

THE REACTION OF BROMOACETYL BROMIDE
WITH
SELECTED ORGANOMETALLIC COMPOUNDS

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Master of Science in Chemistry

by
/Fikru Tafesse
June, 1980

TO Ato Tafese Wondimagegnehu, my father, a
very special person, a friend to
everybody,

and Woizero Roma Negash my mother,

and to

Dr. Ermias Dagne
Dedicated and inspiring teacher

ABSTRACT

THE REACTION OF BROMOACETYL BROMIDE WITH SELECTED ORGANOMETALLIC COMPOUNDS

by

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Research advisor: Makonnen Dilgassa

Organometallic compounds are widely used as heterogeneous and homogeneous catalysts in the industrial productions of important chemicals and synthetic products. In many cases of such industrial transformation, metal carbenes are thought to play important roles as the active catalytic ingredients that bring about the transformation. Such carbenes are classified into two groups electrophilic and nucleophilic. Although several nucleophilic carbenes have been prepared, no general synthetic methods have been developed for the generation of electrophilic metal carbenes. We believe that α -monohaloalkyltransition metal derivatives can be used as precursors of electrophilic metal carbenes via their interaction with Lewis acids (see equation below). For example, the interactions of α -monohaloalkyltransition metal derivatives with Lewis acids may produce metal carbenes capable of catalyzing the olefin metathesis reactions.



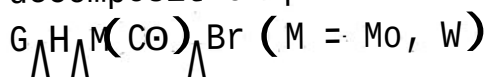
R = alkyl, H, aryl; **In** = Ligand.

Consequently, our main goal is to synthesize α -monohaloalkyltransition metal derivatives by

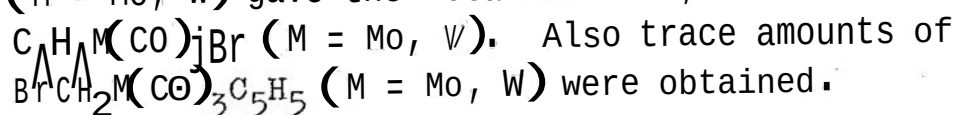
thermal or photochemical decompositions of the haloacetyl metal derivatives.

$\text{BrCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ with traces of $\text{BrCOCH}_2\text{M}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) were made in good yields by allowing $\text{NaM}(\text{CO})_5\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) to react with BrCH_2COBr .

The thermal decompositions of $\text{BrCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) were shown to involve β -halogen elimination. Decarbonylation followed by further decomposition produced the metal halides,



The photochemical decompositions of $\text{BrCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) gave the metal halides,



$\text{Na}_5\text{Fe}(\text{CO})_9$ reacted with BrCH_2COBr giving

$[\text{C}_5\text{H}_5\text{FeCOO}(\text{C}_5\text{H}_5)]_2$ as the major product. Also small quantities of $\text{BrCH}_2\text{COFeCO}(\text{C}_5\text{H}_5)$ and $\text{BrCOCH}_2\text{FeCO}(\text{C}_5\text{H}_5)$

were detected. $(\text{Ph}_3\text{P})_2\text{Pt}$ reacted with BrCH_2COBr giving $\text{Br}(\text{BrCH}_2\text{CO})(\text{Ph}_3\text{P})_2\text{Pt}$ and trace quantity of $\text{Br}(\text{BrCOCH}_2)(\text{Ph}_3\text{P})_2\text{Pt}$. The thermal and photochemical decomposition of $\text{Br}(\text{BrCH}_2\text{CO})(\text{Ph}_3\text{P})_2\text{Pt}$ resulted in the production of $(\text{Ph}_3\text{P})_2\text{PtBr}_2$.

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ABBREVIATIONS

The following abbreviations are used in the main text.

Ac	acetyl
Aq	aqueous
F.P.	boiling point
Bu	butyl, C_4H_9
OH	carbon hydrogen stretch
Cp	cyclopentadienyl
DME	1,2-dimethoxyethane
eq	equation or equations
Et	ethyl C_2H_5
Et ₂ O	diethyl ether
Fig.	Figure
g	gram
IR	infrared
L	ligand
Me	methyl, CH_3
M.P.	Melting point
NMR	nuclear magnetic resonance spectrum
Ph	phenyl, C_6H_5
Pr	propyl, C_3H_7
PPH_3	triphenylphosphine
S	strong
Sh	shoulder
THF	tetrahydrofuran
Vs	very strong

VW

very weak

W

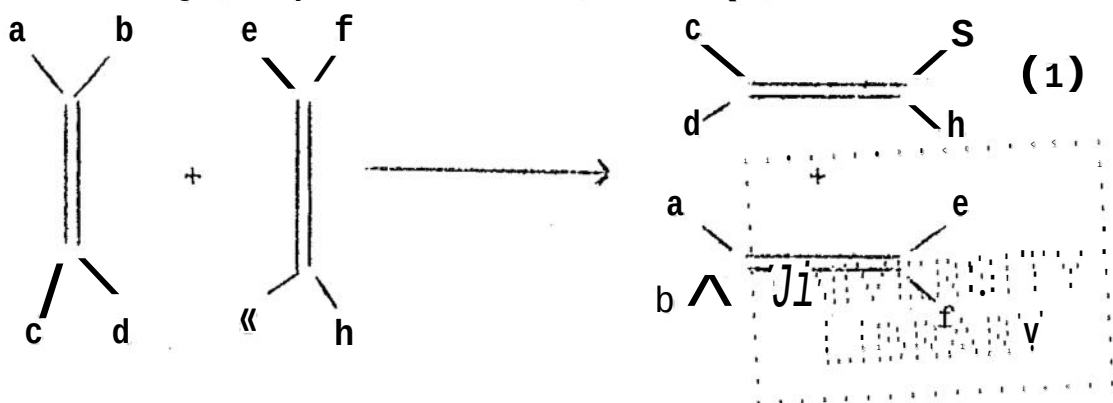
weak

Wt.

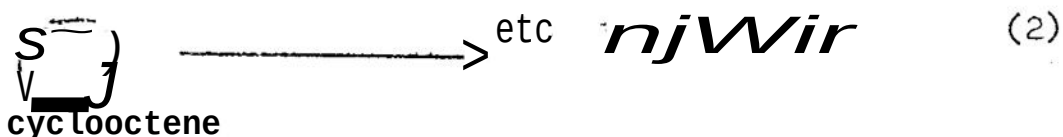
weight

INTRODUCTION

The olefin disproportionation reaction may be carried out with a variety of homogeneous and heterogeneous catalysts. Most commonly the catalysts contain molybdenum, tungsten or rhenium. The reaction converts olefins into equilibrium mixtures of olefins formed formally by breaking double bonds and recombining the pieces¹ - equation (1).

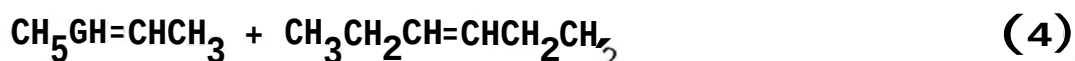
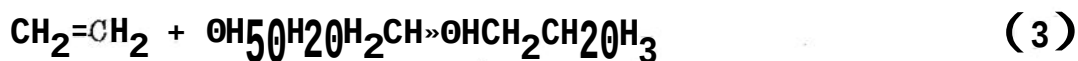
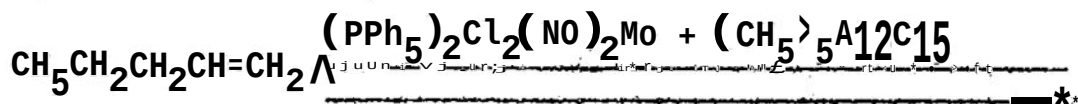


When the olefinic bonds are included in rings, the olefin metathesis reaction produces polymers as shown in equation^{13,14} (2).



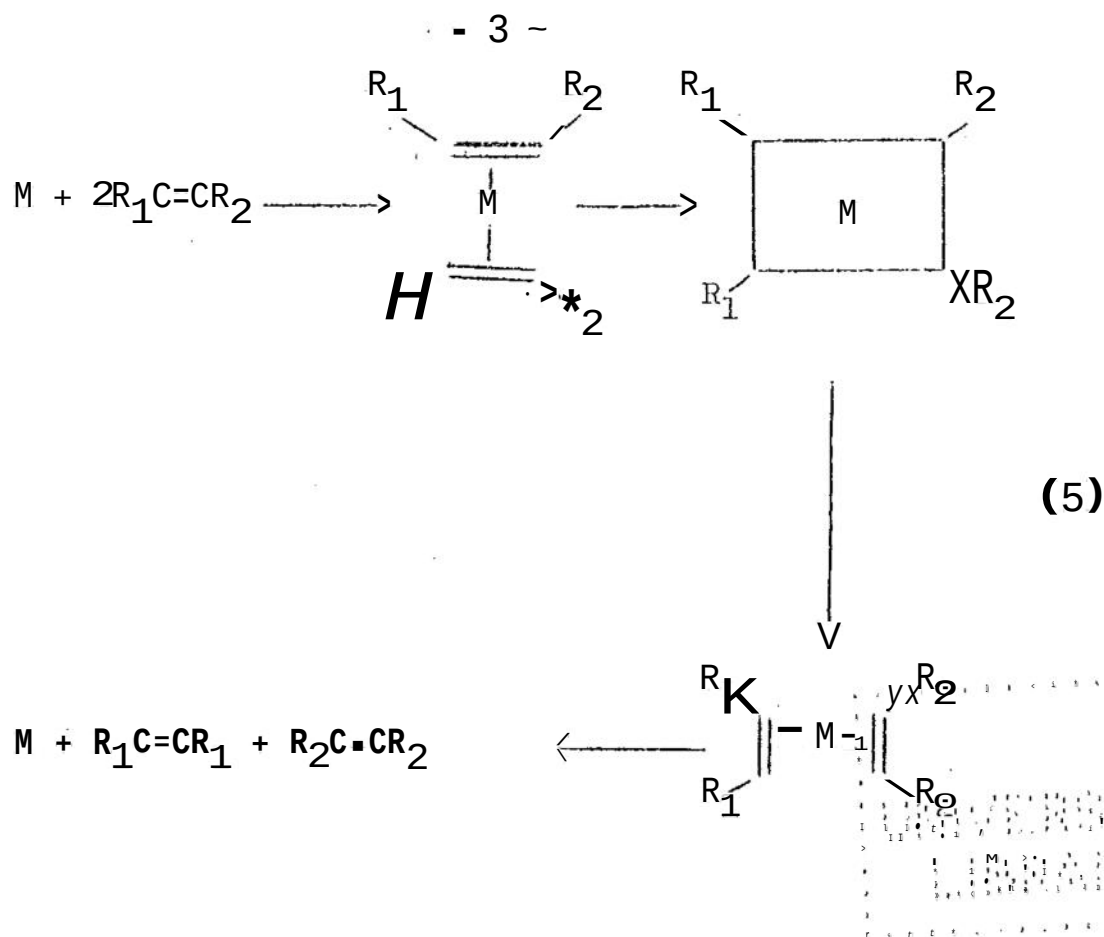
The reaction promises to be of significant value to the petroleum industry since many olefins can be produced from more readily available ones by this method. The following reactions are typical

examples representing homogeneous catalysis.^{15,16}



The catalysts involved in the olefin metathesis may be divided into two groups, "activated" and "non activated". In the former a cocatalyst e.g., aluminium alkyl or other metallating agent, or a hydridic reducing agent has to be added to a transition metal species before any catalytic activity is shown. In the latter, as the name implies, no activating cocatalyst is needed and the transition metal species is capable of effecting olefin disproportionation upon contact with olefins. Some examples of the activated systems are, $\text{VCl}_4 + \text{NaBH}_4$, $\text{L}_2\text{Mo}(\text{NO})_2 + \text{RAlCl}_2$ and $\text{Me}_3\text{Sn} + \text{WCl}_6$, some non activated catalysts are $\text{PhVCl}_4 + \text{AlCl}_3$ and $\text{W}(\text{CO})_6\text{Cl}_2$.

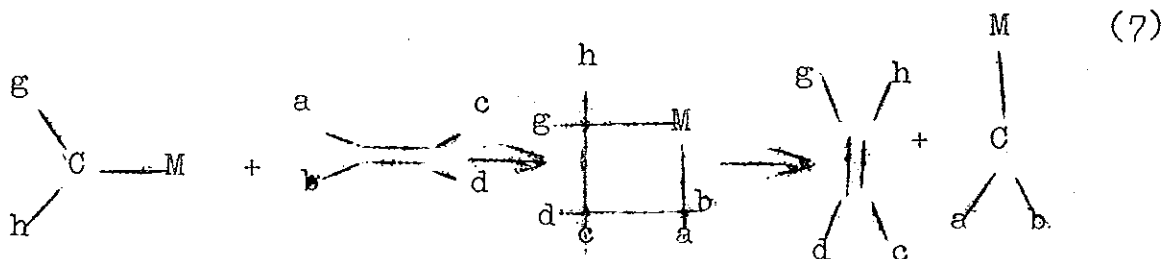
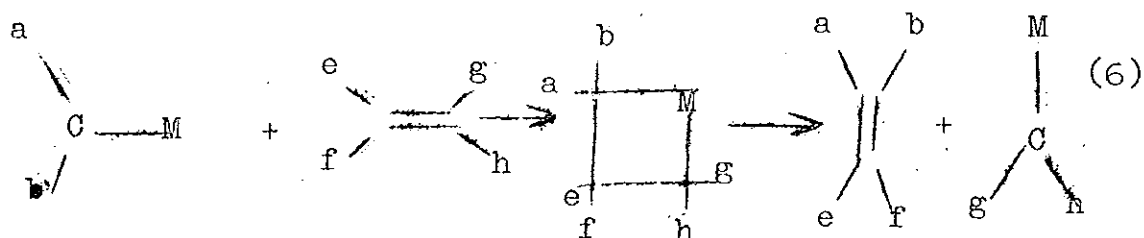
The first attempt at explaining the olefin disproportionation reactions assumed that two olefins unite to form a metallacyclobutane as illustrated in the following equation.



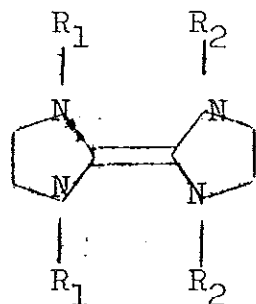
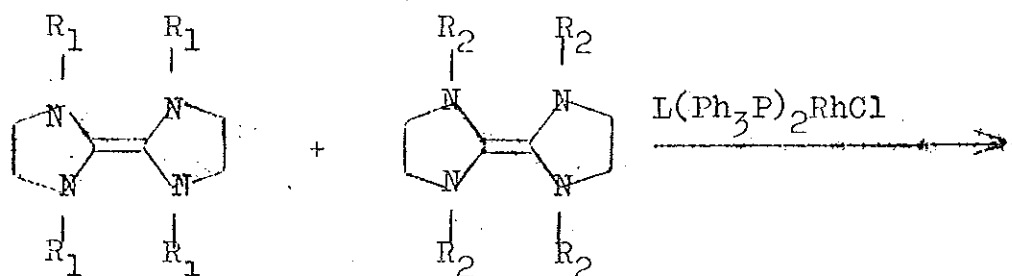
This idea was particularly appealing, not only because it accounts for the gross structural change, but it also suggested that the role of the metal was to circumvent the orbital symmetry prohibition that, in the absence of the metal, prevents 2 + 2 cycloaddition from occurring.^{24 - 29} This was soon to be dropped mainly because experiments clearly demonstrated that cyclobutane is neither formed nor cleaved when added to olefinic metathesis reaction mixtures.^{30 - 33}

It now appears that catalysis of olefin disproportionation is best explained by the intermediacy of 3 ~ carbon metallocycles which are presumed to arise from the interaction of an olefin with a metal carbene complex. Presumably the

carbene is generated from some metal alkyl precursor. This constitutes a chain mechanism propagated by metal carbenes.^{34 - 37}



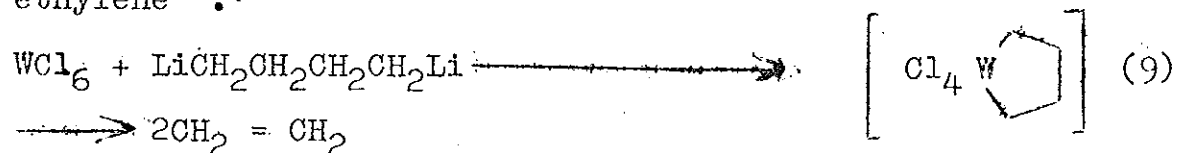
This mechanism clearly accounts for the gross structural change, and also shows that cyclobutane should neither form nor react. This carbene chain mechanism was further strengthened by the fact that (diphenylcarbene) pentacarbonyltungsten initiates not only the metathesis of strained olefins, like 1-methylcyclobutene and 1-methyl-trans cyclooctene, but also of simple olefins like cyclooctene which it converts into a polyoctenamer (eqn. 2) of high molecular weight.³⁷ On top of this the cycle has actually been demonstrated by using an electron rich olefin and an isolable carbene complex. (eq. 8)



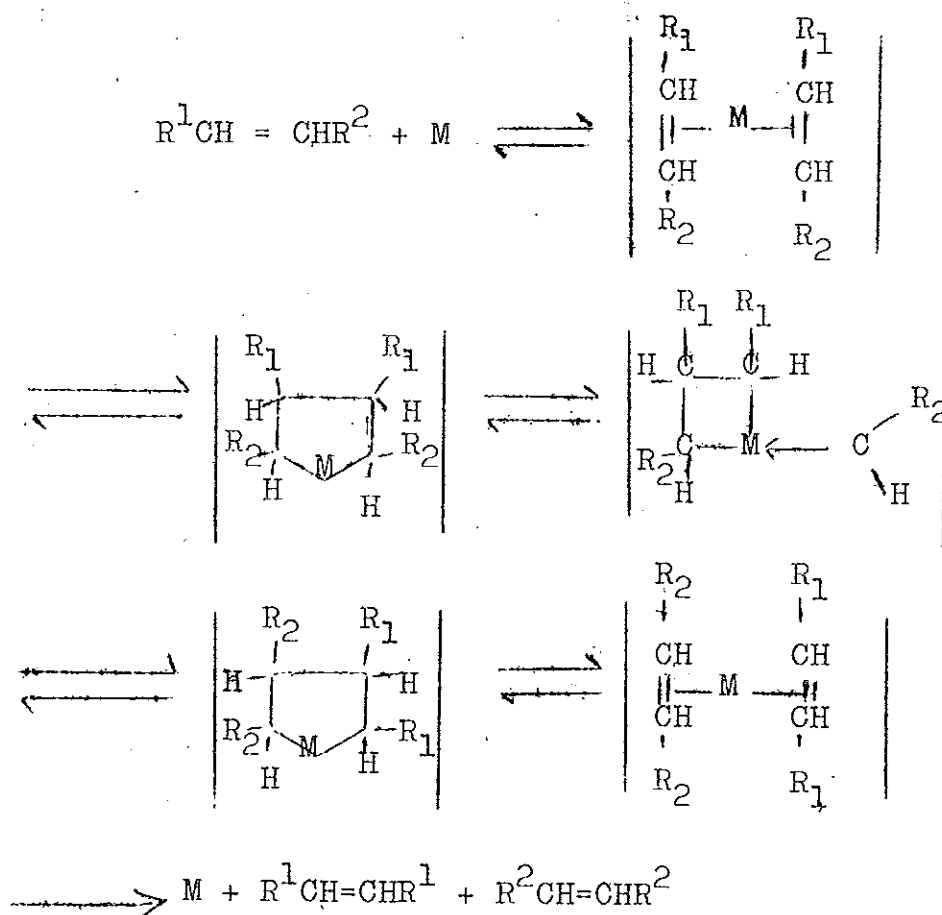
(8)

$R_1 = \text{Ph}$, $R_2 = \text{MeC}_6\text{H}_4$ $L = \text{Ph}_3\text{P}$ or CO

complexed cyclobutane intermediates have been proposed most often to explain the disproportionation, but other mechanisms have not been ruled out. In addition to possible tetracarbene intermediates, metallacyclopentane complexes must be considered. It has been shown, for example, that presumed tetrachlorotungstacyclopentane decomposes to ethylene³⁸.



In the olefin disproportionation the metallocyclopentane intermediate could equilibrate the ring carbons through formation of metallocyclobutane monocarbene complexes. (see scheme - 1)

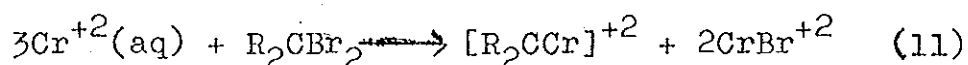
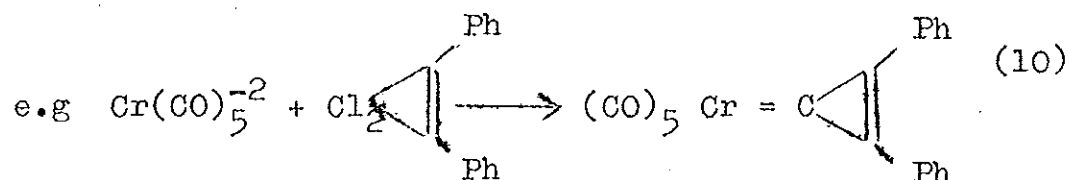


Scheme 1

The preceding discussion unequivocally shows that metal carbene complexes play a central role in the olefin disproportionation reactions. However, in the vast majority of cases where the carbene is presumed to be formed in situ, very little is known about the mode of formation of the carbene species, the oxidation state of the metal, or the number and nature of the remaining ligands. The lack of knowledge in this area stems from the fact that as a rule, stable isolable carbene complexes do not catalyze the olefin metathesis reaction. For the most part stable carbene complexes are coordinatively saturated, therefore relatively drastic conditions are required to get an olefin coordinated to the metal carbene. In addition isolable carbene complexes

usually have the carbene carbon atoms attached to heteroatoms most commonly oxygen or nitrogen. The latter being electron donating atom stabilize the metal carbene complex.

Consequently, the development of a simple and general synthetic route to the unstabilized transition metal carbene complexes would be a desirable project. To date several dialkyl carbene complexes have been synthesized under rather special conditions.^{39,40}



In the next chapter an attempt will be made to discuss the chemistry of carbene complexes because the syntheses and reactions of some of the organometallic compounds pass via the carbene transition state.

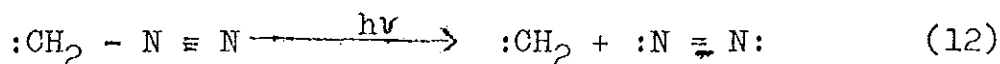
CHAPTER I

CARBENE COMPLEXES

A carbene is a neutral, bivalent carbon intermediate in which a carbon atom is covalently bonded to two other groups and has two valence electrons distributed between two non bonding orbitals. If the two electrons are spin paired the carbene is a singlet. If the spins of the electrons is parallel it is a triplet.

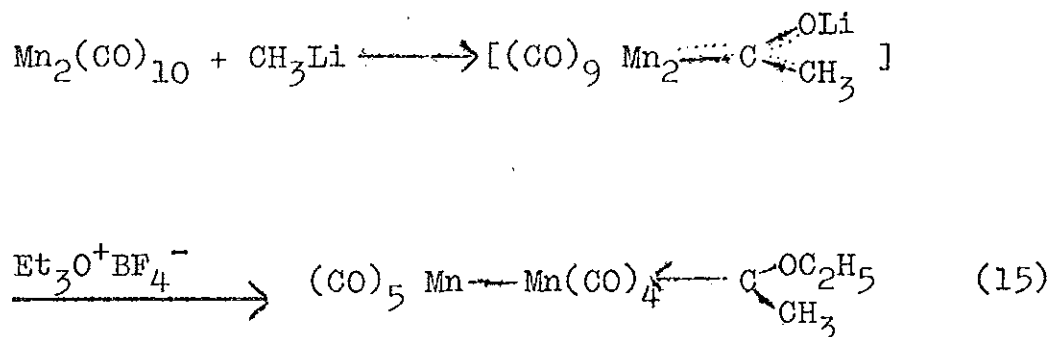
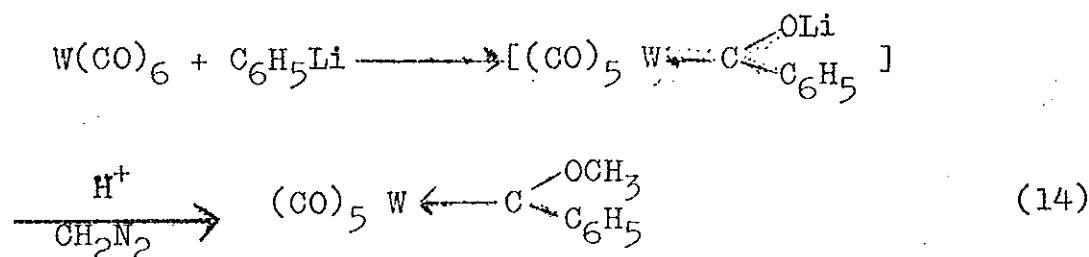
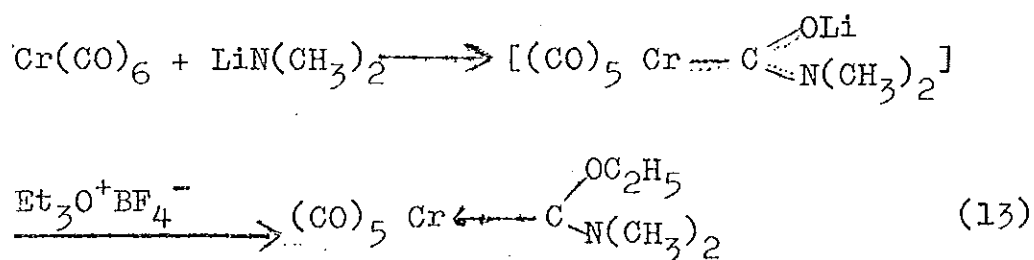
Carbenes in general are very reactive electrophilic species. Their activity depends to some extent on the method of preparation, on the nature of the substituent group, and also on the presence of certain metals or metallic salts. Because of their ability to accept electrons into the unoccupied d orbitals, transition elements and their compounds, specifically transition metal carbenes frequently exhibit catalytic properties.⁴¹

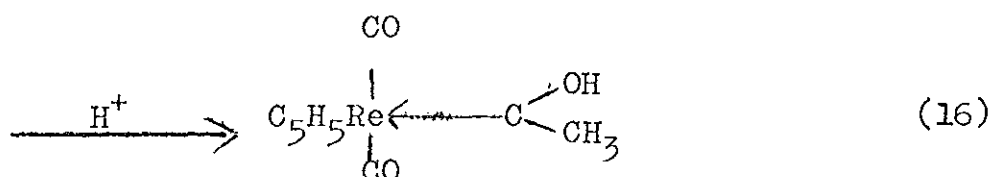
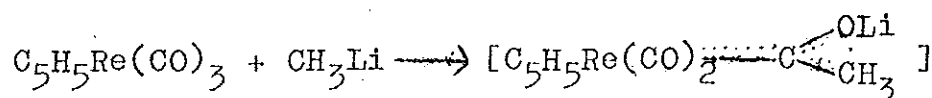
It was recognized that methylene (CH_2) produced via direct photolytic decomposition of diazomethane was extremely reactive.⁴²



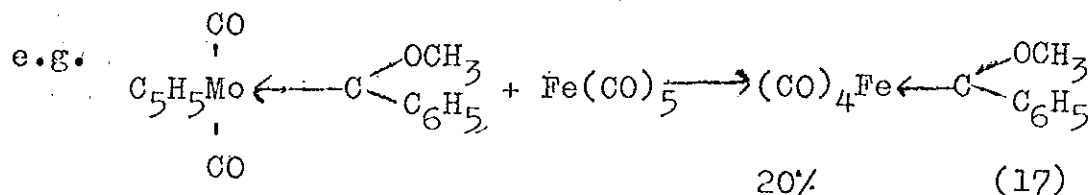
These compounds were of limited synthetic value owing to their high reactivity and low selectivity. However it was found empirically by a large number of investigators that substitution of one or both of the methylene hydrogen atoms either by a heteroatom or alternatively by conjugating electron

hybrids of acyl metal anions and negatively charged coordinated carbene complexes. Protonation gave rather unstable hydroxycarbene derivatives, whereas alkylation produced relatively stable alkoxycarbene complexes. The following equations show typical preparations employing this method of synthesis.⁴⁵⁻⁴⁸

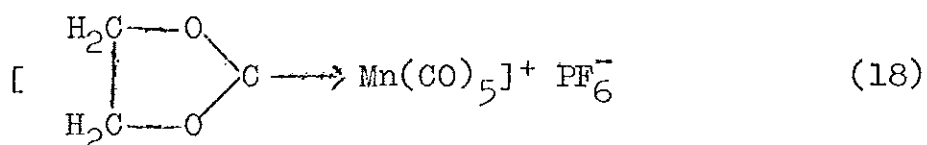
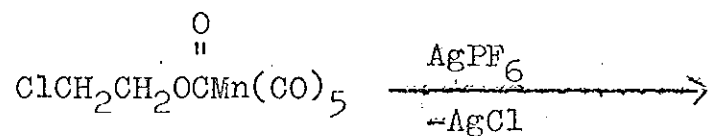
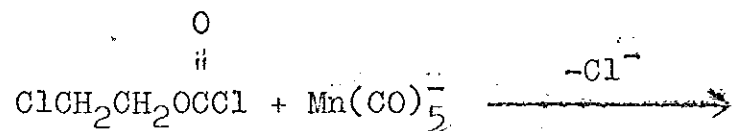




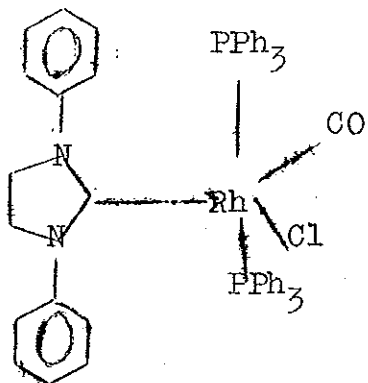
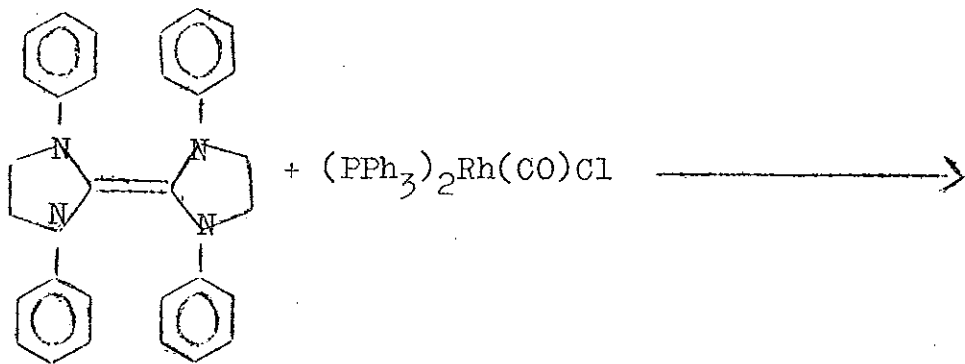
At least seven other methods of preparation of carbene complexes are now known. In one method, carbene ligands are transferred photochemically from one metal to another.⁴⁹ Free carbenes may be involved, but more probably metal - metal bonded intermediates are present and the carbene is transferred by a 1:2 shift mechanism or a coordinately unsaturated metal attacks the carbene ligand and displaces the other metal group.



Nucleophilic attack with acyl metal carbonyls also is capable of producing carbene complexes at least with some manganese and rhenium compounds. For example, pentacarbonyl-2-chloroethoxy-carbonylmanganese (I) reacts with silver hexafluorophosphate to form a cationic cyclic carbene complex.⁵⁰

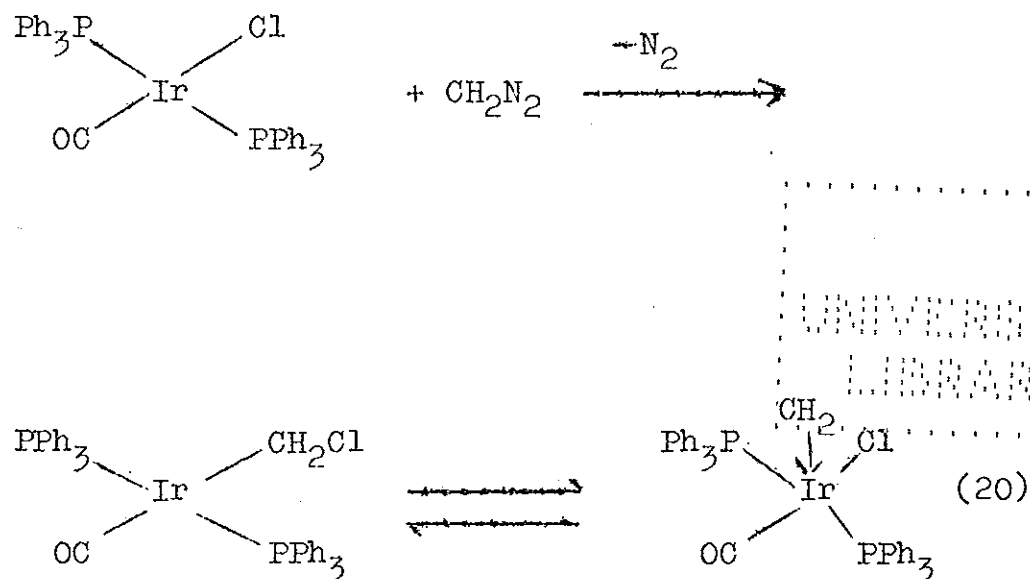


Certain electron rich olefins will react with metal complexes to form carbene derivatives by cleaving the double bond. An example is shown in the following reaction.⁵¹



(19)

Diazo compounds may react with many transition metal derivatives to form carbenelike complexes, although in most cases the complexes are too reactive to be isolated. For example, the reaction of trans-chlorocarbonylbis(triphenylphosphine)iridium (I) with diazomethane gives the four coordinate chloromethyl derivative, but the compound seems to react in the form of the pentacoordinate carbene complex.⁵²

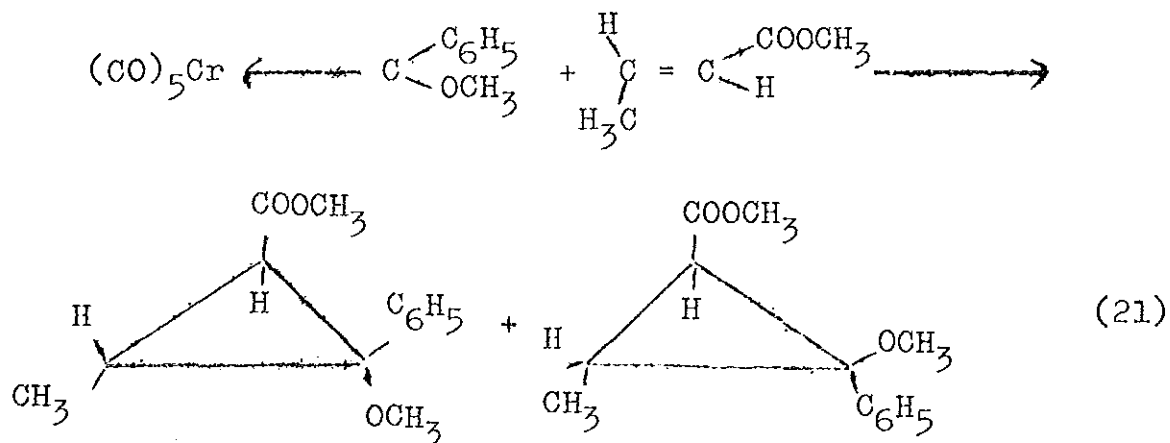


Reactions of carbene complexes

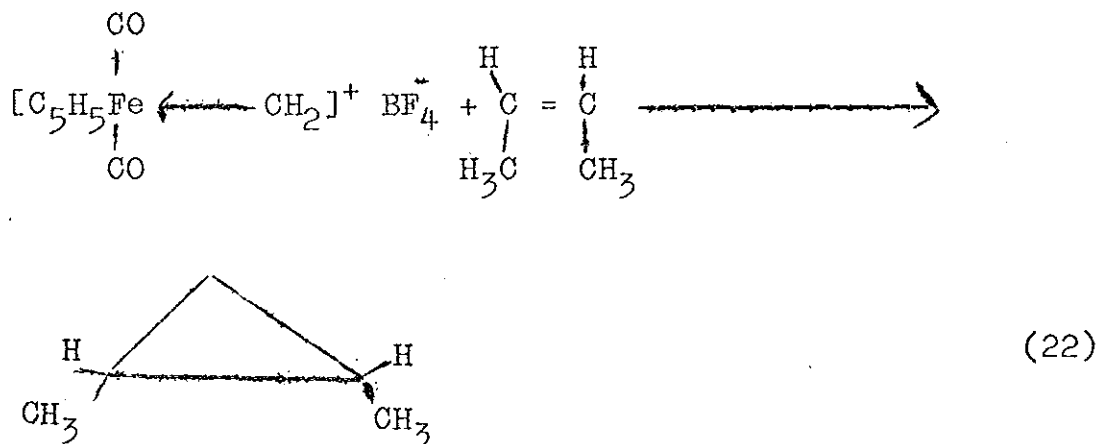
Many of the isolable carbene complexes are capable of transferring the carbene group to olefins to form cyclopropane derivatives.

Methoxyphenylcarbenepentacarbonylchromium (0) on heating reacts with methyl crotonate to produce in 60% yield, two isomeric cyclopropane derivatives.

The trans relationship of the methyl and ester groups is retained in the transfer reaction, while the carbene group adds via two possible ways.⁵³

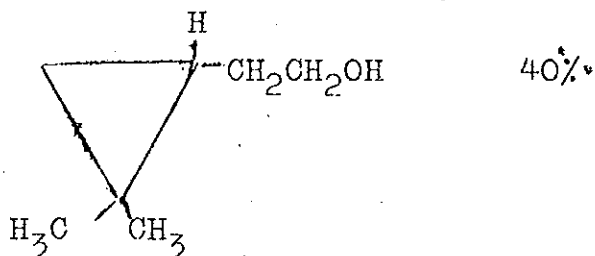
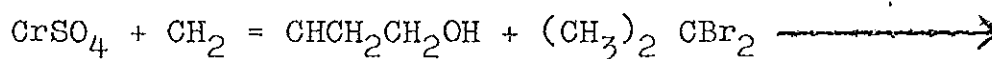


Likewise, the carbenedicarbonylcyclopentadienyliron cation transfers carbene stereospecifically to cis and trans - 2 - butene⁵⁴

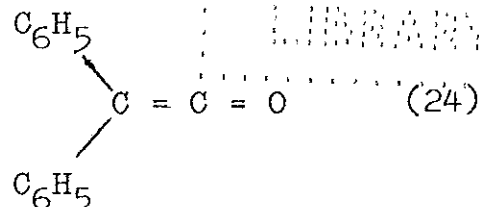
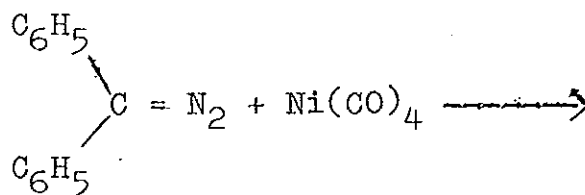


These reactions probably involve addition of the metal carbene group to the olefin, followed

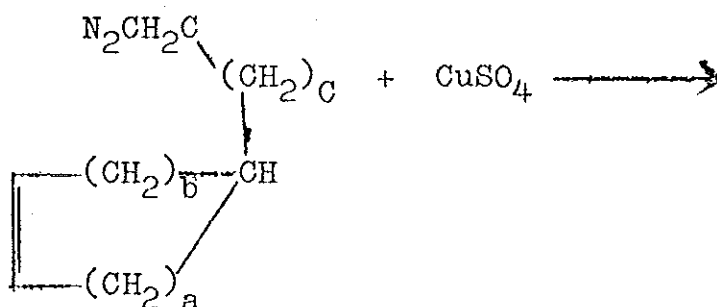
by reductive elimination forming a coordinatively unsaturated metal group and the cyclopropane. Numerous other apparent metal catalysed carbene transfer reactions are known, but intermediates have not been isolated and it is not certain that true metal carbene complexes are involved. Equations 23 to 26 show typical examples.^{55 - 58} The last reaction apparently involves a carbene insertion between the allyl group and the metal, followed by a hydride elimination or a hydride reduction.



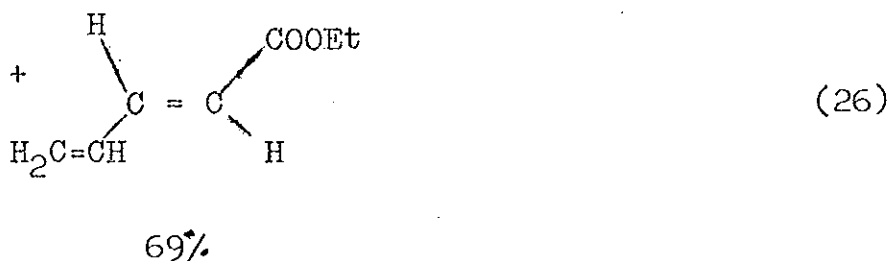
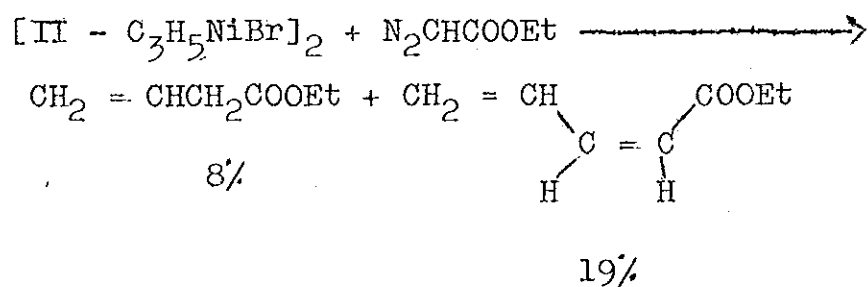
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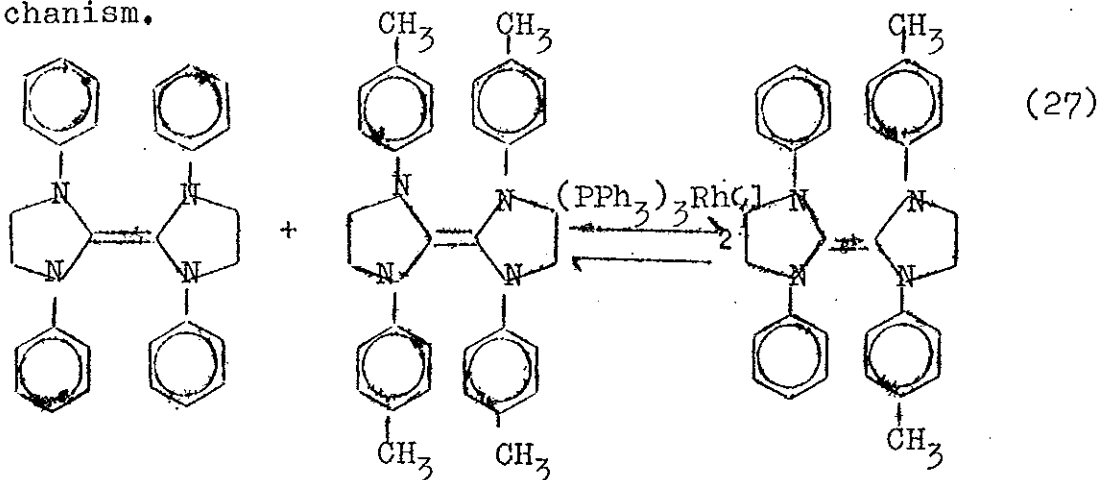
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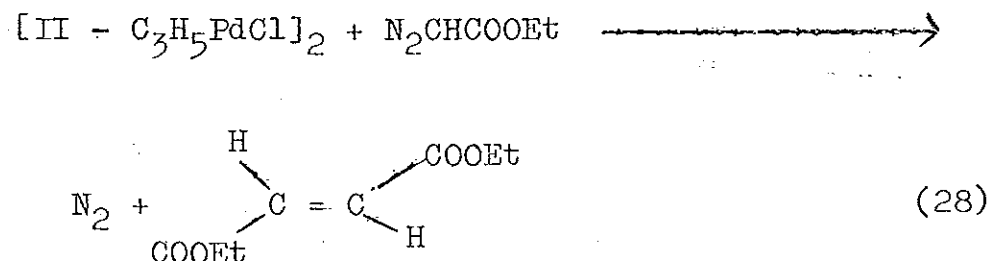
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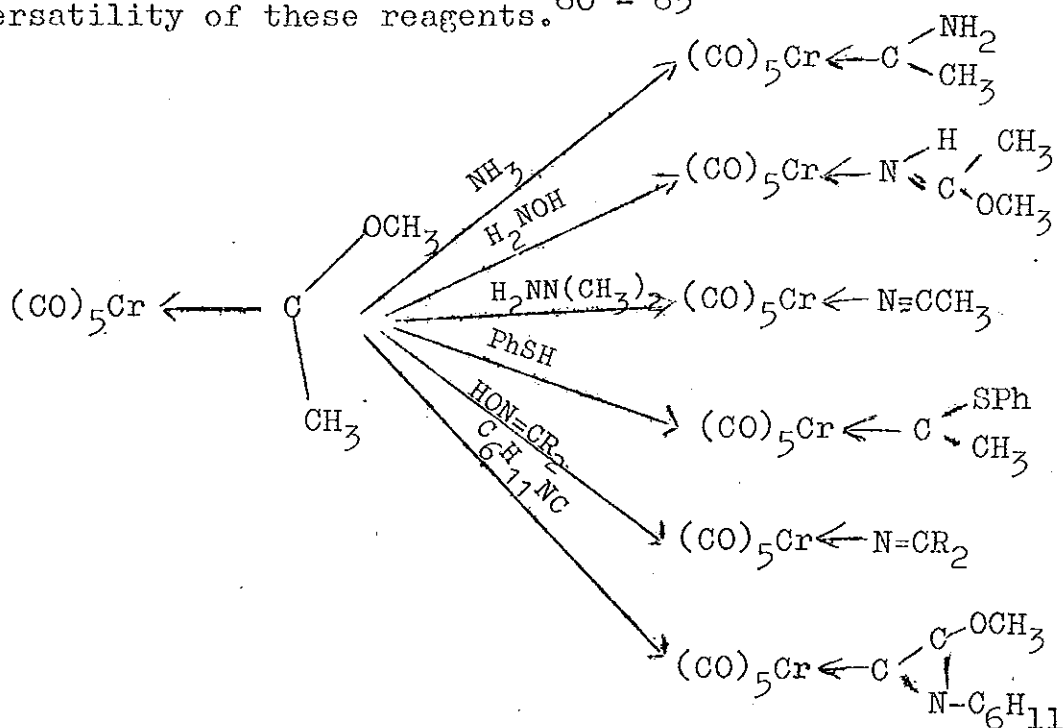
A very interesting carbon - carbon double bond cleavage occurs with certain electron rich olefins and metal complexes. The reaction appears reversible with chlorotristriphenylphosphinerhodium (I) and the amine substituted olefins since mixtures of the two different symmetrically substituted olefins are cleaved and recombined to give mixtures of the unsymmetrical and symmetrical olefins.⁵¹ This reaction is an example of an olefin disproportionation reaction and lends some support to the idea that other known disproportionation catalysts may operate by the same mechanism.



It is already well known that treatment of diazo compounds with some transition metal complexes causes the dimerization of the presumed carbene groups left by the loss of nitrogen. Chloro- π -allylpalladium (II) dimer and ethyl diazoacetate, for example, react to form diethyl fumarate.⁵⁹

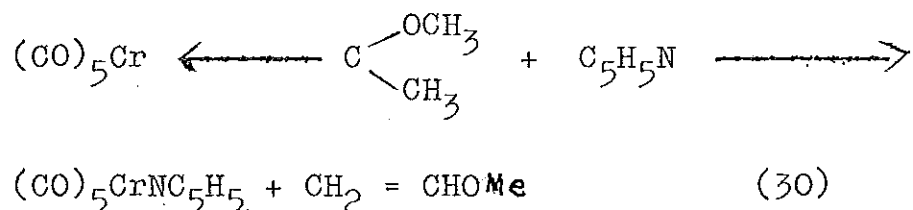
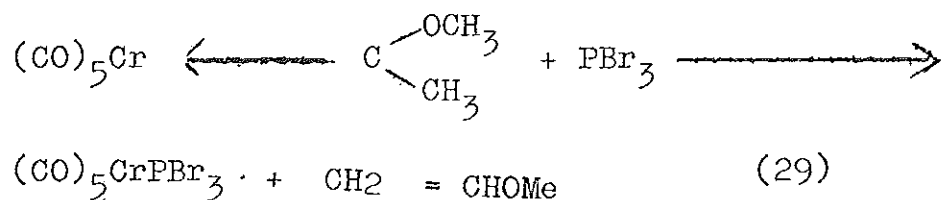


The transition metal carbene complexes are reactive starting materials for preparing a variety of other organometallic and inorganic complexes. E.O. Fischer has demonstrated the conversion of methoxymethylcarbenepentacarbonylchromium (0) into numerous other complexes. Scheme 2 shows the versatility of these reagents.^{60 - 63}

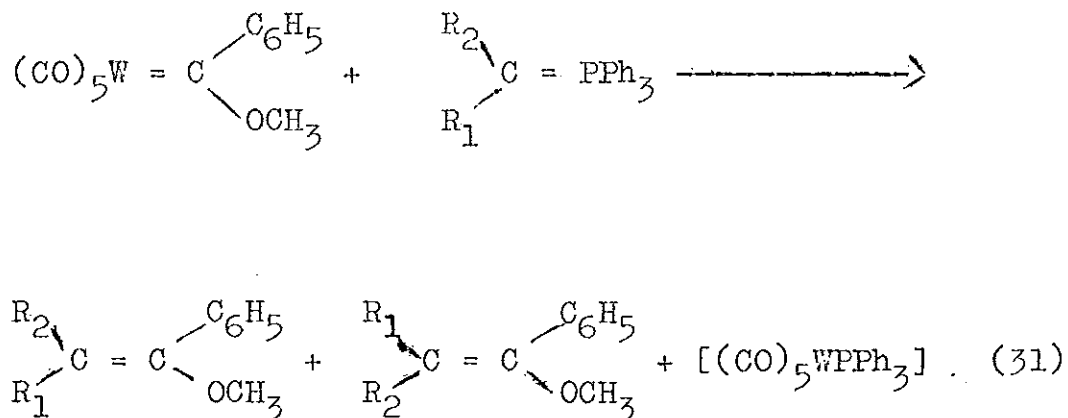


Scheme 2

The carbene ligand in methoxymethylcarbene (pentacarbonyl) chromium (0) is completely replaced when it is reacted with phosphorous trihalides or pyridine.^{64,65}



Some metal methoxycarbene complexes also react with Wittig reagents to produce vinyl ethers in high yield. Both cis and trans isomers are formed.⁶⁶

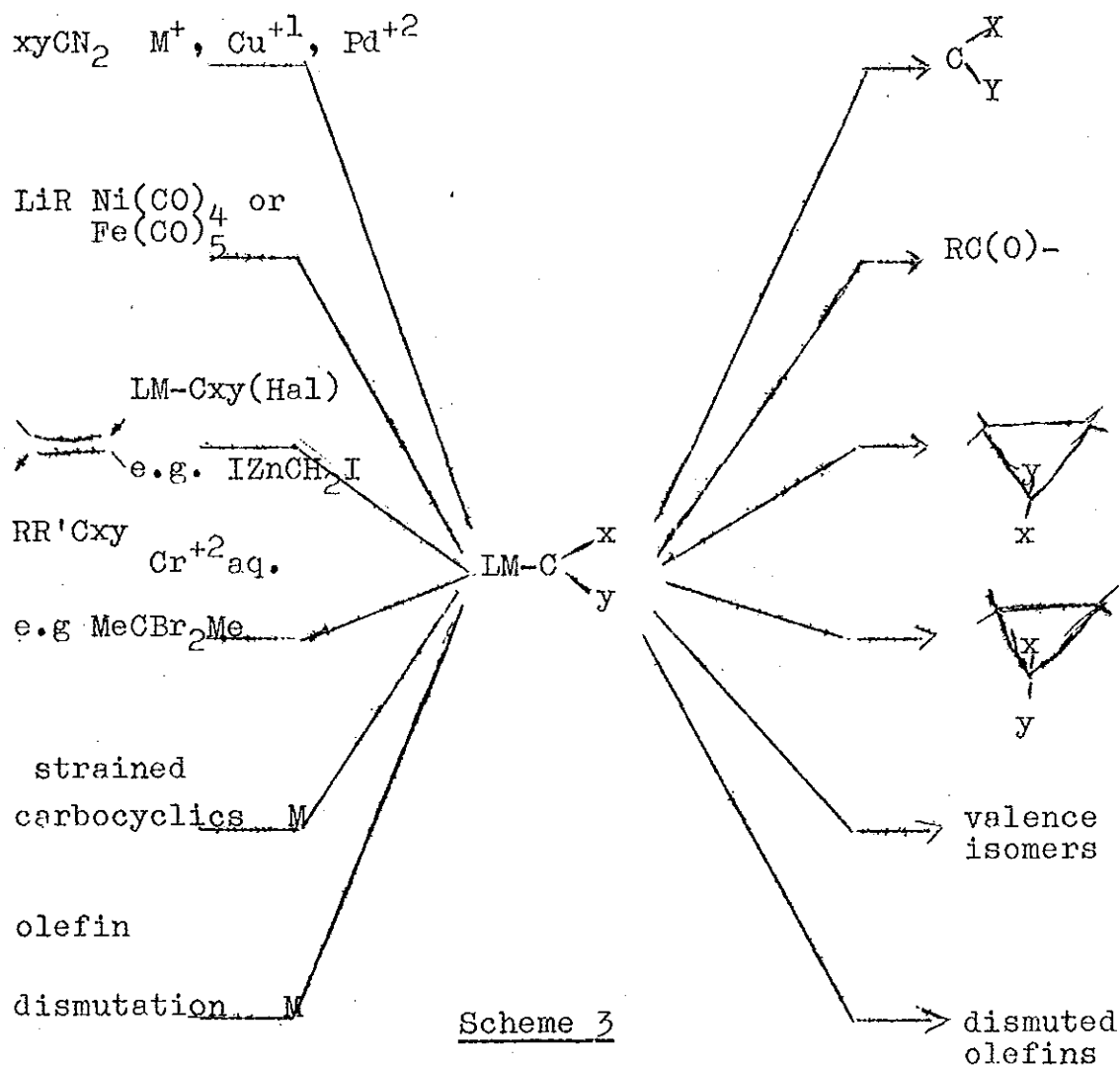


The mechanism of these reactions are not known. The study of transition metal carbene complexes has only just begun and it is apparent that a great deal

of unusual and useful chemistry probably still remains to be discovered.

Several reactions are known for which metal carbene complexes have been postulated as intermediates or transition states. Some of these reactions are synthetically important.

Reactions proceeding via carbene metal complexes⁵¹



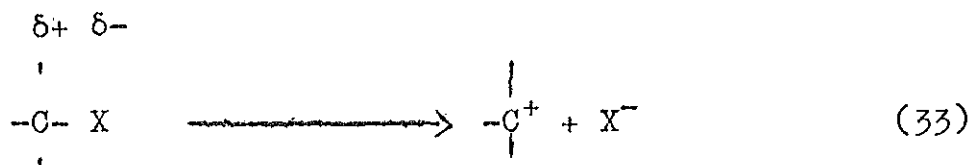
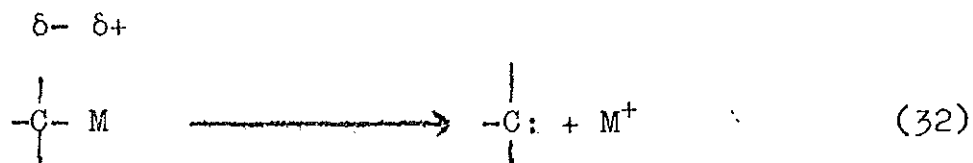
The evidence in favor of intermediate carbene complexes in the reactions shown above is not equally strong in all cases. Thus whereas the metal catalysed decomposition of diazoalkanes and the alkylation of carbonylmetallates leaves little room for doubt concerning such intermediates, the role of the metal in the cyclopropanation reaction is rather different. Many strained carbocyclic rearrangements certainly do not involve complexed carbenes although there is a wealth of circumstantial evidences in favor of such a mechanism in other cases.

In our investigative work, we chose to approach the problem of synthesizing "unstabilized" transition metal carbenes by first developing preparative methods for α -monohaloalkyltransition metal complexes.

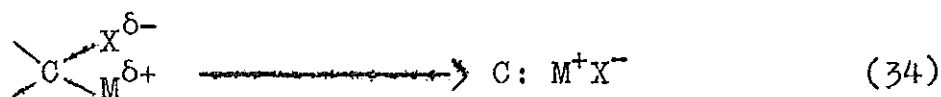
CHAPTER II

α-MONOHALOALKYLTRANSITION METAL COMPOUNDS

When ligands of lower (e.g. alkalimetal, M) or higher (e.g. halogen, X) electronegativity are connected to carbon, the result in both cases is a polarization of the bond in opposite directions. In one case carbon assumes negative charge which explains its nucleophilic reactivity. In the other it carries a positive charge and therefore undergoes electrophilic reactions. The extreme case is the ionization of the polar bonds with the liberation of carb: anions or carbonium ions.



On the other hand when M and X are attached to the same carbon atom, the polarization of the bonds is depicted as in the following equation.



In this case the polarization is even more pronounced owing to the mutual interaction of M and X. Compounds of this nature are rather unstable. Intra- or intermolecular metal - halogen interaction results in metal halide elimination, thereby releasing useful transient species. Some such as those of mercury find useful application as methylene transfer agents.⁶⁷

The stabilities of methylene transition metal carbenes are expected to depend on the kind of transition metal used and the accompanying ligands. Nevertheless, monohalomethyltransition metal compounds appear to be good sources of methylene metal carbenes. Therefore the development of a general synthetic method for monohaloalkyltransition metal compounds from the point of view of the preceding discussion is an extremely useful undertaking. Consequently the main goal of our investigative work is to realize this end.

Review of Monohaloalkyltransition Metal compounds

A number of methods have been developed for the synthesis of halomethyl compounds of the main groups metals and metalloids. Those of silicon and germanium are easily accessible via direct halogenation of methyl compounds of these elements,^{68,69} However, due to the ease with which the halogens cleave metal - to - carbon bonds, methyl group halogenation of methyl derivatives of the heavier metals such as tin, lead and mercury are very limited and not at all satisfactory.

The reaction of diazomethane with metal and organometallic halides often gives halomethyl compounds, including those of tin, lead and mercury.⁷⁰ Unfortunately, the potential hazards associated with handling diazomethane in large quantities impose severe limitation on the scale on which such preparations can be carried out.

A number of haloalkylmetal compounds of the main group elements have been synthesized. However, a simple and general applicable method has not been developed for the preparation of transition metal halomethyls.

To date, only a handful of such compounds have been prepared under special conditions. A number of attempts to prepare chloroalkyltransition metal compounds have resulted in the formation of the corresponding metal chlorides.^{71 - 73} The known monohalomethyltransition metal compounds are summarized in table 1. With the exception of chloromethyliridium and chloromethylchromium derivatives, the rest of the compounds shown in table 1 have been made according to the following equation.⁷⁴

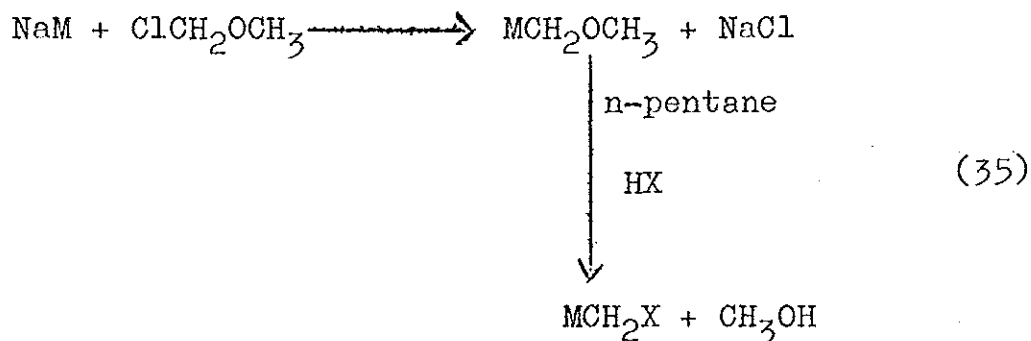
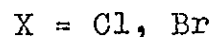
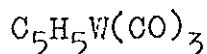
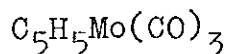
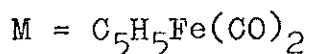


Table 1. Known α -monohalomethyltransition metal derivatives

Compound	Metal Carbonyl Bonds				NMR (δ)	Rela- tive inten- sity	Refer- ence
$C_5H_5Fe(CO)_2CH_2Cl$	2026	(vs),	1960	(vs)	5.09, 4.26	5:2	54,74
$C_5H_5Fe(CO)_2CH_2Br$	2033	(vs),	1977	(vs)	4.83, 3.78	5:2	74
$C_5H_5Mo(CO)_3CH_2Cl$	2037	(vs),	1966	(vw), 1949 (vs), 1924 (vs)	5.42, 4.08	5:2	74
$C_5H_5Mo(CO)_3CH_2Br$	2032	(sh),	2031	(vs), 1945 (vs), 1920 (vs)	5.15, 3.72	5:2	74
$C_5H_5W(CO)_3CH_2Cl$	2026	(vs),	1955	(vs), 1938 (vs), 1913 (vs)	5.53, 4.15	5:2	74
$C_5H_5W(CO)_3CH_2Br$	2030	(vs),	1937	(vs)	5.54 3.86	5:2	74
$(Ph_3P)_2Ir(CO)CH_2Cl$			1942	(vs)	-----	---	52
$C_5H_5Cr(NO)_2CH_2Cl$			-----		-----	-----	69

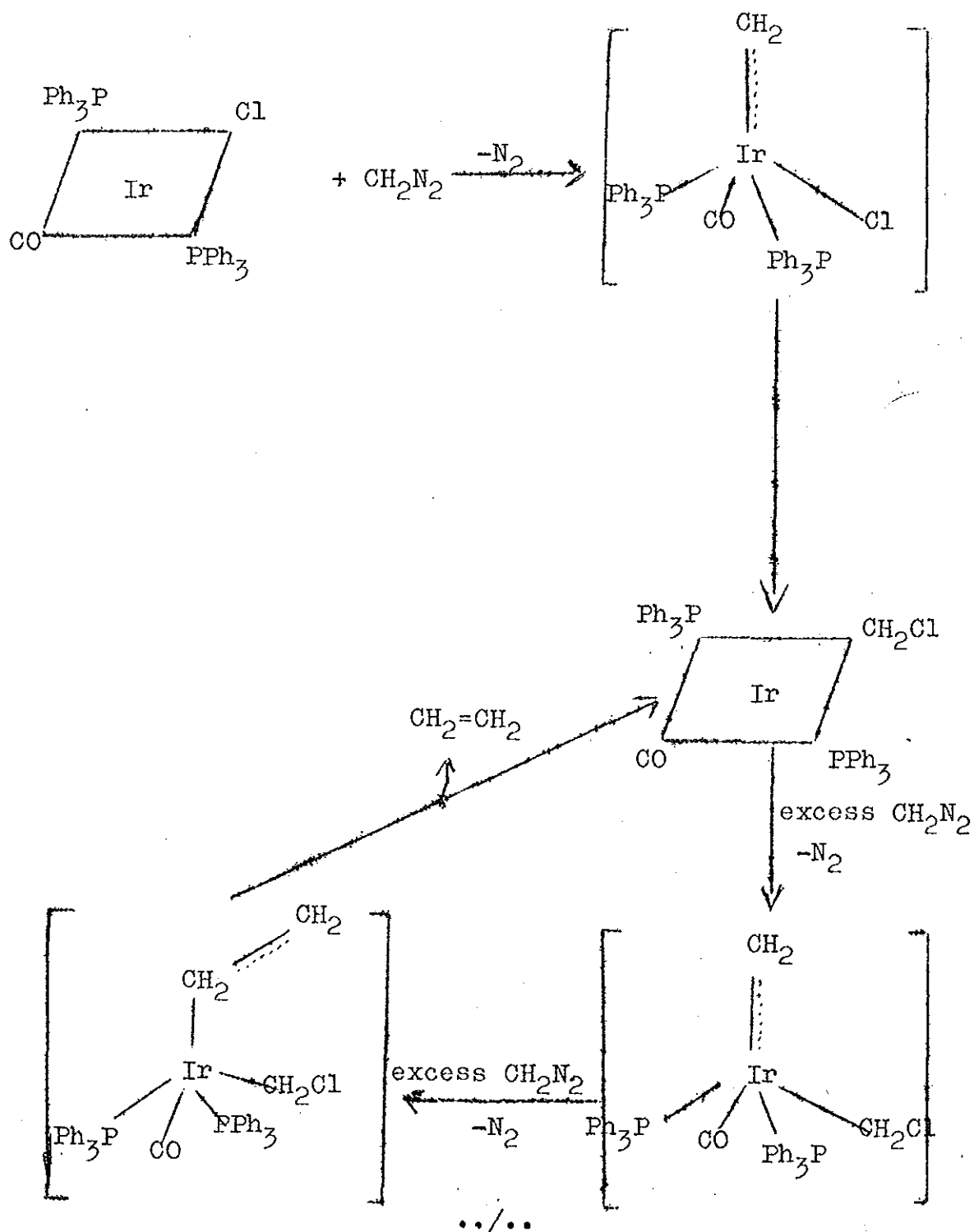


The generality of this reactions is severely limited by the requirement that the metal form a nucleophilic anion, and even then the desired α -methoxymethylmetal compound may not form. Even when the α -methoxymethylmetal complex is readily formed, its conversion into the α -halomethylmetal complex may not be satisfactory. Thus while $CpFe(CO)_2 (CH_2OCH_3)$ in pentane reacts immediately with HCl to give (chloromethyl)-cyclopentadienyldicarbonyliron (II), the complexes $(CO)_5MCH_2OCH_3$ ($M = Mn, Re$) do not give satisfactory results under comparable conditions.⁵⁴ More vigorous experimental conditions are necessary, but these usually result in an extensive decomposition of the resulting chloromethylmetal complex. It appears that the reaction of the α -methoxymethylmetal compound with a hydrogen halide is dependent upon the nature of the metal and its accompanying ligands. The trans-(chloromethyl)-bis(triphenylphosphine)-carbonyliridium (I) is stable in air, although it readily decomposes in solution. In warm chloroform it decomposes yielding $Cl(CO) (Ph_3P)_2Ir$ and polymethylene.⁵²

As a suspension in Et_2O , this chloromethyliridium complex catalytically decomposes diazomethane to ethylene and nitrogen. The following mechanism is offered to explain this property.⁵² Scheme 4.

Scheme 4

Proposed mechanism for the decomposition of diazomethane to ethylene and nitrogen in the presence of $(\text{ClCH}_2)(\text{CO})(\text{Ph}_3\text{P})_2\text{Ir}$.



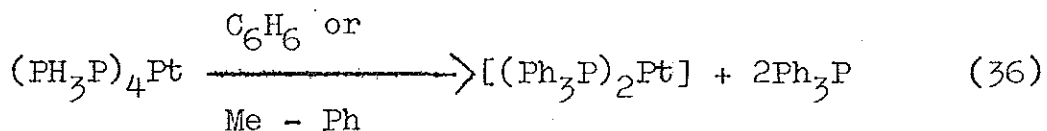
Methods of preparation

In this section an attempt will be made to present the background material for the preparative methods employed in our investigative work.

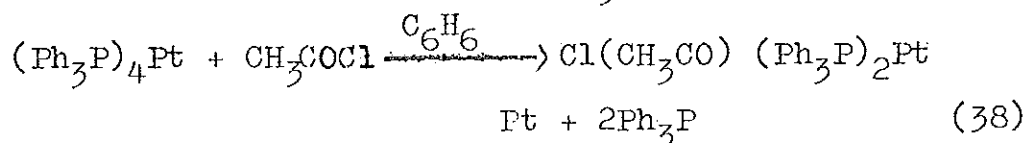
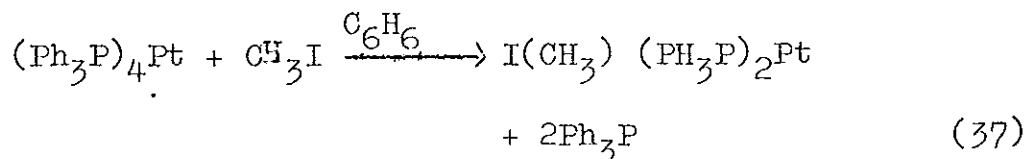
Oxidative addition

One method by which a complex may remain stable although coordinatively unsaturated is the ability to have stable complexes with different coordination numbers. The complex may remain stable and relatively free from unwanted reactions until the appropriate species appears and then expand its coordination shell to receive it. If there is a formal loss of electrons accompanying this change, the reaction is classified as an oxidative addition.⁷⁵ Oxidative addition is the term given to a reaction in which the central metal ion of a coordination complex is formally oxidized by the addition of a covalent molecule to the coordination sphere. For oxidative addition to take place the complex has to be coordinatively unsaturated.

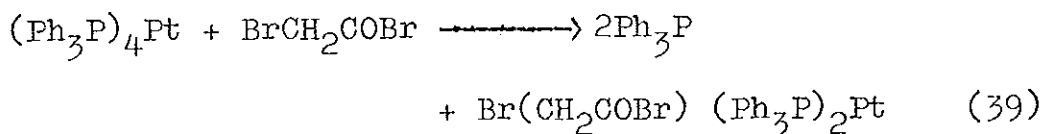
Tetrakis (triphenylphosphine) platinum (0) in benzene or toluene dissociates as shown in equation 36.⁷⁶



The bis (triphenylphosphine) platinum (0) species has never been isolated. However, it is known to react instantly with covalent molecules such as iodomethane⁷⁶ and acetyl chloride⁷⁶ to give oxidative addition products as shown in equations 37 and 38.

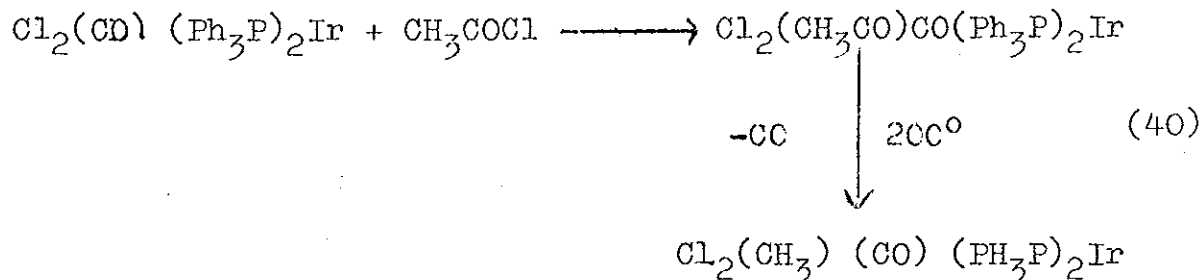


Thus, if bromoacetyl bromide is used in these reactions, the oxidative addition product expected is shown in equation 39.

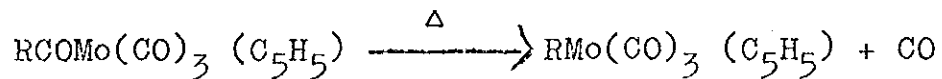


Thermal and photolytic decarbonylation

When transdichloroacetylcarbonylbis-(triphenylphosphine) iridium (III) obtained by the oxidative addition of acetyl chloride to $\text{Cl}(\text{CO}) (\text{Ph}_3\text{P})_2\text{Ir}$ is heated to 200° , it loses carbon monoxide to yield $\text{Cl}_2(\text{CH}_3) (\text{CO}) (\text{Ph}_3\text{P})_2\text{Ir}$.⁷⁷



A related reaction is the decarbonylation of $\text{Cl}(\text{CH}_3\text{CO}) (\text{Ph}_3\text{P})_2\text{Pt}$ when heated at $210 - 220^\circ$ for 2 - 3 hours to give $\text{Cl}(\text{CH}_3) (\text{Ph}_3\text{P})_2\text{Pt}$.⁷⁶



The acyl transition metal derivatives are commonly obtained by the reaction of organotransition metal salts (e.g. $\text{NaFe(CO)}_2(\text{C}_5\text{H}_5)$, $\text{NaMo(CO)}_3(\text{C}_5\text{H}_5)$,) with acyl or perfluoroacyl halides (e.g. CH_3COCl , CF_3COCl).

Thus, examinations of the thermal and photolytic decarbonylation of Bromoacetyltransition metal derivatives promises to offer a logical route to the synthesis of α -Bromoalkyltransition metal compounds.

CHAPTER III

EXPERIMENTAL SECTION

General Techniques

All synthesis involving solutions of air or moisture sensitive compounds were routinely performed under a nitrogen atmosphere. This was made possible by the use of a vacuum line.

Solvents were deaerated with nitrogen, and dried over molecular sieves.

Tetrahydrofuran, was first dried over 4A molecular sieves for about 48 hours then over potassium metal. Benzophenone was added to ascertain the complete removal of air and water. Addition of benzophenone results in an intense blue color if complete removal of oxygen is attained. When required the solvent was directly distilled into the reaction vessel under nitrogen.

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

Infrared spectra were obtained on either perkin elmer 727 B or Pye Unicam SP 2000 grating infrared spectrophotometers. The values are given in cm^{-1} units.

Nuclear magnetic resonance spectra were obtained on a varian T-60 spectrometer. Values are given in $\delta(\text{P.P.M})$ downfield from tetramethylsilane ($\delta = 0$).

Pure carbon di-sulfide was used as a solvent in nuclear magnetic resonance spectroscopy because it is cheaper compared to other solvents and it is generally established as useful in the NMR spectroscopy of transition metal organometallic compounds.⁷⁹

Though carbon tetrachloride is often too reactive with transition metal organometallic compounds, it was used as a solvent in some of the NMR spectroscopy.

Florisil (200 - 300 mesh) was used as an adsorbent, since it was believed to cause less decompositions of organometallic compounds than other common adsorbents.

All apparatus used for the synthesis work were either modified or made in the glass blowing section of the department of chemistry AAU. In this connection vacuum line, sintered glass vacuum filtration, apparatus, schlenk tubes (with different sizes), nitrogen bubblers, pressure equalizing dropping funnels ... etc were made.

1. The Preparation of Bromoacetyl Bromide⁸⁰

Red phosphorous (3.4 g) was added to 20 ml of warm glacial acetic acid. The solution was kept in water bath and 37 ml of Br₂ added dropwise from a dropping funnel. The apparatus was fitted with a reflux condenser and a water-bath. The mixture was allowed to react for about 6 hours. Distillation of the mixture yielded 4.8 ml of an oily liquid which was characterized as bromoacetyl bromide.

Boiling Point: 123-125°C (lit.⁸¹ 147 -150).

NMR 4.8 δ (sharp singlet) (lit.⁸⁰ 4.8 δ)

The yield of bromoacetyl bromide varied from experiment to experiment. The bromoacetyl bromide obtained was kept in a refrigerator for further use in the synthesis work. It was observed that the compound gradually hydrolyzes to bromoacetic acid when it comes in contact with water vapor.

2. The Preparation of tetrakis (triphenylphosphine)-platinum (0).

Triphenylphosphine (5.45 g) was dissolved in 72 ml of absolute ethanol. A solution of KOH (0.5 g) in a mixture 12 ml of ethanol and 3 ml of water was added to the clear ethanolic solution of PPh₃. An aqueous solution of 1.85 gms of potassium tetrachloroplatinate was slowly added dropwise to the alkaline PPh₃ solution, while stirring magnetically at 65°C. The addition was completed in about 20 minutes. A pale yellow precipitate began to separate within a few minutes of the first addition. The compound was recovered by filtration. The product

was washed with 100 ml of warm ethanol, then with 40 ml of cold water and again with 40 ml of cold ethanol. The resulting pale yellow powder was dried in vacuum for 2 hours. The compound was stored under nitrogen to avoid decomposition by atmospheric oxygen.

Yield = 3.8 g

% yield = 76% (based on tetrachloroplatinate)

Melting point = 118 - 120° (lit. 118 - 120°
in air and 159 - 160° in vacuo
1 mm).

3. The reaction of tetrakis (triphenylphosphine)-
platinum (0) with bromoacetyl bromide.

Tetrakis (triphenylphosphine)platinum (0)
(0.5 g) was dissolved in 5 ml of dry benzene. 0.2 ml
of BrCH_2COBr was added to the benzene solution of
 $(\text{PPh}_3)_4\text{Pt}$ dropwise while stirring for 10 minutes.
Immediate color change was observed. The pale
yellow liquid formed a white turbid solution. Then,
the solvent was pumped off giving a yellowish
white greasy residue, which was washed several
times with n-pentane. However, the residue still
remained greasy. Whereupon, the residue was dissolved
in dichloromethane and filtered through florisil to
give an orange solution which was evaporated to a
small volume. Addition of low boiling petroleum ether
gave 0.34 g of an orange precipitate identified as
dibromo-bis(triphenylphosphine)platinum(II)
 $(\text{PPh}_3)_2\text{PtBr}_2$, with trace quantities of bromo(bromoacetyl)
bis(triphenylphosphine)platinum(II), $\text{Br}(\text{BrCH}_2\text{CO})(\text{PPh}_3)_2\text{Pt}$.

% yield of $(PPh_3)_2PtBr_2$ = 81% (based on $(PPh_3)_4Pt$)

Melting point = 180 - 183°C

IR(KBr, acyl-CO) = 1620 cm^{-1}

NMR 3.6 δ (sharp singlet)

7.5 δ (multiplets)

The IR absorption peak at 1620 cm^{-1} disappears with time and the NMR of the product showed a singlet at 3.6 δ which also disappeared on standing. The above phenomenon was also observed when the compound was heated under nitrogen or exposed to light or air. This probably shows that $Br(CH_2CO)(Ph_3P)_2Pt$ and $Br(BrCOCH_2)(Ph_3P)_2Pt$ decomposes to $(Ph_3P)_2PtBr_2$.

4. The Preparation of cyclopentadienylmolybdenum tricarbonyl dimer⁷⁹

Hexacarbonylmolybdenum (10 g) was reacted with dicyclopentadiene (50 ml). The reaction was carried out under nitrogen in a three-necked flask, fitted with a nitrogen inlet, a magnetic stirrer, a straight reflux condenser and a thermometer. The reaction mixture was heated gently at 135 - 145°C until no more white molybdenum hexacarbonyl sublimed out of the reaction mixture. From time to time molybdenum hexacarbonyl that had sublimed in the reflux condenser was pushed back into the reaction mixture. The red violet crystals of the product was washed five times with n-hexane to remove excess dicyclopentadiene and other hydrocarbon impurities. The product was dried in vacuum at 50°C and any remaining $Mo(CO)_6$ sublimed out of the product on to the cooler

parts of the flask.

Yield: 2.5 g

% yield = 18%, (lit 80%) based on Mo(CO)_6

Melting point: $214 - 216^\circ\text{C}$ (lit. $215 - 217^\circ\text{C}$)

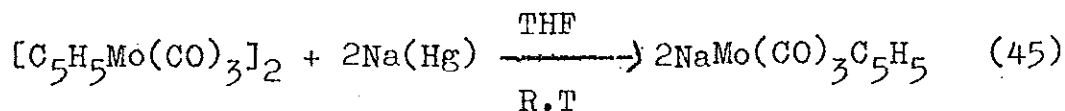
IR(KBr, metal carbonyl absorption)

1950, 1920, 1900, 1890 cm^{-1}

⁷⁹
(lit. 1957, 1926, 1904, 1891 cm^{-1})

5. The reaction of bromoacetyl bromide with cyclopentadienylmolybdenum tricarbonyl dimer.

Sodium (1g) was dissolved in 100 grams of mercury to give a 1% sodium amalgam which was vigorously stirred with a sample of cyclopentadienylmolybdenum tricarbonyl dimer, $[\text{C}_5\text{H}_5\text{Mo(CO)}_3]_2$ (3g) in 100 ml of dry THF for 15 minutes. Subsequently the amalgam was run out via a stopcock in the bottom of the flask and the solution was washed with 50 grams of fresh mercury. Then it was filtered to give yellow $\text{NaMo(CO)}_3\text{C}_5\text{H}_5$.



The yellow solution of $\text{NaMo(CO)}_3\text{C}_5\text{H}_5$ was cooled in an ice salt bath (-10°C) and treated dropwise with 0.8 ml of bromoacetyl bromide in 5 ml of THF. The reaction mixture was stirred in the dark at 0°C for

two hours. At the end of the reaction time the solvent was evaporated under reduced pressure and was first washed with 50 ml of n-pentane (to remove its slightly sticky nature) and then extracted with 90 ml of dichloromethane in three equal portions. The resulting solution was filtered and then evaporated to a small volume. Addition of n-hexane afforded one gram of orange crystals identified as $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ with traces of $\text{BrCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$.

% yield: 45% (based on $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$)

Melting point: $112 - 117^\circ$ (decomposed at 100° , color changed from orange to grey).

IR: CH: 3120(W), 2960(VW)

Mo - CO: 2020 (s), 1950 (s)

acyl-CO: 1645 (s), 1620 (s), 1660 (w)

NMR: 5.6 δ (sharp singlet)

5.2 δ (sharp singlet) with relative intensities 5:2

6. Photochemical decomposition of $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$.

The schlenk tube which contained the product was exposed to the sunlight for three hours. The orange color of the product changed to grey. The grey residue was identified as $\text{BrCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. On further exposure to the sunlight the grey residue darkened. This final product was identified as $\text{Br-Mo}(\text{CO})_3\text{C}_5\text{H}_5$.

IR: The acyl CO absorption bands at 1645, 1660 and 1620 cm^{-1} of the starting compounds disappeared.

NMR: 5.5 δ and 3.6 δ (sharp singlets with relative intensities 5:2.
(The singlet at 3.6 δ disappeared after further exposure to the sunlight. This shows that decarbonylation is taking place. (See experiment number 6.)

7. Thermal decomposition of $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$

The product was placed in a schlenk tube and heated to a temperature of 100°C for one hour under vacuum. A dark grey product was obtained. Its IR and NMR spectra were identical with the one obtained with photolytic decomposition.

IR: No acyl-CO observed.

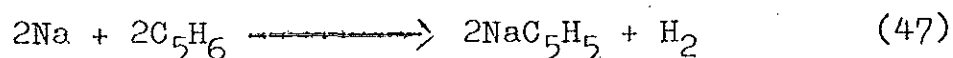
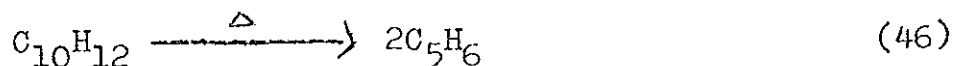
NMR: 5.5 δ (singlet)

The results of the thermal and photolytic decompositions were found to be similar. In both cases the final product was $\text{BrMo}(\text{CO})_3\text{C}_5\text{H}_5$.

8. Preparation of $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ by a different method.

THF (about 150 ml) was distilled under nitrogen on to sodium sheets (0.3 g). The suspension of sodium in the THF solvent was treated dropwise with

excess freshly prepared cyclopentadiene (about 2 ml) by thermal decomposition of dicyclopentadiene to dissolve all of the sodium forming a pink solution of sodium cyclopentadienide.



$Mo(CO)_6$ (3.5 g) was added to the sodium cyclopentadienide solution and the resulting mixture was refluxed under nitrogen for about 20 hours. After filtering and cooling, the resulting $NaMo(CO)_3C_5H_5$ solution was treated dropwise with 1.3 ml of bromoacetyl bromide in 5 ml of THF. The reaction mixture was stirred at $0^\circ C$ for two hours. At the end of the reaction time, the solvent was evaporated under reduced pressure and the resulting residue was first washed with 50 ml of n-pentane (to remove its slightly sticky nature) and then extracted with 100 ml of dichloromethane. The resulting solution was filtered and then evaporated to a small volume. Addition of n-hexane followed by storage of the solutions overnight in a refrigerator afforded one gram of orange red crystals identified as mainly a mixture of $BrCH_2COMo(CO)_3C_5H_5$ and trace quantities of $Br-CO-CH_2-Mo(CO)_3C_5H_5$.

Yield: 1.02 g

% yield: 45% (based on $Mo(CO)_6$)

M.P: $112 - 115^\circ$ (decomp. $100 - 102^\circ$)

IR: CH: 3120 (w), 2960 (v.w)

Mo-CO: 2020 (s), 1950 (s), 1930 (s)

acyl-CO: 1645 (s), 1620 (s), 1660 (w)

NMR: 5.6 δ , 5.2 δ (sharp singlets) (with
relative intensities 5:2)

The product was subjected to thermal and photochemical decomposition. The results were identical to those given in experiments 6 and 7.

9. Preparation of $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$.

Tungsten hexacarbonyl (3.6 g) was refluxed for about 16 hours with a 20% excess of sodium cyclopentadienide in 150 ml of THF to obtain a yellow solution of $\text{NaW}(\text{CO})_3\text{C}_5\text{H}_5$. The yellow solution was filtered while hot, cooled to ice salt temperature and treated dropwise with 1.2 ml of bromoacetyl bromide in 5 ml of THF. The reaction mixture was stirred in the dark at 0°C for two hours. Subsequently the solvent was pumped off under reduced pressure leaving behind an orange red precipitate. The residue was washed with 50 ml of n-pentane to remove the greasy nature of the residue and then extracted with 50 ml of dichloromethane and crystallized by adding 5 ml of n-hexane. 1.01 grams of orange red crystals was obtained. The product was identified as $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ with traces of $\text{BrCOCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$.

% yield: 31% (based on $\text{W}(\text{CO})_6$)

M.P: 118 - 121° (decomp. at 85 - 90°)

IR: CH: 3100 (w), 2950 (vw)

W-CO: 2050 (s), 1960 (s), 1990 (s)

acyl-CO: 1630 (s), 1645 (s).

NMR: 5.7 δ , 5.3 δ (sharp singlets) with
relative intensities 5:2

10. Photochemical decomposition of $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$.

The tungsten compounds synthesized were found to be light sensitive. A solution of the substance in dichloromethane changed its color from orange to greyish black when exposed to the sunlight for about 2 hours. The greyish black residue appeared to be the major product. The residue from the photolysis reaction was identified as $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Br}$.

IR: W-CO 1990 (s), 1950 (s)

NMR: 5.6 δ (sharp singlet)

The CH and acyl COIR absorption bands of $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{BrCOCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ disappeared with photochemical decomposition.

11. Thermal decomposition of $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$.

II-cyclopentadienyl (bromoacetyl) tricarbonyl tungsten (II) was placed in a 100 ml schlenk tube. The system was evacuated and the sample portion heated to 90°C. The orange red color of the sample changed to greyish black. The residue was identified as $\text{II-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Br}$. (see expt. 10).

strong acyl-CO absorption band at 1660 cm^{-1} . It also showed a strong absorption band at 1750 cm^{-1} due to the bridge carbonyls from the dimer. Efforts to separate these were unsuccessful. A mixture of compounds were obtained among which, $\text{BrCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{BrCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ were indentified.

IR (in CCl_4): acyl-CO 1660 cm^{-1}

Fe-CO 2050 (vs), 2010 (vs) 1970 (vs).

NMR (in CCl_4): 3.7 δ (sharp singlet)

4.6 δ (sharp singlet)

4.9 δ (sharp singlet)

4.7 δ (sharp singlet)

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter an effort will be made to discuss the results of each experiment and make a general summary at the end.

The preparation of bromoacetyl transition metal derivatives

A number of compounds with the general formula $R\text{COML}$ and $R_f\text{COML}$ (R = alkyl, R_f = perfluoroalkyl; M = transition metal; L = ligand) have been synthesized and used in the synthesis of some alkyl and perfluoroalkyl transition metal derivatives.^{78,82,83}

In the past years chloroacetyl metal derivatives were prepared and reported.⁶⁷ However no bromoacetyl transition metal derivatives so far have been reported. In this investigative work, the reactions of a number of transition metal derivatives with bromoacetyl bromide were examined. The results are summarized in the following table.

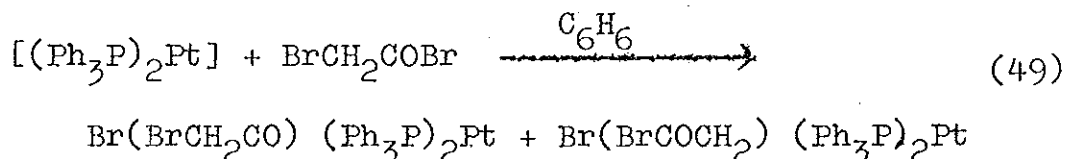
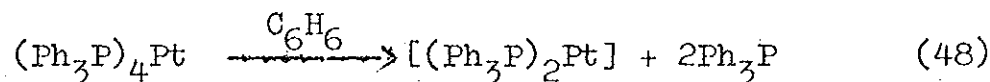
Table 2. The results of the reaction of bromoacetyl bromide with some transition metal derivatives.

Transition metal derivatives	Solvent	Products
$(\text{Ph}_3\text{P})_4\text{Pt}$	C_6H_6	$^+\text{Br}(\text{BrCH}_2\text{CO}) (\text{Ph}_3\text{P})_2\text{Pt}$ $^+\text{Br}(\text{BrCOCH}_2) (\text{Ph}_3\text{P})_2\text{Pt}$ $(\text{Ph}_3\text{P})_2\text{PtBr}_2$
$\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$	THF	$\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ $^+\text{BrCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$
$\text{NaW}(\text{CO})_3\text{C}_5\text{H}_5$	THF	$\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ $^+\text{BrCOCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$
$\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$	THF	$\text{BrCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ $^+\text{BrCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$

⁺trace quantities.

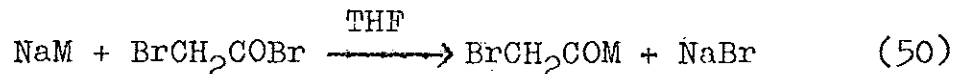
Tetrakis (triphenylphosphine) platinum (0) smoothly reacted with bromoacetyl bromide. The infrared spectrum showed two weak acyl-CO absorption at 1620 and 1640 cm^{-1} probably corresponding to

trace quantities, when the infrared absorption was determined again after two days, the acyl-CO absorption bands were not detected. Based on the two acyl-CO absorption bands one would conclude that the reaction was taking place at both ends of the bromoacetyl bromide.



These reactions of bromoacetyl bromide with $(\text{Ph}_3\text{P})_4\text{Pt}$ shows that the bromoacetylplatinum complexes were formed; but probably decompose spontaneously to give $(\text{Ph}_3\text{P})_2\text{PtBr}_2$.

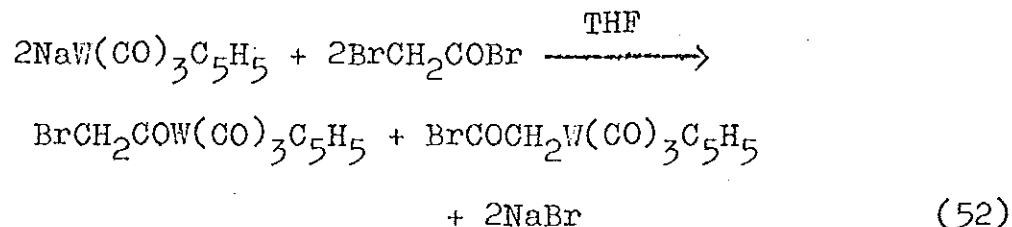
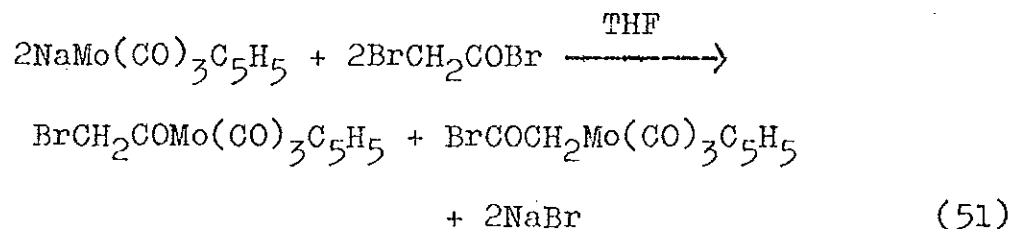
The bromoacetylmethyl derivatives, BrCH_2COM where $\text{M} = \text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ or $\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ were prepared according to the following equation.



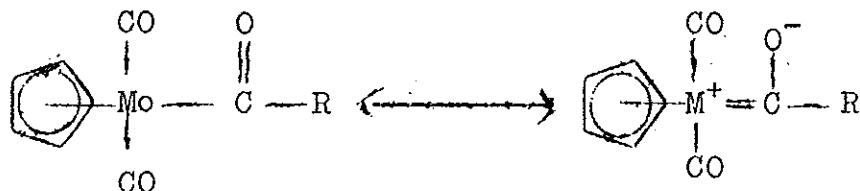
These bromoacetylmethyl derivatives are photosensitive and thermally unstable. Extensive decomposition took place when the experiments were done at room temperature. All of the synthesis of these bromoacetylmethyl complexes were performed at 0°C , and care was taken to avoid prolonged exposure to light. The bromoacetylmolybdenum and tungsten derivatives are orange red in color. The compounds

are readily soluble in dichloromethane, carbon disulfide and carbon tetrachloride, but sparingly soluble in n-pentane and n-hexane.

Both derivatives show two acyl-CO absorptions at about 1645 and 1620 cm^{-1} . Based on the two acyl CO absorption bands, one would conclude that reaction was taking place on both ends of the bromoacetyl bromide.



The acyl-CO absorption frequencies are substantially lower than the carbonyl absorption in ketones. A possible explanation is the significant contribution of resonance structure with metal carbon double bonding which reduces the carbon oxygen bond order.



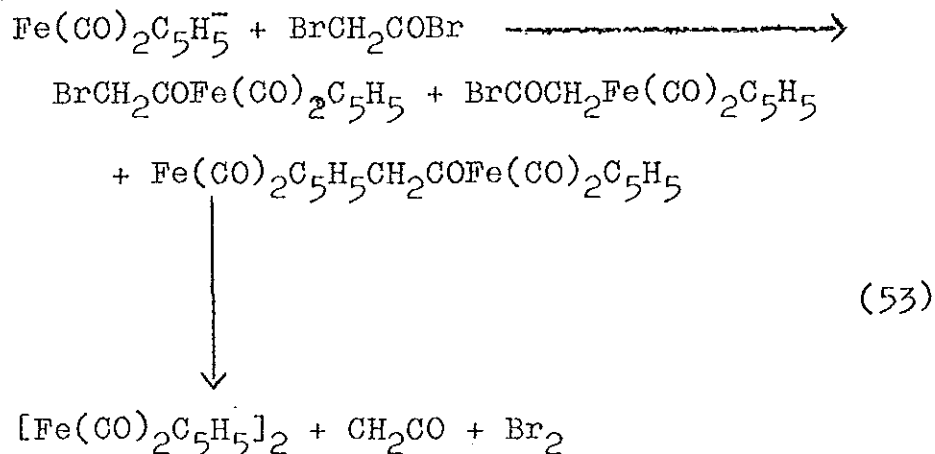
Resonance contributions of this type may have the effect of stabilizing acyl derivatives of transition metals as compared with acyl derivatives of non transition metals which are incapable of forming the type of double bond postulated.⁶⁷

The amount of $\text{BrCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ obtained by reacting $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ with bromoacetyl bromide in THF was in trace quantity. If one takes into consideration the fact that a number of compounds of the general formula $\text{RCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{RfCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (R = alkyl or aryl; Rf = perfluoroalkyl) have already been prepared and have been found to be among the most stable for this class of compounds, one would draw the conclusion, that the bromoacetyl iron complex would be stable, and would be easy to make. However, the synthesis of $\text{BrCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was very difficult. The final product was largely $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ which was the starting compound. Only trace amounts of the desired products i.e. $\text{BrCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{BrCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ as identified by IR with other unidentified compounds were recovered.

The products obtained by reacting $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and BrCH_2COBr were contaminated with tarry products and neither repeated washing with n-pentane nor repeated filtration through florisil could remove the tarry products. It appeared that extensive decomposition took place during purification.

The formation of the dimer, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ in large proportion suggests that in the reaction involving $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and BrCH_2COBr the dicarbonylcyclopentadienyliron (I) anion is highly reactive and least selective, thereby replacing

quantitatively bromine at both ends of bromoacetyl bromide. The resulting product is expected to be unstable and subsequently decomposed to the dimer.



Probably it is assumed that the decomposition of the products gives rise to the dimer, $[\text{C}_5\text{H}_5\text{Fe(CO)}_2]_2$, ketene vapor and bromine. Recent investigation with chloroacetyl chloride has also shown that the resulting chloroacetyl derivative was unstable and subsequently decompose to the dimer.⁶⁷

Thermal and Photolytic Decompositions
of $\text{BrCH}_2\text{COM}(\text{M} = \text{C}_5\text{H}_5\text{Mo(CO)}_3\text{C}_5\text{H}_5\text{W(CO)}_3)$

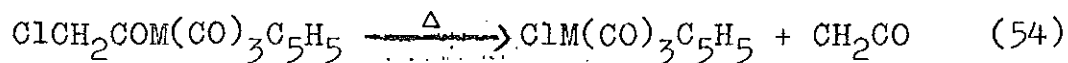
The results of the thermal and photolytic decompositions of $\text{BrCH}_2\text{COMo(CO)}_3\text{C}_5\text{H}_5$ and $\text{BrCH}_2\text{COW(CO)}_3\text{C}_5\text{H}_5$ are summarized in the following table ... (table 3).

Table 3. Thermal and photochemical decompositions of the bromoacetylmethyl derivatives,
 $\text{BrCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ (M = Mo, W).

Bromoacetyl metal complex	Decomposition products	
	Photolytic	Thermal
$\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$	$\text{BrMo}(\text{CO})_3\text{C}_5\text{H}_5$ $^+\text{BrCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$	$\text{BrMo}(\text{CO})_3\text{C}_5\text{H}_5$
$\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$	$\text{BrW}(\text{CO})_3\text{C}_5\text{H}_5$ $^+\text{BrCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$	$\text{BrW}(\text{CO})_3\text{C}_5\text{H}_5$

⁺in trace quantity,

Previous work on chloroacetylmethyl complexes⁶⁷ has shown the formation of ketene and diketene in the thermal decompositions of $\text{ClCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ (M = Mo, W). This reaction showed that β -halogen elimination was taking place.

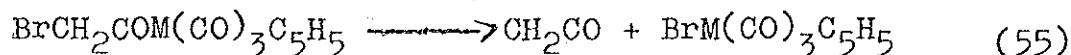


M = Mo, W.

While ketene and diketene were the only identifiable gaseous products obtained in the thermal decomposition of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$, the thermal decomposition of $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ in addition to ketene and diketene,

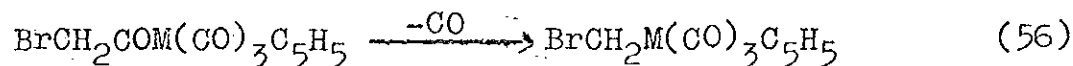
also produced carbon monoxide. It appeared that in the case of the bromoacetyltungsten derivative, both β -halogen elimination and decarbonylation were simultaneously taking place.

Similarly the formation of ketene is predicted, though not actually detected, in the thermal decomposition of $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{BrCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$. The formation of $\text{BrM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) suggests β -bromine elimination or both β -bromine elimination and decarbonylation simultaneously taking place.



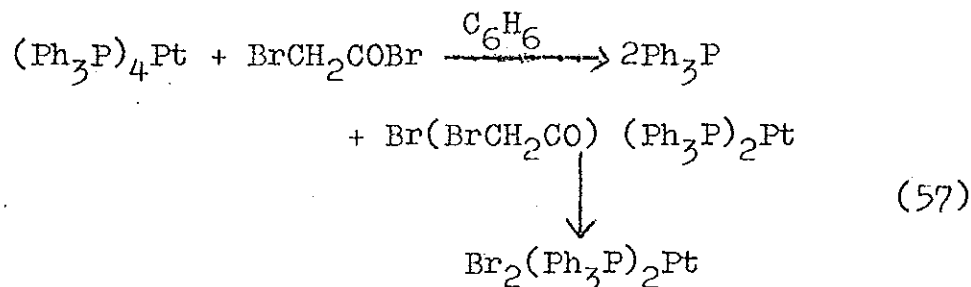
($\text{M} = \text{Mo}, \text{W}$)

The production of trace quantities of $\text{BrCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{BrCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ can be explained by decarbonylation as shown in equation 56.



($\text{M} = \text{Mo}, \text{W}$)

These facile decompositions (β -bromine elimination) of the bromoacetylmolybdenum and tungsten derivatives explain why the attempts to make bromo (bromoacetyl) bis (triphenylphosphine) platinum (II) quantitatively gave dibromo-bis(triphenylphosphine)platinum (II).



Summary

Although a number of α -halomethyltransition metal derivatives such as $\text{BrCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{BrCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ have been obtained in trace quantities, the various attempted preparative methods for the generation of halomethyl metal derivatives did not give satisfactory results.

In conclusion, it is interesting to point out that the synthesis of bromoacetyltransition metal derivatives and the subsequent study of their photochemical and thermal decompositions have not been previously reported and our investigative work appears to be the first venture into this aspect. However, because of the facile β -halogen eliminations, the photochemical and thermal decompositions did not give the expected halomethylmetal derivatives in appreciable quantities.

Further comments and a look into the future

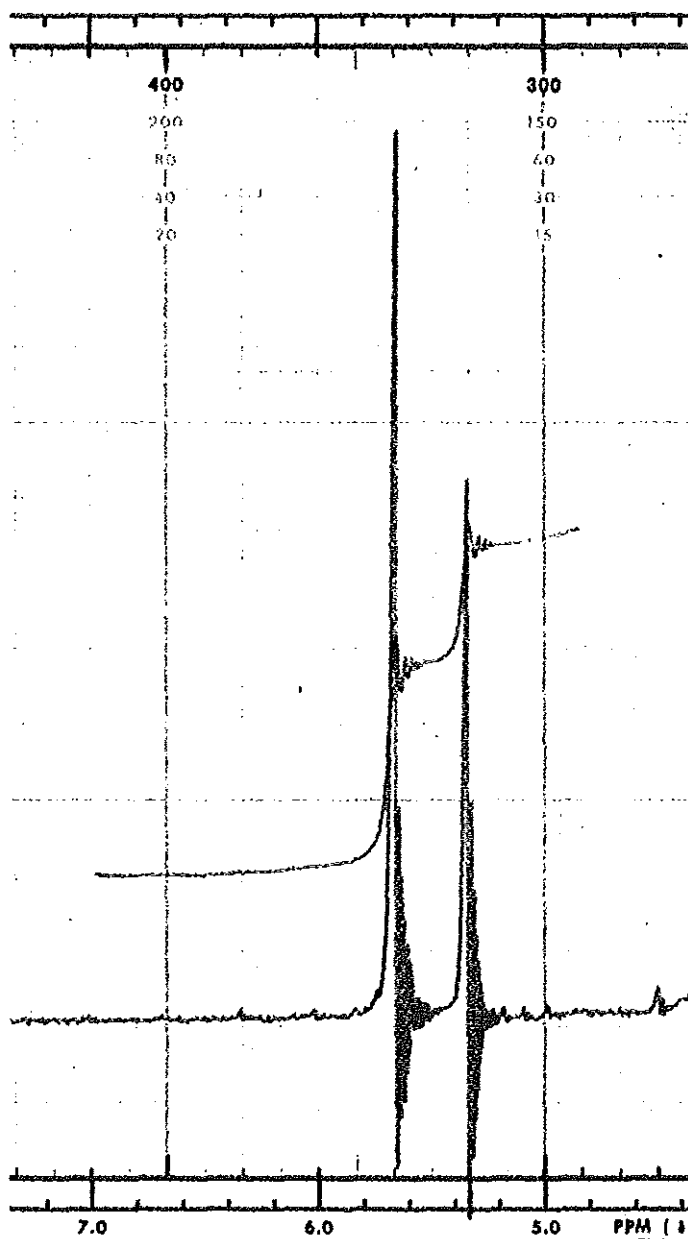
Our main goal was to synthesize α -monohaloalkyltransition metal derivatives by thermal or photochemical decomposition of the haloacetyl metal derivatives. α -monohaloalkyltransition metal derivatives could be used further as precursors of electrophilic metal carbenes via their interaction with Lewis acids.

The ultimate utility of metal carbene complexes in organic synthesis hinges on the discovery of synthetically useful ways of releasing the carbene ligand from its metal complexes. Several useful means of releasing the carbene ligand have already been found and future research will undoubtedly uncover additional transformations.

When carbene ligands were first discovered it was hoped that they might serve as reagents for generating free carbenes. However, to date, no reaction of carbene complexes has been shown to proceed via a free carbene. The thermal decomposition reactions and the alkene addition reactions of carbene complexes (for which the intervention of free carbenes seemed plausible) have been shown not to proceed via free carbenes. The fact that metal carbene complexes do not act as ready sources of free carbenes does not detract from their usefulness. Rather the differences between the complexed and uncomplexed carbenes can be exploited synthetically.

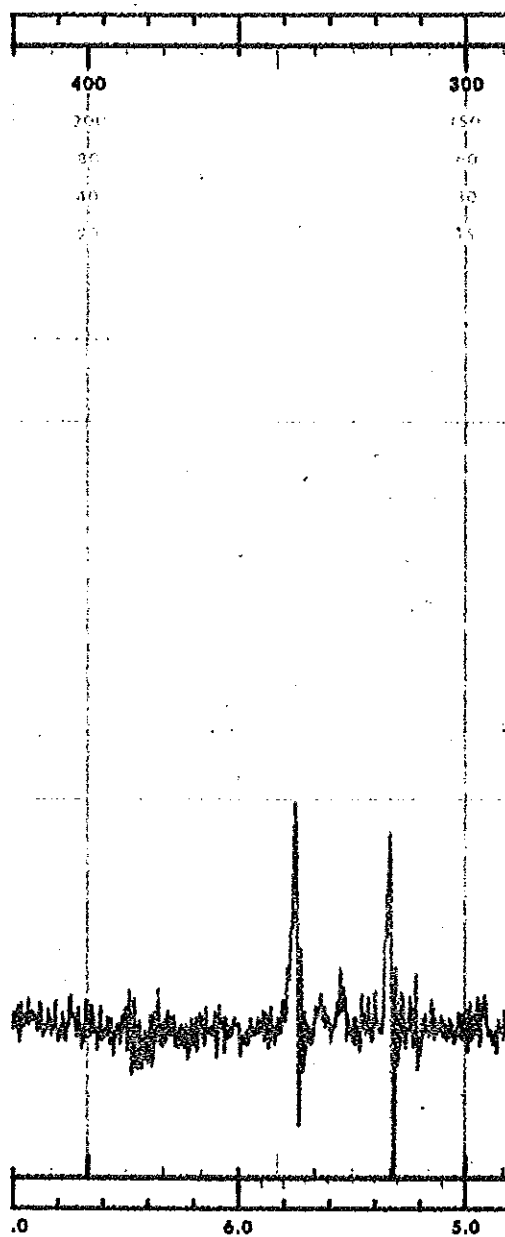
Initially carbene complexes excited a great deal of attention as potential sources of free carbenes. However, in many of the reactions of carbene complexes there is ample evidence against the intervention of a free carbene and in no instance, has a compelling case for the intervention of a free carbene been made. This should not be overly surprising since a free carbene is a high energy species (in contrast to alkenes, CO, phosphines and the like) and should be reluctant to leave the coordination sphere of the metal. Thus from the synthetic point of view, the metal carbene complex is most profitably viewed not as a source of free carbenes, but as a functional group which can be synthesized, modified and ultimately converted into other functional group.⁸⁴

APPENDIX 1



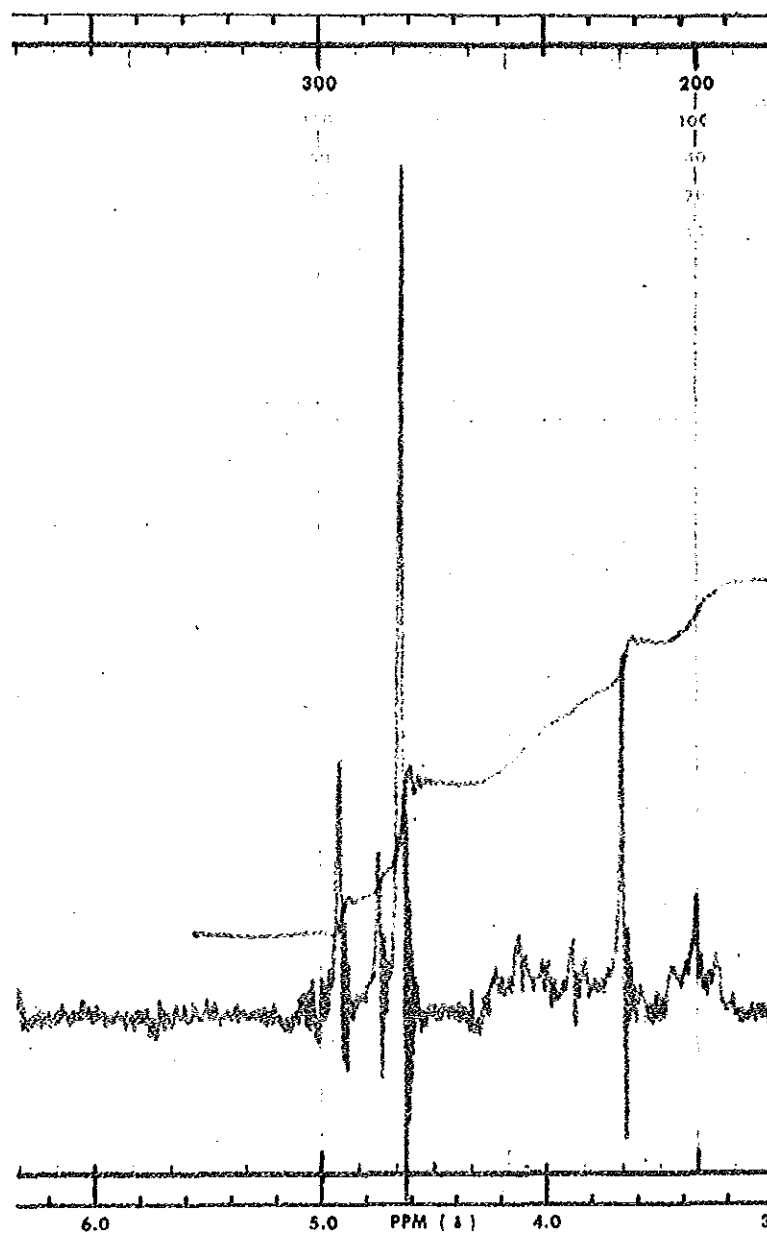
NMR spectrum of $\text{BrCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ in CS_2 .

APPENDIX 2



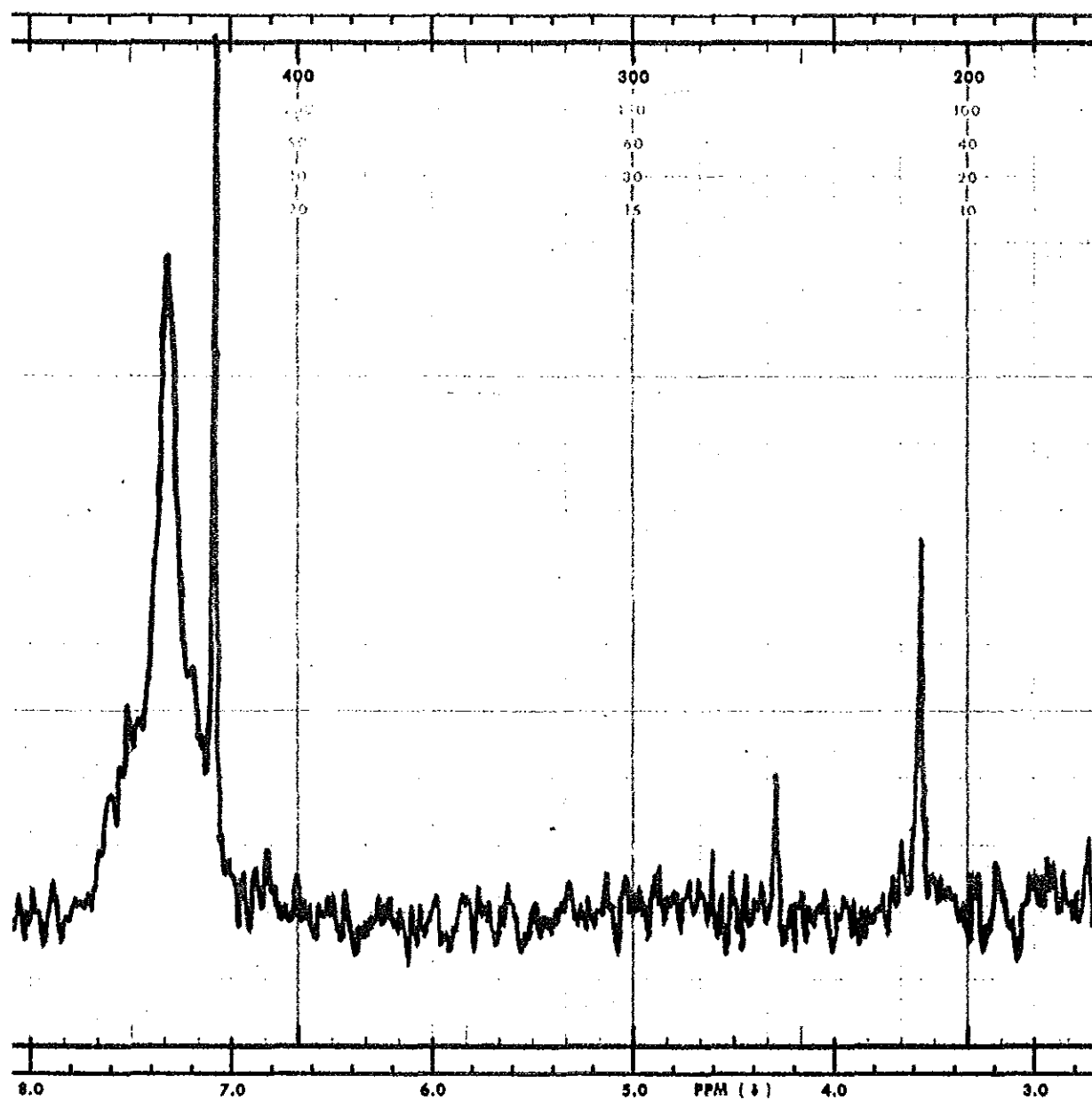
NMR spectrum of $\text{BrCH}_2\text{COO}(\text{CO})_3\text{C}_5\text{H}_5$ in CS_2

APPENDIX 3



NMR spectrum of $\text{BrCH}_2\text{COFe}(\text{CC})_2\text{C}_5\text{H}_5$ in CCl_4

APPENDIX 4



NMR spectrum of $\text{Br}(\text{BrCH}_2\text{CO})(\text{PPh}_3)_2\text{Pt}$ in CS_2

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