Ditertiary Phosphines as Monodentate Ligands in Transition Metal Carbonyl Complexes

Yih-Yau York Sun
Eastern Illinois University

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DITERTIARY PHOSPHINES AS MONODENTATE LIGANDS
IN TRANSITION METAL CARBONYL COMPLEXES

(TITLE)

BY

YIH-YAU YORK SUN

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IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1978

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

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DATE
DITERTIARY PHOSPHINES AS MONODENTATE LIGANDS
IN TRANSITION METAL CARBONYL COMPLEXES

BY

Yih-Yau York Sun
Bachelor of Science
Soochow University
Taipei, Taiwan
June, 1974

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
1978
DITERTIARY PHOSPHINES AS MONODENTATE LIGANDS
IN TRANSITION METAL CARBONYL COMPLEXES

Thesis Approved

Dr. R. L. Keiter, Thesis Advisor

Dr. J. E. Ellis

Dr. J. J. Hamerski

Dr. R. H. Karraker
Title of Thesis: Ditertiary Phosphines as Monodentate Ligands in Transition Metal Carbonyl Complexes

Name: Yih-Yau York Sun

Thesis directed by: Dr. Richard L. Keiter

Carbonyl complexes of chromium, molybdenum and tungsten have been synthesized in which two potentially chelating tetraphenyldiphenophosphino-ethane molecules \((\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\) are bound as monodentate ligands. The reaction of trans-\((\text{CO})_4\text{M(PPh}_2\text{CH}=\text{CH}_2)\_2 \) (\(\text{M} = \text{Cr}, \text{Mo}, \text{W}\)) with diphenylphosphine \((\text{PPh}_2\text{H})\) in the presence of potassium t-butoxide yields trans-\((\text{CO})_4\text{M-} \) \((\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\_2\). The complexes, which represent the first of this type to be synthesized, have been characterized by \(^{31}\text{P}\) nmr. From the \(\text{XAA'}\text{X'}\) phosphorus-31 spectra of the complexes, phosphorus-phosphorus coupling through the metal atom have been determined and have been found to be 26.0, 45.7 and 54.3 Hz respectively for chromium, molybdenum and tungsten. The phosphorus-phosphorus coupling constant for cis-\((\text{CO})_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\_2\), obtained as a minor product, was determined to be 21.3.

The reaction of trans-\((\text{CO})_4\text{W(PPh}_2\text{CH}=\text{CH}_2)\_2\) with \(\text{PPh}_2\text{H}\) in the presence of the free radical catalyst, 2,2'-azobisisobutyronitrile (AIBN), resulted in isomerization and cyclization to give as a major product, a complex in which \(\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH(PPh}_2)\text{CH}_2\text{PPh}_2\) is present as a bidentate ligand. This complex, \((\text{CO})_4\text{W[PPh}_2\text{CH}_2\text{CH}_2\text{CH(PPh}_2)\text{CH}_2\text{PPh}_2]\), and its oxide have been fully characterized by \(^{31}\text{P}\) nmr. The absence of a product in which \(\text{PPh}_2\text{H}\) is
coordinated or in which PPh₂CH₂CH₂PPh₂ is chelated suggests that the isomerization proceeds through an intramolecular mechanism.

The reaction of cis-(CO)₄W(PPh₂H)₂ with PPh₂(CH=CH₂)₂ in the presence of potassium t-butoxide gave (CO)₄W(PPh₂CH₂CH₂PPh₂), a complex in which the phosphorus ligand is chelated. The reaction of cis-(CO)₄W(PPh₂H)₂ with PPh₂H in the presence of AIBN yields the sterically favored trans-(CO)₄W(PPh₂CH₂CH₂PPh₂)₂.

The reactions reported in this thesis represent an approach to controlling the number of metal sites to which a chelating phosphine is coordinated.
DEDICATION

TO MY PARENTS
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CHAPTER I

INTRODUCTION

Trivalent phosphorus derivatives of transition metal carbonyls have been extensively studied in the last decade. The main interest arises from the special use of phosphine complexes in organic synthesis and homogeneous catalysis. Complexes of tertiary phosphines, compared with that of other types of phosphine ligands, are important in this area because of several reasons: (a) The oxidative stability of these ligands is high. (b) For cocatalysts in homogeneous catalysis the phosphine ligands must be inert to the various substrates. (c) Phosphorus ligands with electronegative substituents have a special ability for stabilization of metals in low oxidation state.

Ditertiary phosphines may coordinate to a metal atom in three different ways: (1) Chelation of the phosphine to a transition metal is by far the most common. (Figure 1a) These type complexes have extra thermodynamic stability because they contain chelate rings.

Since 1,2-bis(diphenylphosphino)-ethane was first reported in 1956, a large number of complexes in which diphosphine ligands serve as bidentate ligands have been synthesized. For example, complexes of chromium(0), molybdenum(0), and tungsten(0) which contain ditertiary phosphine, Me₂PCH₂CH₂PMe₂, as a bidentate ligand were synthesized by
reducing CrCl₃, MoCl₅, and WC₆, respectively, with LiAlH₄ or sodium naphthalenide in THF.² Other complexes of zerovalent transition metals with bidentate ligand, Me₂PCH₂CH₂PMé₂, also have been synthesized.²,³

![Diagram of coordination types](image)

(a) M\(\rightarrow\)P\(\leftrightarrow\)P
(b) M\(\rightarrow\)P\(\rightarrow\)P\(\rightarrow\)M
(c) M\(\rightarrow\)P\(\rightarrow\)P

Figure 1. Types of coordination for ditertiary phosphines.

(P\(\rightarrow\)P = ditertiary phosphine)

(2) The ditertiary phosphine may serve as a bridge between two transition metal atoms. (Figure 1b) Complexes of this type also well known. For example, a dimeric complex, [(CO)₂Ni(Et₂PCH₂CH₂PMé₂)]₂, was obtained as a by-product in the preparation of (CO)₂Ni(Et₂PCH₂CH₂PMé₂).⁴

The reaction of [Mn₂(CO)₁₀] with Ph₂PCH₂CH₂PPh₂ or Ph₂PCH₂PPh₂ will provide [Mn₂(CO)₈Ph₂PCH₂CH₂PPh₂] or [Mn₂(CO)₈Ph₂PCH₂PPh₂] in which one of the diphosphine, Ph₂PCH₂CH₂PPh₂, bridges between two metals.⁵ Complexes which contain not only chelating but also bridging diphosphines have also been reported.⁶,⁷

(3) The ditertiary phosphine may coordinate to a metal atom through only one metal site. The complexes of this sort will be stable if the other ligands attached to the metal are sufficiently inert that displacement of these ligands does not take place.
Compared with extensive numbers of investigations of transition metal complexes in which ditertiary phosphine coordinate as bidentate ligand, relatively few studies of complexes with ditertiary phosphine as monodentate ligand have been reported.

Booth and Chatt first found complexes of Ni(II) of the type \([\text{Ni}X_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]\) \((X = \text{Cl}, \text{Br or I})\) in which \(\text{Ph}_2\text{PCH}_2\text{PPh}_2\) is present as a monodentate ligand from the reaction between nickel halides and tetraphenyldisphosphinomethane.\(^8\)

After that, two stable 5-coordinate nickel (II) and cobalt (II) complexes, \([\text{M(CN)}_2(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\), with one of the tetraphenyldiphosphinoethane molecules acting as a monodentate ligand were reported by Rico and Turco. These complexes were obtained by the addition of tetraphenyldiphosphinoethane to a solution of \([\text{M(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)-(\text{CN})_2]\) in \(\text{CH}_2\text{Cl}_2\).\(^6,7\)

In 1972 Keiter and Shah synthesized a tungsten carbonyl complex, \((\text{CO})_5\text{WPH}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\), which contains tetraphenyldiphosphinoethane as a monodentate ligand.\(^9\) The synthesis consists of displacing aniline of pentacarbonylanilinetungsten(O) with the ditertiary phosphine in

![Figure 2](image-url)
benzene at room temperature.

\[(\text{CO})_5\text{WNH}_2\text{Ph} + \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \rightarrow (\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2 + \text{PhNH}_2\]

Connor and coworkers proposed an alternate method for the preparation of complexes in which \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\) is present as a monodentate ligand from the reaction between the ligand \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\), the halogenopentacarbonylmethylate \([\text{XM(CO)}_5^-]\), and a Lewis acid. 10

\[
[(\text{CO})_5\text{MX}^-] + \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 + [\text{R}_3\text{O}][\text{BF}_4^-] \rightarrow (\text{CO})_5\text{MPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2 + \text{RX} + \text{R}_2\text{O} + \text{BF}_4^-\]

After examining both reactions carefully, it was found that neither of the above reactions are satisfactory. Complexes with ditertiary phosphine as monodentate ligand contain an uncoordinated free phosphine which may react with \(\text{M(CO)}_5\text{NH}_2\text{Ph}\) or \([\text{XM(CO)}_5^-]\) to form \((\text{CO})_5\text{MPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{M(CO)}_5\)
bridging complexes. 9

\[
(\text{CO})_5\text{WPPh}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 + [\text{XW(CO)}_5^-] \rightarrow (\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W(CO)}_5 + \text{X}^-\]

Although the quantity of bridging complexes will be reduced by using excess amount of \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\) free ligand, the desired product must be separated from the free ligand and bridging side product and the
yields are low. Further, there is no means to control which end of an unsymmetrical ditertiary phosphine will attach to the metal.\textsuperscript{11} For example:

\[
(CO)_5WNH_2Ph + Ph_2PCH_2CH_2PMe_2 \rightarrow (CO)_5WPh_2CH_2CH_2PMe_2
\]

and \( (CO)_5WPMe_2CH_2CH_2PPh_2 \).

In 1971 King and Kappor developed a new method for the preparation of polytertiary phosphines by the addition of phosphorus-hydrogen bonds across the carbon-carbon double bonds of vinylphosphines in the presence of a base catalyst such as potassium tert-butoxide.\textsuperscript{12} The general reaction can be summarized as in following equation.

\[
\begin{array}{c}
\text{P-H} + \text{CH}_2=\text{CH-P} \\
\rightarrow \text{PCH}_2\text{CH}_2\text{P}
\end{array}
\]

Recently Meek and coworkers have found that the synthesis of polytertiary phosphines can be also achieved by the addition of phosphorus-hydrogen bonds to the carbon-carbon double bonds of vinylphosphines in the presence of free radical, 2,2'-azobis (isobutyronitrile) (AIBN).\textsuperscript{13}

Complexes with polydentate phosphorus ligands, therefore, have received considerable attention in the past few years because of advances made in the synthesis of polydentate phosphorus ligands.\textsuperscript{14}

These new methods for the synthesis of polytertiary phosphines suggested a new approach for the preparation of complexes with a ditertiary phosphine serving as monodentate ligand.
Recently Keiter and coworkers first reported the high yield synthesis of tungsten complex \((\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\) in which \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\) is present as a monodentate ligand.\(^{15}\) Instead of employing substitution reactions, success was achieved by the addition of a secondary phosphine across the carbon-carbon double bond of vinylphosphine ligand of the complex in the presence of AIBN free radical catalyst or a potassium tert-butoxide base catalyst.

\[
(\text{CO})_5\text{WPPh}_2\text{CH} = \text{CH}_2 + \text{Ph}_2\text{PH} \xrightarrow{(\text{CH}_3)_3\text{CO}} \text{or AIBN} (\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2
\]

Brodack\(^{16}\) found further that the same complex can also be synthesized by addition of vinylphosphine to secondary phosphine ligand on the metal complex under similar experimental conditions.

\[
(\text{CO})_5\text{WPPh}_2\text{H} + \text{Ph}_2\text{PCH} = \text{CH}_2 \xrightarrow{\text{AIBN}} (\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2
\]

The results from these addition reactions are encouraging and suggest great potential of the method as a means of the controlling the number of metal sites to which a polydentate phosphine ligand is coordinated.

The purpose of this research is to synthesize the Group VI transition metal carbonyl complexes in which two potentially chelating phosphines, \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\), are present as monodentate ligands. The main reason for synthesizing this type of complexes is to test the generality of the synthetic method in controlling the number of metal sites to which
a chelating phosphine ligand is coordinated. In addition, this type of complexes containing two magnetically and chemically equivalent phosphorus atoms attached to the metal atom and may allow for the direct measurement of phosphorus-phosphorus coupling constants through the metal atom from the proton-decoupled phosphorus-31 nuclear magnetic spectrum, which is very useful in investigating the nature of the metal-phosphorus bond.17

Phosphorus-phosphorus coupling constants, $^{2}J_{PMP}$, through a metal for complexes containing two chemically different phosphorus ligands may be measured directly with the advantage that the value can easily be obtained from the AB or AX type of P-31 spectrum. For the complexes such as $(CO)_4M(PR_3)_2$ ($R$ = alkyl or aryl group) containing two both magnetically and chemically equivalent phosphorus ligands, however, the direct measurement of $^{2}J_{PMP}$ from the proton-decoupled P-31 nmr spectrum becomes impossible. Complexes in which two potentially chelating phosphines, Ph$_2$PCH$_2$CH$_2$PPh$_2$, are present as monodentate ligands may be treated as an AA'XX' spin system. The magnitude of $^{2}J_{PMP}$ for the complexes with this type of spin system can be obtained by the direct measurement of parameters from the spectra. The spin system has been discussed in detail by Harris in 1964.18

Recently two complexes, $[(CO)_5WPh_2PCH_2CH_2PPh_2]_2PtCl_2$ and $[(CO)_5WPh_2PCH_2CH_2PPh_2]_2Ni(CO)_2$, with XX'AA' type of spin system, and their $^{2}J_{PMP}$ values were reported.19,20

So far, only one complex, C$_5$H$_5$Mo(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$[C≡E(CN)$_2$]Cl, in which two ditertiary phosphine molecules coordinate as monodentate
ligands has been reported. This complex was obtained by chance from the reaction of \((\text{NC})_2\text{C} = \text{C(Cl)Mo(CO)}_3\text{C}_5\text{H}_5\) with two moles of \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\).\(^{21}\)

Keiter and coworkers' new approach to the synthesis of the \((\text{CO})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\) complex suggests that there are two possibilities to synthesize the group VI metal complexes in which two ditertiary phosphines serve as monodentate ligands. One possibility is to synthesize the bis-diphenylphosphine complex and allow it to react with two moles of diphenylvinyl compound.

\[
(\text{CO})_4\text{M(PPh}_2\text{H})_2 + 2\text{PPh}_2\text{CH=CH}_2 \xrightarrow{\text{AIBN or (CH}_3\text{)}_3\text{COK}} (\text{CO})_4\text{M(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \]

where

\(M = \text{W, Mo, and Cr}\)

The second possibility is to synthesize bis-diphenylvinyl complex
and allow it to react with two moles of secondary phosphine to obtain the desired complex.

\[
(CO)_4M(PPh_2CH=CH_2)_2 + 2PPh_2H \xrightarrow{AIBN \text{ or } (CH_3)_3COK} (CO)_4M(Ph_2PCH_2CH_2PPh_2)_2
\]

In this thesis both approaches have been examined in our attempts to synthesize cis and trans tetracarbonyl complexes of Group VI metals which contain two tetraphenyldiphosphinoethane molecules as monodentate ligands.
CHAPTER II

RESULTS AND DISCUSSION

The bis(diphenylvinylphosphine) complexes of tungsten, molybdenum, and chromium were synthesized from the following reaction:22

\[ M(CO)_6 + 2PPh_2CH=CH_2 \xrightarrow{\text{diglyme}} (CO)_4M(PPh_2CH=CH_2)_2 + 2CO \]
\[ (M = W, Mo, \text{and Cr}) \]

The crude product from this reaction contained monosubstituted, cis, and trans complexes, with the trans complex present in greatest abundance. The monosubstituted complex was separated from the mixture by extraction with petroleum ether. Attempts to separate the cis compound from the trans by column chromatography were unsuccessful because of decomposition of the sample in the column. However, the purity of the trans complexes can be greatly improved by recrystallizing the crude product several times from dichloromethane-methanol solution. Complexes of this type are air stable at room temperature.

Trans-disubstituted tetracarbonyl metal complexes have \( D_{4h} \) symmetry and only the \( E_u \) mode is infrared active. However, the infrared spectra of these complexes show three absorptions. This is due to the perturbation of \( D_{4h} \) symmetry by the \( \text{Ph}_2\text{P(CH=CH}_2 \) ligands, and the \( A_{1g} \) and \( B_{1g} \) gain slight allowness, thus they become two weak bands.23 Infrared
spectra of trans-(CO)$_4$M(PPh$_2$CH=CH$_2$)$_2$ (M = W, Mo, Cr) are shown in Figure 3-5 and their carbonyl stretching frequencies are shown in Table I.

Compared to the carbonyl stretching frequency at 1940 cm$^{-1}$ of monosubstituted (CO)$_5$WPPh$_2$CH=CH$_2$ complex,$^{24}$ the carbonyl stretching frequency of trans-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$ shift to lower frequency at 1890 cm$^{-1}$. This is due to the effect of increasing substitution of the metal carbonyls by trivalent phosphorus ligands. Trivalent phosphorus ligands are good electron donors, therefore, complexes with two trivalent ligands will have a larger negative charge on the metal atom than for the complexes with only one trivalent phosphorus ligand. The larger negative charge on the metal will increase the pi back-bonding to the carbonyl ligands thus the carbonyl stretching frequency will decrease.

The proton nmr spectra of these complexes are second order spectra (Figure 6-8) and are very complicated. The absorptions of phenyl protons were found around 7.4 ppm, and the absorptions of vinyl protons were found between 5 and 7 ppm.

This type of complex contains both magnetically and chemically equivalent phosphorus atoms and therefore only one signal exhibits on the proton-decoupled P-31 nmr spectrum. (Figure 9-11) The signal of the tungsten compound is different from both the molybdenum and chromium complexes because the P-31 signal of the tungsten compound will be split into a doublet by W-183 (nuclear spin $\frac{5}{2}$, natural abundance 14.3%). The magnitude of the tungsten-phosphorus coupling constant for trans-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$ is 281.1 Hz which was obtained from measuring
Figure 3. Expanded infrared spectrum of $\text{trans}-(\text{CO})_4\text{W(pH}_2\text{CH}_2\text{CH}_2\text{)}_2$. 
Figure 4. Expanded Infrared Spectrum.
trans-(CO)₄CR(PPH₂CH=CH₂)₄

Figure 5: Expanded InfraRed spectrum of
Figure 6. Proton nmr spectrum of \( \text{trans-} (\text{CO})_4 W(\text{PPH}_2 \text{CH=CH}_2)_2 \)
Figure 7. Proton nmr spectrum of trans-\((\text{CO})_4\)Mo\((\text{PPh}_2\text{CH} = \text{CH}_2)_2\)
Figure 8. Proton nmr spectrum of trans-(CO)₄Cr[(PPh₂CH=CH₂)₂]
Figure 9. Phosphorus-31 nmr spectrum of \( \text{trans-}(\text{CO})_4\text{W(PPh}_2\text{CH=CH}_2)_2 \)
Figure 10. Phosphorus-31 nmr spectrum of trans-(CO)$_4$Mo(PPh$_2$CH=CH$_2$)$_2$
Figure 11. Phosphorus-31 nmr spectrum of trans-\((\text{CO})_4\text{Cr(PPh}_2\text{CH=CH}_2)_2\).
the distance between two tungsten's satellites. The P-31 chemical shifts for \( \text{trans-}(CO)_4\text{Cr}(\text{PPh}_2\text{CH}*=\text{CH}_2)_2 \), \( \text{trans-}(CO)_4\text{Mo}(\text{PPh}_2\text{CH}*=\text{CH}_2)_2 \), and \( \text{trans-}(CO)_4\text{W}(\text{PPh}_2\text{CH}*=\text{CH}_2)_2 \) were found at -64.2, -41.8, and -17.9 ppm, respectively. Compared to 13.8 ppm for the free ligand, \((\text{CH}=\text{CH}_2)\text{PPh}_2\), the chemical shifts of these three complexes show a large downfield shift relative to the uncoordinated phosphorus. The electron density on the free phosphine will decrease upon coordination because the sigma bond between metal and phosphorus atom is formed by the donation of the lone electron pair on the phosphorus atom to the metal. A decrease of electron density on the phosphorus atom will cause a decrease in shielding of the phosphorus nucleus thus moving the P-31 chemical shift to a downfield position. It was previously shown that the P-31 chemical shifts of the complexes move to upfield positions as atomic weights of the metal atoms of the complexes increase. Therefore, it is not surprising that the P-31 chemical shifts of these three complexes move upfield in the following metal order: \( \text{Cr}<\text{Mo}<\text{W} \). A small amount of cis isomer which appeared in the P-31 spectrum of the trans complexes indicated that the chemical shift for the cis isomer was in a upfield position relative to the corresponding trans isomer.

An attempt to synthesize \( \text{cis-}(CO)_4\text{W}(\text{PPh}_2\text{CH}*=\text{CH}_2)_2 \) by reacting tetra-carbonyl(norbornadiene)tungsten with diphenylvinylphosphine was unsuccessful probably because of the low quality of the norbornadiene complex.

\[
\text{W(CO)}_6 + 3\text{CH}_3\text{CN} \xrightarrow{\text{refluxing, } 40\text{ hrs}} (\text{CO})_3\text{W(\text{CH}_3\text{CN})}_3
\]
(CO)$_3$W(CH$_3$CN)$_3$ + 2C$_7$H$_8$ $\xrightarrow{\text{hexane} \ 16 \text{ hrs}}$ C$_7$H$_8$W(CO)$_4$

C$_7$H$_8$W(CO)$_4$ + 2Ph$_2$P(CH=CH$_2$) $\rightarrow$ cis-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$

However, cis-(CO)$_4$W(PPh$_2$H)$_2$ was obtained from refluxing W(CO)$_6$ and 2 moles of diphenylphosphine in diglyme.

W(CO)$_6$ + 2PPh$_2$H $\xrightarrow{\text{diglyme} \ 160-165^\circ\text{C}}$ cis-(CO)$_4$W(PPh$_2$H)$_2$ + 2CO$	ext{+}$

Infrared spectrum of this complex is shown in Figure 12 and its carbonyl stretching frequencies are listed in Table 1. This complex has $C_{2v}$ symmetry and therefore the infrared spectrum of this complex should be characterized by four absorptions which are assigned to the $B_1$, $B_2$, $A^1_1$, and $A^2_1$ vibrational modes. In this complex the $B_1$ mode was obscured because of overlap of the $B_2$ and $A^1_1$ modes.

Phosphorus-31 nmr spectrum of this complex is shown in Figure 13. The phosphorus-31 chemical shift was found at 2.8 ppm upfield from the H$_3$PO$_4$ reference peak. $J_{W-P}$ for this complex is 224.1 Hz. This complex slowly decomposes at room temperature in the atmosphere.

It is not surprising that cis-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$ is more difficult to synthesize than the diphenylphosphine complex since diphenylvinylphosphine is more bulky than diphenylphosphine.

In order to obtain the Group VI metal complexes in which two
Figure 12. Expanded infrared spectrum of \( \text{cis-}(\text{CO})_4\text{W}(\text{PPh}_2\text{H})_2 \)
Figure 13. Phosphorus-31 nmr spectrum of cis-(CO)$_4$W(PPh$_2$H)$_2$
ditertiary phosphines serve as monodentate ligands, several different approaches were carried out in this research.

1. \( \text{trans-}(\text{CO})_4M(\text{PPh}_2\text{CH}=\text{CH}_2)_2 + 2\text{PPh}_2\text{H} \xrightarrow{\text{AIBN}} \text{trans-}(\text{CO})_4M(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \)
   \( M = \text{W, Mo, and Cr} \)

2. \( \text{trans-}(\text{CO})_4M(\text{PPh}_2\text{CH}=\text{CH}_2)_2 + 2\text{Ph}_2\text{PH} \xrightarrow{(\text{CH}_3)_3\text{COK}, \text{THF}} \text{trans-}(\text{CO})_4M(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \)
   \( M = \text{W, Mo, and Cr} \)

3. \( \text{cis-}(\text{CO})_4\text{W}(\text{PPh}_2\text{H})_2 + 2\text{PPh}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{AIBN}} \text{cis-}(\text{CO})_4\text{W}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \)

4. \( \text{cis-}(\text{CO})_4\text{W}(\text{PPh}_2\text{H})_2 + 2\text{Ph}_2\text{PCH}=\text{CH}_2 \xrightarrow{(\text{CH}_3)_3\text{COK}, \text{THF}} \text{cis-}(\text{CO})_4\text{W}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \)

From the reaction between \( \text{trans-}(\text{CO})_4\text{W}(\text{PPh}_2\text{CH}=\text{CH}_2)_2 \) and two moles of diphenylphosphine in the presence of AIBN, instead of the desired complex, an air sensitive cyclic complex (Figure 14) in which a tridentate ligand, \( \text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2 \), is present as a bidentate ligand, was obtained in high yield.
The mechanism suggested for this addition reaction may be represented by the following equations:

$$\text{Ph}_2\text{PH} + \text{NC-} \rightarrow \cdot \text{PPh}_2 + \text{NC-CH}$$

$$\text{trans-}(\text{CO})_4\text{W(Ph}_2\text{CH}=\text{CH}_2)_2 + \text{Ph}_2\text{P} \rightarrow$$

$$\text{cis-}(\text{CO})_4\text{W} \rightarrow (\text{CO})_4\text{W}$$
Two possible pathways for the isomerization of the trans isomer to the cis in the cyclization process are (1) dissociative mechanism and (2) intramolecular rearrangement. Since there was no observation of diphenylphosphine or chelated ditertiary phosphine, Ph₂PCH₂CH₂PPh₂, in the coordination sphere of any products isolated, this indicated that the isomerization does not proceed by the dissociative mechanism and suggests that the process is intramolecular. In other words the trans isomer rearranges to form a trigonal prismatic intermediate which then rearranges to form the cis isomer.

The infrared spectrum of this cyclic complex is shown in Figure 15. Complexes of this type contain an unsymmetrical bis-tertiary phosphine chelating ligand which has Cs symmetry and therefore the infrared spectrum of this complex should exhibit four infrared active carbonyl stretching frequencies. The carbonyl stretching frequencies of this complex were found at 2013, 1918, and 1882 cm⁻¹. One of the vibrational mode was obscured because of the overlap of the other two modes.

The proton nmr spectrum of this complex (Figure 16) is very complicated. The absorptions of phenyl protons were found around 7.5 ppm
(CO)₄MCPh₂CH₂CH₂CH(CpH₂)
Figure 16. Proton nmr spectrum of

$$(\text{CO})_4\text{W}[\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH(PPPh}_2\text{)}\text{CH}_2\text{PPPh}_2]$$
and the absorption of the remaining protons were found between 1.8 and 3.2 ppm.

This complex contains three chemically nonequivalent phosphorus atoms and therefore the proton-decoupled phosphorus-31 nmr spectrum of this complex (Figure 17) represents a first order AMX system with three phosphorus-phosphorus coupling constants, $J_{P_1P_2}$, $J_{P_1P_3}$, and $J_{P_2P_3}$. Each phosphorus is represented by a pair of doublets. The chemical shift upfield from the $H_3PO_4$ reference peak at 20.1 ppm can easily be assigned to the phosphorus atom which is not coordinated to the metal. The observed chemical shift of this uncoordinated phosphine is close to the calculated value of 21 ppm which was obtained from the sum of the respective group contributions for the two phenyl groups, 6 ppm, and a pseudo iso-butyl group, 15 ppm. The chemical shifts downfield from the $H_3PO_4$ peak at -17.7 ppm and -4.0 ppm can be assigned to the phosphine(1) and phosphine(2), respectively, which are coordinated to the metal. P-31 nmr data for this complex is listed in Table 2. Tungsten-phosphorus spin-spin coupling constants, $J_{W-P_1}$ and $J_{W-P_2}$, for this complex are 221.1 and 226.5 Hz, respectively. It has been previously determined that the magnitudes of $^{183}W-^{31}P$ spin-spin coupling constants will increase if the substituents on the phosphorus ligand have large electronegativity. Therefore it is reasonable that two tungsten-phosphorus coupling constants for this complex are not very different since the substituents on both phosphorus atoms are similar. Phosphorus-phosphorus coupling constants for this complex may directly be measured.
\[ \delta p^2 = -4.0 \]
\[ \delta p^3 = 20. \]

\[ J_{pp_2} = 21.5 \]
\[ J_{pp_3} = 9.6 \]
\[ J_{p_2p_3} = 3.6 \]
\[ J_{WP_1} = 221.1 \]
\[ J_{WP_2} = 226.5 \]

Spectrum of \((OC)_4 W\)
in the $^{31}$P spectrum since the phosphorus atoms are all chemically non-equivalent. It was quite surprising that we found a long range coupling, P(2) coupling to P(3), which is 3.6 Hz. $^{2}J_{P1P2}$ for this complex was measured to be 21.5 Hz. Grim proposed that the observed phosphorus-phosphorus coupling constant for a chelate complex is the sum of the coupling constant for the coupling through the ligand backbone and through the metal center. $^{29}$ ($J_{pp} = J_{PMP} + J_{PPB}$) For a six membered chelate ring the coupling through the ligand backbone will be too small to be observed and the coupling constant will be approximately zero, thus $J_{pp}$ equals to $J_{PMP}$. Therefore, phosphorus-phosphorus coupling constant, $J_{PMP}$, through the metal for this complex is 21.5 Hz. This is consistent with Grim's prediction of a $^{2}J_{PMP}$ of 22 Hz on average for the six membered chelated rings. $^{29}$

As mentioned earlier, this cyclic complex is air sensitive and therefore small amount of oxidized complex (Figure 18) was also obtained from the reaction.

![Figure 18](image_url)
Infrared spectrum (Figure 19) and proton nmr spectrum (Figure 20) of this oxidized complex are similar to that of the non-oxidized complex. P-31 nmr spectrum is shown in Figure 21 and P-31 nmr data is listed in Table II. Compared to the non-oxidized complex, the chemical shifts for the two coordinated phosphines of this oxidized complex remain fairly constant at -18.2 and -2.3 ppm, respectively. The chemical shift for the uncoordinated phosphine, however, moves to -32.2 ppm downfield upon formation of P=O. This is due to the decreasing of electron density on the phosphorus atom upon oxide formation. Compared to the non-oxidized complex, coupling constants, $J_{W-P_1}$, $J_{W-P_2}$, and $2J_{P_1P_2}$ for the oxidized complex are similar. However, the long range coupling, $5J_{P_2P_3}$, has now disappeared.

In order to support the structures of these two cyclic complexes, carbon-13 nmr spectra (Figure 22) were carried out, and their C-13 nmr data are presented in Table III. For the non-oxidized compound, excluding the phenyl carbons, we found four carbon absorptions: a pair of doublets centered at 34.8 ppm, a doublet centered at 31.2 ppm, a pair of doublets centered at 30.8 ppm, and a pair of doublets centered at 25.9 ppm in the proton-decoupled carbon-13 nmr spectrum. (The metal-carbonyl carbons need not be considered because the chemical shifts of them are much further downfield than that measured in the spectrum.) The proton-decoupled $^{13}$C nmr spectrum for the oxidized compound also contains four carbon absorptions: a pair of doublets centered at 32.9 ppm, a doublet centered at 30.6 ppm, a doublet centered at 30.3 ppm, and a doublet at 25.2 ppm.
Figure 19. Expanded infrared spectrum of 

\[(\text{CO})_4\text{W}^\text{II}\text{Ph}_2\text{CH}_2\text{CH}_2\text{CH}(\text{Ph}_2\text{CH})\text{CH}_2\text{Ph}_2\]
Figure 20. Proton nmr spectrum of \((\text{CO})_4\text{WPPh}_2\text{CH}_2\text{CH}_2\text{CH}(\text{PPPh}_2)_2\text{CH}_2\text{PPPh}_2\)
Figure 22a. Carbon-13 nmr spectrum of 
(CO)₄₆WPh₂CH₂CH₂CH₂CH₂PPh₂₂
Figure 22b. Carbon-13 nmr spectrum of \((\text{CO})_4 \text{W}[\text{PPPh}_2 \text{CH}_2 \text{CH}_2 \text{CH} \text{PPPh}_2] \)
Figure 19. Expanded infrared spectrum of

$(\text{CO})_4\text{W}[(\text{Ph}_2\text{P})_2\text{CH}_2\text{CH}_2\text{CH}((\text{Ph}_2\text{P})_2)\text{CH}_2\text{Ph}_2]_2$
Figure 20. Proton nmr spectrum of

$\text{(CO)}_4\text{WPh}_2\text{CH}_2\text{CH}_2\text{CH(Ph)}\text{CH}_2\text{Ph}_2^3$
\[ \Gamma_{p_1 p_2} = 21.8 \quad \Gamma_{W p_1} = 223.5 \]
\[ \Gamma_{p_1 p_3} = 30.2 \quad \Gamma_{W p_2} = 225.6 \]
\[ \delta p_1 = -32.2 \quad \delta p_2 = -18.2 \]
\[ \delta p_2 = -2.3 \]

Spectrum of \((OC)_4 W\)
Figure 22a. Carbon-13 nmr spectrum of 

$\text{(CO)}_4 \text{W}[\text{PPh}_2 \text{CH}_2 \text{CH}_2 \text{CH(PPh}_2 \text{)} \text{CH}_2 \text{PPh}_2 ]$
Figure 22b. Carbon-13 nmr spectrum of

$$(\text{CO})_4\text{W}[\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH(PPh}_2\text{)_2}\text{CH}_2\text{PPh}_2]$$
We first consider the oxidized complex. The chemical shift centered at 30.6 ppm with a separation of 63.9 Hz between two peaks can be assigned to the carbon which is adjacent to the O=PPh₂. The magnitude of this carbon-phosphorus coupling is consistent with the reported coupling constants between α-carbon and phosphine oxide. The chemical shift centered at 25.2 ppm with 4.4 Hz coupling can be assigned to the carbon which is not bound to phosphorus because this coupling value, 4.4 Hz, is too small to arise from phosphorus bound directly to carbon. However, there is no way to identify whether phosphorus(1) or phosphorus(2) causes 4.4 Hz coupling from this carbon-13 nmr spectrum. Since \( ^2J_{P1C2} \) and \( ^2J_{P2C2} \) were found very small, it is reasonable that the magnitudes of phosphorus(1) coupling to carbon(3) and phosphorus(3) coupling to carbon(3) are too small to be observed because phosphorus(1) is three bonds away and phosphorus(3) is four bonds away from carbon(3), thus \( ^3J_{P1C3} \) and \( ^4J_{P3C3} \) are assumed to be zero. Therefore, C(3) can only be split by phosphorus(2) into a doublet. This is consistent with the chemical shift at 30.3 ppm. Now the chemical shift at 32.9 ppm can be assigned easily to the carbon(1) which is split by P(1) and P(3) into a doublet of doublets.

For the non-oxidized complex, the doublet at 31.2 ppm can be assigned to the carbon(3) because \( ^3J_{P1C3} \) and \( ^4J_{P3C3} \) are too small to be observed and the only coupling was caused from the adjacent P(2). It was found previously that the chemical shift for the carbon which is adjacent to the phosphorus atom moves to downfield position upon
formation of $\mathrm{P=O}$. Since the only absorption at higher field than the doublet of the oxide spectrum is the chemical shift at 25.9 ppm, it must arise from $\mathrm{-CH_2PPh_2}$. Again the doublet of doublets at 30.8 ppm can be assigned to the C(2) which is not bound to phosphorus because the small coupling constant, 4.5 Hz. However, a quite large coupling constant, 16.2 Hz, was found between carbon(2) and phosphorus(3) in this complex. The carbon(1) can then be assigned the upfield doublet of doublets at 34.8 Hz.

The free radical reaction described above was not suitable for synthesizing W, Mo, and Cr complexes in which two ditertiary phosphines present are monodentate ligands. However, the free radical reaction serves very nicely for synthesizing complexes in which a tridentate ligand is coordinated as a bidentate ligand. For example, a complex in which $\mathrm{PPh_2CH_2CH_2CH(PPh_2)PPh_2}$ is present as a bidentate ligand may be synthesized from the reaction between $\text{trans-}(\text{CO})_4\text{M(PPh}_2\text{CH=CH}_2)_2$ and secondary phosphine $\text{Ph}_2\text{PH}$ in the presence of AIBN catalyst. This is consistent with our attempt to develop a method for controlling the number of metal sites to which a polydentate ligand is coordinated.

The successful synthesis for the Group VI metal complexes in which two ditertiary phosphines coordinate as monodentate ligands was achieved from the reaction between $\text{trans-}(\text{CO})_4\text{M(PPh}_2\text{CH=CH}_2)_2$ ($\text{M} = \text{W, Mo, and Cr}$) and diphenylphosphine in the presence of potassium tert-butoxide base catalyst in THF.
This reaction served very nicely for synthesizing \( \text{trans-(CO)}_4\text{M(PPh}_2\text{CH=CH}_2\text{)}_2 \) and \( \text{trans-(CO)}_4\text{Mo(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \) complexes. There is no tendency for cyclization to form the chelated complexes or for the isomerization of \( \text{trans} \) to \( \text{cis} \) to occur. Although \( \text{trans-(CO)}_4\text{Cr(PPh}_2\text{CH=CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \) apparently was formed from the reaction between \( \text{trans-(CO)}_4\text{Cr(PPh}_2\text{CH=CH}_2\text{)}_2 \) and diphenylphosphine in the presence of potassium tert-butoxide, the major product was a chelating complex which has been identified as \( \text{(CO)}_4\text{Cr(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)} \). No explanation for this unexpected cyclization in this reaction can be made at this time.

In order to synthesize the \( \text{cis} \) complex in which two ditertiary phosphines coordinate as monodentate ligands, a mixture of \( \text{trans-(CO)}_4\text{W(PPh}_2\text{CH=CH}_2\text{)}_2 \) and \( \text{cis-(CO)}_4\text{W(PPh}_2\text{CH=CH}_2\text{)}_2 \) in the ratio of 80 to 20 was allowed to react with secondary phosphine under similar experimental conditions. Both \( \text{trans} \) and \( \text{cis-(CO)}_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \) were found from this reaction, also in the ratio of 80 to 20. Although the attempt to separate \( \text{cis} \) complex from the \( \text{trans-(CO)}_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \) was unsuccessful, some important information was obtained: (1) The desired \( \text{cis} \) complex can be synthesized from the reaction between \( \text{cis-(CO)}_4\text{W(PPh}_2\text{CH=CH}_2\text{)}_2 \) and diphenylphosphine. It is very likely that one will be able to obtain the pure \( \text{cis-(CO)}_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \) complex if
one can synthesize the pure cis-(CO)$_4$M(Ph$_2$CH=CH$_2$)$_2$ complexes. (2) Iso-
merization did not take place in this reaction. In order to give further
 evidence for this, the trans-(CO)$_4$W(Ph$_2$CH$_2$CH$_2$PPh$_2$)$_2$ from previous reac-
tion was allowed to reflux in benzene for 24 hours. Only starting material
and chelated complex, (CO)$_4$W(Ph$_2$CH$_2$CH$_2$PPh$_2$), were obtained. (3) P-31
nmr data for the cis-(CO)$_4$W(Ph$_2$CH$_2$CH$_2$PPh$_2$)$_2$ was obtained which is very
useful in investigating the nature of the metal-phosphorus bond.

The proton-decoupled phosphorus-31 nmr spectra of the complexes in
which two Ph$_2$PCH$_2$CH$_2$PPh$_2$ molecules coordinated as monodentate ligands
could be treated as XAA'X' spin system where A and X represent coordi-
nated and uncoordinated phosphorus, respectively.

The analysis of nmr spectra of complexes with X$_n$AA'X$_n'$ spin system
has been discussed in detail by Harris.\textsuperscript{18}

One needs to analyze only X part of the X$_n$AA'X$_n'$ spectrum since the
A part of the spectrum is identical to the X part. An equation has been
derived to express all allowed X transition energies relative to the un-
perturbed resonance frequency of the X and X' nuclei, $\omega_X$.\textsuperscript{18}

\[ (E_X - E_{X-1}) = \pm \frac{\hbar}{2} \left\{ \left[ X^2L^2 + J_{AA'}^2 \right]^{1/2} + \left[ (X - 1)^2L^2 + J_{AA'}^2 \right]^{1/2} \right\} \]

where $X = 1$ to $n$,

\[ L = J_{AX} - J_{AX'} \]

There are total $2n+1$ pairs of lines contain in the X part of spectrum,
assuming $J_{XX'} = 0$. An intense doublet separated by
\[ N = J_{AX} + J_{AX'} \]
disposed symmetrically about $J_X$. The remaining 2n pairs of lines may be divided into two sets, the inner and the outer lines. The inner lines have a separation $S_1(X)$ given by

$$S_1(X) = \left[ x^2 L^2 + J^2_{AA'} \right]^\frac{1}{2} - \left[ (x - 1)^2 L^2 + J^2_{AA} \right]^\frac{1}{2}$$

whereas the outer lines have a separation $S_0(X)$ given by

$$S_0(X) = \left[ x^2 L^2 + J^2_{AA'} \right]^\frac{1}{2} + \left[ (x - 1)^2 L^2 + J^2_{AA} \right]^\frac{1}{2}$$

In the case of $XAA'X'$ spin system, one should find total three pairs of lines in the $X$ part of spectrum, assuming $J_{XX'} = 0$. (Figure 23) The separation of the two most intense peaks is given by $N = J_{AX} + J_{AX'}$.

![Figure 23. Typical X part of spectrum for an XAA'X' system with J_{XX'} = 0.](image)

Since $J_{AX'}$ for the $(CO)_4M(PPh_2CH_2CH_2PPh_2)_2$ type of complexes is considered to be very small compared to $J_{AX}$, $N \approx J_{AX}$ and $3J_{pp}$ may be measured directly from the spectrum. The separations between two inner
lines and two outer lines are given by \( S_1(1) = \left( L^2 + J_{AA}^2 \right)^{1/2} - J_{AA} \) and \( S_0(1) = \left( L^2 + J_{AA}^2 \right)^{1/2} + J_{AA} \), respectively. Therefore, from the separation between outer line and first inner line, \( \frac{1}{2}[S_0(1) - S_1(1)] \), \( J_{AA} \), i.e. \( 2J_{PMP} \) is determined.

The phosphorus-31 nmr spectra of \((CO)_4M(PPh_2CH_2CH_2PPh_2)_2 \) (\( M = W, \) Mo, and Cr) type of complexes are shown in Figure 24-27 and their P-31 nmr data are presented in Table II.

The observation that the P-31 chemical shifts of the complexes move upfield positions as atomic weight of the metal atoms on the complexes increase has been discussed previously in this chapter. The chemical shift for the trans-(CO)_4W(PPh_2CH_2CH_2PPh_2)_2 shows a downfield shift relative to the corresponding cis isomer. This probably can be interpreted in terms of the concept of pi bonding between phosphorus and transition metals. When the phosphorus is trans to the carbonyl ligand, it will not be able to complete the electron density on the metal because carbonyl group is a better pi bonder. Hence the pi bonding between M-P is weaker than the pi bonding between M-C. When the phosphine ligands trans to each other, both phosphine ligands compete equally for electron density from the metal and therefore the pi bonds are equivalent. The increased pi back bonding is result from the increased sigma donor bonding which causes a downfield chemical shift because of the decreasing electron density on the phosphorus atom.

The phosphorus-phosphorus coupling constant through the metal for the trans-(CO)_4W(PPh_2CH_2CH_2PPh_2)_2 was found to be larger than for the
\[ \text{SPECTRUM OF} \quad \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2 \]
Figure 25. Phosphorus-31 nmr spectrum of a mixture of *cis* and *trans* isomers of \((\text{CO})_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\).
Figure 26. Phosphorus-31 nmr spec

\textit{trans-(CO)}_4\textit{Mo(PPh}_2\textit{CH}_2\textit{Cl)}
cis-(CO)_4W(PPh_2CH_2CH_2PPh_2)_2 complex. This is consistent with previous observation that \( ^2J_{PMP} \) values are usually larger for the trans compounds than for the corresponding cis complexes. However, unusually small magnitudes of \( ^2J_{PMP} \) was found in trans chromium complexes and in manganese complexes of the type Mn(CO)_3L_2X. (X = H, Cl, Br, and I) It is very likely that if we are able to synthesize cis-(CO)_4Cr(PPh_2CH_2CH_2PPh_2)_2, we will find that \( ^2J_{PP} \) for the cis isomer will be larger than for the trans isomer. In addition, the magnitudes of \( ^2J_{PMP} \) for the complexes of the type trans-(CO)_4M(PPh_2CH_2CH_2PPh_2)_2 was found in the order: W > Mo > Cr as has been observed by other workers.

Tungsten-phosphorus coupling constant for the trans-(CO)_4-W(PPh_2CH_2CH_2PPh_2)_2 is 279.4 Hz which is similar to the \( ^1J_{W-P} \) for the trans-(CO)_4W(PPh_2CH=CH_2)_2. This suggests that both complexes have very similar metal-phosphorus bond strength.

The infrared spectra (Figure 28-29) for the trans complexes of this type show three absorptions: \( \text{A}_{1g}, \text{B}_{1g}, \) and a strong \( \text{E}_u \) fundamental absorption. The carbonyl stretching frequencies of these complexes are listed in Table 1.

The proton nmr spectra of trans-(CO)_4W(PPh_2CH_2CH_2PPh_2)_2 and trans-(CO)_4Mo(PPh_2CH_2CH_2PPh_2)_2 are shown in Figure 30 and Figure 31, respectively. Again, these second order spectra are very complicated. The absorptions of methylene protons were found between 1.8 and 3.0 ppm.

The desired tungsten complex in which two Ph_2PCH_2CH_2PPh_2 are present as monodentate ligands was also obtained from the reaction between
Figure 28. Expanded infrared spectrum of trans-$(\text{CO})_4\text{W}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$
Figure 29. Expanded infrared spectrum of
\[ \text{trans-(CO)}_4\text{Mo(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2 \]
Figure 30. Proton nmr spectrum of
trans-(CO)$_4$W(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$
Figure 31. Proton nmr spectrum of

\textit{trans-(CO)}_{4}\text{Mo(PPh}_{2}\text{CH}_{2}\text{CH}_{2}\text{PPh}_{2})_{2}
cis-(CO)$_4$W(PPh$_2$H)$_2$ and diphenylvinylphosphine in the presence of AIBN free radical catalyst. Although a small amount of cis isomer was observed, the major product from this reaction was trans-(CO)$_4$W(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$.

$$\text{cis-(CO)}_4\text{W(PPh}_2\text{H)}_2 + 2\text{Ph}_2\text{P(CH=CH)}_2 \xrightarrow{\text{AIBN}} \text{trans-(CO)}_4\text{W(PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$$

It is reasonable that isomerization took place in this reaction because Ph$_2$PCH$_2$CH$_2$PPh$_2$ molecule is too bulky to be in the cis position.

It is quite surprising that the reaction between cis-(CO)$_4$W(PPh$_2$H)$_2$ and diphenylvinylphosphine in the presence of potassium tert-butoxide was not straightforward. Instead of the expected product, a complex with phosphorus-31 chemical shift at -40.8 ppm was found which has been identified as the complex in which Ph$_2$PCH$_2$CH$_2$PPh$_2$ is present as a bidentate ligand. When the ditertiary phosphine complex was first formed, the coordinated secondary phosphine was displaced by the free end of phosphine to form the chelated product.

$$\text{cis-(CO)}_4\text{W(PPh}_2\text{H)}_2 + 2\text{Ph}_2\text{P(CH=CH)}_2 \xrightarrow{(\text{CH}_3)_3\text{COK}} \xrightarrow{\text{THF}} \text{(CO)}_4\text{W(PPh}_2\text{H)}_2 + \text{Ph}_2\text{PH}$$

$$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \rightarrow \text{Ph}_2\text{PH}$$
The phosphorus-31 nmr spectrum and the infrared spectrum of this chelated complex are shown in Figure 32 and Figure 33, respectively.

In conclusion, it is not proper to synthesize the Group VI metal complexes in which two ditertiary phosphines are present as monodentate ligands by the reaction of diphenylvinylphosphine complex with secondary phosphine in the presence of AIBN free radical catalyst or by the reaction of diphenylphosphine complex with diphenylvinylphosphine ligand in the presence of potassium tert-butoxide base catalyst. However, the desired complexes can be synthesized either from the reaction between a diphenylvinylphosphine complex and a secondary phosphine in the presence of potassium tert-butoxide or from the reaction between a diphenylphosphine complex and a diphenylvinylphosphine ligand in the presence of AIBN free radical catalyst. These methods can be taken as a means of controlling the number of metal sites to which a polydentate phosphine ligand is coordinated.
Figure 32.
Phosphorus-31 nmr spectrum of

\[(\text{CO})_4\text{P} \quad \text{pph}_2\]

\[\text{pph}_2 \quad \text{CH}_3 \quad \text{CH}_2\]
Figure 33. Expanded infrared spec

\[(\text{CO})_4\text{W} \quad \text{PPh}_2 \quad \text{CH}_2 \quad \text{PPh}_2 \quad \text{CH}_2\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbonyl Stretching Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans-(CO)₄W(PPh₂CH=CH₂)₂</td>
<td>2021 1946 1890</td>
</tr>
<tr>
<td>Trans-(CO)₄Mo(PPh₂CH=CH₂)₂</td>
<td>2026 1958 1897</td>
</tr>
<tr>
<td>Trans-(CO)₄Cr(PPh₂CH=CH₂)₂</td>
<td>2011 1944 1891</td>
</tr>
<tr>
<td>Cis-(CO)₄W(PPh₂H)₂</td>
<td>2020 1917 1903</td>
</tr>
<tr>
<td>Trans-(CO)₄W(PPh₂CH₂CH₂PPh₂)₂</td>
<td>2020 1945 1888</td>
</tr>
<tr>
<td>Trans-(CO)₄Mo(PPh₂CH₂CH₂PPh₂)₂</td>
<td>2025 1955 1900</td>
</tr>
<tr>
<td>(CO)₄W(PPh₂CH₂CH₂PPh₂)</td>
<td>2017 1915 1899</td>
</tr>
<tr>
<td>(CO)₄W[PPh₂CH₂CH₂CH(PPh₂)CH₂PPh₂]</td>
<td>2013 1918 1888</td>
</tr>
<tr>
<td>(CO)₄W[PPh₂CH₂CH₂CH(PPh₂)CH₂PPh₂]₀</td>
<td>2016 1920 1890</td>
</tr>
<tr>
<td>Compound</td>
<td>δcoord. (ppm)</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
</tr>
<tr>
<td>Trans-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$</td>
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</tr>
<tr>
<td>Trans-(CO)$_4$Mo(PPh$_2$CH=CH$_2$)$_2$</td>
<td>-41.8</td>
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<tr>
<td>Trans-(CO)$_4$Cr(PPh$_2$CH=CH$_2$)$_2$</td>
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</tr>
<tr>
<td>Cis-(CO)$_4$W(PPh$_2$CH=CH$_2$)$_2$</td>
<td>-11.5</td>
</tr>
<tr>
<td>Cis-(CO)$_4$Cr(PPh$_2$CH=CH$_2$)$_2$</td>
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</tr>
<tr>
<td>Cis-(CO)$_4$W(PPh$_2$H)$_2$</td>
<td>2.8</td>
</tr>
<tr>
<td>Trans-(CO)$_4$W(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$</td>
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<tr>
<td>Cis-(CO)$_4$W(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$</td>
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<td>Trans-(CO)$_4$Mo(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$</td>
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<td>(CO)$_4$Cr(PPh$_2$CH$_2$CH$_2$PPh$_2$)</td>
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<td>(CO)$_4$W[P$^2$Ph$_2$CH$_2$CH(P$^1$Ph$_2$)CH$_2$P$^3$Ph$_2$]</td>
<td>-17.7(P$_1$)</td>
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<tr>
<td></td>
<td>-4.0(P$_2$)</td>
</tr>
<tr>
<td>(CO)$_4$W[P$^2$Ph$_2$CH$_2$CH(P$^1$Ph$_2$)CH$_2$P$^3$Ph$_2$]</td>
<td>-18.2(P$_1$)</td>
</tr>
<tr>
<td>0</td>
<td>-2.3(P$_2$)</td>
</tr>
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</table>
Table III

CARBON-13 NMR DATA OF (CO)$_4$W[PPh$_2$CH$_2$CH$_2$CH-$(PPh_2)CH_2PPh_2$] AND ITS OXIDIZED COMPOUND

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>(CO)$_4$W[PPh$_2$CH$_2$CH$_2$CH-$(PPh_2)CH_2PPh_2$]</th>
<th>(CO)$_4$W[PPh$_2$CH$_2$CH$_2$CH-$(PPh_2)CH_2PPh_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>34.8</td>
<td>32.9</td>
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<tr>
<td>C(2)</td>
<td>30.8</td>
<td>25.2</td>
</tr>
<tr>
<td>C(3)</td>
<td>31.2</td>
<td>30.3</td>
</tr>
<tr>
<td>C(4)</td>
<td>25.9</td>
<td>30.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling Constant (Hz)</th>
<th>(CO)$_4$W[PPh$_2$CH$_2$CH$_2$CH-$(PPh_2)CH_2PPh_2$]</th>
<th>(CO)$_4$W[PPh$_2$CH$_2$CH$_2$CH-$(PPh_2)CH_2PPh_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{P_1C_1}$</td>
<td>17.0</td>
<td>16.1</td>
</tr>
<tr>
<td>$J_{P_1C_4}$</td>
<td>6.1</td>
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</tr>
<tr>
<td>$J_{P_2C_3}$</td>
<td>23.5</td>
<td>24.3</td>
</tr>
<tr>
<td>$J_{P_3C_1}$</td>
<td>13.3</td>
<td>4.3</td>
</tr>
<tr>
<td>$J_{P_3C_2}$</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>$J_{P_3C_4}$</td>
<td>13.8</td>
<td>63.9</td>
</tr>
</tbody>
</table>

* For the non-oxidized compound, either $J_{P_1C_2}$ or $J_{P_2C_2}$ equals to 4.5 Hz.

* For the oxidized compound, either $J_{P_1C_2}$ or $J_{P_2C_2}$ equals to 4.4 Hz.
CHAPTER III

EXPERIMENTAL

A. General Considerations

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

The infrared spectra of the carbonyl region (2100-1850 cm⁻¹) were obtained using 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 as a reference and chloroform was used as a solvent for each measurement.

Phosphorus-31 nmr spectra and carbon-13 nmr spectra were obtained by Mr. Lewis W. Cary at Stanford Research Institute, Stanford, California. The 31P spectra were recorded at 40.5 MHz and the 13C spectra at 25.2 MHz on a Varian XL-100-15 NMR Spectrometer equipped with Fourier transform and a pulsed deuterium lock. The 13C-1H and 31P-1H couplings were eliminated using broad-band 1H noise-modulated decoupling. Phosphoric acid (85%) in a 1.0 mm capillary was used as an external reference for the 31P nmr spectra, and TMS was used as an internal reference for the 13C nmr spectra. COCl₃ was used for solvent and lock. Coupling constants are accurate to ±0.1 Hz.
The proton nuclear magnetic resonance measurements were carried out on a Varian T-60 spectrometer. Saturated deuteriochloroform solutions of the compounds were used and contained 2 ml of tetramethylsilane vapor which served as an internal reference.

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

Tungsten hexacarbonyl, molybdenum hexacarbonyl, chromium hexacarbonyl, diphenylvinylphosphine, and diphenylphosphine used in this research were purchased from Pressure Chemical Co.

B. Preparation of Metal Complexes

(1) Preparation of \textit{trans}-tetracarbonylbis(diphenylvinylphosphine)-tungsten(0), \textit{trans}-\((\text{CO})_4\text{W}$(\text{PPh}_2\text{CH}=\text{CH}_2)_2$

Tungsten hexacarbonyl (6.0 g, 0.017 mole) was introduced into a 200 ml round-bottom flask. A teflon coated magnetic stirring pea was added, followed by 50 ml of dry diglyme (diethyleneglycol dimethyl ether). The flask was immersed halfway in an oil bath equipped with a heating coil. A magnetic stirring unit was placed under the oil bath. A thermometer also immersed in the oil bath, indicated the bath temperature. Nitrogen gas was bubbled into the solution through a glass bubbler tube for approximately 10 min. During this period, an excess of diphenylvinylphosphine ($\text{Ph}_2\text{PCH}=\text{CH}_2$) (7.2 ml, 0.054 mole) was injected directly into the flask by means of a syringe. A small condenser with a stopcock
connecting tube on the top was then joined to the flask immediately after the dropper bubbling the nitrogen into the solution was removed from the flask.

The reaction was then carried out by refluxing the solution at 160°C for two hours under a nitrogen atmosphere. When the reaction was over, the solution was cooled to room temperature under nitrogen. The solvent was then removed by a simple vacuum distillation at 60°C. The remaining unreacted tungsten hexacarbonyl was then removed under a high vacuum at 50°C for 5 hours.

After the unreacted tungsten hexacarbonyl was removed, the residue was washed twice with petroleum ether to remove the unreacted diphenylvinylphosphine and monosubstituted complex (CO)₅W(PPh₂CH=CH₂). The crude product was then recrystallized to remove the cis isomer by dissolving the product in a minimum amount of dichloromethane and adding about 30 ml of absolute methanol to produce 3.34 g (27.3% yield) of the desired pure complex. (m.p. 147-149°C) Calcd. for trans-(CO)₄W(PPh₂CH=CH₂): C, 53.36; H, 3.64; P, 8.60 Found: C, 53.53; H, 3.78; P, 8.75.

(2) Preparation of trans-tetracarbonylbis(diphenylvinylphosphine)molybdenum(0), trans-(CO)₄Mo(PPh₂CH=CH₂)₂.

This complex was prepared by the same procedure as for the tungsten complex.

Molybdenum hexacarbonyl (4.5 g, 0.017 mole) and diphenylvinylphosphine (7.2 ml, 0.054 mole) were mixed in 50 ml of diglyme. The solution was allowed to reflux at 160°C for two hours under nitrogen atmosphere.
After the diglyme was removed by vacuum distillation at 60°C, the crude product was allowed to stand under a high vacuum for 5 hours to remove the unreacted molybdenum hexacarbonyl. The yellow solid then was washed twice with petroleum ether to remove the unreacted diphenylvinylphosphine and the monosubstituted compound. This crude product was then recrystallized by dissolving the product in CH₂Cl₂ and CH₃OH to produce a pale yellow complex. (2.5 g, 23% yield) (m.p. 148-150°C) Calcd. for trans-(CO)₄Mo(PPh₂CH=CH₂): C, 60.77; H, 4.14; P, 9.79. Found: C, 60.68; H, 4.18; P, 9.88.

(3) Preparation of trans-tetracarbonylbis(diphenylvinylphosphine)chromium(0), trans-(CO)₄Cr(PPh₂CH=CH₂)₂

This complex was prepared by refluxing 3.74 g (0.017 mole) of chromium hexacarbonyl and 7.2 ml of diphenylvinylphosphine in diglyme for two hours. The crude product was recrystallized by dissolving the product in dichloromethane and absolute methanol to produce 2.1 g (21% yield) (decomposed: 145-147°C) of yellow complex. Calcd. for trans-(CO)₄Cr(PPh₂CH=CH₂): C, 65.31; H, 4.45; P, 10.53. Found: C, 65.14; H, 4.47; P, 9.88.

(4) Preparation of cis-tetracarbonylbis(diphenylphosphine)tungsten(0), cis-(CO)₄W(PPh₂H)₂

This complex was prepared by refluxing 6.0 g (0.017 mole) of tungsten hexacarbonyl and an excess of diphenylphosphine (5.9 ml, 0.051 mole) in diglyme for two hours. The crude product was recrystallized by dissolving the product in dichloromethane and absolute methanol to produce 2.2 g (19% yield) of desired white compound. (m.p. 88-90°C) This complex is air sensitive at room temperature and slowly decomposes with time.
(5) Preparation of (CO)₄W and its oxidized compound.

\[ \text{Trans-} (\text{CO})_4W(\text{PPh}_2\text{CH}=\text{CH}_2)_2 \] (1.8 g, 0.0025 mole) and 0.1 g of AIBN were introduced into a 100 ml round-bottom flask equipped with a side arm stopcock and a Teflon coated magnetic stirring pea. The flask was immersed halfway in an oil bath equipped with a heating coil which was regulated by a Variac. A magnetic stirring unit was placed under the oil bath.

The flask was flushed with nitrogen through the side arm stopcock for 10 min. Diphenylphosphine (1.1 ml) was then injected directly into the flask by means of a syringe. The reaction was then carried out by heating the yellow mixture to 75°C for 24 hours under a nitrogen atmosphere. The unreacted diphenylphosphine was then removed under a high vacuum at 65°C for 2 hours. The oily product was cooled to room temperature under nitrogen. The crude product contained an identified white solid, perhaps \( \text{O}=\text{PPh}_2\text{H}, (\text{CO})_4W[\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2] \) and \( (\text{CO})_4W[\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2] \). Separation was achieved by column chromatography. The column was packed with a petroleum ether-silica gel slurry. The oily product was dissolved in minimum amount of dichloromethane and placed on the column. The column was eluted continuously with 500 ml petroleum ether to remove the unidentified white solid. Continued elution by the solution of 80% petroleum ether and 20% ethyl
acetate yielded a yellow band which was found to contain \((\text{CO})_4\text{W}(\text{PPh}_2\text{-CH}_2\text{CH}_2\text{CH(PPPh}_2\text{)CH}_2\text{PPPh}_2)\). The residues were then recrystallized by dissolving the residues in a minimum amount of dichloromethane and about 30 ml of absolute methanol to produce 1.5 g (65% yield) of the pure product. (m.p. 121-123).

After \((\text{CO})_4\text{W}(\text{PPh}_2\text{-CH}_2\text{CH}_2\text{CH(PPPh}_2\text{)CH}_2\text{PPPh}_2)\) was separated, the column was eluted continuously by the solution of 50% petroleum ether and 50% ethyl acetate to obtain \((\text{CO})_4\text{W}(\text{PPh}_2\text{-CH}_2\text{CH}_2\text{CH(PPPh}_2\text{)CH}_2\text{PPPh}_2)\). The crude product was then recrystallized by dissolving the product in a minimum amount of dichloromethane and about 30 ml of absolute methanol to produce the desired pure product. (m.p. 125-127)

(6) Preparation of \underline{trans-tetracarbonylbis(tetraphenylphosphino)ethane-tungsten(O)}, \underline{\text{trans-}}(\text{CO})_4\text{W}(\text{PPh}_2\text{-CH}_2\text{CH}_2\text{PPPh}_2)_2.

(a) Base Catalyst Reaction

Dry THF (100 ml) (distilled from LiAIH₄) was introduced into a 200 ml round-bottom flask equipped with a ground glass joint and a side arm stopcock. A Teflon coated magnetic stirring pea was added. The flask was then immersed halfway in an oil bath equipped with a heating coil which was regulated by a Variac. A magnetic stirring unit was placed under the oil bath. Nitrogen was bubbled into the solution through a glass bubbler tube for approximately 15 min. During this period, an excess of diphenylphosphine (2.1 ml) was added. This solution was then treated with solid potassium tert-butoxide of two spatula tips. After 15 min, the bubbler tube was removed from the flask. The flask was
then flushed with nitrogen through the side arm stopcock. A small condenser with a separatory funnel joined on the top was then joined to the flask. The solution was heated to boiling. While under reflux it was treated dropwise through separatory funnel with a solution of 2.9 g (0.004 mole) of trans-(CO)₄W(PPh₂(CH=CH₂)₂ dissolved in 20 ml of dry THF over a one hour period all under nitrogen atmosphere. The mixture of two solutions turned bright yellow upon addition. The two solutions were heated under reflux for 40 min.

When the reaction was over, the solution was cooled to room temperature under nitrogen. After 0.5 ml of H₂O was added the solution turned cloudy yellow. Potassium tert-butoxide was removed by filtering the solution through a fritted glass funnel. The filtrate was roter vacuum distilled to remove the THF and which left an oily residue. After addition of 15 ml dichloromethane and 20 ml water, there was a yellowish precipitate in the water layer. The organic layer was separated, saved and dried over MgSO₄ solution overnight. After filtration to remove MgSO₄, 15 ml of absolute methanol was added and the solution was cooled to precipitate out the desired product. (1.2 g, 28% yield) (m.p. 151-152°C)

(h) Free Radical Catalyst Reaction

_Cis-(CO)₄W(PPh₂H)₂_ (1.4 g, 0.0021 mole) and 0.1 g AIBN were introduced into a 100 ml round-bottom flask equipped with a side arm stopcock and a Teflon coated magnetic stirring pea. The flask was immersed halfway in an oil bath equipped with a heating coil which was regulated by a Variac. A magnetic stirring unit was placed under the oil bath.

The flask was flushed with nitrogen through the side arm stopcock
for 10 min. Diphenylvinylphosphine (0.75 ml, 0.005 mole) was then injected directly into the flask by means of a syringe. The reaction was then carried by heating the mixture to 75°C for 24 hours under nitrogen atmosphere. The unreacted diphenylvinylphosphine was removed upon subjection to high vacuum at 65°C for two hours. The oily product was cooled to room temperature under nitrogen. This oil was then dissolved in a minimum amount of dichloromethane and about 30 ml absolute methanol was added to produce 0.34 g (15% yield) of the desired product.

(7) Preparation of trans-tetracarbonylbis(tetraphenyldiphosphino)ethanemolybdenum(0), trans-(CO)₄Mo(PPh₂CH₂CH₂PPh₂)₂

This complex was prepared by the reaction between trans-(CO)₄Mo(PPh₂CH=CH₂)₂ (2.5 g, 0.004 mole) and diphenylphosphine (1.8 ml) in the presence of potassium tert-butoxide. The oily product was dissolved in dichloromethane and methanol to produce 0.33 g (8.2% yield) pure product. (m.p. 134-136°C).

(8) Preparation of trans-tetracarbonylbis(tetraphenyldiphosphino)ethanechromium(0), trans-(CO)₄Cr(PPh₂CH₂CH₂PPh₂)₂

This complex was prepared by the reaction between trans-(CO)₄Cr-(PPh₂CH=CH₂)₂ (1.8 g, 0.003 mole) and diphenylphosphine (1.5 ml) in the presence of potassium tert-butoxide. The crude product was recrystallized from dichloromethane and methanol to produce 0.86 g yellow crystal. Phosphorus-31 nmr showed that both chelate complex (CO)₄Cr(PPh₂CH₂CH₂PPh₂) and the desired complex were present. The impure product decomposed between 137-142°C.
C. Attempted Preparations

(1) Preparation of tetracarbonylbicyclohepta-2,5-dienetungsten(0), $C_7H_8W(CO)_4$

Distilled acetonitrile (50 ml) was introduced into a 100 ml round-bottom flask which contained a magnetic stirring pea. Nitrogen was bubbled into the solution through a glass bubbling tube for 10 min. During this time, 10.6 g (0.0030 mole) of tungsten hexacarbonyl was added. After 10 min, the glass bubbling tube was removed from the flask. A condenser with a 90° standard taper stopcock was joined to the flask immediately. The flask then was immersed halfway in an oil bath with a magnetic stirring bar in it. The mixture was refluxed under nitrogen for 40 hours.

After 40 hours, the liquid part of the mixture was removed by distilling the mixture on 40°C under vacuum. This crude product was recrystallized from 1:1 ratio of acetone-hexane solution to produce 5.5 g (47% yield) of $(CO)_3W(CH_3CN)_3$ compound.

A mixture of 2.3 g (0.0060 mole) of $(CH_3CN)_3W(CO)_3$, excess of bicycloheptadiene (norbornadiene) 2 ml and 80 ml of hexane was refluxed at the boiling point with a magnetic stirring for 20 hours under nitrogen gas. After the reaction period was over, the reaction mixture was filtered hot and the residue was washed with 10 ml boiling hexane under $N_2$ atmosphere. The filtrate was cooled in a liquid nitrogen bath for an hour and put in the refrigerator overnight. The crystals of complex which separated were filtered off and purified by sublimation at 80°C.
for 5 hours was attempted. Only an unidentified dark brown complex was obtained.

(2) Preparation of cis-tetracarbonylbis(tetraphenylphosphino)ethanetungsten(0), cis-(CO)_4W(PPh_2CH_2CH_2PPh_2)_2

An excess of diphenylvinylphosphine (0.75 ml, 0.0050 mole) and small amount of potassium tert-butoxide were added to 100 ml dry THF. The solution was allowed to reflux for two hours. While under reflux it was treated dropwise through separatory funnel with a solution of 1.5 g (0.0022 mole) of cis-(CO)_4W(PPh_2H)_2 dissolved in 20 ml of THF over a one hour period under nitrogen atmosphere. When the reaction was over, the solution was cooled to room temperature under nitrogen. After 0.5 ml of H_2O was added, the solution turned cloudy yellow. Potassium tert-butoxide was then removed by filtration through fritted glass funnel. The filtrate was then roter vacuum distilled to remove the THF. After addition of 15 ml dichloromethane and 20 ml of water, there was a yellowish precipitate in the water layer. The organic layer was collected and dried overnight over MgSO_4. After filtration to remove MgSO_4, 15 ml of absolute methanol was added upon and cooling a precipitate of the desired product occurred. Phosphorus-31 nmr showed that only chelated complex was obtained.
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VITA

Name: Yih-Yau York Sun

Permanent Address: 12052 Wildwing
Plymouth, Michigan 48170

Degree and Date to be Conferred: M.S. (Chemistry)
June, 1978

Date of Birth: November 28, 1952

Place of Birth: Taipei, Taiwan, R.O.C.

Secondary Education: The High School of National Taiwan Normal University

Collegiate Institutions Attended Date Degree Date of Degree
Soochow University (Taiwan) 1970-1974 B.S. June, 1974
Eastern Illinois University 1976-1978

Major: Inorganic Chemistry

Positions Held: Graduate Assistant at the Chemistry Department Eastern Illinois University
August 1976 to May 1978