Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

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Lecture – 36

Classification of Ligands – Oxygen, Phosphorus

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. We have been discussing the classification of ligands by donor atoms. So, far we have completed most of the ligand systems and we are discussing about oxygen donor ligands. We have numerous examples of oxygen donor ligands, let us consider a few prominent ones. For example, if you take alcohols, aryl alcohols or alkyl alcohols, they can be readily deprotonated and reacted with transition metals to form the corresponding alkoxides or aryl oxides.

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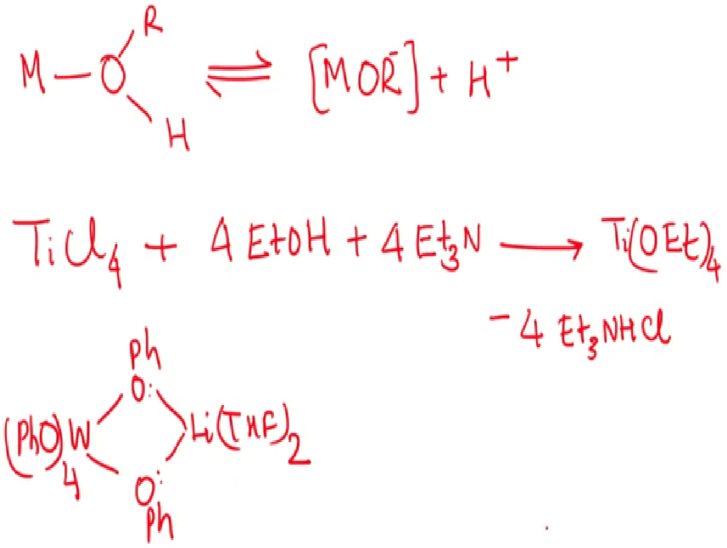

Let me consider a general reaction, so something like this happens and later H^+ can come out and it can form something like this. For example, if we consider titanium tetrachloride and that is treated with 4 equivalents of ethyl alcohol in the presence of a base such as triethylamine, it gives tetraethoxytitanium along with four triethylammonium chloride. And the examples of this type of compounds are also known.

Let us say, we form a phenoxy compound like this and they can also coordinate to hard metals such as lithium something like this. For example, if you are using lithium phenoxide and make this compound and lithium can also get coordinated to this oxygen lone pairs and then the coordination can be saturated with two more THF ligands.

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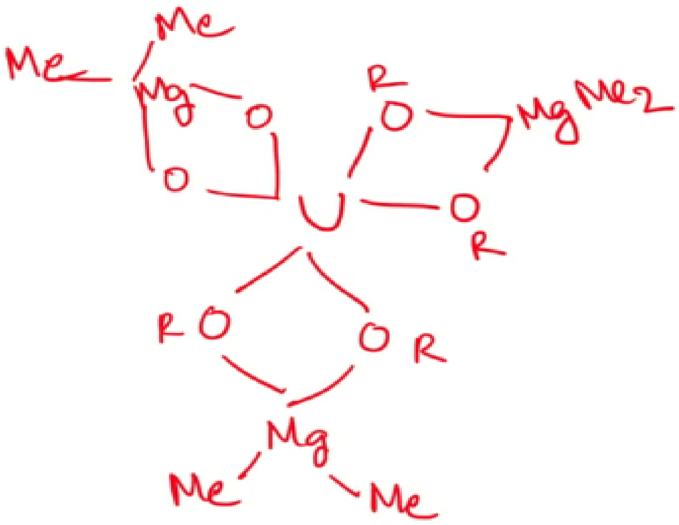

Another interesting complex is with uranium. These are few examples of mixed ligand complexes.

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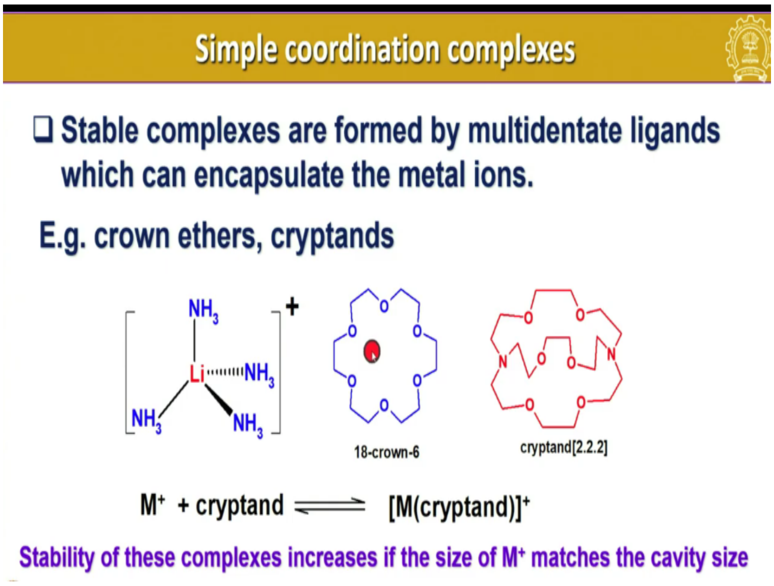

Simple coordination complexes

❑ Stable complexes are formed by multidentate ligands which can encapsulate the metal ions.

E.g. crown ethers, cryptands

$M^+ + \text{cryptand} \rightleftharpoons [M(\text{cryptand})]^+$

Stability of these complexes increases if the size of M^+ matches the cavity size

And another important class of ligands we come across are crown ethers. For example, stable complexes are formed by multidentate ligands and the advantage of multidentate ligands is they can very nicely encapsulate a metal ion and confer very extra stability. In this context, these two ligands are very important, one is crown ethers and other one is cryptands. And these two ligand systems are essentially used to stabilize cations when we have anionic transition metal complexes.

Cation such as alkaline earth metals or alkali metals can very nicely stabilized so that compound is stable and that can also be crystallized very easily to understand the bonding parameters. For example, lithium can bind to ammonia very similar to any transition metal and we have cationic complex here. And nevertheless, if lithium is a counter cation, it is advisable to have some of these crown ethers to stabilize this cation rather than going for monodentate ligands as they are susceptible for further reaction.

So, this is called the 18-crown-6 and it is very simple. We have 18 atoms in the ring and 6 oxygen atoms are there, so that is the reason it is called 18-crown-6. If you start counting from say here 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,14, 15, 16, 17, 18; so 18 atoms are there in the ring and then we have 6 oxygen atoms and usually it looks like a crown, as a result it is named as 18-crown-6.

And in this case what happens we have 2, 2, 2 oxygen atoms in between these nitrogen atoms, it is called cryptand 2.2.2 and in a typical reaction you take a cation and just put into cryptand it can form, even if you have some other hard ligands in there coordination sphere of this cation, the moment you put it because of encapsulation; entropically driven reaction happens, and then this macrocyclic ligands encapsulate the metal to form a stable compound.

The stability of these complexes increases if the size of M^+ matches the cavity of the crown ether or cryptand we have chosen. So, from this point of view, one has to be extremely careful in knowing the size of the metal and also the size of this cavity, so that if the cavity matches well with the size of the cation, then it is very difficult to dislodge the metal centre, as a result this is more stable.

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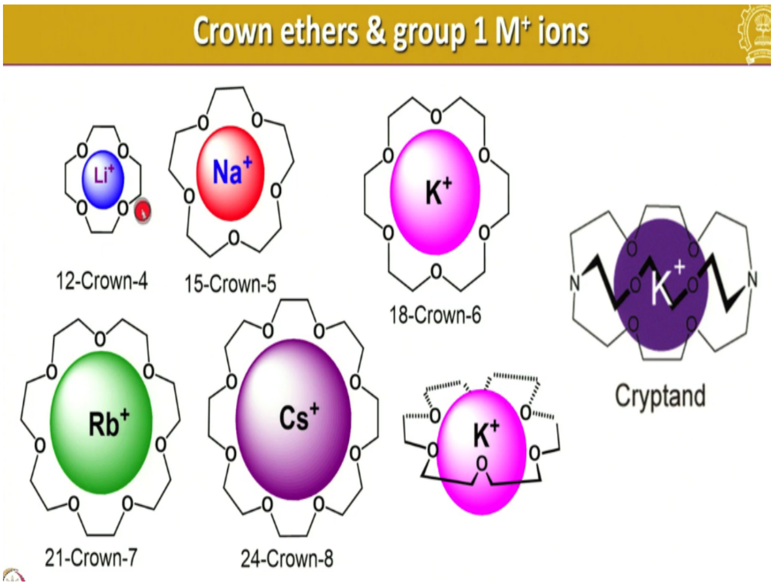

Crown ethers & group 1 M^+ ions

For example, if you have to stabilize lithium ion, then the ideal size is 12-crown-4. And if you want to stabilize a sodium cation the ideal size is 15-crown-5. Similarly, for potassium we need 18-crown-6 or in case of rubidium we need 21-crown-7 and in case of cesium we need slightly larger 24-crown-8 and this is how it can encapsulate a cation, one can see here and now the shape of this crown ether almost looks like crown and hence the name crown here.

And cryptand can encapsulate from 3 different positions like this, as a result what happens it is even more stable compared to the crown ether bound cations and hence this also used in case of alkali metals preferably and also with alkaline earth metals. They are called cryptands where we have oxygen as well as nitrogen donor atoms. In case of crown ether, it is homolyptic, it has only oxygen donor atoms, but one can have alkyl groups and aryl groups combined. Now let me give the preparation of crown ethers.

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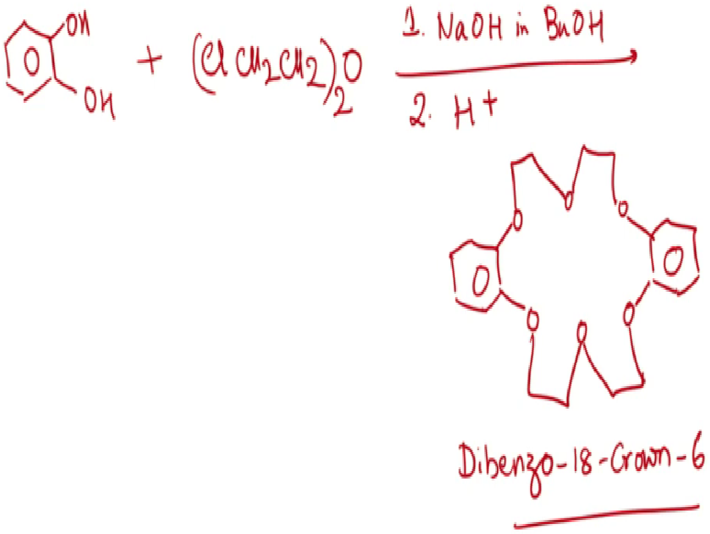

Let us consider this catechol and treat this one with chloro ether in presence of a base such as sodium hydroxide in butanol and then we need H^+ so it forms. So, this is dibenzo 18-crown ether-6 of course, the name given is correct or incorrect you can always check that one. So, this is the typical method of preparation of crown ethers.

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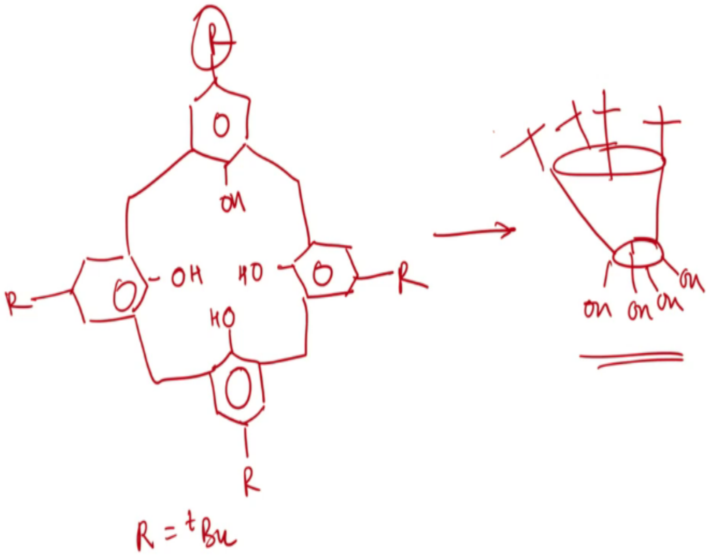

Another important ligand among oxygen donors having caged type structure is called calixarenes. A typical calixarene I shall show you here. Usually, teritiary butyl groups are taken here and because of bulky groups on para position, what happens, it is something like this, it looks like this on the lower rim and upper rim we call. In the lower rim what we have is OH groups and upper rim teritiary butyl groups, something like this we have.

Because of the teritiary butyl group what happens it enlarges something like this, as a result it will be having this kind of shape here and this can also encapsulate and very versatile chemistry is known with this class of ligands. And resorcinol are another class of ligands where hydroxyl groups will be there for further binding. So, with this, let me stop discussion on oxygen donor ligands and move on to another very important class of ligands that is called phosphines.

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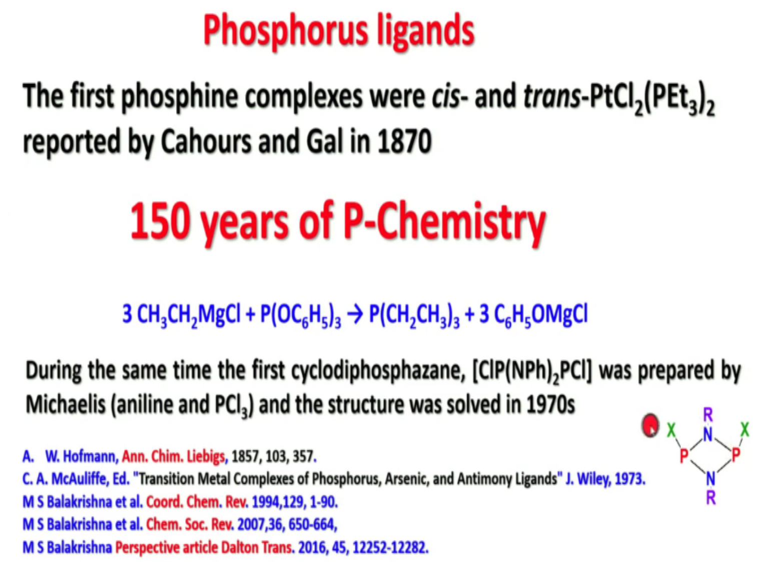

Phosphorus ligands

The first phosphine complexes were *cis*- and *trans*-$PtCl_2(PEt_3)_2$ reported by Cahours and Gal in 1870

150 years of P-Chemistry

$3\ CH_3CH_2MgCl + P(OC_6H_5)_3 \rightarrow P(CH_2CH_3)_3 + 3\ C_6H_5OMgCl$

During the same time the first cyclodiphosphazane, $[ClP(NPh)_2PCl]$ was prepared by Michaelis (aniline and PCl_3) and the structure was solved in 1970s

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You may be surprised to know that phosphines were known for almost 150 years and the first phosphine complex of platinum that is bis(triethylphosphine)dichloroplatinum, both cis and trans, were reported in 1870, that means we have a history of 150 years for phosphine chemistry or phosphine complexes. And how this was made, this phosphine was made initially can be seen from this one, ethyl magnesium chloride was treated with triphenyl phosphide to form triethylphosphine to the elimination of this one.

And of course, during the same time the first cyclodiphosphazane, a saturated four membered ring having alternate phosphorus and nitrogen atoms with phosphorus in trivalent state was reported. Since phosphorus is in trivalent state it has a pair of electrons, so one can use this as a ligand. The first compound was prepared in the 1857 and however the structure of this ligand was solved only in 1970s.

And you can see important review articles, I myself wrote 3 three review articles on this one and we have published more than 50 papers on coordination chemistry and applications. We have studied extensively coordination chemistry of cyclodiphosphazanes, a very interesting ligand system, some very unusual compounds were made especially with copper. The interesting thing about group 15, we call pnictogens.

In fact, when we look into the coordination chemistry that is performed in aqueous medium, nitrogen donor ligands are second to none. In contrast, when we move to the next congener, phosphorus in organometallic chemistry as well as in homogeneous catalysis and also in coordination chemistry, phosphines as neutral ligands with back bonding capability are second to none.

Look at one below has very contrasting and complementing property compared to nitrogen, but on the other hand, we have numerous phosphorus nitrogen compounds in main group chemistry. In main group chemistry one of the important class of compounds are phosphazenes and phosphazanes having phosphorus to nitrogen single bond and phosphorus to nitrogen double bond, excellent ligand system complementing each other, but having contrasting properties. Let us try to understand more chemistry of phosphines as ligands.

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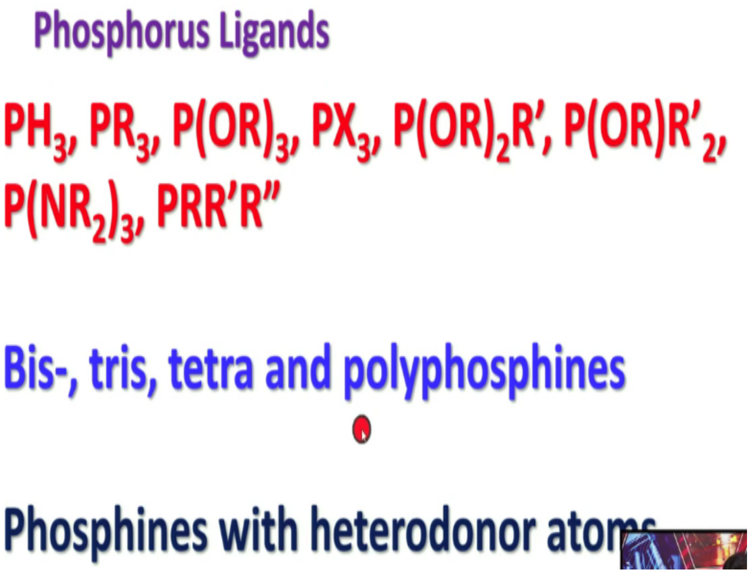

Phosphorus Ligands

PH_3, PR_3, $P(OR)_3$, PX_3, $P(OR)_2R'$, $P(OR)R'_2$, $P(NR_2)_3$, $PRR'R''$

Bis-, tris, tetra and polyphosphines

Phosphines with heterodonor atoms

When we talk about phosphorus donor ligands, the simplest one is a phosphine very similar to ammonia. And then if you keep on substituting hydrogens with R group, organic groups, alkyl or aryl groups then you can have primary phosphine, secondary phosphine and tertiary phosphine. Teritiary phosphines are like PR_3. And also one can have alkoxy or aryloxy groups on phosphorus.

So when alkoxy or aryloxy groups on phosphorus, they are called phosphites. For example, trimethyl phosphite or one can also call as trimethoxyphosphine. Then of course, PF_3, PCl_3, PBr_3 also one can use as ligand. And then we can have a mixed alkoxy or aryloxy group along with this one, this is called phosphonite and if we have one OR group it is called phosphinite.

And also we can have NR_2 groups or we can have all different groups on phosphorus, they are called tertiary phosphines. And apart from this monodentate ligands, we also have new numerous examples of bis, tris, tetra and polyphosphines and also phosphines with heterodonor atoms such as nitrogen are very common. And also we have numerous examples of phosphorus coexisting with other donor atoms such as oxygen, sulfur and selenium.

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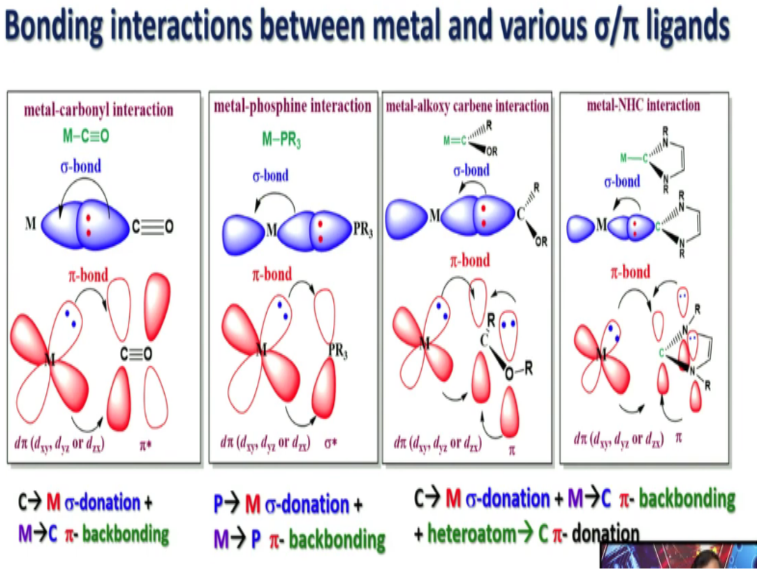

Bonding interactions between metal and various σ/π ligands

$C \rightarrow M$ σ-donation + $M \rightarrow C$ π- backbonding

$P \rightarrow M$ σ-donation + $M \rightarrow P$ π- backbonding

$C \rightarrow M$ σ-donation + $M \rightarrow C$ π- backbonding + heteroatom → C π- donation

Let us try to compare similar ligands which have donor and acceptor properties as phosphines or carbon monoxide and we had spent enough time discussing the binding properties and similarities between carbon monoxide and phosphines. And similarly, Fischer carbenes if you look into it, again you can always make the comparison of sigma donor ability and pi acceptor abilities including heterocyclic carbenes.

And in case of the phosphines, it is sigma star; in case of carbon monoxide or carbenes of these two types it is pi-star are acceptor orbitals. So, that means sigma donation and back bonding is there. The only difference is carbon monoxide what would happen is; of course sigma donor and pi acceptor, but you cannot medal with the nature of carbon monoxide, in order to call this as a carbon monoxide there should be carbon and oxygen.

But in contrast, phosphines: we have an opportunity to perform a variety of substitutions on phosphorus to have different groups that can control the metal activities through both kinetic and electronic ways. For example, phosphine if we consider: more electron withdrawing groups and phosphorus, so that can be poor sigma donor, but very good pi acceptor. On the other hand, if we have more electron donating groups on phosphorus that become very good sigma donor but poor pi acceptor.

But having a combination of electron releasing groups and electron acceptor groups, one can match the ability of carbon monoxide or sometimes even supersede the ability in back bonding. For example, if you take PF_3 or we have like fluorine substituted organic moieties, they can even be better pi-acceptors compared to carbon monoxide. In that context what happens, there is a flexibility in altering the ligating properties of phosphines that normally we do not see in case of carbon monoxide.

This is where we have advantage over carbon monoxide in its utility in organometallic chemistry as homogeneous catalysts for a variety of organic transformations. When we come to Fischer carbene and *N*-heterocyclic carbene, no doubt they are also good sigma donors and pi acceptors, but as I already mentioned in one of my previous lectures that they also have some lone pairs available for back donation to pi star of carbon.

As a result, what happens it is either in this carbene or in this N-heterocyclic carbene, we have nitrogen lone pair, here also lone pair, as a result what happens they have less inclination to take electrons from metal through back donation. They are relatively poor pi acceptors compared to phosphines. So, this is where the phosphines top among best sigma donor and the pi acceptor ligands and hence their utility is enormous in homogeneous catalysis.

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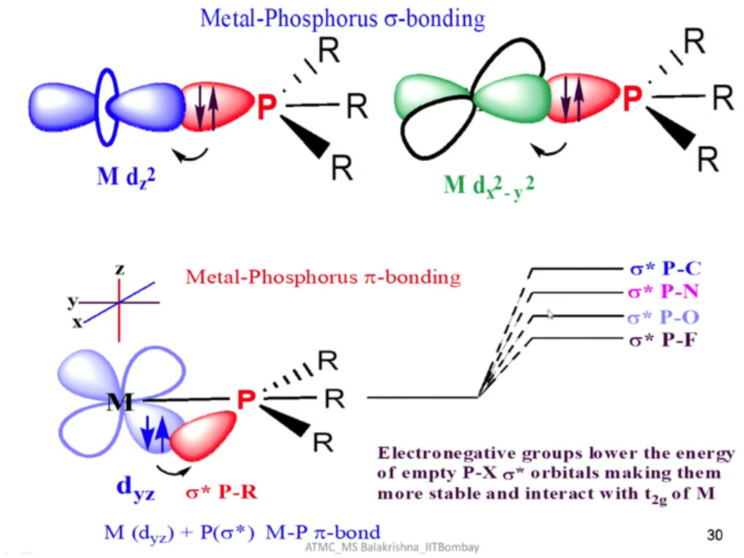

Electronegative groups lower the energy of empty P-X σ* orbitals making them more stable and interact with t_{2g} of M

M (d_{yz}) + P(σ*) M-P π-bond

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Let us look into the binding again. As I mentioned phosphorus in trivalent state has a pair of electrons, so that can go to suitable metal orbital to establish metal to ligand bond that is metal to phosphorus bond. So, preferably it can go to d_{z^2} or $d_{x^2-y^2}$ that depends on the type of geometry adopted by these metal complexes. Now, you can see here, this is about back donation, sigma star.

Sigma star can interact with say d_{yz}, in that case what happens the back donation happens. So, here pi-acceptor ability can be readily monitored by having different substituents on phosphorus. For example, if you put more electron withdrawing group like we have PF_3 or $P(OR)_3$ or $P(NR_2)_3$ or PMe_3, so the relative energy of σ*, I have shown. So, the question is if we say this is a better pi acceptor than P—C bonded, how it is?

Let us say, here the energy of t_{2g} orbitals, or metal donor orbitals or metal pi donor orbitals and here the relative energies are there. That means by adding more electron withdrawing groups, we are pulling down the σ* orbitals to be on par with metal π donor orbitals. So, that means, on the other hand if you put more electron donating groups, the energy of this one is elevated.

As a result, what happens they become good sigma donors, but very poor pi acceptors. So, this is where phosphines have remarkable ability to adjust their donor and acceptor properties and hence they are very important among all ligands in organometallic chemistry and also in homogeneous catalysis.

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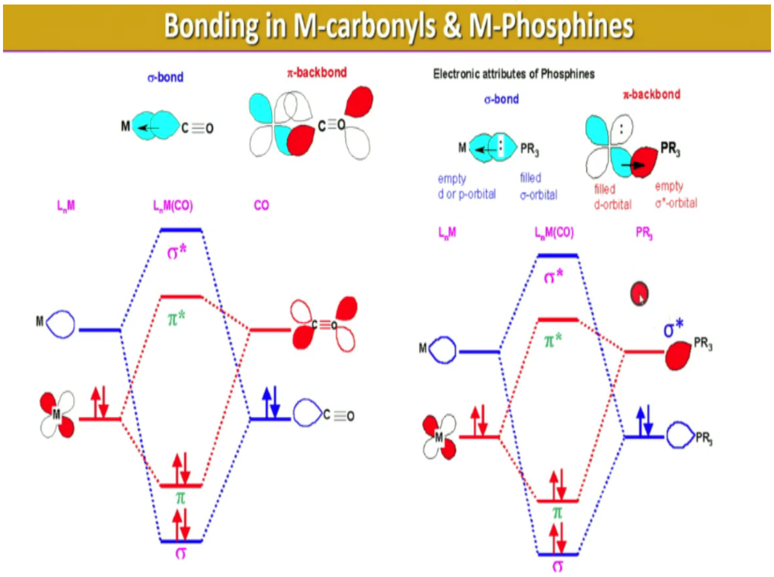

Bonding in M-carbonyls & M-Phosphines

Once again, I have shown here MO diagrams for metal carbonyl complexes and metal phosphine complexes; very similar. This represent back donation, that means σ* is interacting, σ* acts as atomic orbital and then one of the t_{2g} acts as an atomic orbital, they combined together to generate bonding and antibonding orbitals, then electrons are placed in here.

So, why I am elaborating this one is some students were asking question, although electrons are going for σ*, why we call it as π-bonding. The symmetry of that is pi bonding as a result we call it and also the electrons are not going directly to the σ* here, one should remember that one, that is true in case of even carbon monoxide or N-heterocyclic carbenes.

They essentially again combine performing as atomic orbitals with metal atomic orbitals to generate a set of bonding and antibonding and then they stay here, so this is called back bonding here and then the pi symmetry is there, although it goes to sigma star we still call it as pi back bonding for the same reason.

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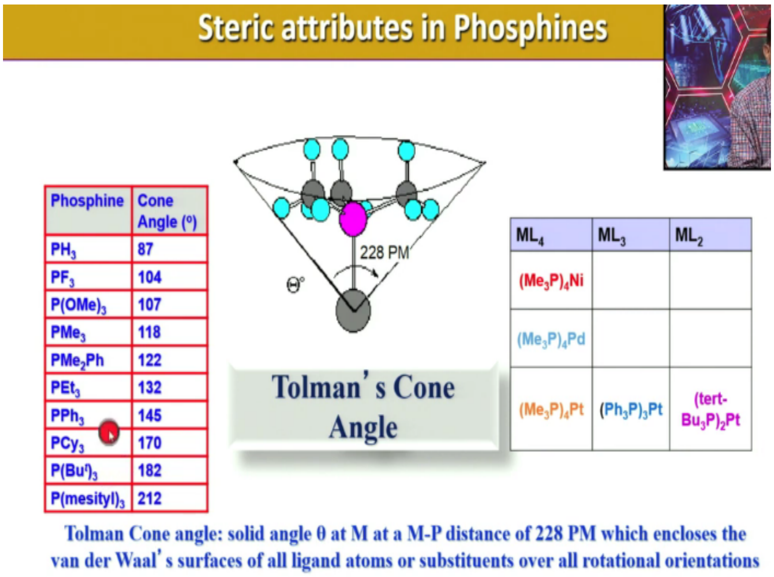

Steric attributes in Phosphines

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

Tolman's Cone Angle

ML_4	ML_3	ML_2
$(Me_3P)_4Ni$		
$(Me_3P)_4Pd$		
$(Me_3P)_4Pt$	$(Ph_3P)_3Pt$	(tert-$Bu_3P)_2Pt$

Tolman Cone angle: solid angle θ at M 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

Another important, that means we know the electronic effect, once again I repeat, so electron withdrawing groups on phosphorus makes it poor sigma donor but strong pi acceptor, on the other hand electron donating groups on phosphorus makes it very good sigma donor but poor pi acceptor. By knowing these two extreme cases, we can have desired groups on that one to have moderate sigma donor and pi acceptor abilities. Then how about steric attributes?

What would happen if we have bulky groups on phosphorus atom? Yes, that is another important thing. This one was shown by Tolman. Tolman showed cone angle when a typical phosphine binds to a metal having a metal to phosphorus distance of 228 picometre, it generates a conical surface like this. **(Video Starts: 22:32)** Let us assume this is a triphenylphosphine, you can see here. Pyramidal structure is there and this the lone pair.

Now, this lone pair goes to the metal and this distance is about 2.28 angstrom unit, this average distance I am talking about. Now, let us imagine a conical surface and I put it here and when I start rotating, that means this cone angle is nothing but the angle subtended at metal with a metal to phosphorus distance of 228 picometre that encloses van der Waal's surfaces of all ligand substituents over all rotational orientations.

I repeat again, this the angle subtended at metal at a metal to phosphorus distance of 228 picometre that encloses van der Waal's surfaces of all ligand substituents for all rotational orientations. For example, now if I can rotate freely without touching this conical surface, this is called cone angle for this particular phosphine. Then if I take a bulky phosphine, let us say take trimethylphosphine. If you take trimethyl phosphine so in order to have free rotation of methyl groups on it, I should expand it.

That means when you have bulky groups, cone angle increases. Then fine, how to correlate this one with its reactivity and its utility in catalysis and other reaction? Let us discuss that one in my next lecture. So, you can see, here I repeat again how to define cone angle. Solid angle theta can be defined as a conical surface that encloses the van der Waal’s surfaces of all ligand substituents over all rotational orientations, this is called cone angle. **(Video Ends: 24:28)**

And here if you see: I have listed some cone angle values here. For example, PH_3 very small groups, the angle is 87 degree. And then if you go for trifluorophosphine you have fluorine with F^-, so with one bond we have 3 pairs of electrons on each fluorine, as a result what happens the cone angle increases. And then we have trimethyl phosphite 107, trimethyl we have 118, dimethyl phenyl phosphine 122, triethylphosphine 132 triphenylphosphine 145.

And if we put cyclohexyl group it goes to 170. And when you have three tertiary butyl groups it is 182 and if you have three mesityl groups we have a maximum, 212 cone angle. That means how these cone angles would define the coordination geometry and coordination number of a metal complex and how we can use this one in homogeneous catalysis, we shall discuss in my next lecture. Until then have an excellent time reading phosphorus chemistry.