Attempts at synthesis of some rhodium(III) complexes of ethylenediphosphine.

John Hugh Carey
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ATTEMPTS AT SYNTHESIS
OF SOME Rh(III)
COMPLEXES OF
ETHYLENEDIIPHOSPHINE

MASTER OF SCIENCE
DISSERTATION

UNIVERSITY OF WINDSOR

JOHN HUGH CAREY, B.SC. (WINDSOR)

Chemistry Department
University of Windsor
Windsor 11, Ontario

September 1971

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ABSTRACT

Attempts to utilize the compound ethylenediphosphine as a ligand bonded to the metal rhodium were made with a view towards the synthesis of complexes useful for kinetic studies. The desired Rh(III) complexes were not produced. Instead a Rh(I) complex was postulated to have been formed.

A general review of rhodium-phosphorus chemistry is given as well as some suggestions for possible synthetic routes to the desired complexes.
ACKNOWLEDGEMENT

I wish to thank Dr. J. E. Drake and Professor M. B. Powley for their reading and comments on this dissertation. I especially wish to thank Dr. E. J. Bounsall for his friendship and direction during the course of this work.

A special word of appreciation should go to Mr. D. Hill for assistance in obtaining the infrared spectra, and to Dr. R. C. Rumfelt for his thoughts on the electronic spectra.

Lastly, I wish to thank my patient wife Anne who not only typed this thesis, but suffered through my many days of procrastination.
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1. INTRODUCTION

1. General Considerations

In the past few years in the field of inorganic reaction kinetics, widespread use has been made of amine ligands because they are commercially available and, in general, form stable complexes with the transition metals. Ethylenediamine is one of the most widely studied amines since it is bidentate and hence forms complexes in which the metal-nitrogen bonds can be considered inert. The diacido-bis(ethylenediamine)rhodium(III) complexes have recently been used to determine effects such as the trans effect, through studies of the anation, acid and base hydrolysis, and equilibrium reactions.

Rhodium has been chosen for these studies since it is a congener of the widely studied cobalt but exists in only two normal oxidation states (III) and (I), with Rh(III) greatly predominating. The reactions of rhodium complexes usually occur at rates which are fast enough to be studied without complications due to usually slow side reactions (eg. trans-cis isomerization) and slow enough to be studied without resorting to fast reaction techniques. Cis-effects are just now beginning to be studied in the rhodium system and there is considerable controversy over whether substitution and anation reactions proceed via $S_N^1$ (essentially bond-breaking) or $S_N^2$ (essentially bond-making) mechanisms.
The latest studies have been unable to assign a mechanism as being unambiguously either $S_{N1}$ or $S_{N2}$ and there has been evidence for both pathways depending on the order of importance one places on the data.\(^{(1,2)}\)

For this reason it was apparent that an analogue of ethylenediamine such as ethylenediphosphine could be important in similar kinetic studies. Whether or not the analogous substitution and anation reactions would even occur with the ethylenediphosphinerrhodium complexes was not known since this type of complex had not even been synthesized.

Another area of reaction kinetics, in which the ethylenediphosphine complexes could assume importance is in the catalysis of rhodium(III) complex formation by reducing agents.

In 1929 Delphine observed that the addition of ethanol to an aqueous solution of hexachlororhodium(III) and pyridine gave an immediate and quantitative yield of transdichlorotetrapyridinerrhodium(III) whereas, without ethanol, trichlorotripyridinerrhodium(III) was produced.\(^{(3)}\) It was later shown that other tetramines could be made in a similar way using as well as ethanol, reducing agents such as hypophosphorous acid, stannous salts, hydrazine, and borohydrides.\(^{(4)}\)

Basolo and coworkers proposed a mechanism, similar to that proposed for the catalysis of Pt(IV) reactions by Pt(II), in which a small amount of Rh(I), present as the
square planar tetrpyridinerhodium(I) is generated in solutions of hexachlororhodium(III), pyridine and the reducing agent. Some investigators later suggested that since all these reducing agents could produce rhodium hydride complexes, it might be a hydride complex which is the catalyzing agent.

In 1968, Rund found catalysts containing Rh(I) were more effective than catalysts containing rhodium-hydrogen bonds or hydride producing reagents. Hydrido complexes of rhodium(III) showed little or no catalytic activity. He proposed a mechanism which closely followed Basolo's in which reducing agents acting on Rh(III) produced tetrpyridinerhodium(I). The rhodium(I) complex then formed a bridged intermediate through its axial position with a molecule of unchanged hexachlororhodium(III).

A sixth ligand was also coordinated to give an intermediate as shown in the (Fig. 1).

![Diagram of Rh(I) complex](Fig. 1)
Finally the two rhodium atoms exchanged oxidation states forming a new rhodium(III) complex and another molecule of rhodium(I). The whole process is shown in equations (I-1) and (I-2)

\[
\text{Rh(I) + X-Rh(III)-X} \rightarrow \text{Rh(I)-X-Rh(III)-X} \quad (I-1)
\]

\[
\text{Rh(I)-X-Rh(III)-X + Z^-} \rightarrow \text{Z-Rh(I)-X-Rh(III)-X} \quad \rightarrow \\
\text{Z-Rh(III)-X + Rh(I) + X^-} \quad (I-2)
\]

Rund concluded that the catalyst was a Rh(I) complex and that the hydride-producing reagents in previous experiments were present in such great excess that they produced some Rh(I) which was responsible for the observed catalytic effects. The reducing agents acted to produce the catalysts and not as catalysts themselves.

In 1970 Gillard and coworkers examined the electrochemical reduction of several Rh complexes in search of a reactive intermediate equivalent to the Rh(I) catalyst. \((8,9)\) Finding that the trans-dichlorotetapyridinerhodium(III) gave some unstable reduced products but was always accompanied by partial decomposition they studied trans-dichlorobis(ethylenediamine)rhodium(III) hoping that the reduction products would be more stable because of the bidentate ligands.

The product of the electrochemical reduction of trans-
dichlorobisethylenediaminerhodium(III) was trans-hydridohydroxobisethylenediaminerhodium(III). The electrochemical reduction may be represented by equations (I-3) and (I-4)

$$\text{trans-}\left[\text{Rh}(\text{en})_2\text{Cl}_2\right]^+ + 2\text{e}^- \rightarrow \left[\text{Rh}(\text{en})_2\right]^+ + 2\text{Cl}^- \quad (\text{I-3})$$

$$[\text{Rh}(\text{en})_2]^+ + \text{H}_2\text{O} \rightarrow \text{trans-}\left[\text{Rh}(\text{en})_2\text{H(OH)}\right]^+ \quad (\text{I-4})$$

Gillard could not isolate the bisethylenediaminerhodium (1) complex. Rhodium(I) complexes using phosphine ligands, however, have been isolated. Two that are close to the proposed square planar structure are di[1,2bis(dimethylphosphino)ethane] rhodium(I) (Fig. 2a) and di[1,2bis(diphenylphosphine)ethane] rhodium(I) (Fig. 2b)(11)
These two complexes suffer from a problem common to most tertiary phosphine complexes, that is they are not soluble in water. This is probably due to the organic groups facing out from the molecule. We believe that similar complexes of the primary phosphine, while adding stability due to the higher ligand field strength of phosphines would be soluble in water since they lack the organic groups. The same sort of behaviour can be noted in amine complexes where primary amine complexes are more soluble in water than tertiary amine complexes.

For this reason if a rhodium(I) complex of ethylenediphosphine could be made it could prove interesting to recheck Gillard's hypothesis.

Outside the field of kinetics, ethylenediamine complexes have seen widespread use in spectroscopy since they have been made with a wide variety of central metal ions. An analog of these complexes where phosphorus had been substituted for nitrogen would have many obvious benefits.

In view of the possible scientific rewards, we felt it was of some merit to initiate a study of the reactions of some rhodium complexes with ethylenediphosphine.

II Rhodium-Phosphorus Chemistry

The study of the co-ordination of phosphorus containing ligands has in the past mainly been confined to ligands of the type PX₃(where X is a halogen, alkoxy or alkyl substitutent). Complexes have been prepared with most of the transition metals with the ligands showing marked preference for the
heavy metals of Group VIIIb. This preference has been explained through the hard and soft acid-base concepts of Pearson; hardness and softness corresponding mainly to high and low polarizability respectively. The heavy metals of Group VIII are included in the soft acids while the heavier donor atoms such as phosphorus are among the soft bases. According to Pearson, hard acids react more readily and more completely with hard bases and soft acids prefer soft bases.

It seems probable that the reason stable complexes with phosphine ligands are formed mainly with elements to the right of the transition series is due to the character of the ligand. Phosphines act as σ-bond donors and π-bond acceptors with the vacant "3d" orbitals of phosphorus being capable of interaction with the filled non-bonding "d" orbitals of the transition metal. Postulated dπ-π bonding for a complex trans-[MX₂(PR₃)₂] is shown in (Fig.3)

![Fig 3.](image)
Generally the most stable complexes are those in which the metal has its low energy 'd' orbitals completely occupied by electrons and its high energy 'd' orbitals vacant. The high ligand field strength of phosphines insures a large energy difference between the low energy and high energy "d" orbitals of the metal. A metal such as Rh(III) which is a d^6 ion fulfills these requirements for all structures but tetrahedral.

A general survey of rhodium phosphorus coordination chemistry can be divided into four sections:

(a) complex formation with phosphine (PH₃)
(b) complex formation with primary phosphines
(c) complex formation with secondary phosphines
(d) complex formation with tertiary phosphines.

(II-a) Complex Formation with Phosphine (PH₃)

A number of complexes using phosphine as a ligand have been prepared and characterized. The central metal in these complexes has included chromium, molybdenum, tungsten, palladium, platinum, ruthenium, nickel, rhodium, and iridium. Two interesting phenomena have been noted. The first is the ease with which complex clusters are generated from simple starting materials. An example of this is shown in equation (II-1)

\[
\text{PH}_3 + \text{Rh}_2(\text{CO})_4\text{Cl}_2 \longrightarrow \text{Rh}_6(\text{CO})_8(\text{PH}_3)_8
\]
The product of this reaction is one of the two reported phosphine-rhodium complexes. The other complex was first given the formula \[\{([C_6H_5]_3P)_2(PH_3)ClRh\}\] and was prepared according to reaction (II-2).

\[
\text{PH}_3 + [\text{Rh}\{([C_6H_5]_3P)_3\}Cl] \rightarrow [\text{Rh}\{([C_6H_5]_3P)_2(PH_3)Cl\}] \quad (\text{II-2})
\]

It was found, however, that in the infrared spectrum of this complex both a P-H and Rh-H stretch were observed. Thus it seems likely that the complex should be represented as \([\text{Rh}\{([C_6H_5]_3P)_2\}H(PH_2)Cl]\) and may have the structure shown in (Fig. 5).

The second interesting phenomenon exhibited by the phosphine complexes, in particular those of chromium, molybdenum, and tungsten, is that whereas phosphine itself is very reactive, igniting on contact with air, the complexes formed by a route shown in equation (II-3) were air-stable and did not decompose upon sublimation.

\[
[M(\text{CO})_4(B_3H_9)]^- + 2\text{PH}_3 \xrightarrow{\text{THF}} [(\text{CO})_4M(\text{PH}_3)_2] + B_3H_8^- \quad (\text{II-3})
\]

\(M = \text{Cr, Mo, W}\)
(II-b) Complex Formation with Primary Phosphines

Very little work has been done with primary phosphines in transition metal chemistry. They are strong reducing agents and have more protonic acid character than amines, so that it may be expected that the coordination reactions might be complicated by oxidation-reduction or dehydrohalogenation reactions. In addition, they are very toxic, have a foul odour and are spontaneously inflammable in air.

There are no reported rhodium-primary phosphine complexes. There are reports, however, of complexes of cobalt (II) with ethylphosphine. A compound of the formula $\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{PH}_2$ was prepared by treating anhydrous cobalt (II) chloride with an excess of ethylphosphine and then pumping off the unreacted base in vacuo. It was later found that if the reaction mixture was allowed to stand before pumping, a second complex of the form $\text{CoCl}_2(\text{C}_2\text{H}_5\text{PH}_2)_2$ was produced. The initial reaction occurred at room temperature and proceeded quickly and vigorously. These complexes appeared air stable. This work was done before it was evident that bridging was important in complex chemistry so it may be of some use to again prepare these complexes, particularly the reported tri-coordinated one, to recheck the structures.

(II-c) Complex Formation with Secondary Phosphines

If transition metal complexes of secondary phosphines are more numerous and well studied than primary phosphine
complexes, it is principally due to the work of R. G. Hayter. Studies were conducted of such complexes using the phosphines, diphenylphosphine, diethylphosphine, ethylphenylphosphine, and dicyclohexylphosphine. The central metal ions involved were nickel, ruthenium, rhodium, and palladium.

In 1963, Hayter reacted diethylphosphine with palladium halides under a variety of conditions and found that the resulting products were mono- and binuclear complexes of palladium. Although the preparations were carried out under nitrogen, it was found that once formed, the complexes did not react with air and could be purified without any particular precautions being taken against oxidation. It was found that in the presence of a base the mononuclear complex lost HX to give phosphorus bridged complexes of the type shown in (Fig. 6)

(Fig. 6)
and the reaction sequence could be represented by equation (II-4)

\[
PdX_2 + 2R_2PH \rightarrow PdX_2(R_2PH)_2 \xrightarrow{-HX} [PdX(PR_2)(HPR_2)]_2 \tag{II-4}
\]

It was found that polar solvents such as ethanol favoured acid elimination and formation of phosphido complexes as in (Fig. 6), whereas reactions in benzene were found to give the mononuclear product. (17)

The reaction of diphenylphosphine with nickel was then studied since previous coworkers\(^\text{(21)}\) in attempting to prepare \([NiX_2(HPR_2)_2]\) had used ethanolic solutions and obtained phosphido complexes of the form shown in equation (II-5)

\[
NiBr_2 + 4(C_6H_5)PH \rightarrow [Ni\{P(C_6H_5)_2\}_2\{HP(C_6H_5)_2\}_2] + HBr \tag{II-5}
\]

Hayter\(^\text{(19)}\) found that by using benzene, toluene, or dichloromethane solutions of the phosphine and dissolving the nickel halides directly into the refluxing solutions, products of the form \(\text{trans-}[NiI_2(HP(C_6H_5)_2)_2]\) and \([NiI_2(HP(C_6H_5)_2)_3]\) were formed.

The reactions of ruthenium, rhodium, and palladium with diphenyl- and diethylphosphine were reported by Hayter in 1964.\(^\text{(20)}\) The complexes formed were of well known types
containing octahedral Ru(II) and Rh(III). The complex $[\text{RhCl}_3\left\{\text{HP(C}_6\text{H}_5)_2\right\}_2]$ was isolated in two isomeric forms from the mixture of hydrated rhodium trichloride and diphenylphosphine in ethanol. $[\text{RhCl}_3\left\{\text{HP(C}_2\text{H}_5)_2\right\}_3]$ was prepared in the same manner but only one isomer was found. $[\text{RhCl}_3\left\{\text{HP(C}_6\text{H}_5)_2\right\}_3]$ was also synthesized from the direct mixture of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]^+$ and the ligand in benzene. The complexes were sufficiently stable to be crystallized without the exclusion of air.

(II-d) Complex Formation with Tertiary Phosphines

A wide number of tertiary phosphine-rhodium complexes have been prepared. Some mixed tertiary phosphine-halogen complexes are listed in Table 1 with their synthetic routes. In Table 2 are listed some of the carbonyl and hydrido-carbonyl phosphine complexes with their preparative routes. Although these complexes would seem to be very useful as a starting point for the primary phosphine complex synthesis, it should be noted that Issleib and coworkers have in many instances demonstrated that primary and secondary phosphines form derivatives often notable for their dissimilarity to the complexes derived from the corresponding tertiary phosphines.

Two ligands of particular interest since they are similar to ethylenediphosphine (edp) in skeletal structure, are $1,2\text{-bis(dimethylphosphino)}$ethane (dmpe), and $1,2\text{-bis(diphenylphosphino)}$ethane (dppe). This similarity of structures is best seen in (Fig. 7)
<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Complex</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>trans-RhCl₃(PR₃)₃</td>
<td>RhCl₃ + PR₃ + EtOH</td>
</tr>
<tr>
<td></td>
<td>(PR₃ = PEt₃, PPr₃, PBu₃, PET₂Ph, PMe₂Ph, PET₂H₂)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>trans-RhBr₃(PPr₃)₃</td>
<td>RhCl₃(PPr₃)₃ + LiBr + EtOH</td>
</tr>
<tr>
<td></td>
<td>Rh₂(PR₃)₄Cl₆</td>
<td>RhCl₃ + PR₃</td>
</tr>
<tr>
<td></td>
<td>(R = Et, Pr₃, Bu₃, pentyln₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cis- and trans-RhCl₃(PR₃)₃</td>
<td>RhCl₃ + PR₃</td>
</tr>
<tr>
<td></td>
<td>(PR₃ = PPh₂H, PET₂H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[RhHCl(dppe)₂]Cl</td>
<td>RhH(dppe)₂ + HCl</td>
</tr>
<tr>
<td>I</td>
<td>RhH(dppe)₂</td>
<td>[Rh(dppe)₂]X + LiAlH₄</td>
</tr>
<tr>
<td></td>
<td>[Rh(dppe)₂]Cl</td>
<td>Rh(CO)₂ + dppe</td>
</tr>
<tr>
<td></td>
<td>Rh(PPh₂H)₃Cl</td>
<td>[Rh(C₂H₄)₂Cl]₂ + PPh₂H</td>
</tr>
<tr>
<td></td>
<td>Rh(PPh₃)X</td>
<td>RhCl₃ + EtOH + PPh₃ + X⁻</td>
</tr>
<tr>
<td></td>
<td>(X = Cl, Br, I)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Complex</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>Rh(CO)Cl\textsubscript{3}(PR\textsubscript{3})\textsubscript{2} \hspace{1cm} (R = Ph, p-Me\textsubscript{6}C\textsubscript{6}H\textsubscript{4}, p-Cl\textsubscript{6}C\textsubscript{6}H\textsubscript{4})</td>
<td>Rh(CO)Cl(PR\textsubscript{3})\textsubscript{2} + Cl\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Rh(CO)X\textsubscript{3}(PET\textsubscript{2}Ph)\textsubscript{2} \hspace{1cm} (X = Cl, Br)</td>
<td>RhX\textsubscript{3} + CO + EtOH + PET\textsubscript{2}Ph</td>
</tr>
<tr>
<td></td>
<td>Rh(CO)ClI\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}</td>
<td>Rh(CO)Cl(PR\textsubscript{3})\textsubscript{2} + I\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Rh(CO)Br\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}</td>
<td>Br\textsubscript{2} + Rh(CO)Br(PPh\textsubscript{3})\textsubscript{2}</td>
</tr>
<tr>
<td>I</td>
<td>Rh(CO)X(PR\textsubscript{3})\textsubscript{2} \hspace{1cm} (X = Cl, Br, I, SCN; R = Et, Ph)</td>
<td>RhCl\textsubscript{3} + PR\textsubscript{3} + X\textsuperscript{-} + CO + EtOH</td>
</tr>
<tr>
<td></td>
<td>Rh(CO)H(PPh\textsubscript{3})\textsubscript{3}</td>
<td>Rh(CO)Cl(PPh\textsubscript{3})\textsubscript{2} + N\textsubscript{2}H\textsubscript{4} + PPh\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>Rh(CO)Cl(dppe)</td>
<td>[Rh(CO)\textsubscript{2}Cl\textsubscript{2}] + dppe</td>
</tr>
</tbody>
</table>
(Y)₂-P-CH₂-CH₂-P(Y)₂

for   edp  Y = H
       dppe Y = C₆H₅
       dmpe Y = CH₃

(Fig. 7)

The 1,2-bis(diphenylphosphino)ethane was the first of these two ligands to be complexed with rhodium. The compound [Rh(dppe)₂]Cl was first synthesized by Sacco and Ugo in 1964 and they reported that this complex was a stable, yellow, crystalline substance, which dissolved readily in polar organic solvents in which it was ionized.₁²¹ The complex was prepared from [Rh(CO)₂Cl]₂ and the diphosphine in benzene by a direct addition reaction. It was also reported at this time that the complex [Rh(dppe)₂]Cl would react with reducing agents such as LiAlH₄ to produce a thermally stable hydrido complex of rhodium(I), [Rh(dppe)₂H]Cl. The hydrido complex was rapidly oxidized by air.

The same complex was also reported by Chatt and Shaw as being the product of the reaction between the ligand and trans-chloro(carbonyl)bis(diethylphenylphosphine)rhodium(I).₁²²

A complex of similar structure, but involving the ligand 1,2-bis(dimethylphosphino)ethane was reported by Chatt and...
Butter in 1967. The compound was prepared by the reaction of the diphosphine with $[\text{RhCl}(\text{PPPh}_3)_2]$ in benzene. It was found to be thermally stable but chemically reactive, and reacted readily with hydrogen, carbon monoxide, hydrochloric acid, hydrobromic acids, chlorine and bromine.

The reactions of this complex were described in another paper by Butter and Chatt in 1970. The complex reacted with chlorine, carbon tetrachloride and chloroform to give cis-$[\text{RhCl}_2(\text{dmpe})_2]\text{Cl}$. The complex cis-$[\text{RhBr}_2(\text{dmpe})_2]\text{Cl}$ could be formed by the reaction of $[\text{Rh}(\text{dmpe})_2]\text{Cl}$ with bromine.

Several other complexes of 1,2-bis(dimethylphosphino)ethane were reported in this paper and are of some interest. Since it was found that $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ in ethanol produced mixed isomers of the desired dichloro complex $[\text{RhCl}_2(\text{dmpe})_2]\text{Cl}$, Chatt attempted to develop preparations which would be specific for each isomer. Thus when mer-$[\text{RhCl}_3(\text{Bu}^n_3\text{P})_2]$ was reacted with the diphosphine, the trans-isomer was precipitated exclusively. Similarly, a specific route to the trans-dibromo complex was found in the reaction between $[\text{Rh}(\text{CO})(\text{dmpe})_2]\text{Cl}$ and bromine in benzene. The complex trans-$[\text{RhBr}_2(\text{dmpe})_2]\text{Cl}$ was formed. The routes to the cis complexes were mentioned above.

Since these routes are specific and do not involve purification of isomers, we decided that if the direct reaction between $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ and ethylenediphosphine produced ambiguous or no results we would attempt to
follow Chatt's procedures. We hoped to study several reactions as listed below in an attempt to produce stable complexes of ethylenediphosphine.

(i) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$

(ii) $[\text{RhCl} (\text{PPh}_3)_3] + \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$

(iii) $\text{mer-}[\text{RhCl}_3 (\text{Bu}^3\text{P})_3] + \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$

Although only a small number of rhodium complexes with phosphine ligands have been mentioned, this not meant to imply that this has been an inactive field. The field of transition metal-tertiary phosphine complexes is very active, due to their excellent catalytic properties for various organic reactions. Researchers such as Issleib and Chatt have been particularly prolific. The complexes mentioned in TABLES 1 and 2 are important only because they show the types of reactions possible with rhodium-tertiary phosphine complexes and are not meant to be a review of rhodium-phosphine chemistry. There are several reviews on the synthesis of various phosphines and their use as ligands with all the transition metals. (34,35,36)
I The Preparation of Ethylenediphosphine

In a typical reaction, 157g(944mM) of triethyl phosphite and 100g(533mM) of 1,2-dibromoethane were mixed and heated under a condenser set for distillation. When heat was applied to the mixture, the temperature climbed to 60°C and the colour of the solution changed from colourless to purple. Then ethyl bromide started to distil. After several hours the mixture turned colourless and ethyl bromide stopped distilling. The resulting yield of ethyl bromide was 79g(731mM).

The reaction mixture was then fractionated by the following method. With reaction flask at room temperature and the receiving flask immersed in an ethanol/dry ice bath, a vacuum was applied to the distilling apparatus. A vigorous bubbling occurred and a clear liquid collected in the trap. When there was no longer any decrease in the volume of the reaction mixture, this distillate in the trap was removed and was shown by IR to be identical to the ethyl bromide that distilled during the reaction. The spectra for these products is given in TABLE 3. The flask was replaced and the distillation continued with heating. The second fraction was trap-collected using ethanol/dry ice as before but for succeeding fractions, only an ice slurry was necessary.

The subsequent fractions were;
(II) diethylethylphosphonate 67g(199mM)
bp 55-60°C/2mm.
(III) diethyl-2-bromoethylphosphonate 9g(22mM)
bp 99-115°C/1mm.
(IV) tetraethylethylenediphosphonate 62g(257mM)
bp 167°C/1mm.

Fraction (IV) was found by IR and elemental analysis to be the desired product. The infrared spectrum is given in TABLE 3.

Calculated for C_{10}H_{24}O_6P_2: C, 39.73; H, 8.00; P, 20.50.
Found: C, 39.36; H, 8.06; P, 19.29%.

The tetraethylethylenediphosphonate was then reduced. To a suspension of 20g(500mM) LiAlH₄ in 150ml ethyl ether, 40g(82mM) of tetraethylethylenediphosphonate were added over a period of several hours. The mixture was then stirred for 48 hours. After 48 hours stirring, the reaction mixture was cautiously hydrolysed with 200ml 1:1 HCl and the ether layer removed and dried with anhydrous Na₂SO₄.

For most of the succeeding attempts at synthesis, the phosphine in the dried ether solution was used since it was found that attempts to purify the phosphine by distillation usually resulted in accelerating the decomposition. The phosphine was purified on a small scale by distillation under nitrogen for the purposes of identification and the pure ethylenediphosphine had a boiling point of 109-112°C (cf 114°C ref. 25) at room pressure, and an IR spectrum
### TABLE 3

Infrared Spectra of Products in the Synthesis of Ethylenediphosphine (cm⁻¹)

<table>
<thead>
<tr>
<th>Ethyl Bromide</th>
<th>TEEDP*</th>
<th>EDP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled during reaction, Distilled under vacuum, Ref.(33)</td>
<td>Found Ref.(32)</td>
<td>Found Ref.(26)</td>
</tr>
<tr>
<td>640</td>
<td>650</td>
<td>780</td>
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<tr>
<td>750</td>
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<td>2994</td>
</tr>
<tr>
<td>3000</td>
<td>3420</td>
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* TEEDP = tetraethyl ethylenediphosphonate

EDP = ethylenediphosphine

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taken neat between AgCl plates consisted of the peaks listed in TABLE 3.

I. Preparation of the Starting Complexes

(i) Preparation of trans-Trichlorotris(tri-n-butylphosphine) rhodium(III)

The complex $\text{trans-}[\text{RhCl}_3 \{\text{P(C}_4\text{H}_9\}_3^3]$ was prepared according to the method of Chatt, Johnson and Shaw.\(^{(26)}\) Rhodium trichloride trihydrate (2g, 7.5 mM) was dissolved in ethanol under nitrogen. Tri-n-butylphosphine (5g, 25 mM) was added under nitrogen and the solution was refluxed for several hours. During this time the solution changed colour from red to orange. The solution was then evaporated to dryness in an air stream. The residue was dissolved in hot methanol and, after cooling for several days at 0°C, dark red prisms and a brown powder formed. When the solution containing these products was allowed to warm, the prisms dissolved while the brown powder remained undissolved. This brown powder was removed by filtration and analysed (see below). The remaining filtrate was heated to boiling and water was added until a yellow precipitate began to form. Hot methanol was added to just dissolve this precipitate. Upon refrigeration, orange-yellow crystals of trans-trichlorotristri-n-butylphosphinerhodium(III) formed.

Calculated for $\text{C}_{36}\text{H}_{81}\text{P}_3\text{Rh}$: C, 52.97; H, 10.00; Cl, 13.63. Found: C, 52.79; H, 10.10; Cl, 13.65%. Yield was 2.1g (36%).
The brown powder mentioned above was identified by melting point and IR spectrum as being di-u-chlorotetra-chlorotetrakistri-n-butylphosphinerhodium(III).

Calculated for $\text{C}_{48}\text{H}_{108}\text{O}_{12}\text{P}_4\text{Rh}_2$: C, 46.95; H, 8.87; Cl, 17.33. Found: C, 47.53; H, 9.29; Cl, 17.46%.
m.p. 172°C, (172-8°C ref. 26), yield was 4g, 8%.

(ii) Preparation of Chlorotristriphenylphosphinerhodium(I)

This complex was prepared according to the methods of Bennett and Longstaff$^{(27)}$ and of Young and coworkers$^{(28)}$ both of whom found that rhodium trichloride trihydrate reacted with an excess of triphenyl phosphine in refluxing ethanol to give dark red crystals of chlorotristriphenylphosphinerhodium(I), m.p. 138°C (decomposed, darkened 125°C).

When the reaction was attempted using 1 g of the rhodium trichloride and a six-fold molar excess of triphenyl phosphine, the dark red crystals were obtained in 90% yield. The crystals darkened at 122°C and decomposed at 138°C and the IR spectrum showed the presence of triphenyl phosphine.

The infrared spectra for all three of the above products, as well as those of the uncoordinated ligands, are given in TABLE 4.

III Attempted Synthesis of Ethylenediphosphine Complexes

(i) Reaction of Rhodium Trichloride with Ethylenediphosphine

An ethanolic solution of rhodium trichloride trihydrate (100mg,) under nitrogen was added to an ether solution of ethylenediphosphine which had been decanted from the
TABLE 4
The Infrared Spectra of the Starting Complexes (cm\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>P(but)(_3^*)</th>
<th>RhCl(_3) P(but)(_3)</th>
<th>Rh(_2)Cl(_6) P(but)(_3)</th>
<th>P(Ph)(_3^*)</th>
<th>RhCl P(Ph)(_3)</th>
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</table>

P(but)\(_3\) = tri-n-butylphosphine
P(Ph)\(_3\) = triphenylphosphine

* Ref. (33)
Na₂SO₄ over which it had been stored. The volume of the ethylenediphosphine solution needed was calculated using Maier's yield\(^{(25)}\) and assuming that four moles of phosphine would be needed for each mole of the rhodium trichloride to ensure complete reaction. After addition, a yellow precipitate formed and was allowed to settle. One or two mls. of the phosphine solution were then added to see if more precipitate would form. When the amounts were calculated in the above manner, the addition of more phosphine did not cause any further reaction to occur. The yellow precipitate was then filtered in air. When the liquid level during the filtration was allowed to reach the precipitate, the product immediately turned orange. Since this seemed to be a decomposition reaction, none of the orange product was sent for analysis. Instead, the procedure was repeated in a glove bag filled with nitrogen so that the filtration could be done in the absence of air. During filtration, when the liquid level reached the level of the precipitate, the product again turned orange. The orange product was sent for analysis and its infrared spectrum was recorded. The IR showed the presence of ethylenediphosphine, but the analysis could not be associated with any simple combination of ethylenediphosphine, rhodium and chloride. (Found: C, 10.70; H, 3.86; Cl, 12.02; P, 23.17%)

Attempts were made, both in the presence of air and under nitrogen, to react the orange product with more
ethylenediphosphine. Refluxing the product for three days with the ether solution of the phosphine produced no results.

The reaction was repeated in air and under nitrogen using half as much of the phosphine. This time, instead of the reaction turning yellow, it remained red. When more of the phosphine solution was added, however, the solution became yellow and a yellow precipitate formed. This precipitate behaved in an identical manner to the one formed above, turning orange upon filtration.

The reaction was also repeated adding the phosphine to the rhodium trichloride instead of the reverse. The same results were obtained. A solution of the yellow product had a peak in the ultraviolet at 240mu.

In order to check the results in the absence of both air and nitrogen, the reaction was repeated on a vacuum line. In a trap on the vacuum line was placed an ethanolic solution of rhodium trichloride trihydrate (200mg, .75 mM). The ligand was distilled in as the ether solution (3 ml.). When the liquid nitrogen was removed, and the contents of the trap allowed to mix, a yellow precipitate formed immediately. The solvents and excess phosphine were removed under vacuum and ethanol was distilled into the trap. Much of the precipitate dissolved in the ethanol to give a yellow solution with a peak at 240mu. When the solution was allowed to sit stoppered in a vial, a yellow product slowly deposited. This product was also sent for analysis and again the values
found did not correspond to any of the expected complexes.

(Found: C, 14.87; H, 4.20; Cl, 9.81; P, 26.63%)

When NaClO\textsubscript{4} was added to the yellow solution, a small amount of precipitate was obtained which partially redissolved in H\textsubscript{2}O to give a yellow solution with a peak again at \( \lambda \text{ max}=240\text{mu.} \) Each time a precipitate formed with NaClO\textsubscript{4}, a large portion of the precipitate would not redissolve even upon refluxing with the following:

(i) H\textsubscript{2}O
(ii) 1:1 HCl
(iii) 1:1 HBr
(iv) NaCl (2M sol'n)
(v) NaBr (2M sol'n)

Only a small portion would redissolve and this gave a solution with a peak at 240mu. When this precipitate was added to a solution of NaOH, however, an orange solution was obtained with a peak at 247mu.

One attempt was made using an ethylenediphosphine/butyl ether solution and an ethanolic solution of RhCl\textsubscript{3}•3H\textsubscript{2}O on both the vacuum line and reflux under nitrogen with the same results being obtained.

(ii) Reaction of Chlorotristriphenylphosphinerhodium(I) with Ethylenediphosphine

An ether solution of chlorotristriphenylphosphine-rhodium(I) (0.5g, 0.5mM) was frozen in a trap and an ether solution of ethylenediphosphine (3 ml.) was distilled on it.
When the trap was warmed and the contents melted and mixed, a yellow precipitate immediately formed. The product was filtered under nitrogen and washed with ether to remove the triphenylphosphine. The yellow complex dissolved in water and the solution had a peak at 247μm. This solution was slightly basic and HCl was added to make the solution acidic. At a pH of 3, a precipitate formed and the solution had a peak at 240μm. This solution could be returned to the 247μm product by increasing the pH greater than 7. A sample spectrum is shown in (Fig. 8). The infrared spectrum of this complex showed co-ordinated ethylenediphosphine. Samples of the precipitate formed in acidic solution were separated for analysis but they turned orange on drying and when sent to the analyst in a closed tube, they arrived as an orange powder and thus were not analysed.

In a second approach, pure ethylenediphosphine (15ml, 3mM) which had been isolated by distillation was added to a methanolic solution of RhCl(PPh₃)₃ (1g, 1mM) by means of a syringe through a serum cap on the reaction flask. The apparatus was well flushed with nitrogen. Upon reflux, a black solid identified as Rh metal by the lack of an infrared spectrum was deposited.

(iii) Reaction of mer-Trichlorotris(tri-n-butylphosphine) rhodium(III) with Ethylenediphosphine

An ether solution of the ethylenediphosphine (3ml) was
distilled onto an ether solution of 300mg of mer-trichlorotri-n-butylphosphine and the solutions allowed to thaw and mix, the colour changed from orange to yellow. A yellow precipitate formed which could be dissolved in water. The addition of NaClO₄ to this solution caused a pale yellow powder to form. This solution had a peak at 245μm. Treatment of the solution with NaOH produced no change in the spectrum. The complex was precipitated with NaClO₄ and dried under vacuum. The dried complex detonated in air but the IR spectrum of a wet sample was taken and showed the presence of ethylenediphosphine. The wet sample weighed 103 mg and if an allowance of 10% is made for moisture and the sample is calculated as Rh(edp)₂Cl₂ as the perchlorate salt, the yield is 64%. The yellow powder could also be precipitated as the chloride using NaCl but the sample turned orange under vacuum drying and a wet sample sent in a sealed tube to the analyst was reported to have turned orange with a noticeable phosphine odour. When the solution of the yellow product was allowed to sit in air, a yellow precipitate formed which could not be redissolved. The IR spectrum of the wet chloride salt revealed peaks assigned to ethylenediphosphine but none assigned to Rh-H, Rh-CO, or Rh-N₂. The yellow solid that had been deposited did not react with HCl, HBr, NaCl, or NaBr, but did dissolve in NaOH to produce an orange solution with a peak at 247μm. Both the yellow
solid that had been deposited and the orange product resulting from the vacuum drying of the chloride salt were sent for analysis.

Found: yellow solid

C, 15.21; H, 4.32; Cl, 7.65; P, 27.87%

orange solid

C, 11.34; H, 3.92; Cl, 11.85; P, 24.34%

In most cases, the preceding attempts at synthesis resulted in products that turned orange upon drying and since analysis revealed that there was a loss of phosphorus content, this was assumed to be decomposition. Since the decomposition products were not known, yields were not calculated.

IV Sources of Supply

RhCl₃·3H₂O (J. Bishop and Co. Platinum Works) was used without further purification as the primary source of Rh(III) for the preparation of the starting complexes. Absolute ethanol, 99.9 Mol % pure methanol, anhydrous ethyl ether, and ion exchanged distilled water were used as solvents. Triethyl phosphite, dibromoethane, tri-n-butylphosphine, and triphenylphosphine were reagent grade and were obtained from Aldrich Chemical Co. Reagent grade sodium salts were used as sources of anions for substitution and precipitation, and were obtained from Fisher Scientific Co.

The electronic spectra were recorded on a Bausch and Lomb Spectronic 505, using water as a solvent unless
otherwise noted. The infrared spectra were recorded on either a Beckman IR 10, or a Beckman IR 12. Solid samples were recorded at 1.0% KBr pellets or Nujol mulls, while liquid samples were used neat between AgCl plates.

The microanalyses were obtained from Spang Microanalytical Laboratories and A. B. Gygli.
Fig. 8
3. DISCUSSION

I. Ligand Preparation

Ethynediethylenediphosphine was obtained following the route

\[
P(OC_2H_5)_3 + BrC_2H_5Br \rightarrow (C_2H_5O)_2P(OC_2H_5)C_2H_5P(OC_2H_5)
\]

+ C_2H_5Br \quad \text{(I-1)}

\[
(C_2H_5O)_2P(OC_2H_5)C_2H_5P(OC_2H_5) \xrightarrow{\text{LiAlH}_4} H_2PC_2H_5PH_2 \quad \text{(I-2)}
\]

The synthesis occurred in two stages. The first involved the preparation of the intermediate tetraethylenediphosphonate from triethylphosphite and dibromoethane following the established procedure of Ford-Moore and Williams. As noted in the Experimental section, the reaction was performed in a distillation apparatus. This was used since one of the products of the reaction, ethyl bromide, had to be removed before it could react with the triethyl phosphite in the manner shown in equation (I-3).

\[
C_2H_5Br + P(OC_2H_5)_3 \rightarrow (C_2H_5O)_2P(OC_2H_5)C_2H_5 + C_2H_5Br \quad \text{(I-3)}
\]

As can be seen, this reaction produces more ethyl bromide and this new molecule recycles and thus all the triethyl phosphite is consumed producing diethylethylphosphonate instead of the desired product. The ethyl bromide can be removed by distillation as it is formed if the reaction temperature is kept above 38°C which is the boiling point of ethyl bromide.

The second stage of ligand preparation involved the reduction of the tetraethylenediphosphonate using lithium aluminium hydride, mainly following the method.
of Maier but using less hydride (2 to 6 times the stoichiometric amount) and much smaller volumes of solvent. Less hydride was needed since the large amounts of solvent used by Maier required drying and this was no longer needed when the volume was reduced. The reaction proceeds according to equation (I-2).

Some difficulty was encountered in handling the free ligand. Maier does not give the details of purification beyond saying that the ethylenediphosphine was separated from the dried ether by distillation at a pressure of 725 Torr. Since it was impossible that this could have been done in air due to the ease of oxidation of the phosphine, the purification was attempted under dry, high purity nitrogen. Unfortunately, it was found that dense white fumes were given off from the hot flask during the distillation. Because of this apparent decomposition, which occurred with several different samples of the ligand, the phosphine was kept as the ether solution in a tightly stoppered flask. The temperature of distillation was lower than that of Maier by 2°C but the spectra given in TABLE 3 show good agreement in the major peaks. Some of the frequencies are slightly shifted since Maier used a gaseous sample.

During all reactions involving the free phosphine it was found that the vile odour of small quantities of the escaping phosphine could be substantially reduced if all effluent gases were passed through a filter. The filter
filter was constructed in the following manner. To a glass tube of 10 cm. diameter and 75 cm. length was added in layers 8 mesh CaCl₂, drierite, lump charcoal, and nuchar as shown.

It was found that when the gas leaving the trap was bubbled through conc. HCl no odour of phosphine could be detected.

II Attempted Synthesis of Ethylenediphosphine Complexes

The three different reactions attempted with the ethylenediphosphine were expected to produce three different results. The rhodium trichloride was expected to become a mixture of cis- and trans-dichlorobisethylenediphosphinerhodium(III). The tri-n-butyl phosphine complex was thought likely to give only the trans-isomer, while it was hoped the triphenyl phosphine complex would give bisethylenediphosphinerhodium(I) chloride. These reactions are summarized below.

\[
\text{RhCl}_3 + 2\text{edp} \rightarrow \text{cis-} \& \text{trans-}[\text{Rh(edp)}_2\text{Cl}_2] \text{Cl} \quad (\text{II-1})
\]

\[
[\text{Rh}\{\text{P(but)}_3\}_3\text{Cl}_3] + 2\text{edp} \rightarrow \text{trans-}[\text{Rh(edp)}_2\text{Cl}_2] \text{Cl} \quad (\text{II-2})
\]

\[
[\text{Rh}\{\text{P(Ph)}_3\}_3\text{Cl}] + 2\text{edp} \rightarrow [\text{Rh(edp)}_2] \text{Cl} \quad (\text{II-3})
\]
The results of the reactions are, however, very similar. All three reactions resulted in species which in acid solution had a peak at 240µ and in basic solution at 247µ. Since we could not isolate as a solid product a substance which did not undergo decomposition, we were unable to determine molar absorptivities to accompany our spectral data. If they had been obtained these values would have shown whether the observed peaks were charge transfer or ligand field transitions. The high dilution which had to be done to allow these peaks to have an absorbance within the range of the spectrometer suggests that these peaks are charge transfer. A comparison of similar complexes reveals that the trans-dichloro species can reasonably be expected to have a maximum near 407µ and the cis-dichloro species near 350µ. These values are listed in TABLE 5.

<table>
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<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$(µ)</th>
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<tr>
<td>trans- [Rh(en)$_2$Cl$_2$]$^+$</td>
<td>406</td>
<td>(30)</td>
</tr>
<tr>
<td>trans- [Rh(cyclam)Cl$_2$]$^+$</td>
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<td>cis- [Rh(dmpe)$_2$Cl$_2$]$^+$</td>
<td>347</td>
<td>(24)</td>
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The peaks at 240 and 247 μm have significant intensity in the visible region when the complexes are in high concentration. They could conceivably have masked any ligand field bands present. The spectra as shown in Fig. 8 have a possible shoulder in the region of 320 μm, since in this region the peak doesn't fall off as rapidly as one might expect from a charge transfer band. The shoulder is not distinct enough to assign a wavelength.

It is interesting that all three reactions seem to produce the same results. Since phosphines are reducing in nature, this could indicate that the product formed is a Rh(I) complex, possibly of the type [Rh(edp)₂]Cl. This was the expected product of the reaction of ethylenediphosphine with chlorotristriphenylphosphinerrhodium(I). This complex can be compared with [Rh(dppe)₂]Cl and [Rh(dmpe)₂]Cl both of which have been synthesized and are known to react with oxygen.²⁴

The electrochemical reduction of trans-[Rh(en)₂Cl₂]⁺ was done by Gillard⁸ who claims to have produced an intermediate with a peak at 338 μm. The final product of the reduction, done under argon, was [Rh(en)₂H(OH)]⁺ which was assigned peaks at 295(323) and 257(272)μm. The numbers in parenthesis are the molar absorptivities. When air was admitted to the reaction vessel, with the solution at its natural pH, a broad shoulder developed at 345-350 μm.(103). The addition of small volumes of acid produced slight
changes in the position of this maximum. The details of the charge transfer spectra are not given. The overall reaction scheme is shown below.

\[ \text{[Rh(en)₂Cl₂]⁺} \rightarrow \text{[Rh(en)₂]⁺} \overset{H_2O}{\rightarrow} \text{[Rh(en)₂H(OH)]⁺} \]

\[ \text{[Rh(en)₂H(OH)]⁺} + O_2 \rightarrow \text{[Rh(en)₂(OH)₂]⁺} \]

Thus if one considers the reaction of the various rhodium complexes with ethylenediphosphine it seems probable that a Rh(I) complex could have been produced which reacted with water to give the hydrido-hydroxo complex. Since the spectra were all taken in 1 cm. cells, there was some contact of this solution with air and possible formation of the di-hydroxo species.

Since the authors of this work don't mention any charge transfer peaks interfering with the observed ligand field bands it may be assumed that there were none in the immediate region. Thus some explanation may be needed for the appearance of a band with the ethylenediphosphine that is not mentioned with ethylenediamine. A similar difference in spectrum has been seen with other rhodium complexes. The spectrum of 1,2,6[Rh(NH₃)₃Cl₃] consists of two ligand field bands at 428(94) and 317(93) and a charge transfer band at 211 mu (39000). Similarly the spectrum of the complex 1,2,6[Rh(dien)Cl₃] consists of two ligand field bands and a charge transfer band at 417(86), 310(330) and 211(34,000).
The spectrum of $1,2,6[Rh\{P(but)_{3}\}Cl_{3}]$ differs from that of the preceding examples in two ways. First there is a marked increase in the intensity of the first ligand field band ($431\mu\text{m}$ $220$) although the second band appears as a shoulder ($320\mu\text{m}$) on a charge transfer band. Secondly, whereas the charge transfer band at $218\mu\text{m}$ ($\sim 30,000$) may be identified with the similar transitions for the amine complexes, the band at $275\mu\text{m}$ ($15,000$) is significantly different in both wavelength and intensity and thus constitutes a new band. The combination of an increase in intensity of the ligand field bands and the appearance of a moderately intense low energy charge transfer band is characteristic of the presence of metal to ligand back-bonding. Normally this is achieved using the anti-bonding $\pi$-orbitals of ligands with intramolecular $\pi$-bonds (e.g., $C_{2}H_{4}$, CN$^{-}$, CO, etc) or alternatively low lying empty ligand d-orbitals, the classic example of which are the 3d-orbitals of tri-valent phosphorus. The 3d-orbitals of nitrogen are too high in energy to effectively participate in back-bonding. Thus, the introduction of back-bonding in the phosphine complex would be expected to give rise to a relatively low energy metal to ligand charge transfer band. At the same time the increased orbital mixing should tend to reduce the 'pure' d-character of the metal orbitals thereby affecting a partial relaxation of the orbital selection rules and providing an explanation for the increased intensity of the ligand field bands. The explosive perchlorate salt
spectrum is given in (Fig. 9).

TABLE 6 gives the infrared spectrum of ethylenediphosphine along with the spectra of the yellow products obtained by all three routes and the orange product from the third reaction obtained when the yellow product was dried. The P-H stretch can be expected between 2290-2320 cm\(^{-1}\). In the obtained ethylenediphosphine spectrum, there is a strong peak at 2320 cm\(^{-1}\) which we assign to the P-H stretch. In the yellow product this peak is shifted to 2360 cm\(^{-1}\) while in the orange product this peak is shifted to 2340. This shift to higher energies is consistent with the strengthening of the P-H bond which could occur if some of the electron density around the phosphorus was withdrawn to form the coordinate bond. The -CH\(_2\)- rocking mode has also been used to indicate coordination of a ligand. This mode occurs for ethylenediamine complexes at 950-850 cm\(^{-1}\). In the experimental spectra there is a band at 840 cm\(^{-1}\) in the free ligand spectrum which is shifted to approximately 880 cm\(^{-1}\) in the products. This shift to higher energy can be accounted for since the complexed ligand would be more restricted in its rocking modes. Nakamoto claims that the M-P stretching modes of triphenyl phosphine and triethyl phosphine complexes occurs between 460 and 170 cm\(^{-1}\). For trans-[PtCl\(_2\)(PET\(_3\))\(_2\)] this vibration occurs at 415 cm\(^{-1}\) while for the cis-isomer of this complex it occurs at 442 and 447 cm\(^{-1}\). (37) Chatt reports unassigned bands
TABLE 6
Infrared Spectra of Ethylenediphosphine and Complexes (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>EDP*</th>
<th>Yellow Product route II-1</th>
<th>Yellow Product route II-2</th>
<th>Yellow Product route II-3</th>
<th>Orange Product route II-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>645</td>
<td>480</td>
<td>480</td>
<td>490</td>
<td>500</td>
</tr>
<tr>
<td>715</td>
<td>700</td>
<td>670</td>
<td>700</td>
<td>710</td>
</tr>
<tr>
<td>830</td>
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<td>670</td>
<td>790</td>
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<tr>
<td>840</td>
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<tr>
<td>971</td>
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<tr>
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<td>1191</td>
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<tr>
<td>3420</td>
<td>3400</td>
<td>3400</td>
<td>3420</td>
<td>3400</td>
</tr>
</tbody>
</table>

* EDP = ethylenediphosphine
routes II-1, II-2, II-3 refer to reactions given on page 35
in the far IR between 456 and 465 cm\(^{-1}\) for various complexes of the type \([\text{RhXY(dmpe)}_2]^+\) where X and Y are halogens or hydrides. In TABLE 6 there is a band listed for the complexes but not for the free ligand at 480-500 cm\(^{-1}\). This could be a Rh-P stretch. Another band which appears in the complexes but not in the free ligand spectra is the 1080-1100 band. Nakamoto lists the Sn-O-H bend as occurring at 1150 cm\(^{-1}\) while for Co-O-H this bend is at 1100 cm\(^{-1}\). Thus the 1080 band may be assigned to Rh-O-H bend. In view of the similarity of the ligand spectra to the complexes it seems evident that the ethylenediphosphine is present and is coordinated. There is also some support for hydroxo-groups being present in the complexes. The Rh-Cl bands generally occur near 300 cm\(^{-1}\) which was out of range for the instrument. The complexes decomposed in a laser beam so that the Raman spectra could not be taken.

An additional alternative could be that binuclear species were forming in solution. These could have been bridging groups of several types although Cl\(^-\), RPH and OH are the most likely. The analysis of one of the products does come close to the chloride bridged structure shown below; (Calculated for \(C_4H_{16}P_4Cl_2Rh_2\); C, 10.31; H, 3.73; Cl, 15.21; P, 26.58%.)

\[
\begin{array}{c}
\text{H}_2\text{C=CH}_2 \quad \text{H}_2\text{P=CH}_2 \\
\text{H}_2\text{C=CH}_2 \quad \text{H}_2\text{P=CH}_2 \\
\text{Rh} \quad \text{Cl} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H}_2\text{C=CH}_2 \quad \text{H}_2\text{P=CH}_2 \\
\text{H}_2\text{C=CH}_2 \quad \text{H}_2\text{P=CH}_2 \\
\text{Rh} \quad \text{Cl} \\
\end{array}
\]
There are however other structures which can be drawn whose analysis should come close to that obtained. Some of these are shown below.

The process of matching structure and analysis is speculative and while the structures above are all possibilities and binuclear complexes are common in the rhodium-phosphorus system, a plausible structure cannot be chosen from such reasoning alone. The analysis calculated for dihydroxo-bisethylenediphosphinerhodium(III) perchlorate is found above and it matches as well as the rest with the results of the analysis of the products.

In retrospect, other routes to the ethylenediphosphine complexes may have been more profitable. One such route

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involves the use of carbonyl complexes as starting materials. Since the displaced ligand would be a gas and any unused ligand could be removed by vacuum, only the products would be left if the process was done under vacuum. While it is not known whether primary phosphines will replace carbynyls as ligands of rhodium, neither was it known if primary phosphines could replace tertiary phosphines. The infrared spectra show that this has happened. If a Rh(I) carbonyl was used as shown in reaction (II-5) the product might be bisethylenediphosphinerrhodium(I). The complex

$$\left[\text{Rh}(CO)_2\text{Cl}\right]_2 + 2\text{edp} \rightarrow \left[\text{Rh}\text{(edp)}_2\right]\text{Cl} + 2\text{CO} \quad \text{(II-5)}$$

di[1,2-bis(dimethylphosphino)ethane]rhodium(I) which is mentioned on page 5 of this thesis can be synthesized in this manner as is shown in TABLE 1. Similarly, a rhodium (III) carbonyl of the type $$\left[\text{Rh}(CO)\text{Cl}_3(\text{PR}_3)_2\right]$$ could be used in an effort to produce a Rh(III) complex.

$$\left[\text{Rh}(CO)\text{Cl}_3(\text{PR}_3)_2\right] + 2\text{edp} \rightarrow \left[\text{Rh}(\text{edp})_2\text{Cl}_2\right]\text{Cl} + 2\text{PR}_3 + \text{CO} \quad \text{(II-6)}$$

The advantage to this type of reaction is that the products and unreacted ligands could be removed and solvent distilled in without the complexes coming into contact with air.
With a properly designed system, the UV spectrum could be obtained with an evacuated cell.\(^{(31)}\)

The attempted reaction of the complexes with I\(_2\) and Br\(_2\) only succeeded in producing I\(_3^-\) and Br\(_3^-\). There was also no reaction with chloride and bromide salts on reflux. If the complex were a simple hydroxo species, some reaction of a replacement type would have been expected. Since the infrared spectrum gives an indication of Rh-O-H bonds, and these are seemingly not reactive, it may be that they are bridging hydroxo groups. Gillard reports several bridged species resulting from reaction of the complexes present in his electrochemically reduced solutions. The change in spectrum with pH does not require hydroxo groups to appear in the complex. Protonation and deprotonation of phosphine groups has also been observed. This is somewhat analogous to the deprotonation of an amine in strong base,

\[
\text{R-P-H}_2 + \text{OH}^- \rightarrow \text{R-P-H}^- + \text{H}_2\text{O}
\]

This area has not been investigated in this case and both explanations must be considered equally until more information is available.

Several results have been obtained from this research. The replacement of tertiary phosphines with chelating primary phosphines has not been noted before. This leaves open many possible routes to primary phosphine complexes since many tertiary phosphine complexes are known.
The primary concern of this project was to synthesize an analogue of ethylenediamine and to form complexes using this as a ligand so that the new complexes could be used in kinetic studies. We have made a beginning by synthesizing the ligand and we have shown that it reacts with rhodium. Although we cannot identify the product of the reaction we know that it doesn't react under conditions where the nitrogen analogue would. This may indicate that the reactions of phosphine complexes are sufficiently different from the reactions of their nitrogen analogues that direct comparisons may not be made. Further work in this area is required.
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VITA AUCTORIS

Born:
   January 28, 1947; Windsor, Ontario, Canada
   Son of Mr. and Mrs. John James Carey.

Primary School:
   John Campbell, Windsor, Ontario, Canada

Secondary School:
   W. C. Kennedy Collegiate Institute, Windsor, Ontario, Canada. 1961 - 1965

University:
   University of Windsor, Windsor, Ontario, Canada.
   B. Sc. Chemistry - 1970

Marital Status:
   Married May 9, 1970 to Anne Kenny.

Accepted into the Faculty of Graduate Studies, University of Windsor, May 1970.