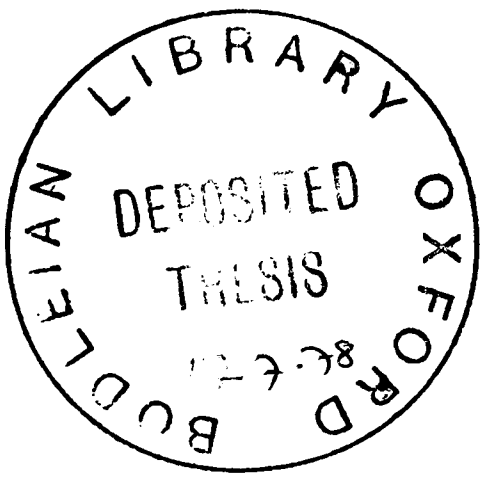
ORGANOMETALLIC CHEMISTRY

OF

MOLYBDENUM AND COBALT AND

RELATED STUDIES



by

Teresa Aviles

A thesis submitted in part fulfilment
of the requirement for the degree of
Doctor of Philosophy
at the
University of Oxford

St. Anne's College
Oxford

February 1978

The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, Oxford, from October 1974 to October 1977 under the supervision of Dr. M.L.H. Green.

All the work is my own unless stated to the contrary, and it has not been submitted previously for a degree in this or any other University.

(Teresa Aviles)

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my supervisor Dr. M.L.H. Green for his great help and encouragement during the course of this work.

I would also like to thank all my laboratory colleagues for their friendship and assistance.

I gratefully acknowledge the services of all those who have contributed to this work by carrying out physical measurements, in particular to Mrs. E. Richards and her staff (n.m.r.), Jane Webb (analysis), Dr. R.T. Aplin and his staff (mass spectroscopy).

I would like to thank Mrs. Judith Adam for her care and patience in typing this thesis.

Finally, I would like to thank the Ministerio de Educacion y Ciencia (Spain) and the Anglo-Spanish Foundation Vicente Cañada Blanch for financial support during the course of this work.

SUBJECT INDEX

FIGURE INDEX

TABLE INDEX

ABSTRACT

Organometallic Chemistry of Molybdenum and Cobalt and related studies.

Teresa Aviles, St. Anne's College

D.Phil Thesis, Hilary Term 1978

The thesis concerns developments in the chemistry of monocyclopentadienylmolybdenum derivatives and (η-allylic)monocyclopentadienylcobalt derivatives.

Improved synthetic routes to the compound $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$ are described.

It is shown that there are structural isomers of the compound $Mo\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_5H_6\}dppe)PF_6$ which differ in the orientation of the $\eta\text{-}C_5H_6$ ligand on the metal.

The new compounds $(Mo\{\eta\text{-}C_5H_5\}_2dppm)(PF_6)_2$, $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}H)PF_6$, $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}Cl)PF_6$ and $(Mo\{\eta\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$ have been prepared.

The new compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ has been synthesised by treatment of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ with $NaAlH_2(OCH_2CH_2OCH_3)_2$. The reaction of the trihydride with butadiene led to isomers of the compound $Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}dppe$. These undergo hydride abstraction giving isomers of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)PF_6$.

New synthetic routes to the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ were investigated. Treatment of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ with $NaBH_4$ and separately with $HSn\{n\text{-butyl}\}_3$ gave the new compounds $Mo\{\eta\text{-}C_5H_5\}\{dppe\}BH_4$ and $Mo\{\eta\text{-}C_5H_5\}\{dppe\}\{Sn(n\text{-butyl})_3\}H_2$ respectively.

The new compounds $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppm$ and $Mo\{\eta\text{-}C_5H_5\}$

{dppm}Cl_3 have also been prepared and characterised.

The chemistry of the (η-allylic)monocyclopentadienylcobalt system was studied with a view to understanding the factors leading to regiospecific addition on the polyene ligands of organometallic cations.

The new compounds (Co{η-C_5H_5}{η-C_3H_5}PR_3)(PF_6), (PR_3 = $PPhMe_2$, PMe_3), (Co{η-C_5H_5}{1-CH_3-η-C_3H_4}L)(PF_6) (L = CO, PMe_3), (Co{η-C_5H_5}{2-CH_3-η-C_3H_4}L)(PF_6), (L = CO, PMe_3, Py, NH_3), Co{η-C_5H_5}{2-CH_3-η-C_3H_4}I and Co{η-C_5H_5}{1-CH_3-η-C_3H_4}Br were prepared and characterised.

The reactions of many of these compounds towards addition of hydride or methyl anion were studied. New reactions observed included the reaction of (Co{η-C_5H_5}{η-C_3H_5}PMe_3)PF_6 with MeLi to give the unexpected product Co{η-C_5H_5}{PMe_3}Me_2.

Reaction of Co{η-C_5H_5}{CO}I_2 with PMe_3 gave (Co{η-C_5H_5}{PMe_3}$_3$)I_2. Treatment of (Co{η-C_5H_5}{PMe_3}$_3$)(PF_6)$_2$ with MeLi gave Co{η-C_5H_5}{PMe_3}Me_2.

The compound (Co{η-C_5H_5}{$PPhMe_2$}$_2$H)PF_6 was isolated in the reaction of Co{η-C_5H_5}{$PPhMe_2$}I_2 with isopropyl magnesium bromide.

The Introductory Chapter of the thesis reviews known chemistry pertinent to the studies described above.

ABBREVIATIONS

Cp	η-cyclopentadienyl
THF	tetrahydrofuran
dppe	1,2-bis(diphenylphosphine)ethane
dppm	1,2-bis(diphenylphosphino)methane

CHAPTER I

INTRODUCTION

I. SOME CHEMISTRY OF MONOCYCLOPENTADIENYLMOLYBDENUM COMPOUNDS.

A very extensive chemistry of the bis(cyclopentadienyl)-molybdenum system is known. However, the two cyclopentadienyl groups occupy essentially six coordination sites around the metal and leave room for only two, or occasionally three, other ligands.

We were interested in developing the chemistry of monocyclopentadienylmolybdenum compounds where the metal was relatively electron rich, in the expectation that this might lead to new areas of reactivity and catalysis.

At the outset of this work, a very extensive chemistry of (carbonyl)monocyclopentadienylmolybdenum derivatives was already known. Some illustrative chemistry is shown in Figure I.1 [1].

Also a related chemistry of the system $Mo\{\eta\text{-}C_5H_5\}\{NO\}_2$ [2 - 4] had been developed. Whilst this chemistry is both extensive and in many respects interesting, we did not wish to develop these systems further since, in general, the effect of carbonyl or nitrosyl ligands on a metal is to reduce significantly electron density at the metal. In other words, $Mo\{\eta\text{-}C_5H_5\}L_x$ compounds, where L = CO or NO, are normally rather electron-poor.

It was our wish to develop other $Mo\{\eta\text{-}C_5H_5\}L_x$ compounds, where the ligands were not very strong π-acids, so that the metal centre remained relatively electron rich.

In this introduction, we will describe some known

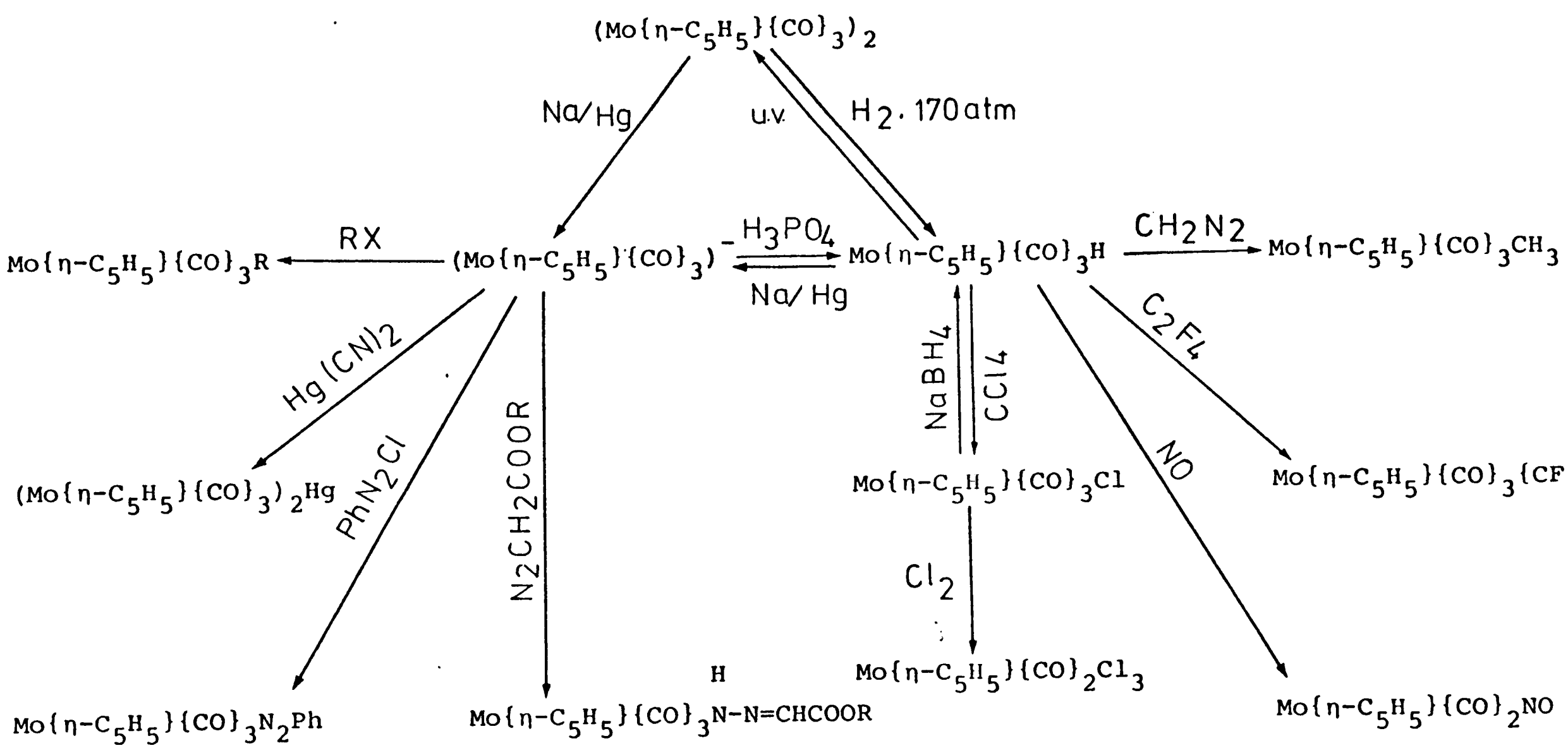
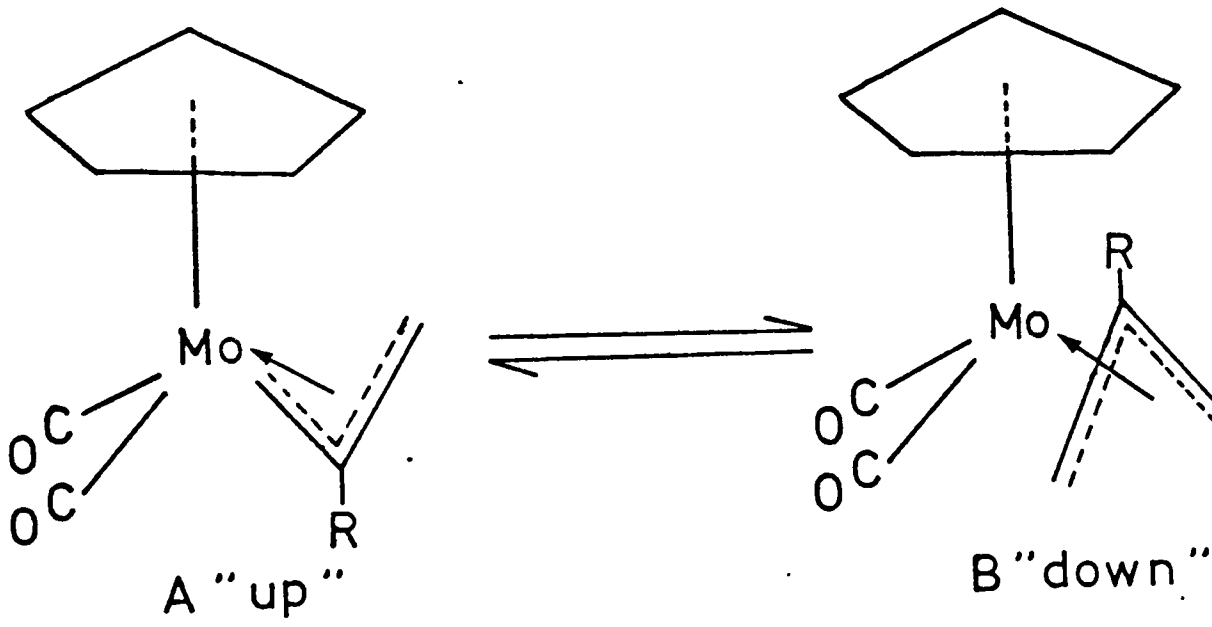


FIGURE I.1. Some chemistry of (carbonyl) monocyclopentadienyl molybdenum system..

chemistry of compounds of the type $Mo\{\eta\text{-}C_5H_5\}L_x$ relevant to the work described in subsequent chapters, where L = CO and other ligands.

1. Configurational isomerism in monocyclopentadienylmolybdenum compounds.

Equilibria between conformers A and B (1a) of η-allyl derivatives of molybdenum and tungsten has been widely noted (5 - 11). Nevertheless, convincing evidence for assigning given configurations was lacking. Faller(12) has provided a method for determining the stereochemistry in these complexes based on measurement of magnetic anisotropies associated with indenyl derivatives. It appears that the major contributor to



(1a)

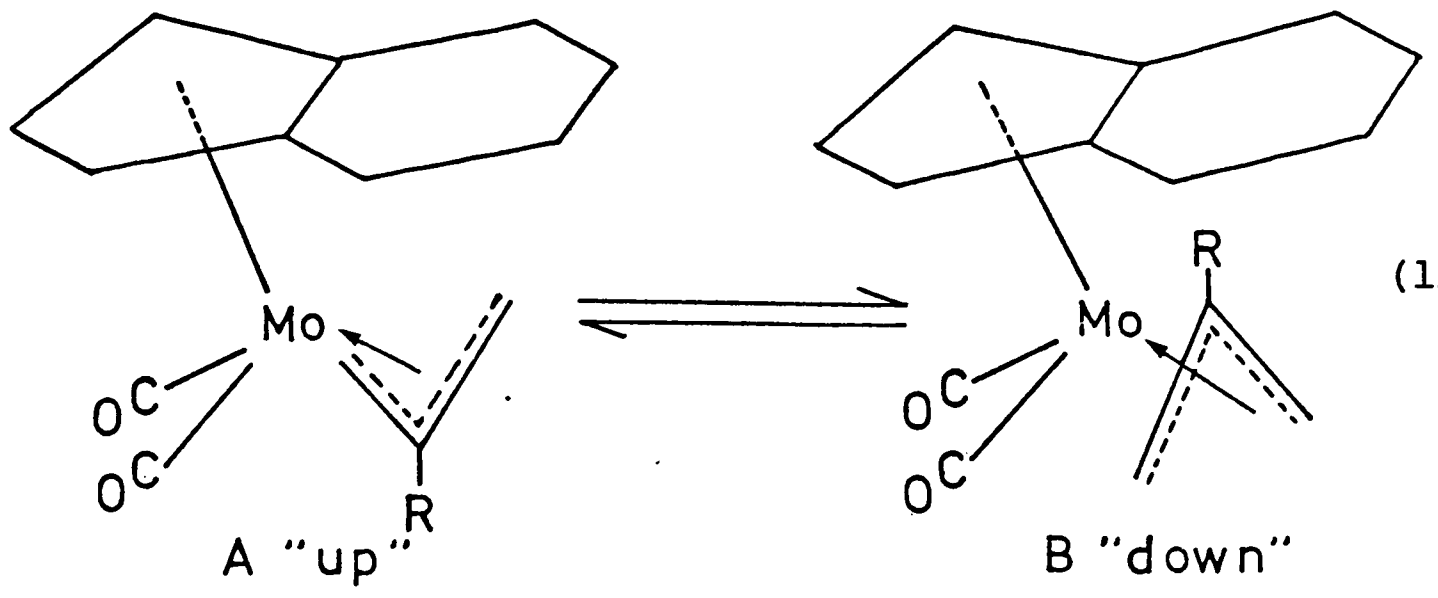
the stability of a particular isomer is the relative magnitude of steric interaction between allyl substituents and the cyclopentadienyl or indenyl ring.

We define the "up" isomer as the one in which the open end of the polyene systems is nearest to the cyclopentadienyl

ring, and the "down" isomer the one in which the open end of the polyene system is further from the cyclopentadienyl ring, and from henceforth, we will refer to them as the "up" and the "down" isomers accordingly.

Substitution of an indenyl ligand for a cyclopentadienyl ligand does not greatly alter the ratio of allyl conformers, although the barrier to interconversion of the conformers is raised somewhat.

A study of the compounds A and B (1b) has led to the suggestion that there is relatively free rotation of the indenyl ligands, but there is a preferred conformation with the six membered ring oriented over the allyl. Appropriate substitution of the allyl offers sufficient steric hindrance to make other conformations more favourable.



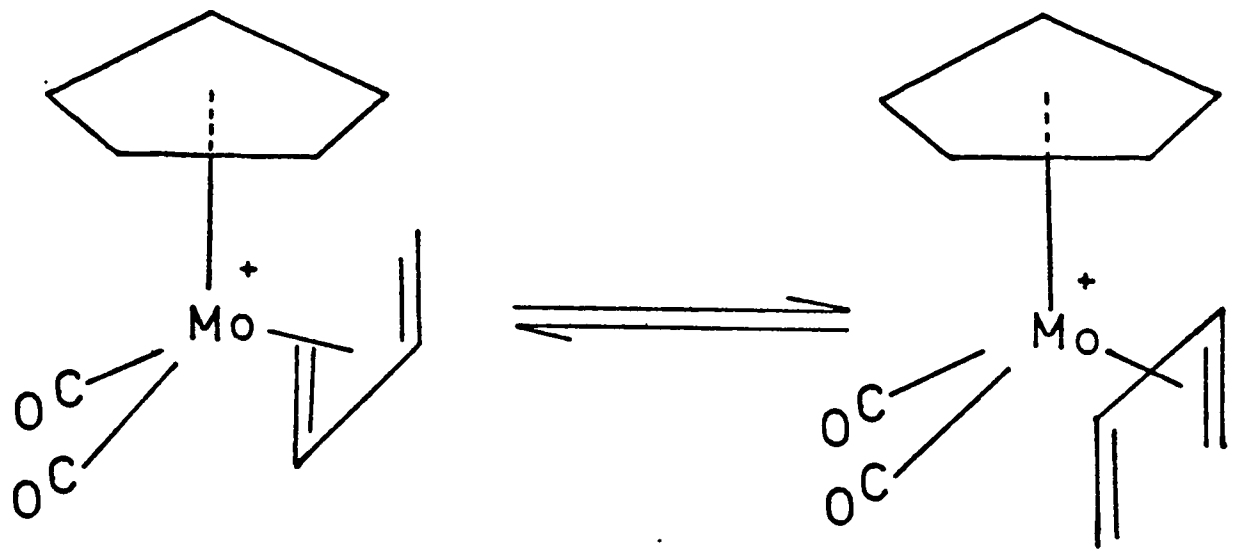
(1b)

For example, for unsubstituted η-allyl, 1-Me, 1,1-Me_2, 1,3-Me_2 and 1,1,2-Me_3-η-allyl derivatives, B is the major conformer, whereas for the 2-Cl, 2-Br and 2-Me-η-allyl derivatives, it is A.

The structure of di(carbonyl)(η-cyclopentadienyl)

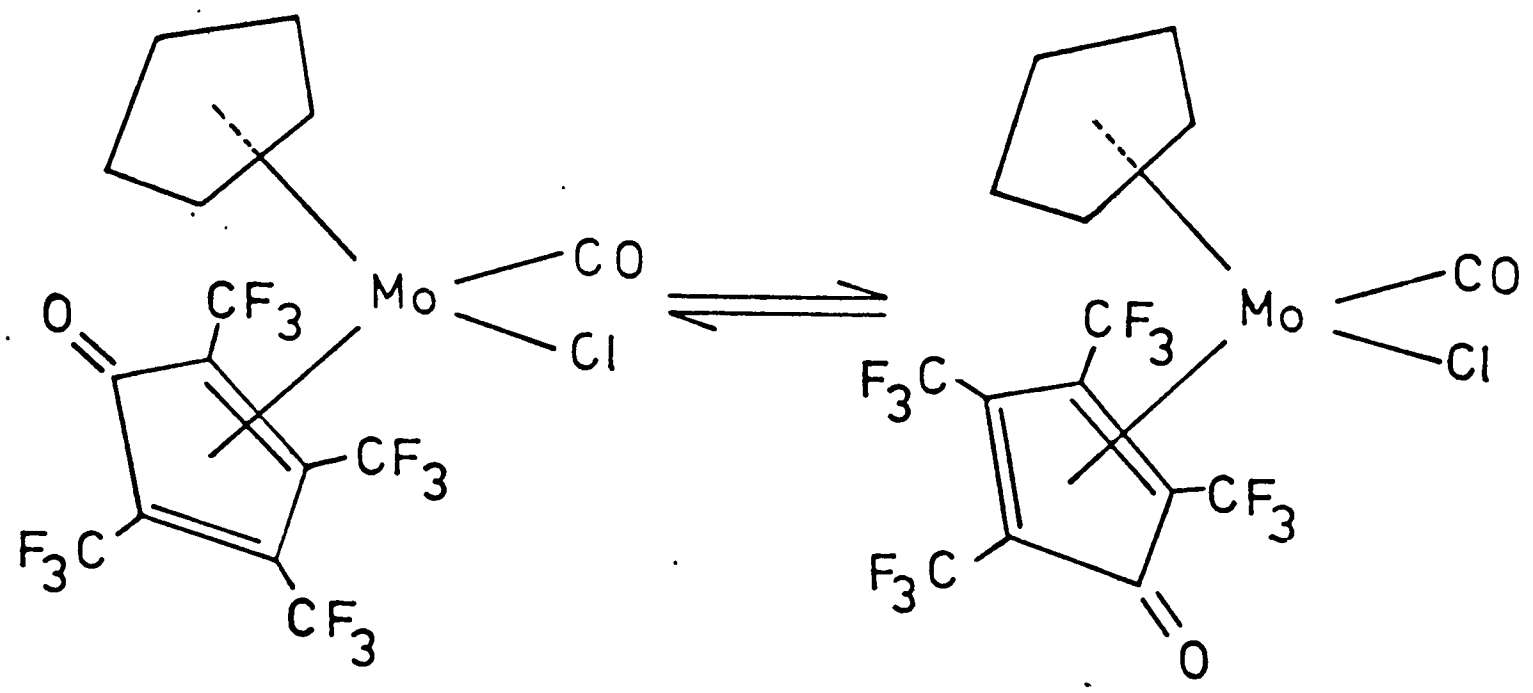
(p-methyl-η-benzyl)molybdenum, which contains a η-allyl-Mo moiety has been determined by X-ray diffraction. Only one of the two possible isomers is formed and this is the "up" isomer[13]

The cationic complexes di(carbonyl)(η-cyclopentadienyl) (η^4-diene) molybdenum have been prepared and characterised. These cations exist as "up" and "down" conformers (1c) and equilibrium is attained by rotation of ligating diene[14].

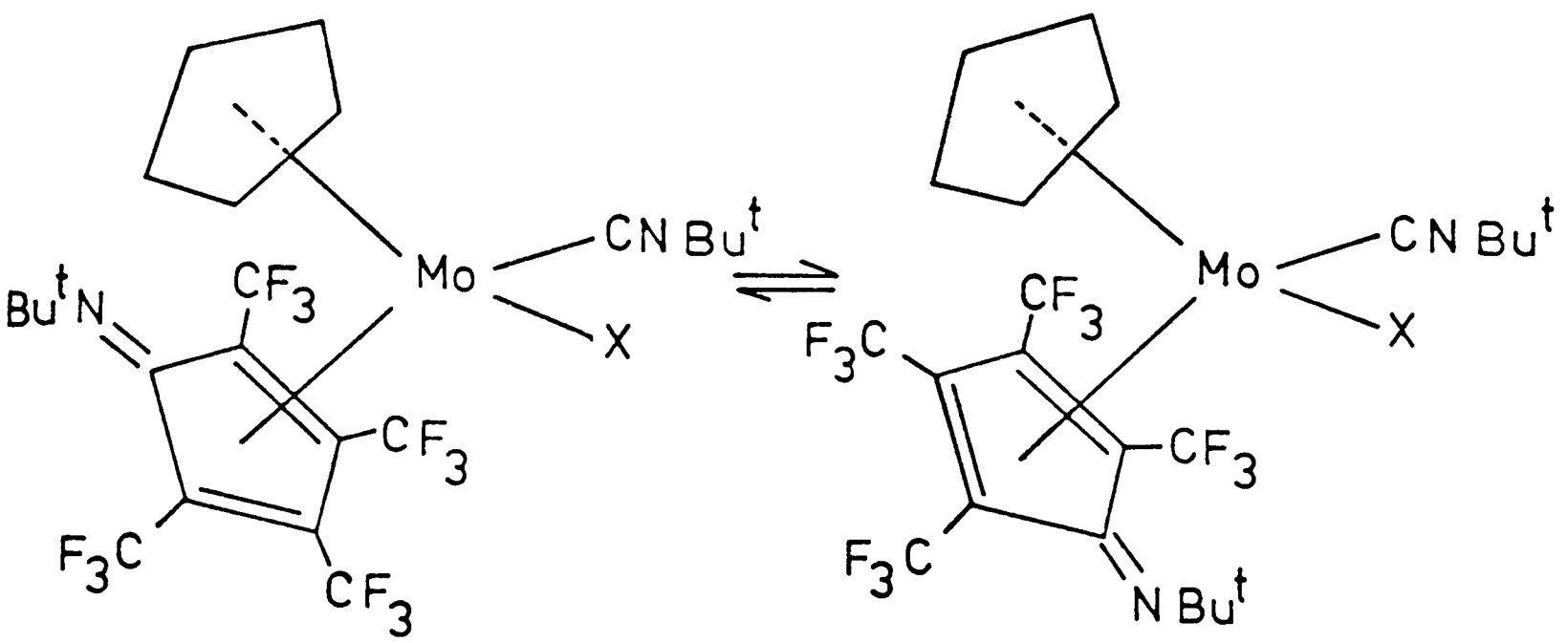


(1c)

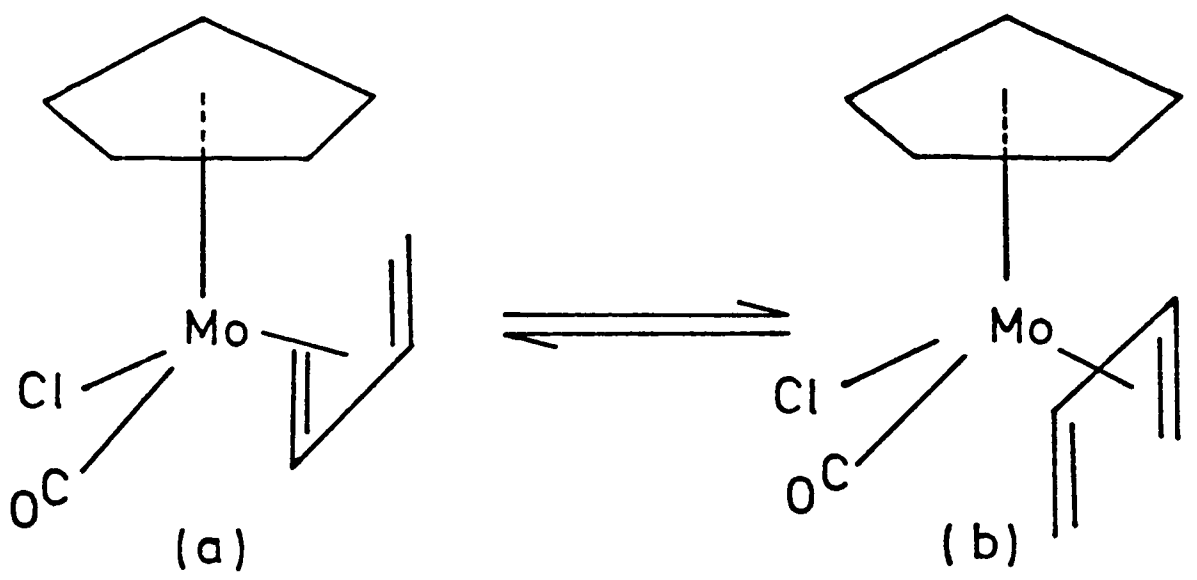
A further example of this type of conformational isomerism is found in the compound ($Mo\{\eta\text{-}C_5H_5\}\{(CF_3)_4C_5O\}\{CO\}Cl$) which is obtained in the reaction $Mo\{\eta\text{-}C_5H_5\}\{CO\}_3Cl$) in excess, with $CF_3C{\equiv}CCF_3$ in hexane. The ^1H n.m.r. spectrum of this compound shows two singlet peaks of equal intensity at 3.55τ and 3.95τ, assignable to a η-cyclopentadienyl ligand. The infrared spectrum shows two ketonic carbonyl bands and ^{19}F n.m.r. was temperature dependent. The presence of interconverting "up" and "down" isomers was proposed[15].



The 16-electron complexes ($M\{\eta\text{-}C_5H_5\}\{F_3CC{\equiv}CCF_3\}_2X$) (M = Mo, X = CF_3; M = W, X = Cl) have been described. Treatment of $M\{\eta\text{-}C_5H_5\}\{CF_3C{\equiv}CCF_3\}X$) with Bu^tNC (1:1) in diethylether at room temperature gave the 18-electron species ($M\{\eta^5\text{-}C_5H_5\}\{CF_3C{\equiv}CCF_3\}_2\{Bu^tNC\}X$) (I). With a 2:1 molar ratio of reactants, the reaction proceeds *via* (I) to give isomeric mixtures of the complexes:



The 16-electron acetylene complexes also react with 1,3-dienes. Treatment at 70°C of ($Mo\{\eta\text{-}C_5H_5\}\{CF_3C_2CF_3\}_2Cl$) with buta-1,3-diene in hexane, or of ($Mo\{\eta\text{-}C_5H_5\}\{PhC_2Ph\}\{CO\}Cl$) with buta-1,3-diene in dichloromethane, afforded the paramagnetic 17-electron species ($Mo\{\eta\text{-}C_5H_5\}\{1,3\text{-}\eta\text{-}C_4H_6\}Cl_2$). In tetrahydrofuran at 70°C, buta-1,3-diene and ($M\{\eta^5\text{-}C_5H_5\}\{PhC_2Ph\}\{CO\}Cl$) (M = Mo, W) give respectively the 18-electron complexes



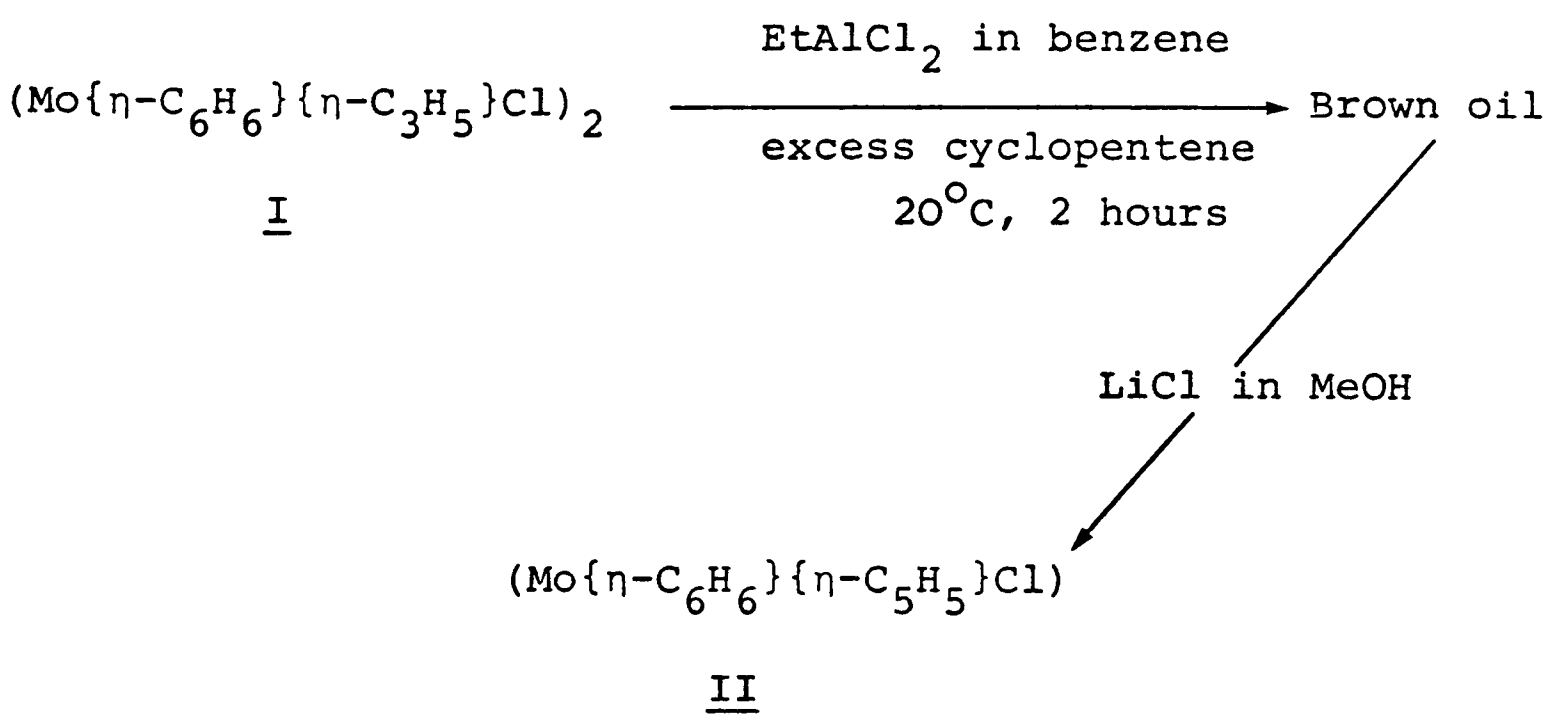
The ^1H n.m.r. spectrum in each case shows a single cyclopentadienyl resonance, and resonances characteristic of 1,4-η^4 bonded buta-1,3-diene consistent with either structure (a) or (b)[16].

2. <u>Some chemistry of monocyclopentadienylmolybdenum systems which do not contain CO or NO ligands</u>.

During the course of this work, others were investigating approaches to monocyclopentadienylmolybdenum chemistry and we

review their conclusions here.

Green, Knight and Segal[17] found a new synthetic route to the mixed η-benzene-η-cyclopentadienylmolybdenum system in which the yield was improved compared with the original one[18, 19]. The new bent mixed sandwich 18-electron compound $Mo\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_6H_6\}Cl$ was prepared in *ca.* 85% yield by the method



The compound II is a versatile precursor for carbonyl-free monocyclopentadienylmolybdenum derivatives[20, 21]. A sequence of reactions is schematically shown in Figure I.2.

FIGURE I.2. Some chemistry of monocyclopentadienyl-molybdenum system.

i; dppe in MeOH, 65°C, 3h. Then NH_4PF_6 or $NaBF_4$.

ii; stoichiometric I_2 in CH_2Cl_2.

iii; $TlPF_6$ in Me_2CO, then cyclooctatetraene, 56°C, 20 min.

iv; O_2 in $CHCl_3$.

v; Solution in MeCN.

vi; CO in MeCN, 80°C, 10 min.

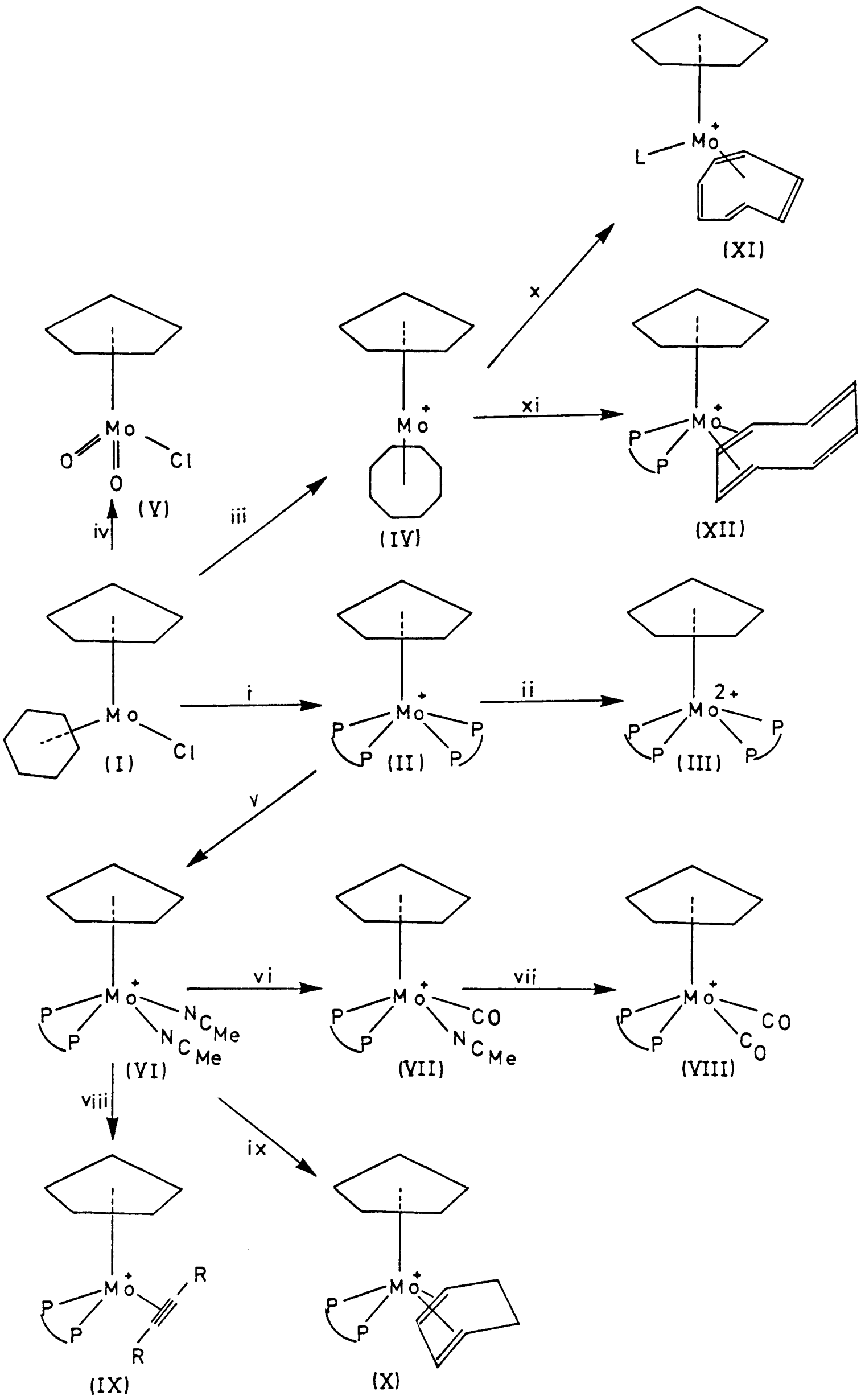
vii; CO in MeCN, 80°C, 12 hours.

viii; C_2Ph_2 or C_2Me_2 in MeCN, 80°C, 1 hour.

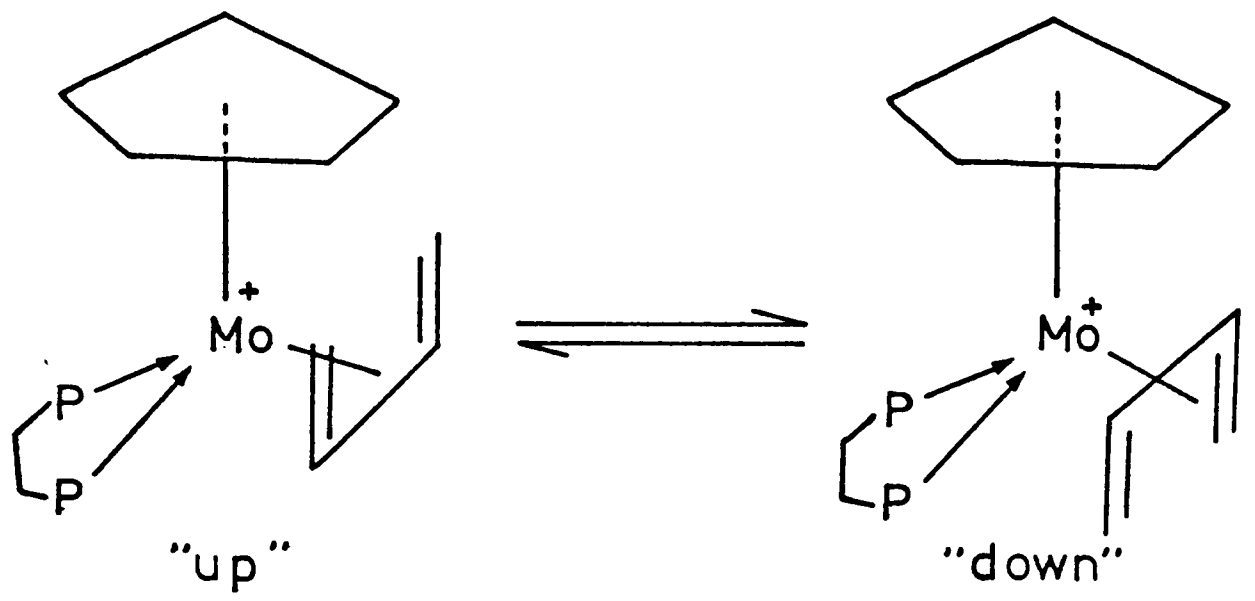
ix; diolefin in MeCN, 80°C, 1 hour.

x; PPh_3 or CO in MeCN, 20°C.

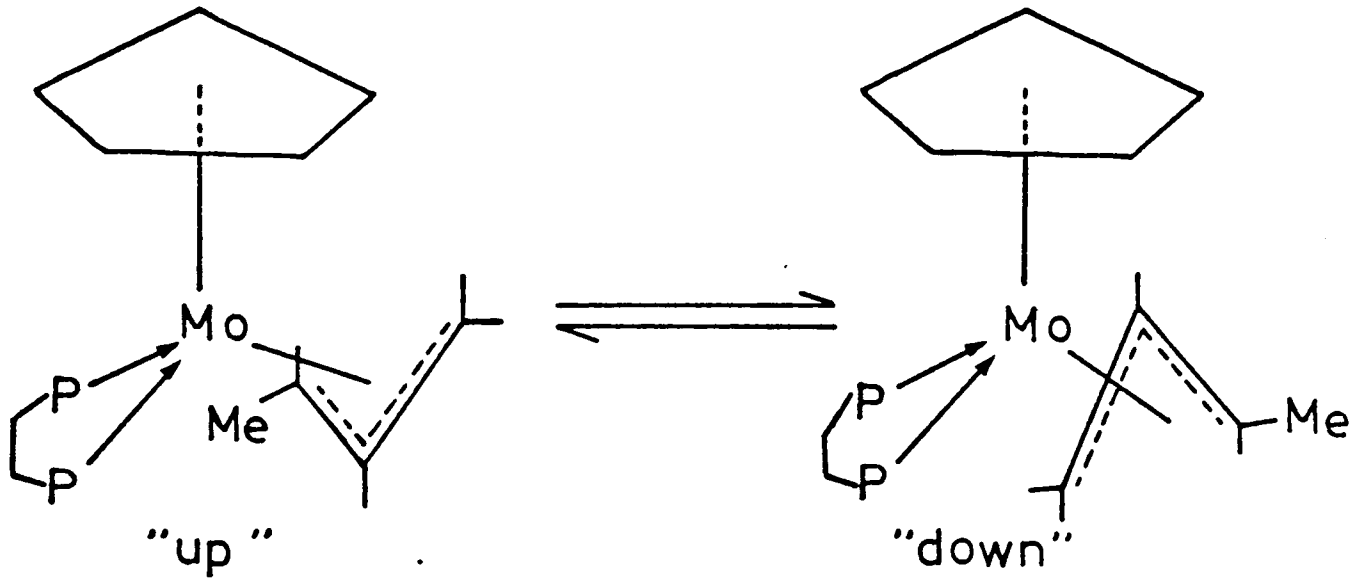
xi; dppe in Me_2CO, 20°C, 5 min.


Mo
Cl
O
(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)
(X)
(XI)
(XII)
P
L
R
CO
N
C
Me
2+
i
ii
iii
iv
v
vi
vii
viii
ix
x
xi

Treatment of compound II with butadiene gives the complex $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)^+$ as a 1:1 mixture of conformational isomers.

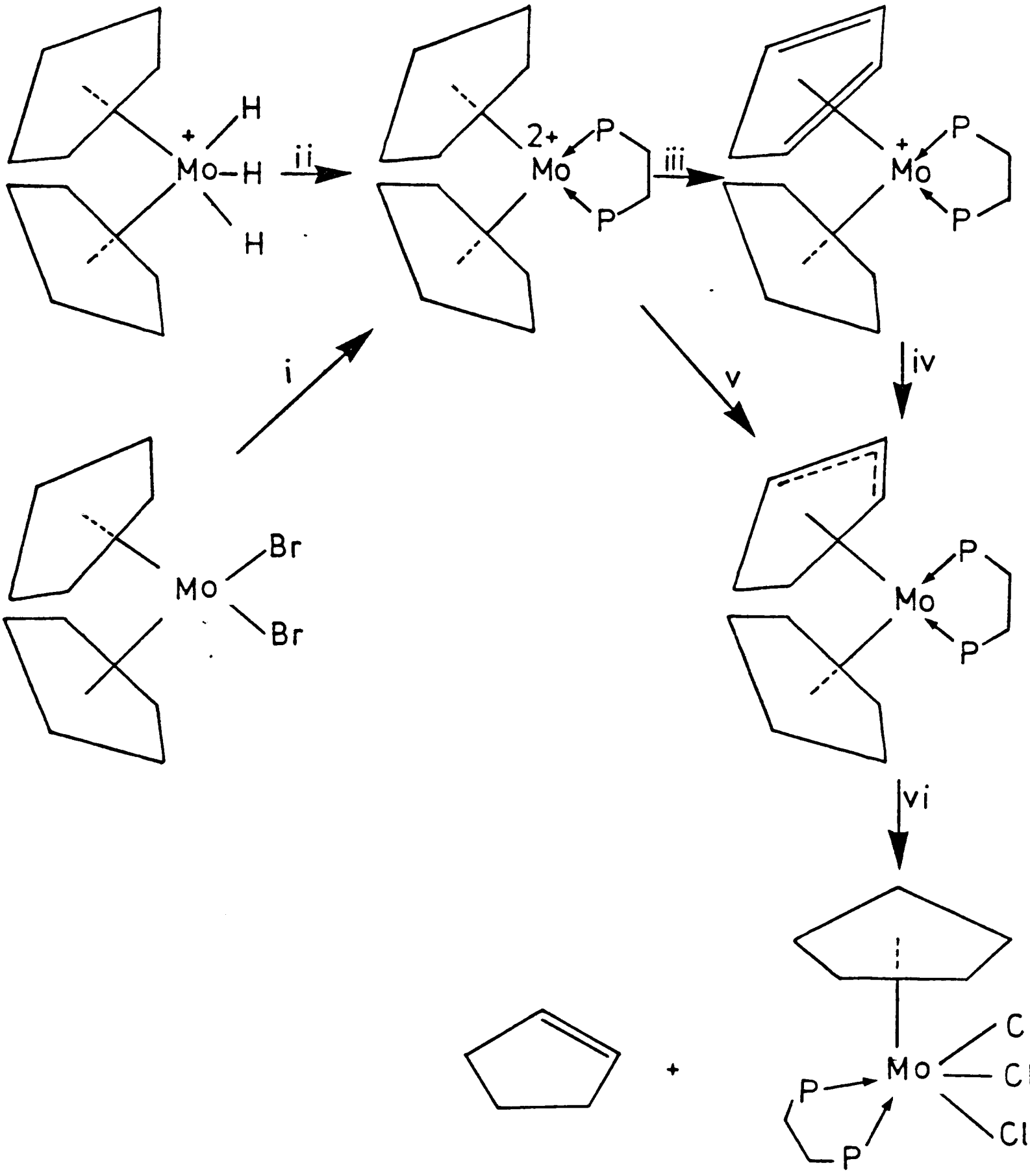


Treatment of a mixture of the two isomers with $NaAlH_2(OCH_2CH_2OMe)_2$ in tetrahydrofuran gives the crotyl derivatives:



which can be partially separated by crystallisation. The crystal structure of compound X has been determined.

Our approach to the synthesis of monocyclopentadienylmolybdenum compounds was via the displacement of one of the cyclopentadienyl rings in biscyclopentadienylmolybdenum systems by other ligands. Some of the reactions which are discussed in Chapter II are anticipated in Figure I.3 as an example.



i dppe in acetone, then $TlPF_6$ in acetone

ii dppe in acetone, 20°C, 12h.

iii 1 equivalent $NaBH_4$ in THF, 20°C

iv 1 equivalent $NaBH_4$ in THF, 20°C

v excess $NaBH_4$ in THF, 20°C

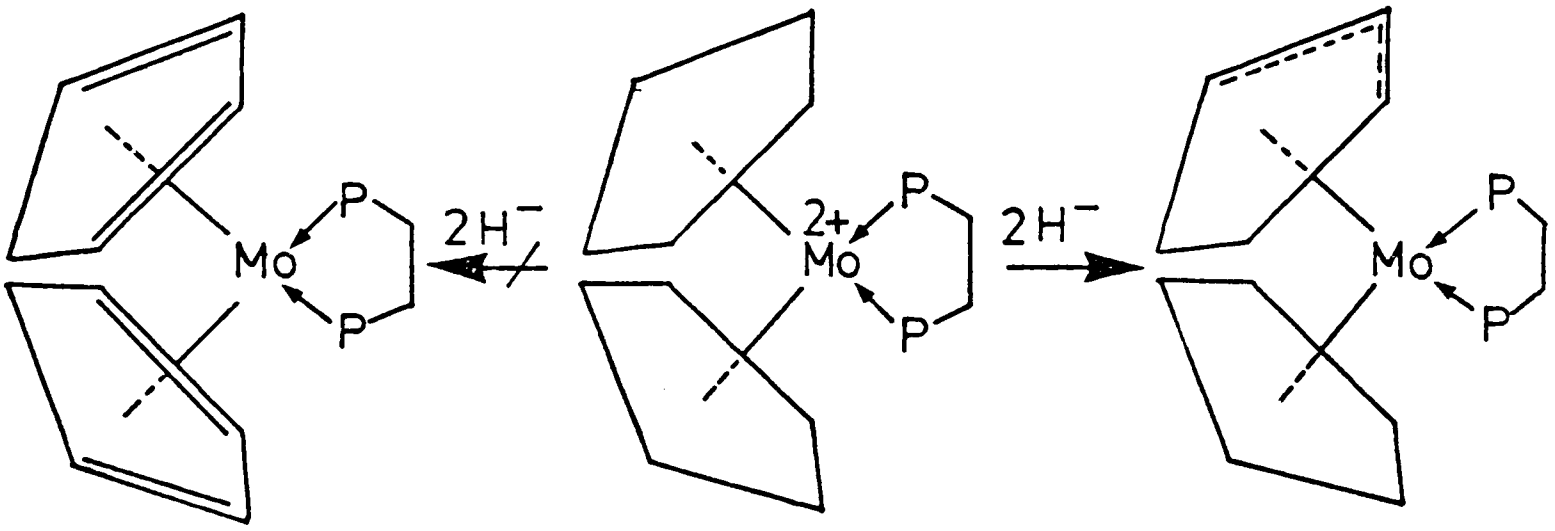
vi HCl (gas) in toluene (140°C)

FIGURE I.3 Synthesis and reactions of $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$

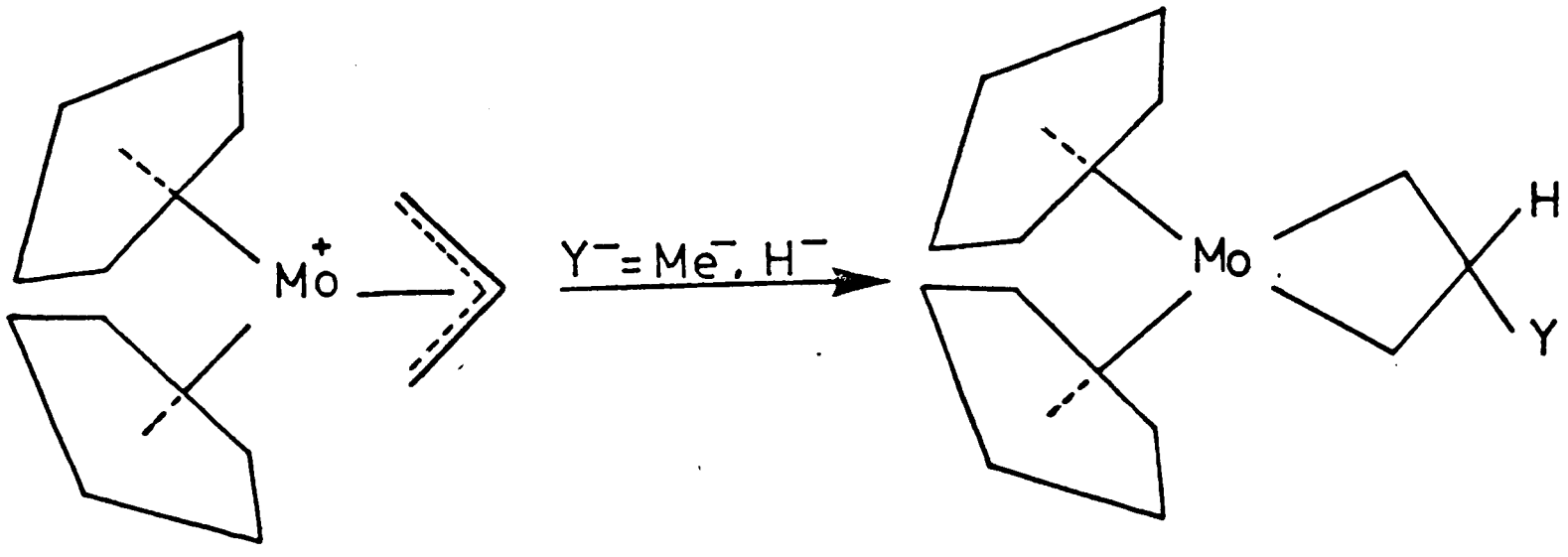
II. CONCERNING NUCLEOPHILIC ATTACK ON SOME ORGANOMETALLIC CATIONS.

Chapter II, in part, and Chapters IV and V in this thesis are concerned with factors controlling the stereochemistry of nucleophilic attack on polyene ligands. Here we describe some rules concerning the regiospecificity of nucleophilic addition to polyene ligands which have recently been proposed[22]

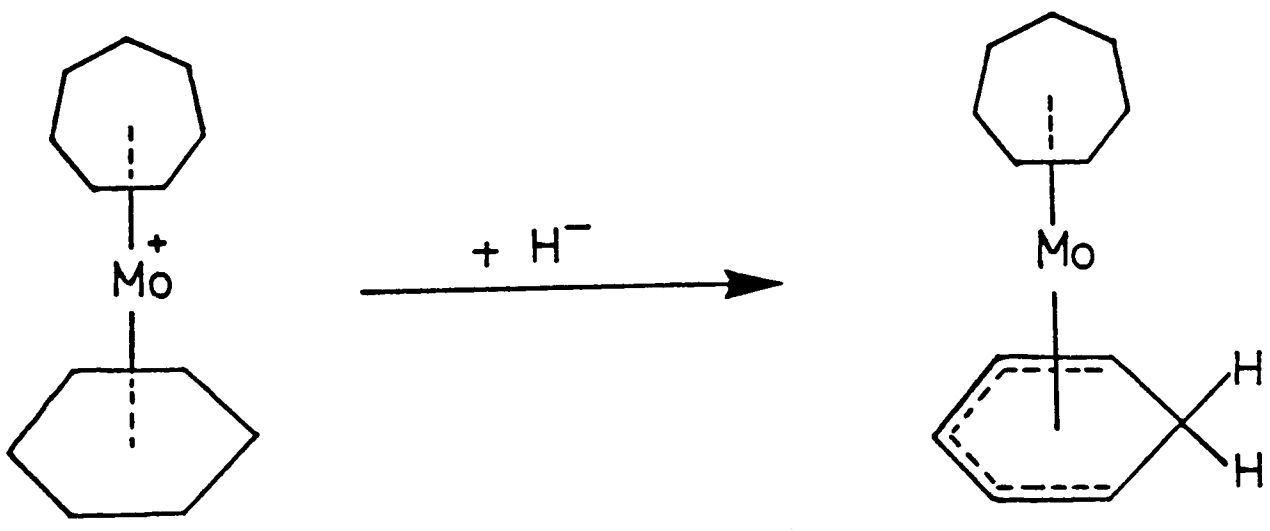
We have seen (Figure I.3) that sequential addition of two hydride ions to II led to the cyclopentenyl compound instead of the bis(cyclopentadiene)compound:



At about the same time, Ephritikhine[23] working at Oxford showed that reaction of $(Mo\{\eta\text{-}C_5H_5\}_2\{allyl\})PF_6$ with nucleophiles such as Me^- and H^- led to metallocyclobutanes, the nucleophile Y having attacked the allyl group in preference to the cyclopentadienyl ring:



Also Knight[24] while working at Oxford showed that H^- attacks the benzene ring rather than the cycloheptatriene ring of the (η-benzene)(η-cycloheptatriene)molybdenum cation.



Observations such as these raised the question of which factors govern the position of nucleophilic attack on an organometallic cation. Further discussion of this question has led to the proposal by Davies, Green and Mingos of three simple rules that enable the prediction of the most favourable

position of nucleophilic attack on 18-electron organotransition metal cations containing unsaturated hydrocarbon ligands. These rules apply to reactions that are kinetically rather than thermodynamically controlled. The rules are described below and briefly illustrated.

1. Rules for predicting the regioselectivity of nucleophilic attack on 18-electron organotransition metal cations containing polyene ligands.

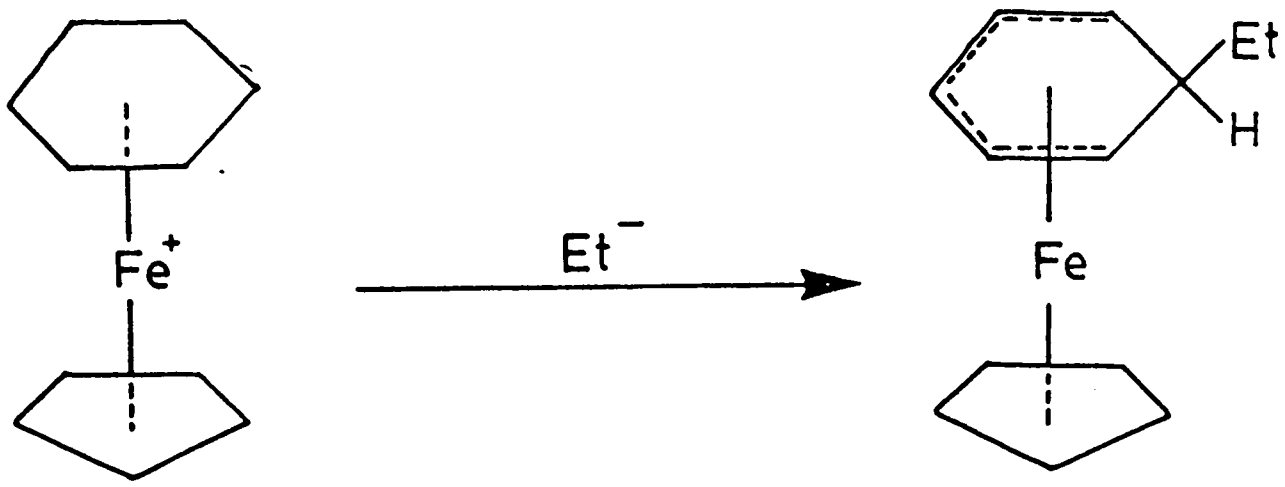
Rule 1: Nucleophilic attack occurs preferentially at even coordinated polyenes which have no unpaired electrons in the h.o.m.o.'s.

Rule 2: Nucleophilic addition to open coordinated polyenes is preferred to addition to closed polyenes.

Rule 3: For even open polyenes, nucleophilic attack at the terminal carbon atom is always preferred. For odd open polyenyls, attack at the terminal carbon atom occurs only if $\dot{M}L_n^+$ is a strong electron withdrawing group.

Some examples of organotransition metal cations which do not contain carbonyl ligands and undergo nucleophilic addition are given below.

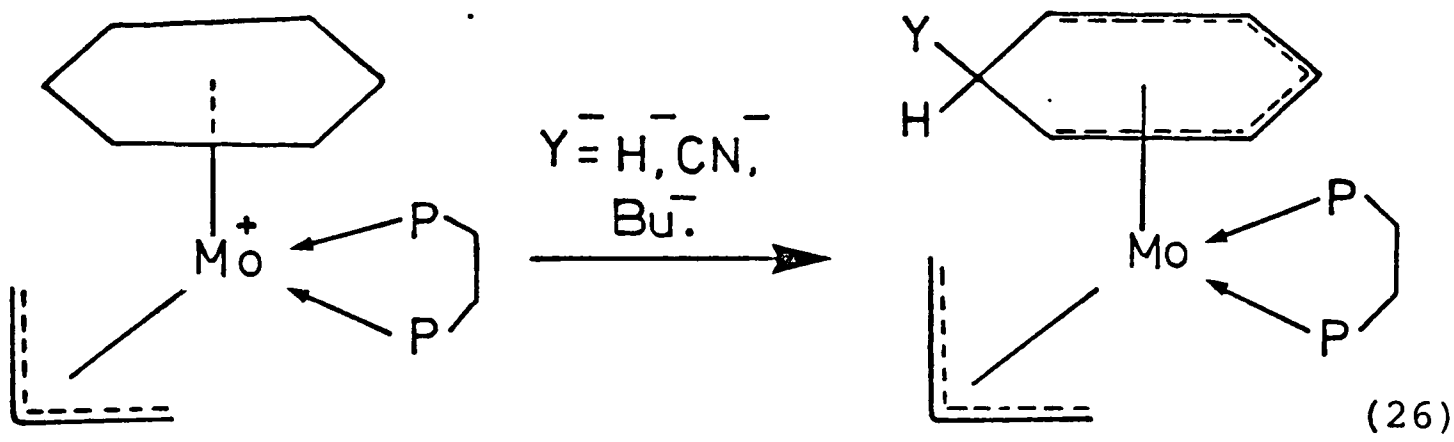
Examples where Rule 1 applies:



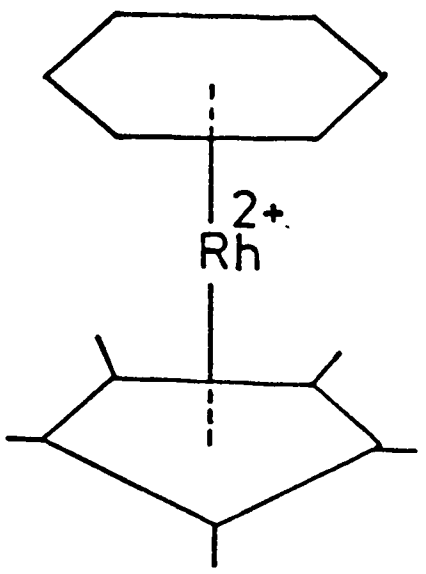
(25)

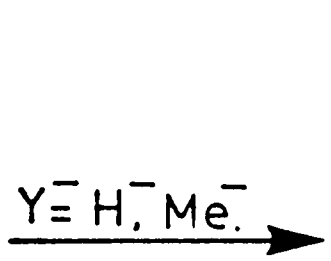
The addition takes place in the <u>even</u> polyene as predicted by Rule 1.

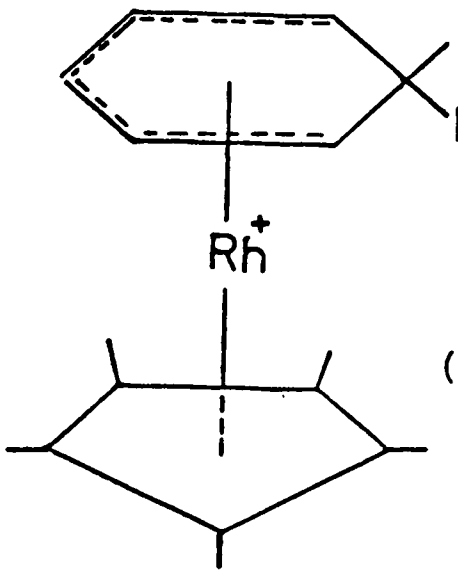
X-ray crystallographic and spectroscopic studies have shown that nucleophilic attack invariably occurs onto the <u>exo</u>-face of the ligand i.e. on the side on the ligand away from the metal.



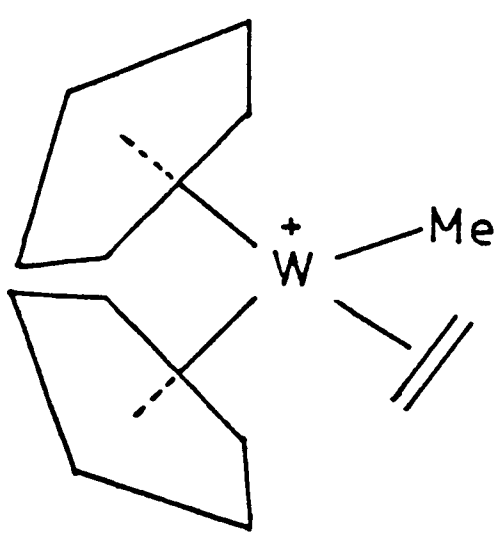
(26)

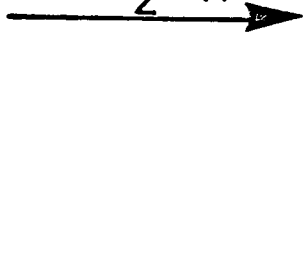


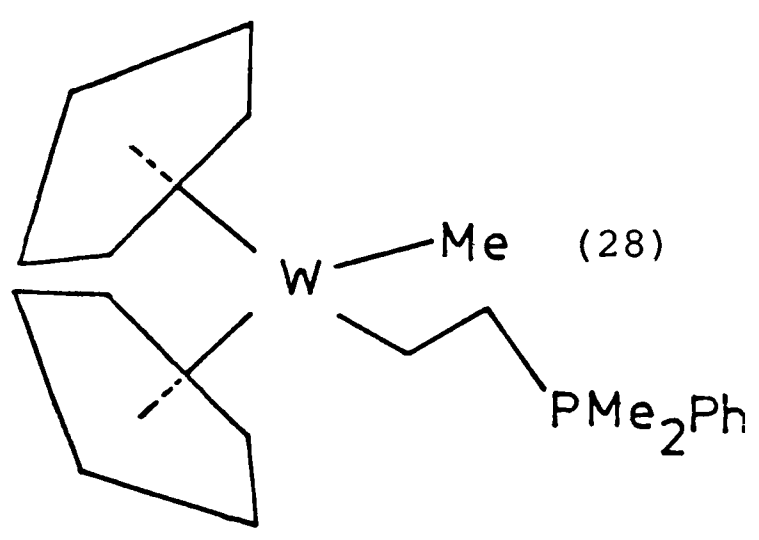




(27)

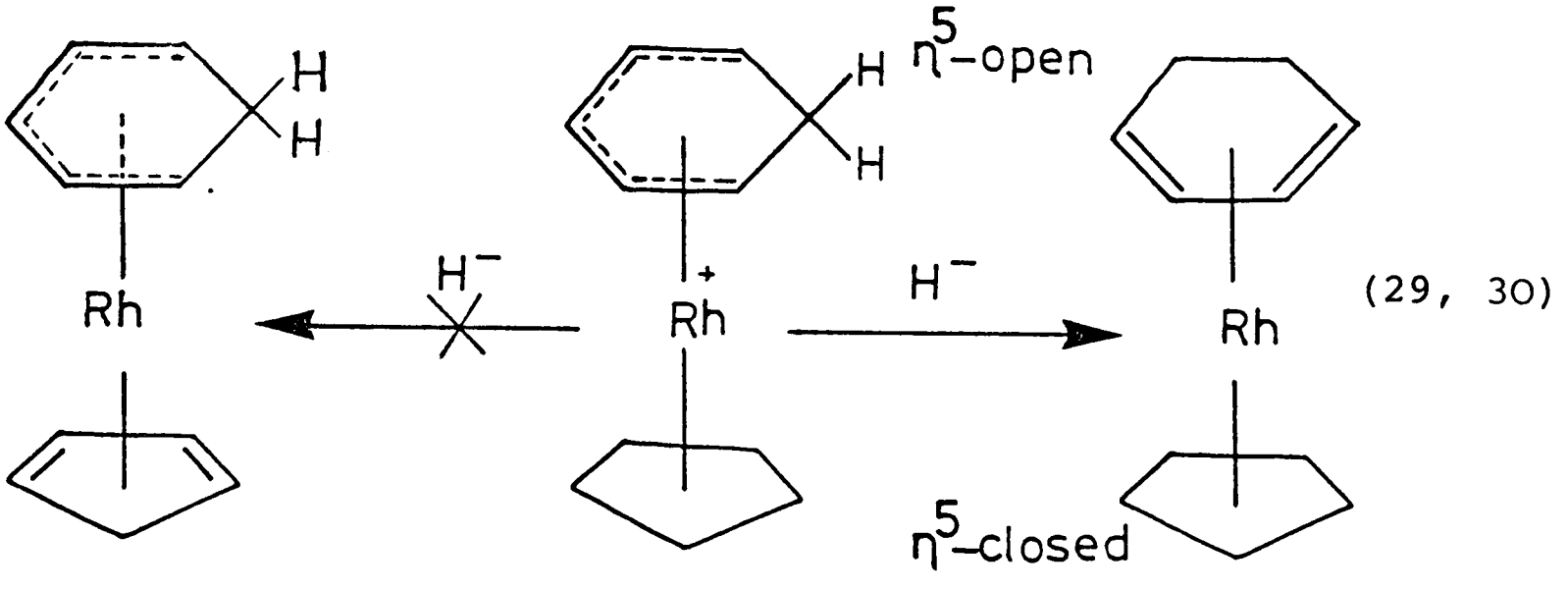






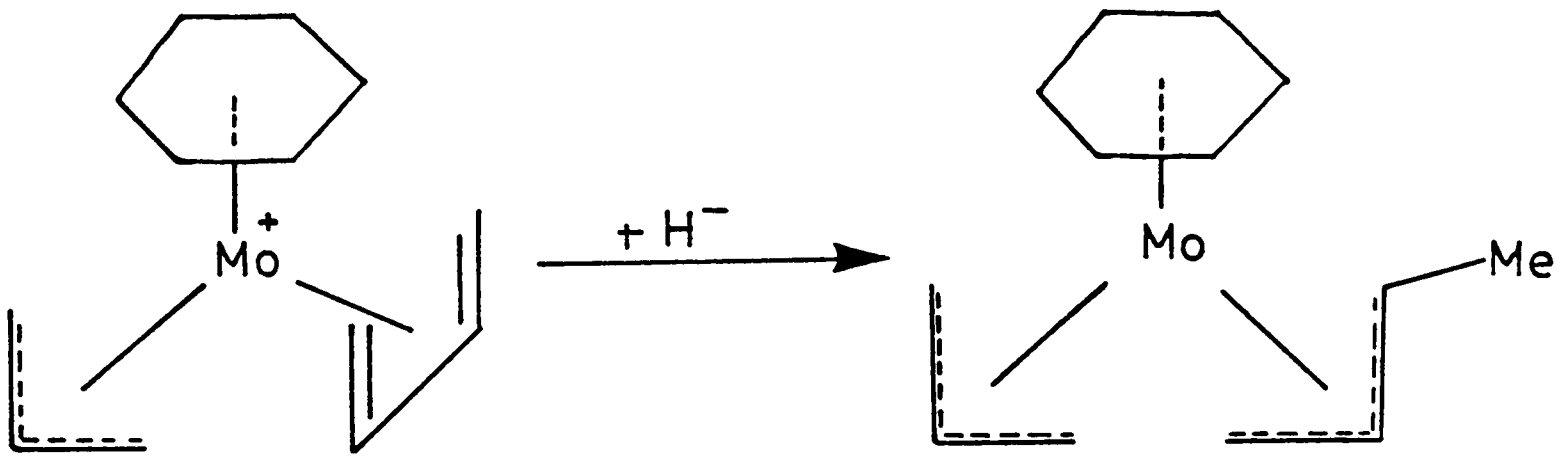
(28)

Rule 2 (open before closed) is illustrated by the reaction given below:



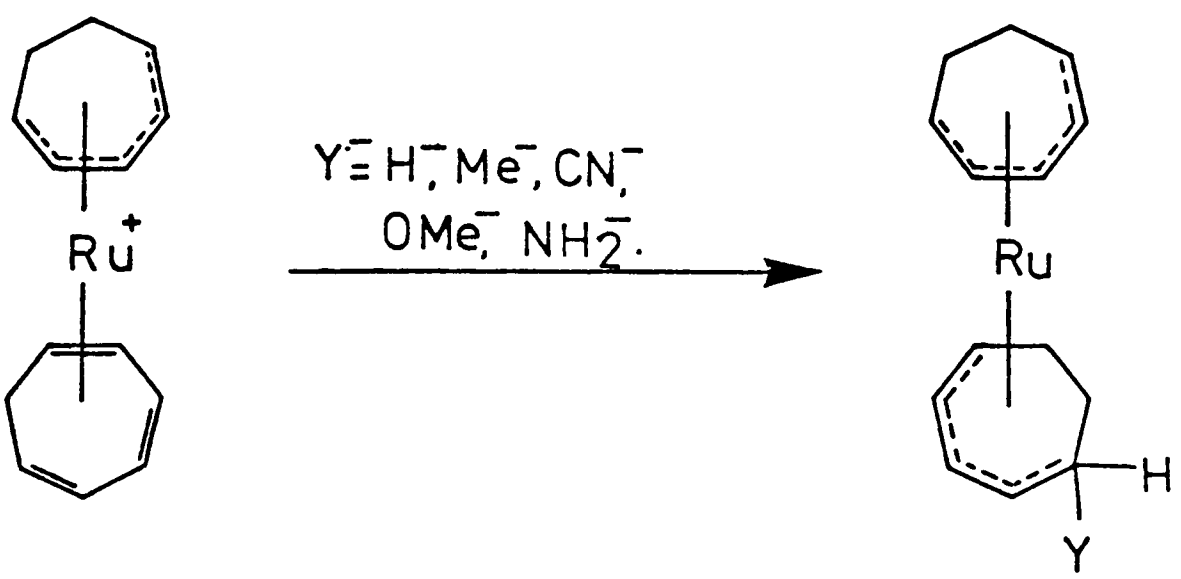
(29, 30)

Some examples are given below where more than one of the three rules apply:



(31)

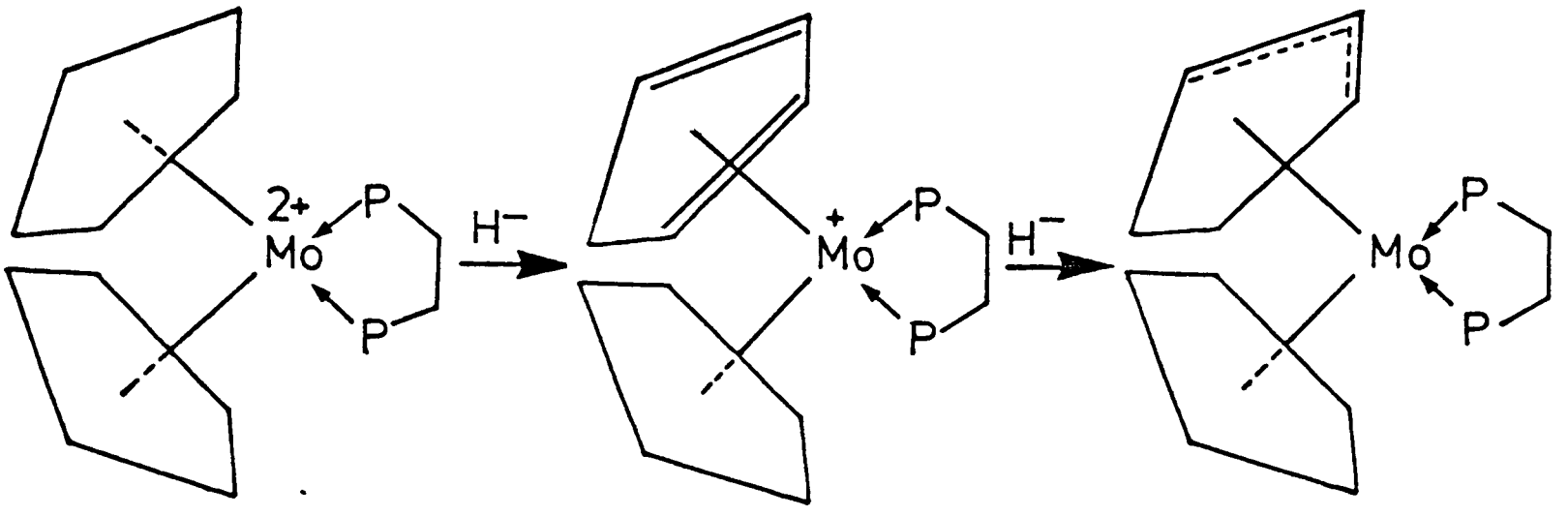
Rule 1 (<u>even</u> before <u>odd</u>) eliminates the possibility of attack on the allyl ligand. Rule 2 (<u>open</u> before <u>closed</u>) suggests nucleophilic attack on the butadiene and attack at the terminal position follows from Rule 3.



(32)

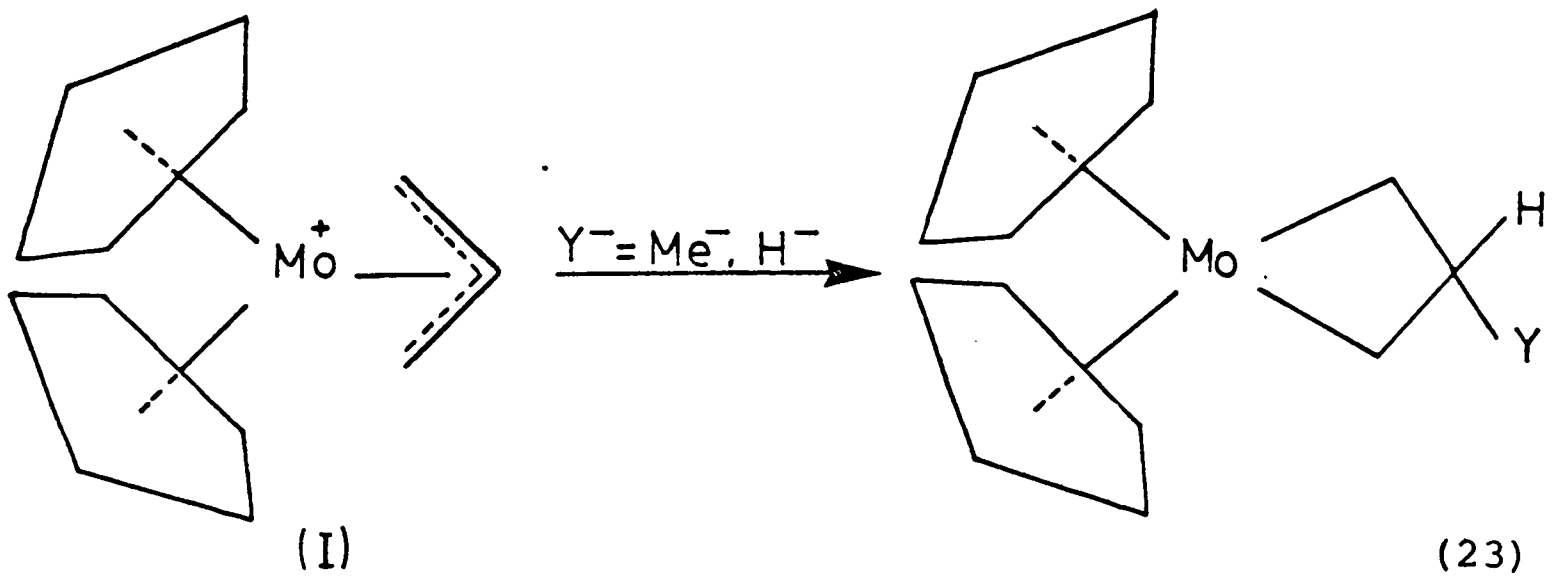
Rule 1 eliminates the possibility of attack on the η^5-cyclo-heptadienyl ring and attack at the terminal carbon of the <u>even</u>, <u>open</u> polyene follows from Rule 3.

The behaviour of the complexes mentioned before with nucleophiles can be explained now using the rules.



In the addition of the second hydride, Rule 1 eliminates the possibility of attack on the cyclopentadienyl ring and Rule 3 predicts the attack at the extreme carbon.

In the case

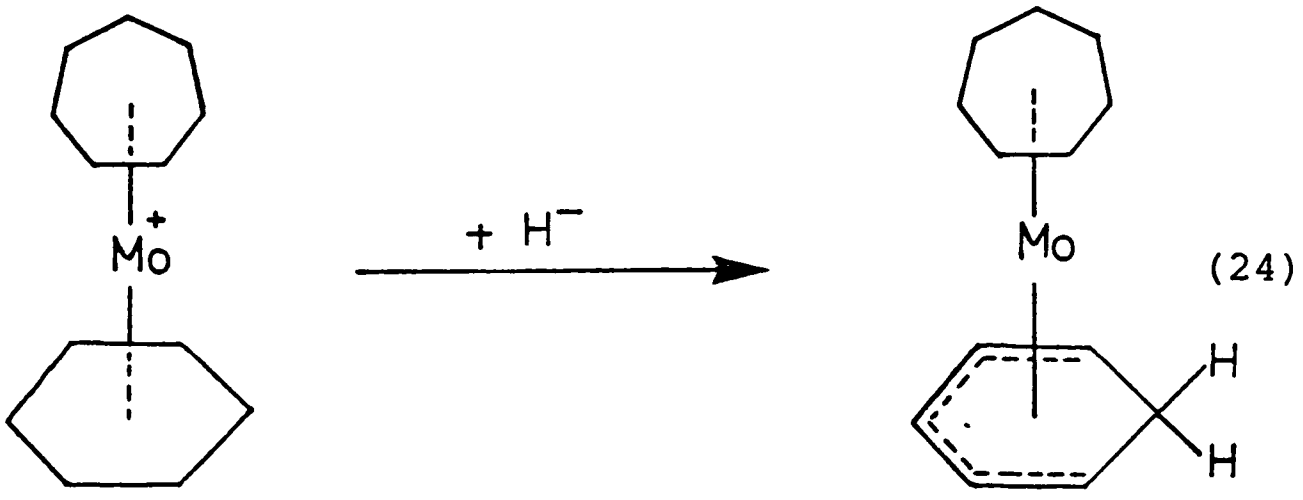


(I) (23)

since both ligands are odd, Rule 1 does not apply. Rule 2 (open before closed) predicts attack on the allyl group and following Rule 3, attack takes place on the central carbon

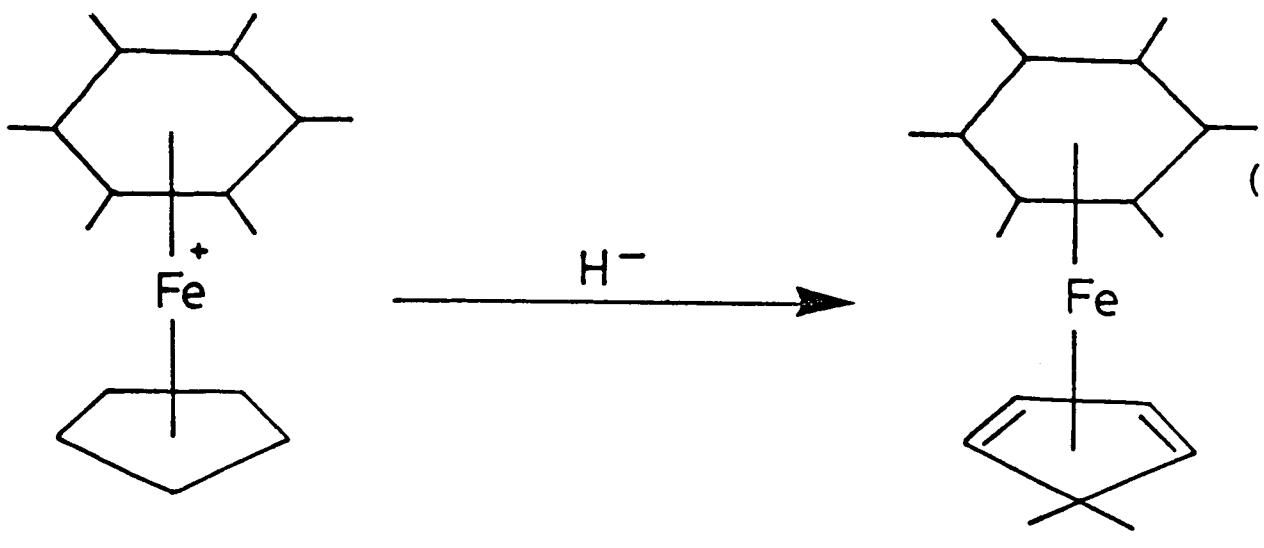
of the allyl group, since the complex (I) is an electron rich compound.

Rule 1 (<u>even</u> before <u>odd</u>) applies in the reaction:



(24)

The few cases which are apparent exceptions to the rules can be explained in terms of the reaction being controlled thermodynamically rather than kinetically. In the reaction:



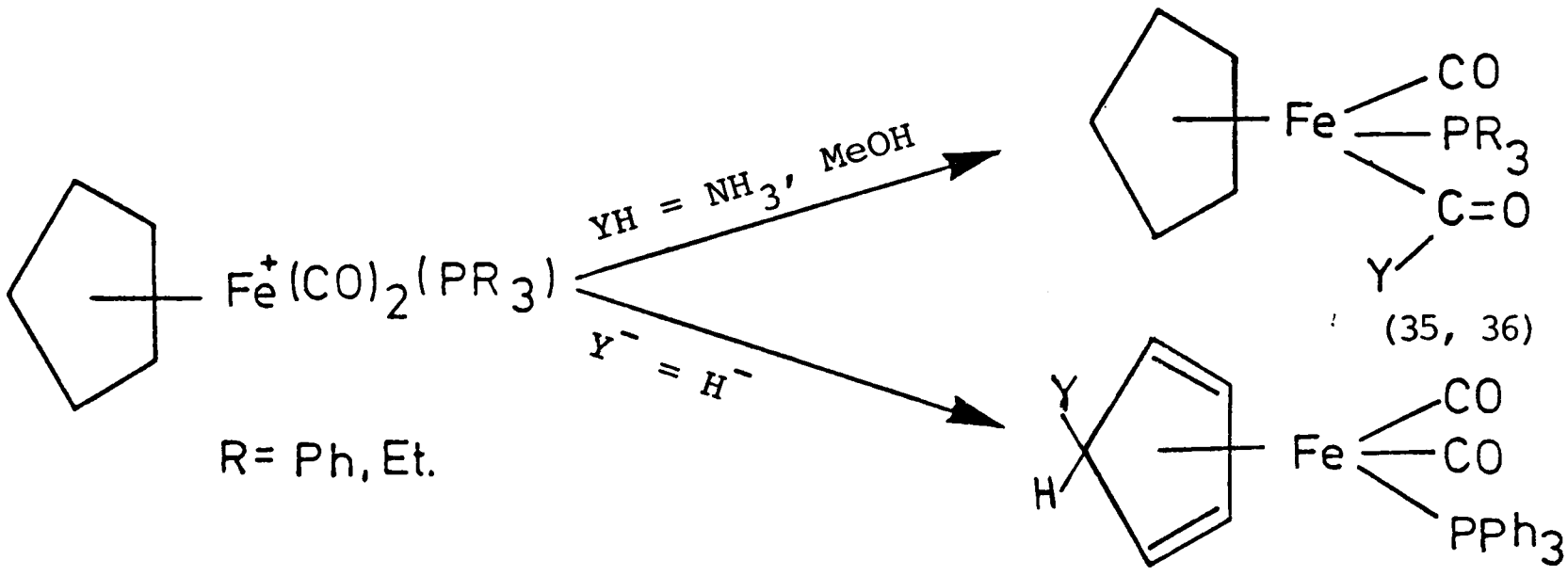
(25)

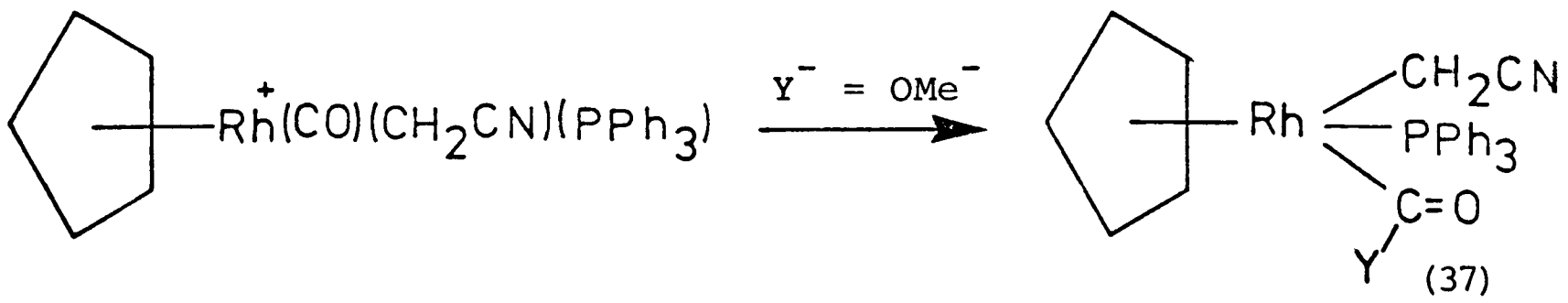
(33, 34)

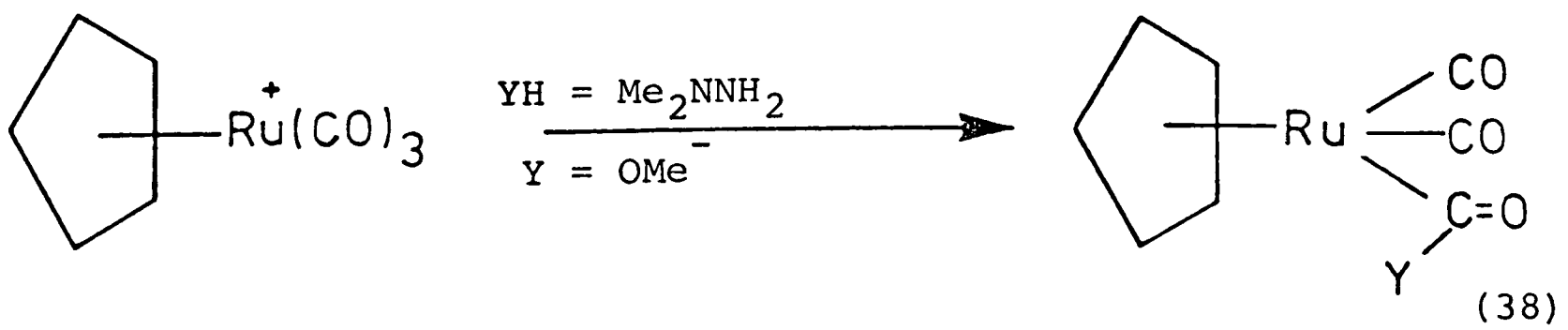
the <u>odd</u> cyclopentadienyl ring is attacked instead of the <u>even</u> hexasubstituted benzene ring. <u>Exo</u>-attack on the benzene

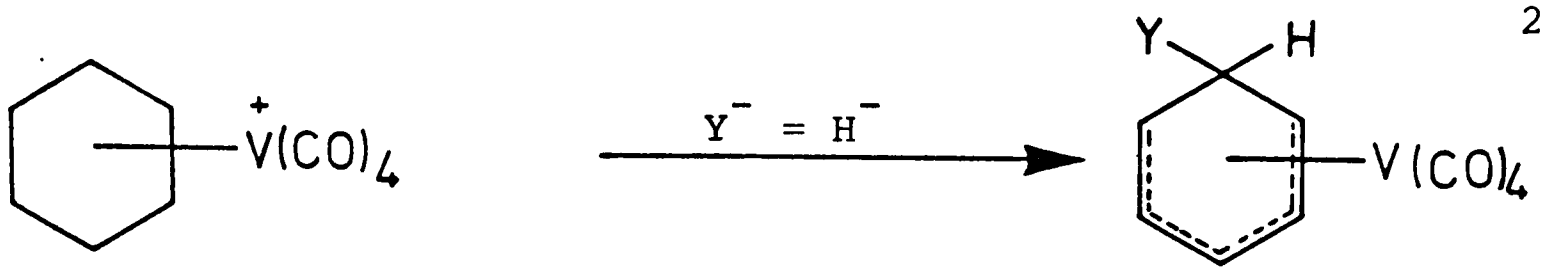
ring would give a sterically unfavourable product with the methyl group in close proximity to the metal. Sometimes the final product is the result of a rearrangement - by hydride migrations to a thermodynamically more stable product.

Organometallic cations which have carbon monoxide coordinated to the metal may undergo nucleophilic attack, either at the organic ligand or the carbon monoxide. For those nucleophiles where attack is kinetically controlled i.e. irreversible, it is generally the hydrocarbon which is attacked. When the nucleophile is such that the product of addition to the unsaturated hydrocarbon is labile, then the isolated product may be derived from attack on the carbon monoxide. Some examples are given below:

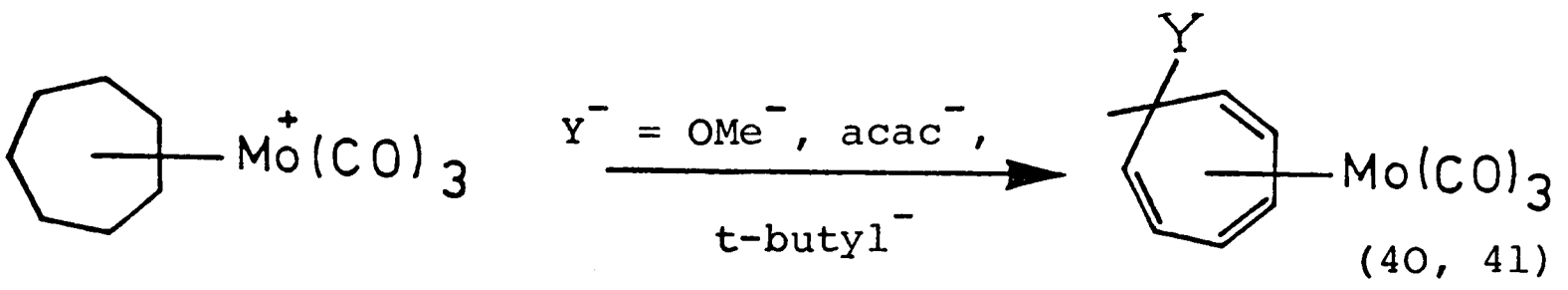




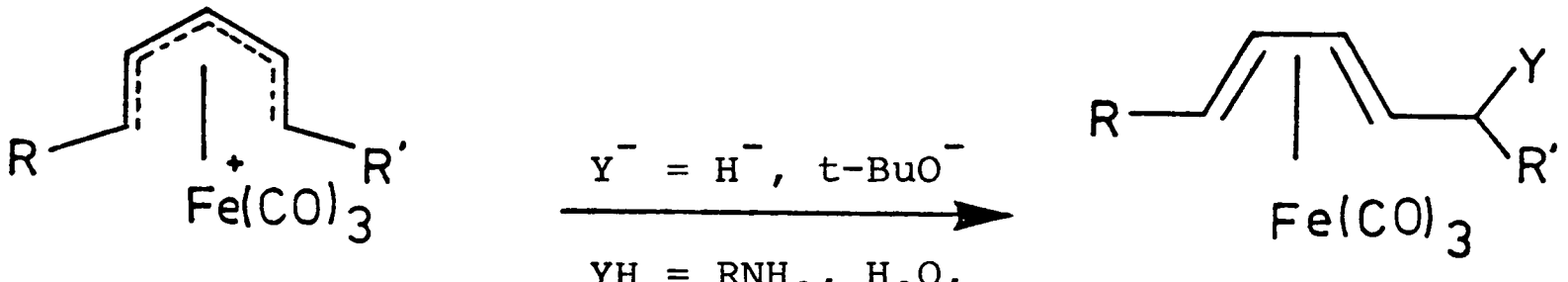




(39)



(40, 41)



(42 - 50)

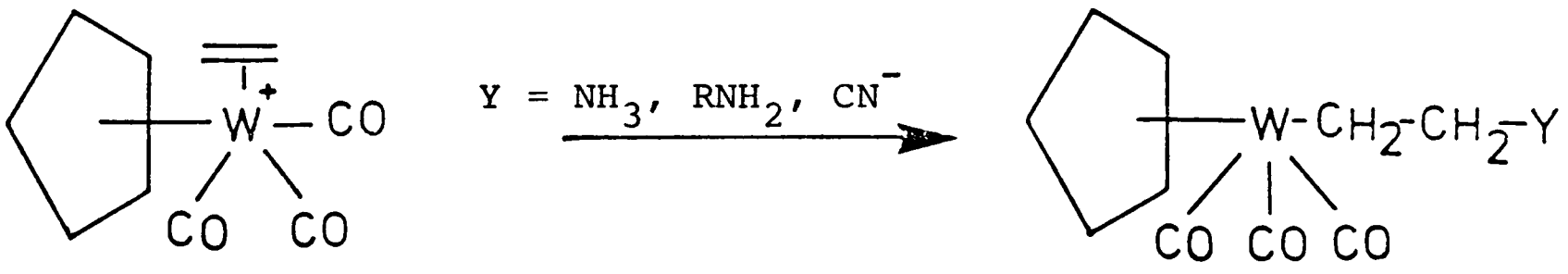
R = R' = H

R = Me, R' = H

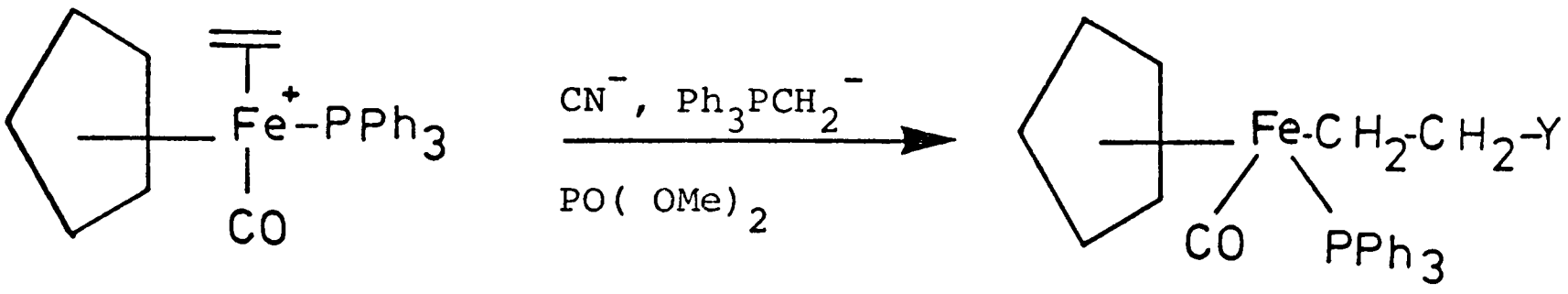
R = R' = Me

R = R' = Ph

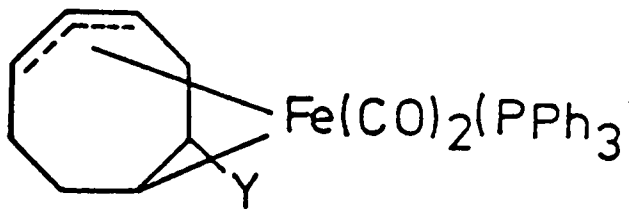
When the organotransition metal cation contains more than one unsaturated hydrocarbon ligand and at least one carbon monoxide ligand, nucleophilic attack can occur either at the carbon monoxide or at one of the organic ligands, following the rules mentioned earlier. In all the examples which have been found in the literature, nucleophilic addition occurs on the unsaturated hydrocarbon ligand. Some examples are given below:

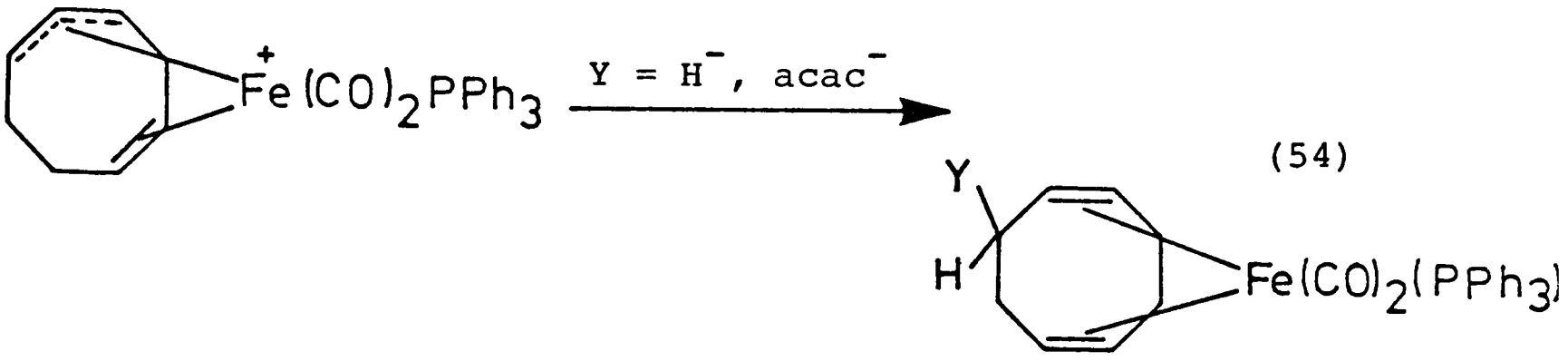


(51)

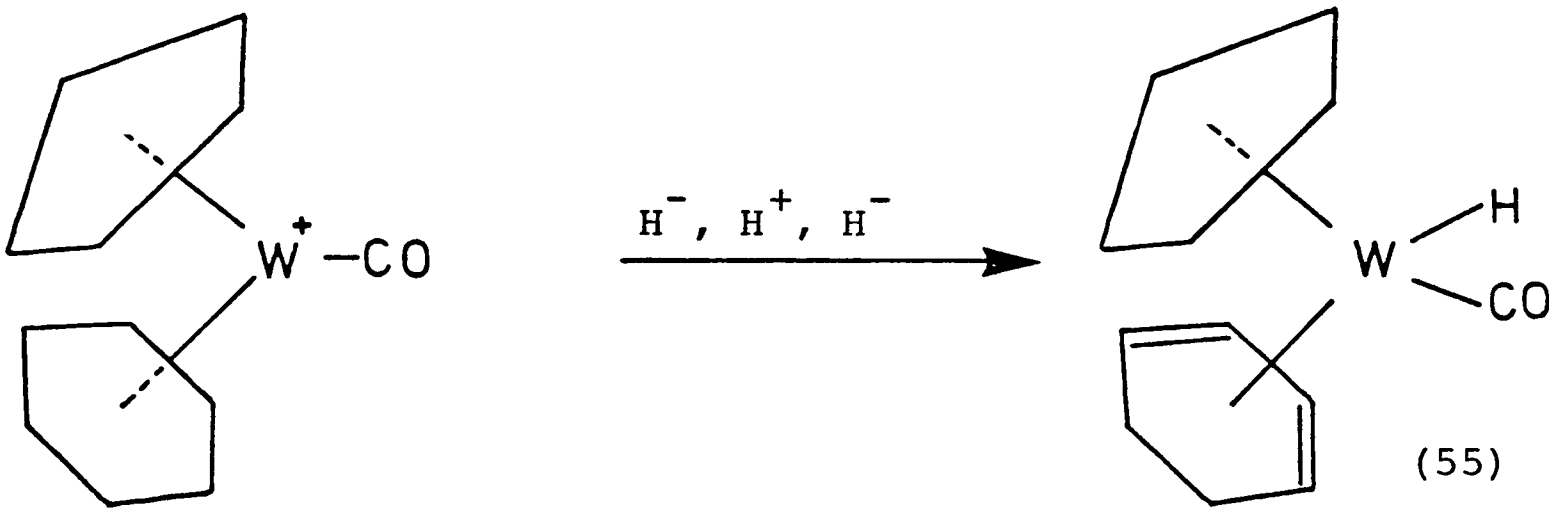


(52, 53)





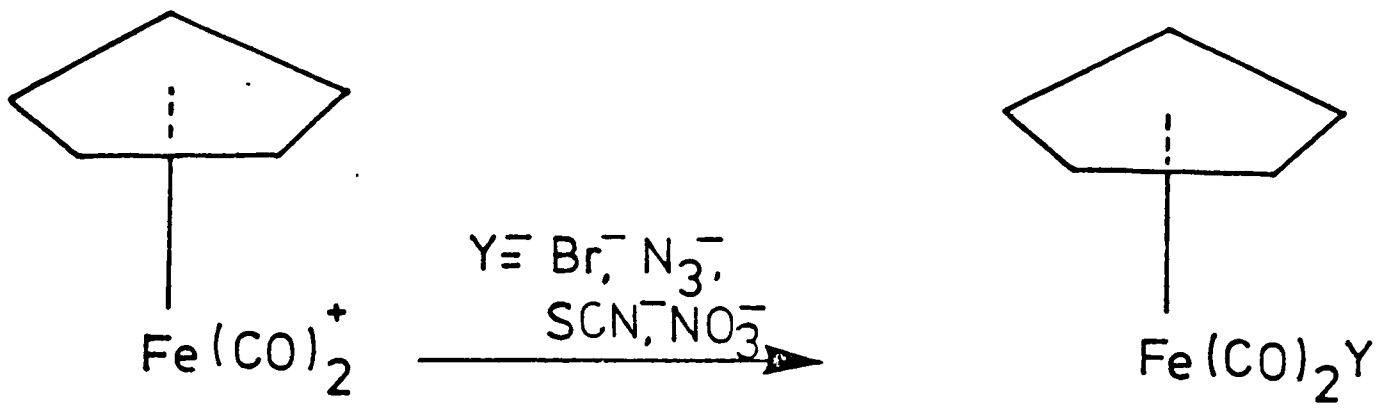
(54)



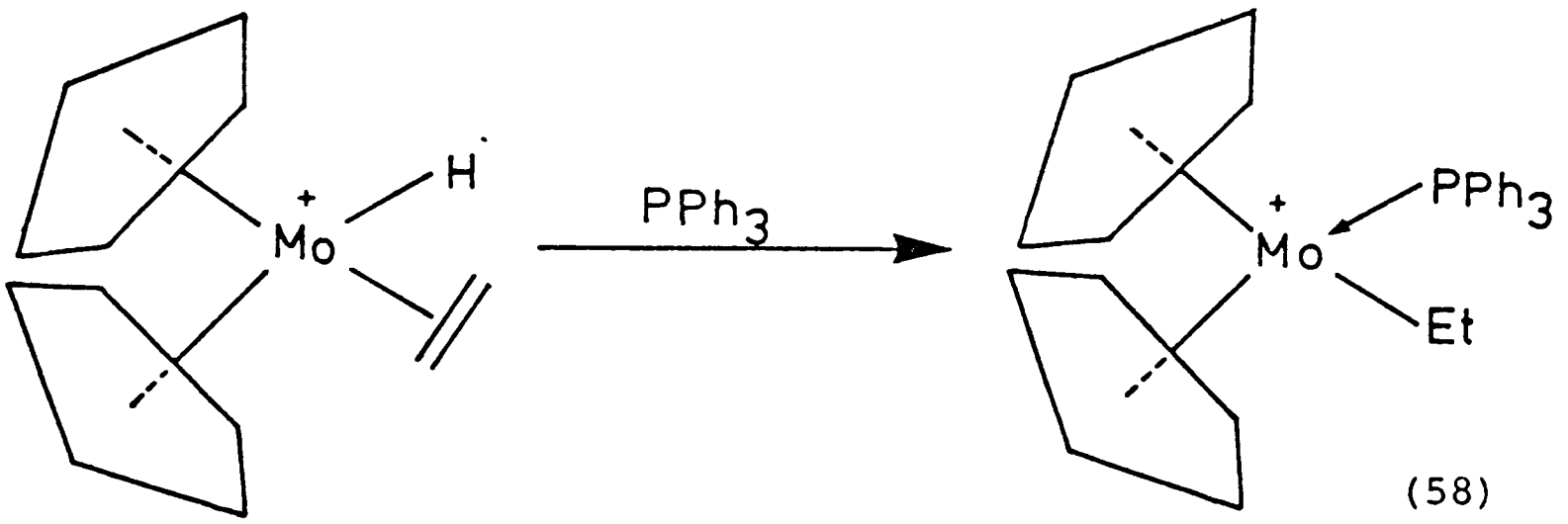
(55)

Some examples are given below of the reaction of organo-transition metal cations with nucleophiles that lead either to addition of the nucleophile to the metal or to ligand substitution. Addition to the metal occurs when the cation has only 16 electrons and gives an 18-electron product. When the 18-electron cation can be readily converted to a 16-electron cation by dissociation of a 2-electron ligand, the nucleophile attacks the 16-electron intermediate cation,

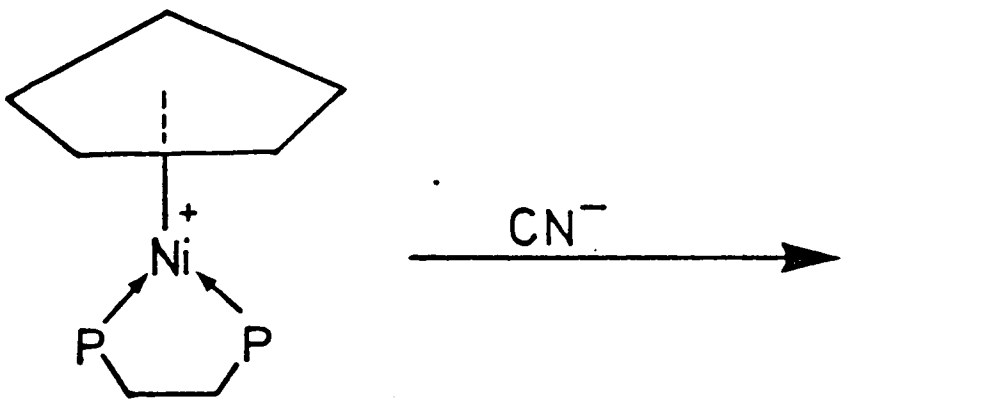
resulting in ligand substitution.



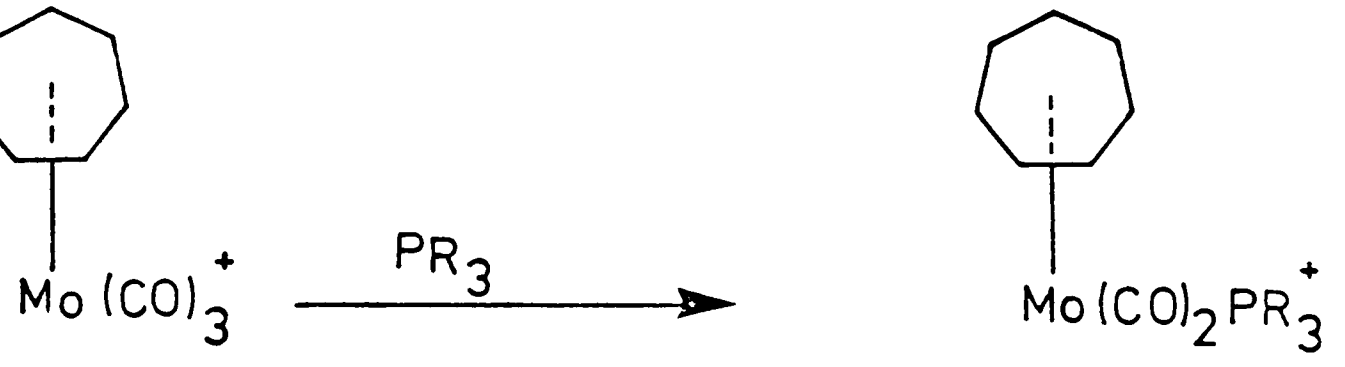
(56, 57)



(58)



(59)

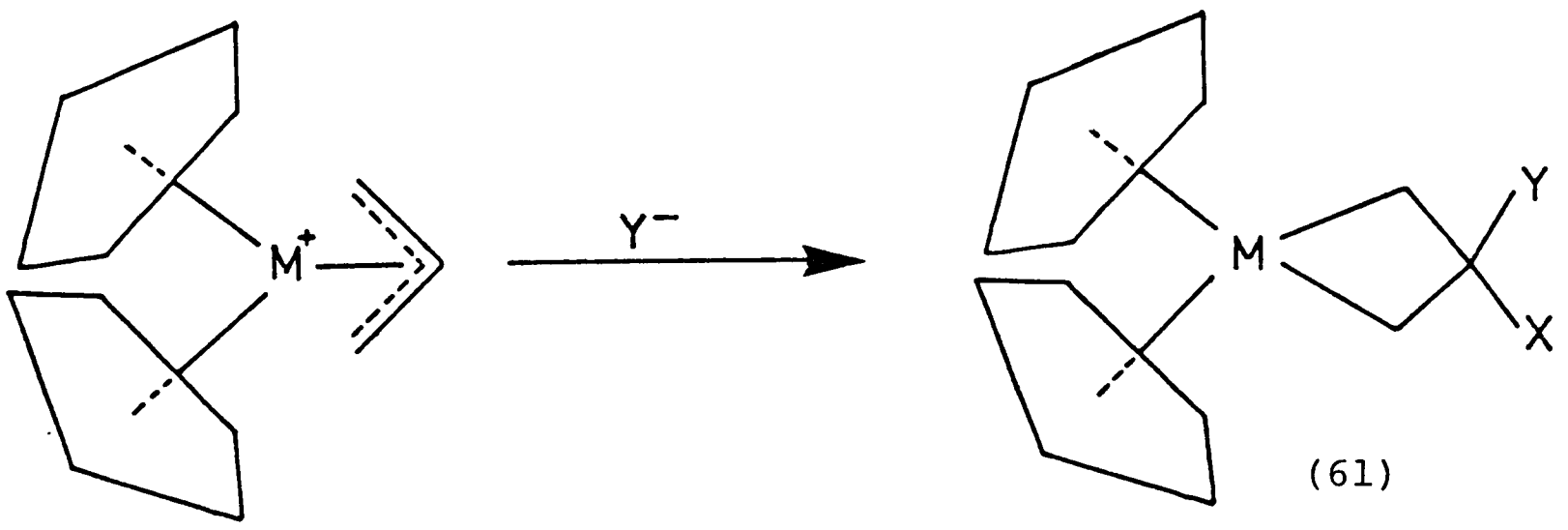


(60)

It was then decided to devise a system which might provide a striking test of Rule 3. The objective was to find a compound where we could increase the electron density of the metal centre, to make it more electron-rich, to see whether we could switch the product from being one where the attack would occur on the terminal carbon of an allyl group to one where the attack would occur on the central carbon.

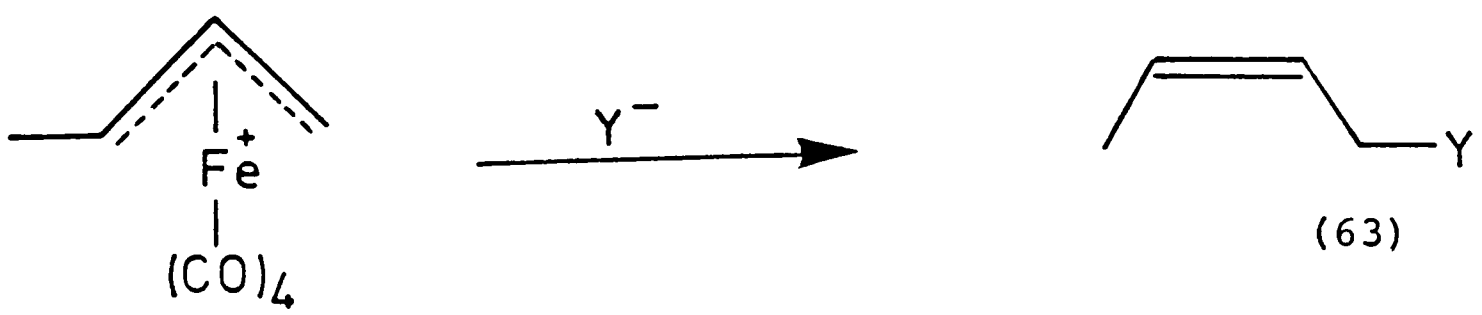
2. Chemistry of attack of nucleophiles on allyl compounds.

Since the allyl ligand is open, the carbon atoms are inequivalent. Therefore there are two possible positions of attack i.e. at the terminal carbon atom (C-1 or C-3) or at the centre carbon (C-2). In the examples shown below, both modes of addition are observed:

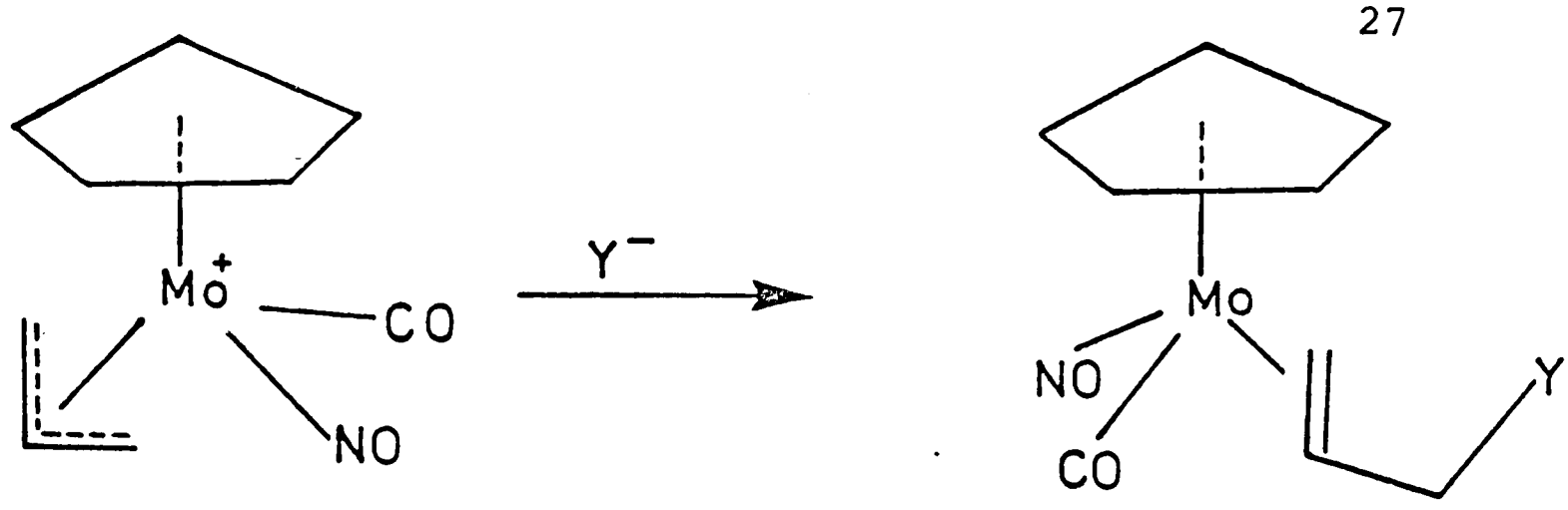


(61)

M = Mo, W

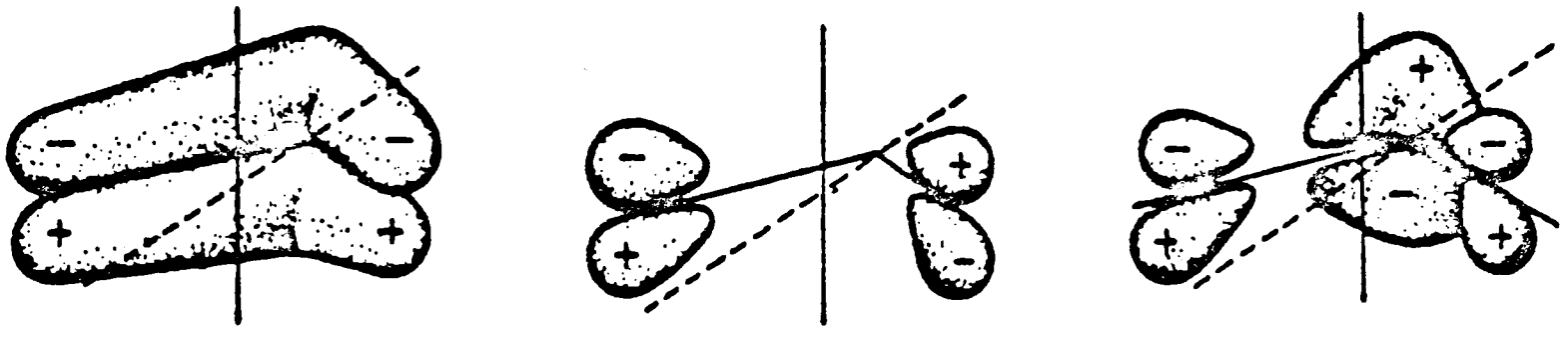


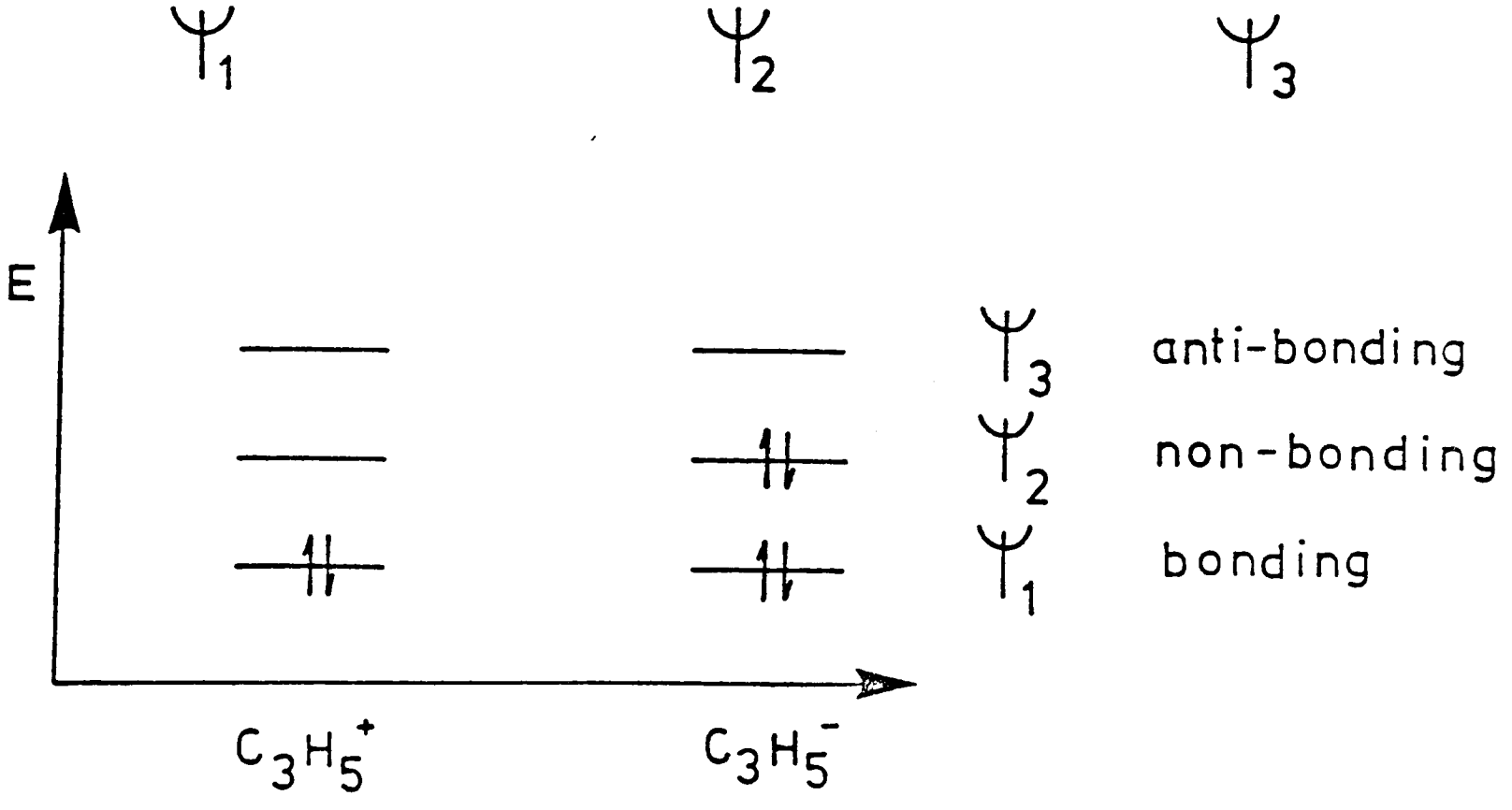
(63)



(62)

The three Molecular orbitals of the allyl group are represented below:





If electron withdrawing ligands such as CO and NO are present, the metal will be electron poor and the allyl group behaves as $C_3H_5^+$, therefore the nucleophile will react with the lowest orbitals in energy Ψ_2, and the attack takes place in the extreme carbon. If the metal is electron rich, the allyl group behaves as $C_3H_5^-$, and the nucleophile will react with the Ψ_3 orbital, and the attack takes place on the central carbon. Given this objective, the question was then to find a suitable compound. The constraints were that we could not have an <u>even</u> ligand together with the allyl group, since attack would not then occur on the allyl group (by Rule 1). Therefore we had to have the allyl group, an <u>odd</u> unsaturated hydrocarbon ligand, and to complete the coordination sites, a ligand which would give rise to a cationic compound and could change the electron density at the metal. Since we did not want to get involved at that stage in a totally new synthetic programme, a suitable system, already in the literature, was investigated.

III. A SURVEY OF THE CHEMISTRY OF $Co(\eta\text{-}C_5H_5)(CO)_2$ DERIVATIVES.

The compound $Co(\eta\text{-}C_5H_5)(CO)_2$ was first synthesised in 1954 by Fischer[64], by treatment of $Co(\eta\text{-}C_5H_5)_2$ with carbon monoxide. Wilkinson[65] prepared it in 1955 by the exothermic reaction:

$$Co_2(CO)_8 + 2C_5H_6 \longrightarrow 2Co(\eta\text{-}C_5H_5)(CO)_2 + 4CO + H_2$$

Several publications have appeared since with modifications in the conditions and improvement in the yield[66].

The carbonyl groups are easily displaced by a variety of ligands. For example, treatment of $Co(\eta\text{-}C_5H_5)(CO)_2$ with X_2 (X = Cl, Br, I) gives $Co(\eta\text{-}C_5H_5)(CO)X_2$. Treatment of the iodide complex $Co(\eta\text{-}C_5H_5)(CO)I_2$ with 2,2'-bipyridyl[67, 68] or o-phenanthroline gives the violet black salts $(Co\{\eta\text{-}C_5H_5\}\{C_{10}H_8N_2\}I)I$ and $(Co\{\eta\text{-}C_5H_5\}\{C_{12}H_8N_2\}I)I$ respectively. Treatment of $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$ with PPh_3 gives $Co\{\eta\text{-}C_5H_5\}PPh_3I_2$

Some typical reactions of $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$ are shown in Figure I.4.

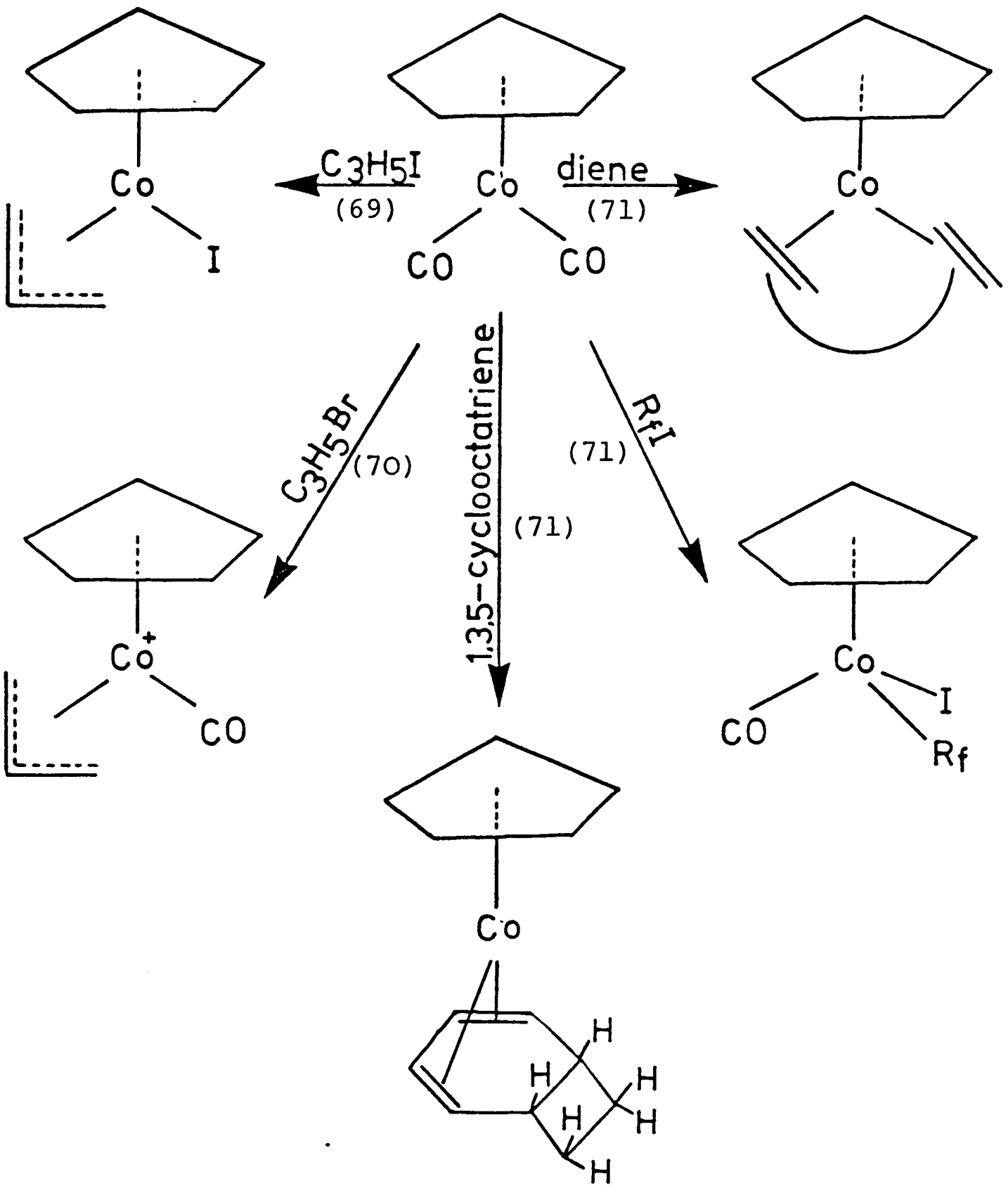
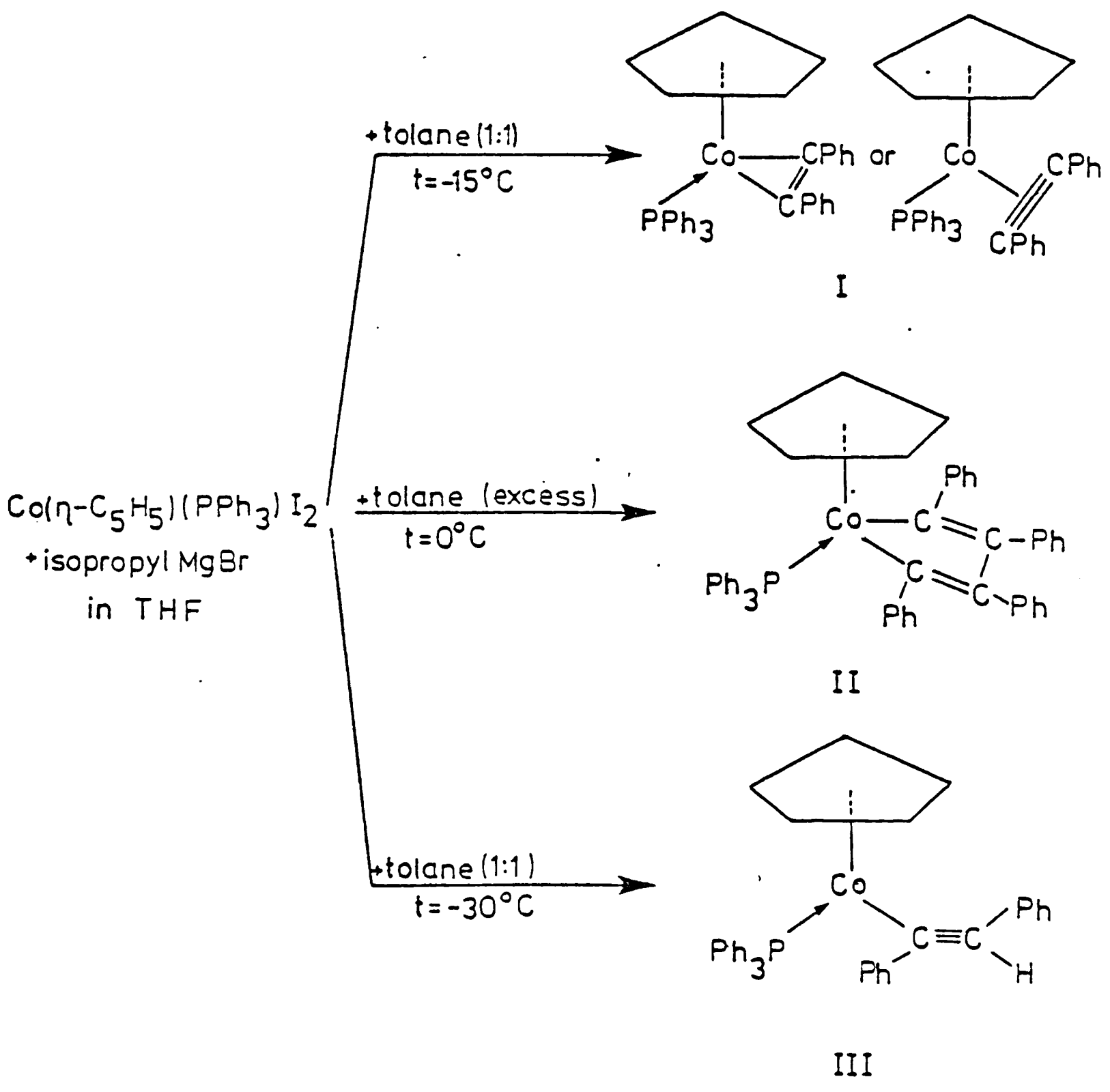


FIGURE I.4. Some reactions of $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$

Complexes of the type $Co(\eta\text{-}C_5H_5)LRR'$ (L = PPh_3, PPh_2Me, $AsPh_3$; R, R' = CH_3, $PhCH_2$ and I) were prepared from the reaction of $Co(\eta\text{-}C_5H_5)(L)I_2$ with Grignard reagents.

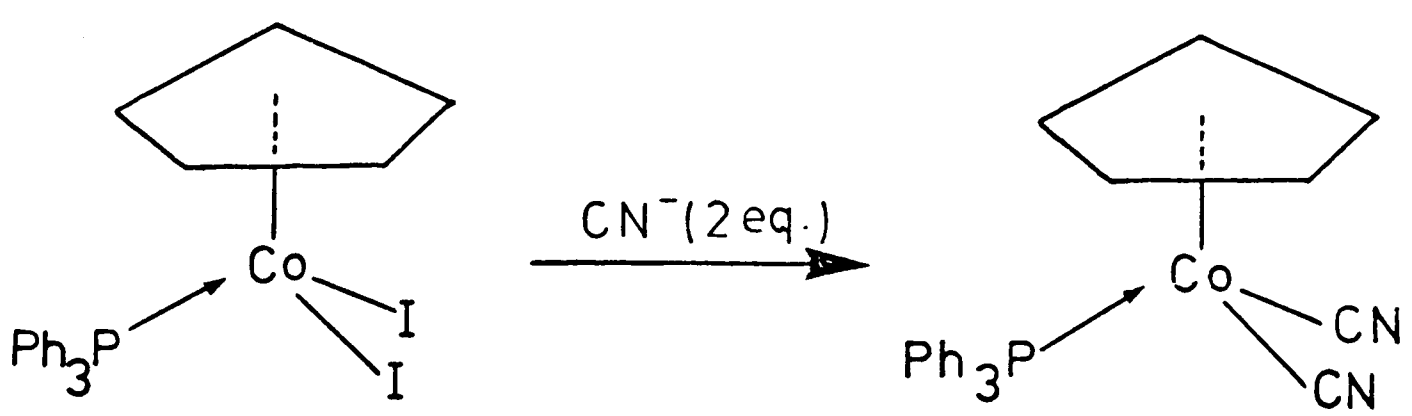
The reaction of $Co(\eta\text{-}C_5H_5)PPh_3L_2$ with isopropyl magnesium bromide in the presence of diphenylacetylene afforded an acetylene complex $Co(\eta\text{-}C_5H_5)PPh_3(PhC{\equiv}CPh)$ (I), a cobalto-cyclopentadiene complex (II) or a stilbenyl complex of divalent cobalt $Co(\eta\text{-}C_5H_5)(PPh_3)(PhC{\equiv}CHPh)$ (III), depending on the conditions used[72].

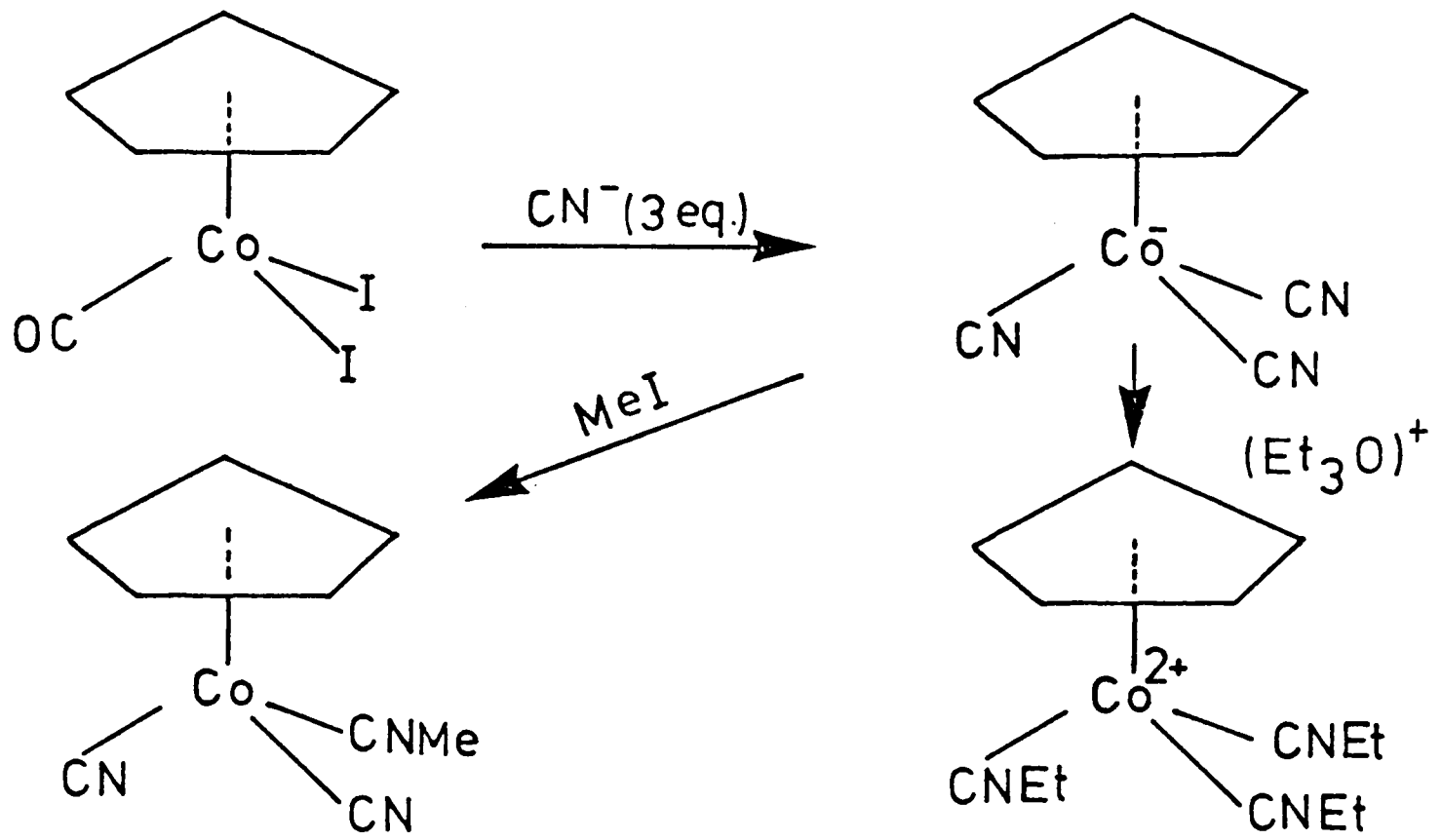


The complex $Co(\eta\text{-}C_5H_5)(CO)I_2$ has been shown to lose CO in solution in light petroleum, to give the insoluble complex $\{Co(\eta\text{-}C_5H_5)I_2\}_n$, which disproportionates when heated in THF to yield the cation $\{Co(\eta\text{-}C_5H_5)_2\}^+$. In contrast, the pentamethylcyclopentadienyl complex did not decompose under these conditions.(73)

The complex $Co(\eta\text{-}C_5H_5)(PPh_3)I_2$ reacted with isopropylmagnesium bromide favourably in the presence of triphenylphosphine to give dark red crystals of $Co(\eta\text{-}C_5H_5)(PPh_3)_2\cdot C_6H_6$.(74)

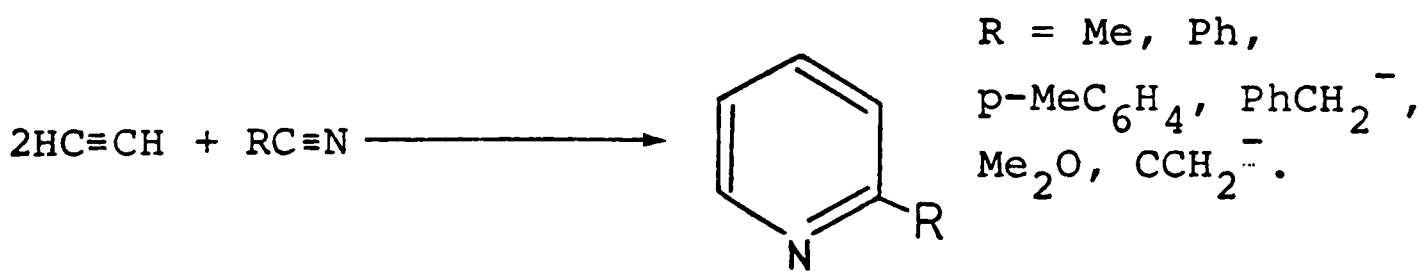
The cyclopentadienyl di- and tri- cyanides of cobalt, $Co(\eta\text{-}C_5H_5)(CN)_2PPh_3$ and $\{Co(\eta\text{-}C_5H_5)(CN)_3\}^-$ have been prepared by reaction of cyanide with $Co(\eta\text{-}C_5H_5)(PPh_3)I_2$ and $Co(\eta\text{-}C_5H_5)(CO)I_2$ respectively. Cyanide and isocyanide ligands are known to favour higher oxidation states than carbonyl groups, and the cobalt(III) complex $Co(\eta\text{-}C_5H_5)(CO)I_2$ was found to be particularly good starting material for the preparation of polycyanide complexes(75).





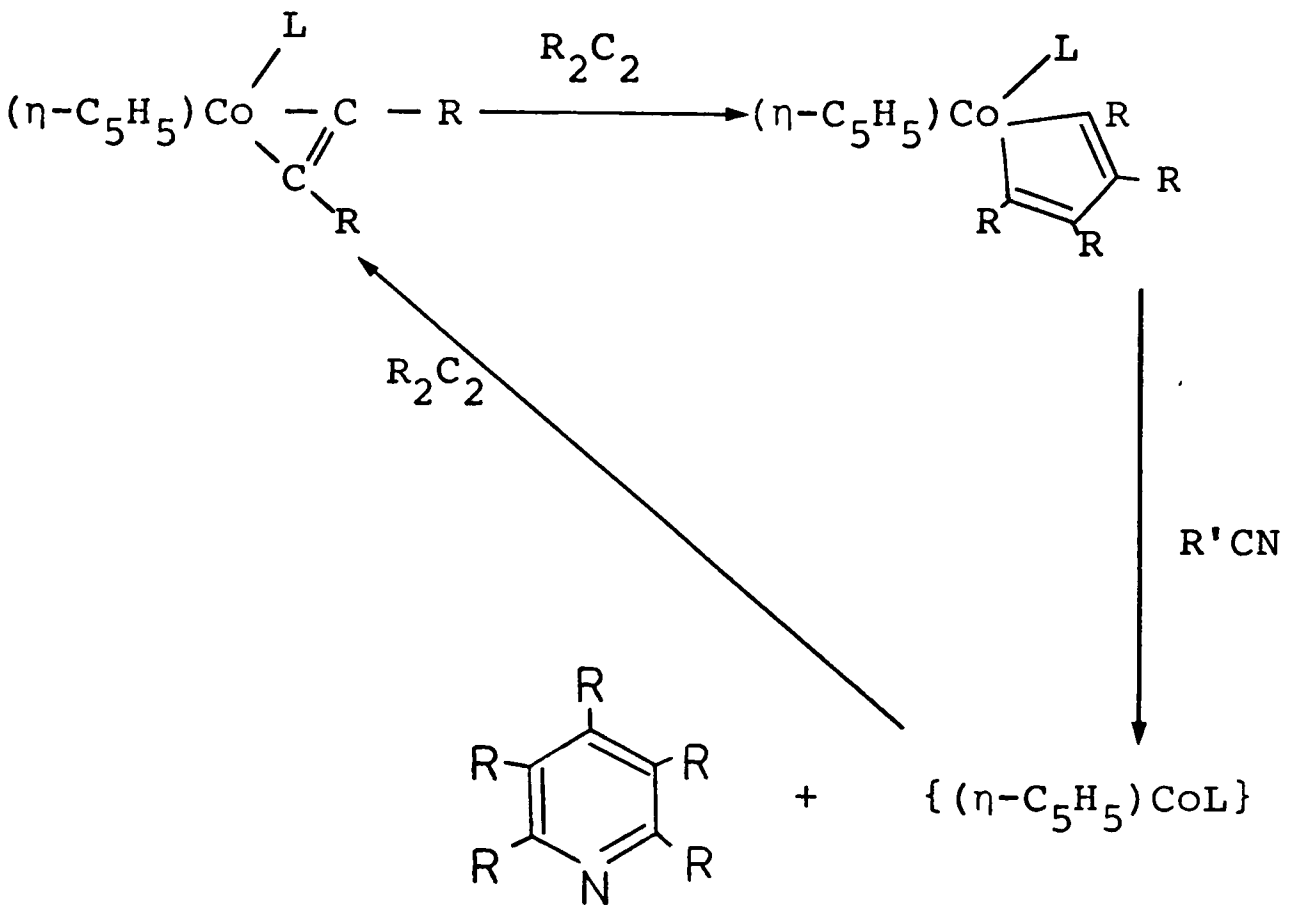
The complexes $M(\eta^5\text{-}C_5H_5)(CO)PPh_3$ (M = Co or Rh) react with $NOPF_6$ in methanol/toluene to form $\{M(\eta\text{-}C_5H_5)(NO)PPh_3\}PF_6$. In contrast, protonation of $Ir(\eta\text{-}C_5H_5)(CO)PPh_3$ takes place in methanol to give the hydride $\{Ir(\eta\text{-}C_5H_5)(CO)(PPh_3)H\}^{+}$(76).

It has been shown that substituted pyridines can be prepared by the reaction of two molecules of acetylene and one molecule of nitrile in the presence of a catalytic amount of η-cyclopentadienyl(triphenylphosphine)cobalta-tetraphenylcyclopentadiene, as shown by the equation:



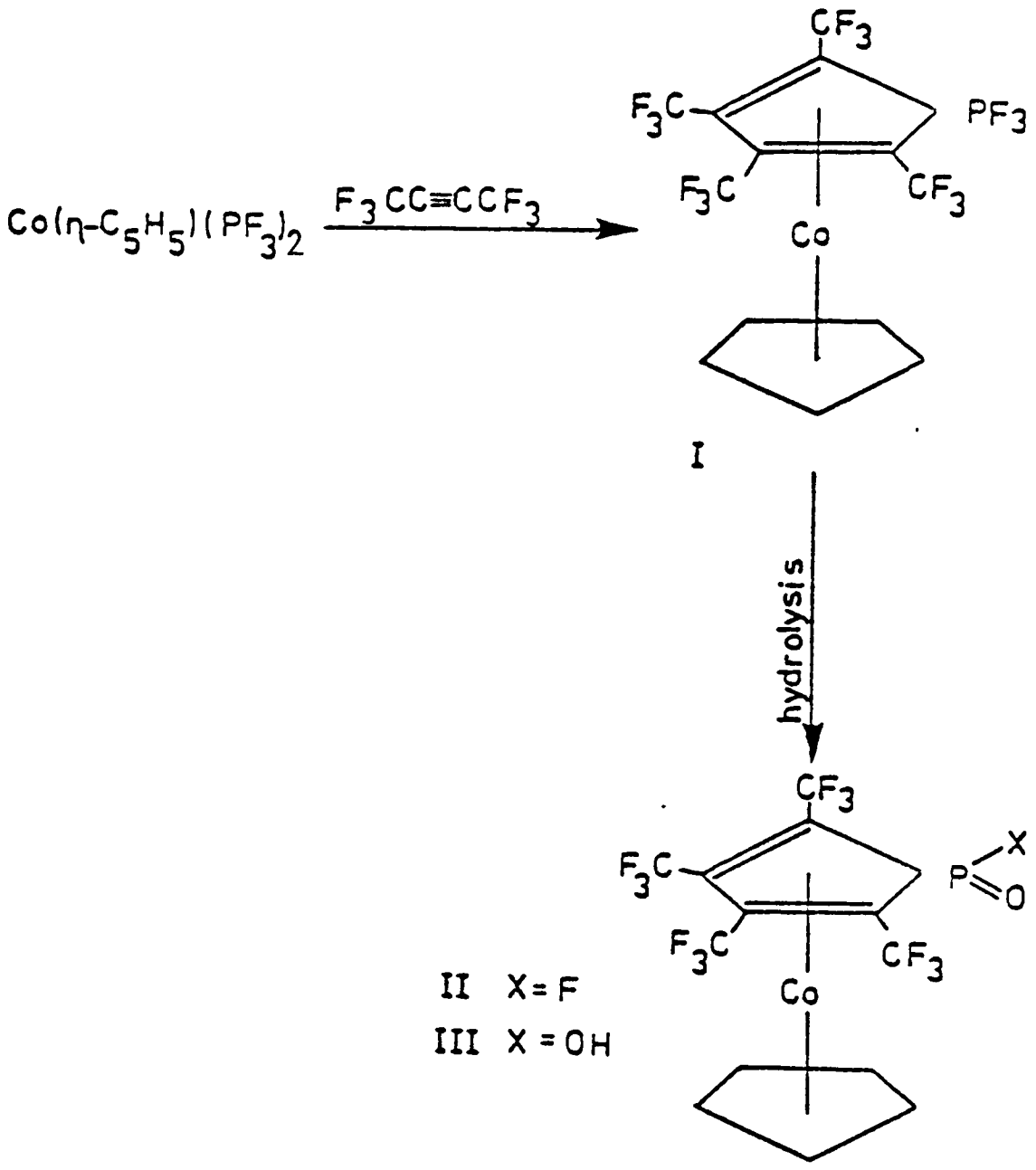
This catalytic reaction can be best explained by means of

cobalta-cyclopentadiene mechanism shown below[77]:

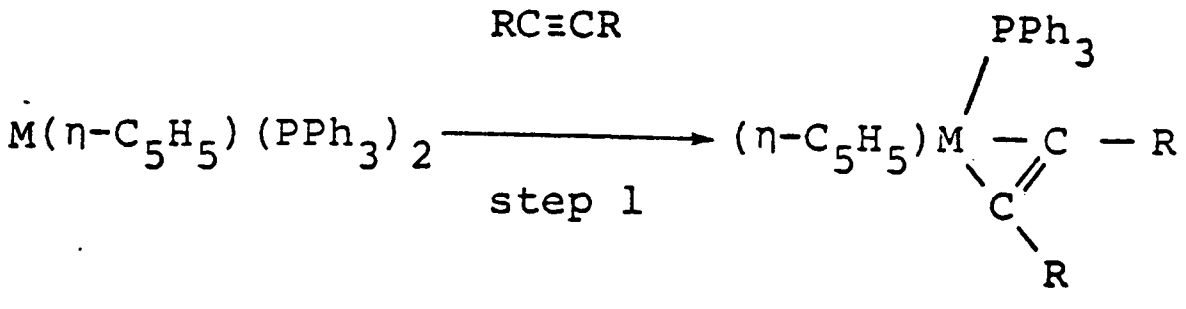


The reaction of $Co(\eta\text{-}C_5H_5)(PF_3)_2$ with $F_3CC{\equiv}CCF_3$ gives I which undergoes hydrolysis to give a mixture of II and III.

Compound III has been characterised by X-ray diffraction. The crystal structure of III shows that the phosphacyclopentadiene ligand assumes an envelope geometry with the phosphorus atom bent out of plane away from the metal atom.[78]



New heterocyclic five-membered metallo-ring complexes of cobalt and rhodium were prepared by the stepwise reaction of $M(\eta\text{-}C_5H_5)(PPh_3)_2$ with acetylenes:

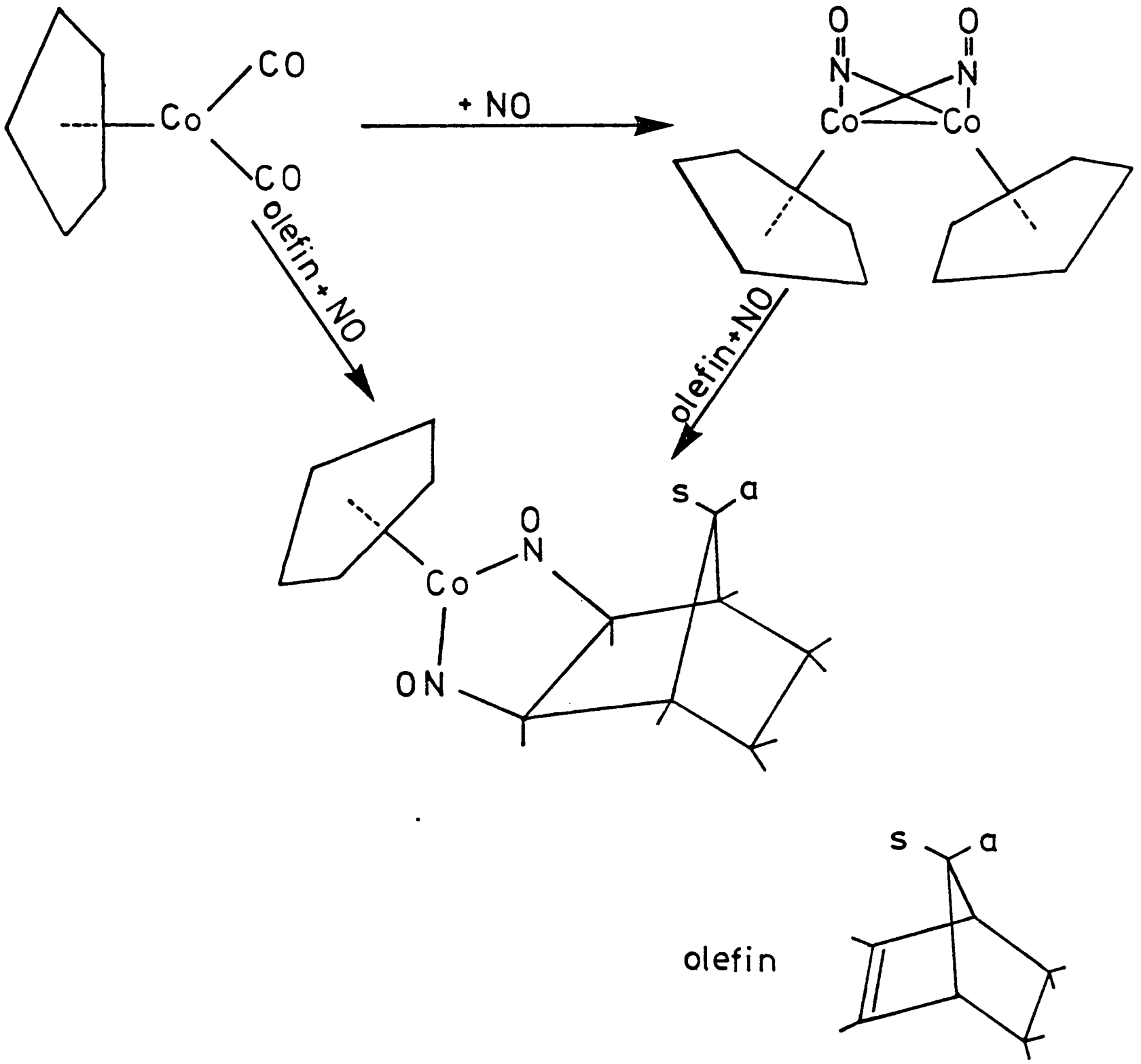


(I)

(I) undergoes insertion of CS_2 or COS to give $(\eta\text{-}C_5H_5)(PPh_3)$-$\underline{MC(R)=C(R)C(X)S}$ (X = S or O).[79]

The complexes $Co(\eta\text{-}C_5H_5)(CO)_2$ and $(Co\{\eta\text{-}C_5H_5\}NO)_2$ react

with NO and olefins of the norbornene type to give the complexes $Co(\eta\text{-}C_5H_5)(NO)_2$olefin, corresponding to addition of the two NO groups to the double bond of the bicyclic ring system. The olefinic protons are in the endo-position.(80)

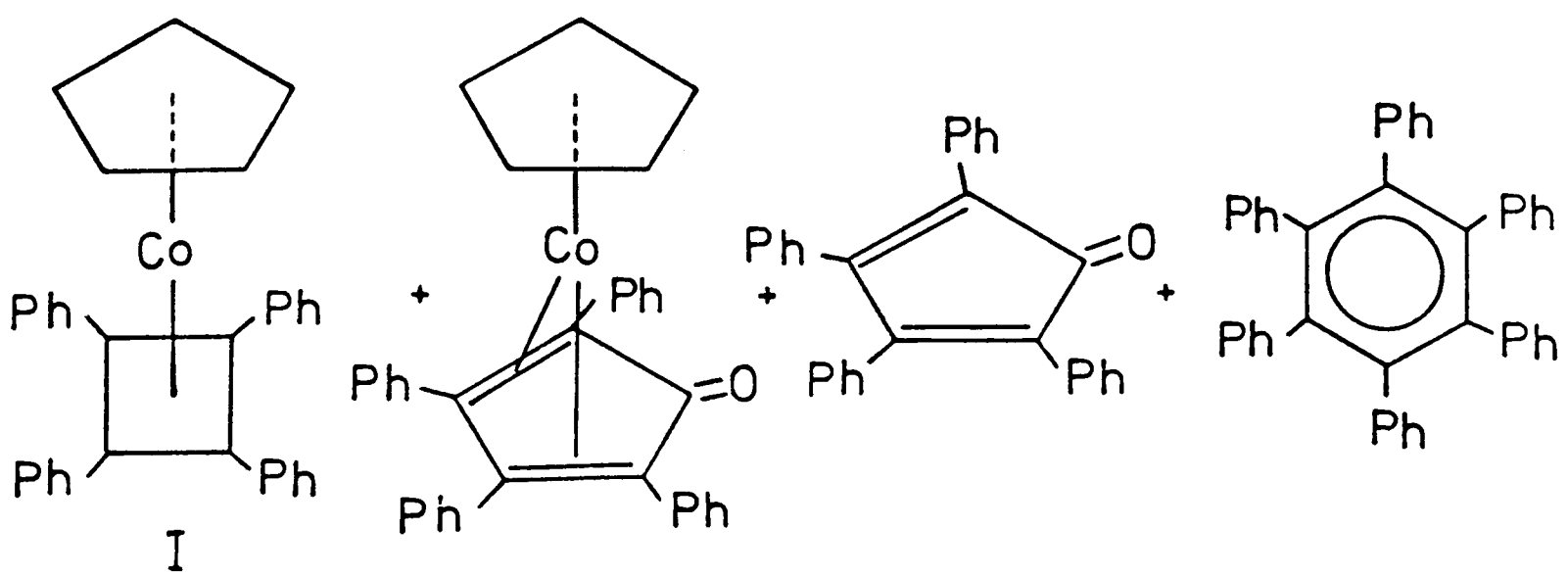


The preparation of neutral, cationic and dicationic η-cyclopentadienylcobalt complexes which also contain isocyanide ligands has been reported. These include $Co(\eta\text{-}C_5H_5)(CNR)I_2$, $\{Co(\eta\text{-}C_5H_5)(CNR)_2I\}PF_6$ and $\{Co(\eta\text{-}C_5H_5)(CNR)_3\}(PF_6)_2$

(R = C_6H_4OMe-p or Me). The other complexes reported have been derived from these by replacement of one or more of the isocyanide groups with other carbon-, nitrogen- or phosphorus-donor ligands.

King[68] previously reported that addition of 2,2',2"-terpyridyl to a solution of $Co(\eta\text{-}C_5H_5)(CO)I_2$ gives an orange-brown precipitate which he claimed to be an impure sample of $\{Co(\eta\text{-}C_5H_5)(C_{15}H_{11}N_3)\}I_2$. The isocyanide complexes were the first well characterised dicationic mononuclear complexes containing a cyclopentadienyl ligand to have been reported. Examples are $\{Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)_3\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)Bipy\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)(CNMe)_2\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)(diphos)\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNMe)_3\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNMe)_2PPh_3\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNMe)diphos\}(PF_6)_2$; $\{Co(\eta\text{-}C_5H_5)(CNMe)Bipy\}(PF_6)_2$[81].

The complex $Co(\eta\text{-}C_5H_5)(CO)_2$ reacts with PhC≡CPh in xylene to give a mixture of products:



50% 10% 15%

The cyclopentadienyl ring in complex I undergoes a variety of electrophilic ring substitutions[82].

CHAPTER II

STUDIES ON THE SYNTHESIS AND REACTIONS OF (1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)BIS (CYCLOPENTADIENYL)MOLYBDENUM DICATION

Chapter I described studies by Romao[83] concerning the synthesis and reactions of (1,2-bis(diphenylphosphino) ethane)bis(cyclopentadienyl) molybdenum dication complexes. His conclusions are summarised in Fig. I.3 which shows that the compound $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$ can be prepared in variable yield by the reaction of $Mo(\eta\text{-}C_5H_5)_2Br_2$ and dppe with $TlPF_6$. $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$ was reduced to the monocation $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6$ which underwent further reduction to the neutral compound $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppe$.

In a preliminary study the cyclopentenyl compound $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppe$ was shown to react with hydrogen chloride giving a red crystalline compound characterised as $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$.

This was the position when the studies described in this chapter were started.

The initial objective of the work was to synthesise, on a suitable scale, the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ and study its chemistry. It was expected that there would be an extensive chemistry of the (1,2-bis(diphenylphosphino) ethane)monocyclopentadienylmolybdenum system which would be of interest with respect to catalysis and for comparison with the chemistry of analogous carbonyl systems.

It was anticipated that the $Mo\{\eta\text{-}C_5H_5\}dppe$ system would be rather more electron-rich than the analogous $Mo\{\eta\text{-}C_5H_5\}\{CO\}_2$ system, because the chelating diphosphine ligand acts as a less powerful π-acceptor ligand than two carbonyl ligands. For example, it has been shown that the $Fe(\eta\text{-}C_5H_5)dmpe$[84] and $Fe(\eta\text{-}C_5H_5)dppe$[85] systems readily form complexes with

molecular nitrogen.

There was an initial problem to be overcome, namely to find a reliable, suitable large scale route to $(Mo\{\eta\text{-}C_5H_5\}_2$ dppe$)^{2+}$ which is the precursor for $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$. We will describe below attempts to improve the yield and convenience of the synthesis. A detailed study of synthetic routes has led to an unexpected and interesting series of observations, which will be described before the chemistry of the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$.

A. RESULTS

SECTION 1:- STUDY OF THE SYNTHESIS OF $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ AND ITS SUBSEQUENT REACTIONS.

The method employed by Romao[83] for the synthesis of $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ (I) was limited in scale to some extent by the fact that $TlPF_6$ is not very soluble in dry acetone, thus substantial quantities of the desired solvent were required. Also $Mo\{\eta\text{-}C_5H_5\}_2Br_2$ is not very soluble. A large scale preparation was carried out very carefully, where a suspension of $TlPF_6$ was added very slowly to a stirred suspension of $Mo\{\eta\text{-}C_5H_5\}_2Br_2$ in the presence of dppe. The reaction is described in detail in the Experimental Section. It was found very difficult to reproduce the conditions of this reaction, which gave satisfactory yields, and there was clearly more that one product present in the reaction mixture. For example, from time to time, in some reactions considerable quantities of a purple material were obtained. This could never be obtained in sufficiently pure state for characterisation. At other times, the yield of the dication $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ (I) would be quite satisfactory, but difficulty was experienced in separating the required product from other materials which were formed. Attempts to improve the yield by variation of the addition rate, the concentrations, or the temperature did not give rise to any significant improvements.

In view of this, an alternative method of synthesis was sought. It has often been observed that dihydrogen is

displaced from a transition metal dihydride system by donor ligands, for example $Co(PPh_3)_3H_3$ even reacts with molecular nitrogen to give $Co(PPh_3)_3(N_2)H$[86]. It was therefore decided to study the reaction between $Mo\{\eta\text{-}C_5H_5\}_2H_3^+$ in acetone solution with dppe. It was found that the reaction took place readily under mild conditions. In initial experiments, the conditions of which are described in the Experimental Section, a deep yellow-brownish solution was formed, from which $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ could be isolated in good yield *ca.* 90%, as the hexafluorophosphate salt, by addition of aqueous NH_4PF_6 to the reaction mixture. Thus it appeared that a convenient and improved route to the $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ had been found.

However, during the course of this research programme, this synthesis was repeated a number of times, and it was observed that from time to time another compound was formed which was of similar appearance to the desired $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$, and which could be isolated as a yellow crystalline compound (II). The reaction between the $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ was studied as a function of the temperature. Conditions of the reaction and the details are described in the Experimental Section. The major observations are summarised here.

When the reaction was carried out by addition of $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ in acetone solution to a cool solution of dppe in acetone, the major product is the dication, $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ (I). However, if $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ in acetone solution is added to a hot solution of dppe in acetone, then the crystalline yellow compound (II) mentioned above is the product formed in higher yield. It was then decided to

attempt to characterise this second product from the reaction.

In a separate attempt to improve the yield and convenience of the synthesis of $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$, the reaction was carried out in acetonitrile instead of acetone. However, a reaction between $Mo\{\eta\text{-}C_5H_5\}_2I_2$ and acetonitrile was observed. A red crystalline compound could be isolated from the reaction mixture.

Elemental Analyses was consistent with the stoichiometry $C_{14}H_{16}F_{12}MoN_2P_2$.

The infrared spectrum had bands of medium intensity at $2329cm^{-1}$ and $2305cm^{-1}$ which are in the region corresponding to C≡N stretching vibration. The spectrum also contained a strong band at $3137cm^{-1}$ and bands at $1423cm^{-1}$ and $1420cm^{-1}$ characteristic of η-cyclopentadienyl ligands, and bands characteristic of the PF_6 anion.

The ^1H n.m.r. spectrum recorded in liquid SO_2, consisted of two sharp singlets of relative intensity in the ratio 10:6, at 4.02τ and 7.6τ assigned to 10 equivalent hydrogens of 2 η-cyclopentadienyl ligands and to 6H of 2 methyl groups of 2 acetonitrile molecules, respectively.

The complex was assigned the formulation: $(Mo\{\eta\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$ on the basis of the analytical and spectral data.

Attempts to prepare $(W\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ analogous to $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ by reacting $(W\{\eta\text{-}C_5H_5\}_2H_3)^{+}$ with dppe gave no tractable products.

SECTION 2:- CHARACTERISATION OF THE SECOND PRODUCT FROM THE REACTION BETWEEN $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ AND dppe.

The yellow compound (II) is moderately stable. It could be recrystallised from a number of solvents and it became apparent that the compound had a marked tendency to crystallise together with solvent of crystallisation. When the compound is recrystallised from acetonitrile, it incorporates some acetonitrile, and when it is recrystallised from mixtures of dichloromethane and methanol or dichloromethane and ethanol it incorporates dichloromethane. Acetone is incorporated when it is recrystallised from acetone. Considerable difficulty was experienced in obtaining good analyses for the compound (II) despite the fact that the crystals obtained from recrystallisation were of excellent appearance. However, by persistent recrystallisation from mixtures of dichloromethane and ethanol a value was obtained which was consistent with the formulation $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6.\frac{1}{2}CH_2Cl_2$.

The ^1H n.m.r. spectrum of the compound (II) has been obtained in deuterated acetone, acetonitrile and nitrobenzene. Solvent of recrystallisation is clearly present since, when recrystallised from mixtures of dichloromethane and methanol or dichloromethane and ethanol, a sharp band is observed at τ4.54 of relative intensity corresponding to half a molecule of crystallisation of dichloromethane. The ^1H n.m.r. spectrum of a number of samples recrystallised from different solvents has been obtained. The data of the different spectra are given in table II.1. A typical spectrum is shown in Figure

II.1 (b). There is a complex series of bands in the region 2.35τ to 3.3τ of relative intensity approximately 20 which may be assigned to the aromatic protons of the 4 phenyl rings. Their appearance is quite characteristic of the phenyl groups of the dppe ligand. There is a sharp band at 5.34τ, of relative intensity 5, which under high resolution can be seen to be a triplet, and this band may be assigned to hydrogens of a cyclopentadienyl ring coupled to two ^{31}P nuclei of the dppe ligand ($J \simeq 1$ Hz). In the region from 5.5τ to 9τ , apart from the bands arising from the solvent, there are a number of broad and complex bands. The band centred at 5.75τ has a relative intensity of approximately 2 hydrogens and it is in the region assignable to olefinic C-H hydrogens of a diene system - we will discuss possible assignment of this later. In the region about 7.05τ there is again a very broad and complex series of bands which integrate approximately to 6. These bands may be assigned to the $P\text{-}CH_2\text{-}CH_2\text{-}P$, 4 hydrogens of dppe group together with 2 more hydrogens arising from a cyclopentadiene system. Finally, there is again a broad doublet centred around 8.7τ of relative intensity 2.

It is instructive at this stage to compare the ^{1}H n.m.r. spectrum of this yellow compound (II) with that of the cyclopentadiene compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6$ (II') described by Romao. The spectrum obtained by Romao of compound (II') is shown together with the spectrum of compound (II) in Figure II.1 (a). Comparison of these spectra clearly show that there are strong similarities between the two different molecules. The phenyl regions both have characteristic sets

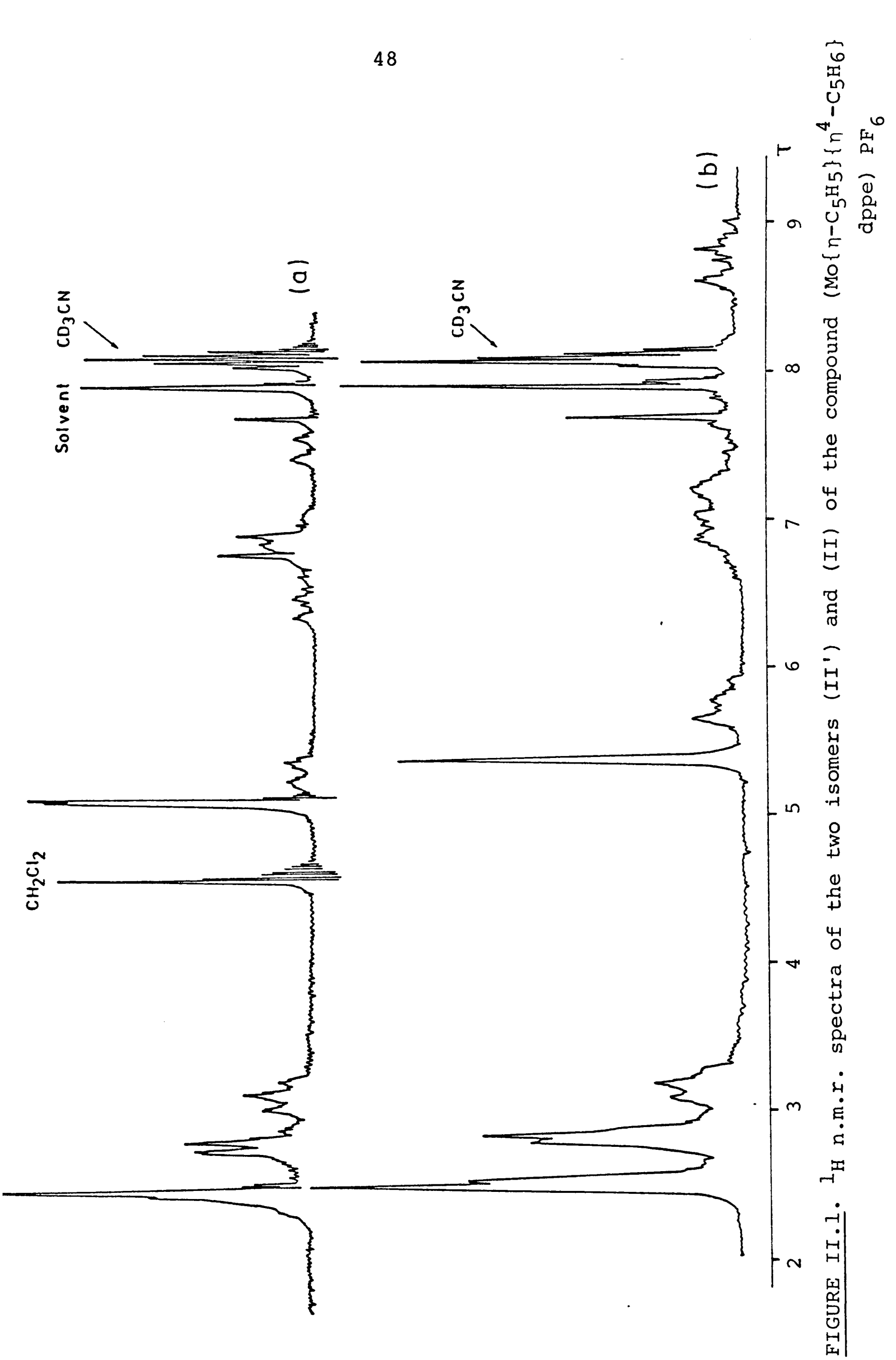


FIGURE II.1. ^1H n.m.r. spectra of the two isomers (II') and (II) of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}$ dppe) PF_6

TABLE II.1. ^{1}H n.m.r. spectra of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6$

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHz in CD_3CN	8.7	2	complex	2H (C_5H_6)
	7.05	6	complex	2H (C_5H_6) + PCH_2CH_2P
$(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6$	5.75	2	complex	2H (C_5H_6)
	5.34	5	triplet (J = 1Hz)	C_5H_5
	3.3 - 2.35	20	complex	4 Ph
90 MHz in $(CD_3)_2CO$	8.82	2	complex	2H (C_5H_6)
	6.31	6	complex	2H (C_5H_6) + PCH_2CH_2P
	4.6	2	complex	2H (C_5H_6)
	4.31	5	triplet (J = 1Hz)	C_5H_5
	1.67 - 0.37	20	complex	4 Ph
60 MHz in $NO_2C_6D_5$	8.45	2	complex	2H (C_5H_6)
	6.55 - 7.7	6	complex	2H (C_5H_6) + PCH_2CH_2P
	5.7	2	complex	2H (C_5H_6)
	5.55	5	singlet	C_5H_5
	2.5 - 3.8	20	complex	4 Ph

of three bands with very similar intensity changes. The cyclopentadienyl peaks occur in similar region and both are triplets. In the spectrum of the compound (II') there is a doublet lying at 5.28τ which corresponds in relative intensity and position to our band centred at 5.75τ. In the spectrum of compound (II'), the bands assigned to cyclopentadiene hydrogens are separated from those which may be assigned to the $P-CH_2-CH_2-P$ hydrogens of the dppe ligand, whereas in the spectrum of compound (II) they have moved close together. Also in the spectrum of compound (II') there is a doublet occurring at 7.47τ which corresponds to the rather broad and less well resolved band at 8.7τ. Comparison of spectra shows that, though they are very similar, clearly (II) and (II') are not the same compound. The analysis data however, suggest that (II) has the same empirical formula as (II').

The infrared spectra of compounds (II) and (II') are shown in Figure II.2. Again, very strong similarities can be seen, and both spectra show bands assignable to cyclopentadienyl stretching frequencies, PF_6 and phenyl groups. Of particular interest is to note that whereas compound (II') shows in the infrared spectrum a relatively intense low frequency band at $2788cm^{-1}$, a corresponding band in compound (II) is not present, so again the spectra are very similar but show distinct differences.

It was observed that treatment of compound (II) with concentrated hydrochloric acid or Ph_3C^+ reform the parent

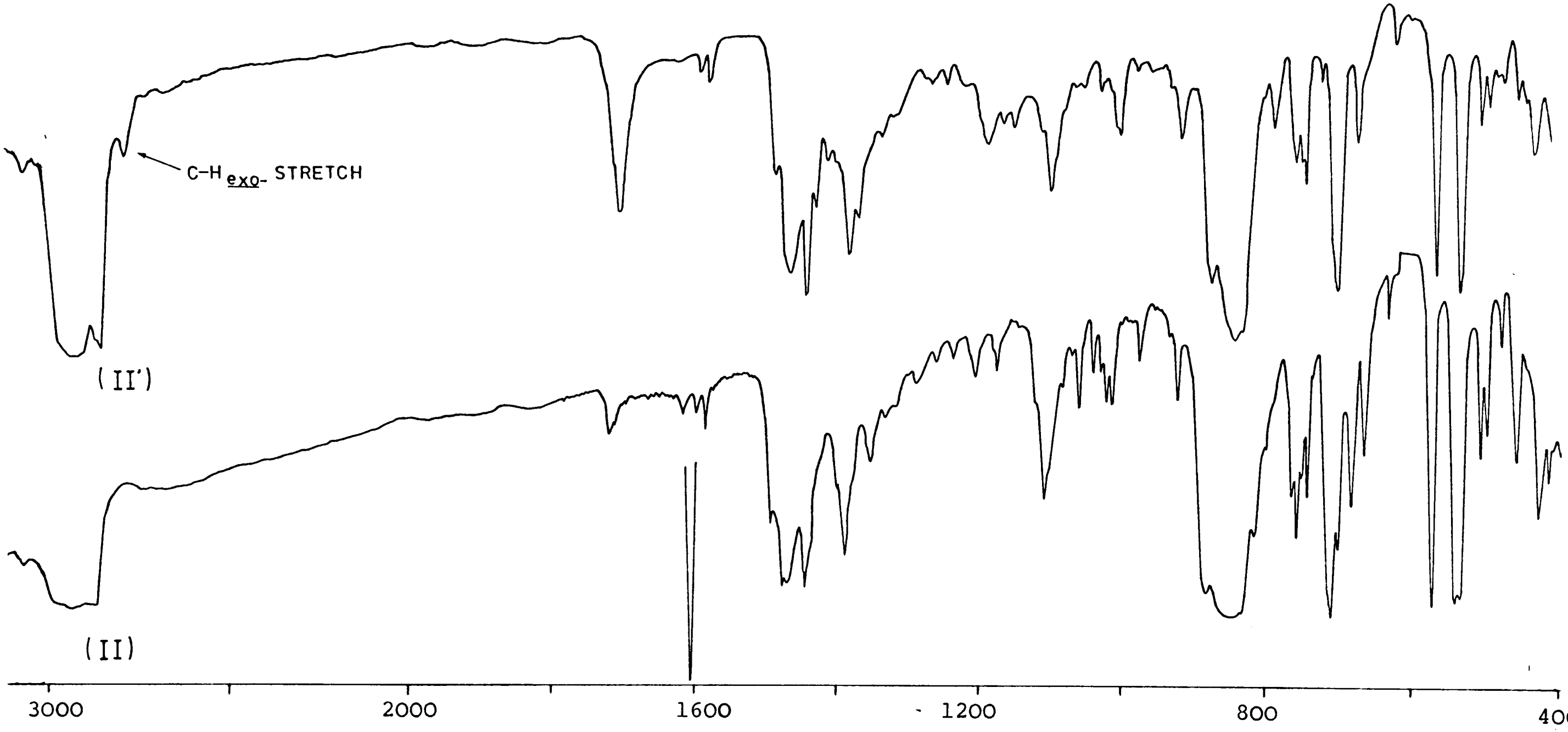
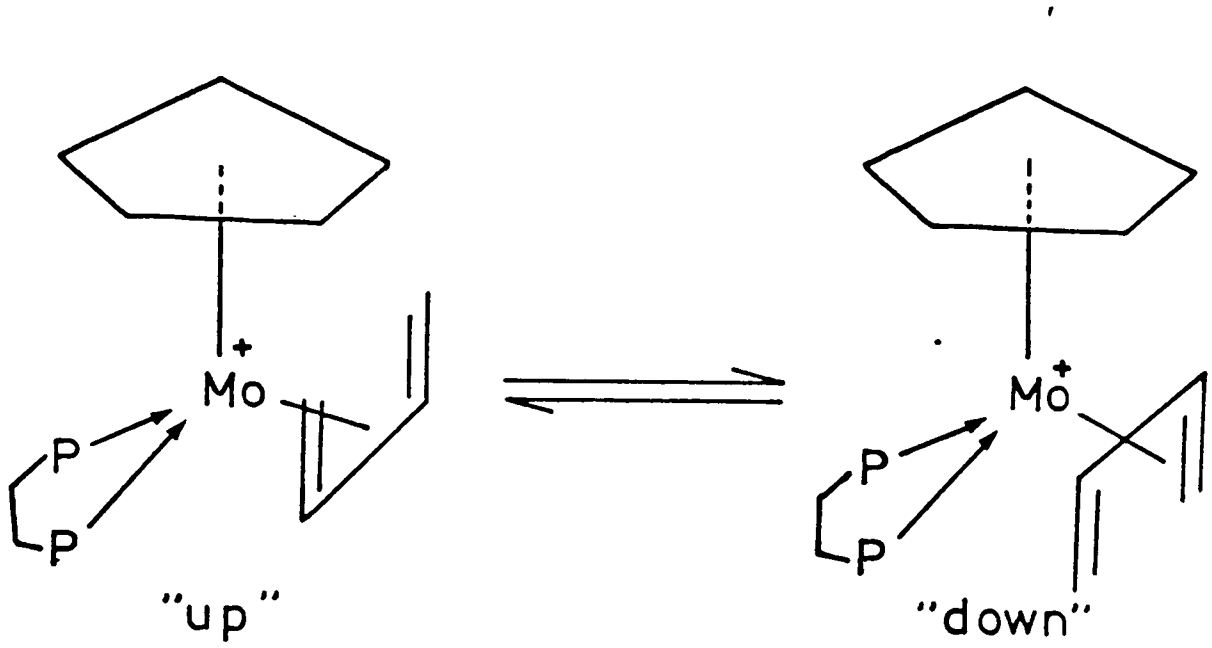


FIGURE II.2. Infrared spectra of the two isomers (II) and (II') of the compound (Mo{η-C_5H_5}{η^4-C_5H_6}dppe)PF_6

dication (I).

On the basis of these data, we came to the preliminary conclusion that compounds(II) and (II') were isomers.

Recent work by J.A. Segal and M.L.H. Green[20, 21] had shown that the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)PF_6$ exists in solution as a mixture of isomers. It has been proposed from the n.m.r. studies that they exist as a mixture of "up" and "down" isomers as shown below:

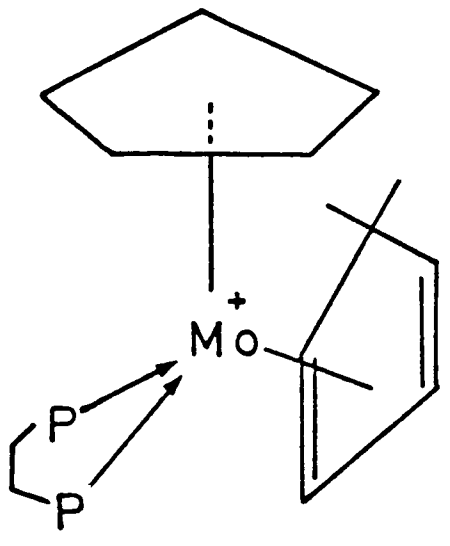


Strong support for this observation arises from the fact that treatment of these isomers with $NaAlH_2(OCH_2CH_2OMe)_2$ gives rise to two compounds which have been characterised as being "up" and "down" isomers of the crotyl compound, and these isomers could be separated by fractional crystallisation.

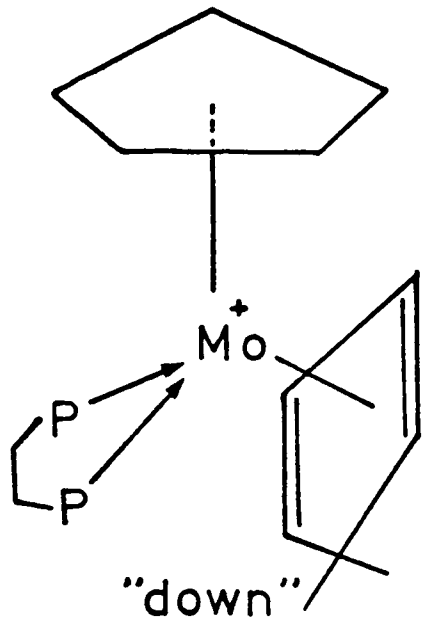
We also note that "up" and "down" isomers of cyclopentadione systems have been described by M. Green and F.G.A. Stone[15]. Other examples of "up" and "down" isomers

are described in Chapter I.

On the basis of these observations, we propose that the compounds (II) and (II') are indeed isomers differing in their configuration as shown below:



"up"



"down"

We also draw attention to the fact that in the synthesis of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_6H_8\}dppe)PF_6$, whose crystal structure has been determined[20], only the "up" isomer of this compound was obtained, and there was no evidence for any rotational freedom of the C_6H_8 ligand, analogous to that observed in the related butadiene compound $(Co\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)^+$. It was concluded that the butadiene compounds were rapidly equilibrating. The equilibrium could not be frozen out, but it was shown that the equilibrium between the "up" and the "down" isomers varied as a function of the different solvents. Furthermore, reduction of the mixture gave a mixture of separable isomers. It proved extremely difficult to obtain analytically pure samples of $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_6H_8\}dppe)PF_6$, again because of the tendency to form

solvates with all the different solvents which were investigated. In fact, the crystal structure shows that it recrystallises with 1 molecule of SO_2. The fact that this compound, which is clearly analogous to our own compound (II) readily forms solvates, accounts for the problems of getting consistently satisfactory analytical data. In the light of all that, we postulate that (II') and (II) are "up" and "down" isomers as drawn, and the question of which isomer has which structure will be discussed later.

Since the compound (II') has been shown to be reduced to $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppe$, (III'), as part of our attempt to characterise compound (II), it was treated with $NaBH_4$, to see whether it gave the same product or an isomer.

On treatment of (II) with $NaBH_4$, a bright yellow crystalline compound (III) was isolated from the reaction mixture, which was very much less soluble than (III'). The new compound (III) was found to be very insoluble in all the ordinary solvents, slightly soluble in hot toluene, being most soluble in dichloromethane, but it reacted with the solvent to give a red solution. It was moderately sensitive to oxygen. Compound (III) could not be recrystallised. Analysis was obtained from the microcrystalline product obtained from the reaction mixture. The analytical data are slightly lower than that corresponding to the formulation $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppe$, due perhaps to the presence of some $NaBH_4$. (Found: C, 66.3%, H, 5.5%. $C_{36}H_{36}MoP_2$ requires: C, 69.0%, H, 5.7%).

No ^{1}H n.m.r. spectrum could be recorded due to its insolubility.

The infrared spectrum (the data are given in the Experimental Section) is very similar to that of the cyclopentenyl compound (III'). It shows bands consistent with the presence of η-cyclopentadienyl and dppe systems.

Attempts to obtain a mass spectrum failed.

It seems probable that reaction of $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}$ dppe$)PF_6$ (II) with $NaBH_4$ gives the neutral cyclopentenyl compound $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}$dppe isomer of (III'), although of course, further evidence will be necessary in order to be able to assign the structure of (III') unambiguously.

We thought it was of interest to see whether $(Mo\{\eta\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$, described above, could be reduced to $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}\{NC\text{-}CH_3\}_2$ compound analogous to the neutral compound $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}$dppe. However, by treatment of $Mo\{\eta\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$ with $NaBH_4$, $Mo\{\eta\text{-}C_5H_5\}_2H_2$ was recovered in good yield.

SECTION 3:- SYNTHESIS OF $(Mo\{\eta\text{-}C_5H_5\}_2dppm)^{2+}$.

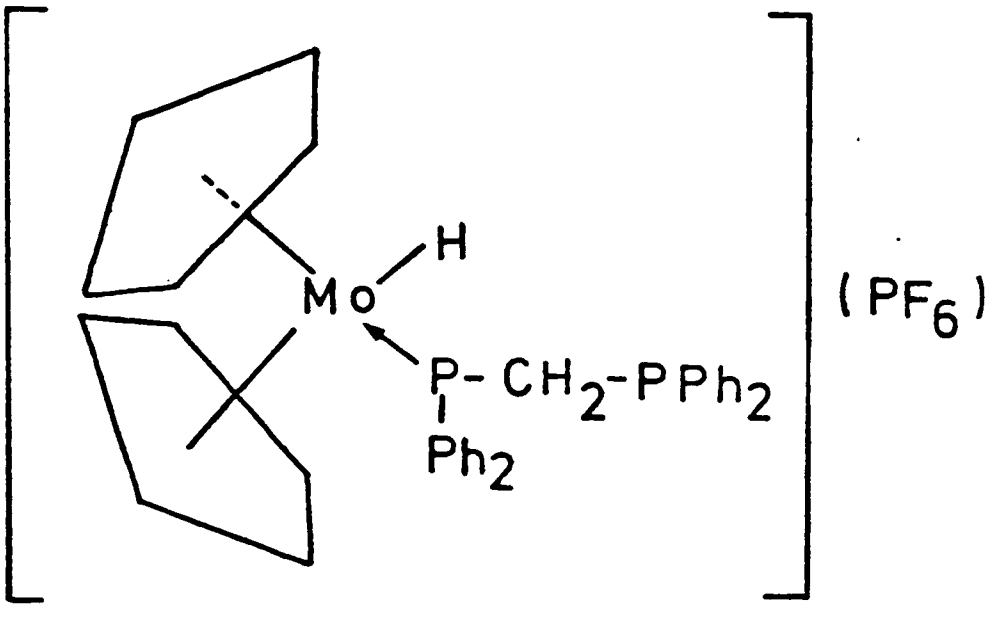
At an early stage in this work and when the difficulties had been experienced in obtaining good yields of the compound $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$ (I), it was thought worth while to explore whether or not it would be simpler to prepare the 1,2-bis(diphenylphosphino)methane analogue. Accordingly the reaction between $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^{+}$ and dppm was studied and two products were isolated, yellow crystals (IV) and orange crystals (V).

The analytical data of compound (IV), given in the Experimental Section, is consistent with the stoichiometry $C_{35}H_{33}F_6MoP_3$.

The ^1H n.m.r. spectrum (the data, together with the assignment, are given in Table II.2) shows that there are two equivalent η-cyclopentadienyl rings split into a doublet and a high field pattern characteristic of hydrogen attached to molybdenum which is also split into a broad doublet due to coupling with one ^{31}P nucleus.

The infrared spectrum (the data are given in the Experimental Section) shows in particular a band of weak intensity at $1870cm^{-1}$ which may be assigned to ν-Mo-H.

On the basis of this evidence, we conclude that compound (IV) has the formula shown below, where the phosphine ligand is acting as a monodentate ligand:



(IV)

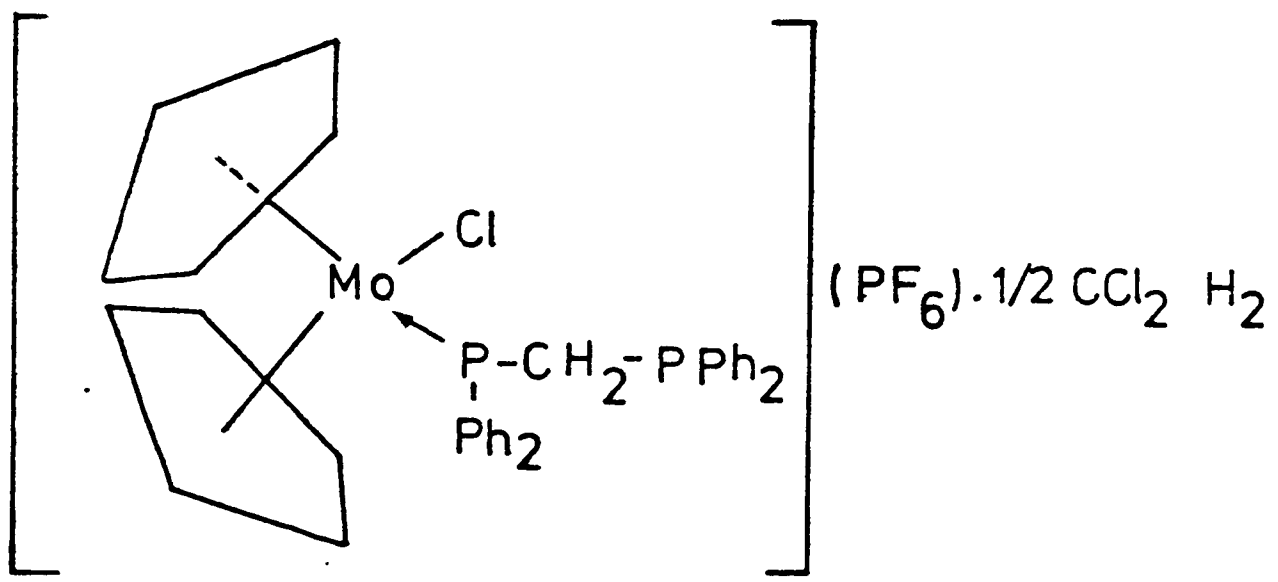
Further evidence for the structure given above was obtained by treatment of compound (IV) with a 1:1 mixture of dichloromethane and chloroform. A purple solution was formed together with a few orange crystals which were found to be identical to compound (V) by comparison of their infrared and ^1H n.m.r. spectra with those of an authentic sample. From the purple solution, purple crystals (VI) were obtained.

The analytical data of compound (VI) given in the Experimental Section is consistent with the stoichoimetry $C_{35}H_{32}ClF_6MoP_3 \cdot \frac{1}{2}CH_2Cl_2$.

The ^1H n.m.r. spectrum (the data are given in Table II.2) contains basically the same peaks as the ^1H n.m.r. spectrum of compound (IV), but their chemical shifts are different. There is no high field peak corresponding to a hydrogen atom attached to molybdenum, however. There is a sharp band at 4.3τ which corresponds to half a molecule of dichloromethane of crystallisation.

The infrared spectrum, given in the Experimental Section, is again very similar to that of $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}H)PF_6$ (IV), except for the absence of the band in the region 1870cm^{-1} assigned to ν-Mo-H in compound (IV).

On the basis of this evidence, we conclude that the compound (VI) has the formula shown below:



(VI)

Compound (V) was recrystallised from mixtures of acetone and water, and acetone and ethanol.

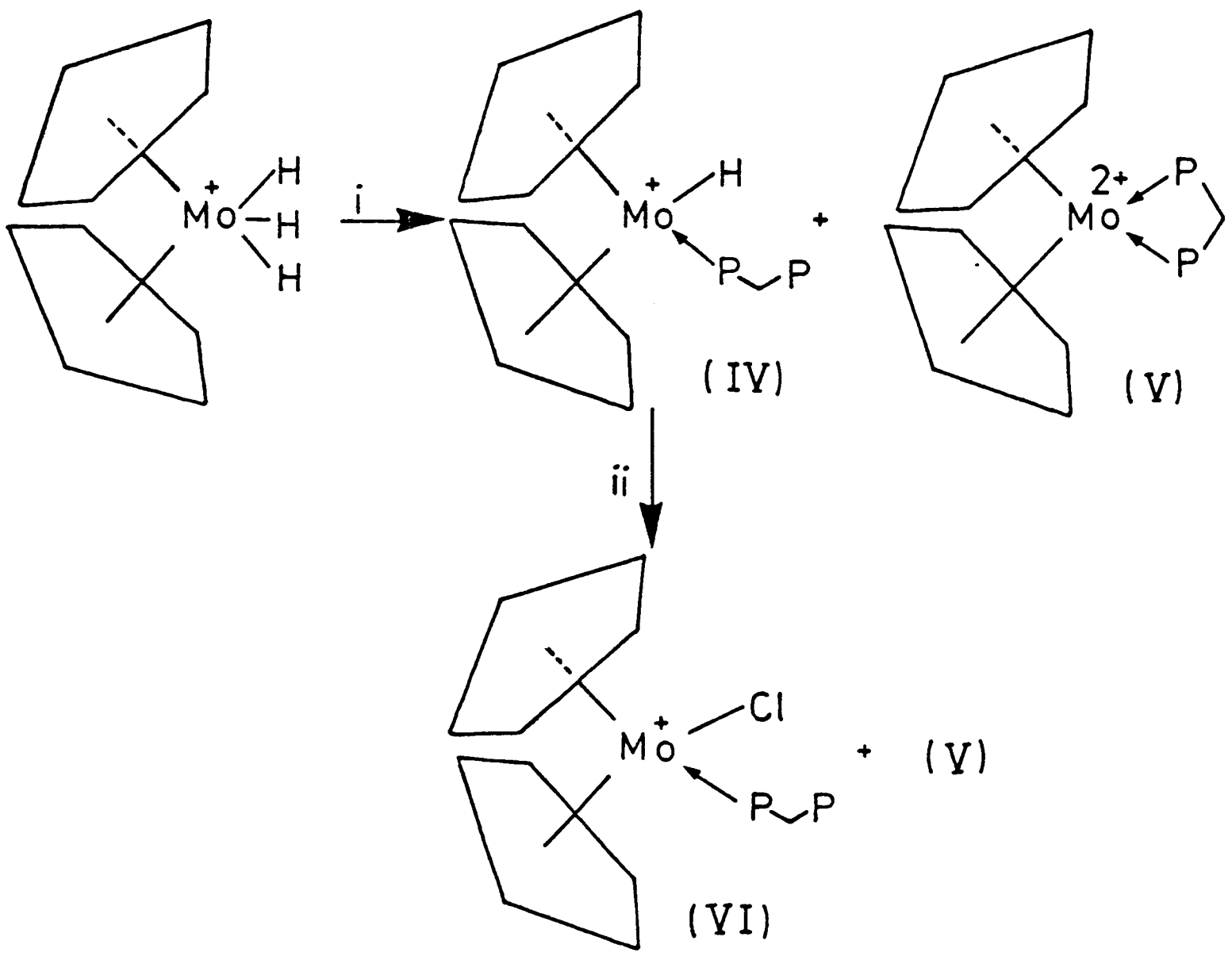
The analytical data given in the Experimental Section are consistent with the stoichoimetry $C_{35}H_{32}F_{12}MoP_4$.

The ^1H n.m.r. spectrum (the data are given together with assignments in Table II.2) is consistent with the compound being the dication $(Mo\{\eta\text{-}C_5H_5\}_2dppm)(PF_6)_2$.

The infrared spectrum, given in the Experimental Section, shows bands characteristic of η-cyclopentadienyl rings,

phenyl groups and PF_6.

In this section, we conclude that from the reaction of $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ and dppm, we obtain two compounds with the structure shown below:



i dppm in acetone

ii $CH_2Cl_2/CHCl_3$

TABLE II.2. ^{1}H n.m.r. spectra of the compounds described in Chapter II, Section III.

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90MHz in $(CD_3)_2SO$	17.84	1	doublet ($J_{^{31}P-H}$ = 36)	Mo-H
	6.05	2	doublet ($J_{^{31}P-CH_2}$ = 9)	$P-CH_2-P$
$(Mo\{\eta-C_5H_5\}_2\{dppm\}H)PF_6$	4.43	10	doublet ($J_{^{31}P-Cp}$ = 2.2)	C_5H_5
	1.85 - 2.4	20	complex	4 Ph
90 MHz in $(CD_3)_2SO$	6.18	2	doublet ($J_{^{31}P-CH_2}$ = 8)	$P-CH_2-P$
	4.39	10	doublet ($J_{^{31}P-Cp}$ = 1.67)	C_5H_5
$(Mo\{\eta-C_5H_5\}_2\{dppm\}Cl)PF_6$	4.3	1	singlet	½ CH_2Cl_2 solvate
	2.9 -2.45	20	complex	4 Ph
90 MHz in $(CD_3)_2SO$	4.32	10	triplet ($J_{^{31}P-Cp}$ = 2.1)	C_5H_5
	3.66	2	triplet ($J_{^{31}P-CH_2}$ = 12)	$P-CH_2-P$
$(Mo\{\eta-C_5H_5\}_2\{dppm\})(PF_6)_2$	2.60-2.05	20	complex	4 Ph

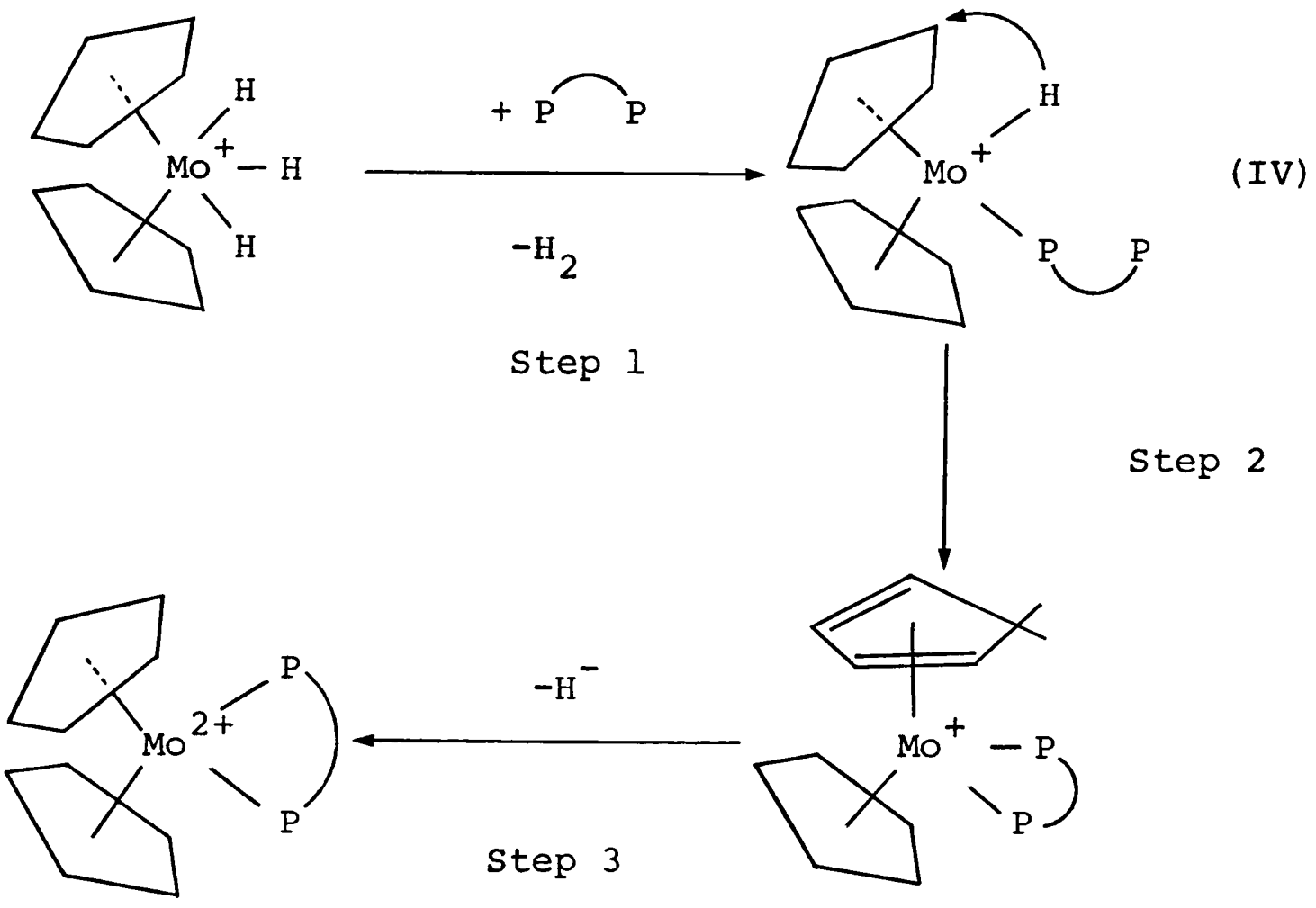
B. DISCUSSION.

It is interesting to enquire which of the isomers (II) and (II'), and which of the cyclopentenyl isomers (III) and (III') have the "up" or the "down" configurations, and also it is interesting to ask what are the factors which lead to the formation of one or the other as a function of the different synthetic routes.

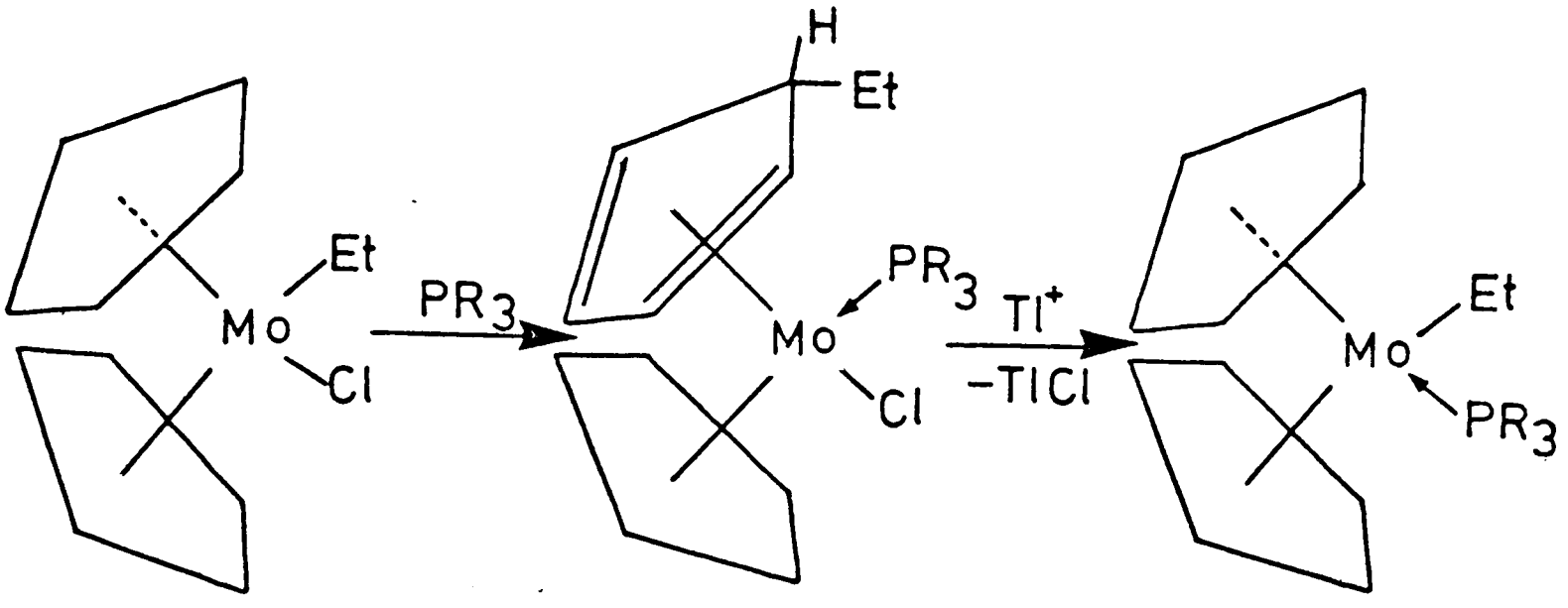
Isomer (II') is prepared by hydride attack on the dication (I), and it is well known that nucleophilic attack on organometallic cations proceeds by addition of the nucleophile in the exo-position relative to the metal. Indeed Romao[83] has studied reaction of the dication (I) with BD_4^- and shown that the low frequency band at 2788cm^{-1}[87] is absent in the deuterated compound and shifted to 2040cm^{-1} and 2070cm^{-1}, corresponding to an exo-C-D stretch.

We observe that reaction of $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ with dppe or dppm, gives the dication $(Mo\{\eta\text{-}C_5H_5\}_2pp)^{2+}$((I) pp= dppe, (V) pp = dppm). The mechanism of formation of these is not clear. Since we isolate $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}H)^+$ from the reaction of $(Mo\{\eta\text{-}C_5H_5\}_2H_3)^+$ with dppm, it is reasonable to assume that this is the first intermediate in the formation of the dications (I) and (V). We can understand the formation of isomer (II) in terms of proton migration from Mo to the endo-position on the ring. We note that treatment of (II) with H^+ or Ph_3C^+ causes formation of the dication $(Mo\{\eta\text{-}C_5H_5\}_2$ dppe$)^{2+}$. Therefore it is possible that these dications are formed by a mechanism shown below, where H^- is lost from

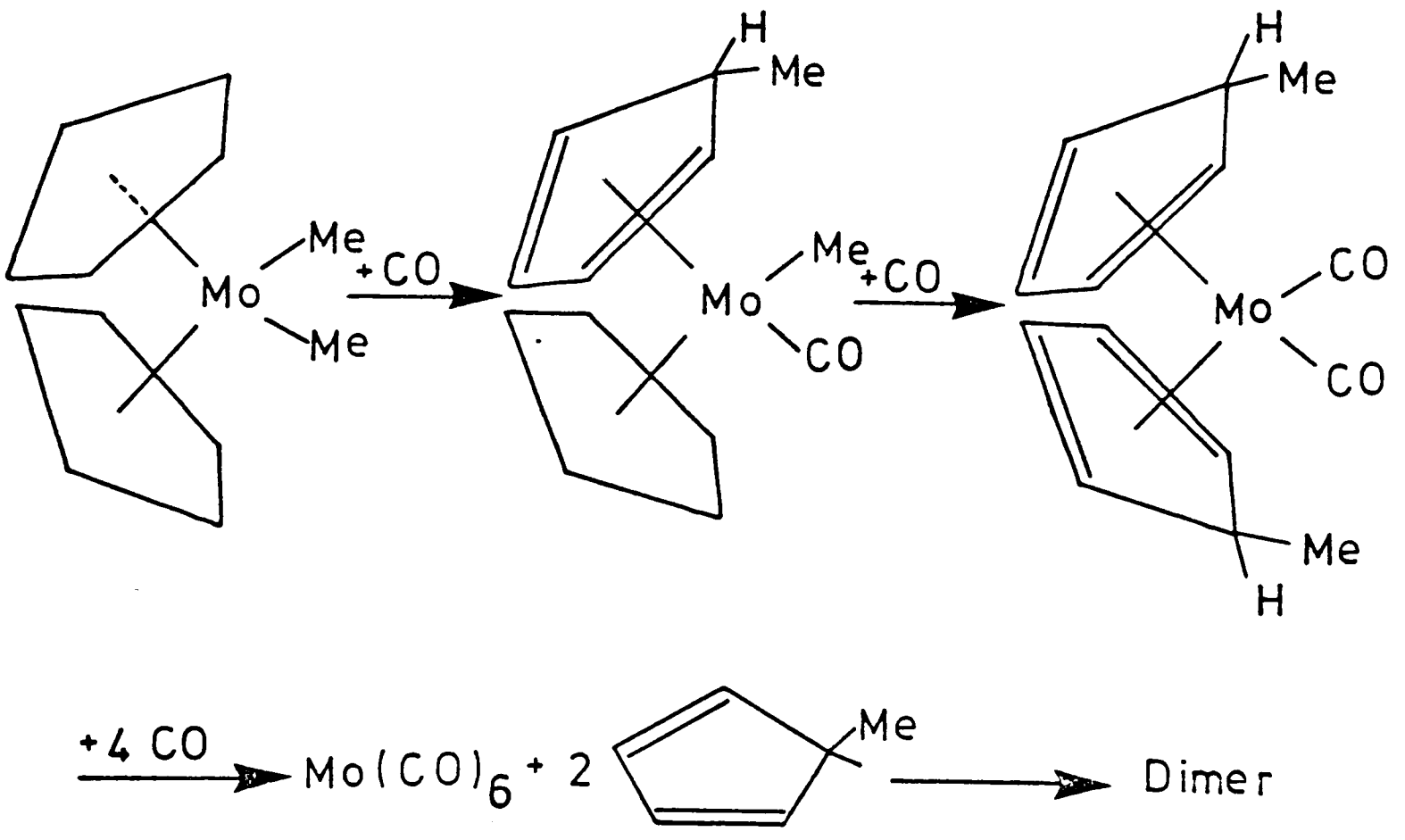
compound (II) or the dppm analogue which has not been isolated.



We then postulate that the formation of isomer (II) may well arise by intra-molecular migration of proton to the cyclopentadienyl ring as a result of the incipient attack on the metal by the uncoordinated phosphine. Benfield[88] has shown that a reversible migration of this type occurs in the reaction of $Mo\{\eta\text{-}C_5H_5\}_2\{Et\}Cl$ with tertiary phosphines, giving the 1-endo-ethylcyclopentadiene derivative, $Mo\{\eta\text{-}C_5H_5\}(1\text{-endo-}EtC_5H_5)(PR_3)Cl$.

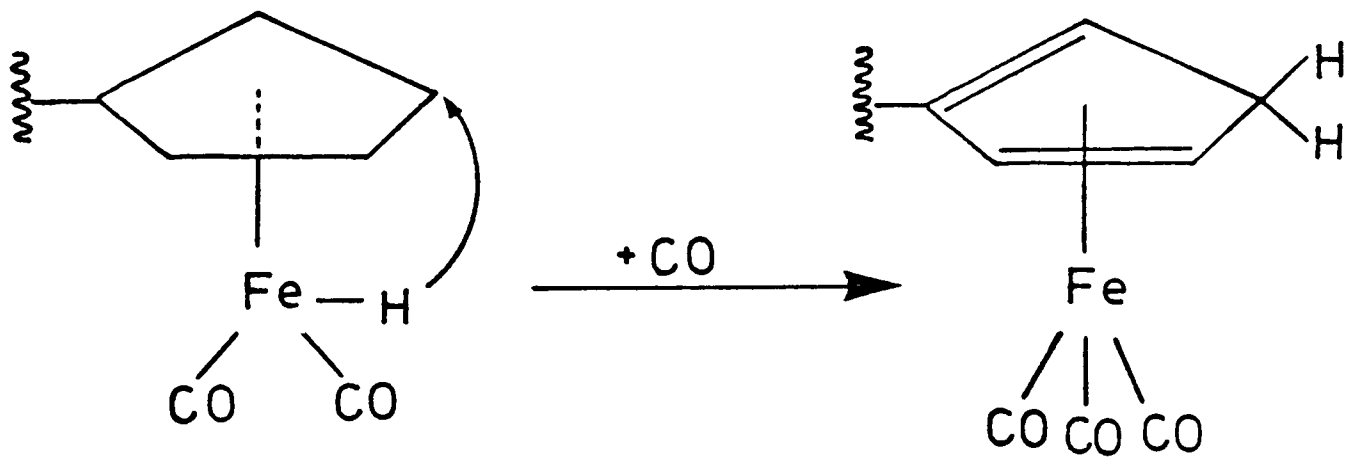


Another example is the reaction of ($M\{\eta\text{-}C_5H_5\}_2Me_2$) (M = Mo, W) with carbon monoxide under pressure, which may involve the following steps:



In the proposed mechanism, it is suggested that the η-cyclopentadienyl ring is lost by a sequential transfer of the two methyls from the metal to the ring.

Brintzinger[89] has reported that the polymer system containing the group $Fe\{\eta\text{-}C_5H_5\text{-}P\}\{CO\}_2H$ (P = polymer) reacts with CO according to:



This provides circumstantial evidence that both hydrogen and alkyl groups on the metal can migrate to an endo-position in the cyclopentadienyl ring.

Thus we postulate that the formation of isomer (II) proceeds by endo-proton migration, whereas the formation of isomer (II') proceeds by exo-attack of hydride on the cyclopentadienyl ring.

The question now arises of why these two different mechanisms should give rise in each case to pure "up" and "down" isomer.

The Figure II.3 shows the dication $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$:

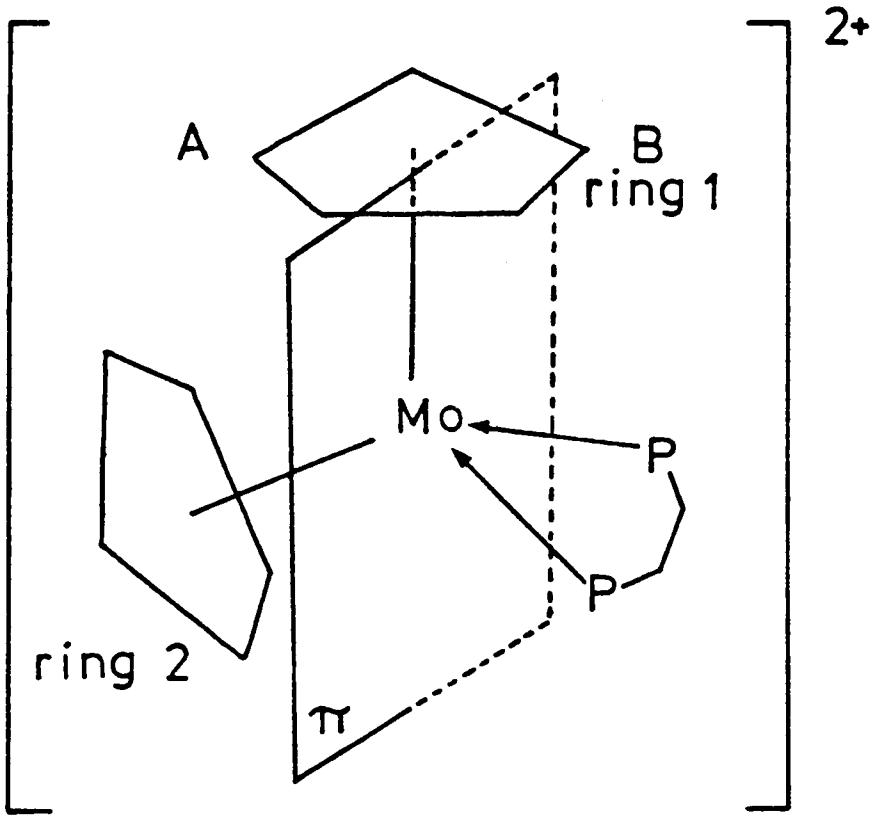


FIGURE II.3 Asymmetric π-electron density of the cyclopentadienyl ring 1 of $(Mo\{\eta\text{-}C_5H_5\}_2dppe)^{2+}$

The plane of symmetry of the molecule lies in the plane of the page. If we draw a plane normal to the plane of the page, plane Π, clearly one can anticipate that the electronic effect of the 1,2-bis(diphenylphosphino)ethane ligand with respect to the side A of the cyclopentadienyl ring 1 will be different from the electronic effect of the cyclopentadienyl ring 2 on the side B of the cyclopentadienyl ring 1. It may be assumed that the trans-effect is the dominant one. This

is normally the case since electronic effects are more important in the trans-position due to the fact that the common orbitals, namely the d orbitals, are involved in metal-ligand interactions. This has been demonstrated many times, notably in square planar platinum complexes. It follows then that the different electronic effects of the cyclopentadienyl ring 2, and dppe in the cyclopentadienyl ring 1, might be to cause some asymmetry in the electron distribution in the π-electrons of the cyclopentadienyl ring 1. Such asymmetry would, of course, be present even while the ring is rotating about the metal-ligand axis, since the electron movement is very much faster than that of molecular motion. It is therefore to be anticipated that the nucleophilic addition of the hydride on ring 1 would occur at the most electron-poor part of the ring. Since the diphosphine ligand is probably a better π-acceptor system than cyclopentadienyl ligand, one might predict that the polarisation of the electron density on the ring 1 is as illustrated in Figure II.3, in which case the isomer which will be predicted to form will be the "up" isomer, as shown in Figure II.4.

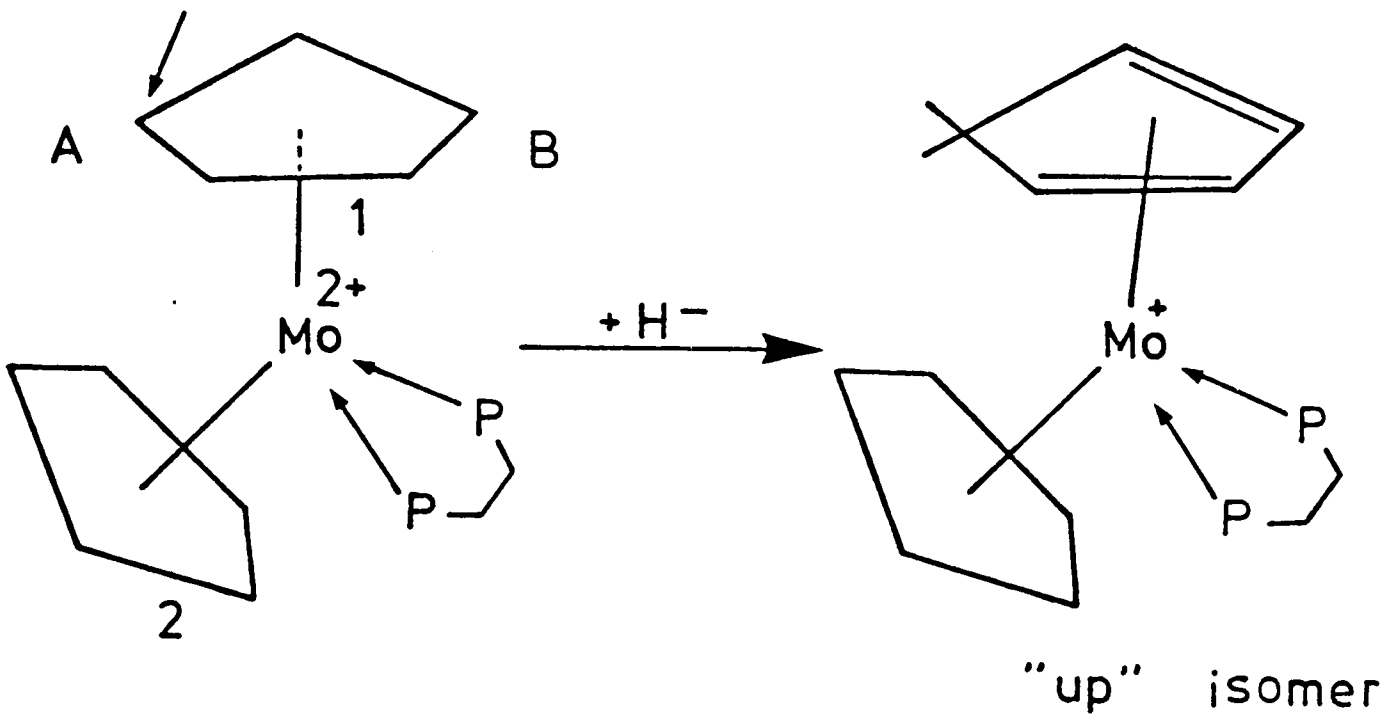


FIGURE II.4 Formation of the "up" isomer of $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}\{dppe\})PF_6$

Certainly one may predict a distortion of π-electron density, and one may argue on this very simple basis that the distortion occurs in this manner. However, in order to substantiate this very tentative and simple argument, a much more detailed consideration of electronic structure and stereochemistry would be necessary.

The observation by Green and Segal[20, 21] that the mixture of "up" and "down" butadiene isomers when reacted with $NaAlH_2(OCH_2CH_2OMe)_2$ gives rise to a separable mixture of "up" and "down" crotyl isomers, clearly shows that there can be a difference of reactivity between diene systems which are orientated differently with respect to the other ligands attached to molybdenum. Ours is a closely analogous system and therefore it is not surprising that stereospecific

attack, giving rise to a particular isomer, is observed in the case of addition of H^- to (II) or (II') giving (III) or (III').

When we considered the formation of isomer (II), then we postulated this to form by proton migration. If we look again at the analogous plane of the proposed precursor, namely $(Mo\{\eta\text{-}C_5H_5\}_2\{dppe\}H)^+$, we can argue that again the cyclopentadienyl ring is much more electron-pushing, giving rise to a greater electron density on side B, and a relatively positive character on side A, in which case we notice from the Figure II.5 that the proton lies on the same side of the ring, which is the one supposed from our previous argument to be the more electron-rich. Thus we can suppose that migration of the proton will preferentially go to the side B of the cyclopentadienyl ring 1, in which case this will give rise to the "down" isomer.

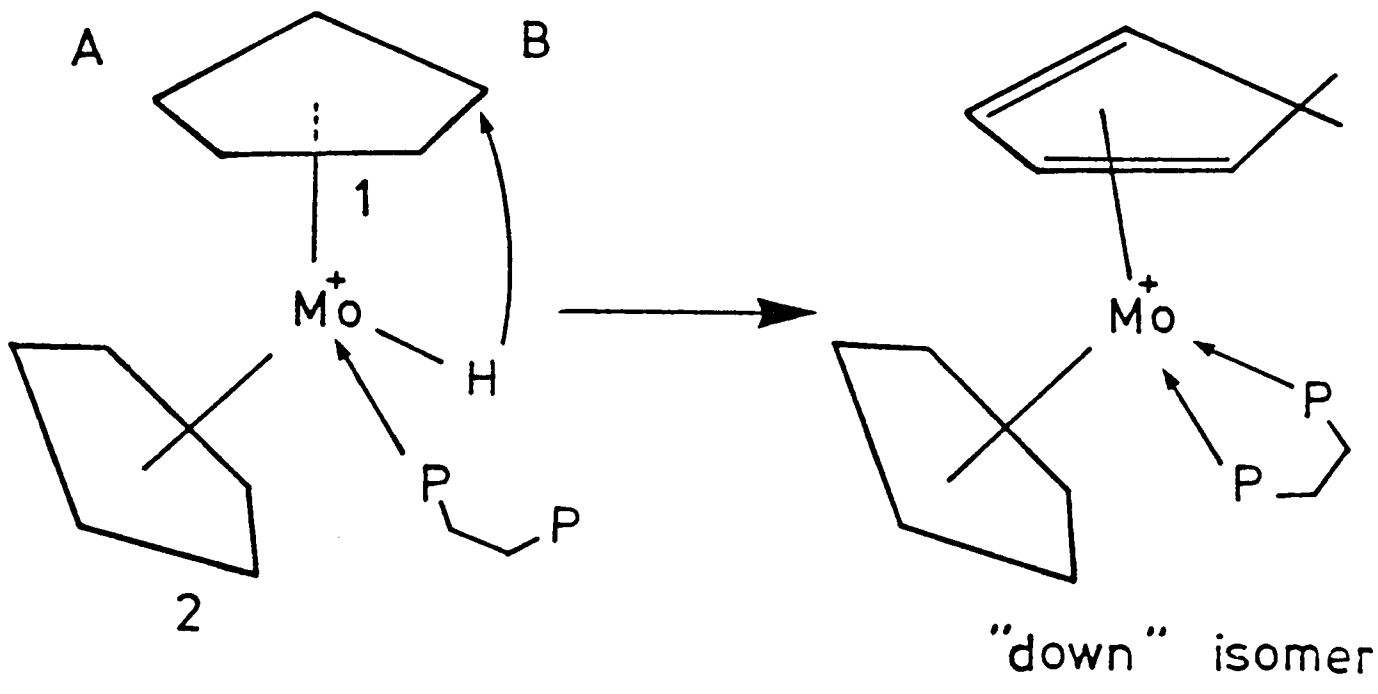


FIGURE II.5. Formation of the "down" isomer of $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_5H_6\}dppe)PF_6$

In summary we are postulating that the asymmetry of the other ligands with respect to the cyclopentadienyl ring 1, is inducing an asymmetry of electron distribution about ring 1, and that hydride attack is occurring on the more positive side, and proton migration is occurring by an <u>endo</u>-process on the more negative side of ring 1.

CHAPTER III

STUDY OF THE CHEMISTRY OF TRI(CHLORO)(η-CYCLOPENTADIENYL) (1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)MOLYBDENUM.

It was thought interesting to study the title compound as a possible starting material for the synthesis of a variety of derivatives of the Mo{η-C_5H_5}dppe system. A number of reactions have been investigated and are described below, in particular the reaction with olefins. It was hoped that it would be possible to obtain olefin complexes which by virtue of the relative electron richness of the system Mo{η-C_5H_5}dppe might give rise to catalytic reactions.

PREPARATION OF Mo{η-C_5H_5}{dppe}H_3

1: Reaction of Mo{η-C_5H_5}{dppe}Cl_3 with $NaAlH_2(OCH_2CH_2OCH_3)_2$:

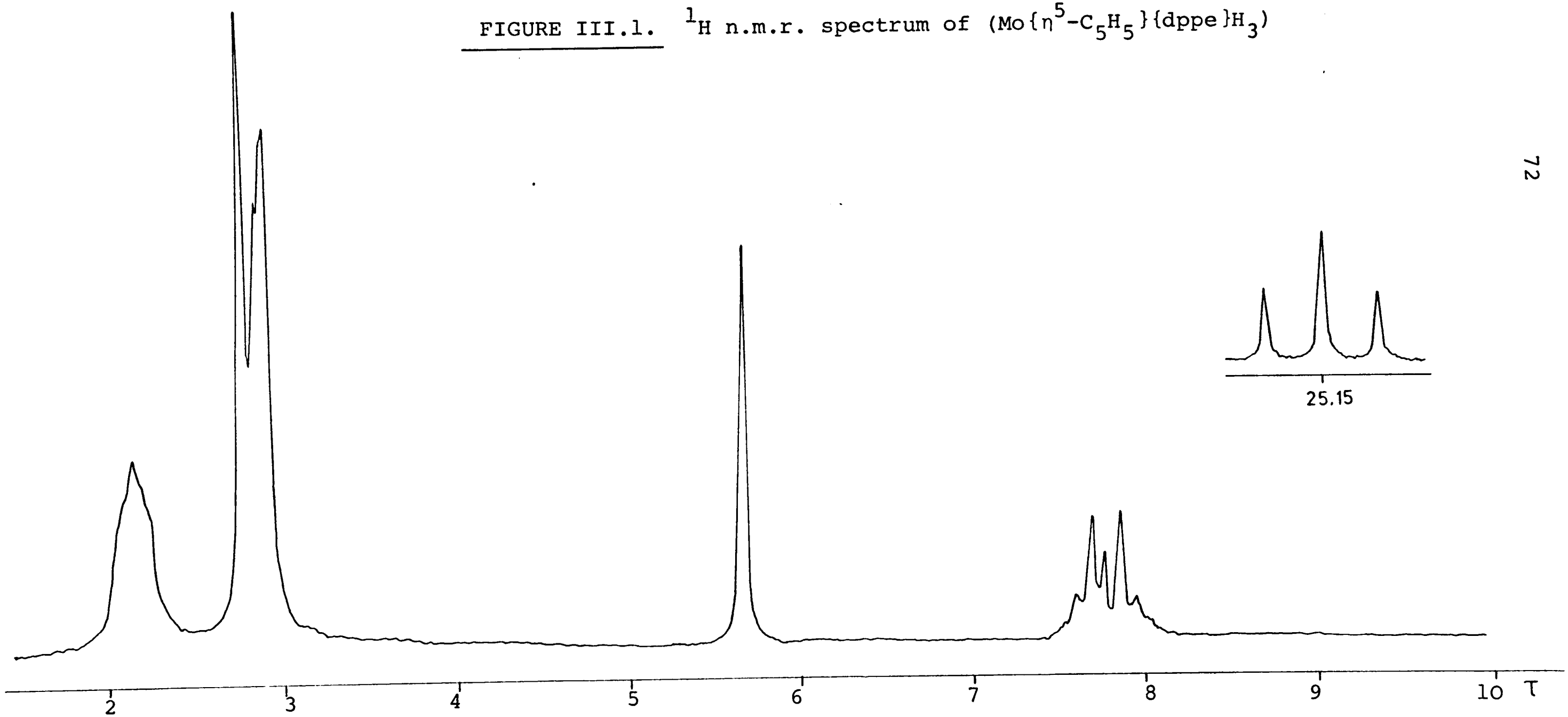
Treatment of Mo{η-C_5H_5}{dppe}Cl_3 with $NaAlH_2(OCH_2CH_2OCH_3)_2$ under the conditions described in detail in the Experimental Section gave a yellow crystalline compound which was sensitive to air. It could be recrystallised from mixtures of toluene and petroleum ether.

The analytical data are consistent with the stoichiometry $C_{31}H_{32}MoP_2$.

The ^1H n.m.r. spectrum is shown in Figure III.1 and the data are given in Table III.1. The spectrum shows there to be a complex series of bands in the region 2.6τ to 3.05τ of relative intensity approximately 20, which can be assigned to the four phenyl rings of the diphenylphosphinoethane ligand.

There is a sharp band at 5.65τ of relative intensity

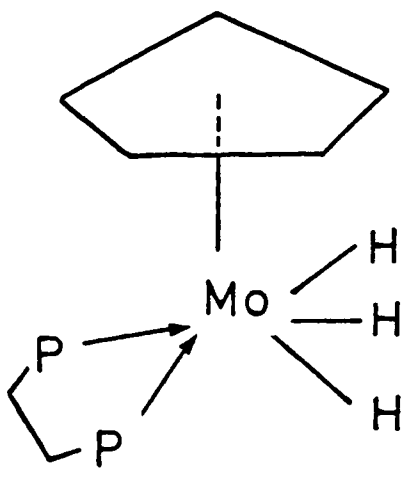
FIGURE III.1. ^{1}H n.m.r. spectrum of ($Mo\{\eta^{5}-C_{5}H_{5}\}\{dppe\}H_{3}$)



approximately 5 which can be assigned to the cyclopentadienyl ring. No coupling with ^{31}P nuclei was observed on expanded scale. There is a symmetric band centred at 7.75τ of relative intensity 4 which may be assigned to the hydrogens of the group $P\text{-}CH_2\text{-}CH_2\text{-}P$. Finally, a 1:2:1 triplet at 25.15τ, of relative intensity 3 may be assigned to hydrogens directly attached to molybdenum. This band shows $H\text{-}^{31}P$ coupling with $J = 37.8Hz$.

The infrared spectrum shown in Figure III.2 (the data are given in the Experimental Section) has broad and moderately strong bands at 1797 and 1780cm^{-1} assignable to Mo-H stretching frequencies and other bands consistent with the presence of cyclopentadienyl and diphenylphosphinoethane ligands.

On the basis of this, we postulate that the molecule has the structure shown below:



We assume that the equivalence on the n.m.r. time scale of the 3 hydrogens attached to molybdenum is due to fluxional behaviour. It is well-known that MH_x system may readily

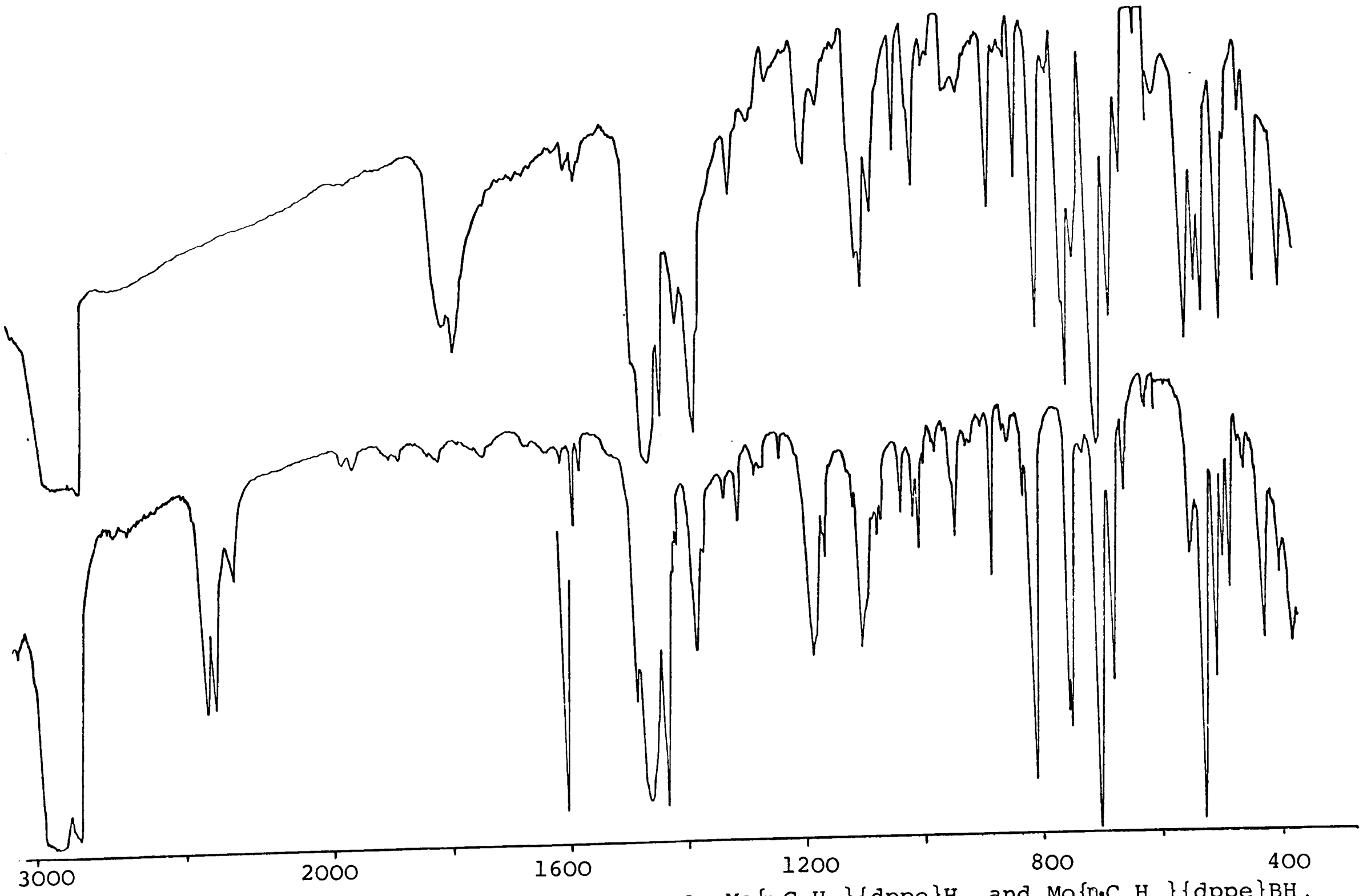


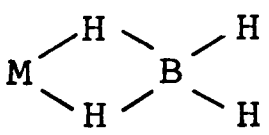
FIGURE III.2. Infrared spectra of the compounds $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ and $Mo\{\eta\text{-}C_5H_5\}\{dppe\}BH_4$

undergo fluxional interchange, for example $ReH_5(PMe_2Ph)_3$ [90], and $OsH_4(PMe_2Ph)_3$ [91 - 93] give only a 1:3:3:1 quartet for the metal hydrogen resonances.

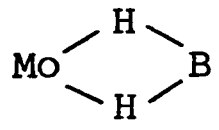
2: Reaction of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ with $NaBH_4$

Attempts to prepare $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ by treatment of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ with $NaBH_4$ in dry THF led to a green solution. The solvent was removed under reduced pressure and the resulting green oily material was extracted with petroleum ether. After partial removal of the solvent, an air sensitive, green powder was isolated. Despite several attempts, this could not be recrystallised.

The infrared spectrum is shown in Figure III.2 and above it is given the infrared spectrum of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$. The spectra are clearly different. The green compound shows strong bands at $2418cm^{-1}$, $2390cm^{-1}$ and $2318cm^{-1}$ which are characteristic of B-H terminal asymmetric stretching vibrations.

Normally the system  shows four major vibrational modes. For example, in diborane, they occur at $\simeq 2500cm^{-1}$ (BH_2 stretching mode), at $1175cm^{-1}$ (BH_2 deformation mode), at $1860cm^{-1}$ (BH_2B out of plane bridge expansion) and at $1600cm^{-1}$ (BH_2B asymmetric in plane bridge stretching). In general, bands in the region of $\simeq 2000cm^{-1}$ remain the most sensitive test for the presence of a hydrogen bridge between the metal and boron atoms. However, this band varies in

intensity, depending on the compound. Thus for $Ti\{\eta\text{-}C_5H_5\}_2BH_4$ there is a band at $1942cm^{-1}$ of strong intensity[94]. However, for the borohydride compounds $MH(BH_4)(PR_3)_2$ (where M = Pd or Ni and PR_3 = Pcy_3 or PPr^i_3) there are only bands of weak intensity in the same region[95].

In the spectrum of the green compound we observe bands of weak intensity in the region $1973cm^{-1}$ and $1953cm^{-1}$ which may be tentatively assigned to  vibrations. However, it is difficult to make conclusive assignment as there are other bands in this region arising fron phenyl groups. Similarly, the band at $1182cm^{-1}$ could arise from BH_2 deformation modes.

The i.r. spectrum is also consistent with the presence of η-cyclopentadienyl and dppe systems.

The ^1H n.m.r. spectrum of the green powder is shown in Figure III.3 and the data are given in Table III.1. The spectrum shows the presence of traces of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$. For example, there is a small peak at 5.65τ and a 1:2:1 triplet at 25.15τ, which may be assigned respectively to the η-cyclopentadienyl ring and the MoH_3 group of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$. The spectrum also shows a complex series of bands in the region 2.65τ to 3.00τ of relative intensity approximately 20, which may be assigned to the aromatic protons of the four phenyl rings of the dppe ligand. There is a very sharp singlet at 5.45τ of relative intensity 5 which can be assigned to the cyclopentadienyl system. No coupling with ^{31}P was observed. There is a complex series of bands in the region

FIGURE III.3

^{1}H n.m.r. spectrum of the compound

$Mo\{\eta\text{-}C_5H_5\}\{dppe\}BH_4$

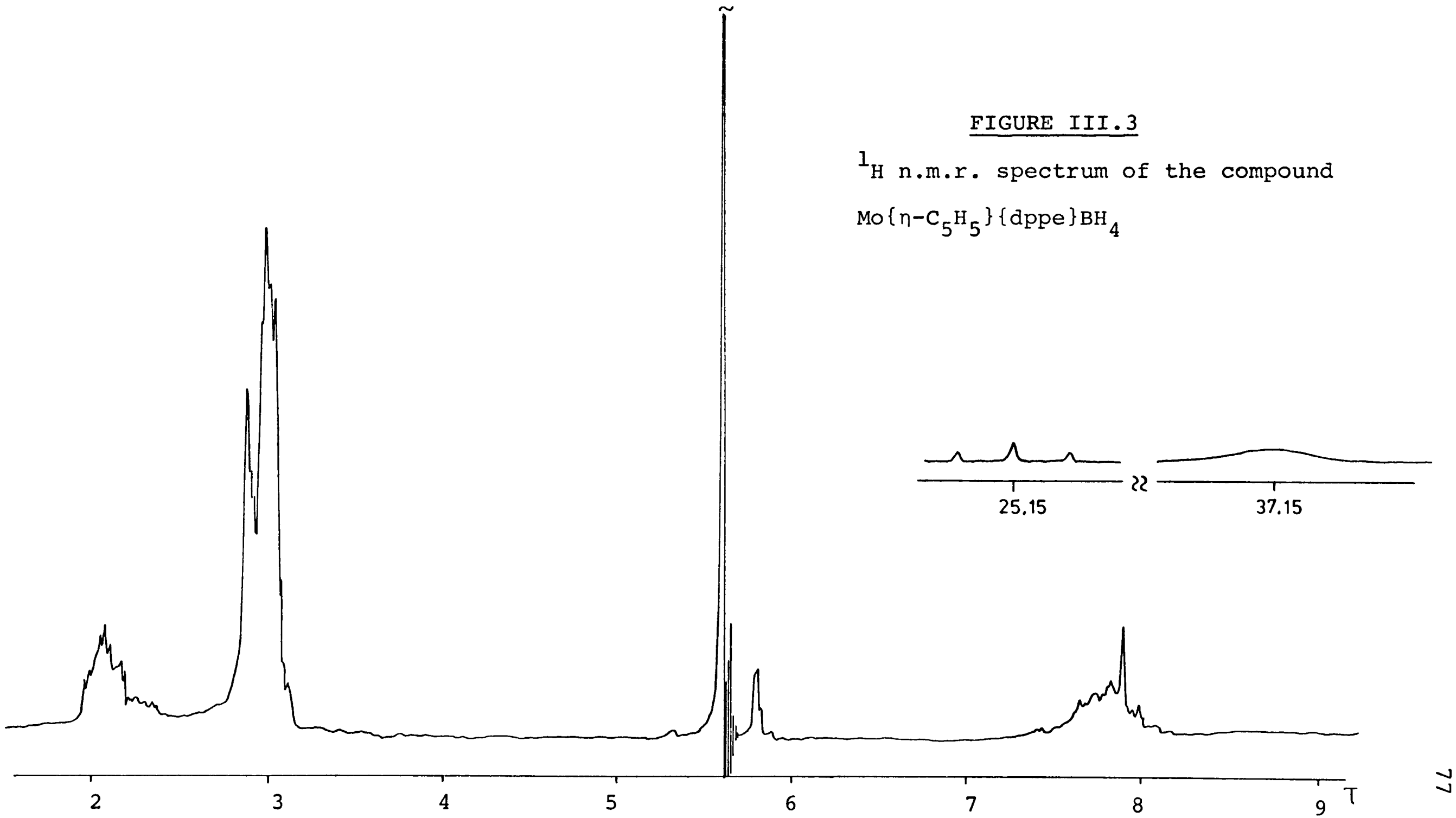
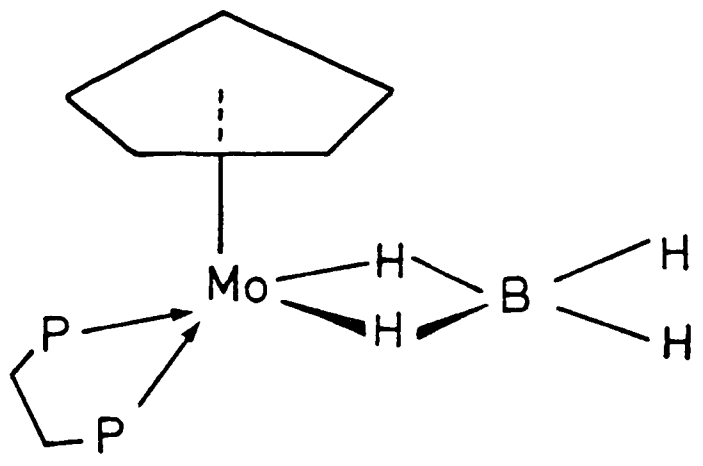


TABLE III.1. ^{1}H n.m.r. spectra of the compounds $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ and $Mo\{\eta\text{-}C_5H_5\}\{dppe\}BH_4$

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHz in C_6D_6	25.15	3	triplet (J = 37.8)	$Mo\text{-}H_3$
	7.75	4	complex	$P\text{-}CH_2\text{-}CH_2\text{-}P$
$Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$	5.65	5	singlet	C_5H_5
	3.05 - 2.6	20	complex	4 Ph
90 MHz in C_6D_6	37.15	≃4	very broad	BH_4
	7.95 - 7.35	4	complex	$P\text{-}CH_2\text{-}CH_2\text{-}P$
$Mo\{\eta\text{-}C_5H_5\}\{dppe\}BH_4$	5.45	5	singlet	C_5H_5
	3.0 - 2.65	≃20	complex	4 Ph

7.35τ to 7.95τ of relative intensity 4 which may be assigned to the 4 hydrogens of the P-CH_2-CH_2-P group of the dppe ligand. Finally, there is a very broad band centred at 37.15τ of relative intensity approximately 4 which can be assigned to a BH_4 system. In most hydroborate systems which have been examined (except in the case of B_2H_6) the protons undergo rapid exchange under the experimental conditions, effectively rendering the bridging and terminal protons equivalent.[96] They occur as a broad band due to coupling of the 4 protons with both ^{11}B and ^{10}B nuclei as well as probably to two ^{31}P nuclei in our case.

On the basis of the evidence presented, we tentatively conclude that the green compound, obtained in the reaction of Mo{η-C_5H_5}{dppe}Cl_3 has the structure shown below:



REACTION OF (Mo{η-C_5H_5}{dppe}H_3) WITH BUTADIENE

A solution of Mo{η-C_5H_5}{dppe}H_3 in toluene was treated with butadiene. The reaction mixture was warmed in a sealed

ampoule at 70°C for twelve hours. Orange crystals were formed. They were collected as described in detail in the Experimental Section, and recrystallised from petroleum ether to give orange crystals.

Analysis of carbon and hydrogen was consistent with the stoichiometry $C_{35}H_{36}MoP_2$.

The infrared spectrum showed bands assignable to the η-cyclopentadienyl system and phenyl groups at 3060cm^{-1}, 3054cm^{-1}, 3042cm^{-1}, 1590cm^{-1} and 1575cm^{-1}.

The ^1H n.m.r. spectrum, shown in Figure III.4 and the data, given in Table III.2, may be interpreted in terms of the presence of two isomers of the compound Mo{η-C_5H_5}{1-CH_3-η^3-C_3H_4}dppe, in the ratio of approximately 10:1. In a separate study, Segal[20, 21] showed that reduction of (Mo{η-C_5H_5}{η^4-C_4H_6}dppe)PF_6 gave two isomers, which he was able to separate by careful fractional crystallisation and obtain the ^1H n.m.r. spectrum of each isomer. Comparison of his data with the spectrum which we discuss here, confirm that the product that we obtain by the reaction of Mo({η-C_5H_5}{dppe}H_3 with butadiene is a mixture of the same two isomers as shown below:

FIGURE III.4

^1H n.m.r. spectrum of the compound $Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}dppe$.

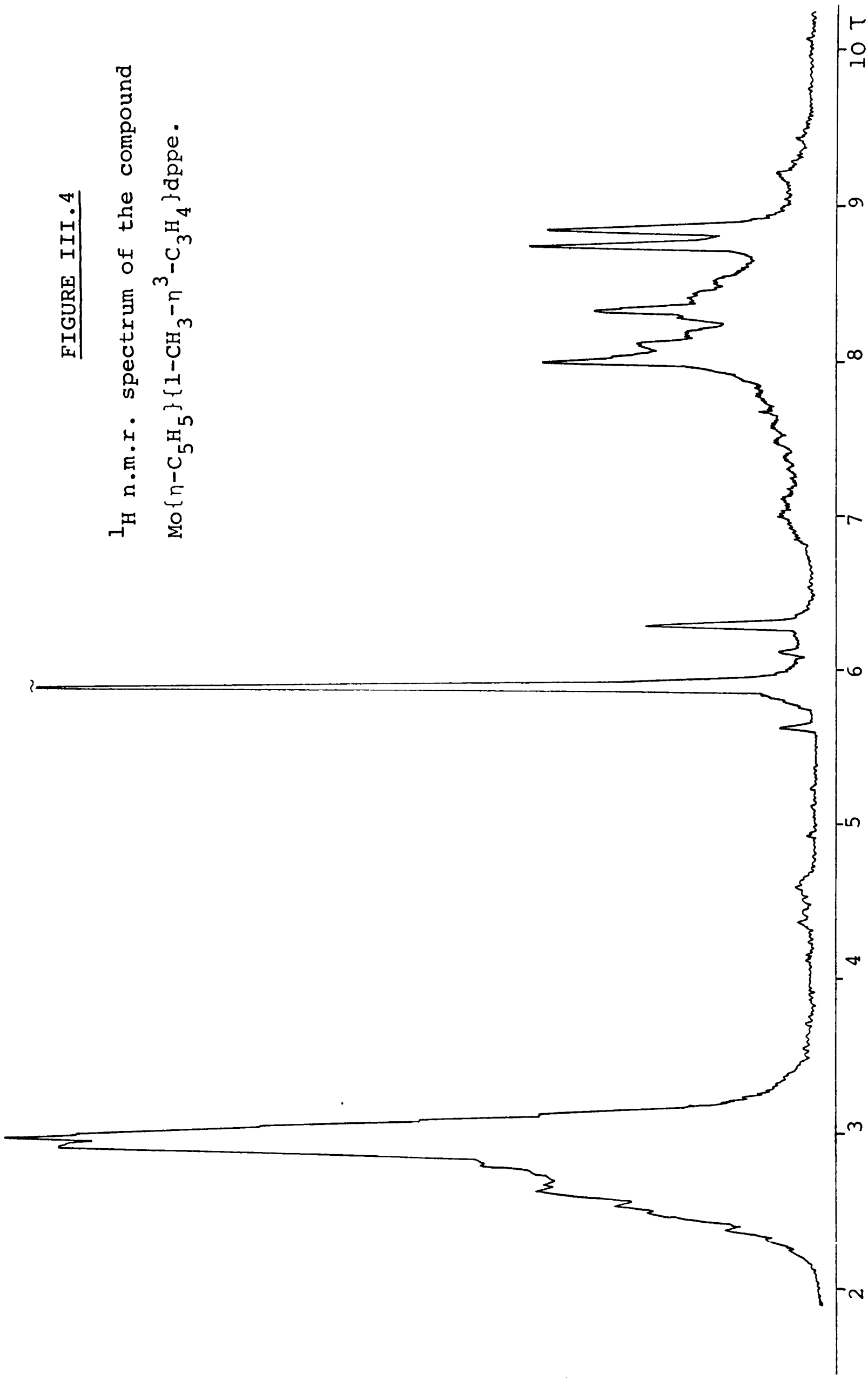


TABLE III.2. ^{1}H n.m.r. spectrum of the compound Mo{η-C_5H_5}{1-CH_3-η^3-C_3H_4}dppe.

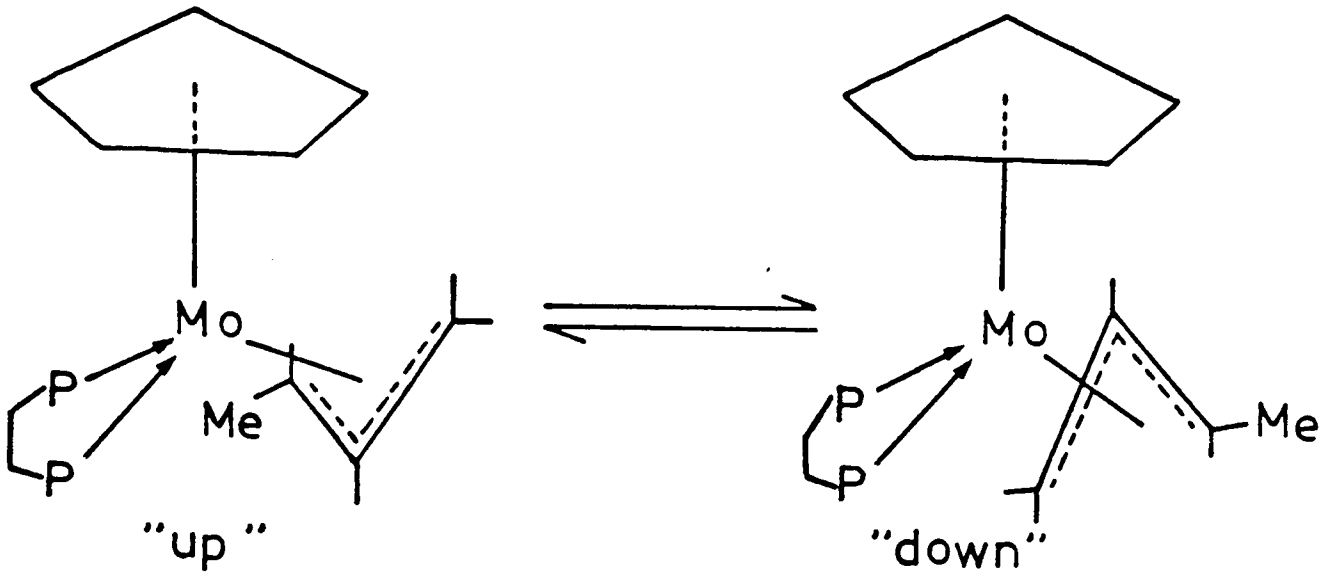
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
60 MHz in C_6D_6	2.74	20	complex	4 Ph
	5.64	6	triplet (J = 0.7)	C_5H_5 + 1H (C_4H_7)
	6.79	1	complex	1H (C_4H_7)
Mo{η-C_5H_5}{1-CH_3-η-C_3H_4}dppe	7.34	1	complex	1H (C_4H_7)
	8.00	5	complex	P-CH_2-CH_2-P + 1H (C_4H_7
	8.50	3	doublet (J = 6.4)	CH_3

TABLE III.3. Mass spectrum of the compound $Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}\{dppe\}$.

m/e	Rel. Int.[a]	Assignment[b]
616	61	$(Mo\{\eta\text{-}C_5H_5\}\{CH_3\text{-}\eta^3\text{-}C_3H_4\}dppe)^+$
561	42	$(Mo\{\eta\text{-}C_5H_5\}dppe)^+$
398	50	$(dppe)^+$

a Relative intensity based on the largest m/e value (for metal containing species = 100).

b Tentative assignment for most chemically probable fragment to fit m/e value.

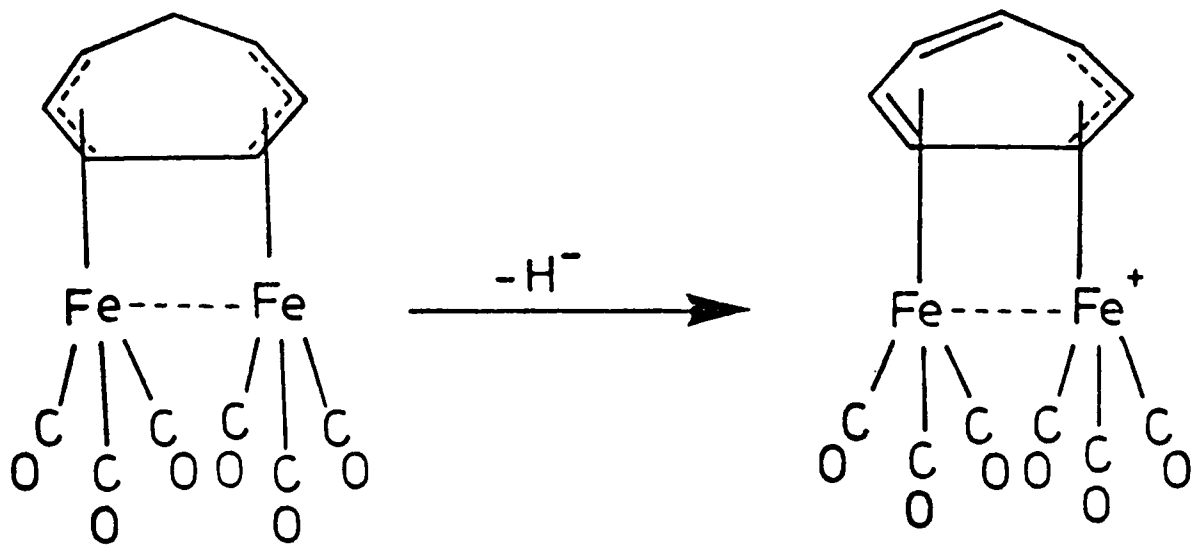


Since Segal[20, 21] had separated in an almost pure state the two isomers, he was able to analyse the ^1H n.m.r. spectra in detail and determine probable coupling constants. However, although he was able to conclude tentatively that the isomers were of the syn-type of configuration, he was unable to distinguish on the basis of the evidence which was the "up" or the "down" isomer.

The mass spectrum of compound $Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}$-dppe showed a parent ion peak at m/e 616, corresponding to $(Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}dppe)^+$ and one peak at m/e 560 which corresponds to $(Mo\{\eta\text{-}C_5H_5\}dppe)^+$, formed by loss of the crotyl group. The data are shown in Table III.3.

REACTION OF $Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}$dppe WITH Ph_3CPF_6

Extraction of a hydride ion from the methyl group of η-crotyl complexes giving η^4-butadiene metal cation derivatives has been well established. For example, in the binuclear complex:



the cycloheptatriene complex undergoes hydride abstraction, and the C_7H_7 ligand formed is presumably acting as both a 3- and 4- electron ligand[97]. Therefore we thought that it would be of interest to prepare a simple butadiene derivative of our ($Mo\{\eta\text{-}C_5H_5\}$dppe) system by this route. Accordingly, a solution of ($Mo\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}$dppe) in dry dichloromethane was treated with CPh_3PF_6 in dry dichloromethane at 0^oC. The reaction mixture was heated at 50^oC for 1 hour, after which time, dry diethyl ether was added. A yellow precipitate was formed. It was separated by filtration and washed with ethanol until the ethanol washings were colourless. The resulting orange solid was recrystallised from a mixture of acetone and ethanol, to give orange crystals.

The elemental analysis was consistent with the stoichiometry $C_{35}H_{35}F_6MoP_3$.

The infrared spectrum showed bands consistent with the presence of cyclopentadienyl, phenyl and PF_6 systems.

The ^{1}H n.m.r. spectrum (part of which is shown in Figure III.5, and the data are given in Table III.4) was initially interpreted in terms of the presence of two isomers of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)^+$ in a 1:1 ratio. This was confirmed by independent studies carried out by Segal[20, 21] who obtained the ^{1}H n.m.r. spectrum of the same compound in a variety of different solvents, and was able to show that the equilibrium concentration of the two isomers was a function of the different solvents. Therefore it is to be presumed that the two isomers may be readily interconverted in the equilibrium mixture.

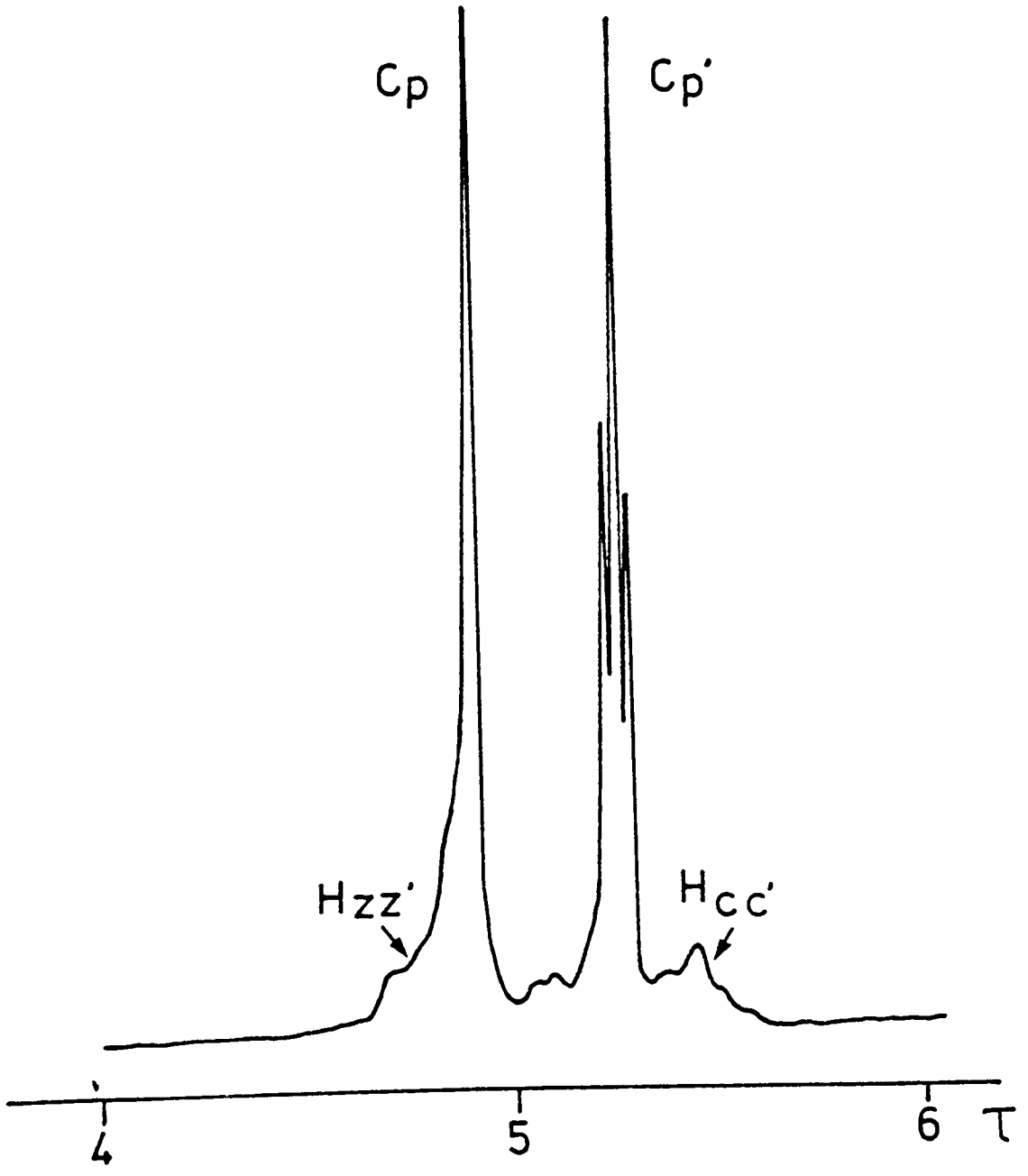
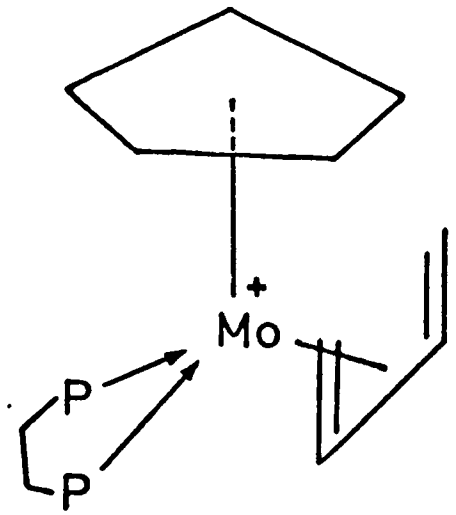
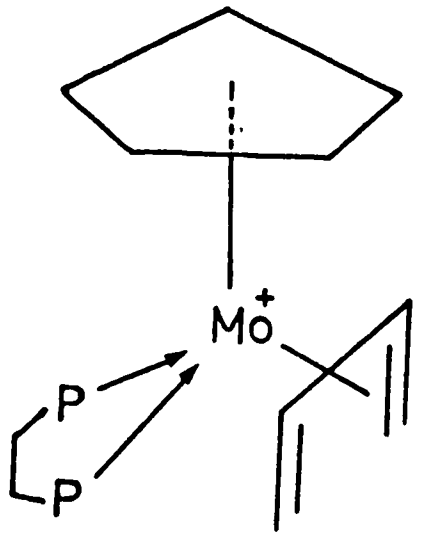
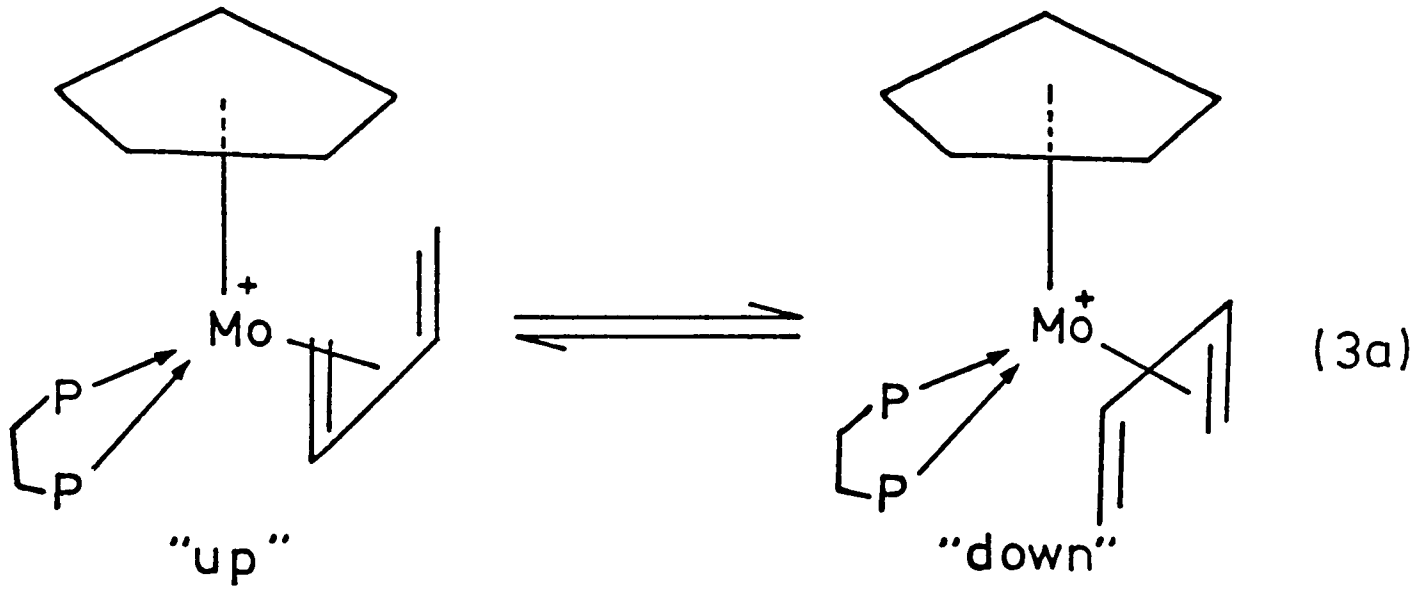


FIGURE III.5. Part of the ^{1}H n.m.r. spectrum of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)PF_6$

TABLE III.4. ^{1}H n.m.r. spectrum of the compound $(Mo\{\eta\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}\{dppe\})PF_6$

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHz in CD_3SO 	8.34	2	complex	2H (C_4H_6)
	8.11	2	complex	2H (C_4H_6)
	6.76	4	complex	$P\text{-}CH_2\text{-}CH_2\text{-}P$
	5.37	2	complex	2H (C_4H_6)
	4.83	5	triplet ($J_{^{31}P\text{-}Cp}$ = 0.8 Hz)	C_5H_5
	2.42	20	complex	4 Ph
90 MHz in CD_3SO 	11.38	2	complex	2H (C_4H_6)
	9.17	2	complex	2H (C_4H_6)
	6.76	4	complex	$P\text{-}CH_2\text{-}CH_2\text{-}P$
	5.22	5	triplet ($J_{^{31}P\text{-}Cp}$ = 2.6Hz)	C_5H_5
	4.78	2	complex	2H (C_4H_6)
	2.42	20	complex	4 Ph

We conclude that the evidence for the formation of ($Mo\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_4H_6\}\{dppe\}$)$^+PF_6^-$ as a mixture of "up" and "down" isomers as shown below (3a) is based in both stoichiometry and comparison of the infrared and ^1H n.m.r. spectra with the very detailed spectral studies carried out by Segal[20, 21] as described above.



(3a)

OTHER PRELIMINARY STUDIES ON THE REACTIONS OF $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$

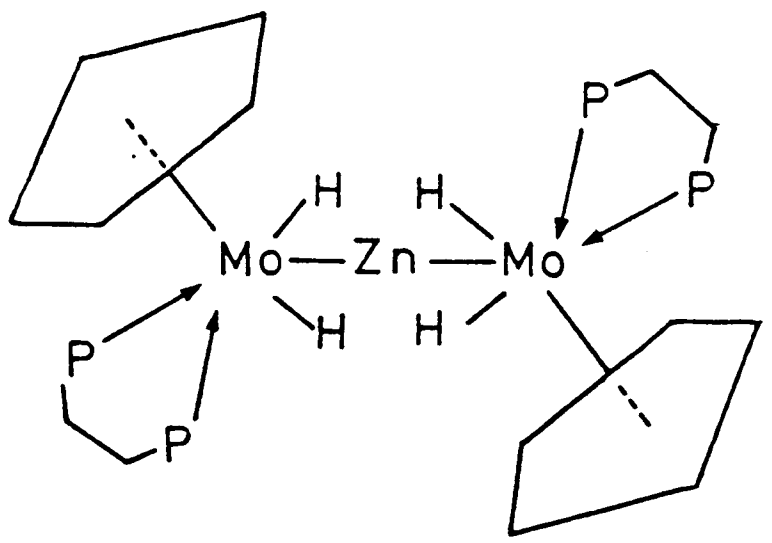
A number of other reactions of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ have been investigated. These experiments are briefly summarised below.

1. Attempts were made to displace a H_2 molecule from $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ with $PPhMe_2$. However, no tractable products could be obtained.

2. $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ was reacted with $CH_3C{\equiv}CCH_3$ and separately with $CH_2{=}CHCN$. Again however no tractable products could be isolated from these reactions.

3. It is well established that $Mo\{\eta\text{-}C_5H_5\}_2H_2$ reacts with organolithium reagents and diethylzinc, giving rise to formation of Mo-Li or Mo-Zn derivatives.[61]

In view of the observed products of the reaction between $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ and $HSn\{n\text{-butyl}\}_3$, which is described later, it was thought, for example, that diethylzinc might react to give a compound such as (3b)



(3b)

However, reaction with diethylzinc gave no tractable products.

Treatment of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ with butyl-Li gave clearly some reaction, but it was not found possible to obtain evidence for the nature of the species, either by reaction with CO_2, which might have been expected to give $Mo\{\eta\text{-}C_5H_5\}\{dppe\}(CO)_2$ or with benzylbromide which might have been expected to give some $Mo\{\eta\text{-}C_5H_5\}\{dppe\}$benzyl derivatives.

4. Transition metal compounds are well known to react with halogenated hydrocarbons, giving rise to exchange and the formation of metal halides. With this reaction in mind, $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ was reacted with MeI. A reaction was clearly

observed which at first sight was promising but after a number of attempts it was not found possible to obtain any tractable products.

Reaction of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ in toluene with $CHBr_3$ as described in the Experimental Section gave a red compound, which could be crystallised from either hot toluene or from a mixture of dichloromethane and methanol. The compound showed a tendency to crystallise together with molecules of solvent. For instance, when it was recrystallised from hot toluene, the ^1H n.m.r. spectrum showed the presence of one molecule of toluene, and the analytical data are very close to those corresponding to the formulation $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_3$. toluene. When the compound was crystallised from a mixture of dichloromethane and methanol, the ^1H n.m.r. spectrum showed a sharp peak in the region corresponding to methyls of MeO groups. The percentage of bromine in this case agreed with the formulation $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_2OCH_3$. It seems therefore that one atom of bromine has been substituted by a MeO group.

The infrared spectrum is consistent with the presence of cyclopentadienyl and dppe ligands.

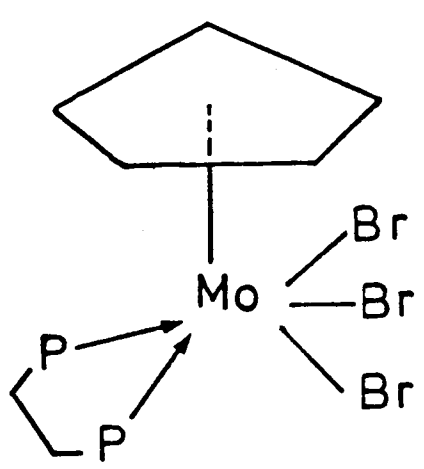
The ^1H n.m.r. spectra of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_3$ (see Table III.5) were recorded in perdeuterochloroform. Apart from the solvent peaks, already mentioned, there was in each case a complex series of bands in the region 1.73τ to 3.08τ, of relative intensity approximately 20, which may be assigned to the phenyl groups of the dppe ligand; a broad band at 5.6τ resolved into a triplet, of relative intensity 5, which

TABLE III.5. ^{1}H n.m.r. spectra of the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_3$

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
60 MHz in $CDCl_3$	8.32 - 7.62	≃4	complex	$P\text{-}CH_2CH_2\text{-}P$
	7.7	3	singlet	CH_3 (toluene)
$Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_3$. toluene	5.52	5	broad triplet ($J_{^{31}P\text{-}Cp} \simeq 1.5$)	C_5H_5
	2.89	5	singlet	Ph (toluene)
	3.22 - 1.77	≃20	complex	4 Ph
60 MHz in $CDCl_3$	8.38 - 7.58	≃4	complex	$P\text{-}CH_2\text{-}CH_2\text{-}P$
	6.65	3	singlet	OCH_3
$Mo\{\eta\text{-}C_5H_5\}\{dppe\}Br_2OCH_3$	5.6	5	broad triplet ($J_{^{31}P\text{-}Cp} \simeq 1.5$)	C_5H_5
	3.08 - 1.73	20	complex	Ph

corresponds to the cyclopentadienyl ring coupled to the 2 ^{31}P atoms of the dppe ligand (J = 1.8 Hz), and finally a series of broad and complex bands in the region 7.58τ to 8.38τ of relative intensity approximately 4, which may be assigned to the $P-CH_2-CH_2-P$ group of the dppe ligand.

On the basis of this evidence, we tentatively conclude that substitution of the 3 hydrogens of $Mo\{\eta-C_5H_5\}\{dppe\}H_3$ by 3 bromine atoms has taken place to give the compound (3c):



(3c)

STUDY OF THE REACTION BETWEEN $Mo\{\eta-C_5H_5\}\{dppe\}Cl_3$ AND $HSn\{n\text{-butyl}\}_3$

As described earlier, attempts to prepare $Mo\{\eta-C_5H_5\}\{dppe\}H_3$ by treatment of $Mo\{\eta-C_5H_5\}\{dppe\}Cl_3$ with $NaBH_4$ gave rise to a borohydride complex in poor yield. The reaction of $HSn\{n\text{-butyl}\}_3$ with $Mo\{\eta-C_5H_5\}\{dppe\}Cl_3$ was also explored as a possible route to $Mo\{\eta-C_5H_5\}\{dppe\}H_3$.

The compound $Mo\{\eta-C_5H_5\}\{dppe\}Cl_3$ was treated with excess

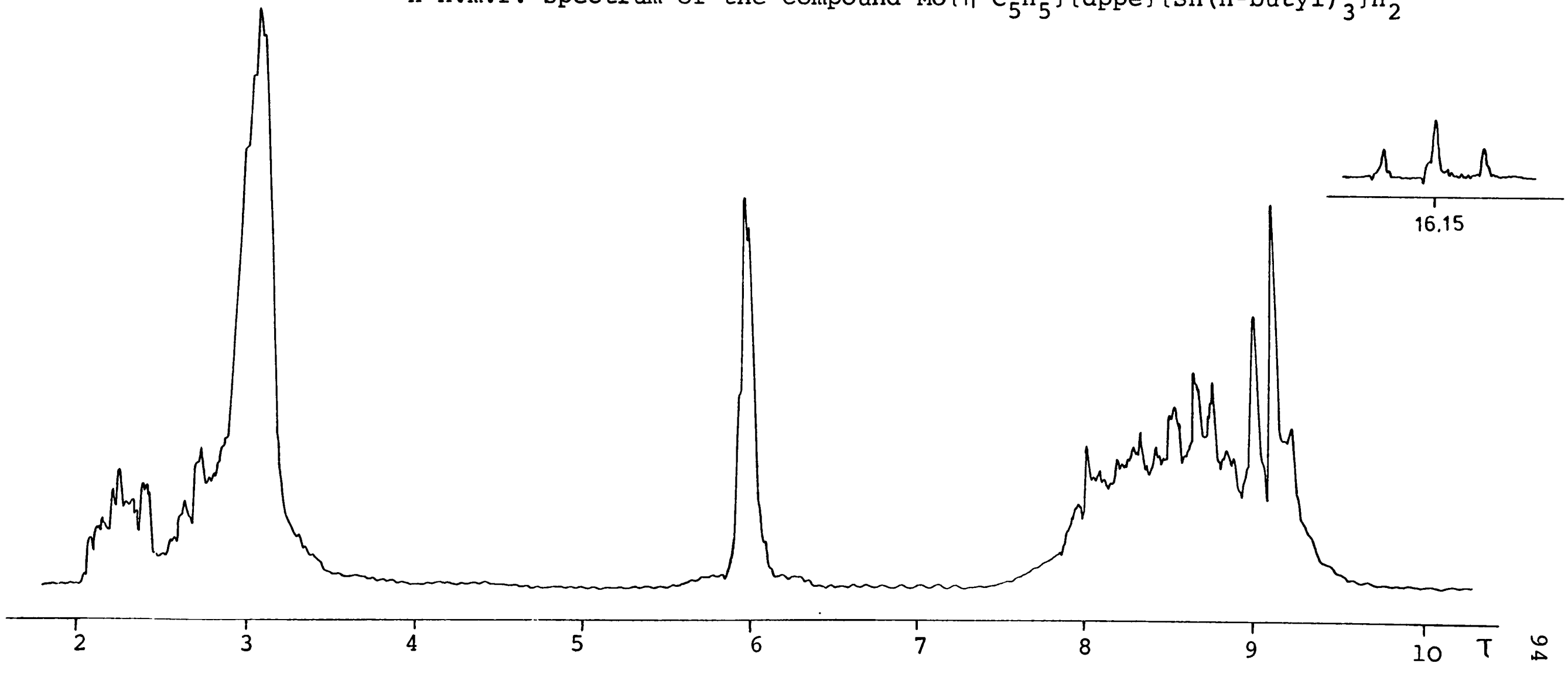
of $HSn(n\text{-butyl})_3$. The reaction mixture was heated at 110°C for 30 minutes, and the solution became a rich yellow colour. The solvent was removed under reduced pressure and the resulting yellow oil extracted with dry toluene. The extract was chromatographed on alumina column. A yellow band was formed which was eluted with a 1:1 mixture of dry toluene and diethylether. The diethylether and part of the toluene were removed under reduced pressure, and addition of petroleum ether followed by cooling at *ca.* -40°C gave a yellow crystalline product.

The infrared spectrum shows a broad band at 1815cm^{-1} characteristic of a terminal Mo-H stretching mode. The spectrum also shows bands characteristic of η-cyclopentadienyl and dppe systems.

The ^1H n.m.r. spectrum (shown in Figure III.6 - the data are given in Table III.6) recorded in perdeuterobenzene, may be interpreted in terms of the presence of 1,2-(diphenylphosphino)ethane ligand and cyclopentadienyl ligand. The cyclopentadienyl peak at 5.95τ shows a triplet structure, $J \simeq 1.5Hz$. There is a complex series of bands in the region 2.2τ to 3.3τ of relative intensity approximately 20, which can be assigned to the phenyl groups of the dppe ligand. There is a very complex set of peaks in the region 7.87τ to 9.37τ of relative intensity approximately 30 which is consistent with the presence of three n-butyl groups together with the 2 CH_2 groups of the diphenylphosphinoethane ligand. Finally there is a 1:2:1 triplet of relative intensity 2

FIGURE III.6

^{1}H n.m.r. spectrum of the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}\{Sn(n\text{-butyl})_3\}H_2$

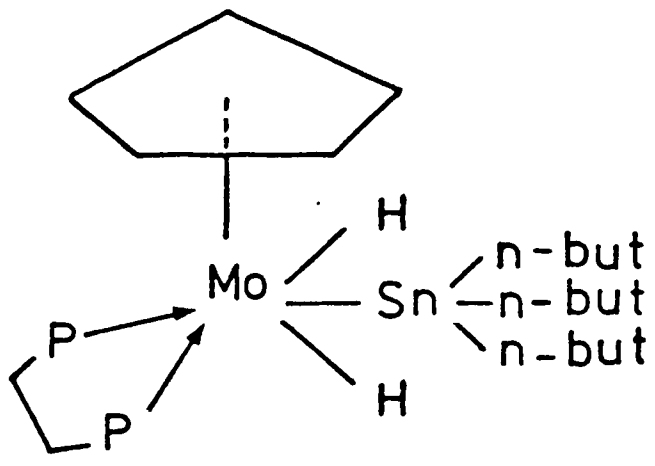


centred at 16.15τ which can be assigned to 2 hydrogens attached to molybdenum, coupled with the two ^{31}P nuclei of the diphenylphosphinoethane ligand (J = 36Hz).

The mass spectrum does not show lines corresponding to the parent ion $(Mo\{\eta\text{-}C_5H_5\}\{dppe\}\{Sn\ \{n\text{-}butyl\}_3\}H_2)^{+\cdot}$ A complex series of lines were present in the region corresponding to the fragment $(Mo\{\eta\text{-}C_5H_5\}\{dppe\}\{Sn\text{-}n\text{-}butyl\})^{+}$ although precise assignment of the fragment has not been made.

On the basis of this evidence, it seems probable that the yellow crystalline compound may be formulated as below:

(3d)



(3d)

Since this reaction was not providing a convenient route to $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$, further study was discontinued.

TABLE III.6. ^{1}H n.m.r. spectrum of the compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}\{Sn\{\eta\text{-butyl}\}_3\}H_2$

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
60 MHz in C_6D_6	16.15	2	triplet ($J_{^{31}P\text{-}H}$ = 36)	MoH_2
	9.37 - 7.87	31	complex	3 butyl + $P\text{-}CH_2CH_2\text{-}P$
$Mo\{\eta\text{-}C_5H_5\}\{dppe\}$ $\{Sn\{\eta\text{-butyl}\}_3\}H_2$	5.95	5	triplet ($J_{^{31}P\text{-}Cp}$ = 1.5)	C_5H_5
	3.3 - 2.2	20	complex	4 Ph

FURTHER STUDIES ON Mo(η-C_5H_5)dppm SYSTEM DERIVATIVES.

Chapter II describes the preparation of (Mo{η-C_5H_5}$_2${dppm})(PF_6)$_2$. During the course of the work described in Chapter III we were interested in finding out whether the Mo{η-C_5H_5}dppm system would lead to more tractable derivatives than the Mo{η-C_5H_5}dppe analogue. Therefore a preliminary study was made with the view to preparing the compound Mo{η-C_5H_5}{η^3-C_5H_7}dppm and studying its reactions with hydrogen chloride to see whether the compound Mo{η-C_5H_5}{dppm}Cl_3 could be isolated.

1. Reaction of (Mo{η-C_5H_5}$_2${dppm})(PF_6)$_2$ with $NaBH_4$.

The compound (Mo{η-C_5H_5}$_2${dppm})(PF_6)$_2$ was suspended in dry tetrahydrofuran and treated with an excess of sodium borohydride. A rapid reaction gave an orange solution, from which an air-sensitive orange crystalline material was isolated. Close examination of the product under a microscope revealed the presence of small quantities of white crystals (presumably free dppm). Repeated recrystallisation did not lead to a separation of the orange and white crystals. Chromatography resulted in decomposition of the orange material.

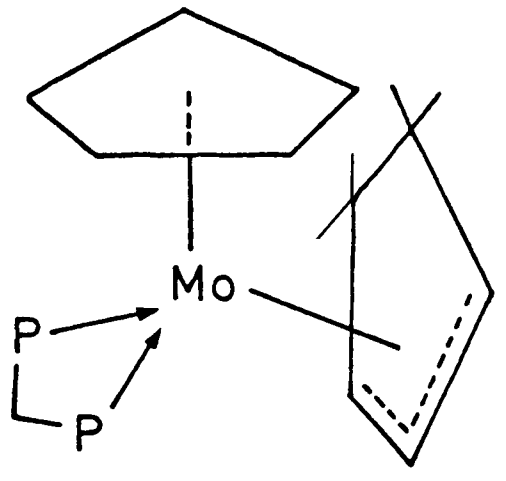
The elemental analysis gives values for percentage of carbon and hydrogen which are higher than the expected (Found: C, 69.9%, H, 5.9%. $C_{25}H_{34}MoP_2$ requires C, 68.6%; H, 5.5%) & this may be understood if there is a small percentage of free dppm present.

The infrared spectrum is consistent with the presence of η-cyclopentadienyl and dppm ligands.

The ^{1}H n.m.r. spectrum (the data are given in Table III.7) is consistent with the expected formulation Mo{η-C_5H_5}{η^3-C_5H_7}dppm. There is a set of complex bands centred at 2.74τ which can be assigned to the protons of the 4 phenyl rings of the dppm ligand. The relative intensity is rather higher than 20, which may be explained by the presence of free dppm. There is a triplet at 5.30τ, which can be assigned to the 5 protons of the cyclopentadienyl ring coupled to the two ^{31}P nuclei of the dppm ligand (J ≃ 1.05). There are a number of other broad and complex bands together with the signal corresponding to the deuterated toluene, in the region 7.14τ to 9.04τ, which are consistent with the presence of η^3-C_5H_7 and in this sense resemble quite closely the complex Mo{η-C_5H_5}{η^3-C_5H_7}dppe.

Attempts to obtain the mass spectrum of the compound were unsuccessful.

We conclude that reaction of (Mo{η-C_5H_5}$_2${dppm})(PF_6)$_2$ with $NaBH_4$ gives rise to hydride attack on the cyclopentadienyl ring in a manner similar to that described for the (Mo{η-C_5H_5}$_2$ {dppe})(PF_6)$_2$ analogue, to yield the neutral compound (3e).



(3e)

2. Reaction of Mo{η-C_5H_5}{η^3-C_5H_7}dppm with HCl.

A toluene solution of Mo{η-C_5H_5}{η^3-C_5H_7}dppm was treated with hydrogen chloride. A red oily precipitate was formed and the solution remained orange. The red precipitate was crystallised from a mixture of dichloromethane and methanol giving purple crystals. The filtrate was allowed to stand for twelve hours and a mixture of purple and yellow crystals was formed, the remaining solution being purple. The solution was filtered and concentrated and more purple crystals were formed. The yellow crystals were formed in a very low yield and no attempts were made to characterise them.

The analytical data of the purple crystals, recrystallised from a mixture of dichloromethane and methanol, were consistent with the stoichiometry $C_{30}H_{27}Cl_3Mo$. The slightly higher content in chlorine may be due to the presence of traces of included dichloromethane. (Found: C, 54.8%; H, 4.4%; Cl, 18.1%. $C_{30}H_{27}Cl_3Mo$ requires C, 55.3%; H, 4.1%; Cl, 16.2%.)

The infrared spectrum is consistent with the presence

of η-cyclopentadienyl and dppm ligands.

The ^{1}H n.m.r. spectrum (the data are given in Table III.7) of the compound crystallised from toluene shows the presence of one toluene molecule of crystallisation. There is a set of complex and broad bands in the region 2.23τ to 2.93τ of relative intensity approximately 25 which corresponds to the protons of the four phenyl rings, together with the protons of the phenyl ring of the toluene molecule. There is a singlet at 4.98τ of relative intensity 5 which can be assigned to the cyclopentadienyl ring, no coupling with ^{31}P being observed. There is a 1:2:1 broad triplet at 5.48τ, of relative intensity 2 corresponding to the methylene protons of the dppm, coupled to the two ^{31}P (J = 9Hz). Finally there is a sharp singlet at 7.7τ of relative intensity 3 corresponding to the protons of the toluene methyl group.

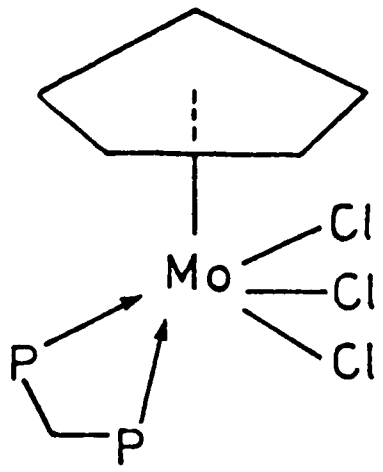
The ^{1}H n.m.r. spectrum of the compound recrystallised from a mixture of dichloromethane and methanol is similar, except for the fact that the bands due to the presence of toluene are not observed.

No mass spectrum of the compound could be obtained.

We conclude that reaction between $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}$ dppm and hydrogen chloride has taken place in a manner similar to that of the $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}$dppe analogue, to give the corresponding trichloride (3f):

TABLE III.7. ^{1}H n.m.r. spectra of the compounds $Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppm$ and $Mo\{\eta\text{-}C_5H_5\}\{dppm\}Cl_3$

Compound and solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
60 MHz in C_7D_8	7.14 - 9.04	≃9	complex	$P\text{-}CH_2\text{-}P$ + C_5H_7
$Mo\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_5H_7\}dppm$	5.30	5	triplet ($J_{^{31}P\text{-}Cp}$ = 1.05)	C_5H_5
	2.74	≃20	complex	4 Ph
60 MHz in $CDCl_3$	5.48	2	triplet ($J_{^{31}P\text{-}CH_2}$ = 9)	$P\text{-}CH_2\text{-}P$
$Mo\{\eta\text{-}C_5H_5\}\{dppm\}Cl_3$	4.98	5	singlet	C_5H_5
	2.93 - 2.23	≃20	complex	4 Ph



(3f)

On the basis of these rather preliminary studies, we concluded that the Mo{η-C_5H_5}dppm system has no clear advantage over the Mo{η-C_5H_5}dppe system and it was decided not to make further, more detailed, studies of the dppm system.

OTHER ATTEMPTS TO DEVELOP THE CHEMISTRY OF Mo{η-C_5H_5}{dppe}Cl_3

Apart from attempts to synthesise the Mo{η-C_5H_5}{dppe}H_3 compound and study its chemistry, as described above, a number of other reactions were attempted. For example:

1. Reduction with sodium amalgam in the presence of dppe was attempted, in the hope that a compound such as (Mo{η-C_5H_5}{dppe}$_2$)$^{2+}$ could be isolated. However, no tractable product was obtained.

2. Similarly, Mo{η-C_5H_5}{dppe}Cl_3 was treated with MeMgBr in order to see whether the corresponding Mo{η-C_5H_5}{dppe}{Me}$_3$ would be formed. However, again no tractable product was

obtained. Similarly, $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ was reacted with MeLi and again no evidence for metal-methyl links was obtained.

CHAPTER IV

SYNTHESIS AND CHARACTERISATION OF (η-ALLYL) (η-CYCLOPENTADIENYL)COBALT CATION COMPOUNDS.

We wished to synthesise a variety of compounds of the type $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$, where L could be CO, PR_3, ammine and related ligands. Our interest in these compounds, some of which have already been reported, was to investigate their reaction with nucleophiles. It was hoped that this might give evidence about the regiospecificity of nucleophilic addition to the η-allylic system, and also, possibly, that it might lead to the isolation of a new metallacyclobutane compound of cobalt.

The $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$ system was chosen for this role, for various reasons. The rules concerning the regiospecificity of nucleophilic attack, given in the Introductory Chapter, show that in order for nucleophilic addition to occur on a η-allylic ligand of an organometallic cation, it is necessary that other polyene ligands on the metal be <u>odd</u> electron ligands rather than <u>even</u>, and also that the ligand be a <u>closed</u> polyene system rather than an <u>open</u> polyene system.

A survey of the literature within this constraint led to the choice of the $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$ system, since there is, as reviewed in the Introductory Chapter, a considerable amount known about the chemistry of this system, so that it was reasonable to expect that the desired compounds would be isolable. Further, cobalt is relatively cheap compared with metals from which similar compounds could be envisaged, such as rhodium or iridium. Thus both the chemical and economic criteria were satisfied.

We have outlined the chemistry of cyclopentadienylcobalt system in the Introductory Chapter, and in our

pursuit of compounds $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$, we have made known compounds by the route previously described, and we have made new compounds as described below based on the previously known chemistry, although as we will see, it was not always a simple question of straightforward analogy.

When the work described in this chapter had been completed results concerning a series of cationic η-allyl rhodium complexes analogous to the cobalt complexes $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$ described in this chapter was published[98].

I. PREPARATION OF COMPOUNDS $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}CO)^+$.

The synthesis of both the known and new title compounds, was attempted following the previously described route, namely direct oxidative addition to $(Co\{\eta\text{-}C_5H_5\}\{CO\}_2)$ of an allylhalide, which proceeds together with a loss of carbon monoxide ligand, so that the general reaction may be written:

$$Co\{\eta\text{-}C_5H_5\}\{CO\}_2 + allylX \longrightarrow (Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}CO)^+X$$

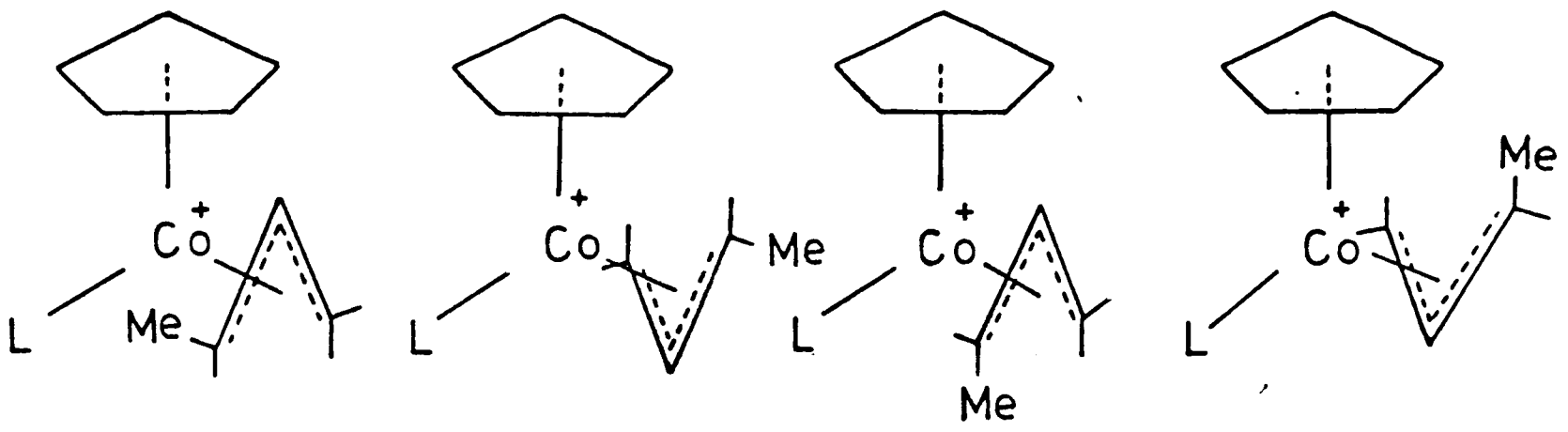
The known compound $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}CO)^+$ (70) was prepared that way and isolated as the hexafluorophosphate salt.

Attempts to prepare the 1- and 2-methylallyl derivatives by this route were made.

In the case of the reaction of 3-methylallylbromide with $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$, the reaction proceeded smoothly and the new compound $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)^+$ was isolated as a yellow crystalline hexafluorophosphate salt.

The elemental analysis is consistent with the formulation $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$.

The ^1H n.m.r. and ^{13}C n.m.r. spectra show that of the four possible isomers of compound $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}L)^+$ (L = CO) similar to that of $Mo\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}\{CO\}_2$ (12) either there is only one isomer present or the energy barrier



syn - "down" "up" anti - "down" "up"

FIGURE IV.1. Possible isomers of $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}Me\text{-}\eta\text{-}C_3H_4\}L)^+$ compound.

of interconversion between the "up" and the "down" isomers is low, and there is a rapid rotation of the η-crotyl ligand around the axis between the metal and the centre of gravity of the η-crotyl ligand, giving rise to an averaged spectrum.

Otherwise, the compound $Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$ is readily and unambiguously characterised by the spectroscopic data given in the Experimental Section, and in particular by the ^1H n.m.r. and ^{13}C n.m.r. spectra, the data of which are given in Tables IV.1 and IV.2 respectively.

The reaction between 2-methylallyliodide (which was prepared as described in the Experimental Section starting from the 2-methylallylchloride) and $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$, also proceeded readily giving in this case two compounds, a toluene soluble product and a water soluble product. The water soluble product was isolated as a yellow crystalline hexafluorophosphate salt in low yield *ca.* 15%, and again it was

unambiguously characterised by the data given in the Experimental Section and the ^{1}H n.m.r. and ^{13}C n.m.r. spectra, given with assignments in Tables IV.1 and IV.2 respectively, as the anticipated $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$.

The ^{1}H n.m.r. and ^{13}C n.m.r. spectra show again that of the two possible isomers of the compound $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}R\text{-}\eta\text{-}C_3H_4\}L)PF_6$ (where L = CO and R = Me), shown in Figure IV.2, only one of them is present, or both isomers are present and rapidly interconverting.

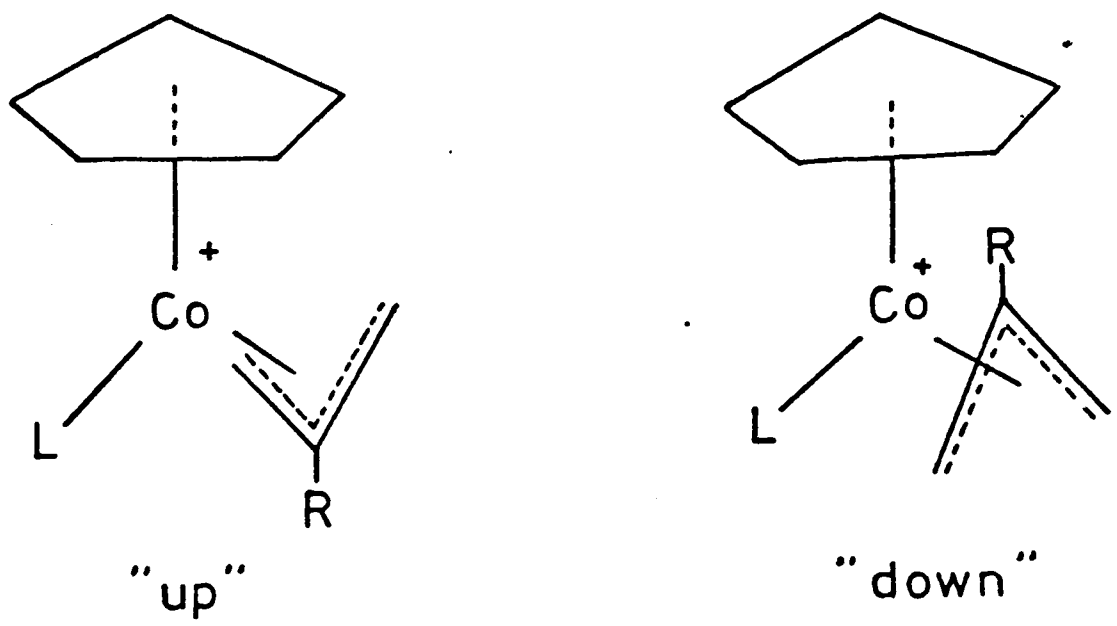
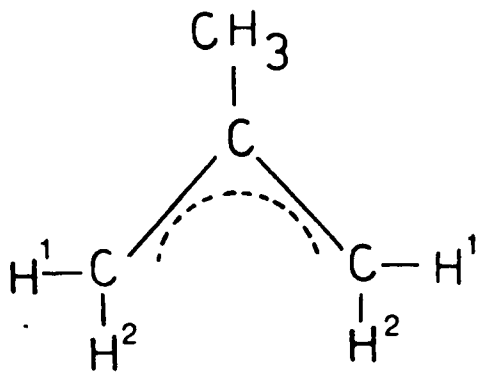


FIGURE IV.2. Possible isomers of $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}R\text{-}\eta\text{-}C_3H_4\}L)^{+}$ compound.

The equivalence of the H^1 and H^2 hydrogens in the 2-methylallyl ligand indicates that the allyl group is bonded symmetrically to the metal:



The toluene soluble product was a black crystalline compound. Yield *ca* 35%.

The analytical data given in the Experimental Section are consistent with the stoichiometry $C_9H_{12}CoI$.

The ^1H n.m.r., the data are given in Table IV.1, and the mass spectrum, which data are given in Table IV.3, show it to be the neutral compound ($Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$). Again either only one isomer, or a mixture of rapidly interconverting "up" and "down" isomers occur. The H^1 and H^2 hydrogens in the 2-methylallyl ligand are again equivalent.

The formation of this compound may be assumed to proceed by displacement of carbon monoxide ligand in ($Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)I$ by iodide attack, although we have no direct evidence to support this observation.

Since the yield of the desired cation, $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)^+$ from this reaction was found to be only 15%, we tried to obtain a greater quantity of this compound by treatment of the neutral compound ($Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$) with carbon monoxide. Reaction takes place giving rise to the desired compound $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)^+$.

Before carrying out this reaction, we had explored the reaction between $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$ with 2-methylallylchloride, since unlike the 2-methylallyliodide and bromide, this was commercially available. The reaction took place as described in the Experimental Section. However, we were unable to isolate any of the desired 2-methylallyl compound - in fact, the only cyclopentadienylcobalt compound that we were able to isolate from the reaction mixture was $Co\{\eta\text{-}C_5H_5\}_2^+$ as the hexafluorophosphate salt in *ca* 23% yield. Clearly, some disproportionation had occurred, but we did not investigate this reaction further and therefore we are unable to offer any mechanism for such a reaction.

II. SYNTHESIS OF THE COMPOUNDS $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}PR_3)^+$.

The compounds of this class were unknown at the outset of this work.

We decided to investigate a number of routes towards these compounds.

In the first case, we thought it might be possible to displace carbon monoxide from compounds of the type $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}CO)^+$ and substitute the CO with the desired PR_3 ligands. With this reaction in mind, $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}CO)PF_6$ was treated with triphenylphosphine. However, the products isolated were the known $Co\{\eta\text{-}C_5H_5\}\{CO\}\{PPh_3\}$which was identified by the data given in the Experimental Section, together with $(PPh_3\{CH_2\text{-}CH{=}CH_2\})PF_6$. Thus it seems possible that the reaction has proceeded by nucleophilic addition of triphenylphosphine to the η-allyl ligand, followed by displacement of the resulting olefin and / or metallacyclobutane intermediate which decomposes with rearrangement to the $(PPh_3\{CH_2\text{-}CH{=}CH_2\})PF_6$ compound. Therefore this route seemed unpromising.

The second route investigated may be summarised as follows. First of all, monophosphine derivatives, $Co\{\eta\text{-}C_5H_5\}\{PR_3\}\{CO\}$ were prepared. This was followed by addition of allylhalide to give the required $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}PR_3)^+$.

This required the preparation of $Co\{\eta\text{-}C_5H_5\}\{PR_3\}\{CO\}$. The compounds of the type $Co\{\eta\text{-}C_5H_5\}\{PR_3\}\{CO\}$ have been described in the literature and were prepared by direct reaction between $Co\{\eta\text{-}C_5H_5\}\{CO\}_2$ and PR_3 [68]. Compounds which were known are as follows: $Co\{\eta\text{-}C_5H_5\}\{PR_3\}CO$ where $PR_3 = PPh_3$ and PMe_2Ph, and

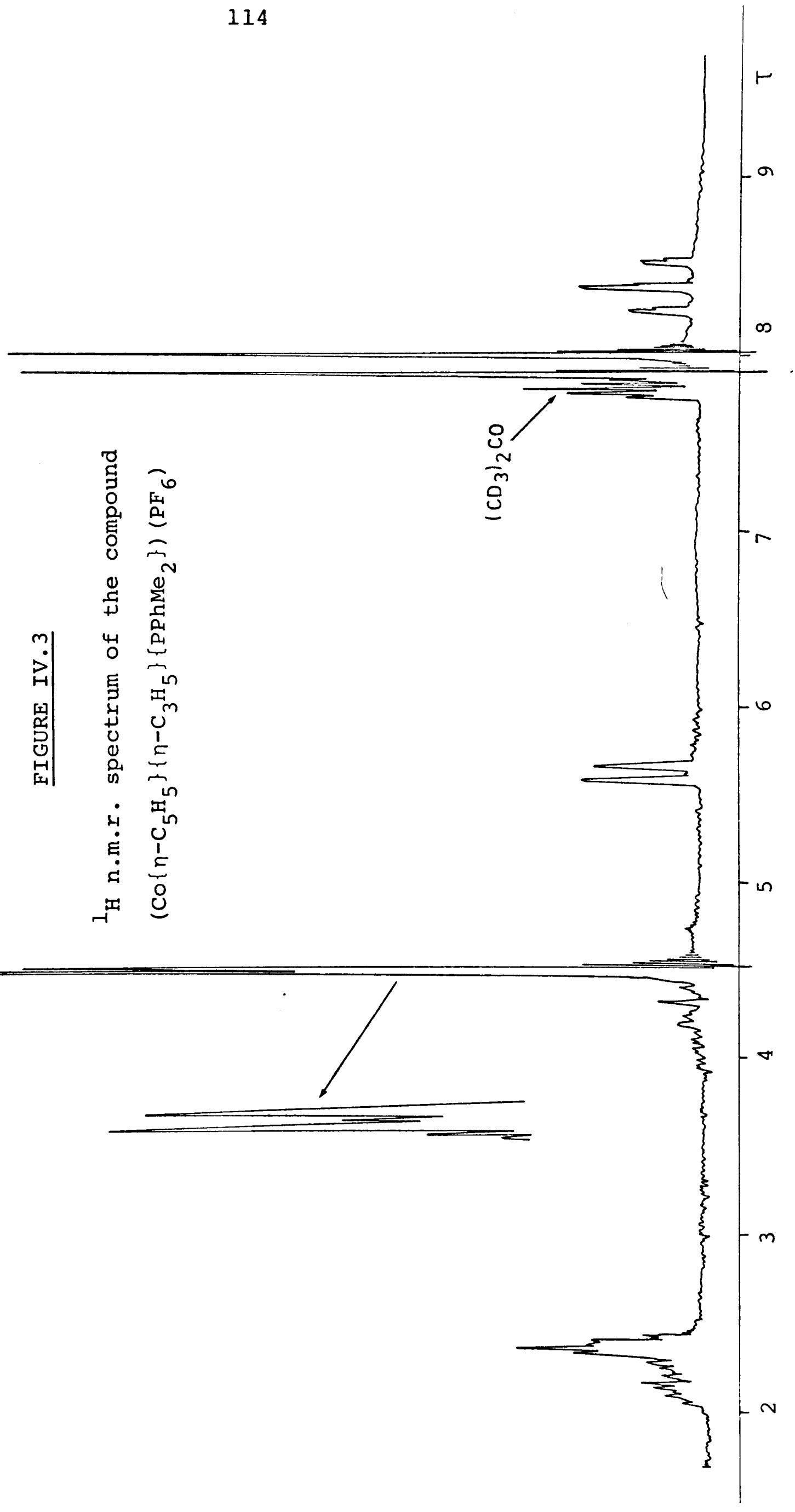
we prepared them by the route described. We prepared $Co\{\eta\text{-}C_5H_5\}\{PR_3\}CO$ ($PR_3 = PMe_3$) by an identical route, the conditions being given in the Experimental Section. The compound $Co\{\eta\text{-}C_5H_5\}\{CO\}PMe_3$ is a red crystalline solid, very soluble in petrol. It was found to be pyrophoric and no elemental analysis was obtained. However, it was characterised by ^1H n.m.r. and mass spectroscopy, the data for which are given in Tables IV.1 and IV.3 respectively.

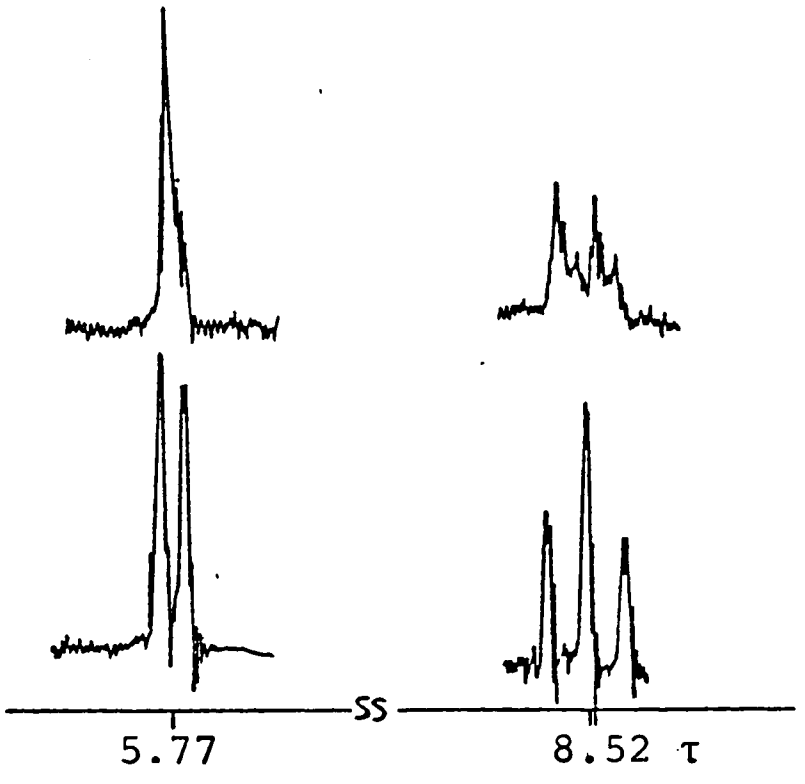
Treatment of $Co\{\eta\text{-}C_5H_5\}\{PMe_2Ph\}CO$ with allylbromide proceeded smoothly, giving two compounds. One, an orange water soluble compound, was isolated as the PF_6 salt. It was characterised by elemental analysis, infrared spectroscopy (the data are given in the Experimental Section) and ^1H n.m.r., as the new compound $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}\{PMe_2Ph\})PF_6$.

The ^1H n.m.r. spectrum is shown in Figure IV.3 and the data with assignments are given in Table IV.1. There is either only one isomer present or a mixture of rapidly interconverting isomers of the type drawn in Figure IV.2 for $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}R\text{-}\eta\text{-}C_3H_4\}L)^+$ ($R = H$, $L = PMe_2Ph$). The presence of a triplet at 8.52τ of relative intensity 2, which can be assigned to the H_a protons of the $\eta\text{-}C_3H_5$ group is a result of the coincidental near equivalence of $J_{31_{P\text{-}H_a}}$ and $J_{H_c\text{-}H_a}$ and this is shown by a double resonance experiment where by irradiation at the central proton H_c = 4.66 to 4.41τ gave rise to a doublet as shown below (4a). Also the doublet at 5.77τ of relative intensity 2, which is assigned to the 2 H_s protons of the $\eta\text{-}C_3H_5$ ligand gave rise to a singlet.

FIGURE IV.3

^1H n.m.r. spectrum of the compound $(Co\{\eta-C_5H_5\}\{\eta-C_3H_5\}\{PPhMe_2\})(PF_6)$





(4a)

The rest of the spectrum can be readily assigned. There is a doublet at 8.09τ of relative intensity 6, which corresponds to the 2 methyl groups of the PMe_2Ph ligand coupled to ^{31}P, J = 9.66Hz. There is a sharp doublet at 4.63τ of relative intensity 5 which can be assigned to the 5 H of the η-C_5H_5 ring coupled to the ^{31}P nucleus of the PMe_2Ph ligand (J = 1.2Hz). Finally, there is a complex band in the region 3.56 to 2.16τ of relative intensity 5, which corresponds to the phenyl group of PMe_2Ph.

We also noticed during the course of this reaction a small quantity of yellow crystalline material which was soluble in petroleum ether. The infrared spectrum shows it to be some carbonyl-containing compound. However, due to the apparent absence of the η-C_5H_5 ring in the ^1H n.m.r., we decided not to make further studies of this product at this stage.

Attempts to prepare $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_2Ph)^+$ by reaction between $Co\{\eta\text{-}C_5H_5\}\{PMe_2Ph\}\{CO\}$ and 3-methylallyl-bromide in conditions analogous to those which successfully led to the preparation of the unsubstituted η-allyl analogue,

gave this time only a very small yield of some yellow crystals. These were identical to those formed in the reaction of the allylbromide with $Co\{\eta\text{-}C_5H_5\}\{PMe_2Ph\}\{CO\}$, which have not been identified. Since no cationic allylic compound was found together with the yellow crystals, the reaction was not further pursued.

The reaction between $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}\{CO\}$ with allyl bromide was then investigated, and it was found to give rise surprisingly to two products, namely the desired $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)^+$ cation, which was isolated as the orange hexafluorophosphate salt (Yield *ca* 60%) together with another yellow crystalline compound, which was also isolated as the hexafluorophosphate salt in *ca* 10% yield. It was separated by chromatography as described in the Experimental Section, from the other product.

The ^1H n.m.r. and ^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)PF_6$ (the data are given in Tables IV.1 and IV.2 respectively) show again that either there is only one isomer present or a mixture of rapidly interconverting isomers, of the type drawn in Figure IV.2 (L = PMe_3 and R = H).

The yellow crystalline compound was unambiguously characterised by elemental analysis, infrared spectroscopy (the data are given in the Experimental Section) and the ^1H n.m.r. spectrum which data are given in Table IV.1, as $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$.

The compound in acetone exhibited unusual behaviour since on warming a solution of $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)^{2+}$ in acetone, a compound precipitated which redissolved when the solution was cooled. This suggests that some reversible reaction with the solvent may be occurring.

Trimethylphosphine is highly volatile but the ^1H n.m.r. spectrum of $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)^{2+}$ in acetone shows a small doublet at 7.86τ as evidence for a trace of free Me_3P ligand.

The ^1H n.m.r. spectrum shows two complex bands of relative intensity in the ratio ≃ 5:27 at 4.21τ and 8.43 to 8.13τ respectively. The former band which may be assigned to $\eta\text{-}C_5H_5$ hydrogens does not show a 1:3:3:1 quartet but is more complex. It is possible to interpret the band as arising from two species. The major component gives a quartet partially superimposed on a less intense band. Similarly, the complex band at 8.43 to 8.13τ which may be assigned to 9 methyl groups of the 3 PMe_3 ligands is less symmetrical than might have been anticipated.

The reaction of $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}\{CO\}$ with 3-methylallylbromide was investigated. The reaction was carried out as described in detail in the Experimental Section by dropwise addition of 3-methylallylbromide to a cool petroleum solution of $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}\{CO\}$. An orange precipitate was formed which was separated by filtration. The precipitate was dissolved in water and addition of aqueous NH_4PF_6 precipitated the cation as the hexafluorophosphate salt. From this precipitate, two products could be separated by chromatography. Orange needles were obtained in *ca* 25% yield and characterised

unambiguously as $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$ by elemental analysis, the infrared spectrum and ^1H n.m.r. and ^{13}C n.m.r. spectra. The data (see Tables IV.1 and IV.2) show again there to be either only one isomer present or a mixture of rapidly interconverting isomers of the type shown in Figure IV.1 ($R = PMe_3$).

A yellow crystalline compound was formed in *ca* 30% yield and it was characterised as $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)$ by comparison of its infrared and ^1H n.m.r. spectra with those of an authentic sample.

After 15 days, some black crystals were formed in the filtrate, together with some more orange precipitate. They were both separated from the mother liquor by filtration and extraction with water left the black crystals. They were recrystallised from a mixture of toluene and petroleum ether.

The elemental analysis is consistent with the stoichiometry $C_9H_{12}BrCo$.

The mass spectrum is given in Table IV.3 and shows the parent ion $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}Br)^+$ as two peaks of equal intensity at m/e 260 and m/e 258, corresponding to the isotopic pattern of one bromine atom containing the isotopes ^{81}Br and ^{79}Br respectively.

The ^1H n.m.r. spectrum (the data are given in Table IV.3) shows that there is again either only one isomer present or

a mixture of rapidly interconverting isomers.

The compound has been characterised as the neutral compound $Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}Br$ which is assumed to be formed, similarly to the analogous neutral compound $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$ previously described, by halide attack, followed by displacement of PMe_3, but again we have no direct evidence to support this observation.

The third route towards the desired compounds was chosen by analogy with our previously described reaction of $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$ with carbon monoxide, giving $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)^+$.

The $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$ was treated with PMe_3 and a rapid reaction took place, giving the desired compound, $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)^+$ in good yield. Similarly, it was found that the compound $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}L)^+$ where L = pyridine or NH_3 could be readily prepared, by reaction of $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$ and either pyridine or NH_3 respectively.

The ^1H n.m.r. spectra of these compounds and the ^{13}C n.m.r. spectrum of compound $Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$ are given in Tables IV.1 and IV.2. They show in all cases that there is either only one isomer present or a mixture of rapidly interconverting isomers of the type shown in Figure IV.2 (R = Me, and L = PMe_3, pyridine or NH_3, respectively).

The H^1 and H^2 hydrogens of the 2-methylallyl ligand are equivalent as in the two 2-methylallyl compounds already described, indicating that the allyl group is symmetrically

bonded to the metal. The evidence for the characterisation of these compounds is given in the Experimental Section and in Tables IV.1 and IV.2. It is quite unambiguous and does not require further discussion.

Finally, we had also suggested a possible synthetic route, namely treatment of $Co\{\eta\text{-}C_5H_5\}\{PR_3\}I_2$ with allylmagnesiumbromide or allyl-lithium to give the desired product, $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}PR_3)^+$, and towards this end we had set out to explore the preparation of compounds of the type $Co\{\eta\text{-}C_5H_5\}PR_3I_2$. The preparation of these compounds where $PR_3 = PPh_3$, by addition of PPh_3 to a CH_2Cl_2 solution of $Co\{\eta\text{-}C_5H_5\}\{CO\}\ I_2$, has been previously described[68]. We therefore reacted $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$ with $PPhMe_2$ and isolated the desired product, $Co\{\eta\text{-}C_5H_5\}\{PMe_2Ph\}I_2$ in *ca* 95% yield, as a purple crystalline product which was characterised readily by the data given in the Experimental Section and by the ^1H n.m.r. spectrum given in Table IV.1.

However, we found that when we treated $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$ with PMe_3, the reaction proceeded further to give $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_2)I_2$, which was isolated as the PF_6 salt. Attempts to obtain $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}I_2$ by treatment of $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$ with the stoichiometric quantity (1:1) of PMe_3 gave instead a mixture of starting material, $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}I_2$ and $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_2)^{2+}$. The salt was separated by filtration. No further attempts to separate the starting material, $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$, from $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}I_2$ were made. An ^1H n.m.r. spectrum of the mixture was recorded which showed that they were present in a 50:50 ratio.

In view of the fact that the route just described above was found successful, this particular route was not explored further.

FIGURE IV.4. Synthesis of the compounds described in Chapter IV.

i I_2 in diethylether, 12h[68]

ii $PPhMe_2$ in CH_2Cl_2, 12h.

iii PMe_3 in CH_2Cl_2

iv PR_3 in petroleum ether, 90°C, 12h[68]

v, vi allylbromide in petroleum ether

vii 1-methylallylbromide in petroleum ether

viii 2-methylallyliodide in petroleum ether

ix L=CO, CO in toluene, 2h, 80°C; L=PMe_3, py or NH_3, PMe_3, py or NH_3 in acetone

x 1-methylallylbromide in petroleum ether

xi 2-methylallylchloride in petroleum ether, 90°C, 48h.

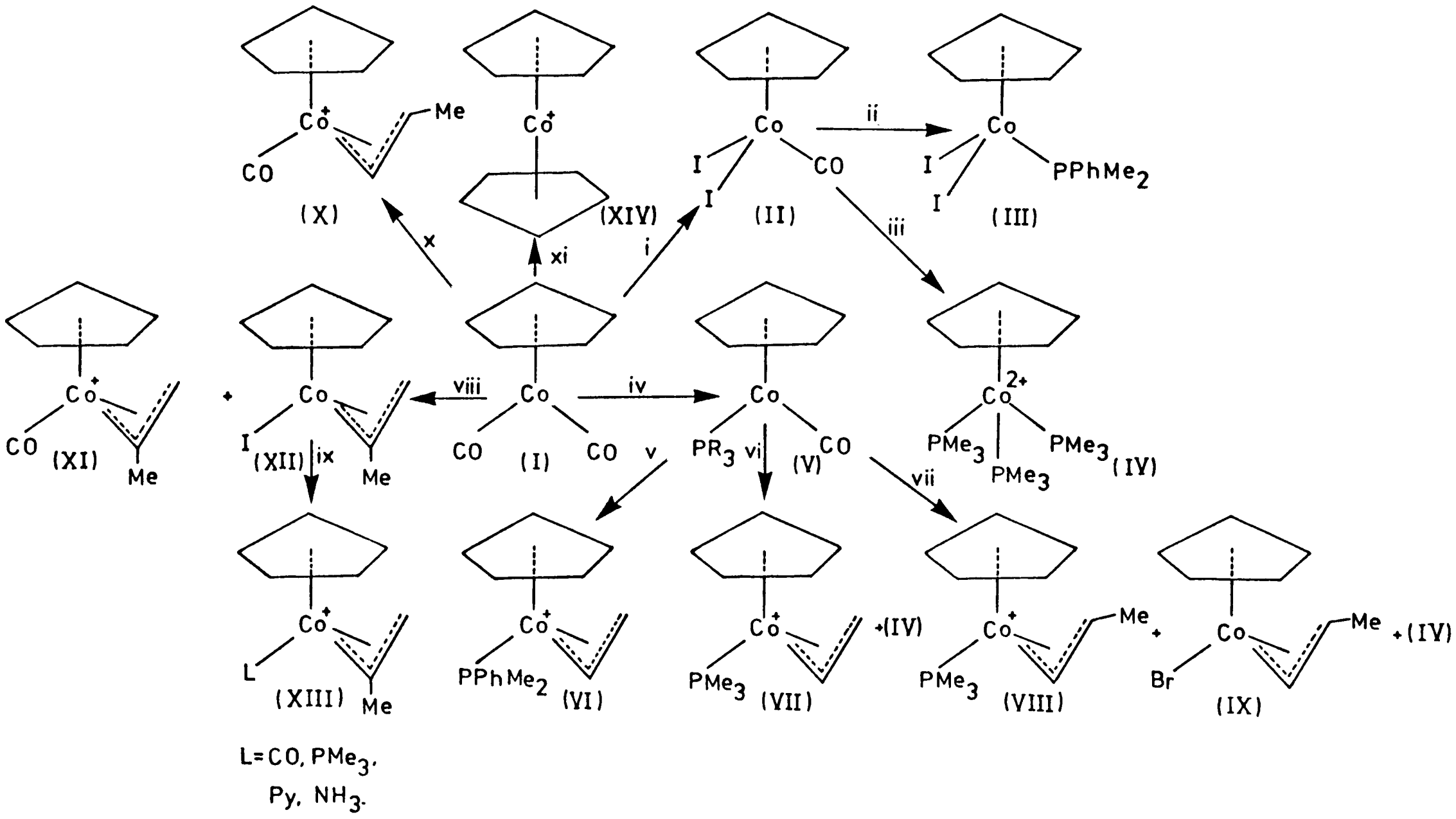

(X)
(XIV)
(II)
(III)
(XI)
(XII)
(I)
(V)
(IV)
(XIII)
(VI)
(VII)
(VIII)
(IX)
i
ii
iii
iv
v
vi
vii
viii
ix
x
xi
L=CO, PMe3, Py, NH3.

TABLE IV.1. ^{1}H n.m.r. spectra of the compounds described in Chapter IV.

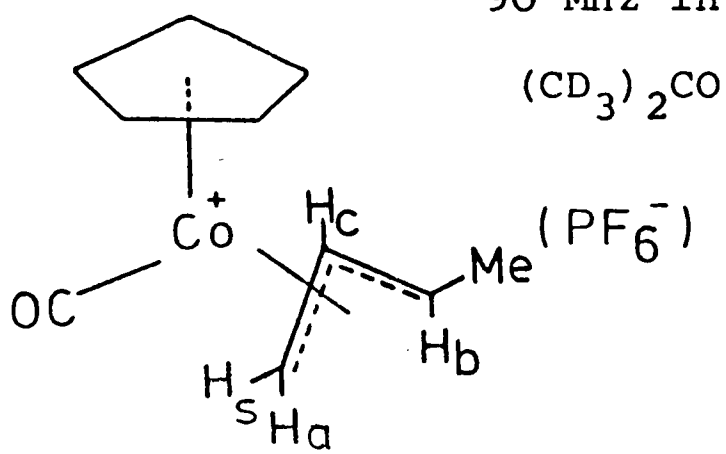
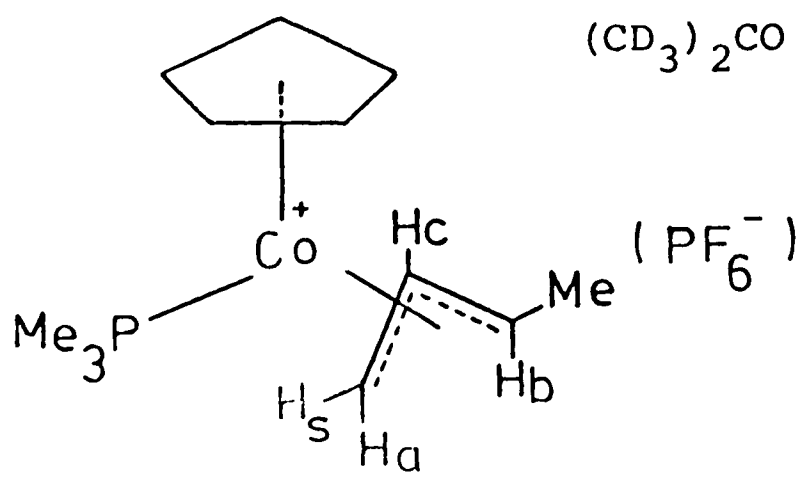
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
 90 MHz in $(CD_3)_2CO$	8.06	3	doublet (J_{H_c-Me} = 6.07	Me
	7.51	1	doublet ($J_{H_c-H_a}$ = 11.78)	H_a
	6.19	1	complex	H_b
	5.58	1	doublet ($J_{H_c-H_s}$ = 6.88)	H_s
	4.47 - 4.10	1	complex	H_c
	4.04	5	singlet	C_5H_5
 90 MHz in $(CD_3)_2CO$	8.75	1	triplet ($J_{^{31}P-H_a}$ = $J_{H_c-H_a}$ = 11.78)	H_a
	8.38	9	doublet ($J_{^{31}P-Me}$ = 9.91)	PMe_3
	8.26	3	doublet (J_{H_c-Me} = 6.22)	Me
	7.66 or 7.27	1	complex	H_b
	6.04	1	doublet ($J_{H_c-H_s}$ = 6.42)	H_s
	4.41 - 4.71	1	complex	H_c
	4.55	5	Doublet ($J_{^{31}P-Cp}$ = 1.32)	C_5H_5

TABLE IV.1 cont.

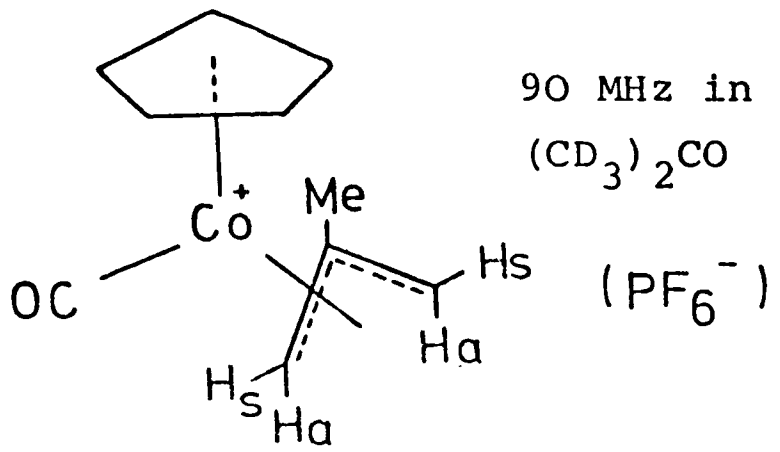
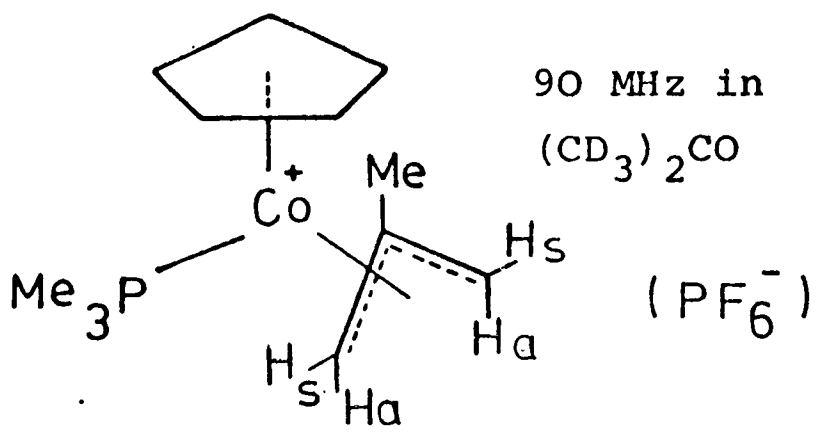
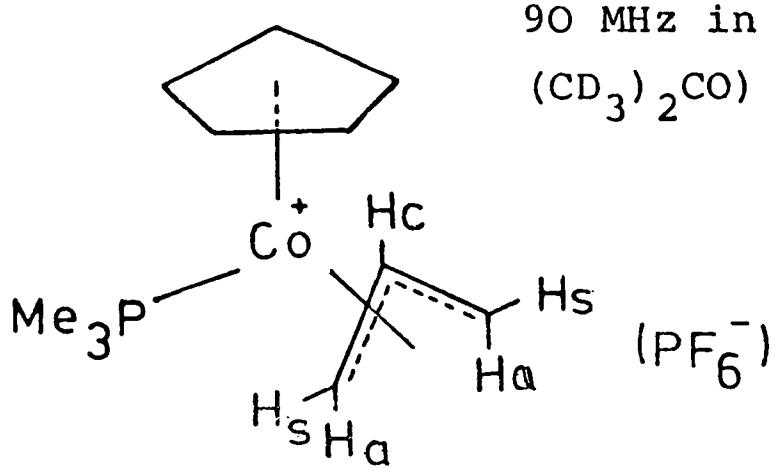
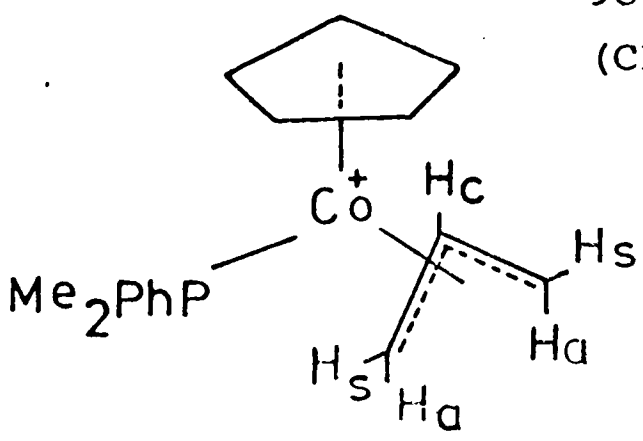
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
 90 MHz in $(CD_3)_2CO$	7.58	3	singlet	Me
	7.24	2	singlet	H_a
	5.38	2	singlet	H_s
	3.94	5	singlet	C_5H_5
 90 MHz in $(CD_3)_2CO$	8.64	2	complex doublet ($J_{^{31}P\text{-}H_a}$ = 12.3)	H_a
	8.42	9	doublet ($J_{^{31}P\text{-}Me}$ = 9.86	PMe_3
	7.73	3	singlet	Me
	6.05	2	complex	H_s
	4.63	5	doublet ($J_{^{31}P\text{-}Cp}$ = 1.15)	C_5H_5

TABLE IV.1 cont.

Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
 90 MHz in $(CD_3)_2CO$	8.54	2	triplet ($J_{^{31}P\text{-}H_a} = J_{H_c\text{-}H_a} = 10.52$)	H_a
	8.4	9	doublet ($J_{^{31}P\text{-}Me} = 9.81$)	PMe_3
	5.91	2	doublet ($J_{H_c\text{-}H_s} = 7.13$)	H_s
	4.52	5	doublet ($J_{^{31}P\text{-}Cp} = 1.2$)	C_5H_5
	4.68 - 4.33	1	complex	H_c
 90 MHz in $(CD_3)_2CO$	8.52	2	triplet ($J_{^{31}P\text{-}H_a} = J_{H_c\text{-}H_a} = 11.17$)	H_a
	8.09	6	doublet ($J_{^{31}P\text{-}Me} = 9.66$)	Me_2
	5.77	2	doublet ($J_{H_c\text{-}H_s} = 6.77$)	H_s
	4.63	5	doublet ($J_{^{31}P\text{-}Cp} = 1.2$)	C_5H_5
	4.66 - 4.41	1	complex	H_c
	3.56 - 2.16	5	complex	Ph

spin decoupling data (see text)

H_a appears as a doublet, and H_s as a singlet when H_c is irradiated.

TABLE IV.1 cont.

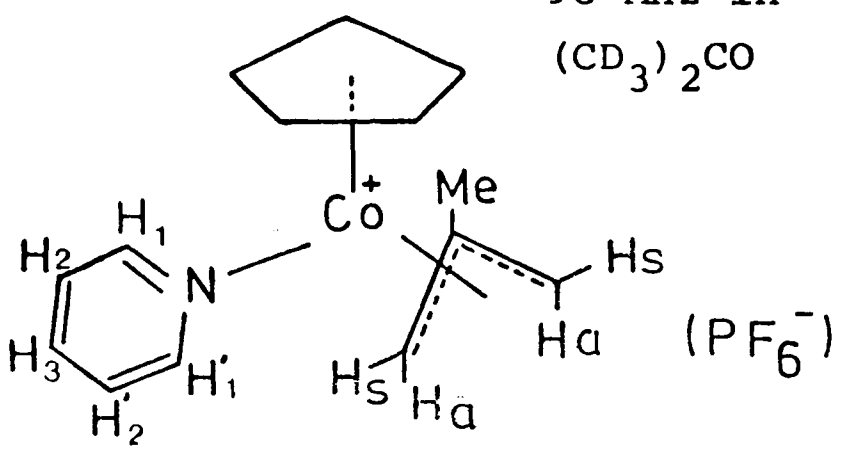
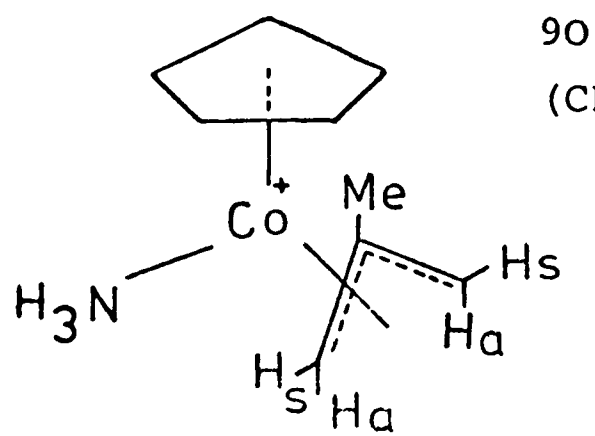
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
 90 MHz in $(CD_3)_2CO$	8.16	2	singlet	H_a
	7.92	3	singlet	Me
	4.62	5	singlet	C_5H_5
	4.51	2	singlet	H_s
	2.61	2	complex triplet (J = 5.97)	H_2, H_2' (Py)
	2.1	1	complex triplet (J = 7.74)	H_3(Py)
	1.02	2	complex doublet (J = 4.65)	H_1, H_1' (Py)
 90 MHz in $(CD_3)_2CO$	8.80 - 8.10	3	broad	NH_3
	8.23	2	singlet	H_a
	7.93	3	singlet	Me
	4.88	2	singlet	H_s
	4.61	5	singlet	C_5H_5

TABLE IV.1 cont.

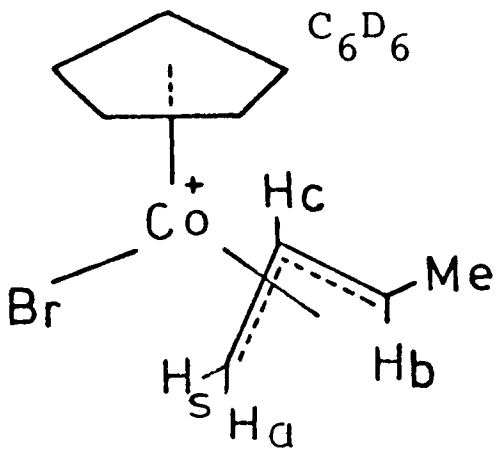
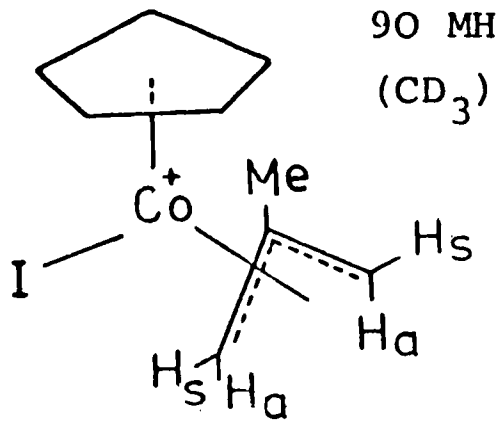
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHZ in C_6D_6 	8.47	3	doublet (J_{H_b-Me} = 4.75)	Me
	7.04	1	doublet ($J_{H_c-H_a}$ = 10.41)	H_a
	6.36 - 5.89	2	complex	H_b, H_c
	5.48	5	singlet	C_5H_5
	5.31	1	doublet ($J_{H_c-H_s}$ = 5.06)	H_s
90 MHz in $(CD_3)_2CO$ 	7.99	3	singlet	Me
	6.92	2	singlet	H_a
	5.17	2	singlet	H_s
	4.79	5	singlet	C_5H_5

TABLE IV.1 cont.

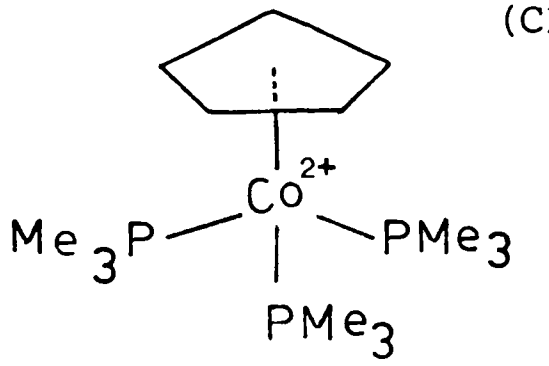
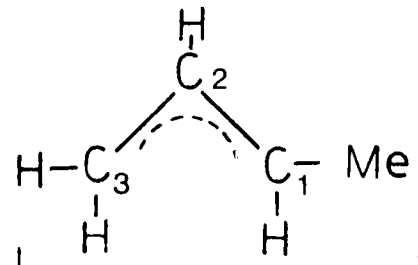
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHz in $(CD_3)_2CO$  $(PF_6^-)_2$	8.43 - 8.13	27	complex	Me
	7.86	2	doublet ($J_{^{31}P\text{-}Me}$ = 9)	PMe_3 (free)
	4.21	5	complex	C_5H_5
90 MHz in C_6D_6 $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}PMe_3)$	8.82	9	doublet ($J_{^{31}P\text{-}Me}$ = 9.35)	PMe_3
	5.2	5	doublet ($J_{^{31}P\text{-}Cp}$ = 1.2)	C_5H_5
60 MHz in CCl_3D	7.25	6	doublet ($J_{^{31}P\text{-}Me}$ = 11.25)	2 Me
	4.62	5	singlet	C_5H_5
$(Co\{\eta^5\text{-}C_5H_5\}\{PPhMe_2\}I_2)$	2.25 - 1.30	5	complex	Ph

TABLE IV.2. ^{13}C n.m.r. spectra of the compounds described in Chapter IV.

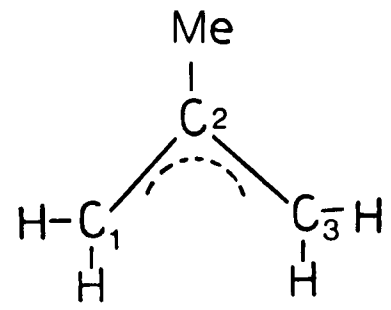
Complexes



Compound and Solvent	Shift in ppm	Multiplicity decoupled (J', J" in Hz)[a]	coupled	Assignment
$(Co\{\eta^5\text{-}C_5H_5\}\{CO\}\{1\text{-methyl-allyl}\})PF_6$ in $(CD_3)_2CO$	91.93	singlet	doublet	C_5H_5
	88.81	singlet	doublet	C_2 or C_1
	83.68	singlet	doublet	C_2 or C_1
	48.84	singlet	triplet	C_3
	21.74	singlet	quartet	Me
$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}\{1\text{-methyl-allyl}\})PF_6$ in $(CD_3)_2CO$	88.42	singlet	doublet	C_5H_5
	84.84	doublet (J'= 2.94)	doublet of doublet	C_1 or C_2
	70.94	singlet	doublet	C_1 or C_2
	42.59	singlet	triplet	C_3
	22.0	singlet	quartet	Me
	17.22	doublet (J" = 33.83)	quartet of doublets	PMe_3

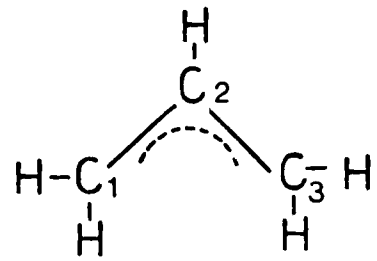
TABLE IV.2 cont.

Complexes



Compound and Solvent	Shift in ppm	Multiplicity Decoupled	Coupled	Assignment
(Co{η^5-C_5H_5}{CO}{2-methyl-allyl})PF_6 in $(CD_3)_2CO$	113.2	singlet	singlet	C_2
	92.19	singlet	doublet	C_5H_5
	52.94	singlet	triplet	$C_1 + C_3$
	33.69	singlet	doublet	Me
(Co{η^5-C_5H_5}{PMe_3}{2-methylallyl})PF_6 in $(CD_3)_2CO$	105.96	doublet (J" = 2.94)	doublet	C_2
	88.87	singlet	doublet	C_5H_5
	46.43	doublet (J" = 3.04)	triplet of doublets	$C_1 + C_3$
	26.16	singlet	quartet	Me
	16.83	doublet (J' = 33.83)	doublet of doublets	PMe_3

TABLE IV.2 cont.

Complexes 

Compound and Solvent	Shift in ppm	Multiplicity Decoupled	Coupled	Assignment
$(Co\{\eta^5\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$ in $(CD_3)_2SO$	90.32	singlet	doublet	C_5H_5
	88.11	singlet	doublet	C_2
	54.05	singlet	triplet	$C_1 + C_3$
$(Co\{\eta^5\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}PMe_3)PF_6$ in $(CD_3)_2CO$	88.29	singlet	doublet	C_5H_5
	84.08	singlet	doublet	C_2
	47.66	doublet (J" = 2.94)	triplet of doublets	$C_1 + C_3$
	17.54	doublet (J' = 33.83)	quartet of doublets	PMe_3

a) J' = coupling constant $J_{^{31}P\text{-}^{13}C}$ in Hz

J" = coupling constant $J_{^{31}P\text{-}Co\text{-}^{13}C}$ in Hz

TABLE IV.3. Mass spectra of the compounds described in Chapter IV.

Compound	m/e	Rel. Int.[a]	Assignment[b]
$(Co\{\eta^5\text{-}C_5H_5\}\{CH_2{=}C\{CH_3\}{=}CH_2\}I)$	306	35	$(Co\{\eta^5\text{-}C_5H_5\}\{CH_2{=}C\{CH_3\}{=}CH_2\}I)^+$
	251	34	$(Co\{\eta^5\text{-}C_5H_5\}I)^+$
	179	100	$(Co\{\eta^5\text{-}C_5H_5\}\{CH_2{=}C\{CH_3\}{=}CH_2\})^+$
	124	68	$(Co\{\eta^5\text{-}C_5H_5\})^+$
	59	26	Co^+
$(Co\{\eta^5\text{-}C_5H_5\}\{CH_3\text{-}CH{=}CH{=}CH_2\}Br)$	260	7	$(Co\{\eta^5\text{-}C_5H_5\}\{CH_3\text{-}CH{=}CH{=}CH_2\}^{81}Br)^+$
	258	7	$(Co\{\eta^5\text{-}C_5H_5\}\{CH_3\text{-}CH{=}CH{=}CH_2\}^{79}Br)^+$
	205	20	$(Co\{\eta^5\text{-}C_5H_5\}^{81}Br)^+$
	203	21	$(Co\{\eta^5\text{-}C_5H_5\}^{79}Br)^+$
	179	33	$(Co\{\eta^5\text{-}C_5H_5\}\{CH_3\text{-}CH{=}CH{=}CH_2\})^+$
	124	100	$(Co\{\eta^5\text{-}C_5H_5\}\ )^+$
	59	40	Co^+

TABLE IV.3 continued.

Compound	m/e	Rel. Int.[a]	Assignment[b]
$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}CO)$	228	41	$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}CO)^+$
	200	100	$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\})^+$
	124	44	$(Co\{\eta^5\text{-}C_5H_5\})^+$
	76	5	$(PMe_3)^+$
	59	14	Co^+

a Relative intensity based on the largest m/e value (for metal containing species = 100)

b Tentative assignment for most chemically probable fragment to fit m/e value.

CHAPTER V

STUDY OF THE REACTIONS OF (η-ALLYL)(η-CYCLOPENTADIENYL)(DONOR LIGAND)COBALT CATION WITH NUCLEOPHILES.

The compounds $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$ were prepared with the purpose of examining regiospecificity, if any, in the attack of nucleophiles on the η-allylic ligand, and in this section we describe the results of studies of the reactions of these compounds with nucleophiles, especially H^- and Me^-. First of all, we will described the general experimental arrangements, and then we will present our results and discuss the conclusions.

I. Procedure for investigating the reaction of cobalt allylic cations with nucleophiles.

The general procedure was to take a sample of the pure and characterised η-allylic cation, in suspension in a suitable solvent, to add the nucleophile and then to monitor the volatile components of the reaction, using gas-liquid chromatography. Attempts were made to isolate any cobalt-containing products by the normal procedures of extraction with petroleum ether, chromatography on an alumina column, crystallisation, distillation, etc., whichever seemed the most appropriate.

The columns used in gas-liquid chromatography were prepared as described in the Experimental Section and they were always checked, before and after each experiment, in order to ensure that they were behaving in the required manner, that they could separate the expected volatile olefins, and that the gas chromatography instrument was behaving to the required degree of sensitivity. Column materials were chosen in the light of the literature and the columns were pre-

pared and checked with calibrating gases before use.

Results

The volatile products are given in Table V.1.

As described in detail in the Experimental Section, with the exception of the reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}PMe_3)^+$ with MeLi, attempts to isolate any organometallic compounds which were expected to have been formed during the reaction were unsuccessful, due to the high reactivity or instability under the conditions employed. Althought promising colours were seen in a number of reactions, we were unable, despite careful attempts, to isolate any characterisable cobalt-containing products.

Discussion

The strategy underlying the above experiments was as follows: consider the cation $Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}L)^+$ (where L = CO or PR_3). Addition of H^- to this compound is predicted, by the rules described in the Introductory Chapter, to occur on the η-allylic ligand, either on the terminal or on the central carbon atom. Addition to the terminal carbon atom would give rise to a neutral η-propene compound $Co\{\eta\text{-}C_5H_5\}\{CH_2{=}CH\text{-}CH_3\}L$. Alternatively, addition to the central carbon would be expected to give rise to the metallacyclobutane compound $Co\{\eta\text{-}C_5H_5\}\{CH_2\text{-}CH_2\text{-}CH_2\}L$ (see scheme).

These are the two products which would be expected, if addition of H^- to the $\eta\text{-}C_3H_5$ ligand had occurred as predicted

TABLE V.1

Volatile Products of the reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}L)^+$ with nucleophiles.

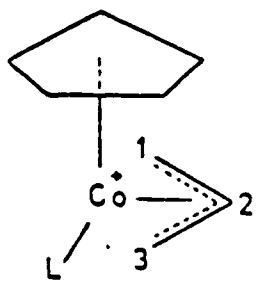
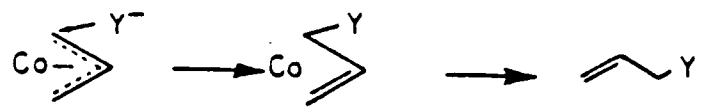
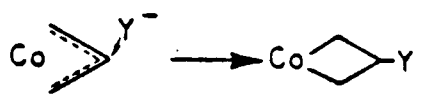
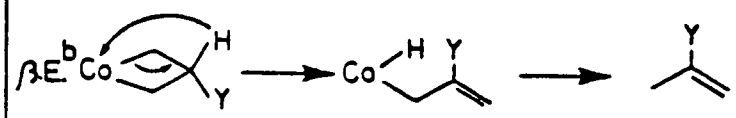
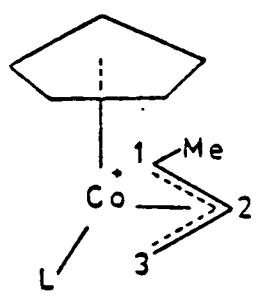
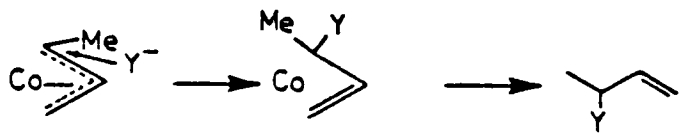
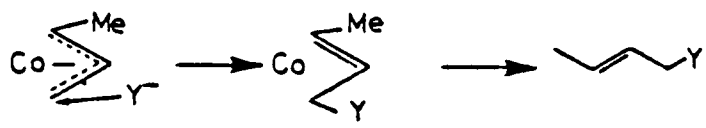
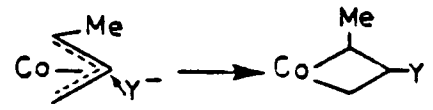
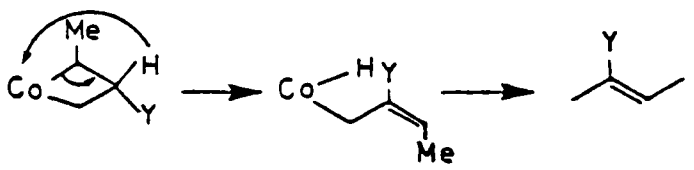
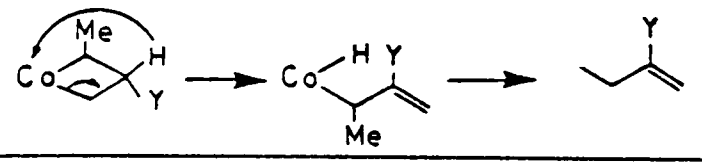
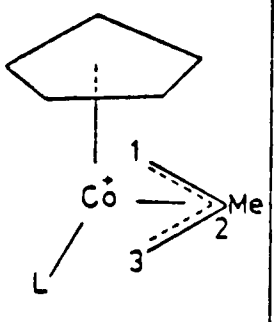
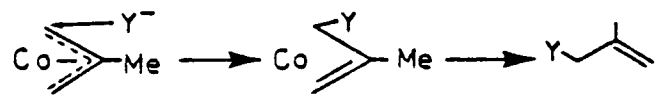
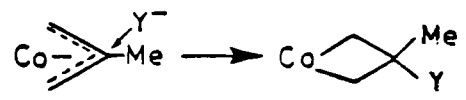
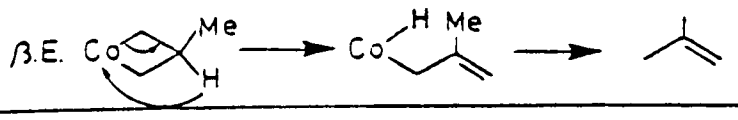
COMPOUND	NUCLEOPHILE[a]	PRODUCTS (b)	PRODUCTS (c)
$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}CO)PF_6$	H^-	propene	propane
	Me^-	propene + but-1-ene (tr)	
$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-allyl}\}PMe_3)PF_6$	H^-	propene	
	Me^-	propene + but-1-ene (tr)	
$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-1-methylallyl}\}CO)PF_6$	H^-	but-1-ene	butane
	Me^-	but-1-ene	cis & trans but-2-ene
$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-2-methylallyl}\}CO)PF_6$	Me^-	isobutene	
$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-2-methylallyl}\}PMe_3)PF_6$	Me^-	isobutene	

(a) The source of H^- was a 70% solution of $Na(AlH_2(OCH_2CH_2OCH_3)_2)$ in benzene, and the source of Me^- was a 2M solution of MeLi in diethylether.

(b) Products formed in the reaction mixture, immediately after reaction had taken place (the products which were already present in the source of nucleophile before the reaction had taken place are not mentioned.

(c) Products which were present in the reaction mixture, after letting the sample stand for 15 days.

tr: traces.

COMPOUND	Position of Nucleophilic Addition	MECHANISM OF DECOMPOSITION	PRODUCTS $Y^- = H^-$	PRODUCTS $Y^- = Me^-$
	1,or 3		Propene	but-1-ene
	2			
		R.E.[a] 	cyclopropane	methylcyclo-propane
		β.E.[b] 	propene	isobutene
	1		but-1-ene	3-methyl-but-1-ene.
	3		but-2-ene	pent-2-ene
	2			
		R.E. 	methylcyclo-propene	1,2-dimethyl-cyclopropane
		β.E. 	but-2-ene	2-methyl-but-2-ene
			but-1-ene	2-methyl-but-1-ene
	1,or 3		isobutene	2-methyl-but-1-ene
	2			
		R.E. 	methylcyclo-propane	1,1'.dimethyl-cyclopropane
		β.E. 	isobutene	

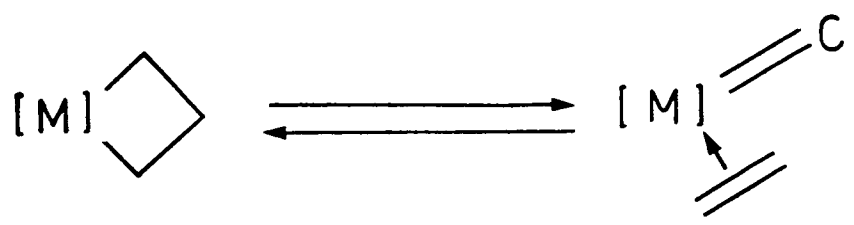
b) β.E. = β-elimination

a) R.E. = Reductive elimination

SCHEME

by the rules.

The subsequent fate of these compounds, if they were not thermally stable, is not readily predictable. However, one would expect, in the case of the η-propene compound, that propene would be evolved, and one would expect in the case of the metallacyclobutane compound either that it will decompose by a reductive elimination mechanism giving cyclopropane or that it will decompose by a β-elimination mechanism, as shown in the scheme, to give propene. Another possible mechanism of decomposition which is not specified in the scheme is an olefin dismutation process such as that occurring in the photochemical decomposition of bis(cyclopentadienyl)metallacyclobutanetungsten [99] which can be formulated as follows:



Thus from this reaction, one might have expected to find: propene, cyclopropane or ethylene, and indeed other possible fragments such as methane. In the event, as shown in the Table, only propene was shown to be the significant product formed, either for the L = CO or L = PMe_3 compounds. Methane and ethylene were evident; especially when the nucleophile used was MeLi, there was always some methane present, but no significant increase of relative intensity occurred. Thus we concluded that the major product was propene,

as shown in Table V.1. The column used for chromatography (polyethylene glycol on Chromosorb P) has been shown to be capable of separating cyclopropane from propene under the typical conditions employed.

The formation of propene in the above reaction does not provide any indication of whether the H^- addition to the η-allylic ligand has occurred on the 1 or the 2 carbon position.

Treatment of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}L)^+$ with MeLi was studied in some detail, and in the case L = PMe_3, it was possible to isolate from the reaction mixture the compound $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$ in good yield. This is a new compound and the evidence for its characterisation is given in the Experimental Section and in Tables V.2 and V.3. The related compound $Co\{\eta\text{-}C_5H_5\}\{PPh_3\}Me_2$ analogue has been described previously[72].

Examination of the volatile products showed that the only major volatile product that we could detect in this reaction was propene and small traces of but-1-ene (see Table V.1).

Addition of Me^- to the terminal carbon (position 1 or 3) would give rise to a neutral compound $Co\{\eta\text{-}C_5H_5\}\{CH_2{=}CH\text{-}CH_2\text{-}CH_3\}L$, whereas addition to the central carbon would be expected to give rise to the 2-methyl-metallacyclobutane compounds $Co\{\eta\text{-}C_5H_5\}\{CH_2CH_2\{Me\}\text{-}CH_2\}L$.

Straightforward thermal decomposition would be expected to give rise, in the case of terminal addition, to but-1-ene, or if isomerisation had occurred but-2-ene, whereas if addition

of Me^- to the central carbon (position 2) had occurred, the product would be expected to be either methylcyclopropane or isobutene (see scheme). However, it is not entirely impossible that the 2-methyl-metallacyclopropane has undergone *via* olefin metathesis, rearrangements to give a 1-methylmetallacyclobutane which in turn has then decomposed to give butenes. Alternatively, olefin metathesis decomposition of the 2-methylmetallacyclobutane compound could give rise to propene as the major product.

The formation as a major product of propene in the reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}L)^+$ with MeLi in both cases, L = CO or L = PMe_3, can be rationalised in terms of either addition of Me^- to the 2 position followed by olefin metathesis decomposition or by a different mechanism.

Formation of traces of but-1-ene can be understood either in terms of Me^- addition to the terminal carbon (position 1) or the much less likely proposal of addition to the central carbon (position 2), followed by rearrangement by olefin metathesis mechanism.

The observation that the compound $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$ is formed in good yield suggests that the reaction between the cation and the MeLi is not proceeding by simple addition of Me^- to the η-allylic system; it seems more likely that the reaction is proceeding *via* addition of Me^- directly to the cobalt. We know that the yield of $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$ is greater than 50%, based on the $Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)^+$ which clearly indicates that the dimethyl compound cannot be formed as a result of simple disproportionation between cobalt compounds.

It is indeed very difficult to formulate any mechanism for the reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}L)^+$ with MeLi which gives rise to propene in high yield, unless one is to suggest that for some reason an allyl radical leaves the cobalt metal and extracts hydrogen from the solvent, although no independent test of this hypothesis has been made.

At the moment we are unable to offer any simple mechanistic explanation for the formation of $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$ compound or indeed for the formation of propene as a major product. We can only conclude from these studies that the evidence we have does not support or detract from the rules which are described in the Introductory Chapter, because the results are so inconclusive.

The reactions of the 1 and 2-methyl allylic cations with either Me^- or H^- were also studied. The major products obtained are shown in Table V.1.

The formation of but-1-ene by H^- addition to the 1-methylallyl cation does not distinguish between terminal or central carbon addition, but there is no evidence in the products for any olefin dismutation reaction.

The formation of butene in the case of Me^- addition reaction with 1-methylallyl, or isobutene in the case of MeLi reaction with 2-methylallyl, corresponds to the observation of propene in the reaction of MeLi with the unsubstituted allyl cations. It is to be presumed that the but-1-ene or alternatively isobutene are formed by similar mechanisms to those given for the formation of propene, whatever they might be. Again, it is not clear what the mechanism is. We can only conclude that these reactions do not provide evidence which

supports or disputes the rules given earlier.

The presence of propane and butane in the products of the reactions of $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}CO)^+$ and $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)^+$ with $NaAlH_2(OCH_2CH_2OCH_3)_2$ respectively, after the reaction mixture was allowed to stand for *ca* 15 days may be explained in terms of catalytic reduction of propene and but-1-ene respectively, due to the presence of some cobalt species formed during the reaction.

II. Exploring reactions of alkylLi and Grignard reagents with compounds other than η-allylic cobalt cations.

Since the reaction of MeLi with $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)^+$ gave the unexpected product $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$, we thought that it might be interesting to examine the reaction of Grignard reagents and MeLi with $Co\{\eta\text{-}C_5H_5\}PR_3$ compounds, which did not contain an allylic ligand, in order to see whether the products obtained in these reactions gave any explanation for the products observed in the reaction of the compound $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)^+$ with MeLi. Accordingly, the following reactions were investigated.

1. Treatment of $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$ with MeLi gave an orange solution from which orange crystals were isolated, as described in detail in the Experimental Section.

   The orange crystals were obtained in good yield. They are air-sensitive and were characterised as $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$. The evidence for its characterisation is

given in the Experimental Section and in Tables V.1 and V.2.

Reaction of $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)^{2+}$ with PhLi however gave no tractable product.

2. Treatment of $Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}I_2$ with isopropyl-magnesiumbromide gave an orange solution from which an orange residue could be isolated, as described in detail in the Experimental Section. The residue was extracted with water, and the cation precipitated as the hexa-fluorophosphate salt by addition of aqueous NH_4PF_6. The yellow precipitate was recrystallised from acetone/water to give yellow crystals. They were identified as $(Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}_2H)PF_6$. The evidence for its charact-erisation is given in the Experimental Section and in Table V.1. Reaction of $Co\{\eta\text{-}C_5H_5\}\{PPh_3\}I_2$ with isopropyl-magnesiumbromide to give $Co\{\eta\text{-}C_5H_5\}\{PPh_3\}_2$ has already been investigated[74]. It seems probable that in the reaction of $Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}I_2$ with isopropylmagnesium-bromide, first $Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}_2$ is formed, which then extracts one proton from water, due to its basicity, to give the hydride $(Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}_2H)PF_6$.

TABLE V.2. ^{1}H n.m.r. spectra of compounds described in Chapter V.

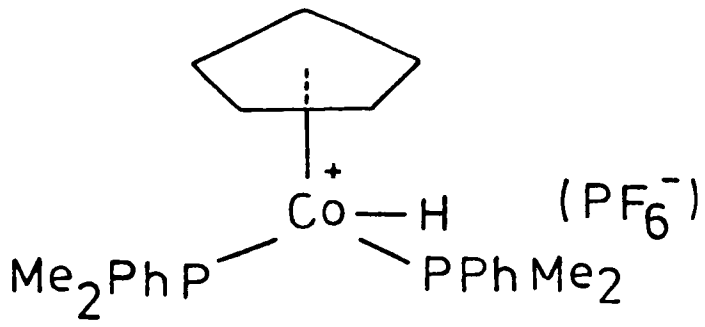
Compound and Solvent	τ value	Rel. Int.	Fine Structure (J in Hz)	Assignment
90 MHz in C_6D_6	9.64	6	doublet ($J_{^{31}P\text{-}Me}$ = 5.81)	Me
$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}\ Me_2)$	8.97	9	doublet ($J_{^{31}P\text{-}Me}$ = 9.10)	PMe_3
	5.44	5	singlet	C_5H_5
90 MHz in $(CD_3)_2CO$ 	8.36 -8.21	12	complex	Me
	4.69	5	singlet	C_5H_5
	2.48	10	complex	Ph
	25.2	1	triplet ($J_{^{31}P\text{-}Co\text{-}H}$ = 76.5)	Co-H

TABLE V.3. Mass spectrum of the compound $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$

Compound	m/e	Rel. int.[a]	Assignment[b]
$Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}Me_2$	230	trace	$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}Me_2)^+$
	215	5	$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}Me)^+$
	200	100	$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\})^+$
	124	92	$(Co\{\eta^5\text{-}C_5H_5\})^+$
	76	23	$(PMe_3)^+$
	59	23	Co^+

a Relative intensity based on the largest m/e value (for metal containing species = 100)

b Tentative assignment for most chemically probable fragment to fit m/e value.

EXPERIMENTAL SECTION

SECTION A - GENERAL

All manipulations were carried out under nitrogen or vacuum unless otherwise stated. The general techniques used have been described elsewhere[100, 101]

Reagents.

"White Spot" or "High Purity" nitrogen was used as supplied by the British Oxygen Company Ltd. or Air Products Ltd. respectively. Petroleum ether, benzene, toluene, cyclohexane, diethylether, tetrahydrofuran, dichloromethane, were dried by refluxing them over finely ground calcium hydride and they were distilled before use, except as stated otherwise. Light petroleum ether refers to AnalaR grade boiling in the range 30^{o}-40^{o}C. The alumina used was 100-120 mesh as supplied by East Anglia Chemicals and was partially deactivated before use by exposure to the atmosphere. Celite refers to the diatomaceous earth Celite 545, used as supplied by Koch-Light Ltd. Standard calibration mixture, Chromosorb P, 80-100 mesh and alumina 80-100 mesh for gas-liquid chromatography were supplied by Phase Separations Ltd. Other reagents were used as supplied.

Analysis.

Microanalyses were carried out by the analytical service of the Inorganic Chemistry Laboratory.

Spectra.

Infrared spectra were recorded as Nujol mulls, between

KBr plates on a Perkin-Elmer instrument and calibrated with polystyrene film. The relative intensity of the bands is indicated as: vw, very weak; w, weak; m, medium; s, strong; vs, very strong. Broad bands are indicated by br. Assignments of the bands are indicated by superscripts as follows: a, C-H stretch of (η-C_5H_5); b, C-H stretch of Ph; c, C-C stretch or ring deformation of (η-C_5H_5); d, skeletal in-plane vibration of Ph; e, PF_6^-. Spectra are quoted in units of cm^{-1}.

^1H n.m.r. spectra at 60 MHz were recorded on a JEOL C60HL, at 90 MHz on a Perkin-Elmer R14, and at 100 MHz on a Perkin-Elmer R32. Spectra were calibrated using the solvent peaks as internal standards or TMS as internal or external standard. All shifts are quoted in ppm relative to TMS = 10. ^{13}C and pulse Fourier transform ^1H n.m.r. spectra were recorded on a Bruker WH 90. ^{13}C spectra were calibrated using solvent peaks as the internal standard. Chemical shifts of ^{13}C resonances are quoted in ppm downfield of TMS.

Mass spectra were recorded on an A.E.I. M.S.9 spectrometer. Only groups of peaks showing Mo isotope pattern or groups with Co are quoted and in the case of Mo compounds these are indicated by quoting the peak of the group observed corresponding to ^{98}Mo. No peaks are observed in the spectra above the highest peak quoted unless stated otherwise.

Chromatograms.

Gas-liquid chromatograms were obtained using a Pye-Unicam programmed instrument, series 104, model 14, with a

flame ionisation detector. Samples were injected either as liquid (0.3μL) or gas (0.3cm^3) and products identified by coincidence of retention times with those of standard samples. Different columns were used depending on the product to be identified. A list is given below and includes the normal operating temperature: KCl 10% on alumina (110^oC) - alkanes. $AgNO_3$, polyethylene glycol on Chromosorb P(R.T.)- alkenes. Polyethylene glycol on Chromosorb P (80^oC) - propene and cyclopropane.

SECTION B DETAILS FOR CHAPTER II

The preparation of $(Mo\{\eta^5\text{-}C_5H_5\}_2H_2)$

All reactions described in Chapters II and III involve derivatives of this compound, which was prepared many times in the course of this work by the method of Green *et al*[102] as modified by Green and Knowles[103].

Preparation of $(Mo\{\eta^5\text{-}C_5H_5\}_2Br_2)$

The compound $(Mo\{\eta\text{-}C_5H_5\}_2H_2)$ in toluene was treated with a large excess of $CHBr_3$. A green precipitate was formed immediately. The reaction mixture was magnetically stirred at room temperature for 10 min. to ensure complete reaction. The precipitate was collected by filtration, washed with acetone and dried under vacuum. No further purification was necessary. Yield 95%.

Preparation of $(Mo\{\eta\text{-}C_5H_5\}_2I_2)$

The complex $(Mo\{\eta\text{-}C_5H_5\}_2H_2)$ in toluene was treated with the stoichiometric amount of I_2 in toluene. A yellowish precipitate was formed immediately. The solution was filtered and the solid washed with acetone and dried under vacuum. No further purification was necessary.

Preparation of (1,2-bis(diphenylphosphino)ethane)bis(η^5-cyclopentadienyl)molybdenum bishexafluorophosphate.

This compound was prepared on a number of occasions.

Different routes and modified conditions were explored in attempts to improve the yield and convenience of the synthesis.

Method A

The compound ($Mo\{\eta^5-C_5H_5\}_2Br_2$) (8.20g, 21.2mmole) and dppe (8.46g, 21.2mmole) in acetone ($1000cm^3$) were magnetically stirred at 60^oC. The suspension was treated in a slow dropwise manner with a suspension of $TlPF_6$ (7.4g, 21.2mmole) in acetone ($600cm^3$) over a period of 12 hours. The reaction mixture was then allowed to stir for a further 6 hours. A further suspension of $TlPF_6$ (7.4g, 21.2mmole) in acetone ($600cm^3$) was then added over a period of 12 hours. After the addition had been completed, the solution was yellow. The solution was filtered through a Celite bed (2 cm) on a glass fritte filtration device. The solvent was removed under reduced pressure and the residual yellow solid was washed with water ($3x50cm^3$) and toluene ($3x50cm^3$). It was extracted with a mixture of acetone and methanol. The extract was filtered and concentrated by removal of the solvent under reduced pressure. Yellow crystals of $(Mo\{\eta^5-C_5H_5\}_2dppe)(PF_6)_2$ separated. They were filtered, washed with methanol and dried under vacuum. Comparison of its i.r. and ^1H nmr. spectra with those of an authentic sample showed them to be identical. Yield = 11.6g ≡ 60%. Yields from this route were found to be unreliable. The following improved method was adopted:

Method B

The compound ($Mo\{\eta^5-C_5H_5\}_2H_2$) (2g, 8.77mmole) was dissolved in dilute aqueous HCl (1:10) and the solution was

treated with NH_4PF_6 (1.47g, 9.0mmole) giving a bulky white precipitate of $(Mo\{\eta^5\text{-}C_5H_5\}_2H_3)PF_6$. This was collected, washed with water ($2x50cm^3$) and dried under vacuum. The salt was then dissolved in acetone ($50cm^3$) and the solution was added to dppe (3.65g, 9.2mmole) in acetone ($600cm^3$). The mixture became deep purple. It was allowed to stand at room temperature for a period of 12 hours, after which time the colour of the solution was yellow. Ammoniumhexafluorophosphate (1.47g, 9.0mmole) in water was added. Then the solvent was removed under reduced pressure giving a yellow-brown solid. This was collected and washed with water ($3x50cm^3$) and toluene ($3x50cm^3$). The residue was extracted with acetone (an orange-yellow solid (II) (1g) remained unextracted). The filtered extract was concentrated under reduced pressure. Addition of water and slow removal of further acetone gave yellow crystals of $(Mo\{\eta^5\text{-}C_5H_5\}_2dppe)(PF_6)_2$. The compound was identified by comparison of its ^1H nmr and i.r. spectra with those of an authentic sample. Yield 7g ≡ 87%. (Found: C, 47.0%; H, 3.7%. $C_{36}H_{34}F_{12}MoP_4$ requires: C,47.3%; H, 3.7%.)

Infrared spectrum

3163w[a], 3149w[a], 3120w[a], 3067vw[b], 1587w[d], 1575w[d], 1443vs, 1424m[c], 1417m[c], 1353w, 1345w, 1323w, 1265vw, 1200vw, 1194vw, 1167vw, 1123vw, 1118vw, 1103m, 1093w, 1082w, 1075vw, sh, 1033w, 1023w, 1007m, 988w, 958vw, 938vw sh, 918w sh, 911m, 885s, 873-823vs br[e], 778m, 770m, 758s, 748s, 733m sh, 713s, 703s, 671m, 624w, 613vw, 567vs[e], 536vs, 531vs, 505m, 489m, 476w, 453w, 433m, 416w, 406m, 393m, 383m.

^{1}H n.m.r. spectrum (recorded at 90 MHz in perdeuterio acetone).

τ: 6.09, 4, d($J_{^{31}P-CH_2}$ = 10.7), P-CH_2-CH_2-P; 4.28, 5, t($J_{^{31}P-Cp}$ = 2Hz), C_5H_5; 2.54 - 2.03, 20, c, Ph.

(II) could be recrystallised from either mixtures of dichloromethane/methanol or dichloromethane/ethanol or acetonitrile. Yield *ca* 15%. The yield of compound (II) seemed to increase when the above reaction was carried out at higher temperature (*ca* 70°C). Yield *ca* 80%. Yields of compound (II) were not consistent. (Found: C, 54.4%; H, 4.5%. $C_{36}H_{35}F_6MoP_3.\frac{1}{2}CH_2Cl_2$ requires: C 54.0%; H, 4.3%).

Infrared spectrum

3124vw[a], 3074vw[b], 1559w[d], 1543w[d], 1528w[d], 1489m, 1442s, 1436s[c], 1430s sh[c], 1374m sh, 1346w, 1324vw, 1310vw, 1280vw, 1254vw, 1228vw, 1198w, 1169w, 1116w, 1104m, 1076w, 1064vw, 1054w, 1034vw, 1024vw, 1016w, 1008w, 969w, 928vw, 917w, 879vs, 869 - 824 vs br[e], 813s, 794m, 759m, 754s, 746m, 736m, 706vs, 694s, 679m, 659m, 625w, 566vs[e], 536vs, 528vs, 501m, 492m, 468w, 452m, 421m, 406m, 392m.

Reaction of the yellow compound (II) with hydrochloric acid.

Approximately 200mg of the yellow compound (II) in CH_2Cl_2 (20cm^3) were treated with HCl (conc) (10cm^3). The reaction mixture was vigorously shaken for 20min, after which time the solvent was removed under reduced pressure. The resulting yellow solid was washed with CH_2Cl_2 and extracted with methanol. NH_4PF_6 dissolved in water was added and the solvent removed under reduced pressure. The resulting

solid was washed with water and crystallised from a mixture of acetone and water to give yellow crystals. They were collected and dried. Comparison of their i.r. and ^{1}H n.m.r. spectra with those of an authentic sample showed them to be $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$. Yield *ca* 60%.

Reaction of the yellow compound (II) with $NaBH_4$

Compound (II) (0.76g) was suspended in dry tetrahydrofuran ($30cm^3$) and treated with an excess of $NaBH_4$. The reaction mixture was magnetically stirred at room temperature for *ca* 4 hours until all the solid was dissolved to give a bright yellow solution. The solution was filtered, leaving a white powder (probably excess of $NaBH_4$) unextracted. Partial removal of the solvent under reduced pressure and cooling the solution to *ca* $-40^{o}C$ gave a bright yellow crystalline powder. It was separated by filtration and dried under vacuum. The product is insoluble in most common solvents, being most soluble in dichloromethane, but it decomposes to give a red solution. It is slightly soluble in warm toluene. No crystals of this product could be obtained. Yield *ca* 60%. (Found: C, 66.3%; H, 5.5%. $C_{36}H_{36}MoP_2$ requires: C, 69.0%; H, 5.7%.)

Infrared spectrum

3054vw[a], 3040vw[a], 3024vw[b], 1584vw[d], 1570vw[d], 1434s, 1428m sh[c], 1366m, 1313vw, 1266vw, 1247w, 1155vw, 1134vw, 1109vw, 1090m, 1084w sh, 1068w, 1042vw, 1025vw, 1011vw, 1003vw, 941vw, 914vw, 866w, 861w, 839w br, 820vw, 799m, 790m, 768w, 740s, 695vs, 689m sh, 655m, 643m, 612w, 556vw, 524s, 509s, 504s, 494vw,

484w, 449vw, 436w, 415m, 388s, 375s.

Reaction of the yellow compound (II) with Ph_3CPF_6.

The compound (II) was suspended in dry acetonitrile and treated with an excess of Ph_3CPF_6. The reaction mixture was magnetically stirred. After five seconds, the suspension became green. After 1 minute, water ($5cm^3$) was added. The solvent was removed under reduced pressure. The oily residue was washed with toluene ($2x5cm^3$) and extracted with ethanol. The solvent was removed under reduced pressure and a yellow residue was obtained. Comparison of its infrared spectrum with that of an authentic sample showed it to be $(Mo\{\eta\text{-}C_5H_5\}_2dppe)(PF_6)_2$.

Preparation of bis(acetonitrile)bis(η^5-cyclopentadienyl)-molybdenumbishexafluorophosphate.

The compound ($Mo\{\eta^5\text{-}C_5H_5\}_2I_2$) (5.47g, 11.4mmole) was suspended in acetonitrile ($60cm^3$). The suspension was magnetically stirred at 85^oC. $TlPF_6$ (8.76g, 25.0mmole) suspended in acetonitrile ($30cm^3$) was added dropwise. Immediately a bright yellow precipitate of TlI was formed and the solution became green. Continued addition gave rise to more precipitate and the solution turned red. After the addition was completed, the reaction mixture was left stirring at 85^oC for 12 hours. The red solution was filtered and the solvent was partially removed under reduced pressure. Addition of diethylether gave red crystals of $(Mo\{\eta^5\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$. The crystals were filtered, washed with diethylether and dried under vacuum. Yield *ca* 70%.

(Found: C, 28.5%; H, 2.7%; N, 5.0%. $C_{14}H_{16}F_{12}MoN_2P_2$ requires: C, 28.1%; H, 2.7%; N, 4.7%.)

Infrared spectrum

3137s[a], 2329m (C≡N stretch), 2305m (C≡N stretch), 1423m[c], 1420m[c], 1367m, 1119vw, 1077vw, 1025w, 1003w, 827 - 867vs br[e], 745m, 726w, 566vs[e], 445vw, 418w, 413w.

^1H n.m.r. spectrum (recorded in liquid SO_2)

τ: 4.02, 10, s, C_5H_5; 7.6, 6, s, CH_3.

Reaction of $W(\eta\text{-}C_5H_5)_2H_3^+$ with dppe.

The compound $(W\{\eta\text{-}C_5H_5\}_2H_3)PF_6$, prepared as described for the molybdenum analogue from $W\{\eta\text{-}C_5H_5\}_2H_2$ (0.72g, 2.28 mmole), was dissolved in acetone ($30cm^3$) and the solution added to dppe (0.91g, 2.29 mmole) in acetone ($100cm^3$). No colour change was observed. After 2 hours, the solution became pale pink and the colour deepened for the next 24 hours until it was red. An excess of aqueous NH_4PF_6 was added. The solvent was removed under reduced pressure. The resulting red solid was washed with water ($30cm^3$x2) and toluene ($30cm^3$x2) and dissolved in hot methanol. On cooling, a red precipitate was formed. Despite several attempts, no crystals could be obtained. An infrared spectrum of the red solid was taken. Further studies were discontinued.

Infrared spectrum

3127w[a], 3103vw[a], 3069vw[b], 3047vw[b], 1587w[d], 1572w[d], 1478m sh,

1435s, 1368m, 1313w, 1263vq, 1190vw, 1178w, 1163w, 1106w, 1097w, 1073w, 1053w, 1028w, 1013w, 1000w, 963vw, 933vw, 878m, 862vs, 843vs br[e], 833vs sh, 778w, 754m, 760m, 750m, 733m, 728m, 708m, 703m, 678w, 565s[e], 533m, 520w, 492w, 486w, 453w, 445vw, 428vw, 393w.

Preparation of (1,2-bis(diphenylphosphino)methane)bis(η^5-cyclopentadienyl)hydrido-molybdenum hexafluorophosphate and (1,2-bis(diphenylphosphino)methane)bis(η^5-cyclopentadienyl) molybdenum bishexafluorophosphate.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}_2H_3)PF_6$ (5.5g, 14.7mmole) in acetone ($30cm^3$) was transferred to a solution of diphenylphosphinomethane (6.21, 16.17mmole) in acetone ($400cm^3$) and the solution immediately became deep purple. The reaction mixture was left to stand at room temperature for 12 hours. After this time, the solution was yellow. NH_4PF_6 (2.6g, 15.95 mmole) in water ($15cm^3$) was added. The solvent was removed under reduced pressure. The resulting yellow product was washed with water ($3x50cm^3$) and toluene ($3x50cm^3$) and dried under vacuum. Dichloromethane extracted part of the precipitate, leaving an orange powder unextracted. From the dichloromethane solution, yellow crystals of $(Mo\{\eta^5\text{-}C_5H_5\}_2\{dppm\}H)PF_6$ were formed by addition of methanol and partial removal of dichloromethane under vacuum. Yield 4.6g ≡ 41%. (Found: C, 55.3%; H, 4.7%. $C_{35}H_{43}MoP_3$ requires: C, 55.6%; H, 4.4%.)

Infrared spectrum

3135vw[a], 3059vw[b], 1890vw (Mo-H stretch), 1587vw[d], 1571vw[d], 1438s, 1418m[c], 1371m sh, 1316w, 1280vw, 1265vw, 1195vw, 1187vw, 1157w, 1143vw, 1118vw, 1096m, 1077w, 1027vw, 1021w, 1000w, 985vw, 937vw, 921vw, 880s sh, 825 - 865vs br[e], 807s sh, 782m, 765m, 755m, 750m, 735m, 707s, 700s, 660w, 635w, 625vw, 567s[e], 545vw, 525m, 514m, 502m, 475vw, 452w, 437w, 427w, 415w, 410w, 387w.

The orange powder was crystallised from a mixture of acetone and ethanol to give pale orange crystals of $(Mo\{\eta^5\text{-}C_5H_5\}_2dppm)(PF_6)_2$. Yield 2.7g ≡ 20%. The yield did not vary significantly when the reaction was carried out at 70°C.

(Found: C, 46.6%; H, 3.5%. $C_{35}H_{42}F_{12}MoP_4$ requires: C, 46.7%; H, 3.6%.)

Infrared spectrum

3155vw[a], 3140w[a], 3100vw[b], 3075vw[b], 1585vw[d], 1575vw[d], 1447s, 1443s, 1411m[c], 1371m, 1345vw, 1325vw, 1195vw, 1166vw, 1121vw, 1141vw, 1095w, 1028vw, 1017vw, 1004w, 999w, 947w, 904w sh, 875s sh, 825 - 865br vs[e], 476w, 762m, 753m, 744m, 728m, 709m, 695m, 567s[e], 535m, 520m, 487w, 475vwm 426m, 397w.

Preparation of (1,2-bis(diphenylphosphino)methane)(chloro)bis (η^5-cyclopentadienyl)molybdenum hexafluorophosphate.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}_2\{dppm\}H)(PF_6)$ (1.22g, 3.78 mmole) in a mixture of dichloromethane (50cm^3) and chloroform (50cm^3) was left to stand at room temperature for *ca*

15 days. After this time some orange crystals were formed (0.1g) and the initially yellow solution became purple. The solution was filtered and removal of part of the dichloromethane under reduced pressure gave purple crystals. These were collected, washed with methanol and dried under vacuum. Yield 0.7g ≡ 52%.

(Found: C, 51.1%; H, 3.8%; Cl, 9.0%. $C_{35}H_{42}ClF_6MoP_3.\frac{1}{2}CH_2Cl_2$ requires: C, 51.2%; H, 4.0%;, Cl, 8.5%.)

Infrared spectrum

3124w[a] 3104w[a] 3060vw[b] 1585vw[d] 1572vw[d] 1480w, 1450m sh, 1438m, 1427w[c] 1415w[c] 1369w, 1358vw, 1337vw, 1312vw, 1365vw, 1230vw, 1210vw, 1190vw, 1165vw, 1160w, 1120vw, 1096w, 1076vw, 1030w, 1012vw, 1002w, 909vw, 882m, 862s, 845vs br[e] 832s, 805w sh, 777w, 762s, 758m sh, 750 m sh, 732s, 705s, 700s sh, 685vw, 670w, 569s[e] 550vw, 521m, 512m, 499m, 474w, 449m, 400m, 375s.

Comparison of the i.r. and ^1H nmr spectra of the orange crystals with those of a separately prepared and fully characterised sample showed them to be $(Mo\{\eta^5\text{-}C_5H_5\}_2\{dppm\})(PF_6)_2$. Yield = 6%.

Preparation of (1,2-bis(diphenylphosphino)ethane)(η^5-cyclopentadienyl)(η^3-cyclopentenyl)molybdenum.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}dppe)(PF_6)_2$, (7g, 7.66mmole) was suspended in tetrahydrofuran (400cm^3) and treated with $NaBH_4$ (3g, 78.9mmole). The reaction mixture was magnetically

stirred at room temperature for 2 hours, and then at 50°C for a further 2 hours to ensure complete reaction. After this time, all the initial solid had dissolved and the solution was dark orange. The solvent was removed under reduced pressure, and the resulting orange oil was extracted with toluene. The toluene solution was concentrated under vacuum and petroleum ether (100°-120°C boiling range) was added. The mixture was cooled at *ca* -40°C to give orange crystals. These were filtered, washed with light petroleum ether and dried under vacuum. Comparison of their infrared and n.m.r. spectra with those of an authentic sample shows them to be ($Mo\{\eta^5-C_5H_5\}\{\eta^3-C_5H_7\}dppe$). Yield *ca* 60%.

Infrared spectrum

3046vw[a], 3032vw[a], 3022vw[b], 2827vs, 2806m, 1586vw[d], 1573vw[d], 1484m, 1436s, 1419vw[c], 1369m, 1314vw, 1272vw, 1264vw, 1257vw, 1223w, 1184w, 1134w, 1109w, 1094w, 1074w, 1044w, 1029w, 1014w, 994w, 970vw, 914vw, 904vw, 870w, 849vw, 839vw, 824w. 801m, 770w, 740s, 724W, 694vs, 657m, 636w, 607vw, 526s, 513s, 493w, 481w, 458vw, 434w, 407m, 401m, 384s.

Mass spectrum

m/e: 628 (4, $(Mo\{\eta-C_5H_5\}\{\eta^3-C_5H_7\}dppm)^+$); 561 (10, $(Mo\{\eta-C_5H_5\}dppm)^+$).

Reaction of $(Mo\{\eta^5-C_5H_5\}_2\{NC-CH_3\}_2)(PF_6)_2$ with $NaBH_4$.

The compound $(Mo\{\eta^5-C_5H_5\}_2\{NC-CH_3\}_2)(PF_6)_2$ (1.6g, 2.67 mmole) was suspended in tetrahydrofuran and treated with

$NaBH_4$ (1g, 26.31mmole). The reaction mixture was magnetically stirred at room temperature for 2 hours. After this time, all the solid had dissolved and the solution was yellow. It was filtered and the solvent removed under reduced pressure. The resulting solid was extracted with toluene. The toluene solution was concentrated under vacuum and petroleum ether (100°-120°C boiling range) added. Yellow crystals with some brown impurity were formed. They were recrystallised (x2) from a mixture of toluene and petroleum ether (100°-120°C boiling range) at -20°C to give yellow crystals. These were identified as $\underline{(Mo\{\eta^5\text{-}C_5H_5\}_2H_2)}$ by comparison of their i.r. and ^1H nmr spectra with those of an authentic sample. Yield *ca* 70%.

SECTION C - DETAILS FOR CHAPTER III.

Preparation of (1,2-bis(diphenylphosphino)ethane)tri(chloro)(η^5-cyclopentadienyl)molybdenum.

The compound (Mo{η^5-C_5H_5}{η^3-C_5H_7}dppe), prepared as described from 5.3g of (Mo{η^5-C_5H_5}$_2H_2$) was dissolved in toluene (500cm^3). The resulting orange solution was cooled to *ca* -40^{o}C and hydrogen chloride gas was passed through the solution for a period of 8 min. A red oily precipitate separated. The solvent was removed under vacuum and the resulting red product was extracted with the minimum quantity of dichloromethane. The extract was filtered into methanol saturated with hydrogen chloride (30cm^3). Red crystals formed immediately. The solution was left to stand at room temperature for 12 hours, to allow the precipitation to be completed. The crystals were collected, washed with methanol and dried under vacuum. Overall yield 7.5g ≡ 49%. Comparison of the i.r. and n.m.r. spectra of the red crystals with those of an authentic sample identified them as (Mo{η^5-C_5H_5}{dppe}Cl_3).

The gaseous products evolved in this reaction were studied by g.l.c. on 10% KCl/Alumina column and shown to be cyclopentene.

Preparation of (1,2-bis(diphenylphosphino)ethane)(η^5-cyclopentadienyl)trihydridomolybdenum.

The compound (Mo{η^5-C_5H_5}{dppe}Cl_3) (3g, 4.5mmole) was suspended in toluene (60cm^3) and treated with a 70% solution

of $Na(AlH_2\{OCH_2CH_2OCH_3\}_2)$ in benzene (3g, 14.9mmole). The reaction mixture was left to stand at room temperature for 12 hours. After this time, all the red solid had reacted, giving a rich yellow solution. This was cooled to approximately -10°C and ethanol added dropwise with vigorous shaking until hydrogen evolution ceased. The solvent was removed under reduced pressure. The resulting yellow oil was extracted with the minimum amount of toluene and placed at the top of an alumina column made up in petroleum ether (60°-80° boiling range). A yellow band was formed, which was washed with light petroleum ether, eluted with toluene and collected. The toluene solution was concentrated under vacuum until it reached saturation. Addition of petroleum ether (100°-120°C boiling range) gave a milky supersaturated solution. This was cooled for 2 hours at -40°C, giving yellow crystals. These were collected, washed with light petroleum ether and dried under vacuum. Yield *ca* 50%.

(Found: C, 66.7%; H, 5.9%. $C_{31}H_{32}MoP_2$ requires: C, 66.2%; H, 5.7%.)

Infrared spectrum

3047vw[a], 1797m (Mo-H stretch), 1780m (Mo-H stretch), 1580 vw[d], 1567vw[d], 1478m sh, 1475m sh, 1433s, 1403m[c], 1369m sh, 1305w, 1270vw, 1262vw, 1237vw, 1177w, 1154vw, 1097m, 1087m, 1067w. 1027w. 1002w sh, 997w, 939vw, 917vw, 870m, 837vw, 824w, 794m, 767vw, 750m, 747s, 697vs, 669m, 647w, 612vw, 591vw, 545m, 527m, 517m, 487m, 472vw, 447vw, 430m, 388m.

Reaction of $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ with $NaBH_4$

The compound $Mo\{\eta\text{-}C_5H_5\}\{dppe\}Cl_3$ (2g, 3.0mmole) in dry tetrahydrofuran ($100cm^3$) was treated with $NaBH_4$ (3g, 79.3mmole). The reaction mixture was stirred magnetically at room temperature for *ca* 2 hours, giving a green solution. The solvent was removed under reduced pressure. The resulting green oily product was extracted with light petroleum ether. The green petroleum solution was concentrated under vacuum, and cooled to *ca* 0^oC, giving a green powder, which was separated by filtration. Attempts to obtain crystals from the green powder failed. Yield *ca* 25%.

Infrared spectrum

3098vw[a], 3070vw[a], 3048vw[b], 2418s (BH_4), 2390s (BH_4), 2318w, (BH_4), 1973vw, 1953vw, 1585w[d], 1570vw[d], 1482s, 1433vs, 1418w[c], 1410w[c], 1368w, 1328vw, 1305w, 1260vw, 1237vw, 1180m, 1158w, 1109vw, 1098m, 1069w, 1064w, 1029w, 1008w, 998w, 988vw, 978vw, 938w, 918vw, 910vw, 878m, 848vw, 814w, 808vs, 753s, 748s, 723vw, 700vs, 678s, 654w, 618vw, 544m, 526vs, 506s, 480m, 490w, 456vw, 425m, 398w, 378m, 354s.

Preparation of (1,2-bis(diphenylphosphino)ethane)(η^5-cyclopentadienyl)(1-methyl-η^3-allyl)molybdenum.

The compound ($Mo\{\eta^5\text{-}C_5H_5\}\{dppe\}H_3$) (0.2g, 0.36mmole) in toluene ($5cm^3$) was transferred into an ampoule and the solution was frozen to -196^oC. Butadiene was condensed into the ampoule ($2cm^3$) which was then sealed under vacuum. The reaction mixture was allowed to warm to room temperature

and then heated at 70°C for 12 hours. Orange crystals were formed. The contents of the ampoule were transferred to a Schlenk tube and the solvent was removed under reduced pressure. The orange residue was extracted with petroleum ether (60°-80°C boiling range). The solution was concentrated in vacuum until saturated and then cooled to -20°C for a period of 12 hours, giving orange crystals. These were collected, washed with light petroleum ether and dried under vacuum. Yield *ca* 70%. Comparison of its i.r. and ^{1}H n.m.r. spectra with those of an authentic sample showed it to be $(Mo\{\eta^5\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}\{dppe\})$.

Found: C, 68.2%; H, 6.1%. $C_{35}H_{36}MoP_2$ requires: C, 68.4%; H, 5.9%.)

Infrared spectrum

3060vw[a], 3054vw[a], 3042vw[b], 1590vw[d], 1575vw[d], 1485m sh, 1437s, 1410w[c], 1372m, 1315vw, 1280vw, 1170w, 1165w, 1115w, 1100m, 1090m, 1075vw, 1060vw, 1035w, 1005vw, 920vw, 868w, 812vw, 800w, 790m, 753s, 750s, 700vs, 687m, 662m, 640m, 625w, 538s, 527s, 520s, 492m, 467vw, 447m, 430w.

Preparation of (1,2-bis(diphenylphosphino)ethane)(η^4-butadiene)(η^5-cyclopentadienyl)molybdenum hexafluorophosphate.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}dppe)$ (0.1g, 0.16mmole) in dry dichloromethane (20cm^3) was treated with CPh_3PF_6 (0.065g, 0.17mmole) in dry dichloromethane (20cm^3) at 0°C. No precipitate was formed. The reaction mixture was heated at 50°C for 1 hour and dry diethylether was added.

A yellow precipitate was formed. The mother liquor was filtered off and discarded. The yellow solid was washed with ethanol until the ethanol washings were colourless. The resulting solid had an orange colour. It was crystallised from a mixture of acetone and ethanol to give orange crystals of $(Mo\{\eta^5\text{-}C_5H_5\}\{\eta^4\text{-}C_4H_6\}dppe)(PF_6)$ identified by comparison of its ^1H nmr and infrared spectra with those of an authentic sample. Yield *ca* 70%.

Found: C, 55.0%; H, 5.1%. $C_{35}H_{35}F_6MoP_3$ requires: C, 55.4%; H, 4.6%.)

Infrared spectrum

3080vw[a], 3060vw[b], 1575vw[d], 1565vw[d], 1484m sh, 1440s, 1432m sh[c], 1425m[c], 1164vw, 1100m, 1057w, 1003w, 954vw, 939vw, 910vw, 885m, 874s, 862s, 845vs br[e], 832s, 822m sh, 800m, 763m, 753m, 749m, 725vw, 705s, 674m, 654w, 625vw, 570s[e], 537s, 532s, 505w, 492vw, 470vw, 450w, 430w, 404w.

Preparation of (1,2-bis(diphenylphosphino)ethane)(η^5-cyclopentadienyl)di(hydrido)tris-n-butyltinmolybdenum.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}\{dppe\}Cl_3)$ (0.6g, 0.9mmole) was suspended in dry toluene ($50cm^3$) and treated with $HSn(n\text{-butyl})_3$ (0.84g, 2.9mmole). The reaction mixture was heated at 110°C for approximately 30min until all the solid had reacted. The solution became a rich yellow colour. The solvent was removed under reduced pressure. The resulting product was washed with dry light petroleum. The petroleum washings were pale yellow, and partial removal of the solvent under vacuum gave a few

yellow crystals. An infrared spectrum of the yellow crystals was recorded. The washed product was extracted in dry toluene giving a rich yellow solution. This was chromatographed on an alumina column, made up in dry petroleum ether (60^{o}-80^{o} boiling range). The resulting yellow band was washed with petroleum ether, then toluene. The first toluene washing had a yellow colour and this was collected. The solution was concentrated under vacuum until saturated and petroleum ether (100^{o}-120^{o}C boiling range) added. On cooling, a few yellow crystals were formed which were not enough for an infrared spectrum. Continued washings with toluene ($500cm^{3}$) moved the yellow band 2cm down the column. The eluent was changed to a 1:1 mixture of toluene and diethylether. The yellow solution was collected and concentrated under vacuum until saturated and petroleum ether (100^{o}-120^{o}C boiling range) was added, giving a small quantity of an oily precipitate. The mixture was filtered and the mother liquor was concentrated and cooled at -40^{o}C for 12 hours. Yellow crystals were formed. They were collected, washed with light petroleum and dried under vacuum. Yield *ca* 50%.

Infrared spectrum

3060vw[a], 3050vw[b], 1815w br (Mo-H stretch), 1588w[d], 1572w[d], 1484m, 1437s, 1435s, 1417vw[c], 1412w[c], 1368w, 1310w, 1375vw, 1186vw, 1160vw, 1110w, 1101m, 1096w, 1050vw, 1030w, 1002w, 927vw, 877w, 850vw, 841vw, 810m, 751m, 732w, 706s, 701s, 672m, 651w, 632vw, 622vw, 582vw, 530s, 520m, 507m, 497vw, sh, 486w, 442m, 417w, 392m.

Reactions of the compound ($Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$)

with CH_2=CHCN: ($Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$) (0.2g, 0.35mmole) in toluene ($50cm^3$) was treated with CH_2=CHCN (5g, 94.0mmole). The reaction mixture was left at room temperature for 12 hours and then heated at 60°C for a further 24 hours. A red precipitate was formed, and it was filtered, giving a red filtrate. The red precipitate was insoluble in most solvents. It was dissolved in acetonitrile and addition of acetone gave a red oily precipitate from which no tractable products could be isolated. From the red filtrate, the solvent was removed under reduced pressure, and the resulting red solid extracted with toluene. Addition of petroleum ether (100°-120°C boiling range) gave an orange-yellow product from which no tractable products could be isolated. The reaction was not further investigated.

with $CH_3\text{-}C{\equiv}C\text{-}CH_3$: $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ (0.5g, 0.89mmole) in toluene ($50cm^3$) was treated with $CH_3\text{-}C{\equiv}C\text{-}CH_3$ (0.048g, 1.78mmole). The reaction mixture was left at room temperature. No change was observed for a period of three hours. The reaction mixture was then heated at 100°C for 4 days. The solution was concentrated under vacuum and chromatographed on an alumina column made up in petroleum ether (60°-80°C boiling range). A yellow band was eluted with toluene. The solvent was partially removed under reduced pressure and petroleum ether (100°-120°C boiling range) added. On cooling, a yellow powder was formed from which no tractable products could be obtained.

with $PPhMe_2$: $(Mo\{\eta^5\text{-}C_5H_5\}\{dppe\}H_3)$ (0.2g, 0.35mmole) in toluene ($25cm^3$) was treated with $PPhMe_2$ (0.5g, 3.62mmole). The reaction mixture was heated at 110^oC for a period of 12 hours. A brown solid precipitated, and the solution became pale yellow. The precipitate was filtered and the filtrate discarded. The brown product was washed with toluene. No tractable products were isolated using common solvent extraction techniques.

with Libutyl: $(Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3)$ (0.2g, 0.35mmole) in dry toluene ($50cm^3$) was treated with Libutyl (1.0, 17.57mmole) and the yellow solution became deep orange. The solution was concentrated under vacuum and petroleum ether (60^o-80^oC boiling range) was added. A small precipitate was formed from which no tractable products could be isolated. The solution was then cooled to -40^oC and hydrolysed with water. The colour of the solution became yellow after hydrolysis. The organic coloured layer was decanted off and concentrated under vacuum, giving yellow crystals on cooling. These were filtered, washed with light petroleum and dried under vacuum. Their infrared spectrum identified them as unchanged starting material.

A portion of the orange solution, prior to hydrolysis, was treated with CO_2 for an hour at room temperature, after which time, ethanol was added to destroy the excess of Libutyl. The solution was concentrated under vacuum and chromatographed on an alumina column made up in petroleum ether (60^o-80^oC boiling range). The starting material, $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ was recovered.

A second portion of the orange solution was cooled at *ca* -10°C and treated with an excess of $PhCH_2Br$ in toluene. The colour of the solution became red. The solvent was partially removed under reduced pressure and the solution was chromatographed on an alumina column made up in petroleum ether (60°C-80°C boiling range). A red band was formed which was eluted with ethanol. Removal of the solvent under reduced pressure gave a red oily solid from which no tractable products could be isolated.

with Et_2Zn: ($Mo\{\eta^5\text{-}C_5H_5\}\{dppe\}H_3$) (0.35g, 0.62mmole) in dry toluene ($50cm^3$) was treated with a 2M solution of Et_2Zn in toluene ($3.11cm^3$, 0.076g, 0.62mmole). The colour of the solution, initially yellow, lightened noticeably and the solution became cloudy. A small grey metallic precipitate was formed. The solution was filtered and the precipitate discarded. An excess of Et_2Zn was added and the reaction mixture was left to stand at room temperature for a period of 12 hours. The solvent was then removed under reduced pressure. No tractable products were isolated from the resulting residue, and the reaction was not further investigated.

with MeI: $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ (0.35, 0.61mmole) in toluene ($40cm^3$) was treated with MeI ($0.04cm^3$, 0.61mmole). The reaction mixture was left at room temperature for 48 hours, after which time, the solution became red and a few pink needles were formed. The solution was separated by filtration and the needles collected. They were formed in low yield and no useful information was found from their i.r.,

^{1}H n.m.r. and mass spectra. Further studies were discontinued. The filtrate was concentrated under vacuum, and a red-brownish precipitate was formed, from which no tractable products could be isolated. The precipitate was redissolved in toluene and together with the rest of the filtrate was chromatographed on an alumina column made up in petroleum ether (60°-80°C boiling range). A red band was formed, which was eluted with toluene. No tractable products could be isolated from the toluene solution.

with $CHBr_3$: $Mo\{\eta\text{-}C_5H_5\}\{dppe\}H_3$ (0.5g, 0.89mmole) in toluene ($30cm^3$) was treated with an excess of $CHBr_3$. The solution, initially yellow, became red. The solution was concentrated warm, under reduced pressure, and allowed to cool to room temperature, giving some red crystals. They were collected, washed with light petroleum and dried under vacuum. Yield *ca* 70%.

Found: C, 49.7%; H, 4.2%; Br, 24.8%. $C_{31}H_{29}Br_3MoP_2.C_6H_5CH_3$ requires: C, 51.2%; H, 4.2%; Br. 26.9% .

The red crystals could be recrystallised from a mixture of dichloromethane and methanol.

Found: Br, 21.0%. $C_{32}H_{32}Br_2MoOP_2$ requires: Br, 21.3%.

Infrared spectrum

3400w br (O-H stretch), 3060vw[a], 1445vs, 1427w[c], 1417w[c], 1320 vw, 1268w, 1195vw, 1165vw, 1140vw, 1108m, 1080w, 1030m, 1010w, 890vw, 817m, 559m sh, 750s, 708s, 681m, 657w, 535vs, 507w, 480vw, 459w, 427w.

Preparation of (1,2-bis(diphenylphosphino)methane)(η^5-cyclopentadienyl)(η^3-cyclopentenyl)molybdenum.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}_2\{dppm\})(PF_6)_2$ (1g, 1.1mmole) was suspended in dry tetrahydrofuran (50cm^3) and treated with $NaBH_4$ (0.3g, 7.8mmole). The reaction mixture was magnetically stirred at room temperature until all the solid had dissolved (15min). The solution became a rich orange colour. The solvent was removed under reduced pressure and the resulting orange oil was extracted with toluene. The extract was concentrated in vacuum and petroleum ether (100°-120°C boiling range) was added. The resulting solution was cooled at -40°C for 48 hours. A mixture of orange crystals and colourless needles was formed. They were washed with acetone, when the colourless needles (probably free dppm) partially dissolved. The remaining orange crystals were dried under vacuum. Yield *ca* 40%.

Found: C, 69.9%; H, 5.9%. $C_{35}H_{34}MoP_2$ requires: C, 68.6%; H, 5.6%.

Infrared spectrum

3050vw[a], 3024vw[b], 1584w[d], 1570w[d], 1479m sh, 1432s, 1365m, 1306w br, 1272vw, 1262w, 1229w, 1195vw, 1189vw, 1132w, 1106w, 1090m, 1080w sh, 1062w, 1039vw, 1030w, 1000m, 845vw, 832vw, 812m, 790w, 753m, 741s, 737s, 708vs, 699vs, 673w sh, 649w, 613w, 535vs, 520vs, 486w, 474w, 458vw, 430m, 394m.

Preparation of (1,2-bis(diphenylphosphino)methane)tri(chloro)(η^5-cyclopentadienyl)molybdenum.

The compound $(Mo\{\eta^5\text{-}C_5H_5\}_2\{dppm\})(PF_6)_2$ (0.8g, 0.89mmole) was suspended in dry tetrahydrofuran ($50cm^3$) and treated with $NaBH_4$ as described above. The orange toluene extract was treated with HCl (gas). A red oily precipitate was formed and the solution remained orange. The red precipitate was crystallised from a mixture of dichloromethane and methanol giving purple crystals. The filtrate was allowed to stand for 12 hours and a mixture of yellow and purple crystals was formed, the solution remaining purple. The solution was filtered and concentrated under vacuum, some more purple crystals being formed. These were recrystallised from a mixture of dichloromethane and methanol, collected and dried under vacuum. Characterisation of the purple crystals showed them to be $(Mo\{\eta^5\text{-}C_5H_5\}\{dppm\}Cl_3)$. Yield *ca* 50%. The yellow crystals were formed in very low yield and no attempt was made to characterise them.

Found: C, 54.8%; H, 4.4%; Cl, 18.1%. $C_{30}H_{27}Cl_3Mo$ requires: C, 55.3%; H, 4.1%; Cl, 16.2%.

Infrared spectrum

3132vw[a], 3122vw[a], 3082vw[b], 3062vw[b], 1602vw[d], 1584vw[d], 1572vw[d], 1497w, 1482m sh, 1437, 1371m sh, 1352vw, 1320vw, 1264vw, 1192vw, 1164w, 1112w, 1095s, 1072w sh, 1032w, 1019w, 1011w, 1002w, 877w, 852w, 841vw, 832vw, 822m, 771vw, 762w, 743vs, 737s sh, 731vs, 702m sh, 699vs, 679w, 672vw, 537s, 516s, 489w, 479w, 444w, 430w, 413m, 404m.

Reactions of the compound ($Mo\{\eta^5-C_5H_5\}\{dppe\}Cl_3$)

with MeMgI: The compound ($Mo\{\eta^5-C_5H_5\}\{dppe\}Cl_3$) (0.8g, 1.2mmole) was suspended in dry diethyl ether ($50cm^3$). The suspension was cooled at approximately -40^oC and treated with MeMgI (3M solution in ether, $1.2cm^3$, 3.6 mmole). The reaction mixture was stirred for 2 hours at room temperature. After this time, all the solid had reacted and the solution became yellow. The solution was cooled at approximately -40^oC and ethanol was added. The solvent was removed under reduced pressure and the resulting yellow product extracted with toluene. Chromatography on an alumina column made up in petroleum ether (60^o-80^oC boiling range) gave a yellow band. This was eluted with toluene and collected. The toluene solution was concentrated under vacuum and petroleum ether (100^o-120^oC boiling range) was added. On cooling, some pale yellow crystals were formed. They were identified as dppe by comparison of their i.r. spectrum with that of an authentic sample.

with MeLi: The reaction was done as described above using dry tetrahydrofuran as the solvent. The only product which could be isolated was dppe.

with sodium amalgam in the presence of dppe: ($Mo\{\eta^5-C_5H_5\}\{dppe\}Cl_3$) (0.3g, 0.45mmole) and 1,2-bisdiphenylphosphinoethane (0.18g, 0.45mmole) in dry toluene ($75cm^3$) were vigorously shaken with sodium amalgam for a period of 10 min. The solution changed from red to yellow. The solvent was

removed under reduced pressure. The resulting product was extracted with warm petroleum ether (60^{o}-80^{o}C boiling range) to give a yellow solution. The solution was concentrated under vacuum and cooled to -20^{o}C. Some yellow crystals were formed with a brown-pink impurity. They were recrystallised (x2) by the same method. The crystals became paler in colour each time. They were filtered, washed with light petroleum ether and dried under vacuum. Comparison of their i.r. and $^{1}_{H}$ n.m.r. with those of an authentic sample showed them to be impure 1,2-bis(diphenylphosphino)ethane.

SECTION D - DETAILS FOR CHAPTER IV.

Preparation of di(carbonyl)(η^5-cyclopentadienyl)cobalt.

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2$) was used as starting material and prepared on a number of occasions as described in the literature[82].

Preparation of (η^3-allyl)(carbonyl)(η^5-cyclopentadienyl) cobalt hexafluorophosphate.

This compound was prepared by the method of Fischer[70].

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2$) ($6cm^3$, 8.4g, 46.68mmole) in dry cyclohexane ($20cm^3$) was treated with allylbromide (10g, 166mmole). The reaction mixture was heated for a period of 16 hours at 60°C. A yellow precipitate was formed, which was separated by filtration, washed with tetrahydrofuran, dried under vacuum and dissolved in water. Addition of NH_4PF_6 to the aqueous solution gave a yellow precipitate, which was recrystallised from acetone/water, to give yellow crystals of $(Co\{\eta^5\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$. Comparison of its infrared spectrum and ^1H n.m.r. spectrum with those of an authentic sample showed then to be identical. Yield 5.3g ≡ 34%.

Preparation of (carbonyl)(η^5-cyclopentadienyl)(1-methyl-η^3-allyl)cobalt hexafluorophosphate.

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2$) ($1\ cm^3$, 1.4g, 7.78mmole) in dry tetrahydrofuran ($10cm^3$) was treated with crotyl-bromide (3g, 22.22mmole). The reaction mixture was heated at

60°C for a period of 5 hours and a yellow precipitate was formed. It was filtered, washed with light petroleum and extracted with water. Addition of NH_4PF_6 dissolved in water, precipitated the cation as the PF_6 salt. The product was recrystallised from a mixture of acetone and water to give yellow flakes of $(Co\{\eta^5\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}CO)PF_6$. Yield = 35%.

Found: C, 34.0%; H, 3.5%. $C_{10}H_{13}CoF_6OP$ requires: C, 34.1%; H, 3.4%.

Infrared spectrum

3140w[a], 3120w[a], 2085vs (C≡O stretch), 1513w, 1413w[c], 1387m sh[c], 1370m, 1120vw, 1072vw, 1042w, 1027w, 990w, 979vw, 929vw, 881s, 840vs br[e], 780vw, 744vw, 726vw, 587w, 563vs[e], 522w, 510w, 483m, 470w, 446w.

Preparation of methallyliodide.

Methallyliodide was not commercially available. It was prepared by the method described in the literature[104]. Methallyl chloride was refluxed for an hour with an excess of a saturated solution of sodium iodide in acetone. The boiling point of the iodide is considerably higher than for the chloride or solvent, so the product was easily separated.

Preparation of (carbonyl)(η^5-cyclopentadienyl)(2-methyl-η^3-allyl)cobalt hexafluorophosphate and (η^5-cyclopentadienyl)(iodo)(2-methyl-η^3-allyl)cobalt.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2)$ (1.0cm^3, 1.4g, 7.78

mmole) in petroleum ether (100°-120°C boiling range) ($30cm^3$) was treated with methallyliodide (6g, 33.0mmole, excess). The reaction mixture was left to stand at room temperature for a period of 12 hours, after which time a mixture of yellow and black crystals was formed. These were separated from the solvent by filtration and washed with light petroleum ether. The yellow crystals were extracted with water and the cation precipitated as the PF_6^- salt by addition of NH_4PF_6. The product was recrystallised from a mixture of acetone/water, giving yellow crystals of $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}CO)PF_6$.

Yield *ca* 15%.

Found: C, 34.1%; H, 3.5%. $C_{10}H_{13}CoF_6OP$ requires C, 34.1%; H, 3.4%.

Infrared spectrum

3138m[a], 2083vs (C≡O stretch), 1418m[c], 1397m, 1371m, 1343w, 1123vw, 1073vw, 1043w, 1029m, 1003vw, 983vw, 963vw, 923w, 878vs, 823 - 858vs, br[e], 783w sh, 745vw, 728vw, 594w, 565vs[e], 523m, 488s, 422m.

The black crystals were insoluble in water. They were dissolved in the minimum amount of toluene giving a dark red solution. Addition of petroleum ether (100°-120°C boiling range) followed by cooling at -40°C for a period of 12 hours gave black crystals of the neutral complex $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}I)$. Yield *ca* 35%.

Found: C, 35.8%; H, 4.4%; I, 41.6%. $C_9H_{13}CoI$ requires: C, 35.3%; H, 3.9%; I, 41.2%.

Infrared spectrum

3098vw[a], 3086vw[a], 3052vw[a], 1440m[c], 1405m[c], 1369m, 1350w, 1330w, 1027vw, 1013vw, 1051w, 1040w, 1020w, 990w, 950vw, 932vw, 928w, 898m, 839s, 837s, 823s, 778w, 740vw, 725vw, 538w, 578vw, 438vw, 413w, 400m, 385m.

Reaction of $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3C_3H_4\}I)$ with CO.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}I)$ (0.3g, 0.98mmole) in toluene ($20cm^3$) was heated at 80^oC, and CO was bubbled through the solution for a period of 2 hours. A yellow precipitate was formed. It was separated by filtration, washed with light petroleum and extracted with water. Addition of an aqueous solution of NH_4PF_6 gave a yellow precipitate that was crystallised from acetone/water to give yellow crystals. Comparison of its i.r. spectrum with that of a separately prepared and fully characterised sample showed it to be $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}CO)PF_6$. Yield *ca* 70%.

Reaction of $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2)$ with methylallylchloride.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2)$ ($1.0cm^3$, 1.4g, 7.78 mmole) in petroleum ether (100^o-120^oC boiling range) ($30cm^3$) was treated with methylallylchloride (3g, 33.15mmole, excess). The reaction mixture was heated for a period of 48 hours at 70^oC and a small yellow precipitate was formed. The temperature was increased to 90^oC and the reaction mixture was left for a further 48 hours, after which time the yellow preci-

pitate was separated by filtration, washed with light petroleum ether and extracted with water, giving a yellow solution from which a yellow precipitate was obtained by addition of NH_4PF_6. This was crystallised from acetone/water. Comparison of its ^1H nmr and i.r. spectra with those of an authentic sample showed that the compound was $(Co\{\eta^5\text{-}C_5H_5\}_2)PF_6$. Yield *ca* 23%.

Reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$ with PPh_3

The compound $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$ (0.35g, 1.03 mmole) in acetone ($30cm^3$) was treated with an excess of PPh_3. The reaction mixture was kept magnetically stirring at 70^oC for a period of 2 hours and the solution, initially yellow, became red. No further changes were observed. The solvent was removed under reduced pressure and the resulting product was extracted with toluene. The toluene extract was red and a white solid remained unextracted. The toluene solution was concentrated in vacuum and petroleum ether (100^o-120^oC boiling range) added. The mixture was cooled to *ca* -20^oC to give red crystals. These were collected, washed with cool light petroleum ether and dried under vacuum. Comparison of their infrared and ^1H n.m.r. spectra with those of an authentic sample showed them to be $(Co\{\eta\text{-}C_5H_5\}\{PPh_3\}CO)$. Yield *ca* 60%.

The white solid which was not extracted with toluene was crystallised from a mixture of acetone and water to give white crystals. They were identified as $(PPh_3\{CH_2\text{-}CH{=}CH_2\})PF_6$ by comparison of their infrared spectrum with that of an authentic sample.

Preparation of the compounds ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PR_3$) (where $PR_3 = PPh_3$, $PPhMe_2$, PMe_3).

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPh_3$) was prepared by the method of King[68].

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}_2$) (1 cm^3, 1.4g, 7.78mmole) in petroleum ether (100°-120°C boiling range) (50cm^3) was treated with PPh_3 (2.1g, 8 mmole). The reaction mixture was heated at 90°C for a period of 12 hours. Gas evolution was observed and the pressure was released twice. The solution was cooled at -40°C for a period of 12 hours, to give prismatic red crystals of ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPh_3$). They were filtered, washed with light petroleum ether and dried under vacuum.

The compounds ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPhMe_2$) and ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PMe_3$) were prepared similarly, using instead of 50cm^3 of solvent, a volume of 20cm^3, due to their higher solubility.

In the preparation of ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PMe_3$), only 2 hours of heating were required. The red crystals were filtered and washed at -78°C.

($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPh_3$) and ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPhMe_2$) were characterised by comparison of their i.r. and ^1H n.m.r. spectra with those of an authentic sample.

($Co\{\eta^5\text{-}C_5H_5\}\{CO\}\{PMe_3\}$) was found to be pyrophoric. Analysis could not be obtained. It was characterised by ^1H n.m.r., i.r. and mass spectroscopy. The yields of these reactions were *ca* 80%.

Infrared spectrum

3120vw[a], 1925vs br (C≡O stretch), 1890vs br (C≡O stretch), 1437vw[c], 1428s[c], 1413vw[c], 1402w[c], 1370w, 1352vw, 1302vw, 1165w br, 1110w, 1015m, 982m sh, 953vs br, 925m sh, 865s, 855w sh, 835vw sh, 798vs, 732vs, 671s, 598m, 577vs, 495m, 405m.

Preparation of (η^3-allyl)(η^5-cyclopentadienyl)(dimethylphenylphosphino)cobalt hexafluorophosphate.

The compound (Co{η^5-C_5H_5}{CO}$PPhMe_2$) (1g, 3.45mmole) in petroleum ether (100°-120°C boiling range) (50cm^3) was cooled to approximately -10°C by occasionally dipping the vessel in liquid nitrogen, and treated dropwise with allylbromide (1.0g, 8.26mmole). An orange brown precipitate was formed immediately, and gas evolution was observed. The precipitate was separated by filtration and washed with petroleum ether (60°-80°C boiling range). The petrol washings had a yellow colour and removal of the solvent under reduced pressure gave yellow crystals, only enough for an infrared spectrum. The orange-brown precipitate was dissolved in water. Addition of an aqueous solution of NH_4PF_6 gave a precipitate. Several attempts were made to crystallise this from acetone/water, but only oily precipitates formed. After several attempts, orange flakes were finally formed by removing the acetone slowly from an acetone/water solution.

Yield = 20%.

Found: C, 42.6%; H, 5.0%. $C_{16}H_{21}CoF_6P_2$ requires: C, 42.9%; H, 4.7%.

Infrared spectrum

3124w[a], 3064w[b], 1575vw[d], 1444s, 1424w[c], 1419m[c], 1395w[c], 1329m, 1314m, 1302m, 1224vw, 1214w, 1167vw, 1114w, 1104w, 1084vw, 1072w, 1064vw, 1024w, 1014w, 1004w, 974m, 964m, 940w, 924s, 909w, 892s, 844vs br[e], 794m sh, 779m, 749s, 719s, 702s, 684m, 579m, 564vs[e], 502vs.

Reaction of $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPhMe_2)$ with crotylbromide.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPhMe_2)$ (2g, 6.9mmole) in toluene ($30cm^3$) was treated with crotylbromide (3g, 22.22mmole). An oily brown precipitate was formed immediately, and gas evolution was observed. The precipitate was separated by filtration and dissolved in the minimum quantity of acetone. It was chromatographed on an alumina column made up in petroleum ether (60^o-80^oC boiling range). The same solvent eluted a yellow band which was collected, and the solution concentrated in vacuum giving yellow crystals. These were filtered, washed with light petroleum ether and dried under vacuum. Yield = 0.25g. Their i.r. spectrum showed them to be identical to the yellow crystals, soluble in petroleum ether, formed as a byproduct in the reaction of $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}PPhMe_2)$ with allyl bromide. Further attempts to characterise them were made. No useful information was obtained from their ^1H n.m.r. and mass spectra and further studies were not carried out.

Infrared spectrum of the yellow crystals.

3050vw, 3020vw, 1967vs, 1900vs br, 1875m, 1867m, 1583vw,

1570vw, 1440m, 1415w, 1405w, 1324vw, 1303w, 1297vw, 1282w, 1112w, 955w, 945m, 910s, 870vw, 855w, 842w, 745m, 720m, 695s, 680w, 572m, 555w, 490m, 429w, 418w.

Further elution with toluene, diethylether and ethanol was tried. Ethanol eluted an orange band which was collected. The solvent was removed under reduced pressure and the resulting residue was extracted with acetone. Addition of water gave a brown oily product from which no tractable product could be isolated and studies were not continued.

Preparation of (η^3-allyl)(η^5-cyclopentadienyl)trimethyl-phosphinocobalt hexafluorophosphate.

The compound (Co{η^5-C_5H_5}{CO}PMe_3) (1.4g, 6.14mmole) in petroleum ether (100°C-120°C boiling range) (30cm^3) was cooled in liquid nitrogen and treated dropwise with allyl bromide (1g, 8.26mmole). While the addition took place, the reaction mixture was vigorously shaken. A yellow precipitate was formed in a few seconds. After the addition had taken place, the reaction mixture was left to stand at room temperature for a period of 30 min. After this time, the precipitate was separated by filtration. (The filtrate was left to stand for three days at room temperature and some more yellow precipitate (300mg) was slowly formed). The yellow precipitate was dissolved in water and transformed into the PF_6 salt by addition of an aqueous solution of NH_4PF_6. The product was separated by filtration and washed with water; it was dissolved in the minimum quantity of acetone and transferred to the top of a 40cm alumina column prepared in petroleum ether (60°-80°C

boiling range). The resulting band was washed with petroleum ether (60^{o}-80^{o}C boiling range), toluene and diethylether. Passage of a 1:1 mixture of diethylether and acetone caused an orange band to develop. The orange solution was collected and the ether and part of the acetone was removed under reduced pressure. Addition of water and slow removal of some more acetone gave a milky supersaturated solution. This was left to stand for a period of 12 hours to give orange needles of $(Co\{\eta^5\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}PMe_3)PF_6$. Yield *ca* 60%.

Found C, 34.6%; H, 5.2%. $C_{11}H_{19}CoF_6P_2$ requires: C, 34.2%; H. 4.9%.

Infrared spectrum

3112w[a], 1420m[c], 1400w[c], 1370m, 1320w, 1300s, 1122vw, 1075vw, 1065vw, 1030w, 1015m, 1002m, 972vs, 910w, 880s, 850 - 830vs br[e], 788m, 737m, 680m, 670vw sh, 590w, 564vs[e], 450m, 420m, 408m.

Further elution of the column with 3:1 acetone:water gave a second yellow band. The solution was collected and the acetone removed under reduced pressure to give yellow crystals. Comparison of its i.r. and ^1H n.m.r. spectra with those of a separately prepared and fully characterised sample showed it to be $(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$. Yield *ca* 10%.

Preparation of (η^5-cyclopentadienyl)(1-methyl-η^3-allyl)trimethylphosphinocobalt hexafluorophosphate.

This compound was prepared as described above. $(Co\{\eta\text{-}C_5H_5\}\{CO\}PMe_3)$ (1.4g, 6.14mmole) was treated with

crotyl bromide (1.4g, 11.1mmole). An orange precipitate was formed which was separated from the mother liquor by filtration. From the precipitate, two compounds were isolated as already described: $\underline{(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2}$ which was identified by comparison of its i.r. and ^1H n.m.r. spectra with those of a separately prepared and fully characterised sample (yield *ca* 30%); and $\underline{(Co\{\eta^5\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}PMe_3)PF_6}$ (yield *ca* 25%). Found: (average of two determinations) C, 36.0%; H, 5.4%. $C_{12}H_{21}CoF_6P_2$ requires: C, 36.0%; H, 5.3%.

Infrared spectrum

3140s[a], 3080vw[s], 1507vw, 1449s[c], 1442s[c], 1430s[c], 1420s[c], 1370m, 1320w, 1300vs, 1203w, 1185vw, 1034s, 1027m sh, 1013w, 1000vw, 955vs br, 820 - 885vs br[e], 780s, 786s, 679s, 600w, 582m, 562vs[e], 492w, 459m, 403s, 391s, 370m.

The filtrate was left to stand for approximately 15 days at room temperature. After this time, some more of the orange precipitate was formed, and a few black crystals were also formed. The mixture of black crystals and orange product was separated by filtration, washed with light petroleum ether and dried under vacuum. Water extracted the orange product. The black crystals were then dissolved in toluene. The dark red toluene solution was concentrated under vacuum until saturated and petroleum ether (100°-120°C boiling range) added. On cooling at -40°C for 12 hours, black crystals of the neutral compound $\underline{(Co\{\eta^5\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}Br)}$ were formed. Yield *ca* 10%. Found: C, 42.0%; H, 4.6%; Br, 31.0%. C_9H_7CrCo requires: C, 41.7%; H, 4.6; Br 30.9%.

Preparation of (η^5-cyclopentadienyl)(2-methyl-η^3-allyl)trimethylphosphinocobalt hexafluorophosphate.

The compound ($Co\{\eta^5-C_5H_5\}\{2-CH_3-\eta^3-C_3H_4\}I$) (0.5g, 1.6 mmole) in acetone ($30cm^3$) was treated with PMe_3 (1g, 13.15 mmole). An orange precipitate was immediately formed and the colour of the supernatant liquid changed from the original dark red to orange. The precipitate was separated by filtration and extracted with water. The cation was precipitated as the PF_6^- salt by addition of NH_4PF_6. The orange precipitate was filtered, washed with water and recrystallised from a mixture of acetone/water to give orange microcrystals of $(Co\{\eta^5-C_5H_5\}\{2-CH_3-\eta^3-C_3H_4\}PMe_3)PF_6$. Yield *ca* 75%.

Found: C, 35.7%; H, 5.4%. $C_{12}H_{21}CoF_6P_2$ requires: C, 36.0%; H, 5.3%.

Infrared spectrum taken from the salt ($Co\{\eta-C_5H_5\}\{2-CH_3-\eta^3-C_3H_4\}PMe_3)I$

3062w[a], 1436m[c], 1427m[c], 1417m[c], 1371w, 1329vw, 1300vs, 1264w, 1052vw, 1042vw, 1032w, 1022m, 992w, 967vs, 948s, 954s sh, 930w, 912vw, 882w, 864m, 852w, 844s, 838m, 798vw, 735s, 681m, 597vw, 452w, 422w, 414m, 404m.

Preparation of (η^5-cyclopentadienyl)(2-methyl-η^3-allyl)pyridinecobalt hexafluorophosphate.

The compound ($Co\{\eta^5-C_5H_5\}\{2-CH_3-\eta^3-C_3H_4\}I$) (0.2g, 0.76 mmole) in acetone ($20cm^3$) was treated with pyridine (0.978g, 12.4mmole). The reaction mixture was heated for approximately 10min at 60°C, during which time the solution lightened notice-

ably in colour. NH_4PF_6 dissolved in water was added to the acetone solution giving a red precipitate which was first crystallised from acetone/water and then recrystallised from hot methanol to give red needles of $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}py)PF_6$. Yield = 75%.

Found: C, 42.0%; H, 4.7%; N, 3.4%. $C_{14}H_{18}CoF_6NP$ requires: C, 41.7%; H, 4.2%; N, 3.5%.

Infrared spectrum

3121w[a], 3074vw[b], 1608w (C≡N stretching), 1453vs, 1413vw[c], 1371m, 1338vw, 1291vw, 1226vw, 1079w, 1043vw, 1033vw, 1021vw, 883m, 863s, 843vs br[e], 800w, 764m, 726vw, 707m, 701w, 563s[e].

Preparation of (ammonia)(η^5-cyclopentadienyl)(2-methyl-η^3-allyl)cobalt hexafluorophosphate.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}I)$ (0.3g, 0.98 mmole) in acetone ($20cm^3$) was treated with NH_3 (0.88g, 6.29 mmole). The colour of the solution, initially dark red, lightened slightly. The acetone was partially removed under reduced pressure and addition of aqueous NH_4PF_6 gave a red precipitate, which was crystallised from acetone/water to give red crystals of $(Co\{\eta^5\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta^3\text{-}C_3H_4\}NH_3)PF_6$. Yield = 75%.

Found: C, 31.9%; H, 4.4%; N, 3.9% (average of two determinations). $C_9H_{16}CoF_6NP$ requires: C, 31.7 %; H, 4.4%; N, 4.1%.

Infrared spectrum

3391s (N-H stretch), 3308m (N-H stretch), 3223w, 3122vw[a],

1632m, (N-H bending), 1415vw[c], 1389s, 1321m, 1336w, 1295s, 1123vw, 1045vw, 1031w, 1003vw, 958w, 931vw, 903m, 883s, 833 - 863vs br[e], 813s, 783w sh, 745w, 590w, 564vs[e], 473vw, 448w, 415m.

Preparation of (carbonyl)(η^5-cyclopentadienyl)di(iodo)cobalt.

This compound was prepared by the method of King[68].

($Co\{\eta-C_5H_5\}\{CO\}_2$) (1.0cm^3, 1.4g, 7.78mmole) in dry diethylether (5cm^3) was treated with I_2 (2g, 7.88mmole) in dry diethyl ether (50cm^3). The formation of a black precipitate occurred immediately with simultaneous gas evolution. The reaction mixture was stirred for a period of 24 hours at room temperature (during this time the pressure was released twice). The solvent was partially removed under reduced pressure, and the black crystalline precipitate separated by filtration, washed with diethyl ether and dried under vacuum. Comparison of the i.r. and ^1H n.m.r. spectra of the black crystals with those of an authentic sample showed them to be ($Co\{\eta^5-C_5H_5\}\{CO\}I_2$). Yield 2.5g ≡ 85%. No further purification of the product was necessary.

Preparation of (η^5-cyclopentadienyl)(dimethylphenylphosphino)di(iodo)cobalt.

This compound was prepared by the method of King[68].

($Co\{\eta^5-C_5H_5\}\{CO\}I_2$) (2.4g, 5.91mmole) in dry methylene chloride (50cm^3) was treated dropwise with PMe_2Ph (1g, 7.25 mmole) in dry methylene chloride (30cm^3). The reaction mixture was kept magnetically stirring at room temperature for a period of 12 hours. The colour of the solution, initially

deep purple, did not change, though gas evolution was observed. The solvent was partially removed under reduced pressure, and hexane ($50cm^3$) was added to give very deep purple crystals. The product was filtered, washed with hexane and dried under vacuum to give $(Co\{\eta^5\text{-}C_5H_5\}PPhMe_2I_2)$. Yield 2.9g ≡ 95%.

Found: C, 30.6%; H, 3.2%. $C_{13}H_{16}CoI_2P$ requires: C, 30.2%; H, 3.1%.

Infrared spectrum

3103vw[a], 3089vw[a], 3077w[b], 1572vw[d], 1434m, 1431w[c], 1423vw[c], 1413m[c], 1366w, 1356w, 1342vw, 1319vw, 1302w, 1294vw, 1284w, 1280w, 1264vw, 1196vw, 1157vw, 1109s wh, 1103m, 1074vw, 1064vw, 1058vw, 1017w, 1019w, 1003vw, 999vw, 995vw, 944m, 937m, 914s, 885w, 873w, 854w, 840m, 835m, 824m, 750m, 747m, 744m, 719m, 699m, 693m, 684vw, 679w, 581m, 494vs.

Preparation of (η^5-cyclopentadienyl)di(iodo)trimethylphosphinocobalt.

$(Co\{\eta^5\text{-}C_5H_5\}I_2CO)$ (1g, 5.55mmole) in dry methylene chloride was treated with the stoichiometric amount of PMe_3 (0.45g, 5.92mmole). Immediately a yellow precipitate of $(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3(I)_2$ was formed. The reaction was not quantitative, the supernatant methylene chloride remaining deep purple. The liquor was filtered off, and the solution concentrated under reduced pressure. Addition of hexane gave purple crystals. Characterisation of these purple crystals by ^1H n.m.r. and i.r. spectroscopy showed them to be a (1:1) mixture of the starting material $(Co\{\eta^5\text{-}C_5H_5\}\{CO\}I_2)$ and

($Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}I_2$). No further attempts to separate them were made.

<u>^1H n.m.r. spectrum</u>

τ: 4.07, <u>5</u>, s (C_5H_5, $Co\{\eta\text{-}C_5H_5\}\{CO\}I_2$); 4.7, <u>5</u>, s ($C_5H_5$, $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}I_2$); 7.88 - 8.13, <u>15</u>, c, (PMe_3 and d^6 acetone).

<u>Preparation of (η^5-cyclopentadienyl)tris(trimethylphosphino) cobalt bishexafluorophosphate</u>.

The compound ($Co\{\eta^5\text{-}C_5H_5\}\{CO\}I_2$) (7.5g, 18.47mmole) in dry methylene chloride ($50cm^3$) was treated with PMe_3 (5g, 67.5mmole). A yellow precipitate was immediately formed and gas evolution observed. The pale purple supernatant liquor was separated by filtration and discarded. The yellow precipitate was extracted with water and the cation precipitated as its hexafluorophosphate salt by addition of NH_4PF_6. The PF_6 salt was crystallised from acetone/water to give bright yellow crystals of <u>$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$</u>.

Yield 70%.

Found: C, 26.2%; H, 4.7%. $C_{14}H_{32}CoF_{12}P_2$ requires: C, 26.2%; H, 5.0%.

<u>Infrared spectrum</u>

3138w[a], 1450s sh[c], 1427m sh[c], 1369m, 1322m, 1318s, 1299w sh, 102Lm, 972s, 950vs, 840vs br[e], 777m, 740m, 677w, 561vs[e], 472vw, 450vw, 421w, 400m, 390m.

SECTION E - DETAILS FOR CHAPTER V

Preparation of the columns

10% KCl on alumina

80-100 mesh alumina was weighed and placed in a 500ml flask. The KCl was then weighed out and dissolved in a small quantity of water. The quantity of water used was such that when this solution was added to the alumina, a slurry was formed. This prevented the mesh size of the alumina from being reduced. This slurry was then dried under vacuum and sieved to 80-100 mesh before packing in the column. The packing was done using a vacuum line and continuous tapping to ensure a reasonable uniformity of packing. The column was conditioned at 120^{o}C for 12 hours.

Silver nitrate / polyethylene glycol on Chromosorb P

0.42g of silver nitrate were dissolved in approximately 30cm^3 of acetonitrile. This was then mixed with 2.55cm^3 of polyethylene glycol and made into a slurry with 14.9g of Chromosorb P. The homogeniser acetonitrile was removed under reduced pressure and the freely flowing material was sieved to 80-100 mesh and packed into a glass column. The column was conditioned at 50^{o}C for 12 hours.

Polyethylene glycol on Chromosorb P.

This column was prepared as described above. 5.01g of polyethylene glycol was taken up in acetonitrile (20cm^3) and 18.9g of support added.

Reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}CHR{=}CR'{=}CH_2\}L)PF_6$ (L = PMe_3, CO) (R, R' = H, Me) with $NaH_2(OCH_3CH_3OCH_3)_2$.

A typical reaction is described.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$ (50mg, 0.15 mmole) was suspended in dry toluene ($1cm^3$). The suspension was cooled at *ca* -20°C and treated with an excess of $NaH_2(OCH_3CH_2OCH_3)_2$. The solid reacted readily giving a red solution. The reaction mixture was allowed to warm to room temperature and the solution became brown. The gaseous products evolved in the reaction were investigated by gas-liquid chromatography using a polyethylene glycol on Chromosorb P column and a 10% KCl on alumina column. The product was shown to be propene. After a period of 15 days, the gaseous products from the same reaction vessel were again investigated, and they were shown to be mainly propane and traces of propene.

Attempts to isolate any tractable organometallic products in previous reactions failed.

Reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}CHR{=}CR'{=}CH_2\}L)PF_6$ (L = PMe_3, CO) (R, R' = Me, H) with MeLi.

A typical reaction is described.

The compound $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}CO)PF_6$ (50mg, 0.15mmole) was suspended in dry diethyl ether cooled at *ca* -20°C and treated with an excess of MeLi ($1cm^3$ of 2M ether sol., 2 mmole). The solid reacted rapidly giving a brownish solution. The reaction mixture was allowed to warm to room temperature and the gaseous products evolved in the reaction were examined by

gas-liquid chromatography using a silver nitrate / polyethylene glycol on Chromosorb P column and a 10% KCl on alumina column. The product was shown to be propene. No changes were observed when the products were examined after 15 days.

Reaction of $(Co\{\eta\text{-}C_5H_5\}\{\eta^3\text{-}C_3H_5\}PMe_3)$ with MeLi

This reaction was carried out as described in the general method.

The reaction mixture had an orange colour and attempts to isolate an organometallic product were made.

The reaction mixture was cooled at *ca* -20°C and water added to destroy the excess of MeLi. The solvent was removed under reduced pressure and the orange oily residue was extracted with petroleum ether (60°-80°C boiling range). Chromatography on alumina column, made up in petroleum ether (60°-80°C boiling range) gave an orange band which was eluted with light petroleum. The solvent was removed under reduced pressure and the resulting orange oil was distilled at high vacuum (t = 45°C). Orange crystals could be obtained by cooling at -78°C a saturated solution of the product in light petroleum. They were characterised as $Co\{\eta\text{-}C_5H_5\}\{Me_2\}PMe_3$, by comparison of their infrared and ^1H n.m.r. spectra with those of a separately prepared and fully characterised sample.

Preparation of (η^5-cyclopentadienyl)bis(dimethyl)phenylphosphino)hydridocobalt hexafluorophosphate.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{PMe_2Ph\}I_2)$ (0.5g, 0.97mmole) in dry tetrahydrofuran (50cm^3) was cooled to approximately -30°C

by dipping the vessel in liquid nitrogen and treated with isopropylmagnesiumbromide (3.0cm^3 of 2M ether sol., 6 mmole). The reaction mixture was stirred magnetically and the colour of the solution changed from the original purple to orange after about 1 min. No further changes were observed. The reaction mixture was then cooled at approximately -10°C and ethanol added to destroy the excess of isopropylmagnesium-bromide. The solvent was removed under reduced pressure, and the resulting solid extracted with water to give a yellow solution. The solution was filtered and addition of an aqueous solution of NH_4PF_6 gave a yellow precipitate, which was separated by filtration, washed with water and recrystallised from acetone/water to give yellow crystals of $(Co\{\eta^5\text{-}C_5H_5\}\{PPhMe_2\}_2H)PF_6$. Yield = 70%.

Found: C, 46.7%;, H, 5.3%. $C_{21}H_{28}CoF_6P_6$ requires: C, 46.2%; H, 5.1%.

Infrared spectrum

3114vw[a], 3064vw[b], 1934m, (Co-H stretch), 1587vw[d], 1570vw[d], 1439s, 1429w[c], 1419w[c], 1405vw[c], 1366w, 1315vw, 1308w, 1301w, 1291w, 1289vw, 1104w, 1020vw, 1030vw, 1004vw, 958w, 946m, 920m, 910m, 884s, 844vs br[e], 779vw, 755s, 742m, 724w, 714m, 703m, 684w, 626w, 574w, 554vs[e], 503w, 492w, 464w, 434w, 405m.

Preparation of (η^5-cyclopentadienyl)di(methyl)trimethyl-phosphinocobalt.

The compound $(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$ (1g, 1.56mmole) was suspended in dry diethylether (20cm^3). The suspension was

cooled by dipping the vessel in liquid nitrogen and treated with MeLi ($3cm^3$ of 2M ether sol., 6 mmole). The solid reacted rapidly to give a rich orange solution. The reaction mixture was cooled at approximately -10^oC and water was added to destroy the excess of MeLi. The diethylether layer was decanted off and the solvent removed under reduced pressure to give an orange oil. This was dissolved in light petroleum ether ($5cm^3$) and chromatographed on an alumina column made up in petroleum ether (60^o-80^oC boiling range). Light petroleum eluted an orange band. The solvent was partially removed from the eluate under reduced pressure and the concentrated petroleum ether solution was cooled at -78^oC. Orange needles were formed which were separated by filtration at -78^oC and dried under vacuum. Yield = 70%.

Found: C, 51.7%; H, 8.8%. $C_{10}H_{20}CoP$ requires: C, 52.2%; H, 8.7%.

Infrared spectrum

3100vw[a], 1423w[c], 1369w, 1302w, 1283m, 1180w, 1147w, 1119vw, 1010vw, 1000vw, 952s, 937m, 849vw, 838vw, 803m, 767vw, 723w, 672w, 670vw, 500vw, 402m.

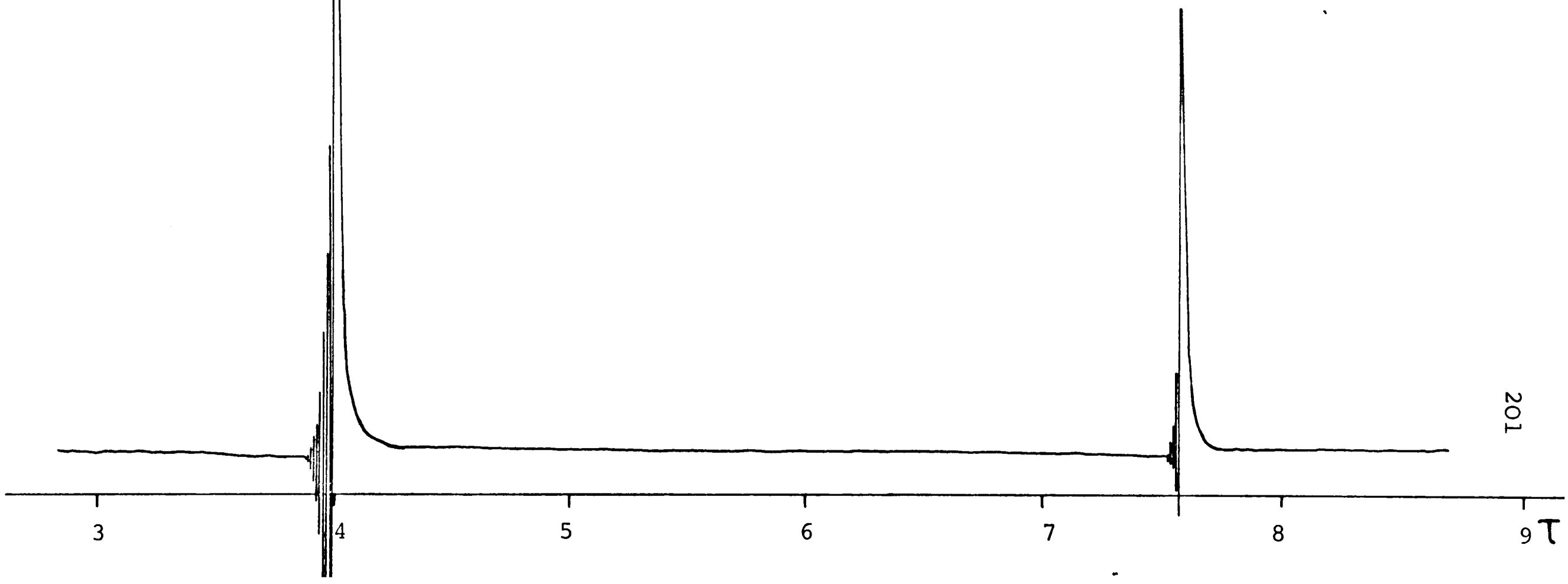
Reaction of $(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$ with phenyllithium.

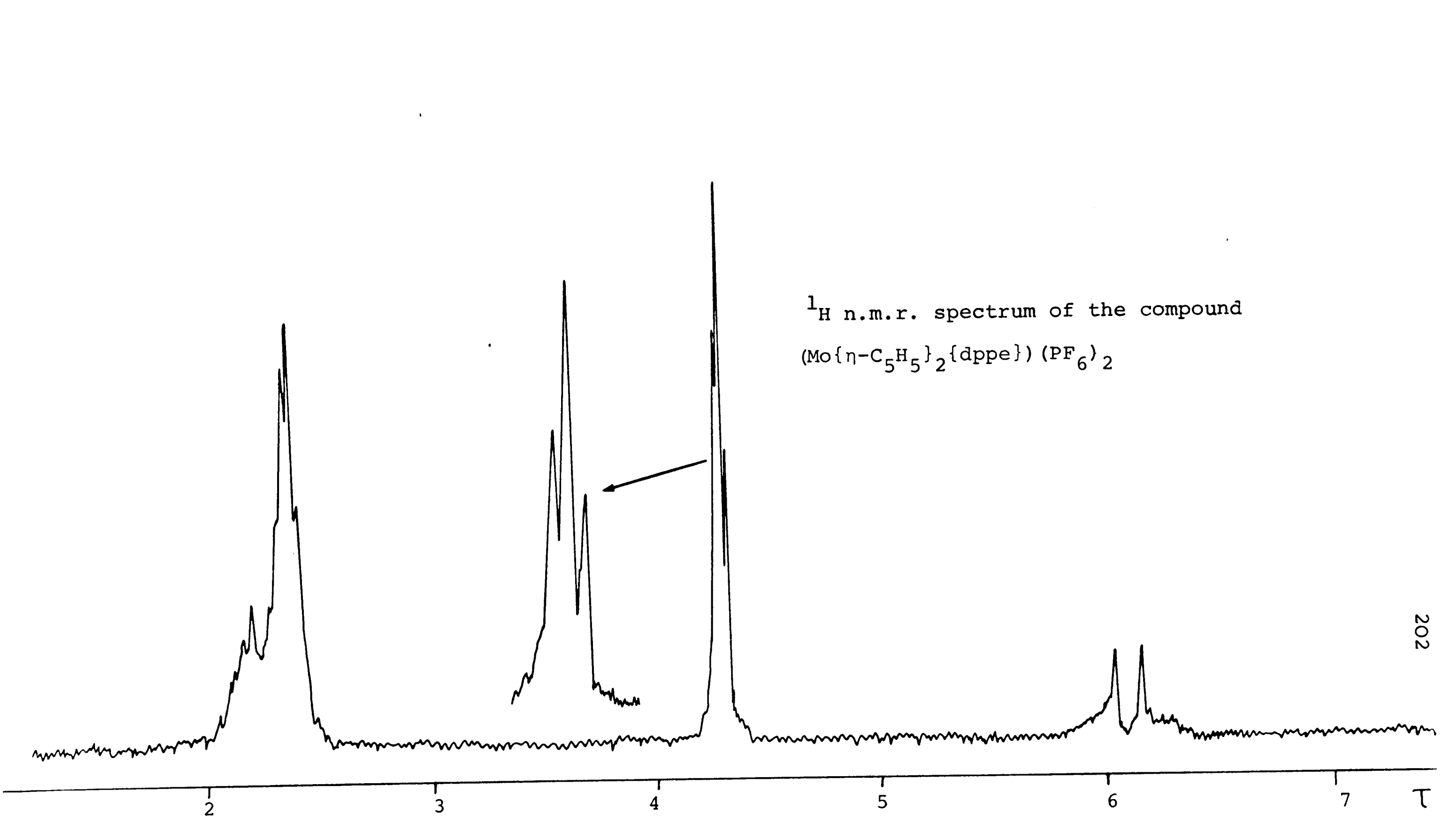
$(Co\{\eta^5\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$ (1.0g, 1.56mmole) was suspended in dry diethylether ($30cm^3$). The suspension was cooled to approximately -10^oC and treated with PhLi ($3cm^3$ of 2M ether sol., 6 mmole). The solid reacted immediately to give a brown-yellowish solution. The reaction mixture was cooled by dipping the vessel in liquid nitrogen and water was added to destroy

the excess of PhLi. The organic layer was decanted off and the solvent removed under reduced pressure. The resulting solid was extracted with the minimum volume of light petroleum, giving on orange solution. Chromatography on an alumina column made up in petroleum ether (60^{o}-80^{o}C boiling range) was performed. The resulting orange band was washed with light petroleum ($100cm^{3}$), eluted with toluene and collected. The solvent was removed under reduced pressure, and the resulting solid extracted with light petroleum. The extract was cooled at -40^{o}C for a period of 12 hours to give a pale yellow solid from which no tractable products could be isolated. The reaction was not further studied.

APPENDIX

^{1}H n.m.r. spectrum of the compound $(Mo\{\eta\text{-}C_5H_5\}_2\{NC\text{-}CH_3\}_2)(PF_6)_2$

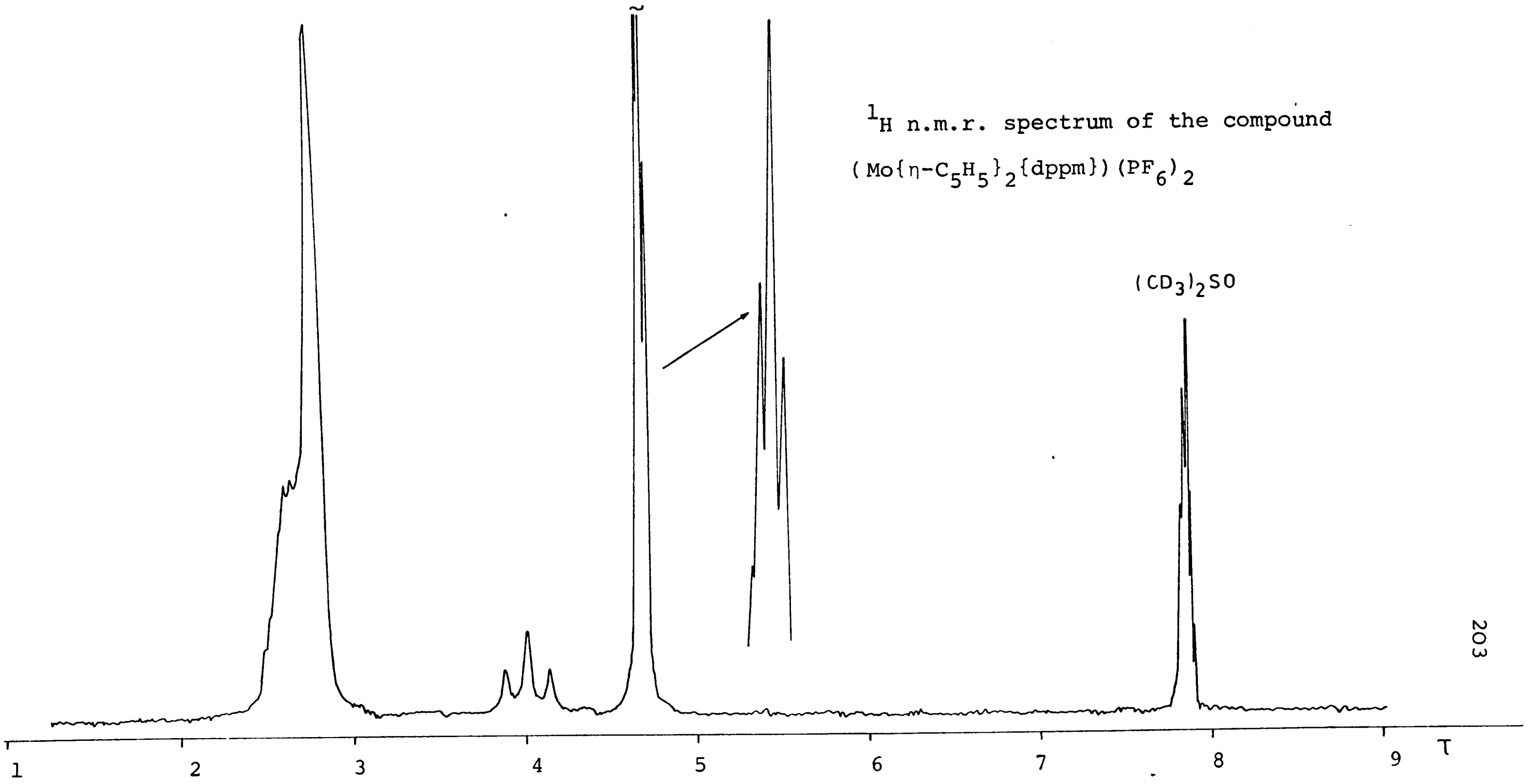


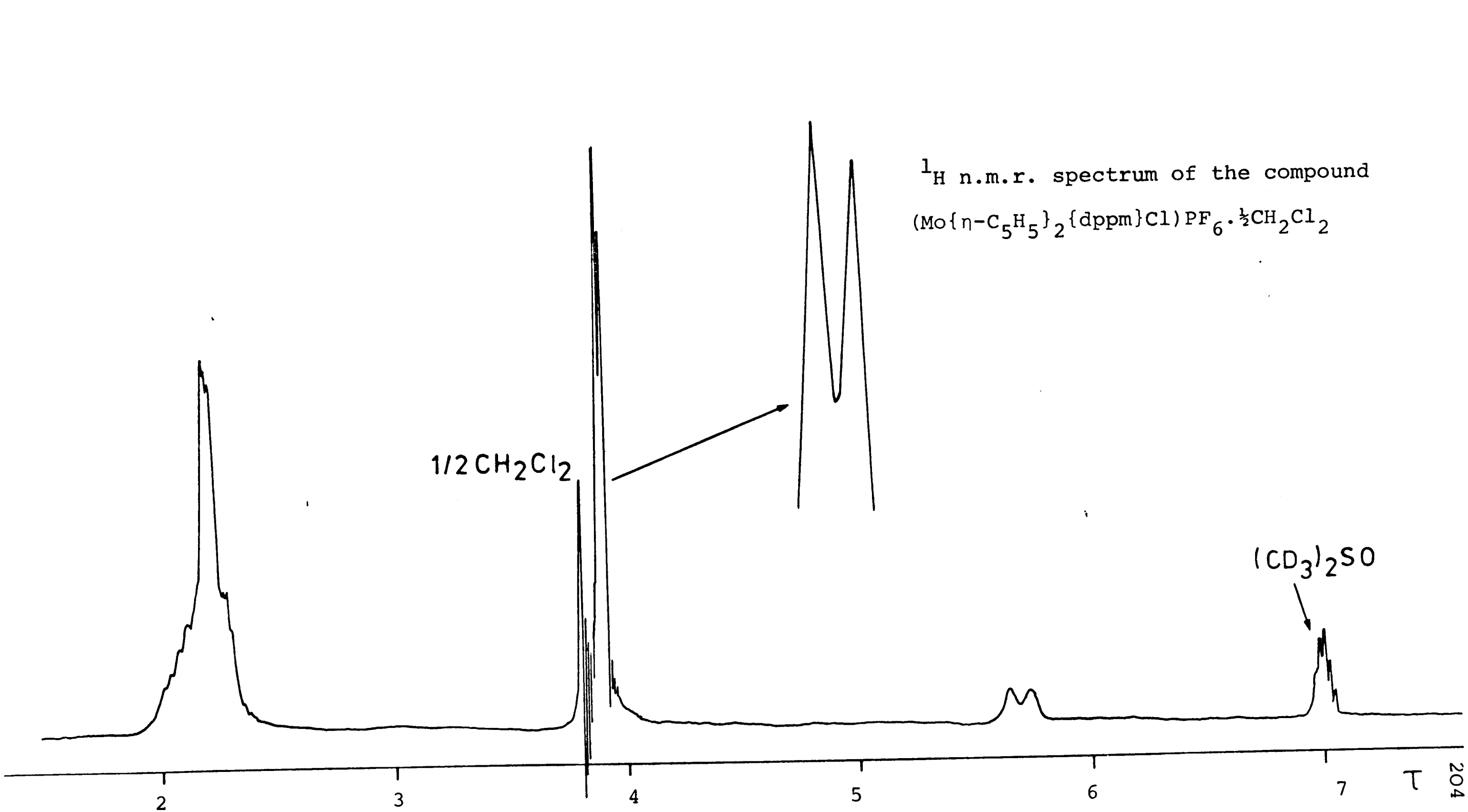


^{1}H n.m.r. spectrum of the compound

$(Mo\{\eta\text{-}C_5H_5\}_2\{dppe\})(PF_6)_2$

^1H n.m.r. spectrum of the compound $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\})(PF_6)_2$

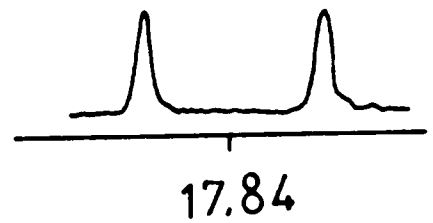




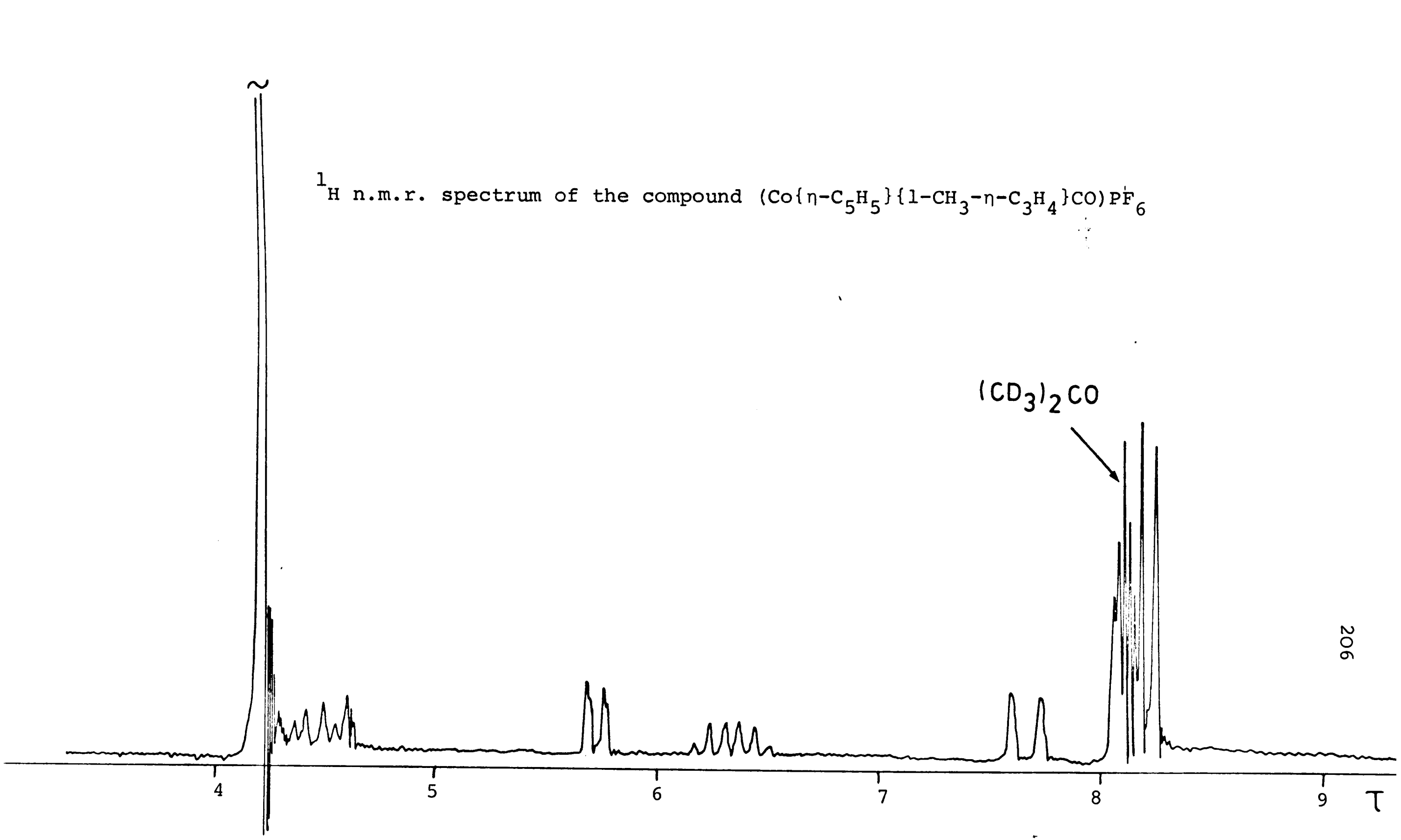
^{1}H n.m.r. spectrum of the compound $(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}Cl)PF_6 \cdot \frac{1}{2}CH_2Cl_2$

^{1}H n.m.r. spectrum of the compound

$(Mo\{\eta\text{-}C_5H_5\}_2\{dppm\}H)PF_6$

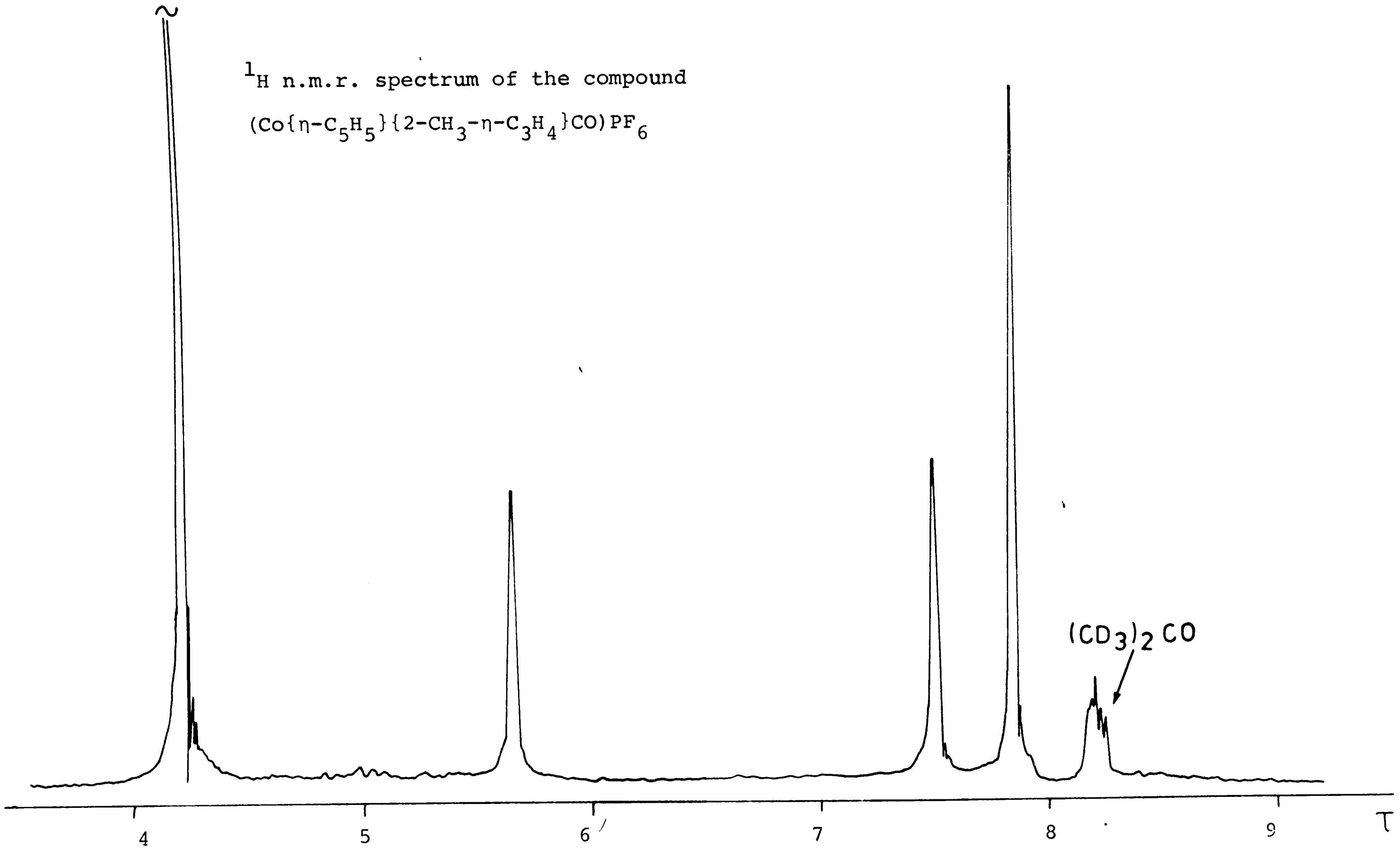


^1H n.m.r. spectrum of the compound $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$



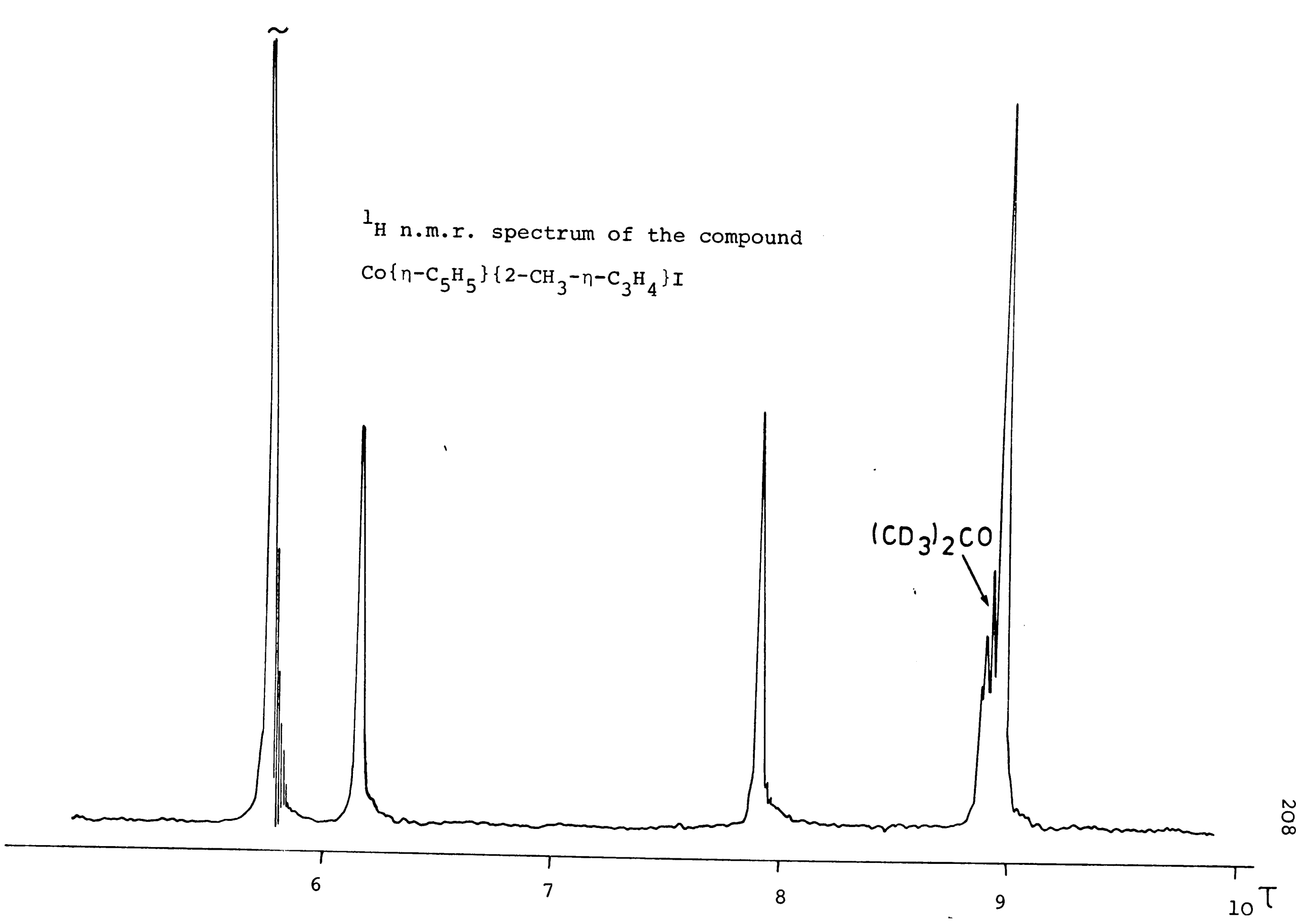
^1H n.m.r. spectrum of the compound

$(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$

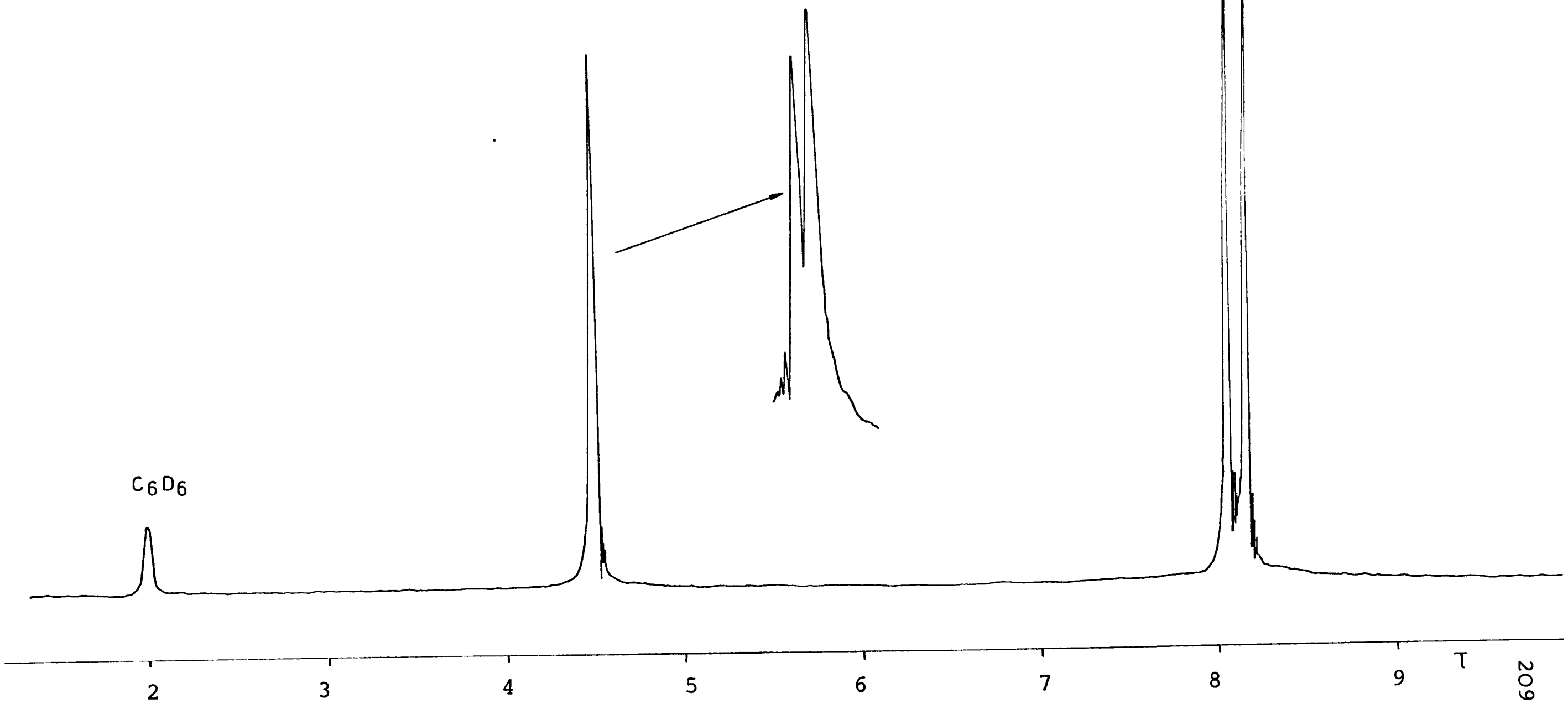


^{1}H n.m.r. spectrum of the compound

$Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}I$

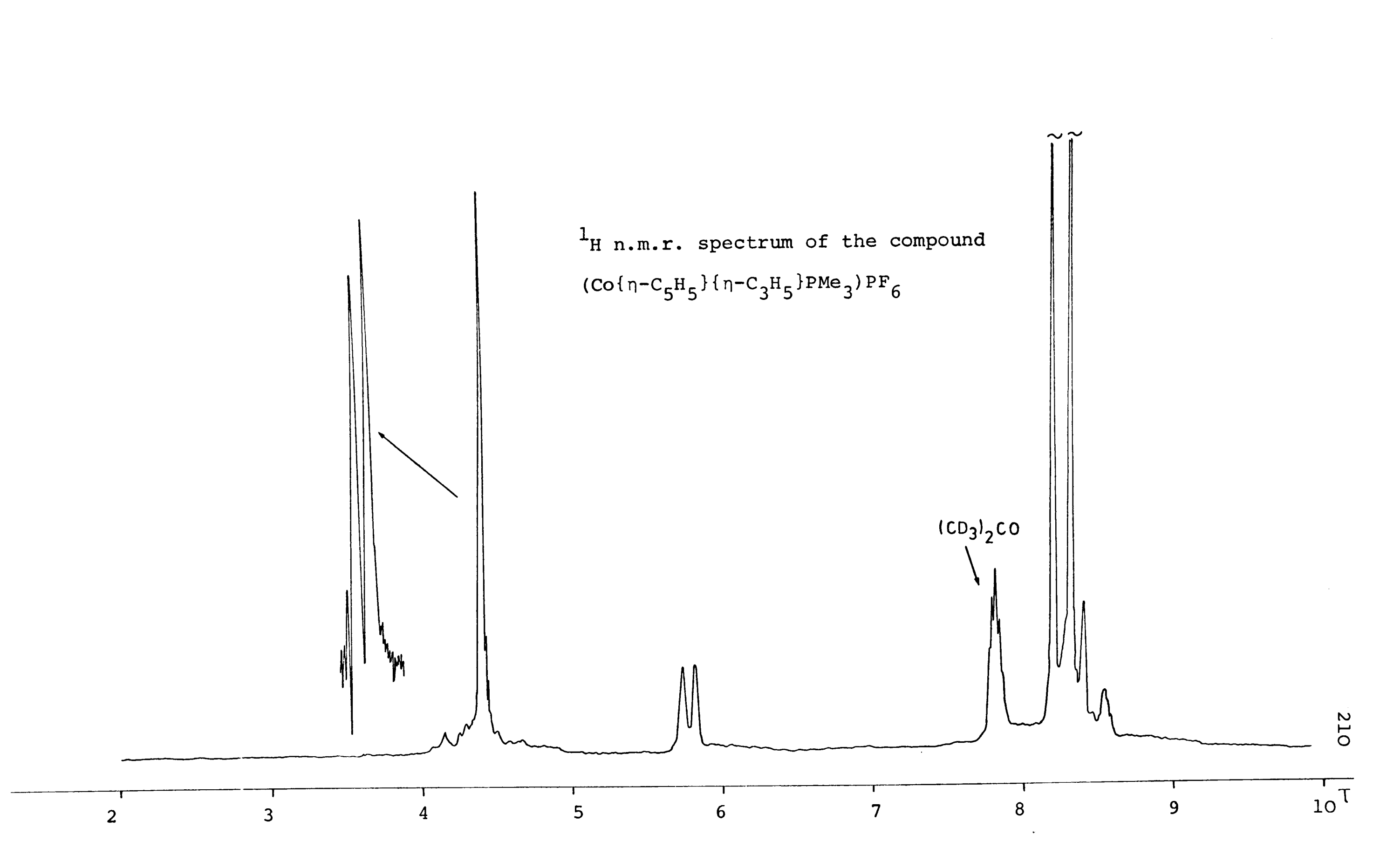


^{1}H n.m.r. spectrum of the compound $Co\{\eta\text{-}C_5H_5\}\{PMe_3\}CO$

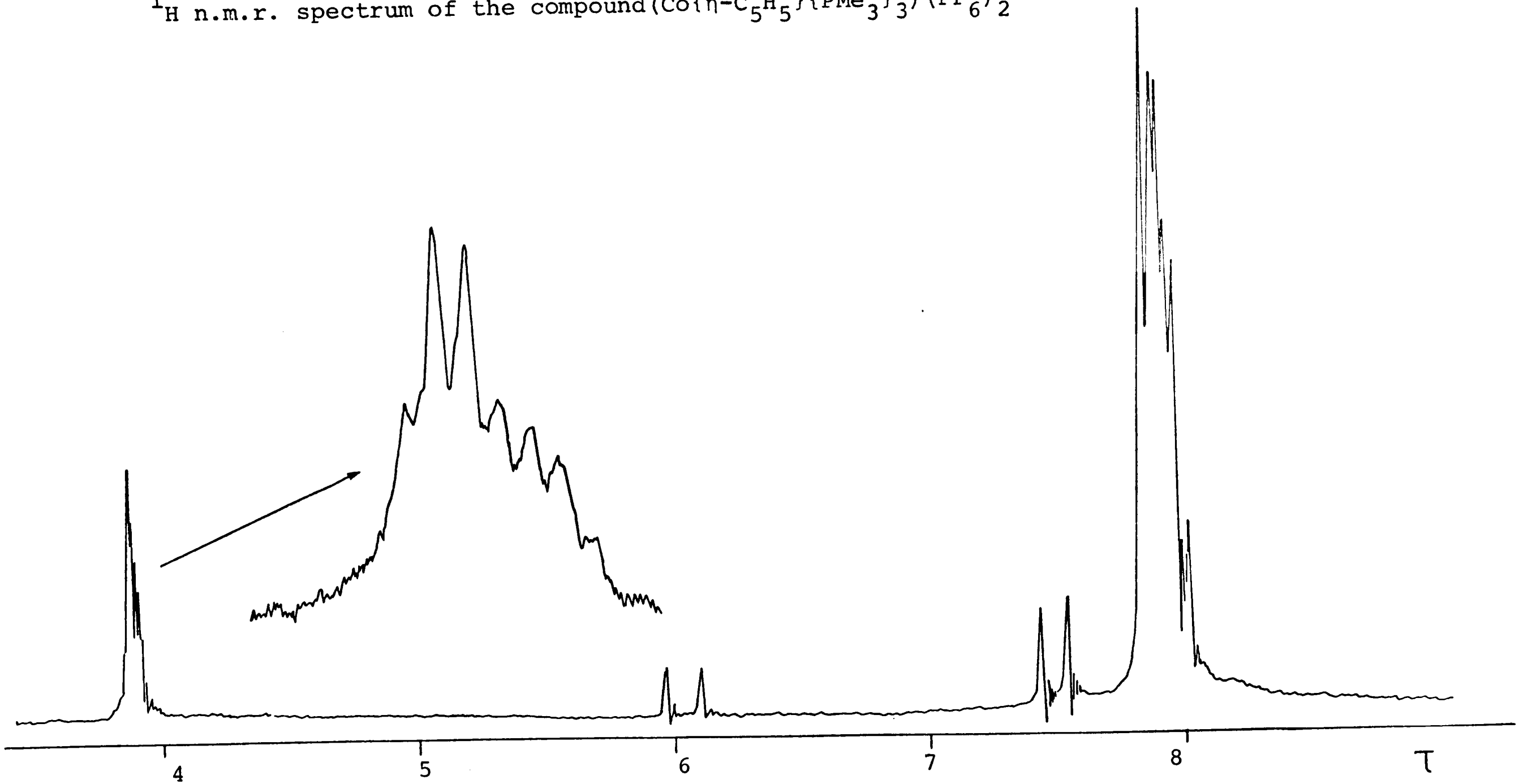


^1H n.m.r. spectrum of the compound

$(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)PF_6$

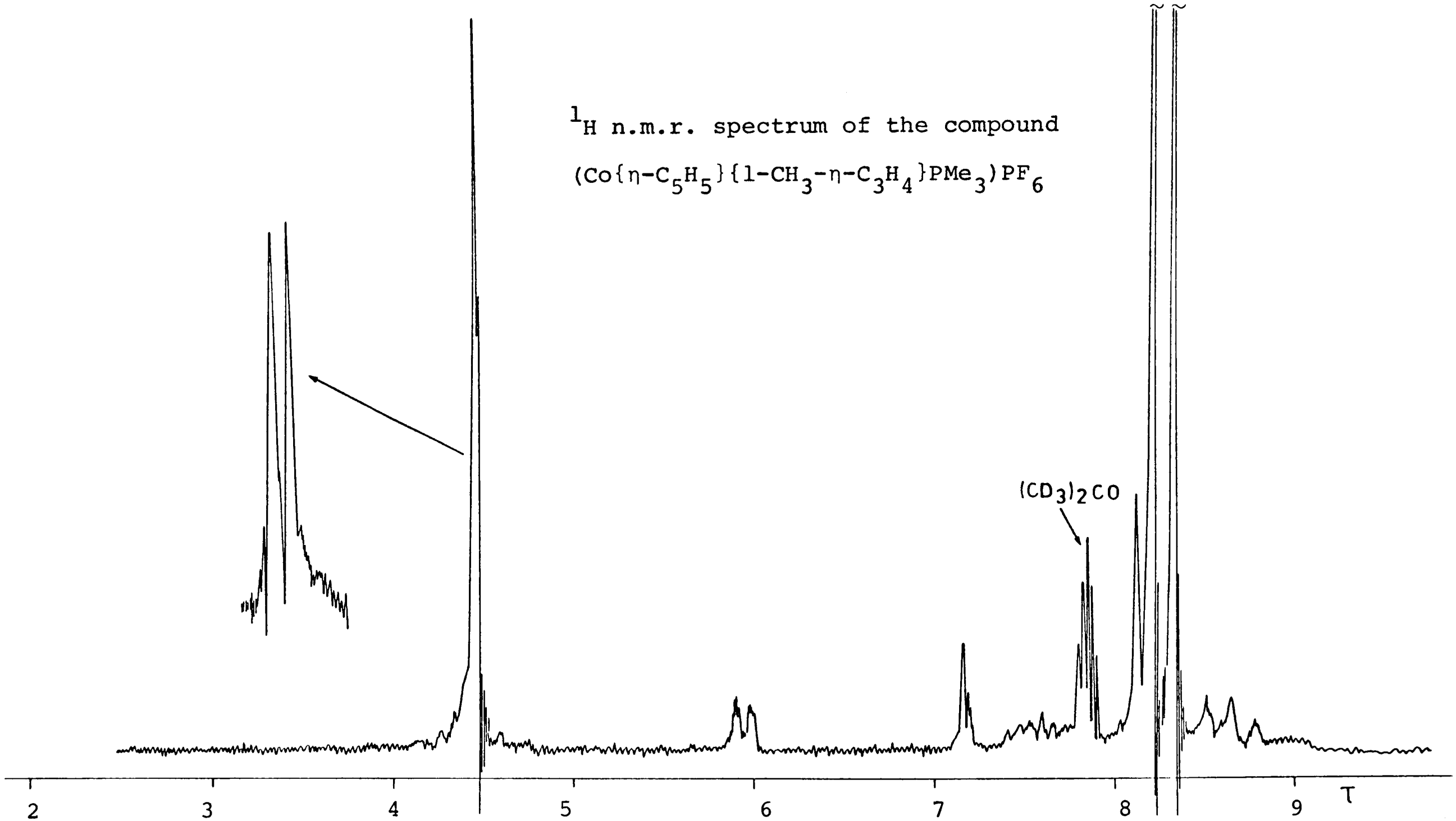


^{1}H n.m.r. spectrum of the compound $(Co\{\eta\text{-}C_5H_5\}\{PMe_3\}_3)(PF_6)_2$



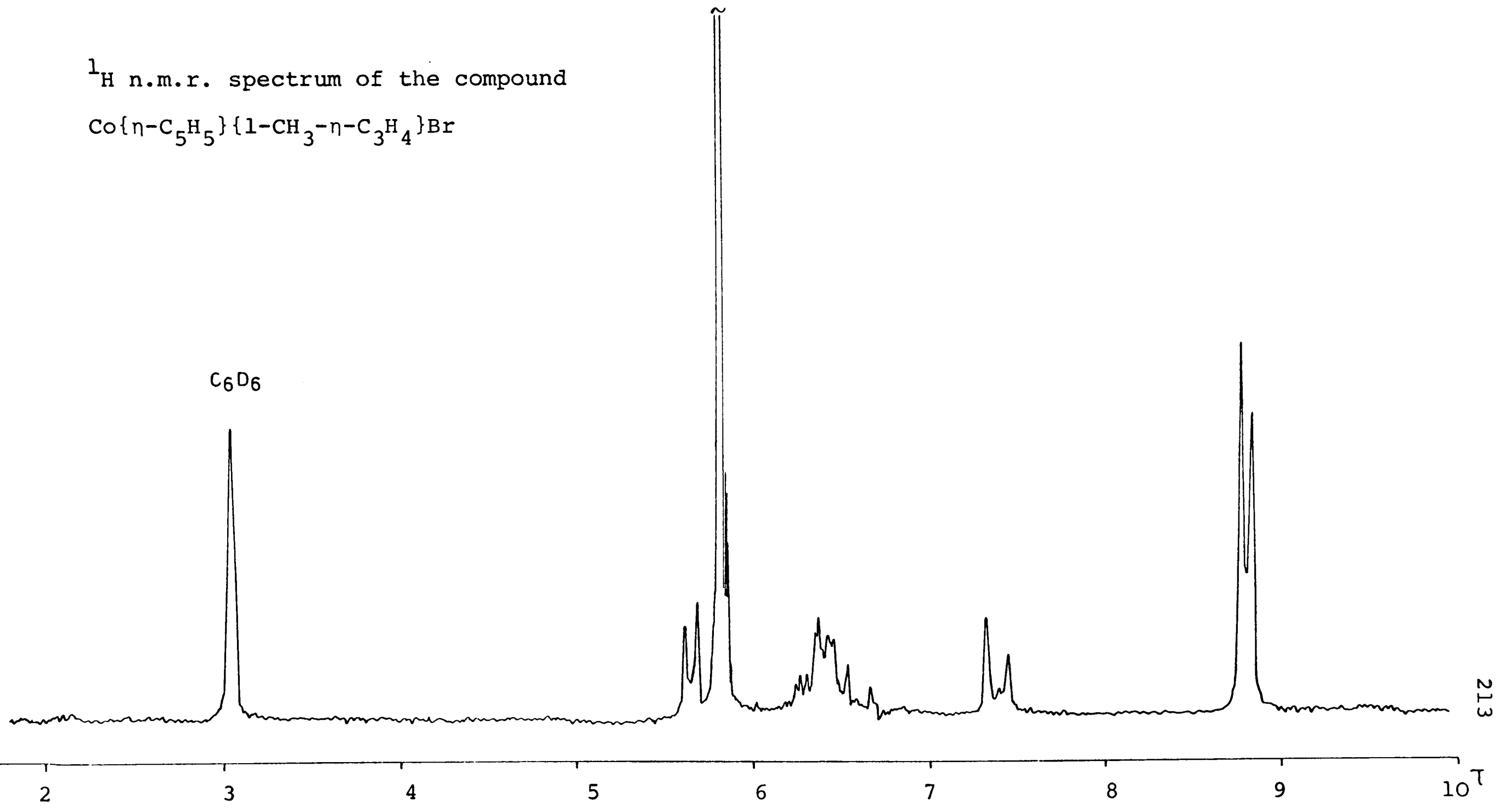
^{1}H n.m.r. spectrum of the compound

$(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$



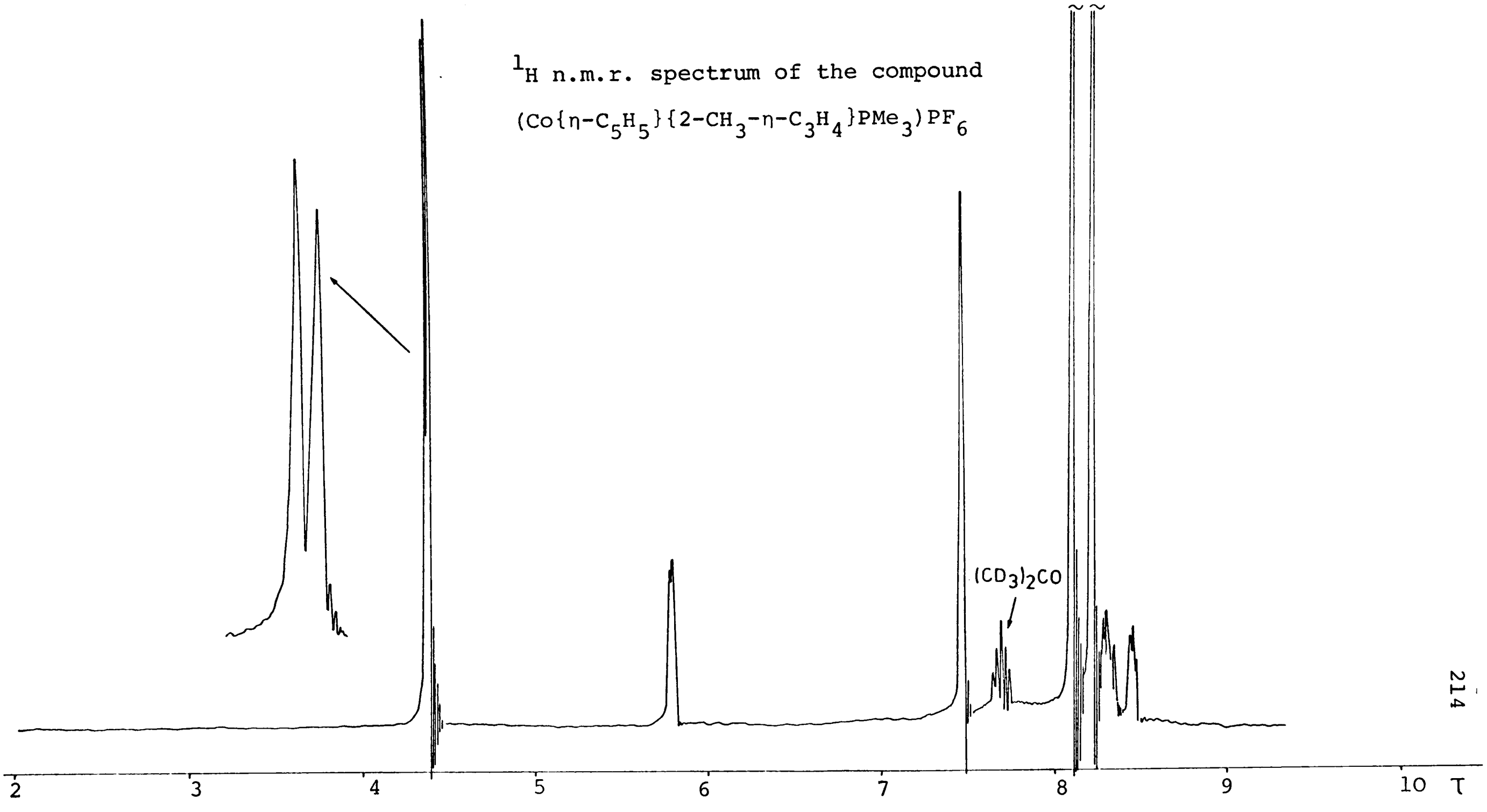
^{1}H n.m.r. spectrum of the compound

$Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}Br$



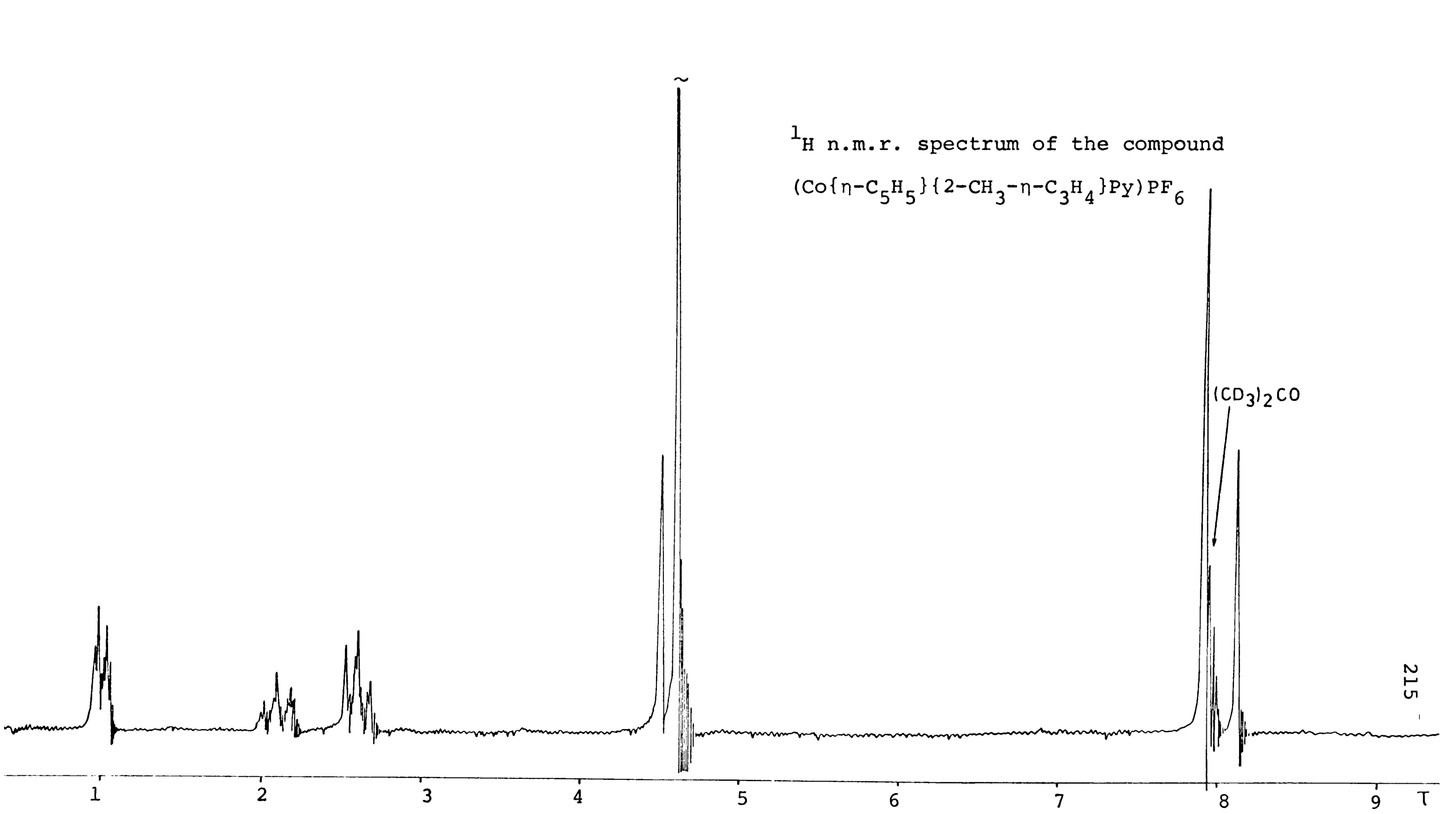
^{1}H n.m.r. spectrum of the compound

$(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$

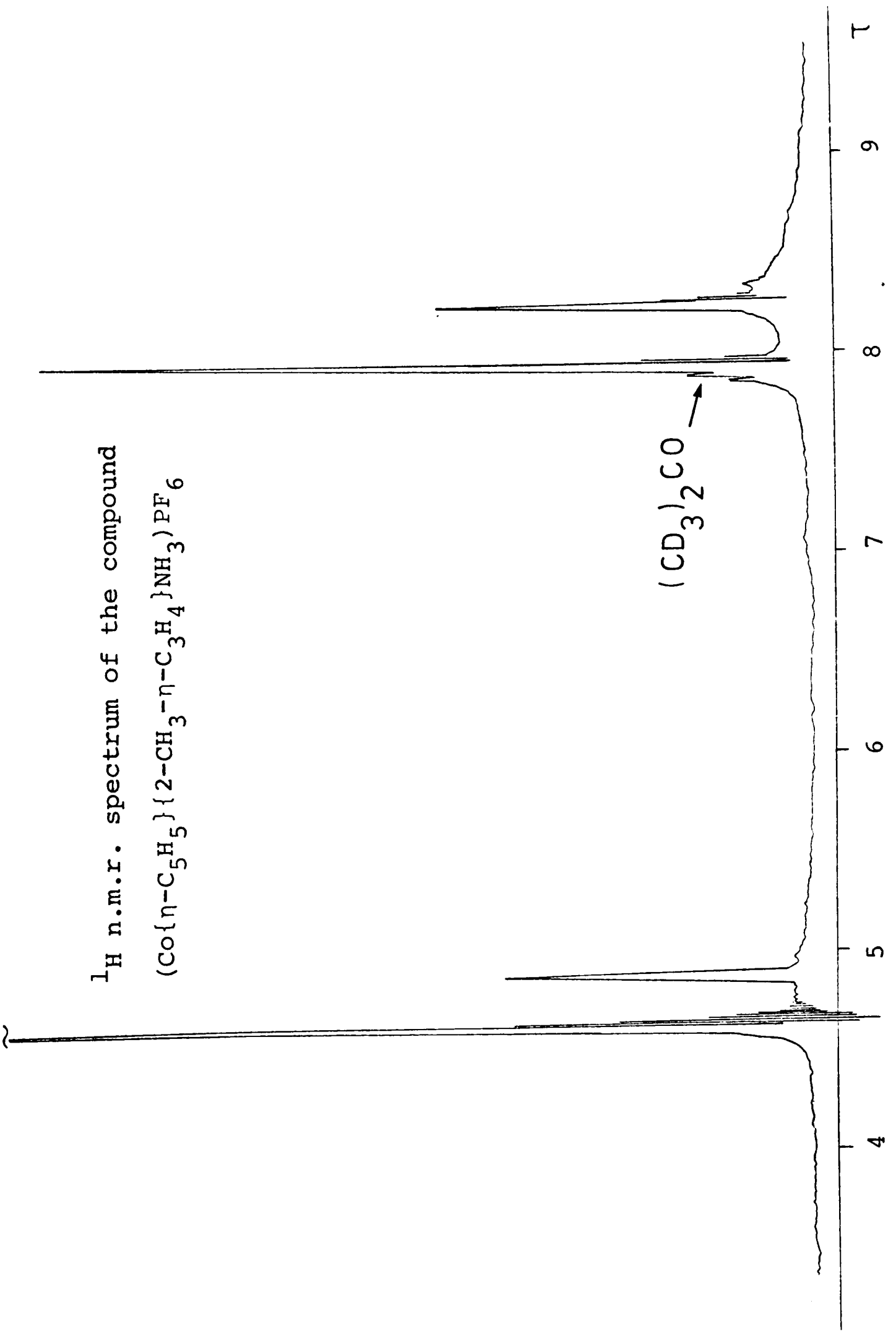


^1H n.m.r. spectrum of the compound

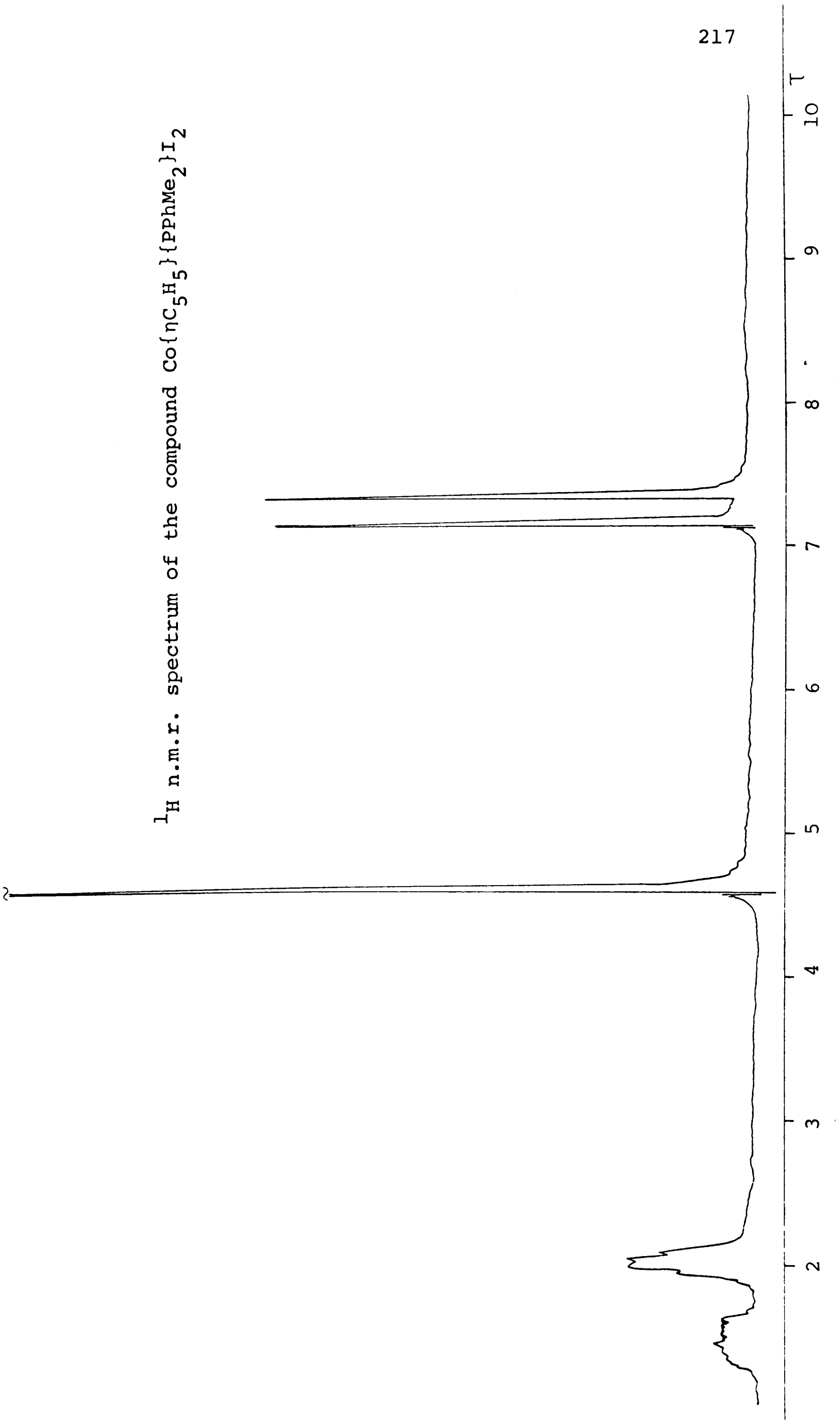
$(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}Py)PF_6$



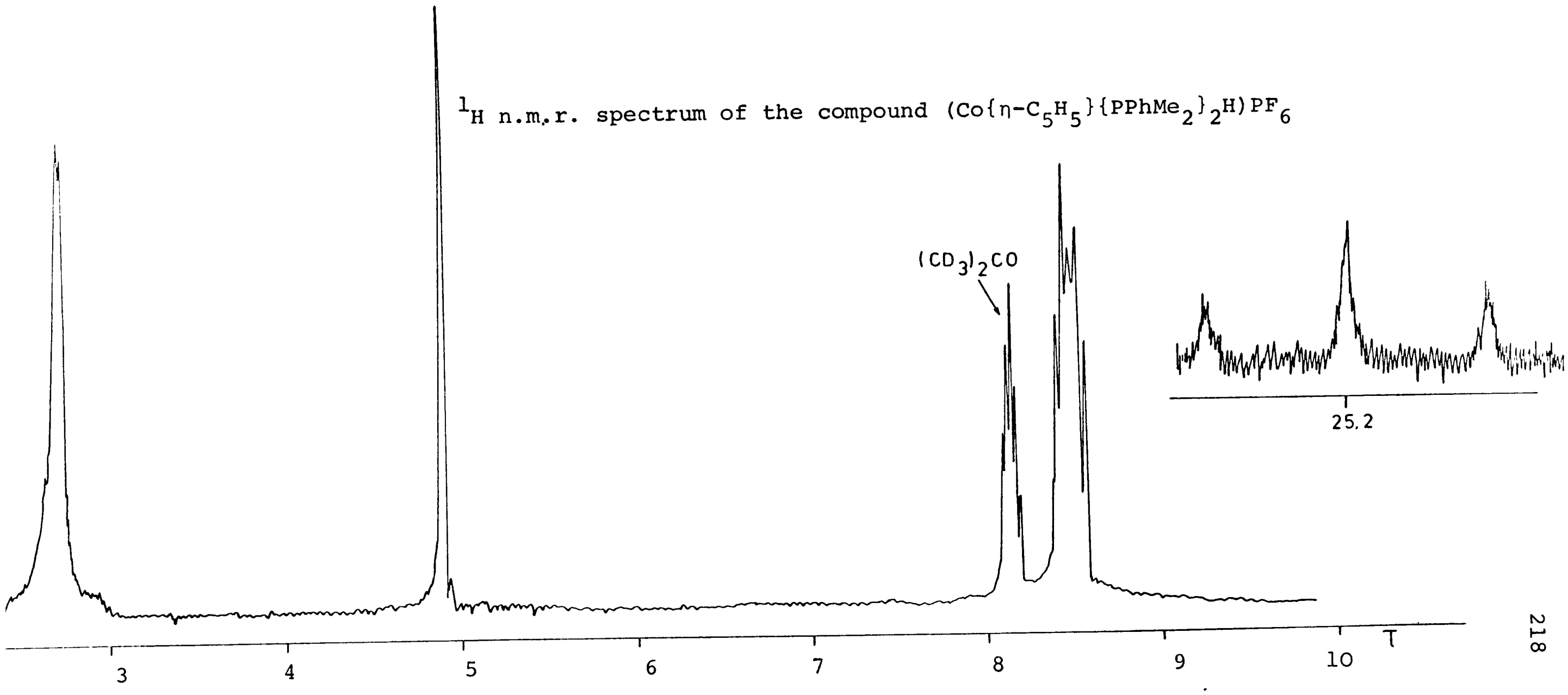
^{1}H n.m.r. spectrum of the compound
$(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}NH_3)PF_6$



^1_H n.m.r. spectrum of the compound $Co\{\eta C_5H_5\}\{PPhMe_2\}I_2$

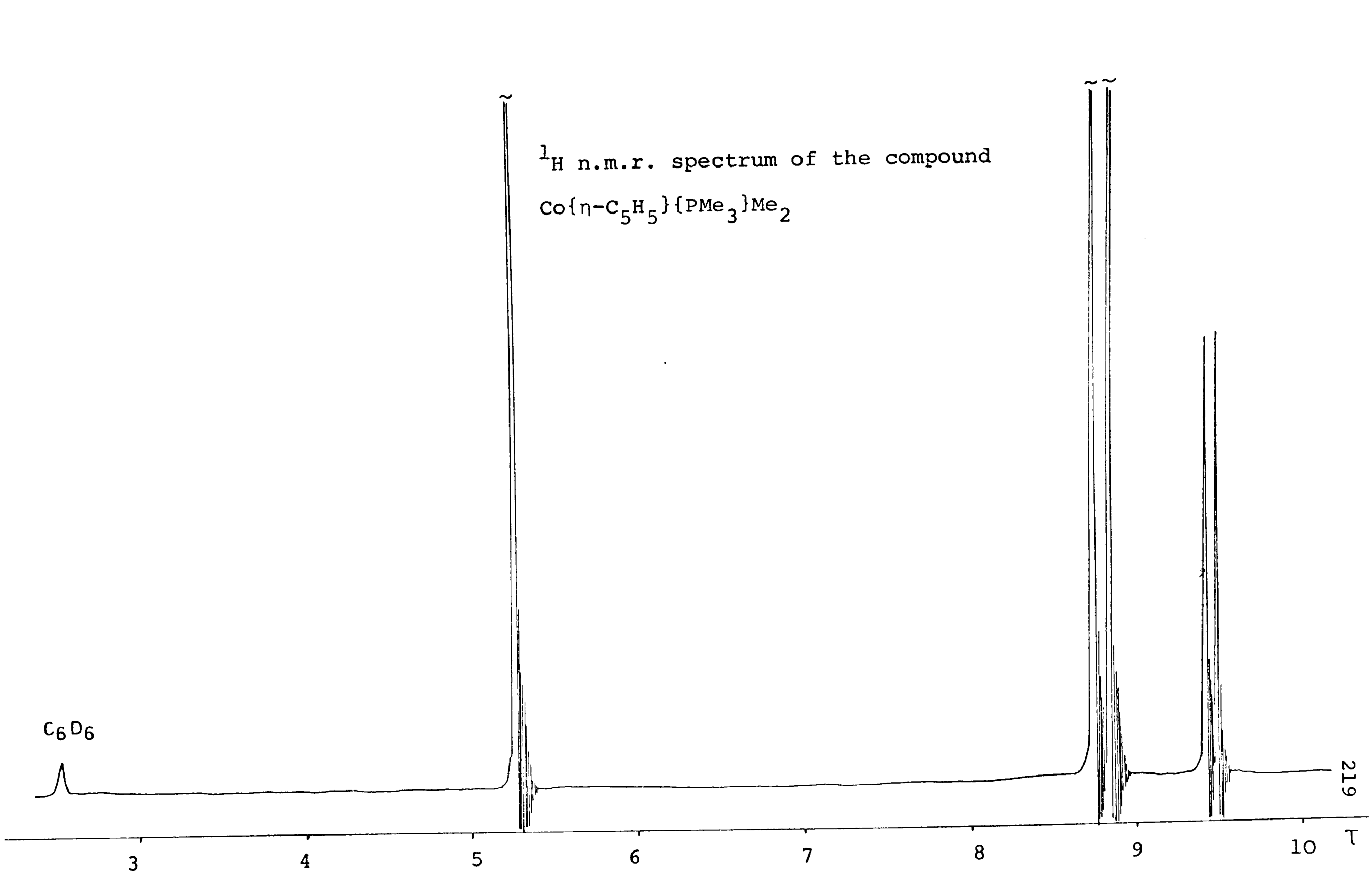


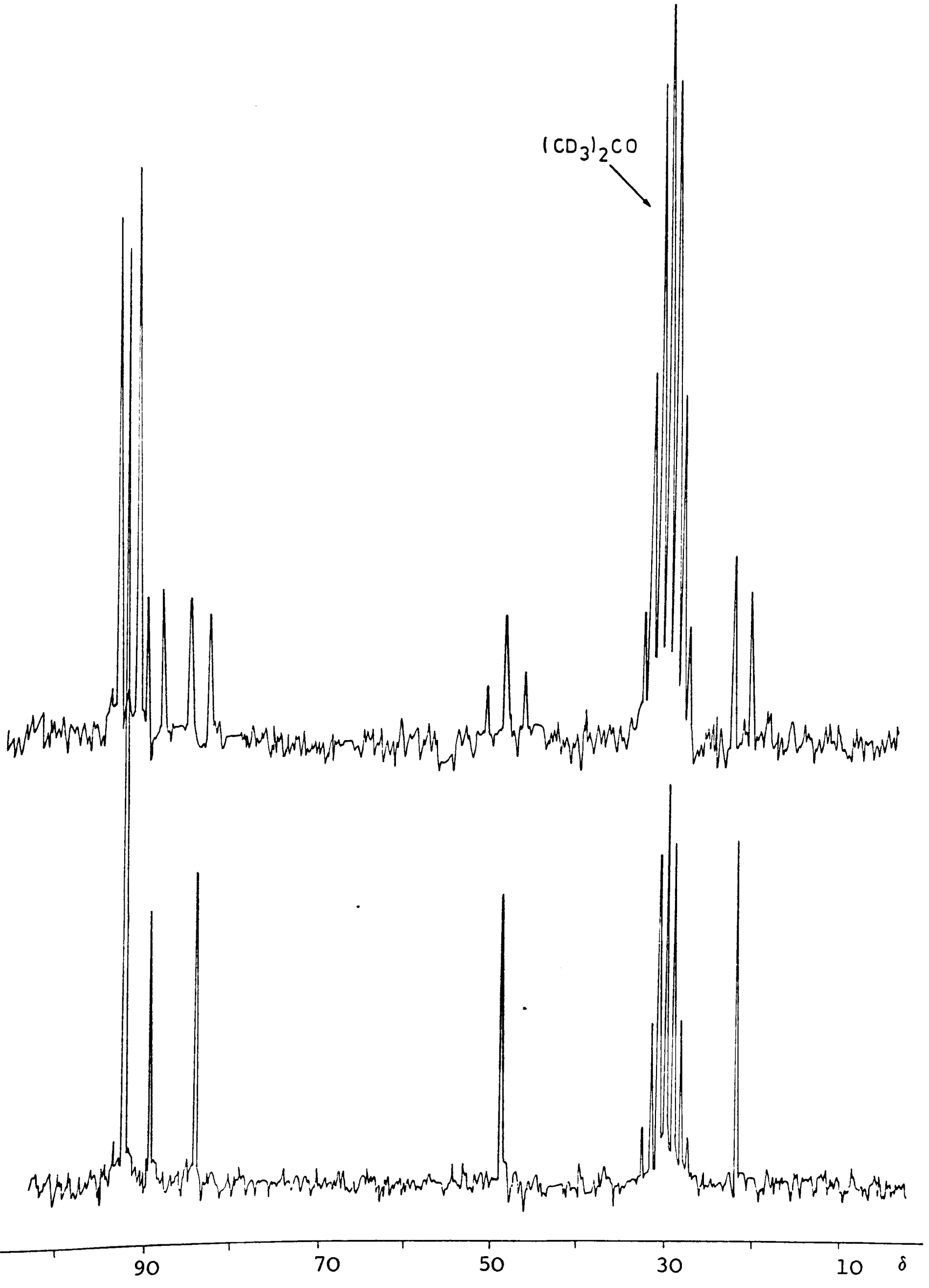
^1H n.m.r. spectrum of the compound $(Co\{\eta\text{-}C_5H_5\}\{PPhMe_2\}_2H)PF_6$



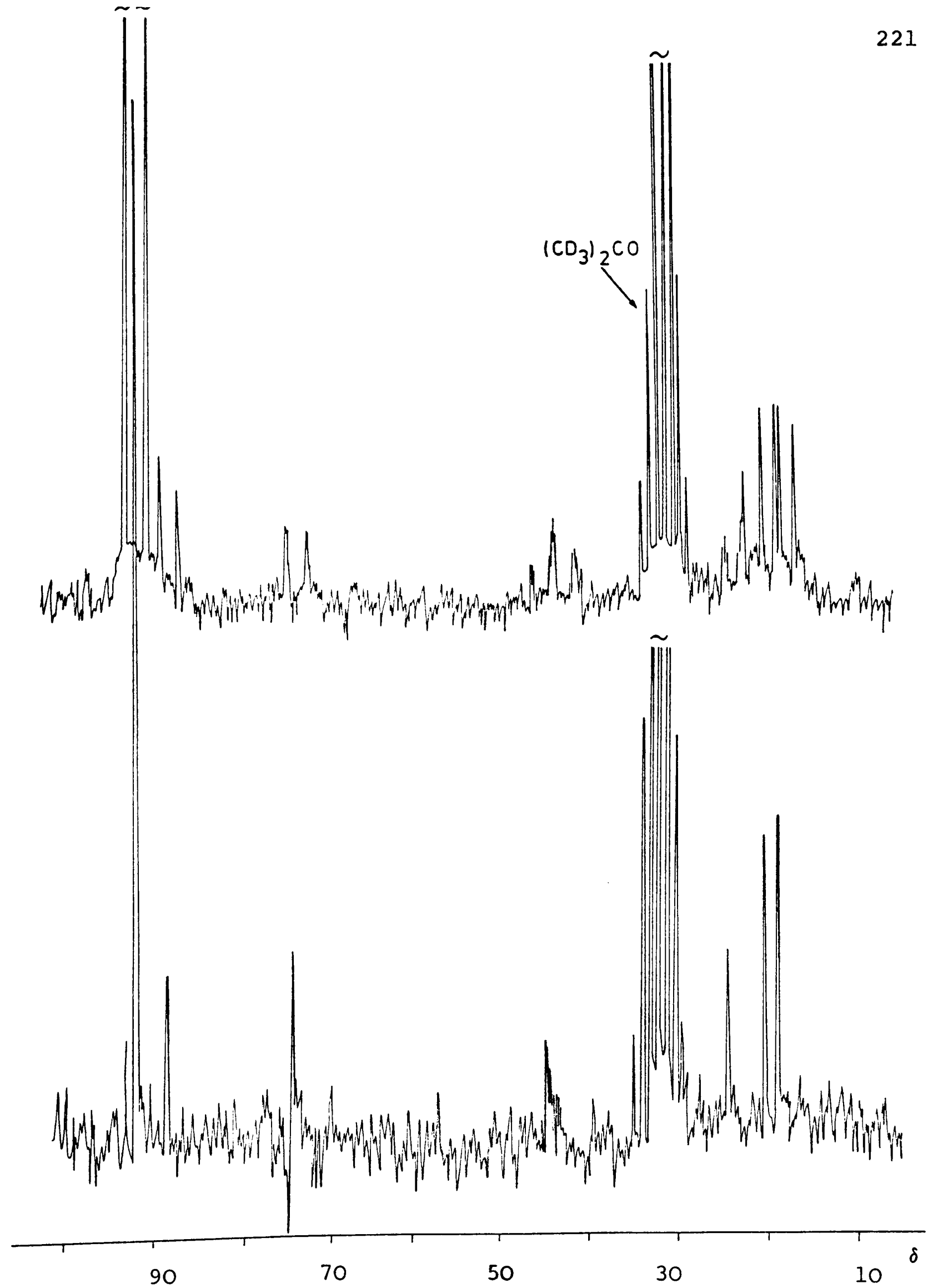
^{1}H n.m.r. spectrum of the compound

$Co\{\eta\text{-}C_5H_5\}\{PMe_3\}Me_2$

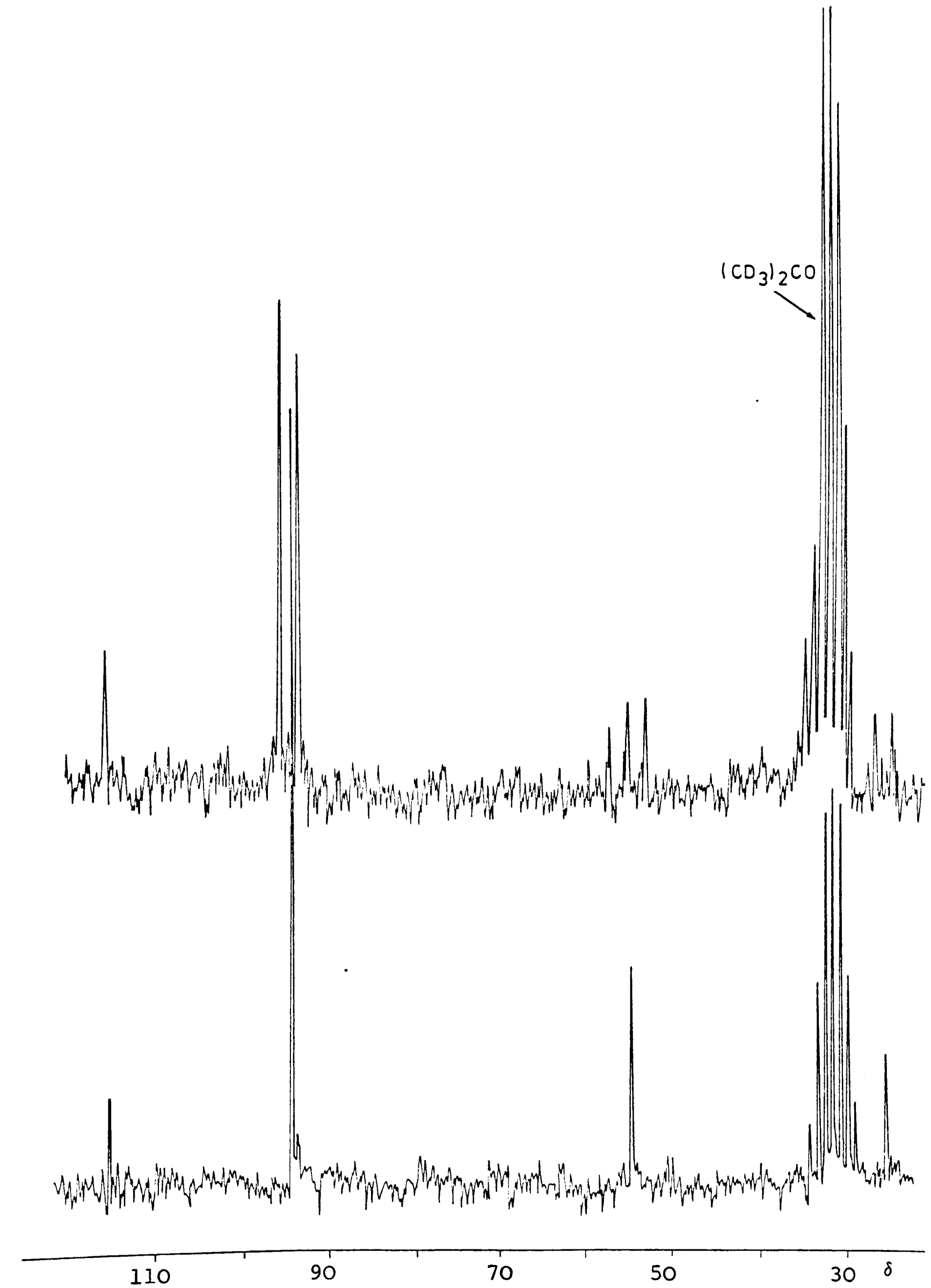




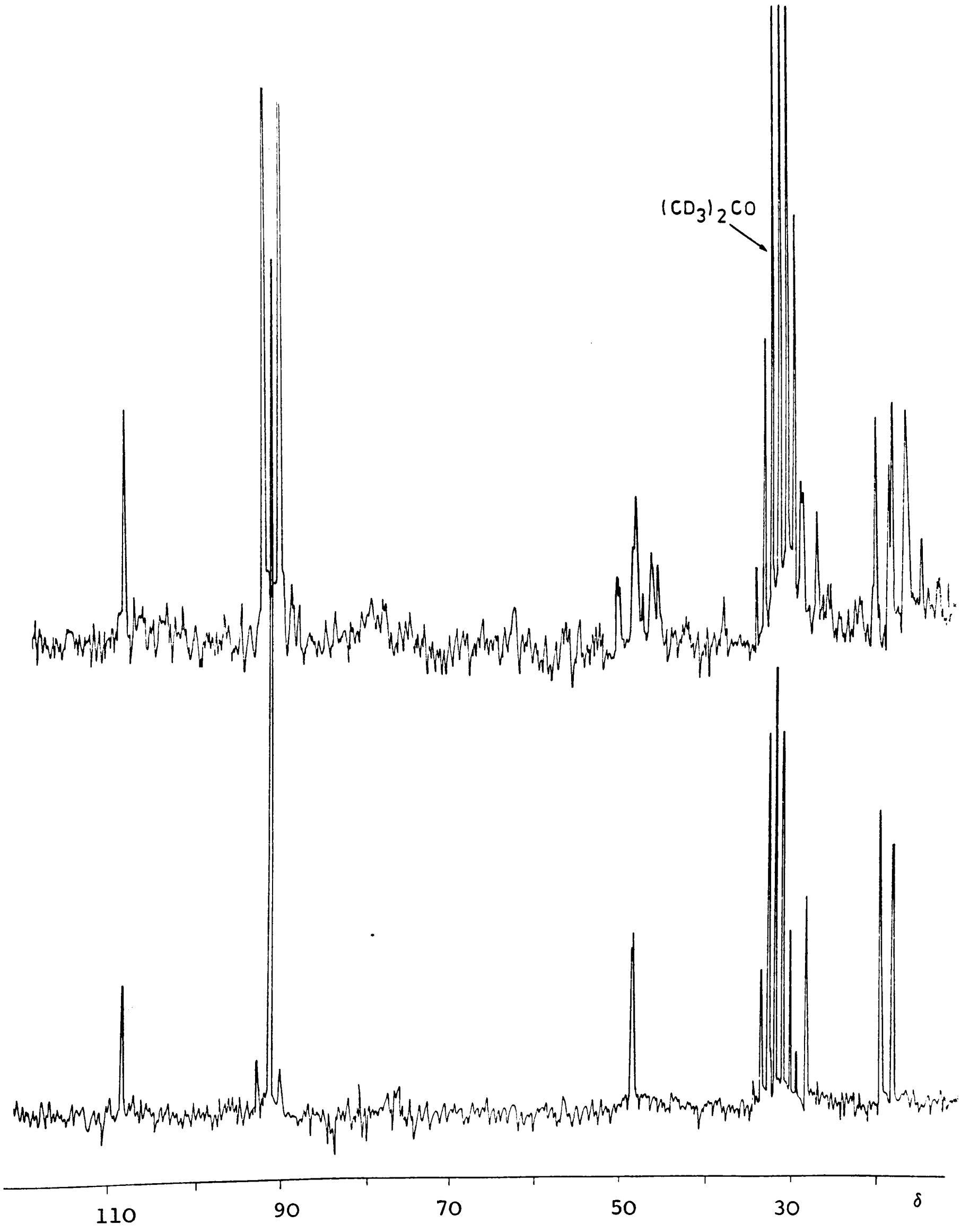
^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$ with and without broad band decoupling of the hydrogen nuclei.



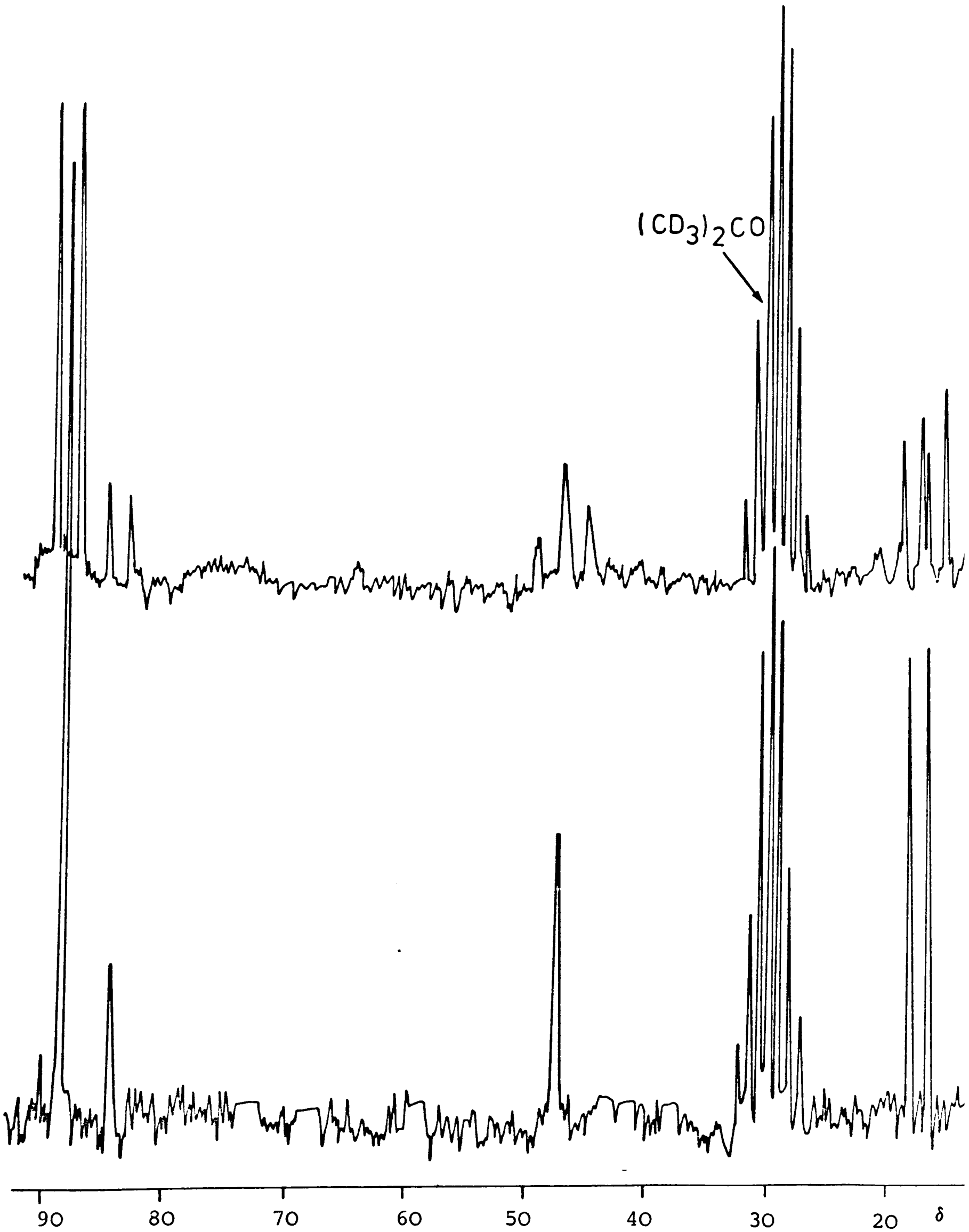
^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{1\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$ with and without broad band decoupling of the hydrogen nuclei.



^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}CO)PF_6$ with and without broad band decoupling of the hydrogen nuclei.



^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{2\text{-}CH_3\text{-}\eta\text{-}C_3H_4\}PMe_3)PF_6$ with and without broad band decoupling of the hydrogen nuclei.



^{13}C n.m.r. spectra of the compound $(Co\{\eta\text{-}C_5H_5\}\{\eta\text{-}C_3H_5\}PMe_3)PF_6$ with and without broad band decoupling of the hydrogen nuclei.

REFERENCES

1) M.L.H. Green, G.E. Coates and K. Wade, "Organometallic Compounds", Vol. II, Methuen, 1968.

2) T.A. James and J.A. McCleverty, *J.Chem. Soc. (A)*, 1971, 1068.

3) T.A. James and J.A. McCleverty , *J. Chem. Soc. (A)*, 1971, 1596.

4) J.A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2526.

5) R.B. King, *Inorg. Chem.*, 5, 1966, 2242.

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

7) S. Trofimenko, *Inorg. Chem.*, 9, 1970, 2493.

8) F.A. Cotton and J.R. Pipal, *J. Amer. Chem. Soc.*, 93, 1971, 5441.

9) F.A. Cotton and T.J. Marks, *J.Amer. Chem. Soc.*, 91, 1969, 931.

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

11) J.W. Faller and M.J. Incorvia, *Inorg. Chem.*, 7, 1968, 840.

12) J.W. Faller, C-C. Chen, M.J. Mattina and A. Jakubowski, *J. Organometal. Chem.*, 1973, 52, 361.

13) F.A. Cotton and M.D. LaPrade, *J. Amer. Chem. Soc.*, 90, 1968, 5418.

14) J.W. Faller and A. Rosan, VIIIth International Conference on Organometallic Chemistry, Kyoto, 1977.

15) J.L. Davidson, M. Green, F.G.A. Stone and A.J. Welch, *J.C.S. Dalton*, 1976, 739.

16) J.L. Davidson, M. Green, J.A.K. Howard, S.A. Mann, J.Z. Nyathi, F.G.A. Stone and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 803.

17) M.L.H. Green, J. Knight and J.A. Segal, *J.C.S. Chem. Comm.*, 1975, 283.

18) H.W. Wehner, E.O. Fischer and J. Muller, *Chem. Ber.*, 1970, 103, 2258.

19) E.O. Fischer and F.J. Kohl, *Chem. Ber.*, 1965, 98, 2134.

20) J.A. Segal, M.L.H. Green, J-C. Daran and K.Prout, *J.C.S. Chem.Comm.*, 1976, 766.

21) M.L.H. Green, J. Knight and J.A. Segal, *J.C.S. Dalton*, 1977, 2189.

22) S.G. Davies, M.L.H. Green and D.M.P. Mingos, *Nouveau Journal de Chimie*, 1, 6, 445.

23) M. Ephritikhine, B.R. Francis, M.L.H. Green, R.E. MacKenzie and M.J. Smith, *J.C.S. Dalton*, 1977, 1131.

24) E.F. Ashworth, M.L.H. Green and J. Knight, *J.C.S. Chem. Comm.*, 1974, 5.

25) A.N. Nesmeyanov and N.A. Vol'kenau, *Izvest. Akad. Nauk. S.S.S.R. Ser. Khim.*, 1151 (1975).

26) M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, *J.C.S. Dalton*, 1973, 2177.

27) C. White and P.M. Maitlis, *J. Chem. Soc. A*, 1971, 3322.

28) N.J. Cooper and M.L.H. Green, *Chem. Comm.*, 1974, 761.

29) B.F.G. Johnson, J. Lewis and D. Yarrow, *Chem. Comm.*, 1972, 235.

30) B.F.G. Johnson, J. Lewis and D. Yarrow, *J.C.S. Dalton*, 1972, 2084.

31) M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, *J.C.S. Dalton*, 1973, 1952.

32) J. Muller and S. Schmitt, *J. Organometal. Chem.*, 97, 1975, 275.

33) E. Roman, D. Astruc and A. Darchen, *Chem. Comm.*, 1976, 512.

34) M.M. Khan and W.E. Watts, *J. Organometal. Chem.*, 108, 1976, C11.

35) H. Brunner, *Ang. Chem. Int. Edn.*, 10, 1971, 249.

36) A. Davison, M.L.H. Green and G. Wilkinson, *J. Chem. Soc.*, 1961, 3172.

37) F.Faraone, F. Cusmano, P. Piraino and R. Pietropaolo, *J. Organometal. Chem.*, 44, 1972, 391.

38) A.E. Kruse and R.J. Angelici, *J. Organometal. Chem.*, 24, 1970, 231.

39) F. Calderazzo, *Inorg. Chem.*, 5, 1966, 429.

40) K.M. Al-Kathumi and L.A.P. Kane-Maguire, *J. Organometal. Chem.*, 102, 1975, C4.

41) M.L. Ziegler, H.E. Sasse and B. Nuber, *Z. Naturforsch*, 30b, 1975, 22, *ibid* 26.

42) J.E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 84, 1962, 1511.

43) J.E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 85, 1963, 3955.

44) J.E. Mahler, D.H. Gibson and R. Pettit, *J. Amer. Chem. Soc.*, 85, 1963, 3959.

45) P. McArdle and H. Sherlock, *J. Organometal. Chem.*, 52, 1973, C29.

46) M. Anderson, A.D.H. Clague, L.P. Blaauw and P.A. Couperus, *J. Organometal. Chem.* 56, 1973, 307.

47) B.F.G. Johnson, J. Lewis, D.G. Parker and S.R. Postle, *J.C.S. Dalton*, 1977, 794.

48) G. Maglio, A. Musco, R. Palumbo and A. Sirigu, *Chem.*

Comm., 1971, 100.

49) G. Maglio, A. Musco and R. Palumbo, *J. Organometal. Chem.*, 32, 1971, 127.

50) T.G. Bonner, K.A. Holder, P. Powell and E. Styles, *J. Organometal. Chem.*, 131, 1977, 105.

51) W.H. Knoth, *Inorg. Chem.*, 14, 1975, 1566.

52) D.L. Reger, *Inorg. Chem.*, 14, 1975, 660.

53) D.L. Reger and E.C. Culbertson, *J. Organometal. Chem.*, 131, 1977, 297.

54) A.J. Deeming, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J.C.S. Dalton*, 1974, 2093.

55) E.O. Fischer and F.J. Kohl, *Chem. Ber.*, 98, 1965, 2134.

56) B.D. Dombek and R.J. Angelici, *Inorg. Chim. Acta.*, 7, 1973, 345.

57) W.E. Williams and F.J. Lalor, *J.C.S. Dalton*, 1973, 1329.

58) F.W.S. Benfield, B.R. Francis and M.L.H. Green, *J. Organometal. Chem.*, 44, 1972, C13.

59) F. Sato, T. Uemura and M. Sato, *J. Organometal. Chem.*, 39, 1972, C25.

60) A. Salzer and H. Werner, *J. Organometal. Chem.*, 87, 1975, 101.

61) F.W. Benfield, B.R. Francis, M.L.H. Green, N-T. Luong-Thi, G. Moser, J.S. Poland and D.M. Roe, *J. Less Common Metals*, 36, 1974, 187.

62) N.A. Bailey, W.G. Kita, J.A. McCleverty, A.J. Murray, B.E. Mann and N.W. Walker, *Chem. Comm.*, 1974, 592.

63) T.H. Whitesides, R.W. Arhart and R.W. Slaven, *J. Amer. Chem. Soc.*, 95, 1973, 5792.

64) E.O. Fischer and R. Jira, *Z. Naturforsch*, 9b, 1954, 618/9.

65) I.S. Piper, F.A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1, 1955, 167/174.

66) R.B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York-London, 1965, S, 115.

67) R.F. Heck, *Inorg. Chem.*, 4, 1965, 855.

68) R.B. King, *Inorg. Chem.*, 5, 1966, 82.

69) R.F. Heck, *J. Org. Chem.*, 28, 1963, 604.

70) E.O. Fischer and R.D. Fischer, *Z. Naturforsch*, 16b, 1961, 475.

71) R.B. King, P.M. Treichel and F.G. Stone, *J. Amer. Chem. Soc.*, 83, 1961, 3593.

72) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, 21, 1970, 431 - 443.

73) D.M. Roe and P.M. Maitlis, *J. Chem. Soc. (A)*, 1971, 3173.

74) H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, 44, 1971, 2260.

75) J.A. Dineen and P.L. Pauson, *J. Organometal. Chem.*, 43, 1972, 209.

76) N.G. Connelly and J.D. Davies, *J. Organometal. Chem.*, 38, 1972, 385.

77) Y. Wakatsuki and H. Yamazaki, *Tetrahedron Letters*, 1973, 3383.

78) M.J. Barrow, J.L. Davidson, W. Harrison, D.W.A. Sharp, G.A. Sim and F.B. Wilson, *J.C.S. Chem. Comm.*, 1973, 583.

79) Y. Wakatsuki, H. Yamazaki and H. Ywasaki, *J. Amer. Chem. Soc.*, 95, 1973, 5781.

80) H. Brunner and S. Loskot, *J. Organometal. Chem.*, 61, 1973, 401.

81) E.W. Powell and M.J. Mays, *J. Organometal. Chem.*, 66, 1974, 137.

82) M.D. Raush and R.A. Genetti, *J. Org. Chem.*, 35, 1970, 3888/97.

83) C.C. Romao, personal communication.

84) W.E. Silverthorn, *J.C.S. Chem. Comm.*, 1971, 1310.

85) D. Sellmann, K Jödden and E. Kleinschmidt, VIIIth International Conference on Organometallic Chemistry, Kyoto, 1977.

86) A. Sacco and M. Rossi, *Chem. Comm*, 1967, 316, see also A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda, *ibid.*, 1967, 79; A. Misono, Y. Uchida, T. Saito and K.M. Song, *ibid.*, 1967, 419; and A. Misono and T. Saito, *Bull. Chem. Soc. Japan*, 40, 1967, 700.

87) G. Winkhaus and H. Singer, *Z. Naturforsch*, 18B, 1963, 418.

88) F.W.S. Benfield, B.R. Francis and M.L.H. Green, *J.Chem. Soc. (Dalton)*, 1974, 1324.

89) H.H. Brintzinger, private communication to M.L.H. Green.

90) J. Chatt and R.S. Coffey, *Chem. Comm.*,1966, 545.

91) G.J. Leigh, J.J. Levison and S.D. Robinson, *Chem. Comm.*, 1969, 705.

92) P.G. Douglas and B.L. Shaw, *Chem. Comm.*, 1969, 624.

93) P.G. Douglas and B.L. Shaw, *J. Chem. Soc. A*, 1970, 334.

94) B.D. James and M.G.H. Wallbridge, Review on Metal Tetrahydroborates, *Progress in Inorg. Chem.*, 11, 1970, 99.

95) H. Munakata, D. Phil Thesis, Oxford 1971.

96) B.D. James, R.K. Nanda and M.G.H. Wallbridge, *J. Chem. Soc.*, 1966, A182.

97) G.F. Emerson, J.E. Mahler, R. Pettit and R. Collins, *J. Amer. Chem. Soc.*, 86, 1964, 3590.

98) P.Powell and L.J.Russell, *J. Organometal. Chem.*, 129. 1977. 415.

99) M. Ephritikhine and M.L.H. Green, *J.C.S. Chem. Comm.*, 1976, 926.

100) M.J. Smith, D. Phil Thesis, Oxford 1971.

101) D.F. Shriver, "The Manipulation of Air Sensitive Compounds", New York, 1969.

102) M.L.H. Green, J.A. McCleverty, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

103) M.L.H. Green and P.J. Knowles, *J.C.S. Perkin I*, 1973 989.

104) F. Northam, J. Oliver and G.A. Crowder, *J. Mol. Spectrosc.* 25, (4), 1968, 434 - 7.