

University of St Andrews



Full metadata for this thesis is available in
St Andrews Research Repository
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

INVESTIGATION OF THE CHEMISTRY OF
PHOSPHORUS FLUORIDES

A Thesis
presented for the degree of
Doctor of Philosophy
in the Faculty of Science of the
University of St. Andrews

by

Charles George Barlow, B.Sc.

September, 1967.

United College of
St. Salvator and
St. Leonard, St. Andrews.



Tm 5458

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.F. Nixon since the 1st October 1964, the date of my admission as a research student.

I hereby certify that Charles George Barlow, has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

ACKNOWLEDGEMENTS

I should like to thank Dr. J.F. Nixon for suggesting the topic of research and for his continued advice and encouragement during the period in which the work was carried out.

In addition, I am indebted to Dr. M. Webster for his invaluable advice, Dr. T. Gilson and R.E. Hester for recording the Raman spectra and Dr. G.S. Reddy for recording some of the nuclear magnetic resonance spectra.

Thanks are also due to the Science Research Council for the award of a Research Studentship for the period during which the work was carried out.

CONTENTS

	<u>Page</u>
<u>PART I, the co-ordination chemistry of fluorophosphines</u>	
<u>Introduction</u>	
Metal Carbonyls	1
Fluorophosphines	20
<u>Discussion</u>	
Results	31
Vibrational Spectra	40
Nuclear Magnetic Resonance Spectra	61
<u>PART II, the reactions of difluorotrichloromethylphosphine</u>	
<u>Introduction</u>	
Difluorotrichloromethylphosphine	74
Dialkylaminodifluorophosphines	76
<u>Discussion</u>	81
<u>EXPERIMENTAL SECTION</u>	90
Purification of Starting Materials	92
Preparations	96

	<u>Page</u>
<u>PART I</u>	
Preparation of <u>trans</u> -(PF ₃) ₃ Mo(CO) ₃	108
" " <u>trans</u> -(CCl ₃ PF ₂) ₃ Mo(CO) ₃	109
" " <u>trans</u> -(CF ₃ PF ₂) ₃ Mo(CO) ₃	110
" " <u>trans</u> -[(CF ₃) ₂ PF] ₃ Mo(CO) ₃	110
" " <u>trans</u> -[(C ₃ F ₇) ₂ PF] ₃ Mo(CO) ₃	112
Reaction between (CF ₃) ₃ P and C ₇ H ₈ Mo(CO) ₃	113
Preparation of <u>cis</u> -(PF ₃) ₂ Mo(CO) ₄	114
" " <u>cis</u> -(CCl ₃ PF ₂) ₂ Mo(CO) ₄	115
" " <u>cis</u> -(CF ₃ PF ₂) ₂ Mo(CO) ₄	117
" " <u>cis</u> -[(CF ₃) ₂ PF] ₂ Mo(CO) ₄	118
" " <u>cis</u> -[(CF ₃) ₃ P] ₂ Mo(CO) ₄	119
" " <u>cis</u> -(PF ₃) ₂ Cr(CO) ₄	120
 <u>PART II</u>	
Reaction between (C ₂ H ₅) ₂ NH and CCl ₃ PF ₂	121
" " C ₅ H ₁₁ N and CCl ₃ PF ₂	122
" " C ₄ H ₉ N and CCl ₃ PF ₂	123
Preparation of C ₄ H ₉ NPCl ₂	124

	<u>Page</u>
Fluorination of $C_4H_8NPCl_2$	126
Action of heat upon $C_4H_8NPF_2$	128
Reaction between $(CH_3)_2PH$ and CCl_3PF_2	129
$(CF_3)_2PH + CCl_3PF_2$	132
$CH_3SH + CCl_3PF_2$	133
$PF_3 + CH_3SH + (C_2H_5)_3N$	133
Reaction between $(CH_3)_2NH$ and <u>trans-</u> $(CCl_3PF_2)_3Mo(CO)_3$	135
Reaction between $C_5H_{11}N$ and <u>trans-</u> $(CCl_3PF_2)_3Mo(CO)_3$	136
Reaction between $C_5H_{11}N$ and <u>cis-</u> $(CCl_3PF_2)_2Mo(CO)_4$	137
Reaction between HCl and <u>cis-</u> $(C_5H_{10}NPF_2)_3Mo(CO)_3$	138

Appendix

Character tables for C_s , C_{2v} groups

Computer Programmes

TABLES

Fluorophosphines	Following page	22
Metal (O) Trifluorophosphines and Carbonyltrifluorophosphines	" "	24
Raman Spectra of Three Fluorophosphine Molybdenum Tetracarbonyls	" "	44
Overtone and Combination Bands	On Page	45
Force Constants for <u>trans</u> -(L) ₃ Mo(CO) ₃ Complexes	Following Page	48
Force Constants for <u>cis</u> -(L) ₂ Mo(CO) ₄ (k _t = 2k _c)	" "	49
Force Constants for <u>cis</u> -(L) ₂ Mo(CO) ₄ (k _t ≠ 2k _c)	" "	49
Calculated and Experimental ¹³ C - O Frequencies for <u>trans</u> -(L) ₃ Mo(CO) ₃	" "	52
Calculated and Experimental ¹³ C - O Frequencies for <u>cis</u> -(L) ₂ Mo(CO) ₄	" "	54
Force Constants of <u>cis</u> -(L) ₃ Mo(CO) ₃ Complexes of Phosphorus-Fluorine Ligands	" "	58
Infrared Spectra of the Fluorophosphine Complexes	" "	60
Changes in N.M.R. Parameters upon Complexation	" "	73

N.M.R. Spectra, Part I	Following Page	73
Infrared Spectra, Part II	" "	89
N.M.R. Spectra, Part II	" "	89

DIAGRAMS

1. Bonding in phosphine-transition metal complexes. Following Page 7
2. Structures of cycloheptatriene molybdenum tricarbonyl and bicycloheptatriene molybdenum tetracarbonyl. Following Page 31
3. Carbonyl stretching modes of $(L)_3Mo(CO)_3$ and $(L)_2Mo(CO)_4$ complexes. Following Page 39
4. Overtone and combination bands of three cis- $(L)_2Mo(CO)_4$ complexes. On Page 45
5. Correlation diagrams of the assignments of carbonyl stretching frequencies. Following Page 45
6. Graph of n against k_1 for $(L)_nMo(CO)_{6-n}$. Following Page 56
7. Infrared Spectra of fluorophosphine complexes. Following Page 60
8. ^{19}F N.M.R. Spectra showing non-equivalence of ligands in some $(L)_3Mo(CO)_3$ complexes. Following Page 63

- 9, 10. ^{19}F and ^{31}P N.M.R. Spectra, experimental
and calculated of cis- $(\text{PF}_3)_2\text{Mo}(\text{CO})_4$ Following Page 66
11. ^{19}F N.M.R. Spectrum, experimental and calculated
of cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ Following Page 67
12. Experimental ^{31}P N.M.R. Spectrum of cis-
 $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ Following Page 67
13. Apparatus for the preparation of CF_3I Following Page 99
-

PART I

The Co-ordination Chemistry
of Fluorophosphines.

INTRODUCTION

The first transition metal carbonyl to be isolated was nickel tetracarbonyl, in 1890¹, as the product in the corrosion of nickel by carbon monoxide. Carbonyls of some other transition metals have also been known for a long time. The direct reaction of carbon monoxide with the metal has produced the corresponding metal carbonyl only with nickel, iron, or cobalt. Other metal carbonyls have been synthesised by reduction of metal salts or complexes in the presence of carbon monoxide, usually under high pressure².

Transition metal carbonyls have been used as intermediates in industrial syntheses such as the "Fischer-Tropsch"³ and "Oxo"⁴ processes, although their importance was not always recognised. The use of metal carbonyls in organic syntheses has been reviewed⁵.

The metal carbonyls were remarkable in their properties, especially in view of the poor donor ability of carbon monoxide towards boron compounds⁶. The lack of any increase in electron density around the metal atom suggested that some mechanism other than just σ bonding between carbon and metal was involved. Electron diffraction studies on nickel tetracarbonyl⁷ and the hexacarbonyls of Group VIB metals⁸ showed the metal-carbon bond lengths to be shorter than expected for a single bond. Pauling suggested that nickel carbonyl contained a partial double bond between nickel and carbon which involved the metal 3d electrons⁹.

Transition metal compounds have been prepared which contain both terminal and bridging carbonyl groups and metal-metal bonds have also been found in some of the compounds. The X-ray structure determination of iron enneacarbonyl, $\text{Fe}_2(\text{CO})_9$, showed the presence of terminal and bridging carbonyl groups and an iron-iron bond¹⁰.

The binary metal carbonyls are usually diamagnetic; vanadium hexacarbonyl is one of the few exceptions, and their structures can be rationalised by the "inert gas rule". Terminal carbonyl groups are assumed to donate two electrons to the metal, bridging carbonyls one electron, and a metal-metal bond is assumed to contain one electron from each metal. Using these assumptions, the metal is usually found to attain the same configuration as the next inert gas.

In the years following 1950 Chatt published the results of studies on the co-ordination chemistry of platinum^{11,12}. Some ligands were found to weaken the bond trans to them much more than bonds in the cis position. The ligands which caused the greatest "trans effect" combined weakly or not at all with electron acceptors such as BH_3 or AlCl_3 , which had no occupied d orbitals. It was proposed that ligands which caused large "trans effects", such as CO , PF_3 , or C_2H_4 formed strong bonds with metals having electrons in their outer d shell because of the formation of a π bond which used the metal d electrons in addition to the normal σ bond between carbon and metal. A similar type of bonding had been postulated by Pauling to explain the properties of some of these ligands¹³.

Theoretical calculations have shown that the existence of $p_{\pi} - d_{\pi}$ and $d_{\pi} - d_{\pi}$ bonding is energetically possible¹⁴.

The bonding molecular orbitals of carbon monoxide may be represented as $(\sigma_s)^2(\sigma_s^*)^2(\pi_{x,y})^4(\sigma_z)^2$, indicating one σ and two π bonds between carbon and oxygen. A lone pair of electrons is left on both carbon and oxygen. The molecular orbital of lowest energy after σ_z is the $\pi_{x,y}^*$ antibonding orbital, which is unoccupied in carbon monoxide. The dative σ bond from carbon monoxide to a transition metal is formed by donation of the unshared pair of electrons on the carbon into an empty σ orbital on the metal. The increase in electron density which this process places on the metal could be diminished by donation of electrons from an occupied metal d_π or dp_π hybrid orbital into the empty $\pi_{x,y}^*$ orbital of carbon monoxide. In this way, the electron density around the metal is unchanged in the formation of a metal carbonyl compound. The two separate parts of the bonding mechanism tend to reinforce each other. The stronger the σ bond, the more electrons will tend to be placed in the π bond by the metal. This is commonly called a "synergic" effect¹⁵. The ability of carbon monoxide to minimise the charge on the metal explains the stabilisation of its compounds which contain a metal in the zerovalent state. The bonding can be represented in valence bond terms by the resonance structure:-



The isocyanides are electronically similar to carbon monoxide and can form similar complexes¹⁶.

The majority of nitric oxide complexes¹⁷ are regarded as being formed from the nitrosonium ion, NO^+ , by initial transfer of an electron from nitric oxide to the metal. The resulting ion is isoelectronic with carbon monoxide.

Anions from the metal carbonyls have been prepared by treatment with alkali hydroxide or Lewis bases. Iron pentacarbonyl with alkali gave the anion $\text{HFe}(\text{CO})_4^-$; acidification then produced the hydride $\text{H}_2\text{Fe}(\text{CO})_4$ ¹⁸. The properties and reactions of carbonylmetallate ions and their derivatives have been studied extensively and the work reviewed¹⁹.

The chemistry of the hydrides has been studied and especial attention drawn to the properties of the hydrogen which they contain²⁰. The hydrogen atom has been shown to have very little effect upon the geometry of the hydrides and it has been suggested that the proton is buried within the electron shell of the metal²¹. However, recent papers dispute this and claim that the metal-proton bond length agrees with the expected covalent bond length²².

A very large number of transition metal compounds containing other ligands, in addition to carbon monoxide, are now known. The usual methods of preparation of these derivatives are the thermal reaction of ligand and metal carbonyl, the photochemical reaction of ligand and metal carbonyl and the displacement of one ligand in a substituted metal carbonyl by another ligand.

Organic ligands may form simple carbon-metal σ bonds or, if the energies and symmetries of the ligand orbitals allow, σ and π bonds. Ethylene, for instance, was shown by Chatt to cause a large "trans effect" in platinum complexes and is believed to form a σ and a π bond to the metal. When the ligand has aromatic character, this is often retained in the complex, as in benzene chromium tricarbonyl, or cyclopentadienyl manganese tricarbonyl.

Ligands which co-ordinate through an atom which has no empty d orbitals available for the formation of the π bond with the metal, such as amines and ethers, cannot assist in the delocalisation of the electron density placed on the metal. Such compounds enhance the metal-carbonyl π bond and lower the carbon-oxygen bond order since the extra density is dispersed by increased back bonding to the remaining carbonyl groups.

Ligands such as cyanide ion can form π bonds with the metal by using empty d_{π}^* orbitals in a way similar to carbon monoxide. Heterocyclic ligands such as dipyridyl or 1,10 phenanthroline donate through the nitrogen atoms but can form a π bond with the metal by interaction of their π aromatic orbitals and the d_{π} orbitals of the metal.

Many derivatives of metal carbonyls have been prepared which contain ligands with a donor atom possessing unoccupied d orbitals. This class of ligands is typified by the Lewis bases, e.g. phosphines and arsines. The chemistry of Lewis base-metal carbonyl chemistry has been reviewed in detail²³. The bonding in a phosphine complex is shown diagrammatically in the figure. The lone pair of electrons on phosphorus is donated into a metal orbital of correct symmetry, the π bond is then formed by overlaps of the filled d_{π} metal orbital with an unoccupied d_{π} orbital of phosphorus. The exact combination of orbitals used will depend upon the symmetry of the molecule. For derivatives of metal hexacarbonyls the metal p orbitals may interact slightly with the ligand π orbitals²⁴. The co-ordination chemistry of phosphines, stibines and arsines has been discussed in a review not restricted to carbonyl complexes²⁵. It has been found difficult to displace all of the carbonyl groups from metal hexacarbonyls by Lewis bases except where the base is phosphorus trifluoride^{26,27}, or a chelating ligand such as dipyridyl²⁸.

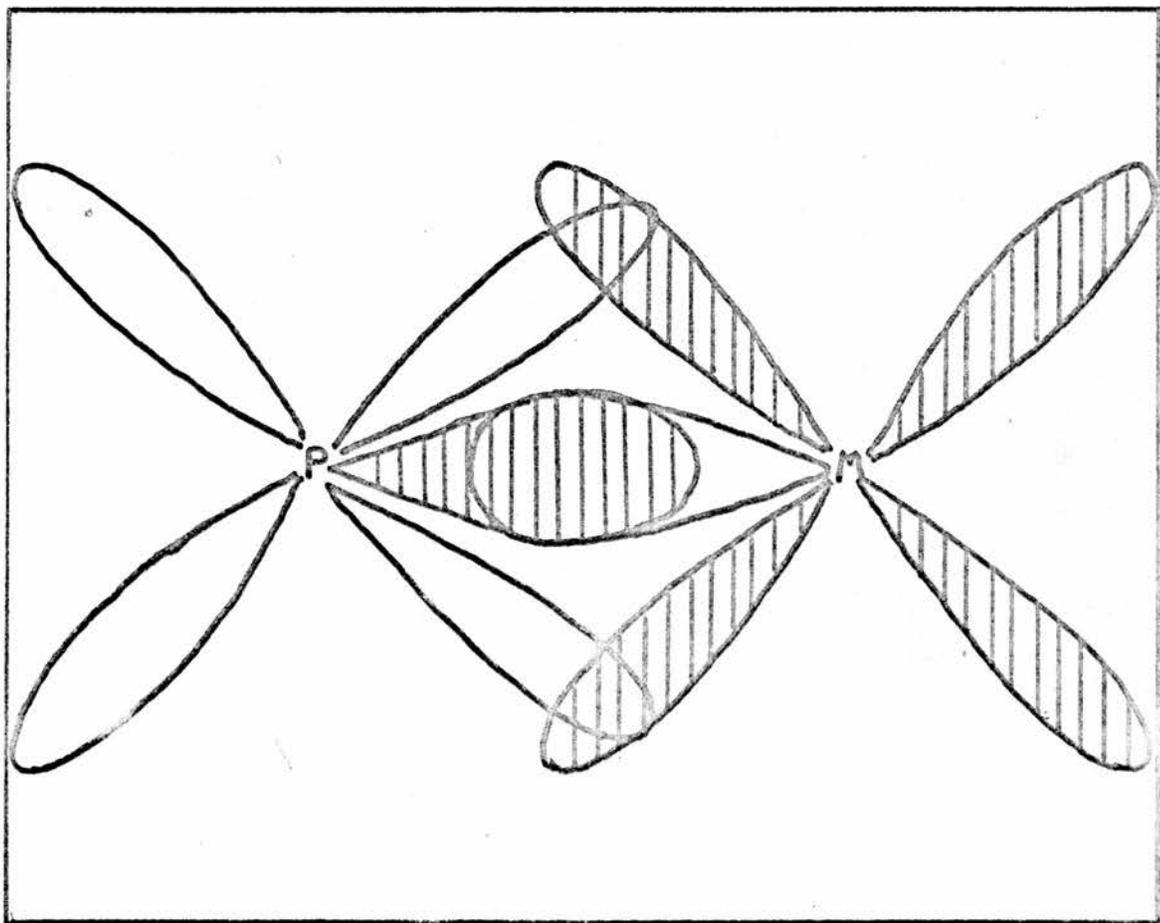


Diagram of the bonding
in phosphine-transition-metal
complexes

Bridging carbonyl groups may be easily distinguished from terminal ones by infrared spectroscopy, the former exhibiting C-O stretching bonds about 1700 cm.^{-1} and the latter around 2000 cm.^{-1} . Since the frequency of absorption depends upon the strength of the carbon-oxygen bond, it has been used as an indicator of the extent of metal-carbon π bonding. The frequency of absorption of the infrared active T_{1u} mode in the binary metal hexacarbonyls is considerably lower than in free carbon monoxide, (2000 cm.^{-1} and 2133 cm.^{-1} respectively²⁹), indicating lowering of the bond order on co-ordination. The effect of a charge on the metal atom is shown by the infrared spectra of the isoelectronic series $Mn^+(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $V^-(\text{CO})_6$, the absorptions occurring at 2096, 2000, and 1859 cm.^{-1} , respectively³⁰.

The transfer of electrons to the metal from donors such as amines causes a lowering of the carbonyl absorption frequency of amine carbonyl complexes. Ligands such as phosphines and arsines, on the other hand, lower the frequency less because they can accept at least some of the charge they donate by forming a back bond. Examples of this are the carbonyl stretching frequencies of cis-(diethylene triamine) $\text{Mo}(\text{CO})_3$ ³¹ and cis $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Mo}(\text{CO})_3$ ³² which have values of 1898, 1758 and 1934, 1835 cm.^{-1} respectively.

The empirical observation that the carbonyl stretching frequency reflected the degree of occupancy of the carbon-oxygen π orbital has been given support by a recent calculation by Kettle³³ which showed that the vibration of the carbonyl groups alters the strength of the carbon-oxygen π bond more than the σ bond.

The theory of the bonding in metal carbonyls proposes that as the bond order of the carbon-oxygen bond decreases that of the metal-carbon bond increases. To substantiate this, it has been found experimentally that the decrease in carbonyl frequency on substitution by a ligand occurs together with an increase in the metal-carbon bond order³⁴.

The shift of the carbonyl stretching frequency upon substitution of a metal carbonyl by a ligand has usually been attributed to the difference in the π accepting abilities of the ligand and the displaced carbonyl group³⁵. A series of ligands have been arranged in a "Spectrochemical Series" in the order of their π bonding abilities³⁶. The ligands with greatest π bonding abilities were shown to be NO, CO, PF₃, the poorest o-phenanthroline and diethylenetriamine. The acceptor property of a ligand depends primarily upon the character of the donor atom but also upon the electronegativity of the substituents bonded to it.

Bigorgne and his co-workers have made many studies on substituted metal carbonyls in order to ascertain the relative importance of the σ and π contributions to the metal-ligand bond. They have shown that the bonding ability depends upon the donor atom, l , and also upon the atom bonded to the donor atom in compounds of the type $r-x-l-Ni-CO$ ³⁷. The conclusion drawn from these studies was that the dominant effect controlling the change in the M-C and C-O bond orders was the σ bonding ability of the ligand³⁷. A graph of the Ingold-Taft constant, σ^* , for the substituents on phosphorus in a series of phosphines against the carbonyl frequency for a series of substituted nickel carbonyl compounds was a straight line³⁴. The σ^* parameter is a measure of the inductive effect of a substituent. It was claimed that calculations showed that the π bonding ability was almost invariant along a series of phosphines, from PF_3 to $P(CH_3)_3$. The variable parameter was the ability to form the dative bond to the metal. The similarity of the bonding abilities of PF_3 and CO is explained in this theory by the low basicity of PF_3 which allows only weak donation of electrons to the metal.

The weak σ bond formed is approximately equal to the π back bond formed; the equality results in little or no extra charge passing into the bond between the metal and remaining carbonyls. A more basic ligand, such as $(\text{CH}_3)_3\text{P}$, will have the same π bonding ability and the extra charge donated by the larger σ bond will be passed into the metal-carbonyl π bonds.

If the π bonding ability was not the controlling factor in ligand-metal bonding, one would expect NF_3 to form complexes similar to PF_3 , but no such complexes of NF_3 are known.

The bonding between a ligand and a transition metal appears to be a combination of σ and π bonding, when the latter is possible, and it is difficult to separate completely the effects of one from the other. Variations of factors such as the electronegativity of the groups bonded to the donor atom will alter the σ and the π bonding abilities of the ligand at the same time.

Most of the detailed studies of the bonding in metal carbonyl derivatives have considered the changes in the carbon-oxygen stretching force constants, rather than the absorption frequencies in the infrared. The use of force constants allows comparisons between compounds of different symmetries. The treatment of molecules containing more than four or five atoms must normally be approximate because the number of force constants exceeds the number of observable frequencies. The binary metal carbonyls are the simplest compounds to treat, being of higher symmetry than their derivatives. The number of vibrational modes active in the infrared or Raman can be obtained by group theoretical methods³⁸. The infrared spectra of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ were reported by Hawkins and co-workers³⁹, although their assignments were later changed by Murata and Kawai⁴⁰, who obtained a set of force constants which only poorly fitted the experimental data. Another set of force constants was calculated by Pistorius and Haarhoff⁴¹. The Raman spectra of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ have been reported⁴². A detailed treatment of $\text{Mo}(\text{CO})_6$ has been made by Jones⁴³, who assigned 12 of the 13 frequencies and calculated a set of force constants.

The force constant for stretching the carbon-oxygen bond obtained was 18.12 m. dynes/Å. Nickel tetracarbonyl has been examined in detail by Jones^{43,44} and by Bigorgne³⁴. The values of the primary force constants obtained were 17.55 and 17.3 m. dynes/Å respectively. The force constant for carbon monoxide is 19.0 m. dyne/Å³⁴. All of the calculations which have been performed have had to include approximations such as assuming some interaction force constants to be zero.

The calculations which have been made on derivatives of metal carbonyls have been less exact. The molecular symmetry is usually determined with the ligands other than carbon monoxide assumed to be point masses. This simplifies the calculations but can lead to erroneous predictions of the number of infrared active vibrational modes, especially if the ligand is large or very asymmetric⁴⁵. Bigorgne has calculated force constants for the series $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{CO})_3(\text{PMe}_3)$, $\text{Ni}(\text{CO})_2(\text{PMe}_3)_2$, $\text{Ni}(\text{CO})(\text{PMe}_3)_3$ and shown that F_{CO} decreases and F_{MC} increases as carbon monoxide is successively replaced. A similar decrease was found in the vibrational frequencies of the compounds.

The majority of the force constants of derivatives of metal carbonyls have been calculated using secular equations derived by Cotton^{31, 35, 46} for the different isomers of the series $L_x M(CO)_{6-x}$ or equations based on assumptions similar to those used by Cotton. All couplings to vibrations other than carbonyl stretching were ignored. There was assumed to be no coupling between σ and π type orbitals. This is true for the octahedral hexacarbonyls, where symmetry does not allow mixing, but is not strictly true for the derivatives with lower symmetry²⁴. Anharmonicity of the vibrations is also ignored.

The use of the equations allows a quantitative comparison to be made between the force constants of different compounds which have the same symmetry and, less accurately, between compounds of different symmetries. The force constants obtained have no absolute meaning, but, since the same assumptions are made each time, comparisons are possible. The force constants obtained are of the correct order, but the effect of the approximations made can be seen from a comparison of the values of F_{CO} for $Mo(CO)_6$ obtained by Cotton (16.52 m. dynes/Å) and by Jones (13.12 m. dynes/Å).

In order that the effect of a ligand on the carbonyl bonding can be ascertained and the correct secular equations used in the calculation of force constants the absorptions observed in the infrared and Raman spectra must be assigned to the vibrational mode causing them. The use of relative intensities of absorptions and comparisons between derivatives of metal hexacarbonyls have been used as guides for assigning absorptions^{46, 47}. The use of intensities has been given a semi-quantitative foundation by Kaesz and El Sayed^{44, 45}. Interaction of infrared radiation and a molecular vibration can only occur if the vibration produces an oscillating dipole in the molecule. Kaesz and El Sayed said that the intensity of an absorption is proportional to the square of the sum of the vectors representing the vibration. The spectra of the compounds $M(CO)_5X$ ⁴⁵ where M = Mn, Re, Tc have been assigned with the aid of this rule. The ratio of the intensity of the asymmetric mode to the intensity of the symmetric mode has been used to calculate the angle between the carbonyl groups in some metal carbonyl compounds and the results shown to agree with X-ray crystal structure results⁴⁸.

The interaction force constants between carbonyl groups are expected to be positive and it follows from this that a symmetric carbonyl mode will absorb at higher frequency than the corresponding asymmetric mode⁴⁷.

The force constants obtained from alternative assignments for a compound have been used to help to find the correct assignment. The assignment giving the set of force constants which were most acceptable was chosen as the correct one. However, the lack of significance of some of the "approximate" force constants has been claimed⁴⁹, and it may be a fallible method of assigning absorptions when the differences between different sets of force constants are small. Whenever the solution of the Cotton equations gave complex roots the assignments were dismissed. More recent work,⁵⁰ however, has suggested that complex roots may not be a sufficient reason for dismissing an assignment.

Raman spectra and polarization data have been reported for some substituted metal carbonyls. Decomposition of the compounds by the exciting light has limited the usefulness of Raman spectroscopy. Decomposition is less likely using new laser spectrometers and so much more data on the Raman spectra of derivatives of metal carbonyls may become available.

Many organoderivatives of transition metal carbonyls have been examined by proton nuclear magnetic resonance⁵¹. The nature of the bonding between the proton and metal in metal hydrides has been studied by proton magnetic resonance. The proton resonance of metal hydrides occurs at abnormally high field strengths suggesting that the proton is strongly shielded. Taken in conjunction with other physical properties this was interpreted as evidence that the proton was buried within the electronic shell of the metal²¹. The high field resonance has more recently been explained by the distortion of the partly filled metal d shell by the magnetic field^{52, 53}.

The ¹³C nuclear magnetic resonance spectra of a series of metal carbonyl derivatives have been examined in the hope that the spectra could be related to the structures of the compounds but no direct correlation appeared⁵⁴. Bicyclo (2,2,1) hepta (2,5)diene molybdenum tetracarbonyl produced two ¹³C resonance absorptions arising from the two pairs of non-equivalent carbonyl groups in the molecule⁵⁴. This indicated that ¹³C nuclear magnetic resonance could be useful in the elucidation of the structures of metal carbonyl derivatives.

The first reported application of phosphorus nuclear magnetic resonance spectroscopy to the study of phosphine complexes was a detailed examination of some nickel carbonyl derivatives⁵⁵. The chemical shift of most of the ligands moved downfield upon co-ordination. A qualitative explanation was proposed but no quantitative relationship between nuclear magnetic resonance parameters and metal-phosphorus bonding was found. The coupling constants J_{P-Pt} between ^{31}P and ^{195}Pt nuclei in some square planar platinum (II) complexes have been measured and found to be greater when two phosphorus atoms were trans to each than when they were mutually cis⁵⁶. Since two trans ligands may share two metal d_{π} orbitals but cis ligands only share one d_{π} orbital, the ratio of the coupling constants may be explained. This is similar to the explanation of the "trans effect" proposed by Chatt^{11, 12}. However, it has now been shown that J_{cis}/J_{trans} is similar for platinum (IV) and platinum (II) complexes. This has been taken as evidence for a σ bonding effect causing the observed ratios since $d_{\pi} - d_{\pi}$ bonding is thought to be less important in platinum (IV) than in platinum (II) complexes⁵⁷.

Fluorine nuclear magnetic resonance spectra have been obtained from fluorocarbon-transition metal complexes. The resonance of a CF_3 or CF_2 group bonded to a transition metal was found at 60 to 70 p.p.m. downfield from the resonance of non-co-ordinated CF_3 or CF_2 . The downfield shift was attributed to mixing of the fluorine p_π electrons and low-lying excited states in the metal-carbon bonds. The mixing alters the paramagnetic screening constant of the fluorine nuclei⁵⁸.

The spectra of some complexes of phosphorus-fluorine ligands have been reported^{27, 59, 60, 61}. The spectra were often considerably more complex than expected and were mirror image patterns of complex bands.

In view of the interest which has been shown in the properties of trifluorophosphine as a ligand, it was decided to study the co-ordination chemistry of its derivatives the fluorophosphines $\text{R}_n\text{PF}_{3-n}$ by infrared and nuclear magnetic resonance spectroscopy.

Fluorophosphines

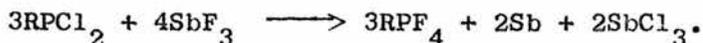
Fluorophosphines are derivatives of phosphorus trifluoride, with a general formula R_nPF_{3-n} , in which one or two fluorine atoms have been replaced by an organic radical or other substituent.

The parent compound, PF_3 , a colourless, toxic gas, was probably first produced in 1875 by the reaction between PCl_3 and AsF_3 ⁶², but was first identified by Moissan in 1884 as the product from the reaction of copper phosphide with lead fluoride⁶³. The usual method of preparation has been by fluorination of phosphorus trichloride using a large variety of fluorinating agents, usually binary fluorides, such as SbF_3 , AsF_3 , ZnF_2 or NaF . The PF_3 produced is sometimes contaminated with partially fluorinated products which can be removed by vacuum fractionation.

The P-F bond length in phosphorus trifluoride has been found to be 0.3\AA shorter than that calculated from the sum of the covalent radii of phosphorus and fluorine^{64, 65}, and this shortening has been attributed to the presence of some π bonding between phosphorus and fluorine^{66, 67}. Phosphorus trifluoride is much more resistant to hydrolysis than phosphorus trichloride.

The general trend amongst the trihalides of phosphorus is that the rate of hydrolysis increases as the electronegativity of the halogen increases. Phosphorus trifluoride is, however, attacked rapidly by aqueous base, giving hydrogen fluoride and phosphorous acid. Dry glass is attacked by phosphorus trifluoride only at high temperatures, when silicon tetrafluoride is produced.

In contrast to phosphorus trifluoride and the chlorophosphines, fluorophosphines have been known for only a short time. Fluorination of allyl or aryl chlorophosphines with the usual agents such as Group V trifluorides produced fluorophosphoranes by a redox reaction⁶⁸:

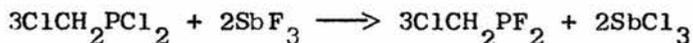


A few difluoroalkylphosphines have been prepared⁶⁸, but only difluoromethylphosphine has been examined in detail. CH_3PF_2 decomposed when stored in a glass tube and gave a cyclic polyphosphine and tetrafluoromethylphosphine:



This rearrangement was also observed by other workers who examined the infrared spectrum and the ^{19}F , ^{31}P and ^1H spectra of CH_3PF_2 ⁶⁹. The original preparation of difluorophenylphosphine⁶⁸ could not be repeated by other workers⁷⁰, but the compound has now been prepared and fully characterised⁷¹.

It has been found that if the group R in a fluorophosphine is electron withdrawing then this redox reaction does not occur. For example, the substitution of one proton by chlorine in CH_3PCl_2 to give $\text{ClCH}_2\text{PCl}_2$ enabled the stable ClCH_2PF_2 to be prepared by the general method of preparation of fluorophosphines, which has been the reaction of antimony trifluoride with the iodo- or chloro-phosphine in a sealed glass tube.



Two fluorophosphines have been formed in very low yields by migration of a fluorine atom from a CF_3 group to phosphorus.

CF_3PI_2 with mercury gave a small amount of CF_3PF_2 ⁷³, and thermal decomposition of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ produced $(\text{CF}_3)_2\text{PF}$ ⁷⁴.

Fluorophosphines

<u>Compound</u>	<u>Preparation</u>	<u>Boiling Point (°C)</u>	<u>Reference</u>
CH_3PF_2	$\text{CH}_3\text{PCl}_2 + \text{SbF}_3$	-28	68
	$\text{CH}_3\text{PCl}_2 + \text{ZnF}_2$		69
ClCH_2PF_2	$\text{ClCH}_2\text{PCl}_2 + \text{SbF}_3$	33.5 - 34.5	72
CCl_3PF_2	$\text{CCl}_3\text{PF}_2 + \text{SbF}_3$	73.1	75
CF_3PF_2	$\text{CF}_3\text{PI}_2 + \text{SbF}_3$	-47.6	76
	$\text{CF}_3\text{PI}_2 + \text{Hg}$		73
$\text{C}_3\text{F}_7\text{PF}_2$	$\text{C}_3\text{F}_7\text{PI}_2 + \text{SbF}_3$	15.8	77
$\text{CF}_2=\text{CFPF}_2$	$\text{CF}_2=\text{CFPCl}_2 + \text{SbF}_3$	2 - 3	78
$(\text{CF}_3)_2\text{PF}$	$(\text{CF}_3)_2\text{PI}_2 + \text{SbF}_3$	-15.4	79
	$(\text{CF}_3)_2\text{P-O-P}(\text{CF}_3)_2$ at 250°		74
$(\text{C}_3\text{F}_7)_2\text{PF}$	$(\text{C}_3\text{F}_7)_2\text{PI} + \text{SbF}_3$	92.2	77
$(\text{CF}_2=\text{CF})_2\text{PF}$	$(\text{CF}_2=\text{CF})_2\text{PCl} + \text{SbF}_3$	63 - 65	78
$\text{C}_6\text{H}_5\text{PF}_2$	$\text{C}_6\text{H}_5\text{PCl}_2 + \text{NaF}$ (in tetramethylene sulphone).	31°	71
$\text{C}_6\text{F}_5\text{PF}_2$	No details given		80

The **known** fluorophosphines, whose methods of preparation are shown in the Table, are colourless gases or liquids, some of which are pyrophoric in the atmosphere. The presence of an electron withdrawing substituent increases the stability of the fluorophosphine. Hydrolysis of trifluoromethyl fluorophosphines by aqueous alkali produced fluoroform quantitatively. The reactions of some fluorophosphines with dimethylamine have been studied^{82 83}, but little else appears to be known of their simple chemistry.

Trivalent phosphorus compounds should be able to act as electron donors or acceptors to form complexes. The high electronegativity of the substituents on phosphorus in fluorophosphines would be expected to enhance their acceptor properties and reduce their donor properties compared to other trivalent phosphorus compounds.

Phosphorus trifluoride appears, however, to have poor acceptor properties since only the adduct formed between phosphorus trifluoride and trimethylamine has been prepared⁸⁴ at -100°C . and no other such adducts have been found.

Phosphorus trifluoride does **act** as an electron donor in a number of complexes. With diborane or with $\text{OC}\cdot\text{BH}_3$, the adduct $\text{F}_3\text{P}\cdot\text{BH}_3$ ⁸⁵ formed, yet no complex was isolated from $\text{PF}_3 + \text{BF}_3$ ¹¹. The properties of $\text{F}_3\text{P}\cdot\text{BH}_3$ are very similar to those of $\text{OC}\cdot\text{BH}_3$. The formation of adducts between phosphorus trifluoride and aluminium trihalide has been reported to occur when phosphorus trifluoride was under pressure⁸⁵.

The co-ordination chemistry of phosphorus trifluoride was examined by Chatt, who prepared $(PF_3)_2PtCl_2$ from phosphorus trifluoride and platinumous chloride, which upon further heating gave $[PF_3PtCl_2]_2$ ¹². The ability of phosphorus trifluoride to displace carbon monoxide from metal carbonyls was demonstrated by the preparation of $Ni(PF_3)_3(CO)$ ¹². Although complete substitution was not achieved in this early study, tetrakis(trifluorophosphine) nickel has since been prepared by several routes including replacement of carbon monoxide from nickel tetracarbonyl.

A recent review²⁶ by one of the leading workers, T. Kruck, illustrates the recent advances in the field of trifluorophosphine complexes of transition metals which have shown the existence of a range of compounds analogous to those of transition metals with carbon monoxide.

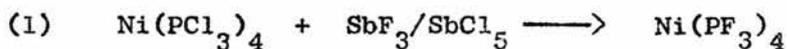
Tetrakis(trifluorophosphine)nickel appears to be the most accessible of the metal (O) trifluorophosphines since it is the only member which can be obtained by the first four methods shown in the Table. Replacement of all the carbon monoxide units from a metal carbonyl by ultra violet irradiation has only been reported for iron and molybdenum carbonyls although the method may have further applications.

Metal (O) Trifluorophosphines

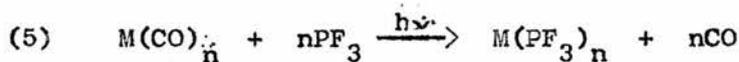
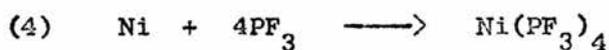
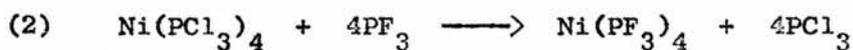
and

Carbonyltrifluorophosphines 26

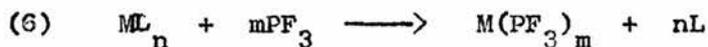
Metal Trifluorophosphines.



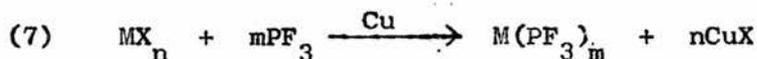
or



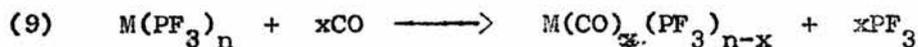
(M = Fe, Mo)



(e.g. L = C₆H₆ or C₅H₅)



Carbonyltrifluorophosphines



The most general route which has been used is the "reductive fluorophosphination" reaction, shown in equation (7), which has produced the mononuclear trifluorophosphines of Mo, W, Fe, Ru, Ni, Pd, Pt, and the binuclear $[\text{Re}(\text{PF}_3)_5]_2$ and $[\text{Rh}(\text{PF}_3)_4]_2$. Very recently the reaction has been used to prepare a cobalt complex containing two, bridging, three electron donating, PF_2 groups ⁸⁷.

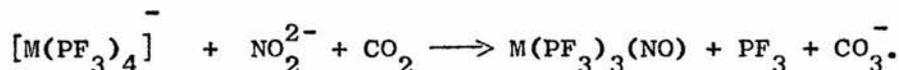
The metal trifluorophosphines have greater stability to heat, oxidation and moisture than the metal carbonyls which they resemble, indeed some of them may even be steam distilled without harm. All of the compounds so far prepared are volatile. Replacement of PF_3 by other ligands is possible, the weaker the donor the more extensive the substitution. Complete ligand exchange is possible with carbon monoxide.

Partial exchange of carbon monoxide or trifluorophosphine provides a facile synthetic route to the carbonyltrifluorophosphine metal complexes from metal carbonyls or metal trifluorophosphines. Alternatively they may be obtained by the displacement of the ligand from substituted metal carbonyls. In the presence of ultra violet light, however, certain substituted metal carbonyls, such as $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, exchange carbon monoxide for trifluorophosphine while the ligand remains bound to the metal ⁸⁸.

Rather similar to the carbonyltrifluorophosphine metal complexes are those containing nitric oxide and trifluorophosphine which may be prepared by an adaptation of the "reductive fluorophosphination" method:-

$$[\text{Fe}(\text{NO})_2\text{Br}]_2 + 2\text{Cu} + 4\text{PF}_3 \longrightarrow 2\text{Fe}(\text{NO})_2(\text{PF}_3)_2 + 2\text{CuBr},$$

or by an aqueous reaction in which carbonate ion is formed from carbon dioxide:-



Trifluorophosphine metal hydrides have been prepared which have increased stability to heat and oxidation over the carbonyl metal hydrides. The nuclear magnetic resonance spectra show a high field shift of the proton resonance similar to that of the carbonyl hydrides. Kruck has suggested that the proton-metal bond is covalent and that the proton is not within the metal electronic shell.

The strongly electron withdrawing nature of trifluorophosphine causes the halogenotrifluorophosphines to lack polarization and to exhibit abnormally high metal-halogen stretching frequencies in the infrared spectra by inducing the donation of electrons from the halogen to the metal in a partial π bond.

The bond between phosphorus trifluoride and a transition metal is similar to that described earlier for other trivalent phosphines but with the important difference that the strongly electronegative fluorine substituents greatly increase the ability of the phosphorus to accept the back π bond and decrease its ability to form the σ bond. Indeed the indications are that the π bond is the dominant factor responsible for many of the remarkable properties of the complexes. The low dipole moment of $(PF_3)_2PtCl_2$ ¹² was explained by the presence of a mechanism for counteracting the transfer of electron density produced by a π bond from phosphorus to platinum.

The stabilisation of zerovalent platinum and palladium by trifluorophosphine is striking evidence for its greater π accepting ability compared to carbon monoxide since $Pt(CO)_4$ and $Pd(CO)_4$ are unknown.

Phosphorus trifluoride being such a good acceptor of electron density through the π bond with the metal, it is able to confer greater stability to the trifluorophosphine metallates than carbon monoxide in the carbonylmetallates.

The reaction between PF_3 and nickelocene has been extended to prepare a variety of tetrakis(fluorophosphine)nickel compounds ⁹⁰ . The use of nickelocene is preferable to that of nickel tetracarbonyl because of the high toxicity of the latter and the fact that only NiL_4 complexes are obtained.

Fluorophosphine metal-carbonyl compounds have also been prepared by fluorination of the corresponding chlorophosphine complexes ⁹¹ or by displacement of cycloheptatriene from its molybdenum tricarbonyl complex ⁹² .

The fluorophosphine complexes which were obtained were more stable than the free fluorophosphines reacting only slowly in the atmosphere.

In co-ordination complexes of fluorophosphines with transition metals the high electronegativity of the substituents on the phosphorus atom should weaken the donor properties of the phosphine, but should enhance any metal phosphorus back π - bonding.

From a comparison of the carbonyl stretching frequencies of the PF_3 metal-carbonyl derivatives with those of other derivatives it has been claimed that PF_3 has better π accepting properties than carbon monoxide³¹. Cotton attempted to confirm this by force constant calculations³¹. However, the carbonyl frequencies of cis- $(\text{PF}_3)_3\text{Mo}(\text{CO})_3$ which he used do not agree with later values obtained for better characterised samples of this compound. His basic argument, nevertheless, still holds true. The value of F_{CO} for $\text{Mo}(\text{CO})_6$ obtained by Cotton's equations is 16.52 m. dynes/ \AA^2 , that for cis- $(\text{PF}_3)_3\text{Mo}(\text{CO})_3$ is 16.62 m. dynes/ \AA^2 ⁹³, showing the higher carbon-oxygen bond order in the latter.

Since phosphorus trifluoride had been shown to have interesting properties as a ligand, it was decided to investigate the ligand properties of several fluorophosphines more closely. It was hoped to find the effect of substituting fluorine atoms by a variety of groups e.g. CCl_3 , CF_3 , C_3F_7 , R_2N etc. The complexes obtained could be examined by ^{19}F and ^{31}P nuclear magnetic resonance spectroscopy in addition to infrared spectroscopy, in an attempt to gain information about the nature of the phosphorus-metal bond.

DISCUSSION

Results.

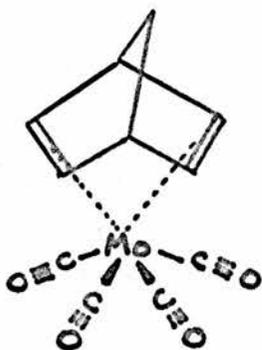
In order to study the co-ordinating abilities of fluorophosphines by physical techniques it was important that mono-isomeric products should be obtained. The reaction between molybdenum hexacarbonyl and a fluorophosphine ligand could in principle produce a variety of substitution and geometric isomers. Phosphorus trifluoride and molybdenum hexacarbonyl are known to react, under appropriate conditions, to give all nine possible products of general formula $(PF_3)_n Mo(CO)_{6-n}$.²⁷

The complexes described in this work were prepared by reaction of the fluorophosphine ligand with an intermediate of known stereochemistry, in the hope that the products would be single isomers. The intermediate used to prepare the tricarbonyl compounds was cycloheptatriene molybdenum tricarbonyl (I)⁹⁴, whose structure has been determined by X-ray crystallography.⁹⁵ The carbon monoxide groups adopt a mutually cis, C_{3v} , configuration about the molybdenum atom and the carbon ring is non-planar with the carbon-carbon double bonds localised as in the free cycloheptatriene. Other workers⁹⁶ have shown that the cycloheptatriene is readily displaced by ligands such as amines, phosphines and phosphites to give products in which the cis carbonyl configuration is retained. The tetracarbonyl complexes were obtained by reaction of the appropriate fluorophosphine with bicyclo (2,2,1)hepta(2,5)diene molybdenum tetracarbonyl (II).⁹⁷



Cycloheptatriene
molybdenum
tricarbonyl

(I)



bicyclo(2,2,1)hepta(2,5)diene
molybdenum
tetracarbonyl

(II)

This compound has been shown by spectroscopic techniques^{93, 54} to have a cis, C_{2v} , arrangement of the carbonyl groups and was expected to react with ligands with retention of the configuration.

The use of other molybdenum carbonyl complexes containing an organic ring system as intermediates in the preparation of substituted molybdenum tricarbonyl compounds, has normally required more vigorous conditions than necessary in reactions with the intermediates used in the present study, and thus the possibility of producing several isomers or further substituted products is enhanced.⁹⁹

A kinetic study of reactions between trimethyl phosphite and arene molybdenum tricarbonyl and cycloheptatriene molybdenum tricarbonyl showed that cycloheptatriene was more easily displaced than arene rings.¹⁰⁰ This may be due to the increased stability arising from the delocalisation of the ring electrons in the arene complexes.

The fluorophosphines studied were PF_3 , CCl_3PF_2 , $(C_3F_7)_2PF$, CF_3PF_2 and $(CF_3)_2PF$. The reactions of $(CF_3)_3P$ were also studied, since it is the last member of the series PF_3 , CF_3PF_2 , $(CF_3)_2PF$, $(CF_3)_3P$.

The reactions were carried out by allowing an excess of the fluorophosphine to stand at room temperature with either (I) or (II). The progress of the reactions could readily be followed by the disappearance of the strong colour of (I) or (II). When gaseous fluorophosphines were employed, the reactions could be followed by the appearance of liquid products. Reaction times under these mild conditions varied from a few hours to several days, depending upon the fluorophosphine. In no case was any significant evolution of carbon monoxide observed which would have been expected if any fluorophosphine molybdenum carbonyl complexes other than the required $L_3Mo(CO)_3$ or $L_2Mo(CO)_4$ derivatives were produced.

Mild reaction conditions were desirable to prevent or minimise re-arrangement of the products since Clark and Hoberman have reported the slow rearrangement and disproportionation of compounds of the type $(PF_3)_x Mo(CO)_{6-x}$, both in the presence of PF_3 and in the absence of PF_3 or CO .²⁷

The reaction between phosphorus trifluoride and bicycloheptadiene chromium tetracarbonyl was, in contrast, much slower. A temperature of 100° was needed to achieve significant reaction. The product from this reaction was shown by ^{19}F nuclear magnetic resonance spectroscopy to be a mixture of PF_3 -containing compounds. There was no sign of reaction between fluorobis(trifluoromethyl)phosphine and cycloheptatriene chromium tricarbonyl or bicycloheptadiene chromium tetracarbonyl after one year at room temperature in a sealed tube. The decreased reactivity of the chromium compounds compared with their molybdenum analogues is in agreement with other studies on Group VIB complexes and is in agreement with very recent kinetic studies by Pidcock and Taylor who showed that the second order rate constants for the reaction between trimethyl phosphite and cycloheptatriene tricarbonyl compounds were in the ratio 1:2210:355 for chromium, molybdenum and tungsten complexes respectively. Two factors have been proposed to account for these observed ratios. The ease of forming a seven co-ordinate transition state is greater for molybdenum and tungsten than for chromium. The metal-ring bond strength increases from chromium to tungsten. For molybdenum and tungsten the former factor appears to be dominant.

The products from the fluorophosphine molybdenum carbonyl reactions are colourless liquids or white crystals, which are sufficiently volatile to be manipulated in the vacuum system at room temperature. It has been reported that the volatility of the compounds $(PF_3)_n Mo(CO)_{6-n}$ increased when $n = 1, 2$ or 3 , then decreased as $n = 4, 5, 6$.²⁷

The fluorophosphine molybdenum carbonyl complexes are much less sensitive to atmospheric oxygen and moisture than the pyrophoric, easily hydrolysed ligands. In the complexes, the lone pair of electrons on phosphorus are used to form the $P \rightarrow Mo$ σ bond, and the empty phosphorus d orbitals can be utilised in $Mo \rightarrow P\pi$ back bonding. The tendency for the phosphorus to oxidise to its five valent state is, therefore, reduced by co-ordination. The compounds decomposed slowly in air, turning dark in colour, possibly caused by the formation of small amounts of finely divided molybdenum. One sample of cis- $[(CF_3)_2PF]_2 Mo(CO)_4$ was observed to fume when handled in air, but this was not normally observed. The solid complexes melted without visible decomposition. Gas-liquid chromatography on a column at $100^\circ C$. showed no decomposition on the column and confirmed the mono-isomeric character of the reaction products. The isomers of the series $(PF_3)_n Mo(CO)_{6-n}$, $n = 1$ to 6 , have been separated on a 27 ft. column;²⁷ the present studies used a 50 metre capillary column of greater resolving power, which should have been better able to separate any isomeric mixtures. The short retention times were unusual in view of the volatilities and molecular weights of the compounds but were in agreement with reports by Kruck.²⁶

The yields in the reactions were normally high. Recovery of the excess fluorophosphine and displaced cycloheptatriene was also close to that expected, based on the amount of complex formation, but in reactions where bicycloheptadiene was displaced the recovery of excess fluorophosphine and of the bicycloheptadiene was not as high, suggesting a possible reaction between fluorophosphines and the bicycloheptadiene. It was noticed that when a mixture of a fluorophosphine and bicycloheptadiene was stored in a sealed tube at room temperature for long periods the mixture turned brown and in some cases a glassy solid was formed.

The reaction of $(CF_3)_3P$ with cycloheptatriene molybdenum tricarbonyl produced a large amount of black involatile solid and a volatile product shown by ^{19}F nuclear magnetic resonance spectroscopy to be a mixture of compounds. With bicycloheptadiene molybdenum tetracarbonyl, however, the volatile product appeared to be a single compound with analytical data fitting the formula $[(CF_3)_3P]_2 \cdot Mo(CO)_4$. The infrared spectrum in the carbonyl region showed four bands as expected for the cis carbonyl C_{2v} configuration, but with different intensity ratios from those of the other cis tetracarbonyl products studied. The failure to form $[(CF_3)_3P]_3Mo(CO)_3$ and the unusual infrared spectrum may be due to the steric requirements of the $(CF_3)_3P$ ligand. Steric effects have been suggested as the reason why it proved impossible to prepare $Ni[(CF_3)_3P]_4$ ⁸⁹ from $Ni(CO)_4$. Steric strain could distort the arrangement of the carbonyl groups around molybdenum in $[(CF_3)_3P]_2Mo(CO)_4$ and so alter the relative intensities in the infrared spectrum.

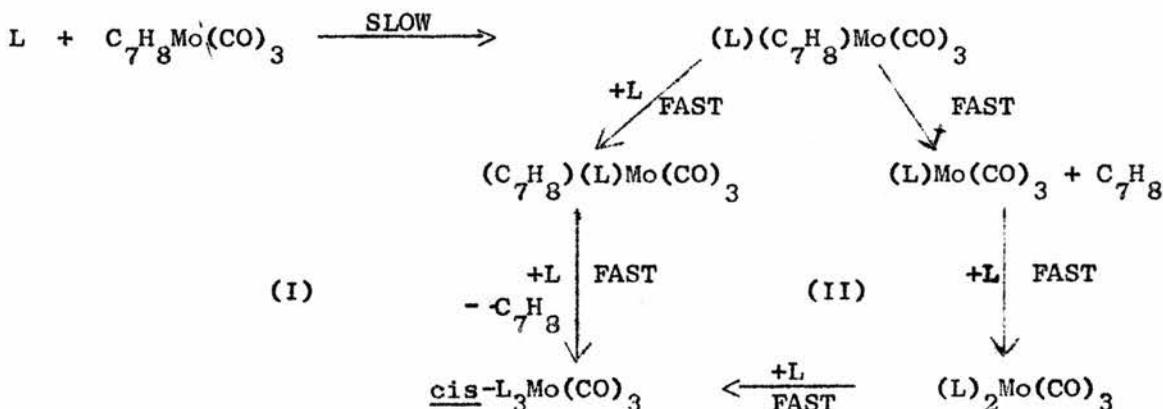
King¹⁰¹ has reported that $[(\text{CH}_3)_2\text{N}]_3\text{P}$ reacts with cycloheptatriene molybdenum tricarbonyl to produce trans- $[(\text{CH}_3)_2\text{N}]_3\text{P}]_2\text{Mo}(\text{CO})_4$ identical to that from reaction of the ligand with bicycloheptadiene molybdenum tetracarbonyl. He considered that in this case steric effects may be responsible or the controlling factor could be the poor π -accepting properties of the phosphorus atom when bonded to three nitrogen atoms.

The configuration of the fluorophosphine and carbon monoxide ligands around the molybdenum atom was determined by spectroscopic techniques. The samples of $(\text{PF}_3)_3\text{Mo}(\text{CO})_3$ and $(\text{PF}_3)_2\text{Mo}(\text{CO})_4$ prepared in the present study melted at temperatures which agreed closely with those reported for the trans and cis isomers respectively.²⁷ In the following sections it will be shown that the infrared and nuclear magnetic resonance spectra supported the trans configuration for the tricarbonyl products and the cis configuration for the tetracarbonyl complexes.

The cis to trans rearrangement which occurred during synthesis of the tricarbonyl complexes was unexpected since a variety of ligands have been reported to react with cycloheptatriene molybdenum tricarbonyl to give cis products. A similar rearrangement was found when cis- $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ reacted with acrylonitrile, the product being trans- $(\text{CH}_2\text{CHCN})_3\text{Mo}(\text{CO})_3$.¹⁰²

The retention of configuration during the reactions of fluorophosphines with bicycloheptadiene molybdenum tetracarbonyl was in agreement with previous observations. Rearrangement has, however, been observed in the reaction of $[(\text{CH}_3)_2\text{N}]_3\text{P}$ with this intermediate when trans- $[(\text{CH}_3)_2\text{N}]_3\text{P} \text{ Mo}(\text{CO})_4$ ¹⁰¹ was isolated. The rearrangement in this particular case could be explained by the large size of the ligand.

From a study of the kinetics of the reaction between cycloheptatriene molybdenum tricarbonyl and trimethyl phosphite, the slow, rate-determining step suggested was the formation of a seven co-ordinate intermediate which then reacted by either of two paths in fast stages to produce the observed cis- $\text{L}_3\text{Mo}(\text{CO})_3$ product.¹⁰⁰



No evidence was available to support one path rather than the other but (I) was considered more likely since cycloheptatriene is known to act as a bidentate ligand in complexes such as $\text{C}_7\text{H}_8\text{Fe}(\text{CO})_3$.¹⁰³ Arene complexes, on the other hand, might be expected to follow (II), in which the delocalisation of the π electrons in the aromatic ring could be retained. Complexes in which arenes are bidentate have been prepared by photochemical reactions¹⁰⁴ so that path (I) cannot be ruled out in this case either.

The reaction mechanism for substitution of bicycloheptadiene molybdenum tetracarbonyl does not seem to have been studied, but a similar compound, cycloocta(1,5)diene molybdenum tetracarbonyl, has been studied.¹⁰⁵ The rate law was similar to that obtained by Pidcock and co-workers for their system and similar mechanisms were proposed.

The kinetic studies were performed in solution but solvolysis was stated to be unimportant in the mechanism. The fluorophosphine reactions in the present work were performed in the absence of solvent and this could possibly account for the differences observed. It is difficult to find an explanation for the rearrangement of the tricarbonyl complexes which would not also cause the unobserved rearrangement in the formation of the tetracarbonyl complexes.

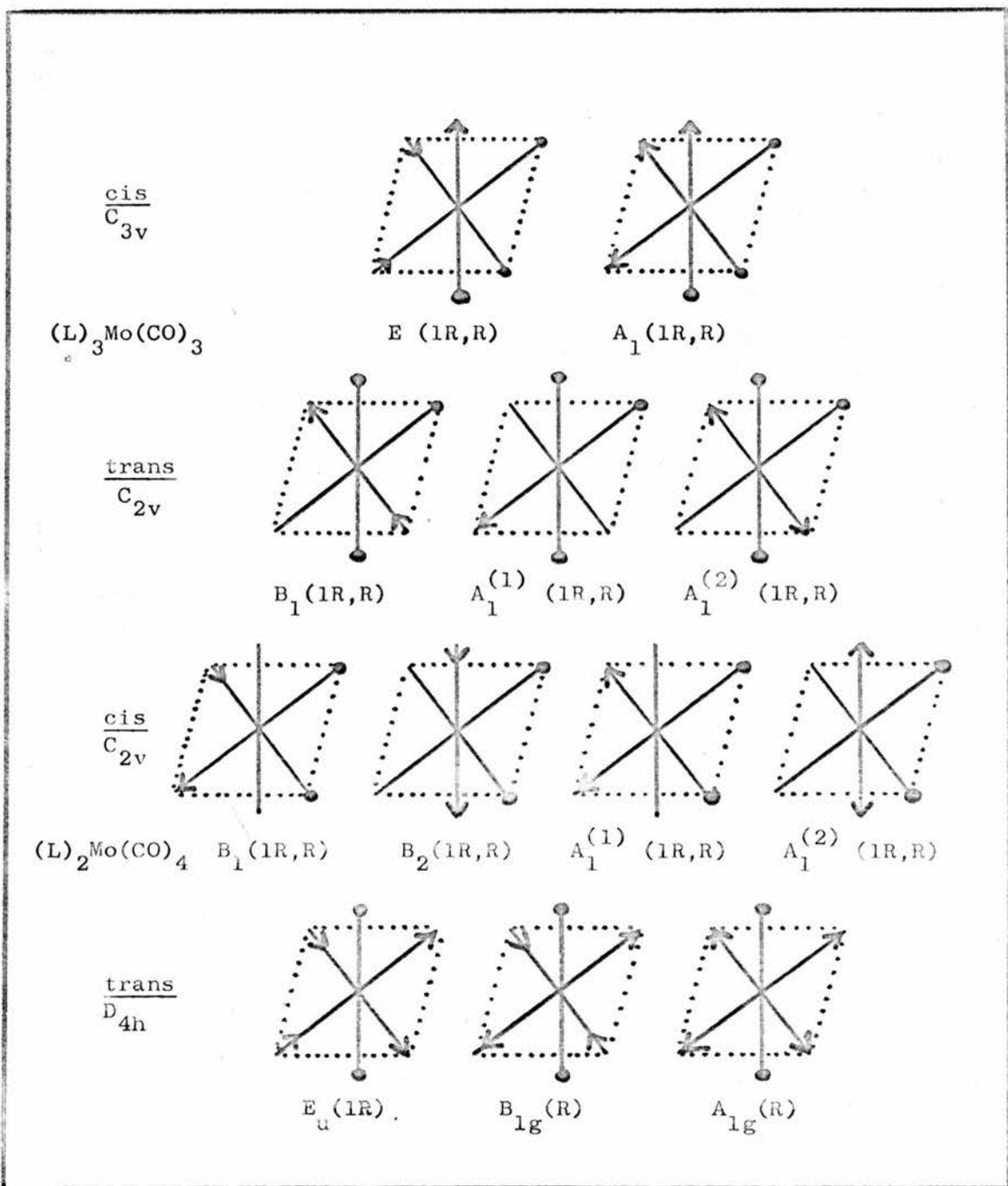
The use of ligands of large size could favour the formation of the less strained trans isomer and such strain would be greater in the tricarbonyl than the tetracarbonyl. However, since the rearrangement occurs with fluorophosphines of smaller size than many ligands which have been shown previously to form the cis product, steric strain can probably be dismissed as a contributory factor.

If the rearrangement occurred by rapid migration of carbonyl groups to give a more stable isomer, then fluorophosphine ligands would allow the breaking of the metal-carbon bond more readily than other ligands. It will be shown in the section on their infrared spectra that in their molybdenum carbonyl derivatives the fluorophosphine ligands are very good π -acceptors, comparable to carbon monoxide.

The metal-carbon bond order will, therefore, be lower than in complexes containing poorer π -acceptors and so be more easily broken. A linear correlation between carbonyl stretching frequency and the energy of activation for the dissociation of some substituted metal carbonyls has shown the connection between the π -accepting ability of ligands and the ease of loss of carbon monoxide.^{10e} If the ligands have greater π -accepting abilities than carbon monoxide, then the effect on the remaining metal-carbon bonds will be greater in the trisubstituted derivatives than in the disubstituted complexes, explaining the lack of rearrangement in the latter.

Such a rearrangement would have been less likely when cycloheptatriene molybdenum tricarbonyl reacted with dialkylamino-difluorophosphines or with fluorophosphites, since, although these ligands are good π -acceptors, they are not as good as the fluorophosphines used in the present study, nor comparable to carbon monoxide. Hence, substitution by these ligands would increase the metal-carbon bond order and favour the formation of the observed cis products.

Without extensive study of the kinetics and mechanisms of the reactions it appears very difficult to rationalise the observations completely.



Carbonyl Stretching Frequencies
 of $(L)_3\text{Mo}(\text{CO})_3$ and
 $(L)_2\text{Mo}(\text{CO})_4$

Vibrational Spectra

The volatility of most of the compounds prepared in this work enabled infrared spectra to be obtained from their vapour. The less volatile compounds were examined in a hexane solution whose concentration was adjusted to produce optimum resolution of the spectra.

The tricarbonyl and tetracarbonyl derivatives of Group VI B metals may exist as either cis or trans isomers and in each case the molecular symmetry of the two isomers is different. The number of normal modes of vibration of the molecule can be obtained using the character table of the molecular symmetry group. Each normal vibration forms a basis for one of the irreducible representations of the group and may be labelled by the Mulliken symbol of that representation. By further use of symmetry arguments, it is possible to deduce the number of carbonyl stretching vibrations active in the Raman effect or which absorb infrared radiation.

The molecular symmetry, the number of vibrational modes active in the Raman or infrared, the Mulliken symbols of the modes and the vector diagrams are shown in the Diagram. The ligands other than carbon monoxide are assumed to be small, point masses which do not grossly influence the molecular symmetry.

The infrared spectra of the tricarbonyl complexes all consisted of three principle absorption bands in the 2000 cm.^{-1} region suggesting that they were trans, C_{2v} , isomers.

The difference in frequency between the lower two carbonyl frequencies was greater for $(PF_3)_3Mo(CO)_3$ than for $[(C_3F_7)_2PF]_3Mo(CO)_3$. For this reason the assignment of these absorptions to a split E mode of a cis, C_{3v} , isomer was dismissed.

The infrared spectra of the tetracarbonyl complexes exhibited three or four absorptions in the carbonyl stretching region, showing that they were cis isomers with C_{2v} symmetry.

Comparisons of infrared frequencies of two compounds can only be made if vibrations of the same symmetry are considered. It was important, therefore, that the observed absorptions were assigned to the correct normal vibrational modes. The assignment of the absorptions was also a necessary prerequisite for subsequent force constant calculations. Guidance as to the correctness of assignments may be obtained from:-

- (1) relative intensities,
- (2) band positions,
- (3) Raman spectra,
- (4) polarisation data from Raman spectra,
- (5) solvent studies,
- (6) force constants obtained from the assignment,
- (7) comparison of calculated and observed ^{13}C -O frequencies,
- (8) study of overtone and combination bands,
- (9) polarised infrared studies on a single crystal.

All but the last of these techniques have been used to some extent in the present study. Polarised infrared spectroscopy requires a single crystal of the compound and a preliminary X-ray structure determination.

The ratio of intensities predicted by the method of Kaes and El-Sayed⁴⁵ for the trans tricarbonyl derivatives is 0:1:4 for the carbonyl-stretching vibrational modes $A_1^{(2)}$, $A_1^{(1)}$, B_1 , and 0:2:2:4 for the $A_1^{(2)}$, $A_1^{(1)}$, B_1 , B_2 carbonyl modes of the cis tetracarbonyl derivatives. The possibility of coupling between vibrations of the same symmetry is not considered in this simplified calculation.

The $A_1^{(2)}$ mode in both isomers is only active in the infrared spectrum because of coupling with other vibrations belonging to the A_1 irreducible representation. The major coupling will be with the $A_1^{(1)}$ carbonyl-stretching vibration since this is closest in frequency to the $A_1^{(2)}$ vibration.

Jones⁴³ has shown that the stretch-stretch interaction force constants in metal carbonyls are always positive. A vibration which involves simultaneous stretching of two carbon-oxygen bonds will, therefore, absorb at a higher frequency than the corresponding vibration involving the stretching of one and contraction of the other of the two carbon-oxygen bonds. One can say in the present case, therefore, that the symmetric A_1 mode will absorb at higher frequency than the corresponding B mode.

The coupling between two trans carbonyl groups has been shown by Cotton⁴⁶ and by Jones⁴³ to be greater than the coupling between two cis carbonyl groups. In the spectra of the tetracarbonyl derivatives, the separation between the frequencies of absorption of the $A_1^{(2)}$ and B_2 modes should, therefore, be greater than the separation between the $A_1^{(1)}$ and B_1 modes.

Using the arguments developed above, the three absorptions in the carbonyl stretching region of the infrared spectra of the tri-carbonyl derivatives were assigned. The intensities of absorption, considered in order of decreasing frequency, were medium, strong, very strong. The assignment chosen, therefore, was $A_1^{(2)}$, $A_1^{(1)}$, B_1 in the above order of frequencies.

The Raman spectrum of trans-(CCl_3PF_2)₃Mo(CO)₃ was examined to obtain confirmation of the proposed assignment. A vibration is Raman active when it causes a change in the polarisability of the molecule. Since this condition is different from that necessary for the absorption of infrared radiation, the intensity of absorption by a vibration may differ in the two spectra. The character table for the C_{2v} group shows that vibrations having A_1 , B_1 , or B_2 symmetry are Raman active. However, a symmetric A_1 mode may be predicted to have greater effect upon the molecular polarisability than the anti-symmetric B_1 or B_2 modes of vibration.

The carbonyl vibrations $A_1^{(2)}$, $A_1^{(1)}$, B_1 of the trans- L_3 Mo(CO)₃ complexes will be expected to have intensities strong:strong:weak in the Raman spectra.

The Raman spectrum of a hexane solution of trans-(CCl_3PF_2)₃Mo(CO)₃ consisted of two lines at 2063 and 2011 cm^{-1} of approximately equal intensities, consistent with the proposed assignments. Attempts to obtain polarisation data were unsuccessful because the compound decomposed slowly in the (4358 Å mercury arc) beam.

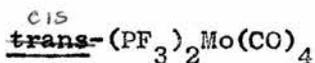
The infrared spectrum of cis-(CCl₃PF₂)₂Mo(CO)₄ contained four lines, two of them very close together, which could be assigned to carbon-oxygen bond stretching vibrations, together with a very much weaker line in the same region. The spectra of cis-(CF₃PF₂)₂Mo(CO)₄, cis-[(CF₃)₂PF]₂Mo(CO)₄ and cis-(PF₃)₂Mo(CO)₄, however, showed only three bands attributable to carbon-oxygen stretching vibrations. Much weaker lines were also present, but were not considered to be due to fundamental vibrations. The latter spectra could be explained by very close proximity of two of the four expected lines.

The assignments suggested by comparison of the observed intensities with those predicted from consideration of the displacement vectors of the four modes of vibration were A₁⁽²⁾, A₁⁽¹⁾, B₁, B₂ or A₁⁽²⁾, B₁, A₁⁽¹⁾, B₂, the central line being assigned to overlapped A₁⁽¹⁾ and B₁ modes when only three bands were seen.

Since the interaction force constants, k_i, are thought to be positive, the following relationships between the frequencies of the vibrations may be obtained:- A₁⁽²⁾ > B₂, A₁⁽¹⁾ > B₁, A₁⁽²⁾ > A₁⁽¹⁾, B₁ or B₂. If k_{i trans} > k_{i cis}, then a further relationship, (A₁⁽²⁾ - B₂) > (A₁⁽¹⁾ - B₁), is obtained. The proposed assignments fulfil all of these conditions.

The Raman spectra of two of the compounds prepared in this study, and one prepared by Grunbaum and Nixon,¹⁰⁷ were examined in an attempt to justify the assignment proposed above. The exciting light was from a Helium-Neon gas laser, 6328Å. The results are shown in the Table. The symmetric A₁⁽²⁾ and A₁⁽¹⁾ vibrations should give rise to more intense bands than the asymmetric B₁ and B₂ vibrations for reasons similar to those discussed for the tricarbonyl complexes.

Raman Spectra of
Three Fluorophosphine Molybdenum
Tetracarbonyl Complexes



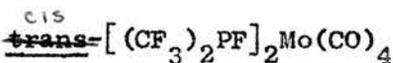
2036 vs, P; 2015 vs, D;

908 vw, D; 881 vw, D; 848 w, D;

561 vw, 521 m, P; 406 vs,

P; 260 m, P; 210 m, P;

96 vs, D; (cm.⁻¹)



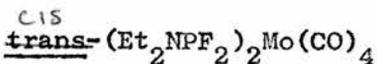
2093 vs, P; 2030 vvs, D;

1220 w, 1153 w, 840 m, D;

757 s, P; 533 m, P; 494 m, P;

404 vvs, P; 290 m, P; 238 vs,

P; 120 m, D; 96 vs, P; (cm.⁻¹).



2057 vs, P; 1970 vs, D; 1943 s, D; 1459 m, D; 1380 vw, D; 1217 w,

D; 1080 m, P; 1022 w, D;

955 w, D; 923 w, D; 818 m,

P; 790 w, D; 692 s, P;

517 w, D; 411 vvs, P;

336 w, D; 222 m, P; 193 m,

P; 96 vs, D; (cm.⁻¹).

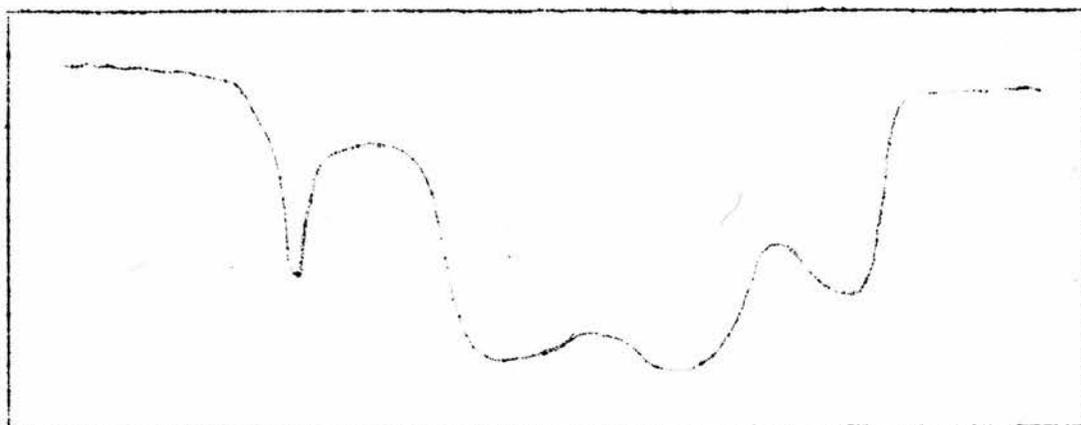
In each spectrum, bands were observed which corresponded to the $A_1^{(2)}$ and $A_1^{(1)}$ absorptions in the infrared spectra. The spectrum of $\text{cis}-(\text{Et}_2\text{NPF}_2)_2\text{Mo}(\text{CO})_4$ also contained a weaker band which corresponded to the infrared absorption of the B_2 vibration. From these results the assignment $A_1^{(2)}$, $A_1^{(1)}$, B_1 , B_2 was chosen rather than $A_1^{(2)}$, B_1 , $A_1^{(1)}$, B_2 .

The $A_1^{(2)}$ band was polarised, as expected for a symmetric vibration, but the $A_1^{(1)}$ band was always depolarised. As expected the B_2 band of $(\text{Et}_2\text{NPF}_2)_2\text{Mo}(\text{CO})_4$ was depolarised.

Adams¹⁰⁸ has shown that the polarity of the solvent shifts the carbonyl stretching frequency of substituted metal carbonyl solutions. The shift was greater for those vibrations involving carbonyl groups trans- to the ligand than for vibrations of carbonyl groups in the cis-position. In hexane solution $\text{cis}-(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ gave four sharp bands but in the more polar solvents, chloroform, acetonitrile, or nitrobenzene, the central two lines could not be resolved because of the increased band-width. There was, however, no noticeable shift in frequency in the more polar solvents. Although the solvent studies did not help in confirming the assignment, the small shifts suggested that the ligand was of comparable π -acceptor ability to CO itself.

Overtone and Combination

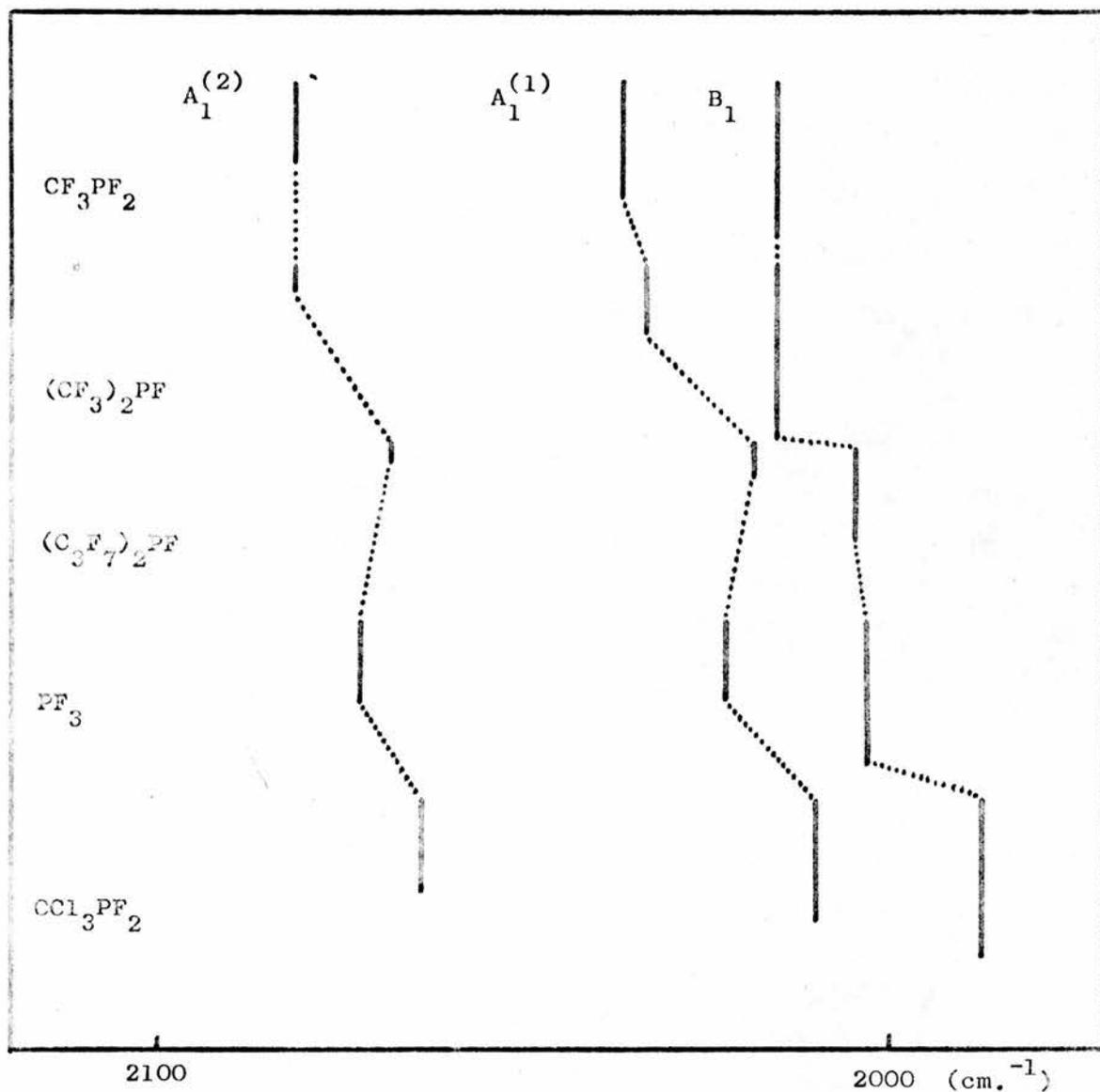
Bands



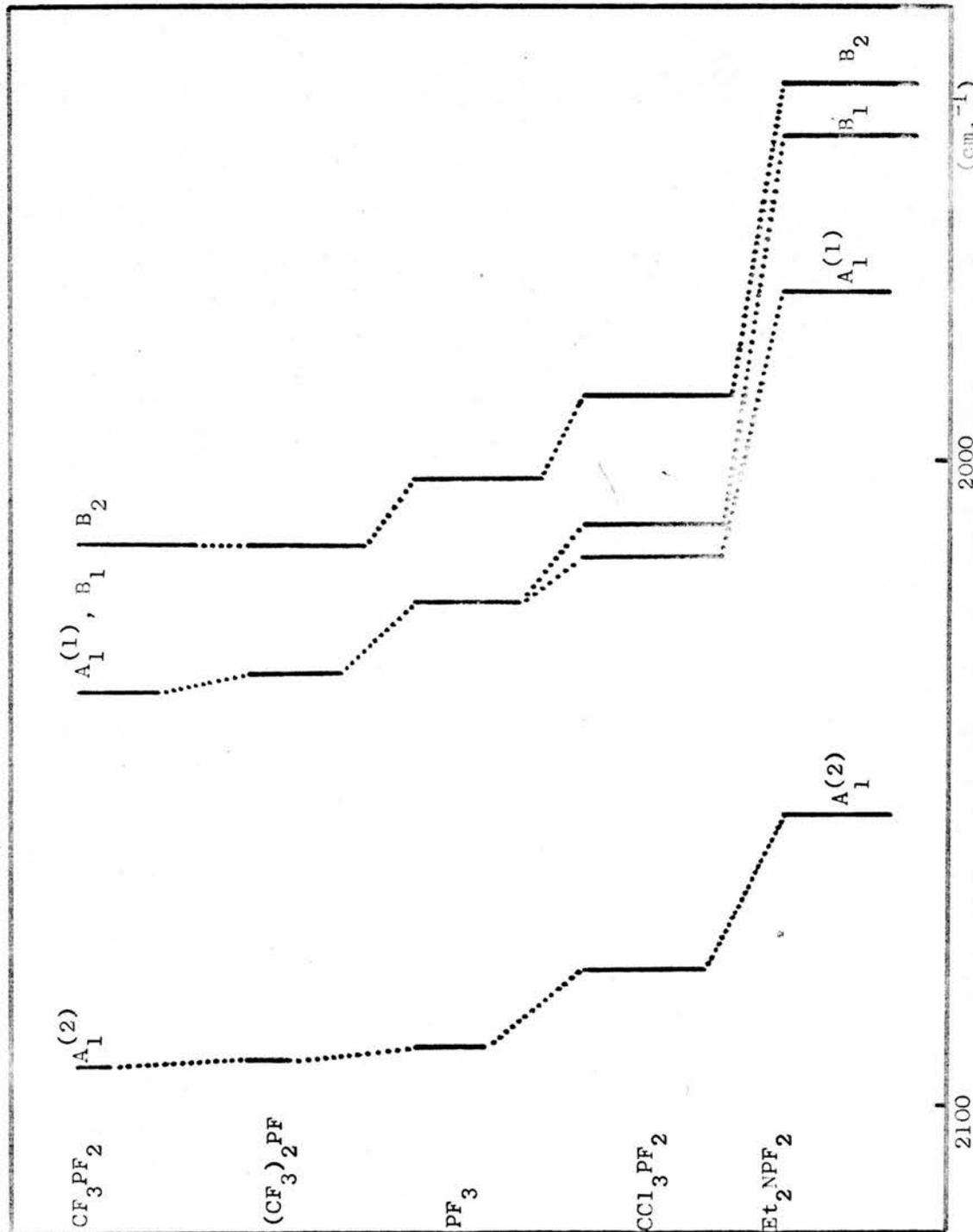
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	
$(PF_3)_2Mo(CO)_4$	4165	4080	4050	3990	$cm.^{-1}$
$[(CF_3)_2PF]_2Mo(CO)_4$	4171	4100	4078	4025	$cm.^{-1}$
$[Et_2NPF_2]_2Mo(CO)_4$	4098	4010	3978	3890	$cm.^{-1}$

Because of breadth of bands, B, C, D are only accurate to

$\pm 5 cm.^{-1}$.



Correlation diagram of
 carbonyl stretching frequencies
 for trans- $(L)_3Mo(CO)_3$ complexes
 (The length of the lines is proportional to
 the observed intensities)



(cm^{-1})

Correlation diagram of carbonul stretching vibrations

2000

2100

When the infrared spectra of $\text{cis}-(\text{PF}_3)_2\text{Mo}(\text{CO})_4$, $\text{cis}-[(\text{CF}_3)_2\text{PF}]_2\text{Mo}(\text{CO})_4$ and $\text{cis}-(\text{Et}_2\text{NPF}_2)_2\text{Mo}(\text{CO})_4$ in the 4000 cm^{-1} region were examined, the carbonyl stretching overtone and combination bands were found to be similar for each compound. Four broad bands were observed whose maxima best fitted the assignments $2A_1^{(2)}$, $A_1^{(2)} + A_1^{(1)}$, $A_1^{(2)} + B_2$, $A_1^{(1)} + B_2$. The large band width may be due to the presence of weaker absorptions which were not completely resolved. The symmetry of the ten possible overtones and combinations can be obtained by multiplying the characters of the irreducible representations to which the two fundamental vibrations belong. The representation given by the products in each case is one of the irreducible representations of the C_{2v} group. All but one of the combination and overtone bands are infrared allowed; the combination $B_1 + B_2$ having A_2 symmetry is infrared forbidden.

The two correlation diagrams show the assignments chosen for the tricarbonyl and tetracarbonyl complexes which have been prepared. The shift in frequency as the ligand changed can also be seen clearly from the diagrams.

Once the assignments had been decided, it was possible to calculate the force constants for carbon-oxygen bond stretching and the interaction between carbonyl stretching vibrations.

A general method of obtaining the values of force constants is by solution of the determinantal equation

$$\begin{vmatrix} GF - E\lambda \end{vmatrix} = 0$$

where G is the kinetic energy matrix and is a function of the atomic masses, F is the potential energy matrix whose elements are functions

of the force constants of the molecule, E is the identity matrix in which all non-diagonal elements are zero and the diagonal elements are unity, λ is the wavelength matrix.

The equation may be simplified by performing a symmetry transformation on G and F so that the matrices become blocked out. Each block may then be solved separately.

By making several assumptions and approximations, secular equations for the series of compounds $L_x M(CO)_{6-x}$ have been derived which require only the carbonyl stretching frequencies as data,^{46, 35} Solution of these equations gives force constants for carbonyl stretching and interaction between carbonyl stretching vibrations which have no true quantitative significance but allow useful comparisons between compounds of similar structures.

Anharmonicity, which for $Mo(CO)_6$ was found to be -10 and -21 cm^{-1} ,⁴³ is neglected in the use of the simplified equations.

All interactions except between carbonyl stretching vibrations were ignored, an assumption justified by the difference in frequency between carbonyl and other vibrations.

From the nature of the bonding in the compounds, several deductions about the carbonyl stretching force constants were made.

- (1) Interaction force constants should be positive.

Stretching of a carbon-oxygen bond lowers the energy of the π antibonding orbital, increasing the overlap with the metal π orbitals. This reduces the availability of metal π electrons for the π bond to the other carbonyl group, whose bond order is increased as a result.

- (2) Interaction force constants between trans carbonyl groups should be approximately twice those between cis carbonyl groups.

Trans carbonyls share two metal π orbitals in the π bond, cis carbonyls one. Jones has shown the validity of this approximation by other reasoning.⁴³

- (3) Primary force constants should decrease with increasing replacement of carbon monoxide by ligands of poorer π bonding ability.

The remaining carbonyl groups must accept an increasing amount of electron density from the metal into their π orbitals.

- (4) Primary force constants of carbonyl groups opposite a ligand should be smaller than those cis.
- (5) Increasing replacement by ligands with poorer π bonding ability should increase the interaction constants.

Interaction increases as the strength of the π back bond to the remaining carbonyl groups increases.

The secular equations obtained after the substitution $k_t = 2k_i$ for the isomers of interest in the present work are:-

cis - L₂Mo(CO)₄

$$\begin{array}{l} A_1^{(2)} \\ A_1^{(1)} \end{array} \left| \begin{array}{cc} \mu(k_2 + 2k_i) - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_1 + 2k_i) - \lambda \end{array} \right| = 0$$

$$B_1 \quad \lambda = \mu(k_1 - k_i)$$

$$B_2 \quad \lambda = \mu(k_2 - 2k_i)$$

trans - L₃Mo(CO)₃

$$\begin{array}{l} A_1^{(2)} \\ A_1^{(1)} \end{array} \left| \begin{array}{cc} \mu k_1 - \lambda & 2 \mu k_i \\ 2 \mu k_i & \mu(k_2 + 2k_i) - \lambda \end{array} \right| = 0$$

$$B_1 \quad \lambda = \mu(k_2 - 2k_i)$$

k_1 is the force constant for carbonyl groups trans to the ligand.

k_2 is the force constant for carbonyl groups cis to the ligand.

k_i is the interaction force constant.

Force Constants for Fluorophosphine

Complexes trans - (L)₃Mo(CO)₃.

<u>Ligand</u>	<u>Force Constants (m.dyne/Å)</u>			<u>Frequencies (cm.⁻¹)</u>		
	k ₁	k ₂	k _i	A ₋₁ ⁽²⁾	A ₋₁ ⁽¹⁾	B ₋₁
PF ₃	16.70	16.68	0.24	2072	2022	2003 <u>obs.</u>
				2072	2023	2003 <u>calc.</u>
CCl ₃ PF ₂	16.53	16.47	0.26	2063	2010	1987 <u>obs.</u>
				2063	2011	1987 <u>calc.</u>
(C ₃ F ₇) ₂ PF	16.61	16.67	0.22	2068	2018	2004 <u>obs.</u>
				2068	2019	2004 <u>calc.</u>
(CF ₃) ₂ PF	16.87	16.85	0.22	2080	2032	2015 <u>obs.</u>
				2080.5	2034	2015 <u>calc.</u>
CF ₃ PF ₂	16.94	16.85	0.23	2081	2036	2015 <u>obs.</u>
				2081	2037	2014.5 <u>calc.</u>

Force constants for the fluorophosphine molybdenum tricarbonyl complexes were obtained by the insertion of guessed values of force constants into part (A) of the programme of Wait and Slezak, which is reproduced in the Appendix. After one iteration by part (B), the force constants gave calculated frequencies which were within $<1\text{cm.}^{-1}$ of the observed frequencies. The computation was performed on an I.B.M. 1620 II computer.

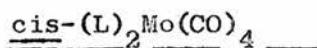
Calculation of force constants for the tetracarbonyl complexes was more difficult since the equations involved three force constants and four observed frequencies.

The calculation was first attempted by using part (A) of the programme to calculate values of λ and the L matrix from estimated force constants $k_1 = k_2 = 16.5 \text{ m.dyne/\AA}$, $k_3 = 0.25 \text{ m.dyne/\AA}$. Part (B) was then used to solve the equations

$$\Delta\lambda_i = \sum_{l,k} L_{il} L_{lk} \Delta F_{lk}$$

for three observed frequencies at a time for each compound. The force constants were thus calculated for each compound from the $A_1^{(2)}$, $A_1^{(1)}$, B_1 and the $A_1^{(2)}$, $A_1^{(1)}$, B_2 frequencies. When frequencies were calculated from the force constants which had been obtained the agreement between calculated and observed values was satisfactory, except for the frequency not used to obtain the force constants. Since the two sets of force constants obtained for each compound by this method did not agree, a different method of calculation was sought.

Force Constants for
Fluorophosphine Complexes

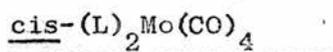


$$k_t = 2k_c$$

Ligand	Force Constants (m.dyne/Å)				Frequencies (cm. ⁻¹)			
	k ₁	k ₂	k _i	A ₁ ⁽²⁾	A ₁ ⁽¹⁾	B ₁	B ₂	
PF ₃				2091	2022	2022	2003 <u>obs.</u>	
	16.65	16.75	0.26	2091	2023	2014*	2004 <u>calc.</u>	
	16.73	16.65	0.27	2091	2023.5	2018	1996* <u>calc.</u>	
CF ₃ PF ₂				2094	2036	2036	2013 <u>obs.</u>	
	16.89	16.84	0.24	2094	2035.5	2030.5*	2013 <u>calc.</u>	
	16.99	16.70	0.25	2087	2024.5	2036	2002.5* <u>calc.</u>	
(CF ₃) ₂ PF				2093	2033	2033	2013 <u>obs.</u>	
	16.81	16.84	0.24	2093	2033	2025*	2018 <u>calc.</u>	
	16.95	16.65	0.26	2094	2031	2033	1998* <u>calc.</u>	
CCl ₃ PF ₂				2079	2015	2010	1990 <u>obs.</u>	
	16.56	16.51	0.26	2079	2014.5	2009*	1990 <u>calc.</u>	
	16.58	16.49	0.26	2079	2014.5	2010	1983* <u>calc.</u>	
Et ₂ NPF ₂ ¹⁰⁷				2055	1974	1950	1942 <u>obs.</u>	
	15.97	15.87	0.32	2055	1974.5	1968*	1942 <u>calc.</u>	
	15.65	16.33	0.27	2059	1976.5	1951	1970* <u>calc.</u>	
C ₅ H ₁₀ NPF ₂ ¹⁰⁷				2053	1977	1952	1942 <u>obs.</u>	
	16.02	15.85	0.31	2053	1976	1972*	1942 <u>calc.</u>	
	15.64	16.39	0.26	2058.5	1970	1952	1983* <u>calc.</u>	

* Frequency not used in the evaluation of the force constants.

Force Constants for
Fluorophosphine Complexes



$$k_t \neq 2k_c$$

<u>Ligand</u>	<u>Force Constants (m.dyne/Å)</u>				<u>Frequencies (cm.⁻¹)</u>			
	k_1	k_2	k_t	k_c	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2
PF ₃	16.70	16.74	0.54	0.19	2091	2022	2022	2003 <u>obs.</u>
					2091	2021	2022	2003 <u>calc.</u>
					2094	2036	2036	2013 <u>obs.</u>
CF ₃ PF ₂	16.94	16.84	0.47	0.20	2094	2036	2036	2013 <u>calc.</u>
					2093	2033	2033	2013 <u>obs.</u>
					2093	2033	2033	2013 <u>calc.</u>
(CF ₃) ₂ PF	16.87	16.84	0.48	0.18	2079	2015	2010	1990 <u>obs.</u>
					2079	2014.5	2010	1990 <u>calc.</u>
					2055	1974	1950	1942 <u>obs.</u>
CCl ₃ PF ₂	16.57	16.51	0.52	0.25	2079	2014.5	2010	1990 <u>calc.</u>
					2055	1974	1950	1942 <u>obs.</u>
					2055	1974	1951	1942 <u>calc.</u>
Et ₂ ¹⁰⁷ NPF ₂	15.83	15.87	0.64	0.46	2053	1977	1952	1942 <u>obs.</u>
					2053	1977	1952	1942 <u>obs.</u>
					2053	1976	1952	1942 <u>calc.</u>
C ₅ H ₁₀ ¹⁰⁷ NPF ₂	15.86	15.85	0.62	0.47	2053	1976	1952	1942 <u>calc.</u>
					2053	1976	1952	1942 <u>calc.</u>
					2053	1976	1952	1942 <u>calc.</u>

By omitting the substitution $k_t = 2k_c$, secular equations for the tetracarbonyl complexes were obtained which contained equal numbers of unknown and known parameters. An unambiguous solution was then possible.

The secular equations became:-

$$\begin{matrix} A_1^{(2)} \\ A_1^{(1)} \end{matrix} \begin{vmatrix} \mu(k_2 + k_t) - \lambda & \mu k_t \\ \mu k_t & \mu(k_1 + k_c) - \lambda \end{vmatrix} = 0$$

$$B_1 \quad \lambda = \mu(k_1 - k_c)$$

$$B_2 \quad \lambda = \mu(k_2 - k_t)$$

Primary force constants obtained by the application of the Wait-Slezak method were similar to those of the corresponding tricarbonyl complexes. The values of k_t and k_c showed that the approximation $k_t = 2k_c$ was not true, the ratio k_t/k_c varied with the ligand. This approximation and others involved in the derivation of Cotton's equations may have been responsible for the discrepancy between the two sets of force constants obtained in the first method used.

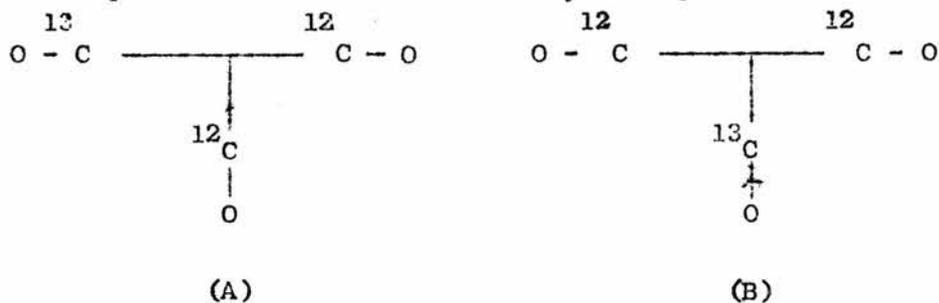
Mixing of vibrations could be seen from the potential energy distribution matrix which was included in the print out of part A of the programme. Mixing of the two A_1 modes was postulated as the main reason for the activity of the $A_1^{(2)}$ mode in the infrared and this was shown to occur to quite a large extent.

		$\%A_1^{(2)}$	$\%A_1^{(1)}$
$(PF_3)_2Mo(CO)_4$	$A_1^{(2)}$ mode	66	31
	$A_1^{(1)}$ mode	34	69
$(CCl_3PF_2)_2Mo(CO)_4$	$A_1^{(2)}$ mode	58	39
	$A_1^{(1)}$ mode	42	61

The total contributions shown do not equal 100% because of small off-diagonal terms. The B_1 and B_2 modes do not mix with any other vibrations.

The force constants obtained for both series of compounds were used in the calculation of the frequencies of absorptions due to the presence of one $^{13}C - O$ group in the molecule.

Inclusion of one $^{13}C - O$ group in a trans tricarbonyl complex produces one of two possible structures which may be represented as:-



Structure (A) is statistically twice as probable as (B) and should, therefore, produce stronger absorption bands in the spectra. The C_{2v} molecular symmetry is retained in (B), which will produce three vibrations of type $A_1^{(2)}$, $A_1^{(1)}$, B_1 symmetries. C_{2v} symmetry is lowered by the presence of a ^{13}C atom in (A) to C_s . Three vibrations are possible which belong to the A' representation although they correspond closely to the vibrations of the C_{2v} structure.

The G matrix used in the calculation of the frequencies was different for the two structures. The position of the reduced mass of the $^{13}\text{C} - \text{O}$ group in the matrix depended upon the site occupied by the ^{13}C atom in the molecule. Both the F and G matrices were used without simplification by symmetry transformations and were:-

$$\begin{array}{l}
 \text{F} = \\
 \\
 \text{G(A)} = \\
 \\
 \text{G(B)} =
 \end{array}
 \begin{array}{|ccc|}
 \hline
 k_2 & 2k_i & k_i \\
 \hline
 2k_i & k_2 & k_i \\
 \hline
 k_i & k_i & k_l \\
 \hline
 \mu^* & 0 & 0 \\
 \hline
 0 & \mu & 0 \\
 \hline
 0 & 0 & \mu \\
 \hline
 \mu & 0 & 0 \\
 \hline
 0 & \mu & 0 \\
 \hline
 0 & 0 & \mu^* \\
 \hline
 \end{array}$$

where μ^* = reduced mass of the $^{13}\text{C} - \text{O}$ group and the substitution $k_t = 2k_c$ has been made. Solution of the new secular equations by a programme provided by Dr. M. Webster, shown in the Appendix, gave frequencies which were close to the fundamental frequencies and, therefore, usually obscured by them. Some calculated values, however, did allow weak observed absorptions to be assigned to ^{13}C substituted isomers and so supported the chosen assignment.

Calculated and Experimental

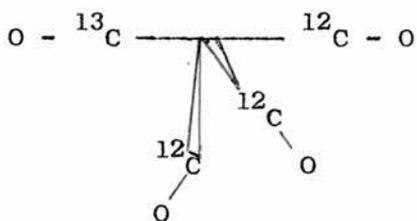
¹³C-O Frequencies of

trans-(L)₃Mo(CO)₃

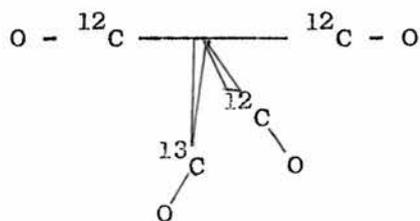
<u>L</u>	<u>Weak Bands</u> <u>Observed</u> (cm. ⁻¹)	<u>Calculated ¹³C-O</u>		<u>¹²C-O Frequencies</u>	
		<u>Positions</u> (cm. ⁻¹)		(cm. ⁻¹)	
		<u>A</u>	<u>B</u>		
PF ₃	2091, 2053, 1983, 1969	A' 2060	A ₁ ⁽²⁾ 2066.5	A ₁ ⁽²⁾	2072
		A' 2020	A ₁ ⁽¹⁾ 1982.5	A ₁ ⁽¹⁾	2023
		A' 1972	B ₁ 2003.5	B ₁	2003
CCl ₃ PF ₂	2055, 2050, 1976, 1957	A' 2051.5	A ₁ ⁽²⁾ 2057	A ₁ ⁽²⁾	2063
		A' 2008	A ₁ ⁽¹⁾ 1971	A ₁ ⁽¹⁾	2010
		A' 1957	B ₁ 1937.5	B ₁	1937
CF ₃ PF ₂	2070, 2001, 1980	A' 2070	A ₁ ⁽²⁾ 2075	A ₁ ⁽²⁾	2081
		A' 2034	A ₁ ⁽¹⁾ 1997	A ₁ ⁽¹⁾	2036
		A' 1983	B ₁ 2015	B ₁	2015
(CF ₃) ₂ PF	2091, 2072, 2057, 2003 1980	A' 2063	A ₁ ⁽²⁾ 2074.5	A ₁ ⁽²⁾	2080
		A' 2031.5	A ₁ ⁽¹⁾ 1993	A ₁ ⁽¹⁾	2033
		A' 1983	B ₁ 2015.5	B ₁	2015

The size of the shift in frequency depends upon the position of the ^{13}C atom in the molecule. In structure (A) the vibrations all have A' symmetry but those involving two trans carbonyls will be affected more than the third vibration which is influenced only by coupling to the other two. Since the ^{13}C atom is only involved in the $A_1^{(1)}$ vibration of the (B) form, the shift of that vibration will be the greatest; coupling to the $A_1^{(2)}$ mode will affect its frequency also, while the B_1 mode should be virtually unaffected.

The presence of a ^{13}C atom in the tetracarbonyl derivative can produce two possible structures, both equally probable:-

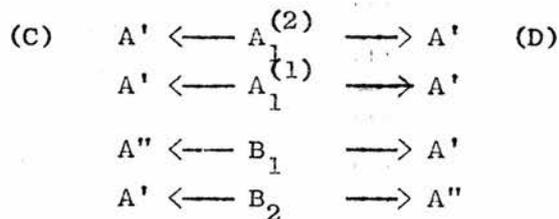


(C)



(D)

Both structures belong to the point group C_s . Four infrared active vibrations are allowed which span the representations $3A' + A''$. The vibrations may be related to those of the unsubstituted C_{2v} structure as follows:-



No alteration in the unfactored F matrix was needed when dealing with different structures but the G matrix was changed to correspond to the position of the ^{13}C atom in the molecule.

$$F = \begin{vmatrix} k_2 & k_t & k_c & k_c \\ k_t & k_2 & k_c & k_c \\ k_c & k_c & k_1 & k_c \\ k_c & k_c & k_c & k_1 \end{vmatrix}$$

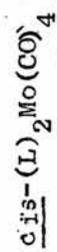
$$G(C) = \begin{vmatrix} \mu^* & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 \\ 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & \mu \end{vmatrix}$$

$$G(D) = \begin{vmatrix} \mu & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 \\ 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & \mu^* \end{vmatrix}$$

The calculated frequencies, shown in the Table, agree with the very weak absorptions found experimentally, although most of them are so close to the much stronger bands of the non-isotopically substituted molecule that they are obscured. In both (C) and (D) the A'' vibration absorbs at the same frequency as the corresponding B mode of the unsubstituted molecule, as expected, since it does not involve the vibration of a $^{13}\text{C} - \text{O}$ group nor is it coupled to a vibration which does. The increase in frequency of the highest frequency mode of $(\text{EtNPF}_2)_2\text{Mo}(\text{CO})_4$ and $(\text{C}_5\text{H}_{10}\text{NPF}_2)_2\text{Mo}(\text{CO})_4$ upon substitution of one ^{12}C by a ^{13}C atom is unexpected and not readily explicable. As predicted by the Teller-Redlich Product Rule, however, the total change in frequency of the

Calculated and Experimental

¹³C - O Frequencies of



<u>L</u>	<u>Weak Bands</u>		<u>¹³C - O</u>										<u>¹²C - O Frequencies</u>					
	<u>Observed</u> (cm. ⁻¹)		A'	A'	A''	A'	A'	A ₁ ⁽²⁾	A ₁ ⁽¹⁾	B ₁	B ₂							
PF ₃	2072	1983 1972	2070	2027	2022	1972	2079	2028	1933	2003	2091	2022	2022	2003				
CF ₃ PF ₂	2108	2080 1975	2080	2036	2036	1931	2084	2039	1996	2013	2094	2036	2036	2013				
(CF ₃) ₂ PF	2108	2076 1979	2076	2035	2033	1931	2082	2037	1993	2013	2093	2033	2033	2013				
CCl ₃ PF ₂	2068	1970 1953	2069	2011	2010	1953	2073	2014	1973	1990	2079	2015	2010	1990				
Et ₂ NPF ₂	2044	- -	2061	1954	1951	1911	2064	1955	1916	1942	2055	1974	1950	1942				
C ₃ H ₁₀ NPF ₂	-	- -	2063	1953	1953	1910	2065	1955	1917	1942	2053	1977	1952	1942				

four carbonyl stretching frequencies is about -45 cm.^{-1} .

The only frequencies which have not so far been assigned are those weakly visible at $2090 - 2110 \text{ cm.}^{-1}$ in several of the spectra. These are possibly due either to a combination or overtone vibration or to a trace impurity common to most of the preparations, which was not detected by other techniques.

The availability of C - O stretching force constants for the fluorophosphine molybdenum carbonyl complexes allows comparisons to be made with those of other neutral ligands already described in the literature.

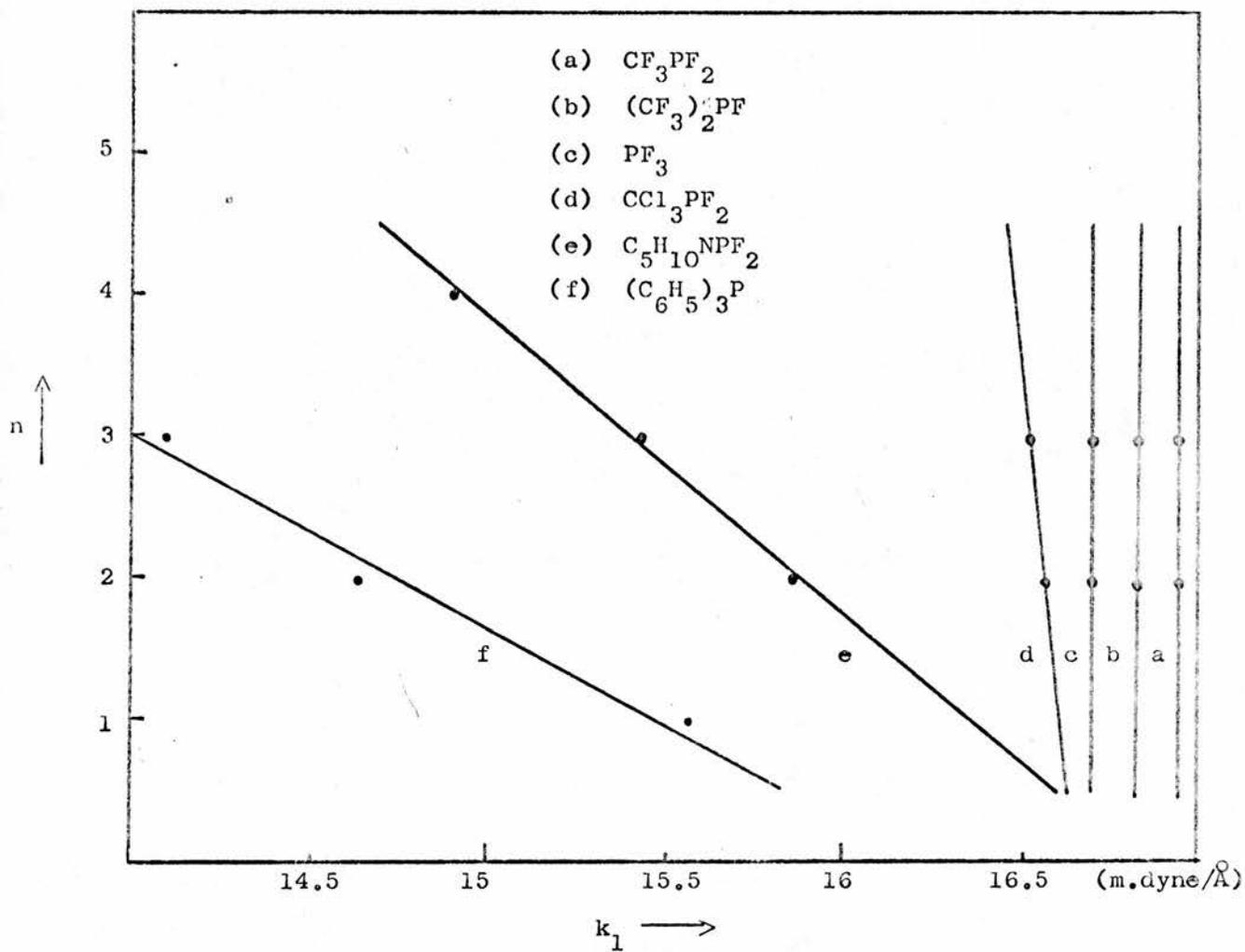
Representative values⁹³ for some complexes containing tertiary phosphines and amines illustrate the very much lower magnitude of the primary C - O stretching force constants and correspondingly larger value of k_i compared with those found for fluorophosphine complexes.

	k_1	k_2 (m. dyne/Å)	k_i
<u>cis</u> -(PCl ₃) ₂ Mo(CO) ₄	16.30	16.44	0.27
<u>trans</u> -(PCl ₃) ₃ Mo(CO) ₄	15.96	16.38	0.27
<u>cis</u> -(Pφ ₃) ₂ Mo(CO) ₄	14.64	15.41	0.35
<u>trans</u> -(PEt ₃) ₃ Mo(CO) ₃	13.86	14.49	0.37
<u>cis</u> -(C ₅ H ₅ N) ₂ Mo(CO) ₄	14.07	15.52	0.42
<u>cis</u> -(diethylenetriamine)Mo(CO) ₃	13.13	-	0.73

The observed trend suggests that in fluorophosphine molybdenum carbonyl complexes the carbon-oxygen bond order is larger than in these similar complexes. Likewise, the amount of π bonding between molybdenum and the carbonyl groups is reduced. The inference may be made that fluorophosphines have very strong π -accepting characteristics which closely parallel their σ bonding abilities towards transition metals.

In all the fluorophosphine molybdenum carbonyl complexes k_1 and k_2 are of comparable magnitude, indeed k_1 is sometimes equal to or greater than k_2 , although the approximations inherent in the calculation limit the significance of this result. In Cotton's original treatment⁴⁶ k_2 was of necessity greater than k_1 , but in this case all the ligands considered had poorer π -acceptor characteristics than CO itself. The fact that in fluorophosphine complexes k_1 and k_2 are almost equal lends support to the suggested similarity in π -acceptor characteristics of carbon monoxide and the fluorophosphines.

Further evidence for the unusual properties of fluorophosphine ligands is provided by a graph of k_1 against n for the series $L_n Mo(CO)_{6-n}$. When L is $(C_6H_5)_3P$, k decreases as n increases in accord with Cotton's predictions. The slope of the line decreases for $L = C_5H_{10}NPF_2$ or CCl_3PF_2 and, finally, when $L = PF_3$, CF_3PF_2 or $(CF_3)_2PF$ the lines are vertical, indicating that increasing replacement of carbon monoxide by the latter three ligands does not alter the bond order of the remaining carbonyl groups.



Graph of the carbonyl stretching force constants against n for complexes $(L)_n Mo(CO)_{6-n}$

Also interesting is the increasing slope of the lines as k increases while n is stationary.

The force constant obtained by Cotton⁴⁶ for $\text{Mo}(\text{CO})_6$, 16.52 m.dyne/ \AA , is smaller than the equivalent force constants, k_2 , found for the molybdenum carbonyl complexes of PF_3 , $(\text{C}_3\text{F}_7)_2\text{PF}$, $(\text{CF}_3)_2\text{PF}$ and CF_3PF_2 , indicating that the latter may have equal or greater π -acceptor abilities than carbon monoxide. Again, however, the approximations involved in the calculations greatly diminish the importance which can be attached to such comparisons of compounds of different symmetries.

It does not necessarily follow that the fluorophosphines are similar π -acceptors to carbon monoxide. The same effect on the carbon-oxygen bond could be produced if they donated less through the σ bond and accepted correspondingly less in the π bond.

An increase in the electronegativity of the substituents on the phosphorus atom might be expected to produce an increase in metal-phosphorus $d_\pi - d_\pi$ bonding by reducing the electron density at the phosphorus atom and also lowering the energy of its unoccupied d_π orbitals. This effect should reach a maximum in phosphorus trifluoride. Opposing the high electronegativity of fluorine, however, is its $p_\pi - d_\pi$ bond with phosphorus which competes with any metal back π bond for the unoccupied phosphorus d_π orbitals. Since the values of $\bar{\nu}_{\text{P-F}}$ increase upon the co-ordination of phosphorus trifluoride in the molybdenum tri and tetracarbonyl complexes, it appears that the $p_\pi - d_\pi$ bonding is greater in the complex than in the free ligand.

The expected maximum of the primary carbonyl stretching force constants for the trifluorophosphine complexes is not observed in the molybdenum carbonyl complexes nor in similar derivatives of nickel tetracarbonyl reported⁸⁹ when the present study was almost complete. The primary carbonyl stretching force constants of the complexes of CF_3PF_2 and $(\text{CF}_3)_2\text{PF}$ with molybdenum carbonyl are higher than those of the corresponding trifluorophosphine derivatives, suggesting that trifluoromethylfluorophosphines have stronger π -acceptor properties than PF_3 itself.

Although the replacement of fluorine by a trifluoromethyl group decreases the total electronegativity of the groups on phosphorus, the inability of CF_3 to π bond to phosphorus more than compensates by leaving the phosphorus d_{π} orbitals more readily available for the formation of the back π bond. Replacement of a second fluorine atom has little further effect on the force constants, suggesting that $\text{P} \leftarrow \text{F} \pi$ bonding is less important in CF_3PF_2 than in PF_3 and that the diminution caused by the introduction of the second CF_3 group parallels the decreased electronegativity of the CF_3 . Unfortunately the carbonyl region of the infrared spectrum of cis- $[(\text{CF}_3)_3\text{P}]_2\text{Mo}(\text{CO})_4$ is difficult to assign, but recent studies⁸⁹ on nickel carbonyl derivatives of $(\text{CF}_3)_3\text{P}$ indicate that the replacement of the third fluorine atom by CF_3 also has little effect upon the π -acceptor ability of the phosphorus atom.

Force Constants for Some
cis-(L)₃Mo(CO)₃ Complexes

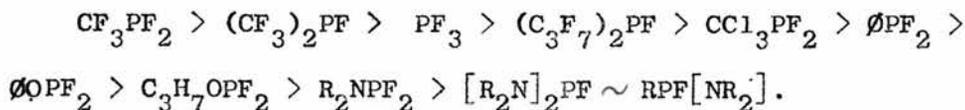
<u>L</u>	<u>Frequencies</u> (cm. ⁻¹)		<u>Force Constants</u> (m.dyne/Å)		<u>Reference</u>
	<u>A₁</u>	<u>E</u>	<u>k</u>	<u>k_i</u>	
(CH ₃) ₂ NPF ₂	2000	1923	15.34	0.41	111
(C ₂ H ₅) ₂ NPF ₂	1995	1919	15.27	0.40	111
C ₅ H ₁₀ NPF ₂	1996	1934	15.43	0.33	111
[(CH ₃) ₂ N] ₂ PF	1969	1873	14.71	0.47	112
C ₃ H ₇ OPF ₂	2020	1947	15.70	0.39	113
C ₆ H ₅ OPF ₂	2025	1954	15.80	0.38	113
C ₆ H ₅ PF ₂	2035	1955	15.86	0.43	71
CH ₃ PF[N(CH ₃) ₂]	1970	1882	14.76	0.46	112
C ₆ H ₅ PF[N(C ₂ H ₅) ₂]	1960	1873	14.71	0.47	112
CH ₂ ClPF ₂	2038	1970	16.04	0.37	114
(C ₅ H ₁₀ NPF ₂) ₄ Mo(CO) ₂	1946	1897	14.91	0.38	111

Examination of the values of $\sqrt{\nu_{P-F}}$ for the complexes of CF_3PF_2 and $(CF_3)_2PF$ shows that there is no general increase or decrease over the values for the unco-ordinated fluorophosphines. The $P \leftarrow F \pi$ bond in CF_3PF_2 and $(CF_3)_2PF$ is little changed upon co-ordination, therefore, and does not counteract any back π -bonding from the metal.

Cotton's secular equations have been used to calculate the force constants of some molybdenum carbonyl complexes of other phosphorus-fluorine ligands in order to compare them with the fluorophosphine complexes. The electronegativity of the substituents is clearly very important in influencing the values of the force constants.

The lowest C - O force constants are found for the alkylamino-fluorophosphines. Not only does the amino group, R_2N- , have a lower overall electronegativity¹⁰⁹ but also the $p_\pi - d_\pi$ bonding¹¹⁰ between the nitrogen and phosphorus can reduce the availability of phosphorus d_π orbitals needed to form the metal-phosphorus π bond.

The phosphorus-fluorine ligands may be placed in an approximate series in order of their decreasing π -acceptor ability from a comparison of the C - O stretching force constants of their carbonyl complexes:-



It is noteworthy that $[R_2N]_2PF$ is a poorer π acceptor than R_2NPF_2 as expected if the $p_\pi - d_\pi$ N \longrightarrow P bond is present.

This study has shown the similarity between fluorophosphines and carbon monoxide in their ability to bond to a zero-valent transition metal. The electronegativity of the substituents on phosphorus is important in determining the bonding ability of a phosphine. Certain trends, however, can best be explained by invoking other factors which can affect the metal-phosphorus π bond. These observations, therefore, give support to the importance of the π back bond in determining the bonding ability of a ligand to a zero-valent transition metal.

The fluorophosphines, including phosphorus trifluoride, appear to be the best π -accepting phosphine ligands so far investigated.

Since the fluorophosphines by definition contain phosphorus and fluorine nuclei, both of which have a spin of $\frac{1}{2}$, it was hoped to obtain more information about the phosphorus to metal bonding by the examination of the changes in the nuclear magnetic resonance parameters produced by the bonding.

Infrared Spectra

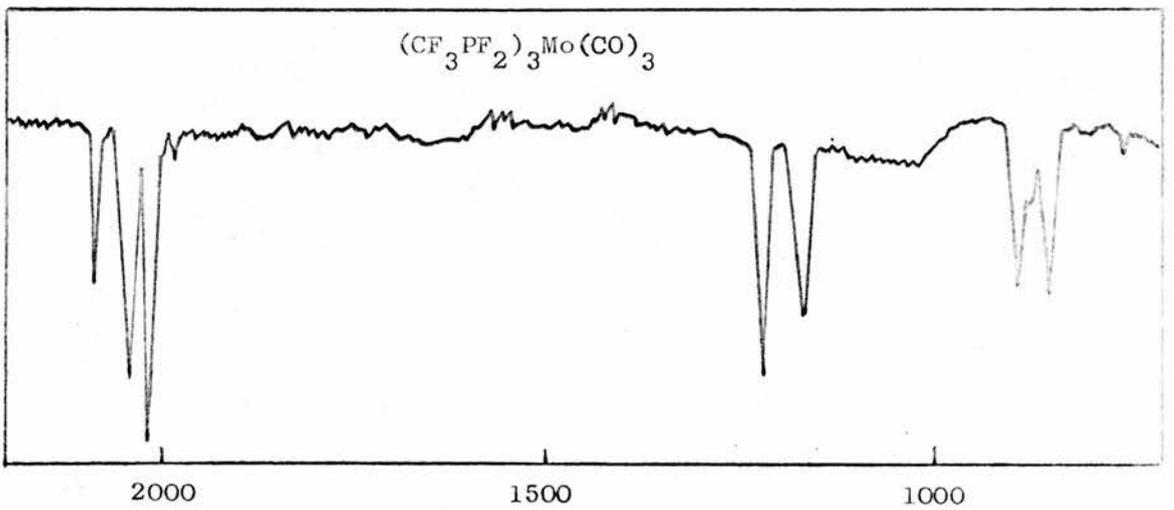
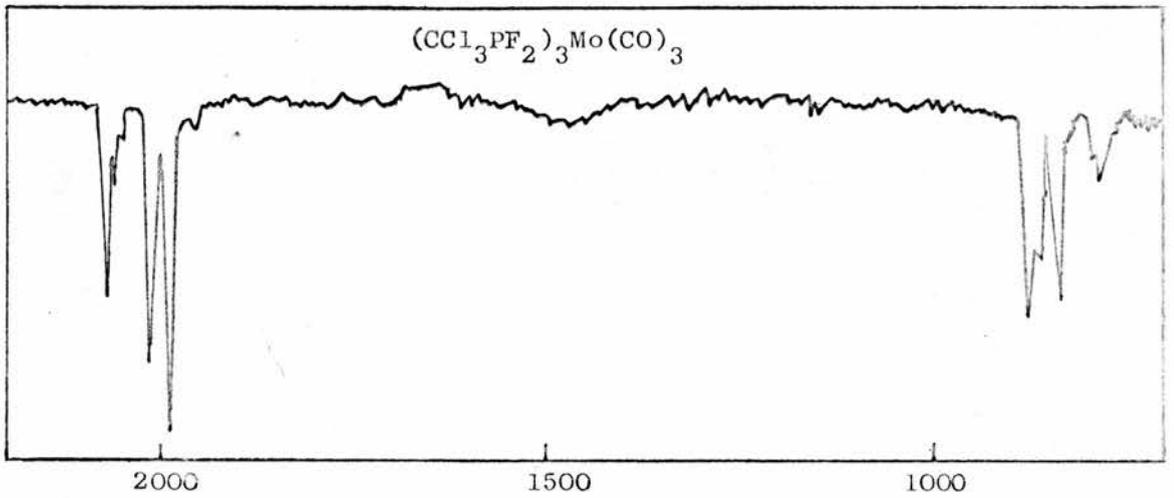
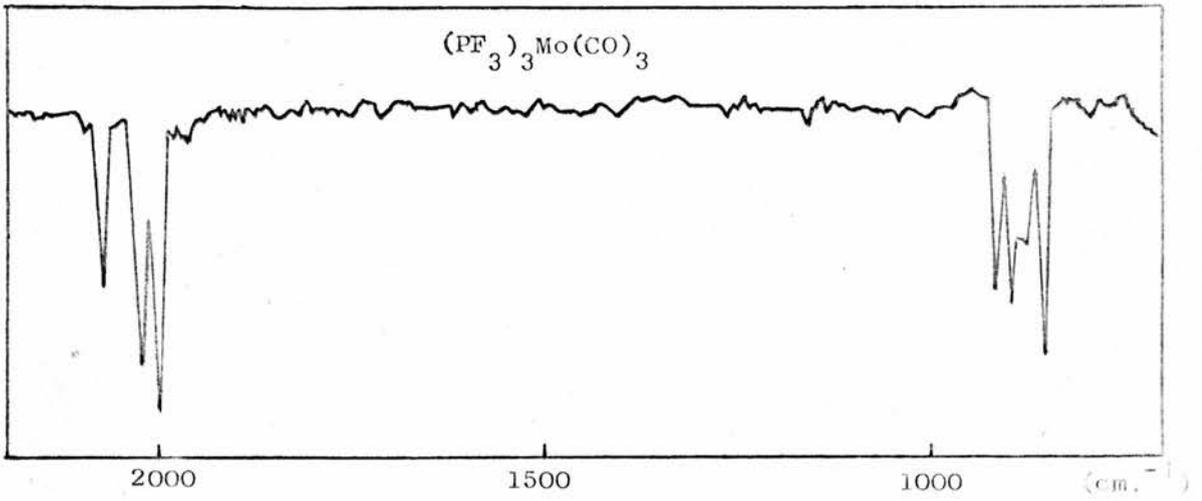
trans-(L)₃Mo(CO)₃

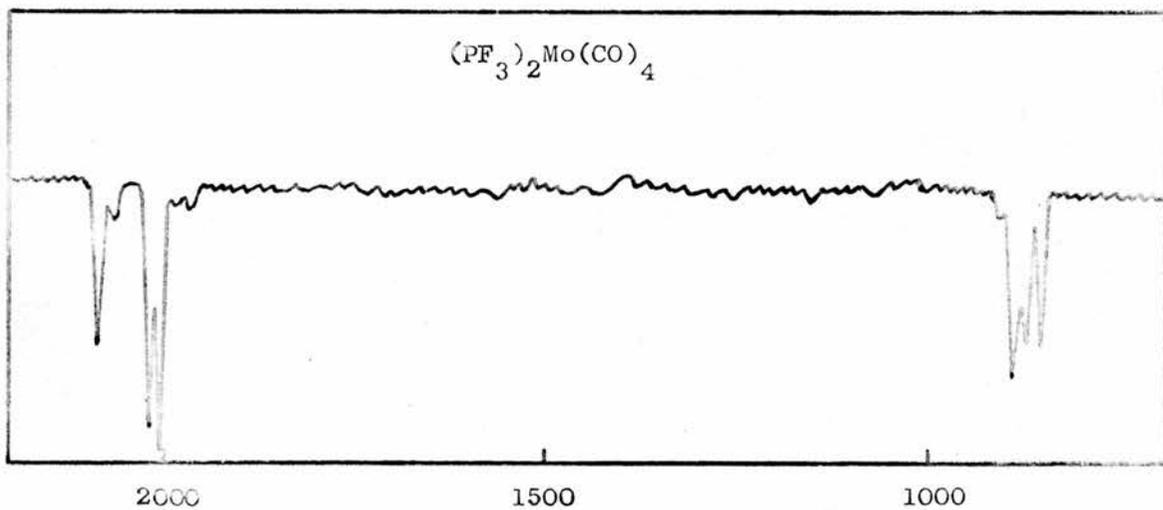
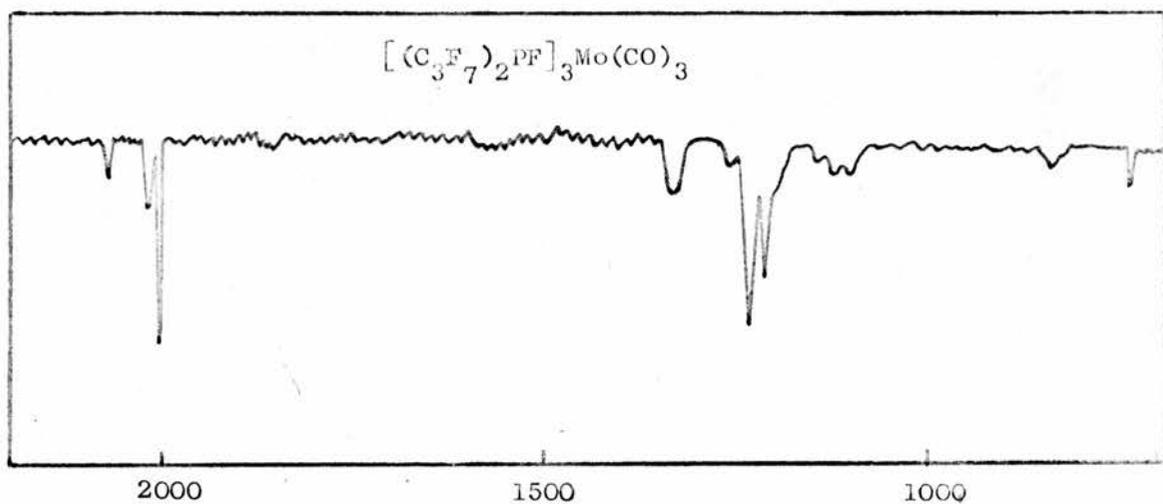
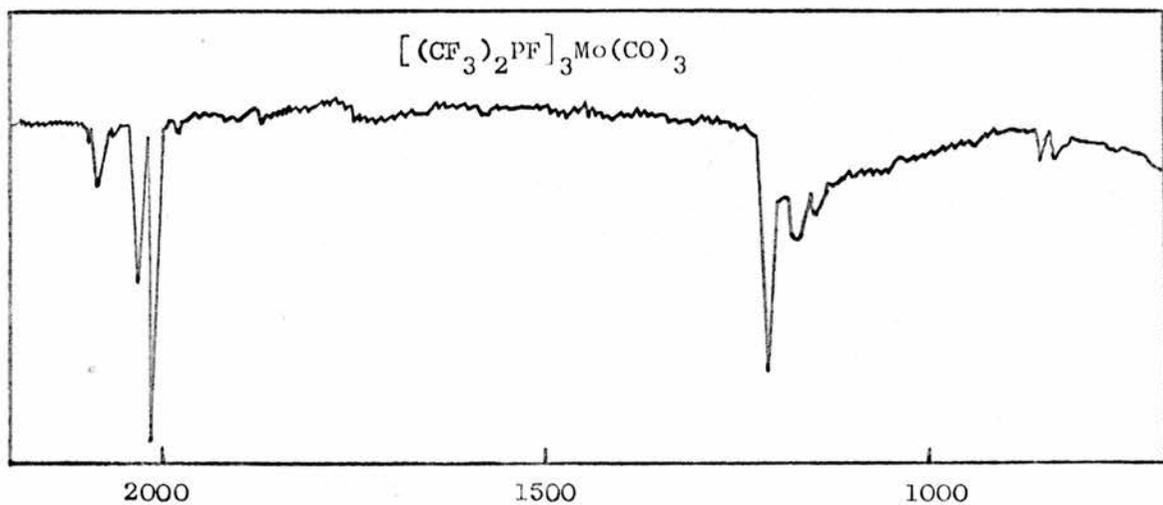
L =	PF ₃	CCl ₃ PF ₂	CF ₃ PF ₂	(CF ₃) ₂ PF ₂	(C ₃ F ₇) ₂ PF [*]	
phase	vapour	solution (hexane)	vapour	vapour	solution (hexane)	(cm. ⁻¹)
	2091 vw			2091 vw		
	<u>2072 m</u>	<u>2064 m</u>	<u>2031 m</u>	<u>2031 m</u>	<u>2063 m</u>	
	2053vw	2055 vw	2070 vw	2072 vvw	<u>2013 m</u>	
	<u>2022 s</u>	2050 vvw	<u>2033 s</u>	2057 vvw	<u>2004 s</u>	
	<u>2003 vs</u>	<u>2010 s</u>	<u>2015 vs</u>	<u>2033 s</u>		
	1983 vw	<u>1987 vs</u>	2001 vvw	<u>2015 vs</u>		
	1969 w	1976 vvw	1980 vw	2003 vvw		
		1957 vw		1980 vw		
					1330 m	
			1212 s	1211 s	1238 s	
			1167 s	1176 m	1216 s	
				1151 m	1150 w	
					1133 w	
	914 m	873 s	836 m	855 w	844 w, br.	
	893 m	865 m	846 m	845 w	740 w	
	874 m	829 s	750 w		672 w	
	856 s	786 w, sh				
		773 w				

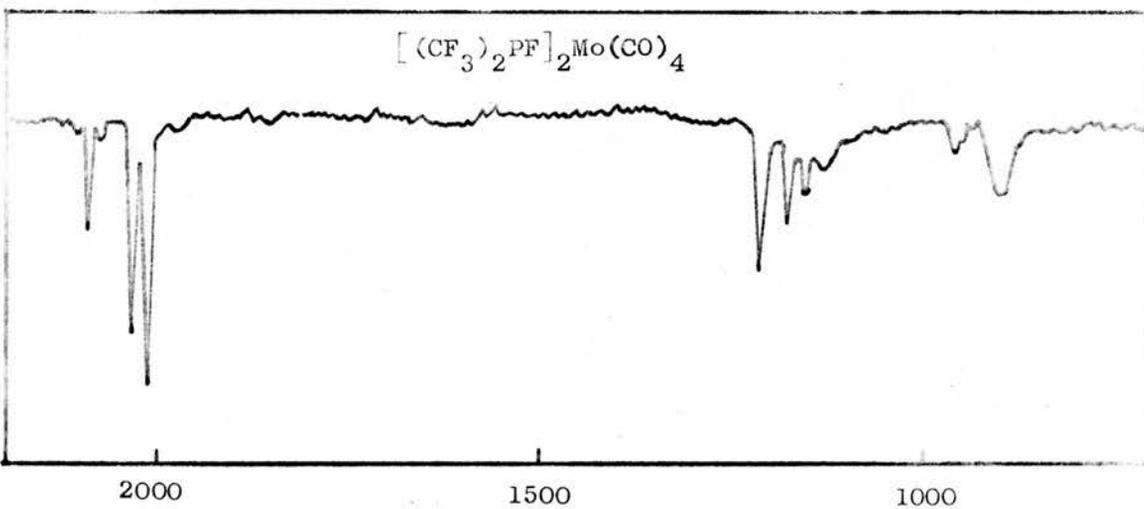
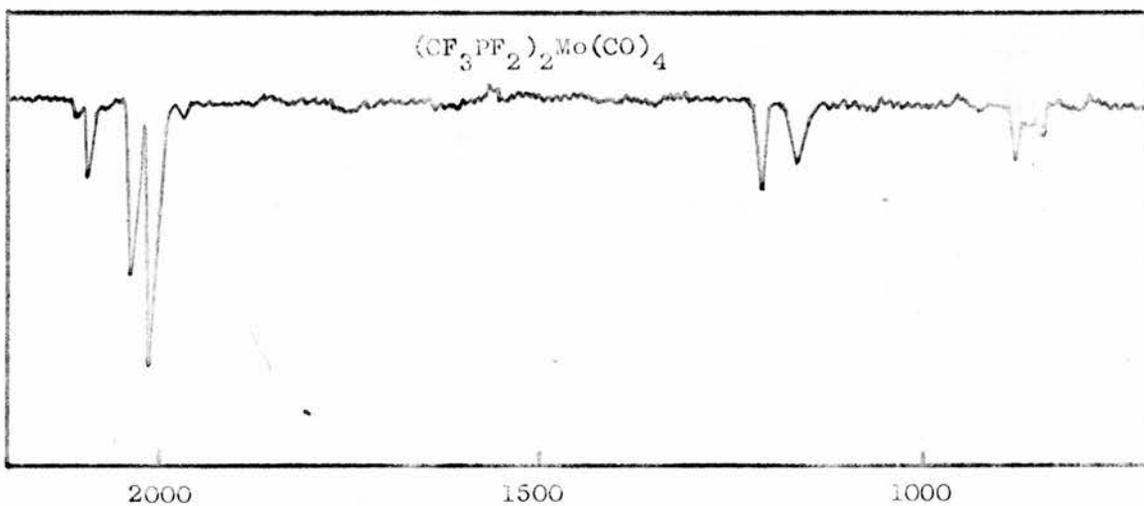
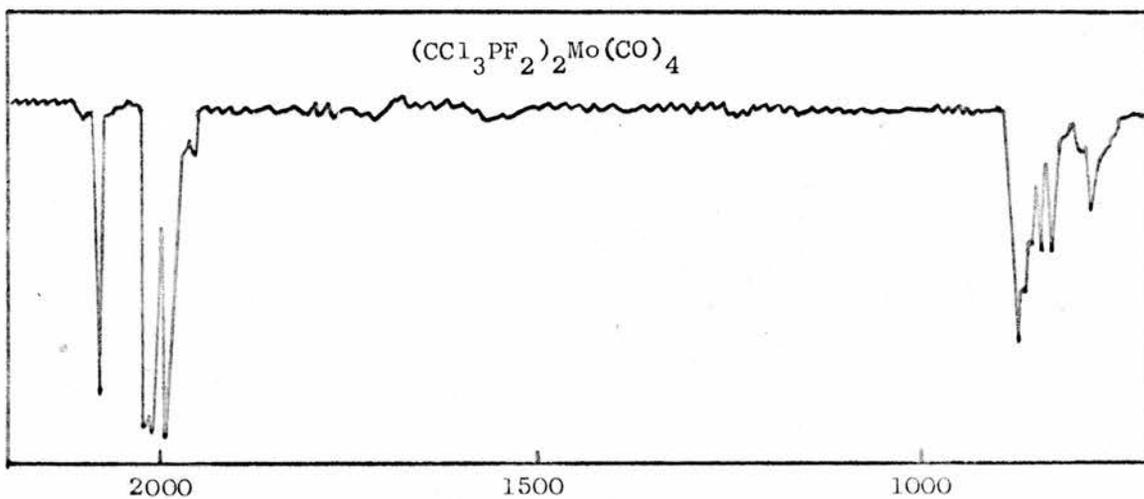
* Recorded on 237 Infracord.

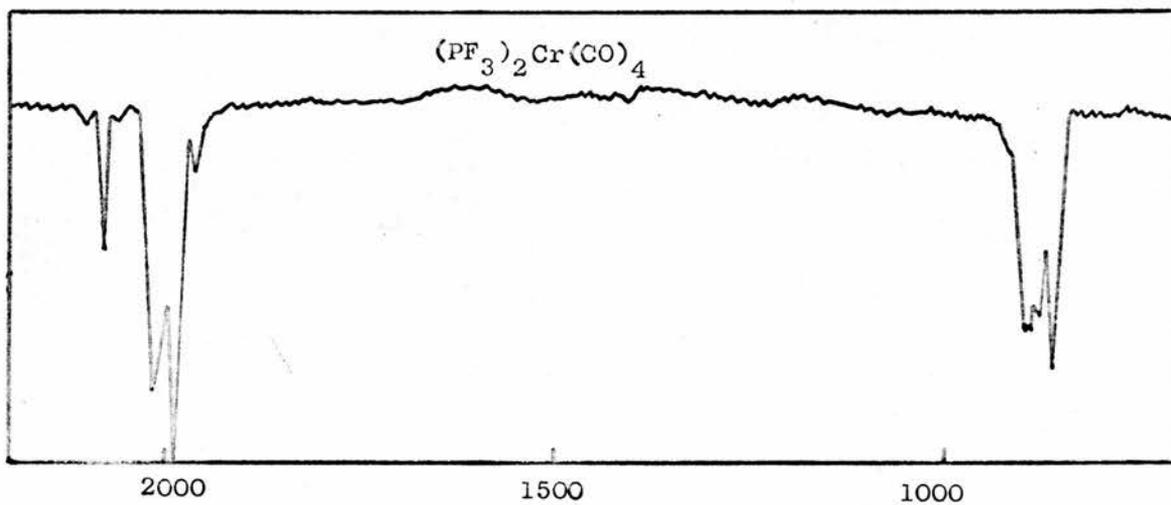
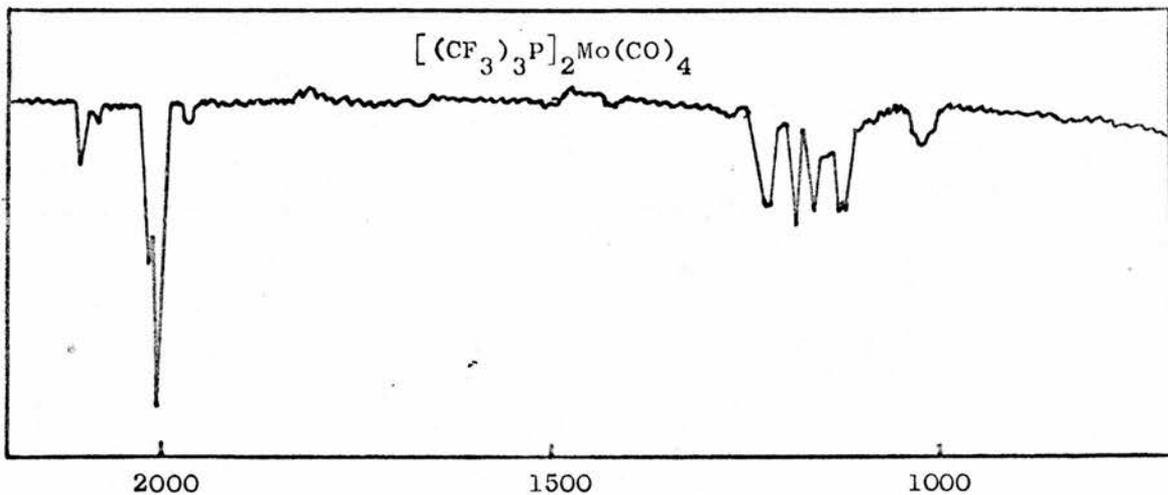
cis-(L)₂Mo(CO)₄

L =	PF ₃	CCl ₃ PF ₂	CF ₃ PF ₂	(CF ₃) ₂ PF	(CF ₃) ₃ P	(PF ₃) ₂ Cr(CO) ₄	
phase	vapour	solution (hexane)	vapour	vapour	vapour	vapour	
			2108 vw	2108 vw	2104 w	2100 vw	(cm. ⁻¹)
<u>2091 m</u>	<u>2079 m</u>	<u>2094 m</u>	<u>2093 m</u>	<u>2084 vw</u>	<u>2083 m</u>		
2072 w	2068 vw	2080 vw	2076 vw	<u>2018 s</u>	2060 vw		
<u>2022 s</u>	<u>2015 s</u>	<u>2036 s</u>	<u>2033 s</u>	<u>2007 vs</u>	<u>2015 s</u>		
<u>2003 vs</u>	<u>2010 s</u>	<u>2013 vs</u>	<u>2013 vs</u>	1970 w	<u>1990 vs</u>		
1983 w	1990 vs	1975 w	1979 w		1960 w		
1972 vw	1970 vw						
	1958 w						
		1212 m	1212 m	1222 m			
		1166 m	1176 m	1184 s			
			1151 m	1183 s			
			1133 vw	1153 m			
				1130 m			
				1126 m			
898 s	872 s	875 w	858 vw		896 s		
879 m	867 sh	862 w	840 vw		892 s		
858 m	858 m, sh	850 w	799 w		878 m		
	844 m				859 s		
	829 m						
	785 w, sh						
	772 m						









Nuclear Magnetic Resonance Spectra

The ^{19}F and ^{31}P isotopes (having nuclear spins of $I = \frac{1}{2}$) are the only isotopes of these two elements which occur naturally. In addition, since the difference in the chemical shifts of the two nuclei is usually far larger than the spin-spin coupling between them, the nuclear magnetic resonance spectra of phosphorus-fluorine containing compounds are invariably first order. It is, therefore, possible to use nuclear magnetic resonance spectroscopy as an aid in the determination of the structures of such compounds. The coupling constant, $J_{\text{P-F}}$, is very large and varies over a considerable range depending upon the compound ¹¹⁴ and the other coupling constants found in $\text{CF}_3 - \text{P} - \text{F}$ compounds may be arranged in order of their magnitude:- $J_{\text{P-F}} \gg J_{\text{P-CF}_3} \gg J_{\text{F-F}}$.

From the general trends in chemical shifts and coupling constants found by the examination of phosphorus and fluorine spectra of a large series of phosphorus-fluorine compounds, it has been shown ^{114, 77} that the parameters can give an indication of the structure of a compound. An application of such measurements was in the determination of the correct structures of the reported $\text{C}_2\text{H}_5\text{PF}_2$ and $\text{C}_2\text{H}_5\text{PClF}$ ⁶⁸ which were shown ¹¹⁵ to be $\text{C}_2\text{H}_5\text{PF}_4$ and $\text{C}_2\text{H}_5\text{POF}_2$.

Unlike the chemical shifts of protons, those of other magnetic nuclei, such as phosphorus or fluorine, are not determined by the electron density about the nucleus. A larger contribution to the shielding or de-shielding of the nucleus, of such elements, arises from a paramagnetic effect caused by the anisotropic electron-environment of the nucleus. In the presence of the applied magnetic field, ground and excited electronic states may mix, allowing partial occupancy of the excited levels. In covalent fluorine compounds for instance, the three 2p orbitals are not equally occupied and the mixing with excited levels produces an anisotropic environment for the nucleus. The paramagnetic term is zero, however, for the fluoride ion which has its 2p orbitals equally occupied. Since the energy difference between the ground and excited levels is much larger for bonds which involve protons, the paramagnetic shielding only contributes a few parts per million to the ^1H chemical shift.

It is the large variation in the paramagnetic term which causes the observed wide variation in the shielding of magnetic nuclei other than the proton.

The electronegativity of a group bonded to an atom may affect its chemical shift by increasing or decreasing the ionic character of the bond and hence the paramagnetic contribution to the shielding of the nucleus. The effect of the electronegativity of X in a series of trivalent phosphorus-fluorine compounds $\text{X} - \text{PF}_2$ has been studied.¹¹⁶ It was found that as the electronegativity increased, δ_{P} increased due to greater ionic bonding of the phosphorus and δ_{F}

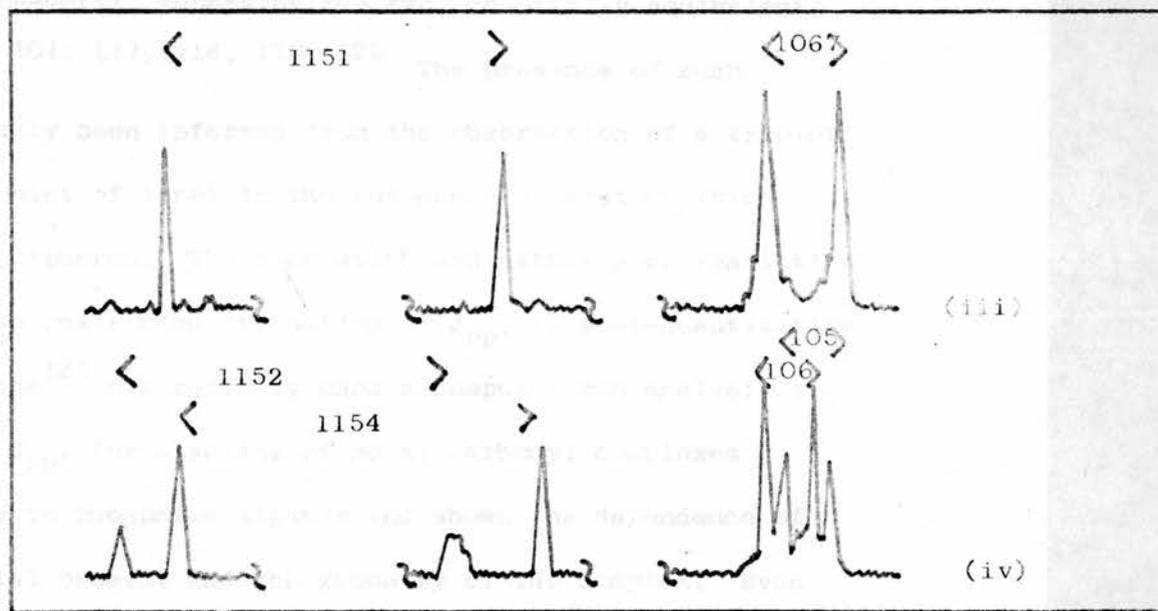
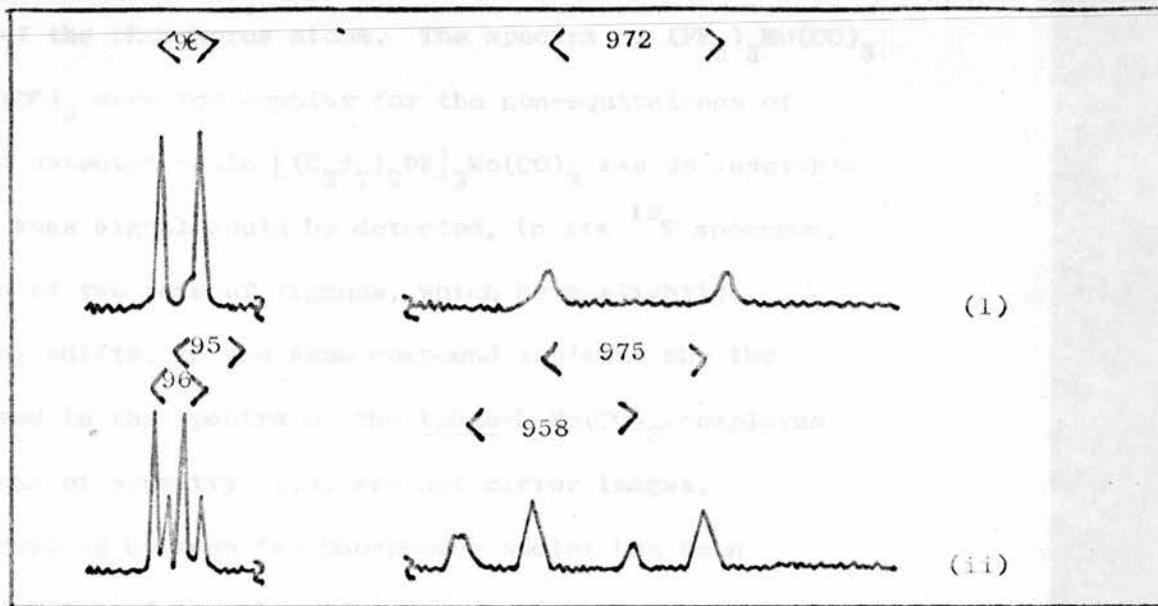
decreased since the decreased electron density at phosphorus lowered the ionic character of the P - F bond.

The coupling constant J_{P-F} was found to increase with increasing electronegativity of X, an observation which supports the importance of the s character of a bond in determining the value of the coupling constant between two magnetic nuclei.

The nuclear magnetic resonance spectra of the complexes showed the number of lines expected from the structure of the ligands, with the correct size of coupling constants, but on closer examination, considerable further fine detail was often visible in each resonance. The interpretation of this detail will be discussed for the complexes $(PF_3)_2Mo(CO)_4$ and $(CCl_3PF_2)_2Mo(CO)_4$.

The CF_3 and P - F fluorine resonances of $[(CF_3)_2PF]_3Mo(CO)_3$ and $(CF_3PF_2)_3Mo(CO)_3$ were each split into a pair of overlapped doublets from coupling with the phosphorus nucleus, with each pair in a 2:1 intensity ratio. This was in contrast to the corresponding resonances of $[(CF_3)_2PF]_2Mo(CO)_4$ and $(CF_3PF_2)_2Mo(CO)_4$ which were simple doublets. The distinctly different types of CF_3 and P - F groups in the tricarbonyl complexes is regarded as evidence supporting their formulation as trans isomers containing two ligands trans to each other while the third is trans to a carbonyl group. This evidence thus corroborates the conclusions obtained from the infrared spectra. Unfortunately, the phosphorus spectra obtained from these two tricarbonyl complexes were so weak that only the strongest lines were visible, so prohibiting the detection of

non-e
and (
the l
that
diffe
multi
do no
obser
atom,
phosp
coupl
rather
are c
obtai
estim
obtai
conta
J_{pp'}
with
large

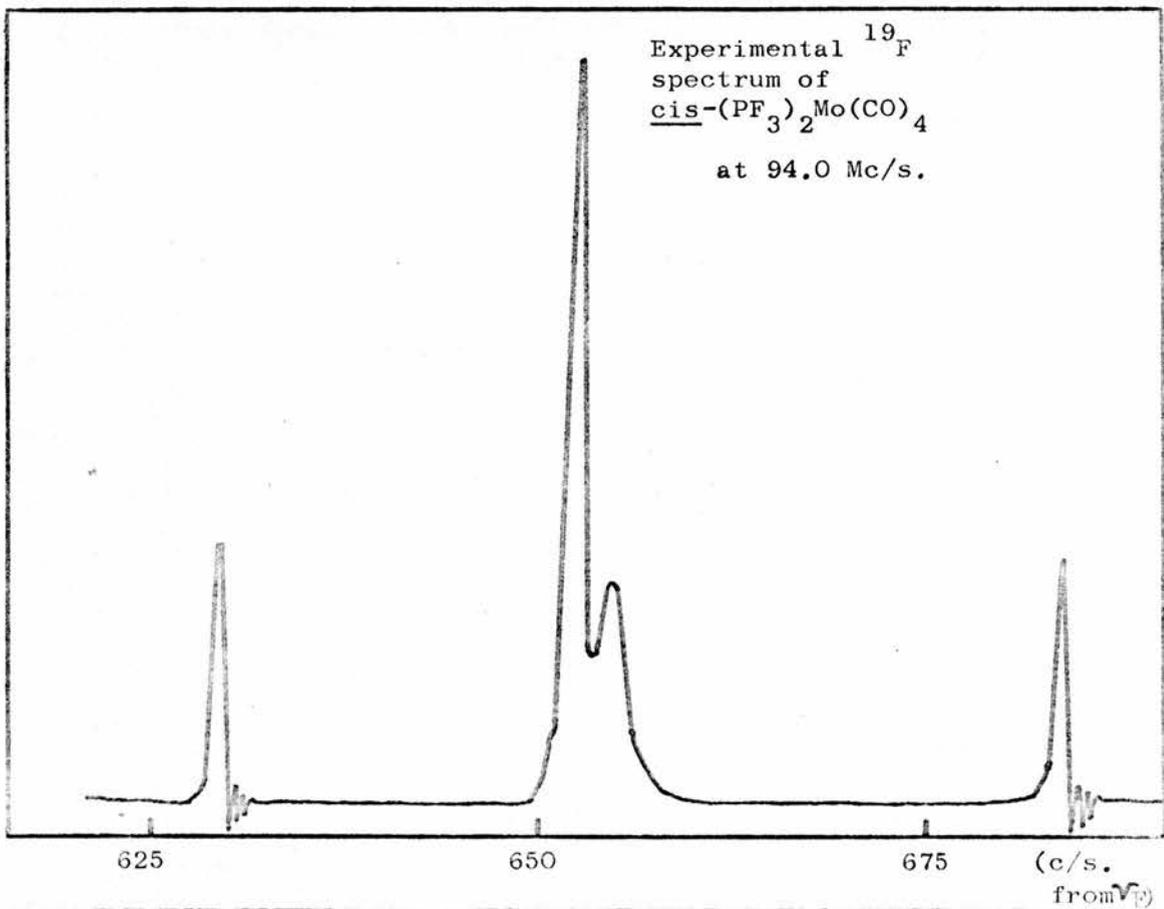


¹⁹F spectra of

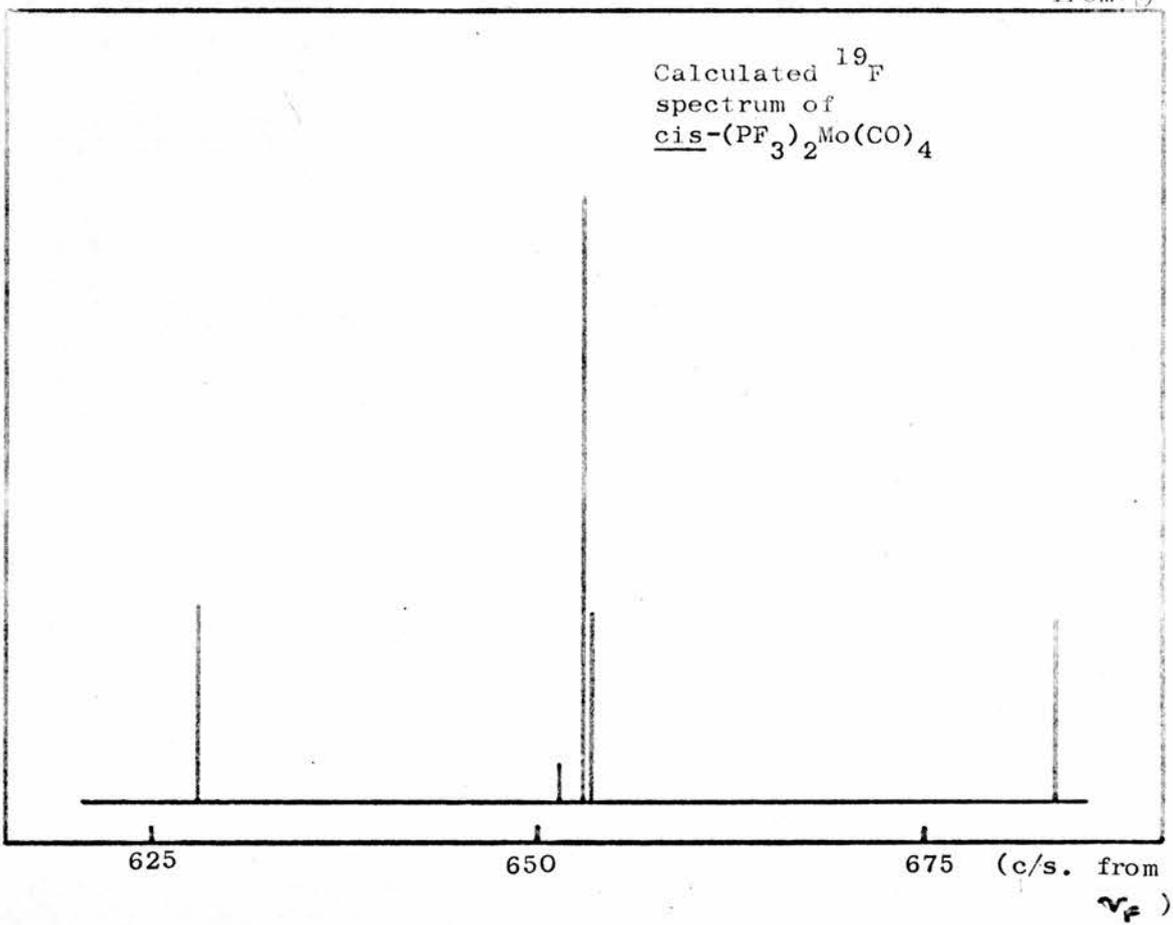
- (i) cis-[(CF₃)₂PF]₂Mo(CO)₄ (iii) cis-[CF₃PF₂]₂Mo(CO)₄
(ii) trans-[(CF₃)₂PF]₃Mo(CO)₃ (iv) trans-[CF₃PF₂]₃Mo(CO)₃

Splittings are given in c/s.

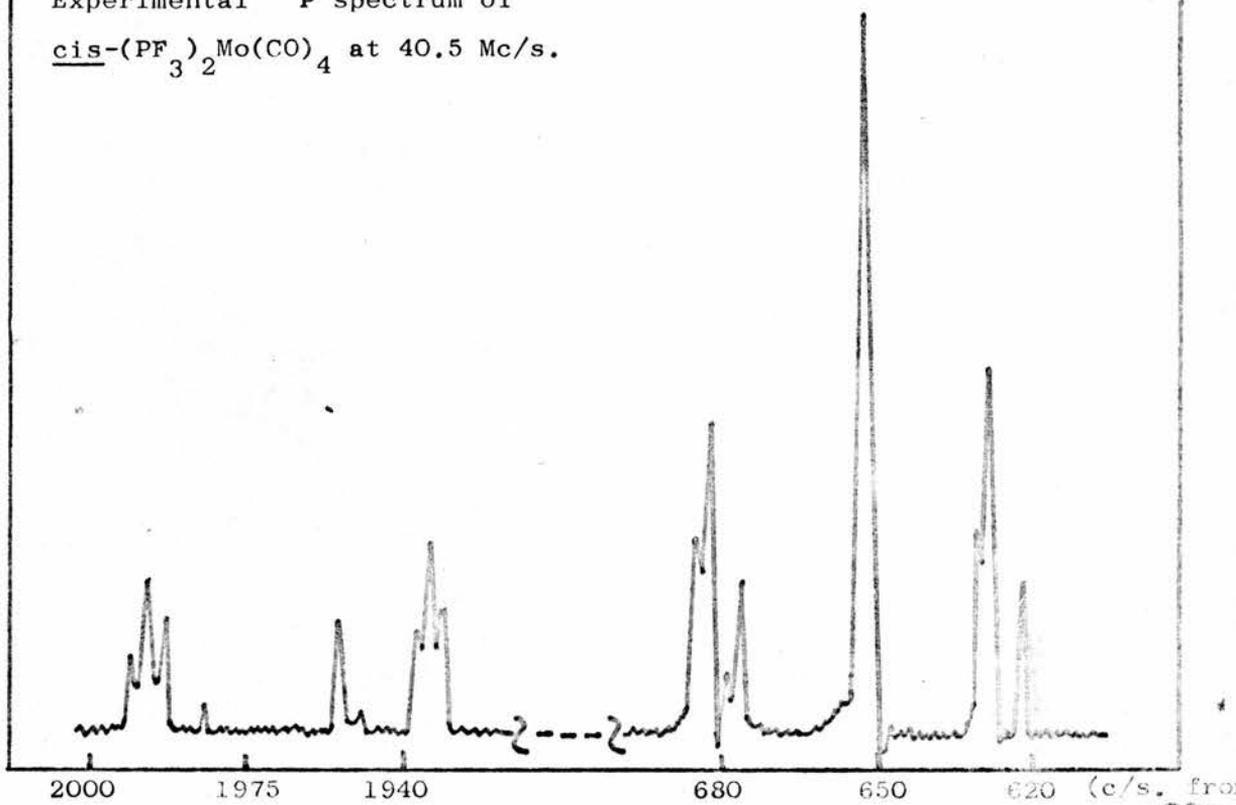
Experimental ^{19}F
spectrum of
 $\text{cis}-(\text{PF}_3)_2\text{Mo}(\text{CO})_4$
at 94.0 Mc/s.



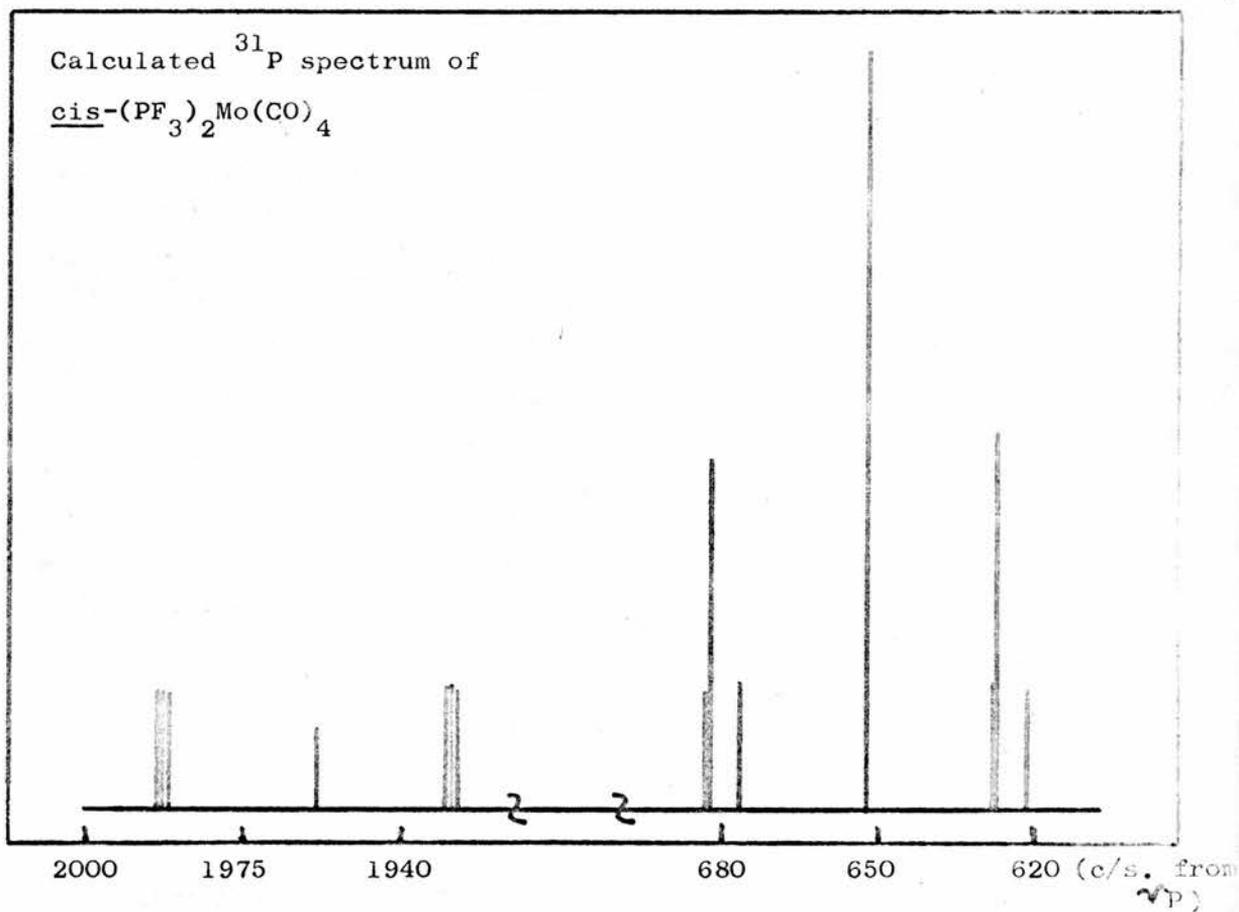
Calculated ^{19}F
spectrum of
 $\text{cis}-(\text{PF}_3)_2\text{Mo}(\text{CO})_4$



Experimental ^{31}P spectrum of
cis- $(\text{PF}_3)_2\text{Mo}(\text{CO})_4$ at 40.5 Mc/s.



Calculated ^{31}P spectrum of
cis- $(\text{PF}_3)_2\text{Mo}(\text{CO})_4$



In an attempt to determine the effect of the metal upon the size of $J_{PP'}$, the preparation of $\text{cis}-(\text{PF}_3)_2\text{Cr}(\text{CO})_4$ was attempted. Unfortunately, the more vigorous conditions needed appeared to cause rearrangement of the product since the fluorine spectrum contained more lines than expected for an $X_3AA'X'_3$ system, and the doublet was not symmetrical about its centre.

The only other complex for which the theoretical spectrum has been calculated is $\text{cis}-(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ which is an $X_2AA'X'_2$ spin system. Application of Harris'¹²⁴ equations for the $X_nAA'X'_n$ system to the irregular triplets obtained as the fluorine spectrum of this compound yielded the values:-

$$J_{PF} = 1194 \text{ c/s.}$$

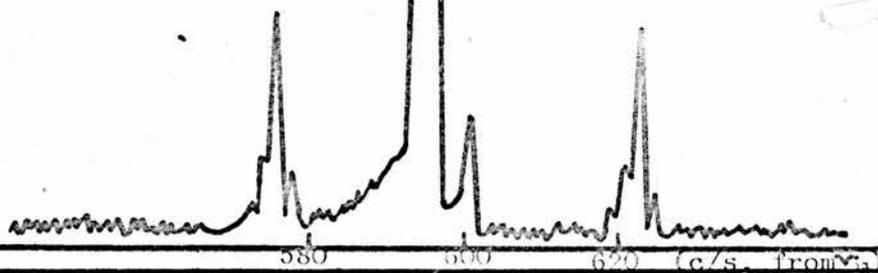
$$J_{PF'} = -4 \text{ c/s.}$$

$$J_{PP'} = 48 \text{ c/s.}$$

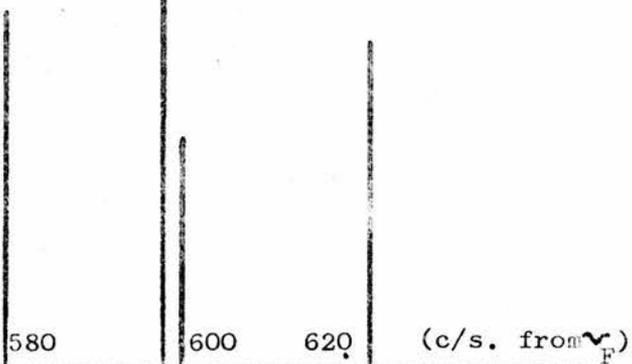
Using these the remaining pair of doublets were calculated to have splittings of 1196 c/s. and 3592 c/s.. The former were visible in the spectrum (as a pair of lines with a splitting of 1200 c/s.) but the latter, calculated to have zero intensity, were not observed experimentally. Further fine structure was clearly present on each of the outer two lines of each triplet and was symmetrically placed about ν_F , suggesting that the system could be more complex with $J_{FF'} \neq 0$ and even with non-equivalence of fluorine atoms on the same phosphorus atom. The theoretical treatment for this more complex system has been reported,¹²⁵ and it is hoped that by computer analysis of the spectrum, more complete information will be available.

Experimental ^{19}F
spectrum of
cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$

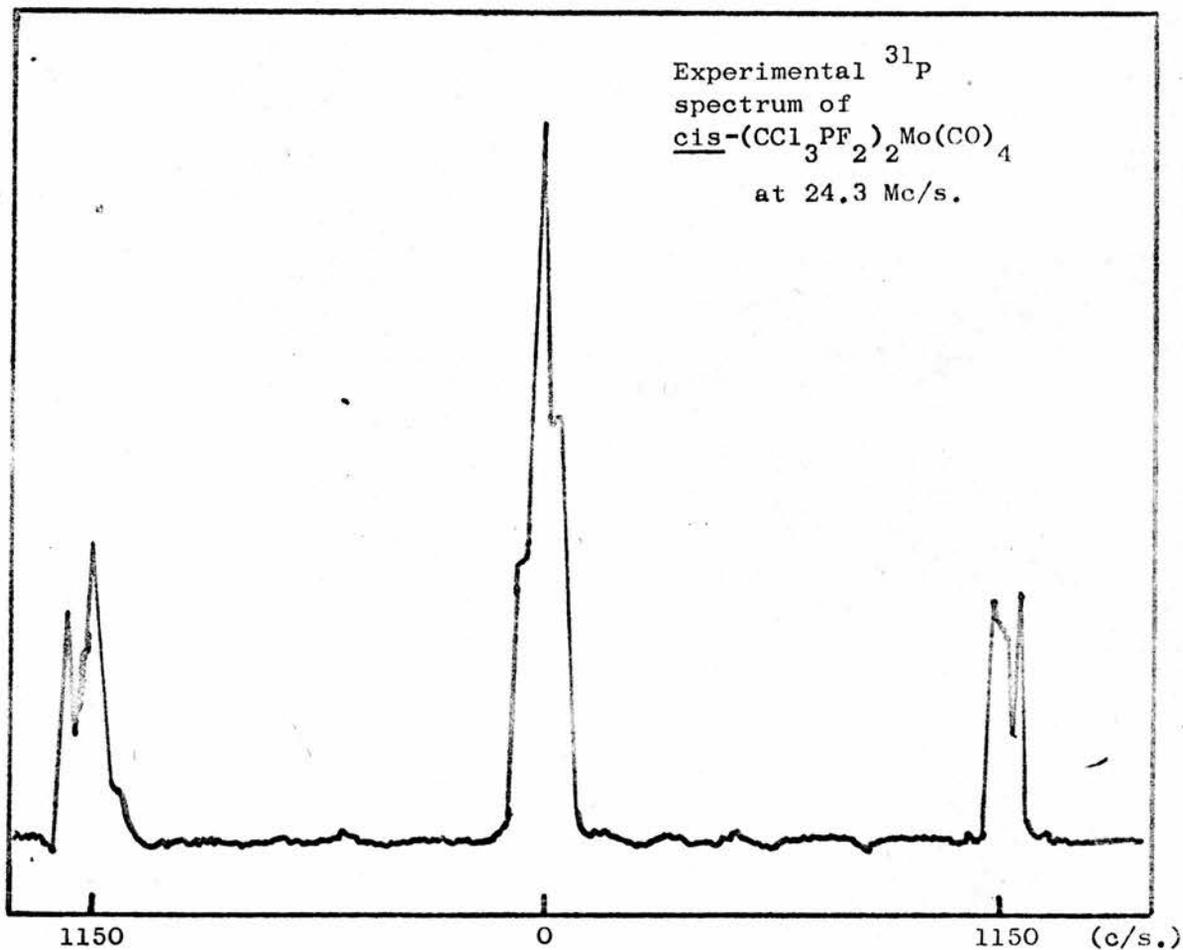
at 94.0 Mc/s.



Calculated ^{19}F
spectrum of
cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$



Experimental ^{31}P
spectrum of
cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$
at 24.3 Mc/s.



The phosphorus spectrum of cis-(CCl₃PF₂)₂Mo(CO)₄ has not been analysed in detail but is very similar in appearance to other X₂AA'X'₂ systems which have been investigated in great detail.^{118, 126}

The above treatment of tetracarbonyl complexes does not enable a distinction to be made between cis and trans isomers since both would have the same spin system. If the theoretical treatment were available, however, it would be possible to confirm that the tricarbonyl complexes were trans isomers since the spin system would be different from the cis isomers in which all the ligands are equivalent. Much useful information may be gained from further studies on P - P coupling in metal carbonyl complexes of phosphorus-fluorine ligands such as correlation between J_{PP} and phosphorus-metal π bonding. The P - P coupling could, however, arise from a through-space mechanism.

Although the other complexes prepared in the present study produced nuclear magnetic resonance spectra which could not be fully interpreted, values of chemical shifts for the mid-points of the resonances and approximate splitting constants could be obtained and interesting comparisons made with the parameters of the free fluorophosphines.

The changes in the parameters upon complexation may be summarised:-

- (1) δ_P decreases by 40 to 65 p.p.m.,
- (2) δ_F decreases by 31 to 82 p.p.m.,
- (3) J_{P-F} decreases,
- (4) J_{P-CF₃} increases.

The first three changes listed overleaf were observed by Reddy and Schmutzler⁶⁰ in the study of nickel and molybdenum complexes of fluorine containing phosphines. This paper, published when the present study was almost complete, also attempts to list the factors responsible for the observed changes in δ_p and δ_F . δ_p could be expected to increase on complexation of the phosphine since it has been observed previously that an increase in the co-ordination number of phosphorus increases its chemical shift.¹¹⁴ δ_p would also increase because of a decrease in the polarisation of the lone pair on phosphorus which is utilised in the phosphorus-metal bond of the complex. The formation of the phosphorus-metal π bond was considered by the authors to lead to a decrease in δ_p . Both δ_p and δ_F are expected to be sensitive to changes in the bond angles at phosphorus but since neither the magnitude nor the direction of these changes are known for the complexes, or for any ligand other than PF_3 , their effects upon the chemical shifts were not discussed by Reddy and Schmutzler. The last factor is the change in the paramagnetic contribution to the screening of the fluorine or phosphorus nuclei caused by the mixing of occupied fluorine or phosphorus orbitals with low lying unoccupied metal orbitals when the latter are anisotropically perturbed by the applied magnetic field. It has been suggested that this paramagnetic effect is responsible for the downfield shift of δ_F observed when $\alpha - CF_2$ groups are co-ordinated to a transition metal which contains unoccupied d orbitals. 58

The factors influencing chemical shifts in such complicated systems are obviously very difficult to discuss quantitatively. However, from the results of Reddy and Schmutzler it does appear that δ_p is influenced more by the effects of π bonding and the paramagnetic anisotropy of the metal than by the increase in the co-ordination number of phosphorus or by the polarisability change. The downfield shift of δ_F may be due largely to the increased paramagnetic contribution to the screening constant since the position of the fluorines, relative to the metal atom, resemble the $\alpha - CF_2$ fluorines in the perfluoroalkyl-transition metal complexes. A comparison of the shifts in δ_p and δ_F , produced by complexation of fluorophosphines to nickel⁹⁰ and molybdenum, confirms the observation of Reddy and Schmutzler that the paramagnetic contribution is greater for molybdenum than for nickel.

The above workers found linear correlations between various parameters of the free and co-ordinated phosphorus fluorides

X - PF₂. These were:-

- (1) the electronegativity of X and the change in δ_p upon complexation $\Delta\delta_p$,
- (2) the electronegativity of X and $\Delta\delta_F$,
- (3) δ_p for the free ligand and $\Delta\delta_p$,
- (4) δ_p for the free ligand and $\Delta\delta_F$.

It was shown, for instance, that the values of δ_p or δ_F were similar for compounds in which the same atom was bonded to phosphorus, viz:-

$\text{Mo}(\text{CO})_3(\text{Et}_2\text{NPF}_2)_3$	δ_p : -38.4,	δ_F : -35.8 p.p.m.
$\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_{10}\text{NPF}_2)_3$	δ_p : -38.3,	δ_F : -34.4 p.p.m.
$\text{Mo}(\text{CO})_3(\text{n - PrOPF}_2)_3$	δ_p : -46.0,	δ_F : -29.4 p.p.m.
$\text{Mo}(\text{CO})_3(\text{C}_6\text{H}_5\text{OPF}_2)_3$	δ_p : -40.0,	δ_F : -31.4 p.p.m.

The relationship with electronegativity may be seen further by the results for the compounds in which X has the smallest and largest values of the compounds studied:-

$\text{Mo}(\text{CO})_3(\text{C}_6\text{H}_5\text{PF}_2)_3$	δ_p : -25.3,	δ_F : -46.2 p.p.m.
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	δ_p : -53.6,	δ_F : -30.7 p.p.m.

These results may be contrasted with the values of δ_p and δ_F shown in the Table of the values of fluorophosphine complexes. Amongst the ligands CCl_3PF_2 , CF_3PF_2 , PF_3 there appears to be no correlation with electronegativity.

Similarly the fluorophosphine complexes do not show the linear relationship between δ_p of the free ligand and $\Delta\delta_p$ or $\Delta\delta_F$ for the complex.

Theoretically derived equations for δ_p in free and co-ordinated phosphines have been obtained by Van Wazer and Letcher¹²⁷ relating δ_p to bond angles, the degree of occupancy of P π orbitals and the electronegativity of the atom bonded to phosphorus. For most practical systems these parameters are unknown, so limiting the usefulness of the equations. Although Van Wazer has applied his results to complexes

of the rigid P_4O_6 ,¹²⁸ their general applicability appears to be limited in the present state of our knowledge of complex systems.

The decrease in J_{P-F} upon complex formation may be compared with the observed decrease as the co-ordination number of some phosphorus-fluorine compounds increases:-¹¹⁴

e.g. PF_3 1410 c/s., $RPCF_2$ 1100 c/s., RPF_4 930 c/s., PF_6^- 707 c/s.

Since complex formation involves an increase in the co-ordination number by the formation of the $P \rightarrow M$ bond the observed behaviour is consistent with expectations. The decrease of J_{P-F} is possibly caused by the change in hybridisation of the phosphorus orbitals which will take place when the co-ordination number increases.

The increase in J_{P-CF_3} is similar to that observed when $(CF_3)_3P$ is co-ordinated to nickel in $[(CF_3)_3P]_2Ni(CO)_2$ or upon going from $(CF_3)_3P$ to $(CF_3)_3P=O$, a change which has been ascribed to an increased involvement of phosphorus 3d orbitals.¹²⁹

No direct correlation appears to exist between the changes in the nuclear magnetic resonance parameters and the carbonyl stretching force constants to indicate any direct relationship between the nuclear parameters and the π -acceptor characteristics of the fluorophosphines. While the primary force constants of their complexes are in the order $CF_3PF_2 > (CF_3)_2PF > PF_3 > CCl_3PF_2$ the values of $\Delta\delta_P$ are found to be $CF_3PF_2 < PF_3 < (CF_3)_2PF < CCl_3PF_2$ and $\Delta\delta_F$, $PF_3 < CCl_3PF_2 < CF_3PF_2 < (CF_3)_2PF$. In such an obviously complex system where so many factors exert some influence on the chemical shifts it is quite possible that the π -acceptor properties

of the ligands are of minor importance.

The analysis of the spectra of two of the complexes points to interesting possibilities. The extension of the analysis to the other complexes could reveal any trends along the series which may exist. What may be more important is that if the appearance of the spectrum of the expected isomer can be predicted from theory then the presence of an isomeric mixture can be detected from the nuclear magnetic resonance spectra even when, as in the case of $(PF_3)_2Cr(CO)_4$, the infrared spectrum appears to indicate a monoisomeric compound.

Changes in Nuclear Magnetic Resonance Parameters
of Fluorophosphines upon Complexation.

$$\Delta x = (x_{\text{complex}} - x_{\text{free ligand}})$$

L	$\Delta \delta_{\text{P}}$ (p.p.m.)	$\Delta \delta_{\text{F}}$ (p.p.m.)	$\Delta \delta_{\text{CF}_3}$ (p.p.m.)	ΔJ_{PF} (c/s.)	ΔJ_{PCF_3} (c/s.)
<u>trans-(L)₃Mo(CO)₃.</u>					
PF ₃	-53.5	-32	-	-104	-
CCl ₃ PF ₂	-65.5	-41.5	-	-109	-
CF ₃ PF ₂	-52	(a) -48.5	-2.0	- 91	+19
		(b) -55	-1.5	- 93	+18
(CF ₃) ₂ PF	-59	(a) -76	+1.0	- 38	+8.0
		(b) -82	+1.5	- 55	+7.0
<u>cis-(L)₂Mo(CO)₄</u>					
PF ₃	-51.5	-31	-	-102	-
CCl ₃ PF ₂	-66.5	-41	-	- 94	-
CF ₃ PF ₂	-41	-50	-1.0	- 94	+19
(CF ₃) ₂ PF	-60	-77	+1.7	- 41	+6.0
(CF ₃) ₃ P	-	-	+4.0	-	-2.5

Nuclear Magnetic Resonance Spectra

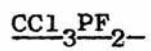
L	δ_p (p.p.m.)	δ_F (p.p.m.)	J_{P-F}^* (c/s.)	δ_{CF_3} (p.p.m.)	J_{P-CF_3} (c/s.)
	relative to 85% H_3PO_4	relative to CCl_3F			
<u>trans-(L)₃Mo(CO)₃</u>					
PF_3	-150.5	2.1	1306	-	-
CCl_3PF_2	-195.5	46.5	1181	-	-
CF_3PF_2	-210	(a) 55.6	1154	79	106
		(b) 50.4	1152	79	105
$(CF_3)_2PF$	-183	(a) 143	975	67	90
		(b) 137	956	68	95
<u>cis-(L)₂Mo(CO)₄</u>					
PF_3	-143.5	2.9	1303	-	-
CCl_3PF_2	-196.5	47.1	1194	-	-
CF_3PF_2	-199	1130	1151	80	106
$(CF_3)_2PF$	-184	1060	972	68	96
$(CF_3)_3P$	-	-	-	55	83

* J_{P-F} is taken from the more intense fluorine spectra.

PART II

The Reactions of

Difluorotrichloromethylphosphine



Introduction

The Chemistry of Difluorotrichloromethylphosphine

Difluorotrichloromethylphosphine is a white, volatile solid which melts at $15.8 - 16.4^{\circ}$. It is very reactive towards air or moisture, a property shared with other fluorophosphines. The presence of the electron-withdrawing trichloromethyl group confers stability on the compound, however, and prevents the formation of the fluorophosphorane during its preparation from the chlorophosphine by fluorination with antimony trifluoride.⁷⁵

With chlorine or bromine, CCl_3PF_2 reacts to give the white, crystalline solids $\text{CCl}_3\text{PF}_2\text{Cl}_2$ or $\text{CCl}_3\text{PF}_2\text{Br}_2$.⁷⁵

The structure of CCl_3PF_2 was confirmed by its ^{31}P and ^{19}F nuclear magnetic resonance spectra, ($\delta_{\text{p}} = -131$ p.p.m., $J_{\text{PF}} = 1290$ c/s.,
 H_3PO_4

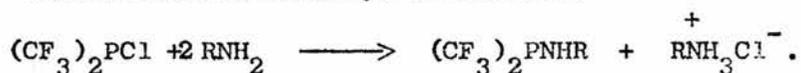
$\delta_{\text{F}}^{\text{CCl}_3\text{F}} = +88.0$ p.p.m., $J_{\text{PF}} = 1285$ c/s.). These parameters are similar

to those of other fluorophosphines and the splitting of the phosphorus resonance into a triplet and the fluorine resonance into a doublet showed the presence of two equivalent fluorine atoms bonded to phosphorus.

Little else was known, at the time of the start of this study, about the chemistry of CCl_3PF_2 except for one report of its reaction with dimethylamine.⁸³ This reaction was unusual, since the products were dimethylamino-N-difluorophosphine and chloroform, indicating cleavage of the phosphorus-carbon bond rather than aminolysis of the

phosphorus-fluorine bond. The anomalous character of this reaction can be seen from the consideration of similar reactions.

Harris showed that the reactions of chlorobis(trifluoromethyl)phosphine with ammonia or amines occurred by the elimination of hydrogen chloride to give the aminobis(trifluoromethyl) phosphines:-¹³⁰



The product from the reaction with a primary amine could not react with a second molecule of the chlorophosphine since the $p_\pi - d_\pi$ bonding between nitrogen and phosphorus reduced the basicity of the nitrogen in $(\text{CF}_3)_2\text{PNHR}$. Both dichlorotri(trifluoromethyl)phosphine and difluorotri(trifluoromethyl)phosphine react with dimethylamine to give trifluoromethylbis(dimethylamino)-N-phosphine, $\text{CF}_3\text{P}(\text{NMe}_2)_2$.⁸² Similarly, dichlorotri(chloromethyl)phosphine, CCl_3PCl_2 , reacts by cleavage of the P - Cl bond when treated with dimethylamine.⁸³

It thus appears that the ease of cleavage of the P - X bond by amines increases along the series $\text{X} = \text{CF}_3 < \text{F} < \text{CCl}_3 < \text{Cl}$. The preferential reactivity of P - Cl than P - F has been shown by the preparation of $(\text{CH}_3)_2\text{NPF}_2$ from the treatment of PF_2Cl with dimethylamine.¹³¹

In view of this apparently anomalous behaviour of CCl_3PF_2 it was decided to investigate its reactions further. The first aspect treated was the generality of the reaction with secondary amines. It was hoped, then, to extend the reaction to include the use of bases other than, but similar to, amines such as phosphines, and lastly to investigate the reactions of difluorotri(chloromethyl)phosphine when co-ordinated to zero-valent molybdenum in the complexes described in Part I.

Dialkylaminodifluorophosphines (dialkylphosphoramidous difluorides).

Although dialkylaminodichlorophosphines have been known for over sixty years, ¹³² the first reports of the corresponding fluorophosphines appeared, as patents, only in 1936. ¹³³ Even these reports, however, were incorrect since they reported diethylamino-N-difluorophosphine as a gas while more recent work, discussed below, has shown that $(C_2H_5)_2NPF_2$ is a colourless liquid boiling at $47^\circ/100$ mm., whose structure has been well characterised by modern physical techniques.

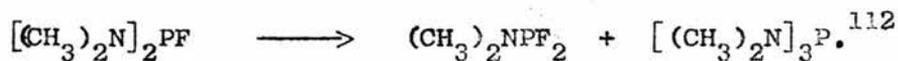
The first correct report of dimethylamino-N-difluorophosphine appeared in 1962 ¹³⁴ although in a later paper its synthesis was claimed to have been achieved in 1959. ¹³⁵ The two methods of synthesis used were, (1) the reaction of phosphorus trifluoride and dimethylamine, (2) the reaction of the adduct $(CH_3)_2NPF_2 \cdot BH_3$ with trimethylamine $(CH_3)_3N$. $(CH_3)_2NPF_2$ has also been prepared by the action of boron trifluoride on trisdimethylamino-N-phosphine ¹³⁶, although other workers had obtained only dimethylamino-N-difluoroborane from this reaction. ¹³⁷ The number of dialkylaminodifluorophosphines known has been increased by the fluorination of the corresponding chlorophosphines using a variety of fluorinating agents:- SbF_3 , ^{111, 130} NaF in tetramethylene sulphone, ¹¹¹ KSO_2F , ¹¹¹ ZnF_2 . ^{136, 138} The use of arsenic trifluoride was reported to give a complex mixture of products. ¹³⁸

The greater reactivity of the P - F bond compared to the P - Cl bond towards aminolysis was shown by Cavell who prepared dimethylamino-N-difluorophosphine by the reaction of dimethylamine with chlorodifluorophosphine.¹³¹

A useful method of obtaining pure $(\text{CH}_3)_2\text{NPF}_2$ from a mixture with $(\text{CH}_3)_2\text{NH}$ and $[(\text{CH}_3)_2\text{N}]_2\text{PF}$ has been described.¹³⁹ The mixture was allowed to stand at room temperature over cobalt dibromide when the impurities were complexed and only pure $(\text{CH}_3)_2\text{NPF}_2$ pumped off.

Dialkylaminodifluorophosphines are strong smelling, colourless liquids which are more stable in the atmosphere than the alkyl, aryl or perfluoroalkyl fluorophosphines.

Upon heating to 50° dimethylamino-N-difluorophosphine reacts further with dimethylamine by eliminating hydrogen fluoride to produce bisdimethylamino-N-fluorophosphine, $(\text{Me}_2\text{N})_2\text{PF}$, which disproportionates slowly at room temperature:-

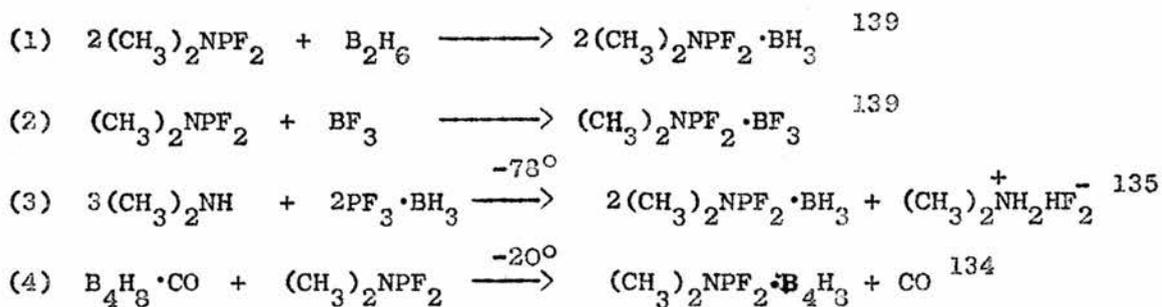


The nitrogen-phosphorus bond in dialkylaminodifluorophosphines is readily cleaved by hydrogen halides or acyl halides to produce the halogenodifluorophosphines, PF_2X ,¹³¹ giving a useful method of their preparation free of other halogeno-fluorophosphines.

Dialkylaminodifluorophosphines are more basic than phosphorus trifluoride in their reactions with electron acceptors.¹³⁵ Any $p_\pi - d_\pi$ bonding between nitrogen and phosphorus involves donation of the lone pair on nitrogen into unoccupied phosphorus d orbitals, thereby increasing the basicity of the phosphorus at the expense of the nitrogen.

This mechanism is further enhanced by the high electronegativity of the fluorine atoms.

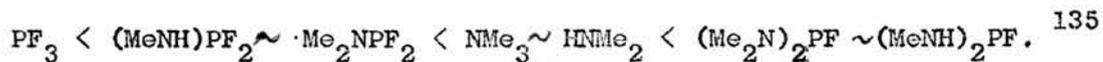
Adducts of dialkylaminodifluorophosphines with boron acceptor compounds may be prepared by direct or indirect syntheses:-



The donor atom in these adducts has been determined by infrared and nuclear magnetic resonance spectroscopy. Compounds containing a phosphorus-boron bond gave a ^{31}P nuclear magnetic resonance spectrum which showed coupling between the ^{31}P and ^{11}B nuclei.¹³⁹ It has been shown that the band at $2760 - 2820 \text{ cm.}^{-1}$ in the infrared spectra of compounds containing the group $\text{>N} - \text{CH}_3$ disappears when the lone pair on nitrogen are used for bonding.¹⁴⁰

Use of these two spectroscopic techniques has shown that while $(\text{CH}_3)_2\text{NPF}_2 \cdot \text{BH}_3$ contains a phosphorus-boron bond, the similar $(\text{CH}_3)_2\text{NPF}_2 \cdot \text{BF}_3$ was co-ordinated through nitrogen.¹³⁹ A phosphorus-boron bond is also believed to be present in $(\text{CH}_3)_2\text{NPF}_2 \cdot \text{B}_4\text{H}_8$.¹³⁴

From studies of their acceptor properties towards borane, a series of compounds have been arranged in order of increasing basicity:-



The co-ordination chemistry of dialkylaminodifluorophosphines with zerovalent nickel and molybdenum has been studied by reacting the appropriate ligand with either the metal carbonyl,¹¹¹ with cycloheptatriene molybdenum tricarbonyl¹¹¹ or with norbornadiene molybdenum tetracarbonyl.¹⁰⁷ Nickel complexes were obtained in which two or four carbonyl groups had been displaced. The molybdenum carbonyl derivatives gave di or tri-substituted products while molybdenum carbonyl itself reacted with piperidino-N-difluorophosphine to give cis- $[\text{C}_5\text{H}_{10}\text{NPF}_2]_2\text{Mo}(\text{CO})_2$ under forcing conditions.¹¹¹

The complexes are stable solids or liquids in which co-ordination to the metal was believed to be from the phosphorus. The infrared absorption at 2780 - 2820 cm^{-1} was present in the spectra of the methyl derivatives and an absorption at 990 cm^{-1} , claimed to be characteristic for the $(\text{CH}_3)_2\text{N} - \text{P}$ group, was unchanged by co-ordination.¹¹¹ The carbonyl stretching frequencies of the complexes were higher than would be expected if co-ordination was through nitrogen. Lastly an X-ray structure determination on $\text{Ni}(\text{C}_5\text{H}_{10}\text{NPF}_2)_4$ also supported co-ordination from phosphorus to the metal.¹⁴¹

It was hoped that in the present study, by preparing dialkylamino-fluorophosphine molybdenum carbonyl complexes from the trichloromethyl-difluorophosphine molybdenum carbonyl compounds prepared in Part I of this thesis, the case for co-ordination through phosphorus in the former would be greatly strengthened since it is the only possibility in the latter.

Discussion

Difluorotrichloromethylphosphine readily reacts at room temperature, in sealed evacuated glass tubes, with secondary amines. Three reactions, involving diethylamine, piperidine and pyrrolidine respectively, followed the same general pattern as that with dimethylamine,⁸³ giving as the major products the appropriate dialkylaminodifluorophosphine and chloroform. One difference, however, was the simultaneous production of small amounts of phosphorus trifluoride.

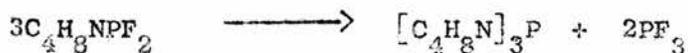
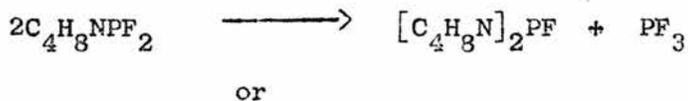
The identity of diethylamino-N-difluorophosphine and piperidino-N-difluorophosphine was confirmed by molecular weight and vapour pressure measurements. Their infrared and nuclear magnetic resonance spectra agreed with those of authentic samples made by fluorination of the corresponding chlorophosphines.¹¹¹ The new compound, pyrrolidino-N-difluorophosphine, was fully characterised by elementary analysis and exhibited the infrared and nuclear magnetic resonance spectra expected from its structure. The proton magnetic spectrum showed two resonances corresponding to the α and β protons.

The ^{31}P spectrum was a 1-2-1 triplet, arising from spin-spin coupling with two equivalent fluorine atoms, which occurred at low field relative to H_3PO_4 ; while the ^{19}F spectrum was the expected doublet, each line of which was further split into five lines by the four α protons of the ring. The large negative value of δ_{P} is characteristic of a phosphine fluoride¹¹⁴ and the value of $J_{\text{P}-\text{F}}$ is in line with other values for trico-ordinate phosphorus fluorides.¹¹⁴

The chloroform and phosphorus trifluoride obtained were identified by molecular weight and infrared measurements.

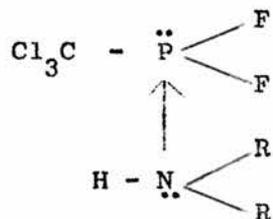
In order to add further confirmation to the synthesis of the pyrrolidine derivative, $C_4H_8NPF_2$, it was also prepared by the fluorination of pyrrolidino-N-dichlorophosphine, using antimony trifluoride. This compound, which was new, was prepared by the action of pyrrolidine on phosphorus trichloride, the reaction being carried out in a large volume of dry ether at -78° to minimize the formation of $[(C_4H_8N)_2]PCl$. The pyrrolidino-N-difluorophosphine obtained was identical in its properties to that from the reaction of difluorotrichloromethylphosphine with pyrrolidine although the yield was much reduced.

The observed evolution of considerable quantities of phosphorus trifluoride during the fluorination reaction suggested that a disproportionation such as:-



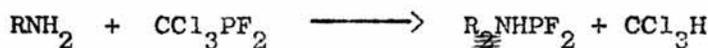
occurred, which may be catalysed by the antimony compounds. Support for such a disproportionation was given by the infrared spectrum of $C_4H_8NPF_2$ which always contained bands attributable to PF_3 , even after repeated fractionation of the sample. Also, when a sample of $C_4H_8NPF_2$ was heated in a sealed tube a 6.6% yield of PF_3 was recovered.

trichloromethyl group, facilitating the elimination of chloroform rather than hydrogen fluoride.



If the steric strain was large enough it could over-ride the other factors and so allow only the formation of chloroform.

Very recently it has been shown that primary amines react readily with CCl_3PF_2 to give two possible products.¹¹⁸



Dimethylphosphine was found to react with difluorotrichloromethylphosphine, at room temperature, to produce a complex mixture of products. The small amount of phosphorus trifluoride produced was fractionated from the two immiscible liquids which constituted the remainder of the volatile products. Infrared and ^1H , ^{19}F nuclear magnetic resonance spectroscopy showed this mixture to consist of chloroform, indicating that some carbon-phosphorus bond cleavage had occurred, trifluorodimethylphosphorane and a further unidentified compound. After repeated fractionation of the mixture enough pure compound was obtained for its infrared spectrum to be recorded. However, on further handling at room temperature it always appeared to decompose since traces of white solid were observed and its ^{19}F spectrum was identical to that of the mixture. The deposition of white solid was observed whenever

the liquid products were allowed to reach room temperature. Each time a sample of the liquids was stored at room temperature, colourless crystals formed which turned to white powder when the liquids were pumped away. The spectroscopic properties of the liquids did not alter during the formation of the solid.

It is also noteworthy that although a mole ratio $(\text{CH}_3)_2\text{PH}:\text{CCl}_3\text{PF}_2 > 1$ was always used in the reaction, no excess of $(\text{CH}_3)_2\text{PH}$ was ever detected in the volatile products.

When the progress of the reaction was followed by ^1H and ^{19}F nuclear magnetic resonance, no reaction occurred in the first two hours but the spectra obtained after three hours showed no evidence of starting materials, only the resonances corresponding to the products being then visible.

Difficulty was experienced in handling the white solid since it was very sticky when handled in the glove box and was insoluble in any of the common organic solvents, polar or non-polar. The reaction of the solid with pyridine showed that it consisted in part of dimethylphosphonium bifluoride, thus confirming the formation of hydrogen fluoride in the reaction.

Analogy with the mode of decomposition of CH_3PF_2 ^{68, 69} suggests that $(\text{CH}_3)_2\text{PF}_3$ could have formed in the present reaction by the decomposition of fluorodimethylphosphine, $(\text{CH}_3)_2\text{PF}$ which could have been produced in two ways:-

of the trifluoromethyl groups supports the postulated importance of the nucleophilicity of the reagent reacting with CCl_3PF_2 .

Methyl thiol also did not react with difluorotrichloromethylphosphine. After thirteen hours at 60° the only sign of any reaction was the formation of a trace of white solid.

The failure to prepare difluoromethylthiophosphine by the reaction of PF_3 and CH_3SH in the presence of triethylamine agrees with the observations of other workers.¹⁴⁶

The reactions of amines with difluorotrichloromethylphosphine were extended to the study of co-ordinated fluorophosphine in trans- $(\text{CCl}_3\text{PF}_2)_3\text{Mo}(\text{CO})_3$ and cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ in the hope of preparing the corresponding dialkylaminodifluorophosphine complexes. In each reaction a high yield of chloroform was obtained, indicating that the reactions followed a similar course to those of the free fluorophosphine. From each reaction the major product was a viscous liquid which could not be completely purified, in spite of repeated attempts using different approaches, even in the case of the product from piperidine and cis- $(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$ which was expected to be the compound cis- $(\text{C}_5\text{H}_{10}\text{NPF}_2)_2\text{Mo}(\text{CO})_4$, a white crystalline solid.¹⁰⁷ The infrared spectra of the tricarbonyl complexes fitted the expected products except that the tricarbonyl products in hexane solution showed more than the expected number of absorptions in the 2000 cm.^{-1} region suggesting an isomeric mixture. The solution spectrum of $(\text{C}_5\text{H}_{10}\text{NPF}_2)_2\text{Mo}(\text{CO})_4$ agreed closely with that of an authentic sample as did its

proton magnetic resonance spectrum. All of the liquids turned brown fairly rapidly in light or upon warming.

It appears, therefore, that the reactions $xR_2NH + (CCl_3PF_2)_x Mo(CO)_{6-x}$ $xCCl_3H + (R_2NPF_2)_x Mo(CO)_{6-x}$ occur as expected but the presence of an isomeric mixture of products or a trace of impurities prevents satisfactory purification of the carbonyl product. The analytical data suggests that the amount of impurity present must be small.

Since amines can co-ordinate to zerovalent transition metals in carbonyl complexes it is possible that the excess of amine used caused some decomposition or rearrangement of the starting or product materials.

Besides demonstrating the extension of the simple amine reactions the production of the aminodifluorophosphine complexes gives support to the proposal¹¹¹ that the donor atom in such complexes is the phosphorus atom, since they have now been prepared from the CCl_3PF_2 complexes in which co-ordination must be through phosphorus.

This work has constituted but a small part in the investigation of the simple chemistry of one fluorophosphine. There remains much to be examined in the chemistry of this and other fluorophosphines.

One concluding experiment to be mentioned is the brief investigation of the reaction of hydrogen chloride and co-ordinated aminodifluorophosphine. The reaction was a great deal slower than that between hydrogen chloride and the free dialkyl aminodifluorophosphines. After heating the reactants, the aminohydrochloride was isolated and also a volatile compound whose infrared spectrum suggested that it was possibly cis- $(PClF_2)_3Mo(CO)_3$. Unfortunately the ease with which it decomposed prohibited a nuclear magnetic resonance study of this compound.

Infrared Spectra

Pyrrolidine-N-difluorophosphine

(Vapour) 2958 vs, 2865 vs, 1453 vw, 1348 w, 1294 vw, 1264 w, 1208 m, 1122 s, 1085 s, 1014 m, 975 m, 907 vw, 890.5 m, 866 s, 851 s, 819 vs, 766 vs, (cm.⁻¹).

Product from Me₂NH + trans-(CCl₃PF₂)₃Mo(CO)₃

(In hexane) 2025 m, 2015 w, 2010 m, 1949 s, 1938 vs, 1918 s, sh.
(Thin film) 2922 vs, b, 2851 s, 2814 m, sh, 2025 m, 2009 m, 1948 s, sh, 1927 vs, 1481 m, 1461 s, 1454 s, 1415 w, 1300 s, 1181 s, 1069 m, 984 s, 805 s, 778 m, sh, 703 s, (cm.⁻¹).

Product from C₅H₁₀NH + trans-(CCl₃PF₂)₃Mo(CO)₃

(In hexane) 2017 s, 2009 vs, 1953 s, 1940 vs, 1921 vs, 1884 vw.
(Thin Film) 2970 m, sh, 2933 s, 2852 s, 2021 s, 1999 s, 1912 vs, b, 1461 m, sh, 1450 m, 1441 m, 1401 w, 1372 s, 1337 m, 1322 w, 1277 m, 1255 w, 1204 s, 1162 s, 1112 s, 1060 s, 1023 m, 957 s, 897 m, 850 m, 793 s, b, 767 s, sh, 694 s, 665 w, (cm.⁻¹).

Product from C₅H₁₀NH + Cis-(CCl₃PF₂)₂Mo(CO)₄

(In hexane) 2055 m, 1973 m, 1963 w, 1950 vs, 1939 s, sh.
(Thin Film) 2937 m, 2855 m, 2054 s, 1930 vs, b, 1462 w, 1450 w, 1441 m, 1371 m, 1339 w, 1279 w, 1260 w, 1205 m, 1164 m, 1112 m, 1060 m, 1024 w, 960 m, 898 w, 852 w, 800 m, b, 780 m, b, 698 m, 668 w, (cm.⁻¹).

cis-(PClF₂)₃Mo(CO)₃

(Vapour) 2068 s, 2019 vs, 2003 w, 890 w, vb, 860 w, 820 vw, 792 w, 772 vw, (cm.⁻¹).

Nuclear Magnetic Resonance Spectra

Chemical shifts and spin-spin coupling constants for R_2NPF_2 systems

Compound	δ_H^*	δ_P^\dagger	δ_F^\ddagger	J_{PF}^{\S}	$J_{PH\alpha}^{\S}$	$J_{FH\alpha}^{\S}$	J_{HF}^{\S}
$\begin{array}{c} \beta \quad \alpha \\ \text{CH}_3 - \text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{NPF}_2 \\ \text{CH}_3 - \text{CH}_2 \end{array}$	-3.15(α) twelve lines -1.13(β) triplet	-147.2 triplet	+64.8 doublet of quintuplets	1204 ^a 1191 ^b	-	3.2	7.5
$\begin{array}{c} \beta \quad \alpha \\ \text{H}_2\text{C} \quad \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{NPF}_2 \\ \quad \quad \quad \text{CH}_2 - \text{CH}_2 \end{array}$	-3.18(α) -1.60(β ,)	-140.5 triplet	+66.4 ^c doublet of quintuplets	1205 ^a 1199 ^b	-	2.9	
$\begin{array}{c} \beta \quad \alpha \\ \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \quad \text{NPF}_2 \end{array}$	-3.30(α) -1.83(β)	-146.2 triplet	+67.9 doublet of quintuplets	1204 ^a 1198 ^b	-	3.3	
$\begin{array}{c} \beta \quad \alpha \\ \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \quad \text{NPCl}_2 \end{array}$	-3.36(α) sextuplet -1.90(β)	-164.5	-	-	3.6	-	

* Chemical shift in p.p.m. rel. to SiMe_4 . † Chemical shift in p.p.m. rel. to H_3PO_4 .

‡ Chemical shift in p.p.m. rel. to CCl_3F .

§ Coupling constant in cycles per second.

^a From ^{31}P spectrum. ^b From ^{19}F spectrum. ^c Measured relative to $\text{C}_6\text{H}_5\text{CF}_3$ (external std.) and corrected to the CCl_3F scale by addition of 63.

^1H spectrum of $\text{cis}-(\text{C}_5\text{H}_{10}\text{NPF}_2\text{Mo}(\text{CO}))_4$

Broad lines at:- δ_H -1.62 (β) protons
 δ_H -3.34 (α) protons.

Experimental

EXPERIMENTAL

Most of the compounds used in this study were very reactive to air and/or moisture. For this reason operations were carried out either under a blanket of dry, oxygen free nitrogen or, preferably, in a high vacuum system. The vacuum system was of the standard type, fitted with greased taps and a train of U-traps. Additional apparatus could be attached to the system by ground glass joints.

A 10 cm. cell with NaCl windows was used for gas phase spectra and a cell of 0.1 mm. path length with NaCl windows for solution spectra. Routine spectra were obtained on a Perkin-Elmer 237 Infracord and a Perkin-Elmer 621 spectrometer was used for more accurate work. The latter was calibrated against atmospheric water and carbon dioxide by conversion to a single beam instrument.

Nuclear magnetic resonance spectra were recorded on the Perkin-Elmer-R10, the Varian Associates HA60 or the Varian HA100. The R10 and HA60 operate at 60 Mc/s. for ^1H , 56.4 Mc/s. for ^{19}F and 24.3 Mc/s. for ^{31}P spectra. The HA100 operates at 100 Mc/s. for ^1H , 94.0 Mc/s. for ^{19}F and 40.5 Mc/s. for ^{31}P spectra. Parameters quoted for the compounds are normally the average values from several measurements.

Gas liquid chromatographic studies were carried out on a Griffin and George D.6 gas density balance instrument or on a Perkin-Elmer F.11 fitted with a flame ionisation detector. A 2 metre column packed with 20% A.P.L. grease on Celite was used in the D.6 and a 50 metre capillary column with A.P.L. grease as stationary phase in the F.11.

Analyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium im Max Planck Institut, Mülheim, Germany.

Purification of Starting Materials

Purification of Solvents

Petroleum ethers and hexane were freed of any unsaturated impurities by shaking with concentrated sulphuric acid, followed by acid potassium permanganate solution. They were then washed with water and given a preliminary drying over anhydrous calcium chloride. Final drying was achieved by refluxing the solvent over phosphorus pentoxide for one hour. The solvent was then distilled from the phosphorus pentoxide through a 60 cm. Vigreux column. The solvents were stored in tightly stoppered bottles over sodium wire.

Acetonitrile was dried by refluxing over phosphorus pentoxide, followed by distillation through the 60 cm. Vigreux column. It was stored in a tightly stoppered bottle.

Benzene was shaken with concentrated sulphuric acid to remove any thiophen present, washed with water and sodium carbonate solution, then dried over anhydrous calcium chloride. The last traces of moisture were removed by reflux and distillation from sodium wire. The pure, dry benzene was stored over sodium wire.

Chloroform and carbon tetrachloride were dried over anhydrous calcium chloride and then distilled through a 60 cm. Vigreux column.

Diethyl ether was dried first over calcium chloride then refluxed over sodium wire. Purification was by distillation through the Vigreux column. The pure, dry ether was stored in a dark bottle over sodium wire.

Diglyme was dried by reflux over calcium hydride and then distilled.

Purification of Red Phosphorus

The commercial sample of red phosphorus was stirred in a 10% sodium hydroxide solution to remove any surface oxides. The solution was decanted off and the phosphorus washed with water until neutral to litmus. The phosphorus was then washed with ethanol and filtered, then dried in a vacuum desiccator over P_2O_5 .

Preparation of Hydrogen Chloride

Concentrated sulphuric acid was added slowly to dry AnalaR sodium chloride in a flask attached to the vacuum line which contained about 200 mm./Hg of dry nitrogen. A vigorous reaction followed the addition of each drop of acid. The hydrogen chloride formed was collected in a trap at $-196^{\circ}C$. The HCl was then fractionated through a trap at -95° to one at -196° under high vacuum. Its purity was checked by molecular weight and infrared, spectroscopy measurements.

Preparation of Phosphorus Trifluoride

A two-necked flask containing freshly sublimed antimony trifluoride, to which a bent side arm containing redistilled phosphorus trichloride was attached, was connected to the vacuum line. The phosphorus trichloride was degassed under vacuum, the vacuum fractionation train and reaction flask were isolated from the pumps and about 400 mm./Hg. of dry nitrogen admitted. The phosphorus trichloride was added slowly from the side arm. When the flask was warmed slightly a reaction started and the phosphorus trifluoride produced passed through a trap at -78° to one at -196° . The rate of reaction was controlled by the addition of the phosphorus trichloride. The phosphorus trifluoride was passed several times through traps at -78° under the nitrogen atmosphere to remove less volatile products such as chlorofluorophosphines $PClF_2$ and PCl_2F . The phosphorus trifluoride was then passed under high vacuum through a -120° trap into one at -196° . Its purity was checked by infrared and molecular weight measurements.

Cycloheptatriene and Bicyclo (2,2,1) hepta (2,5) diene were used as obtained from the Shell Chemical Company and Aldrich Chemical Company respectively.

Molybdenum, chromium and tungsten hexacarbonyls were supplied by the Climax Molybdenum Company and were used without further purification.

Samples of bis(trifluoromethyl)phosphine and fluordbis(heptafluoropropyl)phosphine were supplied by Dr. J.F. Nixon. Before use they were fractionated on the vacuum line and their purity checked by infrared and molecular weight measurements.

Methyl thiol was used as supplied by British Drug Houses, Ltd., after its purity had been confirmed by infrared, molecular weight and vapour pressure measurements.

Preparations

Preparation of $\text{CCl}_3\text{P}^+\text{Cl}_3\text{AlCl}_4^-$. ¹⁴⁷

Carbon tetrachloride (176.5g., 1.14 moles), phosphorus trichloride (117.5g., 0.855 moles) and aluminium trichloride (109.5g., 0.822 moles) were refluxed together in a round bottomed flask, fitted with a condenser, under an atmosphere of dry nitrogen for one hour. During reaction a grey solid was formed. The supernatant liquid was decanted off and the solid extracted with hot, dry methylene chloride. After some of the methylene chloride had been removed by distillation the product, $\text{CCl}_3\text{P}^+\text{Cl}_3\text{AlCl}_4^-$, crystallised, as white crystals which were filtered under nitrogen and dried over P_2O_5 , mpt. $95-100^\circ\text{C}$. The product was extremely reactive towards moisture and in later preparations of CCl_3PCl_2 the intermediate $\text{CCl}_3\text{P}^+\text{Cl}_3\text{AlCl}_4^-$ was not isolated but reduced by MeOPCl_2 immediately. This was more convenient and also led to slightly better yields of CCl_3PCl_2 .

Preparation of CH_3OPCl_2 ¹⁴⁸

Phosphorus trichloride (275 g., 2 moles.) was placed in a three necked flask fitted with condenser, a dropping funnel, and a stirrer. The flask was cooled in an ice-salt bath. The system was flushed with dry nitrogen then kept dry by drying tubes. Methanol (64 g., 2 moles.) was added very slowly while the mixture was stirred continuously. During the reaction hydrogen chloride was evolved. At the end of the reaction the flask was allowed to warm to room temperature when the dissolved HCl escaped. The product of the reaction was distilled, giving a small forerun, followed by a fraction boiling at $86^\circ - 94^\circ$ collected as CH_3OPCl_2 . A considerable amount of yellow solid formed during the distillation and may have been responsible for a yield of only 40%.

Reduction of $\text{CCl}_3\text{PCl}_3^+\text{AlCl}_4^-$ by CH_3OPCl_2 ¹⁴⁹

In a flask fitted with a stirrer, condenser, and dropping funnel, the complex $\text{CCl}_3\text{PCl}_3^+\text{AlCl}_4^-$ was suspended in phosphorus trichloride while dry nitrogen was passed continuously through the system. The contents of the flask were heated to $80^\circ - 90^\circ\text{C}$. when CH_3OPCl_2 was very slowly added with vigorous stirring.

The mixture was refluxed for eight hours after the completion of the addition. The flask then contained a liquid and a white solid. The supernatant liquid was decanted off, the solid washed with PCl_3 and the liquid distilled to remove most of the PCl_3 solvent. The remaining solution of CCl_3PCl_2 in PCl_3 could not be further separated by distillation, even when a packed column was used. The solution was distilled on the vacuum line when the CCl_3PCl_2 was slowly trapped out at -24° while the PCl_3 passed through. The CCl_3PCl_2 was purified by further passes through the -24° until its melting point was sharp and its vapour pressure correct.

Fluorination of CCl_3PCl_2 ⁷⁵

Dichlorotrichloromethylphosphine (1.0184 g., 4.62 moles.) was heated in a sealed, evacuated Pyrex tube at 70°C overnight with a large excess of antimony trifluoride. The tube was opened on the vacuum line and the volatile contents pumped out and fractionated. Unreacted CCl_3PCl_2 stayed in a trap at -24°C . while CCl_3PF_2 (0.6236 g., 3.33 moles.) passed to a trap at -78°C . The purity of the difluorotrichloromethylphosphine was checked by its infrared spectrum and its molecular weight (Found 187.2 Calc. 187.5).

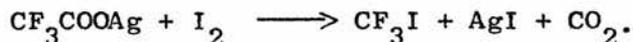
Preparation of Trifluoriodomethane

(a) Silver Trifluoroacetate

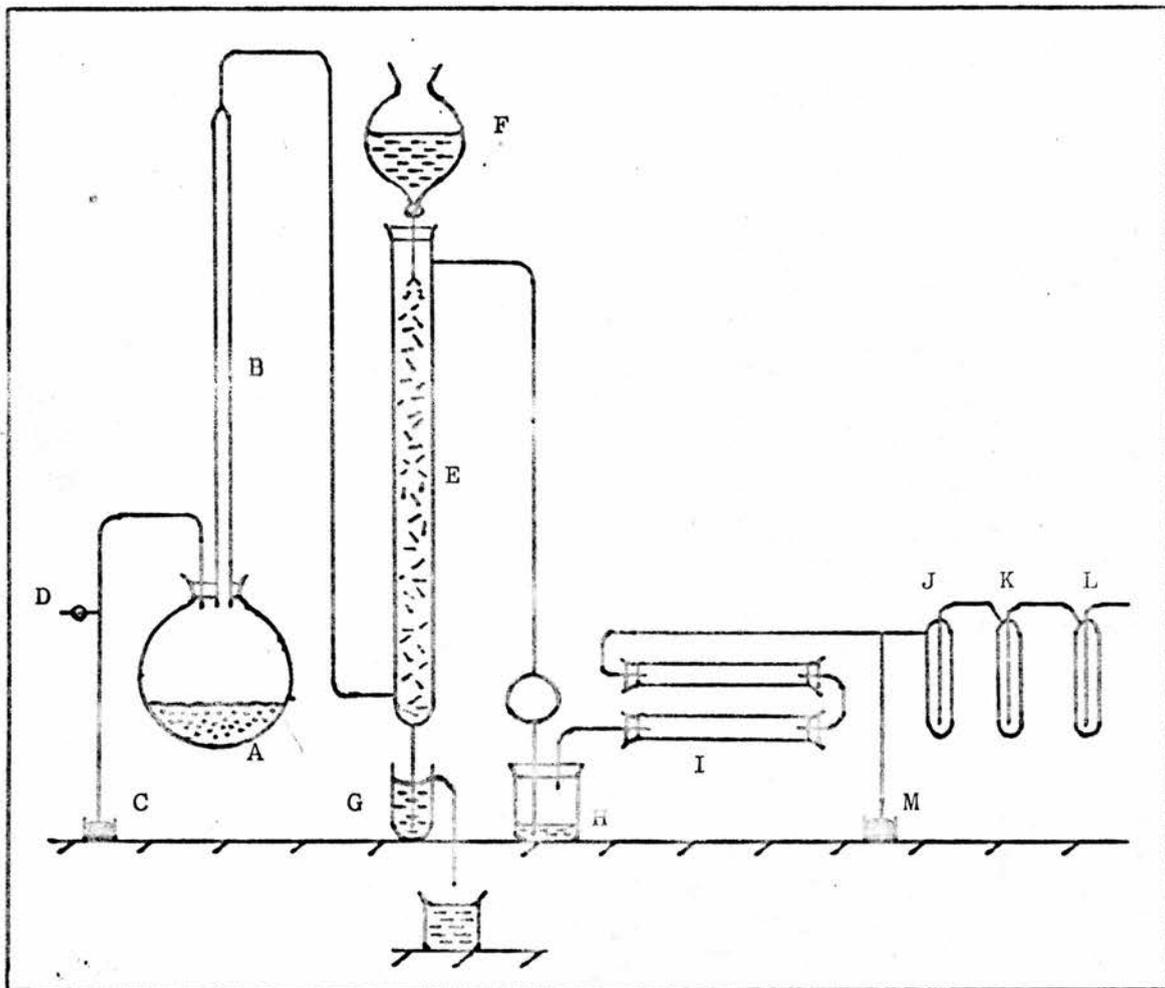
A solution of sodium carbonate (60 g. in 1000 ml. of water) was added slowly to a stirred silver nitrate solution (175 g. in 750 ml. of water). The silver carbonate which precipitated was washed 10 times by decantation. Trifluoroacetic acid was then slowly added to the suspension of silver carbonate until it was neutral to litmus; upon warming the silver carbonate dissolved. The solution was filtered and evaporated to dryness under reduced pressure on a rotary evaporator. The crystals of silver trifluoroacetate were dried in a vacuum desiccator over P_2O_5 .

(b) Trifluoriodomethane¹⁵⁰

Trifluoriodomethane was prepared by heating a mixture of iodine and silver trifluoroacetate:-



In order to prepare CF_3I on a large scale a special apparatus, designed to scrub out the CO_2 and dry the CF_3I , was built. The mixture of iodine and silver trifluoroacetate, both finely ground, were mixed intimately in the flask A. The system was flushed from D with dry nitrogen before the flask was gently heated with a Bunsen.

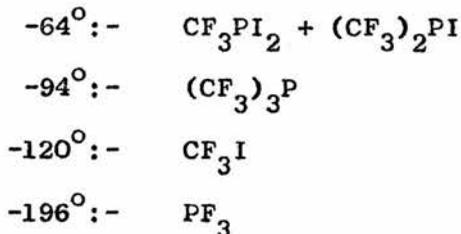


Apparatus for the preparation
of
 CF_3I

The $\text{CF}_3\text{I} + \text{CO}_2$ passed up the glass tube B, where some iodine condensed, and up the scrubbing tower E. The tower was packed with short lengths (1 cm.) of thin glass tubing over which ran a solution of 24% NaOH and 5% $\text{Na}_2\text{S}_2\text{O}_3$ in water, stored in the reservoir F. The rate of production of CF_3I could be followed as it passed the bubbler H. The CF_3I was dried by the tubes of P_2O_5 , I, and collected in the large traps J and K which were cooled to -78° and -196° respectively. Most of the product was retained in J. Mercury safety seals at C and M were included in the system to prevent any pressure build up due to blockage at any point. The traps containing the product were attached to the vacuum line and the contents fractionated through traps at -95° , -120° and -196°C . Water was stopped by the first, CF_3I by the second while any CO_2 passed to the -196° trap. After repeated fractionation the trifluoroiodomethane was stored in an evacuated glass bulb.

Preparation of Tri-trifluoromethylphosphine, Iodobis-trifluoromethylphosphine and Di-iodotrifluoromethylphosphine.

The method used was based on the reported method of Bennett¹⁵¹ et al.. A mixture of pure red phosphorus and resublimed iodine were placed in a glass reaction tube which was then connected to the vacuum line. Sufficient trifluoriodomethane was condensed into the tube to produce about eight atmospheres pressure when the tube had been sealed off and heated at 200° - 210°C. After 48 hours the tube was opened and the volatile products fractionated through traps at -64°, -95°, -120° and -196°C. The traps then contained:-



The tube was refilled with CF_3I and sealed at its second constriction and the reaction repeated. A large excess of phosphorus and iodine was used initially to allow this repetition.

The mixture of iodotrifluoromethylphosphines were separated by fractionation through traps at -24°, -64° and -196°C. Diodotrifluoromethylphosphine stayed in the -24° trap, iodobis-trifluoromethylphosphine in the -64° trap. The two fractions were each recycled and the middle fraction taken each time. Because of their tendency to disproportionate the iodotrifluoromethylphosphines were fluorinated once purified.

Preparation of Difluorotrifluoromethylphosphine

Di-iodotrifluoromethylphosphine was condensed into an evacuated Pyrex tube which contained an excess of dry antimony trifluoride. The tube was sealed and heated at 70° overnight. The volatile products were then taken into the vacuum line leaving antimony triiodide and ~~trichloride~~^{fluoride} in the tube. Fractionation of the products through traps at -78° and -196° separated the di-iodotrifluoromethylphosphine from the difluorotrifluoromethylphosphine which passed to the trap at -196°. The purity of the fluorophosphine was checked by examination of its infrared spectrum, vapour pressure and molecular weight.

Preparation of Fluorobis(trifluoromethyl)phosphine

Iodobistrifluoromethylphosphine and antimony trifluoride were heated together in a Pyrex tube at 70°C. overnight in a similar manner to the previous preparation. The volatile products were fractionated in the vacuum line through traps at -64°, -120° and -196°C. Unreacted iodophosphine was stopped by the first, fluorobis(trifluoromethyl)phosphine by the second and phosphorus trifluoride and silicon tetrafluoride by the last trap. The contents of the -120°C. trap were refractionated until the infrared, molecular weight and vapour pressure measurements were correct for $(CF_3)_2PF$.

Preparation of Tetramethyl biphosphine disulphide 152

Magnesium filings (19 g., 0.78 mole.) were placed in 100 ml. of ether contained in a three necked flask. The flask was fitted with a stirrer, dropping funnel and a cold finger condenser cooled by solid carbon dioxide. A solution of methyl bromide (76.2 g., 0.80 mole.) in 250 ml. of ether were slowly added from the dropping funnel and produced a vigorous reaction to form methyl magnesium bromide. A solution of redistilled thiophosphoryl chloride (45.5 g., 0.27 mole.) in 30 ml. of ether was added very slowly to the cooled, stirred, Grignard solution. 300 ml. of 10% sulphuric acid were then added to the reaction mixture whereupon a white solid precipitated. The solid was filtered, washed with 1.5 litres of water and dried in a vacuum desiccator over P_2O_5 . The crystals were recrystallised from dry ethanol and dried again, giving white crystals of tetramethyl biphosphine disulphide $(CH_3)_2P - P(CH_3)_2$.

S S

mpt. 221-224°C. Yield 9.4 g., 50.5 m. moles.

Preparation of Dimethyl Phosphine 153

A two necked flask; charged with tetramethyl biphosphine disulphide (2.6289 g., 14.15 m. moles.) and lithium aluminium hydride (1.2389 g., 32.8 m. moles), was attached to the vacuum line and the system filled with about 100 mm .Hg of dry nitrogen after it had been evacuated. From a bent side arm, degassed, dry diglyme (8 ml.) was added dropwise. A fairly vigorous reaction started and was moderated by ice cooling. The dimethyl phosphine produced passed through a trap at -78° into one at -196°C . When the reaction had stopped the solvent was pumped off to prevent any further slow production of the pyrophoric phosphine. The dimethyl phosphine in the -196° trap was fractionated twice under vacuum through traps at -78° and -120°C . to give a product whose purity was confirmed by its infrared spectrum, molecular weight and vapour pressure, $(\text{CH}_3)_2\text{PH}$ (1.2776 g., 73%, 2.06 m. moles, M , 61.0, v.p. 337 mms./Hg. at 0°C .). The reported vapour pressure is 338 mm./Hg at 0°C .

Preparation of Cycloheptatriene Molybdenum Tricarbonyl

Under an atmosphere of nitrogen, molybdenum hexacarbonyl (52.8 g., 0.2 mole.), 100 ml. of cycloheptatriene and 400 ml. of 100° - 120° petroleum ether were refluxed for 20 - 24 hours. The solution was then greatly reduced in volume, cooled in solid CO₂ and the red crystals filtered off. The crude product was placed in a sublimator and the excess hexacarbonyl removed at 50°C under high vacuum until no more appeared (usually about 8 - 12 hours). Sublimation at 90° - 100°C. at high vacuum gave red crystals of pure cycloheptatriene molybdenum tricarbonyl (mpt. 100°C). The yield varied but was between 40 and 60%.

Preparation of Bicycloheptadiene Molybdenum Tetracarbonyl

A one litre flask fitted with reflux condenser, stirrer and dropping funnel was flushed continuously with nitrogen. In the flask were placed molybdenum hexacarbonyl (52.8 g., 0.2 mole.) and 400 ml. of 100° - 120°C. petroleum ether. The stirred solution was heated to reflux and bicyclo(2,2,1)hepta(2,5)diene (67.9 g., 0.74 mole.) was added very slowly. Refluxing was continued for 20 - 24 hours after the addition was complete. The cooled solution was then filtered several times through glass wool to remove the brown polymeric material formed during reaction.

The volume of the solution was greatly reduced and cooled in solid CO_2 . The yellow crystals which formed were filtered off and placed in a sublimator. Unreacted molybdenum hexacarbonyl was sublimed off at 50°C under high vacuum for about 8 - 12 hours and then the product was sublimed at $90^\circ - 100^\circ\text{C}$ to give yellow crystals (mpt. 76°C ., yield 32.0 g., 0.107 mole.) of bicycloheptadiene molybdenum tetracarbonyl.

Preparation of Cycloheptatriene Chromium Tricarbonyl ¹⁵⁴

Chromium hexacarbonyl (15.0 g., 0.069 mole.), 50 ml. of cycloheptatriene and 150 ml. of $100^\circ - 120^\circ\text{C}$. petroleum ether were refluxed for about 24 hours under nitrogen. The product was isolated in the same way as the corresponding molybdenum compound. The yield of bright red crystals of cycloheptatriene chromium tricarbonyl (mpt. $128^\circ - 130^\circ\text{dec.}$) was 3.0 g., 0.0133 mole., 22%.

Preparation of Bicycloheptadiene Chromium Tetracarbonyl ¹⁵⁴

25 ml. of bicyclo(2,2,1)hepta(2,5)diene was added very slowly to a refluxing solution of chromium hexacarbonyl (11.0 g., 0.05 mole.) in 175 ml. of $100^\circ - 120^\circ\text{C}$. The mixture was refluxed for about 48 hours after completion of the addition. The product, bright yellow crystals, (mpt. 92° , 3.1 g., 0.0119 mole.) was isolated in the same way as the molybdenum compound.

Preparation of $\text{cis}-(\text{C}_5\text{H}_{10}\text{NPF}_2)_3\text{Mo}(\text{CO})_3$.

Piperidino-N-difluorophosphine (5.69 g., 37.2 m. moles) was added slowly to cycloheptatriene molybdenum tricarbonyl (0.897 g., 3.3 m. moles) and the solution stirred for one hour at 40-50°. The excess piperidino-N-difluorophosphine was taken off by high vacuum distillation, leaving pink crystals in the flask. The impure product was purified by the decolourisation of its hexane solution with charcoal, giving white crystals of cis-tris(piperidino-N-difluorophosphine) molybdenum tricarbonyl (1.753 g., 2.75 m. moles) mpt. 94°C, identified by its infrared spectrum.

PART I

All of the following reactions were performed in sealed, evacuated, Pyrex tubes. Involatile reactants were placed in the reaction tube and thoroughly outgassed before use, volatile reactants were condensed into the tube under vacuum. Reaction tubes were opened under high vacuum.

Preparation of $\text{trans-(PF}_3\text{)}_3\text{Mo(CO)}_3$

Phosphorus trifluoride (0.3995 g., 4.54 moles.) and cycloheptatriene molybdenum tricarbonyl (0.274 g., 1.0 m. moles.) reacted for three days. The volatile contents were then vacuum fractionated through traps at -78° and -196°C . A very little brown solid remained in the reaction tube. The -196° fraction was shown by its infrared spectrum and molecular weight to be phosphorus trifluoride (0.1655 g., 1.88 m. moles., M. 86.0). The fraction in the -78° trap was shown by its infrared spectrum to be a mixture of cycloheptatriene and trans-tris(trifluorophosphine) molybdenum tricarbonyl. Repeated fractionation through cold traps failed to separate the mixture. By repeatedly allowing most of the fraction to pass from a trap at room temperature to one at -196° a sample of pure trans-tris(trifluorophosphine) molybdenum tricarbonyl was obtained.

The remaining mixture could not be resolved further (0.3093 g.). The pure trans-(PF₃)₃Mo(CO)₃ was a colourless crystalline solid (0.1164 g., 0.26 m. moles., mpt. 42.0°C). (Found: C, 8.25; H, 0.15; F, 38.1; P, 21.5. C₃F₉MoO₃P₃ requires C, 8.1; H, 0.0; F, 38.6; P, 20.95%).

Preparation of trans-(CCl₃PF₂)₃Mo(CO)₃

Difluorotrichloromethylphosphine (3.5030 g., 18.7 m. moles.) and cycloheptatriene molybdenum tricarbonyl (1.499 g., 5.52 m. moles.) reacted, with slight evolution of heat, to form an off-white solid and a pale brown liquid. To ensure complete reaction the tube was left overnight before it was opened and the volatile contents distilled into the vacuum line. Repeated fractionation through cold traps failed to separate the volatile products. The mixture was shown by infrared spectroscopy to contain cycloheptatriene and difluorotrichloromethylphosphine (0.8891 g.).

The pale brown solid was removed from the reaction tube and its infrared spectrum examined. The appearance of absorptions in the C-O, P-F and C-Cl stretching regions suggested that it was trans-tris(difluorotrichloromethylphosphine) molybdenum tricarbonyl, (4.0 g., 5.32 m. moles.). Crystallisation from acetonitrile gave white crystals, mpt. 95.5 - 96.0°C. (Found: C, 9.9; H, 0.3; Cl, 42.9; F, 15.3; P, 12.7. C₆Cl₉F₆MoO₃P₃ requires C, 9.7; H, 0.0; Cl, 42.9; F, 15.3; P, 12.5%).

Preparation of $\text{trans}-(\text{CF}_2\text{PF}_2)_3\text{Mo}(\text{CO})_3$

Difluorotrifluoromethylphosphine (0.6944 g., 5.03 m. moles) and cycloheptatriene molybdenum tricarbonyl (0.278 g., 1.02 m. moles.) reacted for two days. A very small amount of pale brown solid remained in the tube when the volatile contents were distilled into the vacuum line. The volatiles were fractionated through traps at -78° and -196°C . The -196° trap was shown by its infrared spectrum to contain difluorotrifluoromethyl phosphine and a little silicon tetrafluoride (0.2781 g., 2.015 m. moles., M, 133). The contents of the -78° trap were passed through a trap at -24° to one at -196° . Cycloheptatriene, identified by its infrared spectrum, passed to the -196° trap (0.0837 g., 0.89 m. moles.).

The -24° trap contained a colourless liquid whose infrared spectrum suggested it was $\text{trans-tris}(\text{difluorotrifluoromethylphosphine})\text{molybdenum tricarbonyl}$ (0.5144 g., 0.87 m. moles.). (Found: C, 12.9; H, 0.1; F, 50.6; P, 16.55. $\text{C}_6\text{F}_{15}\text{MoO}_3\text{P}_3$ requires C, 12.1; H, 0.0; F, 48.0; P, 15.65%).

Preparation of $\text{trans}-[(\text{CF}_3)_2\text{PF}]_3\text{Mo}(\text{CO})_3$

~~Fluoro~~bis(trifluoromethyl phosphine (0.7328 g., 3.90 m. moles) and cycloheptatriene molybdenum tricarbonyl (0.2728 g., 1.00 m. moles.) reacted for four days to produce a brown liquid and a little yellow solid.

The volatile products were fractionated on the vacuum line, leaving the yellow solid in the tube. The unreacted fluoro bis(trifluoromethyl)phosphine, identified by its infrared spectrum, passed a trap at -78° and stopped in the -196° trap (0.1849 g., 0.984 m. moles, M, 184). The contents of the -78° trap were fractionated through traps at -36° , -78° and -196° . The -78° trap contained cycloheptatriene (0.0715 g., 0.78 m. moles.), identified by its infrared spectrum.

The -36° trap contained a colourless liquid which moved slowly under high vacuum. Its infrared spectrum suggested that it was trans-tris (fluorobis trifluoromethylphosphine) molybdenum tricarbonyl (0.6848 g., 0.92 m. moles.). (Found: C, 13.8; H, 0.0; F, 60.3; P, 12.0. $C_9F_{21}MoO_3P_3$ requires C, 14.5; H, 0.0; F, 53.6; P, 12.5%).

Second Preparation of trans- $[(CF_3)_2PF]_3Mo(CO)_3$ —

Fluorobis trifluoromethyl phosphine (1.0258 g., 5.46 m. moles.) and cycloheptatriene molybdenum tricarbonyl (0.2775 g., 1.01 m. moles.) reacted for four days. The more volatile products were removed from the reaction tube by distillation on the vacuum line leaving a red liquid in the reaction tube. The liquid was extracted with hot hexane and the solution boiled with activated charcoal.

The solution was still coloured when the charcoal had been filtered off. The hexane was removed under vacuum and the red liquid was distilled over a short path length at 46 - 49°C under high vacuum. The infrared spectrum of the colourless liquid distillate (0.4788 g., 0.64 m. moles.) was identical to that of the previous preparation.

The volatile products were fractionated through -78° and -196°. Excess fluorobis(trifluoromethyl)phosphine was recovered in the -196° trap (0.4663 g., 2.48 m. moles, M, 185) and was identified by its infrared spectrum and molecular weight. Cycloheptatriene, identified by its infrared spectrum, was recovered in the -78° trap (0.0823 g., 0.89 m. moles.).

Preparation of $\text{trans-}[\text{C}_3\text{F}_7\text{PF}]_3\text{Mo}(\text{CO})_3$

Fluorobisheptafluoropropyl phosphine (1.5025 g., 3.88 m. moles.) and cycloheptatriene molybdenum tricarbonyl (0.2794 g., 1.03 m. moles.) reacted slowly for ten days to produce a light brown solid and a small amount of liquid. Vacuum fractionation failed to separate the volatile products which were shown by infrared spectroscopy to be cycloheptatriene and unreacted fluorobisheptafluoropropyl phosphine (0.4812 g.).

A small amount of the brown solid sublimed at 65 - 70°C to give white crystals. However, when the bulk of the solid was sublimed, extensive decomposition occurred and the solid charred. Crystallisation of the charred residue, from hexane, gave white crystals, mpt. 79.5 - 80.0°C. The infrared spectrum suggested that the crystals were trans-tris-(fluorobis heptafluoropropyl phosphine)molybdenum tricarbonyl (0.388 g., 0.29 m. moles.). (Found: C, 18.7; H, 0.0; F, 61.9; P, 6.7. $C_{21}F_{45}MoO_3P_3$ requires C, 18.7; H, 0.0; F, 63.6; P, 6.9%).

Reaction between $(CF_3)_3P$ and $C_7H_8Mo(CO)_3$

Tris-trifluoromethylphosphine (1.3207 g., 5.55 m. moles.) and cycloheptatriene molybdenum tricarbonyl (0.276 g., 1.00 m. moles.) reacted for seven days to produce a black solid and a red liquid. The volatiles were vacuum fractionated through traps at -24°, -78° and -196°C. The black solid remained in the reaction tube. The trap at -196° was shown by infrared spectroscopy to contain unreacted tris-trifluoromethylphosphine (0.8572 g., 3.60 m. moles.). The -78° trap contained cycloheptatriene (0.0129 g., 0.14 m. moles.), identified by its infrared spectrum.

The trap at -24° contained a colourless solid and liquid of low volatilities, which could not be separated by further fractionation. The infrared spectrum and ^{19}F N.M.R. spectra of this fraction (0.1824 g.) showed it to be a mixture of products containing $(\text{CF}_3)_3\text{P}$ and CO groups.

Extraction of the black solid with hot hexane failed to produce anything when the solvent was removed under vacuum.

Preparation of $\text{cis}-(\text{PF}_3)_2\text{Mo}(\text{CO})_4$

Phosphorus trifluoride (0.2956 g., 3.36 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.3036 g., 1.01 m. moles.) reacted for four days. A very small amount of brown solid stayed in the reaction tube when the volatile contents were vacuum fractionated through traps at -96° and -196°C . The -196° trap contained unreacted phosphorus trifluoride (0.1230 g., 1.40 m. moles.), identified by its infrared spectrum. The contents of the -96° trap were passed through a -36° trap several times to give two fractions. The more volatile fraction (0.0934 g.) was shown by its infrared spectrum to be bicycloheptadiene containing a little cis-bis(trifluorophosphine) molybdenum tetracarbonyl.

The more volatile fraction was shown to be pure cis-bis (trifluorophosphine) molybdenum tetracarbonyl, (0.3120 g., 0.814 m. moles., mpt. $27 - 28^{\circ}\text{C}$.).

Preparation of $\text{cis}-(\text{CCl}_3\text{PF}_2)_2\text{Mo}(\text{CO})_4$

Difluorotrichloromethylphosphine (0.9717 g., 5.18 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.3942 g., 1.22 m. moles.) reacted with slight evolution of heat when brought to room temperature. The reaction was judged to be complete after one day and the volatile contents of the reaction tube were taken into the vacuum line. Infrared spectroscopy showed these to be a mixture of bicycloheptadiene and unreacted difluorotrichloromethylphosphine (0.5344 g.). The mixture could not be separated by fractional condensation. The grey solid in the reaction tube was distilled over a very short path length at high vacuum and at 60 - 65°C. The distillate was a colourless liquid which solidified very slowly when stored under nitrogen. The liquid (0.4298 g., 0.74 m. moles.) was shown by its infrared spectrum to be cis-bis(difluorotrichloromethylphosphine) molybdenum tetracarbonyl. (Found: C, 12.5; H, 0.2; Cl, 36.5; P, 10.6. $\text{C}_6\text{Cl}_6\text{F}_4\text{MoO}_4\text{P}_2$ requires C, 12.35; H, 0.0; Cl, 36.2; P, 10.6%).

When this method of purification was repeated substantial decomposition occurred and the following method was adopted.

Alternative preparation of $\text{cis}-(\text{CCl}_2\text{PF}_2)_2\text{Mo}(\text{CO})_4$

Difluorotrichloromethylphosphine (0.6652 g., 3.55 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.3243 g., 1.08 m. moles.) reacted exothermically when warmed slowly to room temperature. After one day the tube contained a viscous, brown liquid. The volatile contents of the tube were passed into the vacuum line. Vacuum fractionation failed to separate the mixture of bicycloheptadiene and difluorotrichloromethylphosphine (0.2371 g.).

The waxy solid which remained in the reaction tube was extracted with hot hexane and the solution boiled briefly with activated charcoal. The hexane was removed from the filtered solution giving a yellow, waxy solid. Recrystallisation twice from a small volume of 100 - 120° petroleum ether gave white crystals whose infrared spectrum showed them to be cis-bis - (difluorotrichloromethylphosphine) molybdenum tetracarbonyl. (0.465 g., 0.80 m. moles., mpt. 38.5 - 39.5°C.), identical to the product from the previous preparation.

Preparation of cis-(CF₃PF₂)₂Mo(CO)₄

Difluorotrifluoromethylphosphine (0.3370 g., 2.8 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.3265 g., 1.08 m. moles.) reacted for four days. The volatile products were vacuum fractionated through traps at -78° and -196°C. A very small amount of pale yellow solid remained in the tube. The -196° fraction was shown by its infrared spectrum to be unreacted difluorotrifluoromethylphosphine (0.0166 g., 0.12 m. moles.). The -78° fraction was passed through a trap at -36° to one at -196°. Bicycloheptadiene, identified by its infrared spectrum, passed the -36° trap (0.0404 g., 0.43 m. moles.).

The -36° trap contained a colourless liquid whose infrared spectrum suggested it was cis-bis(difluorotrifluoromethylphosphine) molybdenum tetracarbonyl (0.4261 g., 0.88 m. moles.). (Found: C, 14.9; H, 0.1; F, 31.4; P, 12.8. C₆F₁₀MoO₄P₂ requires C, 14.9; H, 0.0; F, 39.3; P, 12.8%).

Preparation of $\text{cis}-(\text{CF}_3)_2\text{PF}_2\text{Mo}(\text{CO})_4$

Fluorobistrifluoromethylphosphine (0.4974 g., 2.65 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.2936 g., 0.97 m. moles.) reacted for four days to produce a little white solid and a yellow liquid. The volatiles were fractionated through traps at -36° , -78° and -196°C . The bicycloheptadiene and excess fluorobis(trifluoromethyl)phosphine could not be completely separated by fractionation. The mixture was condensed into a tube containing 5 ml. of 2 N NaOH, the tube was sealed and allowed to stand at room temperature for several days. When the tube was opened 0.0665 g. of fluoroform, identified by its infrared spectrum, were recovered. Assuming the reaction:-

$(\text{CF}_3)_2\text{PF}_2 + 3 \text{NaOH} \longrightarrow 2 \text{CF}_3\text{H} + \text{NaF} + \text{Na}_2\text{HPO}_3$ to have occurred then the mixture must have contained (0.0893 g., 0.47 m. moles.) of unreacted $(\text{CF}_3)_2\text{PF}_2$. By difference from the weight of the unhydrolysed mixture the weight of recovered bicycloheptadiene was 0.0644 g., 0.70 m. moles.

The -36° fraction was a colourless liquid with an infrared spectrum as expected for $\text{cis-bis}(\text{fluorobistrifluoromethylphosphine})\text{molybdenum tetracarbonyl}$ (0.5221 g., 0.89 m. moles.)

(Found: C, 15.6; H, 0.0; F, 52.2; P, 13.5. $\text{C}_8\text{F}_{14}\text{MoO}_4\text{P}_2$ requires C, 16.45; H, 0.0; F, 45.6; P, 10.6%).

Preparation of cis-[(CF₃)₃P]₂Mo(CO)₄

Tris-trifluoromethylphosphine (0.7899 g., 3.32 m. moles.) and bicycloheptadiene molybdenum tetracarbonyl (0.306 g., 1.02 m. moles.) reacted for ten days to produce a red liquid and a brown solid. The volatile contents were fractionated through traps at -78° and -196°C. The -196° fraction was shown by its infrared spectrum and molecular weight to be tris-trifluoromethylphosphine (0.2950 g., 1.24 m. moles, M, 228). The -78° fraction was shown by its infrared spectrum to be bicycloheptadiene (0.0508 g., 0.50 m. moles.).

After prolonged pumping a colourless liquid moved into the vacuum line from the reaction tube. The brown solid did not move. The infrared spectrum of the liquid suggested that it was cis-bis[tris trifluoromethylphosphine] molybdenum tetracarbonyl (0.457 g., 0.67 m. moles.) (Found: C, 18.1; H, 0.0; F, 58.0; P, 8.7. C₁₀F₁₈MoO₄P₂ requires C, 17.5; H, 0.0; F, 50.0; P 9.1%).

Preparation of $\text{cis}-(\text{PF}_3)_2\text{Cr}(\text{CO})_4$

Phosphorus trifluoride (0.4858g., 5.52 m. moles.) and bicycloheptadiene chromium tetracarbonyl (0.5322 g., 2.08 m. moles.) were allowed to stand at room temperature for ten days. There was no formation of the expected liquid, bicycloheptadiene. The tube was heated for 24 hours at 50°C . and then for 12 hours at 100°C . until the reaction appeared to be complete. The volatiles were fractionated, leaving some yellow solid in the tube. In the -196° trap were phosphorus trifluoride and a small amount of silicon tetrafluoride, shown by infrared spectroscopy, (0.1606 g., 1.82 m. moles.).

The contents of the -78° trap were passed through a trap at -36° several times but the mixture, shown by infrared to be bicycloheptadiene and $\text{cis}-(\text{PF}_3)_2\text{Cr}(\text{CO})_4$ could not be completely separated. The more volatile fraction was the mixture

(0.298 g.,).

The infrared spectrum of the pale yellow liquid in the -36° trap suggested that it was $\text{cis-bis}(\text{tri-fluorophosphine})\text{chromium tetracarbonyl}$ (0.5101 g., 1.50 m. moles.).

(Found: C, 13.8; H, 0.0; F, 27.1; P, 17.4. $\text{C}_4\text{F}_6\text{MoO}_4\text{P}_2$ requires C, 14.1; H, 0.0; F, 33.5; P, 18.25%).

The ^{19}F NMR spectrum suggests that there may be several isomers present in the mixture.

PART II

Reaction between Diethylamine and Difluorotrichloromethylphosphine.

The diethylamine was purified by drying over KOH pellets, distillation, then fractionation on the vacuum line through a trap at -45° to one at -78°C . The middle fraction only was used (M 72.4) and stored under vacuum in a sealed glass tube.

Difluorotrichloromethylphosphine (1.7254 g., 9.22 m. moles.) reacted with diethylamine (0.6834 g., 9.35 m. moles.) upon warming slowly from -196° to room temperature. A very small amount of white solid formed during the rather vigorous reaction, in addition to a colourless liquid. After about five minutes the contents of the tube became yellow and when the volatile products had been pumped into the vacuum line a very little brown liquid remained behind. The products were separated by fractionation through traps at -63° , -96° , and -196°C . The trap at -196° contained phosphorus trifluoride (0.0544 g., 0.618 m. moles.) identified by its infrared spectrum and molecular weight (M, 81). The trap at -96° contained chloroform (0.9320 g., 7.8 m. moles.) identified by its infrared spectrum and molecular weight (M, 120). The colourless liquid in the trap at -63° was identified by its infrared and N.M.R. spectra as diethylamino-N-difluorophosphine (1.003 g., 7.13 m. moles., M. 139). The vapour pressure of $(\text{C}_2\text{H}_5)_2\text{NPF}_2$ at 18.7°C was 44 mm. Hg.

Reaction between Piperidine and Difluorotrichloromethylphosphine.

The piperidine was dried over KOH pellets then distilled at 106-107°C. It was vacuum fractionated and the middle fraction, stopping at -45°C, was taken as pure piperidine and stored in sealed, evacuated, Pyrex tubes.

Difluorotrichloromethylphosphine (1.8342 g., 9.8 m. moles.) reacted with piperidine (0.8256 g., 9.71 m. moles.) when warmed slowly from -196° to room temperature. A colourless liquid and a little white solid were formed by the slightly exothermic reaction. The volatile products of the reaction were fractionated in the vacuum system through traps at -45°, -96° and -196°C. The trap at -196° contained phosphorus trifluoride, (0.1191 g., 1.35 m. moles.) identified by its infrared spectrum and molecular weight (M, 90.0). The trap at -96° contained chloroform (1.0775 g., 8.94 m. moles., M, 119), identified by infrared and molecular weight measurements. The trap at -45° contained a colourless liquid identified as piperidino-N-difluorophosphine (0.7956 g., 5.2 m. moles.) by its infrared and N.M.R. spectra. The vapour pressure of $C_5H_{10}NPF_2$ at 20.6°C was 6.6 mm. Hg.

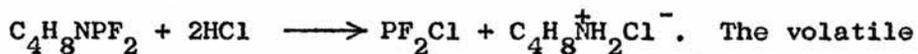
The Reaction of Pyrrolidine with Difluorotrichloromethylphosphine.

The pyrrolidine was dried over KOH pellets and distilled at 86.8-88.0°C. It was then vacuum distilled through a trap at -24° and stored in sealed glass tubes.

Difluorotrichloromethylphosphine (1,801 g., 9.62 m. moles.) and pyrrolidine (0.6935 g., 9.76 m. moles.) reacted exothermically when slowly warmed from -196° to room temperature. A small amount of solid was evident in the reaction tube, together with a yellow liquid, after the reaction had stopped. The volatile products were pumped into the vacuum line leaving a yellow, very viscous oil in the tube. Fractionation of the volatiles through traps at -45°, -96° and -196°C partially resolved the mixture. The trap at -196° contained phosphorus trifluoride (0.1323 g., 1.5 m. moles., M, 88.4) identified by its infrared spectrum and molecular weight. The traps at -96° and -45° both contained a mixture of chloroform and pyrrolidino-N-difluorophosphine as shown by infrared spectra. Repeated refractionation through a trap at -45° separated pure pyrrolidino-N-difluorophosphine (0.4132 g., 2.98 m. moles.) having a vapour pressure of 11.0 mm. at 18.0°C. The infrared and N.M.R. spectra were identical to the product obtained by fluorination of pyrrolidino-N-dichlorophosphine. The remaining mixture of chloroform and pyrrolidino-N-difluorophosphine could not be separated by further fractionation.

The composition of the mixture (1.0760 g.) was determined by reacting it with hydrogen chloride (0.2786 g., 7.63 m. moles., M 36.0).

A white solid was produced as expected from the reaction:



The volatile contents of the tube were fractionated through a trap at -120° where chloroform (0.8699 g., 7.26 m. moles., M, 122.1) was isolated and identified by infrared and molecular weight measurements. The excess hydrogen chloride, together with the difluorochlorophosphine, passed to a trap at -196° . The contents of the mixture (0.3274 g.) were shown by infrared spectroscopy. This reaction shows that the original mixture contained 0.2061 g. of pyrrolidino-N-difluorophosphine. The total amount of pyrrolidino-N-difluorophosphine produced in the reaction was, therefore, 0.6193 g., 4.45 m. moles. .

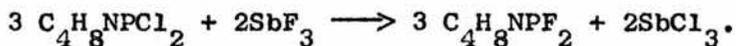
Preparation of Pyrrolidino-N-dichlorophosphine

Phosphorus trichloride (68.75 g., 0.5 mole.) was dissolved in 100 ml. of dry ether and the solution placed in a three necked flask fitted with a reflux condenser and a dropping funnel. The system was kept under an atmosphere of dry nitrogen and the flask cooled in solid carbon dioxide.

Dry, redistilled pyrrolidine (71 g., 1 mole.), dissolved in 100 ml. of dry ether, was added very slowly to the stirred solution of phosphorus trichloride. There was a vigorous reaction as each drop of amine was added and the white insoluble amine hydrochloride formed. When the addition was complete the stirred solution was allowed to warm to room temperature to allow the dissolved HCl to escape. The amine hydrochloride was filtered off and washed with ether (3 x 50 ml.). The ether was distilled off and the last traces were removed under vacuum. The residue was vacuum distilled at $98.5-102^{\circ}\text{C}/19.5\text{ mm.}$ to give a colourless, fuming liquid (41 g., 0.24 mole.). The product was redistilled through a short Vigreux column at $92.5-93.0^{\circ}\text{C}/13\text{ mm.}$ (Found: C, 27.9; H, 5.0; Cl, 36.4; N, 7.0; P, 17.4. $\text{C}_4\text{Cl}_2\text{H}_8\text{NP}$ requires C, 27.9; H, 4.65; Cl, 41.1; N, 8.1; P, 18.0%). The reactivity towards moisture may explain the low chlorine analysis. The structure of the compound was confirmed by its proton and phosphorus N.M.R. spectra.

Fluorination of Pyrrolidino-N-dichlorophosphine by
Antimony Trifluoride.

Pyrrolidino-N-dichlorophosphine was placed in a two necked flask fitted with a reflux condenser and a bent side arm. The system was flushed continuously with dry nitrogen. Freshly refluxed antimony trifluoride was added slowly from the side arm. Slightly more antimony trifluoride was added than required for the reaction:-



The exothermic reaction was controlled by the rate of addition of the antimony trifluoride. During the reaction, at just above room temperature, a colourless gas was evolved as each portion of SbF_3 was added, later observations suggested that this gas was phosphorus trifluoride. When the addition was complete the mixture was kept at $50-60^\circ\text{C}$. for $2\frac{1}{2}$ hours. The liquid in the flask slowly turned brown and more gas was evolved. The liquid product was distilled under vacuum to give only one fraction. The boiling point of the product from two attempts ($64^\circ/16 \text{ mm.}$; and $82^\circ/12 \text{ mm.}$) using the above method suggested that the product was not pure pyrrolidino-N-difluorophosphine but mostly the dichlorophosphine.

A second method of preparation of $C_4H_8NPF_2$ was eventually used. Antimony trifluoride (10g., 5.58 m. moles.) was added slowly to pyrrolidino-N-dichlorophosphine (18.3 g., 10.6 m. moles.) in the manner described above and the reaction mixture then stirred at room temperature for one hour.

The flask was attached to the vacuum line and the volatile products were fractionated through traps at -78° and $-196^\circ C$. The trap at -78° was shown by infrared spectroscopy to contain pyrrolidino-N-difluorophosphine and a small amount of phosphorus trifluoride. Repeated fractionation failed to remove the phosphorus trifluoride completely. The pyrrolidino-N-difluorophosphine produced (2.86 g., 20.6 m. moles.) was a colourless liquid with a very strong smell, its vapour pressure at $20^\circ C$ was 11.0 mm. Hg (Found: C, 35.0; H, 6.1; N, 9.8; P, 21.9. $C_4F_2H_8NP$ requires C, 34.55; H, 5.75; N, 10.1; P, 22.3%).

A slow moving, colourless liquid also moved slowly into the vacuum line and stopped at -24° (1.5915 g.). The ^{31}P N.M.R. spectrum showed that this was unreacted pyrrolidino-N-dichlorophosphine.

Action of heat upon pyrrolidino-N-difluorophosphine.

A sample of freshly purified pyrrolidino-N-difluorophosphine (0.452 g., 3.25 m. moles.) was heated in a sealed, evacuated Pyrex tube at 50°-60°C for four hours. Fractionation of the tube contents gave unreacted starting material and a more volatile fraction, identified as phosphorus trifluoride (0.0.9 g., 0.216 m. moles.) by its infrared spectrum.

Reaction between Dimethyl Phosphine and Difluorotrichloro-
methylphosphine.

Difluorotrichloromethylphosphine (0.6913 g., 3.70 m. moles.) and dimethyl phosphine (0.5357 g., 8.65 m. moles.) were condensed into an evacuated glass tube which was sealed and slowly allowed to warm to room temperature. On reaching room temperature a white solid slowly formed. After one hour the tube appeared to contain a white solid and two immiscible liquids. The tube was opened under vacuum and the liquids moved into the vacuum line where they were fractionated through traps at -78° , -120° and -196°C . The white solid did not move under high vacuum. The trap at -196° was shown by infrared ^{spectroscopy} to contain phosphorus trifluoride (0.0897 g., 1.02m. moles., M, 86). The contents of the traps at -78° and -120° had identical infrared spectra and so were combined. The total weight of this combined fraction was 0.5311 g., it appeared to consist of two immiscible liquids. Each time the liquids were allowed to move from a trap at room temperature, during attempts at fractionation, a small amount of white solid was left behind. The infrared spectrum showed a large number of peaks but those due to chloroform could be picked out at 1216 and 769 cm.^{-1} .

In order to find the constitution of the mixture, its ^1H and ^{19}F nuclear magnetic resonance spectra were examined. The fluorine resonance consisted of a doublet of triplets and a doublet of septuplets and was in complete agreement with a spectrum, provided by Dr. R. Schmutzler, of trifluorodimethylphosphorane.. The ^1H spectrum contained a line at 2.6 τ assignable to chloroform and an irregular doublet at 8.4 τ suggesting the presence of P - H coupling, $J = 8.5\text{c/s.}$ The proton resonance of $(\text{CH}_3)_2\text{PF}_3$ could not be observed.

However, with the new information it was seen that the infrared spectrum of the mixture consisted of three superimposed spectra, those of CHCl_3 , $(\text{CH}_3)_2\text{PF}_3$ and a third unidentified compound. Infrared spectrum of the mixture:- 3170 vw, 3052 vw, 2989 w, 2978 w, 2969 w, 2915 w, 2908 w, 1431 w, 1422 w, 1416 w, 1402 w, 1322 w, sh; 1319 m, 1314 m, 1304 m, sh; 1293 m, 1217 m, 981 s, 951 m, 913 w, sh; 890 s, 382 m, sh; 849 w, 836 w, 770 vs, 762 vs, 753 vs, 686 w, 675 w, (cm.^{-1}).

Slow, repeated passage of the mixture through a trap at -63° yielded a small amount of white solid which melted at about room temperature. The infrared spectrum of this fraction showed it to be free of chloroform and of trifluorodimethylphosphorane. Complete separation of the constituents of the mixture proved impossible, however. Infrared spectrum of the -63° fraction:- 2990 s, 2980 s, 2970 s, 2916 m, P; 2910 s, Q; 2903 m, R; 1442 m, sh; 1439 m, sh; 1434 s, 1428 s, 1419 s, 1413 m, sh; 1407 m, 1300 m, sh; 1297 vs, 1288 s, 1279 m, 1091 vw, 1029 vw, 960 m, P; 955 vs, Q; 946 m, R; 890 s, P; 885 vs, Q; 876 s, R; 851 vw, 705 s, 685 w, 674 w, (cm.^{-1}).

The -63° fraction appeared to decompose at room temperature while being weighed. The ^1H , ^{19}F N.M.R. spectra of this fraction were identical to those of the former mixture.

The white solid product was sealed off under vacuum and the tube opened in the dry-box. The solid was very sticky and difficult to handle. It did not form a very good mull with Nujol but an infrared spectrum was obtained:- 1413 w, 1317 s, 1226 s, 1185 m, 1170 m, 1038 s, 1006 s, 913 s, b, 880 s, 760 m, 704 s, 676 m, 668 m, (cm.^{-1}).

Analysis:- C, 17.32; H, 5.24; P, 5.24; %.

A fresh sample of the white solid (0.2824 g.) was reacted in a sealed tube with pyridine (1.0735 g., 13.6 m. moles). When the volatile tube contents were fractionated through traps at -63° and -196° , they were found to consist of pyridine (0.9737 g., 12.4 m. moles) and dimethylphosphine (0.0398 g., 0.64 m. moles).

Attempted Reaction of Difluorotrichloromethylphosphine with
Bis(trifluoromethyl)phosphine.

Difluorotrichloromethylphosphine (0.7210 g., 3.86 m. moles.) and bis(trifluoromethyl)phosphine (0.6343 g., 3.73 m. moles.) were condensed into a tube at -196°C . The tube was sealed and allowed to warm slowly to room temperature. Since there was no obvious sign of reaction the tube was allowed to stand at room temperature for 9 hours. The contents were fractionated on the vacuum line and examined by infrared spectroscopy which showed only the presence of starting materials. The reactants were resealed in the tube and heated at 60° for 6 hours. The contents were fractionated again, through traps at -78° , -120° and -196°C , and were shown to be unchanged except for the appearance of a small new peak at 1026 cm.^{-1} due to a small amount of silicon tetrafluoride. To ensure that there was no product in the fraction at -78° , this was passed through a trap at -45° , but nothing was condensed out. The -120° fraction did not contain any chloroform, as expected if reaction had occurred.

Reaction between Methyl Thiol and Difluorotrichloromethyl-
phosphine

Difluorotrichloromethylphosphine (1.0787 g., 5.75 m. moles.) and methyl thiol (0.3537 g., 7.37 m. moles.) were allowed to stand at room temperature in a sealed tube for three days. The tube contents were fractionated and examined by infrared spectroscopy. Only starting materials, together with a trace of silicon tetrafluoride, were present. The mixture was resealed and heated at 60° for 13 hours, and again the volatile contents of the tube were found to be starting materials. A very small amount of involatile white solid remained in the tube but was not examined further because of the possible high toxicity of oxidised by-products.

Reaction of Phosphorus Trifluoride with Methyl Thiol in the
presence of Triethylamine.

Phosphorus trifluoride (0.7325 g., 8.32 m. moles.), methyl thiol (0.1445 g., 3.01 m. moles.) and triethylamine (0.3592 g., 3.55 m. moles.) were condensed into a glass tube which was sealed off under vacuum and allowed to slowly warm from -196° to room temperature.

Reaction appeared to occur well below room temperature but the tube was kept at room temperature for 10 minutes to ensure complete reaction. The volatile products were fractionated through traps at -78° , -120° and -196°C . The trap at -196° contained phosphorus trifluoride (0.5003 g., 5.68 m. moles., M, 87.0) identified by its infrared spectrum and molecular weight. The traps at -78° and -120° were shown by infrared spectroscopy to contain triethylamine which was passed through a trap at -24°C to remove any less volatile fraction. The -24° trap then contained a very small amount of liquid, which moved slowly in the vacuum line. The low volatility suggested that this was not MeSPF_2 . The triethylamine passed the -24° trap readily (0.1625 g., 1.60 m. moles., M, 97). The tube contained a yellow solid which was involatile and was presumably triethylamine hydrogen fluoride or bifluoride plus any involatile products. The solid was not investigated further because of the possible high toxicity of compounds containing P^{V} and oxygen, fluorine and methyl thio groups which could have formed during handling.

Reaction between Dimethylamine and *Trans*-tris(difluorotrichloromethyl-
phosphine) molybdenum tricarbonyl.

Dimethylamine (0.5099 g., 11.32 m. moles) and *trans*-(CCl₃PF₂)₃Mo(CO)₃ (0.5012 g., 0.676 m. moles) reacted at room temperature in a sealed, evacuated glass tube overnight. Fine needle crystals were then visible in the brown liquid contained in the tube.

The volatile products (0.5803 g.) were pumped into the vacuum line and identified by infrared spectroscopy as a mixture of chloroform and dimethylamine. The amounts of each compound in the mixture were determined by reacting it with hydrogen chloride to remove the amine as its salt. The chloroform (0.1717 g., 1.44 m. moles) was separated from the excess hydrogen chloride by fractionation through a trap at -120°. From the difference in weights of chloroform and mixture the amount of excess amine was obtained (0.4086 g., 9.08 m. moles).

The involatile, viscous brown liquid from the reaction was extracted with hot hexane and boiled with activated charcoal to produce a cloudy, viscous liquid (0.2188 g., 0.42 m. moles).

It proved impossible to purify this liquid further since it did not crystallise, did not distil, even at high vacuum, was unchanged by passage through an alumina column and could not be

detected on a gas-liquid chromatograph. (Found: C, 21.9; H, 3.4; N, 10.35; P, 17.1. $C_9H_{18}N_3P_3MoO_3$ requires C, 20.8; H, 3.5; N, 10.2; P, 17.9; %).

Reaction between Piperidine and *Trans*-tris(difluorotrichloromethylphosphine) molybdenum tricarbonyl.

Piperidine (0.5942 g., 7.0 m. moles) and *trans*-(CCl_3PF_2)₃Mo(CO)₃ (0.905 g., 1.22 m. moles) reacted at room temperature in a sealed glass tube overnight to produce a brown liquid and fine needle-shaped crystals.

The volatile products (0.3217 g.) were identified by infrared spectroscopy as a mixture of chloroform and piperidine. Reaction of the piperidine with hydrogen chloride and separation of the chloroform from the excess hydrogen chloride showed the mixture to contain 0.3038 g., 2.58 m. moles of chloroform and excess piperidine (0.0179 g., 0.21 m. moles).

Extraction of the involatile product from the reaction tube, followed by boiling with charcoal gave a milky, viscous liquid (0.5112 g., 0.80 m. moles) which could not be purified further by normal techniques.

Reaction of Piperidine and Cis-bis(difluorotrichloromethylphosphine)
molybdenum tetracarbonyl.

Piperidine (0.7847 g., 9.2 m. moles) and cis- $(CCl_3PF_2)_2Mo(CO)_4$ (2.216 g., 3.79 m. moles) reacted overnight at room temperature in a sealed glass tube to produce a brown liquid and small crystals.

The volatile products (0.6167 g.) were pumped into the vacuum line and were identified by infrared spectroscopy as piperidine and chloroform. From the reaction of the mixture with hydrogen chloride its constitution was found to be: chloroform (0.5575 g., 4.66 m. moles) and piperidine (0.0592 g., 0.696 m. moles).

After the involatile product had been extracted from the reaction tube it was decolourised with activated charcoal. The resultant viscous liquid (0.863 g., 1.69 m. moles) could not be crystallised, however, although the expected product, cis- $(C_5H_{10}NPF_2)_2Mo(CO)_4$ has been shown to be solid when pure. (Found: C, 34.82; H, 4.24; N, 5.93; P, 12.68. $C_{14}H_{20}F_4MoN_2P_2O_4$ requires C, 32.7; H, 3.9; N, 5.45; P, 12.05; %).

The infrared and H nuclear magnetic resonance spectra of this product agreed closely with those obtained by Grunbaum and Nixon.

Reaction of Hydrogen Chloride and Cis-tris(piperidino-N-difluoro-phosphine) molybdenum tricarbonyl.

No reaction occurred between hydrogen chloride (0.3403 g., 9.33 m. moles) and cis-(C₅H₁₀NPF₂)₃Mo(CO)₃ (0.967 g., 1.515 m. moles) when they were allowed to stand at room temperature overnight. After three days, however, the tube appeared to contain a dark brown solid and a viscous liquid. Upon fractionation of the volatile tube contents, hydrogen chloride (0.1363 g., 5.1 m. moles) stopped at -196° and a glassy solid (0.1124 g.) remained in the trap at -78°. The hydrogen chloride was resealed with the brown solid and left at room temperature for a further 10 days after which the volatiles consisted of 0.1237 g., 3.4 m. moles of hydrogen chloride and 0.0924 g. of the glassy solid.

The infrared spectrum of the solid suggested that it was cis-tris(difluorochlorophosphine) molybdenum tricarbonyl. Unfortunately its instability prohibited further investigations of its properties.

The black solid was extracted with hot petroleum ether giving a colourless solution which contained a very small amount of sticky white solid, sufficient for an infrared spectrum which showed it to be unreacted cis-(C₅H₁₀NPF₂)₃Mo(CO)₃. Extraction with hot chloroform gave a pink solution which produced pale pink crystals which were purified by recrystallisation from ethanol. The white crystals (0.286 g., 2.365 m. moles) were shown by their infrared spectrum

to be piperidine hydrogen chloride, mpt. $235-7^{\circ}$.

The results of the reaction may be summarised in the percentage yields of the products:- cis- $(PClF_2)_3Mo(CO)_3$, 27%; $C_5H_{10}NHCl$, 52%; HCl reacted, 65.5%

REFERENCES

- 1 L. Mond, C. Langer, F. Quincke, J. Chem. Soc., 1890, 749.
- 2 J.S. Anderson, Quart. Rev., 1947, 1, 33.
- 3 H.H. Storsch, N. Golumbic, R.B. Anderson, "The Fischer-Tropsch and Related Syntheses", Wiley, New York, 1951.
- 4 W. Reppe, "Neue Entwicklungen auf dem Gebiete der Chemie des Acetylen und Kohlenoxids", Springer Verlag, Berlin, 1949.
- 5 C.W. Bird, Chem. Rev., 1962, 62, 283.
- 6 W. Gordy, H. Ring, A.B. Burg, Phys. Rev., 1950, 78, 140.
- 7 L.O. Brockway, P.C. Cross, J. Chem. Phys., 1935, 3, 828.
- 8 L.O. Brockway, R.G. Ewens, M.W. Lister, Trans. Faraday Soc., 1937, 33, 1233.
- 9 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York, 1960, 331.
- 10 H.M. Powell, R.G. Ewens, J. Chem. Soc., 1939, 286.
- 11 J. Chatt, Nature, 1950, 165, 637.
- 12 J. Chatt, A.A. Williams, J. Chem. Soc., 1951, 3061.
- 13 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York, 1939, 231.
- 14 D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel, L.E. Sutton, J. Chem. Soc., 1954, 332.

- 15 F.A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry",
Interscience, London, 1966.
- 16 L. Malatesta, Progr. Inorg. Chem., 1959, 1,
- 17 J. Lewis, Sci. Progr., 1959, No. 187, 506.
- 18 W. Hieber, F. Leutert, Naturwiss, 1931, 19, 360.
- 19 W. Hieber, W. Beck, G. Braun, Angew. Chem., 1960, 72, 795.
- 20 M.L. Green, Angew. Chem., 1960, 72, 719.
- 21 E.O. Bishop, J.L. Down, P.R. Emtage, R.E. Richards, G. Wilkinson,
J. Chem. Soc., 1959, 2484.
- 22 S.L. La Placa, W.C. Hamilton, J.A. Ibers, Inorg. Chem., 1964, 3,
1491.
- 23 T.A. Manuel, Adv. Organometallic Chem., 1965, 3, 181.
- 24 S.F.A. Kettle, Inorg. Chem., 1965, 4, 1661.
- 25 G. Booth, Adv. Inorg. Chem. Radiochem., 1964, 6, 1.
- 26 T. Kruck, Angew. Chem., Internat. Edn., 1967, 6, 53.
- 27 R.J. Clark, P.I. Hoberman, Inorg. Chem., 1965, 4, 1771.
- 28 H. Behrens, W. Harder, Chem. Ber., 1964, 97, 426.
- 29 A.W. Hansen, Acta Cryst., 1962, 15, 930.
- 30 W. Hieber, T. Kruck, Z. Naturforsch, 1961, 16b, 709.

- 31 C.S. Kraihanzel, F.A. Cotton, Inorg. Chem., 1963, 2, 533.
- 32 R. Poilblanc, M. Bigorgne, Bull. Soc. Chim. France, 1962, 1301.
- 33 S.F.A. Kettle, Spectrochim. Acta, 1966, 22, 1388.
- 34 M. Bigorgne, Bull. Soc. Chim. France, 1960, 1986.
- 35 F.A. Cotton, Inorg. Chem., 1964, 3, 702.
- 36 W.D. Horrocks, R.C. Taylor, Inorg. Chem., 1963, 2, 723.
- 37 M. Bigorgne, Adv. Chem. Coord. Chem., 1961, 199.
- 38 F.A. Cotton, "Chemical Applications of Group Theory",
Interscience, New York and London, 1964.
- 39 N.J. Hawkins, H.C. Matraw, W.W. Sabol, D.R. Carpenter,
J. Chem. Phys., 1955, 23, 2422.
- 40 H. Murata, K. Kawai, J. Chem. Phys., 1957, 27, 605.
- 41 W.F.T. Pistorius, P.C. Haarhoff, J. Mol. Spec., 1959, 3, 621.
- 42 A. Danti, F.A. Cotton, J. Chem. Phys., 1958, 28, 736.
- 43 L.H. Jones, J. Chem. Phys., 1962, 36, 2375.
- 44 L.H. Jones, J. Chem. Phys., 1958, 28, 1215.
- 45 H.D. Kaesz, M.A. El-Sayed, J. Mol. Spec., 1962, 9, 310.
- 46 C.S. Kraihanzel, F.A. Cotton, J. Amer. Chem. Soc., 1962, 84, 4432.
- 47 L.E. Orgel, Inorg. Chem., 1962, 1, 25.
- 48 W. Beck, A. Melnikoff, R. Stahl, Angew. Chem., Internatl. Ed.,
1965, 4, 692.

- 49 L.H. Jones, Inorg. Chem., 1967, 6, 1269.
- 50 L.W. Houk, G.R. Dobson, Inorg. Chem., 1966, 5, 2119.
- 51 M.L. Maddox, S.L. Stafford, M.D. Kaesz, Adv. Organometallic Chem.,
1965, 3, 1.
- 52 A.D. Buckingham, P.J. Stephens, J. Chem. Soc., 1964, 2747.
- 53 A.D. Buckingham, P.J. Stephens, J. Chem. Soc., 1964, 4583.
- 54 P.C. Lauterbur, R.B. King, J. Amer. Chem. Soc., 1965, 87, 3266.
- 55 L.S. Meriwether, J.R. Leto, J. Amer. Chem. Soc., 1961, 83, 3192.
- 56 A. Pidcock, R.E. Richards, L.M. Venanzi, Proc. Chem. Soc.,
1964, 184.
- 57 A. Pidcock, R.E. Richards, L.M. Venanzi, J. Chem. Soc. (A), 1966, 1707
- 58 E. Pitcher, A.D. Buckingham, F.G.A. Stone, J. Chem. Phys., 1962,
36, 124.
- 59 G.F. Svatos, E.E. Flagg, Inorg. Chem., 1965, 4, 422.
- 60 G.S. Reddy, R. Schmutzler, Inorg. Chem., 1967, 6, 823.
- 61 R.J. Clark, E.O. Brimm, Inorg. Chem., 1965, 4, 651.
- 62 T.E. Thorpe, Chem. News, 1875, 32, 232.
- 63 H. Moissan, Compt. Rend., 1884, 99, 655.
- 64 L. Pauling, L.O. Brockway, J. Amer. Chem. Soc., 1935, 57, 2684.
- 65 O.R. Gilliam, H.D. Edwards, W. Gordy, Phys. Rev., 1949, 75, 1014.
- 66 J.R. Van Wazer, J. Amer. Chem. Soc., 1956, 78, 5709.

- 67 H.H. Jaffé, J. Inorg. Nucl. Chem., 1957, 4, 372.
- 68 V.N. Kulakova, Y.M. Zinov'ev, Z.Z. Soborovskii, Zhur. obschei Chem., 1959, 29, 3957.
- 69 F. Seel, R. Budenz, Z. anorg. Chem., 1935, 341, 196.
- 70 Z.M. Ivanova, A.V. Kirsanov, Zhur. obschei Chem., 1961, 31, 3991.
- 71 R. Schmutzler, Chem. Ber., 1965, 98, 552.
- 72 R. Schmutzler, Chem. Ind., 1962, 1868.
- 73 A.B. Burg, P.J. Slota, W. Mahler, G.L. Juvinall, W.A.D.C. Technical Report, 56-82, 1956.
- 74 J.E. Griffiths, A.B. Burg, J. Amer. Chem. Soc., 1962, 84, 2309.
- 75 J.F. Nixon, Chem. Ind., 1963, 1555.
- 76 A.B. Burg, G. Brendel, U.S.P. 2,959,620/1960.
- 77 J.F. Nixon, J. Chem. Soc., 1965, 777.
- 78 R.N. Sterlin, R.D. Yatsenko, L.N. Pinkina, I.L. Knunyants, Khim. Nauk i Prom., 1959, 4, 810.
- 79 A.B. Burg, G. Brendel, J. Amer. Chem. Soc., 1958, 80, 3198.
- 80 M.G. Barlow, M. Green, R.N. Hazeldine, H.G. Higson, J. Chem. Soc.(B), 1966, 1025.
- 81 M.A. Bennett, H.J. Emeleus, R.N. Hazeldine, J. Chem. Soc., 1954, 3896.
- 82 J.F. Nixon, R.G. Cavell, J. Chem. Soc., 1964, 5983.

- 83 J.F. Nixon, J. Chem. Soc., 1964, 2469.
- 84 R.R. Holmes, R.P. Wagner, Inorg. Chem., 1963, 2, 394.
- 85 R.W. Parry, T.C. Bissot, J. Amer. Chem. Soc., 1956, 78, 1524.
- 86 E.R. Alton, Diss. Abs., 1961, 21, 3620.
- 87 T. Kruck, W. Lang, Angew. Chem., Internat. Ed., 1967, 6, 454.
- 88 R.J. Clark, Eng. News., 1964, 42, 52.
- 89 A.B. Burg, G.B. Street, Inorg. Chem., 1966, 5, 1532.
- 90 J.F. Nixon, J. Chem. Soc.(A), 1967, 1136.
- 91 F. Seel, K. Ballreich, R. Schmutzler, Chem. Ber., 1961, 94, 1173.
- 92 R. Schmutzler, Amer. Chem. Soc. Adv. Chem., 1963, No. 37, 150.
- 93 G.R. Dobson, I.W. Stolz, R.K. Sheline, Inorg. Chem. Radiochem.,
1966, 8, 1.
- 94 E.W. Abel, M.A. Bennett, G.R. Burton, G. Wilkinson, J. Chem. Soc.,
1958, 4559.
- 95 J.D. Dunitz, P. Pauling, Helv. Chim. Acta, 1960, 43, 2188.
- 96 E.W. Abel, M.A. Bennett, G. Wilkinson, J. Chem. Soc., 1959, 2323.
- 97 R. Pettitt, J. Amer. Chem. Soc., 1959, 81, 1266.
- 98 M.A. Bennett, L. Pratt, G. Wilkinson, J. Chem. Soc., 1961, 2037;
- 99 T. Kruck, A. Prasch, Z. Naturforsch., 1964, 19b, 669.
- 100 A. Pidcock, B.W. Taylor, J. Chem. Soc.(A), 1967, 877.

- 101 R.B. King, Inorg. Chem., 1963, 2, 936.
- 102 B.L. Ross, J.G. Grasselli, W.M. Ritchey, H.D. Kaesz, Inorg. Chem.,
1963, 2, 1023.
- 103 R. Burton, L. Pratt, G. Wilkinson, J. Chem. Soc., 1961, 594.
- 104 W. Strohmeier, H. Hellman, Chem. Ber., 1963, 96, 2859.
- 105 F. Zingales, U. Belluco, M. Graziani, F. Basilo, Abst. Chem. Soc.
Meeting, Brighton, 1966.
- 106 F. Basolo, A.T. Brault, E.M. Thorsteinson, Inorg. Chem., 1964, 3,
772.
- 107 J.F. Nixon, J. Grunbaum, Unpublished results.
- 108 D.M. Adams, Spectroscopy, 1962.
- 109 J.J. Lagowski, Quart. Rev., 1959, 13, 233.
- 110 G.S. Harris, Ph.D. Thesis, University of Cambridge, 1958.
- 111 R. Schmutzler, Inorg. Chem., 1964, 3, 415.
- 112 R. Schmutzler, J. Chem. Soc., 1965, 5630.
- 113 R. Schmutzler, Adv. Chem., 1963, No. 37, 150.
- 114 J.F. Nixon, R. Schmutzler, Spectrochim. Acta, 1964, 20, 1835.
- 115 R. Schmutzler, J. Chem. Soc., 1964, 4551.
- 116 G.S. Reddy, R. Schmutzler, Z. Naturforsch, 1965, 20b, 104.
- 117 J.M. Jenkins, B.L. Shaw, Proc. Chem. Soc., 1963, 279.
- 118 J.F. Nixon, Chem. Comms., 1967, 669.

- 119 R.E. McCarley, D.G. Hendriker, R.W. King, J.G. Verkade,
Inorg. Chem., 1965, 4, 228.
- 120 R.W. Rudolph, R.C. Taylor, R.W. Parry, J. Amer. Chem. Soc.,
1966, 88, 3729.
- 121 D.G. Hendricker, R.E. McCarley, R.W. King, J.G. Verkade,
Inorg. Chem., 1966, 5, 639.
- 122 F.A.L. Anet, J. Amer. Chem. Soc., 1962, 84, 747.
- 123 A.A. Bothner-By, C. Naar Colin, J. Amer. Chem. Soc., 1962, 84,
743.
- 124 R.K. Harris, Canad. J. Chem., 1964, 42, 2275.
- 125 R. Lynden-Bell, Mol. Phys., 1963, 6, 601.
- 126 J.F. Nixon, unpublished observations, private communication.
- 127 J.R. Van Wazer, J.H. Letcher, J. Chem. Phys., 1966, 44, 815.
- 128 J.G. Reiss, J.R. Van Wazer, J. Amer. Chem. Soc., 1967, 89, 851.
- 129 K.J. Packer, J. Chem. Soc., 1963, 960.
- 130 G.S. Harris, J. Chem. Soc., 1958, 512.
- 131 R.G. Cavell, J. Chem. Soc., 1964, 1992.
- 132 A. Michaelis, Annalen, 1903, 326, 129.
- 133 I.G. Farbenindustrie, F.P., 807,789/1936.
- 134 R.W. Parry, Sr. M.A. Fleming, G. Ter Haar, J. Amer. Chem. Soc.,
1962, 84, 1767.

- 135 G. Kodama, R.W. Parry, Inorg. Chem., 1965, 4, 410.
- 136 H. Nöth, H.J. Veiter, Chem. Ber., 1963, 96, 1298.
- 137 R.R. Holmes, R.P. Wagner, J. Amer. Chem. Soc., 1962, 84, 357.
- 138 Z.M. Ivanova, Zhur. obschei Khim., 1965, 35, 164.
- 139 Sr. M.A. Floning, Ph.D. Thesis, University of Michigan, 1962.
- 140 J.T. Braunholtz, E.A.V. Ebsworth, F.G. Mann, N. Sheppard,
J. Chem. Soc., 1958, 2780.
- 141 B. Greenburg, A. Amendola, R. Schmutzler, Naturwiss, 1963, 50, 518.
- 142 D.S. Payne, Quart. Rev., 1961, 15, 173.
- 143 E.L. Muerterties, W. Mahler, R. Schmutzler, Inorg. Chem., 1963,
2, 613.
- 144 A.J. Downas, R. Schmutzler, Spectrochim. Acta, 1967, 23A, 681.
- 145 A.B. Burg, W. Mahler, J. Amer. Chem. Soc., 1961, 83, 2368.
- 146 K. Crosbie, Private Communication.
- 147 A.M. Kinnear, E.A. Porren, J. Chem. Soc., 1952, 3437.
- 148 D.R. Martin, P.J. Pizzolato, J. Amer. Chem. Soc., 1950, 72, 4584.
- 149 V.P. Davydorov, M.G. Voronkov, U.S.S.R., P., 135,485,1961.
- 150 R.N. Hazeldine, J. Chem. Soc., 1951, 584.

- 151 M.A. Bennet, H.J. Emeleus, R.N. Hazeldine, J. Chem. Soc.,
1953, 1535.
- 152 "Organic Syntheses", Wiley, London, 1965, 45, 102.
- 153 N. Niebergall, E. Langenfeld, Chem. Ber., 1962, 95, 64.
- 154 J.J. Eisch, R.B. King, "Organometallic Syntheses", Academic Press,
London, 1965, 122-126.
- 155 J.A. Wait, S.C. Slezak, Q.C.P.E., 78.

Character Tables

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

```

C      GF MATRIX PROGRAM SET --- PART A.  REFERENCE 155
C      WAIT-SLEZAK
C      G F MATRIX PROGRAM
DIMENSION G(10,10),F(10,10),H(10,10),VL(10),VLIWV(10),
1TEMPV(10),VECT(10),VECTNU(10),PCT(10,10),PROBL(10,10)
C      N IS ORDER OF MATRIX, MAX = 10
1000  READ 1,N
1      FORMAT(I2)
      IF(N-10)2,2,999
2      DO 4 I=1,N
4      READ 3,(G(I,J),J=1,N)
      DO 5 I=1,N
5      READ 3,(F(I,J),J=1,N)
3      FORMAT(5F14.8)
      DO 6 K=1,N
      DO 6 I=1,N
      H(I,K)=0.0
      DO 6 J=1,N
6      H(I,K)=H(I,K)+G(I,J)*F(J,K)
      PRINT 800,((C(I,J),I=1,N),J=1,N)
800  FORMAT(/73X,21HKINETIC ENERGY MATRIX/(4F20.8))
801  FORMAT(/73X,23HPOTENTIAL ENERGY MATRIX/(4F20.8))
802  FORMAT(/746X,8HH MATRIX/(4F20.8))
      PRINT 801,((F(I,J),I=1,N),J=1,N)
110  PRINT 802,((H(I,J),I=1,N),J=1,N)
120  NCOL=1
7      DO 10 I=1,N
      TEMPV(I)=0.0
      VECTNU(I)=0.0
10      VECT(I)=0.0
      TEMPV(NCOL)=1.0
      NDCOUNT =1
24      DO 15 I=1,N
      VECT(I)=0.0
      DO 15 J=1,N
15      VECT(I)=TEMPV(J)*H(I,J)+VECT(I)
12      DO 17 I=1,N
      Z=VECTNU(I)-VECT(I)
      IF(ABS(Z)-.10E-4)17,17,16
17      CONTINUE
      NTAG=1
      GO TO 20
16      NTAG=0
      DO 18 I=1,N
18      VECTNU(I)=VECT(I)
20      EIGVL=VECT(1)
      DO 21 I=2,N
      Y=ABS(VECT(I))-ABS(EIGVL)
      H(Y)21,21,24
23      EIGVL=ABS(VECT(I))
21      CONTINUE
      DO 22 I=1,N
22      TEMPV(I)=VECT(I)/EIGVL
      NDCOUNT = NDCOUNT + 1
      IF(NDCOUNT-200)998,998,950
950  PRINT 951
951  FORMAT(10H100 EARLY ITERATIONS)
      GO TO 1000

```

```

998 IF(NTAG-1)24,30,999
30 WAVEN=1302.832*SQRTE(EIGVL)
   PRINT 31, EIGVL,WAVEN
31  FORMAT(//21X,11HEIGENVALUE=F12.8,10X,11HWAVENUMBER=F8.2//)
   PRINT 123, NCOUNT
   123 FORMAT(9H0 NCOUNT=I3)
130 CONTINUE
C   GENERATING L AND L INVERSE VECTORS
   DSQ=0.0
   DO 32 I=1,N
   DO 32 J=1,N
32  DSQ=TEMPV(I)*TEMPV(J)*F(I,J)+DSQ
   D=SQRTE(DSQ/EIGVL)
   PRINT 421
421  FORMAT(46X,8HL VECTOR//)
   DO 33 I=1,N
   VL(I)=TEMPV(I)/D
33  PRINT 42, VL(I)
42  FORMAT(44X,F20.8)
   DO 34 I=1,N
   VLINV(I)=0.0
   DO 34 J=1,N
34  VLINV(I)=VL(J)*F(J,I)+VLINV(I)
   PRINT 381
381  FORMAT(//42X,16HL INVERSE VECTOR//)
   DO 35 I=1,N
   VLINV(I)=VLINV(I)/EIGVL
35  PRINT 42, VLINV(I)
140 CONTINUE
   DO 40 I=1,N
   DO 40 J=1,N
   PRODL(I,J)=VL(I)*VL(J)
40  PCT(I,J)=PRODL(I,J)*F(I,J)/EIGVL
   PRINT 995
995  FORMAT(//12H EIGENVALUE= )
   DO 996 I=1,N
   150 DO 996 J=1,N
   996 PRINT 997, PRODL(I,J),I,J
   997 FORMAT (F20.8,2HF(,I2,1H,,I2,1H) )
   PRINT 43,((PCT(I,J),I=1,N),J=1,N)
43  FORMAT(//35X,29HPOTENTIAL ENERGY DISTRIBUTION//(5F20.8))
160 DO 36 I=1,N
   DO 36 J=1,N
36  H(I,J)=H(I,J)-VLINV(J)*VL(I)*EIGVL
170 NCOL=NCOL+1
   IF(NCOL-N)7,7,1000
999 CALL EXIT
   END

```

C GF MATRIX PROGRAM SET --- PART B.

C SLEZAK SYSTEM OF FOUR EQUONS
DIMENSION A(3,3),B(3),X(3)

30 READ 20,A,B

20 FORMAT(3F14.8)

5 N=3

K=1

10 I=K+1

L=K

24 Z=ABSF(A(I,K))-ABSF(A(L,K))

IF(Z)21,21,25

21 IF(I-N)22,23,22

22 I=I+1

GO TO 24

25 L=I

GO TO 21

23 IF(L-K)26,27,26

26 DO 28 J=K,N

TEMP=A(K,J)

A(K,J)=A(L,J)

28 A(L,J)=TEMP

T1=B(K)

B(K)=B(L)

B(L)=T1

27 I=K+1

4 XM=A(I,K)/A(K,K)

J=K+1

DU 7 J1=J,N

7 A(I,J1)=A(I,J1)-XM*A(K,J1)

B(I)=B(I)-XM*B(K)

IF(I-N)8,9,8

8 I=I+1

GO TO 4

9 IF(K-(N-1))11,12,11

11 K=K+1

GO TO 10

12 CONTINUE

X(N)=B(N)/A(N,N)

I=N-1

17 J=I+1

S=0.

15 S=S+A(I,J)*X(J)

IF(J-N)13,14,13

13 J=J+1

GO TO 15

14 X(I)=(B(I)-S)/A(I,I)

IF(I-1)16,18,16

16 I=I-1

GO TO 17

18 PRINT 19,X

19 FORMAT(3F14.8)

GO TO 30

END

PROG 1 WEBSTER ROOTS,FREQ(K),PERCENT CONT TO POT ENERGY
 REQUIRES G AND F MATRIX ELEMENTS N=ORDER OF F(MAX 20,20)
 IEGEN=0 ROOTS +VECTORS. IEGEN NOT=0 ROOTS ONLY. NEWF=0 READS NEW F
 NEWG=0 READ NEW G. READ F AND G ROW WISE. ONLY TERMS UN AND ABOVE
 MAIN DIAGONAL F,G, AND H=GF PRINTED ROW WISE
 DIMENSION F(20,20),G(20,20),H(20,20),FREQ(20),A(120),B(20,20)
 DIMENSION ROOT(20), C(20,20), D(20,20)

0 READ1, N,IEGEN, NEWF,NEWG

1 FORMAT(4I3)

K=(N*N + N)/2

IF(NEWF) 998,999,998

9 READ2, (A(L), L=1,K)

2 FORMAT (10F7.4)

DO 10 L=1,K

IUM = 0

DO 12 M=1,N

IUM = IUM + N + 1 - M

IF(IUM-L) 12,13,13

12 CONTINUE

13 I=M

JUM=0

DO 17 M=1,I

JUM = JUM + M-1

17 CONTINUE

J=L-M*I+JUM+N

F(I,J)=A(L)

F(J,I) = F(I,J)

10 CONTINUE

98 PRINT 80

80 FORMAT (9H F MATRIX/)

DO 51 I=1,N

PRINT 3, (F(I,J), J=1,N)

PRINT 22

22 FORMAT(1H)

51 CONTINUE

IF(NEWG) 996,997,996

97 READ 3, (A(L), L=1,K)

3 FORMAT (7F10.6)

DO 14 L=1,K

IUM=0

DO 15 M=1,N

IUM=IUM+N+1-M

IF(IUM-L) 15,16,16

15 CONTINUE

16 I=M

JUM=0

DO 18 M=1,I

JUM=JUM+M-1

18 CONTINUE

J=L-M*I+JUM+N

G(I,J)=A(L)

G(J,I)=G(I,J)

14 CONTINUE

996 PRINT 81

81 FORMAT (9H G MATRIX/)

DO 53 I=1,N

PRINT 4, (G(I,J), J=1,N)

4 FORMAT (7F13.8)

```

PRINT 22
53 CONTINUE
C  CALCULATR GF MATRIX AND STORE IN H(I,J)
DO 60 I=1,N
DO 60 J=1,N
H(J,I)=0.0
DO 60 K=1,N
H(J,I)=H(J,I)+G(I,K)*F(K,J)
60 CONTINUE
PRINT 82
82 FORMAT (12H GF=H MATRIX/)
DO 83 J=1,N
PRINT 84, (H(I,J), I=1,N)
84 FORMAT (5E16.7)
PRINT 22
83 CONTINUE
C  USE SUBROUTINE CLEIG TO CALCULATE ROOTS AND VECTORS
NX=20
NY=20
CALL CLEIG(H,B,ROOT,N,NX,NY)
DO 25 I=1,N
IF (ROOT(I)) 30,30,31
30 FREQ(I)=0.0
GO TO 26
31 FREQ(I)=1303.16*SQRTF(ROOT(I))
26 CONTINUE
25 CONTINUE
DO 28 I=1,N
PRINT 29, ROOT(I),FREQ(I)
29 FORMAT (7H ROOT= F12.8, 13H WAVENUMBER= F8.2/)
28 CONTINUE
IF (IEGEN) 100,101,100
101 CONTINUE
PRINT 40
40 FORMAT (13H EIGENVECTORS/)
DO 41 J=1,N
PRINT 42, (B(I,J), I=1,N)
42 FORMAT (10E12.5)
PRINT 22
41 CONTINUE
DO 150 J=1,N
DO 150 I=1,N
C(I,J) = B(I,J) * B(I,J) * F(I,I)
150 CONTINUE
DO 151 J=1,N
SIGMA=0.0
DO 152 I=1,N
SIGMA=SIGMA+C(I,J)
152 CONTINUE
DO 156 K=1,N
D(K,J) = C(K,J) * 100.0/SIGMA
156 CONTINUE
151 CONTINUE
PRINT 153
153 FORMAT (30H POTENTIAL ENERGY DISTRIBUTION/)
DO 154 J=1,N
PRINT 155, (D(I,J), I=1,N)
155 FORMAT (10F8.3)

```