RICE UNIVERSITY

CARBON-13 NUCLEAR MAGNETIC RESONANCE
STUDIES OF SOME ORGANO-RHODIUM COMPLEXES

by

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ABSTRACT OF CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME ORGANO-RHODIUM COMPLEXES

by

Barbara Helene Berman

This study was concerned with the analysis of bonding in rhodium(I) square planar complexes of the type RhCl(CO)L₂ where L= tertiary phosphine,arsine,stibine, and amine.

Since Rh(I) complexes have been shown to be effective decarbonylation, carbonylation, and hydrogenation catalysts, an investigation of the bonding was in order to elucidate the bonding in these complexes. Previous studies have noted that infrared and nuclear magnetic resonance studies are helpful in determining the nature of the pi bonding in the complexes. With the advent of $^{13}$C NMR, a more direct technique of studying the bonding was available, in addition to the already available technique of infrared spectroscopy.

The object of the study was then to determine the relationship of the carbon-13 chemical shift and the infrared carbonyl stretching frequency force constant for the compounds RhCl(CO)L₂. The results of plotting the chemical shift versus the force constant showed a linearity between the two factors.

In addition, some new organo-rhodium complexes were synthesized.
ACKNOWLEDGMENT

The author wishes to thank Dr. Aaron R. Burke who assisted with the NMR studies and the other members of the research group with whom she was affiliated for their help and encouragement.
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<td>milliliter</td>
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<tr>
<td>L</td>
<td>liter</td>
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<tr>
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<td>normal</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>M.W.</td>
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<tr>
<td>$\delta_{ppm}$</td>
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<tr>
<td>$\tilde{\nu}(cm^{-1})$</td>
<td>wavenumber (per centimeter)</td>
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<td>cm</td>
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<tr>
<td>Hz</td>
<td>Hertz or cycles per second</td>
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<tr>
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<td>pounds per square inch</td>
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<td>NMR</td>
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<tr>
<td>mm</td>
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<tr>
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<td>melting point</td>
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Studies of Some Organo-Rhodium Complexes

I. Introduction

One of the few transition metals which has not been extensively studied is rhodium. It is commonly called a platinum group metal, although it is found in the second transition series in the Cobalt triad. Like platinum, it is relatively inert to most reagents, thus serving as a good metal base for construction purposes or razor blades. In addition, it should also serve as a good catalyst for many reactions.

The two most important oxidation numbers of rhodium are the +1 and +3 oxidation states. The latter is the more commonly found and has been investigated more than the +1 state. The +1 state is a $d^8$ system, having an electronic configuration $(\text{Kr})4d^5$. Rhodium(I) complexes are square planar in configuration as are the isoelectronic Pt(II) species rather than the tetrahedral arrangement found in most cobalt (II) cases. Iridium, the third metal of the cobalt triad, behaves in a similar way, forming square planar complexes, the most famous of which is Vaska's compound, chlorocarbonylbis(triphenylphosphine)iridium(I).

One can explain this phenomenon of square planar being favored over either octahedral or tetrahedral arrangements by looking at the electronic configurations of cobalt, rhodium and iridium. Cobalt (II) has a $d^7$ configuration whereas rhodium(I) and iridium are $d^8$ cases. Energetically,
if the xy plane is considered to be that of the complex and the ligands are equidistant in the ±x and ±y directions, the \(d_{(x^2-y^2)}\) orbital points at the ligands would be the least stable \((12,13)\). The \(d_{(z^2)}\) orbital, on the other hand, stretches perpendicular to the plane of the ligands and is more stable. In the square planar complexes, the least stable \(d_{(x^2-y^2)}\) orbital, even though strongly antibonding, is unoccupied, increasing the strength of the sigma bonding. The \(d_{(z^2)}\) orbital, not needed for binding ligands along the z axis, can be used in hybridizing \(s\) orbitals to provide a greater contribution to the in-plane sigma bonding, while the non-bonding electron pair is concentrated above and below the molecular plane. In addition, the \(d_{(xz,yz)}\) and \(p_{(z)}\) orbitals contribute to a higher degree of metal-ligand out-of-plane \(\pi\) bonding than in octahedral complexes. The energy advantage for an octahedral complex is 35,000 to 70,000 \(\text{cm}^{-1}\) which causes it to predominate over square planar coordination for \(d^1 - d^6\) cases. The seventh and eighth electrons are forced into the high energy \(e_g\) levels of octahedral coordination, whereas the much more stable \(d_{xy}\) orbital is available in square planar. This extra stability is what is decisive for the \(d^8\) planar configuration, when the ligand field splitting is large, causing it to favor the square planar configurations. As the atomic number increases, so does the ligand field splitting, hence the configurations for Pt(II), Rh(I) and Pd(II). Ni(II) is usually octahedral as is cobalt (II), although tetrahedral coordination are known for both. Tetrahedral coordination has three disadvantages, four ligands instead of six,
a less stable low energy level, and the necessity of beginning to fill the upper level with the fifth electron rather than the seventh.

Most of the previous work which has been done on the chemistry of rhodium(I) has been initiated using the biscarbonylrhodium-u,u,-dichlorobiscarbonylrhodium(I) dimer which was first made by Hieber(20,21) as well as by McCleverty and Wilkinson(27). The first chlorocarbonylrhodium(I) complexes prepared from the dimer were synthesized by Vallarino (33,34) in 1957. However, no crystal structures were obtained to determine the absolute structure of the complex, leaving the possibilities of the cis or trans structure as shown in figure N. The structure assignment was based solely on dipole moment studies which predicted that the cis structure would be expected to have the larger dipole moment since there would be no counteracting dipole in the molecule. That is, both like ligands would create a dipole which would result from the sum of the two like ligands in one direction and the sum of the Cl and CO in the other direction. In the trans molecule, the dipole created by the like ligands would be cancelled, and the resulting dipole would consist of only the difference of the dipole by the Cl and that of the CO. The actual date which she obtained was, as far as Vallarino was concerned, not entirely conclusive as to structure but strongly indicated that the complexes were trans. In addition, a mechanism proposed for the formation reactions is reproduced in figure A. Further studies established the fact that the complexes are diamagnetic and are neutral species
Figure A- Mechanism of Formation for the Complexes RhCl(CO)L₂
as required for square planar $d^8$ complexes(33,34).

Subsequent to Vallarino's work, the research done mainly established the catalytic properties of the rhodium(I) complexes. These compounds have been shown to be effective decarbonylation catalysts(5,2), hydrogenation(28), and polymerization of olefins (notably ethylene). The usual complex used as a catalyst is the $\text{RhCl}(\text{PPh}_3)_2$ complex. Blum, et al(5), used this complex as a decarbonylation catalyst for aromatic carbonyl compounds, specifically the decarbonylation or aroyl chlorides to the corresponding acyl chlorides. The mechanism which they suggested is reproduced in figure B. The proposed mechanism begins with I as it loses phosphine to the dimeric tricoordinate species IV. This complex then reacts to form V which isomerizes to form VI. The next step is usually loss of carbon monoxide, leading to VII, followed by the elimination of aryl chloride. Thus IV is regenerated and the catalytic activity of IV (and, therefore, I) is explained. As a side reaction, the steps of the decomposition of VI can be reversed; elimination of the aryl chloride leads to II and subsequently liberation of carbon monoxide back to IV. This side reaction is the mechanism proposed by Tsui and Ohno(32) and reproduced in figure C. Practical applications of the mechanism can be used to make the pure trans and cis forms of $\text{RhCl(CO)}(\text{PPh}_3)_2$ from 1-napthaldehyde and 9-anthroyl chloride, respectively.

Similarly, Tsui and Ohno(32) observed that aliphatic acyl chlorides are converted to olefins. There have also been examples of aldehydes
Figure B- Blum's Mechanism for the Decarbonylation of Aroyl Chlorides
undergoing decarbonylation, as well as examples of aroyl cyanides being
decarbonylated by RhCl(PPh$_3$)$_2$ yielding the nitriles of aromatic acids.
The mechanism proposed by Tsui and Ohno(32) considers the compound,
RhCl(CO)(PPh$_3$)$_2$,(II), to be the catalyst rather than the tris(triphenyl-
phosphine) complex suggested by Blum. In addition, they suggest that
II can be an efficient carbonylation catalyst (fig. C) specifically
when converting benzyl chloride to phenyl acetyl chloride at 150$^\circ$ under
100 atm. pressure of CO. As noted before, Tsui's mechanism is repro-
duced in figure C. The path of the decarbonylation reaction which is
catalyzed by II is: (II + RCOX)$\longrightarrow$ IV $\longrightarrow$ III $\longrightarrow$ V $\longrightarrow$ (RX or olefin +
II). The possible pass through using the path II $\longrightarrow$ VI $\longrightarrow$ III cannot
be excluded rigorously. The carbonylation mechanism which is proposed
is (RX + II) $\longrightarrow$ V $\longrightarrow$ III $\longrightarrow$ IV $\longrightarrow$ (II + RCOX).

Baird, et al.(2), have explored the reactions with the RhCl(PPh$_3$)$_2$
complex and hydrogen chloride, and acyl and aroyl chlorides. The
species, RhCl$_2$H(PPh$_3$)$_2$ which is formed as the intermediate, is very
susceptible to insertion or more properly hydrogen-transfer reactions
with ethylene, tetrafluoroethylene, and acetylene to give reasonably
stable rhodium(III) alkyl complexes, RhCl$_2$R(PPh$_3$)$_2$. The mechanism, as
illustrated in figure D, of these reactions appears to be similar to
typical oxidative addition reactions of square planar complexes.
Osborne, et al.(23), have investigated the catalytic homogeneous hydro-
rogenation of olefins and acetylenes and their derivatives. Their studies
Figure C- Tsui and Ohno's Mechanism
Figure D - Baird's Mechanism for the Reactions of bis(triphenylphosphine)dichlorohydrido- and alkylrhodium complexes
even went so far as to derive some kinetic expressions for the reactions involved. Specifically, Osborne and workers have worked with the hydrogenation of hept-1-ene, cyclohexene, and hex-1-yne, using a solution of the tris(triphenylphosphine) complex. These reactions take place at about 1 atmosphere of hydrogen pressure and room temperature, very rapidly, and give homogeneous hydrogenation of compounds containing isolated olefinic and acetylenic linkages. The rates of the hydrogenation of the previously mentioned compounds have been determined, as well as the dependence on factors such as substrate and catalyst concentration, temperature, and pressure. The available data can be accommodated using the following rate expression:

\[
\text{rate} = \frac{K_p (S) (A)}{1 + K_1 P + K_2 P}
\]

where (S) and (A) are the olefin and catalyst concentrations, respectively, and P is the hydrogen concentration in solution. The proposed mechanism for the hydrogenation states that the metal complex serves as a template to which a hydrogen molecule and olefin molecule are briefly coordinated before transfer of one to the other takes place. Isotope studies suggests that synchronous breaking of Rh-H bonds and making of C-H bonds takes place in the transition state involving two simultaneous three center interactions.

In addition to catalytic studies, novel synthetic routes to Rh(I) complexes were found by other workers. Numerous complexes were made, although the majority were tertiary phosphines or even olefins. For
example, the RhCl(CO)L₂ species where L=PMe₃, PPhMe₂, and PPh₂Me were made by Shaw and coworkers (9). Also complexes of the type [Rh(L-L)₂][Rh(CO)₂Cl₂] where L-L = diphosphine or disarsine were made by Mague and Milner (26). The two usual starting materials have been either rhodium trichloride trihydrate or the dimer. The ligands used have been alkyl or alkyl-aryl combinations rather than alkoxy species. No amine complexes have been prepared.

Correlated to catalytic activity is bonding and the structure of the compounds. The most complete description of the bonding as related to the activity of one catalyst can be found in the paper by Baird, et al. (2). Their studies involve more structure determination using NMR and IR studies than bonding studies in the true sense. Their studies relate the observed catalytic activity to the structure of the molecule as determined from observation of the appearance and disappearance of peaks in the NMR and IR spectrum. The paper by Wojcicki and Jennings (36) looks at IR spectra of thiocyanato complexes of rhodium(I) and determines the mode of bonding of this particular ion in the rhodium(I) square planar complexes. The sought for information was found and correlated to previous studies on the same subject using other square planar complexes besides rhodium.

The catalytic activity of the rhodium complexes led to curiosity about the bonding involved in these complexes. We decided to use carbon-13 nuclear magnetic resonance to investigate the bonding in the
iron complexes.

The next part of the problem was to establish conditions for the experiments. Previous work with carbon-13 established the fact that enrichment with $^{13}\text{C}$O enabled an easier interpretation of the spectra. Consequently the next facet of the project emerged as a quantitative study of the exchange rates of CO. Studies done by Basolo and other workers (3, 6, 35) showed that the exchange rate was extremely fast for the triphenylphosphine complex using carbon-$^{14}$ to follow the reactions. This was the only complex studied for exchange rate. Since this was the only study done, much room was left to hypothesize what the other complexes would do. Based solely on the methods used in the synthesis of these species, it was predicted that the phosphine complexes should exchange very readily with a high percentage of label, while the rate would decrease in the order: amine $\approx$ arsine $\approx$ stibine. During the synthesis of these compounds, it was found that the phosphines were formed readily from the dimer, the reaction being quite rapid. In addition, three of the phosphines, the ethyl/phenyl group, were formed from the decarbonylation of alcohols in the presence of a base. The amines were synthesized readily from the addition of amine solution to cool dimer solution. The arsine compound required heat. It was synthesized from the decarbonylation of an aldehyde, plus the rhodium trichloride trihydrate species. An intermediate was formed before decarbonylation, forming the bulk of the material recovered. The stibine required a
slow synthesis which required the dimer to be the initial starting material. The amines did exchange CO more readily than the arsine, which exchanged more readily than the stibine. In fact, the stibine complex needed two exchanges, the latter lasting several days under a CO atmosphere. More detailed discussion will be found in Chapter V of this thesis. The other task was then to locate the region of the Carbon-13 spectrum in which the resonances were to be found. The results will be found in Chapter IV of this thesis. Previous carbon-13 work established that the resonances for all carbonyl species should be near the region of the carbon disulfide carbon-13 peak. We can further reference this resonance from TMS which is considered to be zero ppm. Using this scale, we find that all C-13 resonances are downfield from TMS, the carbon disulfide resonance appearing approximately seven hundred ppm downfield from TMS. The carbonyl resonances are downfield from this disulfide peak.

The availability of a variable probe temperature source was thought to be necessary for the studies as there was an outside chance of intermolecular exchange among the molecules present. The other instrumentation problem which was anticipated was that the signals would be too weak to be clearly found without the use of time-averaging. However, since such high enrichment was achieved, and also the presence of a computer able to do Fourier Transformations, time-averaging was found not to be necessary.
Structure of the amine compounds is still somewhat questionable, but so far the equipment required for dipole moment studies is unavailable at this time. Possible alternatives to help elucidate the structure are proton NMR and Far-Infrared spectroscopy. The former technique has been tried, but the results were not meaningful at all. The latter technique depends on the position of the metal-chlorine stretch which is around 300 cm\(^{-1}\). The variations between the cis and trans species, however, is quite small making the studies not that helpful. The one study that had been done (4) merely noted the positions for the useful compounds which had already been designated as trans, with no corresponding cis complexes mentioned.

The last part of the study was to involve the measurement of the coupling constants for rhodium-phosphorous and phosphorous-carbon. Prior studies which had measured phosphorous-metal coupling showed them to be insensitive to the change in ligand (15,16,17,25).

In summary, then, this study was designed to provide the knowledge about the bonding in metal complexes using carbon-13 NMR along with IR; first as a direct measure of the nature of the bonding in rhodium(I) square planar complexes, secondly to relate this to the catalytic activity of rhodium and synthesize new compounds of the type RhCl(CO)L\(_2\).
II. Experimental

A. SOURCE OF CHEMICALS

Research Inorganic/Organic Chemical Corporation

Rhodium Trichloride Trihydrate
Chlorocarbonylrhodium(I) dimer
Tributylphosphine

Matheson Coleman and Bell

Rhodium Trichloride Trihydrate
Isopropyl ether
Formaldehyde solution, reagent grade A.C.S.
Triphenylphosphite
Triphenylphosphine
Carbon Disulfide, spectral grade
Hydrochloric Acid, reagent grade, A.C.S.
Nitrogen Gas
Carbon Monoxide gas (unlabelled)
Pentane
Carbon Monoxide gas (99.9% labelled)
Dichloromethane
<table>
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<tr>
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<tr>
<td></td>
<td>Tetramethylsilane</td>
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<tr>
<td>Fischer Scientific Chemical Company</td>
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<tr>
<td></td>
<td>Rhodium Trichloridetrihydrate</td>
</tr>
<tr>
<td></td>
<td>Petroleum Ether, light (20-40 and 40-60)</td>
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<td></td>
<td>Toluene</td>
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<tr>
<td>Allied Chemical Company (Baker and Adams)</td>
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<td>Eastman Chemical Company</td>
<td>Triphenylarsine</td>
</tr>
<tr>
<td></td>
<td>Triphenylstibine</td>
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<td>Triphenylbismuthine</td>
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<td></td>
<td>1-Napthaldehyde</td>
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<td>Strem Chemical Company</td>
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<td></td>
<td>Triethylphosphine</td>
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<tr>
<td></td>
<td>Phenyl diethylphosphine</td>
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<td>Stohler Isotope Company</td>
<td>Deuterio Chloroform, spectral quality</td>
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<td>Reagent grade Benzene</td>
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<td>Nujol - a heavy weight mineral oil</td>
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<tr>
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<td>1-pentene</td>
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<tr>
<td>Big Three Industrial Gas Products</td>
<td>Nitrogen, pre-purified (for glove bag)</td>
</tr>
<tr>
<td>Mathey-Bishop Chemical Corporation</td>
<td>Rhodium Trichloride trihydrate</td>
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B. APPARATUS

I. CARBONYLATION TRAIN

The apparatus designed for the synthesis of the rhodium(I) dimer, biscarbonylrhodium-u,u,dichloro-biscarbonylrhodium(I), insured safety in handling the carbon monoxide in and out of the chamber. The three critical points were chamber pressure, evacuation prior to a run, and venting to atmospheric pressure at the conclusion of the synthesis. The basic apparatus (figure E) was made using brass tubing fitted with swagelok fittings using teflon tape as an added safety precaution. All components of the line, the carbon monoxide tank, pressure valves, pressure release valve, and the chamber itself, were similarly sealed into the main line. The operating pressure was 30 psi, with the safety release valve set for 60 psi. The chamber was fitted perpendicular to the line using a T-joint. The third part of the T leads to a needle valve which regulated the vacuum evacuation and venting of the chamber. The system was machined and periodically checked for leaks using SNOOP leak detector.

During a run, the line is secured with wire to a flex-frame rack and also a blast shield was put in front of it and wired in. A magnetic stirrer was clamped to the rack beneath the chamber and served as the base for the oil bath and dry ice-isopropyl alcohol bath.
Figure 5: Apparatus used to synthesize RhCl(CO)$_2$ in situ

A: Carbon monoxide lecture bottle
B: Pressure release valve
C: Pressure gauge: 30 psi
D & E: Needle valves

To Reaction Chamber
To Vacuum Line and Venting Outlet
II. INFRARED SPECTROSCOPY

The Beckmann-IR-18a and IR-20a were used in all infrared work. Sodium Chloride plates were used for solid state mulls and standard liquid cells were used for solution spectra. Calibration of spectra was performed using a polystyrene sample.

III. MASS SPECTROMETRY

Mass spectra were taken in the High Resolution Mass Spectrometer laboratory, Mr. M. R. Hassan, technician.

IV. MICROANALYSIS

Samples were sent to Elek Microanalysis laboratories, P. O. Box 2, Harbor City, California, for analysis.

V. MELTING POINT

Melting points were determined using capillary tubes and a Thomas Hoover Melting Point Apparatus.

VI. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Proton NMR was performed using a 5mm precision tube at room temperature. The instruments used were a Varian A-60 and Varian A 56/60 instrument. Typically, a scan speed would be 250 seconds over a range of 500 Hz, using TMS as an internal reference.

Carbon-13 NMR was performed using a Bruker Model HFX-10 instrument which is equipped with a computer allowing CAT and Fourier analysis to
be done. Also there was a variable temperature control allowing temperature to be changed.

VII. RHODIUM RECOVERY

All rhodium waste material was kept in a waste pot. The metal itself was recovered following:

1. Evaporation of all solvents
2. Reduction with zinc/hydrochloric acid
3. 24-72 hours heating to remove any organic impurity and also to insure complete reduction
4. Finally, extraction with aqua regia and distilled water.

The resulting pure metal was dried in the oven and then converted to the trichloride using the method of Basolo and Anderson (1).
III. Syntheses

A. Biscarbonylrhodium(I)- μ, μ dichloro-biscarbonylrhodium(I)

\[ 2\text{RhCl}_3 + 2\text{RC}=\text{CH}_2 + 4\text{CO} + 4\text{CH}_3\text{OH} \rightarrow 2\text{RhCl(CO)}_2 \text{CH}_3 + 4\text{HCl} \]

Twenty milliliters of absolute methanol and three milliliters of 1-pentene were added to three grams of rhodium trichloride trihydrate in a 150 ml air compression chamber (fig. E). The flask was cooled in a dry ice-isopropyl alcohol bath and evacuated. After warming in a 60°C oil bath, carbon monoxide pressure was raised to 30 psi and maintained until reaction went to completion as denoted by the appearance of a pale yellow solution (19). The chamber was cooled in an ice bath while still attached to the line. After a short period of time, the chamber was vented to atmospheric pressure and removed. The solution was kept cool until it was used. The usual time required for a run was about 12 hours, although Heck said about five hours. The discrepancy can be attributed to a non-constant oil bath temperature.

The dimer was prepared in situ and never isolated until the end of the study when this was attempted solely to prove its existence.
B. Chlorocarbonylbis(Triphenylphosphine)Rhodium(I)

\[ \text{a. } \left[ \text{RhCl(CO)} \right]_2 + 4 \text{P(C}_6\text{H}_5)_3 \rightarrow 2 \text{RhCl(CO)} \left\{ \text{P(C}_6\text{H}_5)_3 \right\}_2 + 2\text{CO} \]

\[ \text{b. } \text{RhCl}_3 + \text{EtOH} \xrightarrow{\text{EtOH}} \text{RhCl} \left\{ \text{P(C}_6\text{H}_5)_3 \right\}_3 + 3 \text{Cl}^- \]

\[ \text{RhCl} \left\{ \text{P(C}_6\text{H}_5)_3 \right\}_3 + \text{CO} \rightarrow \text{RhCl(CO)} \left\{ \text{P(C}_6\text{H}_5)_3 \right\}_2 + \text{PPh}_3 \]

\[ \text{c. } \text{RhCl}_3 + 1\text{-Naphthaldehyde} + \text{PPh}_3 \rightarrow \text{t-RhCl(CO)} \left\{ \text{PPh}_3 \right\}_2 + \text{naphthalene} \]

The above compound has been prepared in a number of ways as illustrated by the three reactions given above, as well as by ones which have not been mentioned. In all cases, however, the intermediate is believed to be the dimer species. In reaction a, a methanolic solution (about eight ml) of the triphenylphosphine is added to the solution containing the dimer while the dimer solution is being chilled. Evolution of CO gas takes place leaving a yellow compound which is recrystallized from chloroform/ethanol solution. The melting point (decomposition) of 209°C and the ν of 1970 cm\(^{-1}\) confirm the synthesis of the compound.

The second method (28) employed involves synthesis of the chlorotris(triphenylphosphine)rhodium(I) complex and then using its properties of the labile triphenylphosphine group trans to the chloride in order to synthesize the carbonyl complex. This method was the same used in the main studies. This method requires 0.1 g of rhodium chloride trihydrate in 5 ml of water added to 25 ml of hot acetone which has dissolved in it 0.6 g of triphenylphosphine. The mixture was refluxed for
Two methods were used in preparation of this compound, due to decomposition of the first batch over a long period of time (six to eight months).

The first method used was the synthesis of the dimer previously mentioned followed by addition of triphenylphosphite to the methanol solution of dimer. The yellow compound formed was recrystallized from chloroform-ethanol and dried in vacuo. The melting point was recorded as 152°C and $\tilde{\nu}$ was 1999 cm$^{-1}$. Analytical results were good: calcd: C 55.1%, H 3.82% rept'd: C 55.2%, H 3.78%.

The second method used was that of Vallarino (33), although half scale reactions were run. The synthetic requirements were 4 mmols of triphenylphosphite in 50 mls of benzene being added to a solution of 1 mmol dimer in 20 ml of benzene. Along with evolution of carbon monoxide a color change of the solution was noted. The solution was evaporated on the roto-vap leaving a yellow oil which was washed with ethanol. The oil was then treated with chloroform and charcoal, then filtered and diluted with ethanol. The crystals which precipitated were recrystallized from chloroform and ethanol.

D. Chlorocarbonylbispyridinerhodium(I)

This compound started with the synthesis of the dimer in solution. The amounts of material had been reduced to 1/3 scale at this point. The pyridine was measured to be about 2-1/2 ml and then...
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D. Chlorocarbonylbispyridinorhodium(I)

This compound started with the synthesis of the dimer in solution. The amounts of material had been reduced to \(1/3\) scale at this point. The pyridine was measured to be about 2-1/2 ml and then deoxygenated
with nitrogen. The solution was cooled while the dimer was added to the deoxygenated pyridine under nitrogen. Carbon monoxide was evolved, and after cooling in an ice bath a yellow crystalline compound was precipitated. Melting point was determined to be 121°C and $\nu_{\text{CO}}$ was 1910 cm$^{-1}$. Microanalysis confirmed the formulation of the compound as $\text{RhCl(CO)(C}_6\text{H}_5\text{N)}$. 

Calc'd: C 40.9%, H 3.21% rep'td: C 40.3%, H 3.3% with M.W. 324.6.

The complex was found to be air and moisture sensitive. All handling had to be done in the glove bag and using deoxygenated solvents.

E. Chlorocarbonylbismorpholinerhodium(I)

Like previously mentioned compounds, the basic starting material was the chlorocarbonylrhodium(I) dimer. The methanolic solution was added to a deoxygenated sample of morpholine. Carbon monoxide was evolved and the solution left to crystallize. Dark crystals were recovered after filtering under nitrogen. Washing with methanol gave lighter colored material which darkened on drying under nitrogen. Infrared spectrometry on the solid state compound confirmed a rhodium(I) complex as well as the microanalysis. Calc'd for $\text{RhCl(CO)(C}_4\text{H}_9\text{NO)}_2$ C 31.8%, H 5.50% reported C 30.1%, H 5.5%, M.W. 344.4, $\nu_{\text{CO}}$ 1990 cm$^{-1}$, M.P. 164°C.

F. Chlorocarbonylbis(Tri-N-Butylphosphine)Rhodium(I)

The compound was prepared according to the method of (19) with modifications. The dimer solution was well chilled on dry Pentane.
was added and the whole thing transferred to a hundred ml round bottom single necked flask. The material was well chilled and the liquid evaporated. More chilled pentane was added and the resulting yellow crystals were obtained via filtration. M.W. 596.4 IR data, and melting point confirmed the compound, \( \bar{v} 1955 \text{cm}^{-1} \) (nujol), m.p. 40-41°C. Analysis gave C 52.2%, H 9.5%. Calcd C 52.5%, H 9.5%.

G. Chlorocarbonylbis(Triphenylarsine)Rhodium(I)

\[
\text{RhCl}_3 + 2\text{As(C}_6\text{H}_5)_3 \text{HCHO} \rightarrow \text{RhCl(CO)}_2\text{As(C}_6\text{H}_5)_3 \text{J}_2 \quad (14)
\]

This synthesis required 2 g of \( \text{RhCl}_2 \cdot 3\text{H}_2\text{O} \) in 70 ml of ethanol is slowly added to 300 ml of boiling ethanol which contains about a two fold excess of triphenylarsine(8,42). Ten to twenty milliliters of 37% formaldehyde is added to turn the solution yellow-orange in a few minutes. Upon cooling, the compound precipitated out. The solution was filtered and the filtrate evaporated to a yellowish solid. Chromatography on a silica column using chloroform as eluent yielded the expected bright yellow crystalline compound. M.P.242°C, 1970 cm\(^{-1}\).

H. Chlorocarbonylbis(Triphenylstibine)Rhodium(I)

\[
(\text{RhCl(CO)}_2 \text{J}_2 + \text{hSb(C}_6\text{H}_5)_3 \rightarrow 2\text{RhCl(CO)}(\text{Sb(C}_6\text{H}_5)_2) + 2\text{CO} \quad (34)
\]

3.5 mmols of triphenylstibine was added to a solution of 0.58 mmols of dimer in 60 ml of benzene. The solution was evaporated to a small
volume using the roto-vap. The remaining material was diluted with ethanol. The crude product was filtered under nitrogen in a glove bag since the compound was believed to be slightly air sensitive. All solutions were deoxygenated prior to use. The crude product was dissolved in dichloromethane and reprecipitated with diisopropyl ether. M.P. 151-53°C and 1976 cm\(^{-1}\). Unlike the rest of the compounds, this one was purple-red prisms. The compound like the amines was bottled and stored under nitrogen. M.W. 872.0

I. Chlorocarbonylbis(Triethylphosphine)Rhodium(I)

\[
\text{RhCl}_3 + 2\text{P(C}_2\text{H}_5)_3 + \text{KOH} + \text{HCl} \rightarrow \text{RhCl(CO)}_2\text{P(C}_2\text{H}_5)_3 + \text{CH}_4\uparrow
\]

This is a unique method for synthesizing the rhodium complex. No mechanism has been given, but it is felt that a base catalyzed oxidative addition (addition of CO) takes place following reduction by hydrogen gas in ethanol, a known reducing medium. This postulation is based on detection of hydrogen gas being given off (8) as well as methane.

The procedure employed utilized 17.8 ml of 1 N potassium hydroxide which was added to RhCl\(_3\) (1.57 g) combined with 2.84 g of triethylphosphine in 15 ml each of methanol and ethanol. This mixture was heated under reflux for 30 minutes, after which concentrated HCl (1.8 ml) was added. This solution was then evaporated to low volume. The compound was isolated with light petroleum ether (40-60°C) and formed prisms from light petroleum ether (50-40°C), \(\tilde{\nu}_{co} 1953\text{cm}^{-1}\) (nujol) and M.P. 75 C.
J. Chlorocarbonylbis(Diethylphenylphosphine)Rhodium(I)

$$\text{RhCl}_3 + 3\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2 \rightarrow \text{RhCl}_3\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2$$

(9)

$$\text{RhCl}_3\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2 + \text{KOH} + \text{HCl} \rightarrow \text{RhCl}(\text{CO})\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2 + \text{CH}_4$$

(8)

The first step in the synthesis (run 1/10 scale) was to make the trichlorotris(diethylphenylphosphine)rhodium(III) compound. The compound was made from 1.52 g of ligand in 100 ml of ethanol which contained 0.716 g of rhodium trichloride trihydrate. The mixture was heated to boiling then cooled. The product separated as orange crystals which were filtered and dried.

Following this, 0.621 ml of 5 N KOH was added to a boiling solution of $\text{RhCl}_3(\text{Pet}_2\text{Ph})_3$ in ethanol. The resultant deep red solution was heated under reflux for 1-1/2 hours. One N HCl was added and the solution heated to boiling and then cooled to 0°C. The product crystallized out readily. Recrystallization from ethanol gave prisms. $\tilde{\nu}_{\text{CO}}$ 1951 cm$^{-1}$, m.p.117°C.

K. Chlorocarbonylbis(Diphenylethylphosphine)Rhodium(I)

The same reaction as in I was used, with slight modification in the quantities of reactants used. The required quantities for this compound were 13.8 ml of 1 N KOH, 1.2 g of $\text{RhCl}_3$, 4.25 g of diphenylethylphosphine, 40 ml of ethanol, 5 ml of concentrated HCl and 10 ml of distilled water.
The compound was recrystallized from a benzene-ethanol solution. 

\[ \tilde{\nu}_{\text{CO}} \text{ 1950 cm}^{-1} \text{ and m.p. 153-160}^\circ \text{C.} \]

The physical properties of the compounds in the solid state are summarized in Table I. A summary of the main synthetic reactions can be found in Figure F.

L. Attempted Synthesis

In addition to the compounds whose syntheses have already been described, a comment should be made on some attempted syntheses. In order to expand the scope of this study, it was desired and attempted to prepare alkylphosphite and alkoxy-phenyl phosphine complexes. These proved to be very unstable species, with lifetimes too short to enable studies to be done. When two crystalline species were obtained, micro-analysis showed them to be of the general formula \( \text{RhCl}_2\text{CO} \text{L} \). The synthesis of the \( \text{RhCl(CO)}_{\text{Bi(C}_6\text{H}_5)_3} \text{L}_2 \) species was tried, but resulted in a black, crystalline solid which gave no IR absorbance in the rhodium(I) carbonyl stretching frequency region.
### TABLE I

**Solid State Properties of the Compounds of the Type RhCl(CO)L₂**

<table>
<thead>
<tr>
<th>L</th>
<th>M.W.</th>
<th>M.P.(°C)</th>
<th>ν₀₀₀(nujol)(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-(C₆H₅)₃</td>
<td>690.4</td>
<td>209-210</td>
<td>1975</td>
</tr>
<tr>
<td>P(OCC₆H₅)₃</td>
<td>786.4</td>
<td>151</td>
<td>1999</td>
</tr>
<tr>
<td>C₅H₅N</td>
<td>324.4</td>
<td>121</td>
<td>1910</td>
</tr>
<tr>
<td>C₄H₉NO</td>
<td>344.4</td>
<td>164</td>
<td>1990</td>
</tr>
<tr>
<td>P-(nC₄H₉)₃</td>
<td>570.4</td>
<td>40</td>
<td>1955</td>
</tr>
<tr>
<td>As(C₆H₅)₃</td>
<td>778.2</td>
<td>242</td>
<td>1970</td>
</tr>
<tr>
<td>Sb(C₆H₅)₃</td>
<td>872</td>
<td>151-53</td>
<td>1976</td>
</tr>
<tr>
<td>P(C₂H₅)₃</td>
<td>402.4</td>
<td>75</td>
<td>1953</td>
</tr>
<tr>
<td>P(C₂H₅)₂(C₆H₅)</td>
<td>498.4</td>
<td>117</td>
<td>1951</td>
</tr>
<tr>
<td>P(C₆H₅)₂(C₂H₅)</td>
<td>594.4</td>
<td>153-60</td>
<td>1950</td>
</tr>
</tbody>
</table>
(1) \([\text{RhCl}(\text{CO})_2]_2 + 4L \rightarrow \text{RhCl}(\text{CO})L_2 + 2\text{CO}\)
\[L = \text{P}(\text{nC}_4\text{H}_9)_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3, \text{C}_5\text{H}_5\text{N}, \text{C}_4\text{H}_9\text{NO}\]

(2) \(\text{RhCl}_3 + 3\text{P}(\text{C}_6\text{H}_5)_3 \rightarrow \text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3 + \text{Cl}_2\)
\[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3 + \text{CO} \rightarrow \text{RhCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2 + \text{P}(\text{C}_6\text{H}_5)_3\]

(3) \(\text{RhCl}_3 + 2\text{As}(\text{C}_6\text{H}_5)_3 \xrightarrow{\text{HCHO} \atop \text{C}_2\text{H}_5\text{OH}} \text{RhCl}(\text{CO})(\text{As}(\text{C}_6\text{H}_5)_3)_2\)

(4) \(\text{RhCl} + 2L + \text{KOH} + \text{HCl} \xrightarrow{\text{CH}_3\text{OH} \atop \text{C}_2\text{H}_5\text{OH}} \text{RhCl}(\text{CO})L_2 + \text{CH}_4\)
\[L = \text{P}(\text{C}_2\text{H}_5)_3, \text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)\]

(5) \(\text{RhCl}_3\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2 + \text{KOH} + \text{HCl} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{RhCl}(\text{CO})(\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2)\)
\[& \text{CH}_4\]
IV. Experimental Methods

The main purpose of this study was to correlate the force constant as calculated from the infrared stretching frequency of the carbonyl group to the carbon-13 nuclear magnetic resonance chemical shift. In addition, examination of the rhodium-carbon coupling constant and the carbon-phosphorous coupling constant was undertaken.

In order to achieve this purpose, the study was divided into three major parts: Synthesis, Infrared studies, and Carbon-13 NMR studies. The previous chapter discussed the synthetic tools used in the study. This chapter will deal with the technique used in the IR and NMR studies.

The IR studies were done in two parts. The first part was solid state, using a nujol mull on sodium chloride plates. This was done to establish structure of the rhodium (I) compounds and to help establish the new synthesis of the pyridine and morpholine compounds, which were made as a part of this study. All spectra were run on a Beckmann-IR 20a instrument for this first part. The spectra were run using a normal 30 minute scan time. The rhodium (I) carbonyl region is generally from about 2000 cm to 1900 cm$^{-1}$. The rhodium (III) carbonyl region has been found to be about 2060 cm$^{-1}$ to 2100 cm$^{-1}$.

The second part of the IR studies was done on a Beckmann IR-18a instrument, using 10x expanded scale, with a scan speed of 60 cm$^{-1}$ per
minute, scan time of 80 minutes, and calibrated against a sample of polystyrene. This was done using liquid cells rather than sodium chloride plates. The solution studies were done in order to eliminate as many variables in the comparison of the IR results and the NMR results. The solution used was composed of about 0.5 g of compound in 4 ml of methylene chloride, 0.5 ml of carbon disulfide, and 1 ml of 1,2-dibromotetrafluoroethane, which was the same solution used for the NMR studies. All of the IR work was done at room temperature, 20-25°C. Unfortunately, there was no way to lower the temperature of the IR studies to the NMR study temperature of -40°C. In general, only the carbonyl region was scanned on the second half of the IR studies, while the fingerprint region was checked on the solid state spectra of the new compounds, as another check on the purity of them.

The next major study was done on the Bruker-model HFX 10 Nuclear Magnetic Resonance Spectrometer.

The basic factors of carbon-13 NMR are that this isotope of carbon has a nuclear spin of I=1/2 which allows it to be studied, and a chemical shift range of 700 ppm. However, the natural abundance of carbon-13 in nature is 1.1% which is great enough to be studied, but low enough to require special enrichment techniques.

The effect of the carbon-13 nucleus has been noted in proton studies. The INDO technique has been developed in order to use the carbon-13 side bands as a means to elucidate structure of many compounds. During
this research the Varian A60 and 56/60 instruments were used merely to observe the proton resonances of the coordinated and free ligands. No quantitative studies were made.

The techniques which have been developed for carbon-13 NMR include Computer Average Time (CAT) and Fourier analysis. The former technique utilizes many scans over periods of hours to achieve a high signal to noise ratio. The premise involved is that noise, being random, will be averaged out while the signal will be enhanced after many scans. The method of Fourier analysis involved applying a high powered pulse for several microseconds to the sample in order to saturate the carbon-13 resonance and distort the normal Boltzmann population distribution in the energy levels. The sample is then left to decay down to the normal Boltzmann distribution, creating a free induction decay pattern which contains the entire spectrum and is what is initially observed. This whole process requires approximately 0.4 second intervals, meaning that in one hour it is possible to scan about 8000 times. The mathematics required, however, to transform the data, the Fourier inverse of the conventional NMR spectrum, is horrendous. A computer connected to the NMR instrument solved this dilemma, and yields a conventional spectrum in a matter of minutes. In addition, the exact position of the resonances can be read out from the computer and transformed to Hertz by use of conventional arithmetic.

Another feature of this instrument is that various fluorine compounds
are used as internal lock systems. The internal reference system can be either TMS of Carbon disulfide, the latter having a well-known carbon-13 resonance peak. Larger sized precision tubes are used, about 10-13 mm in diameter.

The first step in the NMR studies was choosing a solvent which could be used in all cases as well as an appropriate lock compound. The next step involved choosing a trial compound to locate the region of the carbonyl resonance. This first attempt utilized the paramagnetic substance, chromiumtrisacetylacetonate, a shiftless reagent (7) to reduce the relaxation time of the carbonyl group. The observed spectrum consisted of mostly baseline noise with a broad peak suspected to be present in this baseline. It was then decided that the Cr(acac)$_3$ was interacting strongly with the compound and causing extreme broadening of the carbonyl peak. When the Cr(acac)$_3$ was removed, a low intensity, broad doublet emerged. At this point, the sample was enriched with carbon-13 CO, as a measure designed to enhance the signal.

Figure G shows the exchange apparatus. The basic idea is to freeze the labelled CO into the flask holding the sample, seal, and let warm up, undergoing exchange as it does so. Saturated solutions of sample are used as well as a measured volume of the gas. The enriched CO is forced into a toluene filled column and then put onto a vacuum line adjacent to the frozen sample. The major portion of the line is closed off, and cold trapping requires just a few minutes. The flask is then sealed
Figure G - Carbon-13 Labelling Apparatus
using a stopcock and removed from the line while warming. Total elapsed time is about a half an hour to 45 minutes from start to finish. After the solution has warmed, pressure is released and the solvent evaporated. A high percentage of enrichment was achieved using this method as confirmed by IR. The compounds exchanged rapidly, as predicted from previous exchange studies using only the triphenylphosphine complex \((35, 6, 3)\). This is the first time that exchange studies have been done on the other complexes, however. The triphenylstibine complex did not exchange as readily as the others, so that a second exchange was done, this time leaving the complex in solution under a carbon monoxide atmosphere for several days. An IR check for decomposition was done before the NMR was taken, none having been found. The amines were treated with utmost care under nitrogen and sealed under it also.

After enrichment, the trial spectrum was retaken, and an intense broad doublet appeared. However, on the basis of the usual NMR splitting equation (fig. I), a doublet of triplets was expected. Going to \(-40^\circ C\) provided the anticipated spectrum and uncovered a strange phenomenon which heretofore had never been observed. Apparently, the rhodium complexes were rapidly undergoing intermolecular exchange of carbonyls at room temperature (fig. II) due to the extreme lability of the carbonyl. At present, kinetic studies are being done to study the collapse of the NMR signal with rising temperature on a phosphine and the arsine complex. One must also consider the possibility of phosphine exchange contributing
Very Fast $^{A}Rh^{A}CO + ^{B}Rh^{B}CO \rightleftharpoons ^{A}Rh^{B}CO + ^{B}Rh^{A}CO$

Figure H - Intermolecular Exchange of Carbonyls in Rhodium Complexes where Rh refers to the rest of the complex
to the collapse of the triplets.

The entire study was done under the -40°C temperature conditions and the anticipated doublets observed due to solely rhodium coupling (I=1/2) were observed for the amines (I_N=1), arsine (I_As=3/2), and stibine (I_{121}_{Sb}^1=5/2, I_{123}_{Sb}^1=7/2) complexes.* For the phosphines, a doublet of triplets was observed due to phosphorous (I=1/2) coupling and rhodium coupling.

* Since N, As, and Sb have quadrupole moments, which would remove any expected coupling.
V. Results, Analysis and Discussion

The results from the IR and MNR studies are shown in Table II. The IR results are those from part II of the IR study and were done using the same solution as used for the NMR work. The position of the IR stretching frequency is dependent on the extent of \( \pi \) bonding between the metal and the ligands. In this study, the ligand which we are concerned with, CO, has some \( \pi \) back bonding with rhodium in addition to sigma bonding. The changing frequency is dependent on the changing nature of the electron density concentrated in the rhodium-carbon bond, which, in its turn, affects the carbon-oxygen bond. The triphenyl phosphite ligand, for example, is strongly electron withdrawing, concentrating electron density in the rhodium-carbon bond, providing a so called "tightening" of the bond and raising the frequency of the C-O stretch. Conversely, if a ligand is electron donating, one would expect that the rhodium-carbon bond would be electron deficient and the carbon-oxygen bond electron rich. This would lower the stretching frequency.

The data which was required from the stretching frequency is the force constant. Previous studies (15) required the use of the Cotton-Kraihanzel (10) equations relating the simple stretching force constant to the stretch-stretch interaction term (31). Unlike previous studies, there is only one carbonyl in the compound and, more importantly, only one carbonyl absorption band in the IR. Hence, the Cotton-Kraihanzel
TABLE II

Results of IR and NMR Studies on the Compounds of the Type RhCl(CO)L_2

<table>
<thead>
<tr>
<th>L</th>
<th>( \tilde{\nu}_{\text{CO}} ) (cm(^{-1}))</th>
<th>( J_{\text{Rh-C}} )</th>
<th>( J_{\text{p-c}} )</th>
<th>( \delta_{\text{CO}} ) (Hz)*</th>
<th>( k \times 10^6 ) (dynes/cm)</th>
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<tr>
<td>( \text{P(C}_6\text{H}_5\text{)}_3 )</td>
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<td>( \text{As(C}_6\text{H}_5\text{)}_3 )</td>
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<td></td>
<td>7.4</td>
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<tr>
<td>( \text{Sb(C}_6\text{H}_5\text{)}_3 )</td>
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<td>58.0</td>
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<td>1.2</td>
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<tr>
<td>( \text{P(OC}_6\text{H}_5\text{)}_3 )</td>
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</tr>
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<td>( \text{P(C}_6\text{H}_5\text{)}_2\text{(C}_2\text{H}_5\text{)} )</td>
<td>1968.18</td>
<td>74.5</td>
<td>15.9</td>
<td>5.1</td>
<td>1.56</td>
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<td>1971.28</td>
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<td>69.6</td>
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<td>70.8</td>
<td></td>
<td>10.4</td>
<td>1.63</td>
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* In Hz as referenced from carbon disulfide at -40°C.
treatment was unnecessary and the usual equation (fig. I) relating the frequency to the force constant was used. The force constant was calculated from the carbonyl absorption when using the same solution as used in the NMR studies.

In addition to obtaining the carbon-13 chemical shift, we also were able to obtain some coupling constants (table II). Looking at the data, it is observed that the rhodium-carbon coupling constant varies over about seven hertz, neglection the fifty-eight hertz value for the stibine complex. Shaw, in a recent paper (29) measured the $J_{\text{Rh-P}}$ for a selected group of phosphines of the type, $\text{RhCl(CO)L}_2$ and one phosphite, trimethylphosphate. The phosphite coupling was much larger than that observed for the rest of the compounds. The phosphorous-carbon coupling constant is constant, indicating that there apparently is not much difference for alkyl and phenyl substitutes. The high $J_{p-C}$ value observed for the phosphite is probably the result of the presence of oxygen bonded to the phosphorous. The oxygen being a strong electron withdrawing group, stabilized by both the $\pi$ system of the phenyl rings and the $d(\pi)$ orbitals of the phosphorous causes a larger coupling to occur.

As stated previously, the predicted spectra for this system was a doublet of triplets to be observed for the phosphines and a simple doublet for the arsine, stibine, and amine complexes (fig. J). The prediction was based on the general equation predicting the number of lines in an NMR spectrum (fig. I). The doublet originates solely from rhodium
NMR

no. of lines = 2nI + 1

n = no. of nuclei causing the splitting
I = nuclear spin

IR

\[ \bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

\[ \mu (2\pi c \bar{v})^2 = k \]

k = force constant (dynes/cm)
\( \mu \) = reduced mass of carbonyl

Figure I- Equations employed in Calculating NMR Spectra and the Force Constant
Figure J - Typical Carbon-13 NMR Spectrum

\[
\text{RhCl(CO)}(\text{As(C}_6\text{H}_5))_2
\]

\[
\text{RhCl(CO)}\left(\text{P(C}_6\text{H}_5)_2\text{C}_2\text{H}_5\right)
\]
coupling, with the expected 1:1 ratio which agrees with Pascal's triangle for nuclear spin I=1/2 and one interacting nucleus. The triplets, as would be expected, originate from the phosphorous nuclei each with a spin of I=1/2 (fig. K).

The purpose of the study was to see if the force constant and the carbonyl chemical shift are linearly related for rhodium (I) square planar complexes. The study by Gansow (15,15a) finds this to be a linear relationship for some \( \pi \)-cyclopentadienyl iron carbonyl compounds, as well as the study by Gansow, Kimura, Dobson and Brown (16) on some molybdenum, tungsten, and chromium complexes, usually with multiple carbonyls. In addition to trying to substantiate the proposed linearity, these parameters would also shed light on the nature of the bonding in the complexes.

The usual picture of bonding in metal-carbonyls (fig. L) is that of a combination of both sigma and \( \pi \) character in the metal-carbon bond. The sigma bond results from the linear overlap of the filled carbon sigma orbital with a metal sigma orbital. The \( \pi \) bond arises from the dative overlap of a filled \( d_\pi \) or hybrid \( dp_\pi \) metal orbital with an empty anti-bonding \( p_\pi \) orbital of the carbonyl. In addition to consideration of this picture, we must also consider the picture presented to us of bonding in any square planar complex.

In general, the \( d_{x^2-y^2} \) orbital is empty for square planar complexes, increasing the sigma bond stability. In an octahedral complex, the \( d_{x^2-y^2} \)
Figure K- Predicted Splitting Pattern for the Compounds RhCl(CO)L₂ for a) L=Phosphine and b) L=Amine, Arsine, Stibine
Figure L - Bonding in Metal Carbonyls
or, more specifically, the molecular orbital which has the largest amount of $d_{x-y}$ character is strongly anti-bonding, with respect to the four ligands in the xy plane. Thus, it is allowed to hybridize to form the dsp* sigma hybrid orbitals (table III). For more detailed reasoning, one must take into consideration the symmetry requirements imposed on the complex. In addition, the $d_{z^2}$ orbital, having effectively the same symmetry properties of the s orbital, is hybridized along with the s orbital to give greater contribution to the in-plane sigma bond; while a pair of non-bonding electrons occupies the hybrid orbital directed above and below the molecular plane (12). The $d_{xz}$, $d_{yz}$, and $p_z$ orbitals contribute a great deal to out-of-plane metal-ligand bonding (fig. M). This happens since the metals are able to expand their orbitals greater than usual. The extent of this expansion or contraction depends on the nature of the ligand. The back donation which is the major factor in determining bond strength depends on the identity of the donor atom and on the groups attached to it.

In the case of the ligands used in this study, they are all Lewis bases, and except for the amines are $\pi$ acceptors. In addition, the ligands (except for the amines) are using $d_{\pi}$ orbitals (fig. M) to bond with the rhodium. The amines are sigma bonders only. Cotton- and Wilkinson (11) give a qualitative order of various ligands which indicates that the phosphines, arsines and stibines are weaker $\pi$ acceptors than carbonyls. This is consistent with the observation that due to the
<table>
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<th>α Orbitals</th>
<th>π Orbitals</th>
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<td>( d_{x^2-y^2} ), S, Px, Py</td>
<td>Pz, ( d_{xz} ), ( d_{yz} )</td>
</tr>
<tr>
<td>( d_{x^2-y^2} ), ( d_{z^2} ), Px, Py</td>
<td>Pz, ( d_{xz} ), ( d_{yz} )</td>
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</table>
Figure F- Out of Plane Bonding in Square Planar Complexes
lone pairs of electrons on the phosphorous, arsenic, and antimony, that these compounds are electron donors. Also, when there are low-lying d orbitals with the correct symmetry available in both the metal and the ligand, back donation results, which gives overall multiple bond character in the complex. This is especially important when dπ and pπ bonding contributes substantially to bonding in the complex.

Applying the bonding argument to the complexes and results of the study, it is found that as the amount of back donation from metal to carbon increases, the metal-carbon bond strength increases, weakening the carbon-oxygen bond. Then, the weaker the bond, due to occupation of the π* star orbital, the lower the vibrational frequency in the IR. Since the amines are sigma bonders only, this would lead to strengthening of the back donation and increasing the π-character of the rhodium-carbon bond, and hence lowering the stretching frequency. However, the observed frequencies are high, suggesting the possibility of cis (fig. N) complexes rather than the trans compounds (19,14,4,33,34) which are the reported structures for the other compounds. Blum (5) reported that the cis complex of RhCl(CO)(PPh₃)₂ had a carbonyl stretching frequency of 1978 cm⁻¹ whereas the trans species absorbed at 1965 cm⁻¹. Studies have been proposed to measure the dipole moment using capacitance measurements and the Cotton-Madsen equation. It has been observed (33,34) that trans species have lower dipole moments than their cis isomers.

This study is pending the availability of the necessary equipment.
Figure N- Structures of the a)cis and b) trans Isomers of the Compounds RhCl(CO)L₂
Another method which could be employed is that of far infrared studies of the metal-chloring bond. This was found to be insufficient and not feasible since there was not much difference observed in similar studies (4).

Returning to the discussion of the IR stretching frequencies (table II), one finds that the triphenylphosphite ligand, having the highest frequency, is the strongest π-acid of all the complexes studied. This causes the metal d orbitals to overlap with the d orbitals on the phosphorous, decreasing the strength of the metal-carbon bond and tightening of the carbon-oxygen bond. This latter effect would result in a higher infrared stretching frequency which is observed.

Moving on to the NMR results, (table II), we find that from the usual considerations about chemical shifts one would expect to find the more electron withdrawing ligands at a higher magnetic field, indicating increased paramagnetic screening. This can be explained in terms of what is happening in the molecular orbitals. As the electrons are withdrawn from the rhodium, the d orbitals contract. The resulting effect is reduced overlap between d orbitals on the metal and the π star orbitals of the CO. The overall result is a stronger CO bond (high $K_{CO}$) and increased paramagnetic screening or greater local carbon π-bond order. At the same time a contraction of the carbonyl carbon 2p orbital could also contribute to the observed chemical shift (15). All of the resonances which were observed in the study were located downfield from carbon.
disulfide which served as the internal reference for the system.

The plot of the carbonyl chemical shift versus the force constant (fig. 0), is linear since both parameters are a measure of the \( \pi \) electronic character in the carbon-oxygen bond \((24,15,15a,16)\). On first glance, one would expect that the chemical shift of the triphenylphosphine, arsine, and stibine complexes would increase in the order given. However, the stibine has a smaller chemical shift as well as a smaller coupling constant.

One suggestion for this anomalous behavior of the stibine is based on the electronegativity, relative to the arsine and phosphorous. The electronegativity decreases rather than increases as it had been doing (moving down the periodic table) and this could be the cause of its anomalous behavior. Since the IR frequency follows the expected pattern, and even maintains the pattern after enrichment with \(^{13}\)CO and also maintains the pattern in the polar solvent, this is probably not a good assumption. Another suggestion is that stibine is simply a poorer \( \pi \) bonder than either the phosphine or arsine complex, resulting in a smaller chemical shift.

Turning now to the coupling constants (table II), it is observed that the values for \( J_{\text{Rh-C}} \) vary over only about seven hertz, neglecting the \( J \) value for stibine, whose anomalies have just been discussed. It is known that the carbon-13-hydrogen coupling constants are related to the percent \( s \) character in the bond \((18,22,30)\). Several studies which
Figure 0- Plot of the Carbon-13 Chemical Shift versus the Force Constant
have looked at octahedral systems include those of Mather and Pidcock (25), Grant and Lichtman (17), Gansow, et al. (16), and Keiter and Verkade (23). All of these studies have tried to relate $J$, $k$, and the ratio of $\sigma/\pi$ character of the bonds but have found no significant correlation with coupling constants. It seems that in metal systems, the coupling constant, reflecting metal-carbon bond order is apparently insensitive to changes in the nature of the ligand in the system. The data of this study (table II) also bears this out.

The parameters which may be considered to determine relative values of metal to carbon $J$ values are the metal-carbon sigma bond order and the values of $|\Psi_c(0)|^2$, $|\Psi_m(0)|^2$ (17). Substitution of an amine will increase $|\Psi_m(0)|$ but weaken the rhodium-carbon-sigma bond. Thus, we can say that the two effects will probably balance each other. Still another argument which can be applied arises from the study done by Mather and Pidcock. They believe that the value of $J_{\text{Rh-C}}$ is dominated by the percent $s$ character on the Fermi contact term. However, this assumption must be considered tentative, since there is no evidence that the effective nuclear charge ($Z^*$) which is considered important for $J_{13C-H}$ may not be equally important here (fig. P).

In conclusion, then, the linearity of the plot (as confirmed by a linear correlation program) confirms the relationship between the carbon-13 chemical shift and the carbonyl force constant in the IR for rhodium (I) square planar complexes. In addition, King (24) relates a decrease in the carbon-oxygen bond order which in its turn arises from
\[ J(K) = \left( \frac{\Delta_{CH_4}}{\Delta} \right) \left( \frac{N_K}{N_{CH_4}} \right)^2 \left( \frac{\alpha K}{\alpha_{CH_4}} \right) \left( \frac{Z_K}{Z_{CH_4}} \right)^3 J_{(CH_4)} \]

\[ J_{CH_4} = 125 \text{ cps} \]

\( K^{th} \) bond of subst. methane
\( \Delta = \) excitation \( E \)
\( N = \) bond normalization constant
\( \alpha^2 = \) parameter which is proportional to "s" character
\( Z = \) effective nuclear charge appearing in the radial wave function of a carbon 2s orbital of the form

\[ \left( \frac{Z_K}{a_0} \right)^{3/2} \left\{ A + B \left( \frac{Z_K}{a_0} \right) \right\} \exp \left( \frac{Z_K r}{2a_0} \right) \]

*Figure P- The Fidcock-Mather Equation*
increased negative charge on the metal atom. This follows the proposed idea that the ligands cis to the carbonyl change their nature from electron donating to electron withdrawing. This is evident from the force constants and the carbon-13 chemical shift of the carbonyl group.
VI. Summary of Results

I. Two new compounds, chlorocarbonylbispyridinerhodium (I) and chlorocarbonylbismorpholinerhodium (I) were synthesized and physical data reported.

II. The infrared stretching frequency was reported for the compound chlorocarbonylbis(diphenylethylphosphine)rhodium (I) in nujol and dichloromethane/carbon disulfide/1,2-dibromotetrafluoroethane.

III. The carbon-13 δco, $J_{Rh-C}$, and appearance of the spectra reported.

IV. The force constants for the IR carbonyl stretch were calculated.

V. A direct relationship established between the force constant and the carbon-13 chemical shift for rhodium (I) square planar compounds.

VI. A quantitative measure of enrichment using mass spectral technique has established that the tri-nbutylphosphine complex can be enriched 88% of total carbonyl present. The triphenylarsine complex can be enriched 47% of the total carbonyl present.

VII. Temperature dependent NMR studies have shown that the triphenylarsine complex does not undergo intermolecular carbonyl exchange even on warming up to 55 degrees Centigrade.
VII. Literature Cited


12. Ibid., pp. 712-713.


VITA

Barbara Helene Berman was born in Chicago, Illinois, November 13, 1949. She attended the University of Iowa, Iowa City, Iowa, from September, 1967, to June, 1968, transferring to the University of Illinois, Urbana, Illinois. There, she received her Bachelor of Science degree in Chemistry with high honor and high distinction in August, 1970. She entered graduate school at William Marsh Rice University in August, 1970, and will receive her Master of Arts degree in Chemistry in May, 1972.