❖ Tertiary Phosphine as Ligand

The compound phosphine (PH_3) is extremely important in coordination chemistry due to its large number of derivatives which can be used as L-type ligands (2 electron donor neutral ligands) for many metal complexes. These phosphine based ligands are the compounds with the formula PR_nH_{3-n}, and are often classified according to the value of n; the values 1, 2, 3 correspond to primary, secondary and tertiary phosphines, respectively. For instance, the most popular phosphine ligand used is organometallic chemistry is triphenylphosphine, which is obviously a tertiary phosphine. All of these phosphine ligands adopt pyramidal structures that are quite favorable for the metal center to be approached. Unlike most metal ammine complexes, metal phosphine complexes tend to be lipophilic, showing very good solubility in organic solvents. They also are compatible with metals in multiple oxidation states. Therefore, owing to these two features, metal phosphine complexes are quite useful in homogeneous catalysis.

➢ General Methods of Preparation and Reactivity

The first phosphine complexes were *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$, reported by Cahours and Gal in 1870. Being a L-type ligand, the phosphines do not change the overall charge of the metal complex. These complexes may simply be prepared by the addition of phosphines to a coordinatively unsaturated metal precursor, or by ligand displacement of another L-type complex, such as a solvent molecule acting as a ligand. However, it should also be noted that the replacement of X-type ligand (1-electron donor neutral ligand) can also yield such complexes.
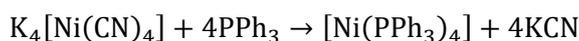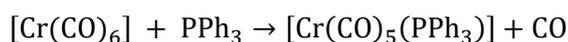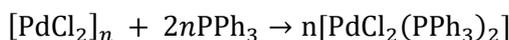
$$[PdCl_2]_n \ + \ 2n PPh_3 \rightarrow n[PdCl_2(PPh_3)_2]$$

$$[Cr(CO)_6] \ + \ PPh_3 \rightarrow [Cr(CO)_5(PPh_3)] + CO$$

$$K_4[Ni(CN)_4] + 4PPh_3 \rightarrow [Ni(PPh_3)_4] + 4KCN$$

As far as the reactivity is concerned, the nature of phosphine ligands is a spectator rather than the actor. Coordinated phosphines generally do not participate in chemical reactions, except their dissociation from the metal center. However, in some high-temperature hydroformylation processes, the scission of phosphorus−carbon bonds is also observed. The thermal stability of phosphine ligands is enhanced when they are incorporated into pincer complexes. Some complexes dissociate in solutions to yield a product with a lower coordination number.

$$[Rh(PPh_3)_3Cl] \rightarrow [Rh(PPh_3)_2Cl] + PPh_3$$

$$[Pt(PPh_3)_3] + MeI \rightarrow [Pt(I)(Me)(PPh_3)_2] + PPh_3$$
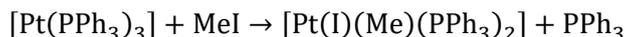
➢ *Structure and Bonding in of Tertiary Phosphine Complexes*

The metal-phosphine complexes are not considered as the organometallic compounds because of the lack of metal-carbon bonds. However, many good inorganic textbooks discuss them in their organometallic section due to their excellent bonding similarities with the carbonyl ligand. For instance, phosphines can act as very good σ-donors as well as respectable π acceptors just like CO ligand. The σ-donation occurs via a hybrid lone pair on phosphorus and the π-acceptance in orbitals that are a mixture of empty *d*-orbital on phosphorus and σ* of the phosphorus-carbon bond. For a long time in coordination chemistry, the pure empty *d*-orbitals of phosphorus were thought to be used for the acceptance of π-electron density; and this theory was also affirmed by the fact that as the R groups attached to phosphorus become more electronegative, phosphine becomes stronger π-acceptor and vice-versa. The concept of mixing of σ* of the phosphorus-carbon bond into empty *d*-orbitals of phosphorus was developed later on.


$3d$ σ*   π-acceptor
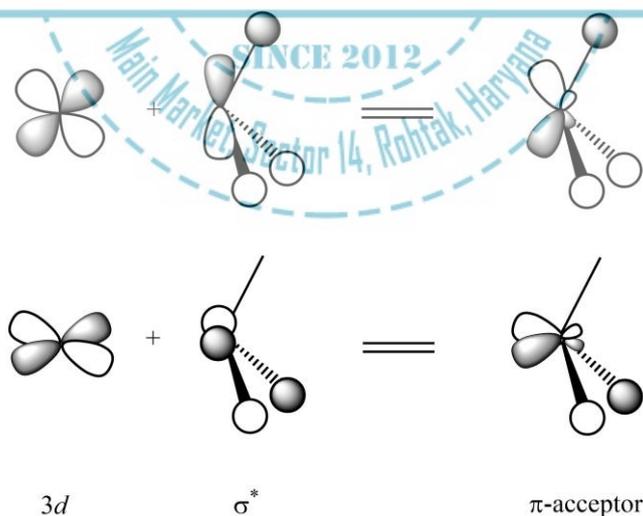
Figure 28. The π-acceptor orbitals of phosphines in metal-phosphine complexes.

Therefore, the nature of R groups in tertiary phosphines governs the relative donor-acceptor strength of the corresponding ligand. For instance, PMe$_3$ acts as a stronger σ donor than PF$_3$ due to the large electron-donating effect of the three methyl groups. However, it is a relatively weaker π-acceptor in comparison to PF$_3$, which easily be explained in terms of a larger electron-withdrawing effect of 3 fluorines. Hence, the σ-donor and π-acceptor strength of tertiary phosphines can be fine-tuned just by changing the R groups.

> ### *Steric and Electronic Properties*

The most valuable thing about tertiary phosphines as ligands is that their steric and electronic properties can easily be manipulated just by changes in one or more of the three organic substituents. This fine-tuning of the electronic and steric profile of phosphine ligands is of great importance in the manipulation of catalytic properties transition metals. The ligand cone angle and Tolman electronic parameter are used to categorize various phosphines on the basis of their steric and electronic behavior, respectively. However, these parameters are not just limited to phosphines but have been extended to other ligand types also.

1. Ligand cone angle: The ligand cone angle is a measure of the size of a ligand. It is defined as the solid angle formed with the metal at the vertex and the other atoms at the perimeter of the cone. Tertiary phosphine ligands are commonly classified using this parameter, but the method can be applied to any ligand. The term cone angle was introduced by the American chemist, Chadwick A. Tolman. Originally applied to phosphines (called Tolman cone angle), the cone angles were originally determined by taking measurements from accurate physical models of them. The concept of the cone angle is most easily visualized with symmetrical ligands, e.g. PR$_3$. Nevertheless, this approach has been refined to include less symmetrical ligands of the type PRR′R″ as well as diphosphines by using equation (1).

$$\theta = \frac{2}{3} \sum_i \frac{\theta_i}{2} \tag{1}$$

Where $\theta_i/2$ are the half of individual angles made by R, R′ and R″ on M−P bond. In the case of diphosphines, the $\theta_i/2$ of the backbone is estimated as half of the bite angle of chelate, taking a bite angle of 90°, 85° and 74°, for propylene, ethylene and diphosphines with methylene backbones, respectively.
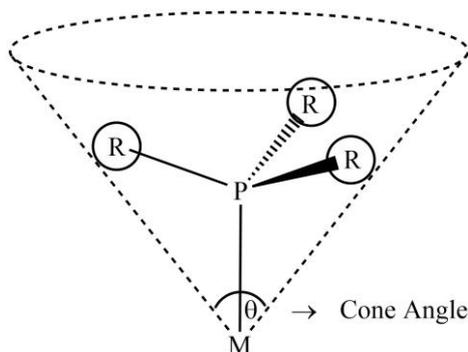

Figure 29. The ligand cone angle in metal-phosphine complexes.

The ligand-cone-angle method accepts empirical bond data and considers the perimeter as the maximum possible circumscription of a substituent which spins freely. The concept of solid-angle derives the bond length and the perimeter from the empirical crystal structure profile obtained from X-ray diffraction of solid sample. Each system has its own advantages. The exact cone angle (θ) can be found if the geometry of a ligand is known from either crystallography or computational studies. Unlike the Tolman route, no assumptions regarding the geometry are made. The cone-angle-concept is practically important in homogeneous catalysis due to the affected reactivity of the metal center from the ligand size. In a famous example, the selectivity of hydroformylation catalysts is strongly affected by the size of the coligands attached. Now though phosphines are monovalent, some are large enough to fill more than half of the coordination sphere around the metal center. The values of the cone angles of selected ligands are given below.

Table 3. The cone angle values of selected ligands.

Ligand	Cone angle	Ligand	Cone angle
PH_3	87°	$P(Me)(PPh)_2$	136°
PF_3	104°	$P(CF_3)_3$	137°
$P(OMe)_3$	107°	$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	141°
$P(OEt)_3$	109°	PPh_3	145°
PMe_3	118°	$P(cyclo\text{-}C_6H_{11})_3$	170°
PCl_3	124°	$P(t\text{-}C_4H_9)_3$	182°
$P(Me)_3Ph$	127°	$P(C_6F_5)_3$	184°
PBr_3	131°	$P(o\text{-}C_6H_4CH_3)_3$	194°
PEt_3	132°	$P(mesityl)_3$	212°

The presence of bulky ligands (ligands with large cone angles) is found to enhance the rate of dissociation; which can be explained in terms of increased steric repulsion due to crowding around the metal center.

2. Tolman electronic parameter: The Tolman electronic parameter (TEP) is named after its inventor, Chadwick A. Tolman, and is a measure of the electron-donating or withdrawing strength of a ligand. It is determined by measuring the frequency of the A_1 vibrational mode of carbonyl stretching frequency of $Ni(CO)_3L$ complex by infrared spectroscopy, where L is the ligand being studied. The $Ni(CO)_3L$ is chosen as the model compound because such complexes can easily be prepared from $Ni(CO)_4$. Moreover, the carbonyl band is quite distinctive, and is rarely obscured by other bands in the observed infrared spectrum; and being a small ligand, steric factors are unable to complicate the analysis.
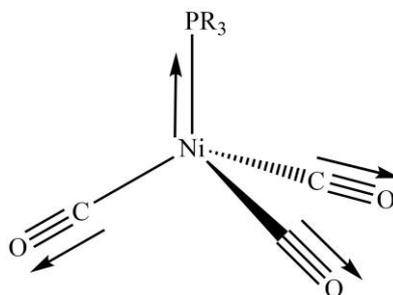
Figure 30. The A_1 stretch of $Ni(CO)_3L$ used to determine the TEP in metal-phosphine complexes.

Upon coordination to a metal, $\nu(CO)$ typically decreases from 2143 cm^{-1} of free CO. This can be explained by π backbonding i.e. the metal is able to form a π-bond with the carbonyl ligand by donating electrons through its d-orbitals into the empty antibonding π^* orbitals on CO. This increases the strength of metal–carbon bond, but also weakens the bond between carbon and oxygen. Moreover, the C–O bond is further weakened if other ligands present increase the π-electrons-density on the metal center, and ν_{CO} decreases. However, if other ligands compete with CO for π backbonding, ν_{CO} would increase. Tolman analyzed a series of seventy ligands in reference to P(t-Bu)$_3$, because three t-butyl groups make it as the strongest donor ligand. Consequently, the A_1 absorption band of carbonyl ligands in $Ni(CO)_3[P(t-Bu)_3]$ complex appears at the lowest wavenumber (2056.1 cm^{-1}), which is obviously due to the largest magnitude of back-bonding among all phosphines. Based on these observations, Tolman proposed a parameter χ_i to show the effect of individual substituents (R, R′, R″) on this band as accorded by equation (2):

$$\nu_{CO} = 2056.1 \text{ cm}^{-1} + \sum_{i=1}^{3} \chi_i \text{ cm}^{-1} \tag{2}$$

Now the calculation of the value of χ_i for each individual substituent in symmetrical phosphines can be done just by putting their observed spectral band. Let's say, we want to calculate the Tolman electronic parameter for PCl$_3$. The infrared absorption of A_1 symmetry for $Ni(CO)_3(PF_3)$ is observed at 2097.0 cm^{-1}. On putting this value for ν_{CO} in the equation (2), we get:

$$2097.0 \text{ cm}^{-1} = 2056.1 \text{ cm}^{-1} + \sum_{i=1}^{3} \chi_i \text{ cm}^{-1} \tag{3}$$

$$2097.0 \text{ cm}^{-1} = 2056.1 \text{ cm}^{-1} + 3 \times \chi_i(\text{Cl}) \text{ cm}^{-1} \tag{4}$$

$$\chi_i = 14.8 \text{ cm}^{-1} \tag{5}$$

The values of χ for different substituents are listed in 'Table 4'; which in turn can easily be used to calculate the theoretical position of A_1 absorption band in case of tertiary phosphine ligands in which R, R′, and R″ are not the same anymore.

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Table 4. Substituent χ Factors for Phosphine and Related Ligands.

Substituent	χ_i (cm^{-1})	Substituent	χ_i (cm^{-1})
–tBu	0.0	–OEt	6.8
–Cyclohexyl	0.1	–OMe	7.7
–iPr	1.0	–H	8.3
–Et	1.8	–OPh	9.7
–Me	2.6	–C_6H_5	11.2
–Ph	4.3	–Cl	14.8
–p-C_6H_4F	5.0	–F	18.2
–m-C_6H_4F	6.0	–CF_3	19.6

The Tolman electronic parameter (TEP) and the ligand cone angle are used to characterize the electronic and steric profile of phosphines, which are very popular ligands for catalysts.

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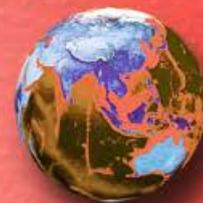
A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

MANDEEP DALAL

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