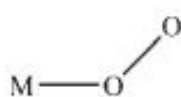


The experimental results show that the bent structure of dioxygen unit in oxyhemoglobin is actually diamagnetic in nature; which suggests that  $\pi^*2p_x$  and  $\pi^*2p_y$  orbitals are not completely degenerate in the complex as they are in free dioxygen. A linear M–O–O structure would result in degenerate set of  $\pi^*2p_x$  and  $\pi^*2p_y$  orbitals with a triplet state. In addition to the  $\sigma$ -bonding, there are two types of interactions between the  $d$ -orbitals of the metal and the  $\pi^*$  orbitals of the dioxygen. One is through an overlap of the  $3d_{xz}$  of the metal with the  $\pi^*$  orbitals perpendicular to the Fe–O–O plane: while the other is through the overlap of the  $3d$  orbital of the metal with the  $\pi^*$  orbital in the Fe–O–O plane. The different bridging modes of dinitrogen ligand are given below.

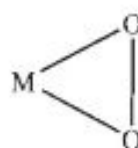
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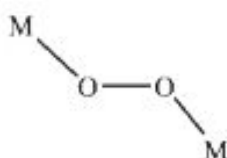
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End-on



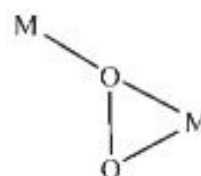
Side-on



End-on/End-on



Side-on/Side-on



End-on/Side-on

Figure 25. Bonding modes of  $O_2$  ligand in metal-dioxygen complexes.

The  $O_2$  ligand binds to a single metal centre either end-on ( $\eta^1$ -) or in a side-on ( $\eta^2$ -) manner. Dioxygen adducts derived from  $Co^{2+}$  and  $Fe^{2+}$  complexes of porphyrin (and related anionic macrocyclic ligands) exhibit this bonding mode. The hemoglobin and myoglobin are two famous examples, and many other synthetic analogues have been reported which behave in similar manner. Binding of  $O_2$  is usually described as proceeding by electron transfer from the metal(II) centre to give superoxide ( $O_2^-$ ) complexes of metal(III) centres. The  $\eta^2$ -bonding is the most common motif seen in coordination chemistry of dioxygen. Since  $O_2$  has a triplet ground state and Vaska's complex is a singlet, the reaction is slower than when singlet oxygen is used. Complexes containing  $\eta^2$ - $O_2$  ligands are fairly common, but most are generated using hydrogen peroxide, not  $O_2$ . The  $O_2$  can bind to one metal of a bimetallic unit via the same modes discussed above for mononuclear complexes. A well-known example in nature is hemerythrin, which features a diiron carboxylate that binds  $O_2$  at one Fe centre. The dinuclear complexes can also cooperate in the binding, although the initial attack of  $O_2$  probably occurs at a single metal. These binding modes include  $\mu^2$ - $\eta^2$ ,  $\eta^2$ -,  $\mu^2$ - $\eta^1$ ,  $\eta^1$ -, and  $\mu^2$ - $\eta^1$ ,  $\eta^2$ -. Depending on the degree of electron-transfer from the dimetal unit, these  $O_2$  ligands can again be described as peroxo or superoxo. In nature, such dinuclear dioxygen complexes often feature copper.

**Structure:** The structures of metal-dioxygen complexes can mainly be classified into two categories; the first one as the metal-complex that contain dioxygen ( $O_2$ ) ligand attached to one metal centre and the second one with  $O_2$  group connected to two or more metal centres. A brief discussion on both of the categories is given below with suitable examples.

*i) Mononuclear metal-dioxygen complexes:* As a ligand,  $O_2$  can bind to single metals centre either as an end-on ligand, or as an a side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

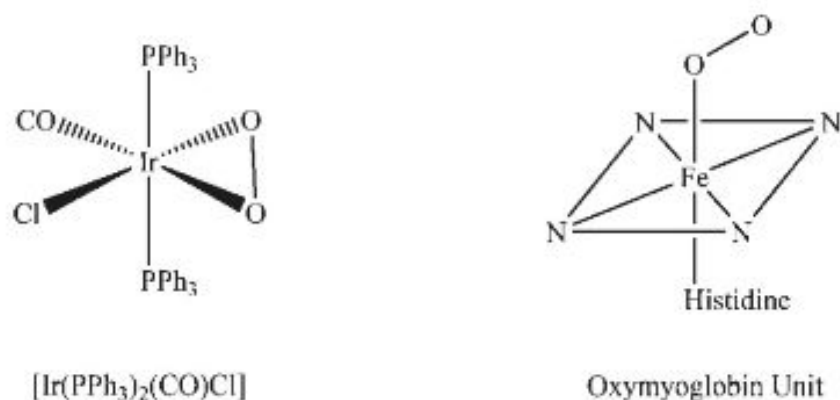


Figure 26. Mononuclear metal- $O_2$  complexes.

*ii) Binuclear metal-dioxygen complexes:* In binuclear metal-dioxygen complexes, the  $O_2$  molecule can bind either to one or both metals centre as an end-on/end-on, end-on/side-on and side-on/side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

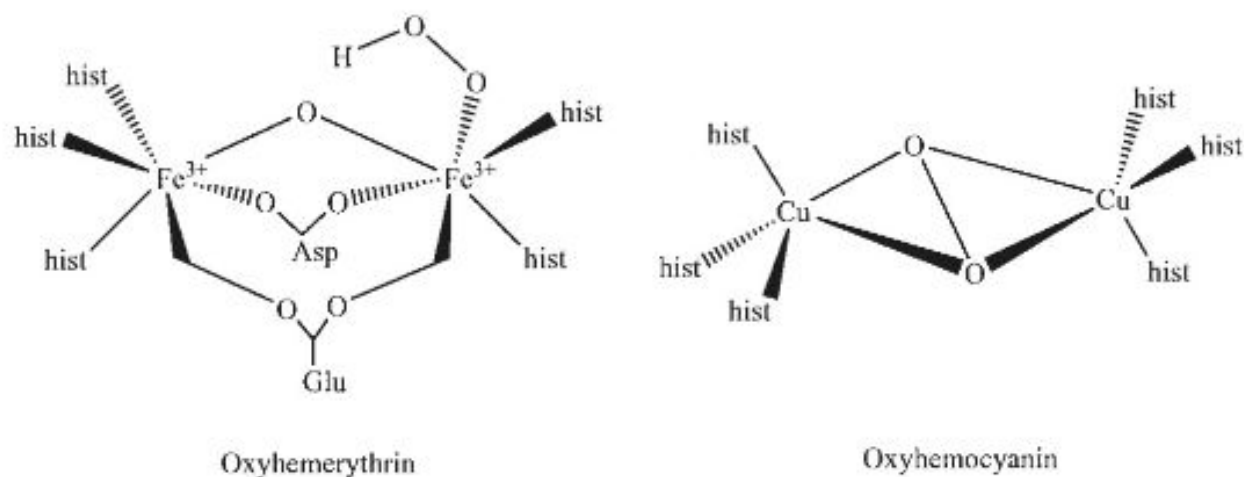
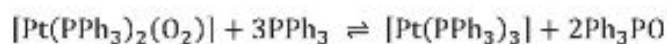
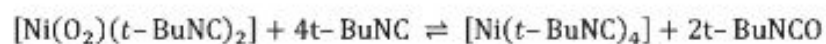
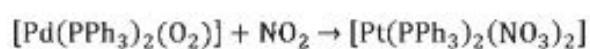
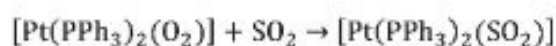
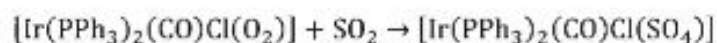


Figure 27. Metal-dioxygen complexes with side-on  $O_2$  ligand.

**Reactions:** i) The displacement of molecular oxygen by some other ligand:



ii) The formation of complexes of oxidized substrates:

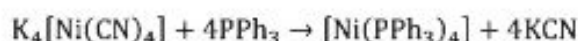
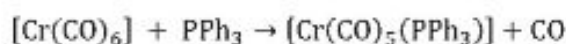
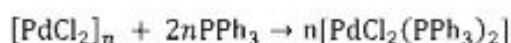


### ❖ Tertiary Phosphine as Ligand

The compound phosphine (PH<sub>3</sub>) 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<sub>n</sub>H<sub>3-n</sub>, 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 in organometallic chemistry is triphenylphosphine, which is obviously a tertiary phosphine. All of these phosphine ligands adopt pyramidal structures that is quite favourable for the metal centre 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<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], 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.



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



➤ **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 bond. 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  $\sigma$ -donors as well as respectable  $\pi$  acceptors just like CO ligand. The  $\sigma$ -donation occurs via a hybrid lone pair on phosphorus and the  $\pi$ -acceptance in orbitals that are mixture of empty  $d$ -orbital on phosphorus and  $\sigma^*$  of 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  $\pi$ -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  $\pi$ -acceptor and vice-versa. The concept of mixing of  $\sigma^*$  of phosphorus-carbon bond into empty  $d$ -orbitals of phosphorus was developed later on.

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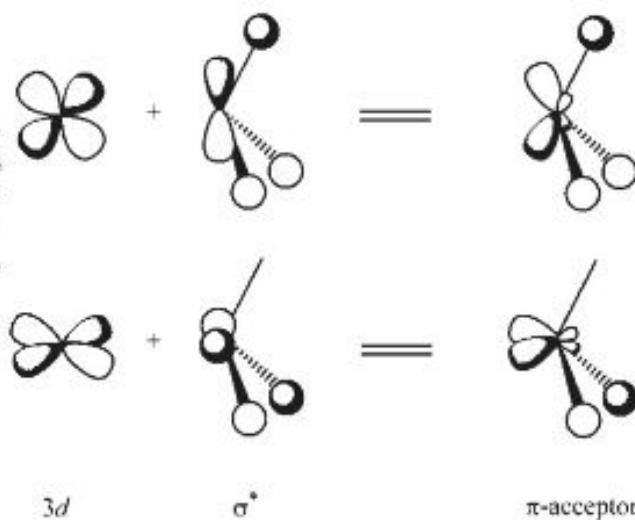


Figure 28.  $\pi$ -acceptor orbitals of phosphines in metal-phosphine complexes.

Therefore, the nature of R groups in tertiary phosphines governs the relative donor-acceptor strength of the corresponding ligand. For instance,  $\text{PMe}_3$  acts as a stronger  $\sigma$  donor than  $\text{PF}_3$  due to large electron-donating effect of the three methyl groups. However, it is a relatively weaker  $\pi$ -acceptor in comparison to  $\text{PF}_3$ , which easily be explained in terms of larger electron withdrawing effect of 3 fluorines. Hence, the  $\sigma$ -donor and  $\pi$ -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 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 behaviour, 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 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 cone angle is most easily visualized with symmetrical ligands, e.g.  $\text{PR}_3$ . Nevertheless, this approach has been refined to include less symmetrical ligands of the type  $\text{PRR}'\text{R}''$  as well as diphosphines by using equation (1).

$$\theta = \frac{2}{3} \sum_i \frac{\theta_i}{2} \quad (1)$$

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  $90^\circ$ ,  $85^\circ$  and  $74^\circ$ , for propylene, ethylene and diphosphines with methylene backbones, respectively.

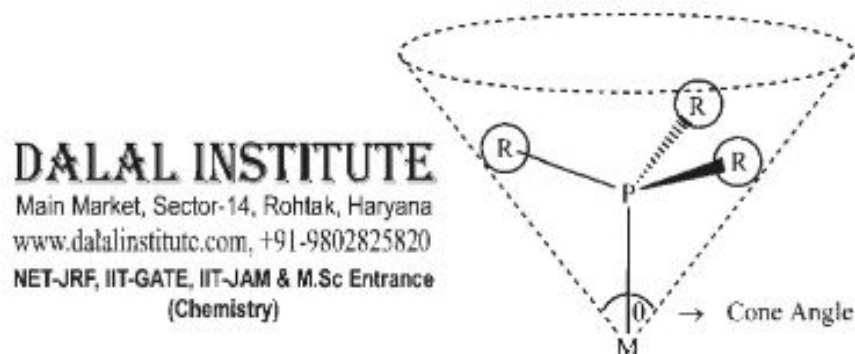


Figure 29. The ligand cone angle in metal-phosphine complexes.