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Bimetallic Complexes of Tungsten and Mercury

Zakariah Abdullah

Eastern Illinois University

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Bimetallic Complexes of Tungsten and Mercury

(TITLE)

BY

Zakariah Abdullah

THESIS

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FOR THE DEGREE OF

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1985

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Bimetallic Complexes of Tungsten and Mercury

by

Zakariah Abdullah
B.A. in Chemistry, June, 1983
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Submitted in partial fulfillment
of the requirement for the degree of
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Charleston, Illinois
1985

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Abstract

A tungsten-mercury bimetallic complex $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ has been synthesized from the reaction of trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$ and $HgCl_2$. The value of n has not been determined due to the insolubility of the complex. The anologous reaction with HgI_2 gave an insoluble, uncharacterizable complex, which best corresponds to $(CO)_4W(PPh_2CH_2CH_2PPh_2)_2Hg_2I_4$.

The geometry about tungsten in $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ is cis as shown by P-31 nmr (J_{W-P}= 230.0 and J_{Hg-P}= 4420 Hz) and by infrared spectroscopy. Isomerization of trans-$(CO)_4W(\eta^1-PPh_2CH_2-CH_2PPh_2)_2$ occured when it reacted with $HgCl_2$. The energy barrier for isomerization is undoubtedly low and the process was probably induced as a result of steric pressure.

The starting material, trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$, was prepared from the reaction of trans-$(CO)_4W(PPh_2CH=CH_2)_2$ and PPh_2H in the presence of base. The reaction of $W(CO)_6$ with $PPh_2CH=CH_2$ in n-butanol in the presence of $NaBH_4$ gave trans-$(CO)_4W(PPh_2CH=CH_2)_2$ (57 % yield).

i

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CHAPTER I

INTRODUCTION

At present, industrial output of chemicals synthesized via heterogeneous catalysis vastly outweighs chemical production via homogeneous catalysis.[1] However, there has been a significant shift toward developing and instituting homogeneous molecular catalysis in industrial processes. This shift is mainly due to several factors. One, due to rising costs in energy and natural resources, the higher selectivity and lower energy requirements of homogeneous catalysts are becoming more important economically. Two, it is easier to modify a homogeneous catalyst to effect a specific reaction than it is to modify a heterogeneous catalyst. Lastly, the chemistry of a homogeneous catalyst can be studied since this soluble species can be examined by IR and NMR during a reaction, whereas heterogeneous catalyst are insoluble and thus are difficult to study even under ideal laboratory conditions.

Much effort has been expended industrially and academically in attempts to understand the mechanistic details of processes which could lead to development of

catalysts with greater selectivity. It has been suggested that in order for a homogeneous catalyst to be very selective, a vacant coordination site is the most important property to be present. The catalyst must have carefully balanced bonding properties such that it can accept the desired ligand and not an alternative.

The preparation of bimetallic complexes which contain two metal atoms of either the same or different elements has received considerable attention.[2,3,4] In some instances, bimetallic complexes may be more selective for catalysis than monometallic complexes. This selectivity may be enhanced by simply choosing the appropriate ligands and metals for the bimetallic complexes. An example of homogeneous catalysis which involves a homobimetallic complex is the water gas shift reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$, which is catalyzed by a Platinum A-frame complex.[1] Although the mechanism is not yet known, the catalysis proceeds according to the following equation.
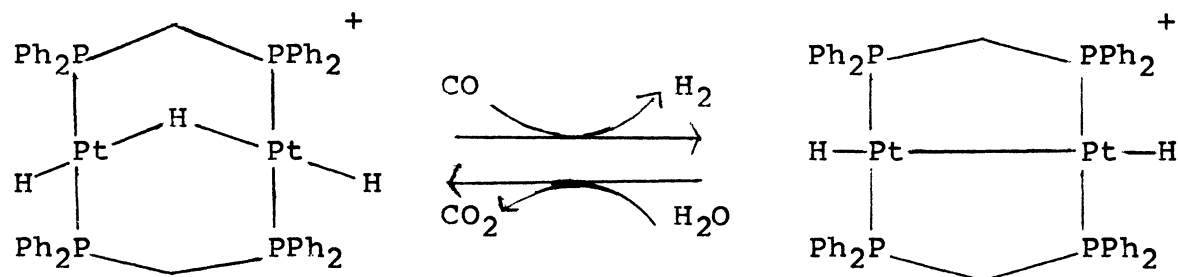
The purpose of this research was to synthesize heterobimetallic carbonyl complexes of the type,

$(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2$ (X=Cl or I) in which W is at an
octahedral center, and Hg is at a tetrahedral center. It
would not be expected that these complexes could function as
catalysts, but they could be used to demonstrate the
possibility of preparing complexes in which two
$PPh_2CH_2CH_2PPh_2$ molecules bridge two different metals. If
metals, (Ir(I) and Rh(I)), known to activate H_2 were used,
one could imagine oxidation-addition occuring, conceivably
followed by the transfer of activated hydrogen to a bound CO
of the metal W.

M= Ir(I), Rh(I)
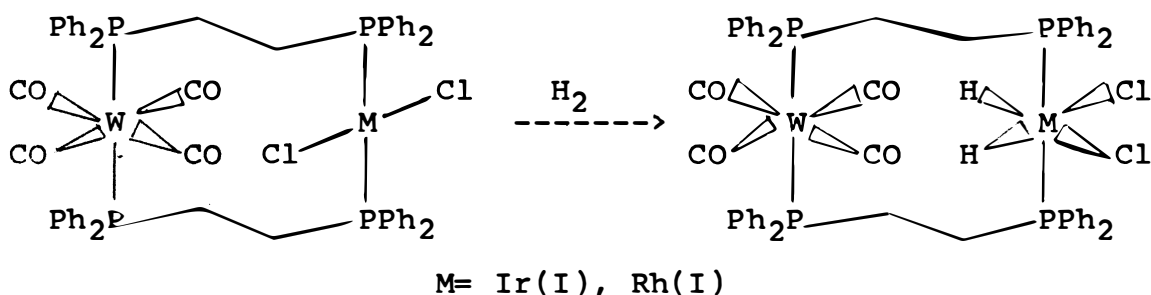
Reduction of coordinated CO could be of considerable
importance in the development of an economically acceptable
Fischer-Tropsch process. It was expected that the formation
of tetrahedral center about Hg would be reasonably
straight-forward. It did not turn out to be the case and
thus plans to examine systems of (Pd(II), Pt(II), Rh(I),
Ir(I)) were not realized.

Substantial activity currently exists in organometallic
laboratories in exploring the chemistry of bridged complexes
of $PPh_2CH_2PPh_2$ (dpm).[5] Shaw and coworkers have successfully

synthesized many heterobimetallic complexes containing two $PPh_2CH_2PPh_2$ bridges. This ligand, which has less tendency for chelation than $PPh_2CH_2CH_2PPh_2$ brings two metal atoms into sufficiently close proximity that organometallic reactions involving two metal centers are promoted. A series of small size ring heterobimetallic complexes of platinum, palladium, silver, gold, rhodium, iridium, mercury, molybdenum, and tungsten metal centers have been reported.[6,7,8,9]

M= Rh, Ir, Ag, Au, Cd
X= Cl, I
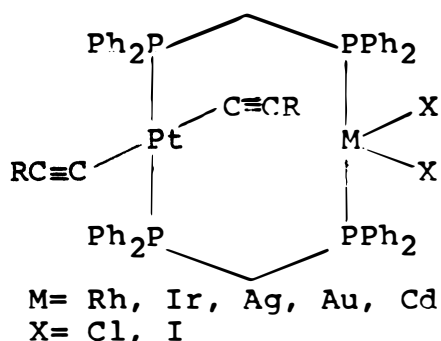
Another example of a heterobimetallic complex that was synthesized previously arises from the reaction of 1,1′-Bis(diphenylphosphino)ferrocene, $(Fe(cpPPh_2)_2)$, with mercuric(II) halides.[10] The products of this reaction were mixtures of structures (I), (II), and (III).

Ph Ph Ph Ph 2+
P   P
Fe   Hg   Fe
P   P
Ph   Ph Ph   Ph
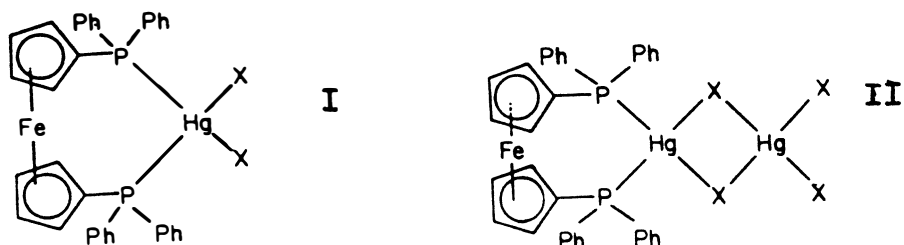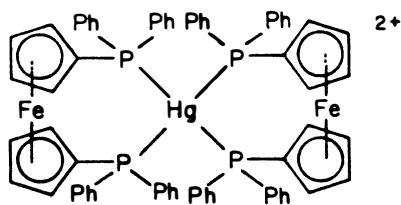
III

In this work $PPh_2CH_2CH_2PPh_2$ (dpe) was chosen to function as a bridging ligand between the two metal centers. Bridged and chelated complexes of dpe have been known nearly as long as the ligand itself.[11] Unidentate dpe complexes are much rarer and in general have been synthesized unintentionally rather than by design. Solution spectroscopic characterization of $Co(NO)_2(CO)_2(\eta^1\text{-dpe})$, appeared early on[12] and was followed by isolation of $Mn(\eta^5\text{-}C_5H_5)(CO)(NO)(\eta^1\text{-dpe})^+$,[13] $Co(\eta^1\text{-dpe})(\eta^2\text{-dpe})(CN)_2$[14] and $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-dpe})^+$.[15] These and other unidentate examples such as $M(CO)_5(\eta^1\text{-dpe})$ (M=Cr, Mo, W),[16] $[V(CO)_5(\eta^1\text{-dpe})]^-$,[17] $Ru(porphyrin)(\eta^1\text{-dpe})_2$,[18] $Fe_3Fe_2(CO)_9(\eta^1\text{-dpe})$[19] and $Fe(\eta^5\text{-}C_5H_5)(CO)H(\eta^1\text{-dpe})$[20] were synthesized by substitution reactions.

Keiter and coworkers have successfully developed a method, based upon addition of PPh_2H to coordinated $PPh_2CH=CH_2$, which have been shown to be effective for the synthesis of unidentate dpe complexes of group VI.[21]

$M(CO)_{6-n}(PPh_2CH=CH_2)_n$ base

PPh$_2$H →

2 PPh$_2$H →
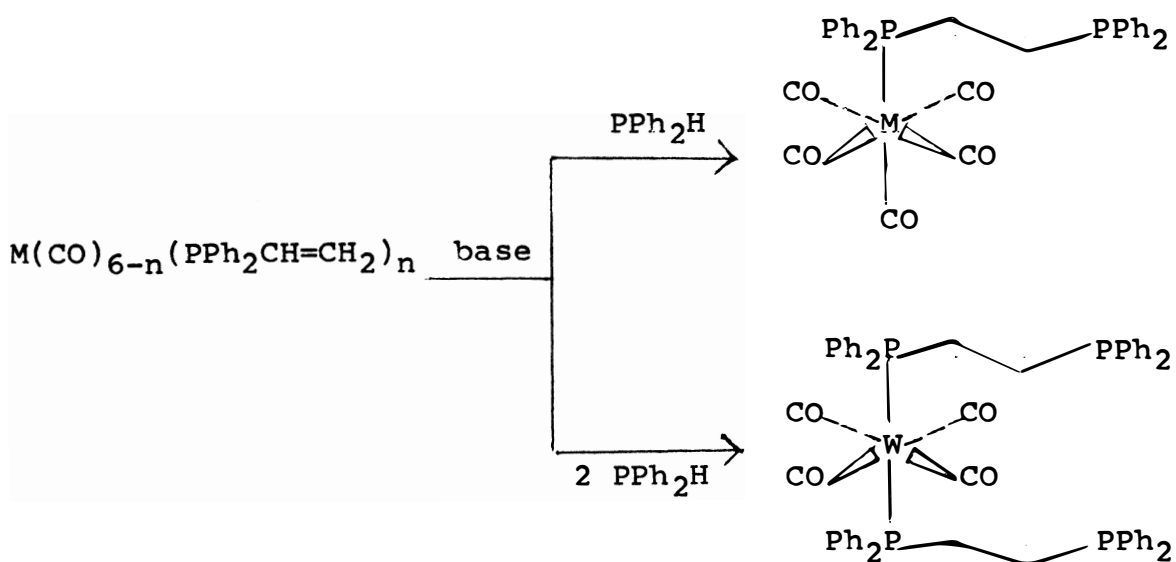
More recently the synthetic approach has been extended to complexes of iron.[22]

$Fe(CO)_{5-n}(PPh_2CH=CH_2)_n$ base

PPh$_2$H →

2 PPh$_2$H →
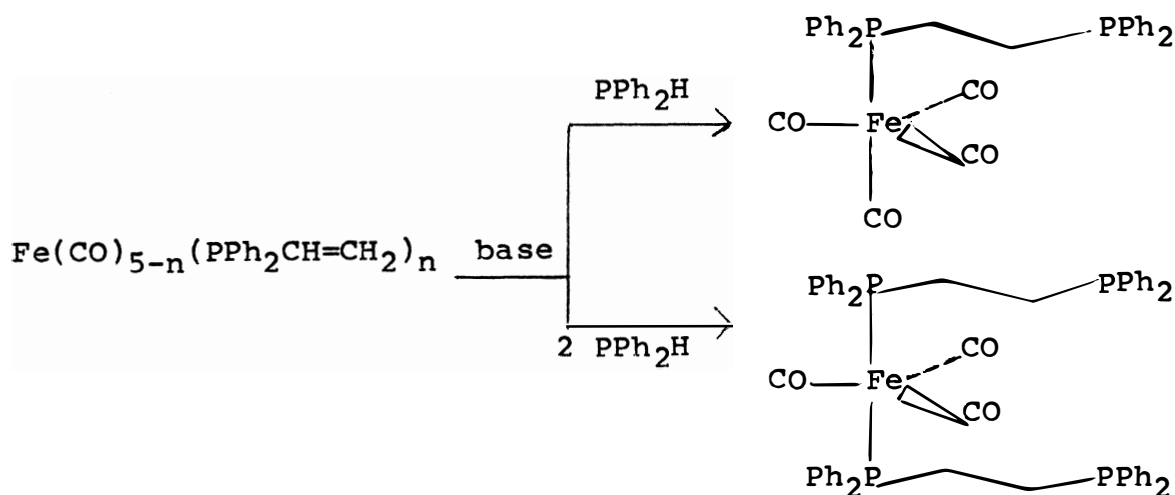
These unidentate dpe complexes are, in general, stable with respect to chelation. For example, $(CO)_5W(\eta^1\text{-dpe})$ melts at $122^{\circ}C$ without decomposition and $(CO)_4Fe(\eta^1\text{-dpe})$, after

melting at 131°C, does not visibly lose CO until the temperature exceeds 180°C. Similarly trans-$(CO)_4W(\eta^1$-dpe$)_2$ (150-151°C) and trans-$(CO)_3Fe(\eta^1$-dpe$)_2$ (162-164°C) resist chelation when conditions are not severe.

In this thesis, reactions of trans-$(CO)_4W(\eta^1$-dpe$)_2$ with $HgCl_2$ and HgI_2 were examined. Several reactions are possible when trans-$(CO)_4W(\eta^1$-dpe$)_2$ is allowed to react with a tetrahedral mercury complexes by a substitution reaction.

(1) cis
(2) trans
(3) polymerization
(4) dimer formation
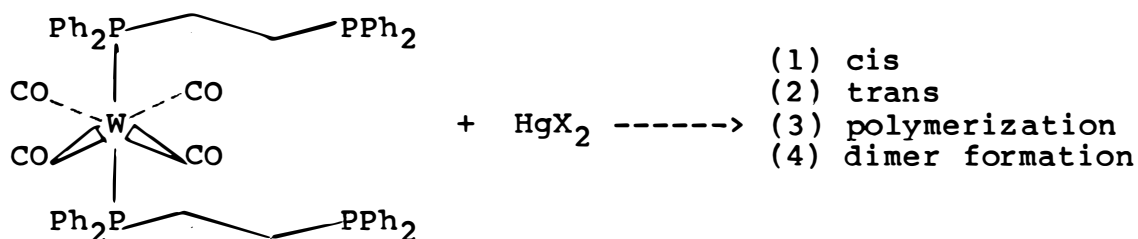
If chelation occurs both cis and trans isomers as shown by structures (1) and (2) are possible products.

(1)   (2)
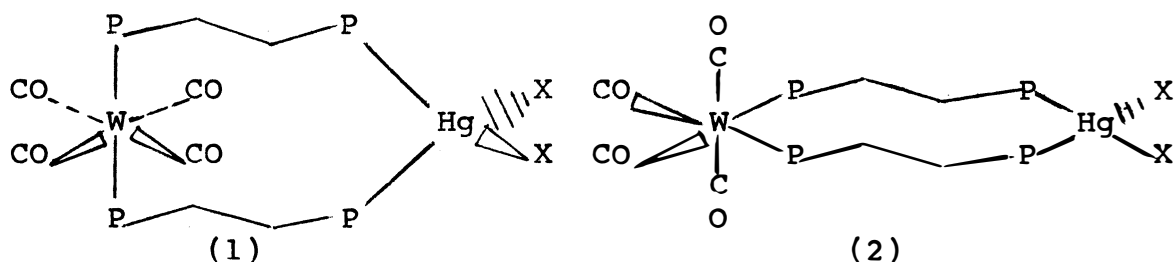
The reason that cis and trans isomers may form is because it is likely that intramolecular isomerization will occur. In $W(CO)_4(PR_3)_2$ complexes it has been shown that the energy

barrier for an intramolecular process is small.[23,24] The ratio of isomers formed will depend on both the steric requirements of the phosphine ligand and upon electronic effects. Electronic effects favor the cis structure while bulky ligands favor the trans isomers.

It is possible that polymerization may be more favorable than the formation of either of the above 10-membered rings. The conclusions of some published literature have shown that the stability of chelated complexes depend on ring size.[25] The entropy effects and favorable conformation appear to make large rings more stable than intermediate size rings. The large-ring complex, $\underline{trans}$-$(PdCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2])_2$, which contains a 26-atom ring[26] has been reported to be very stable complex. Thus, we can postulate that a 20-atom ring complex (and its many isomers) as shown below as a possible product from our reactions.
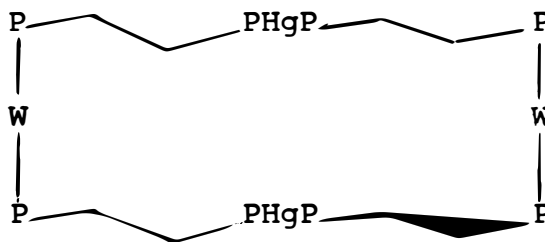
Polymerization can also occur if chelation of the phosphine ligand does not occur.

$$n \quad (CO)_4W \quad \cdots \cdots \cdots \rightarrow$$

with $HgCl_2$ schematic structure.

$$(P\diagdown\diagup P\text{-}W\text{-}P\diagdown\diagup\diagdown P\text{-}Hg\text{-})_n P\diagdown\diagup P\text{-}W\text{-}P\diagdown\diagup P)_n$$
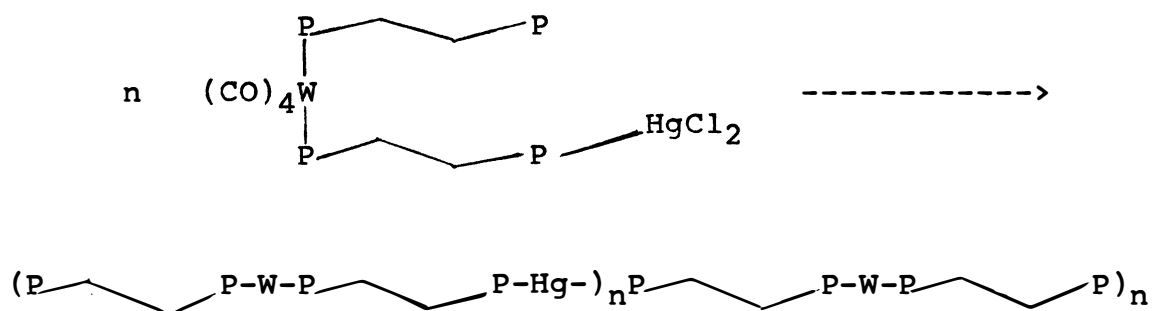
Evans and coworkers have extensively studied mercuric(II) halide phosphine complexes of HgX_2P_2 and $Hg_2X_4P_2$ (where X=halogen, P=phosphine) stoichiometry.[27] The structures of 1:2 complexes are monomeric tetrahedral,[28,29] while the nature of the 1:1 adducts in the solid state depends upon the identity of the phosphine, but the common structure is the centrometric halogen bridged dimers[30,31] as shown below.
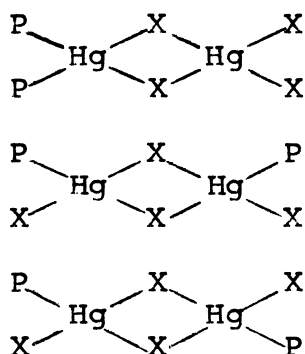
Thus, mercuric(II) halides can form dimers or polymers readily depending upon the reactant stoichiometry. From the observation that the ligand $Fe(cpPPh_2)_2$ formed three different structural products on reaction with mercuric(II) halides, we can deduce that, besides giving products as of

structures (1) and (2) the following products are also possible. The formation of polymers

$$(3)$$

$$(4)$$
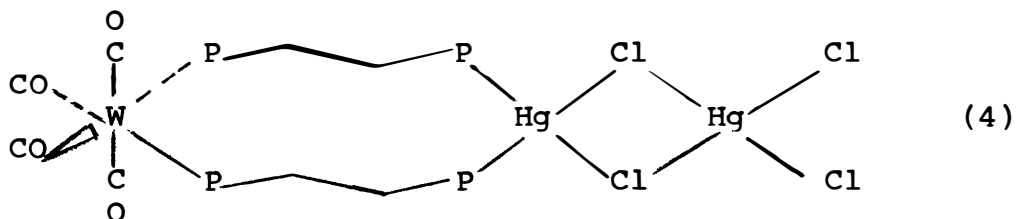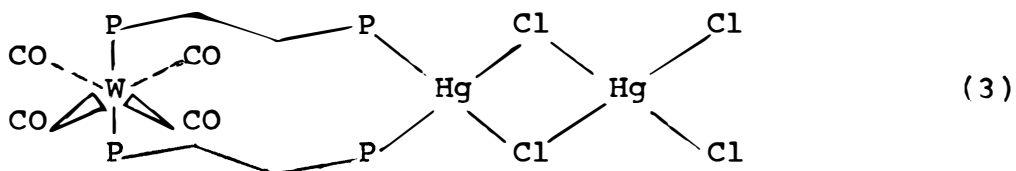
could be avoided or greatly minimized if the concentrations of reactants are small.

In addition to the above approach, i.e by direct reaction of the phosphine with mercuric(II) halides, another approach to the formation of bimetallic complexes was explored. Based on the great success of the base-catalysed addition of P-H to vinyl groups[21] the following reactions were attempted.

$$\text{trans-}(CO)_4M(PPh_2CH=CH_2)_2 + HgX_2(PPh_2H)_2 \xrightarrow{\quad KOBu^t \quad}$$

$$(CO)_4M(PPh_2CH_2CH_2PPh_2)_2HgX_2$$

$$\text{cis-}(CO)_4M(PPh_2H)_2 + HgX_2(PPh_2CH=CH_2)_2 \xrightarrow{\quad KOBu^t \quad}$$

$$(CO)_4M(PPh_2CH_2CH_2PPh_2)_2HgX_2$$

$$X=Cl \text{ or } I$$
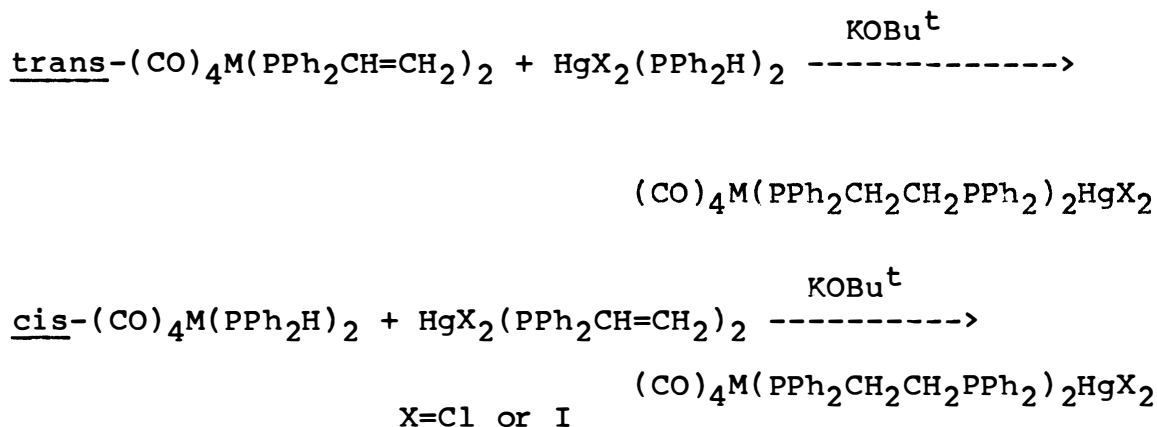
It is possible that tendencies for polymerization which is exist in the direct reaction of <u>trans</u>-$(CO)_4W(\eta^1$-dpe$)_2$ with HgX_2 could be overcome with base-catalysed addition reactions.

CHAPTER II

RESULTS AND DISCUSSION

The syntheses of heterobimetallic complexes of structural formulas $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$ (X=Cl or I) were carried out with the following reaction sequence.

(1) $W(CO)_6 + 2 PPh_2CH=CH_2 \longrightarrow \underline{trans}-W(CO)_4(PPH_2CH=CH_2)_2$

$\qquad\qquad\qquad\qquad + 2 CO$

$\qquad\qquad\qquad\qquad\qquad\qquad KOBu^t$

(2) $\underline{trans}-W(CO)_4(PPh_2CH=CH_2)_2 + 2 PPh_2H \xrightarrow{\qquad}$

$\qquad\qquad\qquad \underline{trans}-W(CO)_4(\eta^1-PPh_2CH_2CH_2PPh_2)_2$

(3) $\underline{trans}-W(CO)_4(\eta^1-PPh_2CH_2CH_2PPh_2)_2 + HgX_2 \xrightarrow{\qquad}$

$\qquad\qquad\qquad [(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$
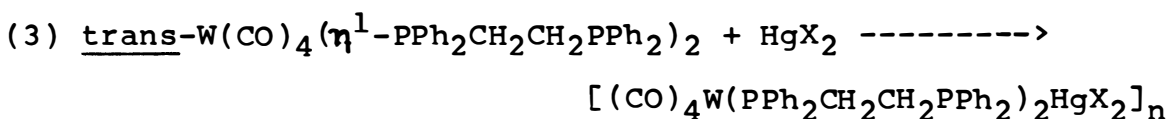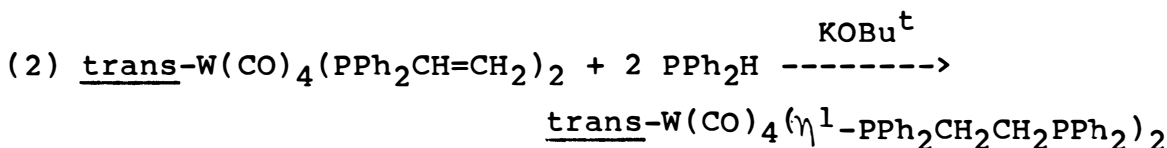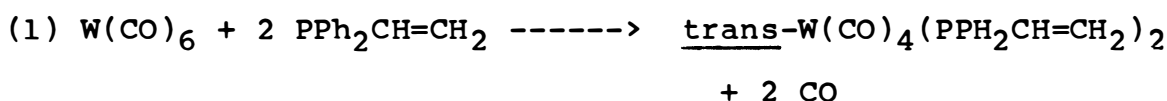
The basic starting material, $\underline{trans}-(CO)_4W(PPh_2CH=CH_2)_2$ was first synthesized following the published method.[21] The crude product from this reaction

$W(CO)_6 + 2 PPh_2CH=CH_2 \xrightarrow{\quad diglyme \quad} (CO)_4W(PPh_2CH=CH_2)_2 + 2 CO$

$\qquad\qquad diglyme=CH_3OCH_2CH_2OCH_2CH_2OCH_3$
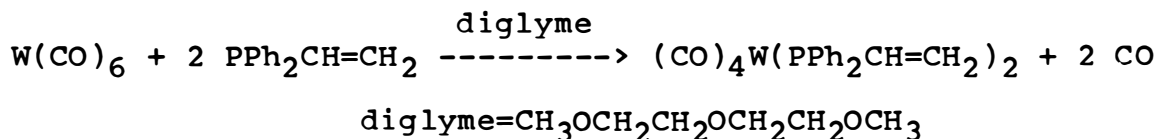
contained $W(CO)_5(PPh_2CH=CH_2)$, $\underline{cis}-W(CO)_4(PPh_2CH=CH_2)_2$, and $\underline{trans}-W(CO)_4(PPh_2CH=CH_2)_2$ complexes.

$$PPh_2CH=CH_2$$

$$CO \diagdown \quad \diagup CO$$
$$W$$
$$CO \diagup \quad \diagdown CO$$

$$CO$$

(monosubstituted)

$$CO$$

$$CO \diagdown \quad PPh_2CH=CH_2$$
$$W$$
$$CO \diagup \quad \diagdown PPh_2CH=CH_2$$

$$CO$$

(cis)

$$PPh_2CH=CH_2$$

$$CO \diagdown \quad \diagup CO$$
$$W$$
$$CO \diagup \quad \diagdown CO$$

$$PPh_2CH=CH_2$$
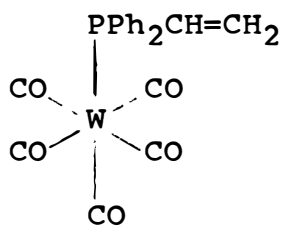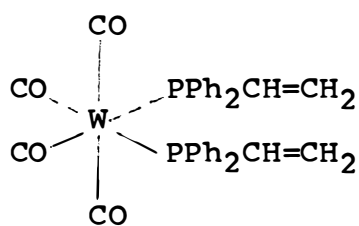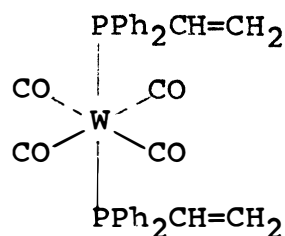
(trans)

The monosubstituted complex was removed from the mixture by extraction with petroleum ether. The trans complex was separated from the cis complex by recrystallizing it from dichloromethane-methanol solution. After several recrystallizations of the product, a rather low yield (26%) of the trans complex was obtained. The reaction was repeated several times to increase the yield of the trans complex but these attempts were not successful. In addition to the low yield several other disadvantages were noted. First, the reaction was done at a high temperature and under these reaction conditions, the tungsten hexacarbonyl tended to sublime from the reaction mixture. This sublimed tungsten hexacarbonyl can be found deposited in the condenser as soon as the reaction starts refluxing. Therefore, it is difficult to maintain the desired 2:1 molar ratio of phosphine to tungsten hexacarbonyl. Secondly, this method required dry diglyme solvent. Considerable work was required for storing and preparing the dry diglyme.

In order to obtain a greater yield of the trans complex, we investigated a reaction reported by Chatt.[32] In his work it was discovered that disubstituted complexes such as $\underline{trans}$-$W(CO)_4(PPh_3)_2$ could be prepared from $W(CO)_6$ under mild conditions in ethanolic $NaBH_4$. The analogous reaction involving $PPh_2CH=CH_2$ was carried out.

$$W(CO)_6 + 2\ PPh_2CH=CH_2 \xrightarrow[NaBH_4]{ethanol} (CO)_4W(PPh_2CH=CH_2)_2 + 2\ CO$$
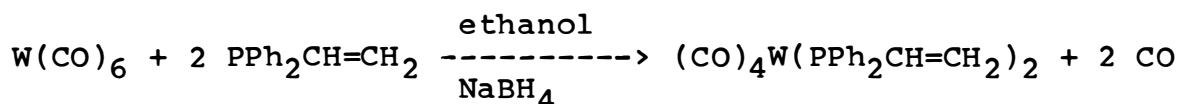
It was found that ethanol was not an appropriate solvent to obtain mainly trans complex. In addition to giving $(CO)_5W(PPh_2CH=CH_2)$, $\underline{cis}$-$W(CO)_4(PPh_2CH=CH_2)_2$, $\underline{trans}$-$W(CO)_4(PPh_2CH=CH_2)_2$, some trisubstituted $\underline{fac}$-$(CO)_3W(PPh_2CH=CH_2)_3$ was found.

When n-butanol was substituted for ethanol in the above reaction a mixture of monosubstituted, trans and cis isomers of $(CO)_4W(PPh_2CH=CH_2)_2$ was obtained with the trans isomer being present in greatest abundance. The trans isomer slowly precipitated from the solution over several days. Recrystallization from CH_2Cl_2/CH_3OH solution gave a greatly improved yield of 50.7%.

The synthesis of $\underline{trans}$-$(CO)_4Mo(PPh_2CH=CH_2)_2$ was also carried out by the $NaBH_4$ method. A much improved yield (48.4%) over that of the diglyme method reported by Sun[33] was obtained.

With this interesting result, the $NaBH_4$ method became

the preferred approach for obtaining

$trans$-$(CO)_4M(PPh_2CH=CH_2)_2$ (M=W or Mo). In addition to the

advantage of greater yield, the method eliminated the

sublimation problem, and the preparation of the solvent and

its storage. However, this method did not eliminate

the formation of both cis and trans isomers.

The formation of both isomers can be explained by the

work of Darensbourg.[23] In his work, it was shown that there

is a thermodynamic preference for either the cis or trans

isomer of $(CO)_4ML_2$ complex depending on the electronic and

steric properties of the ligand L. Sterically demanding or

bulky ligands will lead to the trans isomer as being the

thermodynamically stable species, while a less bulky (small

cone angle) ligand L will lead to the cis isomer as being

the most stable species. In our case, $PPh_2CH=CH_2$, is

somewhat intermediate in bulkiness; hence, a mixture of cis

and trans isomers are formed, with the trans isomer being

more abundant.

The reason for trans complex enhancement which occur

when the crude reaction mixture is allowed to stand for

several days can be explained by the work of Howell.[23]

According to Howell, $trans$-$(CO)_4W(PBu_3)_2$ isomerizes to the

cis isomer intramolecularly at 46°C. This is because the

energy barrier for intramolecular isomerization in

$(CO)_4M(PR_3)_2$ complexes has shown to be small. In this work,

the trans isomer, which is less soluble than the cis isomer

in n-butanol, precipitates from the solution. Hence, assuming there is equilibrium in the solution as shown by the following equation, more cis complex is converted to trans as the less soluble trans precipitates from the solution.

$$\underline{cis}-(CO)_4W(PPh_2CH=CH_2)_2 \rightleftharpoons \underline{trans}-(CO)_4W(PPh_2CH=CH_2)_2$$
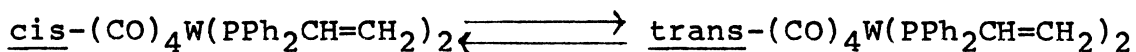
The identification of the cis and trans isomers of $(CO)_4W(PPh_2CH=CH_2)_2$ and $(CO)_4Mo(PPh_2CH=CH_2)_2$ was established with infrared spectra of the carbonyl stretching region. Proton nmr spectra of the complexes were also obtained to compare them with the reported spectra.[33] The infrared spectra of $\underline{trans}-W(CO)_4(PPh_2CH=CH_2)_2$ and $\underline{trans}-Mo(CO)_4(PPh_2CH=CH_2)_2$, of D_{4h} symmetry, show one strong band (E_u) at 1890 cm^{-1} (Figure 1-3). However, the infrared spectra of these complexes also shows two weak absorption bands. These absorptions are due to the perturbation of D_{4h} symmetry by the $PPh_2(CH=CH_2)$ ligands, and thus the A_{1g} and B_{1g} forbidden modes gain slight allowedness and become two weak bands.[34] The infrared spectrum of pure cis-disubstituted tetracarbonyl metal complex was never obtained. Figure 4 shows the infrared spectrum of the mixture of cis and trans isomers of $W(CO)_4(PPh_2CH=CH_2)_2$. The cis isomer of C_{2v} symmetry shows four infrared active bands $2A_1$, B_1, and B_2[34] in the carbonyl stretching region. However, significant overlap of bands occur in the cis/trans
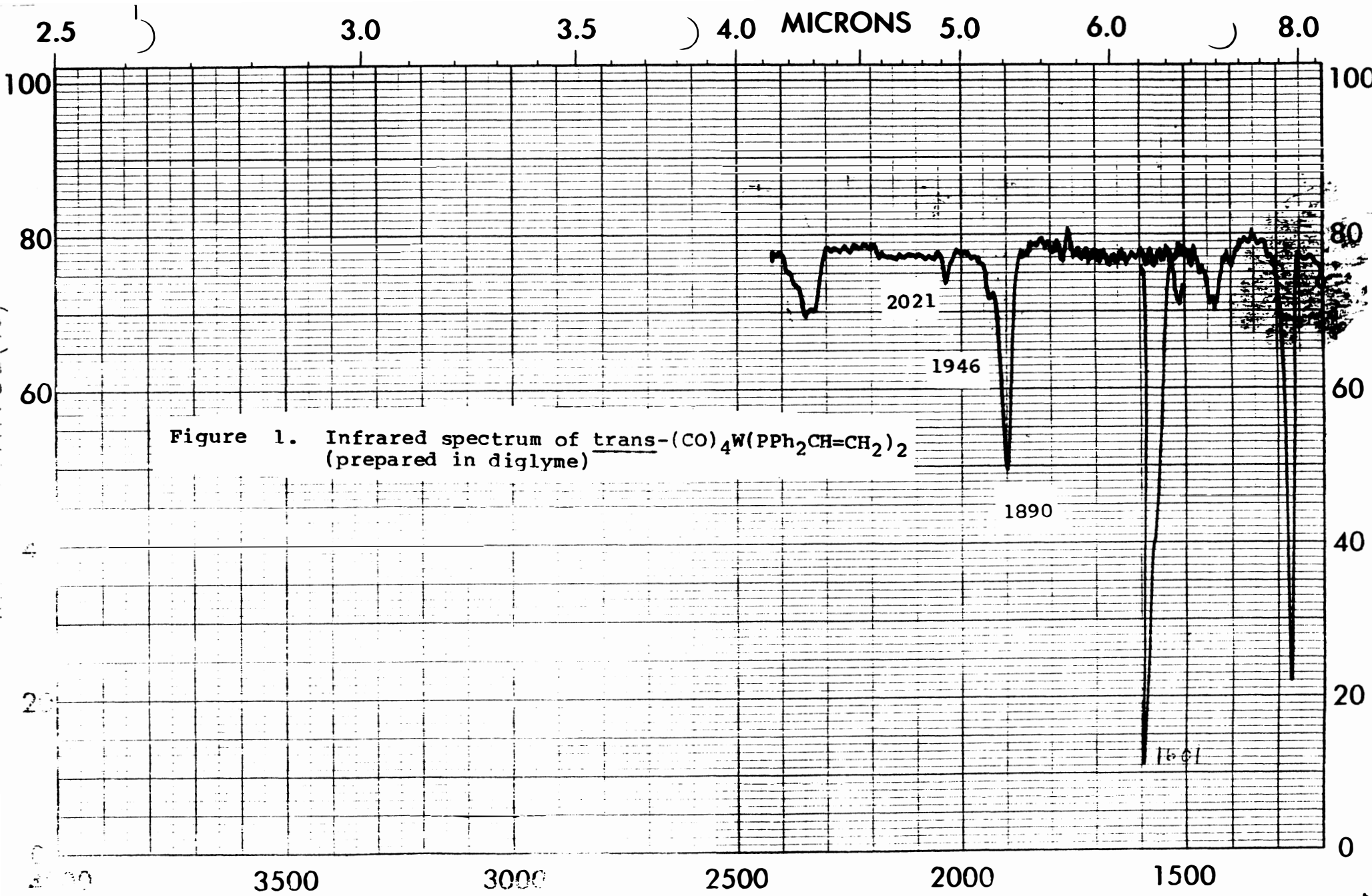
Figure 1. Infrared spectrum of trans-$(CO)_4W(PPh_2CH=CH_2)_2$
(prepared in diglyme)

Peak labels on spectrum: 2021, 1946, 1890, 1661

Figure 2. Infrared spectrum of trans-$(CO)_4W(pPh_2CH=CH_2)_2$ (prepared in n-butanol)
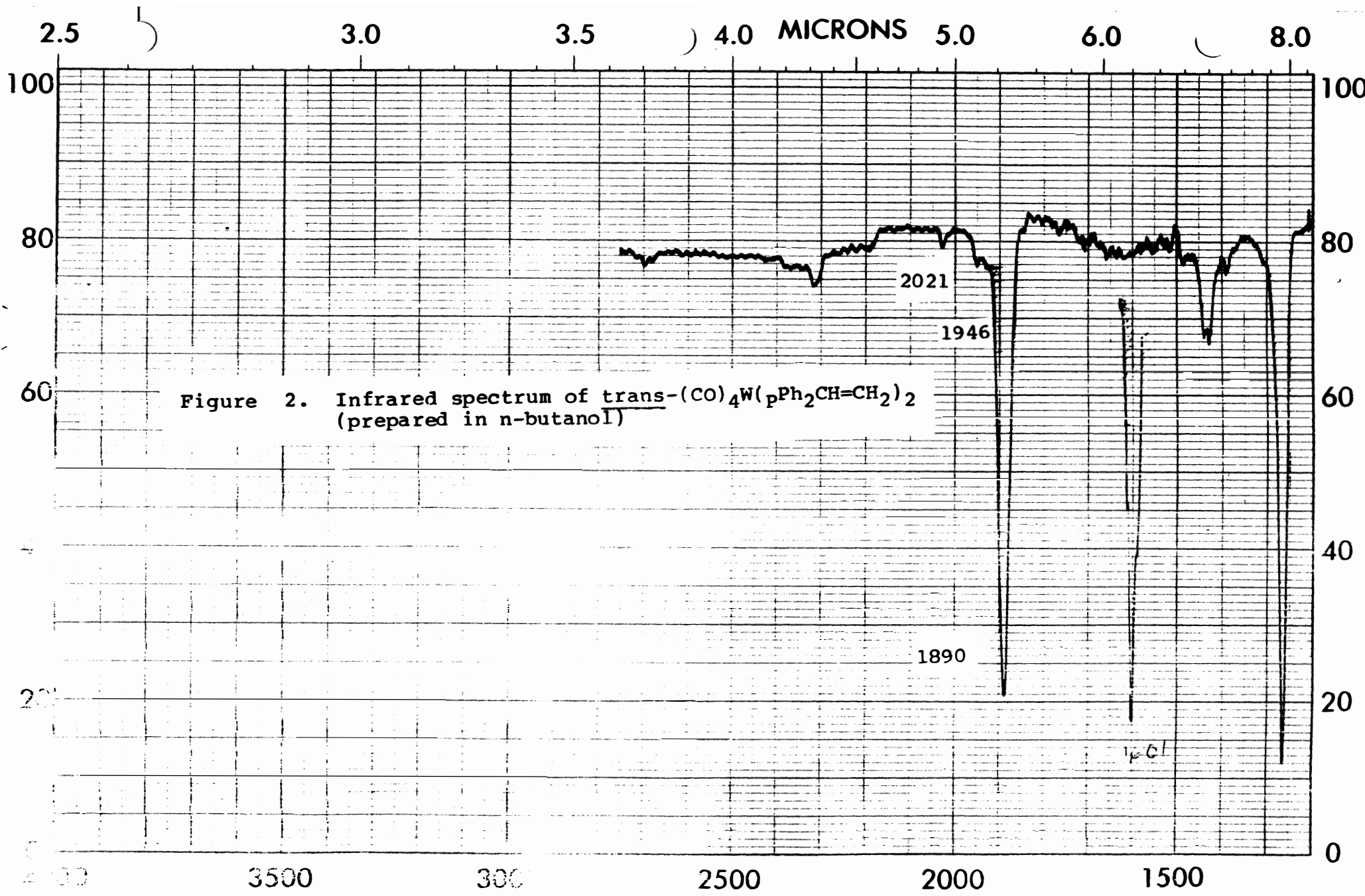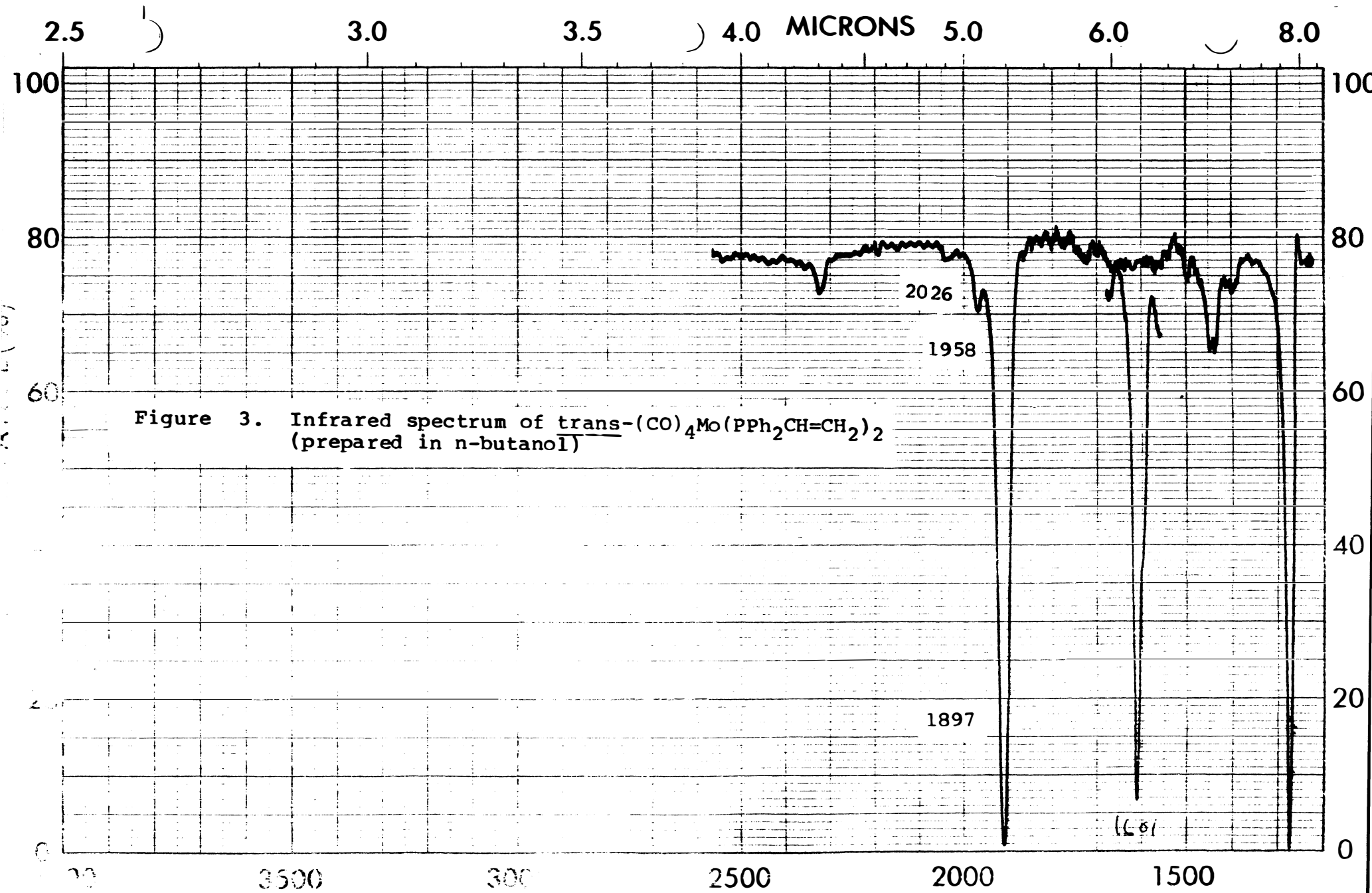
Figure 3. Infrared spectrum of trans-(CO)$_4$Mo(PPh$_2$CH=CH$_2$)$_2$ (prepared in n-butanol)

Labels on spectrum: 2026, 1958, 1897
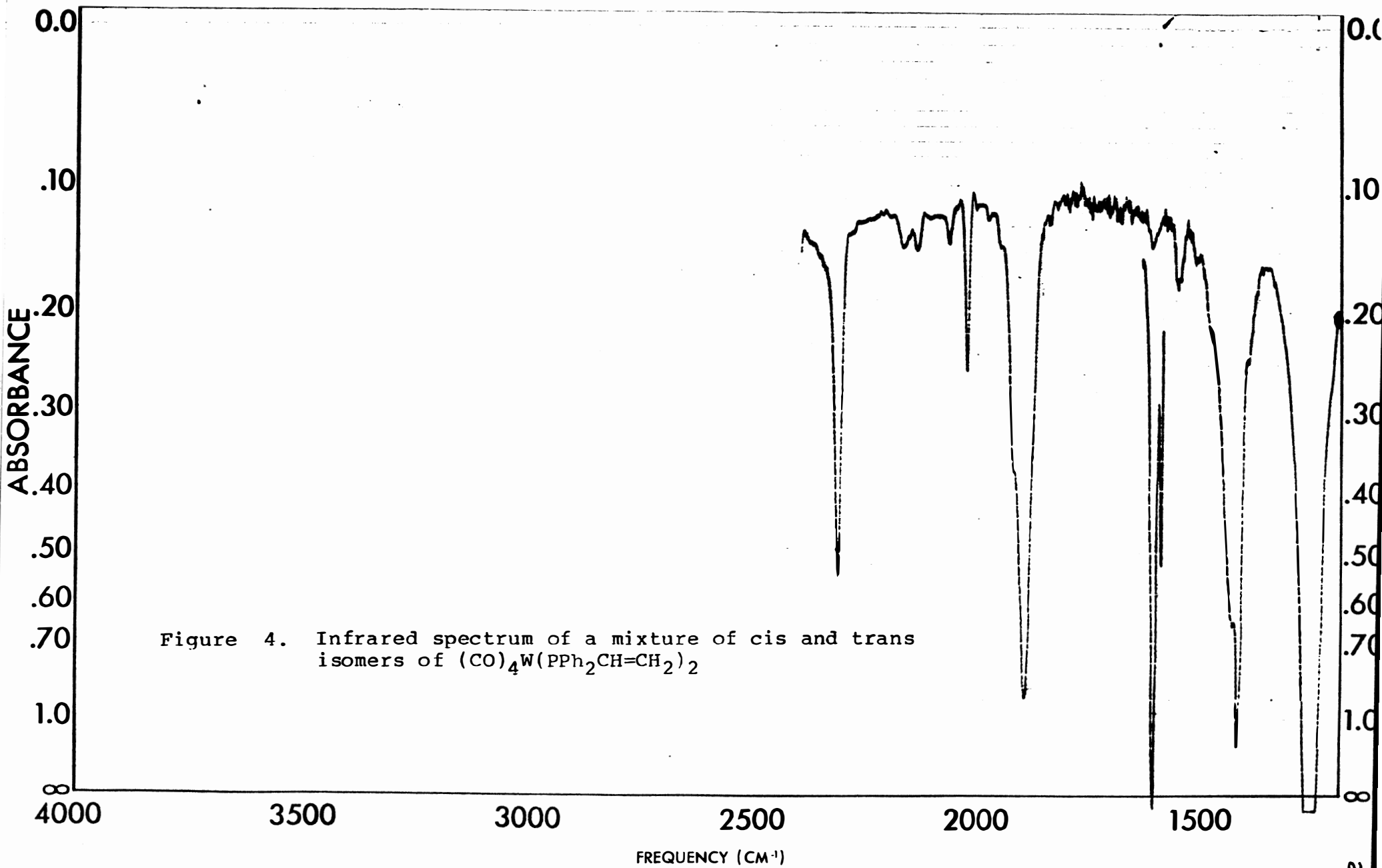
Figure 4. Infrared spectrum of a mixture of cis and trans isomers of $(CO)_4W(PPh_2CH=CH_2)_2$

mixture. The carbonyl stretching frequencies of the complexes are shown in Table I.

The proton nmr spectra of these trans complexes are found to be similar to the one reported.[33] The nmr spectra in Figure 5-7 are of second order and therefore very complicated. The absorptions due to phenyl protons were found around 7.4 ppm, and the absorptions due to vinyl protons were between 5 and 7 ppm.

The $\underline{trans}$-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ complex was synthesized following the literature method.[21]

$$\underline{trans}\text{-}(CO)_4W(PPh_2CH=CH_2)_2 + 2 \ PPh_2H \xrightarrow{\quad KOBu^t \quad}$$
$$\underline{trans}\text{-}(CO)_4W(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$$
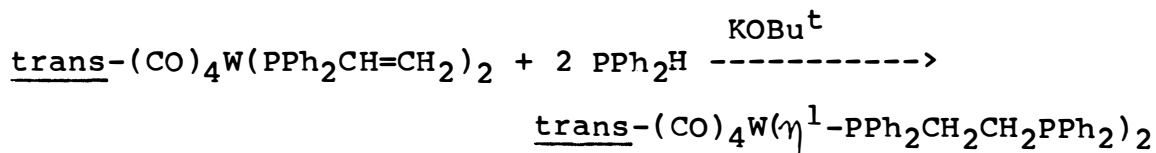
The crude product was recrystallized from CH_2Cl_2/CH_3OH several several times to obtained a pure trans complex. The identification of the trans complex was established with both infrared spectra in the carbonyl stretching region, proton nmr, and proton-decoupled phosphorus-31 nmr spectra. The results are identical to those reported earlier.[33]

Again, this trans complex with D_{4h} symmetry shows a strong E_u mode absorption band at 1890 cm^{-1} and two weak forbidden bands at the carbonyl stretching region. The infrared spectrum and the carbonyl stretching frequencies of this trans complex are shown in Figure 8 and Table I respectively.

The proton nmr spectrum as shown in Figure 9 is second

500   400   300   200   100   0 Hz

8.0   7.0   6.0   5.0   PPM (δ)   4.0   3.0   2.0   1.0   0
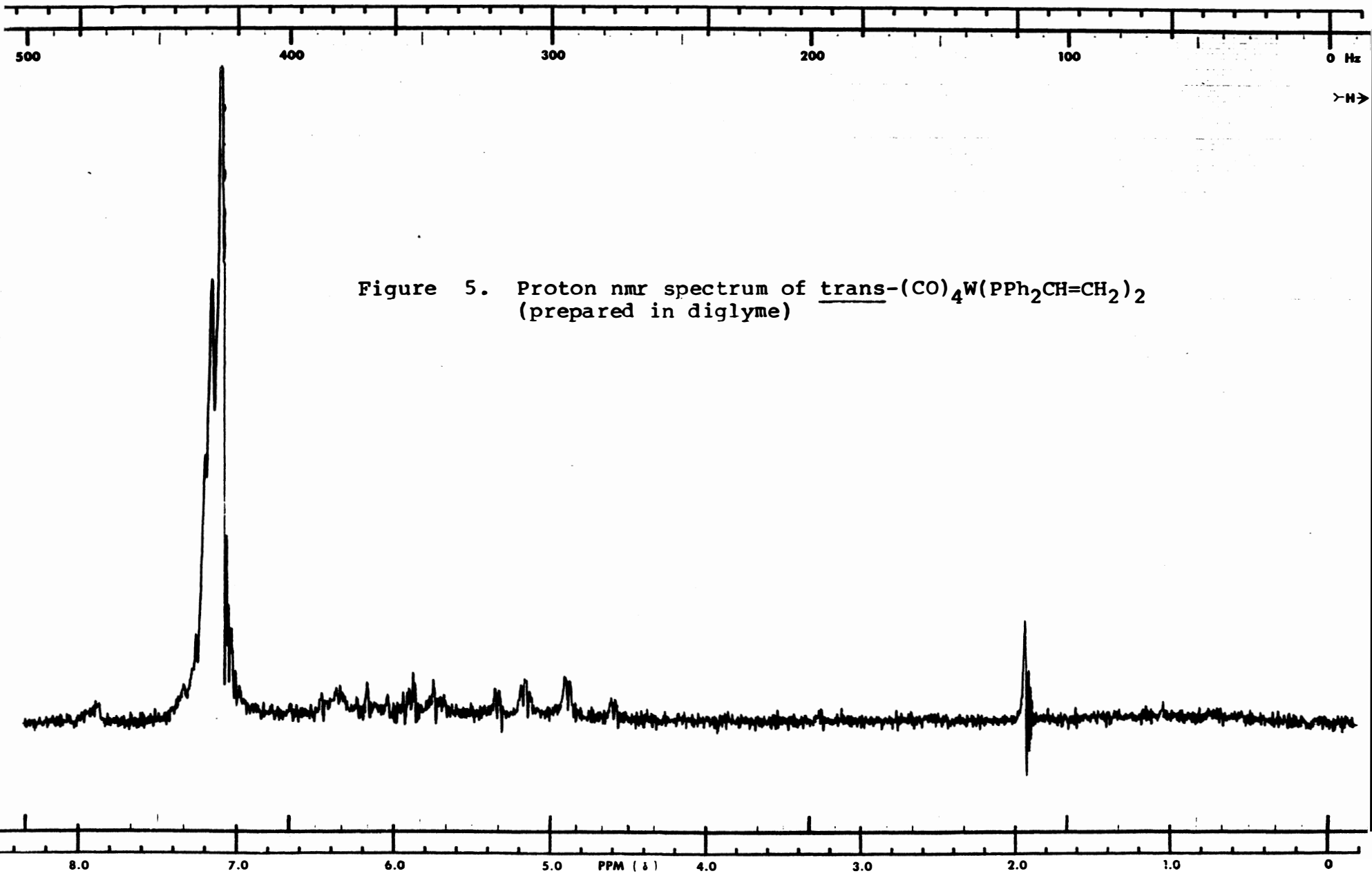
Figure 5.   Proton nmr spectrum of trans-$(CO)_4W(PPh_2CH=CH_2)_2$
(prepared in diglyme)
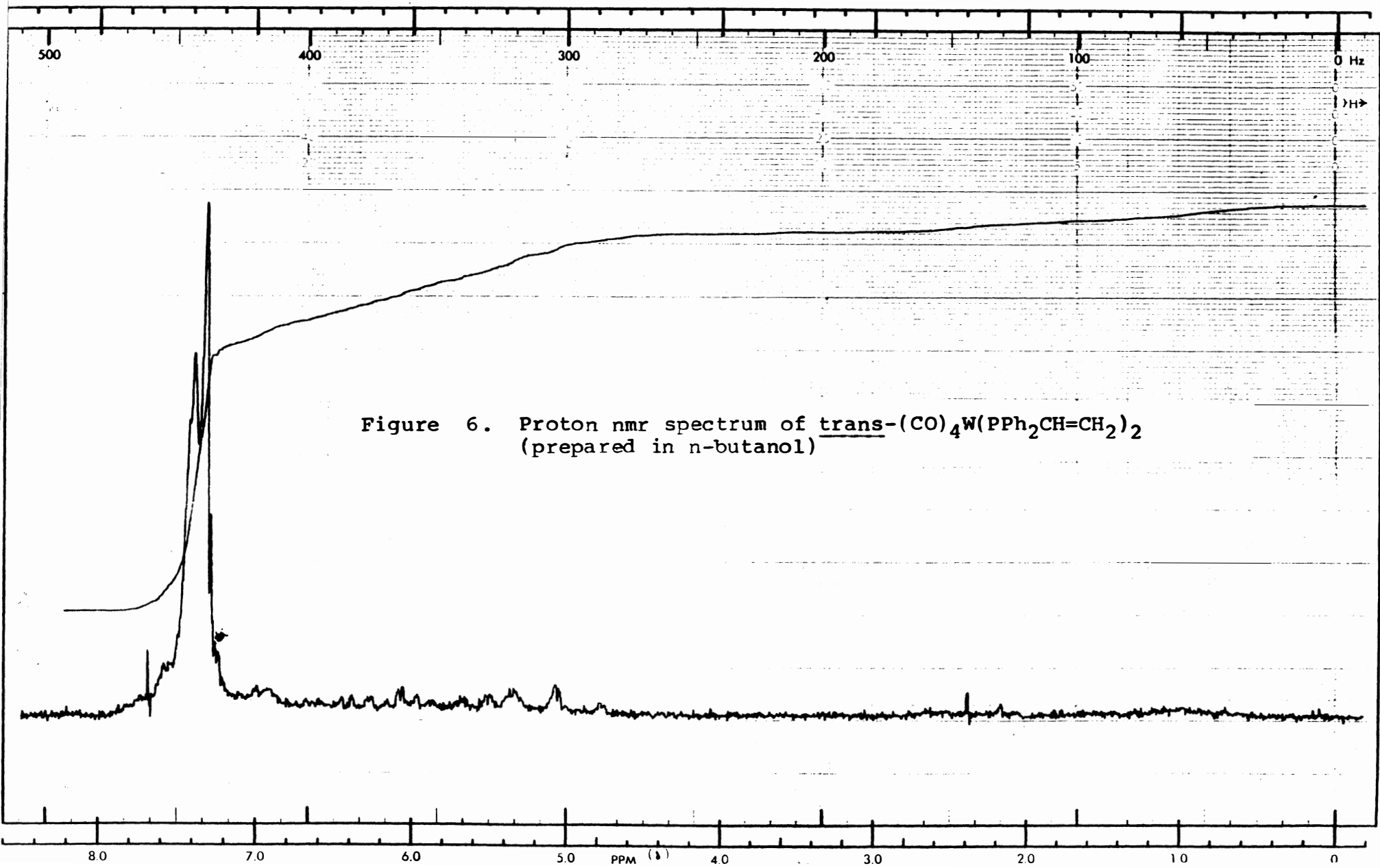
Figure 6. Proton nmr spectrum of trans-$(CO)_4W(PPh_2CH=CH_2)_2$ (prepared in n-butanol)
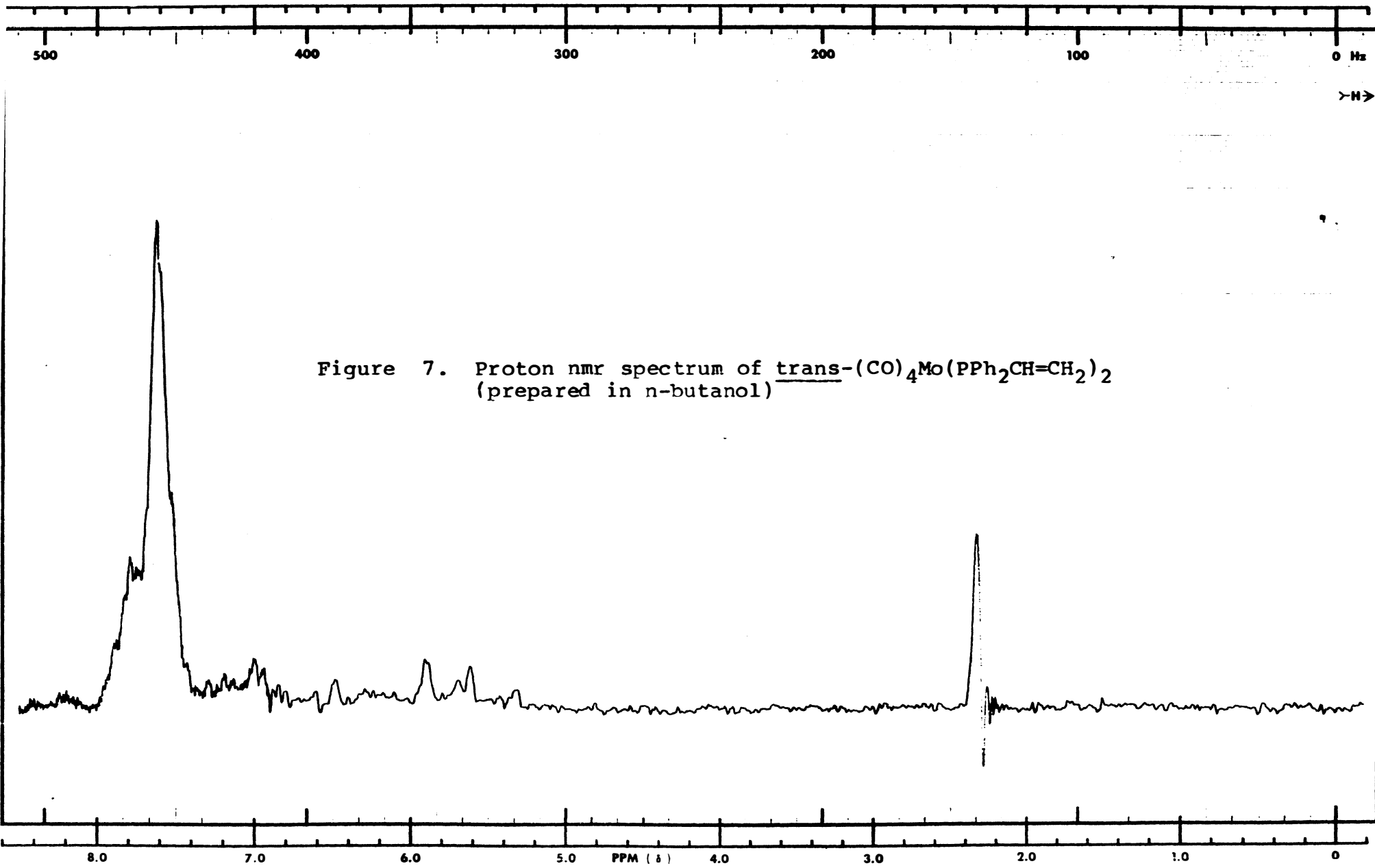
Figure 7. Proton nmr spectrum of trans-$(CO)_4Mo(PPh_2CH{=}CH_2)_2$
(prepared in n-butanol)

Figure 8. Infrared spectrum of trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$

Values marked on spectrum: 2020, 1888
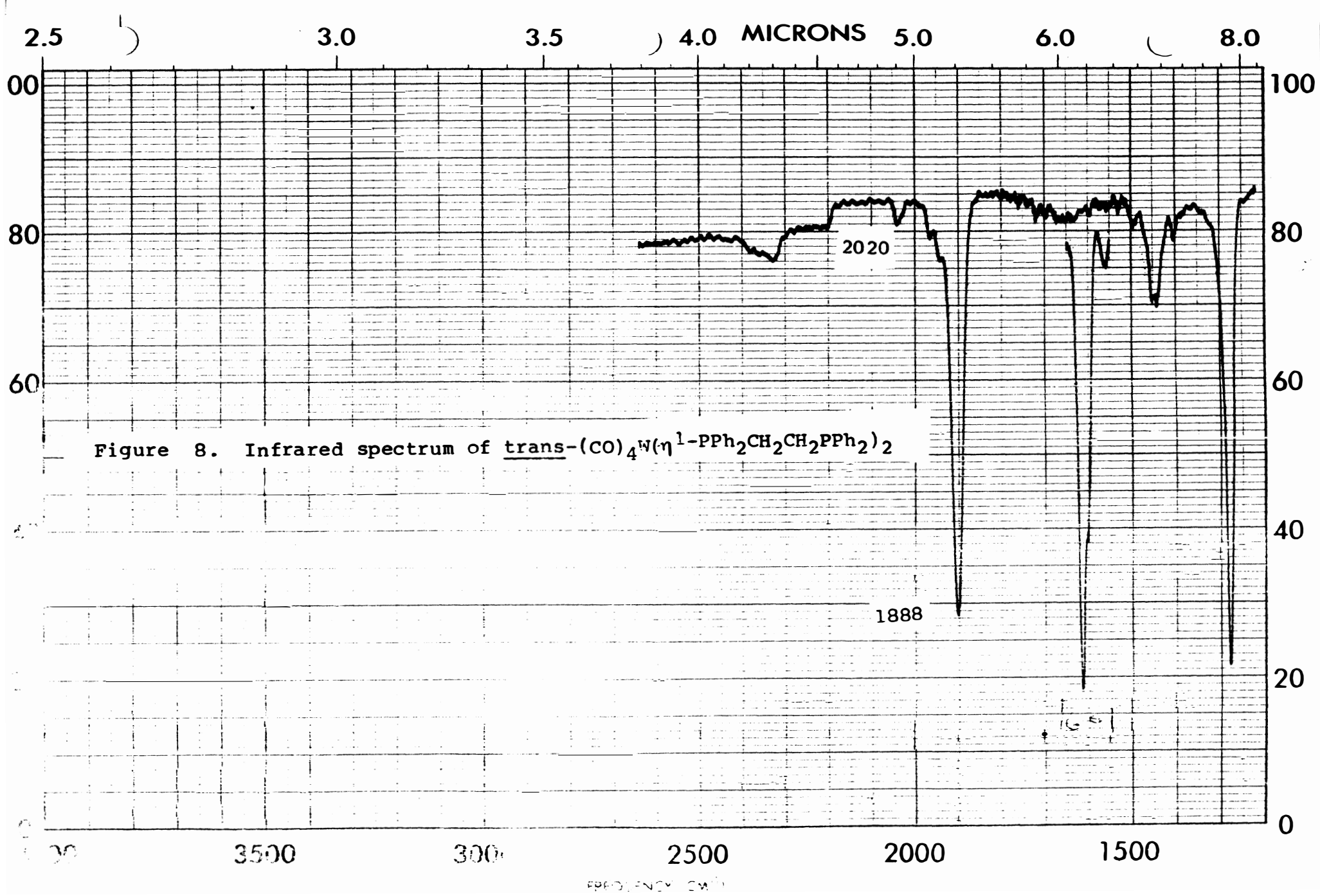
500   400   300   200   100   0 Hz

➤-H➤

Figure 9. Proton nmr spectrum of trans-$(CO)_4W(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$

8.0   7.0   6.0   5.0   PPM (δ)   4.0   3.0   2.0   1.0   0
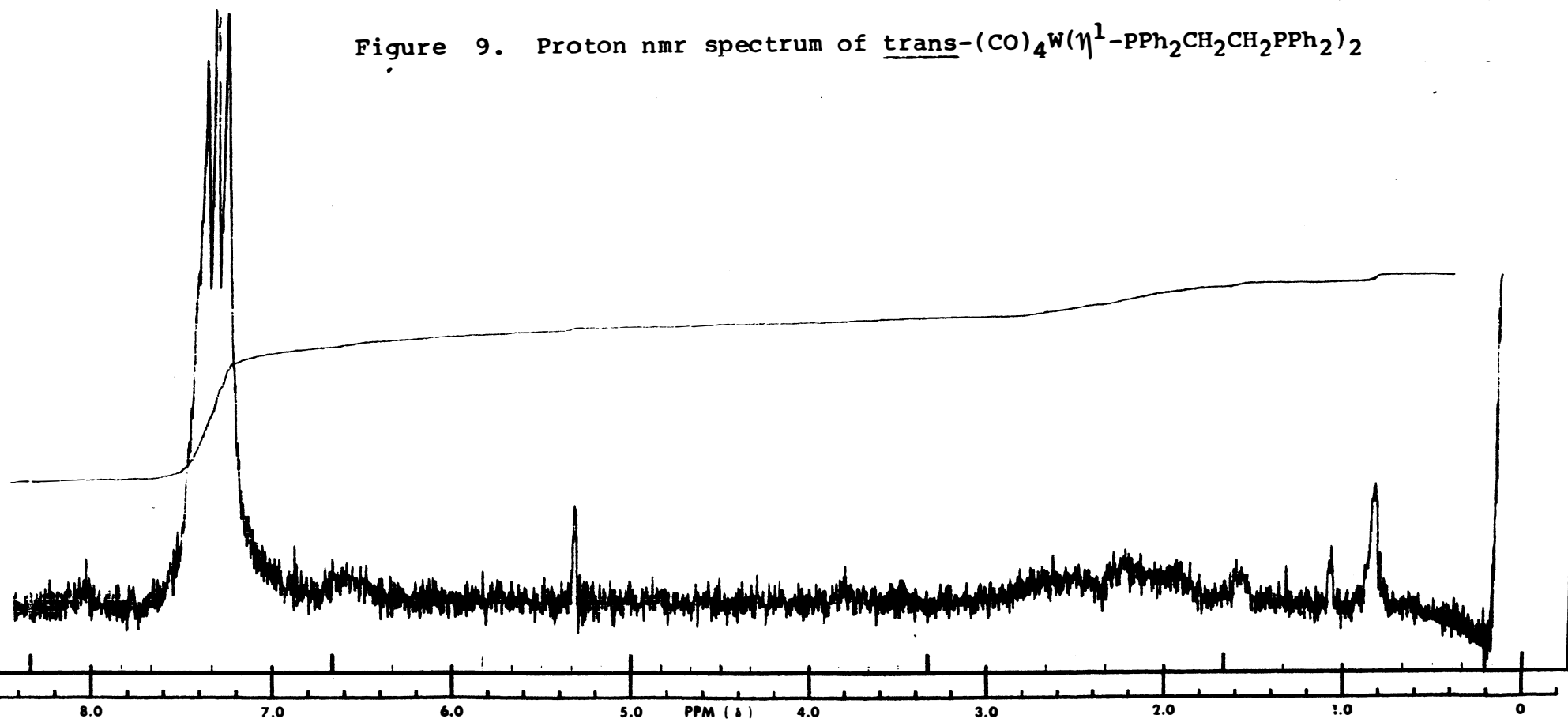
order and therefore complicated. The methylene protons absorptions were found between 1.8 and 3.0 ppm, and the absorptions due to phenyl protons were found around 7.4 ppm.

Figure 10 shows the proton-decoupled phosphorus-31 nmr spectrum of the trans complex, while Figure 11 shows the expanded spectrum of the absorption at 19.6 ppm. The spectra clearly show the coordination of the two unidentate dpe molecules of an AA'XX' spin system. In this spin system all four nuclei are magnetically nonequivalent and form two pairs of symmetrically equivalent nuclei separated from each other by a large chemical shift compared with the coupling constants involved. Thus, as reported earlier by Sun[33] the two principal sets of signals at 19.6 ppm and -11.1 ppm are assigned to this bis(ditertiary)phosphine complex of tungsten. Analysis of nmr spectra of compounds with AA'XX' spin system have been discussed in detailed by Harris.[35] The coupling constants and chemical shifts of this bis(ditertiary)phosphine complex of tungsten are listed in Table II.

A number of attempts have been made to synthesize tungsten-mercury bimetallic complexes. These attempts utilize two different mercuric halides ($HgCl_2$ and HgI_2) and two different solvents (ethanol and dichloromethane) as described earlier by equation (3). Reactions were carried out under very dilute conditions in an attempt to prevent polymerization.

Figure 10. ^{31}P nmr spectrum of <u>trans</u>-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$

19.6 ppm

-11.1 ppm
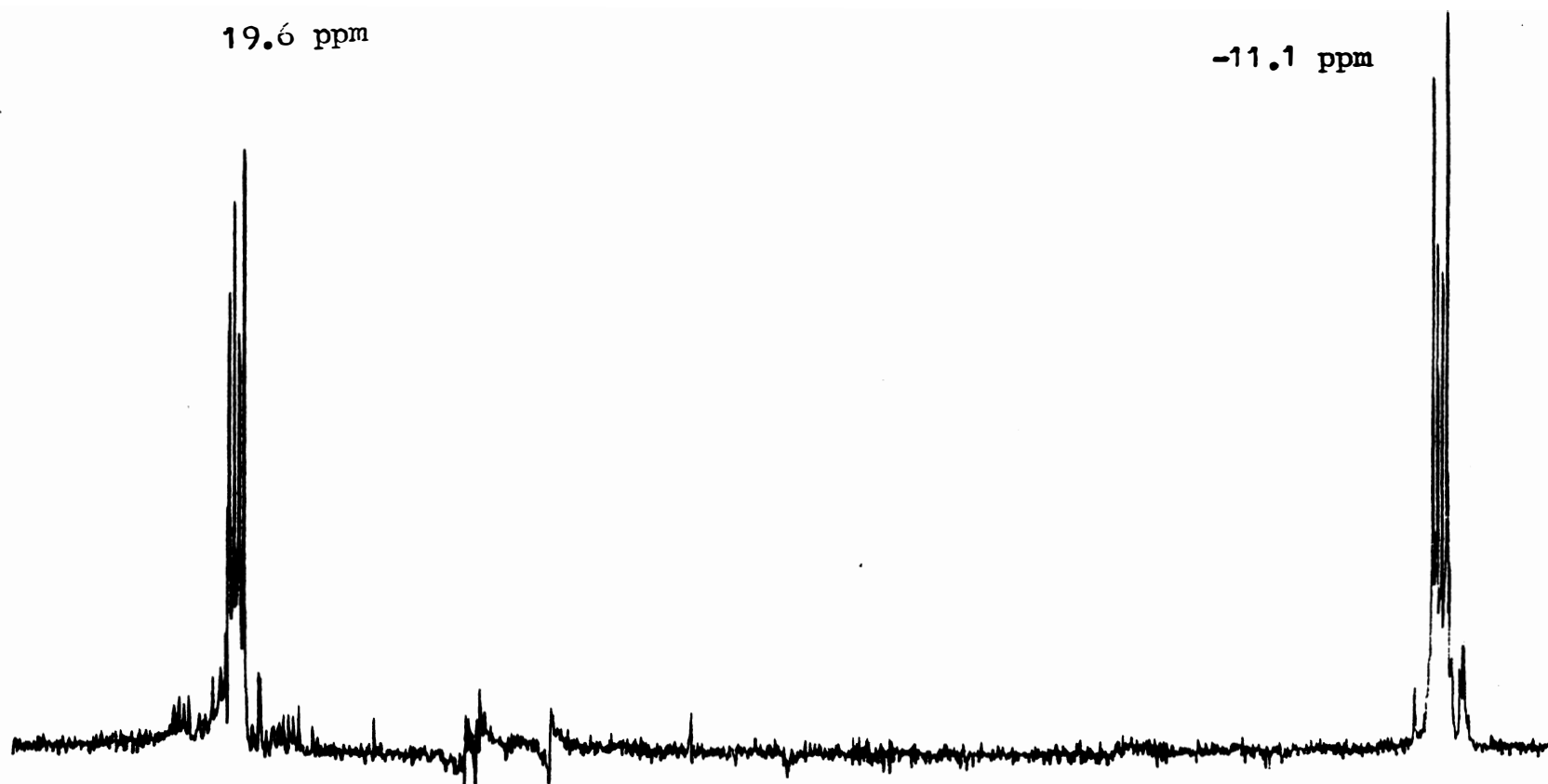
Figure 11.   Expanded ^{31}P nmr spectrum of <u>trans</u>-$(CO)_4W(\eta^1$-PPh_2CH_2-$CH_2PPh_2)_2$ at 19.6 ppm

$^2J_{PMP}$= 54.3 Hz

J_{W-P}= 279.1 Hz
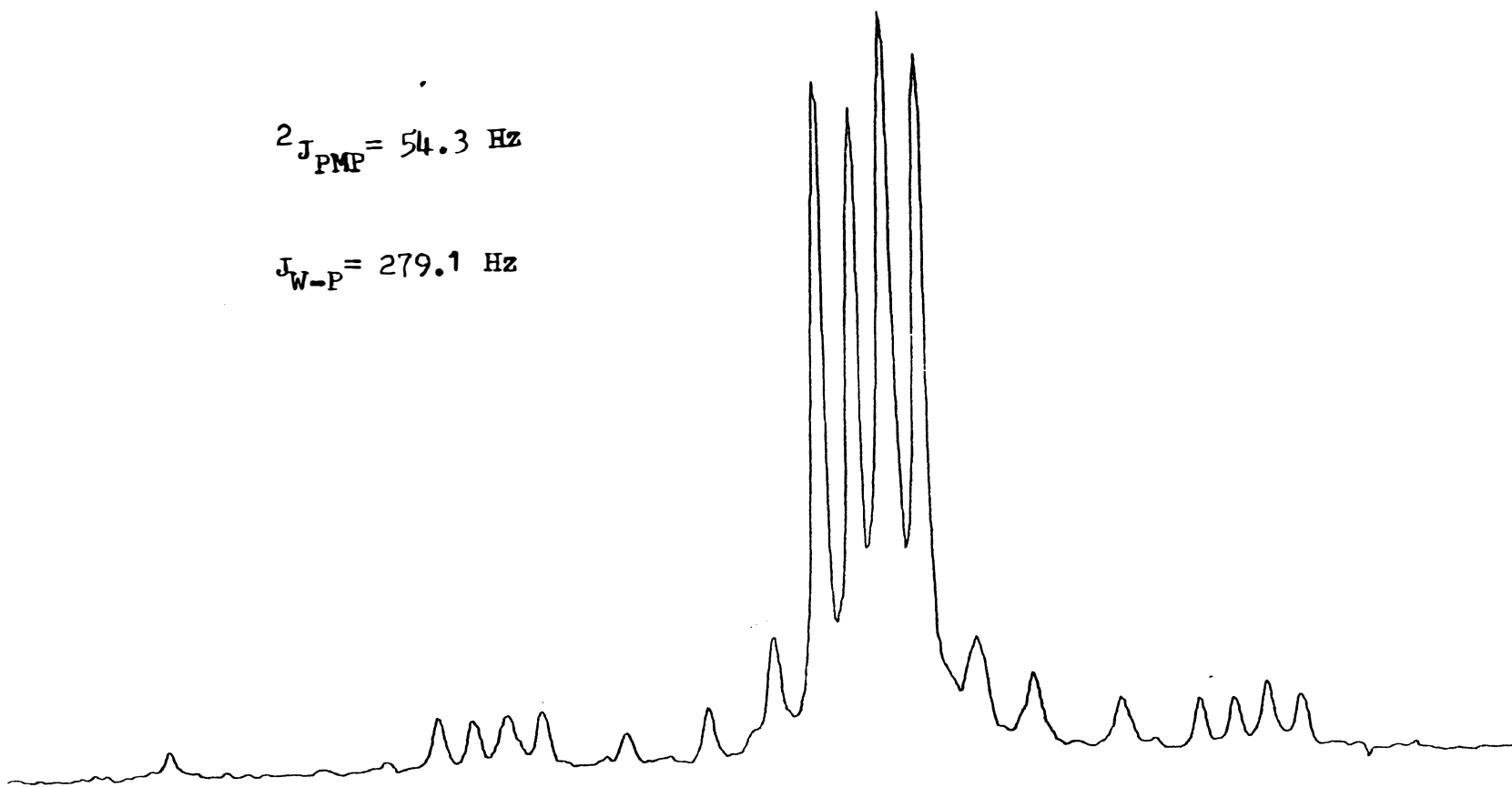
Elemental analysis of the products shown in Table III were very unsatisfactory. The results for $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$, which was synthesized in dichloromethane, were marginal while the results for $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ were completely unacceptable. Reactions of the tungsten ligand with palladium(II) and platinum(II), reported by Wang gave rise to a mixture of dimer, trimer, and polymer.[36] It is likely that mixture of products also resulted from reaction with mercury(II). Identification of the heterobimetallic complexes was attempted by infrared, proton nmr and proton-decoupled phosphorus-31 nmr spectroscopy.

The complexes $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ were extremely insoluble in $CHCl_3$ and CH_2Cl_2. Very poorly resolved phosphorus-31 nmr spectra were obtained for these complexes (Figure 12). Furthermore, infrared spectroscopy and proton nmr spectroscopy were of little value because of the insolubility of the complexes in any solvent.

However, the complex $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$, exhibited slight solubility in $CHCl_3$ or CH_2Cl_2. The infrared spectrum of the chloride product, synthesized in ethanol, is shown in Figure 13, while the product synthesized in dichloromethane is shown in Figure 14. These spectra do not allow firm conclusions to be drawn with regard to the geometry about tungsten. The absorption at 2015 and 1945 cm^{-1} appear to be too intense for forbidden

Figure 12. ^{31}P nmr spectrum of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ (prepared in ethanol)
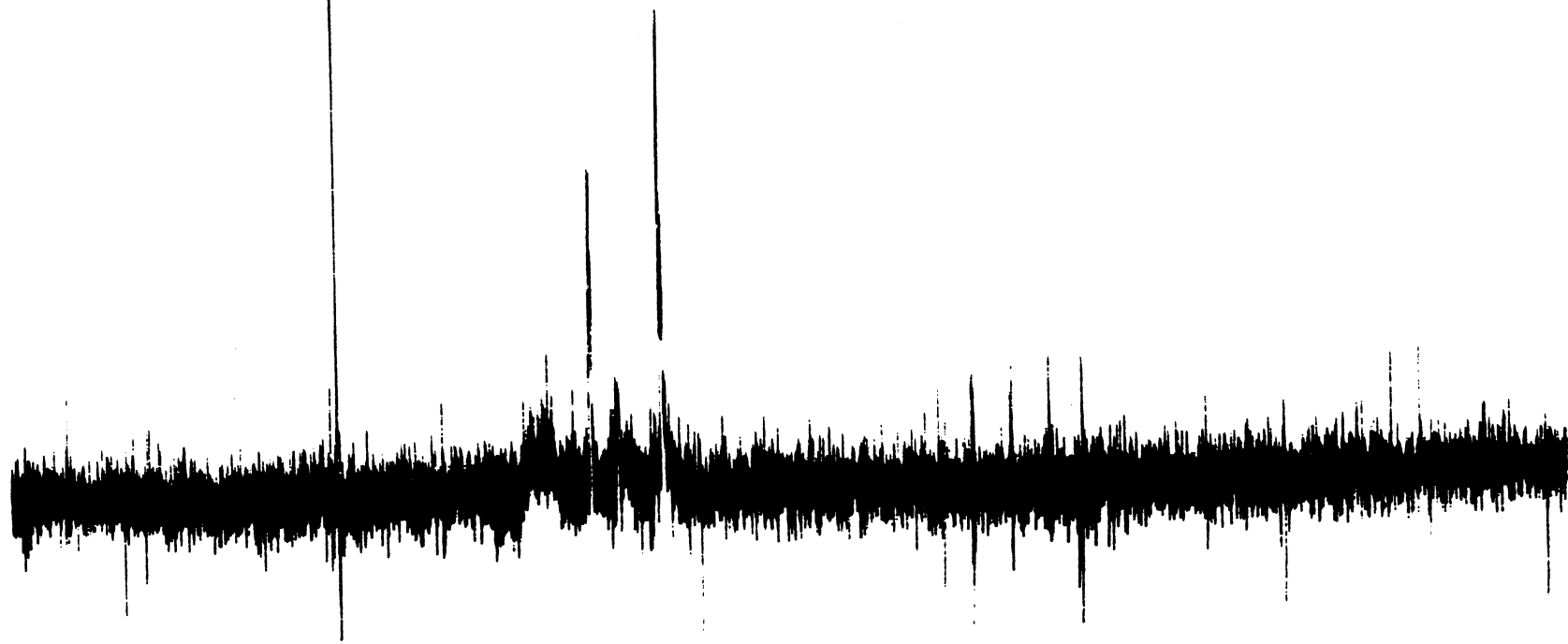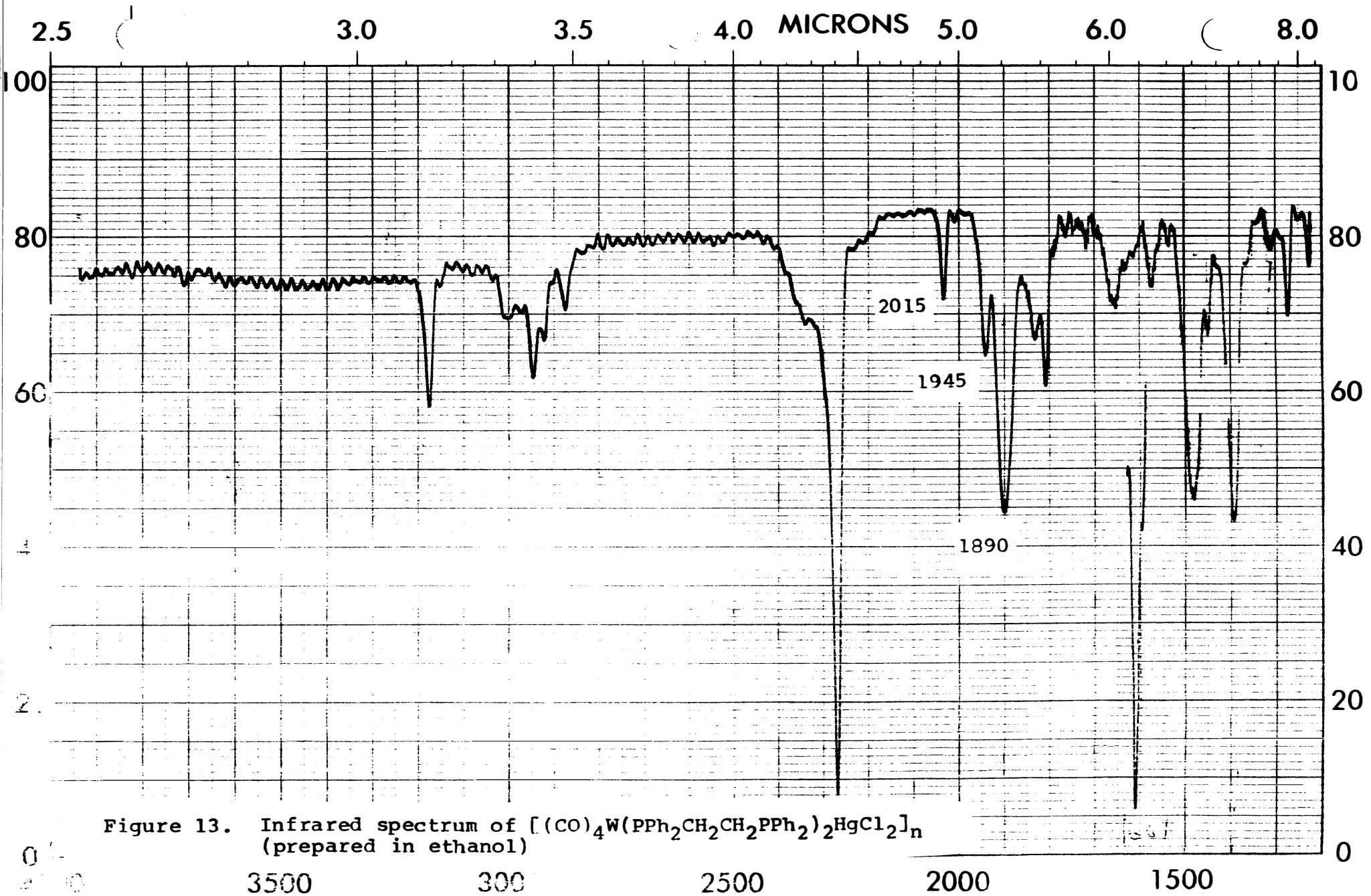
Figure 13. Infrared spectrum of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$
(prepared in ethanol)

Figure 14.   Infrared spectrum of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$
(prepared in CH_2Cl_2)

Peaks labeled: 2015, 1945, 1890

33
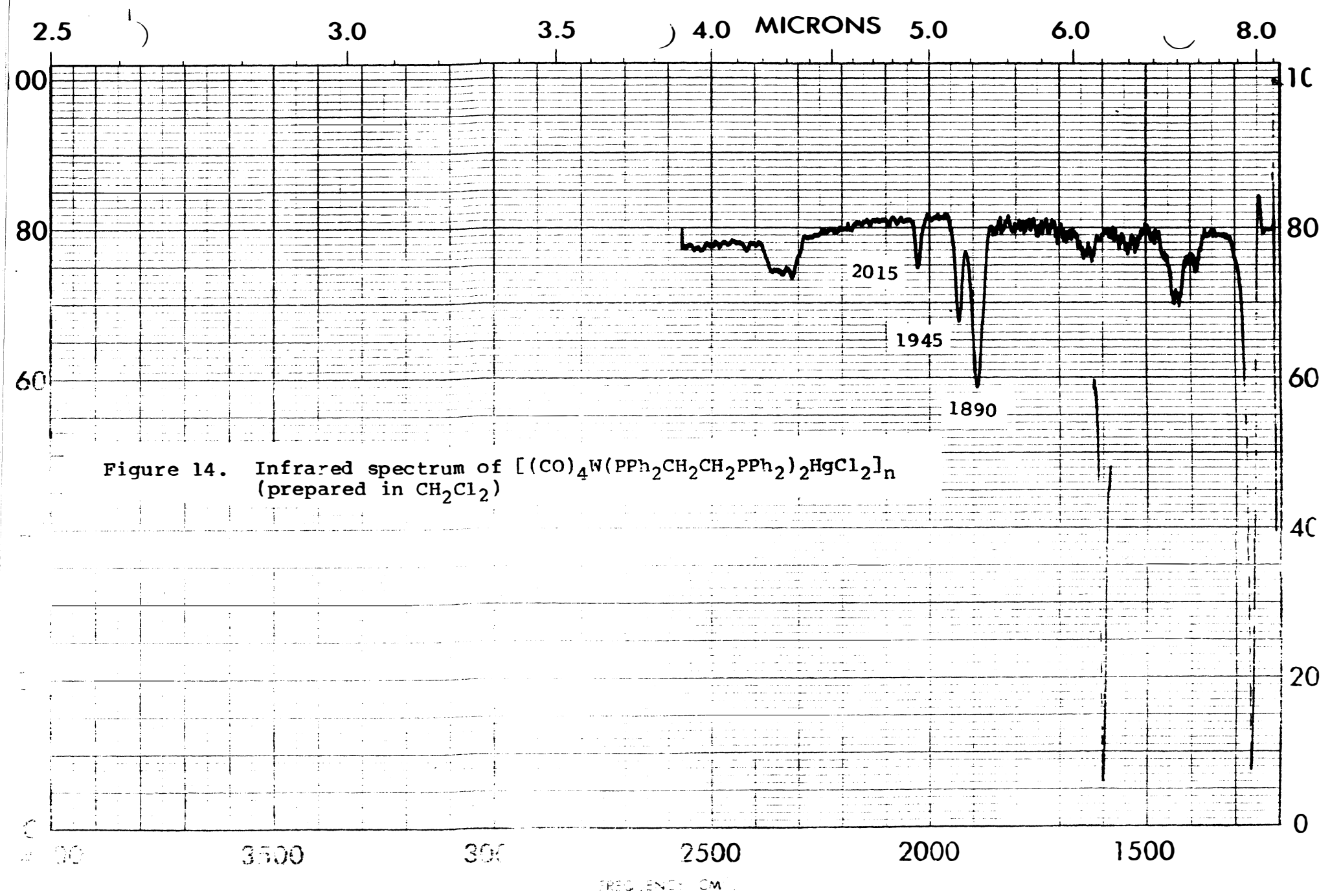
modes of the trans isomer. The strong absorption at 1890
cm^{-1} is correctly positioned to be associated with the trans
isomer but could well result from the overlap of two cis
isomer modes.

The phosphorus-31 nmr spectrum of the complex, which
was synthesized in ethanol, is shown in Figure 15, while
that synthesized in dichloromethane is shown in Figure 17.
Both spectra show two principal signals at approximately 26
ppm and 14 ppm. Expanded spectra of the two principal
signals in Figure 15 is shown in Figures 16, while that in
Figure 17 is shown in Figure 18 and 19. The chemical shift
at 14 ppm is assigned to phosphorus ligands occupying a cis
position in tungsten tetracarbonyl. This chemical shift is
consistent to the one found in
cis-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$ complex.[36] Although the
chemical shift value is slightly larger for the complex to
have cis arrangement around tungsten tetracarbonyl, it is
far too small to be in trans arrangement. The chemical
shift at 26 ppm is close to the published value for the
$Hg(Cl)_2(PPh_2CH_2CH_3)_2$ complex.[37] Both spectra also show Hg-P
satellites (J_{Hg-P}=4420 Hz) arising from 16.9% abundance of
Hg-199 isotope (I=1/2). The W-P satellites are also
resolved in this spectra (J_{W-P}=230 Hz). These
metal-phosphorus coupling constant values are consistent to
published values.[36,37] The exact values of the coupling
constants and chemical shifts of

Figure 15. ^{31}P nmr spectrum of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in ethanol)

14.3 ppm

25.4 ppm
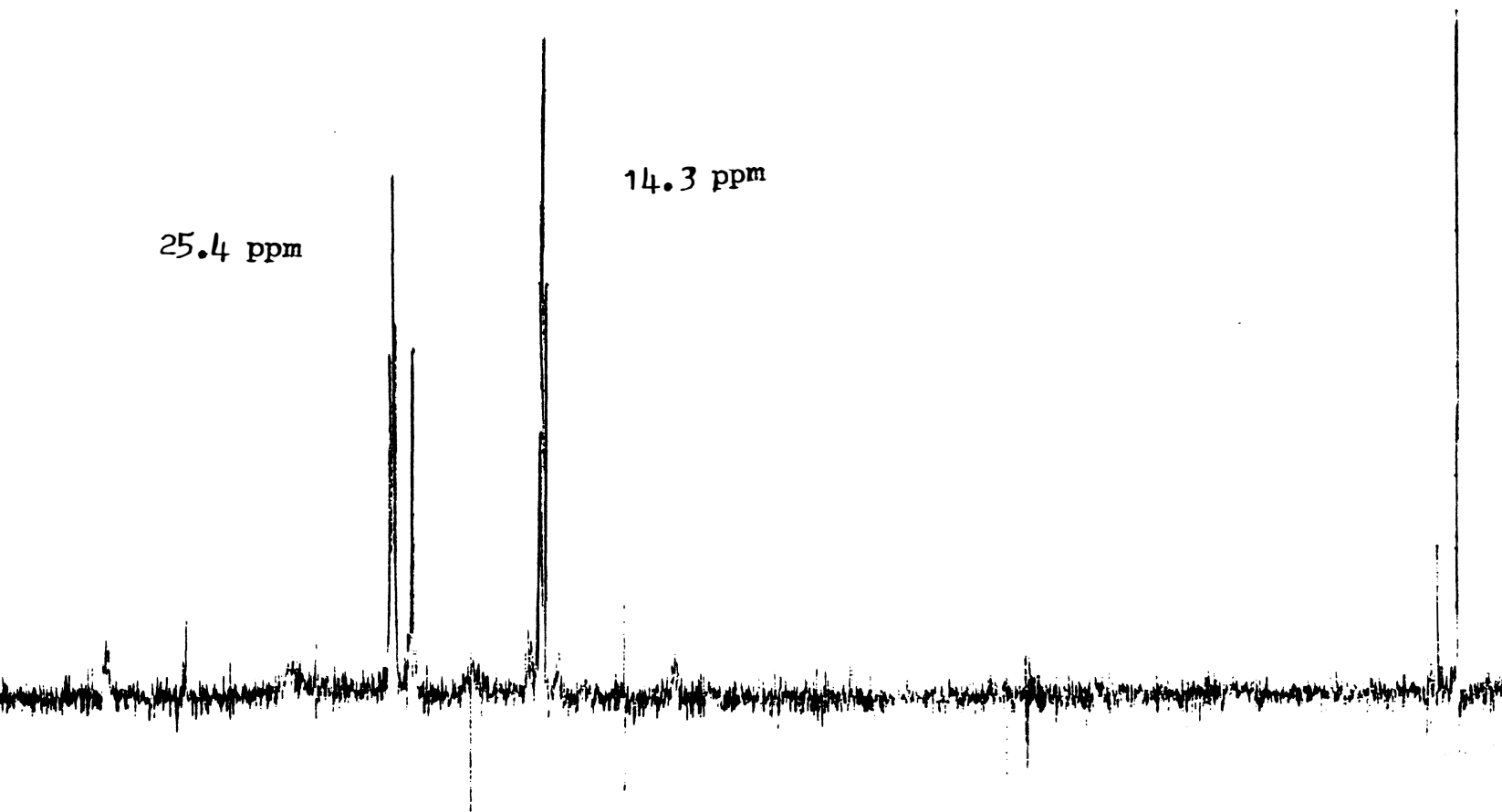
Figure 16. Expanded ^{31}P nmr spectrum (14.3 ppm and 26.0 ppm) of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in ethanol)

$J_{W-P}= 236.4$ Hz

$J_{Hg-P}= 4415$ Hz
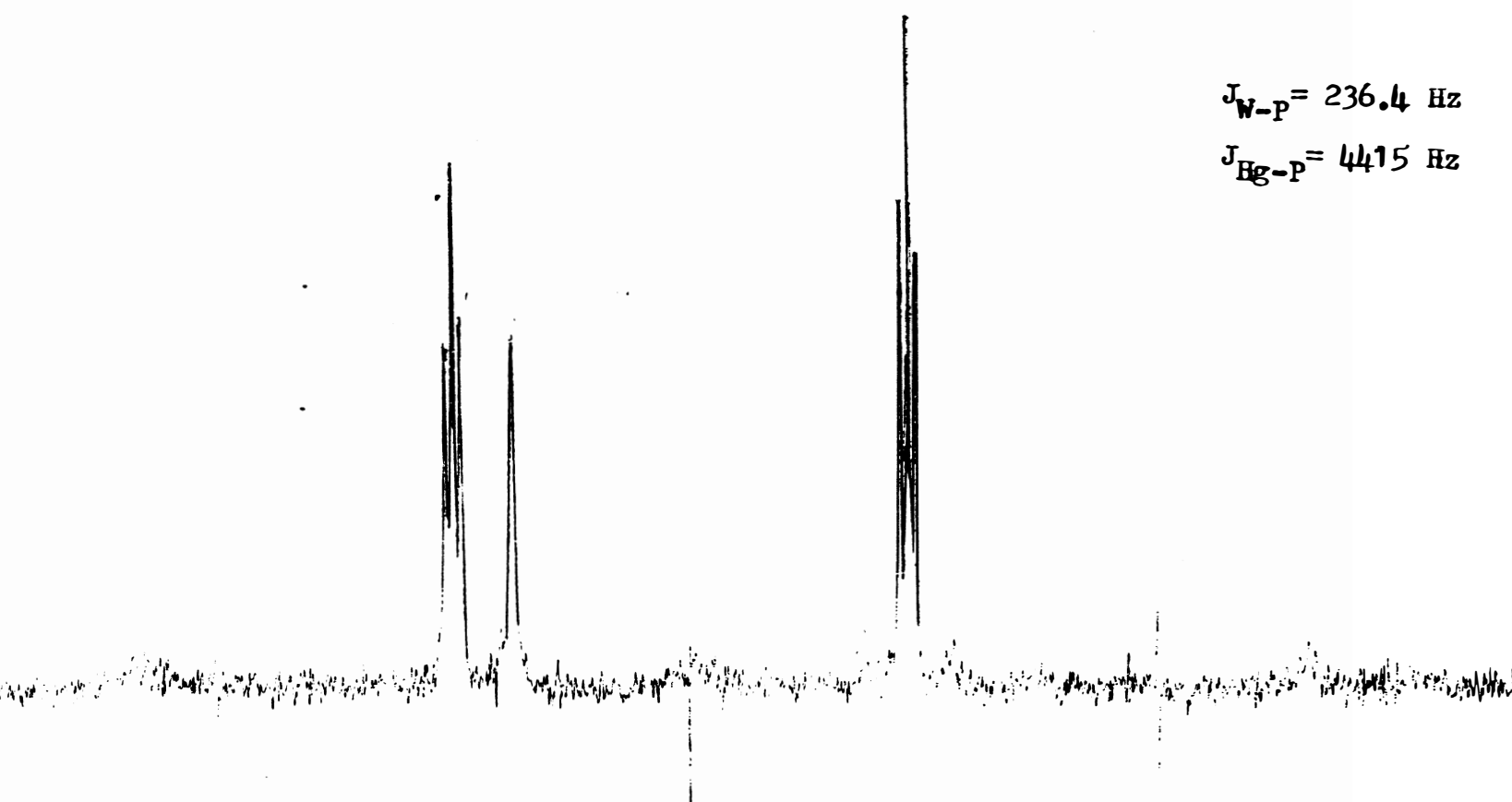
Figure 17. ^{31}P nmr spectrum of $[(CO)_4(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$
(prepared in CH_2Cl_2)

14.5 ppm

26.5 ppm

J_{W-P}= 230.0 Hz

J_{Hg-P}= 4420 Hz

4000   3000   2000   1000   Hz
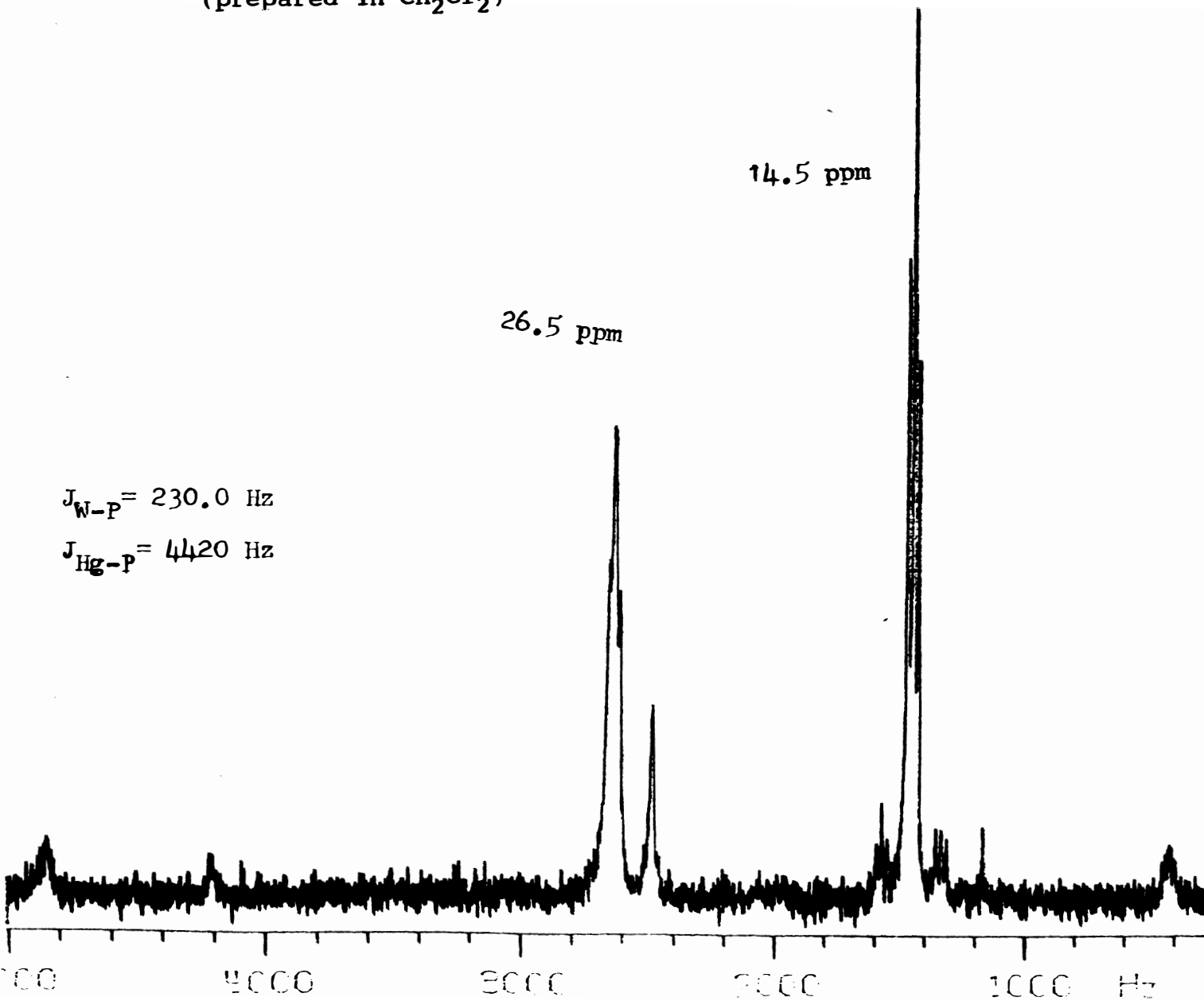
Figure 18. Expanded ^{31}P nmr spectrum (14.5 ppm) of $[(CO)_4W(PPh_2-CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in CH_2Cl_2)
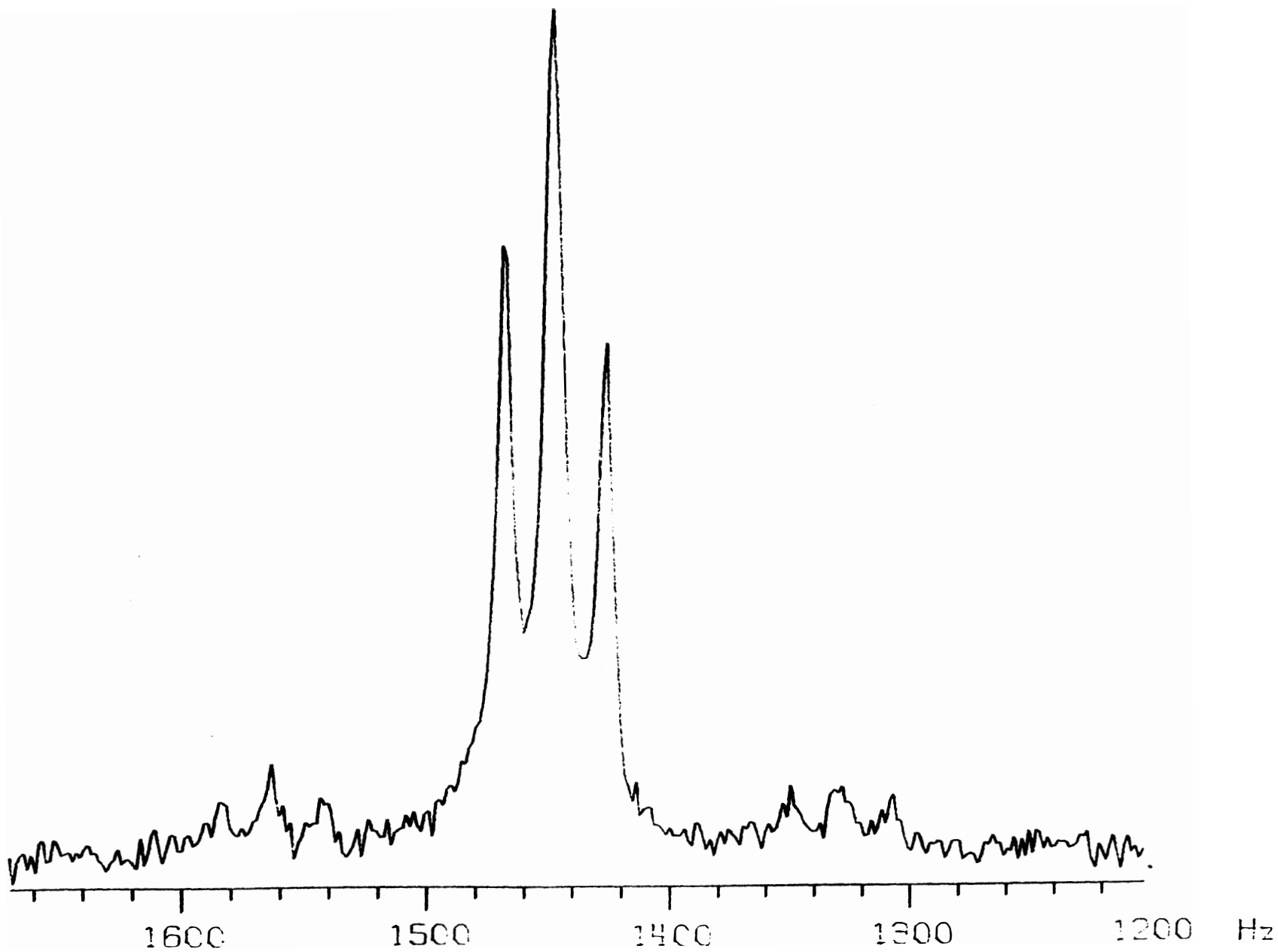
Figure 19. Expanded ^{31}P nmr spectrum (25.5 ppm) of $[(CO)_4W(PPh_2-CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in CH_2Cl_2)
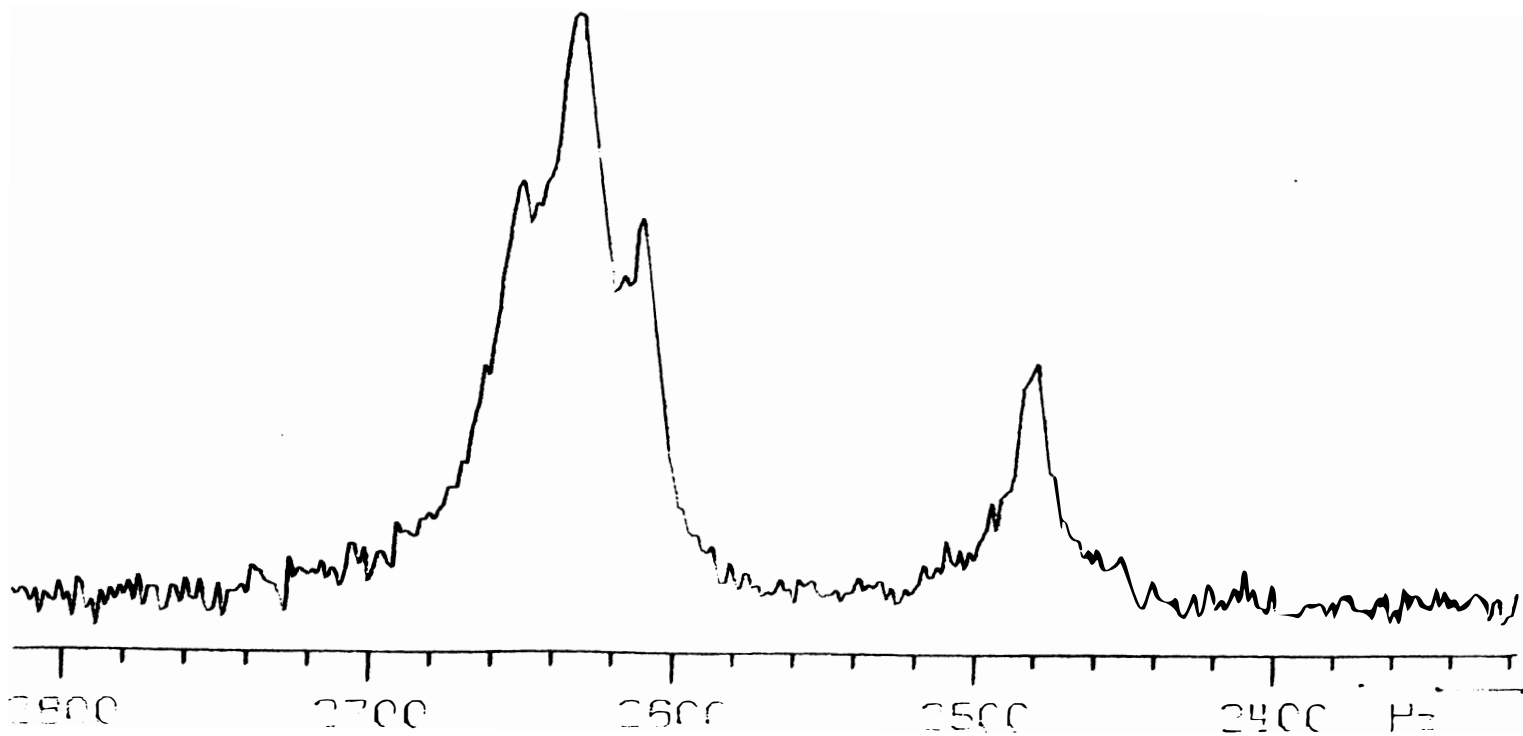
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ complexes are listed in Table II.

The proton nmr spectra of the $(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2$ complex synthesized in CH_2Cl_2 is complicated and is shown in Figure 20. The absorptions at 7.4 ppm are assigned to the phenyl protons and the absorptions between 2.3 and 3.0 ppm are assigned to the methylene group.

Based on the spectral results and the elemental analyses, the following structural formulas are some possibilities for the heterobimetallic complex of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$.
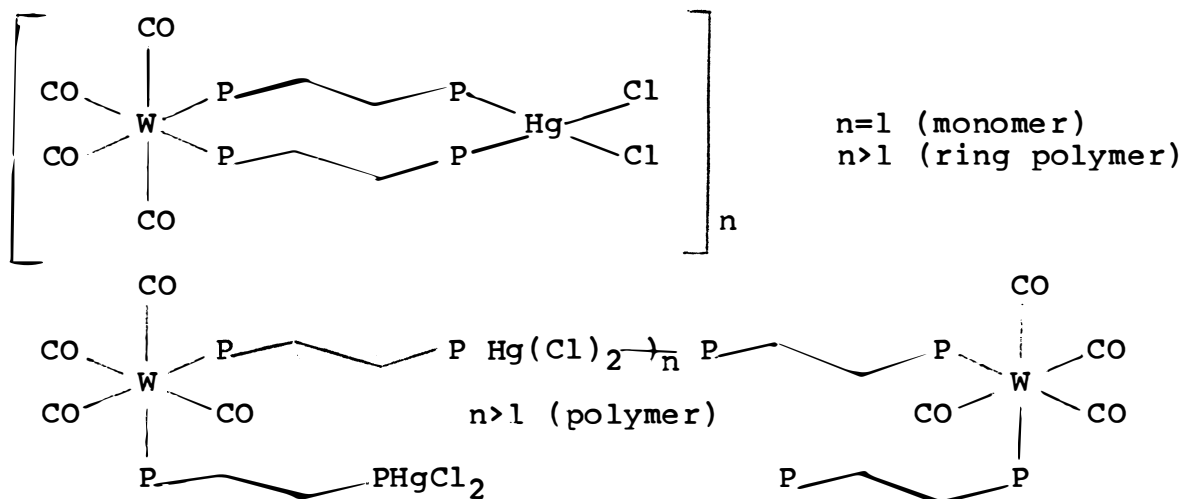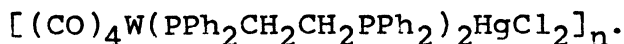
As has been discussed earlier, observation of cis structural arrangement around tungsten center, which implies isomerization, is probably due to the fact that the energy barrier for intramolecular isomerization from the trans to the cis isomer is small.
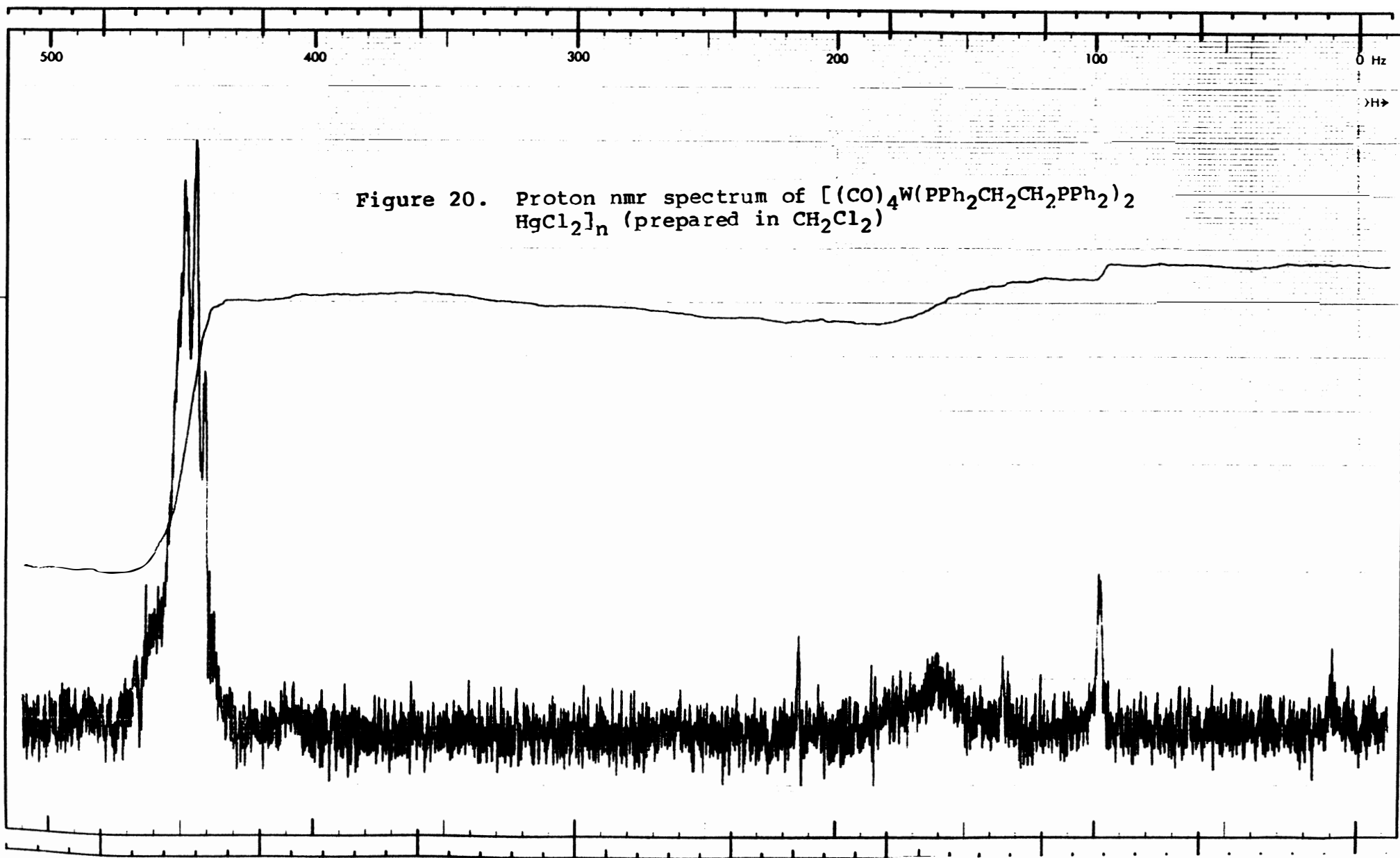
Figure 20. Proton nmr spectrum of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2 HgCl_2]_n$ (prepared in CH_2Cl_2)

The reaction between mercuric iodide and the bis(ditertiary)phosphine led to a product which was not characterized. The elemental analysis was not consistent with a single formulation. Carbon, hydrogen, and phosphorus analysis are in fair agreement with

$$(CO)_4W \begin{smallmatrix} P \diagup\!\!\!\diagdown\!\!\!\diagup P \\ P \diagdown\!\!\!\diagup\!\!\!\diagdown P \end{smallmatrix} Hg \begin{smallmatrix} I \\ I \end{smallmatrix} Hg \begin{smallmatrix} I \\ I \end{smallmatrix}$$
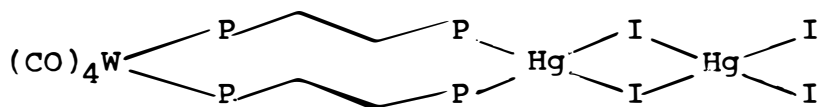
but mercury analysis is 4% too low. Calcd. for $C_{56}H_{48}O_4P_4I_4Hg_2$: C,33.60; H,2.42; P,6.19; Hg,20.04. Found: C,36.99(31.91); H,2.72(2.51); P,5.81(5.64); Hg,16.41(15.96). Results in parenthesis are for analysis of the compound obtained from CH_2Cl_2. A variety of mercury-phosphine complexes are known, as described in the introduction, and mixture of these along with polymer of various molecular weights could account for the results. The lack of resolution and the broadness of the phosphorus-31 spectra, the inability to obtain the infrared stretching frequency of the metal-carbonyl, the inability to observe metal-phosphorus satellites, and above all the insolubility of the complex, all pointed to the formation of polymers.

A computer simulated P-31 nmr spectrum obtained for $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$ complexes is shown in Figure 21.[38] The values used for chemical shifts and coupling constants in this simulation as shown in Table IV were estimated based on the literature values.[21,39]

Figure 21. Computer simulated ^{31}P nmr spectrum of $[(CO)_4W-(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$

26   24   22   20   18   16   14
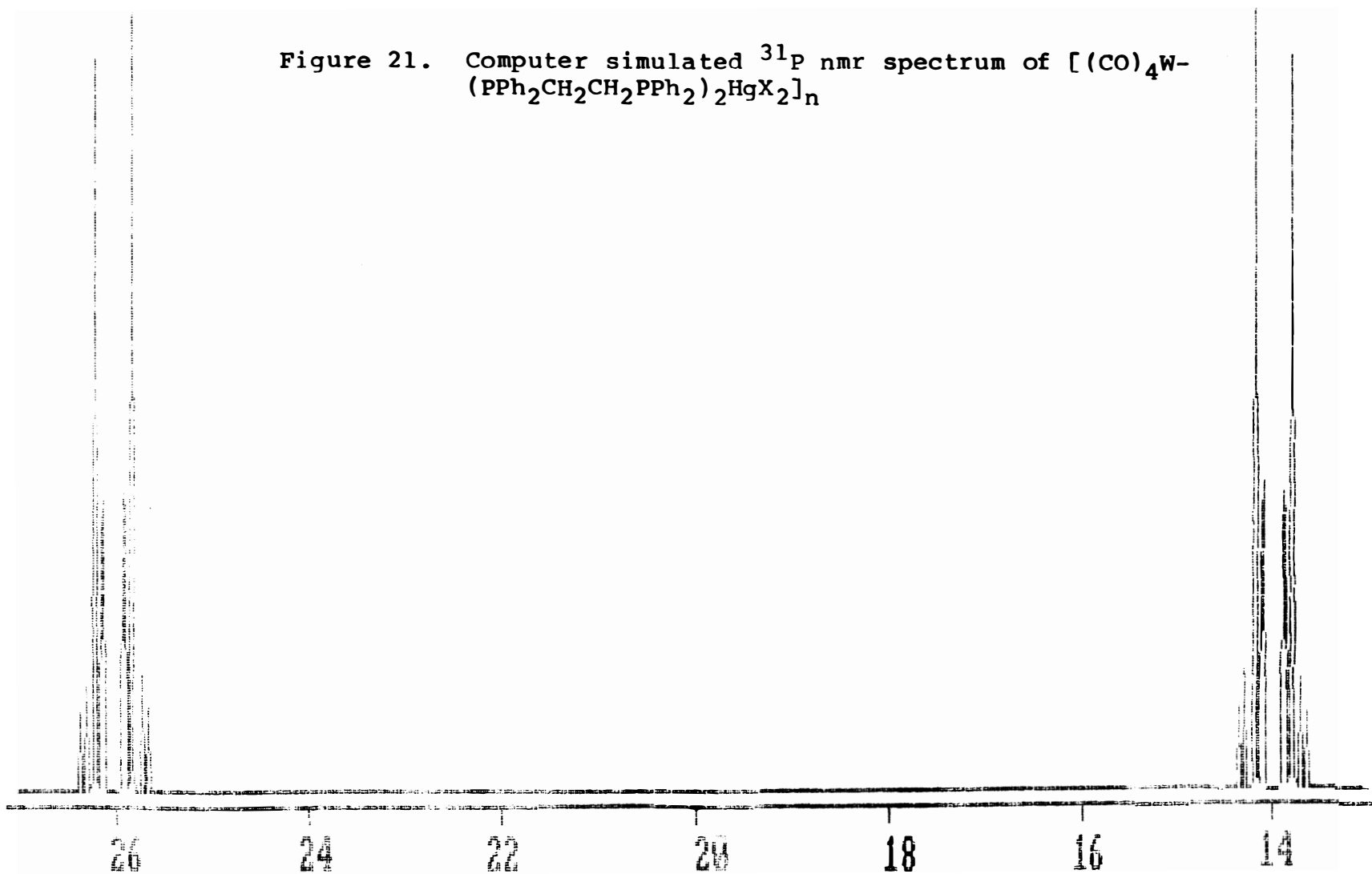
In an attempt to reduce the chances of polymerization, another method of preparing the desired heterobimetallic complexes was proposed. Diphenylphosphine and diphenylvinylphosphine were mixed with mercuric halides in a 2:1 molar ratio in order to form $(PPh_2R)_2HgX_2$ complexes.[37] An addition reaction across the double bond[21] between mercuric complexes and the tungsten complexes, $(CO)_4W(PPh_2CH=CH_2)_2$ and $(CO)_4W(PPh_2H)_2$ was believed to offer the possibility of giving pure monomeric heterobimetallic complexes.

The attempted preparation of mercuric halide phosphine complexes followed the literature method.[37]

(4) $HgX_2 + 2 PPh_2H \xrightarrow{\text{ethanol}} HgX_2(PPh_2H)_2$

(5) $HgX_2 + 2 PPh_2CH=CH_2 \xrightarrow{\text{ethanol}} HgX_2(PPh_2CH=CH_2)_2$
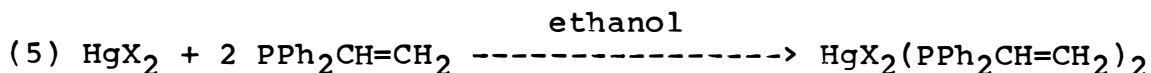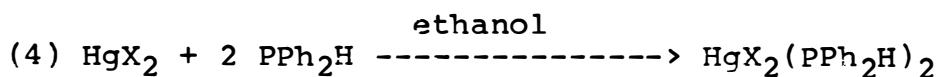
$$X = Cl \text{ or } I$$

However, the products from reaction (4) were so insoluble in CH_2Cl_2 and $CHCl_3$ that the identification of these complexes was not established. Hence, the reaction as described by equation (6) was not carried out. Interestingly, those products from the

(6) $(CO)_4W(PPh_2CH=CH_2)_2 + HgX_2(PPh_2H)_2 \xrightarrow{\text{KOBu}^t}$

$$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$$
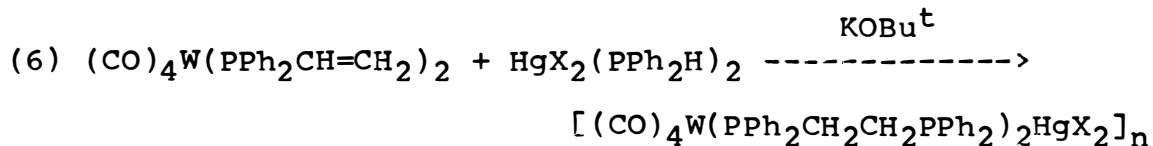
reaction described by equation (5) are very soluble in CH_2Cl_2 and $CHCl_3$. Identification of these soluble complexes

were performed by phosphorus-31 nmr, and proton nmr
spectroscopy. The phosphorus-31 nmr of the product obtained
in reaction (5) is shown in Figure 22. This mercuric
complex contains both magnetically and chemically equivalent
phosphorus atoms, therefore only one major signal is
exhibited mercury-phosphorus satellites are present because
of the coupling of phosphorus to Hg-199. The magnitude of
the mercury-phosphorus coupling constant for
$Hg_2(Cl)_4(PPh_2CH=CH_2)_2$ is 7530 Hz. The chemical shift of the
complex is at 30.7 ppm. The structure of this complex is
probably a dimer instead of the expected monomer.

$$CH_2=CHPh_2P \diagdown \underset{Cl \diagup}{\overset{\diagup Cl}{Hg}} \diagdown \underset{\diagdown Cl \diagup}{Cl} \diagdown \underset{\diagdown Cl}{\overset{\diagup PPh_2Ch=CH_2}{Hg}}$$
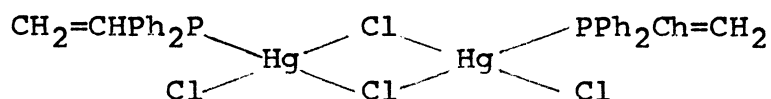
The coupling constant and the chemical shift values are very
close to the published value for $Hg_2(Cl)_4(PPh_2Bu)_2$.[37] No
explanation for this unexpected dimerization in this
reaction can be made at this time.

The proton nmr spectrum of $Hg_2Cl_4(PPh_2CH=CH_2)_2$ shown in
Figure 23, is second order. From the spectrum, the
absorptions of phenyl protons are found to be around 7.4 ppm
and the vinyl protons absorptions fall between 5 to 7 ppm.

The P-31 nmr spectra for the mercury iodide complex is
shown in Figure 24. Due to rapid exchange of the ligands
(phosphorus) with mercury compared to the nmr time scale,
the mercury-phosphorus satellites (J_{Hg-P}) was undetected.

Figure 22. ^{31}P nmr spectrum of $Hg_2(Cl)_4(PPh_2CH=CH_2)_2$

30.7 ppm

$J_{Hg-P}= 7530$ Hz
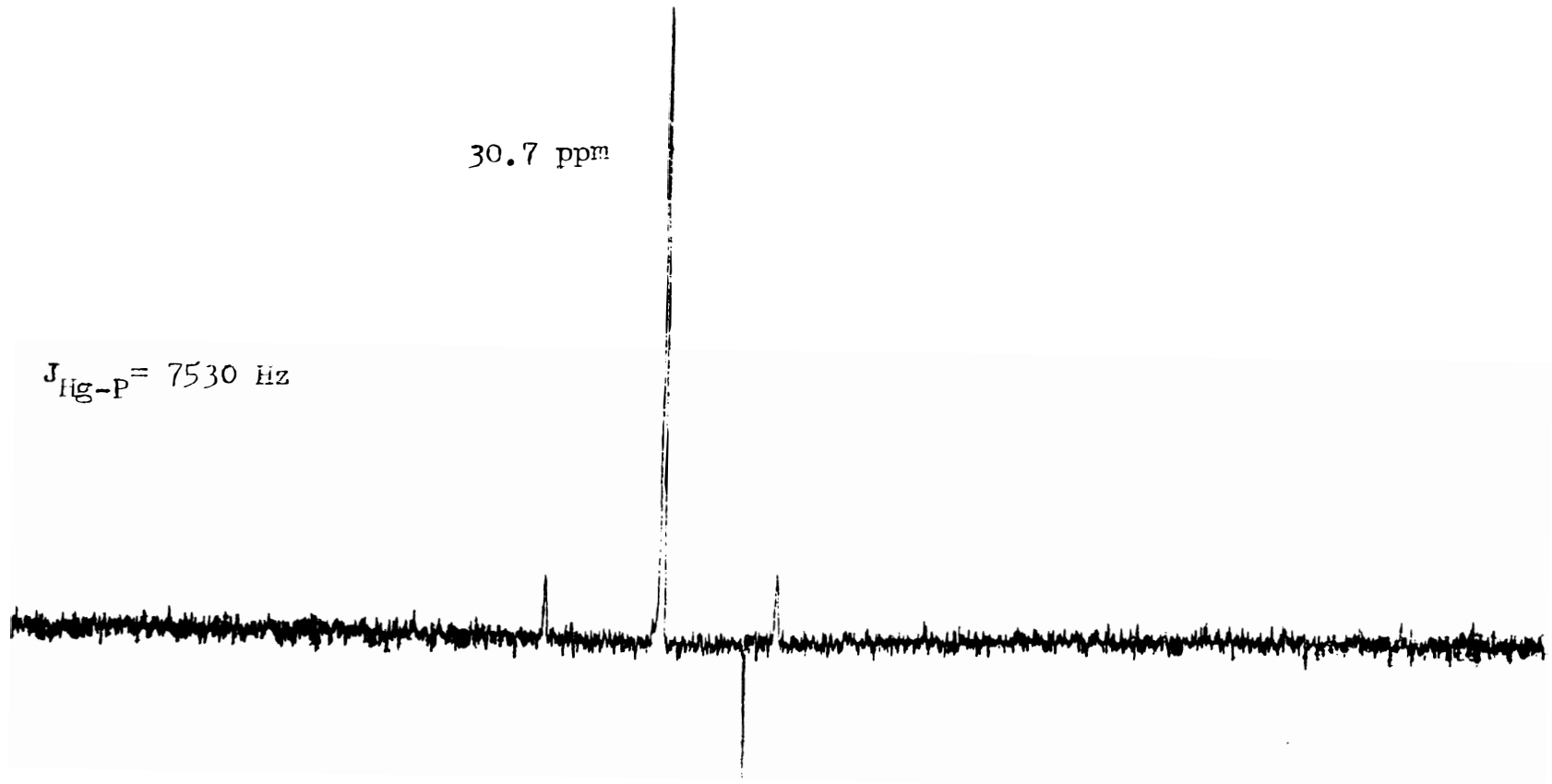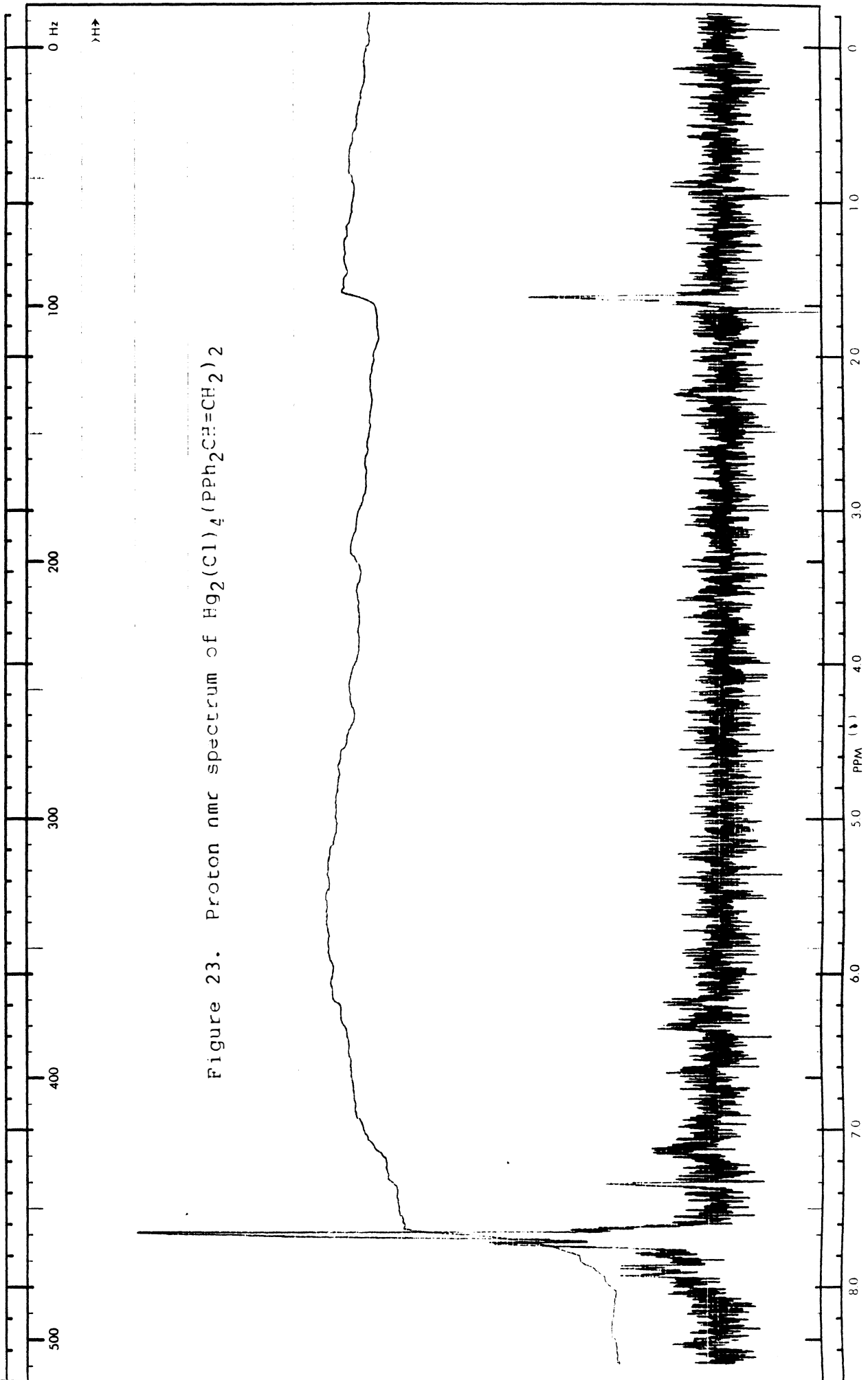
Figure 23.   Proton nmr spectrum of $Hg_2(Cl)_4(PPh_2CH=CH_2)_2$

Figure 24. ^{31}P nmr spectrum of $HgI_2(PPh_2CH=CH_2)_2$
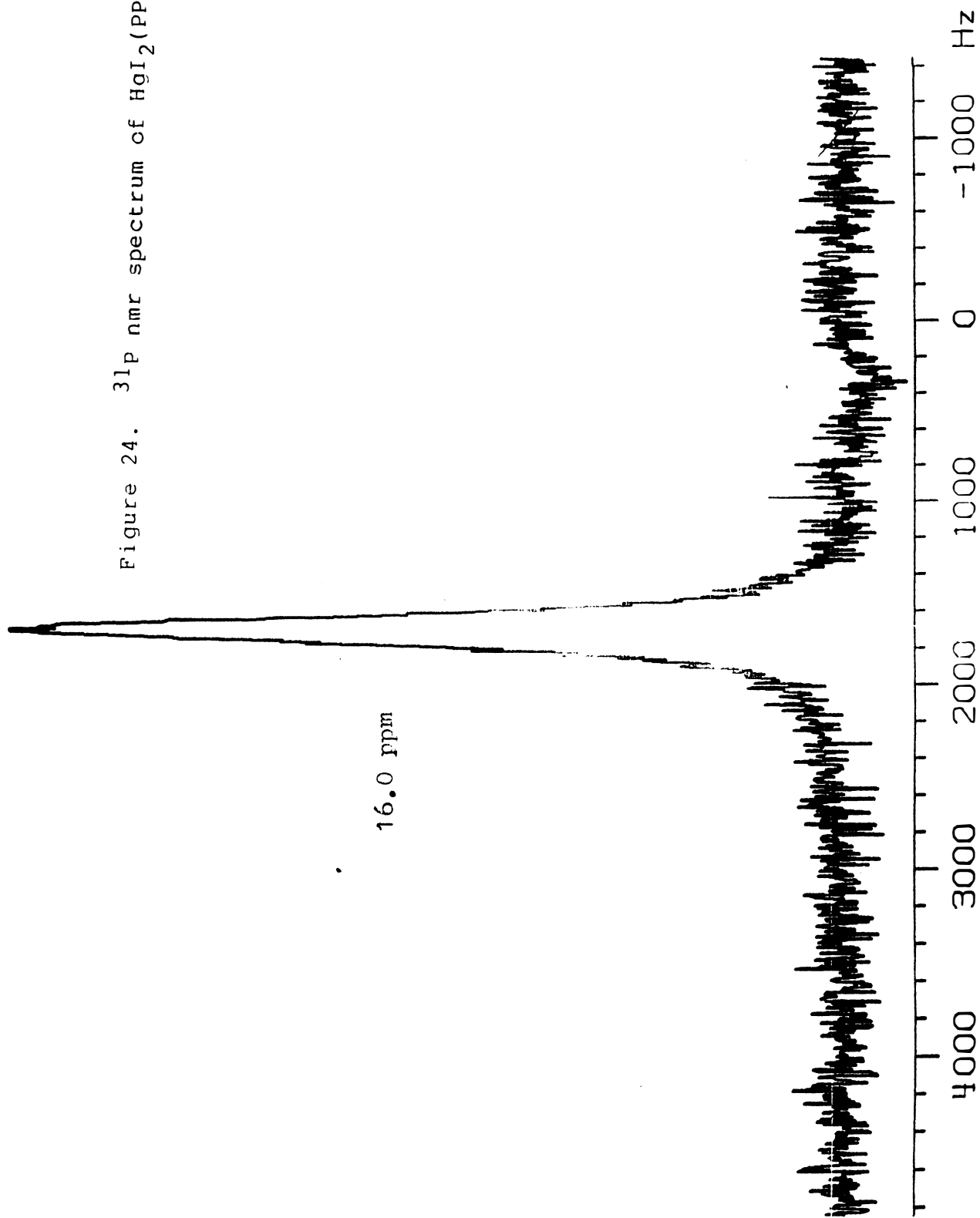
16.0 ppm

The chemical shift of the complex is at 16.0 ppm, is close to the published value for $HgI_2(PPh_2Bu)_2$.[37] The structure of this complex is probably a monomer, $HgI_2(PPh_2CH=CH_2)_2$, although a dimeric structure cannot be ruled out from the phosphorus-31 chemical shift alone.

The attempted preparations of the heterobimetallic complexes as described by equation (7) were terminated due to the inability to synthesize cis-$(CO)_4W(PPh_2H)_2$ complex, and $HgX_2(PPh_2CH=CH_2)_2$. The preparation of the cis-$(CO)_4W(PPh_2H)_2$

$$\text{(7)} \quad \text{cis-}(CO)_4W(PPh_2H)_2 + HgX_2(PPh_2CH=CH_2)_2 \xrightarrow{\quad KOBu^t \quad}$$
$$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$$
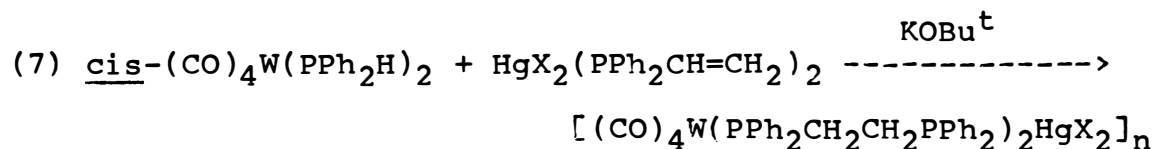
complex by the published method[21] was unsuccessful as decomposition occured under the reaction conditions. To avoid decomposition, the $NaBH_4$ method, discussed earlier in the thesis was used in an attempt to synthesize cis-$(CO)_4W(PPh_2H)_2$. The result was rather surprising. A red complex was obtained when one mole of tungsten hexacarbonyl was allowed to react with two mole of diphenylphosphine in n-butanol in the presence of $NaBH_4$. The reaction mixture was heated under reflux for about five hours. The red product was established by Wang to be a mixture of $W_2(CO)_8(PPh_2)_2$ and $W_2(CO)_7(PPh_2)_2PPh_2H$.[36]

$$(CO)_4W \rightleftarrows^{PPh_2}_{\underset{Ph_2}{P}} W(CO)_4$$

$$(CO)_4W \rightleftarrows^{\overset{Ph_2}{P}}_{\underset{Ph_2}{P}} W(CO)_2(CO)(CO)(PPh_2H)$$
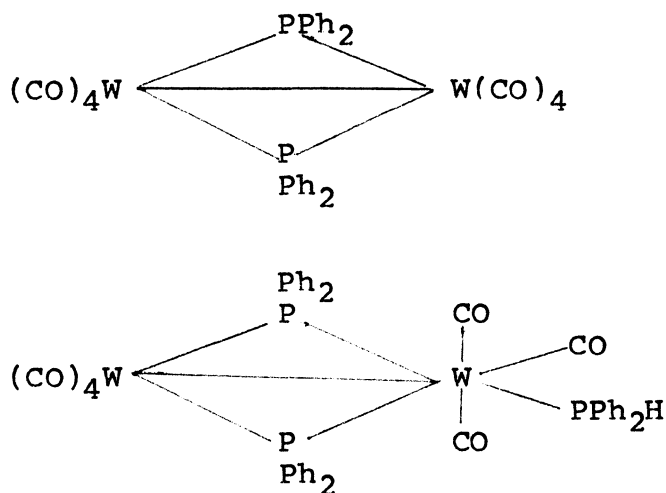
In conclusion, the insolubility of the bimetallic
complexes led us to strongly believe that the direct method
of mixing <u>trans</u>-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ and HgX_2 leads to
polymerization. However, there is no doubt that we have
successfully synthesized complexes containing two different
metals which are bridged by $PPh_2CH_2CH_2PPh_2$ (dpe) ligands.
The molecular weights of these complexes have yet to be
established.

For future research, it is proposed that the carbon
backbone of the starting material should be extended by one
by preparing $PPh_2CH_2CH_2CH_2PPh_2$. The increase in the number
of carbon atoms in the backbone could make the carbon
backbone more flexible and thus the entropy loss upon
coordination would be less significant. As a result it will
be thermodynamically more likely that the dangling phosphine
can chelate with the incoming metal complex. The base
catalyzed addition across the double bond when both PPh_2H

and $PPh_2CH=CH_2$ are coordinated also appears to be promising. This approach should be tried in future research in synthesizing the heterobimetallic complex since it is believed that it can minimize the polymerization process.

Lastly, bimetallic complexes of tungsten and rhodium or iridium should be synthesized since they are more likely to show catalytic activity.

**Table I. Infrared Data in the Carbonyl Stretching
Region of the Tungsten Carbonyl Complexes.**

Compound	Carbonyl Stretching Frequencies (cm^{-1})		
trans-$(CO)_4W(PPh_2CH=CH_2)_2$	2021	1946	1890
trans-$(CO)_4Mo(PPh_2CH=CH_2)_2$	2026	1958	1897
trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$	2020	1945	1888
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in ethanol)	2015	1945	1890
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in CH_2Cl_2)	2015	1945	1890

Table II. Phosphorus-31 NMR Data of the Tungsten-mercury complexes.

Compound	δ uncoord. (ppm)	δ coord. (ppm)	$^2J_{PMP}$ (Hz)	J_{W-P} (Hz)	J_{Hg-P} (Hz)
trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2PPh_2)_2$	-11.1	19.6	54.3	279.1	
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in ethanol)		14.3(W) 25.4(Hg)		236.4	4415
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in CH_2Cl_2)		14.5(W) 26.5(Hg)		230.0	4420
$Hg(Cl)_2(PPh_2CH=CH_2)_2$		30.7			7530
$Hg(I)_2(PPh_2CH=CH_2)_2$		16.0			

Table III. Microanalytical Data for the Heterobimetallic Complexes

Compound	%C		%H		%P		%Hg	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in ethanol)	49.30	47.04	3.54	3.69	9.08	8.39	14.7	17.67
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ (prepared in CH_2Cl_2)	49.30	47.64	3.54	3.46	9.08	8.86	14.7	15.03
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ (prepared in ethanol)	43.47	36.99	3.13	2.72	8.01	5.81	12.96	16.41
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ (prepared in CH_2Cl_2)	43.47	31.91	3.13	2.51	8.01	5.64	12.96	15.96

Table IV. Computer Simulated Phosphorus-31 Data for
$[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgX_2]_n$ Complex

δ W coord.(ppm)	14.0
δ Hg coord.(ppm)	26.0
$J_{AA'}$ (Hz)	21.3
J_{AX} (Hz)	37.6
$J_{AX'}$ (Hz)	0
$J_{A'X}$ (Hz)	0
$J_{A'X'}$ (Hz)	37.6
$J_{XX'}$ (Hz)	5
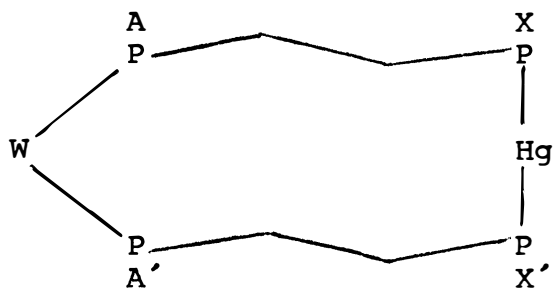
CHAPTER III

EXPERIMENTAL

A. General Considerations

Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tennessee.

The infrared spectra of the carbonyl stretching region (2100-1850 cm^{-1}) were obtained using a Perkin-Elmer 337 infrared spectrometer. Polystyrene was used as a reference and dichloromethane was used as a solvent for each measurement.

Phosphorus-31 nmr spectra were obtained using a 250 MHz homebuilt Fourier-Transform Spectrometer of the University of Illinois, at Urbana-Champaign. The spectra were recorded at 100 MHz. Phosphoric acid (85%) was used as an external reference for the P-31 nmr spectra.

The proton nmr measurement were carried out on a Varian T-60 spectrometer. Deuterated chloroform solutions of the compounds were prepared to obtain the nmr measurement of the

compounds. Tetramethylsilane solution was used as an internal reference for the proton nmr spectra.

Melting points were recorded on an Arthur H. Thomas Unimelt apparatus, and are recorded uncorrected.

Tungsten hexacarbonyl, molybdenum hexacarbonyl, diphenylvinylphosphine, diphenylphosphine, and mercuric halides were purchased from Pressure Chemical Co.

B. Preparation of Monometallic Complexes

(1) Preparation of <u>trans</u>-tetracarbonylbis(diphenylvinyl-phosphine)tungsten(0), <u>trans</u>-$(CO)_4W(PPh_2CH=CH_2)_2$, diglyme method.

Tungsten hexacarbonyl (6.0 g, 0.017 mole) was introduced into a 500 ml round-bottom flask which contained 200 ml of dry diglyme. A magnetic stirring pea was added to the flask. The flask was immersed halfway into an oil bath equipped with a heating coil, a large size magnetic stirring pea, and a thermometer. Nitrogen gas was bubbled into the solution through a gas-inlet tube for about 15 min. During this period, diphenylvinylphosphine ($PPh_2CH=CH_2$) (7.2 ml, 0.054 mole) was injected into the flask by means of a

syringe.

Having purged the solution, a condenser with a stopcock connecting tube on the top was joined to the flask. The reaction was then carried out by refluxing the solution for two hrs at 160°C under a nitrogen atmosphere. When the reaction was over, the solution was cooled under nitrogen to room temperature.

The solvent and the unreacted tungsten hexacarbonyl was removed under a high vacuum for 5 hrs. The residue was washed three times with petroleum ether to remove the unreacted diphenylvinylphosphine and monosubstituted complex, $(CO)_5W(PPh_2CH=CH_2)$. The crude product was recrystallized to remove the cis isomer by dissolving it in a minimum amount of dichloromethane and adding an equal amount of absolute methanol. The solution was kept in the refrigerator for three days to produce 3.2 g (26% yield) of the desired light yellow complex. (m.p. 147-149°C)

(2) Preparation of trans-tetracarbonylbis(diphenylvinyl-phosphine)tungsten, trans-$(CO)_4W(PPh_2CH=CH_2)_2$, in ethanol.

The same procedure and precautions were taken as in the above method. Tungsten hexacarbonyl (3.0 g, 0.0085 mole) and sodium borohydride (0.8 g) were added to 150 ml of ethanol in a round-bottom flask. Diphenylvinylphosphine (2.3 ml, 0.017 mole) was injected into the flask by means of a syringe.

The reaction was carried out by heating the solution

under reflux for 5 hrs under nitrogen. When the reaction was over, the solution was cooled under nitrogen to room temperature. The solution was filtered to removed the unreacted $NaBH_4$. With the aid of a high vacuum pump the solvent was reduced to approximately 50 ml and unreacted tungsten hexacarbonyl was removed.

The solution was placed in the refrigerator for overnight and the product which precipitated was washed with petroleum ether to remove the unreacted diphenylvinylphosphine and the monosustituted tungsten complex. The remaining crude product was recrystallized by dissolving it in a minimum amount of dichloromethane and equal quantity of absolute methanol. However, a mixture of complexes were obtained.

(3) Preparation of <u>trans</u>-tetracarbonylbis(diphenylvinyl-phosphine)tungsten, <u>trans</u>-$(CO)_4W(PPh_2CH=CH_2)_2$, $NaBH_4$ method.

The same procedure and precaution were taken as in the above method. Tungsten hexacarbonyl (3.0 g, 0.0085 mole) and sodium borohyride (0.8 g) were added to 150 ml of n-butanol in a round-bottom flask. Diphenylvinylphosphine (2.3 ml, 0.017 mole) was then injected into the flask by means of a syringe.

The reaction was carried out by heating the solution under reflux at 120°C for 5 hrs under nitrogen. When the reaction was over, the solution was cooled under nitrogen to room temperature. The solution was filtered to remove

unreacted sodium borohydride. With the aid of a high vacuum pump the solvent was reduced to approximately 50 ml and unreacted tungsten hexacarbonyl was removed.

The solution was placed in the refrigerator for 24 hrs and the product which precipitated was washed with petroleum ether to remove unreacted diphenylvinylphosphine and the mono- substituted tungsten complex. The remaining crude product was recrystallized by dissolving it in a minimum amount of dichloromethane and equal quantity of absolute methanol to produce 3.1 g (50.7% yield) of the desired complex. (m.p. 147-150°C)

(4) Preparation of trans-tetracarbonylbis(diphenylvinyl-phosphine)molybdenum(0), trans-$(CO)_4Mo(PPh_2CH=CH_2)_2$, $NaBH_4$ method.

This complex was prepared by heating under reflux molybdenum hexacarbonyl (4.5 g, 0.0017 mole), diphenylvinylphosphine (4.5 ml, 0.034 mole), and 0.8 g $NaBH_4$ in 200 ml of n-butanol for 5 hrs. The crude product was recrystallized from CH_2Cl_2 and absolute CH_3OH to produce 5.19 g (48.4% yield) of the desired complex. (m.p. 147-148°C).

(5) Preparation of trans-tetracarbonylbis(tetraphenyl-diphosphino)ethanetungsten(0), trans-$(CO)_4W(\eta^1-PPh_2CH_2CH_2-PPh_2)_2$, base addition reaction.

Dry THF (100 ml) was introduced into a 250 ml

three-neck round-bottom flask which was connected to a condenser with a stopcock connecting tube on the top. A magnetic stirrer was added into the flask to stir the solution. The flask was then immersed halfway in an oil bath equipped with a heating coil, a magnetic stirrer, and a thermometer. Nitrogen gas was bubbled into the solution through a nitrogen inlet tube for about 30 min. During this period, diphenylphosphine (2.1 ml) and two spatulas of solid potassium tert-butoxide were added to the flask, followed by the addition of $\underline{trans}$-$(CO)_4W(PPh_2CH=CH_2)_2$ (2.9 g, 0.004 mole).

The reaction was carried out by heating the solution under reflux at 65°C for two hours under nitrogen. After the reaction was over, the solution was cooled under a nitrogen atmosphere to room temperature.

The crude solution was filtered with a fritted glass funnel to remove the unreacted potassium tert-butoxide. The solvent of the filtrate was removed with a rotating evaporator. The oily residue obtained was treated with a small amount of dichloromethane and excess amount of methanol to obtain 1.45 g (33.2% yield) of crystalline complex. (m.p. 151-153°C)

C. Preparation of Heterobimetallic Complexes

(6) Preparation of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ in ethanol

Absolute ethanol (200 ml) was introduced into a 500 ml Erlenmeyer flask. A magnetic stirrer was added to the flask. The ethanol solution was purged with nitrogen for about 15 min. Mercuric chloride (0.248 g, 9.153 X 10^{-4} mole) was dissolved in ethanol and 1.0 g of trans-$(CO)_4W$-$(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ was added to the flask. The reaction mixture was stirred slowly for 24 hrs. About 0.71 g of white product was obtained. (56% yield) (m.p. 223-225°C) Calc.: C, 49.3; H, 3.54; P, 9.08; Hg, 14.7. Found: C, 47.04; H, 3.69; P, 8.39; Hg, 17.67.

(7) Preparation of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ in ethanol

Absolute ethanol (300 ml) was introduced into a 500 ml Erlenmeyer flask. A magnetic stirrer was added to the flask. Mercuric iodide (0.187 g, 4.11 X 10^{-4} mole) was dissolved in ethanol, and trans-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ (0.45 g, 4.11 X 10^{-4}) was added into the ethanol solution and the reaction was stirred slowly overnight. Yellow product (0.46 g) was obtained. (72.2% yield) (m.p. 224-226°C) Calc.: C, 43.47; H, 3.13; P, 8.01; Hg, 12.96. Found: C, 36.99; H, 2.72; P, 5.81; Hg, 16.41.

(8) Preparation of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgCl_2]_n$ in CH_2Cl_2

Mercuric chloride (0.1242 g, 4.57 X 10^{-4} mole) was introduced into a 1000 ml round-bottom flask containing approximately 300 ml of dichloromethane. The system was flushed with nitrogen gas for about 20 min. The complex, trans-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ (0.5 g, 4.57 X 10^{-4} mole), dissolved in 300 ml of dichloromethane which had been flushed previously with nitrogen gas, was added dropwise from an addition funnel.

The solution was stirred for four hrs in the dark. The solvent was removed by rotating evaporator. White product (0.28 g, 25.2 % yield) was obtained. (m.p. 178-180°C). Calc.: C, 49.3; H, 3.54; P, 9.08; Hg, 14.7. Found: C, 47.64; H, 3.54; P, 8.86; Hg, 15.03.

(9) Preparation of $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2HgI_2]_n$ in CH_2Cl_2

Mercuric iodide (0.2079 g, 4.57 X 10^{-4} mole) was introduced into a 1000 ml round-bottom flask containing approximately 300 ml of dichloromethane. The system was flushed with nitrogen gas for about 20 min. The complex, trans-$(CO)_4W(\eta^1$-$PPh_2CH_2CH_2PPh_2)_2$ (0.5 g, 4.57 X 10^{-4} mole), dissolved in 300 ml of dichloromethane which had been flushed previously with nitrogen gas, was added dropwise from an addition funnel into the round bottom-flask.

The solution was stirred for four hrs in the dark. The solvent was removed with a rotating evaporator. White

product (0.38 g, 30.2% yield) was obtained. (m.p.
169-172°C) Calc.: C, 43.47; H, 3.13; P, 8.01; Hg, 12.96.
Found: C, 31.91; H, 2.51; P, 5.64; Hg, 15.96.

D. Attempted Preparations of Complexes.

(10) Preparation of <u>cis</u>-$(CO)_4W(PPh_2H)_2$ in diglyme.

This complex was prepared by heating under reflux
tungsten hexacarbonyl (6.0 g, 0.0017 mole) and
diphenylphosphine (5.9 ml, 0.051 mole) in diglyme for two
hrs. The solution turned black indicating that the product
had decomposed.

(11) Preparation of <u>cis</u>-$(CO)_4W(PPh_2H)_2$, $NaBH_4$ method.

Tungsten hexacarbonyl (3.0 g, 8.52 X 10^{-3} mole) and
diphenylphosphine (2.0 ml, 1.70 X 10^{-2} mole) in n-butanol
were heated under reflux for 5 hrs. A red compound was
obtained which corresponded a mixture of $(CO)_8W_2(PPh_2)_2$ and
$(CO)_7W_2(PPh_2)_2(PPh_2H)$ previously identified by Wang.[36]

(12) Preparation of $HgX_2(PPh_2H)_2$ and $HgX_2(PPh_2CH=CH_2)_2$,
where X=Cl or I.

The preparation of these complexes followed the
published method whereby, in obtaining monomeric complexes
the molar ratio of the phosphine to mercuric halide was 2:1.

The mercuric halide was introduced in a 250 ml round-bottom flask with approximately 100 ml of absolute ethanol. The system was flushed with nitrogen gas for about 20 min. The phosphine was injected with a syringe into the flask. The reaction was stirred and refluxed at room temperature for two hrs.

Of the four complexes obtained, only $Hg_2Cl_4(PPH_2Ch=CH_2)_2$ and $HgI_2(PPh_2CH=CH_2)_2$ dissolved in CH_2Cl_2. Following are the percent yields and the melting point of the complexes.

$HgCl_2(PPh_2H)_2$ (64.8% yield, m.p. 168-170°C)

$HgI_2(PPh_2H)_2$ (13.8% yield, m.p. 164-166°C)

$Hg_2Cl_4(PPh_2CH=CH_2)_2$ (36.4% yield, m.p. 178-180°C)

$HgI_2(PPh_2CH=CH_2)_2$ (20.7% yield, m.p. 162-164°C)

E. Preparation of the Solvents (THF and Diglyme)

The solvents used in the preparation of the complexes were dried prior to use.

Commercial solvent, 500 ml, (THF or diglyme) was placed in a round bottom-flask. Magnesium sulfate was added to the flask. The solvent and drying agent were allowed to stand for several days. The solvent was filtered and was transferred to another round-bottom flask. Several small

pieces of sodium metal were added to the solvent. The flask was allowed to stand for several days and benzophenone was added. A calcium chloride trap was used to prevent water vapor from entering the set-up. After several days, the solvent was distilled into a receiving flask for ready use in the preparation of the metal complexes.

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