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Coordination Chemistry of Bidentate Difluorophosphines

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COORDINATION CHEMISTRY OF BIDENTATE

DIFLUOROPHOSPHINES

by

Darrell Lynn Gallup

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of

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<div align="right">Darrell Lynn Gallup</div>

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ABSTRACT

Coordination Chemistry of

Bidentate Difluorophosphines

by

Darrell Lynn Gallup, Doctor of Philosophy

Utah State University, 1978

Major Professor: Dr. Joseph G. Morse
Department: Chemistry and Biochemistry

The reactions of 1,2-bis(difluorophosphino)cyclohexane, $PF_2C_6H_{10}PF_2$,

with hexacarbonyls of Cr(0), Mo(0), and W(0) have been extensively inves-

tigated. The hexacarbonyls react, either under photolytic or thermolytic

conditions, to produce carbon monoxide and oily mixtures of products of

the general formulations, $[M(CO)_4(PF_2C_6H_{10}PF_2)]_x$, where x varies appar-

ently from 1-4. The higher values of x, corresponding to species in-

volving bridging ligands, are more common to the photolysis rather than

the thermolysis reactions. Photolysis reactions of $Mo(CO)_6$ with in-

creasing amounts of the ligand does not result in the higher substitution

products, $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$ and $Mo(PF_2C_6H_{10}PF_2)_3$.

The reactions of $PF_2C_6H_{10}PF_2$ with the norbornadiene tetracarbonyl

complexes of Cr(0), Mo(0), and W(0) produce relatively air-stable chelates

of the general formulation, $M(CO)_4(PF_2C_6H_{10}PF_2)$. $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

will react with more $PF_2C_6H_{10}PF_2$ to give $[Mo(CO)_2(PF_2C_6H_{10}PF_2)_2]_2$. A

slight excess of $PF_2C_6H_{10}PF_2$ also reacts readily with ditoluenemolybde-

num(0) displacing toluene to give $Mo(PF_2C_6H_{10}PF_2)_3$, and air-stable monomer.

Analysis of the infrared spectra of these chelates indicates that the ligand fits into a sequence of π-acceptor strength as: $PF_3 > PCl_3 \sim PF_2C_6H_{10}PF_2 > RN(PF_2)_2 >> Ph_2PC_2H_4PPh_2$. NMR spectral parameters for the chelates verify the very strong coordination of the bidentate ligand to the metals.

1,2-bis(difluorophosphino)cyclohexane has also been found to react with pentacarbonyliron(0), $Fe(CO)_5$ and with pentacarbonylmanganese(I) bromide, $Mn(CO)_5Br$, in hexane, displacing two moles of carbon monoxide per mole of ligand. The products resulting, $(PF_2C_6H_{10}PF_2)Fe(CO)_3$, $(PF_2C_6H_{10}PF_2)_2Fe(CO)$, $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, and $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$, are all air-stable solid monomers indicating that the ligand is an effective chelating agent. Analysis of the ir and nmr spectral data supports the conclusion that $PF_2C_6H_{10}PF_2$ functions as a strong π-acceptor and assists in assigning structures.

The reactions of $PF_2C_6H_{10}PF_2$ in solution with $Co_2(CO)_8$ and the chlorides of Ni(II), Pd(II), and Pt(II) have been investigated. The resultant complexes are not well defined. The characterization of the complexes has given ambiguous results, although the nickel group metal complexes appear to be dimeric.

The ligand, 1,2-bis(difluorophosphino)ethane, $PF_2C_2H_4PF_2$, reacts with tetracarbonylnickel(0), $Ni(CO)_4$, in the gas phase and in solution, to produce carbon monoxide and the polymer, $[Ni(PF_2C_2H_4PF_2)_2]_x$. $PF_2C_2H_4PF_2$ displaces norbornadiene from $(C_7H_8)Mo(CO)_4$ to yield the relatively air-stable complex, $Mo(CO)_4(PF_2C_2H_4PF_2)$. Analysis of the infrared spectrum of the monomeric complex indicates that the ligand exhibits π-acceptor strength equal to $PF_2C_6H_{10}PF_2$.

(212 pages)

INTRODUCTION

During the past twenty-five years a considerable amount of research
has focused on transition metal complexes of tertiary phosphine ligands.[1]
In the early stages of studies on such systems, complexes of many of the
transition metals were prepared employing simple monodentate ligands,
e.g. triphenylphosphine. Transition metal complexes of these phosphines
have been used in a wide variety of catalytic reactions. The Wilkinson
catalyst, $RhCl(PPh_3)_3$, is a prime example of a transition metal complex
which has found use in industrially important reactions requiring a
homogeneous catalyst. The thrust of current research in catalysis re-
quires the continual development of complexes such as transition-metal-
phosphines for use in energy-saving processes. Several reviews describ-
ing transition metal complexes of phosphine ligands are available which
detail much of the work published on the subject.[1,2]

The use of polydentate phosphine ligands (in particular bidentates)
in metal complexes has received much recent attention.[2] The reason for
this emphasis is known as the chelate effect and involves the enhanced
stability of a metal-ligand system containing chelate rings as compared
to the stability of a similar system containing no rings. Compared to
a monodentate ligand, a bidentate ligand containing comparable donor
groups provides enhanced metal complex stability, especially when the
ligand forms five or six-membered chelate rings. Just as triphenyl-
phosphine has found wide use as a monodentate

ligand in metal complexes, the analogous bidentate ligand, 1-2bis(di-
phenylphosphino)ethane ($Ph_2PC_2H_4PPh_2$, known as diphos) has been a
commonly used ditertiary phosphine ligand.

An understanding of the mode of bonding between metal atoms and
phosphorus stoms in metal-phosphine complexes is important to the study
of phosphine ligand coordination. Bonding in metal-phosphine complexes
can be described in terms of π-back-bonding, arising from the donation
of electrons from trivalent phosphorus (a strong Lewis base) to a metal
in a low formal oxidation state (a Lewis acid) in a σ-bonding fashion.
Since phosphorus atoms have available empty d orbitals, acceptance of
electron density is possible from the metal d orbitals. The extent to
which this back donation of electron density occurs depends upon the
identity of the donor atom and on the electronegativity of the groups
attached to it. (See Figure 1) Π-bonding appears to be most important
when ligands with strong electronegative subsituents (such as PF_3), are
used in conjunction with metals in low oxidation states. Trivalent
phosphorus is a carrier of a lone pair of electrons, so not only are the
donor properties of this atom most effectively weakened by the electron
withdrawing power of fluorine in PF_3, but also the acceptor properties
of its 3d orbitals are most strongly enhanced. Phosphine ligands of all
types have thus been classified according to π-acidity, the ability of
the ligand to accept electron density from the metal via the π-back-bond.

The strongest π-acceptor ligands thus classified to date have been
the fluorophosphines. A variety of monodentate fluorophosphine ligands
are known in which one or two fluorine atoms of PF_3 are replaced with
halides, amine, and organic groups. Nixon,[3] has recently reviewed these
fluorophosphines and has described many of the metal complexes of the
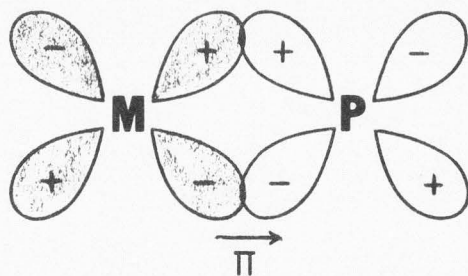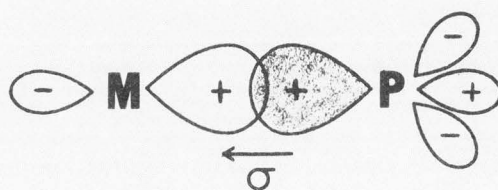
Figure 1. Bonding in Metal–Phosphine Complexes

ligands. The fluorophosphines have been rated with respect to π-acceptor ability, with CF_3PF_2 and PF_3 displaying the greatest π-acidity, even greater than the well-know and intensively studied ligand, carbon monoxide. Only a few bidentate fluorophosphine ligands have been described having the general formula, $RN(PF_2)_2$.

A primary objective of research in this laboratory has been the development of a ligand system in which both strong π-acceptor character and chelating ability are combined. Bidentate difluorophosphine ligands, containing PF_2 groups positioned on a hydrocarbon backbone are prepared by the photoreaction of P_2F_4 with olefins.[4] The ligand, 1,2-bis(difluorophosphino)cyclohexane, $(P_2F_4C_6H_{10})$ is obtained in good yield by photolyzing P_2F_4 in the presence of cyclohexene at 300 nm for twenty minutes. The analogous ligand to diphos, 1,2-bis(difluorophosphino)ethane, $(P_2F_4C_2H_4)$ is prepared by the photoreaction of ethylene and P_2F_4 at 300 nm for six hours. Of the available bidentate difluorophosphines in this laboratory, $PF_2C_6H_{10}PF_2$ was chosen for initial metal coordination studies due to the relative ease of preparation, the favorable yield, and most importantly, the rigidity of the molecule. Construction of molecular models of $PF_2C_6H_{10}PF_2$ shows that the bulk of the cyclohexane ring and the stereochemical rigidity of the PF_2 groups on the ring in either cis or trans positions sterically hinder bridging by the ligand of two metal centers, whereas, chelation to a single metal center is sterically favored.

That $PF_2C_6H_{10}PF_2$ exhibits strong π-acceptor and chelating character was deomonstrated by the initial coordination study of the ligand by Dr. Niel Zack of this laboratory. The reaction of $Ni(CO)_4$ with $PF_2C_6H_{10}PF_2$ in tetrahydrofuran solution at temperatures less than 60°

resulted in the preparation of the very stable complex, bis [1,2-bis(di-fluorophosphino)cyclohexane] nickel(0).[5] In direct contrast to the reaction conditions of high temperature and pressure required for complete displacement of CO from $Ni(CO)_4$ by PF_3, the bidentate difluorophosphine ligand easily displaced CO due to the π-acceptor character, chelating ability, and increased basicity of the ligand at the metal.

STATEMENT OF PROBLEM

The successful synthesis of the new zerovalent nickel complex from the reaction of $Ni(CO)_4$ and the bidentate difluorophosphine ligand, $PF_2C_6H_{10}PF_2$, demonstrated the exceptional coordinating ability of this ligand toward a transition metal. The results of this reaction suggested the importance of a detailed study of the coordination chemistry of $PF_2C_6H_{10}PF_2$ with various transition metals. A description of reaction conditions and product isolation procedures peculiar to $PF_2C_6H_{10}PF_2$ and metal compounds, together with the characterization of the resultant products should provide the systematization required for continuing studies of the coordination of diverse, polydentate difluorophosphine ligands available in this laboratory. Assessment, both qualitatively and quantitatively, of the π-back-bonding ability of $PF_2C_6H_{10}PF_2$ with respect to other phosphine ligands (to stabilize metals in low oxidation states) was to be made by monitoring bond strengths in the complexes by spectroscopic techniques. The chelate effect, as a means of stabilizing the metal complexes, was also to be appraised. The metal complexes of $PF_2C_6H_{10}PF_2$ should be expected to exhibit greater stability than complexes of the analogous monodentate ligand, PF_3.

RESULTS AND DISCUSSION

I. Coordination of $PF_2C_6H_{10}PF_2$ with the Group 6B Metals

A. Introduction

Metal carbonyl complexes are among the most photoreactive transition metal complexes known. Metal carbonyl complexes are known for almost all of the transition metals, the most common being the hexacarbonyls of chromium, molybdenum, and tungsten. The use of light as a synthetic tool for initiating ligand exchange and substitution reactions of the metal carbonyl has become an important part of transition metal carbonyl chemistry. Many photochemical reactions of the metal carbonyls have been studied in solution over the years.[6] It was concluded from many early successes that substituted derivatives of the Group 6B metal hexacarbonyls could be prepared by irradiation of the carbonyl complexes in the presence of a great many coordinating agents. The photochemical formation of $M(CO)_5L$ (where L = coordinating ligand) is outlined in the sequence below. (Reactions 1-3) Several lines of evidence support the very efficient generation of the coordinatively unsaturated intermediate, $M(CO)_5$, which has a substantial lifetime.

$$M(CO)_6 \longrightarrow M(CO)_5 + CO \qquad (1)$$

$$M(CO)_5 + CO \longrightarrow M(CO)_6 \qquad (2)$$

$$M(CO)_5 + L \longrightarrow M(CO)_5L \qquad (3)$$
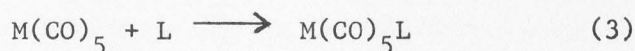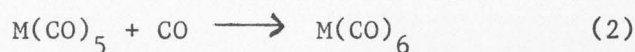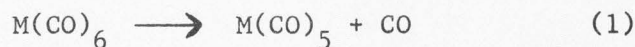
The synthetic utility of the sequence 1-3 has had considerable impact on systematic studies of chemical properties of the metal carbonyl substituted complexes. It was recognized that the photolysis of $M(CO)_5L$

strong σ-donor interaction for the carbonyl ligand (Figure 2). The relative importance of σ and π interactions are difficult to assess, but stronger π-backbonding is generally associated with lower valent metals which have a greater tendency to delocalize electron density into the ligand. As a consequence of the large degree of delocalization of the electrons from the central metal into the ligand, these compounds are highly covalent.

A large number of phosphine-substituted derivatives of the Group 6B metal carbonyls have been prepared over the last 20 years.[7] Direct displacement of CO from the metal carbonyls by a phosphine ligand can be accomplished by refluxing the reactants in an appropriate solvent, heating the reactants in a sealed tube, or irradiating the reactants in solution with an ultraviolet source. In each case, smooth step-wise displacement of CO is acheived affording ligand substitution. The choice of methods is usually dependent upon the products desired and upon the character of the ligand. Using photolysis, Clark and Hoberman[8] prepared the complete series of PF_3 substituted Group 6B carbonyl complexes. Since the coordinating ability of $PF_2C_6H_{10}PF_2$ has been compared favorably with PF_3,[5] the study of the photoreactions of $PF_2C_6H_{10}PF_2$ with the Group 6B metal carbonyls was initiated.

Bonding in the fluorophosphine-substituted metal carbonyls involves a combination of metal carbonyl and metal phosphine bonding, both of which were discussed previously. Both σ bonding and π-backbonding are important in the overall system, especially since the π-acidity of many of the fluorophosphines has been shown to be as great or greater than the π-acidity attributed to CO.[9] This implies that the incoming fluorophosphine ligand will compete with CO in accepting electron density from
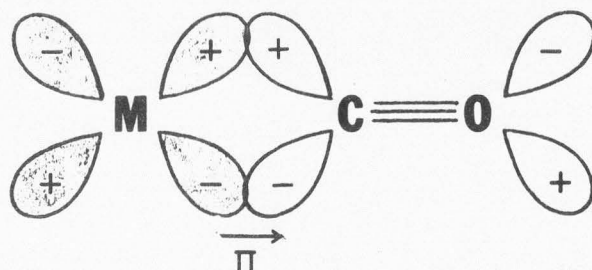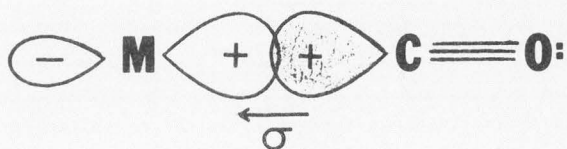
Figure 2. Bonding in Metal Carbonyl Complexes

the metals. The highly electronegative fluorine groups attached to the phosphorus atoms in the fluorophosphine ligands cause progressive increase in the contribution of the triply-bonded resonance form, M-C≡O, relative to the doubly-bonded resonance form, M-C=O, by presumably withdrawing electrons from the metal in the complexes. The C-O ligand competes for this flow of electron density resulting in the triply-bonded C≡O resonance form which will have a shortened C-O bond length, higher C-O bond energy, and consequently, a larger C-O force constant. This means that the fluorophosphine-substituted metal carbonyl complexes are expected to give higher terminal carbonyl stretching frequencies in the infrared spectrum than molecules exhibiting carbon-oxygen double bonds (e.g. ketones) as an indication of enhanced metal → phosphorus π-bonds and subsequent reduced metal → CO π-bonds. Monitoring infrared spectra of the complexes in the CO region will thus allow one to follow reaction progress and to assess the ability of the phosphine ligand as a potential π-acceptor.

Chatt and Watson[10] have shown that thermolysis reactions of the Group 6B metal hexacarbonyls and bidentate phosphine ligands produce monomeric tetracarbonyl derivatives. Direct thermal reactions were therefore undertaken as a means of preparing monomeric complexes of $PF_2C_6H_{10}PF_2$.
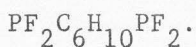
An alternative method of preparing phosphine-substituted carbonyl complexes had employed displacement of weakly bound organic ligands from metal carbonyls.[11] Because direct reaction between bidentate fluorophosphine ligands and the metal hexacarbonyls can produce any one of a number of substitution products or a mixture, syntheses of monomeric tetracarbonyl complexes have been carried out by reactions involving the

displacement of the olefin from norbornadiene metal tetracarbonyls.[11] (Reaction 7) The use of olefin displacement reactions have found wide

$$\underline{cis}-C_7H_8Mo(CO)_4 + L \longrightarrow C_7H_8 + \underline{cis}-LM(CO)_4 \qquad (7)$$
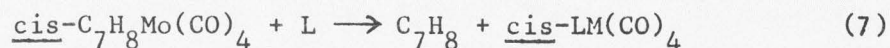
application in recent years as a means of obtaining specific substitution products and isomers. In general, these reactions can be carried out under rather mild conditions and their progress can be followed by the loss of the intense color of the olefin complex and the appearance of the colorless fluorophosphine complex.[9,12]

A few phosphine-substituted dicarbonyl complexes have been prepared of either monodentate or bidentate ligands.[2,10] In the cases of the bidentate ligands, the dicarbonyl complex is often prepared by allowing the phosphine-substituted tetracarbonyl complex to react with excess ligand under vigorous conditions, such as heating to high temperature for prolonged periods of time. (Reaction 8)

$$M(CO)_4L + L \longrightarrow M(CO)_2L_2 + 2CO \qquad (L = bidentate\ ligand) \qquad (8)$$

Complete substitution of CO in the Group 6B metal carbonyls has been acheived only under forcing conditions by the stronger π-acceptor ligands. Attempts to obtain the dicarbonyl complex, $M(CO)_2(PF_2C_6H_{10}PF_2)_2$, and the complex, $M(PF_2C_6H_{10}PF_2)_3$, by the photoreactions of $PF_2C_6H_{10}PF_2$ and the Group 6B metal hexacarbonyls in mole ratios as great as 4:1 have not been successful, in contrast to the photoreaction of excess $CH_3N(PF_2)_2$ and $M(CO)_6$ giving the carbonyl-free complexes, $M[CH_3N(PF_2)_2]_3$, that has recently been reported by King and Gimeno.[13] Complete substitution of CO from these metal carbonyls by bidentate organophosphine ligands has not been acheived, although the $M(diphos)_3$ compounds can be prepared directly.[14,15] The complexes, $M(Me_2PC_2H_4PMe_2)_3$ were formed as yellow solids by reducing Group 6B metal halides with $LiAlH_4$ or sodium

naphthalenide in tetrahydrofuran. Molybdenum(O) complexes, ML_3 (where L = bidentate organophosphine ligands) have been obtained by heating dibenzene molybdenum $[Mo(C_6H_6)_2]$ with the ligand in a sealed tube. Since neither a dicarbonyl complex nor a complex of the type, ML_3, were isolated in the photoreactions of $PF_2C_6H_{10}PF_2$ and the metal hexacarbonyls, these alternatives were to be attempted as methods for obtaining these derivatives.

B. Experimental Results - Photoreactions

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with $Cr(CO)_6$ in Tetrahydrofuran.

The photoreaction of $Cr(CO)_6$ with a 20% mole excess of $PF_2C_6H_{10}PF_2$ in tetrahydrofuran results in the displacement of 0.64 equivalents of CO and the formation of a yellow solid. The solid infrared spectrum of the complex in Nujol and Halogrease mulls consists of several strong broad bands in the CO region including a band cooresponding to unreacted $Cr(CO)_6$ and a strong P-F stretching band at ca 790 cm-1. Elemental analysis of the complex indicates the general formulation as a tetra-carbonyl complex is correct, but the complex is by no means pure, although attempts to purify the solid by recrystallization and sublimation were undertaken. The hydrogen analysis is exceptionally high, suggesting the presence of traces of solvent in the product.

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with $Mo(CO)_6$ in Tetrahydrofuran.

The photoreaction of $Mo(CO)_6$ with a 20% mole excess of $PF_2C_6H_{10}PF_2$ in tetrahydrofuran results in the displacement of 1.32 equivalents of CO and the formation of a light brown solid. Infrared

spectra of the complex exhibit bands assignable to CO and the ligand. Elemental analyses of the solid are inconclusive and suggest impurities due to solvent, although attempts were made to purify the product by sublimation and to dry the product under vacuum.

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with $W(CO)_6$ in Tetrahydrofuran.

The photoreaction of $W(CO)_6$ with a slight excess of $PF_2C_6H_{10}PF_2$ in tetrahydrofuran solution results in the displacement of 0.96 equivalents of CO and the formation of a brown complex upon solvent removal. Infrared spectra of the crude solid indicate the presence of unreacted $W(CO)_6$ and a fluorophosphine-containing product. The brown solid is air sensitive, turning green in color upon exposure to air. Elemental analyses of the solid are inconclusive. The mass spectrum of the solid consists of peaks assignable only to the ligand.

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with $Cr(CO)_6$ in Pentane.

The photoreaction of $Cr(CO)_6$ with a 20% excess of $PF_2C_6H_{10}PF_2$ in pentane results in the displacement of 1.6 equivalents of CO and the formation of a yellow solution. After the irradiation had proceeded for about 10 hours, the solution began to turn brown and an oil began to collect on the reaction vessel walls. The products of the reaction are obtained after removal of the solvent which is maintained at -36° to insure no volatile product loss. The resultant yellow-orange oil is purified by filtration of a pentane solution of the product and pumping to sublime away any unreacted $Cr(CO)_6$.

Characterization of $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The product, where x = 1-3 at least, has been characterized by in-frared and nmr spectral data and by osmometric molecular weight. The vapor phase molecular weight of the oil was determined by $CHCl_3$ to be 949.

Infrared Spectrum

The solution infrared spectrum of the product in the carbonyl region (Figure 3) consists of four or more bands. Frequencies and intensities of the bands are (in cm^{-1}): 2076 m, 2047 m, 2003 m,sh, and 1963 vs,vbr. The band at 1963 cm^{-1} is very broad so as to dominate the spectrum and to hide any underlying bands. A strong band at 801 cm^{-1} is assigned to the P-F stretching mode.

Nmr Spectra

Proton Nmr Spectrum

The 100.1 MHz spectrum of the complex gives a complex multiplet centered near 2.0δ with benzene as the internal reference (free ligand, δ = 1.97, broad multiplet).

Fluorine Nmr Spectrum

The ^{19}F nmr spectrum (Figure 4) displays a set of doublets contered near -63.6 ppm ($CFCl_3$, external reference). The fluorine coordination shift if calculated to be +17.7 ppm. The doublets observed in the spectrum are a result of spin coupling of the fluorine nuclei with the phosphorus nucleus in the PF_2 groups of the ligand. The P-F coupling constant is on the order of 1155 Hz.
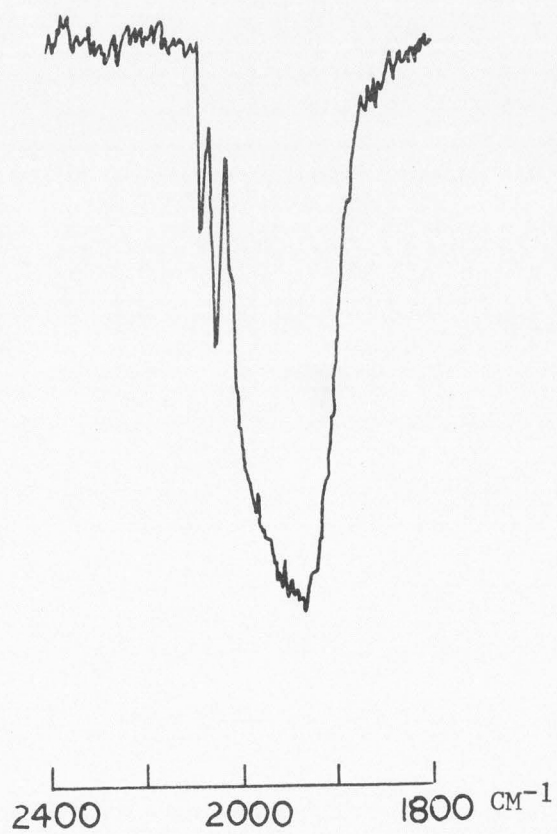
Figure 3.   Ir Spectrum (CO Region) of Photolytically-Prepared
            $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]$ in Hexane
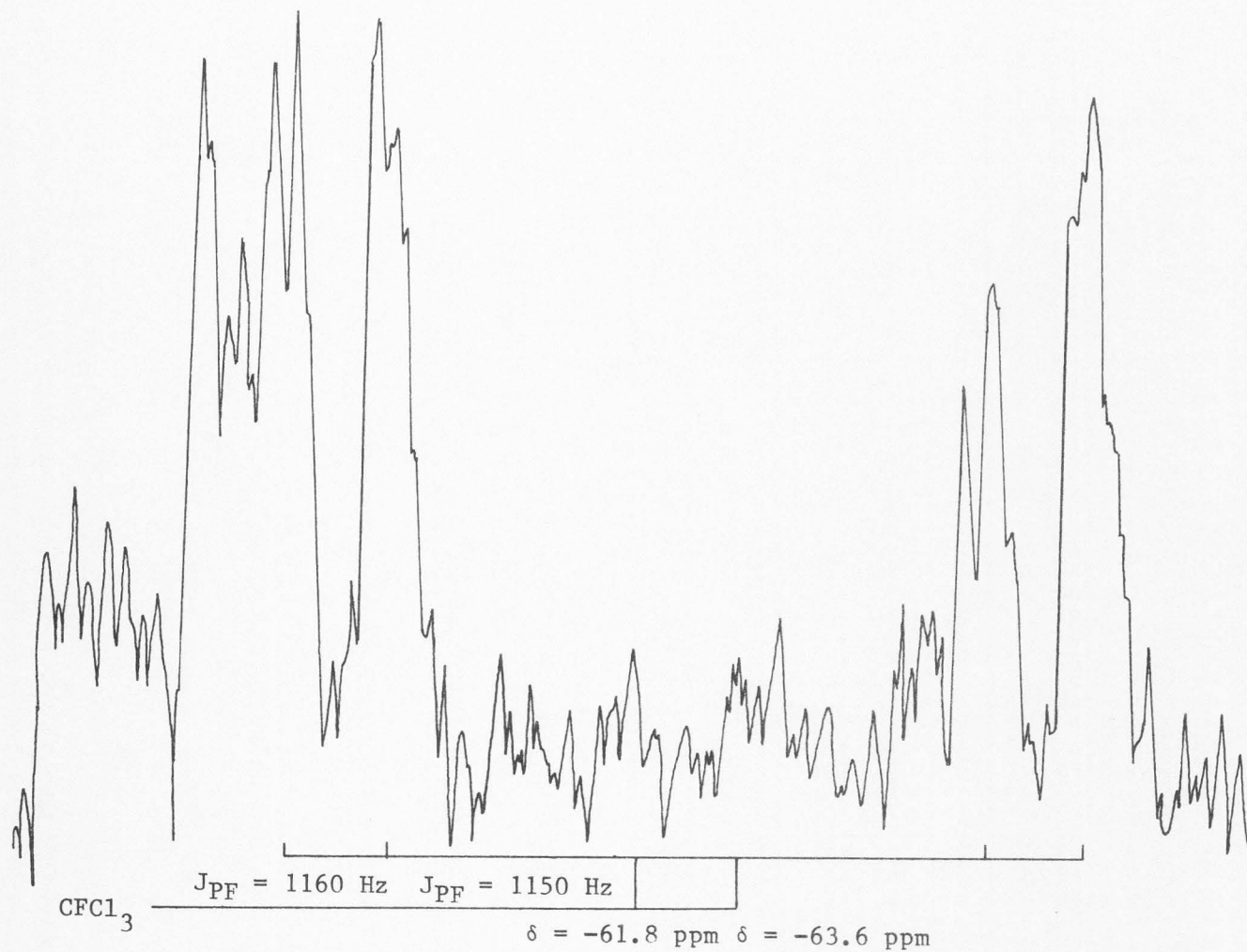
Figure 4. Fluorine NMR Spectrum of Photolytically-Prepared $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$

Phosphorus Nmr Spectrum

The ^{31}P nmr spectrum (Figure 5) gives a series of triplets resulting from the spin coupling of the two fluorine nuclei adjacent to the phosphorus atoms. The primary triplet is centered at +288.9 ppm (85% H_3PO_4). A value of +54.7 ppm is calculated for the phosphorus coordination shift, which is in agreement with chemical shift data reported for complexes of the strong π-acceptor fluorophosphine ligands.[16,17] The F-P coupling constant for the dominant triplet spans 1180 Hz. A triplet of less intensity is observed 5.9 ppm upfield from the dominant triplet, which is probably due to a bridged ligand species.

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with Mo(CO)$_6$ in Pentane.

The photoreaction of Mo(CO)$_6$ with a 20% mole excess of $PF_2C_6H_{10}PF_2$ in pentane results in the displacement of 1.8 equivalents of CO and the formation of a white oil. The oil is purified by filtration and sublimation to remove the volatile unreacted Mo(CO)$_6$. The oil can be separated into four different fractions by column chromatography on Florisil in hexane. Fraction #1 is a white solid identified as unreacted Mo(CO)$_6$, while the remaining fractions consisted of white oils, identified as phosphine-substituted tetracarbonyl complexes.

Characterization of $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The product mixture, where x = 1-3 at least, has been characterized by chromatographic separation of the components and their subsequent identification by mass, infrared, and nmr spectral data and by osmometric molecular weight. (A ^{31}P nmr spectrum of the nonseparated oil could not be obtained due to the low concentration of the complex in the

$J_{FP} = 1180$ Hz $J_{FP} = 1150$ Hz

$\delta = +288.9$ ppm $\delta = +282.9$ ppm

H_3PO_4
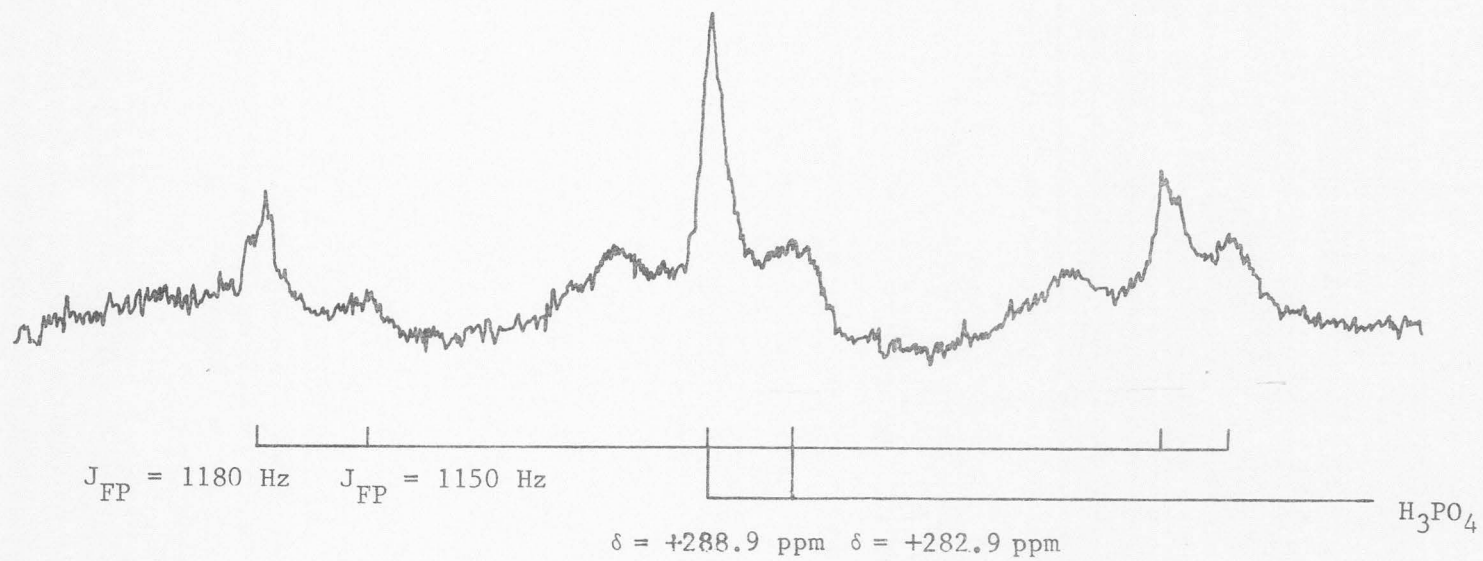
Figure 5.   Phosphorus NMR Spectrum of Photolytically-Prepared $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$

sample tube.) The product mixture gives an elemental analysis in reasonably good agreement with that calculated for $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

Mass Spectra

The osmometric molecular weight of the non-separated mixture in benzene was found to be 968, indicating the presence of high molecular weight species. The mass spectrum of the white solid from Fraction #1 gives a molecular ion at m/e = 264 with six prominent peaks arising at −28 m/e intervals indicating the successive stepwise removal of CO. Molybdenum isotope peaks were present as expected. The mass specta of Fractions #2, #3, #4, give molecular ions at m/e = 428 with four prominent peaks arising at −28 m/e intervals confirming the existence of tetracarbonyl entities. No peaks above the molecular ion are present in the spectra, although the osmometric molecular weight for Fraction #4 was found to be 836 which corresponds to a dimer.

Infrared Spectra

The infrared spectrum of the non-separated mixture (Figure 6) in the carbonyl region consists of two sharp medium intensity bands and a strong broad band containing several shoulders. The frequencies and intensities of the bands are (in cm^{-1}): 2088 m, 2064 m, 2007 w, 1998 sh, 1974 s,br, and 1965 s. A P-F stretching band was observed at 825 cm^{-1} which contained a shoulder at 811 cm^{-1}.

The infrared spectrum of Fraction #1 in the carbonyl region consists of a single band centered near 1990 cm^{-1}. A single carbonyl stretching frequency at 1992 cm^{-1} has been reported for $Mo(CO)_6$ in solution. Frequencies and intensities of the bands in the carbonyl region for the remaining fractions are given in Table #1.
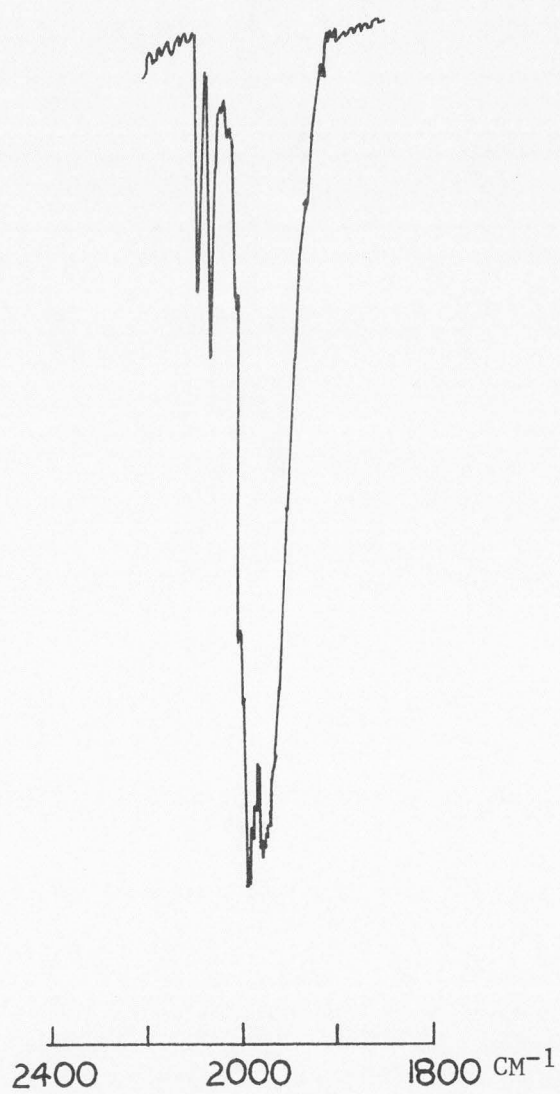
Figure 6. Ir Spectrum (CO region) of photolytically-prepared $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$ in hexane

TABLE 1

CO Frequencies of Fractions Obtained From the Mixture of

the $Mo(CO)_6$ Photolysis Reaction

Fraction #	CO Frequencies (cm^{-1}) and Intensities
2	2055 w, 2000 vw, 1993 vs, 1972 s
3	2065 w, 2050 w, 1995 sh, 1979 s,br
4	1995 m, 1977 s, 1960 sh

23

NMR Spectra

Proton Nmr Spectrum

The 100.1 MHz proton nmr spectrum of the non-separated mixture gives a complex multiplet centered near 2.0δ with benzene as the internal reference (free ligand, $\delta 1.97$, broad multiplet.)

Fluorine Nmr Spectrum

The ^{19}F nmr spectrum of the non-separated mixture (Figure 7) gives two doublets centered near -58 ppm. One of the signals is clearly two peaks whereas the other signal is broad and unresolved and appears as only one peak. The fluorine coordination shifts are calculated to be +30.3 ppm and +11.8 ppm, and the P-F coupling constants span approximately 1160 Hz.

A Study of the Photoreaction of $PF_2C_6H_{10}PF_2$ with $W(CO)_6$ in Pentane.

The photoreaction of $W(CO)_6$ with a 20% mole excess of $PF_2C_6H_{10}PF_2$ in pentane results in the displacement of 1.7 equivalents of CO and the formation of a viscous, white oil. The oil is somewhat stable to air when dry, but decomposes rapidly when exposed to the air in solution, turning a dark blue. The oil was not purified further, although the oil was pumped on the vacuum line overnight in order to sublime away any unreacted $W(CO)_6$.

Characterization of $[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The product, where x = 1-3 at least, has been characterized by infrared and nmr spectral data. The osmometric molecular weight of the product was found to be 1128. The product gives an elemental analysis in good agreement with that calculated for a tetracarbonyl species.
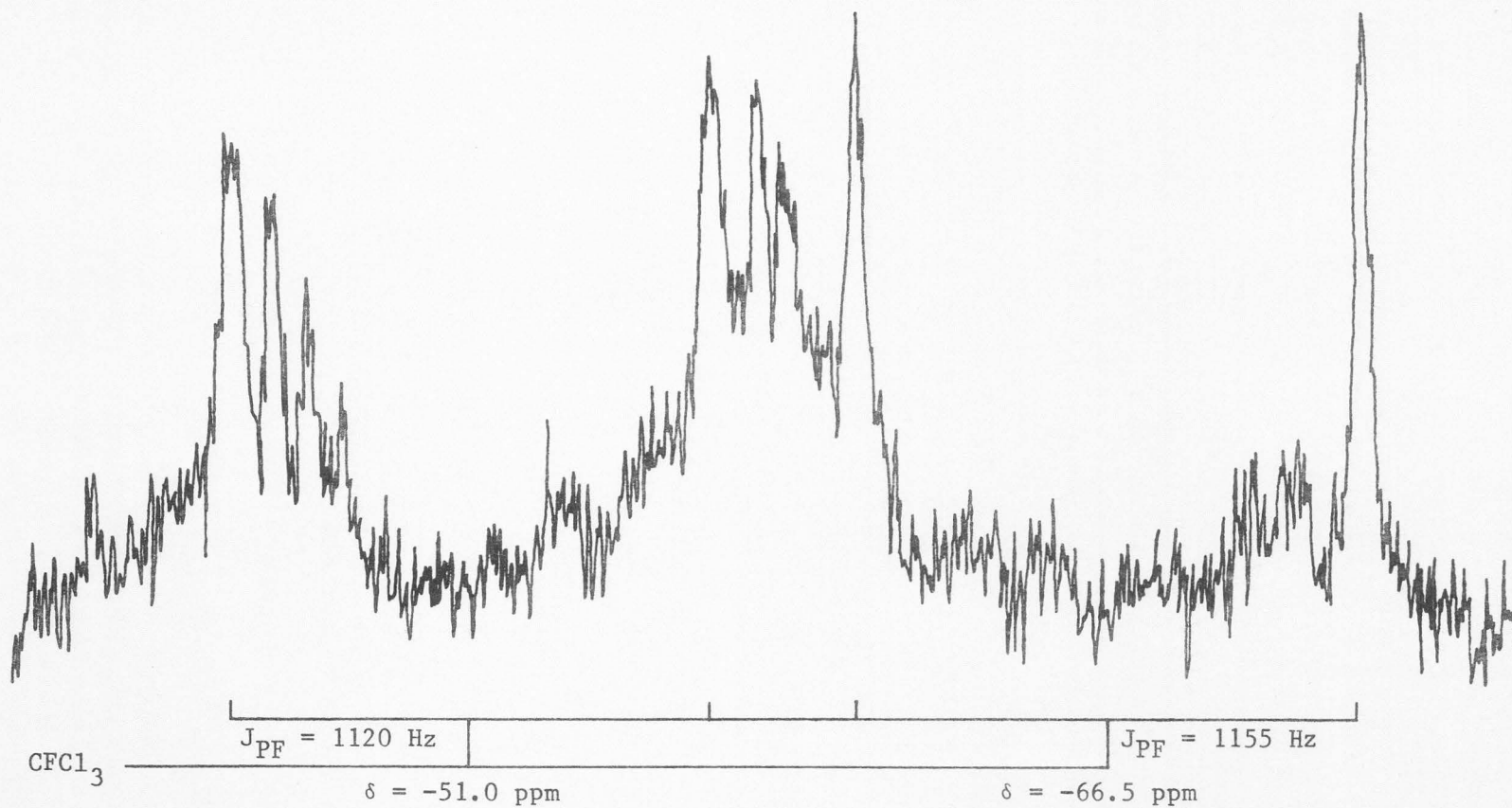
Figure 7. Fluorine NMR Spectrum of Photolytically-Prepared $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$

Infrared Spectrum

The infrared spectrum of the complex (Figure 8) in the carbonyl region exhibits a strong, broad band between 2000 and 1900 cm^{-1}. The band could not be resolved even on an expanded scale. Frequencies and intensities of the bands are (in cm^{-1}): 2081 m, 2056 m, 2006 w, and 1961 s,br. A strong band near 810 cm^{-1} was assigned to the P-F stretching mode.

NMR Spectra

Proton Nmr Spectrum

The 100.1 MHz proton spectrum of the complex consists of a complex multiplet centered near 2.0δ with benzene as the internal reference (free ligand, δ1.97. broad multiplet).

Fluorine Nmr Spectrum

The ^{19}F nmr spectrum of the complex (Figure 9) gives a downfield shift appearing as a large doublet as -66.1 ppm ($CFCl_3$, external standard) and a smaller doublet centered near -63.1 ppm. The fluorine coordination shift for the large doublet was calculated to be +15.2 ppm. The downfield coordination shift and simultaneous decrease of the P-F coupling constant (1150 Hz) are consistent with previous observations.[16] "Satellite" lines arising from further spin coupling of the fluorine nuclei with the ^{183}W nucleus ($I = 1/2$, 14.40% abundance) are not visible.

Phosphorus Nmr Spectrum

The ^{31}P nmr spectrum of the tungsten complex (Figure 10) consists of two distinct triplets (expected for a mixture) centered at 238.8 and 230.8 ppm (85% H_3PO_4). The higher field triplet (phosphorus coordination
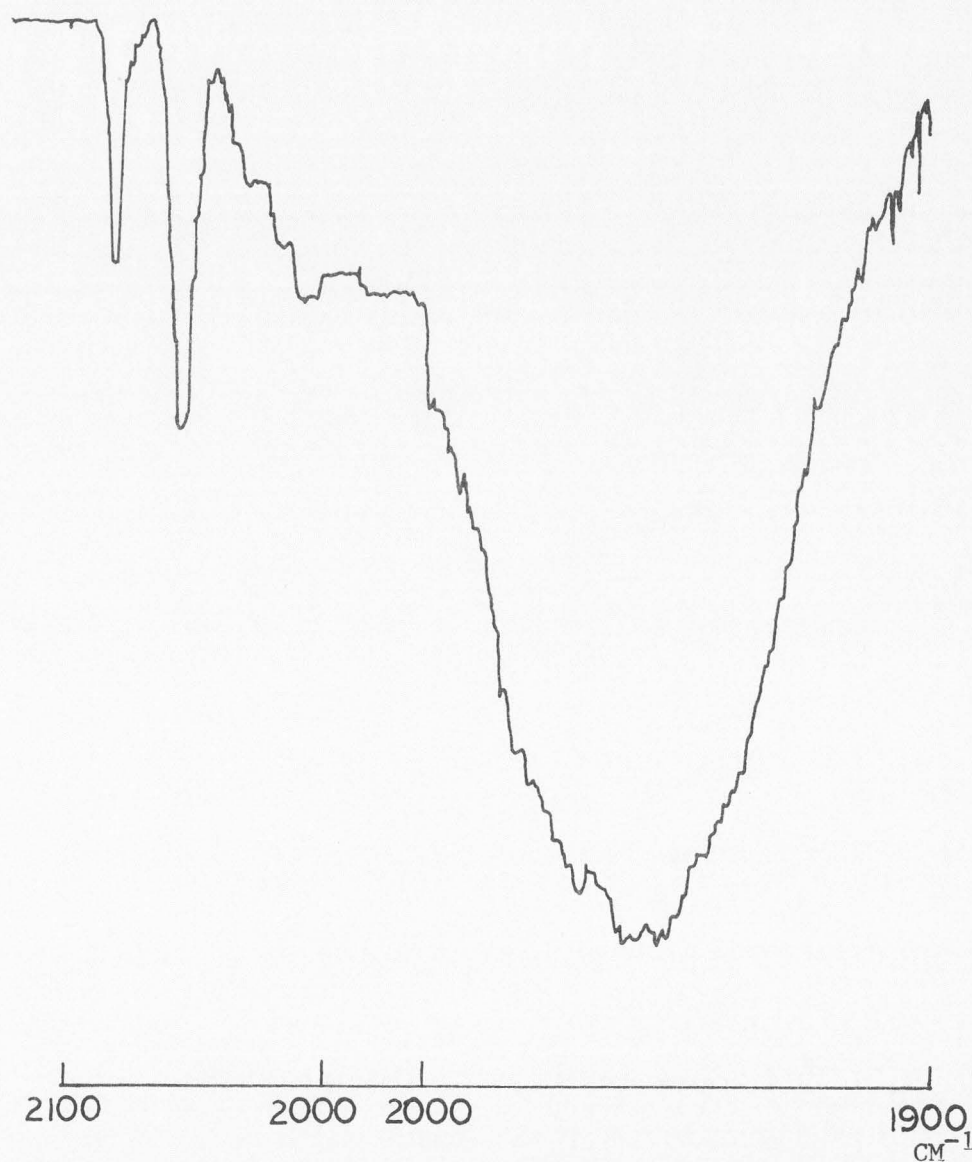
Figure 8. Ir Spectrum (CO Region) of Photolytically-Prepared
$[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$ in Hexane

Figure 9.   Fluorine NMR Spectrum of Photolytically-Prepared
$[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$

$J_{PF} = 1150$ Hz

$CFCl_3$ ————

$\delta = -66.1$ ppm

J_{FP} = 1160 Hz J_{FP} = 1160 Hz

δ = + 238.8 ppm δ = +230.8 ppm

H_3PO_4
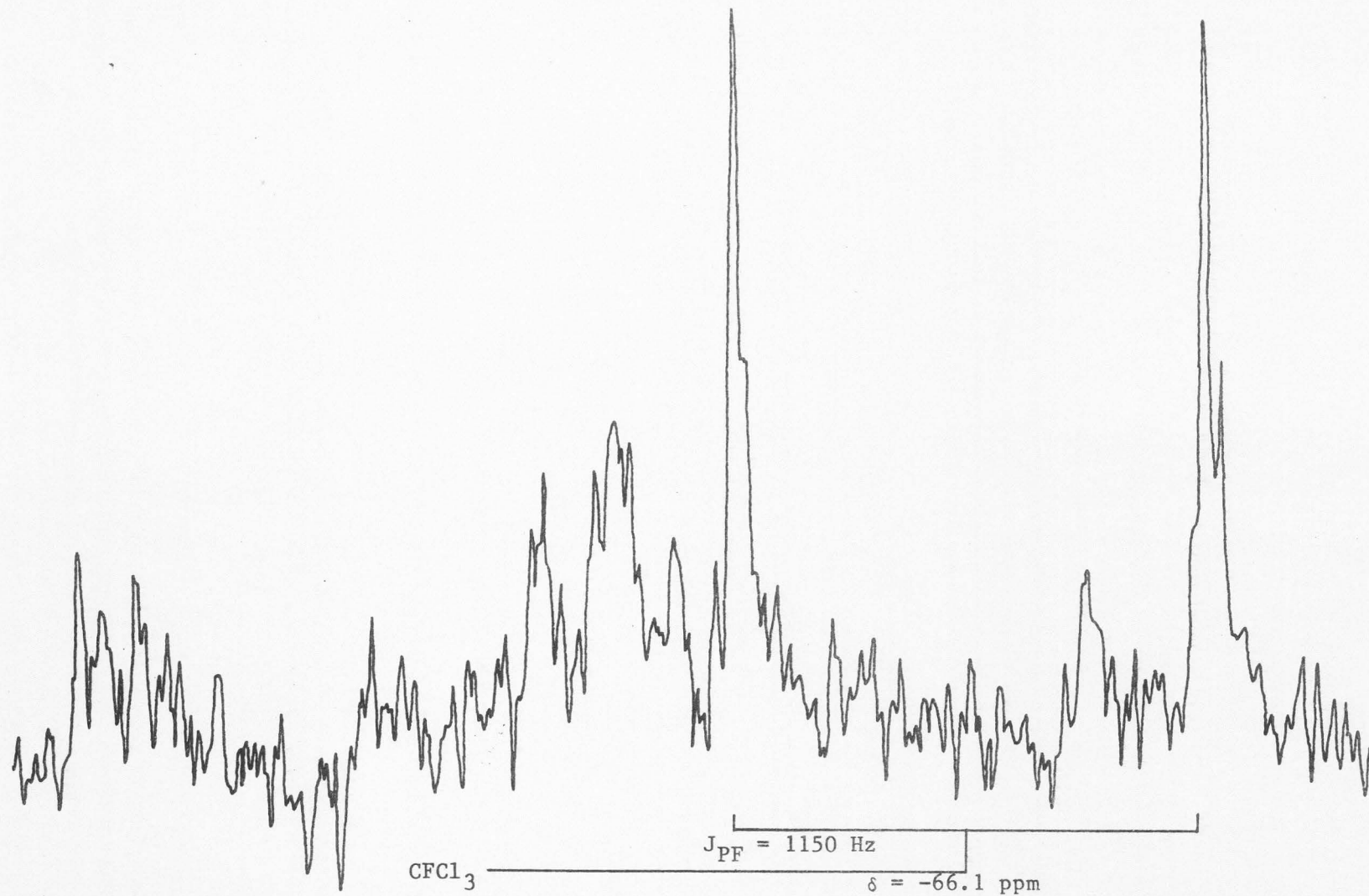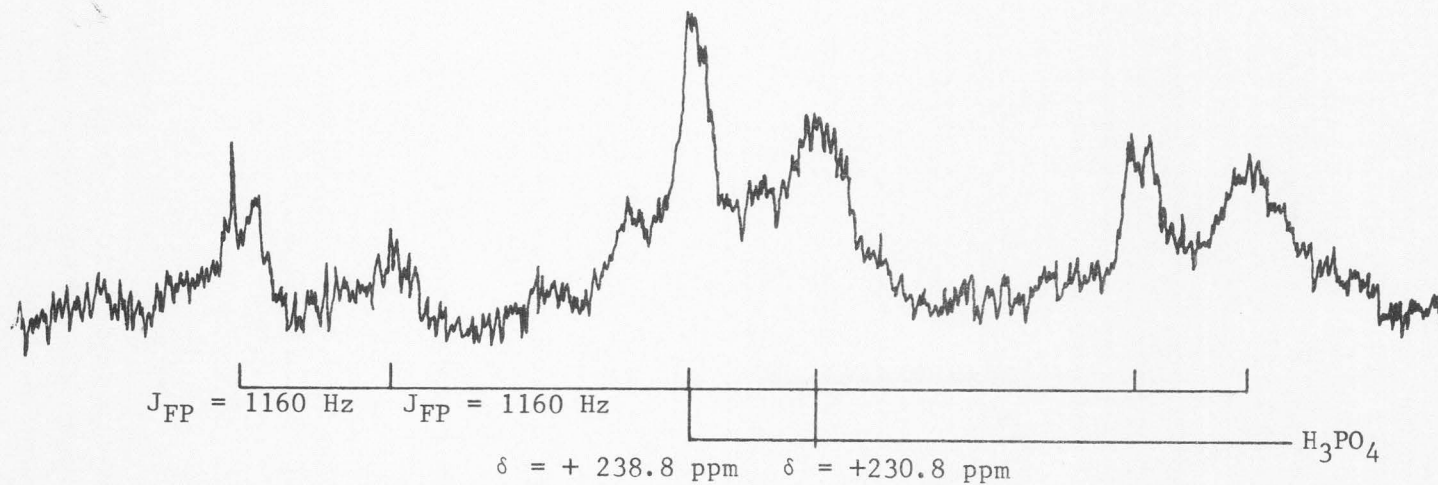
Figure 10.   Phosphorus NMR Spectrum of Photolytically-Prepared
$[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$

shift = -3.3 ppm) is about two-thirds as intense as the lower field triplet (phosphorus coordination shift = 4.7 ppm). The F-P coupling constants for the triplets span approximately 1160 Hz. No peaks due to tungsten-phosphorus spin coupling were discernible.

A Study of the Photoreaction of $Mo(CO)_6$ and Excess $PF_2C_6H_{10}PF_2$ in Pentane.

The irradiation of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ in a 1:2.7 mole ratio at 300 nm in pentane solution results in the recovery of 3.08 equivalents of CO and the formation of a white oil. The product did not sublime up to 130° and is purified by redissolving the oil in pentane, filtering the solution at 0°, and collecting the solid which turned from a solid to an oil upon drying under vacuum. Infrared spectra of the product resembled the spectra obtained for the product of the photoreaction of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ (Figure 6). Since an osmometric molecular weight of 913 indicating polymer formation) is obtained for the oil, the product has not been characterized further. The product probably consists of a mixture of carbonyl-containing species.

A Study of the Photoreaction of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$ in Pentane.

The irradiation of $Ph_2PC_2H_4PPh_2$ and a 10% mole excess of $Mo(CO)_6$ at 300 nm in pentane results in the recovery of approximately one equivalent of CO and the formation of a light yellow solid. The solid is purified by filtration and washing to remove unreacted phosphine. A broad band in the region of 2000-1900 cm^{-1} is obtained in the solution infrared spectrum of the complex (Figure 11). The osmometric molecular weight of the solid in benzene is found to be 600. This value is consistent with the formulation, $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$. Frequencies of bands in the
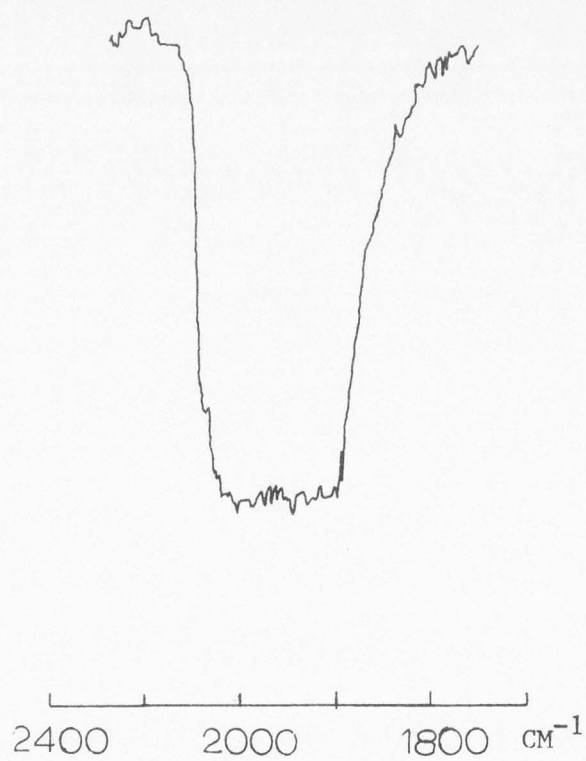
Figure 11. Ir Spectrum (CO Region) of Photolytically-Prepared
$Mo(CO)_4(Ph_2PC_2H_4PPh_2)$ in Pentane

CO region of the infrared spectrum of $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$ (prepared from the thermal reaction of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$)) were reported to be (in cm^{-1}): 2020, 1919, 1907, and 1881.[10]

C. Experimental Results - Thermal Reactions

A Study of the Thermal Reaction of $Ph_2PC_2H_4PPh_2$ and $Mo(CO)_6$.

Chatt and Watson[10] have reported the facile isolation of $Mo(CO)_4$-$(Ph_2PC_2H_4PPh_2)$ by heating $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$ in a 1:1 mole ratio in a sealed evacualted tube. In order to become familiar with the techniques required for thermal reactions of bidentate phosphines and the metal carbonyls, the reaction scheme reported by Chatt and Waston was to be followed. A slight mole excess of $Mo(CO)_6$ is heated in the presence of $Ph_2PC_2H_4PPh_2$ resulting in the recovery of 1.36 equivalents of CO and the formation of a yellow-white solid. The product is purified by subliming away unreacted $Mo(CO)_6$ and filtering off unreacted ligand. The yellow solid is very air-stable, as evidenced by stability of the complex in solution when exposed to air.

Characterization of $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$.

The reaction product has been characterized by osmometric molecular weight and infrared spectroscopy. The osmometric molecular weight of the solid in chloroform was found to be 622. This value is in good agreement with the molecular weight calculated for the monomeric tetracarbonyl product (607). The solution infrared spectrum of the solid (Figure 12) in the carbonyl region suggests the presence of the tetracarbonyl (frequencies in cm^{-1}: 2022, 1926, 1909, and 1889) and unreacted $Mo(CO)_6$

(frequency in cm^{-1}: 1983). The reported values of the frequencies of
the CO bands for $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$ are (in cm^{-1}): 2020, 1919,
1907, and 1881.[10]

A Study of the Thermal Reaction of $Cr(CO)_6$ and $PF_2C_6H_{10}PF_2$.

The thermolysis of $PF_2C_6H_{10}PF_2$ and a slight mole excess of $Cr(CO)_6$
results in the recovery of 1.5 equivalents of CO and the formation of a
light green oil. During the reaction the ligand did not appear to de-
compose up to the reaction temperature of 180°. The oil is dissolved
in a few milliliters of benzene and upon solvent removal, finely-divided,
white crystals appeared which are recrystallized twice from benzene by
cooling to 0° and removing the solvent. The crystals turned light green
in color after storing for a year in the presence of nitrogen.

Characterization of $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The product, where x = 4, at least, has been characterized by in-
frared and nmr spectral data and by osmometric molecular weight. The
product gives an elemental analysis in good agreement with that calculated
for $Cr(CO)_4(PF_2C_6H_{10}PF_2)$. The osmometric molecular weight of the complex
was found to be 1563 which corresponds to a tetramer. The complex is
crystalline (in contrast to the oily mixtures obtained from the photo-
reactions of the metal hexacarbonyls and the ligand) which is indicative
of a pure compound containing no species of higher or lower molecular
weight.

Infrared Spectrum

The infrared spectrum of the complex (Figure 13) in the carbonyl
region exhibits bands not too unlike those obtained for the photolysis
product of $Cr(CO)_6$ and $PF_2C_6H_{10}PF_2$ described above (See Figure 3).
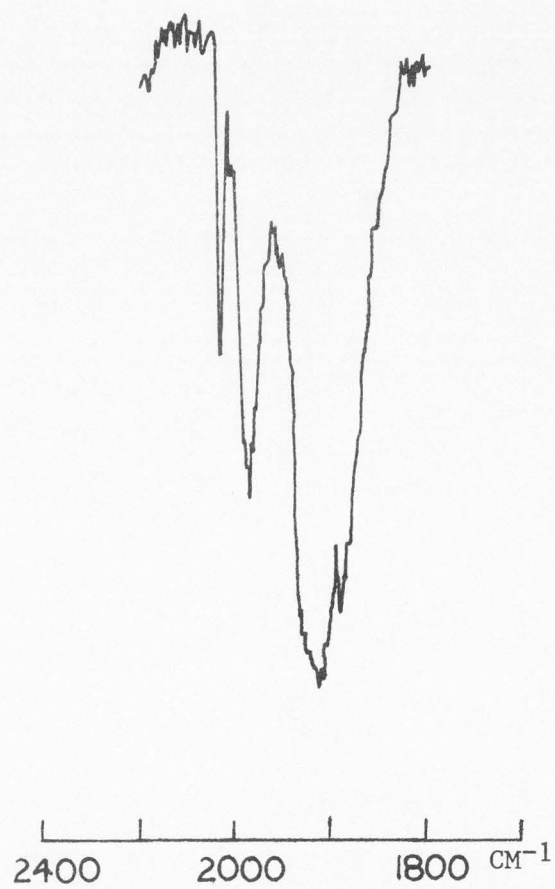
Figure 12.   Ir Spectrum (CO Region) of Thermally-Prepared
Mo(CO)$_4$(Ph$_2$PC$_2$H$_4$PPh$_2$) in Hexane
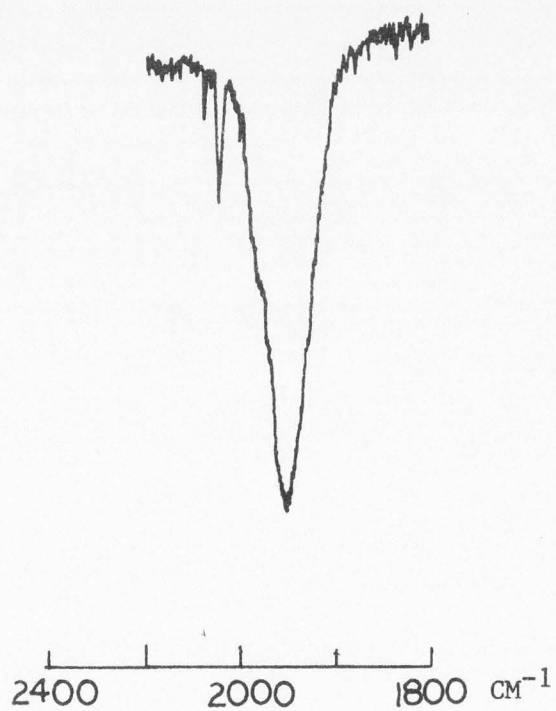
Figure 13. Ir Spectrum (CO Region) of Thermally-Prepared $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$ in Hexane

Frequencies and intensities of the bands are (in cm^{-1}): 2085w, 2055m, 1990sh, 1950s,br. A strong P-F stretching band is obtained at 810 cm^{-1}. The broadness of the band near 1950 cm^{-1} may be due to traces of un-reacted $Cr(CO)_6$.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum consists of a complex multiplet centered near $\delta 2.0$ with benzene as the internal reference (free ligand, $\delta 1.97$, complex multiplet).

Fluorine NMR Spectrum

The ^{19}F nmr spectrum of the complex (Figure 14) consists of a broad doublet centered at -46.7 ppm ($CFCl_3$ external standard). The fluorine coordination shift of the doublet is calculated to be +34.6 ppm, a value much greater than those observed for the photolysis products of the various metals. The width of the resonances (width at half-height spans 180-200 Hz) can arise from longer-range through space PF and FF couplings due to the proximity of ligands in a tetrameric arrangement. The P-F coupling constant spans 1130 Hz. A weak intensity doublet is observed just downfield from the intense, broad doublet.

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum could not be analyzed since the sample had clearly decomposed before the spectrum was obtained. Several signals appeared in the spectrum which could not be assigned to the functional groups of the ligand.

Figure 14. Fluorine NMR Spectrum of Thermally-Prepared
$[Cr(CO)_4(PF_2C_6H_{10}PF_2)]_x$

CFC1$_3$ ——————————
J_{PF} = 1130 Hz

δ = -46.7 ppm

36
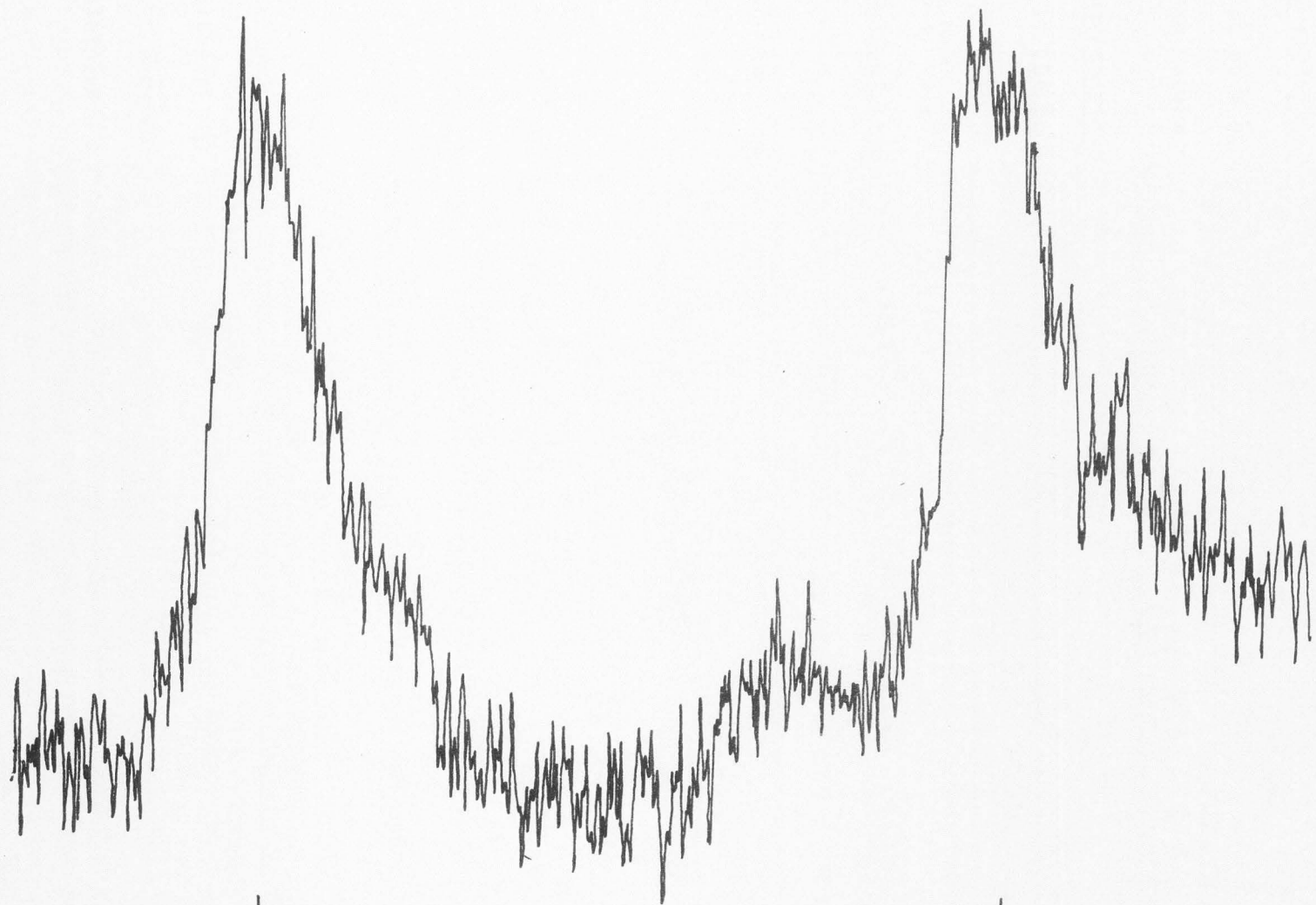
A Study of the Thermal Reaction of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ (A).

The thermal reaction of equimolar amounts of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ at 165° results in the recovery of 1.4 equivalents of CO and the formation of a brown oil. No attempt has been made to purify the oil other than vacuum drying to remove volatile unreacted ligand.

Characterization of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$.

The product has been characterized by nmr spectral data and by osmometric molecular weight. A value of 537 is obtained for the molecular weight in benzene. This weight corresponds to nearly a monomer, (molecular weight = 428) although it may be due to the dicarbonyl substitution product (molecular weight = 572). The nmr data presented below suggest that only a single compound is present. No elemental analysis has been obtained for the oil because of the expected impurities in the product. (Oils were thought to arise from mixtures of products.) No infrared spectrum has been obtained since the infrared spectrometer was not functioning at the time of characterization, and the entire sample was needed for nmr analysis.

NMR Spectra

Proton NMR Spectrum

The 100.1 MHz proton nmr spectrum of the oil consists of a symmetric multiplet (general appearance is that of a quartet) centered at $\delta 2.03$ with benzene as the internal reference (free ligand, $\delta 1.97$, broad multiplet).

Fluorine NMR Spectrum

The ^{19}F nmr spectrum (Figure 15) gives an intense, sharp doublet centered at -64.7 ppm ($CFCl_3$ external reference), and two weak doublets centered at -62.0 and -57.6 ppm. The downfield coordination shift (+16.6 ppm for the large doublet) and the decrease in the P-F coupling constant (1160 Hz; free ligand, 1174 Hz) are expected for fluorophosphine-metal complexes.[16]

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum (Figure 16) exhibits two triplets; the large triplet centered at +264.9 ppm (85% H_3PO_4 external standard) is assigned to the complex containing only the dominant trans, diequatorial ligand conformer. The phosphorus coordination shift of the large triplet is +30.8 ppm. The P-F coupling constant spans 1170 Hz. No higher field triplet attributable to bridging ligand species is observed. Also, no signal is observed for the dicarbonyl complex (two triplets of equal intensity broadened by longer range spin couplings would be expected). This spectral pattern suggests purity of sample typical of a monomeric chelated complex.

A Study of the Thermal Reaction of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ (B).

The thermal reaction of a 20% mole excess of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ at temperatures less than 140° results in the recovery of 1.02 equivalents of CO and the formation of a brown oil. The oil partially dissolves in benzene and the soluble fraction is separated from an insoluble white solid by decanting. The benzene is removed under reduced pressure from the fractions. The white solid has been identified as unreacted $Mo(CO)_6$ by infrared spectroscopy.

$J_{PF} = 1160$ Hz

$CFCl_3$

$\delta = -64.7$ ppm
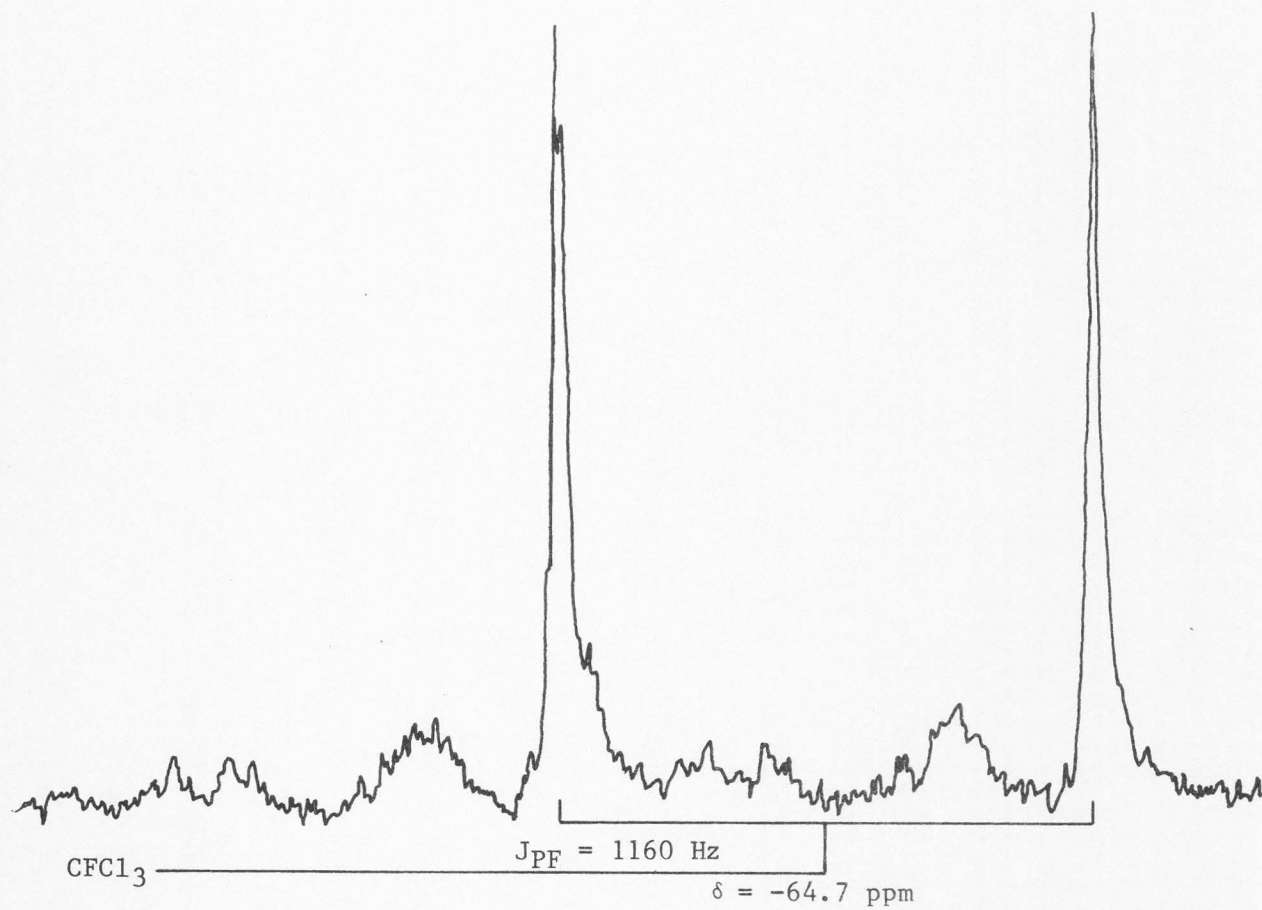
Figure 15.   Fluorine NMR Spectrum of Thermally-Prepared $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

J_{PF} = 1170 Hz

δ = +264.9 ppm

H_3PO_4
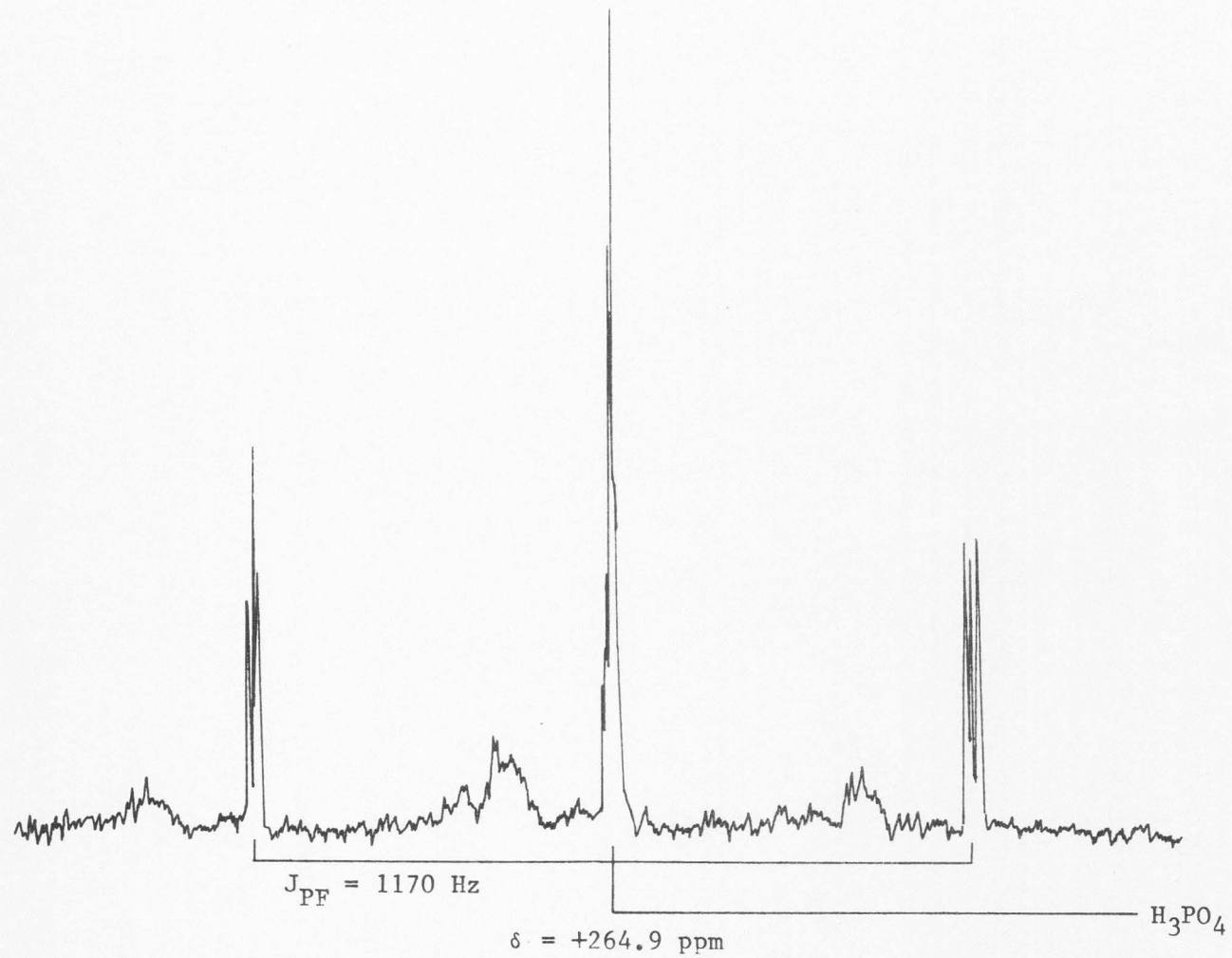
Figure 16.   Phosphorus NMR Spectrum of Thermally-Prepared $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

Characterization of $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The reaction product (oil) has been characterized by infrared and nmr spectra and by osmometric molecular weight. The oil is assumed to result from a mixture and thus no elemental analysis has been performed. The product is determined to have a molecular weight (osmometrically in benzene) of 809 nearly corresponding to a dimer.

Infrared Spectrum

The infrared spectrum of the oil in the CO region is shown in Figure 17. Three bands are visible whose frequencies are (in cm^{-1}): 2057, 2020, and 1980. The broad band centered near 1980 cm^{-1} can be somewhat resolved on an expanded scale with shoulders appearing at 1996 and 1967 cm^{-1}. These carbonyl band positions and intensities are not completely comparable with bands observed for similar tetracarbonyl complexes[7], and may be due to a mixture including traces of unreacted $Mo(CO)_6$. A strong band at 802 cm^{-1} is assigned to the P-F stretching mode.

NMR Spectra

Proton NMR Spectrum

The 100.1 MHz proton nmr spectrum consists of a complex multiplet centered near $\delta 2.0$ with benzene as the internal reference. The free unbound ligand gives a complex multiplet (broad) at $\delta 1.97$.

Fluorine NMR Spectrum

The ^{19}F nmr spectrum gives a broad doublet (Figure 18) centered at -65.7 ppm ($CFCl_3$, external reference). The fluorine coordination shift is +15.6 ppm and J_{PF} spans approximately 1160 Hz. At least one weak
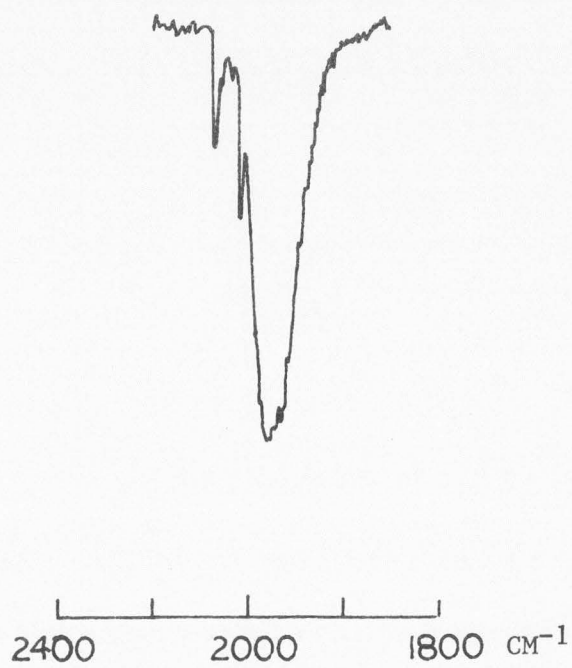
Figure 17. Ir Spectrum (CO Region) of Thermally-Prepared
[Mo(CO)$_4$(PF$_2$C$_6$H$_{10}$PF$_2$)]$_x$ in Hexane

$J_{PF} = 1155$ Hz

$CFCl_3$

$\delta = -65.7$ ppm
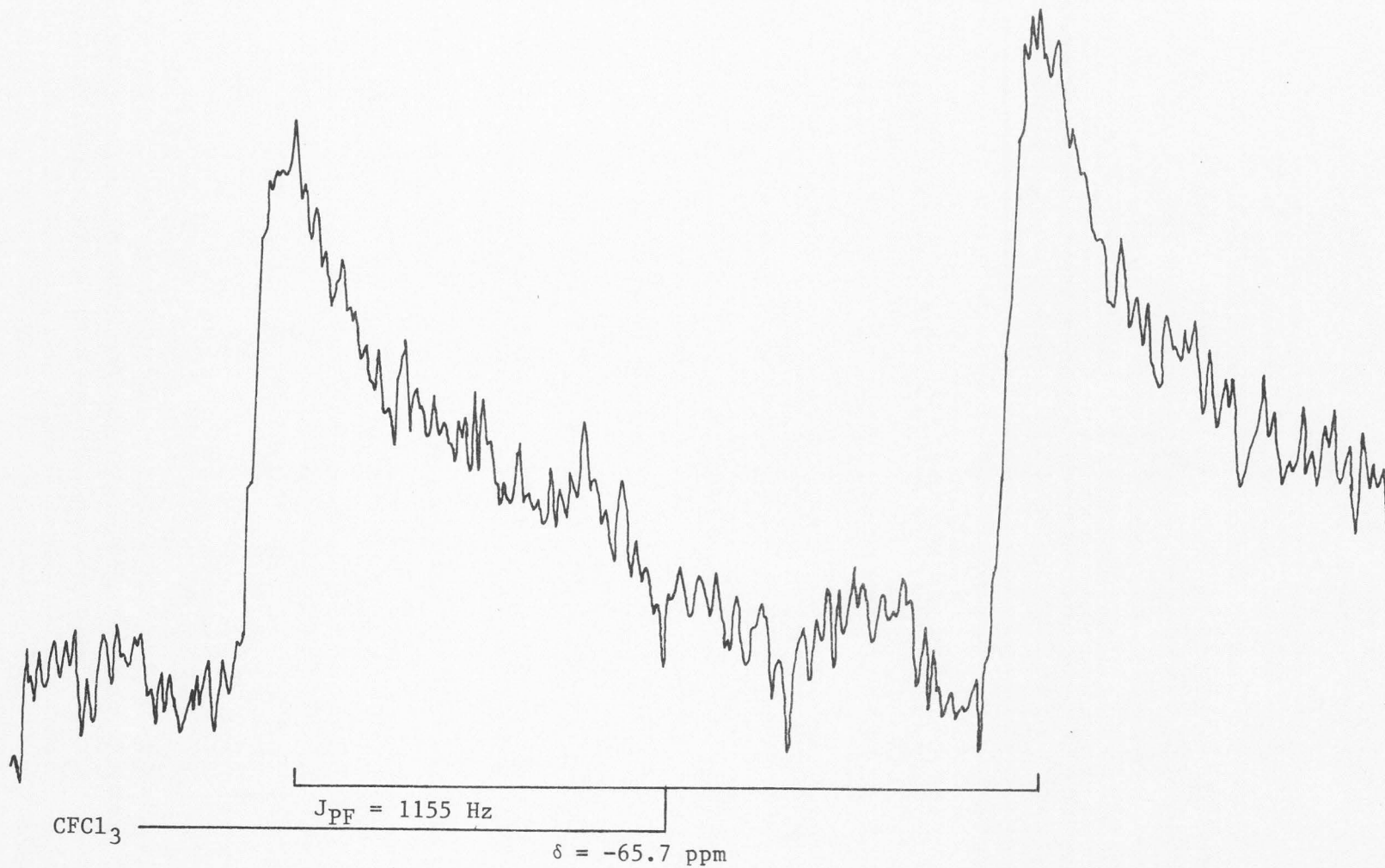
Figure 18. Fluorine NMR Spectrum of Thermally-Prepared $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$

43

intensity doublet is visible above the noise downfield from the large
doublet. The width of the doublet at half-height spans 100-200 Hz.

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum exhibits two triplets shown in Figure 19. The
large triplet is centered at +259.1 ppm (85% H_3PO_4, external reference)
and the small triplet is centered at -268.3 ppm. The lower field
triplet is about one-fourth as intense as the higher field triplet. The
phosphorus coordination shifts of the large and small triplets are
+25.0 and +34.2 ppm, respectively. The F-P coupling constants of the
triplets span approximately 1155 Hz. The resonances are probably due
to a mixture of monomer and polymer.

A Study of the Thermal Reaction of $W(CO)_6$ and $PF_2C_6H_{10}PF_2$.

The reaction of a 20% mole excess of $W(CO)_6$ and $PF_2C_6H_{10}PF_2$ at
45° yields 1.2 equivalents of CO and a yellow solid. Upon extraction of
the solid with benzene and filtering, a yellow oil is separated from a
white solid. The solid is identified as unreacted $W(CO)_6$ by solution
infrared spectroscopy. The yellow solid is very air-sensitive, turning
blue-gray after storing for several days in a nitrogen-filled glove bag.

Characterization of $[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

The yellow oil has been characterized as a polymeric tetracarbonyl
complex by infrared and nmr spectral data and by osmometric molecular
weight. The oil is assumed to consist of a mixture of tetracarbonyl
species, and thus, no elemental analysis has been performed. The
osmometric molecular weight of the oil in benzene is determined to be
873.

J_{FP} = 1160 Hz J_{FP} = 1151 Hz

δ = +268.3 ppm δ = +259.1 ppm H_3PO_4
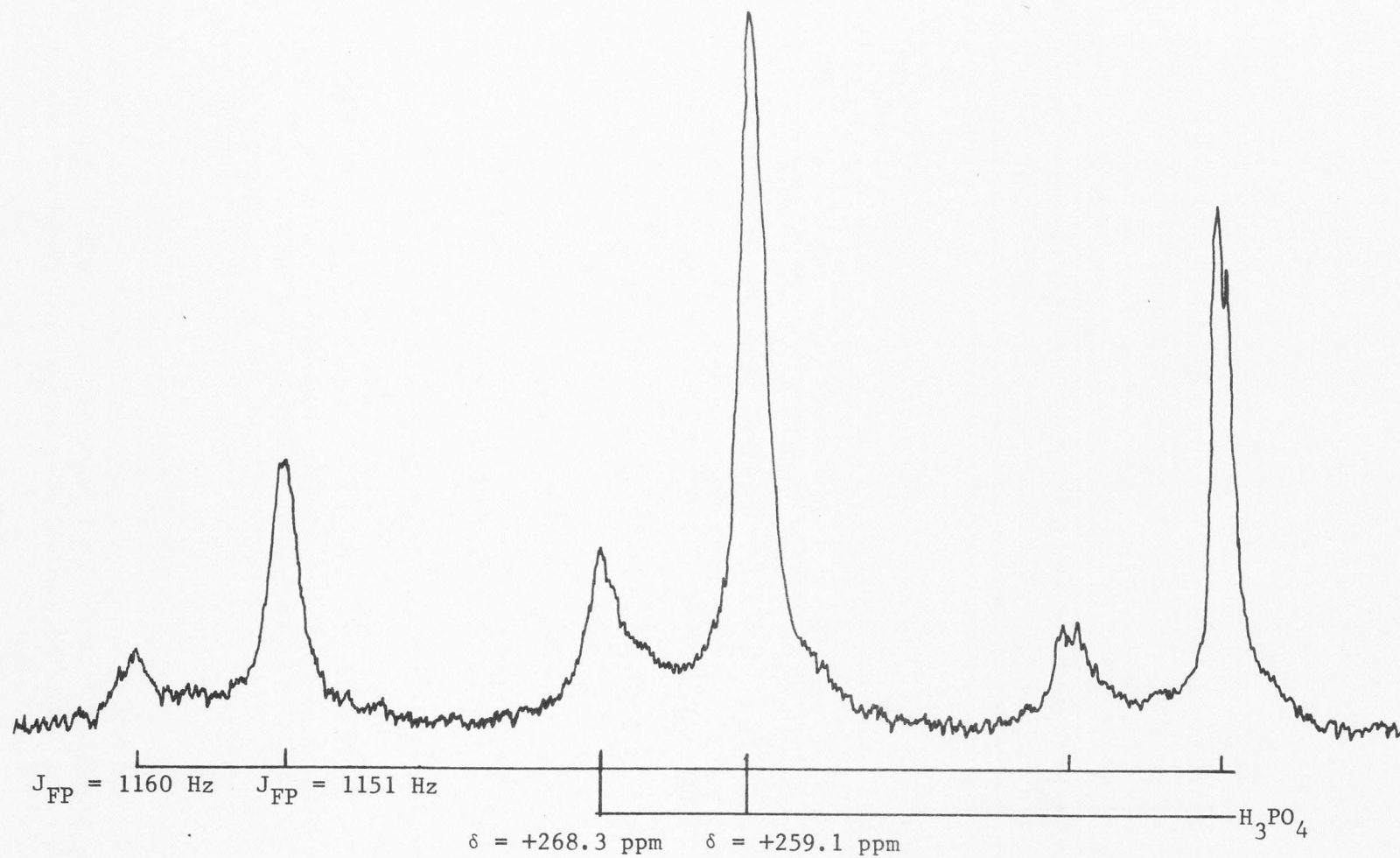
Figure 19.   Phosphorus NMR Spectrum of Thermally-Prepared $[Mo(CO)_4(PF_2C_6H_{10}PF_2)]_x$

Infrared Spectrum

The solution infrared spectrum of the oil in the CO region exhibited bands at 2080w, 2060w, 1980s,br, and 1945sh cm^{-1}. (Figure 20) The strong, broad band in the region of 2000 to 1950 cm^{-1} may be due to traces of unreacted tungsten carbonyl. No P-F stretching band has been observed.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum of the complex consists of a broad resonance centered near $\delta 2.0$ with benzene as the internal reference (free ligand, $\delta 1.97$, broad multiplet).

Fluorine NMR Spectrum

The 94.1 MHz fluorine-19 nmr spectrum of the complex (Figure 21) exhibits a large doublet centered at -70.1 ppm ($CFCl_3$ external standard) and two unresolved smaller doublets downfield from the large doublet. A downfield coordination shift of 11 ppm and simultaneous decrease of the P-F coupling constant of 1160 Hz for the large doublet at indicative of metal complexes of fluorophosphine ligands.[16] A phosphorus nmr spectrum which would complement the fluorine nmr spectrum was not obtained due to loss of the sample.

A Study of the Thermal Reaction of $Mo(CO)_6$ and excess $PF_2C_6H_{10}PF_2$.

A 1:4.3 mole ratio of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ is heated in a sealed evacuated reaction tube for 4 hours at 155° resulting in the recovery of 3.3 equivalents of CO and in the formation of a yellow oil. The oil is

Figure 20. Ir Spectrum (CO Region) of Thermally-Prepared
$[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$ in Hexane
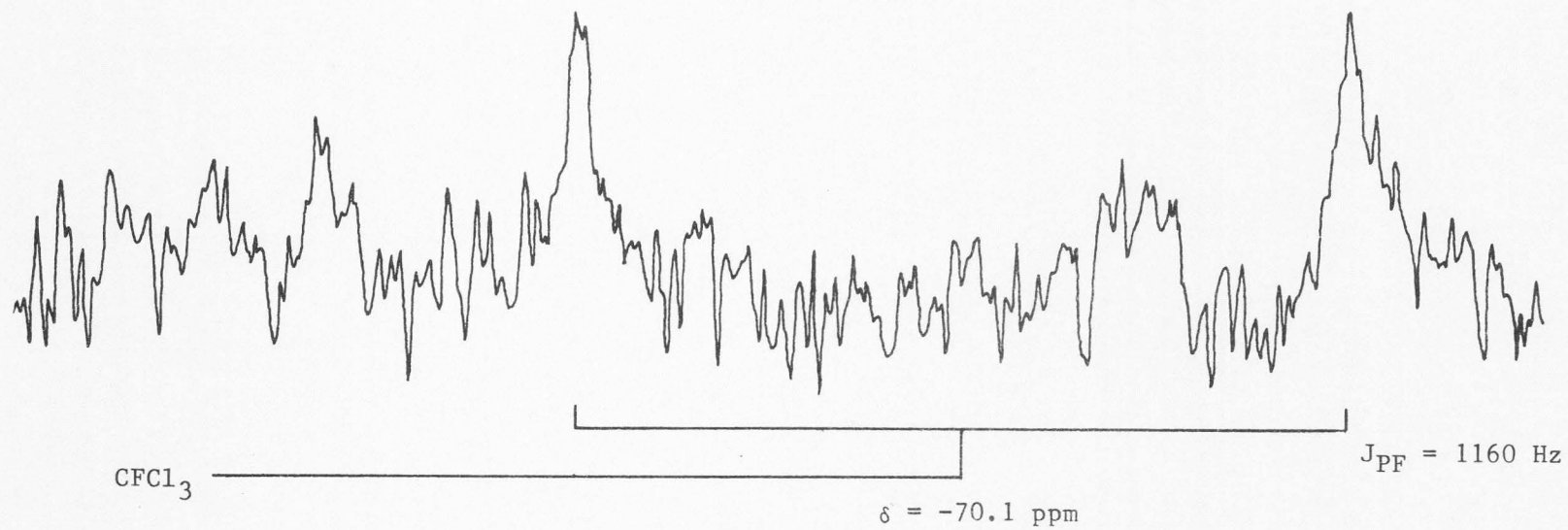
Figure 21. Fluorine NMR Spectrum of Thermally Prepared $[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$

extracted with benzene and the solution filtered. Removal of the

solvent gives a yellow oil.

Attempts to characterize the oil by elemental analysis, osmometric

molecular weight, and infrared and nmr spectroscopy suggest that the oil

consists of a mixture of products. Elemental analysis are inconclusive,

although the elemental percentages are in better agreement with the

formulation, $Mo(PF_2C_6H_{10}PF_2)_3$. The osmometric molecular weight (643) in

benzene is slightly high for a pure dicarbonyl species, while the in-

frared spectrum (Figrue 22) exhibits two broad carbonyl stretching bands

typical of a dicarbonyl complex. The NMR spectra of the complex

(Figures 23 and 24) give a complex multiplet, in the ^1H spectrum, a set

of doublets in the ^{19}F spectrum, and a triplet in the ^{31}P spectrum. The

^{19}F nmr spectrum shows several doublets indicative of a mixture.

A Study of the Thermal Reaction of $Mo(CO)_6$ and PCl_3.

A 1:1.7 mole ratio of $Mo(CO)_6$ and air-free, vacuum-distilled PCl_3

were heated for 2 hours at 145°. 2.2 equivalents of CO were recovered

from the reaction vessel. A black solid was obtained which was not

characterized further, and is most likely the result of an oxidized phos-

phine complex.

A Study of the Thermal Reaction of $Mo(CO)_6$ and PPh_3.

In an effort to obtain a metal complex containing labile ligands

which might be more easily displaced than CO by $PF_2C_6H_{10}PF_2$, a 1:2

mole ratio of $Mo(CO)_6$ and PPh_3 has been heated for 2 hours at 140°. The

reaction yields 2.0 equivalents of CO and a yellow solid. The solid is

extracted with benzene, the solution filtered twice to remove unreacted
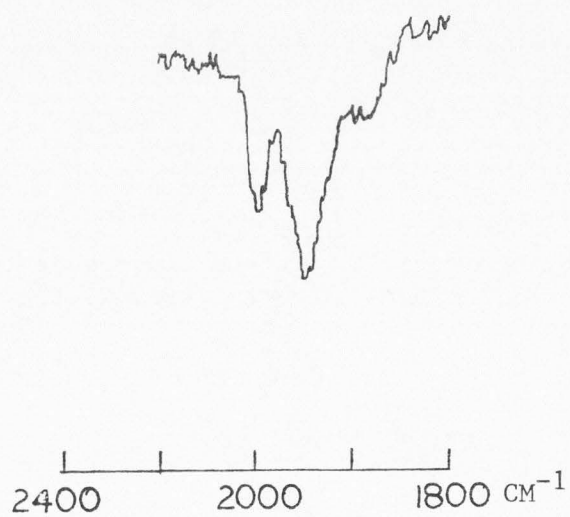
Figure 22. Ir Spectrum (CO Region) of the Product Obtained From the Thermal Reaction of $Mo(CO)_6$ and excess $PF_2C_6H_{10}PF_2$ in Hexane

Figure 23.   Fluorine NMR Spectrum of Product of the Thermal Reaction of Mo(CO)$_6$ and excess PF$_2$C$_6$H$_{10}$PF$_2$

CFCl₃

J_{PF} = 1138 Hz J_{PF} = 1129 Hz

δ = −66.8 ppm δ = − 68.5 ppm

51
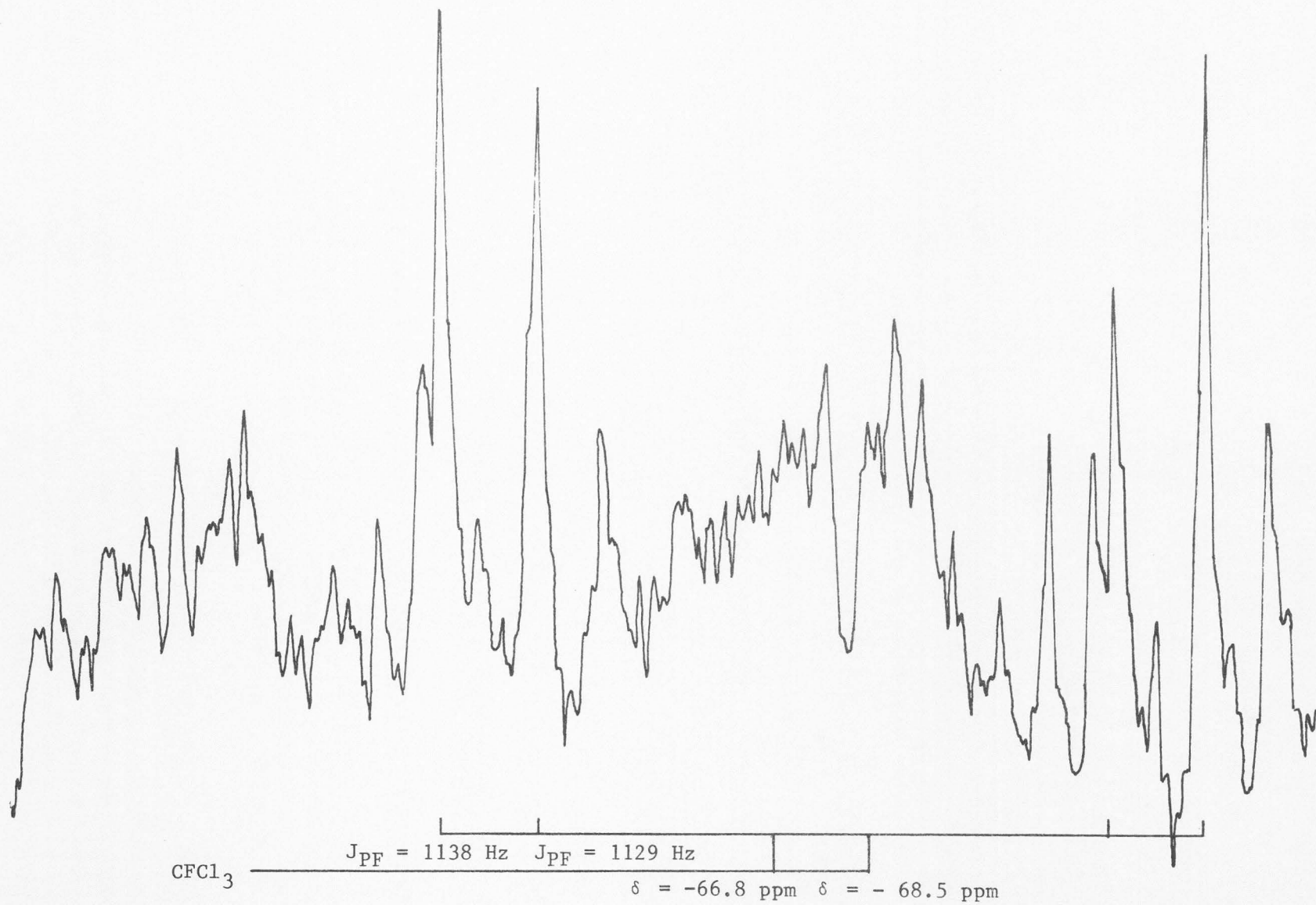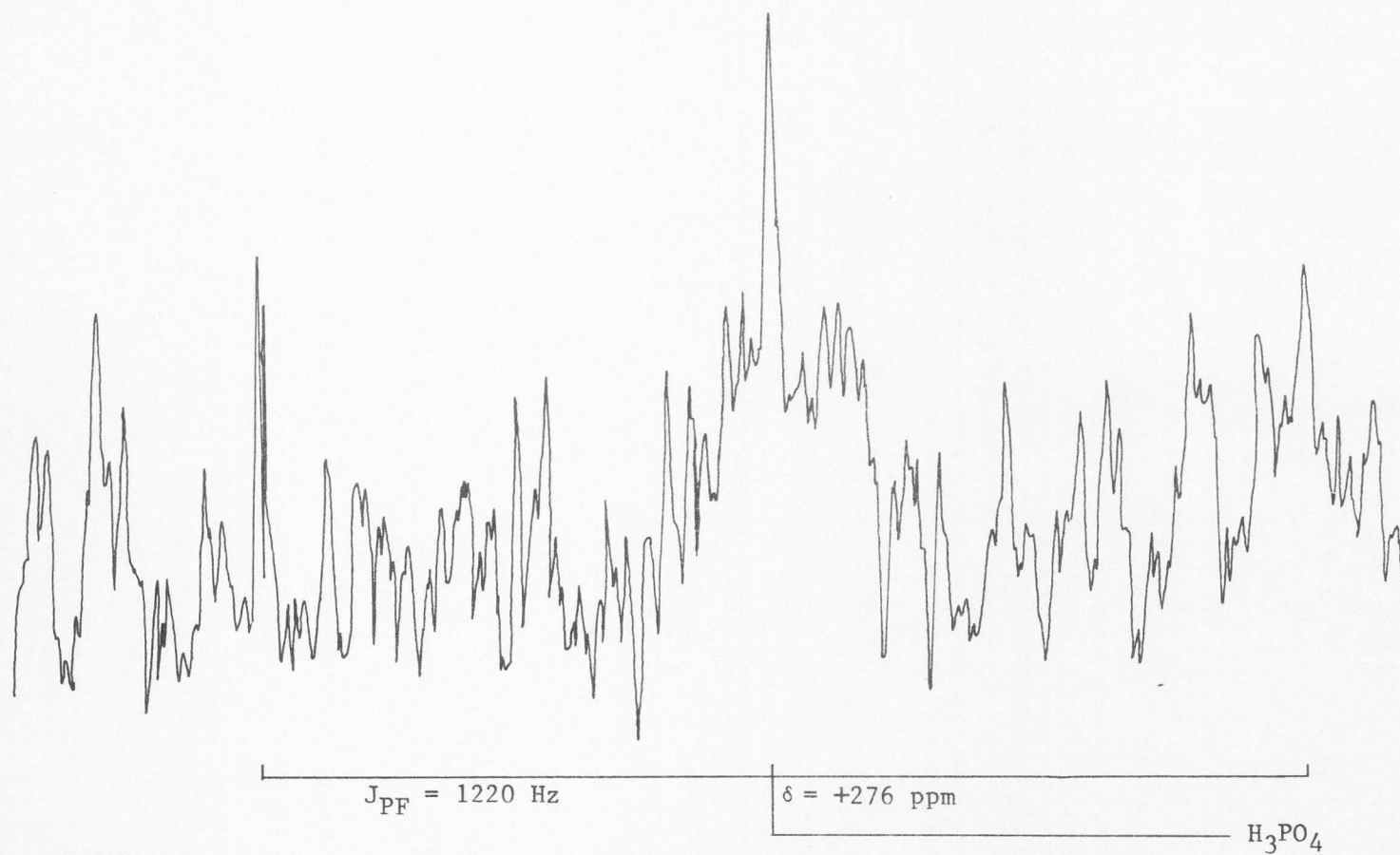
Figure 24.   Phosphorus NMR Spectrum of Product of the Thermal Reaction
of $Mo(CO)_6$ and excess $PF_2C_6H_{10}PF_2$

phosphine, and the solvent removed leaving a yellow solid identified as $Mo(CO)_4(PPh_3)_2$.

Characterization of $Mo(CO)_4(PPh_3)_2$.

The yellow solid has been identified by infrared spectral data. An osmometric molecular weight could not be obtained due to the low solubility of the compound in various solvents.

The solution ($CHCl_3$) infrared spectrum (Figure 25) of $Mo(CO)_4(PPh_3)_2$ in the CO region consists of three bands whose frequencies are (in cm^{-1}): 2010w, 1935w, and 1890s. The band positions and intensities are consistent with a mixture of cis and trans isomers, with the strong, broad band at 1890 cm^{-1} masking several of the bands expected. Poilblanc and Bigorgne[18] report the following frequencies of the CO stretching bands of the two isomers (in cm^{-1}): trans: 1952vw, 1903s; cis: 2202,1929, 1911, 1899.

D. Experimental Results - Ligand Displacement Reactions

A Study of the Reaction of $Mo(CO)_4(PPh_3)_2$ and $PF_2C_6H_{10}PF_2$.

The room temperature mixing of $Mo(CO)_4(PPh_3)_2$ (prepared by the thermal reaction of $Mo(CO)_6$ and PPh_3) and excess $PF_2C_6H_{10}PF_2$ produces no appreciable reaction. The reason for the inability of $PF_2C_6H_{10}PF_2$ to displace PPh_3 is probably due to the insolubility of $Mo(CO)_4(PPh_3)_2$ in the solvent system (benzene). Removal of the solvent gives only unreacted starting material.

A Study of the Reaction of $C_7H_8Cr(CO)_4$ and $PF_2C_6H_{10}PF_2$.

A quasi-equimolar mixture of $C_7H_8Cr(CO)_4$ and $PF_2C_6H_{10}PF_2$ is refluxed in toluene for several days resulting in the loss of the intense
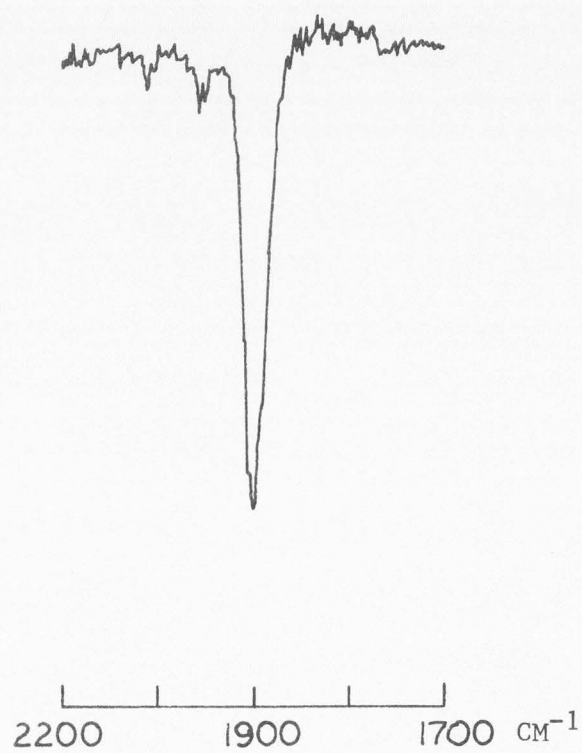
Figure 25. Ir Spectrum (CO Region) of $Mo(CO)_4(PPh_3)_2$ in Chloroform

yellow-green color of the solution and the appearance of a nearly color-less solution. Careful removal of the solvent deposits a yellow-green oil which is applied to a Florisil column. Eluting with hexane allowed for a separation of the yellow fraction from a colorless fraction. The colorless fraction yields a slightly air-sensitive white solid which has been further purified by high-vacuum sublimation.

Characterization of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$.

The yellow fraction obtained from the chromatographic separation has been identified as unreacted $C_7H_8Cr(CO)_4$ by solution infrared spectral data. $Cr(CO)_4(PF_2C_6H_{10}PF_2)$ has been identified by infrared, mass, and nmr spectral data and by osmometric molecular mass. The elemental analyses for the complex are inconclusive; a duplicate analysis varied greatly from the original analysis. The spectral data obtained indicative that the product formulation is correct. An osmometric molecular weight of 377 (theoretical molecular weight = 384) is obtained for the complex in benzene. This molecular weight value suggests that a mono-meric, chelated complex of the bidentate difluorophosphine ligand is synthesizable.

Mass Spectrum

The 70 eV mass spectrum of the complex exhibits five primary sets of peaks. (See Table 2) The parent ion peak is observed at 384 m/e. The four remaining sets of peaks are found at -28 m/e intervals indicat-ing the successive stepwise removal of CO groups from the parent ion. The base peak (relative intensity, 100) is observed at 272 m/e, cor-responding to $Cr(PF_2C_6H_{10}PF_2)^+$. Isotope peaks due to the metal are pre-sent as expected, as are fragmentation peaks of the fluorophosphine

TABLE 2

Assignments, Mass Numbers, and Relative Intensities of
Some Ions in the Mass Spectra of <u>cis</u>-M(CO)$_4$(P$_2$F$_4$C$_6$H$_{10}$)

	M = Cr		M = Mo		M = W	
	Mass	Intensity	Mass	Intensity	Mass	Intensity
LM(CO)$_4$$^+$	384	11	428	94	516	51
LM(CO)$_3$$^+$	356	12	400	59	488	56
LM(CO)$_2$$^+$	328	15	372	35	460	70
LM(CO)$^+$	300	27	344	100	432	100
LM$^+$	272	100	316	53	404	19

ligand. No peaks of higher mass than the parent peak are observed indicating the complex is indeed monomeric.

Infrared Spectrum

The solution infrared spectrum (Figure 26) of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$ in the CO region shows four distinct bands expected for a molecule exhibiting C_{2v} carbonyl symmetry (cis isomer). Frequencies for the four bands are (in cm^{-1}): 2056, 1994, 1982, and 1960. The band shapes and positions are consistent with spectral observations made for tetracarbonyl complexes.[7] A strong P-F stretching band is observed at 823 cm^{-1}.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum consists of a complex multiplet centered near δ2.0 with benzene as the internal reference (free ligand, δ1.97 broad multiplet).

Fluorine NMR Spectrum

The fluorine nmr spectrum of the complex (Figure 27) exhibits two large doublets centered at -63.3 and -61.9 ppm. ($CFCl_3$ external reference). Weak intensity doublets (barely discernible above the noise) downfield from the large doublets are attributed to the coordinated cis ligand isomer. Downfield coordination shifts of the large doublets of 18.0 and 19.4 ppm and a decrease in the magnitude of the P-F coupling constant from 1174 to 1157 Hz is entirely consistent with similar trends reported for fluorophosphine-metal complexes.[16,17]

Figure 26. Ir Spectrum (CO Region) of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$ in Hexane

J_{PF} = 1158 Hz J_{PF} = 1155 Hz

CFCl$_3$

δ = -61.9 ppm δ = -63.3 ppm

Figure 27.   Fluorine NMR Spectrum of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum (Figure 28) exhibits a triplet centered at +287.1 ppm (85% H_3PO_4 external standard). The coordination shift is downfield 53.0 ppm from the free ligand and the P-F coupling constant spans 1158 Hz. The sharpness of the resonances and the absence of triplets upfield from the dominant signal are indicative of a pure monomeric product.

A Study of the Reaction of $C_7H_8Mo(CO)_4$ and $PF_2C_6H_{10}PF_2$.

The room temperature reaction of a slight mole excess of $PF_2C_6H_{10}PF_2$ and $C_7H_8Mo(CO)_4$ in hexane for one hour results in the appearance of a colorless solution. Removal of the solvent and displaced norbornadiene followed by sublimation at 60° of a white solid gives relatively air-stable white crystals in high yield.

Characterization of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$.

The white crystalline product has been characterized by elemental analysis, osmometric molecular weight, and infrared, mass, and nmr spectral data. The complex gives an elemental analysis in excellent agreement with the formula, $Mo(CO)_4(PF_2C_6H_{10}PF_2)$. The osmometric molecular weight of the product in benzene is determined to be 432 which corresponds to a monomer.

Mass Spectrum

The mass spectrum of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ exhibits five major clusters of peaks at m/e values corresponding to the parent ion and the successive stepwise loss of CO from the ion. (See Table 2) The parent ion is observed at 428 m/e and the base peak is observed at 344 m/e and

Figure 28. Phosphorus NMR Spectrum of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$

is due to the ion, $Mo(CO)(PF_2C_6H_{10}PF_2)^+$. The clusters of peaks arise from seven isotopes of molybdenum. Fragmentation peaks due to fluorophosphine ligand are present as expected. No peaks due to ions heavier than the parent ion are observed.

Infrared Spectrum

The solution infrared spectrum (Figure 29) of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ in the carbonyl region gives four bands expected for the cis isomer (C_{2v} carbonyl symmetry). The frequencies of the bands are (in cm^{-1}): 2070, 2003, 1990, and 1971. These band positions are characteristic of monomeric tetracarbonyl complexes.[7] A strong P-F stretching band is observed at 825 cm^{-1}.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ consists of a complex multiplet centered near $\delta 2.0$ with benzene as the internal reference (free ligand, $\delta 1.97$, broad multiplet).

Fluorine NMR Spectrum

The ^{19}F nmr spectrum of the complex (Figure 30) exhibits a large doublet centered at -65.4 ppm ($CFCl_3$ external reference). Two very weak intensity doublets are visible above the noise downfield from the large doublet. The downfield coordination shift (+15.9 ppm) and simultaneous decrease of the P-F coupling constant (1152 Hz) are common to fluorophosphine-metal complexes.[16]

Figure 29. Ir Spectrum (CO Region) of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ in Hexane

$J_{PF} = 1152$ Hz

CFCl$_3$

$\delta = -65.4$ ppm

Figure 30. Fluorine NMR Spectrum of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum (Figure 31) consists of a triplet centered at +263.1 ppm (85% H_3PO_4 external reference). Upon coordination a downfield shift is obtained 29.0 ppm from the free unbound ligand. The P-F coupling constant decreases from 1218 to 1156 Hz. Six weak peaks of equal intensity, symmetrically distributed about the center peak of the triplet arise from coupling of the ^{31}P nucleus with either ^{95}Mo (I=5/2, 15.72% abundance) or ^{97}Mo (I=5/2, 9.46% abundance) or both. Comparable peaks are barely discernible above the noise about the two outside peaks of the triplet, but cannot be assigned with confidence. The Mo-P coupling constant was found to span 215± 5 Hz for the six peaks observed.

A Study of the Reaction of $C_7H_8W(CO)_4$ and $PF_2C_6H_{10}PF_2$.

A 20% mole excess of $PF_2C_6H_{10}PF_2$ is refluxed with $C_7H_8W(CO)_4$ in hexane for four hours. Upon removal of the solvent and the displaced norbornadiene, the white residue is sublimed at 60° yielding white crystals identified as $W(CO)_4(PF_2C_6H_{10}PF_2)$. Of the Group 6B metal complexes prepared by the ligand displacement method, the tungsten complex appears to be most easily oxidized, the white solid turning blue after exposure to air for several days. All the complexes are oxidized rapidly in the presence of solvent.

Characterization of $W(CO)_4(PF_2C_6H_{10}PF_2)$.

The product has been characterized by elemental analysis, osmometric molecular weight, and mass, infrared, and nmr spectral data. The product gives an elemental analysis in excellent agreement with the formulation, $W(CO)_4(PF_2C_6H_{10}PF_2)$. The molecular weight of the complex in benzene is 506 which corresponds to a monomer.

J_{FP} = 1156 Hz J_{MoP} = 215$\pm$5 Hz

δ = +263.1 ppm

H_3PO_4

Figure 31.   Phosphorus NMR Spectrum of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

Mass Spectrum

Further evidence confirming a monomeric tungsten complex is found in the mass spectrum. Assignments of the five major clusters of peaks in the 70 eV mass spectrum are given in Table 2. These prominent clusters (due to tungsten isotopes) arise at the parent ion (516 m/e) and at -28 m/e intervals from the parent peak indicating a successive stepwise removal of CO groups. Fragmentation peaks due to the ligands are present as expected and no peaks of higher mass than the parent ion peak are observed.

Infrared Spectrum

The solution infrared spectrum of $W(CO)_4(PF_2C_6H_{10}PF_2)$ (Figure 32) in the carbonyl region exhibits four well-defined bands common to complexes of the type, cis-$L_2M(CO)_4$, having C_{2v} carbonyl symmetry. Frequencies of the bands are (in cm^{-1}): 2064, 1995, 1983, and 1968. A strong P-F stretching band is observed at 825 cm^{-1}, further indicating the presence of a coordinated fluorophosphine ligand.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum consists of a complex multiplet centered near $\delta 2.0$ with benzene as the internal standard (free ligand, $\delta 1.97$, broad multiplet).

Fluorine NMR Spectrum

The ^{19}F nmr spectrum of the complex (Figure 33) consists of a large doublet centered at -66.1 ppm ($CFCl_3$, external reference). Upon coordination, the doublet is shifted downfield by 15.2 ppm and the P-F coupling

Figure 32.   Ir Spectrum (CO Region) of $W(CO)_4(PF_2C_6H_{10}PF_2)$ in Hexane

Figure 33.   Fluorine NMR Spectrum of $W(CO)_4(PF_2C_6H_{10}PF_2)$

constant is decreased from 1174 to 1143 Hz. Small downfield doublets attributable to the coordinated cis ligand are barely visible above the noise.

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum of the tungsten complex (Figure 34) consists of a large triplet centered at +236.7 ppm (85% H_3PO_4, external reference). The triplet is further split due to second order couplings. The down-field coordination shift (2.6 ppm) and decreased P-F coupling constant (1141 Hz) are consistent with previous observations described above. In the spectrum, two symmetrically positioned "satellite" lines arising from further spin coupling of the phosphorus nuclei with the ^{183}W nucleus (I = 1/2) are observed. A value of 375 Hz for the coupling constant J_{WP} is obtained.

A Study of the Photoreaction of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ and $PF_2C_6H_{10}PF_2$.

An equimolar mixture of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ and $PF_2C_6H_{10}PF_2$ has been irradiated in hexane for 13 hours in an attempt to displace car-bonyl groups resulting in the formation of $Mo(CO)_2(PF_2C_6H_{10}PF_2)$. 1.5 equivalents of CO are recovered from the reaction. A colorless oil is obtained upon solvent removal which has been separated by column chromatography into unreacted $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ and a relatively air-stable colorless oil.

Characterization of $[Mo(CO)_2(PF_2C_6H_{10}PF_2)_2]_x$.

The reaction product has been identified by mass, infrared, and nmr spectral data and by osmometric molecular weight. Elemental analysis of the product is inconclusive, the carbon and hydrogen analyses are a

Figure 34. Phosphorus NMR Spectrum of $W(CO)_4(PF_2C_6H_{10}PF_2)$

$J_{FP} = 1141$ Hz

$J_{WP} = 375$ Hz

$\delta = +236.7$ ppm

H_3PO_4

little high and may be due to traces of solvent. The osmometric molecular weight of the oil in benzene is 943 which corresponds to approximately a dimer and could result from a mixture or traces of unremoved solvent.

Mass Spectrum

The mass spectrum of the oil gives the following major peaks: (assignments and peak intensities are included in brackets) 592 [$Mo(CO)_2$-$(PF_2C_6H_{10}PF_2)_2^+$; 33], 564 [$Mo(CO)(PF_2C_6H_{10}PF_2)_2^+$; 24], and 536 [$Mo$-$(PF_2C_6H_{10}PF_2)_2^+$; 100]. No peaks due to ions heavier than the parent ion are observed, although a high solution molecular weight was obtained. Molybdenum isotope peaks together with ligand fragmentation peaks are present as expected.

Infrared Spectrum

The frequencies of the two bands observed in the carbonyl region of the solution infrared spectrum (Figure 35) are (in cm^{-1}): 2007 and 1974. Another feature of the spectrum is a strong P-F stretching band at 821 cm^{-1}. The carbonyl stretching frequencies are consistent with carbonyl C_{2v} symmetry and a complex of a strong π-acceptor ligand.[7]

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum of $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$ consists of a complex multiplet centered near $\delta 2.0$ and a broad resonance (singlet) at $\delta 3.0$ with benzene as the internal standard. These signals are probably due to differences of the ligand environment of the two coordinated ligands in the complex.

Figure 35. Ir Spectrum (CO Region) of Mo(CO)$_2$(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$ in Hexane

Fluorine NMR Spectrum

The ^{19}F nmr spectrum exhibits a weak intensity doublet barely discernible above the noise (due to a minute quantity of sample available for the nmr studies) centered near -61.9 ppm (CFCl$_3$, external standard). The coordination shift of the signal is +19.4 ppm and the P-F coupling constant spans 1145 ± 10 Hz. These are typical values for metal complexes of fluorophosphine ligands.[16]

Phosphorus NMR Spectrum

The dicarbonyl complex exhibits two triplets of nearly equal intensity in the ^{31}P nmr spectrum (Figure 36). The triplets are centered at +271.2 and +274.7 ppm. The coordination shifts of the signals are +37.1 and +40.6 ppm, respectively. The P-F coupling constants for the triplets each span approximately 1155 Hz. The triplets are attributed to two phosphorus environments in the molecule. (See discussion)

A Study of the Reduction Reaction of MoCl$_5$ by LiAlH$_4$ with PF$_2$C$_6$H$_{10}$PF$_2$.

A three-fold mole excess of PF$_2$C$_6$H$_{10}$PF$_2$ is stirred with MoCl$_5$ in THF under nitrogen. Small portions of LiAlH$_4$ are added to the solution over a period of 1.5 hours to affect reduction of Mo^{5+} to Mo^{o} which could then complex with the bidentate ligand. Upon extraction of the resultant dark-green complex with benzene, a small quantity of colorless oil is obtained. The product has not been identified, although the neat infrared spectrum consists of bands attributable to the fluorophosphine ligand. The osmometric molecular weight of the oil determined in benzene is approximately 2,000.

J_{PF} = 1155 Hz J_{PF} = 1155 Hz

δ = +274.7 ppm δ = +271.2 ppm H_3PO_4

Figure 36.   Phosphorus NMR Spectrum of $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$

A Study of the Reaction of $Mo(C_6H_5-CH_3)_2$ and $PF_2C_6H_{10}PF_2$.

A 1:3.4 mole ratio of $Mo(C_6H_5-CH_3)_2$ and $PF_2C_6H_{10}PF_2$ is mixed together at room temperature. Immediately a reaction occurs, the green mixture turning reddish-brown. Since the fluorophosphine ligand is stable in thermal reactions up to $180°$, the mixture is heated to $140°$ to insure reaction completion. The reaction product is extracted with hexane, filtered, and applied to a Florisil column. Two light yellow bands are eluted, which upon removal of solvent, result in light yellow crystals in low yield. The products comprising the remaining bands have not been characterized. No bright green unreacted $Mo(C_6H_5-CH_3)_2$ is recovered.

Characterization of $Mo(PF_2C_6H_{10}PF_2)_3$.

The yellow solid has been identified as $Mo(PF_2C_6H_{10}PF_2)_c$ by elemental analysis, osmometric molecular weight, and mass, infrared, and nmr spectral data. The elemental analysis of the complex is in reasonably good agreement with the expected formula. More conclusive is the osmometric molecular weight which is determined in benzene to be 772, which corresponds to a monomer.

Mass Spectrum

The mass spectrum of the complex consists of an intense parent ion signal clustered between 752 and 760 m/e in a pattern characteristic of the molybdenum isotope distribution. A weak set of signals corresponding to the ion, $Mo(PF_2C_6H_{10}PF_2)_2^+$ is discernible between 532 and 540 m/e. Ligand fragmentation peaks are present as expected and no peaks due to ions of higher mass than the parent ion are observed.

Infrared Spectrum

The solid phase infrared spectrum (Nujol and Halocarbon 25-5S Grease mulls) of the product (Figure 37) gives the following bands with some tentative assignments as shown (in cm^{-1}): 2941m (νCH); 2868w (νCH); 14400m (νCH_2); 1386w; 1066m; 983m; 789vs,br (νPF). No bands in the aromatic C-H stretching region attributable to unreacted $Mo(C_6H_5-CH_3)_2$ are observed.

NMR Spectra

Proton NMR Spectra

The 60 MHz proton nmr spectrum of $Mo(PF_2C_6H_{10}PF_2)_3$ consists of a complex multiplet centered near $\delta 2.0$ with benzene as the internal reference (free ligand, $\delta 1.97$, complex multiplet).

Fluorine NMR Spectrum

The ^{19}F nmr spectrum of the complex (Figure 38) exhibits three broad doublets; a large doublet centered at -58 ppm and two smaller doublets of equal intensity at -54 and -50 ppm. The smaller doublets are approximately one-half as intense as the large doublet. The fluorine coordination shifts of the doublets are +23, +27 and +31 ppm. The P-F coupling constants of the doublets span approximately 1150 Hz. The broadness of the signals (width at half-height spans 150-200 Hz) arises from longer range P-F couplings through the metal.[17]

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum (Figure 39) consists of a broad triplet centered at +281.5 ppm. The width of the resonances at half peak height spans approximately 155 Hz. This signal broadening (as explained above)

Figure 37. Ir Spectrum of Mo(PF$_2$C$_6$H$_{10}$PF$_2$)$_3$ (mulls)

Figure 38. Fluorine NMR Spectrum of $Mo(PF_2C_6H_{10}PF_2)_3$

$$CFCl_3 \quad \underset{\delta \ = \ -50.4 \ ppm}{\underline{\qquad J_{PF} \ = \ 1165 \ Hz \qquad}} \quad \underset{\delta \ = \ -53.5 \ ppm}{\underline{\qquad J_{PF} \ = \ 1150 \ Hz \qquad}} \quad \underset{\delta \ = \ -57.9 \ ppm}{J_{PF} \ = \ 1130 \ Hz}$$

Figure 39. Phosphorus NMR Spectrum of Mo$(PF_2C_6H_{10}PF_2)_3$

J$_{PF}$ = 1121 Hz

δ = +281.5 ppm

H$_3$PO$_4$

is due to longer range P-F couplings through the metal.[17] The phosphorus coordination shift (+47.4 ppm) is larger than the coordination shifts of $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$ (+40.6 and +37.1 ppm) and $Mo(CO)_4-$ $(PF_2C_6H_{10}PF_2)$ (+29.0 ppm). The P-F coupling constant spans 1121 Hz.

E. Discussion

That pure substitution products obtained from the addition of ligands to solutions of $M(CO)_5(THF)$ (which is obtained upon the photo-reaction of $M(CO)_6$ in a tetrahydrofuran solution) had been reported in the literature[6] led to the assumption that the bidentate ligand, $PF_2C_6H_{10}PF_2$, would freely displace the weakly coordinated THF (Reaction 9). With continuing irradiation, a CO ligand should be displaced affording ring closure of the phosphine chelate to result in the formation of a chelated substitution product. (Reaction 10)

$$M(CO)_5(THF + PF_2C_6H_{10}PF_2 \longrightarrow M(CO)_5PF_2C_6H_{10}PF_2 \qquad (9)$$
$$M(CO)_5PF_2C_6H_{10}PF_2 \xrightarrow{hv} CO + M(CO)_4(PF_2C_6H_{10}PF_2) \qquad (10)$$

The synthesis of pure products from the reactions in tetrahydrofuran of $PF_2C_6H_{10}PF_2$ and the Group 6B metal complexes were unsuccessful. The nature and structure of the crystalline products obtained from these reactions is unexplained and remains to be explored. Possible bridged, solvated, or THF-coordinated species have not been ruled out. The elemental analyses of the products obtained are on the order expected for tetracarbonyl substituted products. The infrared spectra appear to be consistent with phosphine-containing carbonyl complexes. The amounts of CO that were displaced during the reaction of THF suggest that only one carbonyl ligand was displaced giving a pentacarbonyl species. If this were indeed the case, the expected symmetry of the products would

be C_{4v} which would give three infrared active CO stretching modes, labeled $2A_1$ and E.[7] The infrared spectra of the complexes in the CO region are varied and exhibit various numbers of bands. Thus, no conclusion can be drawn with respect to the precise nature of the species. (At this point in the research, purification and characterization techniques had not been sufficiently developed to merit complete identification of the resultant complexes.)

The inability to obtain pure phosphine-substituted tetracarbonyl complexes in tetrahydrofuran required a change in reaction conditions. Reports of the preparation of pure products from photoreactions in non-coordinating solvents, such as the saturated hydrocarbons, are widespread.[6] Thus, the photoreactions of $PF_2C_6H_{10}PF_2$ and the Group 6B metal carbonyls have been reinvestigated in the solvent, pentane.

The preparation of tetracarbonyl complexes of $PF_2C_6H_{10}PF_2$ entailed the direct photolysis in pentane solutions of the metal hexacarbonyls and the bidentate ligand. In these reactions, the amounts of CO that evolved suggested the displacement of approximately two CO ligands. Although non-crystalline products (oils) were obtained, the products were formulated as tetracarbonyl species.

Complexes of the type, cis-$L_2M(CO)_4$ exhibit C_{2v} carbonyl symmetry which predicts the presence of four carbonyl stretching frequencies, $2A_1 + B_1 + B_2$, which are infrared and Raman active. The CO stretching frequencies in the infrared spectra of the complexes synthesized by photolysis are not highly resolved, appear to result from mixtures, and are not comparable with band positions and intensities reported for similar tetracarbonyl complexes.[7] The frequencies have not been labeled according to symmetry modes for this reason. Possible bridging CO

ligands were excluded due to the absence of CO bridging frequencies in the region of 1800-1700 cm^{-1} of the infrared spectrum. The CO stretching bands cannot be sufficiently resolved to distinguish whether the high molecular weight tetracarbonyl polymers exhibit <u>cis</u> or <u>trans</u> (or a mixture) carbonyl symmetry. The <u>trans</u> form of the complexes would allow for ligand bridging under more sterically favored conditions than would the <u>cis</u> form. It has been suggested that the large broad CO band in the infrared spectra may be due in part to traces of unreacted carbonyl starting material.[19] A single CO stretching band is expected in the region of 2000-1950 cm^{-1} for complexes of the type <u>trans</u>-$L_2Mo(CO)_4$.

The oils that were formed in the photoreactions in pentane appear to be mixtures of products as evidenced by the results of the chromatographic separation of the molybdenum product detailed in the Results Section above. These oils gave elemental analyses in reasonably good agreement with those calculated for complexes of the type, $M(CO)_4$-$(PF_2C_6H_{10}PF_2)$. The most unexpected results obtained during the characterization of the photolytically-generated products were the molecular weight data. These results suggest the presence of mixtures of oligimers (dimers or trimers). Mass spectra of the products gave molecular ions attributable only to monomers. The absence of higher peaks than the monomer molecular ion in the mass spectra is interpreted to be due to fragmentation of the polymeric species such that only the apparent spectrum of the monomer is produced.

The observation of high molecular weight fractions in the products is somewhat surprising since the geometry of the ligand was expected to favor chelating as opposed to bridging behavior. Molecular models of the monomer (Figure 40) have been constructed to show that mononuclear metal

Figure 40. Structures of Metal Tetracarbonyl
Complexes of $PF_2C_6H_{10}PF_2$

chelation in the complexes should be the favored structure of the complex.
The ligand appears to be highly sterically crowded in models of bridged
tetracarbonyl structures, (Figure 40) relative to the monomeric structure
as a result of the bulkiness of the cyclohexane ring of the ligand.
Using all possible ligand configurations, these models have shown
extensive steric crowding in all bridged species, although the trans,
diaxial isomer appears to be best suited for bridging two metal centers.

The unexpected high molecular weight data obtained for the photo-
lytically generated products discussed above to give mixtures of polymeric
species, implies that the product selection may be kinetically controlled
under the photoreaction conditions. The first photolytic dissociation
(Reaction 11) may be sufficiently more facile than Reaction 12 to make
the initial bridge formation much more favorable than monomer formation.

$$M(CO)_6 \longrightarrow M(CO)_5 + CO \qquad\qquad (11)$$

$$(CO)_5MPF_2C_6H_{10}PF_2 \longrightarrow (CO)_4M(PF_2C_6H_{10}PF_2) \qquad (12)$$

That is, the most probable reaction of $(CO)_5MPF_2C_6H_{10}PF_2$ may be the
reaction with a second $M(CO)_5$ molecule. This suggested that thermolysis,
rather than photolysis, should favor chelation over bridged species if,
in fact, the chelate is the thermodynamically favored form, particularly
in light of the results of the thermolysis reactions of the Group 6B
metal hexacarbonyls and $Ph_2PC_2H_4PPh_2$ reported by Chatt and Watson.[10]
Monomeric tetracarbonyl phosphine-substituted complexes were prepared by
the latter by heating the reactants at temperatures above 200° in sealed
tubes.

Reactions of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$ were studied using photolytic
and thermolytic methods. The thermolytic method of Chatt and Watson[10]
was employed which resulted in the formation of the expected monomeric

tetracarbonyl complex. Comparison of the osmometric molecular weight and infrared spectral data with the data reported for $Mo(CO)_4$-$(Ph_2PC_2H_4PPh_2)$[10] confirmed the formulation. The photoreaction of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$ has not been reported previously. The irradiation of a 1:1 mole ratio of these reactants for several hours at 300 nm led to the displacement of CO and the formation of a yellow-white solid. Characterization data for the product are consistent with the formulation, $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$. Photoreactions of the Group 6B metal hexacarbonyls with bidentate organophosphine ligands has also resulted in the formation of monomeric tetracarbonyl complexes.[20]

The preparation of high molecular weight tetracarbonyl polymers resulting from the photolysis of the metal hexacarbonyls and $PF_2C_6H_{10}PF_2$ suggested two experimental approaches to prepare thermodynamically favored, monomeric, chelate complexes, neither of which produced unequivocal results. Carrying out the photoreactions at high dilution should favor monomer production, if in fact the polymers result from the reaction of the monoligate complex formed upon dissociation of one CO ligand, $(CO)_5MPF_2C_6H_{10}PF_2$, with a second molecule of photolytically-generated, $M(CO)_5$.[21] No detectable difference in photoproduct formation was observed over a four-fold concentration range. More dilute solutions than 0.01 molar proved impractical with respect to retrieval of sufficient material for analysis.

The second approach, namely thermolysis reactions of the ligand with the metal hexacarbonyls, led again to high molecular weight species, although in the case of chromium, a crystalline material (tetrameric metal polymer) was obtained, in contrast to the previously encountered oils. Comparison of the molecular weight and nmr spectral data of the

molybdenum photolysis and thermolysis products suggests that monomer formation may be more accessible using thermolysis reactions. For example, the osmometric molecular weights of the oils obtained from several photoreactions of 1:1 ratios of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ are 1516, 1083, and 968, whereas, the molecular weights of the oils obtained from two analogous thermolysis reactions are 537 and 809.

That the observed high molecular weights of the complexes determined osmometrically may be due to association of low molecular weight species in solution was ruled out upon comparison of the osmometric molecular weight of the photoproduct (oil) of the reaction of $Mo(CO)_6$ and $PF_2C_6H_{10}PF_2$ at various concentrations. Constancy of the molecular weight (Table 3) (within experimental error limits) determined in benzene over a two-fold concentration range, suggests that the high molecular weights arise from formed polymers rather than the association of species in solution to produce high polymers.

Since attempts to prepare pure monomeric complexes by direct reaction with the hexacarbonyls were unsuccessful, this investigation turned to the use of indirect methods. Several monomeric metal carbonyl complexes of labile monodentate phosphine ligands have been reported,[18] which might serve as intermediates in the synthesis of monomeric $PF_2C_6H_{10}PF_2$ metal complexes by ligand substitution reactions. (Reaction 13)

$$\underline{cis}\text{-}M(CO)_4(PR_3)_2 + PF_2C_6H_{10}PF_2 \longrightarrow cis\text{-}M(CO)_4(PF_2C_6H_{10}PF_2) + 2PR_3 \quad (13)$$

Details of the synthesis of the starting material where R = Cl or Ph are very sketchy[18] and attempts to prepare these complexes proved very difficult, giving rather insoluble complexes which do not serve well for Reaction 13.

TABLE 3

Osmometric Molecular Weight Values in Benzene of Photolytically-
Prepared $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ at Various Concentrations

Molarity (moles/liter)	Molecular Weight
2.4×10^{-3}	1333
3.4×10^{-3}	1294
5.8×10^{-3}	1362

The most successful method for preparing chelate complexes of the Group 6B metal carbonyls utilizes the facile displacement of norbornadiene from cis norbornadiene metal carbonyls complexes. The displacement of norbornadiene by $PF_2C_6H_{10}PF_2$ is carried out under mild conditions to yield the monomeric, chelated complexes, $M(CO)_4(PF_2C_6H_{10}PF_2)$. These complexes, easily purified by high-vacuum sublimation or by column chromatography, are white, relatively air-stable crystalline solids that are obtained in high yield. The procedure of merely pumping on product mixtures to sublime away volatile, unreacted metal carbonyl starting material is not sufficient to purify these products. Column chromatography appears to be most suitable for separating reaction products and removing traces of unreacted starting material.

An important feature of the data obtained on the complexes prepared by ligand displacement is the molecular weights. These molecular weights, in contrast to those obtained for the products of photolysis and thermolysis, are in good agreement with monomeric formulations. Further evidence confirming the existence of monomeric tetracarbonyl complexes is found in the mass spectra, in that parent ions corresponding to $M(CO)_4$-$(PF_2C_6H_{10}PF_2)^+$ are observed. The mass spectra of the polymers obtained from the photoreactions also exhibit parent ions corresponding to $M(CO)_4$-$(PF_2C_6H_{10}PF_2)^+$. The absence of higher m/e peaks than the parent ions in the mass spectra is probably due to cleavage of the polymeric species in such a way as to produce only the apparent spectra of the monomers, and thus, the mass spectra of these complexes must be interpreted with caution. Osmometric molecular weight data appears to be more indicative of the true nature of the complexes prepared with respect to actual molar mass. It is interesting to note that the photoreaction of the

monomer, $Mo(CO)_4(PF_2C_6H_{10}PF_2)$, and $PF_2C_6H_{10}PF_2$ yields a dicarbonyl complex as expected, but a high solution molecular weight is obtained for the complex which suggests that some dimeric complex is present.

As described previously, complexes of the type cis-$L_2M(CO)_4$ or cis-$LM(CO)_4$ exhibit C_{2v} carbonyl symmetry which predicts the presence of four CO stretching bands, labeled $2A_1 + B_1 + B_2$, which are infrared and Raman active. Table 4 shows the CO stretching frequencies obtained from the solution infrared spectra of the tetracarbonyl complexes obtained by olefin displacement, together with the frequencies of similar complexes for comparative purposes. Examination of the CO stretching frequencies of the complexes supports the assumption that $PF_2C_6H_{10}PF_2$ is a good π-acceptor ligand. The frequencies for the complexes of $PF_2C_6H_{10}PF_2$ compare favorably with those reported for the complexes of the stronger π-acceptors as assessed by others.[22] This assessment has been based largely on the assumption that CO stretching frequencies higher than those in the unsubstituted carbonyls imply a greater contribution of the triply bonded resonance form, $M-C\equiv O$, as a direct result of the lower availability of electrons from the metal to the π-antibonding CO orbital, further implying that the substituted ligand competes favorably with CO in accepting electron density from the metal.

A quantitative estimate of this effect can be made by the method of Cotton and Kraihanzel who derived "nonrigorous" secular equations through which sets of force constants for a series of metal carbonyl derivatives may be obtained.[23] (See Appendix)

Although absolute values for these force constants have no significance and thus cannot be compared to force constants for molecules of different structural types, they are claimed to give internally

TABLE 4

CO Frequencies and Force Constants for <u>cis</u>-$L_2M(CO)_4$

and <u>cis</u>-$LM(CO)_4$ Complexes

Compound	Frequencies, cm^{-1}				Force Constants, mdyne/Å[23]		
	A_1^2	A_1^1	B_1	B_2	k_1	k_2	k_i
$Cr(CO)_4(P_2F_4C_6H_{10})$	2056	1994	1982	1960	16.14	16.07	0.28
$Cr(CO)_4diphos$[a]	2009	1914	1899	1877	14.49	15.32	0.36
$Mo(CO)_4(P_2F_4C_6H_{10})$	2070	2003	1990	1971	16.27	16.28	0.28
$Mo(CO)_4(PF_3)_2$[b]	2087	2014	2011	1990	16.59	16.53	0.27
$Mo(CO)_4(PCl_3)_2$[b]	2072	2004	1994	1986	16.30	16.44	0.27
$Mo(CO)_4(CCl_3PF_2)_2$[c]	2079	2015	2010	1990	16.56	16.51	0.26
$Mo(CO)_4(R_2NPF_2)_2$[c]	2055	1974	1950	1942	15.97	15.87	0.32
$Mo(CO)_4[RN(PF_2)_2]$[d]	2066	1991	1973	1963	16.03	16.18	0.31
$Mo(CO)_4diphos$[a]	2020	1919	1907	1881	14.64	15.41	0.36
$W(CO)_4(P_2F_4C_6H_{10})$	2064	1995	1983	1968	16.16	16.20	0.28
$W(CO)_4diphos$[a]	2016	1912	1901	1876	14.58	15.32	0.32

(a. Ref. 10; b. Ref. 7; C. Ref. 9; d. Ref. 17)

consistent results for a particular series of derivatives.

Representative values of the Cotton-Kraihanzel force constants (calculated from the CO frequencies as described in the Appendix) for the series of tetracarbonyl complexes are included in Table 4. From the arguments of Cotton and Kraihanzel, it follows that as the π-acceptor character of the competing, substituted ligand is increased, the magnitude of the CO stretching frequencies and the force consists k_1 and k_2 should increase and k_i, the CO-CO interaction force constant, decrease. The complexes of $PF_2C_6H_{10}PF_2$ exhibit comparable CO force constants to those of the complexes of PF_3, PCl_3, CCl_3PF_2 and $RN(PF_2)_2$. These considerations allow the ligand, $PF_2C_6H_{10}PF_2$ to be placed in the following order of decreasing π-acceptor ability: $CF_3PF_2 > (CF_3)_2PF > PF_3 > CCl_3PF_2 > PCl_3 \sim PF_2C_6H_{10}PF_2 > RN(PF_2)_2 > R_2NPF_2 \gg PPh_3 > Ph_2PC_2H_4PPh_2$. The CO frequencies and force constants for the complexes of $PF_2C_6H_{10}PF_2$ are notably much higher than the corresponding bidentate organophosphine complexes owing to the superior π-acceptor strength of $PF_2C_6H_{10}PF_2$.

$\underline{cis}$-$L_4M(CO)_2$ or $\underline{cis}$-$L_2M(CO)_2$ complexes also have C_{2v} carbonyl symmetry, the two carbonyl stretching vibrations being distributed amongst the symmetry classes of the point group as $A_1 + B_1$, which are infrared and Raman active. The complex prepared by heating $Mo(CO)_6$ with excess $PF_2C_6H_{10}PF_2$ exhibits two poorly-resolved carbonyl bands (Figure 22) in the infrared spectrum that cannot be assigned to the modes with confidence. The complex prepared by photolysis of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ and $PF_2C_6H_{10}PF_2$, $[Mo(CO)_2-(PF_2C_6H_{10}PF_2)_2]_2$, exhibits two carbonyl bands in the infrared spectrum which have been assigned to the modes (See Table 5). Included in Table 5 are the CO stretching frequencies of similar dicarbonyl complexes for comparison, together with the corresponding Cotton-Kraihanzel force

TABLE 5

Force Constants and CO Frequencies for cis-$L_4Mo(CO)_2$

and $\underline{cis}$-$L_2M(CO)_2$ Complexes

Compound	Frequencies, cm^{-1}		Force Constants, mdyne/A[23]	
	A_1	B_1	k	k_i
$Mo(CO)_2(P_2F_4C_6H_{10})_2$	2007	1974	16.00	0.27
$Mo(CO)_2(PF_3)_4$[a]	2048	2010	16.59	0.29
$Mo(CO)_2(diphos)_2$[b]	1852	1786	13.36	0.48

(a. Ref. 7; b. Ref. 10)

constants calculated from secular equations found in the Appendix. As
was previously observed for the tetracarbonyl complexes, the π-acceptor
ability of $PF_2C_6H_{10}PF_2$ in the dicarbonyl complex is shown to be slightly
less than the π-acceptor ability of PF_3, but substantially superior than
the ligand, $Ph_2PC_2H_4PPh_2$.

NMR spectral parameters are also useful in characterizing the com-
plexes of $PF_2C_6H_{10}PF_2$ and in assessing the binding ability of the ligand
toward metals in their low oxidation states, since the three nuclei,
^1H, ^{19}F, and ^{31}P, can be routinely observed. The proton nmr spectra of
the complexes consistently give complex multiplets centered near $\delta 2.0$.
Identical spectra are observed for both the monomeric and polymeric com-
plexes, and thus the ^1H nmr spectra are only useful in a qualitiative
sense of indicating the presence of the ligand. It is also difficult
to distinguish between coordinated and free, unbound ligand since the
free ligand exhibits a complex multiplet at $\delta 1.97$.

The ^{19}F nmr spectra of the polymeric tetracarbonyl complexes are
characteristic of mixtures. Broad resonances are observed for these
species which is not expected to result from extensive longer-range P-F
couplings through the metal centers, except in the cases of the more
highly substituted derivatives, but instead, probably result from mix-
tures of the various oligomers. On the other hand, the ^{19}F nmr spectra
of the monomeric tetracarbonyl complexes exhibit very sharp resonances
which cannot be due to a mixture. The ^{19}F nmr spectra of all of the com-
plexes exhibit downfield coordination shifts and simultaneous decreases
in the P-F coupling constants from that of the free, unbound ligand,
consistent with trends reported for similar fluorophosphine-metal com-
plexes.[16,17] The doublets observed in the spectra are a result of the

spin coupling of the fluorine nuclei with the phosphorus nucleus.
Table 6 presents the data obtained from the spectra, including the
fluorine coordination shifts, $\Delta\emptyset_F$ ($\emptyset_F$ complex - $\emptyset_F$ ligand).

Many of the ^{19}F nmr spectra consist of a large doublet and two
small downfield doublets which are attributed to the presence of coordin-
ated trans and cis difluorophosphino groups in the ligand.[5] The smaller
doublets are always found in a 1:1 area ratio, whereas the area ratio
of the large doublet vs. the smaller doublets varies from complex to
complex. The large doublet is assigned to the dominant[5], coordinated
trans ligand isomer, structure 1. (Figure 41) Inspection of models
indicates that in structure 1, the four fluorine nuclei interact equiva-
lently with the ring protons, especially given rapid ring inversion on
the nmr time scale, giving a single chemical shift for all four nuclei.
The two small doublets are assigned to the coordinated cis ligand isomer,
structure 2. In this case, rapid ring inversion always leads to two
sets of fluorine nuclei (labeled a and b) which interact differently
with the ring protons. It is noteworthy that no evidence for a cis-
trans isomer mixture was observed in the nmr spectra of the uncoordin-
ated ligand.[4] It appears that some ring isomerization may occur during
these reactions and may be a major factor during the reaction of
$Mo(C_6H_5-CH_3)_2$ with $PF_2C_6H_{10}PF_2$. (The ratio of the large doublet to the
smaller doublets approaches 2:1.)

If in fact an isomeric mixture of the ligand exists, it will be
worthwhile to attempt to separate the isomers chromatographically. The
coordination of the pure trans form of the free ligand could then be

TABLE 6

^{31}P and ^{19}F NMR Data for $M(CO)_4L$ and $M(CO)_2L_2$ Complexes[a]

$$L = P_2F_4C_6H_{10}$$

Compound	δ_P Complex[b] (ppm)	$\Delta\delta_P$[c] (ppm)	$J_{FP}(Hz)$[d]	ϕ_F Complex[e] (ppm)	$\Delta\phi_F$[f] (ppm)
$Cr(CO)_4L^g$	+288.8	+54.7	1180	−63.6	+17.7
$Mo(CO)_4L^h$	+264.9	+30.8	1170	−64.7	+16.6
$W(CO)_4L^g$	+238.8 +230.8	+ 4.7 − 3.3	1160	−66.1	+15.2
$Cr(CO)_4L^i$	+287.1	+53.0	1158	−64.7	+16.6
$Mo(CO)_4L^i$	+263.1	+29.0	1156	−65.4	+15.9
$W(CO)_4L^i$	+236.7	+ 2.6	1141	−66.1	+15.2
$Mo(CO)_2L_2^g$	+274.7 +271.2	+40.6 +37.1	1155	−61.9	+19.4

a. Sign convention for chemical shifts: + = downfield

b. Because of second order splitting patterns in the spectra, the chemical shifts and J_{FP} values were measured from the centroids of the signals; c. δ_P ligand = +234.1 ppm; d. J_{FP} ligand = 1218 Hz; e. shifts reported for the dominant doublet; f. ϕ_F ligand = −81.3; g. photolysis product; h. thermolysis product; i. olefin displacement product.
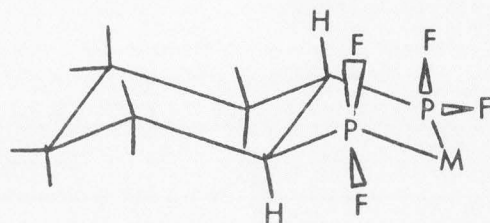
1
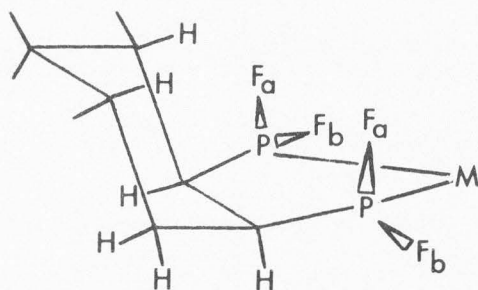
2

Figure 41.   Structures of the Coordinated Ligand
             Isomers in Metal Complexes of $PF_2C_6H_{10}PF_2$

studied with these metal carbonyls. The appearance of the weak doublets in the ^{19}F nmr spectra might then be explained in terms of ring isomerization.

The ^{19}F nmr spectrum of $Cr(CO)_4(PF_2C_6H_{10}PF_2)$ (Figure 27) is quite different from the analogous spectra of the molybdenum and tungsten tetracarbonyl complexes (Figures 30 and 33), two large doublets are observed in the former and a single large doublet in the latter. The two large doublets are further split into doublets. The spectrum appears to be a mirror image of the large doublets about the center point, indicating second order splitting. But such a splitting pattern may be consistent with non-equivalent fluorine environments. (See page 138) The doublet of doublets of doublets (the coupling constants span 115, 169, and 42 Hz, respectively) could arise from $^1J_{PF}$, $^3J_{FH}$, and $^3J_{PF}$ or some combination thereof. Common values reported in the literature for $^3J_{FH}$ are 10-20 Hz and for $^3J_{PF}$, 1-5 Hz.[24,25] Complete analysis and assignment of couplings in the spectrum require computer-assisted techiques.

The general feature of the ^{31}P nmr spectra of the complexes is a triplet with a large P-F coupling constant resulting from the two PF_2 groups. The chemical shift and coupling constant data are summarized in Table 6. The coordination shifts (δ_P complex - δ_P ligand) are all downfield and are in good agreement with chemical shift data reported for complexes of the strong π-acceptor fluorophosphine ligands.[16,17] The coordination shifts decrease in the order Cr Mo W, in agreement with the common observation that the coordination shift is largest for the first-row metal in any particular group.[26]

Two phosphorus triplets of nearly equal intensity are observed for the complex, $Mo(CO)_2PF_2C_6H_{10}PF_2)_2$, (Figure 36) consistent with

nonequivalent phosphorus environments. It has been suggested that the chemical shifts of phosphorus atoms trans to a CO group occurs at higher fields than the chemical shifts of phosphorus atoms trans to another phosphorus atom.[27] This is the only case where a single triplet in a pure compound is not observed.

The coordination shifts of the higher-substituted molybdenum complexes prepared in this study are downfield from the coordination shift obtained for the tetracarbonyl analog, as would be expected for downfield shifts attributable to the adjacency of phosphorus atoms vs. carbonyl groups. There appears to be a linear trend in the coordination shifts of the various substitution products of the same metal (Figure 42) which can be useful as a qualitative analytical technique for distinguishing various substitution products (particularly in a mixture).

Coordination shift data have also been used to distinguish between chelate complexes and bridged complexes, the latter occurring at slightly higher field.[28] Lower field coordination shifts are attributed to ring strain in five-membered chelate rings, whereas ligand-bridged complexes are not expected to introduce this ring strain. Inspection of the ^{31}P nmr spectra of reaction mixtures has been used to determine the relative amounts of chelate product vs. other products (such as bridged poly-metallic species),[29] and is a useful method for identifying possible bridged products in the high molecular weight mixtures described above. Differences in coordination shifts of bridged vs. chelate complexes have been reported to be as great as 10 ppm.[28] For the tungsten complex prepared photolytically, two triplets are observed, whose coordination shifts are -4.7 and +3.3 ppm, a difference of 8 ppm. The higher field triplet is about two-thirds as intense as the lower field triplet. A
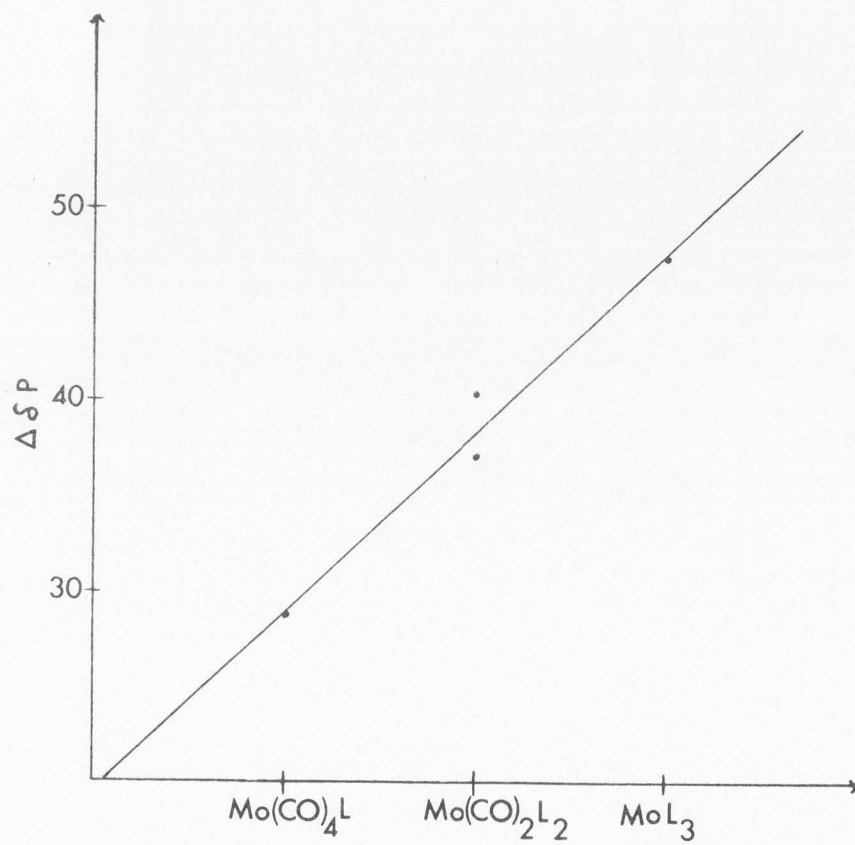
Figure 42.   Correlation Between $\Delta\delta_P$ and the Degree of
Substitution of $Mo-PF_2C_6H_{10}PF_2$ Complexes

similar observation is made for the photolysis product of chromium hexacarbonyl in that a weak intensity triplet is observed 5.9 ppm upfield from the dominant triplet. The lower field triplets arise from chelate species in the product mixtures and the higher field triplets arise from bridged species. The molybdenum tetracarbonyl complex prepared thermally exhibits only a single sharp triplet suggesting the presence of a pure product rather than a mixture. This observation again suggests that thermalysis is a more suitable method than photolysis for preparing thermodynamically favored monomeric chelated complexes of the Group 6B metals. The ^{31}P nmr spectra of the monomeric complexes prepared by ligand displacement all exhibit only a single triplet indicating purity of sample.

Metal-phosphorus coupling constants have been used to assess the binding ability of phosphorus ligands to metals in an analogous fashion that CO stretching frequencies have been used to determine π-acceptor ability.[30] For example, complexes of the strong π-acceptor ligands exhibit unusually large M-P coupling constants reflecting enhanced metal to phosphorus bond strength. A value of 375 Hz for the coupling constant, $^{1}J_{WP}$, obtained from the ^{31}P nmr spectrum of $W(CO)_4(PF_2C_6H_{10}PF_2)$, is much larger in magnitude than those reported for other bidentate phosphine carbonyl complexes,[29,31] attributable to the highly electronegative fluorine atoms located on the phosphorus nuclei of the ligand (which cause the ligand to be a strong π-acid). The coupling constant, $^{1}J_{MoP}$, obtained from the ^{31}P nmr spectrum of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ spans approximately 215 Hz. This value is substantially smaller than the reported for $Mo(CO)_5PF_3$ to be 284 Hz.[32] The smaller coupling constant is consistent with the observations that ring strain in chelates is frequently

associated with smaller coupling constants than are observed in complexes with similar, monodentate ligands[29] and that lower electronegativity of the substituents on phosphorus leads to smaller coupling constants.[32] These rather large metal-phosphorus coupling constants are consistent with enhanced metal-phosphorus bonding expected for the strong π-acceptor ligand, $PF_2C_6H_{10}PF_2$.

Many of the spectra described and shown above exhibit second order splitting patterns, particularly due to $^{31}P-^{31}P$ interactions, which require the chemical shift and coupling constant values reported in Table 6 to be measured from the centroids of the signals. Complete elucidation of these second order splittings, including the coupling constants, $^2J_{PP}$ (which have also been used to assess π-acceptor ability[16]) will require computer-assisted analysis.

F. Conclusion

Several noteworthy observations were made during the study of the photoreactions of $PF_2C_6H_{10}PF_2$ and the Group 6B metal hexacarbonyls with respect to the coordination of the ligand. 1,2-Bis(difluoro-phosphino)cyclohexane has been shown to displace CO from the metal carbonyls resulting in unique substitution products. The ligand is assumed to be a rather strong π-acceptor ligand, because as expected, it shows a marked tendency to compete with carbon monoxide for metal elec-tron density as verified by the shift to higher frequency of the CO bands in the infrared spectra. Most surprising is the ability of the ligand to act as a bridging ligand in direct contrast to the strong chelating ability exemplified by other bidentate phosphine ligands. The bidentate ligands, $Ph_2PC_2H_4PPh_2$ and $CH_3N(PF_2)_2$, show no tendency to bridge

metal centers in their photoreactions with the metal hexacarbonyls.[20,13]
Since no pure chelate complexes were obtained, the stability of these
complexes as a result of the chelate effect could not be ascertained.

An interesting contrast is shown in the reactions of $PF_2C_6H_{10}PF_2$
with the Group 6B metal hexacarbonyls with respect to the reaction con-
ditions used. A pure crystalline tungsten tetracarbonyl compound is
obtained by thermolysis while a mixture of species is obtained by photo-
lysis. Lower molecular weight products are obtained by heating $Mo(CO)_6$
with $PF_2C_6H_{10}PF_2$ particularly at elevated temperatures. Monomeric tetra-
carbonyl complexes might be formed at temperatures above 180°. Sur-
prisingly, the ligand appears to be stable at this temperature and may be
stable at even higher temperatures.

The method most suited for preparing Group 6B metal complexes of
bidentate difluorophosphines is displacement of labile organic ligands
from a proper organometallic precursor. This method is shown to give
pure monomeric tetracarbonyl complexes and monomeric $Mo(PF_2C_6H_{10}PF_2)_3$.
A particularly good feature of the displacement reactions is the non-
forcing conditions required for reaction. This may be a critical point
in future studies of the less thermally-stable bidentate difluorophos-
phines, where low reaction temperatures are required. The ligand,
$PF_2C_6H_{10}PF_2$, also appears to be stable in the presence of a strong re-
ducing agent. Although the desired product was not isolated from the re-
duction of $MoCl_5$ by $LiAlH_4$ in the presence of $PF_2C_6H_{10}PF_2$, there is no
evidence of ligand instability under these conditions. The ir spectrum
of the reaction mixture suggests the ligand may be intact.

The most noteworthy aspects of these results so far is the demon-
stration that $PF_2C_6H_{10}PF_2$ does in fact have the characteristics

anticipated: it binds to low valent metals very strongly to produce relatively stable complexes, reflecting the chelate effect, and with π-acidity which is comparable to the strongest members of the fluoro-phosphine class. One fairly remarkable result is the observation of bridging by the ligand in the carbonyl complexes of the Group 6B metals and its failure to displace all the CO in these cases with ease. The structure of the ligand backbone suggests that bridging should involve significant steric crowding and thus should be disfavored. This is borne out in the ready isolation of a chelate of Ni(0) from the carbonyl.[5] However, with Cr(0), Mo(0), and W(0), polymeric species are obtained from direct reaction with the carbonyls. The ligand does bind well in a chelating mode in these complexes as demonstrated by displacement of olefins. These results contrast markedly with the results obtained recently by King, et. al.,[13] with the similar bidentate difluorophosphine, $CH_3N(PF_2)_2$, in which monomeric complexes having all the CO ligands displaced were formed readily from the carbonyls.

II. Coordination of $PF_2C_6H_{10}PF_2$ with Mn(I), Fe(0), and Co(0).

A. Introduction

Evidence that $PF_2C_6H_{10}PF_2$ functions as an unusually strong π-acceptor in its complexes with the Group 6B metals and with Ni(0) is presented in the preceeding discussion. The ligand functions as a bidentate and/or as a bridging bifunctional ligand in these compounds. Analysis of the Cotton-Kraihanzel CO force constants[23] and NMR parameters results in assignment of π-acidity comparable to that of PCl_3. In order further to characterize the coordinating behavior of $PF_2C_6H_{10}PF_2$, a study of its

reactions with metals having still different stereochemical demands, specifically with Mn(I), Fe(O), and Co(O) was to be undertaken.

Since the common method for preparing phosphine complexes of these metals involves the displacement of CO from metal carbonyls, $PF_2C_6H_{10}PF_2$ was allowed to react with $Mn(CO)_5Br$, $Fe(CO)_5$, and $Co_2(CO)_8$. Carbonyl displacement is usually afforded by photolysis, and thus as a means of comparing the different metal carbonyl photoreactions of $PF_2C_6H_{10}PF_2$, $Mn(CO)_5Br$ and $Fe(CO)_5$ were irradiated in the presence of the ligand. $Co_2(CO)_8$ readily loses CO in the presence of coordinating agents,[2] so mixtures of the carbonyl and $PF_2C_6H_{10}PF_2$ were initially studied at room temperature or below.

Whereas the photoreactions of bidentate phosphine ligands with $Mn(CO)_5Br$ and $Fe(CO)_5$ are straightforward, the reactions with $Co_2(CO)_8$ have produced varied results. $Ph_2PC_2H_4PPh_2$ reacts with $Co_2(CO)_8$ to give an ionic species containing no metal-metal bonds, $[Co_2(CO)_6-(Ph_2PC_2H_4PPh_2)_3]$ $[Co(CO)_4]_2$,[33] or a ligand-bridged complex, $Co_2(CO)_6-(Ph_2PC_2H_4PPh_2)$.[34] Dicobalt hexacarbonyl phosphine-substituted complexes are formed by the reaction of $Co_2(CO)_8$ and bidentate fluoroalicyclic phosphine ligands.[35] $Co_2(CO)_4(Ph_2PC_2H_4PPh_2)_2$ has been obtained by the displacement of the olefin from $(C_7H_8)_2Co_2(CO)_4$ by $Ph_2PC_2H_4PPh_2$.[36]

B. Experimental Results

A Study of the Photoreaction of $Mn(CO)_5Br$ and $PF_2C_6H_{10}PF_2$.

The photoreaction of $Mn(CO)_5Br$ and $PF_2C_6H_{10}PF_2$ in a 1:1 mole ratio at 300 nm over a period of several hours results in the recovery of 1.8 equivalents of CO and in the formation of two substitution products, $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ and $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$. Both complexes are

yellow in color and are exceptionally air stable. The complexes are easily separated by high vacuum sublimation. No decomposition or oxidation of either complex in solution when exposed to the air is observed, in direct contrast to the rapid oxidation of the Group 6B metal carbonyl complexes in solution. The monocarbonyl complex is somewhat soluble in the more polar solvents, while the tricarbonyl complex is soluble in non-polar solvents.

Characterization of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$.

The product has been identified by elemental analysis, osmometric molar mass, and mass, infrared, and nmr spectral data. Elemental analyses (C, H, and P) of the complex compare excellently with the formula given. The osmometric molar mass is consistent with the monomeric formulation.

Mass Spectrum

The 70 eV mass spectrum consists of a series of peaks due to the parent ion (which confirms the monomeric character of the complex) and the successive stepwise loss of CO, Br, and $PF_2C_6H_{10}PF_2$ (in that order). The base peak corresponds to the ion, $(PF_2C_6H_{10}PF_2)MnBr^+$. Isotope peaks (doublets) due to bromine-79 and -81 are easily distinguished. Ligand fragmentation peaks are present as expected and no peaks due to higher molecular weight species than the parent ion are observed. Relative intensities and assignments of major peaks in the mass spectrum are presented in Table 7.

Infrared Spectrum

The solution infrared spectrum (Figure 43) in the CO stretching region exhibits three strong bands whose frequencies are (in cm^{-1}):

TABLE 7

Assignments, Mass Numbers, and Relative Intensities of Some

Ions in the Mass Spectra of the Manganese Carbonyl

Complexes of $PF_2C_6H_{10}PF_2$

$(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$
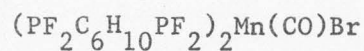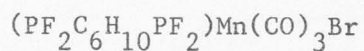
	Mass	Intensity		Mass	Intensity
$LMn(CO)_3{}^{81}Br^+$	440	34	$L_2Mn(CO)^{81}Br^+$	604	18
$LMn(CO)_3{}^{81}Br^+$	438	34	$L_2Mn(CO)^{79}Br^+$	602	19
$LMn(CO)^{81}Br^+$	384	9	$L_2Mn^{81}Br^+$	576	43
$LMn(CO)^{79}Br^+$	382	9	$L_2Mn^{79}Br^+$	574	43
$LMn^{81}Br^+$	356	100	$LMn^{81}Br^+$	356	55
$LMn^{79}Br^+$	354	100	$LMn^{79}Br^+$	354	54
LMn^+	275	25	Br^+	79,81	100
Br^+	79,81	53			

(a)

(b)
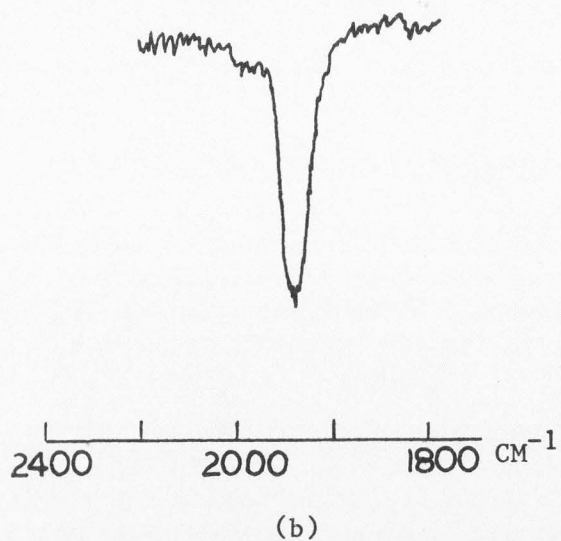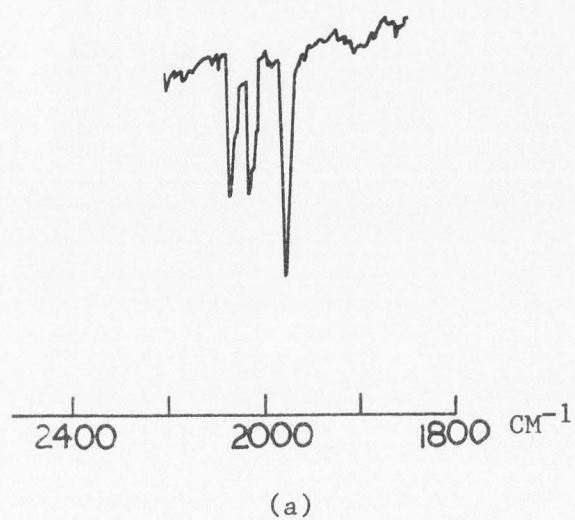
Figure 43. Ir Spectrum (CO Region) of a) $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ and b) $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$

2059, 2017, and 1973. The band positions and intensities are common to tricarbonyl complexes of the facial-cis isomer. A strong P-F stretching band is observed at 815 cm^{-1}.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum consists of a broad multiplet centered near $\delta 2.0$ with benzene as the internal reference. The free, unbound ligand gives a broad, complex multiplet at $\delta 1.97$.

Fluorine NMR Spectrum

The ^{19}F nmr spectrum of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ (Figure 44) consists of at least four sets of doublets which are further split into doublets and quartets. The chemical shifts of the doublets are -60, -70, -79, and -85 ppm ($CFCl_3$, external standard); the fluorine coordination shifts are +21, +11, +2 and -4 ppm; $^1J_{PF}$ span approximately 1120, 1130, 1220, and 1220 Hz, respectively.

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum consists of a broad, weak intensity triplet centered near +272.7 ppm (85% H_3PO_4, external standard). The value of $^1J_{PF}$ is obtained with difficulty due to the broadness of the signals arising from the quadrupole coupling of ^{31}P to ^{55}Mn ($I = 5/2$) and spans about 1135 Hz. A downfield phosphorus coordination shift of +38.6 ppm is observed.

Characterization of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$.

Elemental analyses for the complex were inconclusive, but infrared, nmr, mass spectral and osmometric molar mass data suggest that this
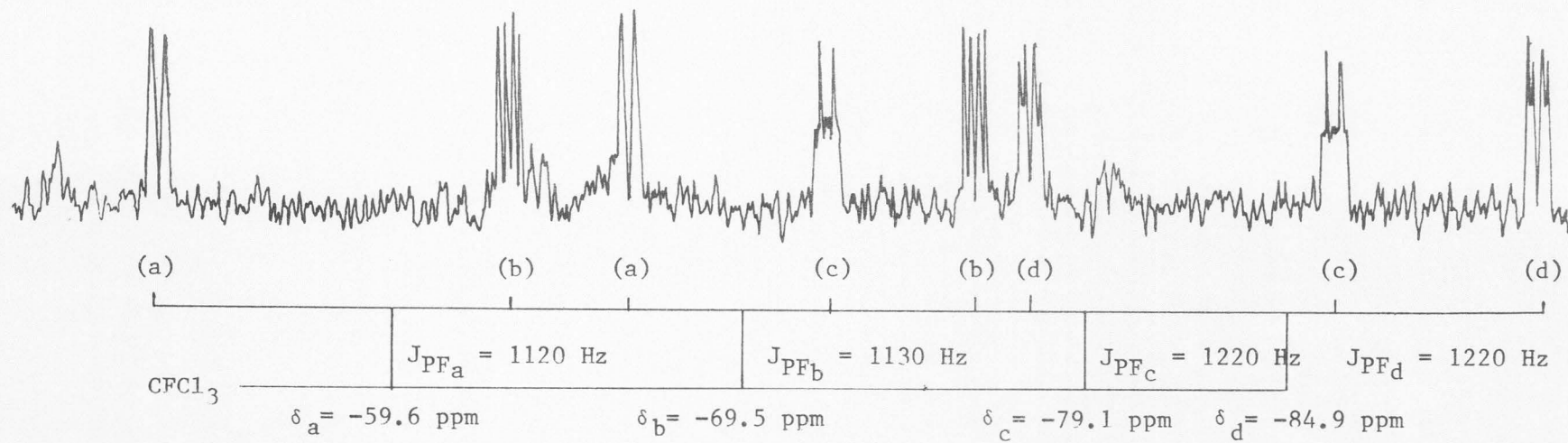
Figure 44. Fluorine NMR Spectrum of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$

formulation is correct. The osmometric molar mass of the complex in $CHCl_3$ is 630 which corresponds to a monomer. The calculated value of the molecular weight is 603.

Mass Spectrum

The mass spectrum consists of three doublets at higher m/e attributable to the molecular ion (which confirms the monomeric character of the complex) and the successive stepwise loss of CO and $PF_2C_6H_{10}PF_2$. Relative intensities and assignments of the major peaks in the spectrum are presented in Table 7. No peaks due to higher molecular weight ions than the molecular ion are observed. The nearly equal intensity doublets arise from the ^{79}Br and ^{81}Br isotopes. Ligand fragmentation peaks are present as expected.

Infrared Spectrum

The presence of only one CO stretching band in the CO region of the solution infrared spectrum (Figure 43) is consistent with this formulation and expected molecular symmetry. The CO band is observed at 1945 cm^{-1} and the strong P-F stretching band is observed at 825 cm^{-1}.

NMR Spectrum

The low solubility of the complex (even in $CDCl_3$) made it difficult to obtain nmr spectra. Proton and ^{31}P nmr spectra are not observed, but the ^{19}F nmr spectrum consists of a very weak doublet barely discernible above the noise. The doublet is centered near -58 ± 3 ppm ($CFCl_3$, external standard). The fluorine coordination shift is downfield +23 ± 3 ppm from the free, unbound ligand and the P-F coupling constant spans 1125 ± 25 Hz.

A Study of the Photoreaction of $Fe(CO)_5$ and $PF_2C_6H_{10}PF_2$.

The 300 nm irradiation of equimolar amounts of $Fe(CO)_5$ and

$PF_2C_6H_{10}PF_2$ in hexane results in the formation of two air-stable sub-

stitution products, $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ and $Fe(CO)(PF_2C_6H_{10}PF_2)_2$, and

the recovery of 1.74 equivalents of CO/equivalent of $Fe(CO)_5$. The

products could be separated by chromatography on Florisil in hexane and

by selective high vacuum sublimation. These products are found to be

very soluble in non-polar solvents and to be resistant to oxidation in

solution upon exposure to air for prolonged periods. Precautions were

taken to avoid exposure of $Fe(CO)_5$ to any light source until irradiation

of the carbonyl with $PF_2C_6H_{10}PF_2$ was initiated. A trace of red-brown

insoluble (in hexane) material appeared during the photoreaction which

was not identified.

Characterization of $Fe(CO)_3(PF_2C_6H_{10}PF_2)$.

The tricarbonyl derivative has been characterized by elemental

analysis, osmometric molar mass, and mass, infrared, and nmr spectral

data. The C, H, and P analyses are in good agreement with the formula-

tion given. The osmometric molar mass in benzene is consistent with a

monomer.

Mass Spectrum

Five dominant clusters are observed in the mass spectrum which are

assigned to the molecular ion and ions resulting from the successive

stepwise loss of CO and the ligand. Iron isotopes are responsible for

the clusters. The relative intensities and assignments of the signals

are given in Table 8. No signals due to higher mass ions than the

TABLE 8

Assignments, Mass Numbers, and Relative Intensities of
Some Ions in the Mass Spectra of the Iron Carbonyl
Complexes of $PF_2C_6H_{10}PF_2$

$Fe(CO)_3(PF_2C_6H_{10}PF_2)$				$Fe(CO)(PF_2C_6H_{10}PF_2)_2$		
	Mass	Intensity			Mass	Intensity
$Fe(CO)_3L^+$	360	16		$Fe(CO)L_2^+$	524	32
$Fe(CO)_2L^+$	332	12		FeL_2^+	496	100
$Fe(CO)L^+$	304	27		FeL^+	276	18
FeL^+	276	100		Fe^+	56	4
Fe^+	56	19				

molecular ion are observed which is evident of a monomer. Peaks due to fragmentation of the ligand are present as expected.

Infrared Spectrum

The solution infrared spectrum in the CO region (Figure 45) exhibits three carbonyl stretching bands whose frequencies are (in cm^{-1}): 2041, 1995, and 1982. No shoulders on these bands are observed which indicates only one isomer is present in solution. A characteristic strong P-F stretching band is observed at 823 cm^{-1}.

NMR Spectra

Proton NMR Spectrum

The 60 MHz proton nmr spectrum consists of a broad multiplet centered near $\delta 1.7$ with benzene as the internal reference (free ligand, $\delta 2.0$, complex multiplet).

Fluorine NMR Spectrum

The complex gives two doublets of equal intensity in the ^{19}F nmr spectrum (Figure 46) centered at -58.3 and -55.6 ppm ($CFCl_3$, external standard). Two weak intensity doublets are observed just downfield from the large doublets. The positions, intensities, and shapes of the large doublets are unchanged over the temperature range, 25-65°. The doublets are clearly not mirror images of one another. The fluorine coordination shifts are downfield from the free, unbound ligand by 23.0 and 25.7 ppm, and the P-F coupling constants span 1125 and 1140 Hz, respectively.

(a)

(b)
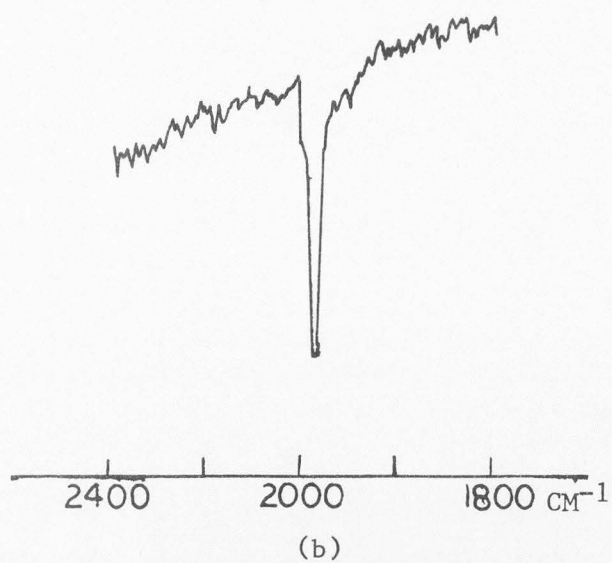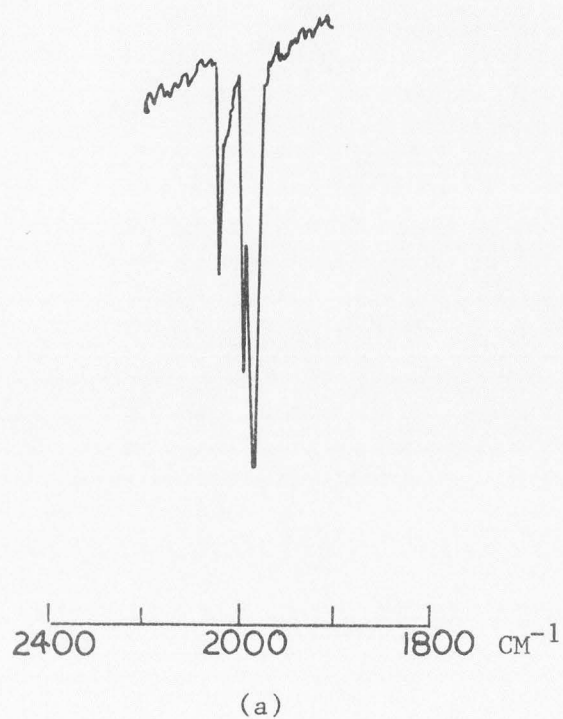
Figure 45.   Ir Spectrum of a) $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ and
b) $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ in Hexane

CFCl₃

J_{PF} = 1140 Hz J_{PF} = 1125 Hz

δ = -55.6 ppm δ = -58.3 ppm
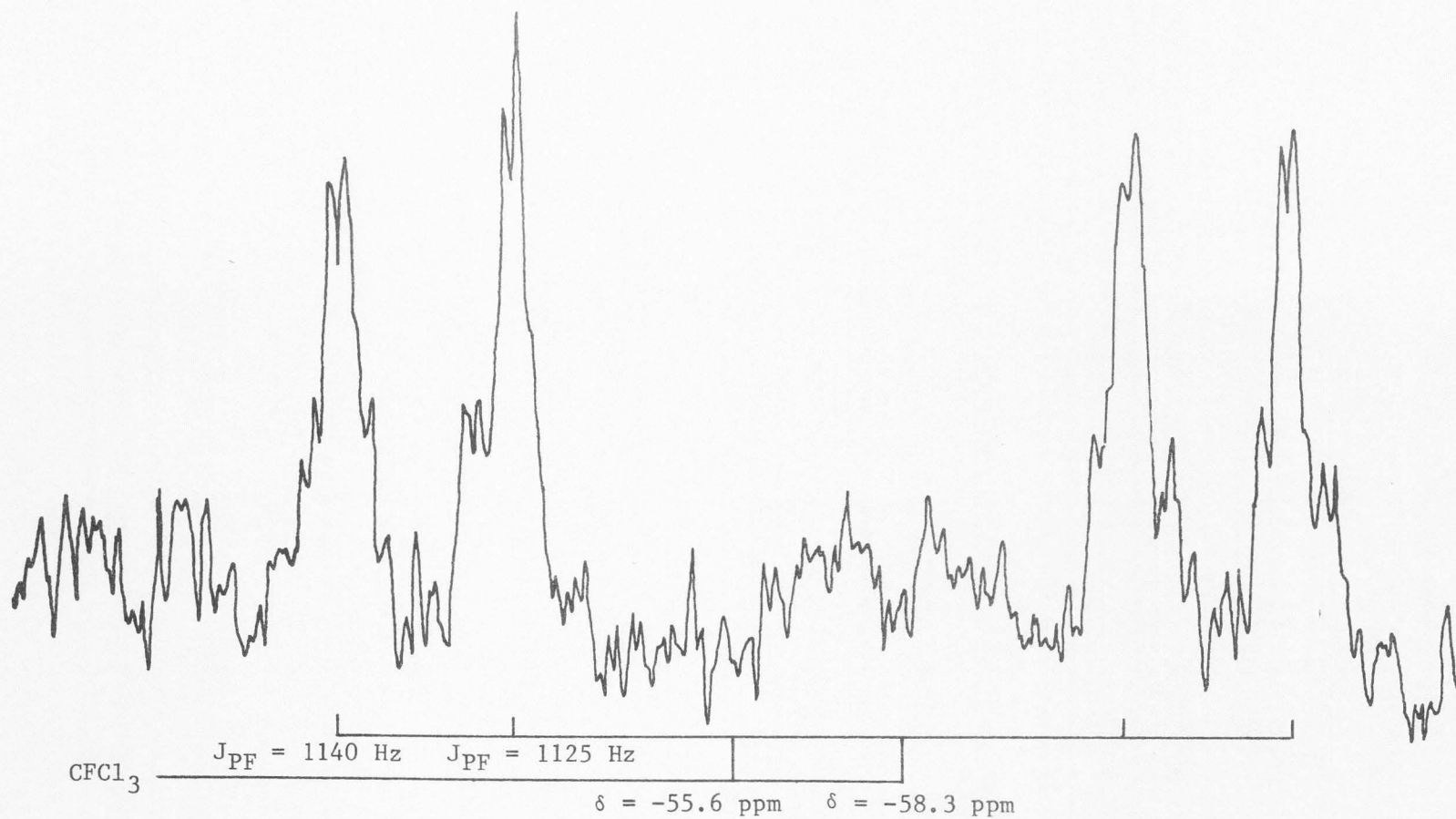
Figure 46.   Fluorine NMR Spectrum of $Fe(CO)_3(PF_2C_6H_{10}PF_2)$

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum (Figure 47) exhibits a single triplet at +271.4 ppm (85% H_3PO_4, external standard). Each member of the triplet is complex, as expected for a second order spectrum in which extensive spin coupling occurs. Upon coordination, the phosphorus signal is shifted downfield by 37.3 ppm from the free ligand. The coupling constant, $^{1}J_{FP}$, spans 1159 Hz.

Characterization of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$.

The monocarbonyl complex is easily distinguished from the tricarbonyl complex and is identified by elemental analysis, osmometric molecular weight, and mass, infrared, and nmr spectral data. The C, H, and P analyses are in good agreement with the formulation, $Fe(CO)$-$(PF_2C_6H_{10}PF_2)_2$. A molar mass value is obtained in benzene by osmometry which indicates the monomeric formulation is correct.

Mass Spectrum

A medium intensity molecular ion at 524 m/e is observed in the 70 eV mass spectrum which corresponds to the ion, $Fe(CO)(PF_2C_6H_{10}PF_2)_2^+$. The base peak is assigned to the ion, $Fe(PF_2C_6H_{10}PF_2)_2^+$, demonstrating loss of CO from the molecular ion. Assignments and relative intensities of the dominant clusters (due to Fe isotopes) in the spectrum are shown in Table 8. As before, no signals are observed at higher m/e above the molecular ion, and fragmentation peaks due to the ligand are also observed, as expected.
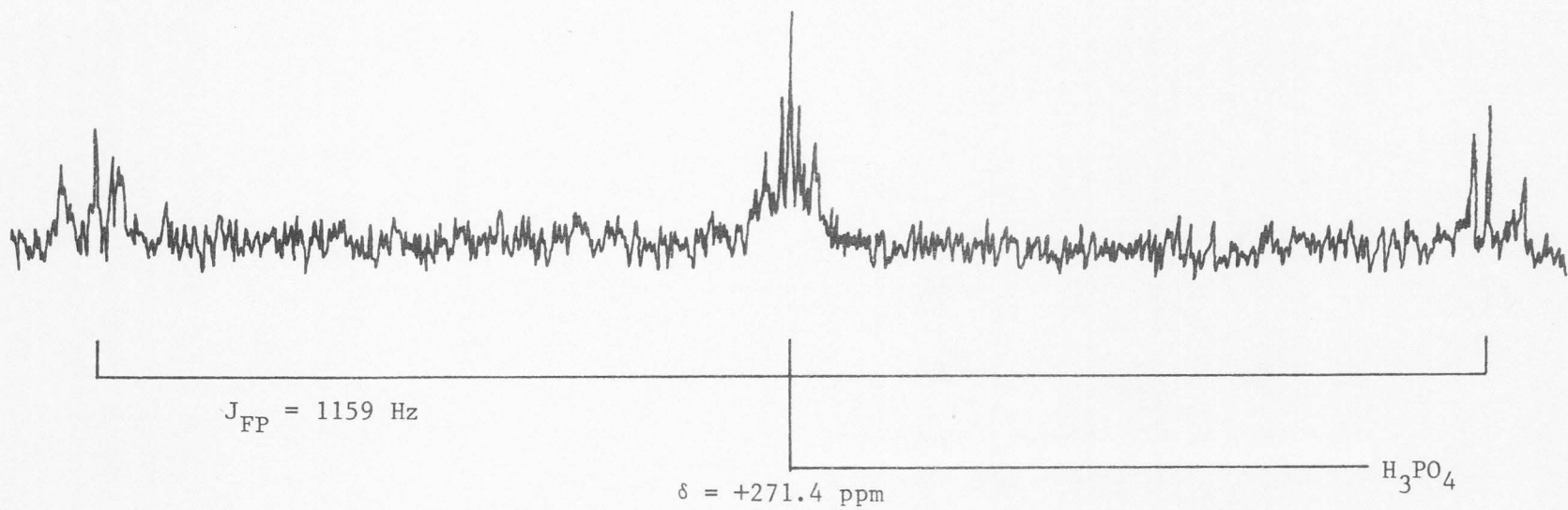
Figure 47. Phosphorus NMR Spectrum of $Fe(CO)_3(PF_2C_6H_{10}PF_2)$

$J_{FP} = 1159$ Hz

$\delta = +271.4$ ppm

H_3PO_4

Infrared Spectrum

For the complex, $Fe(CO)(PF_2C_6H_{10}PF_2)_2$, only one CO stretching band is observed in the CO region of the solution infrared spectrum (Figure 45), indicating the presence of only a single compound and isomer. The frequency of the CO stretching band is 1983 cm^{-1}. Two strong P-F stretching bands are observed at 822 and 841 cm^{-1}.

NMR Spectra

Proton NMR Spectrum

The proton nmr spectrum in benzene (internal reference) exhibits a very broad complex multiplet resembling a 1:2:1 triplet centered near $\delta 2.0$. The free ligand also consists of a complex multiplet centered near $\delta 1.97$.

Fluorine NMR Spectrum

The ^{19}F spectrum (Figure 48) exhibits a broad doublet (width at half-height spans 150 Hz) centered at -52.1 ppm ($CFCl_3$, external reference). The fluorine coordination shift is downfield 29 ppm from the free ligand. The coupling constant, $^1J_{PF}$, spans approximately 1125 Hz.

Phosphorus NMR Spectrum

The ^{31}P nmr spectrum gives the characteristic triplet expected for a PF_2-containing species (Figure 49), and differs from the triplet observed for the tricarbonyl complex in that the resonances are broadened considerably. The width of the signals at half-height spans approximately 100 Hz. The triplet is centered at +272.6 ppm (85% H_3PO_4, external standard). Upon coordination, the triplet is shifted by 38.5 ppm and $^1J_{FP}$ is reduced to 1140 Hz.

CFC1$_3$

J$_{PF}$ = 1125 Hz

δ = -52.1 ppm
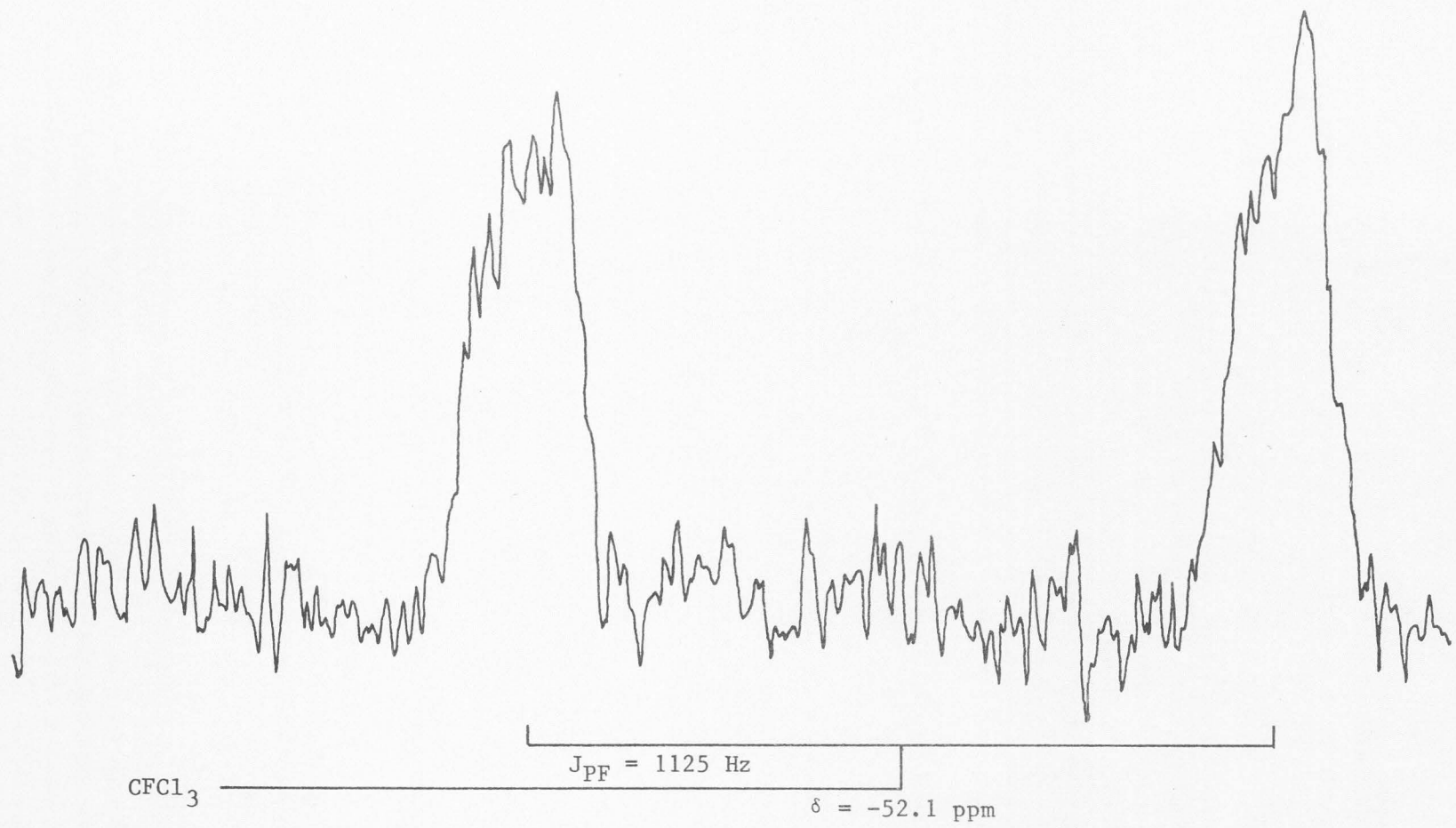
Figure 48. Fluorine NMR Spectrum of Fe(CO)(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$
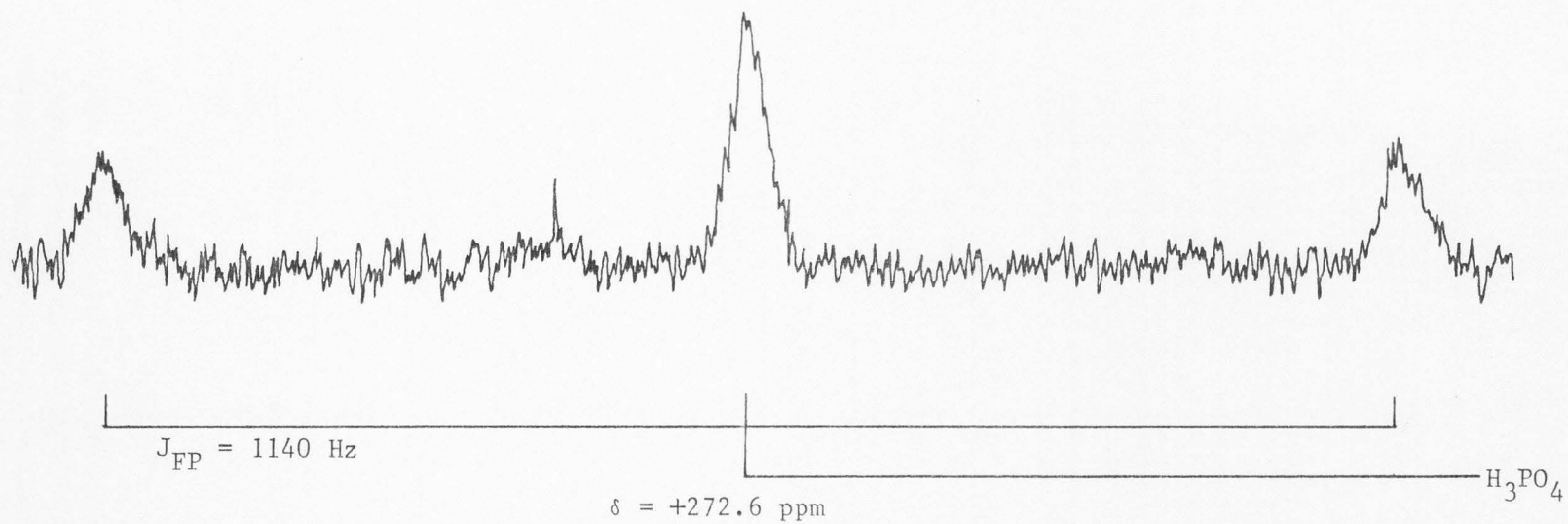
Figure 49. Phosphorus NMR Spectrum of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$

Carbon NMR Spectrum

The 25.2 MHz carbon-13 nmr spectrum (Figure 50) consists of four different resonances; a broad, weak resonance centered at 189 ± 8 ppm, a 1:1:1 triplet (due to the internal standard, $CDCl_3$) centered at 77 ppm, a complex multiplet centered at 51 ppm, and a singlet at 25 ppm (TMS, corrected standard).

A Study of the Reaction of $Co_2(CO)_8$ and $PF_2C_6H_{10}PF_2$.

The reaction of a 1:1 mole ratio $Co_2(CO)_8$ and $PF_2C_6H_{10}PF_2$ in hexane at 0° and 20° results in the displacement of approximately two equivalents of CO/ equivalent of $Co_2(CO)_8$ and the formation of a very air-sensitive brown precipitate. This solid has thus far defied identification particularly since decomposition is observed at room temperature under an inert atmosphere. Elemental analyses are most puzzling in light of the very high hydrogen to carbon ratio. The osmometric molecular weight in $CHCl_3$ is consistent with the formulation, $Co_2(CO)_4-(PF_2C_6H_{10}PF_2)$. The solution infrared spectra vary greatly over a period of several days; terminal CO stretching bands and bridging CO bands are observed initially and later, the bridging bands disappear. A P-F stretching band has not been conclusively identified. The mass spectrum exhibits peaks only attributable to ligand fragmentation ions and the complex is observed to decompose (color change to black and purple) at higher temperature.

A Study of the Reaction of $(C_7H_8)_2Co_2(CO)_4$ and $PF_2C_6H_{10}PF_2$.

A 1:2 mole ratio of $(C_7H_8)_2Co_2(CO)_4$ and $PF_2C_6H_{10}PF_2$ has been allowed to react at refluxing hexane temperature resulting in the formation of a vary air-sensitive brown precipitate and a brown solution. The brown

$\delta = +189 \pm 8$ ppm $\delta = +77$ ppm $\delta = +51$ ppm $\delta = +25$ ppm   TMS
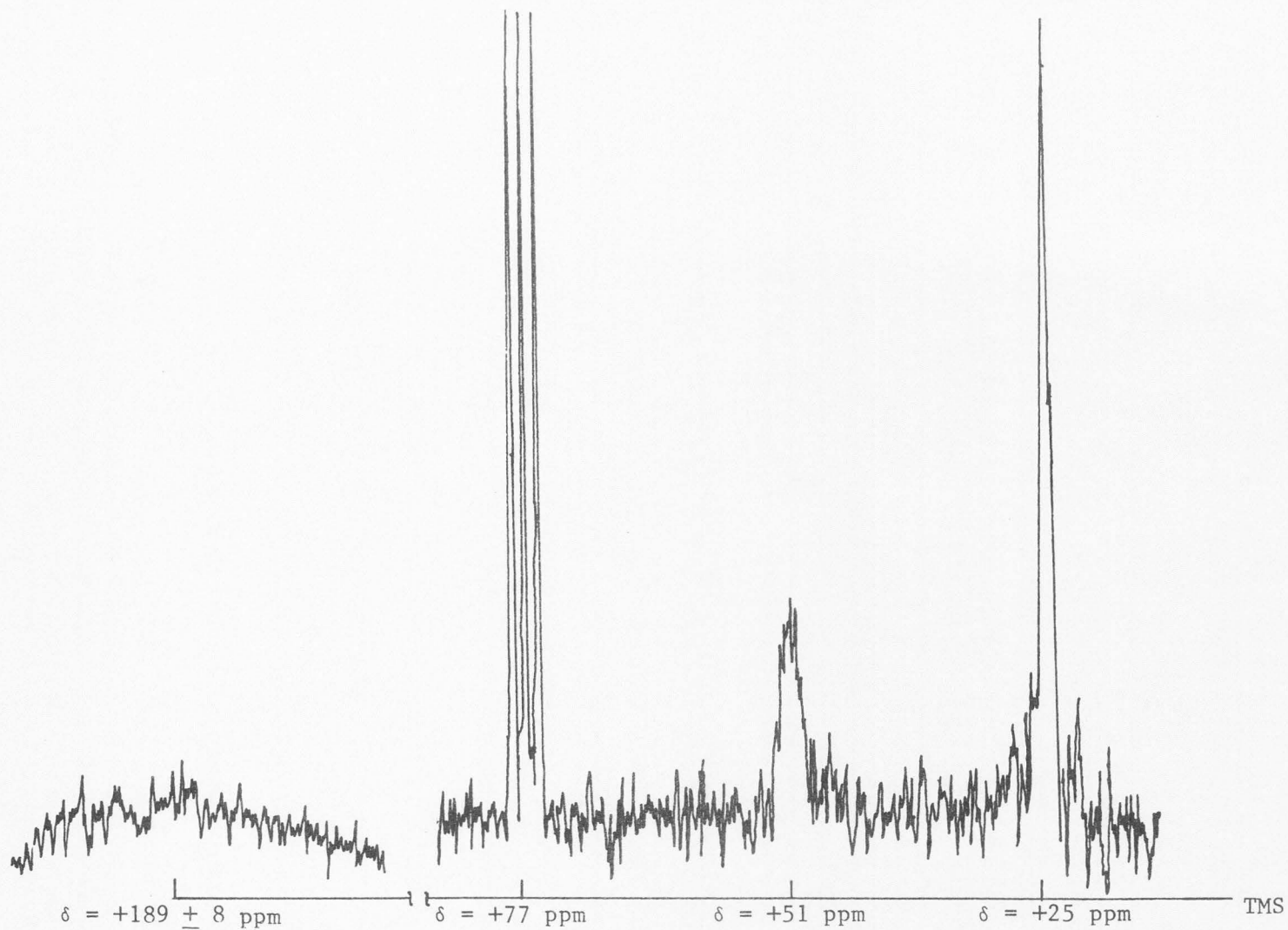
Figure 50.   Carbon NMR Spectrum of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$

precipitate could not be identified, although elemental analyses, osmometric molecular weight, and infrared spectral data have been obtained. The C, H, and P analyses were inconclusive due to the high hydrogen percentage. The osmometric molar mass in $CHCl_3$ suggests a formulation such as, $(C_7H_8)Co_2(CO)_4(PF_2C_6H_{10}PF_2)$, although the elemental analyses are clearly in disagreement. The solution infrared spectrum $(CHCl_3)$ of the solid consists only of peaks attributable to the cobalt tetracarbonyl starting material. Upon solvent removal, the brown solution yields a brown solid that also could not be identified.

C. Discussion

The study of the coordinating ability of $PF_2C_6H_{10}PF_2$ with the first-row transistion metals between chromium of Group 6B and nickel of Group 8 in the form of the metal carbonyls allows for a comparison of the complexes of metals in oxidation states other than zero, with different coordination numbers, and in mononuclear vs. polynuclear environments. The preparation and characterization of complexes of $PF_2C_6H_{10}PF_2$ with Mn(I) and Fe(0), and the reaction with binuclear cobalt (0) have revealed some very interesting and contrasting results.

The most unexpected result was the synthesis of monomeric chelate complexes of Mn(I) and Fe(0), resulting from the photoreactions of the metal carbonyls and the ligand. By contrast, photoreactions of the Group 6B metal carbonyls gave unexpectedly high molecular weight species attributable to bridging ligands across at least two metal centers. Although metal carbonyl-ligand ratios were specifically set with the goal in mind of affording substitution of two CO groups by a single chelate, the higher substituted derivatives, $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ and

Fe(CO)(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$, were obtained in nearly equimolar yield to the respective tricarbonyl complex. In neither of these cases are forcing conditions required for coordination. The exceptional stability of the complexes reflects the chelate effect. The stability of the ligand toward the metal-bromine bond is the Mn(I) complexes is significant, as RPF$_2$ molecules are attacked by HBr yielding phosphoranes.[3] The only metal cluster to be investigated is Co-Co, the carbonyl of which is attacked by PF$_2$C$_6$H$_{10}$PF$_2$ with the loss of CO even at $-78°$. The data obtained for the resultant complexes of these reactions are ambiguous to date.

The tricarbonyl manganese complex, (PF$_2$C$_6$H$_{10}$PF$_2$)Mn(CO)$_3$Br, may exist in two isomeric forms; either meridional-cis or facial-cis, with respect to the ligand environment (C$_s$ carbonyl symmetry). The two isomers (Figure 51) can be distinguished through CO stretching band positions and intensities in the infrared spectrum.[37] Based on these considerations, the tricarbonyl complex has been assigned to the facial-cis isomer. Table 9 shows the CO stretching frequencies obtained from the solution infrared spectrum, along with the frequencies of similar complexes for comparative purposes.

Examination of the CO stretching frequencies in Table 9 supports the previous observation that PF$_2$C$_6$H$_{10}$PF$_2$ exhibits strong π-acceptor character. The CO stretching frequencies for (PF$_2$C$_6$H$_{10}$PF$_2$Mn(CO)$_3$Br are much higher than the frequencies reported for other phosphine-substituted tricarbonyl manganese (I) complexes, implying a greater contribution of the triply-bonded resonance form, M-C≡O, arising from greater back-bonding capabilities expected of a strong π-acid ligand.[22] A semiquantitative value can be assigned to this π-acceptor character by
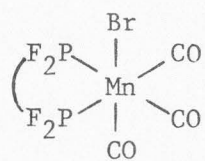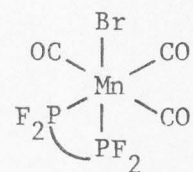
Figure 51.   Structures of Isomers of $Mn(CO)_3(PF_2C_6H_{10}PF_2)Br$

TABLE 9

CO Frequencies and Force Constants for Some Manganese

Tricarbonyl and Monocarbonyl Complexes

Compound	Frequencies, cm^{-1}			Force Constants, mdyne/A			
	A^2	A^1	B	k_a	k_e	k_c'	k_c
$f\text{-}(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$	2059	1973	2017	15.81	16.73	0.24	0.30
$f\text{-}(PPhCl_2)_2Mn(CO)_3Br^a$	2058	1953	2004	15.63	16.55	0.33	0.41
$f\text{-}[P(OPh_3)_3]_2Mn(CO)_3Br^a$	2053	1947	2004	15.56	16.47	0.32	0.40
$f\text{-}[P(OMe)_2Ph]_2Mn(CO)_3Br^b$	2045	1927	1975	15.32	16.16	0.41	0.50
$f\text{-}(Ph_2PC_2H_4PPh_2)Mn(CO)_3Br^c$	2022	1918	1957	15.01	15.93	0.35	0.43
$f\text{-}(PEt_2Ph)_2Mn(CO)_3Br^d$	2021	1902	1954	14.90	15.81	0.39	0.48
$f\text{-}(PMe_2Ph)_2Mn(CO)_3Br^b$	2020	1903	1954	14.91	15.80	0.38	0.48
$(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$	1945			15.26			
$(PF_3)_4Mn(CO)H^e$	2038			16.75			
	2011			16.31			

a. R.J. Angelici, F. Basolo, and A. Poe, J. Amer. Chem. Soc., <u>85</u>, 2215 (1963).

b. R.H. Reimann and E. Signleton, J. Chem. Soc., Dalton, 841 (1973).

c. A.G. Osborne and M.H.B. Stiddard, J. Chem. Soc., London, 4715 (1962).

d. R.J. Angelici, J. Inorg. Nucl. Chem., <u>28</u>, 2627 (1966).

e. W.J. Miles, Jr. and R.J. Clark, Inorg. Chem., <u>7</u>, 1801 (1968).

determination of the appropriate Cotton-Kraihanzel force constants for the CO stretching modes.[23,38] Further, some distinction between π-acceptor effects and σ-donor effects can be made by analysis of these force constant data, determined as described by Dalton, et.al.,[39] for the fac-$L_2Mn(CO)_3Br$ complexes (structure II). According to Wuyts and Van der Kelen[40] the overall changes in force constants expected in such complexes may be expressed as

$$\Delta k_a = 2\Delta(\sigma\to\pi^*) + 2(\Delta\pi/2),$$
$$\Delta k_e = \Delta(\sigma\to\pi^*) + 3(\Delta\pi/2),$$

where k_a and k_e are force constants for the axial and equatorial CO ligands, respectively. The term, $(\sigma\to\pi^*)$ relates to electron density transferred to the CO π^* orbitals by interaction with the σ donor orbitals of the phosphine ligands, while the $\Delta\pi$ term relates to the conventionally considered π orbital interaction. The relative weights assigned to the effects are based on simple geometric considerations. The model assumes negligible change in any Mn-Br π bonding on varying the ligand and also that changes in ligand-metal σ bonding are of minor importance in determining $\nu(CO)$. All values are taken relative to aniline as a ligand. The values of the appropriate force constants for the complex prepared here as well as the complex of $Ph_2PC_2H_4PPh_2$ are included in Table 9 with those for several other Mn(I) complexes (determined by Wuyts and Van der Kelen[40]) for comparison. To the extent that decreasing values of the CO stretching force constants k_a and k_e correspond to increasing π-acceptor strength of the phosphine ligands, it can be seen that the relative π-acidities of these ligands follow the order: $PF_2C_6H_{10}PF_2 > PPhCl_2 > P(OPh)_3 > Ph_2PC_2H_4PPh_2 > Et_2PPh = Me_2PPh$, consistent with the qualitative assessment.

When the possible σ donor effects on the CO stretching force con-
stants are included in the analysis, as outline above,[40] the values shown
in Table 10 are obtained, with those for several other phosphines in-
cluded for comparison. Again, $PF_2C_6H_{10}PF_2$ stands in the same relative
position as a π-acceptor-substantially weaker than CO itself but stronger
than the organophosphines. Both these analyses assume regular octahedral
geometry, i.e., no appreciable distortion due to the bidentate ligands.
The $\sigma \rightarrow \pi^*$ parameters vary only slightly for similar ligands. They do not
necessarily correspond to $\sigma(L \rightarrow M)$ donor strength but may better be viewed
as a measure of the diffuseness of the σ orbital.[40] The relatively small
values of the parameters for the phosphines with the more electronegative
substituents are consistent with this view.

The existence of only one CO stretching frequency in the infrared
spectrum of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ is consistent with this formulation
and expected symmetry. Whether the lone CO ligand is cis or trans to
Br in the molecule is not known, since only one isomer is detected in
the spectrum. (Figure 52) Both isomers have been observed for the mono-
carbonyl complex, $(PF_3)_4Mn(CO)H$, as two different CO stretching fre-
quencies were observed. The CO stretching frequencies and corresponding
force constants for these monocarbonyl complexes are given in Table 9.
Direct comparison of CO stretching frequencies and force constants is
not possible because of the differences in the ligand environment
(Br vs H).

The tricarbonyl iron complex, $Fe(CO)_3(PF_2C_6H_{10}PF_2)$, may also exist
in two isomeric forms; cis, exhibiting C_s carbonyl symmetry or vic,
exhibiting C_{2v} carbonyl symmetry. (Figure 53) Although each isomer
gives rise to three infrared-active bands in the CO region of the

TABLE 10

Bonding Parameters for f-$L_2Mn(CO)_3Br$ Complexes (mdyne/A)[a]

L	$\Delta(\sigma \to \pi^*)$	$\Delta\pi$
CO[a]	0.14	1.055
$PF_2C_6H_{10}PF_2$[b]	-0.23	0.80
$PPhCl_2$[a]	-0.275	0.71
$P(OPh)_3$[a]	-0.29	0.665
$P(OMe)_2Ph$[a]	-0.31	0.475
$Ph_2PC_2H_4PPh_2$[b,c]	-0.43	0.40
PEt_2Ph[a]	-0.45	0.335
PMe_2Ph[a]	-0.44	0.32
$C_6H_5NH_2$	0.00	0.00

a. Reference 40
b. bidentate
c. Calculated from frequencies reported by A.G. Osborne and
   M.H.B. Stiddard, J. Chem. Soc., London, 4715 (1962).
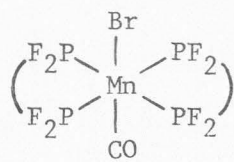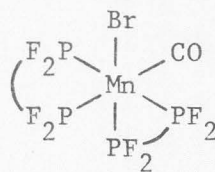
Figure 52.   Structures of Isomers of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$
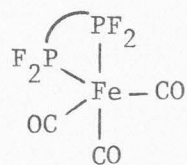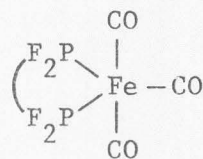
Figure 53. Structures of Isomers of $Fe(CO)_3(PF_2C_6H_{10}PF_2)$

solution infrared spectrum,[41] band positions and intensities have been used to differentiate between the isomers of the tricarbonyliron complexes of PF_3.[42,43] Table 11 shows the CO stretching frequencies obtained for the complex, $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ and similar complexes. Since three CO stretching bands (no shoulders) were observed, only one isomer is present in solution. On the basis of experimental results reported for bidentate phosphine-substituted tricarbonyliron complexes,[44-47] the complex is assigned to the cis isomer. This allows the P-M-P bond to assume an angle of approximately 90° rather than the 120° angle required for the vic isomer, which would introduce much ring strain in the ligand. According to Rechziegel and Bignorgne,[48] considerable distortion of the trigonal-bipyramid of iron tricarbonyl complexes occurs. Such distortions have been reported to give complexes which have structures intermediate between a trigonal-bipyramid and a square pyramid.[44] This flexibility could account for the ready formation of iron chelates relative to the Cr(0) case described above.

Examination of the CO stretching frequencies of tricarbonyliron complexes (Table 11) obtained from solution infrared spectra supports the hypothesis that $PF_2C_6H_{10}PF_2$ is a good π-acceptor ligand. The frequencies given for the $PF_2C_6H_{10}PF_2$ complex are not as high as those reported for the complexes of PF_3, but are substantially higher than the frequencies reported for the tricarbonyl complexes of the bidentate organophosphines. These comparisons are made only through the CO frequency data, since force constants for the penta-coordinate metal carbonyls are difficult to obtain.[43] The results of these comparisons are nonetheless consistent with both expectations and the previous results.

TABLE 11

CO Frequencies for Some Iron Tricarbonyl and Monocarbonyl Complexes

Compound	Frequencies, cm^{-1}	
$cis\text{-}Fe(CO)_3(PF_2C_6H_{10}PF_2)$	2041, 1995, 1982	
$cis\text{-}Fe(CO)_3(PF_3)_2$[a]	2071, 2019, 1992	
$cis\text{-}Fe(CO)_3(Ph_2PC_4F_4PPh_2)$[b]	2008, 1947, 1927	
$cis\text{-}Fe(CO)_3(Ph_2PC_2H_4PPh_2)$[b]	2007, 1946, 1928	
$Fe(CO)(PF_2C_6H_{10}PF_2)_2$	1983	(equatorial)
$Fe(CO)(PF_3)_4$[a]	2037	(axial)
	2008	(equatorial)

a. H. Mahnke, R.J. Clark, R. Rosanske, and R.K. Sheline, J. Chem. Phys., 60, 2997 (1974).

B. W.R. Cullen, D.A. Harbourne, B.V. Liengme, and J.R. Sams, Inorg. Chem., 8, 1464 (1969).

For the complex, $Fe(CO)(PF_2C_6H_{10}PF_2)_2$, only one CO stretching band was observed in the solution infrared spectrum indicating the presence of one isomer. The infrared data alone cannot distinguish whether the lone carbonyl is on an axial or equatorial position of the trigonal-bipyramid (which may be distorted), although the equatorial isomer would be expected to be the preferred isomer due to the bite of the ligand. (Figure 54) Both isomers were observed for the monocarbonyl iron complex of PF_3, the isomer with the axial CO giving the higher CO frequency.[43] The CO stretching frequencies of these monocarbonyl complexes are found in Table 11. The isomers of the PF_3 complex exhibit higher CO frequencies and force constants than the $PF_2C_6H_{10}PF_2$ complex as expected.

The 60 MHz proton nmr spectra of these complexes do not give particularly useful data for describing the complexes since each spectrum gives broad complex multiplets, but they do qualitatively indicate the presence of the ligand. The ^{19}F and ^{31}P nmr spectra, although sometimes very complex, are much more informative as to the nature of the coordination of the ligand in these complexes.

The ^{19}F nmr spectrum of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ is surprisingly complex. The pattern of at least four doublets is no doubt due to two non-equivalent fluorine environments (with respect to Br) and spin coupling of the fluorine nuclei with ^{31}P (I = 1/2), ^{55}Mn (I = 5/2) and $^{79,81}Br$ (I = 3/2). A summary of the chemical shift, fluorine coordination shift, and coupling constant data is found in Table 12. Complete analysis of the spectrum will require computer-assisted techniques, since reports of the couplings of fluorine to manganese and bromine are non-existent. Because the ir spectrum indicates only a single isomer is present and because all the doublets are of equal intensity, a single
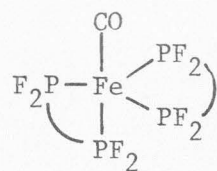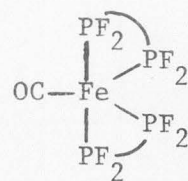
Figure 54. Structures of Isomers of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$

TABLE 12

^{31}P and ^{19}F NMR Data for Manganese and Iron Complexes of $PF_2C_6H_{10}PF_2$[a]

Compound	P Complex[b] (ppm)	P[c] (ppm)	J_{FP} (Hz)[d]	F Complex[e] (ppm)	F[f] (ppm)
$LMn(CO)_3Br$	+272.7	+38.6	1135	−60 −70 −79 −85	+21 +11 + 2 − 4
$L_2Mn(CO)Br$	g	g	h	−58 ± 3	+23 ± 3
$Fe(CO)_3L$	+271.4	+37.3	1159	−58 −56	+23 +25
$Fe(CO)L_2$	+272.6	+38.5	1140	−52	+29

a. Sign convention for chemical shifts: + = downfield.
b. Because of second order splitting patterns in the spectra, the chemical shifts and J_{FP} values were measured from the centroids of the signals.
c. P free ligand = +234.1 ppm.
d. J_{FP} free ligand = 1218 Hz.
e. Shifts reported for the dominant doublets.
f. F free ligand + −81.3 ppm.
g. No data.
h. J_{FP} could not be obtained, but J_{PF} from the ^{19}F nmr spectrum = 1125 ± 25 Hz.

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compound is likely the source of this spectrum (Figure 44). Carefully constructed models show two clearly distinct fluorine environments - above and below the P-Mn-P plane. The further differentiation of fluorine environments is less obvious but is likely due to the difference between approximately equatorial and axial fluorine positions with respect to the chelate ring and the hydrocarbon ring. Table 12 includes the parameters obtained from the spectrum of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$.

An interesting case arises in the ^{19}F nmr spectrum of $Fe(CO)_3^-$ $(PF_2C_6H_{10}PF_2)$. Two large doublets are observed which are clearly not mirror images of one another but are equal in intensity. In a fashion similar to the $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ spectrum, this pair of doublets may arise from two non-equivalent fluorine atom environments with respect to the chelate ring because the two phosphorus atoms are not differentiated in this fluxional molecules (see below) at this temperature $(25-65^{\circ}C)$. Models of the complex show that the axial protons of the ring located on the carbon atoms bonded to the phosphorus atoms should interact differently with the axial and equatorial fluorine atoms. This observation of differentiation of fluorine environments relative to the chelate ring is observed in the ^{19}F nmr spectra of Cr(O), Mn(I), and Fe(O) (Figures 27, 44, and 46) but not for Mo(O) or W(O) (Figures 30 and 33). The larger metal atom radius of Mo(O) and W(O) apparently expands the chelate ring in such a way as to more nearly equalize the axial and equatorial environments in the molecules. The downfield coordination shifts and decreases in the P-F coupling constants for the resonances (Table 12) are consistent with previous results.[3,16] Also included in the Table are the data obtained from the spectrum of the monocarbonyl iron complex.

The fluorine coordination shift of the monocarbonyl is downfield from the coordination shifts obtained for the tricarbonyl. A similar observation was noted for the dicarbonyl and tetracarbonyl molybdenum complexes of $PF_2C_6H_{10}PF_2$.

The PF_2 groups of the ligand account for the triplets observed in the ^{31}P nmr spectra of the complexes obtained in this study. Large P-F coupling constants on the order of 1150 Hz result from the fluorine nuclei adjacent to the phosphorus atoms. Table 12 summarizes the chemical shift and coupling constant data obtained from the spectra. Phosphorus coordination shifts calculated from the difference between chemical shifts of the complexes and the free ligand are all downfield, consistent with coordination shifts reported for the $PF_2C_6H_{10}PF_2$ complexes of the Group 6B metal carbonyls. The anticipated decrease in $^1J_{FP}$ is also observed upon coordination.

The presence of a single triplet in the ^{31}P nmr spectrum of $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ implies a single phosphorus environment inconsistent with the cis isomer unless the molecule is stereochemically non-rigid resulting in a time averaged equivalence of the two positions. This is now well established for several bidentate-Fe(CO)$_3$ molecules including some known to assume the cis form in the crystal.[45-47] Of interest in this regard is a recent theoretical treatment of this question[49] which suggests that there may be essentially free rotation about the metal-bidentate ligand axis yielding effective equivalence of the monodentate ligands, hence of the two ends of the bidentate ligand. This model considers the bidentate bite to be quite rigid and is thus consistent with our data and with those of others who have studied the nmr spectra

of similar bidentate-Fe(CO)$_3$ complexes.[46,47,50] This is quite similar
to the mechanism proposed for the molecule, Fe(CO)$_3$(Ph$_2$PC$_2$H$_4$PPh$_2$).[44]

The absence of well-defined signals in the spectrum of Fe(CO)-
(PF$_2$C$_6$H$_{10}$PF$_2$ masks any detailed structural information though it is
anticipated that the bulk of the cyclohexane ring of the ligand may
hamper ready rearrangement such as that discussed above for the tricar-
bonyl. This broadening of the ^{31}P nmr signal of the complex has made
assignment of the monocarbonyl to the axial or equatorial position im-
possible from the standpoint of ^{31}P nmr since phosphorus equivalence in
the molecule cannot be established. A ^{13}C nmr study of all possible
isomers and substitution products of the Fe(CO)$_5$-PF$_3$ system has shown
that for Fe(CO)(PF$_3$)$_4$, formation of the more symmetrical axial isomer
prevails.[51,52] Three signals were obtained in the ^{13}C nmr spectrum of
Fe(CO)(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$; a broad, weak resonance due to CO, a complex multi-
plet due to the carbon atoms in the cyclohexane ring bound to the phos-
phorus atoms, and a singlet due to the remaining carbon atoms in the
cyclohexane ring. Like the ^{31}P nmr spectrum, the ^{31}P nmr spectrum, the
broadness of the CO resonance does not allow assignment of a specific
structure.

D. Conclusion

The results presented here confirm the conclusion that PF$_2$C$_6$H$_{10}$PF$_2$
has strong π-acceptor character and functions as a bidentate ligand.
Monomeric chelate complexes can be prepared by photolysis of the metal
carbonyls of iron and manganese. The difference in products of these
photoreactions and the photoreactions of the Group 6B metal carbonyls may
be due in part to metal atom size; metal atom radii of the metals
Cr(0) (1.18A), Mo(0) (1.30A), and W(0) (1.30A) are larger than the radii

of Mn(I) (0.8-1.17A) and Fe(0) (1.17A). The bite of $PF_2C_6H_{10}PF_2$ may facilitate chelation to smaller metal atoms rather than the larger metal atoms under photolytic conditions. $PF_2C_6H_{10}PF_2$ is the only ligand having a four atom skeleton which has been shown clearly to exhibit this combination of characteristics and represents a class of ligands accessible through the photoaddition of P_2F_4 to olefins.[4] Unlike monofunctional alkyldifluorophosphines which, as a class, disproportionate very rapidly, these ligands display relatively slow decomposition at room temperature but they are susceptible to hydrolysis. As a consequence wet solvents of alcohols as solvents are avoided of necessity in preparative reactions. Qualitative observation indicates that this sensitivity to hydrolysis is diminished dramatically on coordination. Complexes of $PF_2C_6H_{10}PF_2$ are particularly stable, many being air stable over extended periods. In those instances where reaction is observed, (mostly the solvent wet complexes) it appears to be by way of metal oxidation rather than by a hydrolytic process, as evidenced by a color change of the complex and the non-existance of P-O or P-H stretches in the ir spectra.

The ligand $CH_3N(PF_2)_2$, a three atom skeleton which is receiving much attention, also functions as a bidentate ligand in a bridging or chelating fashion[13,53-56] and is only a little weaker in π-acidity than is $PF_2C_6H_{10}PF_2$, vide supra. At least one noteworthy difference in the chemistry of the two ligands has appeared. While $PF_2C_6H_{10}PF_2$ forms chelates with the Group 6B metals only with special precaution, $CH_3N(PF_2)_2$ has been shown to do so readily.[13,57] On the other hand displacement of CO from $Fe(CO)_5$[57] and $Ni(CO)_4$[57] by $CH_3N(PF_2)_2$ gives bridged dimetal species while $PF_2C_6H_{10}PF_2$ readily gives chelates. This probably reflects the difference in bite between the three and four atom skeletons.

A second feature of $CH_3N(PF_2)_2$ chemistry in its reactions with co-
balt complexes, which has not yet been identified for $PF_2C_6H_{10}PF_2$, is
apparent hydrolysis of a P-N bond on a monodentate ligand to give a
coordinated PF_2NHCH_3 molecule (Figure 55).[55] The equivalent reaction of
$PF_2C_6H_{10}PF_2$ would require hydrolysis of a P-C bond, a process much less
facile as a rule than that of a P-N bond. The implication is that in
comparable circumstances $PF_2C_6H_{10}PF_2$ might be expected to give higher
polymers (Figure 55). This may account in part for the insolubility of
the precipitate obtained in the investigation of the reaction with
$Co_2(CO)_8$ and $(C_7H_8)_2Co_2(CO)_4$.

IV. Coordination of $PF_2C_6H_{10}PF_2$ with Ni(II), Pd(II), and Pt(II).

A. Introduction

Investigation of complexation of charged cations, specifically those
exhibiting the d^8 configuration, with bidentate phosphine ligands has
received only limited attention.[2] After the discovery of the potential
utility of the Wilkinson catalyst, $RhCl(PPh_3)_3$, most of the studies of
phosphine coordination with metal ions has focused on the monodentates.
The few metal (II) complexes of the bidentate phosphines studied to date
are of three main types: $[Ni(L)X_2]$, $[Ni(L)_2X_2]$, and $[Ni(L)_2]X_2$ (where
X = Cl or Br). The general methods of preparation include the reaction
of MX_2 with the diphosphine in aqueous ethanol, acetone, and dichloro-
methane, the actions of halogens on $[M(diphos)(CO)_2]$, or from the chloride
by metathesis with LiX.[2] As noted above, wet solvents or alcohols are
avoided in reactions of the bidentate fluorophosphines since they are
susceptible to hydrolysis. This suggested that the reaction MX_2 (M = Ni,
Pd, and Pt) with $PF_2C_6H_{10}PF_2$ would require dichloromethane as the solvent.

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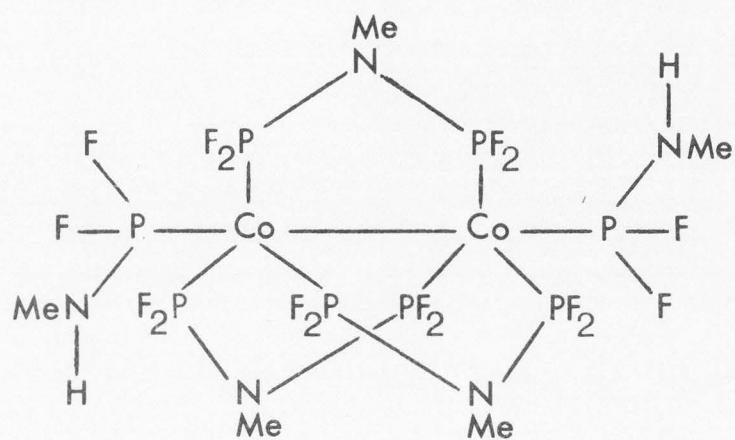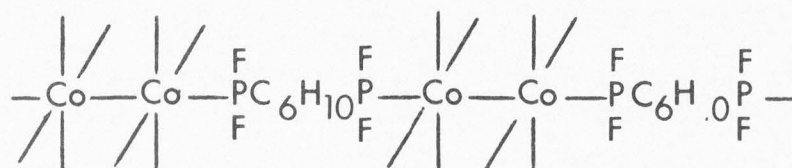
Figure 55. Structures of Dicobalt Complexes
of Bidentate Difluorophosphines

B. Experimental Results

   <u>A Study of the Reaction of</u> $NiCl_2$ <u>and</u> $PF_2C_6H_{10}PF_2$.

   A 1:1 mole ratio of anhydrous $NiCl_2$ and $PF_2C_6H_{10}PF_2$ were refluxed in CH_2Cl_2 for several days resulting in the low yield formation of a yellow oil. Unreacted $NiCl_2$ was recovered by filtration and some ligand was obtained by vacuum distillation. The oil was washed with hexane in an effort to remove traces of unreacted ligand. The oil was not positively identified, although the osmometric molecular weight suggests the formulation, $(PF_2C_6H_{10}PF_2)NiCl_2$. The neat infrared spectrum gives typical peaks attributable to the ligand. A poorly resolved P-F stretching band is observed at 781 cm^{-1} which is shifted from the free ligand value of 799 cm^{-1} suggesting a significant dπ-dπ bonding interaction between phosphorus and nickel.[5] Elemental analyses (C, H, and P) are rather high for all possible coordination products and compare well with the free ligand. The mass spectrum exhibits two major clusters (due to Ni and not Cl) of peaks; a molecular ion at 498 m/e assigned to $Ni(PF_2C_6H_{10}PF_2)_2^+$ (base peak) and a less intense ion at 278 m/e assigned to $Ni(PF_2C_6H_{10}PF_2)^+$. Ligand fragmentation peaks are present as expected and no peaks due to higher mass species than the molecular ion are observed.

   In a similar reaction, anhydrous $NiCl_2$ in dry, air-free ethanol was treated with an equimolar amount of $PF_2C_6H_{10}PF_2$ in CH_2Cl_2 resulting in the recovery of 50% of the $NiCl_2$ by filtration and in the formation of a yellow-orange oil. The oil was applied to a Florisil column; a yellow band was eluted with ethanol, and a colorless fraction was eluted with CH_2Cl_2. The neat infrared spectrum of the colorless oil gives typical bands attributable to the ligand (Figure 56). A strong P-F stretching
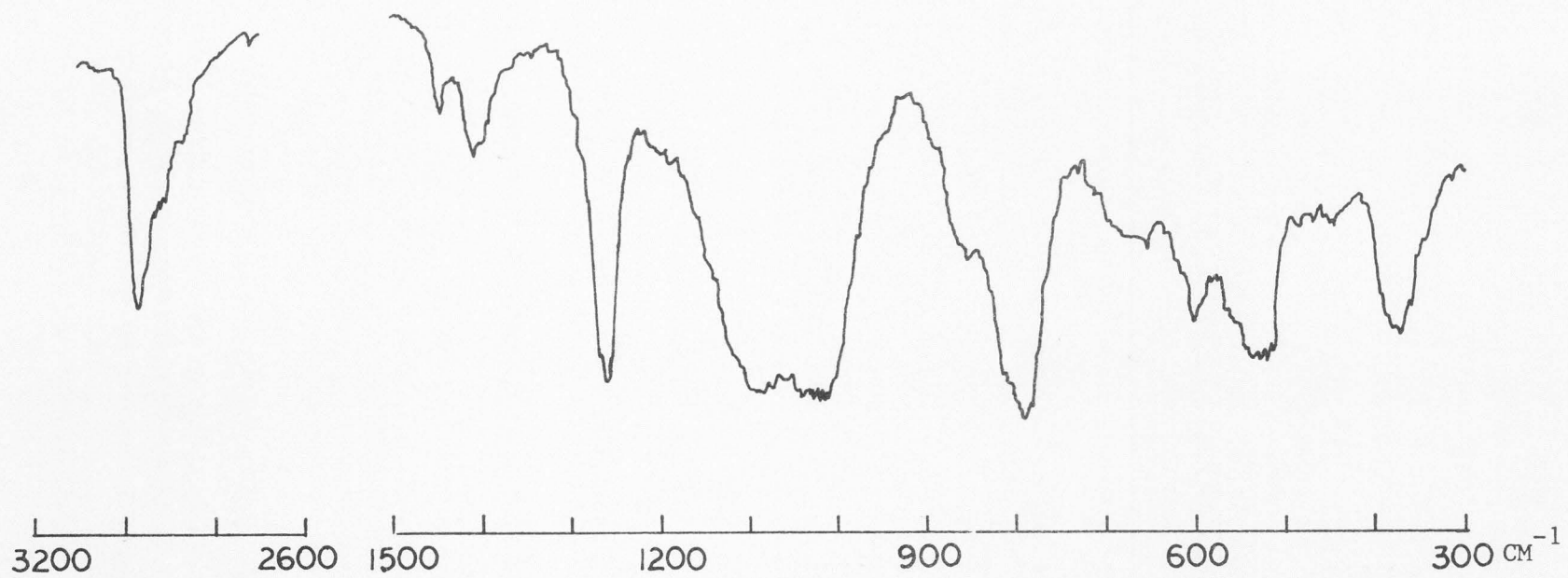
Figure 56. Ir Spectrum of Ni-PF$_2$C$_6$H$_{10}$PF$_2$ Complex (neat)

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band is observed at 790 cm^{-1}. Three bands are observed in the far infrared region whose frequencies are (in cm^{-1}): 539, 525, and 372. The bands at 539 and 525 cm^{-1} may be due to Ni-Cl stretches and the band at 372 cm^{-1} may be due to the Ni-P stretch.[58] The mass spectrum of the oil consists of five major clusters of peaks. The clusters arise from the nickel isotopes and do not appear to result from the chlorine isotopes, ^{35}Cl and ^{37}Cl. Assignments and relative intensities of the clusters are included in brackets: molecular ion-550 [Ni(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$$^+$ + 52, 19], 524 [Ni(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$$^+$ + 26, 37], 498 [Ni(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$$^+$, 65], 304 [Ni-(PF$_2C_6H_{10}PF_2$)$^+$ + 26, 30], and 278 [Ni(PF$_2$C$_6$H$_{10}$PF$_2$)$^+$, 100]. No peaks of higher mass than the peak at 550 m/e are observed and ligand fragmentation peaks are present as expected.

A Study of the Reaction of PdCl$_2$ and PF$_2$C$_6$H$_{10}$PF$_2$.

A 1:1 mole ratio of anhydrous PdCl$_2$ and PF$_2$C$_6$H$_{10}$PF$_2$ was refluxed in CH$_2$Cl$_2$ resulting in the recovery of a small amount of unreacted PdCl$_2$ by filtration and the formation of an orange crystalline solid. The solid was applied to a Florisil column and an orange-brown band was eluted with a methanol-dichloromethane mixture. The resultant orange-red solid was oven and vacuum dried to remove traces of CH$_2$Cl$_2$ believed to be solvated to the complex.

Elemental analyses (C, H, P, and Cl) are inconclusive but best fit the formulas, Pd$_2$Cl$_2$(PF$_2$C$_6$H$_{10}$PF$_2$)$_2$ or Pd$_2$(PF$_2$C$_6$H$_{10}$PF$_2$)$_2\cdot$CH$_2$Cl$_2$. The solid phase infrared spectrum consists of bands attributable to the ligand. The P-F stretching band is observed at 797 cm^{-1}. Five bands are observed in the far-infrared region whose frequencies are (in cm^{-1}): 438, 390, 372, 328, and 284. The osmometric molecular weight of the

complex in $CHCl_3$ was determined twice giving the values 800 and 875. The mass spectrum exhibits peaks due only to CH_2Cl_2 and the ligand.

A Study of the Reaction of $PtCl_2$ and $PF_2C_6H_{10}PF_2$.

A 1:1 mole ratio of anhydrous $PtCl_2$ and $PF_2C_6H_{10}PF_2$ was refluxed in CH_2Cl_2 resulting in the recovery of 40% of unreacted $PtCl_2$ by filtration and the formation of a yellow-orange solid. The solid was applied to a Florisil column and the dominant (yellow) band was eluted with a methanol-dichloromethane mixture. The resultant yellow-orange solid was oven and vacuum dried to remove traces of dichloromethane assumed to be solvated.

As in the case of palladium above, the elemental analyses (C, H, P, and Cl) are inconclusive. The solid phase infrared spectrum consists of bands expected for the ligand. A strong P-F stretching band is observed at 825 cm^{-1}. The osmometric molar mass determined twice in $CHCl_3$ gives the values 845 and 1018. The mass spectrum exhibits peaks attributable only to CH_2Cl_2.

Of particular interest are the proton and phosphorus nmr spectra of the complex (Figures 57 and 58). The 60 MHz proton nmr spectrum consists of a broad multiplet at $\delta1.9$ and a broad resonance at $\delta4.1$ (TMS, external reference). The ^{31}P nmr spectrum exhibits what appears to be a triplet centered at +367.5 ppm (85% H_3PO_4, external reference). Due to the complexity of the spectrum, $^1J_{PF}$ cannot be assigned with confidence.

C. Discussion

The results of the study of the coordination of $PF_2C_6H_{10}PF_2$ with the charged metal cations are completely unexpected and not well understood. The principle difficulty encountered in these reactions is the susceptibility of the ligand P-F bonds to solvents such as, H_2O and C_2H_5OH, so
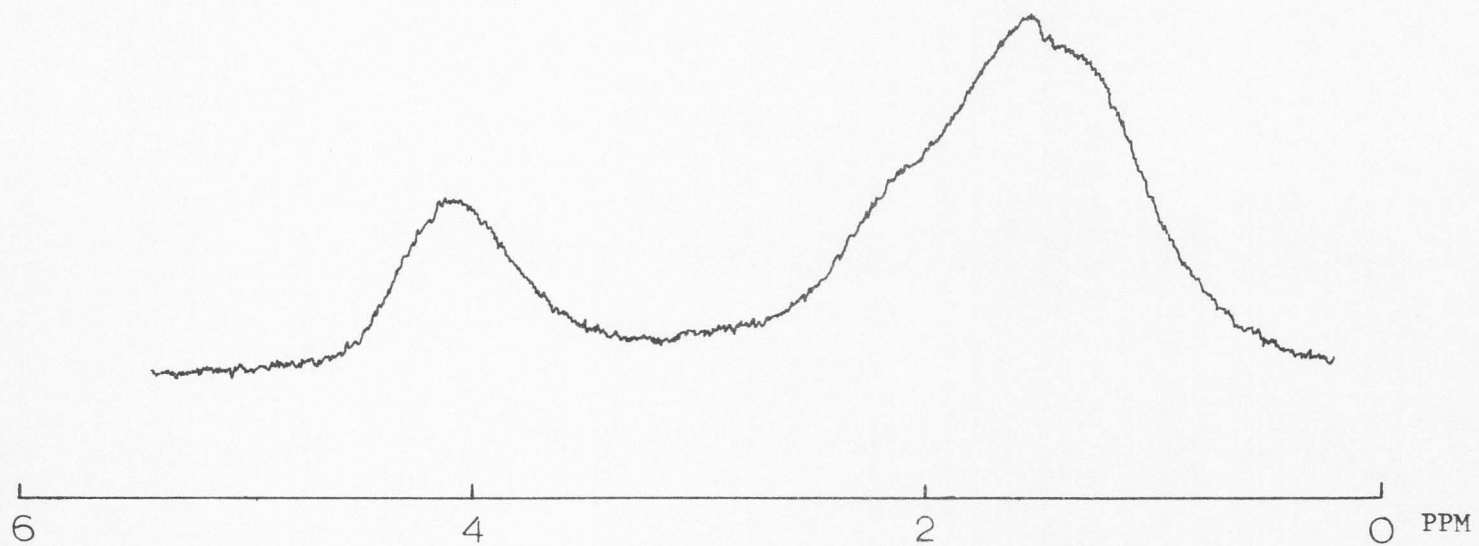
Figure 57. Proton NMR Spectrum of Pt-PF$_2$C$_6$H$_{10}$PF$_2$ Complex

δ = +367.5 ppm
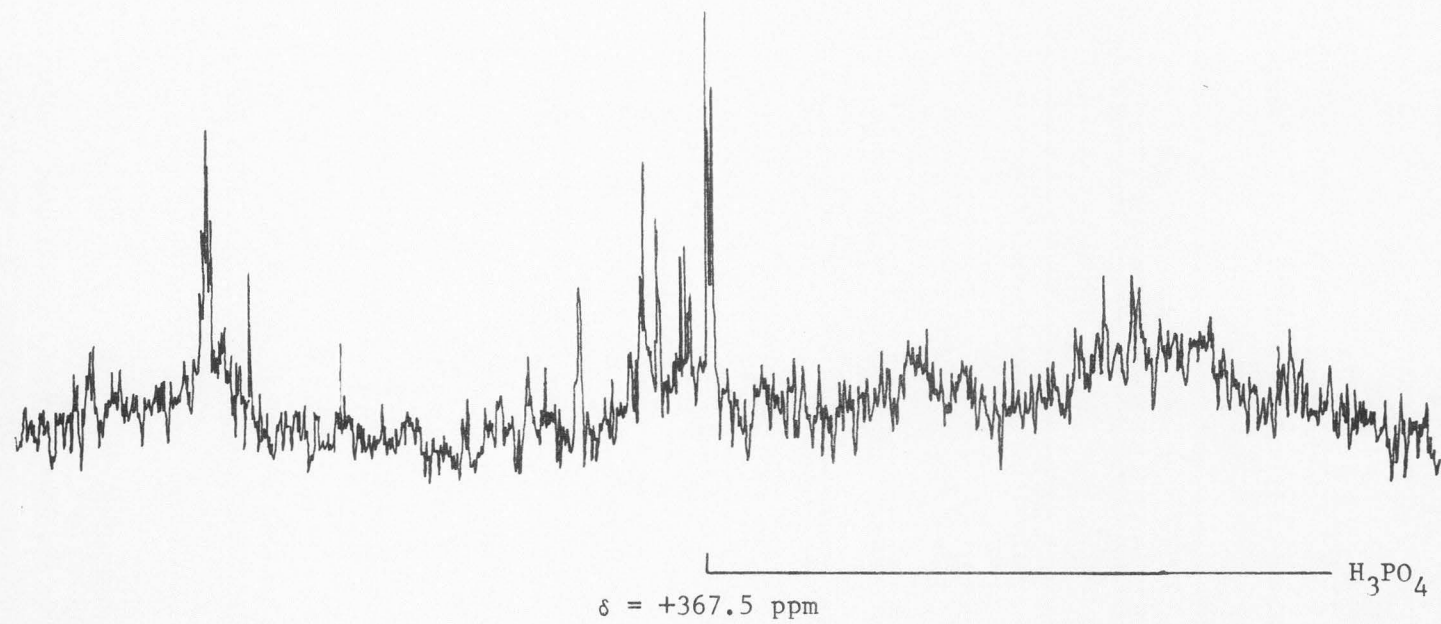
Figure 58.   Phosphorus NMR Spectrum of $Pt-PF_2C_6H_{10}PF_2$ Complex

that a suitable medium in which both ligand and metal halide can be dissolved is hard to find. The limited solubility of the metal halides in CH_2Cl_2 even at reflux results in low yield product formation.

Results of the reaction of $PF_2C_6H_{10}PF_2$ and $NiCl_2$ in CH_2Cl_2 suggest the ligand does indeed coordinate to the metal as verified by the shift to lower frequency of the P-F stretching band in the infrared spectrum[59] and the ions in the mass spectrum attributable to $Ni(PF_2C_6H_{10}PF_2)_2^+$ and $Ni(PF_2C_6H_{10}PF_2)^+$. Similar observation were reported for the complex, $Ni(PF_2C_6H_{10}PF_2)_2$.[5] That nickel has been reduced from the +2 to 0 oxidation state is suggested by the mass spectrum of the complex in that no chlorine isotopes are observed. Whether the chloride ion or some other species in the reaction mixture has been oxidized is not known. It is also not known whether the ligand has been affected in some way by this apparent redox reaction.

When the analogous reaction is performed in a mixed solvent system (ethanol and CH_2Cl_2) coordination of the ligand to the metal is again observed. The P-F stretching band in the infrared spectrum is once more shifted slightly to lower frequency. The most interesting result of the reaction is the apparent product formation as interpreted from the mass spectrum. Prominent peaks in the spectrum are assigned to the ions, $Ni(PF_2C_6H_{10}PF_2)_2^+$ and $Ni(PF_2C_6H_{10}PF_2)^+$. Again, this result indicates that nickel may be reduced in light of the absence of chlorine-containing species. Dominant peaks are observed at 26 m/e above these ions which can only be due to the bound species, CN or C_2H_4. The C_2H_4 moiety could arise from a catalytic reaction producing ethylene from the solvent in such a way as to form a metal ethylene bond in the process. Nickel has been shown to have a high affinity for olefin coordination,[60] although this

interpretation seems suspect since a hexacoordinate species would be formed and nickel(0) is always tetracoordinate. The other possibility is that the fluorophosphine ligand is functioning as a monodentate ligand allowing the metal to assume a coordination number of four.

The reactions of $PdCl_2$ and $PtCl_2$ with $PF_2C_6H_{10}PF_2$ give similar results. Molecular weight data and elemental analyses are consistent with dimers of the type $M_2Cl_2L_2$, although the carbon and hydrogen percentages are high. Due to the difficulty of removing traces of the solvent CH_2Cl_2 and the mass spectral evidence for CH_2Cl_2, the product is probably solvated by CH_2Cl_2. If this is the case, the dimers can be formulated as $M_2L_2 \cdot CH_2Cl_2$, which are also consistent with the osmometric molecular weight and elemental analyses data. The chlorine analyses are particularly convincing that the products contain only two chlorine atoms. The proton nmr spectrum of the platinum derivative exhibits two broad resonances; a higher field signal due to the ligand and a lower field signal at 4.1 which may be due to CH_2Cl_2. Free CH_2Cl_2 gives a single resonance at 5.3. These results are strikingly similar to a dipalladium system in which the addition of sodium acetate to a solution of $PdCl_4^{2-}$ and dibenzylideneacetone followed by recrystallization from CH_2Cl_2 yields the solvated complex, $Pd_2(C_{10}OH_{14})_3 \cdot CH_2Cl_2$,[61,62] the structure of which consists of ligand-bridged Pd atoms (no Pd-Pd bonds). These results again suggest that the metals have been reduced to the zero oxidation state. The nature of the possible reducing agent and the species that is oxidized remain to be explored. The dimeric nature of the products indicate that either metal-metal bonds are formed (an uncommon observation for these metals) or that the ligand functions in a bridging fashion.

D. Conclusion

The ligand, $PF_2C_6H_{10}PF_2$, can function as a coordinating ligand to the nickel group metals apparently giving sufficient stability to merit the complexes described. The ligand may be able to stabilize the metals in the +2 oxidation state, although no evidence is obtained to show that the metals in the complexes prepared are formally +2. Commonly, Pd(0) is less stable and has lower affinity for π-acceptor ligands than Pd(II).[60] The ligand appears to bind to nickel in these reactions in the chelating mode and to bind to palladium and platinum in a bridging fashion (assuming no metal-metal bonds). Questions regarding the nature of these complexes, specifically, the coordination mode in the Pd and Pt complexes and the species bound to the nickel complex exhibiting a mass of 26, and the apparent oxidation-reduction phenomenon remain to be answered.

IV. The Coordination Chemistry of $PF_2C_6H_{10}PF$.

A. Introduction

The availability of another ligand of the bidentate difluorophosphine class in this laboratory, $PF_2C_2H_4PF_2$,[4] allows for comparison of the two structurally different ligands with respect to coordination. The non-rigid hydrocarbon backbone of $PF_2C_4H_4PF_2$ should render the ligand added flexibility in its coordination with the transition metals, specifically with respect to bridging ability. The Lewis base character of the ligand has been demonstrated in the reaction with diborane in which each PF_2 function has been shown to be an active basic site, and thus the ligand is expected to exhibit similar π-acidity to $PF_2C_6H_{10}PF_2$. The study of the coordination chemistry of this ligand is limited since it is obtained in

poorer yield than the cyclohexane derivative. The preparative method of $PF_2C_2H_4PF_2$ is hindered by a less than 50% yield of the photoaddition of PF_2 radicals to the double bond of C_2H_4, which involves handling the unstable and not particularly readily prepared P_2F_4. The study of the coordination chemistry of $PF_2C_2H_4PF_2$ was initiated with nickel(0), as was the study of $PF_2C_6H_{10}PF_2$.[5]

B. Experimental Results

A Study of the Reaction of $Ni(CO)_4$ and $PF_2C_2H_4PF_2$.

The room temperature gas phase reaction of a 1:3 mole ratio of $Ni(CO)_4$ and $PF_2C_2H_4PF_2$ results in the displacement of CO and the formation of a colorless oil which condenses on the reaction vessel walls. The oil solidifies on standing for several hours, turning brown in color. Tbe brown solid is stable in air for prolonged periods, but decomposes in the presence of solvent.

The analogous reaction of $Ni(CO)_4$ and $PF_2C_2H_4PF_2$ was also attempted in benzene solution resulting in the formation of an insoluble brown solid and the recovery of 3.36 equivalents of CO/equivalent of $Ni(CO)_4$. The brown solid was insoluble in polar organic solvents.

Characterization of $[Ni(PF_2C_2H_4PF_2)_2]x$.

The complex obtained from the gas phase reaction was characterized by elemental analyses and infrared spectroscopy. The elemental analyses are in excellent agreement with the formula, $Ni(PF_2C_2H_4PF_2)_2$. The complex, where x is unknown, is probably a polymer because it is insoluble in the common polar organic solvents (including $CHCl_3$ and DMSO). The insolubility of the complex precludes the determination of the osmometric

molecular weight. A mass spectrum could not be obtained (low volatility of the sample) which reflects the polymeric nature of the complex.

Infrared Spectra

The solid phase infrared spectrum of the product obtained from the gas phase reaction consists of the following bands with some tentative assignments given (in cm^{-1}): 2950 m(νCH), 2908 m(νCH), 1170 s, 1075m, and 785 vvs(νPF). Absorptions in the CO region of the spectrum are not observed. The infrared spectrum of the solution product (solid phase) exhibited the same bands and frequencies reported above.

A Study of the Reaction of $(C_7H_8)Mo(CO)_4$ and $PF_2C_2H_4PF_2$.

Equimolar amounts of $(C_7H_8)Mo(CO)_4$ and $PF_2C_2H_4PF_2$ in hexane were warmed to 50° resulting in a nearly colorless solution. Removal of most of the solvent and application to a Florisil column followed by elution with hexane gave a colorless fraction. After solvent removal white crystals were obtained in low yield.

Characterization of $Mo(CO)_4(PF_2C_2H_4PF_2)$.

The product was characterized by elemental anaysis, osmometric molecular weight, and mass and infrared spectral data. The elemental analyses are in excellent agreement with the formula shown. The osmometric molecular weight in benzene corresponds to a monomer.

Mass Spectrum

The mass spectrum consists of six prominent peaks which confirm the assignment of the product as a tetracarbonyl. The molecular ion peak for $Mo(CO)_4(PF_2C_2H_4PF_2)^+$ is observed at 374 m/e. The successive stepwise loss of CO at -28 m/e intervals from the molecular ion is

indicated by clusters of peaks (due to molybdenum isotopes). Ligand fragmentation peaks are present as expected and no peaks due to higher mass ions than the molecular ion are observed.

Infrared Spectrum

The solution infrared spectrum in the CO region (Figure 59) consists of four bands whose frequencies are (in cm^{-1}): 2074, 2005, 1991, and 1973. The bands are well resolved and no shoulders are observed. A strong P-F stretching band is observed at 815 cm^{-1}.

C. Discussion

The ligand, $PF_2C_2H_4PF_2$, displaces CO easily from $Ni(CO)_4$ in both the gas phase and in solution. The mild conditions required for the complete displacement of CO are analogous to the $PF_2C_6H_{10}PF_2$ case,[5] and illustrate the effective π-acceptor ability of $PF_2C_2H_4PF_2$. The insolubility of the resultant complexes is good evidence for polymeric species with assumed high molecular weights. A polymer with the stoichiometry of two bidentate ligands per metal atom (as shown by elemental analyses) requires ligand bridging. Models show the non-rigid ligand, $PF_2C_2H_4PF_2$ can bridge two metal centers to give long chains or networks without appreciable steric crowding. Evidence of ligand coordination is verified by the shift of the P-F stretching band in the infrared spectrum. The coordinated ligand P-F stretch is observed at 785 cm^{-1} as compared to the free ligand P-F stretch at 793 cm^{-1} suggesting,[59] as expected, a significant $d\pi$-$d\pi$ bonding interaction between phosphorus and nickel.

Results of the displacement of norbornadiene from $(C_7H_8)Mo(CO)_4$ by $PF_2C_2H_4PF_2$ show that the ligand can function as an effective chelate. A monomeric complex is obtained (as verified by osmometric molecular
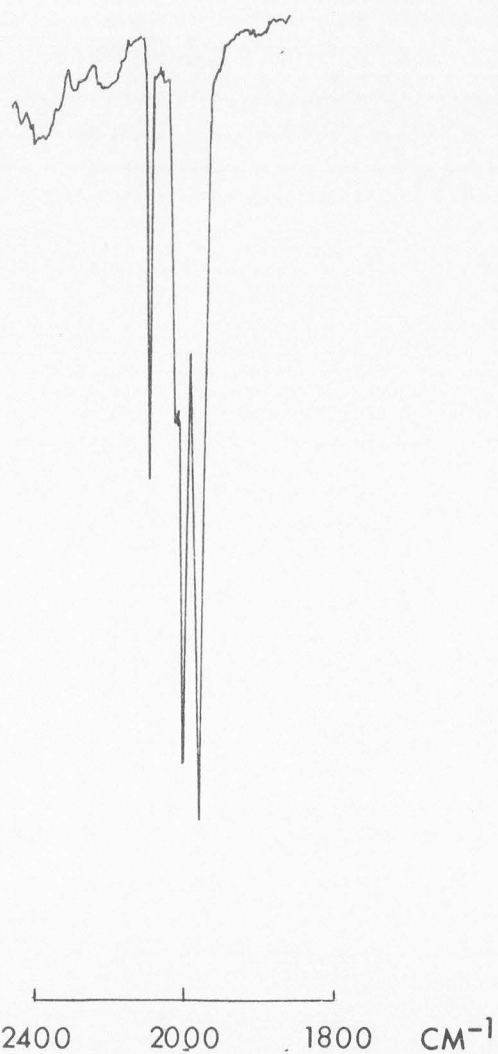
Figure 59. Ir Spectrum (CO Region) of $Mo(CO)_4(PF_2C_2H_4PF_2)$ in Hexane

weight and the mass spectrum) which demonstrates the ligand's ability to coordinate to metals in bridging and chelating modes. The relative stability of the complex toward oxidation when exposed to air reflects the combination of chelate and π-acceptor effects.

That $PF_2C_2H_4PF_2$ is a strong π-acceptor ligand is demonstrated by analysis of the CO stretching bands in the infrared spectrum of $Mo(CO)_4$-$(PF_2C_2H_4PF_2)$. The complex is expected to exhibit C_{2v} carbonyl symmetry which predicts the presence of four CO stretching bands labeled $2A_1 + B_1 + B_2$, which are infrared and Raman active. Bridging CO bands are not observed in the region 1800-1600 cm^{-1}, but four distinct bands (CO terminal stretches) are observed between 2100 and 1950 cm^{-1}. Examination of the CO stretching frequencies supports the assumption that $PF_2C_2H_4PF_2$ is a strong π-acceptor ligand. The frequencies for the bands, $A_1^2 = 2084$ cm^{-1}, $A_1^1 = 2005$ cm^{-1}, $B_1 = 1991$ cm^{-1} and $B_2 = 1973$ cm^{-1}, compare closely with the corresponding frequencies obtained for the molybdenum tetracarbonyl complex of the strong π-acceptor ligand, $PF_2C_6H_{10}PF_2$ ($A_1^2 = 2070$ cm^{-1}, $A_1^1 = 2003$ cm^{-1}, $B_1 = 1990$ cm^{-1}, and $B_2 = 1971$ cm^{-1}). Representative values of the Cotton-Kraihanzel force constants (See Appendix) for the complex of $PF_2C_2H_4PF_2$, $k_1 = 16.30$ mdyne/A, $k_2 = 16.30$ mdyne/A, and $k_i = 0.29$ mdyne/A, are almost exactly equal to the force constants of the analogous complex of $PF_2C_6H_{10}PF_2$ (Table 4).

D. Conclusion

The results of the study of the coordination chemistry of $PF_2C_2H_4PF_2$, although limited, demonstrate that this ligand exhibits the characteristics anticipated: it binds to zero valent metals very strongly, reflecting strong π-acidity which is similar to $PF_2C_6H_{10}PF_2$, and in both

bridging and chelating fashions. The ligand is shown to chelate to

molybdenum(0) only with special precaution. The tendency of the

ligand to bridge metal centers is greater than $PF_2C_6H_{10}PF_2$, as shown by

the polymeric product formation with nickel(0), due to the non-rigid

character of the carbon-hydrogen backbone, as anticipated. Whether

$PF_2C_2H_4PF_2$ will act as a bridging ligand in the photoreactions with the

Group 6B metals remains to be explored.

SUMMARY

This investigation of the coordination chemistry of bidentate difluorophosphines available in this laboratory has shown:

1. That these ligands can function as bidentate ligands. A number of metal complexes of the ligands have been prepared. Coordination of both phosphorus atoms to the low valent metals has been confirmed by ^{31}P and ^{19}F nmr spectra which show single downfield shifts from the free ligand on coordination.

2. That these ligands exhibit strong π-acceptor ability. On coordination with metal carbonyls, an increase is observed in the CO stretching frequencies in the infrared spectra, implying the the substituted ligand competes favorably with CO in accepting electron density from the metal. This effect is measured semiquantitatively by Cotton-Kraihanzel force constants which show the ligands have comparable π-acidity to PCl_3, not quite so good as CO or PF_3, but substantially superior to $Ph_2PC_2H_4PPh_2$.

3. That these ligands are clearly unique. The coordination chemistry of these ligands is unlike any other known ligand type in all general aspects, particularly with respect to chelation vs bridging. High molecular weight polymers are shown to result from bridging ligands (even in stereochemically crowded conditions) by ^{31}P nmr spectroscopy. The chelated complexes exhibit exceptional stability as a result of the chelate effect. The ligands stabilize metals in low oxidation states.

Significant questions regarding the factors affecting the tendency toward polymerization of the complexes, the nature of these polymers, the comparative character of other ligands of this general class, and the oxidation-reduction and potential catalytic behavior of the complexes remain to be answered.

EXPERIMENTAL

I. General Techniques

Due to the reactivities of the fluorophosphine ligands and the resultant complexes toward water and oxygen, all manipulations were carried out using standard high-vacuum techniques or under a dry nitrogen blanket in a glove bag. All glassware employed was dried thoroughly to preclude moisture. The products obtained from the reactions described herein were stored under nitrogen. Since many of the metal carbonyls and phosphines are known to be extremely toxic, it is assumed that these products may also be toxic. Therefore, all reactants and products should be handled carefully in a well-ventilated room and in a fume hood. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. On several occasions elemental analyses were ambiguous which may be due to interference of elements. For example, tungsten analyses are affected by phosphorus. A Rayonet photochemical reactor (Southern N.E. Ultraviolet Co., Middleton, Connecticut) containing RPR-3000A reactor lamps was used as the energy source for the photoreactions.

II. Starting Materials

All organic solvents were dried over Linde 3A Molecular Sieves and degassed before use.

Bicyclo[2.2.1] heptadienetetracarbonylchromium(O) was prepared as reported in the literature.[63,64]

Bicyclo[2.2.1]heptadienetetracarbonylmolybdenum(0) was purchased from
Research Organic/Inorganic Chemical Corp. and sublimed before use.

Bicyclo[2.2.1]heptadienetetracarbonyltungsten(0) was prepared as reported
in the literature.[65]

Bis(bicylco[2.2.1]heptadiene)tetracarbonyldicobalt(0) was prepared as
reported in the literature.[66]

1,2-Bis(difluorophosphino)cyclohexane was prepared by the photoreaction
of P_2F_4 and C_6H_{10}.[4]

1,2-Bis(difluorophosphino)ethane was prepared by the photoreaction of
P_2F_4 and C_2H_4.[4]

1,2-Bis(diphenylphosphino)ethane was purchased from PCR Inc. and used
without further purification.

Bis(toluene)molybdenum(0) was prepared as reported in the literature.[67]

Hexacarbonylchromium(0) was purchased from Strem Chemicals, Inc., and
sublimed before use.

Hexacarbonylmolybdenum(0) was purchased from Ventron Crop. and sublimed
before use.

Hexacarbonyltungsten(0) was purchased from Strem Chemicals, Inc., and
sublimed before use.

Lithium tetrahydridoaluminate was purchased from Ventron Corp. and used
without further purification.

Molybdenum(V) chloride (+99%) was purchased from Apache Chemicals and
used without further purification.

Nickel(II) chloride was purchased from Apache Chemicals and used without
further purification.

Octacarbonyldicobalt(0) was purchased from Strem Chemicals and sublimed
before use.

Palladium(II) chloride (Fisher Scientific Co.) was used without further
purification.

Pentacarbonyliron(0) was purchased from Ventron Crop. and filtered and
distilled before use.

Pentacarbonyl manganese(I) bromide was purchased from Strem Chemicals,
Inc., and sublimed before use.

Platinum(II) chloride was purchased from Apache Chemicals and used
without further purification.

Tetracarbonylnickel(0) was purchased from Strem Chemicals, Inc., and
vacuum-distilled before use.

Trichlorophosphine (Baker Chemical Corp.) was distilled before use.

Triphenylphosphine (Baker Chemical Corp.) was used without further puri-
fication.

III. Instrumental Techniques

Infrared Spectra

Infrared spectra were obtained on a Beckman IR-20A spectrometer.
Solution infrared spectra were obtained with KBr solution plates by
dissolving the solids in the appropriate solvent and introducing the
solution into the salt plates with a syringe. Spectra of volatile
samples were obtained in the gas phase using a standard gas cell (8.5 cm
path). Spectra of volatile samples were obtained in the solid phase
at -196° using a low temperature ir cell.[68] Solid phase spectra were
obtained as mulls of Nujol or Halocarbon 25-5S Grease on NaCl salt plates.
The solids and mull oils were ground together in an agate mortar before
application to the salt plates. Far infrared spectra were obtained as

Nujol mulls using polyethylene plates. Values reported in the text are correct to ±3 cm^{-1} (polystyrene reference). A few spectra were run on an expanded scale using the expansion accessory linked to a single pen recorder.

Mass Spectra

All mass spectral data were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer operating at 70 eV. All samples were introduced in the solid phase and were volatilized by heating the solid sample inlet to appropriate temperatures where the vacuum gauge indicated the sample had indeed volatilized.

NMR Spectra

General

All samples were prepared by dissolving the complexes in a minimum amount of benzene or $CDCl_3$ (depending upon the solubility of the complex) and transferring the solutions to nmr tubes by syringe in the glove bag. The nmr tube was then evacuated and sealed. In keeping with a recent IUPAC ruling, sign conventions for all chemical shifts are: downfield = +, upfield = -.

Proton nmr Spectra

^{1}H nmr spectra were obtained at 100.0 MHz and 60 MHz with a Varian Associates XL-100-12 instrument and a Varian Associates EM 360 instrument, respectively. Benzene was used as the solvent and internal reference.

^{19}F NMR Spectra

Fluorine-19 nmr spectra were obtained at 94.1 MHz with a Varian Associates XL-100-12 instrument. Chemical shift measurements were obtained by the tube interchange technique using $CFCl_3$ as the standard, after minimal drift of the signals was obtained. Fluorine coordination shifts were calculated relative to $CFCl_3$ from the equation:

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

^{31}P NMR Spectra

Phosphorus-31 nmr spectra were obtained at 40.5 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transform mode with proton noise decoupling and a deuterium lock. This required inserting the 5 mm nmr tube containing the sample into a 12 mm nmr tube containing D_2O. The external standard, 85% H_3PO_4, was used for chemical shift measurements. Phosphorus coordination shifts were calculated relative to H_3PO_4 from the equation:

$$\Delta\delta_P = (\delta_P \text{ complex} = \delta_P \text{ free ligand})$$

Because of second order splitting patterns in the spectra, the chemical shifts and coupling constant values were measured from the centroids of the signals.

^{13}C NMR Spectrum

The carbon-13 nmr spectrum was obtained at 25.2 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transform mode with fluorine noise decoupling and a deuterium lock. Chemical shift values are calculated from the internal standard, $CDCl_3$, relative to TMS ($\delta_{TMS} = \delta_{CDCl_3} + 77$, in ppm).

Vapor Pressure Osmometry for Molecular Weight Determinations

Molecular weights of the products obtained in the study were determined osmometrically in benzene or chloroform with a Mechrolab Vapor Pressure Osmometer Model 301A. Solutions were prepared by weighing an appropriate amount of complex in a 1 mL volumetric flask and dissolving the complex in the solvent added to the calibration mark. A standard calibration curve of known molarities of solutions of recrystallized PPh$_3$ was used to obtain the molarities of the solutions.

IV. Reactions Investigated

A. Photoreactions of the Group 6B Metal Hexacarbonyls

General

The following general procedure was employed in the photoreactions of the Group 6B metal carbonyls and PF$_2$C$_6$H$_{10}$PF$_2$ in solution: Sublimed metal carbonyl was weighed and transferred to a 50 mL Pyrex vessel under a dry nitrogen blanket. The Pyrex vessel contained a small Teflon-covered bar magnet and equipped with a Teflon stopcock. The vessel was attached to the vacuum line and evacuated. The appropriate dry, air-free solvent (ca 30 mL) was condensed in to the vessel at -196°. The ligand was weighed in a small weighing vessel (having been condensed into the weighing vessel from a storage tube) and the ligand was condensed into the vessel. The mixture was allowed to warm to room temperature and was irradiated at 300 nm , being continually stirred by a magnetic stirrer located in the photoreactor. The solution was periodically chilled to -196° and the non-condensible product (CO) was removed and carefully measured by a Toepler pump.

<u>Photoreaction of</u> $Cr(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Tetrahydrofuran.</u>

0.1711 g (0.778 mmol) of freshly sublimed $Cr(CO)_6$ and 0.156 g

(0.719 mmol) of $PF_2C_6H_{10}PF_2$ were photolized for 38 hours. Recovery of

0.64 equivalents of CO/equivalent of $Cr(CO)_6$ was made using a Toepler

pump. The solution was transferred to a 50 mL round bottom flask under

Argon in a glove bag. A stopcock adapter was attached to the flask

enabling the flask to be attached to the vacuum line without exposing

the solution to the air. The solvent was then removed under reduced

pressure. After pumping on the remaining yellow solid for 2 days, the

product (0.25 g) was collected in the glove bag. The solid was placed

in a sublimation apparatus. Under vacuum the solid would not sublime,

but began to decompose at 140°. The solid was dissoved in a minimum of

THF and the solution was filtered on a medium porosity glass frit. The

solvent was removed from the solution under reduced pressure leaving

yellow green crystals. <u>Anal</u>. Calcd. fpr $CrP_2F_2C_{10}H_{10}O_4$: C, 31.25;

H, 2.62; P, 16.15. Found: C, 29.32; H, 5.51, P, 18.96.

<u>Photoreaction of</u> $Mo(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Tetrahydrofuran.</u>

0.2773 g (1.05 mmol) of freshly sublimed $Mo(CO)_6$ were photolized

in the presence of 0.284 g (1.29 mmol) of $PF_2C_6H_{10}PF_2$ for 103 hours, at

which time no more CO was observed to evolve from the reaction. Re-

covery of 1.32 equivalents of CO/equivalent of $Mo(CO)_6$ was made using a

Toepler pump. The solution was transferred to a 50 mL round bottom

flask and a stopcock adapter was attached to the flask under nitrogen.

The solvent was removed under reduced pressure and the solid that re-

mained was pumped on for 3 days. The beige colored product was re-

dissolved in THF, filtered, and the solvent was removed under reduced

pressure, leaving a light brown solid. <u>Anal</u>. Calcd. for $MoP_2F_4C_{10}H_{10}O_4$: C, 28.04; H, 2.34. Found: C, 25, 46; H, 5.49.

<u>Photoreaction of</u> $W(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Tetrahydrofuran</u>.

0.2518 g (0.715 mmol) of freshly sublimed $W(CO)_6$ and 0.181 g (0.82 mmol) of $PF_2C_6H_{10}PF_2$ were photolized for 26 hours, at which time no more CO was observed to evolve from the reaction. Recovery of 0.96 equivalents of CO/equivalent of $W(CO)_6$ was made. The solution was transferred to a 50 mL round bottom flask in the glove bag and the stopcock adapter was attached. The solvent was removed under reduced pressure leaving brown crystals. The solid was pumped on for four days and collected. The product was sublimed at 150° giving white crystals. <u>Anal</u>. Calcd. for $WP_2F_4C_{10}H_{10}O_4$: C, 23.27; H, 1.96; W, 35.63. Found: C, 25.81; H, 4.26; W, 39.88.

<u>Photoreaction of</u> $Cr(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Pentane</u>. <u>Preparation of</u> $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]x$.

The reactants, 0.180 g (0.82 mmol) of $PF_2C_6H_{10}PF_2$ and 0.160 g (0.70 mmol) of freshly sublimed $Cr(CO)_6$, were irradiated for ten hours. Recovery of 1.6 equivalents of CO/equivalent of $Cr(CO)_6$ was made. The solution was transferred to a 50 mL round bottom flask and a stopcock adapter was attached to the flask under nitrogen in the glove bag. The vessel was removed to the vacuum line and the pentane was pumped off under reduced pressure. The solution was maintained at -36° (ethlyene dichloride slush) during the solvent removal so that a volatile product would not also be removed. A viscous yellow-orange oil was obtained which was redissolved in pentane, filtered, and obtained by removing the solvent under reduced pressure. The oil was pumped on overnight and

collected. <u>Anal</u>. Calcd. for $CrP_2F_4C_{10}H_{10}O_4$: C,31.25; H, 2.62; P, 16.15;
MW, 384. Found: C, 32.16; H, 3.21; P, 14.26; MW, 949.

<u>Photoreaction of</u> $Mo(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Pentane</u>. <u>Preparation of</u>
$[Mo(CO)_4(PF_2C_6H_{10}PF_2)]x$.

In a typical reaction, 0.225 g (0.852 mmol) of freshly sublimed
$Mo(CO)_6$ and 0.216 g (0.981 mmol) of $PF_2C_6H_{10}PF_2$ were irradiated for 12
hours. Recovery of 1.8 equivalents of CO/equivalent of $Mo(CO)_6$ in-
dicated nearly complete substitution of two CO ligands by the bidentate
phosphine. Under nitrogen the solution was transferred to a 50 mL
round bottom flask and a stopcock adapter was attached to the flask.
The pentane was removed on the vacuum line with pumping. The solvent
was removed slowly by maintaining the solution temperature at -36°.
The white, waxy solid that remained was pumped on overnight at room
temperature to remove the last traces of solvent. <u>Anal</u>. Calcd. for
$MoP_2F_4C_{10}H_{10}O_4$: C, 28.04; H, 2.34; P, 14.49; MW, 428. Found: C, 28.20;
H, 2.51; P, 14.30; MW, 968. The product was dissolved in a few milliliters
of hexane and applied to a 14 cm long column packed with oven-dry
Florisil (100-200 mesh) in a large (X-27-27) glove bag filled with dry
nitrogen. The separation of four different fractions was accomplished
by eluting with hexane. The bands were not visible, so a few milli-
liters of solution were collected at a time in small vials and identi-
fied by infrared spectroscopy (See Results and Discussion).

<u>Photoreaction of</u> $W(CO)_6$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>in Pentane</u>. <u>Preparation of</u>
$[W(CO)_4(PF_2C_6H_{10}PF_2)]_x$.

0.218 g (0.991 mmol) of $PF_2C_6H_{10}PF_2$ and 0.266 g (0.756 mmol) of
freshly sublimed $W(CO)_6$ were irradiated for 13 hours. Recovery of 1.7

equivalents of CO/equivalent of $W(CO)_6$ suggested near completion of
reaction. The solution was transferred in the glove bag under Argon to a
50 mL round bottom flask and a stopcock adapter was attached to the flask.
The pentane was removed slowly under reduced pressure on the vacuum
line with the solution being maintained at -36°. A viscous white oil
was obtained which was pumped on overnight to remove traces of remaining
solvent. <u>Anal</u>. Calcd. for $WP_2F_4C_{10}H_{10}O_4$: C, 23.27; H, 1.96; P, 1
MW, 516. Found: C, 23.50; H, 2.30; P, 11.87; MW, 1128.

<u>Photoreaction of</u> $Mo(CO)_6$ <u>and excess</u> $PF_2C_6H_{10}PF_2$ <u>in Pentane</u>.

0.1726 g (0.654 mmol) of freshly sublimed $Mo(CO)_6$ and 0.297 g
(1.34 mmol) of $PF_2C_6H_{10}PF_2$ were irradiated for 15 hours. Recovery of
1.67 mmol of CO was made using the Toepler pump. Since the amount of
recovered CO was equal to 2.56 equivalents of CO/equivalent of $Mo(CO)_6$,
more $PF_2C_6H_{10}PF_2$ (0.97 g) was condensed into the reaction vessel to in-
sure an excess of ligand. The total amount of ligand used was 0.393 g
(1.79 mmol), placing the ligand in a 2.7:1 ratio with respect to $Mo(CO)_6$.
The solution was irradiated for an additional 6.5 hours. Recovery of
0.33 mmol of CO was made, making a total recovery of 3.08 equivalents
of CO/equivalent of $Mo(CO)_6$. The reaction mixture was transferred to a
100 mL round bottom flask under nitrogen in the glove bag. A stopcock
adapter was joined to the flask and the solvent was removed slowly under
reduced pressure (the solution was maintained at -36°) on the vacuum line.
The white thick oil was pumped on for 20 hours. An attempt to sublime
the product up to 130° failed. The oil was redissolved in pentane,
filtered at 0°, and the pentane was again removed with pumping. An
osmometric molecular weight of 913 was obtained for the product. The

calculated molecular weight for $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ = 428, and for $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$ = 572.

Photoreaction of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$ in Pentane.

In a typical reaction, 0.3614 g (1.37 mmol) of freshly sublimed $Mo(CO)_6$ and 0.5091 g (1.28 mmol) of $Ph_2PC_2H_4PPh_2$ were irradiated for 6 hours. Approximately one equivalent of CO/equivalent of $Mo(CO)_6$ was recovered. A solid precipitated out of the solution during the reaction. The solid was filtered, dissolved in acetone, refiltered to remove insoluble phosphine ligand, and the acetone was removed under reduced pressure. A light yellow solid was obtained which gave an osmometric molecular weight of 600. The calculated molecular weight of $Mo(CO)_4$-$(Ph_2PC_2H_4PPh_2)$ is 606. A similar reaction has been reported by Sandhu and Mehta[20] which gave the dicarbonyl in high yield. The tetracarbonyl was not prepared by a photoreaction.

B. Thermal Reactions of the Group 6B Metal Hexacarbonyls

General

The appropriate metal carbonyl (freshly sublimed) was weighed and placed into a 50 mL Pyrex vessel containing a Teflon stopcock under a dry nitrogen blanket. The flask was evacuated on the vacuum line and then a previously weighed amount of $PF_2C_6H_{10}PF_2$ was condensed into the vessel at -196°. The stopcock was closed tightly and wrapped with foil to keep sand from the plastic parts of the stopcock. The vessel was immersed in a sand bath up to the neck of the vessel so that the Teflon stopcock remained a few centimeters above the surface of the sand. The vessel was thus heated to the reaction temperature. Periodically, the

vessel was removed from the sand bath and the carbon monoxide that was liberated during the reaction was measured and removed by a Toepler pump, the solid mixture being retained at -196°.

Thermal Reaction of $Mo(CO)_6$ and $Ph_2PC_2H_4PPh_2$. Preparation of $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$.

Based on the method employed by Chatt and Watson,[10] 0.2027 g (0.768 mmol) of freshly sublimed $Mo(CO)_6$ and 0.2889 g (0.726 mmol) of $Ph_2PC_2H_4PPh_2$ were heated in the sand bath for 7.5 hours at 160°. Recovery of 1.36 equivalents of CO/equivalent of $Mo(CO)_6$ was made. The yellow-white solid product was dissolved in 10 mL of acetone and the solution was transferred to a 25 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the solvent was removed under reduced pressure on the vacuum line leaving a light yellow solid. An osmometric molecular weight of 622 was obtained for the solid. The calculated molecular weight for $Mo(CO)_4(Ph_2PC_2H_4PPh_2)$ is 606.

Thermal Reaction of $Cr(CO)_6$ and $PF_2C_6H_{10}PF_2$. Preparation of $[Cr(CO)_4(PF_2C_6H_{10}PF_2)]x$.

0.163 g (0.741 mmol) of $PF_2C_6H_{10}PF_2$ and 0.172 g (0.782 mmol) of $Cr(CO)_6$ were heated for 9 hours at 180° in the sand bath. Recovery of 1.5 equivalents of CO/equivalent of $Cr(CO)_6$ was made. A light green oil product was dissolved in 10 mL of benzene and the solution was transferred to a 25 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the solvent was removed under reduced pressure on the vacuum line. The white crystals that were obtained were recrystallized from benzene twice. Anal. Calcd. for $CrP_2F_4C_{10}H_{10}O_4$:

c, 31.25; H, 2.62; P, 16.15; MW, 384. Found: C, 31.19; H, 2.80;
P, 16.24; MW, 1563.

Thermal Reactions of Mo(CO)$_6$ and PF$_2$C$_6$H$_{10}$PF$_2$.

a)   0.238 g (0.902 mmol) of freshly sublimed Mo(CO)$_6$ and 0.200 g
(0.91 mmol) of PF$_2$C$_6$H$_{10}$PF$_2$ were heated for 3 hours at 165° in the sand
bath. Recovery of 1.4 equivalents of CO/equivalent of Mo(CO)$_6$ was made.
A brown oil resulted which was dissolved in a few milliliters of pentane.
The solution was transferred to a 25 mL round bottom flask under nitro-
gen. A stopcock adapter was joined to the flask and the solvent was re-
moved under reduced pressure on the vacuum line, leaving a brown oil.
An osmometric molecular weight of 537 was obtained for this product.

b)   In another reaction, 0.2261 g (0.856 mmol) of freshly sublimed
Mo(CO)$_6$ and 0.159 g (0.723 mmol) of PF$_2$C$_6$H$_{10}$PF$_2$ were heated in the sand
bath for 3 hours at 60° with no measurable CO being recovered from the
reaction. The mixture was heated for an additional 3 hours at 95° with
0.42 equivalents of CO/equivalent of Mo(CO)$_6$ being recovered. Recovery
of an additional 1.02 equivalents of CO per equivalent of Mo(CO)$_6$ was
made after heating the mixture again for 3 hours at 140°. The product
was recovered as before. The brown oil obtained gave an osmometric
molecular weight of 809. The calculated molecular weight for No(CO)$_4$-
PF$_2$C$_6$H$_{10}$PF$_2$) is 428.

Thermal Reaction of W(CO)$_6$ and PF$_2$C$_6$H$_{10}$PF$_2$.

0.133 g (0.605 mmol) of PF$_2$C$_6$H$_{10}$PF$_2$ and 0.280 g (0.706 mmol) of
freshly sublimed W(CO)$_6$ were heated for 7 hours at 145° in the sand bath.
Recovery of 1.2 equivalents of CO/equivalent of W(CO)$_6$ was made. The
yellow solid was extracted with 10 mL of benzene and transferred to a

50 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the solvent was removed under reduced pressure on the vacuum line. The thick, waxy oil was redissolved in benzene and fil-tered on a medium-porosity glass frit. The solvent was again removed from the solution under reduced pressure leaving a yellow oil. An osmometric molecular weight of 873 was determined for the product. The calculated molecular weight for $W(CO)_4(PF_2C_6H_{10}PF_2)$ is 516.

Thermal Reaction of $Mo(CO)_6$ and excess $PF_2C_6H_{10}PF_2$.

0.1394 g (0.528 mmol) of freshly sublimed $Mo(CO)_6$ and 0.498 g (2.26 mmol) of $PF_2C_6H_{10}PF_2$ were heated in the sand bath for 4 hours at 155°. Recovery of 3.3 equivalents of CO/equivalent of $Mo(CO)_6$ was made. The resulting yellow oil was dissolved in 20 mL of benzene and transferred to a 25 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the system was attached to the vacuum line. The solvent was removed under reduced pressure. The yellow oil obtained was redissolved in benzene and filtered on a medium-porosity glass frit. The solvent was removed from the solution under reduced pressure leaving a yellow oil. <u>Anal</u>. Calcd. for $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$: C, 28.37; H, 3.38; P, 20.95; MW, 592. Calcd. for $Mo(PF_2C_6H_{10}PF_2)_3$: C, 28.57; H, 3.97; P, 24.60; MW, 756. Found: C, 30.73; H, 4.75; P, 25.05; MW, 643.

Thermal Reaction of $Mo(CO)_6$ and PCl_3.

0.2764 g (1.050 mmol) of freshly sublimed $Mo(CO)_6$ and 0.240 g (1.75 mmol) of freshly distilled PCl_3 were placed into a 50 mL reaction vessel under nitrogen. The mixture was heated in the sand bath for <u>ca</u>

2 hours at 145°. Recovery of 2.2 equivalents of CO/equivalent of Mo(CO)$_6$ was made. A black oil was obtained which could not be further purified and was not identified.

Thermal Reaction of Mo(CO)$_6$ and PPh$_3$. Preparation of Mo(CO)$_4$(PPh$_3$)$_2$.

In a typical reaction, 0.285 g (1.08 mmol) of freshly sublimed Mo(CO)$_6$ and 0.555 g (2.12 mmol) of PPh$_3$ were heated in a 50 mL reaction vessel in the sand bath for 2 hours at 140°. Recovery of 2.0 equivalents of CO/equivalent of Mo(CO)$_6$ was made. A yellow solid was obtained which was extracted from the reaction vessel with benzene. A fraction of the solid did not dissolve in the benzene and was filtered out of the solution. This insoluble material was tentatively identified as unreacted PPh$_3$. The benzene solution was placed into a 100 mL round bottom flask and the solvent was removed under reduced pressure on the vacuum line. The resultant yellow solid was dissolved in a small amount of chloroform and the solution was filtered on a coarse-porosity glass frit. The solvent was removed as before. The yellow solid was identified as the tetracarbonyl, Mo(CO)$_4$(PPh$_3$)$_2$ upon comparison of data reported previously for the product by Poilblanc and Bigorgne.[18]

C. Ligand Displacement Reactions of Group 6B Metal Complexes by PF$_2$C$_6$H$_{10}$PF$_2$.

Reaction of Mo(CO)$_4$(PPh$_3$)$_2$ and PF$_2$C$_6$H$_{10}$PF$_2$.

A few milligrams of Mo(CO)$_4$(PPh$_3$)$_2$ were placed into a 100 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the flask was evacuated on the vacuum line. An excess of PF$_2$C$_6$H$_{10}$PF$_2$ was condensed into the flask at -196°, along with ca 20 mL of benzene. The mixture was warmed to room temperature and shaken by hand for a

period of 1.5 hours. The tetracarbonyl was rather insoluble and did not appear to react. The solvent was removed under reduced pressure on the vacuum line leaving a brown solid and unreacted ligand. The solid was identified as unreacted $Mo(CO)_4(PPh_3)_2$.

Reaction of $C_7H_8Cr(CO)_4$ and $PF_2C_6H_{10}PF_2$. Preparation of $Cr(CO)_4$- $(PF_2C_6H_{10}PF_2)$.

In a typical reaction, 0.2135 g (0.834 mmol) of freshly sublimed $C_7H_8Cr(CO)_4$ were placed into a 100 mL round bottom flask under nitrogen. A stopcock adapter was joined to the flask and the vessel was evacuated on the vacuum line. Toluene (ca 25 mL) was condensed into the flask, along with 0.150 g (0.682 mmol) of $PF_2C_6H_{10}PF_2$ at -196°. The mixture was allowed to warm to room temperature and in the glove bag under nitrogen, the stopcock adapter was replaced with a plugged reflux condenser. A small magnetic stirring bar was placed in the flask. The closed system was removed from the glove bag, the plug atop the reflux condenser was replaced with a nitrogen flow system containing a bubbler at the end filled with mineral oil, and the solution was refluxed under the nitrogen blanket with stirring for 3.5 days. The reflux condenser was replaced with the stopcock adapter under nitrogen and the solvent was removed slowly under reduced pressure on the vacuum line. The solution was maintained at -36° (ethylene dichloride slush) during the solvent removal process. The resultant yellow-green oil was pumped on overnight. The oil was then dissolved in ca one mL of hexane and was applied to a Florisil column in a large glove bag under nitrogen. The fractions were eluted with hexane in 10 mL portions. A colorless fraction, followed by a yellow fraction were obtained by this procedure.

The yellow fraction was identified as unreacted $C_7H_8Cr(CO)_4$. The colorless elutions were combined, placed into a 50 mL round bottom flask connected to a stopcock adapter, and the hexane was removed under reduced pressure on the vacuum line. White crystals were obtained which sublimed (under high-vacuum) at 55°, m.p. $77-79^o$ (uncorrected), in 42% yield. <u>Anal</u>. Calcd. for $CrP_2F_4C_{10}H_{10}O_4$: C, 31.25; H, 2.62; P, 16.15; MW, 384. Found: C, 33.07; H, 3.49; P, 8.78; MW, 377. Reanalyzed: C, 32.61; H, 2.95; P 3.93.

<u>Reaction of</u> $C_7H_8Mo(CO)_4$ <u>and</u> $PF_2C_6H_{10}PF_2$. <u>Preparation of</u> $Mo(CO)_4$-$PF_2C_6H_{10}PF_2)$.

0.2684 g (0.894 mmol) of freshly sublimed $C_7H_8Mo(CO)_4$ were placed into a 100 mL round bottom flask under nitrogen. A stopcock adapter was connected to the flask and the flask was evacuated on the vacuum line. Pentane (<u>ca</u> 25 mL) was condensed into the flask, along with 0.211 g (0.958 mmol) of $PF_2C_6H_{10}PF_2$ at -196°. On warming to room temperature and agitating for one hour, a colorless solution resulted. The solvent was removed under reduced pressure on the vacuum line, while the solution was held at -36°. A white solid resulted which was charged into a sublimation apparatus. White crystals sublimed at 60° under high-vacuum, m.p. $74-76^o$ (uncorrected) in 60% yield. <u>Anal</u>. Calcd. for $MoP_2F_4C_{10}H_{10}O_4$: C, 28.04; H, 2.34; P, 14.49; MW, 428. Found: C, 28.01; H, 2.34; P, 14.36; MW, 432.

<u>Reaction of</u> $C_7H_8W(CO)_4$ <u>and</u> $PF_2C_6H_{10}PF_2$. <u>Preparation of</u> $W(CO)_4$-$(PF_2C_6H_{10}PF_2)$.

0.329 g (1.00 mmol) of freshly sublimed $C_7H_8W(CO)_4$ were placed into a 100 mL round bottom flask under nitrogen. A stopcock adapter was

connected to the flask and the system was evacuated on the vacuum line.

25 mL of hexane were condensed into the flask, together with 0.263 g

(1.20 mmol) of $PF_2C_6H_{10}PF_2$ at -196°. The mixture was allowed to warm to

room temperature and was shaken by hand for one hour with no appreciable

color change occuring in the solution. The vessel was introduced into

the glove bag and under nitrogen; the stopcock adapter was replaced with

a plugged reflux condenser. A small magnetic stirring bar was placed

in the flask. The system was removed from the glove bag, the plug atop

the reflux condenser was replaced with a nitrogen flow system, and the

solution was refluxed with stirring for 4 hours under nitrogen. The

solution turned from yellow to colorless during reflux. The reflux

condenser was quickly replaced with the stopcock adapter and the solvent

was removed under reduced pressure on the vacuum line. A white solid

was obtained which was placed into a sublimation apparatus. White

crystals sublimed (under high-vacuum) at 60°, m.p. 76-78° (uncorrected)

in 81% yield. <u>Anal</u>. Calcd. for $WP_2F_4C_{10}H_{10}O_4$: C, 23.27; H, 1.96;

P, 1200; MW, 516. Found: 23.40; H, 2.02; P, 11.86; MW, 506.

<u>Photoreaction of</u> $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ <u>and</u> $PF_2C_6H_{10}PF_2$. <u>Preparation</u>

<u>of</u> $[Mo(CO)_2(PF_2C_6H_{10}PF_2)_2]x$.

0.1547 g (0.362 mmol) of freshly sublimed $Mo(CO)_4(PF_2C_6H_{10}PF_2)$

(preparation described above) were placed into a 50 mL Pyrex reaction

vessel containing a Teflon-coated magnetic stirring bar and a Teflon

stopcock under nitrogen. The vessel was evacuated and 25 mL of hexane

were condensed into the vessel, together with 0.083 g (0.38 mmol) of

$PF_2C_6H_{10}PF_2$ at -196°. The mixture was warmed to room temperature and

placed into the photoreactor. The solution was stirred by a magnetic

stirrer located in the bottom of the photoreactor. The solution was irradiated for 13 hours at 300 nm. The vessel was peridically removed from the photoreactor, chilled to -196°, and the liberated CO from the reaction was measured and removed with pumping on the vacuum line. The reaction appeared to be essentially complete within 10 hours due to the absence of CO evolving from the solution. Recovery of 1.5 equivalents of CO/equivalent of $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ was made. The solution was transferred to a 100 mL round bottom flask under nitrogen and a stopcock adapter was attached to the flask. The solvent was removed under reduced pressure on the vacuum line, depositing a colorless oil. The oil was dissolved in a minimum amount of hexane and was applied to a Forisil column in a large glove bag under nitrogen. Elutions of hexane were collected at 6 mL intervals. Two fractions were thus obtained; the first to be eluted was identified by infrared spectroscopy as unreacted $Mo(CO)_4(PF_2C_6H_{10}PF_2)$, the second to be eluted was identified as $Mo(CO)_2$-$(PF_2C_6H_{10}PF_2)_2$. The solvent was removed from the solution under reduced pressure resulting in a colorless oil, in 45% yield. <u>Anal</u>. Calcd. for $MoP_4F_8C_{14}H_{20}O_2$: C, 28.38; H, 3.38; P, 20.95; MW, 592. Found: C, 29.83; H, 4.56; P, 18.15; MW, 943).

<u>Reduction Reaction of</u> $MoCl_5$ <u>and</u> $PF_2C_6H_{10}PF_2$ <u>by</u> $LiAlH_4$.

0.135 g (0.494 mmol) $MoCl_5$ were placed into a 100 mL round bottom flask under nitrogen in a glove bag. 20 mL of dry, degassed tetrahydrofuran were added and the $MoCl_5$ was dissolved with decomposition. A stopcock adapter was connected to the flask and the solution was pumped on the vacuum line while being held at -98° (methanol slush) in an effort to remove any HCl that formed during dissolution. 0.351 g (1.60 mmol)

of $PF_2C_6H_{10}PF_2$ were condensed into the flask at -196°. The mixture was allowed to warm to room temperature and the flask was introduced into a glove bag. Under nitrogen, the stopcock adapter was removed from the flask and small portions (ca 50 mg) of $LiAlH_4$ were added to the solution over a period of 1.5 hours with stirring. The mixture was stirred occasionally by hand over a period of several hours until no more hydrogen gas was observed to evolve from the solution. 10 mL of tetrahydrofuran were added to the flask to wash all of the $LiAlH_4$ into the flask. During the course of the reaction the solution turned from red-brown in color to dark green. The stopcock adapter was reconnected to the flask, the system was attached to the vacuum line, and the solvent was removed under reduced pressure. After complete removal of the tetrahydrofuran, a few milliliters of benzene were condensed on to the mixture at -196°. The mixture was swirled by hand to dissolve any formed products while the solution warmed to room temperature. In the glove bag under nitrogen, the solution was filtered through a medium-porosity glass frit to remove any unreacted, insoluble $MoCl_5$ and $LiAlH_4$. The filtrate was placed into a clean 25 mL round bottom flask, a stopcock adapter was connected to the flask, and the benzene was removed under reduced pressure on the vacuum line. A colorless oil was obtained and collected. The experimental osmometric molecular weight of the oil was determined to be approximately 2000. The calculated molecular weight for $Mo(PF_2C_6H_{10}PF_2)_3$ is 756.

Reaction of $Mo(C_6H_5-CH_3)_2$ and $PF_2C_6H_{10}PF_2$. Preparation of $Mo(PF_2C_6H_{10}PF_2)_3$.

0.261 g (0.932 mmol) of $Mo(C_6H_5-CH_3)_2$ were placed into a 50 mL Pyrex vessel containing a Teflon stopcock (under nitrogen in a glove bag).

Note: The molybdenum complex is extremely air sensitive. The vessel was evacuate on the vacuum line and 0.688 g (3.13 mmol) of $PF_2C_6H_{10}PF_2$ were condensed onto the solid at $-196°$. The mixture was warmed to room temperature, the green solid turning red-brown in color. The vessel was partially immersed in a sand bath, heated for 14 hours at $75°$, and then heated for an additional 30 hours at $140°$ to insure reaction completion. No change in the mixture was observed during the heating process. The heating step can probably be eliminated. Into the vessel was condensed 20 mL of hexane at $-196°$. The mixture was warmed to room temperature and the solid was partially dissolved with shaking. Under nitrogen in the glove bag, the solution was filtered on a medium-porosity glass frit leaving light brown crystals and an orange filtrate. The filtrate was placed into a 50 mL round bottom flask, a stopcock adapter was connected to the flask, and the hexane was removed under reduced pressure on the vacuum line. An orange solid was obtained which was dissolved in a minimum amount of hexane and applied to a Florisil column under nitrogen in a large glove bag. The colored bands were eluted from the column with hexane, hexane-benzene mixtures (the benzene being continually more concentrated), and finally benzene. Five different fractions were obtained. The first two bands (faint yellow in color) were combined. The infrared spectrum of the solution was significantly different from the other fractions and was subsequently identified as the phosphine-substituted complex (See Results and Discussion). Light yellow crystals were obtained after removal of the solvent under reduced pressure. The crystals would not sublime, m.p. $76-80°$ (uncorrected) and were obtained in 22% yield. Anal. Calcd. for $MoP_6F_{12}C_{18}H_{30}$:

c, 28.57; H, 3.97; P, 24.60; MW, 756. Found: C, 30.36; H, 4.18;
P, 24.07; MW 772.

D. Reaction of $PF_2C_6H_{10}PF_2$ with Mn(I), Fe(O), and Co(O).

Photoreaction of $Mn(CO)_5Br$ with $PF_2C_6H_{10}PF_2$. Preparation of
$Mn(CO)_3Br(PF_2C_6H_{10}PF_2)$ and $Mn(CO)Br(PF_2C_6H_{10}PF_2)_2$.

0.2776 g (1.00 mmol) of freshly sublimed $Mn(CO)_5Br$ were placed into
a 50 mL Pyrex reaction vessel containing a Teflon-coated magnetic stir-
ring bar and a Teflon stopcock under nitrogen. The vessel was evacuated
on the vacuum line and 35 mL of hexane were condensed onto the solid,
together with 0.223 g (1.01 mmol) of $PF_2C_6H_{10}PF_2$ at -196°. The mixture
was warmed to room temperature and irradiated with magnetic stirring at
300 nm for 19.5 hours. Recovery of 1.8 equivalents of CO/equivalent of
$Mn(CO)_5Br$ was made by removing the vessel from the photoreactor and
measuring and removing the evolved CO on the vacuum line, the solution
being held at -196°. The solution was transferred to a 50 mL round
bottom flask under nitrogen. A stopcock adapter was connected to the
flask and the solvent was removed under reduced pressure on the vacuum
line. The resulting yellow-white solid was charged into a sublimation
apparatus under nitrogen. A small amount of unreacted $Mn(CO)_5Br$ was
removed by careful sublimation (high-vacuum) below 60°. Sublimation
was continued and yellow-orange crystals were obtained which sublimed at
70°, m.p. 96-98° (uncorrected) in 21% yield. The solid was identified as
$Mn(CO)_3Br(PF_2C_6H_{10}PF_2)$. Anal. Calcd. for $MnP_2F_4C_9H_{10}O_3Br$: C, 24.60;
H, 2.28; P, 14.12; MW, 439. Found: C, 24.80; H, 2.49; P, 13.96; MW, 436.
Light yellow crystals remained in the sublimation apparatus which did
not sublime up to 150°, m.p. 252-258° (uncorrected) in 20% yield. The

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solid was identified (ir and mass spec.) as $Mn(CO)Br(PF_2C_6H_{10}PF_2)$.
<u>Anal</u>. Calcd. for $MnP_4F_8C_{13}H_{20}OBr$: C, 25.87; H, 3.32; P, 20.56; MW, 603.
Found: C, 19.45; H, 3.82; P, 15.41; MW, 630.

<u>Photoreaction of</u> $Fe(CO)_5$ <u>and</u> $PF_2C_6H_{10}PF_2$. <u>Preparation of</u> $Fe(CO)_3$-
$(PF_2C_6H_{10}PF_2)$ <u>and</u> $Fe(CO)(PF_2C_6H_{10}PF_2)_2$.

0.166 g (0.847 mmol) of freshly distilled $Fe(CO)_5$ were condensed
into a 50 mL Pyrex reaction vessel equipped with a Teflon stopcock,
containing a Teflon-coated magnetic stirring bar, at -196°. 25 mL of
hexane and 0.184 g (0.836 mmol) of $PF_2C_6H_{10}PF_2$ were condensed onto the
$Fe(CO)_5$, the mixture was allowed to warm to room temperature, and the
vessel was placed into the photoreactor. The solution was irradiated
for 17 hours with magnetic stirring at 300 nm. Recovery of 1.7 equiva-
lents of CO/equivalent of $Fe(CO)_5$ was made by periodically removing the
vessel from the photoreactor and measuring and removing the evolved CO
on the vacuum line while the solution was maintained at -196°. The
solution which had turned from light yellow in color to orange-brown
during the reaction period, was transferred to a 50 mL round bottom
flask in the glove bag under nitrogen. A stopcock adapter was connected
to the flask and the solvent was removed under reduced pressure on the
vacuum line. The red-brown solid that was obtained was placed into a
sublimation apparatus. Sublimation (high-vacuum) of the solid at 55°
gave beige crystals, m.p. $75-77^\circ$ (uncorrected) in 16% yield identified
as the complex, $Fe(CO)_3(PF_2C_6H_{10}PF_2)$. <u>Anal</u>. Calcd. for $FeP_2F_4C_9H_{10}O_3$:
C, 30.00; H, 2.77; P, 17.22; MW, 360. Found: C, 29.99; H, 3.03; P, 16.66;
Mw, 344. Some of the solid did not sublime which was dissolved in a mini-
mum amount of hexane and applied to a Florisil column under nitrogen in

a large glove bag. A light yellow band was eluted with hexane and the solvent was removed under reduced pressure on the vacuum line in a 50 mL round bottom flask (connected by a stopcock adapter). A pale yellow solid was obtained which was identified as the monocarbonyl complex, $Fe(CO)(PF_2C_6H_{10}PF_2)_2$. Anal. Calcd. for $FeP_4F_8C_{13}H_{20}O$: C, 29.77; H, 3.82; P, 23.66; MW, 524. Found: C, 29.78; H, 3.99; P, 23.35; MW 518.

Reactions of $Co(CO)_8$ and $PF_2C_6H_{10}PF_2$.

In a typical experiment, 0.398 g (1.16 mmol) of freshly sublimed $Co_2(CO)_8$ were placed into a 100 mL round bottom flask containing a Teflon-coated magnetic stirring bar under nitrogen in a glove bag. A stopcock adapter was connected to the flask and the flask was evacuated on the vacuum line, the carbonyl being held at -196°. 20 mL of hexane were condensed into the flask, along with 0.270 g (1.23 mmol) of $PF_2C_6H_{10}PF_2$ at -196°. The mixture was allowed to warm to room temperature and was stirred magnetically overnight. Bubbles of CO gas were observed to evolve from the solution and a brown-yellow precipitate formed. Recovery of 1.4 equivalents of CO/equivalent of $Co_2(CO)_8$ was made by measuring and removing the CO on the vacuum line, the solution being held a -196°. The precipitate was separated from the solution by filtration on a medium-porosity glass frit in the glove bag. The solid was dried and stored under nitrogen. Anal. of the solid. Calcd. for $Co_2(CO)_6(PF_2C_6H_{10}PF_2)$ $[Co_2P_2F_4C_{12}H_{10}O_6]$: C, 28.46; H, 1.97; P, 12.35; MW, 506. Calcd. for $Co_2(CO)_4(PF_2C_6H_{10}PF_2)_2$ $[Co_2P_4F_8C_{16}H_{20}O_4]$: C, 28.66; H, 2.99; P, 18.15; MW, 670. Found: C, 22.16; H, 4.33; P, 16.87; MW, 690. The solvent of the filtrate was removed under reduced pressure on the vacuum line. The dark brown solid obtained was identified (ir) as unreacted $Co_2(CO)_8$.

In an attempt to control the speed of reaction, an experiment similar to that described above was performed. 0.361 g (1.06 mmol) of freshly sublimed $Co_2(CO)_8$ and 0.221 g (1.00 mmol) of $PF_2C_6H_{10}PF_2$ were allowed to react for 2.5 days with magnetic stirring at 0° in 45 mL of pentane. Recovery of 1.5 equivalents of CO/equivalent of $Co_2(CO)_8$ was made. A very air-sensitive brown precipitate was collected. <u>Anal</u>. Found: C, 20.86; H, 4.01; P, 17.05; MW, 667. The solid obtained by removing the solvent from the filtrate was again identified (ir) as unreacted $Co_2(CO)_8$.

<u>Reaction of</u> $(C_7H_8)_2Co_2(CO)_4$ <u>with</u> $PF_2C_6H_{10}PF_2$.

0.2563 g (0.619 mmol) of freshly prepared $(C_7H_8)_2Co_2(CO)_4$ were placed into a 100 mL round bottom flask containing a Teflon-coated magnetic stirring bar, under nitrogen in a glove bag. A stopcock adapter was connected to the flask, which was evacuated on the vacuum line. 30 mL of hexane and 0.274 g (1.25 mmol) of $PF_2C_6H_{10}PF_2$ were condensed onto the solid at -196°. Under nitrogen in the glove bag, the stopcock adapter was replaced with a reflux condenser connected to a nitrogen flow system. The mixture was refluxed for 6 hours with magnetic stirring. The reflux condenser was replaced with the stopcock adapter upon cooling, and all of the volatile material was removed under reduced pressure on the vacuum line. A brown solid was obtained which was dissolved in a few milliliters of hexane and filtered on a medium-porosity glass frit. The precipitate was collected and vacuum-dried. <u>Anal</u>. Calcd. for $Co_2(CO)_4(PF_2C_6H_{10}PF_2)_2$ [$Co_2P_4F_8C_{16}H_{20}O_4$]: C, 28.66; H, 2.99; P, 18.51; MW, 670. Found: C, 29.13; H, 4.81; P, 11.71; MW, 551. The filtrate from

above gave a dark brown solid after removal of the solvent under reduced pressure on the vacuum line, which could not be identified.

E. Reactions of $PF_2C_6H_{10}PF_2$ with Ni(II), Pd(II), and Pt(II).

   Reaction of $NiCl_2$ and $PF_2C_6H_{10}PF_2$.

a) 0.145 g (1.12 mmol) of anhydrous $NiCl_2$ were placed into a 50 mL round bottom flask containing a Teflon-coated magnetic stirring bar under nitrogen in a glove bag. A stopcock adapter was connected to the flask and the flask was evacuated on the vacuum line. 15 mL of dichloromethane and 0.270 g (1.23 mmol) of $PF_2C_6H_{10}PF_2$ were condensed onto the solid at -196°. Under nitrogen, the stopcock adapter was replaced with a reflux condenser. The mixture was refluxed for 67 hours with magnetic stirring under nitrogen. After the solution had cooled to room temperature, it was filtered on a medium-porosity glass frit in the glove bag. Approximately 0.13 g of yellow solid were collected which was identified as unreacted $NiCl_2$. Unreacted phosphine was recovered from the filtrate by vacuum distillation. A trace of yellow oil was obtained after removal of all volatiles. Anal. Calcd. for $NiP_4F_8C_{12}H_{20}Cl_2$: C, 25.26; H, 3.51; P, 21.75; MW, 570. Found: C, 31.82; H, 5.37; P, 30.11; MW, 579.

b) Due to the low yield of a product of the above reaction, the reaction was attempted using a mixed solvent system as described below: 0.104 g (0.80 mmol) of $NiCl_2$ were placed into a 100 mL round bottom flask under nitrogen. A stopcock adapter was connected to the flask and the flask was evacuated on the vacuum line. 5 mL of dry, air-free, absolute ethanol was condensed into the flask at -196°. The mixture was warmed to room temperature and stirred to dissolve the $NiCl_2$. Under

nitrogen in the glove bag, a previously prepared solution of 0.189 g

(0.859 mmol) of $PF_2C_6H_{10}PF_2$ and 20 mL of dichloromethane, was added

dropwise to the ethanolic solution of $NiCl_2$. The mixture was magnet-

ically stirred overnight resulting in the formation of a yellow solution,

although a small amount of undissolved and unreacted $NiCl_2$ was visible

in the bottom of the flask. The mixture was filtered on a medium-

porosity glass frit in the glove bag. The yellow, unreacted $NiCl_2$ was

washed with CH_2Cl_2, dried, and collected in 50% yield. The yellow fil-

trate was placed into a 50 mL round bottom flask joined to a stopcock

adapter and the solvents were removed under reduced pressure on the

vacuum line. A yellow-orange oil was obtained which was dissolved in

a minimum amount of CH_2Cl_2 and applied to a Florisil column under nitro-

gen in a large glove bag. A yellow band was eluted with ethanol. The

ethanol was removed under reduced pressure on the vacuum line, leaving a

small quantity of a light yellow oil, identified (ir and mass spec.) as a

nickel chloride-phosphine complex (See Results and Discussion).

Reaction of $PdCl_2$ and $PF_2C_6H_{10}PF_2$.

0.159 g (0.896 mmol) of $PdCl_2$ were placed into a 50 mL round bottom

flask (containing a Teflon-coated magnetic stirring bar) under nitrogen

in a glove bag. A stopcock adapter was connected to the flask which was

evacuted on the vacuum line. 10 mL of dichloromethane and 0.210 g

(0.955 mmol) of $PF_2C_6H_{10}PF_2$ were condensed into the flask at $-196°$. The

stopcock adapter was replaced with a reflux condenser in a glove bag

and the mixture was refluxed under nitrogen with magnetic stirring for

1.5 hours. The solution had turned orange in color during the reaction

indicating product formation. The solution was filtered on a medium-

porosity glass frit leaving a finely-divided red solid (0.05 g),

identified as unreacted $PdCl_2$. The filtrate was placed into a clean
50 mL round bottom flask and the dichloromethane was removed under
reduced pressure on the vacuum line. An orange crystalline solid was
obtained (0.19 g), dec. 164°. The solid was dissolved in a minimum
amount of dichloromethane and applied to a Florosil column under nitro-
gen in a large glove bag. An orange-brown band was eluted with a 5%
methanol-dichloromethane solution. The solution collected was placed
into a round bottom flask connected to a stopcock adapter an the sol-
vent was removed under reduced pressure on the vacuum line. An orange-
red solid was obtained which was oven and vacuum dried over an 8 hour
period to remove all traces of dichloromethane which was believed to be
solvated to the complex. Anal. C, 23.26; H, 3.80; P, 18.16; Cl, 9.56;
MW, 800.

Reaction of $PtCl_2$ and $PF_2C_6H_{10}PF_2$.

0.266 g (1.00 mmol) of $PrCl_2$ were placed into a 50 mL round bottom
flask (containing a Teflon-coated bar magnet) under nitrogen in a glove
bag. Attached to the flask was a stopcock adapter and the flask was
evacuated on the vacuum line. 20 mL of dichloromethane and 0.238 g
(1.08 mmol) of $PF_2C_6H_{10}PF_2$ were condensed in to the flask at -196°. The
stopcock adapter was replaced with a reflux condenser in the glove bag.
The mixture was refluxed under nitrogen with magnetic stirring for 3 days.
Unreacted, green-brown $PtCl_2$ (0.10 g) was filtered from the solution on
a medium-porosity glass frit. Removal of the solvent from the orange
filtrate under reduced pressure on the vacuum line resulted in a yellow-
orange solid. The solid was dissolved in a minimum amount of CH_2Cl_2 and
applied to a Florisil column under nitrogen in a large glove bag. A
dominant yellow band was eluted with a 5% methanol-dichloromethane

solution. The yellow solution was placed into a round bottom flask connected to a stopcock adapter and the solvent was removed under reduced pressure on the vacuum line. The yellow-orange solid was vacuum and oven dried over a period of 3 days in an effort to remove all traces of dichloromethane which was believed to be solvated (mass spec.).

Anal. C, 20.19; H, 3.35; P, 14.92; Cl, 8.31; MW, 1018.

F. Reactions of $PF_2C_2H_4PF_2$.

Reaction of $Ni(CO)_4$ and $PF_2C_2H_4PF_2$. Preparation of $[Ni(PF_2C_2H_4PF_2)_2]_x$.

In a typical reaction, 2.20 mmol of $PF_2C_2H_4PF_2$ were condensed at $-196°$ into a 200 mL reaction bulb connected via a stopcock to a 500 mL reaction bulb in which 0.76 mmol of $Ni(CO)_4$ were condensed. The reactants were allowed to warm to room temperature (both reactants were completely vaporized) and the connecting stopcock opened. White clouds formed in the larger bulb as the reactants were allowed to react in the gas phase for approximately 20 minutes. When the white clouds dissipated, a colorless oil began to be deposited on the vessel walls. After standing overnight, the oil solidified and turned light brown in color. The noncondensible CO that evolved during the reaction was removed with pumping while the vessel was chilled to $-196°$. The solid product was collected by breaking the vessel open under nitrogen in the glove bag.

Anal. Calcd. for $NiP_4F_8C_4H_8$: C, 12.30; H, 2.05; Ni, 15.03. Found: C, 12.92; H, 2.15; Ni, 14.08.

Reaction of Ni(CO)$_4$ and PF$_2$C$_2$H$_4$PF$_2$ in Benzene.

0.47 mmol of Ni(CO)$_4$ and 1.39 mmol or PF$_2$C$_2$H$_4$PF$_2$ were condensed into a 50 mL Pyrex vessel containing ca 20 mL of dry, air-free benzene at -196°. The mixture was allowed to warm to room temperature and was occasionally shaken by hand over a period of 13 hours. The mixture was warmed to 40° and occasionally shaken over a period of 2.5 hours to insure reaction completion. At periodic intervals, the mixture was chilled to -196° and the CO liberated during the reaction was measured and removed on the vacuum line. 3.36 equivalents of CO/equivalent of of Ni(CO)$_4$ were recovered in this manner. The solution was transferred to Schlenk-ware containing a cold finger under nitrogen. The apparatus was transferred to the vacuum line and the solvent was removed under reduced pressure leaving a brown solid. Cold tap water was allowed to flow through the cold finger and a minute quantity of solid was sublimed onto the finger at 100°. The gummy solid that did not sublime was stirred with CHCl$_3$, resulting in a little of the solid being dissolved. This mixture was filtered on a medium-porosity glass frit. The filtered solid, which could not be dissolved in even the most polar organic solvents, was vacuum dried and stored under nitrogen.

Reaction of C$_7$H$_8$Mo(CO)$_4$ and PF$_2$C$_6$H$_{10}$PF$_2$. Preparation of Mo(CO)$_4$-PF$_2$C$_6$H$_{10}$PF$_2$).

0.160 g (0.533 mmol) of freshly sublimed C$_7$H$_8$Mo(CO)$_4$ were placed into a 200 mL reaction vessel containing a Teflon stopcock under nitrogen. After the vessel was evacuated on the vacuum line, ca 25 mL of dry, air-free hexane were condensed onto the solid, together with 0.48 mmol of PF$_2$C$_6$H$_{10}$PF$_2$ at -196°. On warming to room temperature and heating to 50° overnight, a nearly colorless solution resulted. Under nitrogen,

the mixture was transferred to a 50 mL round bottom flask connected to a stopcock adapter. The hexane was removed under reduced pressure until only 3-4 mL of solution remained. In a large glove bag under nitrogen, the solution was applied to a Florisil column and eluted with hexane. Elutions (colorless) were collected until the yellow band due to un- reacted $C_7H_8Mo(CO)_4$ was about to elute. The colorless fraction was checked for CO and PF stretching bands in the solution infrared spectrum. Upon verification that these groups were present, the solvent was removed under reduced pressure depositing white crystals, m.p. 48-50° (uncor- rected) in 26% yield. Anal. Calcd. for $MoP_2F_4C_6H_4O_4$: C, 19.25; H, 1.07; P, 16.58; MW, 374. Found: C, 19.46; H, 1.20; P, 16.22; MW, 371.

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APPENDIX

Cotton-Kraihanzel CO force constants are calculated in this study from appropriate secular equations.[23] For molecules of the type, cis-$M(CO)_4L$, where M = Cr, Mo, and W, exhibiting C_{2v} symmetry, the following equations are given:

$$\begin{vmatrix} \mu(k_2 + 2k_i) - \lambda_{A_1} & 2\mu k_i \\ 2\mu k_i & \mu(k_1 + k_i) - \lambda_{A_1} \end{vmatrix} = 0 \qquad (1)$$

$$\lambda_{B_1} = \mu(k_2 - 2k_i) \qquad (2)$$

$$\lambda_{B_2} = \mu(k_1 - k_i) \qquad (3)$$

[where the force constants are in dynes cm^{-1}; μ (reciprocal of the reduced mass of CO) = 0.14583; $\lambda = (5.8890 \times 10^{-2})\nu^2$, where ν is the frequency of the appropriate mode in cm^{-1}.]

The force constants were calculated by choosing an arbitrary value of k_i, using equations 2 and 3 to determine k_1 and k_2, and then solving the determinant (1). If the operation did not give a value of zero for the determinant, than a different value was chosen for k_i until, by trial and error, the best force constants were obtained from the frequencies used.

For the molecule, cis-$Mo(CO)_2(PF_2C_6H_{10}PF_2)$, which exhibits C_{2v} symmetry also, the equations from Cotton and Kraihanzel[23] are:

$$\lambda_{A_1} = \mu(k + k_i) \qquad (4)$$

$$\lambda_{B_1} = \mu(k - k_i) \qquad (5)$$

In this case, the force constants can be obtained by solving the two equations simultaneously using the frequencies of the modes A_1 and B_1.

For the molecules, fac-LMn(CO)$_3$Br, where L = PF$_2$C$_6$H$_{10}$PF$_2$ and Ph$_2$PC$_2$H$_4$PPh$_2$, which exhibit C$_s$ symmetry, the equations reported by Cotton[38] are in error, so the equations given by Dalton, et. al.,[39] were used:

$$\begin{vmatrix} k_2 - \lambda_A/\mu & 2kc' \\ 2kc' & k_1 + kc - \lambda_A/\mu \end{vmatrix} = 0 \qquad (6)$$

$$\lambda_B = (k_1 = kc)\mu \qquad (7)$$

$$kc/kc' = 0.81 \qquad (8)$$

The force constants were calculated by choosing an arbitrary value of k$_c$ which fixed the value of k$_{c'}$ (Equation 8) and k$_1$ (Equation 7), and then solving the determinant (6). If the operation did not give a value of zero for the determinant, then different values were chosen for k$_c$ until, by trial and error, the best force constants were obtained from the frequencies used.

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