"STUDIES OF METAL COMPLEXES CONTAINING PHOSPHINE AND SUBSTITUTED-PYRIDINE LIGANDS"

A Thesis Presented by

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The Great Tragedy of Science -

The Slaying of Beautiful Hypothesis by an Ugly Fact.

Thomas Henry Huxley

CONTENTS

SUMMARY

This thesis is concerned with the spectral and structural properties of particular transition metal complexes.

The variable temperature ^{19}F and ^{31}P NMR of platinum, palladium, rhodium and iridium complexes containing one or more trispentafluorophenylphosphine ligands have been examined. It has been shown from the low temperature ^{19}F NMR of these complexes that the structure of this ligand when attached to a metal centre is such that one ring is above and two rings are below the molecular co-ordination plane. Helicity reversal within the complexed ligand occurs by a two ring flip mechanism.

Variable temperature ^{19}F and ^{31}P NMR spectra of the complexes trans -$[MX_2(P(C_6F_5)_3)_2]$ M = Pt or Pd, X = Cl, Br, or I revealed the presence of rotational isomers.

The complex trans -$[RhClCO(P(C_6F_5)_3)_2]$ when dissolved in chloroform produced a phosphorus NMR spectrum which was consistent with the presence of monomeric and dimeric species.

Previous studies of $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$ had suggested that this complex was able to catalyse the addition of chlorine to 1,1-dichloroethane. This system was

fully investigated. In the present study the complex did not exhibit catalytic activity.

Halide substitution reactions of the diphosphine complex were designed to determine the trans-effects of the ends of the complexed asymmetric diphosphine. However very little, if any, preferential substitution of the chlorine atoms was observed.

Attempted preparation of some substituted-pyridine ligands, which are important in the synthesis of herbicides, was carried out. Several dichloroplatinum complexes containing substituted pyridine ligands were prepared and characterised by microanalysis, NMR, and infra-red spectroscopy. Thermogravimetric analyses were obtained for the prepared complexes. Decomposition occurred with the loss of one or more pyridine-type ligands and in some cases with a combination of pyridine ligands and chlorine atoms. Complexes containing one phosphine and one substituted-pyridine ligand were found to be the most thermally unstable with the phosphine ligand being lost first.

SECTION 1

Spectral Investigations of Transition Metal Phosphine Complexes

Section 1

Part 1 - Introduction

1.1.1. General Background

The elements platinum, palladium, rhodium and iridium are members of the group known as the platinum metals. These transition metals are rare elements; platinum itself is the most prevalent with an abundance of about 10^{-6}% of the earth is crust; the other metals have abundancies in the order of 10^{-7} %.

Platinum (sp. platina - silver) was discovered in 1734 but it is known to have been used by pre-columbian indians. Palladium (Gr. Pallus - goddess of wisdom) was named after the asteroid palladus which was discovered at the same time i.e. 1803. These two elements are used extensively as catalysts in various industrial processes. One of the biggest uses of platinum is in the reforming or "platforming" of crude oils. Palladium salts are used for the conversion of alkenes to aldehydes and ketones e.g. propene to acetome. The elements are also used as precious metals for jewellery.

Rhodium (Gr. rodon - rose) and iridium (L. iris - rainbow) were discovered at approximately the same time, round about 1803. Their main uses are as alloying agents, to harden platinum and palladium. The alloys are used as furnace linings for ovens which operate at very high temperatures .

The physical properties of the platinum metals are similar. Their densities increase on going from rhodium to iridium (12.4 g/cm^3 - 22.4 g/cm^3) and decrease from rhodium to palladium (12.4 g/cm^3 - 12.0 g/cm^3). Their melting points as shown in Table 1.1 are all of similar magnitude, iridium having the highest value of 2683k. Covalent radii of elements in the second and third transition series are not very different e.g. Pd - 0.128 nm and Pt - 0.129 nm but those of the first transition series are notably smaller e.g. Ni - 0.115 nm. The filling of the 4f orbitals through the lanthanide elements causesa steady contraction, known as the lanthanide contraction, in the atomic and ionic radii. The expected size increase on going from the second transition to the third, due to increased numbers of electrons and higher principal quantum numbers of the outer shells, is almost entirely offset by the lanthanide contraction. There is usually little difference in covalent radii or physical properties on going from the second to the third transition series and this accounts for the great difficulties previously encountered in the separation of elements of these two series prior to the development of modern experimental techniques.

The chemical properties of the platinum metals have many similarities . They all show variable oxidation states. Table 1.2 contains the oxidation numbers and stereochemistries which are most common for platinum, palladium, rhodium and iridium. All four elements form binary compounds such as

Table 1.1 Physical Properties of the Platinum Metals[1]

Property	Co	Rh	Ir	Ni	Pd	Pt
Density g/cm ^{3}	8.8	12.4	22.4	8.9	12.0	21.4
Melting Point (K)	17 68	2239	2683	1726	1825	2069
Covalent Radii (nm)	0.116	0.125	0.126	0.115	0.128	0.129

Table 1.2 Most Common Oxidation States and Stereochemistries[2]

Species	d species	Co-ord No.	Stereochem.	Example
Rh(I), Ir(I)	d8	4	Planar	$[Rh_2CO_4Cl_2]$
Pd(II), Pt(II)				$[IrCl(CO)(PEt_3)_2]$
				$[PdCl_2]_n$
				$[PtHBr(PEt_3)_2]$
Rh(III) Ir(III) Pt (IV)	d6	6	Octahedral	$[Rh(H_2O)_6]^{3+}$
				$[IrH_3(PPh_3)_3]$
				$[PtCl_2(en)_2]$

sulphides, phosphides and the especially important halides e.g. RhO_2, PtS_2, PdP_3 and IrF_6. Their aqueous complex chemistry is extensive as many of their complexes e.g. the halides and many nitrogen donor ligands are water soluble. The platinum metals form many complexes with π-acid ligands i.e. molecules with a donor atom which have vacant p or d orbitals capable of accepting electron-density from the metals' filled d-orbitals. Investigation of the preparations and reactions of complexes with trialkyl and triarylphosphines which are π-acid ligands is a very wide field of study and much work is now being carried out using analogous arsines. Mixed complexes of trialkyl and triarylphosphines with carbonyls, alkenes, halides and hydride ligands in low-positive, zero or negative oxidation states are common for all these elements. There is a strong tendency for elements of the platinum metal group to form bonds to carbon especially with alkenes and alkynes. The d_8 -species Rh(I), Ir(I), Pd(II) and Pt(II) normally have square planar co-ordination.

Spectroscopy is the chemists's most powerful tool for examining and investigating chemical systems, e.g. molecular structure and molecular bonding.

In the present study Nuclear Magnetic Resonance Spectroscopy has been used extensively as a probe into the structure of various metal phosphine complexes in solution.

1.1.2 Nuclear Magnetic Resonance Spectroscopy [3]

All forms of spectroscopy may be viewed as the interaction of matter and electromagnetic radiation with energy being absorbed or emitted according to the Bohr frequency condition.

$$\Delta E = h\nu$$

Where ΔE is the quantised energy difference between initial and final energy states, h is Plank's constant which is defined as $h = 6.63 \times 10^{-34}$ Joules s molecule^{-1} and ν is the frequency of the electromagnetic radiation.

The topic of spectroscopy is subdivided according to the frequency of the electromagnetic radiation being considered. This is determined by the region of the electromagnetic spectrum or the range of frequencies being used.

In all forms of spectroscopy the given spectra may be described in terms of the frequency, the intensity and the shapes of lines or bands. These physical properties are dependent on the molecular parameters of the system.

In particular Nuclear Magnetic Resonance Spectroscopy examines the interaction of the magnetic energy of the nucleus, in a homogeneous magnetic field, with electromagnetic radiation from the radiowave region of the electromagnetic spectrum. Generally the parameters obtained from NMR spectra are chemical shifts, which give information on the chemical enviroment of the nucleus, coupling constants, which are measurements of the interaction between magnetic

nuclei, and lifetimes of the energy states. Physical or theoretical models can then be used to interpret or predict the spectrum. This information can then be applied to problems of chemical interest e.g. structure determination and evaluation of kinetic or thermodynamic data.

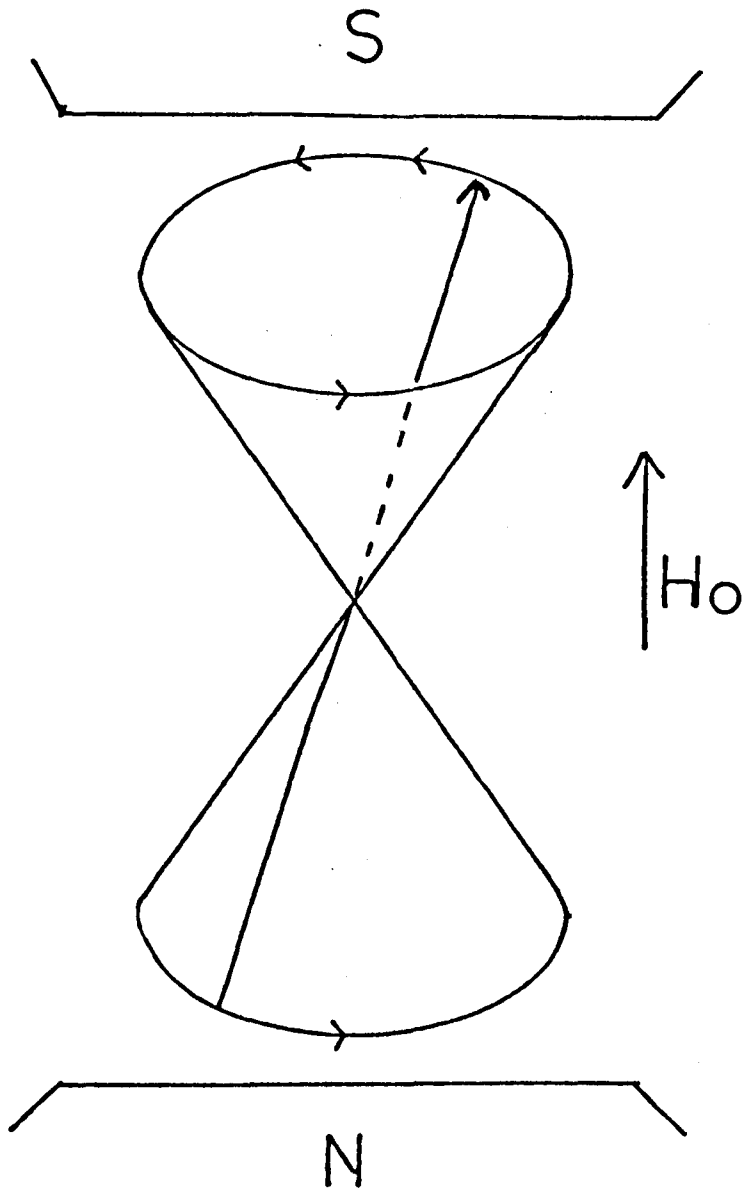
1.1.2(i) The Origins of Nuclear Magnetic Resonance[3]

The nuclei of isotopes which possess an odd number of protons or an odd number of neutrons or both exhibit mechanical spin phenomena and have associated angular momentum. The momentum is characterised by a nuclear spin quantum number I. The nuclei for which I = 0 do not possess spin angular momentum and the magnetic resonance phenomenon cannot be observed for them. The nuclei ^{16}O and ^{12}C fall into this category. Nuclei which have I = $\frac{1}{2}$ include ^{1}H, ^{19}F, ^{13}C and ^{31}P whereas ^{14}N and ^{2}H have I = 1, all these nuclei exhibit some form of magnetic resonance. ^{11}B is an example of a nucleus with I = $\frac{3}{2}$.

Since atomic nuclei are associated with charge, a spinning nucleus gives rise to an electric current which has a magnetic field associated with it. This situation has been compared to a tiny bar magnet, the axis of which coincides with the axis of the spin of the nucleus. The magnitude of the magnetic dipole, $\underline{\mu}$, has a characteristic value for a given nucleus.

When the spinning nucleus is placed in an uniform magnetic field, Ho, the nuclear magnet experiences a torque i.e. a twisting or rotary force, which tends to align it with the field. The interaction of the nucleus with the magnetic field, Ho, causes the spinning nucleus to precess about the field direction; this can be compared to the behaviour of a gyroscope in the earth's gravitational field. (See diagram 1.1).

Diagram 1.1.



Quantum mechanical calculations have shown that the allowed orientations of the nuclear magnet with respect to the field direction are given by 2I+1.

It follows that for protons, fluorine -19 and phosphorus 31 only two orientations are allowed and thus only two energy levels are possible. These levels may be regarded as an alignment of the nucleus with the field, the low energy state and alignment against the field, the high energy state.

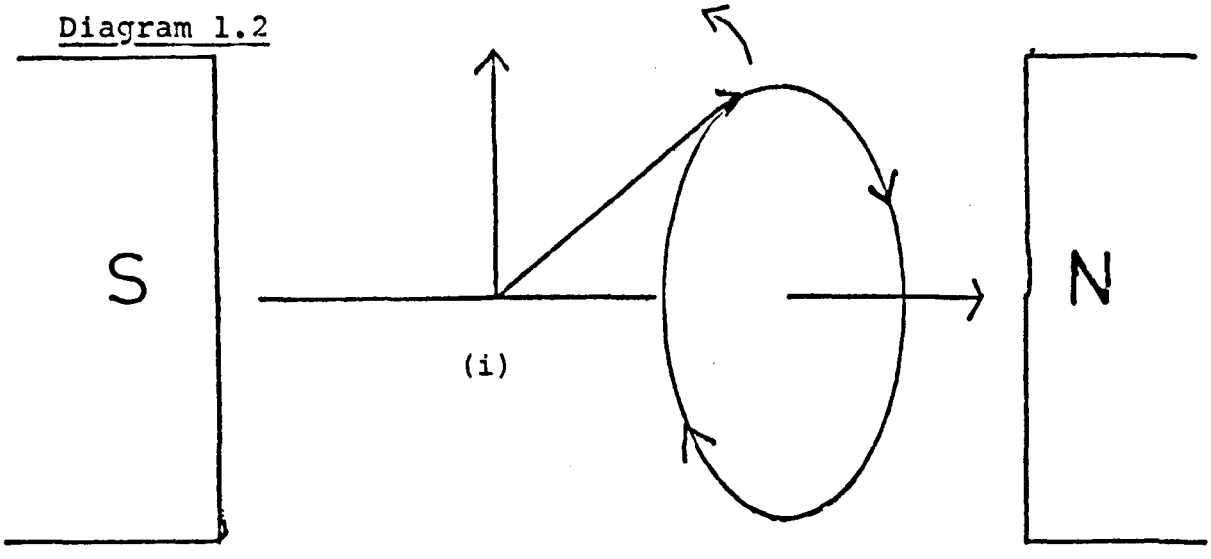
The energy separation is given by

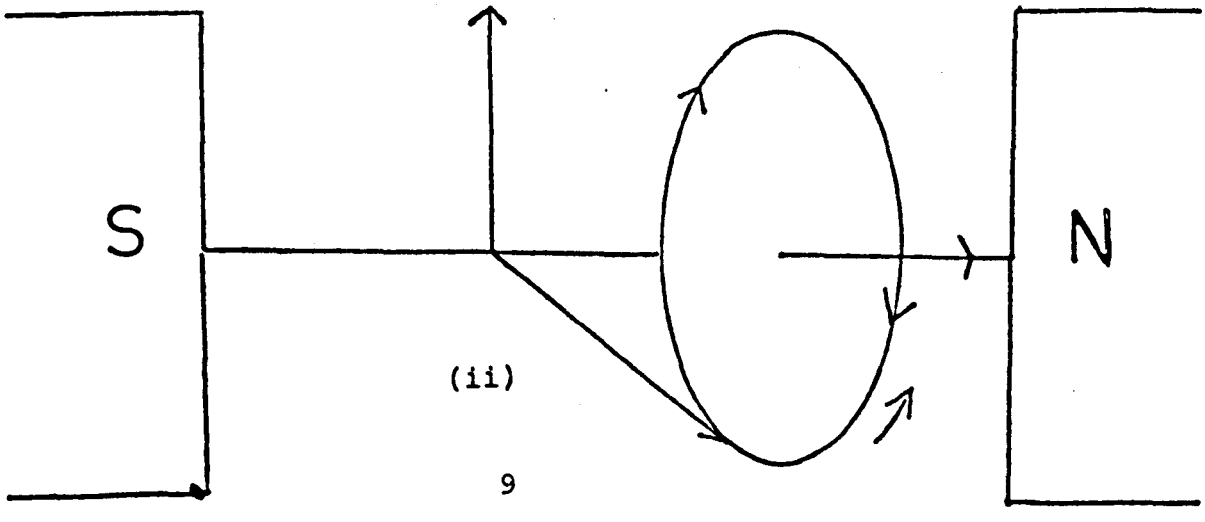
$$E = \frac{\mu Ho}{I}$$

where μ is the nuclear magnetic dipole, Ho the applied field and I the spin quantum number.

If a small magnetic field is applied at right angles to the main magnetic field, the spinning nucleus would be tipped out of the main field (diagram 1.2.(i).) at one instant but half a cycle later in the precession the nucleus would be tipped back into the main field (diagram 1.2.(ii).) The net result is no change.

Diagram 1.2





However when the secondary field rotates at the same rate as the nucleus precesses, as can be achieved using electromagnetic radiation, the nucleus will always be tipped out of the main field. Only when the secondary field and the precessing nucleus are rotating at the same rate does transfer of energy from the tipping field to the nucleus occur and realignment of the nucleus with respect to the main magnetic field takesplace. At this condition the tipping field experiences a drop in amplitude. This effect is termed "Nuclear Magnetic Resonance". The energy absorbed by the nucleus is used to promote it to a higher energy state and so must satisfy the equation

$$\Delta E = h\nu$$

The frequency of radiation used for the tipping field lies in the range 3×10^6Hz to 3×10^8 Hz which is in the radiofrequency region.

From the equation above it follows that

$$\nu = \frac{\mu Ho}{hI}$$

It would be possible to keep the magnetic field, Ho, constant and vary the frequency, ν, of the tipping field until resonance was obtained. Until the advent of Fourier Transform NMR spectroscopy it was simpler in practice to keep the frequency constant and vary the main magnetic field. An NMR spectrum is therefore a plot of intensity of absorption along the ordinate against the magnetic field

strength or frequency as the abscissa. Another feature worth noting is that the intensity of absorption is related to the number of equivalent nuclei in the molecule. By convention the magnetic field strength increases from left to right across the chart. Values towards low field are assigned positive and values to high field are assigned negative.

1.1.2(ii) Chemical Shift

$$h\nu = \frac{\mu H}{I}$$

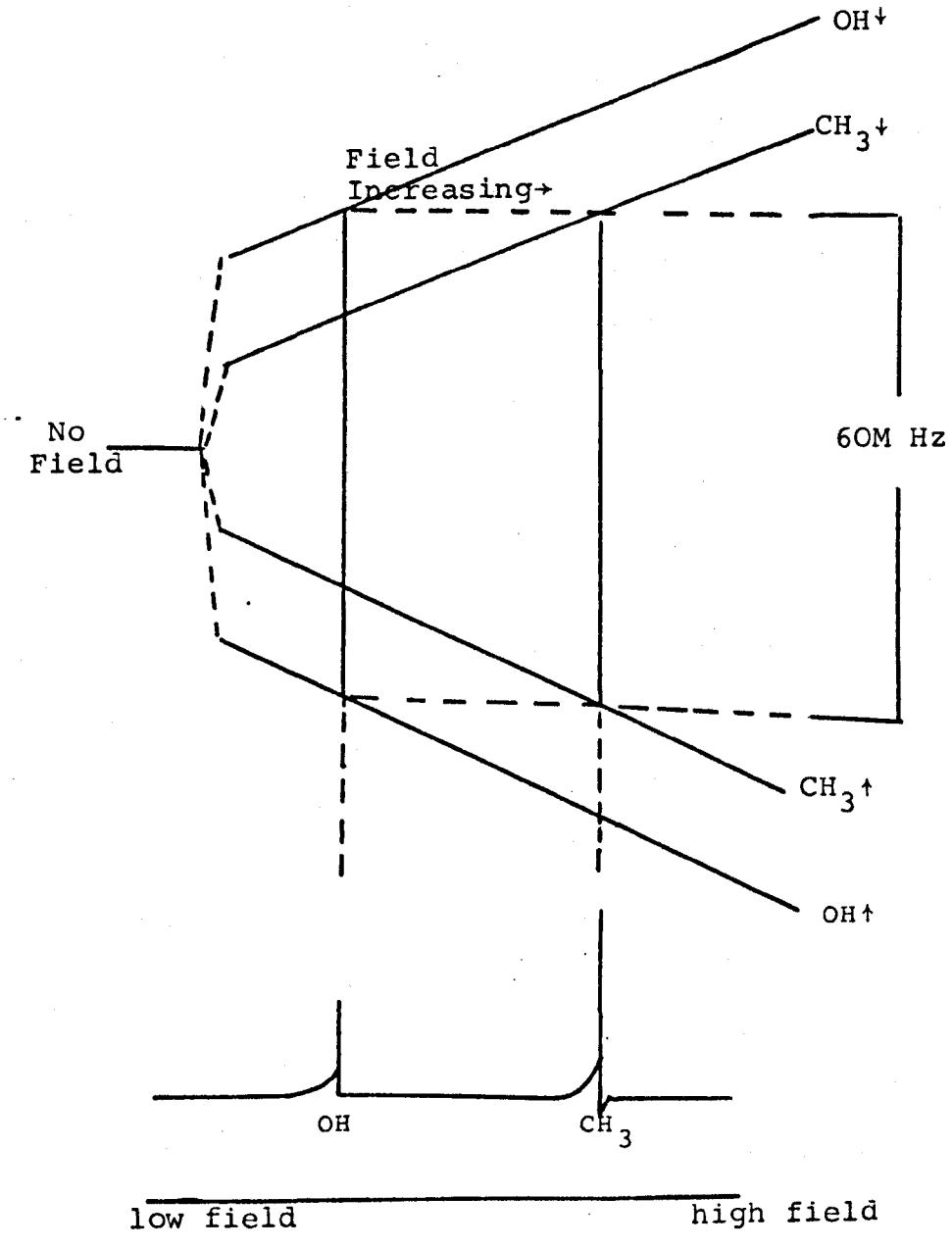
In the above equation the value of the magnetic field H is strictly that experienced by the nucleus and this value is not usually identical with the applied magnetic field. Therefore

$$H = Ho(1 - \sigma)$$

where σ is a screening constant.

The screening constant is a dimensionless quantity associated with the applied magnetic field, Ho. The screening effect has been found to be related to the chemical environment of the nucleus and to the type of chemical bonding involved. Hence chemically different nuclei of, say, hydrogen in a particular molecule will experience slightly different values of the field at resonance. If a hydroxyl-hydrogen nucleus is compared to a methyl hydrogen nucleus it can be seen that the hydroxyl hydrogen nucleus having a smaller shielding constant because of the oxygen atoms electronegativity compared to that of carbon, experiences a greater field at any given applied field strength. Hence its energy levels are more widely spaced than those of the more shielded methyl hydrogen nucleus in the same homogeneous field.

Diagram 1.3


OH↓
CH3↓
Field
Increasing→
No
Field
60M Hz
CH3↑
OH↑
OH
CH3
low field
high field

When this system is irradiated with a beam of radiation at say 60 MHz, while the applied field is increased from zero, the hydroxyl hydrogen nucleus will come into resonance first and so will absorb energy at a lower field. The chemical shifts or position of absorption of the two hydrogen nuclei will be different. (see diagram 1.3).

Chemical shifts of magnetic nuclei are influenced by several interelated parameters. The factors which effect nuclear shielding are not completely understood especially when considering nuclei more complex than hydrogen. It is useful to think of the shielding constant, σ , as arising from well defined groups of electrons in a molecule. This approach was first suggested by Saika and Slichter[4] and later developed by others.

Ramsay[5] derived equations for calculating NMR shielding tensors for systems containing nuclei with net magnetic dipole moments. These equations are complex and difficult to use.

It was later shown by Saika and Slichter[4] that it was possible for the Ramsay equations to be divided into three terms.

a) A diamagnetic correction term for the magnetically active atom which arises from the circulation of the electrons on the atom of the nucleus in question. This contribution opposes the applied magnetic field.

b) A paramagnetic term for this atom. This contribution can be considered as the hindering of the electron cloud about the nucleus, whose shielding is being examined, by the presence of other nuclei in the molecule. This contribution reduces the diamagnetic effect and hence is termed paramagnetic.

c) A contribution from the other atoms in the molecule.

It is generally accepted that for an atom reasonably larger than hydrogen the contribution from the diamagnetic term is negligible. The contribution from other atoms is also considered to be very little because electrons in these atoms are either tightly bound in closed shells or found in valence shells. The former are hard to polarise and generate very small magnetic fields and the latter i.e. the electrons shared with the magnetically active atom are also ineffective while remaining on substituent atoms because of the $\frac{1}{r^3}$, where r is interatomic radius, falling off of the interaction. Therefore the most important term is the paramagnetic contribution from the electrons in the valence shell orbitals associated with the pertinent atom.

For some relatively simple cases in which the screening constants have been calculated the theoretical and experimental results show discrepancies not attributed to theoretical calculations of diamagnetic and paramagnetic terms.[6,7] Such differences must arise from factors not considered by the above terms. The rationale of such differences could be that they arise from contributions from solvents i.e. an intermolecular interaction between solvent and solute or

from intramolecular contribution to the screening constant which could be important. Very little is known about such effects in polyatomic molecules.

In summary the magnitude of the chemical shift is determined by several interrelated factors. In proton NMR spectroscopy the most important contribution is the diamagnetic term. It is quite valid in proton NMR spectroscopy to compare electron donation and withdrawal from a particular hydrogen with differences in chemical shifts. Larger nuclei however such as fluorine-19 and phosphorus-31 have the paramagnetic contribution as the dominant term. The greater range of chemical shifts for these nuclei are attributed to the large paramagnetic contributions. Direct comparison between electron withdrawal or donation by substituents on the larger magnetic atoms with chemical shift is no longer valid unless the relationship can be proved valid empirically, and even then caution must be used when interpreting data.

The chemical shift of any nucleus is dependant on the strength of the magnetic field and is usually expressed in parts per million of the field strength or parts per million of the applied frequency. [3]

The chemical shift range for hydrogen nuclei is approximately 0 to 10 ppm. Fluorine-19 nuclei may have a range of over 1000 ppm; the overall range for aromatic fluorine atoms is 80 ppm. The phosphorus-31 chemical shifts usually occur over 100 ppm approximately.

Absolute values of chemical shifts are difficult to

obtain and chemical shift data is usually quoted relative to an internal or external reference. Tetramethylsilane, TMS, is the usual reference for proton NMR spectroscopy with trichlorofluoro-methane, $CFCl_3$, for fluorine-19 NMR spectroscopy and phosphoric acid, H_3PO_4, for phosphorus-31 NMR spectroscopy

1.1.2(iii) Coupling Constants

The chemically shifted peaks in a NMR spectrum can also show fine structure due to the nucleus associated with a given resonance interacting either through the electronic structure or through 'space' with other magnetically active nuclei in the same molecule.[3] This effect splits the individual peaks of the NMR spectrum into smaller multiplet peaks of the same total intensity. This is called spin-spin splitting. The strength of the coupling between the magnetically active nuclei is measured in terms of a coupling constant J which is expressed in terms of Hertz as it is independant of field strength. There are two types of splitting; simple first order where the chemical shift between the two coupled nuclei is much greater than the coupling constant; second or higher order splitting where the chemical shift between the two coupled nuclei is of a similar magnitude to the coupling constant. Calculation of second order coupling constants is dealt with in greater detail in Appendix A.

In proton NMR spectroscopy the coupling constant can range from a few hertz to ~240 hertz. Directly bonded phosphorus nuclei have coupling constants of some 600 hertz. Coupling fluorine nuclei can give a variety of constants, from a few hertz to approximately 400 hertz. Heteronuclear coupling is also very variable depending on which nuclei are coupled e.g. Phosphorus to platinum coupling is usually between about 2,000 hertz to 4,000 hertz while fluorine to hydrogen coupling is between 50 hertz to 100 hertz in non-aromatic systems.

1.1.2(iv) Fourier Transform Nuclear Magnetic Resonance 8

To date the most commonly used type of NMR spectroscopy is that of continuous wave where the applied frequency of the tipping wave is kept constant and the main applied field strength is slowly increased.

Fourier Transform NMR spectroscopy is a frequency sweep system where the field is kept constant. Pulses of "white" energy which are equivalent to a complete sweep of the frequency range are used. A so called "beat pattern" is obtained which can be converted to a normal spectrum by Fourier Transform methods. This Fourier Transform, which is a purely mathematical conversion, is carried out by a computor. Recent advances in computor technology could well make continuous wave NMR spectroscopy redundant because the availability of computors will increase and their cost decrease.

Fourier Transform NMR spectroscopy has many advantages the main ones being:-

a) The time required to obtain spectrum, for a normal sample usually about 20 seconds.

b) The greater sensitivity obtained. The decreased scanning time enables several scans of the spectrum to be done in a realistic time, this increases the signal to noise ratio and hence improves the sensitivity.

c) The very small quantities of the sample required. These improvements allow investigation of fairly dilute solutions e.g. solution of transition metal complexes many of which tend to be rather insoluble in organic solvents.

1.1.2(v) Double Resonance or Decoupling Technique 8

Complicated spectra which are difficult to analyse could be simplified if coupling between nuclei was destroyed. This decoupling can be achieved if rapid exchange of the spin of one of the nuclei occurs. Two coupled nuclei A and X would give a typical AX spectrum (see Appendix A). Bathing the sample in radiation of ν_A would allow the spectrum of nucleus A to be observed. Application of a strong radio frequency field at frequency ν_X would cause nucleus X to undergo rapid transitions between its two spin states or energy levels. These transitions are not detected by the spectrometer which is tuned to frequency ν_A. The reversals do result in decoupling of the X and A nuclei. Consequently the original doublet would collapse into a single line.

An other use of this technique is the location of particular resonances. If a signal is overlapped and lost beneath another signal decoupling may result in the sharpening up of the missing signal which would then be easily detected.

1.1.2.(vii) Correlation of Fluorine Chemical Shifts with σ- and π-Reactivity Parameters

The magnitude of a fluorine chemical shift is determined by the behaviour of its valence electrons. The fluorine shielding constant is a sensitive probe into the electronic structure of a substituted aromatic compound. Quite large changes in shifts are experienced when substituents are placed at the ortho and para positions of the monfluorophenyl molecules; smaller changes are observed when there is a meta substituent. From the table 1.3 it is apparent that the shifts of fluorine nuclei para to a substituent depend on the π electron distributing nature of the substituents.[9]

Table 1.3

Substituent Chemical Shifts (SCS)

For Fluorine Nuclei in Fluorobenzene

Substituent	SCS (ppm) δ(Para)
H	-6.8
C_6H_5	-3.8
NO_2	-16.0
CHO	-15.9
NMe_2	9.1
NH_2	7.6
OH	3.85

Substituents such as NH_2 and OH, and fluorine itself which produce an increase in π electron density at the para-carbon atom also increase the shielding of the fluorine atom attached to the para-carbon. Those such as NO_2 and CHO which decrease the π electron density at the para-atom cause a decrease in the shielding of the fluorine attached to that atom.

A similar trend is seen with ^{13}C and ^{1}H nuclei.

The first correlation between the Hammett σ parameter and ^{19}F NMR chemical shifts was produced by Gutowsky et al [10] using the chemical shifts of fluorine nuclei in para and meta-substituted monofluorobenzenes.

The Hammett equation[11] is

$$\log \left(\frac{K}{K_o}\right) = \sigma\rho$$

where K and K_o are rate or equilibrium constants for reactions of the substituted and unsubstituted compounds respectively, σ is the substituent "constant" which depends on the nature and position of the substituent and ρ is the reaction constant which depends on the nature of the reaction. The Hammett substituent constant is thought to reflect electronic structure.

The Gutowsky correlation proposes that a relationship exists between nuclear magnetic resonance shielding constants, which may be related to electron density, and parameters derived from the rates of equilibrium constants

of certain reactions.

Taft[12] extended this correlation by proposing that σ could be separated into a resonance contribution σ_R and an inductive contribution σ_I

$$\sigma = \sigma_I + \sigma_R$$

σ_I is considered to be a measure of the substituent's effect on the electron density around the nucleus in question by its ability to attract or repel electrons either through space or via the sigma bonds of the benzene system and σ_R is a measure of the effect due to resonance interaction with the π orbitals of the benzene system. Taft assumed that at the para position both effects were important but at the meta position only the inductive supply or withdrawal of electrons is important. This latter assumption has been used by many workers[13,14] to discuss π donation or withdrawal within substituted benzene rings and also within complexes containing substituted rings as ligands.

Attaching great significance to the observed correlations of chemical shift with Hammett σ is critised severely by J.W. Emsley and L. Philips[9]. These authors also claimed that the division of σ into σ_R and σ_I had no theoretical basis and that it was incorrect to consider that meta ^{19}F chemical shifts and reactivity parameters arise solely from a sigma transmitted effect. The weakest assumption it is claimed is that because there is a linear correlation between Hammett σ and chemical shifts that a simple relationship between changes in potential

energy and changes in the NMR chemical shifts exists. It was postulated by Jaffe[15] that the Hammett equation should be discussed in terms of the potential energy difference between the ground and transition states for correlations involving rate constants and between initial and final states for correlations involving equilibrium constants.

Only a few attempts appear to have been made to apply the Hammett, σ ,correlations to highly fluorinated aromatic compounds. Lawerson[16] found the relationship between the chemical shift of the nucleus <u>para</u> to substituents in ten C_6F_5X molecules was given by

$$\delta F_p = -39.7 \ \sigma_R - 12.9 \ \sigma_I + 154.4$$

and for the meta fluorine atom

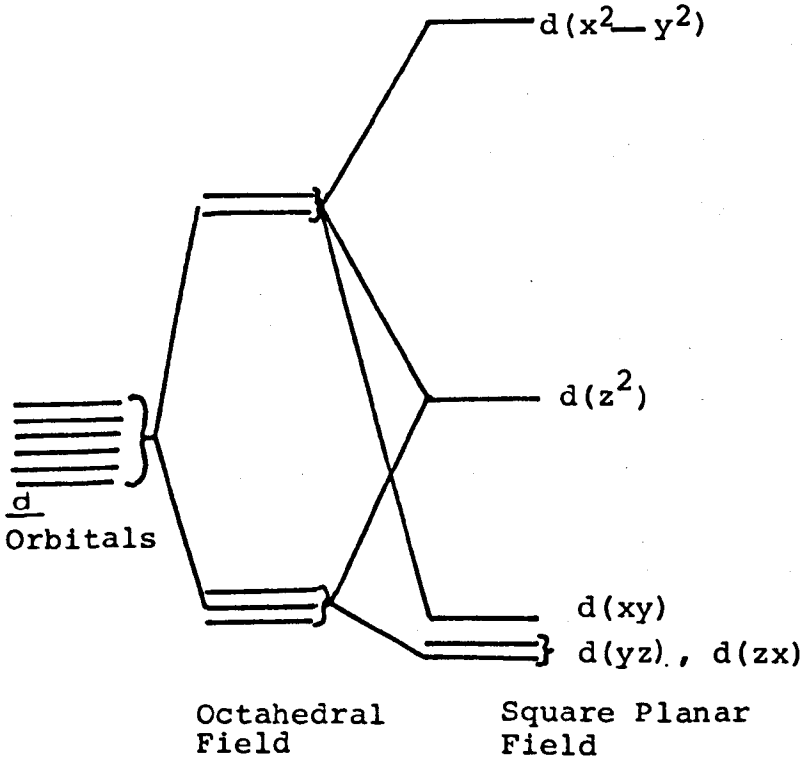
$$\delta F_m = -5.3 \ \sigma_I - 7.2 \ \sigma_R + 162.9$$

Therefore satisfactory correlation requires both resonance and inductive interaction at the <u>meta</u> fluorine atom.

1.1.3. Current Theories of Structure and Bonding

The preference of the d_8 species for square planar configurations can be explained in terms of the Electrostatic Crystal Field Theory [17]. This theory assumes no overlap between the metals atomic orbitals and the ligands orbitals. The interaction between the ligand and the metal is viewed as purely electrostatic. When the metal atom is placed in the electrostatic field produced by the ligands the d-orbitals of the metal are no longer degenerate. The energy difference between the orbitals is called the Crystal Field Splitting Energy. Diagram 1.4 shows the effective orbital splitting in octahedral and square planar structures. The square planar structure is the extreme case of tetragonal distortion of the octahedral system.

Diagram 1.4



The choice of square planar stereochemistry is attributed to the increased value of the crystal field splitting energy which arises from the larger effective nuclear changes of the heavier atoms. The stability of the square planar complexes relative to the tetrahedral depends on the high Crystal Field Splitting Energy of the $\underline{d}_8$ species. The destabilisation of the $d(x^2-y^2)$ orbital in the square planar configuration is so great that the eight d-electrons are paired in the four low energy $\underline{d}$- orbitals making these complexes diamagnetic.

The Crystal Field theory is not strictly valid, although it does account for many transition metal phenomena like magnetic properties and adsorption spectra.[18] There is a great deal of evidence which confirms the existance of metal-ligand orbital overlap. The best piece of evidence arises from electron paramagnetic resonance studies.[19] The classic example is that of the e.p.r. spectrum of $IrCl_6^{2-}$ which can be used to demonstrate the point. The spectrum expected for a group of $\underline{d}$ electrons localised on a particular metal atom should contain a single absorption band with no fine structure. However what is obtained is a complex pattern of sub bands. The hyperfine structure has been explained in terms of orbital overlap between the metal orbitals and the chloride orbitals. The electron is considered not to be localised solely on the metal atom but instead is about 5% localised on each Cl^- ion. The hyperfine splittings are proportional to the probability of each unpaired electron

being found in the chloride ion's orbital. Thus the electron is 70% a Ir(IV) 4d electron instead of the 100% as predicted in the purely electrostatic Crystal Field theory.

Overlap of atomic orbitals is the basic principal of Molecular Orbital Theory[20]. If two atomic orbitals are to make an effective molecular orbital it is necessary that they are of comparable energy. If a molecule is constructed of two different atoms it is unlikely that both atoms would use the same orbitals. Consider the hydrogen chloride molecule; the 1s orbital of the chlorine atom is of a much lower energy than the 1s orbital of the hydrogen atom and therefore the two would not overlap. It is also important to consider the extent of overlap between the combining orbitals. Mathematically the overlap is expressed in terms of the overlap or orthogonality integral.

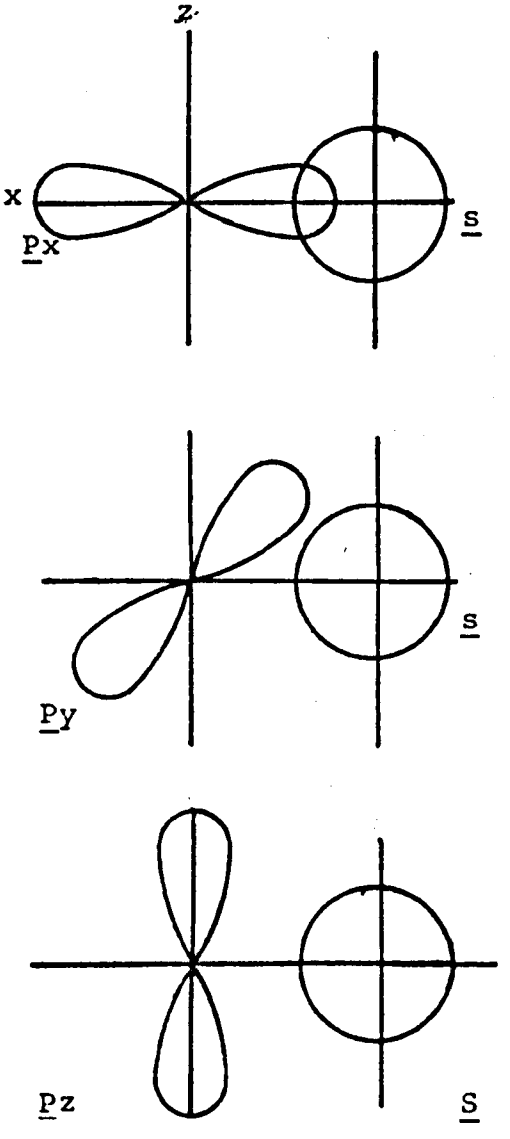
$$Sa,\ b = \int \psi A\ \psi B\ d\tau$$

When $S_{a,b}$ is large the overlap of the orbitals ψA and ψB is large. In directional bonding the overlap criterion is of extreme importance. The symmetry of the two overlapping atomic orbitals must be compatible if they are to form a molecular orbital. Two s orbital can overlap effectively as can a S and a P_x orbital. The symmetry of the P_y and P_z orbitals prevents effective overlap with the S orbital (Diagram 1.5).

Therefore it is evident that the relative energies the extent of overlap and the symmetry of the combining orbitals must be considered when a molecular orbital is being constructed.

Molecular orbitals which are cylindrically symmetric about the molecular axis are called σ (sigma)-bonds. Those whose nodal plane includes the molecular axis are known as π -bonds. If $\underline{P}_x$ is a $\underline{P}$ σ-bond then $\underline{P}_y$ and $\underline{P}_z$ must be $\underline{P}\pi$ -orbitals i.e. orbitals which will form π -bonds.

Diagram 1.5



Molecular orbital theory also predicts the splitting of the d-orbtials on complex formation caused by covalent bonding. Many important phenomena like the magnetism and the absorption spectra of transition metal complexes which are dependent on this splitting can be explained by both Crystal Field Theory and Molecular Orbital Theory.[18, 20]

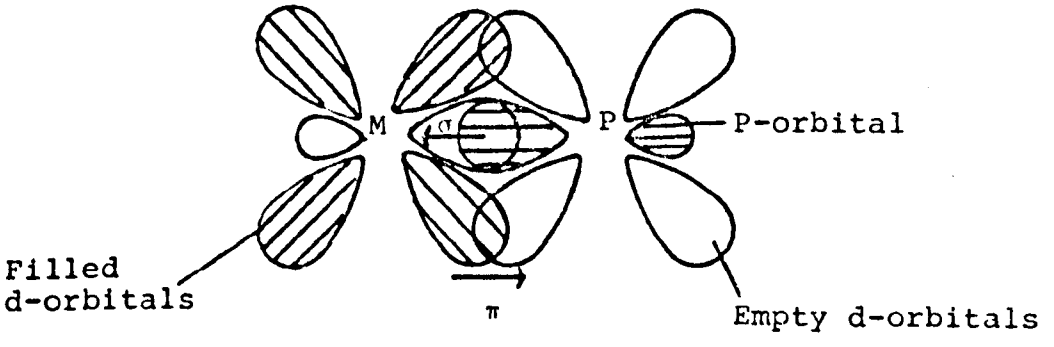
Hybridization[21] of atomic orbitals to form new atomic orbitals which contain both s and p character has been postulated to rationalise the structures of molecules such as methane. The s and p orbitals in the carbon atom are available for bonding with the 1s orbitals of the hydrogen atoms. However all the bond lengths and bond angles in methane are equivalent hence the atomic orbitals used to make the molecular orbitals must be identical. They must all contain the same amount of s and p character. Hybridization of the atomic orbitals of the carbon atom in methane produces sp^3 atomic orbitals. Hybridization involving d-orbitals has also been postulated, d^2sp^3 hybrids for octahedral complexes and dsp^2 hybrids for square planar complexes.

The bonding in transition metal phosphine complexes is generally discussed in terms of molecular orbital overlap.

In 1950 Chatt [22] published his theory of the bonding in metal phosphine complexes. He proposed that ligands which had vacant f or d orbitals could accept electrons

from the filled metal d-orbitals forming ($d\pi - d\pi$) back-bond which is in addition to the ligand-metal σ bond. This transfer of electron density from the metal to the Ligand would be promoted by electronegative groups on the phosphorus. Chatt tested his theory by studying the interaction of phosphorus trifluoride (PF_3) with platinum dichloride ($PtCl_2$) and boron trifluoride (BF_3)[22] Platinum dichloride formed stable complexes but the boron trifluoride did not. The platinum atom has filled d-orbitals whereas the boron trifluoride has none. The idea that the drift of electron density forming the π -bond would partly neutralise the inductive effect of the fluorine atom on the lone pair became an essential part of his theory and was termed the "Synergic Effect". The theory became widely popular and was applied to explain many diverse phenomena such as the (a) and (b) classification of acceptors[23] and the ability of Group VB donors to stabilise transition metal alkyls and aryls.[24] Diagram 1.6 shows a representation of the proposed bonding in metal phosphine complexes.

Diagram 1.6



1.1.3.(ii) π -Bonding?

Doubts about the Chatt bonding explanation were raised by L.M. Venanzi et al[25]. They made the proposal that in platinum (II) complexes π -bonding between the metal and the phosphine ligand had negligible influence on ground state chemical properties. This idea was based on measurements of the J(Pt-P) values for several platinum (II) and platinum (IV) complexes.

Schneider and Buckingham[26] showed that the magnitude of the platinum to phosphine coupling constants was primarily due to an interaction known as the Fermi Contact Term. This interaction depends on the electron densities at the two nuclei and since this is only non-zero for s-atomic orbitals only s-type orbitals can exert nuclear effects.

The approximate expression for a nuclear coupling constant in terms of the Fermi contact term can be expressed as

$$J(P_T\text{-}P) \propto K \alpha_A^2 \alpha_B^2 |\psi_A(0)|^2 |\psi_B(0)|^2$$

K is a constant for the set of compounds examined, α^2 term represents the s-character of each hybrid orbital used by the two atoms when forming the bond and $|\psi_x(0)|^2$ are the electron densities of the orbitals evaluated at the nucleus.[27]

Alteration of the group or groups bonded to one of the coupled atoms can have a large effect on α^2 and $|\psi(0)|^2$

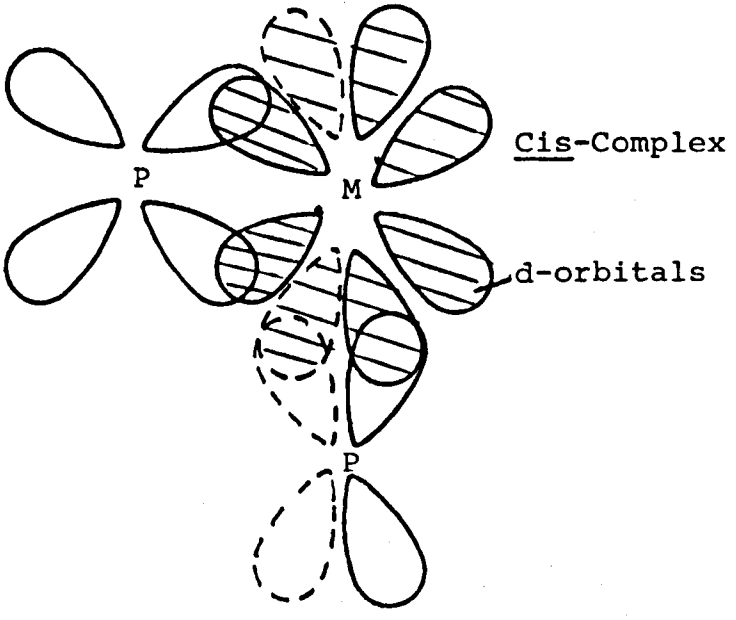
terms for that atom and only a small effect on the corresponding terms of the other coupled atom. Thus the large difference in J(Pt-P) between cis$[PtCl_2(PBu_3)_2]$ (3508Hz) and cis$[PtCl_2(P(EtO)_3)_2]$ (5698Hz) is attributed mainly to a change in α_p^2 and $|\psi_p(o)|^2$ terms

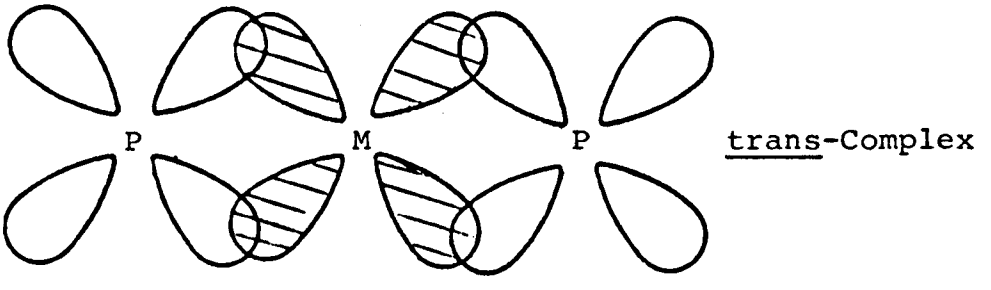
The s-character of the hybrid orbital used by a given atom, α^2 appears to have a larger effect in determining the value of the nuclear spin coupling constant than the $|\psi(o)|^2$ term. The s-character of a bond formed by platinum (II) in a square planar complex $[PtX_2L_2]$ is approximately 0.25 of the total orbital character if it is assumed the metal uses a dsp^2 hybrid. The corresponding octahedral complex $[PtX_4L_2]$ will have approximately 0.17 if the metal uses d^2sp^3 hybrids. It follows that the theoretical ratio of the s-character and hence the coupling constants between analogous platinum (IV) and platinum (II) complexes should be close to 0.67. It is found that the experimental value is $\sim$ 0.6 thereby lending support to the assumption that the s-character of the hybrid is the major factor in determining the value of the nuclear spin coupling constant.

There is considerable evidence showing that in complexes of the type $[PtCl_2(PR_3)_2]$ the platinum phosphorus bonds in the cis isomers are stonger than in the trans isomer [28] this being generally attributed to the difference in the (d_π -d_π) bonds in the cis and trans isomers. In

the trans complex the π -interaction was thought to arise from overlap between a filled metal d-orbital and two empty d-orbitals on the phosphorus atoms. On the other hand a cis complex has two metal d orbitals available for overlap with two phosphorus d-orbitals

Diagram 1.7





This bonding scheme was also used to explain the observed differences in the J(Pt-P) in cis and trans complexes[25] It should be noted that any difference in bonding is detected by the effect it has on the σ -bond and hence the coupling constant. The greater the π -bonding the stronger the σ -bond and the greater the coupling constant. Venanzi[27] pointed out that if this was the mode of bonding, then the expected degree of π -bonding in platinum (IV) complexes would be less than in analogous platinum (II) complexes. The platinum (IV) ion has less associated electron density and a higher formal charge which results in contraction of the d-orbitals and hence a decrease in the ($d\pi$ - $d\pi$) interaction. However Venanzi found that the ratio of J(cis complex)/J(trans complex) was 1.47 for the platinum (II) complexes and 1.41 for the platinum (IV) complexes. This appears inconsistant with the Chatt theory. Venanzi and co-workers favoured the theory put forward by Syrkin[29] which rationalises the difference in the platinum to phosphorus bond strengths in cis- and trans- isomeric platinum complexes exclusively in terms of σ effects.

The most important metal orbitals used to form bonds in square platinum complexes are, in order of their relative stability, 5 $d(x^2-y^2)$ > 6s > 6px; 6py Syrkin showed that if a ligand is bonded to the metal by a strong covalent bond as is the case with phosphine ligands the orbital used by the metal for that bond will have a high s + d character because these atomic

orbitals are more stable than the $6p_x$ orbital. The bond *trans* to this ligand must then have a large metal p_x component and will be less stable. The bonds on the other axis of the molecule could be equivalent and quite strong, or if the ligands are not identical one bond could be strong ($s-dx^2-y^2$) and the other weak (p_y). Thus, in the Syrkin's theory, the strongly covalent bonds also have a large metal s component, so provided that the other parameters effect J_{p-m} are assumed not to vary greatly large coupling constants can be associated with strong (covalent) phosphorus-metal bonds.

However it is generally accepted that the π -back donation plays a part in the bonding of metal complexes where the complex is in a low oxidation state e.g. $[Ni(PF_3)_4]$ [30] support for π bonding in this type of complex comes from photoelectron spectroscopy [31] and *ab initio* S.C.F. MO calculations [32].

The nature of bonding in metal phosphine complexes is reasonably clear at two extremes. Metals in oxidation state (II) or higher form essentially pure σ -bonds with alkyl- and arylphosphines, σ -and π -bonding appears to be established for complexes which have the metal ion in the (0) or (-1) oxidation state. The intermediate situations have yet to be established.

1.1.3. (ii) Cis and Trans-Influence

The kinetic trans effect in square planar platinum (II) complexes was first recognised by Werner[33] and later developed by Chernyaev [34]. The trans-effect is that of a coordinated ligand on the rate of substitution of the group trans to it. The trans influence of a ligand is a measure of the extent to which that ligand weakens the bond trans to it in the equilibrium state of the ligands complex. The terms -effect and -influence are used to distinguish between kinetic and thermodynamic concepts. The cis-influence is the degree to which ligands weaken the bond cis to themselves in the metal complex.

Various theories have been proposed to explain the trans-influence of ligands

(a) The classical polarization theory of Grinberg[35]

(b) The π-bonding theory [36]

(c) The σ-bond rehybridization theory where the platinum to ligand bond has a greater share of the platinum 6s orbital than the platinum bond trans to it.

It is generally accepted that this effect in trans ligands is transmitted through the σ-bonding framework.

If a bond trans to a ligand L is unusually "long" compared with the sum of the covalent radii or with a "normal" bond lengths found in analogous crystal structures, a high trans-influence is usually ascribed to the ligand L However there are other factors to be borne in mind when drawing conclusions from differences in bond lengths. The variations are usually small and intermolecular interactions within the crystal can appreciably effect bond lengths.

Crystal structure determinations on complexes cis-$[MA_2LL']$ have produced the most reliable information on the relative trans-influences of the ligands L and L'.

Mason et al[37] have placed a number of ligands in order of the structural trans-influence by comparing platinum to chloride bond lengths.

$$R_3Si^- > H^- > R_3P > H_2C{=}CH_2, Cl^- > O(acac)$$

This order correlates with the ligand electronegativities. T.C.A. Appleton et al [38] published a similar but much extended series of trans-influencing ligands.

Analogous series have been obtained by examining suitable complexes with techniques other than X-ray crystallography. Allen and Sze [39] obtained a series by measuring the J(Pt-P) values of trans bonds and found the following order of decreasing trans influence but increasing coupling constant.

$SiMePh_2 > Ph^- > Me^- > P(Et_3), P(Bu_3^n) > P(Me_2Ph) > P(Ph_3)$

$P(OPh)_3, CN^- > AsEt_3 > NO_2^- >$ p-toluidine $> EtNH_2 >$

$Et_2NH >$ Py, N_3^-, NCO^-, $NCS^- > Cl^-$, Br^-, $I^- >$

ONO_2^-.

This order represents a decreasing tendency for ligands to concentrate Pt (6s) character into their bonds with platinum (II)

The two series obtained by different techniques show good agreement.

The cis-influence according to predictions made by Zumdahl and Drago [40] from theoretical calculations should be almost as great as the trans influence. However Allen and Sze claimed they obtained evidence for the cis-influence from NMR data but found that a ligand with a large trans influence had a small cis-influence and vice versa. These observations were compatible with Syrkin's theory [29] that a ligand with a large trans influence would strengthen the cis bonds.

More recently work by Muir and Muir [41] has shown that the cis-influence exerted on the platinum to phosphorus bond in complex cis-$[PtCl_2P(Et_3)L]$ by ligands L (where L= Cl^-, $C(NPhCH_2)_2$, C(OEt)NHPh, CNPh, CO, PEt_3, $P(OPh)_3$ or PF_3) is almost as great as the trans-influence exerted on the platinum to chloride bonds.

Muir and Muir claim the cis-influence is predominantly an electronic effect although it is known that in a number of

severely overcrowded complexes e.g. Pt(0) complexes, steric repulsions between the ligands can lengthen the platinum to phosphorus bonds.[42] The authors concluded that cis and trans influences were transmitted through different electronic mechanisms from the fact that different not opposite cis and trans influence series were obtained.

Cis Influence; $Cl < CNPh(CH_2)_2 \simeq CNPh \simeq C(OEt)NHPh < PEt_3 \simeq CO \simeq P(OPh)_3 \simeq PF_3$.

Trans Influence; $CO \simeq Cl^- \simeq PF_3 < CNPh < P(OPh)_3 < PEt_3 \simeq C(OEt)NHPh \simeq C(NPhCH_2)_2$

It is possible that the trans effect and the trans influence are related the latter being put forward as the mechanism of the former, however the two need not be related.

1.1.4. Dynamic NMR Spectroscopy

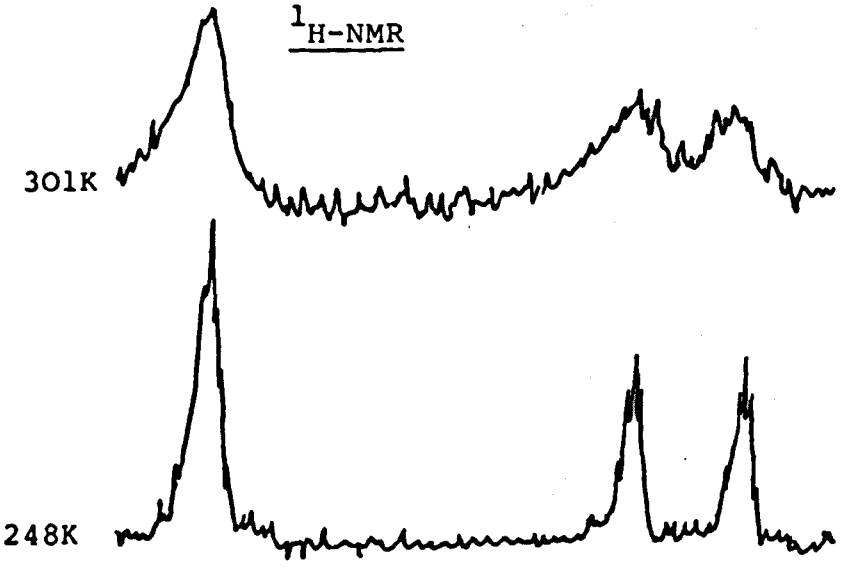
Dynamic NMR spectroscopy has been used extensively for the study of molecular behaviour in solution. This technique enables the study of phenomena such as internal rotations, fast conformational flips, fluxionality, ring "wizzing" and proton transfers. Processes like these occur within the NMR time scale i.e. $\sim 10^3$ sec^{-1}. Great insight has been achieved with regard to reactions between molecules in solution and to the solvated structure of molecules using this technique. Intermolecular processes with activation energies of 21 $KJ/mole^{-1}$ to 105 $KJ/mole^{-1}$ are so fast that resulting isomers (if bond rotation is considered) cannot be separated at room temperature. There are however too slow to be investigated by Infra-red or Raman Spectroscopy. Dynamic NMR is a suitable technique for studying processes with activation energies in the above range. Two examples of the use of DNMR will be looked at more closely.

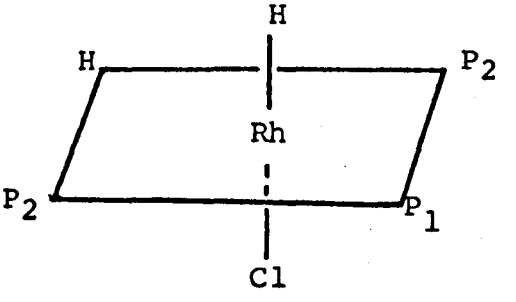
1.1.4.(i) Site Exchange

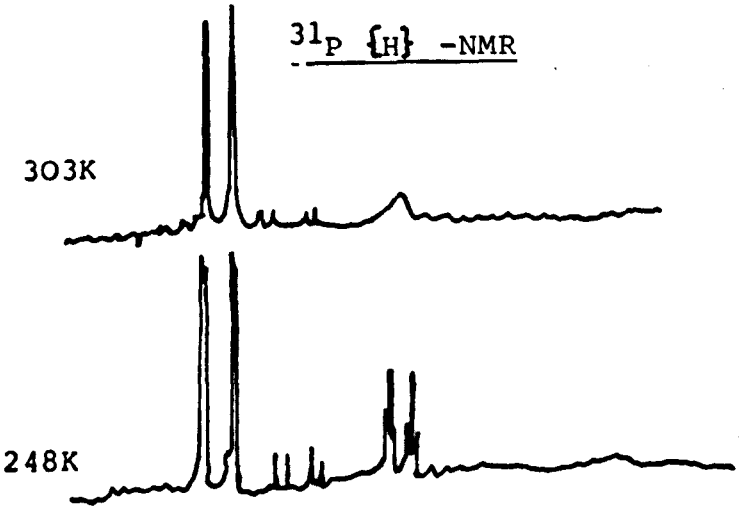
Tolman et al[43] provided an elegant demonstration of the use of Dynamic NMR spectroscopy when they studied the complex $[RhH_2Cl(P(C_6H_5)_3)_3]$ at different temperatures.

The proton NMR spectrum at 248 K as shown in the diagram 1.8 was sharp and contained two non-equivalent hydrogen environments, only one showing large phosphorus to hydrogen coupling. The large coupling is characteristic of a phosphorus atom trans to a hydride and the stereochemistry of the complex is unambiguously established as that with two magnetically equivalent phosphorus nuclei (P_2) and one unique phosphorus nuclei (P_1). On raising the temperature to 301K the hydride spectrum broadens reversibly indicating chemical exchange. Diagram 1.8 shows the ^{31}P NMR spectrum of the complex at a similar set of temperatures. The low-temperature limit spectrum is a doublet of doublets for the phosphorus nuclei P_2, which is coupled with rhodium and P_1. A doublet of triplets is observed for phosphorus nucleus P_1 which coupled with rhodium and the two P_2 nuclei. Coupling to the hydride atoms is presumably masked by the other couplings. The higher temperature spectrum yields quite detailed mechanistic information. It shows that the phosphorus (P_1) to rhodium coupling and the phosphorus to phosphorus couplings are lost while the rhodium to phosphorus (P_2) coupling is still observed. This indicates that the phosphorus (P_1) ligand is dissociating at an appreciable rate at 303 K, providing a site for olefin co-ordination during hydrogenation catalysis.

Diagram 1.8







1.1.4.(ii) Rotational Isomerism

There have been numerous reports of conformational isomerism due to restricted rotation about single bonds in organometallic chemistry. Among the earliest reported examples was that of compounds of the type $[\eta^5C_6H_5Fe(CO)_2MX_2R]$ (M = SiGe; X = Cl, Br, I; R = Alkyl)[44] which existed in solution as mixtures of rotamers with respect to the Fe-M bond. Evidence for these conclusions was based on the appearance of four strong carbonyl stretching bonds in the infra-red spectra of the compounds. Similar observations were made for a number of methyl-thio-bridged and metal-metal bonded bimetallic carbonyl complexes Restricted rotation about transition metal-carbon σ bond has been reported for a wide range of complexes [45]. This has obvious implications to the chemistry of alkyl metal compounds and may have significance in homogeneous catalysis where metal to alkyl bonds are very important.

The presence of rotational isomers in solution of alkyl compounds $[RCOCo(CO)_3L]$ [46] ($R = CH_2FCHF_2$; $L = PPh_3P(OPh)_3$) was inferred from the presence of doubling of bonds in the carbonyl region of the high resolution infra-red spectrum In this case only one set of time averaged resonances was observed in the NMR spectrum suggesting that barriers to rotation in these compounds are very low. However the barrier to rotation in complexes $[IrHX(C_6F_5)(CO)PPh_3]$ [47]. (X = Cl, Br) must be considerable as all five fluorine atoms have been shown to be magnetically non-equivalent.

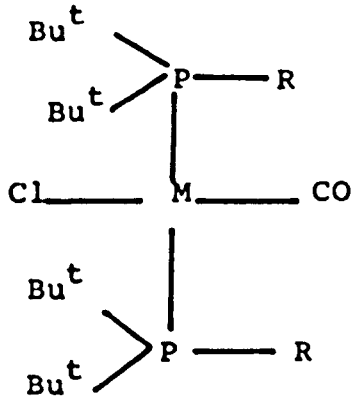
Mann and his colleagues[48] used ^{1}H and ^{31}P NMR spectroscopy to show that complexes of the type trans-$[MX_2(PHBu_2^t)_2]$ (M = Pd, Pt X = Cl, Br, I) and trans-$[MCl(CO)(PBu_2^tR)_2]$ did exist in solution as isomers and they proposed structures for the various isomers these are shown in diagram 1.9.

Restricted rotation which results in rotational isomerism has in most cases been observed in complexes with bulky ligand such as $(Bu^t)_3P$. One exception is the work of Baird et al[49] who proposed rotational isomerism for compounds like $[Cp\ M\ CO(L)CH_2R.]$ (M = Co, Fe, Ni ; L = Phosphorus donor ; R = CF_3, CF_2CF_2, $CF(CF_3)_2$).

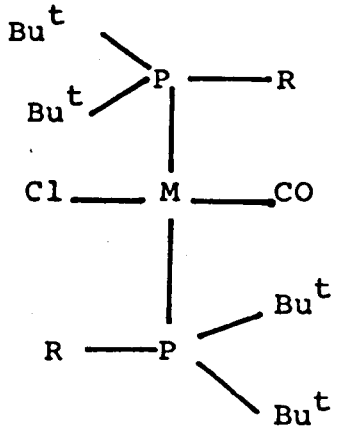
The conclusion that $n^5C_6H_5$ group and bulky phosphines can present significant rotational barriers to coordinated alkyl groups and can force the latter to favour a particular conformation was based on broadening of NMR signals with temperature variation.

The presence of rotational isomers is mainly due to large steric interactions between atoms or groups of atoms on the molecule.

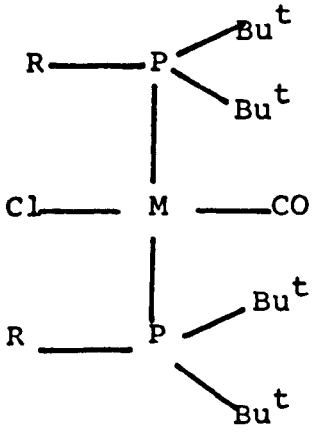
Diagram 1.9



A_2X



A_2X

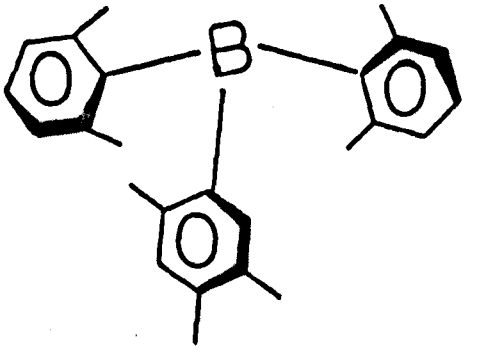


ABX

Trans -[$MCl\ CO(PBu^t_2R)_2$]

1.1.5. Propeller Molecules

A wide variety of molecules of the type A_3Z and Ar_3ZX with propeller-like structures have been known for some time [50]. The aryl rings are considered as blades which radiate from an axis of rotation i.e. the propeller axis, and each blade is twisted in the same sense making each molecule chiral. Although compounds of this type can differ greatly in their constitution Mislow and co-workers showed that their static and dynamic stereochemistries were related [51]. Mislow has discussed extensively in many publications [52,53] the stereochemistry of molecular propellers. He coined the phrase "correlated rotation", for describing the molecular behaviour of these propeller molecules. The conclusion reached by Mislow and others[51] was that when two or more rings are attached to a single atomic centre then the motion of each ring was dependent on and related to the motion of the other rings attached to the centre. The motion of the n-rings was coupled in the sense that none of the rings moved independently. In many papers and reviews published there is considerable evidence for this correlated motion. Proton NMR studies of compounds such as various substituted triaryl boranes[51] eg Diagram 1.10.



have given strong support to this concept

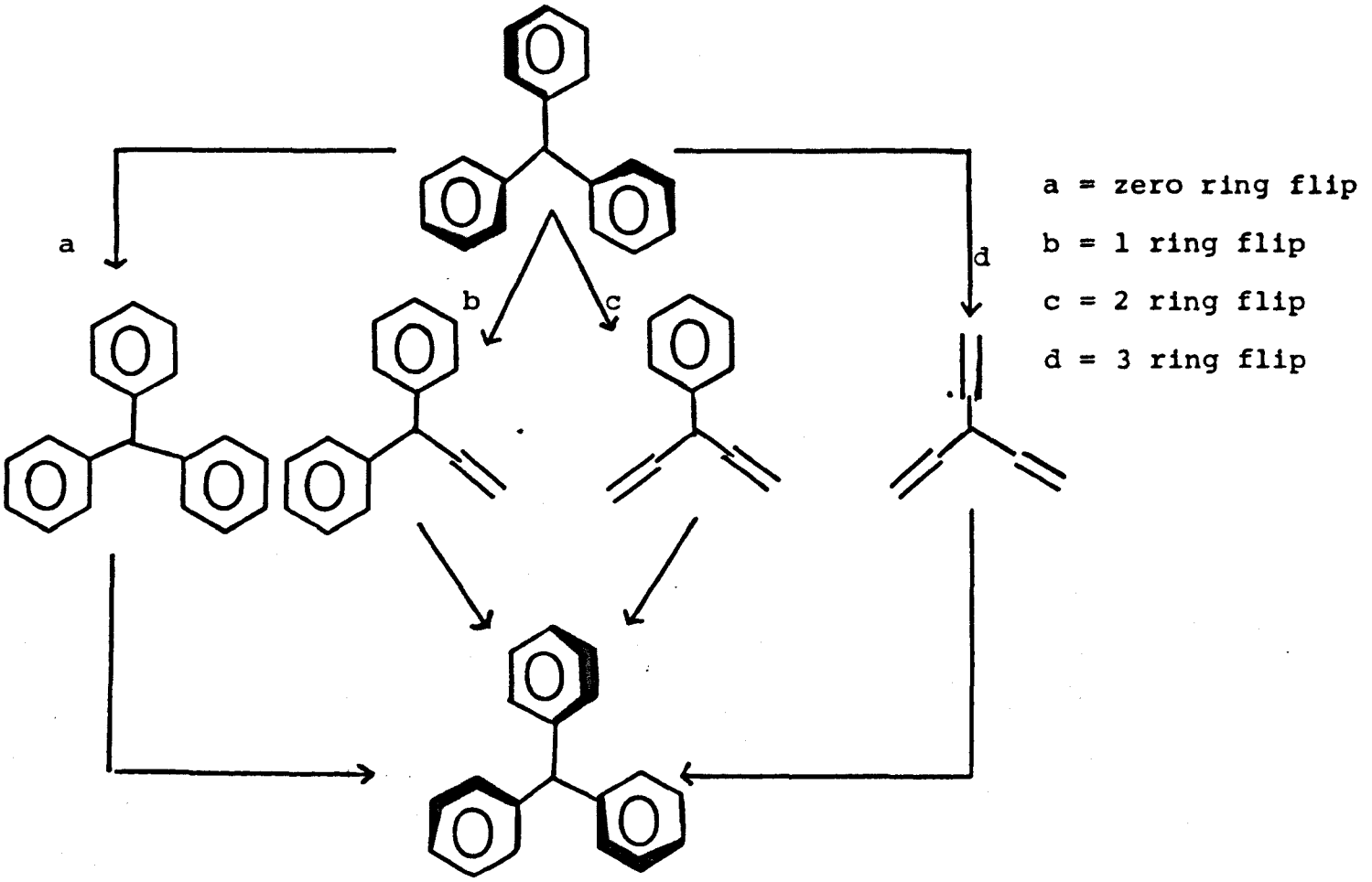
In one particularly comprehensive review[51] Mislow discussed the types of isomers and mechanisms by which isomerisation can occur in molecular propellors. Stereoisomerisation of a molecule of the type Ar_3Z or Ar_3ZX can occur by the rotation of the aryl groups about the Z to carbon bond. There are many modes which could theoretically convert one isomer to another. All the evidence to date has been interpreted in terms of one of four general classes of mechanisms called "flip" mechanisms. There were first suggested by Kurtland et al[54] for the isomerisation of triarylcarbonium ions. In each of the four cases, zero, one, two or all three aryl rings are flipped i.e. rotated through planes perpendicular to the reference plane, while the remaining groups are rotated through the reference plane. Diagram 1.11.
The helicity of the reactant molecule is reversed by each flip mechanism and each mechanism produces a different isomer when the aryl rings are labelled.

In the zero and three ring flips all the rings rotate in the same direction clockwise or anticlockwise. The one and two-ring flips result in two of the rings rotating in the same direction while the third rotates in the opposite direction.

In all systems so far examined the two ring flip, i.e. the mechanism in which one ring passes through the reference plane, is the stereoisomerisation process of lowest energy for molecules of the type Ar_3Z and Ar_3ZX. Mislow's very elegant work using molecular mechanics demonstrated that correlated motion was highly likely in

Diagram 1.11

Mechanisms for Helicity Reversal in Propeller Molecules



these types of molecules.

In the molecules discussed above the motion of the rings is controlled by steric interactions between substituents on the aryl rings.

In the present work propeller molecules attached to metal centres have been examined. In these complexes it is found that other substituents on the central atom can affect the motion of the rings of the propeller molecules.

1.1.6. Asymmetric Tertiary Diphosphines and Related Complexes

The method most commonly used to prepare diphosphines is the reaction between alkali metal phosphines and di-haloalkanes, -alkenes etc.

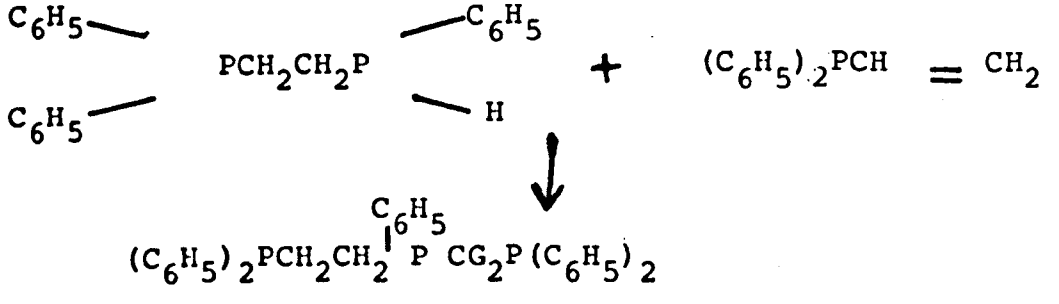
$$2MPR_2 + X\sim\sim X \longrightarrow R_2P\sim\sim PR_2 + 2MX$$ [57]

The bisdiphenyl phosphino alkanes, $R_2P(CH_2)_nPR_2$, are obtained mostly by the reaction between

$X(CH_2)_nX$ + $LiPPh_2$ in tetrahydrofuran in a moisture and oxygen free atmosphere For the case where n = 2 the ligand is also obtained by the base-catalysed addition of diphenyl phosphine, PPh_2H, to diphenylvinyl phosphine, $PPh_2CH{=}CH_2$ [55]. The vinyl phosphine is more difficult to prepare than the metal phosphine.

The reaction involving vinyl phosphine was used by S. O. Grim and co-workers to prepare novel asymmetric bis-(tertiary phosphines)[56] of the type $(C_6H_5)_2PCH_2CH_2P(C_6H_5)R$ where R is methyl, ethyl, or iso-propyl. R.B. King [57] showed the method was useful in the synthesis of poly(tertiary phosphines).

Diagram 1.12



A series of papers was published giving details of the preparation of complexes of asymmetric diphosphines with transition metal carbonyls[58] It was noted that these diphosphines sometimes exhibited preferential bonding at one end of the ligand. The reaction of $Ph_2PCH_2CH_2PMePh$ with $[C_6H_5NH_2W(CO)_5]$ in an 1:1 ratio gave predominantly the isomer with the PPhMe end co-ordinated In general it was found that co-ordination of the smaller phosphine group was preferred.

Platinum(II) and Palladium (II) halide complexes containing the asymmetric biphosphines $Ph_2PC_2H_4PR_2$ where R = CF_3 or C_6F_5 have been prepared.[59] The halide substitutions o $[PtCl_2(C_6H_5)_2PC_2H_4P(C_6F_5)_2]$ were examined and will be discussed later.

Part 2 Experimental Procedure

The following table lists the purchased or gifted chemicals, with suppliers; which were used, in this work.

Table 1.4

Chemical	Supplier
K_2PtCl_4; $PtCl_2$; $PdCl_2$ $RhCl_3.xH_2O$; $IrCl_3.xH_2O$	Johnstone Matthey Chemicals Ltd.
K_2PtBr_4; PtI_2	ICI Mond Division
Diphenylvinylphosphine	BDH Ltd.
Triphenylphosphine	
Chlorine Gas	
Bromopentafluorobenzene	Fluorochem. Ltd.
Magnesium Turnings	Ass. Chem. Ltd.

Volatile materials were transferred by conventional high vacuum techniques using a Pyrex Glass vacuum line with a mercury diffusion pump backed by a N.G.N. high vacuum oil rotary pump. Standard glass joints were greased with Apiezon N, Apiezon L or Edwards high vacuum silicone grease. Polytetrafluoroethylene or glass stopcocks were used when required. The glass vacuum line was 'flamed out' after evacuation and before use to remove moisture.

All solvents used were dried and degassed before use according to methods described in "Purification of Laboratory Chemicals",[60] Chapters 3 and 4.

Photolytic reactions were carried out in Quartz reaction vessels fitted with PTFE stopcocks and irradiated by a Hanovia medium pressure mercury lamp emitting predominantly 254mμ , 265mμ , 297 mμ , 313 mμ and 366mμ wavelengths.

All other reactions were carried out under an atmosphere of dry, oxygen-free, nitrogen.

Characterisation of the ligands and complexes was carried out by conventional methods. Chemical analyses were carried out by the Glasgow University Micro-analysis Service. Infra-Red Spectra were recorded on a Perkin-Elmer P E 577 or a Perkin-Elmer PE 225 spectrometer. Spectra were calibrated against a polyethylene film. The samples were examined as nujol mulls or neat liquid films between KBr or CsI plates. KBr or CsI discs of the solid compounds were used where necessary and solutions of some compounds were also examined.

The following abreviations have been used in the text - s, strong; m, medium; w, weak; sh, shoulder; br, broad, v, very; ν stretch.

The proton NMR were recorded on a Perkin-Elmer R32 at 90 MHz. The ^{19}F and ^{31}P NMR spectra were obtained using a Varian XL100 F.T. spectrometer. The spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ at 94.15MHz for fluorine-19 and 40.5MHz for phosphorus-31. Double irradiation experiments were carried out using the integrated spin decoupler of the instrument. Variable temperature data were recorded directly and the temperature was assumed to be accurate to $\pm$5 K. Additional proton NMR spectra were recorded using a Perkin-Elmer T60 at 60MHz frequency.

1.2.1. Preparation of ligands

1.2.1(i) Pentafluorophenyl magnesium bromide[61]

$$Mg + C_6F_5Br \longrightarrow C_6F_5MgBr$$

The magnesium turnings were dried in an oven at 323 K and cooled in a desicator. A conventional reflux apparatus consisting of a three-necked round bottom flask with a water condensor, dropping funnel, and nitrogen inlet was used. The system was flushed with oxygen-free nitrogen for at least one hour before starting the reaction.

The solution of pentafluorophenyl bromide in sodium-dried ether was placed in the dropping funnel. The magnesium turnings were put into the reaction flask. The reaction was initiated by adding a sufficient volume of pentafluorophenyl bromide solution to the magnesium turnings. Initiation could also be achieved by heating the reaction flask or by scrapping the surface of the magnesium turnings with a glass rod. The reaction was continued by adding the pentafluorophenyl bromide solution at an appropriate rate. As the Grignard preparation proceeded the solution became progressively darker. After the addition of pentafluorophenyl bromide was complete the dark brown solution was left to cool for approximately one hour before continuing to the next stage of the preparation.

1.2.1(ii) Chloro bis (pentafluorophenyl) phosphine[61]

$$2C_6F_5MgBr + PCl_3 \longrightarrow (C_6F_5)_2PCl + \text{by products}$$

$$C_6F_5MgBr + PCl_3 \longrightarrow (C_6F_5)PCl_2 + \text{by products}$$

This reaction yielded different products depending on the molar ratios used.

Freshly distilled phosphorus trichloride in sodium-dried ether was placed in a reaction vessel which had been flushed out with nitrogen. The flask was kept at a temperature of 273 K by placing an ice-bath around it. The Grignard reagent pentafluorophenyl magnesium bromide was added dropwise to the vigorously stirred phosphorus trichloride. When all of the Grignard had been added the remaining mixture was left at ambient temperature for at least two hours. The mixture was then filtered under nitrogen and the solvent was removed by bubbling nitrogen through the solution. The liquid obtained was a mixture of chloro bis(pentafluorophenyl) phosphine and dichloro-(pentafluorophenyl) phosphine. The two oils were separated by fractional distillation with continuous pumping. In normal conditions the first fraction boiled at approximately 313 K to 315 K and the second fraction boiled at approximately 353 K to355 K at 0.1mm Hg pressure. Yields based on moles of C_6F_5 regained as phosphorus halides were typically between 75% and 82%.

1.2.1(iii) Reduction of the Chloro bis(pentafluorophenyl) phosphine [62]

$$(C_6F_5)_nPCl_{3-n} + Me_3SiH \rightarrow (C_6F_5)_nPH_{3-n} + \text{by-products}$$

The oil, chlorobis(pentafluorophenyl) phosphine, was placed in an ampoule-type reaction vessel and attached to a vacuum line. The ampoule was evacuated and trimethylsilane was condensed into the flask and the system was then sealed. The reaction flask was left standing for three days at room temperature or irradiated with UV light for twelve hours. The product precipitated out of solution as a white solid which was collected on a filter funnel and washed with dry methanol. The product, bis pentafluorophenyl phosphine, $(C_6F_5)_2PH$, was purified by sublimation at 353 K at 0.1mm Hg using a conventional sublimation apparatus. If the product did not precipitate out of solution after three days it could be obtained by adding dry methanol to the reaction flask which would cause the product to precipitate. The yield for this stage was usually $\sim$ 80%.

The pentafluorophenyl phosphine,[62] $(C_6F_5)PH_2$, could be similarly prepared. Care had to be taken to exclude moisture completely as this phosphine is very sensitive to air and moisture. The $(C_6F_5)PH_2$ was purified by performing a trap-trap distillation on a vacuum line to separate the product from unreacted starting materials and by-products. The yield was generally $\sim$ 50%.

1.2.1.(iv) Tris pentafluorophenyl phosphine[63]

$$3C_6F_5MgBr + PCl_3 \rightarrow P(C_6F_5)_3 + \text{by-products}$$

This phosphine was prepared by the dropwise addition of phosphorus trichloride to the Grignard, pentafluorophenyl magnesium bromide solution. When the addition was complete the reaction flask was left to stand at ambient temperature for fifteen minutes. Cold 0.01M hydrochloric acid was added to ensure hydrolysis of any chlorophosphines produced. The organic layer was separated from the aqueous layer and the aqueous layer was washed with ether. The combined organic layer and washings were "worked up" by either distilling under reduced pressure or by blowing the solvent off with nitrogen. After removal of the solvent the dark brown solid was placed in a sublimation apparatus and the product sublimed at approximately 373 K at 0.1mm Hg pressure. The yield was generally ~ 80%.

1.2.1.(v) (1-Diphenylphosphino,2-bis pentafluorophenyl-phosphino)ethane[59] i.e. $(C_6H_5)_2PC_2H_4P(C_6F_5)_2$

$$(C_6F_5)_2PH + (CH_2{=}CH)PPh_2 \xrightarrow{UV} (C_6F_5)_2PC_2H_4PPh_2$$

Excess bis(pentafluorophenyl)phosphine was dissolved in dried cyclohexane and then added to diphenylvinyl-phosphine in a quartz reaction vessel which was then placed under a UV lamp for twenty four hours. Care was taken to avoid charring the product by placing the flask at a reasonable distance from the lamp. The product precipitated out of solution and was collected on a filter funnel and washed with dried cyclohexane. The yields obtained were variable from ∿ 50% down to 20%.

1.2.2. Preparation of Phosphine Complexes

1.2.2(i) Dichloro,1-diphenylphosphino,2-bis(pentafluorophenyl)phosphinoethane platinum (II)[59]; i.e. $[PtCl_2\ Ph_2PC_2H_4P(C_6F_5)_2]$

The ligand $Ph_2PC_2H_4P(C_6F_5)_2$, was suspended in benzene and added to a refluxing solution of bis(benzonitrile)dichloroplatinum (II). The reaction mixture was refluxed for twelve hours. The product, a white solid, precipitated out as the solution was allowed to cool. If no precipitation occurred on cooling, the solution was refluxed for a further six hours.

The dibromide and diiodide anologues were prepared by adding excess lithium bromide and lithium iodide to an acetone solution of the dichloride complex.

Yields for the dichloride complex were usually between 50% to 60%. Yields for the dibromide and diiodide were high, between 90% and 95%.

1.2.2.(ii) Trans-carbonylchlorodi(trispentafluorophenyl-phosphine) rhodium(I) i.e. trans-$[RhClCO(PC_6F_5)_3)_2]$

The complex was prepared as described by Peacock et al.[64] Four moles of trispentafluorophenylphosphine was added to one mole of tetracarbonyl-μ-dichlorodirhodium in chloroform solution at ambient temperature. Yellow crystals were obtained immediately. The product was washed with cooled chloroform. Yields of ~ 50% were obtained.

1.2.2(iii) Trans-Carbonyl chloro di(tris pentafluorophenyl phosphine) iridium (i) i.e. Trans $[IrClCo(P(C_6F_5)_3)_2]$

Iridium trichloride hydrate was dissolved in diethylene glycol and trispentafluorophenylphosphine was then added. The solution was refluxed for at least twelve hours and became more yellow as the reaction proceeded. After cooling the solution, a large volume of ethanol was added and a yellow solid separated out. Extraction with acetone yielded the pure product. Yields were ~85% or greater.

1.2.2(iv) Trans-Dihalodi(trispentafluorophenyl phosphine) platinum (II) and Trans-Dihalo di(trispentafluorophenyl phosphine) palladium (II) i.e. Trans-$[Mx(P(C_6F_5)_3)_2]$

The dichloroplatinum (II) complex was prepared by the method described by Peacock et al[65] who first made these complexes i.e. by the addition of an aqueous solution of potassium tetrachloroplatinate to a refluxing methanol solution of tris pentafluorophenylphosphine. The solution turned yellow and yielded yellow crystals on evaporation of the solvent. The dibromide complex was made using sodium tetrabromo platinate. A solution of platinum (II) iodide and the phosphine were refluxed in xylene for twenty four hours and yielded the pink diiodide complex trans-$[PtI_2(P(C_6F_5)_3)_2]$

The dichloropalladium (II) complex was made analogously to the dichloroplatinum (II) complex. The dibromo and diiodo palladium complexes were made by the addition of lithium bromide and lithium iodide to the dichloro complex dissolved in acetone.

1.2.2. (v) Dichlorotriphenylphosphine tris pentafluorophenyl phosphine platinum (II) and Dibromodimethylphenyl phosphine tris pentafluorophenylphosphine platinum (II) i.e. trans-$[PtCl_2(PPh_3)P(C_6F_5)_3]$ and trans-$[PtBr_2(PMe_2Ph)P(C_6F_5)_3]$

The appropriate dimeric species i.e. $[Pt_2Cl_4(P(Ph_3))_2]$[66] or $[Pt_2Br_4(PMe_2Ph)_2]$[66] was suspended in chloroform at ambient temperature. Two equivalents of the tris pentafluorophenyl phospine were added to the suspension. As the reaction proceeded the dimer dissolved and after approximately one hour a clear yellow solution was obtained. Characterisation of the complexes was carried out by nuclear magnetic resonance spectroscopy. The ^{31}P NMR spectrum was a typical ABX type. (A full description and discussion of this type of spectrum is dealt with in Appendix A).

Attempts to recrystallise these complexes resulted in the formation of trans-$[PtCl_2(PPh_3)_2]$ trans-$[PtCl_2(P(C_6F_5)_3)_2]$, trans$[PtBr_2(PMe_2Ph)_2]$ and trans-$[PtBr_2(P(C_6F_5)_3)_2]$ by disproportionation.

1.2.2.(vi) Trans-Dibromo bis(dimethylphenyl phosphine) diphenyldiplatinum (II) i.e. $[Pt_2Cl_2Ph_2(P(Me_2Ph))_2]$

The dimer $[Pt_2Cl_4(PMe_2Ph)_2]$ was prepared according to methods described by F.R. Hartley.[66]

The dimer $[PtCl_2Ph_2(PMe_2Ph)_2]$ was prepared by G.K. Anderson in the following way.[67] A molar equivalent of $[PtCl_2(PMe_2Ph)_2]$ was added to a stirred solution of diphenylmercury (Two equivalents) in benzene at room temperature. This solution was left at room temperature for two hours. The solvent was removed and the complex purified by subliming out the by product PhHgBr.

1.2.2.(vii) Chloro(phenyl)(dimethylphenylphosphine)-tris pentafluorophenyl phosphine platinum (II) i.e. trans-$[PtClPh(PMe_2Ph)P(C_6F_5)_3]$

Tris pentafluoro phenylphosphine (2 equivalents) was added to the dimer $[Pt_2Cl_2Ph_2(PMe_2Ph)_2]$ (1 equivalent) in chloroform. Removal of the solvent yielded the required product. Yield was $\sim$ 50%.

Table 1.5 Infra Red ν(M-Cl) and ν(M-CO) frequencies

Complex	ν(M-Cl)cm^{-1}	ν(CO)cm^{-1}
$[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$[61]	300(s) 335(s)	-
trans-$[PtCl_2(P(C_6F_5)_3)_2]$[63]	349(s)	-
trans-$[PdCl_2(P(C_6F_5)_3)_2]$[63]	363(s)	-
trans-$[PtCl(Ph)PMe_2PhP(C_6F_5)_3]$	338(s)	-
trans-$[RhClCO(P(C_6F_5)_3)_2]$[63]	306(s)	2,005(vs)
trans-$[IrClCO(P(C_6F_5)_3)_2]$	-	1,990(vs)

Table 1.6 Chemical Analysis

ligands		C%	H%	F%	P%
$(C_6F_5)_2PH$	Theory	39.3	0.27	51.9	8.5
	Found	39.2	0.22	52.1	8.4
$P(C_6F_5)_3$	Theory	40.6	-	53.6	5.8
	Found	39.2	-	54.1	5.9
$Ph_2PC_2H_4P(C_6F_5)_2$	Theory	53.9	2.4	32.8	10.7
	Found	54.1	2.5	32.8	10.5

Complexes		C%	H%	F%	Cl%	P%
$[PtCl_2(Ph_2PC_2H_4P(C_6F_5)_2)]$	T	37.0	1.6	22.4	8.4	7.3
	F	37.3	1.7	22.4	8.3	7.1
$[PtBr_2(Ph_2PC_2H_4P(C_6F_5)_2)]$	T	33.4	1.5	20.3	17.1	6.6
	F	34.6	1.2	20.1	16.7	6.3
$[PtI_2(Ph_2PC_2H_4P(C_6F_5)_2)]$	T	30.3	1.3	15.5	24.7	6.0
	F	30.1	1.2	17.4	25.2	5.9
$[RhCl(CO)(P(C_6F_5)_3)_2]$	T	36.0	-	46.3	2.8	5.0
	F	35.3	-	46.3	2.6	-
$[IrClCO(P(C_6F_5)_3)_2]$	T	33.6	-	43.2	2.6	4.6
	F	33.8	-	43.0	2.3	-
$[PtCl_2(P(C_6F_5)_3)_2]$	T	32.4	-	42.9	5.6	4.7
	F	33.1	-	42.5	5.8	4.6
$[PtBr_2(P(C_6F_5)_3)_2]$	T	30.4		40.2	11.2	4.4
	F	31.2		40.1	10.9	4.2
$[PtI_2(P(C_6F_5)_3)_2]$	T	28.5		37.6	16.8	4.1
	F	28.4		37.8	15.9	4.0

Table 1.6 continued

		C	H	F	Hal	P
$[PdCl_2(P(C_6F_5)_3)_2]$	T	34.8	-	45.9	5.7	4.9
	F	34.8		45.3	5.1	5.0
$[PdBr_2(P(C_6F_5)_3)_2]$	T	32.5	-	42.8	12.0	4.6
	F	31.9		42.7	11.9	4.3
$[PdI_2(P(C_6F_5)_3)_2]$	T	30.3	-	40.0	17.8	4.8
	F	30.1		40.5	17.9	4.8
$[PtClPh(PMe_2Ph)P(C_6F_5)_3]$	T	39.3	1.6	29.3	3.6	6.3
	F	38.1	1.4	30.3	4.1	5.9

Part 3 Description of ^{19}F and ^{31}P NMR Spectra

1.3.1. NMR Spectra of Complexes Containing Trispentaflucrophenylphosphine - $P(C_6F_5)_3$.

Various metal complexes containing trispentafluorophenylphosphine were prepared by R.D.W. Kemmitt, D.I. Nichols, and R.D. Peacock[64, 65]. They reported that the ligand was a very weak base which did not protonate in concentrated sulphuric acid and exhibited no complex formation with boron trifluoride, even at 195K. This weak basicity is either the result of electron withdrawal from the phosphorus atom's lone pair by the pentafluorophenyl rings or the result of steric hindrance to the close approach of the proton.

The one surprising feature of this ligand is the comparative weakness of the phosphorus to metal bond. C.A. Tolman[68] showed that the nickel complex $[Ni(P(C_6F_5)_3)_4]$ was extensively dissociated in solution and that this ligand was unable to displace the other phosphine ligands examined from their complexes. Kemmitt et al[64] also reported the displacement of the trispentafluorophenylphosphine from its platinum complex by triphenylphosphine. These observations must reflect either a large steric effect which weakens the phosphorus-metal bond or greatly reduced sigma bonding with very little, if any, π-backbonding. This is contrary to what might be expected from Chatt's bonding proposal.

Kemmitt et al[65] observed temperature dependent NMR signals for the ortho-fluorines of $P(C_6F_5)_3$ in the trans-platinum (11) complexes and suggested that there was restricted rotation about the platinum-phosphorus bond and the carbon-phosphorus bonds but they did not investigate the complete nature of these effects. In this present study the variable temperature NMR of many different complexes containing $P(C_6F_5)_3$ was extensively examined.

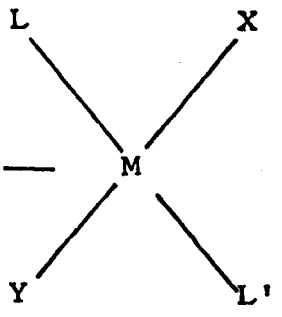
Table 1.7 is a compilation of complexes which have been studied in this work. The observations of similar changes in the NMR spectra of such ligands when complexed to different metals demonstrates that the features observed in the NMR spectra are general for complexes of this ligand and are not peculiar to any particular complex of the ligand.

In this study it was not possible to examine all the complexes in the same solvent because of solubility problems. Diagram 1.13 shows that although differences were observed when complex 1 (table 1.7) was examined using chloroform and acetone, the overall appearance of the spectra confirms that the spectra are essentially the same. When comparisons were made between complexes the same solvent was used as far as possible.

1.3.1(i) The Free Ligand

Each perfluorophenyl ring in the trispentafluorophosphine has three different fluorine environments

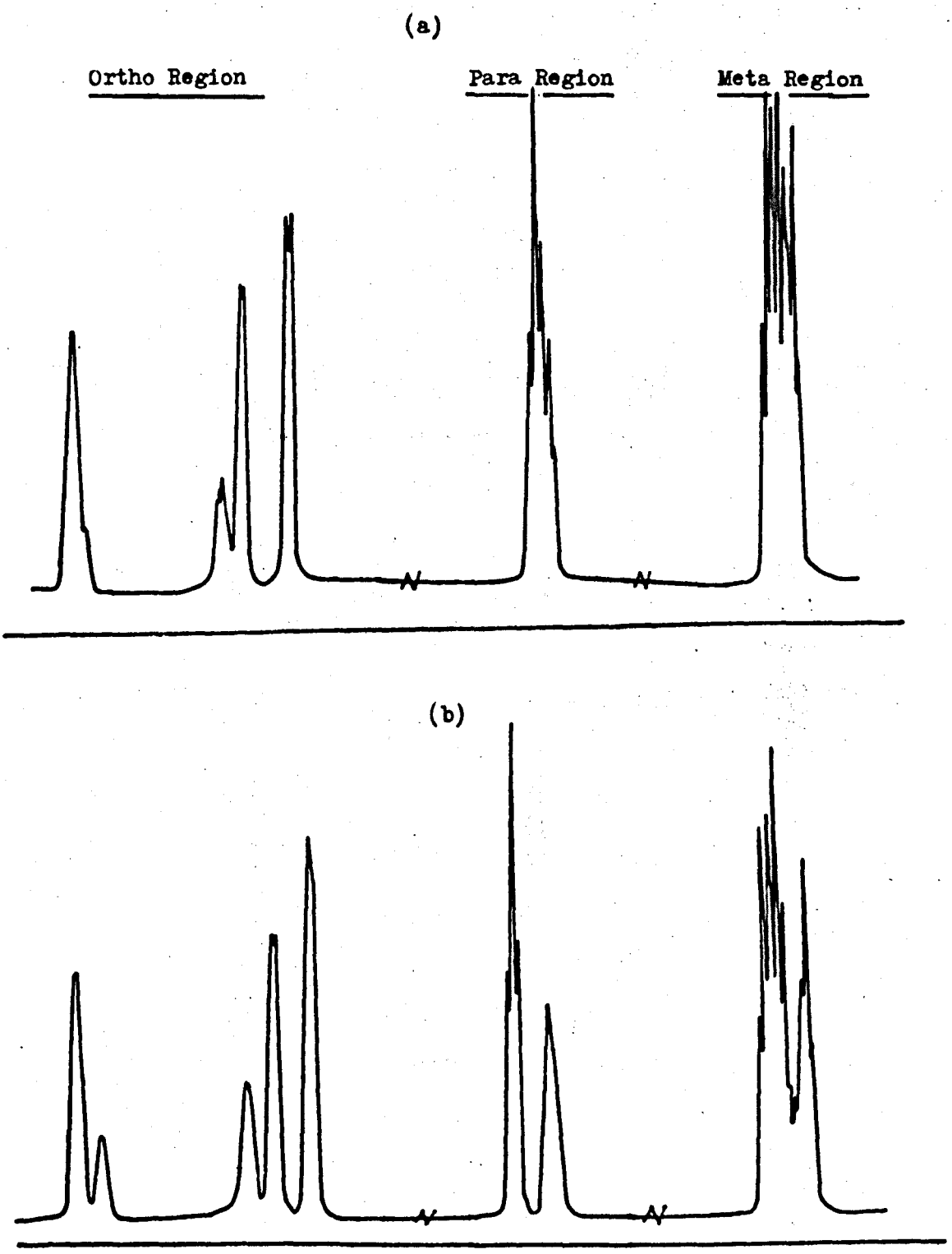
Table 1.7 Index of Complexes



Trans ; L = $P(C_6F_5)_3$

1. L' = $(C_6F_5)_3P$; X = Cl Y = Cl; M = Pt.
2. L' = $(C_6F_5)_3P$; X = Br; Y = Cl; M = Pt.
3. L' = $(C_6F_5)_3P$; X = I; Y = I; M = Pt.
4. L' = $(C_6F_5)_3P$; X = Cl; Y = Cl; M = Pd.
5. L' = $(C_6F_5)_3P$; X = Br; Y = Br; M = Pd.
6. L' = $(C_6F_5)_3P$; X = I; Y = I; M = Pd.
7. L' = $PhMe_2$; X = Br; Y = Br; M = Pt.
8. L' = $(C_6F_5)_3P$; X = Cl; Y = Cl; M = Pt.
9. L' = $PhMe_2$; X = Cl; Y = Ph; M = Pt.
10. L' = $(C_6F_5)_3P$; X = Cl; Y = CO; M = Rh.
11. L' = $(C_6F_5)_3P$; X = Cl; Y = CO; M = Ir.

Diagram 1.13 ^{19}F NMR of Trans-$[PtCl_2(P(C_6F_5)_3)_2]$ at 213K in (a) Acetone and (b) Chloroform.



which consist of the ortho-, the meta-, and the para-fluorine atoms. The chemical shifts of these aromatic fluorine nuclei occur over approximately 80 ppm and so the fluorine environments are well resolved; ortho ∿ - 130.5 ppm; Para ∿ - 148.1 ppm; meta ∿ - 160.0 ppm.

In the fluorine - 19 NMR spectrum of the free ligand $P(C_6F_5)_3$ the ortho signal is a triplet due to coupling with the two meta - fluorine atoms. The meta - signal is a triplet of doublets due to coupling with the two ortho-fluorine atoms and the para-fluorine atom. The para-signal is a triplet of triplets resulting from the coupling of the para-fluorine atom with the two ortho-fluorine atoms and the two meta-fluorine atoms. The solvent used was chloroform. The ortho-signal was further downfield than the para-signal which was in turn further downfield than the meta-signal (Table 1.8). The signals are easily distinquished because of their relative intensities. The ortho- and meta signals being twice as intense as the para-signal.

1.3.1(ii) Trans-$[PtX_2(P(C_6F_5)_3)_2]$ where x = Cl, Br, I

At 333K the fluorine-19 and phosphorus-31 NMR spectra of the dibromide complex contained the following signals. The fluorine spectrum contained ortho-, meta-, and para-fluorine signals. The ortho signal was a broad singlet while the para - and meta-signals were triplets. The phosphorus-NMR of the platinum diiodide complex contained one

large signal, due to the two equivalent phosphorus atoms and two smaller signals resulting from the coupling of the phosphorus nuclei with the platinum-195 nuclei. These smaller signals are known as platinum satallites. Platinum-195 is only 32% abundant and is the only magnetic platinum isotope therefore only 32% of the platinum atoms will couple. (see diagrams 1.14 and 1.15).

All the NMR signals observed for the complexes were shifted downfield from the corresponding free ligand absorptions.

In the fluorine spectrum of the dichloride complex at ambient temperatures, $\sim$ 298K, the ortho-signal was very broad, between -143ppm and -145ppm. The para- and meta-signals although still triplets had broadened. At 253K there were three broad signals in the ortho-fluorine region. The para-signal had separated to give two broad signals with apparent intensities of 2:1. The meta-signal at this temperature was a broad singlet (Table 1.8). The ortho-region at 213K was made up of five signals. The signal at -130 ppm was considered to contain two overlapping signals because of the shoulder on the downfield side of the signal (diagram 1.14). Altogether the spectrum showed the presence of six ortho-fluorine environments. There appeared to be two sets of three ortho-signals. The ratio of intensities of the sets of signals was 3:1. The para-region contained two triplets with the signal

at - 141.5 ppm being twice as intense as that at -143 ppm. The meta-region consisted of three overlapping triplets (diagram 1.14).

The phosphorus NMR also broadened on cooling. At 213K the spectrum had resolved to give two signals, each with corresponding platinum satallites. In chloroform the ratio of the signals was 3:1 but when the solvent was acetone the ratio was approximately 6:1.

The chemical shifts and coupling constants obtained from the NMR spectra, both fluorine and phosphorus, have been recorded in table 1.8 and 1.9. The phosphorus spectra were fluorine decoupled.

The fluorine 19 and phosphorus-31 NMR spectra of the dichloride, the dibromide and the diiodide complexes behaved similarily on lowering of the temperature. The temperature required for resolution of the spectra was usually higher for the dibromide than the dichloride and even higher for the diiodide e.g. the three ortho-signals were seen in the dichloride, dibromide, and diiodide spectra at 213K, 253K, and 298K respectively.

The range of chemical shifts in the fluorine spectra at the low temperatures was slightly larger for the diiodide and dibromide than the dichloride, i.e. 42.5 ppm, 40.5 ppm and 38.9 ppm.

It is interesting to note that the phosphorus to platinum coupling constants for the major signals were smaller than those of the minor signals and that the

Diagram 1.14 ^{19}F NMR of Trans $[PtBr_2(P(C_6F_5)_3)_2]$

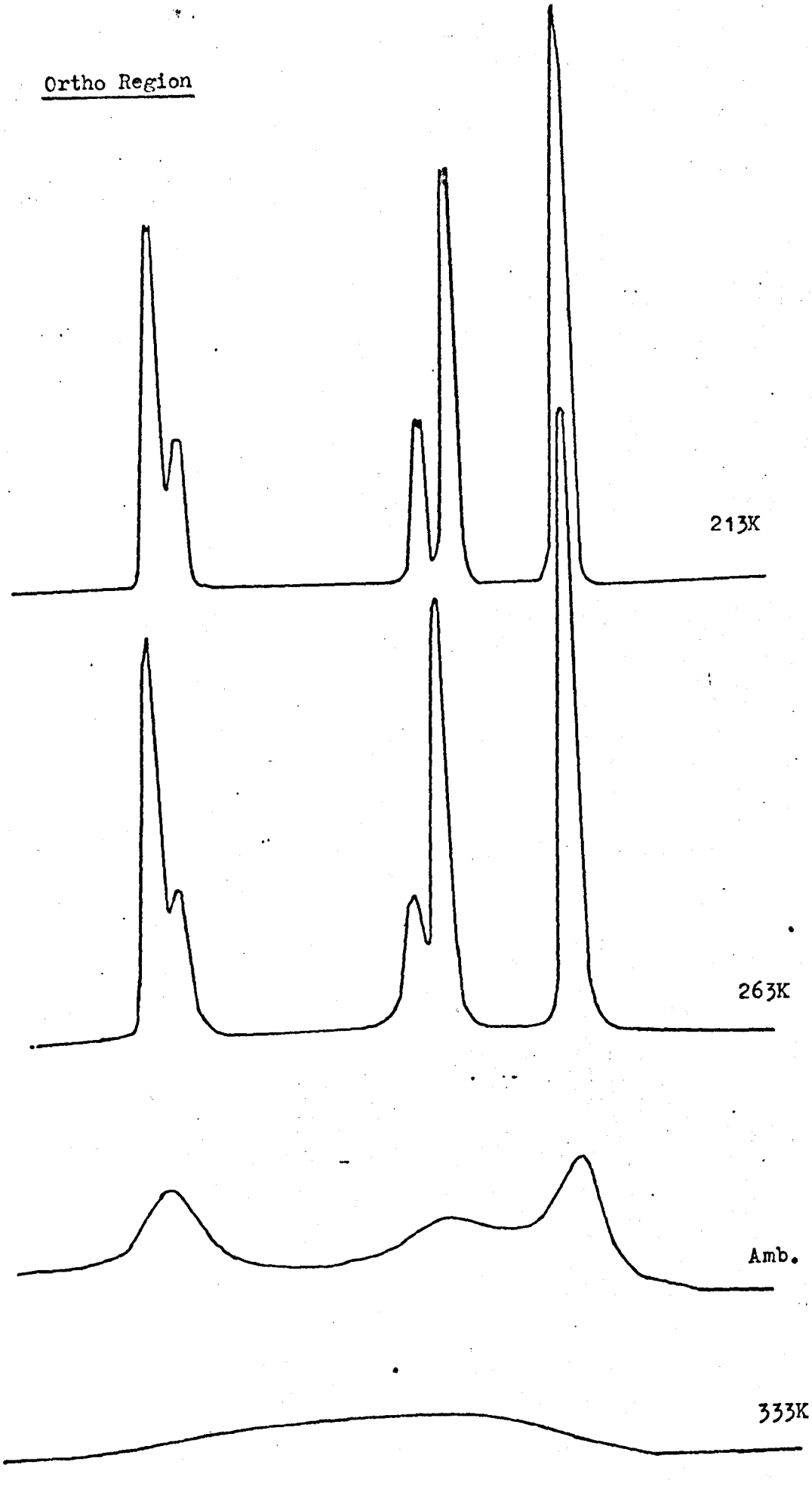


Diagram 1.14 ^{19}F NMR of Trans-$[PtBr_2(P(C_6F_5)_3)_2]$ (Cont)

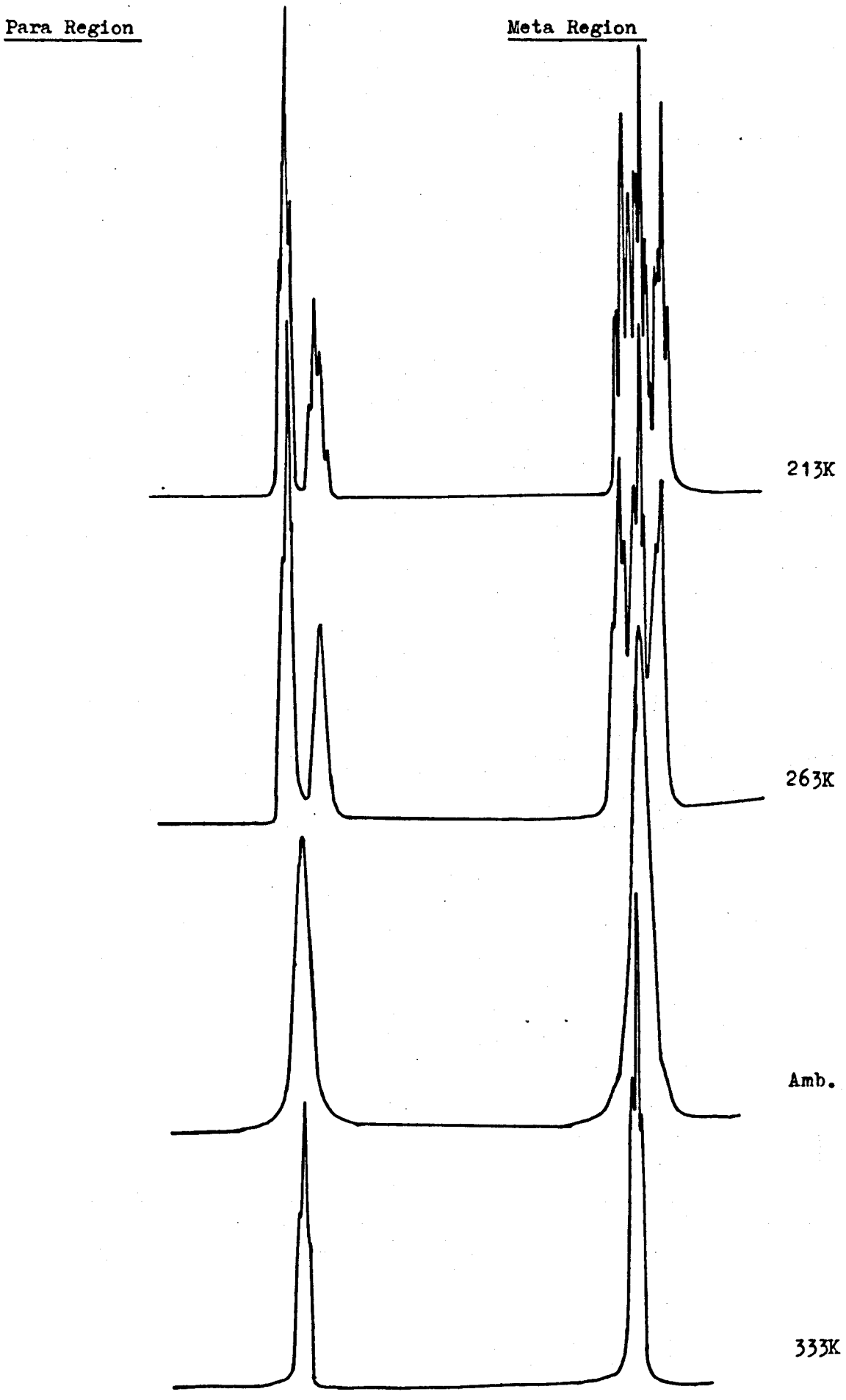
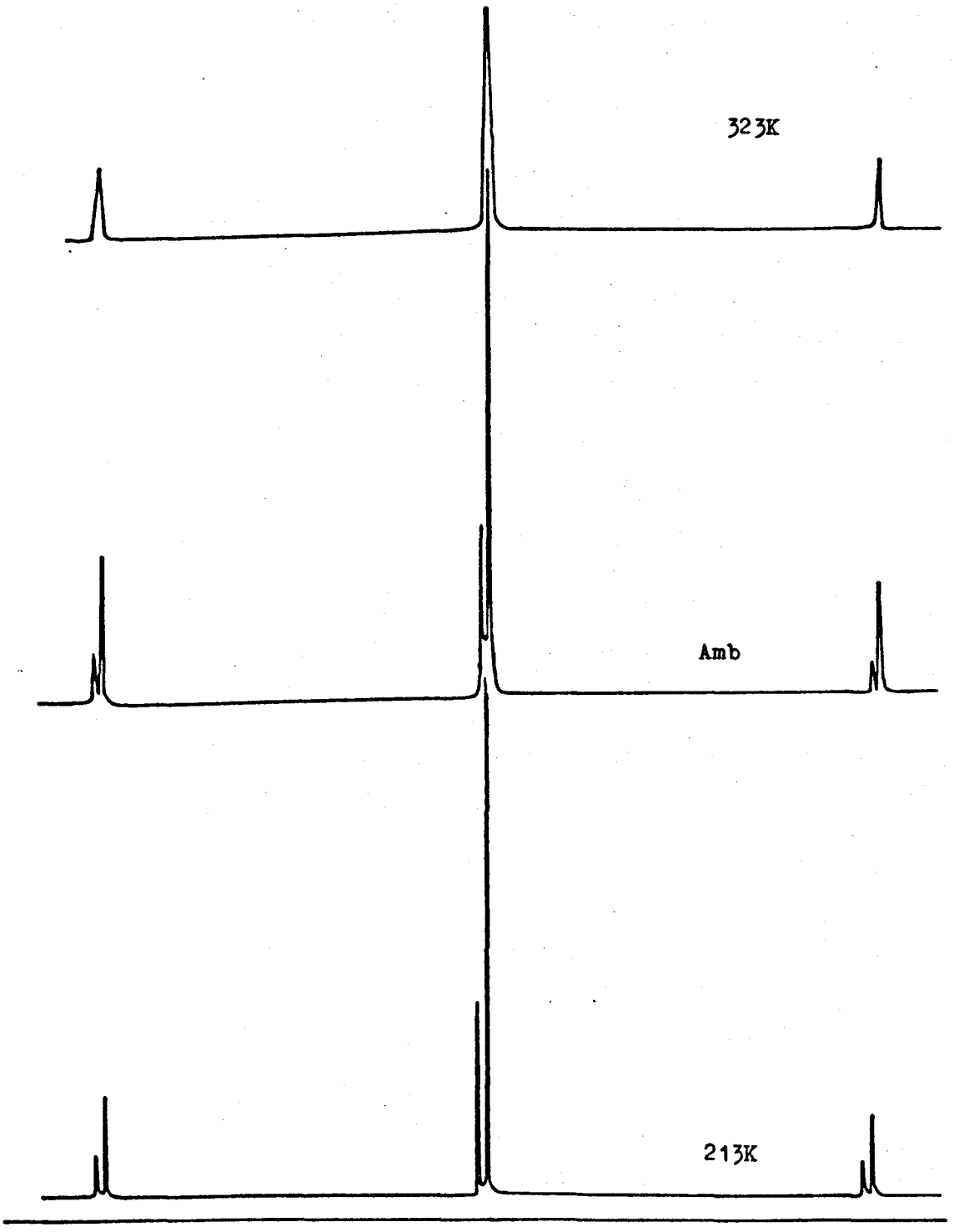


Diagram 1.15 ^{31}P NMR of Trans-$[PtI_2(P(C_6F_5)_3)_2]$



coupling constants decreased when the temperature was lowered.

1.3.1 (iii) Trans-$[Pd\ X_2\ (P(C_6F_5)_3)_2]$ X = Cl, Br, I

The palladium complexes exhibited similar behaviour to the platinum complexes. One significant difference in the NMR spectra of the palladium dichloride was that the meta- and para- signals, although broadened, remained unresolved even at 213K. The ortho-signal did divide to give three ortho signals when the temperature was lowered. The overall chemical shift range for the palladium dichloride complexed in acetone was ∿40.2 ppm which is similar to that of the platinum dichloride complex in acetone i.e. 49 ppm. The palladium complexes did not resolve to give two sets of three ortho-fluorine signals even at 213K. (See diagram 1.16).

The phosphorus NMR of the palladium dichloride complex in acetone at ambient temperature contained two signals in the ratio of 10:1. These signals sharpened when the temperature was lowered to 223K. They coalesced when the temperature was raised to 328K. (Diagram 1.17)

1.3.1 (iv) Trans-$[PtX_2(L)P(C_6F_5)_3]$ and Trans-$[Pt\ X_2(L^1)P(C_6F_5)_3]$. L=$PhMe_2$, x = Br and $L^1=P(C_6H_5)_3$, X=Cl

The fluorine-19 NMR spectra of these complexes exhibited broadening and eventual resolution of the ortho, meta and para fluorine signals when the temperature was lowered from 333K to 208K. At 208K the spectra

Diagram1.16 ^{19}F NMR of Trans -[$PdCl_2(P(C_6F_5)_3)_2$]

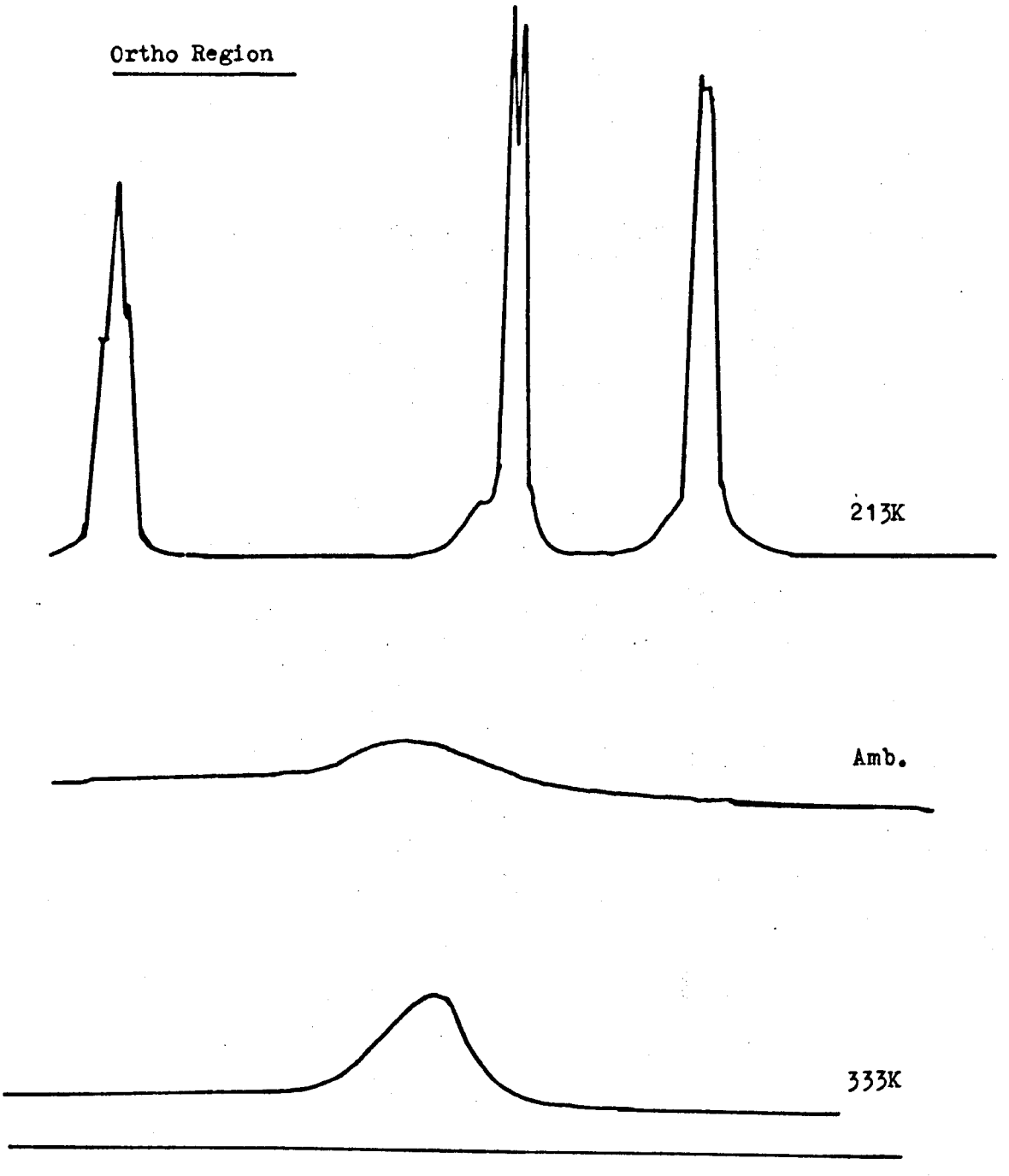


Diagram 1.16 ^{19}F NMR of Trans-[$PdCl_2(P(C_6F_5)_3)_2$]
(Cont)

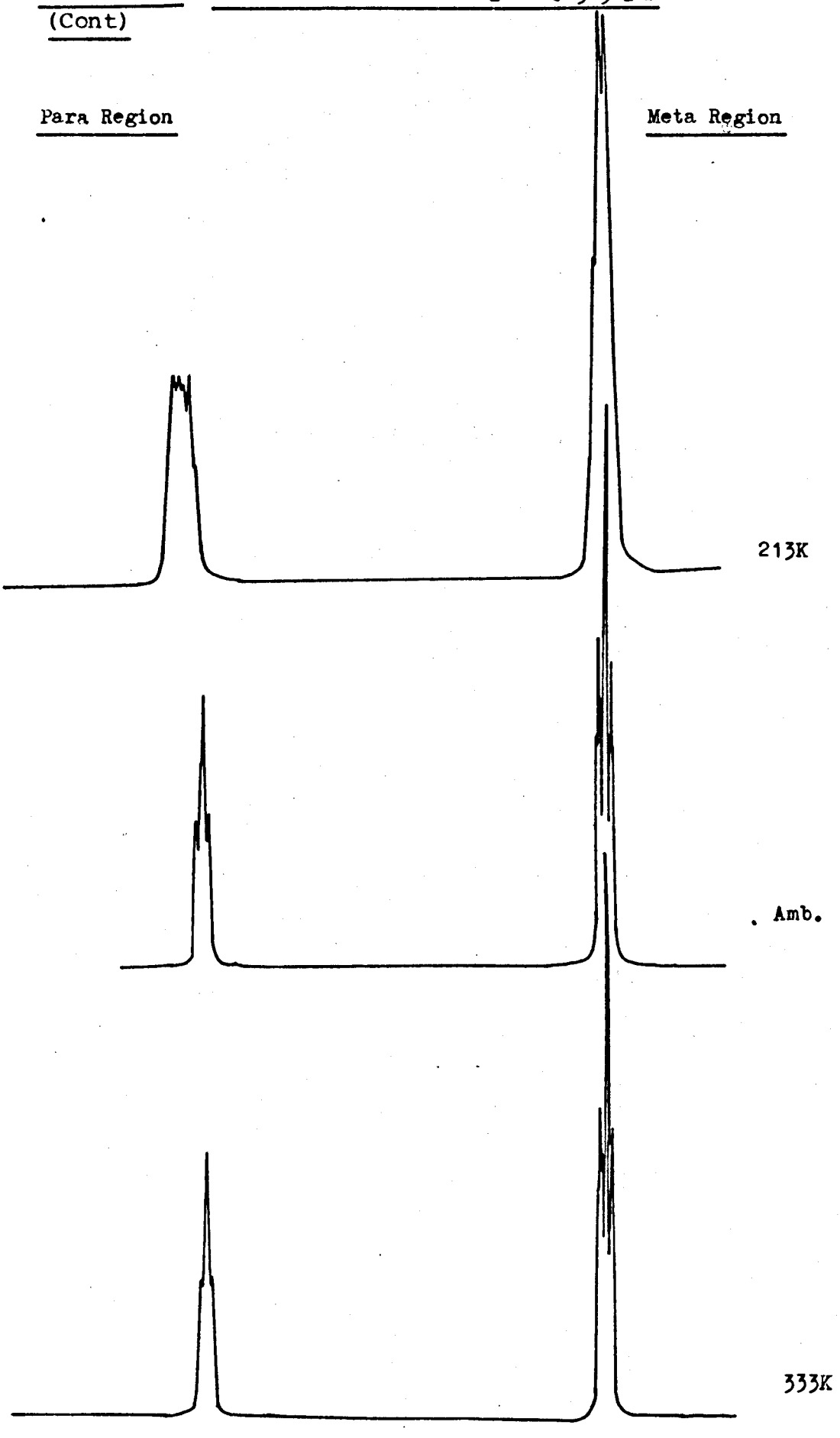
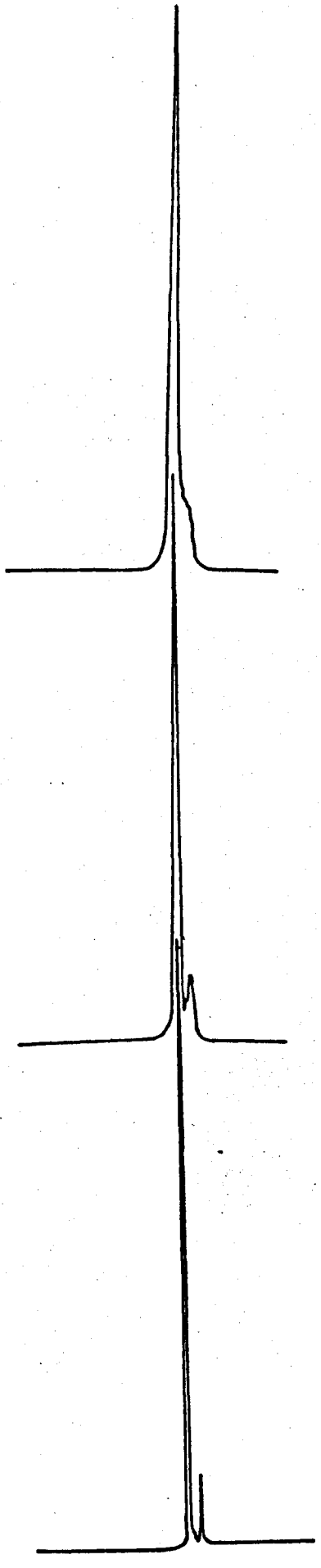


Diagram 1.17 ^{31}P NMR of Trans-$[PdCl_2(P(C_6F_5)_3)_2]$



contained three ortho signals with intensities 2:2:2, two para signals with intensities 2:1 and three meta signals intensities 2:2:2 (Table 1.10).

The phosphorus NMR spectra of these complexes were ABX type spectra (see appendix A) and showed second order splitting. Calculation of chemical shifts and coupling constants was carried out using the conventional methods described in appendix A.

The dibromide complex had sharper signals and was therefore better resolved than the dichloride but both complexes gave essentially the same spectra as those observed for complexes 1-4. (Diagram 1.18).

Relative assignment of fluorine signals in <u>trans</u> $[PtX_2(L)\ P(P_6F_5)_3]$ was made by homonuclear selective irradiation. This technique is a refinement of double resonance or decoupling techniques. It was possible by this method to relate the <u>ortho</u>, <u>meta</u> and <u>para</u> signals which correspond to fluorine atoms on the same aryl ring. The underlying principal is that although coupling between the <u>ortho</u>-, <u>meta</u>- and <u>para</u>- fluorines is not observed in the spectrum it is still occurring, removal of this coupling should affect the signal. Diagram 1.19 is a schematic drawing of the fluorine spectrum of the above complex at 208K. The signals have been labelled A-H with A being the signal furthest downfield. The sample was bathed in radiation in the frequency range $\nu_f - \nu_h$ which resulted in the

Diagram 118 ^{19}F NMR of Trans $[PtBr_2(PMe_2Ph)P(C_6F_5)_3]$

Ortho Region

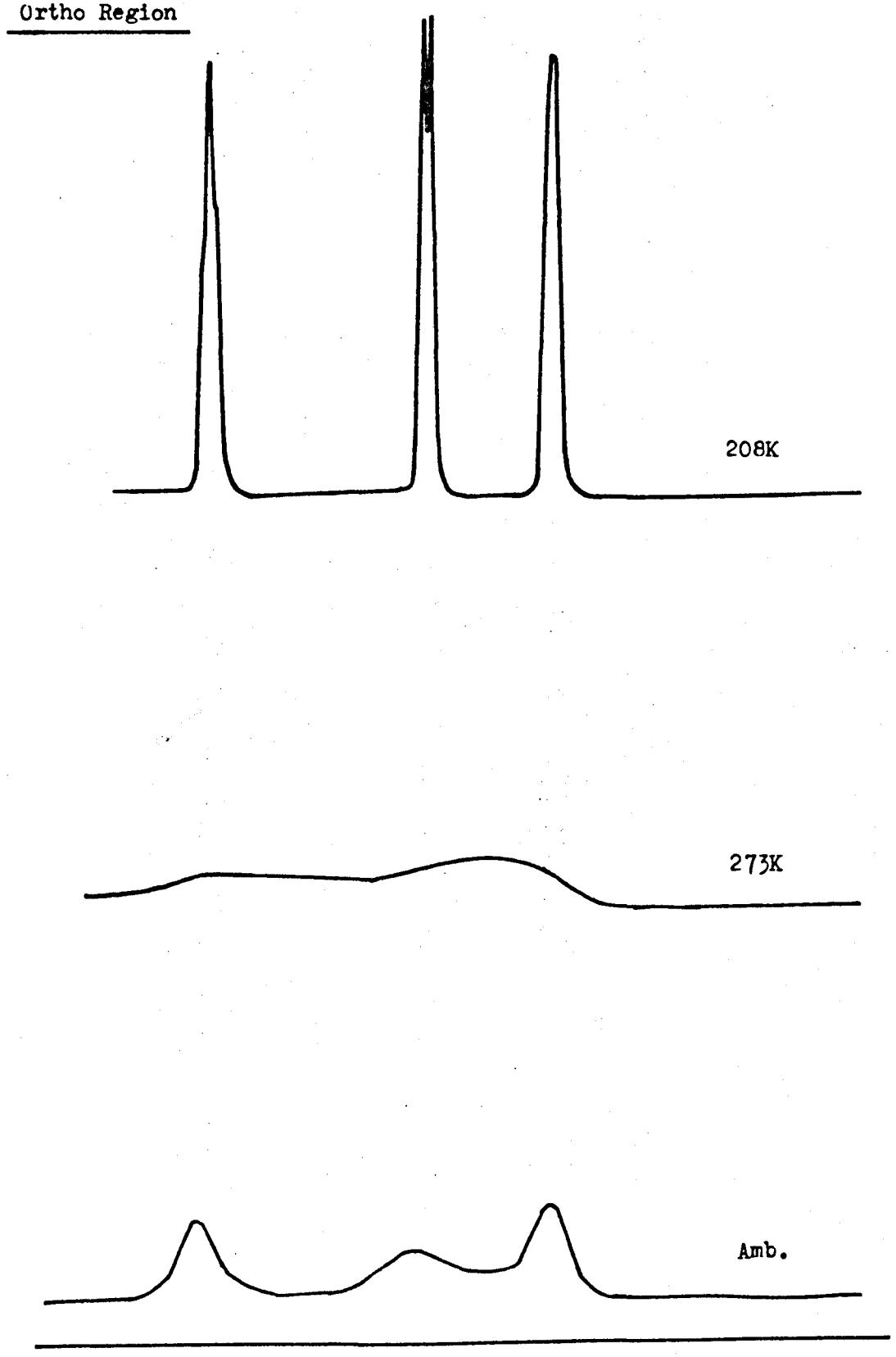


Diagram 1.18 ^{19}F NMR of Trans-$[PtBr_2(PMe_2Ph)P(C_6F_5)_3]$

(Cont)

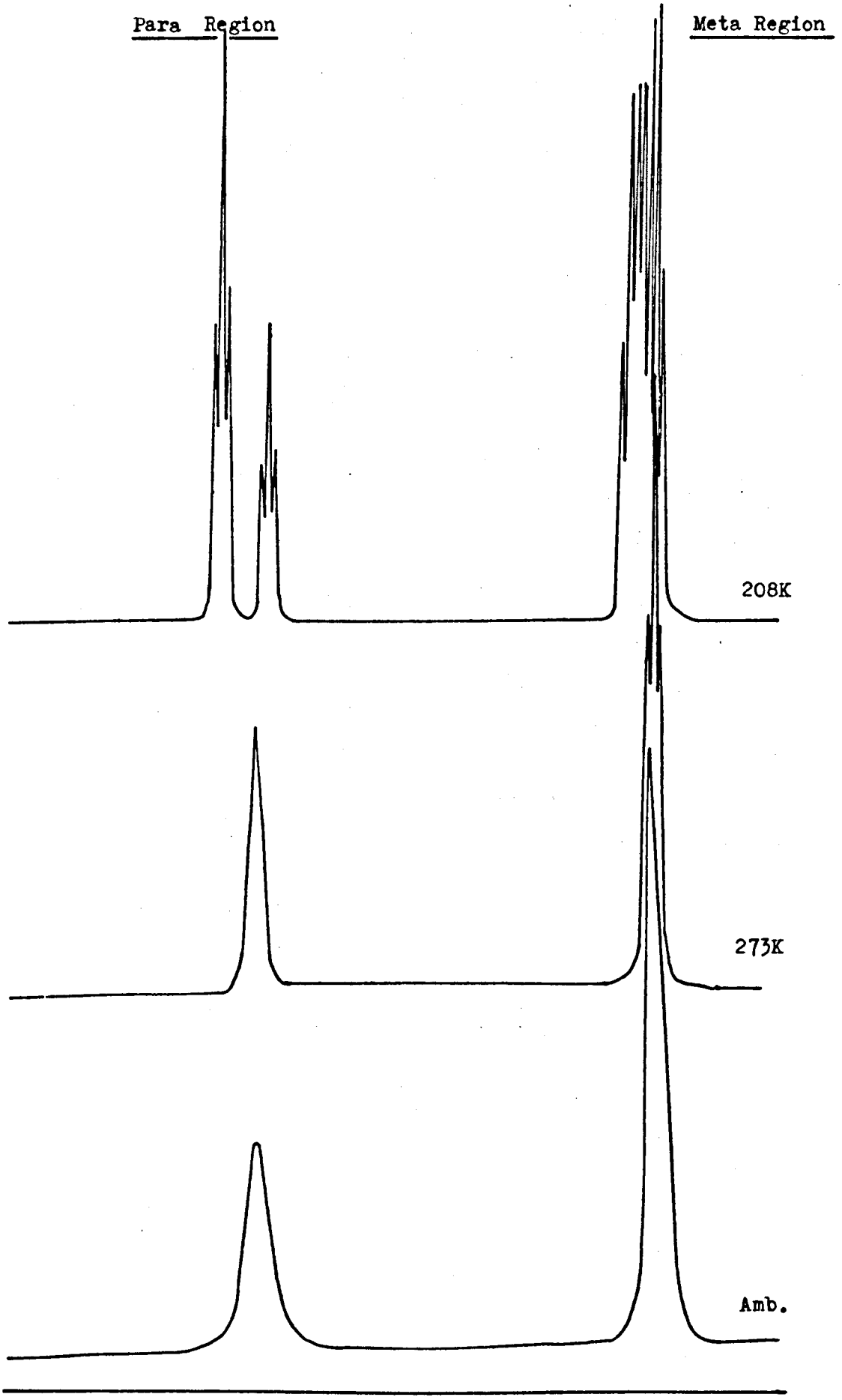
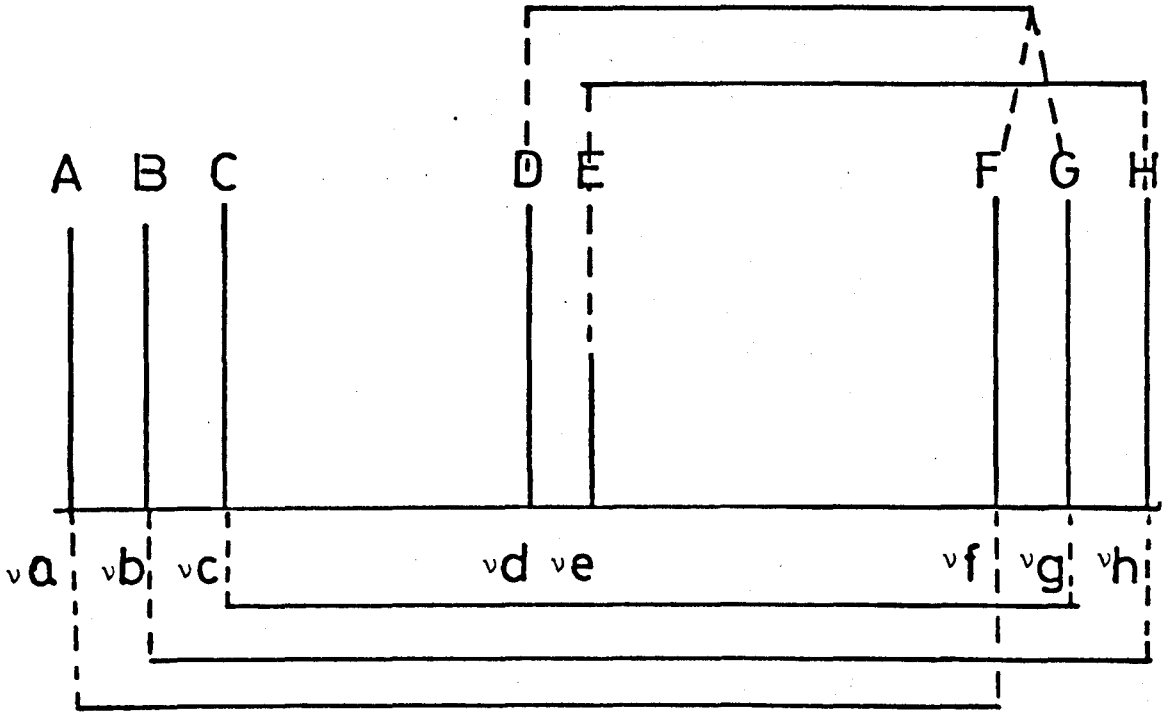


Diagram 1.19



spectrometer monitoring the meta-region. Application of a radiofrequency field of frequency ν_d was seen to broaden the signals F and G. Therefore it was concluded that signals D, F and G were related. Similarly it was shown which of the other signals were related. Assignment of the phosphorus signals to the phosphorus atoms with fluorinated substituents and the phosphorus atoms with protonated substituents was carried out by fluorine and proton decoupling experiments.

1.3.1 (v) Trans-[Pt Cl (Ph) ($P(C_6F_5)_3$) ($P PhMe_2$)]

The fluorine-19 NMR spectrum of this complex at ambient temperature contained the usual three fluorine environments. The signals showed the expected broadening and eventual sharpening with decreasing temperature.

The ortho region at 253K consisted of two broad signals and a very broad hump.(Diagram 1.20.) The para region at this temperature had two signals, the most intense signal being further upfield, which is the reverse of what is seen for the other complexes. The meta region contained two broad signals.

On cooling the sample to 223K the ortho-region resolved to give two fairly sharp singlets and four broad signals. The para region now contained one sharp triplet and one broad singlet. The meta-signals consisted of one triplet and a number of broad overlapping signals.

Diagram 1.20 ^{19}F NMR of Trans-[$PtClPh(PMe_2Ph)P(C_6F_5)_3$]

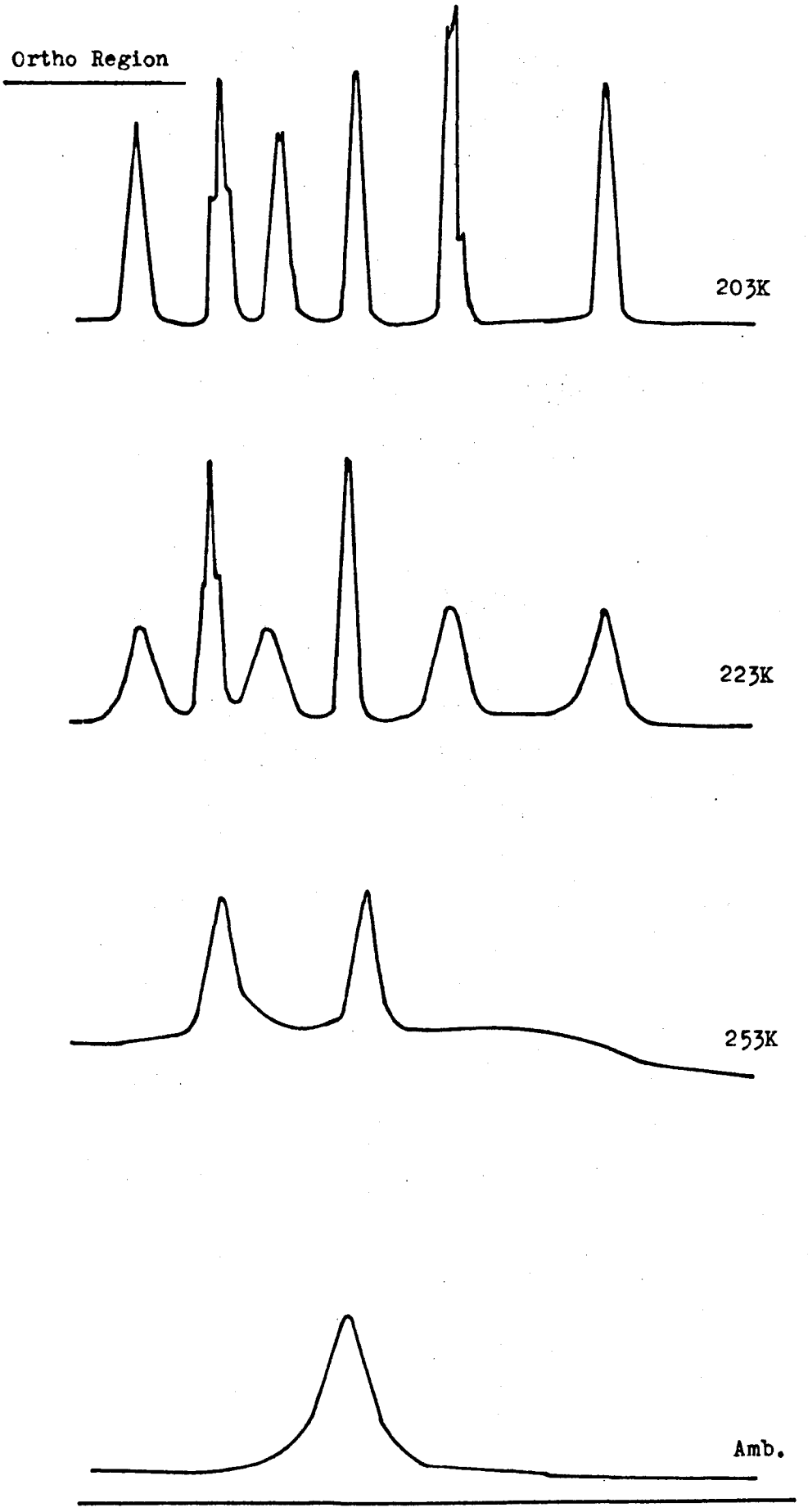
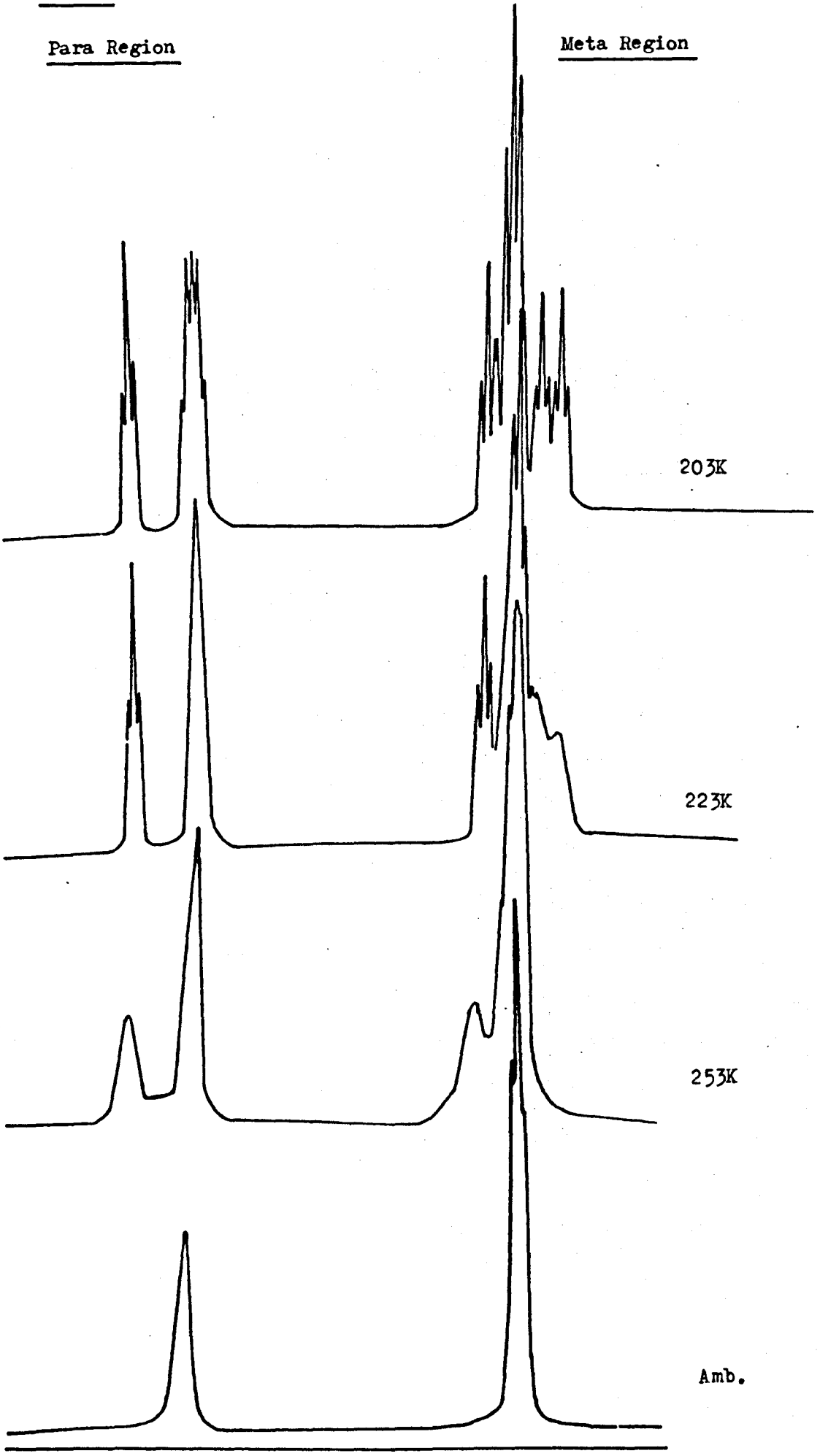


Diagram 1.20 ^{19}F NMR of Trans-[$PtClPh(PMe_2Ph)P(C_6F_5)_3$]

(Cont)



At 203K the original ortho-signal had divided to give six signals which were singlets of equal intensity. The para-region contained three triplets two of which overlapped. Six overlapping triplets made up the meta-region of the spectrum. At this temperature all the signals were of equal intensity (Diagram1.20). The phosphorus spectrum was an ABX type spectrum and was analysed according to the methods described in Appendix A. The spectrum was essentially made up of two phosphorus signals with associated satallites and phosphorus to phosphorus coupling. The signals were assigned by fluorine and phosphorus decoupling experiments. The coupling constant, J(Pt-P), for the co-ordinated trispentafluorophenylphosphine was found to be lower than J(Pt-P) for the dimethylphenylphosphine. A definite decrease in the coupling constants, J(Pt-P) and J(P-P), was observed when the temperature was lowered.

1.3.1(vi) Trans-[$MCl(CO)(P(C_6F_5)_3)_2$], M = Rh, Ir

The fluorine-19 and phosphorus-31 NMR spectra of the rhodium and iridium complexes dissolved in acetone showed similar trends to that of trans-[$PtCl(Ph)(P(C_6F_5)_3)(P\,PhMe_2)$]. At 178K the ortho region contained six signals, the para region had three triplets, and the meta region had six overlapping signals. Resolution in the spectra of the rhodium and iridium complexes was much poorer than in the spectrum of the platinum complex. The temperature needed to obtain

Diagram 21 ^{19}F NMR of Trans-[$RhCl(CC)(P(C_6F_5)_3)_2$] (Cont)

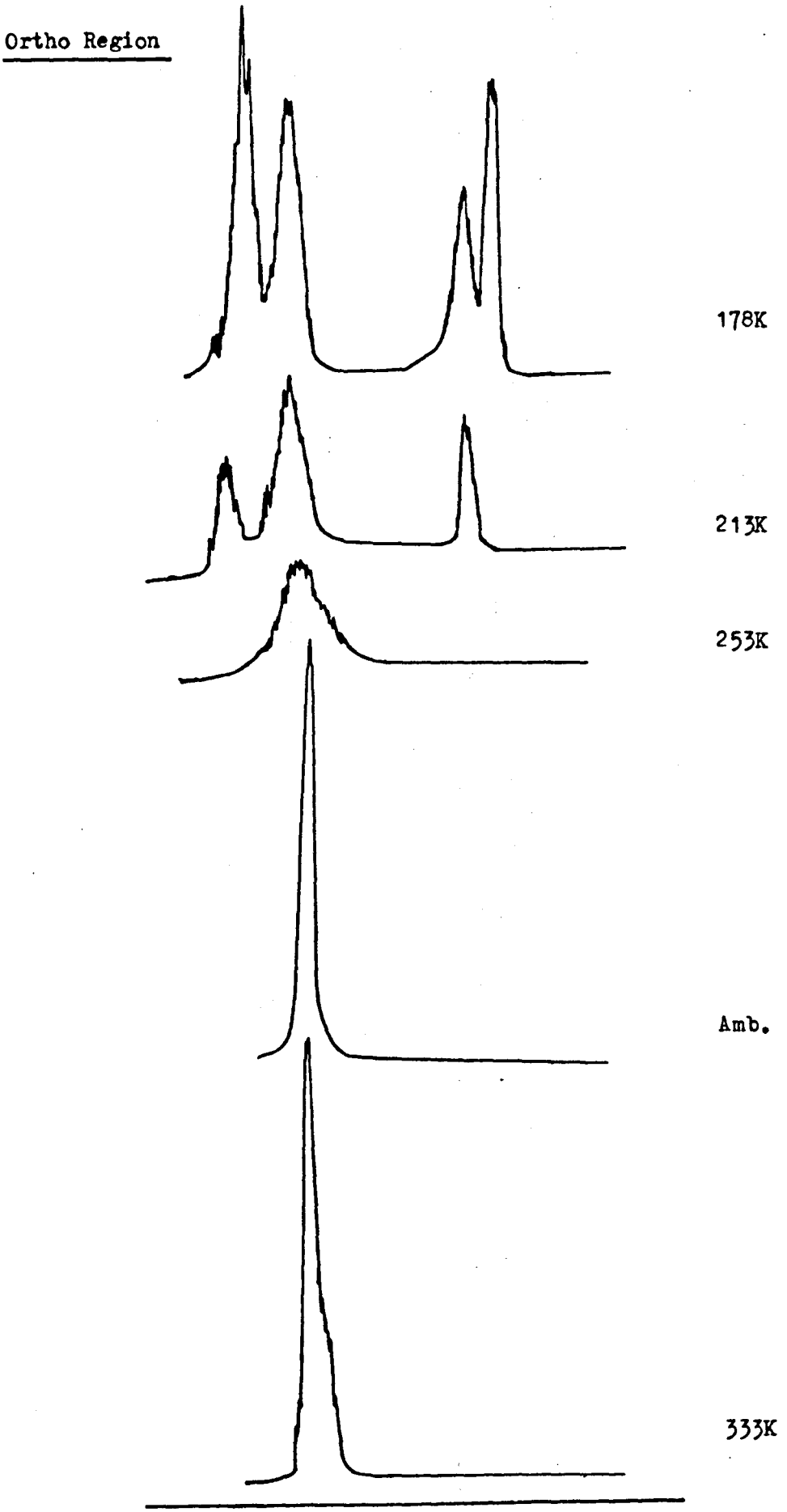


Diagram 121 ^{19}F NMR of Trans-$[RhCl(CO)(P(C_6F_5)_3)_2]$ (cont)

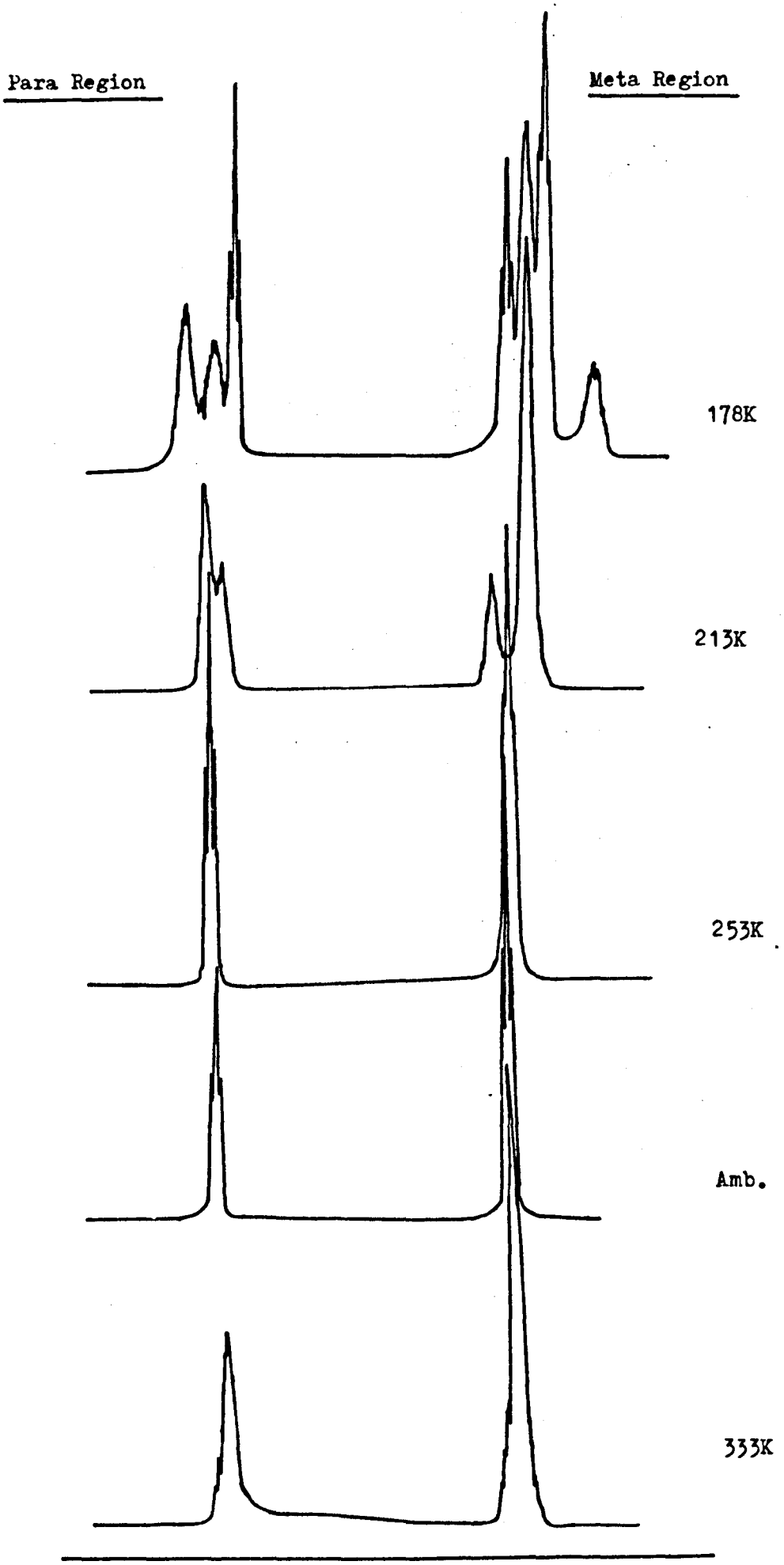


Diagram 1.22 ^{19}F NMR of Trans-[$IrCl(CO)(P(C_6F_5)_3)_2$]

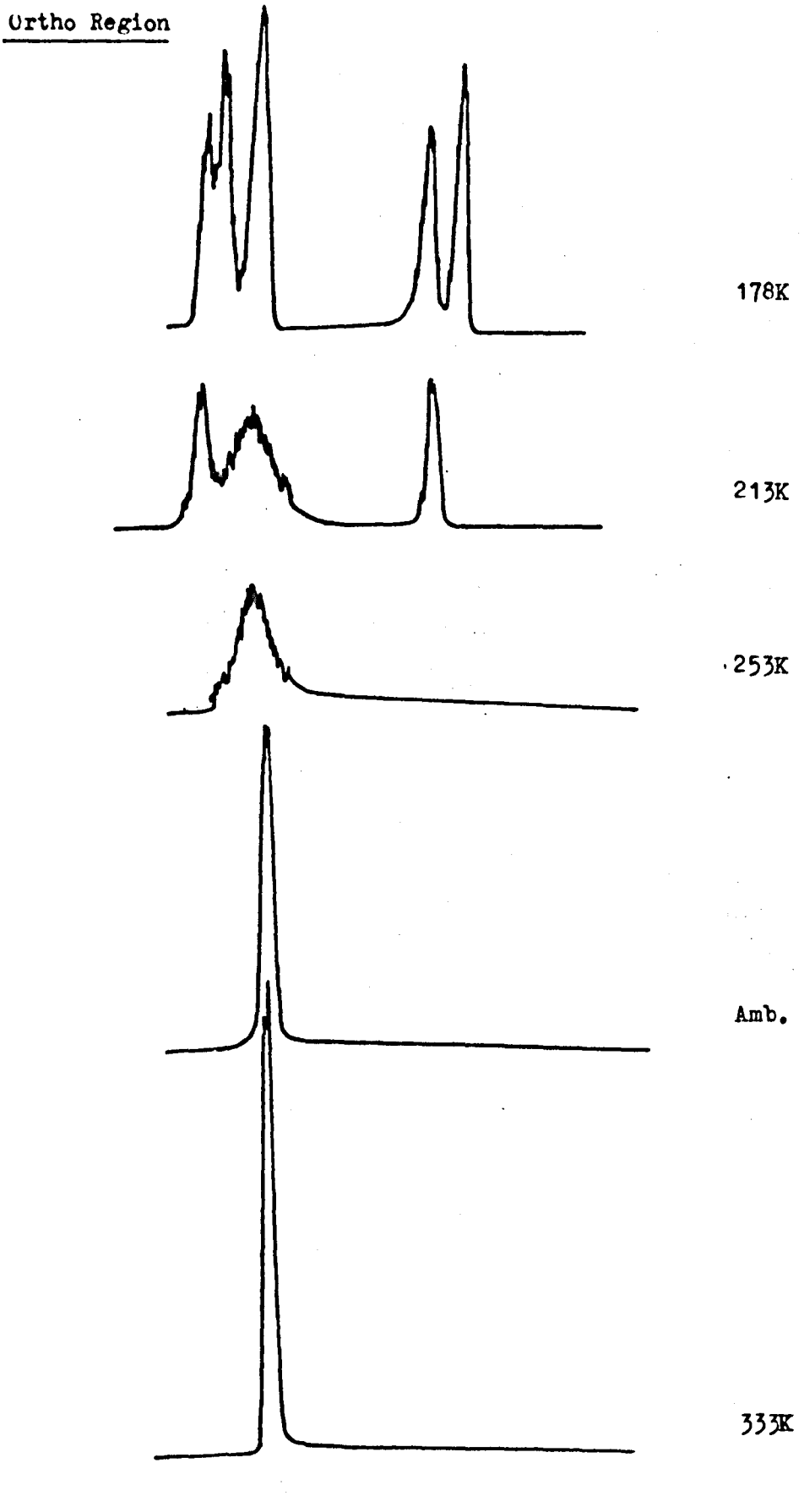
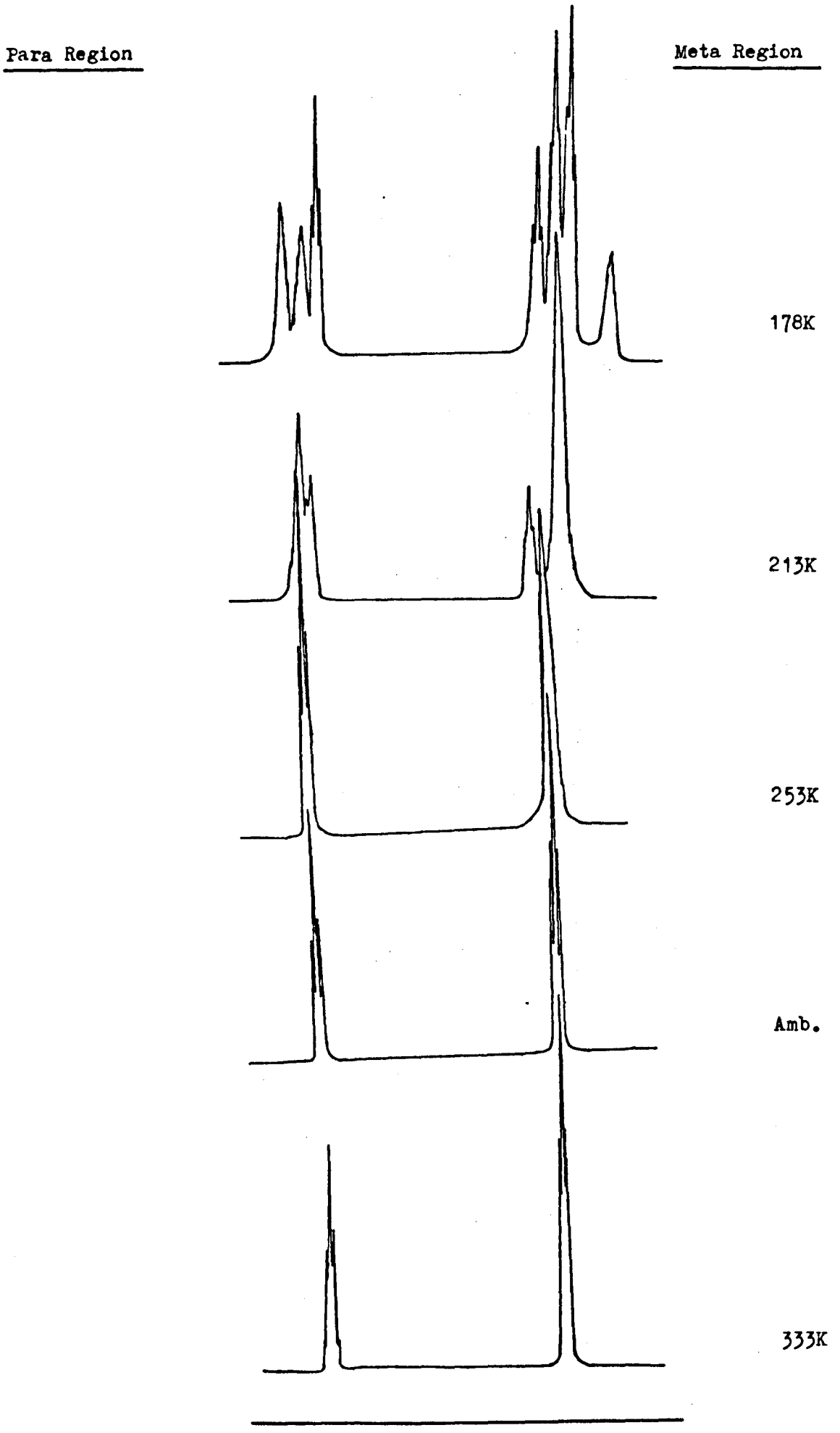


Diagram 1.22 ^{19}F NMR of Trans-$[IrCl(CO)(P(C_6F_5)_3)_2]$



reasonable resolution with the rhodium and iridium complex was 178K whilst with the platinum complex, excellent resolution was obtained at 203K. The ortho signals did not split further to give the two sets of signals as was observed in complexes trans $[PtX_2(P(C_6F_5)_3)_2.]$ (See diagrams 1.21 and 1.22).

The fluorine-NMR spectrum of the rhodium complex exhibited reversible broadening when the sample was heated from ambient to 333K. This broadening was unique to rhodium complex. (Diagram 1.21).

The phosphorus NMR spectrum of the rhodium complex in acetone contained a doublet due to rhodium to phosphorus coupling. The iridium complex in acetone had only one phosphorus signal. No broadening was observed in either spectra when the temperature was lowered.

The phosphorus-31 NMR spectrum obtained when trans-$[RhCl(CO)(P(C_6F_5)_3)_2]$ was dissolved in chloroform contained two doublets, the intensities of which were about 1:2. The sample was left in the NMR tube for twenty-four hours and the ratio of the signals was now 1:4. After a further twenty-four hours the spectrum contained only one set of doublets. The assignment of the signals is discussed in Part 4. (Diagram 1.23).

The iridium complex was insoluble in chloroform.

1.3.2 Rotation of Bonds

Bond rotation in a molecule leads to substituents adopting certain energetically favoured positions e.g.

Diagram 1.23 ^{31}P NMR of Trans-[RhCl(CO)(P(C_6F_5)$_3$)$_2$] In Chloroform

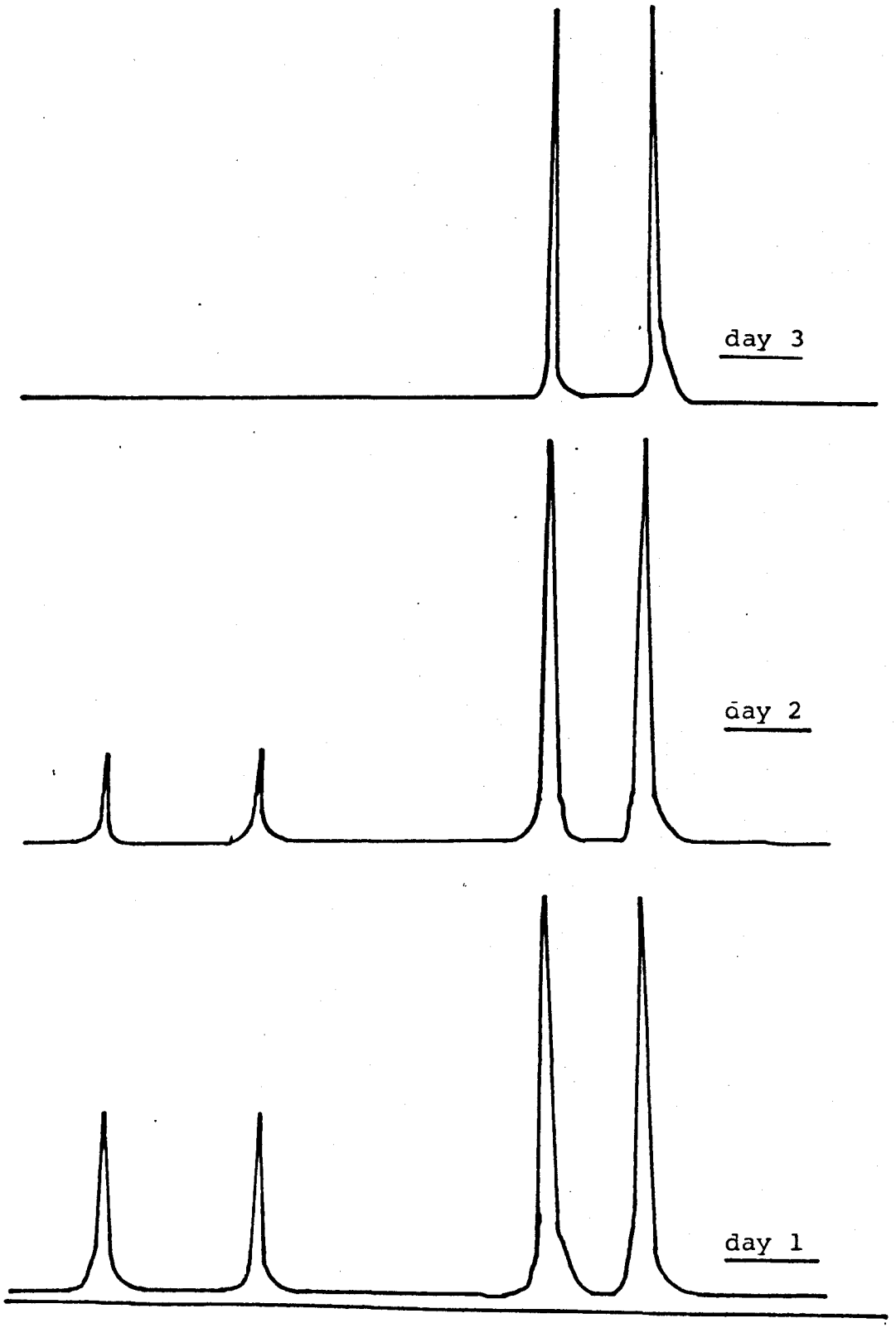


Table 1.8 ^{19}F Chemical Shifts (ppm)

Complex (solvent)		$\delta\ ^{19}F$			Temp (K)
	Isomer	Ortho	Meta	Para	
1		-125.7 br	-158.8 sh	-143.8 sh	333
($CDCl_3$)		V. br	-158.8 sh	-143.4 sh	Amb
		3 br sign	-157.9 br	2 br sign	253
	Major	-119.7	-156.5	-141.5	213
		-130.0	-157.1		
		-128.4	-158.3	-143.0	
	Minor	-120.8			
		-130.0			
		-127.2			
2		br sign	-159.0 sh	-144.2 sh	333
($CDCl_3$)		3 br sign	-158.8 br	-143.8 br	Amb
	Major	-117.9		-142.2	253
		-130.4			
		-126.6		-144.3	
	Minor	-118.6			
		-130.4			
		-125.7			
	Major	-118.0	-156.8	-142.6	213
		-130.2	-157.2		
		-126.9	-158.6	-143.3	
	Minor	-118.7			
		-130.2			
		-125.9			

Table 18 continued

Complex		δ ^{19}F (ppm)			Temp(K)
	Isomer	Ortho	Meta	Para	
2	Major	-118.0	-156.8	-142.6	213
(cont)		-130.2	-157.2		
		-126.9	-158.6	-143.3	
	Minor	-118.7			
		-130.2			
		-125.9			
3		v br sign	-158.9 sh	-144.5 br	333
($CDCl_3$)		-114.9 br	-158.8 br	-144.1 br	Amb
		-130.5 br			
		-115.3 br			
	Major	-115.4	-157.2	-143.0	253
		-130.4	-158.2		
		-123.8	-159.1	-144.3	
	Minor	-115.4			
		-130.4			
		-123.2			
	Major	-115.5	-156.6	-142.3	213
		-130.3	-157.9		
		-124.2	-158.4	-143.4	
	Minor	-115.8			
		-130.3			
		-123.5			

Table1.8continued

Complex (solvent)	$\delta^{19}F$ (ppm)			Temp(°K)
Isomer	Ortho	Meta	Para	
4	-125.0 br	-160.4 sh	-145.2 sh	333
($(CD_3)_2CO$)	v br	-160.3 sh	-145.0 sh	Amb
	-119.5	-159.7 br	-143.8 br	213
	-131.2			
	-127.5			
Free ligand	-130.4	-160.8	-148.1	Amb

Table 1.9 ^{31}P NMR Chemical Shifts (ppm) and Coupling Constants (Hz)

Complex	$\delta^{31}P$		J(P-Pt)		Temp (K)
(solvent)	Major	Minor	Major	Minor	
1	-26.2	-	3131	-	Amb
($CDCl_3$)	-26.7	-	3086	-	213
	-26.8	-26.2	3073	3081	193
2	-30.3	-	3041	-	Amb
($CDCl_3$)	-30.5	-29.9	3023	3024	253
	-30.7	-29.7	3007	3010	213
	-30.7	-30.0	2996	3001	193
3	-42.1	-	2995	-	323
($CDCl_3$)	-42.3	-41.5	2987	2988	Amb
	-42.3	-41.5	2956	2955	213
Free ligand ($CDCl_3$)	-74.9	-	-	-	Amb
1	-26.2	-	3118	-	Amb
($(CD_3)_2CO$)	-26.9	-26.2	3070	3083	193
4	-22.7	-	-	-	328
($(CD_3)_2CO$)	-21.9	-22.9	-	-	Amb
	-21.4	-22.4	-	-	223
	-21.3	-22.3	-	-	203
5	-23.9	-	-	-	Amb
($(CD_3)_2CO$)	-24.3	-	-	-	203

Table 19 continued

Complex	$\delta^{31}P$		J(P-Pt)		Temp (K)
(solvent)	Major	Minor	Major	Minor	
6	-24.7	-	-	-	Amb
$((CD_3)_2CO)$	-24.9	-	-	-	203

Table 1.10 ^{19}F NMR Chemical Shifts (ppm)

Complex (solvent)	$\delta^{19}F$ Ortho	Meta	Para	Temp (K)
7	-119.1	-157.6	-143.5	208
($CDCl_3$)	-130.0	-158.0		
	-126.0	-158.5	-145.1	
8	-120.4	-157.5	-143.4	208
($CDCl_3$)	-130.0	-158.1		
	-127.4	-158.7	-145.2	
9	-125.2br	-158.4	-145.0	273
($CDCl_3$)	-120.9br	-156.6br	-142.6br	253
	-118.6	-156.0	-142.0	203
	-121.2	-156.6	-144.0	
	-123.0	-156.9	-144.6	
	-125.4	-157.2		
	-128.3	-158.1		
	-133.1	-158.9		
10	-126.4br	-160.6br	-146.9br	333
($(CD_3)_2CO$)	-126.6sh	-160.5sh	-146.6sh	Amb
	-126.5br	-166.2sh	-146.0sh	253
	-124.2br	-158.6br	-145.0br	213
	-126.6br	-160.2br	-145.8br	
	-133.5br			

Table 1.10 continued

Complex (solvent)	$\delta^{19}F$ Ortho	Meta	Para	Temp (K)
10 (continued)	-124.2br	-158.2br	-143.0	178
	-125.9br	-159.0br	-144.3	
	-132.5br	-159.9br	-145.3	
	-133.6br	-162.3br		
11	-126.2sh	-160.5sh	-146.5sh	333
$((CD_3)_2CO)$	-126.4sh	-160.3sh	-146.3sh	Amb
	-125.8vbr	-160.0br	-145.6br	253
	-124.1br	-158.4br	-144.7	213
	-126.2br	-160.1br	-145.4	
	-133.6br			
	-123.5	-158.0	-142.8	178
	-124.2	-159.6	-144.0	
	-125.6	-159.9	-144.9	
	-132.5	-162.3		
	-133.9			

Table 1.11 ^{31}P NMR Chemical Shifts (ppm) and Coupling Constants (Hz)

Complex (solvent)	L		L'			Temp K
	δP	J(P-Pt)	δP	J(P-Pt)	J(P-P)	
7 ($CDCl_3$)	-23.7	2315	10.7	2865	578	Amb
8 ($CDCl_3$)	-20.6	2492	20.6	3089	573	Amb
9 ($CDCl_3$)	-19.7	2950	9.5	3630	527	Amb
	-19.8	2945	9.9	3595	522	243
	-19.3	2941	10.2	3576	518	193
10 ($(CD_3)_2CO$)	-23.8	150.3[I]	-	-	-	Amb
	-24.7	148.0[I]	-	-	-	213
11 ($(CD_3)_2CO$)	-31.7	-	-	-	-	Amb
	-32.2	-	-	-	-	213

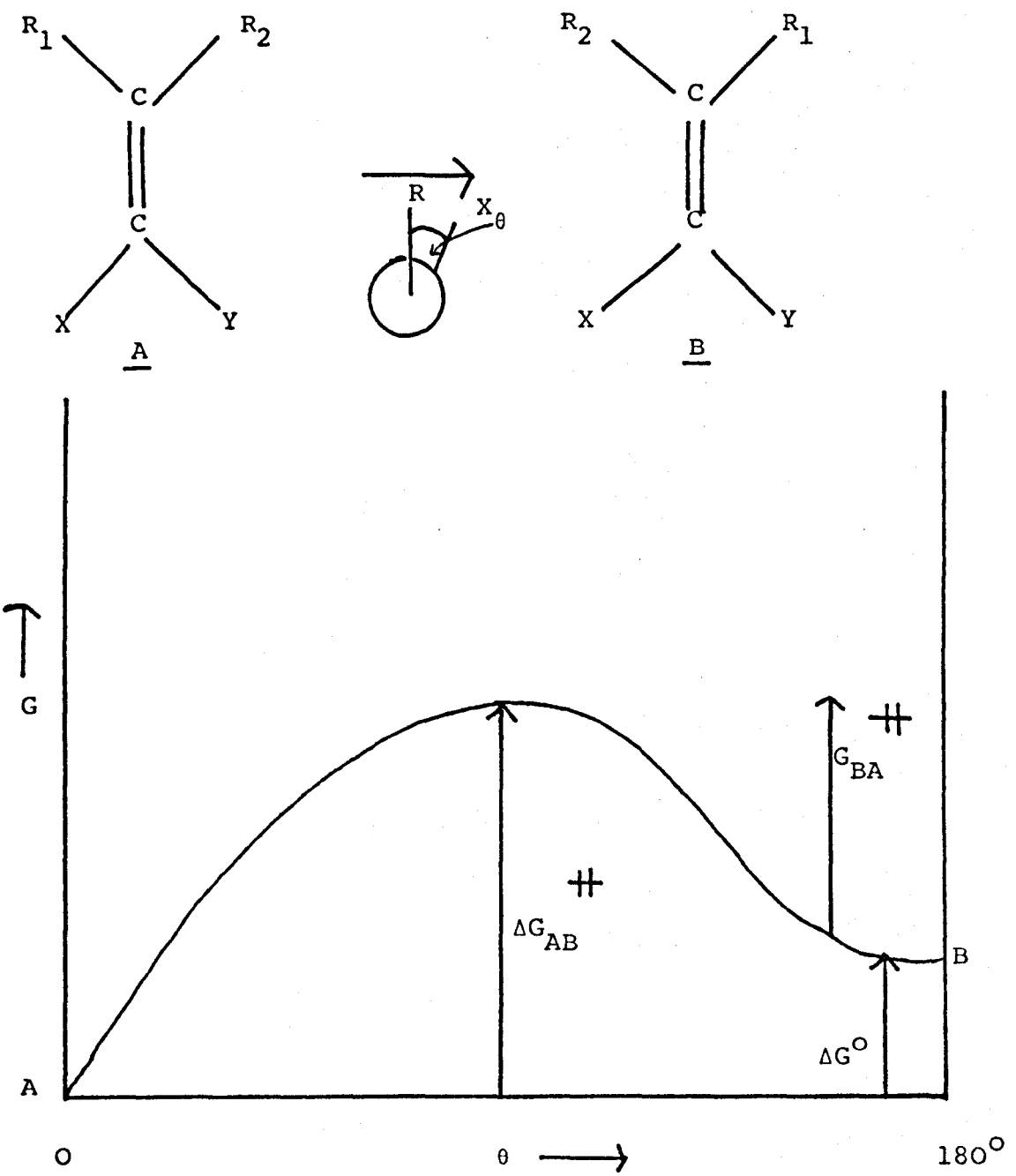
I = J(Rh-P) values

Table 1.12 ^{31}P NMR Chemical Shifts (ppm) and Rhodium-Phosphorus Coupling Constant (Hz)
(Ambient temperature).

Complex (solvent)	δP	J(Rh-P)	ν(CO)
trans[RhCl(CO)(P(C(CH$_3$)$_3$)$_3$)$_2$] (C_6H_6)	-106	183	1923(s)
trans[Rh$_2$Cl$_2$(CO)$_2$(P(C(CH$_3$)$_3$)$_3$)$_2$] (C_6H_6)	-79	124	1970(vs) 1982(w)
trans[RhCl(CO)(P(C_6F_5)$_3$)$_2$] ($CDCl_3$)	-23.5	131	2010(s)
trans[Rh$_2$Cl$_2$(CO)$_2$(P(C_6F_5)$_3$)$_2$] ($CDCl_3$)	-11.8	178	2080(w)

the planar arrangement of substituents on carbon atoms joined by a($P\pi$-$P\pi$) double bond. The dependence of the free energy on the angle of rotation about the double bond is shown in diagram 1.24.

Diagram 1.24



To convert isomer A into isomer B it is necessary to supply the free energy of activation ΔG_{AB}^{+}. The energy ΔG_{BA}^{+} is the activation energy for the reverse process. The magnitude of the free energy of activation determines the rate of thermal isomerization.[69]

If ΔG^{+} is greater than 23 Kcal/mole then the isomers are stable at room temperature. Smaller ΔG^{+} values lead to rapid thermal isomerizations. The rate constants of the processes may be obtained by the equation

$$K_r = \frac{K_B T}{h} \quad \exp \quad \frac{-\Delta G^{+}}{RT}$$

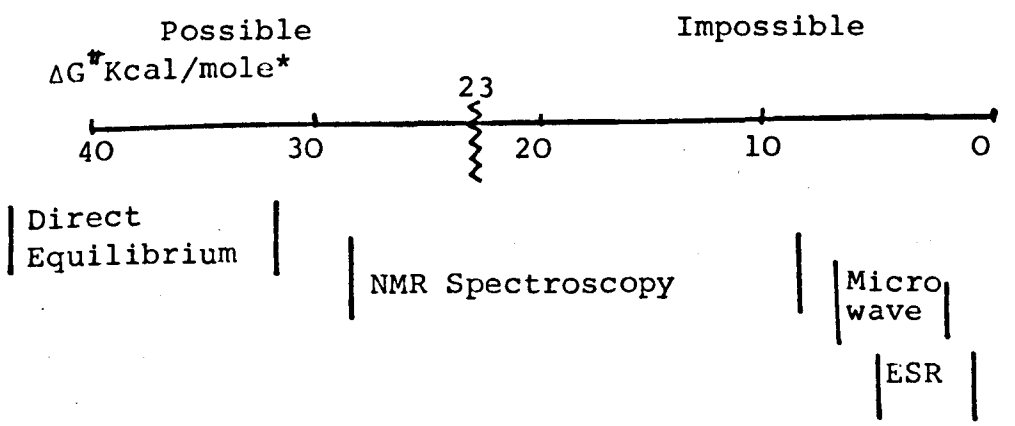
K_B - Boltzmann's constant, h-Plank's constant, R-gas constant, T-absolute temperature.

Then

$$\Delta G^{+} = 4.57T \ (10.32 + \log \frac{T}{Kr})$$

Separation of isomers is possible if the lifetime is of the order of a few hours or more. The NMR method covers a range extending downward from the vicinity of the separation limit. It is difficult to study this region by other methods (diagram 1.25)

Diagram 1.25 Separation of Isomers at Room Temperature



* 1 cal = 4.18 J

If the ΔG^{o} value of the isomerization is small then the process can be followed by NMR spectroscopy.

If $R^1 = R^2$ (Diagram L24) then A and B are chemically identical. However R^1 and R^2 are not equivalent if X and Y are different. Rotation about the double bond leads to exchange of the groups R^1 and R^2. Slow isomerization leads to two separate signals for R^1 and R^2 (Diagram L20). In the NMR spectrum fast exchange gives only one signal with an intermediate chemical shift.

Slow rotation in the NMR timescale means that the rate constant $Kr \ll \pi \Delta\nu / \sqrt{2}$ ($\Delta\nu$ is the chemical shift difference between the two signals in the absence of exchange). "Slow" can be regarded as a statistical kinetic description in this concept. A slow rotation is one in which only a small fraction of molecules can overcome the energy barrier in a unit time. The actual rotation is very fast. Infrequent would be a better term than slow.

The shape of the signal for a transition state can be used to determine rate constants. The theory of "broadening" is well developed and several methods are available in practice,

a) by approximate equations,[70]

b) by graphical evaluation of certain spectral parameters,[71]

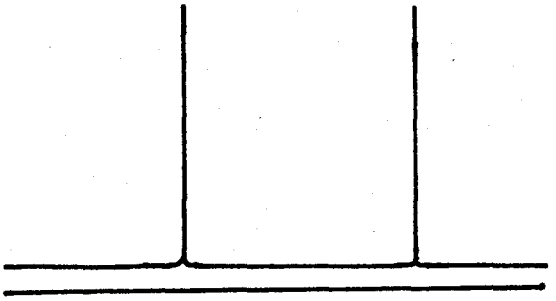
c) by computer matching of measured and calculated spectra.[72]

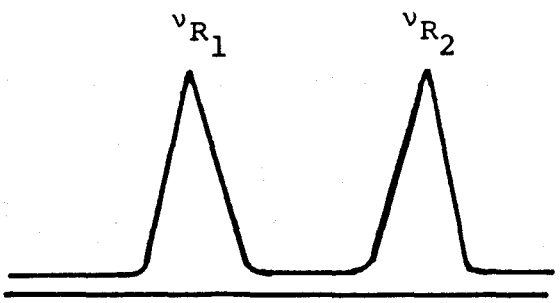
In this work evaluation of rate constants was

Diagram 1.26

Exchange between two equally populated species

Very slow exchange



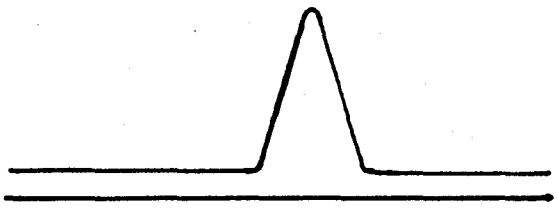


Slow exchange

Broadening $b_{\frac{1}{2}} = \frac{\pi}{K}$ r (Hz)

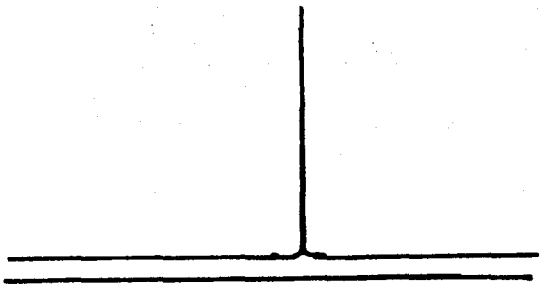
Coalescence Temperature t_c

$$K_c = \frac{\pi (\nu_{R_1} - \nu_{R_2})}{\sqrt{2}}$$



Fast Exchange

Broadening, $b_{\frac{1}{2}} = \frac{\pi (\nu_{R_1} - \nu_{R_2})^2}{2K}$ Hz



carried using method (a).

Diagram 1.26 shows the effect of temperature variation on the NMR spectrum of a system containing two groups of nuclei R_1 and R_2 whose chemical shifts are ν_{R_1} and ν_{R_2}. The equations allow the rate constants at various temperatures to be measured e.g. the temperatures at which slow exchange, coalesence and fast exchange are occurring.

The above equations are only valid when exchange is occurring between two equally populated species.

H. Shannan Atidi and K.H. Bur-Eli[73] developed a method for determining the rate constants for any two exchanging species. i.e. population or concentration R_1 and R_2 do not have to be equal.

The authors presented the expression

$$P_{R_1} - P_{R_2} = \Delta P = \frac{X^2 - 2}{3}^{3/2} \frac{1}{X}$$

where $X = 2\pi\delta\nu\tau$, $\delta\nu$ = chemical shift difference at slow exchange and I is defined $\frac{1}{\tau} = \frac{1}{\tau_{R_1}} + \frac{1}{\tau_{R_2}}$ where τ_{R_1} and τ_{R_2} are the lifetimes of species. A graph of $\frac{X}{2\pi}$ vs ΔP was also presented and this then enabled values of τ and hence K_{R_1} and K_{R_2} to be determined according to

$$K_A = \frac{1}{2\tau}(1 - \Delta P) \qquad K_B = \frac{1}{2\tau}(1 + \Delta P).$$

The variable temperature fluorine NMR spectra of complexes 1-4 (table 1.8) were analysed by examining

Table 1.13 Rate Constants Calculated from ^{19}F NMR spectra

Complex ($CDCl_3$)	$K(sec^{-1})$	Temperature K
Trans$[PtCl_2(P(C_6F_5)_3)_2]$	94.2	233
Trans$[PtBr_2(P(C_6F_5)_3)_2]$	31.4	233
	78.5	253
	125.0	273
Trans$[PtI_2(P(C_6F_5)_3)_2]$	62.0	253

Table 1.14 Rate Constants Calculated from ^{31}P NMR Spectra

Complex (solvent)	K_A (sec^{-1})	K_B (sec^{-1})	$\Delta(P)$	$\Delta\delta$ (Hz)	$Tc \pm 5$ K
Trans$[PtCl_2(P(C_6F_5)_3)_2]$ $(CDCl_3)$	53.3	13.3	0.60	25.0	213
Trans$[PtBr_2(P(C_6F_5)_3)_2]$ $(CDCl_3)$	65.0	25.9	0.43	31.0	258
Trans$[PtI_2(P(C_6F_5)_3)_2]$ $(CDCl_3)$	72.5	27.5	0.45	34.3	298
Trans$[PtCl_2(P(C_6F_5)_3)_2]$ $((CD_3)_2CO)$	57.3	8.9	0.73	27.2	213
Trans$[PtCl_2(P(C_6F_5)_3)_2]$ $((CD_3)_2CO)$	78.7	8.2	0.81	40.0	328

the broadening of the ortho fluorine signals furthest downfield in slow exchange temperature region.

From the variable temperature phosphorus NMR rate constants were obtained for the interconversion of the major and minor isomers using the latter method.

1.3.3 ^{19}F and ^{31}P NMR of Asymmetric Diphosphine Ligands and Corresponding Platinum (II) Complexes

1.3.3(i) The Free and Complexed Ligands

The asymmetric diphosphine $(C_6H_5)_2PC_2H_4P(C_6F_5)_3$ was examined by ^{31}P NMR and ^{19}F NMR spectroscopy. The ^{31}P NMR spectrum contained two signals and by heteronuclear decoupling of the phosphorus, proton and fluorine nucl assignment of the signals was accomplished. The ^{19}F NMR spectrum contained three signals corresponding to the ortho, meta and para fluorine atoms on the pentafluorophenyl rings. The J(P-P) was approximately 42 Hz in this ligand.

The platinum (11) halide complexes contained two sets of signals, each set containing the main phosphorus signal and the platinum satallites. Assignment of the signals was again achieved by heteronuclear decoupling experiments. The J(P-P) was greatly reduced in the complex at $\sim$ 8 Hz. The chemical shifts of the phosphorus atoms of the complexes were all downfield from those of the free ligand's phosphorus atoms. The ^{19}F NMR of the complexes showed that only the ortho and meta signals had shifted significantly. Very little

Table 1.15 ^{31}P NMR Chemical Shifts (ppm) and Coupling Constants (Hz) (ambient temperature)

	δ		J		
	P_H	P_F	$(P_H\text{-Pt})$	$(P_H\text{-Pt})$	(P-P)
$Ph_2PC_2H_4P(CF_3)_2$	-13.1	2.3			42
$Ph_2PC_2H_4P(C_6F_5)_2$	-12.6	-44.4			42
$[PtCl_2Ph_2PC_2H_4P(CF_3)_2]$	45.1	62.5	3120	4013	8
$[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$	41.8	15.1	3434	3820	8
$[PtBr_2Ph_2PC_2H_4P(C_6F_5)_2]$	44.9	16.7	3380	3770	8
$[PtI_2Ph_2PC_2H_4P(C_6F_5)_2]$	46.9	17.4	3213	3554	8
A (Diagram 1.27)	42.2	18.3	3358	3603	-
B (Diagram 1.27)	45.8	12.8	3278	3754	-
C (Diagram 1.27)	44.3	17.2	3417	3954	-
D (Diagram 1.27)	42.4	14.7	3392	3782	-

Table 1.16 ^{19}F NMR Chemical Shifts (ppm)

	Ortho	Meta	Para
$Ph_2PC_2H_4P(C_6F_5)_2$	-132.4	-161.8	-151.8
$[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$	-126.6	-160.2	-146.5
$[PtBr_2Ph_2PC_2H_4P(C_6F_5)_2]$	-126.4	-160.4	-146.9

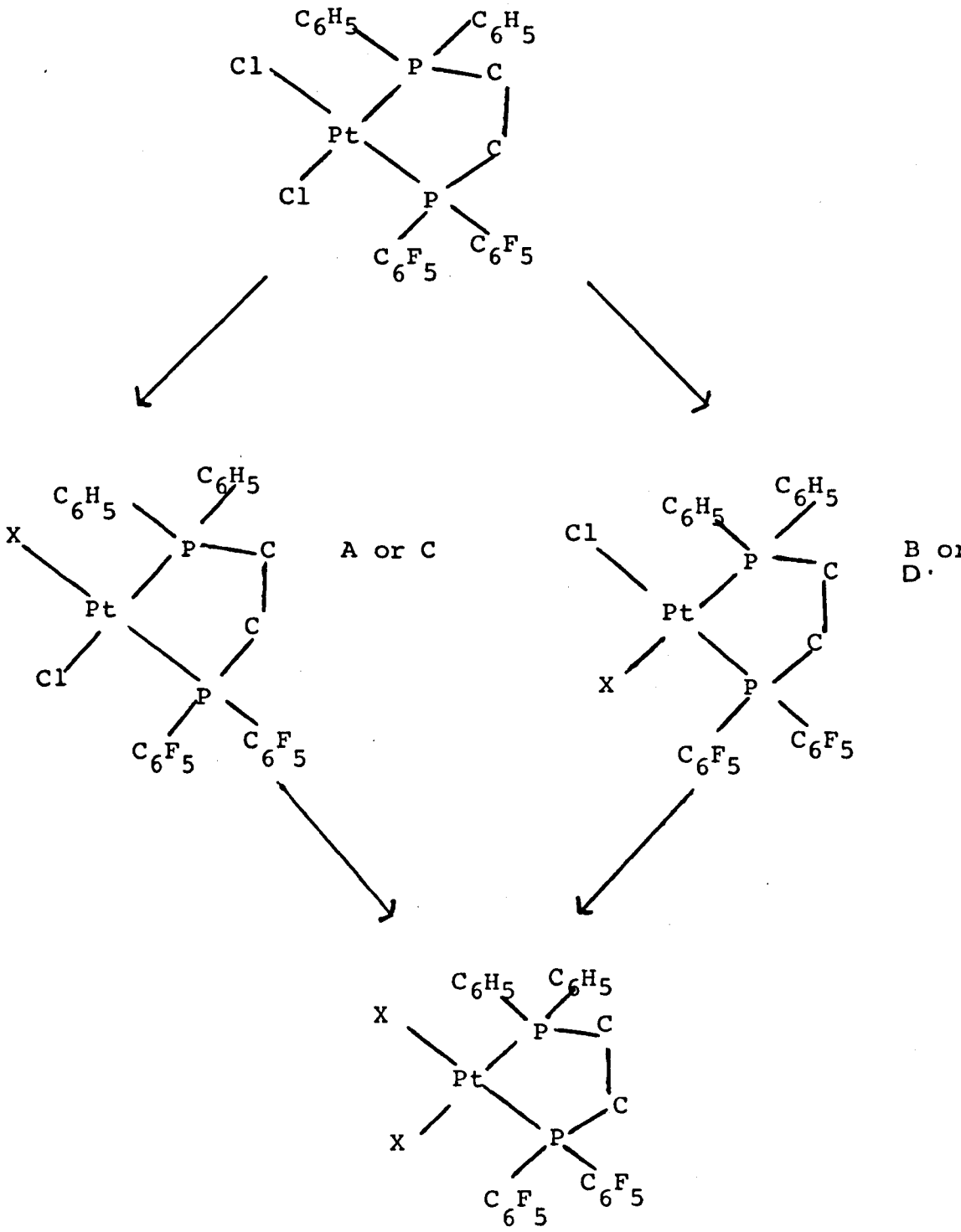
difference in chemical shifts were observed in the ^{19}F NMR signals of the different halide complexes.

1.3.3 (ii) Phosphorus-31 NMR spectra obtained from the Halide Exchange Reactions

The spectra, obtained when a deficiency of lithium bromide and lithium iodide was added to the dichloride complex, contained eight phosphorus environments corresponding to the presence of four complexes. The assignment of the signals to the complexes will be discussed in depth in Part 4. Table 1.15 contains the parameters measured from the spectra. Complexes A,B,C and D are complexes which contain one atom of chlorine and one atom of another halogen.

See diagram.1.27

Diagram 1.27


C6H5
C6H5
Cl
P
C
Pt
C
Cl
P
C6F5
C6F5
X
A or C
B or D.
X
X
A and B; X = Br
C and D; X = I

Part 4 Discussion

1.4.1 Trispentafluorophenylphosphine

1.4.1(i) Complexes Containing $P(C_6F_5)_3$

Tolman et al[68] noted that the ability of phosphine ligands to compete for co-ordination sites on zero-valent nickel could not be explained in terms of the ligand's electronic nature. He introduced the concept of cone-angles to give some measure of the steric congestion around the binding face of the phosphorus atom. The cone angles, calculated from molecular models, were presented for a series of ligands, table1.17 contains a few selected examples.

Diagram 1.28

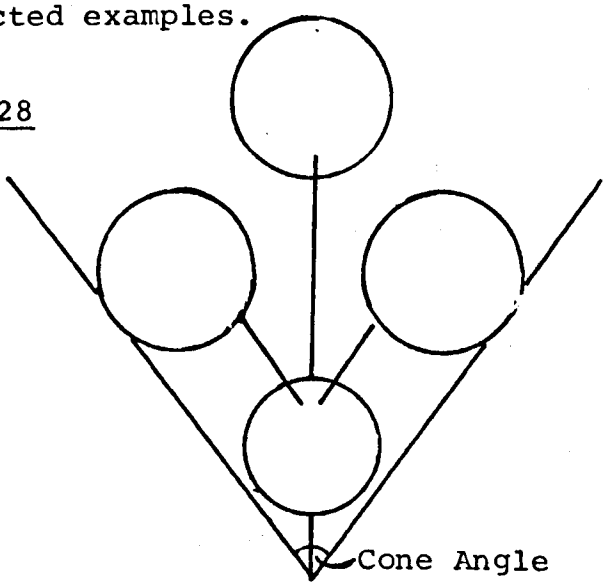


Table 1.17 Calculated Cone-Angles

Ligand	Cone Angles (θ)
$P(C_6F_5)_3$	184
$P(Cy)_3$	170
$P(C_6H_5)_3$	145
$PMe(C_6H_5)_2$	136
(Ph)	105
Cl	102

It was observed that as the binding ability of the ligands on the nickel (o) increased, the value for the predicted cone-angle decreased. The ligand $P(C_6F_5)_3$ was predicted to have one of the largest cone angles and almost the lowest binding ability. It was found in this work and in that of others[65] that $P(C_6F_5)_3$ could be displaced from its platinum (11) complex by triphenylphosphine. The inability of the trispentafluorophenylphosphine to displace other ligands had been observed by Tolman[68] and others.[65] Therefore the phosphorus to platinum bond of the arylfluorinated phosphines must be weaker than that of the other alkyl and aryl phosphine ligands. This weakness was reflected in the platinum to phosphorus coupling constants J(Pt-P). In complexes of the type trans-$[PtX_2LL^1]$ where $L=P(C_6F_5)_3$ and $L^1= PPh_3$ and PMe_2Ph examined in the present work the J(Pt-P(L)) value was always less than J(Pt-P(L^1)) value. The inferior binding ability and smaller J(Pt-P) of the ligand $P(C_6F_5)_3$ may be explained in terms of the reduced s-character in the platinum to phosphorus bond which results from the steric interactions of the pentafluorophenyl rings.

The fluorine-fluorine interatomic steric interactions in the perfluorophenyl phosphine are greater than the hydrogen hydrogen interactions in the non-fluorinated phosphines. This steric strain in the fluorinated phosphine would be relieved if the C-$\hat{P}$-C bond angles were widened. A consequence of the increased bond-angles would

be an increase in the s-character of the carbon to phosphorus bond as the C-P-C bond angles increased towards 180°. This would result in a decrease in the s-character of the platinum to phosphorus bond. The s-character of a bond is thought to be related proportionally to the coupling constant of the two nuclei which are bonded and to the strength of the bond formed. Therefore the reduced coupling constant and bonding ability of the $P(C_6F_5)$ ligand can be accounted for.

In the complexes studied the steric effects of the ligands appear to outweigh any electronic effects which might influence the bonding in the complexes. This is supported by the work of Muir et al[74] who examined the crystal structure of complexes cis-$[PtX_2L_2, L=P(CH_3)_{3-n}(C_6F_5)_n]$ and showed that the electron withdrawing properties of the (C_6F_5) group had little influence on the metal to ligand bond lengths.

It is well known that by changing the solvent the chemical shift and the constants may be altered. This topic has been reviewed in depth by Bhacca and Williams.[75] Dixon, Fakley and Pidcock[76] have conducted a series of experiments to study the effect of varying solvent, concentration and temperature on the ^{31}P NMR parameters of cis and trans - $[PtCl_2(P(Bu^n)_3)_2]$. They found that total change in J(Pt-P) values for the solvents examined was about 3.5%. The concentration effects were found to lie within the range of experimental error. A variation of about 0.5Hz deg^{-1} was found for trans-$[PtCl_2(P(Bu^n)_3)_2]$. It was observed that solvents with high dielectric constants e.g. acetone, (dielectric constant = 20.4), methanol (32.0), dimethylformamide (36.7),

and acelonitrite (38.8) all caused substantial lowering of the J(Pt-P) values for trans $[PtCl_2(PBu^n_3)_2]$. The authors also noted that the solvents, methylene chloride and chloroform, which have fairly low dielectric constants produced significant decreases. Nixon et al did not consider that current theories explaining these effects were satisfactory; a generally used model was that featuring the solute molecule in a cavity within a continuous solvent medium. The authors suggested competitive solvation, primarily in the plane perpendicular to the P-Pt-P plane. This they explained would cause a partial rehybridisation at the platinum with subsequent loss in the s-character of the platinum to phosphorus bond which would lead to a reduced coupling constant. The effect would be greatest for good solvent donors, usually those with high dielectric constants. The effects of chlorinated and aromatic solvents would also be explained by this concept. Their highly effective solvating ability is well known. The reducing effect on the coupling constant should decrease with increase in temperature as the thermal movements would tend to remove molecules from the solvation sphere which would explain the increase in J(Pt-P) values with increasing temperature.

Although there were significant changes in the coupling constant of the cis- and trans-$[PtCl_2(P(Bu^n)_3)_2]$ with variation in temperature and solvent, Dixon et al

observed very little variation in the chemical shifts with temperature and solvent changes.

The variation in coupling constant and chemical shift with solvent and temperature changes was studied for complexes 1-11 (Table 1.7) J(Pt-P) for the complex trans $[PtCl_2(P(C_6F_5)_3)_2]$ is 12 Hz less when acetone instead of chloroform is the solvent. A reduction in the J(Pt-P) values was also noted with temperature decrease e.g. trans -$[RhClCO(P(C_6F_5)_3)_2]$ in acetone has a J(Rh-P) value of 150.3 Hz at ambient temperature and J(Rh-P) of 148.0 Hz at 213 K. Very little change was observed in the chemical shifts with solvent change or temperature reduction. Consider the phosphorus chemical shifts of the complex trans-$[PtCl_2(P(C_6F_5)_3)_2]$; in acetone at ambient temperature δP is - 26.2 ppm; in acetone at 193 K the average shift position between the two isomers is $\sim$-26.5 ppm; in chloroform at ambient temperature δP is - 26.2 ppm; and in chloroform at 193 K the average shift position is 26.4 ppm. (Table 1.8).

It is interesting to note that the decrease in the J(Pt-P)s observed in trans-$[PtCl(Ph)(PMe_2Ph)P(C_6F_5)_3]$ was less for the platinum fluorophosphine than for the platinum-dimethylphenylphosphine. i.e. $J(Pt\text{-}P(C_6F_5)_3)$ decreases from 2950 Hz to 2941 Hz and $J(Pt\text{-}P(Me_2Ph))$ decreases from 3630Hz to 3576 Hz. This may be accounted for by considering the rehybridisation of the platinum

orbitals as the solvent molecules approach the metal atom. The platinum orbitals will rehybridize from dsp^2 to d^2sp^3 to accommodate the co-ordination change i.e. square planar to octahedral. The bulkiness of the $P(C_6F_5)_3$ ligand will tend to repel the complexed solvent towards the other phosphine ligand. This will result in the bond angles $PhMe_2P$-$\hat{P}t$-solvent being less than the $(P_fh)_3P$-$\hat{P}t$-solvent bond angles. The decrease in bond angles is greater for the $P(Me_2Ph)$ ligand than for the $P(C_6F_5)$, ligand. The decrease in the s-character of the Pt-PMe_2Ph bond and hence in the coupling constant between the magnetic nuclei will-be greater for the Pt-P Me_2Ph than for the Pt-$P(C_6F_5)_3$. The total s-character of Pt-PMe_2Ph bond and therefore the J(Pt-P(Me_2Ph)) are still greater than that of Pt-$P(C_6F_5)_3$ bond.

There was no evidence from either the NMR or infra-red spectra of complexes 1-11 for the presence of cis - isomers. The platinum complexes7-9 were assigned trans configuration from the magnitude of J(P-P); it is well known that a trans -J(P-P) is greater than a cis-J(P-P).[77] The infra-red spectra of complexes 1-6 contained only one metal to halogen stretching frequency (table 1.5) and must therefore have trans-stereochemistry. Rhodium (1) and iridium (1) complexes were assigned trans by virtue of the fact that the ^{31}P NMR spectra in acetone contained only one phosphorus environment. If the complexes

were cis the two phosphorus nuclei would be non equivalent and this would have produced a different ^{31}P NMR spectrum, i.e. ABX or AMX type spectra (Appendix A). The spectrum of trans $[RhCl(CO)(P(C_6F_5)_3)_2]$ in chloroform is more complicated and will be discussed later.

The absence of cis-isomers is not surprising if the steric strain in complexes containing $P(C_6F_5)_3$ is considered to be much greater than in other phosphine complexes. It is not unknown however for ligands with large predicted cone-angles to form cis-isomers e.g. cis- $Pt[(C_3H_4)(P(Cy)_3)_2][PF_6]$[78] In this case the rings, unlike aromatic rings, are not rigid and this flexibility allows the cyclohexyl groups to intermesh and so relieve the steric strain. This intermeshing of the ligands was confirmed by the x-ray crystal structure of the molecule.

Masters et al[79] reported the formation of unusual rhodium and iridium complexes when bulky phosphine ligands reacted with rhodium trichloride trihydrate. The phosphine $P(Bu^t)_2R$ where R = Me, Et, Pr^n were observed to react rapidly with $RhCl_3.3H_2O$ in alcohol at 293 K and give rhodium (11) complexes like $[RhCl_2(PBu^t_2R)]_2$ as stable purple or green crystals.

R.D.W. Kemmitt et al[64] in an attempt to prepare rhodium complexes analogous to $[RhCl(P(C_6H_5)_3)_3]$ using fluorinated phosphines $P(C_6F_5)_3$, $P(Ph(C_6F_5)_2)$

and P $Ph_2(C_6F_5)$, observed no monomeric species but found instead the dimers $[Rh_2Cl_2L_4]$.[80]

H. Schuman et al reported the synthesis of a novel type of rhodium (1) dimer. They noticed that different products could be obtained by varying the molar ratios of reactants when they studied the reaction of tri(-t-butyl) phosphine with tetracarbonyl-u-dichlorodirhodium (1) in benzene solution.

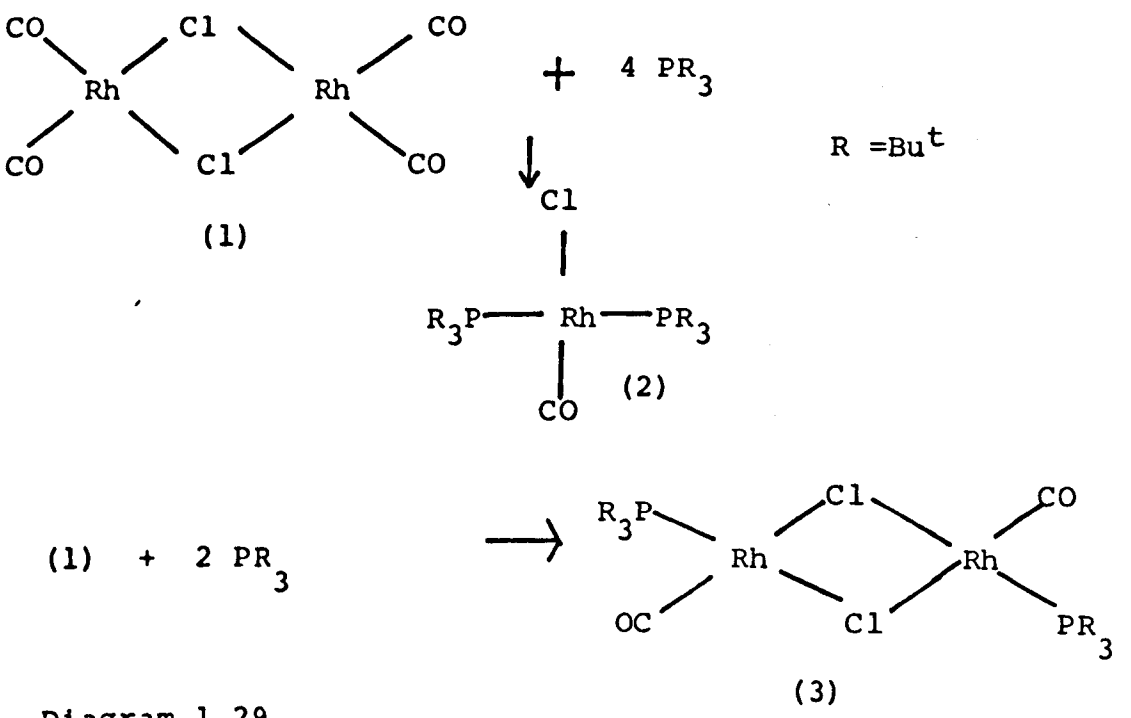
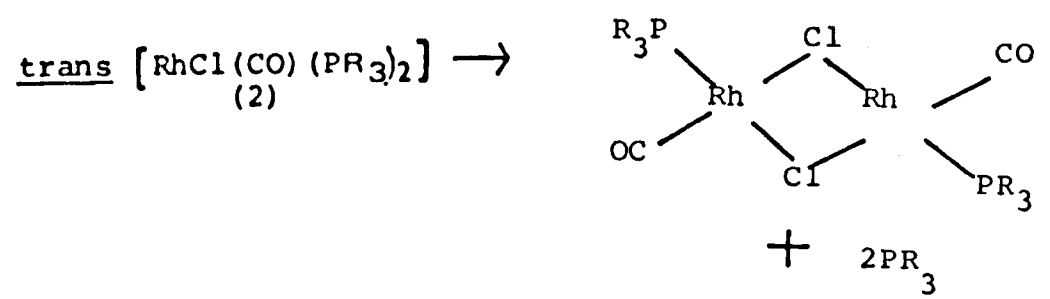


Diagram 1.29

They also found that equilibrium was established between (2) and (3) when a solution of (2) was left standing for seventy two hours.

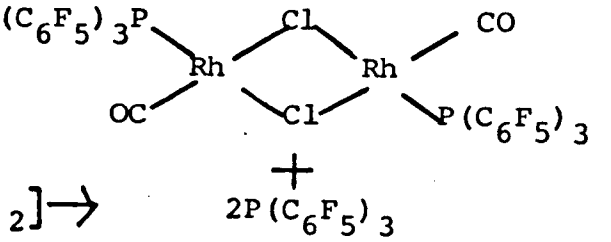
Diagram 1.30



Initially one set of doublets was observed in the ^{31}P-NMR spectrum which corresponded to the monomer (2). After seventy-two hours another set of doublets was observed which were assigned to the dimeric species (3). Evidence for the equilibrium also arose from the infra-red spectrum which contained a sharp band at 1923 cm^{-1} for the monomeric species and two signals one strong 1970 cm^{-1} and one weak 1982 cm^{-1} which corresponded to the ν(CO)s for the dimer. The reaction of monomer to dimer must be very slow. (See table 1.12).

In the present studies the ^{31}P-NMR spectrum of <u>trans-</u> $[RhCl(CO)(P(C_6F_5)_3)_2]$ was obtained in chloroform. The spectrum in chloroform, unlike that of the same complex in acetone, contained two sets of doublets at - 23.5 ppm and - 11.8 ppm, the intensities were in the ratio of 2:1 respectively. The sample was again examined twenty four hours later and the ratio of the sets of doublets was now 4:1. After a further twenty four hours the spectrum contained only one set of doublets at -23.5 ppm. Assuming the chemical shift is approximately the same in chloroform as in acetone, the remaining doublet (-23.5ppm)was assigned to the monomer <u>trans-</u> $[RhClCO(PC_6F_5)_3)_2]$(δP in acetone = -23.8ppm). The other doublet at -11.8ppm is tentatively assigned to the dimer $[Rh_2Cl_2(CO)_2(P(C_6F_5)_3)_2]$. An analogous equilibrium reaction to that found by Schuman et al is envisaged for this complex.

Diagram 1.31



i.e. <u>trans</u>-$[RhCl(CO)(P(C_6F_5)_3)_2] \rightarrow$ $+ 2P(C_6F_5)_3$

Chemical analysis of a sample of complex before it was dissolved in chloroform confirmed that only the monomer was present. In this case the reaction monomer to dimer must be very fast which would account for both being present shortly after mixing. The reverse reaction must be slow in comparison. The driving force for the reverse reaction must be related to relative thermodynamic stability of the complexes which results in all the dimer converting to monomer slowly over forty eight hours. The infra-red spectrum of the chloroform solution on day 1 contained two carbonyl frequencies, a very strong absorption at 2010 cm^{-1} and very weak absorption at 2080(w). On day 2 the weaker of the signals had disappeared and was assigned to the dimer $[Rh_2Cl_2(CO)_2(P(C_6F_5)_3)_2]$.

Another possible explanation was that both <u>cis</u> and <u>trans</u>-isomers of the monomer were present in the original sample. This was rejected in favour of the above explanation for the following reasons.

a) <u>The</u> cis-isomer would have to have magnetically different phosphorus atoms and hence the ^{31}P NMR signal would have exhibited phosphorus-phosphorus coupling. There was no evidence for this; no fine structure or

broadening of the signals, and

b) from steric considerations discussed previously, it is doubtful that the cis-isomer would form at all.

Schuman et al made similar observations on the iridium complex trans-$[IrCl(CO)(P(t\text{-}But)_3)_2]$ in pentane, however the complex trans-$[IrClCo(P(C_6F_5)_3)_2]$ was too insoluble in chloroform or any other organic solvent to be investigated.

The explanation for the difference in structure observed when different solvents are used may lie in the different modes of solvation. Acetone was a very good solvent for this complex whereas chloroform was quite poor. This reflects the donor abilities of the acetone which contains an oxygen molecule compared to those of chloroform.

One important point arises for this type of work. It illustrates the danger of assuming a structure determined by x-ray crystallographic techniques is retained by the molecule when it is in solution and that the structure of the molecule in one solvent is the same as that of the molecule in a different solvent.

1.4.1(ii) Discussion of ^{19}F and ^{31}P NMR Spectra of Complexes 1-11 (Diagrams 1.13-1.22)

The general behaviour of the fluorine NMR of complexes 1-11 with temperature variation can be described in the following way:

a) The initial broadening of the signals on lowering the

temperature,

b) further broadening and eventual separation of signals, which had previously been observed as averaged signals, when the temperature was lowered further and

c) sharpening of the separated signals at very low temperatures.

In phosphines the threshold dynamic process may be either the inversion of the bonds to phosphorus or rotation about the phosphorus bonds. The work by Kessler et al[69] and Negrebetskii et al[81] on molecules like trimesityl phosphine supports the opinion that the dynamic effects observed in these types of molecules are due to phosphorus-carbon bond rotation and not to inversion at the phosphorus atom. In the present work phosphine molecules are complexed to metal centres and very large steric congestion would arise if inversion of the phosphine occurred. Therefore it is assumed that the broadening observed with temperature reduction is due entirely to hindered rotation of phosphorus-carbon bonds and phosphorus-metal bonds. The phenomenon of broadening may be attributed to molecular processes other than bond rotation. As discussed earlier molecular exchange between complexed and uncomplexed ligand can cause broadening of the NMR-signals. Such a process is thought to be responsible for the broadening observed in the fluorine NMR spectrum of <u>trans</u>-$[RhClCO(P(C_6F_5)_3)_2]$ when the temperature is

raised from ambient to 333K. Exchange between free and complexed ligands in metal-phosphine complexes is not unexpected. It is perhaps surprising that no other complex exhibited this type of broadening when the temperature was increased.

The fluorine and phosphorus NMR spectra of complexes 1-9 have been interpreted as showing convincingly that rotation about the phosphorus to metal bond and the phosphorus to carbon bond ceases on the NMR-timescale at temperatures between 213K and 176K.

As mentioned in section 1, Part 3 the fluorine NMR spectra of complexes 7 and 8 (Table 1.10) at 213 K consisted of three-ortho, three meta and two-para fluorine signals. The intensities of the ortho and meta signals were 2:2:2 and the intensity of the para signals were 2:1. (Diagram 1.18). The para signals imply that one of the three aryl rings is in chemically different environment . The ortho - and meta signals may be accounted for if the two ortho fluorines and hence the meta fluorines on the unique ring are equivalent, giving rise to one ortho- and one meta- fluorine signal. The equivalency may be due to the conformation of the ring towards the Cl-Pt-Cl bond or due to the free rotation of the phosphorus-carbon bond. If the two ortho and the two meta fluorine atoms on each of the equivalent rings are not magnetically equivalent to each other but are equivalent

to the corresponding ortho-and meta fluorines on the other equivalent ring, this results in two ortho- and two meta-fluorine signals from the two equivalent rings. Therefore the presence of three ortho and three meta signals of equal intensities can be explained.

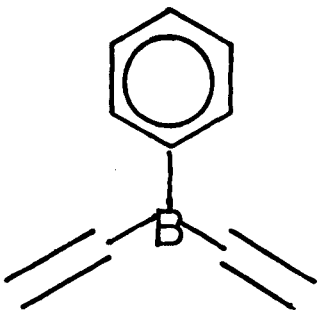
These spectra were interpreted as representing the spectra of two propeller conformations of opposite helicity rapidly converting between conformers. Diagram L35 shows a pictorial representation of one helical form of the complexed ligand.

These observations alone do not require restricted rotation about the phosphorus-metal bond.

A situation can be envisaged where the phosphorus-carbon rotation has ceased but interconversion of the two helical isomers still occurs. In this state the molecule has two equivalent rings and one non-equivalent. The helical interconversion is assumed to be very fast and not detected in the NMR spectrum which at low temperature represents an average structure between the two helical forms. A molecule with an average structure which fits the low temperature NMR spectrum must have two equivalent rings and one unique ring. This can be better appreciated if an analogous situation is considered. In triaryl boranes the boron-carbon bonds form a plane to which the aryl rings, in the extreme cases, may be perpendicular or coplanar. Assuming the interconversion between the

two helices is accomplished by a 2-ring flip. Mislow[51] deduced from molecular mechanics studies that the intermediate structure for the 2-ring flip had one ring perpendicular to the other rings i.e. two equivalent rings and one unique.

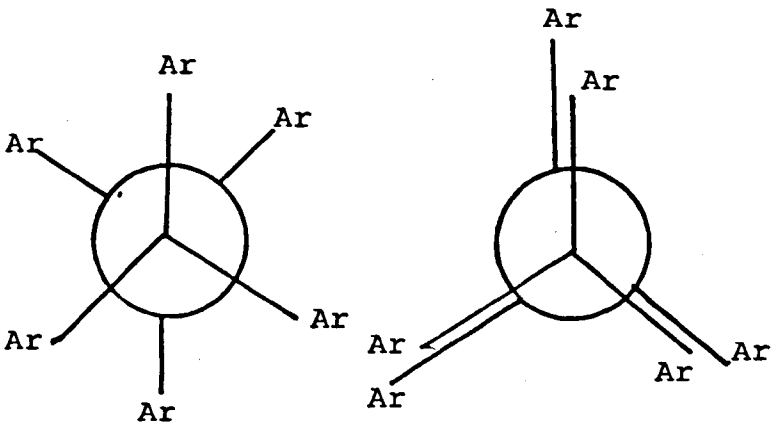
Diagram 1.32



A similar situation can be proposed for triaryl phosphines bearing in mind the fact that the phosphine is not planar but pyramidal. If it is assumed that the average structure for the triaryl phosphines is analogous to that of the triaryl boranes, it is clear that if bond rotation about phosphorous carbon ceases one of the aryl rings must become non-equivalent to the others even if metal-phosphorus bond rotation continues. No broadening was observed in the spectrum of the free ligand at low temperature, therefore if the metal phosphorus rotation continued while carbon-phosphorus bond rotation stopped this would have been due to the bonding of the ligand to the metal and

and not to any steric effects. It is difficult to envisage a situation where the rotation the carbon phosphorus bond is very much slower than the rotation of the phosphorus-metal bond. In order to compare the rate of ring rotation and metal-ligand bond rotation rate constants were obtained from the variable temperature fluorine and phosphorus - NMR for the complexes trans-$[Pt\ X_2(P(C_6F_5)_3)_2]$ where X = Cl, Br, or I.

The low temperature fluorine NMR spectra of complexes 1 (table 1.8) contained two sets of three ortho- fluorine signals, the ratio of intenities being $\sim$ 3:1. The corresponding sets of signals for the meta- and para-fluorine signals were not completely resolved. The most intense para-signal did possess a distinct shoulder (Diagram 1.13). The phosphorus NMR spectrum at 213K contained two phosphorus signals with corresponding platinum satallites. The ratio of the intensities of these signals was again approximately 3:1. The two sets of signals are considered to result from strongly hindered rotation about the platinum-phosphorus bond. This impeded rotation gives rise to two rotamers which are imagined in either a staggered or eclipsed form with respect to the aryl rings.



Staggered Eclipsed

Diagram 1.33

The crystal structure determination of trans-$[Pd\ I_2(P\ Ph_3)_2]$ showed that in the solid state, the staggered form was preferred.[82] In the molecules trans-$[RhClCO(P(t\text{-}C_4H_9)_3)_2]$[80] and trans-$[IrClCO(P(t\text{-}C_4H_9)_3)_2]$[80] the t-butyl groups were found to be in staggered configurations when crystal structures of these molecules were examined. It was not possible in this study to determine which configuration corresponded to the major isomer and which to the minor isomer observed in the low temperature NMR of complex 1. Similar patterns were found for complexes 2 and 3.

The trans-$[PtBr_2(P(C_6F_5)_3)_2]$ and trans-$[PtI_2(P(C_6F_5)_3)_2]$ gave simple ^{19}F and ^{31}P-NMR spectra at 289K and 323K respectively. These observations suggest that barriers to rotation are higher in the diiodide than the dibromide which in turn has higher barriers than the dichloride.

The rate constants calculated from the

phosphorus-NMR were used to reflect the rates of rotation about the phosphorus-metal bond. If the phosphorus siganls are due to the occurrence of rotational isomers then coalesence of these signals is indicative of the onset of metal-phosphours bond rotation within the NMR-timescale.

$$A \underset{K_B}{\overset{K_A}{\rightleftharpoons}} B$$

Minor isomer Major isomer

The K_A and K_B values calculated are rate constants for the conversion of the minor isomer (A) to the major isomer (B) and vice versa. It can be seen from table 1.13 that K_A is much larger than K_B which is expected if B is the major isomer. The rate constants (K_F) from the fluorine NMR were obtained by measuring the broadening, in Hz, of the ortho-fluorine signal furthest downfield with temperature increase. These K_F values are assumed to give some measure of the rates of ring rotation.

The K_F values gave the order of decreasing rate constants, for the <u>trans</u>-$[Pt\ X_2(P(C_6F_5)_3)_2]$ complexes, as

$$K_F\ (Cl_2) > K_F(Br_2) > K_F(I_2)$$

This is also the order of increasing atomic volume. The corresponding values of K_A and K_B obtained from the

^{31}P-NMR, also decrease in this order if the co-alescence temperature is taken into account. The coalescence temperature for the dichloride complex is 213 K and for the dibromide complex is 258K. Therefore at temperature, say, 248K the bond rotation in the dichloride is so fast that the rotamers are not resolved but in the dibromide complex, at this temperature, the bond rotation is such that both isomers are still observed. Therefore bond rotation in the dichloride at this temperature must be greater and hence the rate constant, if measured, would also be greater. A similar argument may be applied when comparing the dibromide and the diiodide complexes. The K_F, K_A and K_B rate constants for the complex trans - $[PtBr_2(P(C_6F_5)_3)_2]$ may be compared since the temperatures at which the values were obtained are approximately the same i.e. K_F-253K, K_A and K_B - 258K. The K_F value of 78.5 sec^{-1} was greater than the K_A and K_B values obtained i.e. K_A-65.0 sec^{-1} and K_B-25.9Sec^{-1}. These observations support the proposal that ring rotation in the complexes studied is faster than rotamer interconversion and hence faster than metal-phosphine bond rotation.

It was not possible to determine other thermodynamic data such as free energies from the fluorine and phosphorus NMR spectra because the nature of the spectra precluded such investigation.

The coalescence temperatures calculated from the ^{31}P-NMR were accurate only to $\pm$ 5 K therefore any free energy value which could be obtained would be somewhat inaccurate. In most of the ^{19}F-NMR spectra examined the coalescence temperatures could not be obtained because broadening near this temperature was so great that the whole spectrum collapsed. The values of rate constants obtained must be regarded as speculative. The broadening observed in the fluorine spectra arises not only from increased phosphorus carbon bond rotation but from other effects such as coupling of magnetic nuclei and metal-phosphorus bond rotation. Ring rotation however is assumed to be the major contributor to the broadening observed.

Rotational isomers were observed in the phosphorus NMR spectrum of <u>trans</u>-$[PdCl_2(P(C_6F_5)_3)_2]$. The coalescence temperature was much higher than that of the anologous dichloroplatinum (11) complex in the same solvent i.e. acetone. This indicates that barriers to rotation in the palladium complex are higher, hence the steric restriction are greater.

When forming square planar complexes palladium uses <u>dsp</u>^{2} hybrid orbitals as does platinum. The palladium use 4<u>d</u> orbitals to make the hybrides while platinum uses 5<u>d</u> orbitals. The 4<u>d</u> -orbitals having a lower quantum number must be less diffused than 5d orbitals. Therefore it is reasonable to predict

smaller bond lengths in the palladium complexes which would result in greater steric restrictions. There are examples of palladium complexes having smaller bond lengths than analogous platinum complexes e.g. Pd-N bond in trans $[PdCl_2(NH_3)_2]$ is 2.044Å while Pt-N bond in trans $[PtCl_2(NH_3)_2]$ is 2.051 Å. Admittedly there are also examples where the converse is true, e.g. Pt-P bond in trans-$[PtCl_2(P(Me_2Ph))_2]$ is 2.28Å while the Pd-P bond in trans $[PdCl_2(PMe_2Ph))_2]$ is 2.333Å.

A possible reason for the absence of rotational isomers in complexes trans-$[MCl(CO)P(C_6F_5)_3)_2]$ (where M=Rh, Ir) is that the chemical shift difference between the two isomers is so small that the rotamers can not be distinquished. This is probably the reason why the fluorine-NMR spectrum of trans $[PdCl_2(PC_6F_5)_3)_2]$ contains only three ortho fluorine signals with no isomers being detected.

An obvious explanation is that barriers to rotation in trans- $[RhClCO(P(C_6F_5)_3)_2]$ and trans-$[IrClCO(P(C_6F_5)_3)_2]$ are much lower than in Pt (11) complexes. Resolution of the ^{19}F-NMR of the rhodium and iridium complex occurs at 233 K and the platinum (11) complex resolves at 253 K therefore it is unlikely that the barriers to rotation are very different between the complexes.

Another view is that the possibility of

isomers does exist but the ratio of isomers is dependent on the free energies of each isomer. It is thought that with the rhodium and iridium complexes the energy difference between the isomers is so great that only one rotomer form is appreciably occupied. In the case of the palladium and platinum the energy difference is not so great and both rotamer forms are occupied.

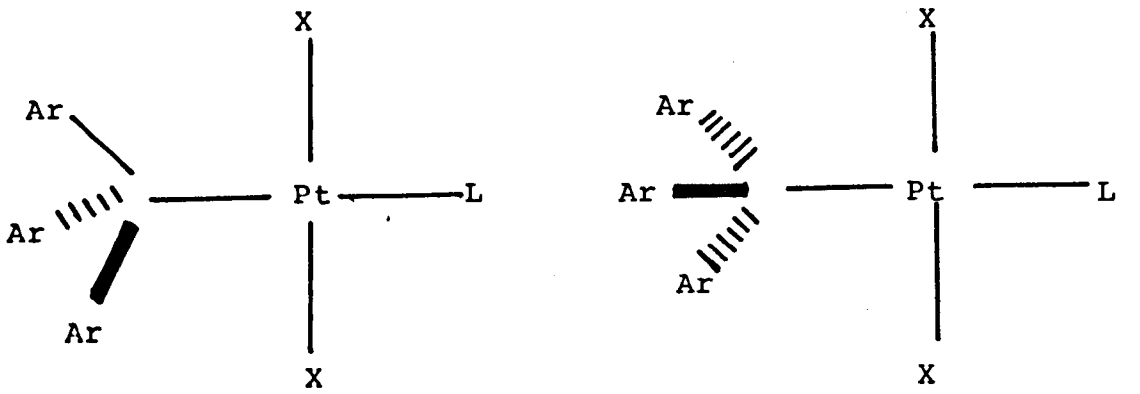
Complexes of platinum containing one tris .pentafluorophenyl phosphine ligand and either triphenylphosphine or dimethylphenyl phosphine do not give rise to rotational isomers. This must mean that rotational barriers are lower in triphenyl phosphine and dimethylphenylphosphine than in tris-.pentafluorophenylphosphine.

If the phosphorus atoms, the halide atoms and the platinum atom are coplanar then the arrangement of the rings relative to this plane can be either;

a) With no phosphorus-carbon bond coplanar and with two of the aryl rings above the plane of the molecule and one ring below the defined plane (configuration B Diagram 1.34); or

b) With one phosphorus-carbon bond co-planar and one ring above and one below the plane (configuration A Diagram 1.34).

Diagram 1.34



It is generally accepted from crystal structure determinations of triphenylphosphine complexes that configuration B is favoured in the solid state. However the work done by Mann et al[48] with trans-$[MClCO(P(t\text{-}C_4H_9)_3)_2]$ (where M = Rh, Ir,) showed that configuration (A) was preferred by some complexes in solution.

No deductions about the preferred conformation of the rings can be made from the spectra of complexes 1-8 (Table 1.7).

In an attempt to clarify this, complexes trans - $[MCl(CO)(P(C_6F_5)_3)_2]$ (where M = Rh and Ir) were prepared.

If conformation (B) is preferred then the three anyl rings should become non-equivalent when bond rotation ceases. However preference for conformation (A) would mean that two of the rings remained

equivalent. An additional consideration was that because the complexes contained two fluorinated ligands it was predicted that rotational isomers would be present. Theoretically, if conformation A was preferred there should have been two sets of six ortho-signals two sets of six meta signals and two sets of three para-signals. If configuration (B) was preferred the predicted spectrum would have contained two sets of three ortho-signals, two sets of three meta-signals and two sets of two para-signals.

The spectra obtained for complexes 10 and 11 in acetone were essentially the same for both complexes. The spectrum at 178 K contained three para-signals of equal intensities and five ortho signals with equal intensities. The number of meta-signals was more difficult to determine because the resolution was insufficient to yield good separation between the signals in the appropriate region of the spectrum. It is not unreasonable however to claim the presence of six meta-signals (diagrams 1.21 and 1.22).

The phosphorus NMR spectrum for the rhodium in acetone exhibited only one phosphorus signal which was a doublet due to rhodium-phosphorus coupling. The iridium complex showed only one phosphorus signal.

The conclusion drawn from these results is that in solution the phosphine ligands in the rhodium and iridium complexes adopt configuration B when bond rotation is stopped within the NMR timescale.

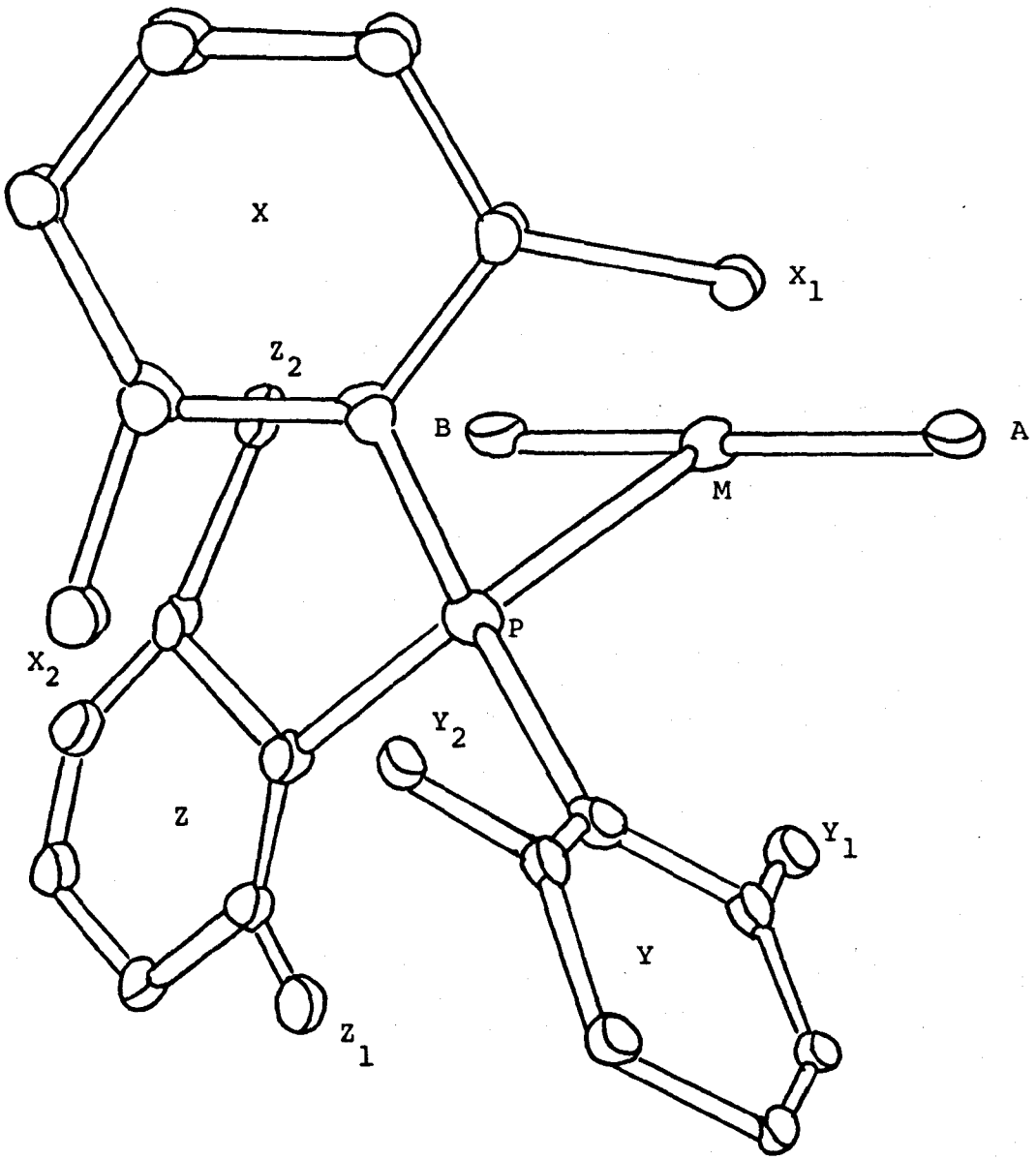
Trans- $[PtCl(Ph)(P\ Me_2Ph)\ P\ (C_6F_5)_3,]$ complex 9 was prepared to determine whether the ligand, $P(C_6F_5)_3$, in a platinum complex would adopt the same configuration. The low-temperature NMR of complex 9 (Diagram 1.20) contained six ortho-fluorine signals, six meta-fluorine signals and three para-fluorine signals; all the signals were of equal intensity. This confirms that the ligand assumes the same configuration in the platinum complex as in the rhodium and iridium complexes.

As previously stated the motion of the propeller "blades" in Ar_3Z- and Ar_3ZX- type molecules during helicity reversal has been well studied. Ring rotation is considered to be an extension of the helicity reversal process and as such concepts applied to helicity reversal may also be applied to ring rotation e.g. the preferred direction, clockwise or anti-clockwise, of the rings' rotations relative to each other.

The rate of bond rotation is governedby the activation energy required to cvercome the steric repulsions experienced when one atom passes near to another.

In the complexes studied steric interactions occur between the ortho-fluorines on the three aryl rings, and between the ortho-fluorines on the rings and the cis-substituents on the platinum atom, i.e. the atoms or molecules cis to the phosphine ligand.

Diagram 1.35 A Propeller Molecule



It is considered that the behaviour of the variable temperature fluorine-NMR is compatible with a ligand structure such that helicity reversal of the propeller molecule occurs by a 2-ring-flip mechanism i.e. two of the rings move in the same direction and the third moves in the opposite direction. Diagram 1.35 is a representation of one helical form of the tris pentafluorophenylphosphine ligand attached to a metal centre. The two equivalent rings, which move in the same direction, are labelled Y and Z and the third ring which is unique is labelled X. The ortho-fluorines on the rings are labelled Y_1 Y_2, Z_1, Z_2 and X_1, X_2.

By analogy to the triarylboranes the directional motions of the three rings are inter-dependent. The correlated motion can be described as a "gear meshing" effect which results from steric interactions between fluorine atoms X_2 and Z_1 and also between Y_2 and X_1 (See Diagram 1.35).

Steric hindrance or "gear-clashing" which slows the rotations of the rings must be experienced between ortho-fluorines Y_1 and the <u>cis</u>- substituent (A) on the platinum, between Z_2 and the <u>cis</u>-substituent (B), and between ortho-fluorines Z_1 and Y_2 during helicity reversal.

By comparing the variable temperature NMR specta of complexes 1-3 (table 1.7) it is seen that the

interactions of the rings with cis substituents must constitutethe prime barrier to rotation about the phosphorus-metal bond.

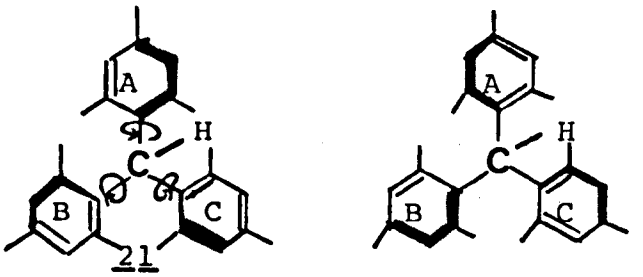
The variable temperature NMR of complexes 1-8 gave no indication which of the "gear-clashing" mechanisms, i.e. ortho - ortho interaction or the ortho - cis interaction described earlier, is the main barrier to rotation of the rings assuming ring rotation continues after metal-phosphorus bond rotation has ceased.

It can be seen from the appearance of the spectra that in complexes 1-8 all the phosphorus-carbons rotate at the same rate as all the ortho signal begin to coalesce at the same temperature.

The low temperature NMR spectrum of complex 9 trans - $[Pt\,Cl(Ph)(P\,Me_2Ph)\,P(C_6F_5)_3]$ contains six ortho signals. When the temperature is raised four of the signals coalesce at 223K while two remain sharp. This is direct evidence for the barrier to rotation being much higher in one ring. (Diagram 1.20).

Analoguous work was that published by M.J.Sabacky et al.[83] dealing with ortho-substituted triaryl methanes as shown in the diagram 1.36.

Diagram 1.36



A - OCH_3 substituted

B,C, - CH_3 substituted.

They found that at 253K the methyl signals had coalesced while the methoxy signals remained sharp. This was taken as showing that the methyl substituted rings rotated at a much faster rate than the methoxy-substituted rings.

The proposed mechanism for rotation was based on considerations of methoxy-methyl interactions and methyl-methyl interactions. They concluded that because the methyl group is bigger than the methoxy group that the methyl methyl interactions would be greater and it was the "gear-clashing" experienced between methyl groups B2 and C1 which determined the mechanism. This was compatible with the ^1H NMR.

A similar interpretation can be applied to explain the variable temperature NMR of complex 9 (Diagram 1.20).

If the ortho-ortho interaction is the dominant effect then substituting one halide atom with a phenyl group should have little or no effect on the ring rotation. The six-ortho signals should then have coalesced at the same temperature because the situation is no different from that of the dihalide complexes from the point of view of the ring rotation. The rate of ring rotation might well have been influenced slightly by substituted a phenyl in the cis-position because this might cause a decrease in C-P-C bond angles but the spectra should have shown all signals coalescing at the same temperature.

If the cis-ortho interaction is more important then the following situation would arise. Rings X and Y would still "gear mesh" as before and ring Z would move until the ortho-fluorine Z_2 approach near to the phenyl group labelled B in diagram 1.35. At the low temperature there would be insufficient energy to overcome this barrier and the ring Z would be prevented from rotating through 180^{o} and it would move back to its original position. Therefore the ortho-fluorines on ring Z cannot exchange and these fluorine atoms would remain in different chemical environments. This fits in well with the

spectral behaviour observed i.e. four signals coalescing due to rings Y and X rotating at a much lower temperature than the other signals. The two sharp signals represent the ortho fluorines on ring Z which cannot exchange by rotation because of steric interactions between fluorine Z_2 and phenyl (B). This holds assuming no change in the mechanism of helicity reversal.

Therefore it can be concluded that barriers to rotations in propeller molecules attached to metal centres arise predominantly from the steric interactions between the ortho-substituents on the ring and the cis-substituents attached to the metal centre.

It has been established that electron-withdrawal or donation by substituents on a fluoro-phenyl ring is related the chemical shift of the para-fluorines on the ring.[9] (Table 1.3). It was thought that because the para-fluorines are least likely to be effected by steric interactions that their chemical shifts might give some measure of the ring's interaction with the substituents without the exact nature of the electronic interaction being defined.

In the trans-$[PtX_2(P(C_6F_5)_3)_2]$ complexes at low temperature the para fluorine signals were moved downfield from the para fluorine signal of the free ligand, e.g. in the free ligand δF_{para} is -148.1 ppm

while in the dichlorocomplex δF_{para} S are - 141.5 ppm and - 143.5 ppm (Table 1.8). Shifts downfield arise from decreases in the electron density around the fluorine nuclei. In this case the shifts were presumably caused by the bonding of the trispentafluorophenylphosphine to the platinum atom. It is noted that the signal of intensity 1 is upfield from the signal of intensity 2 i.e. - 143.5 ppm, (1) and - 143.5 ppm, (2). Therefore there is greater electron-withdrawal from the equivalent rings by the phosphorus atom and hence greater interaction between the equivalent rings and the phosphorus atom than between the unique ring and the phosphorus atom.

In the complex $[PtClPh(PMe_2Ph)P(C_6F_5)_3]$ at low temperature the three perfluorophenyl rings are non-equivalent and therefore the three para fluorine atoms are non-equivalent. As the temperature was increased it was seen from the ^{19}F NMR that one of the para-fluorine signals remained sharp while the other two signals started to coalesce. It has been shown previously that in this complex one of the perfluorophenyl rings has a high barrier to rotation and it is not unreasonable to assign the fluorine signal which remained sharp to the ring which has the highest rotational barrier. Coalescence of this third para-fluorine signal (-1420 PPM) begins at the same temperature (223K) as coalescence the two ortho-signals

assigned to the ring with the highest rotational barrier. The para-fluorine at —142.0 ppm is furthest downfield and hence experiences greatest interaction with phosphorus atom. It appears therefore that there may also be an electronic contribution to the rotational barrier of the fluorophenyl rings. It is well known that electronic features may lead to restricted rotation, consider the carbon-carbon bond rotation in ethane and ethene.

In the ^{19}F-NMR of trans $[RhClCO(P(C_6F_5)_3)_2]$ and trans- $[IrClCO(P(C_6F_5)_3)_2]$ the para-fluorine signal which remains sharp when the temperature is increased is furthest upfield. A possible explanation is that in these complexes unlike the $[PtClPh(PMe_2Ph)\ P(C_6F_5)_3]$ the rotation of all the rings is comparable. The retained sharpness of the signal at -145.3 ppm in rhodium complex and at -144.9 ppm in the iridium may arise from chemical shift differences. The greater the shift difference between two signals the higher the required temperature for coalescence of the signals. Admittedly the differences between the signals which coalesce and those which do not, is not very large.

It seems therefore that para-fluorines chemical shifts do not produce completely reliable measures of the electronic interaction between the ring and its substituents.

Bonding within metal complexes containing substituted fluorophenyl rings has been discussed by many workers[12,13,14] in terms of σ_R and σ_I parameters which were obtained by correlations of the fluorine chemical shifts with Hammitt substituent constants.[11] Parshall[84] used the fluorine chemical shifts of <u>para</u> and <u>meta</u>-fluorophenylplatinum complexes to evaluate the π acceptor capacity of the ligand. A similar approach was used by Hogben et al[85] in their study of pentafluorophenyl phosphine and related complexes.

It is doubtful that σ_R and σ_I parameters have any real meaning in terms of the electron density changes at the <u>para</u>- and <u>meta</u> positions apart from registering that changes exist. The assumption that the magnetic field should be able to differentiate between changes in the electron density produced by the π-system and those produced by a σ system has not been accounted for.

To summerise:

a) The trispentafluorophenylphosphine ligand when complexed to a metal centre retains its propeller shape.

b) The fact the only <u>trans</u>-isomers are found is thought to be due entirely to steric effects.

c) The complexed ligand's configuration in solution is such that one ring is above the plane of the

molecule, defined by the platinum-phosphorus and platinum-halide bonds and two rings are below this plane.

d) The directional motions of the rings when the ligand is attached to the metal centre are interdependent and arise from a "gear meshing" and "gear clashing" effects of the ortho-fluorine substituents. The helicity reversal is accomplished by a two ring flip.

e) The steric interactions of the ortho-fluorine substituents on the rings with the substituents cis to the phosphine ligands on the metal centre are the principal barriers to rotation of the rings and of the phosphorus-metal bond although there are probably small electronic contributions.

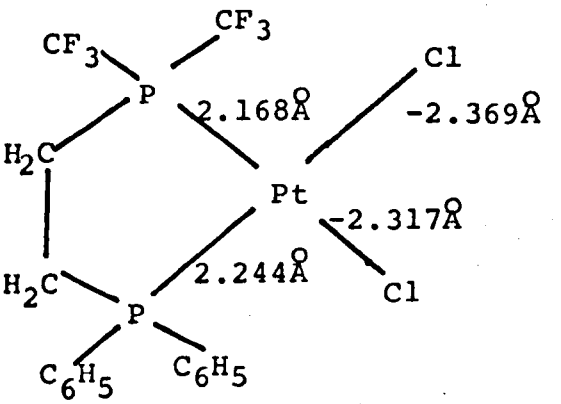
f) Rotational isomers were observed for platinum and palladium complexes containing two fluorinated ligands but rhodium and iridium complexes did not appear to have rotational isomers.

1.4.2 Asymmetric Phosphine Complexes and Halide Exchange Reactions

1.4.2(i) The complex $[PtCl_2(C_6H_5)_2PC_2H_4P(CF_3)_2]$

This complex was prepared by D. Millington and the crystal structure was determined.[59] The structure which was obtained is shown below.

Diagram 1.37



The most striking feature of this structure is the very short $Pt-P(CF_3)_2$ bond *trans* to a short Pt-Cl bond. This platinum-chloride bond is 0.05Å shorter than the Pt-Cl bond *trans* to the $Pt-PPh_2$ bond. From classical models it would be expected that the Pt-Cl bond *trans* to the shorter Pt-P bond would be the longer bond.

The structure of the complex $[PtCl_2(C_6H_5)_2PC_2H_4P(CF_3)_2]$ may be explained in the following way. If it is assumed that (a) the *trans*-influence is transmitted through the molecular σ-bonding system and (b) that π back-bonding between the metal and the ligand does not contribute to the *trans*-influence of that ligand, or effect the length of the bond *trans* to the metal-ligand bond.

The series of increasing trans-influence for ligands presented by Muir and Muir[41] (section 1, part 1) shows that phosphine groups with electronegative substituents should be inferior trans-directors as compared with phosphine groups containing phenyl substituents. Therefore the Pt-Cl bond trans to the PPh_2 end of the diphosphine ligand should be longer than the Pt-Cl bond trans to the $P(CF_3)_2$ end of the bidentate. The shortness of the $(CF_3)_2P$-Pt bond could be accounted for by assuming π-back donation from the metal to the phosphorus atom which would contract the bond length. It is difficult to explain why this removal of electron density does not lengthen the trans Pt-Cl bond greatly.

Alternatively the difference in Pt-P bond lengths between the different phosphine end groups could be a reflection of the greater cis-influence of the $(CF_3)_2P$-groups. The Muir and Muir[41] cis-influence series showed that phosphines with electronegative substituents e.g. PF_3 were comparatively good cis directors. Therefore the Pt-Cl bond lengths found may result from a combination on the one hand of a good trans director, Ph_2P- and a good cis director, $-P(CF_3)_2$, on the other hand a poor trans director, $-P(CF_3)_2$, and a poor cis-director, $-P(Ph)_2$.

The complex $-[PtCl_2(C_6H_5)_2PC_2H_4P(C_6F_5)_2]$ whose crystal structure has not been determined might well at first glance appear analogous to the $[PtCl_2(C_6H_5)_2 PC_2H_4P(CF_3)_2]$ complex. NMR investigations of both

complexes suggest that the former molecule is less distorted i.e. the differences between $-C_6H_5$ and $-C_6F_5$ are not nearly so great as the differences between $-CF_3$ and $-C_6H_5$. The phosphorus chemical shift for the $(CF_3)_2P$ moiety in the free ligand is 2.3 ppm while that of the $P(C_6F_5)_2$-group in the free ligand is -44.4 ppm. This suggests that CF_3 group is more electron withdrawing than the C_6F_5 although the phosphorus chemical shifts are not completely reliable parameters for comparing electron withdrawing properties of substituents. The phosphorus chemical shifts of the Ph_2P-moities are -13.1 ppm and -12.6 ppm in the free ligands. The fact that δp for the $(C_6F_5)_2p$- is upfield from these values and the δp for $(CF_3)_2p$- is downfield suggest great differences between these two groups. When complexed the J(Pt-P) for the $(CF_3)_2P$- end is 4013Hz while J(Pt-P) for the $(C_6F_5)_2P$- is 3820Hz. The values for the Ph_2P- ends are 3120Hz and 3434 Hz. Therefore it can be seen that $(C_6F_5)_2P$- cannot be regarded a completely analogous to the $(CF_3)_2P$- group. However the fact that the $J(Pt-P(C_6F_5)_2)$ is greater than $J(Pt-PPh_2)$ suggests that the $Pt-P(C_6F_5)_2$ bond is shorter than the $Pt-PPh_2$ bond. There has been considerable work done which confirms that the greater the J(Pt-P) the shorter the platinum-phosphorus bond.[86]

1.4.2.(ii) Halide Exchange Experiments

If the J(Pt-P) values reflect trans-influence the order of decreasing trans-influence and decreasing

J(Pt-P) for the phosphine groups attached to the bidendate ligand is;

$$(CF_3)_2P- > (C_6F_5)_2P- > Ph_2P-$$

but if platinum to chloride bond lengths are used to measure trans-influence the order is reversed, i.e. decreasing trans-influence and decreasing trans-Pt-Cl bond length.

$$Ph_2P- > (C_6F_5)_2P- > (CF_3)_2P-$$

Halide exchange experiments to reveal which phosphine group, the group with electro-negative substituents or the group with no electro-negative substituents, has the greatest trans-effect were carried out in the present study. Unfortunately due to time restraints only the complex $[PtCl_2(Ph_2PC_2H_4P(C_6F_5)_2)]$ was examined.

When a deficiency of lithium bromide or lithium iodide was added to a solution of the complex in acetone the resulting ^{31}PNMR contained eight phosphorus environments. These corresponded to four different molecules being present as each molecule contained two non-equivent phosphorus atoms. The complexes found to be present were one dichlorocomplex, one dibromo or one diiodo complex and two isomer each containing two different halogen atoms. (Diagram 1.27). Assignment of the signals was made using ^{1}H and ^{19}F decoupling experiments. Assignment of the mixed halogen complexes was made assuming a trans-substituted halogen would have

greater effect on the J(Pt-P) values than a cis-substitued halogen. The effect of substituting a chloride molecule with a bromide or iodide is to reduce the J(Pt-P).

The phosphorus signals obtained when lithium bromide was used were of equal intensity which immediately suggests there was no preferential substitution occurring. i.e. trans-effect of both phosphine groups is apparently the same (See Diagram 1.27)

When lithium iodide was added there appeared to be a slight preference for substitution to occur at the chloride position trans to the diphenyl phosphine.

Overall there seems to be little difference between the $(C_6F_5)_2P$- group and the Ph_2P-group with respect to their trans-effects.

Similar experimentsusing dithioethane complexes have been studies i.e. the halide substitution of the asymmetric chelate complex $[PtCl_2(CH_3SCH_2CH_2SCF_3)]$[87] . It was found that, initially, preferential bromide substitution occurred trans to CF_3S- group. This was then proceeded with cleavage of the Pt-S bond. In that work preference for the position trans to electronegative group was observed.

There are two possible explanations for the behaviour seen in the present halogen exchange experiments; (a) the trans- effect is the same for both $(C_6F_5)_2P$- group and $(C_6H_5)_2P$- group. Whether this is correlated to the trans-influence of the two groups is impossible to

say at this time; or

(b) the complexes are fairly insoluble in most solvents and the accumulation time necessary to obtain a reasonable spectrum is approximately ten minutes. It is very possible that in this time the isomers have reached an equilibrium position which does not reflect the situation present immediately after mixing.

These experiments are inconclusive. The halide substitution of the complex $[PtCl_2\ Ph_2PC_2H_4P(CF_3)_2]$ would have to be studied before any deductions could be made about trans-effects or trans-influences of the different ends of bidendate phosphine molecules.

Part 5 Future Work

Preparation and NMR investigation of complexes containing ligands such as $PPh_2(C_6F_5)$ and $PPh(C_oF_5)_2$ would be very interesting. Such ligands might exist in different helical forms at low temperatures. If this was the case the complexes would then contain chiral phosphorus centres and perhaps be catalysts for some asymmetric syntheses. These complexes might well exhibit different catalytic properties at different temperatures. A thorough investigation of these complexes as homogeneous catalysts would be a necessary prerequisite.

A fuller investigation, spectral and structural, of the bidentate complexes, $[\,Pt(Cl_2)Ph_2PC_2H_4P(CF_3)_2\,]$ and $[\,PtCl_2Ph_2PC_2H_4P(C_6F_5)_2\,]$ is required. The halide substitution reactions of the former complex might reveal much about the trans-effect and influence of the phosphine groups.

Appendix A

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Calculations of NMR-Parameters from Second-Order Spectra

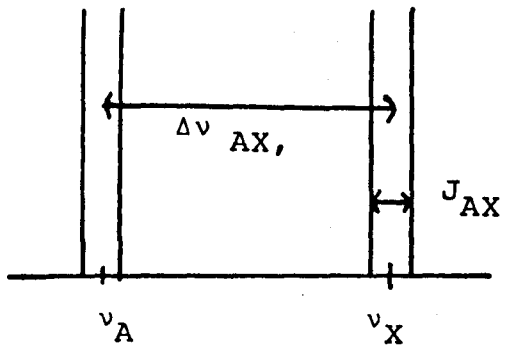
The nomenclature adopted for labelling non-equivalent magnetic nuclei is to give each nucleus a letter from the alphabet. Letters which are well separated in the alphabet are used to label nuclei with large chemical shift differences e.g. $CH_2ClCHCl_2$ is an A_2X system and CH_3CH_2F is an A_3M x system. These spectra are called first order. Second order spectra arise if the chemical shifts between the coupled nuclei are relatively small ; the spins are labelled with letters close together in the alphabet. Two coupled nuclei resonating close together are given letters A and B e.g. the ethyl group in $(CH_3CH_2)_3$ Ga where the methylene and methyl resonate close together is described as an A_3B_2 grouping. Mixed systems are also possible and a commonly encountered system is the three spin ABX group where two nuclei resonate close together and the third is well shifted from the others or is a different nuclear species.

Second order spectra arise when the frequency separation between multiplets due to different equivalent sets of nuclei is similar in magnitude to the coupling constant between them. The effects due to spin-spin coupling and chemical shift are of similar energy and become intermingled leading to alterations in the relative line intensities and in the line positions.

The following diagram shows an AX system and an AB system.

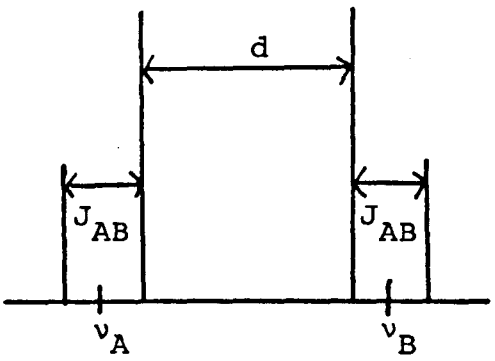
Diagram A.1.

AX SYSTEM



$\Delta\nu_{AX} \gg J_{AX}$

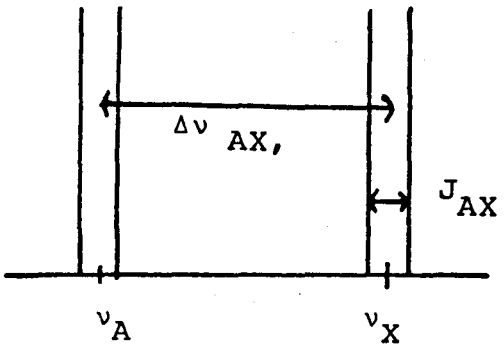
AB SYSTEM



$\Delta\nu AB \simeq J_{AB}$

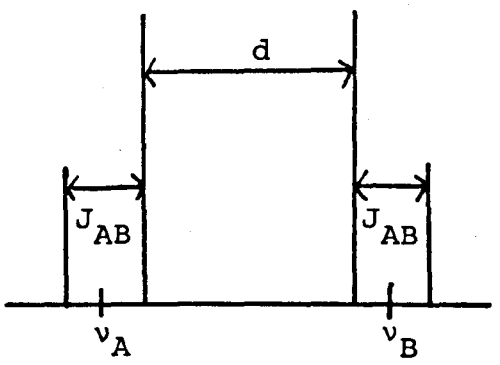
Diagram A.1.

AX SYSTEM



$\Delta\nu_{AX} \gg J_{AX}$

AB SYSTEM



$\Delta\nu AB \simeq J_{AB}$

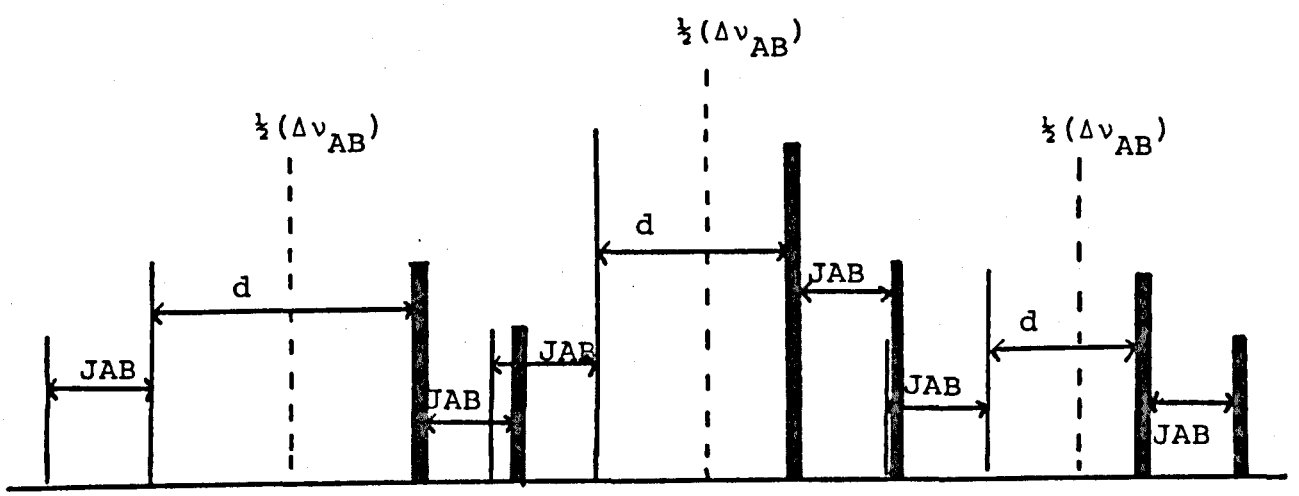
The AB system can be analysed following these simple rules:

1) The spectrum contains two intervals equal to J_{AB} (Diagram A1)

2) The trueAB chemical shift is found using the equation $\nu_{AB} = \sqrt{d(d+2J_{AB}}$ where d is the separation between the innermost lines.

In the case of the ABX type spectrum the AB part is second order and close AB coupling leads to a second order perturbation in the X region of the spectrum also. The AB part can be considered to the made up of AB subspectra, e.g. when X = Pt three subspectra corresponding to $X_{spin} = +\frac{1}{2}$; $X_{spin} = 0$; and $X_{spin} = -\frac{1}{2}$. Where X = Pt only the AB part of the spectrum is usually obtained. An example of which is shown below

Diagram A.2.



This is analysed similarly to the AB spectrum.

1) There are six line spacing equivalent to J_{AB} shown

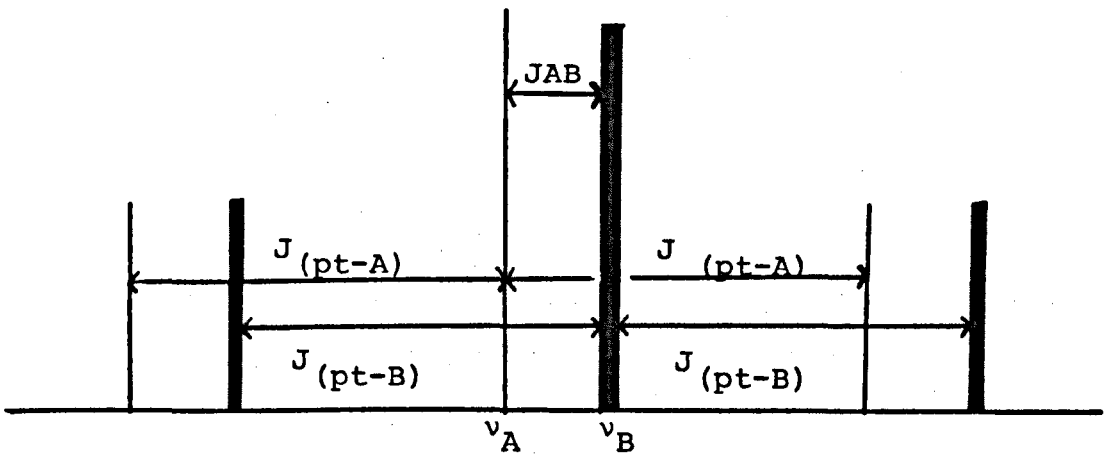
in the diagram. A.2.

2) The true chemical shifts are obtained using the equation $\nu_{AB} = \sqrt{d(d+2J_{AB})}$.

When the true chemical shifts are calculated a spectrum is obtained from which the J(Pt-A) and J(Pt-B) values are obtained.

i.e.

Diagram A.3.



Hence values for δP_H, δP_F, J(P-P), J(Pt-P_H) and J(Pt-P_F) were obtained for the complexes <u>trans</u>-$[PtCl_2(Ph_3P)P(C_6F_5)_3]$, <u>trans</u>- $[PtBr_2(PMe_2Ph)P(C_6F_5)_3]$ and <u>trans</u>- $[PtCl(Ph)(PMe_2Ph)P(C_6F_5)_3]$;

SECTION 2

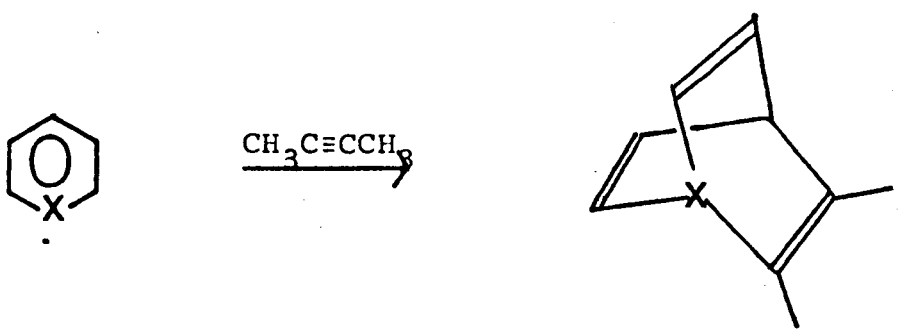
Preparation and Thermal Decomposition of Some Dichloroplatinum (II) Complexes Containing Substituted-Pyridine Ligands

Section 2

Part 1 Introduction

Pyridine is an analogous molecule to benzene in terms of aromaticity and carbon-carbon bond lengths. Replacement of a carbon atom by a heteroatom destroys the symmetry of the ring and it is known that the aromatic character of the ring decreases as the size of the heteroatom increases. Pyridine like benzene has no tendancy to react as a diene but the phosphorus analogue undergoes the Diels Alder reaction at temperatures greater than 283 K and the arsenic compound reacts at room temperature.[89]

Diagram 2.1



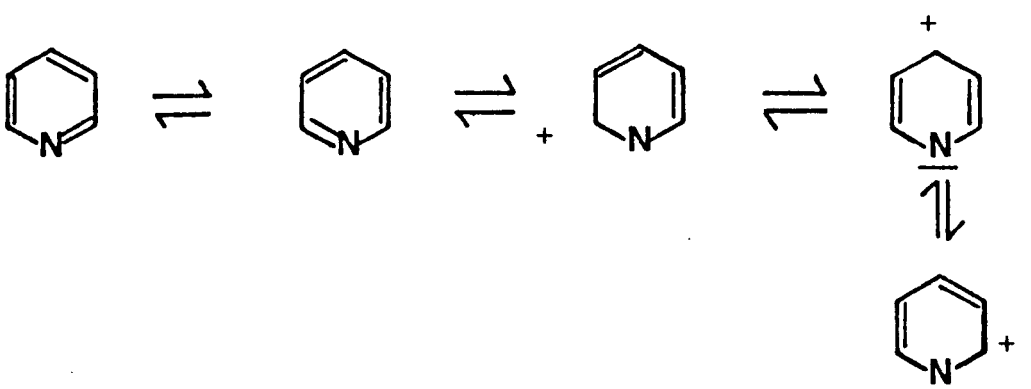
The bond lengths in pyridine are intermediate between double bonds and single bonds as is expected in an aromatic system. Table 2.1 shows that bond lengths in pyridine and benzene, the classic aromatic molecule, are similar in magnitude.

Table 2.1

Molecule	C-C Bond length ^{1} ^{o} (A)
Pyridine	1.39
Ethane	1.54
Ethene	1.34
Benzene	1.39

Introduction of a heteroatom to the benzene structure results in more canical forms of the resonance hybrids.

Diagram 2.2

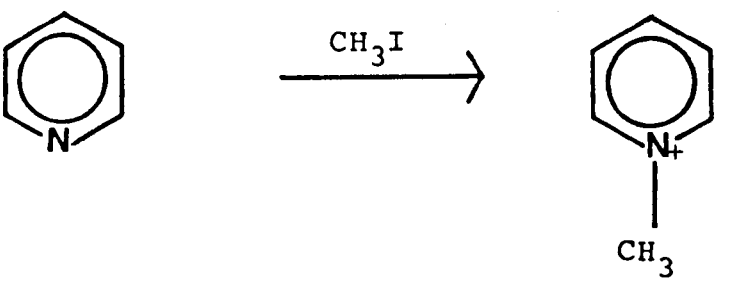


The electronegativity of the nitrogen atom, in the above example , localises the negative charge and it follows that positions 2, 4 and 6 have partial positive charges.

The heterocyclic analogues of benzene are less basic than their corresponding aliphatic compounds, e.g. pyridine-type molecules are less basic than aliphatic amines due to the partial removal of the electron density of the nitrogens lone pair into the aromatic system. In general the heterocycles are still capable of forming stable salts with strong acids.

Pyridine with its electronegative nitrogen atom is more unreactive towards electrophilic reagents than benzene. Many of the reagents react at nitrogen rather than carbon.

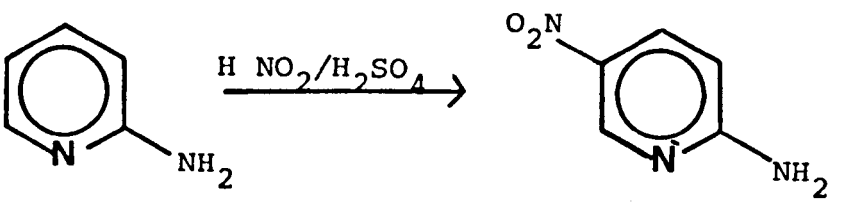
Diagram 2.3



Electrophilic substitution, when it occurs, takes place at positions 3 and 5 on the ring, since these positions have no positive charge.

Electron donating substituents on the ring will encourage electrophilic substitution and will direct replacement to the positions ortho and para to the substituents.

Diagram 2.4



Although deactivated towards electrophilic reagents pyridine will react with strongly necleophilic reagents and nucleophilic substitution will occur at positions 2, 4 and 6 on the ring because these positions are electron deficient.

The lone pair on the nitrogen atom allows pyridine and substituted pyridines to form complexes with transition metals. Cis and trans Dichloro bispyridineplatinum (II) complexes have been known since 1886.[90] Since then there have been many examples of pyridine and substituted pyridines behaving as ligands, e.g. $[\ Ptn(R\text{-}C_3H_4)(C_6H_5N)_2O_2\ ]$[91] and $[MoBr_4(C_6H_5N)_4]$.[92]

The thermal decomposition of transition metal complexes containing pyridine and substituted-pyridine complexes have been extensively studied. Complexes of chromium (II), manganese (II), iron (II), cobalt (II), nickel (II), copper (II) and zinc (II) with ligands pyridine, α, β and γ picoline, 2,6-lutidine and 2,4,6-collidine have been studied.[93]

Many of these complexes were prepared by the thermal decomposition of compounds containing a high ligand to metal ratio. The decomposition patterns varied from metal to metal, however it was generally found that the first decomposition step resulted in the loss of one or more pyridine-type ligands. The octahedral $[\ CoX_2L_4\ ]$ was shown to lose two neutral ligands, L, and form the tetrahedral $[\ CoX_2L_2\ ]$.[94]

Dichlorobispyridinenickel (II) was found to undergo thermal decomposition to give dichloromonopyridinenickel (II) and dichloronickel (II).

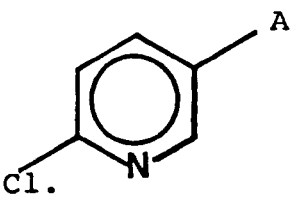
Thermal decomposition was studied in most cases by some combination of the following techniques; thermogravimetric analysis; differential thermal analysis; pyrolysis in the mass spectrometer; and chemical analysis of the residues and the decomposition products.

One very important property of metal complexes with nitrogen-containing ligands is their apparent biological activity. Rosenberg et al[95] reported in 1969 that complexes cis-$[PtCl_4(NH_3)_2]$, cis-$[PtCl_2(NH_3)_2]$, $[PtCl_2(en)]$ and $[PtCl_4(en)]$, (where (en) = $H_2NCH_2CH_2NH_2$) were active as antitumour agents.[92] In quite separate studies Gillard and co-workers noted the antibacterial activity of trans-$[RhL_4X_2]$ complexes (L = pyridine, 4n-propylpyridine or 4-ethyl-pyridine). In 1972 A.J. Thomson et al[96] published a review which discussed the biological activity of transition metal complexes in depth. The authors outlined the types of molecules which have potential biological activity and examined the interaction of metal complexes with biological molecules and macromolecules, e.g. the substitution at the chloro sites in complexes cis and trans- $[PtCl_2(NH_3)_2]$ by amino acid groups $-NH_2$, $-CO_2^-$, $-SCH_3$, etc. There is currently considerable interest and research in this field.

Diagram 2.5 contains a list of the substituted pyridines investigated in the present work. These ligands are potentially useful as starting materials for the manufacture

of herbicides.[97] An attempt to synthesis the ligands from pyridine and 2-chloropyridine was made. Dichloroplatinum (II) complexes containing the various substituted pyridine rings were prepared and characterised. A study of the ligand properties of these molecules was undertaken. A preliminary investigation of the thermal decomposition of the prepared complexes was carried out using the thermogravimetric analysis technique. The influence of the pyridine ligands on the J(Pt-P) of complexes containing a substituted-pyridine ligand trans to a triphenylphosphine ligand was examined.

Diagram 2.5

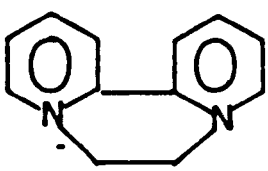


A = H, CH_3, $C Cl_3$, or CF_3,

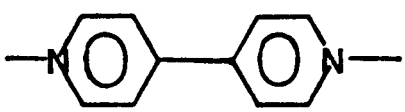
Part 2 Experimental Procedure

2.2.1. Attempted Preparation of the Substituted Pyridine ligands

Substituted pyridines are used as starting materials for the synthesis of many important pharmaceutical and agricultural chemicals,[97] e.g. paraquat and diquat. Diagram 2.6.



Diquat

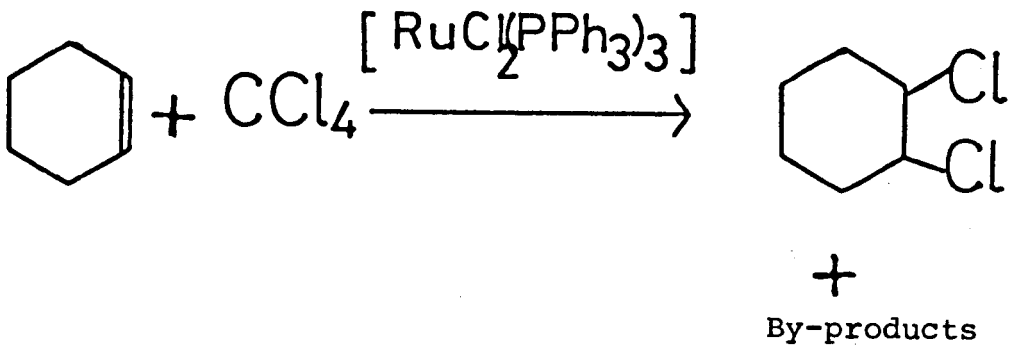


Paraquat

There has in recent years been much interest in finding more ecologically acceptable herbicides. One possibility has 2-chloro, 5-fluoromethyl pyridine as a starting material. Conventional preparation of this type of molecule require severe reaction conditions. Other complications are low yields and the production of unwanted isomers.[98]

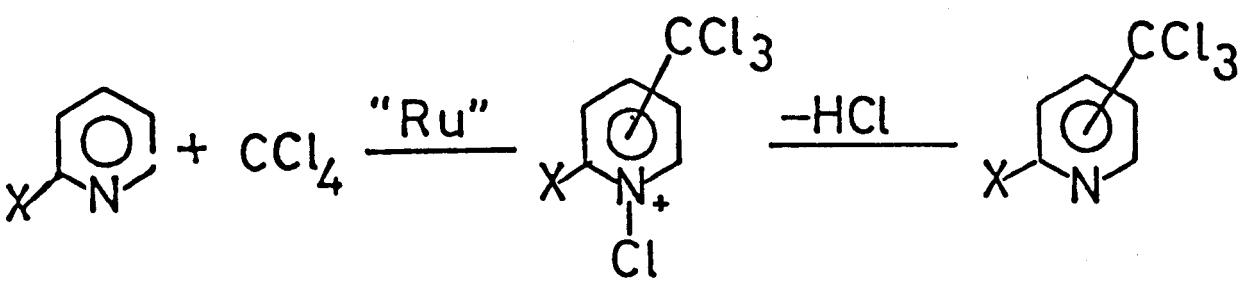
The ruthenium complex dichloro tris(triphenylphosphine) ruthenium (II) was shown by Matsumoto et al[99] to catalyse the addition of carbon tetrachloride across aliphatic double bonds.

Diagram 2.7



Similar experiments have now been carried out replacing the aliphatic substrate with pyridine and 2-chloropyridine to determine whether the ruthenium (II) complex is able to catalyse the addition of carbon tetrachloride to an aromatic system. A possible reaction scheme is shown in diagram 2.8.

Diagram 2.8



The addition of molecular hydrogen to aliphatic and aromatic systems is known to be effected by the same catalysts, e.g. the hydrogenation of benzene and cyclohexane is known to occur over a nickel-silica catalyst.[100] Therefore the proposed addition of carbon tetrachloride to the aromatic pyridine system was not unreasonable.

Table 2.2 contains a summary of the reactions attempted.

Table 2.2

Experiment Number	Reactants	% Reaction
1	$[RuCl_2(PPh_3)_3]$ Cyclohexene (1.65g) CCl_4	82.6
2	$[RuCl_2(PPh_3)_3]$ 2-chloropyridine (1.4g) Cyclohexene (1.60g) CCl_4	60.0
3	$[RuCl_2(PPh_3)_3]$ 2-chloropyridine (2.18g) CCl_4	0
4	$[RuCl_2(PPh_3)_3]$ Pyridine (2.2g) CCl_4	0

The reactions were carried out in sealed 250 ml carius tubes which were air free, sealed and heated to 283 K for twenty four hours. 0.15g of $[RuCl_2(PPh_3)_3]$ and 24.0 g of carbon tetrachloride were standard amounts of complex and reactant used in each of the reactions attempted. Analyses of the reaction products were carried out using a Perkin Elmer F.I.D. chromatographic detector with 16' columns packed with chromosorb 101. The oven temperature was 473 K. The ruthenium complex was prepared using the method described by T.A. Stephanson et al.[101]

Experiment 1 was carried out using freshly prepared $[RuCl_2(PPh_3)_3]$, cyclohexene, and carbon tetrachloride. It was found that 82.6% reaction occurred. The percentage reaction was calculated on the amount of substrate present before starting the reaction and that used up during the reaction. This experiment showed the freshly prepared complex was active for the addition of carbon tetrachloride to cyclohexene. In the second experiment 1.4g of 2-chloro-pyridine was added to ascertain whether the complex remained active in the presence of the substituted-pyridine. 60% reaction was observed in experiment 2 and this confirmed the catalyst was still active. No reaction was observed in experiments 3 and 4 when pyridine and chloro-pyridine but no cyclohexene were present.

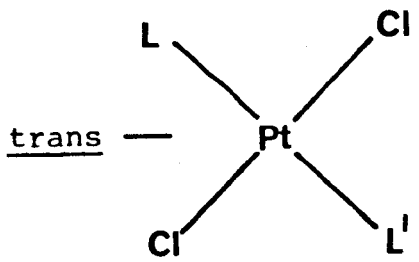
Therefore it appears that the ruthenium complex $[RuCl_2(PPh_3)_3]$ has no ability, under these reaction conditions to catalyse the addition of carbon tetrachloride to an aromatic system

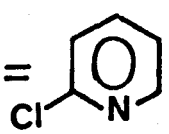
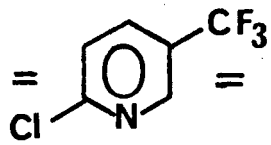
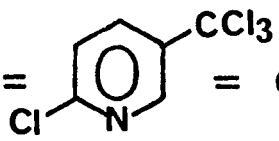
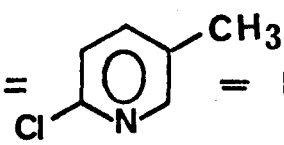
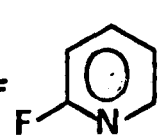
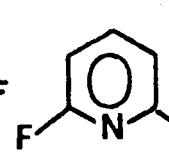
2.2.2. Preparation and Characterisation of Platinum (II) Complexes Containing Substituted-Pyridine ligands

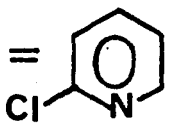
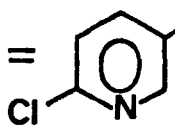
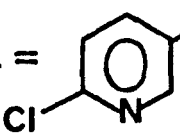
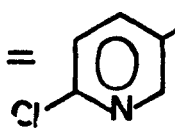
The substituted pyridine molecules (shown in diagram 2.5 were used as ligands. The substituted pyridines were prepared and donated by I.C.I. Mond Division except for the 2-fluoro- and 2,6-difluoropyridines which were purchased from Fluorochem Ltd. The substituted pyridines were prepared by successive alkylation, chlorination and fluorination reactions.

Table 2.3 contains an index of complexes prepared.

Table 2.3



Complex Number	Ligand
1	L = L' =  = A
2	L = L' =  = B
3	L = L' =  = C
4	L = L' =  = D
5	L = L' =  = E
6	L = L' =  = F

Complex Number	Ligands
7	L =  ; $L^1 = PPh_3$
8	L =  ; $L^1 = PPh_3$
9	L =  ; $L^1 = PPh_3$
10	L =  ; $L^1 = PPh_3$

2.2.2.(i) Preparation of Bis(substituted pyridine) Platinum (II) Complexes

The complexes were prepared by the addition of potassium tetrachloroplatinate to an aqueous suspension of the substituted pyridine in a 1:2 molar ratio. The solutions were left with stirring at room temperature for various lengths of time (12 - 36 hours). The colour of the solutions gradually changed from red to yellow and this colour change determined the reaction time. The products were obtained by extracting the complexes with chloroform. The yields obtained with the 2-chloro- and 2-fluoropyridine were high ~ 80%. The other substituted pyridines gave low yields between 25% and 30% due to substantial reduction of the platinum (II). The stoichiometries were obtained by microanalyses (table 2.8). Infra-red spectroscopy was used to determine whether the complexes were cis or trans (table 2.7). ^{1}H NMR was used to confirm, initially, that complex formation had occurred (table 2.4 and 2.5).

2.2.2. (ii) Preparation of the Mono (substituted-Pyridine) Platinum (II) Complexes

The substituted-pyridines A-D (Table 2.3) were added to a chloroform suspension of the dimer $[Pt_2Cl_4(PPh_3)_2]$ in equimolar amounts. The products were obtained by recrystallisation from the chloroform solutions. No reduction of the platinum (II) occurred and yields were approximately 80%. Characterisation was carried out by microanalysis, infra-red and ^{31}P NMR spectroscopy. The J(Pt-P) values obtained were used to determine the trans-influence of the pyridine ligands.

Table 2.4 ^{1}H NMR Chemical Shifts of ligand A-F

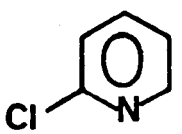
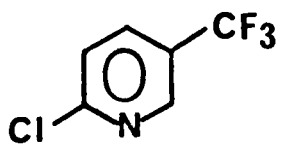
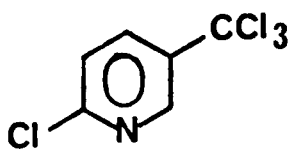
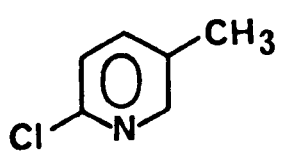
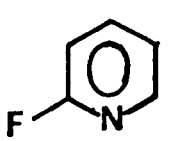
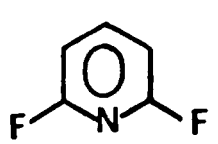
ligands	solvent	^{1}H (ppm)
	$(CD_3)_2CO$	H_3 - 7.54(s) H_4 - 7.81(g) H_5 - 7.36(s) H_6 - 8.42(s)
	$(CD_3)_2CO$	H_3 - 7.69(d) H_4 - 8.18(d) H_5 - 8.75(s)
	$(CD_3)_2CO$	H_3 - 7.65(d) H_4 - 8.35(d) H_6 - 8.97(s)
	$(CD_3)_2CO$	H_3 - 7.23(d) H_4 - 7.55(s) H_6 - 8.15(s)
	$(CD_3)_2CO$	H_3 - 7.13(d) H_4 - 8.10(d) H_5 - 7.51(g) H_6 - 8.57(d)
	$(CD_3)_2CO$	H_3 - 7.19(d) H_4 - 8.31(g) H_5 - 7.19(d)

Table 2.5 ^1H NMR Chemical Shifts (ppm) of Complexes 1 - 4

Complex	Solvent	δ^1H
1 (see table 2.3)	$(CD_3)_2CO$	H_3 - 7.80 (s) H_4 - 7.94 (tr) H_5 - 7.69 (s) H_6 - 8.86 (s)
2	$(CD_3)_2CO$	H_3 - 8.00 (d) H_4 - 8.33 (d) H_6 - 9.34 (tr)
3	$(CD_3)_2CO$	H_3 - 7.87 (tr) H_4 - 8.42 (tr) H_6 - 9.62 (q)
4	$(CD_3)_2CO$	H_3 - 7.35 (d) H_4 - 7.72 (q) H_6 - 8.24 (s)

Table 2.6 ^{31}P NMR Data for Complexes 7 - 10

Complex	$\delta\ ^{31}P$	J(P - Pt)
7	1.5	3825
8	1.4	3895
9	1.14	3933
10	1.5	3804

Table 2.7

Complex Number	1	2	3	4	5	6	7	8	9	10
ν(Pt-Cl)	340	330	335	335	345	340	345	350	349	345

Table 2.8 Micro-analysis Results

Complex		C	H	N	Cl
1	Theory	24.3	0.6	5.6	28.8
	Found	24.3	1.6	5.6	27.7
2	Theory	22.8	0.9.	4.4	22.5
	Found	21.7	0.8	4.2	21.9
3	Theory	19.7	0.8	3.8	48.7
	Found	19.2	0.7	3.2	48.4
4	Theory	27.6	2.3	5.3	27.2
	Found	26.9	2.1	5.2	27.1
5	Theory	26.0	1.7	6.0	15.4
	Found	25.2	1.2	5.5	14.3
6	Theory	24.2	1.2	5.6	14.3
	Found	23.5	1.2	4.6	13.5
7	Theory	43.6	2.8	2.1	16.6
	Found	42.9	2.7	1.5	15.5
8	Theory	40.5	2.5	1.9	15.0
	Found	40.4	2.1	1.7	14.8
9	Theory	37.9	2.3	1.8	28.0
	Found	36.9	1.9	2.4	29.5
10	Theory	43.9	3.2	2.1	16.5
	Found	42.8	3.1	2.0	15.9

2.2.3. Thermogravimetric Analysis of the Prepared Complexes

Thermal behaviour may be used to measure the stability of inorganic complexes.

In this study the decomposition temperature is that temperature at which the complex degrades and evolution of volatile material occurs.

The instrument used was a Dupont 950 Thermogravimetric Analyser. The main components of this system are;

(a) the microbalance which is connected to a photocell which is in turn linked to a pen recorder, and

(b) an oven which is placed around the pan containing the sample. Temperature changes are detected using a thermocouple device.

Hence as the temperature increases the weight loss versus temperature increase is monitored. Diagram 2.9 is an example of the type of trace obtained. The analyses were carried out under a nitrogen stream.

If the calculated weight loss is matched to a theoretical weight loss then a degradation pattern can be obtained for each complex.

The cut out temperature was 673 K and decomposition above this temperature was not examined.

Table 2.9 contains the results of the thermogravimetric analyses. The formulae presented for the decomposition products must be regarded as empirical rather than structural as time did not allow a full analysis of the decomposition products to be carried out.

As can be seen from table 2.9 the temperature at which the first decomposition occurs can be measured assuming all the molecules lost from the complex are volatile at the decomposition temperatures.

Table 2.9 shows the weight loss of the sample in milligrams and also the percentage weight loss calculated from

$$\frac{\text{Weight loss (mg)}}{\text{Initial weight (mg)}} \times 100$$

Included in table 2.9 is the theoretical weight loss in A.M.U.'s and the theoretical percentage weight loss calculated by the same method as the actual percentage weight loss. Table 2.9 also contains the temperatures at which the first decompositions occur. These values were taken as representing the decomposition temperatures of the complexes.

Table 2.9 Thermogravimetric Analyses

Complex (Table 2.3)	Mol Wt	Sample weight mg	Weight loss % (Theoretical)	Temp K
1				
$[PtCl_2(A)_2]$	492	5.0		
$\downarrow -A(Cl)_2$	$\downarrow$	$\downarrow$	35.0 (37.3)	553
$[Pt(A)]_n$	308	3.25		
2				
$[PtCl_2(B)_2]$	629	8.5		
$\downarrow -B$	$\downarrow$	$\downarrow$	27.0 (28.0)	482
$[PtCl_2(B)]_n$	447	6.2		
3				
$[PtCl_2(C)_2]$	728	9.6		
$\downarrow -C$	$\downarrow$	$\downarrow$	33 (31)	507
$[PtCl_2(C)]_n$	426	6.4		
4				
$[PtCl_2(D)_2]$	521	10.0		
$\downarrow -D_2Cl$	$\downarrow$	$\downarrow$	51.0 (55.7)	498
$[Pt(Cl)]_n$	231	4.9		

Table 2.9 continued

Complex	Mol Wt	Sample weight mg	Weight loss %	Temp K
5				
$[PtCl_2(E)_2]$	460	4.75		
↓ -E	↓	↓	22.0 (21.0)	538
$[PtCl_2(E)]_n$	363	3.70		
6				
$[PtCl_2(F)_2]$	496	4.8		
↓ -ClF	↓	↓	27.8 (30.3)	548
$[PtCl(F)]_n$	345	3.5		
7				
$[PtCl_2(PPh_3)(A)]$	641	5.0		
↓ - A	↓	↓	18.0 (17.7)	493
$[PtCl_2(PPh_3)]_n$	528	4.1		
↓ - Cl_2	↓	↓	12.0 (11.1)	563
$[Pt(PPh_3)]_n$	451	3.5		

Table 2.9 continued

Complex	Mol Wt	Sample weight mg	Weight loss %	Temp K
8				
$[PtCl_2(PPh_3)(B)]$	709	4.7		
↓ - B	↓	↓	25.5 (25.6)	448
$[PtCl_2(PPh_3)]_n$	528	3.5		
↓ $- Cl_2$	↓	↓	10.6 (11.1)	556
$[Pt(PPh_3)]_n$	457	3.0		
9				
$[PtCl_2(PPh_3)(C)]$	759	4.0		
↓ - C	↓	↓	30.0 (30.4)	473
$[PtCl_2(PPh_3)]_n$	528	2.8		
↓ $- Cl_2$	↓	↓	10.0 (9.3)	558
$[Pt(PPh_3)]_n$	457	2.4		

Table 2.9 continued

Complex	Mol Wt	Sample weight mg	Weight loss %	Temp K
10				
$[PtCl_2(PPh_3)(D)]$	655	5.0		
↓ -D	↓	↓	20.0 (19.4)	458
$[PtCl_2(PPh_3)]_n$	528	4.0		
↓ $-Cl_2$	↓	↓	10.0 (10.8)	555
$[Pt(PPh_3)]_n$	457	3.5		

Part 3 Discussion

The complexes were prepared as described. The chemical analyses showed the stoichiometry was $[PtCl_2LL']$ (where $L=L^1=A,B,C,D,E,F$ or $L=A,B,C,D$, and $L^1=PPh_3$). Infra-red spectroscopy was used to confirm the trans stereochemistries of the complexes.

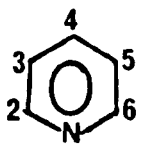
It is well known that complexes of the type trans $[PtCl_2A_2]$ (A is a neutral ligand) will display a single bond in the far infra-red region (200-800 cm^{-1}), usually between 300-375 cm^{-1}, corresponding to the asymmetric vibration of the linear Cl-Pt-Cl unit. In cis-isomers this band is split into two since both the symmetric and asymmetric stretching modes of the angular cis-$PtCl_2$ unit are active in the infra-red. Table 2.7 shows the frequencies of the bands which have been assigned to the Pt-Cl bond vibrations.

Clark and Williams[101] have shown that ν (M -N) occur in the region 287 to $\sim$ 200 cm^{-1} of the infra-red spectrum. Bands near 500 cm^{-1} in some platinum and palladium complexes of pyridine and other heterocycles were assigned by Coates and Parkin[103] to ν(M-N) but according to Adams et al[104] these are due to the internal modes of the ligands. It was not possible in the present work to assign bands to ν(Pt-N) because of lack of facilities capable of accurately scanning below 300 cm^{-1}.

Confirmation of the reactions of ligands A-D with potassium tetrachloro platinate was obtained by comparing the proton NMR of the ligands and the complexes. The signals in the H^1 NMR of the complexes were downfield from the corresponding signals in the ligands spectra. Electron withdrawal from the ligand to the metal as a result of bonding would cause deshielding of the proton nuclei and hence the signal would shift downfield.

Assignment of the signals observed in the 'H NMR of ligands A-F to particular hydrogen atoms on the pyridine ring was achieved by (a) comparison with analogous molecules and (b) consideration of the fine structure of the signals.

Table 2.10 contains proton NMR data for pyridine. This shows that H_6, H_4 and H_2 (8.59 ppm, 7.75 ppm and 8.5 ppm) hydrogen atoms resonate further downfield than H_3 and H_5 (7.38 ppm) hydrogen atoms. Presumably this order is a



reflection of the partial positive charges on positions 2, 4 and 6 which arise from the localisation of electron density by electro-negative nitrogen atom. The proton NMR of 2-chloropyridine had the following order of increasing field strengths and decreasing chemical shifts for the hydrogen nuclei.

H_6 (8.54ppm) > H_4(7.83ppm) > H_3(7.49ppm) > H_5(7.39ppm).

In 2-fluoropyridine a similar order was obtained

H_6(8.61ppm) > H_4(8.03ppm) > H_5(7.40ppm) > H_3(7.17ppm)

In the molecule 2,5 dichloropyridine the order of decreasing chemical shift was

H_6(8.70 ppm) > H_4(8.13 ppm) > H_3(7.68)

The above assignements were confirmed by analyses of deuterated analogues. An example of this type of analyses is shown in Table 2.10. This shows that replacement of one hydrogen by a deuterium atom in 3-methylpyridine causes the signal for this hydrogen atom to disappear and therefore assignment of this particular hydrogen atom to a signal in the undeuterated sample is accomplished. The other hydrogen atoms can be similarly assigned. In the present work the matching of ^{1}H NMR signals to particular hydrogen atoms in the ligands examined i.e. 2-chloro, 5-methyl pyridine, 2-chloro, 5-trifluoromethyl pyridine and 2-chloro, 5-trichloromethyl pyridine was accomplished by comparison of the ligands spectra with the spectrum of 2,5-dichloropyridine. The following order of decreasing chemical shift was obtained for the ligands B-D (Table 2.3 and 2.4) e.g. 2-chloro, 5-methylpyridine.

H_6 (8.15ppm) > H_4 (7.55ppm) > H_3 (7.23ppm)

The assignment was confirmed by the fine structure of the signals. The signals of H_4 and H_3 which couple with each other are doublets but the signal of H_6 whose coupling to H_4 is very small, appears as a singlet.

The proton spectrum of 2,6-difluoro pyridine contained one doublet (7.19 ppm) and a quintet (8.31 ppm). The doublet (intensity 2) corresponded to H_3 and H_5 which are equivalent and the fine structure of the signal results from coupling with H_4. The quintet (intensity 1) results from the resonance of H_4; the fine structure arises from coupling with H_3, H_5 and the two fluorine atoms

Conclusive assignment of the proton signals observed in the NMR of the ligands used in the present work would require analyses using deuterated analyogues of the ligands. Time restraints prevented such an analyses.

It was assumed the same order of proton chemical shifts was observed when the ligand was complexed. The signals in the NMR of the complexed ligands were in general poorly resolved and spectra were not obtained for complexes 5 and 6 because of lack of solubility of the complexes. (see table 2.5).

Table 2.10 ^{1}H NMR Chemical Shifts (ppm)[105]

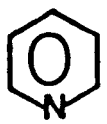
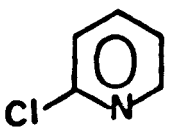
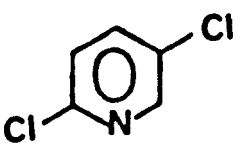
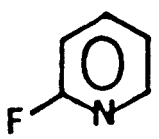
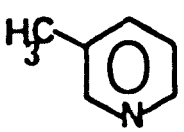
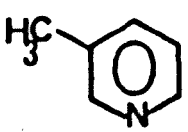
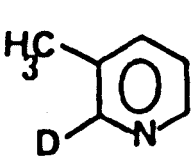
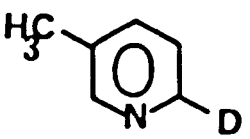
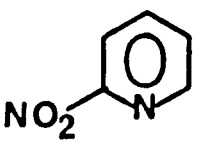
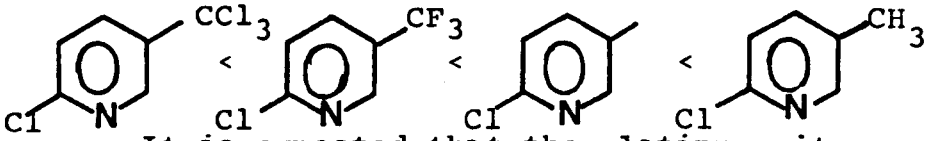
Molecule	Solvent	$\delta_{^1H}$
	DMSO	H_2 - 8.59 H_3 - 7.38 H_4 - 7.75
	Neat	H_3 - 7.49 H_4 - 7.83 H_5 - 7.39 H_6 - 8.54
	Neat	H_3 - 7.68 H_4 - 8.13 H_6 - 8.70
	Neat	H_3 - 7.17 H_4 - 8.03 H_5 - 7.40 H_6 - 8.61
	CH_3CN	H_2 - 8.40 H_4 - 7.50 H_5 - 7.16 H_6 - 8.40
	CH_3CN	H_2 - 8.40 H_4 - 7.50 H_5 - 7.16 H_6 - 8.40
	CH_3CN	H_4 - 7.50 H_5 - 7.15 H_6 - 8.37

Table 2.10 continued

Molecule	Solvent	^1H
	CH_3CN	H_2 - 8.37 H_4 - 7.52 H_5 - 7.13 CH_3 - 2.26
	Neat	H_3 - 8.47 H_4 - 8.42 H_5 - 8.12 H_6 - 8.85

The J(Pt-P)'s obtained from the phosphorus NMR of complexes 7-10 (table 2.6) may be used to determine the trans-influence of the ligands A-D. The platinum-phosphorus coupling constant increases with decreasing trans-influence. The increase in trans-influence with respect to the substituent on position 5 in the pyridine ring is



It is expected that the platinum-nitrogen bond formed in complexes 7 and 10 would be stronger than the platinum-nitrogen bond in complexes 8 and 9 because the hydrogen atom and the methyl group are slightly electron-donating whilst the trifluoromethyl and trichloromethyl groups are electron withdrawing. Therefore the electron-density on the nitrogen atom in complexes 7 and 10 is greater and hence the platinum-nitrogen bond is stronger. The stronger the platinum-nitrogen bond the weaker the trans phosphorus-platinum bond and hence the J(Pt-P). This accounts for the J(Pt-P) values obtained for complexes 7 - 10.

Thermogravimetric analyses for complexes produced decomposition temperatures for the complexes. The temperatures quoted in table 2.9 are the temperatures at which the first decomposition occurred. The following order of increasing thermal stabilities was obtained

Complex 2 < Complex 4 < Complex 3 < Complex 5 < Complex 6 < Complex 1.

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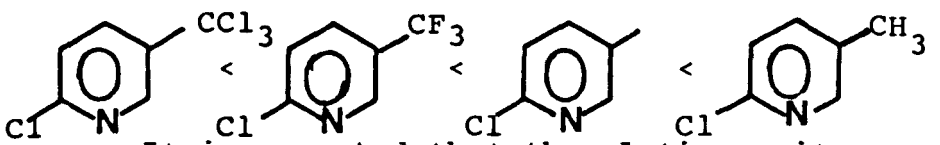

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Thermogravimetric analyses for complexes produced decomposition temperatures for the complexes. The temperatures quoted in table 2.9 are the temperatures at which the first decomposition occurred. The following order of increasing thermal stabilities was obtained

Complex 2 < Complex 4 < Complex 3 < Complex 5 < Complex 6 < Complex 1.

It is noted that the mode of decomposition which was observed is not the same for all the complexes.

The thermal stability of complexes 7 - 10 increased in the order

Complex 8 < Complex 10 < Complex 9 < Complex 7

This preliminary investigation showed that complexes 1, 5 and 6 which contain 2-chloro, 2-fluoro, and 2,6-difluoro substituted pyridine ligands were the most thermally stable.

The weight loss during the first decomposition of complex 1 corresponded to the loss of one neutral ligand and two chlorine atoms. Complex 4 lost the equivalent of two pyridine ligands and one chlorine atom. The weight loss observed for complex 6 was equivalent to losing one pyridine ligand and one chlorine atom. On the other hand in complexes 2, 3 and 5 the first molecule to dissociate was the substituted pyridine.

In previous studies by other workers[94] the thermal decomposition of pyridine complexes occurred initially by the dissociation of the neutral ligand. It is unusual that in complexes 1, 4 and 6 the initial decomposition involves the loss of chlorine atoms. An explanation for this could lie in the bond strengths of the platinum-chlorine and platinum-nitrogen bonds. Another explanation might be that some kind of rearrangement of the complex occurs during decomposition. A full analyses of decomposition products

might provide the answer however time did not permit a fuller investigation during the present work.

Reasons for the different decomposition temperatures and decomposition pathways observed are at present unknown. The variations could possibly arise from different resonance and inductive effects within the differently substituted pyridine rings.

In complexes 7 - 10 the substituted pyridine dissociates before the phosphine or chloride ligands. The temperatures at which the decomposition occurs in these complexes are lower than in complexes 1 - 6. Both these observations are probably consequences of the phosphine ligands high trans-influence which weakens the trans platinum-nitrogen bond.

Part 4 Future Work

Complexes of the substituted pyridines with other transition metals could be prepared e.g. palladium rhodium and iridium complexes.

A more detailed study of the thermal decomposition would be interesting and worthwhile. Chemical and spectral analyses of the decomposition products is necessary before any firm conclusions can be drawn about the decomposition pathways and the structure of the reaction products.

These complexes may also have biological activity, e.g. as antitumour or anti-bacterial agents because similar types of complexes are known to be effective. Therefore testing of the complexes as potential antitumour or anti-bacterial agents is a possibility for future research.

Appendix B(i) Infra-Red Spectral Analysis of Ligands (A - F).

LIGAND	frequency (cm^{-1})			
A (See table 2.3)	3060(s);	3000(w);	1610(w);	1580(vs);
	1520(vs);	1500(w);	1454(vs);	1420(vs);
	1288(s);	1150(vs);	1120(vs);	1084(vs);
	1045(s);	990(s);	965(vs);	725(vs);
	620(s);	480(s);	428(s);	408(s);
B	3100(w);	3050(w);	1600(vs);	1571(vs);
	1470(vs);	1380(s);	1330(vs);	1250(s);
	1220(s);	1170(vs);	1135(vs.br);	1110(vs);
	1080(vs);	1015(vs);	940(s);	840(vs);
	795(s);	750(s);	635(w);	610(w);
	505(s);	415(s);		
C	3099(vs)	3060(w);	3009(s);	1580(vs);
	7560(vs);	1505(s);	1475(s);	1465(s);
	1369(vs);	1352(s);	1300(s);	1245(s);
	1200(s);	1155(s);	1112(s);	1055(s);
	1025(vs);	980(w);	940(s);	880(s);
	810(vs);	770(vs);	725(s);	485(s);
	418(s);	400 (s);	385(s):	
D	3050(w);	3000(w);	2915(w);	1589(us);
	1570(vs);	1460(vs);	1370(s);	1290(w);
	1220(s);	1135(s);	1105(vs);	1081(w);
	1029(s);	821(s);	730(s);	645(s);
	630(s);	490(s);	415(w):	

Ligand	frequency (cm^{-1})			
E	3070(w);	1620(s);	1599(vs);	1560(vs);
	1475(vs);	1435(vs);	1300(w);	1245(vs);
	1145(s);	1100(w);	1050(w);	999(s);
	835(s);	780(vs);	735(w);	625(w);
	555(s);	520(w);	420(w):	
F	3100(w);	1610(s.br);	1445(vs);	1380(w);
	1309(vs);	1130(s);	1230(vs);	1140(s);
	1070(w);	990(vs);	790(vs);	535(vs);
	520(s);	369(s);	300(s):	

Appendix B (ii)

Infra-Red Spectral Analysis of Complexes (1 - 10).

Complex Number	frequency (cm^{-1})			
1	3105(s);	3040(w);	3010(w);	1610(s);
See table 2.3	1592(us);	1560(vs);	1460(us);	1425(vs);
	1282(s);	1160(s);	1140(s);	1095(s);
	1060(s);	770(vs);	735(s);	725(w);
	490(s);	455(s);	340(s);	
2	3109(s);	3025(s);	1620(s);	1575(s);
	1476(s);	1385(s);	1350(s);	1325(us);
	1240(w);	1060(s);	920 (w);	850(w);
	770(w);	721(w);	735 (w);	535(s);
	460(w);	430(w);	330 (s):	
3	3050(s);	1735(vs);	1600(vs);	1570(s);
	1470(s);	1435(vs);	1370(sbr);	1305(s);
	1279(s);	1225(s.br);	1155(s);	1121(s);
	1059(s);	835(s);	765(vs);	700(w);
	550(w.br);	455(w);	335(vs):	
4	3090(s.br);	1600(s);	1571 (s);	1470(vs);
	1405(s);	1375(s);	1289(s);	1245(w);
	1200(s.br);	1155(s);	1125(vs);	1065(w);
	835(s);	750(s.br);	680(w);	645(s);
	515(s);	485(s);	335(s):	

Complex Number	frequency (cm^{-1})			
5	3120(w);	3100(w);	3070(w);	3040(w);
	2915(w);	1615(us);	1570(s);	1482(us);
	1445(s);	1295(s);	1250(w);	1160(s);
	1112(s);	1065(s);	879(w);	839(s);
	775(us);	565(s);	515(w);	460(w);
	345(s):			
6	3008(w.br)	1620(vs);	1570(m);	1485(vs);
	1445(s);	1290(s);	1155(w);	1110(w);
	1065(w);	840(s);	779(us);	565(m);
	520(w);	340(s):		
7	3750(s);	3000(s);	1590(s);	1562(w);
	1483(vs);	1460(vs);	1439(vs);	1428(vs);
	1335(w);	1315(w);	1285(s);	1231(w);
	1185(s);	1160(s);	1145(s);	1100(us);
	1075(w);	1061(s);	1030(s);	1000(s);
	750(vs);	710(vs);	695(vs);	670(s);
	620(w);	552(vs);	519(vs);	500(vs);
	455(s);	430(w);	345(s):	
8	3030(s.br);	2990(w.br);	1620(s);	1600(w);
	1590(w);	1575(s);	1485(s);	1470(w);
	1435(vs);	1385(s);	1325(vs);	1290(s);
	1175(vs);	1145(vs);	1125(vs);	1101(vs);
	1080(vs);	1050(vs);	1030(s);	1025(s);
	1000(s);	929(s);	849(w);	780(s);
	750(s);	710(s);	692(vs);	649(s);
	620(s);	545(vs);	520(vs);	502(s);
	410 (s);	425(s);	395(s);	350(s):

Complex Number	frequency (cm^{-1})			
9	3109(w);	3090(w);	1600(s);	1580(s);
	1565(s);	1482(s);	1465(s);	1435(us);
	1369(s);	1315(w);	1291(s);	1200(s);
	1185(w);	1160(w);	1150(w);	1129(vs);
	1111(vs);	1100(vs);	1055(s);	1021(s);
	1000(s);	900(s);	879(vs);	852(w);
	810(vs);	765(vs);	699(vs);	545(vs);
	520(vs);	498(vs);	349(s):	
10	3060(w);	2915(w);	1600(s);	1575(s);
	1485(s);	1470(us);	1435(vs);	1373(w);
	1315(w);	1289(w);	1245(s);	1189(w);
	1150(w);	1121(s);	1100(vs);	1060(w);
	1030(w);	1000(w);	829(s);	755(vs);
	545 (vs);	520(vs);	500(s);	455(w.br);
	345 (s):			

SECTION 3

Investigations of the Reported Catalytic Activity of Certain Metal Phosphine Complexes

Section 3

Part 1 Introduction

3.1.1 Homogeneous Catalysis in General

One of the first examples of a transition metal complex acting as a catalyst in a homogeneous system was the copper (II) ethanoate - quinoline system[106] which effected the reduction of quinone to 1,4-dihydroxybenzene

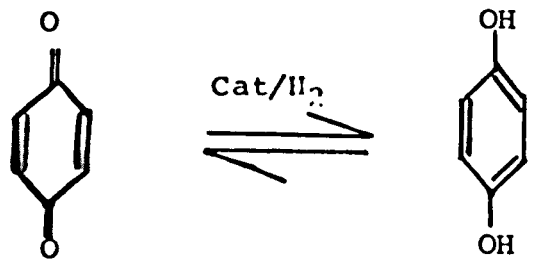


Diagram 3.1

This is an example of homogeneous hydrogenation of an organic molecule by a transition metal complex. In homogeneous catalysis the catalyst and the substrate are usually both soluble in an organic solvent such as chloroform, toluene or benzene and hence during the reaction they are in the same phase. Calvin published these results (Diagram 3.1) in 1938.

It is claimed the first example of heterogeneous catalysis was reported by E. Davy[107] in 1815. It was reported that a few drops of alcohol in a warm vessel was oxidised when platinum wire was present. It is obvious therefore that heterogeneous catalysis has been studied for a much longer period of time than homogeneous catalysis. However the phenomenon of homogeneous catalysis is much better understood and there have been many papers[108] and reviews[109,110] published since Calvins first report.

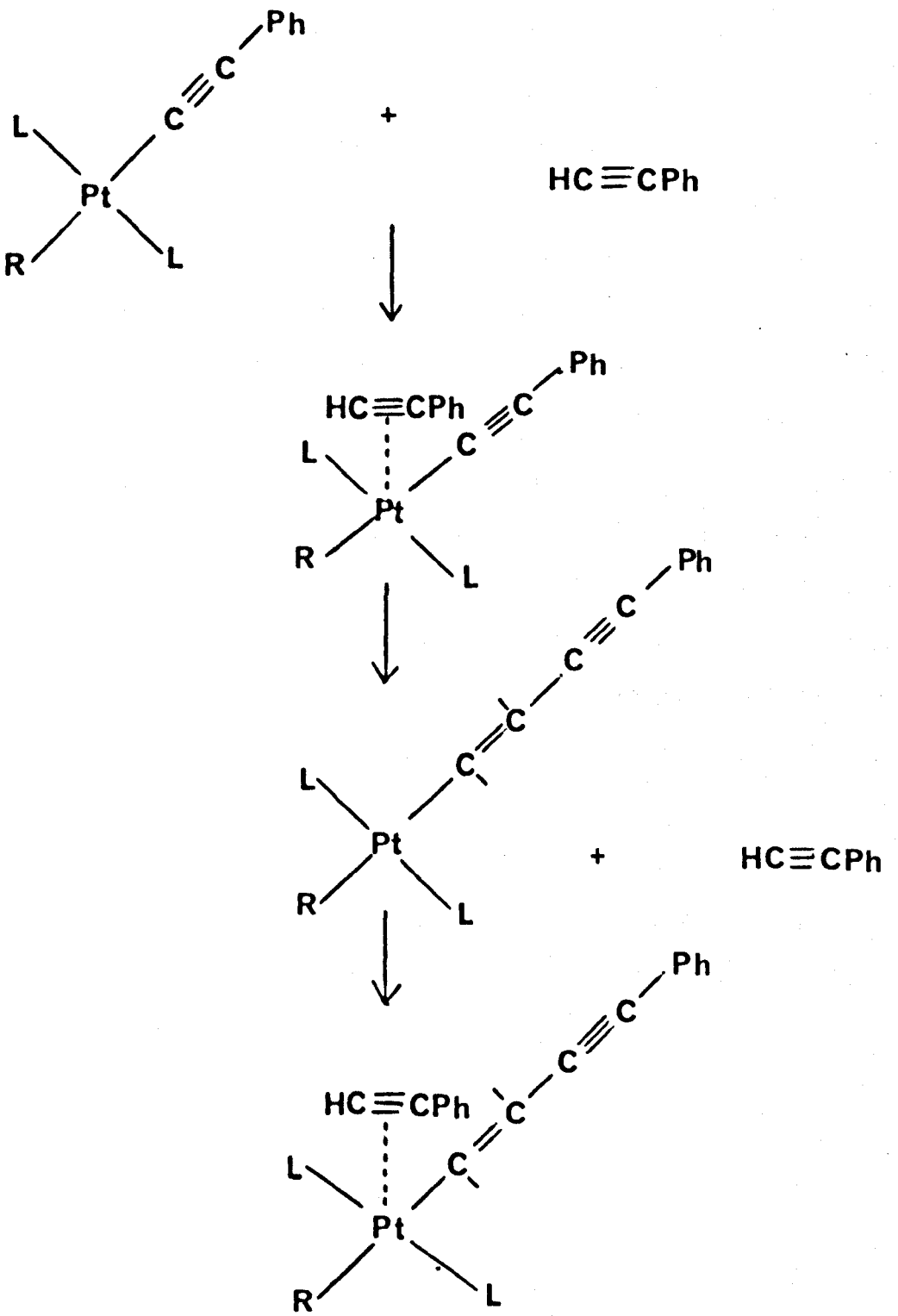
The case of isolation of reaction intermediates in homogeneous catalysis has led to the elucidation of reaction

pathways and in some cases reaction mechanisms.

The polymerisation of phenylacetylene is known to be catalysed by cis and trans -$[PtCl_2(PPh_3)_2]$. Temperatures of 403 K or higher are required for the polymerisation to occur even with the catalysts present. A. Furtani et al[111] studied the system at room temperature and they isolated complexes of the type cis and trans -$[Pt(C{=}CPh_2)_2(PPh_3)_2]$. The stability of the platinum acetytides allowed the complexes to be isolated at room temperature however at the higher reaction temperature they are unstable and polymerisation proceeds.

The platinum(II) acetylides are formed by the attack of an acetylide radical on the platinum phosphine complex. Based on the assumption that the acetylide complexes are reaction intermediates for the catalytic polymerisation the authors proposed a mechanism in which the first molecule of the monomer is σ-bonded to the Pt atom and co-ordination of another phenylacetylene molecule to the active complex is the second step. (See diagram 3.2).

Diagram 3.2

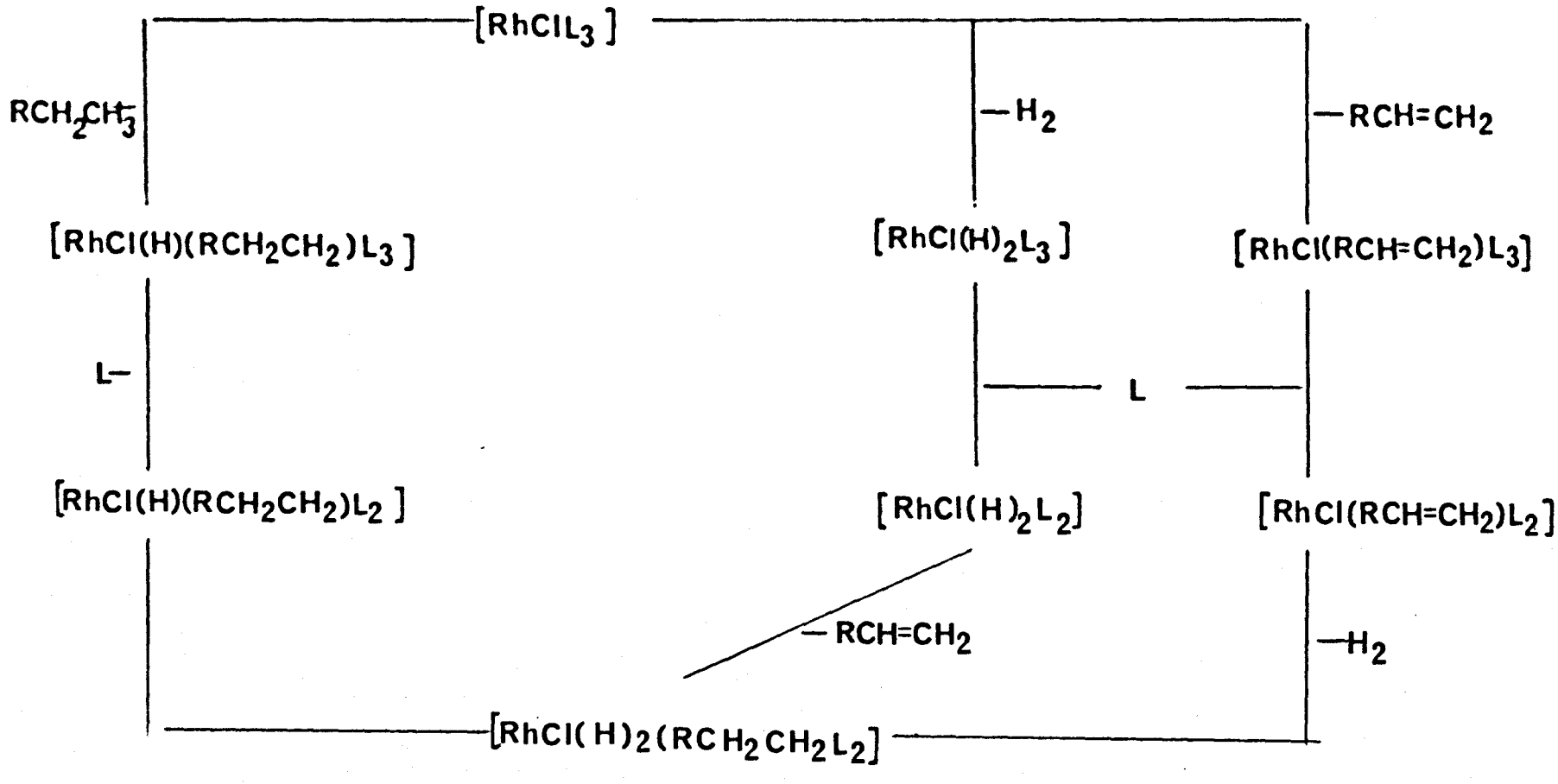

Ph
C
C
L
Pt
R
L
+
HC≡CPh
HC≡CPh
Ph
C
C
L
Pt
R
L
Ph
C
C
C
C
L
Pt
R
L
+
HC≡CPh
Ph
C
C
HC≡CPh
C
C
L
Pt
R
L

The polymer chain begins with insertion of the σ-co-ordinated species into the ethynyl-platinum bond.

The most widely studied and possibly the best understood homogeneous catalyst system is the chlorotris (triphenyl phosphine) rhodium (I) complex. The catalytic activity of this molecule was first reported by Wilkinson et al[112] when they noted that it was a very efficient catalyst for the hydrogen of terminal olefins. The properties of this catalyst have been extensively examined. It is known to reduce olefins and acetylenes with little or no isomerisation, to reduce terminal olefins more readily than internal olefins, to reduce cis-isomers better than trans-isomers and to reduce alkenes faster than alkynes.

The mechanism is very well understood and is shown in diagram 3.3. There are two possible routes. The first step in the mechanism could be either the association of the hydrogen molecule or the association of the olefin acetylene molecule. The route which involves the addition of the hydrogen molecule first is assumed to be the major pathway because isolation of complexes like $[RhClL_2(C_2H_4)]$ demonstrates that the olefinic complex is not readily hydrogenated.

Diagram 3.3 Homogeneous Catalysis



The features of the metal atom which appear to be important for complexes to exhibit catalytic activity can be summarised as follows:-

(a) The metal atom usually has variable oxidation number and more than one co-ordination number, eg platinum exists as Pt(II) and Pt(IV) with complexes which are square planar or octahedral respectively.

(b) The metal atom is usually capable of complexing a large number of ligands, eg R_3P, CO, etc.

(c) The stability of the complex formed by the metal atcm as an intermediate must be balanced between two extremes. The complex must be stable enough to form but unstable enough to allow hydride transfer, in hydrogenation reactions, and subsequent dissociation of the reduced molecule.

The large range of activity shown by $[RhL_3Cl]$ complexes where L = $P(p\text{-}C_6H_5OMe)_3$; $P(p\text{-}C_6H_4Me)_3$; PPh_3; $PEtPh_2$; $p(p\text{-}C_6H_4F)_3$; $P(p\text{-}C_6H_4Cl)_3$; $P(CH_2Ph)_3$; for the hydrogenation of olefins has been related to the basicity of the ligands. It was shown that ligands slightly more basic than PPh_3 gave maximum rate of hydrogenation.[113] It appears therefore that the ligands electronically modify the metal atom and this enhances or depresses the metal atom's catalytic ability by making it or them more susceptible to attack by hydride and olefin or by stabilizing the intermediates.

The main advantages of homogeneous catalysts compared to heterogeneous catalysts are the greater efficiency, better selectivity, and enhanced stereo-specifity of the reactions. The biggest disadvantage of the homogeneous system is the difficulty of separating the products from

the catalysts. This is important in industrial applications. It is desirable, for economic reasons, to have reactants entering the system at one end and products being removed at the other end, i.e. to have a continuous process. This is impossible for most homogeneous systems.

Perhaps the most exciting aspect of homogeneous catalysis is the ability of some catalysts to direct the steric course of a reaction. There is considerable current interest in the use of homogeneous chiral catalysts for asymmetric synthesis where the ligand has one or more chiral centres. One example is the asymmetric reduction of α-keto-esters, which has been achieved via catalytic hydrosilylation followed by hydrolysis using a rhodium catalyst prepared by addition of either (+)- benzlmethylphenylphosphine or (+)-2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenyl-phosphino)butane to $[RhCl(1,5\text{-cod})]_2$ [114]

Diagram 3.4

$$R^1COCO_2R^2 + R^3R^4SiH_2 \xrightarrow{[Rh]^*} R^1CHCO_2R^2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OSiHR^3R^4$$

$$\xrightarrow{MeOH/H^+} R^1{}^*CHCO_2R^2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

3.1.2 Chlorination Reactions

Chlorination of low-molecular weight organic molecules is of particular interest to the organic solvents industry. The chlorination reaction can be carried out by photochemical or catalytic techniques.

3.1.2(i) Gas Phase and Ligand Phase Photochemical Reactions

There has been considerable research into the liquid phase and the gas phase free radical chlorination of asymmetrically chlorinated ethanes.

Hass,McBee and Weber[115] made a classical study of the relative reactivity of primary, secondary and tertiary carbon to hydrogen bonds towards chlorine atoms in the chlorination of isopentane. Table3.1contains the data published on the relative rates of reaction of the carbon to hydrogen bonds with chlorine atoms.

Table 3.1

	Temperature (K)	Tertiary	Secondary	Primary
liquid phase	213	13	8.5	1.0
	373	3	2	1.0
gas phase	573	4.43	3.25	1.0
	873	3.5	2.2	1.0

It was shown that in either phase the relative reactivities of primary secondary and tertiary hydrogens approach unity with increasing temperature. It was noted that the selectivity is lower in the liquid phase. This work was later corraborated by Tedder et al[116].

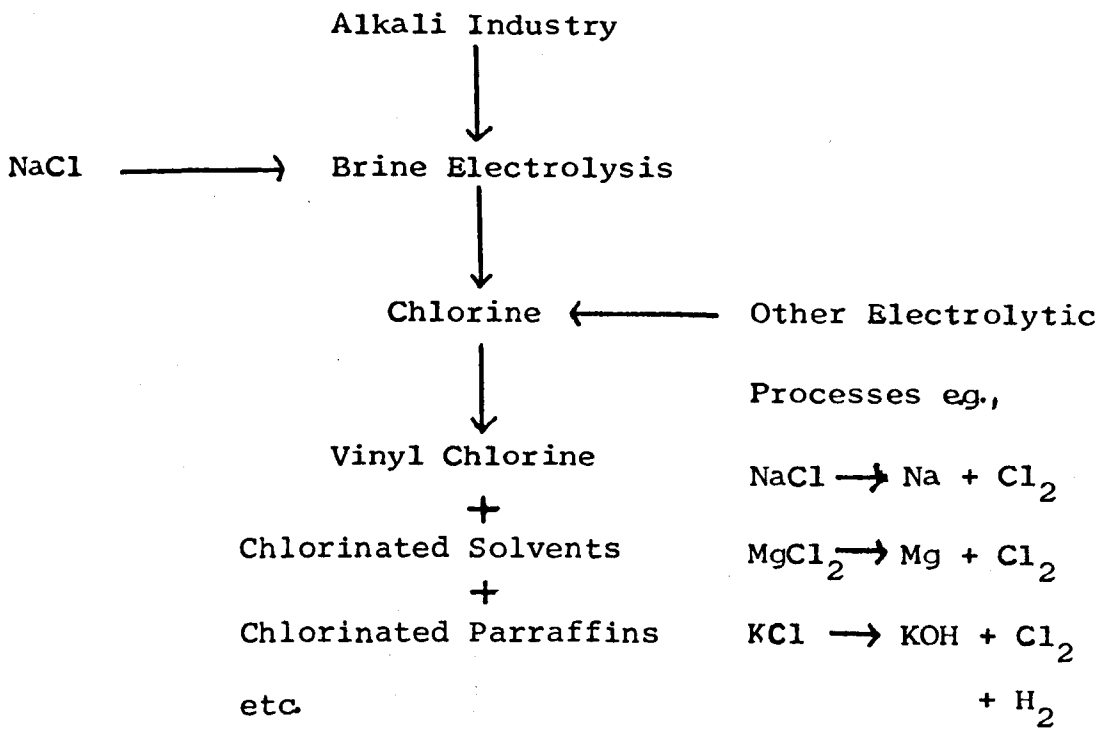
3.1.2(ii) Catalytic Chlorination Reactions

Catalysts for reactions such as chlorination, hydrochlorination, ie addition of a molecule of HCl across an olefinic double bond, and dehydrochlorination, removal of a molecule of HCl, have been known for a long time.[117] The most active catalysts for these types of reactions are iron(III) chloride, iron (II) chloride and copper (I) chloride. There are about twenty patents published yearly dealing with catalysts for chlorination reactions. One example is the process reported by T. Kawaguchi, R. Saito and K. Natanishi[118]. They prepared a catalytic system by dissolving specific amounts of iron (III) chloride in 1,2-dichloroethane. It was claimed this solution plus ethene and chlorine heated to 343 K would give 1,2 dichloroethane in 98% yield with 1,1,2-trichloroethane as a byproduct.

Although many systems which catalyse the chlorination of hydrocarbons have been reported in the literature very little is known about the mechanism of these reactions.

ICI Mond Division, Runcorn, is the biggest U.K. manufacturer of chlorine and chlorinated products such as vinyl chloride and chlorinated paraffins. In addition to this ICI is the sole manufacturer of chlorinated solvents like trichloroethylene, perchloroethylene, 1,1,1-trichloroethane and methylene chloride.

Diagram 3.5



The production of chlorinated products like vinyl chloride and chlorinated solvents usually involves multi-step processes with one or more steps being influenced by catalysts.

ICI Mond Division has a 300,000 t/year capacity for the production of vinyl chloride which is used exclusively in the manufacture of P.V.C.[119].

Modern vinyl chloride processes consist of three stages.

(a) The chlorination of ethylene to give 1,2 dichloroethane. Iron (III) chloride is an excellent catalyst for the ethylene chlorination. In the presence of only 100 ppm

iron (III) chloride the major product (98%) is 1,2-dichloroethane. Various radical and ionic mechanisms have been proposed to explain the iron (III) chlorides involvement but there is still a great deal of research being carried out in order to elucidate the mechanism further.

(b) The thermal cracking of the 1,2 dichloroethane to give vinyl chloride and hydrogen chloride.

(c) The mixing of the hydrogen chloride produced in stage b with ethylene and oxygen. This mixture is then passed, under pressure, into a reactor which containsa fluidized bed of copper (I) chloride catalyst on an inert support, usually alumina. This stage, known as the oxychlorination reaction, produces water and dichloroethane.

The three stages can be summerised as follows

(a) $Cl_2 + C_2H_4 \xrightarrow{FeCl_3} CH_2Cl\text{-}CH_2Cl$

(b) $CH_2Cl\text{-}CH_2Cl + \dot{C}l \xrightarrow{450\text{-}500^oC} CH_2Cl\text{-}CHCl + HCl$

$CH_2Cl\text{-}CHCl \longrightarrow CH_2{=}CHCl + \dot{C}l$ etc

(c) $CH_2{=}CH_2 + 2MCl_x \xrightarrow{CuCl} CH_2Cl\text{-}CH_2Cl + 2MCl_{x-1}$

$2MCl_{x-1} + 2HCl + O \longrightarrow 2MCl_x + H_2O$

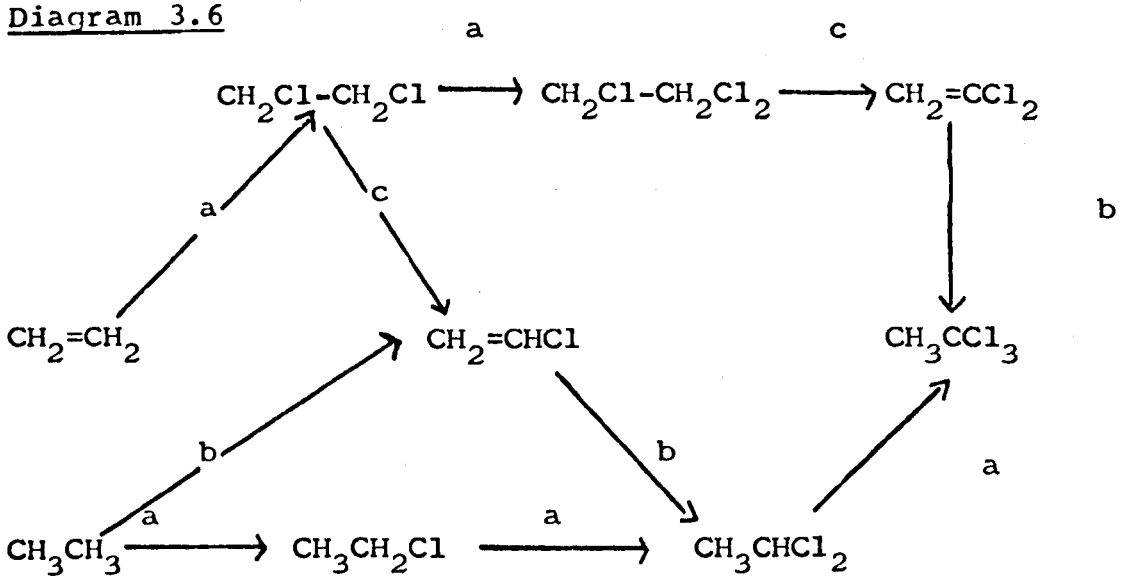
Catalysts are used in two stages of this very important process and so the industrial importance of chlorination catalysts is obvious[119].

Trichloroethylene and perchloroethylene are made by either successive chlorination and dehydrochlorination reactions or by oxychlorination reactions. Both types of processes require the presence of catalysts. The former

reactions are usually carried out in a single reactor at about 623 K - 773 K over an iron catalyst. If this type of process is used the byproduct HCl is recovered for processing elsewhere. The latter process involves ethylene or ethylene dichloride being fed into a fluidised bed reactor which contains a copper catalyst. Mixtures of trichloroethylene and perchloroethylene are obtained[119].

Synthetic routes to 1,1,1 trichloroethane are more complex due to the difficulty of placing three chlorine atoms on one end of the molecule. Ethylene or ethane are used as feedstock. The following diagram shows the different pathways which can be used by building up permutations of chlorination, hydrochlorination and dehydrochlorination reactions.

Diagram 3.6



a - chlorination (photochemical)

b - hydrochlorination

c - dehydrochlorination

The hydrochlorination is usually effected by catalysts such as iron (III) chloride which are Lewis acids.

Dehydrochlorination is achieved by thermal cracking or by the action of a base. The chlorination step can take place in either the liquid phase or the gas phase.

The main difficulty in the production of 1,1,1-trichloroethane or so called "Genklene" is that the required product is not the only isomer obtained at each stage. This is especially significant in the chlorination reactions. Considerable research is being carried out in order to find a process or combination of processes which will give the required product in greater yields.

In the present work an investigation of a reported catalyst for the chlorination step was undertaken.

Part 2 Investigations of $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$ and $[PtCl_2Ph_2PC_2H_4PPh_2]$ as Catalysts for the Chlorination of 1,1 Dichlorethane

3.2.1 Previous Work in this Field

It was reported by I. McLeod and D. Millington that the complexes $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$ and $[PtCl_2Ph_2PC_2H_4PPh_2]$ exhibited catalytic properties[120]. It was claimed that when a suspension of either the above complexes in 1,2-dichlorothane was saturated with chlorine the complex catalysed the chlorination of the solvent. Products like 1,1,2 trichloroethane, tetrachloroethane, pentachloroethane and even hexachloroethane were observed.

These observations stimulated great interest from both an academic and an industrial point of view.

The fact that the complexes were oxidised during the reaction to give a Platinum (IV) species suggested the mechanism of the catalysis might have involved oxidative addition of the solvent and chlorine to the platinum (II). Oxidative addition to platinum has been postulated by many authors[121] and it was therefore a reasonable proposal.

Economically it would be very important for industry to have a catalyst which could catalyse the chlorination of 1,1-dichloroethane or ethane and produce specific products. I. McLeod and D. Millington, it should be noted, made no claims with regard to the selectivity of their catalysts.

These observations laid the foundation for a research project which was initiated to investigate the complexes and their properties further.

3.2.2 Experimental Procedure

The same procedure was used when the catalytic activity of both complexes ie $[PtCl_2Ph_2PC_2H_4PPh_2]$ and $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$ was examined.

3.2.2 (i) Liquid Phase Chlorination of 1,1-dichloroethane

0.5g of the complex was added to 10ml of 1,1-dichloroethane in a three-necked round bottom flask. A similar experimental set-up to that used by the original workers was used in these studies. The chlorine was bubbled through the solution as slowly as possible. The complexes turned bright yellow after approximately ten minutes. After the reaction was stopped, oxygen-free nitrogen was bubbled through the solution to remove any dissolved chlorine. The solution was filtered and the filtrate was distilled under reduced pressure to separate the solvents from the complex. A control experiment, in which there was no complex, was carried out along side each experiment.

The resulting mixture of chlorinated solvents was analysed on a gas liquid chromatographic system. A Perkin Elmer F11 Hot Wire Detector with 5' columns containing Chromosorb 101 packing was used. The inert carrier gas was either nitrogen or helium. The oven temperature was 463K

Calibration of the chromatographic system was carried out using conventional means. Standard mixtures containing known volumes of possible reaction products were analysed. Retention times for each of the components were recorded and a ratio of Peak Area/Volume measured. These parameters are dependant on the oven temperature, the

column used and the flow rate of the inert carrier gas. These factors may vary, therefore it was necessary to run a standard before each set of reaction products were analysed. When the unknown reaction mixtures were analysed components were identified by comparison with the standard. The amounts of the various components presentwere obtained by comparing the peak height of the reaction productswith that of the standard components.

The experiments were repeated using apparatus covered with black tape to exclude light during the reaction. Table 3.2 contains the results of one set of experiments.

Table 3.2

Reaction A Cl_2 + 1,1-dichloroethane + $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$

Control A Cl_2 + 1,1-dichloroethane

Reaction B Cl_2 + 1,1-dichloroethane + $[PtCl_2Ph_2PC_2H_4PPh_2]$

Control B Cl_2 + 1,1-dichloroethane

Components	Reaction A		Control A		Reaction B		Control B	
	hν	Dark	hν	Dark	hν	Dark	hν	Dark
	%		%		%		%	
1,1-dichloroethane	73.8	99.2	67	99.4	12.6	98.1	15.9	97.2
1,1,1-trichloroethane	18.3	0.63	21.5	0.57	82.5	0.4	77.0	1.3
1,1,2-trichloroethane	5.6	-	11.1	-	4.8	trace	7.3	0.29
1,1,1,2-tetrachloroethane	2.3	-	trace	-	trace	-	trace	-
1,1,2,2-tetrachloroethane	trace	-	trace	-	trace	-	trace	-

This set of experiments was repeated but the results above are typical of those obtained. The amount of chlorination observed in the h ν reactions appeared to be related to the brightness of the sunlight.

The most important points which arise from these results are,(a) there is little difference in the extent of chlorination observed between the catalysed reactions and the controls and (b) there are negligible amounts of chlorination observed when light is excluded. This was found for both the catalysed reactions and the controls.

3.2.2.(ii) Gas-Phase Chlorination of 1,1-Dichloroethane

The experimental apparatus used is shown in diagram 3.7.

A mixture of 1,1 dichloroethane (5ml) and chlorine (1 litre) was continually passed over the complex (0.4g) for approximately 4 hours. The vapour of 1,1-dichloroethane and the chlorine gas were circulated using a peristaltic pump. The reaction was carried out in a closed system which had been flushed out with nitrogen before starting. Light was excluded during the reaction. The complexes $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$ and $[PtCl_2Ph_2PC_2H_4PPh_2]$ were both examined.

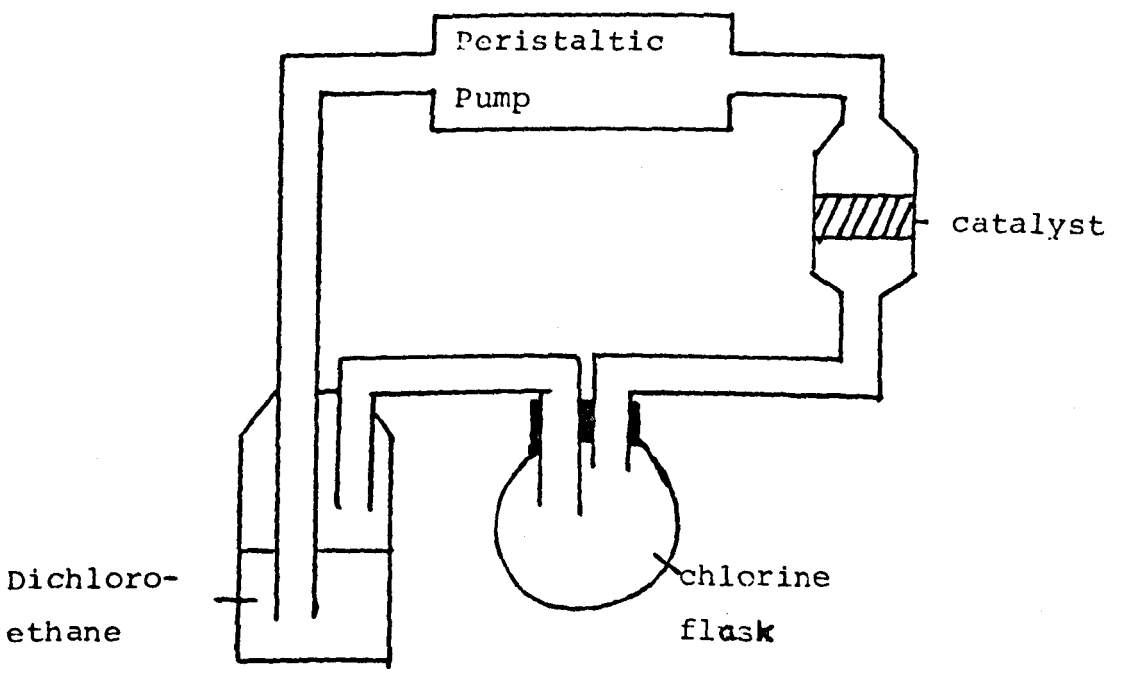
Analysis of the resulting products showed only the presence of starting material.

Therefore no catalytic chlorination was observed when the substrate and chlorine were in the gas phase and the complex in the solid phase.

3.2.2(iii)
Irradiation of the Complex $[PtCl_4Ph_2PC_2H_4P(C_6F_5)_2]$ and and 1,1 Dichloroethane with UV light in the Absence of Chlorine

1g of the complex was added to 0.5ml of 1,1-dichloroethane in a quartz test tube and this was placed under a

Diagram 3.7


Peristaltic
Pump
catalyst
Dichloro-
ethane
chlorine
flask

UV lamp for four hours.

Analysis of the solvent before and after the reaction showed that no chlorination of the 1,1-dichloroethane had occurred.

3.2.2(iv) A Control Experiment using a Partially Darkened System

According to I. McLeod's experimental procedure reports he used a reaction flask which had been covered with black tape, however the condensor was not so covered. McLeod recorded about 16% chlorination in one hour. The percentage chlorination was calculated based on the amount of HCl dissolved in a water trap at the output of the reaction flask.

The original experiment carried out by I. McLeod was repeated without the complex being present. 9.11g of 1,1-dichloroethane was placed in a three-necked round bottom flask. Chlorine was bubbled through the solution at a rate of 15 cm^2/min. The gaseous stream from the reaction flask was passed through a water trap and then through a caustic soda trap. The HCl produced in the reaction was dissolved and was titrated with 1M sodium hydroxide after washing with sodium iodide and sodium thiosulphate to remove any dissolved chlorine.

Volume of 1M NaOH required = 12 ml

No. of moles of HCL produced = 0.012 moles

$\therefore$ 0.012M of 1,1-dichloroethane had reacted, assuming conversion to trichloroethane only

Therefore $\frac{0.012}{.1} \times 100$ = 12% chlorination was observed.

Part 3 Discussion and Conclusions

The complexes used in the preceeding experiments were freshly prepared samples. The asymmetric diphosphine complex, $[PtCl_2Ph_2PC_2H_4P(C_6F_5)_2]$, was made via the preparation described in Section 1 - "Experimental Procedure", and the symmetric diphosphine via the route described by D. Millington,[120] ie addition of diphosphine to a refluxing solution of bis(benzonitrile) dichloroplatinum(II) in benzene and refluxed for twenty four hours.

It became evident very soon after starting the research project that there were differences in the results obtained in these experiments and the results obtained by I. McLeod and D. Millington. Two important differences were firstly, that when the liquid-phase chlorination was carried out with light completely excluded from the system no chlorination occurred and secondly, similar amounts of chlorination were observed in both the control experiment and the actual reaction when light was not excluded (Table 3.2).

These results strongly suggest that the complexes have no catalytic activity.

It was noted that the reaction flask containing the control experiment became very hot during the reaction while the flasks containing the complexes remained cool. This can be accounted for by assuming the photochemical reaction is exothermic and the oxidation of Pt(II) to Pt(IV) is endothermic.

The fact that no interaction was observed between $[PtCl_4Ph_2PC_2H_4P(C_6H_5)_2]$ and 1,1-dichloroethane after UV

irradiation in the absence of chlorine gas would indicate the chlorination observed in the light reaction was due solely to photochemical chlorination, i.e. free radical reaction.

There are several reasons which can be put forward to explain the lack of catalytic activity of the newly prepared complexes.

I. McLeod and D. Millington did not, according to the experimental procedure reports completely exclude light from their water condensors although they did black out their reaction flasks. The chlorination they observed may have been due to a gas-phase photochemical reaction occurring in the condensor. An experiment was carried out following their description of the reaction as closely as possible without any complex being present. I. McLeod reported that he obtained 16% chlorination in one hour and this is similar to the 12% chlorination obtained in the repeated control reaction. Therefore it seems very likely that a gas phase reaction in the condensor had occurred in the previous work.

The complexes of I. McLeod and D. Millington might well have exhibited catalytic activity but this activity would probably have arisen from some impurity which contaminated their complexes. The impurity could possibly have arisen from traces of iron (III) chloride or copper (II) chloride being present in the bulk sample of platinum (II) chloride which could have been used by both workers.

Therefore it would seem, on available evidence, that these complexes are not catalysts for the chlorination of dichloroethane.

Part 4 Future Work

Complexes of this type have been known to be very efficient hydrogenation catalysts[122]. A feasible project for the future would be an investigation of the ability of these complexes to catalyse hydrogenation reactions of unsaturated hydrocarbons. If this proved fruitful investigations of other catalytic properties such as polymerisation and hydrosilylation should be examined.

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