

THE LEWIS BASICITY OF THE GROUP VI TRANSITION METALS

by 3235-

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PART I

INTRODUCTION AND STATEMENT OF PURPOSE

In the course of some research on inorganic derivatives of triphenylphosphoniumcyclopentadienyliid, it was observed that the molybdenum carbonyl complex of the Cpyliid, $(C_6H_5)_3PC_5H_4Mo(CO)_3$ reacted reversibly with boron trifluoride to give a red, air-stable solid. At the time this work was begun there were several reports in the literature that a metal atom in a transition metal organometallic compound may function as a Lewis base toward a boron-containing Lewis acid. As only a few examples of such behavior had been examined, it was not known what metals would function as bases, the extent to which the ligands influenced metal basicity, or if there was a relationship between basicity and atomic weight or d-electron population. Since there was a reasonable possibility that the Cpyliidmetal tricarbonyl-boron trifluoride complex contained a metal-boron coordinate-covalent bond, it became the purpose of this investigation to determine if the solid was indeed a donor-acceptor complex and if the metal was the site of Lewis basicity. Furthermore, since chromium and tungsten analogs of

the Cpylid could be prepared, the series of compounds could be reacted with boron halides in order to determine if there was indeed a relationship between metal basicity and atomic weight.

PART II
NOMENCLATURE

For convenience in reading this thesis, the following abbreviations are used throughout:

Cpylid	- triphenylphosphoniumcyclopentadienyliid
Cp	- π -cyclopentadienyl group
τ	- chemical shift relative to TMS; resonance line of TMS given a value of 10.
Rel. Int.	- Relative Intensity
ϵ	- extinction coefficient
Ar	- Arene group
Ph	- C_6H_5
Me	- CH_3
Et	- C_2H_5
THF	- tetrahydrofuran
TPE	- tetraphenyldiphosphinoethane ($Ph_2P-CH_2-CH_2-PPh_2$)
N.A.	- no absorption
vp	- vapor pressure
DMF	- dimethylformamide
mp.	- melting point
bp.	- boiling point

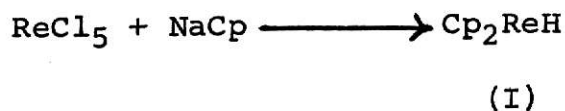
PART III

HISTORICAL INTRODUCTION

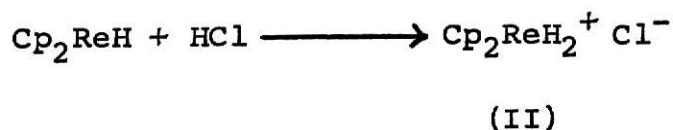
The purpose in presenting this introduction to Lewis acid-base adducts of transition metal compounds is two fold: (1) to give a general background of the application of Lewis acid-base theory to transition metal systems, and (2) to illustrate several characteristics of Lewis acid-base adducts and how they are related to the adducts prepared in the course of this research.

A. Protonation of Organometallic Transition Metal Compounds.

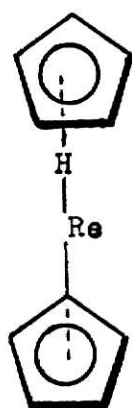
The first example of a transition metal hydride, Cp_2ReH , was prepared by Wilkinson and coworkers by the following reaction.¹



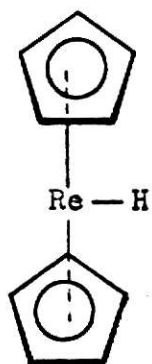
They found that upon dissolving I in a strong acid the dihydride could be formed.



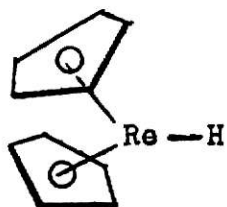
These compounds demonstrated for the first time the high field resonance line characteristic of the ^1H nmr spectra of metal hydrides. The existence of such a high field resonance prompted the following structures to be proposed for Cp_2ReH and $\text{Cp}_2\text{ReH}_2^+$.²



(IB)



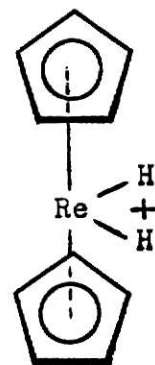
(IE)



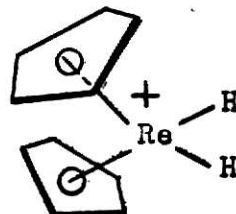
(IC)



(IIB)



(IIE)



(IIC)

Proton nmr data for these two compounds are given below.²

Table III-1.

Proton NMR Data of
Dicyclopentadienylrhenium Hydrides

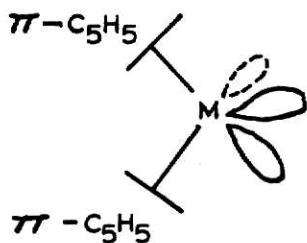
Compound	Assign.	τ ^a	Rel. Int.	Struct. (Δ) ^b	Coupling Constant
Cp ₂ ReH	Cp ring	3.65	10	Doublet (1.9)	1 Hz
	M-H	13.1	1	Broad Singlet (18)	
Cp ₂ ReH ₂ ⁺	Cp ring	3.98	10	Triplet (1.45)	0.56 Hz
	M-H	13.12	2	Broad (8)	

^aoriginal data converted to τ values.

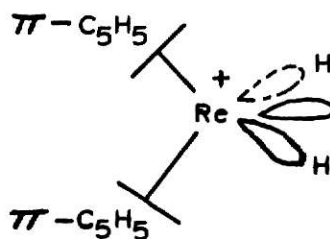
^b Δ = width of signal at half-height in Hz.

Several points should be made concerning the nmr data for these two compounds: (1) The existence of the low field doublet for Cp₂ReH at 3.65 τ is due to coupling between the ring protons and the hydridic proton and not to the existence of two chemically different rings. (2) Since there is coupling between the ring protons and the hydridic proton, an eleven line multiplet would be expected for the hydridic proton. However, only a broad (18 Hz) singlet was observed; it was felt that this was due to the lack of resolution. Therefore, structures IA and IIA can be ruled out; however, based on the nmr data the authors suggested structures (B) or (C) as possibilities.

Bis(π -cyclopentadienyl)rhenium hydride was the first of many compounds to raise the question of whether or not the cyclopentadienyl rings were parallel as in (IB) or non-parallel as in (IC). Dahl and Ballhausen re-examined the molecular orbitals for ferrocene and found that the rings could be bent out of line as much as 45° without effectively changing the overlap integrals between the metal and rings.³ They used six bonding orbitals for the rings; the remaining available orbitals were hybridized into three strongly space-oriented orbitals between the two cyclopentadienyl rings as illustrated below (III).



(III)



(IIC)

These new orbitals contain the non-bonding electrons and are the probable sites for Lewis acid-base interaction, as illustrated by $\text{Cp}_2\text{ReH}_2^+$ (IIC).

Wilkinson and his coworkers have been leaders in the investigation of protonated organometallic transition metal complexes.⁴ Their work will be discussed in two parts:

binuclear and mononuclear metal hydride systems.

The binuclear systems (e.g., $\text{CpW(CO)}_3\text{-W(CO)}_3\text{Cp}$) have exhibited several interesting phenomena. In the case of neutral or unprotonated compounds, the cyclopentadienyl ring protons appear as singlets at low τ values, while a multiplet is observed for these ring protons upon protonation of the metal. The existence of multiplets for the ring protons indicates that there is coupling between the ring and the hydridic protons. Sample nmr data for these systems are given below.⁴

Table III-2.

Proton NMR Data for Protonated Group VI B
Cyclopentadienyl Metal Tricarbonyl Dimers

Compound	Cp (τ)	Rel. Int.	M-H (τ)	Rel. Int. ^a
$(\text{CpMo(CO)}_3)_2\text{H}^+$	4.28	10	30.99	1 s
$(\text{CpW(CO)}_3)_2\text{H}^+$	4.20	10	34.77	1 t
$(\text{CpMoW(CO)}_6)\text{H}^+$	4.20	--	32.88	t

^as = singlet. t = triplet, see Ref. 5.

Two things may be noted in the above table: (1) the extremely high chemical shift of the metal hydride proton relative to that of the bare proton; and (2) in those systems containing

tungsten, the high field line is a multiplet indicating ^{183}W - ^1H coupling.⁵ The existence of the ^{183}W - ^1H coupling is taken as proof that the proton is bonded directly to the metal.

It was also demonstrated that there was a shift in the ultraviolet absorption maximum to higher wavelengths and a tenfold decrease in the extinction coefficient upon protonation of the neutral complex.⁴ This was only a qualitative trend, as there were exceptions to it as shown in the table below.⁴

Table III-3.

Ultraviolet Data for Protonated Metal Carbonyls

Compound	$\lambda_{\text{max.}}$ (m μ)	ϵ
$\text{Mn}_2(\text{CO})_{10}$	343	2.28×10^4
$\text{Mn}_2(\text{CO})_{10}\text{H}^+$	389	1.14×10^3
$\text{CpFeMn}(\text{CO})_7$	388	1.32×10^4
$\text{CpFeMn}(\text{CO})_7\text{H}^+$	395	2.74×10^3
$(\text{CpFe}(\text{CO})_2)_2$	343	7.62×10^3
$(\text{CpFe}(\text{CO})_2)_2\text{H}^+$	287	3.2×10^3

Wilkinson and coworkers found that in the infrared spectra of these compounds there was a shift to higher frequencies for the carbonyl stretching bands upon protonation of the compounds (Table III-4).⁴

Table III-4.

Carbonyl Stretching Frequencies for
Protonated Metal Carbonyls

Compound	$\nu_{\text{CO}} (\text{cm}^{-1})$
$(\text{CpMo}(\text{CO})_3)_2$	1960, 1916
$(\text{CpMo}(\text{CO})_3)_2\text{H}^+$	2074, 2054, 1988
$(\text{CpW}(\text{CO})_3)_2$	1958, 1928, 1983
$(\text{CpW}(\text{CO})_3)_2\text{H}^+$	2028, 1961

The mononuclear systems include the arene metal carbonyls (e.g., $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$) and the metal carbonyls (e.g., $\text{Fe}(\text{CO})_5$).⁴ It was found that arene systems which have electron releasing substituents on the ring are the strongest bases. By basicity Wilkinson referred to stability toward decomposition and narrowness of the hydridic proton resonance in the nmr spectra. That is, complexes of more basic metals were more stable toward decomposition. In addition, the resonance line for the attached proton was narrower, indicating a lower rate of exchange with free acid. The table below contains the chemical shifts for the protonated arene metal carbonyls arranged in order of decreasing ligand basicity.⁴

An investigation of the $\text{Fe}(\text{CO})_5$ system demonstrated that a ligand that is a stronger σ -donor and weaker

Table III-5.

(M-H) Values for Protonated Arene
Metal Carbonyls

Arene Ligand	$\tau(\text{M-H})$ in $\text{ArCr}(\text{CO})_3\text{H}^+$
Mesitylene	14.27 broad (35 cps)
Toluene	13.98 broad (40 cps)
1,2-diphenylethane	14.06 broad
p-fluorotoluene	13.55
Benzene	13.55 broad (95 cps)

π -acceptor than the carbonyl group increases the basicity of the metal carbonyl complex.⁴ That is, the stability of complexes of the type $\text{LFe}(\text{CO})_4\text{H}^+$ decreased in the order $\text{L} = \text{Ph}_3\text{P} > \text{Ph}_3\text{As} > \text{Ph}_3\text{Sb} > \text{CO}$.

It is evident from the foregoing discussion of metal hydrides and protonated metal complexes that a characteristic of such systems is the existence of an unusually high field resonance line in their proton nmr spectra. It was at first felt that the high chemical shift was chiefly due to anisotropy effects and only slightly dependent on the metal involved in the complex. However, using LCAO-MO theory, Lohr and Lipscomb have calculated the M-H chemical shifts for several transition metal systems, an example of which is the $\text{CpM}(\text{CO})_3^-$ system (where $\text{M} = \text{Cr}, \text{Mo}$ and W).⁶ They obtained very good agreement between experimental and theoretical values. Ninety

percent of the shielding of the hydridic proton was attributed to electron density on the proton and ten percent to anisotropy effects. The different aspects of this question have been dealt with in detail by Ginsberg, who concurs with the results of Lohr and Lipscomb.⁷ A zirconium compound, $\text{Cp}_2\text{ZrHBH}_4$, in which the metal hydride chemical shift is τ 5.47, has been reported.⁸ A possible explanation for this low chemical shift is the fact that zirconium (II) is a d^0 case and thus has no d-electron density to transfer to the proton. This causes the proton attached to the metal to be only slightly shielded; a small chemical shift results. Therefore, based on Lohr and Lipscomb's conclusions, there may be a relationship between metal hydride chemical shift (τ) values and the basicity of the transition metals involved: the higher the chemical shift the greater the basicity of the metal.

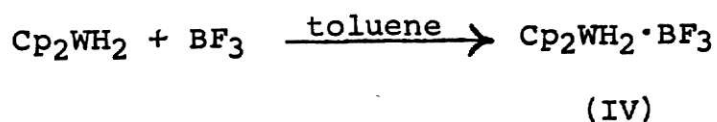
Other characteristics of a metal hydride system are:

- (1) a shift in the ultraviolet absorption maximum to longer wavelengths and a decrease in the extinction coefficient; and
- (2) a shift in the infrared carbonyl stretching bands to higher frequencies.

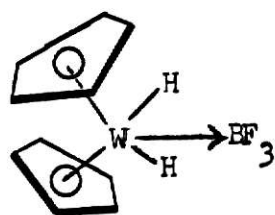
B. Boron Adducts of Organometallic Transition Metal Compounds.

Shriver was the first to isolate boron trihalide adducts of transition metal compounds.⁹ Boron trifluoride and boron

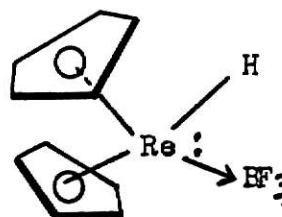
trichloride adducts of Cp_2MH_2 (where $\text{M} = \text{Mo}$ and W) and Cp_2ReH were isolated.^{9,10}



The isolation of borane (BH_3) adducts was not possible, though their existence was expected. Shriver proposed that the boron halides were coordinated to the metal, although only indirect proof was available.⁹



(IV)

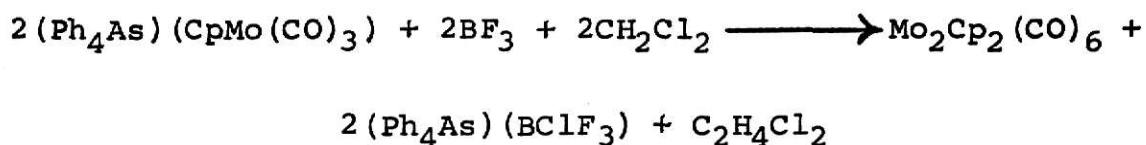


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This proof consisted of the fact that the cyclopentadienyl ring frequencies and metal hydride stretching frequencies were only slightly affected by adduct formation. Thus it seems reasonable that the boron halides are bonded to the metal rather than through the rings or metal hydride protons.

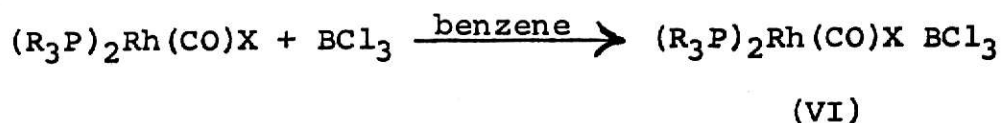
Because Cp_2MH_2 and Cp_2ReH were easily protonated, it was not unreasonable to expect them to form boron halide adducts. Following this same line of reasoning, boron halide adducts of $\text{CpMo}(\text{CO})_3^-$ should also be formed, since $\text{CpMo}(\text{CO})_3\text{H}$ is a

stable molecule. Johnson and Shriver allowed a methylene chloride solution of $\text{CpMo}(\text{CO})_3^-$ to react with BF_3 .¹⁰ However, instead of the boron halide adduct, they isolated the following compounds: $\text{CpMo}(\text{CO})_3\text{H}$ (yellow solid), $(\text{CpMo}(\text{CO})_3)_2$ (red solid) and some grey material assumed to be $(\text{Ph}_4\text{As})(\text{BClF}_3)$. To account for these results, they proposed the following reaction.



Formation of the dimer involves an oxidation which may occur in partially chlorinated solvents but at a much slower rate than observed in the presence of BF_3 . Since solutions of $\text{CpM}(\text{CO})_3\text{H}$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) increase in stability toward decomposition as the atomic weight of the central metal increases, the tungsten analog ($\text{CpW}(\text{CO})_3^-$) was used and methylene chloride was replaced with another solvent, dimethoxyethane. However, the cyclopentadienyl metal tricarbonyl dimer and cyclopentadienyl metal hydride were again isolated.

Nóth and coworkers have also been able to isolate boron halide adducts of transition metals, specifically for the system $(\text{R}_3\text{P})_2\text{Rh}(\text{CO})\text{X}$ where $\text{X} = \text{Cl}, \text{Br}$.¹¹



Upon coordination with the boron halides the carbonyl stretching band was observed to move to a higher frequency ($\Delta\nu_{CO}=20-70\text{ cm}^{-1}$). It will be recalled that a similar shift of the carbonyl bands occurred upon protonation of metal carbonyl complexes. Furthermore, this series of compounds provided proof, for the first time, that the coordinated boron halide was bound directly to the metal. This was demonstrated by the observation that spin-coupling occurred between ^{103}Rh and ^{11}B . Representative data are given below.¹¹

Table III-6.

Boron Trihalide Adducts of Chlorocarbonyl
bis(Triphenylphosphine)rhodium (I)

Compound	$\nu_{CO}(\text{cm}^{-1})$	$^{11}B(\text{ppm})^a$	$J_{Rh-B}(\text{cps})$
$(Ph_3P)_2Rh(CO)Cl$	1968 (s)	--	--
$(Ph_3P)_2Rh(CO)Cl \cdot BCl_3$	1991 (s)	-3.7	146
$(Ph_3P)_2Rh(CO)Cl \cdot BBr_3$	2098 (w)	-4.4	--
	1990 (s)	+1.3	146
	--	+7.3	149
	--	+14.3	146

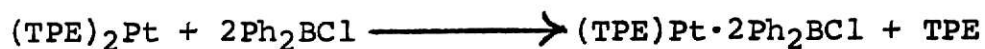
^aChemical shift vs. $Et_2O \cdot BF_3$ as an external standard.

Based on the stability of boron halide adducts, it was suggested that the Lewis acid strength of the boron halides increased from BF_3 to BBr_3 . The reason BF_3 was considered the weakest Lewis acid was because Shriver was unable to isolate a BF_3 adduct of $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$.¹² This order of boron halide Lewis acidity has of course been observed toward other standard Lewis bases.¹³

Boron trifluoride adducts of Vaska's compound, $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ -- a complex analogous with $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ -- were recently reported.¹⁴ When prepared by a rapid tensiometric titration, a 2:1 (BF_3 :complex) adduct resulted. However, when the BF_3 was added slowly, the ratio was greater than 2:1. Similar to the rhodium complex above, coordination with BF_3 moved the carbonyl stretching band to higher frequency. It was also possible to isolate a 1:1 adduct of BF_3 and $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$. This was accomplished by following the reaction via the carbonyl stretching band; the addition of BF_3 was stopped when the carbonyl band for the starting material had disappeared, at which point a ratio of 1:1 existed. However, the 1:1 complex disproportionated into starting material and the 2:1 complex upon removal of the solvent. It was suggested that the most reasonable site for attaching the BF_3 in the 1:1 adduct was on the metal, but no mention was made as to the

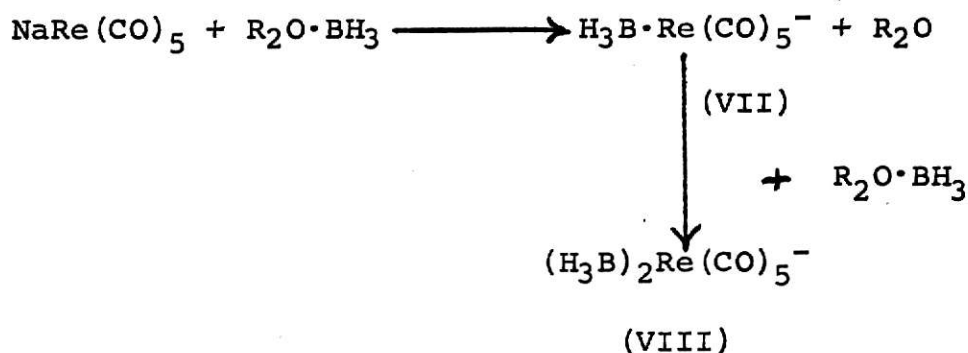
location of the second BF_3 .

It was further found that diphenylboron chloride or bromide would react with bis(tetraphenyldiphosphinoethane)-platinum(0) in boiling hexane according to the equation:¹⁵

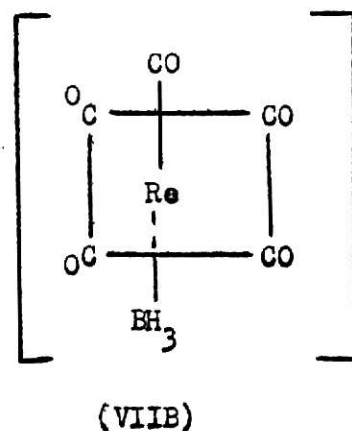
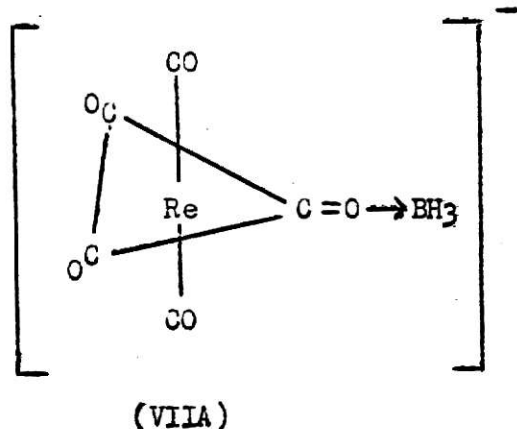


The complex $(\text{TPE})\text{Pt} \cdot 2\text{Ph}_2\text{BCl}$ is thought to be a Ph_2BCl adduct of the compound $(\text{TPE})\text{PtCl}(\text{Ph}_2\text{B})$.

Parshall has been able to isolate 1:1 and 2:1 borane(BH_3) adducts of $\text{Re}(\text{CO})_5^-$ by reacting $\text{Re}(\text{CO})_5^-$ with one or two moles of borane etherate.¹⁶



The possible structures for the 1:1 adduct are shown below:



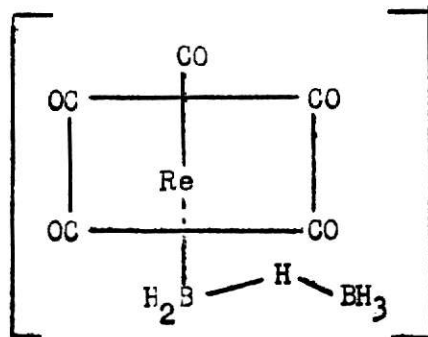
A substantial change in the carbonyl stretching region of the infrared spectrum for VIIA and very little for VIIB relative to the uncomplexed $\text{Re}(\text{CO})_5^-$ was expected. Therefore the infrared data suggested that VIIB is the more reasonable.¹⁶

Table III-7.

BH_3 Complexes of Sodium
Tetracarbonylrhenate (-I)

Compound	$\nu_{\text{CO}}(\text{cm}^{-1})$
$\text{NaRe}(\text{CO})_5$	2085(w), 2070(w), 2058(w), 2036(w), 2014(s), 1972(s), 1922(s), 1887(w).
$\text{Na}(\text{Re}(\text{CO})_5 \cdot \text{BH}_3)$	2060(w), 2002(s), 1974(vs), 1916(s).
$\text{Na}(\text{Re}(\text{CO})_5 \cdot 2\text{BH}_3)$	2005(s), 1950(s), 1901(s), 1863(s).

It is not known with certainty where the second molecule of borane is located in the 2:1 adduct. However, there are two possible sites: (1) on a carbonyl group, as in VIIA or (2) coordinated to the first BH_3 group via a hydrogen bridge as shown below.



(VIII)

It was also possible to prepare a 1:1 BH_3 adduct of $\text{Mn}(\text{CO})_5^-$; however, this adduct was unstable and dissociated if the borane etherate were pumped off. Parshall found that if he substituted triphenylphosphine for one of the carbonyl groups on $\text{Mn}(\text{CO})_5^-$, he could isolate a relatively stable 1:1 adduct. It was felt that, since Ph_3P is a better σ -donor and poorer π -acceptor than the carbonyl group, substitution of Ph_3P for the carbonyl group increased the basicity of the manganese atom and therefore increased the stability of the borane complex. He also attempted to prepare a borane adduct of $\text{Co}(\text{CO})_4^-$ but was unable to do so. Based on the stabilities of the metal carbonyl-borane adducts, he proposed that the Lewis basicity of the metals increased in the following manner: $\text{Re} > \text{Mn} > \text{Co}$.

In the course of their work on the dimerization catalyst $\text{Zn}(\text{Co}(\text{CO})_4)_2$, Schrauzer, et al., found that addition of Lewis acids (e.g., BF_3 , $\text{Et}_2\text{O} \cdot \text{BF}_3$ or AlBr_3) increased the yields but also eventually destroyed the catalyst.¹⁷ They were of the opinion that the Lewis acid functioned in one of two ways:

(1) It causes a more rapid displacement of carbon monoxide from $\text{Zn}(\text{Co}(\text{CO})_4)_2$ to form the reactive intermediate faster, or

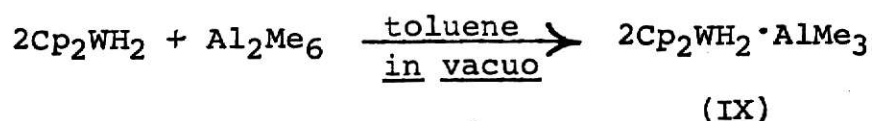
(2) it stabilizes the reactive intermediate once it has formed.

They also found that addition of Lewis bases (e.g., amines or phosphine) decreased the yields or changed the products obtained

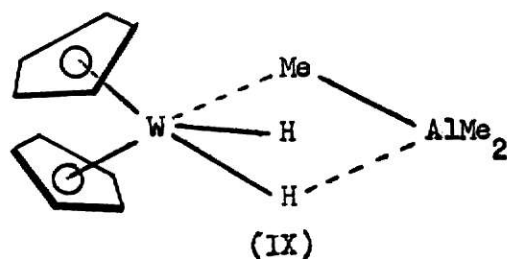
from the reaction. It was felt that the bases were forming adducts with the reactive sites on the catalyst and in this way either stopping the reaction completely or changing the reaction route to yield different products.

C. Alane Adducts of Organometallic Transition Metal Compounds.

Kaes, et al., have isolated AlMe_3 adducts of Cp_2WH_2 and Cp_2ReH by allowing them to react with Al_2Me_6 .¹⁸



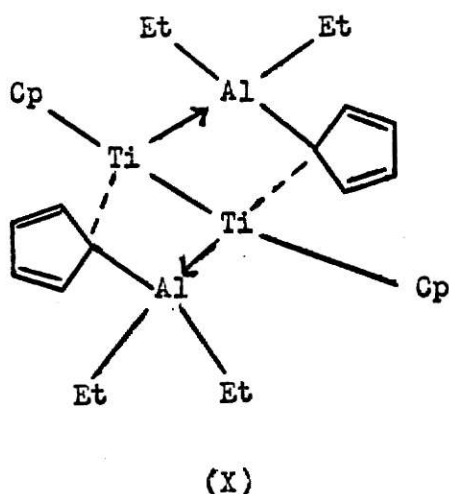
The adducts were found to be 1:1. The only significant change in the infrared spectrum of the adduct from that of the starting material was a small shift to higher frequencies for $\nu_{\text{M-H}}$. Due to this relatively small shift in the M-H stretching frequency, the following bridge structure was ruled out:¹⁸



The proposed structure is therefore the same as that proposed for the BF_3 adducts (IV); that is, AlMe_3 is thought to be coordinated directly to the metal. The isolation of GaMe_3 and BMe_3 adducts was also attempted. However, it was only possible

to find nmr evidence for a GaMe_3 adduct; removal of solvent caused the adduct to dissociate. Apparently no boron analog was formed at all. Therefore, the acceptor power series was found to be $\text{Al} > \text{Ga} > \text{B}$. This series is the same as that found toward donor molecules containing P, As, Sb, S, Se and Te.¹⁹

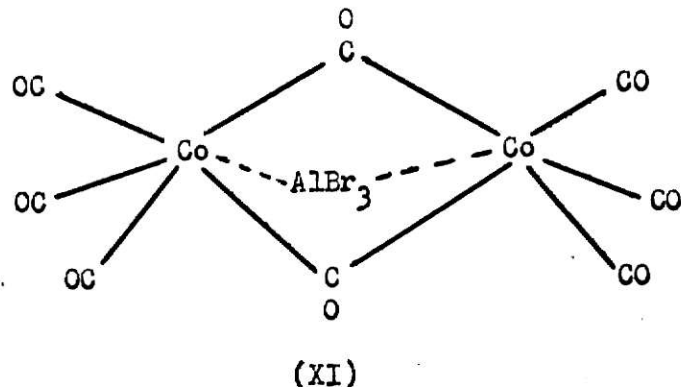
Ziegler-Natta catalysts represent a large number of systems wherein coordinate-covalent metal-metal bonds may be present. An example of a Ziegler-Natta catalyst is $(\text{Cp}_2\text{Ti} \cdot \text{AlEt}_2)_2$, the structure of which is shown below.²⁰



This structure represents only one of the three resonance structures given for this compound. The other two involve covalent Ti-Al bonds rather than coordinate-covalent metal-metal bonds.

Chini and coworkers have prepared the compound $\text{Co}_2(\text{CO})_8 \cdot \text{AlBr}_3$ in which AlBr_3 is apparently acting as a Lewis acid.²¹ Based on the idea of Lewis acid-base interaction, the

following structure was proposed:



They proposed that the AlBr_3 is coordinated to the electron pair of the Co-Co bond. This electron pair is very polarizable and may be more readily available for coordination than lone pairs of electrons at other possible sites. Cotton and Monchamp observed the infrared spectrum of $\text{Co}_2(\text{CO})_8$ and compared it to the AlBr_3 adduct.²² Very little difference between the two spectra was found; therefore, the AlBr_3 group is apparently in a position which has little effect on the carbonyl groups. They therefore concurred with the proposed structure as shown above (XI).

D. Miscellaneous Lewis Acid-Base Adducts of Organometallic Transition Metal Compounds.

Kemmitt's group has been able to prepare complexes of the type $\text{CpM}(\text{CO})_2 \cdot (\text{HgX}_2)_y$ where $\text{M} = \text{Co}, \text{Rh}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $y = 1, 2$.²³ Their contention of acid-base adduct formation was based on the infrared spectra of the complexes and the results

of an x-ray determination of the structure of $\text{CpCo}(\text{CO})_2 \cdot \text{HgCl}_2$. The infrared spectral data for the carbonyl stretching bands and the proton chemical shift data for the Cp rings are given below.²³

Table III-8.

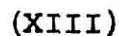
Mercuric Halide Adducts of Cyclopentadienylcobalt
and -rhodium Dicarbonyls

Compound	$\nu_{\text{CO}} (\text{cm}^{-1})$	$^1\text{H}_{\text{nmr}} (\tau)$
$\text{CpCo}(\text{CO})_2$	2017(s), 1949(s).	5.37
$\text{CpCo}(\text{CO})_2 \cdot \text{HgCl}_2$	2074(s), 2042(s).	5.13
$\text{CpCo}(\text{CO})_2 \cdot 2\text{HgCl}_2$	2077(m), 2045(m).	5.13
$\text{CpCo}(\text{CO})_2 \cdot \text{HgBr}_2$	2074(m), 2042(m).	5.27
$\text{CpCo}(\text{CO})_2 \cdot 2\text{HgBr}_2$	2077(m), 2045(m).	5.06
$\text{CpCo}(\text{CO})_2 \cdot \text{HgI}_2$	2065(w).	5.37
$\text{CpRh}(\text{CO})_2$	2041(s), 1947(s).	--
$\text{CpRh}(\text{CO})_2 \cdot \text{HgCl}_2$	2099(s), 2054(s), 2024(m).	--
$\text{CpRh}(\text{CO})_2 \cdot \text{HgBr}_2$	2089(sh), 2040(s), 2002(sh).	--

It was concluded that, since the carbonyl stretching bands moved to higher frequencies, HgX_2 was coordinated to the metal. This was further substantiated by an x-ray structural determination. The following structure was proposed:²⁴



(M' = Cr, Mo, W and M = Mo and W) have been reported recently.²⁵ The metal-metal bond in these molecules was thought to be a coordinate-covalent bond; Cp₂M'H₂ was considered the base and M(CO)₅ the acid. The preparative reaction route is:


$$\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2 + \text{HCl} \longrightarrow \text{IrCl}_2\text{H}(\text{CO})(\text{Ph}_3\text{P})_2.$$

Collman²⁶ and Vaska²⁷ have considered these as reactions of a Lewis base with an acid.

E. Measurements of the Nucleophilicity of Transition Metals in their Organometallic Complexes.

One of the stated objectives of this thesis was the measurement of relative basicities of a series of metals against a standard Lewis acid. Only two such systematic studies have been carried out previously.

Dessy has measured the nucleophilicities of the $\text{CpM}(\text{CO})_3^-$ and $\text{M}(\text{CO})_5^-$ systems.²⁸ The anions of these two systems were generated electrochemically and their nucleophilicities related to the rates of reaction with alkyl halides. Nucleophilicity in the Group VI and Group VII transition metals increases with increasing atomic weight; the opposite trend is true for the Group VIII transition metals. Some data for the two systems are given below.²⁸

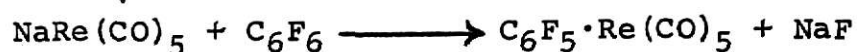
Table III-9.

Nucleophilicities of Some Metal Carbonyl Anions

M:^-	k_2^{a}	$k_2^{\text{'a}}$	M:^-	k_2^{a}	$k_2^{\text{'a}}$
$\text{CpCr}(\text{CO})_3^-$	(5)	500	$\text{Re}(\text{CO})_5^-$	250	2.5×10^4
$\text{CpMo}(\text{CO})_3^-$	0.67	67	$\text{Mn}(\text{CO})_5^-$	0.77	77
$\text{CpW}(\text{CO})_3^-$	0.04	4	$\text{Co}(\text{CO})_4^-$	0.01	1

^aIn this table k_2 represents the measured rate constant for the

F. G. A. Stone, et al., have measured the relative nucleophilicities of transition metal complexes by reacting the different transition metal carbonyl anions with perfluoroalkenes.²⁹



They proposed a series of relative base strengths which demonstrated trends similar to those proposed by Dessy (vide supra).

reaction: $\text{M:}^- + \text{RI} \longrightarrow \text{M-R} + \text{I}^-$, while k_2' is the normalized rate constant obtained by setting k_2 for Co(CO)_4^- equal to 1.

PART IV
EXPERIMENTAL

A. Materials and General Procedures.

1. Reagents. The following reagents were used without further purification:

<u>Reagent</u>	<u>Supplier</u>
$\text{Cr}(\text{CO})_6$	Strem Chemicals, Inc.
$\text{Mo}(\text{CO})_6$	K and K Laboratories, Inc.
$\text{W}(\text{CO})_6$	Pressure Chemicals Co.
Ph_3P	Alfa Inorganics, Inc.
dicyclopentadiene	Eastman Organic Chemicals
Br_2	Baker and Adamson
CF_3COOH	Eastman Organic Chemicals
	Aldrich Chemical Co., Inc.

Methylene chloride (Fisher, Certified Reagent) was purified according to the procedure given by Vogel.³⁰ Diglyme (diethylene glycol dimethyl ether, Ansul Co.) was purified by refluxing over sodium metal for several days and then fractionating and collecting the fraction boiling at 160°C . Another method that gave sufficiently pure solvent consisted of passing diglyme

through a 15 cm column of activated alumina. Acetonitrile (Fisher, Reagent grade) was dried by storing over molecular sieves (Linde 4A, supplied by W. H. Curtin and Co.).

The boron halides (BF_3 and BCl_3) were supplied by Matheson and were purified by trap-to-trap distillation on a high vacuum line: BF_3 , $\text{vp}=298$ torr (lit.=301.0 torr³¹) at -112°C ; BCl_3 , $\text{vp}=476.0$ torr (lit.=476.0 torr³¹) at 0°C .

2. Handling of Air Sensitive Materials. Air sensitive volatile materials were handled in a preparative, high vacuum line equipped with mercury float valves.³¹ Kel-F grease was used on all joints and stopcocks through which boron halides passed. Solids which were air-sensitive were handled in a Vac-Atmosphere HE-43 drybox; the drybox was filled with nitrogen which was circulated through a series of drying and de-oxygenating columns such as those described by Brown.³² Preparations of metal carbonyl complexes were always done under a nitrogen atmosphere.

3. Analysis. Analysis was done by Galbraith Laboratories, Inc. and Schwarzkopf Laboratories, Inc.

4. Spectroscopic Methods. The visible and ultraviolet spectra were run on a Cary 14 recording spectrophotometer. The infrared spectra were run in Nujol mulls on a Perkin-Elmer 337; KBr plates were used throughout. The proton nmr spectra were taken

on a Varian A60 and the ^{11}B nmr spectra on a Varian HA-100 spectrometer.

B. Preparation of Starting Materials.

1. Triphenylphosphoniumcyclopentadienyliid. The compound $(\text{C}_6\text{H}_5)_3\text{PC}_5\text{H}_4$ (Cpyliid) was prepared by the method of Ramirez and Levy.³³ As cyclopentadiene was needed for this preparation, it was necessary to "crack" dicyclopentadiene. The apparatus used for this procedure was an ordinary distillation set-up in which the still-pot was a 100 ml three neck flask equipped with a nitrogen inlet and a Claisen head. Fifty to 60 ml of paraffin oil was placed in this flask and 20 ml of the dimer was added. The mixture was heated under nitrogen until about 11 ml of monomer was distilled over into a 500 ml round bottom flask containing 10 ml of chloroform; the receiving flask was maintained at -20°C by a trichloroethylene-dry ice bath. After collecting the cyclopentadiene the receiving flask was removed and a pressure-equalizing addition funnel attached to the flask. Dry nitrogen was continually passed through the addition funnel during this and subsequent operations. A Br_2 solution (10 ml chloroform and 7.5 ml Br_2) was added dropwise from the addition funnel to the magnetically stirred monomer solution. (At this point the solution should be colorless unless too much Br_2 has been added, in which case the solution is orange.) A

solution of triphenylphosphine (72.1 gm Ph_3P and 220 ml chloroform) was then added slowly, with stirring, to the reaction mixture; the temperature of the reaction mixture was maintained at -40 to -50°C . After the addition of the triphenylphosphine solution, the reaction mixture was slowly warmed to room temperature. After refluxing for six hours, the yellow-orange solution was allowed to stand at room temperature overnight. The reaction mixture was then placed in a separatory funnel and shaken with 302 ml of 1.3 N aqueous sodium hydroxide (15.7 gm. NaOH in 302 ml of H_2O) in 100 ml. aliquots, during which the color changed from orange to magenta. (It is essential for good yields that the mixture be shaken thoroughly.) After separating the aqueous layer, the magenta solution was washed several times with water to remove excess base. The washed chloroform solution was then allowed to stand over Na_2SO_4 for several hours. After filtering off the Na_2SO_4 , the solution was placed in a rotating evaporator and the CHCl_3 was removed.

The sticky, magenta residue was next stirred with small portions of methanol; the methanol dissolved the reaction by-product and left insoluble Cpylid. The crude product, a pink-yellow solid, was collected, washed with methanol and dried.

Recrystallization of the crude product was accomplished by dissolving it in a minimum amount of hot ethanol/ CHCl_3 mixture.

If this solution was filtered while hot, Cpylid crystallized out as golden yellow needles. (mp = 238-41° C) (Yield = 30-50%; 12-20 gm).

Anal. Calcd. for $C_{23}H_{19}P$: C, 85.6; H, 5.9; P, 9.5.

Found: C, 84.75; H, 5.76; P, 9.70.

2. Triphenylphosphoniumcyclopentadienyldichromium Tricarbonyl.

The CpylidCr(CO)₃ was prepared by allowing Cpylid to react under N₂ with Cr(CO)₆ in 100 ml of refluxing diglyme. As Cr(CO)₆ sublimed out of the refluxing solution, it was occasionally returned to the reaction flask by washing it from the condenser walls with diglyme. After the reaction had run for about two hours, the solution had turned red; the mixture was then cooled to room temperature and filtered. The residue was discarded and water was added to the filtrate in small increments until the crude yellow product was completely precipitated. Generally 2 to 3 times as much water as diglyme was used. The crude product was re-crystallized from CHCl₃/petroleum ether to give bright yellow crystals. (mp = 256-258° C dec., sealed tube).

Anal. Calcd. for $C_{26}H_{19}CrO_3P$: C, 67.52; H, 4.14; P, 6.69.

Found: C, 67.53; H, 4.24; P, 6.88.

A sample preparation consisted of reacting 0.6296 gm (1.94 mmol) of Cpylid with 1.7755 gm (5 mmol) of Cr(CO)₆ to yield 0.6594 gm

(1.42 mmoles, 73% yield) of CpylidCr(CO)_3 .

3. Triphenylphosphoniumcyclopentadienyldmolybdenum Tricarbonyl.
The CpylidMo(CO)_3 was prepared by allowing Cpylid to react under N_2 with Mo(CO)_6 in 60 ml of refluxing diglyme. The Mo(CO)_6 which had sublimed into the condenser was occasionally returned to the reaction flask by shaking the reaction mixture. After refluxing for two hours the reaction mixture (yellow-black solution) was cooled to room temperature and filtered, the residue being discarded. Approximately 20 ml of water was added to the yellow-orange filtrate and the mixture allowed to stand 10 to 15 minutes and then filtered. The yellow residue was dissolved in the minimum amount of CHCl_3 (approximately 25 ml) and filtered. Petroleum ether (approximately 25 ml) was added to the filtrate and the mixture was allowed to stand in running water for 10 to 15 minutes before filtering off recrystallized product. (mp = 274-276° C dec., sealed tube.)

Anal. Calcd. for $\text{C}_{26}\text{H}_{19}\text{MoO}_3\text{P}$: C, 61.67; H, 3.78; P, 6.12.

Found: C, 61.50; H, 3.69; P, 6.24.

A sample preparation consisted of reacting 0.6580 gm (2.08 mmoles) of Cpylid with 1.5929 gm (6.05 mmoles) of Mo(CO)_6 to yield 0.6439 gm (1.27 mmoles, 61% yield) of CpylidMo(CO)_3 .

4. Triphenylphosphoniumcyclopentadienylditungsten Tricarbonyl.

An attempt was made to prepare the CpylidW(CO)_3 by the same procedure used for the Cr and Mo analogs; however, little or no product could be isolated.

However, King and coworkers found that $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$ was a very reactive compound and could be used as a starting material in the preparation of substituted W(CO)_3 compounds.³⁴ Hence, it was decided to react Cpylid with $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$ in an attempt to prepare CpylidW(CO)_3 .

Tris(acetonitrile)tungsten tricarbonyl was prepared by allowing W(CO)_6 in acetonitrile to reflux under N_2 for 40 hours.³⁴ Solvent was then removed by distilling it into a vacuum line. The green-yellow product, crude $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$, was used without further purification.

To the crude $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$ was added Cpylid, diglyme and a stirring bar; the mixture was heated under N_2 to 110°C with stirring for three hours. The reaction mixture was cooled to room temperature and the solvent removed on the vacuum line. Chloroform was added to the yellow-black residue, and this solution was passed through a deactivated alumina column (9 cm of alumina) maintained under a N_2 atmosphere. The first fraction off the column was bright yellow when collected but turned slightly orange on standing. A thick black residue remained on

the alumina column. The solvent was removed from the first fraction to yield crude yellow-orange CpylidW(CO)_3 . The solid was dissolved in the minimum amount of CHCl_3 , the solution was filtered and petroleum ether added to the filtrate until a yellow precipitate began to form. The mixture was allowed to stand for 10 to 15 minutes, filtered, and the bright yellow precipitate dried (mp = $266-68^\circ \text{C}$ dec., sealed tube).

Anal. Calcd. for $\text{C}_{26}\text{H}_{19}\text{O}_3\text{PW}$: C, 52.58; H, 3.22; P, 5.21.

Found: C, 49.74; H, 3.12; P, 5.11.

C, 49.87; H, 3.05.

C, 49.40; H, 2.82; P, 5.39.

C, 49.57; H, 2.85.

It was felt that the poor results for the carbon analyses were probably due to incomplete combustion of the samples and possible formation of metal carbides during analysis.

A sample preparation consisted of reacting excess $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$ with 0.6272 gm (2.0 mmoles) of Cpylid yielding, after work up, 0.8289 gm (1.44 mmoles, 73% yield) of CpylidW(CO)_3 .

C. Spectral Properties of the Starting Materials.

1. Infrared Spectra. See Table IV-1 and Spectra IV-1,2,3,4.
2. Ultraviolet and Visible Spectra.

Table IV-1.

Infrared Spectral Data for
Triphenylphosphoniumcyclopentadienylid Complexes

Compound	ν_{CO}	Other Bands
Cpylid		3050(m), 1970(w), 1900(w), 1820(w), 1660(w), 1580(w), 1430(s), 1375(m), 1310(w), 1225(s), 1210(s), 1188(m), 1164(m), 1109(vs), 1070(w), 1050(s), 1030(s), 999(m), 900(w), 960(w), 860(m), 820(w), 760(sh), 746(s), 720(vs), 690(vs), 621(m), 614(m), 565(vs), 529(vs), 510(vs), 469(w), 449(w), 439(w).
CpylidCr(CO) ₃	1900(s), 1805(vs)	1190(s), 1114(vs), 1030(mw), 995(m), 800(m), 750(m), 723(ms), 696(s), 687(s), 656(s), 622(m), 575(m-sh), 552(s), 530(m), 518(w), 509(w).
CpylidMo(CO) ₃	1904(s), 1808(vs)	1187(s), 1106(s), 1021(m), 994(m), 787(m), 747(s), 718(s), 690(s), 632(mw), 620(m), 604(m), 560(s), 526(s), 511(s), 502(m).
CpylidW(CO) ₃	1806(vs), 1916(vs)	1214(sh), 1210(vs), 1172(sh), 1114(vs), 1082(sh), 1022(s), 992(s), 780(vs), 728(vs), 700(vs), 670(vs), 584(s), 568(sh), 530(vs), 496(s), 476(vs).
CpylidMo(CO) ₃ ·BF ₃ ^a	2016(w), 1993(sh), 1957(s), 1935(s), 1896(sh)	1186(s), 1116(vs broad), 996(m), 810(m), 732(m), 704(s), 665(s), 548(sh), 524(s), 500(s), 492(s), 474(sh), 462(m), 428(m), 400(m).

^aRecrystallized complex.

Table IV-1. (Continued)

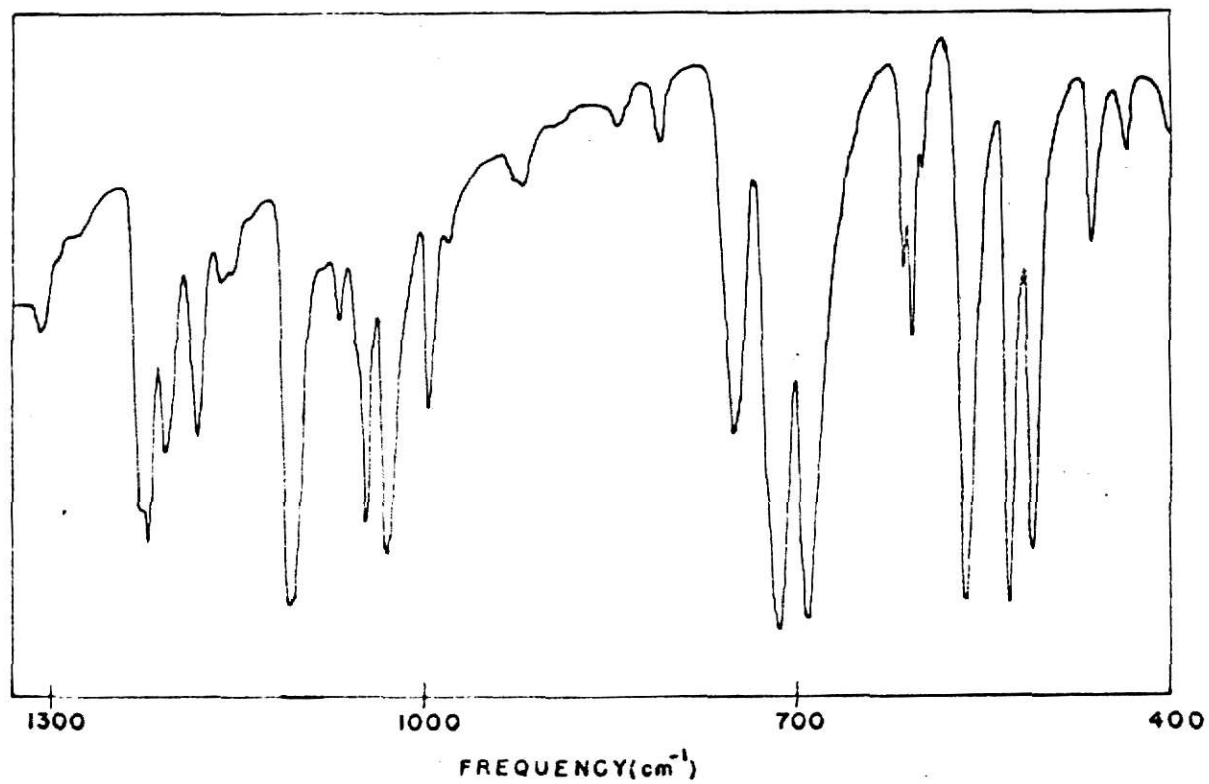
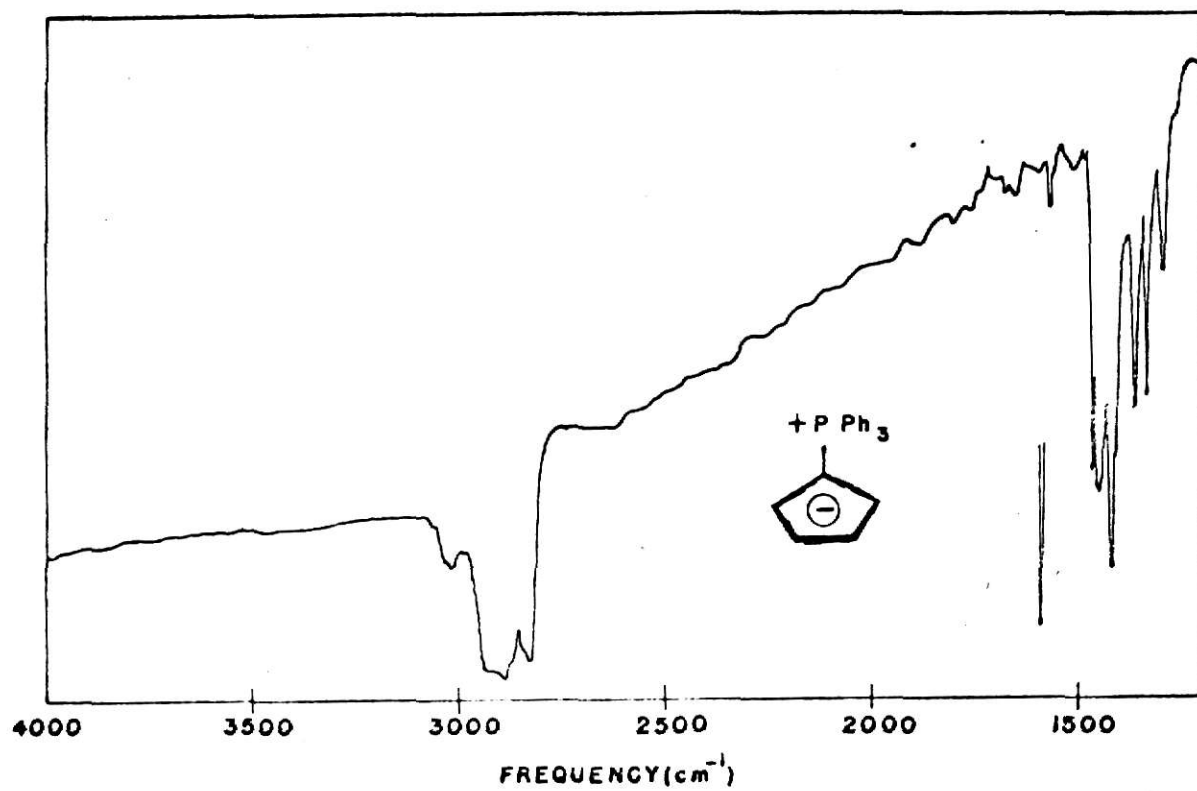
Compound	ν_{CO}	Other Bands
$\text{CpylidW}(\text{CO})_3\text{BF}_3^{\text{a}}$	1941(vs), 1996(vs), 2001(sh), 2036(s)	1216(sh), 1200(m), 1184(m), 1114(s), 1058(vs broad), 990(m), 822(m), 734(s), 704(s), 668(s), 530(m), 524(sh), 512(s), 494(s), 474(s), 485(m), 426(sh), 418(s), 408(s).
$\text{CpylidCr}(\text{CO})_3\text{BF}_3^{\text{b}}$	1811(s), 1956(vs broad), 2041(vs)	1224(m), 1196(s), 1172(sh), 1112(vs), 1068(m), 1040(m), 992(s), 834(s broad), 730(s), 702(s), 666(vs, broad), 632(s), 582(s), 522(vs), 492(vs), 478(s), 454(w).
$\text{CpylidMo}(\text{CO})_3\text{BCl}_3^{\text{b}}$	1896(broad), 2051(vs), 2081(s)	1176(broad), 1112(broad), 990(vs), 814(broad), 722(sh), 702(s), 662(broad), 632(sh), 522(s), 492(s), 478(s), 444(m).

^aRecrystallized complex.^bCrude reaction product.

Explanation of Spectrum IV-1

Infrared Spectrum of Triphenylphosphoniumcyclopentadienyliid.

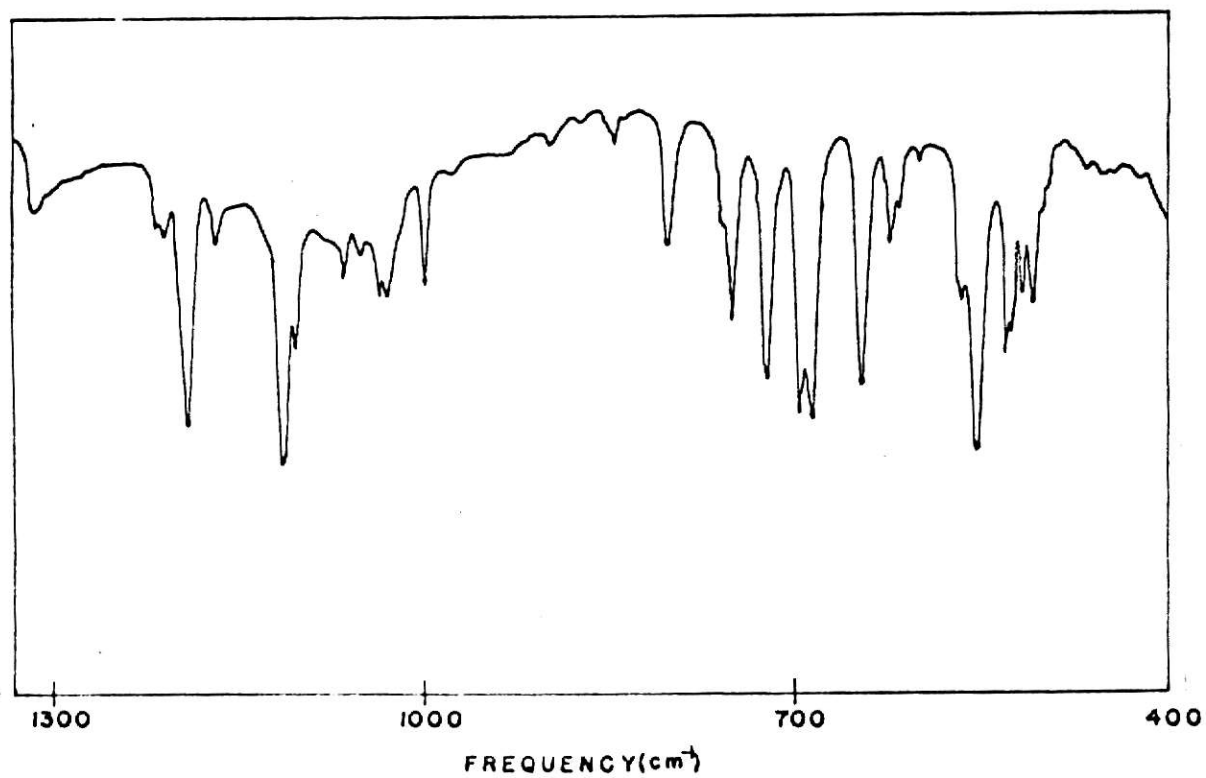
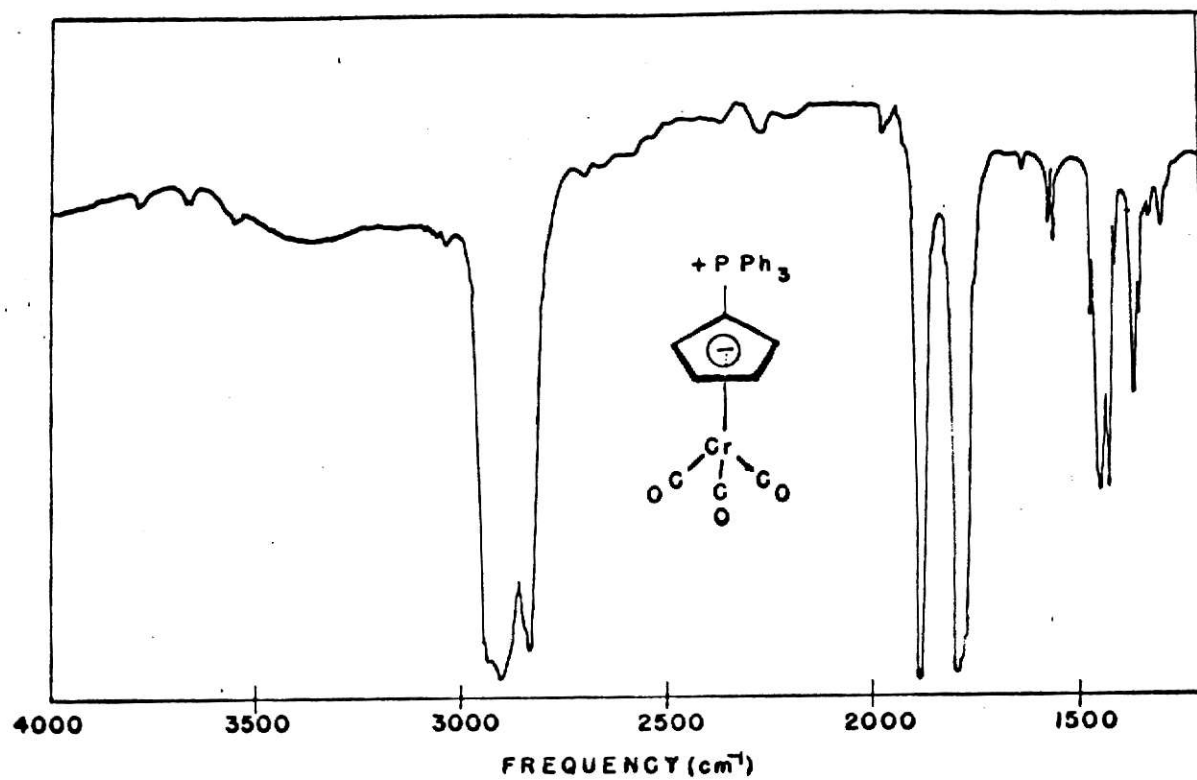
Spectrum was taken as a Nujol mull using KBr plates.



Explanation of Spectrum IV-2

Infrared Spectrum of Triphenylphosphoniumcyclo-
pentadienyldchromium Tricarbonyl.

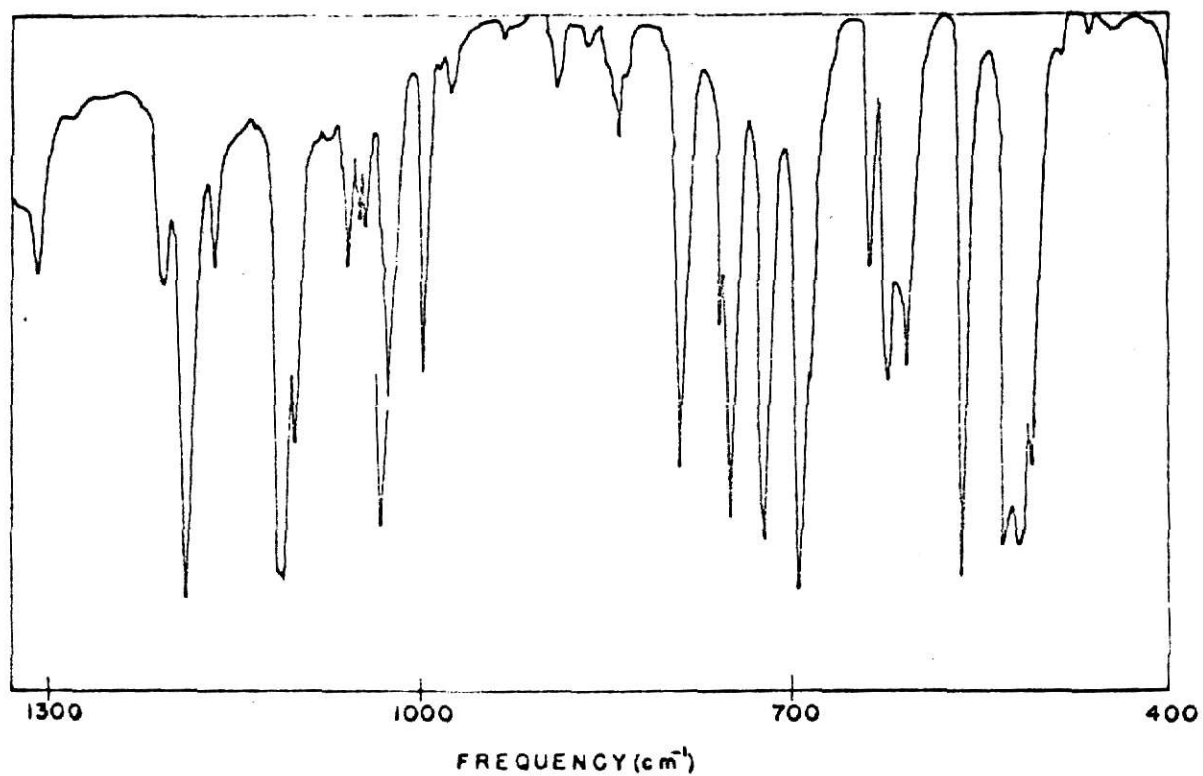
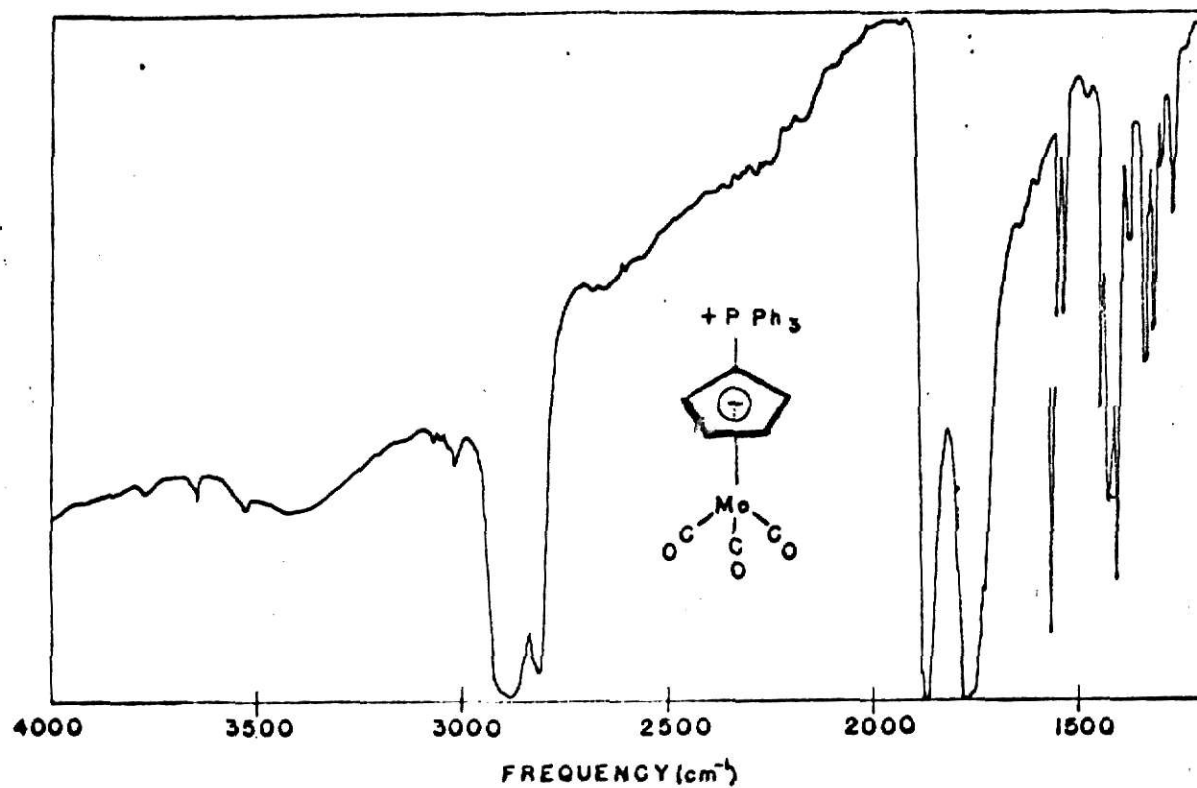
Spectrum was taken as a Nujol mull using KBr plates.



Explanation of Spectrum IV-3

Infrared Spectrum of Triphenylphosphoniumcyclo-
pentadienyldimolybdenum Tricarbonyl.

Spectrum was taken as a Nujol mull using KBr plates.



Explanation of Spectrum IV-4

Infrared Spectrum of Triphenylphosphoniumcyclo-
pentadienyliidtungsten Tricarbonyl.

Spectrum taken as a Nujol mull using KBr plates.

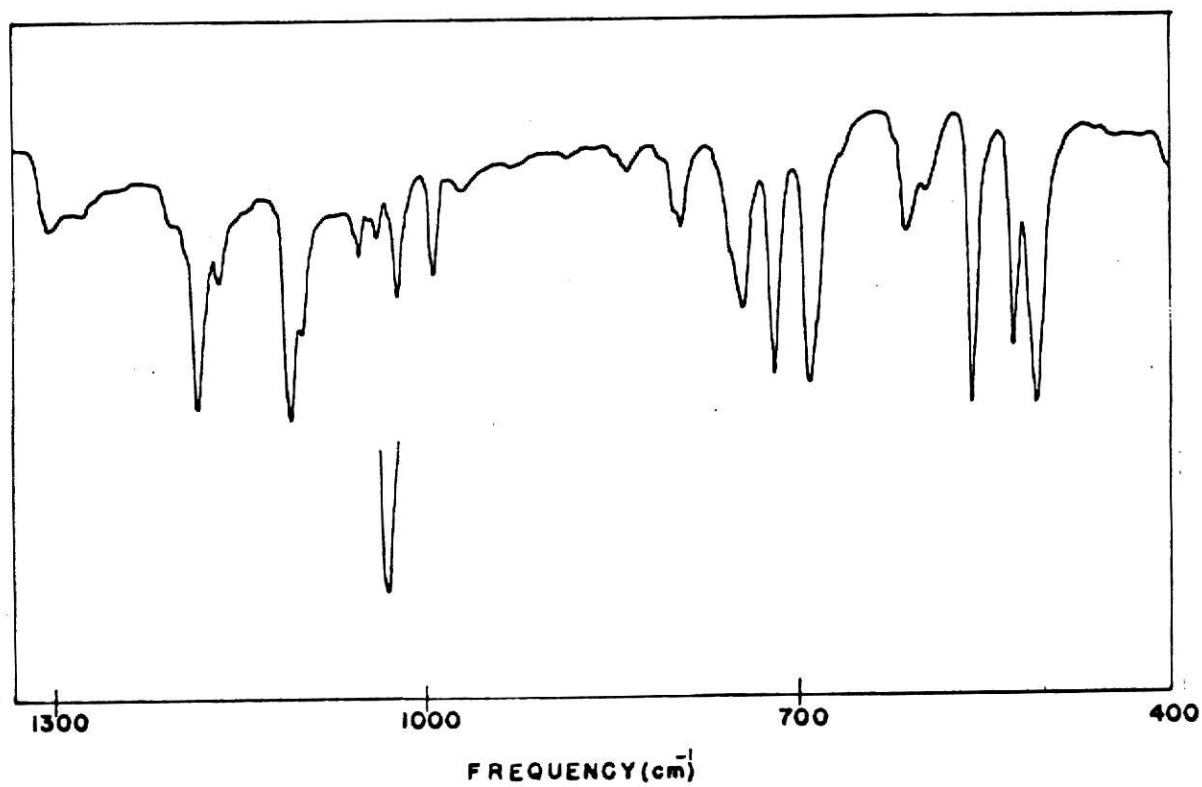
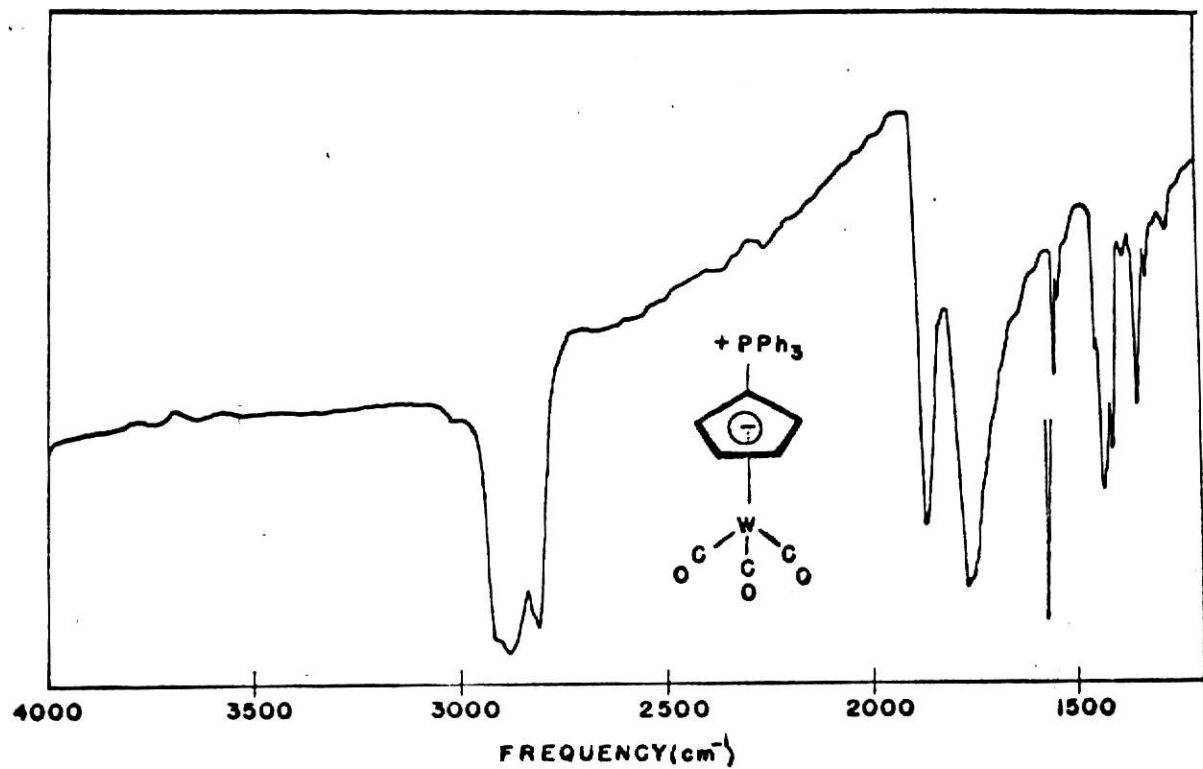


Table IV-2.

Ultraviolet and Visible Spectral Data
for Starting Materials

Compound	Visible	Ultraviolet $\lambda_{\text{max}}(\epsilon)$
Cpylid ^a	N.A.	222 (38,200), 250 (21,600), 295 (5900).
CpylidMo(CO) ₃ ^b	N.A.	275 (7865), 267+ (8870), 259+ (8950).
CpylidW(CO) ₃ ^b	--	274 (10,490), 267 (11,220), 260 (10,800).

^ain CH₃CN solution; see Ref. 33.

^bin CH₂Cl₂ solution.

3. Nmr Data.

Table IV-3.

Nmr Spectral Data for Starting Materials

Compound	¹ H _{C₅H₄} (τ) ^a
Cpylid ^b	3.64
CpylidCr(CO) ₃	5.08, 5.35
CpylidMo(CO) ₃	4.51, 4.77
CpylidW(CO) ₃	4.51, 4.78

^aAll spectra obtained in CDCl₃.

^bRef. 35.

D. Protonation of Triphenylphosphoniumcyclopentadienylidmetal Tricarbonyls.

The protonated Cpylidmetal tricarbonyls were prepared by placing CpylidM(CO)₃ in an nmr tube and distilling CF₃COOH into the tube from the vacuum line. Tetramethylsilane was also distilled in before sealing off the tube. The CF₃COOH solutions of CpylidM(CO)₃ were highly colored: Cr (yellow), Mo (dark red), and W (blue).

1. Ultraviolet and Visible Spectral Data for Cpylid H⁺ and CpylidM(CO)₃H⁺.

Table IV-4.

Ultraviolet and Visible Spectral Data for
Protonated Triphenylphosphoniumcyclopentadienylid
Complexes

Compound	Visible	Ultraviolet $\lambda_{m\mu}(\epsilon)$
Cpylid H ⁺ ^a	--	226(25,200), 262(4,000), 268(4700), 271(3900).
CpylidMo(CO) ₃ H ⁺ ^b	N.A.	274.0, 267.2, 260.0.
CpylidW(CO) ₃ H ⁺ ^b	N.A.	_____

^aThis spectrum was run in EtOH.

^bThese spectra were run in CF₃COOH.

2. Proton Nmr Spectral Data for CpylidM(CO)₃H⁺.

Table IV-5.

Proton Nmr Spectral Data for Protonated
Triphenylphosphoniumcyclopentadienyld Complexes

Compound	C ₅ H ₄ (τ)	Rel. Int.	M-H(τ)	Rel. Int.
CpylidCr(CO) ₃ H ⁺	4.58, 4.80	(broad)	15.09	(broad)
CpylidMo(CO) ₃ H ⁺	4.09, 4.31	3.48	15.34	1.3
CpylidW(CO) ₃ H ⁺	4.00, 4.27	3.28	17.15	0.93

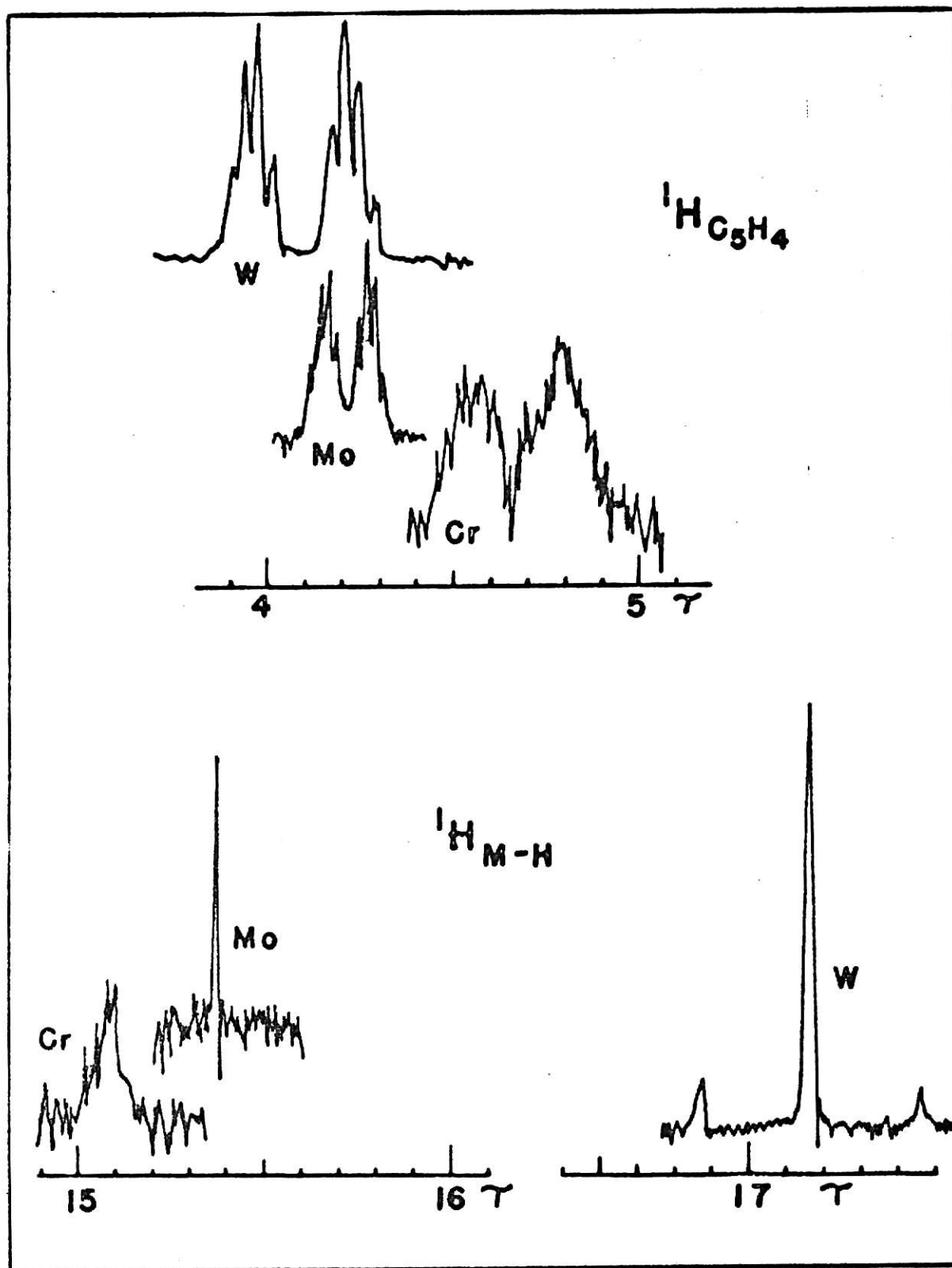
Apparently the broad resonance line for M-H in CpylidCr(CO)₃H⁺ is due to a paramagnetic decomposition product formed by the Cr analog upon dissolving in CF₃COOH. It is felt that this is the case, because it was not possible to obtain good resolution for the internal standard, TMS. (See Spectrum IV-5.)

E. Preparation of Boron Trihalide Adducts by Tensiometric Titration.

The boron trihalide adducts were prepared by allowing approximately one mmole of triphenylphosphoniumcyclopentadienyldmetal tricarbonyl to react with the boron trihalide in methylene chloride during a tensiometric titration. The procedure followed was to place the triphenylphosphoniumcyclopentadienyldmetal tricarbonyl and a stirring bar in a 100 ml round bottom flask, connect this vessel to a high vacuum line

Explanation of Spectrum IV-5

Nmr Spectrum of Protonated Triphenylphosphoniumcyclopentadienylidmetal Tricarbonyl Hydrides
 $\text{CpylidM(CO)}_3\text{H}^+$ (where M = Cr, Mo, or W).



and distill in the solvent. The solvent and metal carbonyl were allowed to warm to room temperature, stirred, and then cooled to various selected temperatures; the pressure was measured at each temperature. Next, successive small increments (0.1 to 0.3 mmoles) of boron trihalide were added to the reaction vessel, and the pressure was measured after each increment. This data was plotted as pressure versus composition graphs. (see Figures IV-1,2.) Table IV-6 gives the results of the tensiometric titrations.

F. Reaction of the Solid Residue from the CpylidM(CO)₃-BF₃

Reaction with Trimethylamine.

The solid residue was obtained by pumping off, at 0° C, all the volatile material from the CpylidM(CO)₃-BF₃ reaction. Fresh CH₂Cl₂ was added to this residue; Me₃N was then titrated into the mixture following the tensiometric titration method. The titration curves indicated a slow and incomplete reaction.

After the titration with Me₃N, all the volatiles were again removed at 0° C. The infrared spectrum of the residue indicated that CpylidMo(CO)₃ was present in the residue.

It was further discovered that if a CH₂Cl₂ solution of the residue from the sublimation was passed through an alumina column, under N₂, only CpylidMo(CO)₃ was collected from the column.

Table IV-6.

Results of the Tensiometric Titration of
Triphenylphosponiumcyclopentadienylidmetal
Tricarbonyl (where the metal is Cr, Mo or W) with
Boron Trihalides^a

Sample Size (mmoles)	CpylidM(CO) ₃ /BF ₃ /CH ₂ Cl ₂		
	Temperature		
	0°	-45°	-78°
<u>Cr</u>			
1.219	0.2	--	1.19
0.598	0.2	--	1.2
<u>Mo</u>			
1.27	--	--	1.00
0.902	--	--	0.97
1.064	0.33	0.4	0.99
0.7898	0.54	--	0.98
0.7755	0.33	--	--
0.7469 ^b	--	--	0.80
1.093	--	--	1.2
0.189	0.45	--	1.04
0.7412	0.4	--	1.05
<u>W</u>			
0.265	1.00	1.00	1.00
0.318	1.00	1.95	1.95
1.012	0.6	1.25	1.45
0.8239	0.55	--	1.65

Sample Size (mmoles)	CpylidM(CO) ₃ /BCl ₃ /CH ₂ Cl ₂		
	Temperature		
	0°	-45°	-78°
<u>Cr</u>			
0.9181	0.7	--	--
0.5646	0.99	--	--
<u>Mo</u>			
0.4623	0.95	--	--
0.6930	1.14	--	--

^aThe data are in the form of F values, where F = mmoles of BX₃/mmoles CpylidM(CO)₃ at the point at which the curve begins to show a positive deviation from the vapor pressure of the pure solvent.

^bToluene used as solvent for this run.

Explanation of Figure IV-1
Tensiometric Titrations of Triphenylphosphoniumcyclo-
pentadienylidmetal Tricarbonyls with
Boron Trifluoride at 0° C.

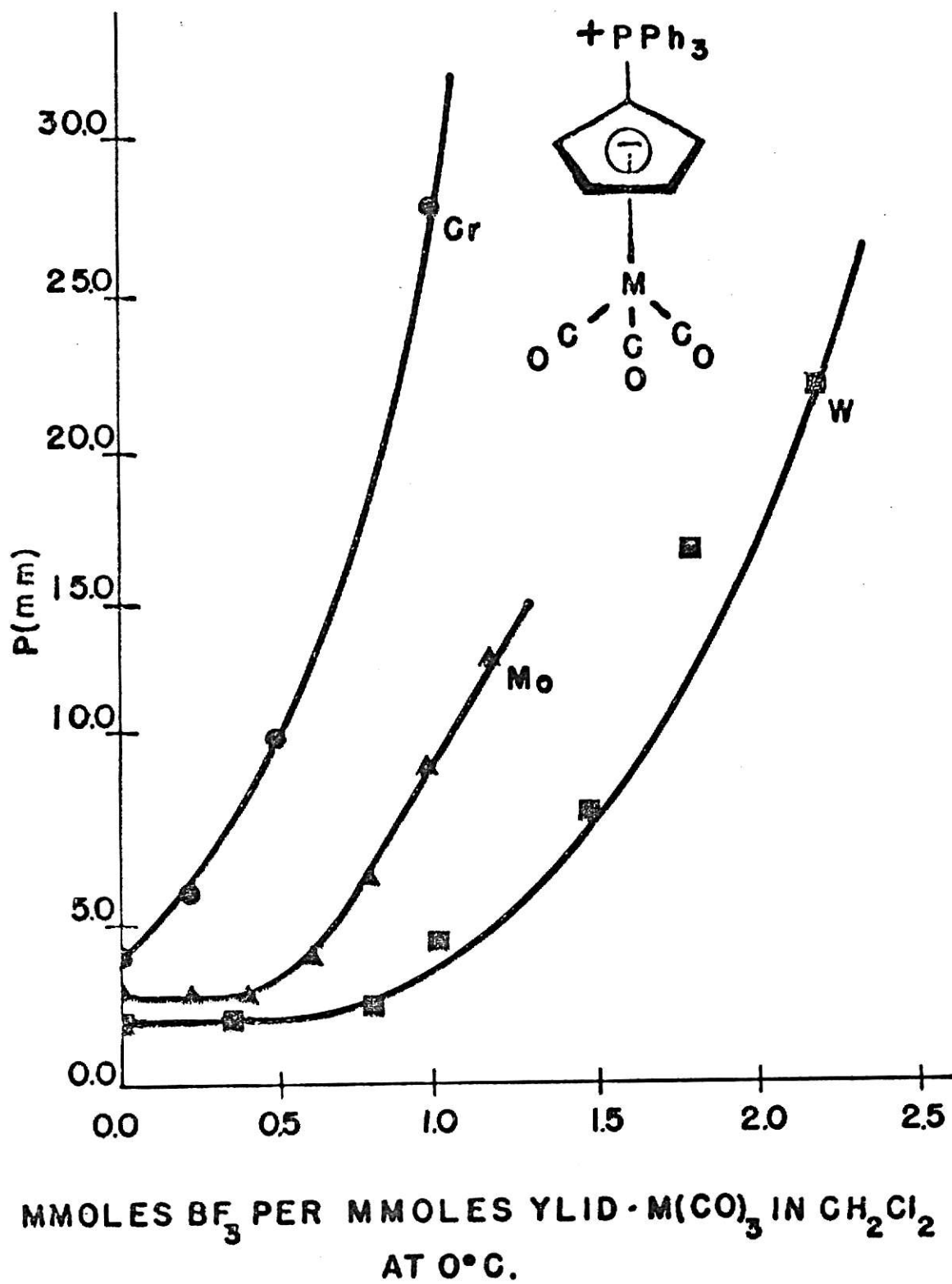
The pressure data for these curves were modified for clarity
by the following equations:

$$\text{Cr} \quad P(\text{mm}) = (x - 140.0)$$

$$\text{Mo} \quad P(\text{mm}) = (x - 141.0)$$

$$\text{W} \quad P(\text{mm}) = (x - 142.0)$$

where x = experimentally measured pressure.



Explanation of Figure IV-2

Tensiometric Titrations of Triphenylphosphoniumcyclo-
pentadienylidmetal Tricarbonyls with
Boron Trifluoride at -78° C.

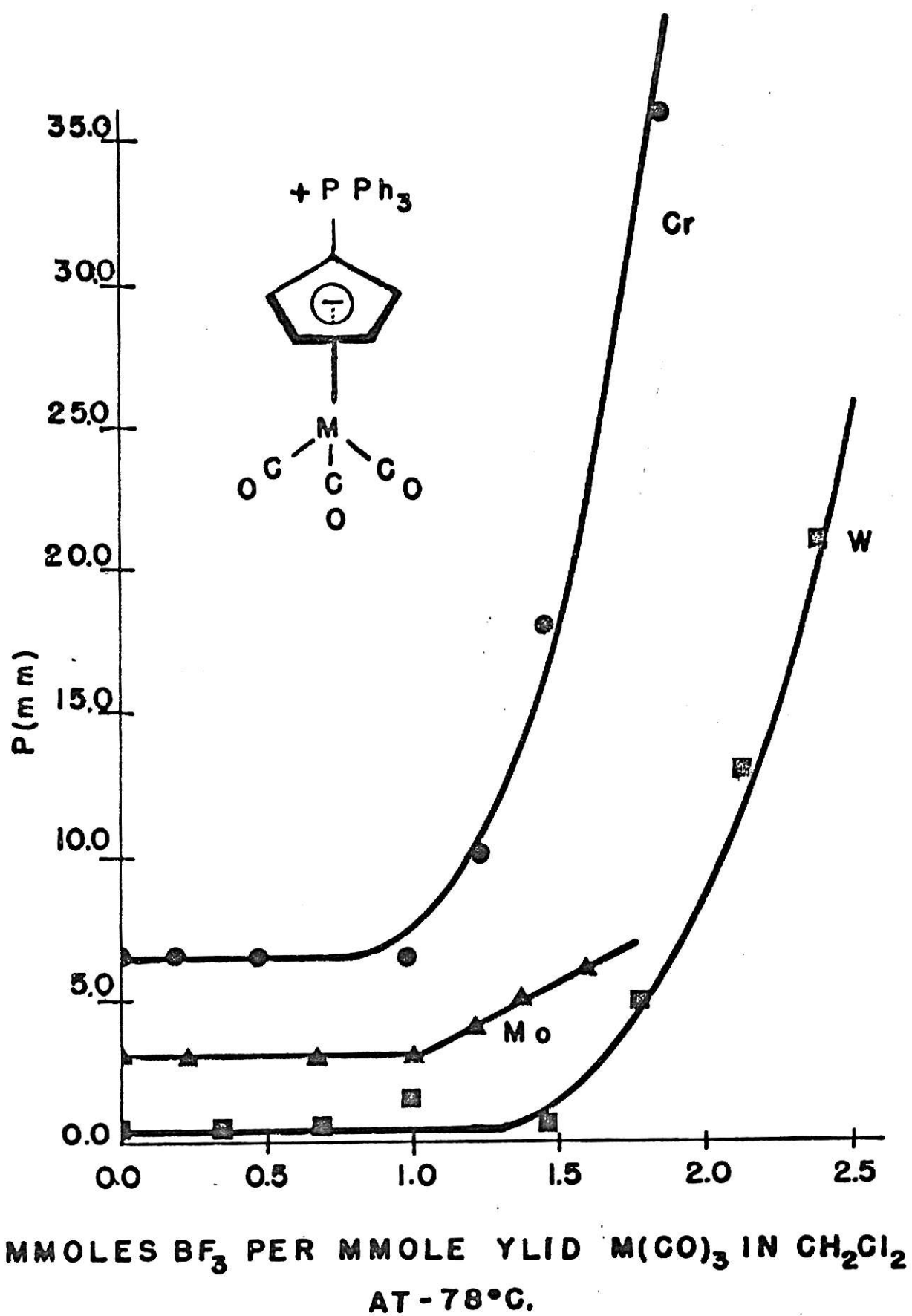
The pressure data for these curves were modified for clarity
by the following equations:

$$\text{Cr} \quad P(\text{mm}) = (x + 5)$$

$$\text{Mo} \quad P(\text{mm}) = (x + 2)$$

$$\text{W} \quad P(\text{mm}) = (x)$$

where x = experimentally measured pressure.



G. Isolation of Boron Trihalide Complexes.

The boron trifluoride adducts of CpylidMo(CO)_3 and CpylidW(CO)_3 were recrystallized from CH_2Cl_2 /toluene in the drybox to yield the 1:1 complex. These adducts were pink in color and air stable. However, the boron trichloride adducts were unstable to recrystallization and no products could be isolated.

Anal. Calcd. for $\text{C}_{26}\text{H}_{19}\text{BF}_3\text{MoO}_3\text{P}$: C, 54.38; H, 3.33; P, 5.37.

Found: C, 54.11; H, 3.13; P, 5.21. (mp = 173°C dec.)

Calcd. for $\text{C}_{26}\text{H}_{19}\text{BF}_3\text{O}_3\text{PW}$: C, 47.19; H, 2.89;

P, 4.68.

Found: C, 46.90; H, 2.77; P, 4.72. (mp = $151-54^\circ\text{C}$ dec.)

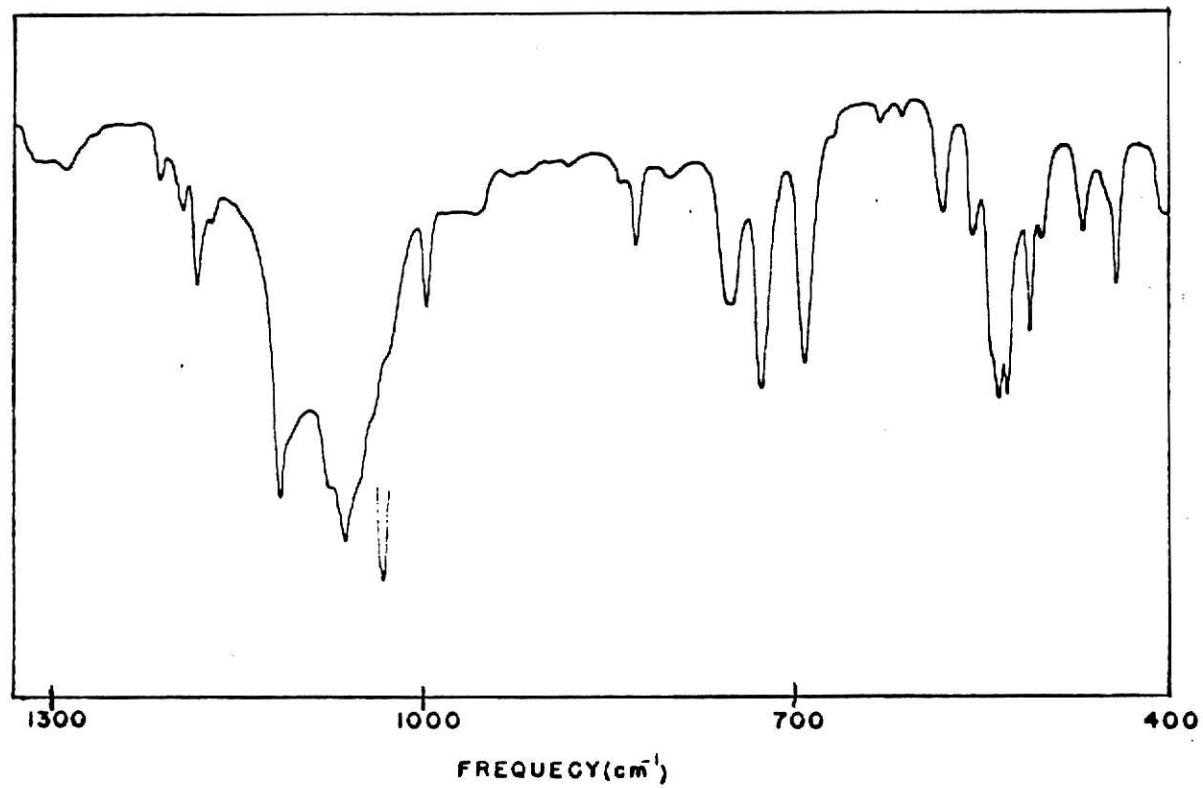
For the infrared spectra of these adducts, see Table IV-1 and Spectra IV-6,7.

Explanation of Spectrum IV-6

Infrared Spectrum of Triphenylphosphoniumcyclo-
pentadienyldmolybdenum Tricarbonyl-

Trifluoroborane Adduct.

Spectrum taken as a Nujol mull using KBr plates.

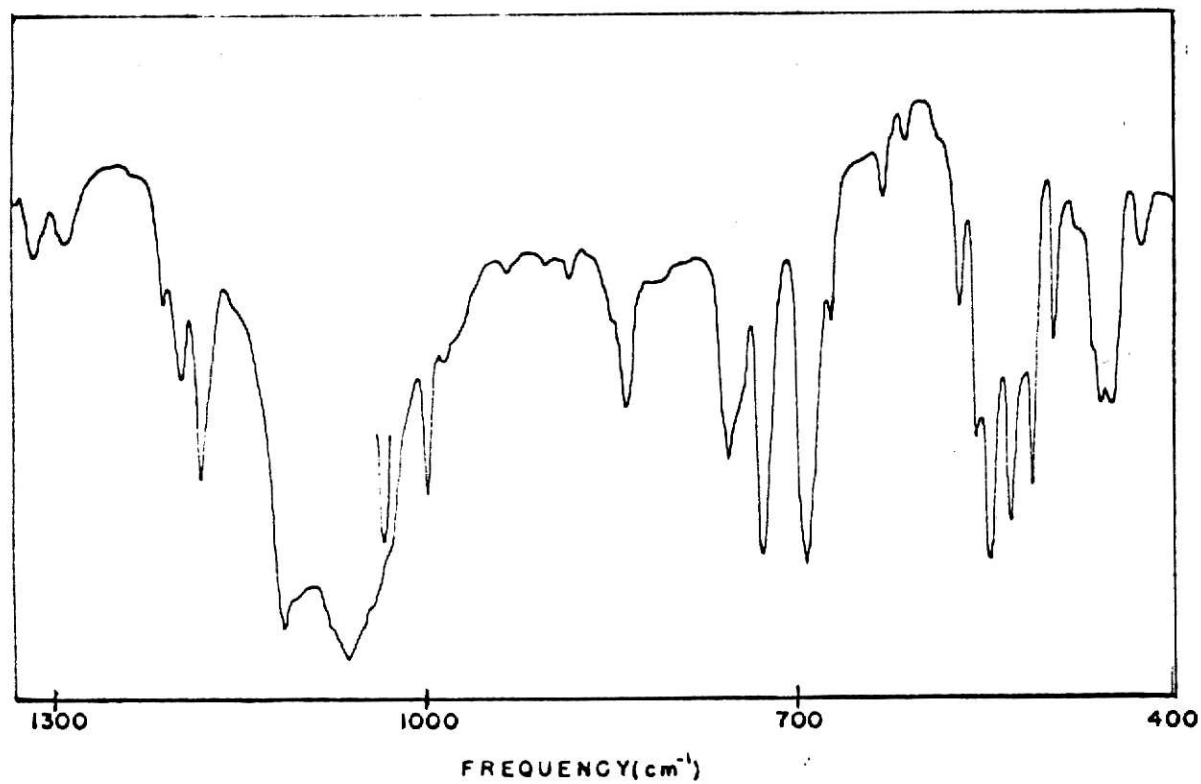
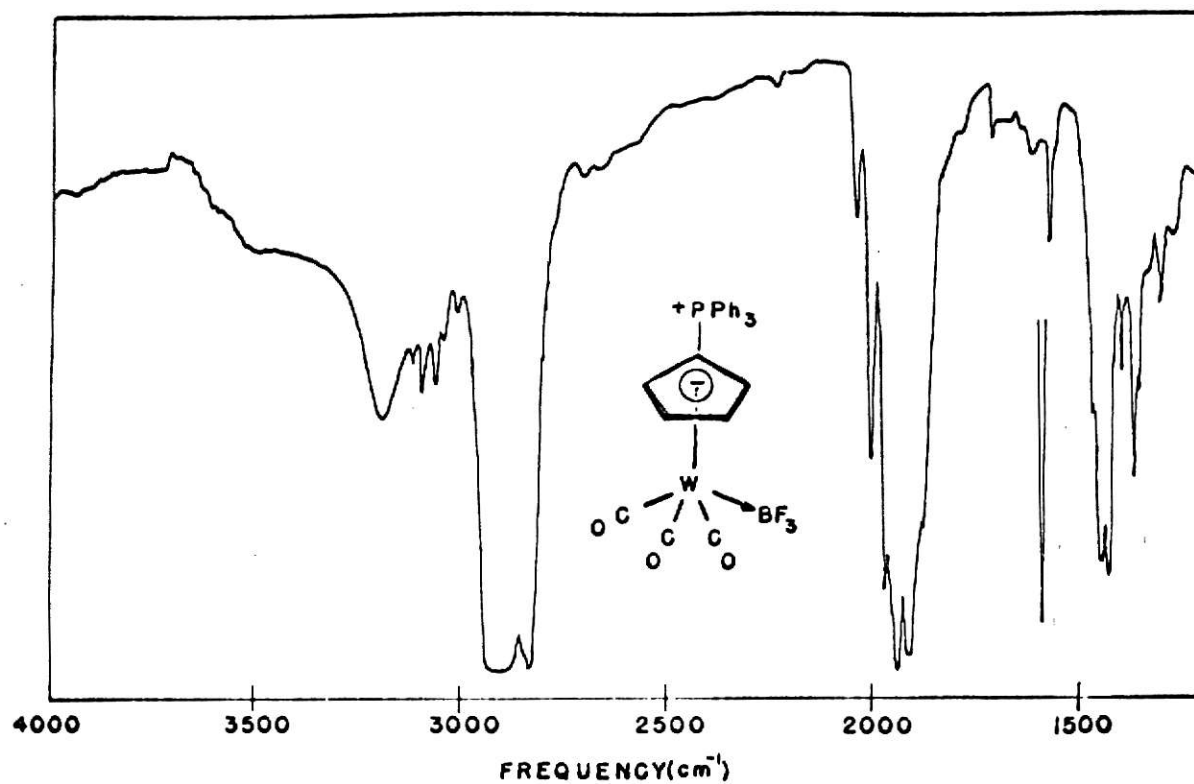


Explanation of Spectrum IV-7

Infrared Spectrum of Triphenylphosphoniumcyclo-
pentadienylidtungsten

Tricarbonyl-Trifluoroborane Adduct.

Spectrum taken as a Nujol mull using KBr plates.



PART V

RESULTS AND DISCUSSION

The experiment which led to the research reported in this thesis involved a reaction between excess BF_3 and CpylidMo(CO)_3 in a toluene/ CH_2Cl_2 mixture. The solvents and BF_3 were distilled from a vacuum line into a flask containing the yellow organometallic tricarbonyl. Upon warming from -196°C to -78°C , a dark red-brown solution had formed. However, on warming to room temperature and distilling some of the BF_3 into an adjoining trap at -196°C , the solution became yellow; this suggested that the solution now contained unreacted CpylidMo(CO)_3 . When the BF_3 which had been removed was allowed to volatilize back into the reaction flask, the solution became less yellow at room temperature and red-brown again at -78°C . Upon removing the solvent at 0°C and examining the infrared spectrum of the yellow-brown residue, a broad band characteristic of coordinated BF_3 was observed in the 1050 cm^{-1} region,¹⁰ and new carbonyl bands were observed (see Table IV-1, page 35) in addition to those for CpylidMo(CO)_3 . This experiment suggested that CpylidMo(CO)_3 was undergoing a reversible

reaction with BF_3 , the interaction being more complete at lower temperatures. To study the reaction in greater detail, the Cpylidmetal tricarbonyls were tensiometrically titrated with BF_3 at various temperatures.

Tensiometric titration curves for the reaction between BF_3 and $\text{CpylidM}(\text{CO})_3$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) in CH_2Cl_2 are shown in Figures IV-1 and IV-2. Only in the case of $\text{CpylidW}(\text{CO})_3/\text{BF}_3$ does the reaction approach a 1:1 stoichiometry at 0°C . These experiments also suggested that the primary reaction was reversible. At any point along the titration curve for a particular metal complex, the temperature could be changed back and forth between 0°C and -78°C ; the vapor pressure appropriate to either temperature did not change over the period of an hour. Furthermore, when volatile materials were removed at 0°C after a tensiometric titration, the infrared spectrum of the solid residue always indicated the presence of some unreacted $\text{CpylidM}(\text{CO})_3$, even though the titration curves showed that the stoichiometry was at least 1:1 for all three metal compounds at -78°C .

Recrystallization of the crude reaction products from the tensiometric titrations led to the isolation of air stable complexes; elemental analyses led to the empirical formulae $\text{CpylidMo}(\text{CO})_3 \cdot \text{BF}_3$ and $\text{CpylidW}(\text{CO})_3 \cdot \text{BF}_3$. However, the fact that

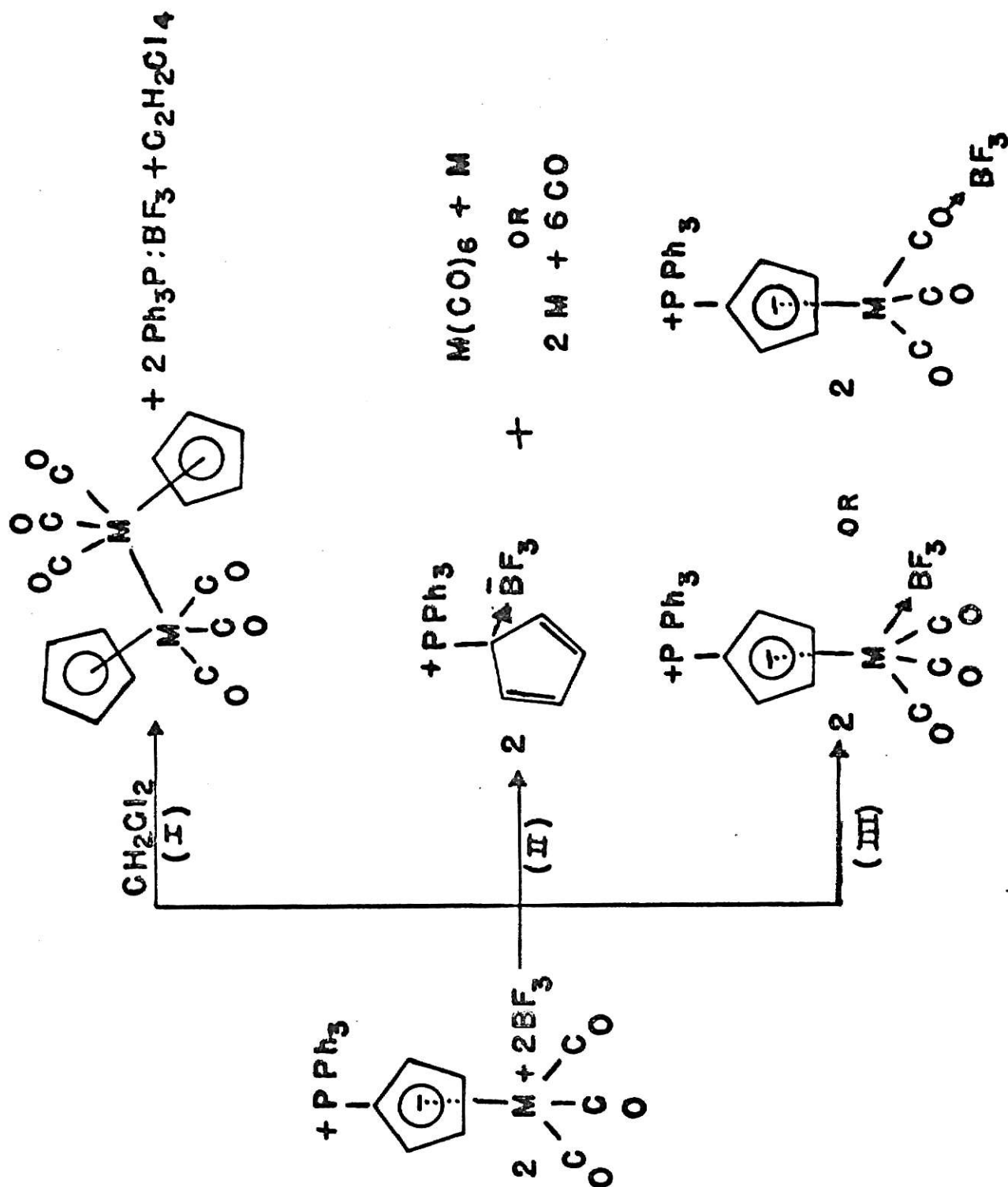
these complexes were isolated only indicated that the primary reaction involved their formation. This did not mean that other reactions had not occurred.

At least three routes (Figure V-1) are possible for the reaction of $\text{CpylidM}(\text{CO})_3$ with BF_3 . That the reaction did not occur by route I was indicated by the fact that neither CO nor $\text{M}(\text{CO})_6$ was isolated. Furthermore, the complex $\text{Cpylid}\cdot\text{BF}_3$ was not observed.

Route II is similar to the reaction of BF_3 with the π -cyclopentadienylmolybdenum and -tungsten tricarbonyl anions¹⁰ which are isoelectronic with the Cpylidmetal tricarbonyls. The dimer $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ is a dark red solid which has carbonyl stretching bands at 1958 and 1898 cm^{-1} ; bands are observed in this vicinity for our crude reaction product. Another product observed by Shriver and Johnson¹⁰ in the $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-/\text{BF}_3$ reaction was $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}$; this hydride has carbonyl bands in the 1900-2000 cm^{-1} region as well. Although the formation of these products in our system seems unreasonable, the solid product was examined for their presence. To this end, Me_3N was added to the crude solid from the BF_3 titrations. If the reaction had occurred only by route III, only $\text{CpylidM}(\text{CO})_3$ and $\text{Me}_3\text{N}\cdot\text{BF}_3$ would be isolated. As noted in the Experimental Section, $\text{CpylidM}(\text{CO})_3$ was indeed obtained.

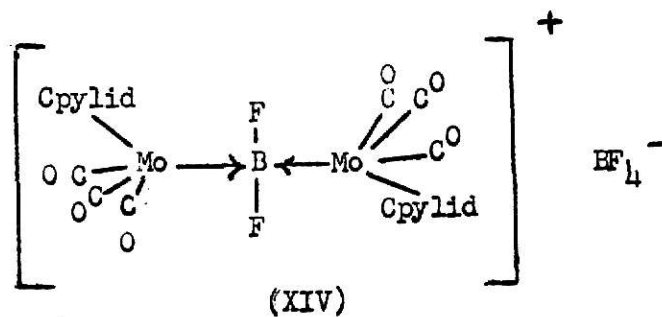
Explanation of Figure V-1

Possible Routes for the Reaction Between a
Triphenylphosphoniumcyclopentadienyldmetal Tricarbonyl
with Boron Trifluoride.



However, $\text{Me}_3\text{N} \cdot \text{BF}_3$ was not found, presumably due to the complicating reaction of Me_3N with the solvent, CH_2Cl_2 .³⁶ No M-H group was detected upon observing the nmr spectra of the purified products.

One additional possibility (XIV) should be considered. Although the reaction between BF_3 and the Cpylidmetal tricarbonyls is apparently reversible, a slow, irreversible



process leading to XIV could occur and not drastically change the titration curve shapes. Based on the elemental analysis results, no other formulations for the products seem likely. A structure similar to XIV was proposed as a possibility for the product of a 1:1 reaction between Cp_2MH_2 ($\text{M}=\text{Mo}, \text{W}$), but it was rejected for steric reasons.¹⁰ The existence of XIV in the $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$ systems is largely ruled out by the observation of only one absorption line in the ^{11}B nmr spectra of mixtures of $\text{CpylidM}(\text{CO})_3$ and BF_3 or the spectra of the purified

products.

Based on the results presented above, the most consistent interpretation of the reaction is that it proceeds predominantly by route III and provides the 1:1 adducts $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$. The next question which must be confronted is that of the site of the Lewis basicity. If the BF_3 were coordinated to the metal, backbonding from the metal to the carbonyl groups would be reduced, and the carbonyl stretching frequencies should increase. Such an increase has been noted upon protonation of organometallic carbonyls and upon formation of the HgCl_2 adducts of $\text{CpCo}(\text{CO})_2$.^{4,23} More applicable to the case of the $\text{CpylidM}(\text{CO})_3$ adducts, however, are the complexes of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with BCl_3 and BBr_3 .¹¹ The observation of ^{103}Rh - ^{11}B spin coupling was the first definitive evidence for the existence of metal-boron dative bonding. Of more consequence to the present discussion, however, is the fact that the stretching frequency of the carbonyl group in these rhodium complexes increased upon adduct formation. The data in Table IV-1 indicate a definite increase in the carbonyl stretching frequencies upon formation of the $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$ adducts. Therefore, the transition metal is apparently acting as the site of Lewis basicity in these organometallic tricarbonyl adducts.

The only other possible basic site is the oxygen atom of the carbonyl group. Several organoaluminum adducts of organometallic carbonyls have been reported recently in which the aluminum is thought to be datively bonded to the oxygen of a carbonyl group.³⁷ In such cases, it has been observed that the stretching frequency of the coordinated carbonyl group decreases significantly due to σ and π polarization.³⁸ The observed increase in ν_{CO} for the $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$ adducts, therefore, rules out oxygen coordination.

In order to further substantiate the conclusion that metal-boron dative bonding is present in the $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$ complexes, several additional experiments were carried out. One of the isotopes of tungsten, ^{183}W , has a nuclear spin of $1/2$ and a natural abundance of 14.3%. If BF_3 or the BF_2^+ group were directly coordinated to the tungsten in $\text{CpylidW}(\text{CO})_3$, spin-coupling between ^{183}W and ^{11}B should be observed. However, on examining the ^{11}B nmr spectrum of a methylene chloride solution of the complex, the satellite peaks expected for metal-boron coupling were not observed. Evidently, the sample was not soluble enough to give sufficient intensity to the peaks. The signal-to-noise ratio of the observed spectrum was about 10 to 1. The signal-to-noise ratio necessary to observe metal-boron coupling satellite peaks should be better than 12 to 1.

The ^{11}B nmr spectra of $\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3$ did provide one piece of information concerning the basicity of the donor site. The ^{11}B chemical shift for the boron in the molybdenum complex was nearly identical with that for $\text{F}_3\text{B} \cdot \text{O}(\text{C}_2\text{H}_5)_2$. Although not as accurate a measurement could be made on the tungsten system since the nmr tube did not contain an external standard, approximate methods showed that the ^{11}B chemical shift in this system was also nearly identical with $\text{F}_3\text{B} \cdot \text{O}(\text{C}_2\text{H}_5)_2$. It should be noted that this chemical shift value is in the same region as those observed for the $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2 \cdot \text{BX}_3$ series.¹¹ No direct comparisons of the rhodium and molybdenum or tungsten complexes may be made, however, due to differences in stereochemistry and attached ligands. A perhaps naive interpretation of our result is that the basicity of the donor site--presumably the metal--is approximately the same as the basicity of diethyl ether toward boron trifluoride. However, much more work must be done before more firm conclusions may be drawn.

Having failed to observe tungsten-boron spin coupling, and, thus to obtain direct proof of metal-boron bonding, an attempt was made to protonate the Cpylidmetal tricarbonyls using a strong acid, CF_3COOH . If it could be shown that the organometallic complexes could be protonated at the metal, it

could be concluded with greater assurance that a boron trihalide would likewise utilize an electron pair localized on the metal in forming the observed adducts.

The Cpylidmetal tricarbonyls dissolve readily in trifluoroacetic acid to give highly colored solutions. The ^1H nmr spectra (Table V-1) of these solutions were examined in the region characteristic of metal hydrides. Very sharp resonance lines (width at 1/2-height = 1 cps) for M-H were observed for the molybdenum and tungsten complexes, and, more importantly, ^{183}W - ^1H spin coupling was observed.³⁹ These spectra demonstrate that there is apparently no exchange of protons between the metal complex and the solvent and that the proton is directly bonded to the metal.

One of the objectives of this research was to determine if there was a relationship between the relative nucleophilicities or Lewis basicities of the three Group VIB metals and the extent of the reaction of their organometallic tricarbonyls with boron trihalides. Nucleophilicity is best thought of as being related to the rate at which a nucleophile reacts with a given electrophilic substrate. Basicity, however, is related to the thermodynamics of the system. When discussing relative basicity or acidity in the Lewis sense, one is usually referring to the relative "coordinating strength" of the acid or base.

Table V-1.

Proton Nmr Data for the Triphenylphosphoniumcyclopentadienyliid and Cyclopentadiene Complexes

Cpylid	CpylidM(CO) ₃	CpylidM(CO) ₃ H ^{+<u>a</u>}	
C ₅ H ₄ (τ)	C ₅ H ₄ (τ)	C ₅ H ₄ (τ)	M-H (τ)
3.64 ^b	Cr 5.08, 5.35	Cr 4.64	15.09
(CDCl ₃)	Mo 4.51, 4.77	Mo 4.20	15.34
	W 4.51, 4.78	W 4.13	17.15
Cp ⁻	CpM(CO) ₃ ⁻	CpM(CO) ₃ H ^{+<u>c</u>, <u>d</u>}	
Cp (τ)	Cp (τ)	Cp (τ)	M-H (τ)
4.93 ^e	Cr --	Cr 5.22	15.46
(CH ₃ CN)	Mo --	Mo 4.70	15.52
	W --	W 4.65	17.33

^ain CF₃COOH

^bRef. 35

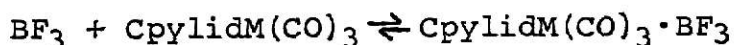
^cRef. 39

^din hexane

^eRef. 40

Drago and Wayland have defined "coordinating strength" as being directly related to the enthalpies of adduct formation measured in the gas phase or in a poorly solvating solvent.⁴¹

As mentioned above, the most consistent interpretation of the tensiometric titration curves is that the primary reaction involves the reversible formation of a 1:1 adduct between BF_3 and $\text{CpylidM}(\text{CO})_3$. The tensiometric curves at 0°C indicate that the chromium compound reacts least readily with BF_3 , and that the reactivity increases on increasing the metal atomic weight. That is, the equilibrium constant for the reaction



$$K = \frac{[\text{CpylidM}(\text{CO})_3 \cdot \text{BF}_3]}{P_{\text{BF}_3} [\text{CpylidM}(\text{CO})_3]}$$

increases with increasing metal atomic weight. If it is assumed that the equilibrium constants reflect enthalpy changes (this requires the reasonable assumption that the entropy changes for all three reactions are nearly equal),⁴² the Lewis basicity of the metal, in these compounds, increases in the same order.

Dessy, Pohl, and King²⁸ have investigated the nucleophilicities of the Group VIB cyclopentadienylmetal tricarbonyl anions, a series isoelectronic with the Cpylidmetal tricarbonyls.

It was found that the anion nucleophilicity increased with increasing metal atomic weight. Although nucleophilicity is not always related to basicity, it is apparent that such a relationship may exist between these two isoelectronic series. Furthermore, it should be noted that the observed anion nucleophilicity parallels $\tau(M-H)$ for the protonated anions, the cyclopentadienylmetal tricarbonyl hydrides.

It may be argued that the chemical shifts observed for the protonated Cpylidmetal tricarbonyls reflect enthalpy changes which occur upon adduct formation. Calculations by Lohr and Lipscomb⁶ have shown that 90% of the high field shift for M-H in $(C_5H_5)M(CO)_3H$ ($M = Cr, Mo, W$) (Table V-1) is due to the presence of an excess of negative charge on the hydrogen, and that the increase in $\tau(M-H)$ with increasing metal atomic weight is due to increasing electron density on the hydrogen. Since the protonated Cpylidmetal tricarbonyls are isoelectronic with the Group VIB cyclopentadienylmetal tricarbonyl hydrides, it does not seem unreasonable to assume that the increase in M-H chemical shifts with increase in metal atomic weight for the Cpylidmetal tricarbonyls is also due to an increase in negative charge on the attached proton; the increase in electron density on the hydrogen may be a reflection of the increasing Lewis basicity of the metals.⁴³

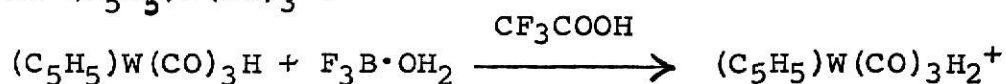
From the above discussion, it seems apparent that the Lewis basicity of the Group VIB metals increases with increasing metal atomic weight in the isoelectronic series $(C_5H_5)M(CO)_3^-$ and $Cp^*M(CO)_3$. However, good correlations of borane adduct stability, anion nucleophilicity, and $\tau(M-H)$ do not always hold for other series of compounds. For the isoelectronic series of carbonyl anions, $Co(CO)_4^-$, $Mn(CO)_5^-$, and $Re(CO)_5^-$, the nucleophilicity of the anions,²⁸ borane adduct stability,¹⁶ and acid ionization constants⁷ all indicate an increase in Lewis basicity with increasing metal atomic weight. However,

$\tau(M-H)$ for the carbonyl hydrides decreases with increasing atomic weight. A breakdown of the correlation at this point is not surprising since $\tau(M-H)$ is the least reliable indicator of metal basicity; $\tau(M-H)$ for a number of metal hydrides is evidently more dependent on the metal TIP than electron density at the hydrogen.⁴⁴

When Nöth reacted $RhCl(CO)[P(C_6H_5)_3]_2$ with BCl_3 and BBr_3 , stable complexes resulted.¹¹ It had been previously reported that this same rhodium complex would not form an adduct with BF_3 .¹² As Nöth pointed out, this result was not unexpected, since the accepted order of Lewis acid strengths of the boron trihalides is $BF_3 < BCl_3 < BBr_3$. We have also experienced an increase in complex stability in the case of BCl_3 . Tensiometric

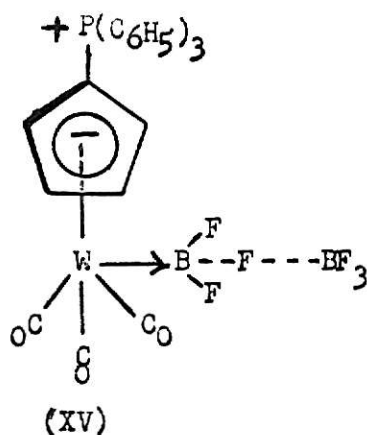
titrations of $\text{CpylidCr}(\text{CO})_3$ and $\text{CpylidMo}(\text{CO})_3$ with BCl_3 indicated that both metal compounds reacted in a 1:1 ratio with this borane at 0°C . On the other hand, we observed little or no interaction between diborane and $\text{CpylidMo}(\text{CO})_3$, even at -78°C . If it is assumed that BF_3 and BCl_3 are hard acids and BH_3 is a soft acid as suggested by Pearson,⁴⁵ our experimental results imply that the $\text{Cpylidmetal tricarboxyls}$ are hard bases. This is in agreement with Shriver's conclusion that the bis(η -cyclopentadienyl)metal dihydrides of molybdenum and tungsten are hard bases toward BF_3 .¹⁰

The $\text{CpylidW}(\text{CO})_3$ system demonstrates an interesting phenomenon: the addition of two molecules of BF_3 at -78°C . Assuming that the first BF_3 goes on the metal, where might the second coordinate? There are several possible sites: (1) the metal, (2) a carbonyl group, or (3) the already coordinated BF_3 . The first possible site is not without precedence since Wilkinson and co-workers were able to form the diprotonated complex of $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3^-$.⁴



The possibility of coordination through the carbonyl oxygen cannot be discounted.³⁷ In reference to the third possibility, H. C. Brown, et al., have found several examples of complexes which appear to have two BF_3 molecules bonded through a single

B---F---B bridge bond.⁴⁶ Furthermore, single fluorine bridges are known to exist in some aluminum compounds.⁴⁷ The structure of $\text{CpylidW(CO)}_3 \cdot 2\text{BF}_3$ may approximate that shown below.



This phenomenon of the coordination of a second molecule of Lewis acid to a transition metal complex has also been found by Shriver, et al.,¹⁴ and Parshall.¹⁶ Shriver did not specify the location of the second boron trifluoride except to say that it was probably not attached to the metal. However, Parshall suggested that a second BH_3 added to $[\text{Re(CO)}_5 \cdot \text{BH}_3]^-$ by coordination to the first BH_3 through a B---H---B bridge.

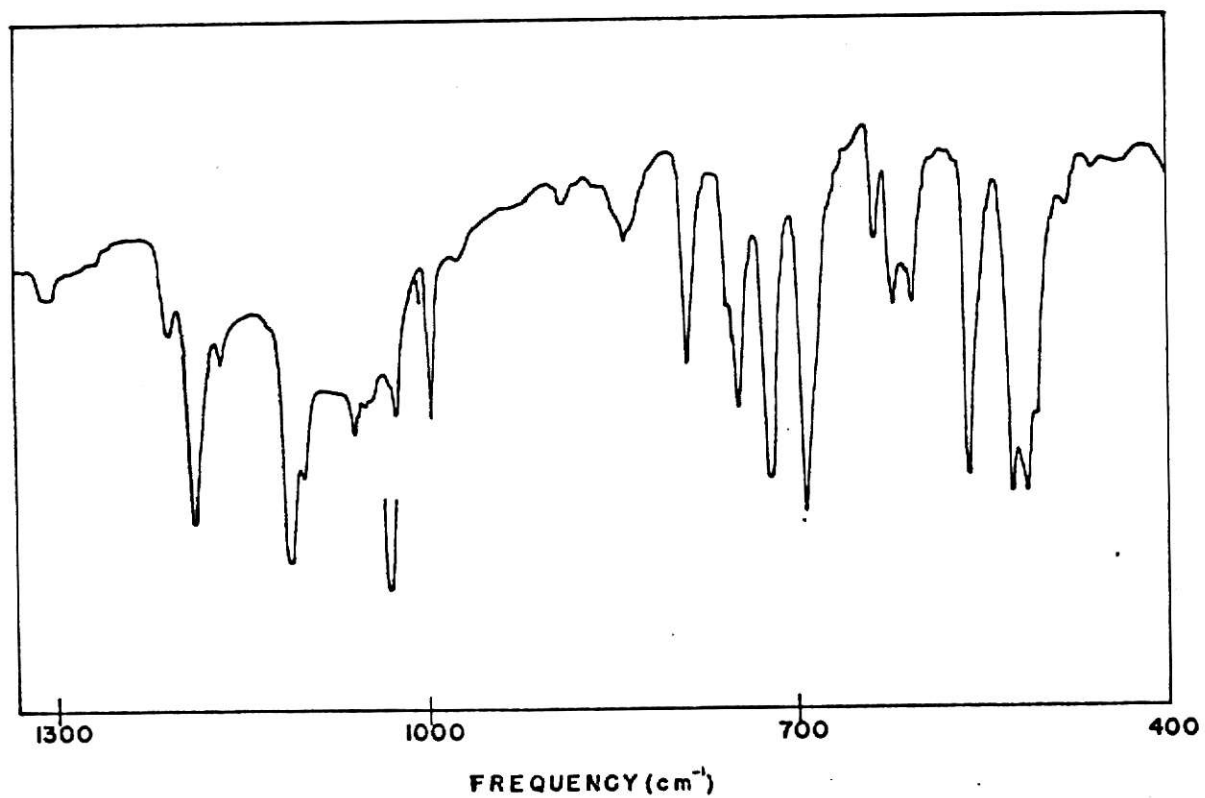
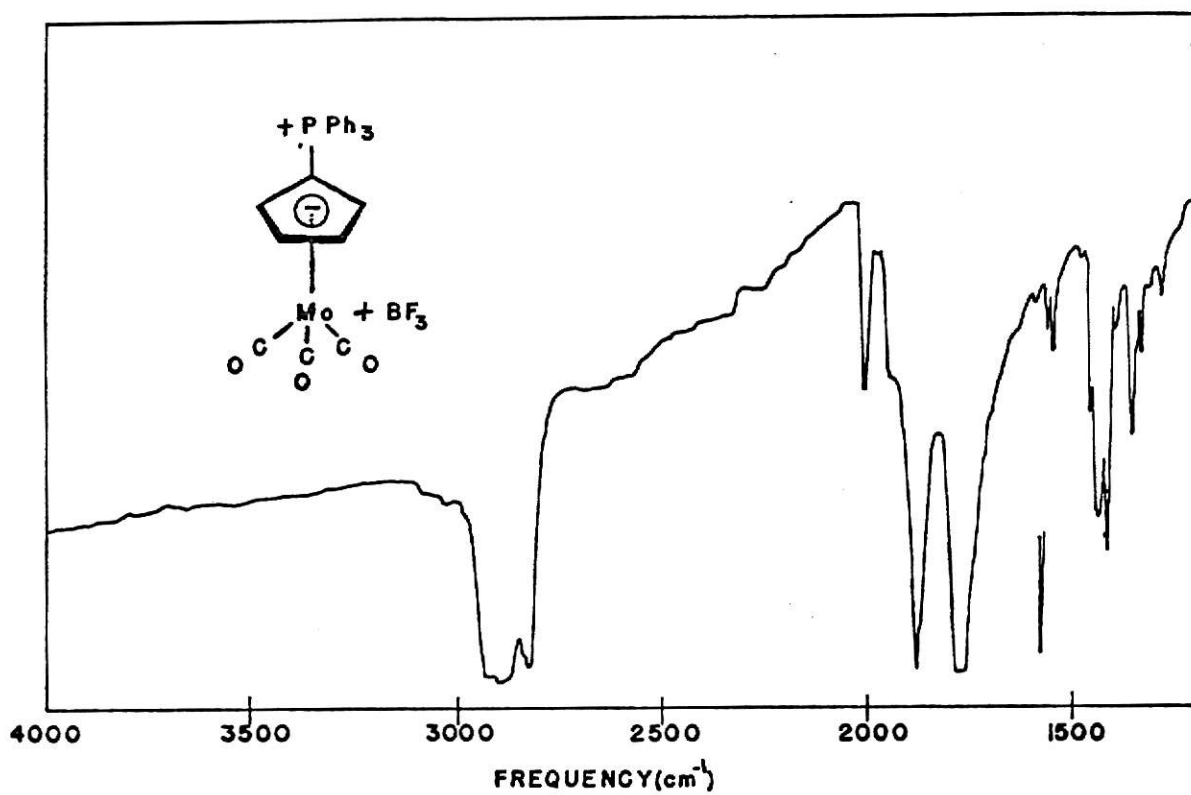
PART VI

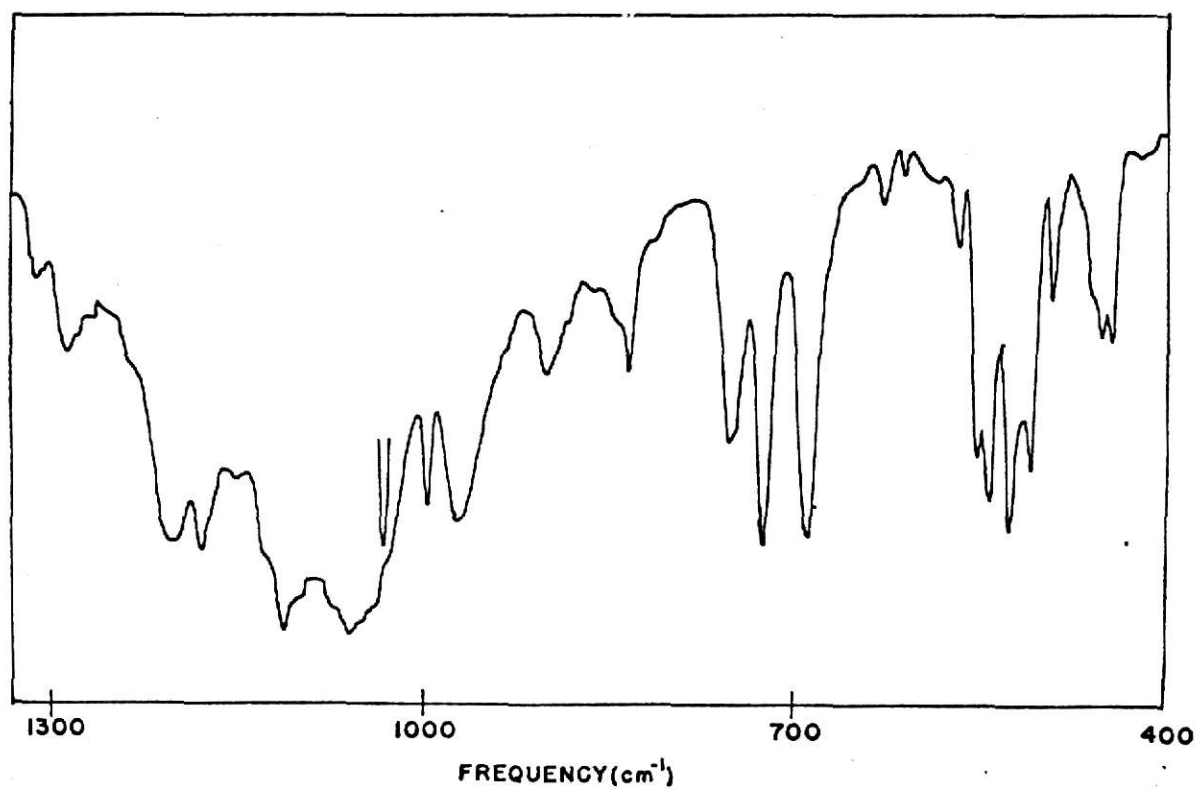
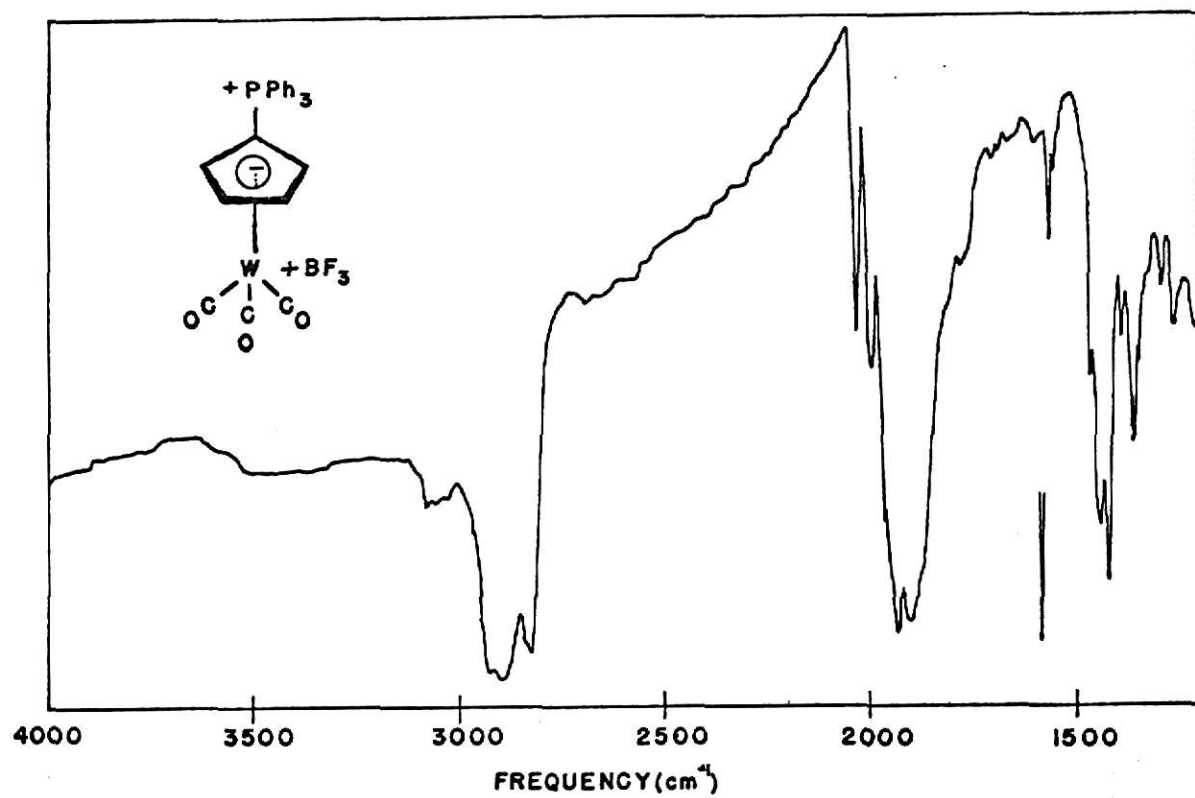
ACKNOWLEDGMENTS

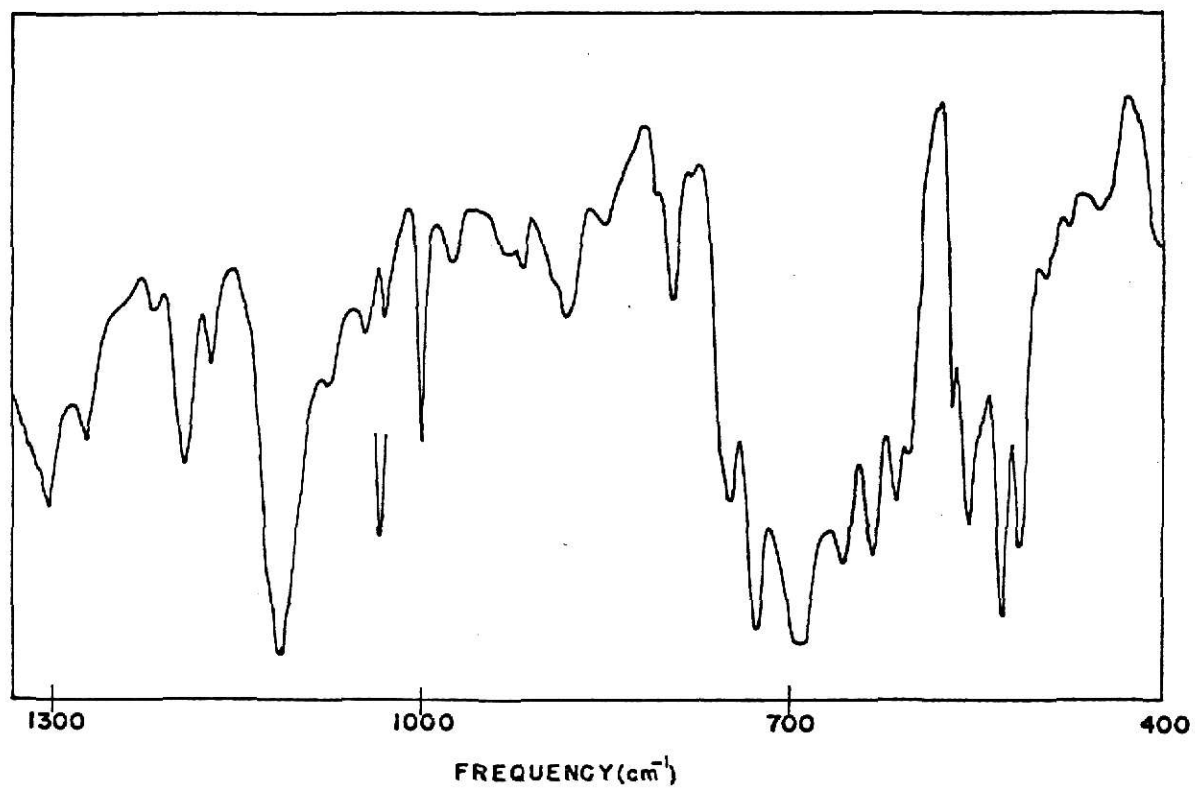
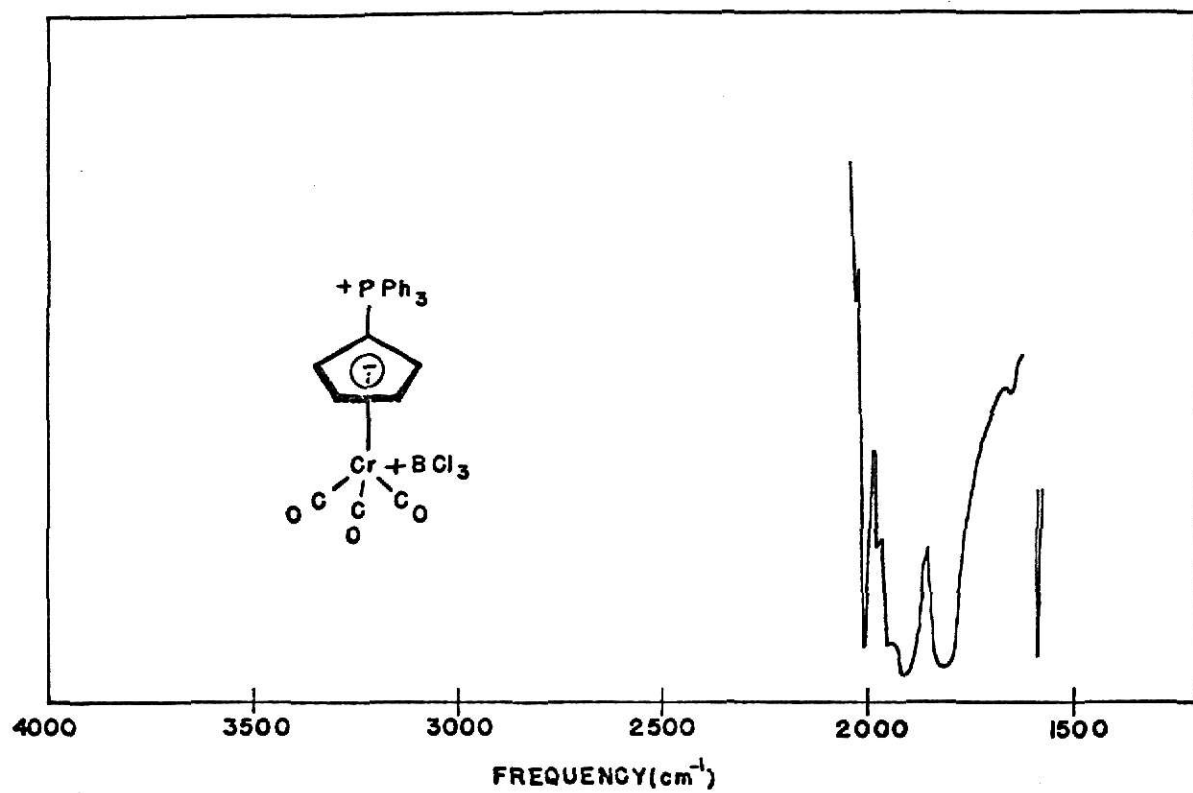
I would like to take this opportunity to express my appreciation to all who played a part in the eventual production of this thesis. Particularly to my wife and family for their continued support, to Dr. J. C. Kotz, without whose interest and assistance this work would not have been possible. My thanks also to the other members of this research group for their friendship and suggestions.

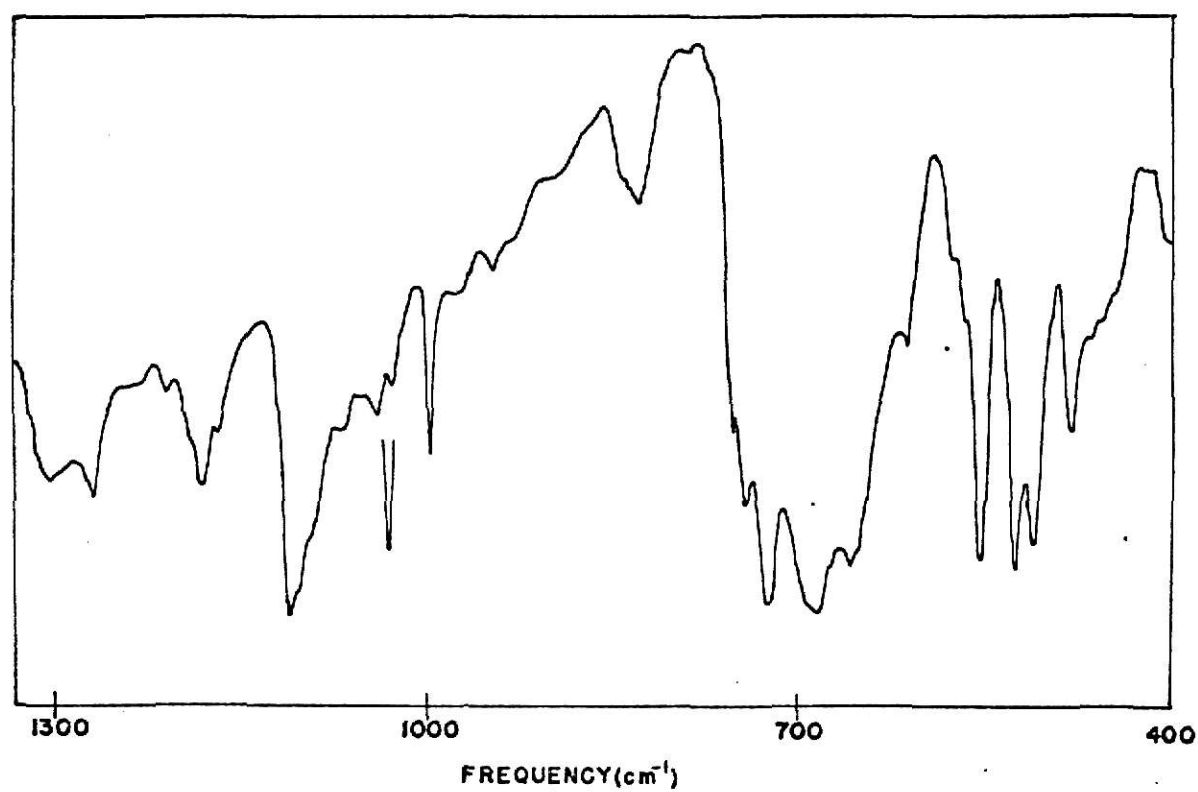
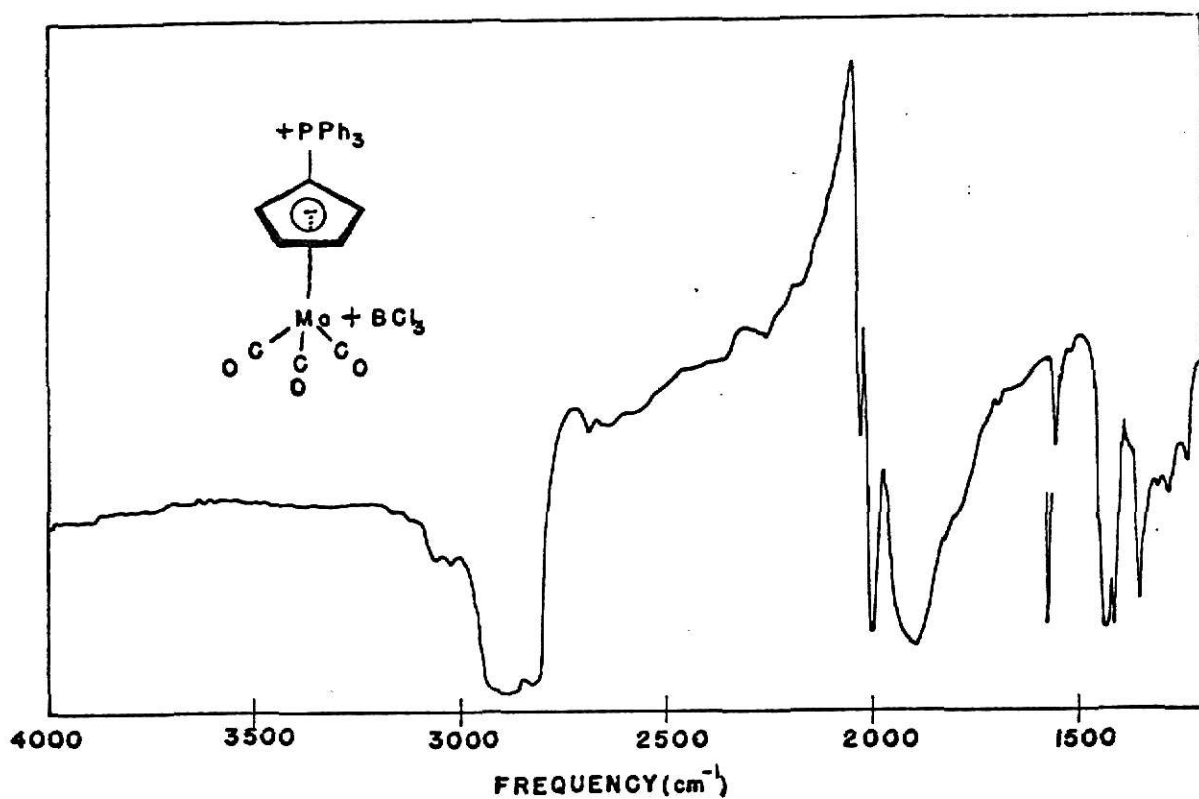
APPENDIX

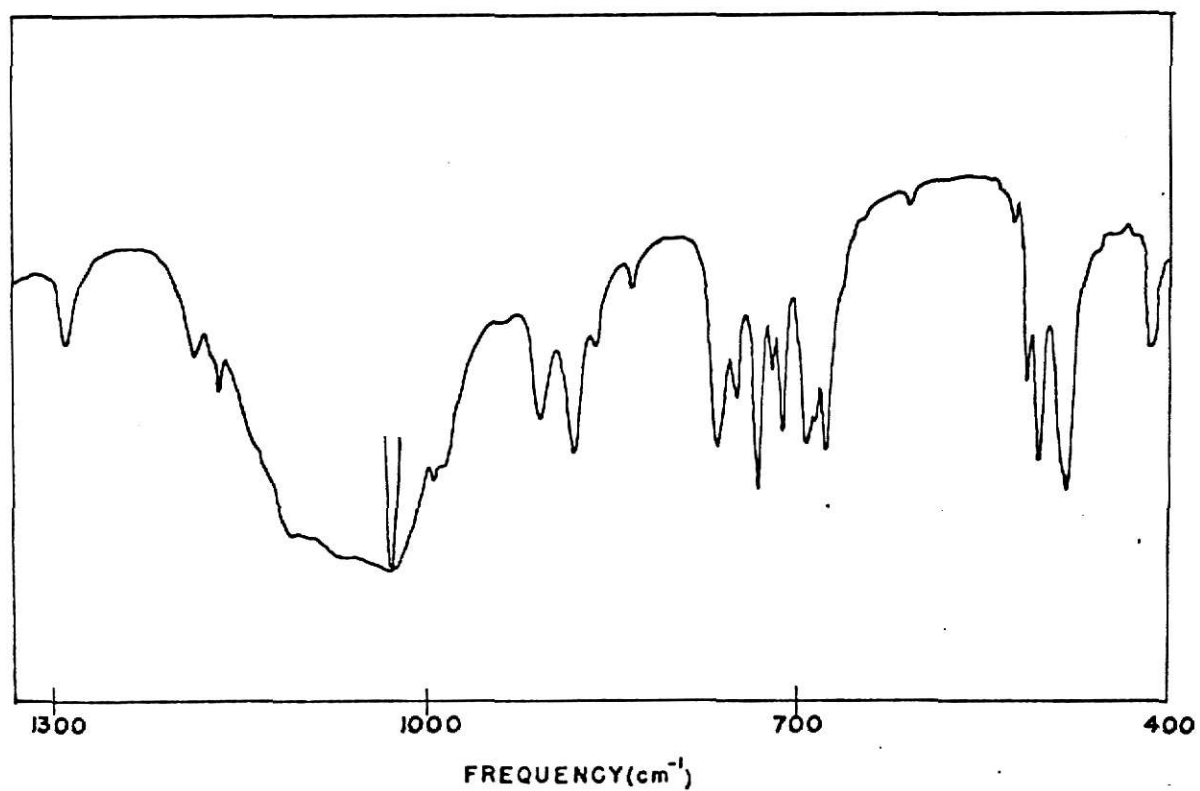
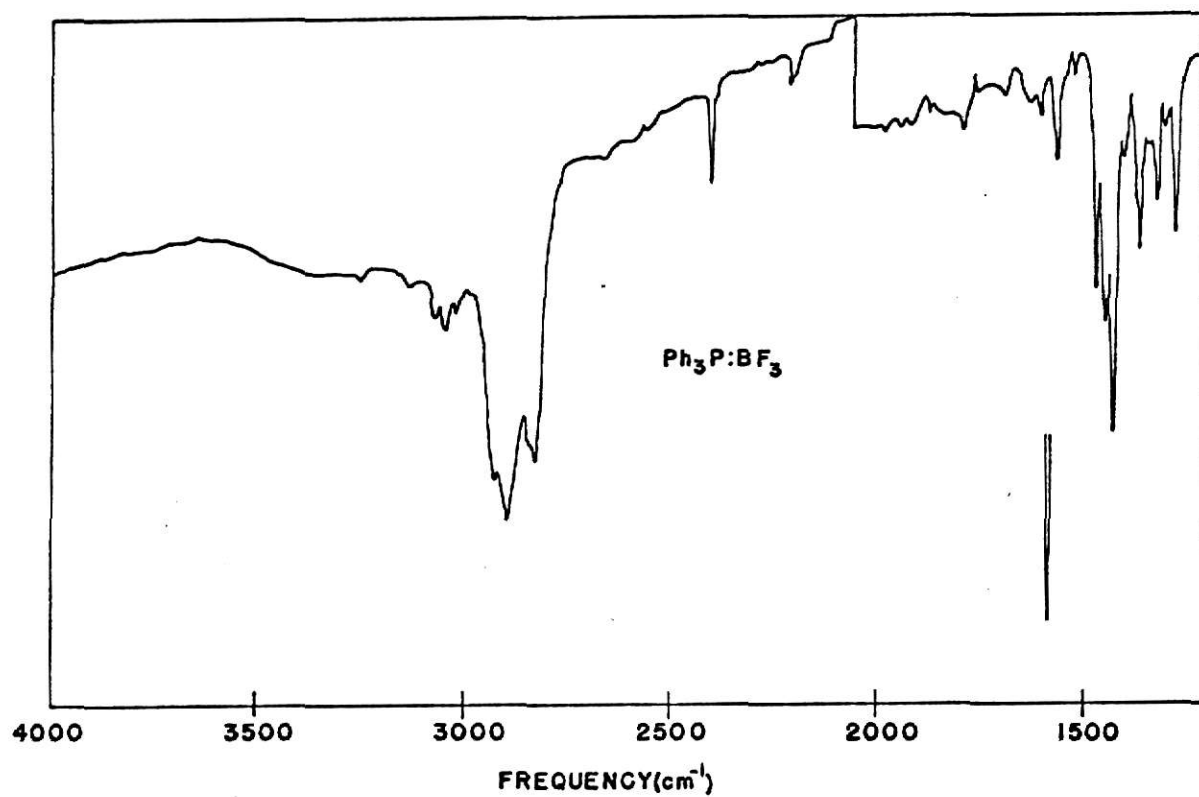
Miscellaneous Infrared Spectra

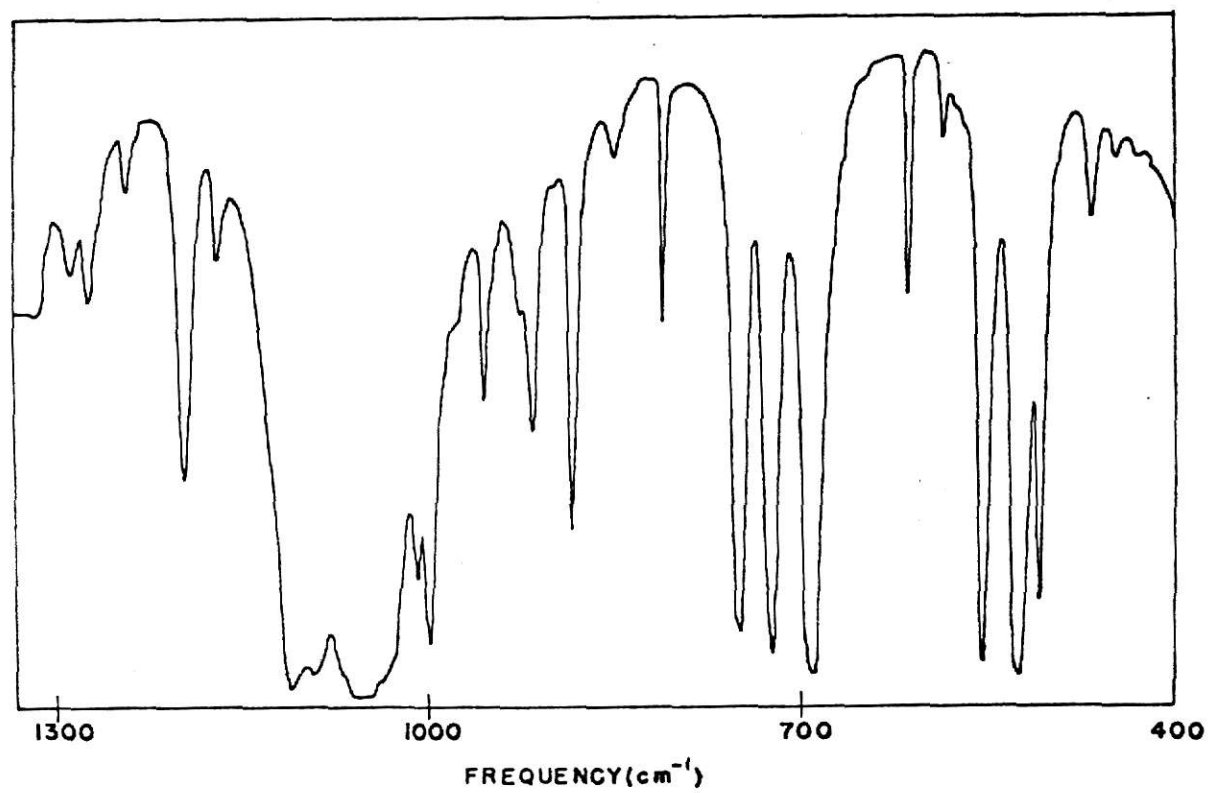
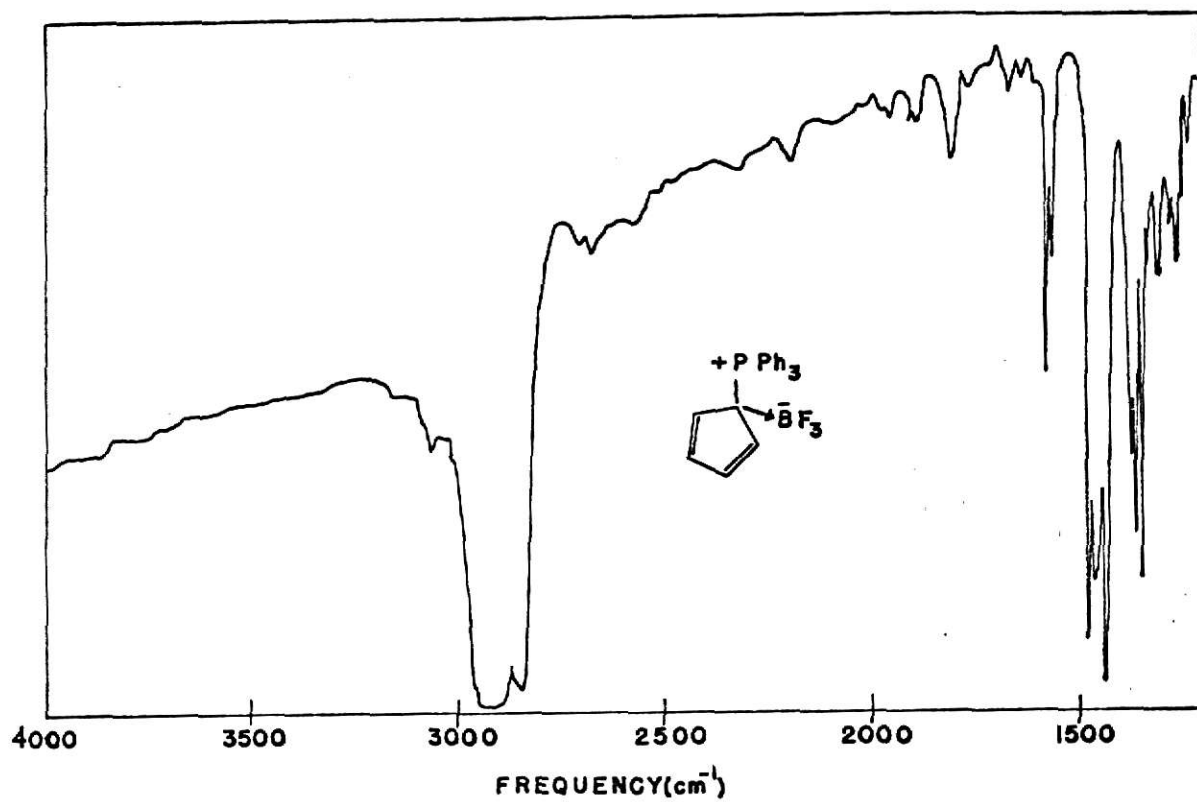












PART VII

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THE LEWIS BASICITY OF THE GROUP VI TRANSITION METALS

by

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B. S., Christian Brothers College, 1965

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1970

The experimental observation which led to the investigation discussed in this thesis was the reaction of boron trifluoride with triphenylphosphoniumcyclopentadienyldimolybdenum tricarbonyl, CpylidMo(CO)_3 . The problem at first resolved itself into determining the product or products of the reaction and the reaction stoichiometry.

It was felt that there were three possible reaction routes. Two of these involved decomposition of CpylidMo(CO)_3 and hence should be irreversible. The postulated products of the third route were 1:1 donor-acceptor adducts involving BF_3 coordination to either the metal or oxygen of a carbonyl group on the CpylidMo(CO)_3 ; this route should be at least potentially reversible. Therefore, the red, air-stable solid from the reaction of CpylidMo(CO)_3 and BF_3 was reacted with trimethylamine; starting material (CpylidMo(CO)_3) was present in the residue. On the basis of this and other results, it was concluded that the third route was the most probable reaction route.

The analogous Cr and W compounds also reacted with BF_3 . The extent of the reactions of BF_3 with all three organometallic compounds was measured by tensiometric titrations with the following results (the value given is the pressure due to unreacted BF_3 at a given temperature and ratio of $\text{BF}_3/\text{CpylidM(CO)}_3$): Cr, 23.0 mm.; Mo, 8.0 mm.; and W, 1.0 mm. at 0°C and a ratio of

1.0; Cr, 16.0 mm.; Mo, 5.0 mm.; and W, 1.0 mm. at -78°C and a ratio of 1.5.

Only indirect information was available for determining the site of Lewis basicity. This information consisted of the observation that the carbonyl bands shifted to higher frequencies upon coordination with BF_3 . A similar effect has been observed for other borane adducts of organometallic compounds in which the site of Lewis basicity is the metal, whereas, it has been found that the carbonyl bands move to lower frequencies if coordination occurs through the oxygen of a carbonyl group. A direct proof for metal-boron coordination would have been the observation of boron-metal spin coupling in the ^{11}B nmr spectrum of the tungsten adduct. However, due to solubility problems, no ^{183}W - ^{11}B spin coupling was observed.

It has been found from the literature that those systems that can be protonated by strong acids may also coordinate borane Lewis acids on the metal. Therefore, an attempt was made to protonate the Cpylidmetal tricarbonyls. The proton nmr spectra of these systems display a high field resonance line indicative of the M-H group. However, most notable of the proton nmr spectral results was the existence of ^{183}W - ^1H spin coupling. This indicated that the proton was bonded directly to the metal; thus, it seemed even more reasonable that the BF_3 was

coordinated to the metal.

The tensiometric titration results at 0° C, indicate an increase in relative equilibrium constants as the atomic weight of the metal increases. The $M-H^+$ proton chemical shifts demonstrated a similar trend; that is, the $M-H^+$ group shifted upfield with increasing metal atomic weight. It should be noted that a LCAO-MO calculation has shown that, for compounds isoelectronic with the Cpylidmetal tricarbonyls, 90% of the M-H proton chemical shift is due to transferred electron density. By definition, a Lewis base donates electrons; therefore, it seems reasonable that the stronger the base the greater the electron density donated and the higher the chemical shift for M-H systems. Thus, based on the observed trend in M-I shifts and equilibrium constants, it has been concluded that, for this system, the Lewis basicity of a Group VI transition metal increases as the atomic weight increases.