48	52
1	7	12	65	79
3	7	12	58	-72
0	8	12	45	43
1	8	12	36	-26
2	9	12	45	-55
4	9	12	32	40
6	9	12	34	-28
0	10	12	76	-75
1	10	12	33	20
2	10	12	40	38
0	11	12	53	-68
2	11	12	39	39
3	11	12	32	41
5	11	12	28	-23
0	13	12	32	-23
1	13	12	42	46
4	0	13	45	-51
8	0	13	31	47
2	1	13	90	-108
3	1	13	35	-45
4	1	13	53	68
5	1	13	41	58
7	1	13	50	-49
8	1	13	56	65
9	1	13	46	41
10	1	13	52	-55
1	2	13	29	-26
5	2	13	35	-28
3	3	13	56	62
5	3	13	46	-53
6	3	13	37	-48
7	3	13	41	60
9	3	13	53	-65
11	3	13	34	33
8	4	13	27	18
4	5	13	44	-57
6	5	13	60	85
8	5	13	41	-56
10	5	13	39	41
2	6	13	34	41
1	7	13	45	41
2	7	13	35	30
3	7	13	43	-49
5	7	13	51	60
6	7	13	42	-47
7	7	13	46	-57
9	7	13	36	45
2	9	13	43	-48
6	9	13	31	-36
4	11	13	31	-29
5	11	13	33	-32
0	0	14	79	95
2	0	14	51	-62
0	1	14	81	-84
1	1	14	45	-49
2	1	14	52	58
3	1	14	58	68
4	1	14	36	-41
0	2	14	57	-60
1	2	14	87	-104
3	2	14	71	97
5	2	14	31	-32
8	2	14	41	-43
1	3	14	73	80
3	3	14	54	-71
4	3	14	34	-41
0	4	14	36	-33
1	4	14	46	58
2	4	14	56	69
4	4	14	68	-84
6	4	14	30	26
0	5	14	38	52
2	5	14	54	-66
4	5	14	48	59
1	6	14	44	59
3	6	14	46	-43
4	6	14	37	61
5	6	14	32	39
1	7	14	53	-65
3	7	14	47	59
5	7	14	35	-40
0	8	14	49	38
3	8	14	37	39
0	9	14	60	-65
1	9	14	37	44
2	9	14	43	53
0	10	14	44	-41
1	11	14	42	38
2	11	14	30	-26
3	11	14	33	-32
1	12	14	44	34
3	12	14	32	-34
2	13	14	29	-14
2	0	15	67	-80
4	0	15	56	65
6	0	15	49	-71
8	0	15	45	54
10	0	15	41	-50
1	2	15	35	-35
2	2	15	38	57
5	2	15	57	-70
7	2	15	57	69

STRUCTURE FACTORS FOR (XII) (CONT'D.)

H	K	L	FO	FC
9	2	15	45	-50
10	2	15	29	25
2	3	15	41	38
4	3	15	42	-50
3	4	15	36	-34
4	4	15	39	-49
6	4	15	50	63
7	4	15	33	-29
9	4	15	29	34
6	6	15	46	-57
8	6	15	33	33
9	6	15	32	37
5	8	15	34	-42
6	8	15	28	-15
7	8	15	34	44
4	10	15	42	-36
0	0	16	77	-83
2	0	16	92	110
4	0	16	52	-66
6	0	16	43	46
0	1	16	54	-55
1	1	16	32	-16
1	2	16	79	88
3	2	16	45	-64
5	2	16	34	33
7	2	16	29	-25
4	3	16	40	-49
0	4	16	68	70
1	4	16	48	-63
2	4	16	44	-55
2	5	16	39	-44
4	5	16	53	60
0	6	16	81	-87
1	6	16	41	-41
2	6	16	52	61
4	6	16	40	-48
1	8	16	58	75
3	8	16	41	-53
5	8	16	36	34
0	9	16	38	-40
0	10	16	41	52
2	10	16	45	-52
6	0	17	32	37
10	0	17	25	17
2	1	17	33	37
6	1	17	33	43
8	1	17	31	-38
5	2	17	36	46
9	2	17	28	22
5	3	17	46	46
7	3	17	40	-48
9	3	17	32	32
2	5	17	29	-22
4	5	17	42	48
6	5	17	36	-50
8	5	17	29	31
4	8	17	31	-21
6	9	17	30	29
6	0	18	32	45
0	1	18	52	57
1	1	18	34	48
2	1	18	45	-52
4	1	18	45	58
1	3	18	74	-94
3	3	18	42	49
0	5	18	91	-100
2	5	18	63	73
4	5	18	35	-36
1	7	18	44	66
3	7	18	42	-51
1	9	18	29	-24
2	9	18	35	-49
4	9	18	37	41
4	0	19	32	-35
6	0	19	44	69
4	1	19	44	29
6	1	19	32	-42
5	2	19	34	47
7	2	19	34	-35
7	3	19	35	36
0	0	20	47	39
2	0	20	40	-53
4	0	20	37	54
1	1	20	29	-18
1	2	20	54	-78
3	2	20	46	51
4	2	20	37	-41
0	4	20	64	-66
2	4	20	44	54
4	5	20	29	17
0	6	20	58	64
1	8	20	46	-43
3	8	20	37	33
5	1	21	30	21
6	2	21	31	32
5	4	21	29	25
6	4	21	31	24
2	6	21	31	-28
0	0	22	41	-57
2	1	22	36	39
1	2	22	31	40
0	5	22	40	52
2	5	22	33	-41
1	7	22	31	-32
0	1	24	37	40
1	1	24	35	32
1	2	24	30	32

APPENDIX III

X-ray data for complex (XXII)

APPENDIX III

Crystal data for $[Mo(\eta^3\text{-}CH_2\text{∸}C(CO_2Me)\text{∸}C(OMe)(Me))(CO)_2(bipy)Cl]$, (XXII):

Suitable crystals of complex (XXII) were grown from a dichloromethane solution. 1721 Independent reflections with $I > 3\sigma(I)$ were measured on a Stoe Stadi-2 diffractometer. Mo, Cl, C, O and N were refined anisotropically and H isotropically. The final R was 0.073. $C_{19}H_{19}MoN_2O_5Cl$, M = 486.8 orthorhombic, space group P_{bca}, Z = 8, a = 13.591(11), b = 14.414(8), c = 20.169(11) Å, U = 3951.1 $Å^3$, F(000) = 1968, D_m = 1.64, D_c = 1.64 gcm^{-3}, μ= 8.23 cm^{-1}, Mo-K_α radiation, λ = 0.7107 A.

MOLECULAR DIMENSIONS IN (XXII)

DISTANCES IN Å, ANGLES IN DEGREES

Mo(1)	-	Cl(1)	2.482(4)
Mo(1)	-	N(1)	2.229(12)
Mo(1)	-	N(12)	2.232(13)
Mo(1)	-	C(31)	1.922(17)
Mo(1)	-	C(41)	2.065(17)
Mo(1)	-	C(60)	2.262(19)
Mo(1)	-	C(61)	2.226(15)
Mo(1)	-	C(62)	2.343(18)
N(1)	-	C(2)	1.322(18)
N(1)	-	C(6)	1.365(18)
N(12)	-	C(7)	1.359(20)
N(12)	-	C(11)	1.338(22)
C(2)	-	C(3)	1.390(22)
C(3)	-	C(4)	1.317(27)
C(4)	-	C(5)	1.379(25)
C(5)	-	C(6)	1.391(23)
C(6)	-	C(7)	1.472(22)
C(7)	-	C(8)	1.367(22)
C(8)	-	C(9)	1.361(25)
C(9)	-	C(10)	1.360(26)
C(10)	-	C(11)	1.411(25)
C(31)	-	O(32)	1.167(19)
C(41)	-	O(42)	1.063(19)

MOLECULAR DIMENSIONS IN(XXII) (CONT'D.)

C(60)	-	C(61)			1.415(26)
C(61)	-	C(62)			1.409(22)
C(61)	-	C(66)			1.473(23)
C(62)	-	C(63)			1.465(24)
C(62)	-	O(64)			1.417(21)
O(64)	-	C(65)			1.440(22)
C(66)	-	O(67)			1.289(23)
C(66)	-	O(68)			1.212(24)
O(67)	-	C(69)			1.426(22)
Cl(1)	-	Mo(1)	-	N(1)	84.18(31)
Cl(1)	-	Mo(1)	-	N(12)	81.66(33)
N(1)	-	Mo(1)	-	N(12)	73.14(46)
Cl(1)	-	Mo(1)	-	C(31)	83.5(5)
N(1)	-	Mo(1)	-	C(31)	166.7(5)
N(12)	-	Mo(1)	-	C(31)	100.1(5)
Cl(1)	-	Mo(1)	-	C(41)	83.7(5)
N(1)	-	Mo(1)	-	C(41)	101.8(5)
N(12)	-	Mo(1)	-	C(41)	164.9(5)
C(31)	-	Mo(1)	-	C(41)	81.7(6)
Cl(1)	-	Mo(1)	-	C(60)	146.1(5)
N(1)	-	Mo(1)	-	C(60)	83.1(5)
N(12)	-	Mo(1)	-	C(60)	123.8(5)
C(31)	-	Mo(1)	-	C(60)	110.0(6)
C(41)	-	Mo(1)	-	C(60)	68.5(7)
Cl(1)	-	Mo(1)	-	C(61)	170.60(41)

MOLECULAR DIMENSIONS IN(XXII) (CONT'D.)

N(1)	-	Mo(1)	-	C(61)	87.9(5)
N(12)	-	Mo(1)	-	C(61)	91.2(5)
C(31)	-	Mo(1)	-	C(61)	103.9(6)
C(41)	-	Mo(1)	-	C(61)	103.0(6)
C(60)	-	Mo(1)	-	C(61)	36.8(6)
Cl(1)	-	Mo(1)	-	C(62)	149.41(43)
N(1)	-	Mo(1)	-	C(62)	121.8(5)
N(12)	-	Mo(1)	-	C(62)	90.5(5)
C(31)	-	Mo(1)	-	C(62)	68.8(6)
C(41)	-	Mo(1)	-	C(62)	104.0(6)
C(60)	-	Mo(1)	-	C(62)	60.4(7)
C(61)	-	Mo(1)	-	C(62)	35.8(5)
Mo(1)	-	N(1)	-	C(2)	124.7(9)
Mo(1)	-	N(1)	-	C(6)	116.8(9)
C(2)	-	N(1)	-	C(6)	118.5(12)
Mo(1)	-	N(12)	-	C(7)	118.4(10)
Mo(1)	-	N(12)	-	C(11)	125.3(12)
C(7)	-	N(12)	-	C(11)	115.7(14)
N(1)	-	C(2)	-	C(3)	122.7(15)
C(2)	-	C(3)	-	C(4)	119.3(17)
C(3)	-	C(4)	-	C(5)	119.8(17)
C(4)	-	C(5)	-	C(6)	119.9(16)
N(1)	-	C(6)	-	C(5)	119.5(14)
N(1)	-	C(6)	-	C(7)	117.2(13)
C(5)	-	C(6)	-	C(7)	123.3(14)

MOLECULAR DIMENSIONS IN(XXII) (CONT'D.)

N(12)	-	C(7)	-	C(6)	114.3(14)
N(12)	-	C(7)	-	C(8)	122.9(16)
C(6)	-	C(7)	-	C(8)	122.5(14)
C(7)	-	C(8)	-	C(9)	120.9(18)
C(8)	-	C(9)	-	C(10)	118.2(17)
C(9)	-	C(10)	-	C(11)	118.8(16)
N(12)	-	C(11)	-	C(10)	123.4(18)
Mo(1)	-	C(31)	-	O(32)	179.9(15)
Mo(1)	-	C(41)	-	O(42)	175.2(17)
Mo(1)	-	C(60)	-	C(61)	70.2(9)
Mo(1)	-	C(61)	-	C(60)	73.0(10)
Mo(1)	-	C(61)	-	C(62)	76.6(9)
C(60)	-	C(61)	-	C(62)	110.3(15)
Mo(1)	-	C(61)	-	C(66)	115.7(9)
C(60)	-	C(61)	-	C(66)	122.3(16)
C(62)	-	C(61)	-	C(66)	127.4(18)
Mo(1)	-	C(62)	-	C(51)	67.5(9)
Mo(1)	-	C(62)	-	C(63)	122.6(12)
C(61)	-	C(62)	-	C(63)	123.5(16)
Mo(1)	-	C(62)	-	O(64)	110.2(11)
C(61)	-	C(62)	-	O(64)	115.5(14)
C(63)	-	C(62)	-	O(64)	111.0(14)
C(62)	-	O(64)	-	C(65)	112.7(14)
C(61)	-	C(66)	-	O(67)	113.8(17)
C(61)	-	C(66)	-	O(68)	123.8(20)
O(67)	-	C(66)	-	O(68)	122.3(17)
C(66)	-	O(67)	-	C(69)	117.3(16)

HYDROGEN COORDINATES (*10**4) IN (XXII)

ATOM	X	Y	Z
H(2)	2475(11)	1925(10)	110(8)
H(3)	2414(17)	1737(13)	-1035(9)
H(4)	981(17)	1299(13)	-1526(9)
H(5)	-431(13)	1108(11)	-884(9)
H(8)	-1542(12)	656(12)	-202(10)
H(9)	-2827(13)	425(14)	535(10)
H(10)	-2638(11)	930(12)	1626(11)
H(11)	-1135(15)	1586(12)	1953(10)
H(61)	2034(92)	3410(102)	609(40)
H(62)	2161(78)	3777(98)	1282(64)
H(631)	-1079(14)	3255(12)	1700(9)
H(632)	-653(14)	4176(12)	1974(9)
H(633)	-789(14)	3332(12)	2442(9)
H(691)	300(18)	4153(15)	-931(9)
H(692)	-666(18)	4199(15)	-523(9)
H(693)	-277(18)	3251(15)	-776(9)
H(651)	1549(23)	5136(14)	2466(11)
H(652)	444(23)	4943(14)	2332(11)
H(653)	1171(23)	5042(14)	1743(11)

ATOMIC CO-ORDINATES (*10**4) FOR COMPLEX (XXII) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESIS

ATOM	X	Y	Z
Mo(1)	1030(1)	2029(1)	1365(1)
Cl(1)	1276(4)	332(3)	1493(2)
N(1)	1070(9)	1716(8)	284(6)
N(12)	-479(10)	1564(8)	1080(7)
C(2)	1863(11)	1782(10)	-94(8)
C(3)	1838(17)	1649(13)	-776(9)
C(4)	1005(17)	1399(13)	-1060(9)
C(5)	171(13)	1284(11)	-681(9)
C(6)	213(11)	1425(8)	1(8)
C(7)	-639(13)	1297(9)	443(8)
C(8)	-1482(12)	862(12)	244(10)
C(9)	-2236(13)	718(14)	676(10)
C(10)	-2122(10)	1003(12)	1314(11)
C(11)	-1220(15)	1411(12)	1502(10)
C(31)	916(11)	2000(12)	2315(8)
O(32)	843(11)	1967(10)	2891(6)
C(41)	2510(13)	2094(13)	1594(8)
O(42)	3260(10)	2084(10)	1742(7)
C(60)	1703(15)	3389(13)	1037(11)
C(61)	670(13)	3490(10)	1103(8)
C(62)	393(14)	3427(12)	1774(9)
C(63)	-625(14)	3519(12)	2004(9)
O(64)	1057(12)	3828(7)	2233(6)
C(65)	1096(23)	4824(14)	2185(11)
C(66)	20(16)	3612(10)	525(10)
O(67)	484(10)	3738(9)	-25(5)
O(68)	-870(12)	3635(10)	559(7)
C(69)	-93(18)	3843(15)	-611(9)

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (XXII)

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 ANISOTROPIC IN THE FORM EXP(-2*PI*PI*(U11*(ASTAR*H)**2 +....
...U23*BSTAR*CSTAR*K*L + ....))

ISOTROPIC     EXP(-8*PI*PI*U*(SIN(THETA)/LAMBDA)**2)

ALL VALUES *1000
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ATOM	U11(OR U)	U22	U33	U23	U13	U12
Mo(1)	69(1)	42(1)	36(1)	-1(1)	-2(1)	-4(1)
Cl(1)	104(4)	41(2)	66(3)	1(2)	-7(2)	5(2)
N(1)	39(6)	46(6)	48(8)	1(5)	0(6)	-5(5)
N(12)	51(7)	38(7)	57(8)	15(6)	0(6)	-7(5)
C(2)	48(8)	49(9)	50(9)	1(7)	-2(7)	-13(6)
C(3)	92(14)	75(12)	47(11)	-9(9)	21(11)	-1(10)
C(4)	100(15)	78(13)	37(9)	-6(8)	16(12)	-7(11)
C(5)	56(10)	62(10)	54(10)	-6(8)	-16(9)	-8(8)
C(6)	75(11)	17(6)	50(9)	4(6)	-6(9)	13(6)
C(7)	73(10)	28(7)	43(9)	-1(6)	-8(8)	8(6)
C(8)	55(10)	62(11)	81(13)	-3(9)	-17(10)	-4(8)
C(9)	54(11)	82(13)	77(14)	-6(10)	5(9)	-7(9)
C(10)	31(7)	69(10)	95(14)	0(11)	13(9)	0(7)
C(11)	99(16)	57(10)	57(12)	10(8)	11(10)	7(9)
C(31)	46(8)	58(9)	60(10)	-4(8)	-6(7)	-15(8)
O(32)	132(13)	85(9)	42(8)	1(7)	0(7)	7(9)
C(41)	56(9)	68(11)	56(10)	-14(9)	-32(8)	0(8)

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS IN (XXII) (CONT'D.)

O(42)	64(8)	100(10)	76(9)	-13(8)	-16(7)	-12(8)
C(60)	66(12)	63(11)	67(12)	3(9)	-19(10)	-13(9)
C(61)	73(11)	35(8)	37(8)	-1(6)	-1(7)	-6(7)
C(62)	79(12)	57(10)	45(10)	-2(8)	8(9)	-7(9)
C(63)	82(13)	55(11)	53(11)	5(8)	0(10)	-5(9)
O(64)	147(12)	41(6)	44(6)	-8(5)	-10(8)	-7(8)
C(66)	77(12)	29(7)	77(13)	3(7)	-24(11)	13(7)
O(67)	100(9)	80(9)	31(6)	10(6)	8(6)	2(7)
O(68)	95(11)	106(12)	61(9)	16(7)	-12(8)	19(8)
C(69)	108(16)	92(14)	36(9)	4(10)	-4(11)	-1(12)
C(65)	171(25)	65(12)	67(13)	-18(11)	-18(16)	0(16)

STRUCTURE FACTORS IN (XXII)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	2	0	104	-98	2	10	0	23	-29	11	3	1	34	-30	6	7	1	62	-64	4	16	1	32	33
4	2	0	125	102	4	10	0	97	-94	12	3	1	40	32	7	7	1	23	21	1	17	1	24	-28
6	2	0	160	140	6	10	0	76	-80	13	3	1	35	32	8	7	1	63	-63	2	0	2	59	61
8	2	0	21	21	8	10	0	33	32	14	3	1	20	16	9	7	1	37	-39	3	0	2	227	-242
10	2	0	105	-82	10	10	0	59	59	0	4	1	168	169	11	7	1	22	-19	4	0	2	174	196
12	2	0	43	-38	12	10	0	18	15	1	4	1	217	216	12	7	1	40	35	5	0	2	121	132
14	2	0	61	51	2	11	0	144	-150	2	4	1	62	61	0	8	1	142	138	6	0	2	104	111
2	3	0	159	148	4	11	0	87	-85	3	4	1	54	57	2	8	1	19	16	7	0	2	147	159
4	3	0	82	72	6	11	0	85	87	4	4	1	153	-138	3	8	1	48	47	8	0	2	17	-16
6	3	0	32	-33	8	11	0	63	65	5	4	1	19	-19	4	8	1	22	-13	11	0	2	24	-39
8	3	0	127	-115	10	11	0	32	-25	6	4	1	127	-121	5	8	1	35	35	2	1	2	43	45
12	3	0	17	15	0	12	0	123	-140	7	4	1	102	-95	6	8	1	56	-57	3	1	2	73	86
14	3	0	17	14	2	12	0	46	-53	8	4	1	24	28	7	8	1	22	-17	4	1	2	90	108
0	4	0	343	-347	4	12	0	82	79	9	4	1	40	-42	9	8	1	16	-21	5	1	2	286	256
2	4	0	222	-218	6	12	0	61	56	10	4	1	80	63	10	8	1	39	37	9	1	2	63	-94
4	4	0	165	-152	8	12	0	43	-47	11	4	1	46	41	11	8	1	16	-7	0	2	2	27	25
6	4	0	31	-32	10	12	0	40	-40	12	4	1	29	23	12	8	1	26	23	1	2	2	147	140
8	4	0	61	53	2	13	0	33	31	13	4	1	44	36	13	8	1	23	15	3	2	2	48	49
10	4	0	25	22	4	13	0	44	42	14	4	1	45	-34	2	9	1	23	-21	5	2	2	38	35
14	4	0	16	-18	6	13	0	18	-14	1	5	1	153	153	4	9	1	38	-35	6	2	2	35	-38
4	5	0	75	-68	8	13	0	20	-26	2	5	1	254	-243	5	9	1	30	-34	7	2	2	106	-90
6	5	0	92	80	0	14	0	41	47	3	5	1	26	-22	8	9	1	16	17	9	2	2	55	-56
8	5	0	27	22	2	14	0	44	42	4	5	1	144	-132	0	10	1	30	-33	11	2	2	32	27
0	6	0	295	301	4	14	0	23	12	5	5	1	151	-137	1	10	1	22	-20	13	2	2	52	45
2	6	0	125	120	6	14	0	25	-26	6	5	1	111	110	4	10	1	22	22	1	3	2	26	26
4	6	0	100	-96	0	16	0	21	-24	8	5	1	118	119	7	10	1	19	16	2	3	2	53	58
6	6	0	36	-35	1	2	1	55	-51	9	5	1	67	60	4	11	1	21	-18	3	3	2	74	71
10	6	0	38	23	2	2	1	69	69	10	5	1	41	-33	0	12	1	57	-62	4	3	2	78	-72
14	6	0	30	-29	3	2	1	100	-97	11	5	1	41	40	1	12	1	34	-33	5	3	2	117	-107
2	7	0	226	-222	4	2	1	94	82	12	5	1	53	-40	3	12	1	29	-33	6	3	2	33	-27
6	7	0	72	79	5	2	1	82	69	13	5	1	39	-28	4	12	1	24	30	9	3	2	56	51
8	7	0	51	61	6	2	1	61	51	0	6	1	367	-371	6	12	1	24	17	11	3	2	46	48
10	7	0	19	-14	7	2	1	131	103	1	6	1	159	-164	1	13	1	32	-34	13	3	2	19	-17
12	7	0	28	-28	8	2	1	56	-50	2	6	1	67	-62	2	13	1	71	72	0	4	2	303	-291
0	8	0	55	-59	9	2	1	27	30	3	6	1	139	-144	3	13	1	44	27	1	4	2	227	-216
2	8	0	89	91	10	2	1	31	-34	4	6	1	197	181	5	13	1	43	39	2	4	2	121	-115
4	8	0	116	118	11	2	1	46	-50	5	6	1	19	16	6	13	1	29	-31	3	4	2	171	-156
6	8	0	57	60	13	2	1	55	-51	6	6	1	110	110	9	13	1	16	-17	4	4	2	32	-25
8	8	0	23	-20	1	3	1	92	-92	7	6	1	74	69	0	14	1	53	55	6	4	2	23	-18
10	8	0	46	-42	2	3	1	41	38	8	6	1	47	-49	3	14	1	28	29	7	4	2	93	80
14	8	0	44	30	3	3	1	65	67	10	6	1	66	-57	4	14	1	36	-36	11	4	2	32	-29
2	9	0	69	71	4	3	1	149	130	11	6	1	18	-15	6	14	1	25	-28	12	4	2	15	-10
4	9	0	102	91	5	3	1	95	84	14	6	1	28	26	7	14	1	20	-20	1	5	2	48	50
6	9	0	42	-47	6	3	1	72	-72	1	7	1	89	-89	1	15	1	25	22	2	5	2	91	87
8	9	0	80	-89	7	3	1	27	25	2	7	1	193	187	2	15	1	30	-30	3	5	2	71	68
10	9	0	22	-24	8	3	1	123	-112	3	7	1	42	41	4	15	1	20	-25	4	5	2	22	-18
12	9	0	38	38	9	3	1	65	-61	4	7	1	129	118	5	15	1	28	-25	7	5	2	45	-39
0	10	0	58	66	10	3	1	16	-9	5	7	1	78	75	0	16	1	37	-42	9	5	2	40	-46

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
10	5	2	21	17
1	6	2	67	-62
4	6	2	28	25
7	6	2	31	33
10	6	2	19	23
11	6	2	25	-15
1	7	2	147	-146
3	7	2	34	34
4	7	2	44	41
5	7	2	109	103
7	7	2	34	-33
9	7	2	41	-41
13	7	2	26	21
0	8	2	54	58
1	8	2	92	89
2	8	2	87	91
3	8	2	125	125
4	8	2	30	33
7	8	2	79	-74
11	8	2	27	30
13	8	2	31	24
1	9	2	23	19
2	9	2	18	-14
3	9	2	22	-21
4	9	2	31	-26
5	9	2	66	-64
7	9	2	32	-28
9	9	2	54	64
11	9	2	32	35
13	9	2	19	-12
0	10	2	72	-75
1	10	2	72	-75
2	10	2	21	-26
3	10	2	110	-111
6	10	2	25	21
7	10	2	85	79
9	10	2	23	26
10	10	2	27	-23
11	10	2	30	-29
1	11	2	69	-70
2	11	2	61	63
3	11	2	68	70
4	11	2	33	29
5	11	2	116	109
6	11	2	28	-27
8	11	2	21	-28
9	11	2	58	-66
11	11	2	22	-26
0	12	2	35	35
1	12	2	78	81
2	12	2	25	-31
3	12	2	68	73
4	12	2	55	-48
7	12	2	63	-63
11	12	2	25	22
1	13	2	64	44
5	13	2	47	-46
9	13	2	23	21
5	14	2	20	-17
1	15	2	30	-34
1	1	3	59	-55
3	1	3	29	36
4	1	3	25	-27
5	1	3	66	82
6	1	3	92	119
0	2	3	79	-85
1	2	3	47	50
3	2	3	86	86
4	2	3	44	42
5	2	3	31	-31
6	2	3	72	64
7	2	3	61	-69
8	2	3	28	-32
12	2	3	31	31
2	3	3	89	-84
3	3	3	25	26
5	3	3	131	-123
6	3	3	114	-99
7	3	3	35	-30
8	3	3	65	-60
9	3	3	71	70
10	3	3	16	21
11	3	3	24	24
12	3	3	35	27
15	3	3	24	-15
0	4	3	84	-76
1	4	3	36	-33
2	4	3	83	82
3	4	3	39	-38
4	4	3	54	-48
5	4	3	26	-24
6	4	3	61	-54
7	4	3	101	97
8	4	3	31	29
9	4	3	54	49
10	4	3	19	16
11	4	3	25	-20
12	4	3	22	-12
13	4	3	47	-34
14	4	3	31	-23
1	5	3	113	-106
2	5	3	98	-98
3	5	3	59	51
4	5	3	22	-16
5	5	3	181	176
6	5	3	48	47
7	5	3	17	-13
8	5	3	35	37
9	5	3	83	-80
10	5	3	38	-38
11	5	3	19	-17
12	5	3	31	-22
0	6	3	107	-114
1	6	3	216	201
3	6	3	152	140
4	6	3	72	67
5	6	3	64	-63
6	6	3	33	32
7	6	3	132	-121
8	6	3	49	-51
10	6	3	42	-40
11	6	3	51	49
13	6	3	40	30
14	6	3	17	14
1	7	3	98	97
2	7	3	76	76
4	7	3	50	48
5	7	3	97	-95
7	7	3	35	-31
9	7	3	49	51
11	7	3	17	27
12	7	3	26	21
13	7	3	16	-15
0	8	3	74	77
1	8	3	80	-71
2	8	3	19	-15
3	8	3	75	-77
5	8	3	24	-20
7	8	3	28	27
9	8	3	22	21
10	8	3	36	35
11	8	3	16	-13
12	8	3	17	15
13	8	3	34	-34
1	9	3	57	-58
2	9	3	66	-64
4	9	3	26	-17
5	9	3	33	27
7	9	3	29	30
8	9	3	20	16
9	9	3	20	-20
11	9	3	15	-17
0	10	3	29	-31
1	10	3	52	56
3	10	3	50	49
4	10	3	37	38
3	11	3	33	-35
5	11	3	25	-17
0	12	3	41	-43
1	12	3	26	24
3	12	3	49	47
4	12	3	22	26
5	12	3	26	-14
10	12	3	21	-17
1	13	3	60	64
2	13	3	46	52
4	13	3	20	12
5	13	3	44	-41
9	13	3	19	24
0	14	3	23	23
1	14	3	42	-37
3	14	3	47	-51
4	14	3	29	-27
7	14	3	27	25
1	15	3	27	-26
5	15	3	34	37
1	16	3	29	34
4	16	3	22	20
1	17	3	34	35
0	0	4	289	-278
1	0	4	284	265
2	0	4	73	76
3	0	4	91	91
4	0	4	183	178
6	0	4	102	99
7	0	4	31	-29
8	0	4	60	-76
10	0	4	55	-57
12	0	4	18	14
14	0	4	21	27
1	1	4	67	69
2	1	4	148	152
4	1	4	57	66
5	1	4	32	-36
6	1	4	109	-137
8	1	4	77	-85
9	1	4	27	40
12	1	4	40	33
0	2	4	164	164
2	2	4	33	38
3	2	4	38	37
4	2	4	97	-90
5	2	4	21	-23
6	2	4	76	-82
7	2	4	20	-19
10	2	4	35	41
13	2	4	25	-23
1	3	4	50	48
2	3	4	71	-72
4	3	4	80	-79
5	3	4	20	26
7	3	4	42	40
8	3	4	75	73
10	3	4	24	-23
12	3	4	50	-37
0	4	4	129	-133
1	5	4	30	25
2	5	4	88	91
4	5	4	25	27
5	5	4	64	-61
6	5	4	38	-35
8	5	4	15	11
10	5	4	42	37
0	6	4	57	-56
4	6	4	63	65
7	6	4	20	14
8	6	4	17	-11
1	7	4	21	24
2	7	4	106	109
3	7	4	40	-42
4	7	4	25	21
5	7	4	37	-31
6	7	4	56	-55
8	7	4	30	-28
10	7	4	25	26
12	7	4	18	10
0	8	4	113	118
1	8	4	19	-20
2	8	4	54	55
3	8	4	36	37

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
4	8	4	54	-54
5	8	4	25	18
6	8	4	50	-45
8	0	4	24	29
10	8	4	27	23
2	9	4	63	-63
3	9	4	26	-30
4	9	4	54	-55
5	9	4	19	15
6	9	4	37	39
7	9	4	24	22
8	9	4	34	30
10	9	4	23	-20
11	9	4	16	-19
12	9	4	39	-32
0	10	4	55	-64
1	10	4	30	26
4	10	4	31	34
6	10	4	50	48
7	10	4	31	-28
8	10	4	32	-34
10	10	4	51	-52
1	11	4	46	45
2	11	4	83	89
3	11	4	21	-19
4	11	4	45	44
5	11	4	35	-35
6	11	4	60	-60
8	11	4	38	-42
9	11	4	32	34
10	11	4	25	25
0	12	4	78	84
1	12	4	33	-37
3	12	4	50	-45
4	12	4	87	-87
6	12	4	39	-36
7	12	4	27	30
8	12	4	37	44
10	12	4	37	35
2	13	4	55	-50
4	13	4	27	-30
6	13	4	24	19
8	13	4	40	45
0	14	4	26	-26
4	14	4	22	25
6	14	4	29	34
2	15	4	24	27
6	15	4	18	-11
0	16	4	43	37
1	1	5	115	-120
2	1	5	136	145
5	1	5	42	46
6	1	5	68	-68
7	1	5	43	44
10	1	5	29	30
11	1	5	17	12
0	2	5	238	233
3	2	5	111	113
4	2	5	122	-115
5	2	5	22	-26
6	2	5	32	-33
7	2	5	52	-63
8	2	5	37	50
10	2	5	47	58
14	2	5	18	-14
1	3	5	121	120
2	3	5	25	27
3	3	5	25	26
4	3	5	20	-21
5	3	5	69	-67
7	3	5	39	-35
8	3	5	43	48
12	3	5	38	-36
0	4	5	170	-165
1	4	5	19	13
2	4	5	24	16
3	4	5	37	-38
4	4	5	47	44
5	4	5	19	-17
6	4	5	54	54
7	4	5	78	73
8	4	5	19	-23
10	4	5	56	-50
11	4	5	25	-29
12	4	5	16	-19
14	4	5	22	25
1	5	5	70	-68
2	5	5	161	151
3	5	5	27	30
4	5	5	50	51
5	5	5	66	63
6	5	5	106	-101
7	5	5	20	-16
8	5	5	89	-90
9	5	5	18	-15
10	5	5	35	23
12	5	5	57	41
0	6	5	195	196
2	6	5	17	11
3	6	5	57	59
4	6	5	158	-149
6	6	5	71	-67
7	6	5	41	-41
8	6	5	42	46
10	6	5	33	27
11	6	5	15	12
14	6	5	34	-29
2	7	5	132	-126
3	7	5	37	-37
4	7	5	72	-72
5	7	5	25	-24
6	7	5	69	72
8	7	5	66	68
9	7	5	29	33
10	7	5	20	-18
11	7	5	26	25
12	7	5	28	-26
0	8	5	40	-40
1	8	5	33	-36
3	8	5	87	-83
6	8	5	71	69
10	8	5	35	-31
1	9	5	48	-46
2	9	5	56	61
3	9	5	38	40
4	9	5	73	75
5	9	5	34	31
6	9	5	25	-27
8	9	5	20	-25
12	9	5	26	21
0	10	5	91	102
1	10	5	30	34
3	10	5	32	39
4	10	5	57	-54
8	10	5	36	41
0	12	5	46	49
3	12	5	22	35
4	12	5	39	-41
6	12	5	26	-22
2	13	5	74	-80
4	13	5	35	-34
5	13	5	26	-21
6	13	5	35	41
8	13	5	17	15
0	14	5	44	-51
1	14	5	22	-21
2	14	5	25	-15
3	14	5	34	-37
4	14	5	36	36
1	15	5	20	-17
2	15	5	30	30
3	15	5	23	19
4	15	5	30	31
5	15	5	25	24
0	16	5	38	46
2	16	5	24	17
4	16	5	28	-29
0	0	6	183	180
1	0	6	190	183
2	0	6	33	-34
3	0	6	225	217
4	0	6	133	-121
7	0	6	101	-104
8	0	6	44	49
9	0	6	34	-39
14	0	6	21	-25
1	1	6	143	136
2	1	6	45	-44
3	1	6	85	-80
4	1	6	129	-123
5	1	6	70	-79
8	1	6	28	33
9	1	6	46	52
10	1	6	20	-30
11	1	6	21	31
12	1	6	21	-18
13	1	6	19	-26
0	2	6	86	-86
1	2	6	92	-91
2	2	6	20	20
3	2	6	150	-151
5	2	6	21	-22
6	2	6	36	38
7	2	6	86	89
9	2	6	32	51
10	2	6	21	-24
11	2	6	19	-27
13	2	6	23	-28
1	3	6	151	-149
3	3	6	51	47
4	3	6	25	12
5	3	6	138	143
6	3	6	48	-49
7	3	6	37	34
8	3	6	22	-29
9	3	6	33	-32
11	3	6	31	-35
15	3	6	22	15
0	4	6	118	117
1	4	6	63	63
3	4	6	56	51
4	4	6	52	-47
5	4	6	40	-36
7	4	6	73	-73
10	4	6	24	19
11	4	6	38	43
1	5	6	75	74
3	5	6	19	-14
4	5	6	54	47
5	5	6	76	-75
6	5	6	63	62
8	5	6	22	25
9	5	6	25	29
0	6	6	33	29
1	6	6	27	27
3	6	6	28	24
6	6	6	21	-14
8	6	6	26	24
9	6	6	21	-22
1	7	6	102	102
2	7	6	68	-76
3	7	6	67	-60
5	7	6	86	-82
6	7	6	52	47
10	7	6	29	-25
0	8	6	75	-75
1	8	6	83	-79
3	8	6	84	-74
4	8	6	50	48
5	8	6	33	34
6	8	6	20	14
7	8	6	74	66
10	8	6	19	-20
11	8	6	34	-32
13	8	6	22	-13
1	9	6	92	-95
5	9	6	84	81
7	9	6	36	34
8	9	6	39	-41
9	9	6	41	-41

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
11	9	6	38	-35	1	3	7	164	-154	11	7	7	27	-26	14	0	8	34	-25	3	6	8	55	-50
12	9	6	19	13	3	3	7	25	19	0	8	7	26	-27	1	1	8	135	-130	4	6	8	22	-20
0	10	6	43	45	4	3	7	33	28	1	8	7	37	34	2	1	8	257	-261	7	6	8	23	21
1	10	6	40	39	5	3	7	102	111	3	8	7	71	62	3	1	8	30	34	1	7	8	69	-70
2	10	6	22	-17	6	3	7	24	20	4	8	7	67	64	4	1	8	117	-112	2	7	8	68	-72
3	10	6	90	79	7	3	7	36	42	5	8	7	30	29	5	1	8	119	123	3	7	8	45	44
6	10	6	25	-22	9	3	7	61	-67	6	8	7	35	32	6	1	8	76	75	5	7	8	84	79
7	10	6	66	-63	11	3	7	40	-49	7	8	7	56	-51	8	1	8	73	84	6	7	8	66	52
11	10	6	30	27	13	3	7	18	16	9	8	7	32	-33	9	1	8	55	-72	8	7	8	30	29
1	11	6	76	77	0	4	7	44	-41	10	8	7	28	-27	12	1	8	47	-47	9	7	8	41	-45
2	11	6	47	-49	1	4	7	96	91	13	8	7	29	26	0	2	8	122	-124	10	7	8	17	-14
3	11	6	42	-37	2	4	7	71	-67	1	9	7	31	35	1	2	8	82	80	12	7	8	24	-21
5	11	6	66	-67	3	4	7	118	118	2	9	7	56	55	2	2	8	44	-44	0	8	8	83	-86
6	11	6	36	40	4	4	7	27	25	3	9	7	29	-22	3	2	8	68	68	1	8	8	71	71
8	11	6	20	20	6	4	7	29	24	4	9	7	22	21	4	2	8	81	79	2	8	8	41	-40
9	11	6	46	56	7	4	7	84	-84	5	9	7	42	-43	5	2	8	32	38	3	8	8	83	83
11	11	6	20	18	8	4	7	18	-16	9	9	7	31	33	6	2	8	98	91	4	8	8	60	60
0	12	6	49	-51	9	4	7	39	-43	11	9	7	20	17	7	2	8	38	-48	6	8	8	25	29
1	12	6	51	-52	11	4	7	33	32	1	10	7	29	-33	8	2	8	19	-29	7	8	8	58	-53
3	12	6	83	-84	13	4	7	36	36	3	10	7	43	-39	9	2	8	18	-23	8	8	8	26	-25
4	12	6	26	30	1	5	7	177	171	5	10	7	30	26	10	2	8	46	-54	10	8	8	39	-40
7	12	6	52	52	2	5	7	39	45	7	10	7	33	32	13	2	8	22	25	11	8	8	19	9
1	13	6	32	-30	3	5	7	68	-62	1	12	7	41	-43	14	2	8	21	21	1	9	8	38	28
3	13	6	28	21	5	5	7	153	-154	3	12	7	50	-60	1	3	8	23	27	2	9	8	48	49
4	13	6	22	12	7	5	7	26	-25	7	12	7	38	36	2	3	8	56	62	5	9	8	44	-39
5	13	6	49	50	8	5	7	33	-31	1	13	7	47	-47	4	3	8	18	-18	6	9	8	42	-43
9	13	6	22	-24	9	5	7	59	61	2	13	7	23	-18	5	3	8	58	-60	7	9	8	30	-26
1	14	6	24	19	11	5	7	41	28	3	13	7	39	46	6	3	8	60	-56	8	9	8	37	-40
3	14	6	29	32	13	5	7	26	-28	4	13	7	21	-18	7	3	8	40	-39	12	9	8	37	33
7	14	6	19	-21	0	6	7	23	20	5	13	7	46	48	8	3	8	38	-39	0	10	8	78	83
1	15	6	19	14	1	6	7	207	-197	1	14	7	30	34	9	3	8	19	27	1	10	8	26	-22
5	15	6	32	-23	2	6	7	30	33	3	14	7	34	40	11	3	8	20	19	2	10	8	21	15
1	1	7	220	208	3	6	7	196	-184	4	14	7	25	22	12	3	8	24	36	3	10	8	27	-29
2	1	7	47	-52	4	6	7	60	-57	7	14	7	30	-32	0	4	8	74	73	4	10	8	59	-59
3	1	7	111	-101	6	6	7	43	-41	1	15	7	20	30	1	4	8	98	-97	7	10	8	32	36
5	1	7	120	-121	7	6	7	114	106	2	15	7	31	31	2	4	8	57	55	8	10	8	19	21
7	1	7	26	33	9	6	7	20	13	5	15	7	33	-32	3	4	8	63	-60	9	10	8	17	19
8	1	7	21	21	10	6	7	19	19	1	16	7	23	-23	4	4	8	34	-32	10	10	8	45	45
9	1	7	47	55	11	6	7	48	-41	0	0	8	176	177	5	4	8	42	36	1	11	8	50	-50
0	2	7	67	-65	13	6	7	25	-22	1	0	8	125	-122	6	4	8	28	-25	2	11	8	82	-86
1	2	7	90	-88	1	7	7	75	-70	3	0	8	113	-110	7	4	8	45	42	4	11	8	46	-42
2	2	7	57	62	2	7	7	108	-104	4	0	8	198	-192	8	4	8	30	34	5	11	8	37	39
3	2	7	78	-77	3	7	7	38	34	6	0	8	109	-103	10	4	8	31	33	8	11	8	27	32
4	2	7	65	58	4	7	7	23	-27	7	0	8	78	83	3	5	8	20	24	0	12	8	54	-60
5	2	7	37	48	5	7	7	87	91	8	0	8	30	37	4	5	8	45	40	1	12	8	38	40
7	2	7	105	108	7	7	7	35	22	10	0	8	46	47	10	5	8	20	-16	4	12	8	72	58
10	2	7	17	14	8	7	7	21	19	11	0	8	21	-35	0	6	8	45	46	5	12	8	23	-21
11	2	7	26	-25	9	7	7	30	-29	13	0	8	21	-26	1	6	8	39	-38	7	12	8	30	-27

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
1	13	8	24	22
2	13	8	48	54
4	13	8	34	38
8	13	8	20	-26
2	14	8	21	19
5	14	8	23	-16
1	16	8	21	12
1	1	9	29	-30
2	1	9	98	-100
3	1	9	44	44
5	1	9	55	49
6	1	9	65	58
8	1	9	18	21
11	1	9	18	13
0	2	9	259	-245
1	2	9	59	55
2	2	9	40	-43
3	2	9	71	70
4	2	9	136	123
6	2	9	53	59
8	2	9	24	-36
10	2	9	24	-36
14	2	9	22	16
1	3	9	70	-70
2	3	9	115	110
4	3	9	60	58
6	3	9	45	-48
7	3	9	28	-23
8	3	9	54	-62
9	3	9	27	-29
12	3	9	44	55
0	4	9	162	160
2	4	9	48	51
3	4	9	44	46
4	4	9	88	-88
5	4	9	29	-30
6	4	9	106	-106
7	4	9	29	-26
8	4	9	29	34
10	4	9	66	67
11	4	9	23	28
14	4	9	31	-33
1	5	9	26	27
2	5	9	210	-220
4	5	9	65	-66
6	5	9	98	98
8	5	9	72	82
10	5	9	20	-13
12	5	9	46	-43
0	6	9	133	-144
2	6	9	26	-29
3	6	9	27	-26
4	6	9	141	134
5	6	9	24	-25
6	6	9	79	80
8	6	9	52	-65
10	6	9	52	-54
2	7	9	99	105
3	7	9	46	49
4	7	9	63	63
5	7	9	29	33
6	7	9	55	-52
8	7	9	60	-68
12	7	9	33	29
0	8	9	27	30
3	8	9	40	39
4	8	9	31	-26
6	8	9	51	-52
10	8	9	36	33
3	9	9	27	-23
4	9	9	34	-31
6	9	9	22	19
8	9	9	22	21
0	10	9	45	-43
1	10	9	39	28
4	10	9	26	21
4	11	9	23	-16
0	12	9	45	-39
4	12	9	32	35
2	13	9	50	56
4	13	9	26	18
6	13	9	41	-41
0	14	9	37	37
4	14	9	28	-31
6	14	9	30	-30
1	15	9	23	11
2	15	9	24	-25
4	15	9	24	-18
0	0	10	149	-140
1	0	10	108	-100
3	0	10	170	-164
4	0	10	129	115
5	0	10	25	28
6	0	10	66	66
7	0	10	149	139
8	0	10	88	-102
9	0	10	28	36
10	0	10	56	-64
11	0	10	46	-50
13	0	10	28	-34
1	1	10	175	-173
2	1	10	32	31
3	1	10	79	84
4	1	10	31	36
5	1	10	105	103
6	1	10	74	-73
8	1	10	52	-52
9	1	10	40	-52
10	1	10	25	17
11	1	10	33	-37
12	1	10	24	26
1	2	10	42	40
2	2	10	23	21
3	2	10	104	107
4	2	10	34	-34
6	2	10	60	-64
7	2	10	87	-83
10	2	10	29	37
11	2	10	31	34
1	3	10	22	31
2	3	10	75	-70
3	3	10	31	-32
4	3	10	61	-62
5	3	10	61	-63
7	3	10	22	-18
8	3	10	37	42
9	3	10	27	28
11	3	10	18	27
12	3	10	18	-18
14	3	10	15	-7
0	4	10	98	-101
3	4	10	41	-36
4	4	10	51	48
6	4	10	27	28
2	5	10	105	106
4	5	10	22	21
6	5	10	32	-25
0	6	10	28	25
1	6	10	37	-32
4	6	10	44	43
5	6	10	33	35
7	6	10	31	27
8	6	10	31	-40
10	6	10	17	-18
1	7	10	24	-27
2	7	10	86	85
3	7	10	32	27
4	7	10	50	41
5	7	10	53	53
6	7	10	41	-43
8	7	10	20	-22
9	7	10	20	-19
10	7	10	23	21
11	7	10	18	-14
0	8	10	45	49
1	8	10	29	30
3	8	10	53	41
4	8	10	48	-45
6	8	10	46	-41
7	8	10	43	-46
10	8	10	20	13
1	9	10	53	51
2	9	10	55	-52
3	9	10	37	-33
4	9	10	57	-54
5	9	10	63	-60
8	9	10	32	34
9	9	10	29	33
11	9	10	17	19
0	10	10	71	-69
1	10	10	21	-28
2	10	10	25	-29
3	10	10	85	-77
6	10	10	38	41
7	10	10	49	50
10	10	10	19	-17
1	11	10	61	-65
2	11	10	66	69
3	11	10	27	25
5	11	10	51	50
6	11	10	41	-43
8	11	10	20	-28
9	11	10	31	-35
0	12	10	81	91
1	12	10	28	30
3	12	10	58	55
4	12	10	49	-47
6	12	10	21	-25
7	12	10	29	-29
1	13	10	29	27
5	13	10	20	-26
3	14	10	27	-15
1	1	11	54	-47
2	1	11	54	56
3	1	11	45	42
5	1	11	42	45
6	1	11	30	-36
2	2	11	39	-35
3	2	11	121	112
7	2	11	56	-55
1	3	11	97	92
2	3	11	38	37
3	3	11	34	-32
5	3	11	98	-105
6	3	11	33	-33
7	3	11	33	-37
9	3	11	28	32
10	3	11	22	23
11	3	11	24	24
0	4	11	42	46
1	4	11	66	-66
2	4	11	30	25
3	4	11	140	-136
7	4	11	96	103
8	4	11	20	18
9	4	11	29	38
11	4	11	32	-37
13	4	11	22	-25
1	5	11	134	-137
3	5	11	60	58
5	5	11	132	136
9	5	11	64	-69
11	5	11	35	-42
13	5	11	18	19
0	6	11	42	40
1	6	11	100	99
3	6	11	143	139
5	6	11	28	-27
7	6	11	115	-112
9	6	11	22	-21
11	6	11	42	43
1	7	11	102	103
2	7	11	26	23
3	7	11	43	-39
5	7	11	81	-79
9	7	11	55	58
11	7	11	39	41
1	8	11	26	-24
3	8	11	58	-57
4	8	11	54	-48

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
7	8	11	54	48
9	8	11	19	22
11	8	11	16	-18
1	9	11	35	-32
5	9	11	19	21
7	9	11	24	21
8	9	11	16	-15
0	10	11	27	31
4	10	11	32	-31
3	12	11	33	31
6	12	11	20	11
1	13	11	40	42
3	13	11	21	-15
5	13	11	31	-34
1	14	11	24	-21
3	14	11	30	-30
1	15	11	31	-27
0	0	12	92	-95
1	0	12	91	93
2	0	12	58	-63
3	0	12	167	152
4	0	12	124	117
5	0	12	27	-26
6	0	12	99	101
7	0	12	106	-100
10	0	12	42	-49
11	0	12	26	25
13	0	12	19	17
1	1	12	89	91
2	1	12	82	88
3	1	12	78	-82
4	1	12	26	29
5	1	12	125	-119
6	1	12	103	-98
8	1	12	54	-63
9	1	12	66	64
11	1	12	31	40
12	1	12	25	27
0	2	12	79	74
1	2	12	26	-26
2	2	12	54	56
3	2	12	42	-41
4	2	12	86	-82
5	2	12	32	-37
6	2	12	61	-66
7	2	12	40	53
8	2	12	23	28
9	2	12	28	33

H	K	L	FO	FC
10	2	12	32	37
13	2	12	20	-21
1	3	12	45	-40
2	3	12	95	-98
4	3	12	50	-50
8	3	12	18	22
11	3	12	22	-26
1	4	12	62	57
3	4	12	54	54
7	4	12	40	-39
1	5	12	55	50
2	5	12	25	30
4	5	12	27	21
6	5	12	40	43
1	6	12	21	11
6	6	12	33	31
1	7	12	29	40
2	7	12	35	36
3	7	12	25	-34
4	7	12	30	32
5	7	12	38	-32
9	7	12	28	27
0	8	12	37	36
1	8	12	34	-31
2	8	12	33	33
3	8	12	57	-51
4	8	12	41	-33
6	8	12	20	-21
7	8	12	33	33
10	8	12	17	18
11	8	12	16	-13
1	9	12	32	-32
2	9	12	72	-74
4	9	12	53	-52
6	9	12	24	19
7	9	12	32	30
8	9	12	17	20
0	10	12	61	-64
1	10	12	51	44
3	10	12	65	61
4	10	12	47	46
6	10	12	20	21
7	10	12	45	-45
8	10	12	20	-21
9	10	12	16	-20
1	11	12	88	87
2	11	12	55	53
3	11	12	34	-37

H	K	L	FO	FC
4	11	12	33	20
5	11	12	71	-72
6	11	12	21	-21
0	12	12	32	35
1	12	12	49	-48
3	12	12	58	-56
4	12	12	27	-30
6	12	12	22	-21
7	12	12	42	45
1	13	12	37	-35
2	13	12	24	-26
5	13	12	34	33
4	14	12	24	22
2	1	13	64	67
3	1	13	34	-31
6	1	13	26	-29
0	2	13	78	82
4	2	13	51	-52
6	2	13	32	-37
7	2	13	21	-25
10	2	13	26	30
2	3	13	132	-136
4	3	13	63	-62
5	3	13	29	-24
6	3	13	33	32
8	3	13	41	46
11	3	13	22	-26
12	3	13	34	-31
0	4	13	118	-119
2	4	13	41	-46
4	4	13	109	103
5	4	13	37	36
6	4	13	65	64
10	4	13	43	-45
1	5	13	54	51
2	5	13	147	145
3	5	13	28	-27
4	5	13	53	46
5	5	13	29	-30
6	5	13	43	-43
8	5	13	52	-56
12	5	13	40	39
0	6	13	136	139
1	6	13	51	-49
2	6	13	49	50
3	6	13	49	-45
4	6	13	100	-95
5	6	13	20	18

H	K	L	FO	FC
6	6	13	65	-65
7	6	13	47	43
8	6	13	32	33
10	6	13	50	49
2	7	13	88	-90
4	7	13	27	-33
5	7	13	29	28
6	7	13	64	61
7	7	13	23	21
8	7	13	39	42
0	8	13	58	-60
2	8	13	33	-35
4	8	13	33	35
6	8	13	48	51
7	8	13	24	-25
8	8	13	18	-18
10	8	13	40	-40
1	9	13	21	-22
2	9	13	19	22
6	9	13	35	-32
8	9	13	25	-29
4	10	13	25	-24
7	11	13	18	-14
0	12	13	28	32
7	12	13	18	18
2	13	13	26	-29
0	14	13	37	-40
0	0	14	193	189
2	0	14	38	39
4	0	14	98	-90
6	0	14	52	-56
8	0	14	57	58
10	0	14	61	62
11	0	14.	21	23
1	1	14	56	57
2	1	14	134	-128
3	1	14	22	-23
4	1	14	55	-55
5	1	14	27	-31
6	1	14	32	33
7	1	14	18	-19
8	1	14	30	35
12	1	14	29	-35
0	2	14	47	-46
1	2	14	33	-37
2	2	14	31	-26
3	2	14	53	-52
4	2	14	41	42

H	K	L	FO	FC
6	2	14	46	52
7	2	14	35	32
10	2	14	43	-40
11	2	14	21	-25
1	3	14	27	-38
2	3	14	49	52
5	3	14	35	35
6	3	14	25	-24
7	3	14	23	-25
8	3	14	41	-50
11	3	14	17	-8
12	3	14	22	22
0	4	14	41	43
3	4	14	24	35
4	4	14	65	-63
6	4	14	43	-44
7	4	14	18	-17
9	4	14	20	-22
1	5	14	26	-25
2	5	14	45	-42
6	5	14	43	48
2	7	14	52	-58
6	7	14	34	35
8	7	14	18	21
0	8	14	38	-36
1	8	14	26	-22
3	8	14	31	-32
4	8	14	55	45
6	8	14	38	39
7	8	14	19	14
10	8	14	24	-21
1	9	14	24	-21
2	9	14	52	53
3	9	14	28	33
4	9	14	24	26
5	9	14	30	26
6	9	14	26	-34
8	9	14	35	-37
9	9	14	24	-25
0	10	14	76	79
1	10	14	24	22
2	10	14	31	33
3	10	14	40	39
4	10	14	53	-48
6	10	14	54	-52
7	10	14	19	-20
2	11	14	84	-87
4	11	14	44	-38

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
5	11	14	26	-22
6	11	14	41	40
0	12	14	77	-80
2	12	14	29	-30
4	12	14	44	44
6	12	14	27	26
1	13	14	25	-28
2	13	14	28	25
4	13	14	21	24
2	1	15	27	-32
3	1	15	33	-29
4	1	15	23	-24
9	1	15	21	20
0	2	15	55	-54
1	2	15	41	-41
2	2	15	25	-25
3	2	15	70	-75
4	2	15	33	33
6	2	15	26	27
8	2	15	21	-24
1	3	15	44	-44
2	3	15	22	20
3	3	15	43	44
4	3	15	52	54
5	3	15	34	29
9	3	15	32	-31
11	3	15	29	-25
0	4	15	35	37
1	4	15	60	57
2	4	15	34	34
3	4	15	66	71
6	4	15	43	-49
7	4	15	37	-36
9	4	15	21	-22
11	4	15	34	31
1	5	15	89	87
2	5	15	59	-61
3	5	15	34	-35
5	5	15	68	-69
6	5	15	36	35
8	5	15	21	18
9	5	15	22	24
11	5	15	24	24
0	6	15	51	-53
1	6	15	40	-37
3	6	15	64	-62
4	6	15	37	39
5	6	15	28	27
6	6	15	29	32
7	6	15	59	60
1	7	15	65	-66
2	7	15	25	23
3	7	15	28	27
5	7	15	69	69
6	7	15	21	-23
7	7	15	19	20
8	7	15	24	-20
9	7	15	28	-31
0	8	15	24	-19
3	8	15	49	45
5	8	15	22	-21
7	8	15	55	-55
1	9	15	30	23
5	9	15	39	-40
3	10	15	31	-23
7	10	15	24	18
5	12	15	30	17
1	13	15	24	-20
2	13	15	26	18
1	0	16	35	-33
2	0	16	34	40
3	0	16	104	-93
4	0	16	40	44
7	0	16	92	94
10	0	16	19	22
11	0	16	23	-27
1	1	16	39	-39
3	1	16	51	51
5	1	16	85	84
9	1	16	50	-53
0	2	16	45	-50
1	2	16	25	19
3	2	16	57	59
4	2	16	46	49
7	2	16	60	-58
8	2	16	20	-13
9	2	16	19	-18
1	3	16	49	50
2	3	16	37	39
5	3	16	39	-41
6	3	16	33	-30
8	3	16	26	-29
10	3	16	16	11
0	4	16	33	-31
1	4	16	39	-37
2	4	16	29	-24
3	4	16	33	-36
4	4	16	39	-40
6	4	16	21	-14
1	5	16	55	-52
8	5	16	17	13
3	6	16	21	-17
7	6	16	29	27
5	7	16	45	43
9	7	16	21	-24
2	8	16	20	16
3	8	16	46	45
4	8	16	30	30
7	8	16	36	-32
1	9	16	55	54
2	9	16	30	32
5	9	16	35	-34
6	9	16	35	-36
0	10	16	20	19
1	10	16	27	-29
3	10	16	47	-47
4	10	16	28	-30
7	10	16	30	30
1	11	16	51	-51
3	11	16	25	24
5	11	16	30	35
1	12	16	33	32
2	12	16	20	-14
3	12	16	37	38
1	1	17	50	-51
2	1	17	38	-40
4	1	17	39	-36
5	1	17	27	27
0	2	17	55	-56
4	2	17	50	51
6	2	17	34	28
7	2	17	20	-15
10	2	17	25	-29
1	3	17	44	35
2	3	17	82	82
4	3	17	63	54
6	3	17	41	-38
8	3	17	30	-31
0	4	17	54	58
2	4	17	32	30
4	4	17	70	-67
6	4	17	39	-38
8	4	17	22	26
10	4	17	43	35
1	5	17	21	-17
2	5	17	62	-62
4	5	17	26	-26
5	5	17	26	30
6	5	17	37	37
8	5	17	28	35
0	6	17	50	-53
1	6	17	25	27
2	6	17	26	-24
4	6	17	51	45
5	6	17	24	-18
6	6	17	29	34
7	6	17	31	-34
2	7	17	32	33
6	7	17	33	-35
8	7	17	25	-27
0	8	17	44	50
4	8	17	28	-34
6	8	17	30	-22
2	9	17	34	-34
6	9	17	21	18
0	0	18	27	-26
4	0	18	99	87
6	0	18	32	36
8	0	18	20	-27
10	0	18	33	-38
2	1	18	72	68
4	1	18	32	28
5	1	18	45	38
6	1	18	57	-51
8	1	18	33	-44
0	2	18	53	56
1	2	18	32	33
2	2	18	23	22
4	2	18	65	-53
5	2	18	21	-11
6	2	18	40	-44
7	2	18	28	-25
8	2	18	22	18
10	2	18	38	38
1	3	18	38	38
2	3	18	65	-66
4	3	18	28	-31
5	3	18	24	-23
6	3	18	28	24
8	3	18	22	24
0	4	18	74	-78
2	4	18	46	-47
2	5	18	20	19
2	7	18	48	48
4	7	18	25	16
6	7	18	24	-25
0	8	18	71	76
2	8	18	28	34
4	8	18	31	-37
6	8	18	25	-25
1	9	18	40	38
2	9	18	50	-53
4	9	18	41	-35
5	9	18	24	-20
6	9	18	22	22
0	10	18	57	-59
2	10	18	30	-26
4	10	18	36	33
2	11	18	38	41
1	1	19	26	-27
2	1	19	42	40
4	1	19	21	9
0	2	19	50	50
1	2	19	33	30
4	2	19	45	-39
1	3	19	64	62
2	3	19	25	-29
4	3	19	24	-21
5	3	19	53	-52
0	4	19	35	-33
1	4	19	56	-56
4	4	19	26	16
5	4	19	22	15
7	4	19	42	40
1	5	19	54	-49
2	5	19	48	49
4	5	19	21	18
5	5	19	72	64
6	5	19	23	-22
0	6	19	33	33
1	6	19	32	31
4	6	19	34	-31
7	6	19	41	-41
1	7	19	51	44
2	7	19	23	-25
5	7	19	48	-46
1	9	19	26	-26
1	0	20	62	54
2	0	20	21	20
7	0	20	50	-51

STRUCTURE FACTORS IN (XXII) (CONT'D.)

H	K	L	FO	FC
1	1	20	78	74
4	1	20	25	16
5	1	20	67	-60
1	2	20	41	-41
4	2	20	25	-21
7	2	20	41	41
1	3	20	42	-37
5	3	20	48	50
2	4	20	24	-21
2	5	20	23	-23
1	7	20	23	20
5	7	20	32	-31
1	8	20	30	-31
1	9	20	40	-39
5	1	21	24	-23
0	2	21	27	27
1	2	21	25	-17
4	2	21	36	-28
6	2	21	23	-20
1	3	21	25	-25
2	3	21	53	-50
5	3	21	33	31
6	3	21	31	32
0	4	21	61	-61
4	4	21	50	49
1	5	21	47	43
2	5	21	42	45
5	5	21	37	-37
0	6	21	27	34
1	6	21	30	-33
4	6	21	32	-28
1	7	21	32	-26
2	7	21	33	-33
0	8	21	29	-30
0	0	22	60	58
4	0	22	47	-46
2	1	22	62	-58
4	1	22	37	-32
0	2	22	53	-50
4	2	22	41	40
2	3	22	31	31
1	3	23	31	-20

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