STUDIES OF GROUP VIII TRANSITION METAL PHOSPHINE COMPLEXES
STUDIES OF GROUP III TRANSITION METAL PHOSPHINE COMPLEXES

by

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SCOPE AND CONTENTS:

This work describes the results of a study of phosphine complexes of some selected members of the group VIII transition metal series. The aim of this work was to investigate possible correlations between the electronic properties of these metal complexes and their stabilities and labilities. It was felt that such a study might prove significant since many of the complexes studied are catalytically active in a number of homogeneous systems. Elucidation of the factors influencing the efficiency of such homogeneous catalytic systems is important from both practical and theoretical points of view.

Some electronic properties of the complexes were investigated using a $^{19}$F Nuclear Magnetic Resonance technique. This method is based upon the measurement of the $^{19}$F chemical shifts of complexes of ($p$-FC$_6$H$_4$)$_3$P and ($m$-FC$_6$H$_4$)$_3$P. The results of this aspect of the work are discussed in Chapter V; i.e., the data is discussed in terms of the "electron affinity" of the central metal.

In order to study the correlation of the "electron affinity" of the central metal with the rates and equilibrium constants for reactions of these complexes, a number of ligand exchange reactions were studied. Chapter III presents the results for such reactions of some palladium(II) phosphine complexes. In the course of this work the formation of four coordinate palladium phosphine cations was demonstrated. The formation
of these cations was shown to be highly sensitive to the nature of the particular phosphine used. Chapter IV presents the results for some phosphine ligand exchange reactions of the complexes trans\([\{(C_6H_5)_3P\}_2MCOX\] (M = Rh and Ir, X = Cl, Br and I) as well as some exchange reactions of the complexes \([\{(C_6H_5)_3P\}_3RhX\] (X = Cl, Br and I). It was shown that the course of these reactions was highly dependent upon the nature of the particular phosphine used in the exchange reaction and on the halide present.

The results described in Chapters III, IV and V are discussed at some length in Chapter VI. In this final chapter, it is argued that the results of the preceding three chapters can be rationalized in terms of the donor and acceptor properties of the ligands and the acceptor and donor properties of the metal. The results of the \(^{19}F\) nmr study are used to provide a measure of the acceptor properties of the metal complexed and data from the literature, based primarily on infrared studies are used as a basis for discussion of ligand donor properties. The results presented are consistent with the hypothesis that maximum stability is achieved by optimum matching of ligand donor/acceptor properties with the acceptor/donor properties of the metal.

Chapters I and II are largely introductory. Chapter I includes a brief review of the chemistry of the complexes and ligands discussed in this work. Chapter II gives the basic theories to nuclear magnetic resonance, and conductivity, the two physical techniques used throughout the experimental work reported in this thesis.
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CHAPTER I
PHOSPHINE, COMPLEXES IN GROUP VIII TRANSITION METAL CHEMISTRY

1.1 INTRODUCTION

Metals of the group VIII series have long been known as active catalysts, being used extensively as heterogeneous catalysts in both industrial and laboratory scale reactions. More recently, complexes of these metals have been found to be active as homogeneous catalysts. Such systems have been extensively studied because of their inherent interest and their potential industrial applications. Several recent studies have led to a rather detailed understanding of the catalytic process. It has been found that the detailed reaction mechanisms of several such processes have a number of features in common. These can be illustrated by considering two of the better known cases.

The "oxo" process is a particularly well understood homogeneously catalyzed reaction in which an aldehyde is produced from a terminal olefin. The proposed mechanism for this reaction is shown below:

\[
\begin{align*}
\text{HCo(CO)}_4 & \rightarrow \text{HCo(CO)}_2 + \text{CO} \\
\text{HCo(CO)}_3 + \text{RCH}_2\text{CH}_2\rightarrow & \text{HCo(CO)}_3 + \text{RCH}_2\text{CH}_2\text{Co(CO)}_3 \\
\text{RCH}_2\text{CH}_2\text{Co(CO)}_3 + \text{CO} & \rightarrow \text{RCH}_2\text{CH}_2\text{Co(CO)}_4 \\
\text{RCH}_2\text{CH}_2\text{Co(CO)}_4 + \text{H}_2 & \rightarrow \text{RCH}_2\text{CH}_2\text{CHO} + \text{HCo(CO)}_3
\end{align*}
\]
The catalytic hydrogenation of ethylene by \([\{(C_6H_5)_3P\}_3\text{RhCl}\]
was first reported by Wilkinson and coworkers\(^2^A\). The mechanism postulated
by these workers has been reinvestigated by several groups\(^2^B,^2^C\) and as
such the original mechanism may not be entirely correct. However, for
the purpose of illustration, Wilkinson's original mechanism is shown
below.

\[
\begin{align*}
[(C_6H_5)_3P]_3\text{RhCl} + [(C_6H_5)_3P]_2\text{RhCl(solvent)} + P(C_6H_5)_3 & \rightarrow [(C_6H_5)_3P]_2\text{RhCl(solvent)} + H_2 + [(C_6H_5)_3P]_2\text{RhH}_2\text{Cl} \\
[(C_6H_5)_3P]_2\text{RhH}_2\text{Cl} + \text{CH}_2\text{CH}_2 & \rightarrow [(C_6H_5)_3P]\text{RhH}_2\text{Cl(CH}_2\text{CH}_2) \\
[(C_6H_5)_3P]\text{RhH}_2\text{Cl(CH}_2\text{CH}_2) + \text{solvent} & \rightarrow [(C_6H_5)_3P]_2\text{RhCl(solvent)} + \text{CH}_3\text{CH}_3
\end{align*}
\]

These mechanisms show features which are common to many
homogeneous reactions.

1. The complex used in such a reaction is often only the precursor
to the catalytically active species and an initial dissociation of
a ligand is often required.

2. The mechanism consists of a series of steps each of which may be
viewed as a ligand exchange reaction. In some cases, there is a
direct exchange between complexed and free ligands. In other cases
the replacement of solvent may be involved. In yet other cases (e.g.,
"insertion reactions") there is a rearrangement of ligands already
present to give new ligands. However, in each case the central
metal has a different ligand environment at the completion of a
step than it possessed at the beginning of that step. Enquiry
into the origin of the driving forces which favour changes in
ligand environment is obviously pertinent to an understanding
of homogeneous catalysis.

It is usual to distinguish steric and electronic factors in discussing the reactivity of metal complexes. Steric factors, although not well understood in detail, are intuitively straightforward, at least in principle. There is obviously a limit to the number of bulky ligands which can be accommodated around a metal atom of a given size. Electronic factors are, however, less straightforward. Ligands are usually regarded primarily as electron donors but it has long been recognized that in these covalent complexes the electron accepting abilities of a ligand can have a marked influence on the bonding. It is also recognized that the electronic requirements of different metal atoms in different oxidation states are not the same. Thus, the range of stable complexes formed with Ni(0) is quite different to that formed by Co(III). Initially it is expected that the stability and lability of a metal complex will depend upon a combination of the donor/acceptor properties of the various ligands and the acceptor/donor properties of the metal centre. The primary objective of the present study is therefore to seek some measures of these donor and acceptor properties and to investigate possible correlations of these properties with the stabilities and labilities of metal complexes.

It is apparent that the factors involved are in part thermodynamic and in part kinetic. Some combinations of certain ligands with a given metal are more stable than others while two complexes of comparable stability may differ markedly in their rates of ligand exchange. Both aspects are important in determining the overall efficiency of catalytic reaction schemes such as those shown above.
It has been often observed that relatively minor changes in the nature of the ligands can very markedly affect catalytic efficiency. Organic chemists have achieved a large measure of understanding of aliphatic and aromatic substitution processes in terms of electronic charge distributions. The above catalytic processes are much more complicated and ready solutions are not to be expected. Nevertheless, the basic driving forces are unlikely to be different from those encountered in other areas of chemistry. This thesis represents an attempt to elucidate some of the factors determining the efficiency of ligand exchange.

The complexes chosen for study were substituted phosphine complexes of group VIII metals. These complexes were chosen for several reasons. A number of them are well-known homogeneous catalysts whereas others are inert, at least in the reactions thus far investigated. In most cases a series of complexes with a variety of phosphines can be obtained and their relative stabilities investigated. Furthermore, many of the complexes have been known for a considerable length of time and their properties and reactivities have been extensively studied. Finally, the complexes are readily available commercially, or can be easily prepared, and are all reasonably stable.

Since all the complexes chosen contain substituted phosphine, the exchange of complexed and free phosphine was chosen as the exchange reaction for study. This exchange of free and complexed phosphine was observed by nuclear magnetic resonance (NMR). The reason for this is two-fold. Since the observed "chemical shift" (see Chapter II) for free and complexed phosphine are usually somewhat different, high-resolution instruments can often distinguish between free and complexed
ligands. This technique also has the advantage that the time scale of observation of the NMR experiment ($\sim 10^{-2}$ sec) is of the same order as the rate of many chemical reactions. This, in favourable cases, makes possible the study of reaction rates which are too fast for classical methods.

In several cases, the exchange reactions studied led to the formation of charged species. The study of such reactions was carried out by means of conductivity measurements. Since conductivity is a measure of the concentration of current carriers (charged species) in solution, this method is particularly suited to the study of reactions producing ionic products.

1.2 \textit{Chemistry of Phosphine and Substituted Phosphines}

Compounds of phosphorus(III) have been known for over one hundred years. The simplest compound which gives this name to the entire range of phosphorus(III) compounds is phosphine $\text{PH}_3$. This compound was first characterized by Rose\textsuperscript{3} in 1826. This compound is very reactive, being rapidly attacked by oxygen or water. The halophosphines $\text{PX}_3 (X = \text{F, Cl, Br, I})$ have also been characterized. Since both types of compounds are very reactive, their use in transition metal chemistry has been somewhat limited.

Alkyl and aryl phosphines $\text{R}_3\text{P}$ where $\text{R}$ is an alkyl or aryl group are also well-known. Triphenylphosphine, $(\text{C}_6\text{H}_5)_3\text{P}$, is particularly stable and readily soluble in a wide range of organic solvents and has been widely used as a ligand in transition metal chemistry. The preparation and properties of substituted phosphines has been thoroughly reviewed.\textsuperscript{4,5} In general, the organophosphorus(III) compounds can be
synthesized by the reaction of the appropriate Grignard reagent with \( \text{PCl}_3 \).

Compounds of phosphorus(III) can be oxidized to phosphorus(V) by a variety of oxidizing agents including atmospheric oxygen, hydroxide in alcohol, or hydrogen peroxide. The ease of oxidation depends markedly upon the substituents. Thus, triethylphosphine is readily oxidized on exposure to air while triphenylphosphine is indefinitely stable towards air.

1.3 Transition Metal Phosphine Complexes

Phosphines are Lewis bases since they possess a lone pair of electrons. This pair of electrons can be donated to a metal to form a complex. The phosphorus-metal bond can be strengthened by back-bonding involving donation of electrons from filled metal orbitals to empty phosphorus d orbitals.

The chemistry of transition metal phosphine complexes has been reviewed by Booth. The ubiquitous nature of phosphine ligands in transition metal chemistry is shown clearly in this review which points out that phosphine complexes are known for every transition metal. Booth has published a more recent review of this subject and the range of data incorporated in this review demonstrates the rapid expansion in the amount of information available on such complexes.

There have been numerous methods devised for the synthesis of phosphine complexes. The preparation generally involves the addition of the phosphine dissolved in some solvent such as acetone to an aqueous solution of the metal halide. The specific reaction conditions vary greatly with the metal oxidation state, the nature of the other
ligands, and the nature of the phosphine.

The wide range of transition metal phosphine complexes is particularly notable with the group VIII metals, constituting perhaps the best known series of organophosphine complexes. The study of these complexes dates back to 1857 with the synthesis of \([\text{C}_2\text{H}_5\text{P}]_2\text{PtCl}_2\)\(^8\). Phosphine complexes are known for the low oxidation states of all the group VIII metals, forming complexes with additional ligands including halide, hydride, carbon monoxide and a wide range of organic moieties. Included are neutral and charged (both anionic and cationic), mono- and polynuclear species. This present study was restricted to simple diamagnetic phosphine complexes with halides or carbon monoxide acting as additional ligands. The complexes studied covered the range of oxidation states of zerovalent (platinum), univalent (rhodium and iridium), divalent (nickel, platinum, and palladium) and trivalent (rhodium and iridium). These different oxidation states show several different stereochemistries which are best classified according to the electronic configuration of the central metal.

1. \(^{10}\text{d}^{10}\)

The complexes studied were those of Pt(0) which at least in the solid are four coordinate. Truly zerovalent \(^{10}\text{d}^{10}\) complexes are tetrahedral as, for example, are the complexes \([\text{Pt(CO)}_2]_n\)\(^{11}\) and \(\text{Pt(PHP}_3)_4\)\(^{10}\). However, some complexes are known such as \([(\text{C}_6\text{H}_5\text{P})_2\text{PtO}_2]_4\)\(^{11}\) and \([(\text{C}_6\text{H}_5\text{P})_2\text{Pt}([\text{CN}]_2\text{C}==\text{C(CH)}_2]^{12}\) which are formally Pt(0) but are square planar with the two phosphorus atoms, the platinum atom, and the two oxygen (or carbon) atoms located in a plane. In valence
bond theory true $d^{10}$ complexes can form only $sp^3$ hybrid orbitals so only tetrahedral species could be formed. The fact that square planar complexes are found indicates the inadequacy of the oxidation state formalism. Previous work has suggested that, although formulated as compounds of Pt(0), these complexes may, in fact, be better described as compounds of Pt(II).

Some results of this present work supporting this view are discussed in Chapter V.

2. $d^8$

(i) M(I), M = Rh, Ir

Univalent complexes of rhodium and iridium are usually 4-coordinate square planar. These complexes are 16 electron systems and can, by adding a fifth ligand, achieve an 18 electron configuration. This is, in fact, realized in some hydride complexes of these metals. Examples of both four and five coordinate phosphine complexes of rhodium(I) and iridium(I) were studied in this work.

(ii) M(II), M = Ni, Pd, Pt

Divalent phosphine complexes of nickel, palladium and platinum are usually four-coordinate. The stereochemistry may be tetrahedral (paramagnetic) or square planar (diamagnetic). Both tetrahedral and square planar complexes are known for nickel while the palladium and platinum complexes are usually square planar. As in the case of the rhodium and iridium complexes discussed above, these complexes are coordinately unsaturated. Examples of addition of a further ligand to give five-coordinate compounds, while known, are not common.
3. \( d^6 \)

Phosphine complexes of this group are commonly six-coordinate and octahedral. Phosphine complexes of Rh(III) and Ir(III) are well-known with both halide and hydride ligands. Complexes of the type \([(C_6H_5)_3P]_2PtX_4\) are known but tend to lose \(X_2\) to form the \([(C_6H_5)_3P]_2PtX_2\) complexes discussed above. All of these six-coordinate \(d^6\) systems are coordinately saturated.

1.4 CHEMISTRY OF GROUP VIII PHOSPHINE COMPLEXES

At the present time so much information regarding the chemistry of these complexes is known, that an exhaustive review is not possible. A brief outline of selected reactions illustrating the type of chemistry observed with these complexes is given below.

1. Oxidative Addition

A remarkable type of reaction observed with many of these complexes is oxidative addition. The term oxidative addition describes the reaction of a metal complex with a variety of neutral covalent molecules in which the neutral molecule is added to the complex which by this process is itself oxidized. This type of behaviour is now well-known and is perhaps best exemplified by Ir(I) carbonyl phosphine complexes although it has been observed for a number of metal complexes. A typical oxidative addition reaction is shown below.

\[
\begin{align*}
(C_6H_5)_3P & \quad \text{Ir} \quad (C_6H_5)_3P \quad \text{CO} \\
\text{Cl} & \quad \text{CH}_3\text{I} \\
\text{Cl} & \quad \text{CH}_3 \quad (C_6H_5)_3P \quad \text{CO}
\end{align*}
\]
This reaction is known for an extensive number of neutral molecules including $H_2$, $X_2$, $CH_3X$, RCOX and $HX$. A similar reaction with $O_2$ is shown below:

\[
\begin{align*}
\text{Cl} & \quad \text{Ir} & \quad \text{P(C}_6\text{H}_5\text{)₃} & \quad + \quad \text{O}_2 & \quad \text{Cl} & \quad \text{Ir} & \quad \text{P(C}_6\text{H}_5\text{)₃} \\
(C_6\text{H}_5\text{)}₃\text{P} & \quad \text{CO} & \quad & \quad & \quad \\
\end{align*}
\]

This reaction differs from that shown above in that the oxygen-oxygen bond is not broken while the corresponding methyl-halide bond is broken. This type of reaction is known for a number of molecules including $O_2$, alkenes, and alkynes. The general phenomenon of oxidative addition has been well documented and the literature reviewed by several authors.\(^{14,15}\)

2. **Stability in Solution**

In general, the phosphine complexes discussed in this work show considerable stability in solution. The platinum (0) complex $[(C_6\text{H}_5\text{)}₃\text{P}]_4\text{Pt}$, however, is known to be somewhat air sensitive both in the solid and in solution, forming amongst other products $[(C_6\text{H}_5\text{)}₃\text{P}]_2\text{PtO}_2$.\(^{16}\) In oxygen-free solvents, the tetrakis complex is dissociated to the tris or even the bis triphenylphosphine complex.\(^{17}\) In such deoxygenated solvents, polynuclear platinum cluster compounds can be isolated.\(^{18}\)

In the initial report\(^2\) of the synthesis and properties of $[(C_6\text{H}_5\text{)}₃\text{P}]_3\text{RhCl}$, molecular-weight studies led to the conclusion that the complex was highly dissociated to the three coordinate species shown below.
\[
[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl} \equiv [(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RhCl} + (\text{C}_6\text{H}_5)_3\text{P}
\]

Later studies demonstrated, both by nuclear magnetic resonance\textsuperscript{19} and by molecular weight measurements,\textsuperscript{20} that in carefully deoxygenated solvents, the dissociation of a triphenylphosphine occurs only to a very minor extent even in very dilute solution. There seems to be no report of the dissociation of any of the other complexes studied in this work although, as pointed out above, the iridium (I) complexes are air sensitive in that they react with oxygen.

In the presence of excess phosphine, the replacement of coordinated halide by phosphine to form a cationic complex has been observed for a series of cobalt complexes, \([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CoX}_2\).\textsuperscript{21} During the course of this work, the formation of similar cationic complexes upon addition of excess phosphine to platinum (II) phosphine complexes was reported by Powell and coworkers.\textsuperscript{22} These authors\textsuperscript{23} recently have shown that cationic intermediates are involved in the cis-trans isomerization of some palladium (II) phosphine complexes. A brief report\textsuperscript{24} of cationic iridium complexes formed by iridium (I) phosphine complexes has also been published. The results of the work reported on the platinum (II), palladium (II) and iridium (I) systems will be discussed in Chapters III and IV.

3. **Mechanism of Substitution**

Substitution reactions of group (VIII) complexes have been a subject of much interest in recent years with the result that the mechanisms for an impressive list of reactions have been determined. Unfortunately, this list contains few reactions of phosphine complexes. Generally, the studies that have been carried out show that substitution
reactions in octahedral complexes proceed via a dissociative mechanism, in which dissociation of a coordinated ligand occurs to give an intermediate of reduced coordination number. Substitution reactions in four coordinate d^{10} complexes also proceed by loss of a ligand. This is the expected reaction mechanism since such systems are coordinately saturated and an associative reaction pathway is not possible. On the other hand, substitution in square planar d^{8} complexes proceeds with retention of configuration and displays a more complicated rate expression than is observed in the dissociative mechanisms discussed above. The observed rate expression for a reaction such as

\[ L_2MX_2 + C \leftrightarrow LCMX_2 + L \]

is

\[ \text{Rate}_{\text{obs}} = K_1[L_2MX_2] + K_2[L_2^{\text{M}}X_2][C] \]

This two-term rate expression implies that there are, in fact, two mechanisms in operation. The first term, characterized by the pseudo first order rate constant \( K_1 \), describes the reaction path in which the displacement of a bonded solvent molecule is rate determining; that is, the term is more correctly formulated as

\[ k_1[L_2^{\text{M}}X_2][\text{solvent}] \]

Since the solvent concentration (or more properly solvent activity) is constant, the pseudo first order rate constant is

\[ K_1 = k_1[\text{solvent}] \]

The second term, characterized by the second order rate constant \( K_2 \), describes the reaction path in which the rate-determining step is the
attack of the ligand C on the complex L₂MX₂ to form the intermediate (usually trigonal bipyramidal) L₂MX₂C. Studies which have shown this type of behaviour have, for the most part, been limited to platinum (II) complexes, since the rates of these reactions are generally slow enough to be amenable to study by classical techniques.

4. **Homogeneous Catalytic Activity**

Complexes used in this study have been widely used as homogeneous catalysts. In fact, it is chiefly because of such activity that these particular complexes were chosen for study.

No attempt will be made to review the literature on the catalytic activity of the complexes discussed in this work for such a review is far beyond the scope of this thesis. However, a few representative reactions will be discussed below.

The square planar rhodium (I) complex \([(C₆H₅)₃P]₂RhCl₃\), known as Wilkinson's compound, was first reported in 1964. In the original publication,² it was shown that this complex is an extremely efficient catalyst for the hydrogenation of olefins. The proposed mechanism for this reaction was shown earlier in this chapter and is somewhat unusual in that a dissociation of a four coordinate d⁸ (coordinately unsaturated complex) is postulated. The rate of reaction appears to depend upon the displacement of the coordinated solvent molecule of \([(C₆H₅)₃P]₂RhCl₃\) (solvent) by the incoming olefin. Such changes in the electronic or steric properties of the complex have a profound effect on the rate of reaction, that is, a change in halide produces a marked change in the rate of reaction. The observed rate of hydrogenation increases as the halide is changed in the order Cl < Br < I. This order was explained
in terms of an increasing trans influence; however, when the halide is replaced by SnCl₃, a ligand with a considerably larger trans effect, the activity of the complex was considerably reduced.

The efficiency of the reaction is also dependent upon the nature of the neutral ligands, for example, the use of the corresponding triphenylarsine or triphenylstibine complexes greatly reduces the catalytic efficiency compared to the triphenylphosphine complex. Even fairly minor changes, such as substitution in the para position of the phenyl rings of the triphenylphosphine, influences the rate of hydrogenation. Since substitution at the para position is unlikely to change the steric properties of the phosphine, changes in the observed rates of hydrogenation which occur as such substitutions are made must reflect the differing electronic properties of such substituted phosphines. Thus, when the tris paramethoxy phenylphosphine complex \((p\text{CH}_3\text{OC}_{6}\text{H}_{15})_3\text{P}_3\text{RhCl}\) is used, the rate constant for the hydrogenation of cyclohexene increases from 0.25 mole\(^{-1}\)sec\(^{-1}\) for the triphenylphosphine complex to 0.34 mole\(^{-1}\)sec\(^{-1}\). Similarly, substitution of F in para position results in a drop in the observed rate to 0.02 mole\(^{-1}\)sec\(^{-1}\). Thus, the electron withdrawing CH₃O substituent facilitates either the solvent displacement or olefin coordination in the \([(\text{CH}_3\text{OC}_{6}\text{H}_{14})_3\text{P}_2\text{RhCl}(\text{solvent})_2\text{F}_2\text{P}_2\text{RhCl}])_2\text{RhCl}((\text{solvent})_2\text{F}_2\text{P}_2\text{RhCl})_2\) intermediate while the F substituent hinders one of these processes. Further studies into the effect of changing the phosphine were carried out by forming the complex in situ by mixing \([\text{RhCl}(\text{C}_8\text{H}_8)_2]_2\) with six moles of phosphine. These results are shown in Table 1-1, where the hydrogen uptake for several such mixtures is quoted. In general, these results show that the rate of hydrogen uptake decreases with increasing basicity of the phosphine. It has also been shown that the phosphite complexes...
TABLE 1-1

Hydrogen Uptake by Mixtures of $[\text{RhCl} (C_6H_5)_2]_2 + \text{phosphine (1:6)}^A$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$H_2$ Uptake (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_2H_5)_3P$</td>
<td>0</td>
</tr>
<tr>
<td>$(C_2H_5)_2(C_6H_5)_2P$</td>
<td>0</td>
</tr>
<tr>
<td>$(C_2H_5)(C_6H_5)_2P$</td>
<td>1.8</td>
</tr>
<tr>
<td>$(C_6H_5)_3P$</td>
<td>12.4</td>
</tr>
</tbody>
</table>

A hydrogenation of cyclohexene in benzene under 500 mm $H_2$ at 25°C.
$[\text{(CH}_3\text{O)}_3\text{P}]_3\text{RhCl}$, $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_3\text{RhCl}$ and $[(\text{C}_6\text{H}_5\text{O})_3\text{RhCl}]$ are inactive as hydrogenation catalysts.

It has been shown that rhodium(I) and iridium(I) carbonyl complexes, $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_{\text{MCOCl}}$ (M = Rh, Ir) are efficient decarbonylation catalysts. Ohno and Ituji have shown that $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_2\text{Rh(CO)Cl}$ decarbonylates $\text{C}_6\text{H}_5\text{COX}$ to form $\text{C}_6\text{H}_5\text{X}$ and carbon monoxide. These workers showed that substrate substitution influences the rate of decarbonylation, that is, reaction with $\text{pCH}_3\text{OC}_6\text{H}_4\text{COCl}$ is slower than the reaction with $\text{C}_6\text{H}_5\text{COCl}$. However, these workers observed no difference in the rate of reaction when $[(\text{CH}_3\text{OC}_6\text{H}_4\text{O})_3\text{P}]\text{RhCOCl}$ was used as a catalyst to decarbonylate $\text{C}_6\text{H}_5\text{COCl}$. The mechanism these workers postulated for the decarbonylation is shown below $(L=(\text{C}_6\text{H}_5\text{O})_3\text{P})$.

\[
\begin{align*}
0 & \rightleftharpoons \text{RCCl + L}_2\text{RhCOCl} \\
\text{RCCl + L}_2\text{RhCOCl} & \rightleftharpoons \text{RCO} \rightleftharpoons \text{RCCl} + \text{L}_2\text{RhCOCl} \\
\end{align*}
\]
A number of complexes studied in this present work are known to be olefin isomerization catalysts. Nicholson and Shaw have observed significant differences in the rate of isomerization of cyclo-octa-1,5-diene to cyclo-octa-1,3-diene by various iridium (III) phosphine complexes as the phosphine was changed. They observed a decrease in the rate of isomerization for the following catalysts $[(C_2H_5)(C_6H_5)_2P)_3IrCl_2 > [(C_2H_5)_3P)_3IrCl_3 > [(C_2H_5)_2(C_6H_5)P)_3IrCl_3 > [(C_2H_5)(C_6H_5)_2P)_3RhCl_3 > [(CH_3)_2(C_6H_5)P)IrCl_3$. These workers also report that $[(C_2H_5)_3P)_2PtCl$ and $[(CH_3)_2(C_6H_5)P)_2PdI_2$ were both very poor catalysts.

The results of Nicholson and Shaw discussed above confirm a number of reports showing that platinum (II) and palladium (II) phosphine complexes do not seem to be particularly active catalysts. This perhaps reflects the fact that such complexes are not particularly labile, although this may be an unwarranted oversimplification. This rationale is substantiated by the observation of olefin isomerization by solutions of $PdCl_2$ as well as by solutions of $(C_6H_5CN)_2PdCl_2$. It is to be noted that $PdCl_2$ has vacant coordination positions while the benzonitrile complex is highly dissociated in solution. Palladium complexes such as $[(C_6H_5)_3P)_2PdCl_2$ can be made catalytic by the use of halide accepting co-catalysts such as $SnCl_2$. Similarly hydrogenation and isomerization of olefins have been observed using a number of platinum (II) phosphine, arsine, and stilbene complexes with $SnCl_2$.

5. **Ligand Exchange Reactions of Group VIII Phosphine Complexes**

Much of the early work on ligand exchange reactions employed Co(III) and Cr(III) complexes since these reactions are generally slow enough to be studied by classical techniques. With the advent of
techniques which made possible the study of much faster reactions, ligand exchange studies have become more diversified and at present considerable information is available on platinum (II) systems. Again, however, the reactions of nickel (II) and palladium (II) tend to be considerably faster than those of platinum (II) and as such have not been investigated extensively. However, the ligand exchange studies which have been made include very few phosphine complexes. The rather limited literature on the ligand exchange reactions of group VIII phosphine complexes is reviewed below.

Eaton and Stuart\(^{33}\) studied the exchange of \([(C\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}\) with \((C\text{C}_6\text{H}_5)_3\text{P}\) and \((p\text{CH}_3\text{C}_6\text{H}_4)_3\text{P}\). Their results show that the distribution of \((C\text{C}_6\text{H}_5)_3\text{P}\) and \((p\text{CH}_3\text{C}_6\text{H}_4)_3\text{P}\) is nearly statistical and that the para tolyl ligand acts only as a labelled triphenylphosphine. Although the exchange of free and complexed ligand was fast at +18°C, cooling to approximately -30°C slowed the rate of exchange sufficiently that the NMR spectrum obtained was typical of a slow exchange process (see Chapter II). These workers found that the rate of cis-trans isomerization in these complexes was faster than the rate of exchange.

Powell and Shaw\(^{34}\) examined the rate of \((\text{CH}_3)_2(C\text{C}_6\text{H}_5)\text{P}\) exchange with a series of iridium (III) phosphine complexes, \(L_3\text{IrHCl}_2\). They found that only the phosphine trans to the hydride is exchanged.

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \\
\text{L} \\
\text{Ir} \\
\text{L} \\
\text{Cl} \\
\text{H}
\end{array}
+ (\text{CH}_3)_2(C\text{C}_6\text{H}_5)\text{P} & \rightarrow \\
\begin{array}{c}
\text{Cl} \\
\text{L} \\
\text{Ir} \\
\text{L} \\
\text{Cl} \\
\text{H}
\end{array}
\end{align*}
\]

and for all complexes studied the reaction proceeded to completion.
The rate of exchange was found to be highly dependent on the nature of L in the iridium complex, the observed order of decreasing rate being

\[(C_2H_5)_3As \rightarrow (C_2H_5)_3P \rightarrow (nC_3H_7)_3P \rightarrow (C_2H_5)_2(C_6H_5)P \rightarrow (nC_3H_2)_2(C_6H_5)P\]

The rhodium carbonyl complex \([(C_6H_5)P]_2RhCO\] has been the subject of several ligand exchange studies. Wojcicki and Basolo found the rate of $^{14}C\text{O}$ exchange too fast to measure using conventional radiocarbon techniques. Similarly, it has been found that $^{35}Cl$ exchange is again too fast to monitor. Shaw et al. showed that phosphine exchange of \([(CH_3)_2(C_6H_5)P]RhCO\] was fast on the NMR time scale. It was postulated that the exchange proceeded via a five coordinate intermediate

\[\{(CH_3)_2(C_6H_5)P\}_2RhCOCl + (CH_3)_2(C_6H_5)P \rightarrow [(CH_3)_2(C_6H_5)P]_3RhCOCl\]

In a later publication from this laboratory it was reported that exchange reactions of the iridium analogue of the complex discussed above, \([(CH_3)_2(C_6H_5)P]_2IrCOCl\], with \((CH_3)_2(C_6H_5)P\) resulted in conducting solutions. Arguing by analogy with the results of some synthetic work published in the same communication, these workers proposed the following alternate pathways for the formation of cationic iridium complexes:

\[
\begin{align*}
{(CH_3)_2(C_6H_5)P}_2Ir(CO)Cl & \quad \rightarrow \quad [(CH_3)_2(C_6H_5)P]_3Ir(CO) + \\
{(CH_3)_2(C_6H_5)P}_2Ir(CO) & \quad \rightarrow \quad [(CH_3)_2(C_6H_5)P]_4Ir(CO) +
\end{align*}
\]

Taylor and Hathaway have shown that the substitution by bromide in \([(C_6H_5)P]_2PtCl_2\) proceeds through an intermediate in which there is considerable platinum-bromine bond formation and little platinum-chlorine bond weakening. However, it has also been reported that the exchange of radiocloride with \([(C_6H_5)P]_2PtCl_2\) shows a zero order dependence on
[Cl\textsuperscript{-}]. This was taken as indicative of a dissociative mechanism for
the exchange. As was pointed out earlier the kinetic expression for
substitution in square-planar d\textsuperscript{8} systems contains two terms.

It is possible that in the above two experiments, the magnitude of the
two rate sets of constants K\textsubscript{1} and K\textsubscript{2} are vastly different such that
in the bromide reaction the second order rate constant is important
while in the chloride exchange the pseudo first order term is dominant.
However, the reason for such a large difference between the chloride
and bromide does not seem clear.

As part of a study on phosphine ligand exchange in "virtually
coupled" systems (see Chapter II), Fackler\textsuperscript{40} observed that the methyl
resonance of cis [[(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})P]\textsubscript{2}PdCl\textsubscript{2}] collapses (loss of phosphorus
hydrogen coupling (J\textsubscript{P-H}) when (CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})P is added. Fackler describes
the observed single methyl resonance as a collapsed triplet. This
interpretation is somewhat puzzling since the observed methyl \textsuperscript{1}H NMR
signal of cis[[(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})P]\textsubscript{2}PdCl\textsubscript{2}] is a doublet. However, even allowing
for this problem, Fackler's interpretation of the collapse of the
observed signal as resulting solely from a simple exchange process is
shown to be in error (Chapter III).

Phosphine exchange reactions of tetrahedral phosphine complexes
of divalent nickel and cobalt complexes, L\textsubscript{2}MX\textsubscript{2} (M = Ni, Co, X = Cl, Br,
I; L = (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P, (pCH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{3}P, and n(C\textsubscript{4}H\textsubscript{9})\textsubscript{3}P) have been studied by L.
Pignolet and Dew Horrocks.\textsuperscript{41} These workers found that the phosphine
exchange was faster for the nickel (II) complexes than for the cor-
responding cobalt (II) complexes.

The rate of phosphine exchange was observed to be halide dependent,
being fastest for Cl. The order of decreasing rate was
Cl > Br > I. The kinetic data obtained by these workers is shown in Table 1-2 and illustrates the metal, phosphine and halide dependence of the rate of exchange. It is to be noted that the rate does not seem to be determined solely by the enthalpy of activation ($\Delta H^\dagger$) but rather by both the enthalpy and entropy ($\Delta S^\dagger$) of activation. The observation of second order kinetics is in accord with the usually observed associative reaction mechanism of substitution in four coordinate $d^8$ systems.

In a study of the ligand exchange reactions of zero-valent phosphinite complexes of the nickel triad, Meier, Basolo and Pearson$^{42}$ showed that the exchange proceeds by a dissociative mechanism. Since four coordinate $d^{10}$ systems are coordinately saturated a dissociative mechanism is the expected reaction pathway. The relative rates of reaction showed the order Ni > Pd > Pt. This order parallels the measured enthalpies ($\Delta H$) for the reaction

$$[(C_2H_5O)_3P]_4M + [(C_2H_5O)_3P]_3M + (C_2H_5O)_3P$$

This implies that the rate of reaction is determined by the strength of the phosphorus metal bond and that while the entropy term for such a reaction, may be large, it is at least constant for the series of complexes studied. In particular, for the nickel complexes studied, the rate was observed to decrease as the phosphate ligands were changed showing the order $(C_6H_5O)_3P > (C_2H_5O)_3P > (CH_3O)_3P > P(OCH_2)_3CCl_3H_7$. The relative ordering of the various phosphate ligands parallels the order of decreasing size and the results of this study were interpreted in terms of the decreasing steric requirements of these ligands. That is, the dissociative (rate determining step) is fastest for the bulkiest
<table>
<thead>
<tr>
<th>L</th>
<th>M</th>
<th>X</th>
<th>$k_2$ (± 0.5)</th>
<th>$\Delta H^\ddagger$ kcal/mole</th>
<th>$\Delta S^\ddagger$ eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C$_6$H$_5$)$_3$P</td>
<td>Ni</td>
<td>Cl</td>
<td>$3.2 \times 10^5$</td>
<td>8.1 ± 0.8</td>
<td>-7 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$6.9 \times 10^3$</td>
<td>4.7 ± 0.4</td>
<td>-25 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$6.4 \times 10^2$</td>
<td>6.9 ± 0.6</td>
<td>-23 ± 3</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$P</td>
<td>Co</td>
<td>Cl</td>
<td>$1.2 \times 10^4$</td>
<td>8.8 ± 0.8</td>
<td>-10 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$8.7 \times 10^2$</td>
<td>7.7 ± 0.5</td>
<td>-19 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$2.6 \times 10^2$</td>
<td>9.1 ± 0.7</td>
<td>-17 ± 4</td>
</tr>
<tr>
<td>[pCH$_3$(C$_6$H$_5$)]$_3$P</td>
<td>Ni</td>
<td>Cl</td>
<td>$1.9 \times 10^4$</td>
<td>5.3 ± 0.8</td>
<td>-21 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$6.1 \times 10^3$</td>
<td>5.2 ± 0.8</td>
<td>-24 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$5.9 \times 10^3$</td>
<td>5.2 ± 0.8</td>
<td>-24 ± 4</td>
</tr>
<tr>
<td>[pCH$_3$(C$_6$H$_5$)]$_3$P</td>
<td>Co</td>
<td>Cl</td>
<td>$2.2 \times 10^3$</td>
<td>4.4 ± 0.9</td>
<td>-29 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$1.8 \times 10^3$</td>
<td>5.5 ± 0.9</td>
<td>-25 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$8.3 \times 10^2$</td>
<td>5.9 ± 0.9</td>
<td>-25 ± 5</td>
</tr>
<tr>
<td>(nC$_4$H$_9$)(C$_6$H$_5$)$_2$P</td>
<td>Co</td>
<td>Br</td>
<td>$8.3 \times 10^3$</td>
<td>7.1 ± 0.5</td>
<td>-17 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$1.1 \times 10^2$</td>
<td>7.7 ± 0.6</td>
<td>-23 ± 4</td>
</tr>
</tbody>
</table>
### TABLE 1-2

Kinetic Parameters for Ligand Exchange in $L_2MX_2$

<table>
<thead>
<tr>
<th>$L$</th>
<th>$M$</th>
<th>$X$</th>
<th>$k_2$ ($\pm 0.5$)</th>
<th>$\Delta H^\dagger$ kcal/mole</th>
<th>$\Delta S^\dagger$ eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_6H_5)_3P$</td>
<td>Ni</td>
<td>Cl</td>
<td>$3.2 \times 10^5$</td>
<td>$8.1 \pm 0.8$</td>
<td>$-7 \pm 4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$6.9 \times 10^3$</td>
<td>$4.7 \pm 0.4$</td>
<td>$-25 \pm 2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$6.4 \times 10^2$</td>
<td>$6.9 \pm 0.6$</td>
<td>$-23 \pm 3$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>Cl</td>
<td>$1.2 \times 10^4$</td>
<td>$8.8 \pm 0.8$</td>
<td>$-10 \pm 4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$8.7 \times 10^2$</td>
<td>$7.7 \pm 0.5$</td>
<td>$-19 \pm 3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$2.6 \times 10^2$</td>
<td>$9.1 \pm 0.7$</td>
<td>$-17 \pm 4$</td>
</tr>
<tr>
<td>[pCH$_3(C_6H_5)]_3P$</td>
<td>Ni</td>
<td>Cl</td>
<td>$1.9 \times 10^4$</td>
<td>$5.3 \pm 0.8$</td>
<td>$-21 \pm 4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$6.1 \times 10^3$</td>
<td>$5.2 \pm 0.8$</td>
<td>$-24 \pm 4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$5.9 \times 10^3$</td>
<td>$5.2 \pm 0.8$</td>
<td>$-24 \pm 4$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>Cl</td>
<td>$2.2 \times 10^3$</td>
<td>$4.4 \pm 0.9$</td>
<td>$-29 \pm 5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>$1.8 \times 10^3$</td>
<td>$5.5 \pm 0.9$</td>
<td>$-25 \pm 5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$8.3 \times 10^2$</td>
<td>$5.9 \pm 0.9$</td>
<td>$-25 \pm 5$</td>
</tr>
<tr>
<td>$(nC_4H_9)(C_6H_5)_2P$</td>
<td>Co</td>
<td>Br</td>
<td>$8.3 \times 10^3$</td>
<td>$7.1 \pm 0.5$</td>
<td>$-17 \pm 3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>$1.1 \times 10^2$</td>
<td>$7.7 \pm 0.6$</td>
<td>$-23 \pm 4$</td>
</tr>
</tbody>
</table>
ligand.

A similar study of nickel (0) phosphine complexes was reported by Tolman who observed similar results to those obtained above. The rate of phosphine exchange in nickel (0) phosphines also seems to be determined by steric considerations.

Finally, phosphine exchange reactions have been commonly used as a synthetic route to the preparation of complexes from triphenylphosphine complexes. Such reactions provide a convenient method to obtain complexes which are not formed by the reactions which yield the common triphenylphosphine complexes.
The combination of a charge and a spin produces a nuclear magnetic moment \( \mu_n \) given by

\[
\mu_n = \gamma_n \hbar = g_n \beta_n
\]  

(4)

where \( \gamma_n \) is the magnetogyric ratio and the nuclear magneton \( \beta_n \) is

\[
\beta_n = \frac{e \hbar}{2mc}
\]  

(5)

and \( g_n \) is a dimensionless constant (nuclear g factor). In (5), \( e \) and \( m \) are the charge and the mass of the proton while \( c \) is the velocity of light.

Upon the application of a magnetic field, an interaction between the field \( \mathbf{H} \) and the magnetic moment occurs. This interaction is described by the Hamiltonian:

\[
H = -\mathbf{\mu}_n \cdot \mathbf{H}
\]  

(6)

Assuming the magnetic direction is \( z \), then expression (6) becomes

\[
H = -\gamma_n \hbar \mathbf{I}_z = -g_n \beta_n \hbar \mathbf{I}_z
\]  

(7)

where \( \mathbf{I}_z \) is the allowed component in the \( z \) direction.

For the case of a proton, the allowed values of \( \mathbf{I}_z \) are \( \pm \frac{1}{2} \).

The energy level diagram (Fig. 2-1) shows that the two states \( (I = \frac{1}{2}) \) are split by a magnetic field. This splitting is given by:

\[
\hbar \nu = g_n \beta_n \hbar
\]  

(8)

and is thus magnetic field dependent. If both \( \beta_n \) and \( g_n \) are positive, as is the case for protons, then the upper level corresponds to the state for which the allowed component of nuclear spin is \( \frac{1}{2} \), while the lower state corresponds to \( -\frac{1}{2} \).
Fig. 2-1  Energy Level Diagram for Proton in a Magnetic Field $H$
(after Carrington and McLachlan 43A)

\begin{align*}
1 \beta > m_I &= -\frac{1}{2} \\
\hbar \nu &= g_B N \mu_N^H \\
1 \alpha > m_I &= +\frac{1}{2}
\end{align*}

Field ($H$) →
Physically this corresponds to the upper state \( \beta \) possessing a nuclear moment opposed to the field while the lower state \( \alpha \) possesses a nuclear moment parallel to the field. Under conditions of thermal equilibrium, the lower \( \alpha \) state will be more populated although the difference in populations is small (approximately one molecule in \( 10^5 \)) due to the small energy separation.

Transitions may be induced between the two energy levels by the application of an oscillating electromagnetic field. Energy absorption occurs when the resonance condition is satisfied (8), where \( \nu \) is the frequency of the oscillating electromagnetic field. The induced transitions in either direction are equally probable and energy absorption is only observed when the \( \alpha \) state is more highly populated. Equation (8) shows that the NMR experiments may be performed by either holding the magnetic field (\( H \)) constant and varying the frequency (\( \nu \)) or by holding \( \nu \) constant and varying \( H \).

As was pointed out above, the observation of energy absorption requires an excess of nuclei in the lower \( \alpha \) state. Time dependent perturbation theory shows that when a time dependent perturbation \( \nu(t) \) is applied to this system, the probability of a transition from \( \alpha \) to \( \beta \) states, \( P_{\alpha \beta} \), is given by:

\[
P_{\alpha \beta} = \frac{2\pi}{\hbar} |<\beta|\nu|\alpha>|^2 \delta(E_\beta - E_\alpha - \hbar \nu)
\]

The matrix element \( <\beta|\nu|\alpha> \) shows that the perturbation mixes states \( \beta \) and \( \alpha \). The Dirac delta function \( \delta \) is zero unless \( \hbar \nu \) is equal to the energy difference \( E_\beta - E_\alpha \).

The rate of change of population of the \( \alpha \) state is

\[
\frac{dN_\alpha}{dt} = N_B P_{\alpha \beta} - N_B P_{\beta \alpha} = P(N_B - N_\alpha)
\]

(10)
where \( P \) is the probability of a stimulated transition. When the population difference is \( n \), equation (10) reduces to

\[
\frac{dn}{dt} = -2P \ n
\]  
(11)

the solution of which is

\[
n = n(0)e^{-2Pt}
\]  
(12)

Thus, although there is an initial population difference \( n(y) \), this difference decreases exponentially to zero. This means that the observed resonance line will disappear.

However, since the system is in thermal equilibrium, the probability of spontaneous transitions are not equal for upward and downward transitions. Thus, the coupling of the spin system to the thermal motion of the lattice results in spin lattice relaxation. The spin lattice relaxation allows energy to be transferred to the lattice from the spin system by radiationless transitions to maintain the population difference.

From the above considerations, the rate of population change is

\[
\frac{dn}{dt} = \frac{n-n_0}{T_1}
\]  
(13)

where \( T_1 \) is the spin lattice relaxation time. Thus, the NMR experiment is possible as long as the spin lattice relaxation time is sufficiently short to maintain the population difference.

The observed frequency at resonance differs from atom to atom in a particular molecule. This difference results from the fact that the application of a magnetic field to a molecule induces an electric current, which generates an opposing magnetic field, which is proportional
to the applied magnetic field. Thus, the effective magnetic field experienced by the particular nucleus is

$$H_{\text{eff}} = (1-\sigma)H$$

(14)

where $\sigma$ is the screening constant and the nuclear Zeeman energy is

$$H_0 = -g_n \mu_n (1-\sigma)H z$$

(15)

The difference in the observed resonance frequency is called the chemical shift.

For a simple system such as CH$_3$CHBr$_2$, there are two types of non-equivalent protons. The methyl protons have four possible spin states

$$
\begin{align*}
&\alpha\alpha \alpha \\
&\alpha\beta\alpha \quad \alpha\alpha \beta \\
&\beta\beta\alpha \quad \alpha\beta\beta \\
&\beta\beta\beta 
\end{align*}
$$

(16)

The coupling of the CHBr$_2$ proton with the spin states of the methyl protons can thus occur in four ways with a probability of 1:3:3:1. This results in the observed spectrum for the CHBr$_2$ proton of four lines of relative intensity of 1:3:3:1, separated by $J$, the coupling constant.

Similarly, the CH$_3$ protons can couple to either of the two equally probable spin states of the CHBr$_2$ proton. Thus, the methyl resonance will be observed as a 1:1 doublet. The complete treatment of this system shows that

$$\nu_{\text{CHBr}_2} = \nu_0 (1-\sigma)_{\text{CHBr}_2} - J_{\text{CH}_3}$$

where $M_{\text{CH}_3}$ is
\[ M_{CH_3} = m_{H_1} + m_{H_2} + m_{H_3} \]

This spin-spin coupling is extremely helpful in interpreting spectra, provided the coupling constant \( J \) between the coupled spins is much smaller than the chemical shift difference. In cases where \( J \) is of the same order as the chemical shift difference, the observed spectra are not first order and the interpretation of such spectra is considerably more difficult.

The screening constant \( \sigma \) is actually a sum of several components:

\[ \sigma = \sigma_d + \sigma_p \]

where \( \sigma_d \) is a diamagnetic contribution and \( \sigma_p \) is a paramagnetic contribution. The diamagnetic contribution depends upon the ground state electron density distribution, while the paramagnetic contribution depends upon the mixing of ground and excited states. Since \( \sigma \) depends upon two contributions, changes in chemical shift, which depend upon changes in \( \sigma \), must be interpreted with considerable care. In proton (\( ^1H \)) NMR, the contribution to \( \sigma \) from both \( \sigma_d \) and \( \sigma_p \) are important. However, for many other nuclei, (\( ^{19}F \) and \( ^{13}C \)) the paramagnetic term usually dominates.

As was pointed out above, the chemical shift is magnetic field dependent and thus the separation of two resonances will increase with increasing magnetic field. Early NMR spectrometers operated at 60 MHz using normal or electromagnets. In order to take advantage of the increased resolution available at higher fields later instruments were designed to operate in the region 90-100 MHz. Such instruments employ an electromagnet. Further increases in magnetic field were not forth-
coming since in addition to high magnetic fields, very uniform and stable fields are required. The stability problem was overcome by the use of a "locked" operating mode in which the instrument was "locked" onto a reference signal, which made possible the use of fields which would not otherwise be stable enough for high resolution work. Recently, the advances in superconductors has made it possible to achieve extremely high magnetic fields using such superconducting magnets. These magnets require very low temperatures (liquid helium temperatures) which presents some cryogenic problems but instruments employing such magnets now operate in the region 200-300 MHz. Such instruments have the advantage of extremely good resolution and extremely stable magnets. In addition the sensitivity depends upon the 3/2 power of the magnetic field. Thus, it is obvious that at higher magnetic fields increased sensitivity is expected. Because of the problems of handling the higher frequency radiation, the expected increase in sensitivity has not been fully achieved. However, there is still a substantial increase in sensitivity available in going from a 100 MHz instrument to a spectrometer operating in the 200-300 MHz range.

Many of the spectra reported in this thesis are characterized by small chemical shift differences between resonances, thus most of the proton (\(^1\)H) NMR results were obtained using a 220 MHz nuclear magnetic resonance spectrometer. Beside the improved resolution available using such an instrument (a factor of 2.2 over the more commonly available 100 MHz instruments), the improved sensitivity facilitated the study of dilute solutions.
2.2 NMR AND RATE PROCESSES

The study of rate processes is a particularly active field of modern chemical research. Since the time scale of the NMR method corresponds to the time scale of many reactions, NMR has proved to be an extremely useful tool in kinetic studies.

For the chemical exchange of a proton between two sites, A and B, the NMR signal observed will depend upon the frequency of this exchange. In the slow exchange limit, the frequency at which the proton jumps from one site to the other is less than the reciprocal of the chemical shift difference. In this case, signals are observed for both A and B species at the resonance frequencies $\omega_A$ and $\omega_B$. The exchange frequency $\omega_E$ is much smaller than the frequency separation of the A and B resonance lines.

When the exchange frequency is small, the lines will be broadened with a width $\delta \omega \approx \omega_E$. Such exchange broadening must, of course, be in excess of the natural line width of the NMR signal to be observed.

In the fast exchange limit, the exchange frequency is much greater than the frequency separation of the A and B lines. This results in the observation of a single peak at the average frequency position and the peak has a width of $\delta \omega = \frac{\Delta \omega^2}{\omega_E}$.

Thus, from the slow exchange limit of two sharp and separate peaks, the increasing exchange frequency first broadens the individual peaks, then begins to shift each peak towards an average position. Finally, the peaks coalesce at the average position and with even higher exchange frequencies, the averaged peak begins to sharpen.

These effects can often be observed by changing the sample temperature and taking advantage of the temperature dependence of the reaction.
rates. Such a process is shown in Figure 2-2, for the hindered rotation of N,N-dimethylnitrosoamine. At low temperature, two resonances for the non-equivalent CH$_3$ groups are observed but at higher temperatures, the rate of rotation increases until only a single averaged resonance is observed.

2.3 EXCHANGE LIFETIMES FROM NMR

The determinations of exchange lifetimes from NMR spectra is a fairly simple process for the case of a proton exchanging between two sites when the limiting (slow exchange) spectrum consists of two single lines.

1. Slow Exchange

In cases where the exchange is slow enough that the only effect is lifetime broadening of the two lines, the signal due to the species A centred at $\omega_A$ will have a width $T_{2a}^{-1}$.

$$T_{2a}^{-1} = T_{2a}^{-1} + \tau_a^{-1}$$

(19)

where $T_{2a}^{-1}$ is the width of the signal in the absence of exchange and $\tau_a^{-1}$ is the mean lifetime for the A state.

2. Intermediate Exchange

For the case of intermediate exchange, the resonance positions are shifted towards each other but the signals have not yet coalesced. The full expression for intensity of the absorption is very complicated, however the value of $\tau$ can be calculated from:

$$\frac{\text{separation of peaks}}{\text{separation of peaks for larger } \tau} = 1 - \frac{1}{2\pi \tau^2 (\nu_A - \nu_B)^2}$$

(20)
Fig. 2-2  Temperature Effect on NMR Line Shapes

40 MHz $^1$H NMR Spectra of N,N-dimethylnitrosamine
where \( \tau \) is \( \tau_A \tau_B / \tau_A + \tau_B \).

A simpler method is the use of the coalescence temperature. The value of \( \tau \) at the coalescence point is given by

\[
\tau = \frac{\sqrt{2}}{2\pi(v_A - v_B)}
\]  

(21)

3. Fast Exchange

In the fast exchange only a single peak is observed and \( \tau_A \) and \( \tau_B \) are small.

The position, \( \omega \), of the resonance will be

\[
\omega = p_A\omega_A + p_B\omega_B
\]  

(22)

where \( p_A \) and \( p_B \) are the fractional populations of the respective sites \( p_A = \tau_A / \tau_A + \tau_B \) and \( p_B = \tau_B / \tau_A + \tau_B \). The width of the line is given by

\[
\frac{1}{T_2} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + \frac{p_A p_B}{p_{AB} + p_{BA}} (\omega_A - \omega_B)
\]  

(23)

2.4 NMR SPECTRA OF COORDINATED METHYL PHOSPHINES

The spectra observed for complexes of methyl phosphines \((\text{CH}_3)_n(\text{C}_6\text{H}_5)_3-n\text{P}(n = 1,2,3)\) are more complicated than might be first anticipated, particularly for trans arrangements of phosphines. This complication arises from strong phosphorus-phosphorus coupling.

For a bis \((\text{CH}_3\text{C}_6\text{H}_5)_2\text{P}\) complex,

\[
\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P} \xrightarrow{X} \text{M} \xrightarrow{P(\text{C}_6\text{H}_5)_2\text{CH}_3}
\]

the spectrum is described as \(X_3\text{AA}^\prime X_3^\prime\). This is a special case of the
The important parameters in this system are the X-A couplings, $J_{AX}$ and $J_{A'X'}$; the X-A couplings $J_{XX}$, and $J_{XX'}$, and the A-A coupling $J_{AA'}$. For the case of the bis CH$_3$(C$_6$H$_5$)$_2$P complexes, this reduces to

$$J_{AA'} = J_{A'A} = J_A$$

$$J_{AX} = J_{A'X'}$$

and

$$J_{AX'} = J_{A'X}$$

Harris defined the quantities;

$$L = J_{AX} - J_{AX'}$$

and

$$N = J_{AX} + J_{AX'}$$

The calculated spectra have the following characteristics in the X (methyl) region.

1. There are a total of $2n + 1$ pairs of lines symmetrically arranged about the resonance position of the X nuclei ($\nu_X$).
2. One-half of the total intensity of the X spectrum occurs as a doublet of separation N centred on $\nu_X$.
3. The remaining half of the intensity is made up by the remaining $2n$ pairs of lines.
4. The intensity of the lines (other than the doublet of separation N) and the position of the lines depends upon $L/J_A$.

The calculated spectra for various values of $L/J_A$ are shown in Figure 2-3. The spectrum shown in Figure 2-3(a) approaches the case of
Fig. 2-3  Calculated Spectra for $X_3AA'^X_3'$ after Harris\textsuperscript{44}

a. $L/|J_A| = 10$

b. $L/|J_A| = 2$

c. $L/|J_A| = 0.5$

d. $L/|J_A| = 0.1$
very small A-A coupling. When L and N are approximately equal, the
two doublets will not be resolved and only a single doublet will be
observed. This is the case normally observed for the cis arrangement
of methyl phosphines. That is, the phosphorus-phosphorus coupling is
small and the methyl resonance is observed as a doublet. Spectra 2-3(d)
approaches the case of very large A-A' coupling. Here a "simple"
triplet will be observed when the inner lines are not resolved. This
simple triplet is the spectrum normally observed for a trans arrange-
ment of phosphines in a bis methyl phosphine complex, since in these
complexes the phosphorus-phosphorus coupling, J_{P-P}, is normally very
large.

This method of determining stereochemistry of transition metal
phosphine complexes was first reported by Jenkins and Shaw. These
workers reported the $^1$H (methyl) NMR spectra of several complexes of
(CH$_3$)$_2$(C$_6$H$_5$)P. The palladium complex, trans [(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PdI$_2$, gave
a triplet resonance while the platinum complex [(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PtCl$_2$
gave a doublet. The complex [(CH$_3$)$_2$(C$_6$H$_5$)P]$_3$IrCl$_3$ gave both a triplet
and a doublet with an intensity ratio 2/1. The ruthenium complex
[(CH$_3$)$_2$(C$_6$H$_5$)P]$_3$Rh(CO)Cl$_2$ gave results similar to the iridium (III)
complex.

Since the publication of the work by Jenkins and Shaw, this
approach has become a standard route to structural elucidation in transi-
tion metal phosphine chemistry and has been applied to such ligands as
(CH$_3$)$_3$P, (CH$_3$)(C$_6$H$_5$)$_2$P, (CH$_3$)$_2$(C$_6$H$_5$)P, and [(CH$_3$)$_3$Cl]$_3$P. A
recent report indicates that the familiar doublet and triplet
patterns occur in the $^{13}$C NMR spectrum of C(1) carbon of complexed tri-
phenyl phosphine.

2.5 THEORY OF CONDUCTIVITY

Since several of the reactions studied in this work resulted on the formation of ionic products, conductivity studies were undertaken (see Chapters III and IV). The theory of conductivity and some particular problems related to conductivity in non-aqueous solutions are given below.

Theory of Conductivity

The fundamental relationship describing electrical conductivity in solids, fused salts or solutions is Ohm's Law, $I = \frac{E}{R}$. For a conductor of length $l$ and cross-section $A$, the resistance $R$ is given by $R = \rho \frac{l}{A}$ where $\rho$ is the specific resistance (resistivity). The reciprocal of the resistance is the conductance (ohm$^{-1}$) and the reciprocal of the resistivity is $K$ (ohm$^{-1}$cm$^{-1}$), the conductivity.

Over a century ago, Kohlrausch defined the equivalent conductivity $\Lambda = 1000 \text{k/c}$ where $c$ is the concentration of solute in gram equivalents per liter. In later work Kohlrausch established that the equivalent conductivity is the sum of the ionic conductivity $\Lambda = \Lambda^+ + \Lambda^-$ where the $\Lambda$'s are contributions due to the cation and anion, respectively.

The fraction of current which an ionic species carries depends upon the transport number, $t$, for that ion.

$$t^+ = \frac{\lambda^+}{\Lambda} \quad \text{and} \quad t^- = \frac{\lambda^-}{\Lambda}$$

Thus, a general expression for conductivity is $K = \sum \left| Z_i e \right| \omega_i$ where $N$ is the number of charge carriers per unit volume, $\left| Z_i e \right|$ is the value
of the charge and \( u_i \) is the mobility of the ion (velocity in electric field of unit strength).

Consideration of this relationship shows that the measured conductivity of a solution depends upon the concentration of charge carriers, their charges and mobilities. More precisely, the dependence of conductivity on concentration is only true at very low solute concentrations, since only under these conditions is the concentration approximately equal to the activity.

2.6 **EXPERIMENTAL CONSIDERATIONS**

Conductivities are normally measured using conductivity bridges which are simply balancing circuits of the Wheatstone-type. Invariably the voltage applied to a cell used for conductance measurements is alternating current. This alleviates the problem of polarization (non-equilibrium) conditions which occur at the electrode when direct currents are used.

The cell may be of any of a number of designs, the common feature being the use of two plates (electrodes), usually fabricated of platinum. Cell constants are normally obtained by measurements of the conductivity of a standard solution (usually one molar potassium chloride in water).

**Conductivity in Non-Aqueous Solvents**

The ability of a solvent to solvate an ion depends upon the dielectric constant of the solvent. Water, with a very high dielectric constant (80.37 at 20°C), is very efficient at ion separation. However, in solvents with much lower dielectric constants, such as most organic solvents, simple salts which are completely ionized in water are only partly
ionized. A considerable amount of even a simple salt such as potassium iodide is undissociated in organic solvents. Table 2-1 shows the dissociation constants $K$ for solvents of different dielectric constants.$^5$1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>$K$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>20.7</td>
<td>8.0</td>
</tr>
<tr>
<td>n propanol</td>
<td>20.1</td>
<td>3.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>12.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

This increases the difficulty of interpreting non-aqueous conductivity results. The ionic conductivities $\lambda^+$, the equivalent conductivities $\lambda$, the transport numbers $t^+$, the mobilities $\mu$ and the dissociation constants for the ion pairs are largely unknown even for simple electrolytes in organic solvents.

Detailed treatment of theoretical and practical aspects of conductivity measurements has been given by Weissberger.$^52$
CHAPTER III

STUDIES OF PALLADIUM(I) PHOSPHINE COMPLEXES

3.1 INTRODUCTION

Phosphine complexes of divalent palladium are well-known. These complexes, formulated as \( \text{L}_2\text{PdX}_2 \) where \( \text{L} \) is a phosphine and \( \text{X} \) is a halide or pseudohalide, are stable, yellow to brown crystalline solids, soluble in many organic solvents. The geometry of the complexes is square planar and as such they may exist as cis or trans isomers as shown in Figure 3-1. The complex \( [(\text{CH}_3)_3\text{P}(\text{C}_6\text{H}_5)]_2\text{PdCl}_2 \) exists as a mixture of both isomers.\(^{53}\)

![Diagram of cis and trans isomers]

Figure 3-1

The complexes may be prepared directly by reaction of the phosphine and \( \text{K}_2\text{PdX}_4 \), or by the exchange of either phosphine or halide with the commercially available \( [(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PdCl}_2 \). The \(^1\text{H} \) NMR spectra of a number of methyl-substituted phosphine complexes have been previously reported. In particular, the complexes \( [(\text{CH}_3)_3\text{P}]_2\text{PdX}_2 \),\(^{54}\) \( [(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PdX}_2 \),\(^{55}\) and \( [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PdX}_2 \)\(^{55}\) have been studied and their \(^1\text{H} \) NMR spectra reported. However, these studies were restricted to structural assignments based upon the virtual coupling phenomenon discussed in Chapter II. Similarly a number of \(^{31}\text{P} \) NMR studies of palladium (II) phosphine complexes have been reported.\(^{56,57}\) In one\(^{56}\) of these \(^{31}\text{P} \) studies it was observed that addition of mixed alkyl-aryl phosphine to alkyl-aryl
phosphines of palladium (II) solutions resulted in a colour change from yellow to red. It was also noted that free and complexed ligands were in fast exchange (on the NMR time scale).

The only attempt to study phosphine ligand exchange in palladium (II) complexes was reported by Fackler. In this publication, Fackler discussed the effect of ligand exchange on line shape, for complexes which show virtually coupled NMR spectra. Fackler observed the collapse of the virtual coupling pattern of the complex cis \([(\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{P}]_2\text{PdCl}_2\) when \((\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{P}\) was added and attributed this observation to a simple exchange process. As pointed out in Chapter I, Fackler's description of the observed single resonance line as a "collapsed triplet" is somewhat puzzling. This observation was further investigated in this present study and the phosphine exchange reactions of a number of palladium (II) phosphine complexes are reported in this chapter.

3.2 EXPERIMENTAL RESULTS

1. \(^1\text{H} \text{NMR}\)

The \(^1\text{H} \text{NMR}\) spectrum of \([(\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{P}]_2\text{PdCl}_2\) in CDCl\(_3\) at 18°C and 220 MHz gave a complex resonance between \(\delta = 7.7\) ppm and \(\delta = 7.3\) ppm. This complex multiplet is easily assigned to the aromatic protons of the complexed \((\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{P}\). Generally, it was found that the aromatic region of the NMR spectra was uninformative, since the resonances due to the various aromatic protons are badly overlapped. In subsequent discussions of such spectra, the aromatic region will not be mentioned.

In addition to the aromatic resonances, the only other observed resonance was a doublet \((J = 11 \text{ Hz})\) at \(\delta = 1.77\) ppm, assigned to the \(\text{CH}_3\) protons of the complexed \((\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{P}\). As discussed in Chapter II, the observation
of a simple doublet shows the complex to have a cis geometry. This resonance can be assigned with some degree of confidence since the coupling constant (J = 11 Hz) is about the magnitude usually found for complexed methyl phosphine while the value of the coupling constant in the free phosphine is only about 3 Hz. Furthermore, the observed chemical shift of δ = 1.77 ppm is considerably different from the shift observed for the free ligand (δ = 1.34 ppm). In addition, the presence of the free ligand can be discounted since, as will be shown below, the presence of free ligand causes collapse of the coupling constant and the appearance (at least at 18°C) of a single resonance.

When \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) is added to a CDCl\textsubscript{3} solution of cis \([\{(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\}_2\text{PdCl}_2] \) at 18° the methyl doublet of the complex collapses to give a single resonance and no resonance due to free \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) is observed. This confirms the observations of Fackler. However, when the experiment is repeated at -50°C, the resonance due to the starting complex decreases in intensity and two new resonances are observed. The new resonances increase in intensity as more \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) is added until, when the mole ratio of added ligand to complex (L:M) equals one, no resonance due to cis \([\{(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\}_2\text{PdCl}_2] \) is observed. These results are shown in Figure 3-2 where the spectra obtained for various values of L:M are reproduced. Obviously, these results show that Fackler's analysis of the collapse of the complex resonance upon addition of free ligand is incorrect since a new species is being formed. Fackler instead, was observing a fast exchange process involving the starting complex, \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\), and some new species.

The low temperature spectrum described above is consistent with the formation of a new species \([\{(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\}_3\text{PdCl}_2\cdot\text{Cl}^-] \). This species
Fig. 3-2  220 MHz spectra ($^1$H) obtained by addition of $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}$ to a CDCl$_3$ solution of cis$[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PdCl}_2$ at -50°C.

1. $L/M = 0$

2. $L/M = 0.4$

3. $L/M = 0.8$

4. $L/M = 1.0$
would be expected to be isostructural with the well-known compound \[ (\text{C}_6\text{H}_5)_3\text{P}_3\text{RhCl} \]. The NMR spectrum shows two non-equivalent phosphine ligands in the ratio 2:1 as expected. The low field triplet shown in Fig. 3-2 can be assigned to the two mutually trans phosphines of the cation which are expected to be virtually coupled while the high field doublet can be assigned to the unique phosphine trans to the chloride.

During the course of this work, complexes similar to that postulated above were reported by Powell and coworkers\textsuperscript{22} for several platinum compounds. These workers found that the reaction of \[ (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{Pt}_2 \] with \( (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P} \) produced \[ (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{PtX}_2^+X^- \]. These complexes were isolated and characterized as the PF\textsubscript{6}^- salts and gave NMR spectra similar to that discussed above. Powell's NMR results are summarized in Table 3-1. In a very recent paper\textsuperscript{23} from the same laboratory, it was shown that cationic palladium complexes are intermediates in the cis-trans isomerization of palladium phosphine complexes. Cationic palladium phosphine complexes have been previously reported by Clarke and coworkers\textsuperscript{58} but these compounds were prepared under somewhat forcing conditions.

\[
\text{L}_2\text{PdX}_2 + \text{L} + \text{NaB}(\text{C}_6\text{H}_5)_4 \rightarrow \text{L}_3\text{PdX}^+\text{B}(\text{C}_6\text{H}_5)_4^- + \text{NaCl}
\]  \( (1) \)

Conductivity results which will be described later in this chapter show that the formation of ionic products indeed occurs. There seems little doubt that the product of the reaction of \[ (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{PdCl}_2 \] and \( (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P} \) is the complex \[ (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{PdCl}_2\text{Cl} \].

Since it seemed interesting to follow this reaction for a number of complexes in order to investigate the effect of changing the nature of the ligands, the following general reaction was investigated by \textsuperscript{1}H NMR
TABLE 3-1

NMR Results for [(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PtX$_2$ and [(CH$_3$)$_2$(C$_6$H$_5$)P]$_3$Pd$^+$X (after Powell$^{22}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$ (ppm from TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis[(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PtCl$_2$</td>
<td>1.78 (11.1)</td>
</tr>
<tr>
<td>cis[(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PtI$_2$</td>
<td>1.91 (10.5)</td>
</tr>
<tr>
<td>trans[(CH$_3$)$_2$(C$_6$H$_5$)P]$_2$PtI$_2$</td>
<td>2.18 (3.6)</td>
</tr>
<tr>
<td>[(CH$_3$)$_2$(C$_6$H$_5$)P]$_3$PtCl$^+$</td>
<td>1.54 (10.8) I = 1</td>
</tr>
<tr>
<td>[(CH$_3$)$_2$(C$_6$H$_5$)P]$_3$PtI$^+$</td>
<td>1.96 (10.8)</td>
</tr>
<tr>
<td></td>
<td>2.46 (3.9)</td>
</tr>
</tbody>
</table>
\[ L_2\text{Pdx}_2 + L \rightarrow [L_3\text{Pdx}^+]X^- \]  

(2)

for \( L = (\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P} \) and \( L = (\text{CH}_3)(\text{C}_6\text{H}_5)\text{P} \) and \( X = \text{Cl}, \text{Br}, \text{I} \). In these cases the observed NMR spectra were recorded at -50°C in CDCl\(_3\) at 220 MHz. The NMR chemical shifts for both the starting complexes \( L_2\text{Pdx}_2 \) and the product \([L_3\text{Pdx}^+]\) are shown in Table 3-2. These results show that, as in the \([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PdCl}_2\) case, the observed low temperature NMR spectra, in the presence of added ligand, are consistent with the formation of the new species \([L_3\text{Pdx}^+]\). In most cases, the resonance due to the starting complex \( L_2\text{Pdx}_2 \) completely disappeared when the ratio of added ligand to starting complex reached unity. This implies that the equilibrium constant \( K \) for the reactions described by equation 2 is very large, where \( K \) is defined as

\[
K = \frac{[L_3\text{Pdx}^+] [X^-]}{[L_2\text{Pdx}_2][L^-]}
\]

There were some differences observed for the two types of complexes studied by \(^1H\) NMR and these are best described under the particular phosphine being considered.

For the complexes \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Pdx}_2\), the resonances due to both \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Pdx}_2\) and \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{Pdx} \) are observed when less than an equivalent amount of \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \) was added. When excess ligand was present \((L:M > 1)\) a new resonance due to the free ligand was observed at \( \delta = 1.62 \) ppm characteristic of the free ligand. Thus, exchange between the neutral and cationic species is slow (due to the large value of the equilibrium constant and virtually no free ligand is present at \( L:M < 1 \)). Similarly the exchange of free ligand with the cation (when \( L:M > 1 \)) is also slow at -50°C. The particular case of the
<table>
<thead>
<tr>
<th></th>
<th>$L_2$Pd$X_2$</th>
<th>$L_3$Pd$X^+X^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^' = \text{Me}(C_6H_5)_2P$</td>
<td>$L = \text{Me}_2(C_6H_5)P$</td>
</tr>
<tr>
<td>A</td>
<td>$\delta$ (trans to $X$)</td>
<td>$\delta$ (trans to L)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (in ppm from TMS)</td>
<td>$\delta$ (in ppm from TMS)</td>
</tr>
<tr>
<td>X</td>
<td>Cl</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>$L^' = \text{Me}(C_6H_5)_2P$</td>
<td>$\delta$ (trans to L)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (in ppm from TMS)</td>
<td>$\delta$ (in ppm from TMS)</td>
</tr>
<tr>
<td>X</td>
<td>Cl</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>--</td>
</tr>
<tr>
<td>II</td>
<td>$L_3$Pd$X^+X^-$</td>
<td>$L = \text{Me}_2(C_6H_5)P$</td>
</tr>
<tr>
<td>A</td>
<td>$\delta$ (trans to L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta$ (in ppm from TMS)</td>
<td>$\delta$ (in ppm from TMS)</td>
</tr>
<tr>
<td>X</td>
<td>Cl</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>$L = \text{Me}_2(C_6H_5)P$</td>
<td>$\delta$ (trans to L)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (in ppm from TMS)</td>
<td>$\delta$ (in ppm from TMS)</td>
</tr>
<tr>
<td>X</td>
<td>Cl</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>1.06</td>
</tr>
</tbody>
</table>
complex \([{(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{PdBr}_2}\] sheds some light on the mechanism of exchange when \(L:M < 1\), i.e., when both neutral and cationic species are present. A series of spectra for various values of \(L:M\) are shown in Fig. 3-3. These spectra show that at \(L:M < 1\), the resonances due to the mutually trans phosphines of the cation \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{PdBr}\] and the resonance due to the starting complex are somewhat broadened. However, the resonance due to the unique phosphine of the cation is sharp. When excess phosphine is present \((L:M > 1)\), the resonance due to the equivalent phosphines of the cation is sharp, while the resonances due to the unique phosphine of the cation and the resonance due to the free ligand are broadened. Thus, when \(L:M < 1\), an exchange process involving the starting complex and the mutually trans phosphines of the cation is indicated. In addition, this process must be occurring in such a manner as to leave the unique phosphine of the cation unaffected. The observation may be rationalized in terms of an exchange between the neutral complex and the cation, in which a bromide from the neutral complex is exchanged for the unique phosphine of the cation while preserving the configuration about each palladium atom, i.e., exchange with retention of configuration. It is apparent that such a process exchanges the unique phosphine between identical sites since at the completion of the exchange this phosphine is again trans to a bromide in the cationic complex. However, equivalent phosphines are exchanging (without Pd-P bond breaking) between cationic and neutral complexes. Thus, the broadening of the two types of mutually trans phosphines is observed while the unique phosphine resonance remains sharp. This process, as pointed out in Chapter II, is fast enough to cause line broadening.
Postulated Exchange Mechanism for

\[ [(CH_3)(C_6H_5)_2P)_2PdBr_2 \text{ and } [(CH_3)(C_6H_5)_2P]_3Pd^+ \]
Fig. 3-3  220 MHz spectra \(^1\text{H}\) obtained by addition of \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) to a CDCl\(_3\) solution of trans[\((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\)_2\text{PdBr}_2\] at -50°C.

3  L/m = 0.9

4  L/m = 1.0

5  L/m' = 1.2
(exchange broadening) without causing shifting of the resonances. The exchange process which occurs when excess \( [L:M > 1] \) ligand is present is somewhat simpler. In this case, the free ligand and the unique phosphine of the cation appear to be exchanging faster than the free ligand and the mutually trans phosphines of the cation. Put more simply, the exchange of free ligand for the phosphine trans to a bromide in \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{Pd}^\text{Br}^+ \) is faster than exchange with the mutually trans phosphines. These exchange processes are shown in Fig. 3-3b.

Another interesting observation was made with the chloride complex \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{PdCl}_2 \). This complex has been reported to exist as a mixture of cis and trans isomers. This report was confirmed in this work as shown by the spectra of the pure complex (Fig. 3-4). The spectra is assigned as a doublet \( (J = 11 \text{ Hz}) \) at \( \delta 2.03 \text{ ppm} \) and a triplet at \( \delta = 2.06 \text{ ppm} \). These resonances are slightly overlapped but the schematic diagram accompanying the spectra shows that both the cis \( (\delta = 2.63 \text{ ppm}) \) and trans \( (\delta = 2.06 \text{ ppm}) \) isomers are present in a ratio of about 1:1. Upon the addition of a small amount of \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \), the resonance due to the trans isomer disappeared and the resonances due to \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{PdCl} \) appeared. Since considerably less \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \) was added than trans\( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{PdCl}_2 \) originally present, the disappearance of the resonance due to the trans isomer cannot be due to preferential reaction of \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \) with trans\( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{PdCl}_2 \) to form \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{PdCl} \) although this product is formed. Instead, the added \( (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \) must catalyze the trans-cis isomerization of the neutral complex. This reaction is so rapid that no sign of the trans isomer remains 30 seconds after addition of small amounts of excess ligand.
Fig. 3-4  220 MHz $^1$H Spectrum of (CH$_3$)$_2$(C$_6$H$_5$)$_2$PdCl$_2$ Showing a Mixture of Isomers

Hz from TMS
Turning now to the complexes of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\), the chloride and bromide behave similarly to the \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\)\(P\) complexes at \(L:M < 1\) at -50°, i.e., the formation of \([((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\)]_3\(PdX^+\) \((X = \text{Cl}, \text{Br})\) is quantitative and the rate of the exchange is slow at -50°C. However, for the iodide complex \([[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\)]_2\(PdI_2\) addition of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\) causes the resonance of the complex to broaden and shift to low field. Simultaneously, a new somewhat broadened resonance appears at \(\delta = 1.06\) ppm which shifts to high field with increasing amounts of added \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\).

In the region \(0.85 < L:M < 0.95\), the resonance which moved downfield is observed at \(\delta = 2.39\) ppm. This behaviour is similar to that observed with \([([\text{CH}_3)(\text{C}_6\text{H}_5)_2\)\(PdI_2\) except that the exchange process is somewhat faster. In this case, the exchange of the starting complex and the mutually trans phosphines of \([((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\)\(PdI^+\) is fast enough to average the two resonances. Thus, as more \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\) is added, a greater fraction of the palladium is in the cationic form and the resonance approaches the limiting resonance position of the mutually trans phosphines of \([([\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\)\(PdI^+.\) In addition, the new resonance which appears at \(\delta = 1.06\) ppm is assigned to the limiting shift of the unique phosphine in \([([\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\)\(PdI^+.\) It appears that the reaction is not quantitative and that some free \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\) is in solution. This free phosphine is in fast exchange with the unique phosphine of the cation. As the amount of added \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\)\(P\) increases, the observed resonance position of this resonance shifts toward the free ligand resonance position \(\delta = 1.34\) ppm.

When excess phosphine was present, the resonances of the cations \(L_3\)\(PdX^+\) coalesced and no resonance was observed which could be assigned to free ligand. Thus, the exchange of excess ligand with \(L_3\)\(PdX^+\)
(L = \( \text{CH}_3 \)\(_2\)(C\(_6\)H\(_5\))P, X = Cl, Br, I) is fast even at -50°C.

In order to study the effect of competing ligands, \((\text{CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\) or \((\text{CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P were added to solutions of \(\text{[(C}_6\text{H}_5\)\(_3\)P\]_2PdX_2\). However, the substitution reaction

\[
\text{[(C}_6\text{H}_5\)\(_3\)P\]_2PdX_2 + 2L \rightarrow L_2PdX_2 + 2\text{(C}_6\text{H}_5\)\(_3\)P
\]

appeared to be quantitative. The addition of two moles of
\((\text{CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\) or \((\text{CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P to one mole of \(\text{[(C}_6\text{H}_5\)\(_3\)P\]_2PdX_2\) (X = Cl, Br, I) caused quantitative displacement of the two triphenylphosphine molecules. Further addition of \((\text{CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\) or \((\text{CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P simply resulted in the formation of the cations discussed above.

However, the reaction of the complexes \(\text{[(CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\]_2PdX_2\) and \(\text{[(CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P\]_2PdX_2\) with large amounts of triphenylphosphine gave some unexpected results. The NMR spectrum of solutions \(\text{[(CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P\]_2PdX_2\) (X = Cl, Br) with large amounts of \(\text{(C}_6\text{H}_5\)\(_3\)P added showed the formation of \(\text{[(CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P\]_3PdX^+\) as observed when the added ligand was \((\text{CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P. The reaction is then assumed to be

\[
3\text{[(CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P\]_2PdX_2 + 2\text{(C}_6\text{H}_5\)\(_3\)P \rightarrow \text{[(C}_6\text{H}_5\)\(_3\)P\]_2PdX_2 + 2\text{(CH}_3\)\((\text{C}_6\text{H}_5\)\(_2\)P\]_3PdX^+
\]

No reaction was observed for X = I.

In contrast, the addition of \(\text{(C}_6\text{H}_5\)\(_3\)P to solutions of
\(\text{[(CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\]_2PdX_2\) gave several new resonances. In addition to resonances due to \(\text{[(CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\]_3PdX^+\), a somewhat broadened triplet was observed. Since this resonance is observed in the region where neutral complex resonances are observed, this new resonance was assigned to the mixed phosphine complex \(\text{[(CH}_3\)\(_2\)(C\(_6\)H\(_5\))P\]_2\text{(C}_6\text{H}_5\)\(_3\)P\]PdX_2\). The reaction appears to be
\[
2\left(\text{CH}_3\right)_2\text{(C}_6\text{H}_5\text{)}_2\text{PdX}_2 + \text{(C}_6\text{H}_5\text{)}_3\text{P} \rightarrow \left(\text{CH}_3\right)_2\text{(C}_6\text{H}_5\text{)}_2\text{PdX}^+ + \left(\text{CH}_3\right)_2\text{(C}_6\text{H}_5\text{)}_2\text{P} + \text{(C}_6\text{H}_5\text{)}_3\text{PdX}_2
\]

When the iodide complex was studied, the resonance due to unique phosphine of 
\[\left(\text{CH}_3\right)_2 \text{(C}_6\text{H}_5\text{)}_2\text{PdI}^+ \] was observed but the resonance due to the starting complex was broadened and slightly shifted to low field and no further methyl resonance was observed. Since the assignable resonance of 
\[\left(\text{CH}_3\right)_2 \text{(C}_6\text{H}_5\text{)}_2\text{PdI}^+ \] was of low intensity, the equilibrium constant for this reaction must be small.

The equilibrium constants for the above reactions were estimated by integration of the NMR spectra and these values as well as the NMR parameters for the mixed phosphine complexes are shown in Table 3-3. It is to be noted that for both reactions, the equilibrium constants are largest for the bromide complexes although they are much smaller than the very large equilibrium constants discussed earlier.

An attempt was made to extend the above study to complexes with ligands such as \((\text{C}_2\text{H}_5\text{)}_2\text{(C}_6\text{H}_5\text{)}_2\text{P} \) and \((\text{C}_2\text{H}_5\text{)}_2\text{(C}_6\text{H}_5\text{)}_2\text{P} \). However, the spectra obtained were very difficult to interpret. The chemical shift difference between the methyl resonances of free and complexed ligands is very small and the signals are badly overlapped. The methylene resonances although not usually overlapped for free and complexed ligands, are split due to spin-spin coupling to the methyl protons. This is further complicated by the effects of virtual coupling. The addition of these ligands to palladium complexes of the ligands results in the formation of cationic species as was observed with the methyl phosphines; however, in several cases the equilibrium constants are quite small. Thus, the spectra consist of methylene resonances due to starting complex,
TABLE 3-3
Equilibrium Constants for Reaction of $L_2\text{PdX}_2 + (C_6\text{H}_5)_3\text{P}$

A. $L = (\text{CH}_3)(\text{C}_6\text{H}_5)\text{P}$

$$K (1^2/\text{mole}^2)$$

$X = \text{Cl}$

1.3

$= \text{Br}$

$2.9 \times 10^2$

$= \text{I}$

small

B. $L = (\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}$

$$K (1/\text{mole})$$

$X = \text{Cl}$

4.9

$= \text{Br}$

$5.6 \times 10^1$

$= \text{I}$

small

A. Reaction

$$3[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{P}]\text{PdX}_2 + 2(\text{C}_6\text{H}_5)_3\text{P} \rightarrow 2[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{P}]_3\text{PdX}^+ + [(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdX}_2$$

B. Reaction

$$2[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PdX}_2 + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow [(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_3\text{PdX}^+$$

$$[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2[(\text{C}_6\text{H}_5)_3\text{P}]\text{PdX}_2$$

NMR Parameters for the complexes

trans $$[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}][(\text{C}_6\text{H}_5)_3\text{P}]\text{PdX}_2$$

$X \delta$ (ppm from TMS)

Cl 1.64

Br 1.84
free ligand and two resonances due to the cationic species. These resonances are badly overlapped as well as being exchanged broadened even at -50°C. These factors make detailed studies of these systems impossible. Since $^1$H NMR proved unsatisfactory for the study of compounds with phosphines more complicated than $(\text{Cl}_3)_3$-$(\text{C}_6\text{H}_5)_n$P ($n = 1,2$), further studies were undertaken using conductometric techniques.

3.3 CONDUCTIVITY RESULTS

Since the reaction of $[(\text{Cl}_3)_3$-$(\text{C}_6\text{H}_5)_n$P]$_2$PdX$_2$ with $(\text{Cl}_3)_3$-$(\text{C}_6\text{H}_5)_n$P produces ionic products, a general study of such reactions was undertaken for a number of phosphines by means of conductivity. This was carried out experimentally by the measurement of the conductivity of a chloroform solution of the complex as a chloroform solution of the phosphine was added. Complex solutions were prepared by dissolving a weighed amount of complex in 20.00 ml of CHCl$_3$, while solutions of the phosphine were prepared by diluting to 1.00 ml weighed amounts of the phosphine in a 1.00 ml volumetric flask. Additions were made using a 50 ml Eppendorf pipette.

The conductometric titration curves for the reaction

$$L_2\text{PdX}_2 + L \rightarrow L_3\text{PdX}^+ + X^-$$

are shown in Figures 3-5, 3-6 and 3-7 in which the conductivity versus the ratio of added ligand to starting complex (L:M) is plotted. These curves generally show a rapid increase in conductivity at low values of L:M and the conductivity levels off at values greater than L:M > 1. These results show that the shape of the curve depends both on the phosphine L and the halide. The results are shown for chloroform solutions of
Fig. 3-5  Conductivity vs L/M for L_2PdCl_2 + L'
(complex concentration = 1.5 \times 10^{-3} \text{ m})
Fig. 3-5 (Continued)

\[ L' = (C_2H_5)_2(C_6H_5)_3P \]
\[ L = (C_2H_5)_2(C_6H_5)_3P \times \]
\[ L = (C_6H_5)_3P \]

conductivity vs concentration for
\[ (C_2H_5)_4N^+Cl^- \]
Fig. 3-6  Conductivity vs L/M for \( L_2^2 \text{PdBr}_2 + L' \)
(complex concentration = \( 1.5 \times 10^{-3} \) m)

\[
L' = (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}
\]
\[
L = (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \times
\]
\[
L = (\text{C}_6\text{H}_5)_3\text{P} \circ
\]

\[
L' = (\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}
\]
\[
L = (\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P} \times
\]
\[
L = (\text{C}_6\text{H}_5)_3\text{P} \circ
\]

\[
L' = (\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}
\]
\[
L = (\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P} \times
\]
\[
L = (\text{C}_6\text{H}_5)_3\text{P} \circ
\]

\[
L' = (\text{C}_2\text{H}_5)_3\text{P}
\]
\[
L = (\text{C}_2\text{H}_5)_3\text{P} \times
\]
\[
L = (\text{C}_6\text{H}_5)_3\text{P} \circ
\]
Fig. 3-6 (Continued)

\[ L^+ = (nC_3H_7)_3P \]
\[ L = (nC_3H_7)_3P \quad \times \]
\[ L = (C_6H_{15})_3P \quad o \]

Conductivity vs concentration for
\((C_2H_5)_4N^+Br^-\)
Fig. 3-7  Conductivity vs. L/M for L₂PdI₂ + L'

(complex concentration 1.5 x 10⁻³ m)

L' = (C₅H₅)₃P
L = (C₂H₅)₃P x
L = (C₆H₅)₃P o

L' = (nC₃H₇)₃P
L = (nC₃H₇)₃P x
L = (C₆H₅)₃P o
Fig. 3-7 (Continued)

\[ L' = (\text{CH}_3)_2 (\text{C}_6\text{H}_5)_p \]
\[ L = (\text{CH}_3)_2 (\text{C}_6\text{H}_5)_p \]
\[ L = (\text{C}_6\text{H}_5)_3 p \]

\[ L_{\text{A} \times 10^{-8}} \text{ ohm} \]

\[ L/M \]

\[ 1 \quad 3 \quad 5 \quad 7 \]
the chloride and bromide complexes. Unfortunately, the change in conductivity observed for the iodide complexes was small in CHCl₃, so the results for these complexes were obtained in nitrobenzene solution.

Assuming, that the degree of ion pairing in the ionic products is similar, regardless of the phosphine, and that the contribution to the observed conductivity from the cation (probably small) is constant, the relative equilibrium constants can be obtained. The equations used in this calculation are given in Appendix I. The relative equilibrium constants referred to the equilibrium constant of the \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) complexes given arbitrary values of unity are given in Table 3-4. The results do not allow comparison between complexes of different halides, since the contribution to the observed conductivity due to the halide (expected to be the major contribution to the conductivity) will differ from halide to halide. However, the results are comparable if the phosphine is varied and the halide kept constant.

These results will be discussed in detail in Chapter VII. However, the important observation is that the value of \(K\) varies with the donor abilities of the phosphine and the halide.

The relative equilibrium constants give no indication of the absolute magnitudes of these constants. The NMR results discussed earlier indicated that the equilibrium constants for the \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) and \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) complexes are very large. This observation was confirmed by comparison with the conductivity of \((\text{CH}_3\text{CH}_2)_4\text{X}\) \((X = \text{Cl, Br})\) which gives conductivities of the same order of magnitude (see Figures 3-5, 3-6 and 3-7) as the complexes shown by NMR to have large equilibrium constants. Any more than a qualitative agreement is not expected since
### TABLE 3-4

Relative Equilibrium Constants

A. \[ L_2^{\text{PdX}} + L = L_3^{\text{PdX}^+} + X^- \]

<table>
<thead>
<tr>
<th>L</th>
<th>( X = \text{Cl} )</th>
<th>( X = \text{Br} )</th>
<th>( X = \text{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((C_6H_5)_3P)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>((CH_3)(C_6H_5)_2P)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>((C_2H_5)(C_6H_5)_2P)</td>
<td>0.91</td>
<td>1.96</td>
<td>7.00</td>
</tr>
<tr>
<td>((CH_3)_2(C_6H_5)P)</td>
<td>1.10</td>
<td>1.20</td>
<td>3.80</td>
</tr>
<tr>
<td>((C_2H_5)_2(C_6H_5)P)</td>
<td>2.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((C_2H_5)_3P)</td>
<td>1.77</td>
<td>0.23</td>
<td>2.80</td>
</tr>
<tr>
<td>((nC_4H_9)_3P)</td>
<td>0.15</td>
<td>0.13</td>
<td>1.93</td>
</tr>
</tbody>
</table>

For \( X = \text{Cl} \) and \( \text{Br} \) results were obtained in \( \text{CHCl}_3 \) while the \( X = \text{I} \) results were obtained in \( C_6H_5NO_2 \).
the degree of ion pairing in chloroform solutions of \((\text{C}_2\text{H}_5)_4\text{H}^+\) is unknown and there is no reason to suppose it is similar to that of the palladium complexes.

The reaction of the \([(\text{C}_6\text{H}_5)_3\text{P})_2\text{PdX}_2\] complexes with various phosphines was also studied by conductivity. The NMR results for the \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P}\) and \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) reactions indicated that \((\text{C}_6\text{H}_5)_3\text{P}\) was quantitatively displaced by more basic phosphines. Conductivity measurements showed no change in conductivity as phosphine was added until the ratio of added phosphine to the triphenylphosphine complex \((L:M)\) exceeded two. Further addition of phosphine caused the conductivity to increase. The resulting titration curves were identical to those shown in Figures 3-5, 3-6, and 3-7 except that they were shifted by two \(L:M\) units. Thus, phosphines more basic than triphenylphosphine quantitatively displace coordinated \((\text{C}_6\text{H}_5)_3\text{P}\). Further additions of phosphine simply cause the formation of the ionic products discussed above. The only exception to this observation was the addition of \((\text{nC}_4\text{H}_9)_3\text{P}\) to \([(\text{C}_6\text{H}_5)_3\text{P})_2\text{PdCl}_2\]. In this case, the conductivity did not begin to rise until the value of \(L:M\) reached 2.9. This indicated that the displacement of coordinated \((\text{C}_6\text{H}_5)_3\text{P}\) by \((\text{nC}_4\text{H}_9)_3\text{P}\) is considerably less than quantitative. No increase in conductivity was observed when \((\text{C}_6\text{H}_5)_3\text{P}\) was added to \([(\text{C}_6\text{H}_5)_3\text{P})_2\text{PdX}_2\]. Thus, formation of \([(\text{C}_6\text{H}_5)_3\text{P})_3\text{PdX}^+\] is unfavourable.

The halide bridged dimers \([(\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}_2\text{X}_4\] were also prepared and the conductivity studied as above. Again it was found that addition of two moles of phosphine was required before increasing conductivity was observed. Thus, it seems that the reaction proceeds through the \(\text{L}_2\text{PdX}_2\) complex before formation of ionic species is observed. Again, no increase
in conductivity was observed for the addition of \((C_6H_5)_3P\).

**Qualitative Rates of Reaction**

Rates of reaction can be determined by NMR spectra as was described in Chapter II. In the reactions described above, small chemical shift differences, and the relatively small changes in line widths, introduce such large uncertainties into the measured rates that these measurements were not undertaken. However, the relative ordering of the rates was qualitatively measured by a combination of line widths and coalescence temperatures. These results are given below.

Rates of \(L_3PdX^+\) and \(L_2PdX_2\)

It was generally observed that the exchange of phosphine when less than an equivalent amount of phosphine had been added to the bis phosphine complex was fast at room temperature, but at -50°C the exchange was slowed sufficiently to give a slow exchange spectrum. The rate of exchange was found to be faster for \((CH_3)_2(C_6H_5)P\) than for \((CH_3)(C_6H_5)_2P\), and faster for iodide than the other two halides. These results are shown in Tables 3-5(a).

Rates of \(L_3PdX^+\) and \(L^+_1\)

When more than an equivalent amount of phosphine was added to a solution of the bis complex, all the bis complex is converted to the cationic species. When excess phosphine is present, there is exchange of free and complexed phosphines. As shown in Table 3-5(b), the order of decreasing rates is somewhat different from that observed above. In this case, the rate of exchange of phosphine is fastest for \((CH_3)_2(C_6H_5)P\)
### TABLE 3-5

Rates for Exchange Reactions of Palladium Complexes

#### A. \( \text{L}_2\text{PdX}_2 + \text{L}_3\text{Pd}'\text{X}'^+ \rightarrow \text{L}_2\text{Pd}'\text{X}_2 + \text{L}_3\text{PdX}'^+ \)

**Order of decreasing rate**

\[
\begin{align*}
\{(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{P})\}_2\text{PdI}_2 \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_2\text{PdI}_2 \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_2\text{PdBr}_2 \\
\{(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{P})\}_2\text{PdCl}_2 \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_2\text{PdCl}_2
\end{align*}
\]

#### B. \( \text{L}_3\text{PdX}'^+ + \text{L} \rightarrow \text{L}_3\text{PdX}^+ + \text{L} \)

**Order of decreasing rate**

\[
\begin{align*}
\{(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{P})\}_3\text{PdCl}^+ \\
\{(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{P})\}_3\text{PdBr}^+ \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_3\text{PdI}^+ \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_3\text{PdCl}^+ \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_3\text{PdBr}^+ \\
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_2\text{PdCl}^+
\end{align*}
\]

**Note:** \( \{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_2\text{PdX}^+ \)

Exchange of free and trans > cis and trans

\[
\{(\text{CH}_3)(\text{C}_6\text{H}_5\text{P})\}_3\text{PdX}^+
\]
complexes with the halide dependence being \( \text{Cl} > \text{Br} > \text{I} \). However, for \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\)P, the halide dependence is reversed, being \( \text{I} > \text{Br} > \text{Cl} \).

**Summary**

1. The addition of phosphines which are more basic than triphenylphosphine quantitatively displace the coordinated \((\text{C}_6\text{H}_5)_3\)P. The only case where this does not seem to hold is the addition of \((\text{nC}_4\text{H}_9)_3\)P. In this reaction, it appears that the equilibrium constant is not as large as in the other reactions studied. In this case approximately three moles of \((\text{nC}_4\text{H}_9)_3\)P are required to displace the two moles of \((\text{C}_6\text{H}_5)_3\)P coordinated.

2. The addition of phosphines more basic than \((\text{C}_6\text{H}_5)_3\)P to complexes of that phosphine results in the formation of a new species in which there are three molecules of phosphine and one halide coordinated to one palladium centre. In these complexes the palladium carries a single positive charge.

3. The equilibrium constant for the reaction of the bis complex is dependent both upon the phosphine and the halide. In general, the results show the reaction does not occur or occurs only to a limited extent with very weakly basic or very strongly basic phosphines. The reaction appears to proceed virtually quantitatively with phosphines of intermediate basicity.

4. The rates of the reactions were fast at room temperature but slow exchange spectra were obtained at -50°C. The rates of the reactions were dependent both upon the phosphine and the halide.
3.4 EXPERIMENTAL

1. Preparation of Complexes $L_2PdX_2$

The complexes were prepared by the addition of a 25% excess of the desired phosphine in acetone to an aqueous solution of $K_2PdX_4$ prepared from $PdCl_2$ and $KCl$ for the chloride complex, or from $Pd(NO_3)_2$ and $KX$ for the bromide and iodide complexes. The products precipitated immediately, were stirred for 30 minutes, filtered, washed with water, and then washed liberally with ether or hexane. The dried product was recrystallized from benzene-hexane, and air dried.

The yields were typically of the order of 85%. The physical properties of the complexes are shown in Table 3-6.

2. NMR Spectra

Nuclear magnetic resonance spectra were recorded on a Varian 220 MHz spectrometer. The spectra were run at approximately $10^{-2}$ molar solution in deuterochloroform (Stohler Isotopes Ltd.).

3. Conductivity

Conductance measurements were made on stirred 20 ml. solution of spectroscopic grade chloroform (J. T. Baker Ltd.) or nitrobenzene (Fisher Chemical Ltd.).

The instrument used in these measurements was an Industrial Instruments Inc. Model RC1682 conductivity bridge equipped with a cell of 0.1 ohm$^{-1}$ cm. cell constant.
<table>
<thead>
<tr>
<th>Complex</th>
<th>mp</th>
<th>lit.</th>
<th>vPd-P</th>
<th>vPd-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(\text{CH}_3)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>191-193</td>
<td>192-193</td>
<td>510</td>
<td>299</td>
</tr>
<tr>
<td>[(\text{CH}_3)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>181-184</td>
<td>180-182</td>
<td>506</td>
<td>190</td>
</tr>
<tr>
<td>cis [(\text{CH}_3)(\text{C}_6\text{H}_5)_2p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>155-158</td>
<td>159-160</td>
<td>516,450</td>
<td>303</td>
</tr>
<tr>
<td>cis [(\text{CH}_3)(\text{C}_6\text{H}_5)_2p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>197-199</td>
<td>201-203</td>
<td>509</td>
<td>494</td>
</tr>
<tr>
<td>[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>215-216</td>
<td>215-213</td>
<td>502</td>
<td>187</td>
</tr>
<tr>
<td>[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>135-137</td>
<td>139-140</td>
<td>507</td>
<td>298</td>
</tr>
<tr>
<td>[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>212-214</td>
<td>211-213</td>
<td>506</td>
<td>296</td>
</tr>
<tr>
<td>[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>200-203</td>
<td>168-171</td>
<td>502</td>
<td>187</td>
</tr>
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<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
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<td>138-139</td>
<td>641</td>
<td>305</td>
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<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>128-131</td>
<td>132-134</td>
<td>637</td>
<td>197</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>66</td>
<td>65-66</td>
<td>650</td>
<td>257</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>74-76</td>
<td>73</td>
<td>657</td>
<td>194</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>63-65</td>
<td>64-65</td>
<td>645</td>
<td>315</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>d 252</td>
<td>250-270</td>
<td>535</td>
<td>315</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{Br}_2</td>
<td>d 250</td>
<td>250-270</td>
<td>535</td>
<td>155</td>
</tr>
<tr>
<td>[(\text{C}_6\text{H}_5)p]_2\text{PdCl}_2 \text{I}_2</td>
<td>d 245</td>
<td>250-270</td>
<td>535</td>
<td>155</td>
</tr>
</tbody>
</table>
CHAPTER IV
STUDIES OF RHODIUM(I) AND IRIDIUM(I) PHOSPHINE COMPLEXES

4.1 INTRODUCTION

The chemistry of phosphine complexes of rhodium (I) and iridium (I) has been extensively studied in the past few years. Although a large amount of experimental data is available, yet little progress has been made in rationalizing the reactivities of these complexes. A brief review of the chemical behaviour of some selected phosphine complexes of rhodium (I) and iridium (I) was given in Chapter II. This review was intended only to indicate the scope of the experimental results currently available. In general, the majority of reports in the recent literature dealing with such complexes have described either the preparation of new complexes or the detailed chemical reactivities of such complexes. The two major types of reaction described are oxidative additions or catalytic processes. Surprisingly, few attempts to study the electronic properties of these complexes have been reported. This chapter describes the results of a study of such properties of some rhodium (I) and iridium (I) complexes.

The work of Vaska is perhaps the best known of the few published studies into the electronic properties of iridium phosphine complexes. In studying the reaction of trans \([\text{C}_6\text{H}_5\text{P}]_2\text{IrCO}(X)(X = \text{Cl}, \text{Br}, \text{I})\), with a number of unsaturated molecules and some small covalent molecules, Vaska found that a large equilibrium constant for adduct formation was associated with a high positive charge on the iridium centre. The relative charge on the metal atom was determined by measure-
ment of infrared stretching frequency \(v_{CO}\) of the adduct. The arguments used in inferring charge on the metal from \(v_{CO}\) are the same as those used by Tolman which will be discussed in Chapter VI. These results suggest that oxidative addition is favoured, i.e., trivalent complex stabilized by formation of an adduct in which the negative charge is effectively dissipated on the ligands.

The work of Faton and Stuart showed that in the exchange of \((p\text{CH}_3\text{C}_6\text{H}_5)_3\text{P}\) with \([((\text{C}_6\text{H}_5)_3\text{P}]_{3}\text{RhCl}\) the phosphine distribution is approximately statistical. The exchange at room temperature is fast by the NMR criterion but moderate cooling reduced the rate of exchange sufficiently so that at \(-30^\circ\text{C}\) a limiting slow exchange spectrum was obtained. Despite the fact that \((p\text{CH}_3\text{C}_6\text{H}_5)_3\text{P}\) is somewhat more basic phosphine than \((\text{C}_6\text{H}_5)_3\text{P}\), there seems to be no appreciable discrimination between the two ligands by the rhodium centre. A second observation made by these workers was that the rate of cis-trans isomerization was faster than the rate of exchange.

A short report by Shaw et al. described the exchange of \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) with trans \([((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\). These workers reported that the exchange at \(30^\circ\text{C}\) is fast by the NMR criterion. In a subsequent paper from the same laboratory, the preparation of eutonic iridium carbonyl phosphine complexes was reported. These workers also reported that the addition of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}\) to a solution of trans \([((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}]_2\text{IrCO(Cl)}\) was accompanied by a marked increase in the conductivity of the solution. By analogy with the results of their synthetic work, the authors presented two pathways by which ionic species could be formed.
They were unable to decide whether one or both of these reaction pathways were involved.

These papers seem to be the only published reports of phosphine exchange reactions of rhodium (I) and iridium (I) phosphine complexes, although a number of papers describing the NMR spectra of such complexes have been published. These publications usually describe complexes of \((\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}\) or \((\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}\) but a few ethyl phosphine complexes have been studied. These complexes have been prepared because of the ease with which structural assignments may be made on the basis of NMR spectra. The chemical shifts observed for some of these complexes will be quoted later in this chapter for comparison with the results of this present work. However, it must be pointed out that the chemical shifts observed for both free and complexed ligands are strongly solvent dependent. For example, the methyl spectrum of \([(\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}]_2\text{RhCl}\) in 

\[\text{C}_6\text{D}_6\]

consists of two resonances, a triplet at \(\delta = 1.63\) ppm and a doublet at \(\delta = 1.45\) ppm. However, in \text{CDCl}_3 the spectrum consists of a triplet at \(\delta = 1.98\) ppm and a doublet at \(\delta = 1.23\) ppm. The rather substantial differences between these two sets of shifts is only a result of the different solvent. The results presented in this chapter refer to chloroform solutions so some variation from the results obtained by other workers in different solvents is to be expected.
4.2 EXPERIMENTAL RESULTS

This chapter reports the exchange of the two phosphines \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) and \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) with a number of rhodium(I) and iridium(I) complexes. The complexes chosen for study were the carbonyl halide complexes \(\text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{MCO}(X)\) (\(M = \text{Rh, Ir; } X = \text{Cl, Br, I}\)). The complexes are known to be catalytically active as well as being capable of oxidative addition. The published studies discussed above indicate that these are labile systems and could be amenable to study by NMR. The previous reports either did not include variable temperature NMR studies, or did not include NMR studies at all. With the availability of a 220 MHz spectrometer capable of operation as low as \(-50^\circ\text{C}\), it was hoped that exchange studies on such systems might shed some light on the electronic properties of these complexes.

4.3 EXCHANGE REACTIONS OF RH(I) AND IR(I) CARBONYL HALIDE COMPLEXES

WITH \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) AND \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\)

The NMR spectrum of the complex \(\text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RhCOCl}\) in \(\text{CDCl}_3\) shows a complex multiplet between \(\delta = 7.6\) ppm and \(\delta = 7.2\) ppm, arising from the aromatic protons. No other resonances are observed for the complex. In the same solvent, \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) also shows resonances due to the aromatic protons in the same region as the metal complex. In addition, a doublet \(\delta = 1.34\) ppm (\(J = 3.5\) Hz) is observed. This resonance is due to the methyl protons and is observed as a doublet due to coupling with the \(I = \frac{1}{2}\) phosphorus atom. On mixing these solutions, the only resonance observed in the methyl region is a somewhat broadened resonance observed at \(\delta = 2.24\) ppm. This resonance grows in intensity as more \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) is added, until the ratio of added ligand to
metal complex (L:M) equals two. The resonance is a somewhat broadened triplet and is assigned to the substitution product trans\([(CH_3)_2(C_6H_5)P]_2RhCl(Ph)]. The chemical shift previously reported\(^{60}\) for this complex in \(CD_2Cl_2\) at 30° and 60 MHz is \(\delta = 2.13\) ppm. Taking into account the solvent shift mentioned above, and the fact that accurate chemical shift measurements are more easily made at 220 MHz, it is felt that this assignment is unambiguous. Thus, it appears that the equilibrium constant for the substitution reaction

\[
\text{trans}[\{(C_6H_5)_3P\} _2 RhCl] + 2(CH_3)_2(C_6H_5)P \rightarrow \text{trans}[\{(CH_3)_2(C_6H_5)P\} _2 RhCl] + 2(C_6H_5)_3P
\]

is very large since no resonance assignable to free ligand is observed prior to the addition of two moles of \((CH_3)_2(C_6H_5)P\) to the solution of the triphenyl phosphine complex. Unfortunately, in such a situation, rate data cannot be obtained by NMR.

Further addition of \((CH_3)_2(C_6H_5)P\) results in a shift to high field and eventually the resonance approaches \(\delta = 1.62\), the resonance position of free \((CH_3)_2(C_6H_5)P\). As the resonance begins to shift, the broadened triplet collapses to a broadened single line. As more \((CH_3)_2(C_6H_5)P\) is added, the resonance first sharpens, then broadens, finally splitting into a doublet. The separation of the two members of the doublet increases and approaches the value of 3.5 Hz observed for the free ligand. Cooling to -50°C caused no change to be observed and the above described results were duplicated at this temperature. As was discussed in Chapter II, the resonance position of the observed line is given by

\[
\omega = \mathbf{p}^\omega_A + \mathbf{p}^\omega_R
\]
where $p_A$ and $p_B$ are the fractional populations of the A and B sites and $\omega_A$ and $\omega_B$ are the resonance frequencies of the A and B species. From this, it can easily be seen that, as the mole fraction of one component approaches unity, the observed resonance position approaches the resonance position of that species. When $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}$ is present in large excess over $t-[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{RhCOC1}$, the observed resonance position is expected to approach that of $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}$. Figure 4-1 shows the concentration dependence of the observed resonance in a plot of $v$ vs. L:M.

The line width of the resonance of a species in fast exchange will depend upon the exchange rate, as was pointed out in Chapter II. However, the situation here is somewhat more complicated. The complex trans-$(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\text{RhCOC1}$ exhibits a triplet pattern due to virtual coupling but rapid exchange with free ligand would remove the strong phosphorus-phosphorus coupling leaving only phosphorus-hydrogen coupling of about 12 Hz. The free ligand shows a coupling of $J_{\text{PH}}$ of 3.5 Hz.

Further, it has been shown that the sign of the coupling constants of free and complexed methyl phosphines are opposite. The exchange process then averages two unequal coupling constants of opposite sign. This accounts for the line widths observed, since the separation of the lines must decrease from the complexed coupling constant of approximately 12 Hz to zero and then increase to 3.5 as observed in the free ligand.

These results are consistent with those of Shaw et al. The use of a high magnetic field (220 MHz) and cooling to -50°C results in no change in the observed spectra.

When the above reaction at -50°C and 220 MHz is repeated using
Fig. 4.1. Chemical Shift of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)P\) vs. 1/m for trans-\([\text{C}_6\text{H}_5)_2P\]_2\text{PrCO}(\text{Cl}) + (\text{CH}_3)_2(\text{C}_6\text{H}_5)P\).
trans\([(C_6H_5)_3P]_2RhCl\) and \((CH_3)(C_6H_5)_2P\), somewhat different results are observed. A \(CDCl_3\) solution of trans\([(C_6H_5)_3P]_2RhCl\) only shows NMR resonances in the aromatic region (\(\delta = 7.2\) ppm) while a \(CDCl_3\) solution of \((CH_3)(C_6H_5)_2P\) shows both aromatic resonances and a sharp doublet (\(J = 3.5\)) at \(\delta = 1.62\) ppm. When these solutions are mixed, a new resonance is observed at \(\delta = 2.24\) ppm. This resonance is observed as a broadened "triplet" which grows in intensity until the ratio of added ligand to starting complex reaches 2. This resonance is assigned to the substitution product trans\([(CH_3)(C_6H_5)_2P]_2RhCl\). The previously reported chemical shift of this complex is \(\delta = 2.13\) ppm in \(CD_2Cl_2\). No shift in frequency of the observed resonance or new resonance assignable to free \((CH_3)(C_6H_5)_2P\) up to \(L/M = 2\). On the basis of these observations the equilibrium constant for the substitution reaction

\[
\text{trans}\([(C_6H_5)_3P]_2RhCl + 2(CH_3)(C_6H_5)_2P \rightarrow \text{trans}\([(CH_3)(C_6H_5)_2P]_2RhCl + 2(C_6H_5)_3P)
\]

must be large. Again, as in the case of the reaction with \((CH_3)_2(C_6H_5)_2P\), rate data for the exchange cannot be determined from NMR data. The addition of excess \((CH_3)(C_6H_5)_2P\) (i.e., \(L:M > 2\)) results in fast exchange of free and complexed ligand and the observed resonance shifts to high field approaching the limiting shift of \((CH_3)(C_6H_5)_2P\). The concentration dependence of the observed resonance is shown in Figure 4-2 where the resonance position is plotted against \(L:M\). As the amount of excess ligand increases, in contrast to the \((CH_3)_2(C_6H_5)_2P\) results, two new resonances begin to appear. These resonances are observed as a triplet at \(\delta = 2.04\) ppm (intensity 2) and a doublet at \(\delta = 1.19\) ppm. Shaw's results show that the addition of \((CH_3)_2(C_6H_5)_2P\) to \(\text{trans}\([(CH_3)_2(C_6H_5)_2P]_2IrCl}\)
Fig. 4-2  Chemical Shift of $(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}$ vs L/m for trans$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RhCO(C1)} + (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}$
results in the formation of ionic complexes. Conductivity measurements shown in Figure 4-3 demonstrate that in the rhodium system, ionic products are also formed. It was then assumed that the new resonances observed at $\delta = 2.04$ ppm and $\delta = 1.19$ ppm were resonances arising from this new ionic product. The observation of a triplet of intensity 2 and a doublet of intensity 1 are strongly indicative of a species having three coordinated $(\text{CH}_3)(\text{C}_6\text{H}_5)_2P$ ligands. These ligands are coordinated in a plane with two being in a mutually trans arrangement and the third being cis to the two equivalent $(\text{CH}_3)(\text{C}_6\text{H}_5)_2P$ ligands. The species is thus expected to be $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2P]_3\text{RhCO}$. The assignment is supported by comparison with the results obtained for the complexes $[(\text{CH}_3)_2(\text{C}_6\text{H}_5)P]_3\text{PdX}$ and $[(\text{CH}_3)_2(\text{C}_6\text{H}_5)P]_3\text{PdX}$ in which the mutually trans phosphines were observed to show methyl resonances (triplets) to low field of the methyl (doublets) resonance arising from the unique (cis) ligand.

In addition to the two resonances attributed to the complex $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2P]_3\text{RhCO}$, a further resonance was observed at 1.92 ppm. This is very close to the chemical shift observed for the neutral substitution product trans$[(\text{CH}_3)(\text{C}_6\text{H}_5)_2P]_2\text{RhCO(Cl)}$. The new resonance at $\delta = 1.92$ ppm is then assigned to a new neutral species. Since complexes of rhodium (I) and iridium (I) are known to form a number of five coordinate species, this new product is assumed to be $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2P]_3\text{RhCOCl}$. The resonance observed for this complex is broadened and no structure is observed. This is undoubtedly a result of an exchange process. Since the observed chemical shift and the observed line width are independent of the concentration of added $(\text{CH}_3)(\text{C}_6\text{H}_5)_2P$, the process causing the broadening is probably due to some intramolecular rearrangement process of the five coordinate (presumably trigonal bipyramidal) complex. This
Fig. 4-3  Conductivity versus L/m for
trans\([\{C_6H_5\}_3P\}_2RhCO(Cl) + \{CH_3\}C_6H_5\}_2P\)
assignment of the resonance observed at \( \delta = 1.92 \) ppm to the five coordinate complex \(((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{RhCO(Cl)}\) requires some further discussion. The exchange of free \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) with trans\(((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{RhCO(Cl)}\) is observed to be fast by the NMR criterion as was discussed above and shown in Figure 4-2. Such an exchange is expected to proceed via an associative mechanism, that is, through an intermediate of higher coordination number. The intermediate is then expected to be five coordinate and trigonal bipyramidal. Since the intermediate in such an exchange process cannot be observed by NMR if the exchange rate is fast on the NMR time scale, the assignment of the \( \delta = 1.92 \) ppm to such a species is at first sight a contradiction. However, it must be pointed out that there are several possible five coordinate complexes, as shown below.

![Diagram showing five-coordinate complexes](image)

It seems possible that the rate of formation of one of these complexes is rapid enough to result in the observed rapid exchange of free and complexed ligand. There are two possibilities for the formation of the \(((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{RhCO(Cl)}\) observed at \( \delta = 1.92 \) ppm. The first is slow isomerization of the easily formed intermediate of the exchange reaction. Such a slow isomerization would result in the observation of a NMR resonance of the neutral five-coordinate species even though the rate of exchange of the free ligand and trans\(((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{RhCO(Cl)}\) is fast. The second possibility is formation of the observed isomer directly by a slow reaction of the free ligand and trans \(((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})\text{RhCO(Cl)}\).

The assignment of the \( \delta = 1.92 \) ppm resonance to a neutral five
coordinate complex is not the only possible assignment. The reaction

\[ \text{trans}[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)} + (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} + [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{RhCl} + \text{CO} \]

might also occur. It has been shown in two ways that this reaction does not occur. First, this reaction would produce free CO but no free carbon monoxide was detected by infrared spectroscopy. Secondly, the complex \([(CH_3)(C_6H_5)_2P)_3RhCl\] under these conditions shows NMR resonances (as shown later in this chapter) which differ drastically from the spectrum obtained above.

At very high values of L:M, another resonance begins to grow, while the resonances due to \([(CH_3)(C_6H_5)_2P)_3RhCO\] and \([(CH_3)(C_6H_5)_2P)_3IrCO(Cl)\] decrease. The new resonance is observed (at L:M \(> 4\)) at \(\delta = 1.56\ ppm.\)

Shaw has shown that the complex \([(CH_3)(C_6H_5)_2P)_4IrCO\] can be prepared from \([(CH_3)(C_6H_5)_2P)_2Ir(CO)_3\] and he has also postulated that this complex is produced by reaction of \text{trans}[(CH_3)(C_6H_5)_2P]_2\text{IrCO(Cl)}\). The NMR spectrum of \([(CH_3)(C_6H_5)_2P)_4IrCO\] is reported as a single broad line centred at \(\delta = 1.61\ ppm\) in CDCl_3. This is very similar behaviour to that observed in the above rhodium system. By analogy then, the resonance observed at \(\delta = 1.56\ ppm\) is assigned to the five coordinate cationic complex \([(CH_3)(C_6H_5)_2P)_4RhCO\]. Again, as in the case of \([(CH_3)(C_6H_5)_2P)_3RhCO(Cl)\], the linewidth and resonance position are independent of the concentration of free ligand in the range \(4 < L:M < 8\). This implies that the broadness is not due to exchange with free ligand but rather must be due to some intramolecular rearrangement process.

The NMR spectrum of \text{trans}[(C_6H_5)_3P]_2\text{IrCO(Cl)}\ in CDCl_3 at -50°C shows the expected aromatic resonances in the region of \(\delta = 7.2\ ppm\) and the methyl region of the spectrum is completely clear. The addition of
\((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) to a CDCl\(_3\) solution of the metal complex at \(-50^\circ\text{C}\) causes a resonance to be observed as a somewhat broadened triplet at \(\delta = 2.25 \text{ ppm}\), well removed from the resonance position \(\delta = 1.62 \text{ ppm}\) observed for free \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\). This resonance grows in intensity until \(\text{L:M} = 2\) with no sign of a free ligand resonance. This resonance is assigned to the substitution product \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{IrCO(Cl)}\) which has been previously reported to have a chemical shift of \(\delta = 2.25 \text{ ppm}\) in CDCl\(_3\). The failure to observe a free ligand resonance indicates that the substitution reaction is quantitative, i.e., that the equilibrium constant for the reaction

\[
\text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCO(Cl)} + 2(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \rightarrow \text{trans}[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{IrCO(Cl)} + 2(\text{C}_6\text{H}_5)_3\text{P}
\]

is large. The addition of excess \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) causes the observed resonance to shift to high field as a plot of the observed chemical shift versus \(\text{L:M}\) shows (Figure 4-4). Again, as in the case of the rhodium complexes, the exchange of free and coordinated \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) is fast on the NMR time scale even at \(-50^\circ\text{C}\).

As this resonance shifts to high field, several new resonances appear. These resonances are observed at \(\delta = 2.23 \text{ ppm}\) (triplet) and \(\delta = 1.14 \text{ ppm}\) (doublet) with an intensity ratio of 2:1. A further doublet is observed at \(\delta = 1.93 \text{ ppm}\). Using similar arguments to those used in the rhodium work discussed above, these resonances are assigned to \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{IrCO(\text{Cl})}\] (\(\delta = 2.23 \text{ ppm and } \delta = 1.14 \text{ ppm}\)), and to the five coordinate complex \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{IrCO(\text{Cl})}\] (\(\delta = 1.93 \text{ ppm}\)). No further resonances were observed up to a value of \(\text{L:M} = 10\).
Fig. 4-4 Chemical Shift of \((\mathrm{CH}_3)(\mathrm{C}_6\mathrm{H}_5)_2\mathrm{P}\) vs L/M for 
\[ t-\{\mathrm{C}_6\mathrm{H}_5\}_{2}\mathrm{P}+\mathrm{IrCOT} \rightarrow (\mathrm{CH}_3)(\mathrm{C}_6\mathrm{H}_5)_2\mathrm{P} \]
The presence of ionic species was again confirmed by conductivity studies. A sharp increase in conductivity is observed when excess \( (L: M = 2) \) \((\text{CH}_3)\text(C_6\text{H}_5)_2\text{P} \) was added to \( \text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCl}(\text{Cl}) \) in \( \text{CDCl}_3 \). A plot of conductivity versus \( L: M \) is shown in Figure 4-5.

The above reaction was repeated using \( \text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCl} \) and \( (\text{CH}_3)\text(C_6\text{H}_5)_2\text{P} \). As above, the methyl region of the NMR spectrum of \( \text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCl} \) is free of any resonances. Upon addition of \( (\text{CH}_3)\text(C_6\text{H}_5)_2\text{P} \) to a \( \text{CDCl}_3 \) solution of the metal complex at -50°C, a resonance appears as a broadened triplet at \( \delta = 2.17 \text{ ppm} \), well removed from the chemical shift observed for \( (\text{CH}_3)\text(C_6\text{H}_5)_2\text{P} \) in \( \text{CDCl}_3 \) (\( \delta = 1.34 \text{ ppm} \)). This resonance, which grows in intensity until \( L: M = 2 \) while no signal due to free ligand is observed, is assigned to the substitution product, \( \text{trans}[(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P}]_2\text{IrCl} \) (literature \( \delta = 1.65 \text{ ppm} \) in \( C_6D_6 \)). Since no free ligand is observed and the observed chemical shift is independent of added ligand in the range \( 0 < L: M < 2 \), the equilibrium constant for the substitution reaction

\[
\text{trans}[(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P}]_2\text{IrCl} + 2(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P} \rightleftharpoons \text{trans}[(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P}]_2\text{IrCl} + 2(\text{C}_6\text{H}_5)_3\text{P}
\]

must be large. When excess \( (L: M > 2) \) ligand is present, the \( \delta = 2.17 \text{ ppm} \) decreases and several new resonances appear. These resonances are observed at \( \delta = 2.04 \text{ ppm} \) (triplet intensity 2) and \( \delta = 1.39 \text{ ppm} \) (doublet intensity 1) and are assigned, respectively, to the two chemically equivalent phosphines and the unique phosphine of the four-coordinate cation \( [(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P}]_3\text{IrCl} \).

In addition, a resonance observed at \( \delta = 1.92 \text{ ppm} \) is assigned to the five coordinate complex \( [(\text{CH}_3)\text(C_6\text{H}_5)_2\text{P}]_3\text{IrCl} \). The rationale behind these assignments is similar to that used above. In contrast to the above cases,
Fig. 4-5  Conductivity versus L/M for
\[ \text{trans}\left[(\text{C}_6\text{H}_5)_3\text{P}\right]_2\text{IrCO(Cl)} + (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \]
the exchange between the substituted complex trans\[\text{trans}((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P})_2\text{IrCOCl} \]
and free (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P} at -50°C is slow on the NMR time scale and free ligand is observed at the usual free ligand position (\(\delta = 1.34 \text{ ppm}\)). At high (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P} concentrations, a further resonance is observed at \(\delta = 1.65 \text{ ppm}\). The position and width of this resonance do not vary with free ligand concentration and this resonance is assigned to the five coordinate cation \[\text{trans}((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P})_4\text{IrCO}. \]
This species was observed by Shaw who quotes the chemical shift in CDCl\(_3\) as \(\delta = 1.61 \text{ ppm}\). The formation of ionic products is shown by the change in conductivity which occurs as excess ligand is added to a CHCl\(_3\) solution of trans\[\text{trans}((\text{C}_6\text{H}_5)_3\text{P})_2\text{IrCOCl} \]
(Figure 4-6).

The addition of (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} to a solution of trans\[\text{trans}((\text{C}_6\text{H}_5)_3\text{P})_2\text{IrCOBr} \]
at -50°C in CDCl\(_3\) results in the observation of a triplet methyl resonance at \(\delta = 2.43 \text{ ppm}\). Again, this resonance is assigned to the substitution product trans\[\text{trans}((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{IrCOBr} \] (literature \(\delta = 2.35 \text{ in CDCl}_3 \) at 30°C). Since the observed resonance position is independent of the concentration of added (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} at L:M < 2, and since in this concentration range no resonance assignable to free ligand is observed, the equilibrium constant for the substitution reaction

\[
\text{trans}((\text{C}_6\text{H}_5)_3\text{P})\text{IrCOBr} + 2(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \rightarrow \text{trans}((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})\text{IrCOBr} + 2(\text{C}_6\text{H}_5)_3\text{P}
\]

must again be large.

When excess (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} is present, the exchange of free and coordinated phosphine is fast and the observed methyl resonance collapses and shifts to high field with increasing concentration of (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} as shown in Figure 4-7, in which the concentration dependence of the observed
Fig. 4-6  Conductivity versus L/M for
\[ \text{trans}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCO(C)} + (\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P} \]
resonance is shown. In the presence of excess \((L/M > 2)\) \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\)
new resonances are observed. Two of the resonances are observed at 
\(\delta = 2.24\) ppm (triplet of intensity 2) and at \(\delta = 1.14\) ppm (doublet of
intensity 1) are assigned to the four coordinate cation [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{IrCO}
and these chemical shifts agree well with the shifts observed for this
complex derived from the chloro substituted starting complex. In addition,
a further resonance is observed at \(\delta = 2.03\) ppm which is assigned to the
neutral five coordinate complex [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{IrCOBr}. No further
resonances are observed up to a value of \(L:M = 10\). A plot of conductivity
versus \(L:M\) shows that ionic products are produced (Figure 4-B).

When \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) is added to a CDCl\(_3\) solution of trans\([(\text{C}_6\text{H}_5)_3\text{P}]\text{IrCO(O\text{Br})}
) at \(-50^\circ\text{C}\), the resonance due to the substitution product [(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]\text{IrCO(Br)}
is observed at \(\delta = 2.06\) ppm. This resonance is observed as a triplet,
due to virtual coupling, and has been previously reported as a triplet with
a chemical shift of \(\delta = 1.75\) ppm in \(\text{C}_6\text{H}_6\). As the ratio of added ligand
to complex is increased, a new resonance at \(\delta = 1.34\) ppm (doublet \(J = 3.5\) Hz)
is observed. This resonance is undoubtedly due to free ligand. Thus, the
exchange of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) with both trans\([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{IrCO(Cl)}\) and
trans\([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_3\text{IrCO(Br)}\) is slow on the NMR time scale. In all other
cases so far discussed, this exchange reaction has been fast. The sub-
stitution reaction

\[
\text{trans\([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCO(Br)}\) + 2(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P} \rightarrow \text{trans\([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{IrCO(Br)}\)}
+ 2(\text{C}_6\text{H}_5)_3\text{P}
\]

is not quantitative as was the case in the chloro complex. This is
shown by the observation of free ligand at values of \(L:M\) considerably
less than two. The ratio of complexes to free \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) at \(L:M = 2\)
Fig. 4-8  Conductivity vs $\frac{L}{M}$ for \((CH_3)(C_6H_5)_2P + t[(C_6H_5)_3P]_2IrCOBr\)
is approximately 3:1 (by integration of the NMR spectrum). This gives an equilibrium constant of $K = 27$ for the reaction

$$2(CH_3)_2(C_6H_5)P + \text{trans}[(C_6H_5)_3P]IrCOBr \rightarrow 2(C_6H_5)_3P + \text{trans}[(CH_3)_2(C_6H_5)P]_2IrCOBr$$

where $K$ is

$$\frac{[\text{trans}[(CH_3)_2(C_6H_5)P]IrCOBr][(C_6H_5)_3P]^2}{[[\text{trans}[(C_6H_5)_3P]_2IrCOBr][(CH_3)_2(C_6H_5)P]]^2}$$

This indicates that although the $(CH_3)_2(C_6H_5)P$ is the preferred ligand, the extent to which substitution occurs is drastically reduced in comparison to the systems discussed above.

As has been discussed above in the presence of a large excess of $(CH_3)_2(C_6H_5)P$, new resonances are observed. The formation of the neutral five coordinate complex $[(CH_3)(C_6H_5)_2P]_3IrCOBr$ is observed and the methyl resonance is found at $\delta = 2.03$ ppm. The four coordinate species is also formed. As in the reaction of $(CH_3)_2(C_6H_5)P$ and trans$[(C_6H_5)_3P]_2IrCOCl$, the four coordinate cationic complex $[(CH_3)_2(C_6H_5)P]_3IrCO$ shows methyl resonances at $\delta = 2.04$ ppm and $\delta = 1.39$ ppm. The formation of this cation from the bromide complex is indicated by the observation of a triplet resonance at $\delta = 2.03$ ppm. The doublet expected at $\delta = 1.39$ ppm is obscured by the large doublet resonance due to free $(CH_3)_2(C_6H_5)P$ at $\delta = 1.34$ ppm. Finally, at very high values of L:M, the resonance due to the five coordinate cation $[(CH_3)_2(C_6H_5)P]_4IrCO$ is observed at $\delta = 1.58$ ppm. The resonance is broad. Furthermore the line shape and position are independent of the concentration of added ligand. This again indicates that the broadening is due to one intramolecular exchange process. The presence of ionic products is shown by
conductivity measurements as shown in Figure 4-9.

The exchange reactions of the iodide complex trans\([\text{C}_6\text{H}_5\text{P}_3]\_2\text{IrCl}_4\) with both \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) and \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) were also studied. The addition of either of these phosphines to CDCl\(_3\) solutions of the iodide complex at -50°C showed no NMR resonances assignable to any complexed \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) or \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\). The only resonance observed was due to the free ligand. Similarly, no change in conductivity was observed on the addition of these ligands to chloroform solutions of the iodide complex. Shaw's results indicate the cationic complexes are formed by the reaction of \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) and trans\([(\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}]_2\)IrCO(I). The failure to observe cationic complex formation in this work seems to be due to the inability of either \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) or \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) to displace coordinated \((\text{C}_6\text{H}_5\text{P})_3\) from trans\([(\text{C}_6\text{H}_5\text{P})_2]_2\)IrCOI.

4.4 EXCHANGE REACTIONS OF \([(\text{C}_6\text{H}_5\text{P})_3]\_2\text{RhX (X = Cl, Br, I)}\]

The NMR spectrum of \([(\text{C}_6\text{H}_5\text{P})_3]\_2\text{RhCl}\) in CDCl\(_3\) shows only aromatic resonance in the region \(\delta = 7.6-7.2\) ppm. When \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\) is added to this solution, a triplet (intensity 2) \(\delta = 2.21\) ppm, and a doublet (intensity 1) \(\delta = 1.86\) ppm are observed. In addition, a further resonance (doublet, \(J = 3.5\) Hz) is observed at \(\delta = 1.64\) ppm which is assigned to the free \((\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}\). The two resonances are assigned to the substituted complex \([(\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}]_3\text{RhCl}\). The triplet arises from the equivalent, mutually trans ligands which are virtually coupled. The remaining resonance \(\delta = 1.86\) ppm is assigned to the unique ligand (trans to chloride). This spectrum is unaltered by heating to 60°C.

The equilibrium constant for the substitution reaction

\[3(\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P} + [(\text{C}_6\text{H}_5\text{P})_3]_2\text{RhCl} \rightleftharpoons [(\text{CH}_3)_2\text{C}_6\text{H}_5\_2\text{P}]_3\text{RhCl} + 3(\text{C}_6\text{H}_5\text{P})_3\]
Fig. 4-9  Conductivity vs. $\frac{L}{M}$ for $(\text{CH}_3)_2(\text{C}_6\text{H}_5)P + t[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrCOBr}$
was estimated by integration of the NMR spectrum at +18°C. The equilibrium constant, given by

\[ K = \frac{\frac{((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{RhCl})[(\text{C}_6\text{H}_5)_3\text{P})]}{\frac{((\text{C}_6\text{H}_5)_3\text{P})_3\text{RhCl})[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})]^3} \]

was found to be $5.9 \times 10^{-2}$ ($\pm 0.6 \times 10^{-2}$). A statistical distribution would yield an equilibrium constant of unity. This shows that in the above system $(\text{C}_6\text{H}_5)_3\text{P}$ is the preferred ligand.

The NMR spectrum obtained at +18°C is a typical "slow exchange" spectrum, which was not altered by heating to +60°C. The exchange rate is slow in contrast to the results discussed for the exchange reactions of trans[((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{IrCl}(\text{Cl})] and trans[((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{RhCl}(\text{Cl})].

The addition of $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P}$ to a chloroform solution of $[(\text{C}_6\text{H}_5)_3\text{P})_3\text{RhCl}$ resulted in the formation of $[(\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P})_2\text{RhCl}$. The NMR spectrum of such a mixture is shown in Figure 4-10. The spectrum consists of two triplets of intensity ratio 4:2 ($\delta = 1.98$ and $\delta = 1.81$ ppm) and two doublets of intensity ratio 2:1 ($\delta = 1.23$ and $\delta = 1.10$ ppm). In addition, a narrow doublet is observed at $\delta = 1.33$ ppm. This resonance is assigned to the free ligand $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P}$. The doubling of the observed resonances in complexes of $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P}$ has been observed previously and has been attributed to restricted rotation about the metal phosphorus bond which makes the individual methyl groups of the ligand nonequivalent.

The equilibrium constant for the substitution reaction, again estimated by integration of the NMR spectrum, was found to be $3.3 \times 10^1$ ($\pm 0.5 \times 10^1$). In this case the $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_3\text{P}$ is the preferred ligand.
Fig. 4-10  220 MHz Spectrum of \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\) Added to \([\{\text{C}_6\text{H}_5\text{P}\}_3\text{RhCl}\)
As in the reaction of \((CH_3)(C_6H_5)_2P\), the exchange of \((CH_3)(C_6H_5)_2P\) with \([(C_6H_5)_3P]_3RhCl\) is slow on the NMR time scale up to 60°C.

The exchange reaction of \([(C_6H_5)_3P]_3RhBr\) with either \((CH_3)(C_6H_5)_2P\) or \((CH_3)(C_6H_5)_2P\) is not as easily studied as the corresponding reactions of the chloride complex. The addition of \((CH_3)(C_6H_5)_2P\) to a chloroform solution of the bromide complex gives an NMR spectrum showing several minor resonances and a strong signal due to free ligand. When the spectrum was recorded twenty times using a computer of average transients (CAT), a complex resonance was observed at \(\delta = 2.25\) ppm. A doublet is observed at \(\delta = 1.85\) ppm and the resonance due to free ligand is off scale. The doublet at \(\delta = 1.85\) ppm probably arises from the unique phosphine of the substituted complex \([(CH_3)(C_6H_5)_2P]_3RhBr\). The very weak spectrum observed indicates that the equilibrium constant for the substitution reaction is very small. Further observation of a sharp signal for the free ligand, and the sharp doublet indicate that the exchange of free \((CH_3)(C_6H_5)_2P\) and the unique phosphine of the substituted complex is slow by the NMR criterion.

The addition of \((CH_3)_2(C_6H_5)_2P\) to the bromide complex gives similar results; a low intensity unresolved resonance is observed at \(\delta = 2.25\) ppm as well as a weak doublet (\(\delta = 1.24\) ppm) assigned to the phosphine trans to the bromide. Again, the equilibrium constant is very small, and the exchange at +18°C appears to be slow.

The addition of \((CH_3)(C_6H_5)_2P\) to a solution of \([(C_6H_5)_3Pi]_3RhI\) results in the observation of the expected NMR spectrum, a triplet of intensity two at \(\delta = 2.21\) ppm and a doublet of intensity one at \(\delta = 1.87\) ppm. The equilibrium constant of the substitution reaction calculated from
integration of the NMR spectrum is 6.0 x 10^{-1} (± 0.4). Again the exchange of free and complexed ligand is slow at +18° and the spectrum is unaltered by warming to 55°C. If this solution is allowed to come into contact with air for a period of about 1 hour, large amounts of (CH₃)₅(C₆H₅)₂PO are formed and a new complex resonance is observed at δ = 2.86 ppm. This spectrum is shown in Figure 4-11. No attempt was made to assign this resonance. Samples used for equilibrium constant determination were prepared under nitrogen and when handled in this way, the δ = 2.86 ppm resonance was not observed.

The NMR results and the data for the equilibrium constants discussed above are collected in Table 4-1, 4-2 and 4-3.

**Summary**

1. The tendency for complete displacement of coordinated (C₆H₅)₃P from trans[[((C₆H₅)₃P)₂MCO(X)] by (CH₃)₂(C₆H₅)P decreases in the order Cl > Br > I, and (CH₃)₂(C₆H₅)P > (CH₃)₂(C₆H₅)P. (M = Rh, Ir).

2. In the rhodium complexes trans L₂RhCO(Cl), the tendency to form cationic complexes is greater for L = (CH₃)₂(C₆H₅)P than for L = (CH₃)(C₆H₅)₂P.

3. In the iridium complexes, trans L₂IrCOX (L = (CH₃)(C₆H₅)₂P and (CH₃)₂(C₆H₅)P and X = Cl, Br) neutral five coordinate and cationic four coordinate complexes are formed by reaction with excess ligand L.

4. The formation of a cationic five coordinate complex L₄IrCO only occurs with the ligand (CH₃)₂(C₆H₅)P.

5. The rate of exchange of trans L₂MCO(X) (M = Rh, Ir; X = Cl, Br; L = (CH₃)(C₆H₅)₂P) with L is fast by the NMR criterion at -50°C.
Fig. 4-11 - 220 MHz $^1$H Spectrum of $(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}$ Added to $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhI}$
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta ) (ppm from TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_2\text{RhCOCl}</td>
<td>2.24</td>
</tr>
<tr>
<td>[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_3\text{RhCO}^+</td>
<td>2.04 (I=2) 1.19 (I=1)</td>
</tr>
<tr>
<td>t-[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_2\text{IrCOCl}</td>
<td>1.92</td>
</tr>
<tr>
<td>t-[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_2\text{IrCOBr}</td>
<td>2.35</td>
</tr>
<tr>
<td>[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_3\text{IrCOCl}</td>
<td>2.43</td>
</tr>
<tr>
<td>[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_3\text{IrCOBr}</td>
<td>1.93</td>
</tr>
<tr>
<td>[((\text{CH}_3))((\text{C}_6\text{H}_5))_2\text{P}]_3\text{IrCO}^+</td>
<td>2.03</td>
</tr>
<tr>
<td>L = ((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}</td>
<td>2.23 (I=2) 1.14 (I=1)</td>
</tr>
<tr>
<td>t-[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_2\text{RhCOCl}</td>
<td>1.92</td>
</tr>
<tr>
<td>t-[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_2\text{IrCOCl}</td>
<td>2.17</td>
</tr>
<tr>
<td>t-[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_2\text{IrCOBr}</td>
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</tr>
<tr>
<td>[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_3\text{RhCOCl}</td>
<td>1.92</td>
</tr>
<tr>
<td>[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_3\text{IrCOCl}</td>
<td>1.92</td>
</tr>
<tr>
<td>[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_3\text{IrCOBr}</td>
<td>1.93</td>
</tr>
<tr>
<td>[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_3\text{IrCO}^+</td>
<td>2.04 (I=2) 1.39 (I=1)</td>
</tr>
<tr>
<td>[((\text{CH}_3))_2((\text{C}_6\text{H}_5))\text{P}]_4\text{IrCO}^+</td>
<td>1.55</td>
</tr>
</tbody>
</table>
TABLE 4-2

NMR Results for $L_3\text{RhX}^*$

$L = (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}$

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (trans to $L$) (ppm)</th>
<th>$\delta$ (trans to $X$) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X = \text{Cl}$</td>
<td>2.61</td>
<td>1.86</td>
</tr>
<tr>
<td>$\text{Br}$</td>
<td></td>
<td>2.25</td>
</tr>
<tr>
<td>$I$</td>
<td>2.21</td>
<td>1.87</td>
</tr>
</tbody>
</table>

$L = (\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}$

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (I=4) (ppm)</th>
<th>$\delta$ (I=2) (ppm)</th>
<th>$\delta$ (I=1) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X = \text{Cl}$</td>
<td>1.98</td>
<td>1.23</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>1.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $\delta$(ppm from TMS)
<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>X</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>([(CH_3)(C_6H_5)_2P])</td>
<td>Cl</td>
<td>fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>fast</td>
</tr>
<tr>
<td>Ir</td>
<td>([(CH_3)_2(C_6H_5)_2P])</td>
<td>Cl</td>
<td>fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br</td>
<td>slow(^1)</td>
</tr>
</tbody>
</table>

\(^1\) Reaction is also slow at +18°.
except in the case of the exchange of trans\([(CH_3)_2(C_6H_5)P)_2IrCO(X)\] 
\((X = Cl, Br)\) and free \((CH_3)_2(C_6H_5)P\).

6. The exchange reactions of \([(C_6H_5)_3P)RhX (X = Cl, Br, I)\] with 
\((CH_3)(C_6H_5)2P\) and \((CH_3)_2(C_6H_5)P\) are slow on the NMR time scale up
to 60°C.

7. The equilibrium for the exchange reactions of \([(C_6H_5)_3P)RhX\] with 
\((CH_3)(C_6H_5)2P\) and \((CH_3)_2(C_6H_5)P\) strongly favours the \((C_6H_5)_3P\)
complex for \(X = Br\). The \((C_6H_5)_3P\) is marginally preferred in the
case of \(X = Cl\), and \(L = (CH_3)(C_6H_5)2P\). In contrast, \((CH_3)_2(C_6H_5)P\)
is the preferred ligand for \(X = Cl\).
CHAPTER V

CHARGE DISTRIBUTIONS IN GROUP VIII TRANSITION METAL COMPLEXES

5.1 INTRODUCTION

The fact that substituents influence the course of organic chemical reactions has been recognized for many years. The first successful attempt to put these observations on a quantitative footing was made by Hammett. Hammett was able to demonstrate a correlation between the substituent and the reactivity for a number of reactions in terms of a reaction constant and a substituent constant. Later work showed that in aromatic systems the substituent constant was better described as a sum of several terms. Still later, Taft suggested the use of $^{19}$F NMR chemical shifts as a measure of the substituent effects in such systems. A few attempts have been made to extend the use of $^{19}$F NMR to determine substituent effects and thus deduce electron densities in inorganic systems. It must be pointed out that the $^{19}$F NMR approach to determining electron densities has been criticized on theoretical grounds, but the empirical foundation of such results tends to lend some confidence to such measurements.

As was pointed out earlier, experimental measurements of charge densities in transition metal complexes are largely unavailable. Since the chemical reactivities of such complexes might well be expected to depend upon such charge densities, the experimental determination of the relative charge densities of a number of group VIII metal phosphine complexes was undertaken. This chapter reports the results of this phase of the study.
5.2 SUBSTITUENT PARAMETERS

The fact that substituents affect organic chemical reactions can be seen by the variation in the acidity of a number of substituted benzoic acids. The acidity measured by the $pK_a$, is shown in Table 5-1 for the reaction

$$RC_6H_4CO_2H \rightarrow RC_6H_5CO_2^- + H^+$$

where

$$K_a = \frac{[RC_6H_5CO_2^-][H^+]}{[RC_6H_4CO_2H]}$$

and

$$pK_a = -\log_{10} K_a$$

Hammett recognized that the $pK_a$'s for a series of substituted phenylacetic acids when plotted against the $pK_a$'s for the same substituents in the benzoic acid series gave a straight line plot as shown in Figure 5-1. Thus, the ratio of the ionization constant for substituted phenylacetic acid to phenylacetic acid plotted against the same ratio for substituted and unsubstituted benzoic acids also yields a straight line as shown in Figure 5-2, and is the more conventional way of displaying the results. The equation of this line is

$$\log \frac{K}{K_0} = p \log \frac{K'}{K'_0}$$

where $K$ refers to the phenylacetic acid series and $K'$ to the benzoic acid series, while the subscript refers in each case to the unsubstituted acid. This relation has been found to apply to a variety of reactions including the ionization of acids, the saponification of esters, the
Fig. 5-1  Plot of pKa benzoic acid series versus pKa phenylacetic acid series

pKa Benzoic acid

pKa Phenylacetic acids

- p-CH₃
- p-Cl
- p-Br
- m-Cl
- m-NO₂
- p-NO₂
- H
Fig. 5-2  Plot of $K/K_0$ for phenylacetic acids versus $K/K_0$ for benzoic acids

$\log K/K_0$
phenylacetic acids

$\log K/K_0$
benzoic acids

$K_0$ ionization constant of parent acid

$K$ ionization constant of substituted acid.
TABLE 5-1

Effect of Changing Substituent on pKa in the Benzoic Acid Series

<table>
<thead>
<tr>
<th>R</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4.19</td>
</tr>
<tr>
<td>m-Cl</td>
<td>3.82</td>
</tr>
<tr>
<td>p-Cl</td>
<td>3.98</td>
</tr>
<tr>
<td>m-Br</td>
<td>3.86</td>
</tr>
<tr>
<td>m-OH</td>
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</tr>
<tr>
<td>p-OH</td>
<td>4.48</td>
</tr>
<tr>
<td>m-I</td>
<td>3.80</td>
</tr>
<tr>
<td>m-NO₂</td>
<td>3.47</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>3.41</td>
</tr>
<tr>
<td>m-CH₃</td>
<td>4.27</td>
</tr>
<tr>
<td>p-CH₃</td>
<td>4.36</td>
</tr>
</tbody>
</table>
TABLE 5-2
Hammet $\rho$ Values for Some Equilibrium Reactions (25°C)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Solvent</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$</td>
<td>$H_2O$</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>40% ETOH</td>
<td>1.668</td>
</tr>
<tr>
<td></td>
<td>50% ETOH</td>
<td>1.601</td>
</tr>
<tr>
<td></td>
<td>70% ETOH</td>
<td>1.738</td>
</tr>
<tr>
<td></td>
<td>80% ETOH</td>
<td>1.791</td>
</tr>
<tr>
<td></td>
<td>90% ETOH</td>
<td>1.896</td>
</tr>
<tr>
<td></td>
<td>ETOH</td>
<td>1.957</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>1.537</td>
</tr>
<tr>
<td>$C_6H_5CH_2CO_2H \rightleftharpoons C_6H_5CH_2CO_2^- + H^+$</td>
<td>$H_2O$</td>
<td>0.489</td>
</tr>
<tr>
<td></td>
<td>$H_2O$</td>
<td>0.212</td>
</tr>
<tr>
<td>$C_6H_5CH=CHCO_2H \rightleftharpoons C_6H_5CH=CHCO_2^- + H^+$</td>
<td>$H_2O$</td>
<td>0.466</td>
</tr>
<tr>
<td></td>
<td>$H_2O$</td>
<td>6.67</td>
</tr>
<tr>
<td>$C_6H_5NH_3^+ + H_2O \rightleftharpoons (C_6H_5)_2CHOH + H^+$</td>
<td>$H_2SO_4$</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td>$H_2SO_4$</td>
<td>2.767</td>
</tr>
<tr>
<td></td>
<td>$H_2O$</td>
<td>3.016</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>3.435</td>
</tr>
<tr>
<td></td>
<td>30% ETOH</td>
<td>3.535</td>
</tr>
<tr>
<td></td>
<td>ETOH</td>
<td>3.256</td>
</tr>
<tr>
<td></td>
<td>45% dioxane</td>
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<tr>
<td></td>
<td>70% dioxane</td>
<td>3.567</td>
</tr>
<tr>
<td>$C_6H_5H(CH_3)_2H^+ \rightleftharpoons C_6H_5N(CH_3)_2 + H^+$</td>
<td>30% ETOH</td>
<td>3.426</td>
</tr>
<tr>
<td></td>
<td>50% ETOH</td>
<td>4.191</td>
</tr>
<tr>
<td></td>
<td>$H_2O$</td>
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</tr>
<tr>
<td></td>
<td>30% ETOH</td>
<td>3.197</td>
</tr>
<tr>
<td></td>
<td>49% ETOH</td>
<td>2.545</td>
</tr>
<tr>
<td></td>
<td>95% ETOH</td>
<td>2.364</td>
</tr>
</tbody>
</table>
solvolysis of benzyl halides, the ionization of phenols and thiophenols and the protonation of anilines.

Equation 5-4 above may be rewritten as

$$\log \frac{K}{K_0} = \rho \sigma$$

where

$$\sigma = \log \frac{K'}{K_0}$$

The reaction constant, $\rho$, measures the sensitivity of a particular reaction to changes in the properties of the reactant, i.e., to substitution, while the substituent constant, $\sigma$, measures the effect of a particular substituent on a given reaction. The values of $\rho$, the reaction constant, are shown in Table 5-2 for a number of reactions. The values of the substituent constant $\sigma$ for a number of common substituents are shown in Table 5-3.

It was pointed out by Taft, that the electronic factors which give rise to these observations can operate by at least two mechanisms, an inductive effect and a resonance effect. A further effect (the field effect) arising from through space interaction of dipoles has been described but will not be considered. The inductive effect operates through bonds and is the result of net electronic charge displacement caused by differing electronic properties of the various substituents, for example, the electronnegative chlorine atom in chloroacetic acid could be expected to stabilize the anion causing chloroacetic acid to be a stronger acid than the parent molecule, acetic acid, which has no such anion stabilization. In going from the acid to the anion of benzoic acid the coulomb integral for the C_1 carbon will change. This
TABLE 5-3
Substituent Parameters

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma$</th>
<th>Substituent</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-NH$_2$</td>
<td>-0.660</td>
<td>M-NH$_2^-$</td>
<td>-0.160</td>
</tr>
<tr>
<td>p-OCH$_3$</td>
<td>-0.268</td>
<td>M-OCH$_3$</td>
<td>+0.115</td>
</tr>
<tr>
<td>p-Cl</td>
<td>+0.226</td>
<td>M$_7$Cl</td>
<td>+0.373</td>
</tr>
<tr>
<td>p-Br</td>
<td>+0.232</td>
<td>M-Br</td>
<td>+0.381</td>
</tr>
<tr>
<td>p-NO$_2$</td>
<td>+0.778</td>
<td>M-NO$_2$</td>
<td>+0.710</td>
</tr>
<tr>
<td>p-I</td>
<td>+0.276</td>
<td>M-I</td>
<td>+0.352</td>
</tr>
</tbody>
</table>

TABLE 5-4
Inductive and Resonance Parameters

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma_I$</th>
<th>$\sigma_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>0.10</td>
<td>-0.76</td>
</tr>
<tr>
<td>OH</td>
<td>0.25</td>
<td>-0.61</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-0.05</td>
<td>-0.13</td>
</tr>
<tr>
<td>F</td>
<td>0.50</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cl</td>
<td>0.47</td>
<td>-0.24</td>
</tr>
<tr>
<td>Br</td>
<td>0.45</td>
<td>-0.22</td>
</tr>
<tr>
<td>CN</td>
<td>0.59</td>
<td>+0.07</td>
</tr>
</tbody>
</table>
will result in a change in the \( \pi \) electron distribution which will be
greatest at the ortho and para positions. Thus, the interaction of an
ortho or para substituent with the changed electron density will in-
fluence the acid strength. Studies of the resonance effect have
chiefly been confined to substitution in the para position since ortho
substitution often gives rise to steric interactions which can con-
siderably complicate the interpretation of results.

From the above considerations it is apparent that the substituent
parameter is a sum of inductive and resonance contributions.

\[ \sigma = \sigma_I + \sigma_R \]

These contributions may be separated if the resonance contribution is
assumed to be zero at the meta position while both contributions are
important at the para position. This type of approach to the measure-
ment of electron density distributions has found widespread acceptance
particularly in the field of physical organic chemistry.

5.3 \( ^{19}F \) NMR CHEMICAL SHIFTS AS AN ELECTRON DENSITY PROBE

The preliminary investigation of \( ^{19}F \) NMR chemical shifts in
substituted fluorobenzenes was carried out by Gutowsky et al.\(^{66}\) In a
series of papers\(^{67-69}\) in the late 1950's and early 1960's, Taft and
coworkers showed that \( ^{19}F \) chemical shifts in fluoroaromatic systems
yield values for inductive and resonance parameters which correlated
well with the values obtained from chemical reactivity measurements.
Taft then showed that the constants derived from such \( ^{19}F \) chemical
shifts are consistent with LCAO-MO calculation.\(^{67}\) The parameters
used by Taft were the inductive and resonance substituent parameters,
\( \sigma_I \) and \( \sigma_R^0 \), and the \( ^{19}F \) chemical shifts, \( \delta_{\text{para}} \) and \( \delta_{\text{meta}} \), for the para and meta substituted fluorobenzene relative to fluorobenzene itself. Table 5-4 shows these parameters for a number of common substituents. The equations used by Taft and later by Rakshys\(^70\) to separate \( \sigma_I \) and \( \sigma_R^0 \) are

\[
\delta_{\text{meta}} = -7.10 \sigma_I + 0.60
\]
\[
\delta_{\text{para}} - \delta_{\text{meta}} = -29.5 \sigma_R^0
\]

These equations have been modified by several authors to better describe particular systems but such modifications usually involve only changes in the numerical constants. In fact, some authors have based their arguments on the magnitudes of \( \delta_{\text{meta}} \) and \( \delta_{\text{para}} - \delta_{\text{meta}} \) without using any proportionality constants at all.

Returning to the substituent parameters \( \sigma_I \) and \( \sigma_R^0 \) shown in Table 5-4, it is obvious that \( \sigma \) withdrawing substituents (e.g., F\(^-\)) are associated with positive \( \sigma_I \)'s (\( \sigma_I = 0.50 \)) while \( \sigma \) donating substituents are associated with negative \( \sigma_I \) (e.g., CH\(_3\) = -0.05). Similar considerations show that \( \pi \) withdrawing substituents are associated with positive \( \sigma_R^0 \) (CN = 0.07) while \( \pi \) donating substituents are associated with negative \( \sigma_R^0 \) (F\(^-\) = -0.04).

Perhaps the best known inorganic application of the \( ^{19}F \) NMR method used as an electron density probe is the work of Parshall. In reporting the \( ^{19}F \) chemical shifts for a series of platinum(II) complexes\(^71,72\) trans\(\{(\text{C}_2\text{H}_5)_3\text{P}\}_2\text{Pt}(\text{C}_6\text{H}_4\text{F})X\), Parshall noted that the \( ^{19}F \) shifts showed a marked dependence upon the nature of the univalent anionic ligand \( X \). These results show that both \( \sigma_R^0 \) and \( \sigma_I \) are generally negative suggesting as discussed above that the substituent trans\(\{(\text{C}_2\text{H}_5)_3\text{P}\}_2\text{PtX}\) is both a \( \sigma \) and \( \pi \) donor. The trans group \( X \) has a marked influence
particularly on $\sigma_1$ showing the order $\text{CH}_3 > \text{C}_6\text{H}_5 > \text{C}_6\text{H}_5\text{C}=\text{C} - > \text{CH} > \text{Cl} > \text{Br} > \text{I}$. This then appears to be the order of decreasing electron donation to the aromatic ring.

In a study of the Co(III) system, Hill and coworkers compared Parshall's results to those obtained for the complex trans $\text{(FC}\text{C}_6\text{H}_4\text{)}\text{Co(DO(DOH))pn}X$ where $X$ is again a series of anions and [DO(DOH)pn] is diacetylimonoimino-diacetylimonoiminoimino propane 1,3. The results for the cobalt complexes again show negative values for both $\sigma_1$ and $\sigma_R^0$, again indicating that the substituent trans Co[DO(DOH)pn] is acting as both a $\sigma$ and $\pi$ electron donor. The $\sigma_1$'s show a similar ordering to that obtained by Parshall, i.e., $\text{CH}_3 > \text{Br} > \text{I}$, however, the cobalt results tend to be somewhat more positive indicating that the cobalt substituent is a poorer $\sigma$ donor than the platinum substituent. On the other hand, the $\sigma_R^0$ values tend to be somewhat more negative for the cobalt complexes showing the cobalt substituent trans Co[DO(DOH)pn]X to be a better $\pi$ donor than the platinum trans$[\text{(C}_6\text{H}_5\text{)}_3\text{P}]_2\text{PtX}$ substituent.

Church and May prepared a series of cationic complexes trans$[\text{(C}_2\text{H}_5\text{)}_3\text{P}]_2\text{Pt(C}_6\text{H}_4\text{F})L^+$ where $L$ was any of a series of neutral ligands. Based upon "generally held ideas that electronegative substituents on a phosphorus ligand increases the $\pi$ acceptor strength" they expected $(\text{CH}_3\text{O})_3\text{P}$ to be a better $\pi$ acceptor than $(\text{C}_2\text{H}_5)_3\text{P}$. They thus expected that the $\pi$ donation to the fluoroaromatic would be reduced when the good $\pi$ accepting ligand $(\text{CH}_3\text{O})_3\text{P}$ was the trans ligand $L$. Thus they looked for a more positive value for $\sigma_R^0$ for the complex trans$[\text{(C}_2\text{H}_5)_3\text{P}]_2\text{Pt(C}_6\text{H}_4\text{F})(\text{CH}_3\text{O})_3\text{P}$ compared to $[\text{(C}_2\text{H}_5)_3\text{P}]_3\text{Pt(C}_6\text{H}_4\text{F})$. In fact, the reverse was found to be true. Commenting that conditions necessary for good $\pi$ overlap between the metal and the fluoroaromatic
centre are not known, these workers dismissed their results as unreliable. With the authors' reservations in mind, it is interesting to compare these results with Parshall's results. Where Parshall found that the substituent trans\((C_2H_5)_3P\)\(_2\)PtX acts as both a \(\sigma\) and \(\pi\) donor, Church and May's results (positive \(\sigma_1\)'s and negative \(\sigma_R^0\)'s) indicated that the substituent trans\((C_2H_5)_3P\)\(_2\)PtL acts as a \(\sigma\) acceptor but a \(\pi\) donor. In addition, the values of the \(\sigma_R^0\) obtained for the cationic complexes are considerably more positive than those obtained for the neutral complexes. Thus, in the cations, the substituent, although still acting as a \(\pi\) donor, shows a donation considerably reduced from that observed with the neutral species. The sigma effect seems reasonable since the cationic species would be expected to display an increased electron affinity over that shown by the neutral species. Similarly a reduction of the \(\pi\) donating ability of the metal centre in a cation is not unexpected. Turning to particular complexes it is apparent that in the carbonyl complex trans\([(C_2H_5)_3P]_2\)Pt\((C_6H_4)\)CO the large value of \(\sigma_1\) and the small value of \(\sigma_R^0\) indicate that the \(C_6H_4\) is acting as a better donor to compensate for the poor donor properties of the carbonyl ligand, while acting as a poor \(\pi\) accepting ligand to compliment the significant \(\pi\) acceptor properties of the carbonyl ligand. At the other end of the scale, the \(C_6H_4\) group in the complex \([(C_2H_5)_3P]_3\)Pt\((C_6H_4)\) is acting as a much poorer \(\sigma\) donor to compliment the increased \(\sigma\) donor properties (see Chapter VI) of the \((C_2H_5)_3P\) group. However, the phosphine is not a particularly good \(\pi\) acceptor so the \(\sigma\) density is donated largely to the \(C_6H_4\) group resulting in a more negative value of \(\sigma_R^0\). This concept of balancing
ligand donor/acceptor properties with metal acceptor/donor properties will be discussed in greater detail in Chapter VI.

A study of gold(I) complexes was undertaken by Nichols, in which a series of complexes LAu(C_{6}H_{4}F) (L = (C_{2}H_{5})_{3}P, (nC_{3}H_{7})_{3}P, (CH_{3})_{2}(C_{6}H_{5})P, (pCH_{3}C_{6}H_{4})_{3}P, (C_{2}H_{5})(C_{6}H_{5})_{2}P, (C_{6}H_{5})_{3}P, (C_{6}F_{5})_{3}P and (C_{6}H_{5}O)_{3}P) were prepared and the $^{19}$F chemical shifts studied as the neutral ligand L was varied. The chemical shift of the meta fluoro complexes was found to be approximately independent of the nature of the phosphine or phosphite ligand L. This indicates that the substituent L Au is not particularly polarizable in the sigma system, that is, the substituent L Au has a fairly well defined electronic requirement in the sigma system. However, these complexes show a marked dependence of $\sigma_R^0$ on the nature of L. Compared to the platinum and cobalt systems, the gold substituent is a very weak $\pi$ donor. In addition, for the ligands L (= (C_{2}H_{5})_{3}P, (nC_{3}H_{7})_{3}P, (CH_{3})_{2}(C_{6}H_{5})P which are usually thought of as good $\sigma$ donors, the value of $\sigma_R^0$ is usually rather negative, thus the fairly basic phosphines (C_{2}H_{5})_{3}P, (C_{3}H_{7})_{3}P and (CH_{3})_{2}(C_{6}H_{5})P give the most negative $\sigma_R^0$'s of this series, while the weaker $\sigma$ donors (C_{6}H_{5})_{3}P and (C_{6}F_{5})(C_{6}H_{5})_{2}P give more positive $\sigma_R^0$ values. This affords then another example of the matching of the ligand donor/acceptor properties with the metal acceptor/donor properties. These gold complexes seem to have a particularly narrow range of acceptable $\sigma$ electron densities as witnessed by the narrow range of $\sigma_1$ values. However, the differing ligands L are accommodated by varying amounts of $\pi$ back-donation so that for a good $\sigma$ donor (C_{2}H_{5})_{3}P the excess negative charge on the metal centre is relieved by increased $\pi$ donation to the C_{6}H_{4}F group. Since (C_{2}H_{5})_{3}P is a poorer $\pi$ acceptor and a better $\sigma$
donor than \((\text{C}_6\text{H}_5)_3\text{P}\), greater amounts of negative charge must be donated \(\pi\) to the \(\text{C}_6\text{H}_4\text{F}\) unit in the \((\text{C}_2\text{H}_5)_3\text{P}\) complex.

Rakhys, Taft and Sheppard\(^70\) have measured the \(^{19}\text{F}\) shifts for a series of phosphines of the type \(\text{mFC}_6\text{H}_4\text{PX}_2\) and have deduced that charge donation from the filled aromatic \(\pi\) orbitals to empty phosphorus \(d\) orbitals and charge donation from the filled phosphorus \(p\pi\) orbitals to the aromatic ring both occur to an extent, depending on the nature of \(X\).

Murray et al.\(^77\) reported several complexes of \((\text{FC}_6\text{H}_4)_3\text{P}\). However, it does not appear that an extensive study of such complexes has been published.

Following from the work of Parshall and others, it was decided to employ the \(^{19}\text{F}\) chemical shift method to a series of group VIII complexes. Rakhys et al.\(^70\), as discussed above, have shown that the separation of \(\alpha_1\) and \(\alpha_0\) is applicable to phosphines and thus it seemed reasonable to assume that the separation of \(\alpha_1\) and \(\alpha_0\) would be possible for complexed fluorophenylphosphines. The results of this study are reported below.

5.4 **EXPERIMENTAL RESULTS**

The trisubstituted phosphines \((\text{FC}_6\text{H}_4)_3\text{P}\) were chosen to avoid shifts arising from charge transfer between inequivalent aromatic rings. The complexes studied were some thirty phosphine complexes of platinum(0) and platinum(1), palladium(II) and nickel(II), rhodium(1), iridium(1), rhodium(III) and iridium(III). The complexes were prepared either by direct synthesis or by ligand exchange with the triphenylphosphine.
complex whereby the desired complex was formed in situ. The ligand exchange method was used because of the experimental simplicity in that the triphenylphosphine complexes were often commercially available. This method gives the additional information of equilibrium constants for the exchange reaction (by integration of the NMR spectrum), as well as a qualitative indication of the rate of this reaction. However, there are three rather serious drawbacks to this method. First, the equilibrium constant for the reaction may very strongly favour the triphenylphosphine complex so that no ligand exchange is observed. Second, the rate of ligand exchange may be fast on the NMR time scale such that, as pointed out in Chapter II, only an averaged signal is observed. Thus, not knowing the equilibrium constant for the exchange reaction or the limiting shift of the fluorophenylphosphine complex, precise values for these unknowns are difficult to obtain. Finally, some doubt inevitably arises concerning the nature of the product, i.e., there is no definitive proof that the only reaction is the exchange of \( \text{FC}_6\text{H}_4\text{P} \) for \( \text{C}_6\text{H}_5\text{P} \). It was for this final reason that in several cases the complexes were prepared by both synthetic routes and the \(^{19}\text{F NMR shifts} \) were found to be identical. Characterization of the complexes prepared by direct synthesis, although a somewhat more time consuming process, at least dispels any doubt concerning the nature of the complex being studied.

The solvent used throughout this stage of the work was \text{CDCl}_3. Although in studying the \(^{19}\text{F NMR spectrum} \) deuteronated solvent is not required it was used since it appeared to be considerably purer than even spectroscopic grade \text{CHCl}_3. This particular solvent was chosen since most of the complexes studied are reasonably soluble.
Since solvent shifts are sometimes appreciable, it was felt that changing solvents for particular complexes which show low solubility in CDCl₃ was inadvisable.

The results for the complexes studied are shown in Table 5-4. For each complex the chemical shifts for both the meta and para tris fluorophenylphosphine are shown. In addition, the values of $\sigma_I$ and $\sigma_R^0$ calculated from equations 5-9 and 5-10 are shown. Finally, the method by which the complexes were prepared is shown. As seen from the table, this method appears to hold considerable promise since the range of observed chemical shifts extends over approximately 7 ppm. This gives a reasonably sensitive probe since the observed chemical shifts can be measured to ± 0.02 ppm. The observation of a 7 ppm range of chemical shifts when compared to the 25 ppm range observed in substituted fluorobenzenes for which the substitution is one atom closer than in the phosphine complexes, indicates that substantial electronic effects are operative.

5.5 DISCUSSION

The ligands in metal complexes generally act as Lewis bases, i.e., as electron donors. The general expectation is that donation of electrons from the phosphorus atom to the metal will leave a greater positive charge on the phosphorus and hence enhance its electron withdrawing properties with respect to the aromatic ring. This will be reflected in a more positive value for $\sigma_I$. It is also recognized though that the phosphine ligands can function as electron acceptors from the metal if metal-ligand $\pi$ bonding is present. Such bonding will decrease the positive charge on the phosphorus and hence make
\[ ^{19}F \text{ Chemical Shifts}^a \text{ of Tri(fluorophenyl)phosphone Complexes} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>( \delta_m^c )</th>
<th>( \delta_p^c )</th>
<th>( \sigma_1^0 )</th>
<th>( \sigma_2^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>d</td>
<td>-1.0</td>
<td>-1.0</td>
<td>0.23</td>
<td>0.00</td>
</tr>
<tr>
<td>L0</td>
<td>d</td>
<td>2.9</td>
<td>-6.8</td>
<td>0.49</td>
<td>0.13</td>
</tr>
<tr>
<td>LMe(^{+})I(^{-})</td>
<td>d</td>
<td>-6.4</td>
<td>-13.5</td>
<td>0.99</td>
<td>0.24</td>
</tr>
<tr>
<td>( L_2\text{PtCl}_2 )</td>
<td>d,g</td>
<td>-2.3</td>
<td>-5.9</td>
<td>0.41</td>
<td>0.12</td>
</tr>
<tr>
<td>( L_2\text{PtBr}_2 )</td>
<td>g</td>
<td>-2.6</td>
<td>-6.0</td>
<td>0.45</td>
<td>0.12</td>
</tr>
<tr>
<td>( L_2\text{PtI}_2 )</td>
<td>g</td>
<td>-1.6</td>
<td>-4.8</td>
<td>0.31</td>
<td>0.11</td>
</tr>
<tr>
<td>( L_2\text{Pt(SCN)}_2 )</td>
<td>g</td>
<td>-3.4</td>
<td>-6.8</td>
<td>0.56</td>
<td>0.12</td>
</tr>
<tr>
<td>( L_2\text{PtO}_2 )</td>
<td>d,e</td>
<td>-2.6</td>
<td>-8.3</td>
<td>0.45</td>
<td>0.19</td>
</tr>
<tr>
<td>( L_2\text{PtCS}_2 )</td>
<td>d</td>
<td>-2.2</td>
<td>-4.4</td>
<td>0.39</td>
<td>0.08</td>
</tr>
<tr>
<td>( L_2\text{PtDPA} )</td>
<td>d,e</td>
<td>-1.0</td>
<td>-1.9</td>
<td>0.23</td>
<td>0.02</td>
</tr>
<tr>
<td>( L_2\text{PtHCl} )</td>
<td>d,e</td>
<td>-2.2</td>
<td>-5.0</td>
<td>0.39</td>
<td>0.10</td>
</tr>
<tr>
<td>( L_2\text{PtFClI} )</td>
<td>d,e</td>
<td>-2.8</td>
<td>-6.3</td>
<td>0.48</td>
<td>0.12</td>
</tr>
<tr>
<td>( L_2\text{PdCl}_2 )</td>
<td>d,e</td>
<td>-2.11</td>
<td>-5.41</td>
<td>0.38</td>
<td>0.11</td>
</tr>
<tr>
<td>( L_2\text{PdBr}_2 )</td>
<td>d,e</td>
<td>-2.13</td>
<td>-4.84</td>
<td>0.38</td>
<td>0.09</td>
</tr>
<tr>
<td>( L_2\text{PdI}_2 )</td>
<td>d,e</td>
<td>-2.00</td>
<td>-4.55</td>
<td>0.37</td>
<td>0.09</td>
</tr>
<tr>
<td>( L_2\text{Pd(SCN)}_2 )</td>
<td>g</td>
<td>-3.4</td>
<td>-7.0</td>
<td>0.56</td>
<td>0.12</td>
</tr>
<tr>
<td>( L_2\text{Ni(NCS)}_2 )</td>
<td>d</td>
<td>-2.4</td>
<td>-4.4</td>
<td>0.43</td>
<td>0.07</td>
</tr>
<tr>
<td>( L_3\text{Rho}_1 )</td>
<td>e</td>
<td>-h</td>
<td>-2.1</td>
<td>0.49</td>
<td>-0.02</td>
</tr>
<tr>
<td>( L_3\text{RhoBr} )</td>
<td>e</td>
<td>-2.9</td>
<td>-2.4</td>
<td>0.49</td>
<td>0.02</td>
</tr>
<tr>
<td>( L_3\text{RhoI} )</td>
<td>e</td>
<td>-2.5</td>
<td>-3.85</td>
<td>0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>( L_2\text{Rho(CO)}_2 )</td>
<td>d</td>
<td>-1.99</td>
<td>-3.85</td>
<td>0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>( L_3\text{RhoCl}_3 )</td>
<td>d</td>
<td>-1.4</td>
<td>-3.80</td>
<td>0.28</td>
<td>0.08</td>
</tr>
<tr>
<td>( L_2\text{Ir(CO)}_2 )</td>
<td>d</td>
<td>-1.95</td>
<td>-4.15</td>
<td>0.36</td>
<td>0.08</td>
</tr>
<tr>
<td>( L_2\text{Ir(CO)}_2\text{HCl} )</td>
<td>d</td>
<td>-2.61</td>
<td>-5.80</td>
<td>0.45</td>
<td>0.11</td>
</tr>
<tr>
<td>Compound</td>
<td>Method</td>
<td>$\delta^c_m$</td>
<td>$\delta^c_p$</td>
<td>$\sigma^i$</td>
<td>$\sigma^o$</td>
</tr>
<tr>
<td>------------------</td>
<td>--------</td>
<td>--------------</td>
<td>--------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>L$_2$Ir(CO)Cl$_3$</td>
<td>d</td>
<td>-2.84</td>
<td>-5.85</td>
<td>0.48</td>
<td>0.10</td>
</tr>
<tr>
<td>L$_2$Ir(CO)ClMeI</td>
<td>d</td>
<td>-2.73</td>
<td>-5.16</td>
<td>0.47</td>
<td>0.08</td>
</tr>
<tr>
<td>L$_2$Ir(CO)ClO$_2$</td>
<td>d</td>
<td>-2.38</td>
<td>-5.62</td>
<td>0.42</td>
<td>0.11</td>
</tr>
<tr>
<td>L$_2$Ir(CO)BrO$_2$</td>
<td>d</td>
<td>-2.39</td>
<td>-5.73</td>
<td>0.42</td>
<td>0.11</td>
</tr>
<tr>
<td>L$_2$Ir(CO)IO$_2$</td>
<td>d</td>
<td>-2.75</td>
<td>-5.75</td>
<td>0.47</td>
<td>0.10</td>
</tr>
<tr>
<td>L$_3$IrCl$_3$</td>
<td>d</td>
<td>1.35</td>
<td>3.25(2)</td>
<td>0.27</td>
<td>0.06</td>
</tr>
</tbody>
</table>

| L$_3$Ir(CO)H    | e      | -0.71        | -0.23        | 0.18      | -0.02     |

\[\text{Shifts in ppm from fluorobenzene}\]

\[^a\] Solvent CHCl$_3$

\[^b\] L = meta or para tri(fluorophenyl)phosphine

\[^c\] Compound synthesized directly

\[^d\] Ligand exchange with triphenylphosphine complex

\[^e\] Data from reference 9

\[^f\] Exchange equilibrium too unfavourable to obtain data

\[^g\] DPA = diphenylacetylene

\[^h\] RF = CCl$_2$CClF$_2$
more negative. In general, it is expected that $\sigma_I$ will depend upon both of these effects. The interpretation of $\sigma_R^0$ is not straightforward. As pointed out by Rakshys et al, in the parent phosphines both donation of electrons to the π system of the ring from the phosphorus lone pair and acceptance of electrons from the π system of the ring into the empty phosphorus d orbitals can be envisaged. The observation of a small or zero $\sigma_R^0$ indicates that these effects either cancel each other out or are negligibly small. If the phosphine is complexed to a metal, the lone pair will no longer be available for donation to the ring. Any excess positive charge on the phosphorus will also tend to enhance donation to the empty d orbitals. Both of these effects will give rise to the positive $\sigma_R^0$. It might be expected that the increase in $\sigma_R^0$ would parallel that in $\sigma_I$. However, the further possibility of donation from the metal d orbitals to the phosphorus d orbitals exists. This could lead to the subsequent donation from the phosphorus d orbitals to the aromatic system. Such a process would make a negative contribution to $\sigma_R^0$. There are obviously some steric restrictions on the conjugation of this type. In most cases, it is not clear whether the aromatic rings will or will not be suitably oriented.

Methyltriphenylphosphonium iodide provides a qualitative indication of the magnitude of the effects to be expected in the absence of metal d orbitals. Compared to triphenylphosphine, the $\sigma_I$ value has increased by 0.76 units (from +0.23 to +0.99) and $\sigma_R^0$ has increased by 0.24 units. This can be taken as a measure of the effect of placing a full positive charge on the phosphorus atom. A rather closer analogy
to complex formation (again without the added complication of d orbitals) is provided by the phosphine oxide results. In this case, $\sigma_I$ has increased by 0.26 units and $\sigma_R^0$ by 0.13 units. This result would indicate about 1/3 or 1/2 of a positive charge on the phosphorus.

For the metal complexes studied, $\sigma_I$ is, in all cases except one, equal to or greater than $\sigma_I$ for the free ligand, i.e., the phosphine is behaving as a Lewis base. The magnitude of the enhancement (0 to 0.33 units) provides a very rough measure of the positive charge on the phosphorus. Turning to specific compounds, the series of diminishing $\sigma_I$ values provided by the various platinum complexes is noted.

$$L_2\text{Pt(SCN)}_2 > L_2\text{PtO}_2 > L_2\text{PtCl}_2 > L_2\text{PtBr}_2 > L_2\text{PtHCl} > L_2\text{PtCS}_2 > L_2\text{PtI}_2 > L_2\text{Pt(DPA)} \quad \text{(DPA = diphenylacetylene)}$$

The range of $\sigma_I$ values ($\sigma_I = 0.56$ to 0.33) covered by this series indicates substantial differences in the amount of negative charge donated to the metal. This series is expected to parallel the charge on the metal. It may be noted that formally Pt(II) complexes tend to occur at the high end of the series and the formally Pt(0) complexes at the low end. There is, however, no sharp line between these two oxidation states. In cases where analogous compounds are involved these results parallel nicely the ESCA energies reported by Cook et al., i.e.,

$$L_2\text{PtCl}_2 > L_2\text{PtO}_2 > L_2\text{PtCS}_2 > L_2\text{PtDPA} \quad (L = (C_6H_5)_3P)$$

Notable in this series is the high $\sigma_I$ value for the oxygen complex. Ibers suggested that the formation of such stable oxygen complexes required donation of $\pi$ electrons to the oxygen moiety which implies that these electrons are less available for donation to other
ligands. This would seem to be reflected in the high $\sigma_I$ value. A similar argument could be applied to the thiocyanate complex. It is also interesting that the hydride complex has a relatively low $\sigma_I$, in accord with the lack of $\pi$ acceptor properties of the hydride ligand. In cases where the change in $\sigma_I$ is close to zero, it is inferred that the negative charge lost from the phosphorus by sigma donation is balanced by the gain from backbonding. Thus, for the diphenylacetylene complex (and probably also for the tetrakis phosphine complex (see Experimental Section) $\sigma$ and $\pi$ bonding are both important. It is thus suggested that $\sigma_I$ values derived in this manner provide an empirical measure of the electron affinity of the metal atoms in differing ligand environments. It would be natural to associate the "electron affinity of the metal" with the positive charge on the metal. This, however, is probably an excessive simplification since the effect of charge transfer from one ligand may be enhanced or diminished by charge transfer from other ligands so that any measurement involving only one ligand will not reflect the true metal charge.

It would be desirable to compare $\sigma_I$ values for the Pt complexes with those of analogous square planar complexes of Pd and Ni. Unfortunately, the data on hand does not allow direct comparison. Many Ni(II) phosphine complexes are tetrahedral and paramagnetic. Interaction with the unpaired electrons prevent analysis of the chemical shifts in the above manner. The Ni(II) isothiocyanate complex cannot be compared directly with the Pd and Pt thiocyanate complexes. From the results for the chloride and the bromide complexes, it would appear that the electron affinity of Pt is rather greater than that of Pd but the iodide gives the opposite indication. However, the Pt
complexes, have cis geometry and the analogous Pd complexes have trans
gamma: The results may, therefore, arise more from extra electron
withdrawing ability of a trans halide io than any intrinsic difference
between Pt and Pd. It is, however, interesting to note that in the
square planar $d^8$ complexes the formally singly charged Rh and Ir do
not have notably lower electron affinities than the formally doubly
charged Pd and Pt.

Perhaps the most interesting comparisons are between the four
coordinate Rh(I) and Ir(I) complexes and the six coordinate Rh(III)
and Ir(III) compounds. Oxidative addition to Vaska's compound ($L_2$IrCOC$\bar{\text{I}}$),
for example, is accompanied by a formal increase in the oxidation state
of the metal from +1 to +3 so that it might be expected that there would
be an increase in the positive charge on the metal, and hence an increase
in $\sigma_1$ for the phosphine ligand. On the other hand, it could be argued
that these compounds tend to be covalent rather than ionic and that
the relevant change is an increase in the number of electrons from
16 in the valence shell of the four coordinate compounds to 18 electrons
in the six coordinate compounds. This would imply an increase in
the negative charge on the metal and hence a decrease in $\sigma_1$ for the
coordinated phosphine. Examination of the results of Table 5-6
shows both types of behaviour. Thus, the $\sigma_1$ value for Vaska's compound
is 0.36. The addition compounds with HCl, Cl$_2$, CH$_3$I, and O$_2$ have
values of 0.45, 0.48, 0.47 and 0.42, respectively. In these cases,$\sigma_1$ has clearly increased. On the other hand, $L_3$RhCl$_3$ and $L_3$IrCl$_3$
both have $\sigma_1$ values of 0.27 which are significantly less than observed
for any of the four coordinate Rh(I) or Ir(I) complexes. It is pos-
sible that this difference in behaviour is associated with the presence or absence of \( \pi \) accepting carbonyl ligands. Thus, \( \text{L}_3\text{IrCl}_3 (\sigma = 0.27) \) may be compared with \( \text{L}_2\text{Ir(CO)Cl}_3 (\sigma = 0.48) \) and the large difference rationalized in terms of the greater \( \pi \) accepting ability of a carbonyl ligand relative to a phosphine. This increases the positive charge on the metal and hence the demand for electrons from the phosphine. However, perhaps the most significant conclusion is that the electron affinity of the metal is much more sensitive to the nature of the ligands than it is to the formal oxidation state.

There have been a number of infrared studies of metal complexes containing triphenylphosphine and carbonyl ligands. High carbonyl stretching frequencies have been associated with diminished back-donation to the carbonyl and hence increased positive charge on the metal. By and large, the carbonyl stretching frequencies correlate reasonably well with the \( \sigma_1 \) parameters derived from this present work. This is illustrated in Table 5-5. The very low \( \sigma_1 \) for the five coordinate \( \text{L}_3\text{Ir(CO)H} \) is particularly notable and is paralleled by a low carbonyl stretching frequency. A quantitative correlation would not be expected since \( \sigma_1 \) is associated with \( \sigma \) bonding where the carbonyl stretching frequencies are associated with changes in \( \pi \) bonding.

A limited study of complexes of \( \text{C}_6\text{H}_4\text{F(C}_6\text{H}_5)_2\text{P} \) was undertaken, and the results of these measurements are shown in Table 5-6. These results closely parallel the results for the corresponding tris fluorophenylphosphines but the magnitude of the values of \( \sigma_1 \) and \( \sigma^0_R \) are somewhat reduced. From this it may be deduced that the metal ion withdraws charge preferentially from the non-fluorinated aromatic
\begin{table}[h]
\centering
\caption{\textsuperscript{19}F Chemical Shifts\textsuperscript{a} of Fluorophenyl Diphenyl Phosphine Complexes}
\begin{tabular}{lcccc}
\hline
Compound & $\delta_m$ & $\delta_p$ & $\sigma_i$ & $\alpha$ & $\beta$ & $\gamma$ & $\delta$ \\
\hline
$L$ & -0.4 & -0.4 & 0.14 & 0.0 & 0.3 & 0.0 & 0.0 \\
$L_2$PdCl$_2$ & -1.2 & -4.0 & 0.25 & 0.09 & 0.0 & 0.0 & 0.0 \\
$L_2$PtO$_2$ & -2.0 & -6.1 & 0.37 & 0.14 & 0.0 & 0.0 & 0.0 \\
$L_2$PtCl$_2$ & -1.6 & -4.6 & 0.31 & 0.10 & 0.0 & 0.0 & 0.0 \\
\hline
\end{tabular}
\textsuperscript{a} Solvent CHCl$_3$
\textsuperscript{b} $L =$ meta or para fluorophenyl diphenyl phosphine
\end{table}

\begin{table}[h]
\centering
\caption{Carbonyl Stretching Frequencies}
\begin{tabular}{lcccc}
\hline
Compound & $\sigma_i$ & $\nu_{CO}$ & Reference \\
\hline
$L = (C_6H_5)_3P$ & 0.36 & 1950 & 1 \\
$L_2$Ir(CO)Cl & 0.44 & 1975 & 1 \\
$L_2$Ir(CO)I & 0.45 & 2024 & 2 \\
$L_2$Ir(CO)HCl$_2$ & 0.48 & 2078 & 2 \\
$L_2$Ir(CO)Cl$_3$ & 0.47 & 2048 & 1 \\
$L_2$Ir(CO)ClMeI & & 2054 & 2 \\
$L_2$Ir(CO)ClO$_2$ & 0.42 & 2000 & 1 \\
$L_2$Ir(CO)BrO$_2$ & 0.42 & 1996 & 1 \\
$L_2$Ir(CO)O$_2$ & 0.47 & 1995 & 1 \\
$L_3$Ir(CO)$_2$ & 0.18 & 1930 & 3 \\
$L_2$Rh(CO)$_2$ & 0.36 & 1960 & 1 \\
\hline
\end{tabular}
\end{table}

ring reducing the effect on the fluorinated moiety. This result is consistent with the report that carbonyl containing complexes involving fluorophenylphosphines have higher CO stretching frequencies than the phenylphosphine compounds. The discussion to this point has omitted the $\sigma_R^0$ values, since they do not provide a direct measure of $\pi$ donation from the metal to the phosphorus d orbitals and hence to the aromatic $\pi$ system. This is due to the fact that the molecular framework is not planar as is required for direct conjugation. As indicated previously, the values of $\sigma_R^0$ are expected to be positive and to parallel the $\sigma_I$ values. Donation from the phosphorus lone pair to the ring $\pi$ system is no longer possible and acceptance into the phosphorus d orbitals will be enhanced by increasing positive charge on the phosphorus, both effects leading to a more positive $\sigma_R^0$. A negative contribution could arise from electron donation from the phosphorus d orbitals to the $\pi$ system if the phosphorus d orbitals are partly filled by donation from the metal. In general, the $\sigma_R^0$'s are positive and parallel the $\sigma_I$'s quite closely. The notable exceptions are the square planar Rh(II) complexes which have large $\sigma_I$'s but small or even slightly negative $\sigma_R^0$'s. It is quite possible that back-donation can be important in these complexes. On the other hand, the platinum oxygen complex has the highest observed $\sigma_R^0$ which is consistent with the suggestion made above that donation to the oxygen molecule inhibits donation to other ligands. It cannot be claimed, however, that the $\sigma_R^0$'s provide any quantitative measure of back-bonding since they obviously represent the relatively small difference between several competing processes.
5.6 EXPERIMENTAL

The synthesis of \((\text{mFC}_6\text{H}_4)_3\text{P}\) and \((\text{pFC}_6\text{H}_4)_3\text{P}\) followed closely the method described by Murray, Roberts and Walker\(^77\) with the exception that the reaction was carried out in dry tetrahydrofuran (THF). The reaction of the appropriate bromofluorobenzene with dry magnesium in THF produced the Grignard reagent, which was reacted with an equivalent amount of \(\text{PCl}_3\) to yield the desired product, in about 20% yield, after recrystallization from the hot ethanol.

The compound \([(\text{FC}_6\text{H}_4)_3\text{P})_2\text{PtCl}_2\] was prepared by the literature method.\(^80\) The addition of an ethanolic solution of \((\text{FC}_6\text{H}_4)_3\text{P}\) to a stirred aqueous solution of \(\text{K}_2\text{PtCl}_4\) caused immediate precipitation of white crystals. After stirring for 10 minutes, the product was filtered and washed with water and hot ethanol. The product was recrystallized from boiling chloroform. The corresponding dibromide and diiodide complexes were prepared from the dichloride complex by stirring for 24 hours in an acetone solution containing a large excess of KBr or KI.

The palladium complexes were prepared by the addition of ethanolic \((\text{FC}_6\text{H}_4)_3\text{P}\) to a stirred aqueous solution of \(\text{Pd(NO}_3)_2\) to which had been added a large excess of \(\text{KX}\). The remainder of the synthesis followed closely the preparation described for the platinum(II) complexes, except that the crude product was recrystallized from chloroform by the addition of hexane.

The tetrakis platinum(0) complex \([(\text{FC}_6\text{H}_4)_3\text{P})_4\text{Pt}\] was prepared by the reaction of \([(\text{FC}_6\text{H}_4)_3\text{P})_2\text{PtCl}_2\] with hydrazine\(^81\) in the presence of excess \((\text{FC}_6\text{H}_4)_3\text{P}\).
The complexes \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{PtDPA}\) (DPA is diphenyl acetylene)\(^{82}\) and \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{PtCS}_2\) were prepared in situ by addition of DPA and CS\(_2\) to the tetrakis complex.\(^{83}\) The compound \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{PtO}_2\) was prepared by passage of air through a chloroform solution of the tetrakis complex followed by precipitation with hexane.\(^{84}\) The complex \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{PtHCl}\) was prepared by the passage of gaseous HCl through a solution of \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_4\text{Pt}\) followed by precipitation and recrystallization from boiling chloroform.\(^{85}\)

The complexes \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_3\text{RhCl}_3\) and \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_3\text{IrCl}_3\) were prepared by literature methods\(^{86},^{87}\) from the appropriate phosphine and the hydrated metal trichloride.

The rhodium(I) and iridium(I) complexes were prepared according to the literature methods\(^{88}\) from the hydrated metal trichloride and the appropriate phosphine in refluxing \(N, N\)-dimethylformamide. The oxidative addition products of the iridium(I) complexes \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{Ir}(\text{CO})\text{HCl}_2\), \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{Ir}(\text{CO})\text{Cl}_3\), \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{IrCH}_3\text{Cl}_2\), and \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{Ir}(\text{CO})\text{ClO}_2\) were prepared by literature methods by the addition of HCl, Cl\(_2\), CH\(_3\) to \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{Ir}(\text{CO})\text{Cl}\).\(^{89}\)

The triphenylphosphine complexes used in the exchange experiments were purchased from Strem Chemical Company and were used without further purification.

The NMR spectra were recorded using a Varian DP60 NMR spectrometer operating at 56.4 MHz using a locked frequency sweep mode. Internal \(\text{C}_6\text{H}_5\text{F}\) was used as an internal lock and spectra were recorded using a proton decoupling frequency of 59,995,200 Hz. Deuterochloroform CDCl\(_3\) was used throughout. Observed chemical shifts are re-
producible to within ±0.02 ppm. All samples were prepared under a nitrogen atmosphere using CDCl₃ previously flushed with nitrogen. In spite of these precautions, small resonances attributed to the phosphine oxides (C₆H₅)₃PO were observed. These were identified by comparison with genuine samples of the phosphine oxides prepared by oxidation of the phosphines by alcoholic potassium hydroxide. In no case was there any evidence for the formation of phosphine oxide complexes.

The tetrakis platinum complex presented some difficulties and the shifts are not reported. Solutions of this complex give ^{19}F resonances at the free ligand position. The complex is known to be dissociated in solution. Addition of free ligand does not cause any shift in position. The most likely interpretation is that there is no chemical shift difference between free and complexed ligand (which would put the [(FC₆H₄)₃P]₄Pt in the expected position in the series of platinum complexes discussed above), but lacking any external probe for complexation it could also be argued that only free ligand is observed with the complex resonance being missed by reason of low intensity or broadening due to rapid exchange.
CHAPTER VI
DISCUSSION

The previous chapters of this thesis have dealt with the results of a number of experiments designed to investigate the relative stabilities and labilities of group VIII phosphine complexes. This chapter will attempt some rationalization of these results in terms of the electronic structures of the complexes. In particular, we will ask whether the stabilities of the complexes can be correlated with the electronic or steric properties of the ligands and whether the labilities are related in any way to the stabilities.

The concept that ligands can be ranked according to their donating ability is generally accepted. On a very simple level, it might be expected that the stability of a complex would increase as the donor properties of the ligands increase. This, however, completely ignores considerations of steric factors. Obviously, the accumulation of a number of bulky substituents around a relatively small metal ion is not conducive to stability, even if the ligands were excellent donors. Secondly, the oxidation state of the metal plays an important role in determining the stability of a complex. Thus, the most stable complexes of metals in low oxidation states are formed with ligands such as CO, which are capable of accepting as well as donating electrons. On the other hand, the most stable complexes of metals in high oxidation states are formed with ligands which are good donors but which cannot themselves be oxidized, for example, F⁻. In both cases the actual charge on the metal in the complex will differ substantially from its formal charge.

Thus, a more reasonable picture is perhaps that optimum stability is attained when the donor and acceptor properties of the ligands are best matched by the acceptor and donor properties of the metal. This implies that there is a preferred net charge for a particular metal ion. The stability of complexes formed with this metal ion will reflect the extent
to which the ligands donate or accept charge to most nearly attain this optimum situation in the particular ligand environment.

This line of argument leads to the hypothesis that minimum lability would be associated with maximum stability. Any intermediate of higher or lower coordination number must be less stable since the net charge on the metal centre must differ. Thus, a very stable complex would require considerable activation energy to pass through an energetically unfavourable intermediate.

Discussion in terms of these concepts requires a more detailed definition of the terms "stability", "lability" and "donor and acceptor properties".

6.1 RELATIVE STABILITY

Relative stability can be defined in terms of a ligand exchange reaction such as

$$ML + L' \neq ML' + L$$

If the equilibrium constant for this reaction is greater than one, the complex ML' is more stable than ML. If the equilibrium constant is less than one, the converse is true. It must be pointed out that equilibrium constants are determined by changes in free energy ($\Delta G$) rather than by enthalpy changes ($\Delta H$) and thus cannot be directly associated with changes in metal-ligand bond strengths. It seems reasonable though to assume that the entropy difference for the exchange of two similar ligands will be small. It is common practice to make this assumption and to ascribe free energy differences in such cases to changes in bond strengths.

However, for a reaction involving ionic species,
ion-pairing in non-aqueous solvents will inevitably lead to a significantly decreased $\Delta S$. If a series of reactions involving a common anion, $X^-$, and closely related $L$'s is considered, it seems reasonable to expect the $\Delta S$ values to remain constant or at least similar, so that again the differences in equilibrium constants will reflect differences in bond energy.

6.2 RELATIVE LABILITY

Relative labilities of different metal complexes may be discussed in terms of the rate of the ligand exchange reaction

$$ML + L' \rightleftharpoons ML' + L$$

in which $L$ and $L'$ are either the same ligand or $L$ is kept constant for a series of $L'$. We have mostly used the latter approach. Again, it must be pointed out that the rate is determined by the free energy of activation, $\Delta G^\ddagger$, rather than by $\Delta H^\ddagger$. It has been common in the literature to assume that $\Delta S^\ddagger$ is constant for similar reactions and to thus discuss the rates in terms of $\Delta H^\ddagger$. Recent work in this laboratory has suggested that for labile systems, this assumption is open to question. For the complexes $(Tu)_2CoX_2$ ($X = Cl, Br, I$), $(Tu =$ thiourea), the rate of thiourea exchange decreases in the order $Cl > Br > I$. It has been shown that this ordering is determined by the values of both $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Apparently, the rate determining step is the formation of a five coordinate intermediate and a more favourable enthalpy term for this process can be outweighed by a less favourable entropy term. Similar considerations could apply to some of the square planar complexes discussed below.
6.3 DONOR-ACCEPTOR PROPERTIES

The donor and acceptor properties of different ligands bonded to the same metal are expected to differ. This is the basis of both the spectrochemical and nephelauxetic series. However, these series can provide no more than a general indication of the ligand donor and acceptor properties since the ordering of ligands in such series have been obtained from electronic spectra and thus will only indirectly reflect the ground state properties of a complex.

For a series of closely related ligands, such as phosphines, the pKa will measure the donor abilities of the ligand. The values of pKa's for a number of phosphines have been correlated by Kabachnik with a set of parameters characteristic of the substituents on the phosphorus atom. Considered alone, it is rather an unjustified extrapolation to apply the set of parameters, which describe a phosphine, hydrogen ion reaction, to describe a phosphine metal ion reaction, since a metal ion differs considerably from a hydrogen ion.

Tolman has studied the donor and acceptor properties of a wide range of phosphines using an infrared technique similar to that suggested by Horrocks and Taylor. This method involves the changes in the CO stretching frequency of complexes of the type Ni(CO)₃L when the phosphine L is varied. Tolman used the argument that a better donor increases the positive charge on the metal thereby increasing the backdonation to the carbonyl group and reducing the carbonyl stretching frequency. Tolman found that such effects were additive and defined a substituent parameter, x, for some 47 phosphine substituents. These parameters reproduced the observed infrared frequencies with high pre-
cision. He further showed that there was an excellent correlation between these substituent parameter, \( \chi \), and Kabuchnik's \( \sigma \) parameters. It is therefore felt that on the basis of this body of consistent data, that Tolman's \( \chi \) values may be taken as a measure of the net donor and acceptor properties of phosphines.

A second comparison of donor and acceptor properties must be considered. This involves the comparison of the donor and acceptor properties of metals in different ligand environments. There seems to be little information available in the literature on this question and this is, in fact, the reason that \( ^{19}F \) chemical shift study of fluoro-phenylphosphine complexes was undertaken. In Chapter V, it was argued that \( \sigma_1 \) reflected the acceptor properties of the metal ions.

Thus, the results of the work described in the previous chapters of this thesis can be discussed in terms of the stability and lability of a complex, as measured by ligand exchange processes and in terms of the donor and acceptor properties of the ligands and metals as measured by \( \chi \) and \( \sigma_1 \).

6.4 PALLADIUM PHOSPHINE COMPLEXES

The donor properties of the phosphines used in the palladium complex study can be ordered using Tolman's \( \chi \) values. These values are shown in Table 6-1 where the better donors are associated with small values of \( \chi \).

Since the \((C_6H_5)_3P\) in any of the complexes \([(C_6H_5)_3P]_2PdX_2\) is displaced by any of the other phosphines \( L \), the complexes \([(C_6H_5)_3P]_2PdX_2\) are less stable than the corresponding \( L_2PdX_2 \) complexes in the sense defined by equation (1) above. Thus, optimum stability requires a
<table>
<thead>
<tr>
<th>Substituent</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_3$C-</td>
<td>0.0</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{11}$</td>
<td>0.1</td>
</tr>
<tr>
<td>o-CH$_3$OC$_6$H$_4$</td>
<td>0.9</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CH-</td>
<td>1.0</td>
</tr>
<tr>
<td>n(C$_3$H$_7$)CH$_2$-</td>
<td>1.4</td>
</tr>
<tr>
<td>CH$_3$CH$_2$-</td>
<td>1.8</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>2.6</td>
</tr>
<tr>
<td>p-CH$_3$OC$_6$H$_4$</td>
<td>3.4</td>
</tr>
<tr>
<td>p-CH$_3$C$_6$H$_4$</td>
<td>3.5</td>
</tr>
<tr>
<td>o-CH$_3$C$_6$H$_4$</td>
<td>3.5</td>
</tr>
<tr>
<td>CH$_3$H$_4$C$_2$H$_2$-</td>
<td>3.5</td>
</tr>
<tr>
<td>m-CH$_3$C$_6$H$_4$</td>
<td>3.7</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>4.3</td>
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<tr>
<td>CH$_3$-CH-</td>
<td>4.5</td>
</tr>
<tr>
<td>p-FC$_6$H$_4$</td>
<td>5.0</td>
</tr>
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<td>p-ClC$_6$H$_4$</td>
<td>5.6</td>
</tr>
<tr>
<td>m-FC$_6$H$_4$</td>
<td>6.0</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO-</td>
<td>6.3</td>
</tr>
<tr>
<td>m-C$_4$H$_9$O-</td>
<td>6.5</td>
</tr>
<tr>
<td>C$_2$H$_5$O-</td>
<td>6.8</td>
</tr>
<tr>
<td>CNCH$_2$CH$_2$-</td>
<td>7.3</td>
</tr>
<tr>
<td>CH$_3$O-</td>
<td>7.7</td>
</tr>
<tr>
<td>H</td>
<td>8.3</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>11.2</td>
</tr>
<tr>
<td>Substituent</td>
<td>X</td>
</tr>
<tr>
<td>-------------</td>
<td>---</td>
</tr>
<tr>
<td>Cl</td>
<td>14.8</td>
</tr>
<tr>
<td>F</td>
<td>18.2</td>
</tr>
<tr>
<td>CF₃</td>
<td>19.6</td>
</tr>
</tbody>
</table>
better donor than \((\text{C}_6\text{H}_5)_3\text{P}\). Since displacement of \((\text{C}_6\text{H}_5)_3\text{P}\) by \((\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}\), \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\), \((\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{P}\), and \((\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}\) is quantitative but displacement of \((\text{C}_6\text{H}_5)_3\text{P}\) is less than quantitative by \((\text{C}_4\text{H}_9)_3\text{P}\), in the chloride system, it appears that optimum stability requires a poorer donor than \(\text{n-Ru}_3\text{P}\). Unfortunately, the formation of ionic compounds prevents the observation of direct ligand exchange between alkyl phosphines. In these cases, added phosphine replaces a halide ion to give a cationic species. This implies that for the alkyl phosphine complexes, enhanced stability can be achieved by increasing the positive charge on the metal ion. In the resulting complex, \(\text{L}_3\text{Pdx}^+\), the metal has a formal positive charge and \(\text{L}\) is a better electron accepting ligand than the \(\text{X}^-\) it has replaced.

Thus, it appears that aryl phosphine complexes require a better donor for maximum stability and alkyl phosphine complexes require a better acceptor for maximum stability. This implies that optimum stability requires some intermediate combination of ligand donor and acceptor properties.

This conclusion is supported by the data on the relative equilibrium constants for the formation of ionic compounds reported in Table 6-2. Figure 6-1 shows the variation of the equilibrium constant for the formation of the ionic product as a function of the ligand donor and acceptor properties measured by \(\text{x}\). This figure shows that the equilibrium constant for the reaction

\[\text{L}_2\text{MX}_2 + \text{L} \rightarrow \text{L}_3\text{MX}^+ + \text{X}^-\]

shows a maximum at a particular value of \(\text{x}\). The maximum moves to poorer electron donors on passing from \(\text{X} = \text{Cl}^-\) to \(\text{Br}^-\) and to \(\text{I}^-\). These results may be rationalized by assuming that at the high \(\text{x}\) end of the scale (poor donors) the donor properties of the ligands are insufficient to compensate for the increased positive charge on the metal. At the low end of the \(\text{x}\) scale (good donors) too much charge is
TABLE 6-2
Relative Equilibrium Constants

A. \( \text{L}_2\text{PdX}_2 + \text{L} \rightleftharpoons \text{L}_3\text{PdX}^+ + \text{X}^- \)

<table>
<thead>
<tr>
<th>L</th>
<th>( X = \text{Cl} )</th>
<th>( X = \text{Br} )</th>
<th>( X = \text{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_6\text{H}_5)_3\text{P})</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P})</td>
<td>0.91</td>
<td>1.96</td>
<td>7.00</td>
</tr>
<tr>
<td>((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P})</td>
<td>1.10</td>
<td>1.20</td>
<td>3.80</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2\text{P})</td>
<td>2.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)_3\text{P})</td>
<td>1.77</td>
<td>0.23</td>
<td>2.80</td>
</tr>
<tr>
<td>((\text{nC}_4\text{H}_9)_3\text{P})</td>
<td>0.15</td>
<td>0.13</td>
<td>1.93</td>
</tr>
</tbody>
</table>
Fig. 6-1. Relative Equilibrium
Constant vs \( \Sigma_X \) for
\[ L_2^2\text{pd}X^2 + L \rightarrow L_3^3\text{pd}X + X^- \]
Fig. 6-1 (Continued)

$x = \text{Br}$
Fig. 6-1 (Continued)

\[ x = 1 \]
donated to the metal and the net charge is excessively negative. Since
the donor abilities of the halides decrease in the order $I^- > Br^- > Cl^-$,
the maximum tendency to form ionic compounds would occur with poorer
donor phosphines as $Cl^-$ is replaced by $Br^-$ and $I^-$. This is in agreement
with the observed trends.

A similar type of behaviour has been reported previously by
Rijo, Gustalla and Turco$^{94}$ who reported the equilibrium constants and
$\Delta H$ values for the reaction

$$L_2\text{Ni(CN)}_2 + L \rightleftharpoons L_3\text{Ni(CN)}$$

where $L$ is a phosphine. Although these authors did not analyse their
data in this manner, a plot of $\Delta H$ (or $K$) versus Tolman's $x$ value for
the different phosphines $L$, goes through a maximum. The behaviour is
shown in Figure 6-2. The values for the equilibrium constants $K$ (or
for $\Delta H$) for the reaction$^{95}$

$$L_2\text{Co(CN)}_2 + L \rightleftharpoons L_3\text{Co(CN)}_2$$

when plotted against $x$ for the particular phosphine, again goes through
a maximum for a particular phosphine as shown in Figure 6-2.

The results for the nickel and cobalt complexes are slightly
displaced, reflecting the different donor and acceptor properties required
to achieve maximum stability for the different metals.

It might be argued that the difference in equilibrium constants
(or stabilities) observed in the palladium work reported in this thesis
could be a result of steric factors. The steric properties of a number
of phosphines have been studied by Tolman.$^{43}$ Such factors have been shown
to determine the relative stabilities of $L_4\text{Ni}$ complexes. The steric
parameters determined by Tolman$^{43}$ are shown in Table 6-3. However,
Figure 6-2  Equilibrium Constants (K) versus Substituent Parameters

Sigma_X for

- O: $L_2Ni(CN)_2 + L \rightleftharpoons L_3Ni(CN)_2$ \(94\)
- X: $L_2Co(CN)_2 + L \rightleftharpoons L_3Co(CN)_2$ \(95\)
TABLE 6-3

Sizes of Various Phosphorus Ligands $R_3P$ (after Tolman\textsuperscript{43})

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Cone angle\textsuperscript{a} (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PX_3$</td>
<td>87 ± 2</td>
</tr>
<tr>
<td>$P(OR)_3$</td>
<td>104 ± 2</td>
</tr>
<tr>
<td>$P(OC_6H_5)_3$</td>
<td>107 ± 2</td>
</tr>
<tr>
<td>$PR_3$</td>
<td>109 ± 2</td>
</tr>
<tr>
<td>$H$</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td></td>
</tr>
<tr>
<td>$OCH_3$</td>
<td>110 ± 2</td>
</tr>
<tr>
<td>$OC_2H_5$</td>
<td>114 ± 2</td>
</tr>
<tr>
<td>$OCH_2CH_2Cl$</td>
<td>118 ± 2</td>
</tr>
<tr>
<td>$O$·-$i$-$C_3H_7$</td>
<td>112 ± 10</td>
</tr>
<tr>
<td>$CH_3$</td>
<td>125 ± 2</td>
</tr>
<tr>
<td>$OC_6H_5$</td>
<td>131 ± 2</td>
</tr>
<tr>
<td>$Cl_3$</td>
<td>131 ± 10</td>
</tr>
<tr>
<td>$Br$</td>
<td></td>
</tr>
<tr>
<td>$OCH_2CCl_3$</td>
<td>132 ± 4</td>
</tr>
<tr>
<td>$CF_3$</td>
<td>130 ± 4</td>
</tr>
<tr>
<td>$C_2H_5$</td>
<td>137 ± 2</td>
</tr>
<tr>
<td>$C_4H_9$</td>
<td>145 ± 2</td>
</tr>
<tr>
<td>$C_6H_5$</td>
<td>160 ± 10</td>
</tr>
<tr>
<td>$iC_3H_7$</td>
<td>165 ± 10</td>
</tr>
<tr>
<td>$C_6H_{11}$</td>
<td>179 ± 10</td>
</tr>
<tr>
<td>$t$-$C_4H_9$</td>
<td>182 ± 2</td>
</tr>
<tr>
<td>$C_6H_{15}$</td>
<td>184 ± 2</td>
</tr>
<tr>
<td>$oC_6H_4CH_3$</td>
<td>194 ± 6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} apex angle of the minimum cone centred 2.28 Å from the centre of the P atom which just touches the outermost extremeties of the ligand fold back while maintaining $C_3$ symmetry.
there seems no indication that these steric factors correlate with the relative stabilities discussed above. It may, therefore, be concluded that electronic rather than steric considerations determine the stabilities of the palladium (II) complexes.

A further illustration of the high stabilities of the complexes \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_3\text{PdX}^+\) and \([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P})_3\text{PdX}^+\) which involve ligands of intermediate donor abilities is provided by the results of the addition of \((\text{C}_6\text{H}_5)_3\text{P}\) to \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PdX}_2\) or \([(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PdX}_2\). The products formed are \((\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdX}_2\), \([(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{CH}_3)(\text{C}_6\text{H}_5)\text{P})_2\text{PdX}_2\) and \(\text{L}_3\text{PdX}^+\). The stability of the cation \(\text{L}_3\text{PdX}^+\) is such that the concurrent formation of the somewhat unstable \((\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdX}_2\) is energetically profitable. It is interesting that the equilibrium constants for these reactions are highest for the bromides, in which the anionic ligand is of intermediate donor ability. It seems then that a combination of ligands with just the right total donor and acceptor properties, is quite critical for obtaining optimum stability.

These observations differ considerably from the exchange of fluoro-phenylphosphines with \([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdX}_2\) reported in Chapter V. In the fluoro-phenylphosphine case, the exchange was slow at room temperature and the distribution of phosphines favour \((\text{C}_6\text{H}_5)_3\text{P}\) slightly. There was no indication that ionic species were formed in these reactions.

Both Tolman's \(\chi\) values and the \(^{19}\text{F}\) results of Chapter V indicate that the fluoro-phenylphosphines are even poorer donors than \((\text{C}_6\text{H}_5)_3\text{P}\). Thus, no net increase in stabilization and perhaps some destabilization is expected when \((\text{FC}_6\text{H}_4)_3\text{P}\) replaces \((\text{C}_6\text{H}_5)_3\text{P}\) in these complexes. Thus, the equilibrium constant is expected to be < 1. Similarly, the forma-
tion of \([\text{(FC}_6\text{H}_4\text{)}_3\text{P}]_2\text{PdX}^+\) would require a significant net positive charge on the palladium centre which could not be sufficiently reduced by the weaker donor phosphine. Thus, the failure to observe cationic species with the \(\text{(FC}_6\text{H}_4\text{)}_3\text{P}\) ligands agrees well with the results for the alkyl phosphine ligands.

The earlier mentioned possibility that decreased stability might be associated with increased lability, does not seem applicable in this system. The relatively unstable \([\text{(C}_6\text{H}_5\text{)}_2\text{P}]_2\text{PdX}_2\) complexes undergo slow exchange with \(\text{(FC}_6\text{H}_4\text{)}_3\text{P}\).

Although little work on platinum complexes of alkyl phosphines was undertaken in this work, Powell's results indicate that exchange between \([\text{(CH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}_2\text{P}]_2\text{PtX}_2\) and \((\text{CH}_3)_2\text{(C}_6\text{H}_5\text{)}_2\text{P}\) results in formation of \([\text{(CH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}_2\text{P}]_3\text{PtX}^+\) species. The exchange of these complexes with free \((\text{CH}_3)_2\text{(C}_6\text{H}_5\text{)}_2\text{P}\) is fast at room temperature. However, as in the palladium case, the exchange of \([\text{(C}_6\text{H}_5\text{)}_2\text{P}]_2\text{PtX}_2\) with \(\text{(FC}_6\text{H}_4\text{)}_3\text{P}\) is slow at room temperature. This exchange reaction is not very favourable and the \(\text{(C}_6\text{H}_5\text{)}_3\text{P}\) is the preferred ligand. These findings indicate that results parallel to those obtained on Pd(II) complexes discussed above may well be obtained on the Pt(II) systems. Such a study might further substantiate the concept of an "acceptable charge" discussed above.

The results for the \(^{19}\text{F NMR}\) study of the Pd(II) complexes showed that the \(\sigma_1\) values of the Cl, Br and I complexes were all in the range 0.37 to 0.38 which is close to the average value for the range of phosphine complexes examined. The two complexes \(\text{L}_2\text{RhCOCI}\) and \(\text{L}_2\text{IrCOCI}\) both have \(\sigma_1\) values of 0.36 and if \(\sigma_1\) is indeed a measure of the electron affinity of the metal it might be expected that the phosphine ligand preference in these compounds might well be similar to the palladium
complexes discussed above. This seems to be generally true; however, the rhodium(I) and iridium(I) complexes are somewhat more complicated. The coordinated \( (C_6H_5)_3P \) of trans\[ (C_6H_5)_3P \]_2IrCO(Cl) or trans\[ (C_6H_5)_3P \]_2IrCO(Br) are displaced by both \( (CH_3)(C_6H_5)_2P \) and \( (CH_3)_2(C_6H_5)P \). Since both \( (CH_3)(C_6H_5)_2P \) and \( (CH_3)_2(C_6H_5)P \) are better donors then \( (C_6H_5)_3P \), enhanced stability is achieved (as discussed above) by replacement of the poor donor \( (C_6H_5)_3P \) by more basic phosphines. This implies that the charge on the iridium is excessively positive in the triphenylphosphine complexes as was found for Pd. Since the donor properties of the halides increased in the order Cl < Br < I, the positive charge on the metal centre will decrease in this order. The equilibrium constant for the exchange of trans\[ (C_6H_5)_3P \]_2IrCO(Br) and \( (CH_3)_2(C_6H_5)P \), while still large, is considerably smaller than the equilibrium constants for the exchange of trans\[ (C_6H_5)_3P \]IrCO(Cl) with \( (CH_3)(C_6H_5)_2P \), and \( (CH_3)_2(C_6H_5)P \) or trans\[ (C_6H_5)_3P \]_2IrCO(Br) with \( (CH_3)_2(C_6H_5)P \). The combination of a better donor halide (Br) and the better donor \( (CH_3)_2(C_6H_5)P \) would result in the largest decrease in the positive charge on the metal centre in trans\[ (CH_3)_2(C_6H_5)P \]_2IrCO(Br). The fact that the exchange is still favourable argues that enhanced stability is again achieved. However, since the displacement is far less than quantitative, the enhanced stability, achieved by replacement of \( (C_6H_5)_3P \) by \( (CH_3)_2(C_6H_5)P \), is somewhat smaller than the enhanced stability achieved by formation of the other substituted complexes. Together, these results indicate that while the complex trans\[ (C_6H_5)_3P \]_2IrCO(Br) is excessively positive, the complex trans\[ (CH_3)_2(C_6H_5)P \]_2IrCO(Br) is excessively negative, although this complex is closer to the optimum charge on the iridium centre than is the \( (C_6H_5)_3P \) complex.
The iodide complex trans\([(C_6H_5)_3P]_2\text{IrCO(I)}\) is expected to bear the least positive charge of the \((C_6H_5)_3P\) complexes since iodide is the best donor halide. Substitution of the \((C_6H_5)_3P\) by either \((CH_3)(C_6H_5)_2P\) or \((CH_3)_2(C_6H_5)_2P\) would again decrease the positive charge on the metal centre. However, since the equilibrium constants for these reactions are both zero, the substitutions do not result in enhanced stability. Thus, it seems that the charge on the complex is excessively negative and the reaction does not occur.

The reaction of trans \(L_2\text{IrCO(X)}\) to form the four coordinate \(L_3\text{IrCO}^+\) species is also favourable for \(L = (CH_3)(C_6H_5)_2P\) and \((CH_3)_2(C_6H_5)_2P\) and \(X = Cl\) and \(Br\). In this work the formation of this four coordinate cation from the iodide complexes was not observed since the complexes trans \(L_2\text{IrCO(I)}\) \((L = (CH_3)(C_6H_5)_2P\) and \((CH_3)_2(C_6H_5)_2P\) were not formed. However, Shaw's work indicates that the formation of \([(CH_3)_2(C_6H_5)_2P]_3\text{IrCO}^+\) from trans\([(CH_3)_2(C_6H_5)_2P]_2\text{IrCO(I)}\) is favourable. The above results indicated that the complex \(L = (CH_3)(C_6H_5)_2P\) and \((CH_3)_2(C_6H_5)_2P\) is favourable. This implies that the formation of the cation results in an increased positive charge on the metal. These results give an ordering to the donor ability of the ligands of \(I > Br > (CH_3)_2(C_6H_5)_2P > (CH_3)(C_6H_5)_2P > Cl\). These results are summarized diagrammatically in Figure 6.3, where the relative charge densities of the metal centres are shown for the various complexes.

It is apparent from the results for the rhodium complex trans\([(C_6H_5)_3P]_2\text{RhCOCl}\), that enhanced stability is achieved by formation of both trans\([(CH_3)(C_6H_5)_2P]_2\text{RhCO(Cl)}\) and trans\([(CH_3)_2(C_6H_5)_2P]_2\text{RhCO(Cl)}\).
However, the formation of the four coordinate cation only occurs for \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\). Since \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}\) is a better donor than \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\), the complex \(\text{trans}[(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\) is expected to bear the least positive charge. Since this complex does not form the four coordinate cation, replacement of chloride by \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}\) must result in destabilization, while replacement of chloride by \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) must result in stabilization. These results imply that the metal in the complex \(\text{trans}[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\) is somewhat too positive while the metal in the complex \(\text{trans}[(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\) is somewhat too negative and that replacement of the chloride by either \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) or by \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}\) results in a decreased positive charge on the metal centre. Such a decreased positive charge on the metal is favourable only for the complex bearing a positive charge on the central metal, i.e., for \(\text{trans}[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\). Put in other terms, in the rhodium complexes the donor abilities of the ligands decreases in the order \((\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P} > (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} > \text{Cl}\). These results are summarized diagrammatically in Figure 6-4.

The comparison of four and five coordinate complexes is somewhat more difficult. At first sight, the addition of a fifth ligand to the complexes \(\text{L}_2\text{MCOX}\) would, on the basis of the above discussion, result in a decrease in the positive charge on the metal. Reference to Figures 6-3 and 6-4 shows that such a process would be unfavourable in several cases, for example, \(\text{trans}[(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}]_2\text{IrCO(Br)}\), and \(\text{trans}[(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}]_2\text{RhCO(Cl)}\). However, the five coordinate neutral species derived from these complexes were observed. Further, the amounts of the five coordinate complexes formed were usually comparable to the amount of four coordinate cation formed. Thus, the stabilities
Fig. 6-3  Variation in Charge for the $t[(C_6H_5)_3P]_2IrCOX$ Series
of the four coordinate cations and the related five coordinate neutral complexes appear to be comparable. Probably this means that the change in coordination number from four to five and the change in geometry from square planar to trigonal bipyramidal results in a sufficiently changed environment about the central metal that the most comfortable charge on the five coordinate complex is somewhat different from that of the four coordinate metal centre.

Similar considerations apply to the five coordinate cationic complex $L_4^{MCO}^+$, as to the five coordinate neutral complexes. However, it may be noted that since the $L_4^{MCO}^+$ species are formed they appear to be somewhat more stable than the $L_3^{MCOX}$ species. This implies that replacement of a halide by $L$ ($L = \text{(CH}_3\text{)}\text{(C}_6\text{H}_5\text{)}_2\text{P or (CH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}\text{P}$) results in increased stability and hence a closer approach to a comfortable charge in the five coordinate species.

The exchange reactions of the hydride species $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{IrCOH}$ provides an interesting comparison with the four coordinate complexes discussed above. The exchange of both $(\text{CH}_3\text{)}(\text{C}_6\text{H}_5)_2\text{P}$ and $(\text{FC}_6\text{H}_4)_3\text{P}$ is slow at room temperature. Since five coordinate Ir(I) is coordinately saturated (18 electrons) substitution will in all likelihood proceed through a complex of reduced coordination. This probable difference in mechanism may account for the dramatic difference in observed rate. However, it is to be noted that the $\sigma_1$ value for the $[(\text{FC}_6\text{H}_4)_3\text{P}]_3\text{IrCOH}$ indicates a very small electron affinity displayed by the metal.

The behaviour of the rhodium(I) complexes $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhX}$ is quite different to the behaviour observed with the Rh(I) and Ir carbonyl complexes discussed above. The chloride complex will exchange $(\text{CH}_3\text{)}(\text{C}_6\text{H}_5)_2\text{P}$
Figure 6-4 Variation in Charge for the trans\([\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{RhCOCl}\] series
for \((\text{C}_6\text{H}_5)_3\text{P}\) to an extent which favours triphenyl phosphine by a factor of two over a statistical distribution. In the analogous reaction with \((\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}\), the latter is favoured by a factor of 1.25. The displacement of \((\text{C}_6\text{H}_5)_3\text{P}\) by \((\text{mFC}_6\text{H}_4)_3\text{P}\) occurs to a considerable extent but the reaction with \((\text{pFC}_6\text{H}_4)_3\text{P}\) is not observed. For the bromide complex, reaction with \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) and \((\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}\) is not favourable while reaction with \((\text{mFC}_6\text{H}_4)_3\text{P}\) and \((\text{pFC}_6\text{H}_4)_3\text{P}\), although observed, is not favourable. The iodide complex resembles the chloride in its reaction with \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) and resembles the bromide in its reaction with \((\text{FC}_6\text{H}_4)_3\text{P}\). It appears that in this case the donor and acceptor properties of \((\text{C}_6\text{H}_5)_3\text{P}\) are well suited to the requirements of the metal and the ligands are not easily displaced by better donor ligands. Unfortunately, data for this series of compounds is incomplete since the unfavourable equilibrium constants for fluorophenylphosphine exchange hampered experiments in this area. The available values for the bromide and iodide would suggest a greater electron affinity for the metal and hence a preference for better electron donating ligands might have been expected. It is possible that steric considerations may determine the stability since there are three bulky phosphine ligands bonded in a planar array. However, Tolman's steric factors do not indicate that \((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}\) or \((\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}\) are bulkier than \((\text{C}_6\text{H}_5)_3\text{P}\). In addition the complexes \([(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{P}^+\) and \([(\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}]_3\text{P}^+\), which are isoelectronic with the rhodium complexes, are very stable. The tentative explanation of these results is that \(\pi\) bonding plays a large role in determining the stability of \([(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhX}\). The \(\sigma^0\text{R}\) values reported in Table 5-4 for these complexes are the most negative observed. Although, as pointed out in Chapter V, \(\sigma^0\text{R}\) cannot be correlated with \(\pi\) bonding directly,
the negative values of $\delta_R^0$ imply that the powerful accepting ability of the metal may be counterbalanced by a strong $\pi$ donation. Thus, it would favour good accepting ligands such as $(C_6H_5)_3P$.

Some mention of the rates of the exchange reactions has been made above. This data will be discussed in detail below.

There is substantial evidence in the literature to suggest that ligand exchange, in most of these square planar $d^8$ complexes proceeds by an associative mechanism involving a five coordinate intermediate. There is evidence to the contrary only for the $L_3RhX$ compounds. The most natural assumption is that the rate of exchange will depend upon the ease of formation of the five coordinate intermediate.

In the case of the palladium complexes, exchange with the fluoro-phenylphosphine is slow. Since the triphenyl phosphine complexes appear to require a better donor, it might be expected that exchange with the methylphenyl phosphines would be more rapid. Unfortunately, this process cannot be observed by NMR because the equilibrium constants lie heavily on the side of the methylphenylphosphine substituted complexes. Two rapid ligand exchange processes can be observed: the exchange between $L_2PdX_2$ and $L_3PdX^+$ and between $L_3PdX^+$ and $L$. In the first of these, line-width observations discussed in Chapter III indicate the exchange process involves the neutral complex and the unique phosphine of the cationic complex. Thus, it seems that the halide of the neutral complex attacks the cation. An intermediate is formed in which the halide of the neutral complex and the unique phosphine of the cation are simultaneously bonded to both metal centres. This intermediate then breaks up with the halide and single phosphine having exchanged. Formation of this
intermediate would be favoured by attack of a better donor halide. This is in agreement with the observed rate ordering, that is $I^- > Br^- > Cl^-$. It can be seen that exchange of $(CH_3)_2(C_6H_5)P$ is faster than for $(CH_3)(C_6H_5)P$ for $X = Cl^-$ and $X = I^-$ while the converse is true for $X = Br^-$. It is inferred from this that maximum stability, and therefore concentration, of the intermediate is achieved by an optimum combination of ligands of intermediate donor abilities, that is, the same considerations apply to five coordinate intermediates as have been discussed for the four coordinate stable compounds.

For the exchange reactions between $L_3PdX^+$ and $L$, the attacking ligand is $L$ rather than a halide. Simple considerations suggest this would be favourable by increasing positive charge and by increasing donor ability of the attacking ligand. This is consistent with the observation that the rate is faster for $(CH_3)_2(C_6H_5)P$ and the halide dependence $Cl^- > Br^- > I^-$ (the order of diminishing positive charge on the metal). However, with $(CH_3)(C_6H_5)P$, the halide dependence shows the order $Cl^- < Br^- < I^-$. This order appears anomalous and there does not appear to be a ready explanation of this observation. However, it is to be noted that in the thiourea complexes mentioned above the ordering of rate of exchange were determined by entropies of activation rather than enthalpies of activation.

In the rhodium and iridium carbonyl complexes, exchange of free and coordinated methylphenylphosphines was fast and could not be frozen out by NMR even at $-50^\circ$C. This contrasts with the slow exchange observed with the cationic rhodium and iridium carbonyl complexes, and the halide complexes of rhodium(I). The complexes $[(C_6H_5)P]_3RhX$ do not
show any broadening up to 60°C. The intermediate inference is that the former complexes readily form five coordinate intermediates while the latter do not. As noted above, \((\mathcal{C}_6\mathcal{H}_5)_3\mathcal{P}\)\(_3\mathcal{RhCl}\) is the only d\(^8\) complex for which a non-associative exchange mechanism has been suggested. These observations are consistent with the data on equilibria discussed above, in that carbonyl complexes show a preference for a better donor phosphine and hence might reasonably accept an additional ligand. Conversely, the \((\mathcal{C}_6\mathcal{H}_5)_3\mathcal{P}\)\(_3\mathcal{RhX}\) compounds have no marked preference for a better donor. The \(\sigma_1\) values show that \(\mathcal{L}_2\mathcal{PdX}_2\), \(\mathcal{L}_2\mathcal{IrCO(X)}\) and \(\mathcal{L}_2\mathcal{RhCO(X)}\) have very similar requirements as far as sigma electrons are concerned. The increased tendency to form five coordinate complexes for Rh and Ir carbonyls could be a reflection of the presence of the \(\pi\) accepting carbonyl ligand.

In summary, the objective of this thesis was the study of the dependence of ligand equilibria and exchange rates of d\(^8\) complexes on the donor and acceptor properties of ligands and metal centres. It is apparent from the above discussion that these relationships are not straightforward in the sense that there exist any linear dependencies of equilibrium constants or the rates on donor or acceptor properties. It seems that the dominant feature is the matching of ligand and metal properties to obtain optimum stability. The above studies have revealed a number of interesting aspects of this problem, and suggest that the use of donor and acceptor properties and optimum charge distributions may contribute towards the organization of the somewhat complex chemistry of these compounds into a single body of related observations.
There are obvious limitations to the application of such an approach to what are basically covalent compounds but it appears that some progress can be made in this direction.
APPENDIX

Determination of Relative Equilibrium Constants:

For the reaction

\[ \text{L}_2\text{PdX}_2 + \text{L} \rightleftharpoons \text{L}_3\text{PdX}^+ + \text{X}^- \]  \hspace{1cm} (1)

the equilibrium constant \( K \) is given by

\[ K = \frac{[\text{L}_3\text{PdX}^+][\text{X}^-]}{[\text{L}_2\text{PdX}_2][\text{L}]} \]  \hspace{1cm} (2)

where the square brackets indicate concentration in moles per liter.

When the concentration of product equals \( \alpha \), the above expression reduces to

\[ K = \frac{[\alpha][\alpha]}{[\text{M}-\alpha][\text{L}-\alpha]} = \frac{\alpha^2}{[\text{M}-\alpha][\text{L}-\alpha]} \]  \hspace{1cm} (3)

where \( \text{M} \) is the initial concentration of metal complex and \( \text{L} \) is the concentration of added ligand \( \text{L} \). Throughout this work the initial concentration of the metal complex was kept constant (1.5 \times 10^{-3} \text{ m/1}). For two such reactions, the ratio of the equilibrium constants \( \frac{k_1}{k_2} \) is given by

\[ \frac{k_1}{k_2} = \frac{[\alpha_1]^2}{[\text{M}_1-\alpha_1][\text{L}_1-\alpha_1]} \times \frac{[\text{M}_2-\alpha_2][\text{L}_2-\alpha_2]}{[\alpha_2]^2} \]  \hspace{1cm} (4)

Assuming that the contribution to the conductivity due to the cation \( \text{L}_3\text{PdX}^+ \) is constant as \( \text{L} \) is varied, and that the degree of ion pairing is constant as \( \text{L} \) is varied for a given \( \text{X} \), then for two conductometric titrations, when the measured conductivities are equal, the concentrations of charged particles are equal. In such a case,
\[ \alpha_1 = \alpha_2 \]

and

\[ M_1 = M_2 \]

Thus the equation reduces to

\[ \frac{k_1}{k_2} = \frac{L_2^{-\alpha}}{L_1^{-\alpha}} \] (4)

Rearranging equation (4) gives

\[ k_1(L_1^{-\alpha}) = k_2(L_2^{-\alpha}) \] (5)

which simplifies to

\[ k_1L_1 - k_2L_2 = k_1^a - k_2^a = a(k_1 - k_2) \] (6)

or

\[ \left( \frac{L_1}{L_2} \right) \right)^{\frac{a(k_1 - k_2)}{L_1}} = \frac{k_1}{k_2} \] (7)

Equation (7) is the equation of a straight line

\[ \frac{L_1}{L_2} = \frac{a(k_1 - k_2)}{k_1} \left( \frac{1}{L_2} \right) + \frac{k_2}{k_1} \] (8)

A plot of \( \frac{L_1}{L_2} \) versus \( \frac{1}{L_2} \) for equal observed conductivities yields a straight line of intercept \( \frac{k_2}{k_1} \). Giving an arbitrary value of \( k = 1 \) to the reaction

\[ [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PdX}_2 + (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} \div [(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_3\text{PdX}^+ + \chi^- \]

\( \chi = \text{Cl, Br, I} \)

allows the relative equilibrium constants for the remainder of the
ligands to be determined.

Providing that the above assumptions are valid, this allows comparison of the equilibrium constants for each of the three series studied. Comparison of one halide with another is not likely valid since the contribution to the observed conductivity from the various halides would probably be considerably different.

The plots of $\frac{L_1}{L_2}$ versus $\frac{1}{L_2}$ for the complexes studied are shown in Figures A-1, A-2 and A-3 for chloride, bromide and iodide complexes, respectively.
A-1 Plot of \( \frac{L_1}{L_2} \) versus \( \frac{1}{L_2} \) for the reaction \( L_2 \text{PdCl}_2 + L \).

\[
\begin{align*}
(CH_3)_2(C_6H_5)_2P & \quad ET(C_6H_5)_2P & \circ \quad 0.37 \\
ET(C_6H_5)_2P & \quad Bu_3P & \times \quad 0.41 \\
(CH_3)_2(C_6H_5)_2P &\quad (CH_3)(C_6H_5)_2P & \cdot \quad 0.91
\end{align*}
\]

\[
\begin{align*}
(CH_3)_2(C_6H_5)_2P = L_1 & \quad \circ \\
(C_2H_5)(C_6H_5)_2P = L_2 & \quad x \\
(C_2H_5)(C_6H_5)_2P = L_1 & \quad x \\
(nC_4H_9)_3P = L_2 & \\
(CH_3)_2(C_6H_5)_2P = L_1 & \quad \circ \quad L_1/L_2 \\
(CH_3)(C_6H_5)_2P = L_2 & \quad x \\
(C_2H_5)(C_6H_5)_2P = L_1 & \quad \circ \quad (C_2H_5)_3P = L_2 \quad L_1/L_2 \\
(C_2H_5)(C_6H_5)_2P = L_1 & \quad \circ \quad 1/L_2 \\
(C_2H_5)(C_6H_5)_2P = L_1 & \quad \circ \quad 1/L_2 \\
(C_2H_5)(C_6H_5)_2P = L_2 & \quad \circ \quad 1/L_2
\end{align*}
\]
A-2 Plot of $\frac{L_1}{L_2}$ versus $\frac{1}{L_2}$ for the Reaction $L_2\text{PdBr}_2 + L$

$\ (C_2H_5)_3P = L_1$

$\ (CH_3)(C_6H_5)_2P = L_2$

$\ (CH_3)(C_6H_5)_2P = L_1$

$\ (CH_3)_2(C_6H_5)P = L_2$

$\frac{1}{L_2}$

$\frac{L_1}{L_2}$
A-2 Plot of $\frac{L_1}{L_2}$ versus $\frac{1}{L_2}$ for the Reaction $L_2PdBr_2 + L$

$(C_2H_5)_3P = L_1$

$(CH_3)(C_6H_5)_2P = L_2$

$(CH_3)(C_6H_5)_2P = L_1$

$(CH_3)_2(C_6H_5)_2P = L_2$
\((\text{C}_2\text{H}_5)_3\text{P} = L_1\)
\((n\text{C}_4\text{H}_9)_3\text{P} = L_2\)

\((\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P} = L_1\)
\((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P} = L_2\)
A-3 Plots of $\frac{L_1}{L_2}$ vs. $\frac{1}{L_2}$ for the Reaction $L_2PdI_2 + L$

\[
(C_2H_5)_3P = L_1
\]
\[
(nC_4H_9)_3P = L_2
\]
\[
(CH_3)_2(C_6H_5)P = L_1
\]
\[
(nC_4H_9)_3P = L_2
\]

\[
(C_2H_5)(C_6H_5)_2P = L_2
\]
\[
(CH_3)_2(C_6H_5)P = L_1
\]
\[
(CH_3)(C_6H_5)_2 = L_2
\]
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