Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

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Lecture – 37

Classification of Ligands – Phosphorus

Hello everyone. I, once again welcome you all to MSB lecture series on transition metal chemistry. I am sure you are having good time reading and understanding chemistry. This is 37th lecture in the series. In my previous lecture, I started discussion on phosphorus ligands and also I did mention about the importance of phosphines in both coordination chemistry and organometallic chemistry and also their utility in homogeneous catalysis, how important phosphines when compared to other similar sigma donor and pi acceptor ligands.

So, let me continue from where I had stopped, two important aspects revolve around phosphorus chemistry when we want to use them as ligands, one is electronic properties and the other one is steric properties. When we talk about electronic properties, we can readily alter the sigma donor ability and pi acceptor capability simply by changing the phosphorus substituents. And if we put more electron donating groups on phosphorus, it becomes a good sigma donor and poor pi acceptor.

On the other hand, if we put more electron withdrawing groups on phosphorus, it makes relatively less or poor sigma donor but very strong pi acceptor. So, this kind of facility you do not come across among carbon monoxide that is the reason tertiary phosphines, whether it is monophosphines, bisphosphonines or polyphosphines play an important role in stabilizing coordination compounds and also organometallic compounds in different oxidation states hence their utility in homogeneous catalysis.

So, I mentioned about electronic properties and also steric attributes can be measured in terms of cone angle and I explained what is cone angle. So, for example let us consider a phosphine bonded to metal and the average metal to phosphorus distance is about 228 picometre or 2.28 Å. So, let us imagine a conical surface at metal that encloses the van der Waal's surfaces of all ligand substituents over all rotational orientations.

That means if the phosphine is less bulky or phosphorus have small groups on it, the cone angle will be very small. On the other hand, if we put more bulky groups, cone angle increases. Once again, I repeat, it is a conical surface defined or imagined 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. So, how we can use this one in utilizing phosphines in catalysis let us look into it.

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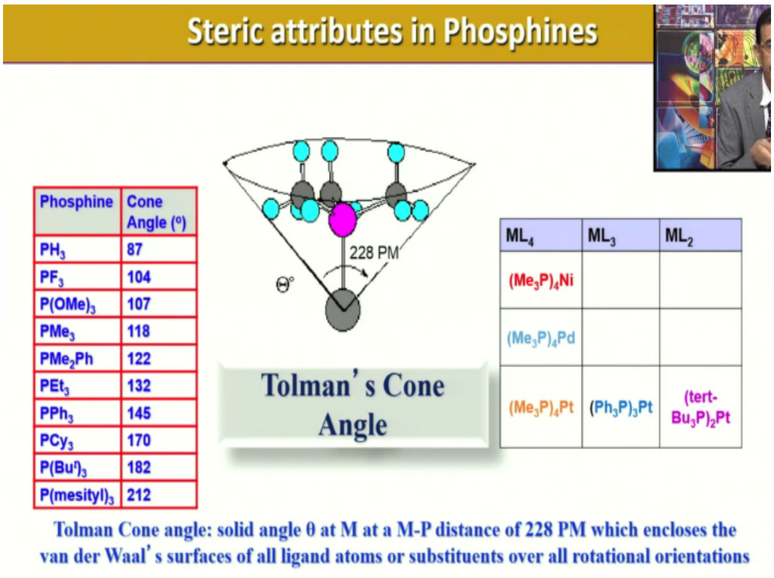

Steric attributes in Phosphines

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

Now, I have shown here and also I have listed corresponding cone angle for various phosphines. As the bulkiness is increasing, cone angle is also increasing.

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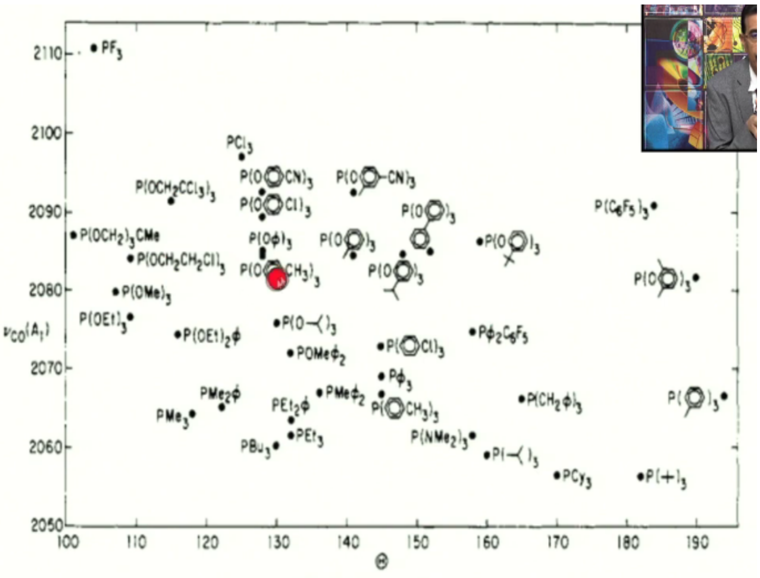

Now, you can see, for example, if we take a metal complex having carbon monoxide as well as phosphines and how the stretching frequency of carbon monoxide varies that determines to what extent a phosphine is acting as a sigma donor and pi acceptor. For example, if you take here, I have put all alkyl phosphines here. If you see here, when we have alkyl phosphines in a metal complex having carbon monoxide, its stretching frequencies are very low.

On the other hand, if you can see here, trifluorophosphine very strong electron withdrawing group here we have, as a result what happens, CO stretching frequency is very high. That means, in these types of ligands there is a competition between both carbon monoxide and tertiary phosphine to take electrons through back bonding and if they are equally competent, then what happens less electron density goes to the pi star of carbon monoxide.

As a result, there is not much change in the stretching frequency. So, that means this can give you a measure of the sigma donor and pi acceptor capability of phosphines with respect to carbon monoxide.

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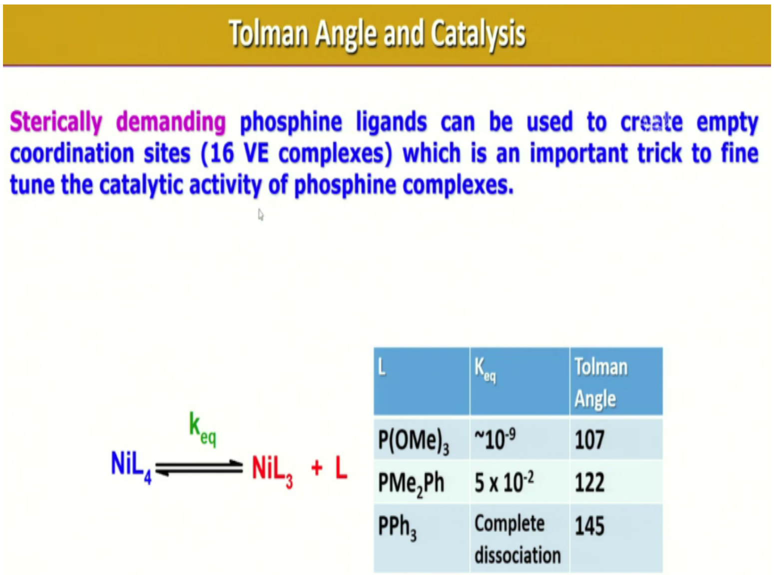

Tolman Angle and Catalysis

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

$$NiL_4 \xrightleftharpoons{k_{eq}} NiL_3 + L$$

L	K_{eq}	Tolman Angle
$P(OMe)_3$	~10^{-9}	107
PMe_2Ph	5×10^{-2}	122
PPh_3	Complete dissociation	145

Now, I have listed three ligands and the corresponding tetrakis-metal complexes. So, one such complex I have taken is NiL_4 where L is a neutral ligand, a phosphine and nickel is in 0 valent state, that means it is an 18 electron complex. Let us say, if you want to use this one in catalysis since it is 18 electron species, we cannot perform any oxidative addition. As a result, what happens, one has to take out or dissociate one or more ligands before we use it as a catalyst.

This is a typical example I have shown. Sterically demanding phosphine ligands can be used to create empty coordination sites or 16 valence electron complexes, which is an important trick to fine tune the catalytic activity of phosphine complexes. That means you see here if you just look into the dissociation constant, here for various ligands that can be compared with Tolman cone angle.

For example, if you take trimethoxyphosphine or trimethyl phosphide, it is very slow, Tolman angle is 107, so that means dissociation is little endothermic in nature. On the other hand, if you go for slightly bulkier ligand such as dimethylphenyl phosphine and here the rate is increasing you can see here, it is 5 x 10^{-2} and Tolman angle is increasing. That means you can see how Tolman cone angle assists in understanding how quickly, how easily it began can be dissociated from metal.

When we go to triphenylphosphine its cone angle is 145, complete dissociation happens within no time, the moment put into the solution. So, that means, in case if you take bulky ligands and even if you make it coordinatively saturated with 18 electron species, the moment we put into solution, dissociation of one or two ligands would be very easy. In that case what happens, we can generate 14 electron species or 16 electron species readily that is essentially an active catalyst and then oxidative addition can be initiated.

So, this is the advantage and this is how Tolman cone angle can be correlated with catalytic efficiency of tertiary phosphines.

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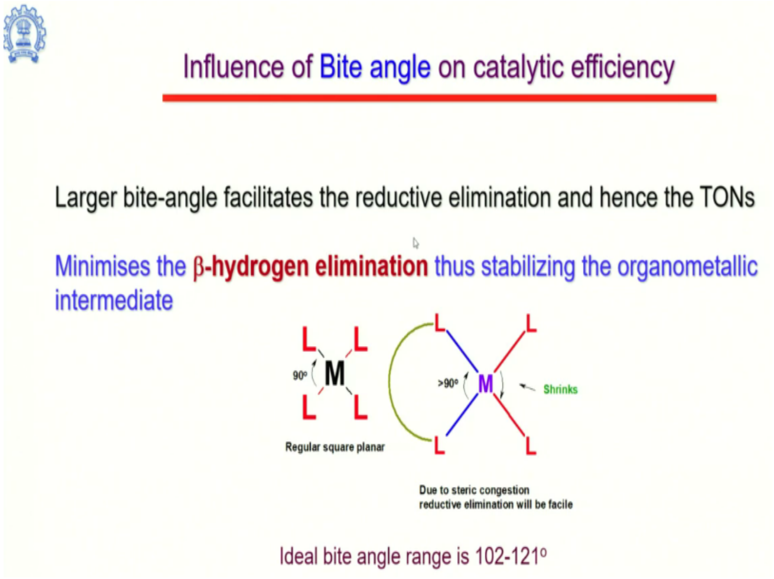

Influence of Bite angle on catalytic efficiency

Larger bite-angle facilitates the reductive elimination and hence the TONs

Minimises the β-hydrogen elimination thus stabilizing the organometallic intermediate

Due to steric congestion reductive elimination will be facile

Ideal bite angle range is 102-121°

Let us look into the influence of bite tangle on catalytic efficiency in a catalytic reaction. So, what is bite tangle? When you use a bidentate ligand, when it chelates to the same metal the angle generated by these two ligands is called bite tangle and this separation between the two donor atoms is called bite separation. If the bite separation is larger, the angle will also be larger.

That means if we have a very bulky link between two phosphorus atoms, then obviously what happens? Bite tangle also increases as a result of increasing bite separation. So, now if you take a typical square printer complex the angle should be 90 degrees. And if the ligand when it forms a square printer complex, so if you just see with bulky ligands what happens? If the angle is increased here, then what happens that distance between these two will shrink to compensate this one.

So, that means basically very bulky ligands would decrease the distance between two groups. If they are leaving groups, then they come very closer and then in the reductive elimination process pre-bond concerted elimination would be very facile. So, that means the ideal bite angle should be around 102 to 121 will make a bisphosphine ideal catalyst for both oxidative addition and also speed up the reductive elimination that is an important step in the coupling reactions.

So, larger bite angle facilitates the reductive elimination and hence the turnover numbers. And also, another advantage with these things are; in case if you have some alkyl groups with beta hydrogen atoms, it can also minimize beta hydrogen elimination because in the beta hydrogen elimination, it is not giving any scope for the expansion of the coordination number of metal, it can also minimize and also increase the stability of a metal complex especially if it is an organometallic compound.

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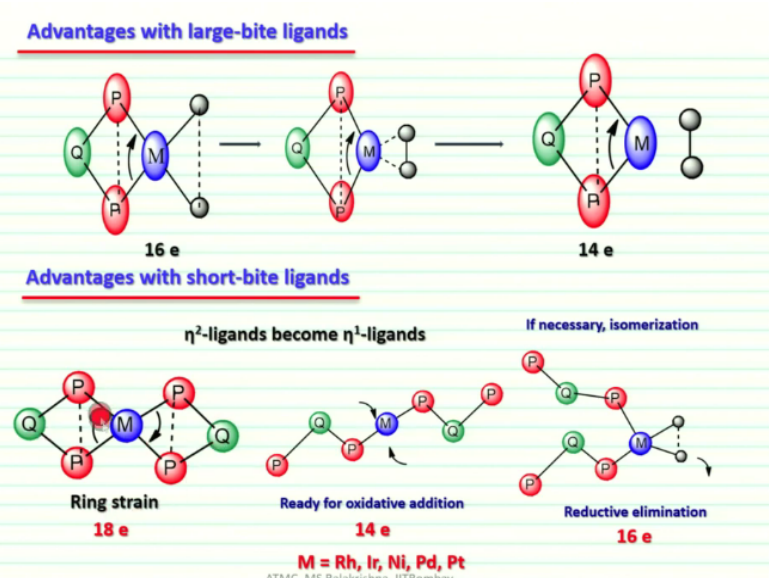

So, now I have shown you with these graphics the advantage with large bite ankles or large bite ligands, for example you can see here, of course this is a 16 electron species with metal in the +2 state, it is a d^8 system. And now you can see, just focus your attention to the separation between these two ligands. Let us assume these two are ready for reductive elimination through the coupling between these two.

And in this case, when you increase this bite angle, so they come very closer and hence facilitate the concerted elimination so that reductive elimination will be much more facile. Now it is a 14 electron species and it is ready for our second cycle of catalysis. This is an advantage with large bite ligand depending upon how we use it. Whether we have a large bite ligand, we have a short bite ligand, we can use according to our convenience if you know how we can use them in particular reaction.

Advantages with short bite ligands: For example, let us say we have short bite ligand, short bite ligands with the two phosphines separated by a small linker like dppm, where it forms a very strained four membered ring, these chelate rings are unstable because of strain. As a result, if you generate a tetradentate tetracoordinated metal complex like this, they should be tetrahedral in nature if it is nickel, palladium or platinum, d^{10} system with 18 electrons.

Now, what happens? The moment you put into the solution and try to add some reagents for oxidative addition, because of ring strain, it is likely that one of the phosphine to metal bond from each ligand would be cleaved to release the strain so that now it forms a 14 electron species and still these phosphorus are in close vicinity and you can perform oxidative addition, and once the reductive elimination happens, you can get back this one.

So, that means whether we have a large bite ligand, whether we have short bite ligand, if you know how to use them, certainly, we can use them in metal complexes and hence their utility in homogeneous catalysis. So, here η^2 ligand, bidentate ligand becomes temporarily monodentate ligand and coordination sites are generated here and it is a 14 electron species. And now we can see once reductive elimination is over, this dangling phosphorus donor atoms will come back and this can be regenerated.

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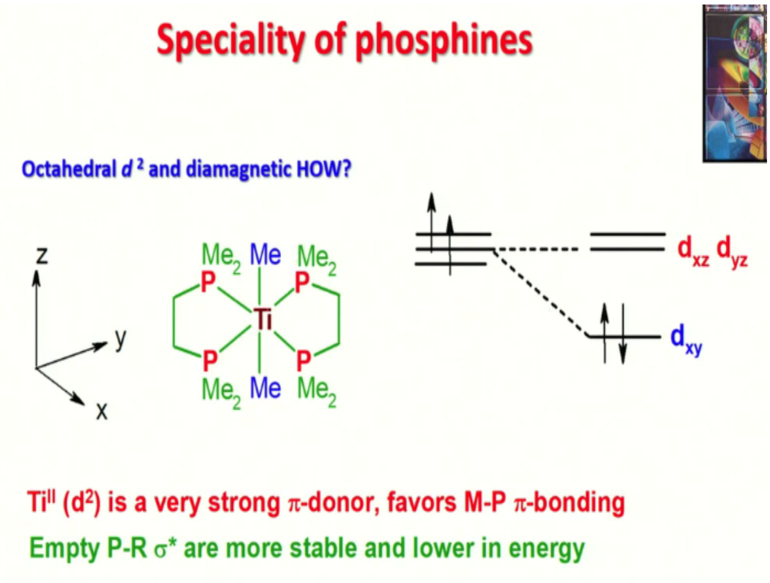

Speciality of phosphines

Octahedral d^2 and diamagnetic HOW?

Ti^{II} (d^2) is a very strong π-donor, favors M-P π-bonding

Empty P-R σ* are more stable and lower in energy

Now, let us look into the speciality of phosphines. I will give you a very interesting example here, just look into this titanium octahedral complex: 2 methyl groups are in axial position and 4 phosphorus atoms from two ligands, they are in the plane. So, now these are anionic ligands, so this is a d^2 system, you know that $3d^2 4s^2$, 2 electrons are gone, it is a d^2 system and d^2 system means we have 2 electrons in the valence shell.

And we know from simple counting electrons that up to 3 electrons if we have whether strong field ligand or weak field ligand they always tend to be paramagnetic. The d^1, d^2 and d^3 system irrespective of what type of ligands we are using, whether we are using strong field ligands or weak field ligands, they remain paramagnetic. Now, the question is this is an octahedral d^2 complex, is it possible to think it as a diamagnetic species?

Very strange, right? How it happens? We have 2 electrons there, under the influence of the sigma donor and pi acceptor ligands, the degeneracy of t_{2g} is destroyed. In t_{2g} we have d_{xy}, d_{xz} and d_{xy}. Let us say 2 electrons would occupy d_{xy} and as a result the energy of this one drops, and these two will remain doubly degenerate d_{xz} and d_{yz}. Now, these electrons are paired unlike a typical d^2 case, where we have 1 electron each 2 orbitals.

In that case, it remains paramagnetic whereas here these two are paired, now this orbit will conveniently overlap with sigma star of phosphines to do back donation. So back donation happens, that means these electrons will be taken by phosphorus sigma star orbitals, and back bonding happens. Because of this despite having 2 electrons and d^2 electronic configuration, this titanium(II) compound is diamagnetic.

So, now we do not have any unpaired electrons. This kind of unusual things can only happen with phosphines. And of course, d^2 is a very strong pi-donor, favours metal to phosphorus pi bonding and the empty P-R sigma star are more stable and lower in energy, they can readily interact with this one and take away their electron density and make it diamagnetic.

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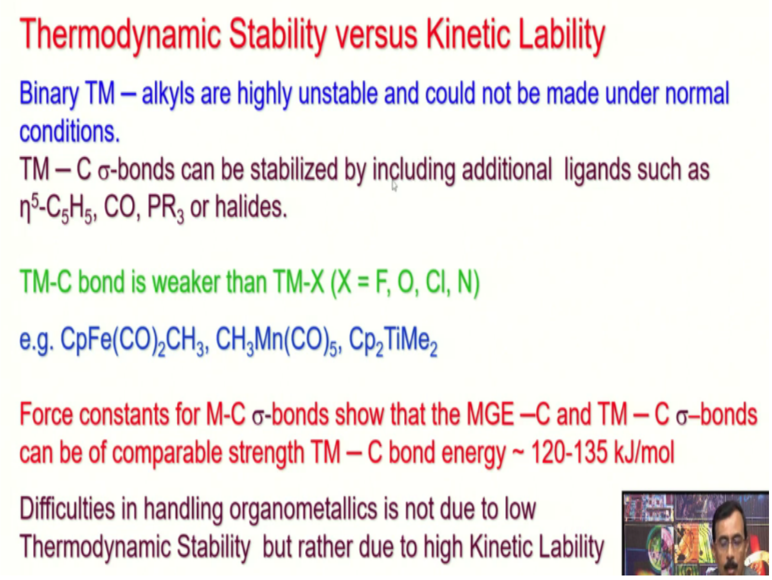

Thermodynamic Stability versus Kinetic Lability

Binary TM – alkyls are highly unstable and could not be made under normal conditions.

TM – C σ-bonds can be stabilized by including additional ligands such as η^5-C_5H_5, CO, PR_3 or halides.

TM-C bond is weaker than TM-X (X = F, O, Cl, N)

e.g. $CpFe(CO)_2CH_3$, $CH_3Mn(CO)_5$, Cp_2TiMe_2

Force constants for M-C σ-bonds show that the MGE –C and TM – C σ-bonds can be of comparable strength TM – C bond energy ~ 120-135 kJ/mol

Difficulties in handling organometallics is not due to low Thermodynamic Stability but rather due to high Kinetic Lability

So, now, let us compare transition metal organic compounds or organometallic compounds with main group compounds having carbon. Let us look into the thermodynamic stability versus kinetic liability of organometallic compounds and also main group compounds where we have element to carbon bond. So, if you consider binary transition metal complexes such as alkyl or aryl compounds or complexes, they are highly unstable and could not be made under normal conditions and also could not be stored at room temperature.

For example, if you take tetraethyl lithium or tetraethyl titanium, they can be stable only up to –60 ºC. And again, among tetramethyl titanium or tetraethyl titanium, tetraethyl is much more reactive and less stable compared to tetramethyl titanium. But if you look into the bond parameters, there is no difference between the transition metal to carbon bond enthalpies and also a main group to carbon bond enthalpies.

Transition metal to carbon sigma bonds can be stabilized by including additional ligands such as cyclopentadienyl group or CO group or a phosphine or even halides. That means transition metal to carbon bond is weaker than transition metal to halogen bond. So, that means if you consider any of these things or even oxygen for that matter, more electronegative, these bonds are weaker compared to transition metal to carbon bond, despite these bonds are stable with respect to this one.

The reason, if you just see here the force constant measurements for metal to carbon sigma bonds shows that main group element to carbon bond as well as transition metal to carbon sigma bonds can be comparable in strength having energy anywhere between 120 to 135 kilojoules per mole. That means why these transition metal to carbon bonds are highly unstable compared to main group elements to carbon bond.

And if the bond enthalpies are same, the difficulties in handling organometallic compounds are not due to low thermodynamic stability, but rather due to high kinetic lability. I repeat again, the difficulties in handling and storing organometallic compounds is not due to low thermodynamic stability but rather due to their high kinetic lability.

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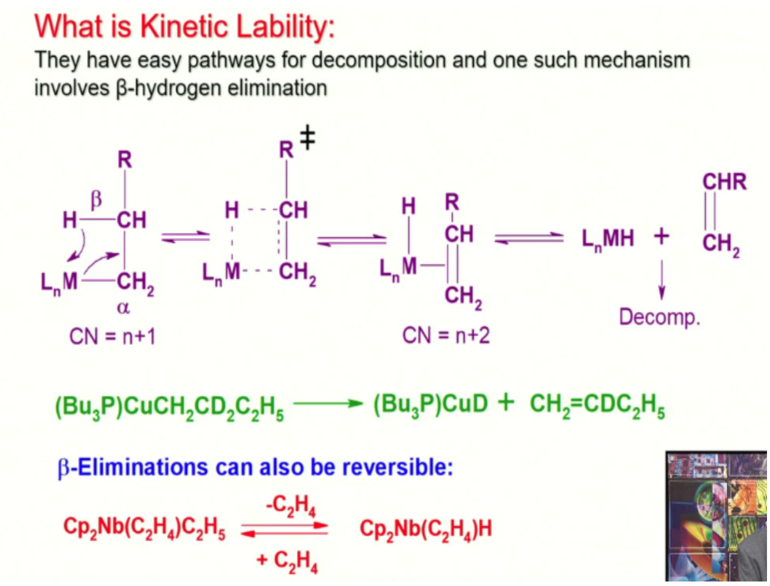

What is Kinetic Lability:

They have easy pathways for decomposition and one such mechanism involves β-hydrogen elimination

$$(Bu_3P)CuCH_2CD_2C_2H_5 \longrightarrow (Bu_3P)CuD + CH_2{=}CDC_2H_5$$

β-Eliminations can also be reversible:

$$Cp_2Nb(C_2H_4)C_2H_5 \underset{+C_2H_4}{\overset{-C_2H_4}{\rightleftharpoons}} Cp_2Nb(C_2H_4)H$$

So, what is the aspect that is responsible for them to make kinetically labile? The culprit is beta hydrogen elimination. So, they have easy pathways for decomposition and one such mechanism involving beta hydrogen elimination is shown in this figure. So, let us say we have a metal bound group like this, where we have beta hydrogens and it can establish a four membered intermediate in this fashion so that hydrogen starts interacting.

Beta hydrogen starts interacting and in this one what happens, eventually the CH bond is cleared and metal to hydrogen bond is established. And now, olefin formation takes place, olefine binding and further what happens here hydrated compound comes and then your olefin comes out and then eventually this may decompose depending upon metal to hydrogen bond enthalpy.

This is exactly opposite to hydrogenation reaction we come across on a metal centre. So, this kind of reactions are responsible for destabilizing organometallic compounds. How to prevent that one? Yes, we have to have some bulky groups like phosphine, cyclopentadienyl or pentamethylcyclopentadienyl groups on metal so that further formation of this kind of four member intermediate can be minimized or one can also look for organic moieties having no beta hydrogen atoms.

And of course, how to know that beta hydrogen elimination is happening in a particular reaction, you can see here. For example, you can take the labelled one, this beta hydrogen is labelled with deuterium and if you see that one eventually, that beta hydrogen should stay on metal. So, CuD is there and other one goes with this one. So, this is how one can also analyse the beta hydrogen elimination process. And is it reversible?

Of course, beta hydrogen elimination is reversible, you can see here. Just look into this example here where we have two cyclopentadienyl groups on niobium and one ethylene group is there and one ethyl group is there, this one on heating eliminates one of the ethylene groups and it forms, this C_2H_5 reverse beta hydrogen elimination to form a compound like this, on addition of ethylene you can regenerate.

And of course, this beta hydrogen elimination is reversible, if not the utility of metal complexes in hydrogenation reaction would not have come very handy for homogeneous catalysts. For example, if you have several very interesting, very bulky tertiary phosphines with us, then why we should go for a bidentate ligand?

Even when you go for bidentate ligand, why we should not go for symmetric bidentate ligand instead we should go for unsymmetrical bidentate ligand or even with unsymmetrical bidentate ligand why we should go for heterodonor ligands; with hetero-donor functionalities, that means one phosphorus can be there, other one can be a nitrogen, oxygen or sulfur donor.

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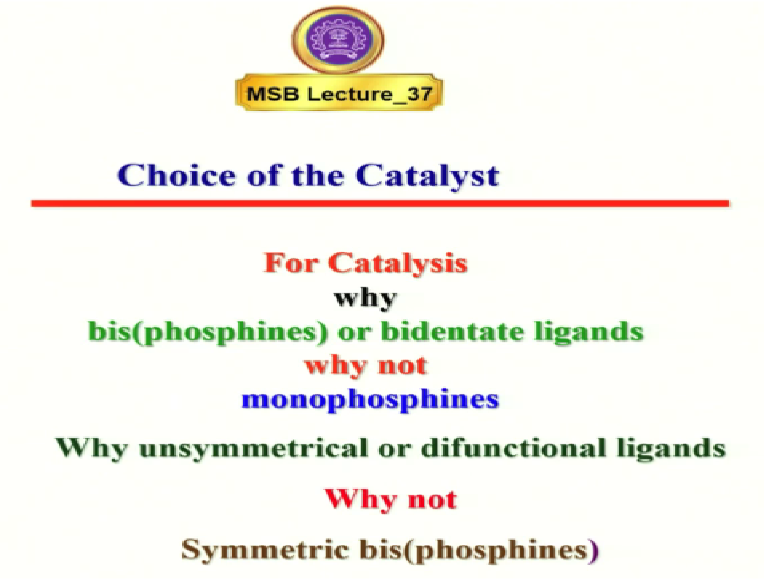

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Choice of the Catalyst

For Catalysis
why
bis(phosphines) or bidentate ligands
why not
monophosphines
Why unsymmetrical or difunctional ligands
Why not
Symmetric bis(phosphines)

So, let us look into the choice of the catalyst and choice of the ligands and choice of the combination of one or more donor atoms in such a way that really facilitates homogeneous catalysis through various processes. Let us look into that one. For catalysis why bisphosphines or bidentate ligands? Why not monophosphines? Obviously, this question would come into the mind.

And yes, if my answer satisfies and convince you, the next question is why unsymmetrical or difunctional ligands? Dppm is there, fine, why I should go for something else where two phosphorus moieties are different or one is phosphorus and other one in something else? And why not symmetric phosphine? I shall convince you about choice of the catalyst, advantage of each one through these cartoons.

I am sure at the end of seeing these couple of slides you will be convinced about what I say about the choice of the catalyst or choice of a particular ligand in a metal complex for its utility in catalytic process.

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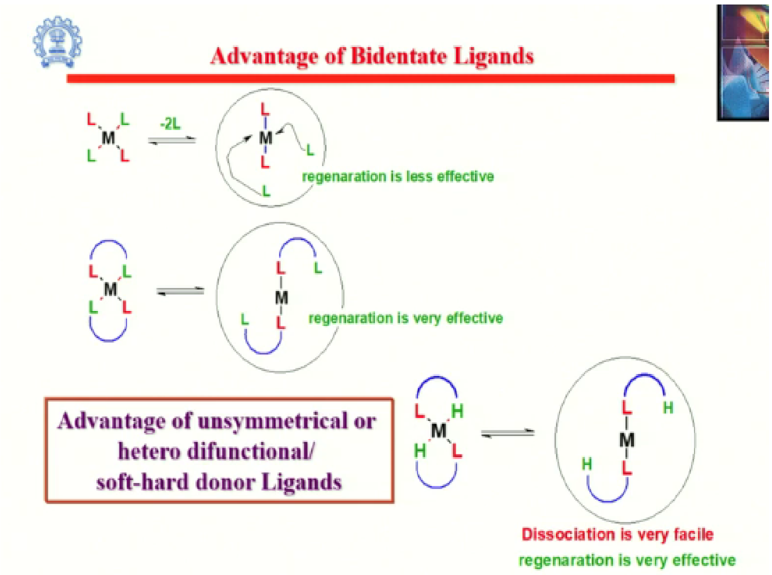

Advantage of Bidentate Ligands

regenaration is less effective

regenaration is very effective

Advantage of unsymmetrical or hetero difunctional/ soft-hard donor Ligands

Dissociation is very facile

regenaration is very effective

Now, advantage of bidentate ligand. First let us look into monodentate ligand. So, assume this is a typical $Pd(PPh_3)_4$ complex. Many organic chemists, for a variety of organic transformation they use it, it is commercially available, it is very unstable, and especially it has to be handled under inert atmosphere. So, when you take this one, you put into solution, initially what happens, it has to get rid of 2 ligands to generate an active species something like this.

And once you generate this one, and these two ligands will be in solution, whatever the organic medium you are taking, and then it is not very easy to regenerate by bringing these back to establish this kind of coordination. We are not talking about an isolated molecule here. If you take even one mole, we have 6.023 x 10^{23} molecules of complexes and then we have so much of solvent molecules.

In that case, what happens, we also talk about efficient collision frequency and all those things. So, considering all those things, when these two ligands are dissociated, again going back to establish this one is next to impossible or efficiency may drop, as a result what happens? In the first round, let us have 100 such molecules were there, in the second step we may be left with 40, in the third way maybe 20.

So, this catalytic cycle will diminish and within no time catalyst is no longer available for further catalytic process. So, that means catalytic turnover number and turnover frequency are going to be very low as regeneration is less effective when you use monodentate ligands.

On the other hand, just look into these two bidentate ligands, very similar to this one except its chelation. And in this case, two ligands are there here and two bidentate ligand, again 18 electron species. So, before we use it for catalysis, we have to dissociate two bonds. And when we dissociate two bonds, what happens still two donor atoms are in close vicinity of the metal centre, they are like dangling, and not going away from the metal centre and they are continuously making efforts to come back to the metal to establish this chelation.

In that process, what happens, when this catalytic process is over, initial oxidative addition and the reductive elimination is over, what happens, they are still in the close vicinity, they will come back and once they come back this catalyst can be regenerated very easily because it does not require much energy to bring back them to establish the bond. This is the advantage of bidentate ligands, regeneration is very effective.

On the other hand, due to some reason, what happens this dangling phosphorus atoms getting oxidized, then it becomes PO. When it forms PO, what happens now with the soft metal is there, hard centre is there, and of course in the absence of any other better ligand what happens, even there can be a soft-hard interaction and this chelation is completed or chelate effect will ensure that even a hard centre like oxygen that can establish a bond.

As a result, again 18 electrons species is generated, in fact this 18 electron species is going to be much more reactive compared to the previous compound, because even dissociation will be very facile because we have to cleave a hard and soft combination, not soft-soft combination. So, that means due to some reason, what happens a freed coordination site getting oxidized to generate a PO and then when the catalyst is regenerated having O bonded to metal, it becomes doubly effective because dissociation can happen within no time.

So, that is the advantage of unsymmetrical or hetero difunctional ligands or having a combination of soft-hard donor ligands. In this context, those who are generating or designing ligands give importance to make not symmetrical ligands but unsymmetrical having labile donor functionalities, also called hemi labile ligands. So let us discuss more about these things in my next lecture. Until then have an excellent time reading chemistry.