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Electronic Transitions of Metal Complexes with Triphenylphosphine as a Ligand

Thomas Zimmer
Western Kentucky University

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Zimmer,
Thomas E.

1975

ELECTRONIC TRANSITIONS OF METAL COMPLEXES WITH
TRIPHENYLPHOSPHINE AS A LIGAND

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Thomas E. Zimmer

August 1975

ELECTRONIC TRANSITIONS OF METAL COMPLEXES WITH
TRIPHENYLPHOSPHINE AS A LIGAND

Approved 7-31-75 :
(Date)

Carl F. Rosen
Director of Thesis

John W. Keenan

John J. Riley

Elmer Gray
Dean of the Graduate School

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Thomas E. Zimmer

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ELECTRONIC TRANSITIONS OF METAL COMPLEXES WITH
TRIPHENYLPHOSPHINE AS A LIGAND

Thomas E. Zimmer

August 1975

54 pages

Directed by: Earl F. Pearson

Department of Chemistry

Western Kentucky University

The spectra of transition metal complexes with triphenylphosphine have been measured near 260 nm and the results interpreted in terms of perturbation of the π electron system of the phenyl ring. All complexes studied show some degree of delocalization of the d-orbital electrons of the metal into the phenyl ring. However, for first row transition metals, the primary effect was found to be polarization of the phenyl ring due to the presence of the metal ion. For second and third row transition metal ions, the primary effect was found to be metal-ligand back-bonding. However, the effect of polarization of the rings due to the metal ion was noticeable.

INTRODUCTION

Few studies have been made of electron distribution in metal ligand complexes. Distortions of the electron cloud cause changes in symmetry which can make forbidden transitions weakly allowed. The intensity of the 260 nm transition in phenyl rings is a sensitive tool for studying changes in electron distribution in benzene derivatives. In triphenylphosphine, the change in symmetry is caused by the interaction between the lone pair of electrons on phosphorus and the ring plus some polarization of the ring caused by the metal ion in the complexes.

The purpose of this study is to see what factors such as metal ion size, back-bonding, covalency, etc. influence this transition in complexes of triphenylphosphine.

I. THEORETICAL

A. Quantum Theory

Since that time in 1900 when Max Planck first assumed that electromagnetic energy was quantized and the subsequent development of quantum theory, much has been learned and applied to the study of electrons in molecules. It took until 1924 for de Broglie to find and understand the dual nature of light and see the relationship between wavelength and momentum of small particles through Planck's constant:

$$\lambda = \frac{h}{p} \quad (1)$$

Where h is Planck's constant, λ is wavelength and p is the momentum of the particle.

In classical mechanics, a mechanical system can be specified to any desired degree of precision. This is not true in small systems. When dealing with small particles, uncertainty is introduced by the measuring process itself. This uncertainty is expressed as the Heisenburg Uncertainty Principle.¹ Therefore, the exact location of a small particle cannot be stated. However, the probability that the small particle is located in a volume of space defined by dx , dy , and dz can be determined.² Since a particle must be somewhere, the integral over all space is unity.

$$\int \psi \psi^* d\tau = 1 \quad (2)$$

Which implies that when the search is extended to all space, the

particle will be found. This equation is referred to as the normalization condition of the probability density p .³

In 1926, working independently W. Heisenburg and Erwin Schrödinger developed a revolutionary concept for applying classical concepts to small particles. This evolved into the present day quantum mechanics. Using Schrödinger's approach referred to as wave mechanics, we can define the motion of a particle by the equation:

$$H\psi = E\psi \quad (3)$$

Where H is the Hamiltonian operator, ψ is the wave function and E is the energy associated with a given wave function.

The Hamiltonian is a complex term containing all the energy terms of the system. Once the wave function, ψ , is known everything about the system can be deduced.

The function ψ must be finite, single valued and continuous at all points in order that its eigenvalues correspond to measurable quantities. The square of the wave function can be defined as the intensity of the wave. Therefore, ψ^2 relates to the probability of finding the electron around the nucleus or at various positions within the atom.

The Schrödinger equation can take many forms, from the simplified version (eq. 3) to the one expressed in Cartesian Coordinates

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad (4)$$

where ψ is the wave function, h Planck's constant, E the energy of the electron, V the potential energy of the electron. The Schrödinger equation expressed in spherical polar coordinates looks more complicated but is easier to solve.

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{8\pi^2 m r^2}{h^2} (E - V) \psi = 0 \quad (5)$$

An exact solution to this equation has been found only for simple systems, e.g. the hydrogen atom. Multiple electron systems require energy terms so complex that approximations must be made. In many cases the approximate results are quite close to experimental data.⁴

Polyatomic molecules are held together by electrons. These electrons have different amounts of energy depending upon the orbitals that they occupy and the interaction of these occupied orbitals with other occupied electronic orbitals in the polyatomic structure. Conversely the total energy of the polyatomic structure determines which specific orbitals are populated. Therefore, states of different energy usually have different shapes as well.

An electronic state may be defined by specifying the exact geometry of the molecule or by the equivalent means of specifying the values of the various quantum numbers applicable to the system. For example, different states may have different values of total angular momentum which is a result of mixing the orbital and spin angular momenta. The angular momentum of a state of the system has a magnitude determined by the manner in which the orbital and spin angular momentum for each electron combines to produce the resultant angular momentum for the entire group of electrons.

From the above reasoning, all molecular wave functions must conform rigorously to basic requirements based on the symmetry of the equilibrium nuclear network of the molecule. These requirements can be very severe. From a knowledge of symmetry it is possible to reach qualitative conclusions about electronic and molecular structure. Even though Group

Theory is a powerful tool, it cannot reveal the absolute intensity of a transition but it can tell if a transition is possible or not.⁵

Through application of Group Theory spectroscopists have developed a group of simple rules applicable to electronic transitions, which predict if a transition can occur.

The electronic transition rules can be summarized in the following equations:

$$\begin{array}{ll}
 g \longleftrightarrow u & g \not\longleftrightarrow g \quad u \not\longleftrightarrow u \\
 \Delta S = 0 & \\
 \Delta L = 0, \pm 1 & L = 0 \not\longleftrightarrow L = 0 \\
 \Delta J = 0, \pm 1 & J = 0 \not\longleftrightarrow J = 0 \\
 \Delta M = 0, \pm 1 &
 \end{array}$$

These rules state that if the electron changes spin, the transition is forbidden. If the change of the spin angular momentum greater than one (1) occurs, the transition is forbidden. If the change of total momentum of the system is greater than one (1), the transition is not allowed. If the change of the magnetic component of total angular momentum in a magnetic field is greater than one (1), the transition is forbidden.

There are cases where it appears that these selection rules are violated and a transition takes place. These transitions are weak and occur because of a mixing of orbitals or some change in symmetry.⁶

B. Crystal Field Theory

An electron in the outermost d energy level of a free metal ion may be located in any of the d-orbitals since all of these orbitals are equal in energy. If the same metal ion is in the presence of six negative point charges (ligands), the d-orbitals of the metal ion are no longer equivalent. If the metal ion is considered to be a sphere with

six negative charges on the surface, the six negative point charges will be located as far apart as they can get due to mutual repulsions. Connecting these six negative point charges from the inside of the sphere describes a regular octahedron with the metal ion in the center.⁷

The five equivalent d-orbitals lie in specific planes about the nucleus of the atoms. The lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals point toward the corners of a regular octahedron (See Figure 1) while the d_{xy} , d_{xz} , and d_{yz} orbitals are directed between the corners. Electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals are closer to the six negative point charges and, therefore, are higher in energy than electrons in the d_{xy} , d_{xz} , and d_{yz} orbitals which are farther away from the point charges. An electron is expected to be located in the lowest energy orbital possible. In this case, the lowest energy orbitals will be the d_{xy} , d_{xz} , and d_{yz} , with the d_{z^2} and the $d_{x^2-y^2}$ of a higher energy.

Thus in the octahedral environment of six negative charges, the metal ion has two sets of d-orbitals. The three orbitals designated as d_{xz} , d_{xy} , and d_{yz} are all equal in energy and have symmetry labeled as t_{2g} . The other set designated as $d_{x^2-y^2}$ and d_{z^2} which are higher in energy than the t_{2g} and labeled collectively as e_g .

Going from the free ion in which all the d-orbitals are equal in energy to the octahedral field of six point charges, the d-orbitals split due to interaction with the charges. The t_{2g} group is lowered in energy while the e_g set is raised in energy. The difference in energy caused by the splitting is designated as Δ_0 . The energy level of a metal ion in an octahedral field lies $3/5 \Delta_0$ above the energy of the metal ion in a spherical field, while the t_{2g} level lies $2/5 \Delta_0$ below this level. The value of Δ_0 , called the crystal field stabilization energy, is different for each ligand. This splitting is illustrated in Figure 2.

Figure 1. Use of $d_{x^2-y^2}$ and d_{z^2} Orbital Lobes in Bonding.

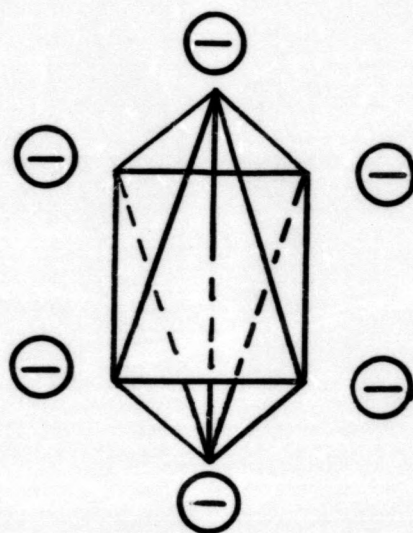
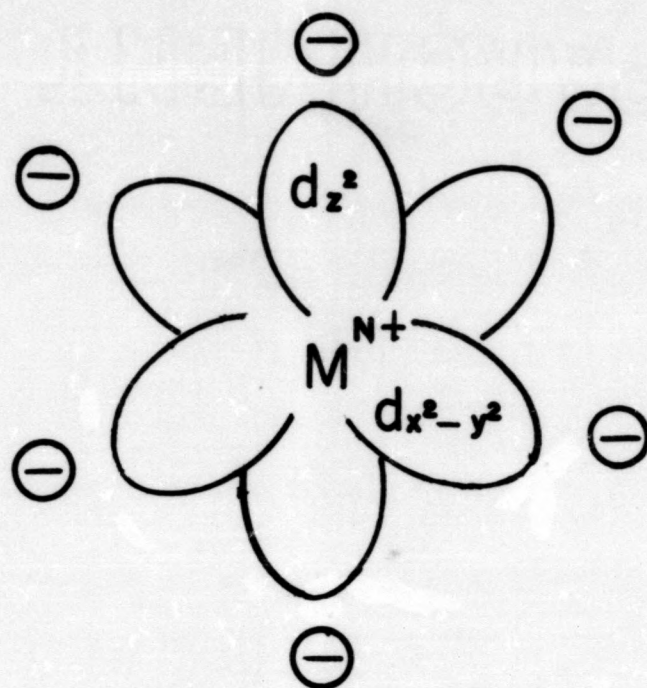
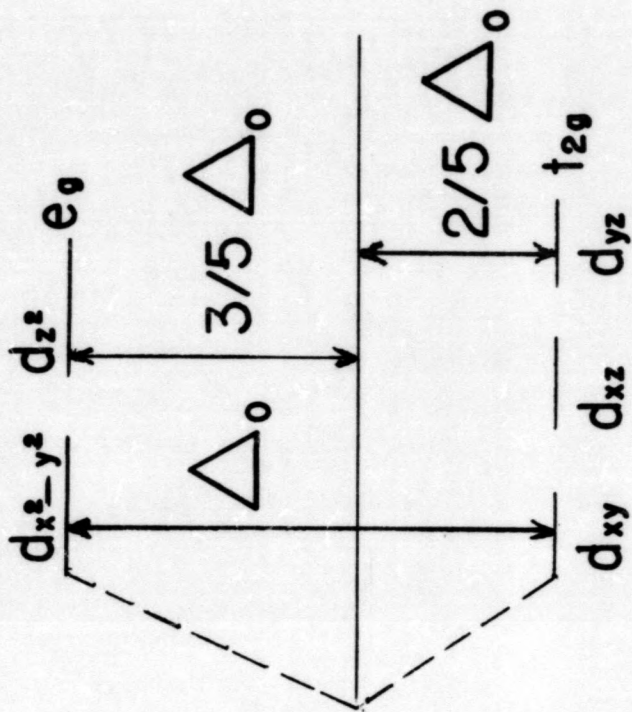


Figure 2. The Effect of an Octahedral Set of Point Charges on the Degenerate Set of d-orbitals of a Metal Ion.

$\frac{d_{xy}}{d_{xz}} \quad \frac{d_{yz}}{d_{z^2}} \quad \frac{d_{x^2-y^2}}{d_{x^2-y^2}}$



FREE ION

OCTAHEDRAL SET
OF POINT CHARGES

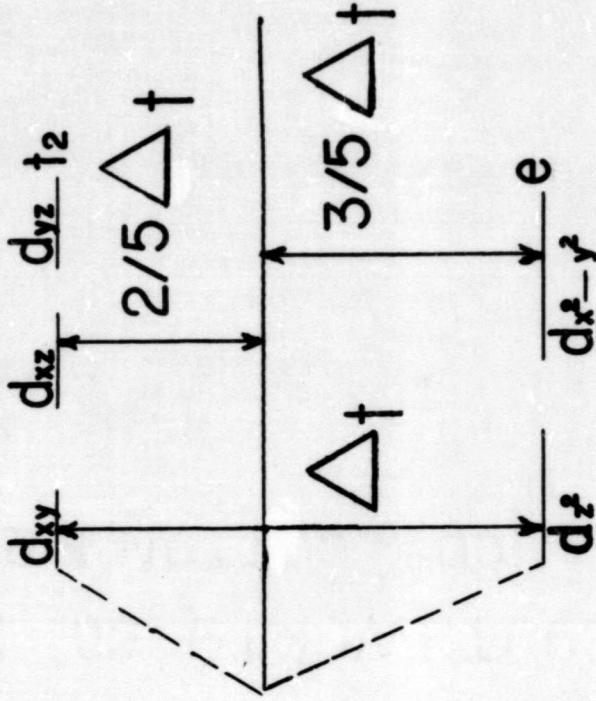
By a similar argument it can be shown that four point charges will arrange themselves around a metal ion at the vertices of a regular tetrahedron with the metal ion at the center. In this case electrons in the d_{xz} , d_{xy} , and d_{yz} orbitals are closer to the point charges therefore higher in energy than electrons in the $d_{x^2-y^2}$ and d_{z^2} . This is the reverse of the octahedral case. In the tetrahedral case, the symmetry labels for the two groups change slightly to t_2 for the d_{xz} , d_{xy} , and d_{yz} , while the label for the $d_{x^2-y^2}$ and d_{z^2} changes to e , since the tetrahedron has no center of symmetry. The energy difference between the t_2 level and e level is designated as Δ_t . The three orbitals of t_2 symmetry lie $2/5 \Delta_t$ above the unsplit metal ion level and the e energy level lies $3/5 \Delta_t$ below the unsplit metal ion level. See Figure 3. In cases where the cation, anion, and cation-anion distances are the same for both octahedral and tetrahedral cases, it can be shown that

$$\Delta_t = 4/9 \Delta_0 \quad (6)$$

The square planar complex can be generated from an octahedral complex by removing two opposing ligands. Slow removal of two opposing ligands gives a tetragonally distorted octahedral complex. If the ligands on the z -axis are pulled away, when the distance between the metal and the ligand on the z -axis is greater than the distance to each of the other orbitals, new energy splitting in the d -orbitals arise. First the degeneracy (states of equal energy) of the e_g orbitals is removed. Because the ligands on the z -axis exert a much more direct repulsive affect on a d_{z^2} electron than upon electrons in the $d_{x^2-y^2}$ orbital, the d_{z^2} orbital becomes more stable as z -axis ligands are removed. At the same time, the degeneracy of the t_{2g} level is also

Figure 3. The Effect of a Tetrahedral Set of Point Charges on a Set of Degenerate Orbitals.

d_{xy} d_{xz} d_{yz} d_z $d_{x^2-y^2}$



FREE ION

TETRAHEDRAL SET
OF POINT CHARGES

removed. As the ligands on the z-axis move away, the orbitals defined in the xz- and yz-planes remain equal in energy but become more stable than the xy orbital. This makes the xy-orbitals less sensitive to changes along the z-axis than the xz- and yz-orbitals. See Figure 4.

It is possible for the d_{z^2} orbital to drop below the d_{xy} in energy if the z-axis ligands are completely removed. In solution, there is always some interaction along the z-axis.⁸

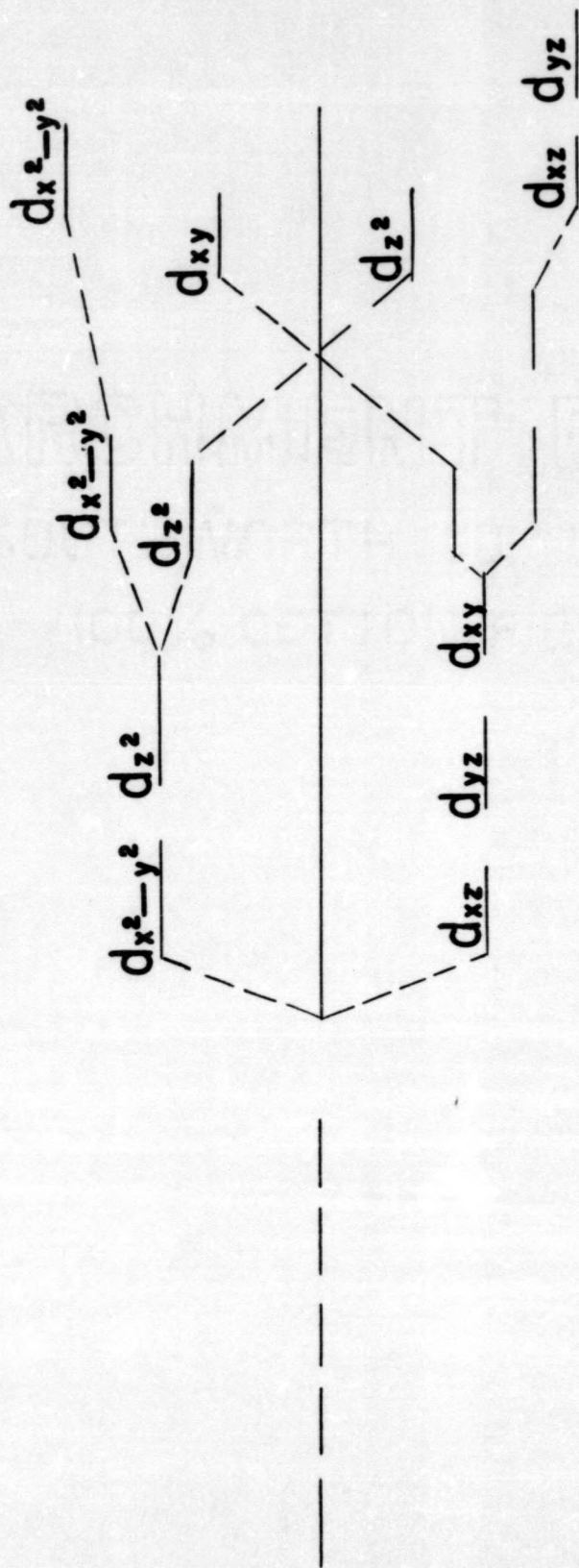
C. Hard-Soft Acid-Base Theory

Bonding in transition metal complexes can also be described by the Pearson Hard-Soft Acid-Base concept. The basic difference between hard and soft is the ability to be polarized. The "hardness" increases with decreasing size and increasing positive oxidation number. Soft acids prefer to associate with soft bases with interactions more covalent in nature than the ionic type found with hard acid-base interactions.⁹

If the same base is used, the type of bonding between the acid and base depends upon the nature of the acid. Metals of zero or low oxidation number or of large size are soft. These are expected to form strong covalent bonds with soft bases. This is brought about because the lone pair of electrons of the donor atom (Lewis base) can delocalize into the d-orbitals of the metal and expand the metal's d-orbitals. This delocalization increases the mean distance between the d-electrons and enhances the covalency of the metal-ligand bond. Increasing the mean distance of the d-electrons in the complex will reduce the interelectronic repulsion.

Furthermore, soft-acids have the potential of d or p-donation into suitable ligands orbitals via π bonds. Some ligands such as CO and $P\phi_3$, with electron acceptor orbitals, can form complexes with transition

Figure 4. Tetragonally Distorted Octahedral Complex. (Not to scale)



TETRAGONAL DISTORTION

metals. These ligands have the lone pair of electrons required of Lewis bases and also vacant π orbitals. The vacant orbitals accept electrons from the filled metal orbitals to form a type of π bonding. This bonding supplements the σ bonding arising from the lone pair of electrons. This supplemental π bonding from the metal back to a ligand has been termed "back bonding." From an electrostatic viewpoint, the stronger the degree of back bonding the stronger the normal σ bonding.¹⁰

D. Electronic States of Substituted Benzene Molecules

In the ground state, the six electrons of the phenyl ring are added to the lowest energy orbitals according to Hund's Rule and the Pauli Principle. The ground state (${}^1A_{1g}$) is formed by the combination of $(a_{2u})^2$ and $(e_{1g})^4$. The lowest excited states are obtained by promoting an electron from the e_{1g} orbital to the next higher orbital of e_{2u} symmetry. This transition is the first known transition of the singlet-singlet ultraviolet absorption of benzene vapor near 260 nm.¹¹

The 260 nm transition in benzene is forbidden by symmetry selection rules applicable to the hexagonal benzene molecule. The intensity of the 260 nm transition in benzene vapor is a measure of the ring distortion due primarily to the ν_{18} vibrational mode. This ν_{18} vibrational mode is a stretching of the benzene ring.¹²

This forbidden transition in benzene becomes allowed due to mixing of the electronic and vibrational motions of the molecule. The transition becomes allowed because the π electron symmetry is reduced from D_{6h} to a lower order of symmetry due to excitation of a nontotally symmetric vibration.

The 260 nm transition of substituted benzene molecules is more intense than in benzene. This $\pi^* \leftarrow \pi$ phenyl ring transition is allowed in the absence of coupling between the electronic and vibrational motions

since the symmetry of substituted benzene molecules is less than

D_{6h} .¹³ The intensity of this transition in triphenylphosphine and other factors will be discussed in more detail in chapter three.

II. EXPERIMENTAL

A. Preparation of Complexes

All chemicals used were reagent grade and used without further purification. All complexes have been previously reported in the literature and the preparations were repeated with little difficulty. The product crystals were purified for use through recrystallization. All physical properties matched those cited in the literature.

1. $\text{Fe}(\text{P}\phi_3)_2\text{Cl}_3$

The compound was precipitated from a mixture of triphenylphosphine (6 g) and anhydrous iron(III) chloride (1.6 g) dissolved in ethyl acetate. The precipitate was filtered and washed with anhydrous ethyl ether. The crystals were recrystallized from a small volume of boiling acetonitrile. The resulting dark green crystals had the following properties: m.p. 98-120°C (reported¹⁴ 114°C); soluble in ethyl acetate, methanol and acetonitrile; unstable in humid air or alcohol; insoluble in ethyl ether and benzene.

2. $\text{Co}(\text{P}\phi_3)_2\text{Cl}_2$

Cobalt(II) chloride hexahydrate was added to molten triphenylphosphine. The blue product was dissolved in hot ethanol, filtered, allowed to cool, and the crystals collected. The product is soluble in chloroform, slightly soluble in ethanol, decomposes in benzene and water, insoluble in n-heptane; m.p. 208-215°C (reported¹⁵ 225°C).

3. $\text{Ni}(\text{P}\phi_3)_2\text{Cl}_2$

Nickel(II) chloride hexahydrate was added to molten triphenylphosphine. The product was separated from excess ligand and recrystallized from hot acetic acid. The compound decomposes in benzene, n-heptane, chloroform, ether; slightly soluble in acetonitrile, methylene chloride; m.p. 235-245°C (reported¹⁵ 244°C).

4. $\text{Cu}(\text{P}\phi_3)_3\text{Cl}$

Copper(II) chloride was added to melted triphenylphosphine. The resulting white paste was dissolved in chloroform. The resulting solution was then treated with n-heptane. The white crystals which formed were collected and washed with n-heptane. The complex is soluble in chloroform, methylene chloride, benzene, acetone, and nitrobenzene; insoluble in water, ethanol, and n-heptane; m.p. 155-165°C (reported¹⁵ 160°C).

5. $\text{Pt}(\text{P}\phi_3)_2\text{Cl}_2$

K_2PtCl_4 was added to melted triphenylphosphine. The resulting white paste was dissolved in methylene chloride and precipitated with n-heptane. The white crystals are soluble in methylene chloride, chloroform, and dimethylformamide; insoluble in water, benzene, and ethanol; m.p. 298-305°C (reported¹⁵ 310°C).

6. $\text{Pd}(\text{P}\phi_3)_2\text{Cl}_2$

Palladium(II) chloride was added to molten triphenylphosphine. The yellow product that was formed was extracted with chloroform. The extract was then treated with n-heptane, filtered and washed with n-heptane. The compound is soluble in chloroform and methylene chloride; sparingly soluble in benzene and methanol; insoluble in water, acetone, ether, and n-heptane; (m.p. reported¹⁵ 298°C with decomposition).

7. $\text{Ag}(\text{P}\phi_3)_4\text{ClO}_4$

A solution of silver perchlorate (1.55 g) in hot absolute ethanol (4 ml) was added to a solution of triphenylphosphine (7.37 g) also in hot ethanol (30 ml). A colorless solid was immediately formed, and the solution filtered after cooling. The crude product was recrystallized from acetonitrile and the colorless crystals were washed with methanol and dried in a vacuum. The compound is insoluble in water, ethyl acetate, n-heptane, cyclohexane, carbon tetrachloride; slightly soluble on heating in the lower alcohols, acetone, chloroform, benzene, toluene, dioxane, and acetonitrile; m.p. 290–298°C (reported¹⁶ 290°C).

8. $\text{Au}(\text{P}\phi_3)\text{Cl}$

A solution of 2 mmoles of triphenylphosphine (0.524 g) in ethanol was added with stirring to 1 mmole of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.394 g) in 10 ml of ethanol. Crystals formed immediately but redissolved. The solution was sealed and placed in a freezer where crystals grew slowly. The crystals were separated, washed with a small volume of ethanol, then again with ethyl ether and dried in a vacuum over copper sulfate. The light yellow prisms are insoluble in water, partially soluble in alcohols, carbon tetrachloride, water free benzene, chloroform, and pyridine. The crystals darkened at 180°C and decomposed at 230°C, as reported.¹⁷

9. $\text{Rh}(\text{P}\phi_3)_3\text{Cl}_2$

A solution of triphenylphosphine (12 g) in hot ethanol (350 ml) was added to a solution of rhodium trichloride trihydrate (2 g) in hot ethanol (70 ml) and this solution was refluxed for thirty minutes. The solution was filtered and the orange crystals of the complex were washed with ether and dried in vacuum.¹⁸

Since these crystals differed in color from one account of the preparation of the complex in the literature, an authentic sample was

obtained commercially. Infrared, ultraviolet spectra, melting points, mixed melting points, and solubility tests were run on both colors. No differences were noted.

B. Spectra

Due to solubility and decomposition of the complexes in various solvents, reagent grade methylene chloride was used as the common solvent for all the spectra. This solvent is transparent above 210 nm. The spectra were recorded on a Cary 14 Spectrophotometer. A matched set of 1 mm quartz Hellma Cells were used for the absorption spectra measurements. Base lines were obtained using the cells filled with pure solvent. In order to test for impurities, comparative solubilities, melting points, and I.R. spectra were run on all complexes.

Figure 5. Ultraviolet Spectrum of 1.156×10^{-4} M $P\phi_3$
Path Length = 1 mm in Dichloromethane.

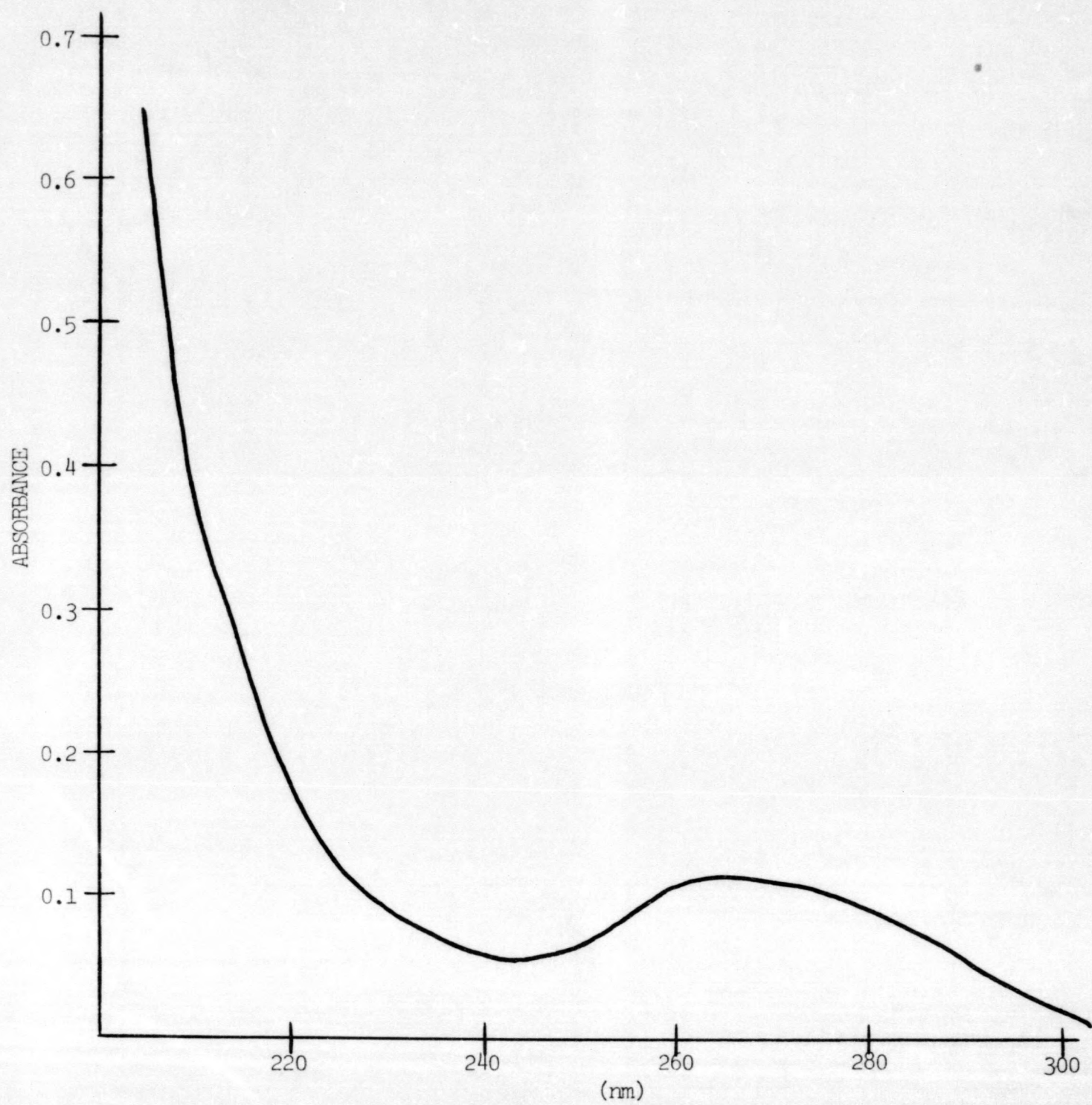


Figure 6. Ultraviolet Spectrum of 3.7×10^{-4} M $OP\phi_3$
Path Length = 1 mm in Dichloromethane.

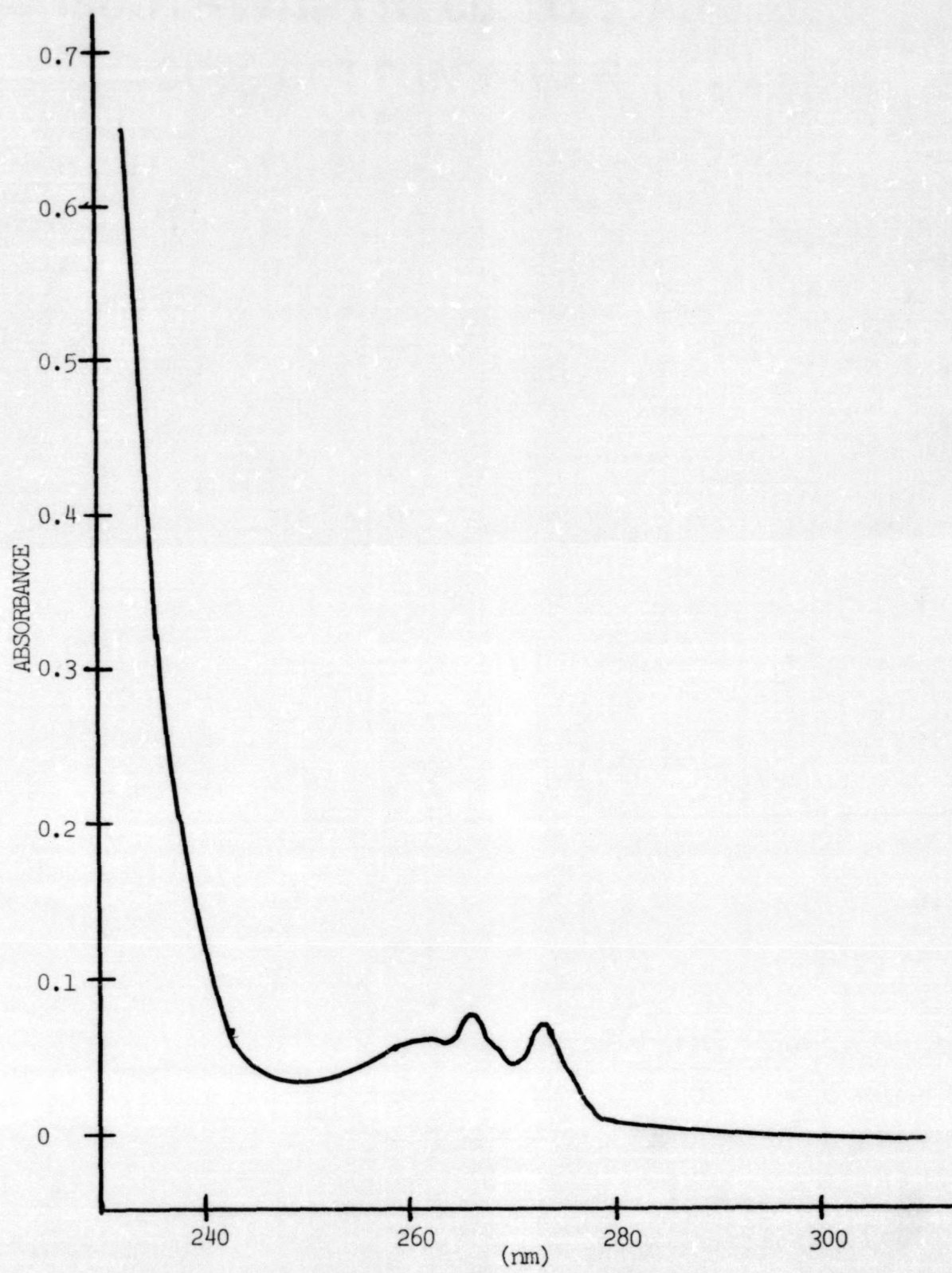


Figure 7. Ultraviolet Spectrum of 1.587×10^{-4} M $\text{Fe}(\text{P}\phi_3)_2\text{Cl}_3$
Pathlength = 1 mm in Dichloromethane.

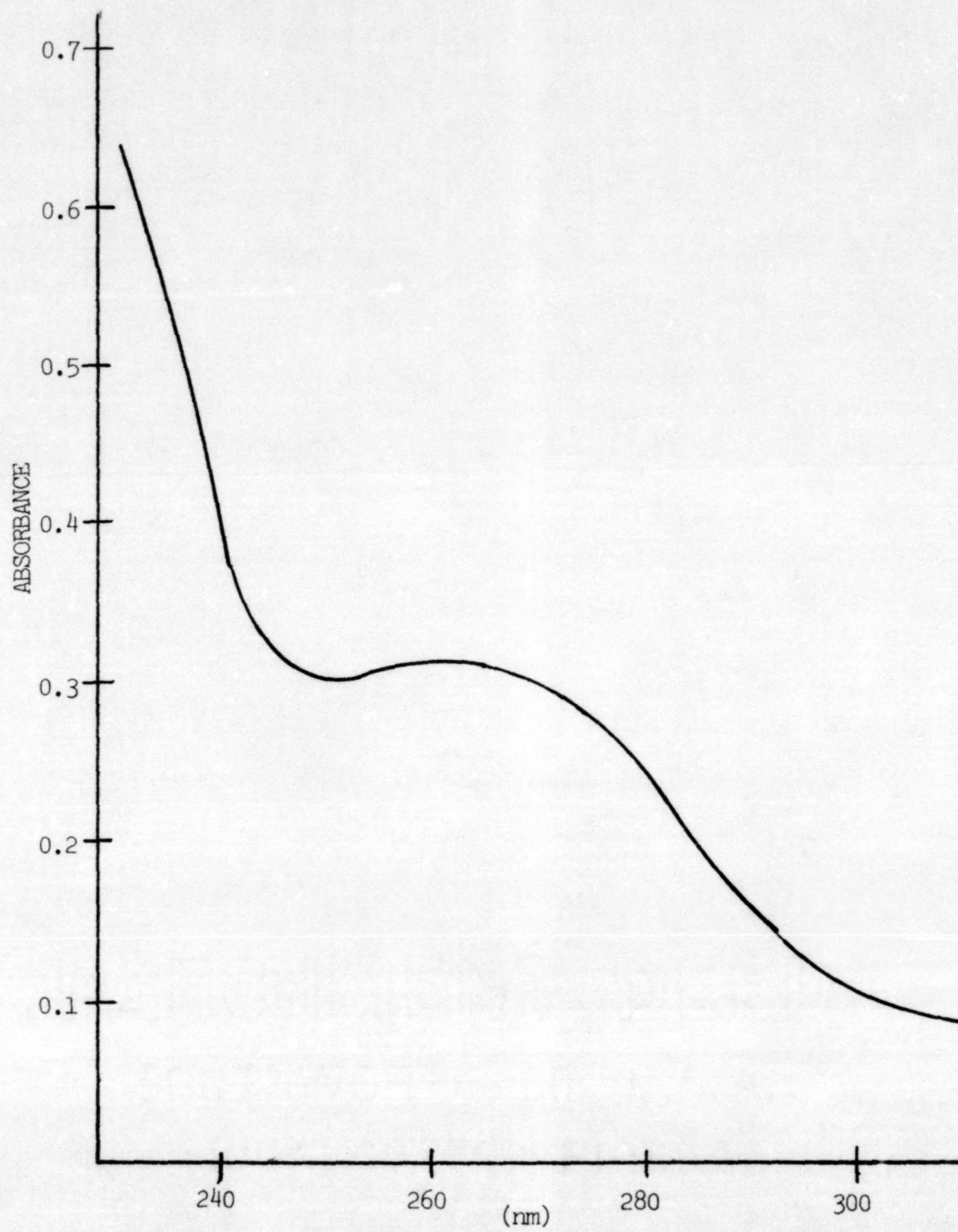


Figure 8. Ultraviolet Spectrum of 1.36×10^{-4} M $\text{Co}(\text{P}\phi_3)_2\text{Cl}_2$
Path Length = 1 mm in Dichloromethane.

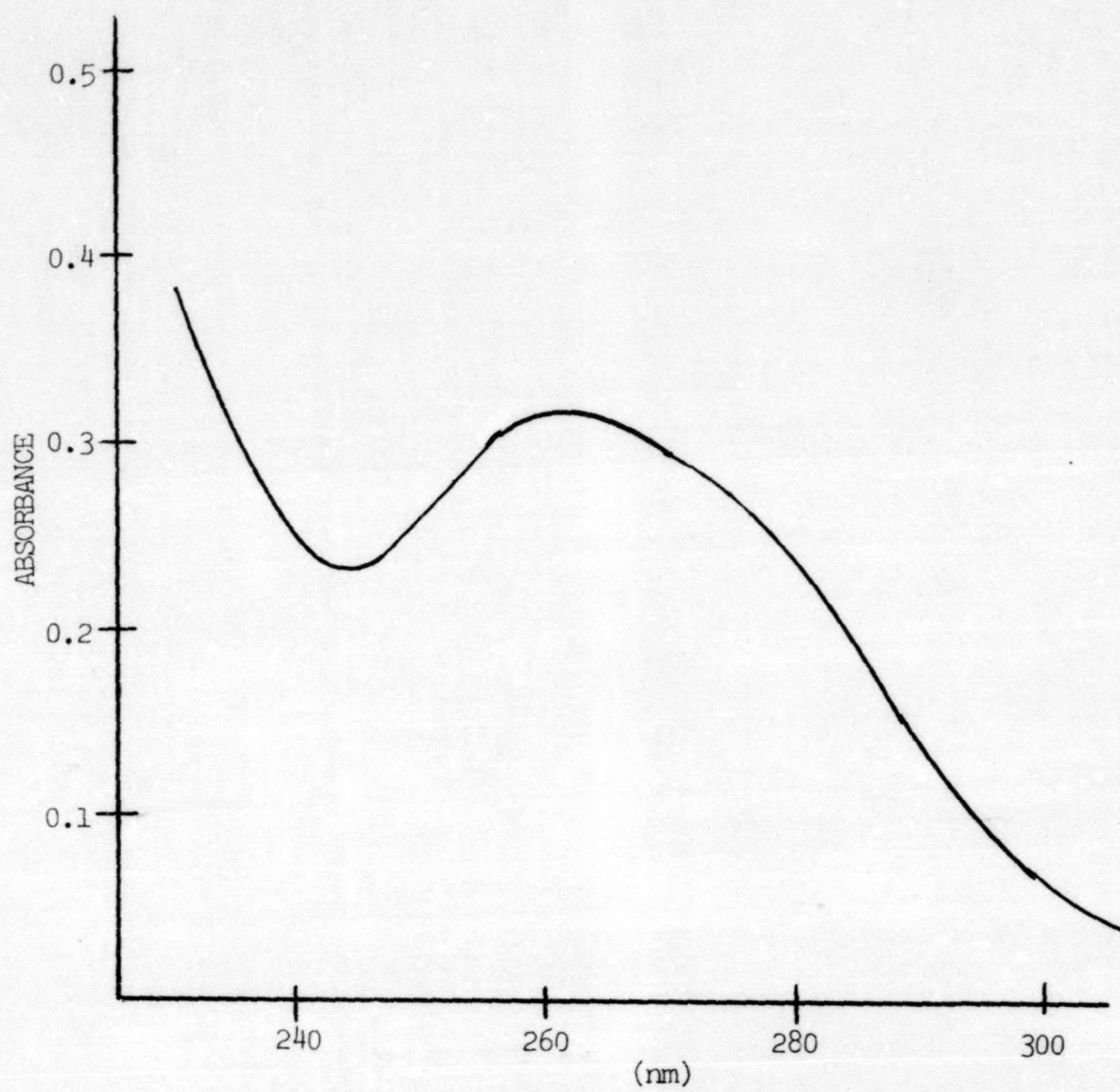


Figure 9. Ultraviolet Spectrum of 6.726×10^{-5} M $\text{Ni}(\text{P}\phi_3)_2\text{Cl}_2$
Path Length = 1 mm in Dichloromethane.

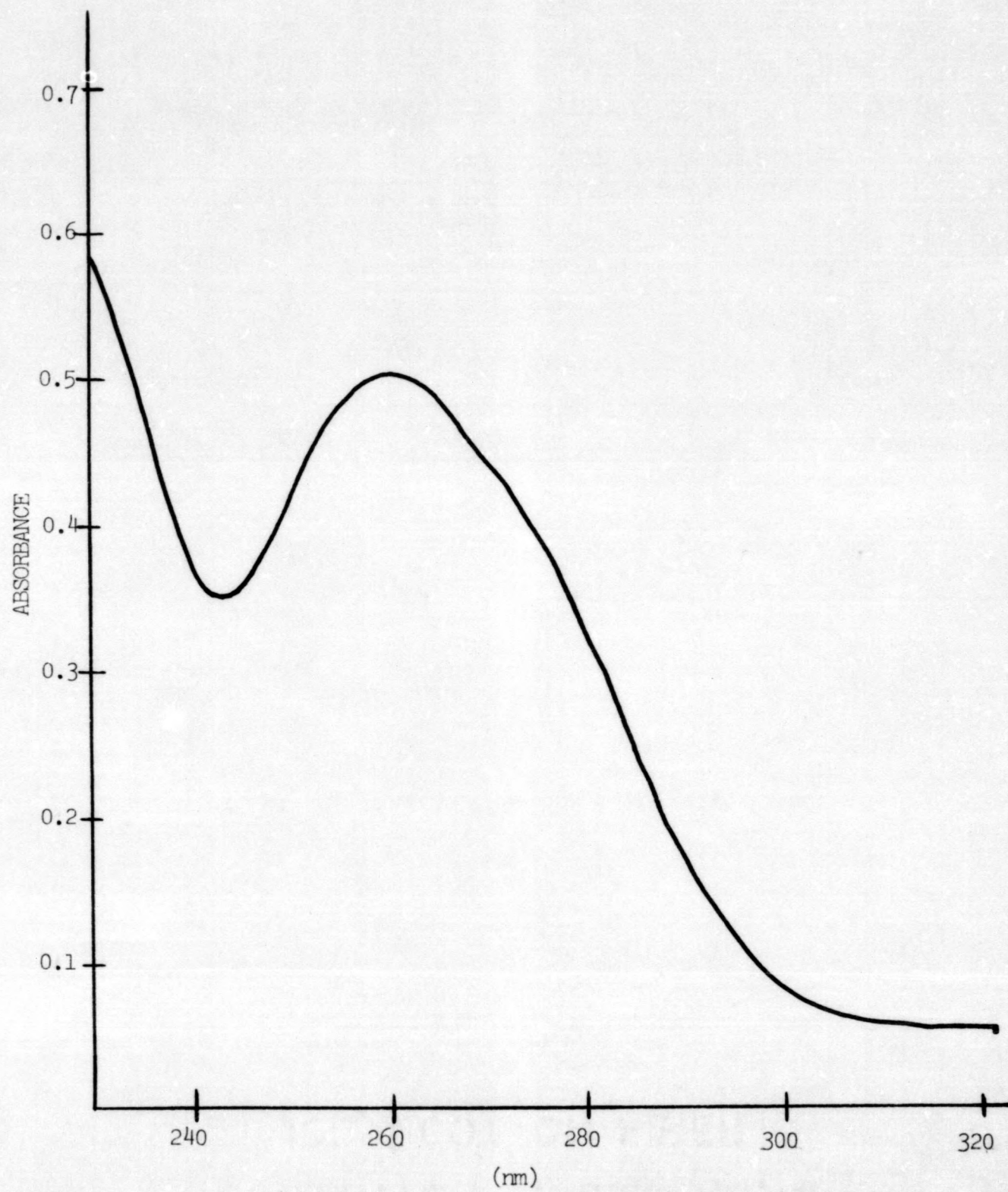


Figure 10. Ultraviolet Spectrum of 2.46×10^{-4} M $\text{Cu}(\text{P}\phi_3)_3\text{Cl}$
Path Length = 1 mm in Dichloromethane.

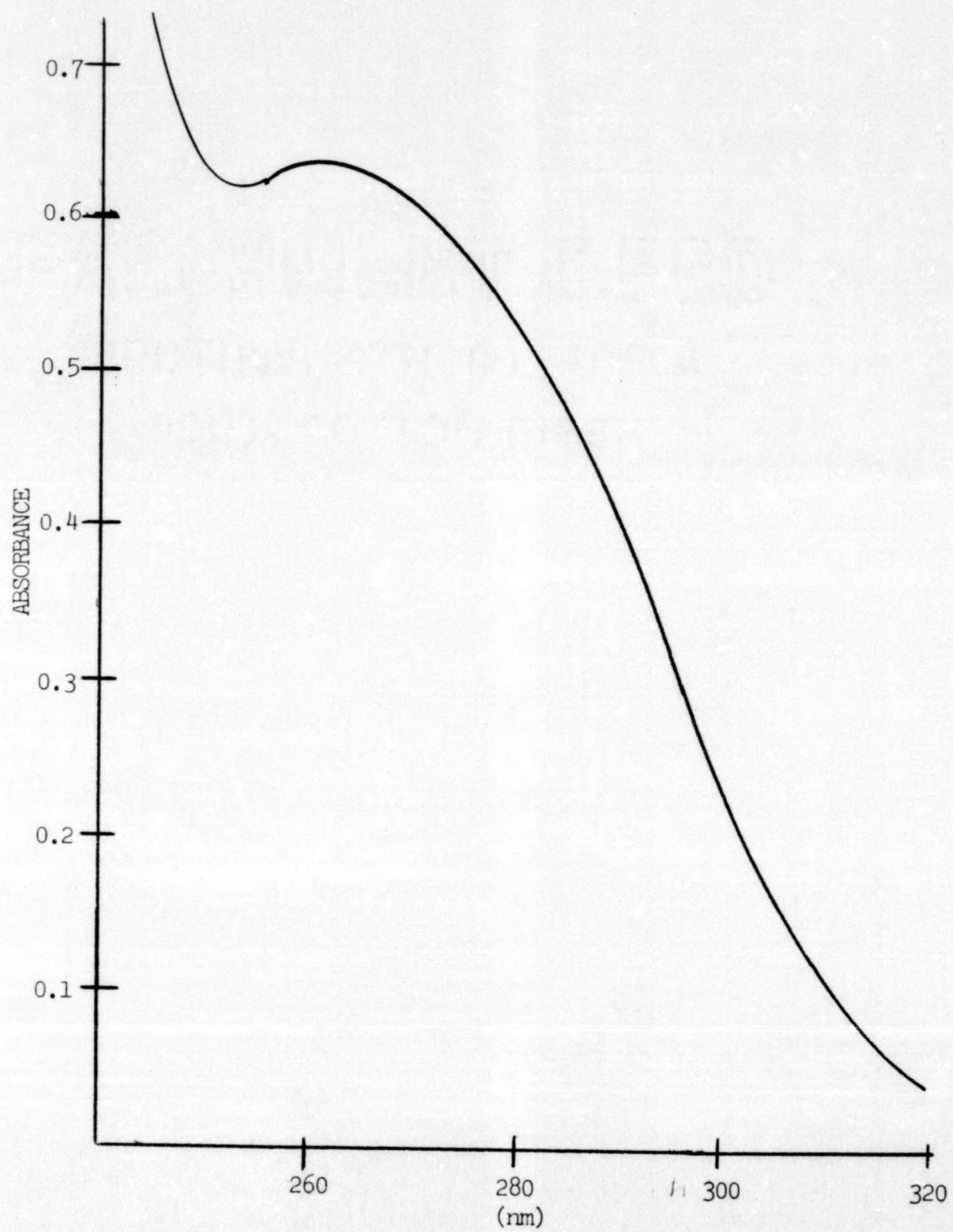


Figure 11. Ultraviolet Spectrum of 1.035×10^{-4} M $\text{Rh}(\text{P}\phi_3)_3\text{Cl}$
Path Length = 1 mm in Dichloromethane.

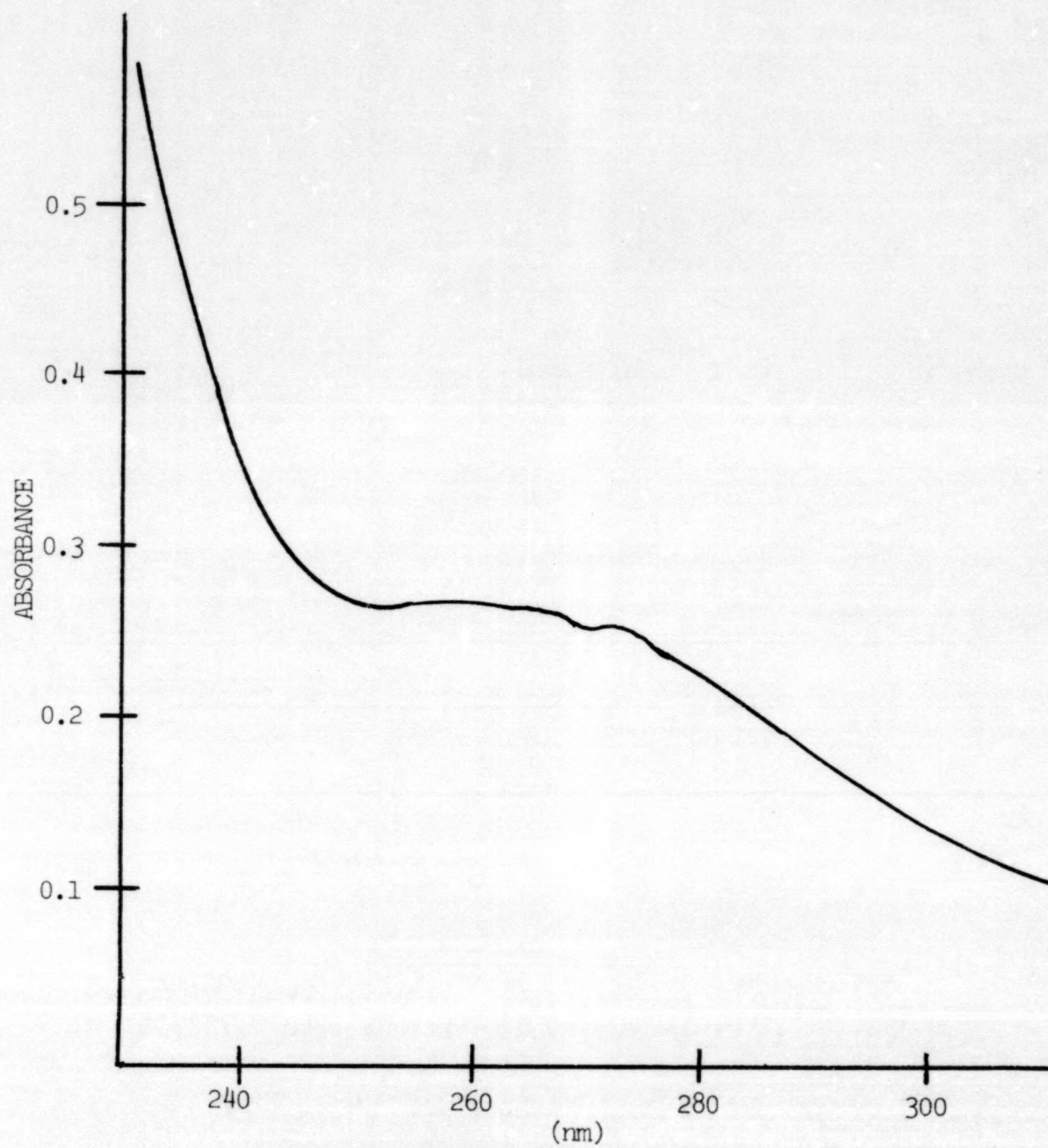


Figure 12. Ultraviolet Spectrum of 1.01×10^{-4} M $\text{Pd}(\text{P}\phi_3)_2\text{Cl}_2$
Path Length = 1 mm in Dichloromethane.

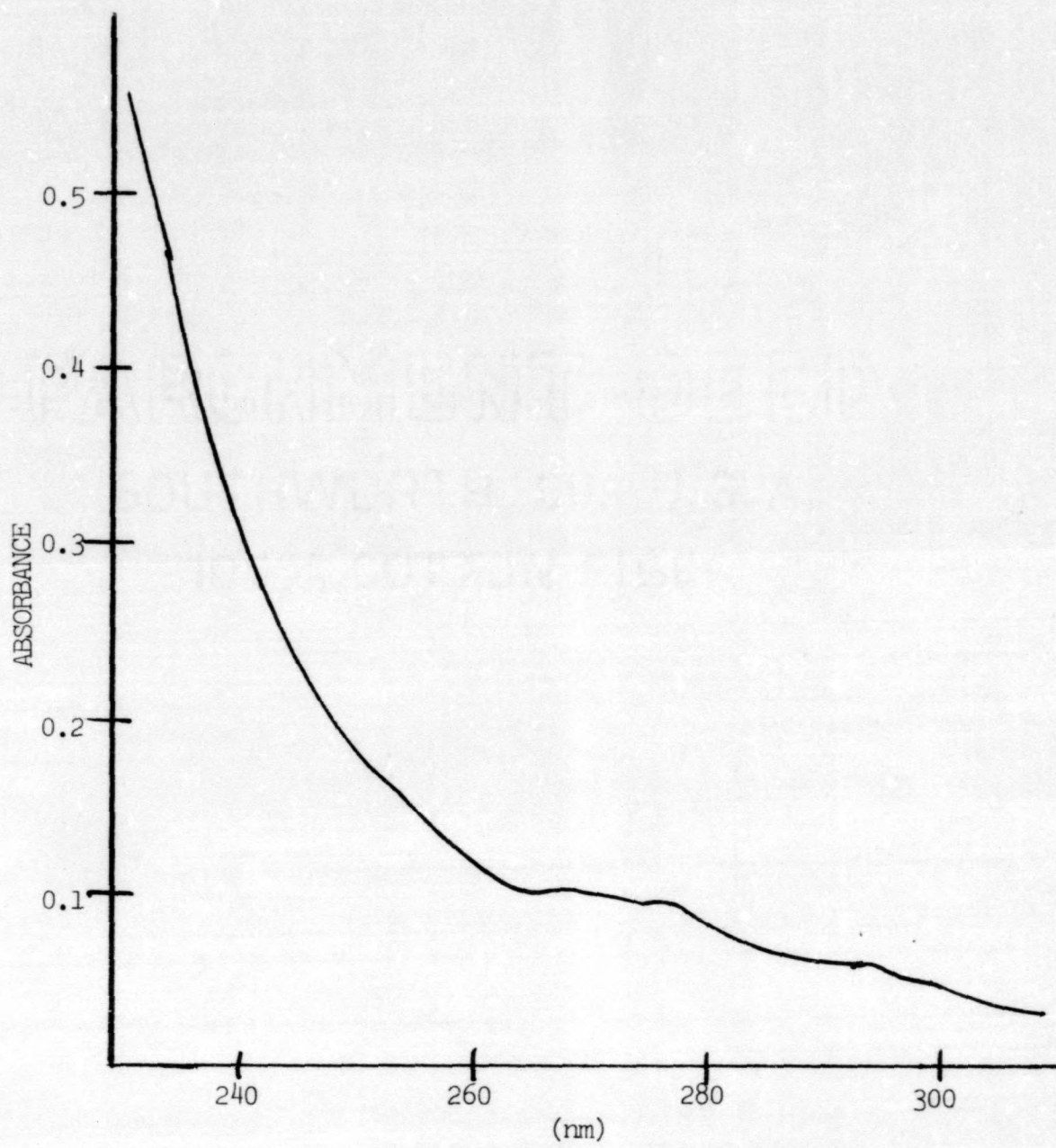


Figure 13. Ultraviolet Spectrum of 1.31×10^{-4} M $\text{Ag}(\text{P}\phi_3)_4\text{ClO}_4$
Path Length = 1 mm in Dichloromethane.

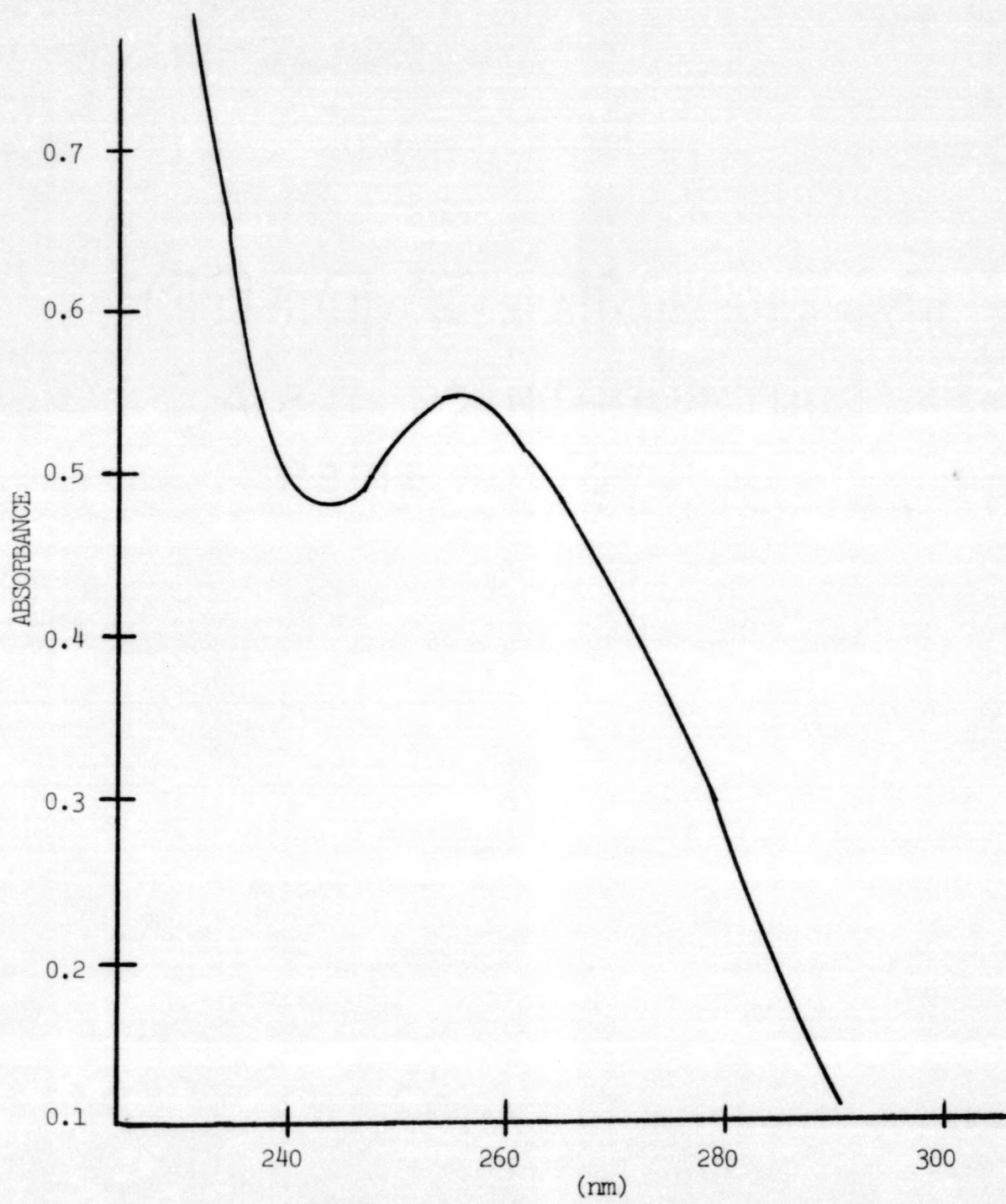


Figure 14. Ultraviolet Spectrum of 4.4×10^{-4} M $\text{Pt}(\text{P}\phi_3)_2\text{Cl}_2$
Path Length = 1 mm in Dichloromethane.

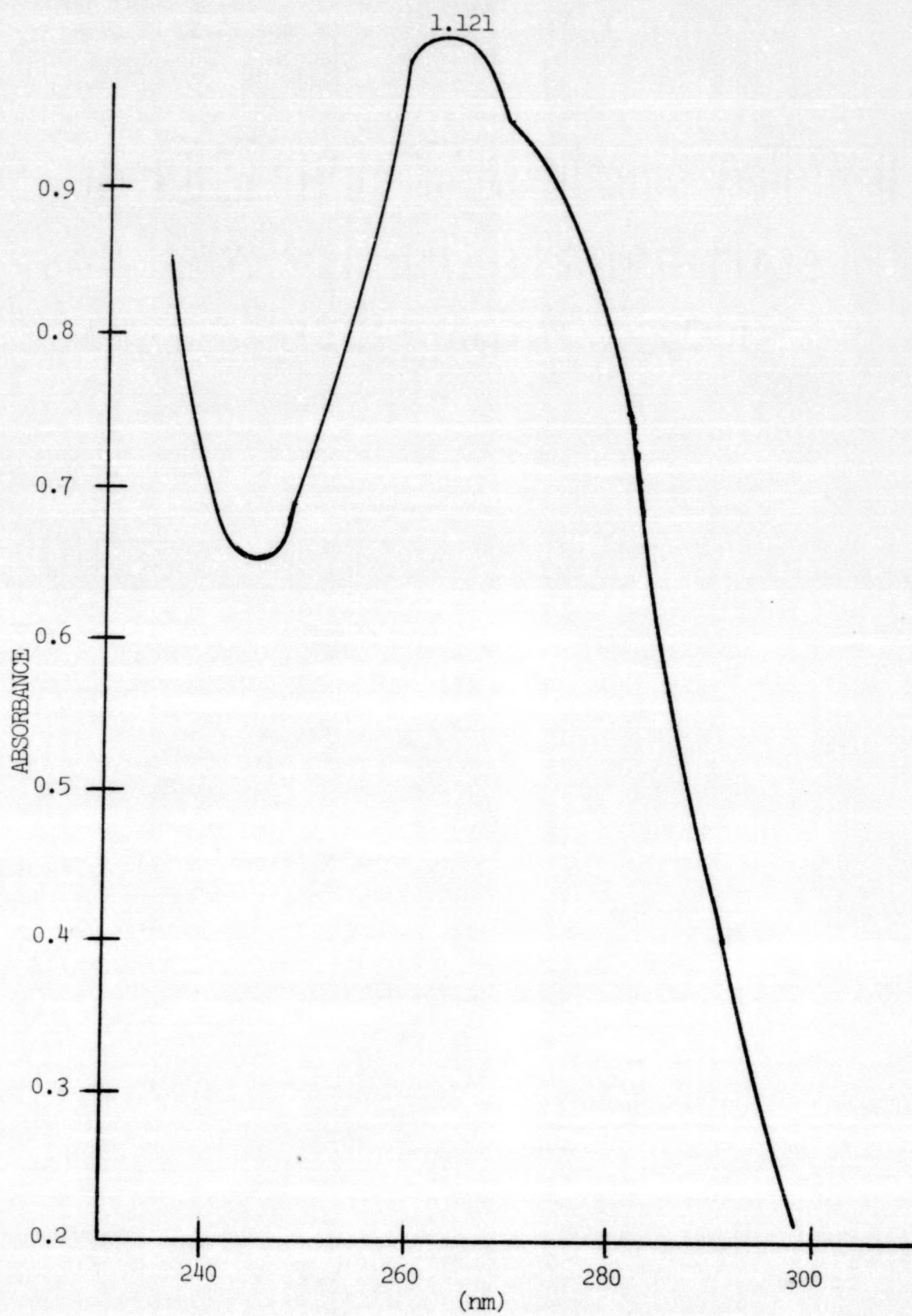


Figure 15. Ultraviolet Spectrum of 1.78×10^{-4} M $\text{Au}(\text{P}\phi_3)\text{Cl}$
Path Length = 1 mm in Dichloromethane.

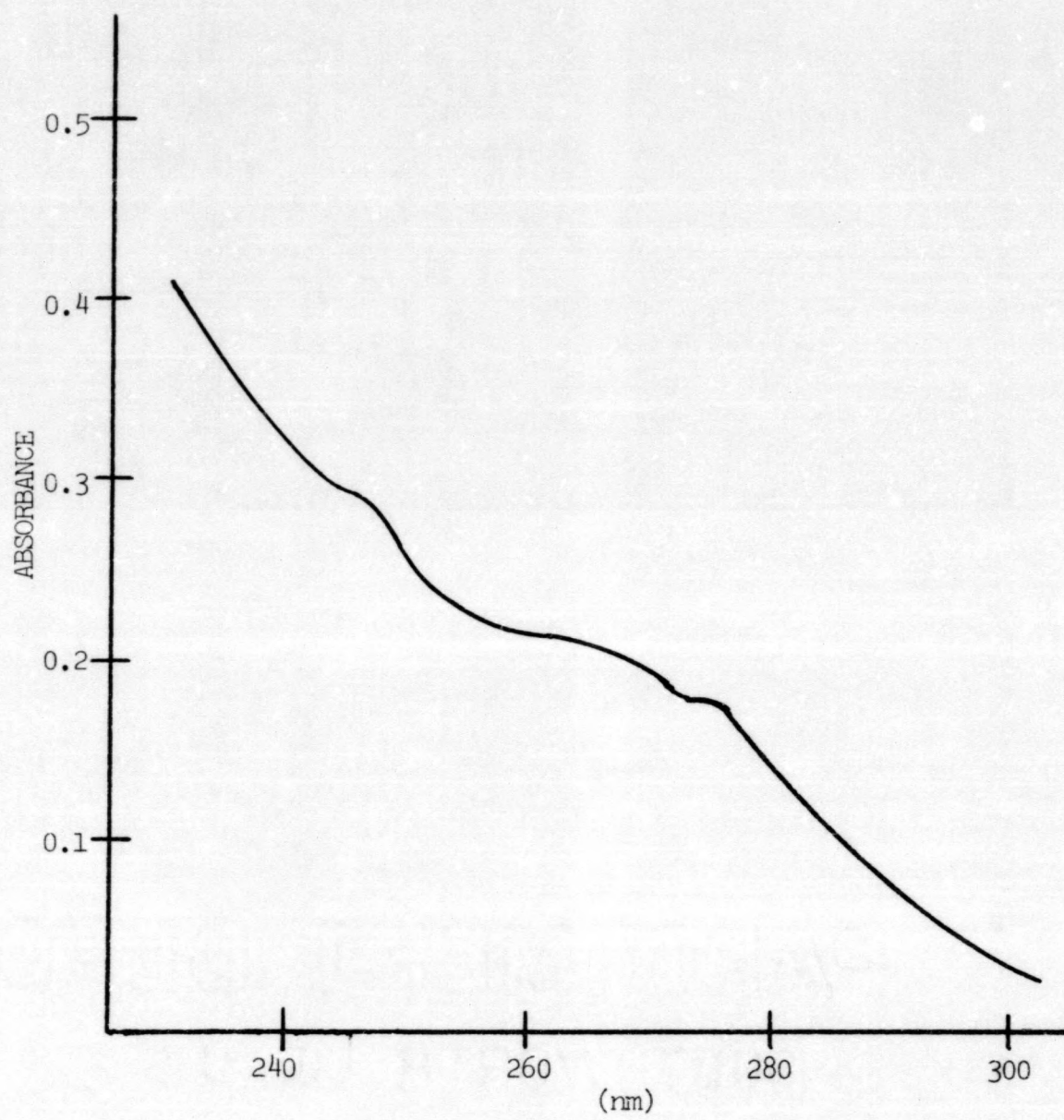


TABLE 1
THE EXTINCTION COEFFICIENT OF LIGANDS IN COMPLEXES

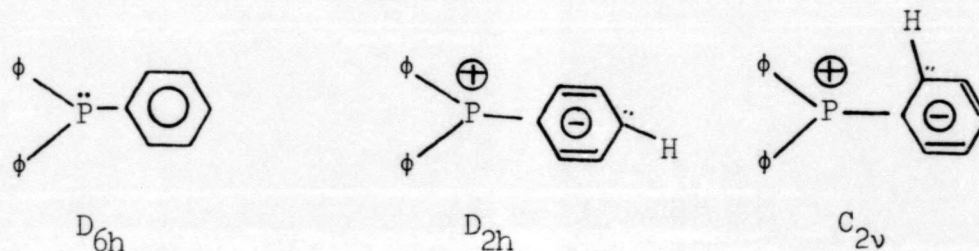
Compound	$\epsilon \times 10^{-4}$ *	ϵ/ϕ
$P\phi_3$.99	3300
$OP\phi_3$.165	550
$Fe(P\phi_3)_2Cl_3$	2.43	4050
$Co(P\phi_3)_2Cl_2$	2.244	3740
$Ni(P\phi_3)_2Cl_2$	2.37	3950
$Cu(P\phi_3)_3Cl$	3.231	3590
$Rh(P\phi_3)_3Cl_2$	1.985	2210
$Pd(P\phi_3)_2Cl_2$.8717	1450
$Ag(P\phi_3)_4ClO_4$	5.580	4650
$Pt(P\phi_3)_2Cl_2$	5.852	8370
$Au(P\phi_3)Cl$.343	1140

*Absorbance reading taken at maximum.

III. DISCUSSION

It has been reported that a $\pi^* \leftarrow \pi$ transition in benzene is forbidden by Laporte Transition Rules.²⁰ This transition becomes allowed because of mixing of electronic and vibrational motions of the benzene ring. These motions cause changes in the π electron symmetry lowering it from D_{6h} to a lower symmetry due to non-totally symmetric vibrations.

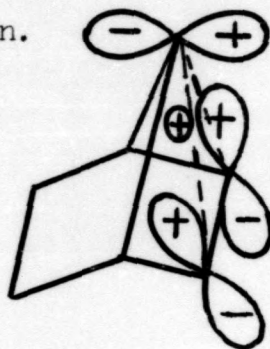
With substituted benzenes, the $\pi^* \leftarrow \pi$ transition is allowed in the absence of coupling of electronic and vibrational motions since the total symmetry is less than D_{6h} . The effect of the substituent is increased with its ability to interact with the π electrons of the benzene ring. To show the greatest effect the species attached to the ring must have nonbonding electrons or empty orbitals. The lone pair of electrons in phosphorus delocalizes into the phenyl rings to change the symmetry of the π electrons in benzene from D_{6h} to a lower symmetry of D_{2h} or C_{2v} .



In Hoffmann's treatment of the interaction of orbitals through space and through bonds,²¹ he shows that orbitals thought to be isolated orbitals actually do have an effect on the electron distribution in distant parts of the molecule.

In cyclopropene and cyclobutene, these double bonds have higher energy than the ethylene π orbitals when a π electron acceptor is substituted on the ring. This π electron acceptor weakens the bonding in the bonding regions and strengthens the bonding in the anti-bonding regions. When a π electron donor is substituted on the ring the bonding in the bonding regions is strengthened and the bonding is weakened in the anti-bonding regions. In both instances, the symmetry of the molecule was reduced.

Hoffmann also pointed out that there is a similar interaction in the 7-norbornenyl cation.



The empty 2-p-orbital at C_7 interacts with the π and π^* orbitals of the double bond. As a result of the interaction, the π^* orbital is unperturbed while the π and 2p levels mix well with each other.

The π orbital is stabilized by through space interaction with the 2p orbital at C_7 . Because of this stabilization, the carbonium ion center is delocalized. Normally it is thought that a carbonium ion is stabilized as a result of some electron transfer to a positive site. Before interaction there are 2 electrons in the π orbital between C_2 and C_3 . After interaction there are still two electrons in this orbital but now the orbital is delocalized over three centers C_2 , C_3 , and C_7 .

In compounds like ethylenediamine,



the two nitrogen lone pairs are too far apart for through-space interaction. Therefore, for any interaction to take place, through-bond coupling is required. The bonding orbital between C_1 and C_2 is overlapped with the nitrogen lone-pair orbitals of like symmetry. This interaction raises the energy of the 2p-orbitals of the nitrogen atoms and lowers the energy of the σ -orbital between C_1 and C_2 . A similar interaction between the nitrogen lone-pair orbitals and the σ^* -orbital between C_1 and C_2 is possible.

Hoffmann's explanations, expanded to benzene derivations, help explain the changes in intensity of the $\pi^* \leftarrow \pi$ transition. The study of the perturbation of the $\pi^* \leftarrow \pi$ transition in benzene derivatives gives a simple means of following small changes in electronic distribution in the benzene ring caused by substituents.

When electron acceptors remove electron density from the benzene ring only occupied orbitals are affected. In the case of orbitals of A_{2u} symmetry in benzene, all occupied orbitals are weakened equally. The symmetry of the π orbital remains D_{6h} . For the orbital of e_{1g} symmetry, the bonds adjacent to the donor group are weakened. The next bonds are strengthened. The remaining pair of bonds are weakened. With this type of stretching, the symmetry is changed from D_{6h} to D_{2h} .

When an electron donor is attached to a phenyl ring, electron density is added to the ring. Electron donors have little effect on filled orbitals. However, empty orbitals adjacent to the donor group are weakened, the next pair strengthened, and the last pair weakened. Similarly the symmetry of the ring is changed from D_{6h} to D_{2h} . Transition metal complexes of aryl substituted phosphines can be both π -electron donors or acceptors.

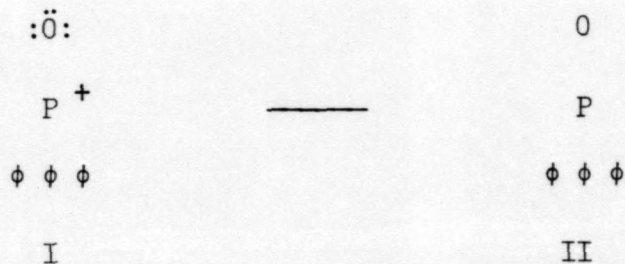
In previous work done by S. B. Chen²² it was noted that the size and charge of the metal ion had a great affect on the intensity of the $\pi^* \leftarrow \pi$ transition in triphenylphosphine complexes of the first row transition metals. Since covalency of the metal phosphorus bond was thought to be important the study was extended to second and third row transition metal complexes. The molar extinction coefficient per phenyl ring (ϵ/ϕ) increases from 550 l/mole·cm for triphenylphosphine oxide to 8370 l/mole·cm for triphenylphosphine complex of platinum(II). The increase in extinction coefficient is accompanied by loss of the vibrational structure characteristic of unperturbed phenyl rings which is observed in the triphenylphosphine oxide spectrum. These completely different spectra indicate that the entire π -electron distribution of the phenyl rings has been altered (See Chapter 1). In triphenylphosphine oxide, the lone pair of electrons on the phosphorus atom are tied up with the oxygen and not available to perturb the electron distribution of the phenyl rings. If the orbitals of the metal were completely independent of the π -orbitals of the ligand, the intensity of transition in the free ligand and the complex would be the same. This increase in intensity observed in all complexes not showing the vibrational structure of triphenylphosphine oxide (See Table 1) implies a delocalization of the d-orbital electrons of the metal ion and the unshared pair of electrons into the phenyl rings. This conjugation causes distortions within the π -system of the phenyl ring which leads to an increase in the intensity of the $\pi^* \leftarrow \pi$ phenyl ring transition over that of the free ligand.

As shown by the data in Table 1, the extinction coefficient per phenyl ring decreases in the order $\text{Fe}^{3+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^+$ with the exception of Ni^{2+} this can be interpreted as following decreasing charge on the metal ion or increasing number of electrons in the d-orbital.

However, the charge density of these metal ions follows this order exactly. The ability of the ions to polarize molecules in its vicinity is determined by the electric field strength at the surface of the ion. If the π -electron system of the phenyl ring is polarized its symmetry will be reduced below D_{6h} and the transition will become more intense (See Chapter 1).

The result of adjusting the extinction coefficient per phenyl ring (See Table 1) for the expected effect due to polarization is shown in Table 2. The adjusted extinction coefficients per phenyl ring are found to increase in the order expected for metal-ligand back-bonding. Nickel(II) and cobalt(II) are out of order, however, the difference is about 2 percent and within the experimental error introduced by overlapping charge transfer bands. It should be noted from the data of Table 1 that the effect of metal ion charge is of great importance. As expected from covalency of the metal-ligand bond, the intensity per phenyl ring increases in going from left to right and top to bottom of the periodic chart. Discrepancies are noted, however, if ions of different charge such as silver(I) and platinum(II) are compared.

The results of this study may shed some light on the bonding in triphenylphosphine oxide. Two resonance structures are expected.



Delocalization of the d-orbital electrons of the metal ion and the unshared pair of electrons on the phosphorus atom into the phenyl ring

TABLE 2
 ADJUSTED EXTINCTION COEFFICIENT OF
 LIGANDS IN COMPLEXES

Compound	q/r^2	$\epsilon/\phi \times \frac{1}{q/r^2}$ *
$\text{Fe}(\text{P}\phi_3)_2\text{Cl}_3$	7.3	560
$\text{Co}(\text{P}\phi_3)_2\text{Cl}_2$	3.9	960
$\text{Ni}(\text{P}\phi_3)_2\text{Cl}_2$	4.2	940
$\text{Cu}(\text{P}\phi_3)_3\text{Cl}$	1.1	3300
$\text{Ag}(\text{P}\phi_3)_4\text{ClO}_4$	0.63	7400
$\text{Pt}(\text{P}\phi_3)_2\text{Cl}_2$	3.1	2700

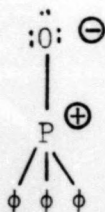
*Absorbance reading taken at the maximum.

system was found to cause the intensity of the $\pi^* \leftarrow \pi$ transition to increase. Therefore, structure I would seem to be favored. Structure II involves conjugation of the π -bond between phosphorus and oxygen and the π -electron system of the phenyl rings and should lead to a high extinction coefficient which is not observed. This conclusion is in agreement with structures proposed for sulfur ylids²³ and arylphosphonium ylids. The triphenylphosphonium ylids have low extinction coefficients in the region of the 260 nm transition with the characteristic fingerprint of unperturbed phenyl rings.

SUMMARY

The spectra of transition metal complexes with triphenylphosphine have been measured near 260 nm and the results interpreted in terms of perturbation of the π -electron system of the phenyl ring. All complexes studied show some degree of delocalization of the d-orbital electrons of the metal into the phenyl ring. However, for first row transition metals, the primary affect was found to be polarization of the phenyl ring due to the presence of the metal ion. For second and third row transition metal ions, the primary effect was found to be metal-ligand back-bonding. However, the effect of polarization of the rings due to the metal ion was noticeable.

This study also indicates the bonding in triphenylphosphine oxide is the dipolar structure similar to that found in sulfur and phosphorus ylids.



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