POLYFLUOROPHENYL DERIVATIVES OF THE GROUP V

ELEMENTS AND THEIR METAL COMPLEXES

A thesis presented for the Degree of

Doctor of Philosophy

in the

Faculty of Science

by

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Myself when young did eagerly frequent

Doctor and Saint, and heard great argument

About it and about: but evermore

Came out by the same door where in I went,

The Rubaiyat of Omar Khayyam, XXVII.

Translated by E. Fitzgerald.

STATEMENT

The experimental work described in this thesis
has been carried out by the author in the Department of
Chemistry of the University of Leicester between
October 1965 and June 1968 under the supervision of
Professor R. D. Peacock and Dr. R. D. W. Kemmitt.
The work has not been presented and is not concurrently
presented for any other degree.

D. I. Nichols.

June 1968.

ACKNOWLEDGEMENTS

I have now the pleasant but impossible task of thanking those who have helped me - impossible because I can only say 'thank you' and the cold print conveys nothing of what I would convey.

After the debts which make me bankrupt to Mrs. Randall for running the n.m.r. spectra and Mrs. Kempston for typing the thesis, I owe a great one to my two supervisors between whose kindnesses and encouragements I will make no attempt to distinguish.

C O N T E N T S

SUMMARY

The introduction is a critical review of the evidence for back-bonding in transition metal phosphine complexes.

The compounds $(C_6F_5)_n Ph_{3-n} M$ (M = P, As, Sb; n = 1, 2 or 3) have been prepared in high yield by an improved method using pentafluorophenyllithium. The reactions of these ligands with various rhodium, palladium and platinum compounds have been investigated and displacement reactions indicate that the complexes L_2PtCl_2 increase in stability in the order of ligands (L), Me_2S < $(C_6F_5)_3P$ < $(C_6F_5)Ph_2As$ < $(C_6F_5)_2PhP$ < tris(2,6 difluorophenyl) phosphine < cycloocta-1,5-diene < Ph_3As < $(C_6F_5)Ph_2P$ < Ph_3P < $(PhO)_3P$.

The reaction of $(C_6F_5)_3P$ with $RhCl_3.xH_2O$ gives the dark green complex $[(C_6F_5)_3P]_4Rh_2Cl_2$. Similar chloro- and bromo- complexes are obtained with $(C_6F_5)_2PhP$ and $(C_6F_5)Ph_2P$. Carbon monoxide readily cleaves the halogen bridge present in these complexes to yield trans $[(C_6F_5)_xPh_{3-x}P]_2RhCOCl$. x = 1, 2 or 3. The reactions of trispentafluorophenylphosphine rhodium complexes with cycloocta-1,5-diene, triphenylphosphine, and triphenylphosphite show that these ligands readily displace the $(C_6F_5)_3P$. Treatment of the Rh(I) complexes of $(C_6F_5)_3P$ with chlorine or methyl iodide gives ill defined Rh(III) materials.

The ^{19}F n.m.r. of the complexes is consistent with $d\pi-d\pi$ bonding between the metal and the phosphorus. Infrared spectra are also reported.

High resolution ^{19}F n.m.r. studies have been carried out
on the compounds $(C_6F_5)_nPh_{3-n}M$ (M = P, As, Sb; n = 1, 2, 3).
A loss in resolution is observed when more than one pentafluorophenyl
group is present. The low temperature n.m.r. studies suggest that
the phosphine $(C_6F_5)_3P$ is rotating about the metal–phosphorus bond
in its platinum or palladium complexes at room temperature.

The production of the carbonyl complexes $L_2RhCOCl$ from high
temperature (120°C) experiments involving fluoro-olefins and the
complexes $L_4Rh_2Cl_2$ (L = $(C_6F_5)_nPh_{3-n}P$, n = 1, 2 or 3) and
$(Ph_3P)_3RhCl$ has been investigated. The reaction has been shown to involve hydrolysis
of an intermediate fluoro-olefin complex, and some tentative
mechanisms are proposed.

I N T R O D U C T I O N

Cur igitur mirumst, animus si cetera perdit

praeterquam quibus est in rebus deditus ipse ?

deinde adopinamur de signis maxima parvis

ac nos in fraudem induimus frustraminis ipsi.

Lucretius. De Rerum Natura. IV, 814.

INTRODUCTION

Very many phosphine complexes of transition metals are known.[1]
The nature of the bond between the metal and the phosphorus atoms
depends on the other groups attached to the metal or phosphorus
atoms. While it is considered that π and σ components are present
in the bond, considerable disagreement occurs about the relative
magnitudes.

A brief account of the molecular orbital representation of
the metal-phosphorus bond is given below. The basis of the treatment
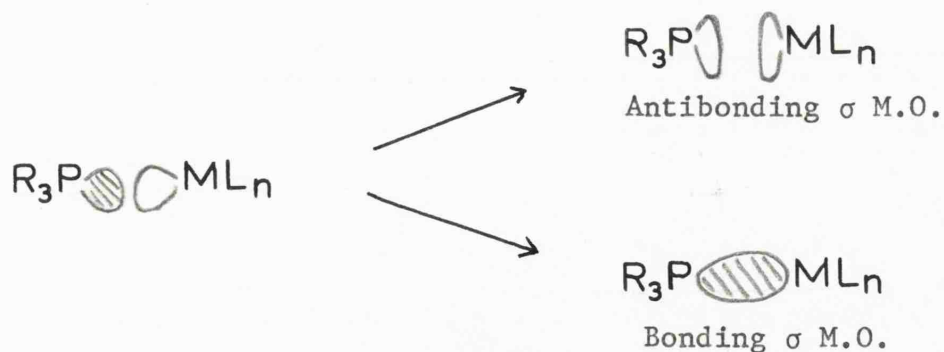is that given by Cotton and Wilkinson.[2]

Antibonding σ M.O.

Bonding σ M.O.

Diagram 1·1.

The σ component is shown in diagram 1·1. The lone pair on
the phosphorus is assumed to be in an sp type hybrid with the exact
character depending on the nature of the groups attached to the
phosphorus. Some contribution to the hybrid from the 3d orbitals

could be present, but the amount is probably small. The metal

σ acceptor orbital is a combination of the s, p, and d atomic

orbitals and the composition is determined by the steric

arrangement of the ligands around the metal atom. In the case

of a monosubstituted octahedral pentacarbonyl $LM(CO)_5$ the

s, p_z and d_{z^2} (L-M bond being the z axis) metal orbitals have

the correct symmetry to act as acceptors for the lone pair on

the phosphorus.

The lone pair which was on the phosphorus enters the σ bonding

molecular orbital as shown in Diagram 1·1. If the contributions

of the phosphorus and metal hybrid orbitals to the molecular

orbital are equal then the electron density is shared equally

between the metal and phosphorus atoms. This is approximately

equivalent to the donation of one electron by the phosphorus to

the metal. However, if the contribution of the acceptor hybrid

orbital on the metal is less than that of the lone pair hybrid on

the phosphorus the σ bonding molecular orbital has more lone pair

character than metal character and the electron density is mainly

associated with the phosphorus. Donation of less than one

electron takes place and in the absence of other effects the metal

atom becomes negatively charged while the phosphorus atom becomes

positively charged.

Just as σ orbitals can combine to yield σ molecular orbitals so orbitals of π character with respect to the metal-phosphorus bond can combine to yield π molecular orbitals. Since d and p orbitals can be π in character dπ-dπ, dπ-pπ, and pπ-pπ bonding can occur.

While the symmetry compatibility of two atomic orbitals is a necessary condition to their effective combination to form a molecular orbital, it is not a sufficient condition. Two other criteria must also be satisfied. The overlap of the charge clouds must be significant, and the energies of the two atomic orbitals must be of comparable magnitude. Thus pπ-dπ bonding involving the interaction of the 3p orbitals of the phosphorus with the metal d orbitals, or the σ bonding molecular orbitals with the phosphorus 3d orbitals is likely to be small since the energies are widely different. The metal d orbitals however are nearer in energy to the 3d orbitals of the phosphorus and significant combination could occur. (Diagram 1·2).

Antibonding π M.O.

Bonding π M.O.
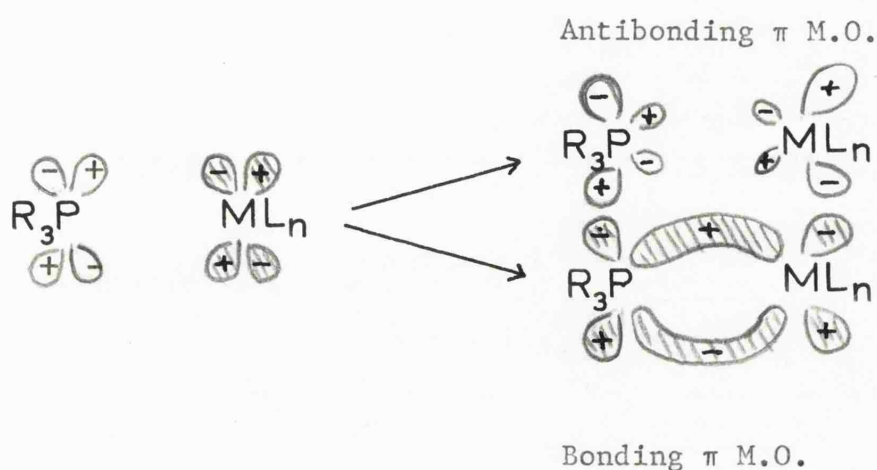
(Diagram 1·2)

Finally another type of bonding involving d orbitals on the metal and the phosphorus atoms is possible. If the orbitals have δ symmetry with respect to the metal-phosphorus bond then δ molecular orbitals can be formed. (Diagram 1·3).
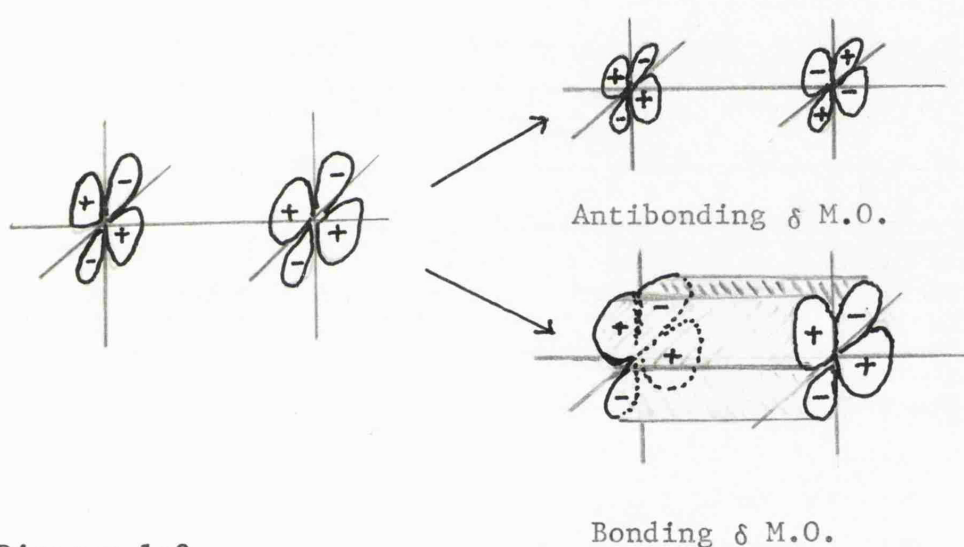

Antibonding δ M.O.

Bonding δ M.O.

Diagram 1·3.

The phosphorus 3d orbitals are empty so that for dπ-dπ bonding to occur those of the metal must have electrons in them. Outside the transition series the d orbitals are too low or too high in energy with respect to the 3d orbitals on the phosphorus to form significantly lower energy bonding molecular orbitals. The formation of occupied π or δ molecular orbitals results in the partial transfer of charge from the metal to the phosphorus.

For dδ-dδ and dπ-dπ combinations, calculations[3] show that the δ overlap integral is much smaller than the π overlap integral. Since the d orbitals involved in both schemes are roughly the same

in energy (for the metal d orbitals they are exactly the same) it seems unlikely that the δ bond is an important component of the metal-phosphorus link.

The partial σ donation of electrons from the phosphorus to the metal tends to make the phosphorus positively charged and the metal negatively charged. The phosphorus 3d orbitals will contract while the occupied metal d orbitals will expand, and the two sets approach each other in energy more closely. Thus a stronger $d\pi$-$d\pi$ bond is formed. At the same time this stronger π bond places electron density on the phosphorus and the metal becomes positively charged, making the phosphorus a better σ donor and the metal a better σ acceptor. Thus up to a point the effects of σ bond formation strengthen the π bond and vice versa. This effect is called a synergic bonding mechanism.

Having established that $d\pi$-$d\pi$ bonding is theoretically possible in metal phosphine complexes the evidence for the existence of such bonding will be considered. The physical evidence will be presented first.

Many physical techniques have been used to probe the nature of the metal-phosphorus bond. The most important of these are nuclear magnetic resonance and infrared spectroscopy. The other methods include dipole moment measurements, kinetic experiments, Mössbauer and electronic spectroscopy.

In the author's estimation the most successful attempt to

separate σ and π effects in metal-phosphorus bonds is reported in a paper by Graham.[4] in which the C-O bond stretching force constants of the carbonyls _cis_ and _trans_ to the ligand in complexes of the type $LM(CO)_5$ were calculated. The basic premise in this paper is that changes in these force-constants are due to changes in the σ and π components of the metal-ligand bond. It is stated that any change in the σ bond character will affect the _cis_ and _trans_ force-constants equally due to alteration of the net charge on the metal altering the $d\pi-\pi^*$ back bonding. It was assumed that the carbonyl frequencies are only slightly affected by changes in the metal-carbon σ bond and that this effect would be isotropic. That this may not be true is shown by the nature of the C-O force constant in BH_3CO, 17.96 m.dynes/$\mathring{A}$[5] compared with 19.0[6] in free CO. However, other authors give a value of 18.96[7] for BH_3CO.

Inferences drawn from the BH_3CO data should be regarded with caution. It is not known whether the boron bonds to the oxygen or the carbon atom of the CO moiety. Hyperconjugative effects involving the electrons in the B-H σ bonds could lead to population of the π antibonding molecular orbitals of the carbon monoxide and thus decrease the force constant.

Parshall's ^{19}F n.m.r. studies on platinum complexes[8] provides evidence for the non-isotropic nature of a σ bond effect. It was

found that the position of the <u>meta</u> fluorine resonance in I was

hardly affected by the nature of the ligand L, but that in the

<u>trans</u> complexes the change was marked.

$$\begin{array}{c} PEt_3 \\ \downarrow \\ Et_3P \rightarrow Pt \\ | \\ L \end{array} \quad\text{—}\bigcirc\text{—}\text{F} \qquad I$$
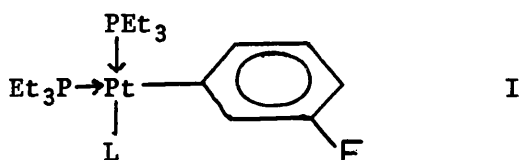
The conclusion was that the σ effects of <u>cis</u> ligands were much

smaller than the σ effects of <u>trans</u> ligands. Also when two

phosphines are <u>trans</u> in a metal complex strong phosphorus-phosphorus

spin-spin coupling occurs,[9] but the <u>cis</u> coupling is much smaller.

If the coupling is assumed to take place through σ bonds then this

supports the view that strong <u>trans</u> σ interactions occur and that

<u>cis</u> interactions are weaker.

The variations in the force constants is small for both the

<u>cis</u> and <u>trans</u> carbonyl ligands in Graham's paper. The possibility

of moderate direct σ interactions and their anisotropic nature may

well alter the conclusions of the work.

Although semi-quantitative π and σ ligand effects were

tabulated these are only relative for the σ effects. The π effects

are absolute since in the absence of hyperconjugative effects a

methyl group or a cyclohexylamine ligand is incapable of π interaction

with the metal. Thus the proportion of the π component to the total

bond strength has yet to be determined.

Other infrared evidence includes the evaluation of the metal-phosphorus bond stretching force constant. In $Ni(PF_3)_4$[10] it was computed to be 2.7 m.dynes/Å, which was stated to be effectively a single bond value. Similarly a value of 2.8 m.dynes/Å was found in $Ni[P(OMe)_3]_4$.[11] In the absence of force constant data in molecules such as F_3P-BH_3 where any π bonding must be due to hyperconjugation these figures do not throw any light on the nature of the metal-phosphorus bond.

A dissent has been entered to the generally accepted views on π bonding in phosphine substituted metal carbonyl complexes. Bigorgne[12] has found that the carbonyl stretching frequency in $(X_3P)_2Ni(CO)_2$ showed a linear correlation with the Taft inductive parameters σ^* of X for many types of X. He suggested that change of the carbonyl frequency is primarily an inductive effect on the metal atom altering the back donation to the carbonyls. If we assume that :

$$\Delta\nu \ CO = k_1\Delta\sigma + k_2\Delta\pi$$

where σ and π refer to the σ and π characters of the metal phosphorus bond, and also that $\Delta\sigma = k_3\Delta\sigma^*$ we get :-

$$\Delta\nu CO = k_1k_3 \ \Delta\sigma^* + k_2\Delta\pi.$$

Bigorgne explained the linearity by putting $\Delta\pi$ equal to
zero and from other studies[13] he estimated that the π component
with R_3P was nearly zero. Hence he concluded that the π components
of all the phosphines studied were nearly zero. However, another
explanation is possible, for if we put $\Delta\pi = k_4\Delta\sigma + k_5$ then we get :

$$\Delta\nu CO = k_1k_3\ \Delta\sigma^* + k_2k_4k_3\Delta\sigma^* + k_2k_5$$

or $\quad \Delta\sigma CO = (k_1k_3 + k_2k_4k_3)\Delta\sigma^* + k_2k_5$

again a linear relationship between σ^* and the carbonyl stretching
frequency.

The linear relationship between $\Delta\pi$ and $\Delta\sigma$ is in accord with
the idea that electronegative ligands on the phosphorus enhance
the π acceptor property while reducing the σ donation. It is
interesting to note that Graham's[4] results show just such a linear
relationship.

The use of ^{19}F n.m.r. spectroscopy has been mentioned earlier.
Here further studies in this field and in the related field of ^{31}P
spectroscopy will be examined.

Graham, Hogben, and Gay[14] have observed the chemical shift of
the para fluorine atom (δp) in pentafluorophenyl phosphines and
their metal complexes. These observations they concluded provided
evidence for metal-phosphorus $d\pi$-$d\pi$ back donation.

Changes in δp are mainly determined by mesomeric effects.[15]
In the phosphine complexes $P.BCl_3$ the decrease in δp with reference

to the free phosphine is due to the $p\pi$–$d\pi$ donation from the
pentafluorophenyl ring to the phosphorus not being countered by
lone pair back donation into the antibonding orbitals of the ring,
since the lone pair is now involved in bonding to the boron.
(Diagram 1·4).

Diagram 1·4.

The observed increase in δp in the metal complexes $PMo(CO)_5$
from δp for the boron trichloride complexes was said to be due to
competition of the d electrons of the metal and the π electrons of
the pentafluorophenyl ring for the vacant 3d orbitals of the
phosphorus. (Diagram 1·5).
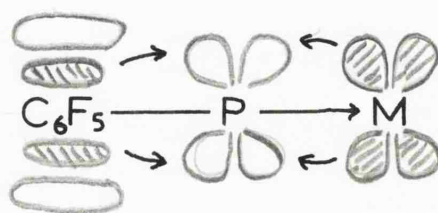
Diagram 1·5.

An alternative explanation to that given above by Graham et al. is

possible. Complexing the phosphine with BCl_3 reduces the lone

pair → ring π^* donation since the lone pair is lowered in energy

by entering the σ molecular orbital between the phosphorus and

the boron atoms. With the metal complex $LMo(CO)_5$ δp increases

from that of the BCl_3 complex due to the decreased binding of the

lone pair and a consequent increase of lone pair → ring π^* back

donation. This explanation requires that BCl_3 is more electronegative

than the $Mo(CO)_5$ group. The Pauling electronegativity values of

1.8 and 2.0 for $Ni(CO)_3$ and BH_3 respectively[16] support this for

BCl_3 would be expected to be even more electronegative than BH_3.

Increasing the charge on the central metal atom results in increased

σ donation and δp falls as is observed (see Chapter I).

[31]P n.m.r. spectroscopy has the advantage that one is looking

at one of the atoms involved. Not enough work as yet has been done

on metal atom n.m.r.[17] for any conclusions about the nature of the

metal-phosphorus bond to be drawn.

Theoretical expressions[18,19] for the chemical shift of the [31]P

nucleus in phosphorus compounds have been derived and the shift

depends on the electronegativity of the ligands, the angles between

them and the occupation of the 3d orbitals. In compounds of the type

$M-PX_3$ it has been calculated[18] that the ^{31}P chemical shift is very

sensitive to changes in the MPX angle when M has a low electronegativity.

This is the situation in most metal-phosphine complexes since the
metal is in a low oxidation state. Thus unless the angles are
accurately known, any meaningful conclusion about π bonding are
hard to arrive at. It has been pointed out[20] that in isostructural-
isoelectronic complexes comparisons are more meaningful.

The pioneer study[21] in this field was the study of mixed
carbonyl phosphine complexes of zerovalent nickel. The coordination
shift (defined as $\delta_P - \delta_{M-P}$) was found to be fairly constant and
negative in most complexes, with the exception of complexes in which
phosphorus chlorine bonds were present, e.g. $(PCl_3)_4 Ni$. It was
concluded from this study that the major contributions to the
coordination shift were changes in angle on coordination, and
inductive effects of the substituents on the phosphorus, $d_\pi - d_\pi$ back
bonding was said to be either small or constant in the series of
complexes.

Another series studied was the monophosphine group VI
pentacarbonyls.[22] The coordination shifts were negative and nearly
constant for a given metal, but decreased in magnitude from chromium
to tungsten. The major contributions were angle changes and
electronegativity, and the decrease of the coordination shift for
the heavier metal atoms was ascribed to a smaller excitation energy
term and to increased anisotropy effects.

P_4O_6 forms the compounds $P_4O_6.BH_3$ and $P_4O_6.Ni(CO)_3$ with diborane and nickel carbonyl respectively.[16] The coordination shift of $P_4O_6.BH_3$ is +20 p.p.m. while that of the nickel compound is -20 p.p.m. The difference was accounted for by the different electronegativity of the acceptor atoms, and theoretical calculations indicate a 3d orbital population of 1.8 electrons on the coordinated phosphorus in both the complexes. It is not possible however in the nickel complex to say whether these electrons came from the nickel or the oxygen atoms in the ligand.

Spin-spin coupling constants between the central metal atom and the phosphorus have also been determined from ^{31}P n.m.r. spectroscopy of metal phosphine complexes.

It has been shown[23] that there are two main contributions to J.

1) The Fermi contact term which involves s orbitals only. Since these can only participate in σ bonding the size of J is related by this mechanism to the proportions of s character the two atoms use in forming the σ bond between them.

2) Dipole-dipole coupling of the nuclear and electron spins. This will operate through π and σ type orbitals. Calculations show that the Fermi contact term is dominant so that changes in J are primarily due to changes in the σ bonding.

The experimental evidence for this conclusion is open to question since an independent measure of σ bonding changes is not available.

Some authors[22,24] link values of J with the π bond between tungsten

and phosphorus.

The coupling constant J_{Pt-H} was found to be 1276 c./sec. in

trans $(Et_3P)_2PtHCl$[25] and here π bonding in the Pt-H bond is very

unlikely.

Venanzi et al.[26] have measured phosphorus-platinum coupling

constants in a large number of cis and trans dichloro-bisphosphine

platinum(II) complexes. They find that J_{Pt-P} in the cis complexes

is greater than in the trans complexes. The π bonding between the

phosphorus and the platinum would be expected to be less in the

trans complex, but similar results are observed in the platinum(IV)

complexes where π bonding would be expected to be much less important.

It was concluded that the s components of the σ bond were greater in

the cis than in the trans series.

In the series of compounds $PW(CO)_5$[22] the value of J_{W-P} was plotted

against νCO for the most intense carbonyl band. A linear correlation

was observed and the coupling constant increased as the number of phenyl

groups increased in the phosphine $Bu_{3-n}Ph_nP$ n = 0,1,2 and 3.

J_{W-P} was stated to be directly related the the π bond order in the

W-P bond, or indirectly as increase in the π bond order will synergically

increase the σ bond order. While the authors' infrared results are

meaningless it should be valid to transfer Graham's[4] results on the

complexes $PMo(CO)_5$ to the isomeric tungsten series. He found that

Bu$_3$P was a better π acceptor and a better σ donor than Ph$_3$P, and attributed the unexpected order to synergic effects. This is clearly not in accord with the values of J$_{W-P}$. A possible explanation is that as the number of phenyl groups increases the metal-phosphorus-carbon bond angles will increase due to steric effects, and the lone pair involved in bonding to the metal will have more 3s character, so that J$_{W-P}$ will increase with the number of phenyl groups present. No support for this is found however from structural studies of [Et$_3$PMn(CO)$_4$]$_2$[27] and (Ph$_3$P)Mn(CO)$_4$SnPh$_3$.[28] These bear a very close relationship to the PW(CO)$_5$ compounds. In both however, the average metal-phosphorus-carbon bond angle is 116°. A similar but relatively smaller effect of increase of J with increase in the number of phenyl groups was found in the cis and trans complexes P$_2$PtCl$_2$.[29]

Very recently J$_{W-P}$ in cis and trans bisphosphinetetracarbonyltungsten(0) complexes have been determined.[24] Higher values were observed in the trans complexes, and the following explanation given. A phosphine trans to a carbonyl group, i.e. cis complex, has less π back-donation due to competition for the metal d electrons by the carbonyl, than two mutually trans phosphines have.

They conclude the J_{W-P} is a direct measure of the W-P bond order.

While in the _cis_ and _trans_ complexes the phosphorus may use the same amount of s character, it is reasonable to expect that the tungsten will use different amounts of 6s character in the hybrids forming σ bonds between the carbon and the phosphine groups. To be consistent with the values of J_{W-P} the 6s character must be greater in the tungsten carbon bond than in the tungsten phosphorus bond.

It is of interest to note that the substitution of phenyl groups for butyl groups on the phosphine results in little change (10 c./sec.) in _cis_ $P_2W(CO)_4$ compared with the much larger (45 c./sec.) change in the $PW(CO)_5$ complexes.

A potentially very powerful method of examining the nature of the metal phosphorus bond is the contact shift in the nuclear magnetic resonance spectrum of paramagnetic phosphine complexes. A good discussion of the effect has been given.[30] The chief chemical limitation is that not many transition metal phosphine complexes are paramagnetic and have short enough relaxation times for the observation of an n.m.r. signal. No e.s.r. experiments seem to have been done.

In the complexes of the type $[(R-\langle\bigcirc\rangle-)_3P]_2NiX_2$ it was calculated[31] from the contact shift of the protons in the proton n.m.r. spectrum that about 0.01 unpaired electron was present in all the phenyl rings.

The total transfer of spin density to a phosphine ligand will
be greater than 0.005 electrons since spin density also is present
on the carbon and phosphorus atoms, and delocalisation from the
phosphorus to the phenyl rings is poor. This figure must also be
multiplied by at least two since only the two unpaired electrons of
the four in the T_2 level are being observed. The factor is probably
greater since the four electrons in the E level are also capable
of being delocalised onto the ligand. Thus the total back-donation
per nickel phosphorus bond is at least .02 electron. It was further
stated that the only mechanism for delocalisation is the d_π–d_π
back-donation from the metal 3d orbitals to the 3d orbitals on the
phosphorus. From these spin density is transferred by their
conjugation with antibonding π levels of the phenyl rings. This is
not true for the unpaired d electrons of the metal are in the
antibonding T_2 orbitals which have some ligand character, resulting
in some spin transfer without dπ–dπ back bonding being considered.
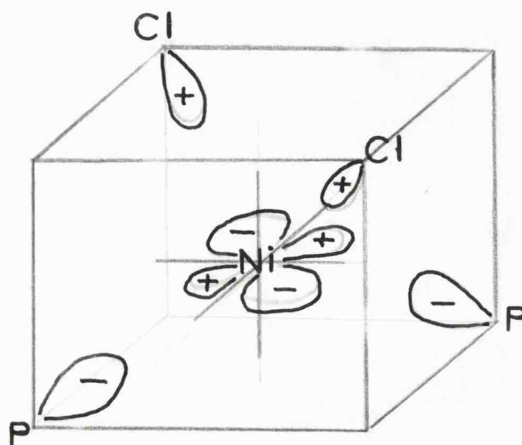
Diagram 1·6 (One of the three T_2 antibonding orbitals.)

Further support for this observation comes from the proton

contact shift of the $(C_6H_5CH_2NH_2)_6Ni^{2+}$ cation[32] where spin density

is found on the phenyl rings in the antibonding π orbitals. Here

no $d\pi$–$d\pi$ back bonding is possible although hyperconjugative effects

are and transmission of spin density probably mainly involves

placing an electron in the σ^* orbitals of the metal–nitrogen bond.

In view of this the attribution of the 0.02 electron back donation

solely to a $d\pi$–$d\pi$ mechanism should be treated with caution.

Dipole moment studies have been done for nickel phosphine

complexes. The greatest difficulty in the method is proceeding from

the observed dipole moment to the value of the nickel–phosphorus

bond moment, since this requires knowledge of the conformation of

the molecule and estimation of all the bond moments for the other

bonds and lone pairs present in the molecule.

Chatt and Hart[33] found a value of about 5.3D for the dipole

moment of $Ni(CO)_2[(PR_2)_2C_6H_4]$ R = Me, Et, Ph. After assuming a

total bond moment of 0.5D for the $Ni(CO)_2$ group and neglecting the

bond moments of the organic residues, they derived a value of 3.4D

for the nickel–phosphorus bond moment. On the basis of a σ transfer

of 0.5 electron (as has been postulated to occur in $R_3P{\rightarrow}BX_3$) they

concluded that $d\pi$–$d\pi$ back donation was responsible for the reduction

to the value of 0.31 electron calculated from the bond moment.

Thus the π bond is at least 40% of the σ bond. This reasoning

assumes that a zero-valent metal complex will accept the same

number of electrons as a powerful Lewis acid such as BCl_3, and the

value of 40% is almost certainly too high. This reasoning may also

be found in the interpretation of the ^{19}F n.m.r. spectra of

pentafluorophenyl phosphine metal complexes (see earlier in the

Introduction).

The opposite view-point to that of Chatt and Hart was taken

by Bigorgne.[34] He used the evaluated bond moments and evaluated

the charges on the ligands assuming no back-bonding occurs. In

$Ni(CO)_3P(OMe)_3$ he calculated that the phosphorus carries a positive

charge of 0.24 electrons. This value is probably less than the

actual σ transfer due to donation of electrons from the neighbouring

oxygens (cf. ^{31}P n.m.r. of $Ni(CO)_3.P_4O_6$) and to the possibility of π

back-donation from the nickel.

The Mössbauer spectra of a series on iron tetracarbonyl

derivatives have been studied.[35] Two quantities can be observed -

the isomer shift and the quadrupole splitting. The isomer shift

depends on the 4s electron density at the iron nucleus while the

size of the quadrupole splitting depends on the electric field

gradient at the iron nucleus. The σ bond of the ligand donates

electrons to the empty 4s orbital causing an increase in the 4s

electron density, while back-bonding removes some shielding of the 4s

electrons and also increases the 4s electron density. Thus the two

effects both cause an isomer shift in the same direction. Both

effects also cause a build-up of electron density between the iron

and the ligand giving an electric field gradient. The larger the σ

and π donations the greater the shift and also the quadrupole

splitting. A linear correlation was found in this study. From the

order of the isomer shifts and the expected changes in forward and

back donation as the nature of the ligands changed it was concluded

that the forward donation is dominant. The expected changes in

forward and back donation were arrived at by chemical intuition so

that the conclusion is of the same order.

The kinetics[36] of exchange of phosphines or phosphites in

$P_2Ni(CO)_2$ were accounted for by assuming the rate determining step

to be dissociation of $P_2Ni(CO)_2$ to yield $PNi(CO)_2$ which then reacts

with the other phosphine. The rate of dissociation was found to be

dependent on the nature of the phosphine, and paralleled the basicities

of the phosphines. It was suggested that as the metal in a

tetrahedral complex forms two strong π bonds these were used for

the carbonyls whereas the phosphines were primarily bound by σ bonds.

In the case of $PNi(CO)_3$ the rate determining step is loss of CO rather

than phosphine, since the third carbon monoxide molecule is less π

bonded than the other two. A note of warning[37] has been given about

assuming dissociative mechanism for these sort of systems. The

carbonyls in $Ni(CO)_4$ exchange with labelled CO and are displaced by

a phosphine.   The kinetics indicate that the reaction is
first-order in $Ni(CO)_4$ and zero order in entering ligands.
It has been assumed that this indicates the rate determining
step is the dissociation $Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the labelled carbonyl
exchange and for carbonyl displacement by a phosphine are very
different, and competition experiments indicate no common
intermediate for the two reactions.

Square planar _trans_ complexes $(piperidine)(L)PtCl_2$ were
studied by ultra-violet spectroscopy.[38]   One of the bands observed
was assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition
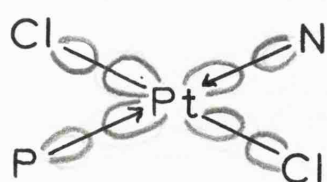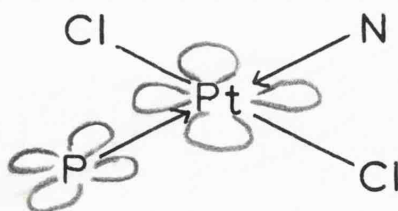
$$d_{x^2-y^2} \qquad\qquad d_{xy}$$

The energy of the transition decreased by about 5 k.cals/mole on
going from $L = P(OMe)_3$ to $L = $ piperidine. This decrease was
attributed to $d\pi-d\pi$ stabilisation of the d_{xy} level rather than σ
destabilisation of the $d_{x^2-y^2}$ level. If it is assumed that the

piperidine ligand has no π acceptor character then this figure

suggests that the total π contribution to the platinum-phosphorus

bond in <u>trans</u> $[P(OMe)_3][C_5H_{11}N]PtCl_2$ is double this or 10 k cal/mole.

This figure may be in error for two reasons. Interelectronic

repulsion terms[39] have not been included to correct the observed

transition energy to the actual energy difference between the

$d_{x^2-y^2}$ and the d_{xy} levels. The inclusion of these effects result

in the actual energy increasing over that calculated from the

observed transitional frequency. Here however, we are concerned

with the difference between the correction terms for the piperidine

and trimethylphosphite complex. As these corrections (Racah

parameters) are to a first approximation a function of the metal

ion and its charge only, the difference will be certainly small or

even zero. The more σ bonding that takes place the more the

$d_{x^2-y^2}$ level will be destabilised. Graham[4] found that $P(OMe)_3$

was a better σ donor than piperidine in $LMo(CO)_5$. If it is

permissible to transfer these results to a bivalent platinum complex

then the phosphite, while stabilising the d_{xy} level would destabilise

the $d_{x^2-y^2}$ level. This means that the calculated 5 k cals/mole

includes both effects. It is not possible to apportion the total

effect to σ destabilisation and to π stabilisation.

The isomerisation of <u>cis</u> $(PEt_3)_2PtCl_2$ to the <u>trans</u> form is

found to be an endothermic reaction. Chatt and Wilkins[40] estimated

that the reaction should be exothermic due to the discharge of

the electric dipole of 10.7D of the cis form. After correcting

for the differing solvation they concluded that the isomerisation

still ought to be exothermic and that the difference of 10 kcal/mole

between the observed and calculated heats of isomerisation was due

to the greater π bond energy in the cis form.

Other physical data[26] suggest that the platinum-phosphorus

bond is stronger in the cis complex. Venanzi et al[26] on the basis

of the platinum-phosphorus coupling constants in the two isomers

consider that the increase in the bond strength of the cis isomer

is primarily an increase in the σ component.

Two interrelated chemical phenomena are generally considered

to support the idea of $d\pi-d\pi$ back donation in metal-phosphine

complexes. As one moves from left to right across the transition

series the number of phosphine complexes known increases, and

they become more stable relative to the amine complexes. The

oxidation state of the metal atom also has an effect and low oxidation

states stabilise phosphine complexes. With the notable exception

of borine and trimethylboron non-transition metal Lewis acid

complexes with amines are more stable than the corresponding

phosphine compound. The generally accepted view[41] is that this

trend follows the d orbital population of the metal and hence the

possibility of π bonding.

It is however very dangerous to argue on the basis of
non-existence of compounds. They may be unstable for entirely
different reasons to those suggested or they may very well be
prepared in the near future using different preparative techniques
and be found to be stable with respect to dissociation, but not
to the conditions of the abortive preparations. The paucity of
phosphine complexes in the early part of the transition series[1]
may well be due to this as donor solvents preferentially complex.
It could also be due to weaker σ bond formation between the metal
and the phosphorus. The quantity of such complexes similarly is
without meaning, since work on phosphine complexes of the platinum
end of the series is fashionable, and also preparatively easier
than work on phosphine complexes of elements such as titanium or
vanadium. To draw any valid conclusions a large body of quantitative
stability data is needed, but little is available concerning
phosphine complexes.

Another point about chemical evidence is that small differences
in the thermochemical parameters of a reaction will completely alter
the observations. A change in ΔG of 2 kcal/mole means a change of
approximately 100 in the equilibrium constant, and this is often
enough to convert what on the bench appears "stable" to "unstable".
All too often entropies and solvation effects are neglected. Thus
to infer from chemical observations evidence about bond strengths

without a quantitative treatment of other factors is invalid.

The present author believes that the physical evidence indicates the existence of $d\pi$-$d\pi$ back donation in metal phosphine complexes but that the π component is much weaker than the σ component. The role of the π bond in explanation of chemical phenomena is probably overemphasised due to the fact that it is often easier to decide which way π bonding effects will operate.

CHAPTER ONE

Since the initial preparation of $(C_6F_5)_3P$[42] a considerable

amount of chemistry has been carried out with Group V elements

containing pentafluorophenyl groups. The source of the

pentafluorophenyl group has been the Grignard reagent[43] prepared

from pentafluorobromobenzene and magnesium. By altering the ratio

of the Grignard reagent to the trichloride it has been possible to

prepare the compounds $(C_6F_5)MCl_2$[44,45] and $(C_6F_5)_2MCl$[44,45] as well as $(C_6F_5)_3M$

(M = P, As). In the hydrocarbon system reaction of the Grignard

with the trichloride cannot be stopped at the intermediate stages

by alteration of the ratio. The chlorophosphines undergo many

further reactions making them very useful synthetic intermediates.

$(C_6F_5)PCl_2$ and $(C_6F_5)_2PCl$ can both be converted into mixed alkyl

or aryl pentafluorophenyl containing tertiary phosphines.[46]

$(C_6F_5)Et_2P$ and $(C_6F_5)_2MeP$ have been made in this way from $(C_6F_5)PCl_2$

and $(C_6F_5)_2PCl$ since the alternative starting materials Et_2PCl and

$MePCl_2$ are not generally available.

Primary amines react with $(C_6F_5)PCl_2$ to yield the corresponding

pentafluorophenylphosphonous diamides $(C_6F_5)P(NHR)_2$.[47] The action of

mercury on $(C_6F_5)PBr_2$[48] gives the ring compound $(C_6F_5P)_5$ while

$(C_6F_5)AsCl_2$ produces a four membered ring $(C_6F_5As)_4$.[45]

The $(C_6F_5)_2MCl$ (M = P, As) compounds undergo similar reactions

to those of $(C_6F_5)MCl_2$. Thus mercury induced chlorine elimination

produced the compounds $(C_6F_5)_4M_2$. The diarsine[45] exists in two

isomeric forms which can be separated by sublimation. Both forms
are interconverted on prolonged heating. It was suggested that
the two forms are trans and gauche rotamers existing by virtue of
restricted rotation about the arsenic-arsenic bond. In the analogous
diphosphine[49] only one isomer was formed. The phosphorus-phosphorus
bond is shorter in the diphosphine than the arsenic-arsenic bond
in the diarsine and the molecule stays locked in the most stable
configuration.

Although other secondary amines give $(C_6F_5)_2PNR_2$ with $(C_6F_5)_2PCl$
dimethylamine does not; further reaction takes place and two fluorines
are displaced from the rings by dimethylamino groups. Mass
spectrometry showed that the product[44] was
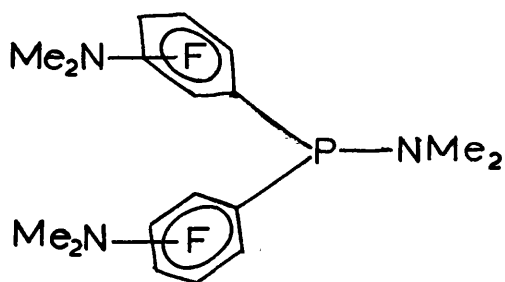
but the orientation of the groups has not been determined.

Other reactions of interest include those in which the
pentafluorophenyl phosphorus or arsenic bond is broken. Chlorination
of $(C_6F_5As)_4$[45] yields arsenic trichloride and pentafluorochlorobenzene,
while the pentameric phosphorus compound gives $C_6F_5PCl_2$.[48]

$(C_6F_5As)_4 + Cl_2 \rightarrow [C_6F_5AsCl_4] \rightarrow C_6F_5Cl + AsCl_3$

$(C_6F_5P)_5 + Cl_2 \rightarrow [C_6F_5PCl_4] \rightarrow C_6F_5PCl_2 + Cl_2$
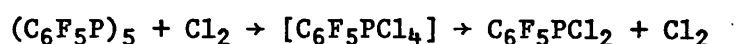
The pentafluorophenyltetrachlorophosphorane[48] can be isolated but is very unstable. Alkaline hydrolysis of $(C_6F_5)_3Sb$,[50] $(C_6F_5)_2AsCl$,[45] or $C_6F_5AsCl_2$[45] produces pentafluorobenzene, although controlled neutral hydrolysis of the last two produced $(C_6F_5)_2AsOAs(C_6F_5)_2$ and $(C_6F_5AsO)_n$ respectively.

A few reactions of $(C_6F_5)_3P$ have been investigated. Oxidation with acid dichromate produced $(C_6F_5)_3PO$,[42] while heating the phosphine with sulphur slowly produced the sulphide.[51] Chlorination gave the trispentafluorophenyldichlorophosphorane $(C_6F_5)_3PCl_2$[51] which was hydrolysed to the oxide.

In contrast to the large body of organic chemistry of pentafluorophenyl compounds of Group V known, the effectiveness of these compounds as ligands has been little studied. $(C_6F_5)Ph_2P$[14] has been shown to form a complex with boron trichloride, and to displace a carbonyl group from molybdenum hexacarbonyl and from iron pentacarbonyl to produce the compounds $LBCl_3$, $LMo(CO)_5$ and $LFe(CO)_4$. Similarly $(C_6F_5)_2PhP$[14] gave $LMo(CO)_5$ when reacted with molybdenum hexacarbonyl. No complexes of $(C_6F_5)_3P$ have been reported up to the present. The only other metal complex known is the bispentafluoro-phenylphosphido bridged compound[49] shown below,

$$(C_6F_5)_2$$

$$
\begin{array}{c}
P \\
(CO)_3Fe \quad\quad\quad Fe(CO)_3 \\
P
\end{array}
$$

$$(C_6F_5)_2$$
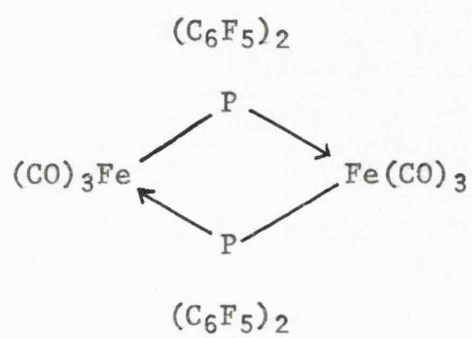
the structure of which is demonstrated by mass spectroscopy.

DISCUSSION

Trispentafluorophenylphosphine is a weaker donor than triphenylphosphine, not only in metal complexes but also towards other acceptors such as BCl_3. The mixed phenylpentafluoro-phenylphosphines are also weaker than triphenylphosphine and the donor ability decreases monotonically with the increase in the number of pentafluorophenyl groups present.

Both triphenylphosphine and diphenylpentafluorophenylphosphine formed complexes with BCl_3 and could be protonated. $(C_6F_5)_3P$ in contrast shows no evidence of complex formation with BCl_3 or BF_3, and a proton n.m.r. of a solution of this phosphine in concentrated sulphuric acid fails to show any peaks corresponding to a phosphorus-hydrogen bond. In agreement with this it has been found that $(C_6F_5)_3P$ is not quaternized with methyl iodide.[42] Phenylbispentafluorophenylphosphine does complex with BCl_3, but $(C_6F_5)Ph_2As$ does not.

Antimony pentachloride and antimony pentafluoride react with $(C_6F_5)_3P$ and coloured materials are produced.

Mercuric chloride, stannic iodide and nickel chloride form complexes[52] with triphenylphosphine but not with trispentafluoro-phenylphosphine. Triphenylphosphine gave the selenide Ph_3PSe[53] on heating with selenium, or on reaction with potassium selenocyanate[54]

in acetonitrile. Trispentafluorophenylphosphine is recovered unchanged when it is substituted for triphenylphosphine in these reactions.

Attempts to make $(C_6F_5)_3PO$ and $(C_6F_5)_3PS$ by reaction of C_6F_5Li with phosphoryl chloride and thiophosphoryl chloride respectively yield only waxy solids from which no pure compounds can be isolated. While some of the required product may be present this reaction is clearly of no use as a preparative route.

Preliminary experiments with $(C_6F_5)_3P$ indicated that platinum(II), and rhodium(I) form complexes readily with this ligand so an investigation of the complexing power of the ligands $(C_6F_5)_xPh_{3-x}M$ where M = As, Sb was undertaken.

A summary of the reactions between the ligands and compounds of rhodium and platinum is given in Table l-2. *(p. 64b)*

Microanalytical data for all the complexes prepared are presented in Table l-3 and in the Experimental section.

Palladium and Platinum Complexes.

These were all of the type L_2MX_2 (X = Cl, Br, I) and since the *p. 64 k/i/).* infrared spectra (400-200 cm^{-1}) (Table l-7) of the chloride and bromide complexes show only one metal-halogen stretching frequency they presumably have a trans configuration. The range of frequencies found for these metal-halogen stretching vibrations is in agreement

with those found for other _trans_ complexes of this type.[55] The

metal-iodine frequencies of the complexes L_2MI_2 have not been

located, but the complexes are presumably _trans_. Attempts to

prepare $[(C_6F_5)_3P]_2PdI_2$ by the action of sodium iodide on an

acetone solution of the dichloride produced a purple solution from

which only PdI_2 and $(C_6F_5)_3P$ could be isolated. Refluxing $(C_6F_5)_3P$

with PdI_2 in xylene did not give a complex.

Preliminary experiments with hydrated nickel chloride and the

phosphines $(C_6F_5)Ph_2P$ and $(C_6F_5)_3P$ give no complexes, but $Ni(CO)_4$

and $(C_6F_5)_3P$ give a pale yellow solid. The carbonyl stretching

frequency pattern indicates that it is $(C_6F_5)_3P\ Ni(CO)_3$.[55]

$$L_2PtCl_2\ +\ 2L'\ \rightarrow\ L_2'PtCl_2\ +\ 2L. \qquad \text{Equation 1.}$$
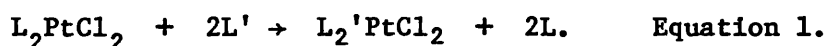
Qualitative displacement reactions of the type illustrated in

equation 1 where L_2 or L_2' is one molecule of a bidentate ligand

or two molecules of a unidentate ligand have been investigated.

The displacement reactions indicate that the complexes increase in

stability in the order of ligands,

Me_2S < $(C_6F_5)_3P$ < $(C_6F_5)Ph_2As$ < $(C_6F_5)_2PhP$ < tris(2,6-difluorophenyl)

phosphine, cycloocta-1,5-diene < Ph_3As < $(C_6F_5)Ph_2P$ < Ph_3P < $(PhO)_3P$.

None of the reactions is reversible, and in no reaction was the

equilibrium displaced by precipitation of a product since all the

products remained in solution. However, in the reaction of $(C_6F_5)_3P$

with _cis_$(Me_2S)_2PtCl_2$ any dimethylsulphide released would escape

from the reaction mixture and so displace the equilibrium.

In agreement with earlier work[41] phosphines are better ligands than arsines of similar structure. Thus Ph_3P displaces Ph_3As from its complex and $(C_6F_5)Ph_2P$ displaces $(C_6F_5)Ph_2As$. In view of this it is not surprising that no complexes of $(C_6F_5)_2PhAs$ can be isolated. It should also be noted that displacement of triphenylphosphine by triphenylphosphite has been observed several times previously.[56,57]

Change in the oxidation state of the central metal atom has also been found to alter the ligand displacement order[41] and we find that $(C_6F_5)Ph_2P$ will displace Ph_3As from $(Ph_3As)_2PtCl_2$ but not from $(Ph_3As)_4Pt$.

It can be seen from the displacement series that as the number of pentafluorophenyl groups increases in the series $(C_6F_5)_nPh_{3-n}$ (n = 0,1,2 or 3) the ligand properties of the phosphine become worse. Similarly, tris(2,6-difluorophenyl)phosphine is a poorer ligand than triphenylphosphine.

The action of pyridine on $[(C_6F_5)_3P]_2PtX_2$ X = Br, Cl, yields the compounds $[(C_6F_5)_3P](C_5H_5N)PtX_2$. The infrared spectra (400-200 cm^{-1}) (Table 1·7), *p. 64 h/i/j.* of these compounds show that the halogen atoms are in a trans configuration.

Two direct methods which have been used previously for the preparation of zerovalent platinum triphenylphosphine complexes were tried using the phosphines $(C_6F_5)_3P$ and $(C_6F_5)Ph_2P$. The method of Malatesta and Cariello[57] using an alcoholic solution of the phosphine

to which potassium hydroxide had been added produces the complexes L_2PtCl_2, while the action of hydrazine^{57} on the complexes L_2PtCl_2, (L = $(C_6F_5)_3P$, $(C_6F_5)_2PhP$ and $(C_6F_5)Ph_2P$) yields dark solutions from which pure compounds were not isolated. The unsuccessful attempt to prepare $Pt[(C_6F_5)Ph_2P]_4$ by displacement of Ph_3As from $Pt(AsPh_3)_4$ has already been noted.

Rhodium complexes.

When trispentafluorophenylphosphine (abbreviated P_f) and hydrated rhodium trichloride in ethanol are refluxed together for 2-3 hours a dark green crystalline solid precipitates. Analysis and molecular weight determinations indicate the formula to be $(P_f)_4Rh_2Cl_2$ for which a chlorine-bridge square planar rhodium(I) structure is proposed. Trispentafluorophenylphosphine oxide may also be isolated from the reaction mixture suggesting that the phosphine is the reducing agent. Further evidence for the structure of tetrakis(trispentafluorophenylphosphine) $\mu\mu'$ dichlorodirhodium(I) is provided by an almost quantitative synthesis from tetrakisethylene $\mu\mu'$ dichlorodirhodium(I) and P_f in refluxing methanol; as expected the compound is diamagnetic and gives no e.s.r. signal at 25° in hexafluorobenzene solution or as a solid at 25° or at -196°.

Tetrakistrispentafluorophenylphosphine $\mu\mu'$ dichlorodirhodium(I) forms green crystals which are dichroic (green purple to light brown).

This colour is unusual for a rhodium(I) compound and it is interesting to note that the paramagnetic rhodium(II) compound <u>trans</u>-dichlorobis(triorthotolylphosphine)rhodium(II)[58] has a similar appearance.

Analogous complexes of rhodium(I) with phenylbispentafluorophenyl phosphine and diphenylpentafluorophenylphosphine are prepared in a similar manner. With these two phosphines the corresponding bromide complexes $P_4Rh_2Br_2$ ($P = (C_6F_5)_2PhP$ or $(C_6F_5)Ph_2P$) are readily isolated using hydrated rhodium tribromide. With P_f no bromo complex can be obtained.

The infrared spectrum (400-200 cm^{-1}) of $(P_f)_4Rh_2Cl_2$ shows two bands at 347 and 306 cm^{-1} in addition to those normally due to the free phosphine (Table 1·7) (p 64 h/i/j) We assign the band at 347 cm^{-1} to the coordinated $(C_6F_5)_3P$ ligand also, since similar bands are observed in <u>trans</u>-$(P_f)_2PtI_2$ and <u>trans</u>-$(P_f)_2PdBr_2$, (the metal halogen frequency is very much lower in these complexes). The lower broad band at 306 cm^{-1} we assign to ν(Rh-Cl). In support of this assignment similar broad bands around 300 cm^{-1} are observed for the complexes (P. 64 h/i/j) $[(C_6F_5)_x(Ph)_{3-x}P]_4Rh_2Cl_2$ ($x = 0,1$ or 2) (Table 1·7) which are not present in the bromide complexes ($x = 1$ or 2).

Group theory predicts that a planar $RhCl_2Rh$ unit (D_{2h} symmetry) should show two infrared active Rh-Cl stretches of b_{2u} and b_{3u} symmetry; a bent $RhCl_2Rh$ unit (C_{2v} symmetry) should show three

infrared active Rh-Cl stretching vibrations ($a_1 + b_1 + b_2$). Thus

on this basis more than one band due to ν(Rh-Cl) would be expected

for our complexes instead of the observed single frequency and it

is possible that the other bridge band may be of lower frequency and

too weak to be observed. A very unsymmetrical rhodium-chlorine

bridge system may be present.[59] It is interesting to note that the

norbornadiene complex $[RhCl(C_7H_8)_2]_2$ also shows only one band due

to ν(Rh-Cl) at 249 cm^{-1}.

The failure to isolate complexes of the type $[(C_6F_5)_xPh_{3-x}P]_3RhCl$

(x = 1,2 or 3) may be the effect of steric repulsion between the

ligands.

$(P_f)_4Rh_2Cl_2$ is sparingly soluble in ether, chloroform, acetone,

pentafluorobenzene and hexafluorobenzene. It is insoluble in benzene,

alcohols and petroleum. Attempts to recrystallise the compound

result in some decomposition. The instability is probably due to

an irreversible dissociation, since decomposition is also observed

in degassed solvents under nitrogen. The osmometric molecular weight

in pentafluorobenzene decreases slowly with time, as does that of

$[(C_6F_5)_2PhP]_4Rh_2Cl_2$, but $[(C_6F_5)Ph_2P]_4Rh_2Cl_2$ decomposes completely

within a minute.

The action of carbon monoxide on $(P_f)_4Rh_2Cl_2$ in pentafluorobenzene

results in bridge cleavage to give trans-$(P_f)_2RhCOCl$. It has been

observed[55] that in complexes containing a carbonyl group trans to a

chlorine, the νCO band occurs at a higher frequency in chloroform

solution than in benzene solution, but if the carbonyl group is

<u>trans</u> to a phosphine, the solution νCO frequency is lowered on going

from benzene to chloroform. Using this criterion (Table 1·10), the

compounds $[(C_6F_5)_x(Ph)_{3-x}P]_2RhCOCl$ (x = 1,2 or 3) are all <u>trans</u>.

TABLE 1·10

ν(CO) frequencies (cm^{-1}).

Compound	Nujol	C_6H_6	$CHCl_3$	$\nu CHCl_3 - \nu C_6 H_6$
$[(C_6F_5)_3P]_2RhCOCl$	2004	1998	2004	+6
$[(C_6F_5)_2Ph\ P]_2RhCOCl$	1998	1992	1996	+4
$[(C_6F_5)Ph_2P]_2RhCOCl$	1974	1978	1982	+4

The carbonyl complexes are readily prepared by reaction of

$Rh_2(CO)_4Cl_2$ with the appropriate phosphine. <u>Trans</u>-$(P_f)_2RhCOCl$ may

also be prepared in low (ca. 30%) yield by refluxing the phosphine

with hydrated rhodium trichloride in β-methoxyethanol.

On refluxing $(P_f)_4Rh_2Cl_2$ suspended in β-methoxyethanol,

decomposition to P_f and a non-carbonyl-containing black solid

(possibly rhodium metal or an oxide) occurs. In refluxing ethanol

no change occurs, but the addition of chloroform to the suspension

produces <u>trans</u>-$(P_f)_2RhCOCl$. The role of the chloroform is to bring

the complex into solution then carbonyl abstraction can proceed

readily. With chloroform alone $(P_f)_4Rh_2Cl_2$ gives unstable solids

which probably contain rhodium(III). $\underline{Trans}$-$(P_f)_2RhCOCl$ is also

obtained by treating $(P_f)_4Rh_2Cl_2$ with propionaldehyde or benzaldehyde

in a similar manner to $(Ph_3P)_3RhCl$[60] which also abstracts carbon

monoxide from aldehydes. The reaction of lithium bromide with

$\underline{trans}$-$(P_f)_2RhCOCl$ failed to produce the corresponding bromide, and

with sodium iodide no pure compound could be isolated.

Cyclo-octa-1,5-diene slowly reacts with a suspension of

$(P_f)_4Rh_2Cl_2$ in benzene to give $(C_8H_{12})_2Rh_2Cl_2$. This reaction is

irreversible. The reaction of norbornadiene with $(Ph_3P)_3RhCl$[61] has

been shown to give $(Ph_3P)(C_7H_8)RhCl$.

Both triphenylphosphine and triphenylphosphite displace P_f

irreversibly from $(P_f)_4Rh_2Cl_2$ to yield the known compounds $(Ph_3P)_3RhCl$[61][62]

and $[(PhO)_3P]_3RhCl$.[56] Triphenylphosphine displaces P_f from

$\underline{trans}$-$(P_f)_2RhCOCl$ to yield $\underline{trans}$-$(Ph_3P)_2RhCOCl$.

The action of pyridine and ethylenediamine on cold chloroform

solutions of $(P_f)_4Rh_2Cl_2$ give unidentified products some of which still

contain coordinated phosphine as shown by infrared spectra.

These substitution reactions indicate that P_f may be displaced

from $(P_f)_4Rh_2Cl_2$ and $\underline{trans}$-$(P_f)_2RhCOCl$.

Trispentafluorophenylphosphine Rhodium(III) Complexes

Attempts to prepare trispentafluorophenylphosphine complexes of rhodium(III) have resulted (with one possible exception) in mixtures, and all the materials isolated dissociate irreversibly in solution.

The passage of chlorine gas through a suspension of $(P_f)_4Rh_2Cl_2$ in carbon tetrachloride gives a red solution which on removal of the solvent gives a red solid. The elemental analysis corresponds approximately to $(P_f)_4Rh_2Cl_6 . 1·5CCl_4$. However, the infrared spectrum of the solid shows a band at 1235 cm^{-1} characteristic of the phosphorus oxygen stretch in $(C_6F_5)_3PO$. This oxide can be isolated from the red solid. Similarly a mixture containing $(C_6F_5)_3PO$ of approximate composition $(P_f)_4Rh_2Cl_6$ can be formed from $(P_f)_4Rh_2Cl_2$ and liquid chlorine in a Carius tube. This $(C_6F_5)_3PO$ is presumably formed by hydrolysis of $(C_6F_5)_3PCl_2$ which results from chlorination of the phosphine.

"$(P_f)_4Rh_2Cl_6.1·5 CCl_4$" dissolves in benzene to give initially a clear solution which slowly deposits a microcrystalline orange solid (uncontaminated by $(C_6F_5)_3PO$) of approximate composition P_fRhCl_3 as shown by analytical and molecular weight data. The residual soluton contains $(C_6F_5)_3PO$. The ^{19}F n.m.r. spectrum of this compound in chloroform solution shows a set of peaks corresponding to that of uncoordinated phosphine, and another set shifted considerably downfield which are assigned to P_f coordinated to Rh(III), (Table 1·5). (p 64 o/f)

The action of liquid chlorine on trans-$(P_f)_2$ RhCOCl gives an

orange solid of composition $(P_f)_2$RhCOCl$_3$. The infrared spectrum

shows a carbonyl stretch at 2132 cm^{-1} typical of a rhodium(III)

species, but a band at 1235 cm^{-1} due to $(C_6F_5)_3$PO is observed

showing this material also to be a mixture. If trans-$(P_f)_2$RhCOCl

is suspended in carbon tetrachloride and reacted with liquid chlorine

a mixture containing $(C_6F_5)_3$PO of composition $(P_f)_2$RhCOCl$_3$.CCl$_4$ is

obtained.

The treatment of $(P_f)_4$Rh$_2$Cl$_2$ in refluxing benzene with methyl

iodide results in the decomposition of the complex. A solution of

trans-$(P_f)_2$RhCOCl in methyl iodide shows only one carbonyl peak in

the infrared corresponding to that of the starting material, and

this solution slowly decomposes with the liberation of the phosphine.

^{19}F N.M.R. Spectra

The ^{31}P n.m.r. spectra[63] of the ligands $(C_6F_5)_x$Ph$_{3-x}$P (x = 1,2,3)

and of their corresponding oxides have shown that the shielding of the

^{31}P nuclei increases with an increase in the number of

pentafluorophenyl groups present. This is consistent with a net flow

of electron density from the pentafluorophenyl ring to the phosphorus;

a similar explanation has been given for trispentafluorophenylboron[15]

and its adducts, in which there is a net flow of electron density

Figure 1
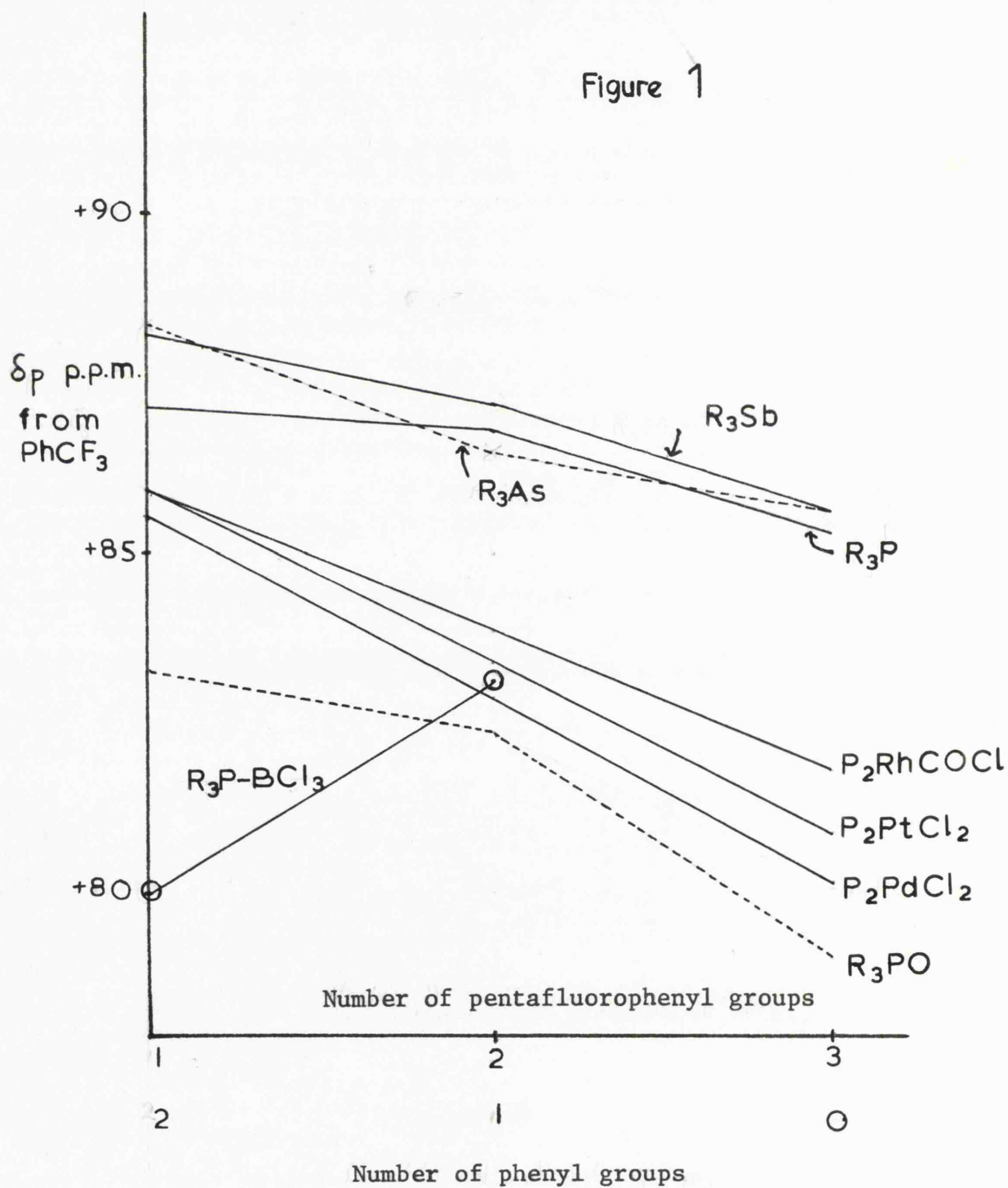
to the boron. A similar effect has been observed in the ^{31}P n.m.r. spectra of the mixed chlorofluorophosphines,[64] in which there is $p\pi$ donation from the fluorine atoms to phosphorus and in the ^{11}B n.m.r. spectra of species such as BF_xCl_{3-x}[65] (x = 0,1,2 or 3) or BF_yCl_{4-y}[66] (y = 0,1,2,3 or 4) where there is $p\pi$ donation from fluorine to the boron. ^{19}F n.m.r. studies of the boron compounds have shown in addition that the shielding of the ^{19}F nuclei increases with an increase in the amount of fluorine present. However, in the mixed chlorofluorophosphines[64,67] a reverse trend has been observed. The shielding of the ^{19}F nuclei in the mixed chlorofluorides of phosphorus(V)[67,68] PCl_xF_{5-x} (x = 0,1,2,3,4), and in the mixed chlorofluorophosphoryl compounds $POCl_xF_{3-x}$ (x = 0,1,2) follows the trend observed in the boron compounds, and the anomalous effect in the chlorofluorophosphines has been ascribed to the lone pair of electrons on the phosphorus atom.

Changes in the chemical shift (δp) of the para fluorine atom in pentafluorophenyl compounds are mainly determined by mesomeric effects,[14,15] and the shielding of the para fluorine in the compounds $(C_6F_5)_xPh_{3-x}M$ and $(C_6F_5)_xPh_{3-x}PO$ (M = P, As, Sb, and x = 1, 2 or 3) decreases with an increase in the number of pentafluorophenyl groups present (see Figure 1). This effect is similar to that observed in the chlorofluorophosphines. In the boron trichloride adducts, in which the lone pair is now involved in bonding to the boron, the

opposite trend is found, as the para fluorine of $(C_6F_5)_2PhP$ is
more shielded than that of $(C_6F_5)Ph_2P$.   The fact that the phosphine
oxides follow the same trend as the phosphines suggests that the
lone pair is not responsible for the effect.

The position of the ^{19}F chemical shift of the para fluorine atom
in transition metal complexes of $(C_6F_5)Ph_2P$ has been related[14] to the
$d\pi-d\pi$ bonding between the metal and the phosphorus.   In the
complexes $P.BCl_3$ the decrease in δp with respect to the free ligand
is due to the $p\pi-d\pi$ donation from the pentafluorophenyl ring to the
phosphorus not being countered by lone pair ring back-donation
(see diagrams A and B).
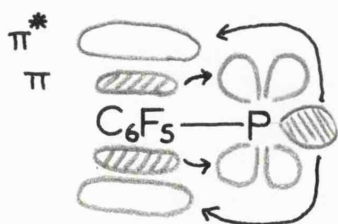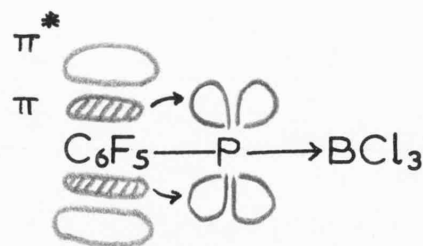
A   B

In the metal complexes the d electrons of the metal and the π
electrons of the pentafluorophenyl rings compete for the 3d orbitals

on the phosphorus. (See diagram C).

<u>C</u>
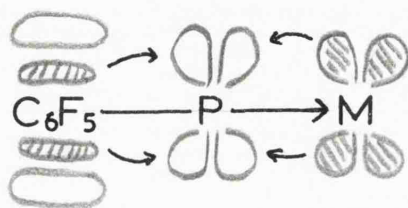
The increase in δp in the metal complex from that of the boron trichloride complex is in agreement with $d\pi$–$d\pi$ donation from the metal to the phosphorus.

TABLE 1·11

δp complex – δp ligand

ligand	$LBCl_3$	$LMo(CO)_5$	$L_2RhCOCl$	L_2PtCl_2	L_2PdCl_2	$LRhCl_3$
$(C_6F_5)_3P$	–	–	–3.6	–4.4	–5.2	–6.4
$(C_6F_5)_2PhP$	–3.8	–2.4[1]	–3.0	–3.5	–4.0	–
$(C_6F_5)Ph_2P$	–7.1[1]	–0.6[1]	–1.2	–1.2	–1.6	–
$(C_6F_5)Ph_2As$	–	–	–1.4	–2.5		–
$[(C_6F_5)_3P](C_5H_5N)PtCl_2$ –3.7						

[1] M. G. HOGBEN, R. S. GAY, and W. A. G. GRAHAM, <u>J. Amer. Chem. Soc.</u>, 1966, <u>88</u>, 3457.

The smaller δp complex $- \delta pL$ is the more metal to phosphorus $d\pi-d\pi$ donation there is. The values in Table 1.11 (p 43) show that the back donation increases in the series Rh(III), Pd(II), Pt(II), Rh(I), Mo(0). A higher formal charge on the central metal atom, as expected, discourages metal to phosphorus back-donation

If the process of back donation is compared with the complete removal of an electron, then the back donating capacity should follow the trend in ionisation potentials. The observation that palladium(II) back donates less than platinum(II) is in line with the ionisation potentials.[69] Platinum 8.2 e.v. Palladium 8.33 e.v.

When one of the $(C_6F_5)_3P$ ligands in _trans_ L_2PtCl_2 is replaced by a pyridine molecule δp complex $- \delta pL$ decreases in magnitude. Explanations based on increased π back-donation or decreased σ donation of the phosphine would account for this.

The para fluorine shifts in Table 1.11 (P. 43) indicate that the amount of back-bonding decreases as the number of pentafluorophenyl groups increases in the phosphines $(C_6F_5)_nPh_{3-n}P$ (n = 1,2,3). Displacement reactions show that the complexing power of the phosphines parallels the decrease in back-bonding. However the σ donor capacity will also decrease with the increase in the number of pentafluorophenyl groups and thus cause the ligands to complex less strongly.

The complexes $P_4Rh_2Cl_2$ (P = $(C_6F_5)_3P$, $(C_6F_5)_2PhP$, and $(C_6F_5)Ph_2P$) were insufficiently soluble for n.m.r. spectroscopy.

The use of infrared to establish the configurations of the complexes L_2MX_2 and $L_2RhCoCl$ has already been mentioned. In $[(C_6F_5)_2PhP]_2MX_2$ (M = Pt, Pd; X = Cl, Br, I) and $[(C_6F_5)_2PhP]_2RhCOCl$ and in the $(C_6F_5)_3P$ complexes P_2PtBr_2, P_2PtI_2 $P_4Rh_2Cl_2$ and $P_2RhCOCl$ an additional band is observed on the high frequency side of the 340 cm^{-1} ligand band at about 347 cm^{-1} which is not present in the spectra of the free phosphines. The complexes of tris(2,6 difluorophenyl) phosphine also show a strong band at 364 cm^{-1} which is absent in the free ligand (Tables 1.6 and 1.7) (p 64g) (p 64h). These additional bands may be due to coupling between the two phosphines or to a change in configuration or environment of the ligand when it is complexed to the metal.   This effect is not observed in the complexes of $(C_6F_5)Ph_2P$ although additional bands in the region 800-400 cm^{-1} are found in all complexes. Triphenylphosphine in the complex cis $(Ph_3P)_2PtCl_2$ also shows additional bands[70] from 1200-400 cm^{-1}.

EXPERIMENTAL

All operations involving butyllithium were carried out in dry apparatus using an atmosphere of dry oxygen-free nitrogen. Pentafluorophenyllithium was prepared from butyllithium and pentafluorobenzene.[71] Sodium-dried tetrahydrofuran was redistilled from lithium aluminium hydride immediately before use. Molecular weights were determined on a Mechrolab vapour pressure osmometer in chloroform as solvent unless otherwise stated. Infrared spectra were recorded using a Perkin-Elmer model 225. ^{19}F n.m.r. spectra were obtained with a Varian Associates model DA60 spectrometer at 56.4 or 19.3 Mc./sec. The e.s.r. spectra were obtained using a Varian Associates e.s.r. spectrometer and an S band spectrometer. Melting points were taken on a Reichart hot stage apparatus and are uncorrected. Ph_2AsCl,[72] $PhAsCl_2$,[72] Ph_2SbCl,[73] $PhSbCl_2$,[73] and 2,6 difluorophenyllithium[74] were prepared by literature methods.

Preparation of pentafluorophenyl derivatives of phosphorus, arsenic and antimony.

Pentafluorophenyl derivatives of phosphorus,[42,46,50] arsenic,[50] and antimony[50] have been prepared in low yield using pentafluorophenyl magnesium bromide. The use of pentafluorophenyllithium, however, gives high yields at lower cost since pentafluorobenzene is the

ultimate starting material. A typical reaction is described below.

A 500 ml three-necked flask fitted with an oil-sealed paddle stirrer was flushed with nitrogen for ten minutes. 91 ml. of 1·1 M butyllithium was added and the flask cooled to -78° by means of a cardice-acetone bath. A solution of 16·7 g. of pentafluorobenzene in 40 ml. of dry ether was then added dropwise over a period of fifteen minutes and the mixture was stirred at -78° for two hours. 9·0 g. of dichlorophenylphosphine in 30 ml. of dry ether was added dropwise and the mixture was allowed to warm to room temperature. The contents of the flask were filtered and the filtrate evaporated to dryness. The solid was crystallised from alcohol (or hexane) to yield 17 g. (75% yield) of phenylbispentafluorophenylphosphine m.p. 68-70°. Lit.[46] 69-70°.

The other pentafluorophenyl derivatives were prepared in a similar manner. Details are summarised in Table 1·1. *(p.64a)* In some preparations an oil was obtained when the reaction mixture was finally evaporated to dryness. Crystallisation of the oil was effected by addition of a little absolute alcohol, removal of the alcohol slowly under reduced pressure, and leaving any oil remaining to stand until crystallisation took place.

Preparation of $(C_6F_5)_3AsCl_2$

1·0 g. of $(C_6F_5)_3As$ was placed in a Carius tube and 1-2 ml. of liquid chlorine was distilled in under vacuum. The tube was

sealed and left to stand for several days. After opening the excess

of chlorine was pumped out. The white residue was washed into a

filter with hexane, then washed with a little methylene chloride and

dried under a vacuum. Quantitative yield of white crystals m.p.

210-218°C. Analysis. Found C, 32.5; Cl, 10.9%. $C_{18}F_{15}AsCl_2$

requires C, 33.4; Cl, 11.0%.

$(C_6F_5)_3SbCl_2$ was similarly prepared. White crystals m.p.

245-247°C. Analysis. Found C, 31.8; Cl, 10.3%. $C_{18}F_{15}SbCl_2$

requires C, 31.2; Cl, 10.2%.

Preparation of $(C_6F_5)Ph_2PO$ and $(C_6F_5)_2PhPO$

The dichlorides $(C_6F_5)Ph_2PCl_2$ and $(C_6F_5)_2PhPCl_2$ made as above

were not isolated but were hydrolysed by shaking the chloroform

solutions with dilute aqueous alkali. The chloroform layer was

separated and evaporated to dryness and the solids recrystallised

from hexane.

$(C_6F_5)Ph_2PO$ m.p.   121-123°   Lit m.p.[46]   123°

$(C_6F_5)_2PhPO$ m.p.   103-104°   Lit m.p.[46]   103°

Attempted Preparations of $(C_6F_5)_3PSe$.

1)   Warm acetonitrile solutions of KSeCN and $(C_6F_5)_3P$ were mixed

and then stirred for thirty minutes. The clear solution was

evaporated to dryness and the solid residue was extracted with

benzene. The resulting suspension was filtered and the filtrate
was evaporated to dryness again. An infrared spectrum of this
solid was identical to that of $(C_6F_5)_3P$ and the m.p. of a sample
recrystallised from hexane confirmed $(C_6F_5)_3P$.

2) 0·5 g. of $(C_6F_5)_3P$ and 0·15 g. of selenium were sealed in a
tube under vacuum. The tube was then heated for one week at 180°C.
The tube was opened and the contents extracted with benzene.
The solution was filtered to remove selenium, and the filtrate
evaporated to dryness. The solid was identified as $(C_6F_5)_3P$ by
m.p. and infrared spectroscopy.

$(C_6F_5)_3P$ + BF_3

BF_3 gas was bubbled through a benzene solution of $(C_6F_5)_3P$ for
thirty minutes. The solution was evaporated to dryness and the solid
identified as unchanged $(C_6F_5)_3P$ by infrared spectroscopy and m.p.

To check whether a labile complex was formed a pressure of BF_3
gas was placed over a toluene solution of $(C_6F_5)_3P$ in a vacuum
system and the absorption followed manometrically. A blank
employing the same volume of toluene was also done. Identical
pressure changes were observed in each case. The experiment was
repeated at -78°C by cooling the bulb containing the toluene solution
in a cardice-acetone bath. Again no difference in absorption between
the solution and the blank was noted.

$(C_6F_5)_3P$ + SnI_4

Carbon tetrachloride solutions of the reagents were mixed and

the mixture left for a week. On evaporation to dryness only

unchanged starting materials were recovered as shown by infrared

spectroscopy.

$(C_6F_5)_3P$ + $HgCl_2$

Hot ethanolic solutions of the two substances were mixed and

allowed to cool. White crystals identified by a mixed melting

point as $(C_6F_5)_3P$ precipitated out. These were filtered off and

the filtrate evaporated to dryness. The 400-200 cm^{-1} infrared spectrum

of the solid left, showed bands attributable to $(C_6F_5)_3P$ and $HgCl_2$ only.

$(C_6F_5)_3P$ + BCl_3

To a dry chloroform solution of $(C_6F_5)_3P$ a few drops of BCl_3

were added. The ^{19}F n.m.r. spectrum was identical to that of

$(C_6F_5)_3P$.

$(C_6F_5)Ph_2As$ + BCl_3

As above. The ^{19}F n.m.r. spectrum was identical to that of

$(C_6F_5)Ph_2As$.

$(C_6F_5)_3P$ + $SbCl_5$

To a dry chloroform solution of $(C_6F_5)_3P$ in an n.m.r. tube were

added a few drops of $SbCl_5$. An orange precipitate which rapidly

turned brown was obtained, together with a dark brown solution.

The ^{19}F n.m.r. showed no peaks in the expected region.

$(C_6F_5)_3P + H_2SO_4$

$(C_6F_5)_3P$ was dissolved in warm concentrated H_2SO_4 and the proton n.m.r. was run of this solution. No peaks were observed in the region 0-10 τ

Experiments with C_6F_5Li

To solutions of C_6F_5Li at -78° were added $POCl_3$, $PSCl_3$, $SbCl_5$ and PCl_5 in ether, the latter as a suspension. The mixtures were allowed to warm up to room temperature. The contents of the flasks were filtered and evaporated to dryness, but only oily or waxy solids were obtained from which no pure compounds could be isolated.

Preparation of Complexes.

The attempts to prepare rhodium, platinum, and palladium complexes are summarised in Table 1·2 (p 64b) Microanalytical data for the complexes isolated are given in Table 1·3 (p 64c) and later in this section.

Palladium and platinum complexes

Complexes of the type L_2PtCl_2 were prepared by dropwise addition of an aqueous solution of K_2PtCl_2 to the ligand in warm alcohol. The complex precipitated out, and was filtered off and recrystallised from chloroform-ethanol. L_2PtBr_2, L_2PdCl_2, and L_2PdBr_2 were prepared in a similar manner using aqueous solutions of K_2PtBr_4, Na_2PdCl_4 and K_2PdBr_4 respectively. The complexes L_2PdI_2 were prepared from sodium iodide and the corresponding

chloro- complexes in acetone solution. The complexes L_2PtI_2
were prepared as follows : PtI_2 and excess of the ligand were
refluxed overnight in xylene. The mixture was filtered hot,
and the filtrate was evaporated to dryness. The solid was washed
with hexane and recrystallised from chloroform-ethanol.

Rhodium complexes.

Complexes of the type $L_2RhCOCl$ were prepared by mixing
benzene solution of $Rh_2(CO)_4Cl_2$ and the ligand. Effervescence
occurred in all successful experiments and after this had subsided
the mixture was evaporated to dryness. The residue was
recrystallised from chloroform-ethanol.

In the reactions attempted between $(C_2H_4)_4Rh_2Cl_2$ and the
ligands, $(C_2H_4)_4Rh_2Cl_2$ was added to a degassed solution of the
ligand in methanol. The mixture was refluxed for one hour when
the complex slowly precipitated out. This was filtered off,
washed with alcohol and ether and dried under vacuum. In some
reactions a brownish solution was obtained from which no pure
compounds could be isolated.

In the reactions between the ligands and hydrated rhodium
trichloride ethanolic solutions of $RhCl_3.xH_2O$ and the ligand were
refluxed for a few hours, when the complex precipitated out.
The crystals were filtered off, washed with alcohol and ether and
dried under vacuum. In some experiments the initial red colour of
the solution slowly faded and a black insoluble precipitate formed.

Miscellaneous preparations.

A Hydrated rhodium tribromide was used in place of rhodium

trichloride with the phosphines $(C_6F_5)_3P$, $(C_6F_5)_2PhP$ and

$(C_6F_5)Ph_2P$. With $(C_6F_5)_3P$ a black insoluble precipitate was

obtained. With the other two complexes of the type $P_4Rh_2Br_2$

were obtained.

Tetrakis(diphenylpentafluorophenylphosphine)$_{\mu\mu}$' dibromodirhodium(I)

Dark red crystals, m.p. 180-185°C. Found: C, 48.6; H, 2.4; Br, 8.9.

$C_{72}F_{20}H_{40}Br_2P_4Rh_2$ requires C, 48.7; H, 2.3; Br, 9.0%.

Tetrakis(phenylbispentafluorophenylphosphine)$_{\mu\mu}$'dibromodirhodium(I).

Purple-black crystals m.p. 190-193°. Found: C, 40.2; H, 1.1; Br, 7.4;

$C_{72}F_{40}H_{20}Br_2P_4Rh_2$ requires C, 40.7; H, 1.0; Br, 7.5%.

B

Bromocarbonylbis(phenylbispentafluorophenylphosphine)rhodium(I).

Carbon monoxide was bubbled through 20 ml. of chloroform for five

minutes and then 0.5 g. of $[(C_6F_5)_2Ph\cdot P]_4Rh_2Br_2$ was added. The

initial purple solution turned yellow almost immediately and the

solution was filtered. The filtrate was evaporated to dryness and

the yellow solid was recrystallised from chloroform-ethanol to yield

yellow crystals, m.p. 214-217°. Found: C, 40.9; H, 1.0.

$C_{37}F_{20}H_{10}BrORh$ requires C, 41.0; H, 0.9%.

C

Trichloro(trispentafluorophenylphosphine)rhodium(III).

Chlorine was passed through a suspension of 0.5 g. of $[(C_6F_5)_3P]_4Rh_2Cl_2$

in carbon tetrachloride until a clear red solution was obtained.

The solution was evaporated to dryness and the red material left

dissolved in benzene. The initially deep red solution slowly

deposited an orange-red solid after several days leaving a pale

yellow solution. The solid was filtered off, washed with benzene,

cold water and cold ether and dried in vacuo to give orange-red

crystals (0.15 g.) decomposing 180-200°. (Found: C, 28.5, 31.0;

F, 40.0, 40.8; Cl, 14.5, 13.9; Rh, 12.9; M in acetone 720.

$C_{18}F_{15}Cl_3PRh$ requires C, 29.4; F, 38.0; Cl, 14.4; Rh, 14.0%, M, 740).

The pale yellow benzene solution contained $(C_6F_5)_3PO$, m.p. 167-168°

(Lit.[42] 167-170°) (Found: M in benzene 560. Calc. 548). Also

identified by an i.r. spectrum.

D

Attempted preparation of Nickel complexes.

1)   Hot solutions in n-butanol of hydrated nickel chloride and the

appropriate phosphine [$(C_6F_5)_3P$ or $(C_6F_5)Ph_2P$] were mixed. No change

was observed. The mixtures were refluxed for thirty minutes and then

cooled, but only starting materials were recovered.

2) $Ni(CO)_4$ was added under nitrogen to an ethereal solution of the

phosphine $(C_6F_5)_3P$ in a 1:2 mole ratio. The mixture was refluxed

for thirty minutes. The contents of the flask were evaporated to

dryness and the pale yellow solid showed two carbonyl peaks in the

infrared at 2110(m) cm^{-1} and 2030(s) cm^{-1}. On attempted work-up

an insoluble green precipitate was formed. This experiment was
not repeated.

E

Attempted preparation of Platinum(0) complexes.

An aqueous solution of K_2PtCl_4 was added dropwise to a hot
alcoholic solution of $(C_6F_5)_3P$ containing KOH (6:1 mole ratio).
The solution was stirred vigorously and kept hot during addition.
After a few minutes a yellow precipitate formed and the reaction
was stopped when no more pink precipitate of unreacted K_2PtCl_4
was visible. The yellow precipitate was washed with water, warm
alcohol and finally hexane. An infrared spectrum (400-200 cm^{-1})
was identical to that of $[(C_6F_5)_3P]_2PtCl_2$. The identification
was completed by a melting point after recrystallisation from
chloroform-alcohol.

When $(C_6F_5)Ph_2P$ was used in place of $(C_6F_5)_3P$ the product was
$[(C_6F_5)Ph_2P]_2PtCl_2$.

Reactions of the Complexes.

A Platinum complexes.

Displacement reactions. Weighed quantities of the reactants were
added to about 20 ml. of the solvent and the mixture was refluxed
overnight. In reactions involving cycloocta-1,5-diene xylene was
used as solvent since the higher reaction temperature ensured complete
displacement in a few hours. Chloroform was the solvent used for

the other reactions. In a typical experiment 0.11 g. of

cycloocta-1,5-diene and 0.5 g. of <u>trans</u>-dichloro bis(tris 2,6

difluorophenylphosphine)platinum(II) (2:1 mole ratio) were refluxed

in 20 ml. of xylene for 10 hr.   The yellow complex slowly

dissolved and gave a colourless solution. This was evaporated to

dryness and the residue was washed with ether. The i.r. spectrum

of the residue was identical to that of (cycloocta-1,5-diene)$PtCl_2$.

It was recrystallised from chloroform to yield white needles,

m.p. 230-280° (decomp.) (Lit.^{75} 220-278°).

It is possible that as much as 25% of the starting complex

could be present in the reaction mixture since the complex isolated

was characterised by infrared spectroscopy.

<u>[$(C6F_5)_3P]_2PtCl_2$ and Pyridine.</u>

0.5 g. of [$(C_6F_5)_3P]_2PtCl_2$ was refluxed in 20 ml. of chloroform

containing 1 ml. of pyridine for four hours. The colour of the

solution gradually changed from yellow to orange. The orange

solution was evaporated to dryness and the solid left was washed

with hexane and filtered off. The residue was recrystallised from

chloroform-alcohol. Orange crystals of [$(C_6F_5)_3P](C_5H_5N)PtCl_2$

were obtained m.p. 225-265 (dec). Found: C, 30.9; H, 0.64; N, 1.60%;

$C_{23}H_5F_{15}Cl_2NPPt$ requires C, 31.5; H, 0.57; N, 1.60%.

<u>[$(C_6F_5)_3P]_2PtBr_2$ and Pyridine.</u>

As above. Orange-brown crystals of [$(C_6F_5)_3P](C_5H_5N)PtBr_2$

m.p. 230-250 (dec). Found: C, 29.2; H, 0.59; N, 1.43%;

$C_{23}H_5F_{15}Br_2NP$ Pt requires C, 28.6; H, 0.52; N, 1.45%.

Hydrazine reactions

To a warm alcoholic suspension of L_2PtCl_2 [L = $(C_6F_5)_3P$,

$(C_6F_5)_2PhP$, and $(C_6F_5)Ph_2P$] containing a 1:2 mole ratio of the

same phosphine were added a few drops of hydrazine hydrate.

The yellow crystals dissolved and the solution gradually turned

dark. After about five minutes the solutions were dark purple.

.The only reaction to be investigated further was that of

$[(C_6F_5)_3P]_2PtCl_2$. In this case the dark solution was evaporated

to dryness, and the solid washed with hexane and filtered off.

The residue was dissolved in methylene chloride and precipitated

with hexane. Pure compounds were not obtained but the final

dark red solid was sent for analysis. Found: C, 36.7; H, 2.66;

N, 9.58%.

The infrared spectrum of the solid showed a weak band at

3370 cm^{-1} attributable to an N-H stretching frequency and strong

bands at 1150 and 1050 cm^{-1} as well as bands attributable to

$(C_6F_5)_3P$.

$(AsPh_3)_4Pt$ and $(C_6F_5)Ph_2P$.

$(C_6F_5)Ph_2P$ and $(AsPh_3)_4Pt$ (6:1 mole ratio) were refluxed in

benzene under nitrogen for thirty minutes. The solution was

filtered and the filtrate evaporated to dryness. The whitish

solid was washed with hexane and the residue filtered off. An

infrared spectrum of the residue was identical to that of

$(AsPh_3)_4Pt$.

B Rhodium Complexes.

Reactions of $[(C_6F_5)_3P]_4Rh_2Cl_2$ with -

(a) Carbon monoxide - Carbon monoxide was passed through a solution

of 0.5 g. $(P_f)_4 Rh_2Cl_2$ in 20 ml. C_6F_5H. The resulting yellow

solution was filtered and evaporated to dryness. The yellow solid

was recrystallised from chloroform-ethanol and identified as

trans- $(P_f)_2RhCOCl$ by an i.r. spectrum and m.p. No $(C_6F_5)_3P$ was

detected in the mother liquor.

(b) triphenylphosphite - 0.40 g. of $(PhO)_3P$ was added to 0.5 g.

$(P_f)_4Rh_2Cl_2$ in 20 ml. benzene (7:1 mole ratio). The mixture was

refluxed for 24 hours and the yellow solution evaporated to dryness.

The solid was recrystallised from benzene-hexane and identified as

$[(PhO)_3P]_3RhCl$ by an i.r. spectrum, m.p. and analysis. (Found:

C, 60.6; H, 4.4; Cl, 3.06, 3.54. Calc. for $C_{54}H_{45}ClO_7P_3Rh$:

C, 60.7; H, 4.2; Cl, 3.32%).

(c) triphenylphosphine - 0.50 g. $(P_f)_4Rh_2Cl_2$ was added to 20 ml.

of a degassed benzene solution of 0.75 g. Ph_3P, (mole ratio 1:15).

The mixture was refluxed under nitrogen for 24 hours and the

resulting red solution was filtered and evaporated to a small volume.

Degassed ethanol was added and evaporation continued until burgundy-

red crystals appeared which were identified as $(Ph_3P)_3RhCl$ by m.p.

and an i.r. spectrum.

(d) <u>cyclo-octa-1,5-diene</u>- 1-2 ml. of cyclo-octa-1,5-diene was

added to 0.5 g. $(P_f)_4Rh_2Cl_2$ in 20 ml. benzene and the mixture refluxed

for 24 hours. The yellow solution was evaporated to dryness, and

the yellow solid was washed with a little hexane and recrystallised

from ethanol to give bis(cyclo-octa-1,5-diene)μμ'dichlorodirhodium(I),

Identified by m.p. and an i.r. spectrum. This reaction was not

reversible. 3 g. of $(C_6F_5)_3P$ was refluxed with 0.5 g. $(C_8H_{12})_2Rh_2Cl_2$

in ethanol for 24 hours. No reaction occurred.

(e) <u>propionaldehyde</u> - 2-3 ml. of C_2H_5CHO was added to 0.5 g.

$(P_f)_4Rh_2Cl_2$ in 20 ml. benzene and the mixture was refluxed for

2-3 hours. The yellow solution was evaporated to dryness and the

solid was recrystallised from chloroform-ethanol to give

<u>trans</u>-$(P_f)_2RhCOCl$ identified by m.p. and an i.r. spectrum.

(f) <u>benzaldehyde</u> - As above to give <u>trans</u>-$(P_f)_2RhCOCl$.

(g) <u>alcohol</u> - 0.5 g. of $(P_f)_4Rh_2Cl_2$ was refluxed in alcohol for

2 days. No change was observed.

(h) <u>β-methoxyethanol</u> - 0.5 $(P_f)_4Rh_2Cl_2$ was refluxed with

β-methoxyethanol for 4 hours. A black solid precipitated which

contained no carbon monoxide or $(C_6F_5)_3P$. $(C_6F_5)_3P$ was present

in the solution.

(i) <u>chloroform</u> - 0.5 g. $(P_f)_4Rh_2Cl_2$ was refluxed with pure dry

chloroform under nitrogen overnight. A dark red precipitate and

red solution were obtained, but no pure compound could be isolated.

(j) <u>chloroform-ethanol mixture</u> - 0.5 g. $(P_f)_4 Rh_2 Cl_2$ was refluxed

with 25 ml. of a 1:1 chloroform-ethanol mixture overnight. The

yellow solution was filtered and evaporated to dryness. The solid

was recrystallised from chloroform-ethanol to give <u>trans-</u>$(P_f)_2$ RhCOCl

identified by m.p. and an i.r. spectrum.

(k) <u>trispentafluorophenylphosphine</u> - 3.0 g. $(C_6F_5)_3P$ and 0.5 g.

$(P_f)_4Rh_2Cl_2$ in 20 ml. benzene were refluxed under nitrogen for

48 hours. No change was observed. The mixture was evaporated to

dryness, placed in a Carius tube and heated at 130° for 24 hours.
Only starting materials were isolated.

(l) <u>pyridine</u> - 1-2 ml. pyridine was added to 0.5 g. $(P_f)_4Rh_2Cl_2$

in 20 ml. chloroform. After 15 min. a clear red solution was

obtained. The solution was evaporated to dryness and $(C_6F_5)_3P$ was

extracted with petroleum. The i.r. spectrum of the residue

indicated a material containing $(C_6F_3)_3P$ and pyridine but no pure

complex could be isolated.

(m) <u>ethylenediamine</u> - as with pyridine. No pure compound could

be isolated.

(n) <u>methyl iodide</u> - 2-3 ml. of methyl iodide was added to 0.5 g.

$(P_f)_4Rh_2Cl_2$ suspended in 25 ml. benzene and was left to stand for

3 days. No change was observed. When the mixture was refluxed

overnight a black precipitate formed which contained no $(C_6F_5)_3P$.

$(C_6F_5)_3P$ was recovered from the solution.

(o) <u>chlorine</u> -

(i) 3-4 ml. of liquid chlorine were condensed onto 0.5 g.

$(P_f)_4Rh_2Cl_2$ in a Carius tube. The tube was sealed and shaken for

24 hours. Excess chlorine was removed and the dark red powder

which remained had the approximate composition $(P_f)_4Rh_2Cl_6$.

(Found: C, 33.8; Cl, 8.18. $C_{72}F_{60}Cl_6P_4Rh_2$ requires C, 33.9;

Cl, 8.37%). An i.r. spectrum showed the presence of $(C_6F_5)_3PO$,

which was extracted from the solid with hexane, and was

characterised further by its m.p. The remaining material was not

investigated further.

(ii) chlorine gas was passed through a suspension of $(P_f)_4Rh_2Cl_2$

in carbon tetrachloride until a clear red solution was obtained.

The solution was filtered and evaporated to dryness to give a solid

of approximate composition $(P_f)_4Rh_2Cl_6.1.5$ CCl_4 (Found: C, 31.8;

Cl, 15.9. Calc. for $C_{72}F_{60}Cl_6P_4Rh_2$ 1.5 CCl_4 : C, 31.7; Cl, 15.3%).

An i.r. spectrum showed bands due to carbon tetrachloride at

787 and 765 cm^{-1} (Lit. 790, 762 cm^{-1})[76] and the presence of

$(C_6F_5)_3PO$. Both could be extracted from the solid with warm

hexane leaving uninvestigated material. The extracted $(C_6F_5)_3PO$

was identified by its m.p.

Magnetic susceptibility of $(C6F5)_3P$ and $[(C_6F_5)_3P]_4Rh_2Cl_2$

The magnetic susceptibilities were determined by the Gouy

method using a magnetic field of 4,000 gauss and a balance capable

of weighing to 5μg. To work out the results the formula[77]

$$10^6 X_g = \frac{\alpha + \beta \ (F - \delta)}{w} \qquad \text{was used.}$$

α is the diamagnetic correction for air displaced by the sample.

β is the magnet constant.

F is the observed weight difference in and out of field.

δ is the diamagnetic correction for the sample tube.

w is the weight of the sample.

If X_g is in c.g.s. units α, F and δ are in milligrams and w is in grams.

α is calculated from the volume of the tube, and the volume susceptibility of air. This is 2.9×10^{-8} c.g.s.[77] The volume of the tube was 0.67 ccs. So α is +0.02 mg. The samples were vacuum dried after being ground to fine powders.

Evaluation of δ.

     Wt of Tube and suspension in field   9.356435 g.

     " " " " "   out of field   9.357515 g.

     Difference = δ = -1.080 mg.

Evaluation of β using Hg[Co(CNS)₄] as the calibrant.

1) Wt in field   10.398525 g.   2) Wt in field   10.408365 g.

Wt out of field 10.382625 g.   Wt out of field 10.391480 g.

F = 15.90 mg.   F = 16.885 mg.

Weight of sample 1.025 g.   Weight of sample 1.043 g.

The temperature was 22°C. X_g Hg[Co (CNS)$_4$]

= 16.34 x 10^{-6} c.g.s. units at 22°C.^{78}

β = 0.985   β = 0.965

The average value of β was 0.945

$(C_6F_5)_3P$

Temperature 25°C

1) Wt in field 9.999000 g.	2) Wt in field 10.163932 g.	3) Wt in field 10.163920 g.
Wt out of field 10.000350 g.	Wt out of field 10.165325 g.	Wt out of field 10.165310 g.
F = -1.350 mg.	F = -1.393 mg.	F = -1.390 mg.
w = 0.643 g.	w = 0.807 g.	w = 0.807 g.
$10^6 X_g$ = -0.374 c.g.s.	$10^6 X_g$ = -0.354 c.g.s.	$10^6 X_g$ = -0.346 c.g.s.

Average X_g is -0.358 x 10^{-6} c.g.s. The molecular weight is 532 so

the molar susceptibility is -190 x 10^{-6} c.g.s. units.

$[(C_6F_5)_3P]_4Rh_2Cl_2$

Temperature 25°C

1) Wt in field 9.941738 g.	2) Wt in field 9.928170 g.	3) Wt in field 9.928197 g.
Wt out of field 9.943020 g.	Wt out of field 9.929485 g.	Wt out of field 9.929485 g.
F = -1.282 mg.	F = -1.315 mg.	F = -1.288 mg.
w = 0.586 g.	w = 0.573 g.	w = 0.573 g.
$10^6 X_g$ = -0.300 c.g.s.	$10^6 X_g$ = -0.356 c.g.s.	$10^6 X_g$ = -0.316 c.g.s.

Average value X_g = -0.324 x 10^{-6} c.g.s.

Assuming the formula $[(C_6F_5)_3P]_4Rh_2Cl_2$ for the complex the

molecular weight is 2405. This yields an average value of

-778×10^{-6} c.g.s. units for the molar susceptibility.

To find the magnetic susceptibility per rhodium atom we must

make corrections for the diamagnetic effect of the ligands.[77]

Phosphine $\qquad$ $4 \times 190 \times 10^{-6}$ = 760×10^{-6} c.g.s.

Chlorine $\qquad$ $2 \times 20 \times 10^{-6}$ = 40×10^{-6} c.g.s.

Total ligand correction is 800×10^{-6} c.g.s.

The contribution per rhodium atom is thus $\dfrac{800 - 778}{2} \times 10^{-6}$ c:.g.s.

$= 11 \times 10^{-6}$ c.g.s. Using the formula $\mu = 2.84 \sqrt{X_M T}$ B.M. we get

a magnetic moment of $+0 \cdot 16$ B.M. per rhodium atom. After assesssing

the errors the range of the magnetic moment is $+0 \cdot 38$ to $-0 \cdot 30$ B.M.

TABLE 1·1

Product	% Yield	Starting material	Melting point °C	Found C	Found H	Analysis required C	Analysis required H	Molecular weight Found	Molecular weight Required
$(C_6F_5)_3P$[1,2]	85	PCl_3	115–116	—	—	—	—	540	532
$(C_6F_5)_2PhP$[3]	75	$PhPCl_2$	68–70	—	—	—	—	436	442
$(C_6F_5)Ph_2P$[3]	75	Ph_2PCl	68–70	—	—	—	—	358	352
$(C_6F_5)_3As$[1]	75	$AsCl_3$	104–106	—	—	—	—	570	576
$(C_6F_5)_2PhAs$	50	$PhAsCl_2$	73–75	44.0	1.0	44.4	1.0	484	486
$(C_6F_5)Ph_2As$	55	Ph_2AsCl	63–64	55.1	2.7	54.6	2.6	403	396
$(C_6F_5)_3Sb$[1]	75	$SbCl_3$	73–75	—	—	—	—	617	622
$(C_6F_5)_2PhSb$	50	$PhSbCl_2$	89–91	40.0	1.0	40.2	1.0	516	532
$(C_6F_5)Ph_2Sb$	25	Ph_2SbCl	30–33	48.4	2.3	48.7	2.3	460	442
$(C_6H_3F_2)_3P$	70	PCl_3	128–130	58.2	2.5	58.6	2.5	368	370
$(C_6H_3F_2)_3As$	75	$AsCl_3$	105–106	51.4	2.4	52.2	2.2	412	414

[1] M. Fild, O. Glemser, and G. Cristoph, Angew. Chem., Int. Ed., 1964, 3, 801;
[2] L. A. Wall, R. E. Donadio and W. J. Pummer, J. Amer. Chem. Soc., 1960, 82, 4846;
[3] M. Fild, O. Glemser, and I. Hollenberg, Naturwiss., 1965, 52, 590.

TABLE 1·2

Ligand	K_2PtCl_4	PtI_2	$RhCl_3 \cdot xH_2O$	$Rh_2Cl_2(C_2H_4)_4$	$Rh_2(CO)_4Cl_2$
$(C_6F_5)_3P$	a	a	a	a	a
$(C_6F_5)_2PhP$	a	a	a	a	a
$(C_6F_5)Ph_2P$	a	a	a	a	a
$(C_6F_5)_3As$	b	b	b	b	b
$(C_6F_5)_2PhAs$	b	b	b	b	b
$(C_6F_5)Ph_2As$	a	a	b	b	a
$(C_6F_5)_3Sb$	c	b	c	c	b
$(C_6F_5)_2PhSb$	c	b	c	c	b
$(C_6F_5)Ph_2Sb$	c	b	c	c	b
$(C_6H_3F_2)_3P$	a	a	a	b	c
$(C_6H_3F_2)_3As$	b	b	b	b	b

<u>Legend</u> a, complex formed, b, no complex isolated,

c, reaction not attempted.

64c

TABLE 1.3

Microanalytical data of the complexes.

Compound	Colour	m.p. °C	% Found		% Required	
$[(C_6F_5)_3P]_2PtCl_2$	Yellow	225–235 dec	C, 32.7; Cl, 5.3		C, 32.5; Cl, 5.3	
$[(C_6F_5)_3P]_2PtBr_2$	Orange Yellow	293–298 dec	C, 30.6; Br, 11.2		C, 30.4; Br, 11.3	
$[(C_6F_5)_3P]_2PtI_2$	Pink	220–240 dec	C, 28.6; I, 16.2		C, 28.5; I, 16.7	
$[(C_6F_5)_3P]_2PdCl_2$	Yellow	230–240 dec	C, 35.2; Cl, 5.6		C, 34.8; Cl, 5.7	
$[(C_6F_5)_3P]_2PdBr_2$	Orange	241–245 dec	C, 32.7; Br, 11.9		C, 32.5; Br, 12.1	
			C	H	C	H
$[(C_6F_5)_2PhP]_2PtCl_2$	Pale yellow	268–270	37.1	0.94	37.6	0.87
$[(C_6F_5)_2PhP]_2PtBr_2$	Cream	260–263	35.2	0.83	34.8	0.86
$[(C_6F_5)_2PhP]_2PtI_2$	Pink	267–272	32.1	0.80	32.4	0.75
$[(C_6F_5)_2PhP]_2PdCl_2$	Yellow orange	245–250	40.4	0.97	40.8	0.95
$[(C_6F_5)_2PhP]_2PdBr_2$	Orange	255–260	36.9	0.83	37.6	0.87
$[(C_6F_5)_2PhP]_2PdI_2$	Yellow brown	222–225	34.6	0.82	34.8	0.80
$[(C_6F_5)Ph_2P]_2PtCl_2$	Pale yellow	225–226	44.4	2.19	44.6	2.06
$[(C_6F_5)Ph_2P]_2PtBr_2$	Yellow	222–225	40.7	1.98	40.7	1.89

Compound	Color	M.P.	Found		Calcd.	
[(C$_6$F$_5$)Ph$_2$P]$_2$PtI$_2$	Orange	241-243	37.8	1.91	37.4	1.83
[(C$_6$F$_5$)Ph$_2$P]$_2$PdCl$_2$	Yellow orange	192-194	49.2	2.33	48.9	2.27
[(C$_6$F$_5$)Ph$_2$P]$_2$PdBr$_2$	Orange	215-218	44.8	2.22	44.6	2.16
[(C$_6$F$_5$)Ph$_2$P]$_2$PdI$_2$	Brown	226-229	40.5	1.90	40.6	1.88
[(C$_6$F$_5$)Ph$_2$As]$_2$PtCl$_2$	Pale yellow	201-206	41.1	1.92	40.9	1.91
[(C$_6$F$_5$)Ph$_2$As]$_2$PtBr$_2$	Light orange	203-210	37.5	1.75	37.8	1.77
[(C$_6$F$_5$)Ph$_2$As]$_2$PtI$_2$	Pink	216-230	34.6	1.63	35.0	1.63
[(C$_6$F$_5$)Ph$_2$As]$_2$RhCOCl	Yellow	138-144	46.5	2.21	46.4	2.10
[(C$_6$H$_3$F$_2$)$_3$P]$_2$PtCl$_2$	Light yellow	300-310	42.3	1.80	42.9	1.79
[(C$_6$H$_3$F$_2$)$_3$P]$_2$PtBr$_2$	Yellow	300-310	39.2	1.61	39.5	1.65
[(C$_6$F$_5$)$_3$P]$_4$Rh$_2$Cl$_2$	Dk. Green	216-218	C, 36.0; F, 48.9; Cl, 2.96		C, 35.9; F, 47.4; Cl, 2.95	
[(C$_6$F$_5$)$_2$PhP]$_4$Rh$_2$Cl$_2$	Dk. Purple	219-221	C, 42.0; H, 1.0; Cl, 3.40		C, 42.3; H, 1.0; Cl, 3.5	
[(C$_6$F$_5$)Ph$_2$P]$_4$Rh$_2$Cl$_2$	Dk. Red	175-185	C, 51.1; H, 2.4; Cl, 4.2		C, 51.3; H, 2.4; Cl, 4.2	
[(C$_6$F$_5$)$_3$P]$_2$RhCOCl	Yellow	243-248	C, 36.1; Cl, 2.72		C, 36.1; Cl, 2.90	
[(C$_6$F$_5$)$_2$PhP]$_2$RhCOCl	Yellow	205-208	C, 42.5; H, 0.90		C, 42.3; H, 0.90	
[(C$_6$F$_5$)Ph$_2$P]$_2$RhCOCl	Yellow	170-174	C, 50.2; H, 2.3		C, 51.1; H, 2.3	

TABLE 1·4

^{31}P n.m.r. chemical shifts in p.p.m. from 85% H_3PO_4,

^{19}F n.m.r. chemical shifts in p.p.m. from CF_3COOH.

Positive values are upfield of the standard.

	^{31}P	^{19}F
PF_3	-97 [a]	-43·4 [b]
PF_2Cl	-176 [a]	-39·9 [b]
$PFCl_2$	-244 [a]	-20·7 [b]
POF_3	+35 [c]	+15·8 [b]
POF_2Cl	+15 [c]	-30·4 [b]
$POFCl_2$	0 [c]	-69·0 [b]
$(C_6F_5)_3P$	+75 [d]	See Table 5
$(C_6F_5)_2PhP$	+49 [d]	"
$(C_6F_5)Ph_2P$	+26 [d]	"
$(C_6F_5)_3PO$	+8 [d]	"
$(C_6F_5)_2PhPO$	-1 [d]	"
$(C_6F_5)Ph_2PO$	-9 [d]	"

[a] A. Müller, E. Niecke, and O. Glemser, Z. anorg. Chem., 1967, 350, 256.

[b] R. R. Holmes and W. P. Gallagher, Inorg. Chem., 1963, 2, 433.

[c] A. Müller, E. Niecke, and O. Glemser, Z. anorg. Chem., 1967, 350, 246.

d O. Glemser, M. Fild, and I. Hollenberg, Z. Naturforsch., 1967, 22b, 253, (Studied in C_6H_6 or $CHCl_3$ solution).

TABLE 1·5

[19]F n.m.r. in p.p.m. upfield from benzotrifluoride (internal standard). Measured at 37°C at 19·3 Mc/sec.[*] or 56·4 Mc/sec. Estimated accuracy ± 0·1 p.p.m.

Compound	Solvent	Ortho	Para	Meta
$(C_6F_5)_3P$[1]	$CHCl_3$	67.2	85.3	97.0
[*]$(C_6F_5)_2PhP$	$CHCl_3$	65.5	86.8	97.2
[*]$(C_6F_5)Ph_2P$	$CHCl_3$	64.1	87.1	97.3
$(C_6F_5)_2PhP + BCl_3$	$CHCl_3$	62.6	83.0	95.8
$(C_6F_5)Ph_2P + BCl_3$	$CHCl_3$	56.6	80.0	95.0
$(C_6F_5)_3PO$[1]	$CHCl_3$	68.2	79.0	94.7
$(C_6F_5)_2PhPO$	$CHCl_3$	67.4	82.3	96.4
$(C_6F_5)Ph_2PO$	$CHCl_3$	65.2	83.2	96.4
$[(C_6F_5)_3P]_2PtCl_2$	$CHCl_3$	62.3	80.8	95.6
$[(C_6F_5)_3P](C_5H_5N)PtCl_2$	$CHCl_3$	62.6	81.6	95.8
$[(C_6F_5)_2PhP]_2PtCl_2$	$CHCl_3$	61.5	83.3	97.0
$[(C_6F_5)Ph_2P]_2PtCl_2$	$CHCl_3$	61.7	85.9	98.3
$[(C_6F_5)_3P]_2PdCl_2$	$CHCl_3$	62.3	80.1	95.2
$[(C_6F_5)_2PhP]_2PdCl_2$	$CHCl_3$	61.0	82.8	96.4
$[(C_6F_5)Ph_2P]_2PdCl_2$	$CHCl_3$	61.5	85.5	97.4
$[(C_6F_5)_3P]_2RhCOCl$	$CHCl_3$	62.9	81.7	95.2
[*]$[(C_6F_5)_2PhP]_2RhCOCl$	$CHCl_3$	61.4	83.8	96.2
[*]$[(C_6F_5)Ph_2P]_2RhCOCl$	$CHCl_3$	61.4	85.9	97.1

Table 1·5 /continued.

Compound	Solvent	Ortho	Para	Meta
$(C_6F_5)_3As$	$CHCl_3$	65.3	85.6	96.3
$(C_6F_5)_2PhAs$	$CHCl_3$	63.2	86.5	95.8
$(C_6F_5)Ph_2As$	"	62.7	88.3	97.3
$[(C_6F_5)Ph_2As]_2PtCl_2$	$CHCl_3$	61.2	85.8	97.0
$[(C_6F_5)Ph_2As]_2RhCOCl$	$CHCl_3$	61.8	86.9	97.5
$(C_6F_5)_3Sb$	"	59.3	85.6	96.0
$(C_6F_5)_2PhSb$	"	57.9	87.2	96.6
$(C_6F_5)Ph_2Sb$	"	56.7	88.2	96.9
$(C_6H_3F_2)_3P$	CH_2Cl_2	38.6	—	—
$(C_6H_3F_2)_3As$	CH_2Cl_2	37.0	—	—
*$[(C_6F_5)_3P]RhCl_3$	$CHCl_3$	66.6; 78.9, 84.8; 94.7, 96.7		

[1] H. J. EMELÉUS and J. M. MILLER, <u>J. Inorg. Nucl. Chem.</u>, 1966, <u>28</u>, 662.

TABLE 1·6

Infrared spectra of the ligands (400–200 cm^{-1}).Nujol mulls

$(C_6F_5)_3P$	394w 377vw 371vw 356vw 328s 314m 284w 236msh 230s
$(C_6F_5)_2PhP$	393s 330sbr 313m 234msh 225m
$(C_6F_5)Ph_2P$	391sbr 373msh 340s 314m 235m 214m
$(C_6F_5)_3As$	393s 386s 373s 353w 313m 283m 256sbr 228s 220s
$(C_6F_5)_2PhAs$	386s 377s 354w 313m 303s 284s 271s 252s 228m 223msh
$(C_6F_5)Ph_2As$	383s 354w 310sbr 284m 271m 253w 232s
$(C_6F_5)_3Sb$	374s 368s 364msh 348w 313s 280m 225sbr
$(C_6F_5)_2PhSb$	394w 369s 364s 349w 312m 280m 256s 233s 204m
$(C_6F_5)Ph_2Sb$	364s 350w 314m 294m 263s 253s 231s 220msh
$(C_6H_3F_2)_3P$	405m 351ssh 346s 334s 305m
$(C_6H_3F_2)_3As$	329s 319m 277m 255s 243s 227m

Table 1.7

Infrared Spectra of the Complexes (410-200 cm^{-1}) in Nujol mulls.
(Metal halogen frequencies are underlined).

[(C6F5)3P](C5H5N)PtCl2	396s <u>351sbr</u> 338s 332s 316m 283m 277wsh 243s 233s
[(C6F5)3P]2PtCl2	395w 366w <u>351ms</u> 338s 317m 284w 240ssh 236s
[(C6F5)3P]2PdCl2	393w <u>365s</u> 336s 317m 284w 240s 236ssh
[(C6F5)3P](C5H5N)PtBr2	394s 349m 339s 331s 317m 283w 277w <u>263s</u> 244s 236msh 216m
[(C6F5)3P]2PtBr2	394w 366w 337s 317s 282m <u>255s</u> 241s 236s
[(C6F5)3P]2PdBr2	391w 365w 343msh 337s 315m 282msh <u>275s</u> 241s 230s
[(C6F5)3P]2PtI2	396w 343msh 338s 317m 283w 238sbr 206m
[(C6F5)2PhP]2PtCl2	383m 369m <u>347ssh</u> 341sbr 318m 286w 243s 236s
[(C6F5)2PhP]2PdCl2	382m <u>357s</u> 344s 337s 317m 285w 242s 235s
[(C6F5)2PhP]2PtBr2	382m 369m 343s 337s 318m 285w <u>255s</u> 244s 236s
[(C6F5)2PhP]2PdBr2	381m 368m 343s 337s 316m <u>282sbr</u> 244m 235m
[(C6F5)2PhP]2PtI2	392m 344ms 338s 317m 245m 237m 228ms 209w
[(C6F5)2PhP]2PdI2	389m 344s 337s 316m 280w 245ms 225ms
[(C6F5)Ph2P]2PtCl2	<u>346ssh</u> 343s 316w 234m

Table 1·7(continued)

$[(C_6F_5)Ph_2P]_2PdCl_2$	<u>359s</u> 343s 316w 243w 223w
$[(C_6F_5)Ph_2P]_2PtBr_2$	370m 344s 318w <u>254s</u> 237mbr 227w
$[(C_6F_5)Ph_2P]_2PdBr_2$	343s 316w <u>278s</u> 233w 223w
$[(C_6F_5)Ph_2P]_2PtI_2$	343s 316w 236m
$[(C_6F_5)Ph_2P]_2PdI_2$	343s 316w 245m 227ms 224wsh
$[(C_6F_5)Ph_2As]_2PtCl_2$	387s 358m <u>340s</u> 330s 323s 316ms 301s 282w 248m 233m 224m 203w
$[(C_6F_5)Ph_2As]_2PtBr_2$	387s 357m 330s 323s 316s 299s 282w <u>247s</u> 232m 224m 203w
$[(C_6F_5)Ph_2As]_2PtI_2$	387s 355m 327sbr 316msh 295s 280msh 235m 222m 203m
$[(C_6H_3F_2)_3P]_2PtCl_2$	364s 353s 348s <u>340s</u> 325m
$[(C_6H_3F_2)_3P]_2PtBr_2$	364s 353s 348s 326m <u>248s</u>

$(Ph_3P)_4Rh_2Cl_2$	325w <u>301sbr</u> 275w
$[(C_6F_5)Ph_2P]_4Rh_2Cl_2$	388w 343s 318msh <u>294sbr</u> 259w 240m/233m
$[(C_6F_5)_2PhP]_4Rh_2Cl_2$	375m 344s 317s <u>304sbr</u> 386w 263w 232m
$[(C_6F_5)_3P]_4Rh_2Cl_2$	387w 367w 347m 340s 319s <u>306sbr</u> 284w 276w 263w 235m
$(Ph_3P)_2RhCOCl$	<u>310s</u>
$[(C_6F_5)Ph_2P]_2RhCOCl$	376w 343s 317s <u>312ssh</u> 235w
$[(C_6F_5)_2PhP]_2RhCOCl$	375w 344s 336s 316m <u>308s</u> 284w 243sbr

/continued.

Table 1.7 (continued)

[(C$_6$F$_5$)$_3$P]$_2$RhCOCl	393m 365m 340s 334s 317s <u>310sh</u> 284w
	232s
[(C$_6$F$_5$)Ph$_2$As]$_2$RhCOCl	385s 357m 326s 320s 314s 297s 282m
	246m 232m 222m 193m
[(C$_6$F$_5$)$_3$P]RhCl$_3$	strong broad 355–330 326s 316sh 228w
[(C$_6$F$_5$)$_2$PhP]$_4$Rh$_2$Br$_2$	375m 344s 318m 284w 277vw 256w 241mbr
[(C$_6$F$_5$)Ph$_2$P]$_4$Rh$_2$Br$_2$	385w 342s 318m 245mbr
[(C$_6$F$_5$)$_2$PhP]$_2$RhCOBr	375w 344s 336s 316s 284m 245sbr

TABLE 1·8

Infrared spectra (2000-400 cm⁻) as Nujol mulls.

The Nujol frequencies have been omitted.

$(C_6F_5)_3P$ 1738w 1650s 1555w 1522vs 1485vw 1445w 1392s

1296s 1268w 1145m 1098vs 1070sh 1030m 980vs 849m 822vw 765vw

755m 662vw 652vw 637m 624m 586m 516s 445m 425s 414m

$(C_6F_5)_2PhP$ 1640s 1585w 1575w 1522vs 1436s 1288s 1228w 1190w

1138m 1090vs 1028m 980vs 842s 832s 768w 750s 728s 695s 638ms

629ms 589m 545ms 520s 485s 452w 436ms 429ms

$(C_6F_5)Ph_2P$ 1638s 1585w 1518s 1433s 1289m 1158w 1090s 1028m

977s 835m 750s 742s 729m 697s 633m 588w 550m 512s 500s 489s

447ms 418w

$(C_6F_5)_3As$ 1640vs 1615w 1587w 1510vs 1280s 1147m 1140m 1085vs

1020m 975vs 810s 760w 750w 726m(doublet) 628m 585w 495m

$(C_6F_5)_2PhAs$ 1640s 1612w 1577w 1548w 1512vs 1435s 1334w 1308w

1278s 1186w 1155w 1136m(doublet) 1080vs 1020m 1010m(doublet)

996m 980vs 844w(doublet) 803 s 736s(doublet) 720m 694s 620m(doublet)

582w 467s

$(C_6F_5)Ph_2As$ 1640s 1610w 1585m 1560w 1513s 1436s(doublet)

1340w(doublet) 1316w 1187w 1160w 1135w 1110w 1080vs 1040w 1025m

1000m 972vs 920w 910w 865w 850w 807m 755w 740vs(doublet) 724m

696s 622m 585w 494w 472s

TABLE 1·8 (continued)

$(C_6F_5)_3Sb$ 1638vs 1610w 1582w 1550m 1510vs 1332w 1327w

1280s 1225w 1140m(doublet) 1080vs 1012m 970vs 785s 748w 720m

616m 611m 583w 487m 445w

$(C_6F_5)_2PhSb$ 1640s 1610w 1577w 1555w 1512vs 1434s 1332w(doublet)

1304w 1277s 1188w(doublet) 1158w 1136m(doublet) 1080vs 1050w

1026w 1020m 1008m 1000m 968vs 848w(doublet) 784m 736s 730s 720mw

696s(doublet) 612w(doublet) 583w 488w 452ms

$(C_6F_5)Ph_2Sb$ 1635s 1578m 1550w 1510vs 1432s 1332m 1302w 1274m

1187w 1157w 1132w 1075vs 1021w 1000m 967vs 780w 730ms 695ms 455m

$(C_6H_3F_2)_3P$ 1610vs 1578-1555vs(complex) 1292m 1285m 1268m

1262s 1230s 1155m 1150w 1109s 1100m 990vs 975m 962m 887w 875w

792vs 784vs 770s(doublet) 720m(doublet) 714s 708s 594w 544w

521s 512m 502w 440ms

$(C_6H_3F_2)_3As$ 1605vs 1578-1555vs(complex) 1286s 1269s 1256s

1228vs(doublet) 1150m(doublet) 1087s(doublet) 990vs(doublet)

975vs 877w 785vs 755vs 710m 702s 696ms(doublet) 595w 564m 558m

545w 535w 520m 508s(doublet)

$[(C_6F_5)_3P]_2PtCl_2$ 1645s 1525s 1490s 1395m 1302m 1165m 1102s

1030w 1020w 988s 772m(doublet) 732m(doublet) 642m 634m(doublet)

593m 530m(doublet) 509m 455m 446m(doublet) 425w.

TABLE 1·8 (continued)

$[(C_6F_5)_2PhP]_2PtCl_2$ 1643s 1590w 1578w 1520vs 1438s 1290s

1190w 1143m 1100vs 1023m 982vs 847m 762s 742s 728s(doublet)

702m 688s 638s 628s 588m 527s 515s 490s 478m 467s 442s 420m

$[(C_6F_5)Ph_2P]_2PtCl_2$ 1640s 1585w   1570w 1510vs 1435s

1330w 1310m 1290s 1185m 1120msh 1100vs 1028w 1012m 1000m 977s

840m 750s 743s 721s 709m 690vs 628s 587m 528s 503s 485s 477s

448w 435m 418m

$[(C_6H_3F_2)_3P]_2PtCl_2$ 1610vs 1575vs 1560ssh 1285m 1268s 1230vs

1150m 1107s 992s(doublet) 890w 878w 790vs 770s 713w(doublet)

592w 584w 547w 523ms 512ms 441s 423m

$[(C_6F_5)Ph_2As]_2PtCl_2$ 1640m 1585m 1575m 1515s 1440s(doublet)

1336w 1309w 1287m 1195w 1182m 1138w 1110w 1090vs 1075m 1031w

1023w 1000m 975vs 813m 742s 731s 720w 690s 670w 620m 490w 480s

455m

TABLE 1·9

Molecular Weight Determinations

Compound	Solvent	Found	Required
[(C$_6$F$_5$)$_3$P]$_2$PtCl$_2$	CHCl$_3$	1360	1330
[(C$_6$F$_5$)$_3$P]$_2$RhCOCl	CHCl$_3$	1193	1230
*[(C$_6$F$_5$)$_3$P]$_4$Rh$_2$Cl$_2$	C$_6$F$_5$H	2270, 2380, 2420	2405
*[(C$_6$F$_5$)$_2$PhP]$_4$Rh$_2$Cl$_2$	CHCl$_3$	1880, 1890	2045
*[(C$_6$F$_5$)Ph$_2$P]$_4$Rh$_2$Cl$_2$	CHCl$_3$	600	1685
[(C$_6$F$_5$)Ph$_2$As]$_2$RhCOCl	CHCl$_3$	895	958
*[(C$_6$F$_5$)$_3$P]RhCl$_3$	Acetone	730, 750, 780	744
[(C$_6$F$_5$)$_3$P]$_2$PdCl$_2$	CHCl$_3$	1170	1242
[(C$_6$F$_5$)$_3$P]$_2$PtBr$_2$	CHCl$_3$	1390	1429
[(C$_6$F$_5$)$_3$P]$_2$PtI$_2$	CHCl$_3$	1500	1513

*Done rapidly. Readings taken about three minutes after making up the solutions.

CHAPTER TWO

ἡ δε κακ τριων τρυπηματων ἐργαζομενη ἐνεκαλει τη φυσει

δυσφορουμενη ὁτι δη μη και τους τιτθους αὑτη εὑρυτερον ἠ νυν

εἰσι τρυπωη ὁπως και ἀλλην ἐνταυθα μιξιν ἐπιτεχνασθαι

δυνατη εἰη

Procopius. Ἀνεκδοτα, IX, 18.

Many pentafluorophenyl compounds have been studied by ^{19}F
n.m.r. spectroscopy.[14,45,51,79-88] The analysis of the spectra is

based on the AA'PXX' spin system. In this system the three

groups of nuclei A, P and X are separated by chemical shifts which

are large compared with the coupling constants. In C_6F_5Y compounds

the A nuclei are those ortho to Y, the X those meta to Y, and the

para fluorine is the P nucleus.
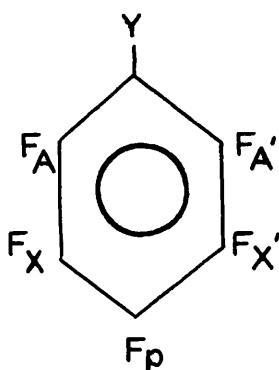
If Y is a substituent not containing any magnetic nuclei then

the high resolution spectrum is as follows. The para resonance

consists of a triplet of triplets due to coupling with the two X

nuclei and the two A nuclei. The meta resonance is the X part of

an AA'XX' system with each band split into a doublet due to coupling

with the para fluorine. The ortho resonance is the A part of the

AA'XX' spectra with each band split into a doublet due to coupling

with the para fluorine.

If Y contains magnetic nuclei which have a very different

chemical shift to the ring nuclei then further first order couplings

must be taken into account. In pentafluorophenylphosphorus

compounds each line in the AA'$\overset{P}{X}$X' spectrum will be split into

doublets although in most cases coupling of the phosphorus to

the meta or para fluorines is too small to be detected.

The analysis of the AA'XX' spin system will be described

in detail.[89]

$$F_{A'} \xleftarrow{\quad J_{AA'} \quad} F_A$$
$$J_{A'X}$$
$$J_{AX}$$
$$F_{X'} \xleftarrow{\quad J_{XX'} \quad} F_X$$
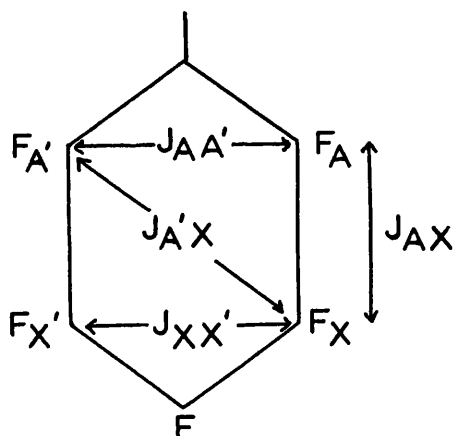
There are four different coupling constants involved since

the symmetry makes $J_{A'X'} \equiv J_{AX}$ and $J_{AX'} \equiv J_{A'X}$. In this system it

is possible to derive analytical expressions for the energies of the

transitions in the A or X parts and these are given below.

Transition	Transition Energy (relative to δ_A).
1,2	$+ \frac{1}{2} N$
3,4	$- \frac{1}{2} N$
5	$+ \frac{1}{2} K + \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$
6	$- \frac{1}{2} K + \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$
7	$+ \frac{1}{2} K - \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$
8	$\frac{1}{2} K - \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$
9	$\frac{1}{2} M + \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$
10	$- \frac{1}{2} M + \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$
11	$+ \frac{1}{2} M - \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$
12	$- \frac{1}{2} M - \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$

$$N = J_{AX} + J_{AX'} \qquad L = J_{AX} - J_{AX'} \qquad K = J_{AA'} + J_{XX'}$$

$$M = J_{AA'} - J_{XX'}.$$

The A part of the system is identical to the X part.
Examination of this table shows that the A (or X) part of the
AA'XX' spectrum is 1) Two bands (1, 2 and 3,4) separated by N
and centred on the resonance frequency of the A nuclei (δ_A). These
bands are intense. 2) Two pairs of symmetrical quartets (5,6,7,8
and 9,10,11,12) also centred on δ_A. Those components of each
quartet nearest the centre of the spectrum will always be the most
intense. To illustrate these points a calculated spectrum is given

below (Diagram 2·1) using typical values of coupling constants

found in pentafluorophenyl compounds.
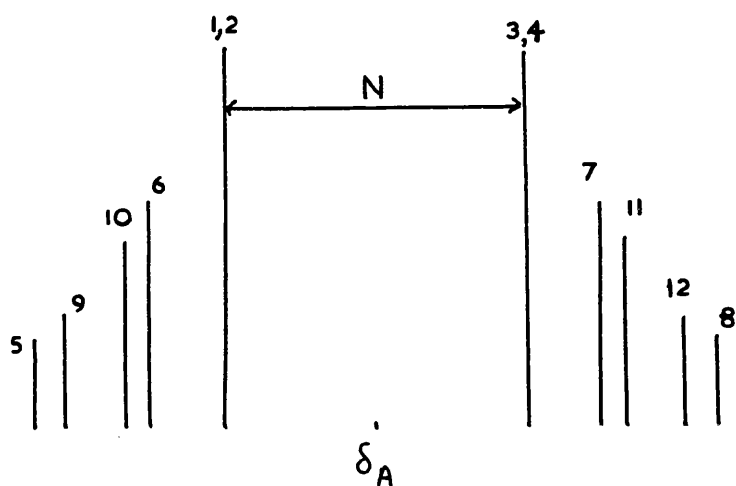
Diagram 2·1

In analysing a spectrum such as this suitable subtractions

are made to determine N, L, K and M. Only the relative signs of

N and L can be obtained and only the moduli of K and M. In

addition to this K and M are indistinguishable. In terms of the

coupling constants J_{AX}, $J_{AX'}$, $J_{AA'}$ and $J_{XX'}$ these limitations mean

that only the relative signs of J_{AX} and $J_{AX'}$ are available; for

$J_{AA'}$ and $J_{XX'}$ only the moduli can be obtained and the assignment

of one value to $J_{AA'}$ and the other to $J_{XX'}$ is arbitrary.

High resolution studies of pentafluorophenyl systems lead to

determination of the following coupling constants:

J_{34}, J_{24}, (from the para resonance); J_{32}, J_{25}, J_{26}, J_{35}, (from

the ortho or meta resonances).

As mentioned before most of the pentafluorophenyl compounds

studied have been found to be examples of the AA'PXX' spin system.

However, in $C_6F_5OCH_3$ [87] the chemical shift between the para signal

and the meta signal is small compared with the coupling constants

involved, while the chemical shift between the para and ortho remains

large, so that this compound is an AA'BXX' spin system.
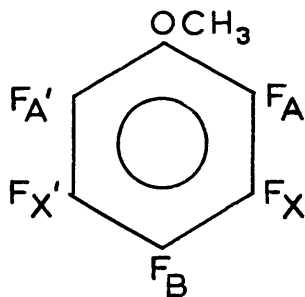
In this system the analysis yields relative signs of all the

coupling constants as well as allowing a unique assignment to be

made for $J_{BB'}$ and $J_{XX'}$. It was found however that $J_{XX'}$ was so small

that the observed spectrum would fit $J_{XX'} = \pm 0 \cdot 8$ c./sec.

The AA'PXX' system of iodopentafluorobenzene at 56·4 Mc./sec.

was transformed into an AA'BXX' system at 6·14 Mc./sec. [81] This was

done in order to extract the maximum amount of information from
the spectrum. The analysis of an AA'BXX' system is more difficult
however, and requires iterative computer techniques.

Figure 2·1. $(C_6F_5)Ph_2Sb$ ^{19}F n.m.r.

ORTHO

PARA

Figure 2·1.

$(C_6F_5)Ph_2Sb$

^{19}F n.m.r.

100

META
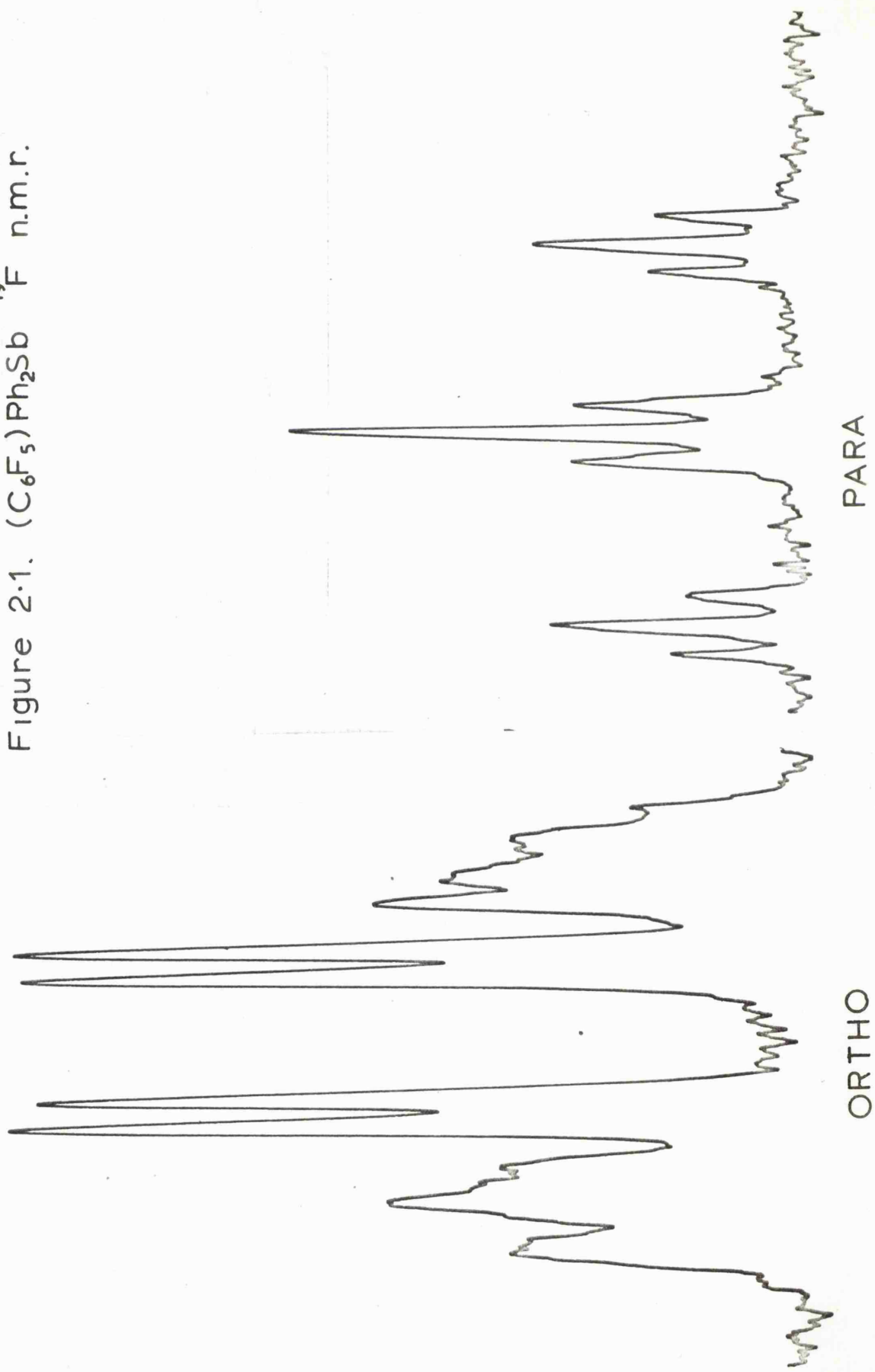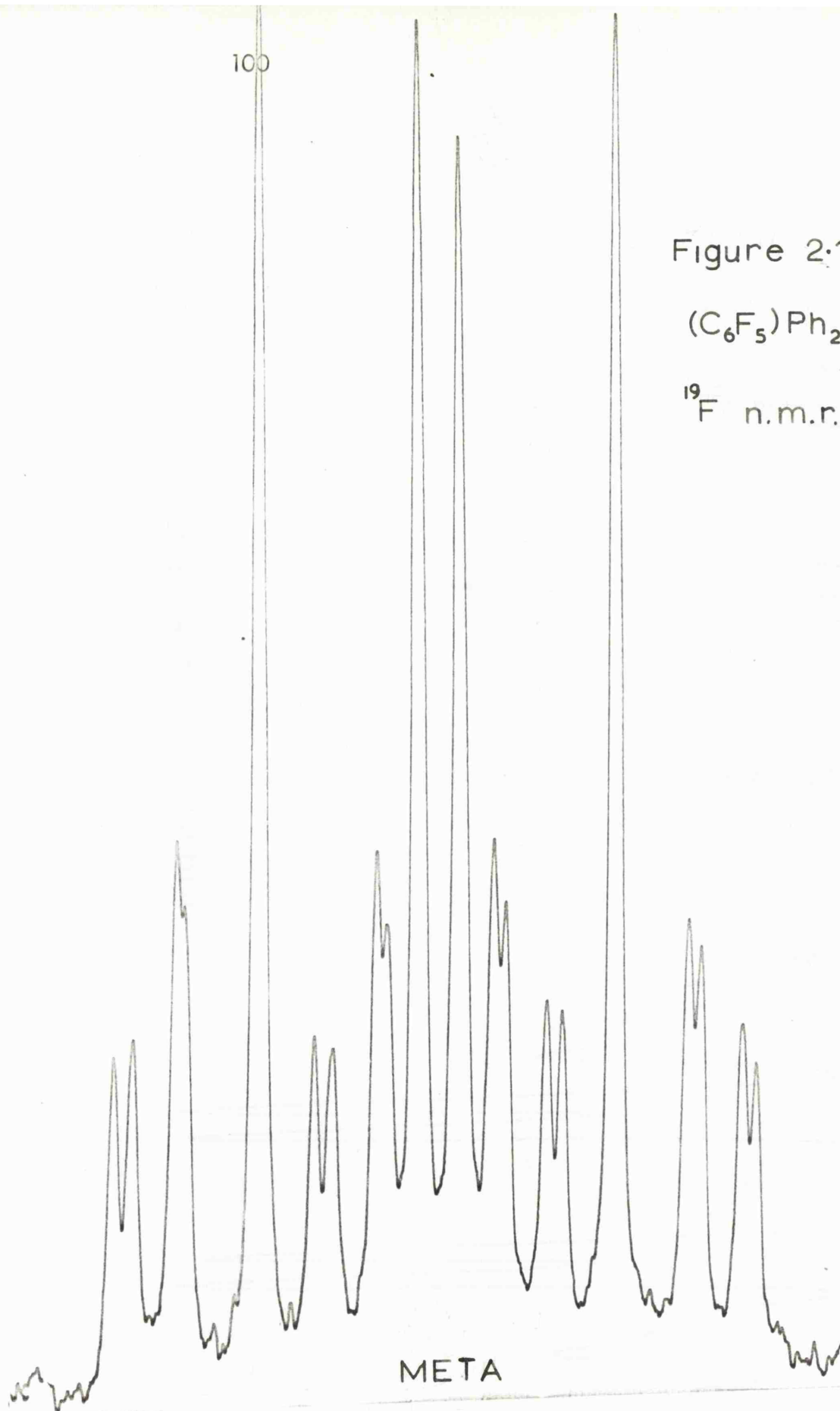
RESULTS AND EXPERIMENTAL

The pentafluorophenyl compounds studies were prepared as described in Chapter 1. ^{19}F and ^{31}P n.m.r. spectra were obtained at 56.4, and 19.3 Mc./sec. on a Varian DA/60 instrument. Calibration was by means of normal side-band techniques. P_4O_6 was used as an external standard for the ^{31}P and $PhCF_3$ as an internal standard for the ^{19}F spectra. The compounds were examined using saturated chloroform or methylene chloride solutions.

Analysis of Spectra

1) The monopentafluorophenyl compounds $(C_6F_5)Ph_2M$, M = P, As, Sb were analysed as an AA'PXX' system. First order coupling by the phosphorus was also included. Figure 2.1 shows the para, meta, and ortho parts of the ^{19}F n.m.r. spectrum of $(C_6F_5)Ph_2Sb$.

The para resonance was examined first and J_{42} and J_{43} calculated. The two overlapping A parts of an AA'XX' system which make up the meta resonance were 'uncoupled' using the value of J_{43}. This enabled J_{23}, J_{25}, J_{35}, and J_{26} to be calculated. The ortho resonance being the X part split by the para fluorine was computed and compared with the observed spectrum. The agreement was good for $(C_6F_5)Ph_2As$ and $(C_6F_5)Ph_2Sb$, and for $(C_6F_5)Ph_2P$ after allowance had been made for $J_{P,F2}$.

Figure 2.2. $(C_6F_5)_2PhSb.$ ^{19}F n.m.r.
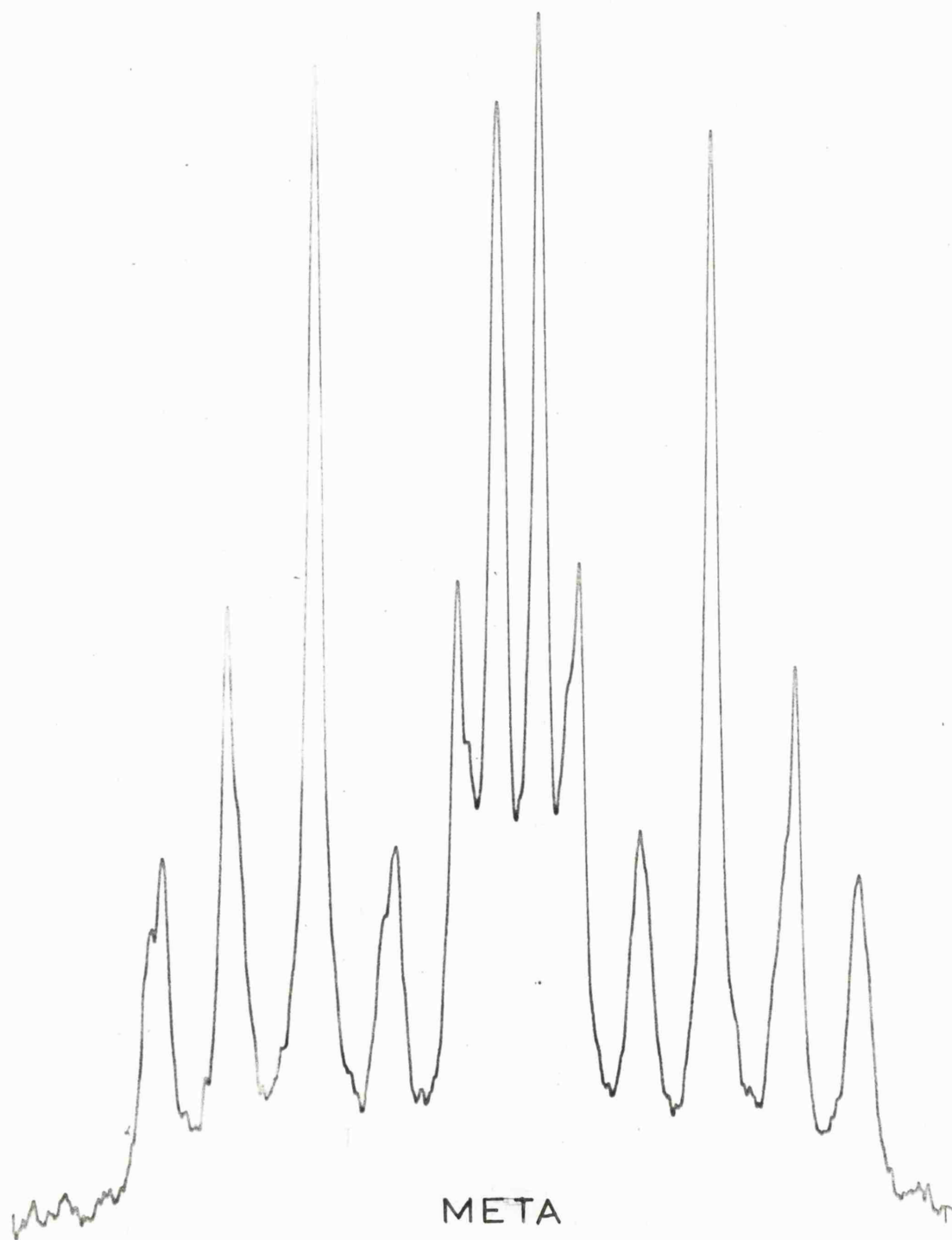
META

2) In all the other compounds examined the meta and ortho

signals were broadened so that the twenty lines of the A or X parts of

the AA'PXX' system were not observed. The para resonance was

unchanged. Fig. 2.2 shows the ^{19}F n.m.r. spectrum of $(C_6F_5)_2PhSb$

as an example of this effect. The n.m.r. spectra of these compounds

were analysed by a modification of the AA'XX' analysis. It will

be seen that the two outer doublets of the meta resonance in Fig. 2.1

are replaced by two broad lines in Fig. 2.2. It was assumed that

the position of the broadened peak corresponded to the mid-point of

the two lines which should have been present for each doublet, as

illustrated by diagram 2·2 below.
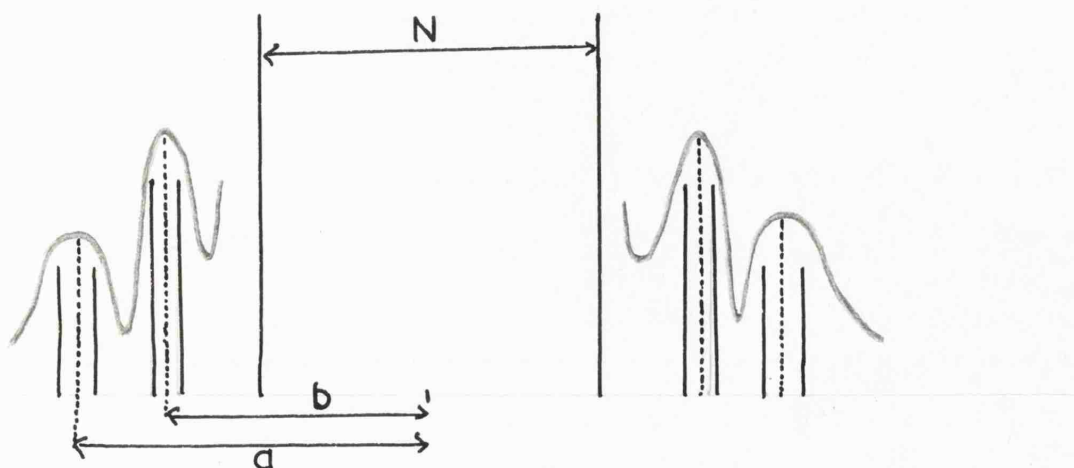
Diagram 2·2

Previous work has shown that in pentafluorophenyl systems J_{23} -20 to -25 c./sec., J_{25} +10 c./sec., $|J_{26}|$, $|J_{35}|$ 5,2 c./sec. Little variation occurs in these values on alteration of the substituent on the pentafluorophenyl ring. Thus $N \sim$ -15 c./sec., $L \sim$ -35 c./sec., $|K|$, $|M|$, $\sim$ 7,4 c./sec. Since K and M are indistinguishable we can arbitrarily set K > M. As L >> K or M the assignment of the transitions 5, 9, 10, and 6 is as follows :

$$5 \equiv \frac{1}{2} K + \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$$

$$9 \equiv \frac{1}{2} M + \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$$

$$10 \equiv -\frac{1}{2} M + \frac{1}{2} (M^2 + L^2)^{\frac{1}{2}}$$

$$6 \equiv -\frac{1}{2} K + \frac{1}{2} (K^2 + L^2)^{\frac{1}{2}}$$

So $b = \frac{1}{2} (10 + 6)$ and $a = \frac{1}{2} (5 + 9)$.

$a = \frac{1}{4} [K + (K^2 + L^2)^{\frac{1}{2}} + M + (M^2 + L^2)^{\frac{1}{2}}]$

$b = \frac{1}{4} [-K - M + (K^2 + L^2)^{\frac{1}{2}} + (M^2 + L^2)^{\frac{1}{2}}]$

and $a - b = \frac{1}{2} (K + M) \equiv J_{26}$ or J_{35}.

$a + b = \frac{1}{2} [(K^2 + L^2)^{\frac{1}{2}} + (M^2 + L^2)^{\frac{1}{2}}]$.

Since L >> K,M $(K^2 + L^2)^{\frac{1}{2}} = L (1 + \frac{K^2}{2L^2})$

and $(M^2 + L^2)^{\frac{1}{2}} = L(1 + \frac{M^2}{2L^2})$.   The error involved here is about 0.03 c./sec.

$$a + b = \frac{1}{2}[L + \frac{K^2}{2L} + L + \frac{M^2}{2L}] = \frac{1}{2}[2L + \frac{1}{2L}(K^2 + M^2)].$$

Now $K^2 + M^2 \approx \frac{1}{2}(K + M)^2$ when K and M are of approximately the same magnitude. The error involved here results in an error of about $0 \cdot 1$ c./sec. in the final value of L. The cruder approximation of neglecting the $\frac{1}{2L}(K^2 + M^2)$ term results in errors of $0 \cdot 5 - 1 \cdot 5$ c./sec. in L.

So $a + b = \frac{1}{2}[2L + \frac{1}{2L}(2(a-b))^2] = L + \frac{(a-b)^2}{L}$

Thus $L^2 - (a + b)L + (a - b)^2 = 0$

and L is obtained as the root of this quadratic.

The spin-spin coupling constants of the compounds investigated are shown in Table $2 \cdot 1$ $\left(p.74a \right)$

The ^{31}P n.m.r. of $(C_6F_5)Ph_2PO$[88a] and $(C_6F_5)_2PhPO$[88a] were studied but only broad lines were obtained and no values of J_{P,F_2} could be derived. In tris(2,6 difluorophenyl)phosphine the ^{31}P resonance was a seven line resonance centred at $+79 \pm 1$ p.p.m. and $J_{P,F}$ was found to be 40 ± 2 c./sec. in agreement with the value of $38 \cdot 2 \pm 0 \cdot 2$ c./sec. derived from the ^{19}F n.m.r. spectrum.

74a

Table 2·1

Spin-Spin Coupling Constants c./sec.

Compound	$J_{P,F2}$	$J_{P,F3}$	$J_{P,F4}$	$J_{24}(+)$	$J_{34}(-)$	$J_{23}(-)$	$J_{25}(+)$	J_{35}	J_{26}
$(C_6F_5)Ph_2P$	38.0	<0.5	<0.5	4.0	20.4	24.2	10.0	4.4	1.6
$(C_6F_5)Ph_2As$	–	–	–	3.2	19.8	25.4	9.8	4.8	1.5
$(C_6F_5)Ph_2Sb$	–	–	–	2.9	20.2	26.9	10.8	5.8	1.5
$(C_6F_5)_2PhP$	31.0	<0.5	<0.5	4.0	20.0	23.3	8.9	3.6	–
$(C_6F_5)_2PhAs$	–	–	–	3.1	18.9	27.3	10.3	5.2	–
$(C_6F_5)_2PhSb$	–	–	–	3.1	19.7	25.0	9.2	5.5	–
$(C_6F_5)_3P$	36.5	<1.0	<1.0	4.3	20.0	24.2	8.8	4.6	–
$(C_6F_5)_3As$	–	–	–	3.9	19.6	24.8	9.8	4.5	–
$(C_6F_5)_3Sb$	–	–	–	3.4	19.5	25.2	9.7	5.7	–
$(C_6F_5)Ph_2PO$	6.5	3.6	2.3	6.3	20.8	23.5	9.5	5.5	–
$(C_6F_5)_2PhPO$	15.0	4.9	2.7	6.6	19.9	23.9	8.6	7.2	–
$(C_6F_5)_3PO$	37.4	<1.0	<1.0	4.4	20.5	26.3	11.5	3.6	–
$[(C_6F_5)Ph_2P]_2PtCl_2$	<1.0	<0.5	<0.5	4.8	20.4	24.0	8.6	6.3	–
$[(C_6F_5)Ph_2P]_2RhCOCl$	<1.0	<0.5	<0.5	4.6	20.6	23.0	7.7	5.8	–
$[(C_6F_5)Ph_2As]_2PtCl_2$	–	–	–	4.6	20.0	24.9	9.2	6.5	0.8
$[(C_6F_5)Ph_2As]_2RhCOCl$	–	–	–	4.2	20.5	24.7	9.2	7.7	–

DISCUSSION

The values of the coupling constants obtained in this study fall inside the range of those reported by other workers. Where the same compounds were studied the coupling constants reported here agree with those of Graham et al.[14] but our values for J_{42} in $(C_6F_5)_3P$ and $(C_6F_5)_3PO$ are in disagreement with those of Eméléus and Miller.[51]

While the fluorine-fluorine coupling constants remain fairly constant in the series of compounds studied here the phosphorus-fluorine coupling constants vary widely, especially J_{P,F_2}. There seems to be no observable correlation between the values and the structure of the compound. A similar variation was noted by Haszeldine et al.[80] in their study.

Ortho fluorine-fluorine coupling constants in a benzene ring show little variation with substituent. The range of values reported is 18 to 26 c./sec. The absolute sign of the ortho coupling constant has been found to be negative in C_6F_6[82] and it is thus likely that all such coupling constants are negative. A similar argument indicates that the para fluorine-fluorine coupling constant is positive although the range of values is larger 18 to 5 c./sec. Thus in Table 2·1 J_{43} and J_{23} are negative while J_{25} is positive.

Graham et al.[14] have found that a linear relationship exists between J_{24} and the chemical shift of the para fluorine (δp) in

Figure. 2·3.

The numbers correspond to the order of the compounds in Table 2·1.

δ_P ppm from PhCF$_3$

J_{24} c./sec.(+)
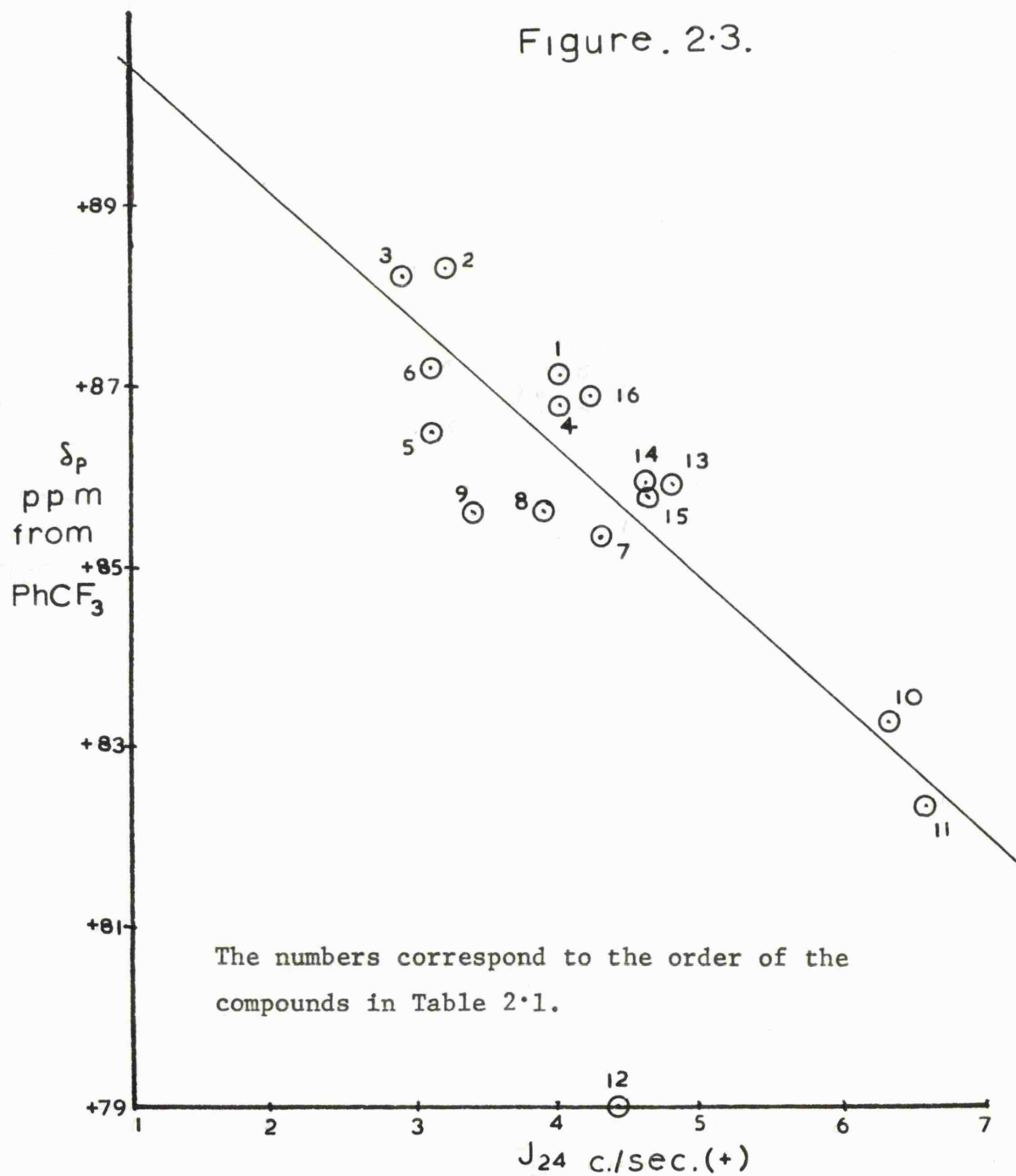
pentafluorophenyl compounds. Fig. 2·3 shows a graph illustrating
this point. The compounds studied here all fall in the region
associated with a positive sign for J_{24}.

δp depends primarily on mesomeric effects. Thus changes in
J_{24} reflect mesomeric changes in the pentafluorophenyl-substituent
bond. A discussion of the δp values of the phosphines and their
metal complexes has been given in Chapter 1. The J_{24} values
(p.74a)
(Table 2·1) in the series $(C_6F_5)_n Ph_{3-n} M$ (n = 1,2 and 3; M = P,As,
and Sb) decrease from phosphorus to antimony for a given number of
pentafluorophenyl rings present in the compounds. An increase in
J_{24} corresponds to a decrease in shielding of the <u>para</u> fluorine atom.
It is not possible to decide whether this decrease in J_{24} on going
from phosphorus to antimony is due to reduction in ring $\pi \rightarrow$ nd of
the central atom (P, As, or Sb) or increase in the lone pair to
ring π^* donation.
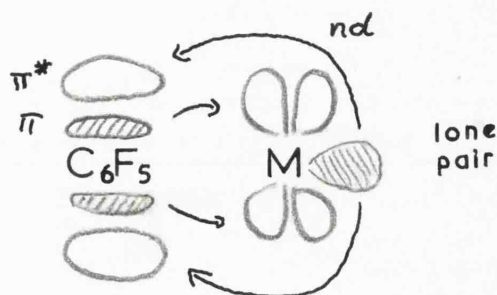
Diagram 2·3

In polyfluorobenzenes it has been found that the meta and

para fluorine-fluorine couplings are determined by additive

substituent contributions from the other groups present.[86]

These substituent parameters can be used to calculate the magnitude

and sign of these coupling constants expected in unexamined compounds.

For the meta J_{FF} there are three different substituent positions.

If we number the two fluorines concerned 2 and 6 then substituents

will have different effects in the 1 (or ortho-ortho) position,

3 and 5 (ortho-para) positions, and 4 (meta-meta) position.
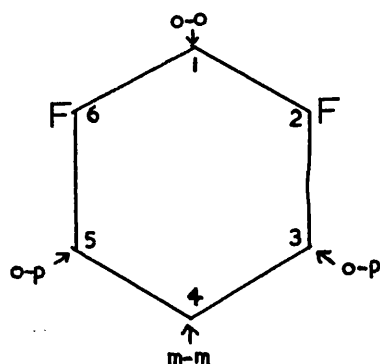
Any meta J_{FF} should therefore be given by the coupling in

m-difluorobenzene (5·8 c./sec.) plus the additive substituent

contributions from each of these three positions.[86] J_{FF} in

m-difluorobenzene has recently been determined[90] and is 6·6 c./sec.

However the substituent contributions used have been evaluated on

the basis of J_{FF} = 5·8 c./sec. and this value will be used here.

Figure 2·4.
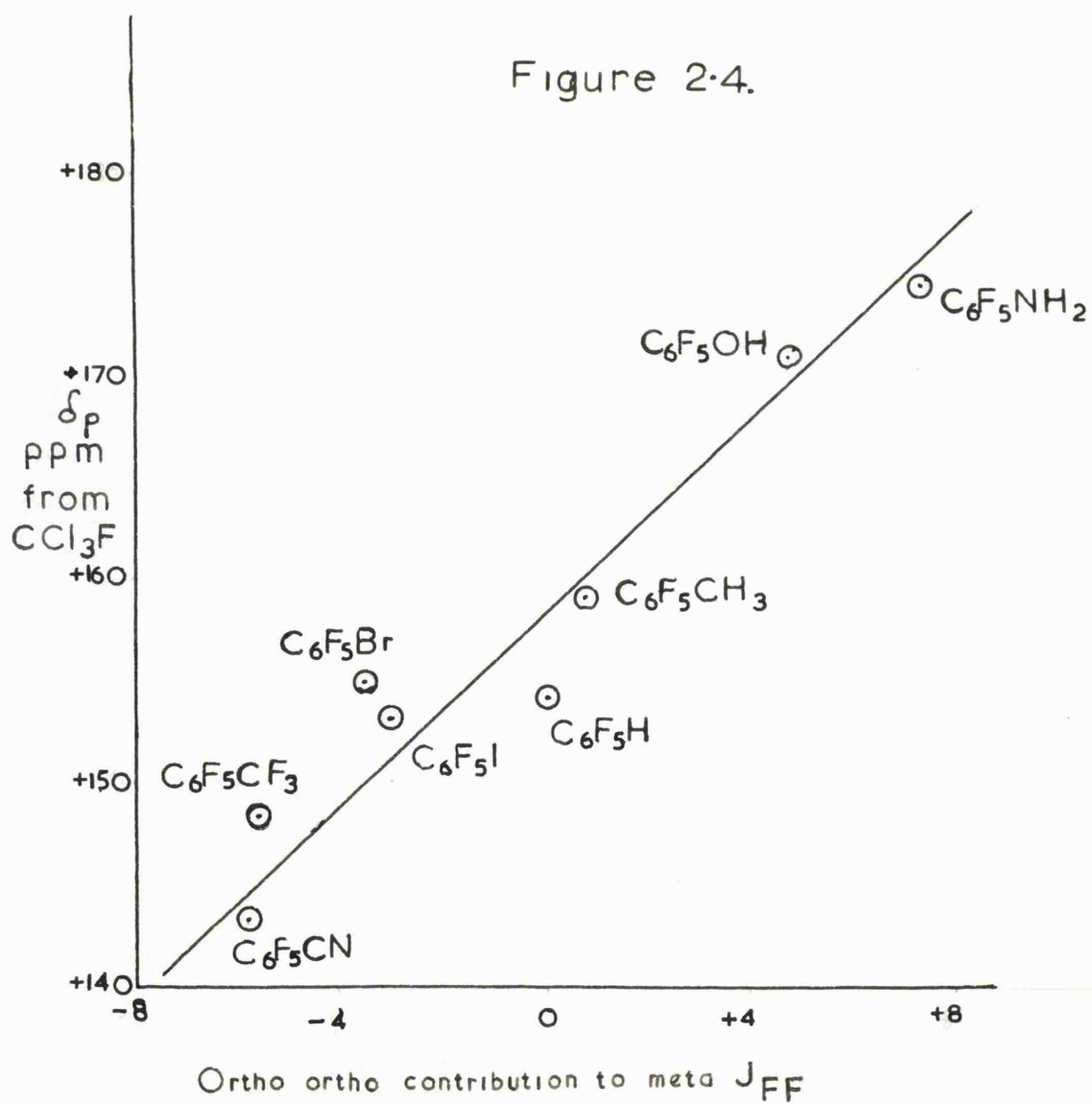
Table 2·2

Compound	$\lvert J_{26} \rvert$ observed c./sec.	J_{26} calculated c./sec.
$(C_6F_5)Ph_2P$	4.4	-5.0
$(C_6F_5)_2PhP$	3.6	-5.2
$(C_6F_5)_3P$	4.6	-5.8
$(C_6F_5)Ph_2As$	4.8	-4.6
$(C_6F_5)_2PhAs$	5.2	-5.3
$(C_6F_5)_3As$	4.5	-5.7
$(C_6F_5)Ph_2Sb$	5.8	-4.6
$(C_6F_5)_2PhSb$	5.5	-5.0
$(C_6F_5)Ph_2PO$	5.5	-6.5
$(C_6F_5)_2PhPO$	7.2	-7.2
$(C_6F_5)_3PO$	3.6	-8.7
$[(C_6F_5)Ph_2As]_2PtCl_2$	6.5	-5.6
$[(C_6F_5)Ph_2As]_2RhCOCl$	7.7	-5.2
$[(C_6F_5)Ph_2P]_2PtCl_2$	6.3	-5.6
$[(C_6F_5)Ph_2P]_2RhCOCl$	5.8	-5.6

In pentafluorophenyl derivatives C_6F_5Y J_{26}, J_{35}, and J_{42} are given by the following formulae in c./sec.

J_{26} = Y ortho-ortho + F meta-meta + 2F ortho-para + 5·8

J_{35} = F ortho-ortho + 2F ortho-para + Y meta-meta + 5·8

J_{42} = F ortho-ortho + F ortho-para + F meta-meta + Y ortho-para + 5·8

Using the known[86] substituent values (in c./sec.) for fluorine

F ortho-ortho = -0·1 , F ortho-para = -3·8, and F meta-meta = -0·3

the formulae reduce to J_{26} = Y ortho-ortho -2·1 , J_{35} = Y meta-meta -1·9,

J_{42} = Y ortho-para + 1·6.

It has been found that the ortho-ortho contribution of a substituent to meta J_{FF} varies in a linear fashion with the Hammett constant σp, the chemical shift of the para fluorine δp is mainly determined by σp too. Thus the ortho-ortho contribution should vary linearly with δp and this can be used to evaluate the ortho-ortho contributions for the compounds studied here. Fig. 2·4 shows that a linear variation of δp with the ortho-ortho contribution is indeed observed. Table 2·2 compares the values of J_{26} calculated on this basis with those obtained. The agreement obtained justifies the assignment to J_{26} rather than J_{35} and makes J_{26} negative. For the values of the ortho-ortho substituent contributions found (-2 to -6) the expected meta-meta contributions would be 0-2 on the

Table 2·3

Compound	$\delta m - \delta p$ c./sec.	J_{34} c./sec.	$\dfrac{\delta m - \delta p}{J_{34}}$
$(C_6F_5)Ph_2P$	575	20.4	27.2
$(C_6F_5)_2PhP$	587	20.0	29.4
$(C_6F_5)Ph_2As$	510	19.8	25.8
$(C_6F_5)_2PhAs$	525	18.9	28.0
$(C_6F_5)Ph_2Sb$	490	20.2	24.3
$(C_6F_5)_2PhSb$	530	19.7	27.0

basis of other substituent contributions. This would make J_{35} range from $-1 \cdot 0$ to 0 c./sec. In approximate agreement with this J_{35} is found to be below 2 c./sec. whenever it could be evaluated.

The compounds studied here with only one pentafluorophenyl group present show typical AA'PXX' spectra. When two or more pentafluorophenyl groups are present the _meta_ resonance has the two outer doublets merged and broadened. Massey et al.[91] found the same effect in the series $(C_6F_5)_n Ph_{4-n} Ge$ ($n = 1,2,3$ and 4) when more than one pentafluorophenyl group was present and attributed the broadening to the large pentafluorophenyl groups causing a restriction of the rotation of the groups about the central atom, and the steric hindrance prevented an averaging out of the dipole-dipole interactions.

As the chemical shift between the _para_ and _meta_ fluorines decreases so second order effects should become apparent. Table 2·3 shows the values of $(\delta m-\delta p)/J_{43}$ for some mono- and bispentafluorophenyl derivatives. It will be seen that in all cases the bispentafluorophenyl derivatives are less likely to show second order effects than the corresponding monopentafluorophenyl compounds. The observed broadening therefore cannot be due to second order effects.

If the central atom has a spin then it will couple to the _meta_ fluorines in the pentafluorophenyl group attached to it. If the coupling constant was less than $0 \cdot 5$ c./sec. the coupling would show as a broadening of the lines. If the central atom possesses a quadrupole moment then again a broadening of the lines might be expected.

While this may explain the broadening in the Group V derivatives,

it seems unlikely to be the explanation for the silanes and germanes

since ^{29}Si $(I = \frac{1}{2})$ and $^{73}Ge(I = \frac{9}{2})$ are in low abundance. It is

also difficult to see why the spin or quadrupole broadening is not

present in the monopentafluorophenyl derivatives.

If small interannular couplings are present from one penta-

fluorophenyl ring to another, but not from a phenyl ring to a

pentafluorophenyl, this would explain the absence of broadening

in the monopentafluorophenyl compounds. Haszeldine et al.[80] noted

a broadening of the ortho resonance in $(C_6F_5)_2PH$ and ascribed it to

this effect. However it does not explain a further observation[91]

that $Me_2Sn(C_6F_5)_2$ is not broadened, while $Ph_2Sn(C_6F_5)_2$ is.

The separation between transitions 5 and 9 as well as 10 and 6

depends on the difference between K and M. If K and M were nearly

equal then instead of two doublets, two broad lines would be seen.

If K and M were equal then transitions 5 and 9, and 10 and 6 would

be superimposed and two sharp lines would be seen. The difference

between K and M is equal to J_{35} and in several pentafluorophenyl

compounds[79,84] this coupling constant is less than 1·0 c./sec.

The compounds in which J_{35} is near zero are those with electronegative

groups attached to the pentafluorophenyl group. It may be that

substitution of a phenyl group by a pentafluorophenyl group causes

the electronegativity of the central atom to increase and thus make

J_{35} smaller. In support of this it is found that $(C_6F_5)Ph_2As$ and

Table 2·4

Line widths at half-height ($\Delta v\frac{1}{2}$) of transitions

1,2 and 3,4 in c./sec.

Compound	$\Delta v^{\frac{1}{2}}$
$(C_6F_5)Ph_2P$	1.85
$(C_6F_5)Ph_2As$	1.25
$(C_6F_5)Ph_2Sb$	1.40
$(C_6F_5)_2PhP$	2.3
$(C_6F_5)_2PhAs$	1.8
$(C_6F_5)_2PhSb$	1.6
$(C_6F_5)Ph_2PO$	1.6
$(C_6F_5)_2PhPO$	1.7
$[(C_6F_5)Ph_2P]_2PtCl_2$	3.4
$[(C_6F_5)Ph_2P]_2RhCOCl$	2.4
$[(C_6F_5)Ph_2As]_2PtCl_2$	1.65
$[(C_6F_5)Ph_2As]_2RhCOCl_2$	1.8
$(C_6F_5)Ph_3Ge$[1]	1.45
$(C_6F_5)_2Ph_2Ge$[1]	1.65
$(C_6F_5)AsCl_2$	1.80

1) Measured from the spectra in Ref. 91.

$(C_6F_5)Ph_2P$ are not broadened whereas $(C_6F_5)AsCl_2$ and $(C_6F_5)PCl_2$ [79] are in spite of the phenyl group being larger than a chlorine atom.

The broadening from steric hindrance should broaden all the lines in the meta resonance, whereas with the near coincidence of K and M the broadening should be confined to the outer doublets, and the line widths of the intense transitions 1,2 and 3,4 should be unaltered. Table 2·4 shows the line widths for the intense transitions in those compounds where those transitions are not affected by overlapping of other lines. While those compounds which do not show a broadening of the outer doublets have small values of $\Delta v_{\frac{1}{2}}$ some compounds which show broadening have values of $\Delta v_{\frac{1}{2}}$ little greater. This evidence is rather inconclusive but tends to support the explanation based on steric hindrance.

Increasing the temperature at which the n.m.r. spectra of the bispentafluorophenyl compounds were run should lead to the broadening being decreased. The monopentafluorophenyl compounds on the other hand should show broadening on cooling the n.m.r. samples. No change was observed in the meta resonance at +150°C in $(C_6F_5)_nPh_{3-n}M$ M = P, As, Sb, n = 2 or 3, or at -60°C in $(C_6F_5)Ph_2M$ M = As, Sb. If there is non-rotation of the penta-fluorophenyl groups in bis- or tris- pentafluorophenyl compounds and further if the broadening the the meta resonance is diagnostic of this, then the free energy of activation associated with the barrier of rotation must increase sharply in going from $(C_6F_5)Ph_2M$

to $(C_6F_5)_2PhM$ M = As, Sb.

In the compound shown below (X = H) the <u>meta</u> resonance

of the C_6F_5 rings is resolvable although molecular models

indicate that the steric hindrance of the <u>ortho</u> fluorines in

the C_6F_5 rings is greater than in $(C_6F_5)_3P$. However when

X = Br the <u>meta</u> resonance is broadened.
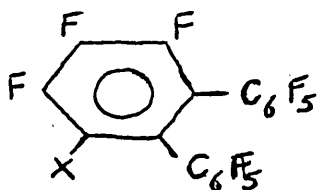
No definite decision between explanations based on steric

hindrance or on the small value of J_{35} can be reached at the

present moment.

<u>Low temperature n.m.r. studies on metal complexes.</u>

On cooling a chloroform solution of $[(C_6F_5)_3P]_2PtI_2$ to 20°C

the very broad <u>ortho</u> signal observed in the room temperature spectrum

splits into three nearly equally spaced sharp lines of equal intensity.

The <u>para</u> signal splits into two lines with an intensity ratio of 2:1.

The <u>meta</u> signal also changes but the splitting appears to be smaller

and obscured by the complex nature of the peak. In the corresponding

bromide and chloride complexes a similar effect is observed on cooling
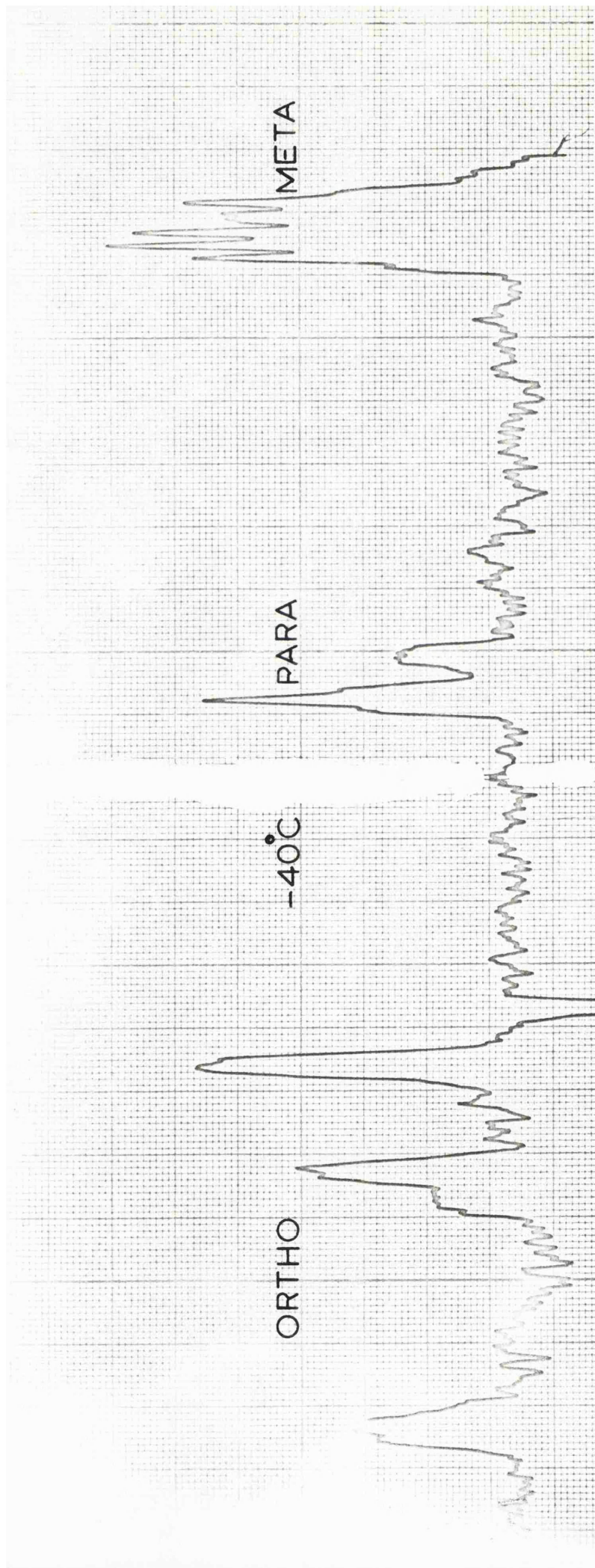
Low temperature ^{19}F n.m.r. of trans $[(C_6F_5)_3P]_2PtBr_2$ Figure 2.5.
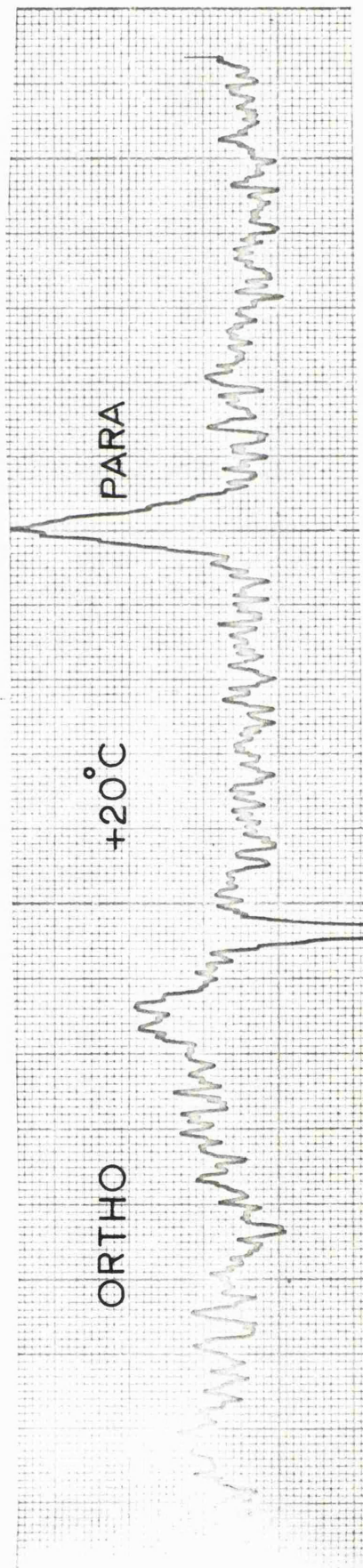
but the three <u>ortho</u> signals are not equally spaced although they
are still of equal intensity. Typical spectra are shown to
illustrate this effect. Fig. 2·5.

The broadening and merging of the lines and subsequent
sharpening as the temperature is raised indicates that an exchange
process whose rate increases with temperature is responsible for
the coalescence. The separation of the <u>ortho</u> resonances is large
($\sim$500 c./sec.) compared with any coupling constant in the system.

An exchange process based on <u>cis</u> – <u>trans</u> isomerisation of
the complexes can be eliminated since infrared spectra in chloroform
solution are identical to the mull spectra in the 400–200 cm^{-1} range.
This indicates that the complexes are <u>trans</u> in solution.

Dissociation of the complexes leading to an equilibrium mixture
of the three species shown below would yield three separate <u>ortho</u>
resonances when the rate of interconversion is slow.
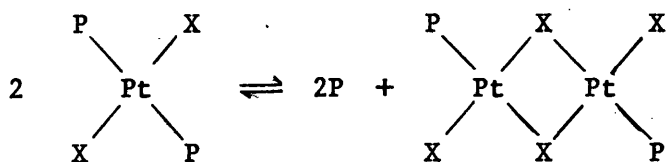
The molecular weights determined osmometrically (Chapter 1) in
chloroform solution show that no dissociation occurs at room
temperature.

These observations may be interpreted as follows. When the

Figure 2·6
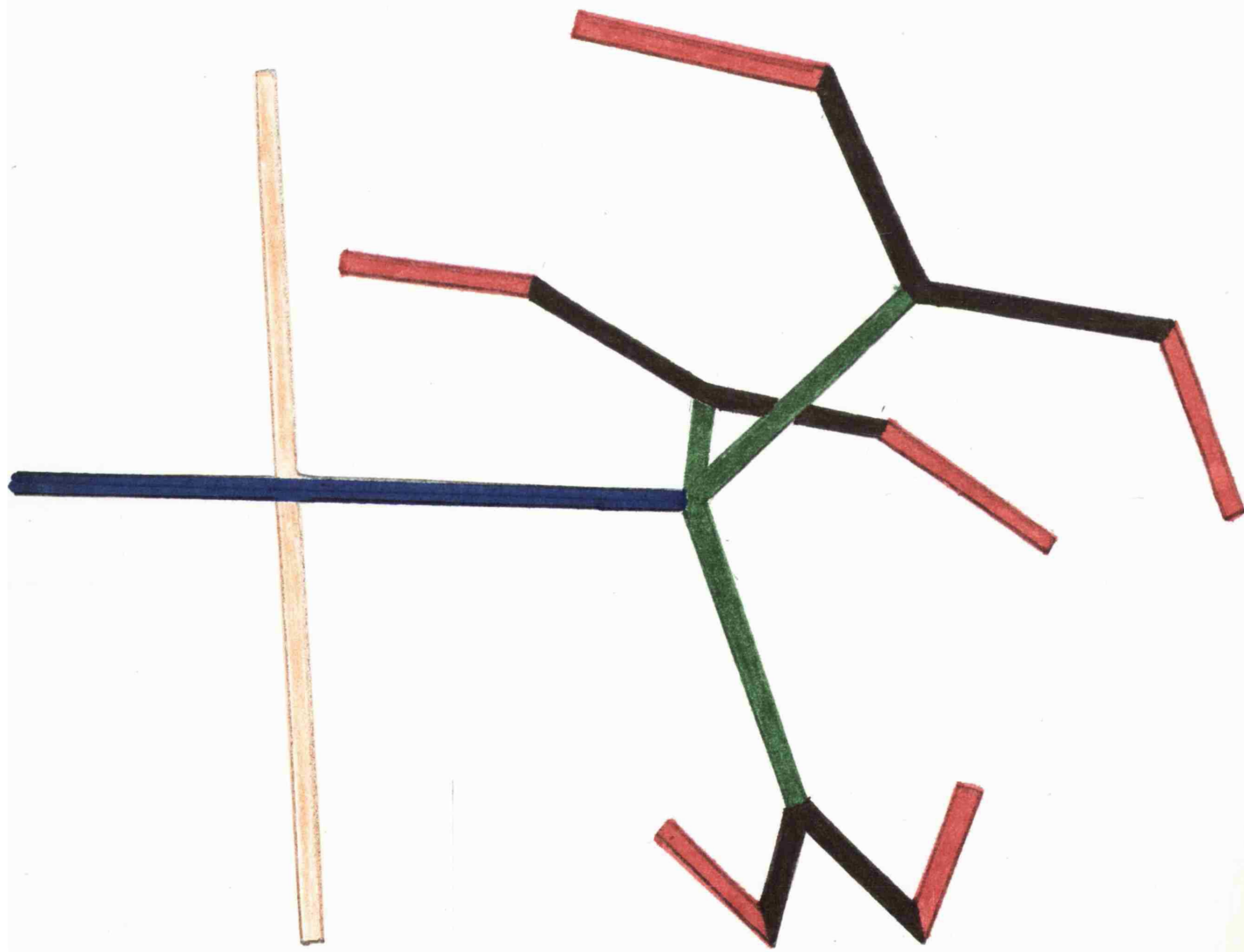
KEY

Pt—Br Orange.

Pt—P Blue.

P—C Green.

C—C Black.

C—F Red.

C_6F_5 rings rotate and the phosphine also rotates about the

platinum-phosphorus bond there is equivalence of all six ortho

fluorine atoms. If the rings and the phosphine are both stationary

then the ortho fluorine atoms become non-equivalent as do the meta

and para fluorine atoms. The number of resonances observed for the

ortho fluorines will be determined by the conformation that the

phosphine adopts when stationary. A tentative structure which

explains the three signals observed is shown in Fig. 2·6.

The two signals of the para fluorine resonance observed at low temperatures

are separated by about 100 c./sec. It seems unlikely that this is a

reflection of different environment since they are well removed from

the metal halogen moiety. A possible explanation is that the chemical

shift of the para fluorines depends to some extent on the chemical

shift of the ortho fluorines so that the non-equivalence of the ortho

fluorines results in non-equivalence of the para fluorines.

Inspection of Fig. 2·6 shows that two of the rings are equivalent

while the third is different. This would lead to two para signals of

intensity ratio 2:1 as is observed.

The coalescent temperatures of the para fluorine signals increase

on going from the chloride to the iodide complex. Molecular models

indicate ortho fluorine steric interactions with the halogen atom

which increase as the size of the halogen atom increases.

The X-ray crystal structures of metal complexes containing Ph_3P as a ligand show that there is no fixed orientation taken up by the phenyl rings. In $(Ph_3P)Mn(CO)_4SnPh_3$[27] the conformation of the phosphine resembles the tentative structure proposed here on the basis of the n.m.r. for $[(C_6F_5)_3P]_2PtX_2$. In $(Ph_3P)_2CuBH_4$[93] and $(Ph_3P)_2Mn(CO)_2NO$[94] however an almost propellor conformation is adopted. The number of lines observed for the _ortho_ fluorines at low temperatures does not necessarily indicate the conformation of the coordinated phosphine, since accidental chemical shift equivalence may be present; nor does it resolve the question of rotation or non-rotation of the pentafluorophenyl rings at higher temperatures, since a rigid conformation with accidental chemical shift equivalence may lead to exchange of sites by rotation about the phosphorus-platinum bond only.

CHAPTER THREE

Felix qui potuit rerum cognoscere causas.

Vergil. Georgics, II, 490.

It has been found previously that carbonyl complexes[95] or
carbon monoxide[96] have been formed in reactions with C_2F_4.
Treatment of $(PEt_3)_2PtHCl$ with C_2F_4 gave a complex initially
formulated as $(PEt_3)_2PtHCl(C_2F_4)$[97] but now known to contain the
$(PEt_3)_2PtCOCl^+$ cation.[95]

Reaction of C_2F_4 with $[(C_6F_5)_3P]_4Rh_2Cl_2$ in a Carius tube at
120° gives the carbonyl complex $[(C_6F_5)_3P]_2RhCOCl$.[98] This reaction
has been extended to other olefins to ascertain the scope and to
elucidate the mechanism. Only fluoroolefins give good yields of the
carbonyl complexes. The chloroolefins C_2Cl_4, C_2HCl_3, C_2H_3Cl give
other products but traces of carbonyl containing species are present.

A few general observations may be made before turning to a
detailed study of possible mechanisms and the compounds isolated.
The production of carbonyl complexes is not limited to the use of
terminal fluoro-olefins since perfluorocyclobutene and $CF_3CF=CFCF_3$
give carbonyl complexes. Although no olefin complexes can be
obtained using the compound $[(C_6F_5)_3P]_4Rh_2Cl_2$ it yields the carbonyl
complex $[(C_6F_5)_3P]_2RhCOCl$ with the cyclic olefins whereas the complex
$(Ph_3P)_3RhCl$ fails to react. The increased reactivity may be a
result of the lower electron density on the rhodium atom since
$(C_6F_5)_3P$ is a weaker ligand than Ph_3P.

After a period of three months at room temperature the complex
$(Ph_3P)_2Rh(C_2F_4)Cl$[99] formed from C_2F_4 and $(Ph_3P)_3RhCl$ in a Carius tube

is uncontaminated with the carbonyl complex. However $[(C_6F_5)_3P]_4Rh_2Cl_2$

had only partially reacted with C_2F_4 after a similar period and

gives exclusively the carbonyl complex $[(C_6F_5)_3P]_2RhCOCl$. If a

C_2F_4 complex is an intermediate in the production of the carbonyl

complexes then the replacement of Ph_3P by $(C_6F_5)_3P$ results in an

increased rate of hydrolysis.

C_2F_4 reacts at room temperature with $[(C_6F_5)Ph_2P]_4Rh_2Cl_2$ to

yield $[(C_6F_5)Ph_2P]_2Rh(C_2F_4)Cl$, and C_2F_3Br reacts with $(Ph_3P)_3RhCl$

to yield $(Ph_3P)_2Rh(C_2F_3Br)Cl$. The similarity of the ^{19}F chemical

shifts (Table 3·1) to those reported for the fluorocarbon moiety

in the complexes $(Ph_3P)_2Rh(C_2F_3X)Cl$[99] X = F,Cl. indicates that the

mode of bonding is the same in all these complexes.

Table 3·1

^{19}F n.m.r. chemical shifts upfield from benzotrifluoride (internal

reference) in p.p.m. Coupling constants in c./sec. The operating

frequency of the DA60 is also shown.

	C_2F_4	ortho	para	meta
$[(C_6F_5)Ph_2P]_2Rh(C_2F_4)Cl$	19.3 Mc./sec.	36.4	60.0	85.0	97.5
$J_{F,P}$ 27.0;	$J_{F,Rh}$ ~ 7.0			
$(Ph_3P)_2Rh(C_2F_3Br)Cl$	56.4 Mc./sec.	Complex peak centred at 24.4.		

The ^{19}F n.m.r. spectrum of $[(C_6F_5)Ph_2P]_2Rh(C_2F_4)Cl$ consists of

a triplet of doublets assigned to the C_2F_4 group. This suggests

that the phosphines are magnetically equivalent and therefore the

complex is _trans_ in configuration.

Carbon monoxide is known to displace C_2F_4 from the complex

$(Ph_3P)_2Rh(C_2F_4)Cl$ [99] and to react with $(Ph_3P)_3RhCl$ or $[(C_6F_5)_nPh_{3-n}P]_4Rh_2Cl_2$

n = 1, 2 and 3 producing the carbonyl complexes. Thus a possible

mechanism for their formation would be hydrolysis of C_2F_4 to CO and HF

and subsequent attack of CO on the metal complex. The HF produced

will attack the glass tube and yield SiF_4 and more water, so that only

small amounts of water are initially needed. However, when a mixture

of C_2F_4, benzene, water, and glass chips is subjected to the conditions

used in the other reactions infrared spectroscopy of the gases showed

the presence of C_2F_4, $CF_3CF=CF_2$ (present initially), and some

perfluorocyclobutane, but no carbon monoxide was detected.

That an olefin complex is an intermediate and that subsequent

hydrolysis occurs in the production of carbonyl complexes, is shown

by the following experiments.

On heating C_2F_3Cl with $(Ph_3P)_3RhCl$ at 120° in a Carius tube for

only 30 minutes, pure $(Ph_3P)_2Rh(C_2F_3Cl)Cl$ [99] is isolated but the

carbonyl is formed after 12 hours heating. Subsequent hydrolysis of this

complex at 120° in a steel bomb produced pure $(Ph_3P)_2RhCOCl$. Also

if the reaction of C_2F_4 with $(Ph_3P)_3RhCl$ is done under anhydrous

Diagram 3·1.

A

$$P_2Rh(Cl)(CF_2CF_2) \xrightarrow{\ H_2O\ } P_2RhCl + [CHF_2CF_2OH]$$

$$[CHF_2CF_2OH] \longrightarrow CHF_2COF + HF$$

CHF₂COF   P₂RhCl
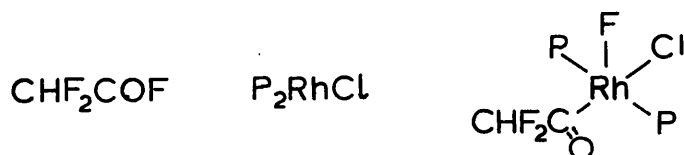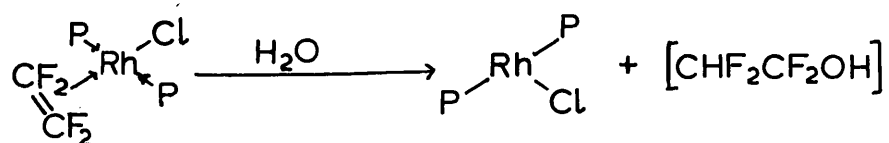
B

C
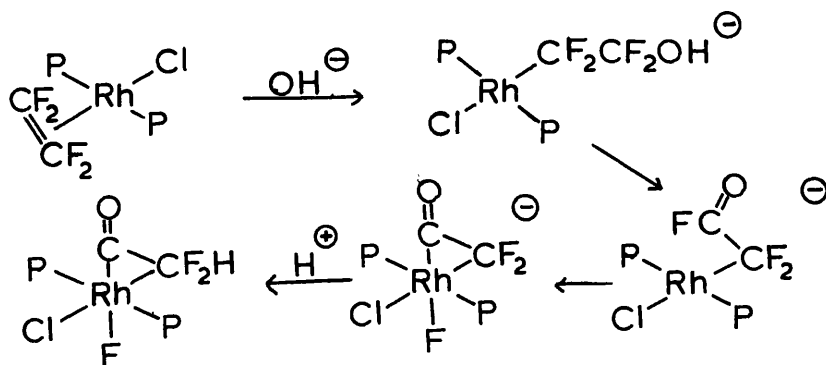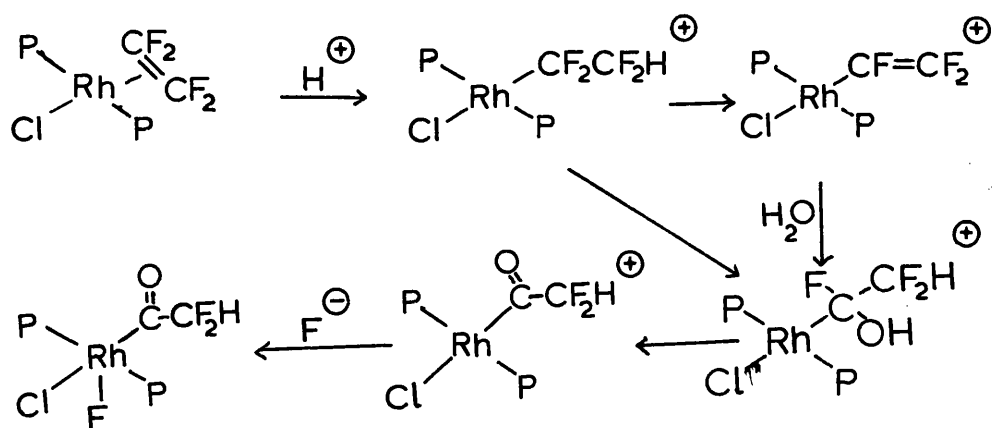
conditions in a Carius tube the olefin complex is formed in high

yield whereas the use of ordinary benzene results in the exclusive

production of the carbonyl complex.

For the mechanism of hydrolysis there are several possibilities.

These are shown in Diagram 3·1 and for convenience C_2F_4 is used

as the olefin.

In mechanism $\underline{A}$ the metal may assist the attack of water on the

coordinated olefin by the transient formation of a six coordinate

hydrido-hydroxo complex. The acyl fluoride produced would attack

the rhodium moiety and the subsequent rearrangement of the rhodium III

acyl complex follows the mechanism proposed by Wilkinson[100] for the

decarbonylation of acyl chlorides. That acyl fluorides can be

decarbonylated is shown by the production of the carbonyl complex

when CH_3COF is used.

Mechanism $\underline{B}$ resembles that proposed for the Wacker reaction.[101]

However the σ bonded fluoroalcohol complex dehydrofluorinates instead

of being eliminated as a carbonium ion.

Mechanism $\underline{C}$ involves initial protonation to yield a

tetrafluoroethyl group. Then displacement of a fluoride ion by a

hydroxide ion or hydration of a vinyl intermediate gives the acyl

complex. The formation of a perfluoro vinyl directly from the olefin

complex is unlikely since the olefin complex in dry solvents remains

unchanged under the conditions of the reaction.

Fluoro-olefins generally resist attack by electrophilic reagents since the strongly electron-withdrawing fluorine atoms reduce the electron density at the olefinic carbon atoms, and nucleophilic attack is the normal mode of reaction. However, on coordination to a metal capable of back donation the anti-bonding orbitals of the olefin become populated and provide a possible centre for electrophilic attack. Protonation of the C_2F_4 moiety would be enhanced by coordination.

Clark[102] in a study of the production of $(PEt_3)_2PtCOCl^+$ from the action of C_2F_4 on $(PEt_3)_2PtHCl$ suggests Mechanism C with the intermediate vinyl for the reaction. In support of Mechanism C the hydrolysis of $(Ph_3P)_2Rh(C_2F_4H)Cl_2$ in the presence of glass gives a quantitative yield of $(Ph_3P)_2RhCOCl$ but in the absence of glass only traces are formed. The role of the glass may be to produce SiF_4, since Clark found that only when this was present would the tetrafluoroethyl complex $(PEt_3)_2PtCl(C_2F_4H)$ dehydro-fluorinate to the vinyl and then add water to yield the acyl. While this may be the course of the reaction in a Carius tube another mechanism must be followed in the steel bomb hydrolyses of complexes $(Ph_3P)_2Rh(C_2F_3X)$ X = F, Cl, Br.

If mechanism A was followed by non-terminal olefins then fluoro-ketones would be produced. Hexafluoroacetone fails to yield carbonyl complexes with $[(C_6F_5)_3P]_4Rh_2Cl_2$ or $(Ph_3P)_3RhCl$ and this suggests that these complexes are not capable of decarbonylating

Diagram 3·2.

CHF₃ +
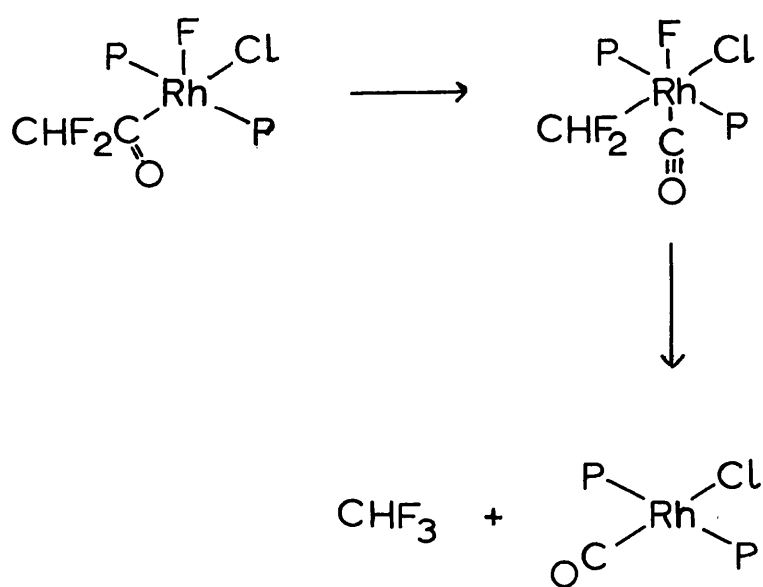
ketones. In mechanism B the ketone remains bonded to the metal

and may be sufficiently activated for decarbonylation to proceed.

All the mechanisms end with the acyl complex $P_2Rh(COCHF_2)FCl$.

Wilkinson[100] has proposed a mechanism for the decarbonylation of

acyl to chlorides in which an acyl complex is an intermediate

(see Diagram 3·2). If the above acyl complex follows this breakdown

pattern then CHF_3 would be expected to be the gaseous product on

hydrolysis of the complex $(Ph_3P)_2Rh(C_2F_4)Cl$. However, large

quantities of CH_2F_2 and CH_4 are detected. In the case of

the complexes $(Ph_3P)_2Rh(C_2F_3X)Cl$ X = Cl, Br. no chlorine or bromine

containing gases were detected. The observation of CH_2F_2 indicates

that a different mechanism must be followed in the presence of water.

In support of this $(Ph_3P)_2Rh(CO)Cl_2Me$ yields methyl chloride[100]

but at 120° in wet benzene only methane could be detected. The

chlorine appears as chloride ions in the aqueous layer.

The complex nature of the gaseous products indicates considerable

secondary reaction. It is not possible on the basis of the

experiments done so far to decide on the mechanism for the conversion

of C_2F_4 into carbonyl complexes.

91a

Table 3·2

Olefin	Complex	Solvent	Temperature	Time	Product
C_2F_4	$[(C_6F_5)_3P]_4Rh_2Cl_2$	C_6H_6	R.T.	3 months	$[(C_6F_5)_3P]_2RhCOCl$
C_2F_4	$[(C_6F_5)Ph_2P]_4Rh_2Cl_2$	$CHCl_3$	R.T.	6 days	$[(C_6F_5)Ph_2P]_2Rh(C_2F_4)Cl$
C_2F_4	$[(C_6F_5)_3P]_4Rh_2Cl_2$	C_6H_6	120°	12 h.	$[(C_6F_5)_3P]_2RhCOCl$
C_2F_4	$[(C_6F_5)_2PhP]_4Rh_2Cl_2$	C_6H_6	120°	12 h.	$[(C_6F_5)_2PhP]_2RhCOCl$
C_2F_4	$[(C_6F_5)Ph_2P]_4Rh_2Cl_2$	C_6H_6	120°	12 h.	$[(C_6F_5)Ph_2P]_2RhCOCl$
C_2F_4	$(Ph_3P)_3RhCl$	C_6H_6	120°	12 h.	$(Ph_3P)_2RhCOCl$
C_2F_4	$(Ph_3P)_3RhCl$	C_6H_6	R.T.	3 months	$(Ph_3P)_2Rh(C_2F_4)Cl$
C_2F_3Cl	$(Ph_3P)_3RhCl$	C_6H_6	120°	12 h.	$(Ph_3P)_2RhCOCl$
C_2F_3Cl	$[(C_6F_5)_3P]_4Rh_2Cl_2$	C_6H_6	120°	12 h.	$[(C_6F_5)_3P]_2RhCOCl$
C_2F_3Br	$(Ph_3P)_3RhCl$	$CHCl_3$	R.T.	2 days	$(Ph_3P)_2Rh(C_2F_3Br)Cl$
CF_2CH_2	$(Ph_3P)_3RhCl$	$CHCl_3$	R.T.	1 month	No reaction.
CF_2CH_2	$(Ph_3P)_3RhCl$	C_6H_6	120°	12 h.	$(Ph_3P)_4Rh_2Cl_2$ and $(Ph_3P)_2RhCOCl$

C$_2$H$_3$Cl	(Ph$_3$P)$_3$RhCl	CHCl$_3$	R.T.	3 weeks	No reaction
C$_2$HCl$_3$	"	"	"	"	"
C$_2$Cl$_4$	"	"	"	"	"
CF$_3$CFCF$_2$	"	"	"	"	"
CF$_3$CFCF$_2$	(Ph$_3$P)$_3$RhCl	C$_6$H$_6$	120°	12 h.	(Ph$_3$P)$_4$Rh$_2$Cl$_2$
CF$_3$CFCF$_2$	[(C$_6$F$_5$)$_3$P]$_4$Rh$_2$Cl$_2$	C$_6$H$_6$	120°	12 h.	[(C$_6$F$_5$)$_3$P]$_2$RhCOCl
CF$_2$CH$_2$	"	"	"	"	"
C$_6$F$_{10}$	(Ph$_3$P)$_3$RhCl	C$_6$H$_6$	R.T.	2 weeks	(Ph$_3$P)$_4$Rh$_2$Cl$_2$
C$_6$F$_{10}$	(Ph$_3$P)$_3$RhCl	C$_6$H$_6$	120°	12 h.	(Ph$_3$P)$_4$Rh$_2$Cl$_2$
C$_6$F$_{10}$	(Ph$_3$P)$_2$Rh(C$_2$H$_4$)Cl	C$_6$H$_6$	R.T.	1 week	No reaction
C$_4$F$_6$	[(C$_6$F$_5$)$_3$P]$_4$Rh$_2$Cl$_2$	CH$_2$Cl$_2$	R.T.	2 months	[(C$_6$F$_5$)$_3$P]$_2$RhCOCl
C$_4$F$_8$	"	C$_6$H$_6$	120°	12 h.	"
C$_4$F$_8$	(Ph$_3$P)$_3$RhCl	C$_6$H$_6$	120°	12 h.	(Ph$_3$P)$_2$RhCOCl
					+ (Ph$_3$P)$_4$Rh$_2$Cl$_2$

The chlorotrifluoroethylene, bromotrifluoroethylene,
1,1 difluoroethylene, hexafluoropropene, hexafluorocyclobutene,
decafluorocyclohexene, hexafluoroacetone, and vinyl chloride used
were the commercially available products and used without further
purification. Tetrachloroethylene and trichloroethylene were
distilled before use. Tetrafluoroethylene was generated by vacuum
pyrolysis of Fluon powder (I.C.I.) and partially purified by
trap to trap distillation. An infrared spectrum of the vapour showed that
small amounts of perfluoropropene were also present. $CF_3CF=CFCF_3$
was made from $CF_3CFClCFClCF_3$ by the literature method.[103]

^{19}F n.m.r. spectra were obtained on a Varian Associates DA-60 machine.
The infrared spectra were taken on Unicam SP200 or Perkin-Elmer 225
models. A Mechrolab vapour pressure osmometer was used for the
determination of molecular weights in chloroform solution. The
mass spectra of gases were done by Mr. Jones of this department on
an A.E.I. MS 9 mass spectrograph. Microanalyses were performed by
Beller, Gottingen, W. Germany. Melting points were taken on a
Reichert hot-stage microscope and are uncorrected. Normal reagent
grade solvents were used except where stated.

(p.91a)
Table 3.2 shows some of the reactions of the several olefins
with the rhodium complexes. The reactions of ethylene with rhodium
complexes are not presented here as it is felt that the trace amounts
of carbonyl complexes obtained may be formed from the impurities
present in commercial ethylene.

A typical experiment is described to indicate the general

procedure.

C_2F_4 and $(Ph_3P)_3RhCl$

0.5 g. of the rhodium complex was placed in a dry Carius tube

and 10 ml. benzene added. It was immediately connected to the

vacuum line and cooled with a liquid nitrogen bath. About 2-3 ml.

of C_2F_4 were distilled in, and the tube then sealed. The sealed

tube was heated at 120°C for 12 hours, cooled and opened. On warming

to room temperature the orange yellow solution was evaporated to

dryness. The yellow solid left was recrystallised from chloroform -

alcohol and identified as $(Ph_3P)_2RhCOCl$ by an infrared spectrum and

a melting point.

The other experiments which do not appear in Table 3·2 will now

be described.

a)   3 ml. C_2F_4 was heated with 5 g. powdered glass, 1 ml. water

and 10 ml. benzene for 24 hours at 120°C in a metal bomb. The

infrared spectrum of the gas in the bomb after this treatment showed

the presence of C_2F_4 and small amounts of CF_3CFCF_2, and

perfluorocyclobutane only.

b)   2-3 ml. C_2F_4 were reacted with 0.5 g. $(Ph_3P)_3RhCl$ and 10 ml.

benzene in a Carius tube at 120°C for 16 hours. All the reagents were

vigorously dried. The products were identified by infrared spectroscopy

as $(Ph_3P)_2Rh(C_2F_4)Cl$ and a very small amount of $(Ph_3P)_2RhCOCl$.

c)   2-3 ml. of C_2F_3Cl was distilled onto 0.5 g. $(Ph_3P)_3RhCl$ in

10 ml. ordinary benzene in a Carius tube. The tube was sealed and

heated at 120°C for 30 mins. The red-orange solution was evaporated

to dryness and the solid recrystallised from chloroform – alcohol

to yield pure $(Ph_3P)_2Rh(C_2F_3Cl)Cl$ as shown by infrared spectroscopy.

d)   2-3 mls. of C_2F_4 was distilled onto 0.5 g. $(Ph_3P)_3RhCl$ in

10 ml. benzene containing a few drops of water in a steel bomb.

This was heated at 120°C for 12 hrs. The yellow solution was

evaporated to dryness and the residue shown to be $(Ph_3P)_2RhCOCl$ by

an infrared spectrum. It was recrystallised from chloroform – alcohol

to yield yellow crystals m.p. 190-197° (Lit.[56] 195-200°).

e) $[(C_6F_5)Ph_2P]_4Rh_2Cl_2$ and C_2F_4.

The reaction conditions are shown in Table 3·2. After reaction

the contents of the Carius tube were evaporated to dryness. The

light yellow residue was recrystallised from chloroform – alcohol at

-30°C to yield very pale yellow crystals. m.p. 170-175°C (dec).

Analysis: Found, C, 47.2; H, 2.18. M, 910. $C_{38}H_{20}F_{14}ClP_2Rh$ requires

C, 48.4; H, 2.14%. M. 942. The compound showed strong bands in the

infrared spectrum at 1115, 1096, 1040, 1025, and 900 cm^{-1} in addition

to peaks due to pentafluorophenyldiphenylphosphine.

f) $(Ph_3P)_3RhCl$ and C_2F_3Br

See Table 3.2 for reaction conditions. The work-up follows

Expt. e). The product was recrystallised from chloroform-ether at

-30°C to yield lemon yellow crystals. m.p. 151-157°C (dec).

Analysis: Found, C, 55.3; H, 3.6; F, 6.5; Br, 9.8%. M. 807.

$C_{38}H_{30}BrClF_3P_2Rh$ requires C, 55.4; H, 3.6; F, 6.9; Br, 9.7%. M. 823.

The compound showed strong bands in the infrared spectrum at

1160(doublet), 1135, 1052, and 790 cm^{-1} in addition to bands due to

triphenylphosphine.

g) C_2F_3Br and $(Ph_3P)_3RhCl$

After heating for 12 h. at 120°C, the contents of the tube

were filtered. The black residue has a weak peak at 2100 cm^{-1} in

the infrared spectrum. The brownish filtrate was evaporated to

dryness and the infrared spectrum of the solid left showed a weak

peak at 2095 cm^{-1} and strong bands in the carbon-fluorine stretching

frequency region.

h) C_2F_3Br and $[(C_6F_5)_3P]_4Rh_2Cl_2$

After heating for 12 h. at 120°C, the contents of the tube were

evaporated to dryness. An infrared spectrum of the dark brown solid

indicated the presence of $[(C_6F_5)_3P]_2RhCOCl$ and another possibly

carbonyl containing species which showed an infrared peak at 2100 cm^{-1}.

The former compound was isolated by extraction of the crude product

with hot benzene. The yellow benzene solution was filtered and

reduced in volume. Addition of alcohol produced yellow crystals

of $[(C_6F_5)_3P]_2RhCOCl$ identified by their m.p.

i) C_4F_6 and $(Ph_3P)_3RhCl$.

After heating at 120°C for 12 h., the contents of the tube

were evaporated to dryness. An infrared spectrum of the residue

indicated that only a trace of a carbonyl containing species

(probably $(Ph_3P)_2RhCOCl$) was presant. Strong bands were observed

at 1760, 1200 – 1000 cm^{-1}.

j) C_4F_6 and $[(C_6F_5)_3P]_4Rh_2Cl_2$.

After heating at 120°C for 24 h. the contents of the tube were

filtered. The black residue was extracted with hot benzene and

filtered again. This residue was insoluble in all solvents and

exhibited no phosphine or carbonyl bands in the infrared. The

yellow solid obtained from evaporating the combined filtrates was

identfied as $[(C_6F_5)_3P]_2RhCOCl$ by infrared spectroscopy and m.p.

k) C_2Cl_4 and $[(C_6F_5)_3P]_4Rh_2Cl_2$.

After heating for 24 h. at 120°C with wet benzene, the contents

of the tube were a black precipitate and a colourless solution.

The black precipitate showed no phosphine or carbonyl bands in the

infrared spectrum. The colourless solution was evaporated to dryness

and the white residue identified as $(C_6F_5)_3P$ by m.p. and infrared

spectroscopy.

1)   Chloroolefins and $(Ph_3P)_3RhCl$.

These were reacted for 12 h. at 120°C in Carius tubes with wet benzene. The contents of the tubes were evaporated to dryness and infrared spectra taken.

C_2Cl_4 weak peaks at 2090, 2050, and 1975 cm^{-1}

C_2HCl_3 "

C_2H_3Cl No peaks   2100 - 1950 cm^{-1}

The brown-yellow solid products were not investigated further.

m) $(Ph3P)3RhCl$ and water.

0.5 g. of the complex was heated for 12 h. at 120°C with 10 ml. benzene and 1 ml. water. Red crystals and a very pale solution was formed. The crystals were filtered off and identified as $(Ph_3P)_4Rh_2Cl_2$ and the solution contained Ph_3P only.

n) CH_3COF and $(Ph_3P)_3RhCl$

0.5 g. of the complex was placed in a Carius tube with 10 ml. of sodium dried benzene. 2 ml. CH_3COF[104] were distilled in under vacuum and the tube heated at 120°C for 12 h. The gaseous products were analysed by infrared spectroscopy. The yellow solution left was evaporated to dryness, and the residue crystallised from chloroform - alcohol, and identified as $(Ph_3P)_2RhCOCl$. The yield was nearly quantitative.

o)   Hexafluoroacetone and $(Ph_3P)_3RhCl$.

2-3 ml. CF_3COCF_3 was distilled into a Carius tube containing

0.5 g. of the complex and 10 ml. benzene. The tube was heated for

12 h. at 120°C. Red crystals of $(Ph_3P)_4Rh_2Cl_2$ (which were filtered

off) and a non-carbonyl containing solid (obtained by evaporation

of the filtrate) were the products as shown by infrared spectroscopy.

p)   Hexafluroacetone and $[(C_6F_5)_3P]_4Rh_2Cl_2$.

As for $(Ph_3P)_3RhCl$, very little reaction took place. A trace

of benzene soluble product was observed.

q)   3.0 g. of $(Ph_3P)_2Rh(C_2F_4)Cl$ were placed in a steel bomb with

10 ml. benzene and 1 ml. water. The bomb was heated for 12 h. at

120°C and then cooled to -78°C. The gaseous products were analysed

by infrared and mass spectroscopy. The bomb was then allowed to warm

up further and further spectra taken. The contents of the bomb were

washed out with benzene into a separating funnel and shaken with water.

Qualitative chemical tests on the aqueous layer indicated the presence

of nickel ions and the absence of chloride ions. The benzene layer

was evaporated to dryness and the yellow solid recrystallised from

chloroform - alcohol. The yellow crystals were identified by infrared

spectroscopy and m.p. as $(Ph_3P)_2RhCOCl$. Other dark brown products

were present in low yield but not identified.

r) The procedure was the same as Expt. p) using $(Ph_3P)_2Rh(C_2F_3Cl)Cl$.

The benzene layer contained exclusively $(Ph_3P)_2RhCOCl$, and the aqueous layer contained nickel and chloride ions.

s) The procedure was the same as Expt. p) using $(Ph_3P)_2Rh(C_2F_3Br)Cl$.

The benzene layer contained mainly $(Ph_3P)_2RhCOCl$, but some dark coloured products were also formed. The aqueous layer contained bromide and nickel ions. A test for chloride in the presence of bromide was negative.

t) $(Ph_3P)_2Rh(CO)Cl_2Me$ was made from $(Ph_3P)_3RhCl$ and CH_3COCl as described in the literature.[100] 1 g. of the products was placed in a steel bomb together with 10 ml. benzene and 0.5 ml. water. After heating for 12 hr. at 120° the only gaseous product was shown by infrared spectroscopy to be methane. No methyl chloride could be detected. The yellow benzene solution in the bomb was evaporated to dryness and shown to be pure $(Ph_3P)_2RhCOCl$ by an infrared spectrum and a m.p. The aqueous layer gave positive tests for nickel and chloride ions.

u) 1.5 g. $(Ph_3P)_2Rh(C_2F_4H)Cl_2$[100] was placed in a steel bomb together with 20 ml. benzene, 1 ml. water, and 5 g. of powdered glass. The bomb was heated for 12 hr. at 120°. The products gaseous at -78° were analysed by infrared spectroscopy. The yellow benzene solution was evaporated to dryness and the residue was pure $(Ph_3P)_2RhCOCl$ as shown by an infrared spectrum and a m.p.

v)   The above experiment (u) was repeated using no glass.

The gases were again analysed. / The dark brown benzene solution

was evaporated to dryness, and an infrared spectrum showed no band

in the region 2100 - 1800 cm^{-1}, but strong bands in the region

1250 - 1000 cm^{-1}.   No pure compounds could be isolated.

Table 3·3

MASS SPECTRA

The main values of e/m are given together with their probable
assignment.   Mass range 16–200.

105

A)   –25°C fraction of the gas from Expt q).

m/e		m/e		m/e		m/e	
16	CH_4	29	C_2H_5?	34	CH_3F	65	$C_2H_3F_2$
18	H_2O	30	C_2H_6?	44vvs	CO_2C_2HF	78	C_6H_6?
26	C_2H_2	31w	CF	45w	C_2H_2F	83w	$C_2H_2F_3$
27	C_2H_3	32	O_2,CHF	47	C_2H_4F,COF	84w	$C_2H_3F_3$
28s	N_2,C_2H_4,CO	33	CH_2F	51vs	CHF_2		

B)   –78°C fraction of the gas from Expt q).

m/e		m/e		m/e		m/e	
16	CH_4	29	C_2H_5?	47s	C_2H_4F,COF	83w	$C_2F_3H_2$
18	H_2O	30	C_2H_6?	51s	CHF_2	84w	$C_2F_3H_3$
		31w	CF				
26	C_2H_2	32	O_2,CHF	65s	$C_2H_3F_2$	95w	C_6H_4F?
27	C_2H_3	44ws	CO_2,C_2HF	69s	CF_3	96w	C_6H_5F?
				76(metastable)	C_6H_6		
28vs	$N_2C_2H_4,CO$	45	C_2H_2F	78s	C_6H_6?	101w	C_2F_4H
						102w	$C_2F_4H_2$

/continued.

Table 3·3 /continued.

C)   -78°C fraction from Expt r).

16	CH_4	29	C_2H_5?	34	CH_3F	51s	CHF_2
18	OH_2	30	C_2H_6?	44vs	CO_2,C_2HF	52	CH_2F_2
26	C_2H_2	31	CF	45	C_2H_2F	63	C_2F_2H
27	C_2H_3	32s	CHF	46w	C_2H_3F	64	$C_2H_2F_2$
28vs	N_2,C_2H_9	33s	CH_2F	50	CF_2	82	C_2F_3H

D)   -25° fraction

As for C) with a peak at 78 (C_6H_6) in addition.

E)   Gaseous products (0°C) from reaction of CH_2CF_2 with

[$(C_6F_5)_3P]_4Rh_2Cl_2$ at 120°C (See table 3·1).

Only peaks due to CH_2CF_2 and SiF_4 were observed.

Table 3·4

Infrared spectra of gaseous products. Pressure 2-5 cms Hg
in a 10 cm. cell fitted with potassium bromide windows.
The probable assignments are also given. ^{105} ^{106} ^{107}

For CF_3H read HCF_2CF_2H in all the following.

1)   -78°C fraction from Expt q).

Intensity	Band	Assignment
S	Complex pattern 3150-2850 Sharp peak at 3020	CH_4, CF_2H_2, CF_3H
w(br)	2330	?
w	1730	CF_2CH_2
s	Complex pattern 1360-1280 Sharp peak at 1304	CH_4, CF_2CH_2
w	1206	CF_3H
vs	1140	CF_3H ?
s	1100	CF_2H_2
s	1088	CF_2H_2
w	800	CF_2CH_2

2)   0°C fraction from Expt q). The peaks due to benzene
     have been left out.

Intensity	Band	Assignment
s	2990	CF_2H_2, CF_3H
w	1380	CF_3H
s	1310(triplet)	?
w	1206	CF_3H ?

Table 3·4 /continued

2)

Intensity	Band	Assignment
vs	1138	CF_3H ?
w	1100,1088	CF_2H_2
m	904(doublet	?
ms	770	?

3) -78°C fraction of gas from Expt r). Run on a Unicam SP.200
Estimated accuracy ± 5 cm^{-1}.

Itensity	Band	Assignment
s(br)	3000	CH_4,CH_2F_2 etc
w	1770	CF_2CFH
m	1720	CF_2CH_2
m	1365	CF_2CFH
m	1350	CF_2CFH
s	1300	CF_2CH_2,CH_4
s	1270,1255	CF_2CFH
m	1160	?
m	1140	CF_3H ?
s	1100,1085	CF_2H_2
m	1045	CH_3F
s(br)	930	CF_2CH_2,CF_2CHF
m	800	CF_2CH_2

The infrared spectrum of the

-25°C fraction was identical

Table 3·4   /continued

4)   Gaseous products from Expt. n).

Intensity	Band	Assignment
m	Complex peak and sharp peak at 3020	CH_4, CH_3COF.
w(br)	1880	?
m	1832(doublet	CH_3COF [a]
m	1305 and complex structure	CH_4
m(br)	1200–1180	CH_3COF [a]
vs	1028	SiF_4
m	828(triplet)	CH_3COF [a]

[a] B. P. Susz and J. J. Wuhrmann, Helv. Chim. Acta., 1957, 40, 722.

5)   −78°C fraction of gas from Expt. s)

Intensity	Band	Assignment
s	Complex 3150–2850 Sharp peak at 3020	CH_4 ,CH_2F_2,CH_3F.
m	1430	CH_2F_2
m	Complex and sharp peak at 1304	CH_4
w	1175	CH_2F_2
vs	1100,1088	CH_2F_2
m	1048	CH_3F ?

The −10°C fraction is identical with the addition of
a band at 674 cm^{-1} attributed to CH_4 and C_6H_6 .

Table 3·4 /continued

6) Gaseous products (0°C) from reaction of CH_2CF_2 with

   $[(C_6F_5)_3P]_4Rh_2Cl_2$ at 120°C (Table 3·1).

   Only CH_2CF_2 and SiF_4 were observed.

7) Gaseous products at -78° from Expt. u).

Intensity	Position	Assignment
m	3150-2850 complex and peak at 3015	CH_4,CH_2F_2,CHF_3 ?
s	1136	CHF_3 ?
s	1106, 1088	CH_2F_2

8) Gaseous products at -78° from Expt. v).

Intensity	Position	Assignment
m	3150-2850 complex peaks at 3015 and 2990	CH_4,CHF_3 ?, CH_2F_2
m	1306 + complex	CH_4
m	1202	CHF_3 ?
vs	1136	CHF_3 ?
m	1106,1088	CH_2F_2
w	674	CH_4

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