

SYNTHESIS AND CHARACTERIZATION OF GROUP IB AND IIB
METAL COMPLEXES WITH DI-TERTIARY PHOSPHINE AND

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and Di-tertiary Arsine Ligands

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SYNTHESIS AND CHARACTERIZATION OF GROUP IB AND IIB
METAL COMPLEXES WITH DITERTIARY PHOSPHINE AND
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by

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Master of Science in Chemistry
Youngstown State University, 1972

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF GROUP IB AND IIB
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This investigation describes the preparation and properties of complexes of the metals copper, silver, gold, zinc, cadmium, mercury, and nickel with ditertiary phosphine and ditertiary arsine ligands.

The experimental work done is described in three parts:

(a) Triphenylphosphine complexes. Some of these have been reported in the literature. Triphenylphosphine complexes of zinc, mercury, copper, and silver have been made either in the molten state¹ by heating a mixture of metal halides and triphenylphosphine, or by mixing hot alcoholic solutions of the reactants.² Analytical information is either completely lacking or at best is only partially reported. An attempt has been made in this study to prepare these complexes in ethanol solvent and determine their complete elemental analysis where feasible.

(b) Ditertiary phosphine complexes. Ditertiary phosphine complexes of the halides of zinc, cadmium, mercury, copper, silver, gold, and nickel having a

composition of 1:1 ligand to metal halide ratio have been prepared, characterized and their properties studied in some detail.

(c) Ditertiary arsine complexes. Ditertiary arsine complexes of the halides of copper, gold, and mercury having ligand to metal halide ratio of 1:1 have been isolated, characterized and their properties are studied in some detail. Attempts to isolate ditertiary arsine complexes of zinc, cadmium, silver and nickel were unsuccessful.

I would like to express my gratitude to my parents who were a constant source of inspiration to me.

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I would like to take this opportunity in expressing my indebtedness and thanks to Dr. Inally Mahadeviah for his suggestions and unlimited help in completing this project.

Also, my special thanks to Dr. Robert Smith and Dr. Elmer Foldvary for their helpful criticism in improving this manuscript.

Finally, I would like to express my gratitude to my parents who were a constant source of inspiration to me.

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Systematization of coordination compounds in terms of structure, properties, and reactions originated with Alfred Werner's theory proposed in 1893. Most of the experimental work which influenced Werner's theory was done using ammonia as a ligand. Ammonia and amines in which the N-atom is the donor atom form salt-like complexes which are soluble in polar solvents. Triaryl and trialkyl phosphines and arsines generally form much stronger metal to ligand (P-atom or As-atom is the donor) bonds than the amines. These phosphine and arsine complexes are generally non-ionic compounds readily soluble in organic solvents.

Perhaps the beginning of triphenyl phosphine and arsine complex chemistry is the report by Oshours and Gal in 1870 on the preparation of palladium, platinum, and gold complexes with tertiary phosphines and arsines.³ From the middle 1950's tertiary, ditertiary phosphines

CHAPTER I

INTRODUCTION

This investigation describes the synthesis and characterization of ditertiary phosphine, $(C_6H_5)_2PCH_2CH_2-P(C_6H_5)_2$, and ditertiary arsine, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$, complexes of some of the post-transition metals. A "complex", or "coordination compound", is a unit in which a metal atom or ion is bound in a definite geometric arrangement to a definite number of groups called ligands. Systematization of coordination compounds in terms of structure, properties, and reactions originated with Alfred Werner's theory proposed in 1893. Most of the experimental work which influenced Werner's theory was done using ammonia as a ligand. Ammonia and amines in which the N-atom is the donor atom form salt-like complexes which are soluble in polar solvents. Triaryl and trialkyl phosphines and arsines generally form much stronger metal to ligand (P-atom or As-atom is the donor) bonds than the amines. These phosphine and arsine complexes are generally non-ionic compounds readily soluble in organic solvents.

Perhaps the beginning of triphenyl phosphine and arsine complex chemistry is the report by Cahours and Gal in 1870 on the preparation of palladium, platinum, and gold complexes with tertiary phosphines and arsines.³ From the middle 1950's tertiary, ditertiary phosphines

and arsines have been used as ligands to prepare a large number and variety of complexes.⁴

An effort has been made to synthesize and characterize ditertiary phosphine and arsine complexes with univalent copper, silver, gold, and bivalent zinc, cadmium, and mercury. The complexes isolated are colorless, crystalline or amorphous materials which are only slightly soluble or almost insoluble in common organic solvents. π -bonding is believed to be important. Particular emphasis will be placed on this aspect of the metal-ligand bond.

Theories of Metal-Ligand Bonding

During the past forty years four theories have been developed to explain the nature of bonding in metal complexes. These are (A) the electrostatic or the crystal field theory, (B) the valence bond theory, (C) the ligand field theory, and (D) the molecular orbital theory. A brief discussion of these theories now follows.

(A) Crystal Field Theory

The electrostatic theory, which has evolved into what is now usually referred to as the crystal field theory, treats bonding in metal complexes as solely due to the coulombic interaction between the central metal

CHAPTER II

METAL-LIGAND BONDING WITH SPECIAL REFERENCE
TO DOUBLE BONDING

The nature of metal-ligand bonding is fundamental to any discussion of metal complexes. Therefore a brief outline of the more important theories of metal-ligand bonding will be considered in this chapter. The complexes discussed in this thesis are those having ligands in which π -bonding is believed to be important. Particular emphasis will be placed on this aspect of the metal-ligand bond.

Theories of Metal-Ligand Bonding

During the past forty years four theories have been developed to explain the nature of bonding in metal complexes. These are (A) the electrostatic or the crystal field theory, (B) the valence bond theory, (C) the ligand field theory, and (D) the molecular orbital theory. A brief discussion of these theories now follows.

(A) Crystal Field Theory

The electrostatic theory, which has evolved into what is now usually referred to as the crystal field theory, treats bonding in metal complexes as solely due to the coulombic interaction between the central metal

ion and surrounding ligands. The ligands may be either negative ions or neutral molecules and these are considered as point charges or point dipoles. Here the strength of the metal-ligand bond is visualized as arising from an attraction between the positively charged central metal ion and negatively charged ions or dipoles possessing lone pair(s) of electrons. The stereochemistry and the coordination number of the complex in such a model depends on its geometry and the tendency for a spherical distribution of negative charge around the central ion. It can be shown that minimum electrostatic repulsion is achieved by having a linear arrangement for two ligands, a tetrahedral arrangement for four ligands and an octahedral arrangement for six ligands.⁵

Based on the electrostatic model it is possible to calculate the bond energies of some simple complexes which are in fair agreement with experiment.⁶ However, there are a number of phenomena which the simple electrostatic theory cannot explain. Examples are as follows.^{7, 8} Generally the coordinating ability of R_3N is greater than R_3P toward group III elements, while it is the reverse with transition metals. The existence of a large number of square planar complexes with d^8 ions cannot be explained. The stability of complexes containing virtually non-polar ligands such as carbon monoxide and isocyanides is difficult to account for on the basis of this model. These and similar phenomena suggest that

in some cases at least, covalent bonding is an important factor.

(B) Valence Bond Theory (VBT)

Sidgwick⁹ applied the electron pair bond model of G. N. Lewis to coordination compounds. He proposed that the coordinate covalent bond was formed as a result of sharing a pair of electrons by the metal and the ligand, both electrons being donated by the ligand. The covalent nature of the bond would explain the stability and the stereochemistry of the complex.

The next major contribution to our understanding of bonding in complexes was provided by Pauling who applied wave mechanics to the study of chemical bonding. The distribution of electron density associated with s-, p-, or d-type atomic orbitals is shown in Figure 1. Bonding results as a consequence of the overlap of such atomic orbitals of suitable symmetry of metal and ligands with a resultant build up of considerable amount of electron density in the regions between the bonding atoms, in such a way as to render the energy of the system a minimum. Pauling¹⁰ proposed that to have a system of minimum energy for the complex, the various bonding orbitals of the metal atom combined to give a new set of equivalent hybrid orbitals which then participated in bond formation. The coordination number and stereochemistry of the complex depend on the way these hybrid orbitals are formed and

Boundary Surfaces

directed in space. The stereochemical arrangements together with the coordination associated with some of the more common hybridization found in transition metal complexes are listed in Table 1.

TABLE 1

Coordination Number	Hybridization	Shape
2	sp	Linear
3	sp^2	Trigonal plane
4	sp^3	Tetrahedron
4	dsp^2, sp^2d	Square plane
5	dsp^3	Trigonal bipyramid
6	d^2sp^3	Octahedron
6	d^3sp^3	Trigonal bipyramid
8	d^4sp^3	Square antiprism and dodecahedron

Approximate values for the lengths of the various hybrid orbitals, taking into account both the angular and radial distribution of the combining atomic orbitals have been made. 11, 12

Bond formation is presumed to occur as a result of the overlap of the metal hybrid orbital with the filled atomic orbital of a ligand atom. In the process of bond formation, if the overlap is along the bond

Fig. 1. Types of Atomic Orbitals

directed in space around the metal ion. The stereochemical arrangements together with the coordination associated with some of the more common hybridization found in transition metal complexes are listed in Table 1.

TABLE 1

Coordination Number	Hybrids	Shape
2	sp	Linear
3	sp^2	Trigonal plane
4	sp^3	Tetrahedron
	dsp^2, sp^2d	Square plane
5	$d_z sp^3$	Trigonal bipyramid
	$d_{x^2-y^2} sp^3$	Square pyramid
6	$d^2 sp^3, sp^3 d^2$	Octahedron
7	$d^3 sp^3$	Pentagonal bipyramid
8	$d^4 sp^3$	Square antiprism and dodecahedron

Approximate calculations of the strengths of various hybrid orbitals, taking into account both the angular and radial distribution of the combining atomic orbitals have been made.^{11, 12}

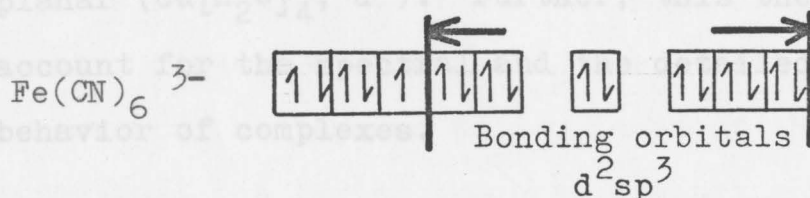
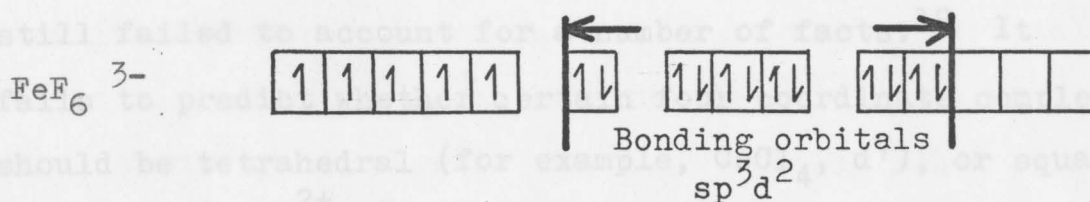
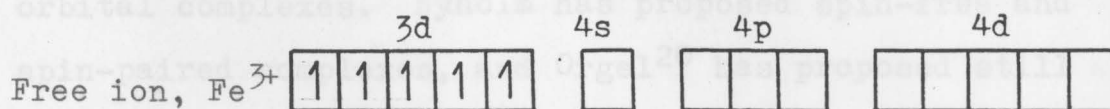
Bond formation is presumed to occur as a result of the overlap of the metal hybrid orbital with the filled atomic orbital of a ligand atom. In the process of bond formation, if the overlap occurs along the bond

axis, a σ -bond is formed, but if there is a sideways overlap a π -bond results. In the case of d-orbitals, if the overlap occurs with the two orbitals oriented in such a way that their lobe planes are parallel to each other, a δ -bond is formed. In addition, a different type of overlap may also take place between a σ -type metal orbital and a filled π -orbital of an unsaturated hydrocarbon, like C_2H_4 in the complex, $K[PtCl_3(C_2H_4)]$. The type of orbital overlap which occurs in the case of metal- π -cyclopentadienyl and related complexes is of this class. Such a bond has been called a μ -bond.¹³ Nyholm¹⁴ has compiled a list of the various types of bonding encountered in complex compounds.

Pauling¹⁵ suggested that the magnetic susceptibility of the complex can be used as a diagnostic of the nature of metal-ligand bond. Pauling's ideas, however, have undergone considerable modification in recent years in order to render the theory more general in nature.^{16, 17, 18}

Complexes of the first transition series can be classified into two groups on the basis of d-electron distribution. For example, it has been suggested in the complex hexafluoroferrate(III) ion, $[FeF_6]^{3-}$, where the magnetic moment is the same as for the free iron(III) ion, the bonding orbitals of the metal are ns , np^3 , nd^2 . In the complex hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$, which has a magnetic moment corresponding to one unpaired elec-

tron, the bonding orbitals are $(n-1)d^2$, ns , np^3 . The electron distribution for the two complexes can be shown as:



(O) Ligand Field Theory (LFT)

In the $[FeF_6]^{3-}$ complex the d-electrons of the metal remain unpaired while in $[Fe(CN)_6]^{3-}$, they are paired. The covalent character of the bond in $[FeF_6]^{3-}$ may be weaker due to the slight overlap involving more diffuse and higher energy 4d orbitals. Stability in such a complex can only be due to coulombic interaction between the ligands and the metal ion, or this amounts to saying bonding in such complexes has a higher degree of ionic character. The theory that 4d-orbitals can be used for bond formation in such cases is supported by the work of

Craig and Nyholm.¹² These workers have demonstrated that ligands of low electronegativity favor electron pairing and hence inner-d type bonding, whereas those of higher electronegativity favor outer-d utilization for bonding. Taube¹⁷ classifies complexes as inner orbital and outer orbital complexes. Nyholm has proposed spin-free and spin-paired complexes, and Orgel²⁰ has proposed still another name--high and low spin complexes.

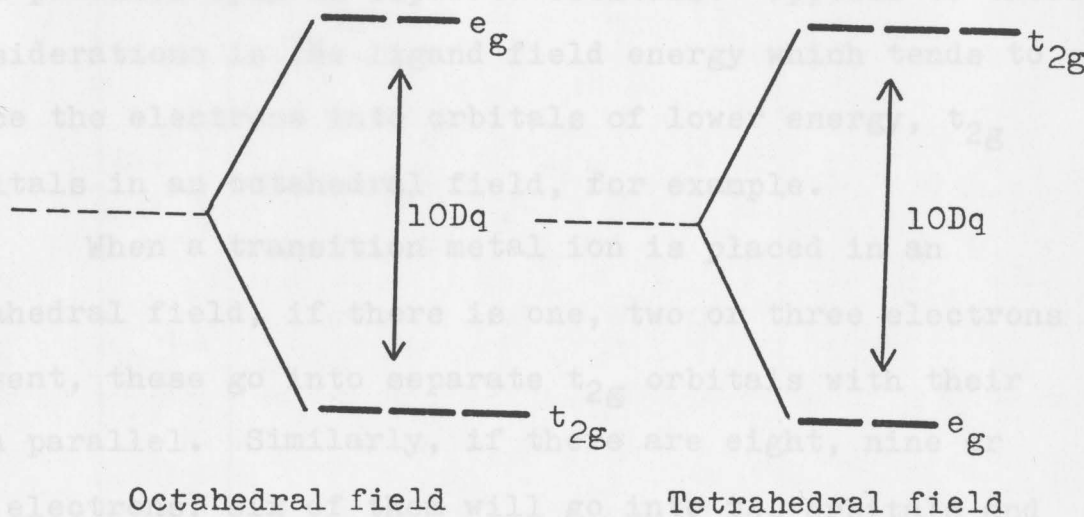
Even after modifications, valence bond theory still failed to account for a number of facts.¹⁹ It fails to predict whether certain four coordinate complexes should be tetrahedral (for example, CoCl_4 , d^7), or square planar ($\text{Cu}[\text{H}_2\text{O}]_4^{2+}$, d^9). Further, this theory fails to account for the spectral and the detailed magnetic behavior of complexes.

(C) Ligand Field Theory (LFT)

Ligand field theory^{21, 22} is essentially crystal field theory in which an allowance is made for covalent character. Thus this is sometimes referred to as adjusted crystal field theory (ACFT). In essence, this theory recognizes the effect of the ligand field produced by the ligands around the metal atom on the non-bonding metal electrons. The resulting ligand field is a combination of σ -bonding, π -bonding and electrostatic effects.

Based on the ligand field theory, properties of complexes are understood in terms of the interaction of metal d-orbitals with σ -atomic orbitals of ligands. In order to properly utilize such interaction and its consequences, it is necessary to know the spacial orientation of d-orbitals around the central metal ion. Let us consider an octahedral complex with a cubic symmetry. Assume the metal ion to be placed in the center of a cube and also at the center of cartesian coordinates of the five d-orbitals. The lobes of the d_{xy} , d_{xz} , and d_{yz} orbitals, called t_{2g} orbitals, point towards the mid-points of the edges of the cube, whereas the $d_{x^2-y^2}$ orbital lobes point towards the center of the four faces of the cube in the x and y direction, and the d_{z^2} orbital lobes towards the centers of the top and bottom faces of the cube in the z direction, the latter two orbitals being referred to as E_g orbitals. When the six lone pairs of electrons associated with the six ligands are brought towards the central metal ion along the x, y and z axes, the electrons in the l_g orbitals are repelled more than the electrons in the t_{2g} orbitals. This destroys the five fold degeneracy of the d-orbitals which will be split into two sets of orbitals, one more stable doubly degenerate set and another less stable triply degenerate set. The energy difference between E_g and t_{2g} sets is known as octahedral splitting or ligand field splitting and is designated D_0 or $10 Dq$. Zero energy is chosen as the weighted mean

of the d-orbitals, thus making the t_{2g} and E_g energies $-4Dq$ and $+6Dq$, respectively, in an octahedral field. In a tetrahedral field the t_{2g} electrons will be nearer to the ligands and hence the tetrahedral splitting will be the reverse of the octahedral one with a smaller energy separation.²³



On the basis of this splitting, the distribution of the non-bonding electrons among the t_{2g} and E_g levels is controlled by the extent of the ligand field splitting. Ligand field splitting is responsible for many optical and magnetic properties exhibited by complexes, although it may not have an important bearing on the strength of the metal-ligand bond.

energies involved are presented in Table 2 according to Sutton.²⁴ It is assumed that every electron pair with parallel spins contributes the same

The d-electrons have a tendency to spread out into as many orbitals as possible. There are two types of interactions among them responsible for this property.^{20, 24} One is the coulombic repulsion between any two electrons occupying the same region of space; the other is the quantum mechanical exchange energy which is zero between two electrons of opposed spin, but is negative and hence increases stability between electrons with parallel spin in separate orbitals. Opposed to these considerations is the ligand field energy which tends to force the electrons into orbitals of lower energy, t_{2g} orbitals in an octahedral field, for example.

When a transition metal ion is placed in an octahedral field, if there is one, two or three electrons present, these go into separate t_{2g} orbitals with their spin parallel. Similarly, if there are eight, nine or ten electrons, six of them will go into t_{2g} orbitals and the rest will go into E_g orbitals. But when the number of d-electrons is four, five, six and seven, there are two possible ways in which these numbers of electrons can be distributed among t_{2g} and E_g orbitals, depending on whether the ligand field stabilization energy is large enough to offset the energy demand for pairing and concomitant loss in exchange energy. These various distributions and the energies involved are presented in Table 2 according to Sutton.²⁴ It is assumed that every electron pair with parallel spins contribute the same

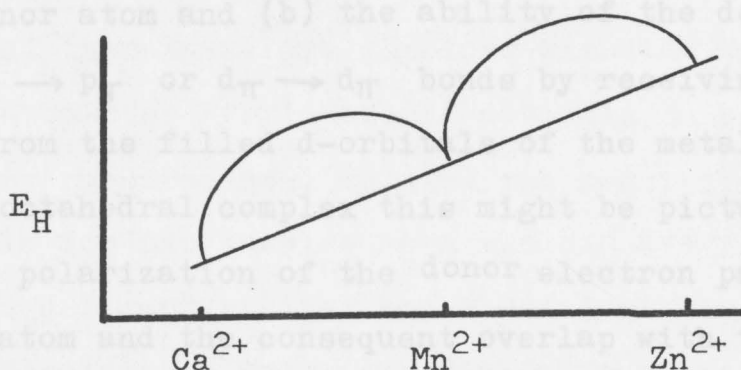
TABLE 2

Number of d-electrons		1	2	3	4		5		6		7		8	9	10
					Spin High	Spin Low	Spin High	Spin Low	Spin High	Spin Low	Spin High	Spin Low			
Electron distribution	Eg				1		2		2		2	1	2	3	4
	t _{2g}	1	2	3	3	4	3	5	4	6	5	6	6	6	6
Resultant spins		1	2	3	4	2	5	1	4	0	3	1	2	1	0
Electrostatic electron repulsion (π_e)		0	0	0	0	+1	0	+2	+1	+3	+2	+3	+3	+4	+5
Spin exchange interaction		0	-1	-3	-6	-3	-10	-4	-10	-6	-11	-9	-13	-16	-20
Energy in ligand field (Dq)		-4	-8	-12	-6	-16	0	-20	-4	-24	-6	-18	-12	-6	0

quantity of exchange energy. Similarly, the electrostatic repulsion energy depends on the number of electron pairs (spins opposed), being π_e per pair.

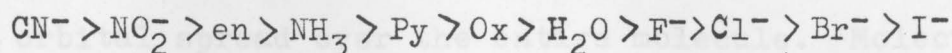
The bottom line in the table gives the stabilization energies of the various fixed electron distribution in the presence of ligands relative to the average distribution.

Orgel²⁰ has applied ligand field stabilization energies to explain the heats of formation of the hydrates of the first row transition metal ions. These values may be expected to vary in the same way as the ionization energies, which rise smoothly for the divalent ions from calcium(II) to zinc(II), but the observed heats of hydration show two maxima (at d^3 and d^8) with a minimum at manganese (d^5) as shown in Figure 3.



Orgel attributes these seeming discrepancies to ligand field stabilization. The Dq values can be evaluated from the spectra of the hydrates of the metal ions and the ligand field stabilization may then be evaluated. If these values are subtracted from the observed heats of hydration, one gets a smooth curve. Similarly the lattice energies of divalent and trivalent metal halides which

show apparent irregularities can be explained.²⁵ The Dq values for a number of ligands have been calculated²⁰ and the order of increasing ligand field strength found for the more common ligands is:



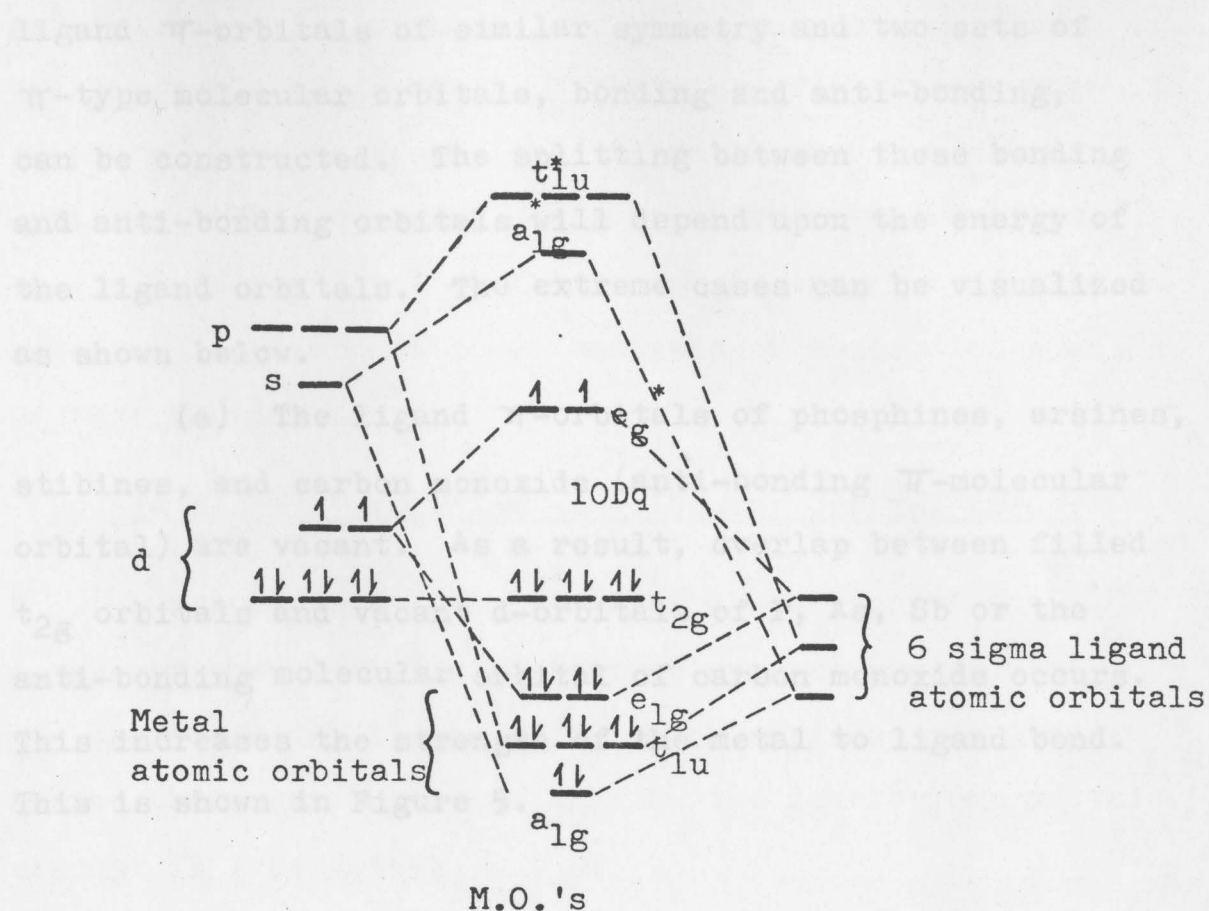
This is known as the spectrochemical series. On the basis of the relative field strengths produced by these ions, one can now more readily explain why hexacyanoferrate(III) is low spin and why hexafluoroferrate(III) is high spin complex.

According to Gillespie and Nyholm^{19, 26} there are two important factors which influence the strength of the ligand field: (a) a readily polarizable electron pair on the donor atom and (b) the ability of the donor atom to form $d_{\pi} \rightarrow p_{\pi}$ or $d_{\pi} \rightarrow d_{\pi}$ bonds by receiving electrons back from the filled d-orbitals of the metal atom or ion. In an octahedral complex this might be pictured as a strong polarization of the donor electron pair by the metal atom and the consequent overlap with the E_g orbitals, forcing any non-bonding electrons in these orbitals to pair-off in the t_{2g} orbitals. Furthermore, the t_{2g} orbitals have the right shapes to overlap with the d_{π} or p_{π} orbitals of the ligand atoms. Thus the t_{2g} electrons may take part in π -bonding, and any such double bond character tends to strengthen and shorten the metal-ligand bond by increasing the overlap.

(D) Molecular Orbital Theory (MOT)

The essential feature of the molecular orbital theory is that the atomic orbitals are delocalized and the bonding electrons are presumed to occupy a molecular orbital spread over the entire molecule. Molecular orbital theory can accommodate at one extreme the completely electrostatic situation which involves no orbital overlap to a maximum of overlap at the other extreme, as well as all the intermediate degrees of overlap. The molecular orbital method employs the same central metal atom orbitals as does the valence bond theory, but in addition it considers the available orbitals of the coordinated ligand atoms. First a set of composite σ -type orbitals for all the ligands is made and then these are combined with the appropriate metal atomic or hybrid-atomic orbitals, in keeping with symmetry requirements, to give the required molecular orbitals for the complex as a whole. Every combination between a ligand orbital and a metal orbital produces two molecular orbitals, one with a lower energy than either of the individual orbitals, called the bonding molecular orbital, and the other with a higher energy, called the anti-bonding molecular orbital. The molecular orbitals thus produced are arranged in the order of increasing energies and the available electrons are fed into them in accordance with Hund's first rule and Pauli's exclusion principle. A molecular orbital diagram for a

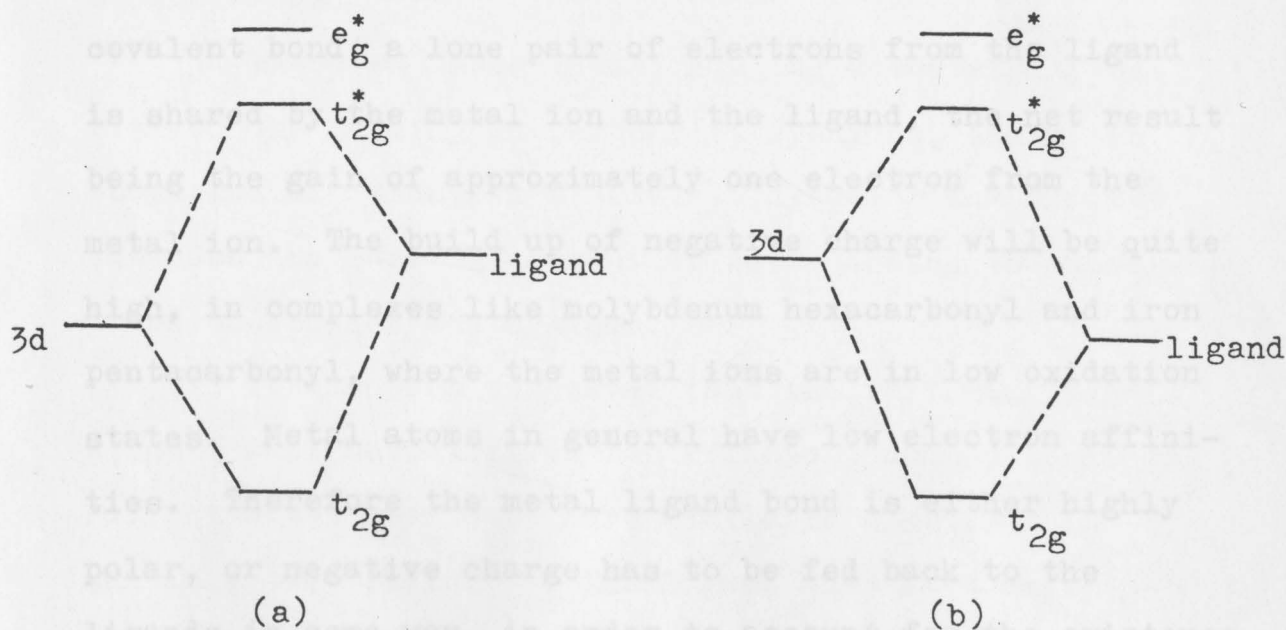
d^6 complex is shown in Figure 4.



The t_{2g} orbitals of the metal are of π -symmetry and cannot combine with the σ -type orbitals of the ligands and these are referred to as non-bonding orbitals. The twelve electrons of the ligands can be housed in six bonding molecular orbitals (one a_{1g} , three t_{1u} , and two e_g). The distribution of d -electrons depends upon the strength of the ligand field. In a strong field a low spin complex results, a t_{2g}^6 configuration, but in a weak field the high spin complex, a $t_{2g}^4 e_g^2$ configuration, will be formed.

The t_{2g} , π -type atomic orbitals can overlap with ligand π -orbitals of similar symmetry and two sets of π -type molecular orbitals, bonding and anti-bonding, can be constructed. The splitting between these bonding and anti-bonding orbitals will depend upon the energy of the ligand orbitals. The extreme cases can be visualized as shown below.

(a) The ligand π -orbitals of phosphines, arsines, stibines, and carbon monoxide (anti-bonding π -molecular orbital) are vacant. As a result, overlap between filled t_{2g} orbitals and vacant d-orbitals of P, As, Sb or the anti-bonding molecular orbital of carbon monoxide occurs. This increases the strength of the metal to ligand bond. This is shown in Figure 5.



(b) π -orbitals of ligands such as halide ions and the oxide ion with filled π -systems, the electrons of which are placed in the t_{2g} orbitals. The nd electrons of the metal have to occupy the t_{2g}^* antibonding molecular orbitals. This causes a decrease in the stabilization energy. Energy level diagrams such as these shown here, have been used for rational analysis of absorption spectra of many complexes.²³

Double Bonding According to Molecular Orbital Theory

According to the preceding discussion of the nature of the metal-ligand bond in some complexes, both σ - and π -bonding is possible, which enhances the strength of the bond. We shall now examine the development of this concept in some detail.

According to Sidgwick's model of the coordinate covalent bond, a lone pair of electrons from the ligand is shared by the metal ion and the ligand, the net result being the gain of approximately one electron from the metal ion. The build up of negative charge will be quite high, in complexes like molybdenum hexacarbonyl and iron pentacarbonyl, where the metal ions are in low oxidation states. Metal atoms in general have low electron affinities. Therefore the metal ligand bond is either highly polar, or negative charge has to be fed back to the ligands in some way, in order to account for the existence of these metal carbonyls.

Pauling incorporated these ideas in his postulate, the electroneutrality principle. This states that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge, the limits being ± 1 and these charges are localized mainly on the most electropositive and the most electronegative atoms. Pauling proposed that the accumulated negative charge on the metal could be fed back to the ligands by (a) assuming the formation of double bonds in which the non-bonding d-electrons of the metal are donated back to the ligand, and (b) by assuming an ionic contribution to the bond. In terms of overlap such back donation can be assumed to take place by the overlap of suitably oriented, filled, t_{2g} orbitals of metal ion with vacant symmetrically compatible p- or d-orbitals on the ligand atoms.

Based on these ideas, Pauling successfully explained the bonding in carbonyls, cyanides, and nitro complexes of transition metals. Nyholm²⁹ and Chatt³⁰ extended the Pauling concept of back bonding to substituted phosphines and arsines.

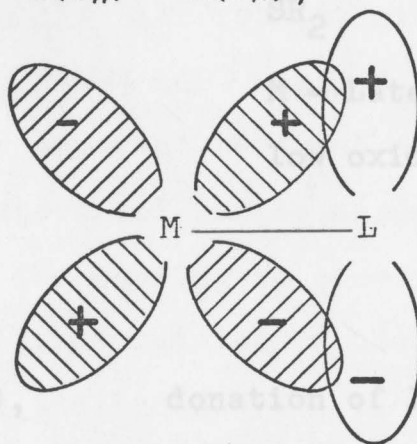
It has been suggested that the following conditions³¹ must be satisfied for efficient double bonding: (a) The metal atom must have available electrons in suitable d-orbitals; (b) The ligand must have empty p- or d-orbitals which can receive these d-electrons; and (c) Sizes of the orbitals of the metal ion and the ligands

must be such as to ensure effective overlap.

Double and multiple π -bonding in metallic complexes is now generally recognized as an important factor in the formation of many stable metal-ligand bonds.

Excluding metal-to-metal bonds in certain complexes and the highly delocalized bonding arising in a large class of complexes having ligands such as olefins and aromatic systems, it is easy to classify the remaining types of π -bonds found in metal complexes:

(a) $M(d\pi) \quad L(P\pi)$,



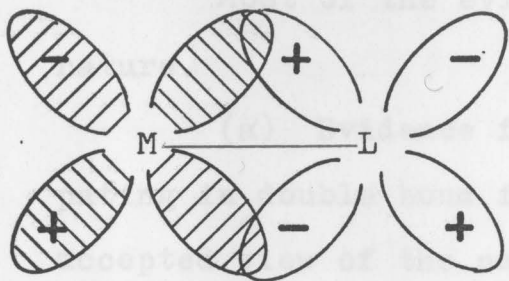
Shaded orbital =
filled orbital.

donation of metal atom d electrons to empty ligand atom $P\pi$ orbitals. Here $L = CO, NO_2^-, CN^-, RNC, NO$

$M =$ Later transition elements in low
oxidation state

Experimental Evidence for Double Bonding
in Complexes

(b) $M(d\pi) \quad L(d\pi)$,



donation of metal atom $d\pi$ electrons to empty ligand atom $P\pi$ orbitals.

Here $L = \text{CO}, \text{NO}_2^-, \text{CN}^-, \text{RNC}, \text{NO}$

$M =$ Later transition elements in low oxidation state.

(c) $M(d\pi) \quad L(d\pi)$,



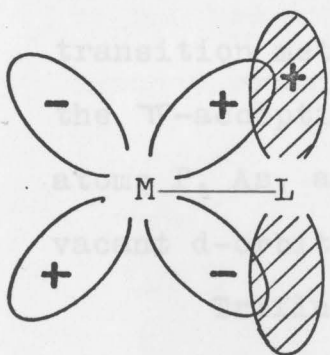
donation of metal atom $d\pi$ electrons to empty ligand atom $d\pi$ orbitals.

Here L may be $\text{PF}_3, \text{PR}_3, \text{AsR}_3$ and

SR_2

$M =$ Later transition metals in low oxidation states.

(d) $L(P\pi) \quad M(d\pi)$,



donation of ligand atom $P\pi$ electrons to empty metal atom $d\pi$ orbitals.

$L = \text{O}^{2-}, \text{F}^-, \text{N}_3^-, \text{NH}_2^-$

$M =$ Early transition metals in high oxidation states.

Experimental Evidence for Double Bonding
in Complexes

Most of the evidence we have is of an indirect nature.

(a) Evidence from the type of ligand participating in double bond formation in complexes: Currently accepted view of the nature of this metal-ligand bond is that it is composed of two parts, the σ -component and the π -component. Generally speaking the coordinating ability of ligands having group V atoms as donors towards $\text{Ga}(\text{Me})_3$ and similar group III metal trialkyls decreases in the order, $\text{R}_3\text{N} > \text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_3\text{Sb}$, provided steric and hyperconjugation effects are absent. But when they combine with transition metals like cobalt, nickel, etc., the order is reversed, $\text{R}_3\text{N} \ll \text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_3\text{Sb}$,³² where R is an alkyl group. This apparent reversal of the order of stability can be accounted for by assuming that with non-transition metals the bonding is purely σ -type, the coordinating ability decreasing in the order given, which is also related to the basicity of the donor atom with transition metals. However, with the exception of R_3N , the π -accepting contribution is more important with donor atoms P, As, and Sb which have energetically favorable vacant d-orbitals.

Trifluorophosphine affords a very interesting example. PF_3 is a poor Lewis base and has little tendency to form a coordinate covalent bond because of the high

electronegativity of fluorine atoms. This is evidenced by the fact that it does not form a stable bond with boron trifluoride. However, it readily forms bonds with transition metals for example, $\text{Ni}(\text{PF}_3)_4$. The existence of this complex, due to the greater contribution of π -bonding in metal-to-phosphorous bond has been suggested by G. Wilkinson.³³

Carbon monoxide forms zero valent diamagnetic carbon only with transition metals having d^6 to d^{10} configuration. The non-existence of non-transition metal carbonyls can only be explained on the basis of the very weak σ -bonding ability of carbon monoxide. The formation of isocyanide complexes has been explained in a similar way.³⁴

(b) Evidence from vibrational frequencies (force constants): Infrared frequency measurements for many carbonyls, and the corresponding force constant calculations, show that the C-O bond in carbonyls is intermediate between a double and a triple bond, as can be shown by the comparison of the values for free CO , CO_2 , metal carbonyls, and ketone group in Table 3.

$\text{Fe}(\text{CO})_5$	2009, 1916, 1880
$\text{Fe}(\text{CO})\text{D}_2$	1953
$\text{Cr}(\text{CO})_6$	2100, 2000, 1985
$\text{Cr}(\text{dien})(\text{CO})_3$	1900, 1760

D = Diarsine,

dien = diethylenetriamine

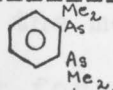
TABLE 3

Compound	Force Constant (dynes/cm)
$\text{CH}_2=\text{C}=\text{O}$	15.5×10^5
CO_2	15.5×10^5
$\text{Ni}(\text{CO})_4$	16.8×10^5
$\text{Cr}(\text{CO})_6$	16.4×10^5
CO	19.0×10^5

When carbon monoxide in a metal carbonyl is substituted by a ligand having a less π -accepting capacity, the carbonyl groups in the resulting mixed carbonyls must accept a greater share of the d-electrons and hence their bond order will be further reduced. This reduction in bond order will result in a further reduction of the CO stretching frequency in the complex. The data in Table 4 provides evidence for what we have just said.

TABLE 4

Compound	C-O Stretch (cm^{-1})
$\text{Fe}(\text{CO})_5$	2028, 1994
$\text{Fe}(\text{CO})_3\text{D}$	2009, 1916, 1880
$\text{Fe}(\text{CO})\text{D}_2$	1953
$\text{Cr}(\text{CO})_6$	2100, 2000, 1985
$\text{Cr}(\text{dien})(\text{CO})_3$	1900, 1760

D = Diarsine, 
dien = diethylenetriamine

On the other hand partial replacement of the CO groups in the metal carbonyls by halogens could be expected to increase the stretching frequency in halogen carbonyl complexes. A halogen atom renders the metal atom more positive and thus causes the flow of electrons from the anti-bonding molecular orbital CO with a resultant increase in bond order for CO. This, of course, will be demonstrated in the increased stretching frequency for CO. For example, $\text{Fe}(\text{CO})_5$ (2028, 1994 cm^{-1}); $\text{Fe}(\text{CO})_4\text{Br}_2$ (2130 cm^{-1}); and $\text{Fe}(\text{CO})_4\text{I}_2$ (2132, 2086 cm^{-1}).³¹

Classification of the More Common Ligands On the Basis of Their Double Bonding Capacity

At present a large body of experimental evidence has been collected from very powerful physical methods like IR, EPS, NQR, to support the hypothesis that there is considerable bonding in certain transition metal complexes. But it must be admitted that most of this evidence is of an indirect nature, with the exception perhaps of electron paramagnetic resonance. Ligands forming double bonds can be classified on the basis of their ability to form double bonds.

(A) Strong π -bonding Ligands

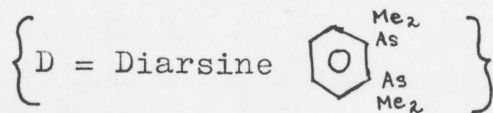
Carbon monoxide, nitric oxide, isocyanides, phosphorus halides, and cyanide ion are strong π -bonding ligands. In the molecular orbital treatment of these ligands (except for the phosphorus halides), all

possess one or more vacant anti-bonding π -molecular orbital(s) which can receive d-electrons from the metal. The evidence in favor of the existence of strong π -bonding in carbonyls has already been cited. The experimental evidence that the carbonyl group in metal carbonyls can be replaced fairly easily by nitric oxide, isocyanides,³⁴ or phosphorus halides³⁵ without any change in the oxidation state of the metal suggests that the latter are as good or even better π -bonding ligands than carbon monoxide.

(B) Moderately Strong π -Bonding Ligands

The phosphines, arsines, and ligands containing sulfur and selenium as donor atoms and ligands of the pyridine type can be grouped in this classification.

Phosphines and arsines are more basic than carbon monoxide and possess considerable σ -bonding capacity. This may well be the reason why these ligands stabilize the higher valence state of the metal as exemplified by the existence of complexes of the type $[\text{NiD}_2\text{Cl}_2]^{2+}$, $[\text{FeD}_2\text{Cl}_2]^{2+}$, where the metal is in a high oxidation state.



Both σ - and π -bonding are considered to be important in pyridine-type ligands. Dipyridyl and phenanthroline form complexes of stability comparable with those of ethylenediamine with transition metal ions in their normal oxidation states, but they also form zero-valent

complexes with titanium, vanadium, chromium, and zirconium.

(C) Poor π -Bonding Ligands

Chloride, bromide, and iodide may be included in this class. With these as ligands ionic character predominates and it increases from chloride to iodide, while the σ -bonding character may increase due to the increase in polarizability and decrease in electronegativity of the ligands. The vacant $d\pi$ orbitals of the ligands are of high energy and thus π -contribution is very low. Paramagnetic resonance experiments³⁸ have shown the existence of some π -bonding in $[\text{IrCl}_6]^{2-}$ and $[\text{IrBr}_6]^{2-}$. Microwave spectroscopy³⁹ supports this and also indicates that the π -bonding decreases from chloride to iodide.

(2) Preparation of Dibromobis(triphenylphosphine) Zinc(II), $(\text{PPh}_3)_2\text{ZnBr}_2$

A hot alcoholic solution of triphenylphosphine (6.5 g, 25 mmol; 150 ml) was slowly added to a stirred hot solution of zinc bromide (1.7 g, 12.5 mmol; 50 ml). The resulting solution was stirred for an additional half hour when white crystals separated out, which were

CHAPTER III

SYNTHESIS

Preparation

All reactions were carried out under an inert atmosphere of nitrogen in ethyl alcohol (absolute) as solvent, hereafter referred to as alcohol.

(A) Preparation of Triphenylphosphine Complexes
of IB and IIB Metal Halides

(1) Preparation of Dichlorobis(triphenylphosphine) Zinc(II),
(Pph₃)₂ZnCl₂

An alcoholic solution of triphenyl phosphine (13.0 g, 50 mmol; 100 ml) was slowly added to a stirred hot solution of anhydrous zinc chloride in alcohol (3.4 g, 25 mmol; 200 ml) and the resulting solution was evaporated to half its original volume on a steam bath. On cooling, dull white crystals separate which were filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 30 per cent.

(2) Preparation of Dibromobis(triphenylphosphine) Zinc(II),
(Pph₃)₂ZnBr₂

A hot alcoholic solution of triphenylphosphine (6.5 g, 25 mmol; 150 ml) was slowly added to a stirred hot solution of zinc bromide (1.7 g, 12.5 mmol; 50 ml). The resulting solution was stirred for an additional half hour when white crystals separated out, which were

filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 82 per cent.

(3) Preparation of Diiodobis(triphenylphosphine) Zinc(II), $(Pph_3)_2ZnI_2$

To a hot alcoholic solution of zinc iodide (8.0 g, 25 mmol; 100 ml) was added slowly with stirring a hot alcoholic solution of triphenylphosphine (13.0 g, 50 mmol; 100 ml). The yellow color of zinc iodide becomes colorless. After heating for a half hour and cooling, dull white crystals separated which were collected by filtration, washed with alcohol and ether and dried overnight in vacuum. The yield was 80 per cent.

(4) Preparation of Dichlorobis(triphenylphosphine) Cadmium(II), $(Pph_3)_2CdCl_2$

A hot alcoholic solution of triphenylphosphine (13.0g, 50 mmol; 150 ml) was slowly added with stirring to a hot alcoholic solution of cadmium chloride (4.5 g, 25 mmol; 300 ml). On cooling, well formed white crystals separated which were collected by filtration, washed with alcohol and ether and dried in vacuum overnight. The yield was 80 per cent.

(5) Preparation of Dibromobis(triphenylphosphine) Cadmium(II), $(Pph_3)_2CdBr_2$

To a hot alcoholic solution of triphenylphosphine (7.0 g, 25 mmol; 125 ml) was slowly added with stirring to an alcoholic solution of cadmium bromide (3.4 g, 12.5 mmol;

75 ml). Stirring, with refluxing, continued for half an hour and then the reaction mixture cooled. White crystals separated which were collected by filtration, washed with alcohol, followed by ether and dried overnight in vacuum. The yield was 72 per cent.

(6) Preparation of Diiodobis(triphenylphosphine) Cadmium(II), $(Pph_3)_2CdI_2$

A hot alcoholic solution of triphenylphosphine (13.0 g, 50 mmol; 150 ml) was slowly added with stirring to a hot alcoholic solution of cadmium iodide (9.0 g, 25 mmol; 300 ml). There appeared a bulky white precipitate which was filtered, washed with alcohol and ether and dried overnight in vacuum. The yield was 95 per cent.

(7) Preparation of Dichlorobis(triphenylphosphine) Mercury(II), $(Pph_3)_2HgCl_2$

A hot alcoholic solution of mercury(II) chloride (2.5 g, 9.0 mmol; 75 ml) was added rapidly with stirring into a hot alcoholic solution of triphenylphosphine (5.5 g, 20 mmol; 100 ml) and the resulting solution was refluxed for a half hour. On cooling, white microcrystals separated which were collected by filtration, washed with alcohol and ether and dried in vacuum overnight. The yield was 81 per cent.

(8) Preparation of Dibromobis(triphenylphosphine) Mercury(II), $(\text{Pph}_3)_2\text{HgBr}_2$

To a hot alcoholic solution of mercury(II) bromide (3.6 g, 10 mmol; 150 ml) was added with stirring a hot alcoholic solution of triphenylphosphine (5.0 g, 20 mmol; 250 ml). There was an immediate separation of white crystals which were collected by filtration, washed with alcohol and ether, and dried overnight in vacuum. The yield was 81 per cent.

(9) Preparation of Diiodobis(triphenylphosphine) Mercury(II), $(\text{Pph}_3)_2\text{HgI}_2$

A hot alcoholic solution of mercury(II) iodide (4.18 g, 10 mmol; 50 ml) was rapidly stirred into a hot alcoholic solution of triphenylphosphine (5.5 g, 20 mmol; 250 ml). Refluxed for half an hour when a pale yellow precipitate was formed. The product was filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 83 per cent.

(B) Preparation of Ditertiary Phosphine, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, Complexes of IB and IIB Metal Halides

(1) Preparation of Dichloro(ditertiaryphosphine) Zinc(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{ZnCl}_2$

An alcoholic solution of anhydrous zinc chloride (0.18 g, 1.35 mmol; 5 ml) was added with stirring to an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 25 ml). The resulting solution was refluxed under

nitrogen for two hours. On cooling white crystals of phosphine complex separated which were filtered from the solution, washed with alcohol and ether, and dried in vacuum overnight. The yield was 42 per cent.

(2) Preparation of Dibromo(ditertiary phosphine) Zinc(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{ZnBr}_2$

A hot alcoholic solution of anhydrous zinc bromide (0.30 g, 1.35 mmol; 10 ml) was added to a well-stirred alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 25 ml). The resulting solution was refluxed under nitrogen for two hours. During the refluxing white crystals separated which were filtered from the reaction mixture, washed with alcohol and ether, and dried overnight in vacuum. The yield was 37 per cent.

(3) Preparation of Dichloro(ditertiary phosphine) Cadmium(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{CdCl}_2$

An alcoholic solution of hydrated cadmium chloride, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, (0.31 g, 1.35 mmol; 10 ml) was added dropwise to an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 20 ml) with stirring under nitrogen atmosphere. The resulting solution was refluxed for an hour during which white crystals of the product separated out. The crystals were filtered from the solution, washed with alcohol and ether, and dried overnight in vacuum. The yield was 47 per cent.

(4) Preparation of Dibromo(ditertiary phosphine) Cadmium(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{CdBr}_2$

An alcoholic solution of cadmium bromide tetrahydrate (0.46 g, 1.35 mmol; 20 ml) was added slowly into a stirred alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 20 ml) under nitrogen and refluxed for 30 minutes. During mixing white crystals of the desired product separated out. The crystals were collected by filtration, washed with alcohol and ether, and dried in vacuum overnight. The yield was 30 per cent.

(5) Preparation of Diiodo(ditertiary phosphine) Cadmium(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{CdI}_2$

An alcoholic solution of anhydrous cadmium iodide (0.46 g, 1.35 mmol; 15 ml) was rapidly added to a stirred alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 25 ml). The resulting solution was refluxed under nitrogen for two hours. The white crystals of the product, ditertiary phosphine cadmium iodide complex, were filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 25 per cent.

(6) Preparation of Dichloro(ditertiary phosphine) Mercury(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{HgCl}_2$

An alcoholic solution of mercury(II) chloride (0.37 g, 1.35 mmol; 20 ml) was added with stirring to a hot alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 25 ml). The resulting solution was refluxed

under nitrogen for two hours. White crystals of the product separated which were collected by filtration, washed with alcohol and ether, and dried overnight in vacuum. The yield was 33 per cent.

(7) Preparation of Diiodo(ditertiary phosphine) Mercury (II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{HgI}_2$

To an alcoholic solution of anhydrous mercury(II) iodide (0.61 g, 1.35 mmol; 30 ml) was added with stirring an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 20 ml). The resulting solution was refluxed under nitrogen for 2.5 hours. The white crystals of the complex separated out which were removed by filtration, washed with alcohol and ether, and dried in vacuum. The yield was 57 per cent.

(8) Preparation of Chloro(ditertiary phosphine) Copper(I), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)_2\text{CuCl}$

Freshly prepared anhydrous copper(I) chloride (0.134 g, 1.35 mmol; 20 ml) in alcohol was added to a stirred alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 15 ml). The resulting solution was refluxed under nitrogen for one hour. A white crystalline solid separated which was collected by filtration, washed with alcohol and ether, and dried overnight in vacuum. The yield was 50 per cent.

(9) Preparation of Bromo(ditertiary phosphine) Copper (I),
 $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})_2)\text{CuBr}$

Copper(I) bromide was prepared by heating an aqueous solution of copper(II) chloride (5 g) with hydrobromic acid and copper turnings until the solution became colorless. The clear solution was filtered hot into distilled water when a creamy white precipitate separated which was removed by filtration, washed well with distilled water and a little alcohol and dried overnight in vacuum.

Dried copper(I) bromide in alcohol (0.197 g, 1.35 mmol; 15 ml) was refluxed with an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 15 ml) under nitrogen for 1.5 hours. The white crystals formed were filtered from the solution, washed with alcohol, dried overnight in vacuum. The yield was 68 per cent.

(10) Preparation of Chloro(ditertiary phosphine) Silver(I),
 $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})_2)\text{AgCl}$

Freshly prepared silver(I) chloride obtained by mixing equimolar aqueous solutions of sodium chloride and silver nitrate, was dissolved in alcohol (0.2 g, 1.35 mmol; 20 ml) and added slowly with stirring to an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 15 ml). The resulting solution was refluxed under nitrogen for two hours. The white crystals formed were filtered from the solution, washed with alcohol and dried overnight in vacuum. The yield was 67 per cent.

(11) Preparation of Dichloro(ditertiary phosphine) Gold(II),
 $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)\text{AuCl}_2$

An alcoholic solution of auric chloride (0.4 g, 1.35 mmol; 4 ml) was added to an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 20 ml) with stirring. The resulting solution was refluxed under nitrogen for two hours. The white crystalline material was filtered from the solution, washed several times with alcohol and dried in vacuum overnight. The yield was 24 per cent.

(12) Preparation of Dichloro(ditertiary phosphine)
Nickel(II), $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Pph}_2)\text{NiCl}_2$

To an alcoholic solution of nickel(II) chloride hexahydrate (0.32 g, 1.35 mmol; 15 ml) was added an alcoholic solution of ditertiary phosphine (0.54 g, 1.35 mmol; 60 ml), slowly with constant stirring. The resulting solution was stirred at 60°C for one hour under nitrogen. The orange colored crystals which separated out during this one hour were filtered from the solution, washed with alcohol and dried in vacuum overnight. The yield was 46 per cent.

(13) Preparation of Dichloro(ditertiary arsine) Gold(II),
 $(\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2)\text{AuCl}_2$

An alcoholic solution of auric chloride (0.304 g, 1 mmol; 10 ml) was added with stirring to an alcoholic

(C) Preparation of Ditertiary Arsine,
 $(C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$, Complexes
 of IB and IIB Metal Halides

(1) Preparation of Chloro(ditertiary arsine) Copper(I),
 $(Ph_2As(CH_2)_2AsPh_2)CuCl$

An alcoholic solution of freshly prepared dried copper(I) chloride (0.098 g, 1 mmol; 10 ml) was added to an alcoholic solution of ditertiary arsine (0.50 g, 1 mmol; 15 ml) and the resulting solution was refluxed under nitrogen for two hours. The white crystals of the diarsine-copper complex were filtered from the solution, washed with alcohol and ether and, dried in vacuum overnight. The yield was 45 per cent.

(2) Preparation of Bromo(ditertiary arsine) Copper(I),
 $(Ph_2As(CH_2)_2AsPh_2)CuBr$

An alcoholic solution of freshly prepared dry copper(I) bromide (0.143 g, 1 mmol; 10 ml) was added to an alcoholic solution of ditertiary arsine (0.50 g, 1 mmol; 20 ml) with stirring. The resulting solution was refluxed under nitrogen for two hours. The white crystals formed were filtered from the solution, washed with alcohol and dried overnight in vacuum. The yield was 80 per cent.

(3) Preparation of Dichloro(ditertiary arsine) Gold(II),
 $(Ph_2As(CH_2)_2AsPh_2)AuCl_2$

An alcoholic solution of auric chloride (0.304 g, 1 mmol; 10 ml) was added with stirring to an alcoholic

solution of ditertiary arsine (0.50 g, 1 mmol; 15 ml). The resulting solution was refluxed under nitrogen for two hours. The white crystals were filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 29 per cent.

(4) Preparation of Dichloro(ditertiary arsine) Mercury(II),
 $(\text{Ph}_2\text{As}(\text{CH}_2)_2)_2\text{AsPh}_2\text{HgCl}_2$

To a hot alcoholic solution of mercury(II) chloride (0.271 g, 1 mmol; 5 ml) was added a hot alcoholic solution of ditertiary arsine (0.50 g, 1 mmol; 10 ml) under nitrogen with stirring. The resulting solution was refluxed for two hours. The white crystals formed were filtered from the solution, washed with alcohol and dried overnight in vacuum. The yield was 59 per cent.

(5) Preparation of Dibromo(ditertiary arsine) Mercury(II),
 $(\text{Ph}_2\text{As}(\text{CH}_2)_2)_2\text{AsPh}_2\text{HgBr}_2$

An alcoholic solution of mercury(II) bromide (0.45 g, 1 mmol; 20 ml) was added to an alcoholic solution of ditertiary arsine (0.50 g, 1 mmol; 15 ml) under nitrogen. The resulting solution was refluxed for two hours. The white crystals formed were filtered from the solution, washed with alcohol and ether and dried overnight in vacuum. The yield was 80 per cent.

CHAPTER IV

ELEMENTAL ANALYSIS

(A) Carbon and Hydrogen

Samples of the complexes, dichloro(ditertiary arsine) mercury(II) and diiodo(ditertiary phosphine) cadmium(II) were sent for analysis to M-H-W Laboratories, P. O. Box 326, Garden City, Michigan 48135. The remainder of the samples were sent to Crobaugh Laboratories, 3800 Perkins Avenue, Cleveland, Ohio 44114.

(B) Halogen Analysis

The halogens were determined by potentiometric titration and by the Volhard method.

A few milligrams of the sample was treated with 100 ml of dilute sodium hydroxide solution and a few drops of 3 per cent hydrogen peroxide were added. The solution was heated to boiling, cooled, and then acidified with dilute nitric acid. The acidified solution was filtered, the residue washed several times with distilled water and the washings were collected in the filtrate. This solution was titrated potentiometrically using standard silver nitrate solution (0.0499 N). This method was found to be suitable for complexes of IIB, but not for IB metals. For IB metal complexes, halogen determination was done using the Volhard method.

Complexes of IB metals were brought into solution by the same procedure as in the case of the potentiometric method. The pH of the solution was adjusted to between 6 and 7. A few drops of potassium chromate (5 per cent) was added and the solution was titrated against standard silver nitrate until a first permanent orange-colored precipitate appears.

(C) Determination of Metals

Reagents: Standard 0.01 F EDTA solution

pH 10 buffer solution

6 N sodium hydroxide

Erichrome Black T

Buffer solution: 3.5 g ammonium chloride and 30 ml of conc. ammonia were mixed and diluted with water to 50 ml.

Erichrome Black T: 0.2 g of Erichrome Black T was ground with 300 g of reagent grade sodium chloride.

(1) Determination of Zinc

Procedure

A carefully weighed sample of zinc-phosphine complex, in the range 0.2 - 0.3 g, was transferred into a Kjeldahl flask to which were added a few mls of conc. nitric acid and a few mls of conc. hydrochloric acid. The complex was then digested at 70-80°C for about two hours. During this period all the brown fumes disappeared and the solution became clear. The resulting solution was

filtered; the flask was washed carefully several times with distilled water and poured over the residue.

Dilute sodium hydroxide was added with stirring until a slight turbidity developed. Twenty milliliters of distilled water and 5 ml of buffer solution (pH = 10) was then added. Approximately 0.1 g of Erichrome Black T was added. The solution became deep red in color. This solution was titrated against standard (0.01 F) EDTA until the color changed from red to pure blue.

(2) Determination of Nickel

Reagents: Standard EDTA solution (0.01 F)

6 N Ammonia

Murexide indicator

Murexide indicator: 0.01 g of murexide was ground with 2.0 g of sodium chloride.

Procedure

Digestion was done in a manner similar to that of the zinc complexes. Dilute ammonia was added to the acidic filtrate until the pH was 10. Murexide indicator was added until the color became yellow. The yellow colored solution was titrated against standard EDTA.

(3) Determination of Copper by Iodometric Method

Reagents: Standard sodium thiosulfate (0.01 F)

Solid potassium iodide

Potassium thiocyanate

One per cent starch solution

1:1 hydrochloric acid

Procedure

A carefully weighed (0.2 to 0.3 g) sample of the phosphine complex was digested with 5-10 ml each of concentrated nitric and hydrochloric acids until the brown fumes disappeared. When the solution turned clear blue it was filtered into an Erlenmeyer flask and washed several times with distilled water and the washings were collected in the same flask.

To the solution was added 175 ml of distilled water, 5 ml of 1:1 hydrochloric acid and 10 ml of potassium iodide containing 2 g KI. The resulting solution was titrated against standard sodium thiosulfate solution until the color changed to pale-yellow. To this solution one gram of potassium thiocyanate and 5 ml of one per cent starch solution was added. Titration was continued until the blue color just disappeared.

CHAPTER V

RESULTS AND DISCUSSION

The synthesis of complexes of group IB and IIB metal halides with ditertiary phosphine and ditertiary arsine ligands has been accomplished.

The complexes were characterized by elemental analysis, melting point, color, and magnetic susceptibility measurements. Molecular weight determination and conductance measurements could not be carried out because of their very poor solubility in most of the common organic solvents.

Attempted preparation of arsine complexes of zinc, cadmium halides and gold chloride were unsuccessful.

TABLE 5

Compound	M.P. (°C)	% Found				% Calc			
		C	H	Hal.	Metal	C	H	Hal.	Metal
ZnCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	295	58.21	4.24	13.31	11.6	58.39	4.49	13.27	12.10
ZnBr ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	265	50.32	3.78	25.49	10.28	50.03	3.84	25.65	10.41
CdCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	257	53.76	4.15	10.31		45.77	3.52	10.40	
CdBr ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	267	46.32	3.53	23.85		46.52	3.58	23.85	
CdI ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	280	40.88	2.99	33.45		40.84	3.14	33.25	
HgCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	280	55.53	4.23	10.56		46.57	3.58	10.59	
HgI ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	247	36.24	2.68	29.41		36.58	2.81	29.78	
CuCl(Pph ₂ CH ₂ CH ₂ Pph ₂)	236	55.91	4.70	7.35	12.70	62.79	4.83	7.13	12.78
CuBr(Pph ₂ CH ₂ CH ₂ Pph ₂)	280	57.39	4.11	14.37	11.88	57.63	4.43	14.77	11.74
AgCl(Pph ₂ CH ₂ CH ₂ Pph ₂)	277	57.51	4.31	6.55		57.64	4.43	6.54	
AuCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	265								
CoCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂) ₂	186	63.80	4.86	7.55		67.38	5.18	7.65	
NiCl ₂ (Pph ₂ CH ₂ CH ₂ Pph ₂)	260	58.89	4.43	13.15	11.12	59.12	4.55	13.43	11.12
HgCl ₂ (AsPh ₂ CH ₂ CH ₂ AsPh ₂)	196	41.11	3.06	9.28		41.19	3.16	9.36	

Table 5 (continued)

HgI ₂ (AsPh ₂ CH ₂ CH ₂ AsPh ₂)	167	33.27	2.33	26.97		33.17	2.55	27.00	
CuCl(AsPh ₂ CH ₂ CH ₂ AsPh ₂)	207	50.88	3.63	6.27	10.58	53.34	4.10	6.06	10.86
CuBr(AsPh ₂ CH ₂ CH ₂ AsPh ₂)	183	49.30	3.59	12.58	10.27	49.57	3.81	12.70	10.09
AuCl ₂ (AsPh ₂ CH ₂ CH ₂ AsPh ₂)	192								
CdCl ₂ (PPh ₃) ₂	298	61.82	4.37	9.95		61.02	4.24	10.02	
CdBr ₂ (PPh ₃) ₂	225	53.98	3.66	20.10		54.23	3.76	19.75	
CdI ₂ (PPh ₃) ₂	238	48.41	3.37	28.51		48.54	3.37	28.52	
HgCl ₂ (PPh ₃) ₂	273	35.15	3.73	8.93		34.34	3.77	8.99	
HgBr ₂ (PPh ₃) ₂	252			18.00		48.87	3.39	18.09	
HgI ₂ (PPh ₃) ₂	217	44.00	3.27	25.73		44.17	3.06	25.97	
CuCl(PPh ₃)	194-203			9.74	16.3	59.50	4.13	9.76	17.6

TABLE 6

Compound	M.P. (°C)	% Found				% Calc.			
		C	H	Hal.	Metal	C	H	Hal.	Metal
ZnCl ₂ (Pph ₃) ₂	298	65.34	4.64	10.64	9.89	65.39	4.54	10.74	9.84
ZnBr ₂ (Pph ₃) ₂	192	57.52	4.4	21.25	8.74	57.62	4.00	21.36	8.66
ZnI ₂ (Pph ₃) ₂	250	51.03	3.75	30.27	7.71	51.75	3.59	30.13	7.71
CdCl ₂ (Pph ₃) ₂	298	61.82	4.37	9.95		61.02	4.24	10.02	
CdBr ₂ (Pph ₃) ₂	223	53.98	3.66	20.10		54.23	3.76	19.75	
CdI ₂ (Pph ₃) ₂	238	48.41	3.37	28.51		48.54	3.37	28.52	
HgCl ₂ (Pph ₃) ₂	273	35.15	3.73	8.93		54.34	3.77	8.99	
HgBr ₂ (Pph ₃) ₂	252			18.00		48.87	3.39	18.09	
HgI ₂ (Pph ₃) ₂	217	44.00	3.27	25.73		44.17	3.06	25.97	
CuCl(Pph ₃)	194-203			9.74	16.3	59.50	4.13	9.76	17.6

BIBLIOGRAPHY

1. C. A. 52, 14679 (1958).
2. Evans, R. C., Mann, F. G., Feiser, H. S., and Purdie, D., J. Chem. Soc., 1209 (1940).
3. Cahours, A. and Gal, H., Ann. Chem. Liebigs, 155, 223 (1870); Ann. Chem. Liebigs, 155, 355 (1870); Ann. Chem. Liebig, 156, 302 (1870).
4. Booth, G., Adv. Inorg. Chem. Radiochem., 6, 1 (1964).
5. Bailar, J. C. Jr., Editor, The Chemistry of the Coordination Compounds, Van Nostrand-Reinhold, New York, 1956, p. 131.
6. Basolo, F. and Pearson, R. G., Mechanisms of Inorganic Reactions, 2nd Ed., Wiley and Sons, New York, 1967.
7. Nyholm, R. S., Rev. Pure Appl. Chem. (Australia), 4, 15 (1954).
8. Emeleus, H. J. and Anderson, J. S., Modern Aspects of Inorganic Chemistry, Routledge and Kegan Paul Ltd., 3rd Ed., 1960, p. 181.
9. Sidgwick, N. V., Electronic Theory of Valency, Oxford University Press, London, 1927.
10. Pauling, L., The Nature of The Chemical Bond, Cornell University Press, New York, 3rd Ed., 1960, p. 145.
11. Mullikan, R. S., J. Am. Chem. Soc., 72, 4493 (1950).
12. Craig, D. P., Maccoll, ., Nyholm R. S., Orgel, L. E., and Sutton, G. J., J. Chem. Soc., 332 (1954).

13. Pauson, P. L., Proc. Chem. Soc., 297 (1960).
14. Nyholm, R. S., Biochem. Soc. Symp., 1 (1958).
15. Reference #6, p. 161.
16. Huggins, ., J. Chem. Phys., 5, 527 (1937).
17. Taube, H., Chem. Rev., 50, 69 (1952).
18. Burstall, . and Nyholm, R. S., J. Chem. Soc., 3570 (1952).
19. Nyholm, R. S., Proceedings 10th Solvay Congress, Brussels, 1956.
20. Orgel, L. E., An Introduction to Transition Metal Chemistry, Methuen and Co., Ltd., London, 1960.
21. Orgel, L. E., Proceedings 10th Solvay Congress, Brussels, 1956.
22. Griffith, W. P. and Orgel, L. E., Quart. Rev., 11, 381 (1957).
23. Orgel, L. E., J. Chem. Phys., 23, 1004 (1955).
24. Sutton, G. J., J. Chem. Ed., 37, 398 (1960).
25. George, P. and McClure, D. S., Progress in Inorganic Chemistry, 1, 381 (1959).
26. Gillespie, R. J. and Nyholm, R. S., Quart. Rev., 11, 339 (1957).
27. Hartmann, H., J. Inorg. Nucl. Chem., 8, 64 (1958).
28. Pauling, L., J. Chem. Soc., 1461 (1948).
29. Kabesh, A. and Nyholm, R. S., J. Chem. Soc., 3245 (1951).

30. Chatt, J., Nature, 165, 637 (1950).
31. Nyholm, R. S., "Tilden Lecture," Proc. Chem. Soc., August, 1961.
32. Ahrland, S., Chatt, J., and Davies, N. R., Quart. Rev., 12, 265 (1958).
33. Wilkinson, G., J. Am. Chem. Soc., 73, 5501 (1951).
34. Malatesta, L., Progress in Inorganic Chemistry, Interscience Publishers, Inc., New York, Vol. 1, p. 283, 1959.
35. Irvine, J. W. and Wilkinson, G., Science, 113, 742 (1951).
36. Nyholm, R. S., J. Chem. Soc., 2602 (1951).
37. Nyholm, R. S. and Parish, R. V., Chem. and Ind., 470 (1956).
38. Owen, J., J. Inorg. Nucl. Chem., 8, 430 (1958).
39. Gordy, W., Discuss. Faraday Soc., 19, 14 (1955).