THE REACTION OF 1-METHYL-1, 2-DICARBACLOSO-DODECABORANE (12) AND 1,2-BIS (DIPHENYLPHOSPHINO) CARBORANE (12) WITH PLATINUM SALTS

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This is to certify that the

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THE REACTION OF 1-METHYL-1,2-DICARBACLOSO-DODECABORANE(12) AND 1,2-BIS(DIPHENYLPHOSPHINO)CARBORANE(12) WITH PLATINUM SALTS

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By

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NOMENCLATURE

The rapid development of research in the area of boron cage compounds was in part responsible for the development of a complete set of rules governing the nomenclature of such systems (1,2). This nomenclature will be employed in naming all compounds in this manuscript with the exception of references to compounds which have been reported previously by other authors. These references will retain the nomenclature used in the original publication. In all work contained in the experimental section of this thesis, the CH_3-$B_{10}C_2H_{10}$-H unit will be referred to as 1-methyl-1,2-dicarbocloso-dodecaborane(12) or by the common name methyl carborane(12).

1. R. Adams, Inorg. Chem., 2, 1087 (1962).
2. R. Adams, Inorg. Chem., 7, 1945 (1968).

INTRODUCTION

The ability of boron to bond with itself and form a series of hydrides was first recognized by Alfred Stock (1). The first boron hydrides to be isolated were the compounds B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. Decaborane-14 ($B_{10}H_{14}$) is the only member of this group that can be handled in air without spontaneous ignition or hydrolysis. It was the high reactivity displayed by these boron hydrides, coupled with their relative scarcity, that led Stock to develop special high-vacuum techniques for their manipulation. These compounds were considered to be mere chemical curiosities. They presented unusual valency problems because their formulation in terms of normal two-electron bonds proved impossible. Most of these structural and bonding problems were resolved during the last twenty years (2). The boron hydrides are characterized by structures that can be recognized as fragments of the icosahedron or the octahedron. Recently, extremely stable polyhedral boron ions and icosahedral carboranes have been prepared (3).

The polyhedral boranes encompass molecules or ions in which boron atoms alone or in combination with other atoms, describe a closed polyhedron ranging from the tetrahedron

to the icosahedron (4). Subsequent investigations of these polyhedral boranes revealed an aromatic character manifest not only in an extraordinary thermal stability, but also in a substitution chemistry centered on the polyhedral boron-hydrogen or carbon-hydrogen bonds. These highly symmetrical species are stabilized by three-dimensional electron delocalization and may be considered to be the aromatic members of the boron hydride series. The low toxicity (5) of these polyhedral boranes and their high stability toward acid and base attack is surprising in view of the toxicity and instability of other boron hydrides (6). The icosahedral carboranes share this stability, but are less stable to basic degradation than $B_{12}H_{12}^{2-}$.

The discovery of this new class of compounds, "aromatic" polyhedral boranes, has resulted in broad areas of research with a variety of synthetic and theoretical problems. Reports on the derivative chemistry have suggested that this class of compounds may rival that of aromatic hydrocarbons. Several reviews on the chemistry of some of these materials, particularly $B_nH_n^{2-}$ and $B_{n-2}C_2H_n$ are available (7-14).

In the late sixties significant developments (15) occurred in the field of research which combines polyhedral carboranes and transition metal chemistries in much the same way as the first metallocenes were synthesized from aromatic organic species and transition metal derivatives. Several groups of polyhedral species are known in which a transition metal resides in the polyhedral surface. Their

remarkable stability suggests that they are stabilized by some degree of electron delocalization similar to that found in the $B_nH_n^{2-}$ ions (3), the carboranes (3), and the more stable metallocenes. This area is of interest since rather unusual formal oxidation states of transition metals may be attained.

The original work in this area of chemical synthesis involved the preparation of the $B_9C_2H_{11}^{2-}$ ligand (15-17), which resembles the well known π-bonding cyclopentadienide ion. The $B_9C_2H_{11}^{2-}$ ion (or dicarbollide ion) is known in two isomeric forms, each of which constitutes an eleven particle icosahedral fragment capable of regenerating an icosahedral surface upon coordination of a transition metal at the open vertex. Later work has demonstrated that bonding of this type is not restricted to the $B_9C_2H_{11}^{2-}$ ions, but can be extended to the $B_{10}CH_{11}^{3-}$ (18-19) and $B_{10}SH_{10}^{2-}$ (20) icosahedral fragment ions and the $B_7C_1H_9^{2-}$ (21) and $B_6C_2H_8^{2-}$ (22) ions of different geometry. The $B_9C_2H_{11}^{2-}$ ion, which can be produced by strong base degradation of 1,2- and 1,7-dicarbacloso-dodecaborane(12), has been employed to generate a series of ferrocene-like "sandwich" compounds (23-29). Various transition metals have been inserted in the open face of the dicarbollide ($B_9C_2H_{11}^{2-}$) ion to form a series of π-complexes (23-29). The structures of some of these compounds have been determined by means of X-ray diffraction (30-31).

In all of these systems the bonding is of π-character in which d orbitals of the transition metal can overlap with the five nearly equivalent sp^3 atomic orbitals (3,9,15), of the open pentagonal face of the eleven particle icosahedral fragment. The research described in this thesis was undertaken with the purpose of synthesizing a sigma-bonded transition metal carborane complex. As of 1968 no sigma-bonded complex had been reported in the chemical literature. After the start of this project, the first literature reports of sigma-bonded transition metal-carborane complexes appeared in the chemical literature (32-34). Hawthorne synthesized 1-[(π-C_5H_5)$Fe(CO)_2$]-2-(CH_3)-(σ-1,2-$B_{10}C_2H_{10}$) via the interaction of the lithium salt (35) of the 1-(CH_3)-1,2-$B_{10}C_2H_{10}$-ion with π-(C_5H_5)$Fe(CO)_2I$ in 1,2-dimethoxyethane solvent (32). These initial results were followed by several other reports of transition metal-carborane complexes containing a sigma bond (34,36). Compounds of copper, gold, and platinum were reported to give sigma-bonded carborane complexes.

Another area of interest is the synthetic investigation of the derivative chemistry which is based on the substitution at the two carbon atoms of 1,2-dicarbacloso-dodecarborane(12) (13). In general, groups which are so substituted act as if they were attached to a very bulky, electron withdrawing moiety (9,11). With the appropriate groups substituted at these two carbon atoms, it is possible to prepare a bifunctional ligand. Very little information is available

regarding the steric and electronic properties of the carborane cage when present in such a ligand.

H. D. Smith (37) has reported that the reaction of nickel(II) chloride 6-hydrate with 1,2-bis(diphenylphosphine)-o-carborane(12), as well as with the corresponding derivatives containing one, two, and three bromine atoms attached to the carborane nucleus, produced complexes which contain one or two molecules of the bisphosphino ligand and one of nickel(II) chloride. Zaborowski and Cohn reported the preparation and characterization of the analogous arsino-1,2-dicarbacloso-dodecarborane(12) (38). They were able to use this compound as a bidentate ligand.

It was of interest to attempt the synthesis of new transition metal carborane complexes. New information about the electron delocalization about the carborane cage system would be of value in attempts to elucidate the similarity of the reaction chemistry between benzene and carborane. The preparation and characterization of stable, inert, transition complexes of platinum was also of interest because of recent work in which platinum complexes were shown to possess potential medical value as anti-tumor agents (39).

EXPERIMENTAL

A. Experimental Methods

A Perkin-Elmer 457 grating spectrophotometer was used to obtain the infrared spectra. Solid spectra were run either as Nujol or as Fluorolube mulls between CsI plates.

Proton nmr spectra were observed by means of a Varian Model 56/60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Tetramethylsilane was employed as an internal standard. Phosphorus and boron nmr absorptions were obtained on an NMR Specialties MP1000 pulsed spectrometer with an operating frequency of 65 MHz, and a field strength of 47.6 and 28.0 kilogauss respectively. Solutions of P_4O_6 and $B(OCH_3)_3$ were employed as internal references, by the capillary insertion technique.

Mass spectral data were obtained by means of an Hitachi-RMU-6 Spectrometer operating with an ionizing voltage of 56V.

The preparations were carried out under an atmosphere of dry nitrogen. Analyses were performed by Spang Laboratories, Ann Arbor, Michigan or by Chemalytics, Inc., Tempe, Arizona. Melting points were obtained by the use of a Thomas-Hoover Capillary Melting Point Apparatus.

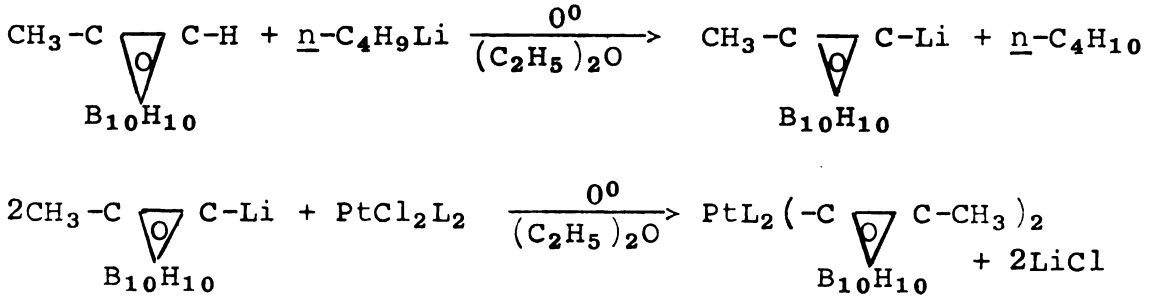
B. Materials

Methyl carborane [1-methyl-1,2-dicarbacloso-dodecaborane(12)], was prepared from purified propargyl bromide (3-bromopropyne), acetonitrile, and decaborane (U. S. Department of the Air Force) by the use of a method previously described (40-41). The procedure was modified in the following manner. Both the number of sulfuric acid-containing traps and the number of empty safety traps in the purification train was increased from the suggested value of one (40) to three traps. Second, the white solid, $CH_3-B_{10}C_2H_{10}-H$ was dried in vacuo over P_2O_5 rather than at atmospheric pressure. The identity of the product was established by its melting point (found, 211 ± 2°, lit. (40) 211-213°) and by a comparison of the ^1H nmr with the reported values. The ^1H nmr spectrum (CS_2) exhibits absorptions at δ 3.50 (broad singlet, intensity 1, due to the C-H on methyl carborane(12)), and δ 2.00 (broad singlet, intensity 3, due to the C-methyl protons) (lit. (40) δ 3.48 and 1.98 respectively). The pure methyl carborane(12) was stored in an evacuated desiccator over P_2O_5 prior to use. The potassium tetrachloroplatinite (K_2PtCl_4) and n-butyllithium were used as supplied by Alfa Inorganics Company.

C. Synthesis: General Reaction Procedures

All reactions which use 1-methyl-1,2-dicarbacloso-dodecarborane(12) as a monodentate ligand were performed in

an analogous manner. Any variation in the experimental procedure for a specific preparation will be mentioned. The general reactions are shown below:



where L is a phosphine ligand. The slurry of lithiomethylcarborane(12), $CH_3\text{-}C_2B_{10}H_{10}\text{-}C\text{-}Li$ was freshly prepared by charging a nitrogen purged 100-ml three-necked flask with 1-methyl-1,2-dicarbacloso-dodecarborane(12) (2 mmol) which contained 50 ml of dry diethyl ether. The flask was fitted with a magnetic stirrer, a nitrogen inlet, and an addition funnel with a nitrogen outlet. This flask was then cooled to 0^0 and a solution of n-butyllithium (2 mmol) in 10 ml of dry diethyl ether was added over a period of 10 minutes via the addition funnel. The solution was maintained at 0^0 and was stirred during this addition procedure. The reaction was allowed to proceed for 30 min at 0^0. At the end of this time a 1 mmol sample of the phosphinoplatinumdichloro complex in a suitable solvent was added over a period of 15 min. (An insoluble platinum complex was added as a suspension in solvent.) The stirred solution was maintained at 0^0 for 45 min and then was allowed to warm to room temperature (25^0) over a period of one hr. That a reaction took place was

indicated either by a color change or by the disappearance of the insoluble platinum slurry. Sometimes the mixture was allowed to reflux for 15 min. The solvent was then removed by distillation *in vacuo*. The products were recrystallized from appropriate solvents and then dried *in vacuo*.

1. Synthesis of the *cis*-Platinum Phosphine Complexes

The following platinum compounds, *cis*-dichlorobis(trimethylphosphine)platinum(II) [*C*-$PtCl_2[P(CH_3)_3]_2$]; *cis*-dichlorobis(dimethylphenylphosphine)platinum(II) [*C*-$PtCl_2[P(CH_3)_2(C_6H_5)]_2$]; *cis*-dichlorobis(methyldiphenylphosphine)platinum(II) [*C*-$PtCl_2[P(CH_3)(C_6H_5)_2]_2$]; and *cis*-dichlorobis(triphenylphosphine)platinum(II) [*C*-$PtCl_2[P(C_6H_5)_3]_2$] were prepared and characterized according to previously described methods (42-44). Characterization data are found in Table I. A typical ir spectrum, as well as ^1H and ^{31}P nmr spectra for *cis*-dichlorobis(methyldiphenylphosphine)platinum(II) is shown in Figures 1-3. No nmr was obtained for the *cis*-dichlorobis(triphenylphosphine)platinum(II) complex because the compound was insoluble.

Table I. Characterization Data of the cis-$Pt(Cl)_2(L)_2$ Complexes.

L	%C (Theory)	%C (Found)	%H (Theory)	%H (Found)	M.P. (Lit.)	M.P. (Found)
$P(CH_3)_3$	17.22	17.05	4.34	4.13	324-326 (44)	323-325
$P(CH_3)_2(C_6H_5)$	35.42	35.13	4.09	3.97	---	221-225
$P(CH_3)(C_6H_5)_2$	46.84	46.76	3.93	3.47	253-258 (43)	254-260
$P(C_6H_5)_3$	54.68	54.60	3.80	3.75	310 (42)	308-309

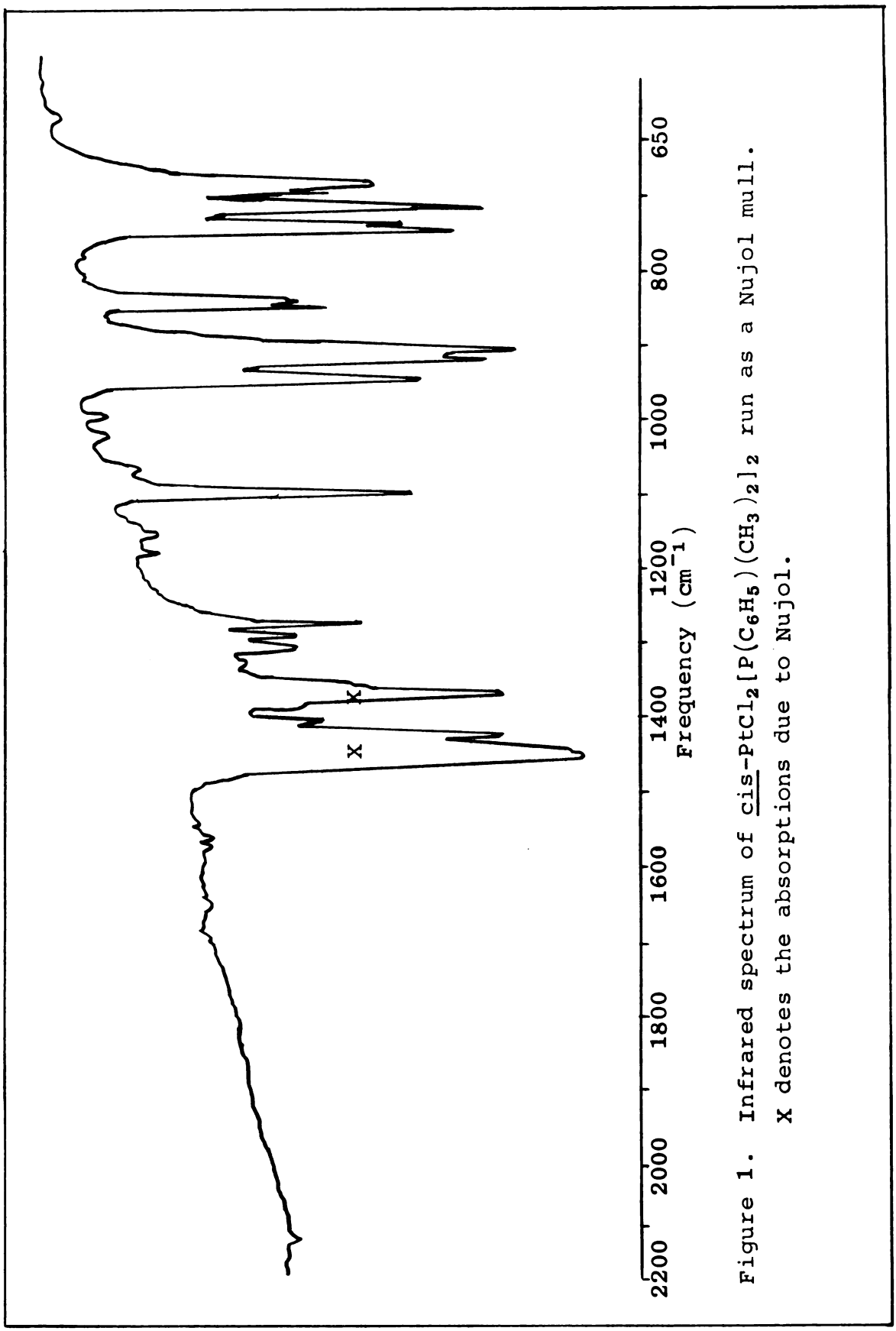


Figure 1. Infrared spectrum of cis-$PtCl_2[P(C_6H_5)(CH_3)_2]_2$ run as a Nujol mull.
X denotes the absorptions due to Nujol.

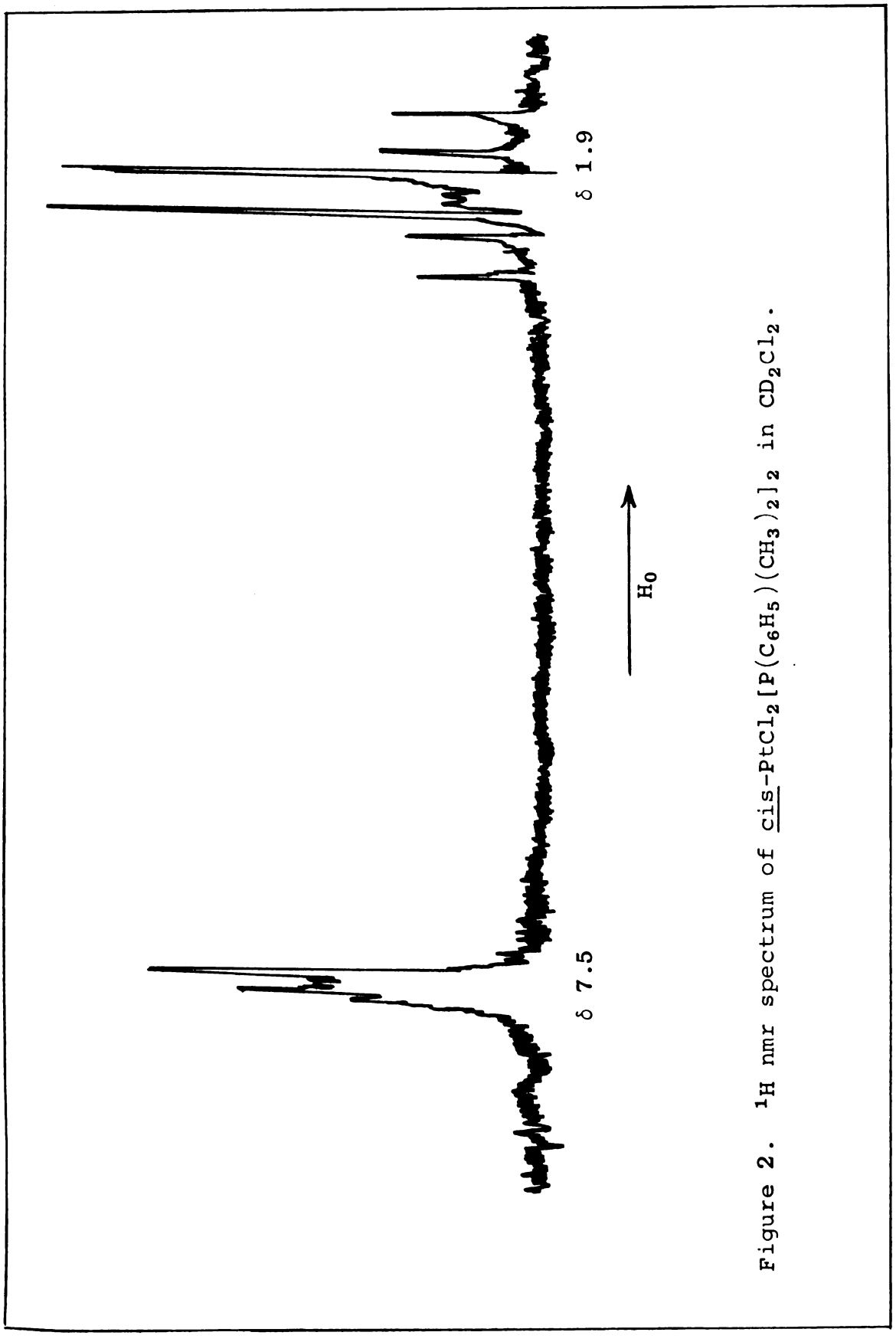


Figure 2. ^1H nmr spectrum of cis-$PtCl_2[P(C_6H_5)(CH_3)_2]_2$ in CD_2Cl_2.

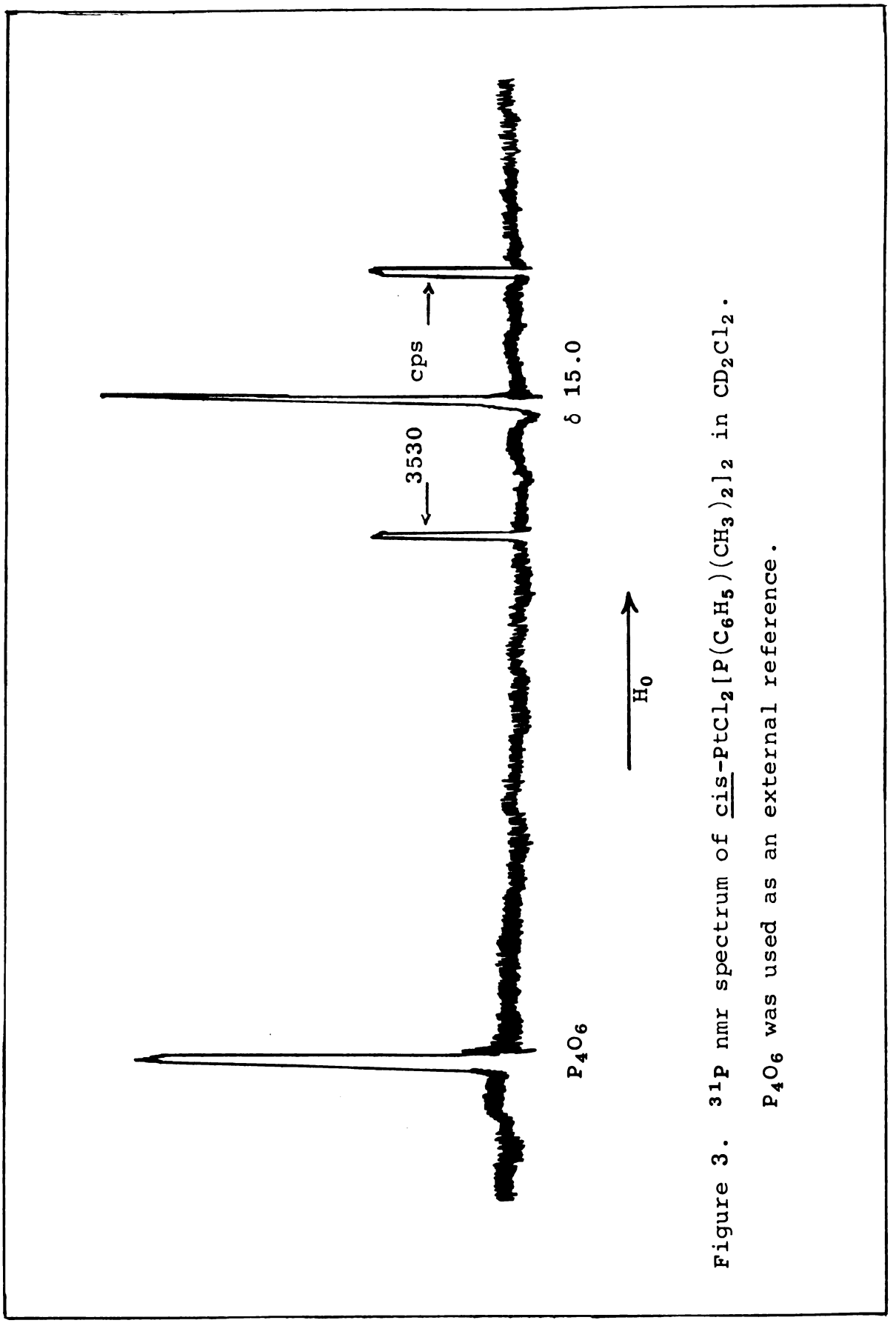


Figure 3. ^{31}P nmr spectrum of cis-$PtCl_2[P(C_6H_5)(CH_3)_2]_2$ in CD_2Cl_2.
P_4O_6 was used as an external reference.

2. The Reaction of 1-Methyl-1,2-dicarbaclosododecaborane(12) with cis-Platinum Phosphine Complexes

a. The Preparation of C-Pt[P(C_6H_5)$_3$]$_2$[-C$_2B_{10}H_{10}$C-CH_3]$_2$

The reaction was carried out as previously described. After the lithiomethylcarborane(12) (2 mmol) was prepared, a slurry of cis-dichlorobis(triphenylphosphine)platinum(II) in dry diethyl ether was added to the stirred lithiomethylcarborane(12) solution maintained at 0^0. This addition took 10 min. The reaction was then allowed to proceed at 0^0 for one hr after which time it was allowed to warm to 25^0 over a one hr period. The disappearance of the insoluble platinum slurry and the appearance of a clear yellow solution was evidence that a reaction took place. The solvent was then removed by distillation in vacuo. The yellow solid, which remained in the reaction flask, was recrystallized from a 70:30 mixture of carbon disulfide and methylene chloride. A small amount of n-pentane was employed to initiate the precipitation of the product from solution. The amber solid was then filtered and dried in vacuo.

The 60 MHz ^{1}H nmr (CS_2) spectrum exhibited two peaks at δ 2.1 (broad singlet, relative intensity 1, due to C-methyl protons of methyl carborane(12)), and δ 7.3 (broad multiplet, relative intensity 5, due to the triphenylphosphine protons). The ^{1}H nmr spectrum is shown in Figure 4. We could not obtain ^{31}P and ^{11}B nmr spectra because of the low solubility of this product.

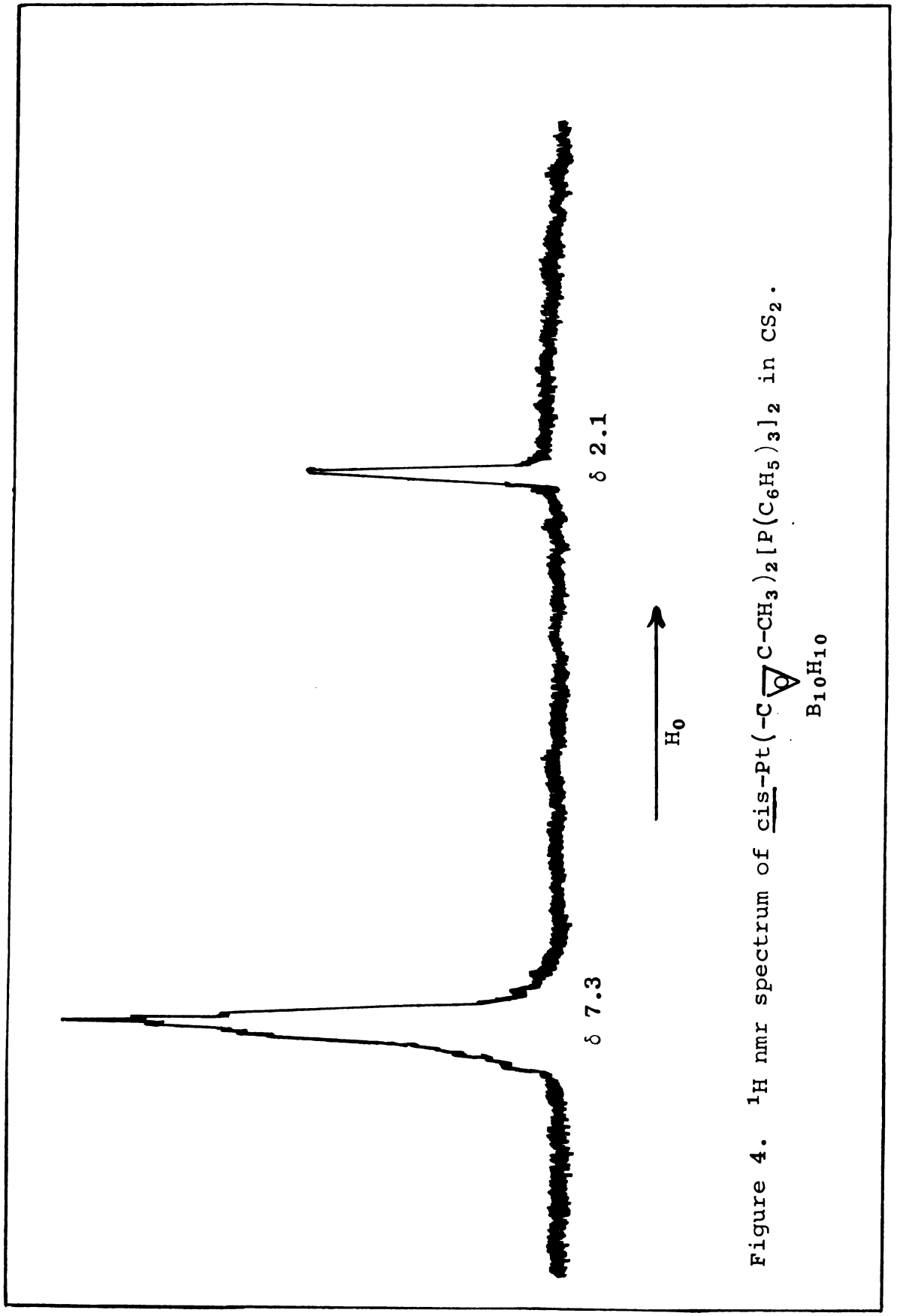


Figure 4. ^1H nmr spectrum of cis-Pt(-C$_{B_{10}H_{10}}$C-CH_3)$_2$[$P(C_6H_5)_3$]$_2$ in CS_2.

The infrared spectrum obtained as a Nujol mull and shown in Figure 5, exhibits characteristic absorptions at 740 (m) and 2550 (s) cm^{-1}. The absorption at 740 cm^{-1} is attributed to the B-H cage structure and the one at 2550 cm^{-1} is ascribed to the B-H stretching mode. Other absorptions appear at 510 (s), 545 (ms), 670 (s), 993 (w), 1020 (mw), 1090 (ms), 1115 (w), 1180 (w), 1305 (w), 1570 (w), and 2720 (w) cm^{-1}. The bands tentatively assigned to Pt-Cl stretches present in the starting material (300, 320 cm^{-1}) were absent from the product. The analytical data for this compound and the subsequent alkylphenylphosphine platinum complexes of methyl carborane(12) are represented in Table II. The compound was slightly soluble in carbon disulfide, methylene chloride, and benzene. It is stable in air.

b. The Preparation of C-Pt$[P(C_6H_5)_2(CH_3)]_2[-C_{B_{10}H_{10}}C-CH_3]_2$

The reaction procedure was identical to the one previously described for the preparation of the triphenylphosphine platinum complex. An amber solid was isolated. The ^1H nmr spectrum (CS_2) exhibited three peaks at δ 1.9 (doublet J = 12 Hz, due to the methyl protons attached to phosphorus), 2.05 (singlet, due to C-methyl protons of the carborane), 7.3 multiplet, due to the phenyl protons of the phosphine ligand). The overlap of peaks at δ 1.9 and 2.05 made the accurate determination of relative peak areas impossible. The ^1H nmr spectrum is shown in Figure 6. This

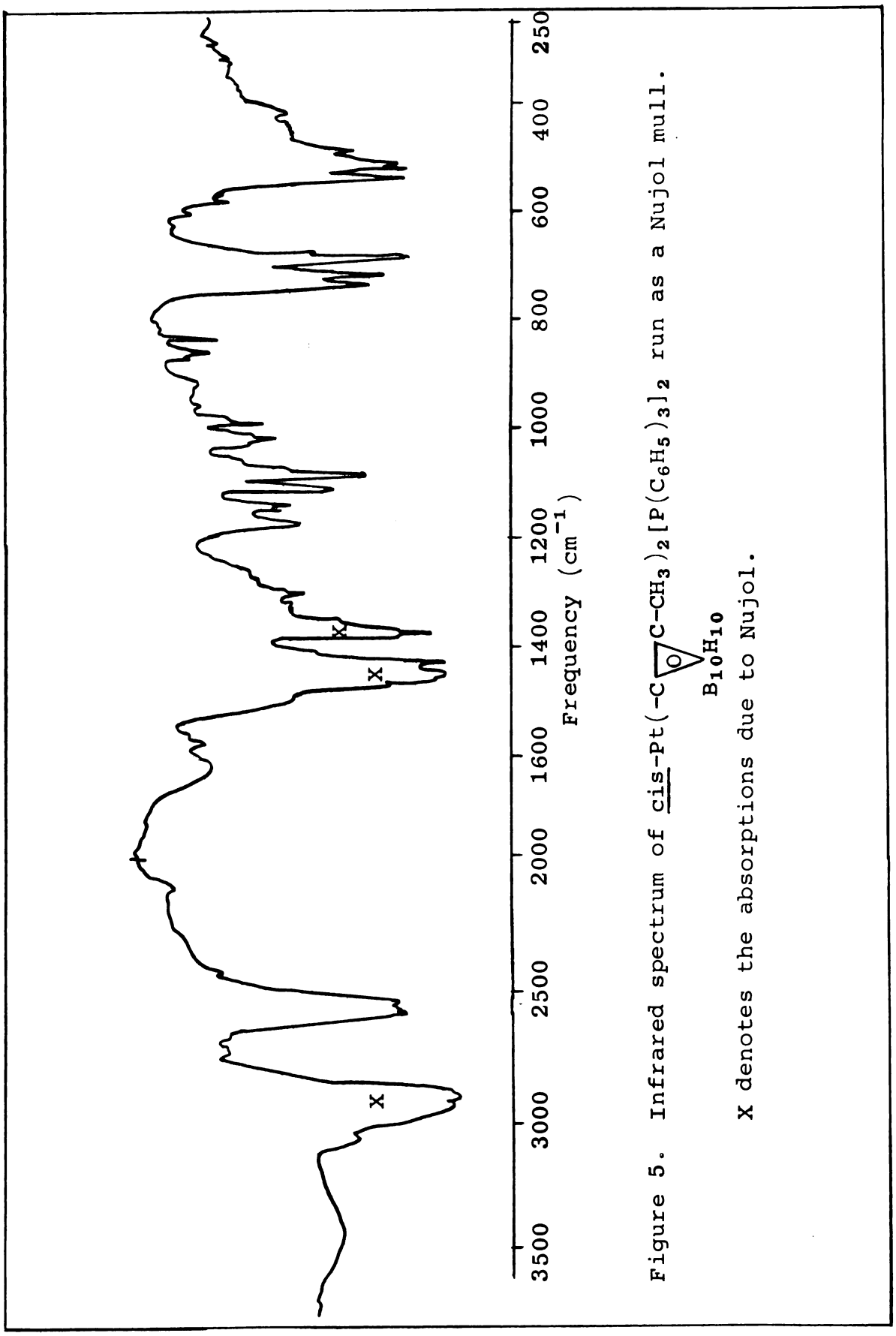


Figure 5. Infrared spectrum of cis-Pt(-C$_{B_{10}H_{10}}$C-CH_3)$_2$[P(C_6H_5)$_3$]$_2$ run as a Nujol mull.

X denotes the absorptions due to Nujol.

Table II. Characterization Data of the cis-Pt(-C$_2B_{10}H_{10}$C-CH_3)$_2$(L)$_2$ Complexes.

L	%C (Theory)	%C (Found)	%H (Theory)	%H (Found)	M.W. (Theory)	M.W. (Found)	M.P.
$P(C_6H_5)_3$	48.74	47.34	5.41	5.04	1033	1002	216-218 (decomp.)
$P(CH_3)(C_6H_5)_2$	42.20	40.94	5.73	5.47	909	891	200-204 (decomp.)
$P(CH_3)_2(C_6H_5)$	33.63	32.84	6.12	5.47	785	739	188-192 (decomp.)
$P(CH_3)_3$	21.78	--	6.65	--	661	--	125-160 (decomp.)

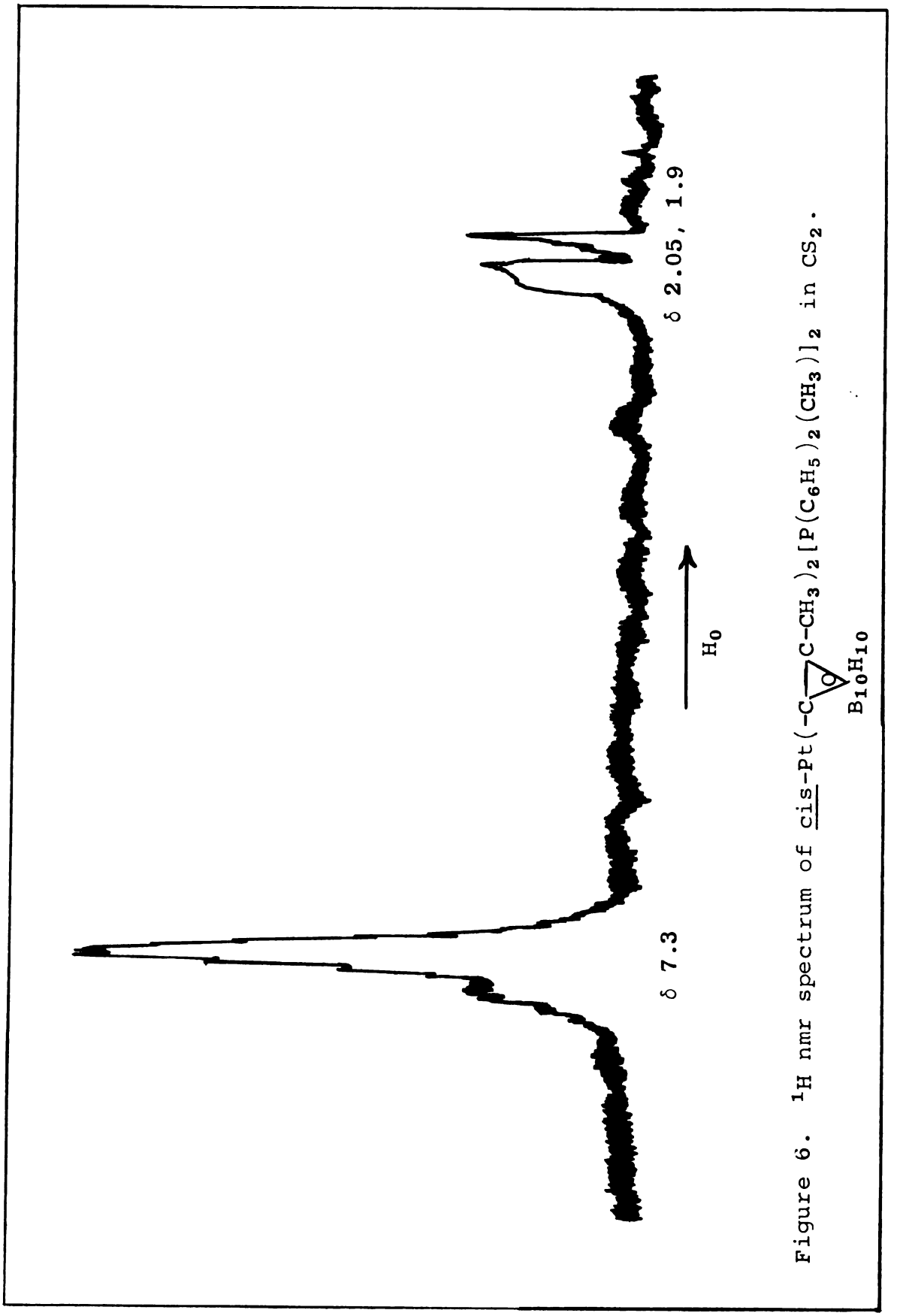


Figure 6. ^1H nmr spectrum of cis-Pt(-C$_{B_{10}H_{10}}$C-CH_3)$_2$[$P(C_6H_5)_2(CH_3)]_2$ in CS_2.

product was too insoluble to obtain ^{31}P nmr spectral data. The ^{11}B signal consisted of a broad doublet at δ29.4 upfield from $B(OCH_3)_3$.

The infrared spectrum of this compound mulled in Nujol is shown in Figure 7. The characteristic absorptions due to the carborane were present, (740 and 2550 cm^{-1}) while the Pt-Cl stretches were absent (320 cm^{-1}).

The solubility of this complex was similar to that described for the triphenylplatinum carborane complex. See Table II for the analytical data obtained from this complex.

c. The Preparation of <u>C</u>-Pt[$P(C_6H_5)(CH_3)_2$]$_2$[-C$_{B_{10}H_{10}}$C-CH_3]$_2$

The reaction was carried out in an analogous manner to that previously described, however, the reaction mixture was allowed to reflux for 15 min at 36^0. The ^1H nmr spectrum (CS_2) exhibited three peaks δ 2.0 (doublet J = 11 Hz, due to the methyl protons attached to phosphorus), 2.1 (singlet overlapped with δ 2.0 doublet, due to the C-methyl protons of the carborane), 7.4 (multiplet, due to the phenyl protons of the phosphine ligand). The nmr spectra are shown in Figures 8 and 9. The ^{31}P nmr (CH_2Cl_2) δ 120.4 (broad singlet). The ^{11}B nmr (CH_2Cl_2) δ 21.4, 22.6, 23.8 (three broad absorptions, intensity 1), 27.7 (broad singlet, intensity 3), 29.4 (broad singlet, intensity 4), 31.0 (broad singlet, intensity 4), 33.4 (broad singlet, intensity 3).

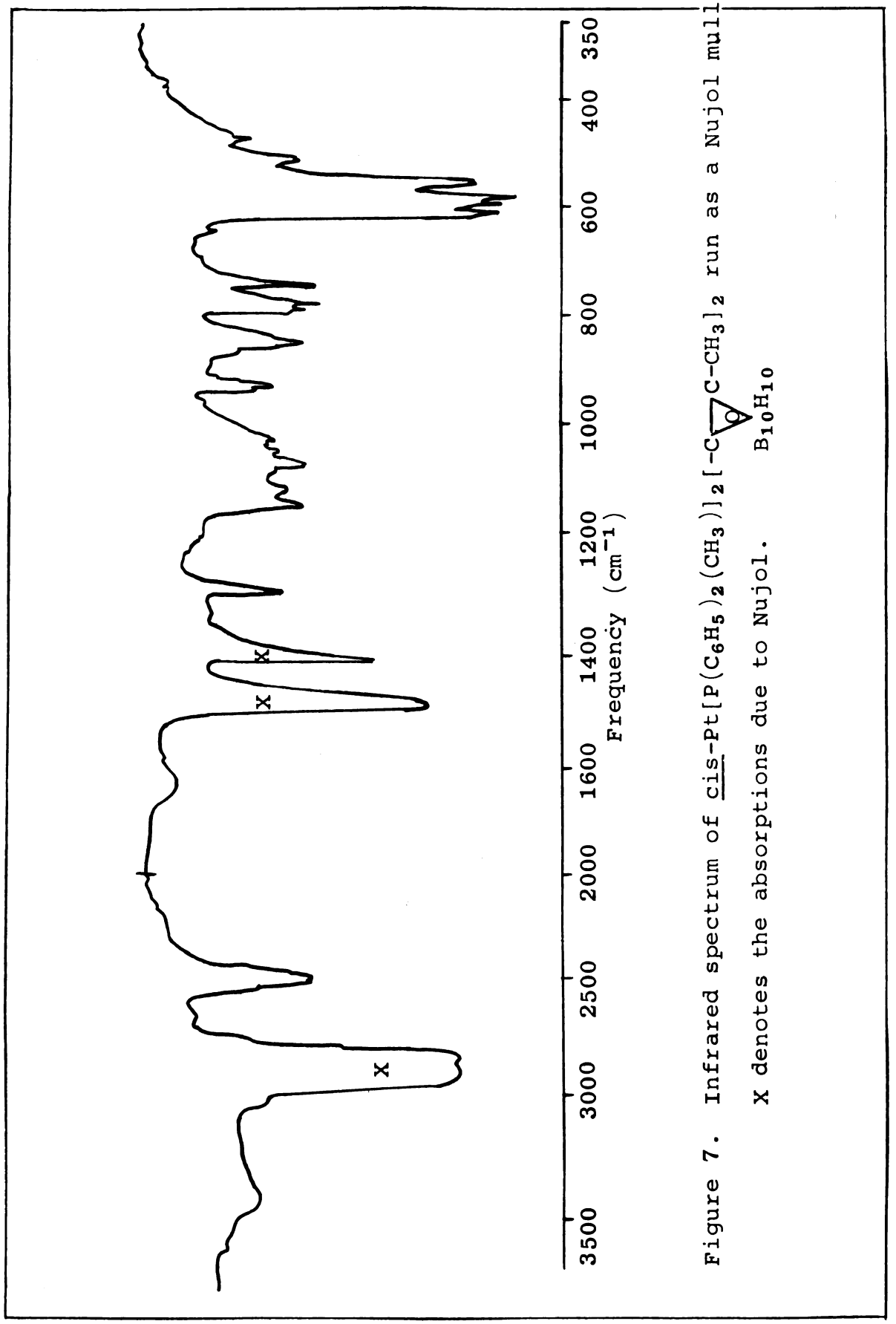


Figure 7. Infrared spectrum of cis-$Pt[P(C_6H_5)_2(CH_3)]_2[-C$ $B_{10}H_{10}$ $C-CH_3]_2$ run as a Nujol mull. X denotes the absorptions due to Nujol.

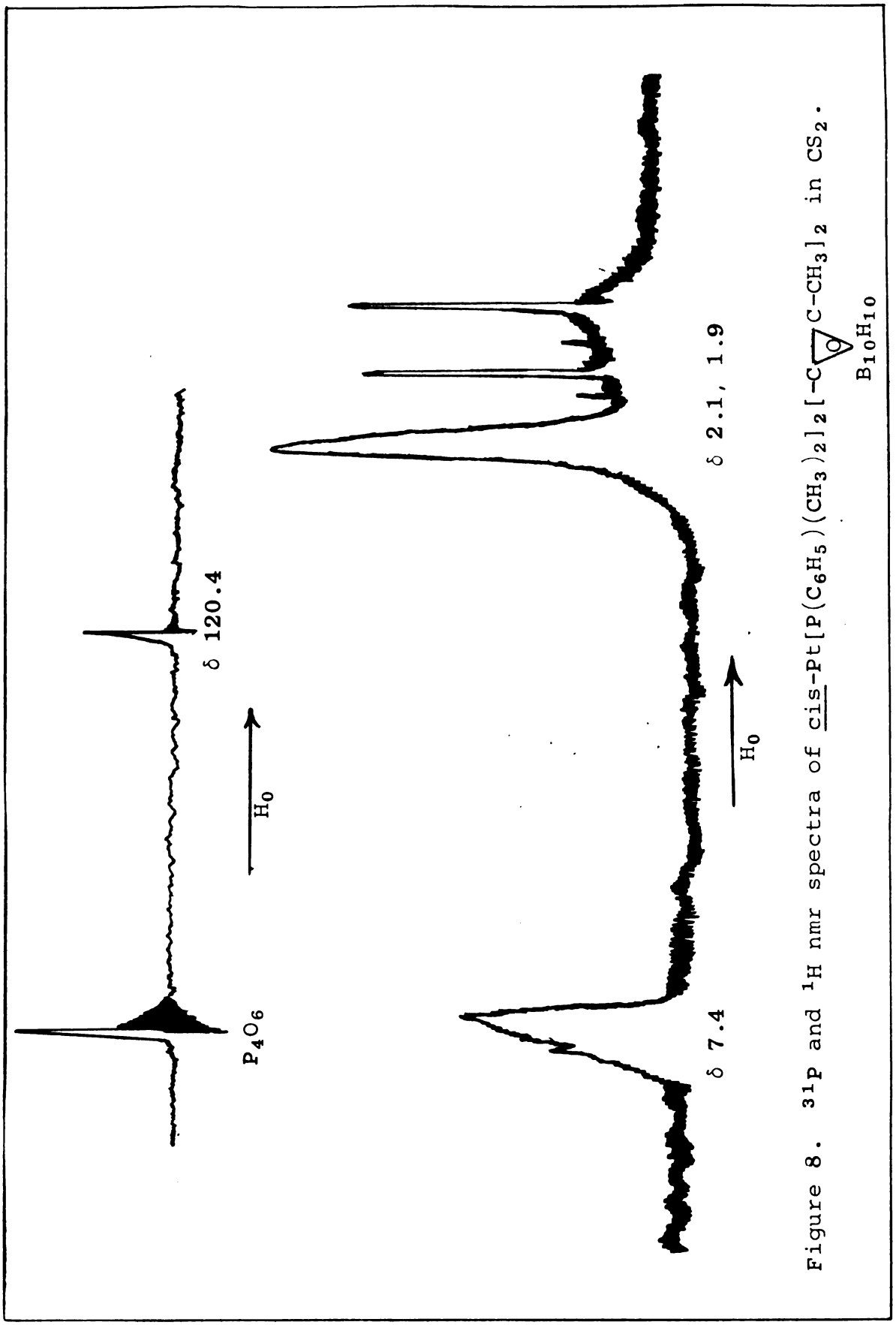


Figure 8. ^{31}P and ^{1}H nmr spectra of cis-$Pt[P(C_6H_5)(CH_3)_2]_2[-C_2B_{10}H_{10}C-CH_3]_2$ in CS_2.

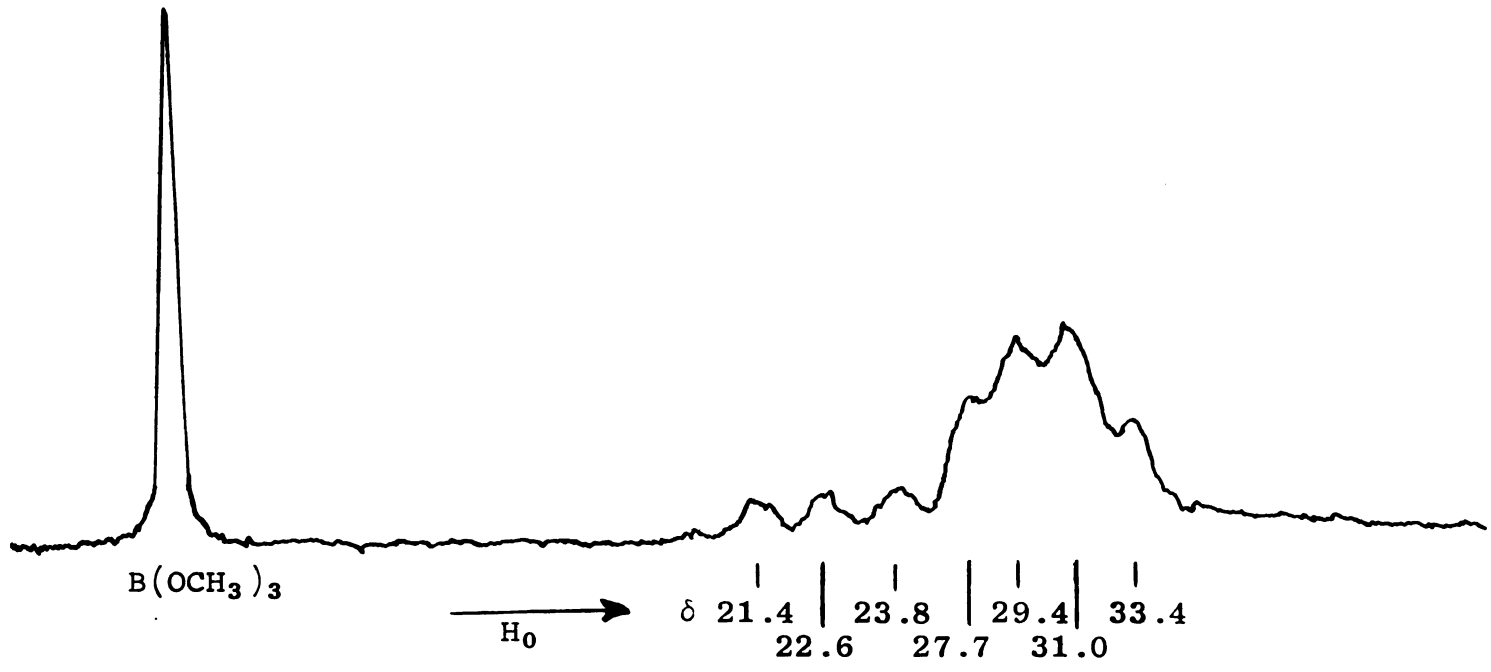


Figure 9. ^{11}B nmr spectrum of cis-$Pt[P(C_6H_5)(CH_3)_2]_2[-C_2B_{10}H_{10}C-CH_3]_2$ in CH_2Cl_2. $B(OCH_3)_3$ was used as an external reference.

The infrared spectrum of this compound mulled in Nujol, is shown in Figure 10. Again the two absorptions characteristic of the carborane cage are present (740 and 2550 cm^{-1}). See Table II for the analytical data. This complex was slightly more soluble in organic solvents than the previous phenylphosphineplatinum carborane complex, but was less stable in air, presumably because of hydrolysis.

d. The Preparation of C-$Pt[P(CH_3)_3]_2[-C_2B_{10}H_{10}C-CH_3]_2$

The general reaction procedure described previously was employed. After allowing the reaction vessel to warm to 25^0 for two hours, some of the insoluble trimethylphosphine platinum complex began to dissolve. After the solution was allowed to reflux for 15 min, it became cloudy and slightly yellow in color. After removal of the diethyl ether solvent by distillation in vacuo, a yellow residue remained in the flask. A buff colored solid was isolated after recrystallization. This solid decomposed when moist. Precise analytical data could not be obtained.

The ^1H nmr spectrum (CS_2) consisted of two resonances, δ 2.0 (broad overlapping singlet and doublet, due to the methyl protons of the phosphine and the C-methyl protons of the carborane). After two hrs the upfield peak decreased and a new resonance δ 3.5 [broad singlet, due to the starting material, 1-methyl-1,2-dicarbacloso-dodecarborane(12)] appeared.

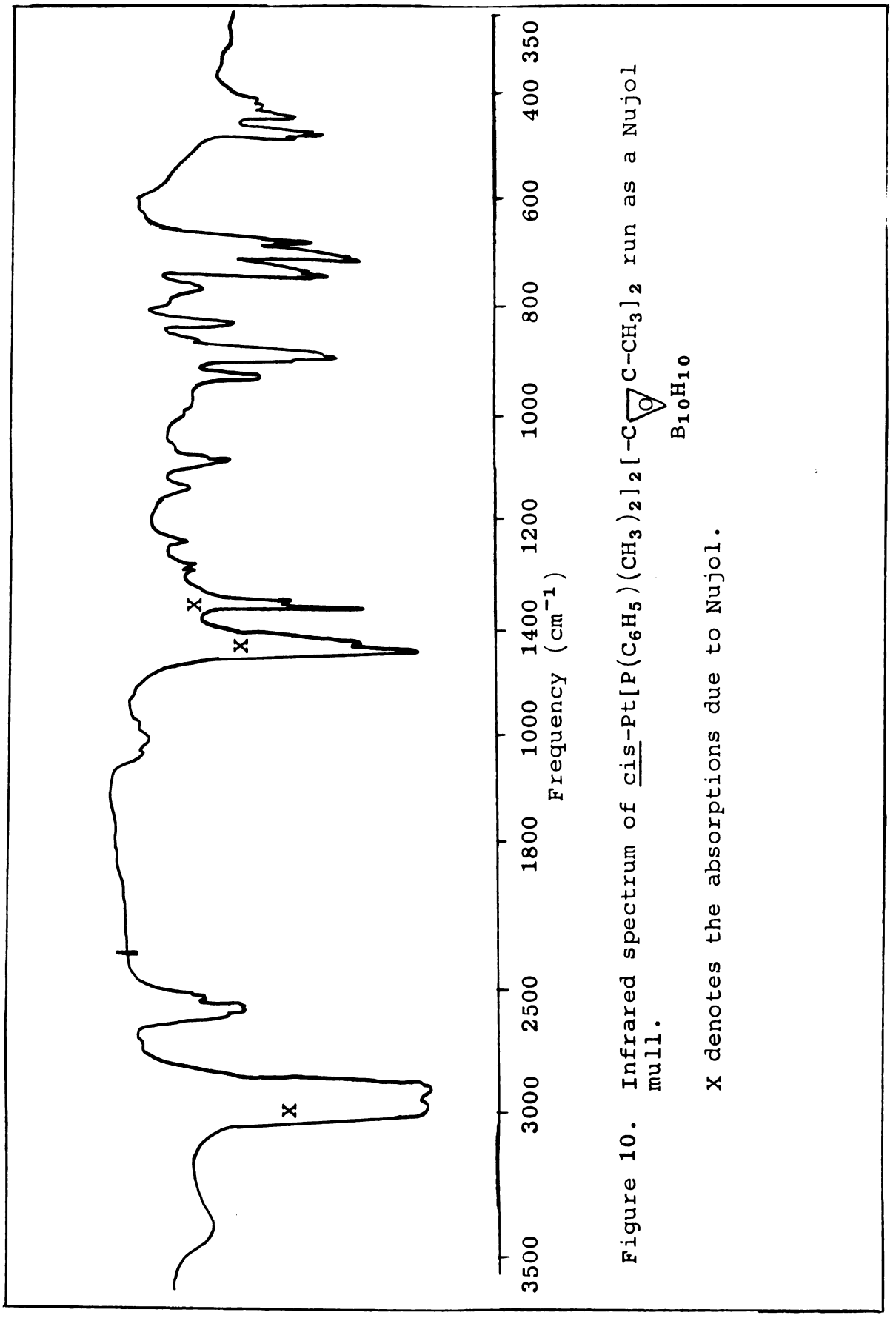


Figure 10. Infrared spectrum of cis-Pt[P(C_6H_5)(CH_3)$_2$]$_2$[-C$_2B_{10}H_{10}$C-CH_3]$_2$ run as a Nujol mull.

X denotes the absorptions due to Nujol.

The infrared spectrum of this compound exhibited the characteristic absorptions of the carborane cage. The appearance of strong bands at 1630 and 3400 cm^{-1} (OH vibrational modes) suggests that hydrolysis and decomposition of the product had occurred. The infrared spectrum is shown in Figure 11.

3. The Reaction of 1-Methyl-1,2-dicarbacloso-dodecarborane(12) with cis and trans-Dichlorobis(tri-n-butylphosphine)-platinum(II)

The cis and trans isomers of dichlorobis(tri-n-butylphosphine)platinum(II) which were used for these reactions were prepared and characterized according to the method described by Kauffman and Teter (45). M.P. 140-144° and 65-66° for the cis and trans complexes respectively (lit. (45) 142-144° and 65-66°). The reaction procedure described in the previous section was employed. Because the trans complex was soluble in benzene, benzene rather than diethyl ether was employed as a solvent. After addition of the yellow trans complex to the reaction flask a small amount of white precipitate appeared. The reaction was allowed to warm to 23°. The benzene was removed by distillation in vacuo, and a golden solid remained in the reaction vessel. This solid was dissolved in 70:30 carbon disulfide-methylene chloride mixture and then recrystallized from n-pentane.

The ^1H nmr spectrum (CS_2) exhibited three resonances, δ 1.0 and 1.6 (broad multiplet, due to the n-butyl groups

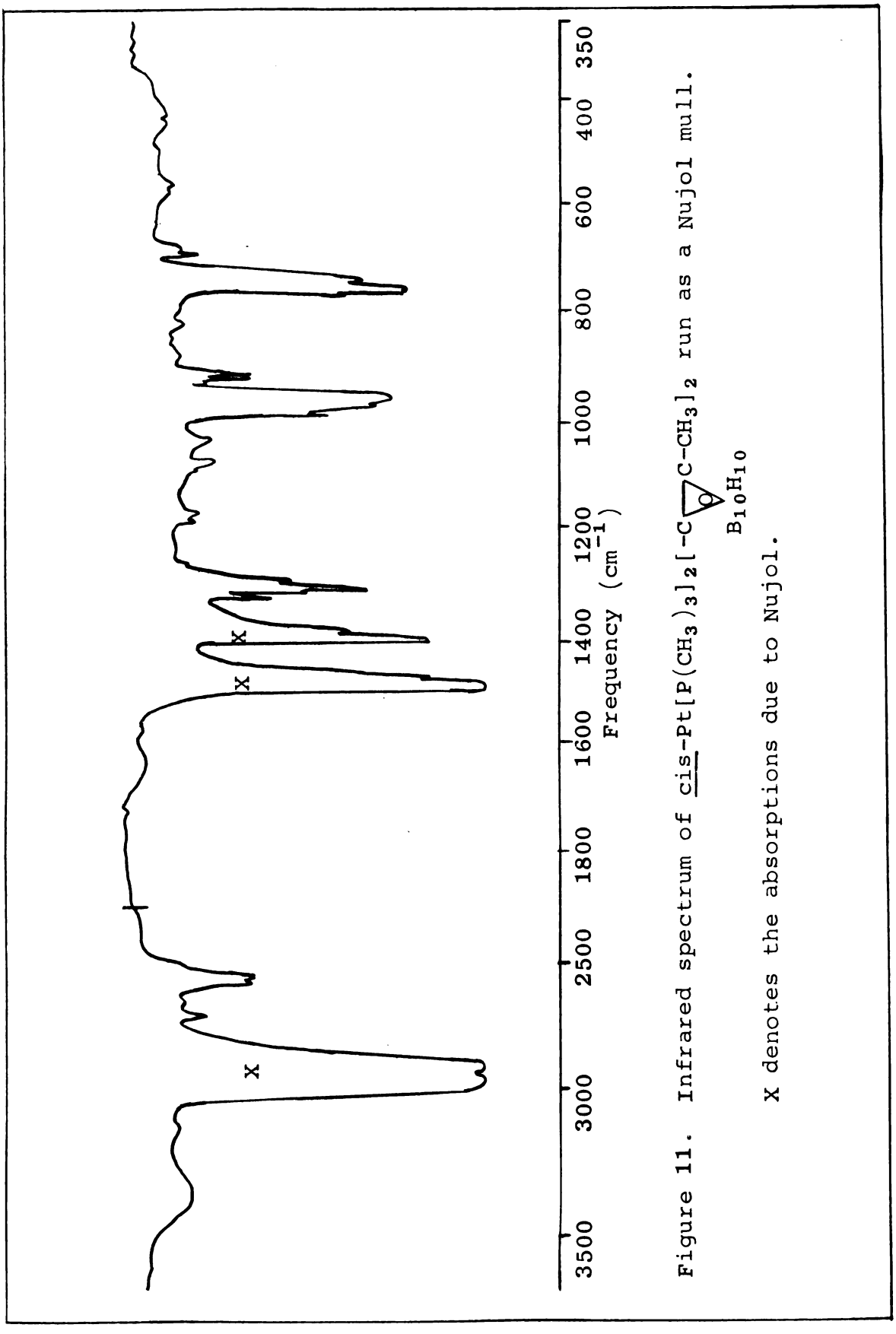


Figure 11. Infrared spectrum of cis-Pt[P$(CH_3)_3$]$_2$[-C$_2B_{10}H_{10}$C-CH_3]$_2$ run as a Nujol mull.

X denotes the absorptions due to Nujol.

on the phosphine), and 2.1 (singlet, due to C-methyl protons of the methyl carborane).

The infrared spectrum of the compound mullen in Nujol, is shown in Figure 12. The characteristic absorptions (725 and 2580 cm^{-1}) of the carborane cage were detected. The peaks at 1630 and 3400 cm^{-1} are attributed to OH stretching modes which arise from the hydrolysis of this complex.

Anal. Calcd. for $C_{30}H_{80}B_{20}P_2Pt$: C, 39.42; H, 8.76.

Found: C, 39.75; H, 8.30.

Molecular weight determined in benzene was 880 (theoretical 913). The melting point was 185 ± 5° (decomposition). The compound was partially soluble in methylene chloride and carbon disulfide. It appears to be moisture sensitive and decomposition was evident upon exposure to air for 15 min. The cis isomer of dichlorobis(tri-n-butylphosphine)platinum(II) was prepared according to the method of Kauffman and Teter (45). The general reaction procedure described for the trans isomer was used. The white cis isomer was insoluble in benzene and in most other organic solvents, thus it was added as a slurry in benzene. Upon warming to 25° the white slurry disappeared and the solution turned yellow. After distillation in vacuo, a yellow oily liquid remained in the flask. After recrystallization of the liquid from a 30:70 mixture of carbon disulfide and n-pentane a pale yellow solid remained.

Attempts to obtain reproducible nuclear magnetic resonance data from this product were unsuccessful. The complex

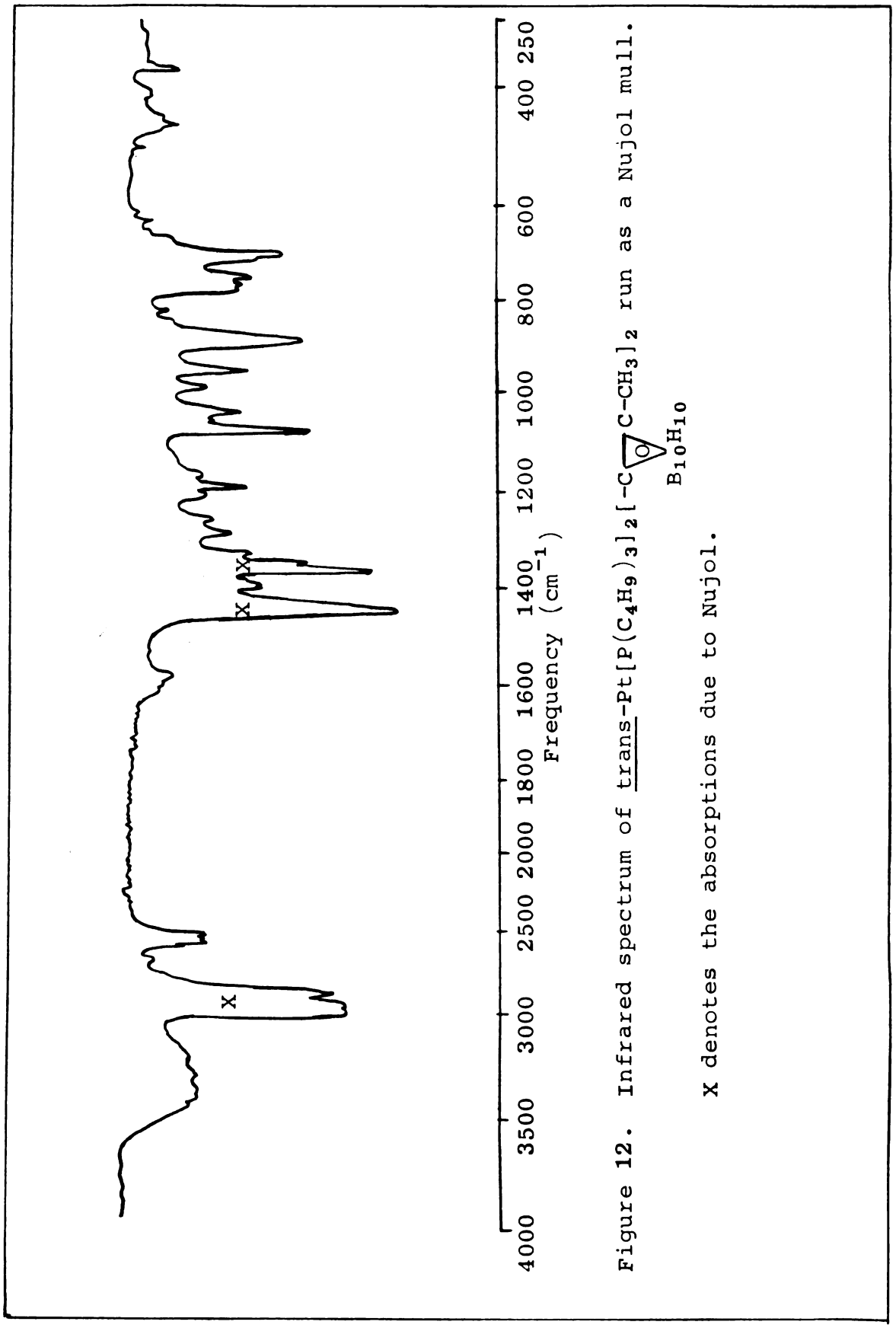


Figure 12. Infrared spectrum of trans-Pt[P(C_4H_9)$_3$]$_2$[-C$_{B_{10}H_{10}}$C-CH_3]$_2$ run as a Nujol mull.

X denotes the absorptions due to Nujol.

proved to be insoluble in most organic solvents. The ^1H nmr spectrum (CS_2) gave three broad peaks at δ 1.0, 1.6, and 2.1. The shifts were approximately the same as for the trans complex. The growth of an absorption peak at δ 3.5, suggests the product undergoes decomposition to the starting methyl carborane(12). The infrared spectrum for the cis compound showed the characteristic carborane cage absorptions as well as OH stretching modes which are attributed to the hydrolysis of this compound. Several attempts to get precise analyses and melting points on this cis compound were unsuccessful.

4. The Preparation of 1,2- bis(diphenylphosphino)carborane(12)

This bidentate carborane ligand was prepared according to the method of Alexander and Schroeder (46). The air-stable white solid was recrystallized from petroleum ether m.p. 217-218° (lit. (46) 219°). Infrared, ^1H, ^{31}P, and ^{11}B nuclear magnetic resonance, and mass spectral data, not previously reported for this compound, are shown in Figures 13-15 and Table III.

Anal. Calcd. for $C_{26}H_{30}B_{10}P_2$: C, 60.93; H, 5.86; P, 12.11.
Found: C, 60.82; H, 5.82; P, 11.10.

a. The Reaction of 1,2-bis(diphenylphosphino)carborane(12) with Potassium Tetrachloroplatinite(II)

Two complexes were obtained when 1,2-bis(diphenylphosphino)carborane(12) was allowed to interact with potassium

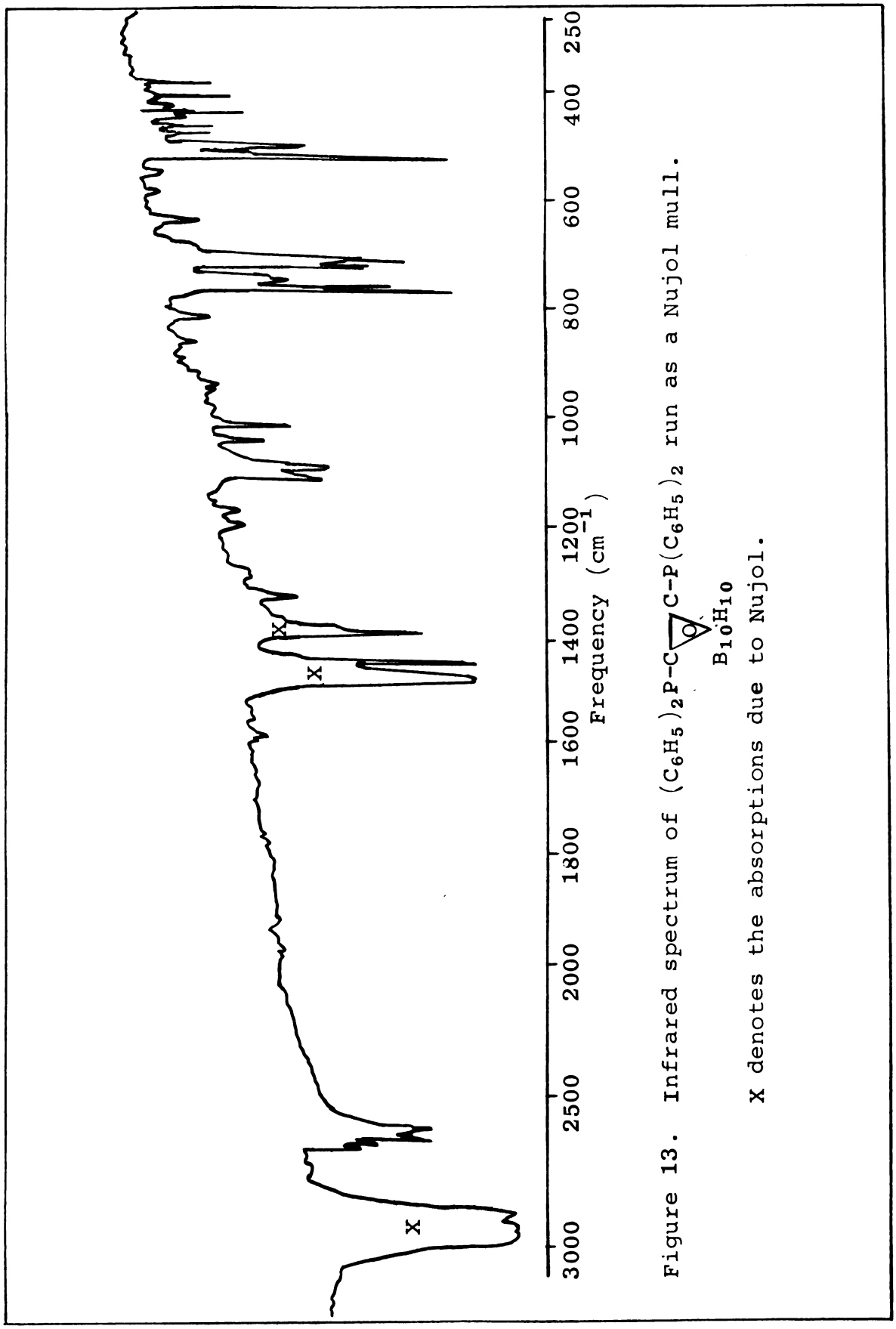


Figure 13. Infrared spectrum of $(C_6H_5)_2P\text{-}C\text{-}C\text{-}P(C_6H_5)_2$ run as a Nujol mull.

$B_{10}H_{10}$

X denotes the absorptions due to Nujol.

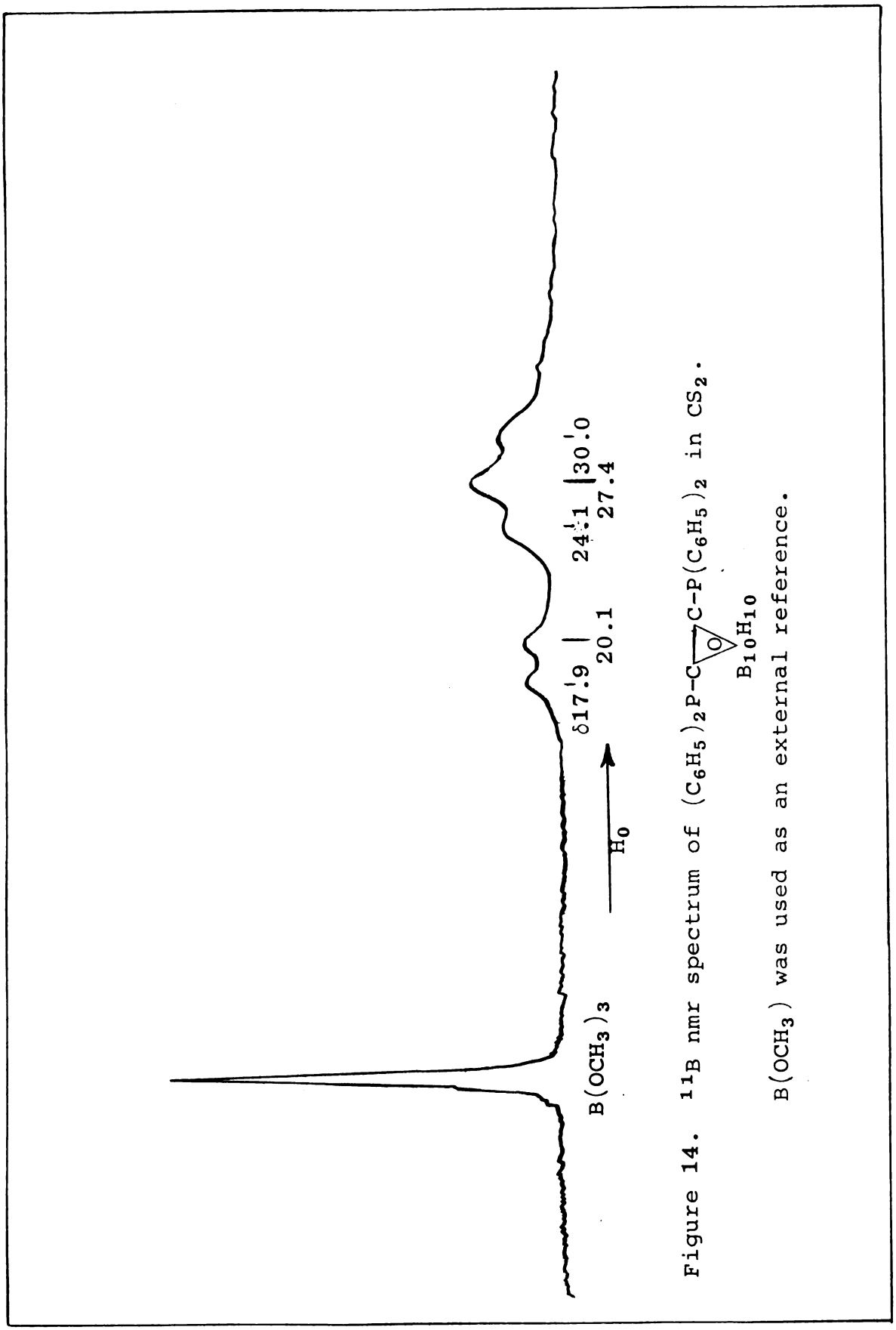


Figure 14. ^{11}B nmr spectrum of $(C_6H_5)_2P-C\overset{O}{\triangle}C-P(C_6H_5)_2$ in CS_2.

$B(OCH_3)$ was used as an external reference.

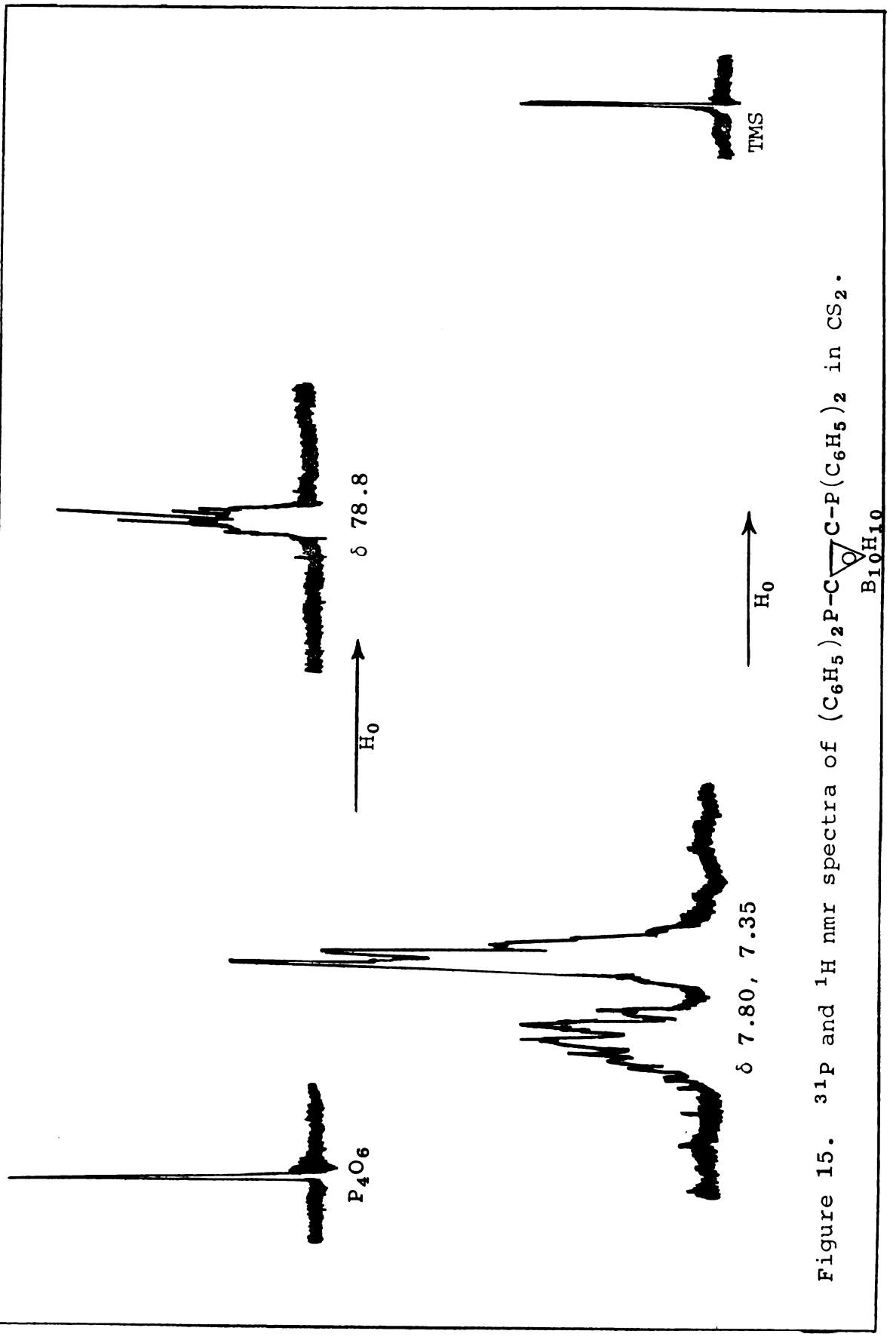


Figure 15. ^{31}P and ^{1}H nmr spectra of $(C_6H_5)_2P-C\overset{C-P(C_6H_5)_2}{\underset{B_{10}H_{10}}{\triangledown}}$ in CS_2.

Table III. Mass Spectrum of $(C_6H_5)_2P\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2$*

(Ionization Voltage 70 eV)

m/e	Relative Intensity	Assignment
512	100	$[(C_6H_5)_2P\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2]^+$
435	37.5	$[(C_6H_5)P\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2]^+$
404	15.5	$[(C_6H_5)\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2]^+$
327	36.5	$[(C_6H_5)_2P\text{-}C_2B_{10}H_{10}\text{-}C]^+$
262	14.5	$[P(C_6H_5)_3]^+$
250	15.0	$[(C_6H_5)P{=}C_2B_{10}H_{10}\text{-}C]^+$
216	12.5	?
185	45.0	$[P(C_6H_5)_2]^+$

* Boron cage compounds appear as a broad distribution due to boron isotopic effects. The center of each distribution is the m/e value reported.

tetrachloroplatinite(II). Both a 2:1 and a 1:1 complex of ligand to metal salt were prepared. To prepare the 2:1 compound, a 0.415 g (1 mmol) sample of K_2PtCl_4 was dissolved in a 60:40 methanol-water mixture and to this magnetically stirred solution a 1.03 g (2 mmol) sample of the 1,2-bis(diphenylphosphino)carborane(12) was added. No immediate reaction was evident so the solution was stirred for 12 hrs at about 30^0. After 12 hrs the solution was darkened by the formation of a gray-violet precipitate. This solution was cooled, filtered, and then washed with three 10 ml portions of cold 50:50 methanol-water mixture. A white residue and a violet precipitate were observed. The white substance was removed by washing the filtrate with benzene. The violet solid was insoluble in carbon disulfide, benzene, methylene chloride, diethyl ether, chloroform, and n-pentane, as well as HCl. A sample of this solid was sublimed in vacuo at 250^0. The small amount of white solid sublimate which was collected was shown by means of its ^1H nmr spectrum to be the starting bisphosphinocarborane(12) ligand. The remaining violet solid did not appear to be altered by the sublimation process.

A nuclear magnetic resonance spectrum could not be obtained due to the extreme insolubility of the violet solid. An infrared spectrum of the solid mulled in Nujol is shown in Figure 16. The absorptions at 750 and 2540 cm^{-1} are characteristic of the bisphosphinocarborane(12) ligand. There was no Pt-Cl stretch observed in the appropriate

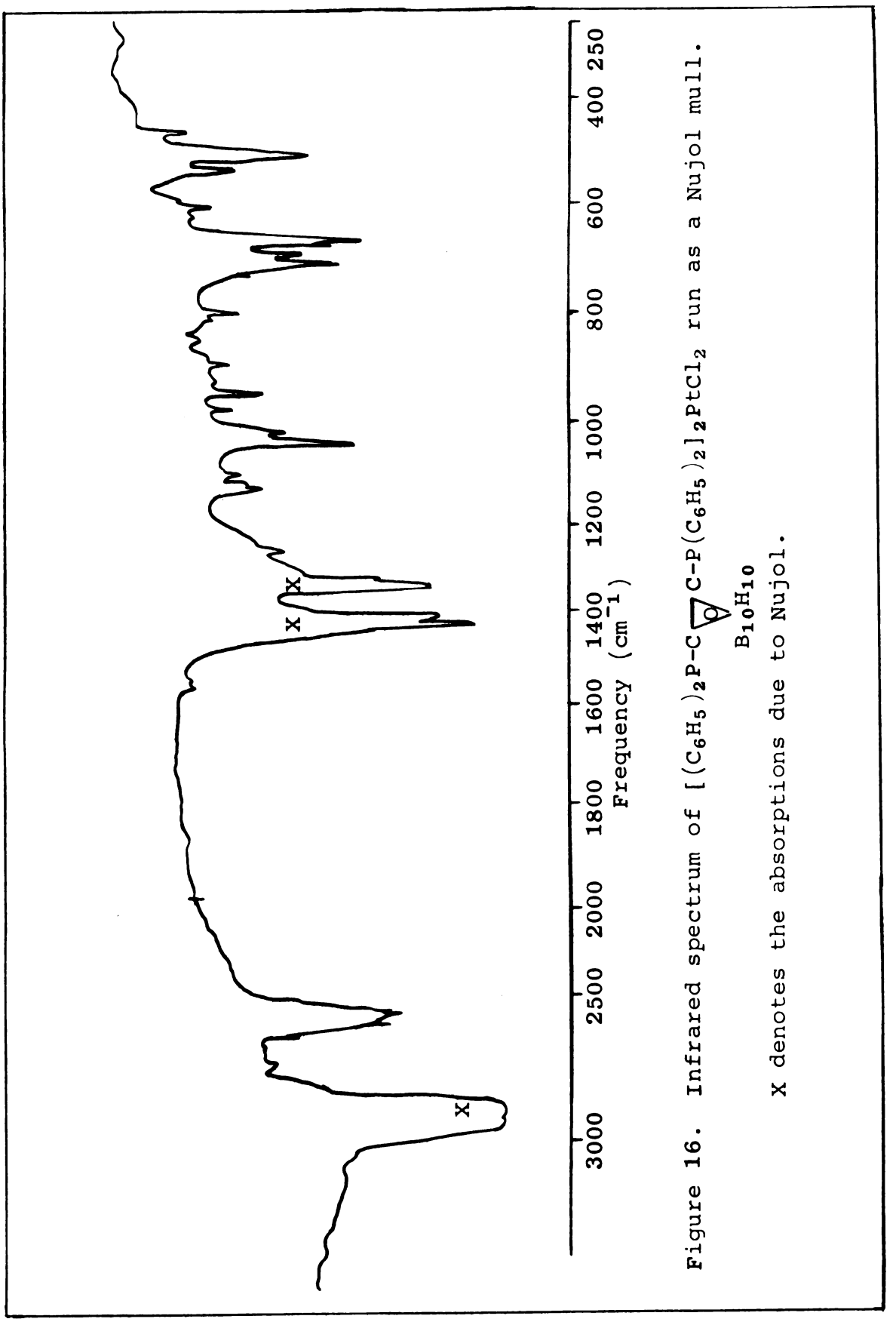


Figure 16. Infrared spectrum of $[(C_6H_5)_2P\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2]_2PtCl_2$ run as a Nujol mull.

X denotes the absorptions due to Nujol.

region of the infrared spectrum (280 to 310 cm^{-1}). This fact together with the chemical analyses suggests that the 2:1 complex of ligand to platinum salt was formed.

Anal. Calcd. for $C_{52}H_{60}B_{20}Cl_2P_4Pt$: C, 48.37; H, 4.65; Cl, 5.50. Found: C, 47.66; H, 4.48; Cl, 6.57. No molecular weight data were obtained due to the insolubility of this compound.

The 1:1 ligand to platinum complex was first prepared by accident in an attempt to prepare the 2:1 complex. A 1 mmol sample of K_2PtCl_4 was dissolved in a 60:40 mixture of ethyl acetate and water. To this stirred solution, a 1 mmol sample of the 1,2-bis(diphenylphosphino)carborane(12) was added. No immediate reaction was observed. The reaction flask was cooled to 20^0. After six hours a white precipitate was observed in the reaction vessel. The mixture was filtered; the precipitate was washed with water and then dried in vacuo. This gray-white solid was insoluble in carbon disulfide, benzene, methylene chloride, diethyl ether, chloroform, and n-pentane. I was unable to recrystallize the product and sublimation in vacuo at 250^0 left the product unchanged.

No nmr spectral data were obtained due to the insolubility of the complex. The infrared spectrum of this complex mulled in Nujol is shown in Figure 17. The bands characteristic of the bis(phosphino)carborane(12) at 750 and 2540 cm^{-1} are again present. There are also bands at 280, 290, and 310 cm^{-1} which we tenatively assign to Pt-Cl

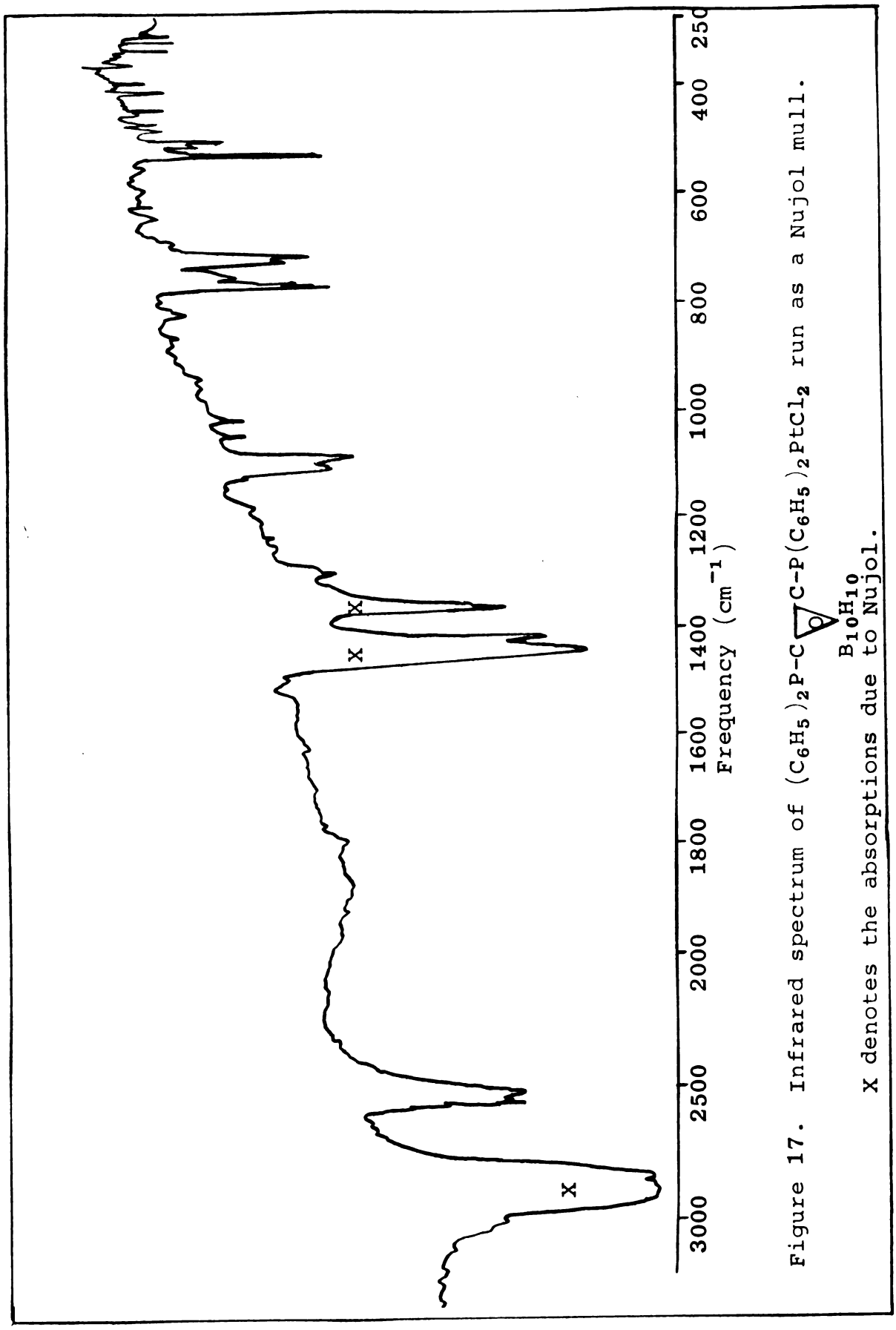


Figure 17. Infrared spectrum of $(C_6H_5)_2P\text{-}C\text{-}P(C_6H_5)_2PtCl_2$ run as a Nujol mull.

$B_{10}H_{10}$

X denotes the absorptions due to Nujol.

stretches. This evidence together with the analytical data support the suggested 1:1 formula for this complex.

Anal. Calcd. for $C_{26}H_{30}B_{10}Cl_2P_2Pt$: C, 40.10; H, 3.89; Cl, 9.11. Found: C, 39.83; H, 3.85; Cl, 8.89. No molecular weight data was obtained due to the insolubility of this product.

D. Attempted Syntheses

1. The Reaction of 1,2-Dicarbacloso-dodecaborane(12) with Dicyclopentadienyldichlorides of Titanium and Vanadium

The similarity of carborane to benzene suggested that $(C_5H_5)_2Ti(-C_2B_{10}H_{10}C-)$ or the dimer, $(C_5H_5)_2Ti(-C_2B_{10}H_{10}C)_2Ti(C_5H_5)_2$, might be prepared through a reaction analogous to the previously reported (47) reaction.

$$(C_5H_5)_2TiCl_2 + 2Li\text{-}C_6H_5 \xrightarrow{THF} (C_6H_5)_2Ti(C_5H_5)_2 + 2LiCl$$

Specifically, a 1 mmol sample of 1,2-dicarbacloso-dodecaborane(12) was dissolved in 50 ml of dried tetrahydrofuran solvent. A 2 mmol sample of n-butyl lithium in n- hexane was slowly added, over a period of 5 min, to the stirred reaction vessel maintained at 0^0. After 30 min the white slurry of the dilithium salt of carborane appeared. The red titanium complex (1 mmol) was added over a 10 min period as a suspension in THF. Immediate evidence of reaction was noted by a color change from red to dark green. After allowing this stirred mixture to react at 0^0 for

30 min, the system was allowed to warm to 25°. The solvent was removed by distillation in vacuo and a dark green oily residue remained in the flask. Attempts to recrystallize this oily product from benzene, methylene chloride, and n-pentane proved futile.

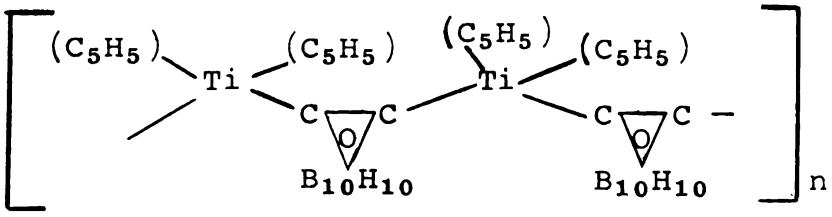
The ^1H nuclear magnetic resonance spectrum of the residue taken in THF revealed peaks attributed to the cyclopentadienyl protons (δ 6.5) as well as the characteristic peak (δ 3.52) of 1,2-dicarbacloso-dodecaborane(12). Several other minor peaks attributed to the unreacted titanium complex and decomposition products were observed. After several hours in solution the ^1H nmr peak attributed to the starting carborane (δ 3.52) increased in intensity. Precise analyses were never obtained.

This reaction was repeated several times with variations in the reaction time (30 min to 3 hrs) and temperature (0° to 36°). All attempts to isolate a stable fraction from the oily residues proved futile.

The vanadium analogue to titanium dicyclopentadienyl-dichloride was then investigated. The reaction procedures were identical to those employed in attempting to prepare the titanium complex, however, vanadium dicyclopentadienyl-dichloride was used as a reactant and THF as a solvent. Again a dark oily residue was the final product and all attempts at recrystallization proved unsuccessful.

The ability of titanium to polymerize may be responsible for the difficulty in isolating a characterizable compound.

The two reactive sites of 1,2-dicarbacloso-dodecaborane(12) may enhance the chance of polymerization. Thus polymers of the type



may form upon reaction. To avoid this problem I used 1-methyl-1,2-dicarbacloso-dodecaborane(12) (40) instead of 1,2-dicarbaclosos-dodecaborane(12). In this moiety, one of the active C-H sites has been blocked by the addition of a methyl group. This would eliminate the possibility of a polymer involving the carborane linkage.

Reaction procedures identical to those previously described (pp 7,8) were employed. After addition of titanium or vanadium dicyclopentadienyldichloride the solution immediately turned from the original color of the starting material to a dark green. Removal of the solvent (THF) by distillation in vacuo left an oily residue. All atte ts at recrystallization were unsuccessful. The nuclear magnetic resonance spectrum exhibited the characteristic peaks ascribed to the starting carborane material. The use of diethyl ether or benzene as the solvent resulted in no noticeable difference in the final product. No acceptable analyses were obtained on the system.

2. The Reaction of 1-Methyl-1,2-dicarbacloso-dodecaborane(12) with Palladium and Nickel Chlorides

Following the successful preparation of platinum-carborane compounds, reactions with palladium analogs of platinum were attempted. The starting materials for these reactions, cis-dichlorobis(triphenylphosphine)palladium(II) and trans-dichlorobis(tri-dimethylaminophosphine)palladium(II) were prepared and characterized according to previously reported methods (48, 49), m.p. 260-265° and 120° (decomp.) (lit. (48,49) 260-270° and 119-120° respectively). The procedures used to make the palladium compounds were identical to those described previously (pp 7-8). In a typical reaction, a 2 mmol sample of the lithium salt of methyl carborane(12) was prepared under nitrogen. This was followed by the addition of 1 mmol of the appropriate palladium complex in diethyl ether. When cis-dichlorobis(triphenylphosphine)-palladium(II) and trans-dichlorobis(tri-dimethylphosphine)-palladium(II) were employed, no immediate reaction was observed but dissolution of the added palladium complex occurred after the reaction flask was allowed to warm to 25° for one hr. The solution underwent a gradual color change from yellow to brown to black over this time period. An oily black residue remained after removal of diethyl ether by distillation in vacuo. These residues were partially soluble in carbon disulfide. A ^1H nuclear magnetic resonance spectrum revealed peaks which can be attributed to the starting material (δ 2.0 and 3.5) and other minor peaks,

(5-10% relative intensity) probably a result of the decomposition of the unreacted palladium complexes, which increased in intensity upon standing. Attempts to recrystallize these products were unsuccessful. A change of the solvent from diethyl ether to benzene had no observable effect on the reaction.

The analogous nickel(II) system was investigated *via* the preparation and characterization of the dichlorobis-(triphenylphosphine)nickel(II) (50,51) (m.p., 245-250°; lit. m.p. (51), 247-250°) and the subsequent interaction of this product with a 2 mmol sample of 1-methyl-1,2-dicarbacloso-dodecaborane(12). The reaction procedure used was identical to that described previously (pp 7-8). There was no evidence of immediate reaction, but upon warming to 25° the solution gradually darkened. The solvent (benzene) was removed by distillation *in vacuo* and a black residue remained in the flask. A ^{1}H nmr spectrum of the black residue in carbon disulfide exhibited peaks which can be ascribed to the starting methyl carborane and a very broad resonance (δ 7.3) due to the paramagnetic nickel complex. No further attempts at synthesis of nickel(II) complexes were carried out.

DISCUSSION

Sigma Bonded Methyl Carborane(12) Complexes

Although no σ-bonded transition metal complexes of methyl carborane(12) were reported at the start of this study, during the time these investigations were underway, three reports of similar complexes appeared (32-34). In these reports, however, detailed spectroscopic data were not presented. In this study the results of a systematic investigation of σ-bonded complexes will be reported, together with spectroscopic data. I was unable to obtain sufficient data, because of experimental difficulties, to fully characterize the influence of the carborane cage on the metal-carbon bond.

The possibility of preparing σ-bonded complexes by the interaction of cis-platinum phosphine compounds with methyl carborane(12) was established.

$$\underline{cis}\text{-}PtCl_2[P(CH_3)_nPh_{3-n}]_2 + 2CH_3\text{-}C_2B_{10}H_{10}\text{-}C\text{-}Li \xrightarrow[(C_2H_5)_2O]{0^0}$$

$$\underline{cis}\text{-}Pt[P(CH_3)_nPh_{3-n}]_2[\text{-}C_2B_{10}H_{10}\text{-}C\text{-}CH_3]_2 + 2LiCl$$

(where Ph is a phenyl group).

Elemental analyses together with molecular weight data suggest that all the complexes are monomeric and non-ionic when dissolved in CS_2.

The ^1H nmr spectral results indicate that bis(alkylphenyl)phosphinoplatinum methyl carborane(12) complexes have been isolated. The ^1H nmr spectral data show the presence of the methyl group on the carborane cage along with the appropriate phenyl and or methyl groups on the phosphine. The absence of the C-H resonance, characteristic of the starting methyl carborane(12), suggests this linkage has been destroyed on complexation, as expected.

The most soluble compound (CS_2, CH_2Cl_2, and benzene) was <u>cis</u>-$Pt[P(CH_3)_2Ph]_2[-C_2B_{10}H_{10}C-CH_3]_2$. The ^{31}P nmr of this complex appears as a broad singlet at δ +120.4. Although the ^{195}Pt-^{31}P coupling constant could be obtained on <u>cis</u>-$PtCl_2[(CH_3)_nPh_{3-n}]_2$, they were not observed in <u>cis</u>-$Pt[(CH_3)_nPh_{3-n}]_2[-C_2B_{10}H_{10}C-CH_3]_2$ because of the lower solubility of the latter complexes.

The ^{11}B nmr of <u>cis</u>-$Pt[P(CH_3)_2Ph]_2[-C_2B_{10}H_{10}C-CH_3]_2$ is shown in Figure 9. The apparently simple low field triplet and high field quartet may be due to overlap of the absorptions or second order spectral effects. For <u>cis</u>-$Pt[P(CH_3)_3]_2[-C_2B_{10}H_{10}C-CH_3]_2$, <u>cis</u>-$Pt[P(CH_3)Ph_2]_2[-C_2B_{10}H_{10}C-CH_3]_2$, and

<u>cis</u>-$Pt[P(Ph)_3]_2[-C_2B_{10}H_{10}C-CH_3]_2$ only very broad ^{11}B resonance absorptions were obtained.

In order to understand what effects the σ-bonded methyl carborane(12) exerts in the platinum complexes, an attempt was made to obtain the ^{195}Pt-^{31}P coupling constants. It has been suggested (52) that as the value of the coupling constant increases there is a corresponding increase in the π-acceptor character of the phosphine ligand. Although I was able to obtain these data for the complexes of the type <u>cis</u>-$PtCl_2[P(CH_3)_nPh_{3-n}]_2$, extensive efforts to obtain similar data for the complexes in which the chloride ligand is replaced by methyl carborane(12) were unsuccessful because the complexes which contained the carborane ligand were much less soluble than those which contained the chloride.

The yields for the <u>cis</u>-$Pt[P(CH_3)_3Ph_{3-n}]_2[-C_2B_{10}H_{10}C-CH_3]_2$ products were about 50%, based upon the amount of methyl carborane(12) recovered. As the phenyl groups on phosphorus were replaced by methyl groups the yields decreased. The complexes which contained greater numbers of methyl groups were more easily hydrolyzed, which may account for the lower yields.

It can be suggested on the basis of these observations that methyl carborane(12) is a poorer π-acceptor than a chloride anion when either of these are <u>trans</u> to phosphines in platinum(II) complexes. Increased stability toward hydrolysis is observed for dichlorobis(methylphenylphosphine)

platinum(II) compounds as the methyl groups on the phosphine are replaced by phenyl groups. This stability has been attributed to the increased π-acceptor character on phosphine because of electron delocalization within the phenyl groups (52,53).

The phenyl groups on phosphorus enhance the π-acceptor character of the phosphine. This results in greater overall bond strength between platinum and phosphorus (53). Methyl groups, however, act as electron donors; this weakens the π-acceptor character of phosphorus and the resultant bond strength between platinum and phosphorus is decreased.

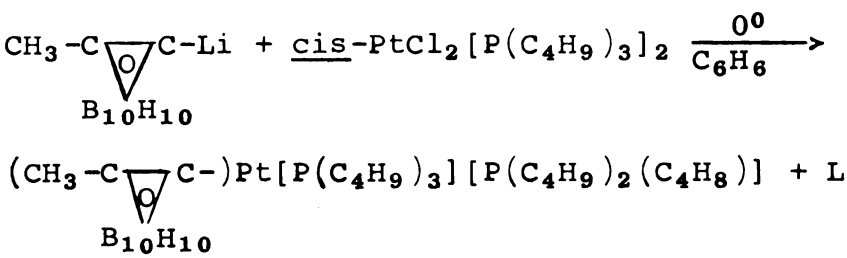
The substitution of methyl carborane(12) for the chloride ligand results in phosphinoplatinum(II) methyl carborane(12) complexes which are more susceptible to hydrolysis than the corresponding dichlorobis(phosphino)-platinum(II) complexes. Since the phosphine groups remain unchanged, hydrolysis apparently is made easier through the replacement of the chloride ligand by methyl carborane(12). This suggests that methyl carborane(12) is a weaker π-acceptor than a chloride ligand.

Such a result is not unreasonable. The chloride anion, which lies in the middle of the trans-effect series, can function as a π-acceptor (53). On the other hand, it has been reported that the o-carborane(12) cage can function as an electron donor or acceptor (54,55). Since the methyl group attached to the boron cage acts as an electron donor

to the cage, the methyl carborane(12) ligand should be a better electron donor and a poorer π-acceptor (56). No kinetic or thermodynamic studies have been attempted on this system.

The cis and trans complexes of dichlorobis(tri-n-butylphosphine)platinum(II) formed upon interaction with methyl carborane(12) were much more susceptible to hydrolysis than the corresponding phenyl phosphine complexes of methyl carborane(12). We suggest this because of the appearance of bands associated with OH vibrations in the infrared spectrum (1600 and 3400 cm^{-1}) and the appearance of an ^1H nmr resonance which can be ascribed to the starting material, methyl carborane(12) (C-H resonance at δ 3.5).

The expected cis complex from the interaction of dichlorobis(tri-n-butylphosphine)platinum(II) and methyl carborane(12) was not isolated. We suggest that a reaction similar to that described below can be used to rationalize the difficulty we encountered in the preparation of the cis-dichlorobis(tri-n-butylphosphine)platinum(II) methyl carborane(12) complex. (Where C_4H_8 is a butyl group which is bonded to both phosphorus and platinum.)



Turco reported similar results for the interaction of dichlorobis(tri-ethylphosphine)platinum(II) with methyl carborane(12) (33). He tentatively formulated the product of this reaction as $[P(C_2H_5)_3]Pt(-C_2B_{10}H_{10}C-CH_3)[P(C_2H_5)_2(C_2H_4)]$. (Where the C_2H_4 group is bonded to both phosphorus and platinum.) The molecular weight data, which was low for the expected methyl carborane(12) complex of dichlorobis-(tri-n-butylphosphine)platinum(II), is near the theoretical molecular weight for the product shown in the reaction (687). Precise analytical results were never obtained. No further investigations were attempted on this system.

Magnetic susceptibility measurements of all the phosphino methyl carborane(12) platinum complexes isolated were made on a Gouy balance. In every case, the compounds were found to be diamagnetic.

Platinum Complexes with 1,2-bis(diphenylphosphino)carborane(12)

The bidentate ligand 1,2-bis(diphenylphosphino)carborane(12) was first isolated by Schroeder (46). The previously unreported ^1H, ^{31}P, and ^{11}B nmr spectra are shown in Figures 12-14.

The proton spectrum (Figure 12) is unusual in that two distinct phenyl resonance absorptions are observed. These are located at δ 7.35 and 7.80 respectively from TMS. This behavior generally is observed when phenyl groups are bonded to systems which allow electron delocalization (57).

The ^{31}P nmr (Figure 13) of 1,2-bis(diphenylphosphino)-carborane(12) is a complex multiplet centered at δ +78.8 from P_4O_6.

The ^{11}B nmr spectrum of 1,2-bis(diphenylphosphino)carborane(12) (Figure 14) may be rationalized in the following manner. In the icosahedral structure for the o-$B_{10}C_2H_{10}$ unit one readily recognizes the existence of four different types of boron atoms, namely, 3(6), 8(10), 9(12), and 4(5,7,11). This would give rise to four singlets of area 2:2:2:4. These absorptions are further split by spin-spin coupling due to the protons attached to the borons to give a predicted spectrum of four doublets of relative integral intensities, 2:2:2:4. Such a spectrum has been reported for the ^{11}B nmr of o-carborane(12) at 60 MHz (58) and has been rationalized in terms of selective overlapping of the expected doublets (59).

The predicted spectrum of o-carborane(12) which appears to consist of four doublets is shown schematically in Figure 18a. It has been suggested that the high field doublet (d) is due to the 3(6) boron atoms located nearest to the carbon atoms of the icosahedral cage of o-carborane(12) (58). When 1,2 bis(diphenylphosphino)carborane(12) is prepared, the 3(6) boron atoms would probably feel the electronic effect of the carbon-phosphorus attachment more than the other boron atoms. A schematic reproduction of the ^{11}B nmr spectrum obtained at 65 MHz of 1,2 bis(diphenylphosphino)-carborane(12) is shown in Figure 18b. It can be suggested,

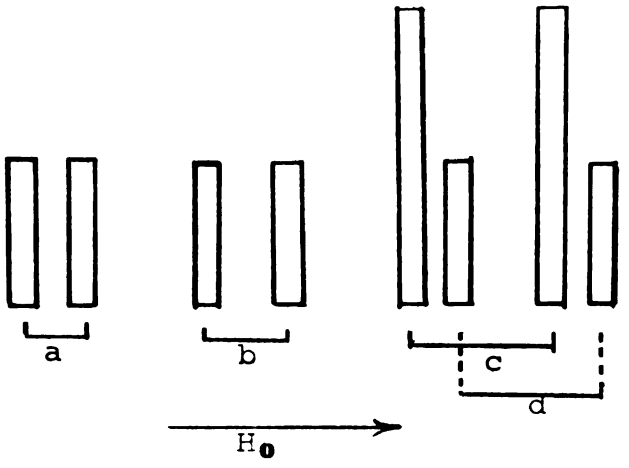


Figure 18a. Schematic representation of predicted spectrum for o-$B_{10}C_2H_{10}$ unit.

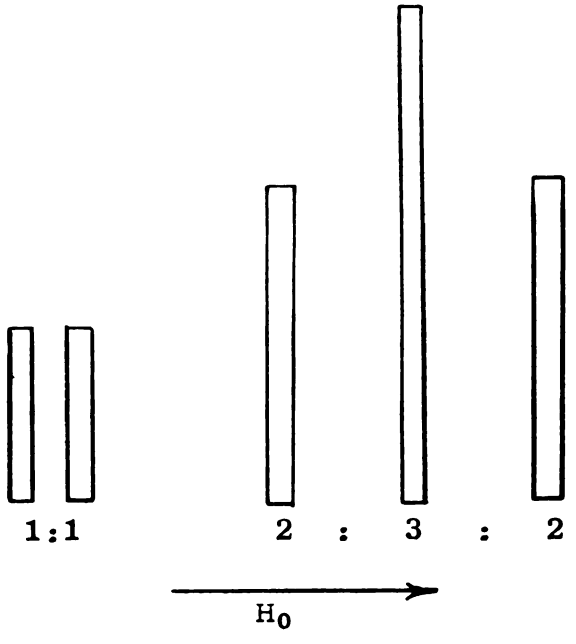


Figure 18b. Schematic representation of spectrum resulting from selective overlapping in $(C_6H_5)_2P\text{-}C_2B_{10}H_{10}\text{-}C\text{-}P(C_6H_5)_2$.

therefore, that the resonances ascribed to the 3(6) boron atoms, (d in Figure 18a), are shifted so as to overlap the high field member of d with the low field member of the resonance due to the 4(5,7,11) boron atoms, (c in Figure 18a). The low field member of d, the resonances ascribed to the 3(6) boron atoms, then overlaps with another low field doublet (b in Figure 18a). It is not possible to determine from the experimental data which boron atoms correspond to the resonances ascribed to the 8(10) and 9(12) atoms (a and b in Figure 18a). The resultant spectrum consists of a low field 1:1 doublet and an apparent 2:3:2 triplet. This is close to the observed ^{11}B spectrum for the 1,2-bis(diphenylphosphino)carborane(12) ligand (Figure 14). It has been reported that the attachment of $As(CH_3)_2$ groups to the o-carborane(12) cage has resulted in a change of electronic environment about the carbon atoms so as to cause such spectral results (55).

The mass spectral assignments for 1,2-bis(diphenylphosphino)carborane(12) are shown in Table III. The main peaks occur at m/e ratios of 512, 435, 404, and 327. These result from the loss of phenyl groups or the phenyl phosphine itself from the boron cage. A strong parent ion peak is observed which suggests that the ligand is thermodynamically stable.

The interaction of 1,2-bis(diphenylphosphino)carborane(12) with potassium tetrachloroplatinite(II) (K_2PtCl_4) gave a monosubstituted, $PtLCl_2$, and a disubstituted, $[PtL_2]Cl_2$

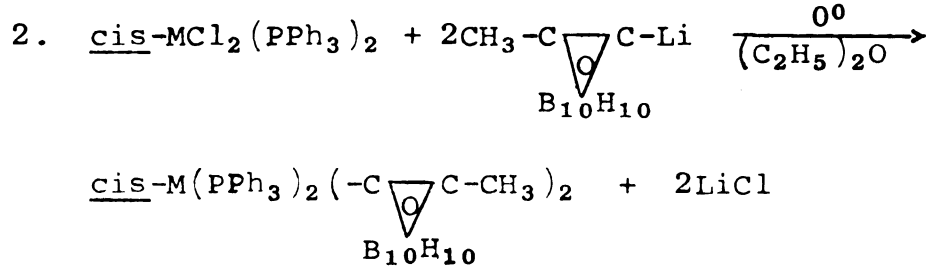
complex (where L is 1,2-bis(diphenylphosphino)carborane(12)). Both of these products were insoluble in carbon disulfide, benzene, acetone, ethyl acetate, methanol, ethanol, methylene chloride, tetrahydrofuran, and hydrochloric acid. The identity of these products is suggested by the analytical and infrared spectral data. Specifically, the C, H, and P analyses agree with the proposed formulations. In addition, the presence of platinum-chlorine stretches is observed in the infrared spectrum of the monosubstituted product (Figure 17), but is absent in the infrared of the disubstituted product (Figure 16). Attempts to obtain molecular weight data by means of mass spectral techniques were unsuccessful. It is generally difficult to volatilize platinum compounds for mass spectral analyses (60).

I attempted to prepare σ-bonded methyl carborane(12) complexes containing titanium, vanadium, palladium, and nickel by the use of similar techniques. The equations for the reactions are:

1. $(\pi\text{-}C_5H_5)_2MCl_2 + 2CH_3\text{-}C_2B_{10}H_{10}\text{-}C\text{-}Li \xrightarrow[(C_2H_5)_2O]{0^0}$

$(\pi\text{-}C_5H_5)_2M(\sigma\text{-}C_2B_{10}H_{10}\text{-}C\text{-}CH_3)_2 + 2LiCl$

(where C_5H_5 is the cyclopentadienyl anion and M is titanium or vanadium).

2. 

(where M is palladium or nickel).

However, no complexes could be isolated. Studies on some of these systems are still in progress by other investigators.

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