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# Complexes of Phosphine Ligands with the Main Transition Elements

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COMPLEXES OF PHOSPHINE LIGANDS WITH

THE MAIN TRANSITION ELEMENTS

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# SECTION I: GENERAL DISCUSSION

In this first section, several general coments will
be made with regard to the phosphorus atom and the
various ligands. While the first portion of this paper
deals in trends and observations on the various phos-
phine types, the second section is very specific.
Part II outlines some of the important complexes formed
by reactions of the ligands with the main transition
metals. The final section is concerned with only one
ligand and one metal. It is a summary of the research
which Dr. W. W. Hess and I have undertaken in an attempt
to form some chromium coordination compounds with 1,2-
bis(diphenylphosphine)ethane.

Phosphorus is the second group Vb element having
a valence shell which is isoelectronic with the valence
shell of nitrogen. It has long been known that ammonia,
as well as many primary, secondary, and tertiary amines,
acts as a ligand forming complexes with the main transi-
tion elements. It then comes as no surprise to find
that the phosphorus analogue of ammonia, phosphine, is
also a ligand.
Phosphine, however, is not the most important of the
phosphorus ligands. It appears that the order of

importance, or at least occurrence is:  tertiary phosphine >
secondary phosphine > primary phosphine > phosphine.
It is probable that this trend is partially due to the
relative stabilities of the phosphine ligands.  The other
factors which enter in will be discussed later.

The chemistry of both nitrogen and phosphorus
involves covalent bonding.  The atoms of both elements
possess lone electron pairs and can act as Lewis bases
in the forming of coordinate covalent bonds.  One may
ask whether or not there is any difference in the chem-
istry of these two elements.  The answer is that a de-
finite difference does exist.  Since the principle
quantum number of nitrogen is two, it only has s and p
orbitals available to accommodate its own five elec-
trons and to take part in bonding.  This means that,
after it has used its three p-orbitals in bonding with
three substituent groups to form     amines, it can
act only as a sigma-donor ligand.  Phosphorus, however,
is not as limited as nitrogen.  Its principle quantum
number is three meaning that it has 3s-, 3p-, and 3d-
orbitals.  The s- and p-orbitals are filled similarly
to those of nitrogen, allowing phosphines to act as
sigma-donors also.  This still leaves phosphorus with
five unused d-orbitals.  These unfilled orbitals give
the phosphorus ligands added versatility since they are
available to accept back-bonding from metals and to

increase the overall conjugation of complexes thereby increasing the stability of the system.

Tertiary phosphines seem to be by far the most prominent and numerous of phosphine ligands. The substituent groups which surround the phosphorus atom vary all the way from the completely saturated systems of the alkyls to the highly conjugated systems of the aryls. As is the case with most new discoveries, the finding that some phosphine compounds made good ligands initiated a full-scale search for many other phosphine compounds. This was of course accomplished by playing the inductive effect against the conjugative effect by varying substituent groups, either from one phosphorus atom to another or on the same phosphorus atom. The importance of having one effect dominant over the other varies from metal to metal. A strongly pi-bonding metal will tend to increase the importance of conjugation.

Tungsten, the heaviest of the group VIa main transition elements, will serve as a good illustration of the relative importance of inductance and conjugation effects in the d-block elements having less than half-filled d-orbitals. Although the relative importance of pi-and sigma-bonding in determining metal-ligand strengths is still not well established, the work of Angelici and Ingemanson with tungsten carbonyls has greatly added to the understanding of such systems.

The tungsten carbonyl work involved a study of the equilibrium $(Am)W(CO)_5 + L \rightleftharpoons (L)W(CO)_5 + Am$ (Where Am represents a given amine and L represents a given phosphine). The entire series of reactions was run first in toluene, and then in other solvents with identical trends being noted for each. When any given phosphine ligand, L, was held constant and the amine group was varied, the values of K increased with amine group as follows: $p\text{-}CH_3OC_6H_4NH_2 <$ $p\text{-}CH_3C_6H_4NH_2 < C_6H_5NH_2 < p\text{-}BrC_6H_4NH_2$. This order also happens to be the order of decreasing basicity. This strongly implies that the strongest Am-W bonds to $W(CO)_5$ are formed by the strongest base. It of course comes as no surprise that this would be true in the amine situation because an amine group has to rely entirely upon its lone electron pair to form the $W\text{-}NH_2R$ bond which is therefore strictly a sigma bond.

When the reverse was tried and Am was held constant while L was varied, the order of decreasing K was this: $P(n\text{-}C_4H_9)_3 \sim P(C_6H_{11})_3 \gtrsim P(OCH_2)_3CC_2H_5 > P(SCH_2)_3CCH_3 \gtrsim$ $P(O\text{-}n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$. It was found that this trend is also the trend in decreasing basicity of the phosphines. It therefore appears that sigma bonding instead of pi-bonding determines the tungsten-phosphine bond strength. Enthalpy and entropy calculations also support this view. This result should be qualified somewhat, however. The complexes $(L)W(CO)_5$ are very favorable

to W-L sigma bonding. This is true because the carbonyl groups are good $\pi$-acceptors and may be rendering the tungsten d-electrons unavailable for pi-bonding. Studies with tungsten complexes having less $\pi$-accepting ligands may show that more $d\pi$-$d\pi$ bonding is possible.[2]

The conclusion made in the above research does seem to be in line with what might logically be deduced. Phosphine ligands must have substantial $d\pi$-$d\pi$ interaction occurring within the phosphorus-metal bond before conjugation effects at this bond become very important. When the metal is tungsten or any other metal with a low number of d-electrons, it is less likely that the electrons will be delocalized in the direction of the phosphorus atom to any great extent. Pi-bonding effects will therefore be minimized for phosphine complexes with metals having a low number of d-electrons.

Platinum lies in the sixth period with tungsten. It will serve well as the opposite situation in which there are nine electrons in its d-orbitals, giving it an almost completely filled subshell. A study has been made of the platinum complexes of the type $(R_nPh_{n-3}P)_2$-$PtCl_2$. Nmr studies of Pt-195 and P-31 coupling constants showed that the sigma-donor ability increases in the order; triethyl- < tripropyl- < tributyl-phosphine. This trend is in line with the fact that the electron-pushing effects of alkyl groups will increase as the

chain length is increased (for the first few carbon atoms).
Coupling constants were found to increase in the order
trialkyl-$<$dialkylphenyl-$<$alkyldiphenylphosphine showing
that the pi-acceptor character of the phosphines increases
as the number of phenyls increases. This may be thought
of as an increasing delocalization of charge which is
brought about by a $p\pi$ -$d\pi$ -$d\pi$ interaction along the
carbon-phosphorus-platinum bond.

These platinum complexes were obtained in both cis-
and trans-planar forms. There is an increased platinum-
phosphorus pi-bonding character in the cis- with respect
to the trans-complex. In the cis case, the platinum
uses $d_{xz}$ and $d_{yz}$ orbitals along with the in-plane $d_{xy}$
pi-bonding orbital. In the trans case, the platinum
can only use the $d_{xz}$ orbital along with the in-plane
orbital. According to this argument, the phosphorus
atoms of the cis compounds have higher electron densities
due to increased back pi-donation from the platinum
d-orbitals.[36]

The platinum study leaves no doubt that conjugative
and, therefore, pi-interactions play extremely influential
roles in the determination of platinum complexes with
phosphines. It should not be inferred from this dis-
cussion that sigma-bonding is no longer important where
phosphine complexes with metals having nearly filled
d-shells are concerned. Sigma-bonding remains important
but its relative effect diminishes.

About as many ditertiary phosphines are known as tertiary phosphines. The two phosphorus atoms may be joined by many types of linkage. They may be joined by saturated or unsaturated carbon chains, they may be ortho to one another on a phenyl ring, or they may be joined by an ether type group. Many polydentate ligands are also known in which other atoms or groups coordinate along with phosphorus. These are oxygen, sulfur, arsenic, selenium, acetylene, olefins, and other groups with coordinating properties similar to those of phosphorus.

Secondary phosphines, though they are not as important as tertiary phosphines, have a characteristic which allows them to form some complexes which tertiary phosphines will not form. In studies with complexes having the general formula $L_2NiX_2$ (where X=halogen, NCS, or CN), it has been found that, when L=tertiary phosphines addition of excess phosphine to the complex results in a trisphosphine complex only if X=NCS or CN. It has been determined that a strong field inducing ligand like cyanide is necessary before five-coordination will occur. Secondary phosphines, however, can form tris complexes with nickel and cobalt even when the anion is bromine or iodine. This higher stability of the tris compounds is attributed to the fact that the tertiary phosphines are much stronger bases therefore decreasing the positive charge on the metal and therefore the

tendency to coordinate a fifth ligand.[58]

An example of a phosphine ligand type in which the phosphorus atom is not directly bonded to the metal is phosphine oxide. In the phosphine oxides, coordination can take place only through the oxygen. An evaluation of some of the data on phosphine oxides will be valuable to the understanding of the nature of the P=O bond. The P-O stretching frequency decreases from the free ligand to the complex. This means that the force constant, $k_{PO}$, will also decrease while the bond order will increase.

Bonding in phosphine oxides involves a coordinate $\overset{+}{P} \rightarrow \overset{-}{O}$ bond and some back-bonding $\overset{-}{P} \leftarrow \overset{+}{O}$ due to overlap of filled oxygen $p\pi$-orbitals with the appropriate empty $d\pi$-orbitals of phosphorus. The back-bonding effect if probably great enough to cause the P-O bond to be essentially a double bond. When complexation occurs, there are three effects upon the P-O bond order. In the first, the oxygen atom being placed near the positive metal ion to which it may also form a covalent bond causes the $\overset{+}{P} \rightarrow \overset{-}{O}$ sigma-bond to be strengthened. This would cause the force constant to increase. Secondly, $p\pi \rightarrow d\pi$ back-bonding will decrease at the same time, causing $k_{PO}$ to decrease. Third, when there are low energy filled d-orbitals in the transition metal, the metal $d\pi$-electrons may drift toward the oxygen $p\pi$-orbitals.

This would displace the $p\pi$-orbitals toward the phosphorus $d\pi$-orbitals and the force constant would increase. Although all of these effects are active to some extent, it appears that the second dominates since $k_{PO}$ decreases experimentally.

The natures of phosphine ligands and the metals to which they coordinate are so varied that no trend which has been mentioned holds for all cases. Section II will attempt to show what these variations are and why some of these occur.

## SECTION II: SPECFIC LIGANDS

This section lists most of the ligand and complex types which are discussed in those articles which appear in the bibliography. Some of the entries state simply that a given ligand has yielded a particular complex with a given metal, while others relate further information. Section II does not have to be read in its entirety to be understood. Each entry is footnoted so that, if further information is desired on any topic, the associated reference can be quickly found. It should be made clear, however, that this section does not contain every phosphine complex or complex type that has been made.

## PART A: MONODENTATE MONOPHOSPHINES

$PH_3$, phosphine: Phosphine has the electron dot formula:     H:P̈:H .
                                                                              H

It has been shown that the P-H bonds mainly involve p-orbitals while the unshared electron pair occupies the s-orbital principally.[72] Phosphine forms complexes with nickel carbonyl.

$P(Ph)_3$, triphenylphosphine:

Ti(IV): Triphenyl phosphine reacts with titanium tetrachloride resulting in a compound which was not

characterized since it is extremely sensitive to moisture. It is assumed, however, to have octahedral coordination and be a unimolecular, non-ionic complex.[15]

Fe(II): Coordination compounds of the type $FeX_2(P(Ph)_3)_2$ have been prepared where X=Cl, Br, or I. Pmr studies show that the bromine complex has a pseudo-tetrahedral structure, however dimeric species are discussed by Naldini.[40,56]

Co(II): This tertiary ligand forms tetrahedral complexes, $Co(PPh_3)_2X_2$, where X=Br or I.[24,70]

Ni(II): The form, $NiX_2(PPh_3)_2$, is general for complexes in which X=Cl, Br, I, NCS, and $NO_3$. Where X=halogen, the complexes have been shown to be tetrahedral by X-ray studies and dipole moment measurements. The X=NCS complex is thought to be trans-planar because of its low dipole moment and diamagnetism. These configurations can be explained as a combination of steric and electronic effects. The field-inducing effect of the halide and triphenylphosphine ligands is too low to form square-planar, diamagnetic compounds and the size of the bulky triphenylphosphine prevents polymerization of the complexes to form octahedral species. The thiocyanato-group is a strong field ligand, on the other hand, which makes the square-planar form desirable.[64,68,70]

The pseudo-pentacoordinated complex $(\pi-C_5H_5)Ni(PPh_3)Ph$ was recently prepared and studied by X-ray techniques. The nickel is bound to one molecule of triphenyl phosphine, one molecule of $\sigma$-phenyl, and one molecule

of the $\gamma$-cyclopentadienyl ligand which is formally a tridentate.[19]

Rh(I): The complex (RhCl(PPh$_3$)$_3$) has activity as a homogeneous hydrogenation catalyst.[20]

Pd(II): (PdX(CO)(PPh$_3$)$_2$)$^+$, (PdX(PPh$_3$)$_3$)$^+$, PdX$_2$(PPh$_3$)$_2$, and (PdH(Ph$_3$P)$_3$)(BPh$_4$) have all been synthesized for X=Cl, Br, and I. They are planar complexes.[20]

Pd(0): The complex (Pd(PhP(o-C$_6$H$_4$·PEt$_2$)$_2$)(PPh$_3$) has been characterized.[14]

W(0), Au(I): PPh$_3$ has been studied in the phosphine-amine equilibrium: (Am)W(CO)$_5$ + PPh$_3$ = (PPh$_3$)W(CO)$_5$ + Am.[2] The layered structure of another tungsten complex, tricarbonyl- -cyclopentadienyltungstiotriphenylphosphine gold, has been deduced by X-ray studies.[59]

Os(0): Crystallographic investigations prove that Os(CO)$_3$(PPh$_3$)$_2$ is trigonal bipyramidal with the carbonyl groups in the molecular plane.[45]

Ir(I): Trans-(IrCl(CO)(PPh$_3$)$_2$) finds use as a homogeneous hydrogenation catalyst and in oxidative addition reactions.[20]

Pt(II): Platinum carbonyls, tetraphenyl borate salts, and halogen complexes containing triphenylphosphine are known.[20,21]

P(Me)$_3$, trimethylphosphine:

Mo(0): Trimethyl phosphine reacts with dibenzene-molybdenum under nitrogen to form a yellow coordination compound too unstable to be characterized.[17]

Ir(III): Octahedral, six-coordinate complexes are formed with Ir(III). These have the form $(IrL_4(P(Me)_3)_2)$ where L=Cl, CO, $CO_2R$, H, $CO_2H$, or combinations thereof. The phosphines occupy trans positions.[26]

$(Et_2N)PF_2$, diethylaminodifluorophosphine:

Ni(0): The complexes of Ni(0) with diethylamino-difluorphosphine are four-coordinated. This ligand either occupies all four positions or just two, the other two being held by carbon monoxide.[61]

$C_6H_4O_2PCl$, 2-chloro-1,3,2-benzodioxaphosphole:

Ni(0): This monodentate tetracoordinates with nickel(0). Nmr studies of the complex formed are compared with studies of the $(Et_2N)PF_2$ complexes to show that, during complexation, the chlorine substituents cause a greater hybridization of phosphorus orbitals than do fluorine substituents.[61]

$(p-Tol)_3P$, tri-p-tolylphosphine:

Fe(II): The complex, $Fe((p-Tol)_3P)_2Br_2$, was prepared and its kinetics of ligand exchange studied by isotopic pmr. The compound has a pseudo-tetrahedral coordination. Second order kinetics were obtained for the ligand exchange indicating an associative mechanism having a five-coordinate transition state. Other dihalobis-(tri-p-tolylphosphine)iron(II) complexes were also formed. It has been found that the lability trend of this ligand is mainly due to an enthalpy of activation effect and is in the order: Fe> Ni> Co.[40]

Co(II): Complexes of the type $((p\text{-Tol})_3P)_2CoX_2$, where X=Br or I, have been formed and found to be tetra-hedral compounds in which the cobalt is in a spin quartet.[70]

Ni(II): The compounds $((p\text{-Tol})_3P)_2NiX_2$, where X=Cl, Br, I, are paramagnetic and have been given pseudo-tetrahedral structures in the solid state. If X=SCN, the complexes are diamagnetic and probably planar. Spectral studies have shown that in benzene solution the chloro- and bromo- compounds have small amounts of dia-magnetic forms. The dipole moments of the compounds increase in the order: X=Cl< Br< I. This trend is attributed to the expansion of the PNiX bond angles.[65]

PEtCy$_2$, dicyclohexylethylphosphine:

Ni(II): The complexes of this ligand are of the type trans-$(Ni(PEtCy_2)_2X_2)$, where X=Cl, Br, or NCS.[58]

PEt$_2$Cy, cyclohexyldiethylphosphine:

Ni(II): The complexes formed by this ligand are very analogous to those of dicyclohexylethylphosphine as might be expected. Square-planar coordination compounds, $(Ni(PEt_2Cy)_2X_2)$, where X=Cl, Br, or NCS are formed.[58]

PEtPh$_2$, diphenylethylphosphine:

Co(II): Stable tris-phosphine, cyano compounds were obtained in the presence of excess phosphine. The equilibrium is of the type $Co(PEtPh_2)_3(CN)_2 = Co(PEtPh_2)_2(CN)_2$. The magnetic moment (2.0 BM) obtained for this compound

is typical of five-coordinate low-spin Co(II) complexes.
It has been found that, in this situation, Co(II) seems to
have a greater tendency to five-coordinate than Ni(II).
This conclusion is based upon the fact that a strong ligand
such as CN is required before Ni(II) will five-coordinate,
whereas a weaker ligand NCS will accomplish the same thing
with Co(II).[7]

Ni(II): The square-planar complex (Ni(PEtPh$_2$)$_2$CN$_2$)
reacts with another mole of diphenylethylphosphine in
solution to give a stable five-coordinated intermediate
as shown by visible spectra. This intermediate is probably
trigonal bipyramidal since the two phosphine ligands are
trans in both cases. The reactions are different for differ-
ent anions and the stable intermediate is not formed. The
CN seems to inhance the metal-phosphine bond. The five-
coordination is not noted either with merely sigma-donat-
ing ligands like amines. It seems to take a $\pi$-donor like
phosphine along with a possible back donation by the
metal.[58]

Complexes of the type (NiX$_2$(PEtPh$_2$)$_2$), where X= Cl,
Br, and I, were prepared and studied by X-ray and other
techniques. The chloride alone was diamagnetic in the
solid state while the bromide and iodide were paramagnetic
having, by analogy with triphenylphosphine complexes, the
tetrahedral structure. In solution, they are similar to
corresponding Ph$_3$P and Ph$_2$-n-Bu-P complexes, being mono-
meric with high dipole moments and similar spectra.

Therefore, even $(NiCl_2(PEtPh_2)_2)$ seems to form some para-magnetic species in solution. The equilibrium between isomers is effected by experimental conditions.

These results lead to the assumption that, in solution, $(NiX_2(PEtPh_2)_2)$ exists as an equilibrium mixture of square-planar and tetrahedral isomers. The isomers of $(NiBr_2(PEtPh_2)_2)$ were the first examples of square-planar-tetrahedral isomerism in complexes of Ni(II) or any metal.[38]

PMePh$_2$, diphenylmethylphosphine:

Pt(II): The coordination compound $(PMePh_2)_2PtCl_2$, exists in both cis- and trans-planar isomers. The Pt-195 and P-31 coupling constants are always greater for the cis compound. The phosphorus chemical shift for the cis compound is upfield from the trans compound. There is an increased Pt-P $\pi$-bonding character in the cis- with respect to the trans-isomer. In the cis case, the Pt uses $d_{xz}$ and $d_{yz}$ orbitals along with the in-plane $d_{xy}$ $\pi$-bonding orbital. In the trans case, the Pt can only use the $d_{xz}$ orbital along with the in-plane orbital. According to this argument, the phosphorus atoms of the cis compounds have higher electron densities due to increased back-donation from the platinum d-orbitals. This compound also dimerizes through chlorine-bridging to give the co-ordination compound, $(MePh_2P)_2Pt_2Cl_4$. The trisphosphine complex can be prepared by adding excess phosphine. This was proven by conductivity and P-31 nmr measurements and isolation of $((MePh_2P)_3PtCl)Cl$.[36]

Diphenylmethylphosphine also combines with platinum in complexes containing the ligands, p-dithiocumate and 3,4,5-trimethoxydithiobenzoate. Since both are bidentate ligands, they form square pyramidal complexes with the single molecule of diphenylmethylphosphine occupying a position above the plane of the two chelate rings of the other ligand. Pmr studies have shown that exchange occurs for the PMePh$_2$ ligand at room temperature even when there is no excess ligand present.[32]

P(C$_3$H$_7$)Ph$_2$, diphenylpropylphosphine:

Ni(II): This ligand forms complexes of the type (NiX$_2$(P(C$_3$H$_7$)Ph$_2$)$_2$), where X=Cl, Br, or I. These compounds are tetrahedral in solid state and monomeric with high dipole moments in solution. In solution, they constitute further examples of square-planar-tetrahedral geometrical isomerism. Both forms have been isolated for (NiBr$_2$-(P(C$_3$H$_7$)Ph$_2$)$_2$) when the propyl group is in both iso and normal forms.[38]

Pt(II): Cis- and trans-planar complexes of platinum having the formula, (P(C$_3$H$_7$)Ph$_2$)$_2$PtCl$_2$ are formed. The cis compound has a higher electron density along the Pt-P bond. The complex will also add another molecule of the ligand to form the trisphosphine complex as shown by the isolation of (((C$_3$H$_7$)Ph$_2$P)$_3$PtCl)BPh$_4$. The chlorine-bridged dimer ((C$_3$H$_7$)Ph$_2$P)$_2$Pt$_2$Cl$_4$ is also formed.[36]

PMe$_2$Ph, dimethylphenylphosphine:

Ir(III): Octahedral, six-coordinated complexes are formed having the formulae (IrL$_4$(PMe$_2$Ph)$_2$), where L=Cl, CO, COOR, COOH, H, or combinations thereof. The phosphines occupy trans positions.[26]
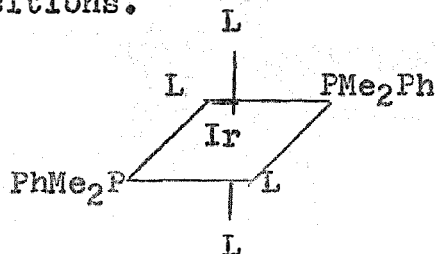


Pt(II): Cis- and Trans-planar bisphosphine compounds are formed with chloride acting as the other ligand. The trisphosphine compound is also formed with one of the two chloride ions in the coordination sphere. The chlorine-bridged dimer, (Ph$_2$MeP)$_2$Pt$_2$Cl$_4$, also has been characterized.[36]

P(C$_3$H$_7$)$_2$Ph, dipropylphenylphosphine:

Pt(II): Like other ligands of its type, dipropyl-phenylphosphine forms compounds cis and trans-((C$_3$H$_7$)$_2$PhP)$_2$-PtCl$_2$ and the trisphosphine. The chloride-bridged dimer has also been isolated.[36]

PBuPh$_2$, butyldiphenylphosphine:

Ni(II): Complexes of the type (Ph$_2$BuP)$_2$NiX$_2$, where X=Cl, Br, and I, are paramagnetic and tetrahedral in the solid state and an equilibrium mixture of paramagnetic tetrahedral and diamagnetic square-planar species exist in benzene solution.[38,67]

Pt(II): Cis- and trans- isomers exist for the complex $(Ph_2BuP)_2PtCl_2$. Addition of excess phosphine leads to the trisphosphine, uni-univalent electrolyte, $((Ph_2BuP)_3PtCl)Cl$. The chlorine-bridged dimer also forms.[36]

PBu$_3$, tributylphosphine:

Cr(III): The ligand reacts with anhydrous $CrCl_3$ in benzene and toluene forming non-electrolytic, binuclear complexes of composition $((Bu_3P)_2CrCl_3)_2$ and structure:[47]
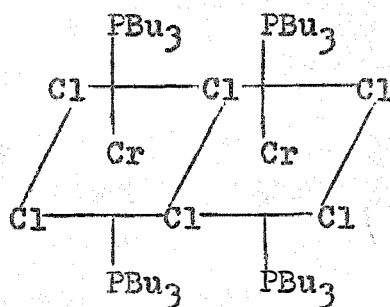


Mn: Tributylphosphine acts as a ligand in the peculiar complex, bis(tetracarbonyl(tributylphosphine)manganese)-mercury, containing a metal-metal-metal bond. The following structure possessing a distorted $D_{4d}$ point symmetry was deduced from infrared spectral studies:[57]
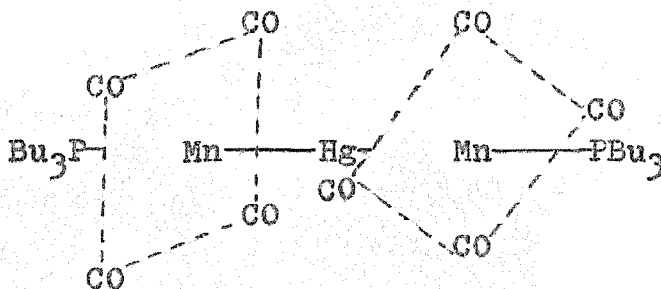


Co(II): The complex $Co(PBu_3)_3(CN)_2$ is stable in solution in the presence of excess phosphine but has not been isolated. This is another example in which the five-coordination in Co(II) is controlled by the anion.[7]

Ni(II): The complex $Ni(PBu_3)_3(CN)_2$ is in an equilibrium with its bisphosphine, four-coordinated counterpart in ethanol. This five-coordination is controlled by the "strong" anion $CN^-$ (or also $NCS^-$).[37]

W(0): The ligand replaces amine groups on tungsten carbonyl to form $(Bu_3P)W)CO)_5$.[2]

Pt(0): The cis- and trans-planar isomers of $(Bu_3P)_2$-$PtCl_2$ form and can react with excess phosphine to give the trisphosphine $((Bu_3P)_3PtCl)Cl$.[36]

$P(C_3H_7)_3$, tripropylphosphine:

Co(II): This ligand forms Co(II) complexes having this equilibrium in solution: $Co(PPr)_3(CN)_2 \rightleftharpoons Co(PPr_3)_2$-$(CN)_2 + PPr_3$. The trisphosphine compound has not been isolated.[7]

Pt(II): The cis- and trans- isomers of the square-planar $(Pr_3P)_2PtCl_2$ have been made and the trisphosphine complex $((Pr_3P)_3PtCl)Cl$ exists in solution.[36]

$PCy_3$, tricyclohexylphosphine:

Cr(II): Tricyclohexylphosphine reacts with $CrCl_2$ and $CrBr_2$ forming coordination compounds of the form $(CrX_2(PCy_3)_2)$. These complexes are unstable and dissociate phosphine to form complex salts which are probably polymeric.[47]

Cr(III): The binuclear, chlorine-bridged dimer of formula $((Cy_3P)_2CrCl_3)_2$ has been characterized along with the monomer $CrBr_3 \cdot 2PCy_3$.[47]

Co(II): The spin-free, tetrahedral complex, $Co(PCy_3)_4$ has been studied.[24]

W(0): The complex $(Cy_3P)W(CO)_5$ has been studied. It was determined that sigma-bonding is responsible for the strength of the W-P bond instead of pi-bonding.[2]

$PBu_2Ph$, dibutylphenylphosphine:

Ni(II): The compounds of type $(PhBu_2P)_2NiX_2$, where X=Cl, Br, or I, are trans-planar and diamagnetic.[67]

$(Cl \cdot CH_2)_3P$, trischloromethylphosphine:

Ni(II): This ligand has substituent groups on the phosphorus which are slightly more electronegative than a phenyl group would be but has no pi-bonding. It was therefore a good ligand to be complexed with Ni(II) to form $((Cl \cdot CH_2)_3P)_2NiX_2$, where X=Cl, Br, and I, in a study of the relative importances of inductance and resonance effects in substituent groups.[67]

$(p-Anis)_3P$, tri-p-methoxyphenylphosphine:

Ni(II): Complexes of the type $((p-Anis)_3P)_2NiX_2$, where X=Cl, Br, and I, are paramagnetic and have been given a pseudo-tetrahedral structure in the solid state. When X=NCS, the complex is probably planar and diamagnetic. Benzene solutions of the chloro- and bromo- complexes have small amounts of diamagnetic species in equilibrium with paramagnetic species. Dipole moments increase in the order X=Cl < Br < I and is attributed to P-Ni-X bond angle expansion.[65]

$(Ph \cdot CH_2)_3P$, tribenzylphosphine:

Ni(II): The complexes of the type $((Ph \cdot CH_2)_3P)NiX_2$, where X=Cl, Br, I, and NCS, were comparable to trialkylphosphines and di-n-butylphenylphosphine for these halogeno- and thiocyanato- complexes. They are monomeric and diamagnetic. They are essentially trans-planar both in solution and solid state. Small amounts of cis- isomer may be present.) This was proven by a comparison of reflectance spectra of the solid to absorption spectra of the liquid.[66]

$(Ph \cdot CH_2)_2PPh$, dibenzylphenylphosphine:

Ni(II): This ligand forms compounds of the type $((Ph \cdot CH_2)_2PPh)_2NiX_2$, where X=Cl, Br, I, and NCS, which are exactly analogous to those formed by another member of its family, tribenzylphosphine.[66]

$(Ph \cdot CH_2)PPh_2$, benzyldiphenylphosphine:

Ni(II): Compounds of the formula $((Ph \cdot CH_2)PPh_2)_2NiX_2$, where X=Cl, Br, I, and NCS, were isolated. The halogeno-complexes can be isolated in both the paramagnetic and diamagnetic isomeric forms. These are interchangeable upon heating or variation of solvent. The thiocyanato complex is of the diamagnetic form. The paramagnetic forms probably contain small amounts of diamagnetic isomer as is deduced from slightly low magnetic susceptibilities along with reflectance spectra. Paramagnetic isomers are tetrahedral (analogous to complexes of triphenylphosphine), while

diamagnetic forms are trans-planar in the solid state (analogous to trialkylphosphine complexes). For benzene solutions of the para-diamagnetic equilibria, the relative percentage of paramagnetic isomer increases in the order $Cl <$ $Br < I$. The equilibria are rapid.[66]

$CH_2:CH \cdot CH_2 \cdot PPh_2$, allyldiphenylphosphine:

Ni(II): The coordination compounds $(CH_2:CH \cdot CH_2 \cdot PPh_2)_2$-$NiX_2$, where $X=Cl$, $Br$, and $I$, were studied. Isomeric solids were diamagnetic only. The para-diamagnetic equilibrium exists in solution in the order of increasing paramagnetic form $Cl < Br < I$.[66]

$P(i-Pr)Ph_2$, diphenylisopropylphosphine:

Ni(II): Complexes $((i-Pr)Ph_2P)_2NiX_2$, where $X=Cl$, $Br$, $I$, exhibit square-planar-tetrahedral isomerism. For $X=Br$, both forms have been isolated in the solid state.[66]

$(m-Tol)_3P$, tri-m-tolyl-phosphine:

Co(II): The complexes of form $((m-Tol)_3P)_2Co$-$X_2$, where $X=Br$ or $I$, are tetrahedral with cobalt in a spin quartet.[70]

Ni(II): The nickel compounds are analogous to the cobalt complexes except that the nickel is in a spin triplet.[70]

$Ph_2PH$, diphenylphosphine:

Co(II): Diphenylphosphine unites with $CoBr_2$ to form three different compounds. The first is the $dsp^3$-

hybrid $((Ph_2PH)_3CoBr_2)_7$ which has a trigonal-bipyramidal structure. The second is $((Ph_2PH)_3CoBr)Br$ which is a uni-univalent electrolyte having a tetrahedral configuration. The third is $((Ph_2PH)_4CoBr)_2Br_2$. This complex is a uni-divalent electrolyte having the bromine-bridged structure:[50]

$$((Ph_2PH)_4Co \underset{Br}{\overset{Br}{\diamond}} Co(HPPh_2)_4)Br_2$$
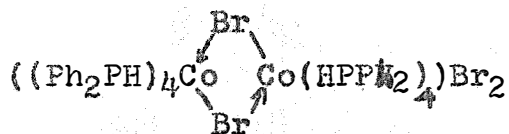
Ni(II): The ligand reacts with Ni-$Br_2$ in the following manner: $NiBr_2 + 4Ph_2PH \quad ((Ph_2P)_2Ni(HPPh_2)_2) + 2HBr$. The complex is square-planar.[50]

Cu(I): Copper (I) halides of the following structures have been obtained: $(Ph_2PHCu\cdot X)_4$, $((Ph_2PH)_2Cu\cdot X)_2$, $(Ph_2PH)_3Cu_2Cl_2$, and $(Ph_2PH)_3Cu\cdot X$.[1,50]

Pd(II): Reactions of the ligand with $PdCl_2$ result in the chlorine bridged dimer:[50]

$$Ph_2PH \quad Cl \quad PPh_2$$
$$Pd \quad Pd$$
$$Ph_2P \quad Cl \quad PHPh_2$$
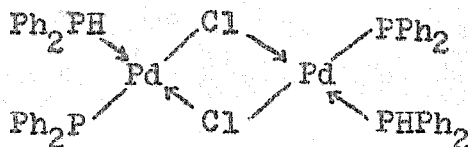
$P(OCH_2)_3CC_2H_5$:

W(0): This ligand forms complexes of the form (ligand)$W(CO)_5$ with tungsten carbonyl.[2]

$P(SCH_2)_3CCH_3$:

W(0): This ligand displaces an amine group from (amine)$W(CO)_5$ giving (ligand)$W(CO)_5$.

P(O-n-Bu)$_3$, tri-n-butoxyphosphine:

W(0): This ligand, along with others mentioned here, was used to displace an amine group of a tungsten carbonyl to form (ligand)W(CO)$_5$. This was done as part of an equilibrium study designed to determine the type of bonding in the W-P bond. It is mostly sigma-type bonding since the value of the equlibrium constant for the various phosphine ligands tried were in direct proportion to the basicities of those ligands.[2]

P(OPh)$_3$, triphenoxyphosphine:

Mn: This ligand, like tributylphosphine, whose Mn-complex structure has previously been shown, forms the complex bis(tetracarbonyl(triphenoxyphosphine)manganese)mercury containing a Mn-Hg-Mn bond.[57]

W(0): The complex (P(OPh)$_3$)W(CO)$_5$ was prepared and used in the study of the W-P bond.[2]

P(Ph)(C≡C-CH$_3$)$_2$, bis(1-propynyl)phenylphosphine:

Rh(I): This ligand reacts with the rhodium dicarbonyl chloride dimer, (Rh(CO)$_2$Cl)$_2$ to form trans-Rh(CO)Cl)ligand)$_2$. This complex is an undissociated monomer in solution and is a squareplanar solid. Infrared spectra have shown that the triple bond does not coordinate since the carbon-carbon multiple bond stretching frequencies are the same for the complex as for the free ligand.[55]

$P(C_{10}H_9Fe)_3$, tris(ferrocenyl)phosphine:

Rh(I): The first transition metal complex of this unusual ligand was recently prepared. It is Rh(CO)-Cl$((C_{10}H_9Fe)_3P)_2$. The infrared spectrum of this compound does not show the expected Rh-Cl stretching frequency but it is believed possible that the ferrocenyl groups are arranged in such a manner as to suppress it.[55]

$Ph_2PC=CHPh$, $\beta$-styryldiphenylphosphine:

Rh(I): This ligand forms the square-planar complex Rh(CO)Cl(ligand)$_2$ for both its cis- and trans- forms. Attempts at coordinating the double bond have been inconclusive.[55]

$SiH_3PH_2$, monosilylphosphine; $(SiH_3)_2PH$, disilyl-phosphine; $(SiH_3)_3P$, trisilylphosphine:
Although no complexes have been formed as yet using these compounds as ligands, it seems probable that they will find such a use in the near future.[31,34]

$PEt_3$, triethylphosphine:

Ti(IV): The ligand reacts with $TiCl_4$ to give an unstable compound which could not be characterized. It is assumed to have octahedral coordination.[15]

Cr(II): $CrCl_2$ and $CrBr_2$ react to form $(CrX_2(PEt_3)_2)$, which may be polymeric.[47]

Cr(III): Anhydrous $CrCl_3$ reacts with the ligand to form the chlorine-bridged dimer $((Et_3P)_2CrCl_3)_2$. Reaction with $CrBr_3$, however, results in $CrBr_3 \cdot 2PEt_3)_3$-$(CN)_2 \rightleftarrows Co(PEt_3)_2(CN)_2$ exists for the cyano complex of this ligand with cobalt. The complex $(Co(mesityl)_2(PEt_3)_2)$ has also been studied.[16]

Ni(II): The complexes of type $NiX_2(ligand)_2$ has been prepared and are square-planar when X=halogen. The complex in which X=CN exhibits a four-coordinate-five-coordinate equilibrium with its trisphosphine counterpart.[37,64]

Ni(III): Dipole moment measurements confirm the structure of $(NiBr_3(PEt_3)_2)$ to be square pyramidal with the two phosphines trans to each other and one bromide at the apex.[51]

Pd(II): Triethylphosphine forms the cations $(PdX(CO)(PEt_3)_2)^+$ and $(PdX(Et_3P)_3)^+$, where X=Cl, Br, I, or H. It also forms tetraphenyl borate and tetra fluoroborates.[20]

Pt(II): The complexes of the ligand with platinum are similar to those of palladium.[20,21]

$PEt_2Ph$, diethylphenylphosphine:

Fe(II): The reactions of Grignard reagent or lithium compound of a complex containing this ligand are: $(FeCl_2(PEt_2Ph)_4)+2MgGrR \rightarrow (FeR_2(PEt_2Ph)_2)+2MgClBr+2PEt_2Ph$ where R=mesityl, 2-biphenyl, 2-methyl-1-naphthyl and

pentachlorophenyl.[16]

Co(II):  (CoBr$_2$(PEt$_2$Ph)$_2$) undergoes reactions with organometallic reagents which are analogous to those for the iron (II) complex mentioned above.[16] The tris-phosphine, Co(PEt$_2$Ph)$_3$(CN)$_2$ has been isolated. It has a magnetic moment of 2.0BM which is typical of five-coordinated low-spin Co(II) complexes.[7]

Ni(II):  Coordination compounds with formula Ni(PEt$_2$Ph)$_2$X$_2$, where X=NCO and CN form, and the cyano complex forms the trisphosphine complex in solution with excess phosphine. This five-coordinated intermediate is probably trigonal bipyramidal since the original two phosphines are trans in both cases.[58]

Ru(II):  The triclinic crystals of tri-$\mu$-chloro-hexakis(diethylphenylphosphine)diruthenium(II)trichloro-tris(diethylphenylphosphine)ruthenate(II) are shown by X-ray to contain units having two atoms of approximately octahedrally coordinated ruthenium bridged by three chlorine atoms.[60]

## PART B:  DIPHOSPHINES WHICH ARE NOT JOINED BY AN AROMATIC RING (AND RELATED POLYDENTATES)

Et$_2$PC$_2$H$_4$SEt, 2-diethylphosphinoethyl ethyl sulfide:

Ni(II):  This ligand acts as a bidentate in almost all complexes of the form Ni(ligand)$_2$X$_2$, where X=Br, I, Cl, NCS, and ClO$_4$ or combinations of these. Most

of these complexes are 5-coordinated with square pyramidal
configurations. The thiocyanato complex, however, appears
as two isomers, which appear to be a diamagnetic, four-
coordinated, square-planar species in which the ligand
is a monodentate bonding at phosphorus:
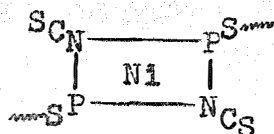


and a paramagnetic, octahedral, six-coordinated species
in which the ligand is a bidentate:
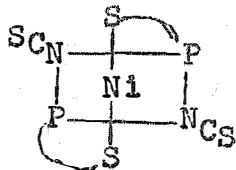


The second isomer shows tetrahedral distortions from the
regular $O_h$ symmetry.[53]

$C_2H_4(PEt_2)_2$, 1,2-bis(diethylphosphino)ethane:

Ti(IV): TiCl₄ reacts with this ligand to form a
presumably octahedrally coordinated complex too sen-
sitive to moisture to be characterized.[15]

Co(II): Co(ligand)$_2$I$_2$ has one unpaired electron
and is uni-univalent in nitrobenzene. It is, therefore,
probably five-coordinated in solution and octahedral
in the solid state.[3]

Co(III): Co(ligand)$_2$X$_2$)X, where X=Cl, Br, and I,
are all uni-univalent in nitrobenzene. They are all
diamagnetic or slightly paramagnetic indicating octahedral
configuration, all electrons being paired. The halogen

atoms may occupy the trans positions.[3]

Ni(0): Nickel carbonyl can be substituted by only one mole of ligand to give $(Et_2PCh_2CH_2PEt_2)N(CO)_2$.[12]

Ni(II): Nickel(II) compounds involving this ligand are square-planar and diamagnetic.[3]

Ni(III): $Ni(ligand)Br_3$ is an octahedral, polymeric solid.[3]

Pd(II): $Pd(ligand)Cl_2$ is a monomer.[3]

Cu(I) and Ag(I): These metal cations form complexes which are conducting in nitrobenzene. They are four-coordinated.[3]

Au(I): Gold differs from the other coinage metals in that it is reluctant to attain four-coordination. Instead, it forms the linear, two-coordinated dimer $IAu(ligand)AuI$. This complex can be oxidized to give $I_3Au(ligand)AuI_3$, a dimer containing two square-planar, 4-coordinated gold atoms.[3]

$C_2H_4(PMe_2)_2$, 1,2-bis(dimethylphosphino)ethane: Tertiary phosphines can stabilize low-valent because of their capacity to form $\pi$-bonds to transition metals. Of the first transition series, only titanium(0) and manganese(0) failed to form complexes which were thermally stable. Cu(0) gave indefinite results. The complexes were prepared by reduction in THF with sodium naphthalenide. The compounds are thermally stable but very sensitive to air oxidation.[18]

Ti(IV): The complex of $TiCl_4$ with this ligand is extremely sensitive to moisture but it probably has an octahedral coordination.[15]

V(O), Cr(O), Mo(O), W(O); The complexes of this type (metal(ligand)$_3$) are octahedral, $d^6$-complexes. Oxidation in air is fast and in the order $V > Cr > Mo >> W$.[17,18]

Fe(O): The four-coordinated, d8-iron(O) complex, is diamagnetic and planar. There may be some metal-metal interactions since the complex is a harder, higher melter than the corresponding species of Co(O) and Ni(O).[18]

Co(O): (Co(ligand)$_2$) is tetrahedral since it is isomorphous with the corresponding nickel complex.[18]

Ni(O), Ni(II), Pd(O), Pd(II): The ligand gives thermally stable, airsensitive, four-coordinated compounds by reduction of the corresponding Ni(II) and Pd(II) complexes with $NaBH_4$.[14]

Rh(I): Although Rh(dpe)$_2$)Cl, where dpe=1,2-bis-(diphenylphosphino)ethane, is inactive toward hydrogen and carbon monoxide under ambient conditions, the analogue with 1,2-bis(dimethylphosphino)ethane is reactive due to the fact that it is less electronegative than dpe, thereby giving the metal atom a higher electron density and encouraging oxidation. The analogue reacts with hydrogen halides to form additional compounds.[11]

Ru(II), Os(II): Complexes of this ligand with these two cations were the first examples of complexes

having both an organic group and a hydrogen atom attached by sigma-bonds to the metal. Formulae are of the types cis-(MR$_2$(ligand)$_2$) and cis- and trans- (MXR(ligand)$_2$), where M=Ru, Os; X=Cl, Br, I, SCN, or H; R=alkyl or aryl.[25]

C$_2$44(PPh$_2$)$_2$, 1,2-bis(dipenylphosphino)ethane(=dpe):

Cr: Dpe would not completely replace CO groups in chromium carbonyl. Two or four CO molecules remained attached to the metal.[17]

Co(II): CodpeX2 compounds, where X=Cl, Br, I, were shown to have pseudo-tetrahedral configurations by comparing their optical electronic spectra and magnetic moments with those of the already characterized pseudo-tetrahedral cobalt(II) phosphine complexes. The magnetic moments increase in the order expected: Cl<Br<I. Additional dpe results in Co(dpe)$_2$X$_2$. Epr spectra along with observations on similar compounds of the type (Co(dpe)$_2$I$^+$)(Y$^-$), where Y is a non coordinating anion like perchlorate or tetraphenylborate. The bonds are similar to those for Co(dpe)$_2$X2 but not identical. This suggests that a penta-coordinated species with the other halogen occupying a sixth coordinated position or a tetragonal hexa-coordinated structure with one Co-X bond short and the other long.[35,41]

Ni(0): The ligand forms Ni(CO)$_2$ dpe and is able to displace all of the carbonyl to yield Ni(dpe)$_2$ which is thermally stable but air-sensitive.[13,14]

Ni(II): Ni(dpe)$X_2$ coordination compounds, where X=Cl, Br, CN, and I, are square-planar on the basis of visible spectra and nmr results, showing them to be diamagnetic in solid state and in solution.

The yellow Ni(dpe)$_2X_2$, where X=Cl, Br, and I, seems to undergo a coordination change from the solid to the red solution. An octahedral coordination is postulated for the solid with dissolution giving dissociation.

$$Ni(dpe)_2X_2 \rightleftharpoons Ni(dpe)X + dpe$$
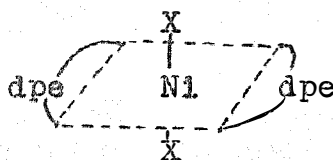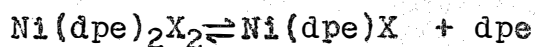


The strong anion, CN, causes the formation of Ni(dpe)$_2$(CN)$_2$, a trigonal bipyramidal, five-coordinated complex in which one dpe molecule acts as a bidentate and the other as a monodentate. A dimer is also formed having the form:[23,43]

$$(CN)_2(dpe)Ni(dpe)Ni(dpe)(CN)_2$$

Ni(III): The dark brown Ni(dpe)Br$_3$ has been isolated.[43]

Mo(0): The diamagnetic compound Mo(dpe)$_3$ is prepared by reaction of dpe with dibenzene-molybdenum. The compound air-oxidizes quickly.[17]

Pd(0): Two molecules of dpe chelate to form a four-coordinated complex. The ligand also forms a mixed diphosphine complex with o-phenylenebisdiethylphosphine.[14]

Pd(II): The dinitrate, (Pd(dpe)$_2$)(NO$_3$)$_2$ has been isolated, along with its dibromo analogue.[14]

Ru(II), Os(II): Formulae for these complexes are
cis-($MR_2dpe_2$) and cis- and trans-($MXRdpe_2$), where M=Ru,Os;
X=Cl, Br, I, SCN, or H; R= alkyl or aryl.[25]

Ir(I): The compounds ($Ir(dpe)_2$)Cl and ($Ir(dpe)_2$)$BF_4$
form adducts, incorporating CO, $PF_3$,$O_2$,$H_2$,$D_2$, $NO_2$, HCl,
HBr, and $SO_2$ into the coordination sphere to become five-
coordinated. This "cationic" coordination compound is in
accord with the concept that coordinately unsaturated and
low-valent metal complexes act as bases toward even such
a weak acid as the hydrogen molecule.[9]

Me·C($CH_2$·$PPh_2$)$_3$, 1,1,1-tris(diphenylphosphinomethyl)-
ethane:

Ni(0); Pd(●): Isomeric configurations of the tri-
phosphine-triphosphine complexes M(ligand)$_2$, where M=Ni or Pd,
are designated $\alpha$ and $\beta$. The two isomers readily convert,
and this new type of isomerism is one in which the only
difference lies in the number of points of attachment of
the potentially tridentate ligand. These possibilities
exist:

(A) ... (tetrahedral)    (B) ... (tetrahedral)

(C) ...    (D) ... (octahedral)
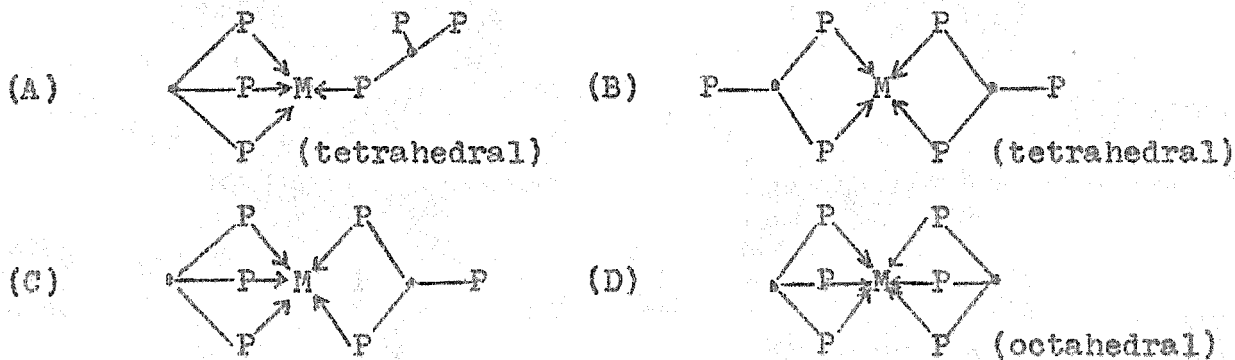
The $\alpha$-isomer has a zero dipole moment and therefore very
high symmetry. The related tetrahedral complexes, e.g.

M(dpe)$_2$, have definite dipole moments of 1-2 D, yet greater symmetry than A, B, or C. The  -configuration is , therefore, D. It is surprising to see Ni(0) and Pd(0) accommodating six donor atoms giving an effective atomic number of four beyond the next inert gas. The ready conversion of these to the more stable, lower-coordination number of 4 is in accord with the expectation that the sixth and possibly fifth phosphorus atoms' binding energy to the zerovalent metal is small.

The expected  -configuration is B since it would show the greatest energy barrier between the two configurations, accounting for the isolation of the two in pure form.[14]

$CH_2(PPh_2)_2$, bisdiphenylphosphinomethane:

Ni(II): The symmetrical Ni(ligand)$_2$X$_2$ complexes have been isolated for X=Cl, Br, and I. These compounds probably are square-planar with the ligand acting as a monodentate. The only complex of Ni(II) in which this ligand acts as a bidentate is Ni(ligand)CO$_2$.[14]

Ru(II); Os(II): Several octahedral, sigma-bonded organo- and hydrido- complexes with this ligand are known.[25]

$C_3H_6(PPh_2)_2$, 1,3-bis(diphenylphosphino)propane:

Co(II): Complexes of the form Co(ligand)X$_2$, where X=Cl, Br, and I, have pseudo-tetrahedral configurations with magnetic moments increasing Cl Br I. If X=CN or NCS, the complexes are dimers having the formulae (Co(ligand)$_{1.5}$X$_2$)$_2$.[7,41]

Ni(II): The complexes Ni(ligand)$X_2$, where X=Cl, Br, and I, exhibit a square-planar-tetrahedral equilibrium in solution. When X=CN, the complexes formed may be five-coordinated monomers and dimers.[23,43]

$(CH_2)_4$-$(PPh_2)_2$, 1,4-bis(diphenylphosphino)butane:

Co(II): This ligand forms Co(ligand)$X_2$ complexes, where X=Br or NCS. They are both probably pserdo-tetrahedral. The dimers of the type (Co(ligand)$_{1.5}X_2$)$_2$ form for X=NCS or CN.[7,33]

Ni(II): Ni(ligand)$Br_2$ is pseudo-tetrahedral with strong distortions of its $T_d$ structure. The thiocyanato analogue is diamagnetic and square-planar. All thiocyanate compounds of nickel with phosphines are planar, even if the corresponding halogen compounds are pseudo-tetrahedral. This may be due to the high nitrogen donor power of the NCS group which is capable of inducing a singlet ground state in all cases.[33] The cyano complexes are dimers, except for the square-planar Ni(ligand)$_2$(CN)$_2$.[23]

$(CH_2)_5$-$(PPh_2)_2$, 1,5-bis(diphenylphosphino)pentane:

Co(II); Ni(II): For M(ligand)$X_2$, X=Br, if M=Co and X=Br,or I, if M=Ni. All of these complexes are pseudo-tetrahedral.[33]

$Ph_2P$-$(CH_2)_2$-O-$(CH_2)_2$-$PPh_2$, bis(2-diphenylphosphino-ethyl)oxide:

Co(II); Ni(II): All complexes Co(ligand)$X_2$, where X=Cl, Br, I, or NCS, are pseudo tetrahedral. The complexes

of nickel are exactly analogous, except that the thio-
cyanate is square-planar. All of these compounds are
monomers and similarities between crystal field spectra
of this ligand and $(PC_nP)$ compounds show that the oxygen
atom is consistently uncoordinated.[33]

$C_3H_6-(PCy_2)_2$, 1,3-bis(dicyclohexylphosphino)propane;
$C_4H_8-(PCy_2)_2$, 1,4-bis(dicyclohexylphosphino)butane; and
$C_5H_{10}-(PCy_2)_2$, 1,5-bis(dicyclohexylphosphino)pentane:

Fe(II); Co(II); Ni(II): These three diphosphines
form compounds of the general composition $((ligand)MX_2)$,
where M=Ni, Co, Fe, and X=Cl, Br, I, and $NO_3$. The cobalt
complexes are tetrahedral, while planar configurations are
found for those of nickel.

Cu(II): Copper forms bromine complexes with the
first and third ligands of this series.[48]

$F_2$⌐──┬─PPh₂
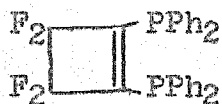
$F_2$└──┴─PPh₂, 1,2-bis(diphenylphosphino)tetrafluoro-
cyclobutene:

Fe(II): This unusual ligand reacts with $Fe_2(CO)_9$
to form $(ligand)(Fe(CO)_3)_2$. The double bond of the ligand
coordinates one iron atom, while the two phosphine groups
coordinate the other. This ligand also acts as a bidentate
with certain metal halides.[8]

$Ph_2PC\equiv CPPh_2$, bis(diphenylphosphino)acetylene(=DPPA):
Cu(I): Complexes $(CuX)_2(DPPA)_3$ (X=Cl, Br, I, $NO_3$,
NCS, $BH_4$) are binuclear with DPPA-bridging. The local sym-

metry around each metal atom is $C_{3v}$ and the structure is:[8]
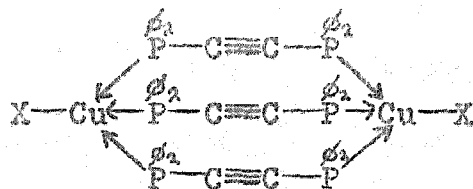


Ag(I); Au(I); Au(III); Pd(II); Pt(II); Pt(IV);
Rh(III); Ir(III); Ir(I): The halides of all of these
metals form DPPA-bridged complexes of varying types. Raman
spectra of DPPA show a $C \equiv C$ stretching frequency which is
much lower than normal. It is so low, in fact, that the
shift cannot be explained solely in terms of the electro-
negative $PPh_2$ group's inductive effect. The change is
at least partially due to a drift of pi-electron density
away from the actylene bond and toward the empty $d\pi$ phos-
phorus orbitals. This weakens the triple bond, but streng-
thens the adjacent P-C bond. The structure of DPPA is
linear with $p\pi$-$d\pi$ overlap:[8]
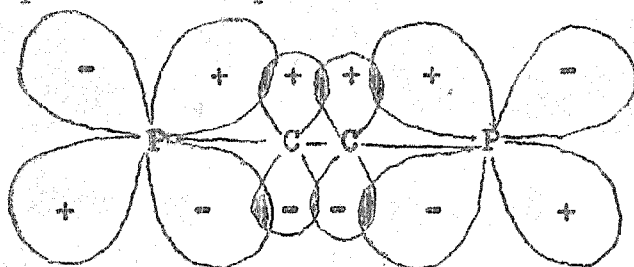


Cis-$C_2H_2$-$(PPh_2)_2$, cis-1,2-bis(diphenylphosphino)-
ethylene:

Rh(I): Ionic complexes, (Rh(ligand)$_2$)X have been
isolated. Dimers also form of the type (Rh(ligand)$_2$)-
(Rh(CO)$_2$X$_2$), where X=Br or Cl.[55]

Trans-$C_2H_2$-$(PPh_2)_2$, trans-1,2,bis(diphenylphosphino)-
ethylene:

Rh(I):  When the rhodium carbonyl chloride dimer, $(Rh(CO)_2Cl)_2$, reacts, polymeric complexes having the formula $(Rh(CO)Cl(ligand)_m$ are obtained.[55]

$Ph_2P-CH_2-O-CH_2-PPh_2$, bis(diphenylphosphinomethyl)ether:

Rh(I):  The ionic complex, $(Rh(ligand)_2)(BF_4)$, shows increased association as solution concentrations are increased.[55]

$Ph_2P(CH_2)_3S(CH_2)_3S(CH_2)_3PPh_2$, 1,3-bis(diphenylphosphinopropylthio)propane:  This tetradentate ligand forms five-coordinate $(M(ligand)X)ClO_4$ complexes, where M=Ni, Pd, Pt).  All of these compounds are diamagnetic, while the analogous five-coordinate series of complexes $(Co(ligand)_2X)Y$ (where X=Cl, Br, I, and $Y=BPh_4$; X=Cl and $Y=ClO_4$)are paramagnetic with one unpaired electron.

Co(II):  The above mentioned cobalt coordination compounds have a square pyramidal structure.

Ni(II):  While the four-coordinate nickel compounds are square-planar, the five-coordinate ones are trigonal bipyramidal.  The most probable structures for these complexes are the following:



or
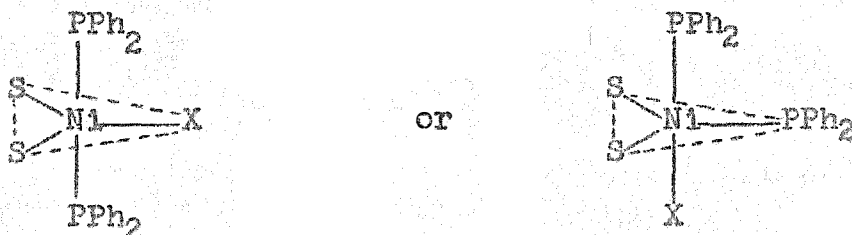
Pd(II); Pt(II): These metals give five-coordinate complexes which are square pyramidal. The possible structures are:[29]
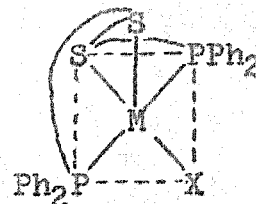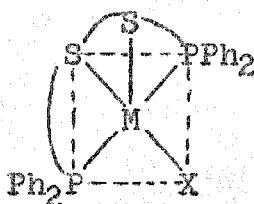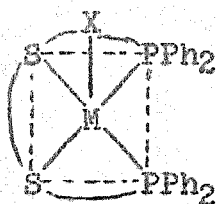


$Ph_2PC_6H_4 \cdot CH:CH \cdot Me$, diphenyl-2-(prop-cis-1-enyl)-phenylphosphine:

Mo(0): The structure of tetracarbonyl(diphenyl-2-(prop-cis-1-enyl)phenylphosphine)molybdenum(0) has been determined by X-ray methods. The configuration is square bipyramidal with the ligand chelating through phosphorus and the olefin bond in the molecular plane.

Cr; W: Similar compounds have been obtained with these metals.[54]

PART C: DIPHOSPHINES IN WHICH THE PHOSPHORUS ATOMS OCCUPY POSITIONS ORTHO TO ONE ANOTHER ON A BENZENE RING (AND RELATED POLYDENTATES)



o-allylphenyldiphenylphosphine(=AP):
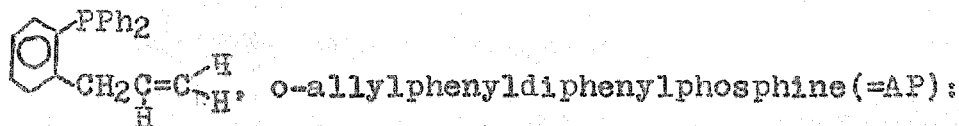
Cu(I): In complexes $(CuX \cdot AP)_2$, where X=Cl, Br, or I, nmr studies show that this ligand acts as a bidentate:[5]
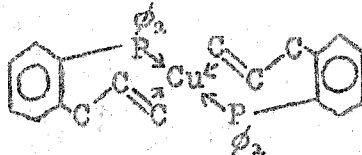
Ag(I): The ligand acts as a monodentate in the silver complexes AgX(AP)$_2$ (where X=Cl, Br, and I), AgI(AP), and AgNO$_3$(AP).[5]

Pd(II), Pt(II): In all of these complexes, the ligand is a bidentate. They take the form MX$_2$(AP) (if M=Pd, X=Cl, Br, orI; if M=Pt, X=Cl, Br, I, and NCS). AP has a stronger tendency to form chelate complexes with Pt(II) than Pd(II) probably because of a weaker metal-olefin bond for Pd(II).[6]
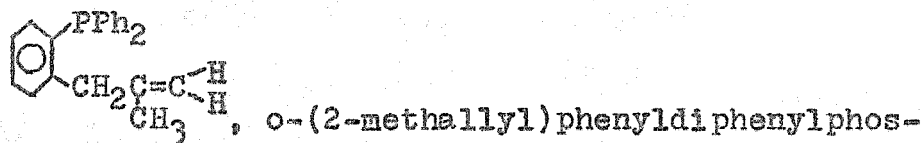


o-(2-methallyl)phenyldiphenylphosphine(=MP):

Cu(I): The compound (CuI·MP)$_2$ is analogous to the cooresponding complex involving AP.[5]

Diphenyl(o-methylthiophenyl)phosphine; bis(o-methylthiophenyl)phenylphosphine; tris(o-methylthiophenyl)-phosphine; tris(o-diphenylphosphinophenyl)phosphine: The structures of these ligands are, respectively:
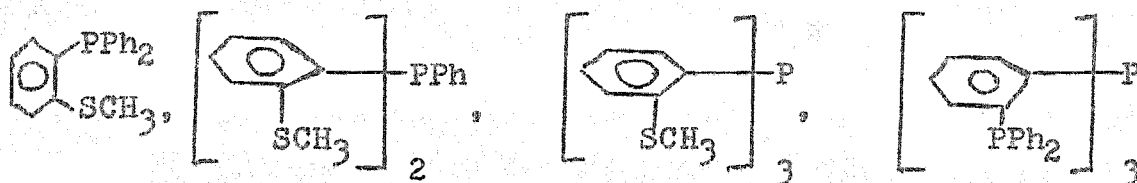


Ni(II), Pd(II): These polydentate ligands showed very little tendency to form five-coordinate Pd(II) complexes, although they readily form them for Ni(II). This goes with the observed trend that, as atomic weight increases

for a given electronic configuration and oxidation state, the tendency to form five-coordinate complexes decreases. The thioether containing ligands have less tendency to form five-coordinate complexes than the polyphosphine ligands, since thioethers are less easily polarized and form less covalent bonds with Pd(II) than phosphorus forms. Steric factors may also enter in to aid five-coordination with the rigid tetradentates like P(o-PhPPh$_2$)$_3$.[28,30]

o-C$_6$H$_4$(PEt$_2$)$_2$, o-phenylenebis(diethylphosphine):

Ti(IV):  The ligand combines with TiCl$_4$ to give a compound too unstable to be characterized.

Ni(0):  This ligand reacts with nickel carbonyl to give the complex:

(I)

Complex I has fair thermal stability and decomposes only slowly in air.  The ligand also replaces carbon monoxide from the complex I to give type II:

(II)

Reactions of type I compounds with halogens results in replacement of the carbon monoxide to give planar, dia-magnetic halogen compounds of high stability.[12,13]

Mo(0):  Three equivalents of ligand react with dibenzene-molybdenum to form Mo(ligand)$_3$.[17]

Pd(0):  Several mixed ligand complexes involving this ligand and o-phenylenebis(diethyl)phosphine have been produced Some Ni(II) and Pd(II) intermediates were also formed.[14]

o-C₆H₄(PMe₂)₂, o-phenylenebis(dimethylphosphine):

Ni(0):   This ligand will replace two of the carbon monoxide on nickel carbonyl.[13]

o-C₆H₄(PPh₂)₂, o-phenylenebis(diphenylphosphine):

Ni(0):   Complexes exactly analogous to those formed by reaction of o-phenylenebis(diethylphosphine) with nickel carbonyl have been isolated.[13]

PhP(o-C₆H₄PEt₂)₂, bis-(o-diethylphosphinophenyl)-phenylphosphine:

Pd(0); Pd(II):   The mixed phosphine complex (Pd-(PhP(o-C₆H₄·PEt₂)₂(PPh₃)) has been isolated.  A Pd(II) complex was an intermediate in its production.[14]
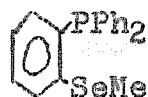

SeMe, diphenyl(o-methylselenophenyl)phosphine(=SeP):

Ni(II):   The complex (Ni(SeP)₂Br)ClO₄ has been isolated.[30]


AsPh₂, diphenyl(o-diphenylarsinophenyl)phosphine (=AsP):

Ni(II):   AsP forms many complexes with this metal having four-, five-, and six-coordination.  The four-coordinate type is (Ni(AsP)X₂, where X=Cl, Br, I, or SCN. Infrared shows SCN groups to be bonded through nitrogen. These complexes are square-planar.  (Ni(Asp)₂X)ClO₄ complexes , where X=Cl, Br, I, NO₂, NCS, NCSe, are diamagnetic and five-coordinated.  Their cations have a square-

pyramidal structure. $(Ni(Asp)_2(NCS)_2)$ is six-coordinated as a solid and five-coordinated in solution. It shows tetragonal distortions from $O_h$ symmetry.[27]

## PART D: OTHERS

$Ph_3PO$, triphenylphosphine oxide:

Mn; Fe; Co; Ni; Cu: The complexes $(Ph_3PO)_2MX_2$ form (where M=Co, X=Cl, Br, I) and the perchlorate complexes $(Ph_3PO)_4M(ClO_4)_2$ (where M=Fe, Co, Ni, Mn, Cu) were also isolated. In phosphine oxides, coordination can take place only through the oxygen.[4,49]

$Me_3PO$, trimethylphosphine oxide:

Co: $(Me_3PO)_4Co(ClO_4)_2$ and $(Me_3PO)_2CoCl_2$ have been isolated.[4,49]

$Cy_3PO$, tricyclohexylphosphine oxide:

Ni(II), Co(II): The complexes $(Cy_3PO_2MX_2$ (where X= halogen or $NO_3$) have been characterized.[46,47]

$Et_3PO$, triethylphosphine oxide: This ligand forms complexes which are similar to its methyl analogue.[49]

$(Et-O)_2-P-(S)_2$, $O,O'$-diethyldithiophosphate:

Pt(II): This ligand bonds through sulfur. The complex which forms with platinum(II) is bis($O,O'$-diethyl-dithiophosphato)platinum(II)methyldiphenylphosphine which has the structure:[32]
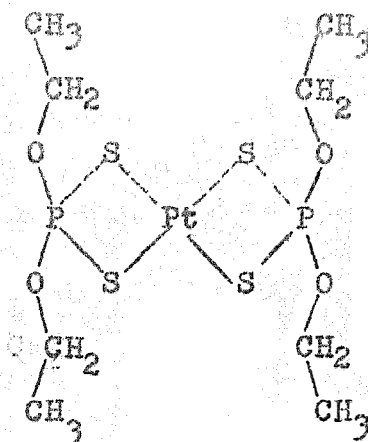
Diphosphine and Diphosphine-like compounds: Diphos-
phine, $P_2H_4$, is an unstable compound to which various
substituent groups can be added to form potentially bi-
dentate ligands. Although these compounds are potentially
bidentates, they generally act as monodentates either in
monomers or bridged complexes. A typical example of such
a bridged species is:

$$(CO)_3Ni-P \overset{CF_3CF_3}{\underset{CF_3CF_3}{\rule{0pt}{0pt}}}P-Ni(CO)_3$$
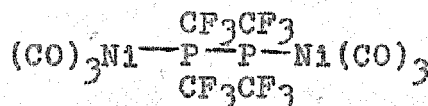
Tetraphenyldiphosphine is a monodentate in complexes with
copper(I), nickel(II), palladium(II), and cobalt(II),
while tetracyclohexyldiphosphine forms three-membered
rings with several transition metal ions. An example of
this unusual system is:[44]
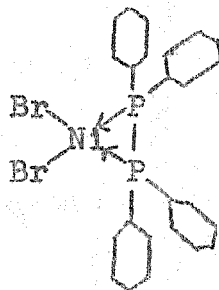
# SECTION III: RESEARCH ON CHROMIUM COMPLEXES

## WITH 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE.

I have been engaged in research with Dr. W. W. Hess
in an attempt to obtain, purify, and characterize the
coordination compounds formed by 1,2-bis(diphenylphosphino)
ethane (=dpe) and chromium(III). This is a continuation
of a project which was begun by Dr. Hess. Although this
research has not as yet been brought to a satisfactory
conclusion, a great deal has been discovered about the
nature of these chromium complexes. A few of those
observations will be elucidated in this section.

The ligand was prepared according to the method of
Chatt and Booth.[71] 1,2-bis(diphenylphosphino)ethane
is quite stable in solid form in atmospheric oxygen, but
it does exhibit a tendency to oxidize to the corresponding
phosphine oxide when it is melted or in solution. This
was demonstrated by bubbling oxygen through a solution of
the ligand in tetrahydrofuran to which a small amount of
2,2-dimethoxypropane had been added. After the oxygen
had been allowed to bubble through the solution for approx-
imately one hour, the solvent system was evaporated and
a melting point of the recovered crystals taken. The
melting point indicated that the white solid was an

incompletely oxidized mixture of the phosphine and its
oxide.

The majority of attempts at isolating chromium
complexes have been centered around a single basic reaction
of $CrCl_3 \cdot 6H_2O$ with the ligand. The hydrated salt is
dissolved in 2,2-DMP and is heated. The salt slowly
dissolves and the heating causes the solution to undergo
a color change from green to deep purple. The metal
solution is then added dropwise to a solution of dpe
in THF to which a little 2,2-DMP has been added. (The
2,2-DMP is used since it seems to act as a scavenger to
remove water molecules from the reaction system. It
is hoped that, by so doing, $H_2O$ will be restrained from
competition with dpe for coordination positions on
chromium(III). Anhydrous chromium chloride was not used
in the first place because it is an extremely stable
molecule which does not dissolve to any extent in most
solvents. Issleib and Fröhlich have however run some
anhydrous chromium reactions in benzene and toluene
so that avenue of research will be studied further.[47]

Most of the early reactions were run under ambient
conditions in the atmosphere. As the metal solution
is added under such conditions, the solution slowly
changes from being clear and colorless to a deep bruish-
purple. After the solution had been allowed to stand
for four or five days in a sealed flask, enough blue

solid formed in the flask that it could be collected
and studied. Under the microscope, the solid appeared
to be clear blue and micro-crystalline and, although its
melting point was questionable, it was sent off for
analysis. The analysis unfortunately did not fit any of
the possible epirical formulae well enough.

By varying this atmospheric method slightly, other
blue compounds having widely divergent melting points
were obtained. The only one which had a really good
melting point was the compound which had been obtained
by adding hexane to the reaction mixture just after the
reaction had occured. The blue compound which precipitated
immediately had a melting point of 135-136.5°C. The
other solids were obtained by other methods and their
nebulous melting points hinted at a solvation effect.

An attempt was then made to prove the theory that
the blue compounds were merely the same compound in
various stages of solvation. Mull and KBr infrared
spectra were taken of all of the compounds along with
the ligand. Spectra were also run of THF and acetonitrile
neat. Meanwhile, a larger reaction was run which dup-
licated the original run. The flask was kept sealed
except when small aliquots of solution were removed for
testing. As several weeks passed, it was realized that
more and more blue solid was precipitating from the reaction

mixture. Because the flask had remained stoppered, this phenomenom could not be explained as merely a concentration effect. Atmospheric oxygen came under suspicion and its effect was investigated. When pure oxygen was bubbled through the reaction mixture, a blue compound precipitated almost immediately, indicating a difinite effect of oxygen upon the complex. Solutions from reactions run under nitrogen, on the contrary, could stand for weeks under nitrogen without any noticeable precipitation occurring.

It seems obvious that some sort of oxidation of either the individual ligands or the complex as a whole is causing the appearance of at least one new species which is insoluble in THF. The fact that the compounds in solution can be altered even after they have fully formed leads one to the following two possibilities. First, that sometimes a ligand which has been attached to the central chromium atom will give up one or both of its coordination positions at least momentarily. At that point, the phosphorus could be oxidized with the result being the formation of a phosphine oxide. Secondly, an alternative mechanism might be an insertion reaction in which the oxygen atom would come to lie between chromium and phosphorus, bonding to both of them. If it is indeed the case that phosphine oxide bonds are involved, it is likely that only one of the two

phosphorus atoms in the chelate ring has been oxidized, since seven-membered rings are quite uncommon due to increased strain.

Recently, one reaction has been run and worked-up entirely under nitrogen atmosphere and another has been run under oxygen. The two resulting compounds are now being studied. The melting point of the compound which was prepared under nitrogen seems to be indicative of some solvation either by THF or water, but the complex prepared under oxygen shows no solvation and has a fairly sharp melt at approximately 330°C. These coordination compounds will be studied further in the hope that they may be representative of two extremes, and that the combination of those two extremes will explain the other compounds which have previously been prepared.

Some zerovalent phosphine complexes have been prepared simply by dissolving zerovalent nickel in the phosphine at elevated temperatures. As an extension of the main project, I attempted this type of a reaction between dpe and chromium metal. The metal and ligand were sealed in an evacuated glass tube and placed in an oven at 200°C. The metal does not seem to be at all soluble in the melted ligand, but perhaps with increased temperature some complexation will occur.

In the course of my research, it became necessary to devise many likely empirical formulae and find the

percent composition of each element involved in each
formula. It was also necessary to take the data which
was received from the analysis of a given compound and
determine the lowest approximate whole number ratio of
the atoms of the elements which had been analysed.
These two tasks can be tedious at best so I wrote two
computer programs, one for each problem, in order to
reduce the time spent in problem solving. They are
written in BASIC language.

Program (I) is designed so that the number of atoms
of each element in a given empirical formula can be
entered as data and the computer will give the percent
composition of each element involved. Program (II)
does the reverse of program (I). Composition data is
entered and the empirical formula is printed out along
with the next four integral multiples of the empirical
formula. Although these programs involve only those
elements directly associated with my work, it can quickly
be seen that the entire periodic chart could easily be
incorporated for added flexibility.

## Program (I)

```
05 INPUT A,B,C,D,E,F
10 LET D2=(A*12.0111)+(B*1.00797)+(C*30.975)+(D*52.01)+(E*35.453)
15 LET D1=D2+(F*15.9994)
20 LET X1=((A*12.0111)/D1)*100
25 LET X2=((B*1.00797)/D1)*100
30 LET X3=((C*30.975)/D1)*100
35 LET X4=((D*52.01)/D1)*100
40 LET X5=((E*35.453)/D1)*100
45 LET X6=((F*15.9994)/D1)*100
50 PRINT "NUMBER OF ATOMS OF C,H,P,CR,CL,O IN COMPOUND"
55 PRINT A,B,C,D,E,F
60 PRINT "PERCENT COMPOSITION OF C,H,P,CR,CL,O"
65 PRINT X1,X2,X3,X4,X5,X6
70 END
```

Program (II)

```
05 INPUT A,B,C,D,E,F,G
10 LET X(1)=A/12.0111
15 LET X(2)=B/1.00797
20 LET X(3)=C/30.9738
25 LET X(4)=D/51.996
30 LET X(5)=E/35.453
35 LET X(6)=F/15.9994
40 LET X(7)=G/14.0067
45 LET J=X(1)
50 FOR I=1 TO 7
55 IF X(I)=0 THEN 70
60 IF X(I) =J THEN 70
65 LET J=X(I)
70 NEXT I
75 LET Y(1)=(X(1))/J
80 LET Y(2)=(X(2))/J
85 LET Y(3)=(X(3))/J
90 LET Y(4)=(X(4))/J
95 LET Y(5)=(X(5))/J
100 LET Y(6)=(X(6))/J
105 LET Y(7)=(X(7))/J
110 PRINT "EMPIRICAL FORMULAE SUBSCRIPTS MULTIPLIED BY 1,2,3,4,5"
115 PRINT Y(1);Y(2);Y(3);Y(4);Y(5);Y(6);Y(7)
120 FOR H=2 TO 5
125 FOR I=1 TO 7
130 LET K(I)=H*(Y(I))
135 NEXT 1
140 PRINT K(1);K(2);K(3);K(4);K(5);K(6);K(7)
145 NEXT H
150 END
```

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