PART I

SUBSTITUTED GROUP VIB METAL CARBONYL COMPLEXES OF DIMETHYL METHYLPHOSPHONITE AND BIS (DIMETHYLAMINO) METHYLPHOSPHINE

PART II

THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME CYANOPHOSPHINES AND THEIR CHROMIUM AND MOLYBDENUM CARBONYL COMPLEXES

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This is to certify that the

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Part I. Substituted Group VIB Metal Carbonyl Complexes of Dimethyl MethylPhosphonite and Bis(Dimethylamino)Methylphosphine. Part II. The Synthesis and Spectroscopic Properties of some Cyanophosphines and their Chromium and Molybdenum Carbonyl Complexes.

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Major professor

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ABSTRACT

PART I

SUBSTITUTED GROUP VIB METAL CARBONYL COMPLEXES OF DIMETHYL METHYLPHOSPHONITE AND BIS(DIMETHYLAMINO)METHYLPHOSPHINE

By

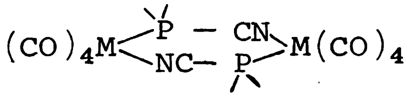
Christopher E. Jones

The syntheses of substituted metal carbonyls of the type $[M(CO)_{6-X}L_X]$ where M = Cr, Mo, and W and where X = 1, 2, or 3 for $L = CH_3P(OCH_3)_2$, and where X = 1 or 2 for $L = CH_3P(N(CH_3)_2)_2$ are described. The infrared data in the CO stretching region and CO stretching force constants are discussed and an order is proposed for the π-acceptor strength of the ligands: $P(OCH_3)_3 \gtrsim CH_3P(OCH_3)_2 > (CH_3)_3P > CH_3P(N(CH_3)_2)_2 > P(N(CH_3)_2)_3$. The proton nmr data is also discussed for these complexes and tentative assignment is made for the sign of $^2J_{PH}$ (coupling of phosphorus to the methyl protons). In the di- and trisubstituted complexes, phosphorus-phosphorus coupling is observed in the proton nmr spectra with the absolute value of $^2J_{PP}$ being larger in the <u>trans</u> isomer than in the <u>cis</u> isomer for a given compound and larger in Mo and W compounds than in analogous Cr compounds. These spectral data are used to help interpret the nature of the metal-phosphorus bond and to determine the stereochemistry of the complexes which are prepared.

Christopher E. Jones

PART II

THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME CYANOPHOSPHINES AND THEIR CHROMIUM AND MOLYBDENUM CARBONYL COMPLEXES

A rapid and easy method of preparation is presented for the routine synthesis of compounds of the type $R_xP(CN)_{3-x}$ (where x = 0, 1, or 2 and R = Ph-, CH_3O-, C_2H_5O-, $(CH_3)_2N$-, or CH_3-). The infrared, proton nmr, phosphorus-31 nmr, and mass spectral data are presented and discussed. From this series of cyanophosphines, the reactions of the compounds Ph_2PCN, $PhP(CN)_2$, $(CH_3)_2PCN$, $(C_2H_5O)_2PCN$, and $[(CH_3)_2N]_2PCN$ with $M(CO)_4C_7H_8$ (M = Cr or Mo and C_7H_8 is norbornadiene) have been investigated. From these reactions, yellow crystalline complexes of the form $[M(CO)_4L]_2$, where L is a bridging cyano-phosphine ligand, have been isolated Their formulation is based on analytical data and their structure is proposed as  $(CO)_4M\left<\begin{matrix}P - CN\\ NC - P\end{matrix}\right>M(CO)_4$ on the basis of the infrared and proton nmr spectral data. These bridged complexes react further with another molar equivalent of ligand (L) or a different ligand (L') to yield complexes of the type $M(CO)_4L_2$ and $M(CO)_4LL'$. The products from these reactions further support the proposed structure for the bridged species. The proton nmr, infrared, and some of the mass spectral data of these bridged complexes are also presented and discussed.

PART I

SUBSTITUTED GROUP VIB METAL CARBONYL COMPLEXES OF DIMETHYL METHYLPHOSPHONITE AND BIS(DIMETHYLAMINO)METHYLPHOSPHINE

PART II

THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME CYANOPHOSPHINES AND THEIR CHROMIUM AND MOLYBDENUM CARBONYL COMPLEXES

By

Christopher E. Nelson Jones

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To Gail

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I would like to extend my appreciation to Dr. Kenneth J. Coskran, for his interest, patience, and encouragement during this investigation.

I am deeply grateful to my wife, Gail, for her inspiration and unrelenting patience. I wish, also, to thank my parents, Mr. and Mrs. Theodore E. Jones of Traverse City, Michigan for their assistance, guidance, and encouragement during my entire educational career.

TABLE OF CONTENTS

PART I

PART II

TABLE OF CONTENTS (Continued).

LIST OF TABLES

PART I

PART II

LIST OF FIGURES

PART I

LIST OF FIGURES (Continued).

PART II

INTRODUCTION

In recent years, metal carbonyl chemistry has been so thoroughly investigated that to attempt any sort of comprehensive review, even in the specific area of group VIB carbonyl chemistry, which is of particular interest here, would be somewhat futile. There have been several reviews in the general area of metal carbonyl chemistry. An excellent review of transition metal complexes of phosphines, arsines, and stibines has been published by Booth (1); reviews of cyclopentadienyl metal carbonyls have been published by Wilkinson and Cotton (2), Fischer and Fritz (3,4), Pauson (5), and Zeiss (6); ultraviolet-induced reactions of metal carbonyls have been discussed by Strohmeier (7); both Abel (8) and Hieber (9) have published very good reviews of metal carbonyls; and a very extensive review of the group VIB metal carbonyl derivatives has been presented by Dobson, Stolz, and Sheline (10). Therefore, except where such information is useful in elucidating the work presented here, repetition of these reviews will be avoided.

A great deal of the work on tertiary phosphorus and amine complexes of the transition metal subgroup VIB (Cr, Mo, W) has been done in the last decade. Emphasis has been placed both on the synthesis of such complexes, and on the nature of the metal ligand bonding. Metal ligand bonding has been studied by means of infrared, nmr, and other spectral techniques. Infrared spectroscopy has by far received the most widespread attention in studying metal carbonyl complexes. The number and shape of the infra-red bands in the carbon-oxygen stretching region can be used to determine the degree of substitution and the geometry of the metal complexes. Shifts in the CO stretching frequency upon substitution can be used to study metal-ligand bonding, but a more rewarding approach involves the use of CO stretching force constants. In 1962 Cotton and Kraihanzel (11) published a rather straight-forward set of secular equations for calculating these force constants for six-coordinate metal carbonyls of octahedral symmetry. These equations were used to begin a comparative study of metal-carbonyl, metal-phosphorus, and metal-nitrogen bonding in complexes of the type $M(CO)_{6-X}L_X$, where M = Cr, Mo, or W; X = 0,1,2, or 3; and L = tertiary phosphorus or amine ligands (11,12,13). Although the carbonyl stretching frequencies had been used previously with some success to discuss the nature of metal ligand bonding, the use of force constants greatly improved the interpretations of the infrared data.

The useful application of nmr techniques to transition metal complex chemistry has been limited somewhat to recent years. Before 1963, proton nmr spectroscopy was used only sparingly in this area. Reports of nmr spectra of metal complexes generally included only changes in chemical shifts

and coupling constants of the ligands upon complexation. In 1963 Jenkins and Shaw (23) observed the phenomenon of "virtual coupling" of phosphorus atoms in the proton nmr spectra of trans-$PdI_2[P(CH_3)_2(C_6H_5)]_2$ and related complexes. They used this virtual coupling to determine the structures of these palladium complexes. The proton nmr spectra of some of the complexes which Jenkins and Shaw investigated displayed a methyl resonance consisting of three lines with the central line varying in intensity from complex to complex. A doublet, due to the splitting of the protons by phosphorus, would have been the expected resonance, however, the resonances of each complexed ligand are further coupled to the phosphorus atom of the ligand cis or trans to it in the complex. The resulting spectrum may appear as a 1:2:1 triplet as is found for cases of large phosphorus-phosphorus coupling, and as was observed for the trans complexes above. If the phosphorus-phosphorus coupling is weak, the intensity of the central peak may be so small that the spectrum appears as a doublet. The cis complexes of palladium were found to give only doublets in the methyl region of the proton nmr. Therefore, Jenkins and Shaw proposed that the geometries of disubstituted palladium complexes could be ascertained from the magnitude of the phosphorus-phosphorus coupling (i.e. the intensity of the third peak in the methyl resonances of the proton nmr). Later in 1963 King (37) reported similar spectra for metal carbonyl complexes of tris(dimethylamino)phosphine, and made

1.

some rough comparisons of the strength of virtual coupling in going from one metal to another. In 1965 Verkade <u>et al</u>. (48) reported more metal-phosphorus complexes which demonstrated this phenomenon, and presented some crude estimates of ^{31}P-^{31}P coupling strengths. They also observed coupling in some complexes of <u>cis</u> geometry and made further comparisons between metals. Verkade's work was followed by a theoretical interpretation by Harris (16,17) of the virtual coupling of phosphorus atoms in the proton nmr spectra of these systems. Complexes which have two or more phosphorus ligands bound to a metal are classified as $X_nAA'X'_n$ type systems, where X and A represent the protons and phosphorus, respectively of one ligand bound to a metal and X' and A' represent the protons and phosphorus, respectively, of a second ligand bound to the same metal. The subsequent development and application of this theory by Verkade (18, 19,20,21) and Shaw (22,27) greatly improved the interpretation of proton nmr for transition metal complexes. Because of their work, proton nmr became a useful tool in the determination of structures of transition metal complexes and in the study of metal-phosphorus bonding.

Phosphorus-31 nmr has also been applied to metal complex chemistry in recent years. In 1961, Meriwether and Leto (41) reported ^{31}P chemical shifts of metal complexes. In 1966 the ^{31}P chemical shifts for several phosphine substituted tungsten carbonyl complexes were reported by Grim

<u>et al</u>. (42), and for molybdenum carbonyl complexes by Lenzi and Poilblanc (43). Bertrand <u>et al</u>. (19) also reported ^{31}P data for several metal carbonyl complexes, and other authors (44,45,49) lent interpretation and data to this area of nmr spectroscopy.

Relatively little use has been made of ultraviolet and visible spectra in studies of the group VIB carbonyl complexes. In 1969 Abel <u>et al</u>. (28) studied the ultraviolet and visible spectra of the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, $W(CO)_6$, and $Re(CO)_6^+$, and discussed the results in terms of metal-ligand π-bonding.

A significant amount of the work involving chromium, molybdenum, and tungsten carbonyl complexes of phosphorus and nitrogen donor ligands, has been concerned with the nature of metal-ligand bonding. The accepted metal-carbon bonding scheme in metal carbonyls is a "synergic" one in which bonding is accomplished through σ-donation of a lone pair of electrons from the carbon atom to an empty d orbital of the metal (Figure 1) in conjunction with a back donation of electron density from filled metal d-orbitals to vacant p-π^* antibonding orbitals on the carbonyl group (Figure 2).

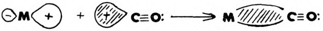


Figure 1.- σ-bonding through donation of carbon lone pair to an empty metal d-orbital (39).

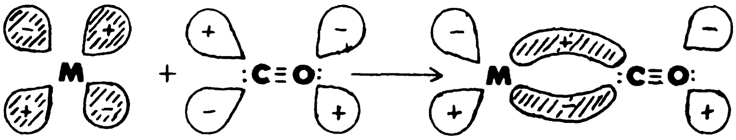


Figure 2.- π-bonding through donation of metal d- electrons to CO antibonding orbitals (39).

Bonding between a metal and a coordinately bound ligand can take place, in general, in one of three ways. The bonding can invoke a σ-bond (ligand to metal donation) reinforced by a d-π to p-π^* metal to ligand π-bond as stated for the carbonyls. A second method of bonding involves back donation of metal d-π electron density to empty ligand d-π orbitals in addition to the coordinate σ-bond, and is the bonding system generally accepted for phosphorus-metal coordinate bonding. The third method is that believed to exist in nitrogen-metal coordinate bonding which uses only a σ-bond and little or no π-bonding.

In octahedral (or very nearly octahedral) metal complexes, the metal σ-orbitals and the metal π-orbitals are essentially separate with little or no mixing, and therefore, can be treated independently ("symmetry factoring") (11). When this idea is applied to metal carbonyl systems such as $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ and their derivatives, it is possible to discuss metal to ligand π-bonding in terms of carbonyl stretching frequencies. Since metal d-π to carbonyl p-π^* donation involves an antibonding orbital on

the CO group, the carbon oxygen bond should be weakened, and should cause a lower energy infrared stretching frequency to be observed. This involvement of CO antibonding orbitals is borne out by a comparison of free CO, which has a stretching frequency of 2133 cm^{-1} (10), with group VIB metal carbonyls which have stretching frequencies at approximately 2000 cm^{-1} (10). This assumption that the shift to a lower stretching frequency is a result of donation of metal electron density into the CO antibonding orbitals is also reflected in the isoelectronic series, $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$ which exhibit CO stretching frequencies of 2096, 2000, and 1859 cm^{-1}, respectively (15). These observations substantiate that the stretching frequency is dependent on the available metal electron density (reflected by the net charge on the metal).

Since all of the carbonyl groups bonded to a metal are essentially in competition with each other for metal π-electron density, if a CO group is replaced by a ligand of weaker π-accepting ability, the remaining CO groups should withdraw more electron density into their p-π^* antibonding orbitals. This withdrawal in turn should weaken the CO bond and produce a lower energy infrared stretching frequency. Such a shift to lower energy is in fact observed when carbonyls are replaced by phosphorus and nitrogen ligands, unless the ligand is PF_3, which appears to be comparable to or better than CO in π-accepting ability (13,38). The idea that there

is an increase in the donation of metal d-π electron density to the remaining carbonyl groups in these substituted metal carbonyls is also supported by the available information on metal-carbon bond strengths and bond lengths in group VIB carbonyls. Adams (29) and others (30,31) have provided some information on metal carbon stretching frequencies, ν(M-C), and metal-carbon-oxygen deformation frequencies, δ(MCO), for metal carbonyls and their derivatives. Verkade et al. (32,33) investigated similar infrared data for a variety of substituted metal carbonyls and made correlations to the π-bonding ability of the various ligands as compared to a carbonyl group. As poorer π-accepting ligands replaced carbonyl groups, the metal-carbon stretching frequency increased. Thus, as the CO bond gets weaker, the M-C bond gets stronger as a result of the increased metal-carbonyl π-bonding. Problems with this hypothesis arise from the difficulty in assignment of these low energy infrared absorptions as well as from the difficulty which arises from the coupling of ν(M-C) and δ(M-C-O) (10). An indication as to the validity of this interpretation of the changes in the metal-carbon stretching frequencies could be obtained from crystal structure data, since increases in metal-carbon multiple bonding should be accompanied by a shortening of the M-C bond. Unfortunately there are few structural data available on these systems. Crystal structures have been reported for $Cr(CO)_6$ (34) and for $Cr(CO)_3(PH_3)_3$ (35),

and the average metal-carbon bond distance indeed does shorten from 1.909 ± 0.003Å for $Cr(CO)_6$ to 1.84 ± 0.01Å for $Cr(CO)_3(PH_3)_3$. Even more conclusive are the structural determinations by Grim et al. (46) of $Cr(CO)_5[P(C_6H_5)_3]$ and $Cr(CO)_5[P(OC_6H_5)_3]$. The Cr-C distances in both of these complexes are shorter than the corresponding distances in $Cr(CO)_6$. In addition, if changes in the strength of metal-carbonyl π-bonding are the cause of changes observed in the infrared spectra, one would predict that Cr-C distances which are trans to the phosphorus ligand should be shorter than Cr-C distances for CO's cis to phosphorus ligands and trans to other CO's. Also C-O distances for CO's trans to a phosphorus ligand should be longer than those cis to a phosphorus ligand. And lastly, since infrared data predict that $P(OC_6H_5)_3$ is a better π-acceptor than $P(C_6H_5)_3$, the Cr-P distances and the C-O distances should be shorter, and all of the Cr-C distances should be longer for the $P(OC_6H_5)_3$ complex than for the $P(C_6H_5)_3$ complex. Everyone of these predictions is found to hold. It is of further interest to note that a comparison of the bond lengths of these two complexes with those of $Cr(CO)_3(PH_3)_3$ also fits the prediction by infrared data that the order of π-accepting ability for these ligands is $P(OC_6H_5)_3 > P(C_6H_5)_3 > PH_3$.

Some authors (30, 36, 47) have argued that the observable changes in the spectra of group VIB carbonyl complexes upon substitution of a carbonyl group with a ligand of

weaker π-accepting ability can and should be attributed to σ-bonding effects. Brown and Darensbourg (36) presented an interesting argument to this effect based on infrared intensities, frequency measurements, and dipole moment derivatives. However, both the far infrared data and the slight bit of structural data which are available are in direct contradiction to their suggestion.

Several substituted metal carbonyl complexes of the type $[M(CO)_{6-x}L_x]$, where M = Cr, Mo, or W, x = 1, 2, or 3, and L = a tertiary phosphorus ligand (in particular, $P(OCH_3)_3$ (14), $P(CH_3)_3$ (14,33), and $P(N(CH_3)_2)_3$ (37)) have been investigated previously using infrared and proton nmr techniques. However, no study has been made on substituted metal carbonyls with ligands of the type CH_3PY_2 and $(CH_3)_2PY$, where Y = $-OCH_3$ or $-N(CH_3)_2$. In this work, group VIB hexacarbonyl complexes of dimethyl methylphosphonite, $CH_3P(OCH_3)_2$, and bis(dimethylamino)methylphosphine, $CH_3P(N(CH_3)_2)_2$, are reported. Although the proton nmr spectra of metal complexes of $P(OCH_3)_3$ (20) and $P(N(CH_3)_2)_3$ (37) have been reported, the invariance of the chemical shifts and coupling constants has prevented interpretation in terms of phosphorus metal bonding. Because of the closer proximity of the methyl protons to the phosphorus atom in the ligands used in this work, meaningful changes in the nmr spectra can be observed and correlated with infrared data to obtain information about the metal phosphorus bond.

Cotton and Kraihanzel (11) type force constant calculations have been combined with the proton nmr results to help explain the stereochemistry and bonding in various substituted group VIB metal carbonyls.

EXPERIMENTAL SECTION

The infrared spectra were obtained on a Perkin-Elmer Model 225 grating spectrophotometer. Sodium chloride optics were used and, in all cases, hexane was used as a solvent. Proton nmr spectra were taken in chloroform solutions on a Varian Associates Model A-56/60-D instrument with tetramethylsilane as an internal standard. The phosphorus nmr spectra were obtained on a Varian associates Model DA-60 spectrometer at 24.29 MHz and are referenced to 85% *ortho*-phosphoric acid as an external standard. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The *n*-isomers of pentane, hexane, and octane were used where these solvents are involved. Melting points were taken in glass capillaries using a Hoover melting point apparatus.

Materials.- The molybdenum and tungsten hexacarbonyls were purchased from Pressure Chemical Co., and chromium hexacarbonyl was purchased from Strem Chemical Co. (All hexacarbonyls were used without purification.) The ligands, dimethyl methylphosphonite ($CH_3P(OCH_3)_2$) and *bis*(dimethylamino)methylphosphine ($CH_3P(N(CH_3)_2)_2$), were prepared according to previously described methods (51). Purification

was achieved by vacuum distillation at the reported temperatures. Molybdenum norbornadiene tetracarbonyl (52), molybdenum mesitylene tricarbonyl (53), tungsten mesitylene tricarbonyl (53,54), and chromium cycloheptatriene tricarbonyl (52) were also prepared as described elsewhere. Acetonitrile pentacarbonyl tungsten and cis-bis(acetonitrile)-tetracarbonyl tungsten were prepared by a modification of previously described methods (55). These complexes were prepared by irradiation with ultraviolet light (Hanovia Lamp 654-A10) in a quartz tube for 2 and 5 hours for the mono- and disubstituted species, respectively. They were identified by their infrared spectra (55); no further purification was performed.

(Dimethyl methylphosphonite)pentacarbonylchromium, $[(CH_3)(CH_3O)_2PCr(CO)_5]$.- A magnetically stirred mixture of 2.1 g (9.5 mmole) of chromium hexacarbonyl and 1.0 g (9.2 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of octane was caused to reflux for 12 hr under nitrogen. The solution was then allowed to cool to room temperature and concentrated under vacuum to about 2 ml. Approximately 5 ml of pentane was added, and fractional crystallization of this solution in a dry ice-isopropyl alcohol bath gave first, $Cr(CO)_6$ and $((CH_3)(CH_3O)_2P)_2Cr(CO)_4$ (both identified by their infrared spectra), and then the white, crystalline $(CH_3)(CH_3O)_2PCr(CO)_5$. The solvent was decanted, and when the solid (mp 6°) was warmed to room temperature a yellow liquid product

remained. Repeated fractional crystallizations gave the pure product, and any remaining solvent was removed under vacuum. Anal. Calcd. for $C_8H_9PCrO_7$: C, 32.00; H, 3.00; P, 10.03. Found: C, 32.20; H, 3.15; P, 10.57.

(Bis(dimethylamino)methylphosphine)pentacarbonylchromium, $[(CH_3)((CH_3)_2N)_2PCr(CO)_5]$.- A magnetically stirred mixture of 3.0 g (13 mmole) of chromium hexacarbonyl and 1.8 g (13 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of octane was caused to reflux for 15 hr under nitrogen. The resulting solution was concentrated under vacuum to about 2 ml of a brown liquid. Five milliliters of pentane was added, and the solution, when cooled to -78°, yielded pale yellow crystals of $(CH_3)((CH_3)_2N)_2PCr(CO)_5$, mp 74-76°. The pentane was then decanted, and any remaining solvent was removed under vacuum. Vacuum sublimation at about 100° and 1 torr produced pale yellow crystals of the complex. Anal. Calcd. for $C_{10}H_{15}N_2PCrO_5$: C, 36.80; H, 4.60; P, 9.50. Found: C, 36.61; H, 4.73; P, 9.61.

cis-Bis(dimethyl methylphosphonite)tetracarbonylchromium, $[((CH_3)(CH_3O)_2P)_2Cr(CO)_4]$.- A magnetically stirred mixture of 5.0 g (9.2 mmole) of chromium hexacarbonyl and 2.1 g (20 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of octane was caused to reflux for 24 hr under nitrogen. The solution was concentrated to about 10 ml under vacuum, and cooled in a -78° bath, which caused precipitation of white, needlelike

crystals of cis-$((CH_3)(CH_3O)_2P)_2Cr(CO)_4$, mp 75-76°. Recrystallization was achieved in pentane. Anal. Calcd. for $C_{10}H_{18}P_2CrO_8$: C, 31.60; H, 4.74; P, 16.32. Found: C, 31.70; H, 4.87; P, 16.60. The trans isomer of $((CH_3)(CH_3O)_2P)_2Cr(CO)_4$ was observed (infrared spectra) after several recrystallizations. It was not, however, produced directly from the reaction of the carbonyl and ligand.

trans-Bis(bis(dimethylamino)methylphosphine)tetracarbonylchromium, $[((CH_3)((CH_3)_2N)_2P)_2Cr(CO)_4]$.- A magnetically stirred mixture of 5.0 g (9.1 mmole) of chromium hexacarbonyl and 2.5 g (19 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of octane was caused to reflux for 28 hr under nitrogen to give a brown colored solution. After it had cooled to room temperature, this solution was filtered. The filtrate, when further cooled in a -78° bath, yielded yellow crystals. The octane was decanted, and recrystallization from pentane gave yellow, needlelike crystals of trans-$((CH_3)((CH_3)_2N)_2P)_2$-$Cr(CO)_4$, mp 88-90°. Anal. Calcd. for $C_{14}H_{30}N_4P_2CrO_4$: C, 38.89; H, 6.95; P, 14.35. Found: C, 38.82; H, 6.89; P, 14.44.

Tris-(dimethyl methylphosphonite)tricarbonylchromium, $[((CH_3)(CH_3O)_2P)_3Cr(CO)_3]$.- A mixture of 0.3 g (1.0 mmole) of chromium cycloheptatriene tricarbonyl and 0.4 g (3.7 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of methylcyclohexane was caused to reflux for 1 hr during which the initially dark

red solution gradually turned to light yellow. This solution was then cooled to room temperature and filtered. The solvent was removed under vacuum and about 5 ml of octane was added to the oily residue. When this solution was cooled in a -78° bath, the oily residue formed again. After the solvent had been decanted, the residue was again dissolved in octane and cooled at -20° for 2 hr before the very pale yellow mixture of *fac*- and *mer*-$((CH_3)(CH_3O)_2P)_3$-$Cr(CO)_3$, mp 152-155°, was produced. The product was recrystallized from pentane. *Anal.* Calcd. for $C_{12}H_{27}P_3CrO_9$: C, 31.31; H, 5.88; P, 20.22. Found: C, 31.15; H, 5.88; P, 20.09.

(Dimethyl methylphosphonite)pentacarbonylmolybdenum, [$(CH_3)(CH_3O)_2$[$Mo(CO)_5$].- A magnetically stirred mixture of 4.1 (15 mmole) of molybdenum hexacarbonyl and 1.6 g (15 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of methylcyclohexane was caused to reflux for 4 hr under nitrogen. The clear to yellow liquid $(CH_3)(CH_3O)_2PMo(CO)_5$ was isolated in a manner completely analogous to that used for the isolation of $(CH_3)(CH_3O)_2PCr(CO)_5$. *Anal.* Calcd. for $C_8H_9PMoO_7$: C, 27.91; H, 2.62; P, 9.01. Found: C, 27.99; H, 2.88; P, 9.26.

(Bis(dimethylamino)methylphosphine)pentacarbonylmolybdenum, [$(CH_3)((CH_3)_2N)_2PMo(CO)_5$].- A magnetically stirred mixture of 2.5 g (9.3 mmole) of molybdenum hexacarbonyl and 1.2 g (9.2 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of

methylcyclohexane was caused to reflux for 4 hr under nitrogen. The resulting black solution was cooled to room temperature, filtered, and concentrated under vacuum to about 2 ml of a brown liquid. The white, crystalline $(CH_3)((CH_3)_2N)_2PMo(CO)_5$, mp 45-47°, was isolated and purified in a manner completely analogous to that used for the isolation of $(CH_3)((CH_3)_2N)_2PCr(CO)_5$. Anal. Calcd. for $C_{10}H_{15}N_2PMo(CO)_5$: C, 32.41; H, 4.05; P, 8.38. Found: C, 32.60; H, 4.21; P, 8.19.

cis-Bis(dimethyl methylphosphonite)tetracarbonylmolybdenum, $[((CH_3)(CH_3O)_2P)_2Mo(CO)_4]$.- A mixture of 1.0 g (3.3 mmole) of molybdenum norbornadiene tetracarbonyl and 1.0 g (9.2 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was caused to reflux for 1 hr. After the solution was cooled and filtered and the hexane removed under vacuum, a yellow solid remained. Recrystallization from pentane gave white, needlelike crystals of cis-$((CH_3)(CH_3O)_2P)_2Mo(CO)_4$, mp 67-68°. Anal. Calcd. for $C_{10}H_{18}P_2MoO_8$: C, 28.30; H, 4.25; P, 14.62. Found: C, 28.43; H, 4.36; P, 14.78.

trans-Bis(bis(dimethylamino)methylphosphine)tetracarbonylmolybdenum, $[((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4]$.- A magnetically stirred mixture of 0.9 g (3.0 mmole) of molybdenum norbornadiene tetracarbonyl and 1.3 g (9.0 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was caused to reflux for 1 hr under nitrogen. In a manner identical to that used

for the isolation of *cis*-$((CH_3)(CH_3O)_2P)_2Mo(CO)_4$, yellow, needlelike crystals of *trans*-$((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4$, mp 88-90°, were obtained. *Anal*. Calcd. for $C_{14}H_{30}N_4P_2MoO_4$: C, 35.29; H, 6.30; P, 13.03. Found: C, 35.26; H, 6.37; P, 13.10.

fac-Tris(dimethyl methylphosphonite)tricarbonylmolybdenum, $[(CH_3)((CH_3)_2N)_2P)_3Mo(CO)_3]$.- A magnetically stirred mixture of 0.4 g (1.4 mmole) of molybdenum mesitylene tricarbonyl and 0.5 g (4.6 mmole) of $CH_3P(OCH_3)_2$ in 25 ml of hexane was caused to reflux for 3/4 hr under nitrogen. When the clear solution was allowed to cool to room temperature, precipitation of white, needlelike crystals of *fac*-$((CH_3)(CH_3O)_2P)_3Mo(CO)_3$, mp 171-173°, was observed. *Anal*. Calcd. for $C_{12}H_{27}P_3MoO_9$: C, 28.60; H, 5.36; P, 18.50 Found: C, 28.56; H, 5.30; P, 18.33.

(Dimethyl methylphosphonite)pentacarbonyltungsten, $[(CH_3)(CH_3O)_2PW(CO)_5]$.- A magnetically stirred mixture of 3.0 g (8.4 mmole) of tungsten hexacarbonyl and 0.8 g (7.4 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of octane was caused to reflux for 72 hr under nitrogen. The pale yellow liquid, $(CH_3)(CH_3O)_2PW(CO)_5$, was isolated in a manner completely analogous to that used for the isolation of $(CH_3)(CH_3O)_2P$-$Cr(CO)_5$. Anal. Calcd. for $C_8H_9PWO_7$: C, 22.21; H, 2.09; P, 7.16. Found: C, 22.59; H, 2.14; P, 7.01.

(Bis(dimethylamino)methylphosphine)pentacarbonyltungsten, [$(CH_3)((CH_3)_2N)_2PW(CO)_5$].- A magnetically stirred mixture of 1.7 g of $(CH_3CN)W(CO)_5$ 4.6 mmole) and 0.6 g (4.5 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was caused to reflux for 4 hr under nitrogen. The solvent was removed under vacuum and a yellow solid which contained a mixture of $W(CO)_6$, $(CH_3)((CH_3)_2N)_2PW(CO)_5$, and trans-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$ remained. These complexes were identified by their infrared spectra. Repeated attempts to purify the desired monosubstituted product failed.

cis-Bis(dimethyl methylphosphonite)tetracarbonyltungsten, [$((CH_3)(CH_3O)_2P)_2W(CO)_4$].- A magnetically stirred mixture of 2.0 g (5.2 mmole) of $(CH_3CN)_2W(CO)_4$ and 1.5 g (13 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was caused to reflux for 11 hr under nitrogen. The solvent was removed under vacuum, and the remaining solid when recrystallized from pentane yielded white crystals of cis-$((CH_3)(CH_3O)_2P)_2$-$W(CO)_4$, mp 49-51°. Anal. Calcd. for $C_{10}H_{18}P_2WO_8$: C, 23.50. H, 3.52; P, 12.12; Found: C, 23.71; H, 3.42; P, 12.14.

trans-Bis(bis(dimethylaminomethylphosphine)tetracarbonyltungsten, [$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$].- A magnetically stirred mixture of 3.1 g (7.8 mmole) of $(CH_3CN)_2W(CO)_4$ and 2.1 g (16 mmole) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was caused to reflux for 9 hr under nitrogen. The yellow, crystalline trans-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$, mp 91-93°, was

isolated in a manner completely analogous to that used for the isolation of cis-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$. Anal. Calcd. for $C_{14}H_{30}N_4P_2WO_4$: C, 29.80; H, 5.32; P, 11.00 Found: C, 29.95; H, 5.19; P, 11.23.

fac-Tris(dimethyl methylphosphonite)tricarbonyltungsten, [$((CH_3)(CH_3O)_2P)_3W(CO)_3$].- A magnetically stirred mixture of 0.5 g (1.3 mmole) of tungsten mesitylene tricarbonyl and 0.5 g (5.6 mmole) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was caused to reflux for 12 hr under nitrogen. This solution was cooled to room temperature, filtered, and the hexane removed under vacuum. The remaining yellow solid, when recrystallized from pentane, gave white crystals of fac-$((CH_3)(CH_3O)_2P)_3W(CO)_3$. (See below.)

mer-Tris(dimethyl methylphosphonite)tricarbonyltungsten, [$((CH_3)(CH_3O)_2P)_3W(CO)_3$].- mer-$((CH_3)(CH_3O)_2P)_3$-$W(CO)_3$ was prepared in a manner completely analogous to the preparation of fac-$((CH_3)(CH_3O)_2P)_3W(CO)_3$ except that the reaction was caused to reflux for 6 hr in methylcyclohexane. When this reaction was stopped after 2 hr, infrared analysis of the product showed the presence of the fac-isomer. Since attempts at purification of either isomer resulted in the loss of the compounds because of decomposition, elemental analyses were not obtained, and identification was accomplished with infrared and nmr spectral data.

RESULTS AND DISCUSSION

The monosubstituted compounds, $(CH_3)(CH_3O)_2PM(CO)_5$ (M = Cr, Mo, W), were prepared in good yields from reaction of equimolar mixtures of the hexacarbonyl and ligand. The ease with which the reactions took place decreased in the order Mo > Cr > W. These complexes are liquids at room temperature, as Poilblanc and Bigorgne (14) reported for similar complexes of $P(OCH_3)_3$. The isolation and purification of these compounds was most easily achieved by fractionally crystallizing a pentane solution in a dry ice-isopropanol slush bath. This procedure removed the unreacted hexacarbonyl and any disubstituted complex which may have formed, and left the monosubstituted compound in solution. Further cooling caused precipitation of white crystals of the monosubstituted complex which melted on warming to room temperature to give a pale yellow liquid.

The monosubstituted complexes of $CH_3P(N(CH_3)_2)_2$ were prepared in a similar manner. However, these compounds existed as crystalline solids at room temperature and were easily sublimed. The monosubstituted tungsten complex of $CH_3P(N(CH_3)_2)_2$ has not been isolated in a pure state. The infrared spectrum of the reaction product obtained from a 1:1 mixture of $W(CO)_6$ and $CH_3P(N(CH_3)_2)_2$

showed a mixture of unreacted hexacarbonyl and both the mono- and disubstituted compounds. Attempted purification by fractional crystallization did not free the monosubstituted compound of these impurities. The monosubstituted compound may be unstable and may disproportionate to the disubstituted compound and the hexacarbonyl. It is interesting to note that when tris(dimethylamino)phosphine, $(P(N(CH_3)_2)_3)$, was allowed to react with $W(CO)_6$, only the disubstituted compound was observed although both mono- and disubstituted compounds of Cr and Mo were isolated (37).

The disubstituted complexes of chromium for either $CH_3P(OCH_3)_2$ or $CH_3P(N(CH_3)_2)_2$ were prepared by refluxing the hexacarbonyl in octane, whereas, the molybdenum complexes were very easily prepared from molybdenum norbornadiene tetracarbonyl. Previously, disubstituted tungsten carbonyl complexes had been prepared either by direct reaction of the ligand with the hexacarbonyl or with a tungsten-diene complex such as tungsten cyclooctadiene tetracarbonyl (32) or tungsten norbornadiene tetracarbonyl (33). These diene intermediates were prepared from $(CH_3CN)_3W(CO)_3$ according to the methods of King and Fronzaglia (54). In the course of this work it was found that $(CH_3CN)_2W(CO)_4$ could be prepared easily and in good yields by irradiation of an acetonitrile solution of $W(CO)_6$ with ultraviolet light. When this complex was allowed to react directly with $CH_3P(OCH_3)_2$ or $CH_3P(N(CH_3)_2)_2$, the disubstituted compounds were produced in almost quantitative yields.

The tri-substituted compounds of $CH_3P(OCH_3)_2$ were easily formed in good yields from either the metal mesitylene tricarbonyl complex or the metal cycloheptatriene tricarbonyl complex. The ligand $CH_3P(N(CH_3)_2)_2$ would not form a trisubstituted complex with any of the metals, regardless of the manner of preparation. When $CH_3P(N(CH_3)_2)_2$ was allowed to react with molybdenum mesitylene tricarbonyl, the disubstituted compound $((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4$ was obtained. This reaction is similar to that of $P(N(CH_3)_2)_3$ with molybdenum cycloheptatriene tricarbonyl where again, only the disubstituted compound was isolated (37).

Infrared Spectra.- Table I lists the infrared data for the carbonyl region of all the compounds studied in this work. The monosubstituted compounds exhibited the three infrared bands, $A_1^{(2)}$, $A_1^{(1)}$, and E_1 for C_{4v} symmetry (Figure 3-A). An additional weak band which is assigned to the Raman active B_1 mode was observed. This Raman active band becomes weakly active in the infrared since the ligand, which has a symmetry lower than the C_{4v} assumed for the complex, lowers the overall symmetry of the complex. The disubstituted compounds of $CH_3P(OCH_3)_2$ were primarily the cis isomers as was indicated by the four carbonyl stretching frequencies expected for C_{2v} symmetry (Figure 3-C) (11). Indications of the trans isomers for Cr and W were observed in both the infrared and the nmr spectra, but no trans isomer was observed for Mo. Both the cis and trans

Table I. CO stretching frequencies and force constants .

	Frequencies^b, cm^{-1}				Force Constants^c, mdynes/Å		
$ML(CO)_5$	$A_1^{(2)}$	$A_1^{(1)}$	B_1	E	k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2](CO)_5$	2071.0	1963.5	1987.0	1947.0	15.80	15.90	0.30
$Cr[CH_3P(N(CH_3)_2)_2](CO)_5$	2061.0	1948.5	(1974.0)^d	1938.0	15.55	15.76	0.30
$Mo[CH_3P(OCH_3)_2](CO)_5$	2078.5	1967.0	1989.0	1953.0	15.85	16.01	0.30
$Mo[CH_3P(N(CH_3)_2)_2](CO)_5$	2070.5	1950.0	(1980.0)^d	1946.0	15.56	15.89	0.30
$W[CH_3P(OCH_3)_2](CO)_5$	2077.0	1961.0	1983.0	1947.5	15.76	15.94	0.31
$W[CH_3P(N(CH_3)_2)_2](CO)_5$	2069.5	1946.0	(1972.0)^d	1928.0	15.55	15.69	0.34
cis-$ML_2(CO)_4$	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2]_2(CO)_4$	2022.0	1934.0	1911.5	1909.5	15.08	15.47	0.36
$Mo[CH_3P(OCH_3)_2]_2(CO)_4$	2031.5	1940.5	(1940.5)^d	1921.0	15.20	15.81	0.30
$W[CH_3P(OCH_3)_2]_2(CO)_4$	2028.5	1943.0	1934.5	1912.5	15.10	15.77	0.33
trans-$ML_2(CO)_4$	A_{1g}	B_{1g}	E_u			k_2	k_i
$Cr[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	. . .^{e}	. . .^{e}	1883.0			15.00	(0.34)^f
$Mo[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	. . .^{e}	(1919.0)^d	1894.0			15.17	(0.34)^f
$W[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	. . .^{e}	(1910.0)^d	1886.0			15.05	(0.34)^f

Table I. (Continued).

	Frequencies[b], cm^{-1}			Force Constants[c], mdynes/Å		
fac-$ML_3(CO)_3$	A_1	E			k_1	k_i
$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1960.0	18.71.0			14.59	0.46
$Mo[CH_3P(OCH_3)_2]_3(CO)_3$	1970.0	1891.5			14.86	0.41
$W[CH_3P(OCH_3)_2]_3(CO)_3$	1966.0	1885.0			14.86	0.52
mer-$ML_3(CO)_3$	$A_1^{(2)}$	$A_1^{(1)}$	B_1	k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1972.0	1871.0	1887.0	14.38	14.92	(0.27)[f]
$W[CH_3P(OCH_3)_2]_3(CO)_3$	1984.0	1878.0	1899.0	14.53	15.10	(0.27)[f]

[a] Hexane solutions.

[b] Frequencies are in cm^{-1} (± 2.0 cm^{-1}).

[c] Force constants are ~ ± 0.2 mdyne/Å.

[d] Tentative assignment.

[e] Not observed.

[f] Value of k_i is assumed after comparison with similar compounds (ref. 13).

isomers have been reported for disubstituted complexes of Cr, Mo, and W hexacarbonyls with the similar ligands $P(CH_3)_3$ (14,33) and $P(OCH_3)_3$ (14,18). The disubstituted compounds of $CH_3P(N(CH_3)_2)_2$, which were prepared here, were exclusively trans, as was shown by their infrared spectra which conformed to D_{4h} symmetry (Figure 3-B). The same trans configuration was reported for the disubstituted complexes of $P(N(CH_3)_2)_3$ (37), although in the case of Mo, Verkade, et al. (18) have recently reported the isolation of the cis isomers of both $P(N(CH_3)_2)_3$ and $P(NCH_3Ph)_3$. This $P(N(CH_3)_2)_3$ complex of Mo, however, readily isomerized to the trans isomer in benzene solution at room temperature. Both fac- and mer- isomers were observed for the trisubstituted compounds of Cr and W, however, only the fac- isomer was obtained for Mo. These isomers were identified by their infrared (Figure 4-C and 4-D) and nmr spectra.

Substituted Group VIB hexacarbonyl complexes of tertiary nitrogen and phosphorus ligands have been the subject of many previous studies (10). An integral part of most of these studies has been the interpretation of the carbonyl stretching frequencies and the stretching force constants in terms of the metal ligand bonding (12,13). Substitution of a CO group by another ligand of weaker π-acceptor capacity causes the frequencies of the remaining CO groups to decrease inasmuch as the weaker π-accepting capacity of the ligands (relative to CO) increases the available metal d-π electron

Figure 3.- Examples of the CO stretching region of the infrared spectra for mono- and disubstituted complexes. *A* is $Mo(CO)_5(CH_3P(OCH_3)_2)$; *B* is *trans*-$Mo(CO)_4[CH_3P(N(CH_3)_2)_2]_2$; *C* is *cis*- $Mo(CO)_4[CH_3P(OCH_3)_2]_2$.

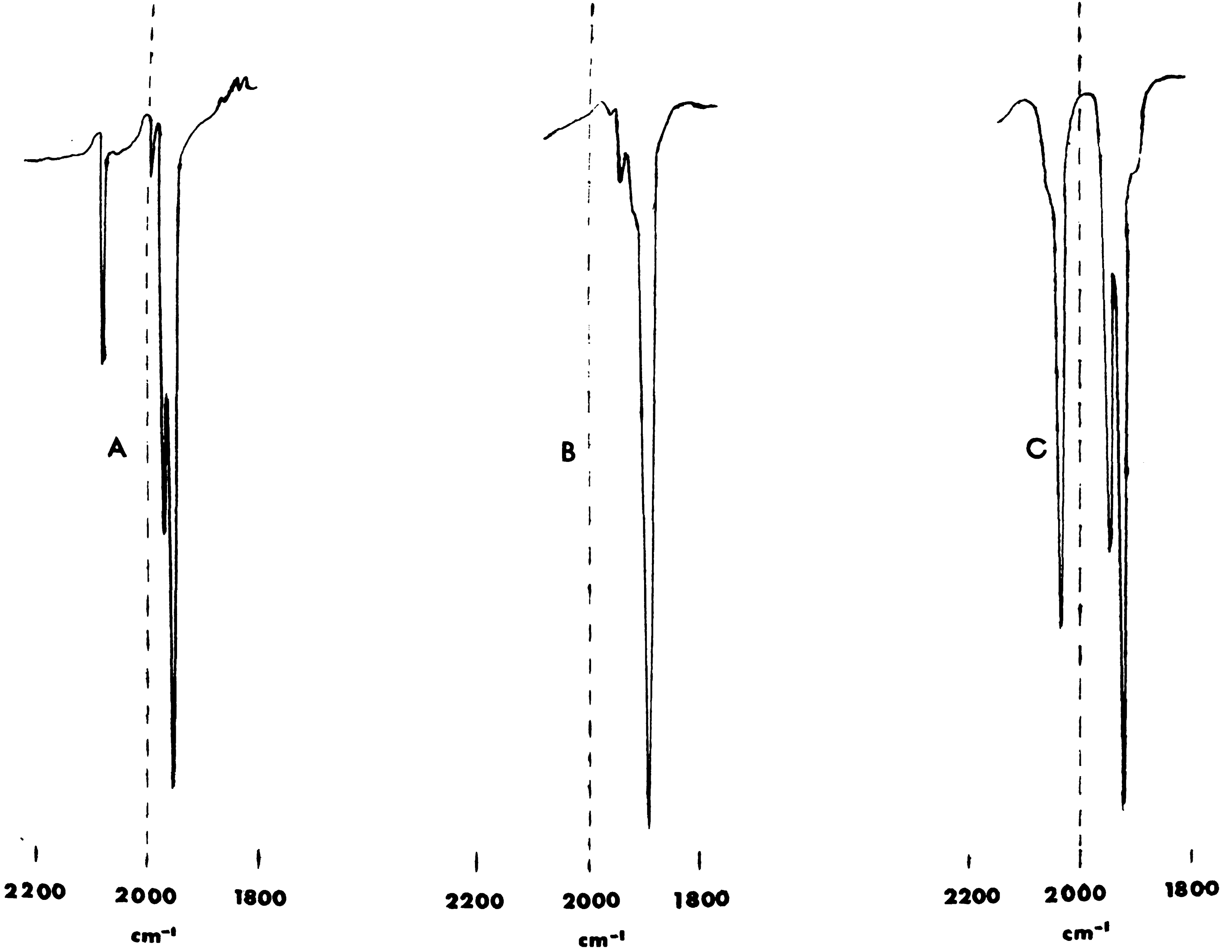


Figure 3.

Figure 4.- Examples of the CO stretching region of the infrared spectra for *fac*- and *mer*-trisubstituted complexes. *D* is *fac*-$Mo(CO)_3[CH_3P(OCH_3)_2]_3$ and *E* is *mer*-$W(CO)_3[CH_3P(OCH_3)_2]_3$.

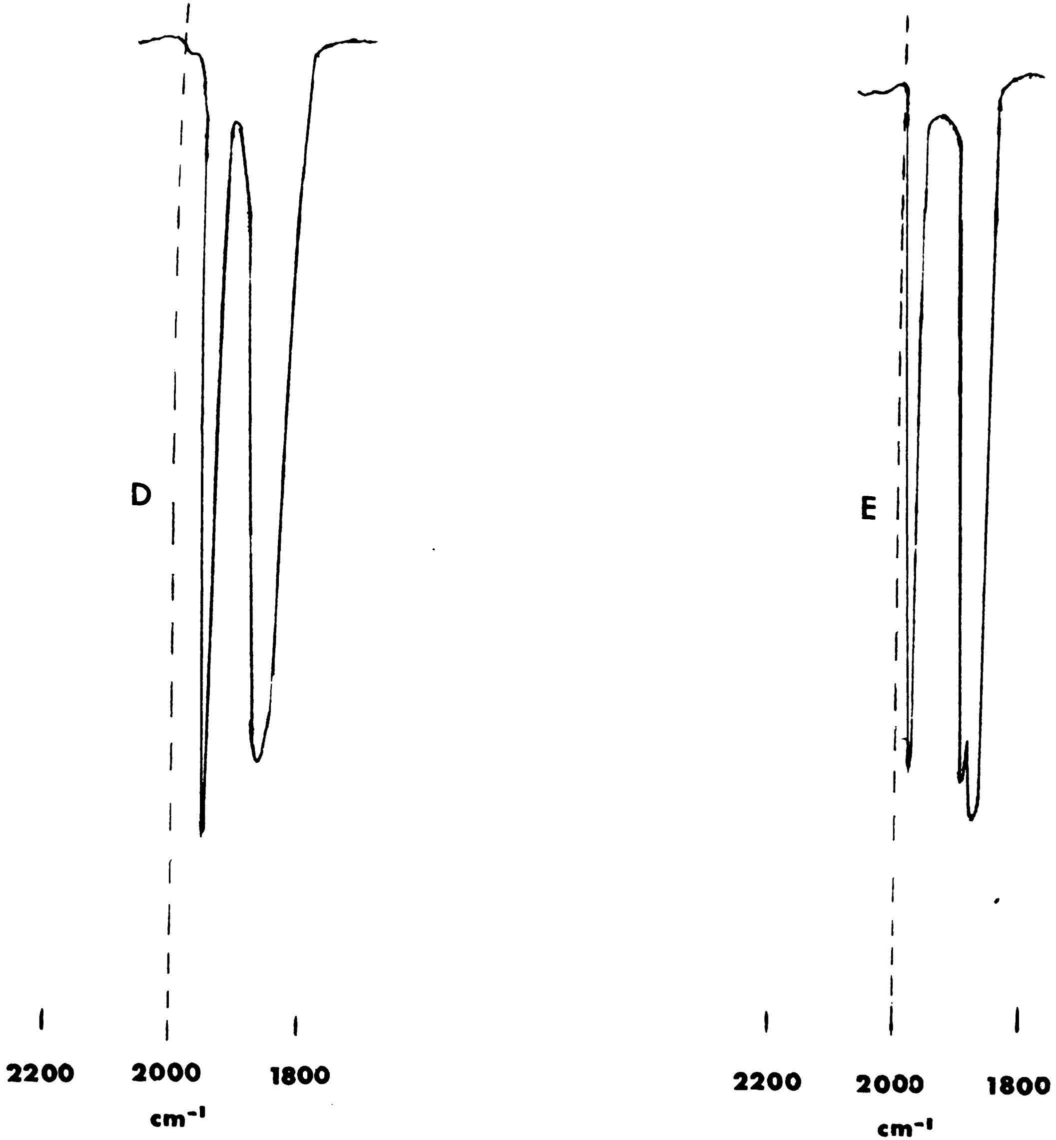


Figure 4.

density for back donation to the CO p-π* antibonding orbitals. Trends in such experimentally observable shifts may then be interpretable in terms of relative changes in the π-acceptor properties of the metal-ligand bond.

The method of Cotton and Kraihanzel (11) was used to calculate force constants from the frequencies given in Table I. Secular equations for $M(CO)_5L$, C_{4v} molecular symmetry; cis-$M(CO)_4L_2$, C_{2v}; trans-$M(CO)_4L_2$, D_{4h}; fac-$M(CO)_3L_3$, C_{3v}; and mer-$M(CO)_3L_3$, C_{2v}, were solved (see Table 2). In these equations k_1 is the stretching force constant for a CO group trans to a ligand, k_2 is for the CO force constant cis to a ligand, and k_i is a measure of the interaction constant between CO groups. All stretching interactions between CO groups should give rise to a term in the potential energy expression with a positive coefficient (k_i), since as the CO bonds stretch the π bonds are weakened slightly and the energies of the CO p-π* orbitals are lowered. This energy lowering results in an increase in metal to ligand π bonding to that CO group and a decreasing availability of electrons for other CO p-π* orbitals with the result that those CO bonds are strengthened (11). In addition, consideration of the metal d-π orbitals shows that two mutually trans CO groups share two metal orbitals while CO groups cis to each other share only one. Therefore, interactions should be approximately twice as large between

Table 2. Secular equations for CO stretching modes (11).

Molecule	Molecular Symmetry	Stretching Mode	Activity	Secular Equations
$M(CO)_5L$	C_{4v}	$A_1^{(1)}$ $A_1^{(2)}$	Infrared and Raman	$\begin{vmatrix} uk_1-\lambda & 2uk_i \\ 2uk_i & u(k_2+4k_i)-\lambda \end{vmatrix} = 0$
		B_1	Raman	$\lambda = uk_2$
		E	Infrared and Raman	$\lambda = u(k_2-2k_i)$
cis-$M(CO)_4L_2$	C_{2v}	$A_1^{(1)}$ $A_1^{(2)}$	All Infrared and Raman	$\begin{vmatrix} u(k_2+2k_i)-\lambda & 2uk_i \\ 2uk_i & u(k_1+k_i)-\lambda \end{vmatrix} = 0$
		B_1		$\lambda = u(k_2-2k_i)$
		B_2		$\lambda = u(k_1-k_i)$
trans-$M(CO)_4L_2$	D_{4h}	A_{1g}	Raman	$\lambda = u(k_2+4k_i)$
		B_{1g}	Raman	$\lambda = uk_2$
		E_u	Infrared	$\lambda = u(k_2-2k_i)$
cis-$M(CO)_3L_3$	C_{3v}	A_1	Infrared and Raman	$\lambda = u(k_1+2k_i)$
		E		$\lambda = u(k_1-k_i)$
trans-$M(CO)_3L_3$	C_{2v}	$A_1^{(1)}$ $A_1^{(2)}$	Infrared and Raman	$\begin{vmatrix} uk_1-\lambda & \sqrt{2}k_i \\ \sqrt{2}uk_i & u(k_2+2k_i)-\lambda \end{vmatrix} = 0$
		B_1		$\lambda = u(k_2-2k_i)$

u = reciprocal of the reduced mass of CO group.
$\lambda = (5.8890 \times 10^{-2})\nu^2$, where ν is in cm^{-1}.

two trans CO groups as between two cis CO groups. Finally, both k_1 and k_2 should decrease as CO groups are replaced by weaker π-acceptors, with k_1 (trans to the ligand) decreasing more than k_2, while k_i should increase in value (11). Therefore, if the force constants are calculated, from the CO stretching frequencies, an estimate of π-accepting ability of various ligands, relative to CO, can be made.

If the values of the CO stretching frequencies and force constants calculated here (Table 1) for the metal complexes in which both $CH_3P(N(CH_3)_2)_2$ and $CH_3P(OCH_3)_2$ are ligands, are compared with those reported for the CO groups in complexes in which either $P(OCH_3)_3$ (13), $P(CH_3)_3$ (13), or $P(N(CH_3)_2)_3$ (56) are ligands, the relative order of π-acceptor strength of these ligands can be determined. For these ligands the π-acid strengths were found to decrease in the order: $P(OCH_3)_3 \gtrsim CH_3P(OCH_3)_2 > P(CH_3)_3 > CH_3P(N(CH_3)_2)_2 > P(N(CH_3)_2)_3$. The position of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ in this order may be expected, since a certain degree of $p\text{-}\pi \rightarrow d\text{-}\pi$, nitrogen to phosphorus π bonding is anticipated. Support for this statement comes from structural data available for the compound $F_2PN(CH_3)_2$ (57), in which a short P-N bond length was observed along with a nearly planar arrangement for the P, N, and C atoms. This trigonal planar arrangement of nitrogen σ-bonding orbitals suggests an sp^2

hybridization about the nitrogen. This hybridization must arise from the donation of the lone pair of electrons from the nitrogen p-π orbital to the empty phosphorus d-π orbital. This partial filling of the phosphorus d-π orbitals causes the ligand to be a poorer acceptor of metal d-π electron density than a ligand such as $P(CH_3)_3$ which has no internal p-π —> d-π bonding. Further support for the assumption that there is some nitrogen to phosphorus π bonding in these compounds comes from some force constant data of Nixon, et al. (58). For di- and trisubstituted molybdenum complexes of a variety of fluorophosphines they determined a π-accepting capacity of $ROPF_2 > R_2NPF_2 > RP(F)NR_2 > (R_2N)_2PF$. In the case of $P(OCH_3)_3$ and $CH_3P(OCH_3)_2$, although there may be some degree of oxygen to phosphorus p-π —> d-π bonding, the important factor must be that the electronegativity of the oxygen creates a slight lowering of the energy of the phosphorus d-π orbital and an increase in its π-accepting capacity. In addition, with only one inductive methyl group on the oxygen, as opposed to the two on the nitrogen, the oxygen to phosphorus π-bonding is expected to be somewhat less than the nitrogen to phosphorus π-bonding (59).

Proton N.M.R. For each ligand, the proton nmr spectrum consists of two doublets arising from the two types of protons coupled to the phosphorus (see Table 3). The

Table 3. Proton nmr data[a].

Compound	CH_3[b]	${}^2J_{PH}$[c]	OCH_3[b]	${}^3J_{PH}$[c]
$CH_3P(OCH_3)_2$	1.10	8.5	3.50	11.0
$Cr[(CH_3P(OCH_3)_2](CO)_5$	1.70	4.0	3.60	11.5
$Mo[(CH_3P(OCH_3)_2](CO)_5$	1.70	3.0	3.55	12.0
$W[(CH_3P(OCH_3)_2](CO)_5$	1.80	4.0	3.55	12.0
cis-$Cr[CH_3P(OCH_3)_2]_2(CO)_4$	1.70	3.5	3.60	11.5
cis-$Mo[CH_3P(OCH_3)_2]_2(CO)_4$	1.65	2.5	3.55	12.0
cis-$W[CH_3P(OCH_3)_2]_2(CO)_4$	1.85	4.0	3.55	12.0
fac-$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1.70	2.5	3.57	11.0
mer-$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1.65[d]	2.5	3.50[d]	11.0
	1.70[e]	2.5	3.57[e]	11.0
fac-$Mo[CH_3P(OCH_3)_2]_3(CO)_3$	1.65	1.0	3.55	11.0
fac-$W[CH_3P(OCH_3)_2]_3(CO)_3$	1.75	3.0	3.50	11.0
mer-$W[CH_3P(OCH_3)_2]_3(CO)_3$	1.75[d]	3.0	3.48[d]	11.0
	1.80[e]	3.5	3.53[e]	11.0
$CH_3P(O)(OCH_3)_2$	1.42	17.0	3.65	11.0
			$N(CH_3)_2$[b]	
$CH_3P(N(CH_3)_2)_2$	1.05	8.0	2.60	9.0
$Cr[CH_3P(N(CH_3)_2)_2](CO)_5$	1.65	4.5	2.60	10.0
$Mo[CH_3P(N(CH_3)_2)_2](CO)_5$	1.65	3.8	2.60	10.5
$W[CH_3P(N(CH_3)_2)_2](CO)_5$	1.80	4.5	2.60	11.0
trans-$Cr[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	1.60	4.0	2.60	10.0
trans-$Mo[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	2.65	3.0	2.60	10.5
trans-$W[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	1.80	4.0	2.60	10.5

[a] Chloroform solutions.

[b] Chemical shifts are in ppm (± 0.05) and are referenced to tetramethylsilane.

[c] Coupling constants are in Hz (± 0.5) and are given as the absolute value. See text for discussion of signs.

[d] Apparent "doublet" for ligand *cis* to the two *trans* ligands.

[e] Apparent "triplet" for the two ligands *trans* to each other.

more shielded methyl group protons resonate at a higher field than either the OCH_3 or the $N(CH_3)_2$ protons, and the $N(CH_3)_2$ protons resonate at a higher field than those of the OCH_3 group. When the ligands are complexed to the metals, there is a downfield shift for the CH_3 resonances due to partial oxidation (as a result of donation of the lone pair of electrons) of the phosphorus. However, the chemical shifts and coupling constants of both the $N(CH_3)_2$ and the OCH_3 groups are relatively insensitive to complexation because of their greater distance from the phosphorus atom. The absolute value of $^2J_{PH}$ (coupling to the methyl protons) is decreased upon complexation to less than half of its free ligand value, while the absolute value of $^3J_{PH}$ (coupling to either the OCH_3 or $N(CH_3)_2$ protons) remains unchanged or is increased slightly.

The nmr spectra of the monosubstituted compounds consist of two doublets, while the spectra of the disubstituted and the fac-trisubstituted compounds consist of two resonances, each of which appears as a "triplet", the center peak of which shows a wide variation in intensity from compound to compound. This apparent "triplet" results from both phosphorus-hydrogen coupling and phosphorus-phosphorus coupling, and is an example of an $X_nAA'X'_n$ type spectrum which has been observed in a variety of other phosphorus complexes (18,21,22,37). The subscript n refers to the number of protons (X) that are coupled to a

phosphorus (A). Thus n equals 3, 6, or 12 for the CH_3, OCH_3, or $N(CH_3)_2$ resonances, respectively, in the ligands $CH_3P(OCH_3)_2$ and $CH_3P(N(CH_3)_2)_2$. (Figure 5.) The center line of the observed "triplet" arises from the near coincidence of a large number of X lines and the spectrum may appear as a 1:2:1 triplet in the limiting case (16). The intensity of the central peak is then dependent upon this coincidence of many other spectral lines and the value of $^2J_{PP}$ is a maximum when the central peak is most intense (16,17). By using the qualitative approach outlined here, results similar to those obtained in previous studies (18, 22,37) can be achieved, namely, that $^2J_{PP}$ for <u>trans</u> compounds is larger than that for analogous <u>cis</u> compounds, except perhaps for Cr, and that coupling for <u>trans</u> compounds decreases Mo > W >> Cr, and for <u>cis</u> compounds Cr > Mo > W. Unfortunately, the two ligands used in this study do not form complexes of the same geometry, so comparisons of the effect of the ligand on $^2J_{PP}$ cannot be fully ascertained. One unique feature of the nmr spectra of the complexes prepared in this work is that two resonances are observed for each complex (the CH_3 resonance and the OCH_3 or $N(CH_3)_2$ resonance), thus allowing for the possibility of two independent determinations of $^2J_{PP}$.

For the compound mer-$((CH_3)(CH_3O)_2P)_3W(CO)_3$ in addition to the two "triplets", both the CH_3 and the OCH_3 protons exhibited a "doublet" at approximately 0.05 ppm higher field

Figure 5.- Examples of ^1H nmr spectra of metal complexes which illustrate spectra with and without the presence of phosphorus-phosphorus coupling. In both spectra L = $CH_3P(N(CH_3)_2)_2$. The more intense downfield peaks are for the $(CH_3)_2N$-group while the less intense upfield peaks are from the CH_3- resonances. The trans-$W(CO)_4L_2$ is a good example of an $X_nAA'X_n'$ type spectrum.

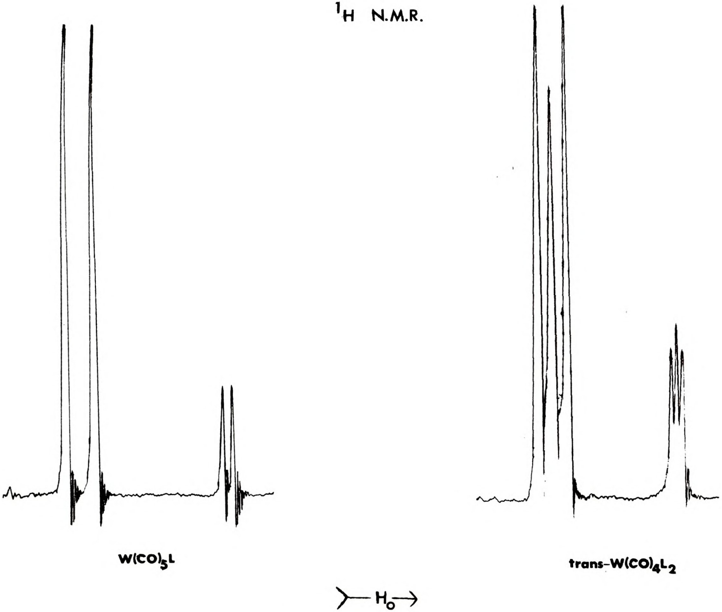


Figure 5.

Figure 6.- Shapes of the proton nmr resonances of some trisubstituted complexes of $CH_3P(OCH_3)_2$ (L). A is mer-$W(CO)_3L_3$; B is fac-$W(CO)_3L_3$; and C is mer-$Cr(CO)_3L_3$. The methyl resonance is at higher field in all cases. Those resonances in the mer-complexes labeled with the letter t are assigned to the two ligands trans to each other, and give rise to a near "triplet". Those resonances labeled d refer to the "doublet" which results from the ligand cis to the other two ligands (see text). In C, assignment of the central resonance in the "triplets" is not obvious, and is, therefore, not labeled.

(Figure 1A). These "doublets" can be attributed to the ligand which is uniquely trans to a CO group and cis to the other two ligands. These resonances represent one of the limiting cases of the $X_nAA'X'_n$ type spectrum where $^2J_{PP}$ is small for phosphorus atoms cis to one another while the slightly lower-field "triplets" represent the X part of an $X_nAA'X'_n$ type spectrum wherein $^2J_{pp}$ is appreciable for two ligands trans to each other. The mer- Cr compound exhibited a spectrum consisting of two sets of overlapping "doublets" (Figure 1C). In the OCH_3 proton resonance, where the phosphorus-hydrogen coupling is quite large, some indication of a very weak peak could be observed near the middle of this "doublet" grouping. However, it was impossible to assign this resonance unambiguously to either the trans ligands or the cis ligands. Again the chemical shift difference between the two resonances is approximately 0.05 ppm. Similar spectra have been observed by Shaw, et al. (22), for the trisubstituted Cr compound of $PhP(OCH_3)_2$ and the analogous Mo compound of $(CH_3)_2PPh$.

The slight change observed in $^3J_{PH}$ for the $P{-}OCH_3$ system upon complexation is typical (22). The relatively large change observed in $^2J_{PH}$ for the CH_3 group is of interest because it aids in the assignment of the sign of the P-C-H coupling. Manatt, et al. (60) have suggested that the geminal coupling, P-C-H, ($^2J_{PH}$), in a variety of trivalent phosphorus compounds is positive and that $^2J_{PH}$

becomes more negative as the s character of the phosphorus bonding orbitals to carbon increases. Thus, $^2J_{PH}$ in $(CH_3)_3P$ is +2.66 Hz while $^2J_{PH}$ in $(CH_3)_4P^+$ and $(CH_3)_3P{=}O$ are -14.4 Hz and -13.4 Hz, respectively (60). In the latter two compounds, the hybridization around phosphorus is nearly pure sp^3 and consequently the phosphorus-carbon bonds should have more s character than do phosphorus-carbon bonds in compounds in which the phosphorus has not been partially oxidized from loss of its lone pair. In $CH_3P(OCH_3)_2$ and $CH_3P(N(CH_3)_2)_2$ the values of $^2J_{PH}$, 8.5 Hz and 8.0 Hz (Table 3), respectively, are probably positive (Manatt, et al. (60)) while the value of 17.0 Hz for $^2J_{PH}$ in $CH_3P(O)(OCH_3)_2$ (Table 3) is taken as negative. Therefore, as the phosphorus is oxidized, the s character of the P-C bond increases and the phosphorus-hydrogen coupling constant becomes more negative. In the metal carbonyl complexes the phosphorus is partially oxidized because of donation of the lone pair. The result of this donation should be an increase in the s character of the P-C bond, and the value of $^2J_{PH}$ for the complexed ligand should be more negative than that for the free ligand. Since the absolute values of $^2J_{PH}$ in the complexes are less than those in the free ligands, (Table 3) this coupling in the ligand is very likely positive if the s character effect is dominant. Although the $^2J_{PH}$ couplings could be either positive or negative in the complexes,

some evidence can be cited for suggesting that they are negative. As the carbonyl groups on a metal are successively replaced by one, then two, then three phosphorus ligands (which are more basic than CO groups), there is an increase in the effective negative charge on the metal. Therefore, each phosphorus atom is oxidized to a lesser extent in a trisubstituted complex than in a disubstituted complex, and to a lesser extent in a disubstituted complex than in a monosubstituted one. Consequently, there should be less s character in the P-C bonds and $^2J_{PH}$ should become more positive with increased substitution. Reference to Table 3 shows that the regular decrease in $^2J_{PH}$ from $|3|$ to $|1|$ Hz for the molybdenum complexes of $CH_3P(OCH_3)_2$ parallels the degree of substitution from the mono- to the trisubstituted complex. These values of $^2J_{PH}$, therefore, are probably increasing from -3 to -2.5 to -1 for the complexes $Mo(CO)_5L$, $Mo(CO)_4L_2$, and $Mo(CO)_3$ respectively ($L = CH_3P(OCH_3)_2$). Similar trends can be noted (Table 3) for the Cr and W compounds. It is, of course, consistent with this rationale that $^2J_{PH}$ for the trisubstituted molybdenum complex could have passed through zero, and is actually +1.

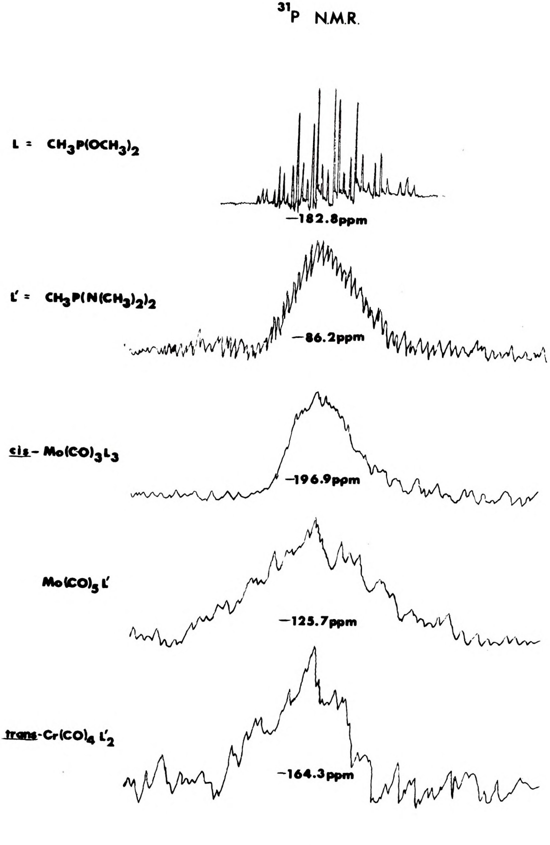
If it can be assumed that $^2J_{PH}$ in these complexes is a reflection of the extent of phosphorus to metal σ-donation, then the methyl coupling constants give an indication of the strength of the σ-bond. As the metal atom is varied

for a given substitution and ligand, the ${}^2J_{PH}$ value consistently becomes more positive from tungsten to chromium to molybdenum although the change in ${}^2J_{PH}$ is relatively small. Since this change in ${}^2J_{PH}$ is small, it could very well be that the σ-interaction is either very nearly the same or perhaps becoming slightly weaker along the series $W \gtrsim Cr \gtrsim Mo$.

It should be pointed out that in an $X_nAA'X'_n$ spectrum, the separation of the two most intense peaks (the outer peaks of the apparent "triplet") is given by $|J_{AX} + J_{AX'}|$ (16). If $J_{AX'}$ is considered to be very small or almost negligible compared to J_{AX}, then $J_{AX} \cong |J_{AX} + J_{AX'}|$ and ${}^2J_{PH}$ may be taken directly from the spectrum. The relatively large number of bonds (four) through which AX' coupling takes place makes this assumption plausible for these complexes. The values reported in Table 3 for both ${}^2J_{PH}$ and ${}^3J_{PH}$ have been determined directly from the spectra in this manner.

Phosphorus-31 Nmr.- Phosphorus-31 nmr spectra were obtained for three of the metal complexes, and for each of the two ligands (see Figure 7). The spectrum of the ligand dimethyl methylphosphonite which consisted of a septet of quartets at $\delta = -182.8$ ppm, relative to the external standard (85% *ortho*-phosphoric acid), arises from the splitting of the phosphorus nucleus by both the three methyl and the six methoxy protons. The ligand bis(dimethylamino)-methylphosphine exhibited an unresolvable broad peak at

Figure 7.- ^{31}P nmr spectra of $CH_3P(OCH_3)_2$, $CH_3P(N(CH_3)_2)_2$, and three of the metal complexes of these ligands.



^{31}P N.M.R.
L = $CH_3P(OCH_3)_2$
−182.8ppm
L′ = $CH_3P(N(CH_3)_2)_2$
−86.2ppm
cis- $Mo(CO)_3L_3$
−196.9ppm
$Mo(CO)_5L'$
−125.7ppm
trans-$Cr(CO)_4L'_2$
−164.3ppm

Figure 7.

δ = -86.2 ppm. The spectra of the complexes were quite weak and revealed a simple broad absorption from which only a chemical shift (Table 4) could be ascertained. These data are consistent with similar data reported for other complexes (Table 4) in which the phosphorus atom is deshielded upon complexation with a metal. Meriwether and Leto (41) have suggested that the factors which affect ^{31}P chemical shifts upon complexation to a metal include: extent of σ bond formation, extent of d-π —> p-π back donation, rehybridization of phosphorus orbitals, electronegativities of substituents, and steric effects. The use of ^{31}P chemical shift data to describe bond types is very tenuous because of both the number of factors involved and the interdependence of these factors. Indeed, the only thing that can be said about these data is that the phosphorus is deshielded because of the donation of its lone pair to the metal.

It is interesting that although the chemical shift of $CH_3P(N(CH_3)_2)_2$ falls between the values reported for $P(CH_3)_3$ (50) and $P(N(CH_3)_2)_3$ (50)(Table 4), and the shift of trans-$Cr(CO)_4[CH_3P(N(CH_3)_2)_2]_2$ falls between the shifts reported for trans-$Cr(CO)_4[P(CH_3)_3]_2$ (19) and trans-$Cr(CO)_4[P(N(CH_3)_2)_3]_2$ (19), the chemical shift of $CH_3P(OCH_3)_2$ does not occur, as expected, between the shifts of $P(CH_3)_3$ (50) and $P(OCH_3)_3$ (50). It is in fact significantly more negative than the chemical shift observed for

Table 4. ^{31}P nmr spectral data.

Compound	Chemical Shift (ppm)	Reference
$P(CH_3)_3$	+ 62.0 (±1.0)	(50)
$CH_3P(OCH_3)_2$	-182.8 (±1.0)	
$P(OCH_3)_3$	-141.0 (±0.5	(49)
$CH_3P(N(CH_3)_2)_2$	- 86.2 (±1.0)	
$P(N(CH_3)_2)_3$	-121.9 (±0.5)	(50)
cis-$Mo(CO)_3[CH_3P(N(CH_3)_2]_3$	-196.5 (±1.0)	
$Mo(CO)_5[CH_3P(N(CH_3)_2)_2]$	-125.7 (±1.0)	
trans-$Cr(CO)_4[CH_3P(N(CH_3)_2)_2]_2$	-164.3 (±1.0)	
$Mo(CO)_5[P(OCH_3)_3]$	-161.2 (±0.5)	(19)
trans-$Cr(CO)_4[P(N(CH_3)_2)_3]_2$	-178.2 (±0.5)	(19)
trans-$Cr(CO)_4[P(CH_3)_3]_2$	- 21.0 (±0.5)	(19)

$P(OCH_3)_3$. In addition, the ^{31}P chemical shift of the cis-trisubstituted molybdenum complex of $CH_3P(OCH_3)_2$ is shifted downfield to -196.5 ppm. Although the magnitude of this change is as expected (19), the value of -196.5 is still more negative than the chemical shifts for complexes of $P(OCH_3)_3$ (19). Van Wazer et al. (50) have reported an extensive study of ^{31}P nmr for many phosphorus compounds and discussed the factors influencing the chemical shifts. Among these factors are bond angles, bond hybridization, electronegativity of substituents, and the amount of π-character in the phosphorus bonds. Along the series of compounds $(CH_3)_nP(OCH_3)_{3-n}$ $(n = 0,1,2,3)$ there should be a regular change in all of the above effects and this change should be reflected in the ^{31}P chemical shifts of the compounds in this series. Since these changes in chemical shifts should be regular, it is not clear at this time why $CH_3P(OCH_3)_2$ has a larger negative value for its chemical shift than does $P(OCH_3)_3$.

Stereochemistry.- The observance of both cis and trans and fac- and mer- isomers for the disubstituted and trisubstituted complexes of $CH_3P(OCH_3)_2$, respectively, with the apparent predominance of the cis and fac- isomers, is consistent with the stereochemistry reported previously for complexes with similar ligands (13,14). I expected that no stable trisubstituted compounds would be formed with $CH_3P(N(CH_3)_2)_2$ since similar observations had been reported

for $P(N(CH_3)_2)_3$ (37). If these nitrogen-containing phosphorus ligands are actually strong σ-donors (37) the increased charge on the metal would be too large to accommodate three such ligands. The suggestion (37) that electronic rather than steric effects are the primary cause for the lack of formation of trisubstituted complexes with $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ (37) gains support from the fact that the bulky ligand $P(C_6H_5)_3$ (14) forms stable fac-complexes. Moreover, the ligands, $FP(N(CH_3)_2)_2$, $CH_3P(F)(N(CH_3)_2)$, and $C_6H_5P(F)(N(C_2H_5)_2)$ all form fac-complexes with molybdenum (61). The stability of such complexes may result from an increase in the π-acceptor strength for these fluorine containing ligands over that of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ because of the electronegative fluorine atom. This increase in π-acidity and corresponding decrease in σ-basicity reduces the increased negative charge on the metal that must arise when three CO groups are replaced by three phosphorus ligands.

It is interesting that $CH_3P(N(CH_3)_2)_2$ would not form an isolable monosubstituted complex with tungsten (see Experimental Section) even though it would form such complexes of chromium and molybdenum. King (37) observed the same results when he reacted $P(N(CH_3)_2)_3$ with tungsten. This latter observation was not expected since monosubstituted tungsten complexes with various amine ligands, which should also be strong σ-donors, are well known (40,62).

In order to explain this observation, an important role might be invoked for the metal to phosphorus π-bond in stabilizing these compounds. Whether or not the σ-bond is indeed the stronger bond, it alone is probably not sufficient in this system to stabilize a metal-phosphorus bond. Thus the π-contribution to the synergic bonding-mechanism must be sufficiently large before the phosphorus ligand will form a M-P bond. This assumption is supported by the observed reactions of tungsten. For the Group VI hexacarbonyls, the order of metal-CO π-bonding is W > Cr > Mo (11,63). If a single CO group in $W(CO)_6$ is replaced by either $CH_3P(N(CH_3)_2)_2$ or $P(N(CH_3)_2)_3$ a poor π-accepting ligand is placed trans to and in direct competition with the strong π-acid, CO, and an unfavorable situation is created. Stable monosubstituted amine complexes of tungsten do form, however, because the increased basicity of the ligands over that of $CH_3P(N(CH_3)_2)_2$ or $P(N(CH_3)_2)_3$ and the resultant stronger σ-interaction must be sufficient for bond formation. Consistent with this argument are the observations that the most stable disubstituted metal complexes of the ligands $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_2$ (18,37) are the trans isomers, while amine substituted compounds are of the cis geometry (12). When the ligand on the metal is one of these phosphorus containing ligands, the trans isomer allows for the increase in metal-phosphorus π-bonding necessary to stabilize the compounds, especially for the tungsten

complex, since the ligand is then removed from direct competition with a CO for the metal π-electron density. On the other hand, the <u>cis</u> isomer allows for maximum metal-CO π-bonding in the case of the poor π-accepting amine ligands.

PART II

THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME CYANOPHOSPHINES AND THEIR CHROMIUM AND MOLYBDENUM CARBONYL COMPLEXES

INTRODUCTION

Although the metal coordination chemistry of tertiary phosphine compounds has been investigated extensively in recent years (1), there has been relatively little attention given to cyanophosphine compounds of the type $[R_xP(CN)_{3-x}]$ (x = 0,1, or 2). The preparation and characterization of of several cyanophosphine compounds have been reported (51, 65,66,68,69), however, these preparations usually involved rather extensive reaction times and the characterizations involved little spectral data. In 1963, Noth and Vetter (67) reported the preparation of a disubstituted nickel carbonyl complex of $[(CH_3)_2N]_2PCN$ in which coordination presumably occurred through the phosphorus atom. More recently, Kirk and Smith reported that $P(CN)_3$ forms unstable adducts with AlH_3, $AlCl_3$, and $AlBr_3$ (69) and that in solution it forms an adduct with pyridine (70) which was identified by ^1H nmr spectroscopy. In this pyridine adduct $P(CN)_3$ was probably acting as the acceptor with coordination occurring through the phosphorus atom. In this same work some association of the cyanide groups in both $P(CN)_3$ and $PhP(CN)_2$ with N,N-dimethylformamide was proposed on the basis of ^1H nmr data (70).

Because of the very little amount of work reported on the coordination chemistry of cyanophosphine compounds, I decided to prepare several of these phosphines and attempt to form transition metal complexes with them. In this work, a rapid and easy method of preparation is presented for the routine synthesis of compounds of the type $R_xP(CN)_{3-x}$ (where x = 0, 1, or 2 and R = Ph-, CH_3O-, C_2H_5 -, $(CH_3)_2N$-, or CH_3-). The infrared, proton nmr, and mass spectral data of these compounds are also given. Several of these phosphines were then used in reactions with chromium and molybdenum norbornadiene tetracarbonyls. Emphasis has been placed on determining the effect of the cyanide group on the coordinating properties of the phosphorus atom to which it is bound, and on determining if the nitrogen atom, as well as the phosphorus atom, is a potential σ-donor site. The following cyanophosphine ligands were used: Ph_2PCN, $PhP(CN)_2$, $(CH_3)_2PCN$, $(C_2H_5O)_2PCN$, and $[(CH_3)_2N]_2PCN$. Metal carbonyls were selected as reactants for these ligands because carbonyl substitution is known to occur for both trivalent phosphorus compounds (1,10) and for nitriles (10, 55,80).

During the course of this work Nixon and Swain (83) proposed a dimeric structure for the complexes $[M(CO)_4P(CF_3)_2CN]_2$ (M = Cr or Mo) with $(CF_3)_2PCN$ acting as a bridging ligand. I therefore wished to determine, by means of chemical and spectroscopic evidence, the structure

of dimers of this type and if this process could be observed for other cyanophosphine ligands.

EXPERIMENTAL

The infrared spectra were run on a Perkin-Elmer model 225 grating spectrophotometer. $CHCl_3$ was used as a solvent for all metal complexes and for $P(CN)_3$ and $CH_3P(CN)_2$. Hexane was used as an infrared solvent for all of the other cyanophosphines. Proton nmr spectra were taken on a Varian Associates Model A-56/60-D instrument with tetramethylsilane as an internal standard. For all of the nmr spectra $CHCl_3$ was used as a solvent, except for the spectra of complexes of Ph_2PCN where CH_2Cl_2 was used. The phosphorus-31 nmr spectra were obtained on a Varian Associates Model DA-60 spectrometer at 24.29 MHz and are referenced to 85% ortho-phosphoric acid as an external standard. Mass spectra for the cyanophosphine compounds were recorded on an Hatachi-Perkin Elmer model RMU-6 instrument using the liquid inlet system with an ion source temperature of 200^0 and an ionizing voltage of 70 eV for all samples except $P(CN)_3$, where the solid inlet was used at a temperature of 50^0 and an ionizing voltage of 70 eV. Mass spectra of the metal complexes of the cyanophosphine ligands were performed by the Chemical Physics Research Laboratory of the Dow Chemical Co., who used the direct probe method with temperatures ranging from $110\text{-}215^0$. Elemental analyses and

osmometric molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Materials.- The compounds $PhPCl_2$, Ph_2PCl, $(C_2H_5O)_3P$, were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin, and CH_3PCl_2 was obtained as a gift from the Department of the Army, Edgewood Arsenal, Edgewood, Maryland. The compounds, $C_2H_5OPCl_2$ (71), $(C_2H_5O)_2PCl$ (71), $(CH_3)_2PCl$ (72), $(CH_3)_2NPCl_2$ (66), and $[(CH_3)_2N]_2PCl$ (66) were prepared by previously described methods. Molybdenum norbornadiene tetracarbonyl (52) and chromium norbornadiene tetracarbonyl (52) which were used for the preparation of the metal complexes were also prepared by previously described methods.

The compounds, $(CH_3O)_2PCl$ and CH_3OPCl_2 were prepared when appropriate molar ratios of $(CH_3O)_3P$ and PCl_3 were mixed in a manner described as follows. When a 2:1 molar ratio of $(CH_3O)_3P$ to PCl_3, for example, was stirred in a N_2 atmosphere at room temperature for several min, an exothermic reaction ensued forming $(CH_3O)_2PCl$. This product was identified in the ^1H nmr spectrum by a doublet resonance which was, as expected, downfield (due to decreased shielding) from the similar doublet for $(CH_3O)_3P$; stirring for 24 hr at room temperature insured complete reaction. The extent of reaction was easily monitored by following the $(CH_3O)_3P$ doublet in the ^1H nmr spectrum. When the opposite molar ratio of $(CH_3O)_3P$ and PCl_3 was mixed at room temperature,

$(CH_3O)_2PCl$ again formed, however, if the reaction mixture was warmed slightly (~70^0) for 3 hr, CH_3OPCl_2 formed. This reaction was also followed by ^1H nmr spectroscopy; CH_3OPCl_2 exhibited a doublet resonance down field from the resonance of $(CH_3O)_2PCl$. Although some decomposition was evidenced by formation of an unidentified orange solid and CH_3Cl (singlet in the ^1H nmr at 2.95 ppm) the reactions were essentially quantitative. Caution: It was not found possible to purify these chlorophosphites by distillation (either at reduced or at atmospheric pressure) because decomposition was accelerated by the application of heat, and invariably an explosion resulted. These compounds, whose purity was checked by ^1H nmr, were used without purification and with good results. It was later found that these two compounds could be made easily if the appropriate molar ratio of methanol was added dropwise to PCl_3 and allowed to stir for approximately 6 hr. The nmr spectra of the products from these preparations indicated that less CH_3Cl formed with this method than with the above method. No attempt was made to distill the products of these preparations.

Preparation of Cyanophosphine Compounds.- The compounds, $P(CN)_3$ (65), $(CH_3)_2NP(CN)_2$ (66), $[(CH_3)_2N]_2PCN$ (66), $(C_2H_5O)_2PCN$ (68), $C_2H_5OP(CN)_2$ (68), and $PhP(CN)_2$ (70) were prepared previously when the appropriate phosphorus halide was caused to reflux with AgCN for 12 to 24 hr in solvents

such as $CHCl_3$, CCl_4, and $(C_2H_5)_2O$. This method of preparation was modified slightly for preparation of the above compounds and the compounds of this work. If acetonitrile was used as the reaction solvent, the compounds were quickly formed when the reactants were stirred for about 2 hr at rrom temperature under a nitrogen atomosphere. The compound, $CH_3P(CN)_2$ was prepared previously (51) when acetonitrile was used as the solvent, however, reflux temperatures were employed for five hr.

Two methods were used for isolation of the products from these reaction mixtures: A. After about 2 hr of stirring, the reaction mixture was filtered under nitrogen to remove the AgCl (and any unreacted AgCN). The acetonitrile was then removed from this filtrate by water aspiration, and the remaining liquid was vacuum distilled (vacuum sublimed for solids) (see Table 5) to give the colorless liquid or white solid product. B. The entire reaction mixture was vacuum distilled, after about 2 hr of stirring. The acetonitrile was collected first, followed by the cyanophosphine product. The silver salts were left in the reaction vessel. This second method of isolation was particularly effective for those phosphorus compounds which formed insoluble complexes with the silver salts in the reaction mixture and which would have been lost in filtration, but it could also be used as a general method for the isolation of the lower boiling liquid products.

Table 5. Experimental data for cyanophosphines.

Compound	Method of Isolation	$b_{(mm)}$
Ph_2PCN	A	$110^{0}_{(0.1)}$
$PhP(CN)_2$	A	$68\text{-}70^{0}_{(0.1)}$
$(CH_3O)_2PCN$	B	$58^{0}_{(10)}$
$CH_3OP(CN)_2$	B	$65^{0}_{(6)}$
$(C_2H_5O)_2PCN$	A	$51^{0}_{(5)}$
$C_2H_5OP(CN)_2$	B	$51^{0}_{(5)}$
$[(CH_3)_2N]_2PCN$	B	$48^{0}_{(1)}$
$(CH_3)_2NP(CN)_2$	B	$65\text{-}69^{0}_{(8)}$
$(CH_3)_2PCN$	B	$40\text{-}45^{0}_{(10)}$
$CH_3P(CN)_2$	A	$50\text{-}60^{0}_{(0.1)}$[a]
$P(CN)_3$	A	$50\text{-}60^{0}_{(0.1)}$[a]

[a] Sublimed.

It should be noted that $(CH_3O)_2PCN$, which was prepared by method B, was also prepared by method A. With method A, after approximately half of the material had been distilled the distillation pot exploded rather violently, perhaps due to some unreacted $(CH_3O)_2PCl$. Therefore, method B is recommended.

Reactions of $P(CN)_3$ with Various Metals.- The compound $P(CN)_3$ was caused to react with a number of transition metals under many different conditions, and with a variety of solvents. In every case, no identifiable complex was isolated. Reactions of this phosphine with nickel compounds were studied extensively. These compounds included $Ni(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6CH_3CN$, $Ni(BF_4)_2 \cdot 6DMSO$, $Ni(CN)_2$, $NiBr_2$, and NiI_2. (When used in these reactions the Ni(II) hexahydrates were first dihydrated with 2,2-dimethoxypropane.) The compound $Ni(CO)_4$ was used in attempts to prepare nickel(0) complexes of $P(CN)_3$. All of these reactions with nickel were run on a scale of approximately a mmole of metal, and a ligand to metal molar ratio of anywhere from 1:1 to 10:1. A wide range of temperatures was used as well as a wide variety of solvents. The solvents which were employed included acetone, ether, halocarbons, alcohols, acetonitrile, and benzene as well as others. A brown amorphous solid, which was not identifiable by infrared spectra or elemental analysis, invariably was obtained from reactions with $Ni(CO)_4$, while a yellow to green powder was isolated from an initially yellow to orange solution for the reactions of Ni(II) salts with the

ligand. The various ligand:metal ratios, solvents, and reaction temperatures appeared to have little effect on the outcome of these reactions.

Reactions of $P(CN)_3$ were also attempted with Co(II) and Cu(I) salts and with Fe(0), Cr(0), Mo(0), and W(0) carbonyls. In almost all cases (except chromium, molybdenum, and tungsten which required heat) the addition of $P(CN)_3$ to a solution of the metal salt or carbonyl was followed by an immediate reaction, as evidenced by a rapid color change. In all cases of reactions attempted with this ligand no product other than unidentifiable non-crystalline powders could be isolated. Even in the cases where elemental analyses were obtained for the products, no meaningful interpretation could be gathered from the results, and despite the many reactions no definite metal complex of $P(CN)_3$ was ever isolated.

Preparation of Metal Complexes of Cyanophosphine Ligands Other Than $P(CN)_3$

Bridged Complexes.- All of the bridged complexes were prepared when equimolar mixtures of either chromium or molybdenum norbornadiene tetracarbonyl and one of the cyanophosphine ligands were stirred in *n*-hexane for several minutes (see Table 6). The *n*-hexane was removed by water aspiration and the remaining solid was recrystallized from CH_2Cl_2 to give yellow crystalline solids of the form

Table 6. Experimental and analytical data for metal complexes.

Compound	Rxn	% C		% H		% P	
	Time	Calc.	Found	Calc.	Found	Calc.	Found
$[Mo(CO)_4L]_2$							
L =							
Ph_2PCN	5 min	48.69	48.68	2.39	2.50	7.40	7.26
$PhP(CN)_2$[a]	5 min	39.13	36.62	1.36	1.60	8.43	7.81
$(CH_3)_2PCN$	5 min	28.47	28.29	2.03	2.07	10.51	10.39
$(C_2H_5O)_2PCN$	5 min	30.42	30.31	2.82	2.88	8.73	8.59
$[(CH_3)_2N]_2PCN$	5 min	30.59	30.29	3.40	3.45	8.78	8.65
$[Cr(CO)_4L]_2$							
L =							
Ph_2PCN	5 min	54.50	54.64	2.67	2.75	8.27	8.46
$(CH_3)_2PCN$	5 min	33.47	33.27	2.39	2.40	12.35	12.50
$(C_2H_5O)_2PCN$[a]	12 hr	--	--	--	--	--	--
$[(CH_3)_2N]_2PCN$	12 hr	34.95	34.70	3.88	3.84	10.03	10.22
$Mo(CO)_4L_2$							
L =							
Ph_2PCN	2 hr	57.14	57.12	3.17	3.23	9.84	9.65
$(CH_3)_2PCN$	1 hr	31.41	31.18	3.14	3.22	16.23	15.92
$(C_2H_5O)_2PCN$[a]	2 hr	--	--	--	--	--	--
$[(CH_3)_2N]_2PCN$[a]	1 hr	33.73	31.18	4.82	4.84	12.45	11.31
$Cr(CO)_4L_2$							
L =							
Ph_2PCN	4 hr	61.43	59.81	3.41	3.89	10.58	10.28
$(CH_3)_2PCN$[a]	2 hr	--	--	--	--	--	--
$[(CH_3)_2N]_2PCN$[a]	1 hr	36.99	35.97	5.28	5.69	13.64	10.28
$Mo(CO)_4LL'$							
L =							
$[(CH_3)_2N]_2PCN$	1 hr	30.19	30.30	4.40	4.52	13.00	12.88
L' = $(CH_3O)_3P$							

Table 6. (Continued)

Compound	Rxn Time	% C		% H		% P	
		Calc.	Found	Calc.	Found	Calc.	Found
$Cr(CO)_4LL'$							
L =							
$[(CH_3)_2N]_2PCN$	1 hr	33.26	32.72	4.85	4.77	14.32	14.25
$L' = (CH_3O)_3P$							

---

[a] Readily decomposed and, therefore, not isolated in purity suitable for good analysis, however, infrared and nmr spectra gave unequivocal evidence as to the identity of these complexes.

$[M(CO)_4L]_2$. A molecular weight measurement of $[Mo(CO)_4Ph_2PCN]_2$ produced a value of 910; calculated, 838.

Disubstituted Complexes.- The disubstituted complexes (both $M(CO)_4L_2$ and $M(CO)_4LL'$) were prepared when a 1:1 molar mixture of the appropriate ligand and the bridged metal complex were caused to reflux in n-hexane for one to four hr (see Table 6). The n-hexane was then removed by water aspiration, and the remaining solid was recrystallized. The $M(CO)_4L_2$ complexes were recrystallized from n-hexane to which a minimum of dichloromethane was added to dissolve the complexes, while the $M(CO)_4LL'$ complexes were recrystallized from n-pentane.

RESULTS AND DISCUSSION

Cyanophosphine Compounds.- In contrast to the previously reported preparative methods for cyanophosphines, the preparations in acetonitrile proceeded rapidly at room temperature. All of the compounds were hygroscopic and usually became yellow to red in color after brief exposure to air. This apparent decomposition, however, did not seem to affect further reactions of these compounds in any appreciable way, and several of these compounds were used as ligands to form chromium and molybdenum carbonyl complexes.

Mass Spectra of Cyanophosphines.- Mass spectra were obtained to confirm the identity of the cyanophosphines and, perhaps, to gain some information about the strengths of the phosphorus-cyanide bonds. (My interest in the phosphorus-cyanide bond strengths in these compounds arose from the somewhat peculiar behavior of $P(CN)_3$. Apparently $P(CN)_3$ has fairly strong intermolecular nitrogen-phosphorus interactions, both as a solid (76) and in solution (64). In addition, some of the work of Kirk and Smith (69), as well as some of the work I did with $P(CN)_3$, seems to indicate that at least one cyanide is easily removed from the phosphorus atom under reaction conditions.) Parent ions were observed for all of the compounds.

These data are presented in Table 7 along with other major identifying peaks. For $P(CN)_3$, I found that the peak at m/e 57 which can be represented as PCN^+, was the most intense peak, followed by CN^+ (86% relative intensity and then $P(CN)_3^+$ (25%). The intensity of the PCN^+ ion, perhaps demonstrates the ease with which two of the cyanides are cleaved from the phosphorus, and further, indicates that under these conditions (temperature of 50^0, ionizing voltage of 70 eV), $P(CN)_2^+$ (8.3% intensity) is easily cleaved to give PCN^+. This trend was, in general, paralleled in the other compounds, especially in the dicyano species where mass spectral peaks for PCN^+ and $P(R)CN^+$ were always found to be stronger than the peaks for $P(CN)_2^+$. In the compound $PhP(CN)_2$, $C_6H_4PCN^+$ was the most intense peak and was formed when a neutral HCN molecule split off of the parent compound, as evidenced by the metastable peak observed at m/e 110.6 (calculated at m/e 110.56).

$$m^* \; 110.6 \quad C_6H_5P(CN)_2^+ \rightarrow C_6H_4PCN^+ + HCN$$

The phenyl derivatives exhibited fairly strong parent peaks. The ion peak at m/e 211 for Ph_2PCN^+ showed a 96% relative intensity, and the ion peak m/e for $PhP(CN)_2^+$ exhibited a relative intensity of 50%.

The phosphites showed strong peaks for those species in which the phosphorus-oxygen bond remained intact. For example, in the spectrum of $(CH_3O)_2PCN$, the most intense peak was at m/e 93 corresponding to $P(OCH_3)_2^+$ with $P(OCH_3)(OH)^+$ being next strongest at 56% relative intensity.

Table 7. Mass spectral data for cyanophosphines.

	(Relative Intensity of Identifying Peaks in Percentages)							
Ion	R_2PCN	R_2P	RP	RPCN	PCN	$RP(CN)_2$	$P(CN)_2$	$P(CN)_3$
Compound								
Ph_2PCN	96	2.8	100	4.3	7.1			
$PhP(CN)_2$			12.5	15.3	9.7	50.0	2.4	
$(CH_3O)_2PCN$	15.9	100	9.5	7.9	9.5			
$CH_3OP(CN)_2$			21.9	100	35.8	38.7	8.8	
$(C_2H_5O)_2PCN$	15.3	18.1	16.2	20.0	8.6			
$C_2H_5OP(CN)_2$			3.5	8.8	49.2	5.3	26.4	
$[(CH_3)_2N]_2PCN$	25.6	14.0	10.5	53.5	3.5			
$(CH_3)_2NP(CN)_2$			6.2	100	21.2	27.5	3.0	
$(CH_3)_2PCN$	100	6.6	9.8	67.2	24.6			
$CH_3P(CN)_2$			91.8	47.1	83.5	67.1	11.8	
$P(CN)_3$					100		8.3	25

In the spectra of the compounds $[(CH_3)_2N]_2PCN$ and $(CH_3)_2NP(CN)_2$, some ions were observed in which the P-N bond had been cleaved, as evidenced by the presence of immonium ions. However, there was a high abundance of ions in which the P-N bond remained intact. This observation can be contrasted to the observation that the dimethylaminodihalophosphines showed a high abundance of fragments, which contained only phosphorus and the halogen, but a low abundance of fragments which contained P and N (75). In the spectrum of $(CH_3)_2NP(CN)_2$, the ion peak at m/e 101, represented as the fragment $P(CN)[N(CH_3)_2]^+$ (relative intensity 100%), was found to be much stronger than the mass peak at m/e 57 for the PCN^+ ion (20%) and very much stronger than the peak at m/e 83 for $P(CN)_2^+$ (4%).

<u>Nmr Spectra of the Ligands</u>.- The proton nmr resonances for these cyanophosphines (see Table 8) were observed to be shifted downfield (less shielding) from the corresponding chloride compounds, and were, therefore, easily identified in the reaction mixtures.

The ^{31}P nmr chemical shifts are shown in Table 8. These resonances shifted upfield as cyanide groups replaced organic groups on the phosphorus atom. This observed trend in the chemical shifts is opposite to the downfield trend exhibited by the corresponding chloride compounds (50). For example, the ^{31}P chemical shifts for $(CH_3O)_2PCl$, CH_3OPCl_2,

Table 8. Infrared and nmr spectral data of cyanophosphines.

Compounds	^1H (ppm)	J_{PH} (Hz)	^{31}P (ppm)	CN^a (cm^{-1})
Ph_3P			+ 6.0[b]	----
Ph_2PCN	7.20	9.0[d]	+ 36.4	2173 (s)
$PhP(CN)_2$	7.60[c]	10.0[d]	+ 75.6	2184 (s)
$(CH_3O)_3P$	3.43	10.5	-141.0[b]	----
$(CH_3O)_2PCN$	3.75	10.3	-122.4	2186 (s)
$CH_3OP(CN)_2$	3.88	9.0	- 24.4	2179 (s) 2030 (w)
$(C_2H_5O)_3P$	3.85[e] 1.19[f]	7.5[g]	-139.0[b]	----
$(C_2H_5O)_2PCN$	4.08[e] 1.30[f]	7.5[g]	-117.0	2180 (s)
$C_2H_5OP(CN)_2$	4.20[e] 1.40[f]	7.0[g]	- 17.6	2178 (s) 2133 (w)
$[(CH_3)_2N]_3P$	2.44[h]	8.9[h]	-123.0[b]	----
$[(CH_3)_2N]_2PCN$	2.75	10.0	- 66.1	2168 (s)
$(CH_3)_2NP(CN)_2$	2.90	14.0	+ 5.7	2179 (s) 2060 (w)
$(CH_3)_3P$	0.90	2.7	+ 62.0[b]	----
$(CH_3)_2PCN$	1.47	4.5	+ 62.6	2172 (s)
$CH_3P(CN)_2$	1.90	7.5	+ 81.4[i]	2191 (s) 2095 (m)
$P(CN)_3$	----	----	+138.3[i]	2186 (s) 2096 (m)

[a] s = strong, m = medium, w = weak. [b] See reference 50.
[c] Most intense peak. [d] Approximate coupling to ortho-protons
[e] Methylene protons. [f] Methyl protons.
[g] Coupling to methylene protons. [h] See reference 37.
[i] CH_3CN solution.

and PCl_3 are -169, -180, and -220 ppm, respectively (50). Therefore, a cyanide magnetically shields the phosphorus atom while a chloride deshields it. This positive shielding effect from the cyanides, as well as the trends in the ^1H chemical shifts may be attributed at least partly to the diamagnetic anisotropic shielding arising from the cyanide triple bond. An X-ray diffraction study of solid $P(CN)_3$ (76) indicated that the P-C≡N linkage was nearly linear (172^0 angle). Therefore, if the same linkage is linear in the organic substituted compounds the phosphorus atom should lie in the positive region of acetylenic shielding and experience an upfield shift, while the protons of the organic groups may lie in the negative region of shielding and experience a downfield shift (73). In addition, it is noteworthy to point out that the small C-P-C bond angle of 94^0 found in $P(CN)_3$ (76) indicates that the lone pair on phosphorus has a large percentage of s character. This should also contribute to the effective magnetic shielding of the phosphorus nucleus and give rise to the upfield shifts.

The phsophorus-hydrogen coupling constants, also listed in Table 8, varied with the different organic groups on the phosphorus. The coupling, J_{PH}, increased in absolute value when either $-CH_3$, $-N(CH_3)_2$, or -Ph was replaced by cyanide However, as cyanide groups replaced either $-OCH_3$ or $-OC_2H_5$, J_{PH} decreased in absolute magnitude.

Metal Complexes of Cyanophosphines.- If one to one molar ratios of ligand and metal norbornadiene tetracarbonyl were allowed to react, dimeric complexes involving bridging cyanophosphine ligands were obtained.

$$M(CO)_4C_7H_8 + R_2PCN \longrightarrow [M(CO)_4R_2PCN]_2$$

These bridged complexes were easily prepared when molybdenum norbornadiene tetracarbonyl was allowed to react with the ligands. The chromium analogs, however, were prepared with slightly more difficulty. For both metals the formation of the bridged complexes was observed as the appearance of a bright yellow precipitate. A facile reaction was observed for diphenyl- and dimethylcyanophosphines for both metals, however, the diethylcyanophosphite and bis(dimethylamino)-cyanophosphine ligands, although readily reacting with molybdenum, reacted substantially slower with chromium. In addition, these latter complexes of chromium were not nearly as stable to decomposition as the other complexes which were prepared.

When two moles of ligand were added to the metal norbornadienetetracarbonyl complex, the bridged complex would again precipitate from solution. However, if this solution was then refluxed for about an hour, the bridged species gradually went into solution as the monomeric disubstituted complex [$M(CO)_4L_2$] formed. In similar manner, the bridged species could undergo a reaction with a second mole of a different phosphorus ligand (L') to give $M(CO)_4LL'$.

$$M(CO)_4C_7H_8 + R_2PCN \longrightarrow [M(CO)_4R_2PCN]_2 + R_2PCN \longrightarrow [M(CO)_4(R_2PCN)_2]$$

These disubstituted monomeric species were found to be unstable to air possibly because of the hygroscopic nature of the cyanide group. (The compound, $P(CN)_3$, is reported to be extremely sensitive to moisture, yet inert to oxygen at room temperature (74).)

Infrared Spectral Data of Metal Complexes of Some Cyanophosphine Ligands.- Table 9 lists the infrared data for the carbonyl and cyanide stretching regions for all of the complexes isolated and characterized from the reactions of some of these cyanophosphines with either molybdenum or chromium carbonyls. Figure 8 shows the shapes and intensities of the infrared bands in the CO region of the disubstituted complexes and the bridged complexes which were prepared. All of the disubstituted complexes of molybdenum were white and of the cis configuration, while the chromium analogs were yellow and trans-disubstituted with the exception of the chromium complex of $(CH_3)_2PCN$ which was cis. The C_{2v} (cis) and D_{4h} (trans) symmetries of these complexes were easily determined from the number and intensity of the carbonyl stretching frequencies (11) (Table 9, Figure 8). The trans- configuration found in the disubstituted complexes of chromium may indicate that a sterically hindered arrangement exists in the cis isomers of the bulkier ligands and

Table 9. Cyanide and carbonyl infrared frequencies for metal complexes.[a]

Compounds	ν C≡N[b]	ν C≡O[c]
$[Mo(CO)_4L]_2$		
L =		
Ph_2PCN	2161	2031,1945,1886
$PhP(CN)_2$	2170,2155	2044,1965,1920
$(CH_3)_2PCN$	2163	2028,1935,1887
$(C_2H_5O)_2PCN$	2164	2037,1946,1906
$[(CH_3)_2N]_2PCN$	2159	2025,1932,1881
$[Cr(CO)_4L]_2$		
L =		
Ph_2PCN	2158	2023,1930,1885
$(CH_3)_2PCN$	2161	2020,1934,1885
$(C_2H_5O)_2PCN$	2150	2025,1985,1930
$[(CH_3)_2N]_2PCN$	2155	2018,1927,1886
$Mo(CO)_4L_2$		
L =		
Ph_2PCN	2183	2039,1955,1932
$(CH_3)_2PCN$	2183	2040,1950,1925
$(C_2H_5O)_2PCN$	2183	2062,1997,1970
$[(CH_3)_2N]_2PCN$	2176	2037,1945,1924
$Cr(CO)_4L_2$		
L =		
Ph_2PCN (trans)	2182	1925
$(CH_3)_2PCN$	2182	2031,1945,1918
$[(CH_3)_2N]_2PCN$ (trans)	2173	1917

Table 9. (Continued)

Compound	ν C≡N[b]	ν C≡O[c]
$Mo(CO)_4LL'$		
$L = [(CH_3)_2N]_2PCN$	2175	2035,1960,1920
$L' = (CH_3O)_3P$		
$L = [(CH_3)_2N]_2PCN$	2175	2040,1965,1930
$L' = P(OCH_2)_3CCH_3$		
$Cr(CO)_4LL'$ (trans)		
$L = [(CH_3)_2N]_2PCN$	2185	1918
$L' = (CH_3O)_3P$		

[a] $CHCl_3$ solutions.

[b] CN stretching frequencies were all medium to very weak in intensity.

[c] Disubstituted monomeric complexes were of cis configuration unless otherwide indicated.

Figure 8.- Shapes of the infrared bands in the CO region. *A* represents the general shape of the *cis*-disubstituted complexes and *B* the bridged complexes.

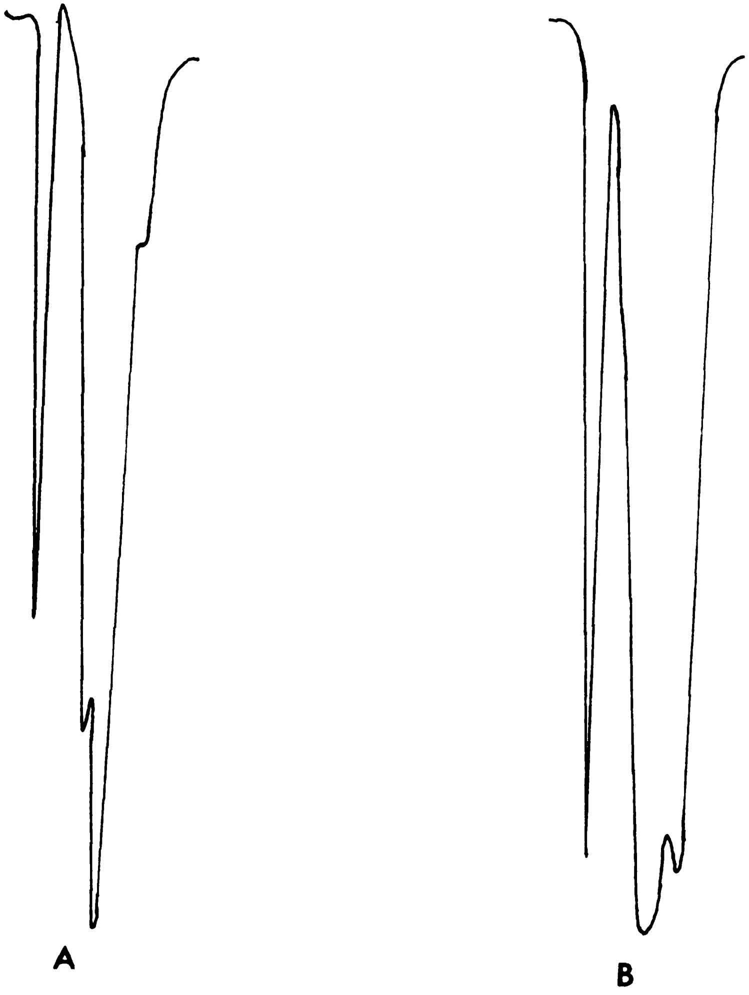


Figure 8.

that a cis-trans rearrangement takes place after initial attack of the bridged complex by a ligand (see later). This steric hindrance is apparently not significant for the larger molybdenum atom, and the cis configuration is reretained. For the cyanophosphine-bridged metal complexes, the CO stretching vibrations probably conform to a local C_{2v} carbonyl environment (about each metal) which requires four CO stretching frequencies ($2A_1 + B_1 + B_2$). The more intense B_2 band is generally of lower energy than the B_1 band for the cis-disubstituted complexes (13). For the dimers studied, however, the reverse may be true, since the B_1 band appears to be a lower energy shoulder of the B_2 band (Figure 8). Regardless of the assignment of these bands, however, the shapes of the infrared absorptions in the CO region (Figure 8) were always indicative of the type of complex present (monomer or dimer).

The cyanide stretching mode (ν_{CN}) was helpful in identifying the resulting complexes, although not nearly as useful as the carbonyl bands. The CN stretching frequency for the bridging ligands occurred at lower energy than that for the free ligand. The observed shifts to lower energy for the bridging ligands ranged from 9 to 30 cm^{-1}. The largest shift occurred for the dimeric Cr complex of $(C_2H_5O)_2PCN$. Nixon and Swain (83) observed a similar shift of 40 cm^{-1} for the Cr and Mo complexes of $(CF_3)_2PCN$. This shift to lower energy for the CN stretch in these bridging

cyanophosphines is opposite to the shift observed for a bridging thiocyanate ion in the complex [$Pt_2(PBr_3)_2Cl_2(SCN)_2$] (77). Bridging SCN groups are reported to have higher energy CN stretching frequencies than terminal SCN groups. Furthermore, the CN stretching frequencies for nitrile (RCN) complexes (55,78) are similarly reported to be of higher energy than the stretching frequencies of uncomplexed nitriles. Gerrard, et al. (79) and Stolz, et al. (80) have discussed the increase in ν_{CN} for nitriles upon coordination in terms of mesomeric forms of the uncoordinated nitrile which are not possible in the complexed nitrile. In the R_2PCN bridged complexes the lower value of ν_{CN} (lower than the value of the free ligand) may be the result of the strain on the M-P-C-N angles in these bridged complexes. If the nitrogen atom is sp hybridized ($-C\equiv N:$) then a nearly linear arrangement of the atoms P-C-N-M would result (M = Cr or Mo). This linear arrangement would place a strain on the M-P-C angles. (If the P-C-N system is nearly linear, the M-P-C bond angle would have to be close to 90^0 for the bridged complex.) However, if the sp hybrid orbital on nitrogen has some additional p character, which in the limit would be sp^2 hybridized ($-C\equiv\ddot{N}:$), then a smaller C-N-M angle would result. This smaller bond angle would be more compatible with a bridged structure since some ring strain would be relieved. The relatively small shift from free to complexed ligand in ν_{CN}, indicates that the CN bond

is still a triple bond. (An sp^2 hybridization on nitrogen would require a CN double bond.) However, the addition of some slight amount of p character to the sp orbitals would leave the triple bond intact, yet not only relieve ring strain but lower ν_{CN} slightly.

The cyanide stretching region for the bridged molybdenum complex of the ligand $PhP(CN)_2$ exhibited two different cyanide stretching frequencies. These frequencies indicated the presence of two distinct cyanide groups, one coordinated and one not coordinated. Therefore, despite the two available nitrogen bonding sites, the P-C-N bridge is preferred. For the disubstituted monomeric metal complexes of these cyanophosphines, the CN stretching frequency for the terminal CN group either remained essentially the same as the free ligand or actually increased slightly in energy from the value of the free ligand.

Proton Nmr of Metal Complexes.- The proton nmr spectra of the bridged complexes are not significantly different from the spectra of the free ligands except for a general downfield shift in the resonances (Table 10). If the organic groups attached to the phosphorus were either -Ph or $-OC_2H_5$, the spectra were complicated by the addition of proton-proton coupling to phosphorus-proton coupling. However, for complexes of either $(CH_3)_2PCN$ or $[(CH_3)_2N]_2PCN$ simpler spectra were obtained which were

Table 10. ^{1}H nmr of complexes[a].

Compounds	δ[c]	J_{P-H}
$[Mo(CO)_4L]_2$		
L =		
Ph_2PCN	7.55m	----
$PhP(CN)_2$[d]	----	----
$(CH_3)_2PCN$	1.94d	6.0
$(C_2H_5O)_2PCN$	1.30m (CH_3)	----
	3.70m (CH_2)	7.0
$[(CH_3)_2N]_2PCN$	2.82d	11.6
$[Cr(CO)_4L]_2$		
L =		
Ph_2PCN	7.50m	----
$(CH_3)_2PCN$	1.92d	5.0
$(C_2H_5O)_2PCN$	1.41m (CH_3)	----
	4.20m (CH_2)	7.0
$[(CH_3)_2N]_2PCN$	2.79d	11.0
$Mo(CO)_4L_2$		
L =		
Ph_2PCN	7.40m	----
$(CH_3)_2PCN$	1.95"t"	5.7
$(C_2H_5O)_2PCN$	1.45m (CH_3)	----
	4.20m (CH_2)	7.0
$[(CH_3)_2N]_2PCN$	2.82"t"	11.6
$Cr(CO)_4L_2$		
L =		
Ph_2PCN	7.40m	----
$(CH_3)_2PCN$	1.93"t"	6.8
$[(CH_3)_2N]_2PCN$	2.76"t"	11.8

Table 10. (Continued)

Compounds	δ^c	J_{P-H}
$Mo(CO)_4LL'$		
L = $[(CH_3)_2N]_2[CN$	2.71"t"	11.8
L' = $(CH_3O)_3P$	3.55"t"	11.2
L = $[(CH_3)_2N]_2PCN$	2.75"t"	11.6
L' - $P(OCH_2)CCH_3$	4.19"t" (CH_2)	4.1
$Cr(CO)_4LL'$		
L = $[(CH_3)_2N]_2PCN$	2.74"t"	11.6
L' = $(CH_3O)_3P$	3.64"t"	11.2

[a] All spectra of complexes taken in $CHCl_3$, except nmr spectra of phenyl derivatives which were obtained in CH_2Cl_2.

[b] Chemical shifts are in ppm (± 0.05) and are referenced to tetramethylsilane. Coupling constants are in Hz (±0.5).

[c] m = multiplet, d = doublet, "t" = apparent triplet due to virtual coupling.

[d] Not sufficiently soluble for nmr spectrum.

useful in structural determinations (see below). The disubstituted complexes $[M(CO)_4L_2]$ of these latter two ligands exhibited $X_nAA'X'_n$ type spectra (16,23) where X and A are the protons and phosphorus of one ligand and X' and A' are are the protons and phosphorus of a second identical ligand cis or trans to the first. These spectra consisted of a doublet of separation $|J_{AX} + J_{AX'}|$ (16) plus a central peak of varying intensity. The magnitude of this central resonance has been related to the magnitude of $J_{PP'}$ (16,18,48). The disubstituted molybdenum and chromium complexes which were cis and trans respectively, (with the exception of cis-$Cr(CO)_4[(CH_3)_2PCN]_2$) exhibited very weak central peaks, small ^{31}P-^{31}P coupling, consistent with other disubstituted complexes of this geometry (18,21,22,23,37). It has been observed that cis- disubstituted chromium complexes have very strong phosphorus-phosphorus coupling (18,21,22,82,89) (stronger than trans-disubstituted chromium). This coupling is demonstrated by the intense central peak observed for the complex cis-$Cr(CO)_4[(CH_3)_2PCN]_2$ (see Figure 11).

The proton nmr spectra of the mixed ligand complexes $[M(CO)_4LL']$ can be considered to be M_mABY_n spin systems similar to those discussed by Ogilvie, et al. (82), where A and B are the two phosphorus atoms and M and Y are the protons of the organic groups attached to the phosphorus atoms A and B, respectively. For these systems, if $J_{AB} <<$ $(\nu_A - \nu_B)$ (where ν_A and ν_B are the chemical shifts of the

Figure 9.- ^{1}H nmr spectra of the mixed ligand complexes. In both the Cr and the Mo complexes, L = $[(CH_3)_2N]_2PCN$ and L' = $(CH_3O)_3P$. (See Table 10 for chemical shifts and coupling constants.)

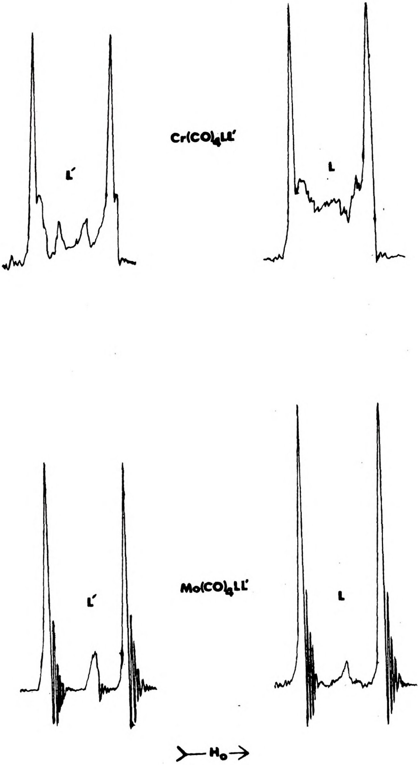


Figure 9.

protons on ligands A and B), then a doublet is observed for each set of protons split by the adjacent phosphorus atom. If $J_{AB} \approx (\nu_A - \nu_B)$, then perturbation of the doublet spectrum occurs (see Figure 9), and if $J_{AB} \gg (\nu_A - \nu_B)$, apparent "triplets" due to virtual coupling are observed (see Figure 9). Of the three mixed ligand complexes reported in Table 10 only the Mo compound, where L = $[(CH_3)_2N]_2PCN$ and L' = $(CH_3O)_3P$, exhibited apparent "triplets" in the ^1H nmr spectrum with very weak central peaks (Figure 9). In a previous study (82) of mixed ligand complexes, only examples of the first two cases outlined above, $J_{AB} \ll (\nu_A - \nu_B)$ and $J_{AB} \approx (\nu_A - \nu_B)$, were observed The spectrum of the lone Cr mixed ligand complex is best described as that of a perturbed doublet, $J_{AB} \approx (\nu_A - \nu_B)$, (Figure 9), while the spectrum of the remaining Mo complex with L = $[(CH_3)_2N]_2PCN$ and L = $P(OCH_2)_3CCH_3$ is essentially just two doublets; an example of the case where $J_{AB} \ll (\nu_A - \nu_B)$.

Mass Spectra of Complexes .- Nixon and Swain reported (83) that they observed mass spectra for their dimeric complexes of $(CF_3)_2PCN$ characterized by fragmentation patterns showing stepwise loss of all eight carbonyl groups while the $(MPCN)_2$ ring system remained intact. Of the complexes reported in this work, mass spectra have been obtained for $[Mo(CO)_4L]_2$ where L = Ph_2PCN, $PhP(CN)_2$, $(CH_3)_2PCN$, and $[(CH_3)_2N]_2PCN$ and for $\{Cr(CO)_4[(CH_3)_2N]_2PCN\}_2$. In these

cases, only the complexes with L = $[(CH_3)_2N]_2PCN$ showed parent ions and displayed fragmentation patterns similar to those reported by Nixon and Swain (83). For the Ph_2PCN and $(CH_3)_2PCN$ complexes, the predominant fragmentation patterns originated from the recombination ions of $(CO)_5MoL^+$ and $Mo(CO)_6{}^+$. In these cases there may very well be rapid cleavage of the dimer, as a result of the metal-nitrogen bonds breaking, leaving a species of the form $M(CO)_4L^+$, followed by combination with CO. The $PhP(CN)_2$ complex, however, showed only rapid decomposition of the entire complex.

Structure of Bridged Complexes.- The identity of the yellow crystalline solids obtained by the displacement of norbornadiene from $C_7H_8M(CO)_4$ with these cyanophosphine ligands was established by elemental analysis as being $[M(CO)_4L]_n$, and the value of 2 for n, which was expected because of the two potential bonding sites on each ligand, was confirmed by molecular weight measurement in one case (see Experimental) and by the observation of some parent ions in the mass spectra. Therefore, as suggested by Nixon and Swain for the Cr and Mo complexes of the ligand $(CF_3)_2PCN$ (83), a dimeric structure involving two bridging cyanophosphine ligands is assumed.

There are two possible isomers for this type of dimer (excluding CO bridging) (see Figure 10): one in which a given metal atom is bound to the phosphorus atom of one of

Figure 10.- Two possible isomers for the bridged dimeric complex. Dotted lines indicate expected cleavage by a phosphorus ligand.

ISOMERS

Figure 10.

the cyanophosphine ligands and to the nitrogen atom of the other (A), and a less symmetric isomer with both phosphorus atoms bound to the same metal (B). The products obtained from the reactions of these bridged complexes with other ligands, as well as the proton nmr and infrared spectra, indicate that the more symmetric of the two isomers is the only isomer present.

When a dimeric complex bridged with ligand L reacts with L', I would expect the metal-nitrogen bond to be cleaved to yield two moles of a disubstituted product. If I assume that the less symmetric structure (B) is present, then the bridged complex would be expected to cleave asymmetrically when it reacts with L' to yield two distinct complexes, $M(CO)_4L_2$ and $M(CO)_4L'_2$. However, if the more symmetric structure (A) is present, I would expect symmetric cleavage of the complex to yield two moles of $M(CO)_4LL'$. The mixed ligand complex is isolated exclusively from reactions of $[M(CO)_4L]_2$ with L'. Therefore, if no rearrangement occurs during reaction, isomer B can be ruled out. Additional support for isomer A comes from the nmr and infrared spectra. The more symmetric isomer A has only one carbonyl environment, while structure B would have two distinct carbonyl environments (one about each metal). In the infrared spectra only one carbonyl environment is observed. The nmr spectra of the <u>cis</u> disubstituted complexes, $M(CO)_4L_2$, where L = $(CH_3)_2PCN$ or $[(CH_3)_2N]_2PCN$,

clearly show the presence of virtual coupling. If in the bridged complex, isomer B were present, with two phosphorus atoms bound in a *cis*-configuration to a single metal atom, one would similarly expect to see some indication of virtual coupling in the nmr spectra. The spectra of the dimers, however, are sharp doublets (Figure 11) with no evidence of virtual coupling, a further indication of the presence of the more symmetric isomer (A).

Figure 11.- Examples of the proton nmr spectra used to determine structure of bridged complex.

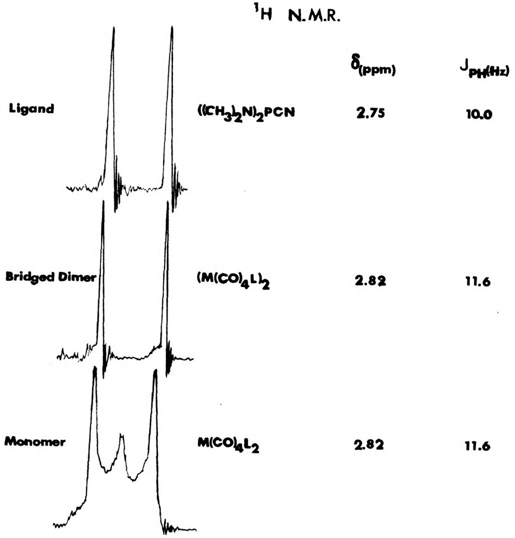

^{1}H N.M.R.
$\delta_{(ppm)}$
$J_{PH}(Hz)$
Ligand
$((CH_3)_2N)_2PCN$
2.75
10.0
Bridged Dimer
$(M(CO)_4L)_2$
2.82
11.6
Monomer
$M(CO)_4L_2$
2.82
11.6

Figure 11.

CONCLUSION

It was found that cyanophosphines could be easily prepared from the corresponding phosphorus chlorides and silver cyanide if acetonitrile was used as a solvent. These compounds were then observed to form coordination compounds with chromium and molybdenum carbonyls. Because of the potential donor sites on both phosphorus and nitrogen, the formation of the cyanophosphine bridged dimers was not totally unexpected. The ease with which these reactions took place was somewhat surprising, however, since even though nitrile coordination is well known (10, 55,80), replacement of a diene with a nitrile is not common. In fact nitriles have been used as intermediates for the formation of diene or triene metal carbonyls (54). The second step in these reactions, cleavage of the dimer by the phosphorus of a second mole of ligand was anticipated since phosphines are known to replace nitriles in group VIB metal carbonyl complexes (89).

Comparison of the infrared spectra of the molybdenum complexes of $(CH_3)_2PCN$, Ph_2PCN, and $(C_2H_5O)_2PCN$ to those of $P(CH_3)_3$, PPh_3, and $P(OC_2H_5)_3$, indicates that the cyanophosphine complexes always exhibit the higher CO stretching frequencies. This observation

indicates that the π-accepting capacity of the phosphorus atom is increased by the bonding of cyanide group to it. An indication of the strong effect that these cyanide groups have on the phosphorus-metal bonding can be obtained by comparison of the cyano group to a chloride. Halides, as substituent groups on a phosphorus, are generally thought to cause a pronounced increase in the π-accepting capacity of phosphorus ligands (13). The complex $Mo(CO)_4(PCl_2OC_2H_5)_2$ with two chlorides on the phosphorus, has CO stretching frequencies at 2063, 1977, and 1968 cm^{-1} (13), while $Mo(CO)_4[P(CN)(OC_2H_5)_2]_2$ has CO frequencies at 2062, 1997, and 1970 cm^{-1}. This shift may indicate that cyanide groups cause an even larger increase in the ability of a phosphorus ligand to accept metal d-π electron density than do chlorides.

Figure 10 shows the two possible isomers of the bridged complexes. The drawings are not intended to indicate a planar molecular structure of the ring system. Nixon and Swain (83) suggested by comparison to the planar arrangement of the eight membered ring in the thiocyanate bridged Pt complex, $Pt_2(PBr_3)_2Cl_2(SCN)_2$, for which a crystal structure is known (87), that their complex might have a planar ring system. If, as I have suggested in the infrared section here, the nitrogen (or carbon) atoms have some added p character to the sp orbitals, the PCN bonds might bow out slightly to relieve ring strain. If this

in fact happens, then a planar arrangement of the ring system should result. If, however, these sp orbitals on both C and N acquired a significant amount of p character, the ring would pucker, thereby eliminating the possibility of planarity.

SUGGESTIONS FOR FUTURE WORK

There are several logical extensions of the chemistry investigated here. The most obvious work would be to study further the complexes already prepared. A thorough study of the carbonyl stretching frequencies and force constants would help to clarify the nature of the bonding in these cyanophosphine complexes. More interesting, however, would be a crystal structure determination to discover the exact configuration of the proposed eight membered ring. This ring structure would give information suggesting the orbital configurations (hybridizations) about the phosphorus, carbon, and nitrogen. Since the P-C-N bond angles in $P(CN)_3$ are about 172° (76), and in PF_2CN approximately 165° (88), a remarkable deviation from linearity for this P-C-N group might be found in these complexes.

A most interesting reaction to investigate might be that of the cis-disubstituted complexes of the type cis-$M(CO)_4(R_2PCN)_2$ with another diene complex, $M'(CO)_4$diene. This reaction could produce a bridged dimer with two different metals (Mo and Cr), or if the same metal were to be used for both groups, and if there were no rearrangement upon reaction, the less symmetric of the two isomers given in Figure 10 would be produced in which both phosphorus atoms are bound

to the same metal

Two other areas of interest for the extension of this work would be, first, to attempt the preparation and characterization of other metal complexes to determine if cyanophosphine bridges will form with other metals, such as Fe, Ni, Pd, and Pt, and secondly, to investigate the reaction of these cyanophosphines, R_2PCN and $RP(CN)_2$, with various boron Lewis acids. This study should provide information about the relative basicities of phosphorus *versus* the cyanide lone pair of electrons.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).
2. G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1(1959).
3. E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1964).
4. E. O. Fischer and H. P. Fritz, *Angew. Chem.*, **73**, 353 (1961).
5. P. L. Pauson, in "Organometallic Chemistry," (H. Zeiss, ed.), New York: Reinhold, 1960, p. 346.
6. H. Zeiss, in "Organometallic Chemistry," (H. Zeiss, ed.), New York: Reinhold, 1960, p. 380.
7. W. Strohmeier, *Angew. Chem. Intern. Ed. English*, **3**, 730 (1964).
8. E. W. Abel, *Quart. Rev. (London)*, **17**, 133 (1963).
9. W. Hieber, *Adv. Organometal. Chem.*, **8**, 1 (1970).
10. G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).
11. F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).
12. F. A. Cotton and C. S. Kraihanzel, *Inorg. Chem.*, **2**, 533 (1963).
13. F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
14. R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).
15. W. Hieber and T. Kruck, *Z. Naturforsch.*, **16b**, 709 (1961).
16. R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
17. R. K. Harris, *Inorg. Chem.*, **5**, 701 (1966).

18. F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970).

19. R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970).

20. F. B. Ogilvie, R. L. Keiter, G. Wulfsberg, and J. G. Verkade, *Inorg. Chem.*, **8**, 2346 (1969).

21. R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

22. J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.* (A), 2796 (1969).

23. J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

24. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (A), 770 (1966).

25. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (A), 1407 (1966).

26. J. R. Moss and B. L. Shaw, *J. Chem. Soc.* (A), 1793 (1966).

27. P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (A), 1709 (1967).

28. E. W. Abel, R. A. N. Mclean, and S. P. Tyfield, *J. Molec. Spect.*, **30**, 29 (1969).

29. D. M. Adams, *J. Chem. Soc.*, 1771 (1964).

30. M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

31. A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc.* (A), 1817 (1967).

32. A. C. Vandenbroucke, Jr., D. G. Hendricker, R. E. Mc Carley, and J. G. Verkade, *Inorg. Chem.*, **7**, 1825 (1968).

33. J. M. Jenkins and J. G. Verkade, *Inorg. Chem.*, **6**, 2250 (1967).

34. A. Whitaker and J. W. Jeffery, *Acta. Cryst.*, **23**, 977 (1967).

35. G. Huttner and S. Schelle, *J. Organometal. Chem.*, **19**, p9 (1969).

36. D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).

37. R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

38. R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771(1965).

39. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," New York: Interscience Publishers, 1967, p. 728.

40. R. J. Angelici and Sr. M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

41. L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.*, **83**, 3192 (1961).

42. S. O. Grim, W. McFarlane, and D. A. Wheatland, *Inorg. Nuc. Chem. Letters*, **2**, 49 (1966).

43. M. Lenzi and R. Poilblanc, *Compt. Rend. Series C*, **263**, 674 (1966).

44. S. I. Shupack and B. Wagner, *Chem. Commun.*, **547** (1966).

45. G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967).

46. H. J. Plasts, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

47. R. E. Dessey and L. Wieczorek, *J. Amer. Chem. Soc.*, **91**, 4963 (1969).

48. J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

49. K. J. Coskran, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, **89**, 4535 (1967).

50. V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. VanWazer, *Topic in Phosphorus Chem.*, **5**, 227 (1967).

51. L. Maier, *Helv. Chim Acta*, 2667 (1963).

52. R. B. King, *Organometal. Syn.*, **1**, 124 (1965).

53. R. J. Angelici, *J. Chem. Educ.*, **45**, 119 (1968).

54. R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

55. B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

56. R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969).

57. E. D. Morris, Jr. and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

58. C. G. Barlow, J. F. Nixon, M. Webster, *J. Chem. Soc.* (A), 2216 (1968).

59. J. G. Verkade, private communication.

60. S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

61. R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

62. W. Strohmeier and K. Gerlack, *Chem. Ber.*, **94**, 398 (1961).

63. R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

64. P. G. Kirk and T. D. Smith, *J. Inorg. Nucl. Chem.*, **30**, 892 (1968).

65. P. A. Staats and H. W. Morgen, *Inorg. Syn.*, **6**, 84 (1960).

66. H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1109 (1963).

67. H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1479 (1963).

68. K. A. Petrov, L. G. Gatsenko, and H. A. Neimysheva, *Zh. Obshch. Khim*, **29**, 1827 (1959).

69. P. G. Kirk and T. D. Smith, *Chem. Commun.*, 42 (1968).

70. P. G. Kirk and T. D. Smith, *J. Chem. Soc.* (A), 2190 (1969).

71. Van Ebbelhard Fluck and J. R. VanWazer, *Z. Anorg. Allg. Chem.*, **307**, 113 (1961).

72. G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

73. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Englewood Cliffs, N.J.: Prentice Hall, Inc., 1965, p. 74-79.

74. V. J. Goubeau, H. Haiberle, and H. Ulmer, *Z. Anorg. Allg. Chem.*, **311**, 110 (1961).

75. W. Z. Borer and K. Cohn, *Anal. Chim. Acta*, **47**, 355 (1969).

76. K. Emerson and D. Britton, *Acta Cryst*., **17**, 1134 (1964).

77. J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956).

78. H. J. Coerver and A. C. Curran, *J. Amer. Chem. Soc*., **80**, 3522 (1958).

79. W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960).

80. I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963).

81. T. R. Johnson, R. M. Lynden-Bell, and J. F. Nixon, *J, Organometal. Chem*., **21**, p15(1970).

82. F. Ogilvie, R. J. Clark, and J. G. Verkade, *Inorg. Chem*., **8**, 1904 (1969).

83. J. F. Nixon and J. R. Swain, *J. Organometal. Chem.*, **21**, 13 (1970).

84. F. A. Miller, S. G. Frankiss, and D. Sala, *Spectrochim. Acta*, **21**, 775 (1965).

85. F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc*., 1565 (1953).

86. K. J. Packer, *J. Chem. Soc*., 960 (1963).

87. P. G. Owston and J. M. Rowe, *Acta Cryst*., **13**, 253 (1960).

88. K. Cohn, private communication.

89. C. E. Jones and K. J. Coskran, *Inorg. Chem.*, **10**, 55 (1971).