

4.3: Phosphines

Learning Objectives

In this lecture you will learn the following

- Classification of ligands.
- Nature of bonding in phosphines.
- Steric and electronic properties of phosphines.
- Bonding in phosphines and CO.
- Cone angle and its application in catalysis.

Classification of Ligands by donor atoms

Ligand is a molecule or an ion that has at least one electron pair that can be donated. Ligands may also be called Lewis bases; in terms of organic chemistry, they are 'nucleophiles'.

Metal ions or molecules such as BF_3 (with incomplete valence electron shells (electron deficient) are called Lewis acids or electrophiles).

Why do molecules like H_2O or NH_3 give complexes with ions of both main group and transition metals. E.g $[\text{Al}(\text{OH}_2)_6]^{3+}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$

Why other molecules such as PF_3 or CO give complexes only with transition metals.

Although PF_3 or CO give neutral molecules such as $\text{Ni}(\text{PF}_3)_4$ or $\text{Ni}(\text{CO})_4$ or $\text{Cr}(\text{CO})_6$.

Why do, NH_3 , amines, oxygen donors, and so on, not give complexes such as $\text{Ni}(\text{NH}_3)_4$.

Classical or simple donor ligands

Act as electron pair donors to acceptor ions or molecules, and form complexes of all types of Lewis acids, metal ions or molecules.

Non-classical ligands, π -bonding or π -acid ligands: Form largely with transition metal atoms.

In this case special interaction occurs between the metals and ligands

These ligands act as both σ -donors and π -acceptors due to the availability of empty orbitals of suitable symmetry, and energies comparable with those of metal t_{2g} (non-bonding) orbitals.

e.g. Consider PR_3 and NH_3 : Both can act as bases toward H^+ , but P atom differs from N in that PR_3 has σ^* orbitals of low energy, whereas in N the lowest energy d orbitals or σ^* orbitals are far too high on energy to use.

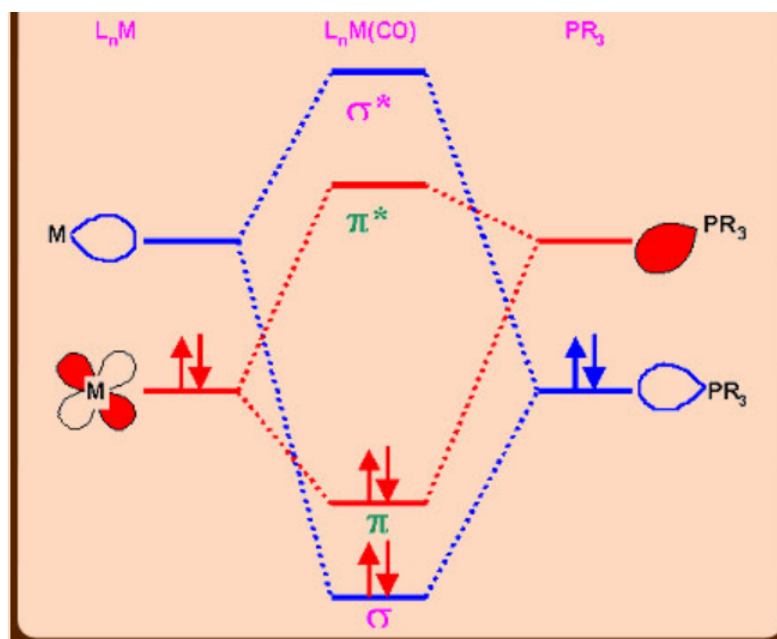
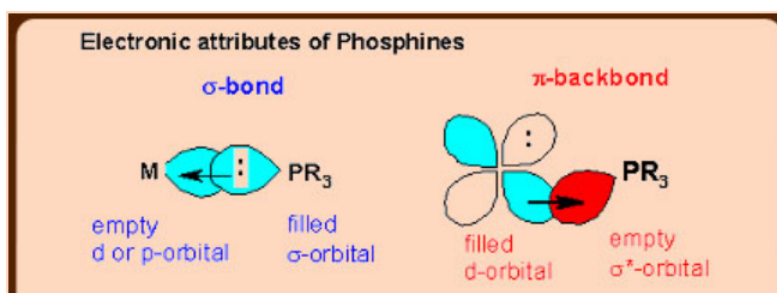
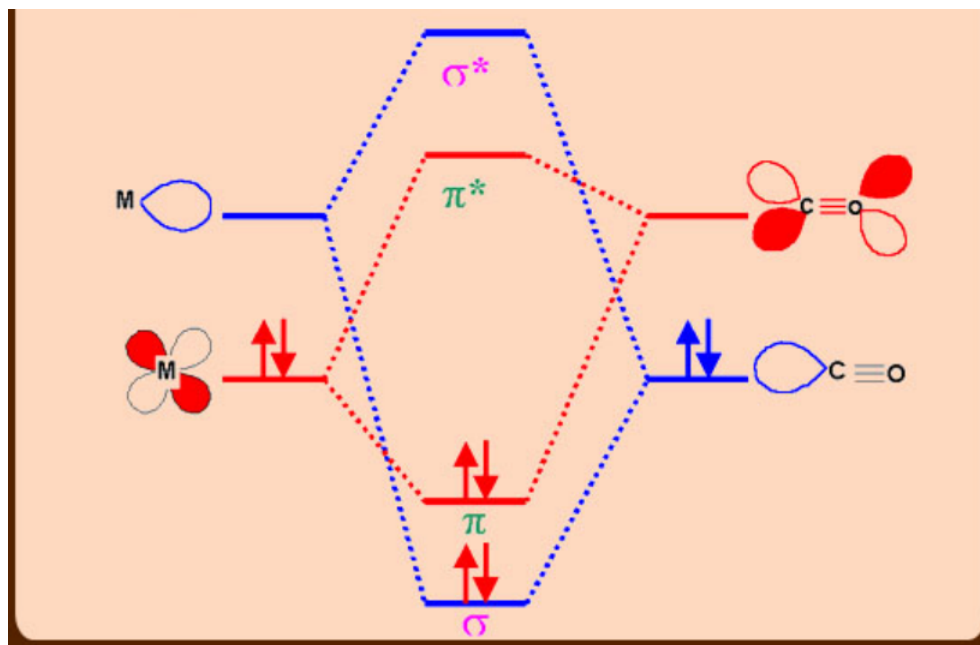
Consider CO that do not have measurable basicity to proton, yet readily reacts with metals like Ni that have high heats of atomization to give compounds like $\text{Ni}(\text{CO})_4$.

Ligands may also be classified electronically depending upon how many electrons that they contribute to a central atom. Atoms or groups that can form a single covalent bond are one electron donors.

EXAMPLES: F, SH, CH_3 etc.,

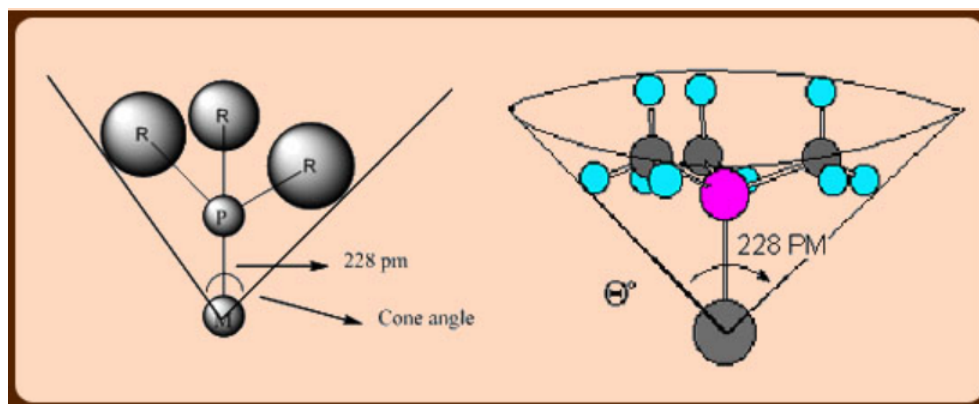
Compounds with an electron pair are two-electron donors

EXAMPLE: NH_3 , H_2O , PR_3 etc.,



Steric factors in phosphines (Tolman's cone angle)

Cone angle is very useful in assessing the steric properties of phosphines and their coordination behavior.



The electronic effect of phosphines can be assessed by IR and NMR spectroscopic data especially when carbonyls are co-ligands. In a metal complex containing both phosphines and carbonyl, the $\nu(\text{CO})$ frequencies would reveal the σ -donor or π -acceptor abilities of phosphines. If the phosphines employed are strong σ -donors, then more electron density would move from M (t_{2g} orbitals)- $\pi^*(\text{CO})$ and as a result, a lowering in the $\nu(\text{CO})$ is observed. In contrast, if a given phosphine is a poor σ -donor but strong π -acceptor, then phosphine(σ^* -orbitals) also compete with CO for back bonding which results in less lowering in $\nu(\text{CO})$ frequency.

Another important aspect is the steric size of PR_3 ligands, unlike in the case of carbonyls, which can be readily tuned by changing R group. This is of great advantage in transition metal chemistry, especially in metal mediated catalysis, where stabilizing the metals in low coordination states is very important besides low oxidation states. This condition can promote oxidative addition at the metal centre which is an important step in homogeneous catalysis. The steric effects of phosphines can be quantified with Tolman's cone angle.

Cone angle can be defined as a solid angle at metal at a M—P distance of 228 pm which encloses the van der Waal's surfaces of all ligand atoms or substituents over all rotational orientations. The cone angles for most commonly used phosphines are listed in the following table.

Phosphine	Cone Angle (°)
PH_3	87
PF_3	104
$\text{P}(\text{OMe})_3$	107
PMe_3	118
PMe_2Ph	122
PEt_3	132
PPh_3	145
PCy_3	170
$\text{P}(\text{Bu}^t)_3$	182
$\text{P}(\text{mesityl})_3$	212

Phosphines with different cone angles versus coordination number for group 8 metals:

ML_4	ML_3	ML_2
$(\text{Me}_3\text{P})_4\text{Ni}$		
$(\text{Me}_3\text{P})_4\text{Pd}$		

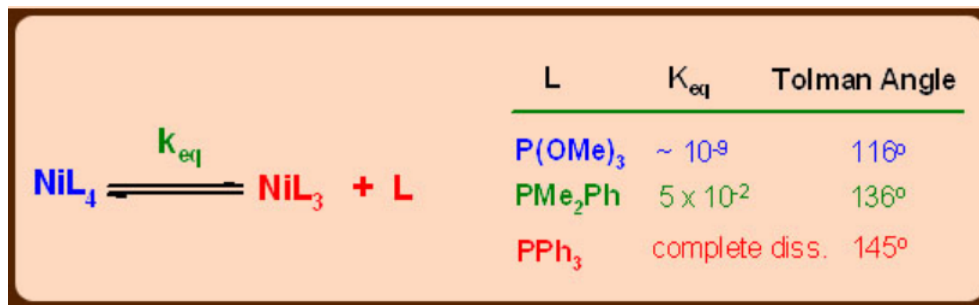
(Me₃P)₄Pt

(Ph₃P)₃Pt

(tert-Bu₃P)₂Pt

Tolman Angle and Catalysis

Sterically demanding phosphine ligands can be used to create an empty coordination site (16 VE complexes) which is an important trick to fine tune the catalytic activity of phosphine complexes.



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