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Tungsten Carbonyl Complexes Containing Positively Charged Phosphorus Ligands

Dilip Poonamchand Shah

Eastern Illinois University

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Tungsten Carbonyl Complexes containing Positively Charged Phosphorus Ligands

(TITLE)

BY

Dilip Poonamchand Shah
B.S. (1966)
The University of Bombay
Bombay, India

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1971
YEAR

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TUNGSTEN CARBONYL COMPLEXES
CONTAINING POSITIVELY CHARGED
PHOSPHORUS LIGANDS

BY

Dilip Poonamchand Shah
Bachelor of Science
The University of Bombay
Bombay, India
January, 1966

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
1971

TUNGSTEN CARBONYL COMPLEXES
CONTAINING POSITIVELY CHARGED
PHOSPHORUS LIGANDS

Thesis Approved

Dr. R. L. Keiter, Thesis Advisor

Dr. D. W. Ebdon

Dr. R. H. Karraker

DEDICATION

To my Mother and Father

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ABSTRACT

Title of Thesis: Tungsten Carbonyl Complexes Containing
Positively Charged Phosphorus Ligands

Dilip P. Shah, Master of Science, 1971

Thesis directed by: Dr. Richard L. Keiter

Two positively charged complexes, $(CO)_5WP(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ Br^-$ and $(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$, were synthesized, and their carbonyl stretching frequencies and force constants were compared to those of the uncharged complexes, $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ and $(CO)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$. Within experimental error, no differences in infrared data were noted for $(CO)_5WP(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ Br^-$ and $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$. The complex $(CO)_5WP(C_6H_5)_2CH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$ had a significantly larger k_1 force constant than did $(CO)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$. This effect is interpreted as arising from the ability of the positive charge to withdraw electron density from the metal which weakens the metal-carbon bond and strengthens the C O bond.

A tungsten-phosphorus coupling constant of 270 Hz was recorded for $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ which suggests a metal-phosphorus bond of the same strength as the metal-

phosphorus bond in $(CO)_5WP(C_6H_5)_3$. A phosphorus-phosphorus coupling value of 32.1 Hz was noted.

Synthetically, it was observed that $C_6H_5NH_2W(CO)_5$ reacts with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ to give a mixture of $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ and $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2(W(CO)_5)$ with the formation of the latter being favored. The monometallic product can be obtained predominantly if a large excess of free ligand is employed in the reaction. With $(C_6H_5)_2PCH_2P(C_6H_5)_2$, there is no tendency for the formation of the dimetallic complex nor does the monometallic complex $(CO)_5W(C_6H_5)_2CH_2P(C_6H_5)_2$ react with benzyl bromide. The inactivity of the dangling phosphorus is thought to be steric in nature because quaternization does occur with iodomethane. Attempts to prepare a complex such as $(CO)_5WP(C_6H_5)_2\overset{+}{N}(C_2H_5)_3\ BF_4^-$ with the positive charge in the position alpha to phosphorus were unsuccessful.

Infrared evidence is presented which suggests that the reaction between $(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5Br^-$ and $C_6H_5NH_2W(CO)_5$ in methanol yields predominantly $(CO)_4Br\overset{-}{W}P(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5$ which represents a new class of compounds.

CHAPTER I

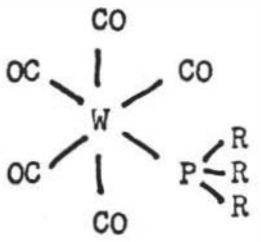
INTRODUCTION

During the last twenty years, studies of the chemistry of phosphorus-containing complexes have expanded enormously. This has been the result of several factors. It has been found that trivalent phosphorus ligands have the ability to stabilize a number of very interesting and useful complexes. Many of these complexes are of commercial importance as a result of their use in homogeneous catalysis.

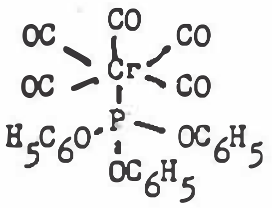
Phosphorus ligands are more interesting than amine ligands from a bonding point of view. When the nitrogen of an amine ligand, R_3N, coordinates to a metal, there is a formation of a dative σ bond, $M \leftarrow NR_3$, which is the result of the lone pair of N (consisting of some 2s and some 2p character) being donated to available empty orbitals of the metal which have the appropriate symmetry. Any d orbitals of the metal which contain potentially back donating electrons, cannot overlap with empty d orbitals of N, as there are none available of suitable energy. When the phosphorus of R_3P is coordinated to a metal, the dative σ bond is formed and the possibility of a $d\pi$-$d\pi$ bond from metal to ligand exists. The d orbitals of the metal are of appropriate energy and symmetry for overlap to take place.

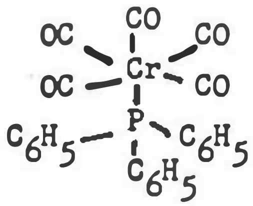
Considerable discussion can be found in the literature regarding the relative importance of π-bonding in the metal-phosphorus bond. Some, such as R. J. Angelici, are convinced that such bonding is minimal.[1] Others, such as S. O. Grim, are convinced that back donation has considerable influence in determining the nature of the phosphorus-metal bond.[2]

The type of complexes discussed in this thesis are pseudo-octahedral complexes of C_{4V} symmetry, where five carbonyl groups are bound to tungsten and the sixth group is a trivalent phosphorus ligand, R_3P.



There are several methods by which one could get some measure of the strength of the phosphorus-metal bond. These include crystal structure, metal-phosphorus coupling constants, metal-phosphorus stretching frequencies and C-O stretching frequencies. For example, Stewart and Grim have done the structural study of two complexes, one containing a phosphite and one containing a phosphine.[2]





For the phosphite, the M-P bond distance is 2.309 A, and for the phosphine it is 2.422 A. These data suggest a stronger M-P bond in the phosphite complex. Grim has attributed this to the better π accepting ability of the phosphite complex. Others would argue that the more electronegative substituent on P in the phosphite complex would enhance the s electron density in the Cr-P bond, thereby drawing the two atoms closer together.[3]

A number of tungsten-phosphorus coupling constants have been determined. Tungsten-183, which is about 14% abundant has a nuclear spin of $\frac{1}{2}$ as does phosphorus-31. A typical P-31 spectrum excluding any phosphorus-hydrogen coupling would consist of an apparent 1:11.5:1 triplet as shown in Figure 1.

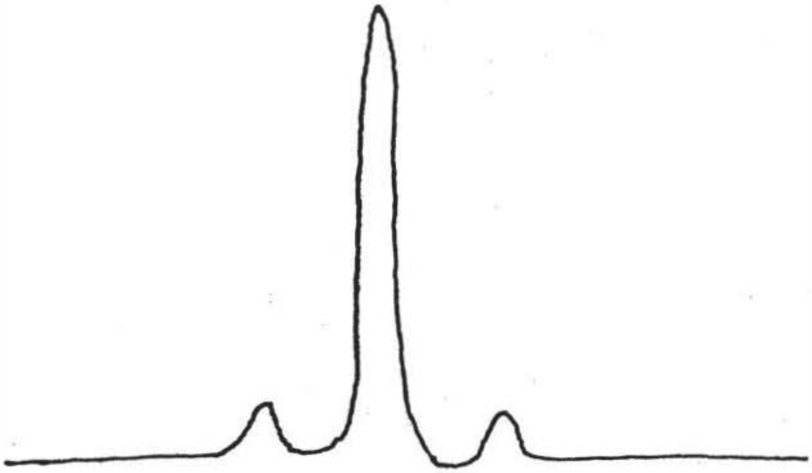


Fig. 1 A Typical P-31 Spectrum of an $LW(CO)_5$ Complex

The satelite peaks arise from the $^{183}W-^{31}P$ coupling while the center line is the result of those P-31 nuclei which are bonded to tungsten not possessing a nuclear spin of ½. Studies have shown that the magnitudes of the coupling constants are quite related to the electron withdrawing ability of substituents on phosphorus.[4] In Table I are found some representative complexes which show this trend.

Table I Phosphorus-31 NMR Data[4]

Compound	$J_{^{183}W-^{31}P}$
$(C_4H_9)_3PW(CO)_5$	200
$(C_4H_9)_2C_6H_5PW(CO)_5$	235
$(C_4H_9)(C_6H_5)_2PW(CO)_5$	250
$(C_6H_5)_3PW(CO)_5$	270
$C_5H_{11}C(CH_2N(CH_3))_3PW(CO)_5$	318
$C_5H_{11}C(CH_2O)_3PW(CO)_5$	393
$F_3PW(CO)_5$	485

In these complexes the same two bonding arguments are applicable. However, it appears that the $d\pi$-$d\pi$ argument is a less cogent explanation of these data. This results primarily from the theoretical description of coupling constants. It is felt that nuclei can only couple via s electron density, and that other coupling mechanisms, such as dipole-dipole interactions, contribute very little to coupling magnitude. If the theoretical equations are correct, it is unlikely that the diffuse d orbitals contribute to the magnitude of coupling constants. Regardless of the bonding arguments used, it does appear that as the electronegativity of substituents on phosphorus increases, a stronger metal-phosphorus bond is created.

A third and more indirect approach to the metal phosphorus bond strength comes from the evaluation of the C-O force constants. It is well accepted that CO is a very good π-bonding ligand as a result of its ability to accept electron density into its antibonding 2p orbitals.

When a phosphorus ligand replaces a CO group of $W(CO)_6$, the charge on the metal increases considerably. The excess charge finds its way into the d orbitals of the metal, which increases the electron density in the antibonding orbitals of CO and this in turn weakens the C-O bond. Therefore, one observes the C-O stretching frequency falling to a lower value. One may also compare the π-bonding strength of CO with R_3P, and in doing so, the CO group is found to be much superior. Therefore, CO should be more successful than R_3P at withdrawing π electron density from the metal. It must be added that the observed CO stretching frequency lowering can also be rationalized by assuming that the π bonding ability of R_3P is insignificant. R_3N groups put even more charge on the metal than do R_3P groups, and as expected, replacing a CO group with R_3N lowers CO stretching frequencies even more than R_3P groups.

The number of CO bands that are observed in a monosubstituted tungsten hexacarbonyl under ideal conditions is 3. As can be shown from group theory calculations, three infrared bands should be found for complexes of C_{4V} symmetry. Figure 2 shows a typical infrared spectrum for complexes of this type. The C-O stretching frequency is invariably found in the region from 1900 to 2100 cm^{-1}.

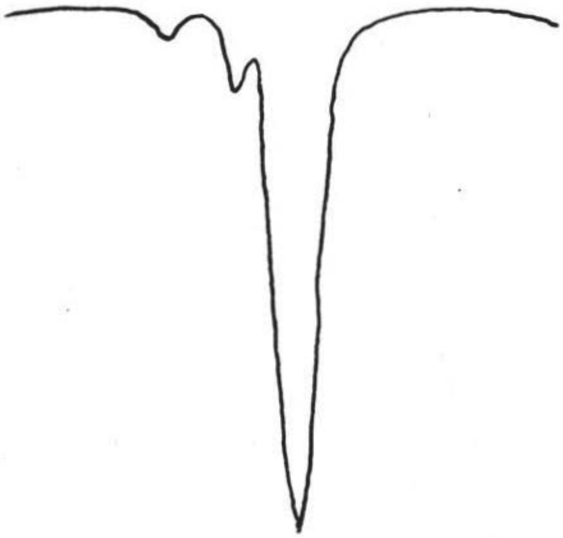


Fig. 2 C-O Stretching Region of the Infrared Spectrum of a $LW(CO)_5$ Complex

The $^{2}_{1}A$ mode is the result of equatorial and axial interaction, while E corresponds to equatorial CO groups and $^{1}_{1}A$ to the CO group trans to L. The stretching frequencies are not nearly as indicative of the strength of the CO bond as are force constants.

From the three stretching frequencies, three force constants can be calculated. F. Cotton has used an approximate force field to derive secular equations that enable approximate force constants to be found.[5] The secular equations used for C_{4v} symmetry are

$$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_2 + 4k_i) - \lambda \end{vmatrix} = 0 \quad \text{and} \quad \lambda = \mu(k_2 - 2k_i)$$

where μ = reciprocal of reduced mass for CO = $\frac{16.0 + 12.01}{16.0 \times 12.01} = 0.1458$ and $\lambda = (5.8890 \times 10^{-2})\nu^2$ with ν expressed in cm^{-1}. The force constants are expressed in mdynes cm^{-1}.

The algebraic solution to the equations and the computer program for obtaining values are found in Appendix I.

Compared with extensive numbers of investigations of transition metal complexes of neutral and anionic ligands, relatively few studies with positively charged ligands have been reported. The purpose of this research has been to prepare positively charged phosphorus ligands, coordinate them to tungsten, measure carbonyl stretching frequencies, obtain tungsten-phosphorus coupling constants and compare these positively charged ligands to neutral ligands. As has been pointed out, the metal-phosphorus bond becomes stronger as more electronegative groups are attached to phosphorus.

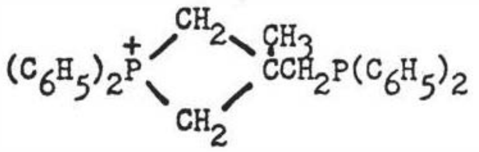
It would seem reasonable that as a positive charge is moved closer and closer to the coordinated phosphorus atom, electron density would be drawn toward the positive charge to a greater and greater extent. In fact, a positive charge in the alpha position to phosphorus would probably create an effect similar to the excellent electron withdrawing group F. As of this work, no systematic attempts had been made to evaluate the characteristics of complexes of positively charged ligands.

The complexes chosen to be made for the study were:

$Br^{-}Ph_3\overset{+}{P}CH_2CH_2PPh_2W(CO)_5$
$Br^{-}Ph_3\overset{+}{P}CH_2PPh_2W(CO)_5$
$Br^{-}Ph_3\overset{+}{P}PPh_2W(CO)_5$
$Br^{-}Et_3\overset{+}{N}PPh_2W(CO)_5$

None of these complexes was known and for some of them, as will be described in the discussion, synthesis was not an easy task.

There are a few examples of complexes of positively charged complexes in the literature. Bergland and Meek[6] prepared a positively charged phosphorus ligand,



Cl^{-} , abbreviated $P\text{-}\overset{+}{P}$,

which was coordinated to form $M\text{-}(P\text{-}\overset{+}{P})X_3$ where M=Co, Ni, Pd, Cu and X=Cl, Br, I. These complexes are quite stable, have pseudotetrahedral structure, and the coordination tendency of the diphenyl phosphino group was not affected by the presence of the quaternary phosphorus atom. Studies of this ligand were continued by Bergland and Meek[9] but no additional significant information was obtained.

Bertrand, et al[7], were successful in preparing a complex of the same general class as those in this thesis. The ligand $P(OCH_2)_3P$ was coordinated and quaternized to form $(CO)_5WP(OCH_2)_3\text{-}\overset{+}{P}CH_3\ BF_4^-$. They detected no noticeable effect of the charge on the metal-phosphorus bond. It should be pointed out, however, that in the study done by Bertrand and also in the one by Bergland the positive charge was never very close to the metal-phosphorus bond and hence little effect would be expected.

The only other studies of positively charged phosphorus ligands were done by Quagliano and coworkers[8]. They studied the donor properties of positively charged pseudotetrahedral Co(II) and Ni(II) complexes containing monoquaternized ditertiary phosphines, $MX_2(Ph_2PCH_2CH_2\overset{+}{P}Ph_3)X$ and $MX_2(Ph_2PCH_2\overset{+}{P}Ph_3)X$, where M=Co, Ni and X=Cl, Br, I. The authors concluded that the presence of a positive charge on the phosphine cationic ligand, although it undoubtedly contributes to the stability of the complexes and favors their formation by providing the suitable 1:3 metal to halide ratio, has very little influence on the ligating character of the phosphorus donor atom. The complexes with which they worked were very insoluble. For this reason, except for solid state uv, they had no experimental method to determine effects of the positive charge. Table II contains a compilation of positively charged phosphorus complexes.

Table II. Compilation of Complexes Containing Ligands of Positively Charged Phosphorus

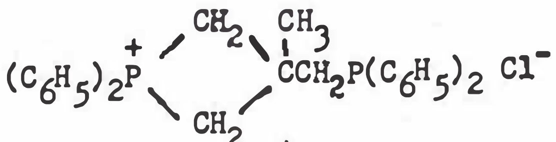
Formula	mp, °C	Color	Comment	Ref.
$(OC)_5WP(OCH_2)_3\overset{+}{P}CH_3BF_4^-$			${}^2J_{PH}$=-5.6 Hz ${}^3J_{PH}$=+6.1 Hz ${}^3J_{PP}$=143.2 Hz	7
 (Abbreviated $\overset{+}{P}$-P)	268-272	White crystals	Reported magnetic susceptibilities, conductivities, visible and UV studies.	6
$Ni(\overset{+}{P}\text{-}P)Cl_3$		Blue		9
$Ni(\overset{+}{P}\text{-}P)BrCl_2$		Turquoise		9
$Ni(\overset{+}{P}\text{-}P)Br_2Cl$		Bluish		9
$Co(\overset{+}{P}\text{-}P)Cl_3$		Blue		9
$Co(\overset{+}{P}\text{-}P)I_3$		Bluish green		9
$Pd(\overset{+}{P}\text{-}P)Cl_3$		Orange		9
$Pd(\overset{+}{P}\text{-}P)Cl_2(ClO_4)_2$		Orange		9
$Au(\overset{+}{P}\text{-}P)Cl_3$		Orange		9

Table II. Continued

Formula	mp, °C	Color	Comment	Ref.
$(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5$ (Abbreviated $PCH_2CH_2\overset{+}{P}$)			UV and IR study in solid state	8
$CoCl_3(PCH_2CH_2\overset{+}{P})$		Blue		8
$CoBr_3(PCH_2CH_2\overset{+}{P})$		Blue		8
$CoI_3(PCH_2CH_2\overset{+}{P})$		Yellow green		8
$NiCl_3(PCH_2CH_2\overset{+}{P})$		Blue		8
$NiBr_3(PCH_2CH_2\overset{+}{P})$	dec 280	Turquoise		8
$NiI_3(PCH_2CH_2\overset{+}{P})$		Dark brown		8
$(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5$ (Abbreviated $PCH_2\overset{+}{P}$)			UV and IR study in solid state	8
$CoCl_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Blue		8
$CoBr_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Blue		8
$CoI_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Chartreuse blue		8

Table II. Continued

Formula	mp, °C	Color	Comment	Ref.
$NiCl_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Greenish blue		8
$NiBr_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Green		8
$NiI_3(PCH_2\overset{+}{P})\ (CH_3)_2CO$		Brown		8

CHAPTER II

RESULTS AND DISCUSSION

A. Synthetic Aspects

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

In the preparation of the positively charged complex, $(C_6H_5)_2(CH_2C_6H_5)\overset{+}{P}(CH_2)_xP(C_6H_5)_2PW(CO)_5\ Br^-$ (x=1,2), the first approach was to prepare the neutral ligand, $(C_6H_5)_2P(CH_2)_xP(C_6H_5)_2$ (x=1,2), quaternize one end of it and coordinate the other end by utilizing a displacement reaction. The neutral ligands were prepared by a standard procedure which involved the following reactions:

1) $Li + P(C_6H_5)_3 \longrightarrow C_6H_5Li + LiP(C_6H_5)_2$
2) $C_6H_5Li + (CH_3)_3CCl \longrightarrow C_6H_6 + LiCl + (CH_3)_2CH{=}CH_2$
3) $LiP(C_6H_5)_2 + Cl(CH_2)_xCl \longrightarrow (C_6H_5)_2P(CH_2)_xP(C_6H_5)_2$

The nmr spectrum of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ is shown in Figure 3. Excluding phenyl protons, the compound represents an $XA_2A_2'X'$ type. The apparent triplet is the result of strong hydrogen-hydrogen coupling which makes the spectrum second order. The nmr spectrum (Figure 4) of $(C_6H_6)_2PCH_2P(C_6H_5)_2$ is an A_2X_2 type with very small phosphorus-hydrogen coupling of 1.6 Hz.

Following the procedure of Quagliano[8], one end of $(C_6H_5)_2$-

$PCH_2P(C_6H_5)_2$ and of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ were quaternized with $BrCH_2C_6H_5$ to form $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ Br^-$ and $(C_6H_5)_2P$-$CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ Br^-$.

Thermally, tungstenhexacarbonyl undergoes a Lewis base reaction with nucleophilic ligands (:B) to give *cis* and *trans* disubstituted and monosubstituted products.

$$W(CO)_6 + :B \xrightarrow[\text{diglyme (polyether)}]{130^\circ} \underline{\text{cis-}} \text{ and } \underline{\text{trans-}}W(CO)_4B_2 + W(CO)_5B$$

A similar type of reaction occurs when tungstenhexacarbonyl is irradiated with ultraviolet light.

$$W(CO)_6 + :B \xrightarrow[\text{THF(dry)}]{\text{uv}} \underline{\text{cis-}} \text{ and } \underline{\text{trans-}}W(CO)_4B_2 + W(CO)_5B$$

It is possible to use column chromatography to separate monosubstituted complexes from disubstituted ones, but this procedure is time-consuming and yields are low. In addition, a chelating ligand such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ has a great tendency to form cis products exclusively if conditions as drastic as those above are employed.

Recently it was shown by Keiter and Verkade[4] that an excellent synthetic approach to monosubstituted tungstenhexacarbonyl complexes involves the displacement of $C_6H_5NH_2$ in $C_6H_5NH_2W(CO)_5$. It was assumed that such a synthesis would be applicable in this work. The aniline complex was prepared from the reaction of $W(CO)_6$

and aniline by irradiating the reaction mixture with uv light. Amines such as aniline, which put considerable charge on the metal, never form disubstituted products. The following reaction was attempted in methanol.

$$C_6H_5NH_2W(CO)_5 + (C_6H_5)_2P(CH_2)_x\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ \ Br^- \longrightarrow$$

$$C_6H_5NH_2 + W(CO)_5(C_6H_5)_2\overset{+}{P}(CH_2)_xP(C_6H_5)_2(CH_2C_6H_5)\ \ Br^-.$$

Methanol was used because the positively charged ligand was sparingly soluble in nonpolar solvents.

It was surprising to find that the reaction was not straightforward. The compound recovered from the reaction mixture was clearly not a complex of the type $LW(CO)_5$ (L= ligand). This was confirmed by its infrared spectrum (Figure 5). The spectrum was taken as a nujol mull, because the compound was insoluble in chloroform. The spectrum consisted of five bands, the most significant of which are those at 1903 and 1834 cm^{-1}. These bands are much too low in frequency for a monosubstituted complex but fit nicely for a cis substituted complex of the type $L_2W(CO)_4$. A complex of this type, which is of C_{2v} symmetry, is expected to have four infrared active bands. The band at 1982 cm^{-1} may be due to $W(CO)_6$ impurity. The insolubility of the complex prevented the application of the usual purification techniques, and the compound was, therefore, not analyzed. The infrared spectrum strongly suggests that the following reaction took place.

$$W(CO)_5C_6H_5NH_2 + (C_6H_5)_2\overset{+}{P}CH_2CH_2P(C_6H_5)_2(CH_2C_6H_5)\ \ Br^- \longrightarrow$$

$CO + (CO)_4Br\overset{-}{W}(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5 + C_6H_5NH_2$

The reaction was repeated several times and the same product appeared each time. Furthermore, $(C_6H_5)_2PCH_2\overset{+}{P}(CH_2C_6H_5)_2\ Br^-$ reacted in a similar manner, and the infrared spectrum of the product of this reaction is shown in Figure 6. The band at 1834 cm^{-1} is noticeably missing. A search of the literature revealed no zwitterionic complex of this nature, although it was found that $W(CO)_6$ reacts with $(C_2H_5)_4\overset{+}{N}Br^-$ to form $[W^-(CO)_5Br][(C_2H_5)_4\overset{+}{N}]$ with the evolution of CO.[15,16] As the halide in this reaction behaves as a Lewis base, it may do likewise as part of the positively charged ligand. Further work needs to be done with this reaction, but since it did not represent the basic purpose of this research, it was not explored further.

The next approach which was used to prepare a positively charged complex involved coordinating the neutral ligand by displacing aniline and then quaternizing the dangling end.

$$W(CO)_5C_6H_5NH_2 + (C_6H_5)_2P(CH_2)_2P(C_6H_5)_2 \longrightarrow$$

$$W(CO)_5(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2 + C_6H_5NH_2$$

It was found that when the aniline complex and the neutral ligand were allowed to react in a mole ratio of 1:1 that the predominant product was $(CO)_5W(C_6H_5)_2CH_2CH_2P(C_6H_5)_2W(CO)_5$. The nmr spectrum, Figure 7, reveals immeasurable small phosphorus-hydrogen coupling at 2.3 ppm. An expanded spectrum did not reveal any splitting. The molecular weight of the compound was confirmed by mass spectral analysis.

Isolated as a minor product was the desired complex, $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, the structure of which was proven by P-31 nmr. This compound will be discussed in section B. When the ratio of aniline complex to free ligand was increased to 3:1, the desired complex was found in good yield. The nmr spectrum (Figure 8) of the XA_2B_2M type complex was quite complicated in the methylene region. This complex reacted with $BrCH_2C_6H_5$ to give the desired positively charged complex, $(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(CH_2C_6H_5)(C_6H_5)_2\ Br^-$. The essentially second order spectrum (Figure 9) shows the benzyl proton coupled to phosphorus (J_{P-CH_2}= 15.5 Hz). No further coupling can be observed in the expanded spectrum of the methylene region (Figure 10). The analysis of the complex was somewhat low (see experimental section) which is due to the hygroscopic nature of the phosphonium salt. The complex was converted to the hexafluorophosphate salt.

$$(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ Br^- + NH_4PF_6 \longrightarrow$$

$$NH_4Br + (CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ PF_6^-$$

This compound is not hygroscopic and a good analysis was obtained. Figure 11 shows its nmr spectrum. The $P-CH_2$ coupling remains 15.5 Hz but has been shifted upfield as the result of a solvent effect. Acetone was used as the solvent for solubility reasons.

When $(C_6H_5)_2PCH_2P(C_6H_5)_2$ was treated with the aniline complex, only a complex with one end coordinated, $(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5)_2$, could be isolated regardless of the ratio of reactants. Apparently, when one end becomes coordinated, the other end is sufficiently deactivated to prevent further reaction. The nmr spectrum (Figure 12), an XA_2M type, consists of a doublet of doublets in which phosphorus-hydrogen coupling is $J_{W-P-CH_2} = 8.6$ Hz and $J_{P-CH_2} = 2.4$ Hz. The inactivity of the dangling end created a problem in quaternizing that end. No reaction occurred with $BrCH_2C_6H_5$, and no product was isolated with the good alkylating agent, $Et_3O^+BF_4^-$.

In one reaction, the aniline complex, benzylbromide, and the neutral ligand were mixed together in benzene and stirred for a few hours. Precipitation slowly occurred. This solid was washed with water to remove any $C_6H_5\overset{+}{N}H_2CH_2C_6H_5\ Br^-$ and washed with benzene to remove any $(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5)_2$. The nmr spectrum (Figure 13) showed that the compound was $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5\ Br^-$. This was established by synthesizing the compound from stoichiometric quantities of benzyl bromide and the free ligand. This reaction took place rapidly. On the basis of the benzyl chemical shift when this group is attached to a quaternized phosphorus atom (see Figure 9), the doublet at low field was attributed to phosphorus-hydrogen coupling (15.5 Hz) and the trivalent phosphorus-hydrogen coupling was too small to be measured.

There is good evidence that the low activity of $(CO)_5W(C_6H_5)_2P$-

$CH_2P(C_6H_5)_2$ toward quaternization is a steric factor. The complex did not react with benzyl bromide or the aniline complex, but both the benzyl group and the $W(CO)_5$ moiety are somewhat bulky. To prepare a positively charged complex of $(C_6H_5)_2PCH_2P(C_6H_5)_2$, iodomethane was employed. First, one end of the ligand was quaternized to give $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$. The nmr spectrum of this ligand is shown in Figure 14. The phosphorus-methyl proton coupling at 2.7 ppm was 14.2 Hz and the quaternized phosphorus-methylene coupling was 15.6 Hz. The trivalent phosphorus-methylene coupling was not resolved. When $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3I^-$ was treated with a stoichiometric amount of $C_6H_5NH_2W(CO)_5$, the desired positively charged $(CO)_5WP(C_6H_5)_2CH_2\overset{+}{P}(C_6H_5)_2I^-$ was obtained. The nmr spectrum of this complex (Figure 15) shows the phosphorus-methyl proton doublet of doublets centered at 4.8 ppm. In this case, both phosphorus nuclei are quaternized. The expanded spectrum (Figure 16) shows coupling of 18.6 Hz and 7.6 Hz, but since there are no model compounds available for comparison, it is not possible to make definite assignments for these couplings.

$(C_6H_5)_2PP(C_6H_5)_2$ is an air sensitive ligand and was prepared as described in the experimental section. No characterizable compounds were isolated from the reaction of this ligand and the aniline complex. Attempts to prepare a positively charged complex of this ligand were thus abandoned.

A similar ligand which is not air sensitive is $(C_6H_5)_2PN(C_2H_5)_2$.

It was prepared from the reaction of $(C_6H_5)_2PCl$ and $(C_2H_5)_2NH$ in good yield. The nmr spectrum (Figure 17), a first order XA_2M_3 system, shows $J_{P-N-CH_2} = 9.8$ Hz (expanded spectrum - Figure 18) with $J_{CH_2-CH_3} = 7.5$ Hz. This ligand reacts with $C_6H_5NH_2W(CO)_5$ to produce in good yield $(CO)_5W(C_6H_5)_2PN(C_2H_5)_2$. As amines do not displace aniline, only phosphorus becomes coordinated. The nmr spectrum (Figures 19 and 20) showed little change from the free ligand. The $P-N-CH_2$ coupling increased to 11.6 Hz and the CH_2-CH_3 coupling value decreased to 7.2 Hz. Attempts to quaternize the dangling diethylamino group were unsuccessful in that a characterizable compound was never isolated. Benzyl bromide and iodomethane did not react with $(CO)_5W(C_6H_5)_2PN(C_2H_5)_2$. Some infrared data suggested that quaternization occurred when $(C_2H_5)_3O^+BF_4^-$ was used (Figure 21). The spectrum of the product is the same as that of $(CO)_5WP(C_6H_5)_2N(C_2H_5)_2$ with an extra ${}^{2}_{1}A$ band (the small one). Attempts to isolate this material gave an oil which still contained some neutral complex (Figure 22). Attempts to purify the compound were not successful and therefore this evidence is somewhat tenuous. Further efforts should be made to characterize the compound.

B. Theoretical Aspects

The carbonyl infrared stretching frequencies and calculated force constants are found in Table III.

The complexes, $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, $(CO)_5W(C_6H_5)_2P$-

Table III. **Infrared carbonyl stretching frequencies and force constants of monosubstituted pentacarbonyl complexes**

Complex	B	${}_1^2A$	${}_1^1A$	E	K_i	K_1	K_2	Fig.
	cm^{-1}				mdynes cm^{-1}			
$(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	1986	2074	1945*	1940	0.324	15.50	15.84	23
$(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2W(CO)_5$	1983	2075	1947*	1942	0.322	15.53	15.87	24
$(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ PF_6^-$	1990	2076	1943*	1938	0.338	15.44	15.81	25
$(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5)_2$	1981	2072	1944*	1939	0.321	15.48	15.82	26
$(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$	1989	2078	1952	1938	0.336	15.63	15.84	27
$(CO)_5W(C_6H_5)_2PN(C_2H_5)_2$	—	2077	1946*	1941	0.329	15.52	15.87	28
$(CO)_5WP(C_6H_5)_3$[17]	1981	2075	1947*	1942	0.322	15.53	15.87	
$(CO)_5WPF_3$[4]	—	2103	2007	1983	0.29	16.59	16.45	

*Values were estimated to be 5 cm^{-1} larger than E as was estimated by R. J. Angelici.[1]

$CH_2CH_2P(C_6H_5)_2W(CO)_5$ and $W(CO)_5(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ PF_6^-$ have essentially the same stretching frequencies and force constants. This is not too surprising as the second phosphorus atom is five bonds away from the nearest carbonyl group.

It is of interest that the ligands $(C_6H_5)_3P$ and $(C_6H_5)_2P$-$CH_2CH_2(C_6H_5)_2$ have very similar donor and acceptor properties. This agrees with the fact that $(C_6H_5)_3P$ and $(C_6H_5)_2PCH_2CH_2(C_6H_5)_2$ are both stable in air whereas many phosphines are air sensitive.

Tunsten-phosphorus coupling constants are a more sensitive probe to the metal-phosphorus bond strength than infrared data (see page 3). A P-31 spectrum has been obtained only for $(CO)_5W$-$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (Figure 29). A tungsten-phosphorus coupling value of 270 Hz was recorded. The tungsten-phosphorus coupling value for $(C_6H_5)_3PW(CO)_5$ has been reported to be 270 Hz.[17] This again shows the great similarity of the two ligands. The compound $(C_6H_5)_2C_2H_5PW(CO)$ (a complex of an air sensitive ligand), reported by Grim,[17] has a W-P coupling constant of only 240 Hz which shows that it is a weaker ligand than either of the two complexes. It is expected that the positively charged complex would show a somewhat higher J_{W-P} value.

The phosphorus-phosphorus coupling of $(CO)_5W(C_6H_5)_2PCH_2CH_2$-$P(C_6H_5)_2$ (32.3 Hz) is rather large. The P-31 chemical shifts are relative to P_4O_6. The coordinated phosphorus value is +98.7 ppm and the dangling phosphorus value (Figure 30) is +123.4 ppm. That the coordinated phosphorus is downfield from the uncoordinated phosphorus is in agreement with data of other tungsten-phosphorus systems.[18]

No tungsten-phosphorus coupling constant values have been obtained for complexes of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ because of a solubility problem. The carbonyl stretching frequencies and force constants for $(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5)_2$ are very much like those for $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, indicating the similarity of these ligands. However in the case of $(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2$-$CH_3$ I^-, the effect of the positive charge is shown. Here the charge is four bonds from the neutral CO, but the great sensitivity of carbonyl groups to electronic charge is evident. The CO force constant(k_1) for the ^1A mode (corresponding to CO opposite to the ligand) has become larger. A change of 0.15 mdynes/cm is noted.

Finally, the carbonyl stretching frequencies and force constants for $(CO)_5WP(C_6H_5)_2N(C_2H_5)_2$ are similar to $(C_6H_5)_2P$-$CH_2P(C_6H_5)_2$ values. If $(CO)_5WP(C_6H_5)_2\overset{+}{N}(C_2H_5)_3BF_4^-$ could have been synthesized, a dramatic effect on CO force constants would probably have been noted.

The force constants are quite large for the $(PF_3)W(CO)_5$ complex. The values are 0.29, 16.59 and 16.45 mdynes cm^{-1}. This shows that PF_3 is a far better acceptor of electron density than is a positively charged ligand with the charge in the position β

to phosphorus.

C. Summary

In this study it has been shown that the ligand $(C_6H_5)_2P$-$CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)$ PF_6^- forms a metal-phosphorus bond very much like $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. It has also been shown that $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3$ I^- is a slightly better ligand than $(C_6H_5)_2PCH_2P(C_6H_5)_2$.

Finally, a complex such as $(CO)_5W(C_6H_5)_2P\overset{+}{N}(C_2H_5)_3$ BF_4^- could not be synthesized and so the effect of a positive charge in the α position is yet unknown.

Synthetically, it was found that $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ reacts with $C_6H_5NH_2W(CO)_5$ to form $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$-$W(CO)_5$ and $(CO)_5W(C_6H_5)_2PCH_2CH_2(C_6H_5)_2$. The dimetallic complex is favored and a large excess of free ligand is needed to form the monometallic complex in good yield. The monometallic complex may be quaternized with benzyl bromide. In the reaction of $C_6H_5NH_2W$-$(CO)_5$ with $(C_6H_5)_2PCH_2P(C_6H_5)_2$, there is no tendency for the dimetallic complex to form even when the aniline complex is present in excess. Nor is the monometallic complex quaternized by benzyl bromide. That steric factors are present here is suggested by the fact that quaternization with CH_3I takes place.

Electronically, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_3P$ are very similar ligands. When coordinated to $W(CO)_5$, nearly identical force constants and CO stretching frequencies are obtained, and identical values of tungsten-phosphorus coupling constants are found. Infrared data support the formation of $(CO)_4Br\overset{-}{W}P(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)$ when $(C_6H_5NH_2)W(CO)_5$ and $P(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5\ Br^-$ are allowed to react in methanol.

CHAPTER III

EXPERIMENTAL

A. General considerations

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Phosphorus-31 nmr spectra were measured with a Varian S-T60 nmr equipped with a phosphorus probe and a time averaging computer. These measurements were performed by Varian Associates, Palo Alto, California. An external reference of P_4O_6 was employed. By convention, chemical shifts upfield from P_4O_6 are assigned a positive value and all chemical shifts downfield are given a negative value.

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

Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 grating infrared spectrometer. Expanded spectra were recorded with an E. H. Sargent recorder SR, and are considered to be accurate to ± 2 cm^{-1}.

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

B. Preparation of Ligands

1. 1,2-Bisdiphenylphosphinoethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$[10]

Triphenylphosphine (50.0 g, 0.19 mole) was dissolved in 500 ml of anhydrous tetrahydrofuran (THF) which contained lithium metal (3.0 g, 0.432 mole). The solution was stirred for three hours, and a dark red solution of lithiumdiphenylphosphide ($LiP(C_6H_5)_2$) and phenyllithium (C_6H_5Li) resulted. A solution of t-butylchloride (17.6 g, 0.19 mole) was added to destroy the phenyllithium. The resulting solution was cooled to 0°C, and 1,2-dichloroethane (18.8 g, 0.19 mole) was added in small portions over one hour. The solution was stirred for 5 hours, and 200 ml of water was added to remove the inorganic layer. After separation, THF was removed from the organic layer with a rotary evaporator. Sufficient petroleum ether (30°-60°C) was added to the resulting oil to crystallize the product. The product (yield 40%) was recrystallized from absolute alcohol (mp 141°C[11]).

2. Bis(diphenylphosphino)methane, $(C_6H_5)_2PCH_2P(C_6H_5)_2$

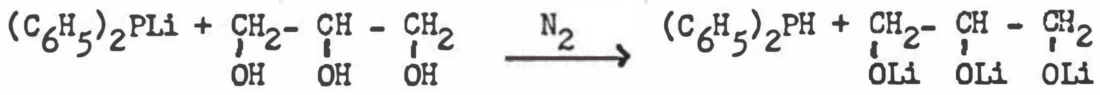
This ligand was prepared by a modification of the procedure for the ethane analog.

To a solution of lithium diphenylphosphide at 0°C was added dibromomethane (33.0 g, 0.19 mole) over a period of one hour. The solution was stirred for 5 hours, and 200 ml of water was added to remove the inorganic layer. After separation, tetrahydrofuran (THF) was removed from the organic layer with a rotary evaporator. Sufficient petroleum ether (30-60°C) was added to the resulting oil to crystallize the product. The product (yield 50%) was recrystallized from absolute alcohol (mp 121°C[12]).

3. Tetraphenylbiphosphine, $(C_6H_5)_2PP(C_6H_5)_2$

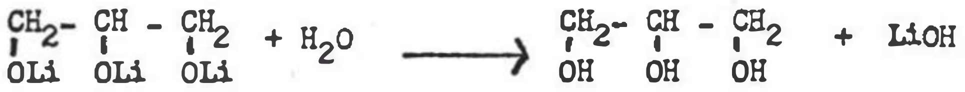
This air sensitive compound is generally made from lithiumdiphenylphosphide and chlorodiphenylphosphine.[13] After mixing the two reactants in tetrahydrofuran (THF), the solution is extracted with ether and the organic layer is separated. The ether is removed from the organic layer by evaporation under an inert atmosphere to give the desired product.

By accident, in the first stage of the preparation, glycerol (used in a nitrogen bubbler) was drawn into a solution containing lithiumdiphenylphosphide.



$$(C_6H_5)_2PLi + \underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2} \xrightarrow{N_2} (C_6H_5)_2PH + \underset{OLi}{CH_2}-\underset{OLi}{CH}-\underset{OLi}{CH_2}$$

The lithium salt of glycerol was destroyed by adding distilled water.



$$\underset{OLi}{CH_2}-\underset{OLi}{CH}-\underset{OLi}{CH_2} + H_2O \longrightarrow \underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2} + LiOH$$

The aqueous layer containing glycerol was separated from the THF layer. The THF was distilled and $(C_6H_5)_2PH$ was distilled at 125°C (0.05 torr). All the operations were done under nitrogen. Chlorodiphenylphosphine (22.23 g, 0.119 mole) was added to diphenylphosphine (26.40 g, 0.119 mole) to yield a white tetraphenylbiphosphine (yield 35.7 g, 80%). The compound was stored under nitrogen.

4. 1-Diphenylphosphino-2-benzyldiphenylphosphonium-ethane bromide, $(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5\ \ Br^-$

This ligand was prepared by treating $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (1.0 g, 0.0025 mole) in acetone (25 ml) with a stoichiometric quantity of benzylbromide (0.44 g, 0.0025 mole). The white solid which separated after several hours was washed with acetone and recrystallized by dissolving it in isobutylalcohol and reprecipitating with hexane (yield 1.05 g, 74%). The pure product was obtained as white crystals (mp 240-245°C).

5. 1-Diphenylphosphino-1-benzyldiphenylphosphonium-methane bromide, $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5\ \ Br^-$

This ligand was prepared by treating $(C_6H_5)_2PCH_2(C_6H_5)_2$ (1.0 g, 0.0026 mole) in acetone (25 ml) with the stoichiometric quantity of benzylbromide (0.42 g, 0.0026 mole). The white solid which separated after several hours was washed with acetone and recrystallized by dissolving it in isobutylalcohol and reprecipitating with hexane (yield 1.03 g, 71%). The pure product was obtained as white crystals (mp 230-235°C).

6. 1-Diphenylphosphino-1-methyldiphenylphosphonium-methane iodide, $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ \ I^-$

This ligand was prepared by treating a solution of $(C_6H_5)_2PCH_2$-

$P(C_6H_5)_2$ (1.0 g, 0.002 mole) in benzene (25 ml) with iodomethane (0.369 g, 0.0026 mole). The white solid separated after several hours. The yield was essentially stoichiometric.

7. Diethylaminodiphenylphosphine, $(C_2H_5)_2NP(C_6H_5)_2$[14]

Diethylamine (73.0 g, 1.0 mole) in dry ether (10.0 ml) was added dropwise, with stirring, to chlorodiphenylphosphine (83 g, 0.38 mole) in 300 ml of dry ether at room temperature. Entry of air into the mixture was prevented by the use of a nitrogen stream. The mixture was stirred for 1 hour to ensure an easily filterable precipitate. The hydrochloride was separated by filtration under nitrogen and washed with dry ether. The washings were combined with the filtrate, and the ether was removed by distillation. The fraction boiling at 165°C (2.0 torr) was collected as the required product (yield 34 g, 64%).

C. Preparation of Neutral Complexes

1. Anilinepentacarbonyltungsten, $C_6H_5NH_2W(CO)_5$[1]

Tungstenhexacarbonyl (8.7 g, 0.024 mole) and aniline (10.0 g, 0.10 mole) were dissolved in 500 ml of dry tetrahydrofuran (THF) and irradiated with uv light for 7 hours. (A diagram of the irradiation cell is found in Appendix II). The resulting yellow solution was evaporated to a thick oil, and water and dilute hydrochloric acid were added until the oil became a yellow solid. Excess $W(CO)_6$ was removed by sublimation (yield 87 g, 87.9%).

2. Bis(diphenylphosphino)ethanepentacarbonyltungsten(0), $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

This complex was prepared by dissolving $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (3.0 g, 0.0075 mole) in 100 ml of benzene. To this solution was added $W(CO)_5C_6H_5NH_2$ (1.0 g, 0.0023 mole). The solution was allowed to stand for 12 hours at room temperature, and was taken to a thick oil with a rotary evaporator. The oil was dissolved in dichloromethane, and an equal volume of methanol was added. The solution was cooled to 5°C, and white crystals slowly formed. These crystals were recrystallized from methanol (yield 1.8 g, 33%) (mp 116-117°C).

3. Bis(diphenylphosphino)ethanebis(pentacarbonyltungsten)(0), $(W(CO)_5(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2W(CO)_5$

This complex was prepared as the preceding one except that the mole ratio was 1:1 (ligand to aniline complex).

$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (6.8 g, 0.017 mole) was dissolved in 100 ml of benzene, and $W(CO)_5C_6H_5NH_2$ (6.0 g, 0.014 mole) was added to the solution. The solution was allowed to stand for 12 hours at room temperature and was then taken to a thick oil with a rotary evaporator. The oil was dissolved in dichloromethane, and an equal volume of methanol was added. The solution was cooled to 5°C, and white crystals slowly formed. These crystals were recrystallized from methanol (dec 205-206°C).

4. Bis(diphenylphosphino)methanepentacarbonyltungsten(0), $(C_6H_5)_2PCH_2P(C_6H_5)_2W(CO)_5$

This complex was prepared by dissolving $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (1.2 g, 0.003 mole) in 25 ml of acetone and treating it with $W(CO)_5C_6H_5NH_2$ (0.43 g, 0.0013 mole) in 50 ml of benzene. After 24 hours, the benzene was removed and a thick oil resulted. The oil was dissolved in equal volumes of dichloromethane and methanol. The solution was cooled to 5°C, and white crystals slowly formed. These crystals were recrystallized from methanol (yield 0.8 g, 37%) (dec 188-189°C).

Anal. Calcd. for $C_{29}H_{27}O_5P_2W$: C, 50.60; H, 3.17; P, 8.87. Found: C, 50.87; H, 3.13; P, 8.74.

5. Diethylaminodiphenylphosphinopentacarbonyltungsten(0), $W(CO)_5P(C_6H_5)_2N(C_2H_5)_2$

Diethylaminodiphenylphosphine (2.50 g, 0.0097 mole) and $C_6H_5NH_2W(CO)_5$ (4.35 g, 0.010 mole) were mixed in 50 ml of benzene. The solution was allowed to stand for 24 hours at room temperature and was then taken to a thick oil with a rotary evaporator. The oil was dissolved in equal volumes of dichloromethane and methanol. This was cooled to 5°C, and yellow crystals slowly formed. These crystals were recrystallized from methanol to give white crystals (yield 2.8 g, 49%) (mp 84-85°C).

D. Preparation of Positively Charged Complexes

1. 1-Diphenylphosphino-2-benzyldiphenylphosphonium-ethanepentacarbonyltungsten(0) bromide, $W(CO)_5(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5CH_2)$ Br^-

This complex was prepared by treating $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (1.0 g, 0.0014 mole) with benzylbromide (0.237 g, 0.0014 mole) in benzene. The white solid which separated after several hours of stirring was washed with benzene (yield 1.2 g, 96%). Anal. Calcd. for $C_{38}H_3P_2WO_5Br$: C, 50.54; H, 3.32; Br, 9.09; P, 7.04. Found: C, 54.39; H, 4.28; Br, 10.67; P, 7.01.

2. 1-Diphenylphosphino-2-benzyldiphenylphosphonium-ethanepentacarbonyltungsten(0) hexafluorophosphate, $W(CO)_5(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(C_6H_5CH_2)\ PF_6^-$

This complex was prepared by mixing $W(CO)_5(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5CH_2)Br^-$ (0.8 g, 0.0009 mole) with 50 ml of water and treating the mixture with ammonium hexafluorophosphate, $(NH_4)PF_6$ (0.3 g, 0.0018 mole). The white product which formed was washed with water and dried under vacuum (yield 0.8 g, 92%) (dec 175-185°C). Anal. Calcd. for $C_{38}H_{31}P_3WO_5F_6$: C, 47.62; H, 3.26; P, 9.69; F, 11.89. Found: C, 47.37; H, 3.29; P, 9.71; F, 11.59.

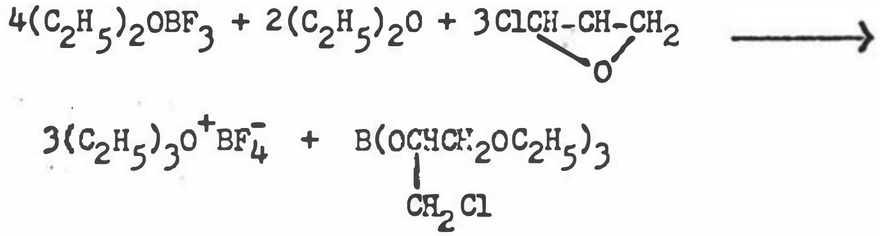
3. 1-Diphenylphosphino-2-methyldiphenylphosphonium-methanepentacarbonyltungsten(0) iodide, $W(CO)_5(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$

This complex was prepared by dissolving $(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\ I^-$ (1.367 g, 0.0026 mole) in chloroform (25 ml) and treating with $NH_2C_6H_5W(CO)_5$ (1.0842 g, 0.0026 mole). The solution was allowed to stand for 12 hours at room temperature and was then taken to a thick oil with a rotary evaporator. Extraction of the oil with benzene left the desired compound as a white solid (dec 145-150°C).

E. Attempted Preparations

1. Triethyldiphenylphosphinoammoniumpentacarbonyltungsten(0) tetrafluoroborate, $(C_6H_5)_2W(CO)_5PN(C_2H_5)_3\ BF_4^-$

The $(C_2H_5)_3O^+BF_4^-$ was prepared according to Meerwin.[19]



$$4(C_2H_5)_2OBF_3 + 2(C_2H_5)_2O + 3\,ClCH_2\text{-}CH\text{-}CH_2(O) \longrightarrow 3(C_2H_5)_3O^+BF_4^- + B(OCH(CH_2Cl)CH_2OC_2H_5)_3$$

Sodium dried ether (250 ml) and 126 ml(1.0 mole) of freshly distilled fluoride etherate were placed in a flask. Epichlorohydrin (60 ml, 0.75 mole) was added dropwise for 1 hour, and the mixture was stirred at a sufficient rate to allow it to reflux. The white crystals which formed were washed with dry ether and dried under vacuum. All the operations were performed under nitrogen. The triethyloxoniumfluoroborate was colorless (yield 120 g, 85%) (mp 92-92°C).

$W(CO)_5(C_6H_5)_2PN(C_2H_5)_2$ (2.0 g, 0.0034 mole) was dissolved in 30 ml of benzene, and $(C_2H_5)_3O^+BF_4^-$ was added to the solution which was stirred for 12 hours under nitrogen. No reaction occurred. The solution was then heated under reflux for 6 hours. An nmr of the solution showed that only starting material was present.

The same reaction was attempted with other solvents, such as methanol, chloroform, acetone, ether and methylene chloride, but no significant changes were observed.

$(CO)_5W(C_6H_5)_2PN(C_2H_5)_2$ (0.8 g, 0.0014 mole) and $(CH_3CH_2)_3O^+ BF_4^-$ (excess) were heated under nitrogen until molten in an oil bath at 95°C for 15 minutes. The oily mass was extracted with petroleum ether and benzene. Most of the mixture did not dissolve. The insoluble oil was extracted with chloroform and taken to an oil with a rotary evaporator. The oil showed a very promising carbonyl stretching frequency in the infrared spectrum. An nmr of the oil showed that very little starting material was present. Several attempts at crystallizing this oil by various methods failed.

2. Benzyldiethyldiphenylphosphinoammoniumpentacarbonyltungsten(0) bromide, $(C_2H_5)_2(C_6H_5CH_2)\overset{+}{N}P(C_6H_5)_2W(CO)_5\ Br^-$

$W(CO)_5(C_6H_5)_2PN(C_2H_5)_2$ (2.0 g, 0.0034 mole) was dissolved in 30 ml of benzene, and benzylbromide (1.76 g, 0.010 mole) was added. The solution was stirred for 12 hours under nitrogen. No reaction occurred. The solution was then heated under reflux for 6 hours. Starting material was recovered.

3. Methyldiethyldiphenylphosphinoammoniumpentacarbonyltungsten(0) iodide, $(CH_3)(C_2H_5)_2NP(C_6H_5)_2W(CO)_5\ I^-$

$W(CO)_5(C_6H_5)_2PN(C_2H_5)_2$ (1.8 g, 0.0030 mole) was dissolved in benzene, and methyl iodide (11.3 g, 0.08 mole) was added. The solution was heated under reflux for several hours. No reaction occurred. Starting material was recovered. The neutral complex was dissolved in pure methyl iodide. No change in the nmr spectrum appeared after 24 hours.

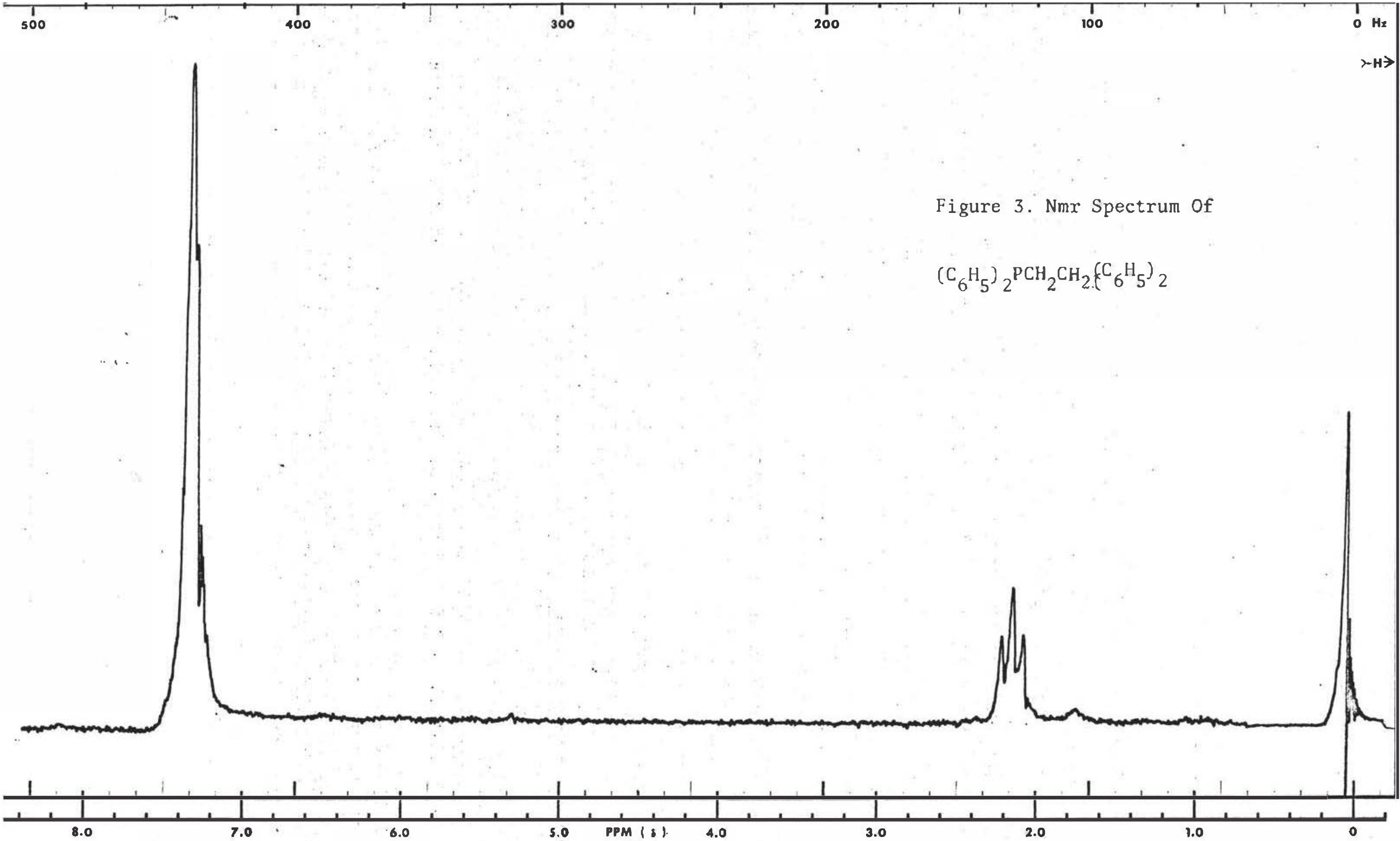


Figure 3. Nmr Spectrum Of

$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

MANUAL

VEEP OFFSET (Hz): 00

ECTRUM AMPLITUDE: 12.5

ITEGRAL AMPLITUDE:

INNING RATE (RPS):

SWEEP TIME (SEC): 50 | 250 (250)

SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500 (500)

FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 (2)

RF POWER LEVEL: (.05)

AUTO ☐

SAMPLE: $Ph_2P(CH_2)_2PPh_2$

SOLVENT: $CDCl_3$

REMARKS: Free Ligand

varian
analytical instrument division

DATE:

OPERATOR:

60 MHz NMR
SPECTRUM NO. DK-40-A

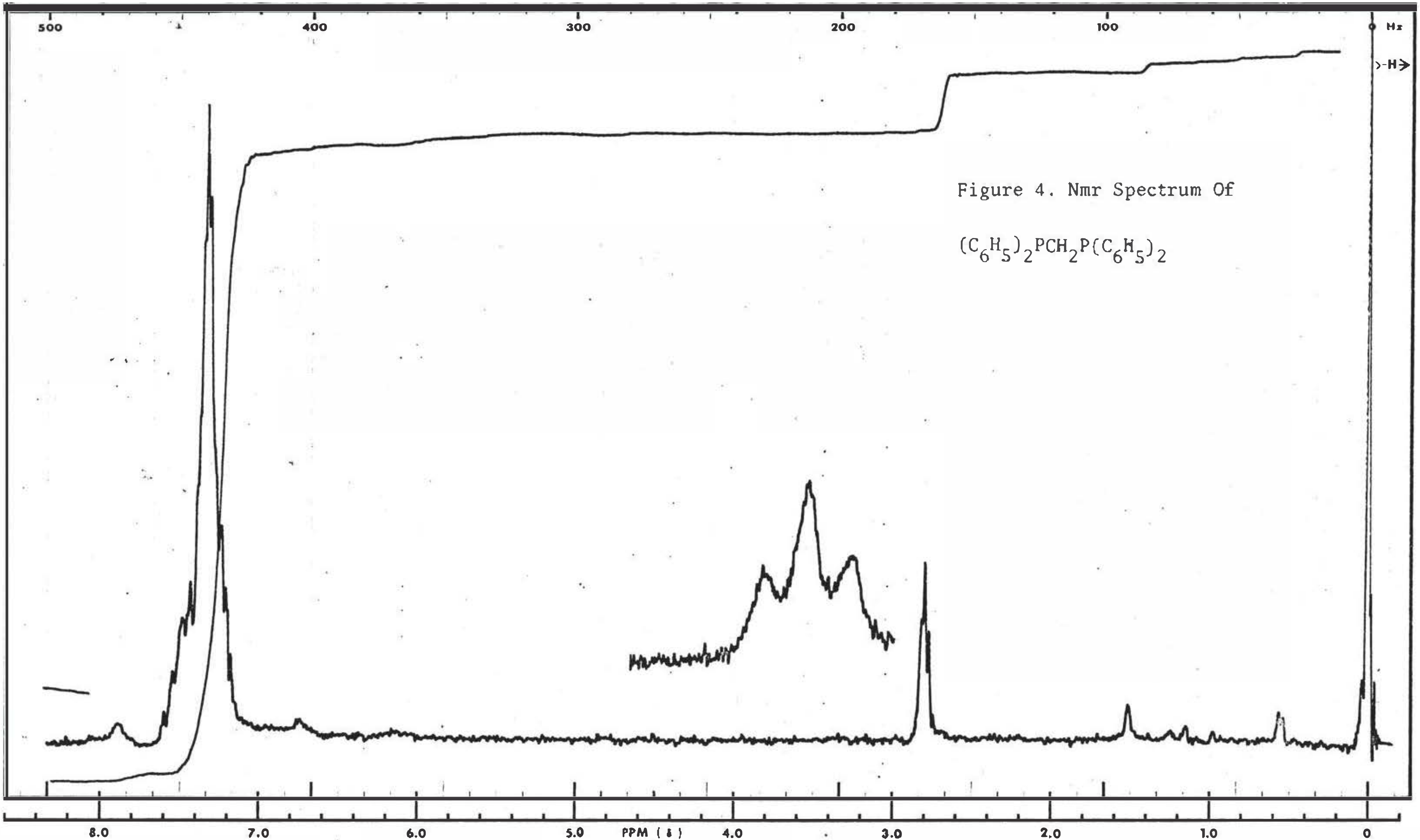


Figure 4. Nmr Spectrum Of

$(C_6H_5)_2PCH_2P(C_6H_5)_2$

MANUAL

SWEEP OFFSET (Hz): 145
SPECTRUM AMPLITUDE: 40
INTEGRAL AMPLITUDE: ~7
SPINNING RATE (RPS): 40

SWEEP TIME (SEC): ☒ 50 ☐ 250
SWEEP WIDTH (Hz): ☐ 25 ☒ 50 ☐ 100 ☐ 250 ☒ 500
FILTER: ☐ 1 ☒ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8
RF POWER LEVEL:

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

SOLVENT:

REMARKS:

$\phi h_2 PCH_2 PPh_2$

varian
analytical instrument division

DATE: 1/21/70

OPERATOR:

60 MHz NMR
SPECTRUM NO.

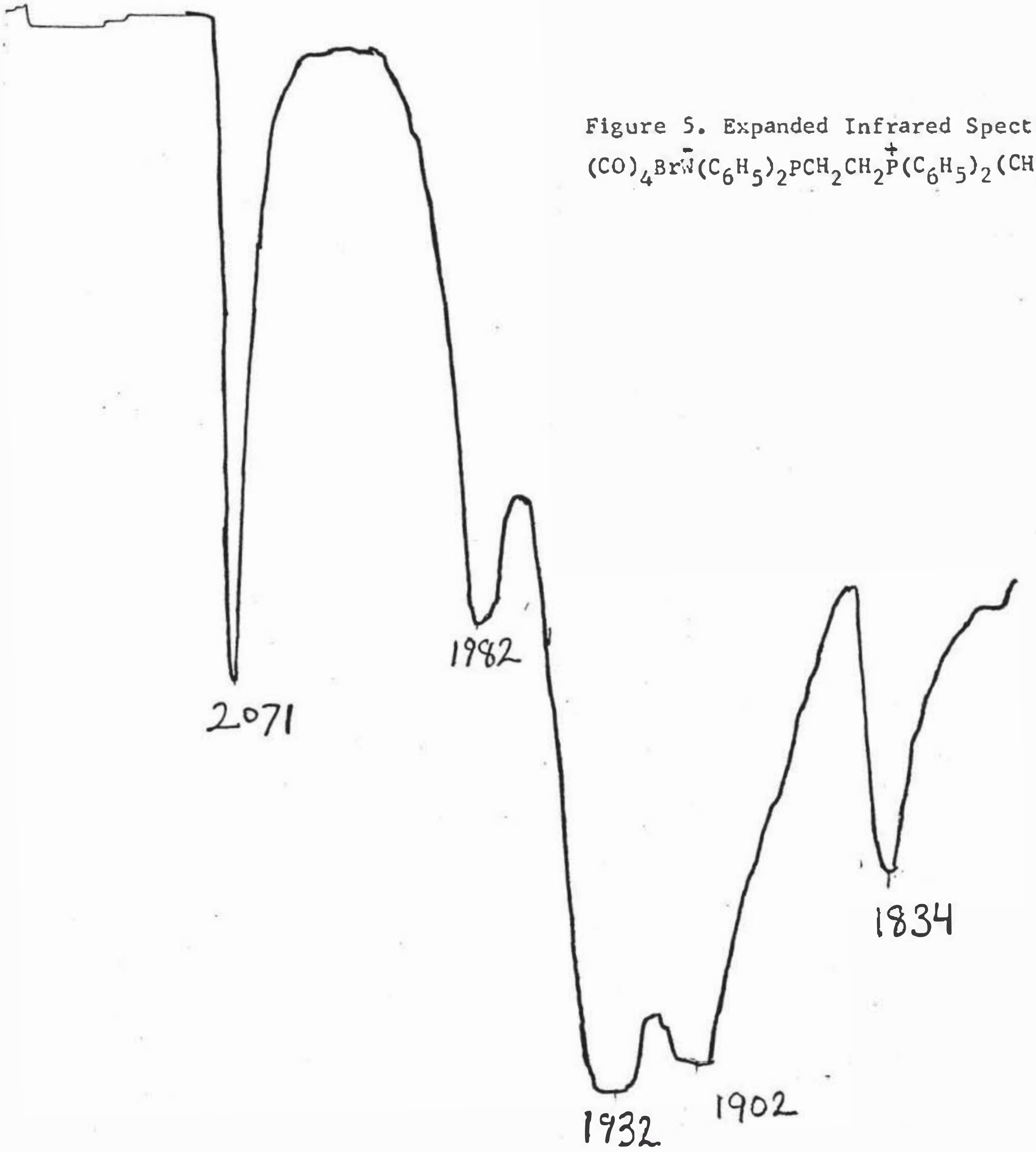
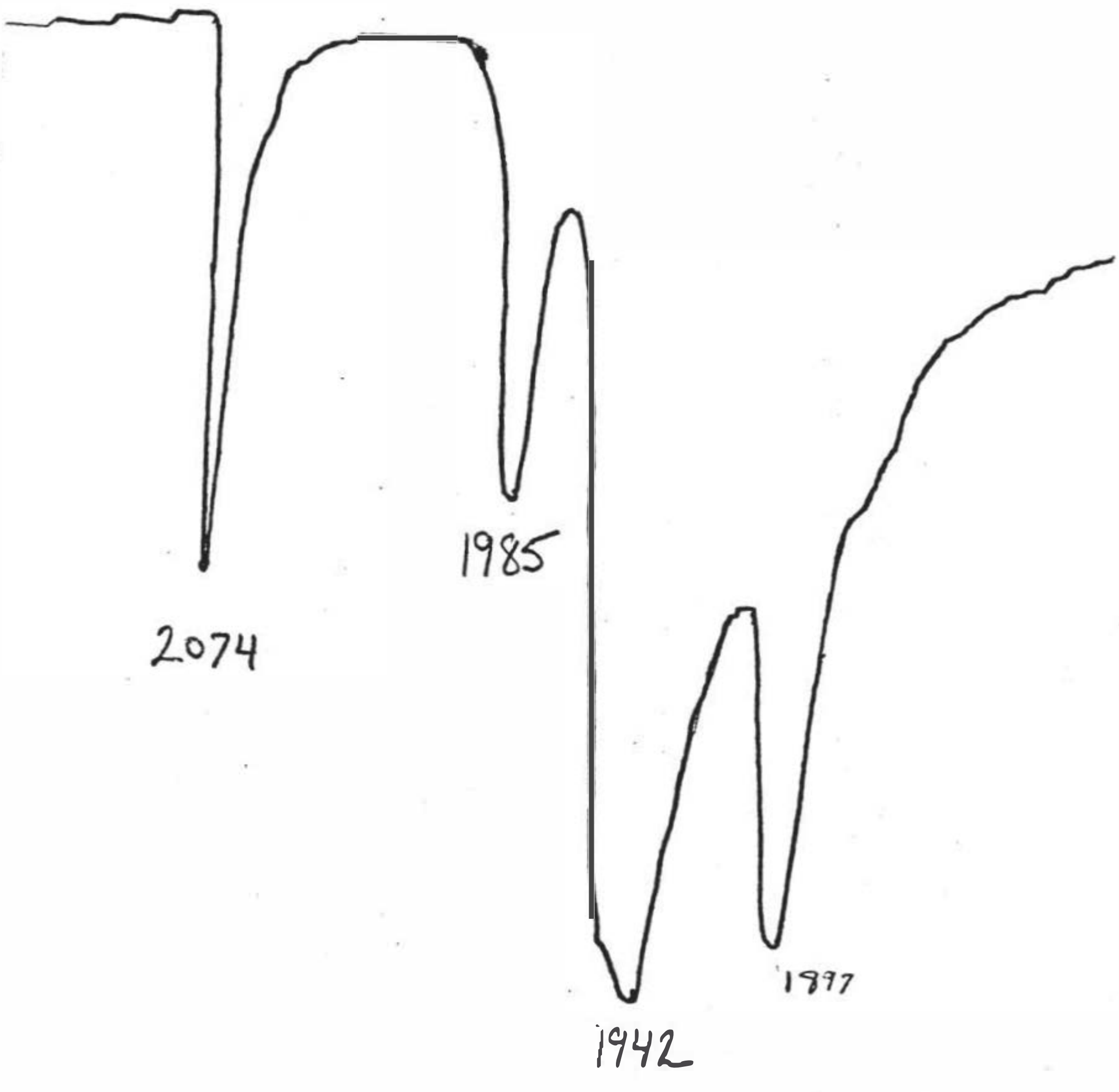


Figure 5. Expanded Infrared Spectrum of $(CO)_4Br\overset{-}{W}(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)$

Figure 6. Expanded Infrared Spectrum of $(CO)_4Br\bar{W}(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)$



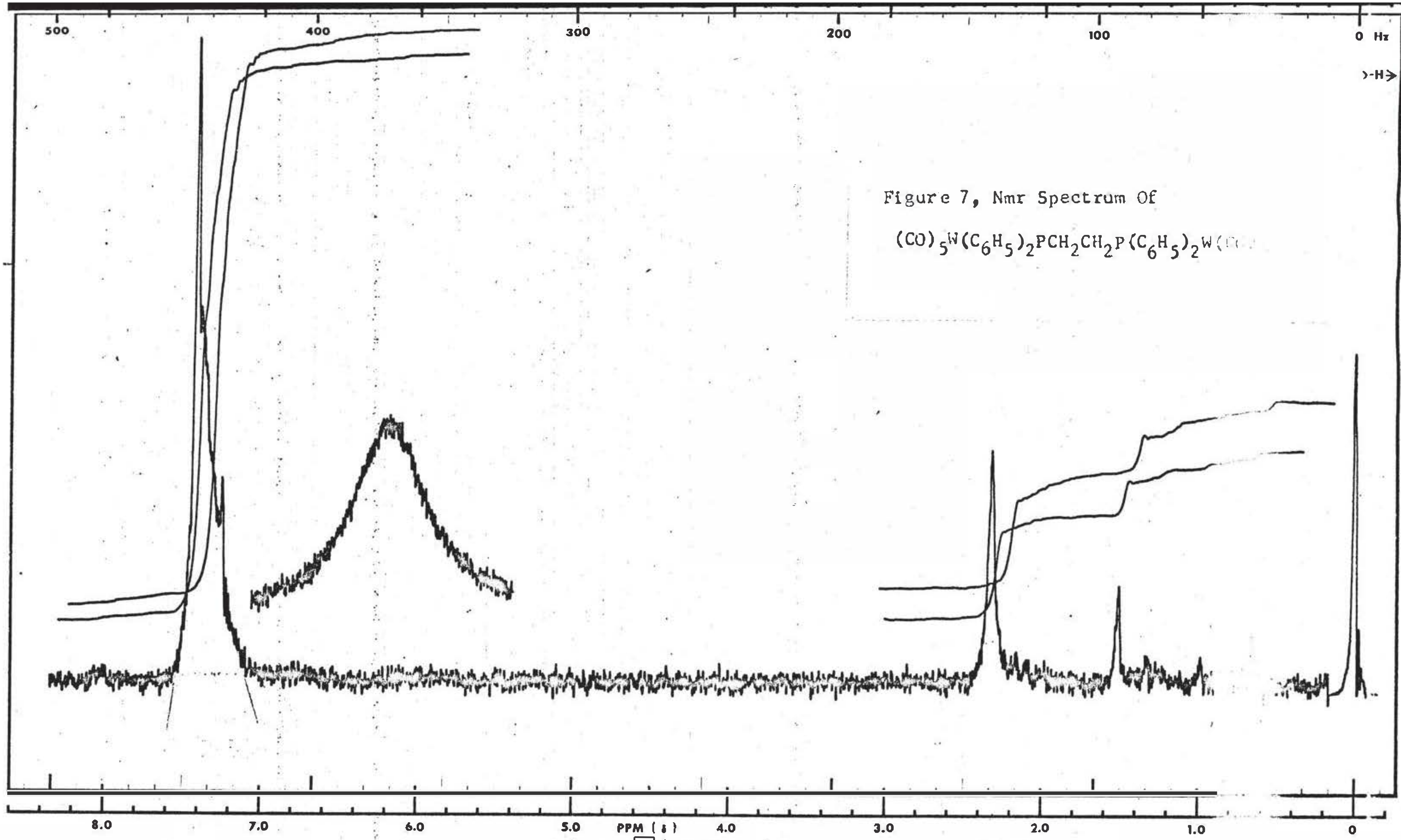


Figure 7, Nmr Spectrum Of

$(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2W($

MANUAL

SWEEP OFFSET (Hz): 110
SPECTRUM AMPLITUDE: 40
INTEGRAL AMPLITUDE: 6.5
SPINNING RATE (RPS): 40

SWEEP TIME (SEC): [illegible]
SWEEP WIDTH (Hz): 25 50 ~~100~~ 250 ~~500~~
FILTER: ☒ 2 3 4 5 6 7 8
RF POWER LEVEL: 0.1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $(CO)_5WPh_2PCH_2CH_2PPh_2W(CO)_5$
REMARKS:

SOLVENT: $CDCl_3$

varian
analytical instrument division

DATE: 10-19-70

OPERATOR:

60 MHz NMR
SPECTRUM NO. DK- 12

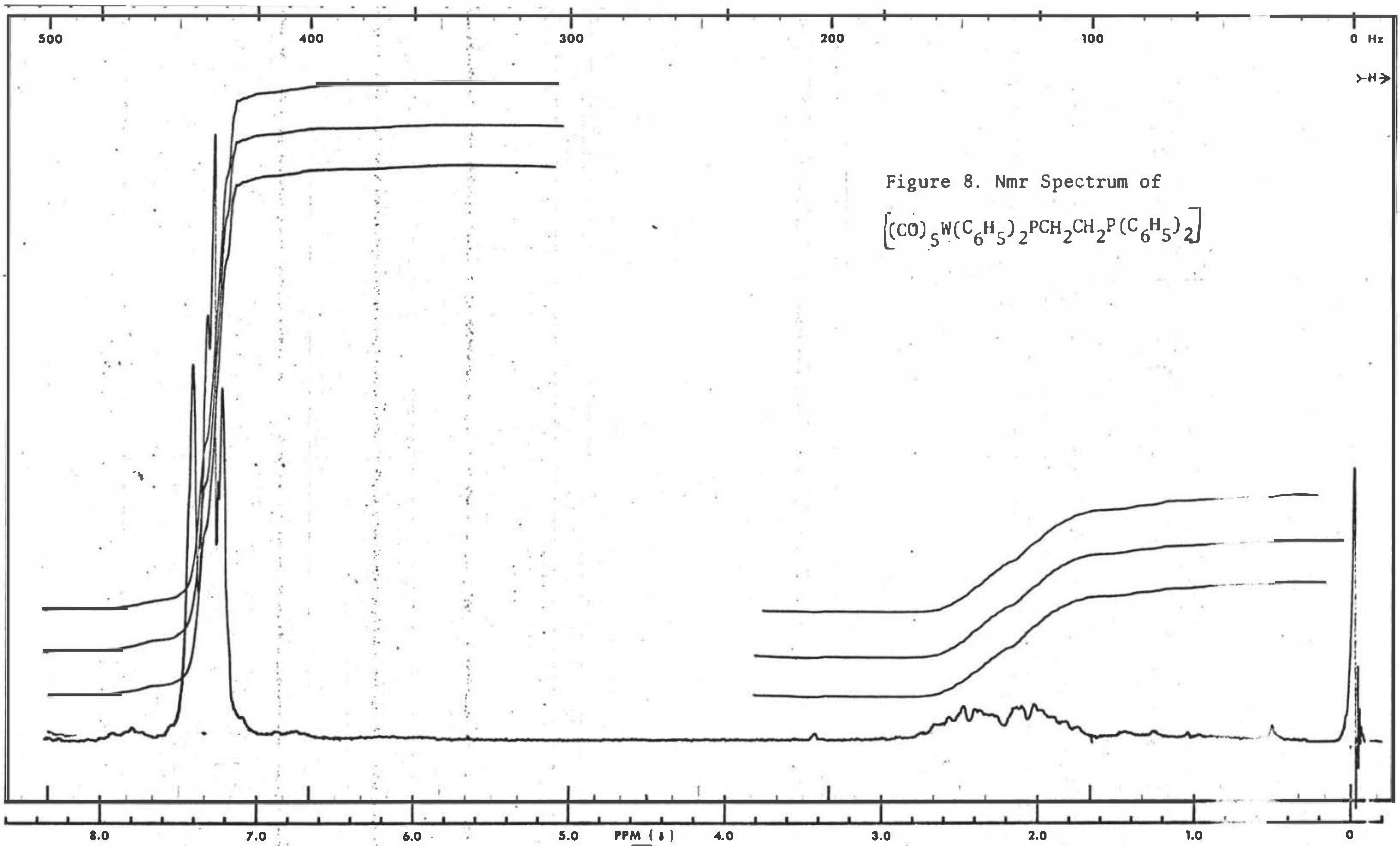


Figure 8. Nmr Spectrum of $[(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$

MANUAL

AUTO ☐

SWEEP OFFSET (Hz): 00

SPECTRUM AMPLITUDE: 6.3

INTEGRAL AMPLITUDE: 6

SPINNING RATE (RPS): 32

SWEEP TIME (SEC): [✓ 50] 250 (250)

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500] (500)

FILTER: ☒ 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: .075 (.05)

SAMPLE: $(CO)_5W Ph_2PCH_2CH_2PPh_2$

SOLVENT: $CDCl_3$

REMARKS:

43

varian
analytical instrument division

DATE: 10/15/70

OPERATOR:

60 MHz NMR
SPECTRUM NO. D 11

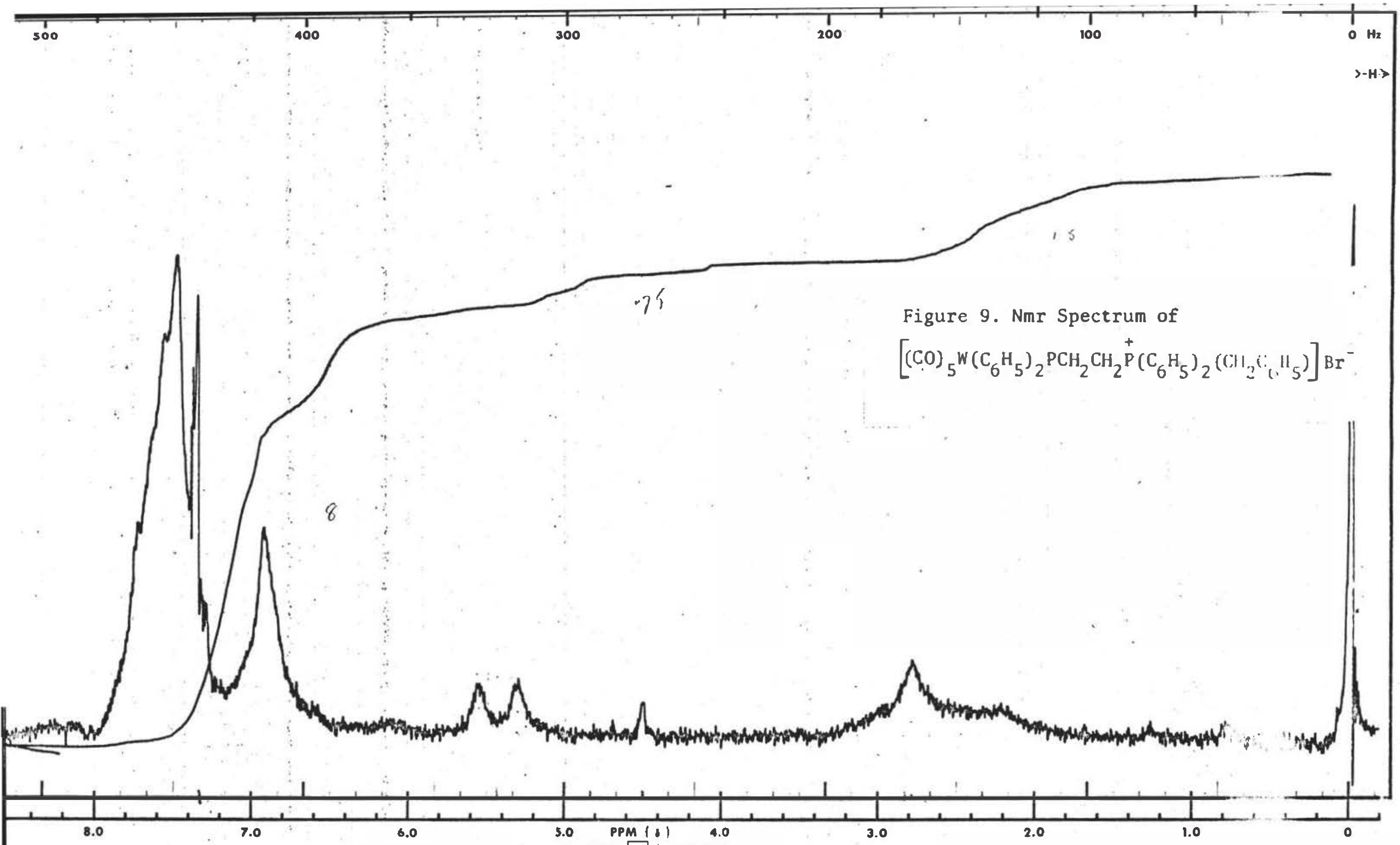


Figure 9. Nmr Spectrum of $\left[(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\right]Br^-$

	MANUAL	AUTO ☐
WEEP OFFSET (Hz):	SWEEP TIME (SEC): 50 250	(250)
PECTRUM AMPLITUDE:	SWEEP WIDTH (Hz): 25 50 100 250 500	(500)
NTEGRAL AMPLITUDE:	FILTER: ☒ 2 3 4 5 6 7 8	(2)
PINNING RATE (RPS): 43	RF POWER LEVEL: 0.1	(.05)

SAMPLE:

SOLVENT:

REMARKS:

varian
analytical instrument division

DATE:

OPERATOR:

60 MHz NMR
SPECTRUM NO. DK

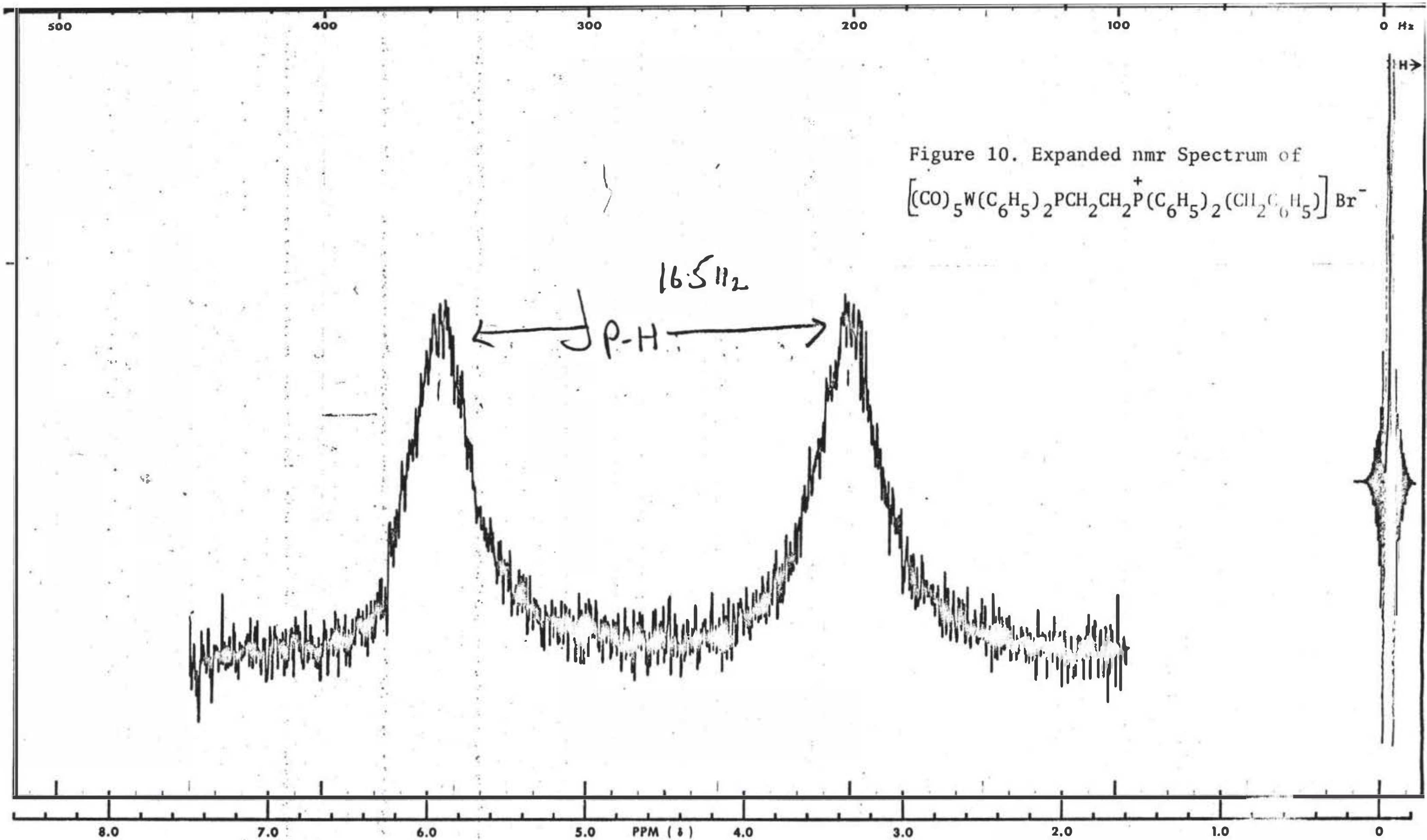


Figure 10. Expanded nmr Spectrum of $[(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)]Br^-$

MANUAL

AUTO ☐

SAMPLE:

REMARKS:

SWEEP OFFSET (Hz): 300

SPECTRUM AMPLITUDE: 160

INTEGRAL AMPLITUDE:

SPINNING RATE (RPS): 30

SWEEP TIME (SEC): 50 250 (250)

SWEEP WIDTH (Hz): 25 50 100 250 500 (500)

FILTER: 1 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: 0.1 (.05)

SOLVENT:

+vely charged 1st lig

2.8-C5
136

varian
analytical instrument division

DATE: 11/12/70

OPERATOR:

60 MHz NMR
SPECTRUM NO.

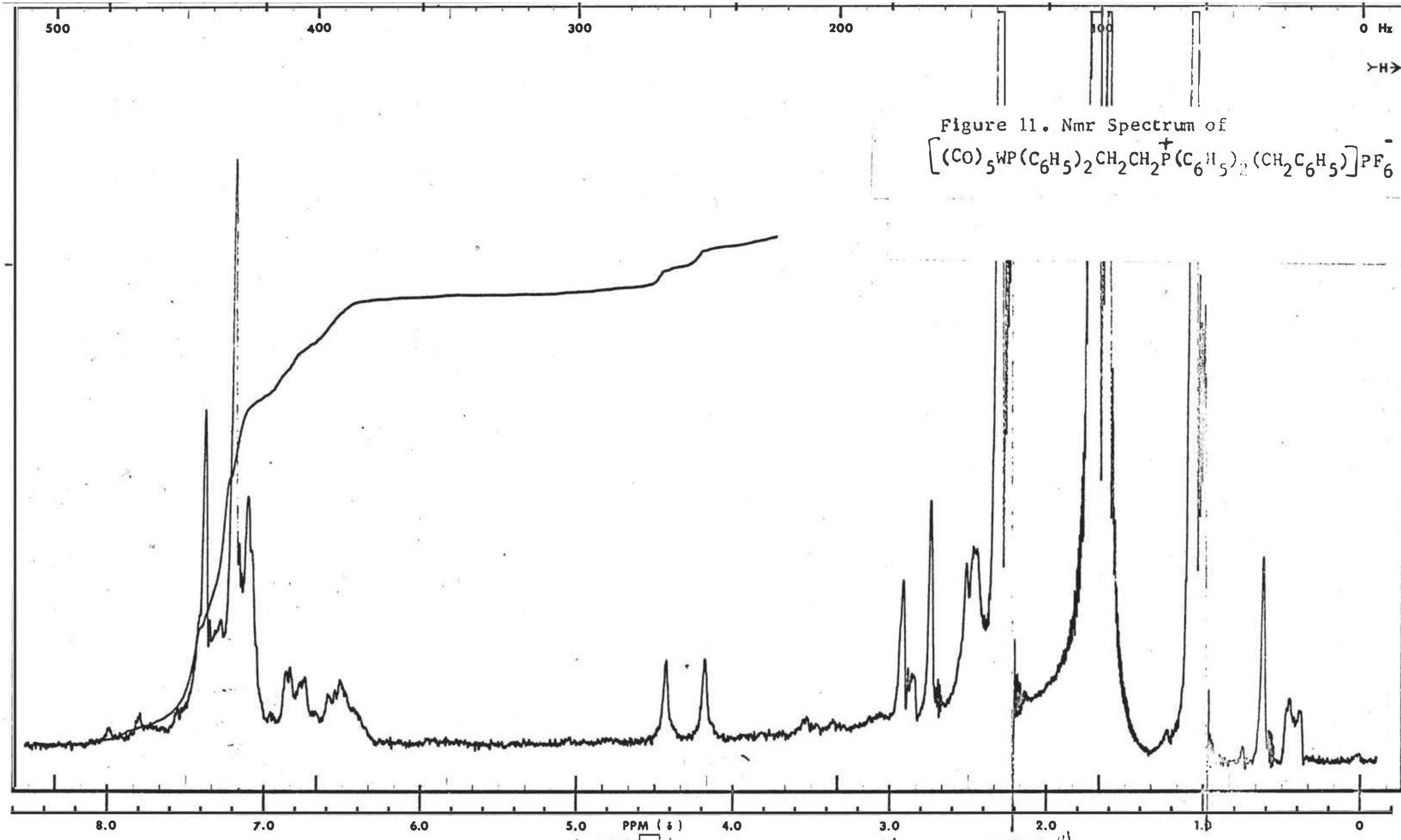


Figure 11. Nmr Spectrum of $[(CO)_5WP(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)]PF_6^-$

MANUAL

SWEEP OFFSET (Hz): 0.0

SPECTRUM AMPLITUDE: 20

INTEGRAL AMPLITUDE: 5

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 [✓ 250]

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]

FILTER: [✓ 1] 2 3 4 5 6 7 8

RF POWER LEVEL: 0.05

AUTO ☐

(250)

(500)

(2)

(.05)

SAMPLE: $(CO)_5W\,PPh_2CH_2CH_2\overset{Ph_2}{\underset{(+)}{P}}-CH_2C_6H_5\ PF_6^-$

REMARKS:

SOLVENT: $CH_3\underset{O}{\overset{\|}{C}}CH_3$

varian
analytical instrument division

DATE:

OPERATOR:

60 MHz NMR
SPECTRUM NO.

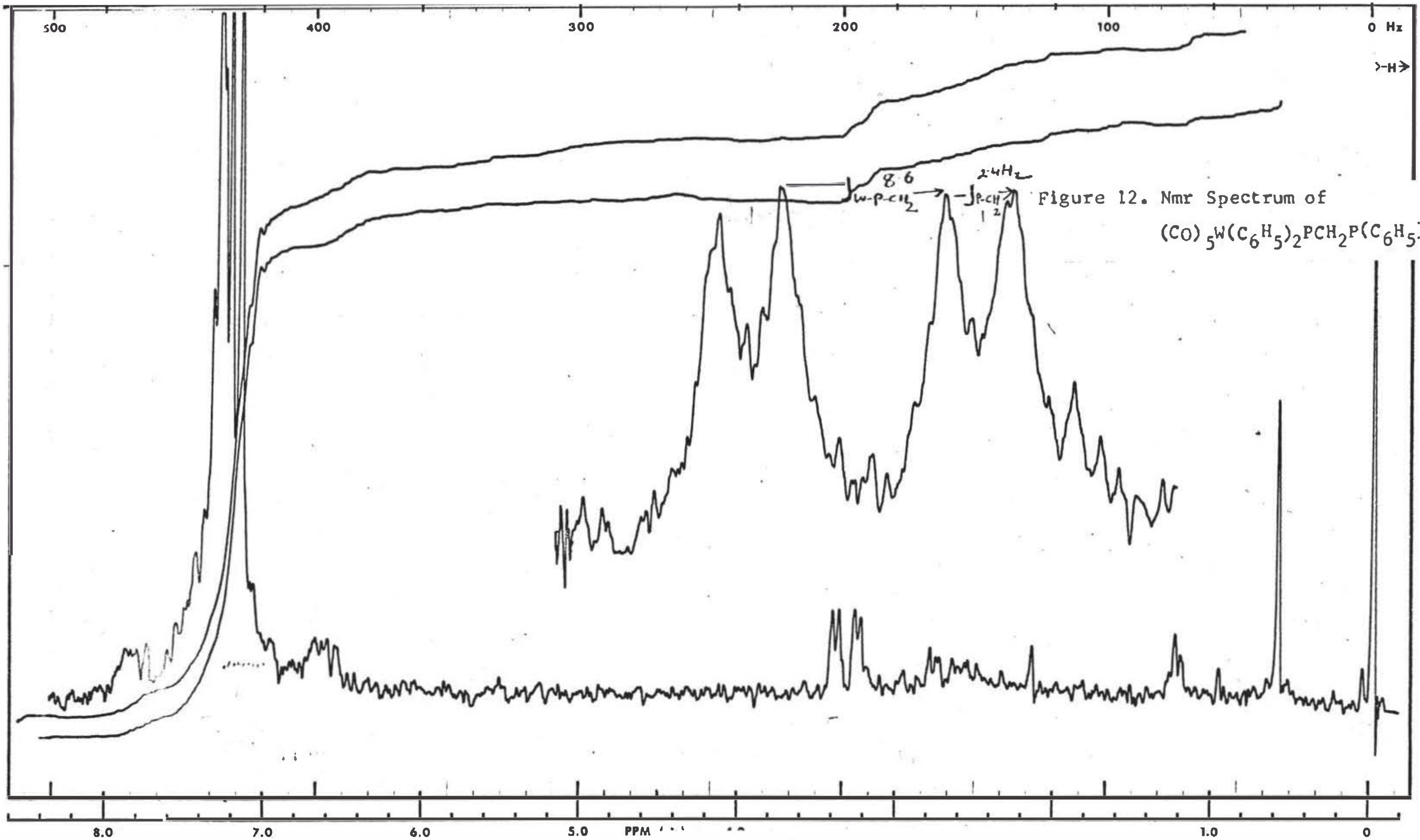


Figure 12. Nmr Spectrum of $(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5$

MANUAL

AUTO ☐

SWEEP OFFSET (Hz): [illegible]
SPECTRUM AMPLITUDE: 80
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 [✓ 250] (250)
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500] (500)
FILTER: 1 2 [✓ 3] 4 5 6 7 8 (2)
RF POWER LEVEL: .05 (.05)

varian
analytical instrument division

DATE: 10/9/70

OPERATOR:

SPECTRUM NO.

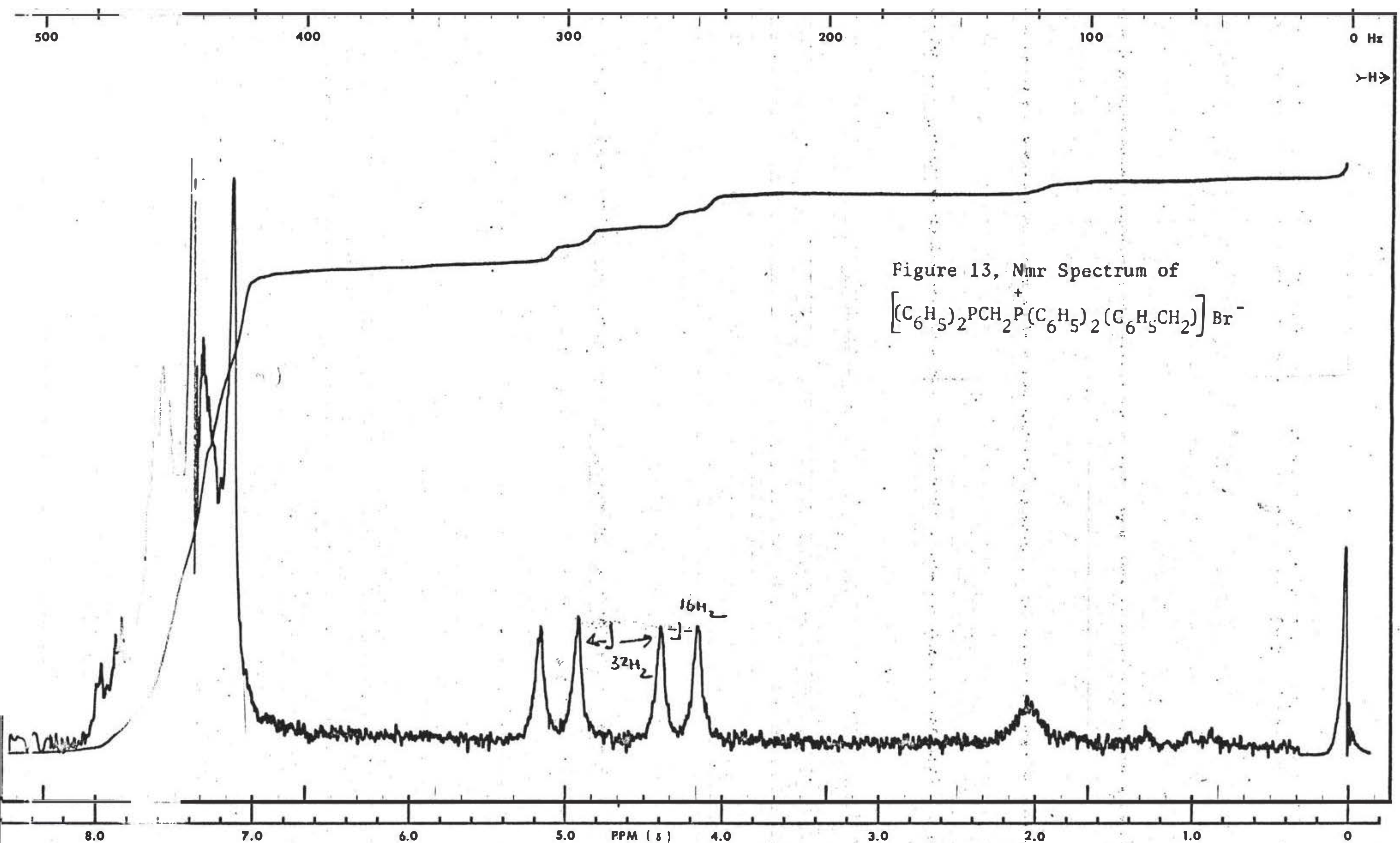


Figure 13, Nmr Spectrum of $\left[(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2(C_6H_5CH_2)\right]Br^-$

MANUAL

SWEEP OFFSET (Hz): [illegible]
SPECTRUM AMPLITUDE: [illegible]
INTEGRAL AMPLITUDE: [illegible]
SPINNING RATE (RPS): [illegible]

SWEEP TIME (SEC): ☒ 50 ☒ 250
SWEEP WIDTH (Hz): 25 50 100 250 ☒ 500
FILTER: 1 ☒ 2 3 4 5 6 7 8
RF POWER LEVEL: .075

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $Ph_2PCH_2\overset{+}{P}Ph_2CH_2Ph$ Br^-

SOLVENT: $CDCl_3$

REMARKS:

varian
analytical instrument division

fig 13
DATE: 10/31/2

OPERATOR:

60 MHz NMR
SPECTRUM NO. DK-41-B

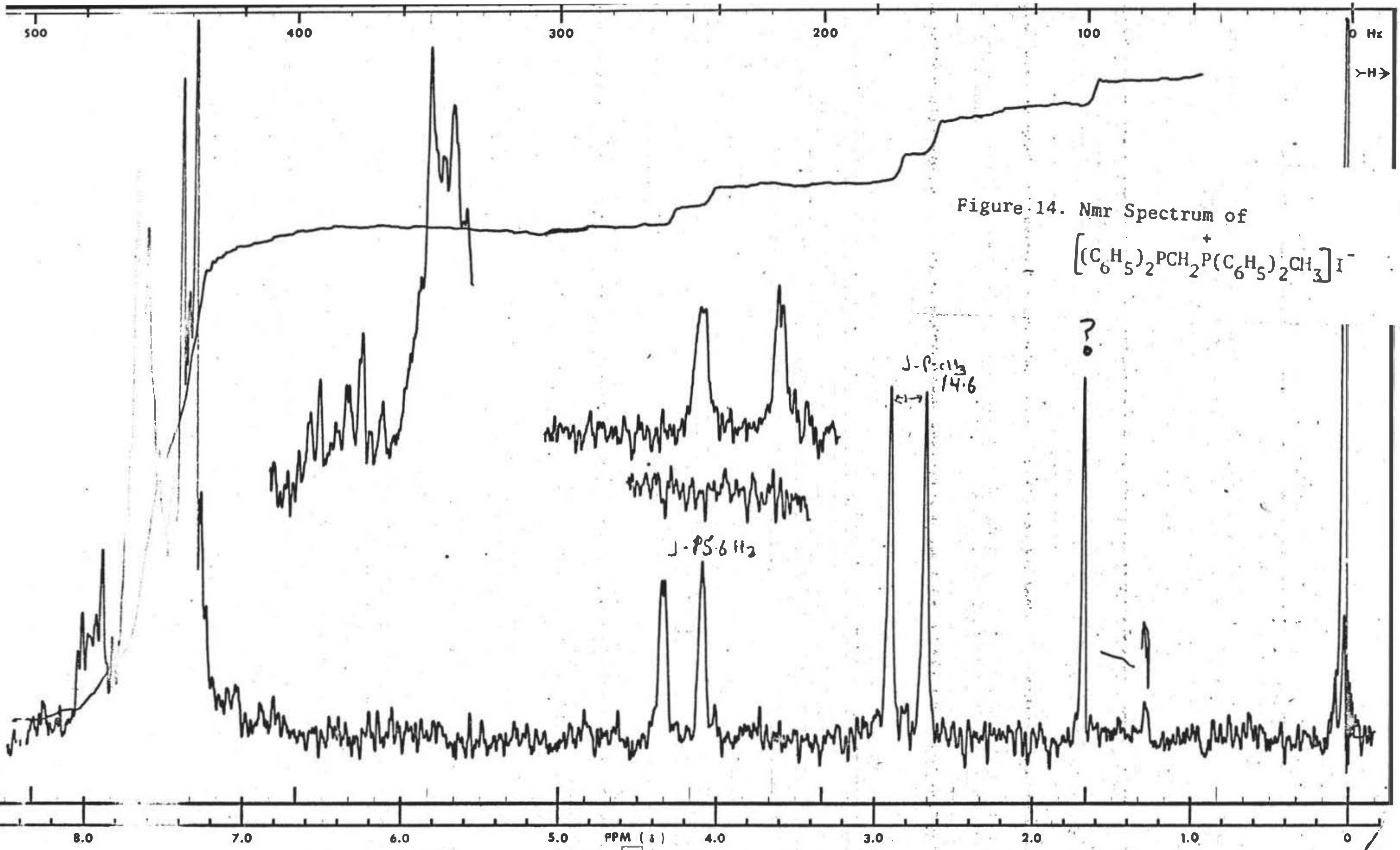


Figure 14. Nmr Spectrum of $[(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3]I^-$

WEE OFFSET (Hz):		SWEEP TIME (SEC): ☐ 50 ☐ 250	(250)
PECTRUM AMPLITU		SWEEP WIDTH (Hz): ☐ 25 ☐ 50 ☐ 100 ☐ 250 ☐ 500	(500)
NTEGRAL AMPLITU		FILTER: ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8	(2)
PINNING RATE (RPS		RF POWER LEVEL:	(.05)

MANUAL

AUTO ☐

SAMPLE: $Ph_2PCH_2\overset{+}{P}Ph_2CH_3\ I^-$

SOLVENT:

REMARKS:

2.25 ppm

varian analytical instrument division

DATE: 12/23/70

OPERATOR:

60 MHz NMR SPECTRUM NO.

49

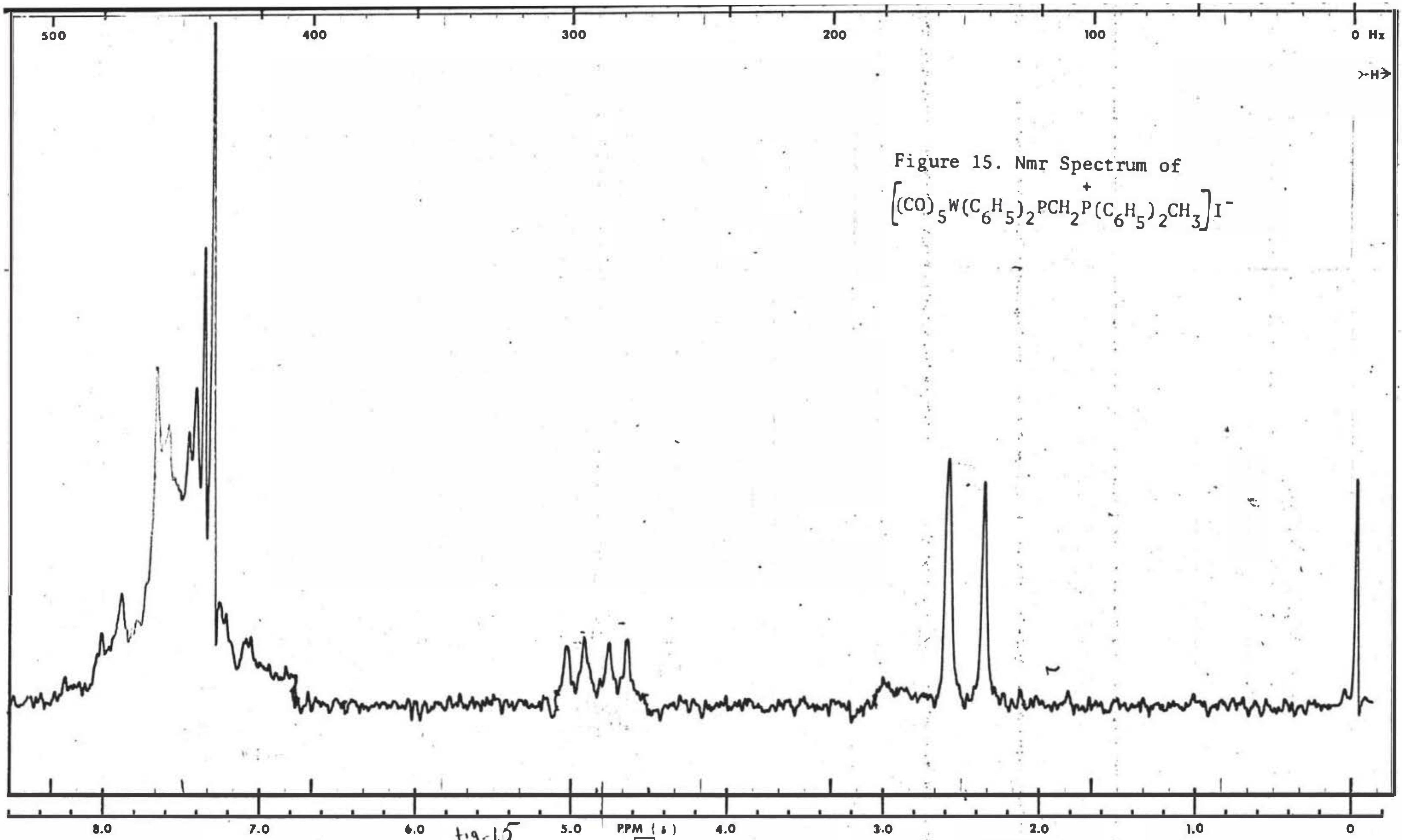


Figure 15. Nmr Spectrum of $\left[(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3\right]I^-$

fig-15

MANUAL

SWEEP OFFSET (Hz): -------

SPECTRUM AMPLITUDE: -------

INTEGRAL AMPLITUDE: -------

SPINNING RATE (RPS): -------

SWEEP TIME (SEC): 50 [✓ 250]

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]

FILTER: 1 2 ☒ 4 5 6 7 8

RF POWER LEVEL: -------

AUTO ☐

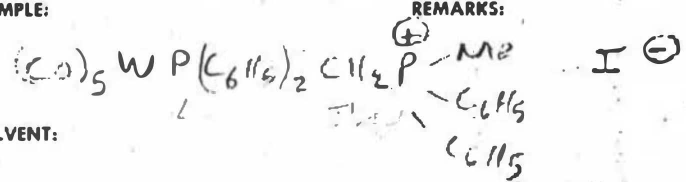
(250)

(500)

(2)

(.05)

SAMPLE:



$(CO)_5WP(C_6H_5)_2CH_2\overset{\oplus}{P}(Me)(C_6H_5)(C_6H_5)\ I^{\ominus}$

SOLVENT:

REMARKS:

50

fig-13

DATE: 1/15/71

OPERATOR:

varian
analytical instrument division

60 MHz NMR
SPECTRUM NO.

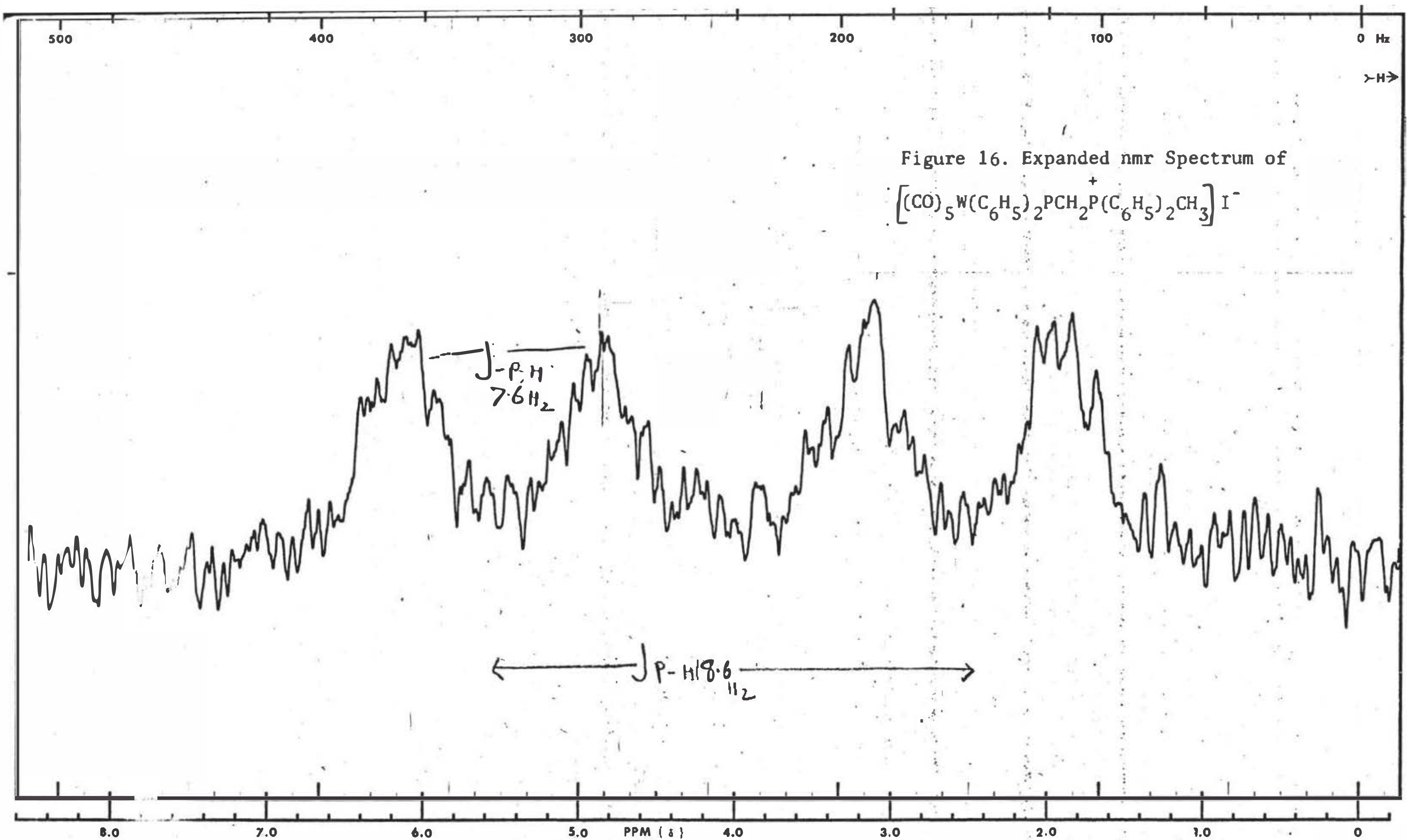


Figure 16. Expanded nmr Spectrum of $[(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2CH_3]\ I^-$

MANUAL

AUTO ☐

SWEEP OFFSET (Hz): ------

SPECTRUM AMPLITUDE: 100

INTEGRAL AMPLITUDE: ------

SPINNING RATE (RPS): ------

SWEEP TIME (SEC): 50 [✓ 250] (250)

SWEEP WIDTH (Hz): 25 [✓ 50] 100 250 500 (500)

FILTER: 1 2 3 [✓ 4] 5 6 7 8 (2)

RF POWER LEVEL: 0.05 (.05)

SAMPLE: $(CO)_5WPh_2PCH_2\overset{+}{P}$ -Me -C_6H_5 -C_6H_5

REMARKS: methylene region

SOLVENT: $CDCl_3$

varian
analytical instrument division

DATE: 12/31/79

OPERATOR:

60 MHz NMR
SPECTRUM NO.

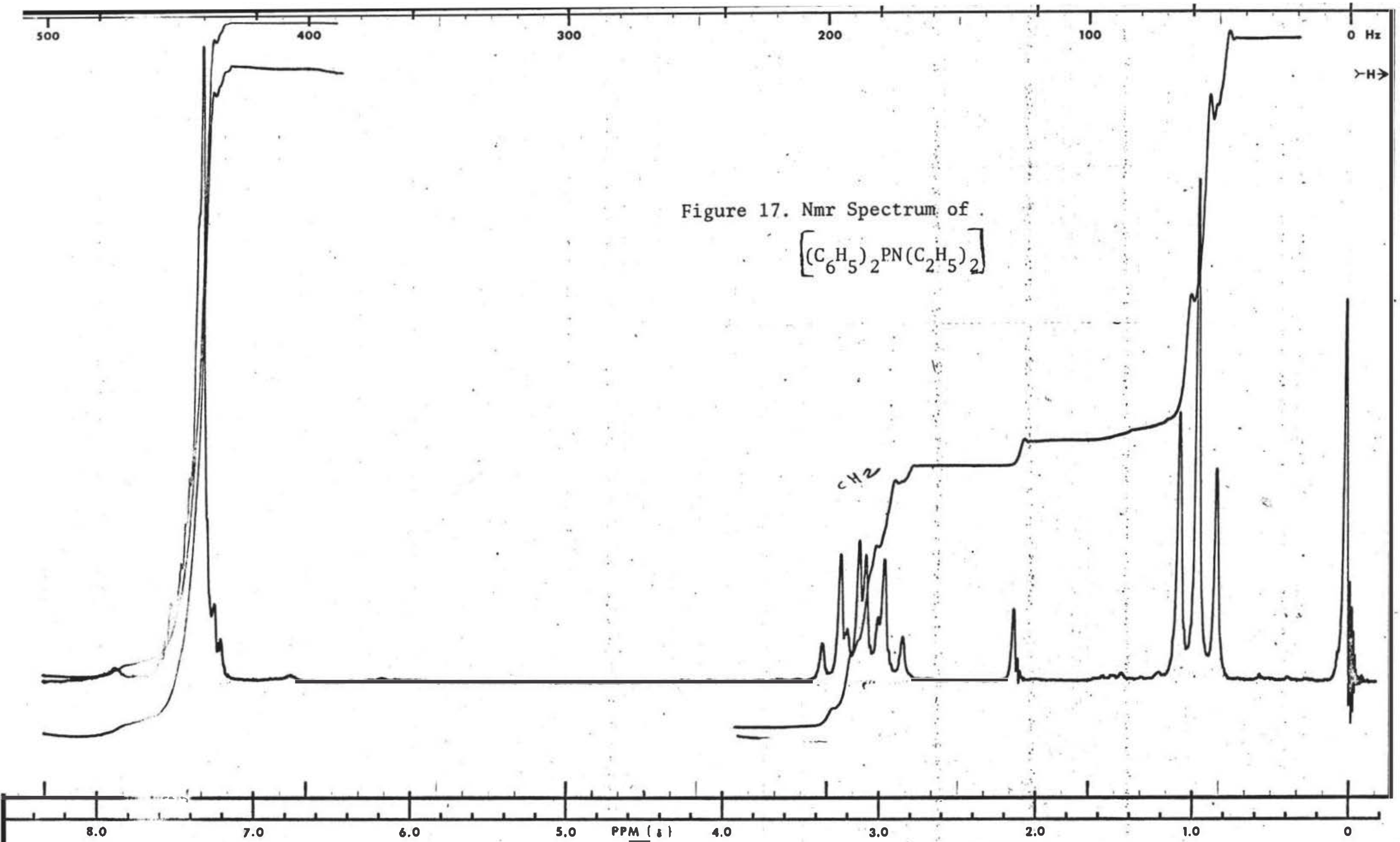


Figure 17. Nmr Spectrum of $[(C_6H_5)_2PN(C_2H_5)_2]$

	MANUAL	AUTO ☐	SAMPLE: $(C_6H_5)_2PNEt_2$
SWEEP OFFSET (Hz):	SWEEP TIME (SEC): 50 [✓ 250]	(250)	
SPECTRUM AMPLITUDE: 3	SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]	(500)	
INTEGRAL AMPLITUDE: 8	FILTER: [✓ 1] 2 3 4 5 6 7 8	(2)	
SPINNING RATE (RPS): 2	RF POWER LEVEL: .075	(.05)	SOLVENT:

REMARKS:

OK 39-1

varian analytical instrument division

DATE: 10 - 1?

OPERATOR:

60 MHz NMR SPECTRUM NO.

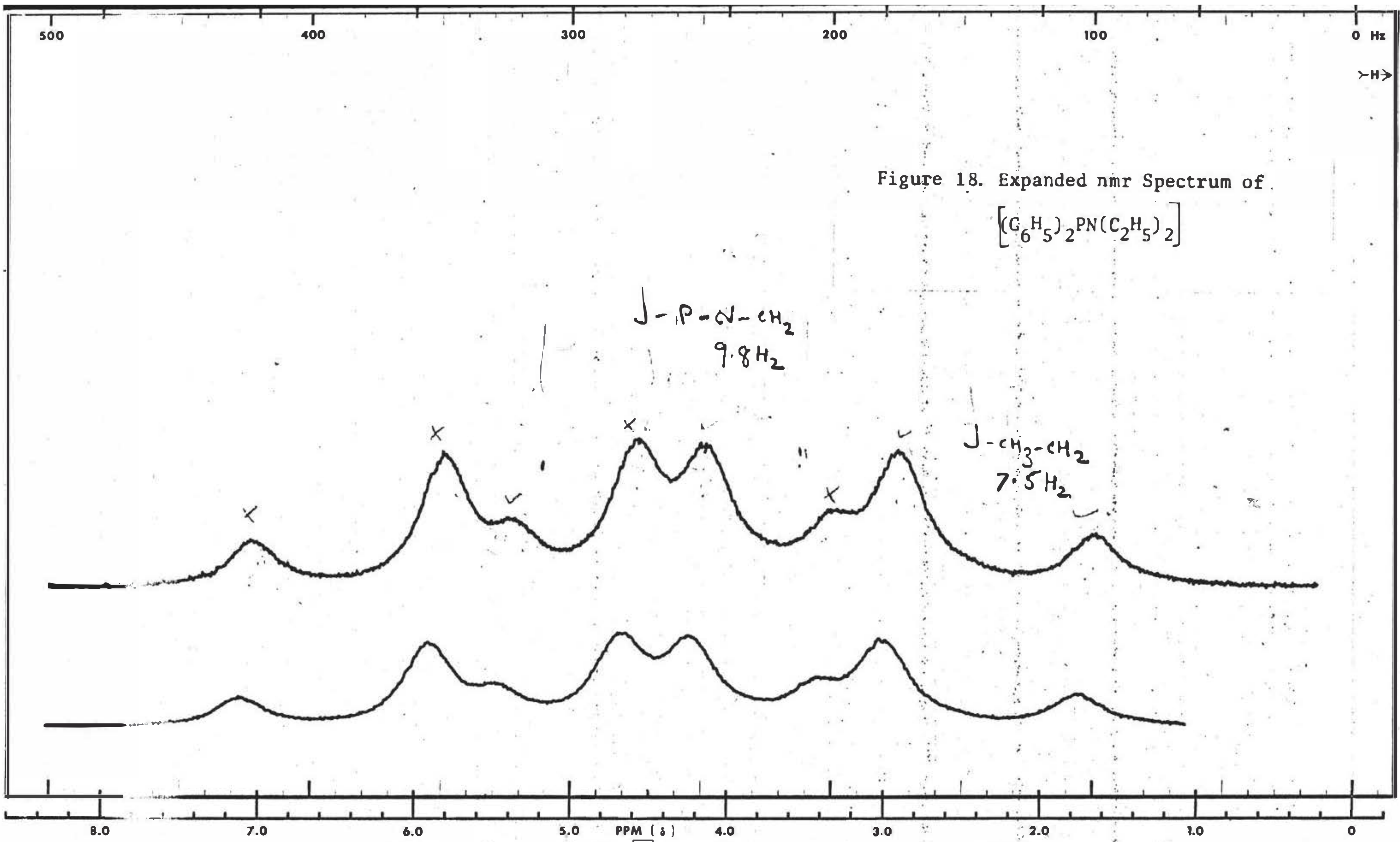


Figure 18. Expanded nmr Spectrum of $[(C_6H_5)_2PN(C_2H_5)_2]$

SWEEP OFFSET (Hz): [illegible]	MANUAL	AUTO ☐	SAMPLE: Ph_2PNEt_2
SPECTRUM AMPLITUDE: [illegible]	SWEEP TIME (SEC): 50 [✓ 250]	(250)	
INTEGRAL AMPLITUDE: [illegible]	SWEEP WIDTH (Hz): 25 [✓ 50] 100 250 500	(500)	
SPINNING RATE (RPS): [illegible]	FILTER: [✓ 1] 2 3 4 5 6 7 8	(2)	
	RF POWER LEVEL:	(.05)	SOLVENT:

REMARKS:

1

varian
analytical instrument division

DATE: 10/70

OPERATOR:

60 MHz NMR
SPECTRUM NO. DK-39-1

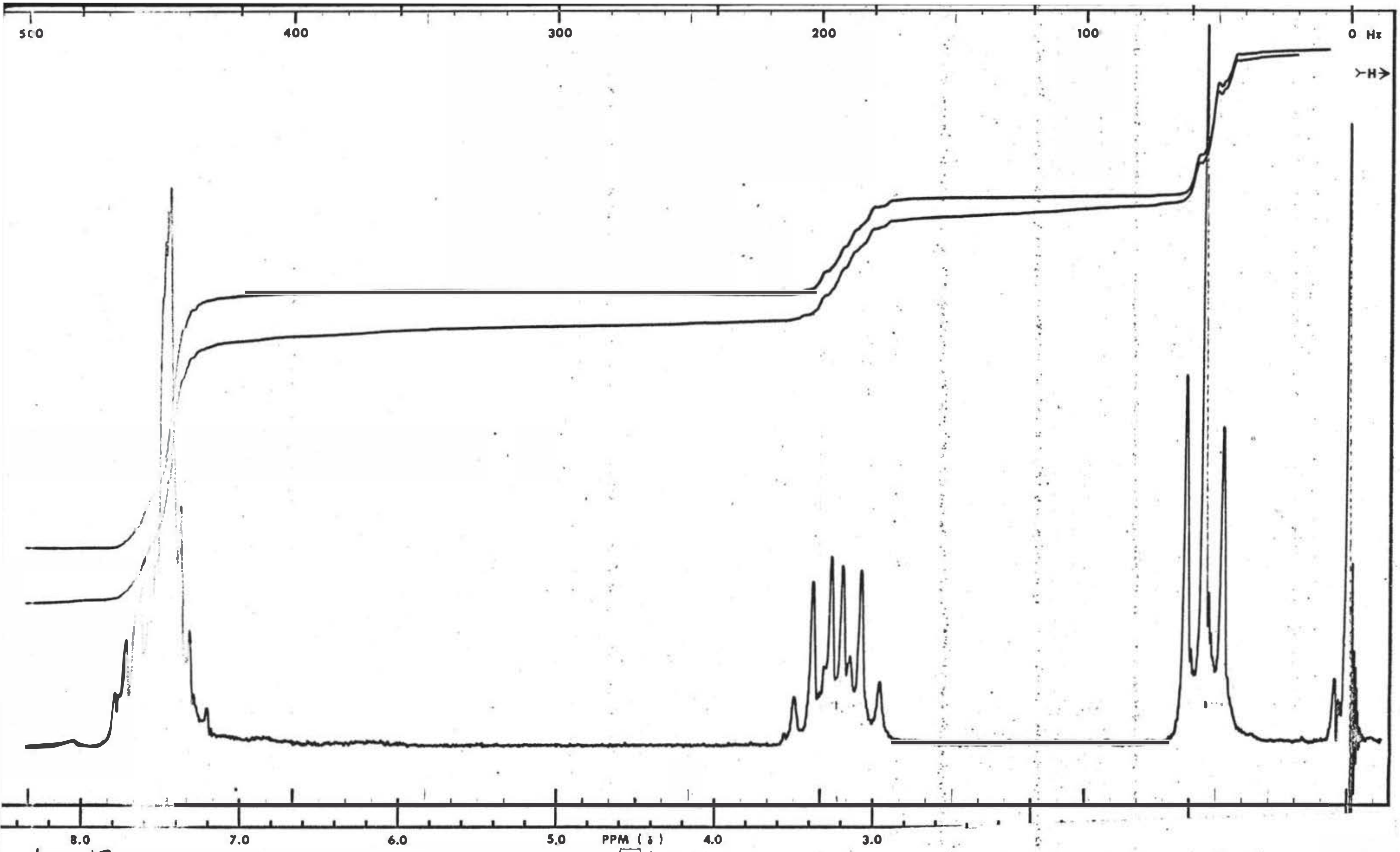


fig-19

EEP OFFSET (Hz): 0
ECTRUM AMPLITUDE: 10
TEGRAL AMPLITUDE: 40
INNING RATE (RPS): 40

MANUAL
SWEEP TIME (SEC): 50 [✓ 250]
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]
FILTER: [✓ 1] 2 3 4 5 6 7 8
RF POWER LEVEL: .075

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:
SOLVENT: CDCl3

varian
analytical instru[illegible] division

DATE: 10/70
OPERATOR:
60 MHz NMR SPECTRUM NO. OK-40-A

Figure 19. Nmr Spectrum of $[W(CO)_5(C_6H_5)_2PN(C_2H_5)_2]$

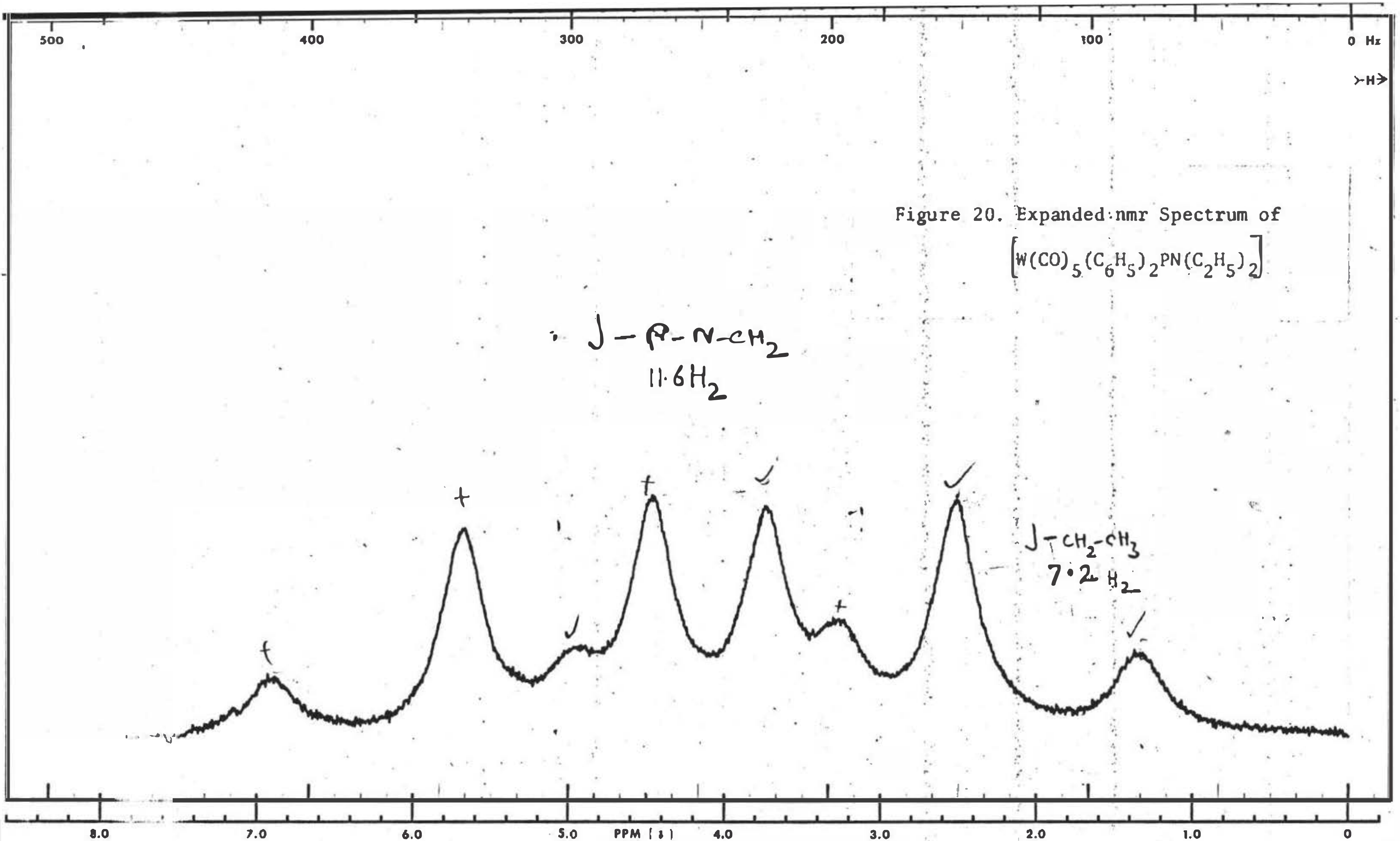


Figure 20. Expanded nmr Spectrum of $[W(CO)_5(C_6H_5)_2PN(C_2H_5)_2]$

J – P – N – CH_2
11·6 Hz

J – CH_2 – CH_3
7·2 Hz

MANUAL

SWEEP OFFSET (Hz): 70

SPECTRUM AMPLIT: 10

INTEGRAL AMPLITU: 3

SPINNING RATE: 40

SWEEP TIME (SEC): 50 [✓ 250]

SWEEP WIDTH (Hz): 25 [✓ 50] 100 250 500

FILTER: [✓ 1] 2 3 4 5 6 7 8

RF POWER LEVEL: .05

AUTO ☐

(250)

(500)

(2)

(.05)

SAMPLE: $(CO)_5W Ph_2PNEt_2$

SOLVENT: $CDCl_3$

REMARKS:

55

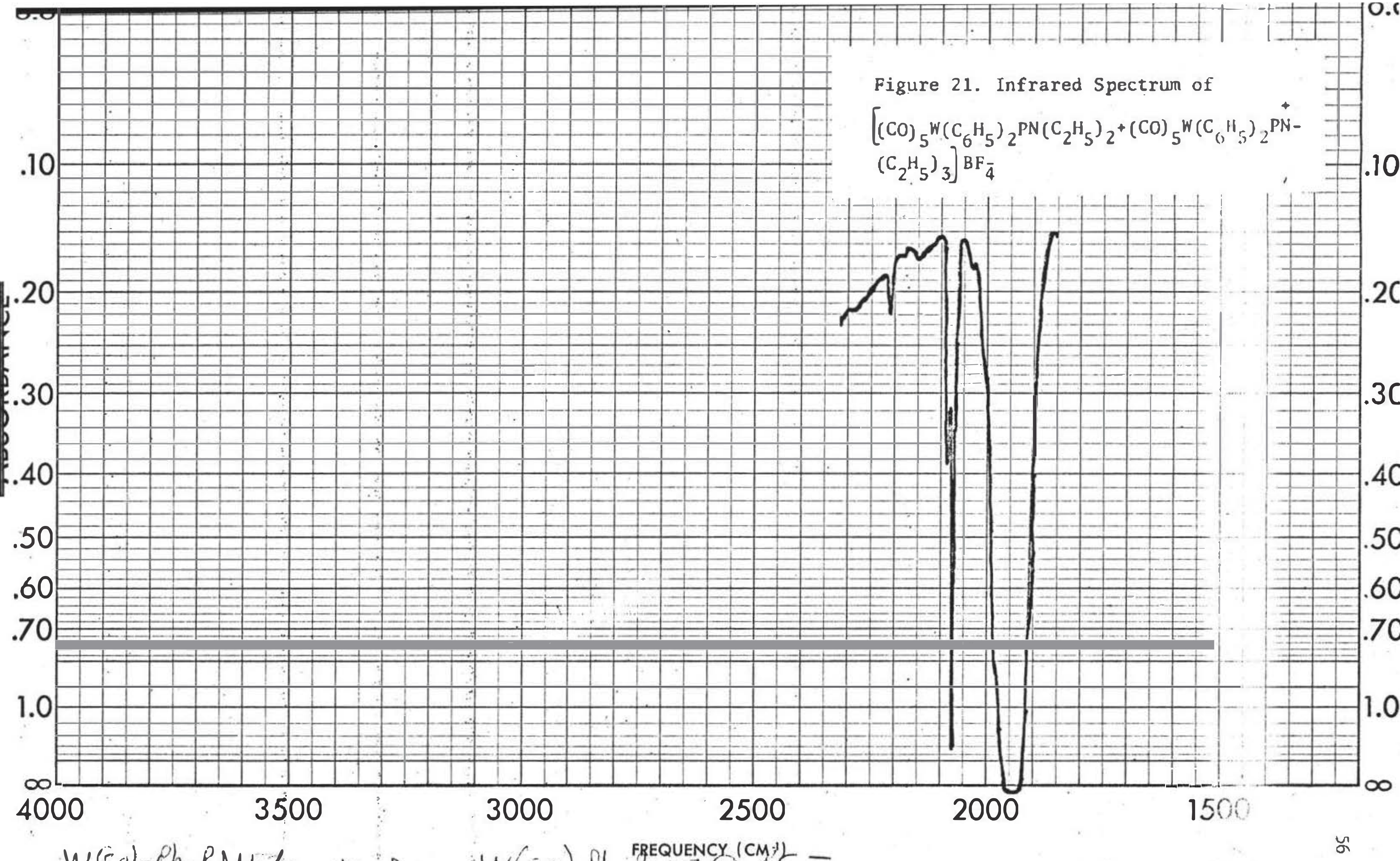
varian analytical instrument division

DATE: 10/70

OPERATOR:

60 MHz NMR SPECTRUM NO.

Figure 21. Infrared Spectrum of $\left[(CO)_5W(C_6H_5)_2PN(C_2H_5)_2 + (CO)_5W(C_6H_5)_2\overset{+}{P}N(C_2H_5)_3\right]BF_4^-$



$W(CO)_5Ph_2PNEt_2$ + Amine $W(CO)_5Ph_2PNEt_3^{\oplus}$ BF_4^-

SAMPLE

ORIGIN

SOLVEN

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS DK-43

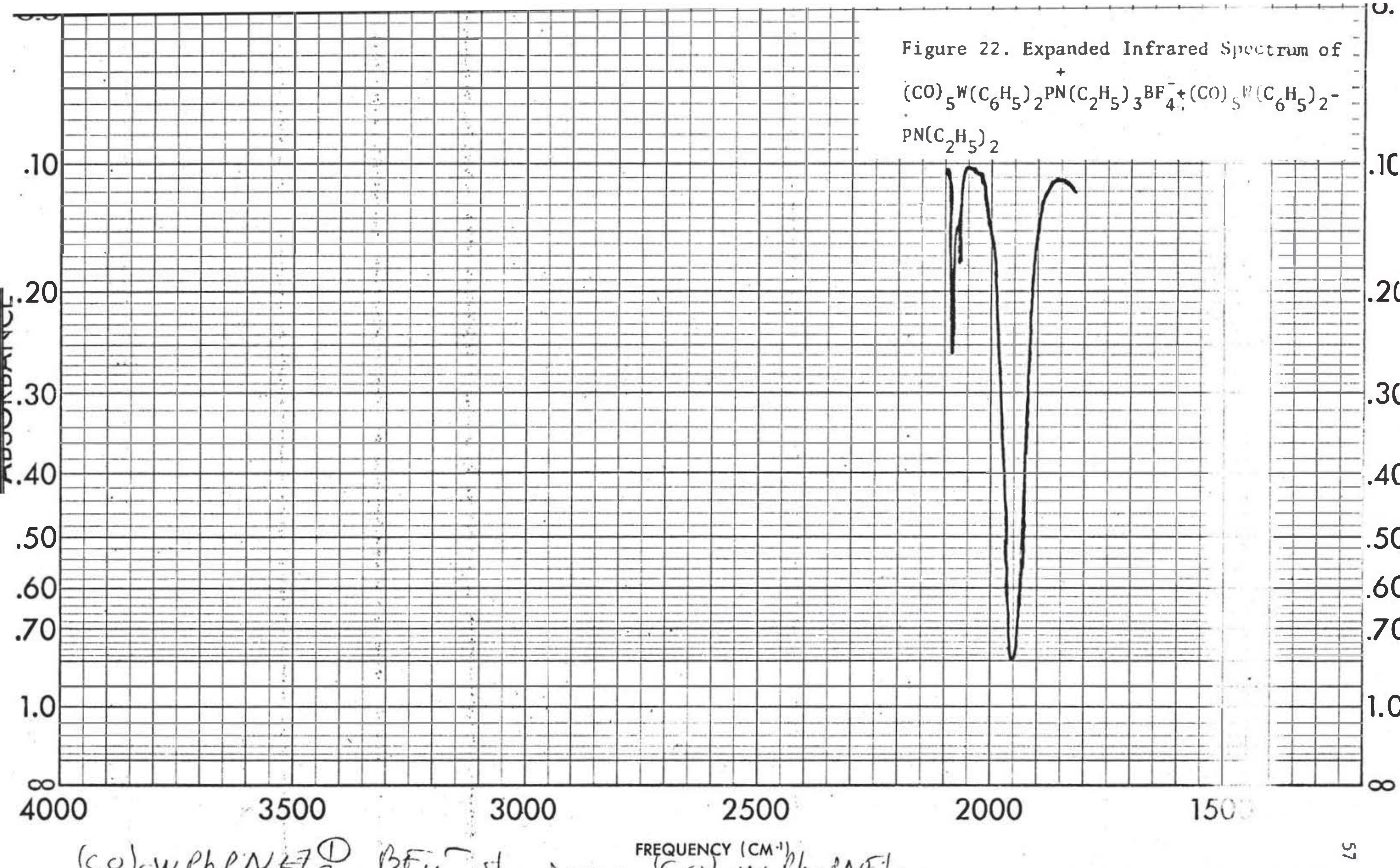


Figure 22. Expanded Infrared Spectrum of $(CO)_5W(C_6H_5)_2\overset{+}{P}N(C_2H_5)_3BF_4^- + (CO)_5W(C_6H_5)_2$-$PN(C_2H_5)_2$

$(CO)_5WPh_2PNEt_2$ ① BF_4^- + some $(CO)_5W\,Ph_2PNEt_2$

SAMPLE	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH DK-43-1	REMARKS	
SOLVENT	REFERENCE		

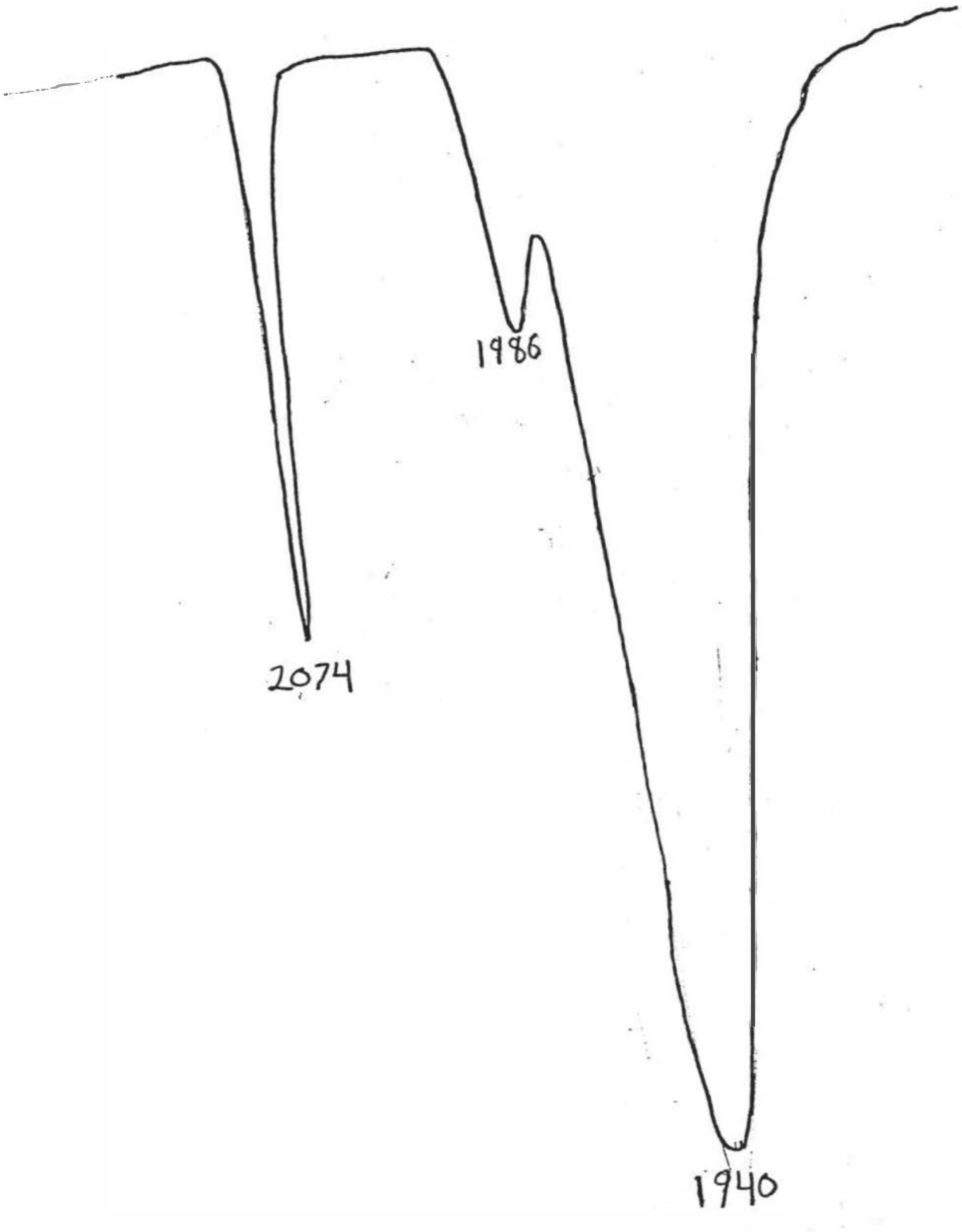


Figure 23. Expanded Infrared Spectrum of $W(CO)_5(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

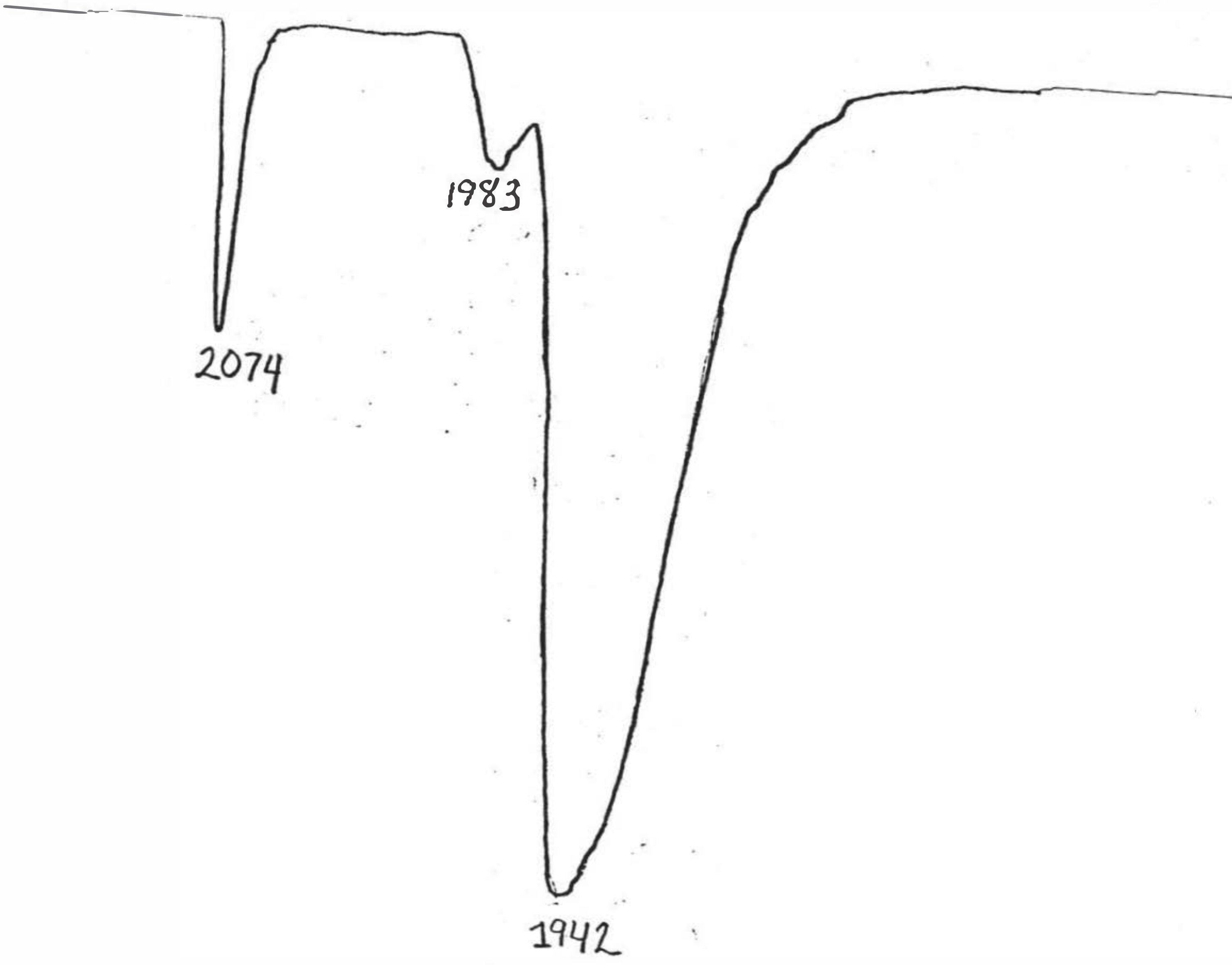


Figure 24. Expanded Infrared spectrum of $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2W(CO)_5$

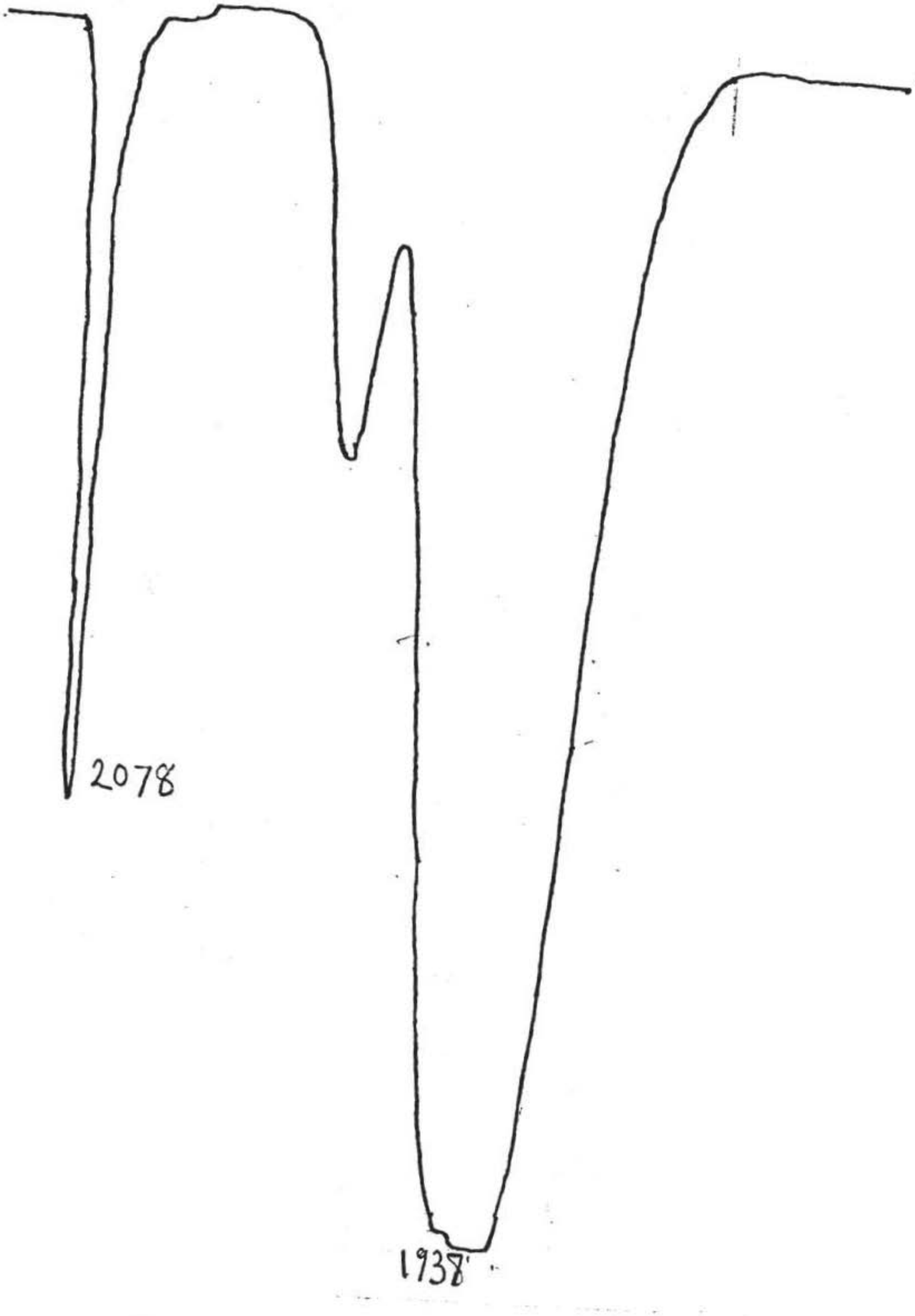


Figure 25. Expanded Infrared Spectrum of $(CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2(CH_2C_6H_5)\ PF_6^-$

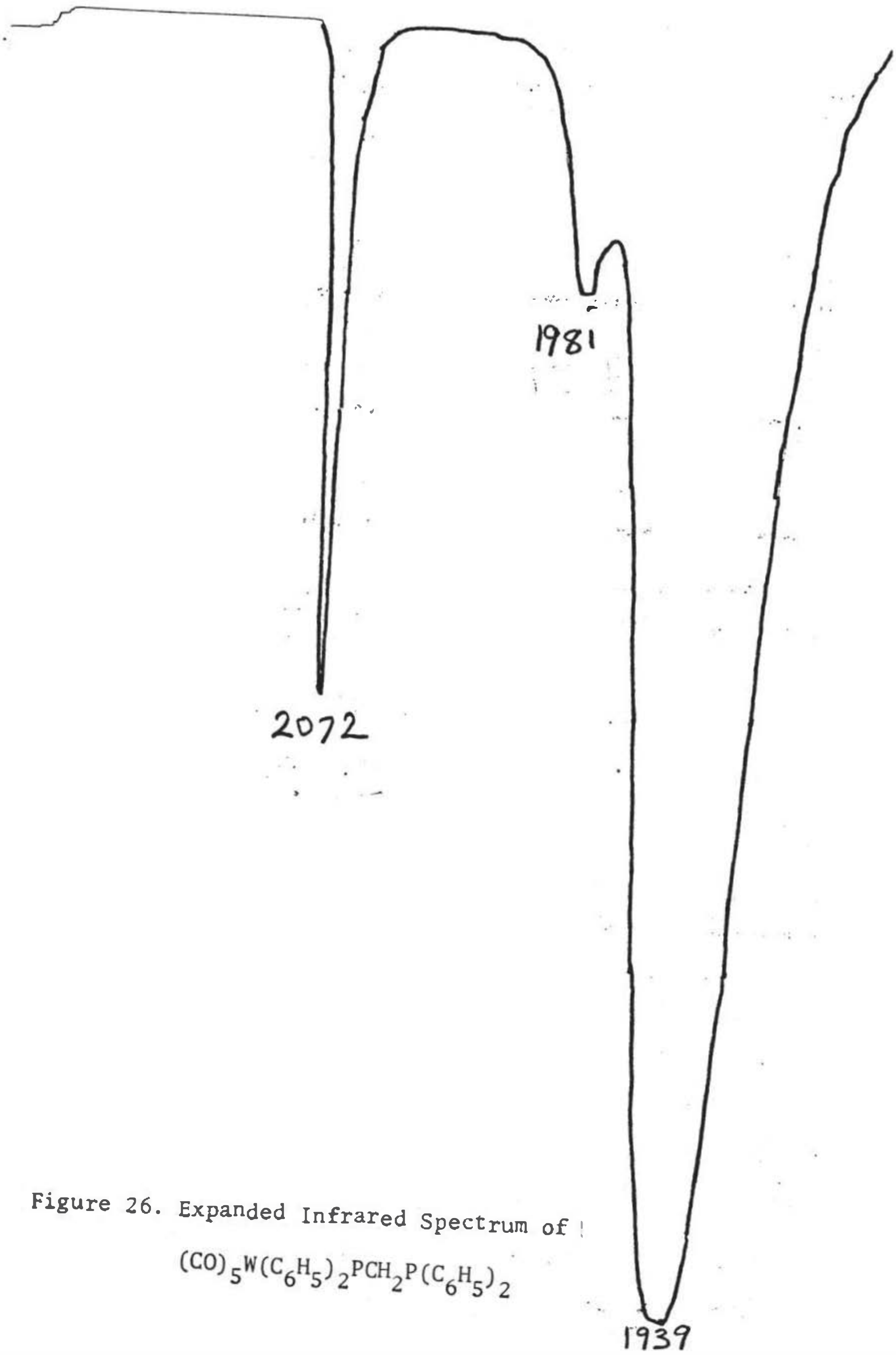


Figure 26. Expanded Infrared Spectrum of

$(CO)_5W(C_6H_5)_2PCH_2P(C_6H_5)_2$

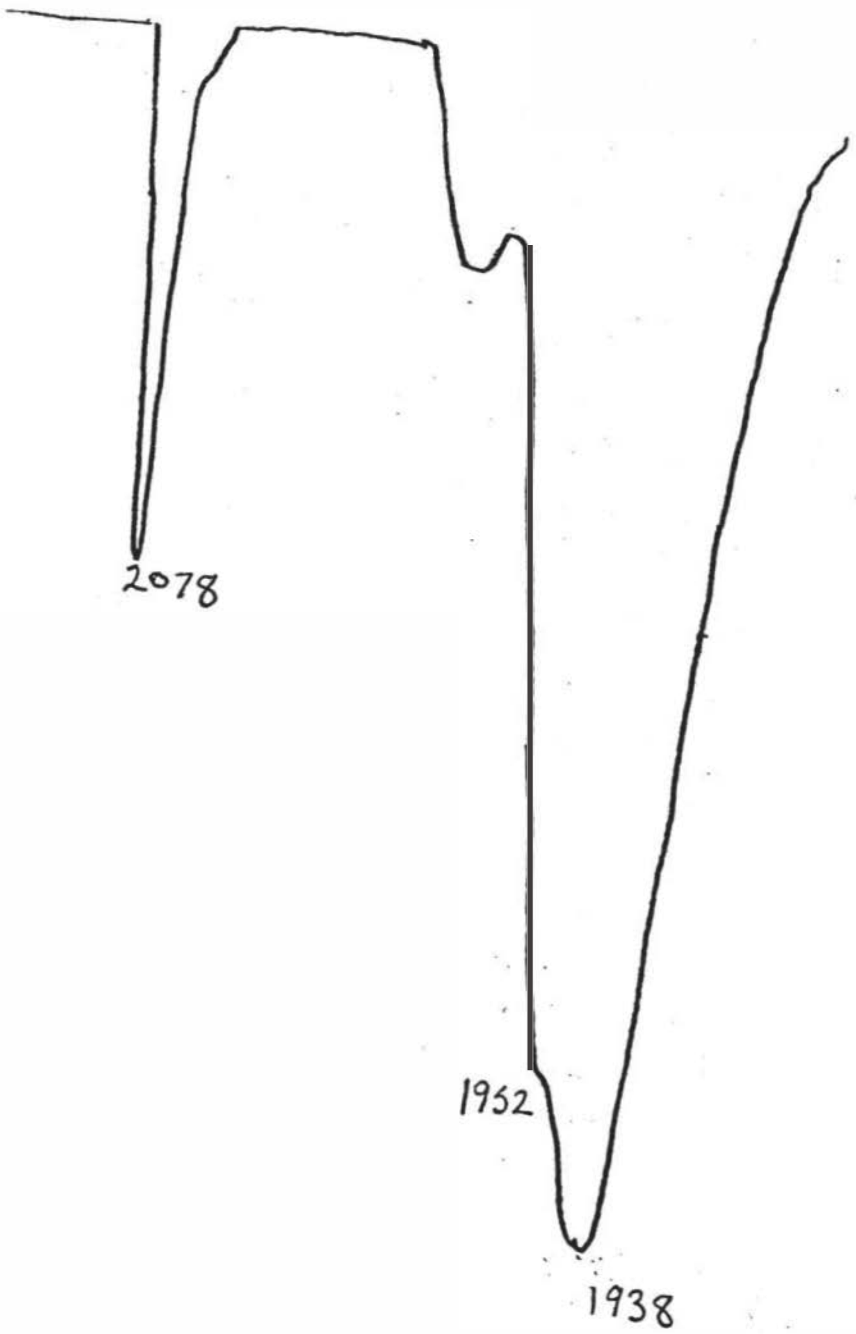


Figure 27. Expanded Infrared Spectrum of $(CO)_5W(C_6H_5)_2PCH_2\overset{+}{P}(C_6H_5)_2(CH_3)I^-$

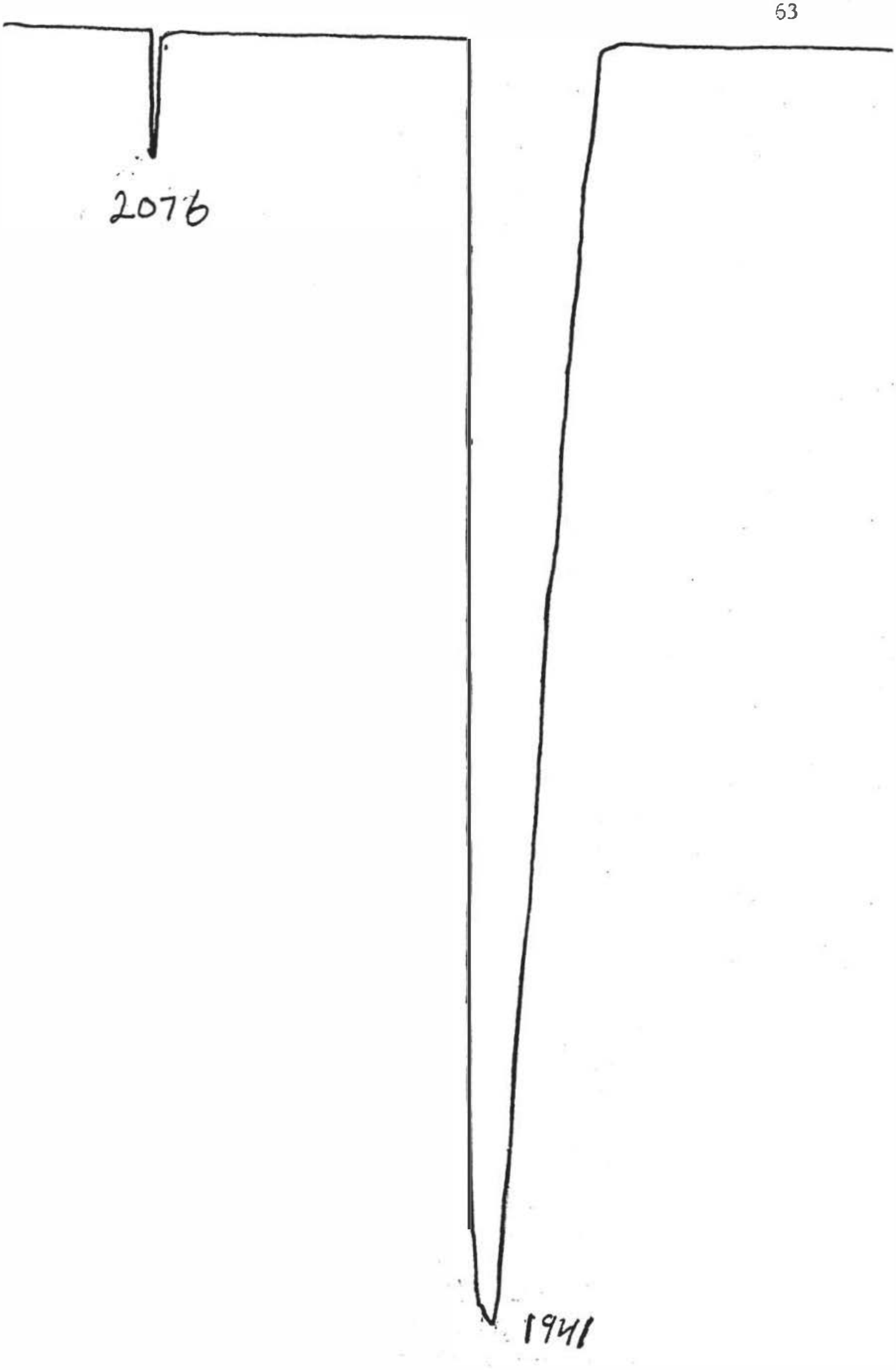


Figure 23. Expanded Infrared Spectrum of $(CO)_5W(C_6H_5)_2PN(C_2H_5)_2$

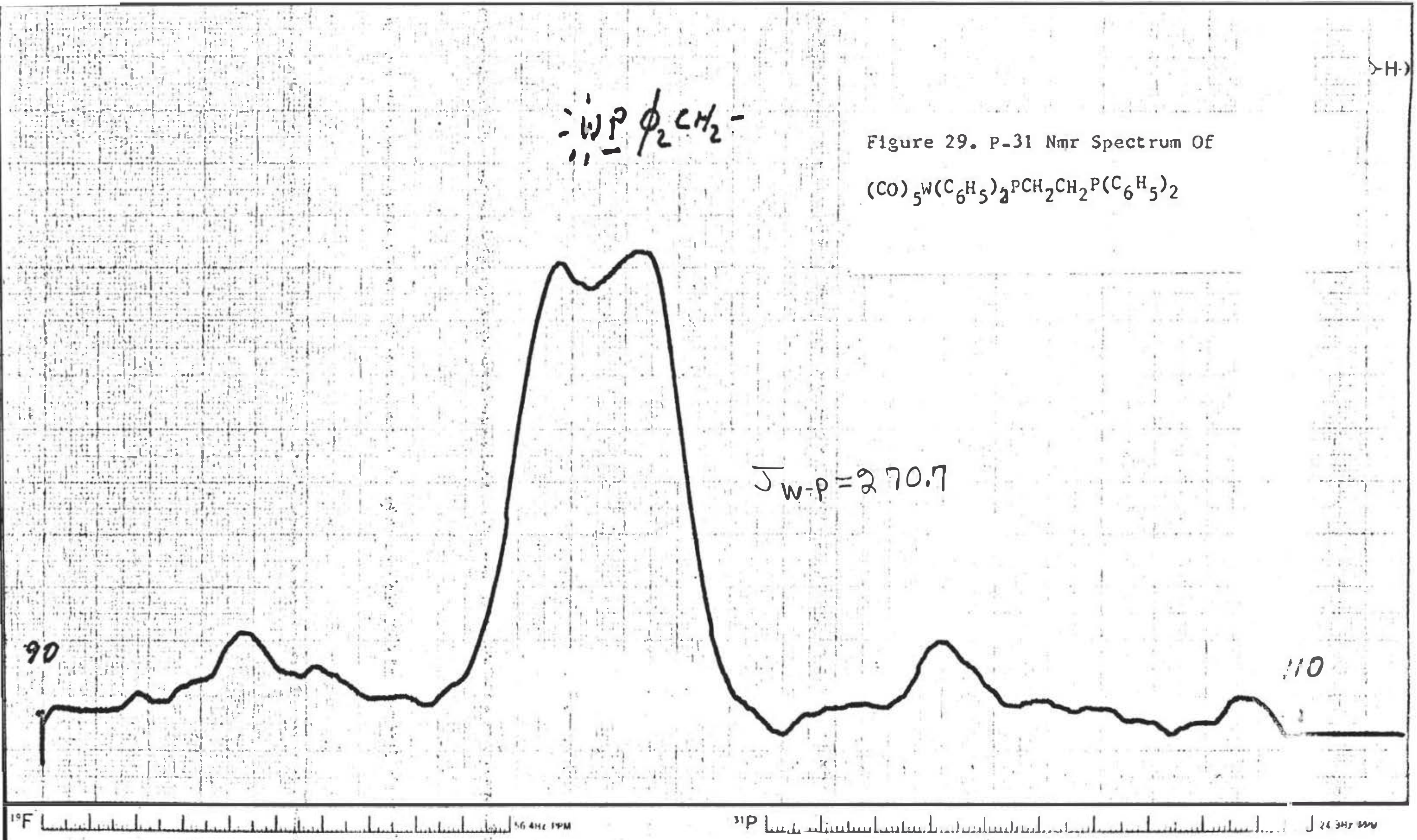


Figure 29. P-31 Nmr Spectrum Of $(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

IDE SWEEP OFFSET	120	PPM	SWEEP TIME	10	SEC	SAMPLE 3
WEEP OFFSET	-10	PPM	SWEEP WIDTH	20	PPM	
PECTRUM AMPLITUDE	32		FILTER	3		50 scans
TEGRAL AMPLITUDE			RF POWER LEVEL	.2		
PINNING RATE	40	RPS	NUCLEUS	19F☐, 31P☑, 11B☐, 13C☐		

DATE 9/30/70 OPERATOR SOLVENT CHCl3 14.1KG NMR SPECTRUM NO. 111661

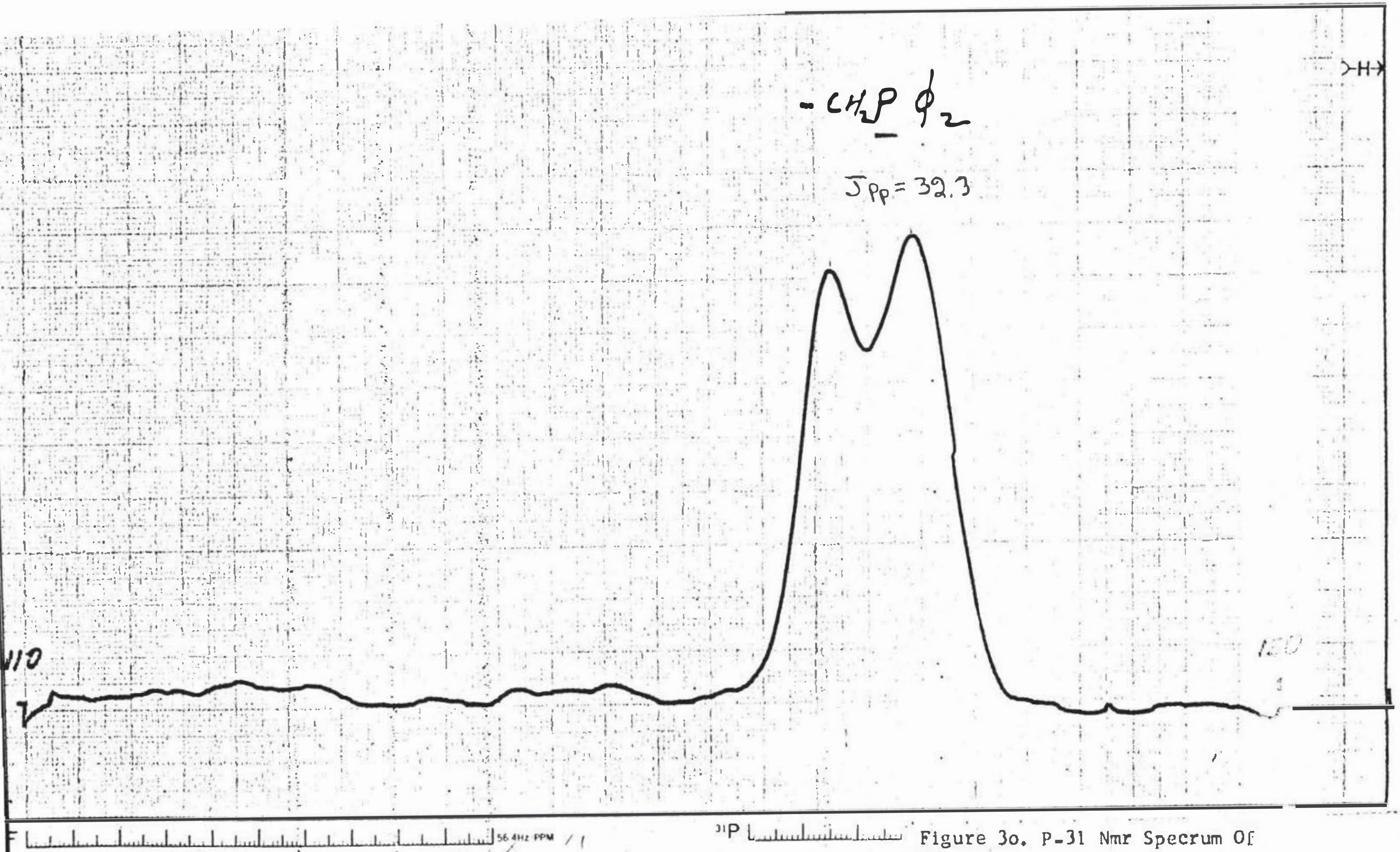


Figure 3o. P-31 Nmr Specrum Of

$(CO)_5W(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

E SWEEP OFFSET 110 PPM

EP OFFSET -10 PPM

CTRUM AMPLITUDE 32

GRAL AMPLITUDE

NING RATE 40 RPS

SWEEP TIME 10 SEC

SWEEP WIDTH 20 PPM

FILTER 3

RF POWER LEVEL .2

NUCLEUS ¹⁹F☐, ³¹P☐, ¹¹B☐, ¹³C☐

SAMPLE 3

64 scns

DATE 9/30/70 OPERATOR

SOLVENT CHCl3

14.1KG NMR SPECTRUM NO 11166

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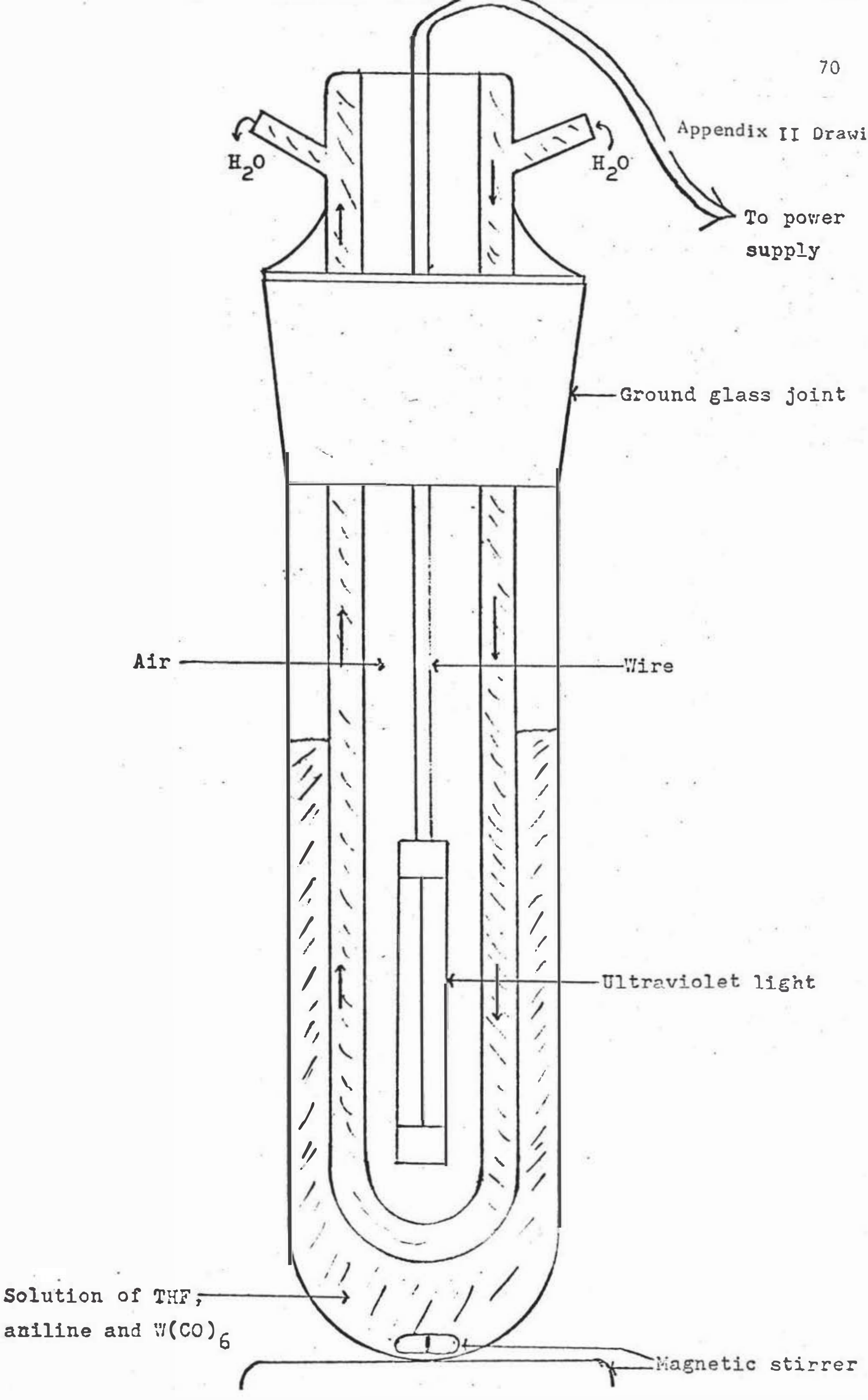
```
C     THIS RESEARCH IS DONE UNDER THE DIRECTION OF DR. R.L. KEITER.
C     DK---- REPRESENTS COMPOUNDS MR.DILIP P. SHAH HAS MADE IN THE LAB
C     WE WILL ALSO HAVE THREEE EXTRA VALUES OF K'S WHICH ARE DUE TO QUADRATI
C     EQATIONS
C     THIS PROGRAME IS TO CALCULATE FORCE CONSTANTS.
C     V1(1) IS ASSUMED TO BE HIGHER BY +5 CM-1 THEN A(E) AS IT IS UNRESOLVED
C     V(1) IS A FRQUENCY DUE TO C-O  WICH IS TRANS TO THE LIGAND
C     V1(2)IS A FRQUENCY DUE TO C-O  WICH IS INERACTING BETWEEN TRANS AND CI
C     V(E) IS A FRQUENCY DUE TO C-O  WICH IS EQITORIAL TO THE LIGAND
C     WE WILL BE CALCULATING FORCE CONST, OF MONOSUBSTITUTED COMPLEXES
C     ALL THE DATA FOR ONE COMPOUND SHOULD BE PUNCHED ON THE SAME CARD
C     ALL THE FRQUENCIES ON DATA CARDS ARE PUNCED FOLLOWING WAY
C     FIRST ONE IS PUNCHEO IN ONE TO TEN.
C     SECOND ONE IS PUNCHED FROM 11 TO 20.
C     THIRD ONE WILL BE PUNCHED FROM 21 TO 30
C     COMPOUND REF. SHOULD BE PUNCHED FROM 31 TO 35.
C     LAST CARO OF THE DATA SHOULD HAVE 9999.9 FROM 1 TO6.
C     GO MAN GO .
C     SOCK TO YOU
C     WE THANK MR. LARRY SHEDWICK FOR HIS HELP IN MODIFYING THIS PROGRAME.
      DOUBLE PRECISION CNO
      REAL LCON,LA1,LA2,LE,KIPOS,KINEG,K1,K2,K1N,K2N
      TRIP=9999.9
      LCON=5.8890E-2
      U=0.14583
      WRITE(6,100)
  100 FORMAT('1FORCE CONSTANT CALCULAAION OF   W(CO)5L       & W(CO)5LW(CO)5
     1  BY MR. DILIP SHAH FOR HIS M.S RESEARCH' ///'    V 1      V
     2  V         K +             K              K             K -
     3       K              K'/'     A        A        E         I
     4         1              2             I              1
     5   2'///)
C     CNO REPRESENTS THE REF. OF COMPLEXES
    3 READ (5,101)VSUBA1,VSUBA2,VSUBE,CNO
  101 FORMAT (3F10.1,A6)
      IF(VSUBA1-TRIP)1,9,1
    1 LA1=LCON*VSUBA1**2
      LA2=LCON*VSUBA2**2
      LE=LCON*VSUBE**2
      A=40*U**2*(LA1-LA2)
      B=6*U*(2*LE*(LA1-LA2)-(LA1**2-LA2**2))
      C=LE**2*(LA1-LA2)-LE*(LA1**2-LA2**2)+LA1*LA2*(LA1-LA2)
      ROOT=B**2-4*A*C
      IF(ROOT)8,2,2
    2 KIPOS=(-B+SQRT(ROOT))/(2*A)
      KINEG=(-B-SQRT(ROOT))/(2*A)
      K1=0
      K2=0
```

Appendix I Computer programme for calculation of force constants

```
                KIN=0
                K2N=0
                IF(KIPOS)5,5,4
            4   K2=(LE+2*U*KIPOS)/U
                K2=(U*LA1*K2+4*LA1*U*KIPOS-LA1**2+4*U**2*KIPOS**2)/
             1     (U**2*K2+4*U**2*KIPOS-U*LA1)
            5   IF(KINEG)7,7,6
            6   K2N=(LE+2*U*KINEG)/U
                KIN=(U*LA1*K2N+4*LA1*U*KINEG-LA1**2+4*U**2*KINEG**2)/
             1     (U**2*K2N+4*U**2*KINEG-U*LA1)
            7   WRITE (6,102)VSUBA1,VSUBA2,VSUBE,KIPOS,K1,K2,KINEG,KIN,K2N,CNO
          102   FORMAT (F7.1,2F9.1,6E15.5,A6)
                GO TO 3
            8   WRITE (6,103)VSUBA1,VSUBA2,VSUBE
          103   FORMAT (F7.0,2F9.0,'      KI SQUARE ROOT GIVES IMAGINARY VALUE')
                GO TO 3
            9   RETURN
                END
```

Appendix II Drawing of UV cell



Vita

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February, 1971

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University of Bombay	1962-1966	B.Sc.	December 1966
Eastern Illinois University	1969-1971	M.S.	February 1971

Major: Inorganic Chemistry

Minor: Zoology

Positions Held	Date	Institutions
Data Analyst	January 1969-August 1969	University of Akron
Graduate Assistant	March 1970-November 1970	Eastern Illinois University