THE SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF DIPHOSPHINE MONOXIDE COMPLEXES OF SELECTED TRANSITION METALS

FONTAINE COSBY BRADLEY
University of New Hampshire, Durham

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University of New Hampshire

Ph.D. 1984

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
THE SYNTHESIS, CHARACTERIZATION, AND
REACTIONS OF DIPHOSPHINE MONOXIDE
COMPLEXES OF SELECTED TRANSITION METALS

BY

Fontaine C. Bradley
B.S., Tufts University, 1973

A DISSERTATION

Submitted to the University of New Hampshire
In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy

in

Chemistry

December 1984
This dissertation has been examined and approved.

Edward H. Wong  
Faculty Advisor  
Associate Professor of Chemistry

Frederick G. Hochgraf  
Associate Professor of Materials Science

Paul R. Jones  
Professor of Chemistry

Frank L. Pilar  
Professor of Chemistry

James H. Weber  
Professor of Chemistry

August 3, 1984  
Date
Acknowledgements

I would like to thank Ed Wong for being ever available and ever tolerant of my incessant badgering. He is a great chemist and a great friend.

I would like to thank Ms. Kathleen Gallagher for her help in running the NMR. Without Kathy and therefore without the NMR this work would not have been possible.

Finally I would like acknowledge the invaluable collaboration between Dr. Eric J. Gabe at the National Research Council of Canada and this laboratory. Dr. Gabe solved a great many problems by means of his expertise in x-ray crystallography.
This dissertation is dedicated to the memory of my father

Thomas Bradley
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ABSTRACT

THE SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF DIPHOSPHINE MONOXIDE COMPLEXES OF SELECTED TRANSITION METALS

By

Fontaine C. Bradley
University of New Hampshire, December, 1984

The synthesis, characterization and reactions of transition metal complexes containing diphosphine oxide, \( \text{R}_2\text{P-P(0)PR}_2 \), and diphosphoxane, \( \text{R}_2\text{P-O-PR}_2 \), ligands have been studied. The diphosphoxane tautomer, which is unstable in the free state has been observed to be stabilized by coordination to Mo(0) and Cu(I).

The reactivity of cis-(\( \text{CO} \))\(_4\text{Mo(} \text{R}_2\text{P-O-PR}_2 \)) (\( R = \text{Ph, p-tolyl} \)) towards halogen-oxidation has been studied. The new seven-coordinate complexes (\( \text{CO} \))\(_3\text{Mo(} \text{R}_2\text{P-O-PR}_2 \))\(_2 \) (\( R = \text{Ph, } X = \text{I} ; R = \text{p-tolyl, } X = \text{Br} \)), as well as the known (\( \text{CO} \))\(_3\text{Mo(} \text{Ph}_2\text{PCH}_2\text{PPh}_2 \))\(_2 \text{I}_2 \) have been observed to exhibit temperature-dependent \( ^{31}\text{P} \) NMR consistent with rapid topological isomerization and intramolecular rearrangement of a given isomer.

The reaction of coordinated aminophosphines has been shown to lead, via fluoride exchange, to mixed fluorophosphine-aminophosphine complexes. This result is in agreement with published reports of fluoride exchange reactions which occur via initial coordination of BF\(_3 \) etherate to the nitrogen donor of free aminophosphines.
The reaction of Ph$_2$P-P(0)Ph$_2$ with [cp(CO)$_2$FeTHF]BF$_4$ has resulted in a redistribution reaction leading to [cp(CO)$_2$FePh$_2$P-PPh$_2$Fe(CO)$_2$cp][BF$_4$]$_2$. A mechanism for this unusual transformation has been proposed based on $^{31}$P NMR evidence.

Five new complexes, cis-(CO)$_4$Mo(Ph$_2$P-O-PPh$_2$), cis-(CO)$_4$Mo(Ph$_2$P-O-P(0)(Ph)PPh$_2$), trans-(CO)$_4$Mo(Ph$_2$P-P(0)(OEt)$_2$)$_2$, (CO)$_3$Mo(Ph$_2$P-O-PPh$_2$)I$_2$, and [(CuCl)$_2$Ph$_2$P-O-PPh$_2$]$_2$ have been structurally characterized by x-ray crystallography. $^{31}$P NMR and IR spectroscopy have been used extensively throughout the research described in this dissertation and the results of these spectroscopic investigations have been discussed.
Note: In this dissertation a convention will be used to simplify the drawing of metal carbonyl complexes. In this convention a

![Diagram: Mo(CO)\textsubscript{6}]

will be used to represent a metal carbonyl. The above drawing is a representation of Mo(CO)\textsubscript{6} in which the octahedral arrangement of the six carbon monoxide groups is shown simply as six lines radiating from the metal center. Substitution of carbon monoxide by a phosphine will be explicitly shown, i.e.,

![Diagram: Ph\textsubscript{2}PCL\textsubscript{2}Mo(CO)\textsubscript{4}]

is a drawing of the complex trans-(CO)\textsubscript{4}Mo(Ph\textsubscript{2}PCL\textsubscript{2}).
INTRODUCTION

One of the central themes of recent inorganic chemistry is that metal-metal interactions present in the bulk metal may, on some level, be mimicked by the metal-metal interactions present in polymetallic molecular complexes. The hope has been that the soluble complexes, being easier to study than the bulk metals, can provide useful models for the physical and chemical behavior of the bulk metals.

Compounds containing direct metal-metal bonds have been known for many years but in the past ten years there has been a tremendous increase in the synthesis and study of these compounds. While it is becoming apparent that there are as many differences as there are similarities between polymetallic clusters and bulk metals, there is much to be gained from studying metal-metal interactions in simple complexes and clusters.

From a purely scientific point of view the availability of simple metal-metal bonded complexes will lead to physical models for metal-metal interactions which can be tested. The compounds may also be used as starting materials in the synthesis of complexes which cannot be made by other means and which may have novel properties.

In a more practical arena, metal-metal bonds play a central role in biological and industrial catalysis, magnetism, electrical conduction and electrode processes.
As deliberate variations in the structures of organic compounds have led to the production of drugs with specifically sought properties, the ability to manipulate and understand the structures of inorganic compounds will lead to the ability to design, at the molecular level, materials with specifically sought properties.

Quite removed from these grandiose claims is the problem of the synthesis and study of complexes containing two or more metal sites within bonding distance of one another. Often the lowest unoccupied and the highest occupied molecular orbitals in these complexes are metal-metal molecular orbitals which translates into metal-metal bond scission in many reactions. A stable framework is necessary to hold the two metals within bonding distance such that their interaction can be probed without causing the complex to come apart. It was the search for synthetically accessible metal-metal bridging ligands that provided a starting point for this research.

In the first chapter, reactions leading to complexes containing diphosphine monoxide ligands, \( \text{R}_2\text{P-P(O)PR}_2 \) and diphosphoxane ligands, \( \text{R}_2\text{P-O-PR}_2 \) are discussed. These are complexes of group 6B metal carbonyls, most specifically, molybdenum carbonyl. In fact the work described in the first chapter is paralleled by similar studies of the chromium and tungsten carbonyls but these reactions were studied to only a limited extent by this author and are not discussed here.
In the second chapter, the reactivity of a coordinated diphosphoxane complex towards halogen oxidation is described. This is a well known type of reaction\(^{31}\) and the results were observed to be similar in many ways to those obtained from the oxidation of similar compounds containing the diphosphine \(R_2PCH_2PR_2\). In addition, \(^{31}\)P NMR studies of these complexes show some interesting temperature dependent processes which were previously unreported for complexes of this type.

In Chapter 3, the effect of coordination of \(R_2P-P(0)R_2\) (\(R=\text{phenyl}\)) to copper (I) and iron (II) ions is explored. These reactions gave results which were not anticipated and were quite removed from the context of this work. Also described in this chapter is a study of the reaction of coordinated aminophosphines, again with an eye towards making nitrogen-linked diphosphine bridged bimetallics similar to the oxygen linked diphosphines described in Chapter 1. The results of these reactions were also unanticipated and contained structures quite different from those desired.
In a somewhat arbitrary fashion, transition metal clusters can be divided into two classes depending on the oxidation state of the metal. These two classes are, 1, the complexes containing metals in a high oxidation state and 2, the complexes containing metals in a low oxidation state. These have also been called high valent and low valent metal complexes respectively. The distinction is useful because the donor ligands in the two types of clusters are different and are themselves divided into two classes, hard donors and soft donors.

Hard-soft acid-base theory is a description of the properties of donor-acceptor complexes in inorganic chemistry. Hard donors, Lewis bases like oxygen or nitrogen, tend to form more stable complexes with hard acceptors, which are metal atoms in higher oxidation states. Soft donors like phosphorus or sulfur, form stable complexes with later transition metals and metals in lower oxidation states.

Zero valent metals - zero valent being a strange term meaning that the oxidation number of the metal is formally zero - are soft acceptors which prefer soft donors such as
phosphorus or sulfur. All transition metal ligands are Lewis bases with a free pair of electrons available to form coordinate covalent or dative bonds, although as we shall see, a salient feature of the bonding between zero valent metals and their ligands is that both centers act as both donors and acceptors of electron density. Phosphorus(III) ligands are particularly suited to serve as both $\sigma$-donors and $\pi$-acceptors of electron density and form strong bonds with transition metals in low oxidation states.

Our interest has been to use hetero-atom (N, O, S) bridged diphosphines, $R_2P-E-PR_2$, $E=N, O, S$, to link two metal centers together. There are several ways this can be accomplished.

Diphosphines of the type $R_2P-P(E)R_2$ ($E=O, S, NR$), can exist in one of two isomeric forms (eq. 1).

$$R_2P-P(E)R_2 \rightleftharpoons R_2P-E-PR_2 \text{ eq. 1}$$

These two forms, 1 and 2, can be viewed formally as valence tautomers. Both forms are known. $^2$ $^2$ 2 contains two trivalent phosphorus atoms each with a lone pair available for bonding to transition metals. It is the more stable form for electronegative or bulky substituents such as $(CF_3)_2P-O-P(CF_3)_2$, $(EtO)_2P-O-P(0Et)_2$ and $(t-Bu)_2P-O-P(t-Bu)_2$. The more common form of these ligands, however, is the mixed valent form with a direct phosphorus-phosphorus bond, 1. The free ligands are known to interconvert such that the kinetic product 3,
slowly tautomerizes to yield the thermodynamically more stable phosphoxane 4 (eqs. 2, 3). It was interesting to us to see whether transition metal coordination would have an effect on the position of the equilibrium shown in eq. 1. It is reasonable to expect the metal complex to act as both a bulky substituent and an electron-withdrawing substituent (vide infra) and thus favor the diphosphoxane form. If this were the case, coordination of the diphosphine oxide would result in the formation of a species which, through tautomerization would yield a monodentate metal-containing ligand, 5, useful in the synthesis of bi-metallics (eq. 4).

A variation of the nucleophilic substitution reaction shown in eq. 2 but with coordinated reactants, provides an alternative approach to the synthesis of hetero-atom-bridged diphosphines. The reaction of a free ligand with a coordinated ligand (eq. 5)
yields the same metal containing monodentate ligand 5.

Reactions of coordinated halo-phosphines with H₂O, results in the formation of hetero-atom bridged bimetallic diphosphines (eq. 6).

\[ 2 \text{MR}_2\text{PX} + \text{E(H)}_n \rightarrow \text{MR}_2\text{P-E-PR}_2\text{M} \quad \text{eq. 6} \]

The reactivity of coordinated phosphines is modified with respect to the uncomplexed ligands. Reactions 4-6 are examples of reactions of coordinated phosphines.

Phosphorus-containing ligands are able to bridge two metal centers in a variety of ways. By far the most common bridges contain either a phosphido-bridge or else are carbon bridged diphosphines.

The phosphido-anion 6 can be viewed as a bivalent phosphorus anion with two pairs of electrons available for bonding. As such it can form complexes as either a terminal ligand, 7, or bridging ligand 8. There are many examples of both homo- and heterobimetallic complexes containing phosphido-bridges. In most cases the phosphido-bridge has appeared very stable, but a recent report has demonstrated the addition of ethylene across a phosphido-metal bond.

Diphosphine-bridging ligands, particularly the carbon bridged diphosphines, have been used to prepare a variety
of homo- and heteronuclear bimetallic and chelate complexes, whereas heteroatom bridged diphosphines, P-O-P or P-S-P for example, have not been used much in the preparation of coordination compounds and deserve more attention as synthetic routes to bimetallics. There are potentially more routes available to this type of diphosphine than to the carbon bridged species. The carbon nucleophiles such as Grignard and lithium reagents are extremely reactive in phosphorus chemistry and the reactions are difficult to control.

Nitrogen or oxygen nucleophiles do not require the highly energetic conditions for their reactions that are needed to generate carbanion nucleophiles. Kraihanzel has demonstrated that the hydrolysis of coordinated diphenylchlorophosphine results in the formation of a mixture of the coordinated phosphinous acid and a bimetallic diphosphoxane complex (eq.7).

\[
\begin{align*}
(CO)_5\text{Mo}(\text{Ph}_2\text{PCl}) & \xrightarrow{\text{H}_2\text{O, Base}} \\
9 & \\
(CO)_5\text{Mo}(\text{Ph}_2\text{POH}) + [(CO)_5\text{Mo}(\text{Ph}_2\text{P})]_2\text{O} & \text{eq.7}
\end{align*}
\]

10 11
Direct reaction of diphenyl phosphine oxide gave the coordinated phosphinous acid (eq. 8).

$$\text{Mo(CO)}_6 + \text{Ph}_2\text{P(OH)} \rightarrow \text{(CO)}_5\text{Mo(Ph}_2\text{POH)} \quad \text{eq. 8}$$

Further, it was shown that the coordinated phosphinous acid had appreciable acid character and provided a simple route to the diphosphoxane bridged bimetallic (eq. 9).

$$\text{(CO)}_5\text{Mo(Ph}_2\text{PCl) + (CO)}_5\text{MoPh}_2\text{P-O}^- \rightarrow [(\text{CO})_5\text{MoPh}_2\text{P}]_2\text{O} + \text{Cl}^- \quad \text{eq. 9}$$

By contrast, in this lab, the hydrolysis of diphenylchlorophosphine was observed to yield diphenylphosphine oxide or a mixture of diphenyl phosphine and diphenylphosphinic acid, the outcome depending on the reaction conditions (eq. 10).

$$\text{Ph}_2\text{P(OH)} + \text{Ph}_2\text{P-P(O)Ph}_2 + \text{Ph}_2\text{PH} + \text{Ph}_2\text{P(O)OH} \quad \text{eq. 10}$$

The reactivity of chlorophosphines towards hydrolysis is modified by coordination to molybdenum. This is probably the result of the steric crowding of the coordination sphere of the metal and the changes in the charge distribution around the phosphorus resulting from the donation of the phosphorus lone pair and the population of the phosphorus d orbitals.

In light of these results and Kraihanzel's convenient
preparation of the coordinated diphenylphosphinous acid, it was our intention to extend the work in a study of the general utility of the diphosphoxane linkage in the synthesis of multimetallic complexes.

In a reaction (eq.11)

\[
(CO)_5 MoPh_2 PO^- + \text{Ph}_2 \text{PCl} \rightarrow (CO)_5 \text{Mo(Ph}_2 \text{POPOPPh}_2) + \text{Cl}^- \quad \text{eq.11}
\]

analogous to that shown in eq.3, reaction of 12 with uncomplexed Ph\(_2\)PCl yielded tetraphenyldiphosphoxanemolybdenumpentacarbonyl, 13, a metal-containing monodentate ligand which then served as the starting point for the bimetallics shown in eq.12-14.\(^{13}\)

\[
13 + \text{Fe}_2(CO)_9 \rightarrow (CO)_5 \text{MoPh}_2 \text{POPOPPh}_2 \text{Fe(CO)}_4 \quad \text{eq.12}
\]

\[
13 + \text{CH}_3\text{CNCr(CO)}_5 \rightarrow (CO)_5 \text{MoPh}_2 \text{POPOPPh}_2 \text{Cr(CO)}_5 \quad \text{eq.13}
\]

\[
2(13) + \text{trans-L}_2 \text{PdCl}_2 \rightarrow \text{trans-((CO)}_5 \text{MoPh}_2 \text{POPOPPh}_2 \text{)}_2 \text{PdCl}_2 \quad \text{eq.14}
\]

The related anion 17 and diphosphoxane complex 18 have yielded a similar series of polymetallics.\(^{13}\)

\[
(CO)_5 \text{Mo(EtO)}_2 P-O^- \quad (CO)_5 \text{Mo(EtO)}_2 \text{POPOPPh}_2
\]

\[17 \quad 18\]

It seemed reasonable that trans-diphenylchlorophosphinetetracarbonylmolybdenum(0), 19, would provide a
convenient route to the trans-bis-phosphinous acid 21. This complex would then serve as a starting material in the synthesis of a variety of stable bimetallics. The resulting 'A' frame structure is a stable geometry in the complexes of the carbon bridging diphosphines.6

Results

The room temperature hydrolysis of 19 in THF in the presence of triethylamine yielded 20 as the triethylammonium salt in greater than 90% yield and not the trans-bis-phosphinous acid 21 (eq.15). It is likely that 21 is an intermediate in the reaction but it has not been observed.

\[
\begin{align*}
\text{Ph}_2\text{PCl} & \quad \text{Et}_3\text{N} \\
\text{Mo} & \quad \text{H}_2\text{O} \\
\text{Ph}_2\text{PCl} & \quad \text{Ph}_2\text{POH} \\
19 & \quad 20 \\
\text{H}+ & \quad \text{Et}_3\text{NH} \\
\end{align*}
\]

In a similar reaction trans-(tolyl\(_2\)PCl\(_2\))Mo(CO)\(_4\) 22 was observed by \(^{31}\)P NMR to hydrolyze and isomerize more slowly and a species giving a singlet resonance at 127ppm was observed. Heating this sample to 40 C in the NMR tube for
about five minutes converted this species to the analogous hydrogen bridged chelate compound. This intermediate is most likely the trans-bis-phosphinous acid.

Complex 20, containing a six-membered chelate ring with a symmetric hydrogen-bridge, was first reported by Kraihanzel and Gray in 1978\textsuperscript{14} resulting from the hydrolysis of cis-\((\text{Ph}_2\text{PCl})_2\text{Mo(CO)}_4\) \textsuperscript{23}. While 20 could be viewed as the anion of a dibasic acid with the charge and the remaining proton localized on two phosphinite oxygens, the distance between the two oxygens is \(2.415(4)\) \text{Å} as determined by x-ray crystallography.\textsuperscript{15} A distance of < 2.50\text{Å} is taken as evidence of a strong symmetric hydrogen bridge.\textsuperscript{16}

The complex also has the potential to serve as the starting point in the synthesis of coordinated diphosphoxanes. A number of attempts to prepare the diphosphines by Kraihanzel resulted in the formation of \(24\), a complex featuring a four-membered phosphoxane chelate ring.\textsuperscript{19} Thus, the reaction of 20 with diphenylchlorophosphine resulted in the formation of \(24\) (eq.16).

\[
\text{Ph}_2\text{P} = \text{O}\quad \text{Mo} \quad \text{H} + \text{Ph}_2\text{PCl} \quad \rightarrow \quad \text{Mo} \quad \text{O} \quad \text{Ph}_2\text{P} \quad \text{Ph}_2\text{P} \quad +\text{Cl}^- 
\]

Similar reactions in our lab gave the same result such that
the variety of reagents leading to this common product is quite large (Ph$_2$PCl, PCl$_3$, RC(O)Cl, (CO)$_5$Mo(MePCl$_2$), H$^+$, trifluoroacetic anhydride). This compound is an acid anhydride of the cis-bis-phosphinous acid, and its formation can be represented formally as a protonation followed by dehydration. The reaction of trifluoroacetic anhydride, a dehydrating reagent, is consistent with this. The reaction also occurs with a trace of aqueous H$^+$ and it may be the presence of HCl in some of the above mentioned reagents that is actually responsible for the reaction.

In the crystal structure$^{12}$ of 20, the chelate ring is planar; the P-M-P angle is 63.82(3), the P-O-P angle is 103.3(1) and the normalized bite (bite=2sin $\alpha$/2, $\alpha$=P-M-P angle) is 1.05 (Figure 1, page 14, and Appendix B for selected bond distances and angles).$^{27}$ Although it would be expected$^9$ that such a small ring would be quite strained, the compound is quite stable in solution and can be stored as a solid in the dark without any appreciable change for years.
Figure 1
The Crystal Structure of
$\text{cis-} (\text{CO})_4 \text{Mo(Ph}_2\text{POPPh}_2)$
The reaction of the disodium salt of 20 with diphenylchlorophosphine (eq. 17),

\[
\begin{align*}
\text{Mo} & \quad \text{Ph}_2\text{P}-\text{O}^- \quad + \quad 2 \text{Ph}_2\text{PCl} \quad \rightarrow \quad \text{Mo} \quad \text{Ph}_2\text{P}-\text{O}^- \quad + \quad 2 \text{Cl}^- \\
\text{Ph}_2\text{P}-\text{O}^- & \quad \text{Ph}_2\text{P}-\text{O}^- \\
\end{align*}
\]

\[\text{Ph}_2\text{P}-\text{O}^- + \text{Ph}_2\text{PCl} \quad \rightarrow \quad \text{Ph}_2\text{P}-\text{P(O)}\text{Ph}_2 \quad \text{eq. 17}
\]

in contrast to the triethylammonium salt, gave the transient bis-diphosphoxane complex 26. This complex could be observed by $^{31}$P NMR and isolated as a crude solid, but it decomposes in solution within 6 hours to give 24 and tetraphenyldiphosphine monoxide.

The reaction of 20 with PhPCl$_2$ (eq. 18),

\[
\begin{align*}
\text{Mo} & \quad \text{Ph}_2\text{P}-\text{O}^- \quad + \quad \text{PhPCl}_2 \quad \rightarrow \quad \text{Mo} \quad \text{Ph}_2\text{P}-\text{O}^- \quad + \quad 2 \text{Cl}^- \\
\text{Ph}_2\text{P}-\text{O}^- & \quad \text{Ph}_2\text{P}-\text{P(O)}\text{Ph}_2 \\
\end{align*}
\]

\[\text{Ph}_2\text{P}-\text{P(O)}\text{Ph}_2 \quad \text{eq. 18}
\]

However, does not lead to the four-membered chelate ring.
complex 24 but instead yields a compound containing a five-membered ring, in fair yield. This ring contains a phosphinite donor, a tetravalent phosphinate phosphorus and a phosphine donor. This structure was confirmed by an x-ray crystal structure determination (Figure 2, page 17, and Appendix B for selected bond distances and angles). An intermediate triphosphoxane is observed by $^{31}\text{P}$ NMR which rapidly contracts to a five-membered ring by tautomerization (eq. 18).

The sodium salt of coordinated diphenylphosphinous acid, 12, acting as a nucleophile, displaced chloride from a series of chlorophosphines to form polyphosphoxane complexes (eq. 19-21).^13

\[
\text{Ph}_2\text{PCl} + (\text{CO})_5\text{Mo(Ph}_2\text{PO})^- \rightarrow 12 (\text{CO})_5\text{Mo(Ph}_2\text{POPPh}_2) \quad \text{eq. 19}
\]

\[
\text{PhPCl}_2 + 2 (\text{CO})_5\text{Mo(Ph}_2\text{PO})^- \rightarrow [(\text{CO})_5\text{Mo(Ph}_2\text{PO})]_2\text{PPh} \quad \text{eq. 20}
\]

\[
\text{PCl}_3 + 3 (\text{CO})_5\text{Mo(Ph}_2\text{PO})^- \rightarrow [(\text{CO})_5\text{Mo(Ph}_2\text{PO})]_3\text{P} \quad \text{eq. 21}
\]

With the exception of 13 as shown in eq. 12-14, the trivalent phosphorus in these complexes has not been observed to replace a weakly-bonded donor. The preparation
Figure 2
The Crystal Structure of
$cis-(CO)_4Mo(Ph_2POP(0)(Ph)PPh_2)$
of these compounds is fairly straightforward although the yields have been low such that their reactivity has been studied to only a limited extent.

The reaction of sodium diethylphosphite, \((\text{EtO})_2\text{PONa}\) 30, with both free and coordinated chlorophosphines yielded compounds containing the diphosphine monoxide tautomer with a direct phosphorus-phosphorus bond (eq. 22-26).13

\[
\begin{align*}
(\text{EtO})_2\text{PO}^- + \text{Ph}_2\text{PCl} & \rightarrow \text{Ph}_2\text{P}(\text{O})(\text{OEt})_2 & \text{eq. 22} \\
(\text{EtO})_2\text{PO}^- + (\text{CO})_5\text{Mo}(\text{Ph}_2\text{PCl}) & \rightarrow (\text{CO})_5\text{Mo}(\text{Ph}_2\text{P-P(O)(OEt)})_2 & \text{eq. 23} \\
(\text{EtO})_2\text{PO}^- + \text{trans-}(\text{Ph}_2\text{PCl})_2\text{Mo(}\text{CO})_4 & \rightarrow \text{trans-}(\text{CO})_4\text{Mo(Ph}_2\text{P-P(O)(OEt)})_2(\text{Ph}_2\text{PCl}) & \text{eq. 24} \\
2 (\text{EtO})_2\text{PO}^- + \text{trans-}(\text{CO})_4\text{Mo(Ph}_2\text{PCl})_2 & \rightarrow \text{trans-}(\text{CO})_4\text{Mo(Ph}_2\text{P-P(O)(OEt)})_2_2 & \text{eq. 25} \\
2 (\text{EtO})_2\text{PO}^- + \text{cis-}(\text{CO})_4\text{Mo(Ph}_2\text{PCl})_2 & \rightarrow \text{cis-}(\text{CO})_4\text{Mo(Ph}_2\text{P-P(O)(OEt)})_2_2 & \text{eq. 26}
\end{align*}
\]

The AA'BB' spectrum expected for 34 has not yet been simulated but the structure has been confirmed by an x-ray crystal structure (Figure 3, page 19, and Appendix B for a table of selected bond distances and angles). Complex
Figure 3
The Crystal Structure of trans-\((\text{CO})_4\text{Mo(Ph}_2\text{P-P(O)(OEt)}_2\)
32 has also been independently synthesized by direct reaction of \( \text{Ph}_2\text{P-P(O)(OEt)}_2 \) and \( \text{Mo(CO)}_6 \). An alternate route to \( \text{35} \) has been found via reaction of the free diphosphine monoxide and \( \text{(NBD)Mo(CO)}_4 \) (NBD = bicyclo[2.2.1]-hepta-2,5-diene).

**Discussion**

For the characterization of the compounds presented in this thesis we have relied most heavily on \( ^{31}\text{P} \) NMR and IR spectroscopy. As this dissertation is the first to come out of this lab concerned with metal carbonyl chemistry, there is to be included in the discussion a preamble in which the basic principles of IR spectroscopy, as they apply to the study of metal carbonyl complexes, are outlined.

IR spectroscopy has played a central role in understanding the structure of metal carbonyl complexes. Carbon monoxide vapor absorbs very strongly in the IR around 2130 cm\(^{-1}\). In coordination compounds it absorbs in the range from 2100 to 1600 cm\(^{-1}\). The intense absorptions, occurring in a range relatively free from interference by other group frequencies makes the assignment of the CO absorption relatively easy and extremely useful. The position of the CO stretch depends on the strength of the bond.

Low valent metals are electron-rich, and, in the absence of stabilizing ligands, tend to become oxidized. Carbon monoxide stabilizes low valent transition metals by
its ability to remove electron density from the electron rich metal center by way of π-back bonding. The electrons which are distributed to the CO ligands originate in the highest occupied molecular orbitals\textsuperscript{22} of the complex. Since these orbitals are slightly antibonding in character, they most closely resemble the metal d atomic orbitals. The acceptor orbitals of the carbon monoxide are a degenerate pair of π-orbitals ideally situated to accept π-symmetry electron density from the occupied d metal orbitals. This metal dπ-ligand π overlap, leading to transmission of electron density from the metal to the ligands, is called π-back bonding. π-back bonding leads to an increase in the metal-carbon bond order both because the metal-carbon bond is a bonding orbital and also because electron density has been decreased in a metal molecular orbital which was somewhat antibonding in character. The carbon-oxygen bond-order is decreased, however, as π-back bonding populates a carbon-oxygen antibonding orbital.

The effects of π-back bonding are readily observed by IR spectroscopy as a lowering of the carbon-oxygen stretching frequency to around 2000 from 2130 cm\textsuperscript{-1} for free CO. The greater the extent of back bonding the lower the energy of the CO stretch.

Carbon monoxide is one of the best π-acceptor (π-acid, in the Lewis sense) ligands known. Replacement of a
CO with a neutral ligand such as a phosphine will further lower the position of the CO stretching frequencies of the remaining CO's as the phosphine acts as a better donor and poorer acceptor than CO. Replacement of CO with one, two, or three good donor ligands results in a steady shift of the CO stretching frequencies to lower and lower energies. It should be remembered that increasing the extent of back bonding increases the metal-carbon bond order which makes replacement of each additional CO more difficult. Metal carbonyl complex stability is the result of the right combination of acceptor and donor ligands around the metal.

The application of group theory to the interpretation of the CO stretching region of the spectra results in detailed structural information.\(^{22,28}\) The point symmetry of the complex is determined. The local symmetry of the non-CO ligands is ignored in making this determination, which results in the assignment of higher symmetry for the complex.

For example, \(\text{Ph}_2\text{PCl}\) is of \(C_3\) symmetry but the CO region of the IR spectrum of the complex \((\text{CO})_4\text{Mo(Ph}_2\text{PCl})_2\) is analyzed as though the complex were of \(D_{4h}\) symmetry. This is physically reasonable as the CO's are isolated from the ligands and their normal modes of vibration are many times greater than most other group frequencies.\(^{20}\) Reference to the appropriate character table allows the number and the irreducible representations of the IR-active stretching modes to be determined. The
actual assignments as to which band corresponds to which transition are not so conveniently made. The following rules are useful as guide lines in the assignment of spectra.

1) As the CO bond stretches the \( \pi \) -bonding within it decreases. This lowers the energy of the \( \pi^* \)-orbital so that it more closely matches the energy of the metal d-orbitals which increases the extent of the \( \pi \)-back bonding to that CO. This increase in back bonding to one CO occurs at the expense of the other CO's. The CO bond-order increases in these CO's which makes the bond harder to stretch. Thus, concerted bond stretch deformations are more difficult than bond stretches in concert with bond compressions, ie,

\[
\begin{align*}
\text{cis:} & \quad \text{trans is more difficult than} \quad \text{cis}\end{align*}
\]

2) Cis-CO's interact more weakly than trans-CO's:

\[
k_{\text{trans}} = 2k_{\text{cis}}
\]

where \( k \) represents the contribution of the stretch-stretch interaction to the position of the IR band. ie,

\[
\begin{align*}
\text{cis:} & \quad \text{trans is easier than} \quad \text{cis}
\end{align*}
\]

3) This follows directly from 2; CO trans to a good donor has a lower stretching frequency than CO cis to a good donor.

The above outlined procedure for the point groups of interest gives the following results.
A mono-substituted group 6B metal complex has $C_{4v}$.
symmetry which results in three IR-active bands in the CO stretch region, \( 2 \, A_1 + E \) (Figure 4 and Table 1). These terms refer to the irreducible representations of the stretching deformations under \( C_{4v} \) symmetry. They have the forms shown in Figure 4. The cis-disubstituted complexes are of \( C_{2v} \) symmetry and have four IR-active bands in the CO region, \( 2 \, A_1 + B_1 + B_2 \) (Figure 5). The trans-disubstituted complexes are \( D_{4h} \) and have but one active band, \( E_u \) (Figure 6). Examination of the spectrum of a trans-disubstituted complex shows that in addition there are some weak bands above 2000 cm\(^{-1}\). These are described as symmetry-forbidden transitions, and their appearance is a demonstration of the fact that the term symmetry-forbidden really means that the transition is less likely to occur than a symmetry-allowed transition. It also demonstrates the weakness of the assumption that the ligand symmetry does not affect the appearance of the CO spectrum.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Point Group</th>
<th>IR Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )Mo(CO)(_5)</td>
<td>( C_{4v} )</td>
<td>( 2 , A_1 ) active, ( E ) active</td>
</tr>
<tr>
<td>cis-( L_2)Mo(CO)(_4)</td>
<td>( C_{2v} )</td>
<td>( 2 , A_1 ) active, ( B_1 ) active, ( B_2 ) active</td>
</tr>
<tr>
<td>trans-( L_2)Mo(CO)(_4)</td>
<td>( D_{4h} )</td>
<td>( A_{1g} ) inactive, ( B_{1g} ) inactive, ( E_u ) active</td>
</tr>
</tbody>
</table>

Table 1
Irreducible Representations of the CO Stretches of Some Metal Carbonyls

The phosphorus-oxygen single and double bond stretching-frequencies also give rise to prominent bands in
the IR which have been useful in characterizing these compounds. The strongest of these two, the phosphorus-oxygen double bond, has a strong IR-active stretching mode in the range 1400-1150 cm\(^{-1}\). The phosphorus-oxygen single bond stretch occurs in the range 1030-820 cm\(^{-1}\). The diphosphoxane (\(R_2POP\)) stretch in the free ligands gives rise to two bands associated with symmetric (720-680 cm\(^{-1}\)) and asymmetric (980-930 cm\(^{-1}\)) stretches. The symmetric band is weak and it is not clear that two strongly coupled modes occur in the coordination compounds. We have assigned one band to the diphosphoxane stretching frequency in the range 900-750 cm\(^{-1}\).

In the following discussion the principles outlined above will be used in the analysis of the IR spectra of the new compounds reported in this thesis.

When molybdenum hexacarbonyl and \(\text{Ph}_2\text{PCl}\) are refluxed in toluene a mixture of three compounds, the monosubstituted and the cis- and trans-disubstituted, is formed. These three compounds can be separated fairly easily and their identity determined by examination of the IR spectrum.

\((\text{CO})_5\text{Mo(Ph}_2\text{PCl)}\) (C\(_4\)v, three bands around 2000 cm\(^{-1}\)) and \(\text{cis-(CO)}_4\text{Mo(Ph}_2\text{PCl)}_2\) (C\(_2\)v, four bands around 2000 cm\(^{-1}\)) both have \(A_1\) transitions in the CO region above 2000 cm\(^{-1}\) (Figure 7). Though the number of bands around 2000 cm\(^{-1}\) is different for the two complexes, in practice it is
Figure 7
$L=\text{Ph}_2\text{PCl}$
sometimes difficult to resolve the bands below 2000 cm\(^{-1}\). Nonetheless they can be distinguished by noting that the monosubstituted compound's higher energy \(A_1\) band occurs at 2072 cm\(^{-1}\) because of the lower electron density at the metal. Substitution of a second CO by the better \(\sigma\)-donor phosphine lowers the position of this \(A_1\) band to around 2028 cm\(^{-1}\). Trans-(CO)\(_4\)Mo(Ph\(_2\)PCl)\(_2\) \(\left(D_{4h}\right)\) has only a single strong band at 1939 cm\(^{-1}\).

Hydrolysis of cis- or trans-(CO)\(_4\)Mo(Ph\(_2\)PCl)\(_2\) gave the same compound with four well resolved bands around 2000 cm\(^{-1}\). A trans to cis isomerization occurred in the reaction of the trans-starting material (Figure 8, page 29). The higher energy \(A_1\) band appeared at 2000 cm\(^{-1}\), a fairly low value, which is consistent with increased negative charge at the metal expected for an anion.

This six-membered hydrogen-bridged structure has been found recently in a number of transition metal complexes and has been used as the starting point in the synthesis of a variety of bimetallic complexes containing a phosphinite bridge.\(^{18}\) The phosphinite-bridge contains a soft phosphorus donor and a hard oxygen donor such that it can bridge metals in different oxidation states. That it results from the hydrolysis of the trans- as well as the cis-chlorophosphine complex is likely the result of the very favorable free energy of formation of the hydrogen-bridged ring.
With bulky phosphine ligands the trans-compounds are usually slightly favored over the cis.\textsuperscript{24} The isomerisation of octahedral Mo(0) complexes can occur by a dissociative or intramolecular mechanism. The bulkier ligands, \( \text{Ph}_3\text{P} \), favor the dissociative path while the less bulky ligands, \( \text{n-Bu}_3\text{P} \) have a lower activation barrier associated with an
intramolecular mechanism. The thermal cis-to-trans rearrangement occurs quite rapidly at elevated temperature and is reversed photochemically. Since this isomerization (eq.15); occurs rapidly at room temperature, results in an intramolecular hydrogen bridge and is probably driven by the formation of that bridge, it is reasonable to propose an intramolecular nondissociative mechanism.

It is interesting to speculate on the effect of the coordination geometry of coordinated acids. By bringing the coordinated phosphinous acid moieties into close proximity the pKa may decrease as the conjugate base can distribute the charge over two oxygen atoms instead of one by allowing the remaining proton to bridge between the two. This should render the cis-di-acid a stronger acid than the trans-isomer. Furthermore, the phosphinous acid ligand is trans to an electron-withdrawing CO in the cis-isomer capable of stabilizing the conjugate base more effectively by the CO's trans-influence.

The C2v symmetry of cis-(CO)4Mo(Ph2POHOPPh2)− 20, cis-(CO)4Mo(Ph2POPPh2) 24, cis-(CO)4Mo(Ph2POP(O)(Ph)PPH2 27, and cis-(CO)4Mo(Ph2POPOPPh2)2 26 (Figure 8 page 29) should result in four bands, 2A1, B1 and B2 from the CO stretching modes. These bands are not very well resolved below 2000 cm−1 in the spectrum of compound 26 but this was isolated only as a crude solid so this is not surprising. The CO stretching frequencies for a number of complexes prepared in this laboratory have been tabulated in Appendix A at the
The P-O and P-O-P stretching modes vary considerably in these compounds. A striking feature in the solid-state spectrum of 24 is the appearance of the diphosphoxane stretch as a doublet at 773 and 758 cm\(^{-1}\). The appearance of this band at such a low value is related to the small P-O-P angle, 103.3(1). The P-O bond lengths, 1.659(2) Å, 1.667(2) Å, av. 1.663 Å,\(^{12}\) are 0.028 Å longer than in 9, 1.630(3) Å, 1.641(3) Å, av. 1.635 Å,\(^{26}\) for example. This is a reflection of the increasing p-character in the P-O bonds in the chelate ring necessary to accommodate the small angle. The appearance of two bands in this region is most likely a solid state effect. The diphosphoxane stretch observed in the IR of 26 (Figure 8) is typical of the acyclic compounds; it is a very strong broad line at 835 cm\(^{-1}\).

In the IR spectrum of 28 the diphosphoxane stretch appears as a pair of lines at 895 and 846 cm\(^{-1}\). From the limited data on these cyclic diphosphoxane complexes it appears that the diphosphoxane stretch is broadened with a substantial shoulder on the band compared to the acyclic analogues. The fact that a phosphoryl stretch at 1230 cm\(^{-1}\) is also present shows that the initially formed triphosphoxane has tautomerized to give a five-membered ring containing a phosphoryl group.

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The IR spectra of 33 and 34, both of nominal D\(_{4h}\) symmetry, show a single strong band below 2000 cm\(^{-1}\). Two weak bands from the forbidden A\(_{1g}\) and B\(_{1g}\) stretches can be seen in both spectra. Since the two phosphorus donors in 33 are different these two bands have greater relative intensity an observation consistent with a lowering of the symmetry about the metal.

The phosphoryl stretching frequency is shifted to higher energy in the coordination compounds of Ph\(_2\)P-P(O)(OEt)\(_2\) compared to the free ligands. By contrast, little or no shift is observed in the position of the phosphoryl stretch on coordination of Ph\(_2\)P-P(O)Ph\(_2\). It is interesting to note in this context the as yet unexplained very low value of the phosphoryl stretch, 1206 cm\(^{-1}\), in the asymmetric compound 33, as compared to 1228 and 1226 cm\(^{-1}\) for 34 and 35, respectively. The P-O-P and P-O stretching frequencies for a number of complexes prepared in this laboratory have been tabulated in Appendix A at the end of this chapter.
With the development of Fourier NMR, $^{31}$P NMR ($I=1/2$, receptivity/$C^{13}=377$) has become one of the most conveniently observed nuclei by magnetic resonance. It has a very large shift range, about 500 ppm, and with broadband proton decoupling the resonance lines are on the order of 3 Hz wide at half-height. Most of the compounds prepared in this laboratory thus far have contained one to four phosphorus nuclei so the interpretation of the spectra has been relatively straightforward.

In contrast to IR spectra which contain many lines, $^{31}$P NMR spectra are often fairly simple. Nonetheless, structures and geometries cannot be assigned simply on the basis of the NMR spectra because the theories of phosphorus NMR shifts and coupling constants are very complex and require a fairly detailed knowledge of the molecular orbital diagram for each complex. Nonetheless, once the structures of several complexes have been determined, a number of useful empirical trends emerge which allow for ready interpretation of results obtained in analogous systems. These empirical trends must be used with caution, however, as they are consistent only within a narrow range of structural types.

Perhaps the greatest single application of $^{31}$P NMR has been to monitor reactions in progress, to determine the number of compounds formed in the reaction and to get an idea of how many types of phosphorus atoms are in the
complex by examining the coupling constants. The reactions can be examined with no workup because most solvents do not contain phosphorus.

The most consistent observation has been the downfield shift which occurs when a phosphine ligand is coordinated to a transition metal. Beyond this there are particular trends noted for very specific types of complexes, and these are best discussed in context.

Diphenylchlorophosphine gives rise to a single line 81 ppm down field from external 85% phosphoric acid. Unless otherwise noted all shifts are reported in this manner. Positive values refer to lower field (higher frequency) positions relative to the reference. The $^{31}$P NMR shift of diphenylchlorophosphine appears at 122 ppm in $(\text{Ph}_2\text{PCl})\text{Mo(CO)}_5$. Substitution of a second phosphine produces a further downfield shift of 2ppm to 124ppm if the substitution is cis and 14ppm to 136ppm if the substitution is trans.

In general, the greater the extent of phosphine substitution, the further the downfield shift of the resonance. Also, phosphines trans to a better donor than CO, such as a second phosphine, resonate at lower field than phosphines trans to a better acceptor ligand such as CO.

The $^{31}$P NMR spectra of compounds 20 and 24 are single lines at 113 and 134 ppm respectively. The shift for 20 varies from 109 to 125 ppm and is presumably a function of
the proton concentration in the the solution. The addition of aliquots of \( \text{Ph}_2\text{PCl} \) to a solution of \( \text{20} \) to generate \( \text{24} \) causes a shift of the resonance position of \( \text{20} \) to lower field with each addition as well to increase the intensity of the resonance due to \( \text{24} \).

The proton coupled spectra of these phenylphosphine complexes has been uninformative. The three bond phosphorus ortho-phenyl proton coupling is only poorly resolved.

The \( ^{31}\text{P} \) NMR spectrum of \( \text{Ph}_2\text{P-P(O)Ph}_2 \), \( \text{36} \), contains an AX pattern (\( \delta \) 35ppm (d), -23ppm (d), \( ^1J_{pp}=224\text{Hz} \)) with the trivalent phosphorus resonating at higher field. Coordination of this ligand through the phosphorus in \( (\text{CO})_5\text{Mo(Ph}_2\text{P-P(0)Ph}_2) \) shifts this resonance downfield by 54 ppm to a value of 31 ppm.\(^{30}\)

The \( ^{31}\text{P} \) NMR of \( (\text{CO})_4\text{MoPh}_2\text{P-0-PPh}_2 \)\(^1\text{12}\) \( \delta \) 148 ppm (d), 108 ppm (d), \( J=60\text{Hz} \), a coordinated valence tautomer of \( \text{36} \) is shifted to lower field, an observation which has made it quite simple to determine whether the diphosphine oxide is in the P-P(0) or P-O-P form. \( \text{R}_2\text{P-0-} \) resonates far down field from \( \text{R}_2\text{(0)-} \).

Although it was expected that reaction of \( \text{20} \) with \( \text{PhPCl}_2 \) would yield a coordination compound containing the triphosphoxane linkage, the NMR of the final product indicated that this was not the case. By analogy to the \( ^{31}\text{P} \) NMR spectrum of \( \text{13} \), the \( ^{31}\text{P} \) NMR should appear below 100ppm and to consist of a doublet and a triplet. Instead
an AMX pattern was observed in which eight of the twelve lines lay between 30 and 55 ppm, far upfield from where they were expected. The position of these eight lines indicated the presence of a diphosphine oxide like system and this was confirmed by a crystal structure (Figure 2 page 17).  

This determination shows molybdenum at the center of an octahedral arrangement of ligands with a five membered chelating ring containing a complexed valence tautomer of bis-diphenylphosphorylphenylphosphine. This ligand was heretofore unknown. The details of the structure have been reported.  

The $^{31}$P NMR spectrum of 26 provides the best evidence for the formulation of a bis-diphosphoxane complex. The spectrum consists of two complex patterns (AA'BB') centered around 148 and 108 ppm which is the same as the shift range reported for the monosubstituted complex 13.  

This complex could not be isolated in pure form, however, because it decomposes overnight to form a mixture of 24 and Ph$_2$P-P(O)Ph$_2$. The driving force for this reaction could be the formation of two very stable species. That 26 decomposes so slowly to the chelated diphosphoxane complex 24, rules out its being a significant intermediate in the rapid formation of 24 from the triethylammonium salt, 20, and diphenylchlorophosphine. This again indicates a role for the proton in the several reactions of
the hydrogen-bridged chelate structure which result in the formation of the diphosphoxane chelate \( 24 \). The complex \( 26 \) is stable as a solid and its IR spectrum can be easily obtained. The IR spectrum further supports the bis-diphosphoxane structure assignment. Attempts to purify this compound or to trap it by reaction with \( \text{CH}_3\text{CNCr(CO)}_5 \) or \( \text{Fe}_2\text{(CO)}_9 \) have thus far been unsuccessful.

The IR spectra of complex \( 29 \), though not completely resolved around \( 2000\text{cm}^{-1} \), has the expected appearance. The high energy \( A_1 \) band is at \( 2080\text{cm}^{-1} \) and the diphosphoxane stretch appears at \( 830\text{cm}^{-1} \).

**Conclusions**

Reaction of coordinated phosphines has led to the isolation of isomers of phosphine oxides which are unknown in the uncomplexed state.

Two complexes, \((\text{CO})_4\text{Mo(Ph}_2\text{POPPh}_2)\) and \((\text{CO})_4\text{Mo(Ph}_2\text{POP(O)(Ph)PPh}_2)\) containing unusual four- and five-membered chelate rings and have been fully characterized by spectroscopic analysis and single crystal x-ray structural determinations. The effort to synthesize trans-bis-phosphinous acid complexes was thwarted by the facile formation of a chelate ring. The result is surprising as the four-membered ring is unstrained and the complex is quite stable. A study of the reactivity of these and related complexes is well under way in our laboratory and also forms the subject of the next chapter in this dissertation.
EXPERIMENTAL

All manipulations were carried out by using standard Schlenk techniques. THF and diethyl ether were pre-treated with calcium hydride and distilled under nitrogen from purple sodium benzophenone ketyl. Toluene was distilled under nitrogen from sodium metal. Methylene chloride and hexane were distilled under nitrogen from calcium hydride. Tetrachloroethane was purified by standard techniques and vacuum distilled before use.

NMR spectra were recorded on a JEOL 90FXQ or a Varian 360A. IR spectra were recorded on a Perkin Elmer 283 B instrument. Solution spectra were observed with a Wilkes 0.1 mm NaCl cell and were referenced to air. Elemental analyses were performed at the University of New Hampshire Instrumentation facility with a Perkin Elmer 240 B Elemental Analyzer.

X-ray crystal structure determinations were carried out by Dr. Eric J. Gabe, Chemistry Division, National Research Council of Canada, Ottawa K1A 0R9 (Canada).

Synthesis of cis- and trans-(Ph₂PCl)₂Mo(CO)₄. 10 g Mo(CO)₆ (38 mmol) and 12 mL Ph₂PCl (65 mmol) were held at reflux in 50 mL of toluene for 3 hours. During this time 1400 mL of CO was evolved and the solution turned dark brown. The solution was cooled to room temperature and stirred during the addition of 50 mL hexane. The mixture was then filtered, the solvent distilled and the brown
residue further evacuated overnight. The resulting brown paste was evacuated at 90 °C for 2 h, cooled to room temperature and stirred with 8 mL methylene chloride to make it smooth. 50 mL hexane was added and the mixture stirred in ice followed by suction filtration to give 6.4 g (25%) trans-(Ph₂PCl)₂Mo(CO)₄ as a brown solid. This can be recrystallized from methylene chloride/hexane to give a bright yellow crystalline solid. ³¹P NMR 136 (s); IR hexane, ν CO 1939s.

The filtrate from the above isolation was concentrated under vacuum until an oil began to form, a small sample of cis-(Ph₂PCl)₂Mo(CO)₄ was added and with chilling and scratching with a glass rod 8 g (31%) cis-(Ph₂PCl)₂Mo(CO)₄ was isolated as a tan solid which can be recrystallized with a little more difficulty from methylene chloride/hexane to give a bright yellow crystalline solid. ³¹P NMR 124 (s), IR xane, 2028m, 1961m, 1936s.

Et₃NH(CO)₄Mo(Ph₂POHOPPh₂). This compound was synthesized by Kraihanzel's method from either cis- or trans-(Ph₂PCl)₂Mo(CO)₄. Yields were about 80%.

(CO)₄Mo(Ph₂POPOPPh₂). To 13 g (18 mmol) 15 in 70 mL methylene chloride at 0 °C was added 4 g trifluoroacetic anhydride which caused the immediate darkening of the solution followed by deposition of a solid. As the solution was concentrated more solid precipitated. The two solids were combined, washed with water, ethanol and dried under vacuum to give 10 g bright yellow solid. This
compound can be conveniently recrystallized from CH$_2$Cl$_2$/hexane. $^{31}$P NMR $\delta$ 134; IR KBr $\nu$ CO, 2025, 1936, 1915, 1900, $\nu$ P-O-P 773,758.

$(CO)_4$Mo(Ph$_2$P=O(0)(Ph)PPh$_2$)$_2$. To a solution containing 3.16 g (4.4 mL) 4 in 50 mL methylene chloride was added 6 mL 0.83M PhPCl$_2$ in meapidly paled to yellow. In the corresponding tungsten complex the color change occurred overnight. The reaction was stirred and the filtrate concentrated to a small volume. Addition of methanol caused a solid to form (1.8g) which was collected and recrystallized from methylene chloride/methanol. $^{31}$P NMR 166 (doublet of doublets), $^2$$J_{pp}$=39Hz (Ph$_2$P=O-P(0)(Ph)), $^2$$J_{pp}$=23Hz (Ph$_2$P-M-PPh$_2$), 53 (doublet of doublets), $^2$$J_{pp}$=63Hz (Ph$_2$P=P(0)(Ph)), 42 (doublet of doublets); IR 2022m, 1930s, 1897s, 1884sh.

cis-$(CO)_4$Mo(Ph$_2$P=OPPh$_2$)$_2$. This compound has been observed by $^{31}$P NMR and isolated only as a crude solid. 0.5 g (0.7 mmol) 15 and 100 mg NaH (50% oil dispersion) were stirred together in 25 mL THF. The mixture, which effervesced for about one minute, was filtered through a carefully dried frit. 309 mg(1.72 mmol) Ph$_2$PCl was added to the filtrate which caused the solution to pale and become cloudy. $^{31}$P NMR at this time showed cis-$(CO)_4$Mo(Ph$_2$P=OPPh$_2$)$_2$ and tetraphenyldiphosphine monoxide. After ten minutes 19 was also observed. Decomposition in the NMR tube was complete overnight.
If the reaction mixture was kept at 0°C, filtered rapidly, and the solvent distilled, a solid residue was obtained.

\[ \text{[(CO)}_5\text{Mo(Ph}_2\text{PO)}]_3\text{P} \]

To a mixture of about 0.250 g hexane-washed NaH (50% oil dispersion) and 1.3 g (2.4 mmol) \((\text{Et}_3\text{NH})\text{(CO)}_5\text{Mo(Ph}_2\text{PO)}\) was added 10 mL THF which caused strong effervescence for several minutes. Careful filtration through a dry frit using no celite gave a faintly turbid yellow solution. The solvent was distilled under reduced pressure to remove all triethylamine, and the residue was redissolved in 20 mL THF. To this was added 0.120 g (0.87 mmol) \(\text{PCl}_3\) in 10 mL THF over 5 minutes. As the reaction was allowed to stir, the yellow color faded and the solution became turbid. After filtration and solvent distillation under reduced pressure a gummy residue remained. This residue was dissolved in \(\text{CH}_2\text{Cl}_2\) and filtered several times to remove turbidity. Slow addition of hexane and careful reduction of solvent volume under vacuum, followed by scratching resulted in the formation of a precipitate which was collected and dried under vacuum to give 0.254 g (22%) of product. \(^{31}\text{P NMR } \delta 143 \text{ (d), 139 (q), } \)

\[ ^2\text{J}_{\text{PP}}=21\text{Hz; IR KBr, } \nu \text{ CO } 2080\text{m, 1998, 1945, } \nu \text{ P-O-P } 830; \]

Anal. Calcd. for \(\text{C}_{51}\text{H}_{30}\text{Mo}_3\text{O}_{18}\text{P}_4\) C, 45.63; H, 2.25. Found: C, 45.89; H, 2.33.

\[ \text{trans-(CO)}_4\text{Mo(Ph}_2\text{Cl)(Ph}_2\text{P-P}(\text{O})(\text{Et})_2) } 0.66\text{CH}_2\text{Cl}_2. \]

There are no complete records of the synthesis of this compound. To 0.206 g (1.5 mmol) \((\text{EtO})_2\text{P(O)}\) in 20 mL THF
was added 0.100 g 50% oil dispersion NaH. After the reaction subsided the turbid solution was filtered and 12 mL, (0.9 mmol) of this was added to a THF solution of 0.302 g, (0.46 mmol) trans-(CO)$_4$Mo(Ph$_2$PCl)$_2$. Despite the use of excess (EtO)$_2$PONa, $^{31}$P NMR of this mixture showed the primary component of the reaction to be trans-(CO)$_4$Mo(Ph$_2$PCl)(Ph$_2$P=P(O)(OEt)$_2$)$_2$. The solvent was distilled under reduced pressure and the gummy residue column chromatographed on silica gel, eluent 28% ethyl acetate/hexane. The solvent was distilled from this column eluant and the residue recrystallized from CH$_2$Cl$_2$ by the slow addition of hexane. The analysis and $^1$H NMR both showed the inclusion of CH$_2$Cl$_2$ in the solid. IR KBr (ν CO) 2020w, 1958w, 1900s, (ν PO 1202m); $^{31}$P NMR δ 139 (d), $^2$J$_{PP}$=83Hz, 29 (doublet of doublets), $^1$J$_{PP}$=46Hz, 24; Anal. Calcd. for C$_{100}$H$_{94}$Cl$_7$Mo$_3$O$_7$P$_3$: C, 48.58; H, 4.29. Found: C, 48.55; H, 4.10.

trans-(CO)$_4$Mo(Ph$_2$P=P(O)(OEt)$_2$)$_2$CH$_2$Cl$_2$. To 1.5 g (2.3 mmol) was added a total of 9.6 mmol (EtO)$_2$PONa in 20 mL THF, the amount necessary to consume all the starting material. It is most likely that the sodium salt was being protonated during the manipulations. The reaction was allowed to stir overnight; the solvent was distilled under reduced pressure and the residue recrystallized from CH$_2$Cl$_2$/hexane. $^{31}$P NMR δ 35.5 (m), 24.7 (m); IR KBr (ν CO) 2017m, 1933sh, 1915s, 1900s, 1989sh, (ν PO) 1228m;
Anal. Caled. for C$_{37}$H$_{42}$Cl$_2$MoO$_6$P$_4$: C, 47.41; H, 4.52. Found: C, 47.47; H, 4.58.
### Appendix A

**Carbonyl Stretching Frequencies for Diphosphoxane Complexes of 6B Metal Carbonyls in cm⁻¹**

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*All disubstituted complexes are cis unless otherwise marked.

**As the triethylammonium salt.
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*As the triethylammonium salt.
**Appendix B**

Selected Bond Distances and Angles For 
$(\text{CO})_4\text{Mo(Ph}_2\text{P}2\text{PPh}_2\text{)}$

### Bond Distances (Å)

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### Bond Angles (°)

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### Selected Bond Distances and Angles

**For (CO)$_4$Mo(Ph$_2$P(0)(0Et)$_2$)**

#### Distances (Å)

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### Selected Bond lengths and Angles

**for trans-(CO)$_4$M(Ph$_2$P-P(0)(0Et)$_2$)$_2$**

#### Bond Distances (Å)

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#### Bond Angles (°)

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CHAPTER 2

Halogen Oxidation of (CO)$_4$Mo(Ph$_2$POPPh$_2$)

In the previous chapter, group 6B metal carbonyl complexes containing a coordinated diphosphine oxide or tautomeric diphosphoxane ligand were discussed. The diphosphoxane linkage, which is rarely observed in the free ligand, was seen to be stabilized by coordination to group 6B carbonyls. In this chapter the reactivity of these complexes towards halogen oxidation will be discussed. The reactivity of these complexes towards nucleophiles and electrophiles is of interest because there are a number of potentially reactive sites for the incoming reagent.

Hydroxide, acting as a nucleophile, attacks the phosphorus of the diphosphoxane complex giving a complex with a six-membered chelate ring$^{12}$ containing a hydrogen-bridge (eq. 1).

\[
\begin{array}{c}
\text{Ph}_2\text{P} \\
\text{Mo} \\
\text{Ph}_2\text{P}
\end{array}
+ \text{OH}^- \rightarrow
\begin{array}{c}
\text{Ph}_2\text{P}-
\\
\text{O} \\
\text{Ph}_2\text{P}
\end{array}
\text{eq. 1}
\]

In like manner, hydroxide will cleave the diphosphoxane of bridged bimetallics$^{13}$ to give the mono-metallic phosphinous acids (eq. 2).

\[
[(\text{CO})_5\text{Mo(Ph}_2\text{P})]_2\text{O} + \text{OH}^- \rightarrow
\begin{array}{c}
\text{Ph}_2\text{P} \text{OH}
\\
\text{CO}_5\text{Mo(Ph}_2\text{P})
\\
\text{CO}_5\text{Mo(Ph}_2\text{P})
\end{array}
\text{eq. 2}
\]

Other nucleophiles may attack the ligand or the
carbonyl carbon. Electrophiles may form simple adducts with any suitable donor such as the phosphoryl or carbonyl\textsuperscript{30} oxygen or the metal center (eq. 3),

\[
\text{Mo} \begin{array}{c} \text{Ph}_2\text{P} \\ \text{Ph}_2\text{P} \end{array} \overset{\text{O}}{\longrightarrow} \overset{\text{E}^+}{\longrightarrow} \overset{\text{E}}{\longrightarrow} \text{Mo} \begin{array}{c} \text{Ph}_2\text{P} \\ \text{Ph}_2\text{P} \end{array} \overset{\text{O}}{\longrightarrow} \overset{\text{eq. 3}}{\longrightarrow}
\]

or oxidation of the metal may occur (eq. 4).

\[
\text{Mo} \begin{array}{c} \text{Ph}_2\text{P} \\ \text{Ph}_2\text{P} \end{array} \overset{\text{O}}{\longrightarrow} \overset{\text{XY}}{\longrightarrow} \overset{\text{Y}}{\longrightarrow} \text{Mo} \begin{array}{c} \text{Ph}_2\text{P} \\ \text{Ph}_2\text{P} \end{array} \overset{\text{O} + \text{CO}}{\longrightarrow} \overset{\text{eq. 4}}{\longrightarrow}
\]

The reaction of group 6B metal carbonyls with halogens has been studied by a number of groups and a variety of compounds have been produced.\textsuperscript{31} Iodine and bromine oxidation leads often to metal(II) compounds while chlorine can oxidize tungsten to give WCl\textsubscript{6}.

The reaction products vary with the halogen, the nature of the ligands on phosphorus and the metal. Halogen oxidation of the central metal atom to the 2+ state in phosphorus and arsenic complexes of group 6B metal carbonyls results in a d\textsuperscript{4} electronic configuration for the central metal atom. Satisfying the 18-electron rule requires seven ligands in the coordination sphere of the d\textsuperscript{4} atom and while seven coordination is commonly observed for Mo and W, it has rarely\textsuperscript{63} been found in Cr. An important result of this crowding of ligands is that steric plays a
major role in determining the structure of these compounds. In addition, as the metal becomes more electron deficient it loses CO more readily. This is most likely the result of the metal having less electron density available for back bonding.

In the chemistry of the 6B metal(0) complexes, the replacement of three CO's around 80 to 100°C to give \((\mathrm{CO})_3\mathrm{ML}_3\) \((\mathrm{L}=\mathrm{PR}_3)\) complexes which are resistant to further substitution. The 6B metal(II) complexes will undergo rapid substitution of CO by group 5 donors at room temperature to give complexes with two or three CO's remaining.\(^{32}\) It appears at present that the optimum number of CO's for a metal(II) complex is two.\(^{33}\) The use of chelating ligands leads most commonly to bis-chelated complexes (eq. 5).

\[
\begin{align*}
\text{Mo(CO)}_4\text{X}_2 + \text{L} \rightarrow \text{M(CO)}_2\text{(L L)}_2\text{X}_2
\end{align*}
\]

\(\text{L=R}_2\text{P(CH}_2\text{)}_n\text{R}_2\) \(\text{R=phenyl, CH}_3; n=1,2,3\)

The geometry of seven-coordination is complicated. There are no regular or semiregular polyhedra containing seven vertices. Of the 92 nonuniform convex polyhedra, three have seven vertices: the pentagonal bipyramid, capped octahedron and capped trigonal prism (Figure 1).\(^{34}\) These three topologies are actually observed for seven-coordinate species though commonly the solid state structures observed may show significant distortion from these idealized geometries.
Figure 1
The Low Energy Topologies of Seven-Coordinate Complexes
Kepert has devised a model for calculating repulsion energies between ligands for seven-coordinate compounds assuming that the centers of repulsion lie on or close to the surface of a sphere. The function of the model is to predict the geometry with the minimum overall repulsion energy. This assumption is valid when all the ligands are extremely similar but becomes less so as the kinds of ligands become more and more varied. Nonetheless it has worked quite well for a large variety of complexes.

The result of these calculations is that the three topologies mentioned have extremely similar energies and the barriers to their interconversion are low. This energy surface of shallow valleys and low hills results in room-temperature intramolecular rearrangements which can be observed by variable-temperature NMR. The processes which lead to intramolecular rearrangements can be expected to traverse one of the above mentioned topologies as an intermediate.

The presence of chelate rings in the coordination sphere of these seven-coordinate compounds introduces an additional steric effect which Kepert has codified as the ligand's normalized bite. This is defined as \( b = 2 \sin \frac{\theta}{2} \), in which \( \theta \) is the ligand-metal-ligand bond angle (Figure 2). The normalized bite is, in effect, an additional constraint placed on the energetically reasonable topologies a particular complex may adopt. Kepert has been able to predict quite accurately the geometry of a number
Figure 2

Normalized Bite $2\sin \alpha/2$
of complexes based on the normalized bite. The model predicts that \((\text{CO})_3\text{Mo(Ph}_2\text{P(CH}_2\text{)}_3\text{PPh}_2)\text{I}_2\), \(b=1.33\), and \((\text{CO})_3\text{Mo(Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2)\text{I}_2\), \(b=1.24\) should form complexes best represented as having ligands at the corners of a capped trigonal prisms. On the other hand \(\text{W(Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2)(\text{CO})_3\text{I}_2\), \(b=1.09\) should adopt a pentagonal bipyramidal geometry, and these complexes do in fact have the stereochemistries predicted.

The chelate rings of all the existing 6B-metal carbonyl halide complexes have contained group 5 donors bridged by carbon chains of one, two or three carbons. The diphosphoxane chelates described in this work could be expected to yield compounds analogous to those known and provide additional tests for Kepert's predictions of structure. The presence of the heteroatom in the the chelate ring, on the other, hand may also provide an additional site of attack for the halogen. With these possibilities in mind, the halogen oxidations of the coordinated diphosphoxane complexes discussed in Chapter 1 were studied under conditions analogous to those found in the literature.
Results

\[(\text{CO})_4\text{Mo}(\text{R}_2\text{PEPR}_2) + \text{X}_2 \rightarrow (\text{CO})_3\text{Mo}(\text{R}_2\text{PEPR}_2)\text{X}_2 + \text{CO}\]

1 \(\text{R=Ph, E=O}\)  \hspace{1cm} 4 \(\text{R=Ph, X=I, E=O}\)
2 \(\text{R=p-tolyl, E=O}\)  \hspace{1cm} 5 \(\text{R=p-tolyl, X=I, E=O}\)
3 \(\text{R=Ph, E=CH}_2\)  \hspace{1cm} 6 \(\text{R=p-tolyl, X=Br, E=O}\)
7 \(\text{R=Ph, X=I, E=CH}_2\)  

Scheme 1

The halogen oxidations shown in Scheme 1 all result in stereochemically nonrigid seven-coordinate Mo(II) complexes with pentagonal bipyramidal solid state stereochemistries as predicted for the small ligand bite found in 4 \((b=1.01\ \text{R=Ph, E=O})\). As a consequence of the crowding of the seven ligands around the metal, stereochemical-nonrigidity on the NMR time scale is commonly observed. An AX 'P NMR spectrum is observed for 4 at -60 C, while at room temperature, a single extremely broad resonance (100Hz) is observed. It is unusual to observe low-temperature limiting spectra for seven-coordinate complexes.\(^{35}\)

A second species of unknown structure (4a), which gives a singlet resonance from -60 C to room temperature, is observed in solutions of 4. There are reports\(^{41}\) of solution-equilibria in complexes of this type, but this is the first reported observation of this type of behavior by NMR.

In a typical reaction, a methylene chloride solution of the halogen was added to a rapidly stirred solution of the metal complex at room-temperature. Addition of bromine caused rapid CO evolution and the reaction was complete.
within a minute or so. The reaction with iodine was much slower, reaching completion only after about half an hour. Orange powders precipitated from the solution after the addition of hexane to the reaction mixture. Yields ranged from 50-70%.

These compounds were not observed to be stable in air for long periods of time. 4 showed some decomposition on standing in air in the dark after several days. After several months it became a black powder which showed no CO stretch in the IR spectrum.

The structures of 4 and 6 have been determined by x-ray diffraction although 6 decomposed during data collection. It is still apparent, however, from the low resolution that 6 has the same general pentagonal bipyramidal arrangement of ligands as 4. The structure of (CO)3W(Ph2PCH2PPh2)I2 7 was determined by x-ray diffraction by Kepert in 1980. In all these compounds the axial positions of the pentagonal bipyramid are occupied by CO while the equatorial plane contains mutually cis halogens in addition to the chelating phosphorus atoms and the third CO (Figure 3).

Bromine oxidation of 1 yielded a pair of highly insoluble compounds which have not yet been identified. Their IR spectra were quite different in the CO region from the other pentagonal pyramidal complexes reported in this
Figure 3
$(\text{CO})_3\text{Mo(Ph}_2\text{POPPh}_2)\text{I}_2$
In order to improve the solubility of the bromine oxidation products, the p-tolyl analogue of 1 was synthesized and its halogen oxidations studied. As would be expected, iodine oxidation of 2 gave compound 5, \((\text{CO}_3\text{Mo(tolyl}_2\text{POPOPtolyl}_2)\text{I}_2\) which is similar in all respects to 4. The bromine oxidation of 2 yielded 6, \((\text{CO}_3\text{Mo(tolyl}_2\text{POPOPtolyl}_2)\text{Br}_2\) which undergoes the same kind of intramolecular rearrangement as 4 although at a somewhat slower rate. Long accumulation times resulted only in a barely discernible lump in the baseline at room temperature. This implies a slower exchange rate for the AX system of 6. The low temperature spectrum of 6 is again an AX quartet, \((\delta 91\text{ppm} \text{ d; } \delta 119\text{ppm} \text{ d; } J=205\text{Hz})\), but there is no second species observed. Warming the sample to above room temperature under \(N_2\) in deoxygenated tetrachloroethane resulted in the appearance of a single line with a width of about 50 Hz but also caused its steady decomposition to a compound which gave no signal at high temperature. The solution also turned green.

**Discussion**

All of these compounds undergo various intramolecular rearrangements giving rise to temperature-dependent NMR spectra.\(^{35}\) In the \(^{31}\text{P}\) proton-decoupled NMR spectrum of 4 it can be seen (Figure 5) that the two nonequivalent phosphorus nuclei of the pentagonal bipyramid undergo rapid mutual exchange at room temperature giving rise to a
Variable Temperature $^{31}$P NMR of $(\text{CO})_3\text{Mo(Ph}_2\text{POPPh}_2)\text{I}_2$
single, broad (109Hz at half-height) resonance centered at 93ppm. As the temperature is lowered the line broadens into the baseline and then sharpens at -60 C to give an AX quartet, (\delta 81ppm d; \delta 112ppm d; J=193Hz) (Figure 6) consistent with the nonequivalence of the two phosphorus nuclei in the solid. In addition, a second slower process interconverts the pentagonal bipyramidal compound with an as yet unidentified species (\#) which gives a single line at 76ppm with a width at half-height of 10Hz at room temperature.

Three lines of evidence support the conclusion that this unidentified compound (4a) is in equilibrium with 4. First, it is present in carefully recrystallized samples of 4 in a constant ratio of 0.32/1 (4a/4) at room temperature. Second this ratio varies as a function of temperature favoring the AB quartet at -60 C (0.14/1.0 4a/4) and the singlet at +70 C (0.42/1.0 4a/4). Third, as the temperature is raised, the single line from 4a broadens to a width of about 100Hz at 100 C (Figure 4). This is expected to happen as the rate of interconversion of 4 and 4a becomes rapid on the NMR time scale. Cooling the sample to room temperature restores the original spectrum of the two species in the same 0.32/1 ratio. Heating the sample above 100 C causes rapid decomposition and an actual coalescence cannot be observed. If it is assumed that coalescence occurs around 120 C, then a barrier of
approximately 17 kcal/mol can be calculated by simulation of the high temperature NMR. 37

By carrying out the iodine and bromine oxidations at -50 °C and observing the 31P NMR at low temperature without allowing the sample to warm, an intermediate can be detected. The 31P NMR spectrum of the reaction mixture of iodine and (CO)₄Mo(Ph₂P(OPh)₂) at -60 °C (Figure 7) shows the starting metal(0) complex at 134 ppm, the AB spectrum of the intermediate centered at 85 ppm and an unidentified singlet at 90 ppm.

Shaking the sample at room temperature for ten minutes causes rapid conversion of most of the intermediate to product and disappearance of the remainder of the starting material (Figure 8).

In a comparable experiment with bromine it can be seen that this reaction is faster (Figure 9). Most of the intermediate has gone on to product. This is the result of an experimental limitation in which a room-temperature methylene chloride solution of bromine was added to the solution containing the metal complex which had been chilled to -76 °C. Since the spectrum shows no change on standing at -60 °C, the intermediate must have been converted to product during the time it took the added bromine solution to reach thermal equilibrium with the chilled sample in the NMR tube. This is consistent with the experimental observation that the bromine reaction appears to be more rapid, with vigorous CO evolution which
Figure 7
Intermediate (*) in the Reaction of cis-(CO)₄Mo(Ph₂POPPh₂) and I₂

Figure 8
3¹P NMR After Warming to Room Temperature

-60°C
Figure 10
31P NMR After Warming to Room Temperature

Figure 9
Intermediate (*) in the Reaction of cis-(CO)₄Mo(tol₂POPtol₂) and Br₂
rapidly subsides. Again, warming the NMR tube to room temperature converts the remainder of this intermediate to product.

These intermediates have not been identified. Their $^{31}$P NMR spectra are similar to the respective isolated compounds (Table 1), but shifted to higher field and with somewhat smaller coupling constants. The definitive identification of these intermediates must await the accumulation of a more complete collection of $^{31}$P NMR data for complexes of this type.

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<td>-</td>
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<tr>
<td>7a -6 -30</td>
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Table 1

$^{31}$P NMR Shifts of Seven-Coordinate Complexes, Solution Isomers and Intermediates

There are a number of possible structures for these intermediates. The simplest to consider is a seven-coordinate topomer, stable at low temperature, which rearranges to product at room temperature. This seems unlikely. The relatively slow rate of conversion of the intermediate to product observed for the iodine reaction,
is inconsistent with the low barriers associated with these topological isomerizations. The barriers associated with the rearrangement processes for the seven-coordinate compounds are low enough such that the rearrangement would be complete within a few seconds at room temperature.

A six-coordinate intermediate appears unlikely as the result of some preliminary observations of the reaction between 4 and silver tetrafluoroborate. Silver tetrafluoroborate should react with 4 to give a six-coordinate ionic compound (eq. 6).

\[
\text{(CO)}_3\text{Mo(Ph}_2\text{POPPh}_2\text{)I}_2 + \text{AgBF}_4 \rightarrow \text{[(CO)}_3\text{Mo(Ph}_2\text{POPPh}_2\text{)I}^+\text{BF}_4^- + \text{AgI}} \quad \text{eq. 6}
\]

This reaction, when carried out at low temperature, in fact yields what appears to be a stereochemically rigid compound which gives a single resonance at 120 ppm in the \( ^{31}\text{P} \) NMR. The stereochemical rigidity and the shift are consistent with the above proposed reaction. Thus, it appears from this and some other as yet unpublished results, that there is a substantial shift to higher field in the \( ^{31}\text{P} \) NMR of phosphorus bound to seven-coordinate molybdenum complexes compared to the six-coordinate complexes.

Two other candidates for this intermediate are both ionic compounds which differ from one another by a single CO. These are \( [(\text{CO})_4\text{Mo(Ph}_2\text{POPPh}_2\text{)I}]^+ \) and \( [(\text{CO})_3(\text{Ph}_2\text{POPPh}_2\text{)MoI}]^+ \). On the basis of the above
discussion the seven-coordinate complex, 
\[(\text{CO})_4\text{Mo(Ph}_2\text{POPPh}_2\text{I})^+\], would seem the most likely candidate. A report by Connor\(^3\) of a redox equilibrium (eq. 7) supports this postulate.

\[
\begin{align*}
(\text{CO})_4\text{Modmpe} + \text{I}_2 & \rightleftharpoons [(\text{CO})_4\text{Modmpe}]\text{I} \\
\text{slow} & \rightarrow (\text{CO})_3\text{ModmpeI}_2 & \text{eq. 7}
\end{align*}
\]

The more rapid conversion of \(6a\) to \(6\) is therefore the result of the greater polarity of the metal-bromine bond versus the metal-iodine bond in the ionic seven-coordinate intermediate. The bromo-intermediate metal center is more electron-deficient than the iodo-intermediate and loses the electron-withdrawing CO more readily.

Though \((\text{CO})_3\text{Mo(Ph}_2\text{PCH}_2\text{PPH}_2\text{I}_2)\) \(7\) has been known for some time, its \(^{31}\text{P}\) NMR spectrum has not been reported. It also gave a temperature-dependent NMR spectrum. At room temperature a single, moderately broad resonance at -22ppm was observed (Figure 11), which broadens as the temperature is lowered (Figure 12), and is resolved as a pair of \(\text{AX}\) spectra, \((\delta \ 0 \ (d), \delta -47 \ (d), J=68\text{Hz}; \delta -5 \ (d), -30 \ (d), J=122\text{Hz})\), with coalescence temperatures that differ by about 15°C (Figures 13–15). At about -80°C both sets of resonances are sharp. By contrast, 
\((\text{CO})_3\text{Mo(Ph}_2\text{POPPh}_2\text{I}_2)\) is static at -60°C.

The observed temperature dependence in the NMR of \(7\) is consistent with the processes depicted in Scheme 2.
$^{31}$P of $\text{Mo}($PPH$_2$-CH$_2$-PPh$_2$)(CO)$_3$I$_2$
If stereochemistry (2) gives rise to the AX spectrum which sharpens at the lowest temperature, then the rate of path 1 is the fastest and results in the broadened lines of Figure 13. Since at room temperature, a single line is seen, path 2 must interconvert stereochemistries (1) and (2). It cannot be determined from this data if another process, path 3, exchanges nuclei i and j or whether this results from a traverse of stereochemistry (2) via paths 1 and 2.

The theory of NMR shifts and coupling constants for phosphorus NMR is fairly involved. This, and the lack of any systematics in the $^{31}\text{P}$ NMR data for group 6B metal(II) complexes, makes interpretation of these results difficult. Through-metal cis-phosphorus-phosphorus coupling constants in molybdenum(0) complexes containing similar phosphines are on the order of 40 Hz. The magnitude of the phosphorus coupling constants for the molybdenum(II) complexes reported, varies considerably from around 200 Hz for the compounds prepared in this laboratory, to 120 and 69 Hz for the two isomers of 7, to 10 Hz for compounds of
the type (CO)\textsubscript{2}Mo(PMe\textsubscript{3})\textsubscript{3}Cl\textsubscript{2}.\textsuperscript{40} From the limited data there appears to be correlation between the number of atoms in the coordination sphere of the metal and the NMR shift. The seven-coordinate complexes thus far appear to have higher field shifts than the six-coordinate complexes.

**IR Spectra**

Both the description and interpretation of the IR spectra of the compounds discussed in this chapter are difficult because the appearance of the spectra vary significantly, depending on the solvent from which the sample was recrystallized as well as the phase of the sample (KBr disc or solution) from which the spectrum was recorded.

Differences in the appearance of solid and solution spectra are common in IR spectroscopy. In dilute solution, a molecule is isolated from its neighbors and, in the best cases, interacts weakly with the solvent.\textsuperscript{28} The IR-active stretching modes are determined by the molecular symmetry of the compound.\textsuperscript{21} For this reason most useful structural data for metal carbonyls comes from the spectra measured in dilute hexane solutions.

In a rigid crystal lattice, the IR-active bands are determined by the site symmetry of the lattice, which cannot be higher, and is often lower, than the molecular symmetry. In addition, the molecules are no longer isolated and therefore can interact. These two effects can cause an increase in the number of bands observed in a KBR
disc spectrum compared to a solution spectrum.

The pentagonal bipyrmidal geometry in tricarbonyl metal complexes gives rise to three IR-active stretches, $2A'+A''$. The high energy $A'$ CO stretch in the solution IR of 4 is split (2060 m, 2040 m cm$^{-1}$) into two bands of roughly equal intensity. This splitting of the $A'$ band must be independent of any lattice effects. Moreover, single crystals of 4 grown from solutions of tetrachloroethane and methylene chloride were different from one another. The crystals grown in tetrachloroethane showed one band at 2040 m cm$^{-1}$ and the crystals grown in methylene chloride showed two bands at 2058 m, 2034 m cm$^{-1}$. The x-ray analysis of the two samples showed virtually identical structures. Both x-ray analyses showed there to be solvent incorporated into the lattice so there may be some solvent interaction giving rise to the differences in the IR spectra. The carbonyl and diphosphoxane stretching frequencies are tabulated in table 2 (page 71), as well as the phase in which the spectra were measured.

In light of the $^{31}$P NMR results which show solution equilibria between two isomers, it is possible that the $A'$ band-doubling arises from the presence of the unidentified species (4a) in equilibrium with 4. Colton has reported the existence of a solution equilibrium between two forms of (CO)$_3$W(Ph$_2$PCH$_2$PPh$_2$)I$_2$ which can be separated. The solution spectrum of these is a composite of the solid state spectra
of the two individual compounds. The x-ray evidence, however, flatly contradicts this hypothesis.

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<tbody>
<tr>
<td>1 2054sh</td>
<td>2036m</td>
<td>1971s</td>
</tr>
<tr>
<td>4 2054m</td>
<td>2034m</td>
<td>1972s</td>
</tr>
<tr>
<td>4 2060m</td>
<td>2040m</td>
<td>2005w</td>
</tr>
<tr>
<td>5 2046m</td>
<td>2015w</td>
<td>2002w</td>
</tr>
<tr>
<td>5 2059m</td>
<td>2038m</td>
<td>2010w</td>
</tr>
<tr>
<td>6 2049m</td>
<td>2015w</td>
<td>1975sh</td>
</tr>
<tr>
<td>6 2054m</td>
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<td>1976</td>
</tr>
<tr>
<td>7 2031m</td>
<td>1959s</td>
<td>1923sh</td>
</tr>
</tbody>
</table>

Table 2
Carbonyl and Diphosphoxane Stretching Frequencies (cm⁻¹) of Molybdenum(II) complexes

Kepert, in his report of the solid-state structure of (CO)₃W(Ph₂PCH₂PPh₂)I₂, makes no mention of separable isomers in its preparation, and the IR spectrum of the crystal is not reported. Solvent incorporation has also been reported frequently for complexes of this type.

Two bands have been assigned to the P-O-P stretching frequency for (CO)₄Mo(Ph₂POPPh₂) (24, Chapter 1) at 773 and 758 cm⁻¹. The position of the P-O-P bands in the free ligands is thought to be a function of the P-O-P bond angle.²³ This angle is slightly smaller in 4, (61.9) than in 24 (Chapter 1) (63.82(3)). It is most likely that the appearance of two bands assigned to the P-O-P stretch in 24 (Chapter 1) is the result of a solid state effect and the actual band position falls between the two values (
765 cm\(^{-1}\)). A single band, observed at 761 cm\(^{-1}\), is assigned to the P-O-P stretching frequency of \(\mathbf{4}\), which has therefore moved to a slightly lower frequency as predicted.

The IR spectra of \((\text{CO})_3(\text{tolyl}_2\text{POPtolyl}_2)\text{MoBr}_2\), \(\mathbf{6}\) are also extremely variable. KBr disc spectra of \(\mathbf{6}\) vary greatly in the CO region, while the rest of the spectrum remains essentially constant from one sample to another. However, the tetrachloroethane-solution spectra of all samples are identical in the CO region, as was the case for Colton's tungsten DPM complex just described.\(^4\) \(\mathbf{6}\) has not been successfully recrystallized from tetrachloroethane and decomposes rapidly in tetrachloroethane solution at elevated temperature.

**Conclusions**

The halogen oxidations of molybdenum carbonyl complexes containing the diphosphoxane linkage as a chelating ligand, has resulted in the formation of molybdenum(II) seven-coordinate stereochemically non-rigid complexes analogous to the bis(diphenylphosphino)methane complexes synthesized first by Colton.

The IR and crystal data show that these complexes have solid-state structures similar to the reported complexes containing a chelate ligand with a small normalized bite. The variable-temperature NMR data also indicates that changes in the halogen or ligand bridge result in substantial differences in solution behavior. Direct NMR
observation of a solution equilibrium between seven-coordinate complexes has also been reported here.

It is well established that changes in the halogen, central metal atom and donor ligand produce a wide variety of structures, depending on the particular combination of atoms in the metal coordination sphere. The NMR evidence described here further demonstrates that this variability extends to solution behavior as well, for even minor changes in the coordination sphere. This is another indication of the delicate balance of forces which determines the structural chemistry of seven-coordinate metal complexes.
EXPERIMENTAL

(CO)$_3$Mo(Ph$_2$P$_2$PPh$_2$)I$_2$. To 1 g (CO)$_4$Mo(Ph$_2$P$_2$PPh$_2$) (1.68 mmol) in 10 mL freshly distilled CH$_2$Cl$_2$ was added dropwise 20.7 mL (20.6 mg/mL) I$_2$ in CH$_2$Cl$_2$ with rapid stirring. CO was evolved slowly and continuously for about 5 minutes after the addition was complete. The reaction was stirred for 0.5 h at which time TLC (eluent 28% ethyl acetate/hexane) showed some starting material. The best yields were obtained when a slight deficiency of iodine was used. The solvent volume was reduced under vacuum by 20-30% and 10 mL hexane slowly added. 0.667 g (53%) (CO)$_3$Mo(Ph$_2$P$_2$PPh$_2$)I$_2$ was deposited as a microcrystalline solid over about 3 h. This solid was filtered off, washed with ether and dried under vacuum in the dark. The mother liquor was stripped of solvent, the residual oil redissolved in freshly distilled tetrachloroethane and an additional 280 mg (combined yield 75%) precipitated by the slow addition of hexane. IR ν CO 2060m, 2040m, 2005w, 1983s br, 1932s; $^{31}$P NMR 213 K 81 (d), 112 (d), $^{2}$J$_{pp}$=193Hz, 76 (s); Anal. Calcd. for C$_{27}$H$_{20}$I$_2$Mo$_4$P$_2$ C, 39.54; H, 2.46. Found: C, 39.14; H, 2.40

Single crystals of 4 were grown by dissolving 50 mg of material in 2 mL CH$_2$Cl$_2$ and allowing 4 mL hexane to diffuse slowly into the solution overnight. The Schlenk tube was stored in the dark.
(CO)$_3$Mo(tolyl$_2$PO$_2$tolyl)$_2$I$_2$. To 0.419 g (0.644 mmol) (CO)$_4$Mo(tolyl$_2$PO$_2$tolyl) in 5 mL CH$_2$Cl$_2$ was added 4 mL 0.165 mmol/mL I$_2$ in CH$_2$Cl$_2$. TLC as above showed some starting material still present. The reaction was stirred for about 10 minutes and then 4.8 mL solvent was removed under vacuum. Slow addition of 8 mL hexane resulted in the precipitation of 0.327 g (58%) bright orange (CO)$_3$Mo(tolyl$_2$PO$_2$tolyl)$_2$I$_2$ which was filtered, washed with ether and dried under vacuum. IR C$_2$H$_2$ClCO 2059m, 2038m, 2010w, 1975s, 1929s, 1885w; $^{31}$P NMR 213 K $81$ (d), 111 (d), $^{2}J_{pp}$=193Hz.; No analysis.

(CO)$_3$Mo(tolyl$_2$PO$_2$tolyl)$_2$Br$_2$. To 0.457 g (0.7 mmol) (CO)$_4$Mo(tolyl$_2$PO$_2$tolyl)$_2$) in 8 mL CH$_2$Cl$_2$ at 0 C was added 5.6 mL (0.7 mmol) Br$_2$ in CH$_2$Cl$_2$. CO evolution was rapid during the addition and ceased immediately when the addition of bromine was complete. As the reaction appeared nowhere near completion by TLC, two additional 0.3 mL of Br$_2$ solution were added. This caused the spot corresponding to starting material to become more faint. 8 mL hexane was added and the solvent volume reduced under vacuum until 0.220 g (40%) bright yellow solid was deposited. This was filtered off, washed with ether and dried under vacuum. The mother liquor deposited an additional 0.182 g (combined yield 73%) orange-yellow solid on standing overnight. The KBr disc spectra of these solids were quite different from one another in the CO region but the finger print regions were identical. The CO
regions in tetrachloroethane were the same. IR
tetrachloroethane \( \neq \) CO 2054 m, 1990 s, 1976 s, 1885 sh; \( ^{31} \)P NMR 91 (d), 119 (d), \( \frac{2J_{PP}}{=119Hz} \). No analysis.

X-ray crystals of 6. 0.85 mg (0.13 mmol)
(CO)\(_4\)Mo(toly\(_2\)P0Ptolyl\(_2\)) was dissolved in 1 mL CH\(_2\)Cl\(_2\) in a Schlenk tube and 1.8 mL 0.07 M Br\(_2\) in CH\(_2\)Cl\(_2\) was added slowly with stirring. The orange solution was stirred in the dark for 24 h, the stir-bar removed and 10 mL hexane layered in slowly. This was stored in the dark for 48 hrs during which time it deposited bright orange crystals. IR KBr \( \neq \) CO 2040 m, 2015 w, 1975 s, 1961 s, 1925 m, 1877 sh.

(CO)\(_4\)Mo(Ph\(_2\)PCH\(_2\)PPh\(_2\)). A convenient preparation of this compound compared to published methods is as follows:
0.638 g (1.69 mmol) (CO)\(_4\)Mo(NHC\(_5\)H\(_{10}\))\(_2\) and 0.648 g (1.69 mmol) Ph\(_2\)PCH\(_2\)PPh\(_2\) were stirred at room temperature in 30 mL CH\(_2\)Cl\(_2\) for 4 hrs. During this time the solution became cloudy. The solution was filtered through celite, the solvent volume reduced under reduced pressure, and methanol slowly added. 0.605 g (60%) bright yellow (CO)\(_4\)MoPh\(_2\)PCH\(_2\)PPh\(_2\) was deposited, filtered in air, washed with methanol and dried under vacuum. \( ^{31} \)P NMR -23 (s); IR KBr 2008 s, 1920 sh, 1904 s, 1862 sh 1829 sh.

(CO)\(_3\)Mo(Ph\(_2\)PCH\(_2\)PPh\(_2\))\(_2\). To 0.605 g (1.02 mmol)
(CO)\(_4\)Mo(Ph\(_2\)PCH\(_2\)PPh\(_2\)) in 10 mL CH\(_2\)Cl\(_2\) was added dropwise 6.2 mL 0.165 mmol/mL I\(_2\) in CH\(_2\)Cl\(_2\) over several minutes. CO was
evolved slowly and continuously for several minutes after the addition was complete. The solvent was distilled under vacuum and the brown residue was recrystallized from CH$_2$Cl$_2$/hexane to yield a brick-colored microcrystalline solid. $^{31}$P NMR -23; IR C$_2$H$_2$Cl$_4$ CO 2031m, 1959s, 1923m.
CHAPTER 3

The Reactions of Ph\textsubscript{2}P-P(0)Ph\textsubscript{2} with CuCl and [cp(CO)\textsubscript{2}FeTHF][BF\textsubscript{4}].

The Reaction of Coordinated Aminophosphines with Boron Trifluoride Etherate.

In this last chapter, three different types of reactions will be described. These reactions gave unexpected results, and while it is sometimes useful to follow up on these serendipitous results, it is also important to know when to stop. The three reactions are interesting in and of themselves, are not particularly useful in any obvious way, but nonetheless, the products were characterized satisfactorily and the results are reported herein.

Two of these reactions were studied because of an interest in the effect of transition metal coordination on the position of the tautomeric equilibrium of diphosphine monoxides (eq. 1).

\[
R_2P-P(0)R_2 \rightleftharpoons R_2P-O-PR_2 \quad \text{eq. 1}
\]

Previous studies in this laboratory were concerned almost exclusively with the group 6B carbonyls and we wanted to extend these studies to some of the other transition metals. If an effect is to be ascribed solely to the steric and electronic influence of the metal, the reaction conditions must be mild such that they do not interfere
with the results. Thus two substrates, \((\text{cpFe(CO)}_{2}\text{THF})\text{BF}_4\) and CuCl, were chosen for study because they undergo substitution at room temperature. In the former, phosphine donors were known to replace THF at room temperature\(^4\) and the latter is a kinetically labile \(d^{10}\) metal with free and bound ligand equilibrating rapidly in solution at room temperature\(^4\).

The third reaction type is the direct result of our studies on the reactions of coordinated phosphines. In Kraihanzel's experiments\(^1\), nucleophilic displacements carried out on \((\text{R}_2\text{PCl})_2\text{Mo(CO)}_4\) as the substrate with oxygen, sulfur, and nitrogen nucleophiles, resulted in the formation of chelate rings. This suggested a route to coordinated diphosphines via the reaction of these same nucleophiles with the corresponding trans-starting material. As we have seen, hydrolysis of trans-\((\text{Ph}_2\text{PCl})_2\text{Mo(CO)}_4\) led to an isomerized product. Since the amine is not as strong an acid, aminolysis would be expected to leave the trans-geometry unchanged.

These reactions have been described in two sections, each containing results and discussion. In the first section, reactions of tetraphenyldiphosphine monoxide with the copper and iron species, which are prone to substitution have been discussed. The reactions of coordinated aminophosphines have been described in the second section. Experimental details have been included at the end of the chapter.
Reactions of Ph₂P-P(O)Ph₂ with [Cp(CO)₂FeTHF]BF₄ and CuCl

The cpM(CO)₂ fragment is a ubiquitous structural feature in organometallic chemistry. The iron(II) containing species cpFe(CO)₂⁺ (Figure 1), hereafter referred to as Fp⁺, is particularly common, with the olefin complexes receiving particular attention.

Cp(CO)₂FeL, in which L is a loosely bound donor solvent molecule such as acetone or THF, can be isolated as a salt and is readily available from [cpFe(CO)₂]₂ (Figure 2).

Our interest in cpFe(CO)₂THF⁺ complex was stimulated by a report of its convenient preparation and reaction with phosphines, in which the phosphine replaces the solvent rapidly at room temperature. Treichel also reported the hydrolysis of FpPh₂PCl⁺ to give a hydrogen-bridged dimer,
analogous to the hydrogen-bridged chelate complex described earlier. Since this species contains the stable phosphinous acid tautomer, it seemed reasonable to suppose the Fp\(^+\) fragment might also stabilize the diposphoxane ligands. Though the Fe(II) center of Fp\(^+\) can be expected to \(\pi\)-backbond to the phosphine ligand,\(^{42}\) the higher effective nuclear charge of Fe(II) compared to Mo(0) makes Fe(II) a more electronegative atom which would favor the P-O-P tautomer of the diphosphine oxide. This would be analogous to the effect of electronegative organic substituents on phosphorus which, are known to favor the diposphoxane form.\(^{10}\)

Results

The reaction of FpTHFBF\(_4\) with one equivalent of Ph\(_2\)P-P(0)Ph\(_2\) in methylene chloride resulted in the isolation of only one identifiable compound, FpPh\(_2\)P-PPh\(_2\)Fp(BF\(_4\))\(_2\)\(^5\), in which the phosphoryl oxygen has been lost (eq. 1).

\[
\begin{align*}
\text{FpTHFBF}_4^+ + \text{Ph}_2\text{P-P(0)Ph}_2 & \rightarrow (\text{FpPh}_2\text{P-PPh}_2\text{Fp})^{2+} \\
\text{eq. 1}
\end{align*}
\]

This bimetallic species has been characterized by \(^{31}\)P and \(^1\)H NMR, IR and elemental analysis.

Monitoring the reaction while in progress by \(^{31}\)P NMR revealed several reaction intermediates. During the course of the reaction the solution became turbid. The material giving rise to this turbidity was never isolated although
the mass of the turbidity is most likely insignificant.

One of the intermediates observed in the reaction, FpPh₂P-PPh₂(BF₄)₄, has been synthesized by reaction of FpTHFBF₄ with Ph₂P-PPh₂ (eq.2), and characterized by ³¹P NMR, IR and elemental analysis.

\[ \text{FpTHF}^+ + \text{Ph}_2\text{P-PPh}_2 \rightarrow \text{FpPh}_2\text{P-PPh}_2^+ \quad \text{eq.2} \]

Reaction of this complex with another equivalent of FpTHF(BF₄) converted it to FpPh₂P-PPh₂Fp(BF₄)₂ (eq.3), as observed by ³¹P NMR.

\[ \text{FpPh}_2\text{P-PPh}_2^+ + \text{FpTHF}^+ \rightarrow \text{FpPh}_2\text{P-PPh}_2\text{Fp}^2+ \quad \text{eq.3} \]

The reaction of Ph₂P-P(O)(OEt)₂ with FpTHF⁺ resulted in the isolation FpPh₂P-P(O)(OEt)₂, identified by it ³¹P NMR. However, the analysis and the proton NMR integration were not satisfactory. The fact that significant decomposition in d⁶-acetone was observed overnight may account for these results. Indeed, this diphosphine oxide complex may undergo a similar decomposition to that observed for FpPh₂P-P(O)Ph₂⁺, but at a sufficiently slow rate to allow for its isolation.

**Discussion**

It was hoped that coordination of Ph₂P-P(O)Ph₂ to an electronnegative and bulky group such as the Fp iron(II)
cation, would result in a room temperature tautomerization from diphosphine monoxide to diphosphoxane. There is evidence that this did occur, but the only compound isolated from the reaction was a diiron-diphosphine species in which the strong phosphorus-oxygen double bond appears to have been broken.

Since a certain amount of turbidity was seen to develop during the reaction and the identity of the material was never determined, it is possible that the oxygen was removed from the system by its precipitation as an insoluble phosphine oxide. It seems unlikely that the mass of this material was sufficient to support this explanation.

It appears unlikely that the solvent plays a role in this reaction which occurs in both methylene chloride and THF, two solvents with very different properties. Indeed, the reaction rate in THF is increased because the product is insoluble and the reaction is driven to completion in about an hour, as opposed to a three hour reaction time in methylene chloride.

The reactivity of \((\text{FpPh}_2\text{P-PPh}_2\text{Fp})^{2+}\) has not yet been studied. Preliminary results indicate that the phosphorus-phosphorus bond is not rapidly cleaved by iodine. It may be that attack by iodine is blocked by the \(\text{Fp}^+\) bonded to each phosphorus.

Related iron(I) and (II) complexes have long been known. Hayter\(^{45}\) reported the reductive cleavage of \(\text{R}_2\text{P-PR}_2\)
(R=Ph,Me) by \((\text{cpFe(CO)}_2)_2\) in refluxing toluene to give a diphosphido-bridged iron dimer (eq. 4).

\[
(\text{cp(CO)}_2\text{Fe})_2 + \text{R}_2\text{P-PR}_2 \rightarrow \begin{array}{c}
\text{cp} \\
\text{R} \\
\text{P} \\
\text{Fe} \\
\text{Fe} \\
\text{R} \\
\text{P} \\
\text{cp}
\end{array} \text{ + cis} \quad \text{eq. 4}
\]

An analogous diphosphine-diiron (0) complex is also known\(^4^6\) which was prepared by thermal reaction of the diphosphine with \(\text{Fe(CO)}_5\) (eq. 5).

\[
\text{Fe(CO)}_5 + \text{Me}_2\text{P-PMe}_2 \rightarrow (\text{CO})_4\text{FeMe}_2\text{P-PMe}_2\text{Fe(CO)}_4 \quad \text{eq. 5}
\]

This complex, on heating, loses two equivalents of CO and undergoes an internal redox reaction which results in an iron(I) diphosphido-bridged dimer (eq. 6).

\[
7 \quad \rightarrow \quad (\text{CO})_3\text{Fe} \quad \text{Fe(CO)}_3 \quad \text{eq. 6}
\]

Thus a formal scheme illustrating the relationships between these diiron complexes can be composed as shown in Scheme 1 on page 85. In principle, \(9\) and \(5\) are related by redox reactions at the phosphorus ligand. It remains to be seen whether this transformation can be effected under chemical or electrochemical redox conditions.
Scheme 1

**Phosphorus NMR**

The reaction in progress was followed by $^{31}$P NMR and the results analyzed in terms of coordination shifts observed for some known compounds.

$$\text{Ph}_2\text{P}-\text{P}(\text{O})\text{Ph}_2 + \text{Fp}^+ \rightarrow (\text{FpPh}_2\text{P}-\text{P}(\text{O})\text{Ph}_2)^+$$

1

$$(\text{FpPh}_2\text{P}-\text{P}(\text{O})\text{Ph}_2)^+ \rightarrow (\text{FpPh}_2\text{P}-\text{O}-\text{PPh}_2)^+$$

2

$$2 + 1 \rightarrow (\text{FpPh}_2\text{P}-\text{O}-\text{P}(\text{O})\text{Ph}_2)^+ + (\text{FpPh}_2\text{P}-\text{PPh}_2)^+$$

3

4

$$3 + 4 \rightarrow (\text{FpPh}_2\text{P}-\text{PPh}_2\text{Fp})^{2+} + \text{Ph}_2(\text{O})\text{P}-\text{P}(\text{O})\text{Ph}_2$$

5

6

Scheme 2

In the proposed scheme (Scheme 2), compound 1 which is observable (52.4 ppm d; 34.6 ppm d; J = 68.36 Hz.), slowly
tautomerizes to give 2 (eq. 7) which is not observed.

\[ \text{Ph}_2\text{P-P(O)Ph}_2 + \text{Fp}^+ \rightarrow (\text{FpPh}_2\text{P-P(O)Ph}_2)^+ \]

\[ 1 \rightarrow (\text{FpPh}_2\text{P-O-PPh}_2)^+ \quad \text{eq. 7} \]

Compound 2 rapidly abstracts an oxygen atom from 1 to give 3 and 4 (eq. 8).

\[ (\text{FpPh}_2\text{P-P(O)Ph}_2)^+ + (\text{FpPh}_2\text{P-O-PPh}_2)^+ \]

\[ 1 \quad 2 \rightarrow (\text{FpPh}_2\text{P-O-P(O)Ph}_2)^+ + (\text{FpPh}_2\text{P-PPh}_2)^+ \quad \text{eq. 8} \]

3 4

Both of these latter species are observed and 4 has been independently synthesized and characterized. It has also been observed to form 5 by reaction with one equivalent of added Fp⁺ in an NMR tube. In the reaction between 3 and 4, a redistribution of iron and oxygen occurs to give 5 and 6 (eq. 9).

\[ (\text{FpPh}_2\text{P-O-P(O)Ph}_2)^+ + (\text{FpPh}_2\text{P-PPh}_2)^+ \]

\[ 3 \quad 4 \rightarrow (\text{FpPh}_2\text{P-PPh}_2\text{Fp})^2+ + \text{Ph}_2\text{(O)P-P(O)Ph}_2 \quad \text{eq. 9} \]

5 6

5 has been isolated in moderate yield and 6 is observed in the NMR at 27.5 ppm (s) which agrees with published values. Rationalization of the evidence for this scheme depends on additivity relationships which are summarized in
A coordination shift in the range +75.6 to +68.4 ppm has been observed for Fp⁺ with a number of ligands. Thus, the signal for Ph₂PCl occurs at 81 ppm while the signal for the coordination compound FpPh₂PCl⁺ is at 151.3 ppm. A coordination shift of 70 ppm therefore occurs when diphenylchlorophosphine coordinates to Fp⁺. The trivalent phosphorus of Ph₂P-P(O)Ph₂ has a shift of -23 ppm. The AX quartet assigned to FpPh₂P-P(O)Ph₂ has a doublet centered at 52 ppm which corresponds to a change of 75 ppm downfield.

<table>
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<th>Shift P</th>
<th># Shift PO</th>
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<td>-</td>
</tr>
<tr>
<td>Ph₂P-P(O)(OEt)₂</td>
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<td>-</td>
</tr>
<tr>
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<td>-</td>
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<td>75.6</td>
</tr>
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<td>116.5 **</td>
</tr>
<tr>
<td>FpPh₂P-O-P(O)Ph₂⁺</td>
<td>167.9</td>
<td>114.6 **</td>
</tr>
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</table>

Table 1
* The change in shift on coordination in ppm
** Value reflects the sum of two contributions to the shift: P(O)P to P-O-P and coordination to the metal
A comparison of \((\text{CO})_5\text{MoPh}_2\text{P-}\text{P(0)Ph}_2\) and \((\text{CO})_5\text{MoPh}_2\text{P-0-PPh}_2\) shows the coordinated phosphorus in the diphosphoxane species 115ppm downfield from the diphosphine monoxide form. This compares well with a difference of 115ppm between the coordinated phosphorus atoms in the proposed \(\text{FpPh}_2\text{P-P(0)Ph}_2^+\) and \(\text{FpPh}_2\text{P-0-P(0)Ph}_2\) structures. \(\text{Ph}_2\text{(O)P-O-P(0)Ph}_2\) resonates at 33.1ppm which again compares favorably with the shift of 31ppm assigned to the uncoordinated tetravalent phosphorus in 3.

The \(\text{3}^1\text{P NMR shift of 5}\) is at anomalously high field. Because this complex is a dication and would be expected to resonate at lower field than the related monocations, this result is perplexing.

It is also interesting to note that the free phosphorus of \(\text{Ph}_2\text{P-PPh}_2\) has moved 17ppm to lower field on coordination to \(\text{Fp}^+\), which contrasts with a very slight coordination shift to higher field observed for most the diphosphine monoxides. Electronegative substituents are known to shift the trivalent phosphorus signal to lower field, while the opposite trend is observed for the tetravalent \(\text{P=O}\) resonance, which moves to slightly higher field on substitution of electronegative groups. Therefore, \(\text{Fp}^+\), acting like an electron-withdrawing group, is causing a slight upfield shift in the remote phosphoryl group of \(\text{Fp(Ph}_2\text{P-P(0)(OEt)}_2\) and a more substantial downfield shift in the remote trivalent phosphorus of
Fp(Ph₂P-PPh₂)+.

**IR Spectra**

The IR spectra for both complexes 4 and 5 show the expected two intense bands in the CO region assigned to A' and A'' transitions. The KBr disc spectrum of 5 shows three bands in the CO region, the additional band occurring at 2013 cm⁻¹. This band is ascribed to a solid state effect. There is little or no difference in the positions of the CO bands in the KBr and solution spectra. Most important is the absence of the strong absorption associated with the P=O stretch in the spectrum of 5.

**Reaction of Ph₂P-P(O)Ph₂ with CuCl**

A 1:1 complex, (CuCl)(Ph₂P-P(O)Ph₂) 10, was isolated as a white solid from the reaction of CuCl and Ph₂P-P(O)Ph₂ in methylene chloride (eq. 10),

\[ \text{CuCl} + \text{Ph}_2\text{P}-\text{P(O)Ph}_2 \rightarrow [\text{CuClPh}_2\text{P-P(O)Ph}_2] \text{ eq. 10} \]

by precipitation with diethyl ether. This complex has been characterized by IR, ³¹P NMR and analysis. The complex is kinetically labile, equilibration between free and bound ligands being rapid on the NMR time scale. This equilibrium can be suppressed by addition of excess free ligand or the ligand can be replaced by addition of excess Ph₃P (eq. 11).
\[ \text{[CuClPh}_2\text{P-P(O)Ph}_2] + P\text{Ph}_3 \rightarrow \text{[CuClPPh}_3] \quad \text{eq. 11} \]

It appears that the coordination of phosphines to CuCl activates the ligand toward nucleophilic attack which is in sharp contrast to the deactivation of phosphines observed on their coordination to the earlier transition metal carbonyls.

During an attempt to isolate single crystals of this complex suitable for x-ray analysis, a different complex was isolated, 11, (eq. 12),

\[ \text{[CuClPh}_2\text{P-P(O)Ph}_2] \xrightarrow{\text{3 days}} \text{[(CuCl)}_2\text{Ph}_2\text{P-O-PPh}_2\text{]}_2 \quad \text{eq. 12} \]

which contained the diphosphoxane linkage as observed by \(^{31}\text{P}\) NMR. An x-ray crystal structure revealed a dimeric step-like structure (Figure 3 page 91) strictly analogous to a series of complexes, \([(\text{CuX)}_2\text{DPM}]_2, \text{X}=\text{Cl,Br,I,} \]

\(\text{DPM} = \text{bis(diphenylphosphino)-methane, reported by} \]

\(\text{Randaccio.}^{49}\)

An independent synthesis of this phosphoxane complex was achieved by hydrolysis of \((\text{Ph}_2\text{PCl})(\text{CuCl})\) with one half an equivalent of water (eq. 13).

\[ 2 \text{[CuClPh}_2\text{PCl}] + \text{H}_2\text{O} \rightarrow \text{[(CuCl)}_2\text{Ph}_2\text{P-O-PPh}_2\text{]}_2 \quad \text{eq. 13} \]

Variable temperature NMR experiments confirmed the exchange processes which are well known for complexes of this type\(^{48}\) and also implied the existence of complexes of higher than a 1:1 ligand to metal ratio in the presence of
Figure 3
The Structure of \([(\text{CuCl})_2 \text{Ph}_2 \text{PPOPPh}_2]\)_2
excess ligand at low temperature. A similar report has been made by Muetterties for copper complexes of $\text{Ph}_3\text{P}$.\textsuperscript{50}

**Discussion**

The solid-state structure of 2 consists of discrete centrosymmetric dimeric units containing four copper atoms arranged at the corners of a parallelogram and bridged in pairs by the tetraphenyldiphosphoxane ligand (Figure 3). There are two crystallographically distinct copper atoms, one of which is sixteen-electron tri-coordinate and the other, eighteen-electron tetra-coordinate. Each copper is bonded to a trivalent capping halogen and to a divalent asymmetrically-bridging halogen. Finally, each copper is bonded to a single phosphorus of the diphosphoxane-bridging ligand which links the two distinct coppers of each pair.

A large number of complexes of the type $(\text{M}\text{X})_4\text{L}_4$, $(\text{M}\text{=Cu,Ag, X}\text{=Cl,Br,I, L}\text{=AsR}_3,\text{PR}_3)$ monodentate or bidentate, are known. The solid state structures of many of these complexes have been determined by Churchill\textsuperscript{51} and others. It is generally accepted that no metal-metal bond exists in these complexes and the structures are thought to be the result of non-bonded interactions. There are two basic structural types, a cubane-like structure consisting of two interpenetrating tetrahedra, one of four metal atoms and the other of four halides, while the other structure is step-like consisting of an eight-membered ring with alternating halogens and metal atoms. The structure reported in this work is of the latter type.
From the study of a large number of clusters has emerged the observation of a dependence of structure on nonbonded interactions. The complex((Et$_3$P)CuCl)$_4$ contains a fairly undistorted cubane core. As changes in the ligands, metal and halide cause the coordination sphere to become more crowded, the cubane structure becomes progressively more distorted. With the most bulky groups on the ligands and with those atoms that form the shortest bonds, and hence, the largest steric interaction, the step structure is observed. If the group 5 donors are chelating ligands then the step structure is observed regardless of the other atoms in the cluster. One interesting cluster (AgIPh$_3$P)$_4$, has been observed to crystallize as either a highly distorted cubane or as a step depending on the conditions. Another, for which there is Raman and IR data indicating a step structure, has been shown to form crystals of the cubane structure. The following atoms are listed in order of their increasing tendency to cause the formation of the step structure: Cl<Br<I; Ag<Cu; As<P.

An anomalous distorted cubane structure has recently been reported for [[CuX](t-Bu$_3$P)]$_4$, X=Br. IR and Raman data are consistent with a cubane structure for X=Cl,I as well. The bulky substituents on phosphorus are expected to favor the step structure. 

[[CuCl$_2$]DPM]$_2$, DPM=Ph$_2$P-CH$_2$-PPh$_2$, provides an exact
analogy to the diphosphoxane complex reported here, the only difference being the methylene bridge vs. the oxygen bridge. With the exception of the specific differences in lengths and angles associated with the oxygen and methylene bridges the two structures are essentially the same. The Cu-P bond length in the phosphoxane-bridged structure reported here is 0.28Å shorter than the sum of the covalent radii of copper, (1.35Å) and phosphorus, (1.10Å). This suggests an additional contribution to the simple sharing of a pair of electrons such as a dipolar bond or \( \pi \)-back bonding from the metal. It is noteworthy in this context that the Cu-P bond length in \([(CuCl)_{2}Ph_{2}P-O-PPh_{2}]_{2}\) is 0.027Å shorter than in the DPM complex.

The methylene-bridged chelate complexes and the oxygen-bridged chelate \( \text{11} \) show a pronounced compression of the M(1)-X-M(2) angle, (\( \sim 75^\circ \)) and a shorter Cu(1)-Cu(2) distance than in the analogous but unbridged step structures reported. This is the result of the chelate ligand bite which forces the step geometry on the complexes presumably allowing a closer approach of the bridged copper atoms than is possible across the diagonal of the cubane face.

One other point of note in the comparison of the POP and PCP structures is the short-short-long pattern in the capping halogen copper bond-lengths which is observed for both complexes \([(CuX)_{2}PEP]_{2}, (X=Cl, E=CH_{2}, O) \) but not for \([(CuX)_{2}PCP]_{2} (X=Br, I) \). The six membered P-C-P-Cu-X-Cu
ring has a chair conformation for X=Cl, and a boat in the Br and I cases. A table of selected bond distances and angles for \([(CuCl)_2(Ph_2P-O-PPh_2)]_2\) is included in an appendix at the end of the chapter.

31P NMR

The 31P NMR spectra Ph₂P-P(0)Ph₂)(CuCl) are interesting because rapid ligand dissociation, which is well known for phosphine complexes of copper(I), broadens only the doublet resonance of the phosphorus directly bonded to the copper (Figure 4). The phosphoryl phosphorus doublet remains a sharp pair of lines shifted to slightly higher field compared to the free ligand and with a reduced coupling constant of 109Hz. This decrease in coupling constant has been observed uniformly for the coordination of diphosphine monoxide to a variety of transition metals.

As the temperature is lowered (Figures 5 and 6), the high-field lines sharpen as expected with a slowing of the exchange, while the down-field lines remain unchanged. This process continues to -70°C. No coupling to ⁶³Cu (nat. abun. 69%, I=3/2, Q=-0.18) was observed at this low temperature. ¹J_CuP has been reported in Cu[P(OMe)₃]ClO₄, ¹J_CuP=1190Hz ± 30Hz.

The temperature-dependent 31P NMR spectrum of (CuCl)(Ph₂P-P(0)Ph₂) in the presence of excess ligand is complex, and the low-temperature limiting spectrum, in which all rates are slow on the NMR time scale, has not yet been observed. In the absence of a computer simulation
Variable Temperature $^{31}$P NMR of $(\text{CuCl})(\text{Ph}_2\text{P-P(O)Ph}_2)$
only some cautious simple statements can be made about these spectra.

The addition of excess ligand to a methylene chloride solution of \(\text{(CuCl)(Ph}_{2}\text{P-P(0)Ph}_{2})\) causes the lines at high field to sharpen somewhat (Figure 8). The left hand of the pair of downfield lines (3) broadens substantially while the right hand of this pair remains essentially unchanged. Raising the temperature causes further sharpening of the broad resonances (Figure 7).

In the absence of excess ligand, the low-field lines are sharp as the exchange is more rapid than the shift difference between the bound and free ligand. The high-field lines are very broad as the exchange is of the same magnitude as the shift difference between the bound and free ligand.

The addition of excess ligand increases the concentration of free ligand and slows the exchange. This makes the high-field lines sharper as the exchange rate is now slower than the shift difference between the free and bound ligand (compare Figure 4 and Figure 8). The upfield portion of the spectrum presumably approaches a closely spaced pair of doublets. The appearance of the low-field lines after the addition of excess ligand, is the result of the coalescence of two pairs of lines, with the coalescence for each pair occurring at different rates. As the temperature is lowered further to \(-10^\circ\text{C}\) (Figure 11), the two pairs of lines emerge. Lines 1 and 3 are a coupled
Variable Temperature $^{31}$P NMR of $(\text{CuCl})(\text{Ph}_2\text{P-P(O)Ph}_2)$ and Excess Ligand
Variable-Temperature $^{31}$P NMR of (CuCl)(Ph$_2$P-P(O)Ph$_2$) and Excess Ligand
pair, lines 2 and 4 are a coupled pair. Lines 1 and 3 coalesce more slowly than do lines 2 and 4 because initially they were farther apart. The downfield halves of two AX spectra can be seen quite clearly at -20° C (Figure 12). A low-temperature limiting spectrum is not observed, however, as on lowering the temperature further (Figures 13-15), the spectrum becomes a good deal more complex, indicating additional equilibrium processes. This continues down to the limits of the operating temperature of the instrument. Muetterties and Lippard, and more recently Morse, have reported multiple equilibria of the type:

\[
2L_3\text{CuX} \rightleftharpoons (L_2\text{CuX})_2 + 2L \\
(L_2\text{CuX})_2 \rightleftharpoons 2L_2\text{CuX} \\
(L_2\text{CuX})_2 \rightleftharpoons L_3\text{Cu}_2\text{X}_2 + L
\]

The NMR analysis of such a system containing diphosphine ligands is far beyond the scope of this investigation.

Presumably, the variation in the appearance of the spectra around room temperature is the result of the temperature-dependence of the exchange rate between free ligand and a simple 1:1 complex. Muetterties has observed multiple equilibria in the low temperature spectrum of (Ph3P)CuCl and similar processes may be at work here, producing very complex spectra. It is obvious that much remains to be done if we are to understand these solution processes.
Variable Temperature $^{31}$P NMR of $(\text{CuCl})(\text{Ph}_2\text{POPPh}_2)$ and Excess Ligand
The Effect Of Coordination Of Ph$_2$P-P(0)Ph$_2$ To CuCl On The Phosphorus-Phosphorus Bond

From an independent study of ligands of the type Ar$_2$P-P(0)Ph$_2$, Ar=p-tolyl, it was apparent that these diphosphine monoxide ligands are not stable in methylene chloride solution.$^{64}$ By refluxing a sample of Ar$_2$P-P(0)Ph$_2$ in methylene chloride for eight hours, a mixture of four diphosphine monoxides, Ar$_2$P-P(0)Ar$_2$, Ph$_2$P-P(0)Ph$_2$, Ar$_2$P-P(0)Ph$_2$ and Ph$_2$P-P(0)Ar$_2$ was produced.

In the study of the complexes of CuCl, slow diffusion of hexane into a solution of (CuCl)(Ph$_2$P-P(0)Ph$_2$) in CH$_2$Cl$_2$ at room temperature, caused the deposition of crystals of [(CuCl)$_2$(Ph$_2$P-O-PPh$_2$)]. Simply allowing methylene chloride solutions of (CuCl)(Ph$_2$P-P(0)Ph$_2$) to stand overnight at room temperature resulted in the formation of a mixture of Ph$_2$P(OH), [(CuCl)$_2$(Ph$_2$P-O-PPh$_2$)] and (CuCl)(Ph$_2$POH). The scrambling of the free diphosphine monoxide ligand in CH$_2$Cl$_2$ occurred at reflux overnight. These results imply activation of the P-P bond resulting from coordination to CuCl. Thus, while the coordination of Ph$_2$P-P(0)Ph$_2$ to CuCl ultimately yielded complexes containing the diphosphoxane ligand, it appears likely this resulted from the decomposition of the ligand in methylene chloride accelerated by CuCl coordination. The tautomerization of the diphosphine oxide to diphosphoxane remains an intriguing possibility. Regardless of the mechanism, the P-O-P linkage has been observed to be
stabilized by coordination to the d\textsuperscript{10}\ copper(I) ion in addition to the stabilization observed by coordination to the d\textsuperscript{6} 6B metal carbonyls described in Chapter 1.

**Conclusions**

The proper interpretation of the above results is not entirely clear. The reaction of the diphosphine monoxide with both the iron(II) and copper(I) species was mediated in one way or another by the formation of the diphosphoxane tautomer of tetraphenyldiphosphine monoxide. In the former case the evidence is more speculative. The diphosphoxane is assumed to have formed because of the observation by phosphorus NMR of a coordinated P-O-P(0) linkage. A scheme was proposed to support this assumption. Nonetheless, the structure may have formed as the result of phosphorus-phosphorus bond rupture promoted by Fp\textsuperscript{+}. In the latter case, it appears most likely that reaction of Ph\textsubscript{2}P-P(0)Ph\textsubscript{2} with CuCl resulted in the labilization of the phosphorus-phosphorus bond so that it was readily hydrolyzed and subsequently formed the P-O-P linkage. The hydrolysis of CuClPh\textsubscript{2}PCl led to this product directly in a reaction analogous to the hydrolysis of chlorophosphines coordinated to molybdenum(0) discussed in Chapter 1.
The Reaction of Coordinated Aminophosphines

A series of nucleophilic displacements of chloride from cis-(Ph₂PCl)₂Mo(CO)₄ by oxygen and sulfur nucleophiles yielded chelated products which were the result of the close proximity of the sites of attack in the substrate (eq. 14 and 15).¹⁹

\[
\begin{align*}
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂PCl} \\
\text{Ph₂PCl}
\end{array} \\
\text{H₂O} & \quad \text{Et₃N} \\
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂P-O⁻} \\
\text{Ph₂P-O⁻}
\end{array}
\end{align*}
\]

(eq. 14)

\[
\begin{align*}
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂PCl} \\
\text{Ph₂PCl}
\end{array} \\
\text{H₂S} & \quad \text{Et₃N} \\
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂P} \\
\text{Ph₂P}
\end{array}
\]

(eq. 15)

The reaction of the corresponding trans-substrate would not be expected to give such structures.

We have seen, however, that hydrolysis of trans-(Ph₂PCl)₂Mo(CO)₄ resulted in an isomerized product. This is the same compound formed as in eq. 14 above, the driving force for the isomerization being the formation of the hydrogen-bridged structure. Aminolysis of cis-(CO)₄Mo(Ph₂PCl)₂, however, yielded the unchelated bis-aminophosphine (eq. 16)

\[
\begin{align*}
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂PCl} \\
\text{Ph₂PCl}
\end{array} \\
\text{NH₃} & \\
\text{Mo} & \quad \begin{array}{c}
\text{Ph₂PNH₂} \\
\text{Ph₂PNH₂}
\end{array}
\end{align*}
\]

(eq. 16)

Kraihaunzel demonstrated further the reaction of the
coordinated aminophosphine with BF$_3$ etherate to form a diphosphazene ring (eq. 17).\textsuperscript{19}

\begin{equation}
\text{Ph}_2\text{PNH}_2 + 2\text{BF}_3\text{OEt}_2 \rightarrow \text{Ph}_2\text{P} - \text{Mo} - \text{NH} + \text{F}_3\text{BNH}_3
\end{equation}

It seemed, therefore, that aminolysis of trans-$(\text{CO})_4\text{Mo(Ph}_2\text{PCl})_2$ should result in the formation trans-$(\text{CO})_4\text{Mo(Ph}_2\text{PNH}_2)$ which would show no tendency to isomerize. Further, the reaction of the trans-bis-aminophosphine with BF$_3$ etherate, which resulted in the formation of a P-N-P linkage in its reaction with the cis-substrate, could lead to a P-N-P bridged dimer in its reaction with trans-$(\text{CO})_4\text{Mo(Ph}_2\text{PNH}_2)_2$. It also seemed possible that a similar trans-to-cis isomerization could occur resulting in the diphosphazene ring shown in eq. 17.

**Results**

**Aminolysis of trans-$(\text{Ph}_2\text{PCl})_2\text{Mo(CO)}_4$ with NH$_2$R,**

\begin{equation}
\text{Ph}_2\text{PCl} \quad \text{R NH}_2 \rightarrow \text{Ph}_2\text{PN(H)R}
\end{equation}

12 $R=H$

13 $R=\text{Me}$
R=H, CH₃ resulted in the formation of trans-(Ph₂PN(H)R)₂Mo(CO)₄ in good yield (eq 18). The complexes are pale yellow crystalline solids which are stable indefinitely in air. They show the expected single CO stretch in the IR spectrum for the trans-geometry, a single sharp resonance in the ³¹P NMR and they gave satisfactory analyses.

Subsequent reaction of these complexes with boron trifluoride etherate resulted in a fluoride-exchange reaction to give trans-(Ph₂PF)(Ph₂PN(H)R)Mo(CO)₄ complexes (eq. 19).

\[
\begin{align*}
\text{Ph}_2\text{PN(H)R} \quad \text{Mo} \quad + \quad \text{BF}_3 \quad \text{OEt}_2 & \quad \rightarrow \quad \text{Ph}_2\text{PF} \quad + \quad [\text{R(H)N BF}_2] \\
\text{Ph}_2\text{PN(H)R} \quad \text{Ph}_2\text{PN(H)R} & \\
\end{align*}
\]

These complexes have been fully characterized by multinuclear NMR, IR, analysis and one, R=H by an x-ray crystal structure.

From the reaction of trans-(Ph₂PN(H)CH₃)₂Mo(CO)₄ with BF₃ etherate was isolated 900mg (50% by weight) of ether-insoluble material which is tentatively identified as cis-(CO)₄Mo(Ph₂P-N(CH₃)-PPh₂)BF₃ by its ³¹P NMR (s 77.6ppm d₆-acetone) and its IR spectrum ( CO 2010cm⁻¹ s, BF 1070-1090).
Discussion

Aminophosphines are an interesting class of compounds because they contain lone pairs of electrons on adjacent atoms.\(^5^7\) Competition experiments have shown that amines are stronger bases than phosphines but aminophosphines react at phosphorus with Lewis acids such as CH\(_3\)\(^+\), alkyl\(_3\)B, PF\(_5\) and (alkyl)\(_3\)Al. This is thought to be due to N-pπ-P-dπ-dative bonding. Reports of restricted P-N bond rotation, and short P-N bond lengths support this explanation.

With boron Lewis acids, however, the site of quaternization has been shown to depend on the boron substituents.\(^5^9\) BF\(_3\) coordinates F\(_2\)PN(H)CH\(_3\) at nitrogen (eq. 20),

\[
\text{BF}_3 + \text{F}_2\text{PN(CH}_3\text{)}_2 \rightarrow \text{F}_2\text{PN(CH}_3\text{)}_2\text{BF}_3 \quad \text{eq. 20}
\]

\(-78\, ^\circ\text{C}\)

BF\(_3\) coordinates at nitrogen while BH\(_3\) coordinates at phosphorus. These BF\(_3\) N-bonded adducts are unstable above -50 \(^\circ\text{C}\) decomposing by fluoride shift to give aminoboranes and PF\(_3\) (eq. 21).

\[
\text{F}_3\text{BF}_2\text{PN(CH}_3\text{)}_2 \xrightarrow{\text{RT} \ 24\text{hrs}} \ [\text{(CH}_3\text{)}_2\text{NBF}_2\text{]}_2 + \text{PF}_3 \quad \text{eq. 21}
\]

Greenwood\(^5^8\) has also reported a fluoride-shift resulting from the reaction of aminoperfluoromethylphosphines and BX\(_3\) (X=Cl,F). The N-bonded adduct is formed at low temperature but decomposes on warming. Other examples of fluoride-shift involving silylamines\(^6^0\) and aminoboranes are known.\(^5^9\)
In this laboratory the reaction of a coordinated aminophosphine with BF$_3$ has resulted in a fluoride shift to give the mixed fluorophosphine-aminophosphine complexes. The reactions have not been exhaustively studied and the yields are low. The complexes are ether-soluble and can be recrystallized from ether with hexane.

Preliminary data indicates the presence of small amounts of the mixed cis-fluorophosphine-aminophosphine complex cis-(Ph$_2$PN(H)CH$_3$)(PPh$_2$PF)Mo(CO)$_4$ observed by $^{31}$P NMR in the residue of the reaction of the N-methyl complex with BF$_3$. Reaction of this cis-complex with more BF$_3$ may yield the methyl substituted analogue of the diphosphazine complex isolated by Kraihanzel from the reaction of BF$_3$ with cis-(CO)$_4$Mo(Ph$_2$PNH$_2$)$_2$ (eq. 17 page 105).

**IR Spectra**

The trans-stereochemistry of complexes 1-4 is confirmed by the single intense band below 1950 cm$^{-1}$ corresponding to the single CO stretch of Eu symmetry. The position of this single band is a measure of the electron density at the metal which decreases in a logical order (Table 2 page 109). The fluorophosphines are more electronegative than the aminophosphines and the unsubstituted aminophosphine is more electronegative than the N-substituted aminophosphine.

The NH-stretch region, 3500-3300 cm$^{-1}$, of 12 shows a pair of bands corresponding to $A'$ and $A''$ transitions for
C₅ symmetry around nitrogen. This same region shows each band further split to give a total of four bands in the spectrum of cis-(Ph₂PNH₂)₂Mo(CO)₄. This doubling may be related to the proximity of the two ligands in the cis-configuration.

### CO(cm⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 (Ph₂PN(H)CH₃)₂Mo(CO)₄</td>
<td>1896</td>
</tr>
<tr>
<td>12 (Ph₂PNH₂)₂Mo(CO)₄</td>
<td>1903</td>
</tr>
<tr>
<td>15 (Ph₂PN(H)CH₃)(Ph₂PF)Mo(CO)₄</td>
<td>1915</td>
</tr>
<tr>
<td>14 (Ph₂PNH₂)(Ph₂PF)Mo(CO)₄</td>
<td>1916</td>
</tr>
</tbody>
</table>

**Table 2**  
Carbonyl Stretching Frequencies  
For Coordinated Mixed Fluorophosphine Aminophosphine Complexes

There are two moderate bands observed in the spectra of complexes 12 and 14 around 850 and 960 cm⁻¹. Bands reported in this region have been assigned to P-N stretching.²³ The absence of any bands in this region for complexes 13 and 15 casts some doubt on the assignment in this case.

Other tentative assignments include PF-stretching at 770 and 755 cm⁻¹ for 14 and 15, respectively.

**³¹P NMR Spectra**

The large coupling to ¹⁹F and the large downfield shift produced in atoms bonded to fluorine make the ³¹P NMR spectra of complexes 14 and 15 interesting. Prior to the work by the crystallographer the presence of fluorine in the complexes made the ³¹P NMR quite perplexing as...
well. The coordinated fluorophosphine phosphorus of 14 and 15 resonate below 200ppm, show large coupling to fluorine, 800Hz, and approximately 80 Hz coupling to the trans-aminophosphine phosphorus. The aminophosphine phosphorus resonates around 80ppm, at about roughly the same position as observed for the starting complexes. In addition to the 80Hz coupling to the trans-ligand phosphorus, there is a 2 Hz coupling to fluorine.

**Conclusions**

The reaction of coordinated aminophosphines with boron trifluoride etherate resulted in an unexpected, but not unprecedented, fluoride exchange. Reaction of free aminophosphines with BF$_3$ etherate has been reported to lead, via initial coordination of BF$_3$ to nitrogen at low temperature, to fluoride exchange. BH$_3$ has been reported to coordinate initially to the phosphorus of free aminophosphines. In the case of the transition metal coordinated aminophosphine, which is coordinated through phosphorus, BF$_3$ coordination must occur at nitrogen.

The reaction has not been studied in detail. The reported mixed-ligand complexes represent about 50% of the total product mixture. The remainder has not been identified, although it is likely a chelated phosphazaine complex of the type reported by Kraihanzel. If this is the case then the formation of chelate rings is a favorable enough process such that both trans-bis-phosphinous acids
and aminophosphines isomerize to cis-complexes rapidly at room temperature.
EXPERIMENTAL

trans-(Ph₂PNH₃)₂Mo(CO)₄. This procedure is essentially the same as that used by Kraihanzel for the synthesis of the corresponding cis-complex. Ammonia gas, first dried by passing it through a tube packed with ground KOH, was bubbled through a solution containing 5.9 g (9 mmol) trans-(Ph₂PCl)₂Mo(CO)₄ in 80 mL THF at 0°C for 15 min. The solution paled in color and NH₄Cl precipitated. The mixture was filtered and the solvent vacuum-distilled from the filtrate to leave 5.2 g, 93% crude product. This was recrystallized to give a pale yellow crystalline product.

1H NMR δ 7.70 (m) 8H, 7.38 (m) 12H, 3.39 br s 4H; 31P NMR δ 75.6 s; IR ν CO 2014w 1957w 1903s CH₂Cl₂; Anal. Calcd. for C₂₈H₂₄MoN₂O₄P₂ C, 55.10; H, 3.96; N, 4.59. Found: C, 55.39; H, 3.99; N, 4.59.

trans-(Ph₂PN(H)CH₃)₂Mo(CO)₄. Methylamine, dried as above with KOH, was bubbled through a solution containing 2.6 g (4 mmol) trans-(Ph₂PCl)₂Mo(CO)₄ in 20 mL THF for 15 min at 0°C. Care must be taken not to allow the reaction to continue for too long because the amine will condense into the reaction mixture making the subsequent distillation difficult. The amine-hydrochloride was filtered from the solution and the filtrate stripped of solvent by vacuum-distillation. The residue was recrystallized from CH₂Cl₂/hexane and a second crop isolated from the mother liquor for a combined yield of 1.6
trans-(Ph$_2$PNH$_2$)$_2$(Ph$_2$PF)Mo(CO)$_4$. To a stirred solution containing 1.2 g (1.96 mmol) trans-(Ph$_2$PNH$_2$)$_2$Mo(CO)$_4$ in 20 mL THF, was added dropwise 0.610 g (4.3 mmol) BF$_3$OEt$_2$ via syringe. The solution was stirred for an hour during which time it darkened and became cloudy. The solvent was vacuum-distilled to leave a nougat-colored mass. This mass was extracted with 10 mL CH$_2$Cl$_2$, the extract filtered and the solvent removed from the filtrate by distillation. The residue was dissolved in 1.5 mL CH$_2$Cl$_2$ and chromatographed on a 30 mL silica gel column (2 cm ID, eluent, 28% ethylacetate/hexane) The resulting clear yellow column eluate was stripped of solvent by vacuum-distillation to leave a yellow oil. This oil was ground under hexane to give a tan solid, 380mg, (32%), which was dried under vacuum. $^1$H NMR 7.73 (m) 2.90 (br s); $^{31}$P NMR 201.3 doublet of doublets $^1$J$_{PF}$ = 867.5Hz, $^3$J$_{PP}$ = 76.4Hz, 73.5 doublet of doublets $^3$J$_{PP}$=2Hz; $^{19}$F NMR 139.7 (rel. to ext. trifluoroacetic anhydride) $^1$J$_{FP}$ = 867.3Hz. $^3$J$_{FP}$ not observed; IR ν CO 2025w, 1969w, 1916s CH$_2$Cl$_2$; ν PF KBr 770s; Anal. Calcd. for C$_{28}$H$_{22}$FMoN$_2$O$_4$P$_2$: C, 54.83; H, 3.62; N, 2.28. Found: C, 55.14; H, 3.48; N, 2.28. 

The hexane from above was vacuum-distilled to leave a
residue which proved, by phosphorus NMR, to be mostly the desired product. This material was recrystallized from ether/hexane and then crystallized slowly from hot ether/hexane to give small off-white transparent crystals suitable for x-ray crystallography.

\[ \text{trans-(Ph}_2\text{PN(H)CH}_3\text{)(Ph}_2\text{PF)Mo(CO)}_4 \]. To a solution containing 2.6 g (4.2 mmol) trans-(Ph\textsubscript{2}PN(H)CH\textsubscript{3})\textsubscript{2}Mo(CO)\textsubscript{4} in 10 mL CH\textsubscript{2}Cl\textsubscript{2} was added dropwise 4.7 mL 1.78 M BF\textsubscript{3}OEt\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}. There was no immediate change in the appearance of the solution. It became cloudy over the course of an hour. The solvent was vacuum-distilled to leave a gummy solid. To this was added 10 mL Et\textsubscript{2}O which caused the formation of a white solid which was isolated by filtration, 0.9 g (24\% by weight), but never identified. To the filtrate was added small portions of hexane to give a small quantity of a tan solid. This material was column chromatographed as above, the solvent distilled and the residue ground under hexane to give a tan solid (material not weighed!!). \textsuperscript{1}H NMR 7.50 (m), 2.4 (d) \textsuperscript{3}J_{PH} = 11Hz. 2.63 (s br); IR \textsubscript{CO} 2025m 1976m 1930 1918 KBr; \textsubscript{PF} \textsuperscript{31}P NMR 207.2 doublet of doublets \textsuperscript{1}J_{PP} = 859.4Hz \textsuperscript{2}J_{PP} 73.2Hz, 89.4 doublet of doublets \textsuperscript{2}J_{PP} = 2.4Hz; Anal. Calcd. for C\textsubscript{29}H\textsubscript{24}FMoNO\textsubscript{4}P\textsubscript{2}: C, 55.52; H, 3.86; N, 2.23. Found: C, 55.28; H, 3.87; N, 2.26.

\[ [(\text{cpFe(CO)}_2)_2\text{Ph}_2\text{P-PPh}_2][\text{BF}_4]_2 \]. \text{cpFe(CO)}_2\text{I}^{61} and \text{[cpFe(CO)}_2\text{THF}]\text{BF}_4^{43} were synthesized by published methods.
0.304 g (.787 mmol) Ph₂P-P(0)Ph₂ and .261 g (0.777 mmol) were stirred in THF. The solution turned bright orange after about .5 h and then precipitated a bright yellow solid which was filtered and dried to yield .127 g, (18%), [(cpFe(CO)₂)₂Ph₂P-PPh₂][BF₄]₂ as a crude solid. This was recrystallized from methylene chloride/ether. Analysis Calcd. for C₃₈H₃₀B₂F₈Fe₂O₂P₂: C » 50.83; H , 3.37; Found: C , 51.15; H , 3.63

(cpFe(CO)₂Ph₂P-PPh₂)BF₄. 0.521 g (1.55 mmol) [cpFe(CO)₂THF]BF₄ and 0.575 g (1.55 mmol) Ph₂P-PPh₂ were dissolved in 10 mL methylene chloride and stirred for 1.5 h. ³¹P NMR showed the reaction complete at this time. The solvent was distilled and THF was added to the residue which formed a solution. The dropwise addition of ether to this solution caused an oil to form which was trituted with small added amounts of methylene chloride, which caused a solid to form. 400mg (41%) of crude material was isolated and recrystallized from methylene chloride/ether to give a bright yellow solid. Anal. Calcd. for C₃₁H₂₅BF₄FeO₂P₂: C, 58.72; H, 3.97, Found: C, 58.69; H, 4.00

CuCl(Ph₂P-P(0)Ph₂. 1.0 g (2.7 mmol) Ph₂P-P(0)Ph₂ 0.27 g (2.7 mmol) CuCl were stirred together in 10 mL CH₂Cl₂ in a heterogeneous reaction which yielded a solution after a few minutes. The solution was filtered and ether added to the filtrate, which resulted in the precipitation of 0.598
g (46%) CuCl(Ph$_2$P-P(0)Ph$_2$) as a white solid which gave a satisfactory analysis. $^{31}$P NMR $\delta$ 32 (d), $^1J_{pp}$=110Hz, -22 (br. doublet); The IR spectrum is virtually indistinguishable from that of the free ligand from 4000 to 200cm$^{-1}$. Anal. Calcd. for C$_{24}$H$_{20}$ClCuOP$_2$: C, 59.39; H, 4.15, Found: C, 59.00; H, 4.26.

X-ray crystals of [(CuCl)$_2$Ph$_2$P-O-PPh$_2$]$_2$ were prepared as follows: Ether was layered into a solution of CuCl(Ph$_2$P-P(0)Ph$_2$) in CH$_2$Cl$_2$ and the sample allowed to stand undisturbed in the dark. Crystal formation was observed after 24 h. After 4 days the crystals were removed from the tube, the solvent decanted, and the crystals carefully dried under nitrogen. $^{31}$P NMR 101 (br. singlet); IR $\nu$ P-O-P 875cm$^{-1}$.

An independent synthesis of this complex was achieved by the reaction of CuCl(Ph$_2$Cl) in CH$_2$Cl$_2$ with one half equivalent of water in THF. CuCl(Ph$_2$PCl) was extremely unstable to hydrolysis and has not been isolated in pure form.
## Bond Distances and Angles in the Cu₄Cl₄ Core of \([(\text{CuCl})_2(\text{Ph}_2\text{PO} \text{PPh}_2)]_2\)

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<th>Distances</th>
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<td>Cu(1) Cl(1)</td>
<td>2.365(1)</td>
<td>Cu(1) Cl(1) Cu(2) 75.59(4)</td>
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<td>Cu(1) Cl(2)</td>
<td>2.355(1)</td>
<td>Cu(1) Cl(1) Cu'(1) 87.03(5)</td>
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<tr>
<td>Cu(1) Cl'(2)</td>
<td>2.574(2)</td>
<td>Cu(2) Cl(1) Cu'(1) 72.89(4)</td>
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<td>Cu(2) Cl'(2) Cu'(1) 80.21(5)</td>
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<td>Cu(2) Cl(1)</td>
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<td>Cl'(2) Cu(2) Cl(1) 100.84(5)</td>
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<td>Cl'(2) Cu(2) P(2)  141.42(6)</td>
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<td>P(1) O P(2)        124.44(18)</td>
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