THE SYNTHESIS, CHARACTERIZATION AND INVESTIGATION OF THE CATALYTIC ACTIVITIES OF SOME 1,5-CYCLOOCTADIENE AND 2,5-NORBORNADIENE GROUP VIB TRANSITION METAL CARBENE CARBONYL COMPLEXES

by

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To my father Hirpo Mullata,
who was deeply concerned for the
education of his children and could see
only the flowers, but not lucky
enough to see the fruits.

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ABBREVIATIONS

The following abbreviations are used in the main text.

app.	apparent
br	broad
COD	1,5-cyclooctdiene
d	doublet
Et	ethyl (C_2H_5)
ir	infrared
Me	methyl (CH_3)
mg	milligram
ml	millilitre
mmole	millimole
M.P	melting point
NBD	2,5-norbornadiene
NMR	nuclear magnetic resonance
q	quartet
s	strong
t	triplet
vs	very strong
w	weak

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CHAPTER

ABSTRACT

THE SYNTHESIS, CHARACTERIZATION AND INVESTIGATION OF THE CATALYTIC ACTIVTIES OF SOME 1,5-CYCLOOCTADIENE AND 2,5-NORBORNADIENE GROUP VIB TRANSITION METAL CARBENE CARBONYL COMPLEXES

by

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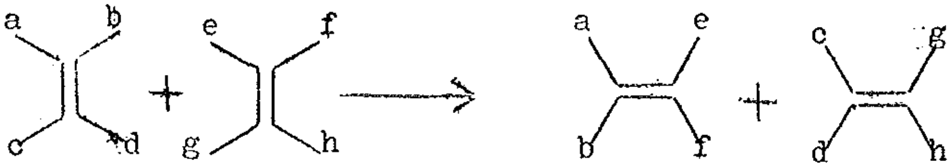
Research Advisor: MAKONNEN DILGASSA

The reaction of 1,5-cyclooctadiene tetracarbonyl tungsten (O) with methyllithium gave products in which the diene is no more coordinated to the metal. It was investigated that the compound is catalytically active and could metathesize 2-pentene into 2-butene and 3-hexene in the presence of $EtAlCl_2$ as a cocatalyst.

A series of some $(diene)M(CO)_4$, [$(diene)M(CO)_4$ = (1,5-cyclooctadiene)$W(CO)_4$, (2,5-norbornadiene)$W(CO)_4$, (2,5-norbornadiene)$M_O(CO)_4$, (2,5-norbornadiene)$Cr(CO)_4$], and $(CH_3CN)_3M_O(CO)_3$ complex were tested in the ratio of M to cocatalyst to 2-pentene to be 1:6:1000. For comparison the active WCl_6-C_2H_5OH-$C_2H_5AlCl_2$ System was used. Gas chromatographic analysis of the reaction products showed that (2,5-norbornadiene)-$W(CO)_4$ is able to give 59.24% conversion after 24 hours at room temperature. The other complexes showed different percentage conversions and (NBD)$Cr(CO)_4$ was found to be completely inactive.

INTRODUCTION

In the presence of catalysts, most commonly containing tungsten, molybdenum, or rhenium, olefins undergo the reaction generalized as Eq.(1) and known as olefin metathesis reaction.[1-12] Metathesis results in polymers called polyalkenamers when the olefinic bonds are included in rings, Eq.(2).[13,14]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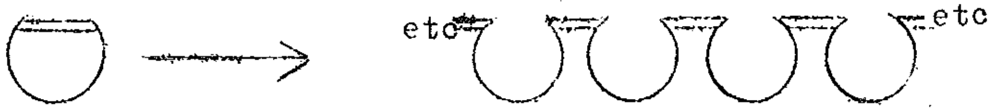
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Such reactions are most often brought about by the metal catalysts in the presence of cocatalysts such as organoaluminim compounds[15-20] or organic derivatives of other metals, notably tin. Some catalyst systems need traces of oxygen or oxygen containing species as an activator,[18,19,23] while, others initiate the reactions only in the presence of some Lewis acids[24] or light[25] and even at the absence of any cocatalyst at all.[26]

The metathesis reaction is gaining a wide application primarily in petroleum industry due to its use for synthesis of some olefins which would otherwise be difficult to obtain through some other common synthetic methods. Terminal olefins can be synthesized by ethylene cleavage of an unsymmetrical internal alkenes or by reaction of symmetric internal ole-

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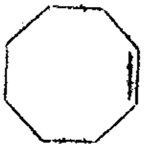
fins with ethylene. For example 1-hexene was prepared by metathesis of 2-heptene and ethylene with a homogeneous molybdenum catalyst, Eq.(3).[25]

$$CH_3(CH_2)_3CH{=}CHCH_3 \quad + \quad C_2H_4 \longleftrightarrow CH_3CH{=}CH_2 \quad + \quad CH_2{=}CH(CH_2)CH_3 \qquad (3)$$

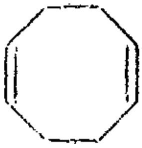
Metathesis of acyclic dienes can yield either cycloalkenes (intramolecular metathesis) or acyclic polyenes (intermolecular metathesis). A convenient route to multiple unsaturated derivatives has been attained by cross-metathesis of an acyclic and cyclic alkenes. With ethylene as the acyclic reactant, α,ω-dienes are formed. W.B.Hughes and his coworkers[25] have prepared 1,9-decadiene and 1,13-tetra-decadiene from cyclooctene and cyclododecene, respectively, by using a homogeneous molybdenum catalyst, Eqs.(4) and (5).



$$+ \quad C_2H_4 \rightleftharpoons CH_2{=}CH(CH_2)_6CH{=}CH_2 \qquad (4)$$

$$+ \quad C_2H_4 \qquad CH_2{=}CH(CH_2)_{10}CH{=}CH_2 \qquad (5)$$

In a matter of 2hr at 0°C, 1,5,9-decatriene could be obtained in 18% yield by the metathesis of ethylene with 1,5-cyclooctadiene, Eq.(6).



$$+ \quad C_2H_4 \rightleftharpoons CH_2{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH_2 \qquad (6)$$

The preparation of polyalkenameres by metathesis is one of the most widely studied areas since the discovery of the disproportionation reaction. The synthesis of perfectly

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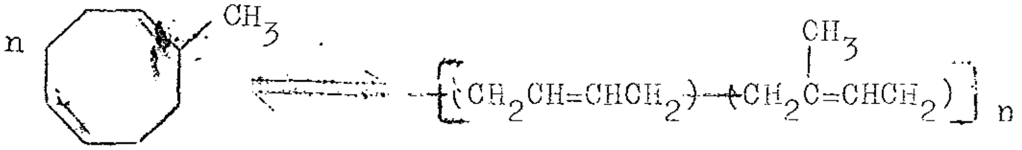
alternating interpolymers, the synthetic objectives not attainable by any other technique is one of the most attractive applications. By use of conventional methods, the copolymerization of butadiene and isoprene yields polymers that contain random sequences of $-CH_2CH=CHCH_2-$ and $-CH_2C(CH_3)=CHCH_2-$ units. In contrast, metathesis of 1-methyl-1,5-cyclooctadiene yields a polymer in which these units are more than 97% perfectly alternating, Eq.(7).[27]



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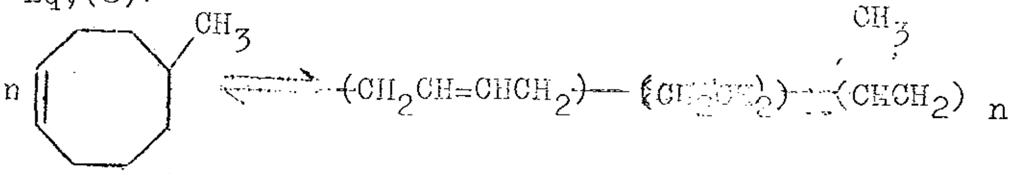
Metathesis of 5-methylcyclooctene gives the perfectly alternating terpolymer of butadiene, ethylene, and propylene, Eq,(8).



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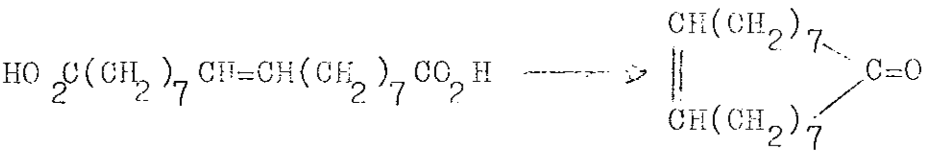
The synthetic utility of the metathesis reaction would be greatly extended by the metathesis of alkenes that bear functional groups. Boelhouwer et al were able to metathesize long chain fatty acids esters by use of a $WCl_6/(CH_3)_4Sn$ catalyst.[29] Methylester of 9-octdecene gives the 9-octadecene dimethylester, Eq.(9) which is changed to the corresponding diacid providing a starting material for the preparation of civetone, a valuable perfume component, Eq.(10) and for the preparation of an unsaturated valcanizable polyesters.

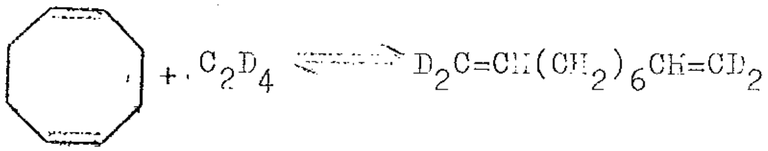
$$2CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + CH_3O_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \quad (9)$$



$$HO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2H \longrightarrow \begin{matrix} CH(CH_2)_7 \\ \| \\ CH(CH_2)_7 \end{matrix} C{=}O \quad (10)$$

The metathesis of alkynes is also gaining attention, though most of the works done in this area so far have centred on alkenes. By use of $WO_3(SiO_2)$ catalyst the conversion of 2-pentyne into 2-butyne and 3-hexyne could be accomplished in a 23% yield.[30] In this respect terminal acetylenes seem to be less useful since the major reaction becomes cyclotrimerization to benzene derivatives.[31] Cycloalkynes undergo ring-opening metathesis, like their olefinic counterparts; the conversion of cyclodecyne to a series of oligomers, $(C_6H_{16})_n$, upto the hexamer (n=6) has been demonstrated.[32]

The application of the metathesis reaction for organic synthesis is expanding at such a tremendous rate that it is not easy to cite all examples. Neverthless, two last points are worth mentioning. These are, the synthesis of isotopically labelled olefins like the reaction of tetradeuteroethylene with cyclooctene to produce terminally deuterated, diene Eq.(11), and the synthesis of Muscalure (cis-9-tricosene), the sex pheromone of the common housefly (Musca



$$+ C_2D_4 \rightleftharpoons D_2C{=}CH(CH_2)_6CH{=}CD_2 \quad (11)$$

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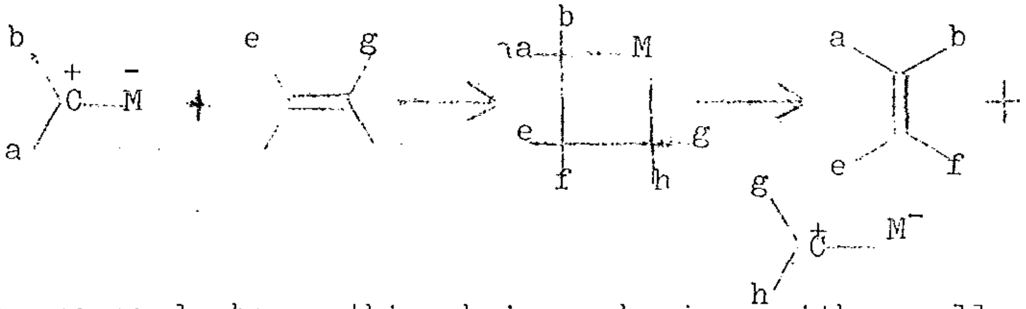
in the absence of metals prevent 2 + 2 cycloadditions from occuring.[31-41] Consequently one would expect either of the following two things to occur,

a) the formation of cyclobutanes as side products from olefin metathesis reaction.

b) the cleavage of the cyclobutanes when added to metathesis reaction mixtures.

This first mechanism proposed was ruled out when experiments to demonstrate either showed that neither occured.[42-45]

The most reasonable mechanism so far forwarded emphasizes the involvement of the metal-carbene species to propagate the chain reaction, Eq.(15).[46-53] Unlike the mechanism proposed above, this chain mechanism neither calls for cyclobutanes to be formed nor react, but yet, it nicely accounts for the gross structural change. The metal-carbene species involved were thought to be of high energy and difficult to isolate.



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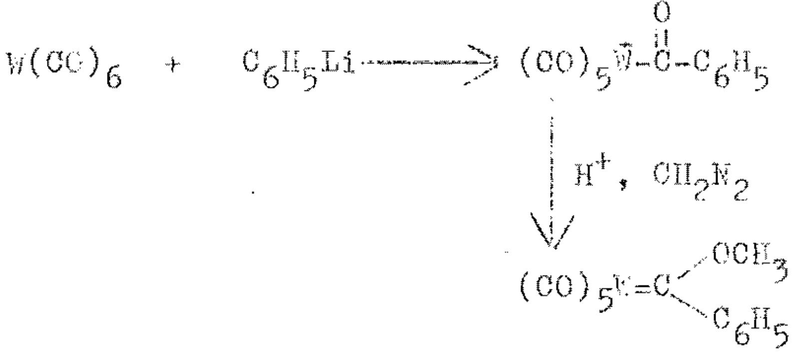
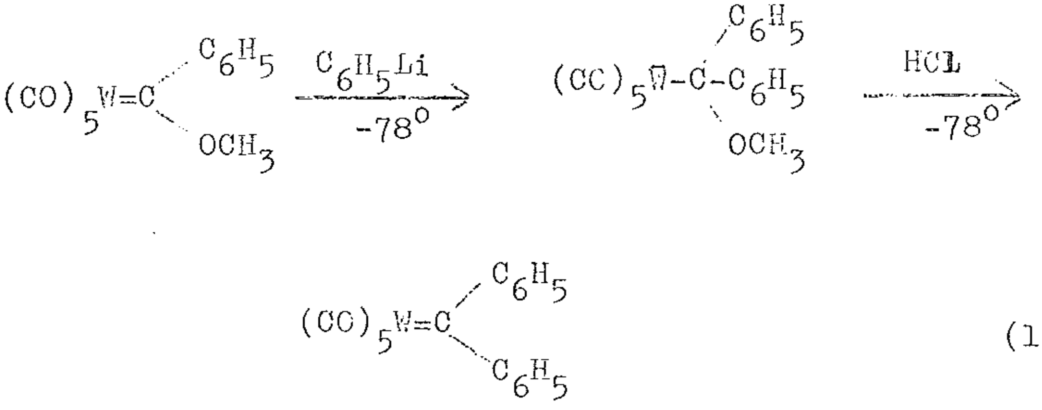
It was in 1964 that the first stable transition metal carbene complexes were synthesized and characterized by

E.O. Fischer's group.[54] They found that metal carbonyls react with organolithium reagents to produce acylmetal anions which could subsequently be alkylated on oxygen to give transition metal carbene complexes, Eq.(16). Since then many stable transition metal carbene complexes have been synthesized and these are shortly reviewed in the coming chapters. The heteroatom stabilized carbenes known which are coordinatively saturated are not so efficient as catalysts in the olefin metathesis reaction except under some drastic conditions. It is generally believed that the catalytic activity diminishes as the stability of the carbene complex is enhanced.



$$\mathrm{W(CO)_6} + \mathrm{C_6H_5Li} \longrightarrow \mathrm{(CO)_5\overset{-}{W}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5} \xrightarrow{\mathrm{H^+,\ CH_2N_2}} \mathrm{(CO)_5W{=}C}\begin{matrix}\mathrm{OCH_3}\\ \mathrm{C_6H_5}\end{matrix} \qquad (16)$$

The isolation of a non-heteroatom stabilized metal carbene complex 1 was achieved by Casey and Burkhardt.[47] This compound (diphenylcarbene) pentacarbonyl tungsten (0) was synthesized by the route shown in Eq.(17), and it was found to be catalytically active in the olefin metathesis reaction.



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If a central metal is catalytically inactive in the olefin-metathesis reaction one would theoretically expect the isolation of a metal carbene to be possible in the presence of an olefin coordinated to the central metal. What would be rather interesting is to know what happens when an olefin is coordinated to a catalytically active metal centre. An attempt to isolate an active metal carbene in the presence of an olefin coordinated to the metal and subsequent studies to know the fate of the olefin could be a desirable project. This in a way can support the attempts to explain the mechanism of the olefin-metathesis reaction. It was from this point of view that the project was designed.

The first part of theproject is directed towards the development of methods for the syntheses of some (diene)-$M(CO)_4$ complexs, [diene=1,5-cyclooctadiene (COD), or 2,5-norbornadiene (NBD) and M=Cr, Mo, W], and reaction of $(COD)W(CO)_4$ with methyllithium and subsequent methylation following similar procedures as Fischer's[54], so as to isolate the carbene complex. An attempt is also done to isolate the trimethylsilane derivative of the carbene complex.

The second part of the project is investigation of some of the (diene) $W(CO)_4$ complexes, whether they can catalytically metathesize 2-pentene into 2-butene and 3-hexene or not. (Trisacetonitrile) tricarbonyl molybdenum (0), $(CH_3CN)_3Mo(CO)_3$ is also included in the series of compounds subjected to catalytic test just for comparative reasons. Since the acetonitrile ligand has less pΠ-dΠ back bonding character and is more labile than the diene ligands, it is reasonable to know if this has any effect on the activity of the central metal as compared to the diene complexes. The well known cocatalyst, $C_2H_5AlCl_2$ is used in these catalytic tests, since it is believed that its role in the catalytically active transition metal carbonyl complexes is to generate the acyl metal anions which then lead to metal-carbene compounds.[55,56]

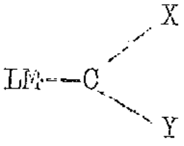
In the following chapters, some attempts will be done to present a bird's-eye-view of the bonding in the transition metal carbene complexes and some general methods used to synthesize such complexes. This is followed by a chapter dealing with a short review of different catalyst systems known in the olefin metathesis reaction.

CHAPTER 1

THE ORIGINS OF TRANSITION METAL CARBENE COMPLEXES

1.1. The Nature of Bonding

The transition metal carbene complexes have the general formula 2, where CXY is defined as a ligand with approximately SP^2 hybridized electron deficient carbene carbon. The Ccarb. is directly attached to the metal without a formal Ccarb-X or Ccarb-Y multiple bonds.



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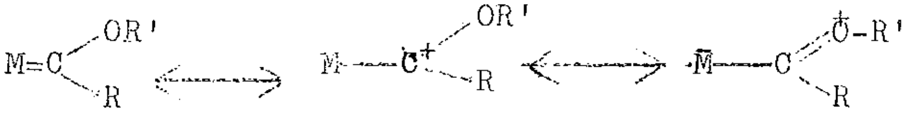
C=Ccarb (Carbene carbon)
L=Ligand
M=Metal
X,Y,= substituents attached to Ccarb.

For the alkoxy substituted Fischer type carbene complexes, there are three important resonance structures(3a, 3b,3c).



3a 3b 3c

The bonding of the carbene ligand to a transition metal is conveniently described in terms of the donation of the SP^2 hybridized lone-pair electrons of the carbene carbon to the metal atom together with a concomitant acceptance of electrons from the filled d orbitals of the transition metal into the empty Pz atomic orbitals of the carbene. The metal-carbon length and the degree of double bond character is determined by the extent to which these two processes occur. The electron donation from the lone pair of adjacent heteroatoms into the empty Pz orbital of the carbene carbon atom generates double bond character in the carbon-heteroatom bond.[57]

Carbene complexes are now known for many of the latter transition metals. The central metal electron configuration range from d^3 to d^{10} with d^5 and d^9 with yet unpresented, oxidation states from 0 to +4, and coordination numbers from 2 to 7. The corresponding configurations around the central metal include linear, square planar, tetrahedral, trigonal bipyramidal and octahedral. The majority of carbene complexes are neutral, mononuclear and have single coordinated carbene. However, cationic species are known, as are a number of di- and tri-nuclear derivatives. To date no anionic carbene compexes have been reported, although the acyl metallates $(LM-COR)^-$ are intermediates in a number of syntheses.

The stable metal carbene complexes are derived from nucleophilic carbenes and that Ccarb is highly electrophilic. This results in multiple bonding with the heteroatoms (x or y) of the ligand (see 4a) and not in (d-P) Π (Back bonding) with the metal. As a ligand, we can therefore describe the

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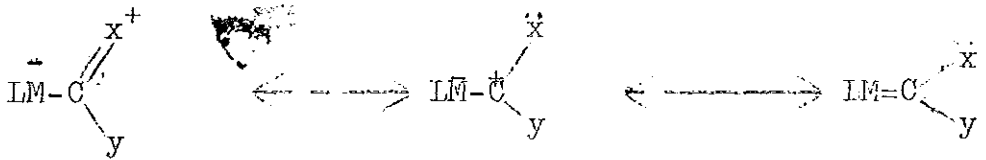
coordinated carbene as a strong -donor, but a weak II-acceptor. In this context the polarity clearly differentiates it from the 'ylide' (eg. $R_3\overset{+}{P}-\overset{-}{C}H_2$), structure.



4a 4b 4c

The conclusion that 4a and 4b are the principal canonical forms implies (i) the absence of a bond order significantly greater than unity in M-Ccar, (ii) the considerable multiple bond character in Ccarb-x, (iii) the electrophilic character of Ccarb, (iv) the analogy between Ccar-OR or Ccar-NR'R^2 and Cacyl-OR or Cacyl-NR'R^2, rather than Calkyl-OR or Calkyl-NR'R^2 organic compounds, and (v) an electronic effect of the carbene ligand on M. The clearest evidence for (i), (ii), and (iv) is crystallographic.[58]

1.2. Some Synthetic Approaches

Chugaev Salts were first prepared as early as 1915[59] but they were only recently recognized to contain carbene complexes.[60,61] The success of E.O.Fischer[54] in isolating and characterizing the first heteroatom stabilized transition metal carbene complexes, has been a good basis for the further development of different synthetic routes.

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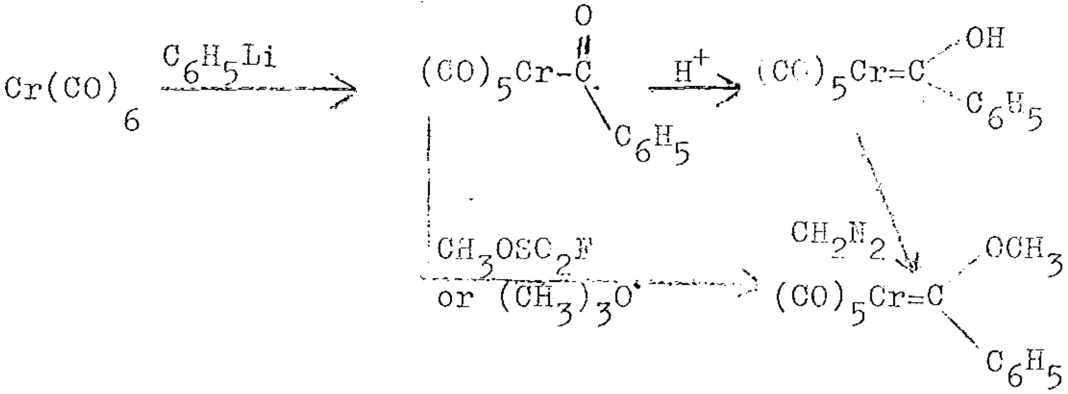
1.2.1 Nucleophilic Attack on Metal Carbonyls:

For the direct synthesis of carbene complexes from non-carbene complex precursors, Fischer's original preparation[54] (Scheme I) is the most useful, though different methods seem to appear nowadays. The anionic acyl complexes have been



Scheme I

isolated and characterized as stable tetraalkylammonium salts.[62] In the initial preparation of $(CO)_5WC-(C_6H_5)OCH_3$ Fischer reacted the anionic acyl complex with diazomethane in acidic solution to give 55% yield of the carbene complex. The preferred alkylating agents for the synthesis of alkoxy-substituted metal-carbene complexes are trialkyloxonium salts[63] and CH_3OSO_2F[64] which give yields in excess of 80%. A great number of carbene complexes have been prepared by this route from $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe(CO)_5$, $Ni(CO)_4$, and many substituted metal carbonyl compounds.[65,66] The lithium reagents widely employed are CH_3Li, n-butyllithium, substituted aryllithiums,

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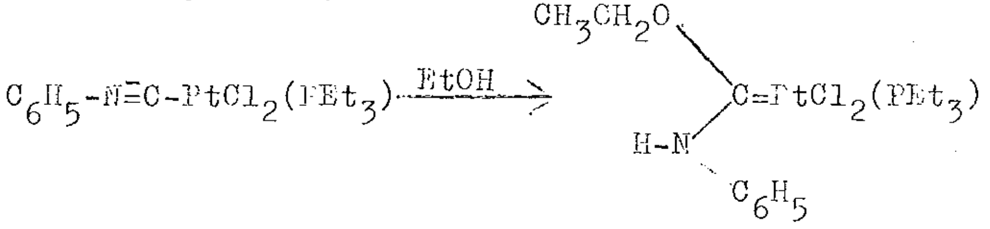
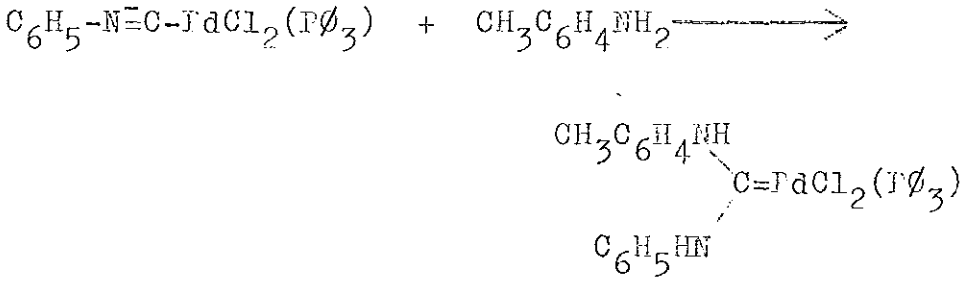
furyllithium and ferrocenyllithium. Amides can also be used to prepare metal carbene complexes from metal carbonyls.[67,68]

1.2.2. Nucleophilic Attack on Isocyanide Complexes

Alcohols add across the carbon-nitrogen bond of complexed isocyanides, Eq.(18).[69] Amines also readily add to complexed isocyanides, Eq.(19).[70]



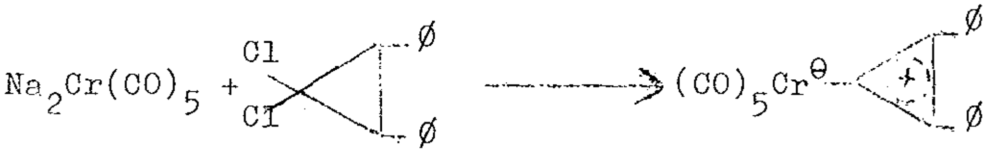
$$C_6H_5\text{-}N{\equiv}C\text{-}PtCl_2(PEt_3) \xrightarrow{EtOH} \begin{matrix} CH_3CH_2O \\ H\text{-}N(C_6H_5) \end{matrix}\!\!>\!C{=}PtCl_2(PEt_3) \qquad (18)$$



$$C_6H_5\text{-}N{\equiv}C\text{-}PdCl_2(P\phi_3) + CH_3C_6H_4NH_2 \longrightarrow \begin{matrix} CH_3C_6H_4NH \\ C_6H_5HN \end{matrix}\!\!>\!C{=}PdCl_2(P\phi_3) \qquad (19)$$

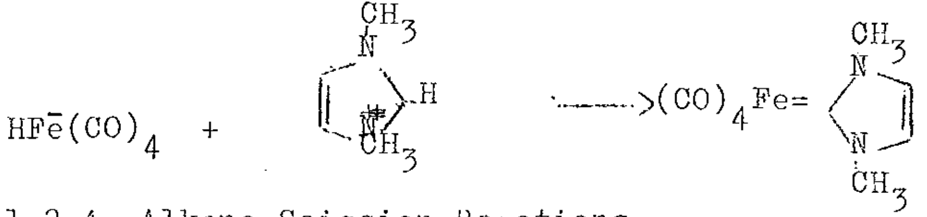
1.2.3. Reactions of Metal Carbonyl Anions

The reaction of $Na_2Cr(CO)_5$ with 1,2-diphenyl-3,3-dichlorocyclopropene gives the novel carbene complex, (Eq.20).[71]



(20)

The reaction of $NaFe(CO)_4H$ with the 1,3-dimethylimidazolium ion gives a carbon-bonded imidazole complex (Eq.21)[72]



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1.2.4. Alkene Scission Reactions

Electron-rich alkenes react with metal complexes to split the alkene and give carbene complexes, Eq.(22)[73] By a similar route a bis-carbene complex of chromium was prepared, Eq.(23).[74]

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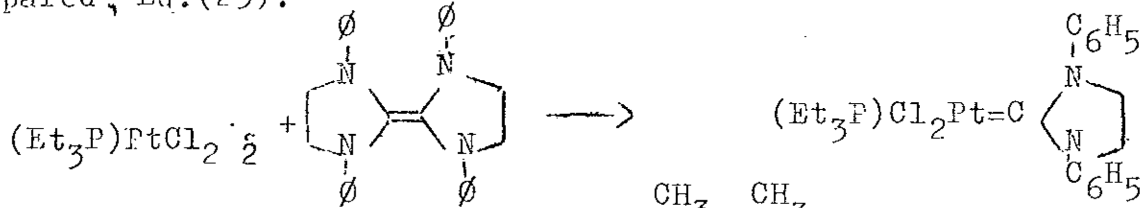

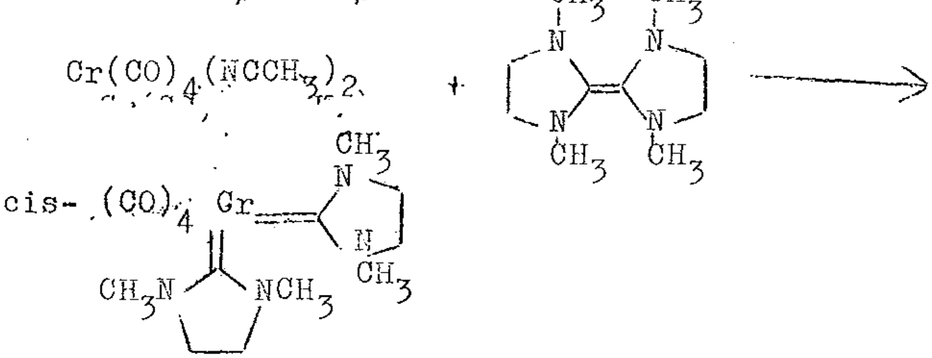

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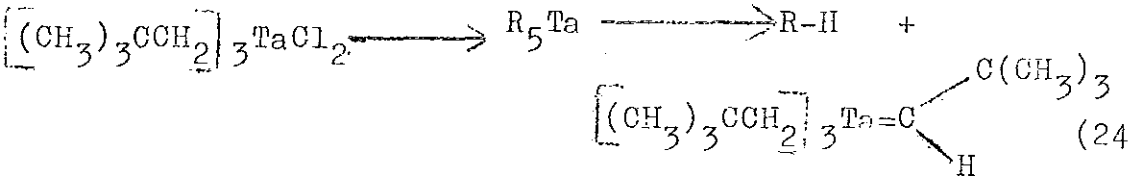
1.2.5. α-Elimination Reactions

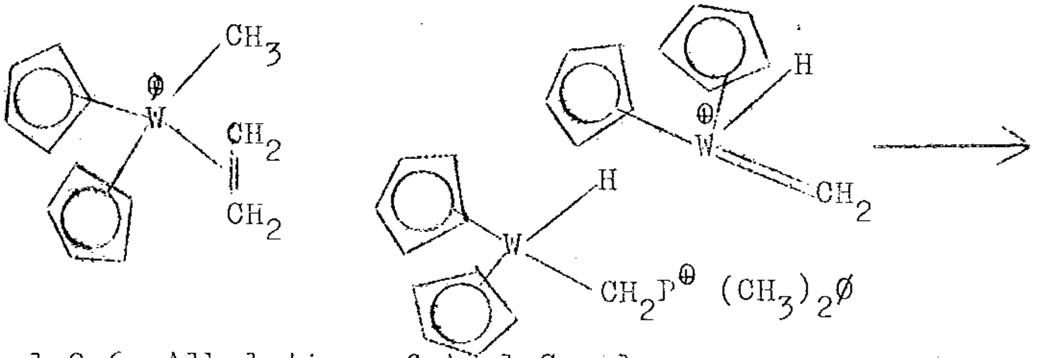
Reaction of $[(CH_3)_3CCH_2]_3TaCl_2$ with $(CH_3)_3CCH_2Li$ gives a tantalum-carbene complex.[75] Labeling studies indicate that the reaction proceeds via α-elimination from an intermediate R_5Ta compound, Eq.(24).



$$[(CH_3)_3CCH_2]_3TaCl_2 \longrightarrow R_5Ta \longrightarrow R\text{-}H + [(CH_3)_3CCH_2]_3Ta{=}C\begin{matrix} C(CH_3)_3 \\ H \end{matrix}$$

(24)

Reversible α-elimination of hydrogen from a methyl-tungsten compound to give a tungsten-methylene hydride derivative has been proposed as a key step in the reactions of $(C_5H_5)_2W(CH_2{=}CH_2)CH_3^+$ with $P(CH_3)_2C_6H_5$ Eq. (25).



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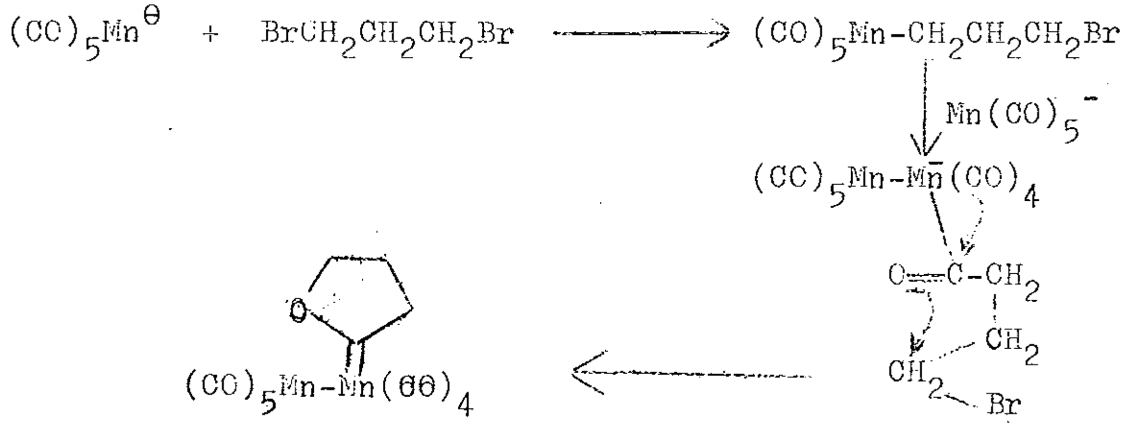
1.2.6. Alkylation of Acyl Complexes

The reaction of $NaMn(CO)_5$ with 1,3-dibromopropane produces the cyclic carbene complex 5 [77] presumably via intramolecular alkylation of an intermediate acyl complex (Scheme II)



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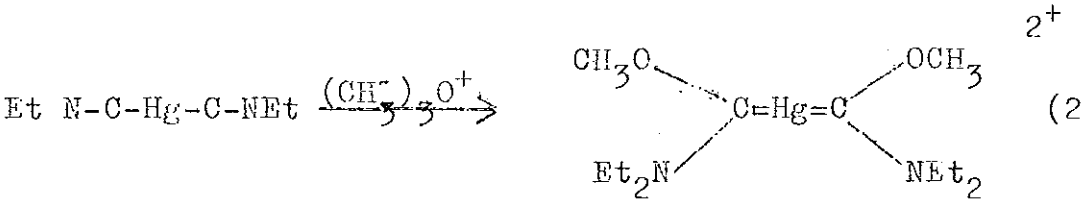
Scheme II

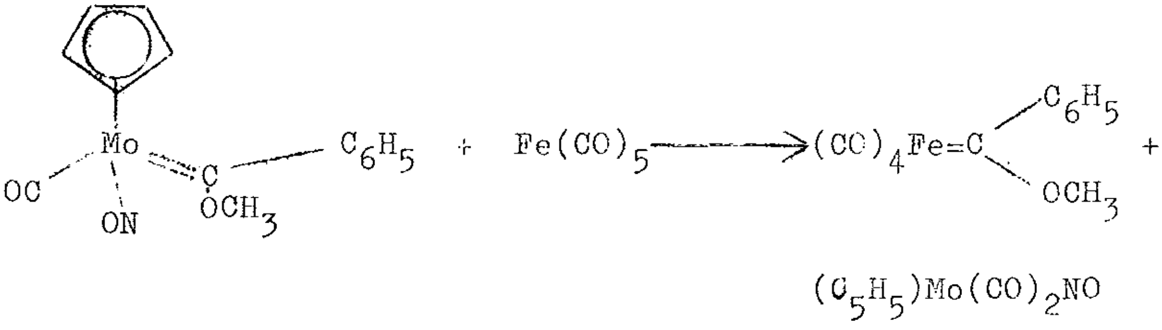
The O-alkylation of acyl mercurials produces cationic carbene complexes Eq.(26).[78]



(26)

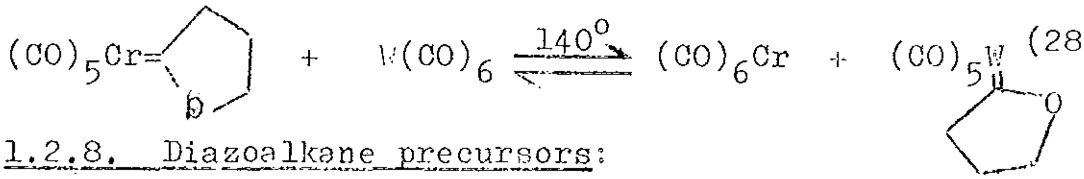
1.2.7. Carbene Transfer Reactions:

Light-catalyzed transfer of a carbene ligand from molybdenum to iron has been obserbed, Eq.(27)[79] though it is not known whether light activated the iron or the molybdenum complex to catalyze this reaction.



(27)

Casey and Anderson were able to transfer a barbene legand from chromium to tyngsten by thermal activation, Eq.(28).[80]



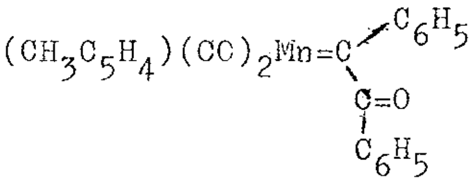
(28)

1.2.8. Diazoalkane precursors:

The reaction of diazo compounds with metal complexes has recently been reported to give carbene complexes Eq.(29).[81]

Complexes of electron poor carbenes can be prepared via this route.

$$(CH_3C_5H_4)Mn(CO)_2(THF) \quad + \quad C_6H_5COCN_2C_6H_5 \longrightarrow$$



$$(CH_3C_5H_4)(CO)_2Mn{=}C(C_6H_5)(C({=}O)C_6H_5)$$

(29)

CHAPTER 2

A SHORT SURVEY OF THE OLEFIN METATHESIS REACTION CATALYSTS

As early as 1954,[82] norbornene was polymerized by a mixture of titanium tetrachloride and either ethylmagnesium bromide or lithium tetrabutylaluminium, but the product was recognized as a polyalkenamer only in 1960.[83] The first description of the metathesis reaction was given in 1957,[84] when molybdenum oxide on alumina combined with trisoboutyl aluminium could transform propene into ethene and butene. When the same catalyst, molybdenum oxide on alumina was used in the presence of lithium-aluminium hydride and hydrogen, norbornene and cyclopentene were changed into their respective polyalkenamers.[85] In 1963, tungsten or molybdenum halides with organoaluminium compounds as cocatalysts were introduced as metathesis catalysts, when they were found to polymerize cyclobutene and [86] norbornene,[87] and the significance of their application became apparent the following year when they were found to polymerize the unstrained cyclopentene to trans-polypentenamer.[88] Ruthenium trichloride in ethanol was discovered to be a catalyst the following year.[89,90] Soluble catalyst, notably the combinations WCl_6-C_2H_5OH-$C_2H_5AlCl_2$

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and Mo $[(C_6H_5)_3P]_2Cl_2(NO)_2(CH_3)_3Al_2Cl_3$[92,25] were also found to be effective.

Certain metal carbene complexes such as $[(CH_3)_4N]$ $[(CO)_5WCOPh]$ and $(CO)_5WC(OC_2H_5)Ph$ in combination with PR_3, sulfides, sulfoxides, quinones, or N-Chlorosuccinimide, together with $TiCl_4$ cocatalyst, were also effective cocatalysts, at monomer /W molar ratios of up to 5000/1.[93]

The majority of the metathesis inducing catalysts contain either tungsten or molybdenum as the transition metal. Rhenium is the only other metal that has shown general catalytic activity. Other transition metals have been used in special cases. The olefin metathesis reaction has been found to be general for a large number of olefins and can be catalyzed by a variety of complexes. The catalysts in many cases are very active. For example, one homogeneous system will convert 10^4 moles of olefin per mole of catalyst to an equilibrium mixture of products in a matter of seconds at 25°C.[91,94] Procedures employed in the preparation of catalyst systems are diverse in many aspects. Different oxidation states can initiate the metathesis reaction under different conditions. For example, tungsten based catalysts can be prepared from precursor compounds ranging from W(0) to W(VI) oxidation states. The composition of the ligand field surrounding the metal is not very restricted. However, the ligand field does affect specific catalyst features, such as oveall efficiency, capacity to metathesize certain substrates, stereospecificity, and retention of activity in polar environments.

The metathesis catalysts can be classified into three major rather arbitrary categories.

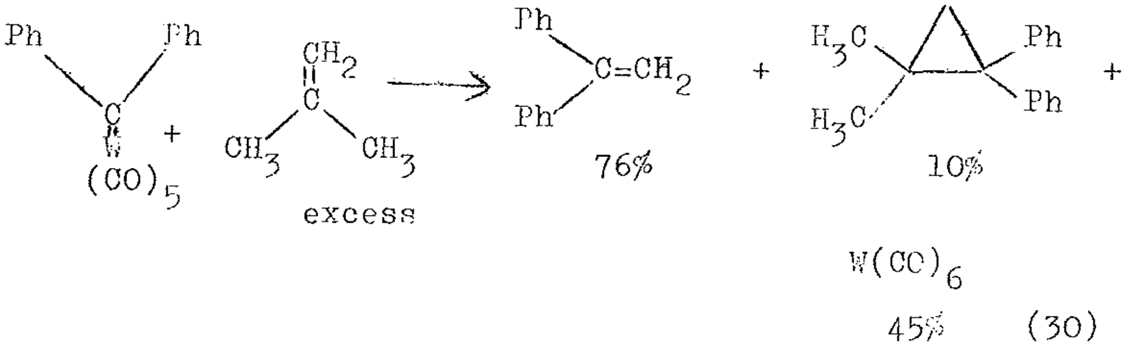
i) Catalyst systems utilizing a relatively stable and well-characterized carbene which is attached to the metal.

ii) Catalyst systems that are activated by organometallic cocatalysts which presumably form σ-bonded R-M transients, wherein M is the transition metal

iii) Catalyst combinations that do not involve a prior carbene or an organometallic component.

2.1. Catalysts Possesing Carbene Metal Ligands:

After the novel synthesis of the first non-heteroatom stabilized carbene, diphenylcarbene (pentacarbonyl) tungsten(O) complex[47], Katz and coworkers demonstrated that this stable W(O) complex may also be employed as a metathesis catalyst Eq.(30).



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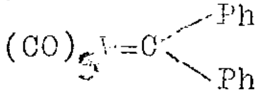
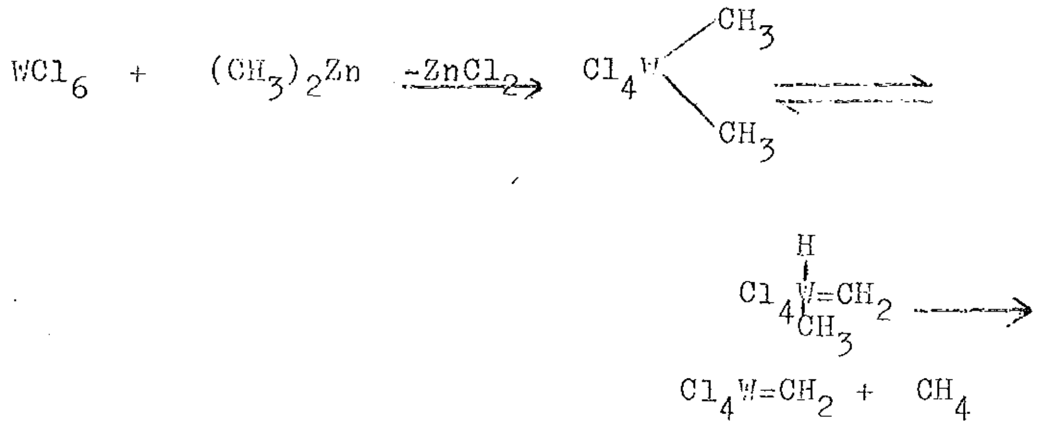
In comparison to other catalysts, the coordinatively saturated  $(CO)_5W{=}C\begin{smallmatrix}Ph\\Ph\end{smallmatrix}$ is surprisingly sluggish.[95] Recently, Banasiak from Phillips Petroleum Company,[97] has demonstrated that the stable (methoxyphenylcarbene) pentacarbonyl tungsten (0), $(OC)_5W{:}CPhOMe$ is capable of converting 1-pentene to 4-octene in a yield of 37.2 mol % in ≈72h when heated to 55°C. For this coordinatively saturated heteroatom stabilized carbene the promoters found to be effective were halogenated compounds of general formula [$RCCl_3$, $R+CCl_3CO$, Ph, Br etc], and tin alkyl compounds R_4Sn, [R=Me,Et,BU] or $BuSnCl_3$.

2.2. Catalysts Activated by Organometallic Cocatalysts.

It has been well documented that organometallic cocatalysts do provide σ-bonded alkyl groups when reacted with transition metal derivatives, particularly when the transition metal is at a high oxidation state. Typical examples of active catalyst systems are unmodified and alcohol-modified WCl_6/R_mAlCl_n (m+N=3), WCl_6/RLi, WCl_6/R_4Sn, WCl_6/R_2Zn, $MoCl_5/R_3Al$, and $Mo(Ph_3P)_2Cl_2(NO)_2/\ R_3Al_2Cl_3$. Carbene metal-generation from σ-bonded alkyl groups was first proposed by Muetlerties when he observed CH_4 generation by reacting $(CH_3)_2Zn$ with WCl_6. Muetterties' schemes are presented in Eqs.(31) and (32).



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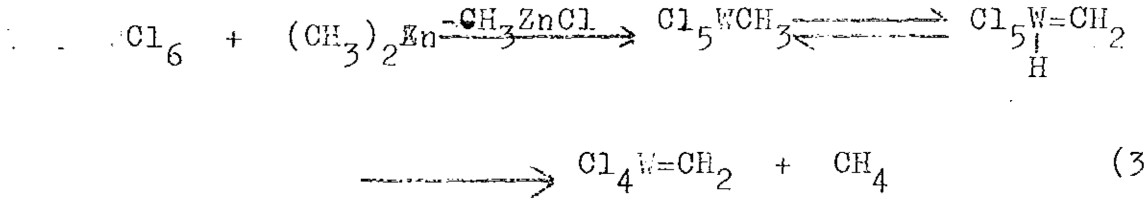


$$WCl_6 + (CH_3)_2Zn \xrightarrow{-CH_3ZnCl} Cl_5WCH_3 \rightleftharpoons Cl_5\underset{H}{W}{=}CH_2 \longrightarrow Cl_4W{=}CH_2 + CH_4$$

(32)

The $CH_3\text{-}W \rightleftharpoons CH_2{=}W\text{-}H$ equilibrium, proceeding by -hydrogen migration from the -alkyl to the metal, has been demonstrated by Green.[100] Shrock has also reported that abstraction of -hydrogens is a route to isolable alkylidenetantalum complexes, after which an addion evidence for the formation of carbenoid species in the reactions of $(CH_3)_3Al_2Cl_3$ and Mo $[(Ph_3P)_2Cl_2(No)_2]$ as well as $(CH_3)_4Sn$ and WCl_6 was recently reported by Grubbs.[102] When $(CD_3)_4Sn$ was used as a cecatalyst predeutrated methane and ethylene were produced Eq.(33).

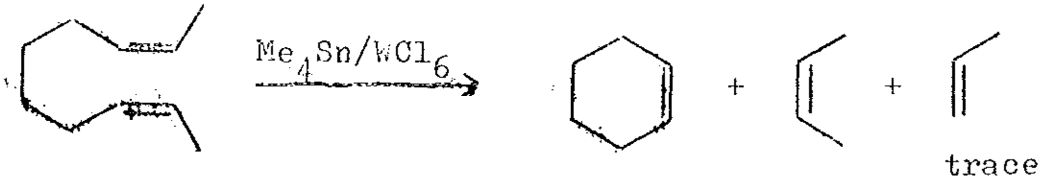
$$WCl_6 + (CD_3)_4Sn \longrightarrow CD_4 + CD_2{=}CD_2 + W - \text{catalyst}$$

(33)

The suggested scheme for ethylene formation is dimerization of methylene metal complexes:

$$2LnM{=}CH_2 \longrightarrow CH_2{=}CH_2$$

Evidence for a methylene-metal initiating species was provided by detection of propylene early in the course of metathesis of 2,8-decadiene with Me_4Sn/WCl_6, in addition to normal metathesis products, Eq. (34). Proper deuterium-



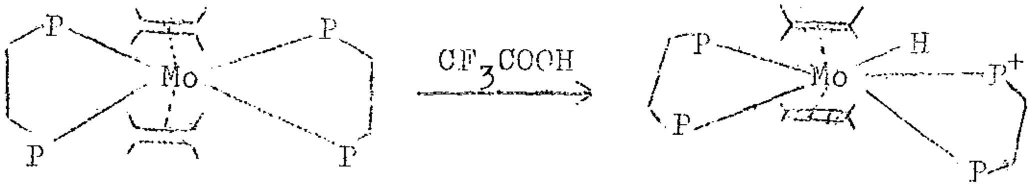
(34)

labeling experiments involving $(CD_3)_4Sn$ and $[1,1,1,10,10,10,-D_6]$-2,8-decadiene confirmed that propylene is indeed the first formed olefin, and its structure indicated that the methylidene and ethylidene moities originated from Me_4Sn and 2,8-decadiene, respectively.

2.3. Catalysts Void of Organometallic Cocatalysts.

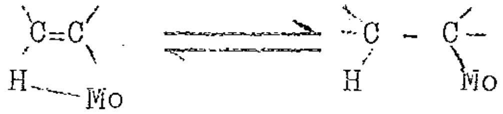
Whereas formation of the original carbene metal species in catalysts from the above two categories is reasonably accounted for and substantiated by experimental work, pathways for carbene formation in systems that do not employ organometallics are in most cases still unresolved. Nevertheless it is suggested nowadays, that hydrogen transfer processes in

Mo and W complexes with olefins take place, which may be related to carbene generation in olefin metathesis catalysts. Osborn observed that $Mo(C_2H_4)_2$ $(diphos)_2$ having a trans octahedral structure, undergoes protonation when reacted with CF_3COOH Eq.(35). NMR studies clearly indicated that a



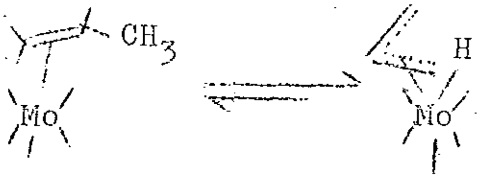
(35)

rapid and reversible ethylene insertion-deinsertion process takes place Eq.(36).



(36)

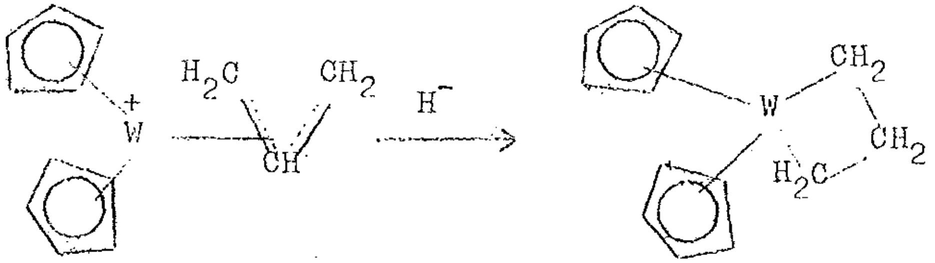
A different reaction occurs when propylene is employed. A II-allyl hydride complex is the observed stable product, thus suggesting the following equilibrium.



(37)

The two significant items confirmed in this work were that (i), Molybdenum, and most probably tungsten, can expand its sphere of coordination beyond 6 and, (ii) hydride shifts transforming olefins to allyls or II-allyls, via II- and II-η^3 processes, respectively, are feasible in metals that are known to produce active metathesis catalysts.

According to Green[104] a Π-allyl complexed to W or Mo can undergo a nucleophilic attack by H^- on thecentral carbon of the ^{3} allylic group, forming a stable metallocyclobutane Eq.(38). Cyclopropane and propylene were evolved[105] on heating the metallocyclic product of Eq.(38). Irradiation of the complex produced ethylene and some methane.



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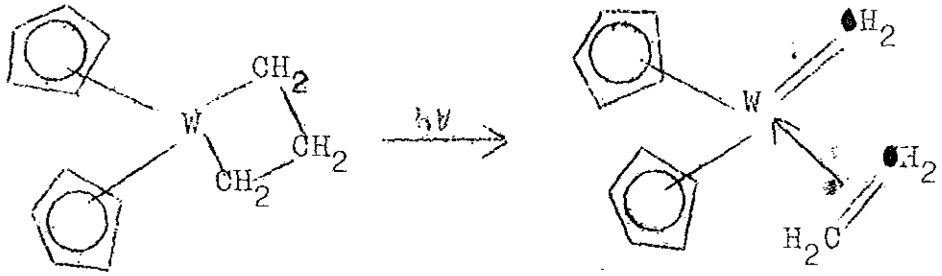

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Osborn and Green's elegant result are instructive but their relevance to metathesis must be qualified. Until actual catalytic activity with the respective complexes is demonstrated, it remains uncertain whether this chemistry indeed relates to olefin metathesis.

The route to carbene initiation for systems catalyzed solely by transition metal salts[106] or their combination with Lewis acids such as $AlCl_3$, is not well established. Nevertheless, some evidence suggests reduction of the metal by the olefinic substrate.[105]

It is quite obvious that, the number of catalysts, and the different conditions needed for metathesis to take place are nowadays becoming so vast and fastly developing that it would be unwise to attempt to discuss all. Just for the sake of partial completness the different catalyst systems, their selectivities and speed of reactions are summarized in Table 1 below.

Table 1. Common Catalyst Systems, their Selectivities and Speed of Reactions.

Catalyst system	Speed	Selectivity	Ref
Molybdenum			
$MoCl_2(NO)_2L_2/Al_2(CH_3)_3Cl_2$			
$L=\emptyset_3P, EtPy, \emptyset_3PO, \emptyset_3As$	fast	9 5	15,16,17
$Mo(CO)_5/Cl(NR_4^+)$	slow		107
$MoCl_5/(Et_3Al)/O_2$	slow	71	19
$MoCl_5/Et_3Al$	slow		19
$Mo(CO)_6/SiO_2/Al_2O_3$			108
Tungsten			
$WCl_6/EtAlCl_2(4)/EtOH(1)$	very vast	99.6	18
$WCl_6/Et_3Al(0.5)(O_2)$	fast	96	19
$WCl_6/LiAlH_4(1)$	fast	93	109

Catalyst system	Speed	Selectivity	Ref
$WCl_6/BuLi$ (?) (O_2)	slow	100	23
WCl_6/n-Pr-MgCl(2).ether	very slow		110
WCl_6/Bu_4Sn	slow		21
$W(Pyr)_2Cl_4-EtAlCl_2(8)CO$	fast		111
$WCl_6CH_3CN/Bu_4Sn(4)$	fast	97	22
$W(CO)_6CCl_4$.light (80^o)	slow	85	112
$W(C_6H_6)Cl_3/AlCl_3$	slow		24
WO_3SiO_2			113
$W(\emptyset_2C)(CO)_5(50^o)$	slow		95
W(arene)$(CO)_3$	slow		114
$WO(OCH_3)_4$ or $W(CCH_3)_6/EtAlCl_2$	fast	high	115
Rhenium			
$ReCl_5Et_3Al.O_2$	fast	100	19
$Re(CO)_5Cl.EtAlCl_2(90^o)$	fast		20
Re_2O_7/SiO_2			116
Other metals			
$RHCl(\eta^3-C_3H_5)_2/Al_2(CH_3)_3Cl_3$	slow		17
$CrCl_2(NO)_2(\emptyset_3PO)_2$	inactive		17
$[Ir(cyclooctene)_2Cl]_2$	only with strained olefins		117

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CHAPTER 3

RESULTS AND DISCUSSION

3.1 The Synthetic Part

The change in colour of the reaction solution, the change in their spectrum in the carbonyl absorption and the NMR data clearly indicate that reaction has taken place between (COD)W$(CO)_4$ and methyllithium.

The sharp absorption bands at 2041, 1946, and 1898 cm^{-1} which correspond to the starting material, are clearly observed to change during the progress of the reaction by continuous decreament in the intensity of the bands at 2041 and 1898 cm^{-1}, which finally disappeared when a completely brownish-red solution I was obtained. The band at 1946 cm^{-1} was shifted to 1965 cm^{-1} with a shoulder at 1925 cm^{-1}.

In addition to the change in the terminal carbonyl absorption region, the other observation was a development of another peak at 1620 cm^{-1}. Though free olefins show a C=C stretching vibrations in this region the coordinated 1,5-cyclooctadiene in the starting material doesn't give an absorption band in the same region presumably due to the decreament in the bond order by complex formation with tungsten metal. This fact is also theoretically supported since the antibonding orbitals of theolefinic carbons accept electron from the metal by back donation. The new peak suggests the formation of a ketonic type carbonyl, $CH_3-\underset{\overset{\|}{O}}{C}-W$. This is also supported by the fact that $C_5H_5W(CO)_3COCH_3$ absorbs at 1631 cm^{-1} which corresponds to the C=O stretching frequency in the $CH\ -\underset{\overset{\|}{O}}{C}-W$.

The NMR spectrum of <u>Ia</u> doesn't indicate the presence of any olefinic protons which are expected to appear at a lower field. This obviously tells us that 1,5-cycloctadiene is no more coordinated to the metal as an olefin after the reaction. The resonance at 2.2 δ corresponds to CH_3-protons introduced by methyllithium. This can be compared with the CH_3-protons introduced by the reaction of $W(CO)_6$ with methyllithium in the Fischer type complexes with a resonance at 2.32δ [54]. The shift to the upfield region in out case is consistent with the theoretical expectation in that in the Fishcher type complexes the metal is surrounded by five carbonmonoxide ligands which have a very strong Π-back accepting capacities to their antibonding orbitals and hence a decrease in the electrondensity on the metal, and that has the effect of further decreasing the electron cloud on the attacked carbonyl carbon. Further the quartet at 3.45 δ and the triplet at 1.2δ of <u>Ia</u> correspond to the protons of diethylether, which is similar to that of the coordinated diethylether of Fisher complex, $(OC)_5Cr(CN(CH_3)_2Oli.2O(C_2H_5)_2$[67]

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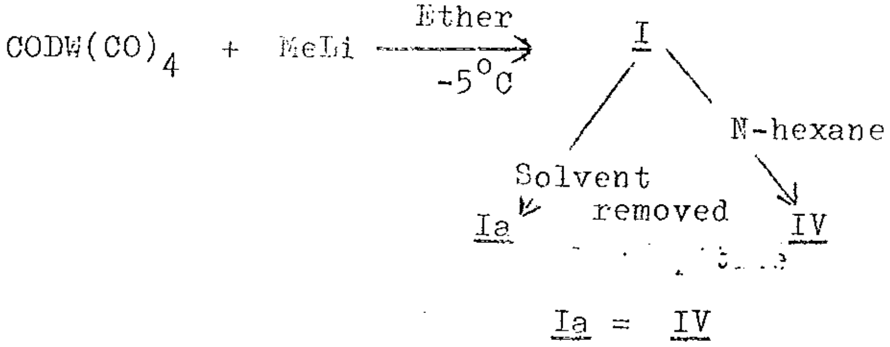
The multiplet at 1.2ppm for Ia could be the formation of the σ-type complex which might have occured by disappearance of the olefins by attack of the methy from methyllithium, but this idea is not yet established.

The compound II formed after treatment with aqueous acid and diazomethane which showed the multiplet at 0.9δ and a siglet at 2.0δ are similar to the others above, with the appearance of another peak at 3.2δ which is thought to be the CH_3O-protons, but the other peaks are not in accordance with what is expected.

The red-brown compound IV precipitated from the red-brown solution I by treatment with n-hexane gave the same product as compound Ia, (Scheme III).



Scheme III

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Treatment of the red-brown solution I with $(CH_3)_3SiCl$ which gave a precipitate of LiCl and a deep red solution demonstrates that the red brown solution contains lithium ion in some form which in this case is as a lithium salt of the complex, and this idea is supported by the high solubility of the initial residue after removal of the ether. The NMR spectrum shows that $(CH_3)_3Si\text{-}O$ is presumably present (see Scheme IV) which corresponds to the sharp singlet at 1.2 δ, which would be expected to appear upfield nearer to the standard TMS if the silicon was not bonded to an heteroatom. The resonance at 2.0 δ in this cas corresponds to the CH_3- initially introduced by the methyllithium, and the multiplet and singlet at 0.9 δ and 0.75 δ respectively, could possibly be the alkyl type ligand as suggested above...

$$\left[>C\text{-OLi} \right] + (CH_3)_3SiCl \longrightarrow \left[>C\text{-O-Si}(CH_3)_3 \right] + LiCl$$

Scheme IV

The absence of the olefinic protons cannot be surprising since the catalytic investigation has shown that $(COD)W(CO)_4$ has the capacity to disproportionate 2-pentene into 3-hexene and 2-butene (See table III). Eventhough it can be ambiguous to predict what has exactly happened to the 1,5-cyclooctadiene ligand, it is not expected to remain

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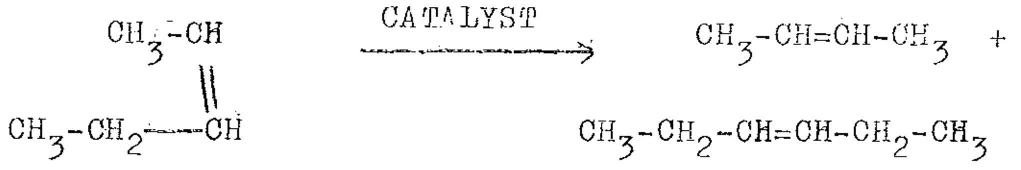
coordinated to the metal centre in the presence of the carbene which is expected to be generated by the reaction with methyllithium. Presumably the absence of the olefinic protons after the reaction suggests that an active metal centre which in this case consists of a metal carbene bond must have been formed.

It is expected that the isolation of the carbene in the presence of a diene coordinated to the metal is possible for catalytically inactive compounds like (NBD)Cr$(CO)_4$. The kinds of products formed from the reactionof alkylmetals reagents with the diene tetracarbonyl metal complexes and the comparisons of the products obtained from active and inactive systems can give hints to the actual path of the metathesis reactions. The complete characterization of the products should include elemental analysis and mass spectra. Yet, the high sensitivity of carbene complexes to air and moisture seem to halt their complete characterization to some extent. In olefin metathesis reaction the success to establish the fully correct mechanism go side by side with the different attempts to isolate the catalytically active complex. Though it should not be frustrating, the isolation and characterization of the active species from a catalytic solution is one of the most difficult tasks that should be given special attention in this area of inquiry.

3.2. The Catalytic Investigation Part

In the analysis of the products obtained from the catalytic reactions, it is ascertained that from the active systems the products obtained are 2-butene and 3-hexene. The formation of 3-hexene was confirmed by distilling it out and characterizing by NMR spectroscopy, which gage resonances at 5.3δ (a triplet), at 2.0δ (a multiplet) and at 1.0δ (a Triplet in the ratio of 1:2:3). The comparison of the distilled 3-hexene retention time, with the peaks obtained in the unknowns clearly demonstrates that 3-hexene is obtained. Further the formation of 3-hexene is supported by the fact that after distilling away the hexene the chromatogram obtained didn't give the hexene peak. The addition of 3-hexene into the catalyst solution after deactivation, lead to increament in the peak area of the 3-hexene.

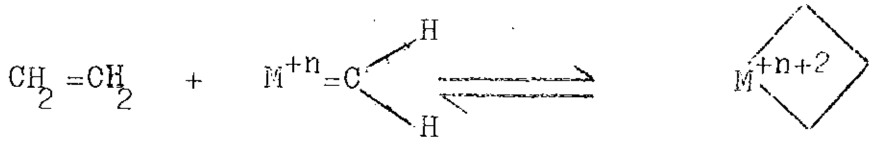
In all systems where the 3-hexene peak appeared in the chromatogram, there is always another peak of almost the same area as that of 3-hexene which comes just before the 2-pentene peak. This presumably corresponds to 2-butene which comes as a product of the metathesis reaction. Eq. (40)



$$\begin{array}{r} CH_3-CH \\ \| \\ CH_3-CH_2-CH \end{array} \xrightarrow{\text{CATALYST}} \begin{array}{l} CH_3-CH=CH-CH_3 \quad + \\ CH_3-CH_2-CH=CH-CH_2-CH_3 \end{array} \qquad (40)$$

The comparison of our systems with the WCl_6-C_2H_5OH-$EtAlCl_2$ system which is known to be a metathesis active system[91] has further helped identification of the reaction products, 2-butene and 3-hexene.

It is quite interesting to note that in general, the tungsten compounds are more active than the molybdenum complexes. The chromium complex tested $(NBD)Cr(CO)_4$ is infact completely inactive with no traces of 3-hexene even after 24 hours. The inactivity of the chromium complex is not so surprising since so far there is no chromium complex put among the most active systems since the discovery of olefin metathesis reaction. The best activity of the tungsten complexes among the sub-group can be explained by the fact that the formation of the metallo-cyclobutane intermediate is favoured more since the oxidation of themetal, the last element in the subgroup can easily take place. It is believed that the oxidation state of the metal has to change by two units to form the metallocyclobutane intermediate, Eq.(41).[118]



(41)

This mechanism explains the activity of the WCl_6 system where the oxidation state of tungsten is changed from +6 to where the oxidation state of tungsten is changed from +6 to +4($W^{IV} \rightleftharpoons W^{VI}$). Muttertis and his coworkers found that the standard tungsten hexachloride based catalyst systems were inactive when prepared under completely oxygen free conditions.[115] The introduction of oxygen or oxygen containing species induced high activity.

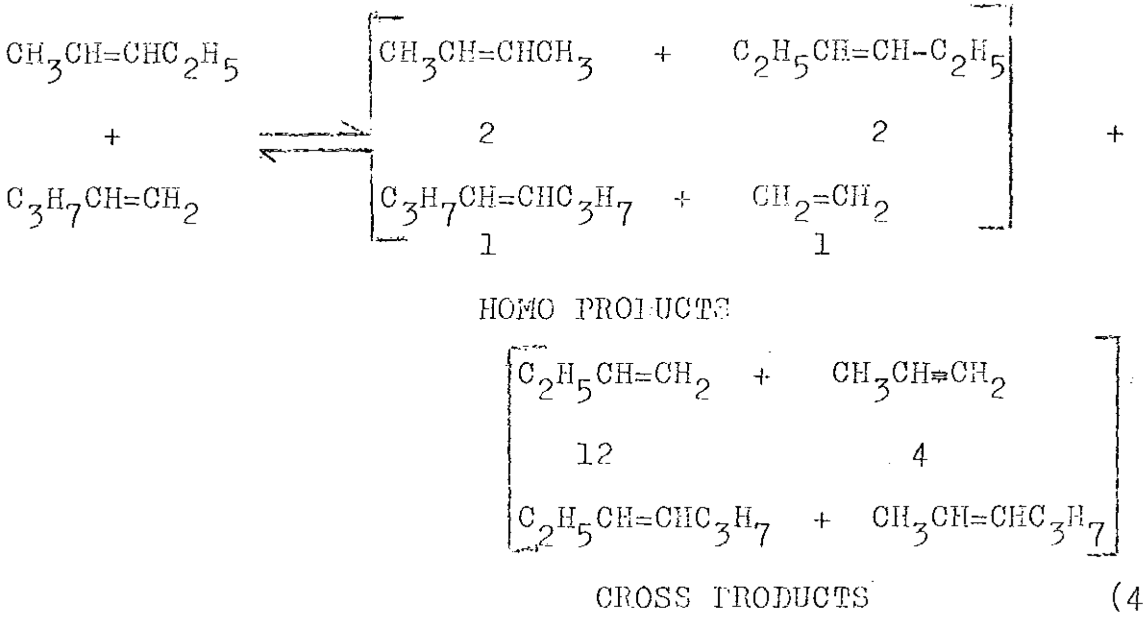
In our systems also it is believed that the oxidation of the metals to a higher oxidation state is essential. Eventhough the catalyst systems were prepared under oxygen free conditions, the introduction of oxygen through syringe transfer of solvents, or rubber serum caps etc. is sufficient to activate the systems.

In the catalysts prepared from tungsten and molybdenum carbonyl complexes, it has been proved[119] that, they require oxygen as an activator. It was shown that, a mixture of 1 equivalent of $W(CO)_5$-$P(C_6H_5)_3$ and 4 equivalents of $C_2H_5AlCl_2$ showed no catalytic activity until 12 equivalents (based on W) of O_2 was introduced. Introduction of the oxygen oxidizes the alumin um alkyl to increase its acidity. This observation is consistent with the fact that the increased activity of the WCl_6 system in the presence of an alcohol is due to the formation of W-O systems.[20]

Of the diene-tetracarbonyl and acetonitrile tricarbonyl metal complexes we tested the systems which show activity, have one common feature, and that is the equilibrium seems to be attained slowly. In other words, all catalysts which show some activity at the end of the 1st hour give more reaction products at the end of 24 hours. In these systems no attempt was done to deactivate the catalysts after a few seconds or minutes. The break as was shown in table III was chosen after 1 and 24 hours. This data is not quite sufficient to say that equilibrium is attained after several hours. It is possible that the catalyst becomes active in the first very few seconds after addition of theolefin and start being deactivated, but this needs further studies to be conclusive.

The chromatogram of all the active systems showed a small peak just before the 2-butene peak, (see apencices III and IV), which presumably corresponds to a 3-carbon propene peak which arises from the cross metathesis of 2-pentene with 1-pentene, which can be present as an impurity.

It was observed that [120] a mixture of 1-pentene and 2-pentene when subjected to metathesis conditions, gave homo and cross products of which the latter were the major products Eq.(42).



$$\begin{array}{l} CH_3CH{=}CHC_2H_5 \\ \quad + \\ C_3H_7CH{=}CH_2 \end{array} \rightleftharpoons \left[\begin{array}{ccc} CH_3CH{=}CHCH_3 & + & C_2H_5CH{=}CH{-}C_2H_5 \\ 2 & & 2 \\ C_3H_7CH{=}CHC_3H_7 & + & CH_2{=}CH_2 \\ 1 & & 1 \end{array}\right] + \left[\begin{array}{ccc} C_2H_5CH{=}CH_2 & + & CH_3CH{=}CH_2 \\ 12 & & 4 \\ C_2H_5CH{=}CHC_3H_7 & + & CH_3CH{=}CHC_3H_7 \end{array}\right] \tag{42}$$

HOMO PRODUCTS

CROSS PRODUCTS

This result indicates that a primary olefin can compete with the internal olefin in the cross reaction but does not undergo metathesis with itself. The formation of propene as one of the cross products from the above experimental result is in support of the idea that the propene peak is present in the chromatogram.

The remarkable result obtained from complexes subjected to catalyst tests is the high activity of (NBD)W(CO)$_4$ whic gave a complet conversion after 24 hours (table III). The fact that olefin metathesis is a reversible equilibrium controlled reaction and that for simple acyclic alkenes, the heat of reaction is essentially zero, the equilibrium concentration being dictated by entropy factors and hence the maximum conversion expected to be 50%,[121] may seem to contradict the experimental result (59.24%) at a first glance.

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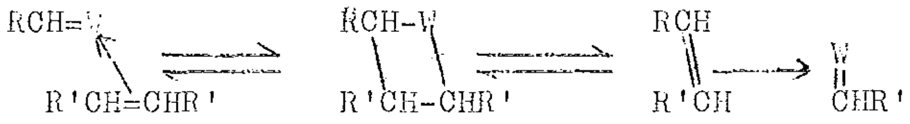
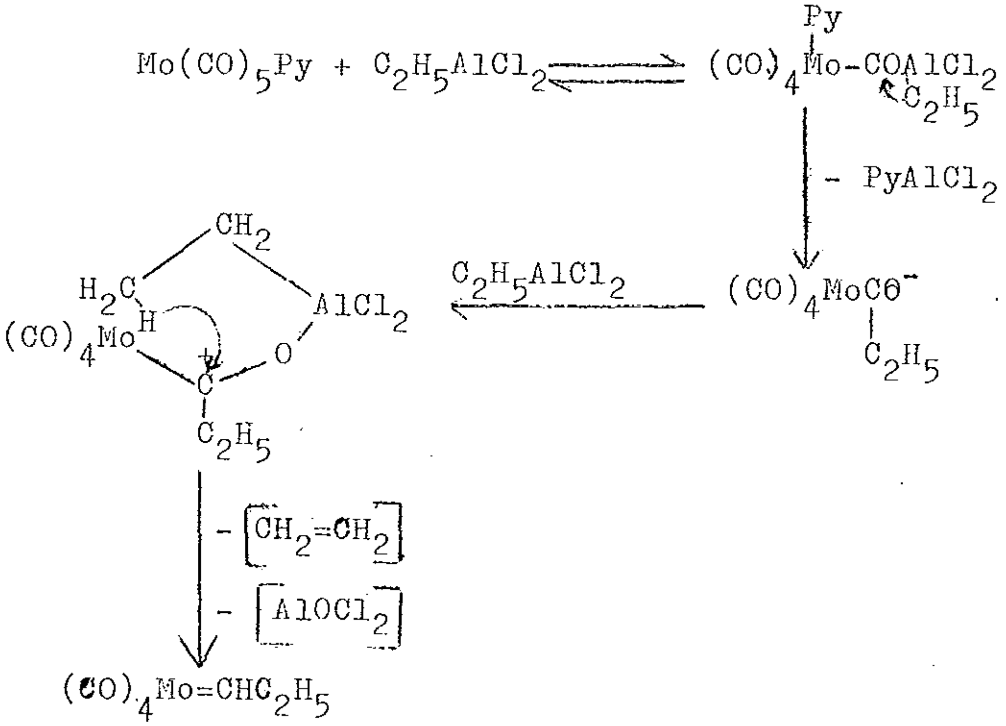
The presence of 1-pentene as an impurity can be one factor for this discrepancy. As was shown in Eq.(42) above the cross products are the major products which contain higher ratios of the isomers of 4-carbon and 6-carbon. Since the percentage conversions were calculated referring to the peak area of 3-hexene the calculation didn't exclude the the area which comes from the cross product as these were not resolved in the chromatographic analysis. The use of an internal standard and a very pure 2-pentene can minimize this error. It is also possible that 2-butene, one of the reaction products which is a gas at room temperature escapes out of the reaction solution thus shifting the equilibrium towards the formation of more of 3-hexene which may also support the high percentage conversion. In any cas it is quite interesting that (NBD)W$(CO)_4$ can be put among the most active catalysts in the olefin metathesis reaction.

So far no attempt was done to explain the mechanism of the reactions for the particular complexes tested for catalytic activity. In this respect Casey's Scheme[47], Eq.(43) which emphasizes a need to accommodate the incoming olefin within the coordination sphere of the metal prior to rearrangement to a metallocycle in the explanation of the mechanism, followed by the first non-heteroatom stabilized (diphenylcarbene) tungsten pentacarbonyl seems to be attractive.



(43)

The scheme calls for an empty coordination site on the metal in addition to the complexed carbene. The generation of the carbene for the metathesis active carbonyl complexes Re(CO)$_5$Cl/RAlCl$_2$ and Mo(CO)$_5$Py/RAlCl$_2$ was proposed by Farona and coworkers.[55,56,122] In their explanations it is stressed that the key step is the insertion of CO ligand in the R-AlCl$_2$ followed by a sequence of steps that produce the initial carbene Eq.(44).



(44)

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The need for an empty coordination site after the carbene generation before metathesis takes place can be a key step in the (NBD)M$(CO)_4$, (COD)M$(CO)_4$ and $(CH_3CN)_3M(CO)_3$ (M=Cr or Mo or W) complexes considered. The lability of the acetonitrile and olefin complexes is expected to be higher than carbonmonoxide ligand due to the high back accepting capacity to its empty antibonding orbital of the latter.

Casey has also demonstrated the carbonyls of $(CO)_5W{=}CPh_2$ are vulnerable to exchange processes under relatively mild conditions Eq.(45)[123]. Under conditions where carbonyl

$$(CO)_5W{=}CPh_2 \xrightarrow[33^oC]{^{13}CO} (^{13}CO)(CO)_4W{=}CPh_2 \qquad (45)$$

exchange is suppressed, the highly reactive $(CO)_2W{=}CHPh$ did not exhibit any carbene exchange. The ligand exchange to the logistics aspects of olefin metathesis[3,4,124] is enormous. The inefficiency of $(CO)_5W{=}CPh_2$ as a metathesis catalyst is thought to be due to the slow rate of displacement of carbonyl ligands. The hypothesis is supported by Chauvin's report [125] on a catalyst derived from $(CO)_5W{=}C(OEt)C_4H_9$, which is highly stable carbene W(0) compound but displays an efficient catalyst system by photochemical or thermal activation, or when mixed in dark with $TiCl_4$, where the latter is expected to promote the carbonyl displacement. Eventhough the whole work done was not directed to the study of the actual path of the reaction, extension of Farona and his co-workers proposal for the mechanism followed by the $(CO)_5MoPy$ complex ,Eq.(44) to the catalyst systems studied here which showed activity in the disproportionation of 2-pentene is quite reasonable;The role of the co-catalyst $EtAlCl_2$ used is most likely to produce the metal carbene species which immediately co-ordinate the olefin and subject it to metathesis. The lability of COD, NBD and acetonitrile ligands as compared to CO support the idea that a free co-ordination site is initially formed with a better ease. The better lability of the acetonitrile ligand as compared to the NBD dose not seem to enhance the catalytic activity of molybdenum, but more experimental details are needed to be conclusive.

In our opinion $(NBD)W(CO)_4$ can polymerize cyclic olefins like norbornene which are more strained than 2-pentene. In the catalytic investigations done the ratio of the metal complexes to 2-pentene was only 1:1000, far less than stoichiometric ratio. Hence it was not possible to detect whether some olefinic compounds formed from metathesis of 2,5-norbornadiene with 2-pentene were also formed or not. This may be achieved by using higer concentration of the catalyst, but in this case the system turns out to be a

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CHAPTER 4

EXPERIMENTAL SECTION

General Techniques

All syntheses of moisture and air sensitive compounds were done under dry nitrogen atmosphere.

Diethylether was dried over potassium metal. It was treated with benzophenone and the stable blue solution refluxed for several hours and distilled for an immediate use.

Hexane was dried over lithiumaluminium hydride and distilled under an inert atmosphere.

Infrared spectra were obtained on Perkin Elmer 727B Infrared Spectophotometer. The values are given in cm^{-1} units.

Nuclear magnetic resonance spectra were obtained on varian T-60 spectrometer. Values are given in (ppm) downfield from tetramethylsilane (δ =0).

Melting points were determined in a capillary tube on a Hoover capillary melting point apparatus and are uncorrected.

Gas chromatography was obtained by Helwett Packard 5710A Gas Chromatograph using 3% SE-30/80/10V chromosorp

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$(CH_3CN)_3W(CO)_3$ gradually dissolved forming a solution with a yellow characteristics colour of the complex. However, some insoluble matter remained during the entire reaction period. After the reaction period was over, the reaction mixture was filtered hot and the residue washed with a few milliliters of boiling hexane. The filterate was cooled for four hours in a -40°C bath, and bright yellow crystals were collected and characterized to be $(COD)W(CO)_4$.

Yield: 30%

M.P: 159-163°C (dec.), lit.[128] 159-162°C(dec.)

ir : 2043 cm^{-1}(s), 1952 om^{-1}(vs), 1907 om^{-1}(vs).

lit[128]: 4.25 δ (app.t), 2.48 δ (app.d) in the ratio of 4:8

lit:[128] 4.25 δ (app.t), 2.48 δ (app.d) in the ratio of 4:8

4.4. Preparation of (2,5-norbornadiene) tetracarbonyl tungsten(0), $(NBD)W(CO)_4$.[128]

A mixture of 1.17 g (3 mmole) of $(CH_3CN)_3W(CO)_3$, 3 ml of 2,5-norbornadiene, and 50 ml of n-hexane was refluxed at the boiling point with magnetic stirring for 16 hours. The yellow reaction mixture was filtered hot and the residue washed with a few milliliters of boiling hexane. The filterate was cooled for four hours in a -40°C bath to obtain yellow crystals. The yellow crystals identified to be pale yellow crystals characterized to be $(NBD)Mo(CO)_4$ were filtered and the unreacted $Mo(CO)_6$ removed by sublimation.

Yield: 32%

M.P.: 76-77°

ir: 2030 cm^{-1}, 1990 cm^{-1}, 1960 cm^{-1}, 1925 cm^{-1}, 1880 cm^{-1}.

lit[129]: 2030 cm^{-1}, 1980 cm^{-1}, 1920 cm^{-1}, 1870 cm^{-1}.

4.7. Reaction of $(COD)W(CO)_4$ with methyllithium.

In dry air free diethyl ether, 0.5 g of $(COD)W(CO)_4$ was dissolved and the solution cooled to -5°C. The solution was treated with 3 ml of a 0.5 M methyllithium (prepared according to Gilman et al [130]) in 25 ml diethyl ether from a dropping funnel in 15 minutes time with constant stirring. The reaction was followed by taking the infrared spectra of the reaction solution at different stages. A brownish red solution I was obtained at the end of the reaction.

$$(COD)W(CO)_4 \quad + \quad MeLi \xrightarrow[-5^{\circ}C]{\text{diethyl ether}} \underset{\text{I}}{\text{brown-red solution}} \qquad (46)$$

ir: ν_{co} of I, 1965 cm^{-1} (s), 1925 cm^{-1}(w), 1620 cm^{-1}(s)

The solvent from I was decreased and the solution cooled in a -40°C bath for 2 hrs. No crystals were obtained. The solvent was completely removed and a brownish-red gummy residue Ia soluble in water insoluble in n-hexane and

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CH_2Cl_2 and sparingly soluble in chloroform was obtained.

M.P. of Ia 130°C (decomp.)

ir (in nujol): 1965 cm^{-1}(s), 1925 cm^{-1}(w), 1620 cm^{-1}(s)

NMR (in $CDCl_3$): 2.25 δ (s), 3.45 δ (q), 1.25 δ (t), 0.82 δ (m).

The NMR indicates that CH_3 is introduced (2.25 δ) and diethyl ether is coordinated in some form 3.45 δ (q) and 1.25 δ (t), but there is no indication for the presence of olefinic protons.

4.8. Methylation of Ia

The brown-red solution I was obtained as in expt. 4.7. Solution I was first treated with an aqueous solution of 1.24 mmole of diazomethane in diethylether. Removing the solvent under vacuum pump led to traces of yellowish-red residue which was further treated with 10 ml of n-hexane and cooled in a -40°C bath for 2 hours. Traces of yellow crystals II were formed.

ir: 3400 cm^{-1}(br), 1960 cm^{-1}(s), 1620 cm^{-1}(s).

NMR(in $CDCl_3$): 3.2 δ (s), 2.7 δ (d), 21 δ(s), 1.7 δ (s), 0.9 δ (m).

4.9 Reaction of I with $(CH_3)_3SiCl$, trimethylchlorosilane.

Solution I was obtained as in 4.7 above and treated with 0.13 g of $(CH_3)_3SiCl$. A deep-red solution III and a

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greyish white precipitate IIIb were obtained. IIIb gave a positive test for chloride, and was discarded. Removal of the solvent from the deep-red solution III led to a reddish brown residue IIIa.

$$\underline{I} \quad + \quad (CH_3)_3SiCl \longrightarrow \underset{\underline{III}}{\text{A deep-red solution}} + \underset{\underline{IIIb}}{LiCl} \qquad (47)$$

$$\underline{III} \quad \xrightarrow{\text{Solvent removed}} \underline{IIIa}$$

ir of IIIa (in Nujol): 1600 cm^{-1} (s), 1960 cm^{-1}(s)

NMR (in $CDCl_3$): 2.0 δ (s), 1.5 δ (s), 1.2 δ (s), 0.75 δ (s)

There is an indication for the formation of $-O-Si(CH_3)_3$ from the NMR spectrum, 0.75 δ (s) .

4.10. Precipitation of Ia with n-hexane

Solution I was prepared as in 4.7 above and after filteration treated with n-hexane drop by drop. A reddish-brown precipitate IV was obtained. After filteration, IV was characterized to be the same as compound Ia above.

4.11. An attempt to Precipitate Ia as its tetra ethylammonium Salt.

Solution I was treated with 1.24 mmole of an aqueous solution of tetra ethyl ammoniumchloride drop by drop. No precipitate was obtained.

[illegible]

4.12 Investigation of the Catalytic Activities of some $(diene)M(CO)_4$ [diene=NBD or COD, M=Cr,Mo,W], and $(CH_3CN)_3Mo(CO)_3$ Complexes.

Chlorobenzene wad dried by refluxing on lithium aluminium hydride for three days. Ethylaluminum dichloride $EtAlCl_2$ was prepared in our laboratory according to literature.[131] As an olefin, 2-pentene was chosen, and it was prepared by dehydration of 2-pentanol with concentrated phosphoric acid. Prior to use 2-pentene was dried by refluxing over sodium metal for 3 hours and then distilling from $EtAlCl_2$ for an immediate use.

All the chromium, molybdenum and tungsten NBD, COD tetracarbonyl complexes and (trisacetonitrile) tricarbonyl Mo(O) complexes were prepared in our laboratory. The NBD and COD tetracarbonyl metal complexes were used after sublimation but the acetonitrile molybdenum complex was used without further purification. Tungsten hexachloride, WCl_6, was obtained from Fluka AG,Buchs SG and was used as purchased.

The catalyst solutions were prepared in the ratio of M to $EtAlCl_2$ to 2-pentene to be 1:6:1000 as follows [M=Cr, Mo,W] .

Eleven Schlenk flasks were labeled from 1 to 11. They were all equipped with one stirring bar each and the complexes to be tested were weighed as shown in table II.

Table II. Weights of Cr, Mo, W Compounds Taken.

FLASK NUMBER	COMPLEX	WEIGHT OF COMPLEX mg	(mmole)
1	$(COD)W(CO)_4$	12.12	(0.03)
2	$(NBD)W(CO)_4$	11.64	(0.03)
3	$(NBD)Mo(CO)_4$	9.00	(0.03)
4	$(CH_3CN)_3Mo(CO)_3$	9.08	(0.03)
5	WCl_6	11.89	(0.03)
6	$(COD)W(CO)_4$	12.12	(0.03)
7	$(NBD)W(CO)_4$	11.64	(0.03)
8	$(NBD)Mo(CO)_4$	9.00	(0.03)
9	$(CH_3CN)_3Mo(CO)_3$	9.08	(0.03)
10	WCl_6	11.89	(0.03)
11	$(NBD)Cr(CO)_4$	7.68	(0.03)

The complexes were dissolved in 1.5 ml of chlorobenzene. Contents of the flasks 5 and 10 were each treated with 1.75 µl (0.03 mmole) of ethanol. From another flask which contains 400 µl of $EtAlCl_2$ in 28.75 ml of Chlorobenzene, 1.5 ml was added to each of the flasks 1 through 11.

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The contents were then stirred for 15 minutes, and subsequently 1.5 ml of 2-pentene was transferred to each of the flasks and the stirring continued at room temperature.

After one hour the contents of the flasks labelled 1 to 5 were each treated wtith 400 µl of 2-pentanol which was chosen for deactivation of the catalyst solutions. The contents of the flasks labelled 6 through 11 were deactivated after 24 hours in the same manner.

4.13 Gas Chromatographic Analysis

The following set of conditions was chosen for a better resolution.

Oven temperature:	50-150°C
Injection port temperature:	50°C
Detector temperature:	100°C
Injection volume:	2 µl
Chart speed	30 in/hr

The comparison of the retention times of the peaks obtained with retention times of standard fresh samples of chlorobenzen, 2-pentene, 2-pentanol and 3-hexene (distilled from one of the active samples and characterized by its NMR spectrum) led to identification of the reaction products. The percentage conversion was calculated for all active systems by referring to the peak areas of the consti-

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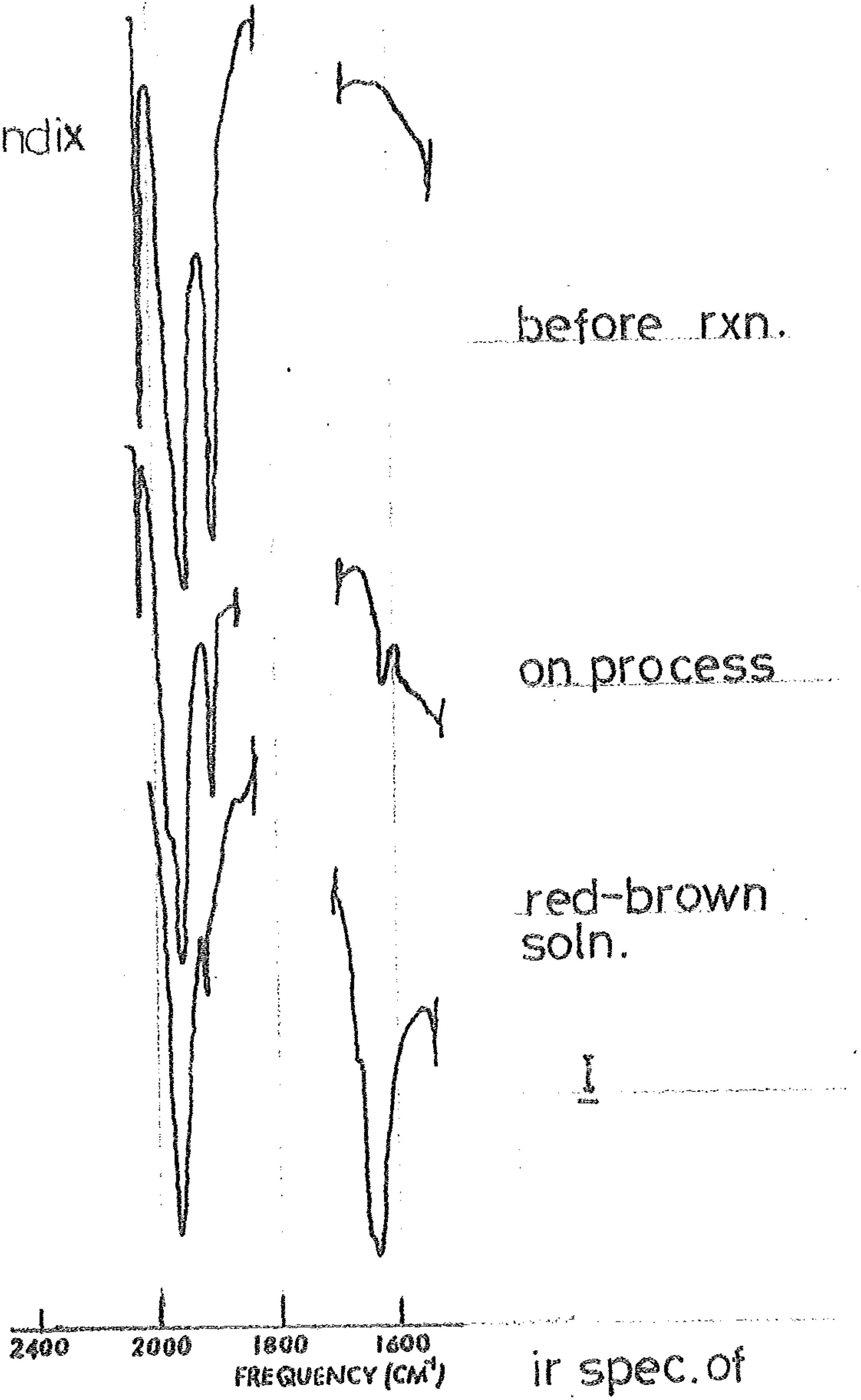
tuents and the analysis result is given in table III.

Table (III): Percentage Conversion of 2-pentene into
2-butene and 3-hexene

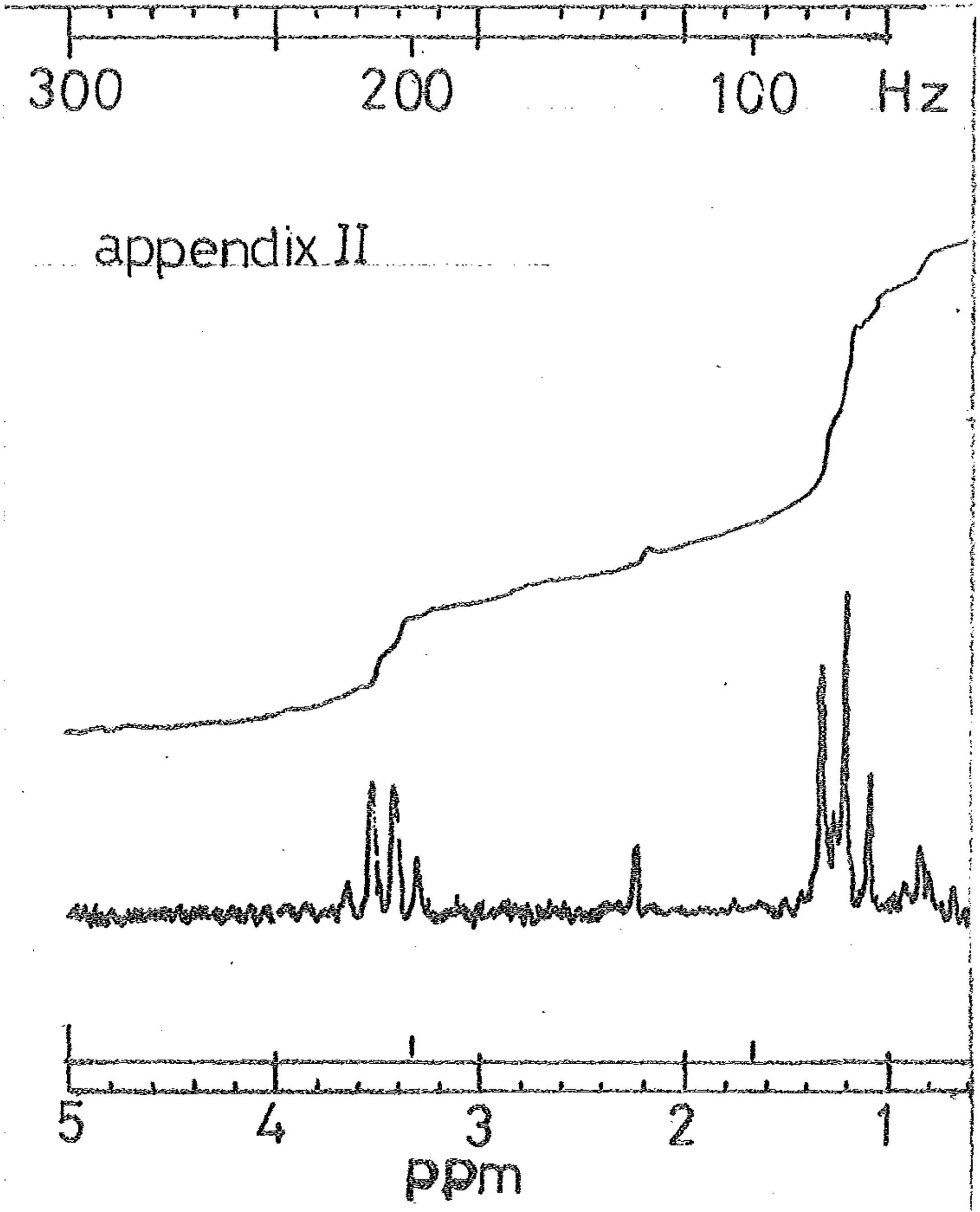
FLASK NUMBER	COMPLEX	PERCENTAGE CONVERSION	
		AFTER 1 hr	AFTER 24 hrs
1	$(COD)W(CO)_4$	7.44	-
2	$(NBD)W(CO)_4$	18.23	-
3	$(NBD)Mo(CO)_4$	trace	-
4	$(CH_3CN)_3Mo(CO)_3$	trace	-
5	WCl_6	7.78	-
6	$(COD)W(CO)_4$	-	9.48
7	$(NBD)W(CO)_4$	-	59.24
8	$(NBD)Mo(CO)_4$	-	3.4
9	$(CH_3CN)_3Mo(CO)_4$	-	0.84
10	WCl_6	-	23.63
11	$(NBD)Cr(CO)_4$	-	NO CONVERSION

appendix
I



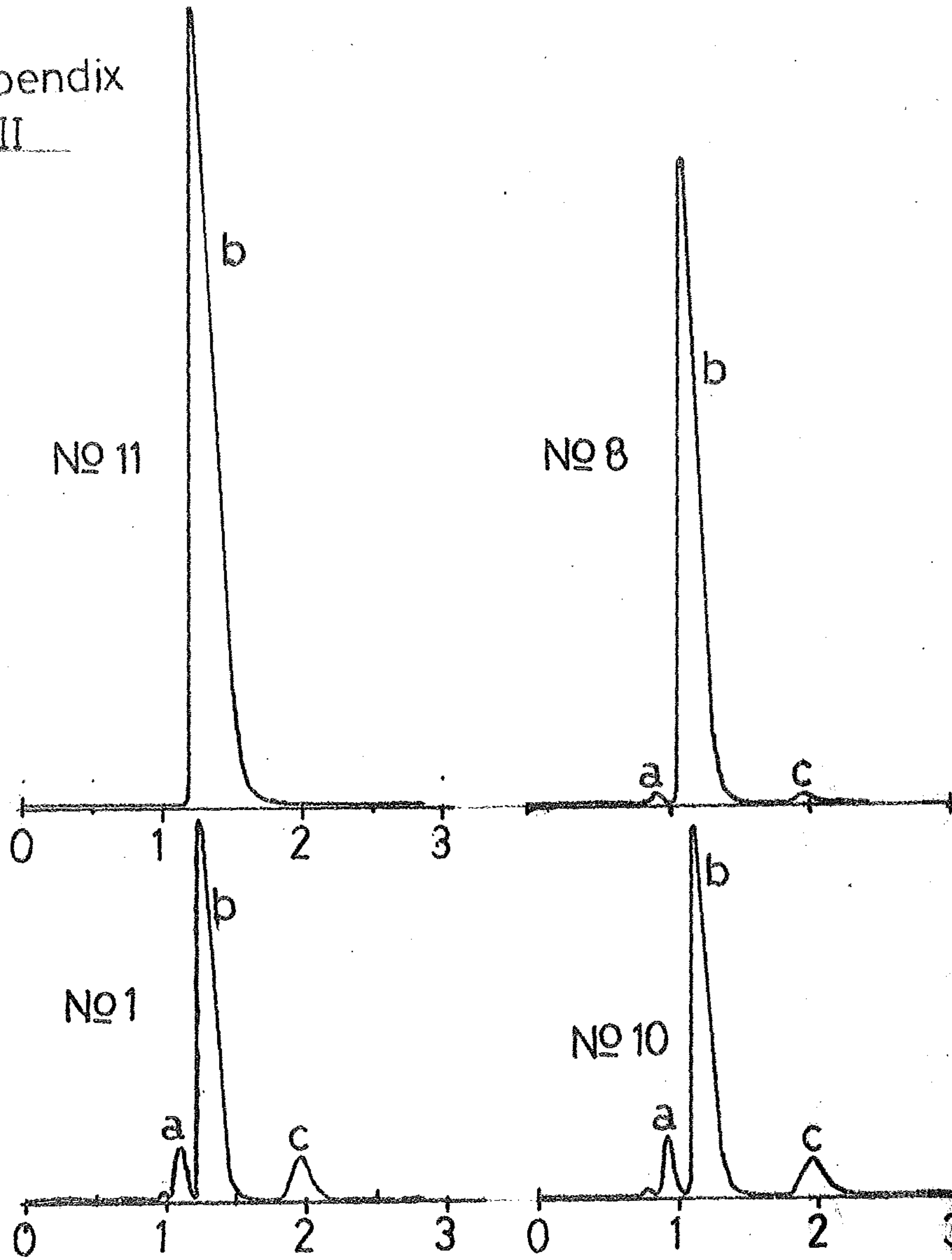
ir spec. of
rxn. soln.

$(COD)W(CO)_4$ + MeLi



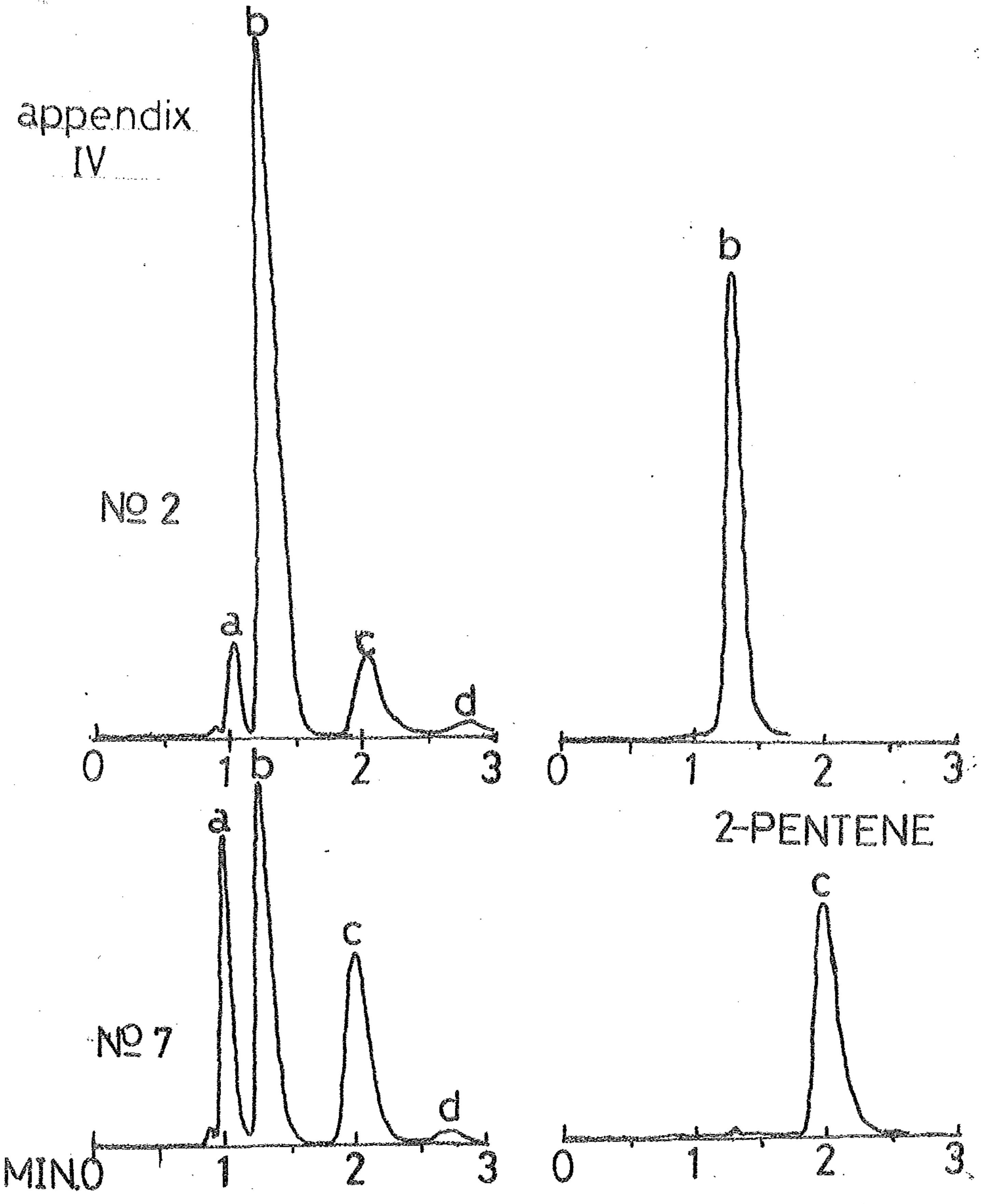
NMR spectrum of Ia

appendix III



GC of №S 1,8,10&11

appendix
IV



GC of NoS 2,7, 2-PEN.& 3-HEX.

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