Skills to Develop

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$_2$O or NH$_3$ give complexes with ions of both main group and transition metals. E.g \([\text{Al(OH}_2\text{)}_6]^{3+}\) or \([\text{Co(NH}_3\text{)}_6]^{3+}\)
- 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 Ni(PF$_3$)$_4$ or Ni(CO)$_4$ or Cr(CO)$_6$.
- Why do, NH$_3$, amines, oxygen donors, and so on, not give complexes such as Ni(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 Ni(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, CH₃ etc.,
Compounds with an electron pair are two-electron donors

EXAMPLE: NH₃, H₂O, PR₃ etc.,

Bonding in Metal –Carbonyl and Metal-Phosphines
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 \( \sigma \)-donor or \( \pi \)-acceptor abilities of phosphines. If the phosphines employed are strong \( \sigma \)-donors, then more electron density would move from \( M \left( t_{2g} \text{ orbitals} \right) - \pi^*(\text{CO}) \) and as a result, a lowering in the \( \nu(\text{CO}) \) is observed. In contrast, if a given phosphine is a poor \( \sigma \)-donor but strong \( \pi \)-acceptor, then phosphine(\( \sigma^* \)-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 \( \text{PR}_3 \) 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 \( M-\text{P} \) 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.

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Cone Angle (°)</th>
</tr>
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<tbody>
<tr>
<td>( \text{PH}_3 )</td>
<td>87</td>
</tr>
<tr>
<td>( \text{PF}_3 )</td>
<td>104</td>
</tr>
<tr>
<td>( \text{P(OMe)}_3 )</td>
<td>107</td>
</tr>
<tr>
<td>( \text{PMe}_3 )</td>
<td>118</td>
</tr>
<tr>
<td>( \text{PMe}_2\text{Ph} )</td>
<td>122</td>
</tr>
<tr>
<td>( \text{PET}_3 )</td>
<td>132</td>
</tr>
<tr>
<td>( \text{PPH}_3 )</td>
<td>145</td>
</tr>
<tr>
<td>( \text{PCy}_3 )</td>
<td>170</td>
</tr>
<tr>
<td>( \text{P(Bu}^3\text{)}_3 )</td>
<td>182</td>
</tr>
<tr>
<td>( \text{P(mesityl)}_3 )</td>
<td>212</td>
</tr>
</tbody>
</table>

Phosphines with different cone angles versus coordination number for group 8 metals: \( \text{ML}_4 \) \ ML_3 \ ML_2 \ (\text{Me}_3\text{P})_4\text{Ni} \ (\text{Me}_3\text{P})_4\text{Pd} \ (\text{Me}_3\text{P})_4\text{Pt} \ (\text{Ph}_3\text{P})_3\text{Pt} \ (\text{tert-Bu}_3\text{P})_2\text{Pt}

### 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.

Contributors

http://nptel.ac.in/courses/104101006/15

In this lecture you will learn the following

- Know about metal phosphine complexes.
- Have an understanding of the steric and electronic properties of the phosphine ligands.
- Obtain a deeper insight about the metal phosphine interactions.
- Be introduced to other π–basic ligands.

Phosphines are one of the few ligands that have been extensively studied over the last few decades to an extent that the systematic fine tuning of the sterics and electronics can now be achieved with certain degree of predictability. Phosphines are better spectator ligands than actor ligands. Tolman carried out pioneering infrared spectroscopy experiments on the \( \text{PR}_3\text{Ni(CO)}_3 \) complexes looking at the \( v(\text{CO}) \) stretching frequencies for obtaining an insight on the donor properties of the \( \text{PR}_3 \) ligands. Thus, a stronger σ–donor phosphine ligand would increase the electron density at the metal center leading to an enhanced metal to ligand π–back bonding and thereby lowering of the \( v(\text{CO}) \) stretching frequencies in these complexes. Another important aspect of the phosphine ligand is its size that has significant steric impact on its metal complexes. Thus, unlike CO ligand, which is small and hence many may simultaneously be able to bind to a metal center, the same is not true for the phosphine ligands as only a few can bind to a metal center. The number of phosphine ligands that can bind to a metal center also depends on the size of its R substituents. For example, up to two can bind to a metal center in case of the PCy\(_3\) or P(i–Pr)\(_3\) ligands, three or four for PPh\(_3\), four for Me\(_2\)PH, and five or six for PMe\(_3\). The steric effect of phosphine was quantified by Tolmann and is given by a parameter called Cone Angle that measures the angle at the metal formed by the \( \text{PR}_3 \) ligand binding to a metal (Figure 1).
The Cone Angle criteria has been successfully invoked in rationalizing the properties of a wide range of metal phosphine complexes. One unique feature of the phosphine ligand is that it allows convenient change of electronic effect without undergoing much change in its steric effects. For example, PBu$_3$ and P(O^{i}Pr)$_3$ have similar steric effects but vary in their electronic effects. The converse is also true as the steric effect can be easily changed without undergoing much change in the electronic effect. For example, PMe$_3$ and P(o-tolyl)$_3$ have similar electronic effect but differ in their steric effects. Thus, the ability to conveniently modulate the steric and the electronic effects make the phosphine ligands a versatile system for carrying out many organometallic catalysis.

**Structure and Bonding**

Phosphines are two electron donors that engage a lone pair for binding to metals. These are thus considered as good σ-donors and poor π-acceptors and they belong to the same class with the aryl, dialkylamino and alkoxo ligands. In fact they are more π-acidic than pure σ-donor ligands like NH$_3$ and, more interestingly so, their π-acidity can be varied significantly by systematic incorporation of substituents on the P atom. For example, PF$_3$ is more π-acidic than CO. Analogous to what is observed in case of the benchmark π-acidic CO ligand, in which the metal $d_{π}$ orbital donates electron to a π* orbital of a C−O bond, in the case of the phosphines ligands, such π−back donation occurs from the metal $d_{π}$ orbital occurs on to a σ* orbital of a P−R bond (Figure 2). In phosphine ligands, with the increase of the electronegativity of R both of the σ and the σ* orbitals of the P−R bond gets stabilized. Consequently, the contribution of the atomic orbital of the P atom to the σ*−orbital of the P−R bond increases, which eventually increases the size of the σ* orbital of the P−R bond. This in turn facilitates better overlap of the σ* orbital of the P−R bond with the metal $d_{π}$ orbital during the metal to ligand π−back donation in these metal phosphine complexes.
Figure 2. Back donation from the metal $d_{\pi}$ orbital to a $\sigma^*$ orbital of a P–R bond.

Starting from CO, which is a strong $\pi$–acceptor ligand, to moving to the phosphines, which are good $\sigma$–donors and poor $\pi$–acceptor ligands, to even going further to other extreme to the ligands, which are both good $\sigma$–donors as well as $\pi$–donors, a rich variety of phosphine ligands thus are available for stabilizing different types of organometallic complexes. In this context the following ligands are discussed below.

π-basic ligands

Alkoxides (RO$^-$) and halides like F$^-$, Cl$^-$ and Br$^-$ belong to a category of π–basic ligands as they engage a second lone pair for π–donation to the metal over and above the first lone pair partaking $\sigma$–donation to the metal. Opposite to what is observed in the case of π–acidic ligands, in which the $\pi^*$ ligand orbital stabilizes the $d_{\pi}$ metal orbital and thereby affecting a larger ligand field splitting, as consistent with the strong field nature of these ligands (Figure 3), in the case of the π–basic ligands, the second lone pair destabilizes the $d_{\pi}$ metal orbitals leading to a smaller ligand field splitting, which is in agreement with the weak field nature of these ligands. The orbitals containing the lone pair of the ligands are usually located on the more electronegative heteroatoms and so they are invariably lower in energy than the metal $d_{\pi}$ orbitals. Hence, the destabilization of the metal $d_{\pi}$ orbitals occurs due to the repulsion of the filled ligand lone pair orbital with the filled metal $d_{\pi}$ orbitals. In case of the situations in which the metal $d_{\pi}$ orbitals are vacant, like in $d^0$ systems of Ti$^{4+}$ ions, the possibility of the destabilization of the metal $d_{\pi}$ orbitals do not arise but instead stabilization occurs through the donation of the filled ligand lone pair orbital electrons to the empty metal $d_{\pi}$ orbitals as seen in the case of TiF$_6$ and W(OMe)$_6$. Thus, this scenario in π–basic ligands is opposite to that observed in case of the π–acidic ligands, for which the empty $\pi^*$ ligand orbitals are higher in energy than the filled metal $d_{\pi}$ orbitals.
Figure 3. Orbital interactions in the presence of the π–acceptor, (pure) σ–donor and π–basic ligands are shown.