SYNTHESIS AND STRUCTURE OF NEW ORGANOMOLYBDENUM COMPLEXES CONTAINING PYRAZOLE-DERIVED LIGANDS

A THESIS

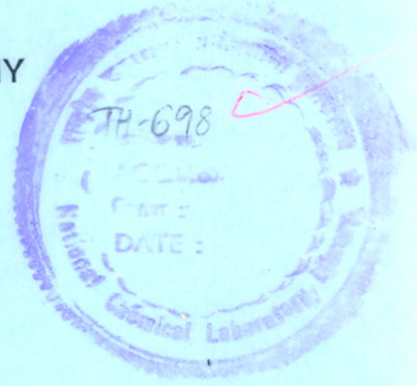
SUBMITTED TO THE

UNIVERSITY OF POONA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY



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PUNE - 411 008

December 1993

ACKNOWLEDGEMENTS

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I am thankful to the scientific and supporting staff of the Division and my numerous friends for their wholehearted help in many ways. I share my heartfelt thanks for the encouragement and support given by my husband during the course my work.

Finally, I am thankful to the Director, National Chemical Laboratory, Pune, for permitting me to submit this work in the form of thesis.

V. S. Joshi

Dedicated to

Him

CERTIFICATE

*This is to certify that the work incorporated in the thesis entitled "**Synthesis and Structure of New Organomolybdenum Complexes Containing Pyrazole-derived Ligands**" submitted by **Mrs. Vijaya S. Joshi** was carried out by her under my supervision at the National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.*

Date: 20 Dec. '93

National Chemical Laboratory,
Pune 411 008.

(Dr. A. Sarkar)
Research Guide

GENERAL REMARKS

1. IR spectra for all organic compounds and metal complexes were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 599-B as nujol mulls, chloroform solutions or neat liquid samples. The absorption values were expressed in frequency (cm^{-1}).
2. ^{1}H NMR spectra of all compounds were recorded on a varian FT - 80 (Varian 80 MHz FT NMR Spectrometer), Bruker WH - 90 (Bruker 90 MHz FT NMR Spectrometer), Bruker AC - 200 (Bruker 200 MHz FT NMR Spectrometer) and Varian T - 60 instruments. Variable temperature NMR spectra were recorded on Bruker WH - 90, AC - 200 and MSL - 300 spectrometers. Chemical shifts were recorded in parts per million (δ) using tetramethylsilane/chloroform signal as internal standard. The abbreviations s, d, t, q and m refer to singlet, doublet, triplet, quartet and multiplet respectively. Coupling constants (J), wherever mentioned, have been given in Hz.
3. ^{13}C NMR spectra were recorded on Bruker MSL - 300 and Bruker AC - 200 instrument operating at 75.5 MHz and 50 MHz respectively. For the solid state NMR, chemical shifts were reported in ppm with reference to methylene carbon resonence of adamantane at 37.8 ppm (External standard).
4. ^{31}P NMR spectra were recorded on a Bruker MSL - 300 instrument operating at 121.6 MHz. Chemical shifts were reported in ppm with reference to 85% H_3PO_4 as external standard.
5. ^{95}Mo NMR spectra were recorded on a Bruker MSL - 300 instrument operating at 19.554 MHz. Chemical shifts were reported in ppm with reference to 2M Na_2MoO_4 as external standard.
6. X-Ray crystal diffraction data were obtained from Enraf Nonius CAD-4 diffractometer.
7. All melting points (recorded on Thermonik Campbell melting point apparatus) and boiling points (bath temperature) were recorded on Celsius scale and are uncorrected.
8. Mass spectra were recorded on Finning MAT-1020 instrument using direct inlet system.

9. Elemental analysis were performed by Perkin-Elmer, Bio-nics, Leco Corp (USA) and CSMCRI (India) with their instruments. In NCL some of the complexes were analysed using a Carlo-Erba CHNS analyser Model EA-1108.

10. Chromatography: Thin layer chromatography (TLC) were performed on 6*2 cm glass plates coated with commercial grade silica gel G and visualisations of the spots on the plates was achieved by exposure to iodine vapour or under UV light. Column chromatography was performed using SD's commercial grade silica gel (60 - 120 mesh) activated at 130°C for 5h. Flash chromatography was done with IOLAR nitrogen using flash silica gel (230 - 400 mesh).

11. Inert gases: Iolar grade argon and nitrogen cylinders were used for inert gas atmosphere.

12. ***Representative spectra of compounds have been appended at the end of each chapter.***

CHEMICALS : 3,5-Dimethylpyrazole was prepared by a known route and was used without further purification. $Mo[CO]_6$, $POCl_3$ and 2-methylallyl chloride were purchased from *Fluka* and were used as such. Allyl chloride and allyl bromide (BDH) were distilled prior to use. 2-Phenyl-3-bromo-1-propene, crotyl chloride and cinnamyl chloride were prepared by known routes and freshly distilled before use.

SOLVENTS : Acetonitrile was dried over P_2O_5 and freshly distilled prior to the reaction. Other solvents were dried by usual drying techniques and degassed with argon.

EQUIPMENTS : The glassware used for the reaction was cooled with argon after heating at 120°C for 24 hrs. The reaction flask was maintained under argon atmosphere with evacuation and purging technique, using balloon, during the course of reaction. After removal of solvent under low pressure, vacuum was released with argon balloon.

ISOLATION OF COMPLEXES : Work up and isolation of products could be carried out in air without any problem. The products in pure form, were air stable crystalline solids which could be stored in the refrigerator for months.

CRYSTALLIZATIONS : All complexes could be recrystallized from mixed solvent systems.

SYNOPSIS OF THE THESIS

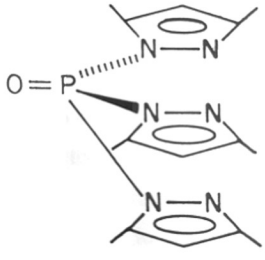
SYNTHESIS AND STRUCTURE OF NEW ORGANOMOLYBDENUM COMPLEXES CONTAINING PYRAZOLE-DERIVED CHELATING LIGANDS

Chapter - I *Review of Pyrazole-derived Ligands (1986-1992)*
Background to the Problem

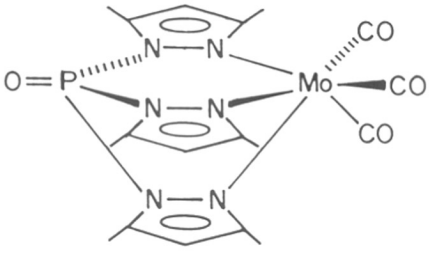
The literature on pyrazole-based ligands and their application in organometallic synthesis for the period 1986-1992 has been reviewed. Emphasis is laid on the design of such ligands, the synthetic methods and the structural aspects of the metal complexes derived thereof. Structure of molybdenum π-allyl complexes has been discussed in detail as a background to the work that is undertaken during the present investigation.

Chapter - II *Tris(3,5-dimethylpyrazolyl)phosphoramide as a Ligand for New Organomolybdenum Complexes*

An improved synthetic procedure for the preparation of the ligand was developed. Consistent good yield of the phosphoramide (**1**) was obtained by heating three equivalents of 3,5-dimethylpyrazole with one equivalent of phosphorus oxychloride in the presence of excess triethylamine in benzene. Complexes were prepared with Co(II), Ni(II), Cu(II) and Cu(I) salts. They were characterized by infrared spectroscopy and elemental analyses. When the ligand was heated under reflux with an equivalent amount of molybdenum hexacarbonyl in acetonitrile, the expected molybdenum tricarbonyl complex (**2**) was obtained in good yield. On heating one equivalent of this complex with three equivalents of dimethyl acetylenedicarboxylate in dimethylformamide, hexacarbomethoxybenzene was obtained as the major product in moderate yield.



1



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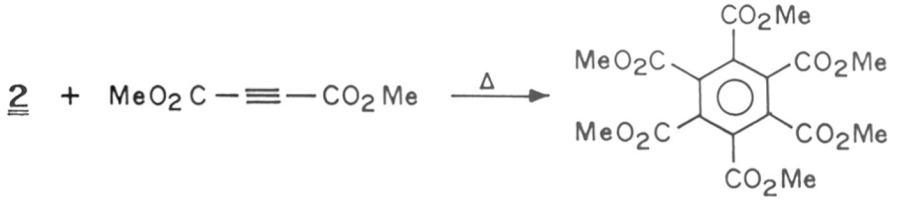
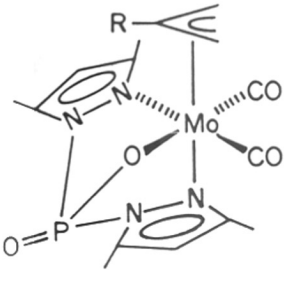
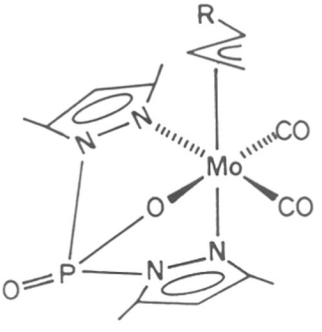




3a-c

R	
a :	H
b :	CH_3
c :	C_6H_5



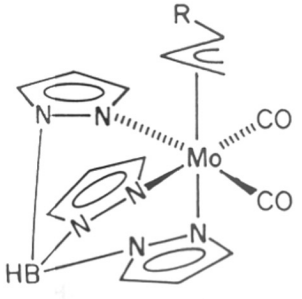
3d-f

R	
d :	CH_3
e :	C_6H_5
f :	p-OCH_3-C_6H_4

Three new π-allyl complexes of molybdenum (**3a-c**) were prepared by ligand-exchange reaction. It was observed that one of the pyrazole was displaced by oxygen in these complexes. The NMR spectra of these compounds revealed stereochemical non-rigidity and the intramolecular motion could be arrested at low temperature. The X-ray crystal structure of the complex **3c** showed that oxygen occupied an equatorial site in the distorted octahedron while the allyl group occupied an apical position. EHMO calculations indicated that this was the preferred orientation of the ligands. It was also found that the energy barrier of trigonal twist involving the ligand was lower in **3b** while those of **3a** and **3c** were comparable. Three additional complexes **3d-f** were prepared where the allyl group carried a terminal substituent, since these are more relevant in the context of regio- and stereoselective syntheses. The broad lines in NMR spectra of **3e** and **3f** indicated fluxionality in these complexes as well and low-temperature proton NMR spectra were investigated to determine conformational preferences. The two conformers (A and B) were almost equally populated at low temperature. The X-ray structure of **3e**, however, revealed that the molecules in the crystalline state have the conformation where the aromatic ring lies closer to the equatorial pyrazole ring and shields the 3-methyl group. For **3d**, only one set of sharp lines were observed which showed no appreciable broadening even at -50°.

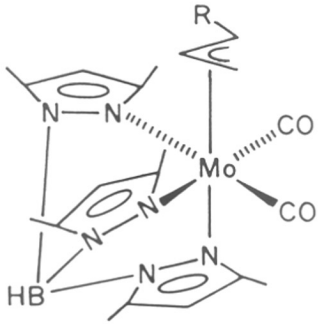
Chapter - III *Steric Effect of Pyrazole Substituent on the Conformation of Molybdenum π-Allyl Complexes*

The synthesis and structure of four new π-allyl complexes (**4a,b** and **5a,b**) of molybdenum containing hydridotris(pyrazolyl)borate and hydridotris(3,5-dimethylpyrazolyl)borate were studied. The allyl groups were terminally substituted. In the case of unsubstituted pyrazole-derived ligand, the fluxional molecules showed near-average NMR spectra as expected for a slow trigonal twist involving the ligand. With 3-methyl substitution, the barrier of this rotation was sufficiently raised so that sharp signals were obtained. The crotyl complex **5a** showed at least two species in solution. The compound **5b** showed only one set of peaks assignable to a single species in solution. The central proton of the allyl group was significantly deshielded in both **5a** and **5b** indicating significant distortion in the allyl group. This could arise due to considerable steric interaction between the 3-methyl group of the pyrazole and the terminal substituent on the π-allyl. An X-ray structure solution of the complex **5b** revealed substantial deviation from the usual orientation of the allyl group in such complexes.



4

a : R = CH_3 , b : R = C_6H_5



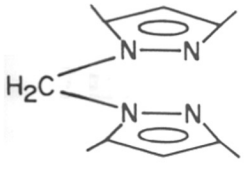
5

a : R = CH_3 , b : R = C_6H_5

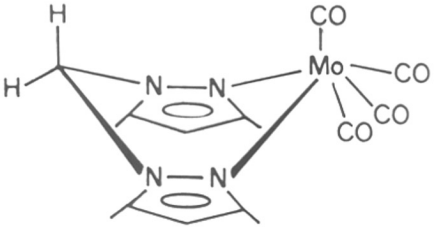
Chapter - IV *New Organomolybdenum Complexes Containing Bidentate bis(3,5-Dimethylpyrazolyl)methane Ligand*

The bidentate ligand was prepared by an improved procedure using dibromomethane as the alkylating agent and a phase-transfer catalyst. On refluxing the ligand with an equivalent amount of molybdenum hexacarbonyl in acetonitrile or toluene, the tetracarbonyl complex **6** was

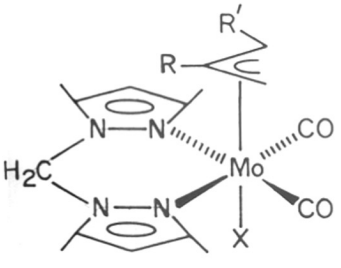
obtained in good yield. Five new π-allyl complexes (**7a-e**) were synthesized and characterized by spectroscopy (IR, PMR and CMR) as well as elemental analyses. The conformation of the chelating ring was unambiguously determined by X-ray crystallography for two compounds. The stereochemistry was found to be dependent on the pyrazole substitution. In **7c**, the methylene protons are highly shielded by the phenyl ring anisotropy. When dipyrazolylmethane was used as the ligand, no such upfield shift was observed for the analogous complex. Also, the compound **7b** was extremely unstable and underwent rapid aerial oxidation, while the corresponding complex with dipyrazolylmethane ligand was rather stable and could be prepared and isolated in good yield.



(L)



6



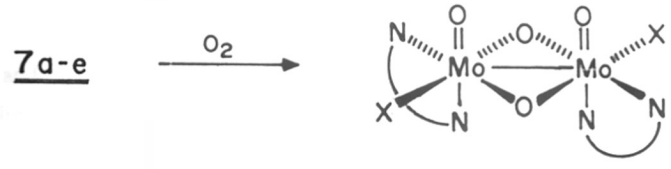
7

	R	R′	X
a :	H	H	Cl
b :	CH_3	H	Cl
c :	C_6H_5	H	Br
d :	H	CH_3	Cl
e :	H	C_6H_5	Cl

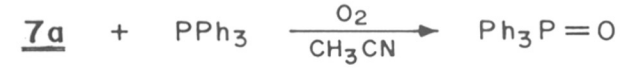
Chapter - V : *Unusual Formation of Molybdenum(V) Binuclear Oxo Complexes*

Molybdenum π-allyl complexes with bis(3,5-dimethylpyrazolyl)methane were found to undergo slow oxidation in acetonitrile or dichloromethane solution to furnish crystalline Mo(V) oxo complexes. The X-ray crystal structure revealed that the compounds had a bimetallic core containing two singly bonded molybdenum atoms in a distorted octahedral environment. These

diamagnetic molecules had an overall C_2 symmetry and contained no allyl group. An EPR signal was observed during the period of their formation from allyl complexes, and it was tentatively assigned to monomeric Mo(V) species. Triphenylphosphine was oxidized to the phosphine oxide by aerial oxygen in the presence of a catalytic amount of molybdenum π-allyl complex. This is the first example of dioxygen activation and transfer initiated by a Mo(II) complex.
The corresponding acetonitrile, triphenylphosphine, bipyridyl or phenanthroline derived complexes do not undergo such a reaction under similar conditions.



X = Cl, Br



1equiv. 20 equiv. 94 %

Serial numbers of the compounds in the synopsis are different from those in the thesis.

Publications

1. Synthesis and Structure of New Molybdenum π-Allyl Complexes : Unexpected Hydrolysis of Tris(3,5-dimethyl-1-pyrazolyl)phosphine Oxide
   Vijaya S. Joshi, Vasumati K. Kale, Kashinath M. Sathe, Amitabha Sarkar, S.S. Tavale and C.G. Suresh
   Organometallics *1991*, **10**, 2898.

2. Synthesis of New Stereochemically Non-rigid Molybdenum Allyl Complexes Containing the Bis(3,5-dimethylpyrazolyl)methane Ligand
   Vijaya S. Joshi, Amitabha Sarkar and P.R. Rajamohanan
   J.Organomet.Chem. *1991*, **409**, 341.

3. Isolation and Structure of a Dimeric Mo(V) Oxo Complex with bis(3,5-dimethylpyrazolyl) methane ligand : An Unusual Case of Dioxygen Activation
   Vijaya S. Joshi, Malay Nandi, Hongming Zhang, Brian S. Haggerty and Amitabha Sarkar
   Inorganic Chemistry (*in press*)

4. Structure and Dynamic Stereochemistry of Molybdenum π-Allyl Complexes Containing Pyrazole-derived Ligands
   Vijaya S. Joshi, Kashinath M. Sathe, Malay Nandi and Amitabha Sarkar
   (to be submitted to Organometallics)

CONTENTS

CHAPTER - I

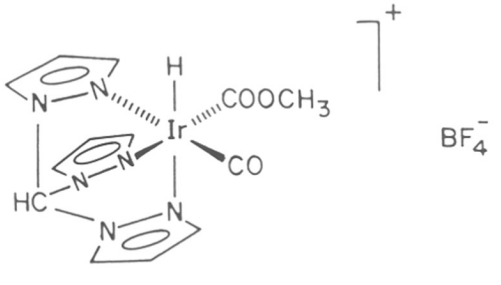
REVIEW OF PYRAZOLE-DERIVED LIGANDS (1986-1992): BACKGROUND TO THE PROBLEM

INTRODUCTION

The chemistry of pyrazole-derived ligands was initiated by Trofimenko and has been extensively reviewed by him.[1] Although initially developed as an isoelectronic alternative to the ubiquitous cyclopentadienyl ligand, it was soon realised that the pyrazole-derived ligands have a rich chemistry of their own. In particular, these ligands have markedly different stereoelectronic requirements compared to the conventional pyridine or phosphine-derived ligands. Therefore, the structures and reactivities of metal complexes containing pyrazole-derived ploydentate ligands varied widely from previously known analogues.

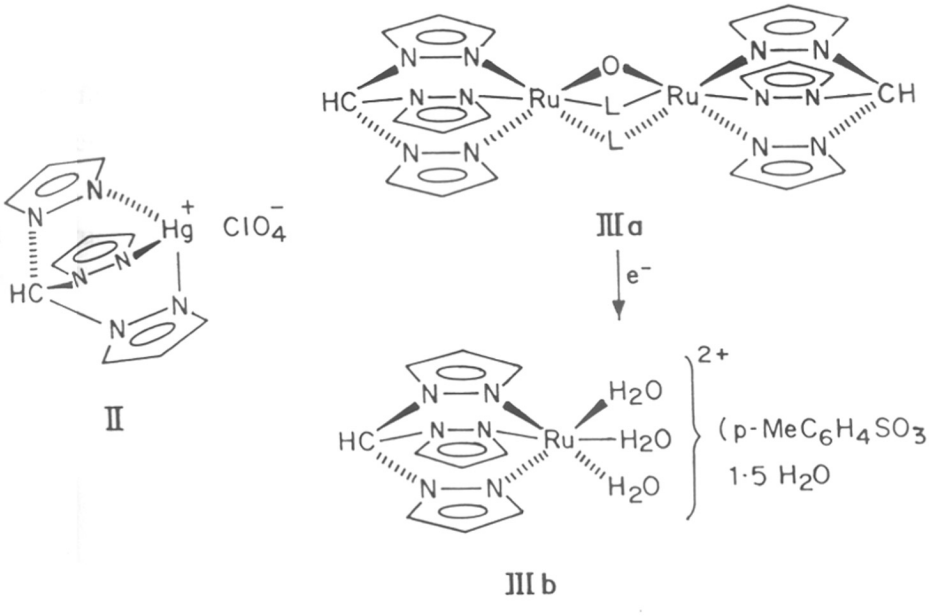
Over the years, the ligand modifications concerned variation of ring size of the chelates and substituents on the pyrazole. Such changes allowed fine tuning of steric and/or electronic influences on the metal centres. The following discussion provides an overview of this general trend from current literaure. The polypyrazolylborates have been excluded in view of a recent review[1a], and the literature was scanned from 1986 for the various other pyrazole-derived ligands since earlier reports were already reviewed.[1b]

Trofimenko described[2] the preparation of polypyrazolylmethanes and some of their ligation properties. The *tris*-pyrazolylmethane derivatives can be regarded as the neutral analogue of the uninegative *tris*-pyrazolylborates. The olefin-complexes of rhodium and iridium were characterised[3] and formation of alkoxycarbonyl derivatives (I) were later reported.[4]



I

Moderately stable derivatives were prepared from zinc[5], cadmium[5] and mercury[6] (II), and characterised by IR and NMR spectroscopy. Structurally characterised mononuclear aquo complex[7] as well as the ones containing bipyridyl ligand[8] were reported for ruthenium. A bridged diruthenium complex (III) was also prepared.[9] Upon reduction of this dimeric species, the mononuclear *tris*(aquo) complex was obtained quantitatively.

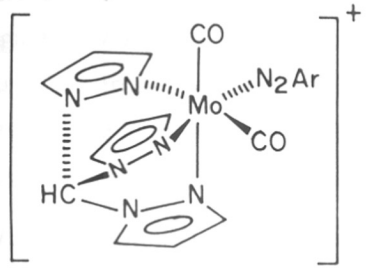


II

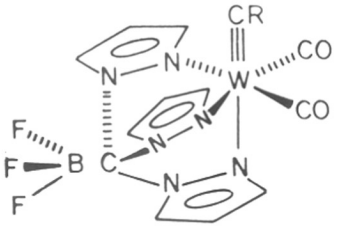
IIIa

IIIb

While an interesting molybdenum diazonium complex could be prepared using the tridentate *tris*-pyrazolylmethane ligand[10], a number of Mo and W alkylidyne complexes were reported by Angelici[11] and Stone.[12]



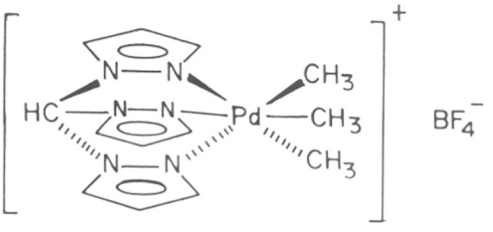
IV



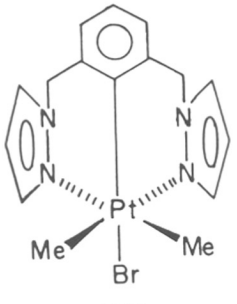
$R = Me / C_6H_4 Me\text{-}4$

V

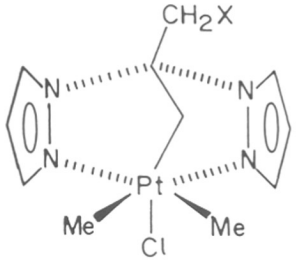
The first isolable complex (VI) of Pd(IV) featured this tridentate ligand.[13] Intramolecular oxidative addition of R-X on suitably designed substrate was also possible[14], as shown in (VII) and (VIII).[15] Palladium complexes were also prepared with a structuurally related mixed ligand where one pyrazole was replaced by a pyridine.[16]



VI



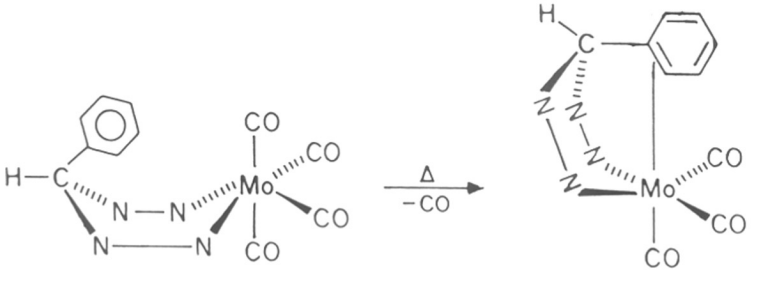
VII



VIII

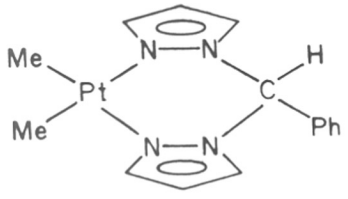
The chemistry of bidentate *bis*-pyrazolylmethane derivatives has also been investigated by several groups. A number of complexes are known with zinc[17], cadmium[17], mercury[18] and tin[19]. Solution behaviour and X-ray structure of silver complexes have been studied[20]. The stoichiometry of metal:ligand is 1:1 in most of the complexes with the exception of some complexes of mercury and silver.

While a copper(I) complex featuring this bidentate ligand was prepared and characterised[21], a great deal of activity centred around molybdenum and tungsten complexes. The $M(CO)_4$ derivatives were prepared[22,23] and converted to M(II) dihalides[24] or π-allyl complexes[22]. An unusual η^2-arene complex (IX) was structurally characterised by X-ray crystallography[25] when the bridging carbon was linked with a phenyl ring.

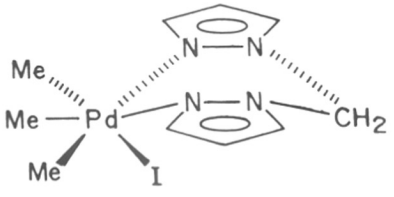


IX-A IX-B

A number of complexes were prepared from palladium(II) and platinum(II) metal centres[26] as well as those metals in IV state.[27] Some of the latter complexes were reported to be fluxional (X) and (XI).[27b]



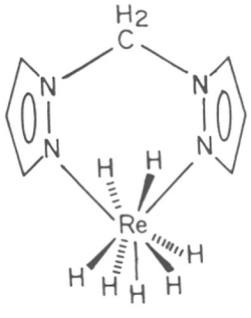
X



XI

Formation of heterobimetallic complexes of palladium and platinum with the *bis*-pyrazolylmethane ligand as bridged, has been reported.[28]

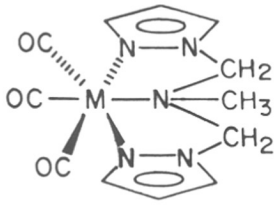
Crabtree[29] reported the first transition metal polyhydride complex featuring this bidentate ligand (XII).



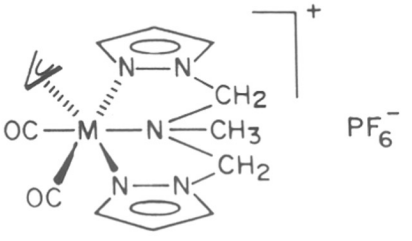
XII

Ligands have been synthesised where nitrogen was retained as the capping atom of *bis* or *tris*-pyrazolyl derivatives. In most instances, the capping nitrogen took part in complexation through its lone pair.

Shiu[30] investigated several molybdenum and tungsten complexes of structures (XIII) and (XIV).



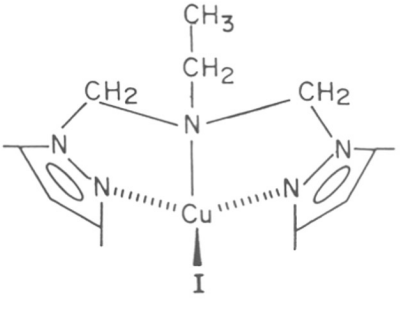
XIII



XIV

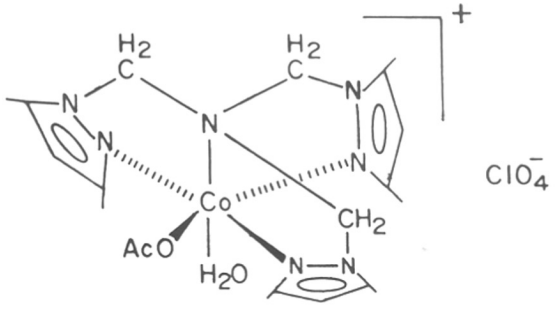
The π-allyl complex was shown to be fluxional and the dynamic structure was believed to have resulted from a *trigonal twist* involving the tridentate ligand. In the X-ray structure it was observed that the capping nitrogen as well as one pyrazole occupied positions *trans* to the CO ligands.

A large number of copper complexes were prepared and characterised using ligands derived from pyrazoles, a capping nitrogen atom and variable spacer connection between the capping nitrogen and the pyrazoles. Among the complexes derived from the ligand N,N-*bis*(3,5-dimethyl-1-pyrazolylmethyl) aminoethane[31a], a tridentate ligand environment was characterised by X-ray crystallography (XV).[31b]



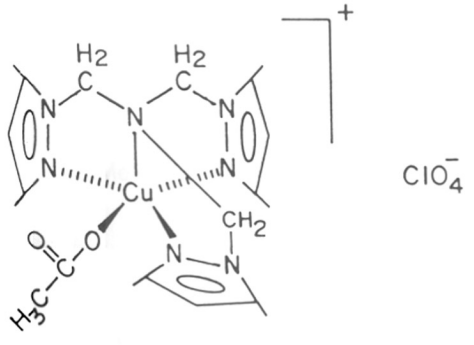
XV

Dimeric complexes of cobalt, copper, nickel and zinc with this ligand were reported (XVI).[32] Hexacoordinated and pentacoordinated structures have been characterised (XVII)).[33]

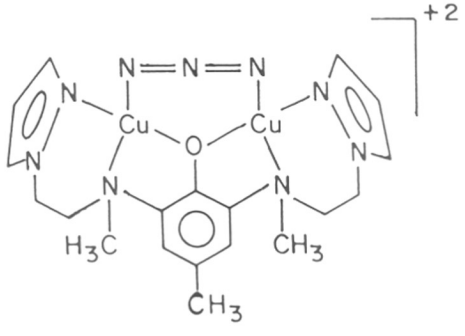


XVI

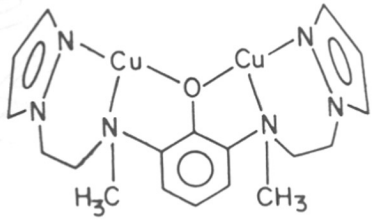
Another form of ligands featured two pyrazoles in conjunction with a phenolate ion and copper complexes were investigated[34] in the context of bioinorganic interests. Examples of these and related complexes[35] follow (XVII), (XIX) and (XX):



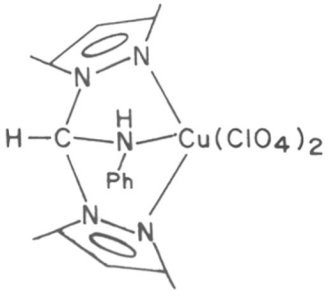
XVII



XVIII



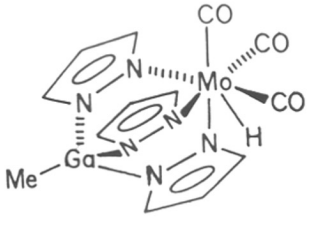
XIX



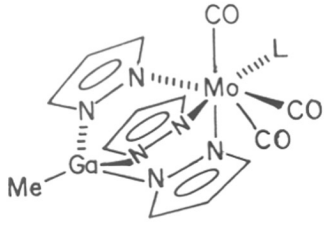
XX

Various other ligands[36] were studied where pyrazoles were used as mixed donor sites with nitrogen and sulfur.

A large number of complexes were prepared with ligands derived from pyrazoles and gallium as the capping atom. *Tris*-pyrazolylgallates have been used in different complexes ranging from monomeric[37] to heterobimetallic with direct[38] or bridging linkages (XXI), (XXII), (XXIII) and (XXIV).[39]

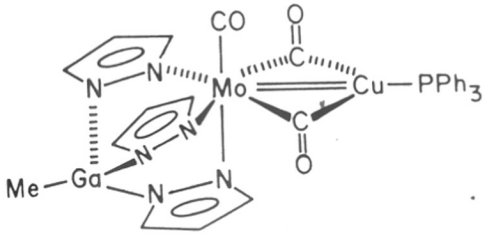


XXI

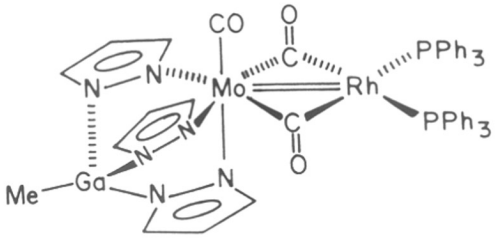


L = Ph_3Sn, Me_3Sn, Me_2ClSn

XXII

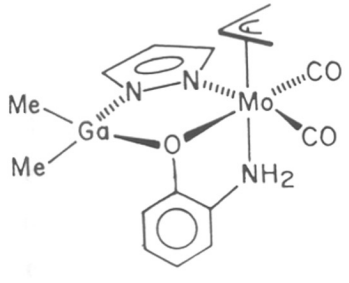


XXIII

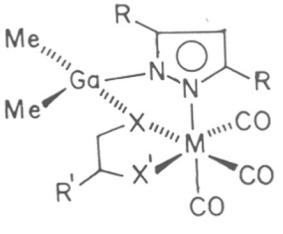


XXIV

The other aspects of the gallium derived ligands[40] concern complexes like XXV and XXVI, as shown below :



XXV

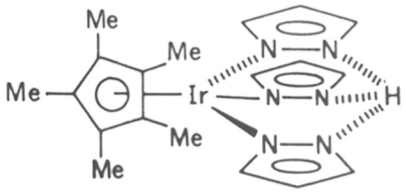


XXVI

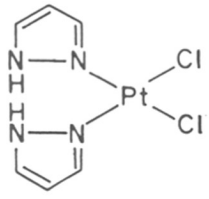
M = Mn, Re
R = H, Me
R = H, Me, Et
X = O, S
X′ = NH_2, NMe_2, SPh, SEt.

The unsymmetrical ligand environment generated interesting stereochemical features and occasionally resulted in fluxional structures.

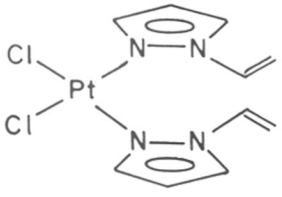
As with gallium, if a metal atom could be used as capping atom in such pyrazole-bridged complexes, the bimetallic species would be interesting both from the consideration of reactivity and as potential precursors for material applications. Progress in this direction awaits future endeavours. However, certain related structures[41] should be noted. The last three structures represent potential ligands for heterobimetallic complexes (XXVII), (XXVIII) and (XXIX).



XXVII



XXVIII



XXIX

In view of the above literature data, it was clear that numerous possibilities existed in terms of ligand design with pyrazoles. From the standpoint of synthetic organic chemistry, no such ligand has so far been used in C-C bond formation. Therefore, it was of interest to investigate the viability of such a proposition in the present study. The molybdenum π-allyl complexes were selected as the central structure since this moiety has previously been used extensively in organic synthesis with high stereoselectivity[42]. Once the stereochemistry of a particular set of complexes comprising a pyrazole-derived ligand was understood, reactions to generate new carbon linkages could be predictably effected with desired steric outcome.

The account presented in the following chapters concerns synthesis and structural characterisation of three classes of pyrazole-derived ligands with emphasis on the stereochemistry of the allyl group and unexpected oxygen affinity of a certain class of complexes.

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CHAPTER - II

TRIS(3,5-DIMETHYLPYRAZOLYL)PHOSPHORAMIDE AS A LIGAND FOR NEW ORGANOMOLYBDENUM COMPLEXES

Part of this work was published in

Organometallics, *1991*, **10**, 2898.

INTRODUCTION

While pyrazole-derived chelating ligands have been extensively used in the synthesis of organometallic complexes,[1] no attempt was made to study systematic variations in the structure or reactivity of such complexes consequent to variation in ligand structure or substitution. A long-term objective of the present work was to understand and correlate ligand-modified structure and reactivity of organometallic complexes in a designed series of new compounds.

Molybdenum π-allyl complexes were selected as the general class of complexes in the present study for the following reasons :

a) The structure and reactivity of these complexes are well-studied.[2] Thus comparison with various related compounds will be possible.

b) The π-allyl complexes are particularly relevant for catalytic[3] and sequential C-C bond formation.[4] This study, therefore, can be usefully directed towards developing efficient synthetic methods for organic molecules.

c) The compounds are usually air-stable and thus easier to handle under ordinary laboratory conditions.

d) For a series of π-allyl complexes, diversely substituted pyrazole derivatives can be readily prepared for comparative study.

RESULTS

The reaction of phosphorus oxychloride with three equivalents of pyrazolate or 3,5-dimethylpyrazolate was reported[5] to yield a phosphoramide, the coordination chemistry of which was not explored. The compound was a potential tridentate ligand which appeared to be an attractive, neutral analogue of the uninegative tripodal ligand *tris*-pyrazolylborate. Co-ordination of this ligand to form molybdenum(II)dicarbonyl complex with π-Allyl group would probably afford cationic complex and hence susceptible to nucleophilic attack.

Therefore, a modified procedure for the preparation of *tris*(3,5-dimethylpyrazolyl)phosphoramide was developed, and synthesis of molybdenum π-allyl complexes were undertaken, as described below.

Preparation of the Ligand 1

The preparation consisted of addition of $POCl_3$ to a benzene solution of three equivalents each of 3,5-dimethylpyrazole (readily obtained from acetylacetone and hydrazine hydrate) and triethylamine at 0°C followed by heating under reflux for 12h. The precipitated amine hydrochloride was filtered and the benzene solution was concentrated to yield the crude product. Attempts to purify the product by column chromatography failed since the compound underwent decomposition. Several attempts were made to crystallize the product. The CCl_4-hexane was found to be the best solvent mixture to obtain the pure product as colourless crystals. The crystallization was a slow process lasting over two weeks. The compound was extremely hygroscopic. However, it could be preserved under the mother liquor at 5°C for months.

The IR spectrum of the ligand showed P=O absorption as a sharp peak at 1180 and C=N at 1560. The NMR spectrum of this compound showed two sharp singlets for pyrazole methyls at 2.15 and 2.25 and a doublet at 5.95 ($J_{P\text{-}H}$ = 4 Hz). The mass spectrum of this compound showed M^+ at 332 with a base peak at 95. The ^{13}C NMR spectrum showed peaks at 11.9 and 13.6 corresponding to pyrazole methyls; 110.6 and 110.8 for pyrazole C-4; 147.6 and 147.9 for pyrazole C-5; 154.3 and 154.6 for pyrazole C-3 carbon.

Preparation of metal complexes

Acetonitrile solution of ligand **1** was treated with aqueous solution of cobalt nitrate, nickel chloride, copper sulphate and cuprous iodide. Immediate precipitation of solids indicated the formation of complexes. Filtration and drying afforded complexes in 30-40% yields. The Co(II), Ni(II) and Cu(II) complexes were found to be insoluble in organic solvents. The Cu(I) complex was soluble in most of the organic solvents. The IR spectrum of above complexes showed a peak of medium intensity at 1560 corresponding to pyrazole ring C=N absorption and a peak at 1180 for P=O absorption. The NMR spectrum of Cu (I) complex showed two sharp singlets at 2.45 and 2.50 corresponding to the pyrazole methyl protons. Pyrazole 4H appeared at 5.95 and 6.00 as two broad singlets.

Preparation of Molybdenum Tricarbonyl Derivative 2

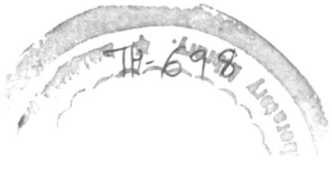
On heating equivalent quantities of $Mo(CO)_6$ and the ligand **1** in acetonitrile under argon for one hour, the complex **2** was isolated as a bright yellow, microcrystalline solid which was sparingly soluble in common organic solvents. The IR spectrum of this compound showed a sharp peak at 1910 with a shoulder at 1920 and an intense peak at 1790 corresponding to CO absorptions. A sharp peak at 1580 was characteristic of pyrazole ring C=N absorption and a sharp peak at 1180 corresponded to P=O absorption. The ^{13}C NMR spectrum (recorded in the solid state) of this compound showed peaks at 12.7, 14.2, 14.9, 15.6, 16.2 and 17.3 corresponding to pyrazole methyls; 108.9, 112.3 for pyrazole C-4; 150.2 and 151.9 for pyrazole C-5; 161.5 for pyrazole C-3 ring carbons; 232.4 and 234.4 for carbonyl carbons. Elemental analysis was consistent with the formulation of the complex.

Reaction of Dimethyl Acetylenedicarboxylate with Complex 2

In an attempt to prepare metal-alkyne derivatives by the displacement of CO ligands by alkynes,[6] the complex **2** was heated with three equivalents of dimethyl acetylenedicarboxylate in dimethylformamide at 110°C for two hours. Attempts to isolate a stable metal complex failed, but removal of the solvent followed by column chromatography afforded hexacarbomethoxybenzene in 35% yield based on dimethyl acetylenedicarboxylate. The ^1H NMR of this compound showed a single sharp peak at 3.80. The ^{13}C NMR spectrum of this compound showed peaks at 53.2 corresponding to methyl carbon, 133.7 for aromatic carbon, 164.9 for carbonyl carbon. The mass spectrum showed M^+ at 426. Identity of this product was readily established by spectral means (^{13}C NMR and Mass), and comparing the values with those reported in literature.[7]

Preparation of π-Allyl Complexes of Molybdenum(II) 3a-f

The preparative method for the molybdenum π-allyl complexes was adopted from literature[8] with minor variations in isolation step. The *bis*-(acetonitrile) π-allyl complexes were first prepared from $Mo(CO)_6$ and the allyl halide. Ligand exchange was carried out subsequently.



The complex **3a** was obtained by heating $Mo(CO)_6$ and allyl bromide or allyl chloride in acetonitrile for 5h. The resulting complex was treated with the ligand **1** in acetonitrile and heated under reflux for 10 min. The product **3a** was isolated by precipitation with degassed water as an orange solid and purified by crystallization with hot acetonitrile-water to get needle shaped crystals in 52% yield.

The IR spectrum of **3a** showed two sharp peaks of equal intensity at 1940 and 1840 corresponding to the CO ligands. A medium peak at 1560 (pyrazole ring C=N) and a sharp peak at 1180 for P=O absorption were also observed. The ^1H NMR spectrum recorded at -50 °C showed two sets of doublets at 1.40 and 1.70 for *anti* allyl protons; broad singlets at 2.40, 2.45 and 2.90 corresponding to pyrazole methyl protons; and broad multiplets at 3.40 and 3.75 corresponding to *syn* and central allyl protons. The ^{13}C NMR spectrum showed peaks at 11.5 and 14.3 for pyrazole methyl carbons, 55.2, 65.3 for allyl terminal carbons and 78.6 for allyl central carbon, 109.5 for pyrazole C-4, 146.2 and 147.4 for pyrazole C-5, 155.8, 157.2 for pyrazole C-3 ring carbons[9] and at 227.4, 228.6 for carbonyl carbons.

The ^{31}P NMR spectrum showed a singlet at -12.09. The ^{95}Mo NMR spectrum showed a broad peak at -787.6 with a peak width of 499.2 Hz.

The complex **3b** was similarly obtained from the *bis*-acetonitrile Mo-methallyl complex by ligand substitution. The product **3b** was isolated as yellow crystals in 44% yield.

The IR spectrum of **3b** showed two sharp peaks of equal intensity at 1925 and 1830 for carbonyls, a peak of medium intensity at 1560 corresponding to pyrazole C=N vibration and at 1180 a sharp peak corresponding to P=O vibration. The ^1H NMR spectrum recorded at room temperature showed two broad singlets at 1.40 for *anti* protons and at 3.30 for *syn* protons. A singlet at 1.75 for central CH_3 and broad singlets at 2.40 and 2.60 appeared for pyrazole CH_3 and a doublet at 5.90 for pyrazole 4-H. The ^{13}C NMR spectrum of **3b** showed peaks at 11.4, 14.2 for pyrazole-CH_3, 19.6 for allyl-CH_3. A broad peak at 59.4 was assigned to terminal allyl carbons and 88.4 for allyl central carbon, 109.5 for pyrazole C-4, 146.6 for pyrazole C-5 and 156.1 for pyrazole C-3 ring carbons and 226.9 and 228.2 for carbonyl carbons. The ^{31}P NMR spectrum showed a sharp peak at -12.13. The ^{95}Mo NMR spectrum featured a broad peak at -746.5 (peak width 332.8 Hz).

The complex **3c** was obtained by heating $Mo(CO)_6$ with α-methylstyryl bromide in acetonitrile for 5h, followed by addition of the ligand solution and work up (as in the case of **3a**). Crystallization from toluene-hexane afforded the orange crystalline complex **3c** (23%).

The IR spectrum of **3c** showed two sharp peaks of equal intensity at 1940 and 1850 for carbonyls, a peak of medium intensity at 1560 corresponding to pyrazole C=N stretch and a sharp peak at 1180 corresponding to P=O. The ^1H NMR spectrum recorded at -18°C showed a broad singlet at 1.45 for *anti* proton and two broad singlets at 3.90 and 4.20 for *syn* protons. Singlets at 2.10, 2.25, 2.50 and 2.80 appeared for the pyrazole CH_3 protons. Two broad singlets at 5.75 and 5.90 were assigned to pyrazole 4-H proton while the multiplets at 7.05 and 7.25 corresponded to the phenyl ring protons. The ^{13}C NMR spectrum of **3c** showed signals at 11.1, 14.1 for pyrazole CH_3; 55.1 and 57.4 for allyl terminal carbons and 85.3 for allyl central carbon; 109.1, 147.1, 156.5, for pyrazole C-4, C-5 and C-3 ring carbons respectively. 124.3, 126.6, 135.9, and 154.5 for phenyl ring carbons, and, 225.1 and 227.4 for carbonyl carbons. The ^{31}P NMR spectrum displayed a sharp peak at -12.46. The ^{95}Mo NMR spectrum displayed a peak at -762.3 (peak width 332.8 Hz).

The complex **3d** was obtained in a similar manner. On heating $Mo(CO)_6$ with cinnamyl chloride in acetonitrile for 5h afforded the *bis*-acetonitrile cinnamyl complex as a red solution. After cooling to room temperature, the solution of the ligand in acetonitrile was added in one portion. The reaction mixture was stirred for 10 minutes. Degassed water (2 ml) was added till slight turbidity appeared. It was preserved under argon at O°C for 48 hrs. Orange Crystals of complex **3d** were obtained which were filtered and dried(48%).

The IR spectrum of **3d** showed two sharp peaks of equal intensity at 1930 and 1840 for carbonyls, a peak of medium intensity at 1560 corresponding to pyrazole C=N and a sharp peak at 1170 corresponding to P=O. The ^1H NMR spectrum recorded at room temperature showed broad lines. On cooling the sample to -31 °C, two sets of well-resolved peaks were obtained, assignable to two different conformers. One set showed doublet at 1.90 for *anti* proton, doublet at 3.85 for *syn* proton, doublet at 2.65 for benzylic *anti* proton, broad singlets at 5.90 and 5.97 corresponding to pyrazole 4-H, and singlets at 2.30, 2.50, 2.51 and 2.58 for pyrazole methyls. Another

set showed doublet at 1.55 for *anti* proton, doublet at 3.20 for *syn* proton, doublet at 3.45 for benzylic *anti* proton. Sharp peaks appeared at 6.00, 5.95 and 5.65 in the ratio 7:4:3 corresponding to pyrazole 4-H. For pyrazole CH_3 signals, one out of four singlets appeared at high field, i.e. 1.15, while the other three singlets appeared at 2.45, 2.80 and 2.85 respectively. Central allyl proton of both conformers appeared together as a multiplet at 4.60. The multiplet between 6.60 and 7.70 were assigned to the phenyl ring protons. The ^{13}C NMR of **3d** at -31 °C also showed signals corresponding to the pair of conformers and were consistent with the structures.

The complex **3e** was prepared by heating $Mo(CO)_6$ with *p*-methoxycinnamyl chloride in acetonitrile for 5h to obtain the intermediate *bis*-acetonitrile complex as a dark red solution, followed by ligand substitution. Usual aqueous work up afforded a brown solid, which was recrystallized from toluene-hexane as brown crystals (9%).

The IR Spectrum of **3e** showed sharp peaks at 1920 and 1840 corresponding to carbonyls, a medium peak at 1560 for pyrazole C=N and a sharp peak at 1180 for P=O absorption. The ^1H NMR at low temperature (-15°C) showed two sets of well-resolved peaks, assignable to two separate conformers. The first set comprised a doublet at 1.90 for *anti* proton, a doublet at 3.80 for *syn* proton, a doublet at 2.80 for the other *anti* proton, peaks at 5.90 and 5.95 corresponding to pyrazole 4-H and singlets at 2.30, 2.48, 2.50 and 2.55 for pyrazole CH_3 protons. Another set showed a doublet at 1.55 for *anti* proton, a multiplet at 3.45 for *syn* proton, a doublet at 3.30 for another *anti* proton, peaks at 5.95, and 5.70 corresponding to pyrazole 4-H, and singlets at 1.25, 2.45, 2.80 and 2.82 for pyrazole CH_3. The singlet at 3.85 for methoxy group, the multiplet at 4.50 for central proton and the multiplet from 6.60 to 7.70 for phenyl ring protons overlapped on the same region of spectrum.

The complex **3f** was obtained by heating $Mo(CO)_6$ with crotyl chloride in acetonitrile for 5h followed by ligand substitution. Usual work up and crystallization from acetone-water furnished the complex **3f** as yellow crystals (25%).

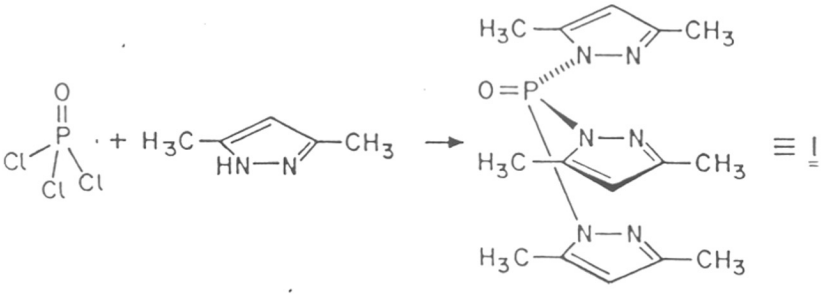
The IR spectrum of **3f** showed two sharp peaks of equal intensity at 1940 and 1850 for carbonyls, a peak of medium intensity at 1560 corresponding to pyrazole C=N and a sharp peak at 1180 corresponding to P=O absorption. The ^1H NMR spectrum showed sharp peaks which were assignable to a single conformer. A singlet

at 1.55 and a multiplet at 1.90 were assigned to the *anti* protons of the allyl group, a doublet at 2.00 was assigned to the allylic methyl, the *syn* configuration was deduced from comparison of the chemical shift values to the literature values of similar compounds.[10] A set of singlets between 2.30 and 2.70 could be assigned to the pyrazole methyls. The doublet at 3.50 was assigned to the *syn* proton of the allyl group. The central allyl proton appeared at 3.70 as a multiplet. Two doublets at 5.80 and 5.90 corresponded to the pyrazole 4-H. The ^{13}C NMR spectrum of **3f** showed signals at 11.4, 11.7, 14.2, 14.4 for pyrazole CH_3; 16.0 for allyl terminal CH_3; 62.1, 73.9, 81.6 for allyl carbons; 109.3, 110.0, 146.1, 147.4, 155.7 and 157.4 for pyrazole ring carbons, and, 229.1 and 230.0 for carbonyl carbons.

DISCUSSION

Preparation of the compound *tris* (3,5-dimethyl-1-pyrazolyl)phosphine oxide was reported in the literature.[5] The procedure involved the reaction of potassium 3,5-dimethylpyrazolate with phosphorus oxychloride. For the present study (**Scheme-1**), the method was simplified by using excess triethylamine as a base, thereby obviating the need for pyrazolate anion generation.

SCHEME-1



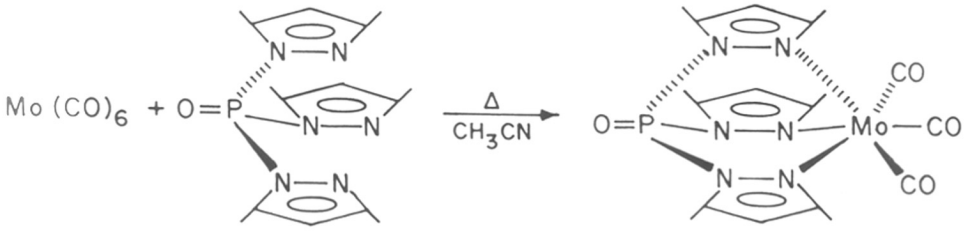
The modified procedure gave consistent yield of 55-60% over several batches of 10-15 g. The storage of this compound proved a little difficult since it was extremely hygroscopic. Later it was found that it could be stored for a prolonged period under a solvent cover. The spectral and physical properties of this compound were identical with those reported.

In order to learn about the ligation behaviour of the ligand **1** with transition metals, preliminary experiments were carried out to prepare metal complexes from readily available first row transition metal salts. The complexes could be easily prepared and isolated as stable solids.

The complexation of ligand to Molybdenum was immediately evident from IR absorption at 1560 and 1180 corresponding to pyrazole C=N and P=O for all complexes. The ligand-to-metal ratio could be either 1:1 or 2:1.[11] Microanalytical data did not accurately correspond to a 2:1 complex for Co(II), Ni(II) and Cu(II), though the values were somewhat close. These complexes were, however, insoluble in common organic solvents and as such the NMR spectra could not be recorded. For the complex derived from Cu(I), the microanalytical data was consistent with the formation of a metal-ligand ratio 1:1. This implied that the ligand was not hydrolysed during complexation in aqueous medium. The ^{1}H NMR spectrum of the complex showed two sharp singlets at 2.45 and 2.50 while the parent ligand **1** showed sharp peaks at 2.13 and 2.25 corresponding to pyrazole CH_3. This change in chemical shift positions was consistent with complexation of ligand **1** to the metal.

Encouraged by the above results which demonstrated efficient ligation capability of the ligand **1**, organomolybdenum complexes were attempted to be made. Thermal displacement of three CO ligands from molybdenum hexacarbonyl by **1**, resulted in the facile formation of the complex **2** (**Scheme-2**).

SCHEME-2

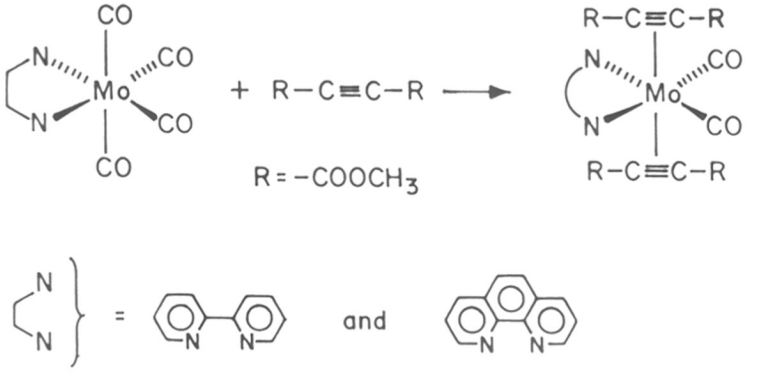


1 **2**

The complex **2** was sparingly soluble in usual organic solvents and thus its utility was rather limited. Its identity was established by spectral and analytical data.

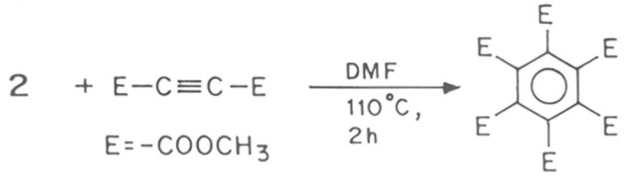
Recently it has been reported that[12] complexes of the type (L-L)$Mo(CO)_4$, where L-L is a bidentate N-donor ligand, can react with dimethyl acetylenedicarboxylate to produce bis(alkyne)(L-L)$Mo(CO)_2$ complexes (**Scheme-3**), in which the two alkynes remain *trans* to each other and *cis* to the ligand (L-L).

SCHEME-3



In order to explore similar ligand substitution chemistry of the new complex 2, it was heated with three equivalents of dimethyl acetylenedicarboxylate in DMF (**Scheme-4**). The solvent DMF was chosen in view of the poor solubility of the complex 2 in other solvents. Instead of affording any alkyne-bound complex, the reaction yielded hexacarbomethoxybenzene as the major product.

SCHEME-4

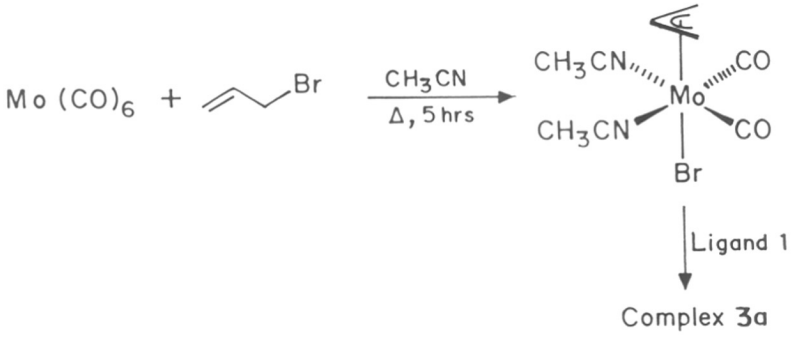


Although acetylene trimerisation mediated by Mo(0) compounds was observed earlier,[13] the yield of this reaction was poor in most of the cases. The present yield was respectable in comparison. However, it was found that the reaction was not general for other acetylenes and it was not pursued further.

The oxidative addition of allyl halides to Mo(0) compounds were known to yield π-allyl complexes.[14] If such addition would take place on the complex **2**, it would lead to a cationic π-allyl complex. Such a complex would be useful to study C-C bond formation by reaction with C-nucleophiles. Unfortunately, no reaction took place when the complex **2** was heated with allyl bromide for several hours in acetonitrile. There could be two possible reasons for the failure : a) poor solubility of the complex did not permit appreciable reaction, or, b) the methyl groups of pyrazoles shielded the molybdenum centre from attack of the reagent. There is a precedent in literature in support of the second possibility; *tris* (3,5-dimethylpyrazolyl)borato- tricarbonylmolybdenum anion failed to react with allyl halides.[15] Therefore, the allyl complexes were sought to be made by an alternative approach - ligand substitution of a preformed π-allyl complex, as detailed below.

On heating $Mo(CO)_6$ in acetonitrile with allyl bromide for 4-5 h, the π-allyl complex (**Scheme-5**), $(CH_3CN)_2$-$Mo(CO)_2$-Br-(π-allyl), was obtained as an orange solution, as described in the literature.[16]

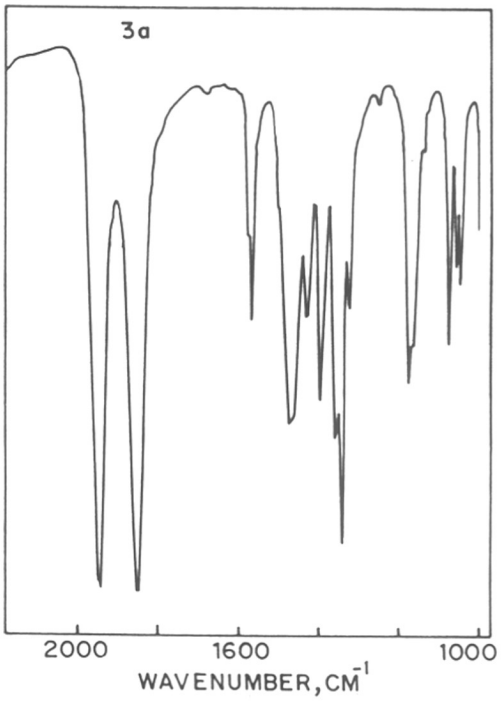
SCHEME-5



This complex could be isolated as a crystalline solid, though in the present case, ligand substitution was performed without isolation. The ligand **1** was added to this solution and heating was continued for a brief period of time. After aqueous work up, a orange crystalline product **3a** was obtained. The experiment was repeated

with allyl chloride and the same complex **3a** was obtained again. The IR spectrum revealed two strong CO absorptions at 1950 and 1850 (**Figure-1**), characteristic of a *cis* dicarbonyl complex.[17]

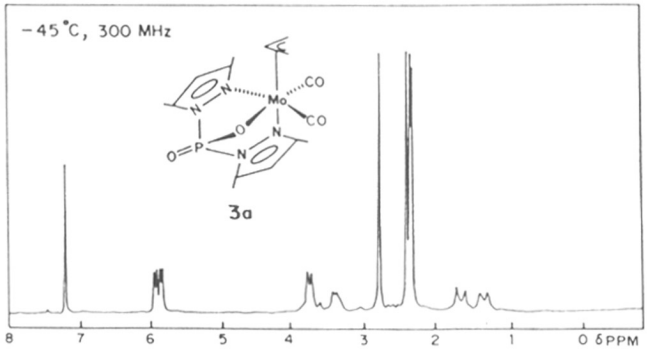
FIGURE-1



A band of medium intensity at 1560 was also observed for the C=N stretching in the pyrazole. However, the ^{1}H NMR spectrum showed broad lines at room temperature indicating that the complex was fluxional.

At -30°C, the signals were sharp and well-resolved to permit first order analysis. It was immediately noticed that the pyrazole 4-H displayed two signals of equal intensity, and only four methyl resonances were observed in the place of six. This suggested loss of one pyrazole group from the ligand. Two sets of *syn* and *anti* allyl-H signals were observed which showed coalescence phenomena. A multiplet corresponding to the central allyl proton was observed at 3.75 ppm (**Figure-2**).

FIGURE-2



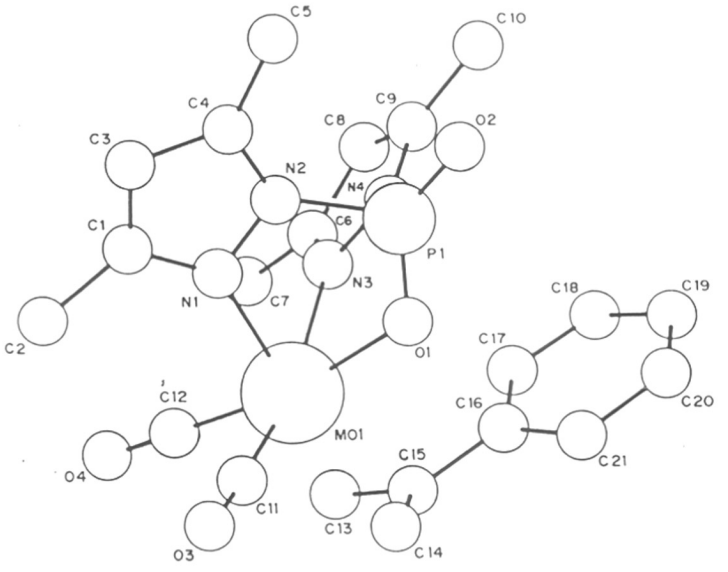
The same complex was also obtained when allyl chloride was used in the place of allyl bromide indicated the absence of halide in the complex.

When allyl bromide was replaced by methallyl chloride in an otherwise identical reaction, similar loss of a pyrazole was noticed in the new compound **3b**. The NMR spectrum showed an exchange-averaged spectrum for this compound at room temperature. The peaks decoalesced and gave rise to two sets at lower temperature. However no change was observed for the methyl signal of the methallyl group.

The reaction of 2-phenylallyl bromide (prepared from α-methylstyrene and N-bromosuccinimide) under similar condition provided the complex **3c**. While the IR spectrum of the complex was comparable with those described above, the ^{1}H NMR spectrum featured broad lines at room temperature. On cooling, decoalescence resulted in sharp signals. Loss of a pyrazole was evident in this case also.

In order to ascertain the identity of these complexes, it was necessary to carry out X-ray crystal structure analysis of one of the complexes (**Figure-3**). While aqueous acetonitrile furnished crystals of high purity, they were invariably twinned. Such difficulties in obtaining single crystals of pyrazole-derived molybdenum complexes were reported by Cotton earlier.[18] Finally, a single crystal of the complex 3c was grown from toluene-hexane, and subjected to X-ray crystal structure determination. The structure of the complex is depicted in the PLUTO diagram.

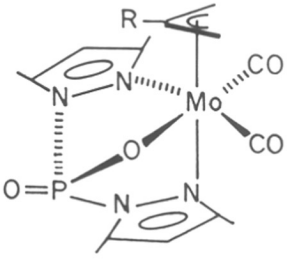
FIGURE-3



The X-ray structure solution was carried out by Dr. S. S. Tavale and Dr. C. G. Suresh at NCL, Pune.

From the diagram, it was clear that an oxygen atom was incorporated in the place of a pyrazole, and the overall charge was thus balanced. The oxygen atom occupied a position *cis* to the π-allyl group and *trans* to a CO ligand. One of the pyrazoles occupied a position *cis* to the Oxygen and *trans* to a CO ligand while the other pyrazole remained *trans* to the allyl group. The plane of the phenyl ring was nearly coplanar with the allyl group, but the central carbon was slightly tilted away from the metal. This structure unambiguously established the identity of this series of complexes as shown below (**Scheme-6**).

SCHEME-6

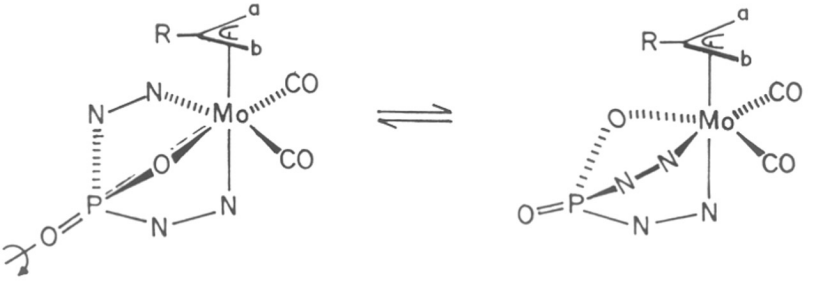


3

R
3a : H
3b : CH_3
3c : C_6H_5

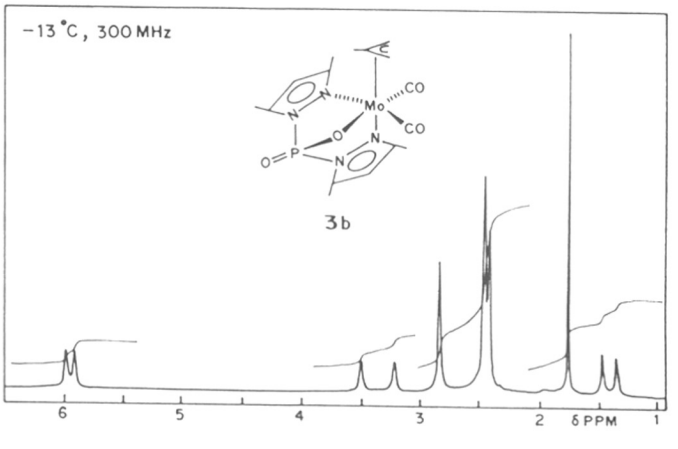
In such a structure, the two termini of the allyl group were in non-identical environment, one end proximal to the oxygen while the other was close to a pyrazole, and there was no plane of symmetry for the molecule. This resulted in two sets of ^{1}H NMR signals for the *syn* and *anti* protons of the allyl group, for a static environment observed at low temperature. Averaging of these two sites at higher temperature would occur due to a fast *trigonal twist*[19] about the Mo-P=O axis. Such a twist is depicted in **Scheme-7**

SCHEME-7



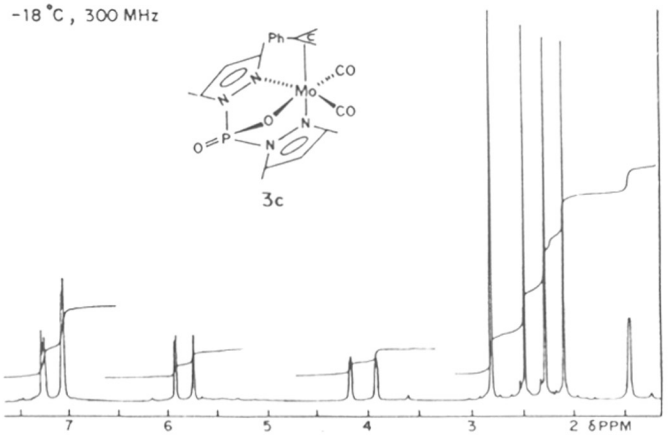
The barrier to *trigonal twist* was lower for the complex **3b** which displayed average spectrum at room temperature. At low temperature (**Figure-4**), the spectrum showed two sets of peaks for the allyl terminal protons as well as the pyrazole signals.

FIGURE-4



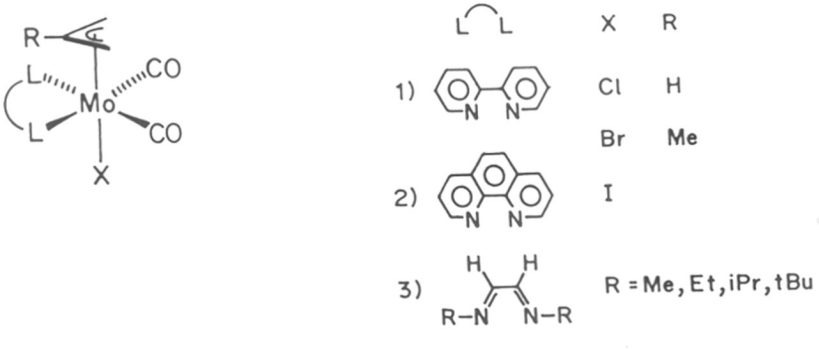
The barrier being relatively higher for the complexes **3a** and **3c**, the room temperature spectra showed broader lines. On cooling the sample, however, similar features were observed (**Figure-5**), two sets of signals were obtained for the terminal allyl protons and the pyrazole signals. Averaging of signals took place above 50 °C.

FIGURE-5



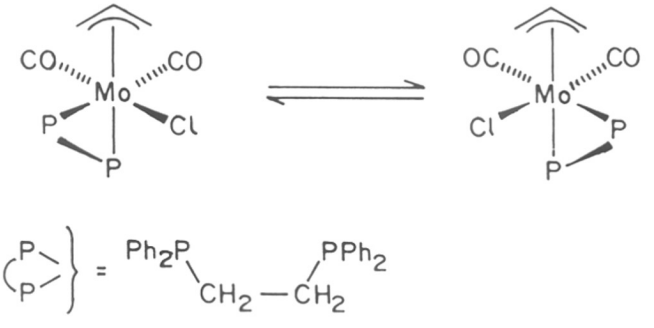
No conformer was identified where two pyrazoles occupied positions *trans* to the CO ligands and the oxygen was placed *trans* to the allyl group. Such a structure would have a mirror plane symmetry and the allyl group termini would have equivalent environment. For bipyridyl or phenanthroline ligands,[20] the heterocyclic donors invariably occupied positions *trans* to the CO groups when the counter ion occupied a position *trans* to the allyl group in similar complexes (**Figure-6**).

FIGURE-6



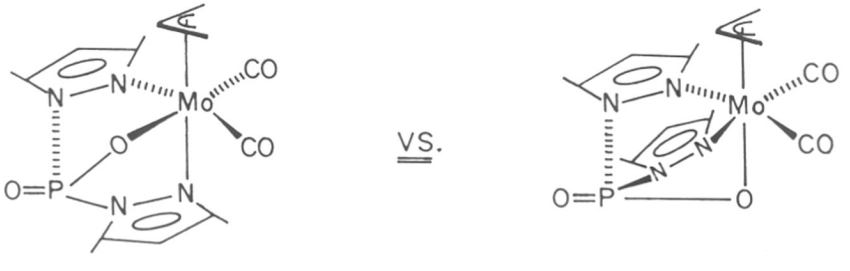
However, such a structure has never been obtained when two pyrazoles and the third donor belong to the same molecule of the ligand[21]. Only in the complex featuring 1,2-diphenylphosphinoethane ligand, however, one phosphorus preferentially occupied a position *trans* to the allyl group (**Figure-7**). Trigonal twist was observed in this case.[22]

FIGURE-7



To gain a supporting evidence that oxygen in apical position *trans* to the allyl group is inherently destabilized compared to the observed conformer, an EHMO calculation was performed[23] on a pair of conformers generated by simulating trigonal twist on the crystal structure (**Figure-8**).

FIGURE-8

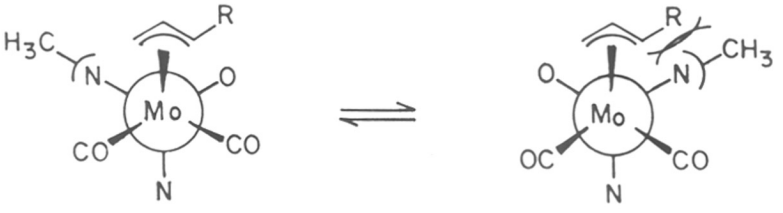


It was ensured that such twist did not disturb interatomic distances. Such calculations usually provide reliable data for relative stability of molecules having closely related structures. The calculations revealed that the observed conformer was energetically more favoured by 28 kcal/mol. Even if the energy difference is

considered to be largely exaggerated, the trend is consistent with the present observation. Detailed investigation into the orbital interactions was beyond the scope of this thesis.

If the allyl group is terminally substituted, the unsymmetrical ligand environment would imply that two conformers are still possible (**Figure-9**). In one, the terminal allyl substituent will reside close to the pyrazole while in the other, it will remain located near the vicinity of the oxygen.

FIGURE-9



Since the pyrazole contains a 3-Me group, in the former case, one would expect steric interaction dictating its stability.

The cinnamyl complex **3d** was obtained by the same preparative procedure described earlier. The room temperature NMR spectrum of this complex displayed broad lines indicating slow conformational interconversion. The rate was arrested at -40 °C, when the peaks were sharp (**Figure-10**). Clearly, two sets of conformers could be identified and assigned based on integration of peaks.

Significantly, one methyl singlet was shifted upfield from the rest by about 1.2 ppm. Such a shift could result from an anisotropic effect of the proximal phenyl ring of the allyl group (**Figure-11**). Thus, this upfield methyl singlet was assigned to the conformer where the phenyl substituent of the allyl group resides near the pyrazole. This was the minor conformer and the ratio of conformers was 3:4.

FIGURE-10

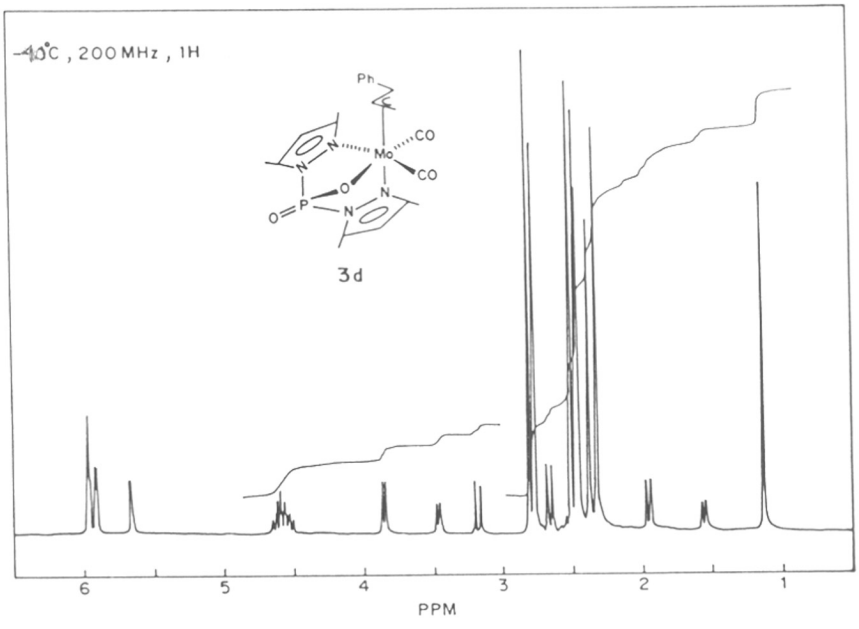
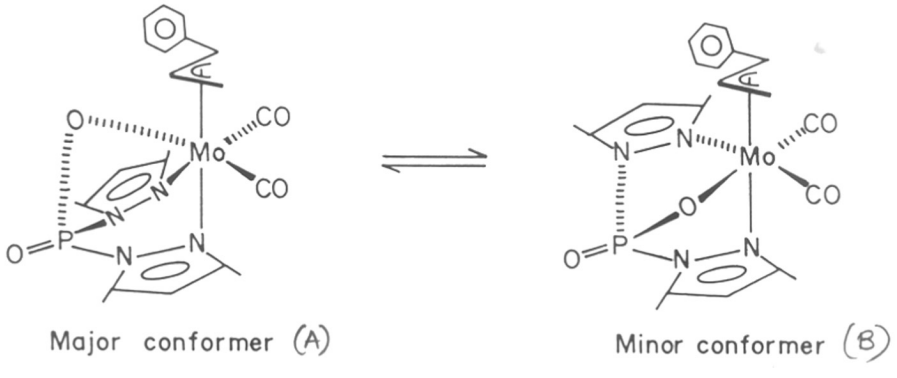


FIGURE-11

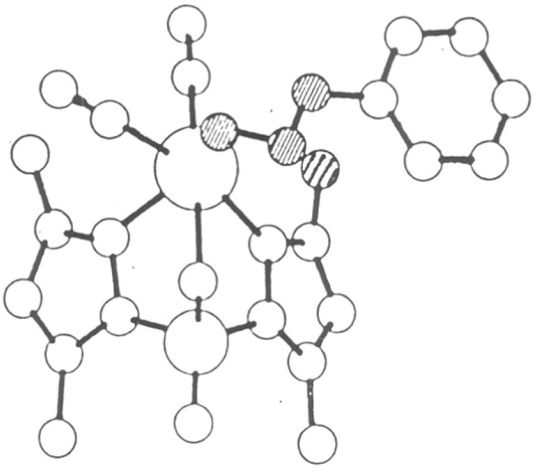
3d



It was noted, however, that a proximal Ph / Me steric interaction was not highly destabilising, as was perceived prior to experiment.

An X-ray structure determination of this complex revealed that only one conformer was present in the crystal, and that was the minor one (**Figure-12**).

FIGURE-12



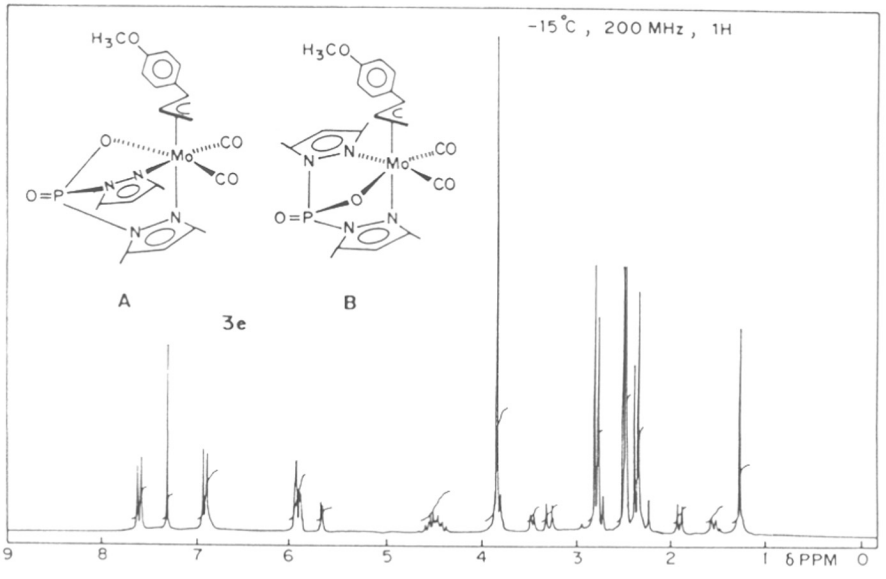
The X-ray structure solution was determined by Dr. S. S. Tavale and Dr. Mrs. V. Puranik, NCL, Pune.

While it was fortuitous to have the minor conformer structurally characterized beyond doubt, it was now possible to identify this conformer in solution from the upfield shift of the pyrazole methyl signal in related complexes. The allyl signals for both the conformers were identified with the help of 2-D NMR .The distance between the *ipso* carbon of the phenyl group and the proximal Me carbon was 3.22 A, i.e. they were within van der Waal's distance. It was surprising that such proximity did not result in severe steric destabilisation.

An analogous complex **3e** was similarly prepared, where the aromatic ring contained a *p*-OMe group. Two sets of signals were obtained at low temperature corresponding to two possible conformers (**Figure-13**).

In this case, the upfield methyl signal was observed at 1.25, and based on integration of signals, the ratio of conformers was found to be 1:1. Thus, the stability of the conformers were comparable. Also, this result further established that a Ph/Me interaction in these complexes was minimal despite the proximity of these two groups.

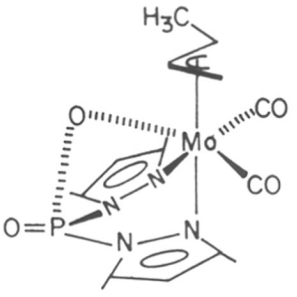
FIGURE-13



In recent times, C-H/π interaction has been identified as a stabilizing influence.[24] Such interaction is described to be between a C-H bond and a proximal π-bond.[25] It is possible that these complexes provide additional evidence for such an effect.

The corresponding crotyl complex **3f** showed sharp lines in the NMR spectrum indicating the presence of one conformer. Lowering the temperature had no effect on the line shape. The chemical shift of the allyl methyl doublet and the vicinal allyl proton confirmed that the methyl group adopted the *syn* orientation. It was tentatively concluded that the complex **3f** existed exclusively in the more stable conformation where the methyl group resided on the side of the basal oxygen. The Me/Me interaction between the allyl and the pyrazole could destabilize the other possible conformer (**Figure-14**).

FIGURE-14



3f

SUMMARY

A new class of molybdenum π-allyl complexes were prepared and structurally characterized by variable-temperature NMR spectroscopy and X-ray crystallography. The extent of steric interaction between a terminal substituent of the allyl group and the proximal 3-Me group of a pyrazole was probed. The present experimental observation appeared to indicate that a Ph/Me interaction was less severe than a Me/Me interaction.

EXPERIMENTAL:

Preparation of *tris*-(3,5-dimethyl-1-pyrazolyl) phosphine oxide 1

This compound has been prepared from potassium-3,5-dimethyl pyrazolide and phosphorus oxychloride in 65% yield. A modified procedure was used in the present case.

To a solution of 3,5-dimethyl pyrazole (12.66 g, 0.13 mol) and triethylamine (18.5 g, 0.18 mol) in benzene (125 ml) maintained at 0 to 5 °C, $POCl_3$ (8.2 g, 53.5 mmol) in benzene (25 ml) was added dropwise over a period of 30 minutes with stirring. The reaction mixture was stirred for 1h at room temperature and then heated under reflux for 10h (monitered by TLC). Then the mixture was cooled to room temperature, it was filtered and washed with dry benzene. Benzene was removed on a rotary evaporator. The colourless sticky residue so obtained was dissolved in CCl_4 (9 ml) and diluted with petroleum ether (50 ml). The slightly turbid solution was kept in a refrigerator for 15 days to furnish white crystals of compound **1** (8.5 g, 59%).

COLOUR	:-	Colourless Crystals
MP	:-	105 °C (lit.[5] 105 to 108 °C).
IR	:-	1560 (s); 1180 (s).
^{1}H NMR	:-	2.15 (s, 9H); 2.25 (s, 9H); 5.95 (d, 3H, J = 4Hz)
^{13}C NMR	:-	11.96; 13.61; 110.65; 110.82; 147.67; 147.91; 154.33; 154.64.
MS	:-	332 (M^+); 95(100%)

Preparation of metal complexes

Metal complexes of general formula L_2M were prepared by treating aqueous solution of metal salts with acetonitrile solution of ligands. Immediate precipitation of solids indicated formation of metal complexes.

Preparation of $Co^{(II)}$ complex

A solution of $Co(NO_3)_2$, $6H_2O$ (0.291 g, 1 mmol) in water (1 ml) and a solution of ligand **1** (0.8 g, 2.5 mmol) in acetonitrile (3 ml) was mixed. Immediate precipitation of pink coloured solid was noted. It was filtered, dried and recrystallized from hot ethanol to give pink crystals (0.236 mg) of CoII complexes.

IR :- 1560 (s). 1180 (s).

ANALYSIS :- $(C_{10}H_{14}N_4O_2P)_2Co$

Cal. C = 42.5; H = 4.9; N = 19.0.

Found C = 42.6; H = 4.8; N = 18.28.

Preparation of $Ni^{(II)}$ complex

To a solution of $NiCl_2$. $6H_2O$ (0.238 g, 1 mmol) in water (1 ml), a solution of ligand **1** (0.8 g, 2.5 mmol) in hot acetonitrile (3 ml)) was added. The pale green precipitate thus obtained was filtered. Then it was dried in vacuum and recrystallized from hot ethanol to give green crystals (0.186 mg) of Ni(II) complex.

IR :- 1560 (s). 1180 (s).

ANALYSIS :- $(C_{10}H_{14}N_4O_2P)_2Ni$.

Cal. C = 42.5; H = 4.9; N = 19.83.

Found C = 42.75; H = 4.98;

Preparation of $Cu^{(II)}$ complex.

To a solution of $CuSO_4$. $5H_2O$ (0.250 g, 1 mmol) in hot water (1 ml) a solution of ligand **1** (0.8 g, 2.5 mmol) in acetonitrile (3 ml) was added. Immediate precipitation of blue solid was observed. This powdery solid was filtered, dried under vacuum and recrystallized from hot ethanol to give 0.214 g of Cu(II) complex.

IR :- 1560 (s). 1180 (s).

ANALYSIS :- $(C_{10}H_{14}N_4O_2P)_2Cu$.

Cal. C = 42.1; H = 4.9; N = 19.6.

Found C = 41.9; H = 4.0; N = 19.4.

Preparation of $Cu^{(I)}$ complex

A solution of 190.5 g (1 mmol) cuprous iodide in hot water (1 ml) was mixed with a solution of 0.8 g of ligand **1** in hot acetonitrile (3 ml). Yellowish green precipitate thus appeared was filtered, dried under vacuum to get 0.082 g. of complex.

IR :- 1560 (s). 1180 (s).

^{1}H NMR :- 2.45 (s, 9H); 2.5 (s, 9H); 5.95-6.00 (bs, 3H).

ANALYSIS :- $C_{15}H_{21}N_6OPCuI$.

Cal. C = 34.4; H = 4.01; N = 16.07.

Found C = 34.5; H = 3.85; N = 15.59.

Preparation of *tris*-(3,5-dimethyl-1-pyrazolyl) phosphine oxide tricarbonylmolybdenum(0) 2

Molybdenum hexacarbonyl (2 g, 7.56 mmol) was suspended in acetonitrile (50 ml) containing ligand **1** (3.6 g, 10.84 mmol). It was heated under reflux for 2h. Precipitation of a yellow solid commenced after 0.5h. It was then cooled to room temperature. The solid was filtered, washed with CH_3CN (10 ml) and dried in air to afford yellow crystals of the complex **2** (2.24 g, 58%).

Insolubility of this complex in standard NMR solvents did not permit recording of ^{1}H or ^{13}C NMR spectra in solution. The ^{13}C NMR was recorded in the solid state by MAS technique.

COLOUR :- Bright yellow

MP :- Above 250 °C (decomposition)

IR :- 1920(sh), 1910(s), 1790(s), 1580(s), 1180(s).

^{13}C NMR (Solid) :- 12.7; 14.2; 14.9; 15.6; 16.2; 17.3; 108.9; 112.3; 150.2; 151.9; 161.5; 227.5; 229.1; 231.1; 232.4; 234.4.

ANALYSIS :- $C_{18}H_{21}MoN_6O_4$

Cal. C = 42.18; H = 4.10; N = 16.40.

Found C = 42.15; H = 4.05; N = 16.27.

Preparation of Molybdenum [*bis* (3,5-dimethyl-1H-pyrazol-1-yl)phosphinato] dicarbonyl (η^3-2-propenyl) complex 3a

Molybdenum hexacarbonyl (1 g, 3.78 mmol) was taken in a two neck 50 ml round bottom flask under argon. To this allyl chloride (2 ml, excess) and acetonitrile (15 ml) was added. The flask was evacuated and purged with argon several times and it was heated under reflux on a water bath for 5h. The formation of *bis* acetonitrile π-allyl Mo $(CO)_2$ chloro complex resulted in an orange coloured solution. The reaction flask was then cooled carefully under argon to room temperature. A solution of ligand **1** (1.3 g, 3.9 mmol) in acetonitrile (5 ml) was then added to the reaction mixture with a syringe. The reaction mixture was refluxed on a water bath for 15 minutes, cooled and poured into distilled and degassed water (100 ml). The yellow precipitate was collected by filteration and dried under vacuum (0.882 g, 52%). Analytically pure crystals of complex **3a** were obtained by crystallization from aqueous acetonitrile.

COLOUR :- Bright orange.

MP :- Above 260 °C (decomposition)

IR :- 1940(s), 1840(s), 1560(m), 1180(s).

^{1}H NMR :- (-50 °C, 90MHz, $CDCL_3$); 1.40 (bd, 1H); 1.70 (bd, 1H); 2.40 (bs, 6H); 2.45 (s, 3H); 2.90 (s, 3H); 3.40 (bm, 2H); 3.75 (bm, 1H)

^{13}C NMR :- (75.5MHz, $CDCl_3$); 11.5; 14.3; 55.2; 65.3; 78.6; 109.5; 146.2; 147.4; 155.8; 157.2; 227.4; 228.6.

^{31}P NMR :- (121.6MHz, $CDCl_3$); -12.09.

^{95}Mo NMR :- (19.554MHz, $CDCl_3$); -787.6.

ANALYSIS :- $C_{15}H_{19}MoN_4O_4P$

Cal. C = 40.35; H = 4.25; N = 12.55.

Found C = 40.06; H = 4.17; N = 12.04.

Preparation of Molybdenum [*bis* (3,5-dimethyl-1H-pyrazol-1-yl)phosphinato] dicarbonyl [1,2,3, ... n]-2-methyl-2-propenyl complex 3b

Molybdenum hexacarbonyl (1 g, 3.78 mmol) was taken in a two necked flask equipped with a rubber septum and reflux condenser under argon. To this flask, 2-methallyl chloride (1 ml, excess) and acetonirile (15 ml) were added through syringe. The reaction mixture was heated under reflux for 5h to obtain clear orange solution of *bis* acetonitrile π 2-methallyl Mo $(CO)_2$ chloro complex. A solution of ligand **1** (1.3 g, 3.9 mmol) in acetonitrile (5 ml) was added to the refluxing solution through a syringe. Heating was continued for additional 10 minutes and then the flask was cooled to room temperature under argon. The reaction mixture was then poured into distilled and deaerated water (90 ml). The bright yellow precipitate was collected by filteration. Recrystallization from acetonitrile-water afforded yellow crystalline product **3b** (0.77 g, 44%).

COLOUR :- Bright yellow.

MP :- Above 260 °C (decomposition)

IR :- 1925(s), 1830(s), 1560(m), 1180(s).

^{1}H NMR :- (25°C, 90MHz, $CDCl_3$). 1.40 (bs, 2H); 1.75 (s, 3H); 2.40 (bs, 6H); 2.60 (bs, 6H); 3.3 (bs, 2H); 5.90 (d, J = 3Hz, 2H).

^{13}C NMR :- (75.5MHz, $CDCl_3$) 11.4; 14.2; 19.6; 59.4; 88.4; 109.5; 146.6; 156.1; 226.9; 228.2.

^{31}P NMR :- (121.6MHz, $CDCl_3$) -12.13.

^{95}Mo NMR :- (19.554MHz, $CDCl_3$) -746.5.

ANALYSIS :- $C_{16}H_{21}MoN_4O_4P$

Cal. C = 41.75; H = 4.56; N = 12.17.

Found C = 41.74; H = 4.58; N = 12.10.

Bromination of α methyl styrene

To a solution of α-methyl styrene (9.44 g, 80 mmol) in carbontetra chloride (5 ml), freshly recrystallized NBS (90 g, 50 mmol) was added and the reaction mixture was slowly heated in an oil bath till the temperature of the oil bath reached 160 °C. At this temperature the reaction commenced spontaneously. The flask was raised from the oil bath. After 10 minutes, the vigorous reaction subsided then

carbontetrachloride (20 ml) was added and the mixture was heated under reflux for 30 minutes. It was then cooled to room temperature and filtered (*caution :- lacrimater).* The succinimide was washed with carbontetrachloride (20 ml). The concentration of the filtrate on the rotary evaporator furnished a yellow oily residue. It was fractionally distilled to remove α-methyl styrene (b.p. 35°C / 1mm) (4.1g). The fraction collected at 90-95 °C / 1mm was found to be of pure 2-phenyl-3-bromo-1-propene (4.6 g, 52%).

Preparation of Molybdenum [*bis* (3,5-dimethyl-1H-pyrazol-1-yl)phosphinato] dicarbonyl [1,2,3, ... n]-2-phenyl-2-propenyl complex 3c.

A mixture of molybdenum hexacarbonyl (1 g, 3.78 mmol), 2-phenyl-3-bromo-1-propene (0.75 ml, excess) and acetonitrile was heated under reflux for 5h. A deep red solution, thus obtained, was cooled to room temperature under argon. Ligand **1** (1.3 g, 3.9 mmol) was dissolved in 5 ml acetonitrile and added to the reaction mixture through a syringe. The solution was heated under reflux for 10 minutes and then cooled to room temperature. On pouring it into water (100 ml), a crude solid was obtained. Crystallization from toluene-hexane afforded the crystalline complex **3c** (0.436 g, 23%).

COLOUR :- Bright orange

MP :- Above 260 °C(decomposition)

IR :- 1940(s), 1850(s), 1560(m), 1180(s).

^{1}H NMR :- 1.45 (bs, 2H); 2.10 (s, 3H); 2.25 (s, 3H); 2.50 (s, 3H); 2.80 (s, 3H); 3.90 (bs, 1H); 4.20 (bs, 1H); 5.75 (bs, 1H); 5.90 (bs, 1H); 7.05 - 7.25(m, 5H).

^{13}C NMR :- (75.5 Hz, $CDCl_3$) 11.1; 14.1; 55.1; 57.4; 85.3; 109.1; 124.3; 126.6; 135.9; 147.1; 154.5; 156.5, 225.1, 227.4.

^{31}P NMR :- (121.6MHz, $CDCl_3$) -12.46.

^{95}Mo NMR :- (19.554MHz, $CDCl_3$) -762.3.

ANALYSIS :- $C_{21}H_{23}MoN_4O_4P$

Cal. C = 48.27; H = 4.40; N = 10.72.

Found C = 48.27; H = 4.38; N = 10.76.

Preparation of cinnamyl chloride from cinnamyl alcohol

Triphenylphosphine (34.09 g, 0.13 mmol) was added portionwise to a stirred solution of cinnamyl alcohol (13.41 g, 0.1 mmol) in CCl_4 ((90 ml, CCl_4 was passed through neutral alumina column before use). The flask was heated under reflux for 2h on a water bath. After cooling to room temperature, petroleum ether (50 ml) was added and filtered. Residue of triphenylphosphine oxide was washed with petroleum ether (50 ml) and the solvent was removed from the turbid solution. Petroleum ether (100 ml) was again added to the residue and left overnight at 0 °C. The residual triphenylphosphine oxide was filtered and the solvent was removed from the filtrate to get a yellow oily liquid as crude product. It was distilled under vacuo and the constant boiling fraction (90 °/5mm) to get 11.2g (73.2%) of the pure product.

Preparation of the cinnamyl complex 3d

Molybdenumhexacarbonyl (0.528 g, 2 mmol) was taken in a two necked flask fitted with a septa and a reflux condenser connected to an argon balloon. Cinnamyl chloride (0.5 ml, excess) and acetonitrile (20 ml) were added to the flask through a syringe. The reaction mixture was heated under reflux for 5h to obtain a red solution of *bis* acetonitrile π cinnamyl Mo $(CO)_2$ chloro complex. The reaction mixture was cooled to room temperature and a solution of ligand **1** (0.996 g, 3 mmol) in acetonitrile (10 ml) was added with a syringe. After stirring at room temperature for 10 min degassed water (2 ml) was added to the reaction mixture till slight turbidity appeared. The reaction mixture was preserved under argon at 0°C for 48h. The orange crystals deposited in the flask were filtered and washed with 50% aq. acetonitrile (10 ml), dried under vacuo to obtain complex **3d** (0.505 g, 48.4%) as an orange crystalline solid.

COLOUR :- Bright orange

MP :- 239 °C (decomposition)

IR :- 1930(s), 1840(s), 1560(m), 1170(s).

^{1}H NMR :- (200 MHz, -31 °C, $CDCl_3$):

:- **Conformer-A**

1.90 (d, 1H, $J_{HA\text{-}HC}$ = 10Hz); 2.32 (s, 3H); 2.50 (s, 3H); 2.51 (s, 3H); 2.58 (s, 3H); 2.65(d, 1H, $J_{HA'\text{-}HC}$ = 10Hz); 3.85 (d, 1H, $J_{HS\text{-}HC}$ = 6Hz); 4.60 (m, 1H); 5.90 (d, 1H, $J_{P\text{-}H}$ = 2Hz); 5.97 (d, 1H, $J_{P\text{-}H}$ = 2Hz)

:- **Conformer-B**

1.15 (s, 3H); 1.55 (d, 1H, $J_{HA\text{-}HC}$ = 10Hz); 2.44 (s, 3H); 2.80 (s, 3H); 2.83 (s, 3H); 3.17(d, 1H, $J_{HA'\text{-}HC}$ = 10Hz); 3.45 (d, 1H, $J_{HS\text{-}HC}$ = 6 Hz); 4.60 (m, 1H); 5.65 (d, 1H, $J_{P\text{-}H}$ = 2Hz); 5.97 (s, 1H).

6.6 to 7.7 (m, 5H) **for both isomers.**

^{13}C NMR :- (200MHz,-31 °C, $CDCl_3$) 11.7; 12.1; 14.6; 49.4; 62.3; 89.2; 109.2; 110.3; 125.2, 127.4, 127.9, 128.3, 130.3, 136.9, 137.7, 145.6; 146.0; 147.2, 147.3, 148.0, 155.7; 156.6; 157.1, 159.1, 229.3; 230.0, 230.1, 231.7.

ANALYSIS :- $C_{16}H_{21}MoN_4O_4P$

Cal. C = 48.27; H = 4.4; N = 10.73.

Found C = 48.55; H = 4.39; N = 10.6.

Preparation of Ethyl p-methoxy cinnamate

Zinc wool (8 g, 0.12 mmol), polished with sand paper and dried in an oven (110 °C) overnight, was cut into small pieces and placed in a three necked flask equipped with a condenser, a $CaCl_2$ guard tube and a dropping funnel. A solution of *p*-anisaldehyde (16.34 g, 0.12 mmol) and ethylbromo acetate (16.7 g, 0.1 mmol) in benzene (16 ml) and ether (4 ml) was added to the dropping funnel. Reaction flask was kept in hot waterbath and a 5 ml portion of the above solution was added. The reaction mixture was stirred vigorously. After the reaction was set addition was continued dropwise in such a rate that gentle reflux was maintained (15 minutes). The reaction mixture was further heated for 30 minutes at 100°C. It was cooled to room temperature and then in an ice bath and then 40 ml of 10% H_2SO_4 was added dropwise to quench the reaction. It was stirred for 15 minutes and the layers were separated. Aqueous layer was washed with 30 ml of ether and the ether extract was

combined with the organic layer. Washing with brine and removal of solvent gave the crude hydroxy ester as yellow oil (25 ml). The oil was dissolved in dry benzene (120 ml) and refluxed with a catalytic amount of *p*-toluenesulfonic acid in a dean-stark apparatus for 4h. The dehydration reaction was monitered by TLC. Removal of benzene followed by column chromatography with silica gel afforded pure Ethyl *p*-methoxycinnamate (20.1 g, 81%)

Preparation of *p*-methoxy cinnamyl alcohol

Ethyl *p*-methoxycinnamate (4 g, 19.4 mmole) was dissolved in dry ether (80 ml) and lithium aluminium hydride (0.6 g, 15.7 mmole) was added in portions. The reaction mixture was heated under reflux for 1 hour. The flask was cooled in ice bath. Water (1 ml), 15% NaOH (1 ml) and water (3 ml) were added successively by dropping funnel with stirring. Then tartaric acid solution (2 g. in 10 ml water) was added. After ether extraction, drying with Na_2SO_4 and removal of solvent afforded yellow oil which, upon column chromatography with silica gel afforded (2.1 g, 66%) of *p*-methoxy cinnamyl alcohol.

Preparation of *p*-methoxycinnamyl chloride

Triphenylphosphine (7.86 g, 30 mmol) was added portionwise to a stirred solution of *p*-methoxycinnamyl alcohol (4 g, 24.4 mmol) in carbontetr achloride (80 ml). The reaction mixture was heated under reflux and monitered by TLC After completion of the reaction (2h), CCl_4 (50 ml) was removed by distillation. It was then cooled, diluted with petroleum ether (40 ml) and filtered to remove the solid. The filtrate was concentrated and the residue was distilled under high vacuum to get *p*-methoxy cinnamyl chloride as yellowish oil (1.7 g, 38%).

Preparation of *p*-methoxycinnamyl complex 3e

A mixture of molybdenum hexacarbonyl (0.264 g, 1 mmol), *p*-methoxycinnamyl chloride (0.31 g, 1.7 mmol) and acetonitrile (15 ml) was heated under reflux for 5h to obtain a dark red solution of *bis* acetonitrile π-p-methoxycinnamyl Mo $(CO)_2$ chloro complex. A solution of ligand **1** (0.5 g, 1.5 mmole) in acetonitrile (5 ml) was added to this refluxing solution and refluxsation was continued for 5 minutes. After cooling to room temperature and partial removal of solvent afforded dark brown liquid, which was added in ice cold degassed water (100 ml).The gummy solid was separated

which was redissolved in toluene (100 ml). The toluene solution was concentrated to 5 ml and kept in a jar containing pet ether for recrystallization. Brown crystals were obtained after 48 h. They were collected by filteration and dried to afford the desired complex **3e** (49 mg, 9%).

COLOUR :- Brown.

MP :- Above 260 °C (decomposition)

IR :- 1920(s), 1840(s), 1560(m), 1180(s).

^{1}H NMR :- (200 MHz, -15 °C, $CDCl_3$):

:- **Conformer-A**

1.90 (d, 1H, J_{HA-HC} = 10Hz); 2.30 (s, 3H); 2.48 (s, 3H); 2.50 (s, 3H); 2.55 (s, 3H); 2.80 (bs, 1H); 3.80 (bs, 1H); 3.85 (s, 3H); 4.50 (m, 1H); 5.90 (d, 1H, J_{P-H} = 2Hz); 5.95 (bs, 1H).

:- **Conformer-B** 1.25 (s, 3H); 1.55 (d, 1H, J_{HA-HC} = 10Hz); 2.45 (s, 3H); 2.80 (s, 3H); 2.82 (s, 3H); 3.30 (d, 1H, J_{HA-HC} = 10Hz); 3.45 (m, 1H); 3.85 (s, 3H); 4.50 (m, 1H); 5.70 (d, 1H, J_{P-H} = 2Hz); 5.95 (bs, 1H).

6.60 to 7.70 (m, 5H) **for both conformers.**

ANALYSIS :- $C_{22}H_{25}MoN_4O_5P$

Cal. C = 47.82; H = 4.52; N = 10.73.

Found C = 47.71; H = 5.34; N = 9.7.

Preparation of crotyl chloride from crotyl alcohol

In a 50 ml RB flask equipped with a 50 ml dropping funnel and an argon balloon, PCl_3 (11 g, 80 mmol) was placed and cooled in an ice water bath. A mixture of crotyl alcohol (14.4 g, 200 mmol) and pyridine (4.45 g, 56.2 mmol) was added dropwise with stirring over a period of 15 min. After the completion of the addition, the ice bath was replaced by oil bath and the crotyl chloride formed was distilled (bath temp. 70 - 100 °C). The distillate was washed with water (10 ml) and 5% aq K_2CO_3 to remove traces of HCl. It was dried over anhydrous K_2CO_3 and fractionally distilled. The distillate collected at 60 - 80 °C provided pure crotyl chloride (9.36 g, 52%).

Preparation of crotyl complex 3f

A mixture of molybdenum hexacarbonyl (0.528 g, 2 mmol), crotyl chloride (1 ml, excess) and acetonitrile (20 ml) was heated under reflux for 5h to afford an orange solution of *bis* acetonitrile π allyl Mo $(CO)_2$ chloro complex. The reaction mixture was cooled to room temperature and ligand **1** (0.835 g, 2.5 mmol) in acetonitrile (10 ml) was added to it with a syringe. The reaction mixture was stirred for 10 min and concentrated to about 10 ml. It was poured in to an ice cold water (100 ml) and the yellow sticky mass separated was extracted with dichloromethane (25 ml). The residue obtained after the removal of dichloromethane was crystallized from acetone - water to furnish yellow crystals of complex **3f** (0.228 g, 24.7%).

COLOUR :- Bright yellow

MP :- Above 260 °C (decomposition)

IR :- 1940(s), 1850(s), 1560(m), 1180(s).

^{1}H NMR :- (200 MHz, 25 °C, $CDCl_3$): 1.55 (s, 1H); 1.90 (m, 1H); 2.00 (d, 3H, $J_{H\text{-}CH_3}$ = 6Hz); 2.30 (bm, 9H); 2.70 (s, 3H); 3.5 (d, 1H, $J_{H_c\text{-}H_s}$ = 6Hz); 3.70 (m, 1H); 5.85 (d, 2H, $J_{P\text{-}H}$ = 2Hz).

^{13}C NMR :- (200MHz,25°C, $CDCl_3$) 11.4; 11.7; 14.2; 14.4; 16.0; 62.1; 73.9; 81.6; 109.3; 110.0; 146.1; 147.4; 155.7; 157.4; 229.17; 230.01.

ANALYSIS :- $C_{16}H_{21}MoN_4O_4P$

Cal. C = 41.75; H = 4.56; N = 12.17.

Found C = 41.73; H = 4.52; N = 11.84.

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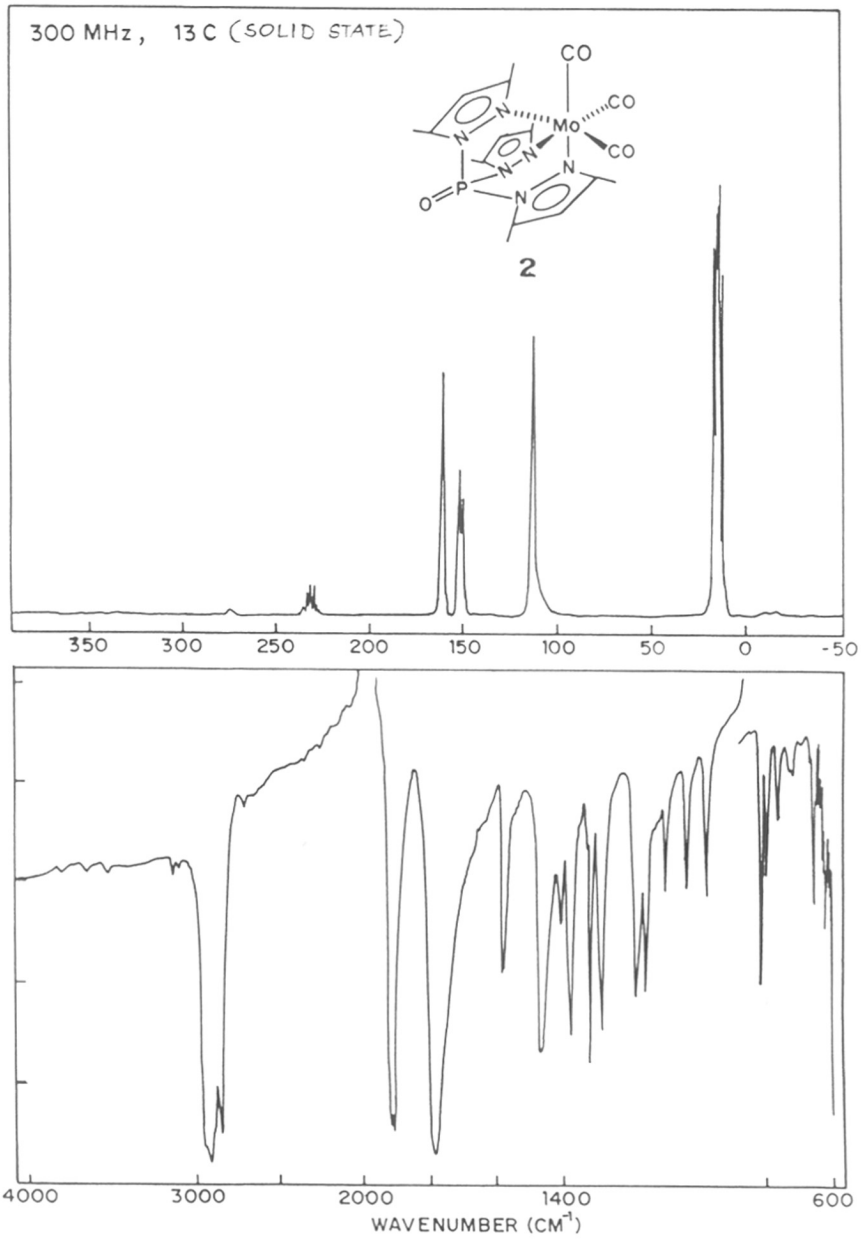
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CO
CO
Mo
N
N
N
N
N
N
O=P
2
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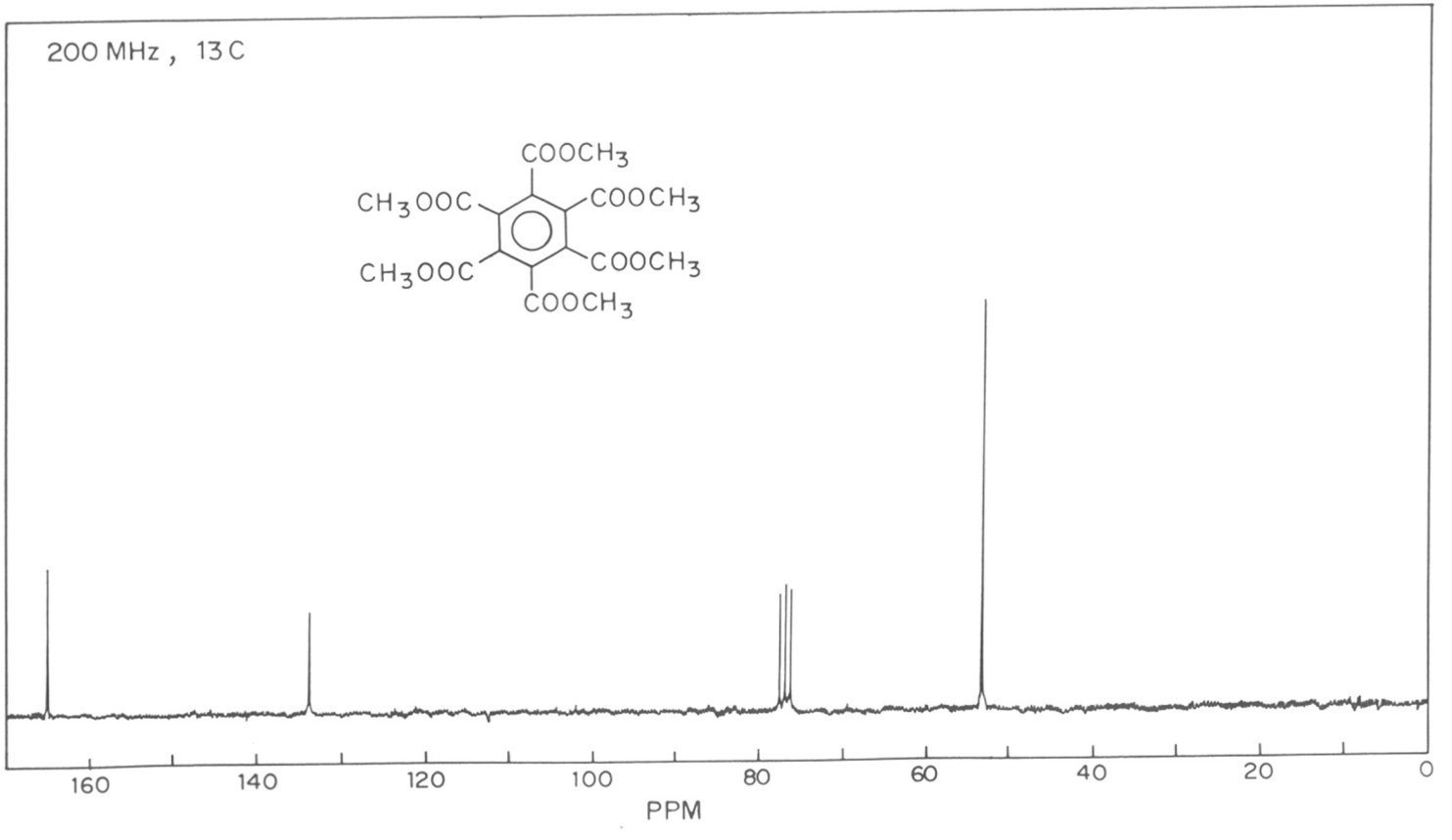
300
250
200
150
100
50
0
-50
4000
3000
2000
1400
600
WAVENUMBER (CM-1)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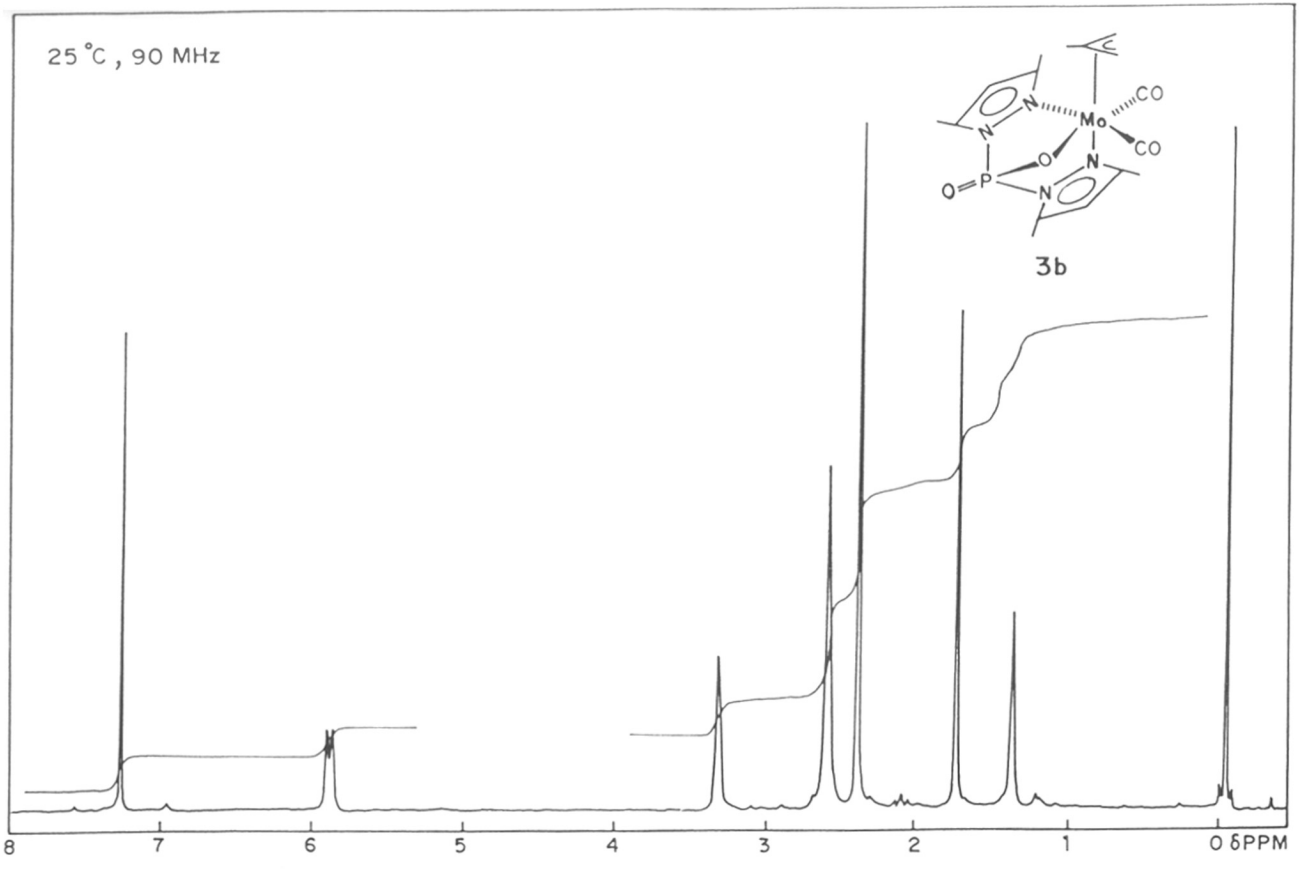
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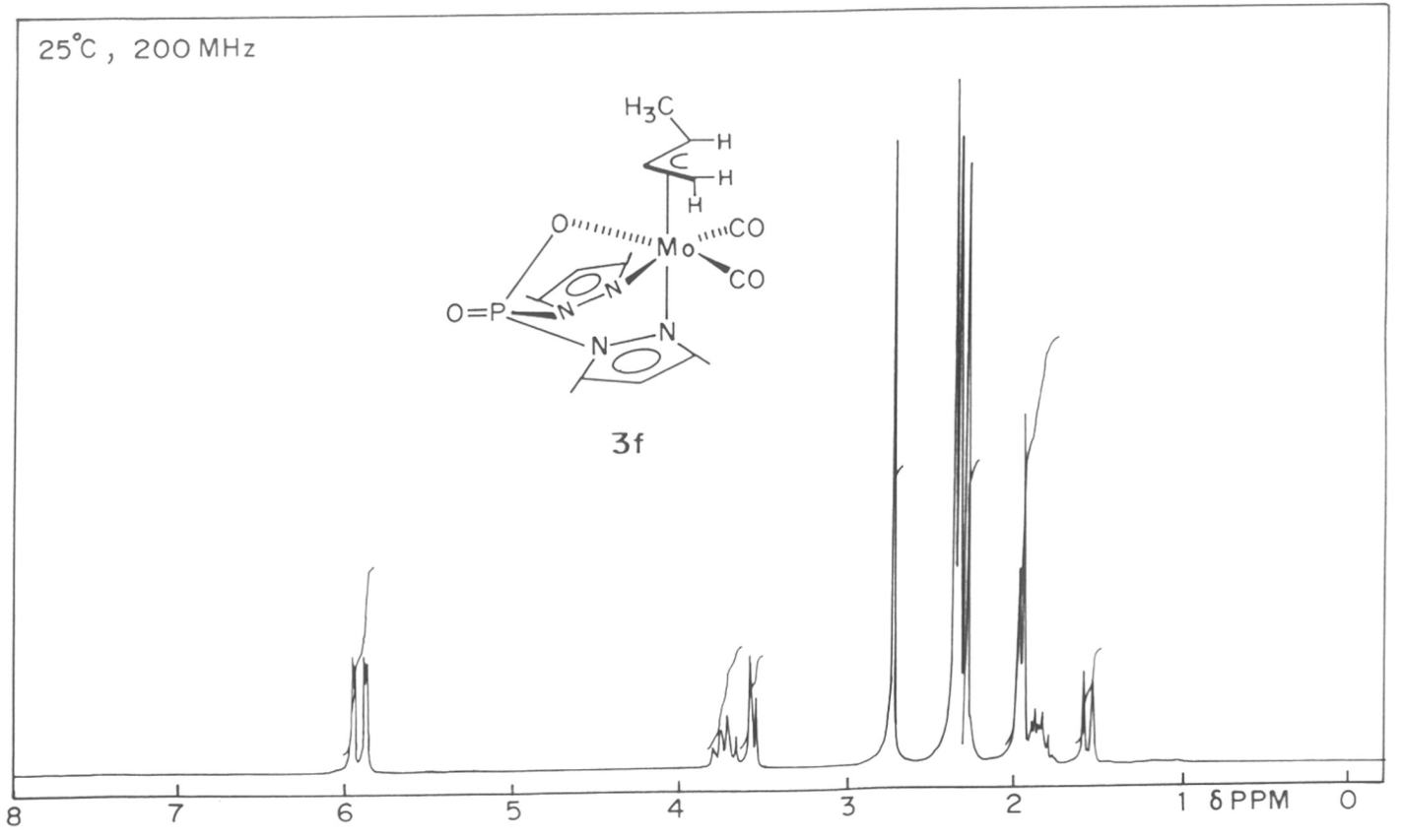
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H
H
O
Mo
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7
6
5
4
3
2
1
δ PPM
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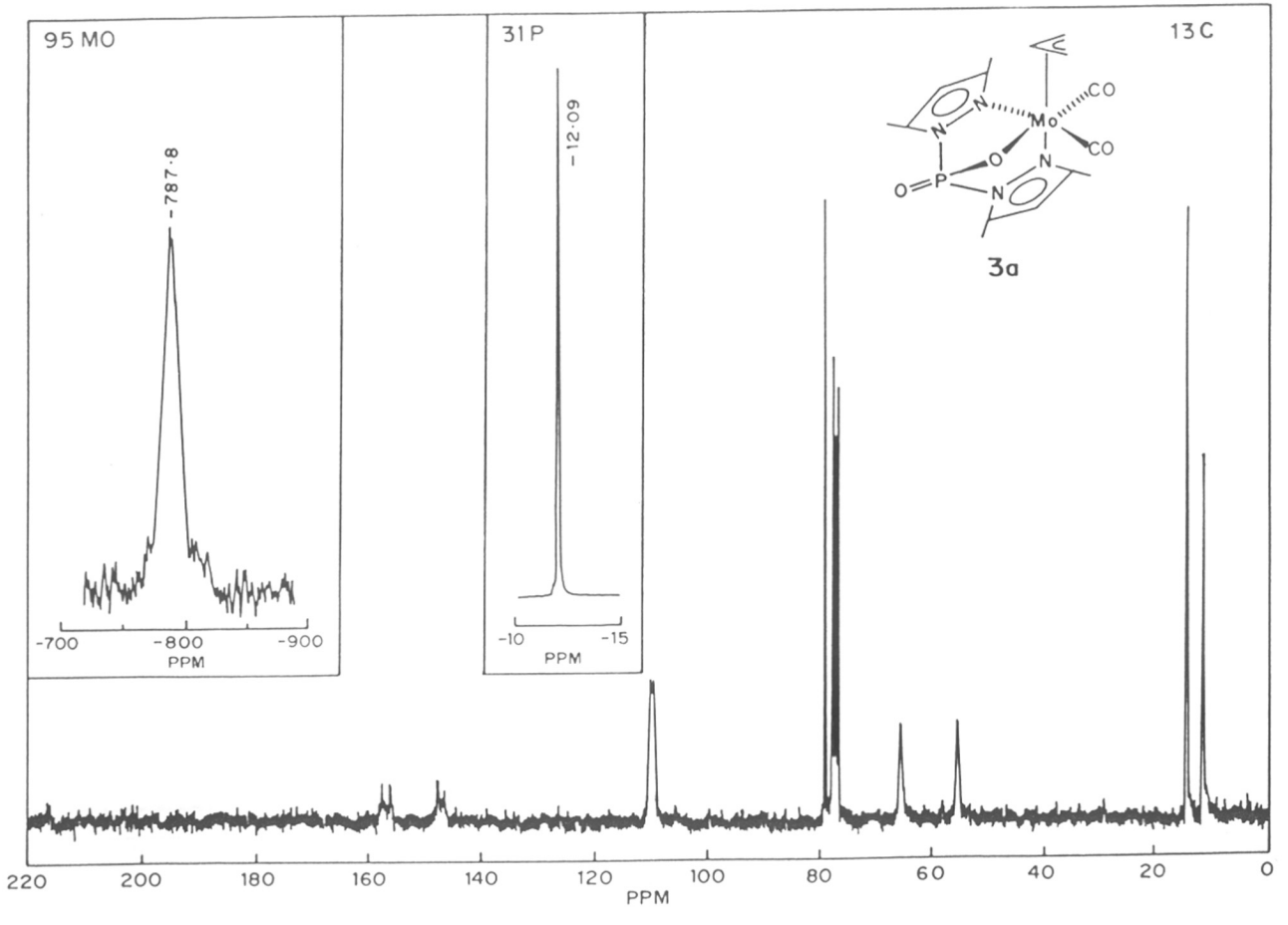
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-700
-800
-900
PPM
31P
-12·09
-10
-15
PPM
13C
CO
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Mo
O
N
N
N
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O=P
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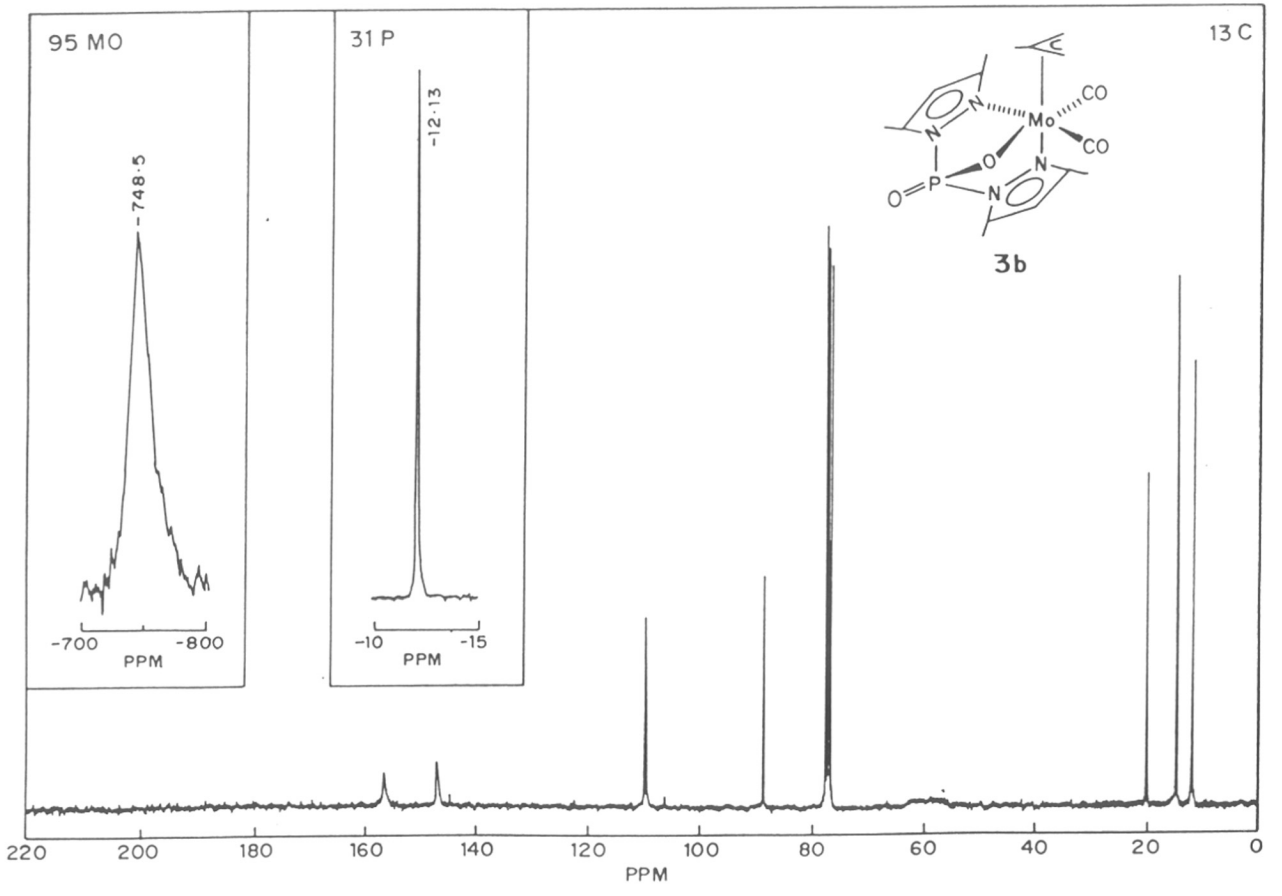
20
0
PPM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-700
-800
PPM
31 P
-12·13
-10
-15
PPM
13 C
CO
CO
Mo
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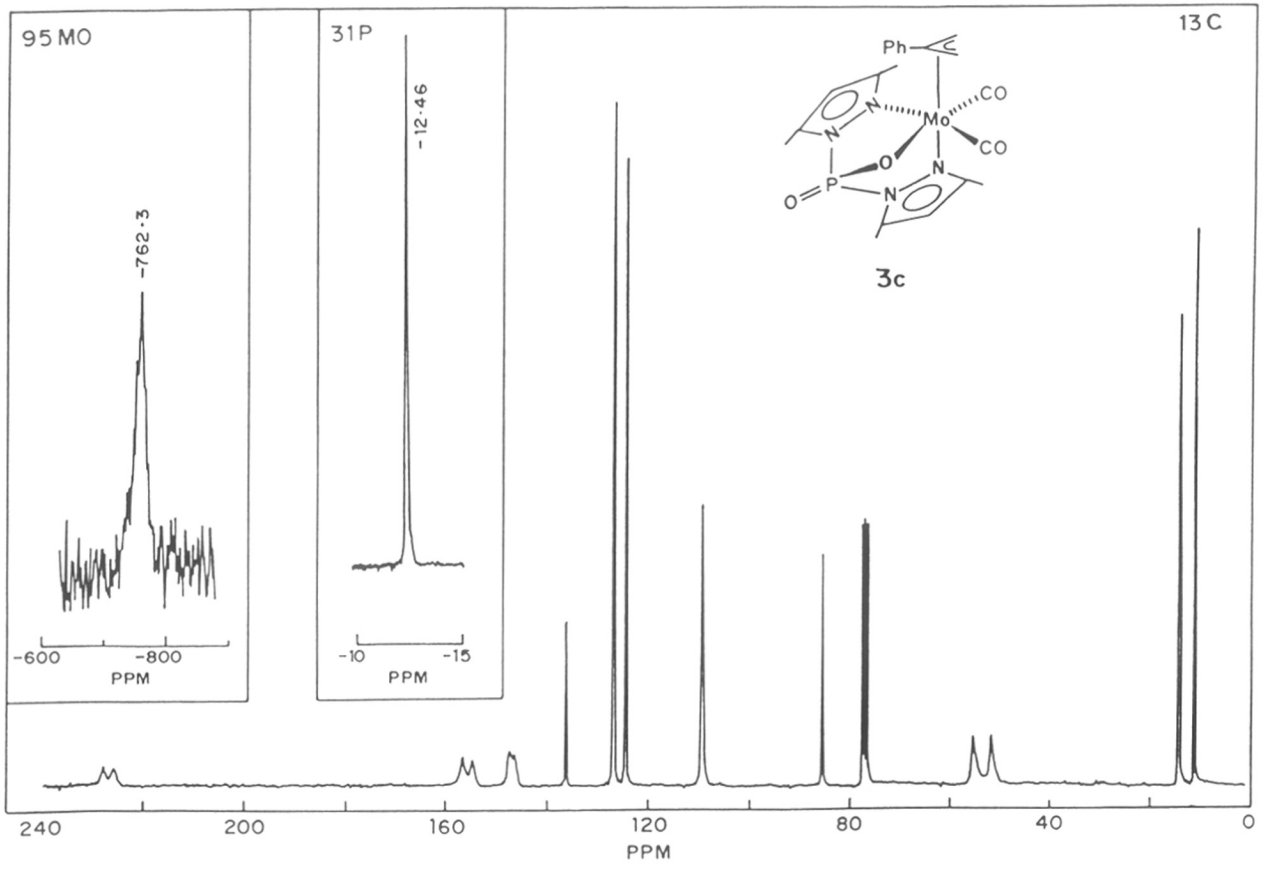
PPM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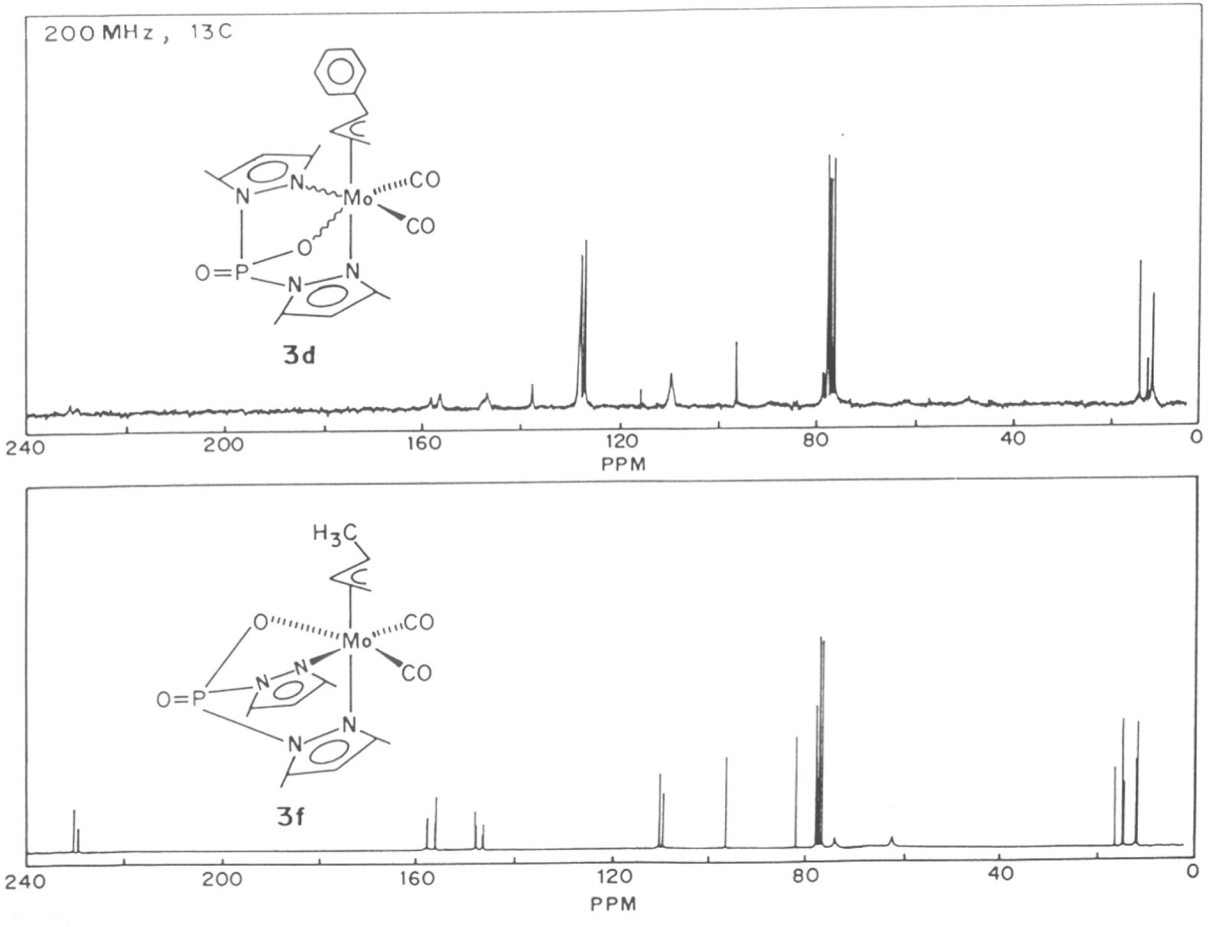
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240
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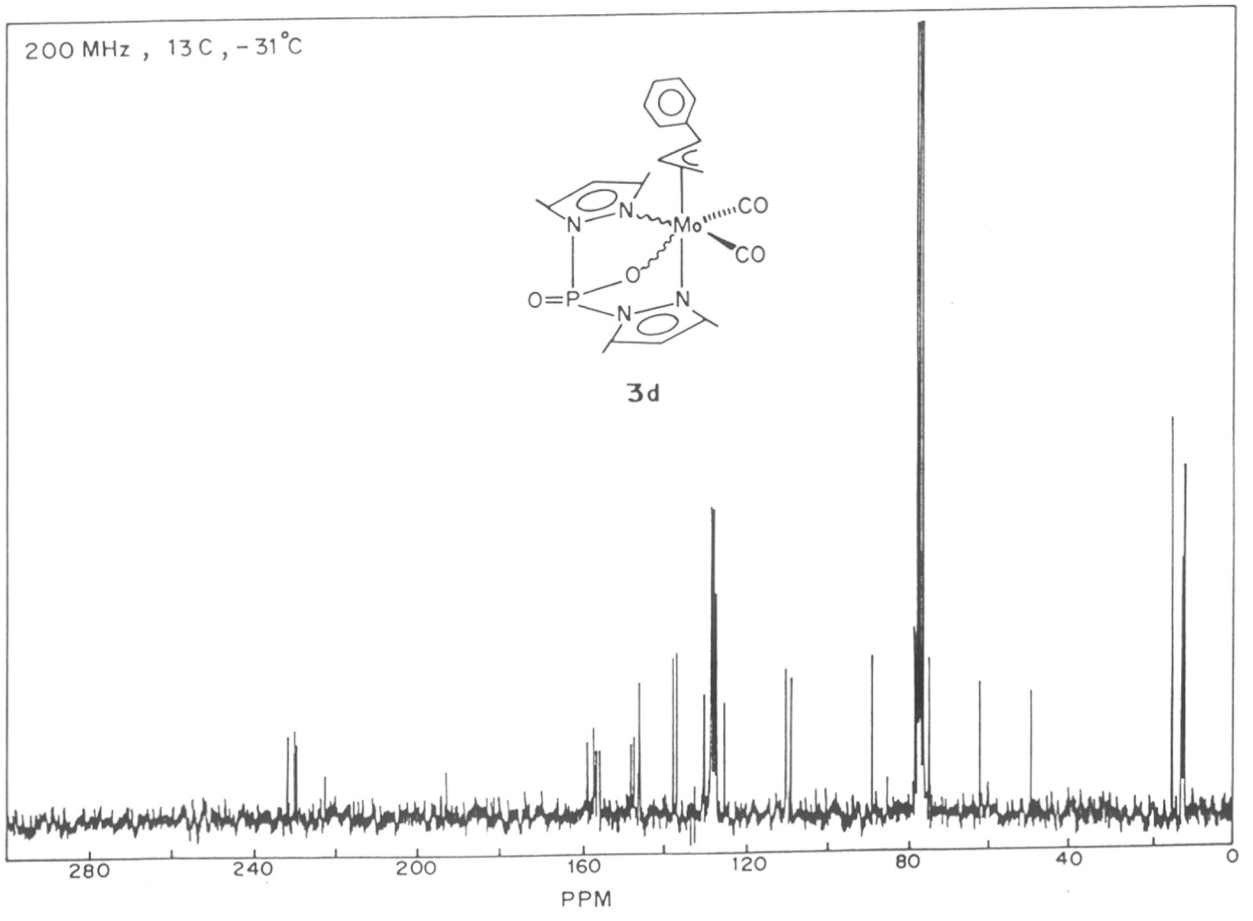
PPM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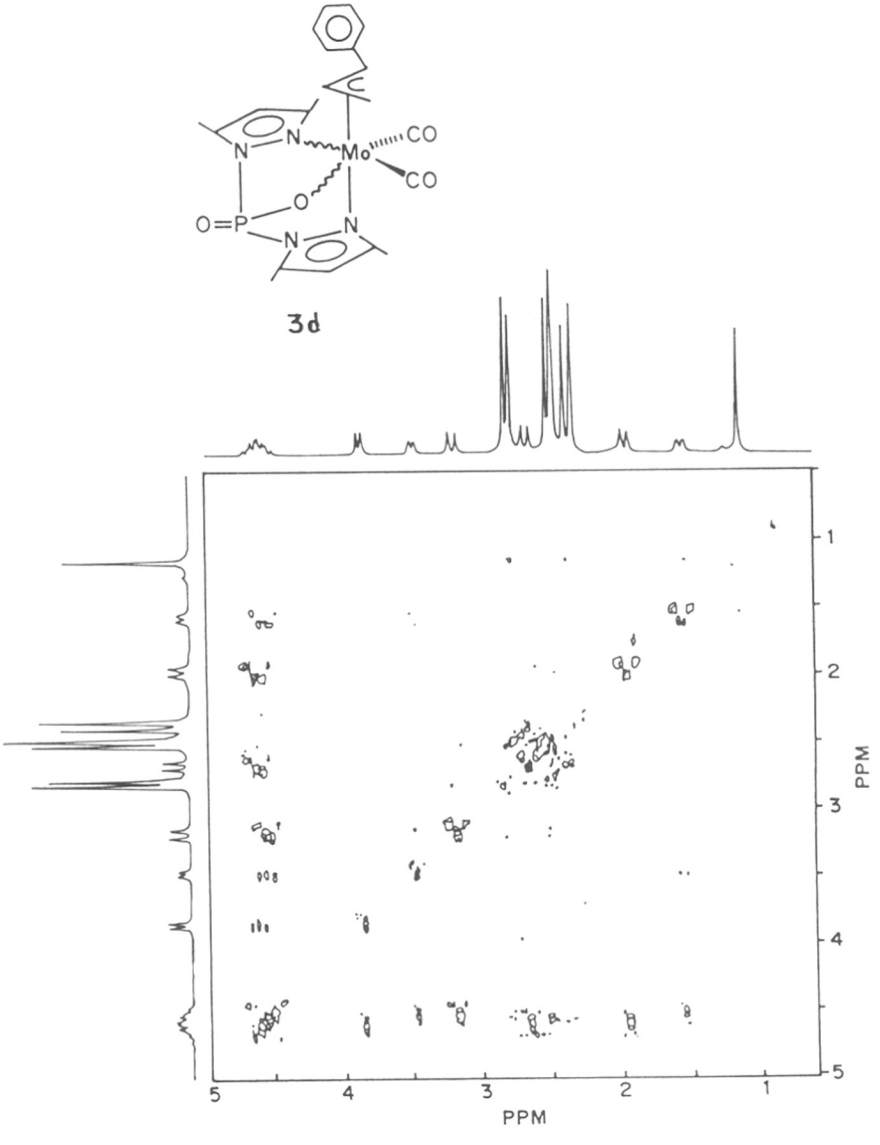
PPM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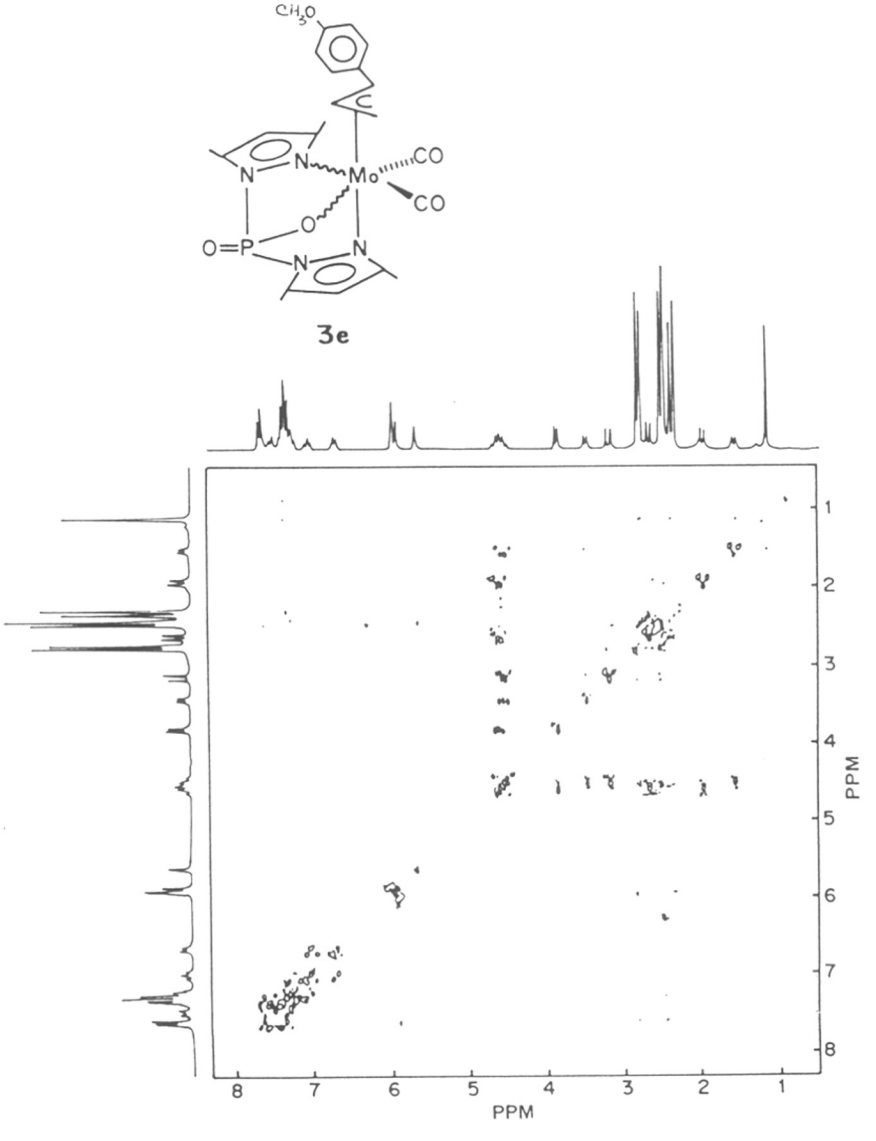
PPM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8
PPM
8
7
6
5
4
3
2
1
PPM

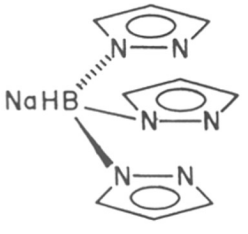
CHAPTER - III

STERIC EFFECT OF PYRAZOLE SUBSTITUENT ON THE CONFORMATION OF MOLYBDENUM Π-ALLYL COMPLEXES

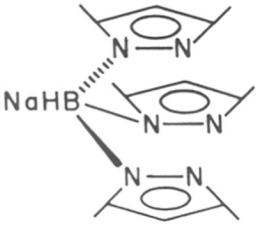
INTRODUCTION

In continuation with the question of steric interaction between the terminal allyl substituent and the proximal pyrazole 3-Me group, it was decided to examine the stereochemistry of η^3-crotyl and η^3-cinnamyl complexes of molybdenum (complexes **3** and **4**) containing hydridotripyrazolyl borate **1** and hydrido*tris*(3,5-dimethylpyrazolyl)borate **2** ligands (**Figure-1**), as depicted below.

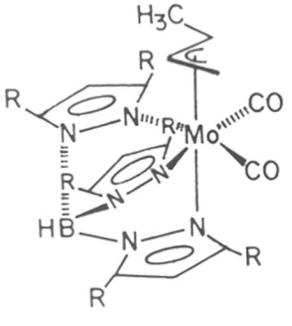
FIGURE-1



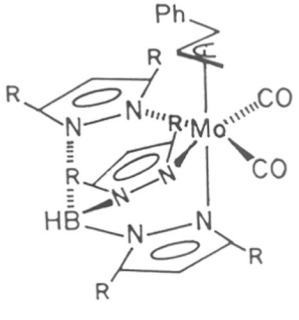
Ligand 1



Ligand 2



R
3a: H
3b: CH_3



R
4a: H
4b: CH_3

Since both the ligands **1** and **2** are symmetrical, a *trigonal twist* of the ligand would not affect the η^3-allyl environment. Hence, the ^{1}H NMR spectral lines corresponding to the allyl protons would remain sharp and distinct. Also, for the

ligand **2**, there are two equatorial pyrazoles, both containing 3-Me groups. Thus, steric interaction with the terminal substituent of the π-allyl ligand cannot be avoided. A comparison of the NMR spectra of the same allyl group in two ligand environments (one without and one with proximal 3-Me of pyrazole) should indicate steric consequence of Me/Me and Me/Ph interaction, as the case may be.

RESULTS

Preparation of ligands

Ligands **1** and **2** were prepared by Trofimenko's procedure.[1] Sodium borohydride and pyrazole or 3,5-dimethylpyrazole (3.5 equivalents) was ground together into a fine powder and slowly heated in an oil bath. Gas evolution ceased around 200°C to 240°C indicating completion of the reaction. The melt was cooled to 160°C and it was poured into toluene with stirring. Ligands were obtained in pure form as powdery solids from toluene with yields around 70%. Melting points and spectral data were comparable with the reported values.[1]

Preparation of Complexes 3 and 4

The terminally substituted π-allyl complexes of molybdenum were prepared essentially by following Trofimenko's method.[2] Solutions of *bis* (acetonitrile)π-allyl complexes were prepared as before (Chapter-II) and treated with ligand solutions *in situ* to effect the ligand exchange. Column chromatography followed by crystallization afforded pure complexes.

Preparation of complex 3a

Complex **3a** was prepared from its precursor *bis*-acetonitrile molybdenum η^3-crotyl complex. Refluxing $Mo(CO)_6$ with excess crotyl chloride in acetonitrile for 5 hrs resulted in an orange solution of the above complex. Acetonitrile solution of ligand **1** was injected for ligand exchange. Immediate precipitation of NaCl in reaction flask was observed. Cooling, evaporation of solvent followed by column chromatography afforded **3a** in 62% yield.

The IR spectrum of complex **3a** showed a singlet of medium intensity at 2500 corresponding to B-H stretching. Sharp peaks at 1830 and 1920 were assignable to CO absorption. A peak at 1520 could be assigned to the pyrazole C=N. The room temperature NMR spectrum of **3a** displayed sharp lines . The *anti* and *syn* protons of the unsubstituted terminus of the allyl group appeared at 1.20 (J_{HA-HS} = 3Hz, and J_{HA-HC} = 9Hz) and 3.30 (J_{HS-HA}=3Hz, and J_{HS-HC}=6Hz)) as doublets of doublets. The terminal *syn*-methyl group of the allyl appeared at 2.05 as a doublet (J_{CH3-HA} = 6Hz,). The *anti*-proton at this terminus appeared as a multiplet at 2.25. The central proton appeared as a multiplet at 3.80. Pyrazole ring hydrogens appeared as broad singlets at 6.10, 7.50 and 7.95 respectively. The ^{13}C spectrum of **3a** showed methyl carbon of the allyl at 18.5. Allyl terminal carbons appeared at 50.1 and 69.9, allyl central carbon showed chemical shift of 80.29 and 80.9 respectively. Pyrazole C-4 appeared at 105.1, pyrazole C-5 at 135.2 and pyrazole C-3 at 144.1 respectively.

Preparation of complex 3b

Following a similar procedure as described above, the complex **3b** was obtained in 57 % yield.

The IR spectrum of complex **3b** showed a singlet of medium intensity at 2540 corresponding to B-H absorption. Sharp peaks at 1810 and 1930 were assignable to CO group. A sharp peak at 1550 corresponded to pyrazole ring C=N. The ^1H NMR spectrum of **3b** displayed several sharp peaks assignable to allyl protons. After keeping the solution for a long time (2 weeks), the relative peak heights were found to have been altered. This indicated an equilibrium between the two conformers in solution. The 2D-COSY experiments were done to assign the peaks to two interconverting conformers.

For one conformer, the *anti* methyl showed a doublet at 1.20 (J_{CH_3-HS} = 6Hz) while the proton at this terminus appeared at 4.70 as a multiplet. At unsubstituted terminus, *syn* and *anti* protons appeared at 3.60 and 3.05 respectively. Central proton appeared at 4.30 as a multiplet.

For the other conformer, the *anti* and the *syn* protons at the unsubstituted terminus appeared as broad doublets at 2.00 and 2.70 respectively. At the substituted terminus, *anti* proton appeared at 2.70 and *syn* methyl group appeared at 2.25 ($J_{CH_3\text{-}HA}$ = 6Hz) respectively. Central proton appeared at 5.20 as a multiplet.

Pyrazole methyls were difficult to assign to individual conformers. They appeared as several singlets in the region from 2.00 to 2.90 and pyrazole 4H appeared as a multiplet at 5.80.

The ^{13}C spectrum of **3b** showed pyrazole methyl carbons at 12.6, 12.8, 14.0, 14.5, 14.9, 15.2. The methyl carbon of the allyl appeared at 19.8. Terminal allyl carbons appeared at 64.4 and 68.1, central allyl carbon appeared at 88.9. The pyrazole C-4 appeared at 106.8, and 107.2, pyrazole C-5 at 144.1 and 144.8, and pyrazole C-3 at 150.3 and 151.0 respectively. The carbonyl carbons appeared at 233.6 and 234.2.

Preparation of complex 4a

Bis-acetonitrile π-cinnamyl complex was prepared in solution by refluxing molybdenum hexacarbonyl with cinnamyl chloride in acetonitrile for 5h. Acetonitrile solution of the ligand **1** was injected to the red solution. Removal of solvent and column chromatography afforded **4a** in 72% yield.

The IR spectrum of complex **4a** showed a singlet of medium intensity at 2500 corresponding to B-H stretching. Sharp peaks at 1830 and 1910 were assignable to CO ligands. A peak at 1510 corresponded to pyrazole ring C=N. Room temperature ^1H NMR spectrum of **4a** displayed sharp lines indicating the presence of single conformer in solution. The *anti* and *syn* protons of the unsubstituted terminus of the allyl group appeared at 1.40 ($J_{HA\text{-}HS}$ = 2Hz, $J_{HA\text{-}HC}$ = 9Hz) and 3.50 ($J_{HS\text{-}HA}$ = 2Hz, $J_{HS\text{-}HC}$ = 6Hz) as doublets of doublets. The terminal *syn*-phenyl group of the allyl appeared as a multiplet from 7.00 to 7.20, while the *anti* proton at this terminus appeared as a doublet at 3.25 ($J_{HA'\text{-}HC}$ = 10Hz,). The central allyl proton appeared as a multiplet at 4.30. Pyrazole ring hydrogens appeared as broad singlets at 6.10, 7.50 and 8.30 respectively. The ^{13}C spectrum of **4a** showed peaks due to the terminal

allyl carbons at 47.6 and 77.8, central allyl carbon appeared at 86.0. The pyrazole C-4 was observed at 105.3, pyrazole C-5 at 135.9 and 135.4 and pyrazole C-3 at 145.0. The aromatic carbons appeared at 125.2, 126.9, 127.4, 128.1, 128.4 and 128.8. The carbonyl carbons appeared at 227.7 and 233.8.

Preparation of complex 4b

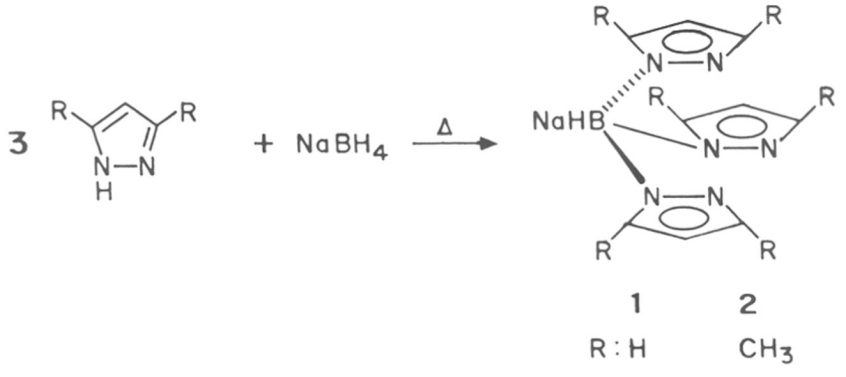
After preparing *bis*-acetonitrile cinnamyl complex in solution, ligand exchange was carried out with ligand **2** in acetonitrile. The complex **4b** was obtained as a red solid in 45% yield.

The IR spectrum of complex **4b** showed a singlet of medium intensity at 2510 corresponding to B-H stretching. Sharp peaks at 1820 and 1930 were assignable to CO groups. A peak at 1540 corresponded to the pyrazole ring C=N. In the ^{1}H NMR spectrum of **4b**, pyrazole methyls appeared as six singlets from 2.25 to 2.55. *Anti* and *syn* protons of the unsubstituted terminus of the allyl group appeared at 2.10 and 3.70 as doublets. ($J_{HA\text{-}HC}$ = 12Hz, $J_{HS\text{-}HC}$ = 6Hz) Terminal *syn*-phenyl group of the allyl appeared as a multiplet from 6.90 to 7.10 and *anti*-proton at benzylic center appeared as a doublet, at 4.25 ($J_{HA'\text{-}HC}$ = 12Hz). Central proton was a multiplet at 5.40. Pyrazole 4H appeared as broad singlets at 5.50 and 5.80 respectively. The ^{13}C spectrum of **4b** showed methyl carbons at 12.4, 12.5, 12.8, 14.8, 15.4, and 15.5. Allyl terminal carbons at 57.3 and 82.2, allyl central carbon showed chemical shift of 89.6. The pyrazole C-4 appeared at 106.5, 106.8, 107.6; pyrazole C-5 at 144.2, 144.7 and pyrazole C-3 at 151.9 respectively. The carbons of phenyl ring appeared at 125.2, 126.9, 127.4, 128.1, 128.4, 128.8. The carbonyl carbons appeared at 227.7 and 233.8.

DISCUSSION

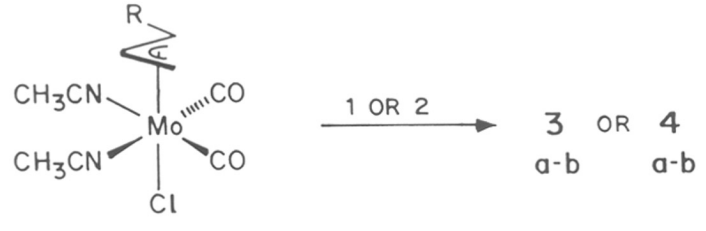
The ligands **1** and **2** were prepared by following a reported procedure in good yields (**Scheme-1**).

SCHEME-1



The complexes were prepared by ligand exchange with the corresponding *bis* (acetonitrile)-π-allyl complexes (**Scheme-2**).

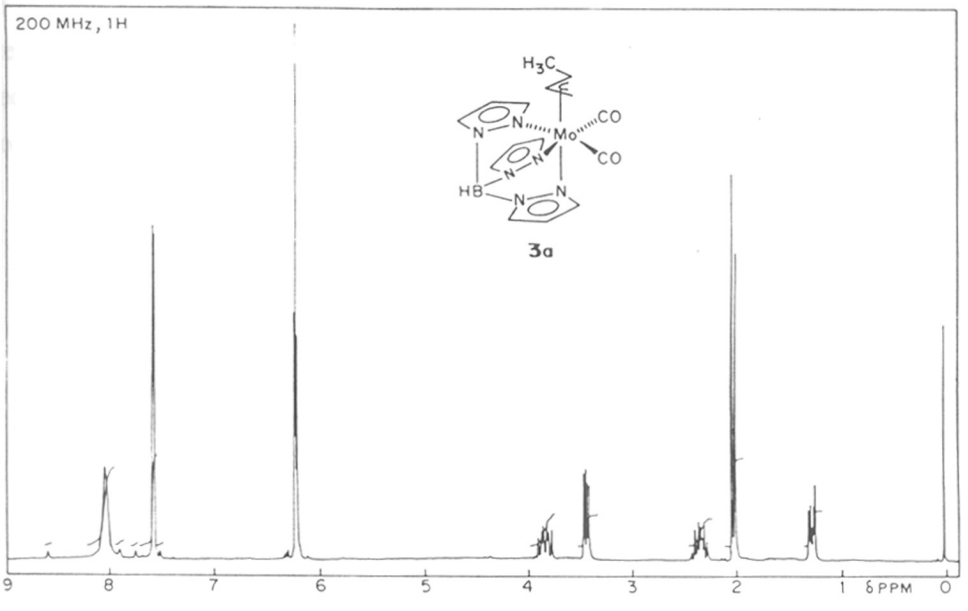
SCHEME-2



The complexes **3a-b** and **4a-b** were isolated by rapid chromatography and purified by crystallization. The crotyl complexes were yellow-orange solids while the cinnamyl complexes were orange to dark brown solid compounds stable in air.

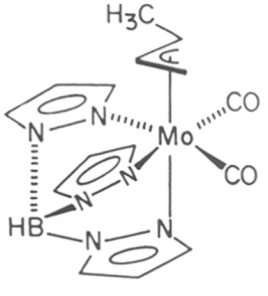
The ^{1}H NMR spectrum of the complex **3a** (**Figure-2**), indicated the presence of a single allyl conformer at room temperature.

FIGURE-2



The three-proton singlet at 2.00 implied that the methyl group was oriented *syn* to the central proton. The multiplet at 2.25 was due to the *anti* proton at the same terminus. Thus, in the absence of a steric perturbation, this was the preferred conformation of the crotyl group (**Figure-3**).

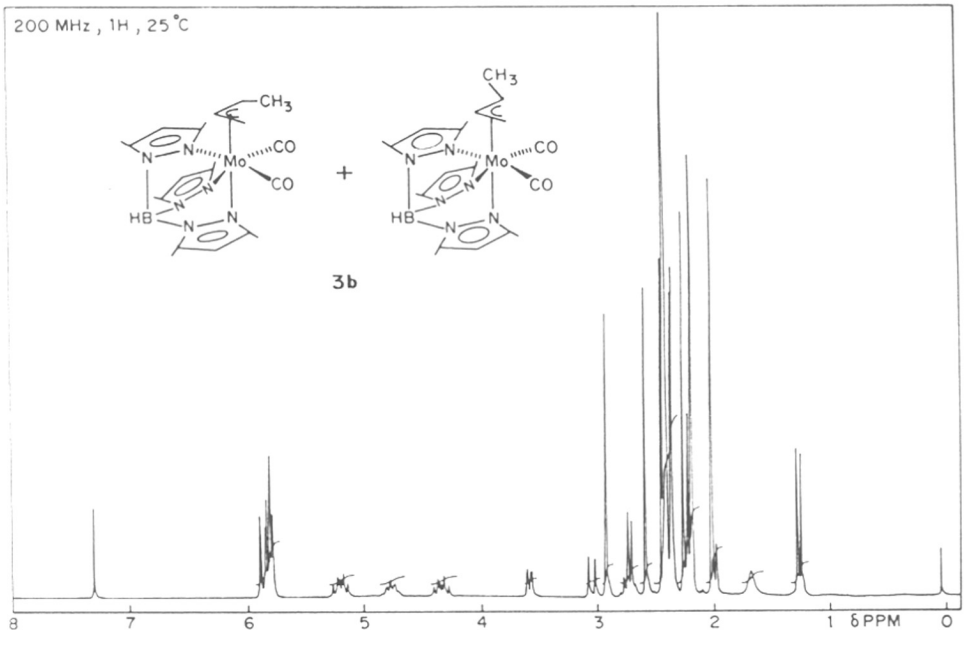
FIGURE-3



3a

The complex **3b** featured the ligand **2** derived from 3,5-dimethylpyrazole, and the methyl group on the allyl terminus was expected to have considerable steric interaction with the proximal 3-Me group of pyrazole. The room temperature ^{1}H NMR spectrum showed two unequal sets of allyl resonances indicating the presence of two allyl conformers (**Figure-4**).

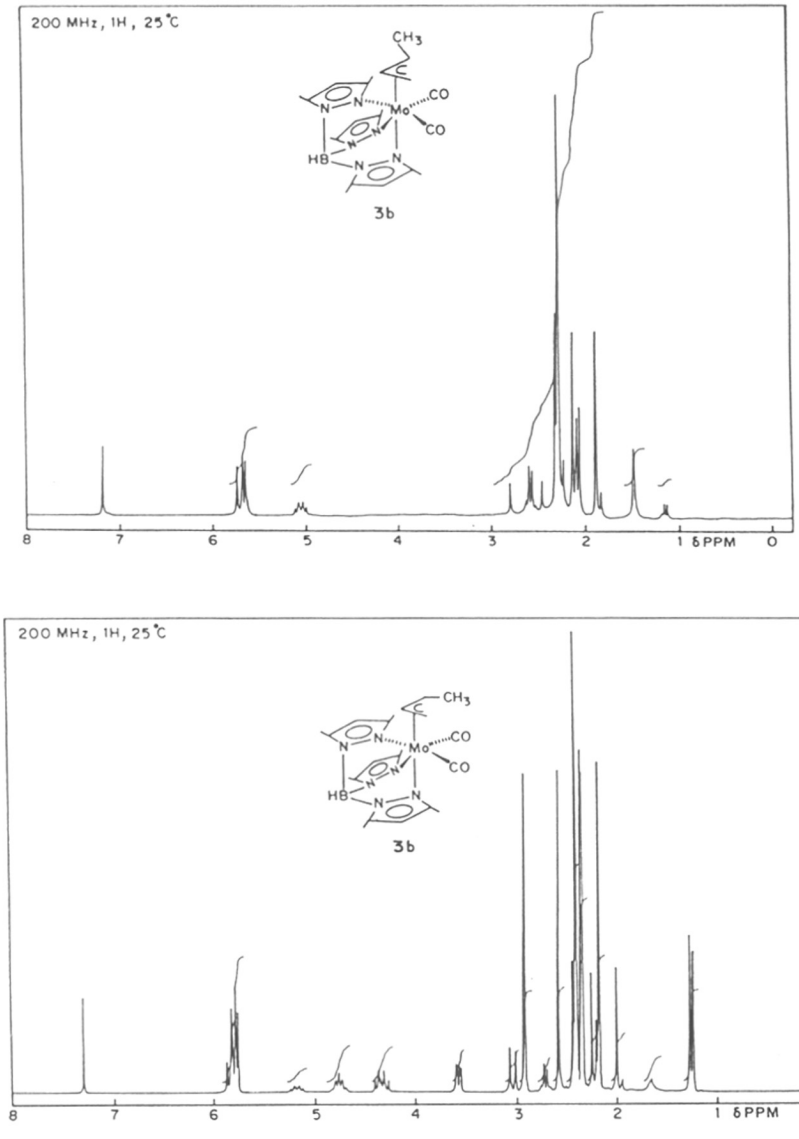
FIGURE-4



The allyl methyl doublets appeared at 1.25 and 2.25, one for the *anti* orientation and the other for the *syn* orientation respectively. The *syn* allyl proton adjacent to the *anti* methyl group was observed at 4.70 and identified by a COSY experiment.

The change in conformer population with time was indicative of a slow interconversion of conformers. Two sets of ^{1}H NMR spectra (**Fig. 5 and 6**), revealed the enrichmentt of one conformer over a period of time, and permitted convenient assignment of signals in the mtxture.

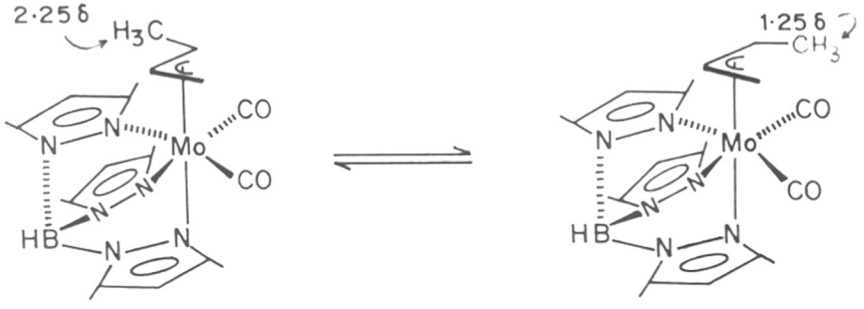
FIGURE-5



It was also of interest to note that the central allyl proton resonance in the case of *syn* methyl conformer was deshielded considerably and appeared at 5.20 (compared with 4.30 for the other conformer).

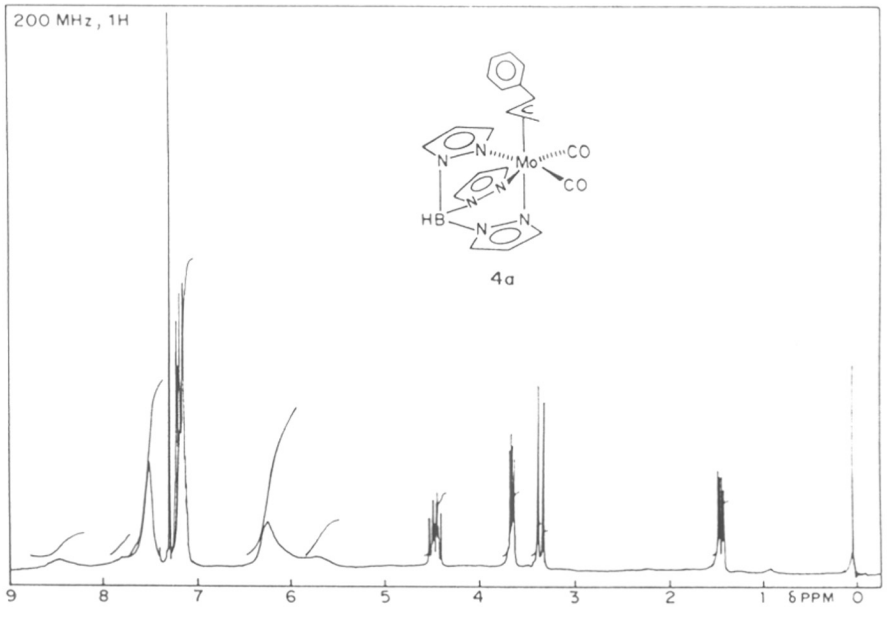
This observation suggested that the Me/Me steric interaction was indeed considerable as anticipated, and it was repulsive in nature (**Figure-6**).

FIGURE-6



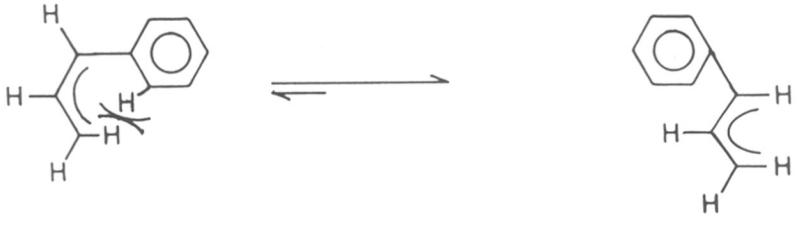
For the cinnamyl complex **4a**, the presence of one conformer with a *syn* phenyl group was readily discernible from the ^{1}H NMR spectrum (**Figure-7**). The central allyl proton appeared as a multiplet at 4.30.

FIGURE-7



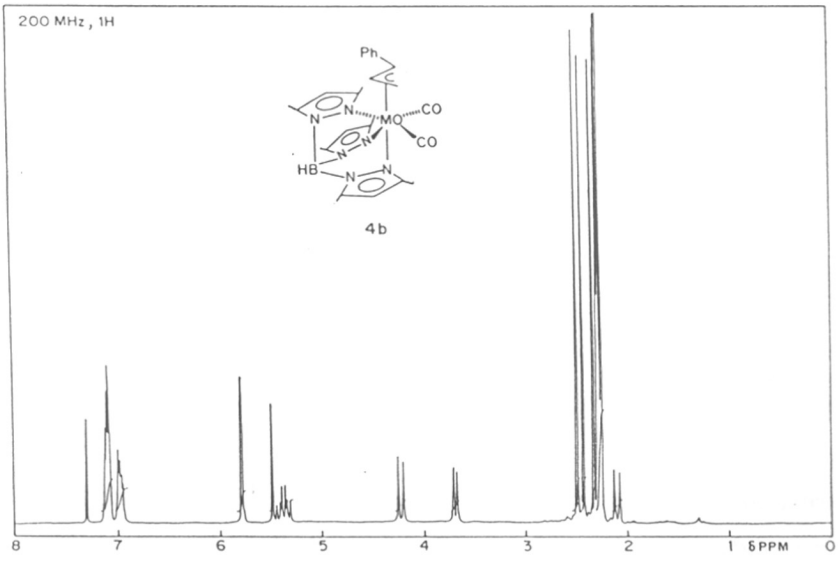
Unlike the crotyl complex **3b**, a phenyl ring at the allyl terminus could not adopt an *anti* orientation with respect to the central proton on account of severe 1,3-allylic strain (**Figure-8**).

FIGURE-8



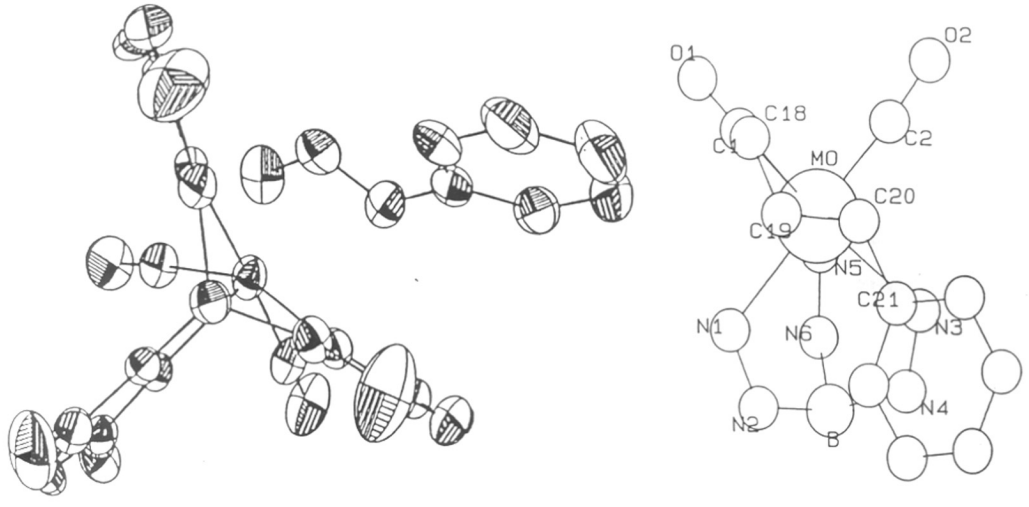
It was anticipated that one of the pyrazole 3-Me group which was proximal to the phenyl ring of the allyl moiety in complex **4b**, would undergo an upfield shift (as observed for the complex **3d** described in Chapter-II) as a result of ring current anisotropy. No such upfield shift of a methyl signal was observed in the ^{1}H NMR spectrum of the complex **4b** (**Figure-9**), which featured sharp lines.

FIGURE-9



The central proton was deshielded (5.40) compared to that of the analogous complex **4a** (4.30). This difference in chemical shift of the central allyl proton was also observed for the crotyl complexes **3a** and **3b** (4.30 and 5.20 respectively). Such deshielding appeared to be systematic for the ligand containing 3-Me group on the pyrazole. Since the NMR spectrum of complex **4b** featured sharp signals, it was decided to carry out a crystal structure determination of this complex. The structure has been depicted in **Figure-10,** as shown below.

FIGURE-10



The X-ray structure was determined by K. M. Sathe, M. Nandi and P. Chakrabarti, NCL, Pune.

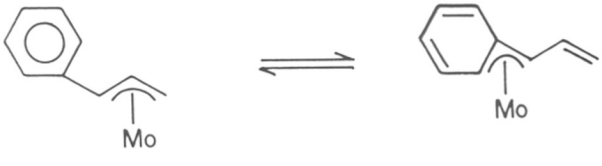
The crystal structure clearly revealed a severe distortion of the allyl group from its normal orientation. In all the structures of similar molybdenum π-allyl complexes[3], the allyl groups are oriented almost parallel to the two CO ligands. The

EHMO calculations of Curtis and Eisenstein[4] also suggested this to be most preferred orientation in terms of bonding. Such a structural distortion of a π-allyl group has been observed for the first time.

It was also of interest to note that the phenyl ring actually moved in between the two pyrazoles, presumably in a bid to release steric strain, while a similar distortion away from the pyrazoles and towards the CO would have led to a less congested environment for the phenyl ring. In the observed orientation, the central allyl proton approached the deshielding zone of the pyrazole ring current anisotropy, and thus the downfield shift could be explained. A similar situation should be considered for the complex **3b** as well.

The origin of the distortion of allyl orientation could be steric, but the implication of the direction of distortion is not immediately apparent. For this class of allyl complexes, a σ-allyl was never observed. The bond lengths of the allyl fragment and the distances of the allyl carbons from molybdenum did not provide any evidence for a σ-bonding mode. A second possibility of an equilibrium involving an η^3-benzyl to η^3-allyl interconversion (**Figure-11**), would, however, be consistent with the sense of distortion. But it would remain still a conjecture in the absence of evidences.

FIGURE-11



SUMMARY

In a series of structurally related complexes, it has been clearly demonstrated that the 3-Me substituent on the pyrazole of the chelating ligand has definite steric interaction with the terminal substituent of the π-allyl moiety, and could lead to structural distortion. However, the results indicated that such interactions are repulsive in character.

EXPERIMENTAL

Preparation of ligand 1

Sodium borohydride (3.04 g, 80 mmol) and pyrazole (16.32 g, 0.24 mmol) were ground together in a mortar. This fine powder was transferred into the reaction flask. It was fitted with an air condenser and 2-way stopcock connected to bubbler. The reaction mixture was slowly heated in silicone oil bath with magnetic stirring. Reaction mixture melted at 90 °C with vigorous gas evolution. So, it was heated very slowly from 90 °C to 125 °C. (2h) and from 125 °C to 190 °C (4h). When hydrogen gas evolution nearly stopped (around 200 °C), the reaction mixture was cooled to 160 °C and poured in hot toluene. It was stirred for 5 minutes and left overnight at room temperature. The powdery solid appeared in the flask which was filtered and dried under high vacuum to get 13.63 g (72%) of ligand **1**. (m.p. 100 °C) lit[1a].

Preparation of ligand 2

3,5-Dimethylpyrazole (23.28 g, 0.24 mmol) was grounded together with sodium borohydride (3.04 g, 80 mmol). The fine powder was transferred into 100 ml RB flask fitted with air condenser and two way stopcock connected to bubbler. The reaction flask was slowly heated in an oil bath with stirring. Vigorous gas evolution started at 100 °C and the solid initially melted at 140 °C (4h) but again solidified at 160 °C (6h). It was furtther heated slowly upto 238 °C and this temperature was carefully maintained for 2h. When the gas evolution nearly ceased, the heating was stopped. The hard solid in the flask was stirred with hot toluene for 1 hour and filtered. It was dried under high vacuum to obtain 12 g, (47%) of **2**. Ligand **2** so obtained was pure enough for complexation reactions.

preparation of complex 3a-Standard method.

Molybdenum hexacarbonyl (0.528 g, 2 mmol) and crotyl chloride were heated under reflux in acetonitrile,(20 ml) for 5 hours. After cooling the reaction mixture to room temperature, a solution of ligand (0.8 g, 2.5 mmol) in acetonitrile (10 ml) was added with syringe. Immediate precipitation was observed. After stirring at

room temperature for 5 minutes, solvent was removed and residue was chromatographed with flash silica gel under argon with dichloromethane as eluent. A yellow coloured band is collected. After removal of solvent, complex **3a** was obtained as yellow powdery solid. (0.52 g, 62%)

COLOUR :- Bright yellow

MP :- Above 222 °C (decomposition)

IR :- 2500, 1920(s), 1830(s), 1520(m).

^{1}H NMR :- (200 MHz, 25 °C, $CDCl_3$):
1.20 (dd, 1H, J_{HA-HS} = 3Hz, J_{HA-HC} = 9Hz) 2.05 (d, 3H, $J_{CH_3-HA'}$ = 6Hz); 2.25 (m, 1H); 3.30 (dd, 1H, J_{HS-HA} = 3Hz, J_{HS-HC} = 6Hz); 3.80 (m, 1H); 6.10 (bs, 3H); 7.50 (bs, 3H); 7.95 (bs, 3H);

^{13}C NMR :- (200MHz,25 °C, $CDCl_3$)
18.5; 50.1; 69.9; 80.2; 80.9; 105.1; 135.2; 144.1.

ANALYSIS :- $C_{15}H_{17}MoN_6O_2B$

Cal. C = 42.9; H = 4.00; N = 20.00.

Found C = 42.9; H = 4.09; N = 19.6.

Preparation of 3b

With 0.528 g, (2 mmol) of molybdenum hexacarbonyl and 1 ml (excess) crotyl chloride in 30 ml of acetonitrile and 0.8 gms (2.5 mmol) of ligand **2**, 0.572 gms, (57%) of **3b** was obtained as shiny red solid.

COLOUR :- Bright red

MP :- 227 °C (decomposition)

IR :- 2540, 1930(s), 1810(s), 1550(m).

^{1}H NMR :- (200 MHz, 25 °C, $CDCl_3$):
1.20 (d, 3H, $J_{CH_3\text{-}HA'}$ = 6Hz); 3.05 (d, 1H, $J_{H_A\text{-}HC}$ = 10Hz); 3.60 (d, 1H, $J_{H_S\text{-}HC}$ = 6Hz); 4.30 (m, 1H); 4.70 (m, 1H) 2.00 (d, 1H, $J_{H_A\text{-}HC}$ = 10Hz); 2.25 (d, 3H, $J_{CH_3\text{-}HA'}$ = 6Hz); 2.70 (m, 2H); 5.20 (m, 1H); 2.00 (s, 3H); 2.10 (s, 3H); 2.20 (s, 3H); 2.30 (s, 3H); 2.35 (s, 3H); 2.55 (s, 3H); 2.90 (s, 3H); 5.80 (m, 3H).

^{13}C NMR :- (200MHz, 25 °C, $CDCl_3$)
12.6, 12.8, 14.0, 14.5, 14.9, 15.2, 19.8, 64.4, 68.1, 88.9, 106.8, 107.2, 144.8, 150.3, 151.0, 233.6, 234.2.

ANALYSIS :- $C_{21}H_{29}MoN_6O_2B$

Cal. C = 50.0; H = 5.70; N = 16.6.

Found C = 49.89; H = 5.97; N = 16.52.

Preparation of 4a.

With 1.05 g, (4 mmol) of molybdenum hexacarbonyl and 1 ml (excess) cinnamyl chloride in 40 ml of acetonitrile and 1.18 gms (5 mmol) of ligand **1**, 1.4 gms, (72%) of **4a** was obtained as shiny orange solid.

COLOUR :- Bright orange

MP :- 192 °C (decomposition)

IR :- 2500, 1910(s), 1830(s), 1510(m).

^{1}H NMR :- (200 MHz, 25 °C, $CDCl_3$):
1.40 (dd, 1H, $J_{H_A\text{-}HS}$ = 2Hz, $J_{H_A\text{-}HC}$ = 9Hz); 3.25 (d, 1H, $J_{H_A'\text{-}HC}$ = 10Hz); 3.50 (dd, 1H, $J_{H_S\text{-}HA}$ = 2Hz, $J_{H_S\text{-}HC}$ = 6Hz); 4.30 (m, 1H); 6.10 (bs, 3H); 7.50 (bs, 3H); 8.30 (bs, 3H); 7.00 to 7.20 (m, 6H).

^{13}C NMR :- (200MHz,25 °C, $CDCl_3$)

47.6; 77.8; 86.0; 105.3; 125.2; 126.9; 127.4; 128.1; 128.4; 128.8; 135.4; 135.9; 145.0; 227.7; 233.8.

ANALYSIS :- $C_{20}H_{19}MoN_6O_2B$

Cal. C = 49.8; H = 3.97; N = 17.4.

Found C = 50.1; H = 3.95; N = 17.08.

Preparation of 4b

With 0.528 g, (2 mmol) of molybdenum hexacarbonyl and 0.75 ml (excess) cinnamyl chloride in 30 ml of acetonitrile and 0.8 g (2.5 mmol) of ligand **2**, 0.510 g, (45%) of **4b** was obtained as shiny red solid.

COLOUR :- Bright orange

MP :- 195 °C (decomposition)

IR :- 2510, 1930(s), 1820(s), 1540(m).

^{1}H NMR :- (200 MHz, 25 °C, $CDCl_3$):

2.10 (d, 1H, $J_{H_A\text{-}HC}$ = 10Hz); 2.25 to 2.55 (m, 18H); 3.70 (d, 1H, $J_{H_S\text{-}HC}$ = 6Hz); 4.25 (d, 1H, $J_{H_A'\text{-}HC}$ = 9Hz); 5.40 (m, 1H); 5.50 (s, 1H); 5.80 (bs, 2H); 6.90 to 7.10 (m, 5H).

^{13}C NMR :- (200MHz,25 °C, $CDCl_3$)

12.4, 12.5, 12.8, 14.8, 15.4, 15.5, 57.3, 82.3, 89.6, 1o6.8, 125.9, 127.3, 127.5, 139.2, 144.2, 144.4, 151.9, 230.1, 234.2.

ANALYSIS :- $C_{26}H_{31}MoN_6O_2B$

Cal. C = 55.12; H = 5.4; N = 14.8.

Found C = 55.12; H = 5.63; N = 14.74.

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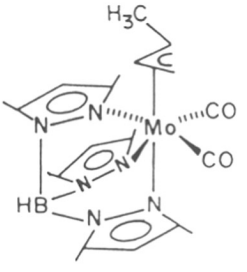
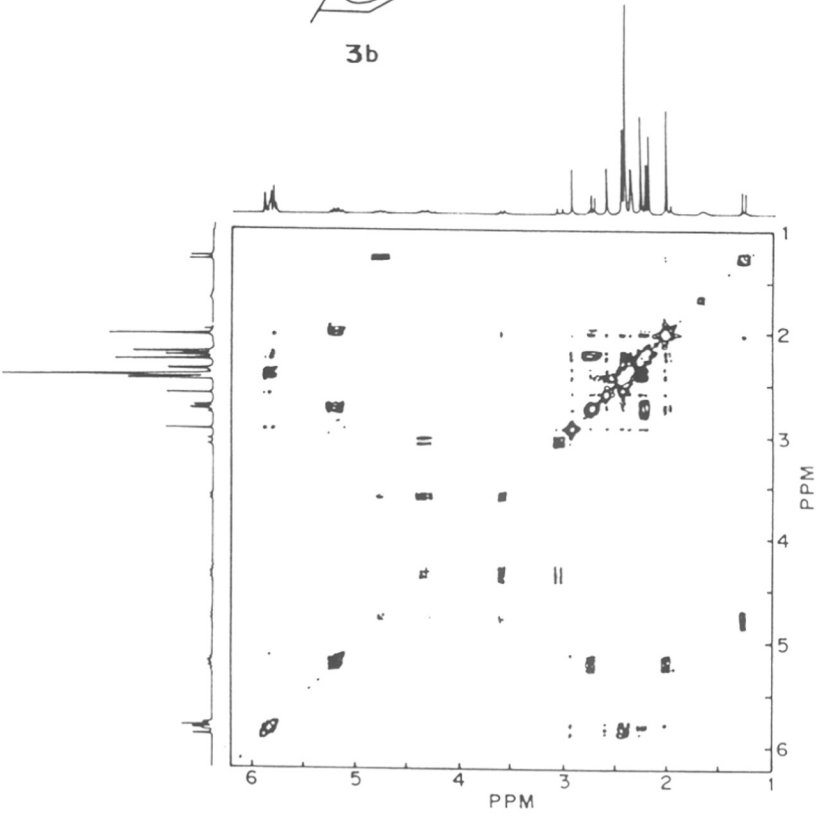
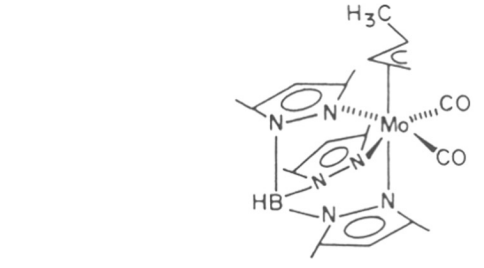
4 Curtis, M. D.; Eisenstein, O. *Organometallics,* **1984,** *3,* 887.



3b





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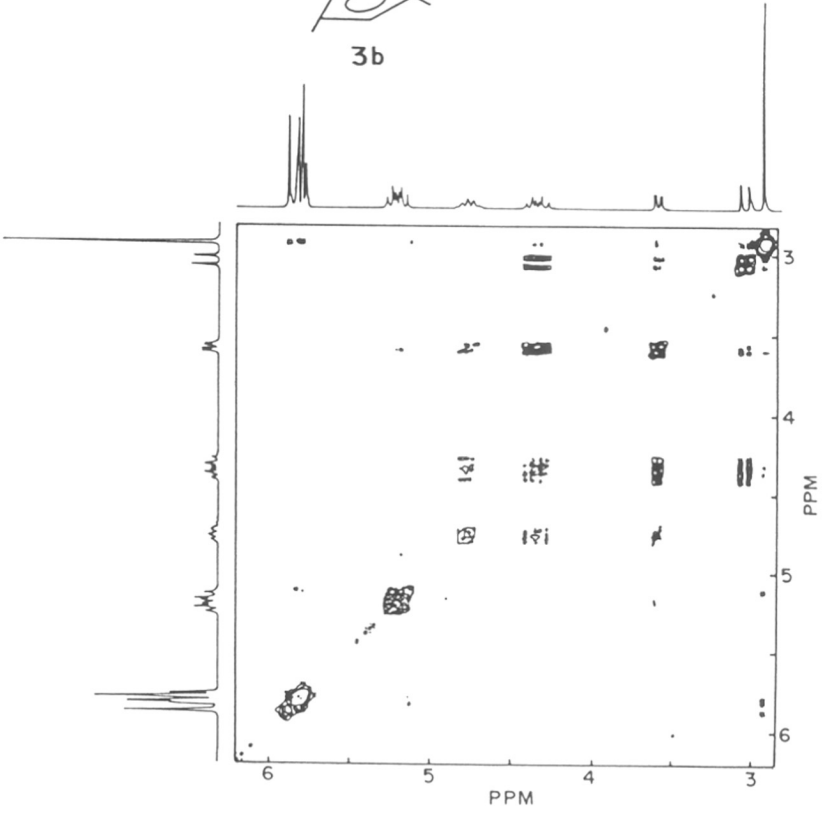

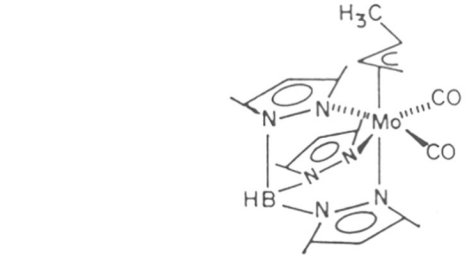

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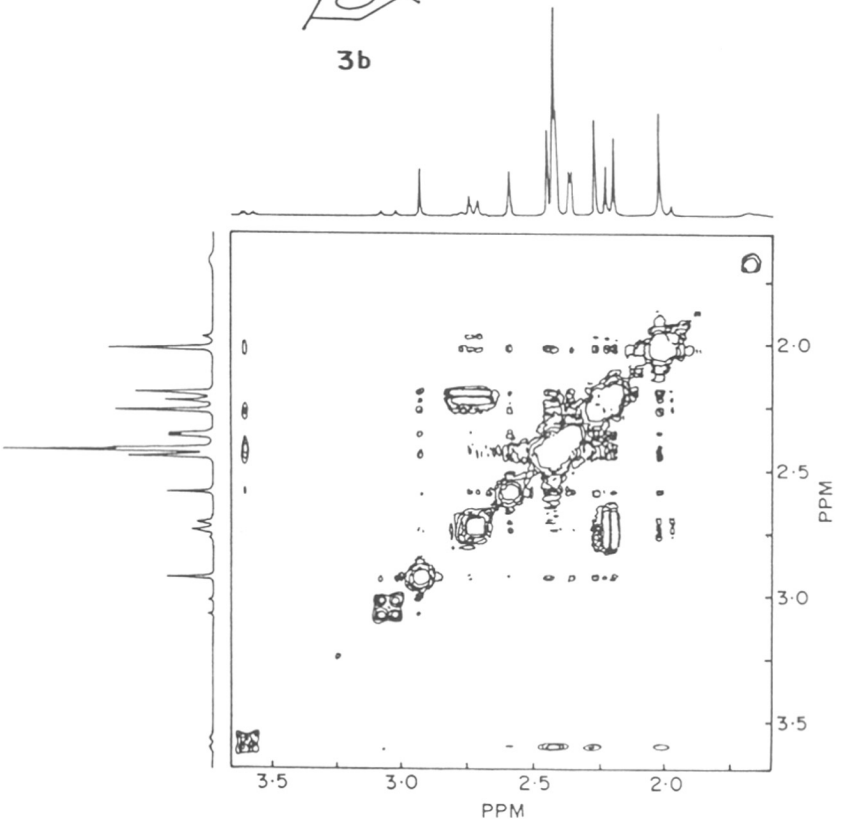

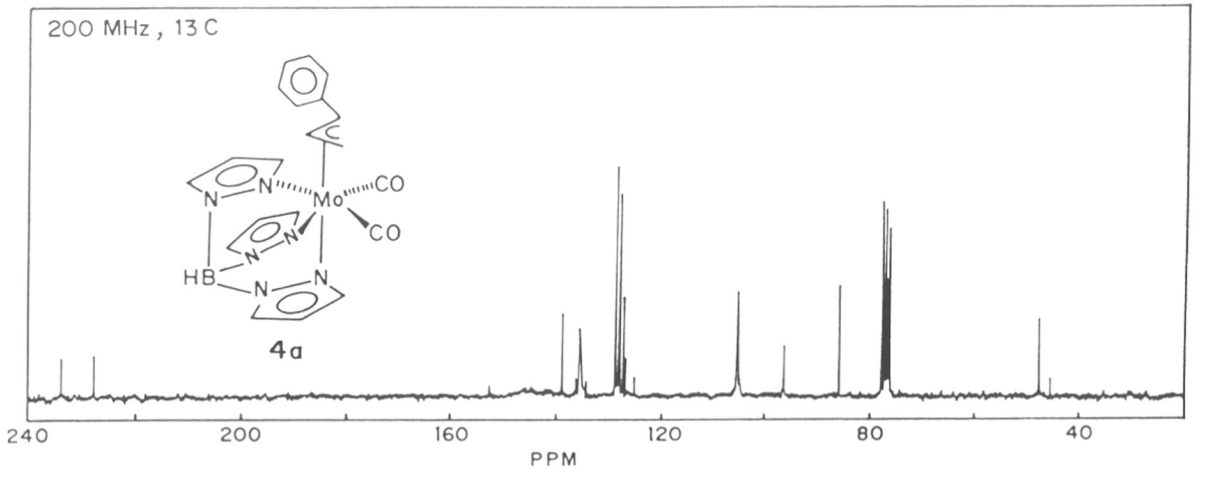
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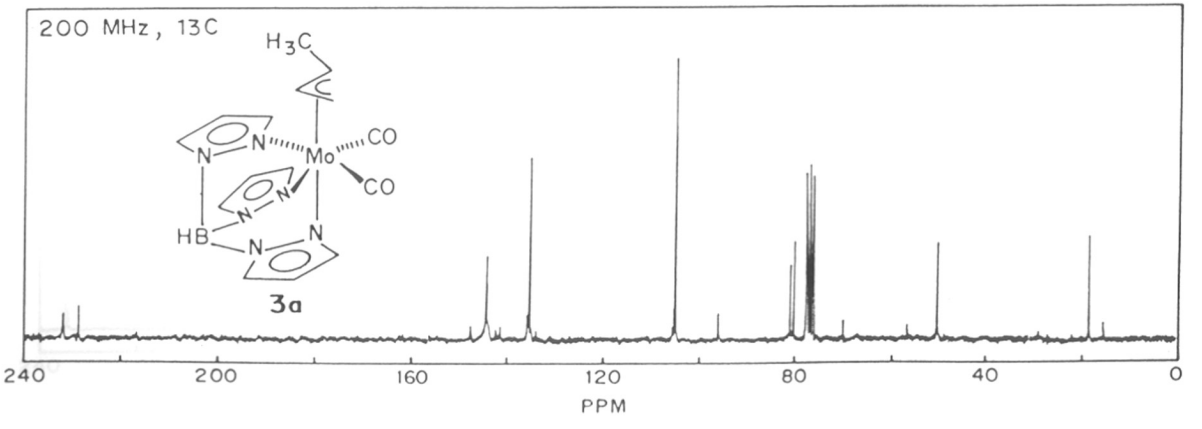
Mo
HB
4a
240
200
160
120
80
40
PPM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CO
CO
Mo
HB
3a
240
200
160
120
80
40
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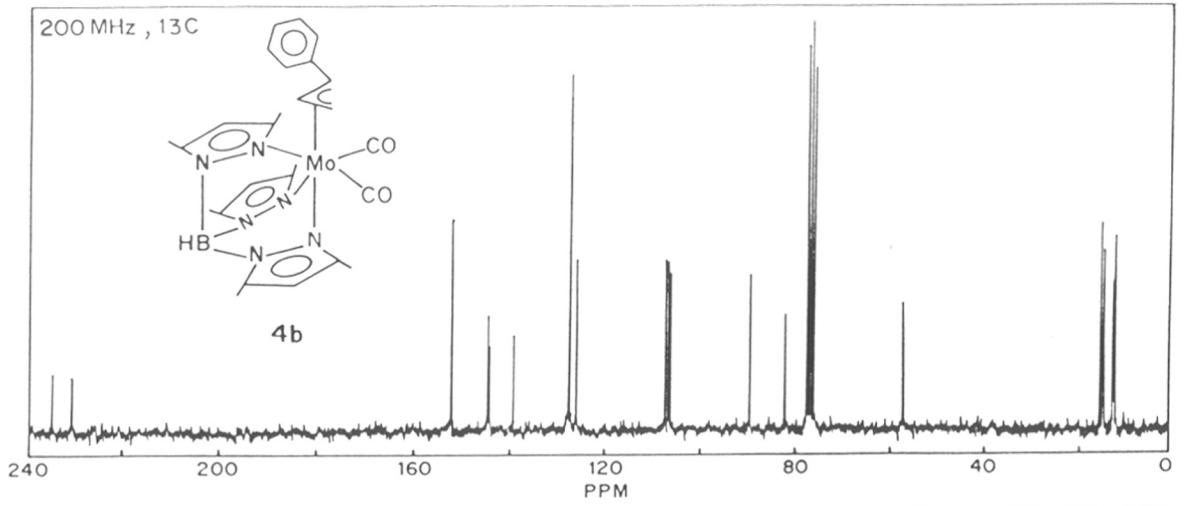
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CO
CO
Mo
HB
N
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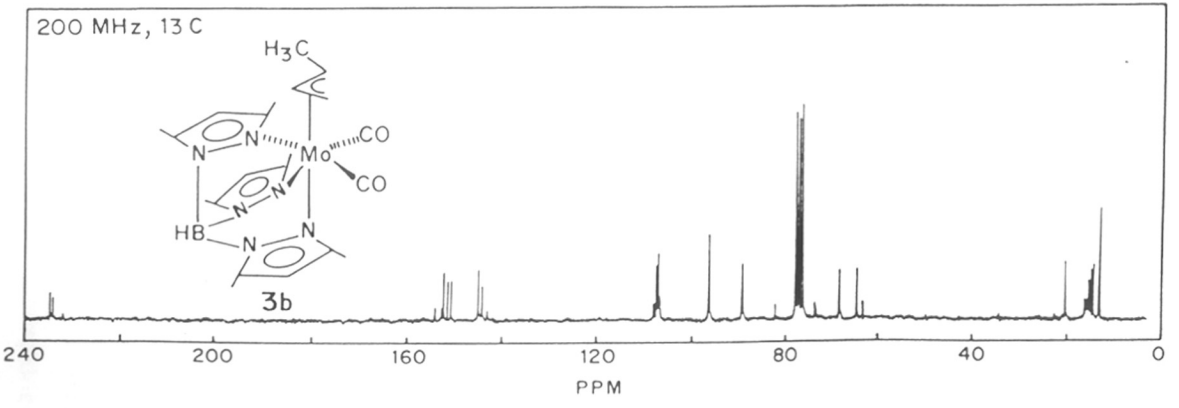
160
120
80
40
0
PPM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CO
Mo
HB
N
3b
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200
160
120
80
40
0
PPM

CHAPTER - IV

NEW ORGANOMOLYBDENUM COMPLEXES CONTAINING BIDENTATE BIS(3,5-DIMETHYLPYRAZOLYL)METHANE LIGAND

Part of this work was published in

J. Organomet. Chem., *1991*, **409**, 341.

INTRODUCTION

Pursuing our interest in ligand-modified structure and reactivity of molybdenum π-allyl complexes containing pyrazole-derived ligands, attention was turned to pyrazolylmethanes. Trofimenko introduced[1] polypyrazolylmethanes as a class of ligands which can coordinate as *bidentate* or *tridentate* N-donor ligands analogus to polypyrazolylborates. The chemistry of tridentate ligand was explored but the bidentate ligand was not studied.

These ligands are neutral and non-hydrolysable, unlike the phophorus-derived ligands described in Chapter-II. While the present work was in progress, a few reports appeared in the literature from other groups working on related interest.[2]

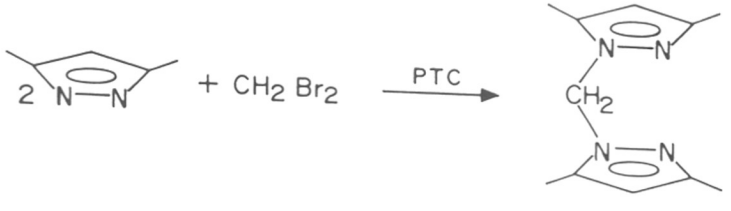
The objective of the present investigation was to standardize the preparation of a series of structurally related complexes and investigate their stereochemical features, in order to assess their potential for application in organic synthesis. The ligand *bis*(3,5-dimethylpyrazolyl)methane was selected for the investigation.

RESULTS

Synthesis of *bis*(3,5-dimethyl-1-pyrazolyl)methane (1).

The ligand **1** was synthesized by the following reaction (**Scheme-1**).[1]

SCHEME-1



Ligand 1

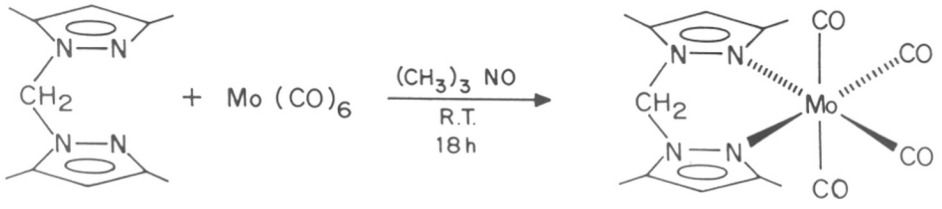
Two Molar equivalents of 3,5-dimethylpyrazole were alkylated with methylene bromide under phase-transfer conditions using 50% aq. sodium hydroxide as the base, benzene as the organic phase and $Bu_4N^+Br^-$ as PTC. The reaction mixture was

stirred and heated under reflux for 4h. The compound **1** was obtained as white needles on crystallization from pet ether in 98% yield. The spectral data and elemental analysis were in agreement with the literature report.[3]

Synthesis of Complex 2

The reaction of molybdenum hexacarbonyl with *bis* (3,5-dimethyl-1-pyrazolyl)methane was carried out at room temperature in the presence of trimethylamine N-oxide (**Scheme-2**).

SCHEME-2



Ligand-1 Complex-2

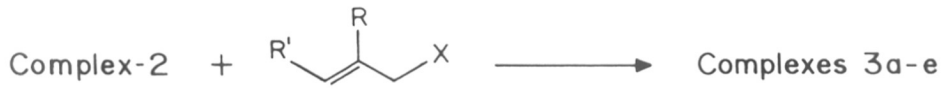
Complete conversion of the hexacarbonyl to the complex **2** took 18h. It was a yellow crystalline solid (59%). Spectral and analytical data were found to be consistent with the literature values.[2a] Heating in toluene to effect ligand exchange, on the other hand, did not furnish an analytically pure product.

Synthesis of Complexes 3a-e.

Attempted preparation of π-allyl complexes by direct oxidative addition to complex **2** did not afford workable yield of products (**Scheme-3**).

Therefore, these complexes were prepared from corresponding *bis*(acetonitrile)π-allyl complexes by ligand exchange with **1** (**Scheme-4**).

SCHEME-3



	R	R'	X
a :	H	H	Cl
b :	H	CH_3	Cl
c :	H	Ph	Cl
d :	Ph	H	Br
e :	CH_3	H	Cl

SCHEME-4

	R	R'	X
a :	H	H	Cl
b :	H	CH_3	Cl
c :	H	Ph	Cl
d :	Ph	H	Br
e :	CH_3	H	Cl

Ligand exchange was done by injecting a solution of ligand **1** to hot solutions of these pre-formed complexes. Cooling at 5°C overnight afforded crystals of complexes **3**. Since this method gave consistent yields, it was used as a standard method of preparation. The compounds were generally insoluble in common organic solvents and their structures were established on the basis of IR and elemental analyses. For some complexes, the ^{1}H NMR could be recorded, but ^{13}C NMR could not be recorded owing to poor solubility.

Freshly prepared hot orange solution of *bis*(acetonitrile) π-allyl chloro complex was subjected to ligand exchange with ligand **1** in acetonitrile. Cooling and preservation of the reaction mixture overnight at 0°C followed by filtration and drying afforded **3a** as yellow crystals (72.6%).

The IR spectrum of **3a** showed carbonyl absorptions at 1910 and 1810 as sharp peaks. A peak of medium intensity at 1550 was observed due to pyrazole ring C=N. This complex was found to be sparingly soluble in chloroform.

Using a similar procedure for crotyl chloride, the complex **3b** was obtained from the reaction mixture as yellow crystals in 79% yield.

The IR spectrum of **3b** showed carbonyl absorptions at 1950 and 1830 as sharp peaks. A peak of medium intensity at 1560 corresponded to pyrazole ring C=N. This complex was found to be moderately soluble in chloroform. The ^{1}H NMR spectrum of this complex, recorded in $CDCl_3$ showed broad humps assignable to allyl protons. Ligand methylene protons appeared at 5.80 as a multiplet. Sharp singlets at 2.00 and 2.35 were assigned to pyrazole methyls and pyrazole 4-hydrogens appeared as a singlet at 5.90.

The complex **3c** was obtained (60%) as orange crystals from cinnamyl chloride in an analogous manner.

The IR spectrum of **3c** showed carbonyl absorptions at 1920 and 1830 as sharp peaks and a peak of medium intensity at 1555 (pyrazole ring C=N). NMR spectrum of this complex, recorded in DMSO-D_6 showed broad doublet at 1.15 (J = 9 Hz) assigned to *anti* proton at the unsubstituted end. The *syn* proton at this end showed chemical shift 3.10 (J = 9 Hz). Allyl proton at the substituted end could not be located. The central allyl proton appeared as a multiplet at 4.10. Singlets at 2.00 and 2.30 were assigned to pyrazole methyls. Pyrazole 4-H appeared at 5.95 as a singlet. Methylene protons of the ligand **1** appeared as a multiplet at 5.70 and terminal phenyl ring protons appeared as a multiplet at 7.30.

Freshly prepared deep red solution of *bis*-acetonitrile π-phenylallyl complex was subjected to ligand exchange with solution of the ligand **1** in acetonitrile to afford the complex **3d** as orange crystals (35%). This complex was highly soluble in most of the organic solvents in contrast to the earlier complexes.

The chair conformation is an intermediate stage when one boat conformer is converted to the other. Since the pyrazole rings are planar, a direct boat-boat interconversion is the more reasonable conformational equilibrium.[2b] The synthesis and structural characterisation were undertaken for a series of structurally related molybdenum π-allyl complexes containing ligand **1**. Structurally defined complexes of rigid conformation are of immediate interest in the context of synthetically useful C-C bond forming reactions. Prior to the present work, no such complex was definitively characterized by X-ray crystallography. Also, these compounds were expected to be less susceptible to ligand degradation than those described in Chapter-II.

The ligand **1** was synthesized by a modified procedure from dibromomethane and two equivalents of 3,5-dimethylpyrazole in a biphasic medium using conc. NaOH as base in the presence of $Bu_4N^+Br^-$ as a phase transfer catalyst. The reaction was clean and could be conveniently carried out in multigram scale in excellent yield (95-97%).

Initially, the tetracarbonylmolybdenum derivative **2** was prepared by heating equimolar quantities of $Mo(CO)_6$ and the ligand **1** in toluene. The yield of this reaction was variable and the product purity was often unsatisfactory. Difficulty in obtaining this complex by thermal reaction was noted earlier.[2c] Later, the desired product with a better purity was readily obtained in good yield (60%) by using two equivalents of trimethylamine N-oxide in benzene containing about 15% *(v/v)* methanol (to dissolve the N-oxide) at room temperature.[4] The complex **2** was identified[2a] by its characteristic IR absorption and ^{13}C NMR spectrum. The compound was found to be air-sensitive and was preserved in the refrigerator under a cover of argon.

Heating the complex **2** with allyl chloride in acetonitrile for three hours (**Scheme-3**) provided the allyl complex in poor yield. When THF was used as the solvent, no product was obtained. Thermal sensitivity of the complex **2** could be a possible factor contributing to such dismal yield. Therefore, the preparative route involving ligand exchange from the preformed *bis*(acetonitrile) π-allyl complex of molybdenum was pursued.

The IR spectrum of **3d** showed carbonyl absorptions at 1940 and 1860 as sharp peaks. A peak of medium intensity at 1560 corresponded to pyrazole ring C=N absorption. The ^{1}H NMR spectrum of this complex recorded in $CDCl_3$ showed singlet at 1.40 assignable to *anti* protons. The *syn* protons appeared as a singlet at 3.70. Singlets at 2.10 and 2.30 were assignable to pyrazole methyls. Pyrazole 4-H appeared at 5.85 as a singlet. Methylene protons of the ligand **1** showed two distinct doublets(J = 16Hz) at 3.40 and 4.70. The phenyl protons appeared as a multiplet at 7.15.

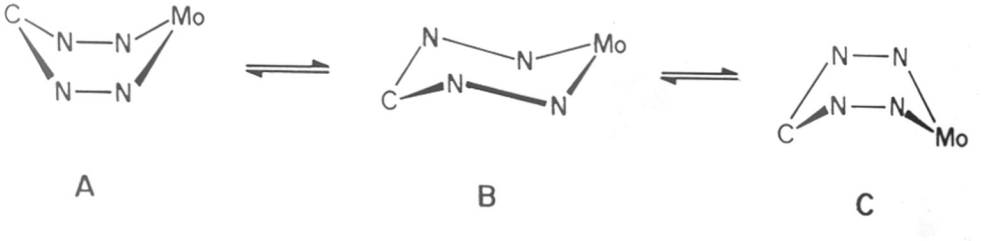
Bright yellow crystals of *bis*-acetonitrile π-methallyl complex which was isolated from acetonitrile solution, was stirred with ligand **1** in methanol for 10 minutes at room temperature. A change of colour from orange to brown indicated partial decomposition of product. Partial evaporation of solvent afforded yellow solid which was quickly filtered to get 20 mg of complex **3e** which was decomposed after half an hour.

The IR spectrum of **3e** showed carbonyl absorptions at 1920 and 1830 as sharp peaks. A peak of medium intensity at 1560 corresponded to pyrazole ring C=N absorption.

DISCUSSION

Bis (3,5-dimethylpyrazolyl)methane **1** is a bidentate N-donor ligand which gives rise to a six-membered chelate. Compared to the conventional ligands like 2,2'-bipyridyl or 1,10-phenanthroline, which provide rigid five-membered chelates, the ligand **1** afforded a chelate with greater conformational flexibility : two boat (A and C) and one chair-like (B) conformers are possible (**Figure-1**).

FIGURE-1



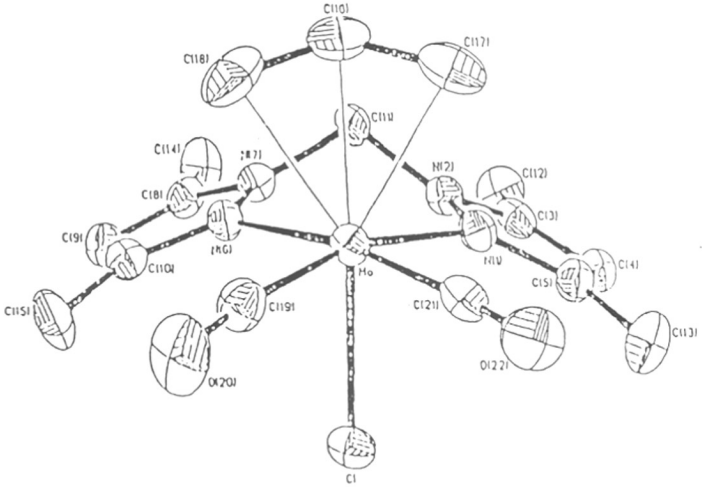
The *in situ* preparation of *bis*(acetonitrile)π-allyl dicarbonylmolybdenum has been described in Chapter-II. Appropriate allyl halides were used for the preparation of different complexes. The ligand exchange was generally carried out in refluxing acetonitrile for a few minutes (**Scheme-4**). The products were obtained on refrigeration overnight, as analytically pure crystalline solids.

As an exception, isolation of the complex **3e** proved extremely difficult. The complex decomposed very rapidly during isolation. The ligand exchange was carried out in methanol at room temperature for 5 min and the complex **3e** was precipitated on partial evaporation of the solvent. The complex underwent decomposition within half an hour from isolation. Such rapid decomposition was a result of oxidation which was common for all these complexes, as discussed in Chapter-V.

The IR spectra for all the complexes (**3a-e**) featured absorptions due to *cis*-CO ligands. The pyrazole C=N stretch was the other prominent band. The ^{1}H NMR spectra of complexes were difficult to record on account of their poor solubility in standard solvents. Extensive ligand dissociation and decomposition occurred in DMSO over a period of an hour. Line broadening was observed in certain cases indicative of slow conformational interchange.

The X-ray crystal structure solution of the complex **3a** established its structural identity (**Figure-2**).

FIGURE-2

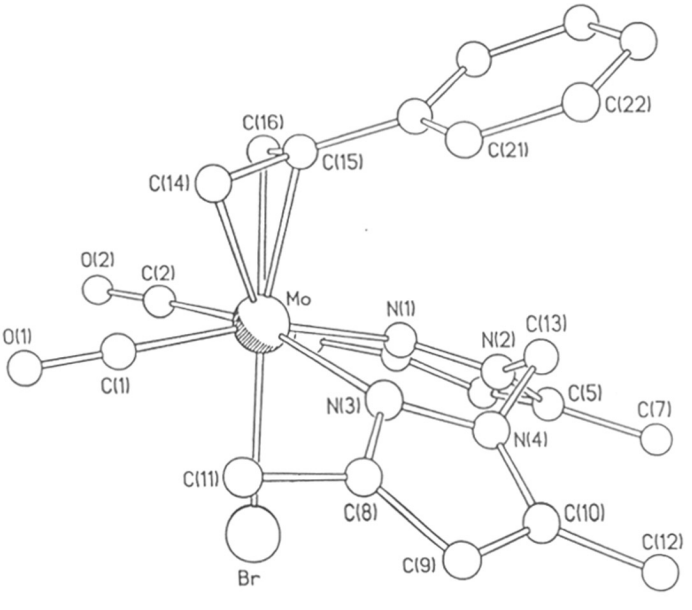


The X-ray structure determination was carried out by H. Zang, Southern Methodist University, USA.

In the symmetrical, distorted octahedral structure, the pyrazoles were found to occupy positions *trans* to the CO ligands. The allyl group was placed *trans* to the chlorine. The ligand **1** and the metal adopted a boat conformation where the CH_2 group was bent towards the allyl group and the pyrazole rings towards the chlorine. This was expected to be the more stable conformation. In the other possible boat conformation, the pyrazoles would point towards the allyl group and the two methyl substituents on the pyrazole would render such arrangement sterically unfavourable.

In the ^{1}H NMR spectrum of the complex **3d**, the methylene protons of the ligand appeared as two separate doublets (J = 16 Hz) which were considerably shielded (3.40 and 4.70 instead of 5.80-6.00). From the conformation of the molecule described above, such shielding could be accounted for by the phenyl ring anisotropy. The X-ray structure of this complex substantiated this conclusion (**Figure-3**).

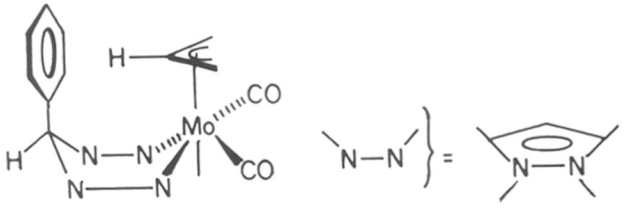
FIGURE-3



The X-ray structure determination was carried out by B. S. Haggarty, University of Dalware, USA.

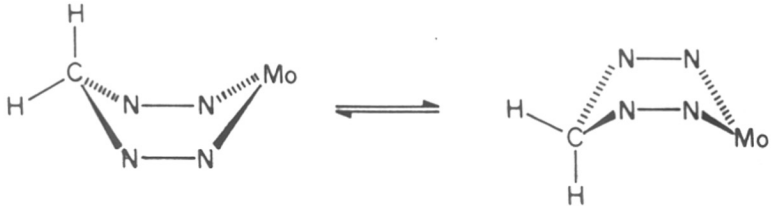
It may be mentioned here that a similar phenomenon was independently reported by Shiu[5] for an analogous molecule, after our results were published. In this case, the central allyl proton experienced an upfield shift as a result of phenyl ring anisotropy from the ligand (**Figure-4**).

FIGURE-4



The relative insolubility of many of these complexes in common NMR solvents discouraged extensive investigation. However, there has been no positive indication to believe that a boat-boat interconversion occurred at a rapid rate. Though the overall symmetry of the molecule would be retained during the boat-boat interconversion (**Figure-5**), the distance of the CH_2 group from the allyl group would alter and hence its chemical shift. These protons displayed a geminal coupling of about 16 Hz. A minimal chemical shift difference between these protons would make the signal appear as a broad singlet, as was observed in these cases except for **3d**. It appears more reasonable to assume that the methyl substituents on the pyrazole would destabilize the alternative boat conformation to a considerable extent. A dynamic spectrum can rather be explained in terms of a *trigonal twist* involving the ligand and the halogen (**Figure-5**).

FIGURE-5



Since the pyrazole rings were oriented away from the allyl ligand, the methyl substituents on the pyrazole rings were no longer proximal to the terminal substituents on the allyl group. Hence, the crotyl and the cinnamyl complexes showed no special features.

Owing to poor solubility of these complexes, no further chemistry was explored with these compounds.

SUMMARY

A series of structurally related molybdenum(II) π-allyl complexes featuring *bis* (3,5-dimethylpyrazolyl)methane were prepared and structurally characterized. A number of these complexes exhibited fluxional motion which could not be investigated in detail for lack of solubility in normal NMR solvents.

EXPERIMENTAL

General

Trimethylamine N-oxide was prepared by a known method[7]. All allyl complexes were crystallized in the reaction mixture. The mother liquor gave brown crystalline complexes after isolation of all π allyl complexes. Due to the moderate solubility of π allyl complexes in organic solvents ^{13}C NMR spectrum was possible only for complex **3d**. The C and H analyses were performed at RSIC Chandigarh and analyses for N were not available.

Preparation of *bis* (3,5-dimethyl-1-pyrazolyl)methane 1

Ligand **1** was prepared by a slightly modified literature[3] procedure as follows.

3,5-Dimethyl pyrazole (7.68 g, 80 mmol) was dissolved in benzene (80 ml) and dibromomethane (8 g, 44 mmol) was added to it. This solution was added to a solution of sodium hydroxide (9 g) in water (9 ml). Then tetraethylammonium bromide (100 mg) was added to the reaction mixture. The two phase mixture was stirred vigorously and heated under reflux. The progress of the reaction was monitered by TLC. After 4h the reaction was complete. The reaction mixture was then cooled to room temperature. Sodium sulphate (5 g) was added to the reaction mixture. The reaction mixture was filtered and the residue washed with benzene (40 ml). The combined organic layer was evaporated under reduced pressure and the white solid residue obtained after recrystallization from hot petroleum ether afforded pure ligand **1** (7.9 g, 96%).

COLOUR :- Colourless crystals

MP :- 105°C(lit.[3] 105°C)

IR :- 1560(s), 1040(s), 780(s).

^{1}H NMR :- 2.10 (s, 3H); 2.30 (s, 3H); 5.65 (s, 2H); 6.00 (s, 2H).

Mass :- 204 (M^+), 95 (100%).

Preparation of *bis*(3,5-dimethyl-1-pyrazolyl)methane-tetracarbonyl molybdenum 2

Method A

This procedure is a modification of the literature method[4] to prepare **2** by oxidative decarbonylation with triethylamine-N-oxide.

To a stirred suspension of $Mo(CO)_6$ (1.05 g, 4 mmol) in benzene (120 ml) was added a solution of trimethylamine-N-oxide (1 g, 13.3 mmol) in dry methanol (15 ml). Then *bis* (3,5-dimethyl-1-pyrazolyl) methane **1** (1 g, 4.9 mmol) was added in one portion and the mixture was stirred under argon at room temperature for 18h. The slightly turbid yellow solution was concentrated to about 20 ml and quickly filtered. Methanol (3 ml) was added to the filtrate and it was cooled to 0° C to afford **2** as yellow crystals, which were filtered off and dried to yield 0.982 g (60%) of analytically pure **2**.

Method B.

This method involved the thermal decarbonylation followed by ligand substitution. It was used earlier to prepare bipyridyl and phenanthrolin ($Mo(CO)_4$) complexes[6]. By this method, the complex obtained was not analytically pure.

Molybdenum hexacarbonyl (0.8 g, 3 mmol) was suspended in toluene (20 ml) and ligand **1** (0.7 g, 3.5 mmol) was added to it. The reaction mixture was refluxed under argon for 1h. Then the reaction mixture was cooled in an ice bath for 1.5h. The yellow crystalline solid separated was filtered, washed with petroleum ether and dried under vacuo to give 1.13 g (91%) of pure complex **2**.

COLOUR :- Bright yellow

MP :- 170°C (Decomposed).

IR :- 2000(s), 1910(m), 1870(s), 1810(s), 1560(s).

^{1}H NMR :- 2.40 (s, 6H); 2.45 (s, 6H); 5.95 (s, 2H); 5.90 to 6.40 (m, 2H).

ANALYSIS :- $C_{15}H_{16}MoN_4O_4$

Cal. C = 43.68; H = 3.88;

Found C = 43.61; H = 3.77;

Preparation of π-allyl complexes 3a-e (*method A*).

Following π-allyl complexes were prepared by ligand exchange of freshly prepared *bis* acetonitrile dicarbonyl π-allyl and substituted allyl complexes with ligand **1**.

General procedure for preparation of π-allyl complexes

Preparation of complex 3a

Molybdenum hexacarbonyl (0.528 g, 2 mmol) was suspended in acetonitrile (10 ml). Allyl chloride (1 ml, excess) was added to it. The flask was connected to the reflux condenser and argon balloon with two way stop-cock and it was evacuated and purged with argon several times. Then the reaction mixture was refluxed for 5h. Ligand **1** (0.408 g, 2 mmol) was dissolved in acetonitrile (5 ml) and the solution was added to the reaction flask through a syringe. Heating was continued for 5 min and the reaction flask was cooled to room temperature and preserved in the refrigerator overnight. The yellow crystals were filtered and dried under vacuo to give 0.628 g (73%) of analytically pure **3a**.

COLOUR :- Bright yellow

MP :- 232°C.

IR :- 1910(m), 1810(s), 1550(m).

ANALYSIS :- $C_{16}H_{21}MoN_4O_2Cl$

Cal. C = 44.39; H = 4.85;

Found C = 44.39; H = 4.33;

Preparation of complex 3b

Molybdenum hexacarbonyl (0.528 g, 2 mmol), crotyl chloride (0.75 ml, excess), ligand **1** (0.5 g, 2.4 mmol) and acetonitrile (10 ml) afforded 0.708 g (79%) of **3b**.

COLOUR :- Bright yellow

MP :- 236°C.

IR :- 1950(s), 1830(s), 1560(m).

^{1}H NMR :- 1.00 (bs, 1H); 1.20 (bs, 3H); 2.35 (s, 6H); 2.60 (s, 6H); 3.40 (bs, 1H); 4.20 (m, 1H); 4.70 (bs, 1H); 5.90 (s, 2H); 6.00 (bs, 2H).

ANALYSIS :- $C_{17}H_{23}MoN_4O_2Cl$

Cal. C = 45.68; H = 5.15;

Found C = 45.59; H = 5.52;

Preparation of complex 3c

Molybdenum hexacarbonyl (0.8 g, 3.03 mmol), cinnamyl chloride (1 ml, excess), ligand **1** (0.7 g, 3.43 mmol) and acetonitrile (12 ml + 3 ml) afforded 0.942 g (60%) of **3c**.

COLOUR :- Orange

MP :- 225°C.

IR :- 1920(s), 1830(s), 1555(m).

^{1}H NMR :- 1.15 (bd, J = 9.6Hz, 1H); 2.00 (s, 6H); 2.30 (s, 6H); 3.10 (bd, J = 9Hz, 1H); 4.10 (m, 1H); 5.70 (s, 2H); 5.95 (s, 2H); 7.30 (m, 5H).

ANALYSIS :- $C_{22}H_{25}MoN_4O_2Cl$

Cal. C = 51.91; H = 4.91;

Found C = 51.53; H = 5.25;

Preparation of complex 3d

Molybdenum hexacarbonyl (0.8 g, 3.03 mmol), α-methylstyril bromide (1 ml, excess), ligand **1** (0.9 g, 4.4 mmol) and acetonitrile (15 ml + 5 ml) afforded 0.6 g (35%) of **3d**.

COLOUR :- Orange

MP :- 219°C.

IR :- 1940(s), 1860(s), 1560(m).

^{1}H NMR :- 1.40 (s, 2H); 2.10 (s, 6H); 2.30 (s, 6H); 3.40 (d, J = 16Hz, 1H); 3.70 (s, 2H); 4.10 (m, 1H); 4.70 (d, J = 16Hz, 1H); 5.85 (s, 2H); 7.15 (m, 5H).

ANALYSIS :- $C_{22}H_{25}MoN_4O_2Br$

Cal. C = 47.73; H = 4.52;

Found C = 46.83; H = 4.55;

Preparation of complex 3e

Molybdenum hexacarbonyl (0.164 g, 0.62 mmol) and 2-methylallyl chloride (0.5 ml, excess) were heated under reflux in acetonitrile (8 ml) with argon balloon for 5h. The orange solution was cooled to room temperature and preserved under argon overnight in a refrigerator. The *bis*-acetonitrile complex **4e** was separated as orange crystals. The supernatent solution was decanted and the crystals were dried in vacuo (0.1 g, 50%). To this solid, ligand **1** in methanol (10 ml) was added and the flask was purged with argon. The reaction mixture was stirred for 10min at room temperature. During this time the colour of the solvent darkened. After partial evaporation of the solvent a small amount of yellow solid separated in the flask. It was quickly filtered to give 21 mg of complex **3e**.

The product turned into a dark brown mass within 30 min at room temperature.

COLOUR :- Bright Yellow

IR :- 1920(s), 1830(s), 1560(m).

Preparation of complexes 3a-d (*method B*)

This method involved heating complex **2** with excess allyl halide in acetonitrile for several hours. The yield and purity of the complexes were inferior to those described above.

Preparation of complex 3a

Complex **2** (0.3 g, 0.72 mmol) and allyl chloride (1 ml, excess) was dissolved in acetonitrile (15 ml). The reaction mixture was refluxed for 3h. During this time the pale yellow colour of the solution turned orange. The reaction mixture was then

cooled to room temperature and preserved in refrigerator overnight. Next day the yellow crystals separated were filtered, washed with acetonitrile and dried under vacuo to yield 0.046 g (15%) of complex **3a**.

Preparation of complex 3b

From complex **2** (0.2 g, 0.48 mmol), crotyl chloride (1 ml, excess) and acetonitrile (10 ml) afforded 0.054 g (25%) of complex **3b**.

Preparation of complex 3c

From complex **2** (0.3 g, 0.72 mmol), cinnamyl chloride (0.8 ml, excess) and acetonitrile (10 ml) afforded 0.073 g (20%) of complex **3c**.

Preparation of complex 3d

From complex **2** (0.3 g, 0.72 mmol), α-methylstyril bromide (0.6 g, 3.04 mmol) and acetonitrile (10 ml) afforded 0.063 g (15.7%) of complex **3d**.

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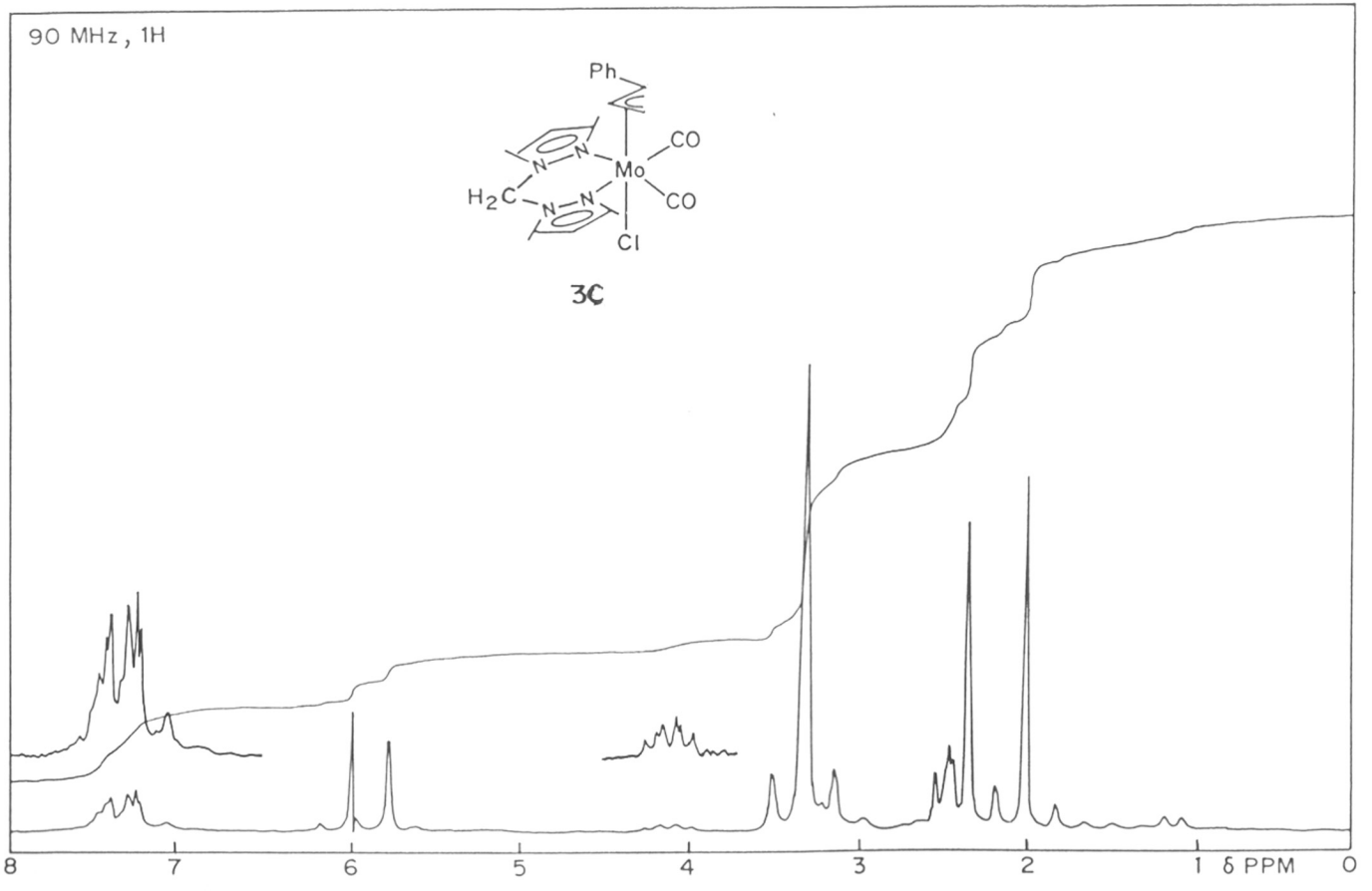

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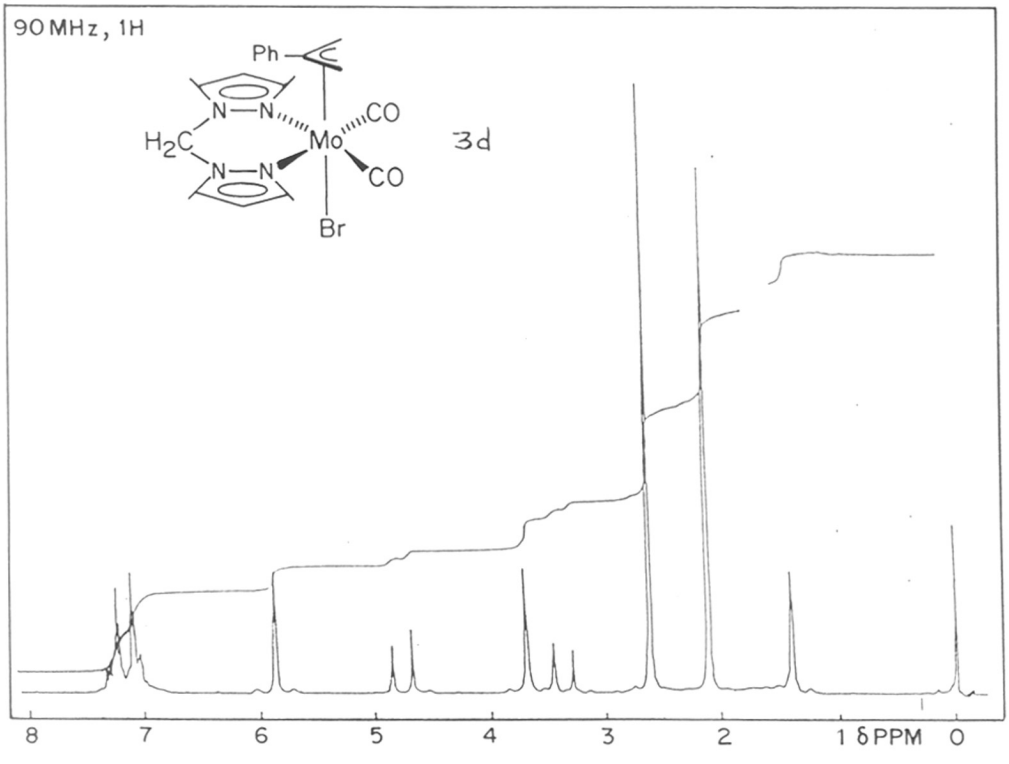
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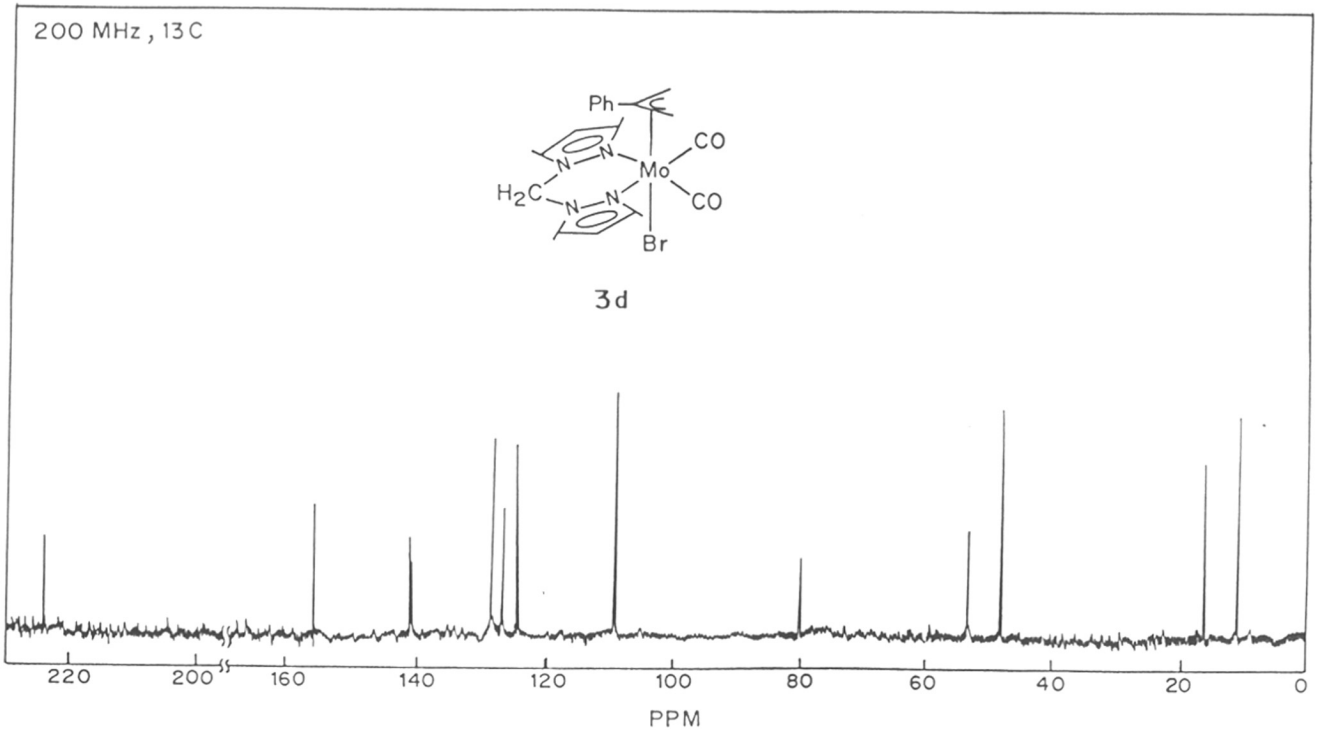
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PPM

CHAPTER - V

UNUSUAL FORMATION OF MOLYBDENUM(V) BINUCLEAR OXO COMPLEXES

Part of this work was published in

Inorganic Chemistry, *1993*, **32**, 1301.

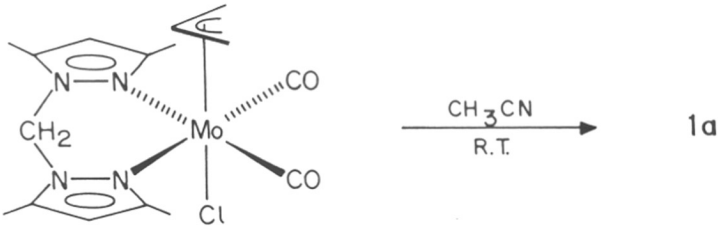
INTRODUCTION

Organometallic chemistry of Group VI transition metals essentially follows a distinct pattern. The chemistry of π-complexes have the metal in a low oxidation state (0 to IV), while the reactive oxo and alkylidyne complexes have the metal in a high oxidation state (IV to VI). The oxo complexes are biologically significant and are implicated in dioxygen activation and transfer reactions. In the course of our investigation on molybdenum π-allyl complexes, there was a chance diversion into the Mo(V) oxo complexes, as described below.

RESULTS

When π-allyl complex **3a** described in Chapter-IV was isolated as crystalline solid from the reaction mixture by filtration, mother liquor was left in air at room temperature. After 48 hours, brown crystalline solid was deposited in the flask. This solid was stable to air and moisture, but it was not soluble in most of the organic solvents. Similarly, when an acetonitrile or dichloromethane solution of **IV-3a** was left at room temperature for 48 hrs, a similar type of solid was obtained (**Scheme-1**).

SCHEME-1

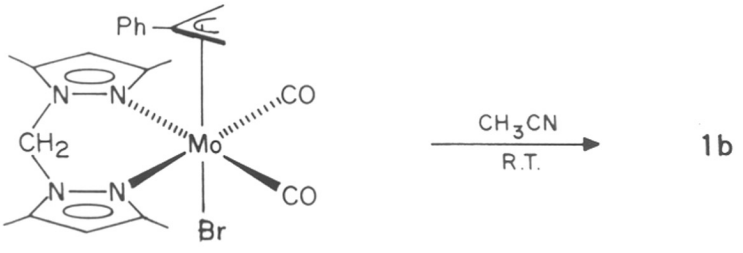


IV-3a

The IR spectra of these solids were identical. Both these solids have m.p. at 260°C (decomposition). Elemental analysis of these solids established their identity.

Similarly solutions of complexes **IV-3b, IV-3c,** and **IV-3e** when exposed to air also gave **1a** as brown crystals. A different complex **1b** obtained from the mother liquor of **IV-3d** was found to be the same as obtained from exposure of a solution of **IV-3d** in air (**Scheme-2**). The colour of this solid **1b** was darker than **1a** and it was also practically insoluble in common organic solvents.

SCHEME-2



IV - 3d

The IR spectra of complexes **1a-b** indicated absence of carbonyl absorptions and presence of absorptions at 960 and 820 characteristic of Mo=O bonding.[4] Other peaks at 1560, 1290, 1040 and 720 were absorptions corresponding to the ligand *bis* (3,5-dimethylpyrazolyl)methane. ^{1}H NMR spectra of complex **1a** recorded in DMSO-D_6 showed two sharp peaks at 2.05 and 2.30 corresponding to pyrazole methyls, and two sharp peaks at 5.70 and 5.95 corresponding to pyrazole 4-H.

In order to learn about the solution behavior of similar complexes, solutions of known (2,2' bipyridyl)-π-allyl dicarbonyl Molybdenum chloro complex[5] **3** and (1,10 phenanthroline) π-allyl dicarbonyl Molybdenum chloro complex[6] **4** were kept at room temperature for 48 hours. No change was observed.

When an acetonitrile solution of complex **IV-3a** was treated with 2 equivalents of PPh_3 and left at room temperature, no brown solid was formed. Isolaion of the organic product indicated that it was 100% triphenylphosphine oxide. This reaction could be extended to 10 equivalents of PPh_3, to attain quantitative conversion to Ph_3PO.

Solutions of other known π-allyl complexes like *bis* (tryphenylphosphine)-π-allyl dicarbonyl Molybdenum chloro complex[7] **5** and *bis* (acetonitrile)-π-allyl dicarbonyl Molybdenum chloro complex[8] **6** in acetonitrile were unable to oxidise PPh_3.

DISCUSSION

After isolation of Mo(II) allyl complexes (**IV-3a-c,e**) from the reaction mixture, the mother liquor was left aside in air at room temperature. After 48 hours, brown crystals appeared in the flask. Filtration and drying under vacuo afforded air stable brown crystals of complex **1a.** This complex was found to be insoluble in almost all organic solvents.

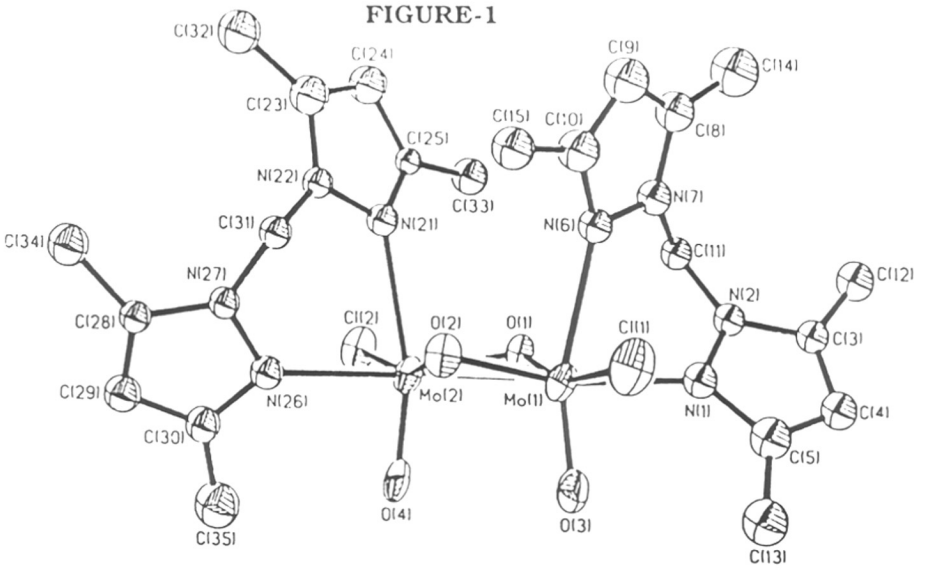
It was also found that dissolving complexes (**IV-3a-c,e**) in acetonitrile or methylene chloride and leaving overnight at room temperature afforded identical crystalline complexes.

After isolation of complex (**IV-3d**), mother liquor afforded complex **1b**. Similarly, solution of complex (**IV-3d**) afforded same complex.

These two complexes (**1a** and **1b**) displayed very similar spectral characteristics. The X-PES recorded for the complexes[9] revealed that chlorine was present in **1a** while bromine was present in **1b**, and that the molybdenum atom was in a high oxidation state.

The identity of these complexes were determined by X-ray crystal structure. The X-ray crystal structure of complex **1a** was determined, and the ORTEP diagram is shown below (**Figure-1**). It indicated that[10] it was a Mo (V) complex with Mo_2O_4 moiety. The six membered metallacycle exists in the boat form, which is known for the complexes of this ligand (Chapter-IV). The Mo-Mo distance of 2.56 A is within the range of a single bond. These compounds were found to be diamagnetic at room temperature, as would be expected for Mo-Mo bonding. Each metal has a distorted octahedral ligand environment with a molecular *C2* symmetry. The bond between molybdenum and a terminal oxygen atom (**Table**) is shorter than that between a metal and a bridging oxygen atom as would be expected.[4]

FIGURE-1



The X-ray structure determination was carried out by H. Zang, Southern Methodist University, USA.

TABLE

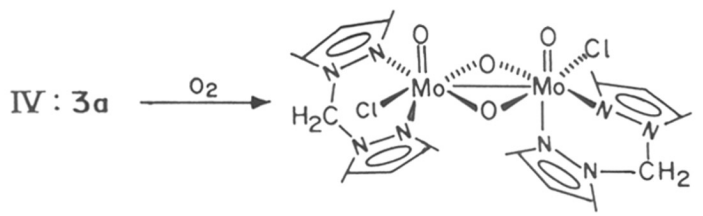
Mo(1)–Mo(2)	2.559(3)	Mo(1)–Cl(1)	2.444(6)
Mo(1)–O(1)	1.939(12)	Mo(1)–O(2)	1.927(13)
Mo(1)–O(3)	1.650(14)	Mo(1)–N(1)	2.267(16)
Mo(1)–N(6)	2.418(16)	Mo(2)–Cl(2)	2.448(6)
Mo(2)–O(1)	1.930(12)	Mo(2)–O(2)	1.943(13)
Mo(2)–O(4)	1.687(14)	Mo(2)–N(21)	2.434(16)
Mo(2)–N(26)	2.275(16)		

Cl(2)–Mo(2)–O(4)	92.8(5)	O(3)–Mo(1)–N(1)	86.1(6)
Cl(2)–Mo(2)–N(21)	79.4(4)	Cl(1)–Mo(1)–N(6)	79.3(4)
Mo(1)–Mo(2)–N(26)	134.1(4)	O(2)–Mo(1)–N(6)	90.4(5)
O(4)–Mo(2)–N(26)	85.9(6)	N(1)–Mo(1)–N(6)	76.6(6)
Mo(2)–Mo(1)–O(1)	48.4(4)	Mo(1)–Mo(2)–O(1)	48.7(4)
O(1)–Mo(1)–O(2)	92.9(5)	Mo(1)–Mo(2)–O(2)	48.3(4)
O(2)–Mo(1)–O(3)	106.3(6)	O(1)–Mo(2)–O(2)	92.7(5)
O(2)–Mo(1)–N(1)	166.5(6)	O(2)–Mo(2)–O(4)	105.4(6)
O(1)–Mo(1)–N(6)	81.1(5)	O(2)–Mo(2)–N(21)	81.5(5)
Mo(1)–Mo(2)–Cl(2)	136.8(2)	O(1)–Mo(2)–N(26)	168.1(6)
Cl(2)–Mo(2)–O(2)	160.8(4)	Mo(1)–O(1)–Mo(2)	82.8(5)
O(1)–Mo(2)–O(4)	105.6(6)	Mo(2)–Mo(1)–O(2)	48.9(4)
O(1)–Mo(2)–N(21)	87.8(5)	Cl(1)–Mo(1)–O(3)	93.8(5)
Cl(2)–Mo(2)–N(26)	88.6(4)	Cl(1)–Mo(1)–N(1)	87.0(4)
N(21)–Mo(2)–N(26)	80.4(6)	Mo(2)–Mo(1)–N(6)	100.2(4)
Mo(2)–Mo(1)–Cl(1)	135.6(2)	O(3)–Mo(1)–N(6)	161.6(6)
Cl(1)–Mo(1)–O(1)	160.3(4)	Cl(2)–Mo(2)–O(1)	88.1(4)
Cl(1)–Mo(1)–O(2)	86.8(4)	Mo(1)–Mo(2)–O(4)	96.4(5)
Mo(2)–Mo(1)–O(3)	96.6(5)	Mo(1)–Mo(2)–N(21)	98.6(4)
O(1)–Mo(1)–O(3)	105.1(6)	O(4)–Mo(2)–N(21)	164.3(6)
Mo(2)–Mo(1)–N(1)	136.6(4)	O(2)–Mo(2)–N(26)	86.7(6)
O(1)–Mo(1)–N(1)	89.0(6)		

The nitrogens are coordinated to the metal in such a way that one nitrogen remains *cis* to the terminal oxygen atom, while the other one was *trans* to it. The Mo-N bond *trans* to the terminal oxo group is longer. The two bridging oxygens are slightly below the plane containing the two molybdenum atoms and the pair of

equatorial ligands. Since these are dimeric complexes of Mo(V) containing two terminal and two bridging oxygen atoms, one halogen on each metal and one bidentate ligand with each metal centre, the net reaction could be represented as shown in **Scheme-3**:

SCHEME-3

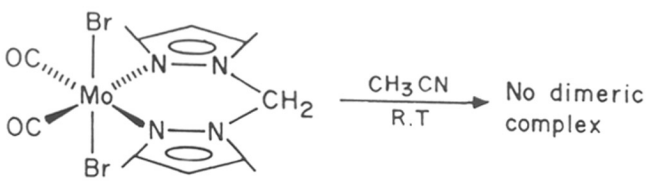


1a

In order to establish whether formation of such isomeric Molybdenum(V) oxo complexes was a general reaction, similar Molybdenum(II) complexes were prepared and allowed to react with oxygen.

Dimerisation of complex **2**[11] was tried under similar conditions. No dimeric complex **1b** was isolated from **2**. This indicated that release of the allyl radical could lead to facile dimerisation (**Scheme-4**).

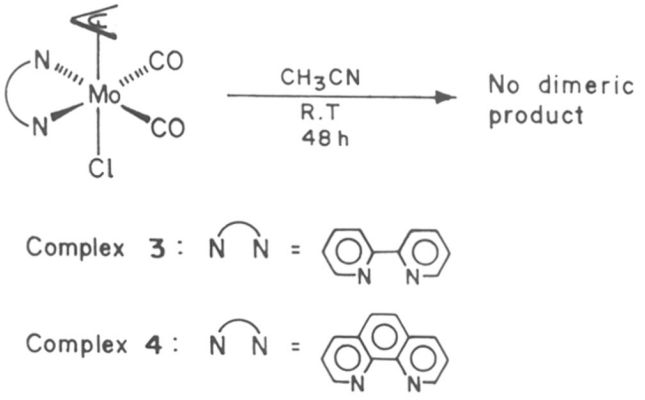
SCHEME-4



Complex -2

Complexes **3** and **4**[12] did not give dimer after exposure to air for 48 hours (**Scheme-5**). This indicates that ligation of *bis*(3,5 dimethyl 1-pyrazolyl) methane to Molybdenum was contributing to dimerisation.

SCHEME-5



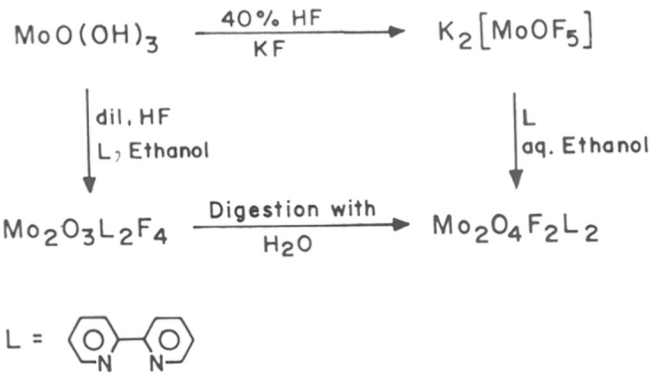
The mechanism for this oxidation is not clear. A peroxo intermediate could be involved, since its formation is feasible under these conditions.

Molybdenum(V) oxo complexes play a major role in molybdenum biochemistry.[13] Ligation of oxomolybdenum centers can prevent dimerisation and hence stabilize the formation of monomeric $\{MoO\}^{+3}$ centers as observed in the oxomolybdoenzymes, since in general chemistry of Molybdenum(V) state is dominated by spin-paired dimerisation.

Molybdenum(V) oxidation state is closely associated with significant number of biological processes like dinitrogen fixation and nitrate reduction. Molybdoenzymes are important for catalysis in the metabolic cycles of carbon, nitrogen, sulphur and chlorine. Strong evidence has been obtained to indicate that the redox states of molybdenum involved in the normal catalytic cycle of these enzymes are Molybdenum(IV), Molybdenum(V) and Molybdenum(VI). The EPR spectra obtained by Gutteridge and Bray[14] have demonstrated that oxygen ligands are bound to Molybdenum(V) centers of the enzymes.

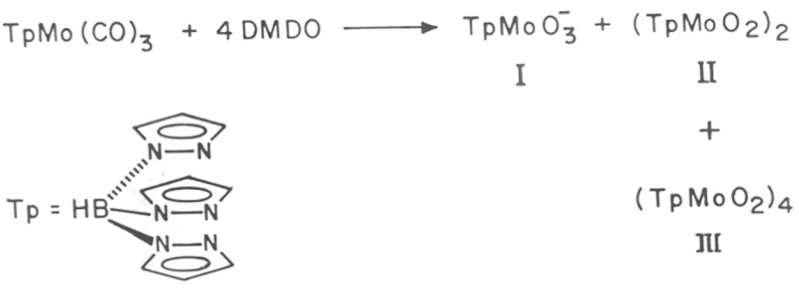
The preparation of Molybdenum(V) oxo complexes usually involve reduction of Molybdenum(VI) species or oxidation of low-valent molybdenum complexes. Dimeric Molybdenum(V) oxo complexes have been prepared[15] from monomeric Molybdenum(V) complexes (**Scheme-6**).

SCHEME-6



Low valent molybdenum complexes were oxidized by the use of various reagents. Kochi[1] found that the complexes $Tp[Mo(CO)_3]^-$ {Tp = Hydrotris(1-pyrazolyl) borate} could be oxidatively decarbonylated to the corresponding oxo complexes by treating with dimethyl dioxirane [DMDO] in anhydrous acetone solutions, at 0 °C temperature. Reaction took place with 4 equivalents of DMDO per equivalent of the complex (**Scheme-7**).

SCHEME-7

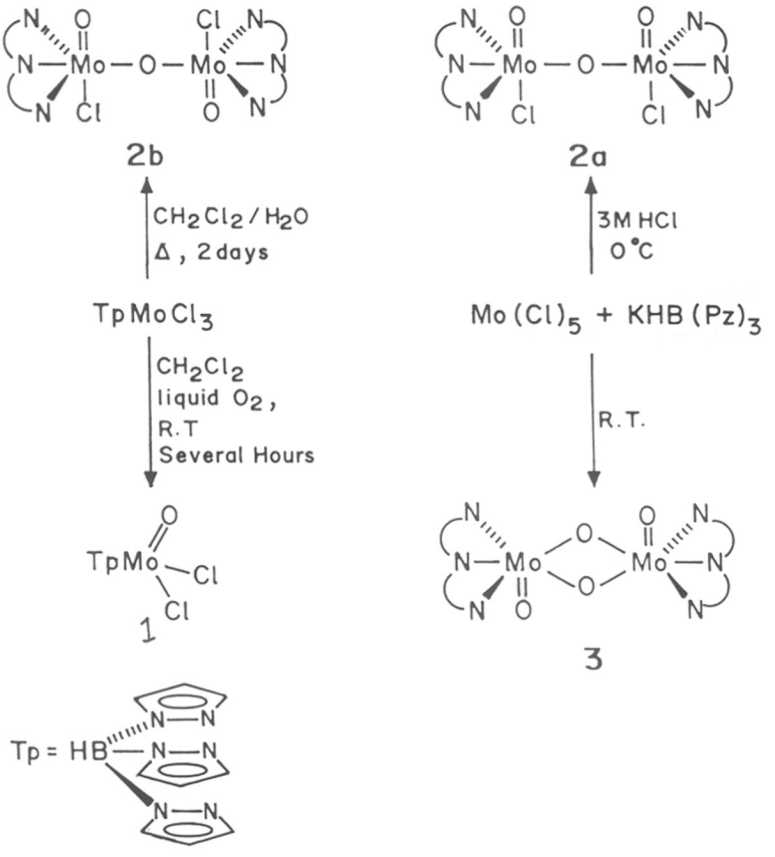


Treatment of the 3,5-dimethyl analogue $T_p^*Mo(CO)_3^-$ [T_p^* = *tris* (3,5-dimethyl pyrazolyl)borate] under the same conditions afforded a similar mixture of complexes.

X-Ray structures of all three complexes were obtained and it was found that II and III were Molybdenum(V) complexes. It was also found that II and III were intermediates in formation of I as treating $[T_pMo(CO)_3]^-$ with DMDO led to a single Molybdenum(VI) product I.

Lincoln[2a] prepared and characterized oxomolybdenum (V) complexes with the hydrotrispyrazolylborate [$HB(Pz)_3$] ligand (**Scheme-8**)

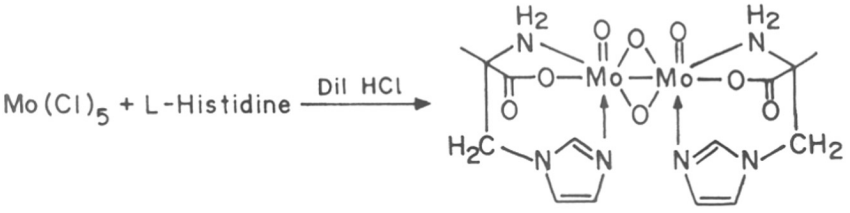
SCHEME-8



The complexes **1**, **2a**, **2b** and **3** were Molybdenum(V) complexes; **2a** and **2b** were geometrical isomers. X-ray structures indicated that complex **1** was a monomer and **2a** and **2b** were dimeric geometrical isomers with *cis* and *trans* Mo=O bonds. Complex **3** was Molybdenum(V) dimer.

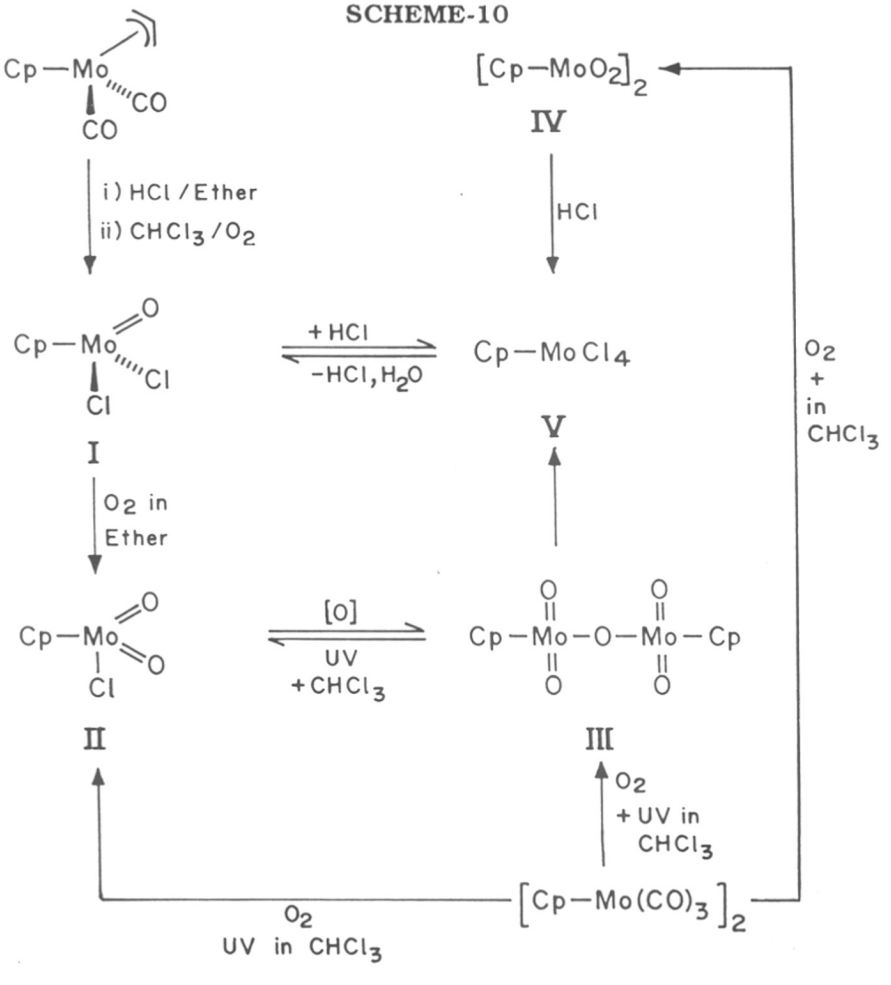
Biologically important Molybdenum(V)-L-histidine complex **1** (**Scheme-9**) was prepared by Melby[16a] starting with a Molybdenum(V) halide.

SCHEME-9



From its crystal structure,[16b] the terminal oxygens were found to be *cis*. The Mo-Mo bond distance was 2.552 A. The only report of an allyl complex of Molybdenum(II) being converted to a Molybdenum(V) complex was reported by Green.[17] He prepared various Molybdenum(V) oxo complexes and oxochloro complexes starting from Molybdenum(II) π-allyl complex (**Scheme-10**).

SCHEME-10



Oxidation of this complex with oxygen and treatment with dry HCl afforded Molybdenum(V) monooxo, oxychloro and dimeric Molybdenum(V) oxo complexes.

The structures of the Molybdenum(V) oxo complexes were deduced from spectral and analytical data. Many dimeric Molybdenum(V) complexes are diamagnetic due to interactions between the two molybdenum (V) atoms either directly and/or via the bridging atoms which lead to spin pairing of the two unpaired electrons.

The *syn* conformation of $[Mo_2O_4]^{+2}$ centers seem to be favoured[18] **(Figure-2)** because this allows a more effective, direct overlap of the orbitals containing the unpaired electrons on each centre leading to the formation of a stronger Mo-Mo bond than is possible for the corresponding *anti* isomer.

FIGURE-2

Syn Anti

The molybdenum centre of the enzyme molybdenum oxidase and nitrate reductase appears to cycle between the VI^+, V^+ and IV^+ states during catalysis of electron transfer between substrate and electron donors or acceptors.[19a] No direct evidence for dioxygen activation with Molybdenum (II) centre was found in the literature, but Molybdenum(VI) to Molybdenum(IV) transformations accompanied by oxo abstraction with triphenyl phosphine were reported.

R. Barral[19b] *et al* had reported that triphenylphosphine abstracts an oxo group from dioxo *bis* (N,N-dialkyldithiocarbamato) molybdenum (**Equation-1**).

EQUATION-1

$$\overset{IV}{Mo}O_2(S_2CNR)_2 + PPh_3 \longrightarrow \overset{IV}{O}Mo(S_2CNR_2)_2 + PPh_3O$$

EQUATION-2

$$Mo_2O_3(S_2CNR_2)_4 \rightleftharpoons MoO_2(S_2CNR_2)_2 + OMo(S_2CNR_2)_2$$

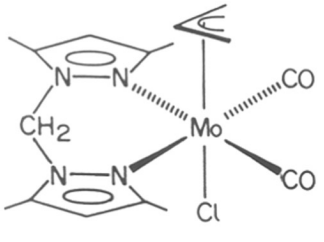
This reaction, together with the equilibrium shown in **Equation 2**, was used in the design of a system for the catalytic aerial oxidation of phosphines.

Chen[20] *et al* prepared complexes $MoO_2(S_2PPh_2)_2$, $MoO_2(S_2P(i\text{-}Pr)_2$ and utilized these complexes in the synthesis of Molybdenum(IV)-oxo and Molybdenum(V)-Molybdenum(V) dimeric complexes by treating them with PPh_3. It was observed that in the oxo abstraction reactions from the complexes MoO_2L_2, the degree of reduction to Molybdenum(IV) or Molybdenum(V) depends on the ligands involved.

In view of possible intermediates which could effect catalytic oxygen transfer to suitable acceptor molecule, reaction of the Molybdenum-π-allyl complexes (**IV-3a**) with O_2 was studied in the presence of PPh_3.

When two molar equivalents of triphenylphosphine were treated with acetonitrile solution of π-allyl complex **IV-3a** at room temperature, no dimer formation was observed even after 48 hours. After complete consumption of PPh_3 (2 days) to form a new product, the reaction was worked up. Inorganic part was a dark green solid which was not stable enough for crystallization. The organic part was 100% triphenylphosphine oxide (**Scheme-11**).

SCHEME-11



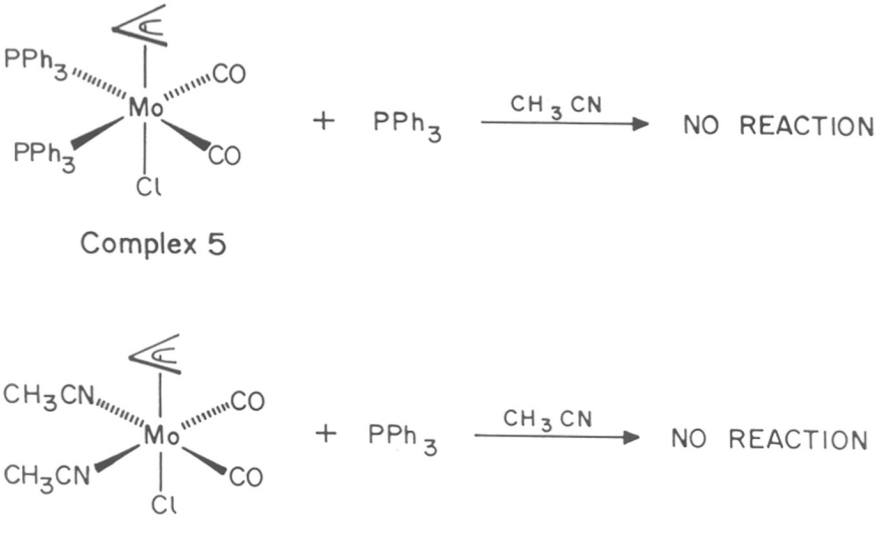
IV-3a

+ PPh_3 $\xrightarrow{CH_3CN}$ PPh_3O

The catalytic efficiency of this process was tested by treating 10 fold excess of PPh_3 with the substrate. Complete conversion of PPh_3 to PPh_3O was achieved after 12 days. This is the first example of aerial oxidation of PPh_3 catalysed by Molybdenum oxo intermediates generated from a Molybdenum(II)-π-allyl complex.

To see whether this process is associated with complexation and decomplexation of PPh_3 to the metal, solution of complex **5** was treated with PPh_3 and exposed to air. No conversion of PPh_3 to PPh_3O was observed. This showed that complexation of PPh_3 was not involved in this process at any stage. Similarly *bis*(acetonitrile)-π-allyl complexes of molybdenum also did not effect oxidation of PPh_3 (**Scheme-12**).

SCHEME-12



It was also found that dichloromethane was not a suitable solvent for oxygen transfer to PPh_3, though dimeric Molybdenum(V) complex could be obtained.

Results so far obtained, thus indicated that pyrazole ligation was crucial to dioxygen activation on the Molybdenum(II) centre.

SUMMARY

The molybdenum π-allyl complexes containing *bis* (3,5-dimethyl 1-pyrazolyl)methane as the chelating ligand underwent facile oxidation to furnish crystalline, dimeric Molybdenum(V) oxo complex whose structure was determined by X-ray crystallography. It was further observed that acetonitrile solutions of such complexes could catalytically oxidise PPh_3 to PPh_3O in air.

EXPERIMENTAL

Preparation of 1a from IV-3a

Allyl complex **IV-3a** (50 mg, 0.11 mmol) was dissolved in acetonitrile (5 ml) and the flask was closed with loose cotton plug and left at room temperature for 48h. The brown crystalline solid, **1a** settled at the bottom of the flask was collected by filtration, washed with CH_3CN and dried under high vacuum to get 28 mg (66%) of **1a**.

Preparation of 1a from IV-3b

Following the same procedure from 0.05 g (0.11 mmol) of **IV-3b** in 5 ml of acetonitrile, 0.032 g (78%) of **1a** was obtained.

Preparation of 1a from IV-3c

Following the same procedure from 0.05 g (0.1 mmol) of **IV-3c** in 5 ml of acetonitrile, 0.023 g (63.7%) of **1a** was obtained.

COLOUR:- Brown

MP Above 260°C (decomposition)

IR 1560, 1290, 1040, 960, 820, 720.

^{1}H NMR 80 MHz, DMSO-D_6:- 2.05 (s, 3H); 2.30 (s, 3H); 5.70 (s, 1H); 5.95 (S, 1H).

ANALYSIS $C_{22}H_{32}N_8Cl_2O_4Mo_2$

Cal: C = 35.91; H = 4.35; N = 15.23.

Found: C = 36.08; H = 4.43; N = 15.26.

Preparation of 1b from IV-3d

Following the same procedure from complex **IV-3d** (0.05 g, 0.09 mmol) in dichloromethane (10 ml), 0.029 g (78%) of complex **1b** was obtained.

COLOUR:- Dark brown

MP Above 260°C (decomposition)

IR 1560, 1290, 1040, 960, 820, 720.

ANALYSIS $C_{22}H_{32}N_8Br_2O_4Mo_2$

Cal: C = 32.03; H = 3.80; N = 13.59.

Found: C = 31.93; H = 3.48; N = 13.18.

Oxidation of Triphenylphosphine.

Complex **1a** (216 mg, 0.5 mmol) and Triphenylphosphine (264 mg, 1 mmol) were dissolved in acetonitrile (20 ml), and the solution was allowed to stand in air. After 2 days, complete disappearance of triphenylphosphine was observed by TLC. The solvent was removed under reduced pressure, and the residue was treated with dichloromethane (10 ml). On addition of petroleum ether (10 ml) to this solution, precipitation of the metallic residue occurred as a green solid. After filtration and concentration of the filtrate, the residue was triturated with petroleum ether to obtain a pure sample of triphenylphosphine oxide as a white solid (268 mg, 94%). The experiment was repeated with the same quantity of complex **1a** and excess of PPh_3 (1.32 g, 5 mmol). The complete conversion of the phosphine required 12 days, and the product phosphine oxide was isolated as before (1.18 g, 84%).

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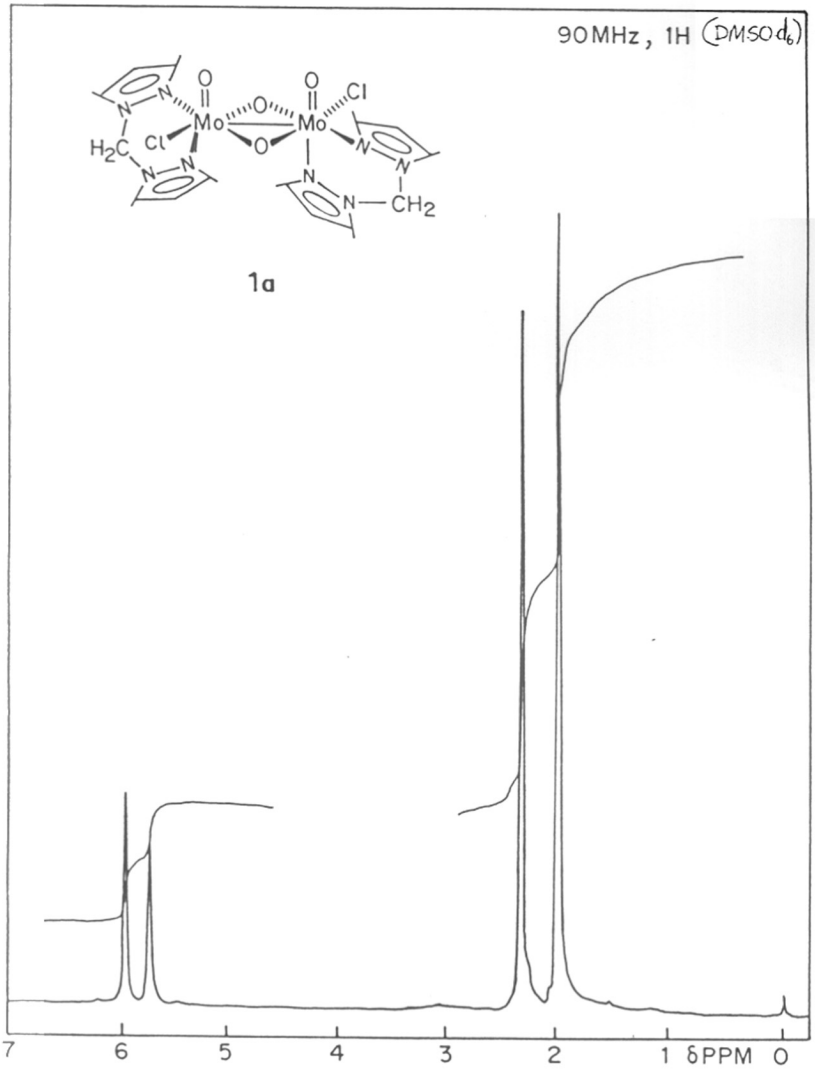

1a