1981

Controlling the Number of Metal Sites to Which a Polytertiary Phosphine Coordinates in Tungsten Carbonyls

Rodney D. Borger
Eastern Illinois University

Recommended Citation

Borger, Rodney D., "Controlling the Number of Metal Sites to Which a Polytertiary Phosphine Coordinates in Tungsten Carbonyls" (1981). *Masters Theses*. 2967.
https://thekeep.eiu.edu/theses/2967

THESIS REPRODUCTION CERTIFICATE

TO: Graduate Degree Candidates who have written formal theses.

SUBJECT: Permission to reproduce theses.

The University Library is receiving a number of requests from other institutions asking permission to reproduce dissertations for inclusion in their library holdings. Although no copyright laws are involved, we feel that professional courtesy demands that permission be obtained from the author before we allow theses to be copied.

Please sign one of the following statements:

Booth Library of Eastern Illinois University has my permission to lend my thesis to a reputable college or university for the purpose of copying it for inclusion in that institution's library or research holdings.

June 25, 1981

Date

I respectfully request Booth Library of Eastern Illinois University not allow my thesis be reproduced because ______________________________

____

____

Date

Author

m

CONTROLLING THE NUMBER OF METAL SITES TO WHICH A POLYTERTIARY PHOSPHINE COORDINATES IN TUNGSTEN CARBONYLS

(TITLE)

BY

RODNEY D. BORGER

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

1981
YEAR

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

June 25, 1981
DATE

June 25, 1981
DATE

June 25, 1981
DATE

June 25, 1981
DATE

CONTROLLING THE NUMBER OF METAL SITES TO WHICH A POLYTERTIARY PHOSPHINE COORDINATES IN TUNGSTEN CARBONYLS

By

Rodney D. Borger
Bachelor of Science
Eastern Illinois University
Charleston, Illinois
May 1977

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
1981

CONTROLLING THE NUMBER OF METAL SITES TO WHICH A POLYTERTIARY PHOSPHINE COORDINATES IN TUNGSTEN CARBONYLS

Thesis Approved

Dr. R. L. Keiter, Thesis Advisor

Dr. D. H. Buchanan

Dr. R. H. Karraker

Dr. E. O. Sherman

ABSTRACT

Title of Thesis: Controlling the Number of Metal Sites to Which a Polytertiary Phosphine Coordinates in Tungsten Carbonyls

Name: Rodney D. Borger

Thesis directed by: Dr. Richard L. Keiter

Judiciously selected coordinated fragments of $\mathrm{Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2}$ [$\mathrm{(OC)_5WPPh_2H}$, $\mathrm{(OC)_5WPPh_2CH{=}CH_2}$ and $\mathrm{(OC)_5WPPh(CH{=}CH_2)_2}$] were used to construct its five possible nonchelated pentacarbonyltungsten complexes. These are the trimetallic $\mathrm{(OC)_5WPPh[CH_2CH_2PPh_2W(CO)_5]_2}$ and the two pairs of constitutional isomers, $\mathrm{(OC)_5WPPh[CH_2CH_2PPh_2]_2}$ and $\mathrm{(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2}$, and $\mathrm{PPh[CH_2CH_2PPh_2W(CO)_5]_2}$ and $\mathrm{(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2}$. Their syntheses, based on free radical and base catalyzed addition reactions, demonstrate a successful approach to ligation control of a polydentate phosphorus ligand.

The reactions used to synthesize these complexes are as follows:

I. $\mathrm{(CO)_5WPPh(CH{=}CH_2)_2 + 2\ HPPh_2 \xrightarrow{AIBN} Ph_2PCH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2}$

II. $\mathrm{PPh(CH{=}CH_2)_2 + HPPh_2 \xrightarrow{AIBN} Ph_2PCH_2CH_2PPhCH{=}CH_2}$

$\mathrm{Ph_2PCH_2CH_2PPhCH{=}CH_2 + (CO)_5WPPh_2H \xrightarrow{AIBN} Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2W(CO)_5}$

III. $\mathrm{2\ (CO)_5WPPh_2CH{=}CH_2 + PPhH_2 \xrightarrow{AIBN} (CO)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2W(CO)_5}$

IV. $\mathrm{(CO)_5WPPh(CH{=}CH_2)_2 + (CO)_5WPPh_2H \xrightarrow{KOBu\text{-}t} (CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH{=}CH}$

$\mathrm{(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH{=}CH_2 + HPPh_2 \xrightarrow{KOBu\text{-}t}}$

$\mathrm{(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2}$

V. $(CO)_5WPPh(CH{=}CH_2)_2 + 2\ (CO)_5WPPh_2H \xrightarrow{KOBu\text{-}t}$

$$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2W(CO)_5$$

The new complexes were characterized structurally by phosphorus-31 nuclear magnetic resonance and infrared spectroscopy and their purity established with elemental analyses.

DEDICATION

TO MY PARENTS

ACKNOWLEDGEMENT

I wish to express my sincere appreciation to Dr. Richard L. Keiter for his suggestion of the problem and his guidance, inspiration and encouragement throughout this project.

I would like to thank the members of Dr. Keiter's research group, especially Jim Brodack for some experimental work. I also thank the other members of the faculty for their active interest and help. In addition, I wish to thank Mr. Lewis W. Cary for obtaining ^{31}P NMR spectra.

Finally, I would like to thank Ms. Pat Beaulieu for typing this thesis and Mrs. Peggy Ballard for drawing the apparatus figures.

Table of Contents

Chapter — Page

I Introduction 1

II Results and Discussion 18

III Experimental 56

A. General Considerations 56

B. Preparation of Complexes 57

References 68

List of Figures

Figures		Page
1	^{31}P NMR of $(CO)_5WPPh_2H$	21
2	^{31}P NMR of $(CO)_5WPPh_2CH{=}CH_2$	23
3	^{31}P NMR of $(CO)_5WPPh(CH{=}CH_2)_2$	24
4	Expanded IR spectrum of $(CO)_5WPPh_2H$	25
5	Expanded IR Spectrum of $(CO)_5WPPh_2CH{=}CH_2$	27
6	Expanded IR spectrum of $(CO)_5WPPh(CH{=}CH_2)_2$	28
7	Expanded IR spectrum of P⁄∖⁄ P(W) ⁄∖⁄ P	30
8	^{31}P NMR of P ⁄∖⁄ P(W) ⁄∖⁄ P	31
9	^{31}P NMR of P ⁄∖⁄ P(W) ⁄∖⁄ P(O)	33
10	Expanded IR spectrum of WP⁄∖⁄ P ⁄∖⁄ P	35
11	^{31}P NMR of WP⁄∖⁄ P ⁄∖⁄ P	36
12	^{31}P NMR of WP⁄∖⁄ P(O) ⁄∖⁄ P and WP ⁄∖⁄ P ⁄∖⁄ P(O)	37
13	Expanded IR spectrum of WP⁄∖⁄ P ⁄∖⁄ PW	39
14	^{31}P NMR of WP ⁄∖⁄ P ⁄∖⁄PW	40
15	^{31}P NMR of WP⁄∖⁄ P(O)⁄∖⁄ PW	41
16	Expanded IR spectrum of WP⁄∖⁄ P(W)/=	43
17	^{31}P NMR of WP ⁄∖⁄ P(W)/=	44
18	Expanded IR spectrum of WP ⁄∖⁄P(W) ⁄∖⁄ P	46
19	^{31}P NMR of WP⁄∖⁄ P(W) ⁄∖⁄ P	47
20	^{31}P NMR of WP⁄∖⁄ P(W) ⁄∖⁄ P(O)	48
21	Expanded IR spectrum of WP⁄∖⁄ P(W)⁄∖⁄ PW	50
22	^{31}P NMR of WP⁄∖⁄P(W) ⁄∖⁄ PW	51
23 a&b	Figure of UV reaction vessel	58-59
24 a&b	Figure of molecular still	60-61

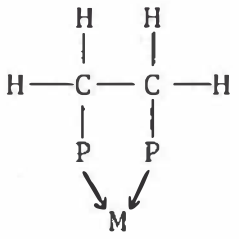
List of Tables

Table		Page
I	Physical Data of Complexes	53
II	^{31}P NMR Data of Complexes	54
III	IR Data of Complexes	55

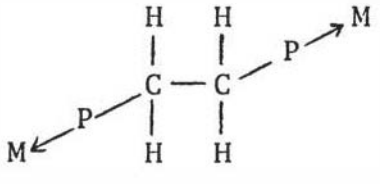
INTRODUCTION

Tertiary phosphines have become important in coordination chemistry during the last 25 years. To be a good chelating ligand a properly designed polydentate ligand should provide (1) control of the coordination number, stereochemistry and magnetic properties of a complex, (2) increased basicity (or nucleophilicity) at the metal and (3) high yields in catalytic synthesis. It is thought that further studies on the coordination chemistry of poly tertiary phosphines are likely to lead to major contributions to areas of practical importance such as nitrogen fixation, fuel cell technology, homogenous hydrogenation and new catalytic processes for the synthesis of useful organic chemicals.

In this study the polytertiary phosphine of interest is bis(2-diphenylphosphinoethyl)phenylphosphine, $PhP(CH_2CH_2PPH_2)_2$, hereafter called triphos. The interest in triphos stems principally from its ability to bind to one, two or three metal atoms. Triphos has structural units consisting of three phosphorus atoms connected by two ethylene bridges. These PCH_2CH_2P units form 5-membered rings with a metal as in I or they can span two different metal atoms as in II.



I



II

Triphos was first reported in 1962 by Hewertson and Watson.[1] Their reaction sequence can be outlined as follows:

$$PhP(CH_2CH_2OEt)_2 \xrightarrow[HOAc]{HBr} PPh(CH_2CH_2Br)_2$$

$$2\ NaPPh_2 + PhP(CH_2CH_2Br)_2 \xrightarrow{liq\ NH_3} 2\ NaBr + PhP(CH_2CH_2PPh_2)_2$$

This procedure was found to be quite lengthy and complicated due to the rather unstable and inaccessible halide, $PhP(CH_2CH_2Br)_2$, starting material. The halide was found to undergo self-quaternization after isolation and therefore could not be stored. This reaction sequence gave a 16% yield of triphos whose melting point is 131-132°C. The obtained low yield of triphos explains why interest in the ligand lagged in the sixties.

In 1969 R. B. King and P. N. Kapoor[2] reported a new and novel way of synthesizing triphos which consisted of using a base-catalyzed addition of phosphorus-hydrogen bonds to carbon-carbon multiple bonds of vinylphosphines and ethynlphosphines. King and Kapoor[3] reported the following simple synthetic routes.

Method A $PhP(CH{=}CH_2)_2 + 2\ Ph_2PH \longrightarrow PhP(CH_2CH_2PPh_2)_2$

Method B $2\ Ph_2PCH{=}CH_2 + PhPH_2 \longrightarrow PhP(CH_2CH_2PPh_2)_2$

In method A the solvent was benzene which contained a catalyst of ether-PhLi giving a 50% yield of triphos. Method B was examined in three ways: (1) A benzene solvent and a catalyst of potassium tert-butoxide (KOBu-t) gave an 87% yield, (2) A THF solvent and a catalyst of KOBu-t gave a 74-83% yield and (3) A benzene solvent and a PhLi catalyst gave a 55% yield. The ^{31}P NMR spectrum of triphos revealed chemical shifts of -13.5ppm and -16.6ppm for the Ph_2P and PhP groups, respectively.

These base-catalyzed additions are a special case of the Michael addition reaction[4] and proceed according to the following sequence.

$$R^1R^2PH \quad + \quad base^- \longrightarrow base\text{-}H \quad + \quad R^1R^2P^-$$

$$R^1R^2P^- \quad + \quad H_2C{=}CHPR^3R^4 \longrightarrow R^1R^2PCH_2\text{—}\bar{C}HPR^3R^4$$

$$R^1R^2PCH_2\text{—}\bar{C}HPR^3R^4 \quad + \quad base\text{-}H \longrightarrow R^1R^2PCH_2CH_2PR^3R^4 \quad + \quad base^-$$

While working to improve the base-catalyzed reactions King and Cloyd[5] reported that the reactions of $PhPH_2$ with $Ph_2P(CH{=}CH_2)$ not only produced triphos, a 1:2 product, but also a 1:1 product, $PhP(H)CH_2CH_2PPh_2$. The 1:1 product was isolated from the filtrate after crystallization of triphos in a yield that was less than 20% of triphos. The yield of the 1:1 adduct suggests that the base-catalyzed addition of primary phosphines to vinylphosphine derivatives containing tricoordinated phosphorus atoms cannot be efficiently controlled to give the 1:1 adduct. The intermediate carbanion, $RP(H)CH_2\bar{C}HPR^3R^4$, which forms was found to be in equilibrium with its tautomeric phosphide anion $R\bar{P}CH_2CH_2PR^3R^4$. The equilibrium constant is dependent on the relative acidities of the CH_2 hydrogens and the PH hydrogens. If the CH_2 hydrogens are relatively acidic, the carbanion will be favored. Since the carbanion ion is a relatively poor nucleophile, the carbanion will not undergo a second Michael addition. The reaction will then stop at this stage to give $RP(H)CH_2CH_2PR^3R^4$. If the PH hydrogens are relatively acidic, the phosphide anion will form $R\bar{P}$-. Thus in the second step the phosphide anion $R\bar{P}CH_2CH_2PR^3R^4$ will add readily to a second equivalent of the vinylphosphorus compound to yield $RP(CH_2CH_2PR^3R^4)_2$ after protonation.

Cloyd and Meek[6] developed concurrently with King and Kapoor a different three step synthesis of triphos, which gave comparable yields of

80%. This reaction sequence is much simpler than that of Hewertson and Watson, but more complex than that of King and Kapoor. Cloyd and Meek's synthesis can be outlined as follows:

$$\mathrm{Ph_2PK} + \text{(excess) } \mathrm{ClCH_2CH_2Cl} \longrightarrow \mathrm{Ph_2PCH_2CH_2Cl} + \mathrm{KCl}$$

$$\mathrm{Ph_2PCH_2CH_2Cl} + \mathrm{PhPHNa} \xrightarrow{\text{liq } \mathrm{NH_3/THF}} \mathrm{Ph_2PCH_2CH_2P(H)Ph} + \mathrm{NaCl}$$

$$\mathrm{Ph_2PCH_2CH_2P(H)Ph} \xrightarrow[\text{b) } \mathrm{Ph_2PCH_2CH_2Cl/THF}]{\text{a) BuLi/Hexane}} \mathrm{PhP(CH_2CH_2PPh_2)_2}$$

In 1971 Issleib and Weichmann reported a new synthetic method to produce triphos involving the free radical catalyst 2,2'-azobis-(isobutyronitrile) (AIBN).[7] Their reaction sequence was as follows:

$$\mathrm{R_2PCH{=}CH_2} + \mathrm{R'PH_2} \xrightarrow[\mathrm{THF}\ \Delta]{\mathrm{AIBN}} \mathrm{R_2PCH_2CH_2P(H)R'} + \mathrm{R'P(CH_2CH_2PR_2)_2}$$

Meek and co-workers[8] have shown that the free-radical catalyzed addition of phosphorus-hydrogen across carbon-carbon double bonds in vinylphosphines is a useful method for the preparation of polytertiary phosphines. Meek's reaction produced triphos in 91% yield.

$$\mathrm{PhP(CH{=}CH_2)_2} + 2\ \mathrm{HPPh_2} \xrightarrow[\Delta]{\mathrm{AIBN}} \mathrm{PhP(CH_2CH_2PPh_2)_2}$$

The advantages of the free-radical catalyzed method over any other method are: (1) The ease of making the polydentate ligands by choosing the correct P-H and vinyl derivatives, (2) The simplicity of the one-pot reaction, (3) Faster reaction times than any other method, (4) Impurities and most by-products can be removed in high vacuum in the initial workup yielding a crude material that is relatively pure to use in the next step, (5) Yields of this method are 85-99%, (6) The solutions are homogeneous and therefore easily handled, (7) Workups are simple, fast and the reaction conditions are relatively mild.

Triphos was found to be a slightly air sensitive (oxygen) compound. King and Heckley[9] have reported the preparation and properties of its oxides and sulfides. To oxidize all of the trivalent phosphorous atoms in triphos, the following reaction was carried out:

$$PhP(CH_2CH_2PPh_2)_2 \quad + \quad 2\ H_2O_2 \longrightarrow PhP(O)[(CH_2CH_2(O)PPh_2]_2$$

Similarly trisulfide was produced:

$$PhP(CH_2CH_2PPh_2)_2 \quad + \quad S \longrightarrow PhP(S)[CH_2CH_2(S)PPh_2]_2$$

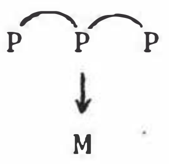
King *et al*. found that there was no obvious difference observed between ν(P=O) for all three phosphorus atoms in triphos (ν = 1180 cm^{-1}). The polytertiary phosphine sulfides did not provide an unambiguous spectrum for ν(P=S) due to the numerous bands from the organic groups in the 500-600 cm^{-1} region where ν(P=S) is expected to absorb.

The oxides were found to be insufficiently soluble in organic solvents for satisfactory ^{31}P NMR analysis. The sulfides were found to be sufficiently soluble to exhibit the expected large downfield shift of phosphorus atoms bonded to a sulfur, two aryl groups and a saturated aliphatic bridge. The resonance appears at 44± .8ppm. For a phosphorus atom bonded to a sulfur, one aryl group and two saturated aliphatic bridges, the resonance appears at 51± 1 ppm. This order of chemical shifts is the opposite of that found for the phosphorus atoms in the free polytertiary phosphines. This suggests that the deshielding effects of sulfur addition is greater for the more basic phosphorus atoms bearing larger numbers of saturated aliphatic rather than aromatic substituents.

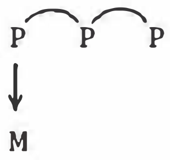
Dean[10] reported the ^{31}P NMR spectrum of $PhP(Se)(CH_2CH_2(Se)PPh_2)_2$ as a AB_2 type in appearance, much resembling that of the free ligand.

It consists of the AB_2 part of an AB_2X spin system overlapping with the ABC part of an ABCX spin system.

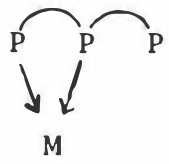
King et al.[11] were the first to use triphos as a chelating ligand. They reported that a polytertiary phosphine will complex with transition metals in a variety of different ways depending on the choice of metal atom and the other ligands surrounding the metal atom. In the particular case of the tritertiary phosphine, triphos, six possible coordination modes are as follows: (1) Monoligate monometallic (IIIa and IIIb); (2) Biligate monometallic (IVa and IVb); (3) Triligate monometallic (V); (4) Biligate bimetallic (VIa and VIb); (5) Triligate bimetallic (VIIa and VIIb); (6) Triligate trimetallic (VIII).



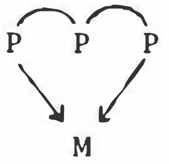
IIIa



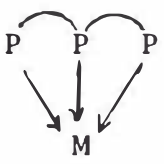
IIIb



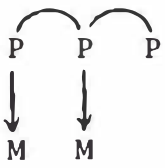
IVa



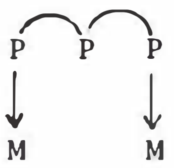
IVb



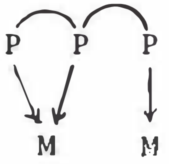
V



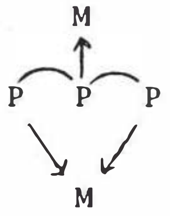
VIa



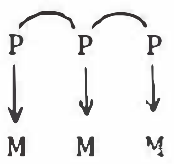
VIb



VIIa

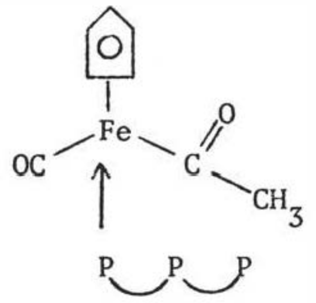


VIIb

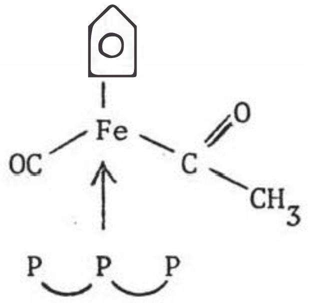


VIII

Although King and coworkers were able to prepare complexes which demonstrated each of these six fundamentally different types of bonding, they were not able to distinguish between the different isomers.[11] The preparation of a monoligate monometallic complex (III a or b) of triphos by substitution requires a transition metal system in which exactly one vacant coordination position is readily generated. The rate of reaction for this substitution must be sufficiently slow if formation of polymetallic species is to be prevented. This type of reaction can be seen in the formation of (Triphos)Fe$(CO)_4$ and $CH_3COFe(CO)(Triphos)C_5H_5$. The structure of the latter complex in its two isomeric forms is

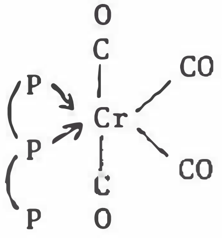


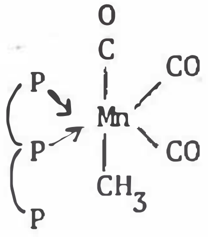
or

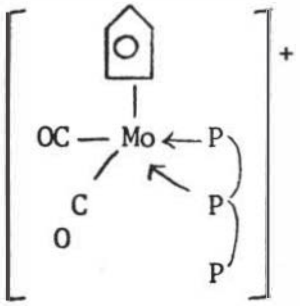


More common than monoligate monometallic complexes are the biligate monometallic complexes (IV a and b). These complexes form readily since there are several types of metal carbonyl derivatives in which exactly two reactive coordination positions are generated by loss of carbonyl groups and/or other ligands. Specific examples can be seen in these examples: $(Triphos)OsCl_4$, $(Triphos)M(CO)_4$, M = Cr and Mo, $CH_3Mn(CO)_3(Triphos)$, $C_5H_5Mo(CO)_2(Triphos)$ and $[C_5H_5Mo(CO)_2(Triphos)]Cl$.

Examples of their structures are:

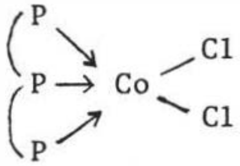


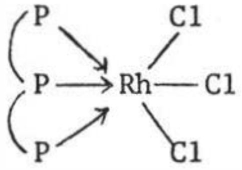


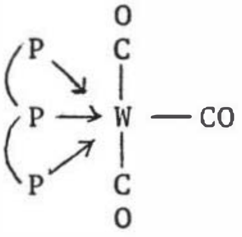


Triligate monometallic complexes (V) of triphos are also formed. Examples of such complexes are as follows:[11] (Triphos)MCl$^+$ (M = Ni, Pd, and Pt), (Triphos)CoCl$_2$, (Triphos)MCl$_3$ (M = Rh and Ir), (Triphos)IrH$_3$, (Triphos)M(CO)$_3$ (M = Cr, Mo and W), (Triphos)Mn(CO)$_2$Br, C$_5$H$_5$Mo(Triphos)Cl and C$_5$H$_5$Fe(Triphos)$^+$.

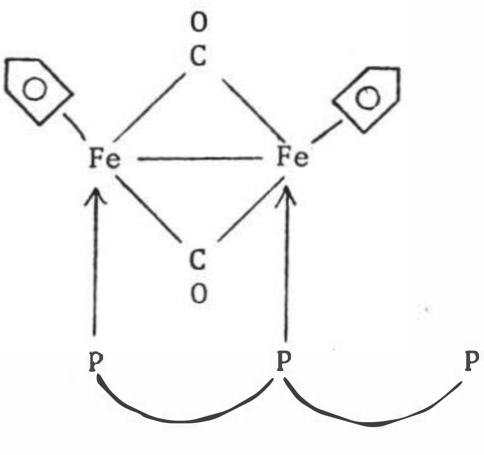
The substitution formation of a triligate monometallic complex from triphos and a transition metal derivative only requires that three reactive coordination positions on the transition metal atom can be readily generated.[11] Such structures are shown as



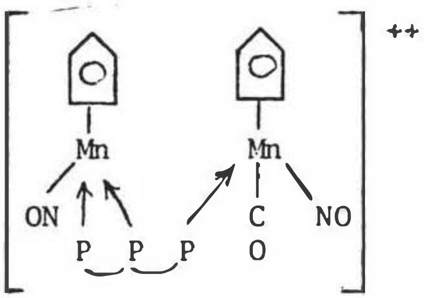




King's one example of a biligate bimetallic (VI a and b) complex is (Triphos)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$ and is thought to have the following structure:



The first known complex of a triligate bimetallic (VII a and b) is $[(C_5H_5)_2Mn_2(CO)(NO)_2(\text{Triphos})][PF_6]_2$ which has the following structure:[11]



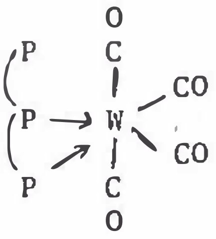
An example of a triligate trimetallic complex (VIII) can be seen in the complex $(\text{Triphos})[Mo(CO)_2(COCH_3)(C_5H_5)]_3$ but it is not clear whether King synthesized it or not.

A paper by King and Cloyd[12] surveys the proton decoupled pulsed Fourier transform ^{31}P NMR of some metal complexes of phenylated poly tertiary phosphines. In it King states that for the complexes of interest, the ^{31}P data are:

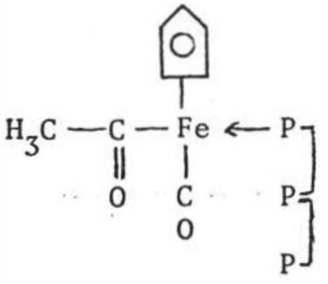
	Chemical Shifts (ppm)		
	PhP	Ph_2P	J(PP) Hz
Triphos $W(CO)_3$	78.1	40.3	∼6
Triphos $W(CO)_4$	39.6	30.5, -13.2	39, 36
Triphos	-16.5	-12.9	27

Triligate monometallic ligands can be identified by their characteristic ^{31}P NMR spectra. A biligate monometallic derivative such as $(\text{Triphos})W(CO)_4$, (IX), in which an uncomplexed phosphorus atom is present exhibits a phosphorus-31 chemical shift nearly unchanged from that of the free ligand.

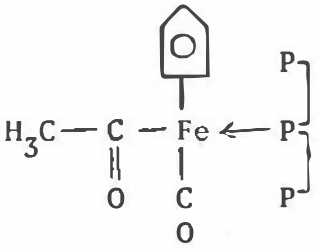
The monoligate complex $(C_5H_5)Fe(CO)(\text{Triphos})(COCH_3)$ can exist as isomer Xa in which an end phosphorus atom is bonded to the iron atom, or isomer Xb in which the center phosphorus is bonded to the iron atom. The ^{31}P NMR spectra of this complex exhibits two distinct resonances separated by 5 ppm in the region assigned to complexed phosphorus atoms of the triphos ligand. This indicates that the King sample of $(C_5H_5)Fe(CO)(Triphos)(COCH_3)$ is a mixture of two isomers, Xa and Xb, a fact that would be difficult to demonstrate unequivocably by any technique other than ^{31}P NMR spectroscopy.



IX



Xa



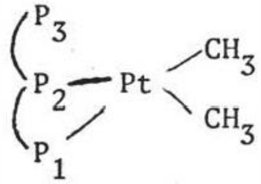
Xb

Meek[13] has attempted to design polyphosphine complexes in which the rhodium atom is more basic than in $Rh(Ph_3P)_3Cl$ (Wilkinson's catalyst)[14] and which would simultaneously minimize the tendency of one or more phosphine donors to be displaced in chemical reactions. The triphos ligand was found to fulfill these criteria, although in some instances the phosphine donors often bridged to another rhodium atom producing polynuclear rhodium complexes.

It was found that the addition of a benzene solution of triphos to a suspension of $[Rh(C_8H_{12})X]_2$ (X = Cl, Br, I) in refluxing ethanol readily produces the corresponding square-planar complex Rh(Triphos)X in high yields (∿80%). It was observed that the complex Rh(Triphos)Cl reacts with a variety of small molecules to form the five-coordinate nonionic adducts, Rh(Triphos)Cl·A (A = BF_3, CO, $HgCl_2$, SO_2, O_2 and S_2).

On the basis of the increased stability and reactivity patterns of these four and five-coordinated rhodium complexes of the chelating triphos ligand as compared to other tertiary phosphine-rhodium systems, it was concluded that the Rh(Triphos)Cl complex offers tremendous potential for future study because: (1) It functions as a stronger Lewis base, (2) It forms qualitatively more stable adducts of small molecules (i.e., the increased stability of the O_2, SO_2 and BF_3 adducts) and (3) It simplifies the stoichiometry of the products as all three phosphine groups remain bonded in the resulting complexes.

Later Meek _et_ _al_.[15] reported the ^{31}P NMR of various platinum (II) dimethyl polyphosphine complexes. It was found that the chelating polyphosphine ligands easily displace 1,5-cyclooctadiene from $Pt(CH_3)_2(COD)$ to give the corresponding phosphine complexes. For the ligand of interest Meek reports the structure of $Pt(CH_3)_2$(Triphos), its ^{31}P data and that of other complexes as



Compound	Chemical Shifts (ppm)			Coupling Constants (Hz)	
	P_1	P_2	P_3	P_1-P_2	P_1-P_3
$Pt(CH_3)_2$(ttp)	-3.7	3.5	-18.9	18.0	0
$Pt(CH_3)_2$(Cyttp)	4.0	0.2	-7.9	19.0	0
$Pt(CH_3)_2$(Triphos)	49.4	48.5	-15.5	0.8	37.5
$Pt(CH_3)_2$(eptp)	44.0	47.4	-18.9	3.7	0

(ttp) = $PhP(CH_2CH_2CH_2PPh_2)_2$ (Cyttp) = $PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$
(eptp) = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$

The interesting feature of these compounds is the variability of the phosphorus-phosphorus coupling constants which change with the chelatechain length. When a ligand forms a six-member chelate ring, the P-P coupling increases relative to the value in the free ligand. Whereas the P-P coupling observed for a chelating ligand that forms a five-member ring containing two phosphorus atoms decreases upon coordination to the metal as compared to the free ligand.

The first reported substitution reaction of a low-valent iron organophosphorus complex was by Felkin et al.[16] This new compound was of interest for the possibility of obtaining a potential hydrogenation catalyst. The compound of interest was formed from the following reaction:

$Fe(cot)_2$ + Triphos $\longrightarrow$ Fe(cot)(Triphos), cot = cyclooctatetraene

Proton NMR spectra showed a singlet resonance for coordinated cyclooctatetraene ($\delta 4.89$) indicating that the cot is fluxional and presumably η^4-coordinated. The variable temperature ^{31}P NMR spectra indicated the fluxional nature of the phosphorus ligand. The ^{31}P NMR at 0°C showed two absorptions at 99.9(d J=9Hz) and 117.4 ppm (t, J=9Hz) in an intensity ratio of 2/1. Upon cooling, the spectrum changed considerably until at -80°C three broad signals of comparable intensity at 92, 95, and 188 ppm were observed.

The first triphos complexes were made by the simple method of refluxing the starting materials together to yield various products. Muller and Rehder[17] introduced the photo-induced introduction of triphos to various vanadium complexes. This was accomplished by taking triphos and photolytically reacting it with $[Et_4N][V(CO)_6]$ or $[\eta^5\text{-}CpV(CO)_4]$ to give the complexes $[Et_4N][V(CO)_4Triphos]$, mer-$[Et_4N][V(CO)_3Triphos]$, cis-$[\eta^5\text{-}CpV(CO)_2Triphos]$ and trans-$[\eta^5\text{-}CpV(CO)_2Triphos]$.

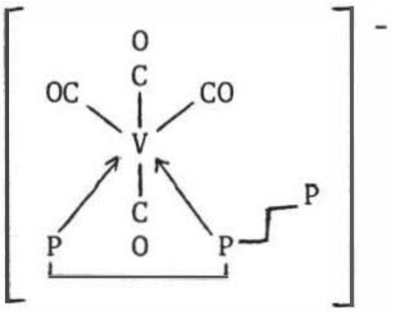
The reaction of $[Et_4N][V(CO)_6]$ and triphos upon UV irradiation of the THF solution is thought to take place in three steps corresponding to the formation of mono-, *cis*-, and *mer*-trisubstituted anions (eqn 1-3). By varying the time of irradiation, either *cis*- or *mer*- complexes were formed.

$$[V(CO)_6]^- + \text{Triphos} \dashrightarrow [V(CO)_5\text{Triphos}]^- + CO \qquad (1)$$

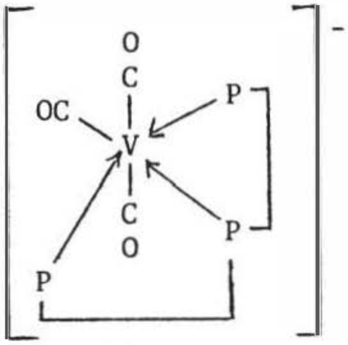
$$[V(CO)_5\text{Triphos}]^- \longrightarrow \underline{cis}[V(CO)_4\text{Triphos}]^- + CO \qquad (2)$$

$$\underline{cis}\text{-}[V(CO)_4\text{Triphos}] \longrightarrow \underline{mer}\text{-}[V(CO)_3\text{Triphos}]^- + CO \qquad (3)$$

Rehder proposed the following structures for $[Et_4N][V(CO)_4\text{Triphos}]$ (XI), and *mer*-$[Et_4N][V(CO)_3\text{Triphos}]$ (XII) on the basis of IR, ^{31}P NMR, and ^{51}V NMR data.



XI



XII

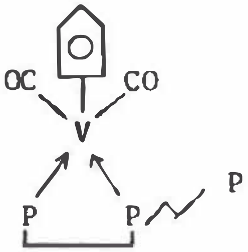
The following is a list of ^{31}P data of Rehder's complexes.

^{31}P Chemical Shifts (ppm)

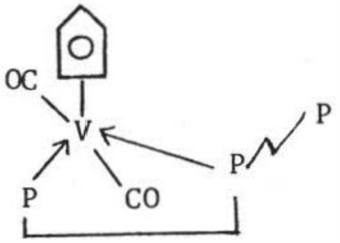
Complex	Unligated		Ligated	
	PPh_2	PPh	PPh_2	PPh
Triphos	-12.8	-16.6		
cis-$[Et_4N][V(CO)_4\text{Triphos}]$	-16.4		68	83
mer-$[Et_4N][V(CO)_3\text{Triphos}]$			62	87
cis-η^5-$CpV(CO)_2\text{Triphos}$	-15.5		102	114
trans-η^5-$CpV(CO)_2\text{Triphos}$	-15.7		122	
fac-$[V(CO)_3\text{Triphos}]_2$			90	

The photo reaction of triphos with η^5-CpV(CO)$_4$ gave the cis- and trans-[η^5CpV(CO)$_2$Triphos] products. It may be noted that King[3] made the analytically impure cis complex by refluxing starting materials in toluene. Rehder found that mono-substituted species vanished after 10 minutes of irradiation. The cis product is formed simultaneously as the formation of the trans product commences. The complete production of the trans product via the cis product takes 45 minutes of UV irradiation.

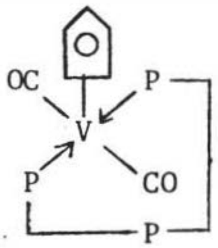
The structure of cis-[η^5-CpV(CO)$_2$Triphos] is



It was discovered that the trans product could bond in two ways. The trans positions are spanned either by the -PPh$_2$ and -PPh functions (XIII) or by two terminal PPh$_2$ groups (XIV). These complexes were found to be in an isomeric mixture.



XIII



XIV

When cis-[V(CO)$_4$Triphos] is passed through a column of silica gel, partial oxidation of vanadium occurs. Rehder originally suggested that the product was {fac-[V(CO)$_3$Triphos]}. Rehder and Puttfarcken[18] later reported that this compound is actually $HV(CO)_3Triphos$. The hydrogen ion in the product is apparently abstracted from the acidic [Si-OH] group according to $[H^+]$ + cis-$[V(CO)_4Triphos]^- \longrightarrow HV(CO)_3Triphos$.

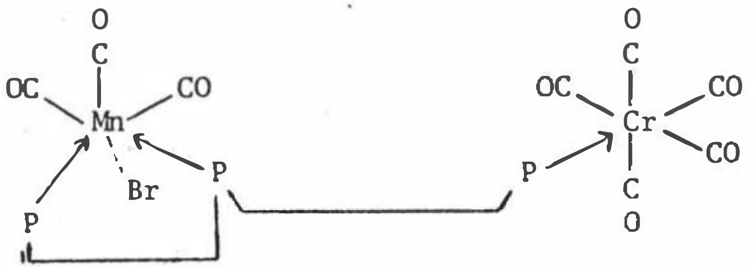
Butler et al.[19] reported the first crystal structure of a triligate bimetallic triphos complex, $Br(CO)_3Mn(Triphos)Cr(CO)_5$. This complex was synthesized by the following reactions:

$Mn(CO)_5Br$ + Triphos $\longrightarrow Mn(CO)_3(Triphos)Br$

$Mn(CO)_3(Triphos)Br$ + $Cr(CO)_5$-THF $\longrightarrow Br(CO)_3Mn(Triphos)Cr(CO)_5$

XV

The complex XV was found to consist of two diastereomers that differ solely on the orientation of the phenyl group on the centrally coordinated phosphorus atom with respect to the bromine atom.

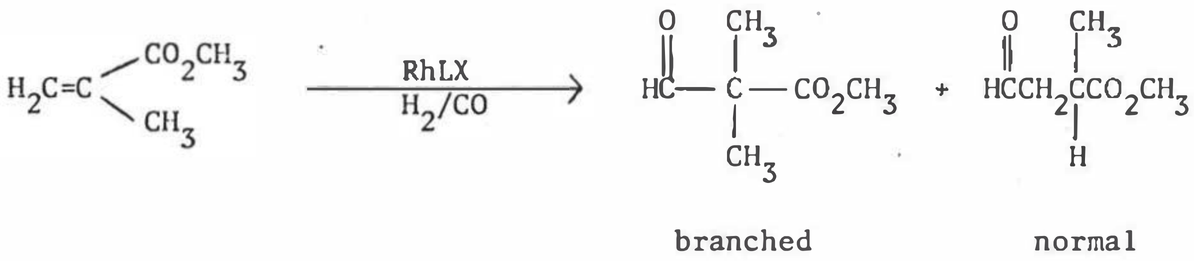


XV

Butler[20] reported another complex like XV, $C_5H_5Mn(CS)(triphos)Cr(CO)_5$ that has two diastereomers that differ solely in the orientation of the phenyl group on the centrally coordinated phosphorus atom with respect to the CS molecule.

Triphos complexes are thought to be possible catalytic reagents as indicated earlier. The Olivés[21] report that alkylbenzenes, $C_6H_5(CH_2)_nH$ (n = 1-5), are formed in a Fischer-Tropsch type synthesis if triphos is used as a co-catalyst in a solution of $W(CO)_6$ and $AlCl_3$ in benzene. It was found that if triphos was not incorporated into the mixture, no xylenes were detected but small amounts of methane, ethane and ethylene were generated.

Pittman and co-workers[22] report that hydroformylation of methyl methacrylate can be catalyzed by phosphine rhodium complexes. They found that two products could be formed from the reaction depending upon the catalyst chosen based upon the following reaction sequence.



If the catalyst Rh_2O_3 only is used, at low temperatures the branched product was favored; at high temperatures the normal product dominated. The addition of a phosphine ligand to rhodium favored the branched isomer when the reaction was run at lower temperatures. It was also noted that different phosphine ligands resulted in different mixtures of the isomers. When triphos was compared to PPh_3 at equal P/Rh ratios, triphos resulted in higher selectivities to the branched product at constant temperature and pressure, 59% vs 45%.

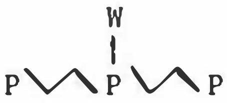
From the above history one can see that triphos has a large variety of possible uses. It is the synthesis of organometallic complexes that are of interest in this thesis rather than their catalytic properties. The method of construction of most of the triphos complexes has been to take triphos plus a metal complex and reflux these materials in a suitable solvent. This method and the photo-induced syntheses do not lead to predictable complexes. Instead, yields of any of the six fundamentally different complexes (page 6) may be obtained.

Synthesis for triphos complexes are here proposed which enable one to predict where and how many metal groups will be bonded to triphos. This different approach has been used by Keiter et al.[23] on diphos complexes and is exemplified by the following reactions:

$$\text{(CO)}_5\text{WPPh}_2\text{CH=CH}_2 + \text{HPPh}_2 \xrightarrow[\text{KOBu-t}]{\text{AIBN}} \text{(CO)}_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$$

$$\text{(CO)}_5\text{WPPh}_2\text{H} + \text{PPh}_2\text{CH=CH}_2 \xrightarrow{\text{AIBN}} \text{(CO)}_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$$

By using similar methods we have built triphos complexes of the five possible nonchelated triphos complexes of pentacarbonyl tungsten by judiciously selecting the proper coordinated fragments.



XVI

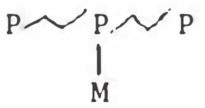
XVII

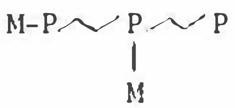
XVIII

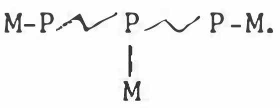
XIX

XX

RESULTS AND DISCUSSION

Traditionally the inorganic chemist has thought in terms of substitution when he considers the synthesis of a new transition metal complex. Such thinking can be limiting especially when one is dealing with polydentate phosphorus ligands. As pointed out in the introduction, difficulties arise when one seeks to obtain a particular isomer of triphos by a substitution reaction. Suppose, for example, one sought to prepare a hypothetical complex, $\mathrm{M{-}P}\diagup\!\diagdown\!\diagup\,\mathrm{P}\diagup\!\diagdown\!\diagup\mathrm{P}$, in which an end phosphorus is coordinated. One could imagine starting with M-Y, a complex in which Y is a good leaving group. The reaction: $\mathrm{M{-}Y} + \mathrm{P}\diagup\!\diagdown\!\diagup\mathrm{P}\diagup\!\diagdown\!\diagup\mathrm{P} \dashrightarrow \mathrm{M{-}P}\diagup\!\diagdown\!\diagup\,\mathrm{P}\diagup\!\diagdown\!\diagup\,\mathrm{P} + \mathrm{Y}$ could be imagined. In practice, however, such a reaction would not only produce the product as written but might also produce  $\mathrm{P}\diagup\!\diagdown\!\diagup\underset{\substack{|\\ \mathrm{M}}}{\mathrm{P}}\diagup\!\diagdown\!\diagup\mathrm{P}$

plus the dimetallic species such as $\mathrm{M{-}P}\diagup\!\diagdown\!\diagup\mathrm{P}\diagup\!\diagdown\!\diagup\mathrm{P{-}M}$ or  $\mathrm{M{-}P}\diagup\!\diagdown\!\diagup\underset{\substack{|\\ \mathrm{M}}}{\mathrm{P}}\diagup\!\diagdown\!\diagup\mathrm{P}$

and the trimetallic species  $\mathrm{M{-}P}\diagup\!\diagdown\!\diagup\underset{\substack{|\\ \mathrm{M}}}{\mathrm{P}}\diagup\!\diagdown\!\diagup\mathrm{P{-}M}$. These complexes would be

difficult to separate and chances are the synthesis would not be attempted or as in the case of King's work,[11] the obtained mixture of products could not be separated. Tedious separation can be avoided by designing syntheses based on addition rather than substitution reactions. In this work we have designed such syntheses and have been successful in synthesizing the complexes listed below: $Ph_2PCH_2CH_2P(Ph)[W(CO)_5]CH_2CH_2PPh_2$ (XVI)

$(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$ (XVII),

$(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2Ph_2PW(CO)_5$ (XVIII),

$(OC)_5WPPh_2CH_2CH_2P(Ph)[W(CO)_5]CH_2CH_2PPh_2$ (XIX),

$(OC)_5WPPh_2CH_2CH_2P(Ph)[W(CO)_5]CH_2CH_2Ph_2PW(CO)_5$ (XX).

To construct the five complexes of interest (XVI - XX), it was first necessary to synthesize some of the starting materials that would be needed to make the metal triphos complexes. These starting materials were $(CO)_5WPPh_2H$, $(CO)_5WPPh_2CH{=}CH_2$ and $(CO)_5WPPh(CH{=}CH_2)_2$. A number of approaches could be used for obtaining these complexes but most would not provide the formation of a clean product. Pyrolysis in a high boiling solvent in the presence of the appropriate ligand tends to give cis and trans products as well as the monosubstituted product. Photolysis of $W(CO)_6$ in the presence of ligand offers the same disadvantages. Strohmeier[24], more than anyone else, solved the problem of high yield production of monosubstituted product by using an indirect method. The method is based on production of an unisolated THF complex by a photolytic method followed by addition of phosphine ligand.

$$W(CO)_6 \xrightarrow[h\nu]{THF} (CO)_5W\text{-}THF \quad + \quad CO\uparrow$$

$$(CO)_5W\text{-}THF \quad + \quad L \longrightarrow (CO)_5WL$$

$L = HPPh_2,\ PPh_2CH{=}CH_2$ and $PPh(CH{=}CH_2)_2$

The crude reaction mixture realized from the above sequence was found to contain tungsten hexacarbonyl, free ligand, unidentified decomposed material and the desired product. It is known that tungsten hexacarbonyl is sparingly soluble in dichloromethane whereas the complex and free ligand are very soluble. By dissolving the oily crude mixture, after the THF was stripped off, in dichloromethane and cooling in a freezer for two days, most of the tungsten hexacarbonyl precipitated out of solution leaving the ligated complex, free ligand and decomposed material in solution. The tungsten hexacarbonyl was filtered out of solution and the dark filtrate was treated with charcoal and filtered to remove the decomposed material to give a yellow colored solution.

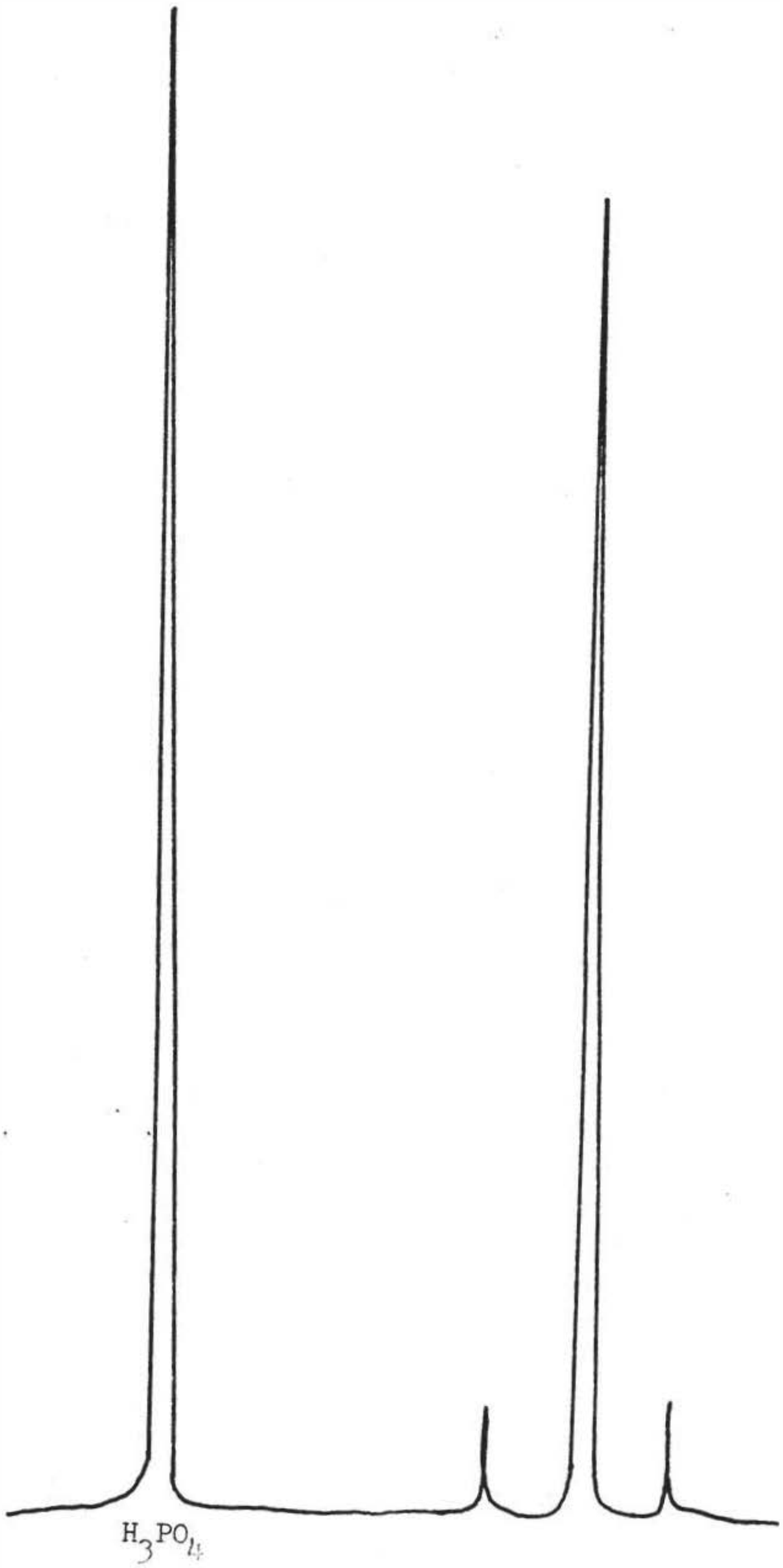
The $(CO)_5WPPh_2H$ and $(CO)_5WPPh_2CH{=}CH_2$ were worked up in the same manner. A different procedure was used for $(CO)_5WPPh(CH{=}CH_2)_2$ to be discussed later. An equal volume of methanol was added to the dichloromethane solution and the new solution was cooled in a freezer for a few days, after which the complex crystallized. These crystals were further purified by subliming out trace tungsten hexacarbonyl. The pure $(CO)_5WPPh_2H$ complex is a whitish crystalline product that has a melting poing of 91-93°C. The complex $(CO)_5WPPh_2CH{=}CH_2$ is a whitish crystalline product with a melting point of 64-65°C. It is noted that prolonged exposure to light caused the complexes to slowly decompose turning the crystals brown. This procedure yields pure products that can be verified by infrared, ^{31}P NMR as well as elemental analysis. Table I (page 53) lists these compounds and the best yields obtained.

The work-up of the dichloromethane solution of $(CO)_5WPPh(CH{=}CH_2)_2$ required removing the dichloromethane and distilling with a molecular still the nonviscous dark yellow oil which resulted. The nonviscous yellow liquid complex was obtained in high yield (Table I). The complex is stable in air at room temperature and can be stored for long periods of time if protected from light.

The complex $(CO)_5WPPh_2H$ contains only one phosphorus atom and therefore its ^{31}P NMR proton decoupled spectrum (Figure 1) contains one major resonance signal. The upfield chemical shift at -13.7 ppm is somewhat unusual as most tungsten carbonyl complexes show chemical

Figure 1

^{31}P NMR of $(CO)_5WPPh_2H$



shifts downfield from the reference, 85% H_3PO_4.[25,26] Diphenylphosphine in the uncoordinated form has a shift of -41 ppm,[25] thus a downfield shift is noted upon coordination. This is due to a decrease in electron density of the coordinated phosphorus atom as compared to the free ligand phosphorus. It occurs because of the formation of a sigma bond which results when the phosphorus lone pair is donated to the metal. This causes a deshielding effect on the phosphorus atom thus moving the phosphorus-31 chemical shift to a downfield position. Due to tungsten-183 (nuclear spin $\frac{1}{2}$, natural abundance 14.3%) the phosphorus resonance signal is flanked by satellite signals which reveal a tungsten-phosphorus coupling constant of 229.6 Hz. This value is taken as the separation between the two tungsten satellite signals (Table II, page 54).

The complex $(CO)_5WPPh_2CH{=}CH_2$ has a phosphorus-31 NMR spectrum (Figure 2) that shows a singlet downfield at 11.4 ppm. The tungsten-phosphorus coupling constant of 239.4 Hz is somewhat larger than for $(CO)_5WPPh_2H$, consistent with replacing -H with the more electronegative $-CH{=}CH_2$ group (Table II).

The phosphorus-31 NMR spectrum of $(CO)_5WPPh(CH{=}CH_2)_2$ is shown in Figure 3. The phosphorus-31 chemical shift is at 2.27 ppm. The tungsten-phosphorus coupling constant for this complex is 236.3 Hz (Table II).

The compound $(CO)_5WPPh_2H$ exhibits the characteristic IR spectrum of a monosubstituted complex, $(CO)_5WL$, of C_{4v} symmetry, as do all the complexes studied in this thesis. This spectrum clearly shows that $W(CO)_6$ has been substituted. The infrared spectrum (Figure 4) exhibits three stretching bands in the carbonyl region. These three bands can be identified as 2077 cm^{-1} $A_1^{(2)}$ strong; 1985 cm^{-1} B_1 weak (a forbidden

Figure 2

^{31}P NMR of $(CO)_5WPPh_2CH=CH_2$

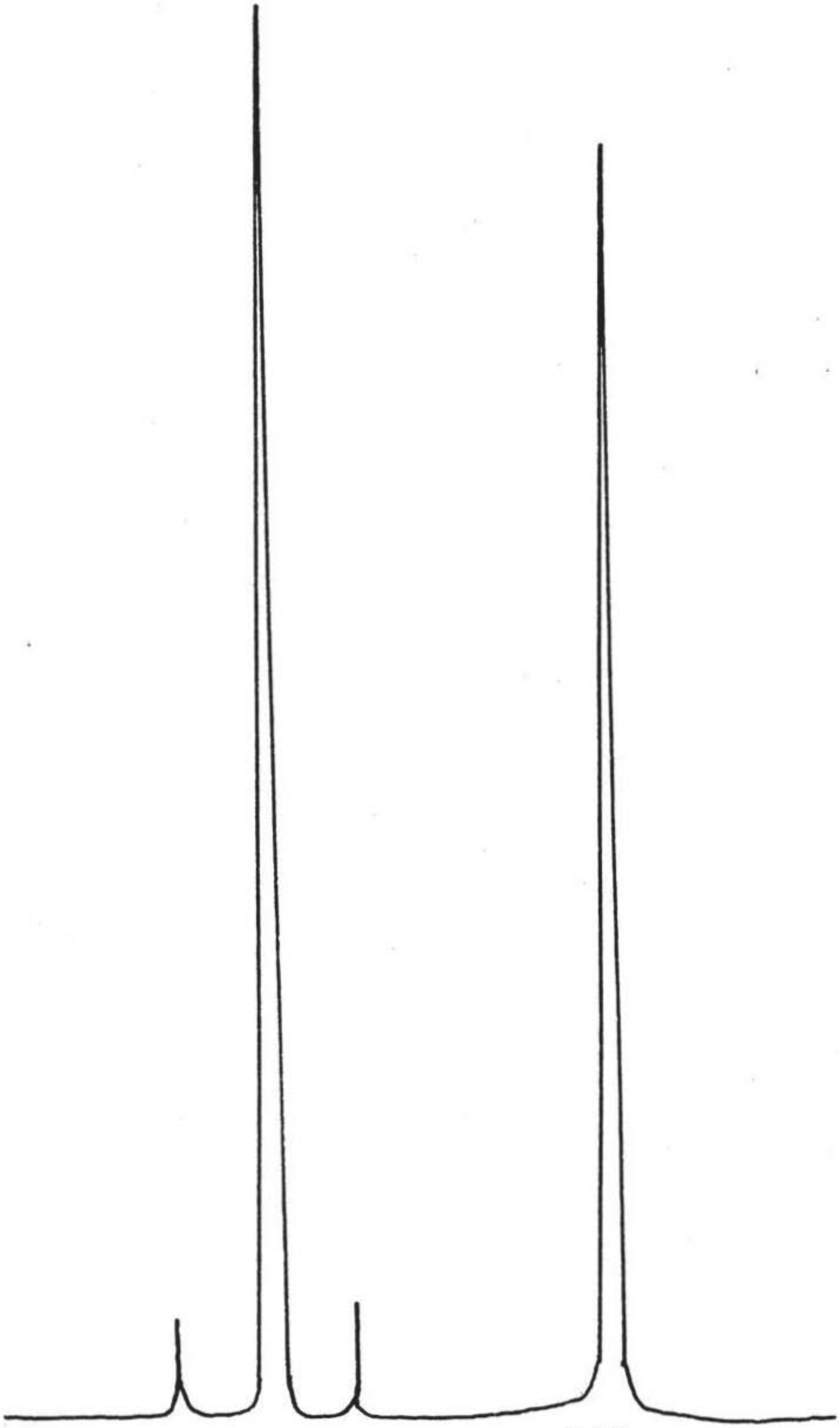


Figure 3

^{31}P NMR of $(CO)_5WPPh(CH=CH_2)_2$

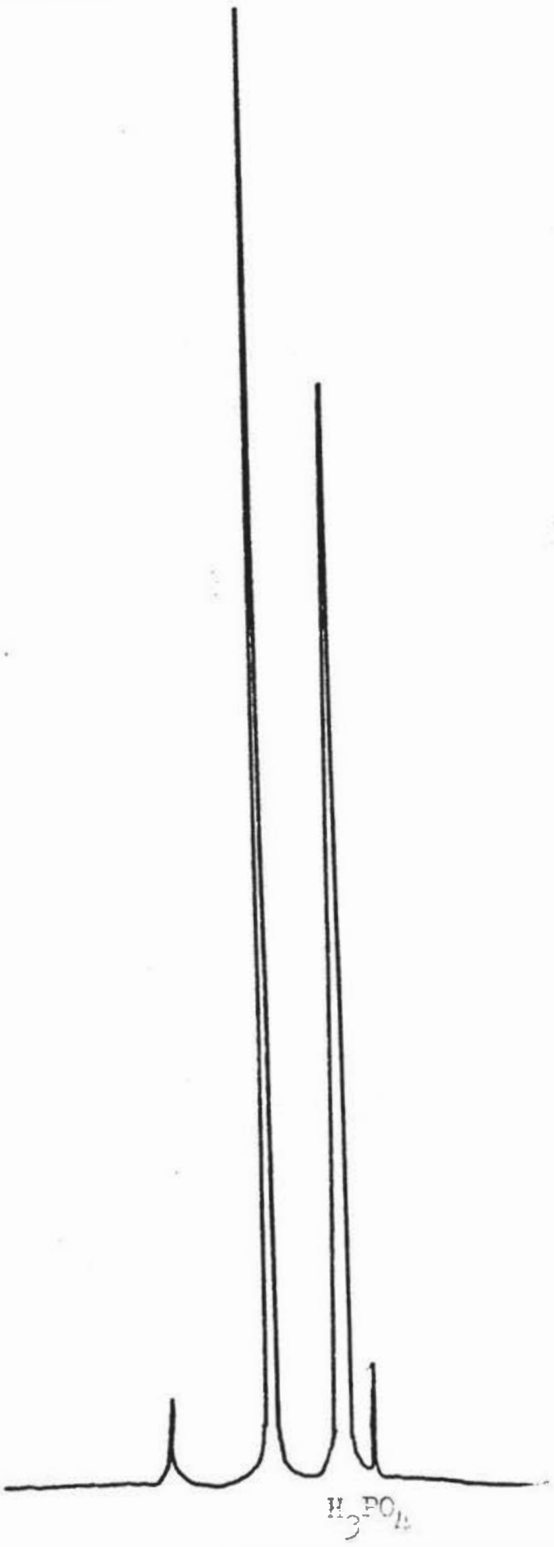
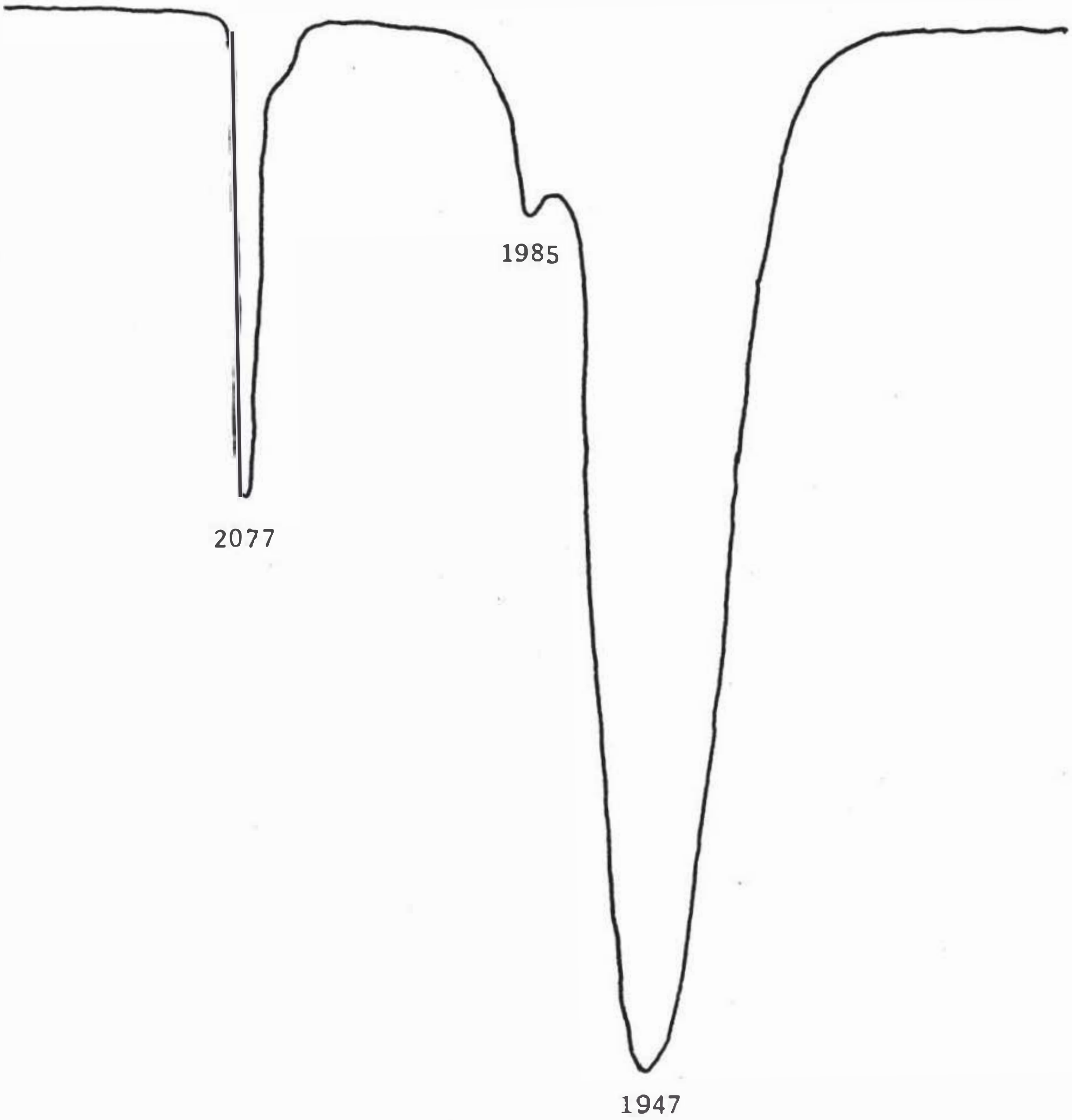


Figure 4

Expanded IR spectrum of $(CO)_5WPPh_2H$



transition which gains some intensity because the symmetry of the complex is less than C_{4v}) and 1947 cm^{-1} ($E + A_1^{(1)}$) very strong (Table III, page 55).

The infrared spectrum of the $(CO)_5WPPh_2CH{=}CH_2$ complex (Figure 5) displayed the characteristic C_{4v} symmetry spectrum and its stretching frequencies are listed in Table III.

The infrared spectrum of $(CO)_5WPPh(CH{=}CH_2)_2$ is shown in Figure 6 (Table III).

Several approaches could be envisioned for the synthesis of $(CO)_5WPPh(CH_2CH_2PPh_2)_2$. Possibilities are:

$$(CO)_5WPPh(CH{=}CH_2)_2 \;+\; 2\ PPh_2H \longrightarrow (CO)_5WPPh(CH_2CH_2PPh_2)_2$$

or

$$(CO)_5WPPhH_2 + 2\ PPh_2(CH{=}CH_2) \longrightarrow (CO)_5WPPh(CH_2CH_2PPh_2)_2$$

The first reaction was choosen because it eliminated working with the extremely air sensitive phenylphosphine. The free radical catalyst, AIBN, was chosen for this reaction rather than the base catalyst, KOBu-t. We have found that the free radical induced reaction will proceed without solvent if the reaction mixture is liquid at 75°C. In general, the base catalyst requires dry THF and so our method eliminates a solvent drying step.

The complex $(CO)_5WPPh(CH{=}CH_2)_2$ is an excellent starting material for the production of $(CO)_5WPPh(CH_2CH_2PPh_2)_2$ (XVI). The reaction proceeds quite smoothly aided by the homogenity of the starting materials. The excess diphenylphosphine was removed by high vacuum. The work-up of the complex consisted of several crystallizations which finally yielded a white crystalline product (melting point 69-74°C) (Table I, page 53).

Figure 5

Expanded IR spectrum of $(CO)_5WPPh_2CH=CH_2$

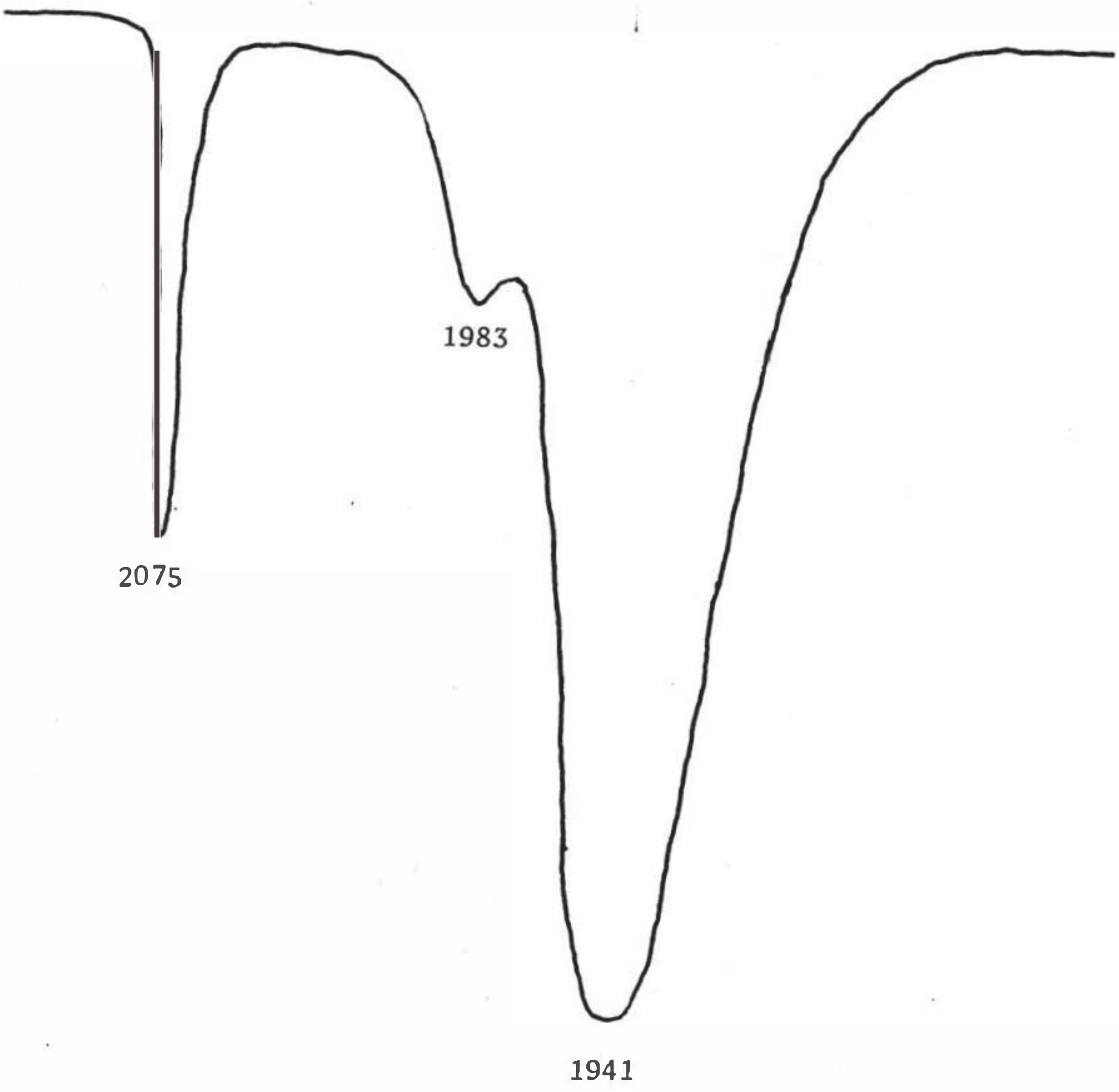
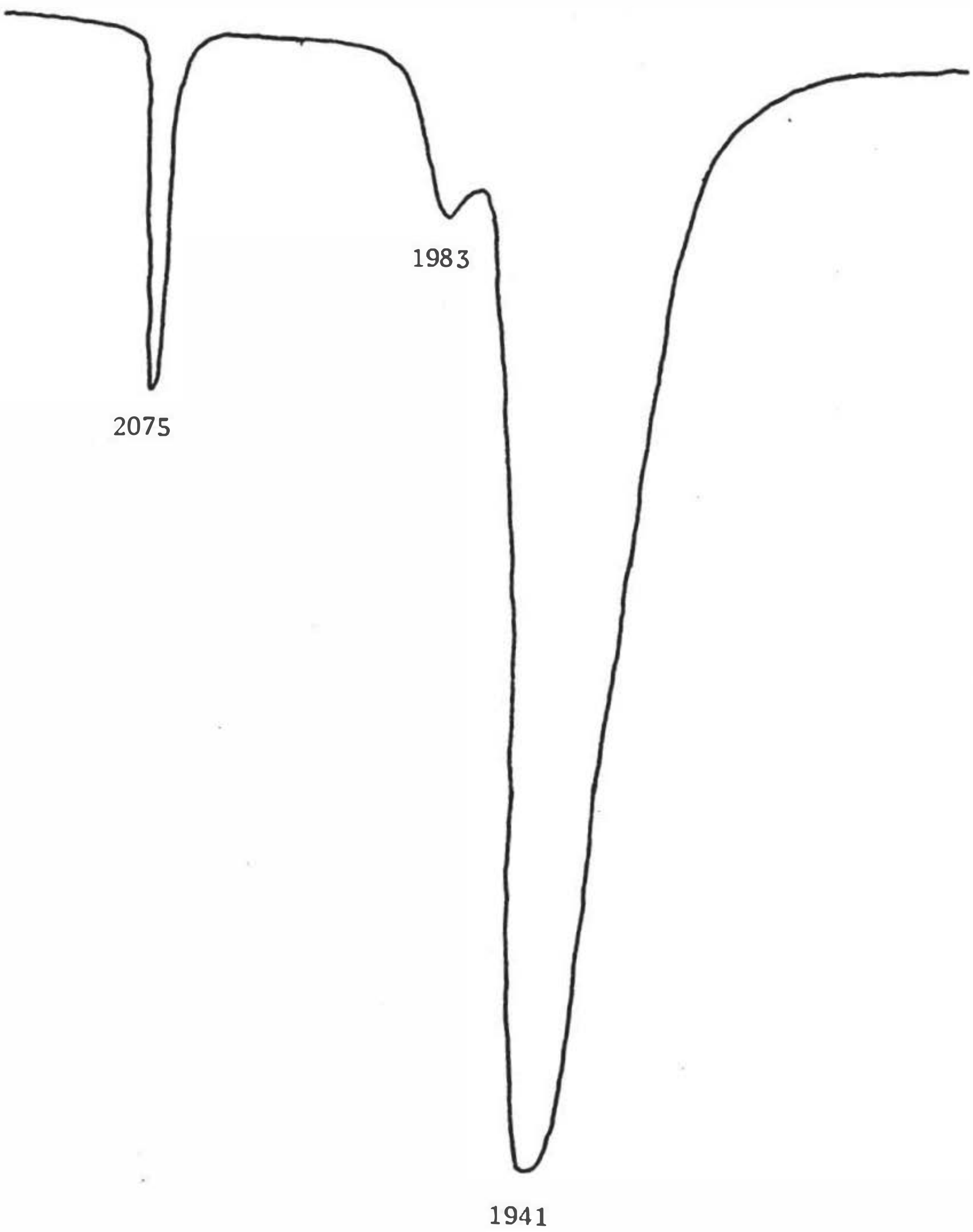


Figure 6

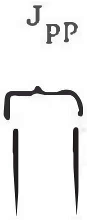
Expanded IR spectrum of $(CO)_5WPPh(CH{=}CH_2)_2$



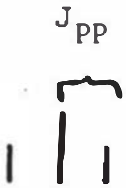
The infrared spectrum of this complex is shown in Figure 7; its carbonyl stretching frequencies are listed in Table III (page 55).

The phosphorus-31 NMR spectrum of this complex, as shown in Figure 8, unambiguously establishes the structure of this complex. The multiplicity of a phosphorus-31 peak due to first-order splitting is predicted by simple rules. The number of signal is given by (n+1) when the n other nuclei are also of spin $\frac{1}{2}$ or, in general, by (2nI + 1) where I is the nuclear spin of the coupled nuclei. For $I = \frac{1}{2}$ the relative intensities of the (n + 1) peaks are given by the binomial coefficients. This follows as a natural consequence of the number of different ways which n spin $\frac{1}{2}$ nuclei can be distributed among two possible energy states and the relative statistical probabilities of each of the possible distributions.[27] From this (2nI + 1) rule one would expect to see a downfield triplet for the WPPh and such is found at 7.3 ppm. In addition an upfield doublet for $-PPh_2$ is found at -12.5 ppm. These signals gave the intensities expected.

The phosphorus-phosphorus coupling constant ($^3J_{pp}$) is found to be 33.8 Hz. This coupling constant can be measured from either the distance between the doublet or from the triplet.



or



Both measurements should yield the same coupling constant since the terminal phosphorus and center phosphorus atoms are coupled. In the expression $^3J_{PP}$, the 3 indicates the number of chemical bonds between the coupled phosphorus atoms.

Figure 7

Expanded IR spectrum of P∕∖∕P(W)∕∖∕P

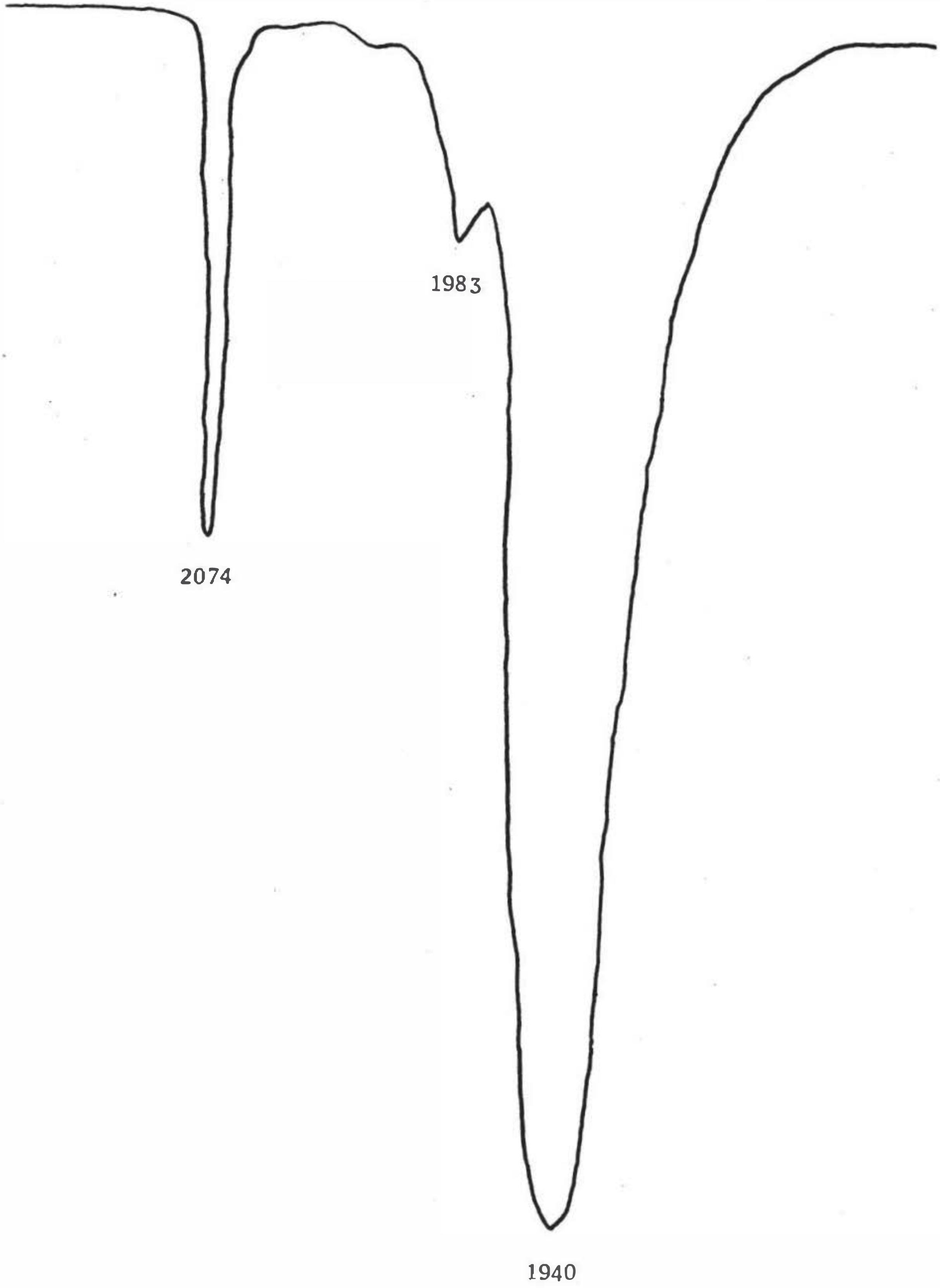
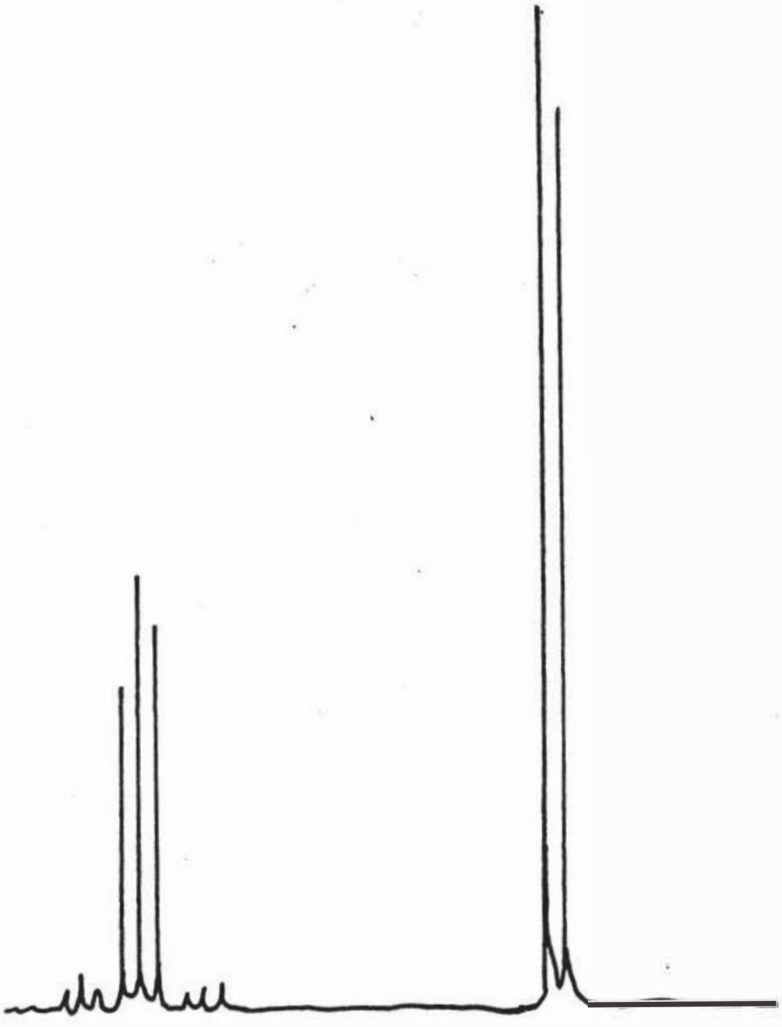
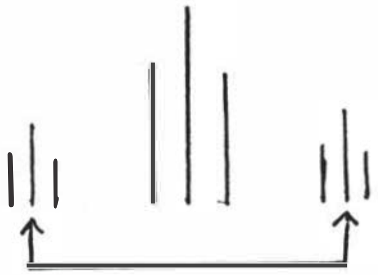


Figure 8

^{31}P NMR of P ∼ P(W) ∼ P



The tungsten-183 satellites, two triplets, are observed for the coordinated phosphorus atom and J_{WP} is 236.7 Hz. To obtain the tungsten-phosphorus coupling-constant from a triplet the separation between the mid peaks of the triplet can be measured



= J_{WP}

Long range tungsten-phosphorus coupling is not observed (Table II).

In solution, XVI is slowly oxidized to a monoxide which shows phosphorus-31 chemical shifts (Figure 9) at -12.6, 7.4 and 31.1 ppm for the uncoordinated phosphorus atom (doublet), phosphorus coordinated to tungsten (a doublet of doublets that appears as a triplet) and phosphine oxide (doublet) respectively. The phosphorus-phosphorus coupling between coordinated (tungsten and oxygen) phosphorus atoms is 43.2 Hz and between coordinated phosphorus and the phosphine oxide atoms is 34.2 Hz.

Obtaining $(CO)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$ (XVII), a structural isomer of XVI, was synthetically difficult and was best accomplished by a two step reaction involving $Ph_2PCH_2CH_2PPh(CH{=}CH_2)$ as an unisolated intermediate. The reaction sequence taken is as follows:

$$PhP(CH{=}CH_2)_2 \;+\; PPh_2H \xrightarrow{AIBN} Ph_2PCH_2CH_2PPh(CH{=}CH_2)$$

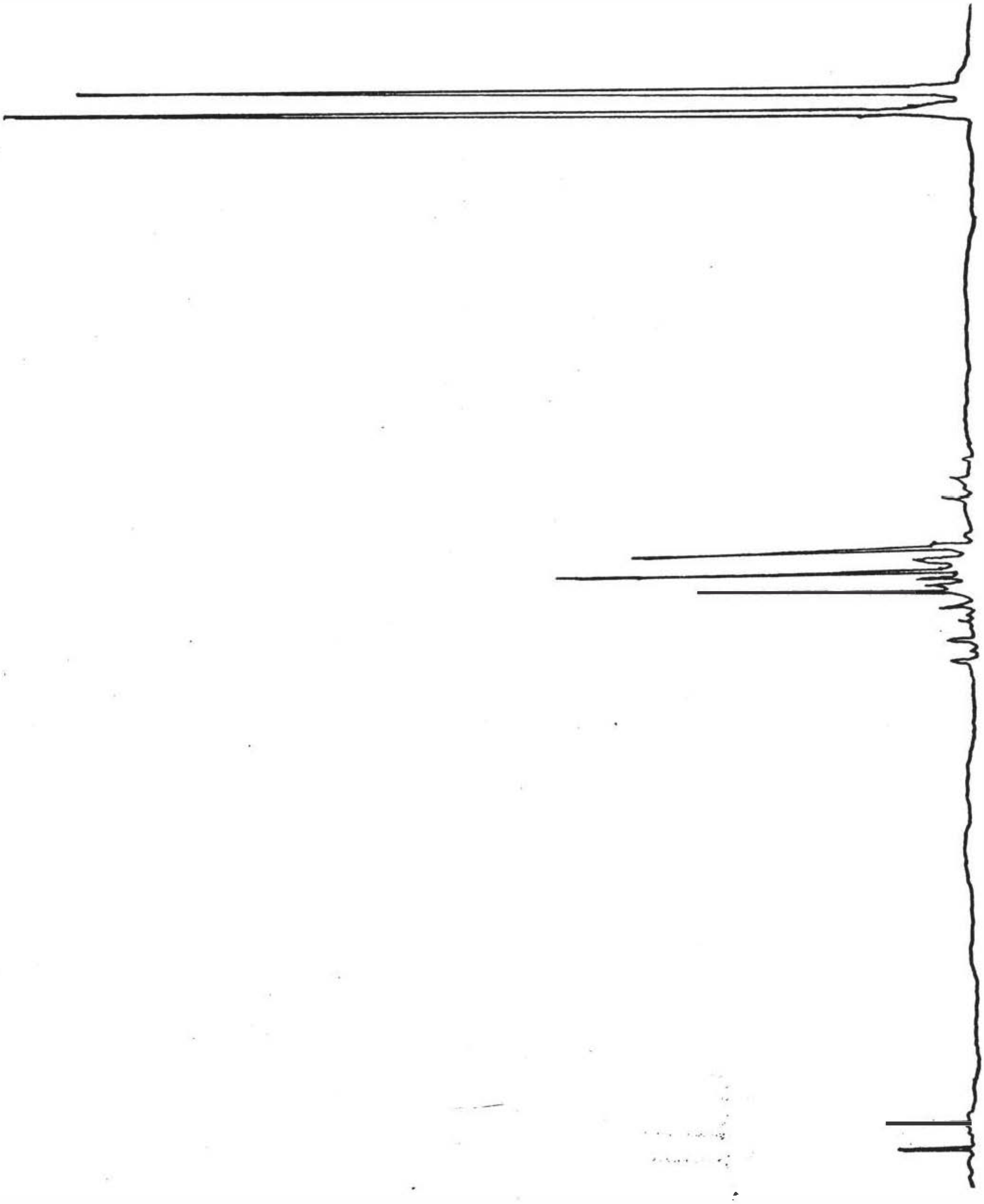
$$Ph_2PCH_2CH_2PPh(CH{=}CH_2) \;+\; (CO)_5WPPh_2H \xrightarrow{AIBN} Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2W(CO)_5$$

This two step method allowed us to remove excess starting material after the first step to accomplish a better separation in the final

Figure 9

^{31}P NMR of P /\/ P(W) /\/ P(O)

and ^{31}P NMR of P /\/ P(W) /\/ P



product. The intermediate was not isolated, diminishing oxide formation. After the second step the work-up of the tungsten complex proceeded in the same manner of trying to crystallize the oily crude mixture from a 1:1 dichloromethane/methanol solution. An oil was obtained which was again submitted to the crystallization step but an oil once again resulted. This yellow oil was examined by TLC, IR, ^{31}P-NMR and CHP elemental analysis. The TLC showed only one spot upon separation so the oil was presumed to be the product (Table I). The infrared spectrum (Figure 10) of the oil displayed the expected C_{4v} symmetry and its stretching frequencies are listed in Table III. The CHP analysis gave the expected results within experimental error.

The phosphorus-31 NMR spectrum (Figure 11) displays the characteristic spectrum of three chemically nonequivalent phosphorus atoms of a first order AMX spin system. The doublet chemical shift downfield of the H_3PO_4 reference peak at 12.5 ppm was assigned to the tungsten coordinated phosphorus. A tungsten-phosphorus coupling constant of 239.4 Hz and a phosphorus-phosphorus coupling constant of 29.4 Hz were observed. The furthest upfield chemical shift doublet at -12.8 ppm was assigned to the terminal phosphorus atom by the (2nI + 1) rule and showed a phosphorus-phosphorus coupling constant of 31.1 Hz. The upfield chemical shift doublet of doublets at -16.6 ppm was assigned to the central phosphine. This assignment clearly identifies the complex and dramatically distinguishes it from its isomer XVI (Table II). Isomer XVII is somewhat more air sensitive than isomer XVI and mixtures of $(CO)_5WPPh_2CH_2CH_2P(Ph)(O)CH_2CH_2PPh_2$ and $(CO)_5WPPh_2CH_2CH_2P(Ph)CH_2CH_2PPh_2(O)$ could be observed spectroscopically (Figure 12) but were not isolated. The chemical shifts for the oxides were $\delta_{P=O}$ = 40.7 and $\delta_{P=O}$ = 32.7 ppm respectively.

Figure 10

Expanded IR spectrum of WP∿P∿P

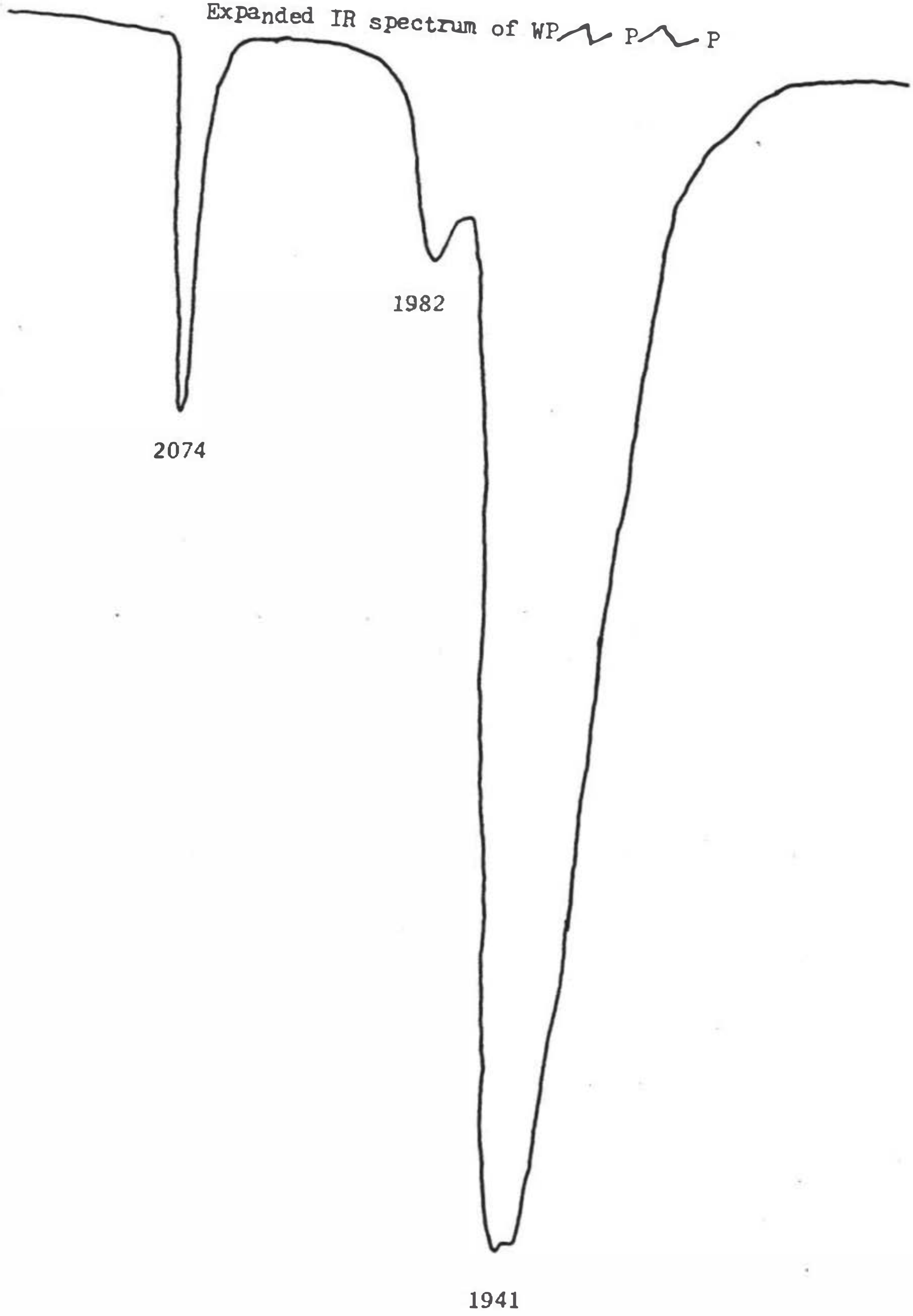
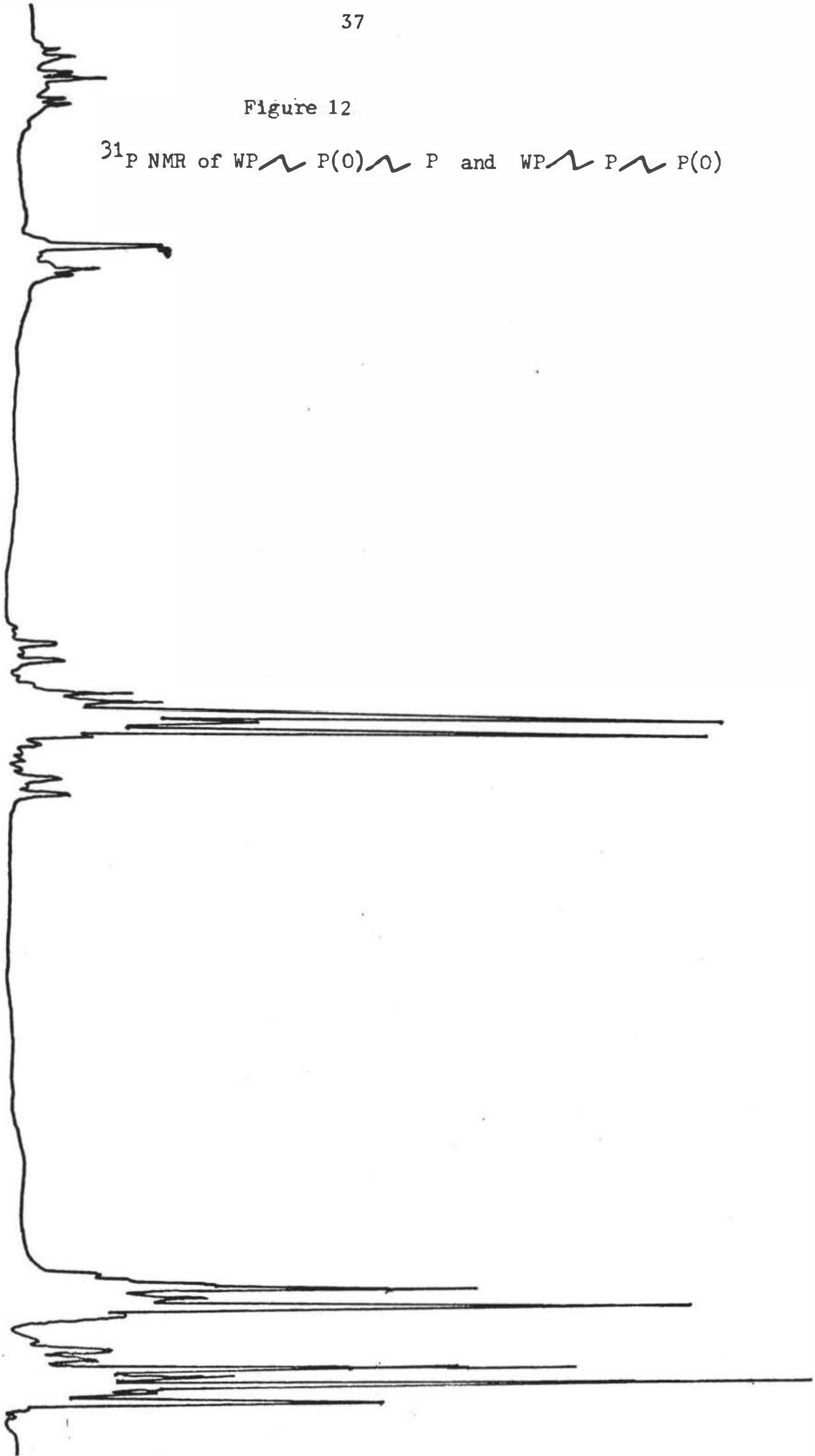


Figure 11

^{31}P NMR of 

Figure 12

^{31}P NMR of WP∿P(O)∿P and WP∿P∿P(O)



Other reported examples of monoligate complexes are the unseparated isomers of $CH_3COFe(CO)(Triphos)\eta^5-C_5H_5$ (X a and b) and $(CO)_4Fe(Triphos)$.[11,12] In addition $[V(CO)_5(Triphos)]^-$ has been observed in solution by IR and ^{51}V NMR.[17]

Complex XVIII was also obtained by a free radical addition.

$$2(CO)_5WPPh_2CH{=}CH_2 \quad + \quad PPhH_2 \xrightarrow{AIBN} (CO)_5WPPh_2CH_2CH_2P(Ph)CH_2CH_2PPh_2W(CO)_5$$

The work-up of XVIII involved the removal of unreacted $PPhH_2$ by high vacuum. The attempts to crystallize XVIII from dichloromethane and methanol resulted in an oil which when checked by TLC showed several compounds. Column chromatography (silica gel) using 80% petroleum ether/20% ethyl acetate as the eluting solvent gave the best separation. The oil which resulted crystallized from a dichloromethane/methanol mixture after two months. The complex appears as a white solid (Table I).

The infrared spectrum (Figure 13) of the crystals displayed the expected C_{4v} symmetry spectrum. The stretching frequencies are listed in Table III.

The phosphorus-31 NMR spectrum (Figure 14) is first order and arises from two equivalent phosphorus atoms and a third nonequivalent to the two; the chemical shift of the upfield triplet is at -17.3 ppm and the downfield doublet at 13.6 ppm with a J_{PP} of 30.7 Hz and a J_{WP} of 239.9 Hz. This spectrum establishes the structure of XVIII (Table II).

This compound was found to air oxidize to $(CO)_5WPPh_2CH_2CH_2P(Ph)(O)$-$CH_2CH_2PPh_2W(CO)_5$. Its spectrum (Figure 15) reveals a downfield triplet (assigned to the phosphoryl group) chemical shift at 45.6 ppm with a phosphorus-phosphorus coupling constant of 46.4 Hz.

Figure 13

Expanded IR spectrum of WP$\sim$P$\sim$PW

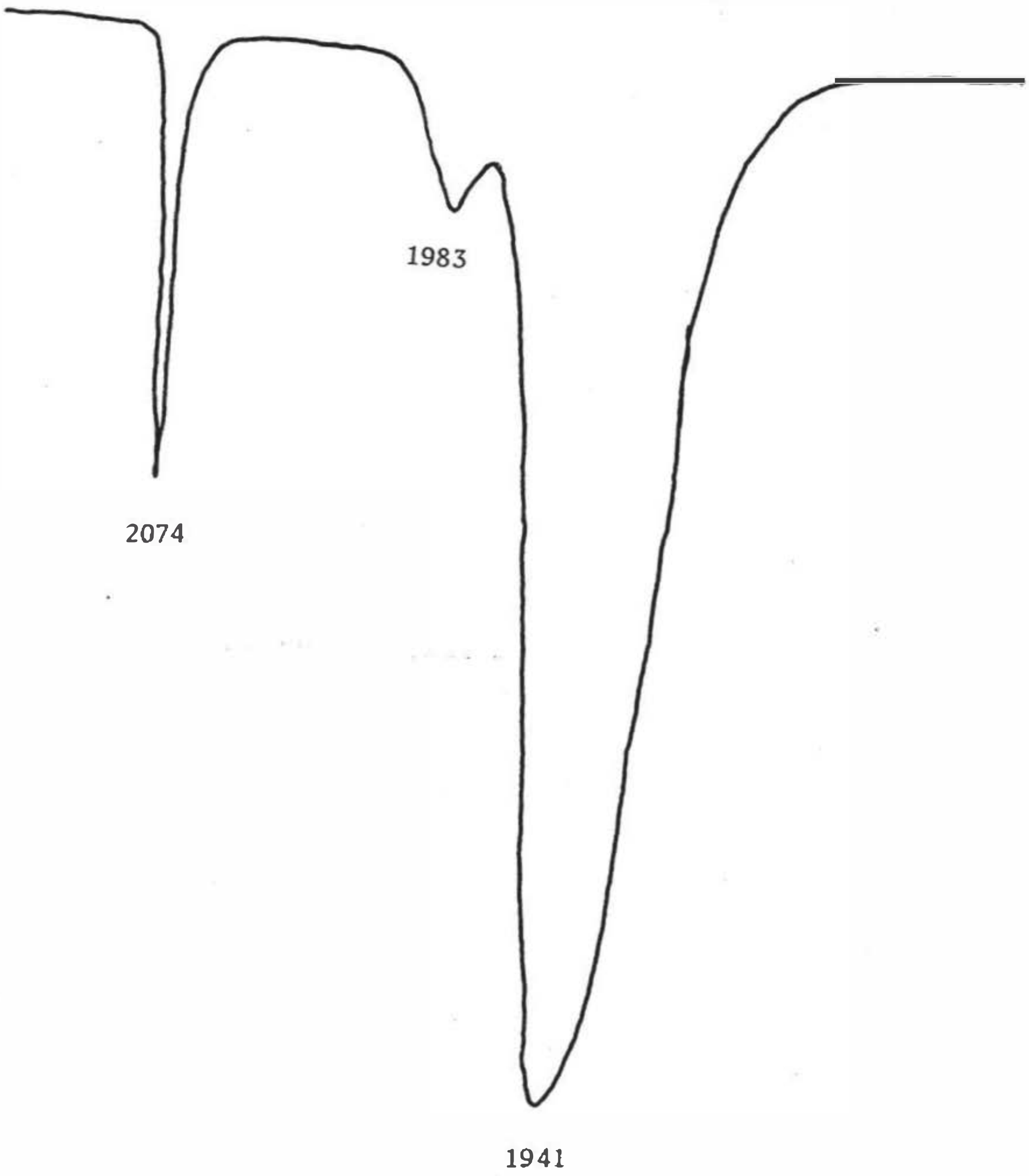


Figure 14

^{31}P NMR of WP$\sim$P$\sim$PW

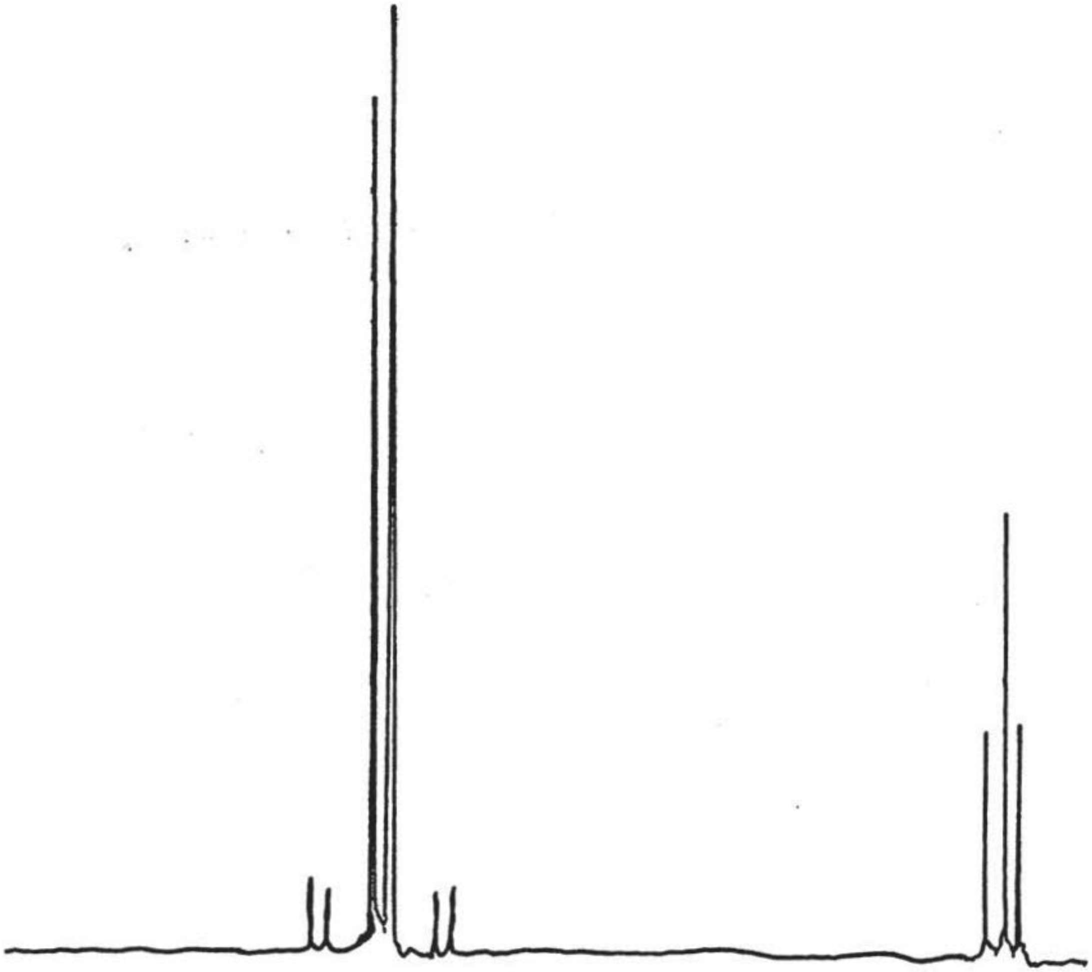
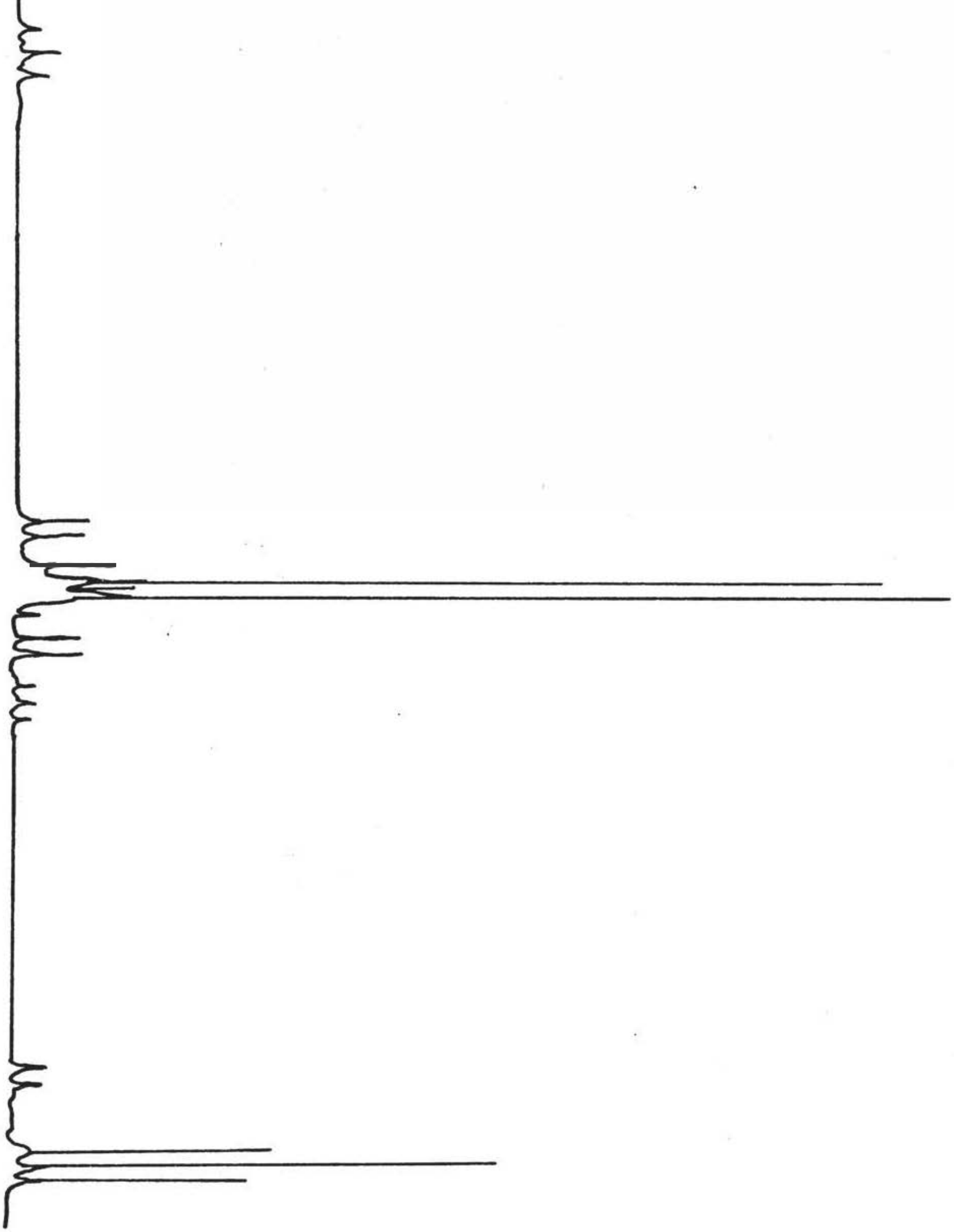


Figure 15

^{31}P NMR of WP∿P(O)∿PW and WP∿P∿PW



Complex XIX, the isomer of XVIII, was prepared by a two step base catalyzed method in which the intermediate was isolated from its starting materials and the trimetallic complex (XX) by fractional crystallization. The reaction sequence was as follows:

$$(CO)_5WPPh(CH{=}CH_2)_2 + (CO)_5WPPh_2H \xrightarrow{KOBu\text{-}t} (CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$$

$$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2) + PPh_2H \xrightarrow{KOBu\text{-}t}$$

$$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$$

In the first step the base catalyzed method had to be used because the free radical method does not work when both secondary and vinyl phosphines are coordinate. Apparently once the active free radical phosphorus species forms it becomes involved in a competitive reaction which proceeds faster than vinyl addition. Blue decomposed product was noted which usually signals higher order polytungstates. The intermediate was isolated as a white solid by the standard dichloromethane/methanol crystallization procedure described earlier. Crystal formation took several days (Table I).

The infrared spectrum (Figure 16) of the intermediate displays the typical C_{4v} symmetry spectrum. Since the two $-W(CO)_5$ moieties have slightly different electronic environments, one might expect to see this difference reflected. Such is not the case presumably because instrumental resolution is not adequate (Table III). The phosphorus-31 NMR spectrum shows the expected spectrum for two nonequivalent phosphorus atoms (Figure 17). This spectrum has two doublets that are downfield, one at 12.8 ppm ($^3J_{PP}$ = 35.7 Hz) with a tungsten-183- phosphorus coupling constant of 240.9 Hz. This signal is assigned to the diphenylphosphorus atom. The upfield doublet at 4.5 ppm (J_{WP} = 238.6 Hz) is

Figure 16

Expanded IR spectrum of WP~P(W)=

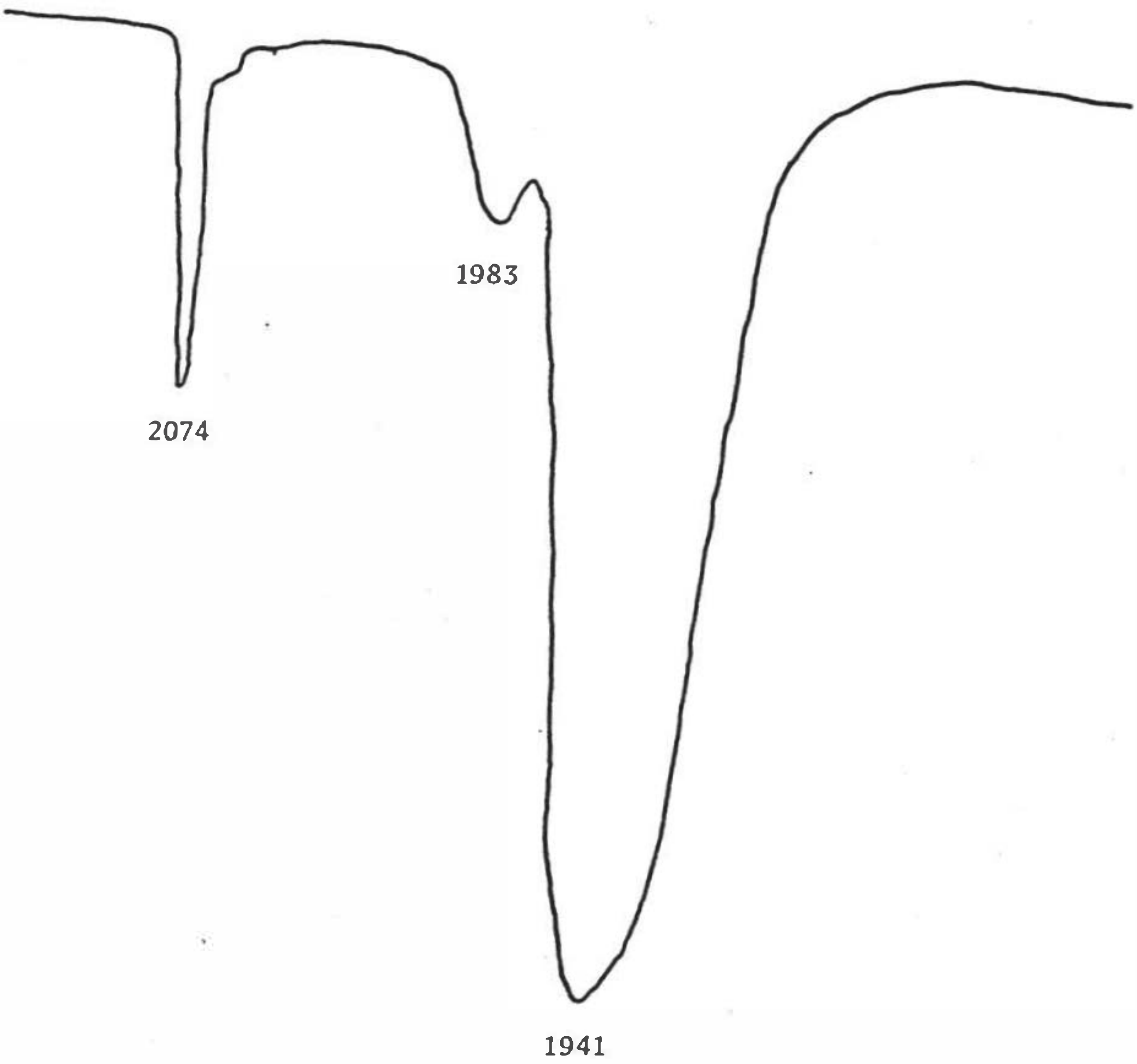
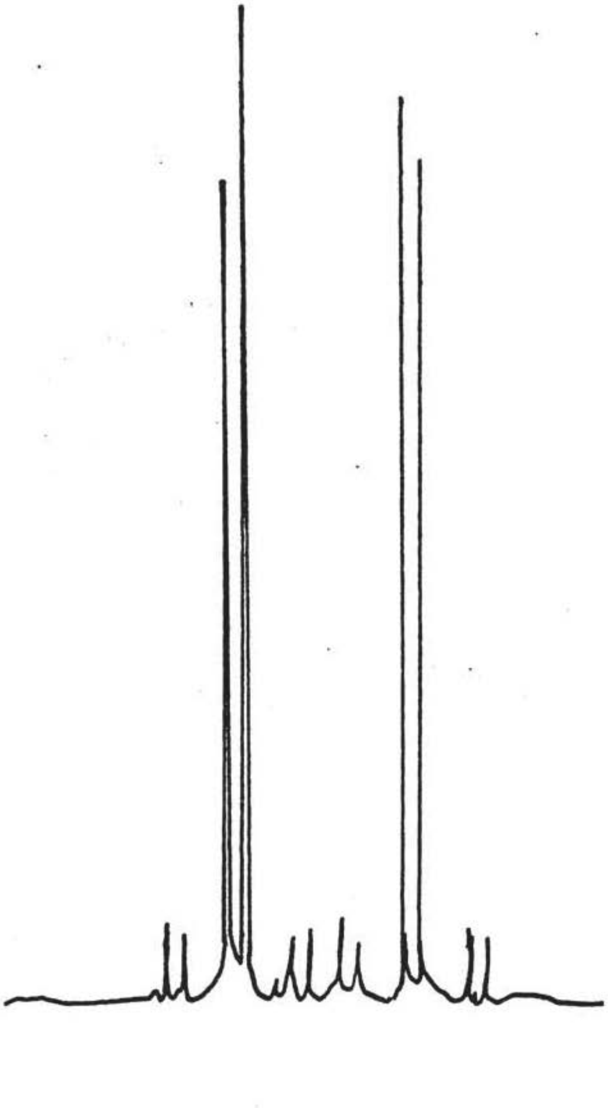


Figure 17

^{31}P NMR of WP/\/P(W)/=



assigned to the phenylphosphorus atom (Table II).

The second step of this reaction proved to be the most difficult step of all the reactions done due to the fact that the oxide of XIX, $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2(O)$, was so easily formed. To over come this oxide formation the atmosphere was rigorously excluded from the work-up. Deoxygenated solvents were used to obtain pure white product of unoptimized yield (Table I).

The product XIX gave the characteristic infrared spectrum for a C_{4v} symmetry complex (Figure 18). The stretching frequencies for this compound are listed in Table III. The phosphorus-31 NMR spectrum of this compound (Figure 19) can be seen to be a typical ABX spectrum and confirms its structural arrangements. The uncoordinated phosphorus atom gives rise to an upfield doublet at -12.1 ppm with a phosphorus-phosphorus coupling constant of 36.5 Hz. The terminal coordinated phosphorus atom gives rise to a downfield doublet chemical shift at 12.7 ppm with a phosphorus-phosphorus coupling constant of 32.7 Hz and a tungsten-183-phosphorus coupling constant of 239.9 Hz. The central coordinated phosphorus atom appears as a downfield doublet of doublets at 6.84 ppm (J_{WP} = 238.6 Hz) (Table II).

The oxide, $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2(O)$, was obtained in most reactions as a contaminant. It gives rise to a phosphorus-31 spectrum (Figure 20) that shows two doublets. The farthest downfield doublet is attributed to the oxide (29.2 ppm, $^3J_{PP}$ = 46.3 Hz). The second downfield doublet at 12.4 ppm is attributed to the terminal tungsten coordinated phosphine ($^3J_{PP}$ = 31.9 Hz). The center coordinated phosphorus which should give a doublet of doublets is obscured by signals from its precursors. The tungsten-183 satellites were not observed because of low concentrations.

Figure 18

Expanded IR spectrum of WP∕∖∕ P(W)∕∖∕ P

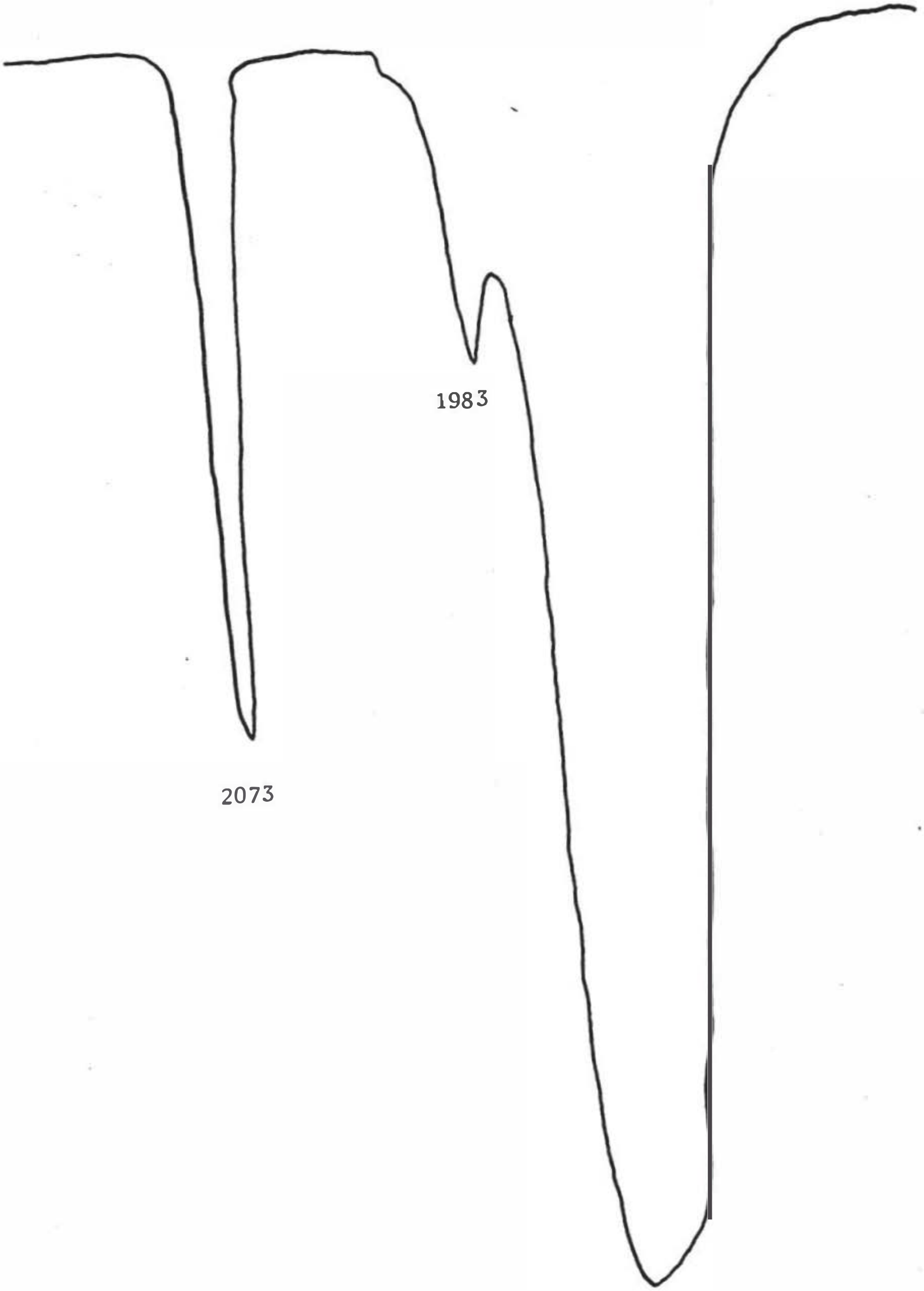


Figure 19

31P NMR of WP∿P(W)∿P

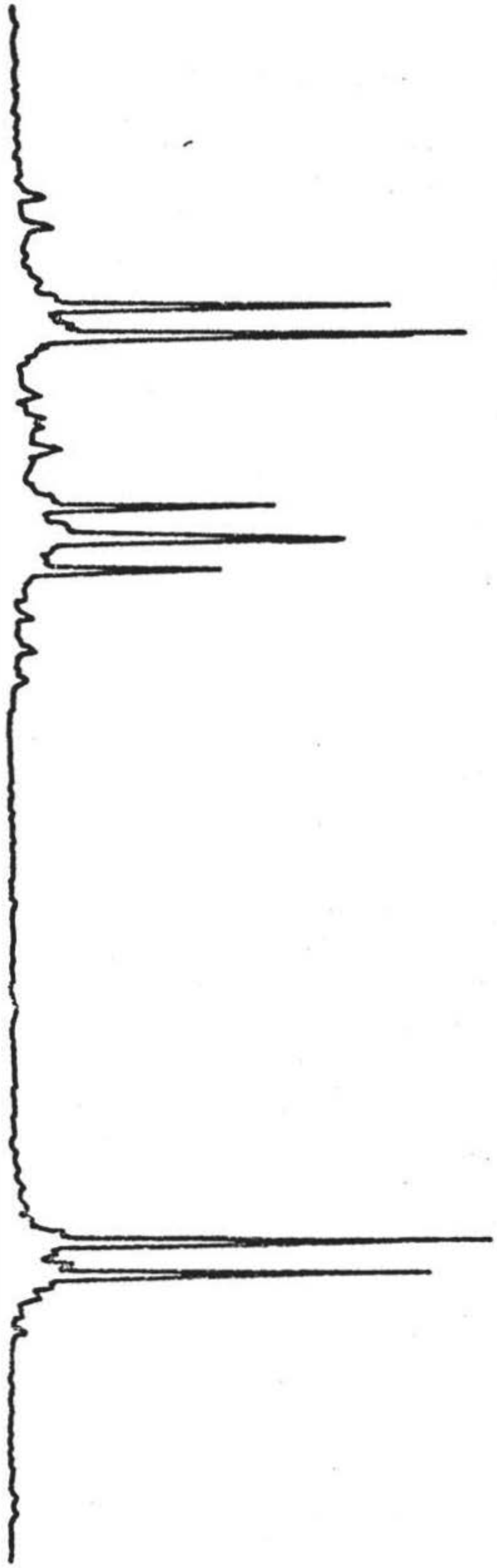
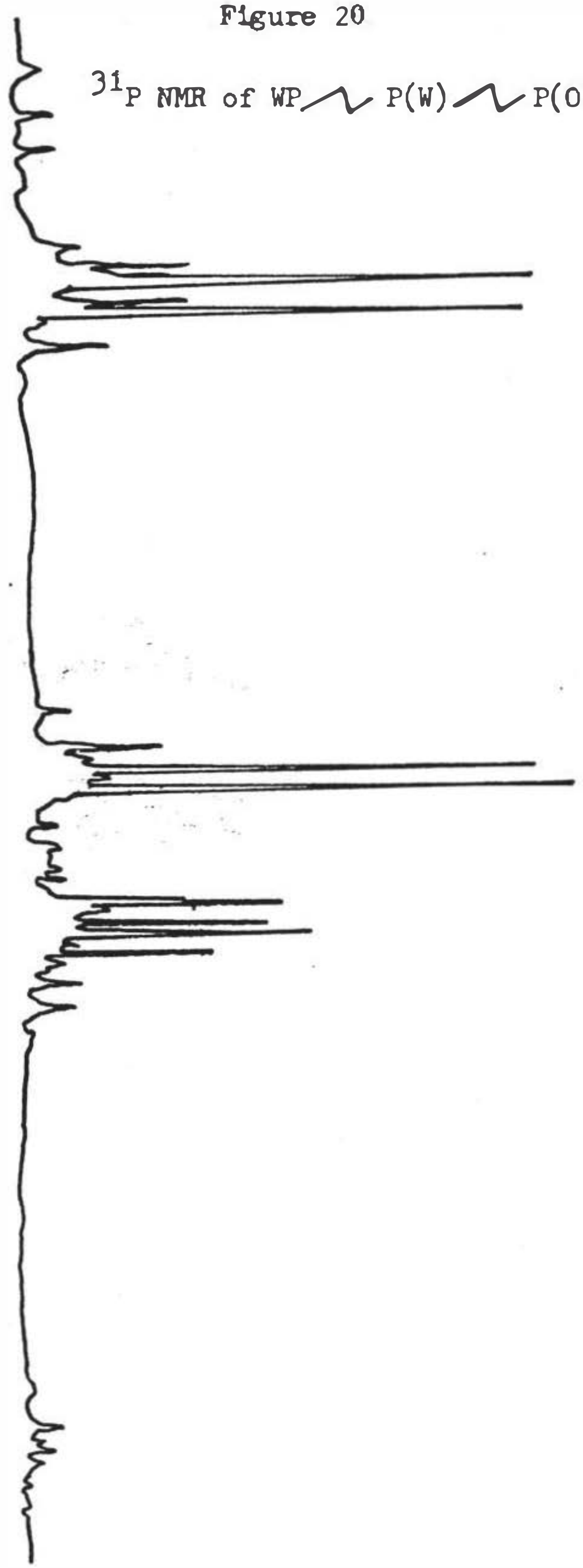


Figure 20

^{31}P NMR of WP∿P(W)∿P(O)



Isomers XVIII and XIX are particularly unusual because these are the first reported examples of two independent metal moieties attached to nonchelating triphos. The complex, $Fe_2(CO)_2(C_5H_5)_2$(Triphos) (page 8) is thought to be a biligate bimetallic complex in which the end and center phosphorus atoms are bound to the two carbonyl bridged iron atoms.[11,12] Two metal atoms are attached to triphos in the case of $Br(CO)_3Mn$(Triphos)$Cr(CO)_5$ (XVI)[17] and $[\eta^5\text{-}C_5H_5)_2Mn_2(CO)(NO)_2(\text{Triphos})]\text{-}[PF_6]_2$ (page 9)[12] but these contain chelated manganese. Triphos may also chelate through the two end phosphorus atoms as has been shown for trans-$[\eta^5\text{-}C_5H_5V(CO)_2(\text{Triphos})]$[17] (XIII and XIV).

Of the five complexes reported in this study, XX can be synthesized in the highest yield, is most readily crystallized as a white product and is the least soluble (Table I). Its reaction sequence is given as:

$$2(CO)_5WPPh_2H + (CO)_5WPPh(CH{=}CH_2)_2 \xrightarrow{\text{KOBu-t}} (CO)_5WPPh[CH_2CH_2PPh_2W(CO)_5]_2$$

The infrared spectrum is shown in Figure 21. The stretching frequencies for this compound are listed in Table III. The phosphorus-31 NMR spectrum (Figure 22) is a characteristic AB_2 type in appearance, much resembling that of the free triphos ligand.[19] The satellite spectrum can be compared to that of $Ph_2P(Se)CH_2CH_2P(Se)PhCH_2CH_2PPh_2(Se)$ which was recently analyzed.[10] It consists of the AB_2 part of an AB_2X spin system overlapping with the ABC part of an ABCX spin system. The center phosphorus resonance is found at 7.46 ppm with a phosphorus-phosphorus coupling constant of 34.7 Hz (J_{WP} = 239.4 Hz). The end phosphorus atoms are found at a chemical shift of 13.5 ppm (J_{WP}=242.0 Hz) (Table II).

Figure 21

Expanded IR Spectrum of WP∼ P(W) ∼ PW

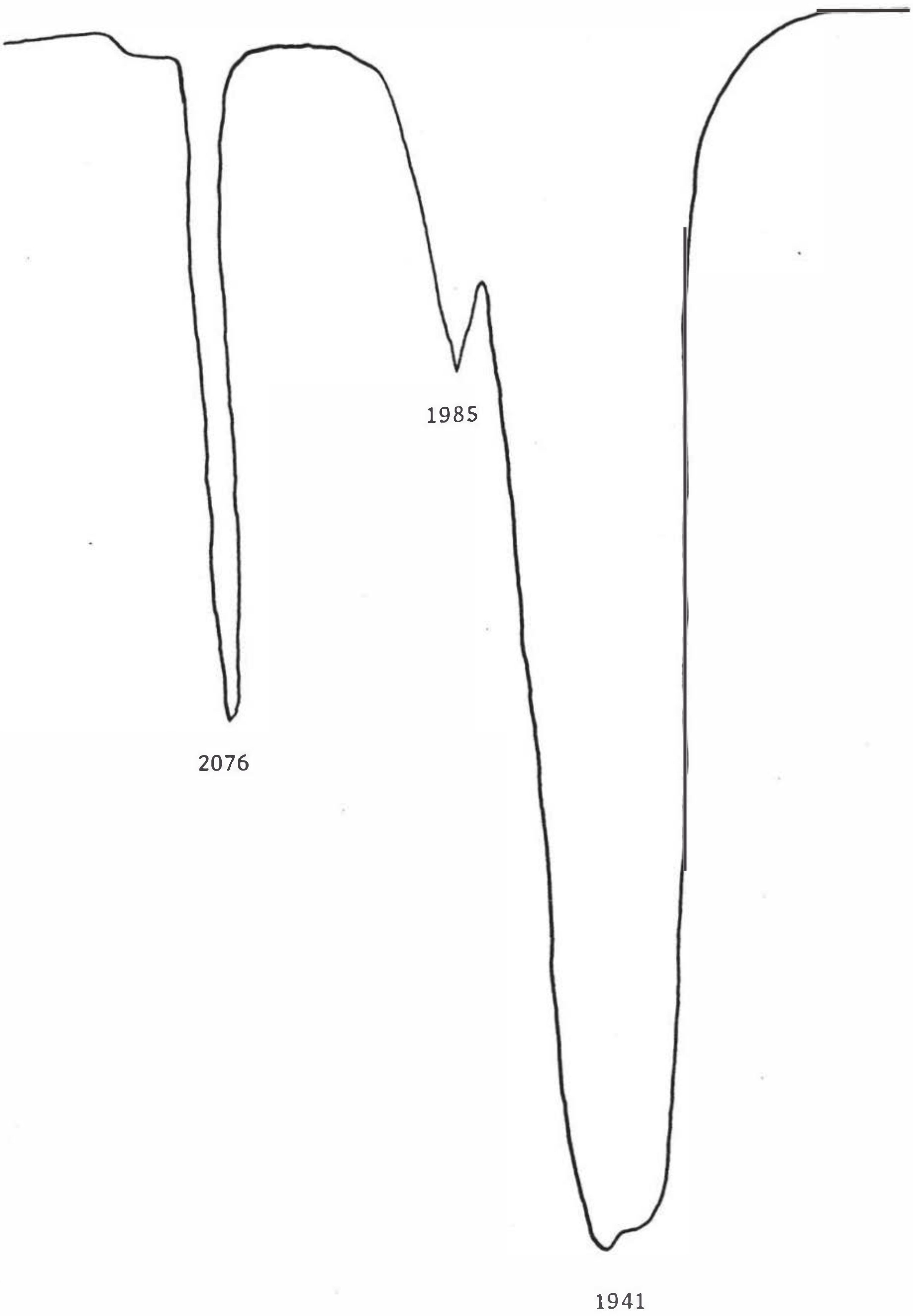
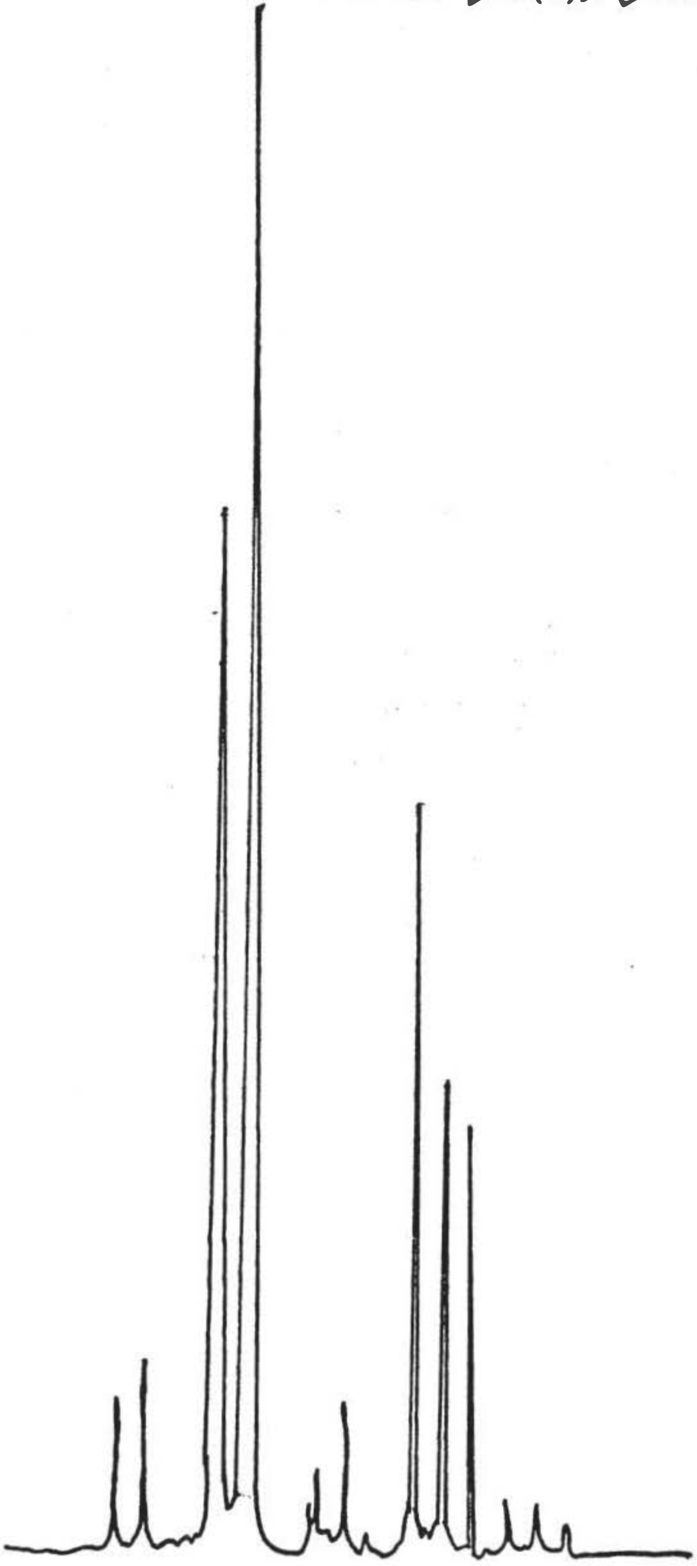


Figure 22

^{31}P NMR of WP~P(W)~PW



The enormous potential of using addition reactions for ligation control becomes apparent in this study. Many complexes, until now considered chemical oddities because of their synthetic inaccessibility, will become commonplace and available for catalytic, mechanistic and spectroscopic studies.

The same methods employed in this study should be useful for introducing different metals into the same triphos complex. For example, it should be possibe to synthesize

$(CO)_5CrPPh_2CH_2CH_2P(Ph)[W(CO)_5]CH_2CH_2PPh_2Mo(CO)_5$

and its isomers. Such a complex would be the first all encompassing Group 6 complex ever to be synthesized.

TABLE I: PREPARATIVE DATA

	Compound	M.P.	Color	Best Yield
	$(CO)_5WPPh_2H$	90-92°	White	60%
	$(CO)_5WPPh(CH=CH_2)_2$	Oil	Yellow	80%
	$(CO)_5WPPh_2CH=CH_2$	64-65°	White	79%
XVI	 = $(CO)_5WPPh(CH_2CH_2PPh_2)_2$	69-74°	White	40%
XVII	 = $(CO)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$	Oil	Yellow	20%
	 = $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH=CH_2$	123-125°	White	56%
XVIII	 = $PhP(CH_2CH_2PPh_2W(CO)_5)_2$	80-85°	White	58%
XIX	 = $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$	139-141°	White	40%
XX	 = $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2W(CO)_5$	160-162°	White	79%

TABLE II: ^{31}P NMR DATA

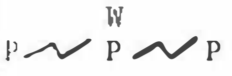
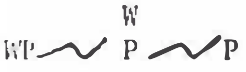
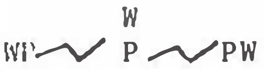
	Compound	$\delta WPPh_2$ ppm	$\delta WPPh$ ppm	δPPh_2 ppm	δPPh ppm	$^1J_{WPPh_2}$ Hz	$^1J_{WPPh}$ Hz	$^3J_{PP}$ $WPPh_2PPhW$ Hz	$^3J_{PP}$ $WPPh_2PPh$ Hz	$^3J_{PP}$ PPh_2PPhW Hz	$^3J_{PP}$ $PPhPPh_2$ Hz	J_{PH} Hz
	$(CO)_5WPPh_2H$	-13.7				229.6						344.9
	$(CO)_5WPPh(CH=CH_2)_2$		2.27				236.6					
	$(CO)_5WPPh_2CH=CH_2$	11.4				239.4						
XVI			7.25	-12.47			236.7			33.8		
XVII		12.47		-12.81	-16.6	239.4			29.4		31.1	
		12.76	4.52			240.9	238.6	35.7				
XVIII		13.57			-17.25	239.9			30.7			
XIX		12.75	6.84	-12.1		239.9		32.7		36.5		
XX		13.49	7.46			242.0	239.4	34.7				

TABLE III: INFRARED DATA (cm^{-1})

	Compound	$A_1^{(2)}$	B_1	$(E+A_1^{(1)})$
	$(CO)_5WPPh_2H$	2077	1985	1947
	$(CO)_5WPPh(CH=CH_2)_2$	2075	1983	1941
	$(CO)_5WPPh_2CH=CH_2$	2073	1984	1940
XVI	$(CO)_5WPPh(CH_2CH_2PPh_2)_2$	2074	1983	1940
XVII	$(CO)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$	2074	1982	1941
	$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH=CH_2$	2074	1983	1941
XVIII	$PhP(CH_2CH_2PPh_2W(CO)_5)_2$	2074	1983	1941
XIX	$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$	2073	1983	1941
XX	$(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2W(CO)_5$	2076	1985	1941

EXPERIMENTAL

General Considerations

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

The infrared spectra of the carbonyl region (2100-1850 cm^{-1}) were obtained from a Perkin-Elmer 337 Infrared spectrometer. These spectra were expanded with a Beckman 10" recorder and are considered to be accurate to ±2 cm^{-1}. Polystyrene was used to calibrate and chloroform was used as a solvent for the measurements.

Phosphorus-31 NMR spectra were obtained by Mr. Lewis W. Cary at Nicolet Technology Corporation, Mt. View, California. The ^{31}P spectra were recorded at 40.5 MHz on a Varian XL-100-15 NMR Spectrometer equipped with Fourier transform. The ^{31}P - ^{1}H couplings were eliminated using broad-band ^{1}H noise-modulated decoupling. Phosphoric acid (85%) in a 1.0 mm capillary was used as an external reference for the spectra. Coupling constants are accurate to ±0.1 Hz.

All melting points were recorded on an Arthur H. Thomas Unimelt apparatus and are reported uncorrected.

Tungsten hexacarbonyl, phenylphosphine, diphenylphosphine, diphenylvinylphosphine, and phenyldivinylphosphine, used in this research, were purchased from Pressure Chemical Company and used without further purification. All reactions were carried out under a nitrogen atmosphere.

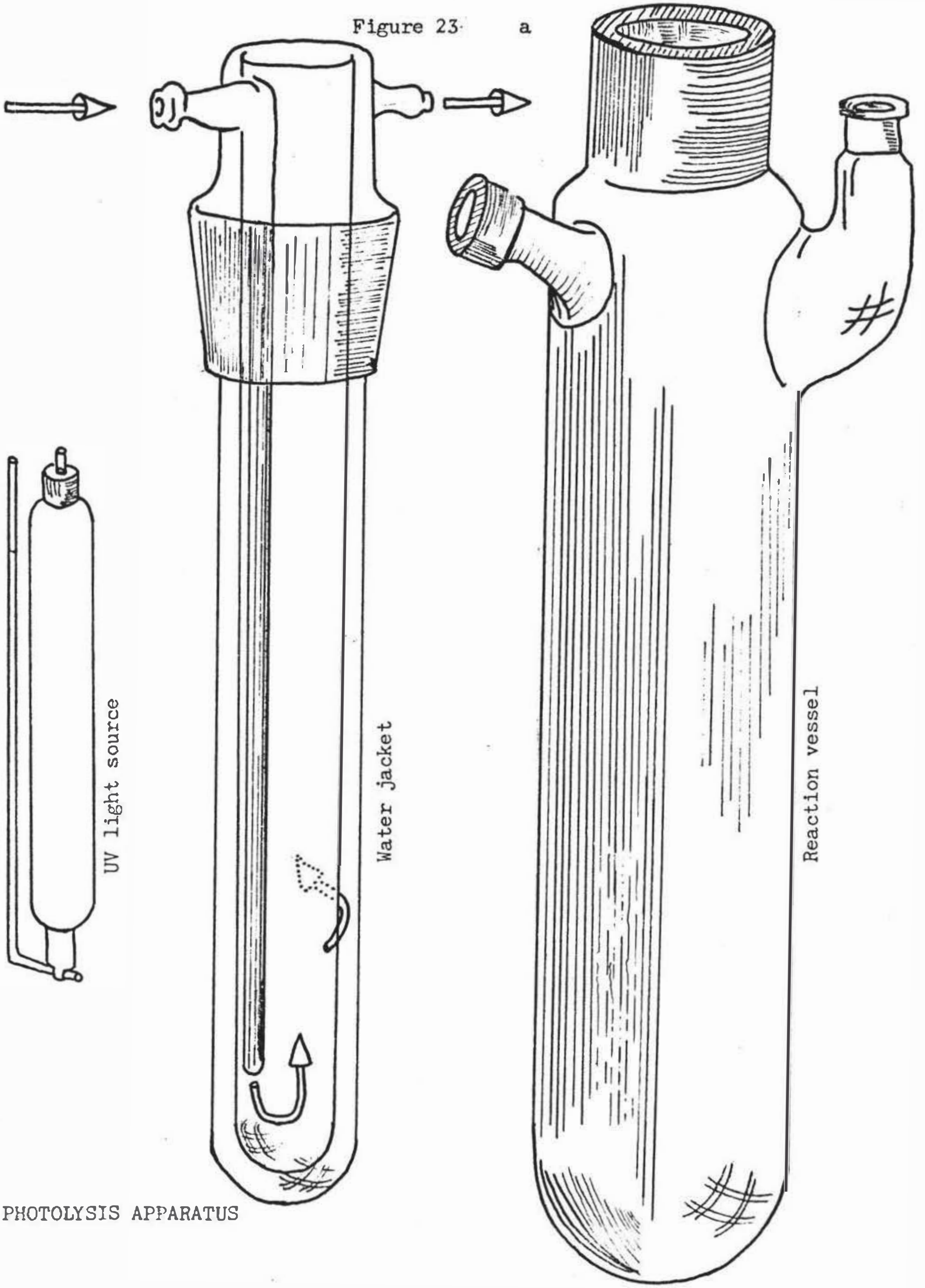
THF used in these reactions was dried by refluxing over sodium. Benzophenone was used to indicate dryness. THF was collected by distillation under nitrogen.

Preparation of Complexes

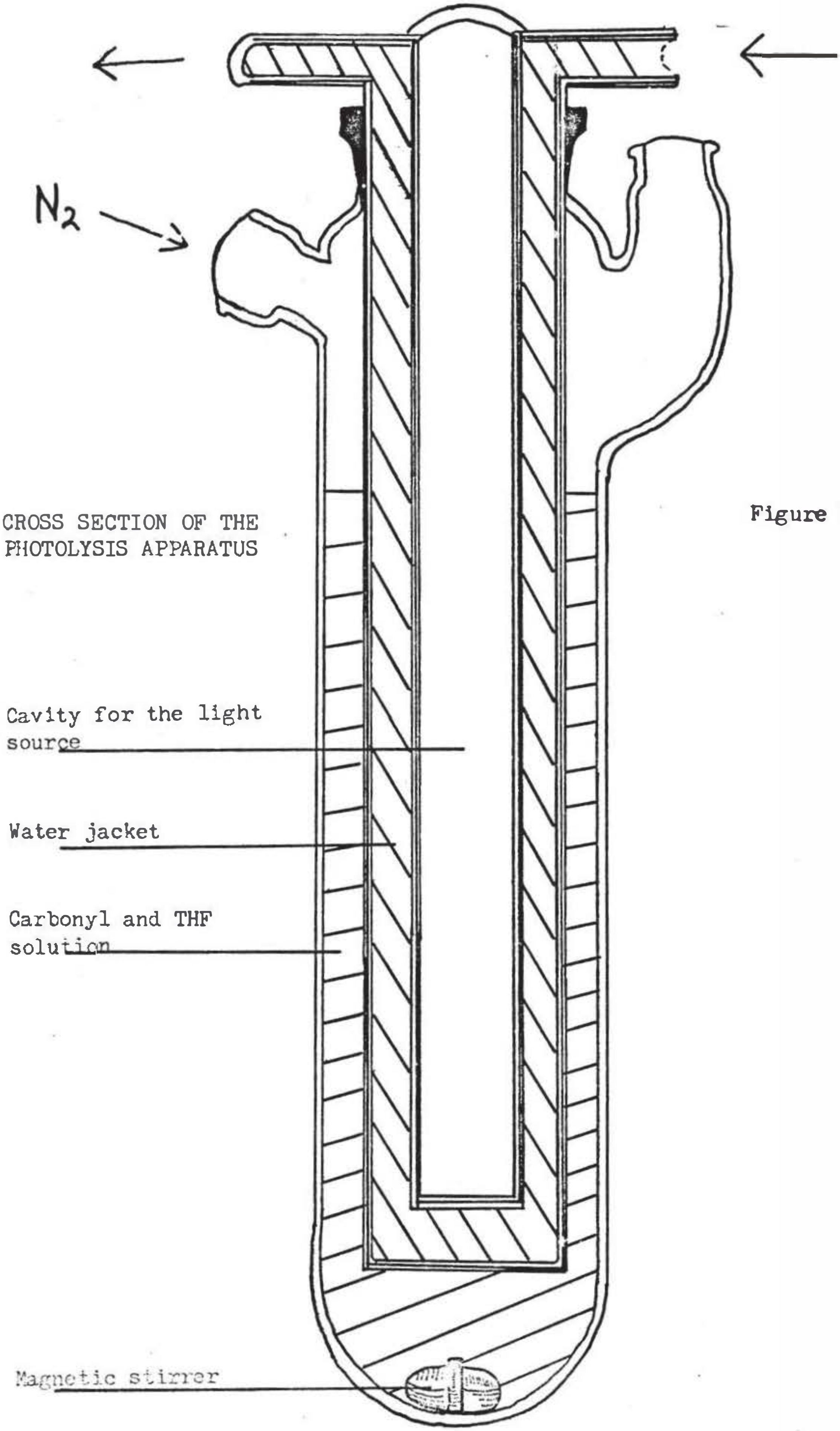
Preparation of $(CO)_5WPPh(CH=CH_2)_2$. A 450 Watt UV reaction vessel (Figure 23) as described by Marcovitch[28] was charged 200-250 ml dried THF and tungsten hexacarbonyl (6.0g, 0.017 mole). This mixture was purged with nitrogen for 10 minutes. The solution was irradiated for one hour. The solution was allowed to cool for ten minutes after which phenyldivinylphosphine (2.5 ml, ≈0.015 mole) was transferred to the reaction flask with a syringe. The solution was stirred for 1.5 hours, transferred to a 300 ml one neck round bottom flask and stripped to an oil with a Buchi evaporator. The resulting oil was dissolved in a minimum of dichloromethane and cooled in a freezer for two days under nitrogen. The solution was filtered to remove any unreacted tungsten hexacarbonyl. The solution was stripped to an oil which was stored under nitrogen in the dark.

About half of the oil was transferred to a molecular still (Figure 24). The molecular still was placed under high vacuum and heated to 60°C for 24 hours. About half of the material distilled over and the crude mixture in the still formed a coating. After 24 hours the temperature was raised to 80°C for 24 hours where more of the product distilled over and the crude mixture in the still became tar. The temperature was raised to 100°C for 24 hours to distill over the last traces of product leaving a thin layer of tar in the still. This completed the distillation of the first half of the oil, and this was repeated for the second half. The final product is a light yellow oil that is light sensitive and obtained in 80% yield.

Figure 23 a



PHOTOLYSIS APPARATUS



CROSS SECTION OF THE PHOTOLYSIS APPARATUS

Figure 23 b

Figure 24 a

Molecular still

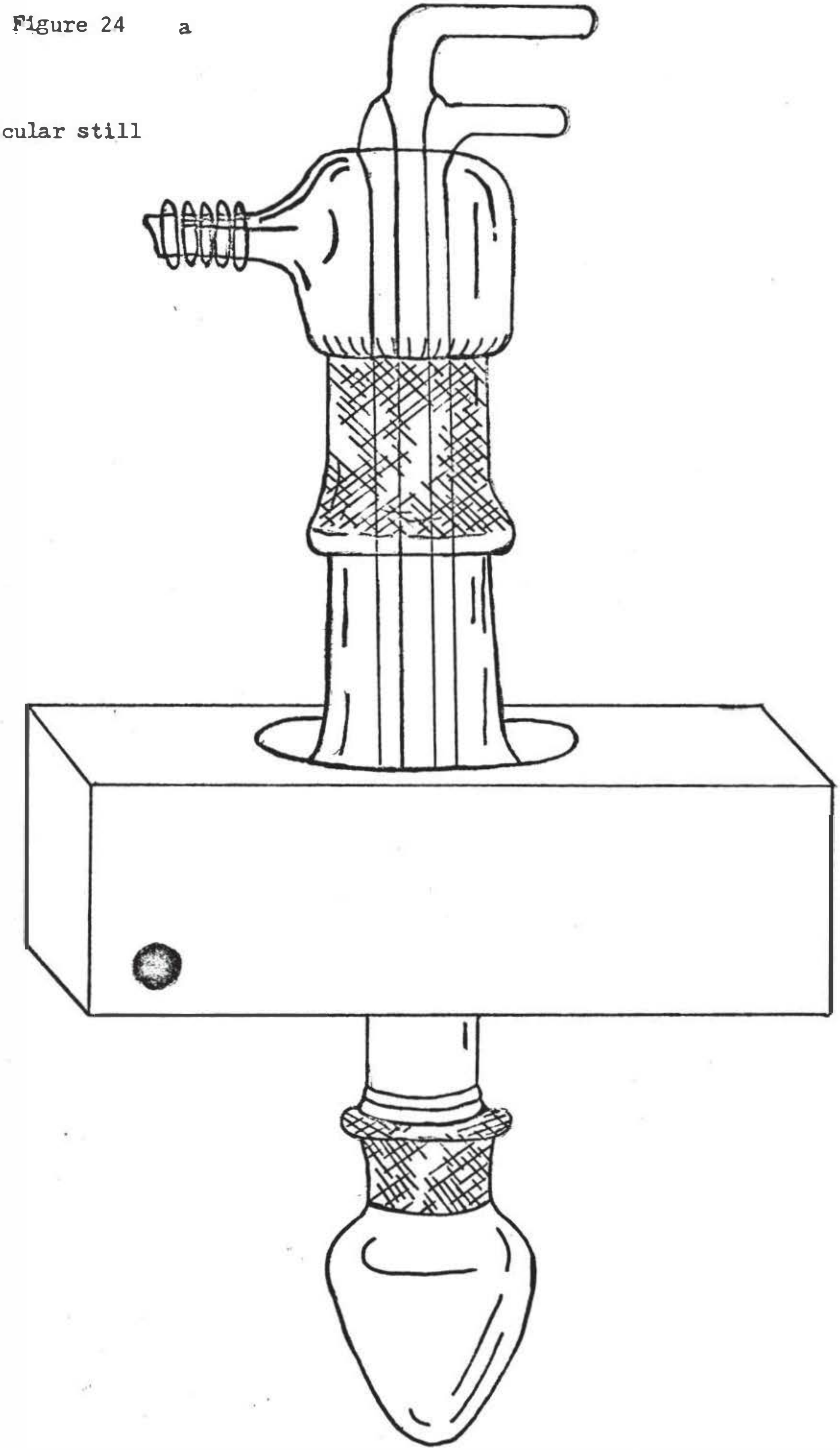
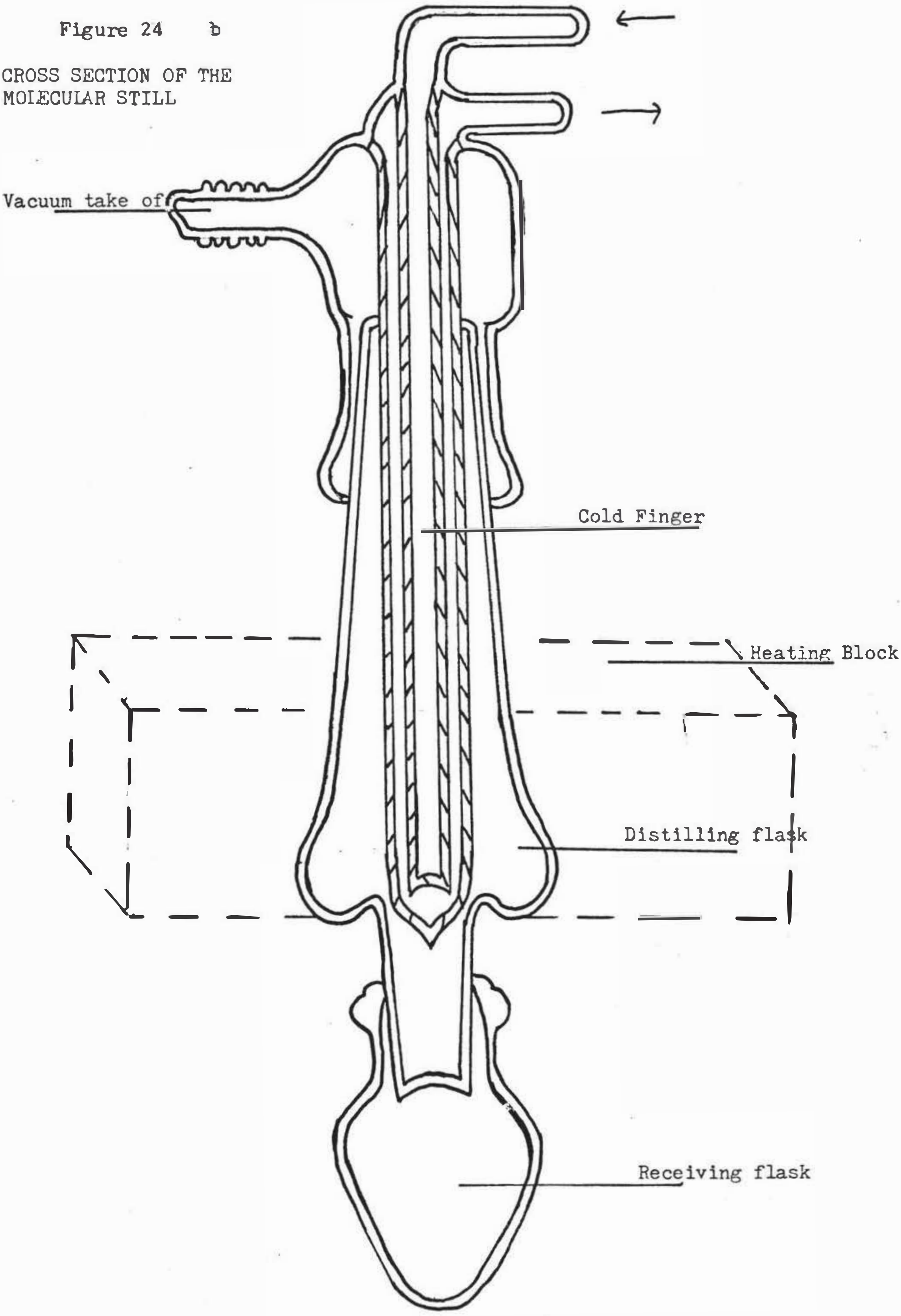


Figure 24 b

CROSS SECTION OF THE MOIECULAR STILL



IR: 2075 ($A_1{}^{(2)}$), 1983 (B_1), 1941 ($E + A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ2.27 ppm (J_{WP} = 236.3 Hz)

Anal. Calcd. for $C_{15}H_{11}O_5PW$: C, 37.07; H, 2.28; P, 6.37

Found: C, 36.91; H, 2.44; P, 6.46

Preparation of $(CO)_5WPPh_2H$. The 450 Watt UV reaction vessel (Figure 23) was charged with 200-250 ml dried THF and tungsten hexacarbonyl (6.0g, 0.017 mole). This mixture was purged with nitrogen for 10 minutes. The solution was irradiated for one hour. The solution was allowed to cool for ten minutes, after which diphenylphosphine (3.0 ml, ≈0.017 mole) was transferred to the reaction flask with a syringe. The solution was stirred for 1.5 hours, transferred to a 300 ml one neck round bottom flask and stripped to an oil with a Buchi evaporator. The resulting oil was dissolved in a minimum of dichloromethane and cooled in a freezer for two days under nitrogen. The solution was filtered to remove any unreacted tungsten hexacarbonyl. To the filtrate was added an equal volume of methanol. Solid formed when this solution was placed in the freezer for 2 days. This solid was recovered and to the filtrate was added 2 ml of methanol which produced yet more solid after cooling.

The crude product (80%) was sublimed at 40°C for one day under high vacuum to remove tungsten hexacarbonyl yielding a pure product 60% having a melting point of 90-92°C[29].

IR: 2077 ($A_1{}^{(2)}$), 1985 (B_1), 1941 ($E + A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ13.7 ppm (J_{WP} = 229.6, J_{PH} = 344.9 Hz)

Preparation of $(CO)_5WP(Ph)_2CH{=}CH_2$. The 450 Watt UV reaction vessel (Figure 23) was charged with 200-250 ml dried THF and tungsten hexacarbonyl (6.0g, 0.017 mole). This mixture was purged with nitrogen for 10 minutes. The solution was irradiated for one hour. The solution was allowed to cool for ten minutes after which diphenylvinylphosphine (3.2g, 0.015 mole) was transferred to the reaction flask with a syringe. The solution was stirred for 1.5 hours, transferred to a 300 ml one neck round bottom flask and stripped to an oil with a Buchi evaporator. The resulting oil was dissolved in a minimum of dichloromethane and cooled in a freezer for two days under nitrogen. The solution was filtered to remove any unreacted tungsten hexacarbonyl. To the filtrate was added an equal volume of methanol. Solid formed when this solution was placed in the freezer for two days. This solid was recovered and to the filtrate was added 2 ml of methanol which produced yet more solid after cooling.

This crude mixture was sublimed at 40°C for one day under high vacuum to remove tungsten hexacarbonyl yielding a pure product (79%) having a melting point of 64-65°C [23].

IR: 2073 ($A_1^{(2)}$), 1984 (B_1), 1940 ($E+A_1^{(1)}$) cm^{-1}

^{31}P NMR: $\delta 11.4$ ppm ($J_{WP} = 239.4$ Hz)

Preparation of $(CO)_5WPPh(CH_2CH_2PPh_2)_2$. To a 50 ml one neck round bottom flask equipped with a stirring bar, placed in an oil bath on a magnetic stirrer, was added $(CO)_5WPPh(CH{=}CH_2)_2$ (1.0g,2.1mmole) by syringe and 0.1g AIBN. The flask with contents was purged with nitrogen. Diphenylphosphine (0.75g, 4.3mmole) was added with a syringe to the mixture. The mixture was then heated to 75°C for 24 hours. The nitrogen inlet tube was replaced by a high vacuum line and the vessel was placed under high vacuum at 75°C for 24 hours to pull off excess diphenylphosphine. This oily mass was dissolved in 5 ml of dichloromethane and 5 ml of methanol was added to the solution. Solid formed when this solution was placed in the freezer. This crude mixture was recrystallized from a 1:1 mixture of dichloromethane/methanol yielding a pure product (40%) having a melting point of 69-74°C.

IR: 2074 ($A_1{}^{(2)}$), 1983 (B_1), 1940 ($E+A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ7.25, -12.47 ppm (J_{WP} = 236.7, J_{PP} = 33.8 Hz)

Anal. Calcd. for $C_{39}H_{33}P_3O_5W$: C, 54.56; H, 3.87; P, 10.82

Found: C, 54.40; H, 3.80; P, 10.99

Preparation of $PhP[CH_2CH_2P(Ph)_2W(CO)_5]_2$. To a 50 ml one neck round bottom flask equipped with a stirring bar, placed in an oil bath on a magnetic stirrer, was added $(CO)_5WP(Ph)_2CH{=}CH_2$ (2.0g, 3.7mmole) and 0.1g AIBN. The flask with the contents was purged with nitrogen. Phenylphosphine (0.25g, 2.3mmole) was added with a syringe to the mixture. The mixture was then heated to 75°C for 24 hours. After 24 hours the system was placed under high vacuum at 75°C for 24 hours to pull off unreacted phenylphosphine. The oily mass was dissolved in 5 ml of dichloromethane and diluted with an equal volume of methanol. The mixture was cooled in a freezer for one month to result in an oil. The oil was chromatographed on silica gel with an eluent of 80% pet ether/20% ethyl acetate. The eluting liquid with product was stripped down and crystallized from a 1:1 dichloromethane/methanol mixture to yield a pure product (58%) with a melting point of 80-85°C.

IR: 2074($A_1{}^{(2)}$); 1983 (B_1); 1941 ($E+A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ13.57, -17.25 ppm (J_{WP} = 239.9, J_{PP} = 30.7 Hz)

Anal. Calcd. for $C_{44}H_{33}P_3W_2O_{10}$: C, 44.68; H, 2.79; P, 7.86

Found: C, 44.81; H, 2.78; P, 7.56

Preparation of $(CO)_5WPPh[CH_2CH_2PPh_2W(CO)_5]_2$. To a 250 ml three-necked round bottom flask equipped with a stirring bar, stirrer, heating mantle, dropping funnel with stopper and a reflux condenser with a nitrogen inlet was charged $(CO)_5WPPh_2H$ (2.12g, 4.15 mmole) and 0.2g potassium tert-butoxide in 150 ml dry THF. The yellow mixture was heated to reflux. Upon reflux a solution of $(CO)_5WPPh(CH{=}CH_2)_2$ (1.03g, 2.12 mmole) in 25 ml dry THF was added dropwise with a dropping funnel over half an hour. After the addition was complete the mixture was refluxed for one hour. The mixture was cooled and transferred to a 300 ml flask and stripped to an oil on a Buchi. The oil was dissolved in a minimum amount of dichloromethane and an equal volume of methanol was added to the solution. Solid formed when this solution was placed in the freezer. The product was filtered and recrystallized in a 1:1 mixture of dichloromethane and methanol to give a product (79%) with a melting point of 160-162°C.

IR: 2076 ($A_1{}^{(2)}$); 1985 (B_1); 1941 ($E+A_1{}^{(1)}$) cm^{-1}
^{31}P NMR: δ = 13.49, 7.46 ppm (J_{WP} = 242.0, 239.4, J_{PP} = 34.7 Hz)
Anal. Cald. for $C_{55}H_{33}O_{15}W_3P_3$: C, 39.07; H, 2.21; P, 6.17
Found: C, 38.92; H, 2.49; P, 5.92

Preparation of $(CO)_5WPPh_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$. A 50 ml round bottom flask equipped with a stirring bar and stirrer and flushed with nitrogen was charged with phenyldivinylphosphine (2.0g, 1.2 mmole), diphenylphosphine (1.0g, 0.6 mmole) and 0.1g AIBN. This mixture was heated to 75°C in an oil bath with stirring for 24 hours. After 24 hours the nitrogen line was replaced by a high vacuum line for 24 hours at 75°C. The system was flushed with nitrogen after which the mixture was charged with $(CO)_5WPPh_2H$ (3.0g, 0.6mmole) and 0.1g AIBN. This mixture was heated to 75°C for 24 hours after which the flask was placed under high vacuum for

24 hours. The resulting oil was dissolved in a 1:1 mixture of dichloromethane and methanol. The solution was cooled in a freezer to result in an oil. The process was repeated twice more to give an oil which gave an unoptimized yield of 20%.

IR: 2074 ($A_1{}^{(2)}$); 1982 (B_1); 1941 ($E+A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ = 12.47, -12.81, -16.6 ppm (J_{WP} = 239.4 Hz, J_{PP} = 29.4, 31.1 Hz)

Preparation of $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$. To a 250 ml three-necked round bottom flask equipped with a stirring bar, stirrer, heating mantle, dropping funnel with stopper and a reflux condensor with a nitrogen inlet was added $(CO)_5WPPh(CH{=}CH_2)_2$ (2.67g, 5.45mmole) and 0.2g potassium tert-butoxide in 150 ml dry THF. This yellow mixture was heated to reflux. Upon reflux a solution of $(CO)_5WPPh_2H$ (1.39g, 2.72mmole) in 25 ml dry THF was added dropwise with a dropping funnel over half an hour. After the addition the mixture was refluxed for one hour. The mixture was cooled and transferred to a 300 ml flask and stripped to an oil with a Buchi. The oil was dissolved in a minimum amount of dichloromethane and an equal volume of methanol was added to the solution. The solution was cooled in a freezer for a few days to produce crystals. The product was filtered and recrystallized in a 1:1 mixture of dichloromethane/methanol to yield a product (56%) with a melting point of 123-125°C.

IR: 2074 ($A_1{}^{(2)}$); 1983 (B_1); 1941 ($E+A_1{}^{(1)}$) cm^{-1}

^{31}P NMR: δ = 12.76, 4.52 ppm (J_{WP} = 240.9, 238.6 Hz, J_{PP} = 35.7 Hz)

Anal. Cald. for $C_{32}H_{22}O_{10}W_2P_2$: C, 38.57; H, 2.21; P, 6.22

Found: C, 38.30; H, 2.09; P, 6.08

Preparation of $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$. To a 250 ml three-necked round bottom flask equipped with a stirring bar, stirrer, heating mantle, dropping funnel with a stopper and a reflux condenser with a nitrogen inlet was added $(CO)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH=CH_2)$ (1.16g, 1.12mmole) and 0.2g potassium tert-butoxide in 150 ml dry THF. This yellow solution was heated to reflux. Upon reflux a solution of diphenylphosphine (1.2g, 1.2mmole) in 25 ml dry THF was added dropwise with a dropping funnel over half an hour. After the addition the mixture was refluxed for one hour. The mixture was cooled and transferred to a 300 ml flask and stripped to an oil by the use of a vacuum pump. The oil was dissolved in a minimum amount of deoxygenated dichloromethane; then an equal volume of deoxygenated methanol was added to the solution. The solution was cooled in a freezer for a few days to produce crystals. The product was filtered and recrystallized in a 1:1 mixture of dichloromethane/methanol to yield a pure product (40%) with a melting point of 139-141°C.

IR: 2073 ($A_1^{(2)}$); 1983 (B_1); 1941 ($E+A_1^{(1)}$) cm^{-1}

^{31}P NMR: δ = 12.75, 6.83, -12.1 ppm (J_{WP} = 239.9, J_{PP} = 32.7 Hz)

Anal. Calcd. for $C_{44}H_{33}P_3W_2O_{10}$: C, 44.68, H, 2.79; P, 7.86

Found: C, 44.61; H, 2.80; P, 8.11

REFERENCES

1. W. Hewertson and H. R. Watson, J. Chem. Soc., 1490 (1962).
2. R. B. King and P. N. Kapoor, J. Am. Chem. Soc., 91, 5191 (1969).
3. R. B. King and P. N. Kapoor, J. Am. Chem. Soc., 93, 4153 (1971).
4. E. D. Bergman, D. Ginsburg and R. Pappo, Org. React., 10, 179 (1959).
5. R. B. King and J. C. Cloyd, Jr., J. Am. Chem. Soc., 97, 46 (1975).
6. J. C. Cloyd, Jr. and D. W. Meek, Inorg. Chim. Acta, 6, 607 (1972).
7. K. Issleib and H. Weichman, Z. Chem., 11, 188 (1971).
8. D. L. DuBois, W. H. Meyers and D. W. Meek, J.C.S. Dalton Trans., 11, 1011 (1975).
9. R. B. King and P. R. Heckly, Phosphorus, 3, 209 (1974).
10. P. A. W. Dean, Can. J. Chem., 57, 754 (1979).
11. R. B. King, P. N. Kapoor and R. N. Kapoor, Inorg. Chem., 10, 1841 (1971); R. B. King, Acc. of Chem. Res., 5, 177 (1972).
12. R. B. King and J. C. Cloyd, Jr., Inorg. Chem., 14, 1550 (1975).
13. T. E. Nappier, Jr. and D. W. Meek, J. Am. Chem. Soc., 94, 306 (1972).
14. J. A. Osborn, F. H. Jurdina, J. F. Young and G. Wilkinson, J. Chem. Soc. A, 1711 (1966).
15. K. D. Tau, R. Uriate, T. J. Mazane and D. W. Meek, J. Am. Chem. Soc., 101, 22 (1979).
16. H. Felkin, P. W. Lednor, J. Normat and R. A. J. Smith, J. Organometal. Chem., 157, C64 (1978).
17. I. Muller and D. Rehder, J. Organometal. Chem., 139, 293 (1977).
18. U. Puttfarcken and D. Rehder, J. Organometal. Chem., 15, 321 (1978).
19. M. L. Schneider, N. J. Coville and I. S. Butler, J.C.S. Chem. Comm., 13, 799 (1972).
20. I. S. Butler and N. J. Coville, J. Org. Chem., 80, 235 (1974).
21. G. Henric-Olivé and S. Olivé, Ang. Chem., 91, 83 (1979).
22. C. U. Pittman, Jr., W. D. Honnick and J. J. Yang, Inorg. Chem., 45, 684 (1980).

23. R. L. Keiter, R. D. Borger, J. J. Hamerski, S. J. Garbis and G. S. Leotsakis, J. Am. Chem. Soc., 99, 5224 (1977); R. L. Keiter, Y. Y. Sun, J. W. Brodack and L. W. Gary, J. Am. Chem. Soc., 101, 2638 (1979).

24. W. Strohmeier and F. Muller, Chem. Ber., 102, 3608 (1969).

25. G. M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Vol. I Wiley-Interscience, N.Y., N.Y. (1972), p. 115.

26. P. S. Pregosin and R. W. Kunz, NMR 16, ^{31}P and ^{13}C NMR Complexes, Springer-Verlag, Berlin Heidelberg, N.Y. (1979).

27. M. M. Crutchfield and J. R. Van Wazer, Topics in Phosphorus Chemistry, Vol. 5, "P^{31} Nuclear Magnetic Resonance," J. Wiley & Sons, Inc., N.Y. (1967).

28. D. Marcovitch, Eastern Illinois University, M.S. Thesis (1975).

29. J. G. Smith and D. T. Thompson, J. Chem. Soc. A, 1694 (1967).

VITA

Name: Rodney D. Borger

Permanent Address: 309 W. Phillips
Freeburg, Illinois 62243

Degree and Date to be Conferred: M.S. (Chemistry)
August 1981

Date of Birth: April 7, 1954

Place of Birth: Belleville, Illinois

Secondary Education: Freeburg High School, June 1972

Collegiate Institutions Attended	Date	Degree	Date of Degree
Belleville Area College	8-72/8-74	Assoc. of Science	May, 1974
University of Illinois	8-74/5-75		
Eastern Illinois University	8-75/5-77	B.S.	May, 1977
Eastern Illinois University	8-79/5-81	M.S.	August, 1981

Major: Inorganic Chemistry

Positions Held:	Date	Institution
Production Chemist	5-77/8-79	Aldrich Chemical Co.
Graduate Assistant	8-79/5-81	Eastern Illinois Univ.