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I am submitting herewith a thesis written by Celeste Reneé Daffron entitled "An Infrared and Phosphorus-31 Nuclear Magnetic Resonance Spectroscopic Study of Some Square Planar Rhodium(I) Complexes." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Clifton Woods

Clifton Woods, Major Professor

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AN INFRARED AND PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC STUDY OF SOME SQUARE PLANAR RHODIUM(I) COMPLEXES

A Thesis

Presented for the

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Degree

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Celeste Reneé Daffron

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DEDICATION

This work is dedicated to my mother, Dean Daffron and my two brothers, John and Howard.

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ABSTRACT

The electronic environment of rhodium in some square planar complexes has been monitored using both infrared spectroscopy and nuclear magnetic resonance spectroscopy. Efforts have been made to determine the importance of σ and π contributions of the ligands to the observed variations in spectral parameters. The pK_a's of some substituted pyridines have been used as a measure of the σ donor ability of these ligands toward Rh in <u>trans</u>-$[Rh(CO)L(PPh_3)_2]PF_6$ complexes. It has been found that the pK_a is related linearly to the carbonyl stretching frequency for some pyridine complexes. In <u>trans</u>-$[Rh(CO)A(PPh_3)_2]$ complexes (A = anionic ligand), no obvious correlation was observed between $\nu(C\equiv O)$ and a parameter called the sigma electronegativity of A ($\chi_{A(\sigma)}$).

Rhodium-phosphorus coupling constants have been measured for the complexes. A meaningful correlation between J_{Rh-P} and $\chi_{A(\sigma)}$ was not observed; however, for most pyridines a general increase in J_{Rh-P} is observed with increasing pK_a. It has also been observed that J_{Rh-P} varies by a constant amount as the pyridines or the anionic ligands are varied in these square planar complexes.

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CHAPTER I

INTRODUCTION

Several techniques have been used to study changes which occur in the electronic nature of metal ions when the coordinated ligands are varied. These techniques have included x-ray crystallography, vibrational spectroscopy, nuclear magnetic resonance, nuclear quadrupole resonance and photoelectron spectroscopy.[1] The work presented in this thesis will focus on two of these techniques, infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR).

Infrared Spectroscopy

Infrared spectroscopy is one of the primary tools used to investigate the electronic environment of the metal atoms in transition metal complexes. The reason this method is often useful is best illustrated by reviewing its application in studies of the *trans*-influence.

The *trans*-influence was defined in 1966 by Pidcock[2] as the extent to which a ligand, L, weakens the bond trans to itself in the equilibrium state of a metal complex. This is not to be confused with a related phenomenon, the *trans*-effect, defined by Basolo and Pearson[3] as the effect a coordinated group, A, has upon the rate of substitution of the group trans to A. One class of compounds for which *trans*-influence studies by IR are well suited are square planar complexes in which a carbonyl (CO) is trans to the influencing ligand. The stretching frequency ν(CO) is readily observed, and a correlation

of ν(CO) and various properties of the trans ligands can readily be investigated.

One of the earliest theories of the trans-influence, known as the Polarization Theory, was proposed by Grinberg.[1] The theory proposes that a metal-induced dipole in a ligand L induces a dipole in the metal M. The dipole in M opposes the negative charge on ligands A trans to L, thus weakening the M-A bond, without significantly affecting the ligands cis to L. Since this theory is concerned with the electrostatic component of the M-L bond it does not sufficiently explain the pronounced trans-influence in complexes where there is a high degree of covalency in the M-L bond.

A more recent consideration of the trans-influence is the role that metal-to-ligand π backbonding plays. When a ligand has vacant orbitals of the correct symmetry to interact with filled "nonbonding" d orbitals of a metal, the resulting complex is stabilized as a result of the overlap of the metal d orbitals and the ligand π acceptor orbitals. This overlap permits the flow of electron density from the metal to the ligand. Some common ligands which can participate in this type of bonding are phosphines, arsines and the carbon monoxide. Phosphines and arsines have vacant d orbitals available for overlap with metal d orbitals, whereas carbon monoxide has vacant π^* orbitals which serve as the ligand acceptor orbitals.

At present there is no clear cut way of separating σ and π effects on the stretching frequency of CO as the trans ligand varies. The following discussions illustrate the complexity of the problem and explain why this area is still being actively studied.

In a complex such as trans-$MX(CO)L_2$, changing X can affect $\nu(CO)$ in a variety of ways. If X^- is a good σ donor it will transfer part of its electronic charge to the metal. This increased electron density on M will cause expansion of its $d\pi$ orbitals and increase M-CO π bonding. Occupation of the π^* orbitals of CO decreases the bond order between C and O and reduces $\nu(CO)$. The increased M-CO π bonding tends to increase OC-M σ bonding because of the accumulation of negative charge on CO from the M-CO backbonding. An increase in OC-M σ bonding will cause an increase in $\nu(CO)$. If X^- has a high trans-influence, the OC-M σ bond will be weakened by X^-, causing the M-C bond to lengthen. The longer M-C bond will reduce the degree of π overlap between the metal and carbonyl group, thus increasing $\nu(CO)$. Finally, if X^- has available d orbitals it will compete with CO for the electron density in the metal d orbitals. This competition for electron density will decrease the amount of M-CO π backbonding and increase the M-CO σ bonding. The result of these effects is an increase in $\nu(CO)$.

Several studies have been conducted in efforts to separate the σ and π influences on $\nu(CO)$ for various trans ligands in trans-$MX(CO)L_2$ type complexes. One of these studies was by Vaska and Peone.[4] They attempted to determine whether a correlation exists between $\nu(CO)$ and the total electronegativity, or acceptor strength, of anionic ligands trans to CO in the square planar rhodium(I) complexes. The total electronegativity, as they define it, combines a σ component and a π component of a given ligand and is related to $\nu(CO)$ by equation 1;

$$\chi_{A(T)} = \chi_{F(T)} \frac{(\Delta\nu(CO)^2)_F}{(\Delta\nu(CO)^2)_A}, \qquad (1)$$

where $(\Delta\nu(CO)^2) = (\nu(CO)^2_{gas}) - (\nu(CO)^2_{complex\ in\ CHCl_3})$, $\chi_{A(T)}$ and $\chi_{F(T)}$ are the total electronegativities of the ligand and the fluoride ion respectively. Equation 1 is based on the assumption that the fluoride ion has no π electronegativity, i.e., $\chi_{F(T)} = \chi_{F(\sigma)}$. Values for $\chi_{A(\sigma)}$ were calculated using equation 2 which relates $\chi_{A(\sigma)}$ $\nu(HA)$ and was derived by Wilmshurst.[5]

$$\chi_{A(\sigma)} = 1.104 \times 10^{-3} \left(1 + \frac{M_H}{M_A}\right)^{-\frac{1}{2}} \nu(HA) - 0.24 \qquad (2)$$

Some doubts have been raised as to the validity of the results obtained by Vaska and Peone.[1] It has been pointed out that $\chi_{A(\sigma)}$ obtained from the Wilmshurst equation might not be a measure of σ effects only, but of the overall tendency of A to gain electrons. Also, this method assumes that electron flow from metal to ligand will affect $\nu(CO)$ to the same extent whether the removal of electronic charge from the metal is via σ bonding or via π bonding. Appleton, et. al.,[1] suggests that $\nu(CO)$ is more probably related to $\chi_{A(\sigma)} + \lambda\chi_{A(\pi)}$ where λ is a constant. The Vaska-Peone calculation lead to a value of 1.25 for $\chi_{Cl(\pi)}$ in Ir(III) complexes as compared to a value of 2.94 for $\chi_{Cl(\sigma)}$. It is somewhat surprising that the π electronegativity of Cl^- is assumed to be 43% of the σ electronegativity when Cl^- is generally considered to be a weak π donor. Studies such as those of Vaska and Peone point out the difficulties of separating σ and π effects of trans-influencing ligands.

An IR study by Reddy and Ramesh[6] was conducted to determine whether ν(CO) can be correlated with the basicity of substituted imidazoles (Y) in trans-$MY(CO)L_2$ complexes. It was suspected that an increase in the basicity of Y would increase the electron density on the metal and that such an increase might be reflected in changes in ν(CO). However, no meaningful correlation was found for the imidazole complexes. Adequate explanations for these results could be due to the lack of inclusion of possible variations in π acidity of Y and steric factors.

A final example of attempts to monitor changes in electronic environment of metals in $MY(CO)L_2$ complexes involves the correlation of the electron donor property of ligands with the polarographic halfwave potential of trans-$MX(CO)(PPh_3)_2$ complexes.[7] It is assumed that the difference in halfwave potential reflects changes in the charge density on the metal center. If only one ligand is changed, namely X, the variation in the charge density of the metal (measured by the halfwave potential) should lead to a relative scale of electron donor abilities of the ligands. The scale produced by this method is in fair agreement with the scale prepared by Vaska and Peone.

The types of techniques used to determine the electronic nature of metal centers in transition metal complexes are varied. Infrared spectroscopy has been used more frequently than most. However, recent advances in NMR technology have made it a very popular tool for probing the electronic environment of metals. The importance and usefulness of NMR in studies such as these will be discussed in the next section.

Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance signal of an atom which has a non-zero nuclear quantum number, I, can be split by neighboring nuclei

if they also have a non-zero value of I. This phenomenon is called spin-spin splitting. The separation of the split resonances is measured in Hertz (Hz) and is denoted by J, which is referred to as the spin-spin coupling constant. The magnitude of J is independent of the applied field strength.

There are several mechanisms for spin-spin coupling between neighboring nuclei. However, a single mechanism, the Fermi contact mechanism, has been found to dominate the coupling in many heavy atom systems where atoms A and B are bound by a covalent bond, and both A and B have $I = +\frac{1}{2}$.[1] This assumes that the contributions of orbital and spin-dipolar mechanisms to the coupling of A and B are negligible.

The Fermi contact mechanism involves the transmission of the orientation of the nuclear moment of A to B through the bonding electrons of A and B.[8] The electron with a spin of $-\frac{1}{2}$ will have a higher probability of being found nearer the nucleus with a spin of $+\frac{1}{2}$, A for instance. Since electron spins are paired, the electron with a spin of $+\frac{1}{2}$ will have a higher probability of being found near B. This is the mechanism responsible for transmitting the spin of one nucleus to another. This polarization process occurs regardless of the orientation of the two atoms A and B in the field.

The dominance of the Fermi contact term is seen in one-bond platinum-phosphorus coupling. Pidcock and co-workers,[2] using the equation of Pople and Santry[9] for the Fermi contact contribution, have obtained an approximate expression (Equation 3) for the platinum-phosphorus coupling constant, J_{Pt-P}.

$$J(Pt-P) \propto \gamma_{Pt}\gamma_{P}(\Delta E)^{-1}\alpha_{Pt}^{2}\alpha_{P}^{2}|\Psi_{Pt(6s)}(0)|^{2}|\Psi_{P(3s)}(0)|^{2} \qquad (3)$$

The value of J_{Pt-P} involves contribution from the magnetogyric ratio (γ), the fraction of s character of the hybrids used by Pt and P in the Pt-P σ bond (α_{Pt}, α_P), the electron density of the ns valence orbital at the Pt and P nuclei ($|\Psi_{Pt(6s)}(0)|^2$, $|\Psi_{P(3s)}(0)|^2$), and an average excitation energy (ΔE).

The more important terms in evaluating the value of ΔE are the singlet-to-triplet excitation energies, and the least energetic transition energy. Since J_{Pt-P} has an inverse dependence on ΔE, it is reasonable to expect complexes with the weaker ligand fields (smaller ΔE values) to have larger coupling constants. Results from a study by Pidcock and co-workers[2] show a decrease in J_{Pt-P} with increasing ligand fields. It is suggested that any variations in ΔE are negligible relative to changes in the other parameters in equation 3. The expected dependence of J_{Pt-P} upon ΔE is not seen.

For phosphine ligands, as the groups bound to the phosphorus are changed, the product $\alpha_P^2|\Psi_{P(3s)}(0)|^2$ changes significantly because of the variation in s character of the phosphorus orbital and s electron density at the nucleus. If upon varying the phosphine ligands the metal oxidation state is unchanged, the $\alpha_M^2|\Psi_{M(ns)}(0)|^2$ term is essentially invariant. Evidence for these conclusions is obtained from the ratio of $J_{Pt-Phosphite}/J_{Pt-Phosphine}$ for complexes of the type PtL_2X_2 (L = phosphorus containing ligand).[2] Changing X causes no significant change in the ratio of coupling constants, leaving changes in L responsible for the ratio deviating from one (one being the value expected if $\alpha_P^2|\Psi_{P(3s)}(0)|^2$ is unaltered by changing the atoms bound to P).

In order to determine the contribution of $\alpha_{Pt}^2|\Psi_{Pt(6s)}(0)|^2$ to J_{Pt-P}, complexes with a single type of phosphine ligand were studied,

namely $[PtX_4(Bu_3P)_2]$ and $[PtX_2(Bu_3P)_2]$.[2] The ratio of the coupling constants, $J_{Pt(IV)}/J_{Pt(II)}$, was evaluated when X = Cl^- and Br^-. Since the 6s orbital of Pt is shared by 4 bonds in the Pt(II) complex and 6 bonds in the Pt(IV) complex, the 6s character of the Pt hybrids (α_{Pt}) in the octahedral complex should be two thirds of those in the square planar complex. This is reflected in the values of the ratios for both the cis and trans isomers, their values being 0.59 and 0.61, respectively. These results also suggest that a change in oxidation state of Pt does not affect the value of $|\Psi_{Pt(6s)}(0)|^2$. Further support for the significant contribution of α_{Pt} to J_{Pt-P} is provided by the NMR spectrum of cis-$[Pt(CH_3)Cl(Et_3P)_2]$. Two phosphorus resonances are observed with very different J_{Pt-P} values. Since each J_{Pt-P} value receives the same contribution from $|\Psi_{Pt(6s)}(0)|^2$, the large difference must be due to widely different α_{Pt} values.

The s character of the Pt hybrid orbital seems to be the dominant term in equation 3. The same studies that led to this conclusion, show that $d\pi$-$d\pi$ interactions are of minor importance and have no appreciable synergic effect on the Pt-P σ bond. Competition by the phosphines for Pt d orbitals is no longer considered to be responsible for the value of J_{Pt-P} being smaller for the trans isomer of $[PtCl_2(Bu_3P)_2]$ than for the cis isomer. Instead, a mechanism involving only the Pt-P σ bonds is presently accepted as an explanation for the difference in the two coupling constants.

It is also unnecessary to invoke π bonding in rhodium complexes similar to the platinum complexes that have been so widely studied.[1] The ratios J_{Rh-P}(trans to P)/J_{Rh-P}(trans to Cl) for the complexes

$[RhCl(PPh_3)_3]$ and $[RhCl_3(PPh_3)_3]$ are both equal to 0.75. If Rh-P π bonding does indeed exist, it should be seen in a decrease of the value of the above ratio of coupling constants from the Rh(I) complex to the Rh(III) complex. Since the values are equal, the coupling constants must not be dependent upon Rh-P π bonding. Also the ratio $J_{Rh(III)-P}/J_{Rh(I)-P}$ has been evaluated for $[RhCl(PPh_3)_3]$ and for both the cis and trans isomers of $[RhCl_3(PPh_3)_3]$.[1] A value of 0.6 for this ratio is almost identical to the corresponding value of $J_{Pt(IV)-P}/J_{Pt(II)-P}$ and is comparable with the theoretical value of 0.67. These results allow discussion of variations in J_{Rh-P} values in terms of equation 3, where Rh-P π bonding does not contribute, and changes in α_{Rh}^2 are dominant. It is clear that the mechanism of coupling for J_{Rh-P} is similar to that for J_{Pt-P}.

From the collection of physical data obtained in efforts to better understand the trans-influence for transition metal complexes, another phenomenon has emerged, the cis-influence. Defined in a similar manner as the trans-influence, it is the extent to which a ligand weakens a M-L bond cis to itself in a complex. This phenomenon, although not as pronounced as the trans-influence has been observed in both Rh and Pt complexes.[1]

In a series of Pt(II) complexes, it has been observed that a ligand with large trans-influence has a small cis-influence.[10] This is in conflict with the prediction by Zumdahl and Drago[11] that a large trans-influencing ligand should also have a large cis-influencing ability. Sykrin[12] suggests that cis bonds are strengthened by a ligand with a large trans-influence, and this suggestion is supported by ^{31}P NMR data of Pt(II) complexes with P containing ligands. There is no explanation

offered for the observation that the high trans-influence ligand $(PhO)_3P$ has a high cis-influence. Presently, there seems to be no simple relationship between the cis-influence and trans-influence.

Statement of the Problem

In an attempt to relate CO stretching frequencies to the basicities of ligands in $[Ir(PPh_3)_2Y(CO)]ClO_4$ complexes, Reddy and Ramesh chose substituted imidazoles for their study. No meaningful relationship between ν(CO) and the pK_a of Y was found. Since these ligands appear to have been chosen without regard to possible steric problems, one goal of this research is to conduct a similar study with more carefully chosen ligands to see if there is a correlation between basicity of ligands L and ν(CO) in some Rh(I) complexes. Para-substituted pyridines were chosen for the study because these ligands eliminate steric hindrance as a variable and allow a more accurate analysis of the correlation between ν(CO) and basicity or other properties of Y.

The purpose of the ^{31}P NMR study is to evaluate the extent of M-A σ interaction in $[Rh(CO)A(PPh_3)_2]$ complexes (A = anionic ligand) and $[Rh(CO)L(PPh_3)_2]PF_6$ complexes (L = substituted pyridines). Since the rhodium-phosphorus coupling constant is mostly sensitive to the s character in the rhodium orbitals, it is expected that there is a relationship between J_{Rh-P} and a parameter related to the σ donor character such as Wilmshurst σ electronegativities of the anionic ligands or the pK_a's of the substituted pyridines.

Another goal of this study is to establish a ranking of ligands based on their cis-influencing ability. Variations in Rh-P coupling constants should reflect different cis-influencing abilities of the ligands.

CHAPTER II

EXPERIMENTAL

A. Chemicals

1. Solvents

a. Methylene Chloride, (CH_2Cl_2). Both spectroanalyzed and Certified ACS CH_2Cl_2 (Fisher Scientific) were used without further purification.

b. Chloroform, ($CHCl_3$). Both spectroanalyzed and Certified ACS $CHCl_3$ (Fisher Scientific) were used without further purification.

c. Acetone. Certified ACS acetone (Fisher Scientific) was used without further purification.

d. Methanol. Certified ACS methanol (Fisher Scientific) was used without further purification.

e. Distilled water, (water). Water from the department still was used.

f. Benzene. Certified ACS benzene (Fisher Scientific) was used without further purification.

g. Diethyl Ether, (ether). Certified ACS anhydrous ether (Fisher Scientific) was used without further purification.

h. Pentane. Certified ACS pentane (Fisher Scientific) was used without further purification.

i. Absolute Ethanol, (ethanol). Certified ACS ethanol (Aaper Alcohol) was used without further purification.

2. Reagents

a. Rhodium(III) Chloride Trihydrate, ($RhCl_3 \cdot 3H_2O$). Reagent grade $RhCl_3 \cdot 3H_2O$ (Strem) was used without further purification.

b. 1,5-Cyclooctadiene, (COD). Reagent grade COD (Aldrich) was used without further purification.

c. Triphenylphosphine, (PPh_3). Certified ACS PPh_3 (Fisher Scientific) was used without further purification.

d. Potassium Hexafluorophosphate, (KPF_6). Reagent grade KPF_6 (Aldrich) was used without further purification.

e. Pyridine, (py). Certified ACS py (Fisher Scientific) was used without further purification.

f. 4-Acetylpyridine. Reagent grade 4-acetylpyridine (Aldrich) was used without further purification.

g. 4-Cyanopyridine. Reagent grade 4-cyanopyridine (Aldrich) was used without further purification.

h. 4-Dimethylaminopyridine. Reagent grade 4-dimethylaminopyridine (Aldrich) was used without further purification.

i. 4-Methylpyridine, (γ-picoline). Reagent grade γ-picoline (Aldrich) was used without further purification.

j. 4-Benzoylpyridine. Reagent grade 4-benzoylpyridine (Aldrich) was used without further purification.

k. Acetonitrile, (CH_3CN). Certified ACS CH_3CN (Fisher Scientific) was used without further purification.

l. 4-Hydroxypyridine. Technical grade 4-hydroxypyridine (Aldrich) was used after recrystallization from hot ethanol.

m. 3-Chloropyridine. Reagent grade 3-chloropyridine (Aldrich) was used without further purification.

n. Sodium Thiocyanate, (NaSCN). Analytical reagent grade NaSCN (Mallinckrodt) was used without further purification.

o. Hydrofluoric Acid, (HF). ACS reagent grade 49% aqueous HF (Fisher Scientific) was used without further purification.

p. Diethylamine, (Et_2NH). Certified ACS Et_2NH (Fisher Scientific) was used without further purification.

q. Potassium Cyanate, (KCNO). Certified ACS KCNO (Fisher Scientific) was used without further purification.

r. Sodium Nitrate, ($NaNO_3$). Certified ACS $NaNO_3$ (Fisher Scientific) was used without further purification.

s. Sodium Nitrite, ($NaNO_2$). Bakers Analyzed $NaNO_2$ (J. T. Baker) was used without further purification.

t. Sodium Acetate, (NaOAc). Purified NaOAc (J. T. Baker) was used without further purification.

u. Potassium Bromide, (KBr). Certified ACS KBr (Fisher Scientific) was used without further purification.

v. Sodium Benzoate. Sodium benzoate, U.S.P. powder (Merck) was used without further purification.

w. Carbon Monoxide, (CO). CP grade CO (Air Products) was used without further purification.

B. Spectroscopic Measurements

1. Infrared Spectroscopy

Infrared spectroscopy (IR) was carried out using a Digilab FTS-20 C/V Fourier Transform Infrared Spectrometer. Solutions were prepared

by dissolving maximum amounts of solute in spectroanalyzed chloroform or spectroanalyzed methylene chloride. Barnes Engineering IR liquid cells equipped with NaCl or KBr salt plates were used for liquid samples.

2. Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

Phosphorus-31 nuclear magnetic resonance spectroscopy (NMR) was carried out using a Joel FX90Q Fourier Transform NMR Spectrometer operating at 36.19 MHz. Solutions were prepared by dissolving 0.1 to 0.2 g of solute in approximately 2 mL of spectroanalyzed chloroform or spectroanalyzed methylene chloride. Chemical shifts are given relative to external 85% H_3PO_4.

C. Elemental Analysis

All elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

D. Preparation of Rhodium Complexes

1. Di-μ-Chlorobis(η^4-1,5-cyclooctadiene)dirhodium(I), $[Rh(Cl)COD]_2$, 1.

A procedure outlined by Giordano and Crabtree[13] was used for the synthesis of this complex. To 1.0 g of $RhCl_3 \cdot 3H_2O$ dissolved in 20 mL of 5:1 ethanol/water solution was added 1.5 mL of 1,5-cyclooctadiene. The mixture was refluxed under a nitrogen atmosphere for 18 hours at 91-93°C. The yellow-orange product was filtered and rinsed with pentane, followed by washing with 1:5 methanol/water solution to ensure removal of chloride ions. The yield was 85-90%.

2. (η^4-1,5-cyclooctadiene)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(COD)\{P(C_6H_5)_3\}_2]PF_6$, 2.

A procedure outlined by Schrock and Osborn[14] was used to prepare this complex. To 1.0 g $[Rh(Cl)COD]_2$ dissolved in 20 mL of CH_2Cl_2 was added 20 mL of H_2O containing 1.0 g of KPF_6. This solution was stirred vigorously while 4.0 g of PPh_3 was added. Stirring was continued for 15 minutes after the addition of PPh_3 was completed. The CH_2Cl_2 layer was removed and washed three times with a total of 20 mL of H_2O. To the CH_2Cl_2 layer 20 mL of ethanol was added, followed by addition of 20 mL of ether to precipitate dark orange crystals. The product was filtered and washed with benzene, then ether, and dried in vacuum. The yield was 90-95%.

3. Tricarbonylbis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)_3\{P(C_6H_5)_3\}_2]PF_6$, 3.

In 15 mL of acetone 1.5 g of $[Rh(COD)\{P(C_6H_5)_3\}_2]PF_6$ was dissolved. Carbon monoxide was bubbled through the solution until the volume was reduced to 3-5 mL. To complete precipitation of the pale yellow complex, several milliliters of ethanol were added. The product was filtered and rinsed with ether while under a CO atmosphere. The yield was 80-85%.

4. Carbonylpyridinebis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_5H_5N)\{P(C_6H_5)_3\}_2]PF_6$, 4.

While stirring 0.3 g of $[Rh(CO)_3\{P(C_6H_5)_3\}_2]PF_6$ in 2 mL of CH_2Cl_2, 0.08 mL of pyridine was added. Evolution of CO was observed upon addition of the ligand. After evolution of CO subsided, 2-3 mL of ethanol was added followed by an equivalent amount of ether to complete precipitation of yellow product. The product was filtered and recrystallized

from CH_2Cl_2 and ether, and dried in vacuum. The yield was 70%. Anal. Calcd for $C_{42}H_{35}F_6NOP_3Rh$: C, 57.36; H, 4.01; N, 1.59. Found: C, 57.70; H, 4.15; N, 1.56.

5. (4-Acetylpyridine)carbonylbis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(C_7H_7NO)(CO)\{P(C_6H_5)_3\}_2]PF_6$, 5.

This complex was prepared by the same method used to prepare compound 4. The yield was 85%. Anal. Calcd for $C_{44}H_{37}F_6NOP_3Rh$: C, 57.35; H, 4.04; N, 1.52. Found: C, 55.92; H, 4.11; N, 1.58.

6. Carbonyl(4-cyanopyridine)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_6H_4N_2)\{P(C_6H_5)_3\}_2]PF_6$, 6.

This complex was prepared by the same method used to prepare compound 4. The yield was 86%. Anal. Calcd for $C_{43}H_{34}F_6N_2OP_3Rh$: C, 57.10; H, 3.79; N, 3.10. Found: C, 56.95; H, 3.71; N, 3.03.

7. Carbonyl(4-dimethylaminopyridine)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_7H_{10}N_2)\{P(C_6H_5)_3\}_2]PF_6$, 7.

This complex was prepared by the same method used to prepare compound 4. The yield was 87%. Anal. Calcd for $C_{44}H_{40}F_6N_2OP_3Rh$: C, 57.28; H, 4.37; N, 3.04. Found: C, 56.77; H, 4.47; N, 3.04.

8. Carbonyl(4-methylpyridine)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_6H_7N)\{P(C_6H_5)_3\}_2]PF_6$, 8.

This complex was prepared by the same method used to prepare compound 4. The yield was 90%. Anal. Calcd for $C_{43}H_{37}F_6NOP_3Rh$: C, 57.80; H, 4.17 N; 1.57. Found: C, 57.48; H, 4.21; N, 1.62.

9. (4-Benzoylpyridine)carbonylbis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(C_{12}H_9NO)(CO)\{P(C_6H_5)_3\}_2]PF_6$, 9.

This complex was prepared by the same method used to prepare compound 4. The yield was 67%. Anal. Calcd for $C_{49}H_{39}F_6NO_2P_3Rh$: C, 59.86; H, 3.99; N, 1.42. Found: C, 59.28; H, 4.00; N, 1.46.

10. Acetonitrilecarbonylbis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CH_3CN)(CO)\{P(C_6H_5)_3\}_2]PF_6$, 10.

This complex was prepared by the same method used to prepare compound 4. The IR spectrum of a CH_2Cl_2 solution shows $\nu(C\equiv O)$ at 2014 cm^{-1} (s) (lit.[14]: 2016 cm^{-1} (s)). The phosphorus-31 NMR spectrum shows J_{Rh-P} = 119 Hz (lit. for perchlorate salt[14]: J_{Rh-P} = 119 Hz).

11. Carbonyl(3-chloropyridine)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_5H_9ClN)\{P(C_6H_5)_3\}_2]PF_6$, 11.

This complex was prepared by the same method used to prepare compound 4. Anal. Calcd for $C_{42}H_{34}ClF_6NOP_3Rh$: C, 55.19; H, 3.75; N, 1.53. Found: C, 54.76; H, 3.81; N, 1.57.

12. Carbonyl(4-hydroxypyridine)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate, $[Rh(CO)(C_5H_5NO)\{P(C_6H_5)_3\}_2]PF_6$, 12.

To 0.30 g of $[Rh(CO)_3\{P(C_6H_5)_3\}_2]PF_6$ dissolved in 2 mL of CH_2Cl_2, 0.035 g of 4-hydroxypyridine was added. No appreciable evolution of CO was observed upon addition of the ligand. To this solution, 3-5 mL of ethanol was added to dissolve the remaining 4-hydroxypyridine. After the ligand had dissolved, more ethanol was added, followed by 5-8 mL of ether to precipitate the product. The product was filtered and recrystallized from CH_2Cl_2 and ether. The yield was 70%. Anal. Calcd for $C_{42}H_{35}F_6NO_2P_3Rh$: C, 56.33; H, 3.94; N, 1.56. Found: C, 56.28;

H, 4.06; N, 1.41.

13. Carbonylfluorobis(triphenylphosphine)rhodium(I), [Rh(CO)F{P(C_6H_5)$_3$}$_2$], 13.

A procedure given by Reed and Roper[15] was used for the synthesis of this complex. A 49% solution of HF, diethylamine, and ethanol, in a 2:5:20 ratio, was prepared as a source of fluoride ions for this reaction. A methylene chloride/ethanol solution containing 1.5 g of [Rh(CH_3CN)(CO){P(C_6H_5)$_3$}$_2$]PF_6 was stirred while 5.9 mL of the ethanolic fluoride solution was added; the mixture was stirred for an additional 30 minutes. The volume was reduced and ethanol was added to complete precipitation. The product was filtered and recrystallized from CH_2Cl_2 and ethanol. The yield was 96%.

Coordination of F^- was confirmed by the absence of phosphorus resonances of the PF_6^- anion in the ^{31}P NMR spectrum of the product. The IR spectrum of a $CHCl_3$ solution shows $\nu(C\equiv O)$ at 1980 cm^{-1} (s) (lit.[4]: 1971 cm^{-1} (s)).

14. Carbonylnitratobis(triphenylphosphine)rhodium(I), [Rh(CO)(NO_3){P(C_6H_5)$_3$}$_2$], 14.

A procedure given by Vaska and Peone[4] was used for the synthesis of this complex. To approximately 20 mL of hot methanol (70°C) 0.52 g of $NaNO_3$ was added. Addition of 0.20 g of [Rh(CO)F{P(C_6H_5)$_3$}$_2$] turned the solution yellow. It was allowed to stir at 70°C for 10 minutes. After cooling the solution, water was added to complete precipitation. The product was filtered and recrystallized from CH_2Cl_2 and ether. The yield was 56%.

The IR spectrum of a $CHCl_3$ solution shows $\nu(C\equiv O)$ at 1979 cm^{-1} (s) (lit.[4]: 1985 cm^{-1} (s)).

15. Carbonylnitritobis(triphenylphosphine)rhodium(I), [Rh(CO)(NO_2){$P(C_6H_5)_3$}$_2$], 15.

This complex was prepared by the same method used to prepare compound 14. The yield was 81%.

The IR spectrum of a $CHCl_3$ solution shows ν(C≡O) at 1981 cm^{-1} (s) (lit.[4]: 1996 cm^{-1} (s)).

16. Acetatocarbonylbis(triphenylphosphine)rhodium(I), [Rh($C_2H_3O_2$)(CO){$P(C_6H_5)_3$}$_2$], 16.

This complex was prepared by the same procedure given for compound 14. The yield was 20%.

The IR spectrum of a $CHCl_3$ solution shows ν(C≡O) at 1973 cm^{-1} (s) (lit.[4]: 1972 cm^{-1} (s)).

17. Benzoatocarbonylbis(triphenylphosphine)rhodium(I), [Rh($C_7H_5O_2$)(CO){$P(C_6H_5)_3$}$_2$], 17.

This complex was prepared by the same procedure given for compound 14. The yield was 20%.

The IR spectrum of a $CHCl_3$ solution shows ν(C≡O) at 1973 cm^{-1} (s) (lit.[4]: 1973 cm^{-1} (s)).

18. Carbonylcyanatobis(triphenylphosphine)rhodium(I), [Rh(CO)(CNO){$P(C_6H_5)_3$}$_2$], 18.

This complex was prepared by the same procedure given for compound 14. The yield was 70%.

The IR spectrum of a $CHCl_3$ solution shows ν(C≡O) at 1982 cm^{-1} (s) (lit.[4]: 1982 cm^{-1} (s)).

19. Carbonylthiocyanatobis(triphenylphosphine)rhodium(I), [Rh(CO)(SCN){P(C_6H_5)$_3$}$_2$], 19.

To 0.10 g of [Rh(CH_3CN)(CO){P(C_6H_5)$_3$}$_2$]PF_6 dissolved in 5 mL of CH_2Cl_2 was added 10 mL of ethanol containing 0.03 g of NaSCN. This solution stirred vigorously for about 30 minutes. The volume was reduced and precipitation of the product was completed by addition of ether. The product was recrystallized from CH_2Cl_2 and ether. The yield was 60%.

Coordination of SCN^- was confirmed by the absence of phosphorus resonances of the PF_6^- anion in the ^{31}P NMR spectrum of the product. The IR spectrum of a $CHCl_3$ solution shows $\nu(C\equiv O)$ at 1990 cm^{-1} (s) (lit.[4]: 1990 cm^{-1} (s)).

20. Bromocarbonylbis(triphenylphosphine)rhodium(I), [RhBr(CO){P(C_6H_5)$_3$}$_2$], 20.

To 10 mL of hot methanol (70°C) containing 0.76 g of KBr, 0.20 g of [Rh(CO)F{P(C_6H_5)$_3$}$_2$] was added. This solution was stirred for 15 minutes at 70°C before being cooled. Addition of 15 mL of water to the cooled solution caused the product to precipitate. The product was filtered and recrystallized from $CHCl_3$ and ether. The yield was 78%,

The IR spectrum of a $CHCl_3$ solution shows $\nu(C\equiv O)$ at 1978 cm^{-1} (s) (lit.[4]: 1980 cm^{-1} (s)).

21. Carbonylchlorobis(triphenylphosphine)rhodium(I), [Rh(CO)Cl{P(C_6H_5)$_3$}$_2$], 21.

This compound was prepared by David Abbott[16] according to the procedure of McCleverty and Wilkerson.[17]

The IR spectrum of a $CHCl_3$ solution shows $\nu(C\equiv O)$ at 1980 cm^{-1} (s) (lit.[4]: 1980 cm^{-1}(s)).

22. Rhodium(I) complexes of substituted imidazoles.

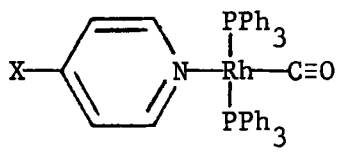
Complexes of substituted imidazoles were prepared as perchlorate salts by Paul Anderson[18] by a procedure similar to the one used for the synthesis of compound 4. The following complexes were prepared: carbonylimidazolebis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(CO)(C_3H_4N_2)\{P(C_6H_5)_3\}_2]ClO_4$, 22; benzimidazolecarbonylbis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(C_7H_6N_2)(CO)\{P(C_6H_5)_3\}_2]ClO_4$, 23; carbonyl(2-methylbenzimidazole)bis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(CO)(C_8H_8N_2)\{P(C_6H_5)_3\}_2]ClO_4$, 24; carbonyl(2-ethylbenzimidazole)bis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(CO)(C_9H_{10}N_2)\{P(C_6H_5)_3\}_2]ClO_4$, 25; carbonyl(2-methylbenzthiazole)bis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(CO)(C_8H_7NS)\{P(C_6H_5)_3\}_2]ClO_4$, 26; carbonyl(2-methylbenzoxazole)bis(triphenylphosphine)rhodium(I) perchlorate, $[Rh(CO)(C_8H_7NO)\{P(C_6H_5)_3\}_2]ClO_4$, 27.

CHAPTER III

RESULTS AND DISCUSSION

In a study by Reddy and Ramesh,[6] an attempt was made to find some relationship between the pK_a of substituted imidazoles (Y) and $\nu(CO)$ in trans-$[Ir(PPh_3)_2Y(CO)]ClO_4$ complexes. It was suspected that changes in the basicity of Y would be reflected in the $\nu(CO)$ values since the electron density on the Rh atom should vary as a result of changing Y. However, no meaningful relationship between ligand basicities and $\nu(CO)$ was found. It was suggested that the π acidity might not vary in the same manner as the σ basicity, thereby precluding the expected correlation. Steric problems presented by these bulky ligands might also be responsible for these complexes not exhibiting the expected correlation between pK_a and $\nu(CO)$. This thesis presents results of a similar study using more carefully chosen ligands.

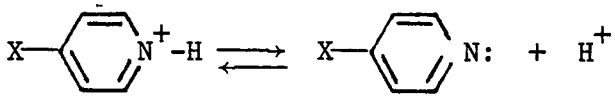
Pyridines, substituted at the positions three or four, were considered to be ideal ligands for this study because the steric demands of the pyridine ligands in trans-$[Rh(CO)L(PPh_3)_2]PF_6$ complexes are essentially the same (Structure I).



I

Changing X results in a variation of the σ basicity of the coordinating site. This basicity, taken as the tendency to coordinate with H^+,

is given by the pK_a of the conjugate acid (Equation 4) of the substituted pyridine.



(4)

If the tendency of N to coordinate with H^+ can be assumed to be proportional to its sigma donor ability toward Rh, the pK_a should be a good measure of the sigma basicity of L in complexes with structure I. With this in mind, IR data have been collected for complexes of this type in which various substituents are attached to the pyridine ring. The IR data are presented in Table I.

Figure 1 consists of a plot of pK_a for the substituted pyridines and the imidazoles listed in Table I versus ν(CO) of the complexes. The linear relationship observed for most of the pyridine complexes suggests that a correlation does exist between pK_a and ν(CO) for some pyridines. This linear correlation also suggests that the sigma donor ability of those ligands is the dominant factor determining the variations in ν(CO). This follows from the fact that the proton has no π bonding capability and the pK_a is therefore a measure of the strength of the sigma interaction with the proton.

The empirical relationship given in equation 5 follows from the plot in Figure 1, and relates ν(CO) with pK_a's of only those pyridines that lead to the linear correlation.

$$\nu(CO) = 2017\ cm^{-1} + pK_a(L)m \qquad (5)$$

This equation can therefore be used, under certain conditions, to predict ν(CO) for other pyridine complexes. A least squares analysis gives

TABLE I

pK_a's AND C≡O STRETCHING FREQUENCIES FOR

$[Rh(CO)L(PPh_3)_2]PF_6$ COMPLEXES

Compound No.	Ligand	pK_a of L[a]	ν(C≡O)
pyridines			
4	pyridine	5.23	2008 (s)
5	4-acetylpyridine	3.51	2011 (s)
6	4-cyanopyridine	1.88	2014 (s)
7	4-dimethylaminopyridine	9.71	2001 (s)
8	4-methylpyridine	5.98	2007 (s)
9	4-benzoylpyridine	3.35	2012 (s)
11	3-chloropyridine	2.82	2012 (s)
12	4-hydroxypyridine	3.27, 11.09	2000 (sh), 1988 (s)
imidazoles			
22	imidazole	7.00	2001 (s)
23	benzimidazole	5.52	2000 (s)
24	2-methylbenzimidazole	6.10	2000 (s)
25	2-ethylbenzimidazole	6.15	2001 (s)

[a]The pKa values are taken from reference 19 for complexes 4-12; reference 20 for complex 22; and reference 21 for complexes 23-25.

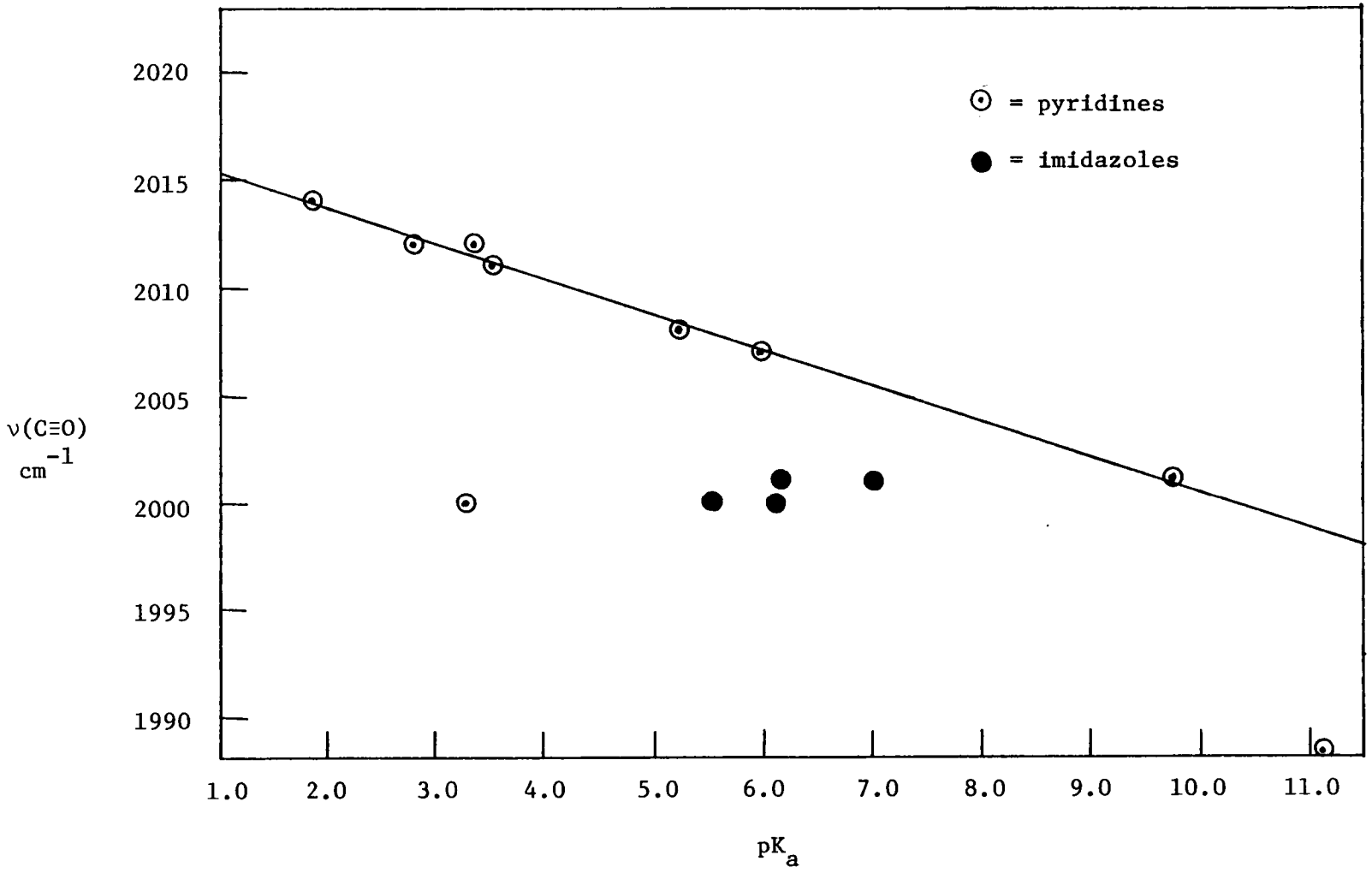
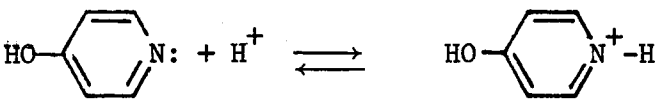
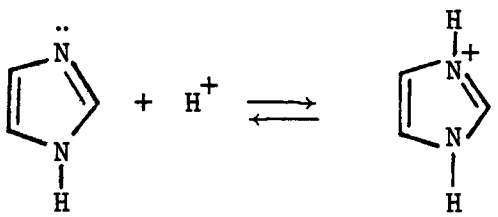


Figure 1. Plot of pK_a of pyridines and imidazoles versus ν(C≡O) for <u>trans</u>-[Rh(CO)L(PPh_3)$_2$] complexes.

a value of -1.63 for m (correlation coefficient = 0.9969).

Figure 1 shows several points which do not lie on the straight line plot. The complexes represented by these points are those containing 4-hydroxypyridine, imidazole, benzimidazole, 2-methylbenzimidazole and 2-ethylbenzimidazole. These compounds have a common feature. They all have conjugate acids which possess two potentially ionizable hydrogens (Equation 6).





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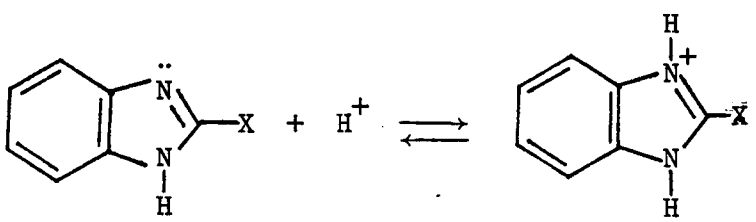


The existence of two potentially ionizable hydrogens could affect the pK_a of the ligand in such a way that the pK_a no longer has the same relationship with the σ basicity of the binding site toward Rh(I) as exists for the other substituted pyridines.

A related study by Tolman[22] involves the measurement of ν(CO) in $Ni(CO)_3L$ complexes where L is a phosphorus containing ligand. From the IR data, Tolman derived substituent parameters (χ_i) for the groups bound

to the phosphorus in the ligands L. A correlation was found to exist between these χ_i values and σ parameters reported by Kabachnik.[23] Kabachnik's σ parameters are similar to Taft's σ parameters except that Kabachnik's σ values are based on the transmission of inductive effects through phosphorus rather than carbon. Tolman also observed a correlation between χ_i and the pK_a of the phosphonium ligands. Since H^+ cannot π bond to P, it is the σ donor ability of P which determines the pK_a values of the phosphonium ions. The fact that the correlation between χ_i and Kabachnik's σ parameters is nonlinear is recognized by Derencsenyi.[24] This nonlinearity was attributed to either reduced σ donation or enhanced π acceptor ability of the phosphorus ligand. The contribution to the reduced electron density on Ni by each of these two effects is not known.

The separation of the σ and π contributions to the electron density on M in <u>trans</u>-$[M(CO)A(PPh_3)_2]$ complexes (M = Ir, Rh, A = anionic ligand) was the result sought in an IR study by Vaska and Peone.[4] An equation for the total electronegativity ($\chi_{A(T)}$) of A was derived (Equation 1, Page 4). Pi electronegativities were obtained using $\chi_{A(T)}$ and the Wilmshurst sigma electronegativities. Although a linear relationship exists between $\chi_{A(T)}$ and ν(CO), the plot in Figure 2 shows that there is no linear correlation between $\chi_{A(\sigma)}$ and ν(CO). All the electronegativities and IR data are given in Table II.

It was thought that $\chi_{A(\sigma)}$ might show a correlation with J_{Rh-P} since variation in $\chi_{A(\sigma)}$ is expected to be reflected in changes in the distribution of the s electron density on the metal, and since the magnitude of J_{Rh-P} is related to the s character in the metal orbital.

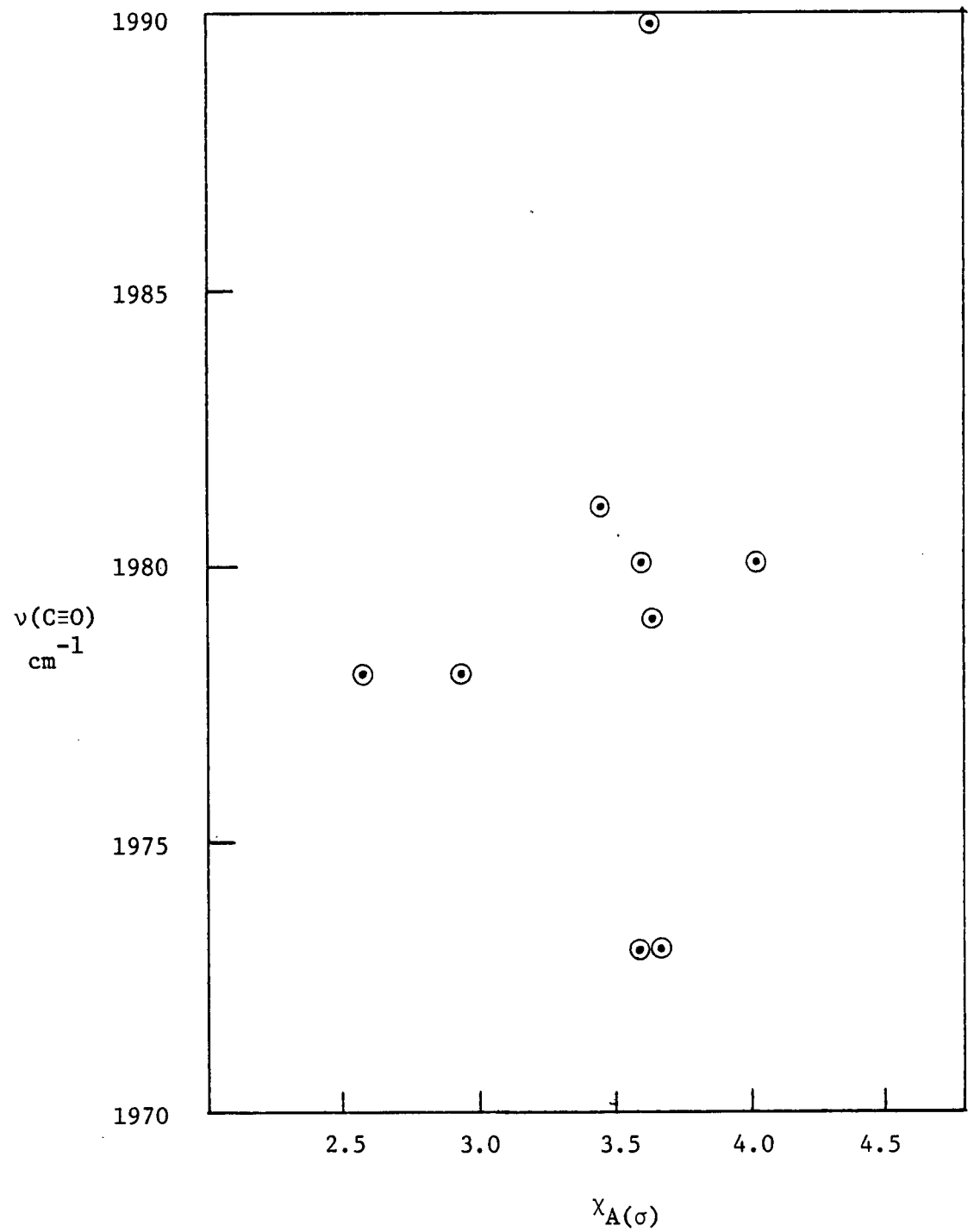


Figure 2. Plot of $\chi_{A(\sigma)}$ versus $\nu(C\equiv O)$ for <u>trans</u>-$[Rh(CO)A(PPh_3)_2]$ complexes.

TABLE II

TOTAL AND SIGMA ELECTRONEGATIVITIES

OF A AND C≡O STRETCHING FREQUENCIES

OF $[Rh(CO)A(PPh_3)_2]$ COMPLEXES[a]

Compound No.	Ligand A	$\chi_{(T)}$	$\chi_{(\sigma)}$	ν(CO)
13	F^-	4.02	4.02	1980
14	NO_3^-	4.36	3.65	1979
15	NO_2^-	4.67	3.45	1981
16	CH_3COO^-	4.04	3.60	1973
17	$C_6H_5COO^-$	4.06	3.67	1973
18	CNO^-	4.28	3.60	1982
19	SCN^-	4.50	3.64	1990
20	Br^-	4.23	2.58	1978
21	Cl^-	4.23	2.94	1978

[a]Taken from reference 4.

To investigate this possibility, ^{31}P NMR data were collected for complexes 5 - 21. These data are given in Table III. A plot of $\chi_{A(\sigma)}$ versus J_{Rh-P} for complexes 5 - 21 is shown in Figure 3 and demonstrates that there is no meaningful correlation. This lack of correlation could be due either to the fact that the $\chi_{A(\sigma)}$ values are not a true measure of the sigma electronegativities or that in these complexes J_{Rh-P} is affected by other parameters.

Phosphorus-31 NMR data were collected for the pyridine complexes and are given in Table IV. Figure 4 shows a plot of the pK_a of the pyridine ligands versus J_{Rh-P}. It was thought that there might be a direct correlation between J_{Rh-P} and the pK_a since J_{Rh-P} is related to the s character of the Rh orbitals and the pK_a is a measure of the σ donor ability of the ligand. Even though a general increase in J_{Rh-P} with an increase in pK_a can be seen in Figure 4, there is an exception to the trend. The ligand, 4-acetylpyridine, has a much larger coupling constant than expected on the basis of its pK_a and the coupling constants for other ligands with similar pK_a values. There is no obvious reason why the 4-acetylpyridine should have such a large J_{Rh-P} value. There appears to be no simple relationship between J_{Rh-P} and pK_a; however, if the 4-acetylpyridine complex is assumed to be an exception, the plot in Figure 4 appears to have the form of a step function.

It should be noted that Table IV shows two Rh-P coupling constants for $[Rh(CO)L(PPh_3)_2]$ when L is 4-hydroxypyridine. Figure 5A shows the ^{31}P NMR spectrum of 8. This spectrum is typical of all other complexes except the hydroxypyridine complex which appears in Figure 5B. The simple doublets result from the coupling of Rh (100%, I = ½) to the

TABLE III

^{31}P NMR DATA AND SIGMA ELECTRONEGATIVITIES FOR

$[Rh(CO)A(PPh_3)_2]$ COMPLEXES

Compound No.	Ligand A	J_{Rh-P} (Hz)	$\chi_{(\sigma)}$	δ(ppm)
13	F^-	136.72	4.02	26.36
14	NO_3^-	131.84	3.65	30.59
15	NO_2^-	139.16	3.45	29.35
16	CH_3COO^-	136.72	3.60	32.55
17	$C_6H_5COO^-$	136.72	3.67	32.01
18	CNO^-	129.39	3.60	29.35
19	SCN^-	126.96	3.64	29.05
20	Br^-	126.96	2.58	29.05
21	Cl^-	126.95	2.94	28.98

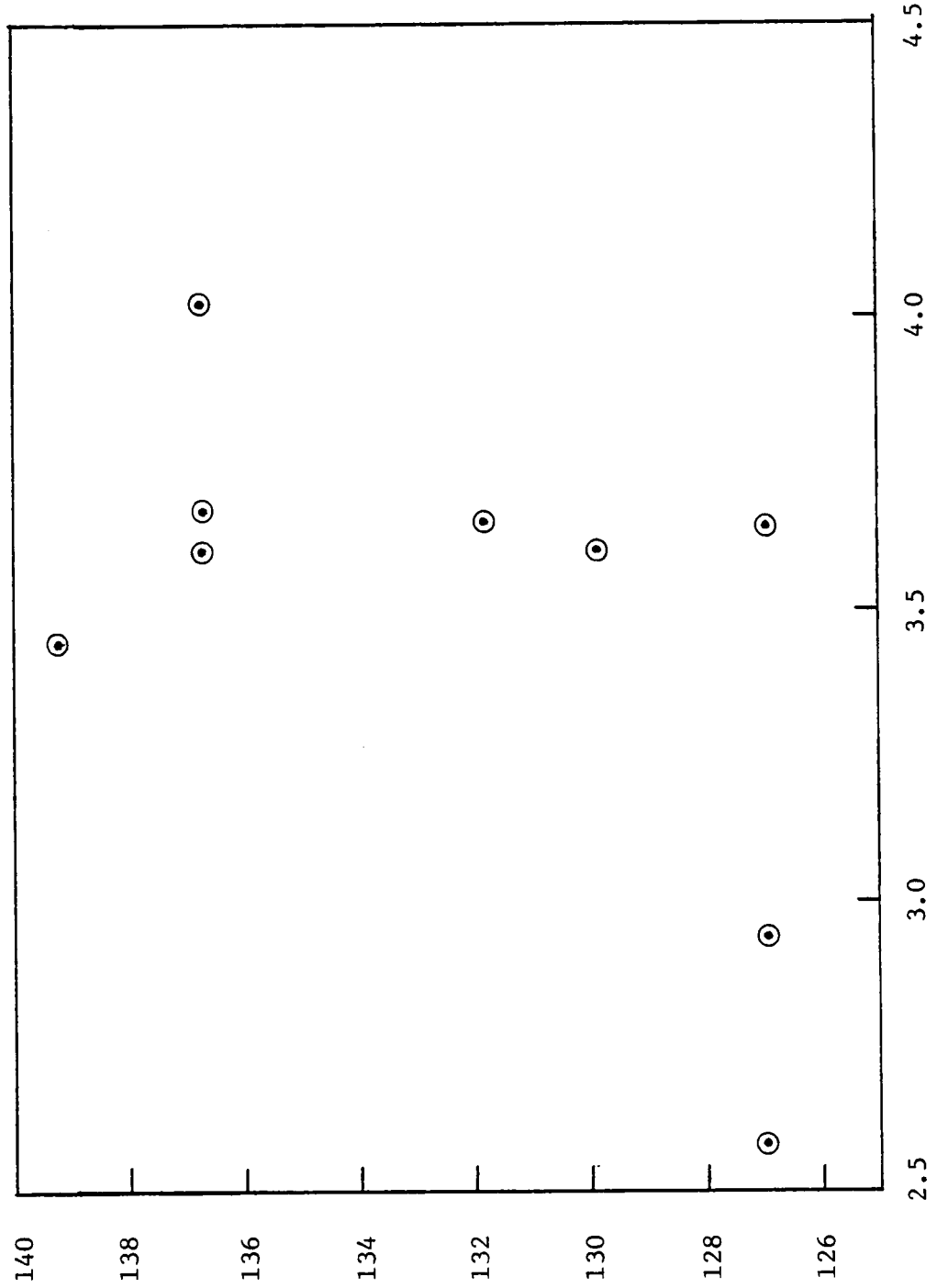


Figure 3. Plot of $\chi_{A(\sigma)}$ versus J_{Rh-P} for trans-$[Rh(CO)A(PPh_3)_2]$ complexes.

TABLE IV

pK_a's AND ^{31}P NMR DATA FOR $[Rh(CO)L(PPh_3)_2]$ COMPLEXES

Compound No.	Ligand L	J_{Rh-P} (Hz)	pK_a[a]	δ(ppm)
pyridines				
4	pyridine	129.40	5.23	31.44
5	4-acetylpyridine	131.84	3.51	31.41
6	4-cyanopyridine	126.96	1.88	31.07
7	4-dimethylaminopyridine	131.83	9.71	31.34
8	4-methylpyridine	129.39	5.98	31.31
9	4-benzoylpyridine	126.96	3.35	31.21
11	3-chloropyridine	126.96	2.82	31.54
12	4-hydroxypyridine	126.96, 131.84	3.27, 11.09	31.34, 30.67
imidazoles				
22	imidazole	129.39	7.00	30.77
23	benzimidazole	126.96	5.52	31.47
24	2-methylbenzimidazole	126.96	6.10	31.00
25	2-ethylbenzimidazole	126.95	6.15	30.26

[a]The pK_a values are taken from reference 19 for complexes 4-12; reference 20 for complex 22; and reference 21 for complexes 23-25.

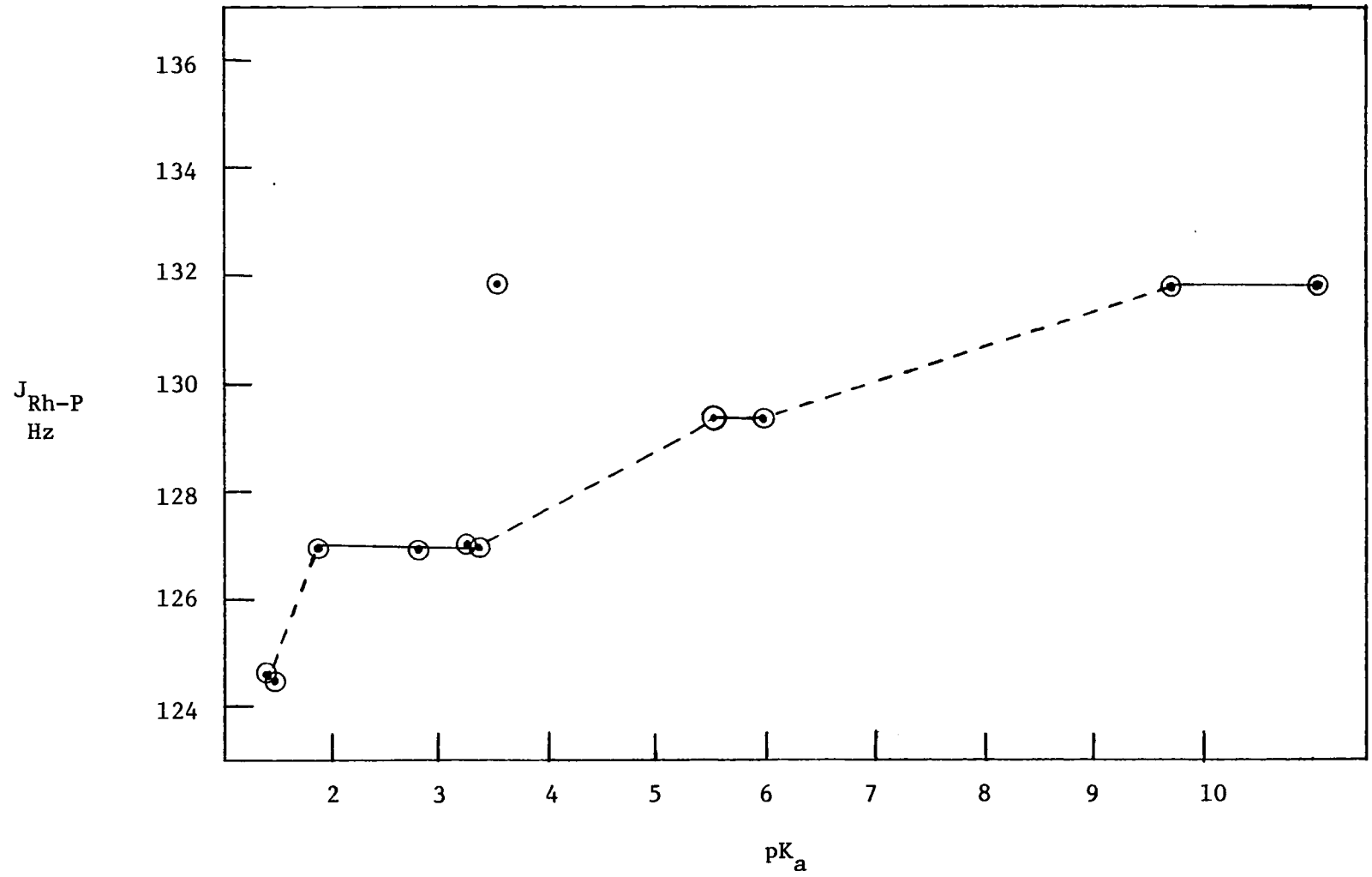


Figure 4. Plot of pK_a of pyridines versus J_{Rh-P} for <u>trans</u>-$[Rh(CO)L(PPh_3)_2]PF_6$ complexes.

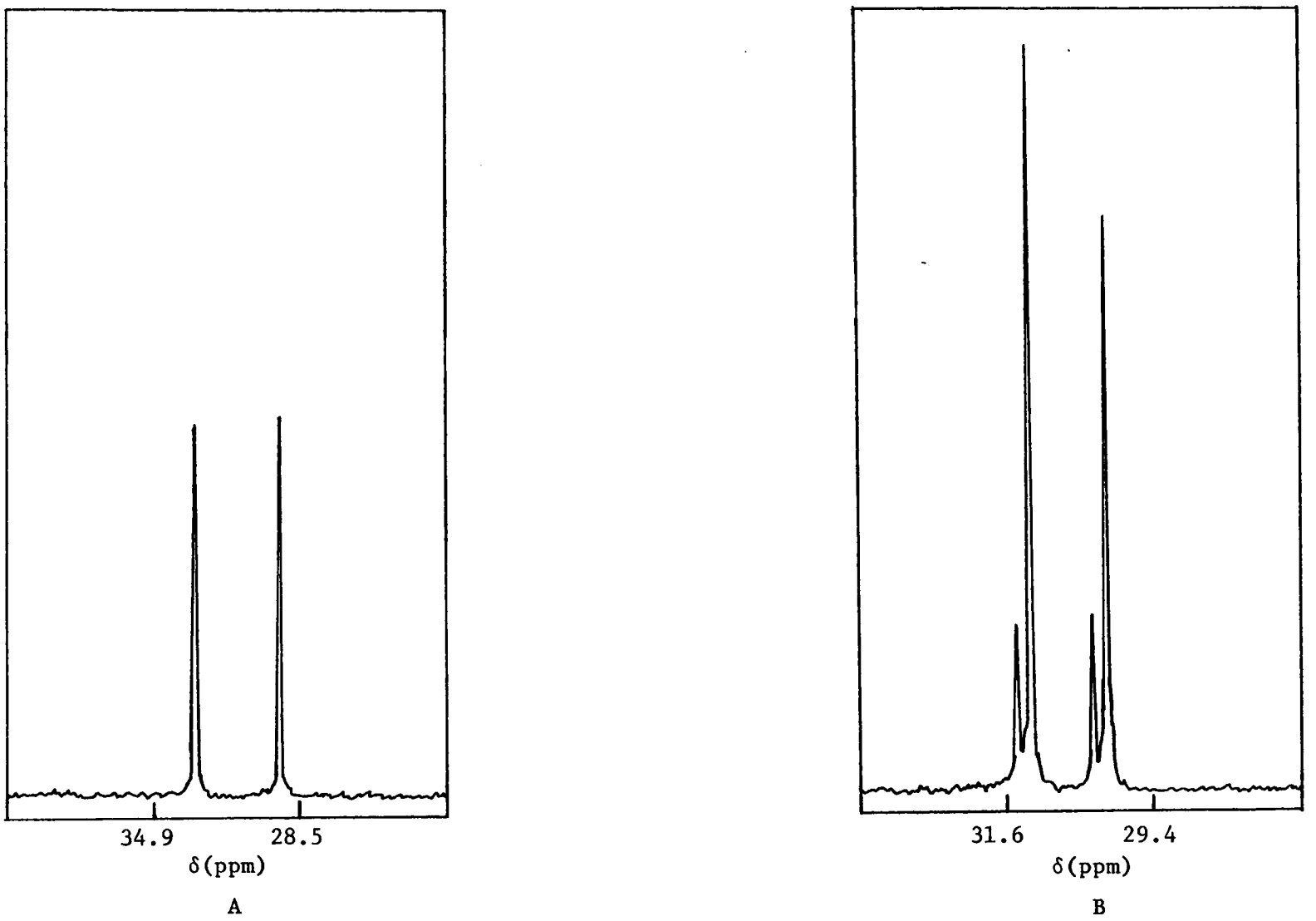
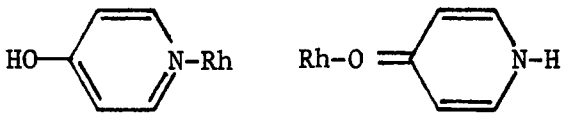


Figure 5. ^{31}P NMR spectra of $[Rh(CO)L(PPh_3)_2]PF_6$. (A) L = 4-methylpyridine; (B) L = 4-hydroxypyridine.

phosphorus nuclei. The ^{31}P NMR spectrum of the hydroxypyridine complex (Figure 5B) shows two doublets, representing two phosphorus resonances. These two resonances are due to the presence of of two linkage isomers resulting from two tautomeric forms of 4-hydroxypyridine (Structures II and III).



II III

A C=O stretching frequency at 1638 cm^{-1} supports the presence of the pyridone form (Structure III) in the hydroxypyridine complex. Two $\nu(C\equiv O)$ values at 1988 cm^{-1}(s) and 2000 cm^{-1}(sh) indicate the presence of two rhodium complexes for the 4-hydroxypyridine ligand.

Careful examination of Table V will show that only certain values of J_{Rh-P} are observed for square planar Rh complexes of the type $[Rh(CO)X(PPh_3)_2]$. Also, it should be noted that there is a constant variation of 2.44 Hz in successive J_{Rh-P} values. A summary of ligands and their corresponding coupling constants is given in Table V. Three ligands not previously discussed, acetonitrile, 2-methylbenzoxazole and 2-methylbenzthizaole have been included because their complexes show J_{Rh-P} values that fit in the series and show the 2.44 Hz variation. The J_{Rh-P} values for the chloride complex and the acetonitrile complex are in agreement with literature values.[14,25] No complex was found to have a J_{Rh-P} value of 134.27 Hz, but this value is expected to be a possible coupling constant for complexes of this type since it lies 2.44 Hz from the next higher (136.72 Hz) and the next lower (131.84 Hz) coupling constants observed. If the Fermi contact mechanism is assumed, these results suggest that there is a ligand property, yet to be identified,

TABLE V

SUMMARY OF LIGANDS AND Rh-P COUPLING CONSTANTS FOR $[Rh(CO)X(PPh_3)_2]^{n+}$ COMPLEXES[a]

J_{Rh-P} (Hz)[b]	Ligands, X
119.63	acetonitrile
122.07	2-methylbenzoxazole
124.51	2-methylbenzthiazole
126.95	4-hydroxypyridine, 4-cyanopyridine, 4-benzoylpyridine, 3-chloropyridine, benzimidazole, 2-methylbenzimidazole, 2-ethylbenzimidazole, thiocyanate, chloride, bromide
129.39	pyridine, 4-methylpyridine, imidazole, cyanate
131.84	4-acetylpyridine, 4-dimethylaminopyridine, nitrate, 4-hydroxypyridine
134.27[c]	
136.72	fluoride, benzoate, acetate
139.16	nitrite

[a] n = 1 when X = the neutral ligands L; n = 0 when X = anionic ligands A.

[b] Coupling constants obtained from CH_2Cl_2 solutions for the neutral ligands and $CHCl_3$ solutions for the anionic ligands.

[c] No compound having this J_{Rh-P} value was prepared.

which causes a constant variation in the s character of the Rh orbitals. At the present, there is no obvious reason why the variation in s character of the Rh orbitals should occur in constant increments.

In summary this work has shown that under certain conditions there appears to be a linear relationship between the pK_a and $\nu(CO)$ in $[Rh(CO)L(PPh_3)_2]PF_6$ complexes. This correlation suggests that changes in $\nu(CO)$ can be attributed predominantly to σ interaction of the ligand and the metal. Since an increase in ligand basicity (increase in pK_a), increases the electron density on Rh, there should be an increase in the flow of electron density from the Rh into the C≡O π^* orbitals via the metal d-orbitals. An increase of electron density in the carbonyl π^* orbitals results in a decrease in the C≡O stretching frequency. The data presented in this thesis is consistent with this interpretation.

This work has also shown that their is a <u>cis</u>-influence which is reflected by the Rh-P coupling constants. It has been revealed that only certain J_{Rh-P} values are possible for the square planar rhodium complexes. However, this investigation has not led to the identification of the particular ligand parameter which is responsible for the limited number and constant variation of the rhodium-phosphorus NMR coupling constants.

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