

1975

Reactions of Tungsten Carbonyl Complexes Containing Diphenylvinylphosphine

George S. Leotsakos

Eastern Illinois University

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REACTIONS OF TUNGSTEN CARBONYL COMPLEXES

CONTAINING DIPHENYLVINYLPHOSPHINE

(TITLE)

BY

George S. Leotsakos

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1975

YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

3/11/75
DATE

ADVISER

3/11/75
DATE

REACTIONS OF TUNGSTEN CARBONYL COMPLEXES
CONTAINING DIPHENYLVINYLPHOSPHINE

George S. Leotsakos
Bachelor of Science
Eastern Illinois University
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August, 1971

Submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Chemistry
at the
Graduate School
of
Eastern Illinois University
CHARLESTON, ILLINOIS
1975

REACTIONS OF TUNGSTEN CARBONYL COMPLEXES CONTAINING
DIPHENYLVINYLPHOSPHINE

Thesis Approved

Dr. R. L. Keiter, Thesis Advisor

Dr. D. W. Ebdon

Dr. R. H. Kerraker

DEDICATION

To my Parents

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Richard Keiter for suggesting the problem and for his guidance, inspiration, and infinite patience throughout the investigation.

The author would like to give thanks to other members of the faculty for their active interest and help. Special thanks are in order for the author's wife, Sherri, for her constant understanding, encouragement and moral support.

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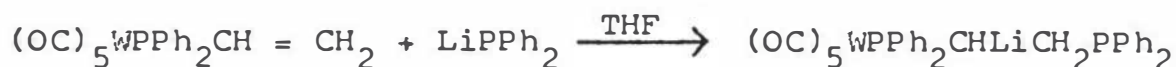
ABSTRACT

Title of Thesis: Reactions of Tungsten Carbonyl Complexes
Containing Diphenylvinylphosphine

Name: George S. Leotsakos

Thesis directed by: Dr. Richard L. Keiter

A new synthetic route for the production of the tungsten carbonyl complex $(OC)_5WPPh_2CH_2CH_2PPh_2$ has been discovered. It has been found that lithiumdiphenylphosphide reacts with diphenylvinylphosphinepentacarbonyltungsten(0) in tetrahydrofuran to produce upon hydrolysis a good yield of the pentacarbonyl product:



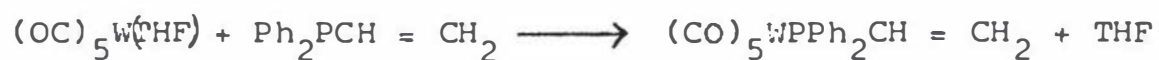
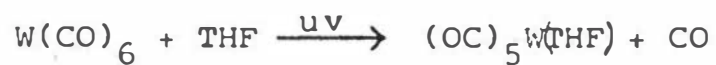
No evidence for the formation of secondary products was noted nor was there evidence for preferential attack of the carbonyl group by $LiPPh_2$ to form a carbene complex.

Diphenylvinylphosphinepentacarbonyltungsten(0) (mp 62-64°C), was prepared for the first time by two different methods.

I. Displacement of aniline from anilinepentacarbonyltungsten(0) complex with diphenylvinylphosphine.



II. Displacement of THF from $(OC)_5W(THF)$ complex with diphenylvinylphosphine.

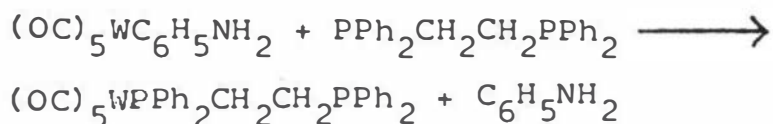


Of the two methods the latter produced better yields and eliminated the need for the unstable aniline complex intermediate necessary in the former method.

CHAPTER I

INTRODUCTION

Syntheses of transition metal complexes in which a potentially bidentate ligand serves as a monodentate are uncommon. In 1970 Rigo and co-workers¹ synthesized a five coordinate cobalt complex, $\text{Co}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\text{CN})_2$, in which one of the diphosphines served as a monodentate ligand. The first zerovalent complex, in which $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (diphos) was present as a monodentate ligand, was reported in 1972 by Keiter and Shah² from the reaction



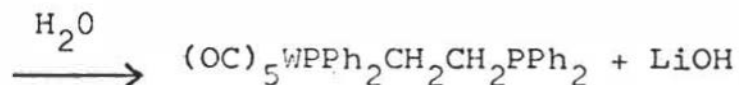
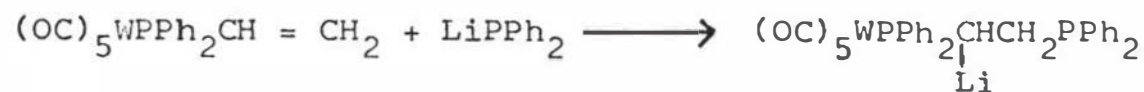
The reaction depends upon the thermodynamic instability of the aniline complex.³ A large excess of the diphos ligand was needed for the reaction, however, in order to obtain the desired product. If equimolar amounts of ligand to aniline complex were employed for the reaction, a mixture of the dimetallic complex $(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W}(\text{CO})_5$ as well as the desired monodentate product was obtained, with the formation of the first being favored. Attempts to directly synthesize $(\text{OC})_5\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ from $\text{W}(\text{CO})_6$ and diphos photolytically or thermally were unsuccessful because of the formation of disubstituted products of the type $(\text{OC})_4(\text{diphos})\text{W}$.

More recently complexes containing potential chelating ligands as monodentates have been synthesized by an alternate method in which an anionic carbonyl halide is allowed to react with the diphosphine.⁴

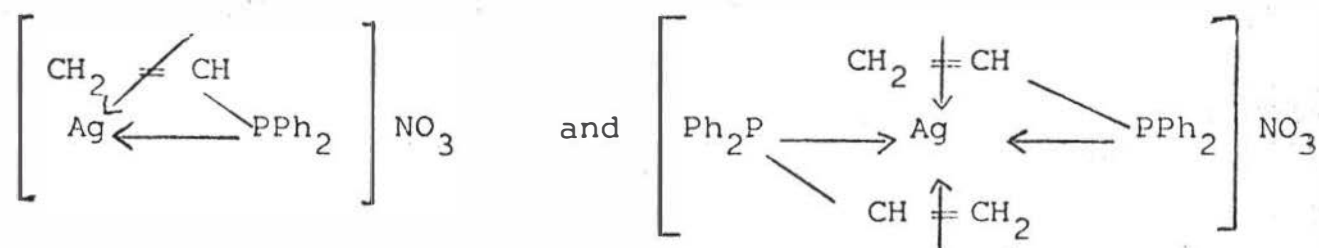


The disadvantage of this synthesis lies with the instability of the halogenometalpentacarbonyl complex.⁵

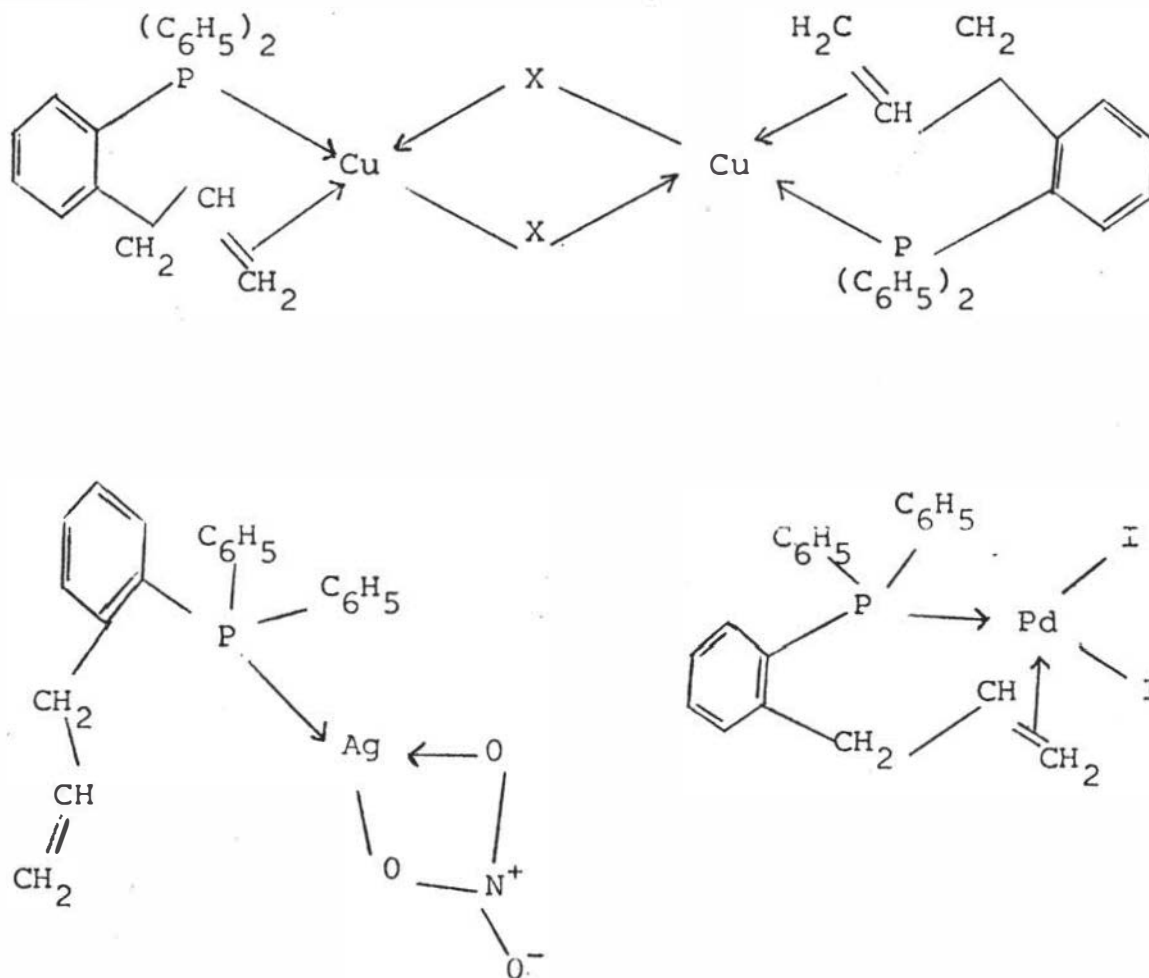
It has been the purpose of this research to find a new synthetic route for the production of $(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$. The reaction specifically investigated involves the addition of an alkali metal phosphide to a tungsten carbonyl complex containing diphenylvinylphosphine



Since $(\text{OC})_5\text{WPPh}_2\text{CH}=\text{CH}_2$ had not been previously reported in the literature, the first task was to determine if the affinity of the metal for the lone pair of phosphorus is greater than the affinity of the metal for the double bond of the olefinic group. The only complexes of $\text{PPh}_2\text{CH}=\text{CH}_2$ previously reported are those of Ag(I) in which it is found that both the phosphorus atom and the double bond coordinate to give 1:1 and 2:1 complexes.⁶

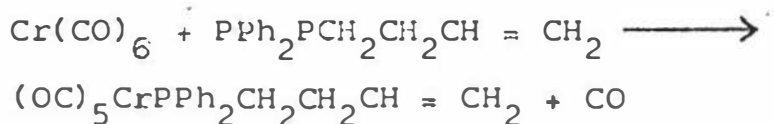


The coordination chemistry of a number of other ligands containing both phosphorus and olefinic groups has been reported.^{7,8} Some examples of these complexes are shown below:



It should be noted that in all reported examples, phosphorus is coordinated to the metal whereas the double bond may or may not be coordinated. Other phosphine ligands containing an unsaturated site have been reported to coordinate to the central atom of Group VI metal carbonyls. K. Issleib and coworkers⁹ reported that 3-butenyldiethylphosphinepenta-

carbonylchromium(0) can be prepared when $\text{Cr}(\text{CO})_6$ is irradiated in the presence of 3-butenyldiethylphosphine.



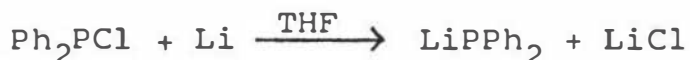
Only the phosphorus atom of the ligand is coordinated to the metal. Taylor and coworkers¹⁰ have reported the syntheses of $(\text{OC})_5\text{W}(\text{cis} - \text{PPh}_2\text{CH}=\text{CHPPh}_2)$, $(\text{OC})_5\text{W}(\text{trans} - \text{PPh}_2\text{CH}=\text{CHPPh}_2)$, and $(\text{OC})_5\text{WPPh}_2\text{C}\equiv\text{CPh}_2$ and in each complex only phosphorus is coordinated.

The reaction of olefins and alkynes with lithium diphenylphosphide, LiPPh_2 , has been studied by several investigators. Angular and coworkers¹¹ first reported a method of conveniently synthesizing LiPPh_2 from triphenylphosphine, $\text{PPh}_3 + \text{Li} \xrightarrow{\text{ether}} \text{LiPh} + \text{LiPPh}_2$.

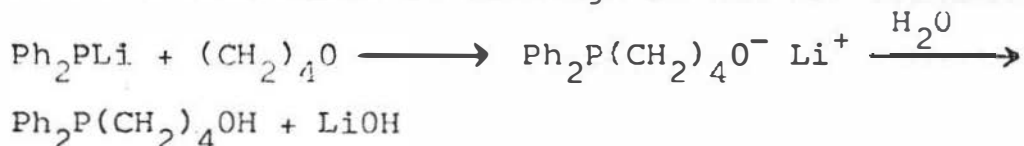
The LiPh which is produced in the reaction is a stronger base than LiPPh_2 and can be destroyed conveniently with t-butyl chloride.



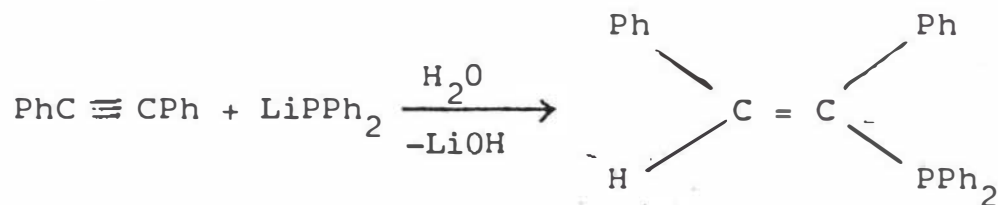
Another method of synthesizing LiPPh_2 has been reported¹² in which lithium metal is allowed to react with Ph_2PCl .



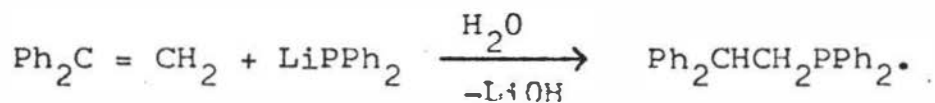
It is essential that a stoichiometric amount of Li be used as an excess leads to cleavage of the THF solvent.¹³



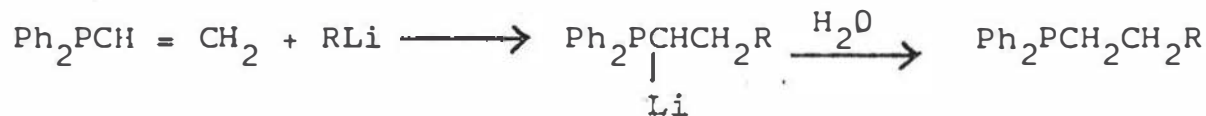
Anguilar and coworkers¹⁴ have found that LiPPh_2 reacts with diphenylacetylene to give high yields of the pure vinyl phosphine.



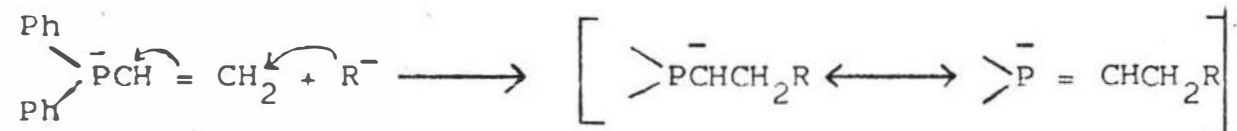
Extensive work on the addition of LiPPh_2 to olefins has been reported by Issleib and coworkers.¹⁵ It was found that LiPPh_2 adds to the double bond of $\text{Ph}_2\text{C} = \text{CH}_2$.



Organolithium reagents have been shown to react with vinyl phosphines. Peterson and coworkers¹⁶ first reported that the unsaturated linkages of vinylphosphines are subject to Michael-type addition reactions of the type



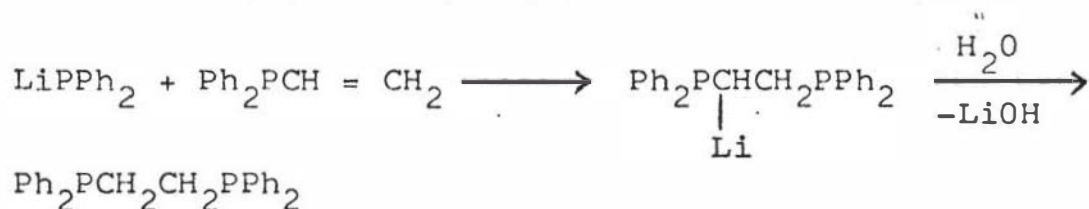
and postulated the mechanism



It appeared that the phosphino group activated the alkene linkage of the vinylphosphine toward nucleophilic addition. The activating effect was believed to be a result of the ability of trivalent phosphorus atom to stabilize the transition state for the addition reaction, by delocalization of

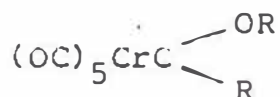
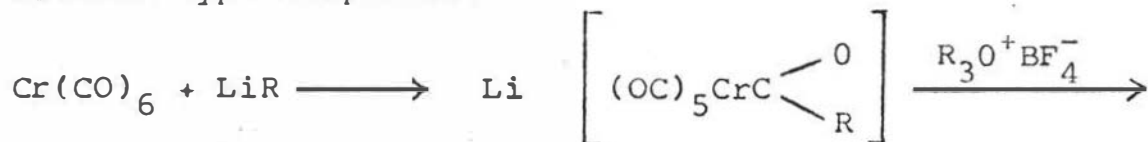
the negative charge on the α -carbon atom into its vacant d-orbitals.

Extension of the addition of LiPPh_2 to vinyl phosphines was reported by Keiter.¹⁷ It was found that LiPPh_2 reacts with diphenylvinylphosphine to form upon hydrolysis good yields of 1,2,-bis(diphenylphosphino)ethane.



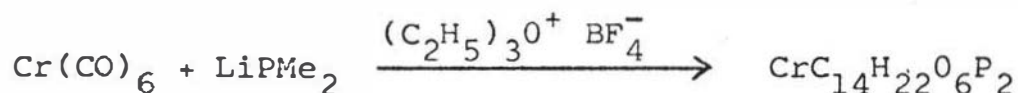
Other unsymmetrical bis tertiary phosphine ligands of the type $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhR}$ where R is methyl, ethyl, or isopropyl were synthesized by this method.¹⁸ The coordination chemistry of these ligands with Group VI metal carbonyls has also been reported in the literature.¹⁹

Though it is well established that LiPPh_2 will add across the double bond of diphenylvinylphosphine, it was not certain that it would do so when the phosphine is coordinated to a metal carbonyl. Several reactions are possible besides the addition to the double bond. It is known that organolithium reagents attack metal carbonyls to form carbene type complexes.²⁰

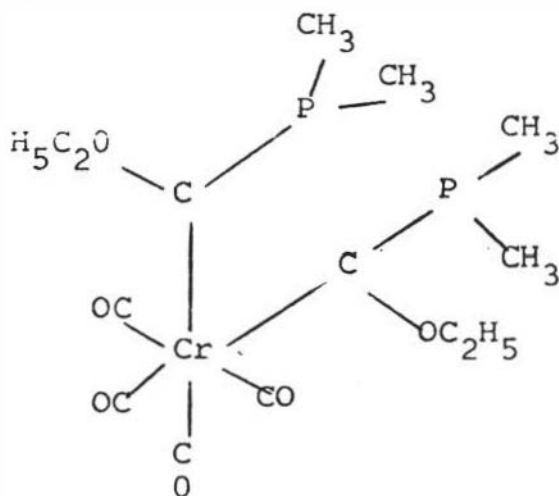


where R, R' = Me, Et, Ph.

Fischer and coworkers²¹ have reported that when LiPMe_2 reacts with Cr(CO)_6 and then is subsequently treated with $[(\text{C}_2\text{H}_5)_3\text{O}]^+\text{BF}_4^-$, a cis-(bisdimethylphosphinoethoxycarbene) tetracarbonylchromium(0) complex is formed instead of the expected dimethylphosphinoethoxycarbenepentacarbonylchromium(0).

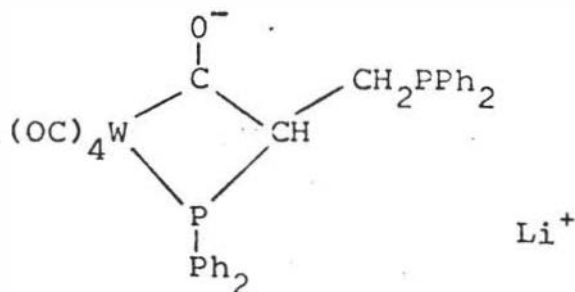


The hypothetical structure of $\text{CrC}_{14}\text{H}_{22}\text{O}_6\text{P}_2$ is thought to be as follows

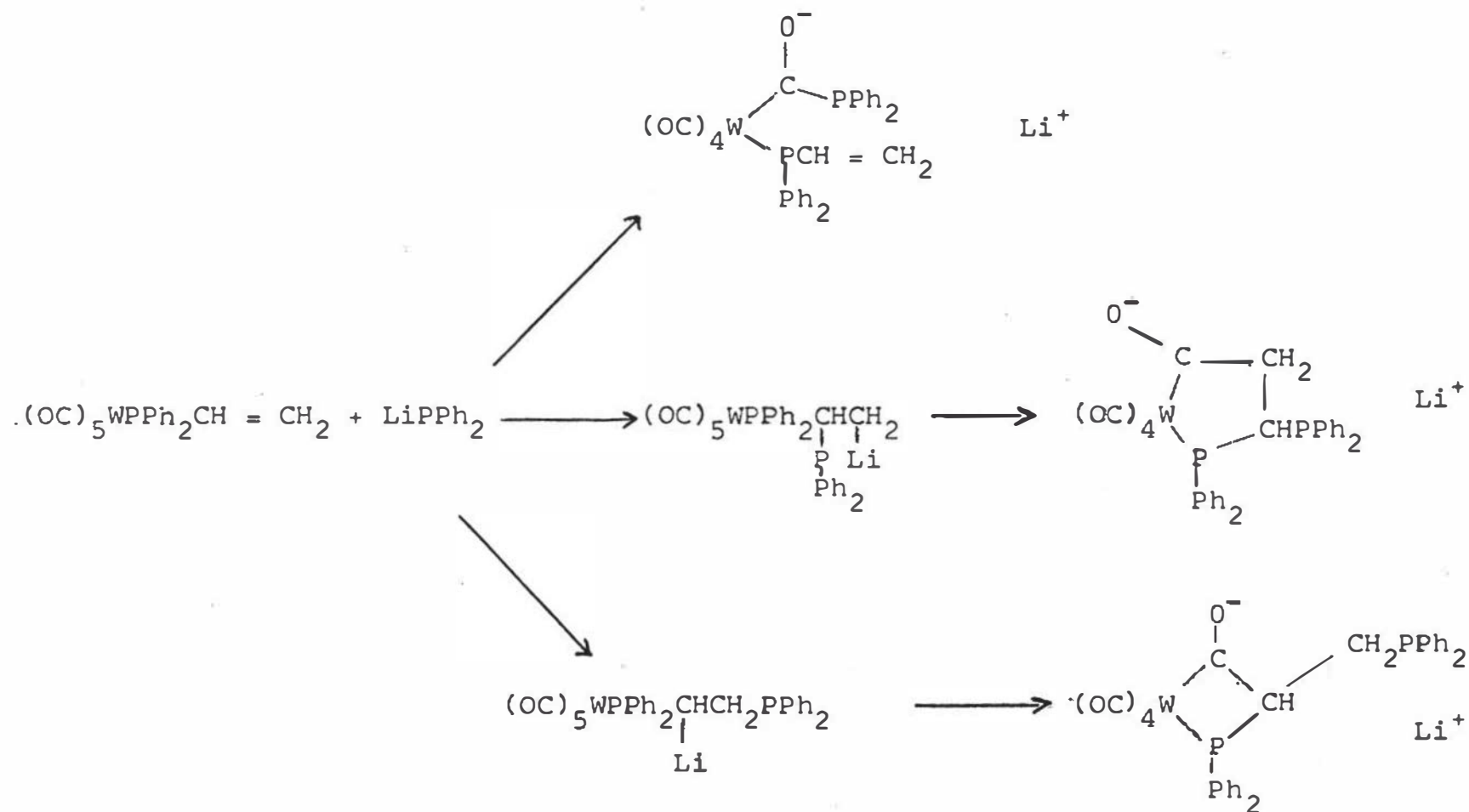


It also seemed possible that if LiPPh_2 added to $(\text{OC})_5\text{WPPh}_2\text{CH}=\text{CH}_2$ to form $(\text{OC})_5\text{WPPh}_2\text{CHCH}_2\text{PPh}_2$ the reaction

might proceed to a cyclic carbene complex



Thus at the outset of the research, based upon reactions presented above, the following possibilities had to be considered. These are shown on the following diagram.

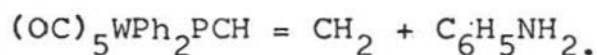
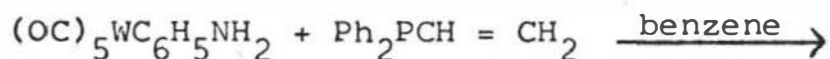


CHAPTER II

RESULTS AND DISCUSSION

The details of all syntheses described in this section are found in the experimental section.

In preparing $(OC)_5WPh_2PCH = CH_2$ the first approach was to coordinate aniline to tungsten by displacing one carbonyl of $W(CO)_6$ and then displacing aniline with $Ph_2PCH = CH_2$.



Coordination of aniline to $W(CO)_6$ was found to occur readily, and column chromatography was employed in separating the product from the starting materials. The product $(OC)_5WPh_2PCH = CH_2$ exhibits the characteristic spectrum of a monosubstituted complex $(OC)_5WL$ of C_{4v} symmetry. This spectrum strongly suggests that only the phosphorus atom is coordinated to the metal. Its ir spectrum (Figure 1) exhibits three bands in the carbonyl region of strong, weak, and very strong intensities, the 2_1A , B_1 , and E vibrational modes respectively. The 1_1A mode lies hidden within the E mode absorption. Comparison of these CO

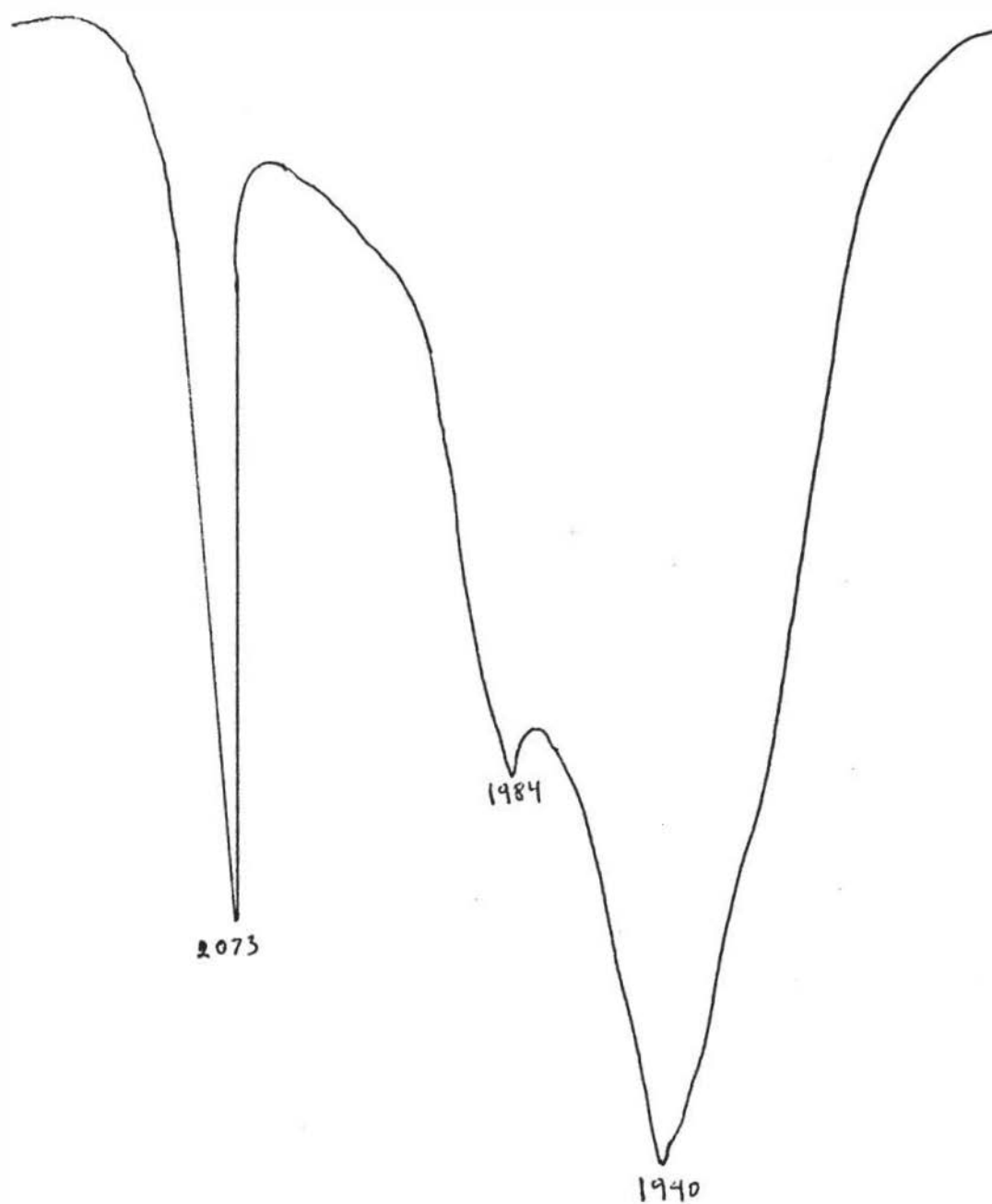
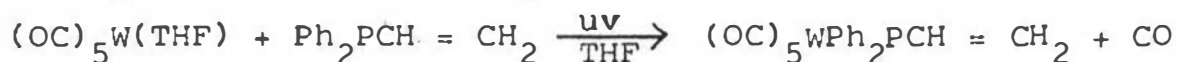
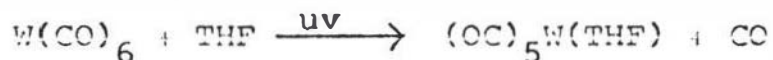


Figure 1. Expanded infrared spectrum of
 $(OC)_5WPh_2PCH=CH_2$

stretching frequencies to known frequencies of C_{4v} complexes in which only phosphorus is coordinated to the tungsten are shown in Table I.

The proton NMR spectrum of the $(OC)_5WPh_2CH=CH_2$ complex excluding phenyl protons is a complicated one of the type A_2BX . The vinyl protons are shifted downfield near the phenyl protons, and are found to absorb in the general region of 5-7 ppm (Figure 2).

A more efficient synthetic approach than that described above was found to be the direct coordination of $Ph_2PCH=CH_2$ to tungsten by displacing THF from $(OC)_5W(THF)$.



Better yields of $(OC)_5WPh_2CH=CH_2$ were obtained by this method. The product was recrystallized from methanol in which it has limited solubility, but since the melting point of the complex is low ($64^\circ C$), recrystallization was somewhat inefficient and the obtained yields were low (57%).

The double bond of the $(OC)_5WPh_2PCH=CH_2$ complex which remained free and uncoordinated to the metal was found to be subject to a Michael-type addition reaction. $LiPPh_2$, a strong Lewis base, was prepared by two different methods.

I. Reaction of Li with triphenylphosphine

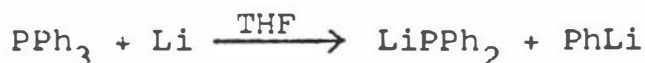


Table I

INFRARED SPECTRA OF THE CARBONYL
REGION FOR MONOSUBSTITUTED COMPOUNDS*

<u>Compound</u>	<u>Carbonyl Stretching Frequency (cm⁻¹)</u>			
Ph ₃ PW(CO) ₅	2075 s	1981 w	1942 vs	
Ph ₂ BuPW(CO) ₅	2073 s	1978 w	1938 vs	
PhBu ₂ PW(CO) ₅	2071 s	1975 w	1937 vs	
Bu ₃ PW(CO) ₅	2070 s		1934 vs	
Ph ₂ MePW(CO) ₅	2073 s	1979 w	1939 vs	
Ph ₂ EtPW(CO) ₅	2073 s	1979 w	1938 vs	
Ph i-PrPW(CO) ₅	2074 s	1979 w	1937 vs	
Ph ₂ t-BuPW(CO) ₅	2072 s	1979 w	1937 vs	
CH ₂ =CHPh ₂ PW(CO) ₅	2073 s	1984 w	1940 vs	

s, strong; w, weak; vs, very strong

*D. A. Wheatland, Ph.D. Dissertation, "Tertiary Phosphine Derivatives of the Group VI Metal Carbonyls," University of Maryland (1967)

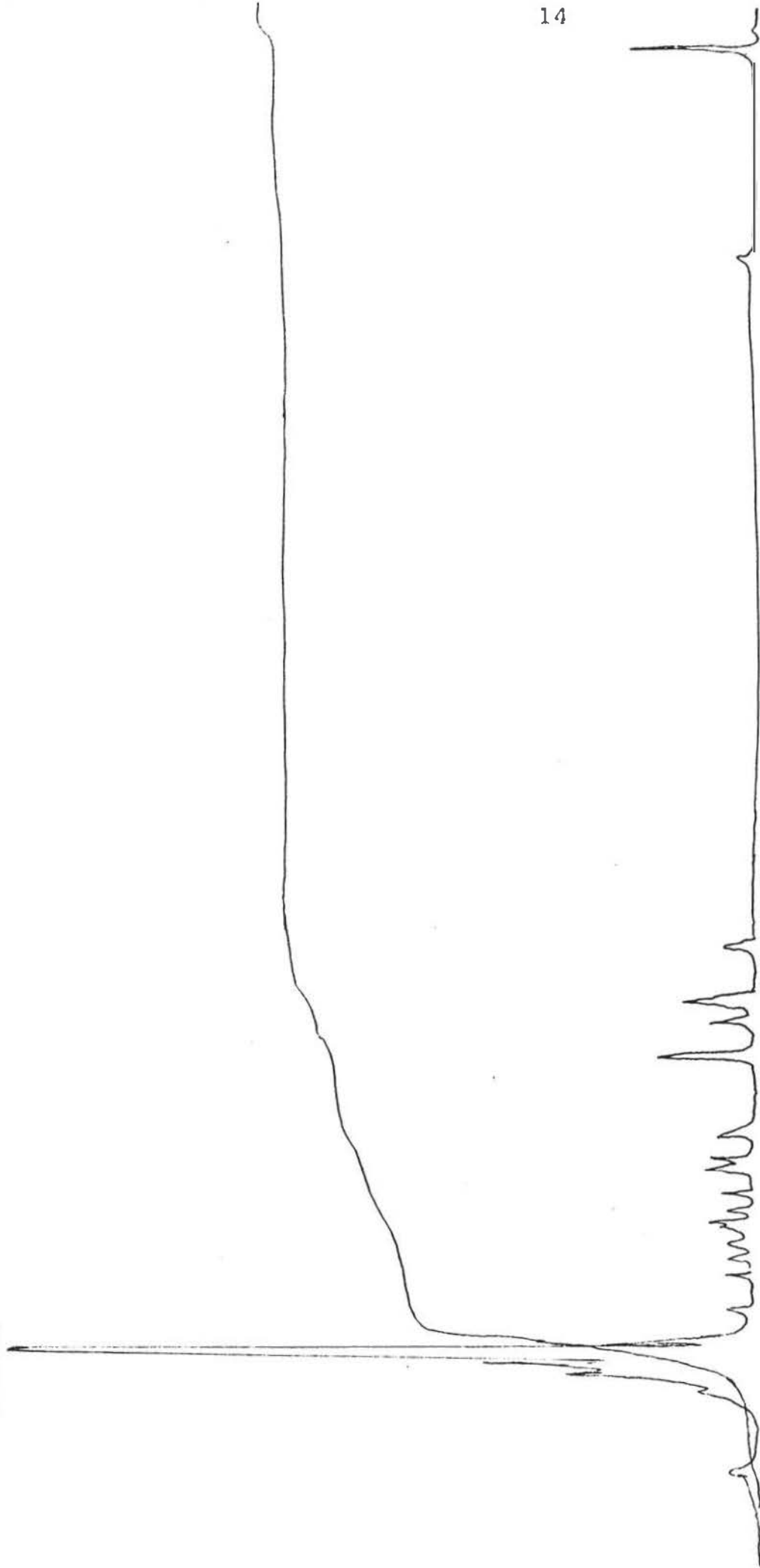
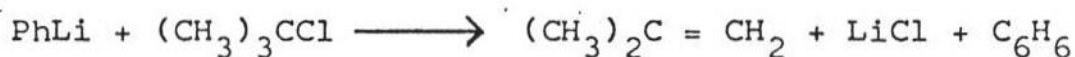


Figure 2. NMR Spectrum of $(OC)_5WPh_2PCH=CH_2$

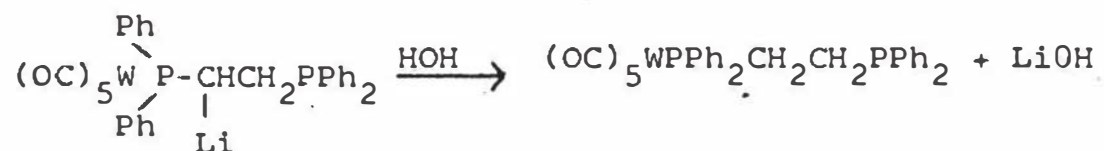
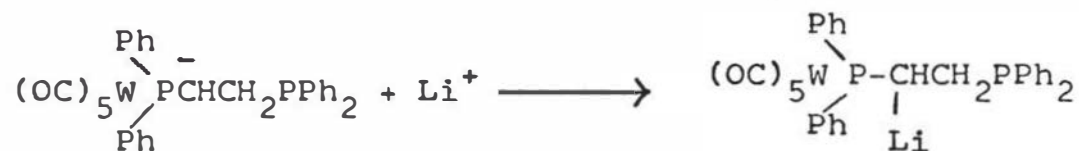
A stoichiometric amount of t-butyl chloride was added to destroy the PhLi.



II. Reaction of Li with chlorodiphenylphosphine



The second method was more efficient than the first since it involved only a single reaction, but care must be taken to avoid an excess of Li. Excess Li may react with THF (See page 4). In both methods the deep-red color of the resulting solutions served as an indicator of the existence of LiPPh_2 in the solution. LiPPh_2 adds readily across the double bond of $(\text{OC})_5\text{PPh}_2\text{CH} = \text{CH}_2$. The following reaction was found to have taken place and is believed to proceed by the mechanism presented.



The melting point, infrared spectrum (Figure 3) and proton NMR spectrum (Figure 4) of the hydrolyzed product are in agreement with those reported in the literature² for

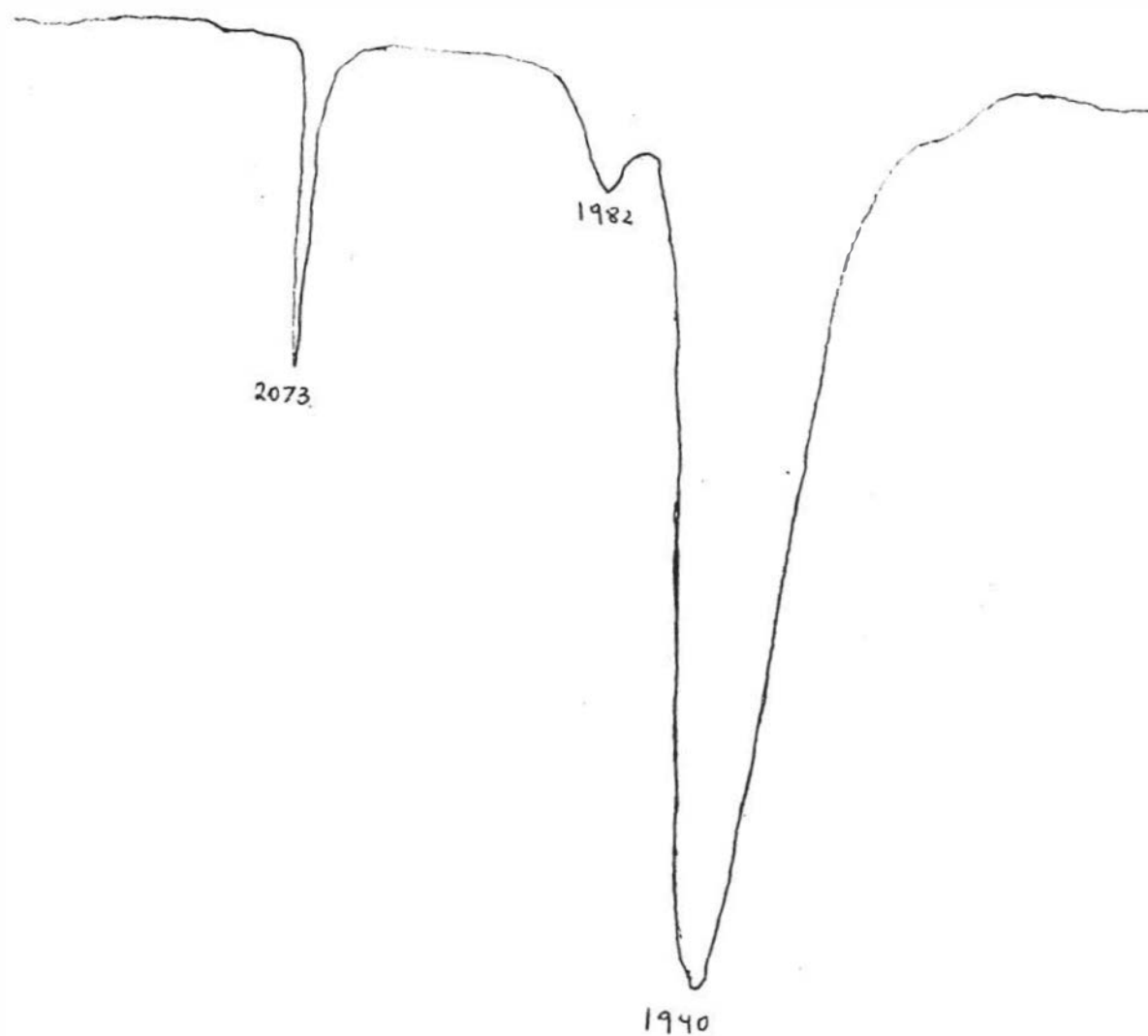


Figure 3. Expanded Infrared Spectrum of
 $(OC)_5WPh_2PCH_2CH_2PPh_2$

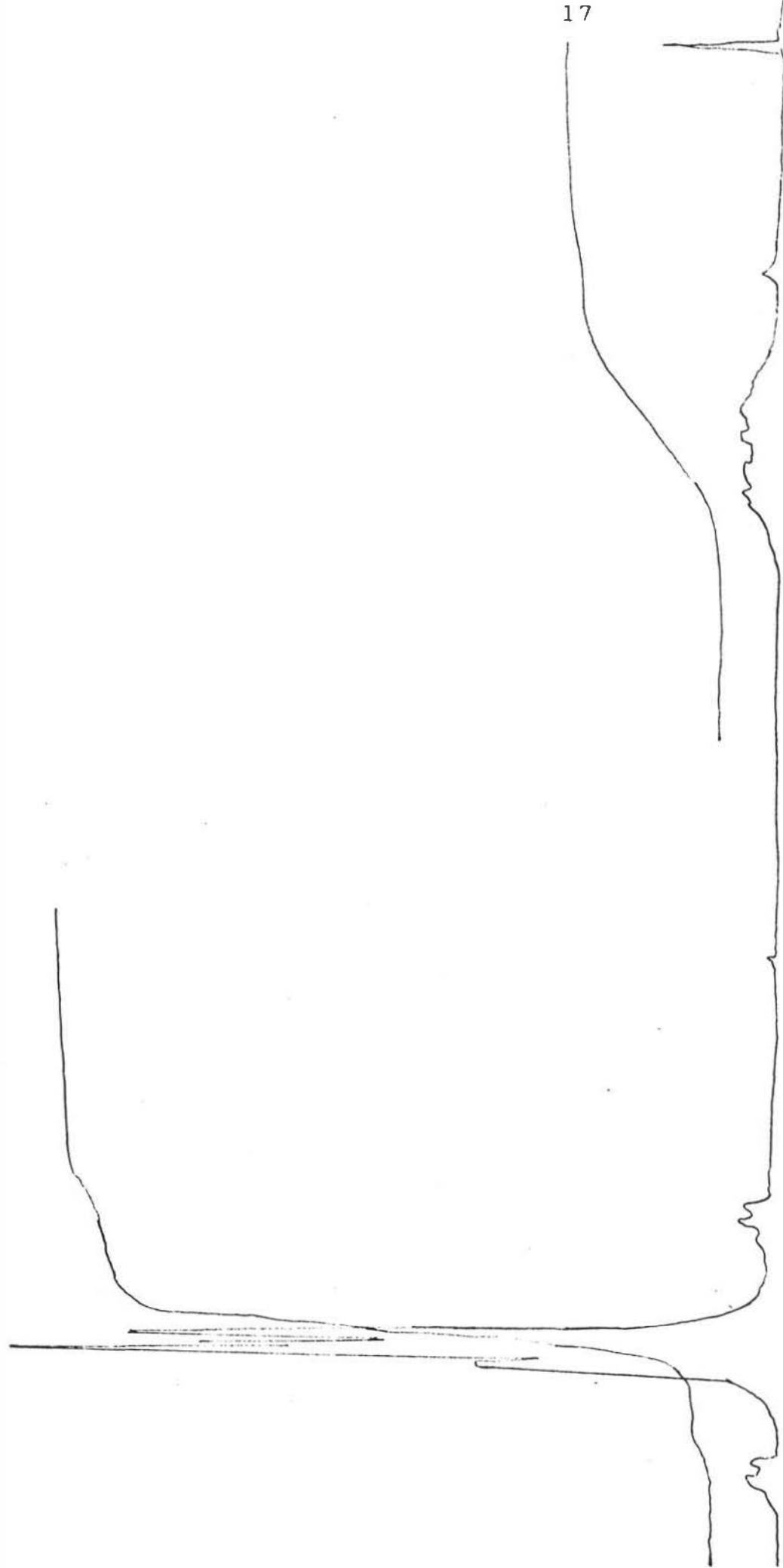
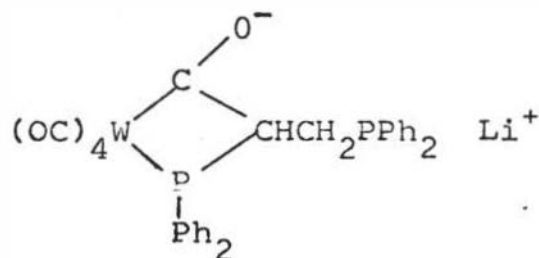


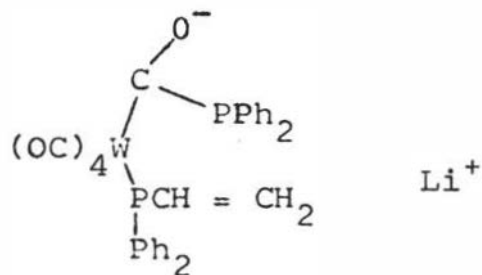
Figure 4. NMR Spectrum of $(OC)_5WPh_2PCH_2CH_2PPh_2$

$(OC)_5WPh_2CH_2CH_2PPh_2$. The ir spectrum exhibited the three bands, 2A_1 , B_1 , E , of a C_{4v} symmetry complex at 2074 cm^{-1} , 1988 cm^{-1} , and 1940 cm^{-1} respectively. The NMR spectrum excluding the phenyl protons is of the type XA_2B_2M and is quite complicated in the methylene region. An unresolved peak is found at 1.6-2.7 ppm.

No evidence of the formation of secondary products was obtained. The Li complex did not cyclize to form a cyclic carbene product



This could be interpreted in terms of the strain that such a ring would have and the instability of the resulting complex. Also, there was no evidence of the formation of a carbene complex of the type

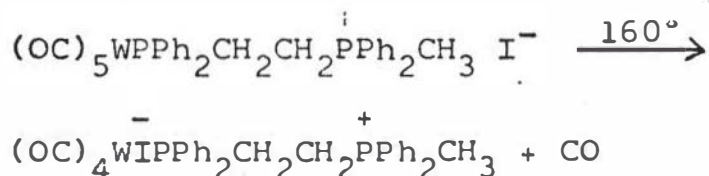


The LiPPh_2 preferentially attacked the double bond of the phosphine ligand over the carbonyls.

The quaternized salt of $(OC)_5WPh_2PCH_2CH_2PPh_2$ with CH_3I was easily obtainable when excess of CH_3I was employed. The product $(OC)_5WPh_2CH_2CH_2PPh_2CH_3^+ I^-$ (mp 168°C) exhibited the characteristic infrared bands of C_{4v} symmetry the

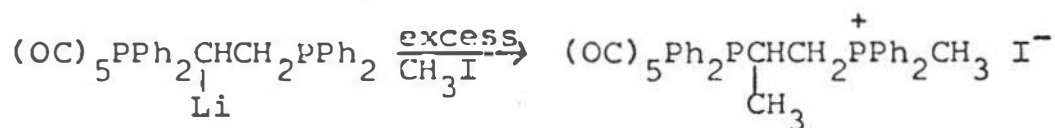
2_1A , B_1 , and E modes at 2076 cm^{-1} , 1980 cm^{-1} , and 1938 cm^{-1} respectively (Figure 5). The proton NMR spectrum (Figure 6) showed a doublet centered at 3.1 ppm. The coupling constant of phosphorous to the methyl protons was measured to be 13.6 Hz.

During the melting point determination of the $(OC)_5WPPh_2CH_2CH_2P^+Ph_2CH_3 I^-$ salt, at temperatures near 160°C it was noted that the pale yellow crystals started changing to a green-yellow color accompanied by the evolution of gas. This was attributed to the removal of one of the carbonyls from the coordination sphere of the tungsten and the insertion of the iodine ion as indicated in the following reaction



A search in the literature revealed that this interpretation was consistent with the recently reported²² syntheses of carbonyl halide zwitterionic complexes of the type $cis-(OC)_4X^+M^+PPh_2(CH_2)_nP^+Ph_2R$ in which M is tungsten and X is iodine.

An attempt to add CH_3I to the $(OC)_5PPh_2CHCH_2PPh_2Li$ complex was made before hydrolyzing the complex. The methyl group of CH_3I would be expected to replace lithium and form the salt, $(OC)_5PPh_2CHCH_2P^+Ph_2CH_3 I^-$ when excess CH_3I is employed.



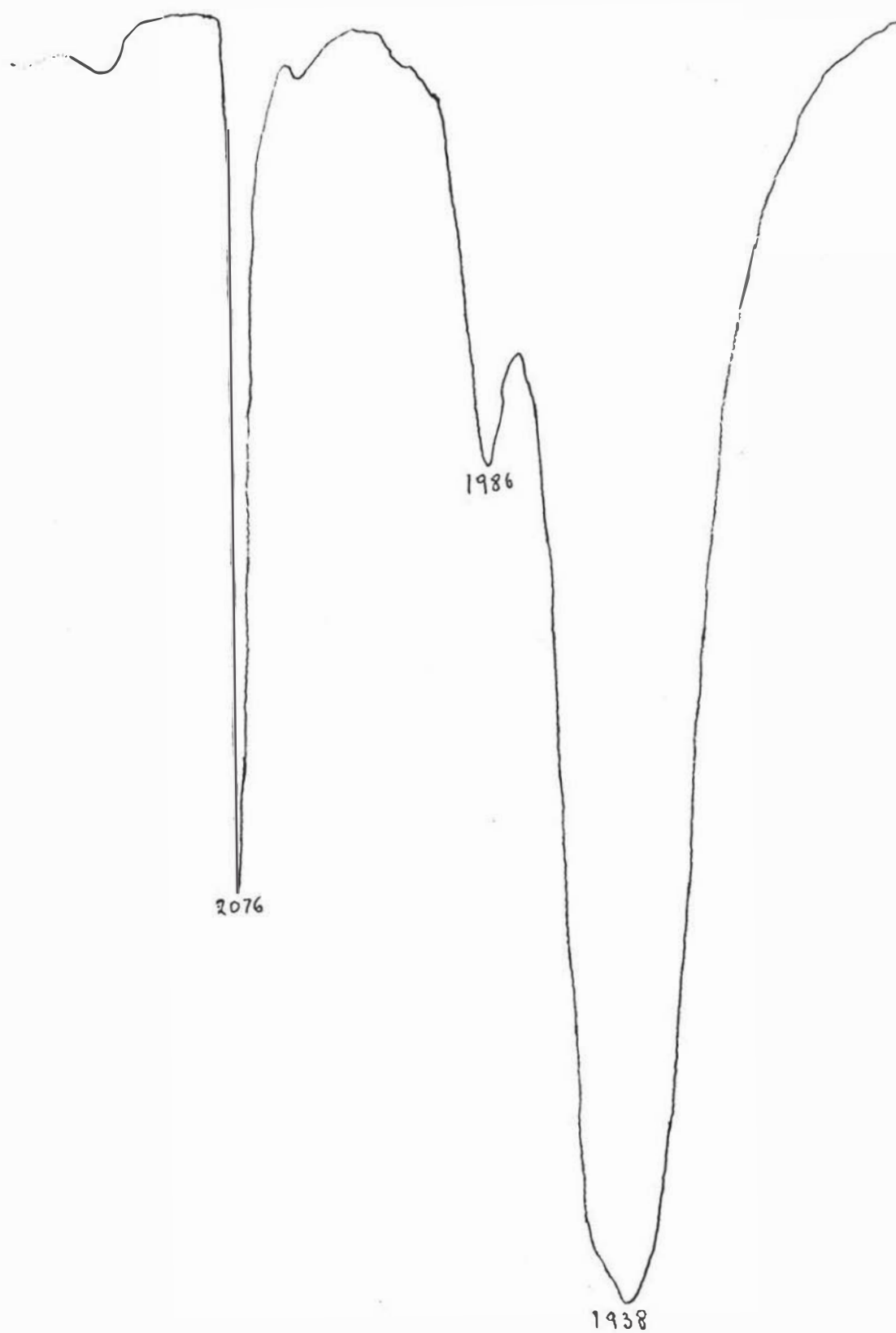
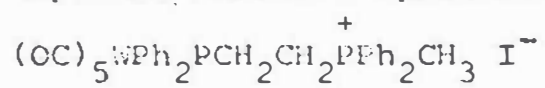


Figure 5. Expanded Infrared Spectrum of



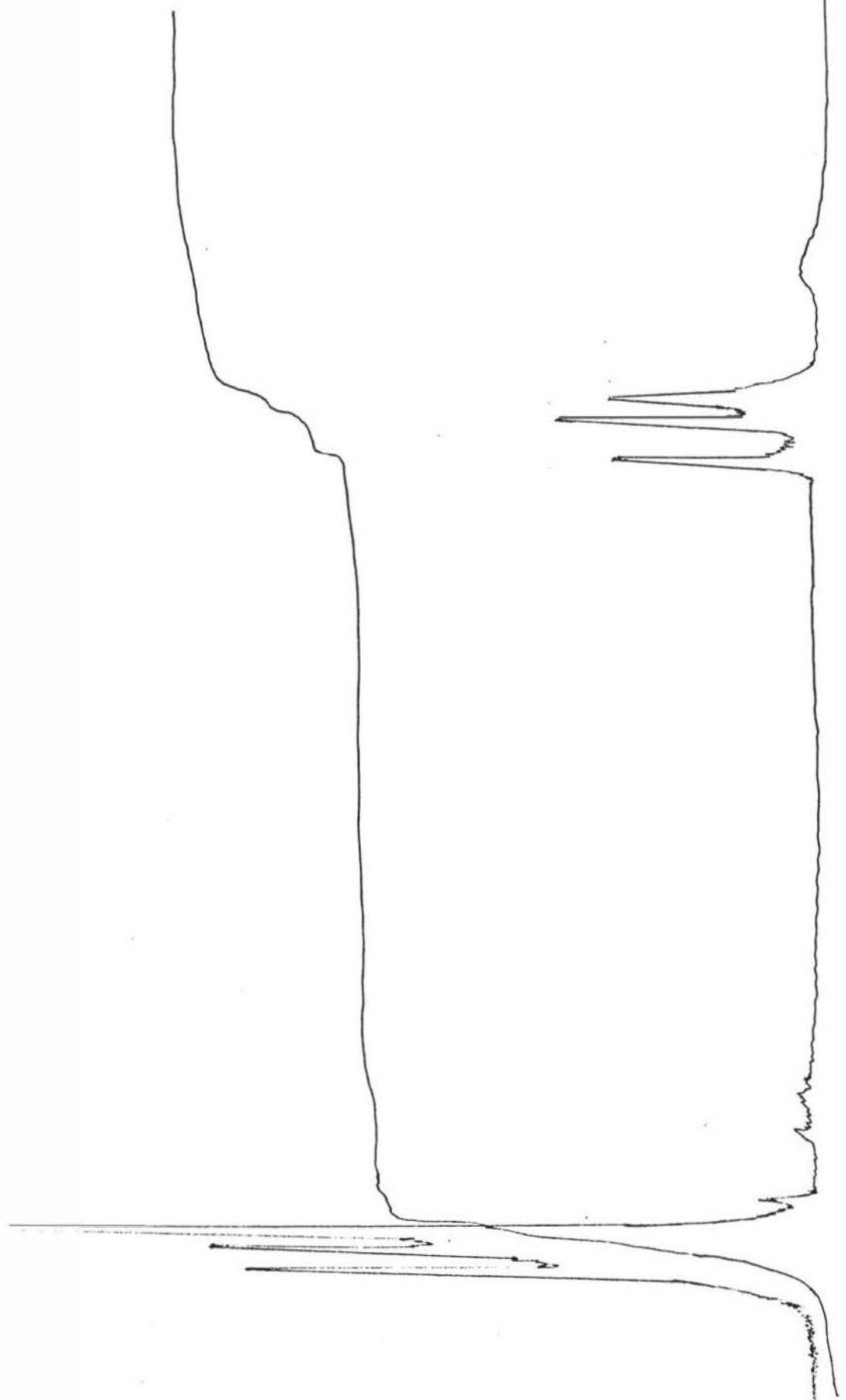


Figure 6. NMR Spectrum of $(OC)_5WPPh_2CH_2CH_2PPh_2CH_3 I^-$

The first time the reaction was run $(OC)_5WPPh_2CH_2CH_2CH_2^+PPh_2CH_3 I^-$ was obtained as the only product. The lithium complex had been hydrolyzed during the process. Apparently moisture in the apparatus was sufficient to hydrolyze the complex. The reaction was repeated and all equipment was dried with a heat gun under a stream of dry nitrogen. The reaction was not straightforward, and a mixture of products was obtained. Thin layer and column chromatography were employed in separating the reaction products and only one solid residue was obtained. The rest of the products remained as an oil and were not identified. An ir spectrum of the impure residue exhibited three bands at 2073 cm^{-1} , 1980 cm^{-1} , and 1938 cm^{-1} characteristic of a monosubstituted $W(CO)_6$ product (Figure 7). The NMR spectrum was complicated in the methylene region though one observes a doublet centered at 1.4 ppm (Figure 8) which could be interpreted as splitting of the methane protons attached to the methylene group ($J_{H-CH_3} = 6.0\text{ Hz}$). All attempts to recrystallize this solid residue failed.

The potential formation of a carbene complex from $(OC)_5WPPh_2CHCH_2PPh_2$ was further investigated by heating the lithium complex in diglyme under carefully dried conditions. The precipitate of the reaction was a high melting point solid (mp $> 250^\circ\text{C}$). The insolubility of this solid prevented the application of the usual purification techniques and the compound was therefore not analyzed. An infrared

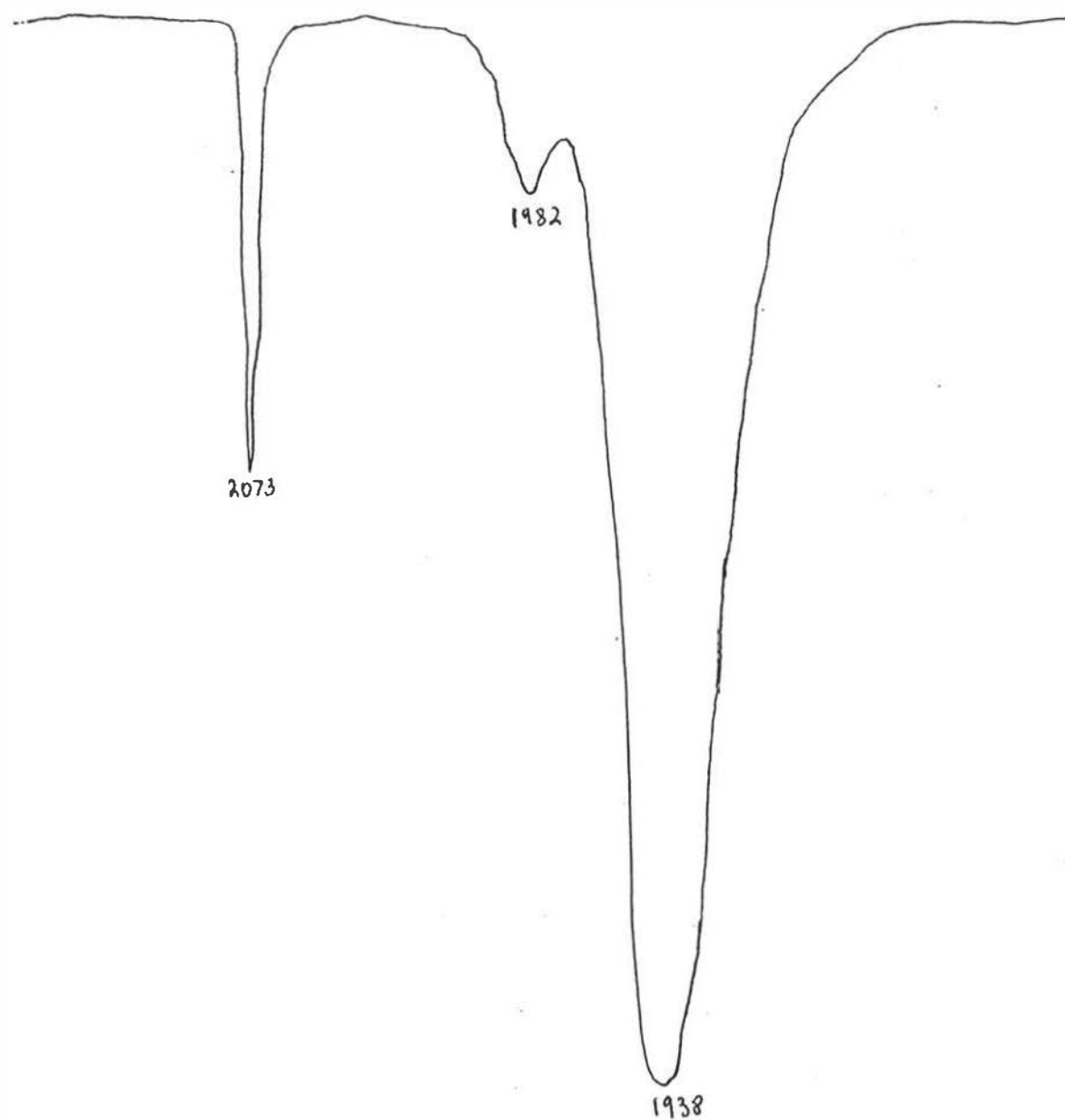
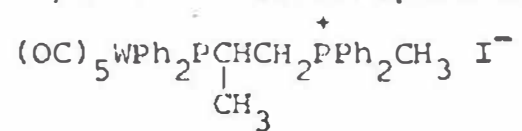


Figure 7. Expanded Infrared Spectrum of



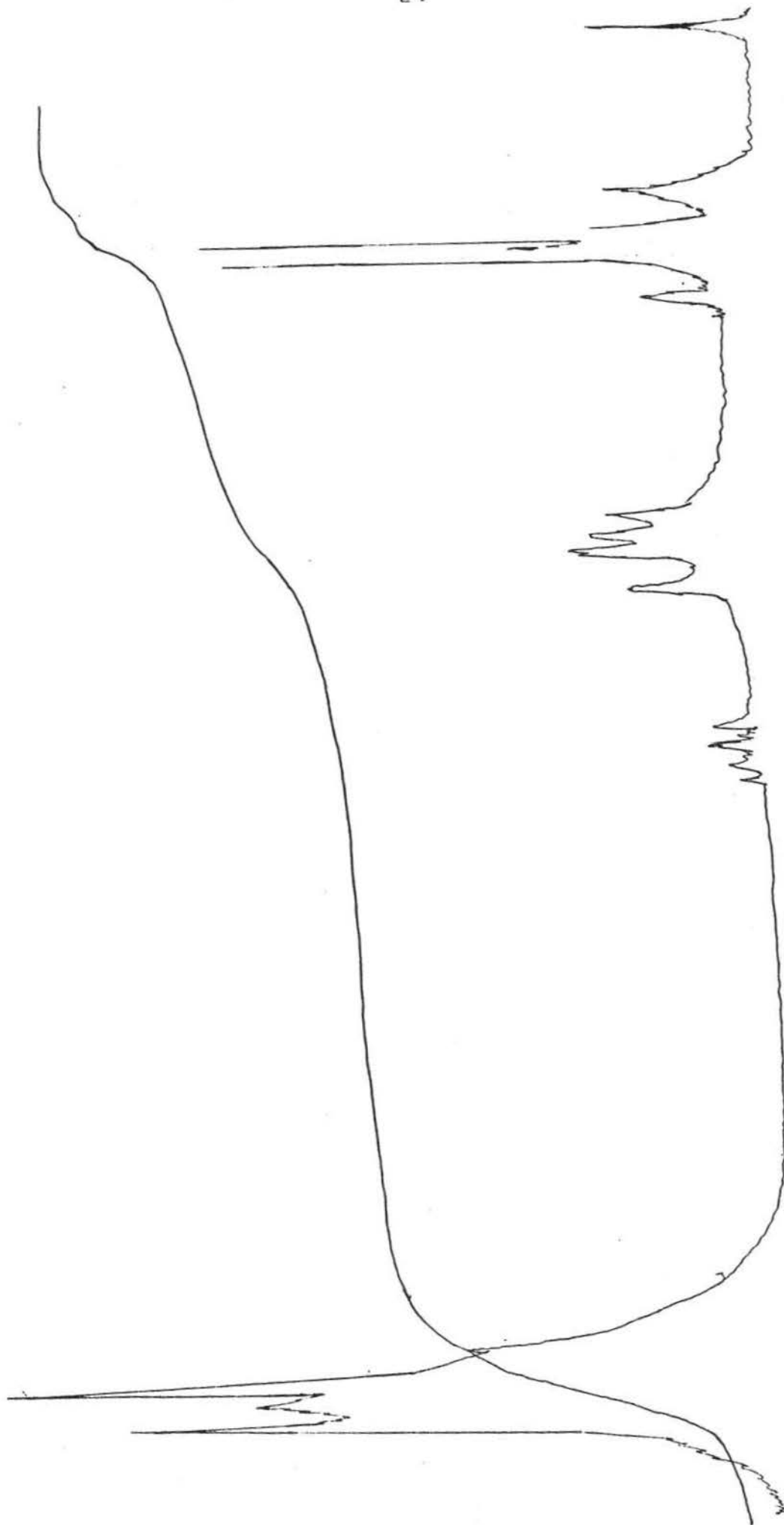


Figure 8. NMR Spectrum of $(OC)_5WPPh_2PCH(CH_3)_2PPh_2CH_3 I^-$

spectrum of the impure solid (Figure 9) did not indicate the formation of a monosubstituted or disubstituted $W(CO)_6$ alone. It appears that a polymer had formed and as the product is only partially soluble in $CDCl_3$ no NMR spectrum could be obtained.

Since it was evident that $LiPPh_2$ preferentially attacks the double bond of $(OC)_5WPPh_2CH = CH_2$, the activity of the vinyl bond towards addition reactions was further investigated. A 1% Br_2 in CCl_4 solution was added to $(OC)_5WPh_2PCH = CH_2$. A white precipitate immediately formed. As the addition proceeded the color of the precipitate started changing from white to blue. This indicated that oxidation of the metal to tungsten blue had taken place. The possibility of a polymer formation was also investigated. A search in the literature²³ revealed that Group VI metal carbonyls in the presence of CCl_4 may act as initiators for the free radical polymerization of molecules containing an unsaturated site. The reaction was repeated and the very first precipitate was collected. A quantitative analysis of this product was indicative of polymer formation. The infrared spectrum (Figure 10) of this precipitate indicated a monosubstituted $W(CO)_6$, but the NMR spectrum showed that starting material was not present (Figure 11).

More puzzling results were obtained when $PhLi$ was allowed to react with $(OC)_5WPPh_2CH = CH_2$. Since $PhLi$ is a stronger base than $LiPPh_2$, one would expect that $PhLi$ would have been added even more readily across the double bond

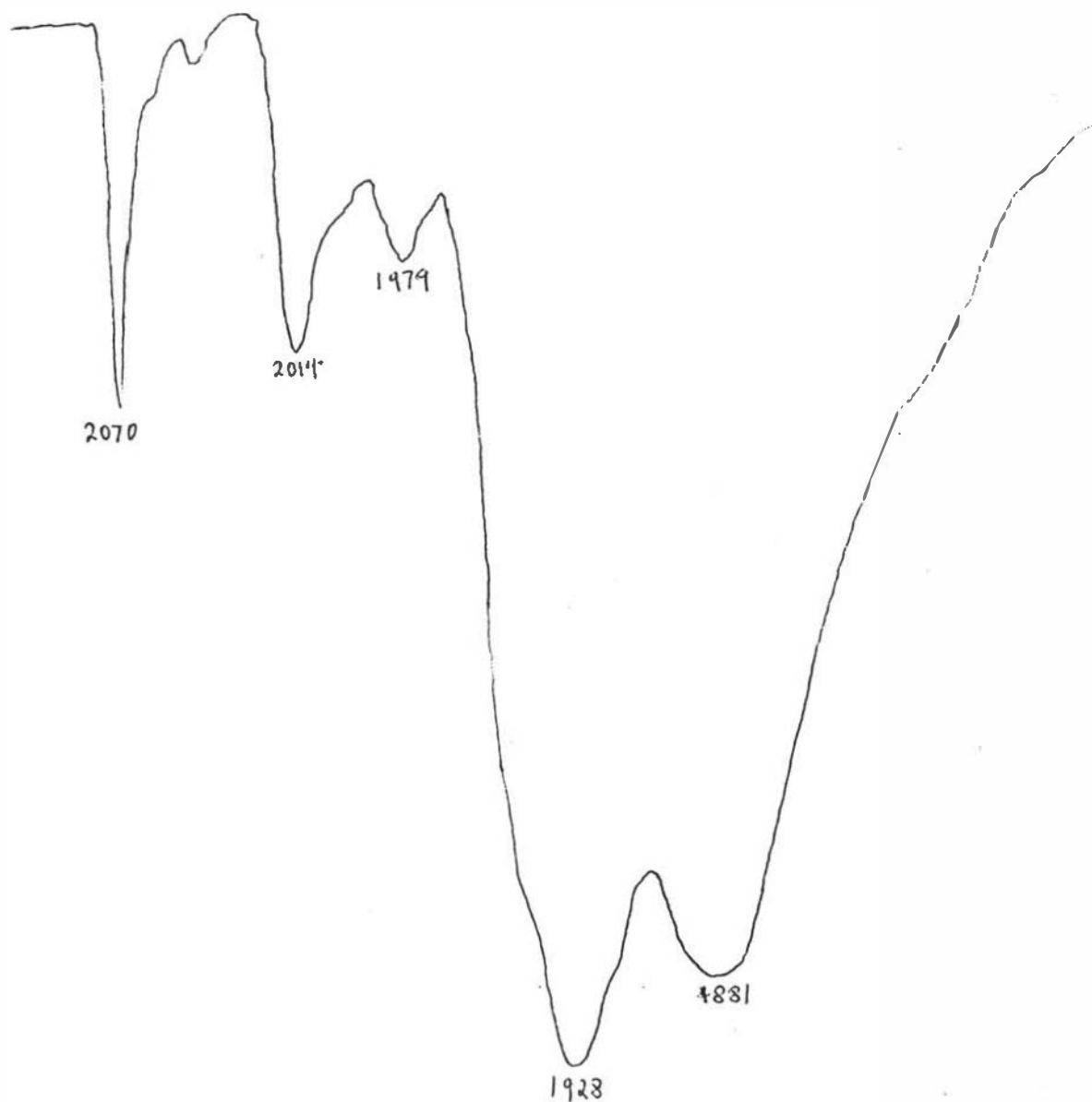


Figure 9. Expanded Infrared Spectrum of the product resulted after refluxing $(OC)_5LiPh_2PClCH_2PPh_2$

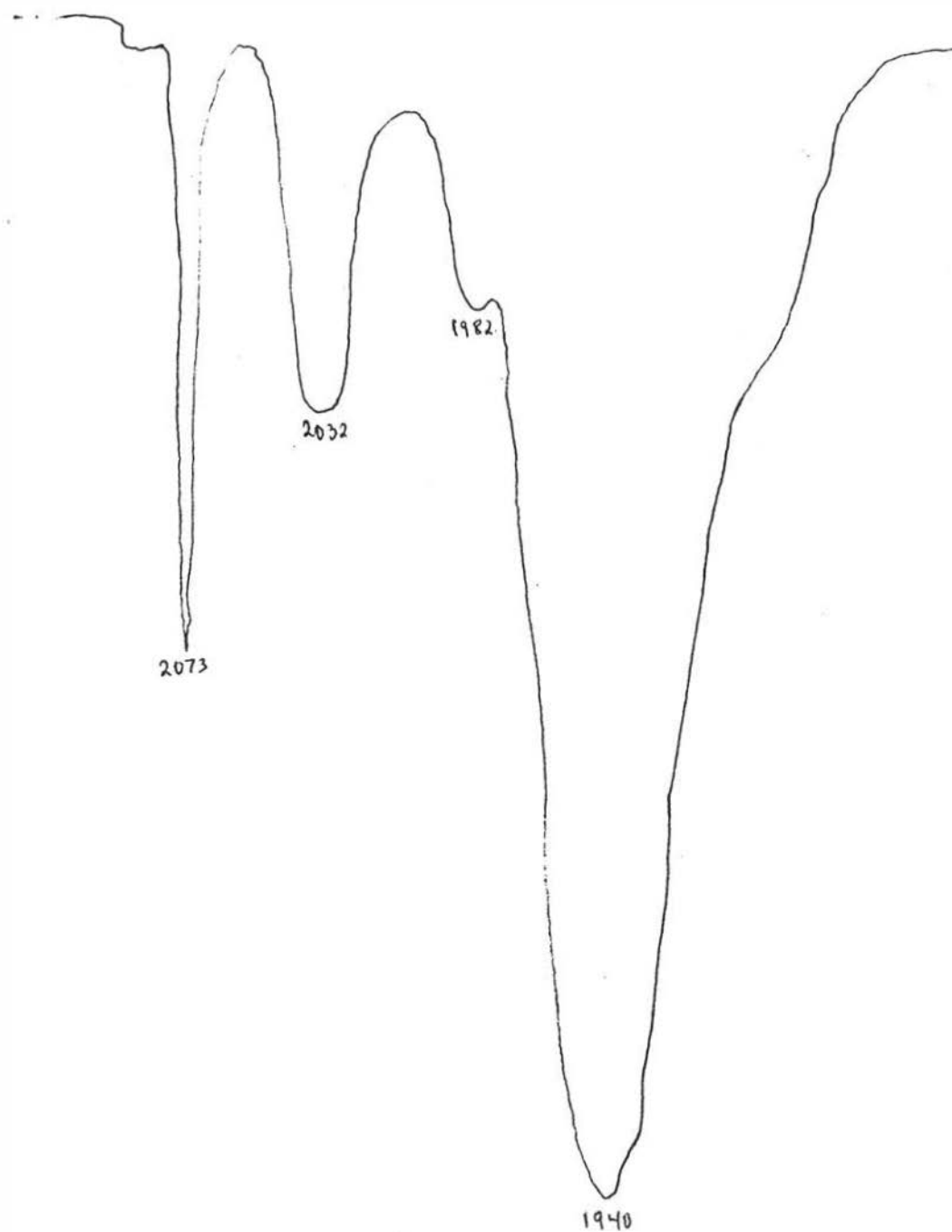


Figure 10. Expanded Infrared Spectrum of the product from the Reaction $(OC)_5WPh_2CH = CH_2 + Br_2$

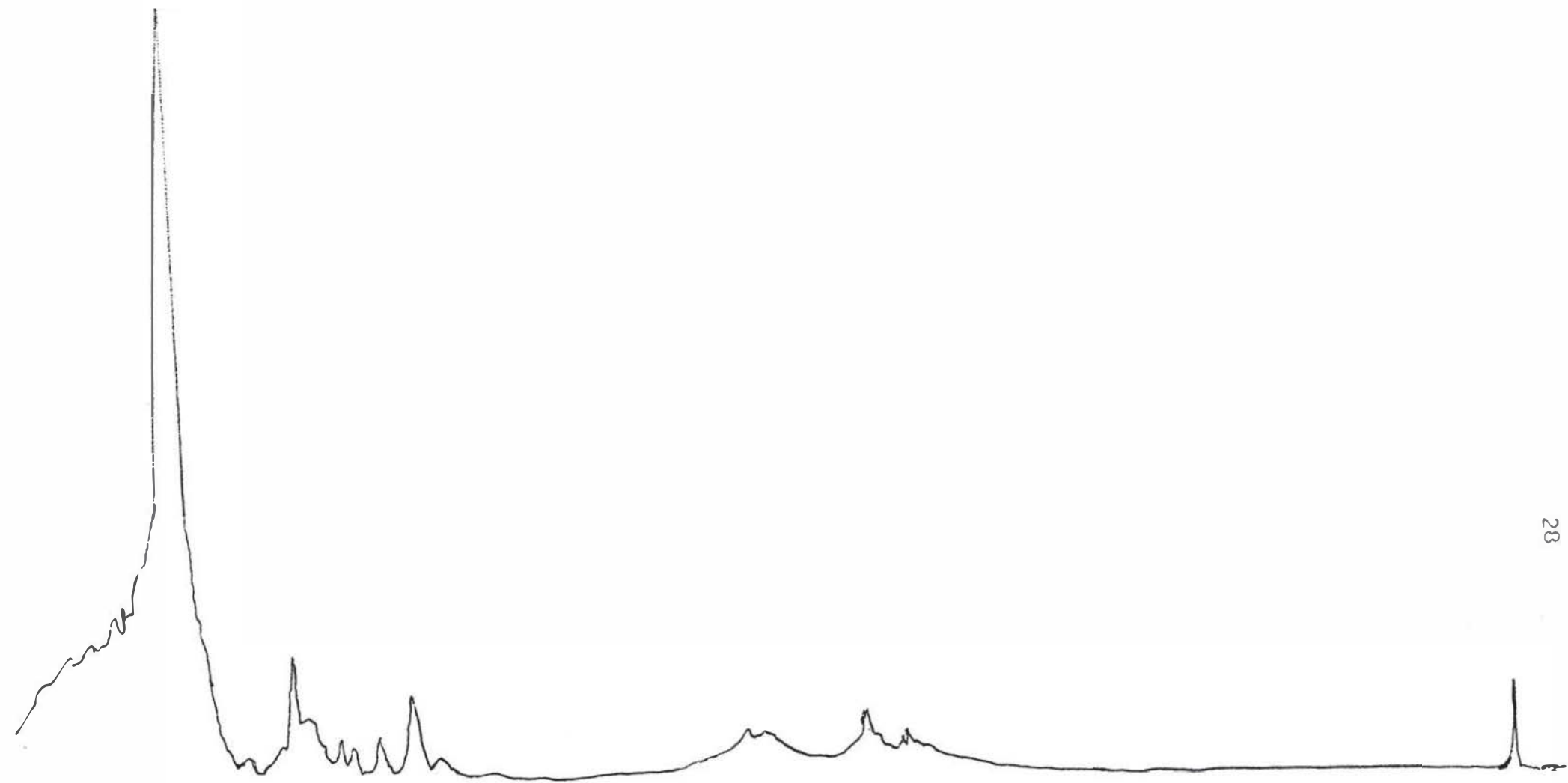
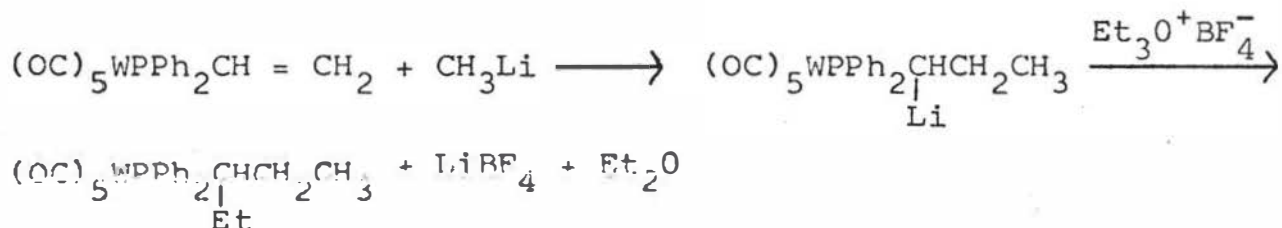


Figure 11. NMR Spectrum of the product from the reaction
 $(OC)_5WPh_2CH = CH_2 + Br_2$

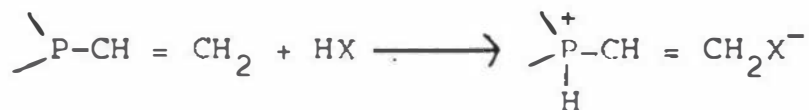
than LiPPh_2 . The same experimental procedure with the one used for the LiPPn_2 addition was employed, but no evidence of a reaction was obtained and an NMR spectrum of the resulting product indicated that only starting material was present (Figure 12).

The same results were obtained when CH_3Li was allowed to react with $(\text{OC})_5\text{WPPh}_2\text{CH}=\text{CH}_2$. The alkylating agent $\text{Et}_3\text{O}^+\text{BF}_4^-$ was also employed for the reaction in order to remove the Li from the α -carbon of the expected product.



No reaction occurred and an NMR spectrum of the recovered material (Figure 13) indicated that only starting material was present.

The unexpected results from the above reactions, however, are not unique. A search in the literature on Michael-type addition reactions to vinyl phosphines revealed that similar results have been obtained; Kabachnik and co-workers have reported²⁴ that di-n-butylvinylphosphine is inert to piperidine at 160° . However, the desired addition reaction was realized when run in the presence of an acid catalyst.



As suggested by Kabachnik this finding would appear to be



Figure 12. NMR Spectrum of the recovered material from the reaction

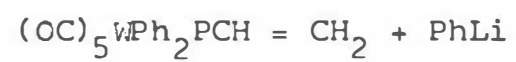
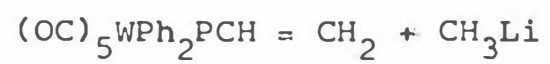




Figure 13. NMR Spectrum of the recovered material from the reaction



consistent with the addition reaction being preceded by a conversion of the vinylphosphine to the more reactive vinylphosphonium salt. Therefore, no final conclusion concerning the inactivity of the vinyl bond of $(OC)_5WPPh_2CH = CH_2$ toward the addition of CH_3Li or $PhLi$ may be drawn from this study until further investigation of the reaction conditions.

CHAPTER III

EXPERIMENTAL

A. General Considerations and Comments on the Preparative Methods

The handling of tertiary and halophosphines used in the preparations requires a great deal of care. The compounds are sensitive to oxidation by air, toxic to some degree, and there is also a somewhat unpleasant odor associated with these compounds. For these reasons all reactions involving phosphines were performed under an atmosphere of nitrogen and in a well-ventilated hood. Direct exposure to the atmosphere was kept at a minimum.

The solvents employed in the preparations, tetrahydrofuran (THF) and diethyleneglycolmethylether (diglyme) have to be extremely dry. Drying was accomplished by refluxing the solvent in the presence of sodium metal and benzophenone under an atmosphere of nitrogen. Sodium will react with benzophenone to form a deep blue ketyl;²⁵ however, the ketyl will not form in the presence of water or oxygen. The blue color therefore serves as an indicator of dryness. Dry solvent was distilled from the deep blue solution just before use for the reactions.

Tungsten hexacarbonyl and diphenylvinylphosphine were obtained from Pressure Chemical Company and

chlorodiphenylphosphine, methyllithium and phenyllithium were obtained from Ventron Chemical Co.

Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 grating infrared spectrometer. Expanded spectra were recorded with an E. H. Sargent recorder JR, and are considered to be accurate to $\pm 1 \text{ cm}^{-1}$.

Proton NMR spectra were measured with a Varian T60 spectrometer. Saturated deuteriochloroform solutions containing tetramethylsilane as an internal reference were used for all ligands and complexes.

Melting points were taken with an Arthur H. Thomas Unimelt apparatus, and are reported uncorrected.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

B. Preparations of Complexes

1. Preparation of 1,2-bisdiphenylphosphinoethane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$

Diphenylvinylphosphine 6.0 g (0.028 mol) was dissolved in 50 ml of anhydrous tetrahydrofuran (THF), and the solution was placed in a three neck flask equipped with a reflux condenser, a pressure-equalizing addition funnel and a nitrogen flow stopper. The solution was cooled to $+2^\circ\text{C}$ by immersion of the flask in an ice bath, and 5.4 g (0.028 mol) of lithium diphenylphosphide (LiPPh_2) in 75 ml of anhydrous tetrahydrofuran was added dropwise over a period of half an hour. The solution was allowed to warm to room temperature and

stirred vigorously under reflux for a period of two hours. The flask was then cooled in an ice bath and a 11 ml saturated ammonium chloride solution was added and the color of the solution changed from red to green. The solvent was removed by means of the rotary evaporator and a thick gray oil resulted. Sufficient petroleum ether (30°-60°C) was added to crystallize the product. The product (yield 40%) was recrystallized from absolute ethanol (mp 141°-142°C).

2. Preparation of Lithium diphenyl phosphide, $\text{LiP}(\text{C}_6\text{H}_5)_2$

A. Triphenylphosphine method:

Triphenylphosphine (10.0 g, 0.038 mol) was dissolved in 100 ml of anhydrous tetrahydrofuran (THF) which had previously been de-oxygenated by bubbling nitrogen through it for 10 min. The solution was placed in a 250 ml three-neck flask equipped with a nitrogen flow stopper and a magnetic stirrer. Strips of clean lithium wire were added in excess, (1.0 g, 0.14 mol) and the solution was stirred at room temperature under nitrogen for several hours. A dark red solution of lithium diphenylphosphide, $\text{LiP}(\text{C}_6\text{H}_5)_2$ and phenyllithium ($\text{C}_6\text{H}_5\text{Li}$) resulted. A solution of t-butylchloride (3.5 g, 0.038 mol) in 25 ml of tetrahydrofuran was added to destroy the phenyllithium. The resulting solution was filtered through glass wool, under nitrogen, directly into a reaction vessel for further use.

B. Chlorodiphenylphosphine method:

Chlorodiphenylphosphine (1.1 g, 0.0050 mol) was dissolved in 50 ml of anhydrous, de-oxygenated tetrahydrofuran, and the solution was placed in a similar reaction apparatus as the preceding one. Strips of lithium wire were added in excess (0.5 g, 0.07 mol) and the solution was stirred at room temperature for a period of 2 hrs. A dark red solution of lithiumdiphenylphosphide, $\text{LiP}(\text{C}_6\text{H}_5)_2$, and a fine precipitate of lithium chloride, LiCl , resulted. The solution was filtered through glass wool under nitrogen directly into a reaction vessel for further use.

3. Preparation of Anilinepentacarbonyl tungsten, $\text{C}_6\text{H}_5\text{NH}_2\text{W}(\text{CO})_5$

Tungstenhexacarbonyl (8.7 g, 0.024 mol) and freshly redistilled aniline (10.0 g, 0.10 mol) were dissolved in 300 ml of dry tetrahydrofuran (THF) and placed in a light reaction vessel equipped with a magnetic stirrer and wrapped with aluminum foil to keep exposure of the radiation to the environment at a minimum. The solution was irradiated with a uv light for a period of seven hr. The resulting yellow solution was evaporated to a thick oil by means of a rotary evaporator, and water and dilute hydrochloric acid were added until the oil became a yellow solid. The mixture was then filtered and the collected precipitate was dissolved in a minimum amount of benzene and filtered again, to remove most of the unreacted tungsten hexacarbonyl. The filtrate was brought to dryness and an infrared spectrum of the resulting

solid indicated the presence of $C_6H_5NH_2W(CO)_5$ and some $W(CO)_6$. These traces of $W(CO)_6$ were removed by sublimation leaving pure product (6.5 g, 66.0%).

4. Preparation of diphenylvinylphosphinepentacarbonyl-tungsten(0), $(CO)_5WP(C_6H_5)_2CH = CH_2$

A. Anilinepentacarbonyl tungsten method

In a 200 ml round bottom flask containing 75 ml of benzene 3.2 g (0.0076 mol) of anilinepentacarbonyl-tungsten was dissolved, and to the solution 1.5 ml (1.62 g, 0.0076 mol) of diphenylvinyl phosphine was added by means of a calibrated syringe. The operation was performed in a nitrogen bag. The solution was allowed to stand for 24 hours at room temperature, and then it was filtered and taken to a thick oil with the rotary evaporator. The oil was dissolved in a minimum amount of dichloromethane-methanol mixture, but failed to produce crystals upon refrigeration. The solution was then brought to dryness and the residue was eluted on a silica gel column with a solution of petroleum ether-ethyl acetate (4:1). The diphenylvinylphosphine pentacarbonyl tungsten came off first, followed by the starting carbonyl complex and aniline. A third component did not come off and remained unidentified. The derived product was dissolved in a minimum amount of absolute methanol and cooled to $-5^\circ C$. Pale yellow crystals slowly formed. These crystals were recrystallized from methanol

to produce white crystals (yield 1.6 g, 40%)
(mp 62–64°C).

B. Direct Photolysis method:

In a light reaction vessel containing 300 ml of dry tetrahydrofuran (THF), 6.0 g (0.017 mol) of freshly sublimed tungsten hexacarbonyl was dissolved and the resultant solution was photolyzed for a period of seven hr. The vessel was joined to a nitrogen source and a gas bubbler (filled with mineral oil) by means of rubber tubing and a three-way stopcock. Thus carbon monoxide produced during the irradiation could escape from the vessel. The light source was turned off and 2 ml (1.8 g, 0.0087 mol) of diphenylvinylphosphine was added to the solution by means of a calibrated syringe under a constant flow of nitrogen. The mixture was agitated for a period of half an hour, stoppered, and stored in the refrigerator at -5°C for 24 hours. The cold solution was filtered to remove a small amount of unreacted $\text{W}(\text{CO})_6$ and the filtrate was evaporated to dryness on a rotary evaporator. The crude product was dissolved in a minimum amount of dichloromethane and again filtered to remove a small quantity of $\text{W}(\text{CO})_6$. Addition of methanol to the cold solution precipitated a pale yellow solid. An infrared spectrum of this solid indicated the presence of $(\text{CO})_5\text{W}(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CH}_2$ and some $\text{W}(\text{CO})_6$. This material was vacuum sublimed at

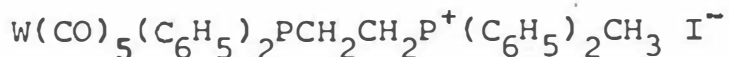
40°C/0.2 torr in order to remove the residual traces of $W(CO)_6$. A total of 1.9 g was obtained. An additional 0.7 g of product was isolated from the filtrate upon addition of more cold methanol. The overall yield based on the ligand was 47% (mp 62-64°C).

5. Preparation of bis(diphenylphosphino)ethanepentacarbonyltungsten(0), $W(CO)_5(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

In a 250 ml three-neck flask containing 75 ml of dry THF and equipped with a magnetic stirrer, 2.6 g (0.0050 mol) of diphenylvinylphosphinepentacarbonyltungsten(0) was dissolved. To this solution 0.95 g (0.0050 mol) of lithium diphenylphosphide, dissolved in 50 ml of dry THF, was added in the following manner. The lithium diphenylphosphide solution was contained in a 200 ml round bottom flask equipped with a nitrogen flow inlet tube and joined to the 3-neck flask by means of an inverted U-shaped connecting tube filled with glass wool. A glass stopper, which functioned as a gas release valve, was fitted loosely into the third neck of the flask. Under a constant stream of nitrogen the apparatus was tilted in order to allow the lithium diphenylphosphide solution to pour slowly through the glass wool into the 3-neck flask. The resulting solution was left to stir for a period of 12 hours at room temperature and then hydrolyzed by the addition of 1 ml of H_2O . The color of the solution changed from red to orange. The solution was then filtered and the solvent was removed by means of a rotary evaporator. The resulting

oil was dissolved in an equal volume of dichloromethane-methanol (1:1) solution and cooled to -5°C . Yellow crystals slowly formed. The precipitate was filtered and 1.5 g was collected. A work-up of the mother liquid produced an additional 0.70 g. These crystals were recrystallized from absolute methanol (yield 2.20 g, 57%) (mp $116-117^{\circ}\text{C}$).

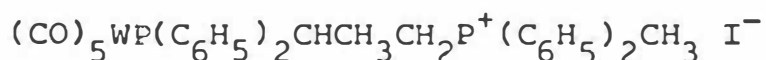
6. Preparation of 1-Diphenylphosphino-2-methyldiphenylphosphoniummethanepentacarbonyltungsten(0) iodide,



This reaction was carried out essentially the same way as the preceding one. In a 250 ml three-neck flask containing 75 ml of dry THF 2.5 g (0.0049 mol) of diphenylvinylphosphinepentacarbonyl tungsten was dissolved. To the solution 0.95 g (0.0049 mol) of lithium diphenylphosphide in 50 ml of dry THF was added and the solution was stirred under nitrogen for a period of 12 hr. To the solution 2 ml of methyl iodide was introduced in excess by means of a calibrated syringe and the resulting mixture was allowed to stir for an additional 12 hr during which a fine precipitate formed. The solution was then filtered and the collected precipitate was identified as lithium iodide. The filtrate was evaporated to dryness with a rotary evaporator, and the residue was eluted on a silica gel column with a solution of petroleum ether-ethyl acetate (4:1). A first component that came off was identified as starting material. A second component did not move and was eluted with 100% acetone

solvent, collected and brought to dryness on a rotary evaporator. The solid was then dissolved in a minimum amount of dichloromethane-methanol (1:1) solution and cooled to -5°C . Yellow crystals slowly formed. These crystals were recrystallized from methanol (yield 1.6 g, 40%) (mp $166-168^{\circ}\text{C}$). The product was identified with proton NMR.

7. Preparation of 1-methyldiphenylphosphino-2-methyldiphenylphosphoniummethanepentacarbonyltungsten(0) iodide,



Diphenylvinylphosphinepentacarbonyltungsten(0)

(3.1 g, 0.0073 mol) was dissolved in 50 ml of dry THF and lithium diphenylphosphide (1.4 g, 0.0073 mol) was added to the solution which was stirred for 12 hours under nitrogen. All equipment used was previously dried with a heat gun under a stream of dry nitrogen. To the solution excess methyl iodide (3 ml) was added and the mixture was allowed to react for a period of 12 hours. The solvent was then removed by means of a rotary evaporator and the residue was dissolved in a minimum amount of dichloromethane and refrigerated. A fine precipitate formed which was filtered and identified as lithium iodide. The solvent was removed from the filtrate and a drop of the resulting oil dissolved in a mixture of dichloromethane-methanol solution (1:1) was placed on a thin layer plate with a capillary. The spot was eluted with petroleum ether-ethyl acetate solution (1:1) and the plate was developed in an iodine chamber. Two mobile spots

developed and one non-mobile. Separation of the two mobile components from the non-mobile component was achieved by extracting the crude oil with benzene. The non-mobile component did not dissolve and was not identified. The benzene solution was brought to dryness on the rotary evaporator and the resulting oil was eluted on a silica gel column with a solution of petroleum ether-ethyl acetate (1:1). Two separate components were collected. The components were vacuum dried, one of which remained as an oil, and the other crystallized to a solid residue. Several attempts to recrystallize the products failed. An ir spectrum of the impure solid component indicates a monosubstituted pentacarbonyltungsten complex. An NMR spectrum identified the solid as the desired product (dec $> 146^{\circ}\text{C}$).

C. Attempted Preparations

- 1,2-dibromo-1-diphenylphosphinoethanepentacarbonyltungsten(0), $(\text{OC})_5\text{WPPH}_2\text{CHBrCH}_2\text{Br}$

Diphenylvinylphosphinepentacarbonyltungsten(0)

1.3 g (0.0025 mol) was dissolved in 50 ml of carbon tetrachloride, and to the solution a 1% bromine in carbon tetrachloride solution was added dropwise by means of a calibrated burette. After 1 ml of bromine solution was added a white precipitate formed. The precipitate was filtered, and an additional 1 ml of Br_2/CCl_4 solution was added, and a new light-green precipitate formed. Four precipitates were collected in this manner, the colors of which gradually became

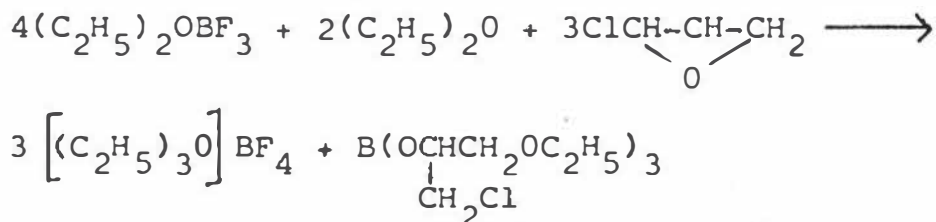
deep blue-green. An ir spectrum of the first precipitate indicated a monosubstituted carbonyl. A quantitative analysis of the unidentified product gave an empirical formula of $W_xO_yC_{43}H_{43}P_3Br_2$ (Found: %C 49.42, %H 4.13, %P 8.87, %Br 15.18).

2. 1-Diphenylphosphino-2-phenylethanepentacarbonyl-tungsten(0), $(OC)_5WPh_2CH_2CH_2Ph$

In a 200 ml round bottom flask placed in a nitrogen bag 1.6 g (0.0031 mol) of diphenylvinylphosphinepentacarbonyltungsten(0) was dissolved into 50 ml of benzene. To the solution 1.6 ml of 1.8 M solution of phenyllithium in 70:30 mixture benzene-ether solvent was added by means of a calibrated syringe. The solution was allowed to stir overnight at room temperature and then 2 ml of saturated ammonium chloride solution was added dropwise. The solvent was removed on the rotary evaporator and the residue was dried under high vacuum. A NMR spectrum of the resulting solid showed that only starting material was present. The same reaction was attempted by refluxing the reactants for a period of 6 hr but no reaction occurred. Different solvents were also tried, such as tetrahydrofuran and pentane, but no significant changes were observed.

3. 1-ethanediphenylphosphino-2-methylethanepentacarbonyl- tungsten(0), $(OC)_5WPPh_2CHC_2H_5CH_2CH_3$

The triethyloxoniumfluoroborate was prepared according to Meerwin.²⁶



Into a dry 3-neck flask protected from atmospheric moisture was placed a solution of 91 g (0.64 mol) of freshly redistilled boron trifluoride etherate in 300 ml of anhydrous ether. Epichlorohydrin 44 g (0.48 mol) was added dropwise at such a rate that the stirred solution remained in a state of constant gentle reflux. When the epichlorohydrin had been added the oil which initially formed began to solidify. The mixture was stirred at room temperature for 2 hours and the solvent was decanted. The triethyloxoniumfluoroborate was washed with anhydrous ether (72 g, yield 72%). The boric acid ester formed is retained in the mother liquor.

Diphenylvinylphosphinepentacarbonyltungsten(0) (1.0 g, 0.0019 mol) was dissolved in 25 ml of dry THF, and methyllithium (1.0 ml of 1.8 M ether solution) was added to the solution. The mixture was stirred for 12 hours at room temperature under nitrogen, and 1.5 g of triethyloxonium-fluoroborate in 25 ml of dichloromethane was added. No reaction occurred. The solution was stirred for an additional 12 hours but no significant changes were noted. Starting material was recovered.

4. Preparation of $(\text{CO})_4\text{W}(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2 \text{Li}^+$ carbene complex

Diphenylvinylphosphinopentacarbonyltungsten(0), 3.3 g (0.0060 mol), was dissolved in 50 ml of dry diglyme and 1.5 g (0.0060 mol) of lithiumdiphenylphosphide solution was added. The mixture was refluxed under reduced pressure (28 torr) for a period of two hours during which a precipitate formed. The precipitate was filtered under nitrogen and washed several times with petroleum ether to remove the diglyme. The residue was dissolved in a minimum amount of dichloromethane, but several attempts to recrystallize the product by various methods failed. The mixture was then dried under vacuum and an ir and NMR spectrum of the resulting solid indicated that no starting material was present and that a polymer had formed. The product remained unidentified (mp > 250°C).

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