Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms
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Lecture – 38
Classification of Ligands – Phosphorus

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. I am sure you are enjoying the classification of ligands by donor atoms. In my previous lecture, I was telling you about how important it is to make the right kind of phosphines so that you can perform catalysis very efficiently under homogeneous catalysis. So, let me continue from where I had stopped.

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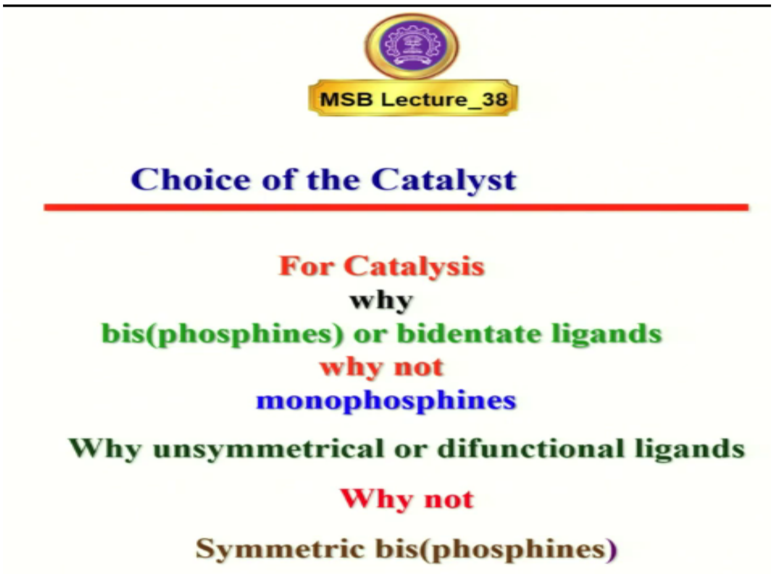

MSB Lecture_38

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)

I was telling you about the choice of catalysts and for catalysis, why we prefer bidentate ligands, even when you have bidentate ligands, why we prefer unsymmetrical bidentate ligands or difunctional ligands having hemilabile nature or of hybrid in nature.

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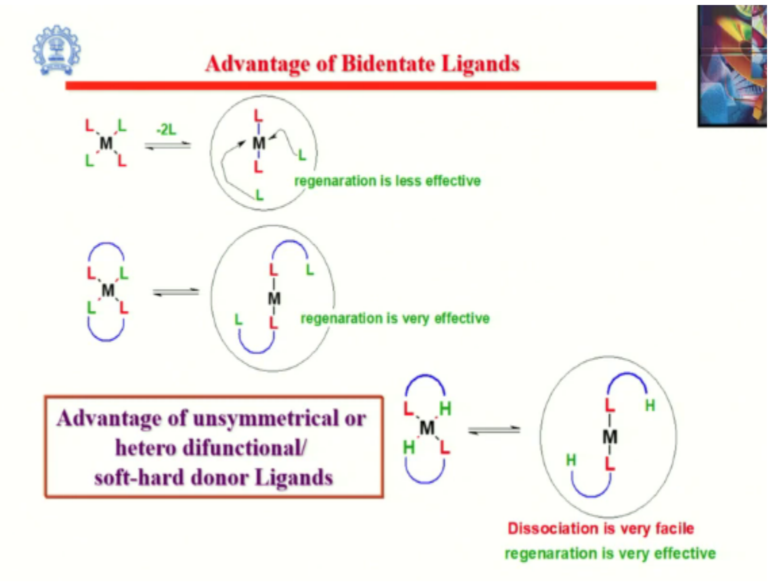

Advantage of Bidentate Ligands

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

So now let me show you, these things I showed you and also I showed you advantage of bidentate ligands versus monodentate ligands. And now, I shall try to convince you using these following cartoons why bidentate ligands are much more efficient and have longer life and can yield products with high turnover number and turnover frequency.

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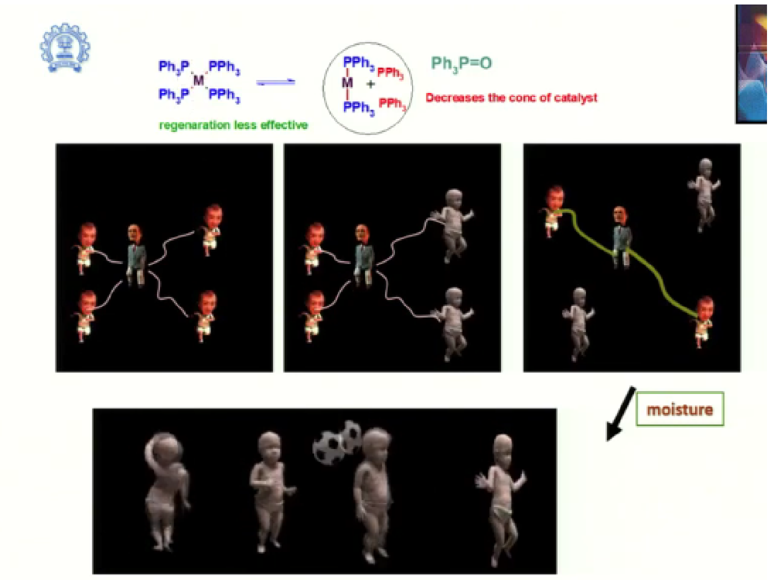

regenaration less effective

$Ph_3P{=}O$

Decreases the conc of catalyst

moisture

Let us assume $Pd(PPh_3)_4$ ligands are there and metal is here. And now we have to activate couple of bonds. The moment you put into solution, what would happen? Two bonds would be getting activated, as a result what happens, the bond distance also increases, that means they are ready for cleavage, you can see and also it is activated. So in the next step, they are completely detached.

You imagine a father goes with 4 children to some sort of mela where millions of people are there. In case, if he loses 2 children, it is highly unlikely that they will come back to father, and like that if 100 parents are going where millions of people are gathered, I am sure at least few parents would lose their children, they go empty handed or with fewer children in case if they are coming with 4 children with them.

This is what happens to $Pd(PPh_3)_4$ in solution when we are using it as a homogeneous catalyst for a particular organic transformation. So that means basically regeneration efficiency is very low. As a result, what happens, number of catalytic cycle one can perform will decrease. If moisture intervenes, these compounds are highly susceptible for oxidation, phosphines can be readily form phosphine oxide.

As a result, what happens? If the moisture comes, what happens the entire metal complex is decomposed and you can never get back this one from this condition. So, this is the fate of metal complex having 4 monodentate ligands when you want to use them in homogeneous catalysis. Organic chemists, what they do is they use large excess of that one, as a result what happens, they are not worried about the catalytic efficiency.

What they want is small quantity of catalytic product, there should not be any problem. But as an inorganic chemist if you want to use this one in very small quantity with the efficiency like 1 mole percent, 0.5 mole percent. I do not think it is an ideal case if you think about monodentate ligands.

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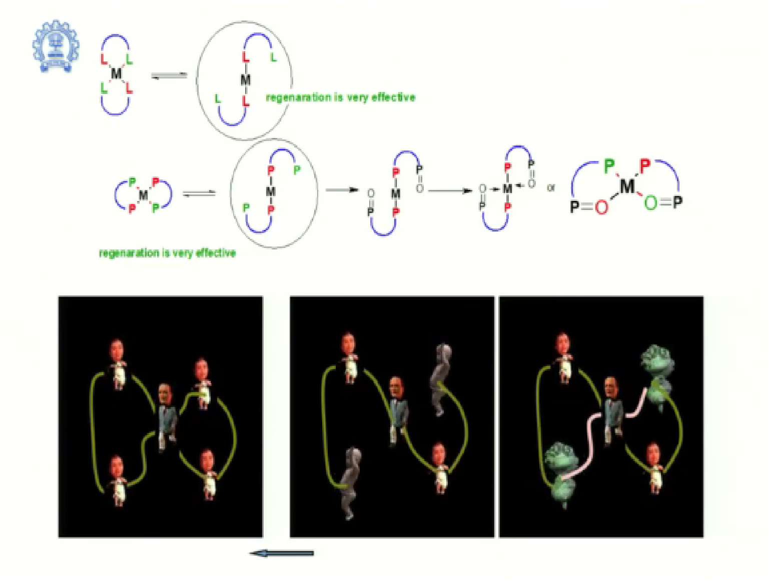

So, let us look into bidentate ligand in the same context. Now, you can see the difference between them is these two children are again tied. Now father knows that it is likely that he cannot control all the 4 together and even if his attention is diverted a little bit, these 2 kids can go away, as a result what he does is he ties the hands of children like this. In that case what happens, in case if he loses the grip on 2 children, they cannot go because their hands are tied with another one which he has a firm grip.

As a result, what happens? These two try to go away, but they cannot go away, they are in the vicinity of father and they will try to make bond or try to establish a bond, and once oxidative addition and reductive elimination are completed, they can establish so that father can go happily with 4 children. No matter how many people are gathered, it is highly unlikely that he loses children here.

This is what exactly one can compare with bidentate ligand in homogeneous catalysis. Due to some reason, what happens if it is getting oxidized, that means if get wounded let us say, wounded here baby or if the phosphine is getting oxidized to form a PO bond and now PO bond means it is a hard donor atom now, P is no longer a donor atom, but oxygen lone pairs can be donated to the metal, sometime it happens, if you take THF, diethyl ether they can also bind to metals which are soft.

So, as a result what happens now, it is no longer a trivalent phosphorus, it is a pentavalent tetracoordinated phosphorus having P=O and O has lone pair and then from this one once the reductive elimination is over, still we can establish a bond so that the bond is established here. So, that means again you can generate a more active species compared to the parent catalyst.

And it is much more easy to dissociate these bonds because this is a soft centre and these two are hard centres, dissociation would be very easy; there is a competition to dissociate this one and this one, you know that these bonds are soft, soft, stable and that is what we want. They want to be ancillary ligands, they have to be held on to the metal, whereas these two bonds should be cleaved, so that is what exactly happens. Now in the second cycle, if this happens, second cycle even much faster.

That means some damage that happens to uncoordinated or dangling phosphorus moieties can enhance the catalytic efficiency, something unusual unheard of, but it is true that happens in case of phosphines and this is the advantage of having unsymmetrical phosphines. I am sure you are convinced why we are very particular about designing appropriate phosphines with appropriate characteristic so that we can use them efficiently and also they can be more durable.

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Research Activities

- Phosphane/phosphinite/phosphonite Synthesis
- Phosphorus-Nitrogen Chemistry
- Pincer Chemistry
- Coordination and Organometallic Chemistry
- Coordination Polymers, Metal Clusters and Cages
- Homogeneous Catalysis
- Anticancer Studies
- Photophysical Studies
- Material Applications

When we look into the phosphorus bound metal complexes, their application are plenty and of course, when we talk about phosphines, we come across a variety of groups on phosphorus. They can be phosphanes also called phosphines, phosphonites, phosphinites and phosphorus nitrogen compounds. Of course, pincer chemistry comes into picture and then in coordination and organometallic chemistry, they are second to none.

And coordination polymers, metal clusters and metal cages phosphines play major role. And of course, homogeneous catalysis they are the leading ligands. And of course, with less toxic phosphines one can think of them in anticancer studies. And they can also show interest in photophysical studies and also they can be very handy in material applications.

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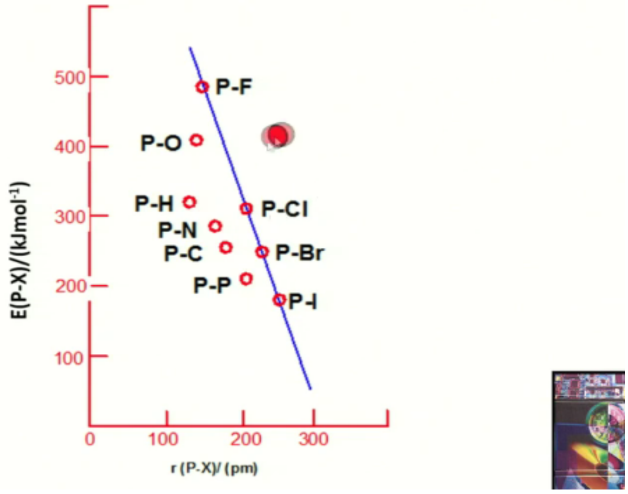
Bond enthalpies *vs* bond lengths for phosphorus bonds



Now, we should look into this bond enthalpies and if you see here phosphorus to fluorine bonds are quite strong, whereas phosphorus to iodine bonds are very weak. And of course, these compounds are quite expensive and not very easy to handle. But on the other hand, P—Cl and P—Br bonds can be handled nicely; P—Br$_3$ is also used as a brominating agent in organic chemistry. And the most appropriate and economical compounds are phosphorus chlorine compounds that means having 3 chlorine atoms on phosphorus or phosphorus trichloride.

Phosphorus trichloride has optimum properties, one can perform a series of nucleophilic substitution reaction to generate a desired phosphorus compound either by using lithium reagents or Grignard reagents or even Friedel-Crafts reaction for that matter or several other reactions where one can replace chlorine with right kind of substituents to have moderate or desired steric and electronic attributes on it.

Now how to replace? In my previous lectures when I was talking about several metal complexes, I showed you how you can generate labile complexes and eventually replace those with phosphines or the other ligands. For example, if you have acetonitrile, benzonitrile, cyclooctadiene or norbornadiene, they are very easily replaceable ligands, one can make those compounds as intermediates.

And then under mild conditions, one can generate a phosphine complex whether a monophosphine, bisphosphonate or even a phosphorus compound having tridentate properties. So, now I will show you how one can replace carbon monoxide using mild condition. For example, one can also perform for the chemical reaction, you can shine UV light and you can detach or dissociate CO.

And in its place another phosphorus ligand can come or one can also do thermal reaction by refluxing in appropriate metal carbonyl with ligand in a right kind of solvent, but how to do substitution of carbon monoxide with phosphine under mild conditions at room temperature, there is an option one can use trimethylamine-N-oxide, let me show you this trick.

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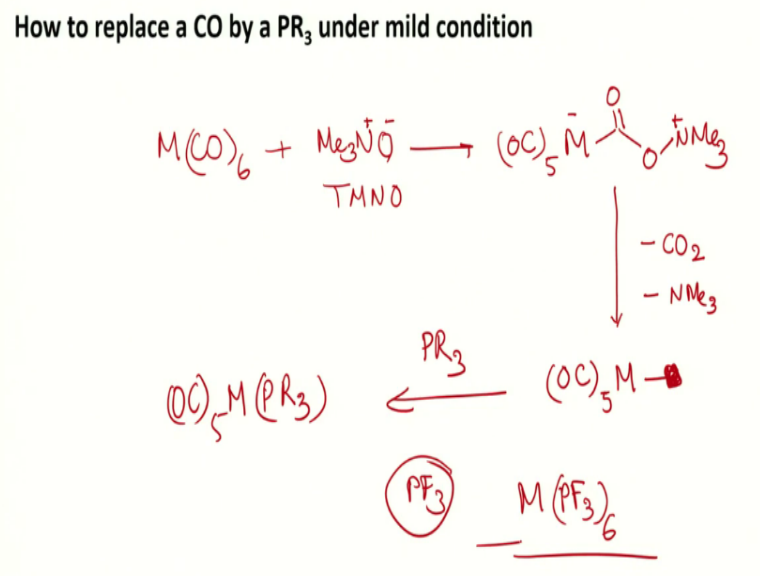

How to replace a CO by a PR_3 under mild condition

So, let us consider a hexacarbonyl, so it can be molybdenum or tungsten. Then treat this one with 1 equivalent of trimethylamine-N-oxide, this is also called as TMNO. Then it forms an intermediate, of course here you should remember it has something like this, bond is polarized here, it forms a compound of this type here.

So, now we have plus charge and we have negative charge here. Now, what happens, it readily loses a molecule of carbon dioxide and a molecule of trimethylamine to generate a vacant site on metal, this the vacant site now. So, now if we add at this stage a tertiary phosphine, we can make very conveniently a phosphine complex something like this. Of course, one can do stepwise.

Now, we can add one more equivalent of TMNO and we can substitute for one more carbon monoxide, we can keep on doing. And if the phosphine taken is not very bulky and the phosphorus substtuents are very strong electron withdrawing groups, then probably we can replace all carbon monoxide from hexacarbonyl, examples: if you take trifluorophosphine this is one such ligand whose sigma donor and pi acceptor abilities can be compared to carbon monoxide.

It can knock off all carbon monoxide and one can form a homolyptic complex like this. So, there are not many ligands we have which can replace all CO, of course one can also take a nitrogen donor ligand. If you ask a question take metal hexacarbonyl or trimethylamine N oxide and it generates a vacant site, how about adding ammonia? Yes, you can add ammonia, triethylamine you can add, you can add acetonitrile still you can form.

But only thing one should remember is if you want to replace carbon monoxide with nitrogen donor ligands which are only sigma donor you cannot go beyond 3, and at most you can get $M(CO)_3L_3$, where L can be any nitrogen donor ligand, whereas in case of phosphines it is possible. So, this is one mild reaction method where a carbon monoxide can be replaced at room temperature using a solvent such acetonitrile or even toluene.

Now, the question is, is they remain always ancillary ligands or silent spectator, phosphines or is it possible to perform some reactions on coordinated phosphines? Yes, I showed you when talking about ortho-metalation, triphenylphosphine can undergo ortho metalation through CH activation and then it can be added oxidatively and then if the condition is suitable HCl can be eliminated or if the metal has a halide that can still be retained having higher coordination number or higher oxidation state.

But if we can perform reaction on coordinated phosphorus, yes, it is possible, then again we are thinking of an interesting catalytic system.

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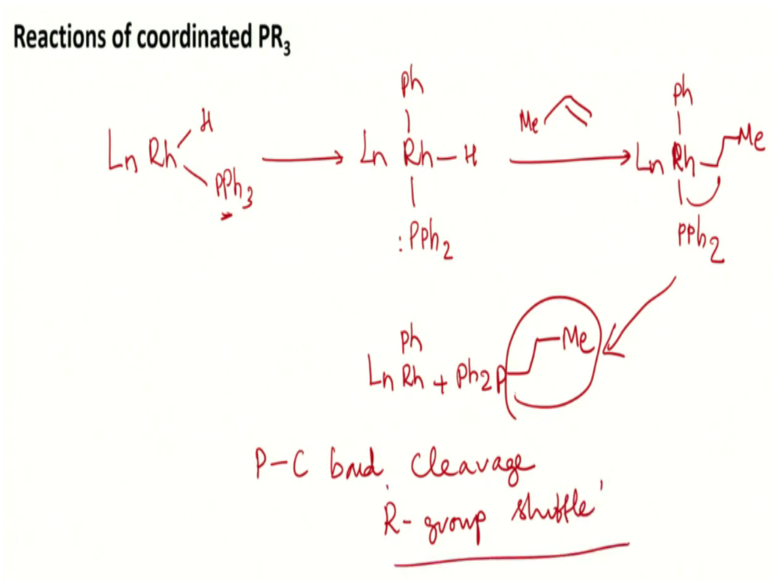

Reactions of coordinated PR_3

So, let us look into what would happen if we make an attempt to do P-C bond cleavage. So, let us consider a complex like this. We have some other ligands along with a triphenylphosphine and hydride. So, if we take this one there can be cleavage of P-C bonds to generate a rhodium to phenyl bond and now we have a phosphido group is there and this lone pair is intact now, and then it can generate a species of this type.

So, now let us say we are adding inorganic compound, it can give something like this. One can eventually eliminate triphenylphosphine as a different ligand now, which can eliminate this diphenylphosphino moiety through this coupling reaction. That means, it is possible to activate P-C bond of coordinated tertiary phosphine. Earlier we had a phenyl group there, if and now phenyl group has come out and then in its space we have a new moiety here.

That means this is a typical P-C bond cleavage and this is also called as R-group reshuffle or R-group shuffle So, this also comes very handy in generating a new kind of tertiary phosphines having different substituents on phosphorus. I shall tell you more about these kinds of reactions at later stage. In fact, in our own group we have seen P-C bond cleavage and also migration of phosphorus bound group onto the metal, very interesting chemistry carried out recently. I shall tell you some time before I conclude phosphorus donor ligands.

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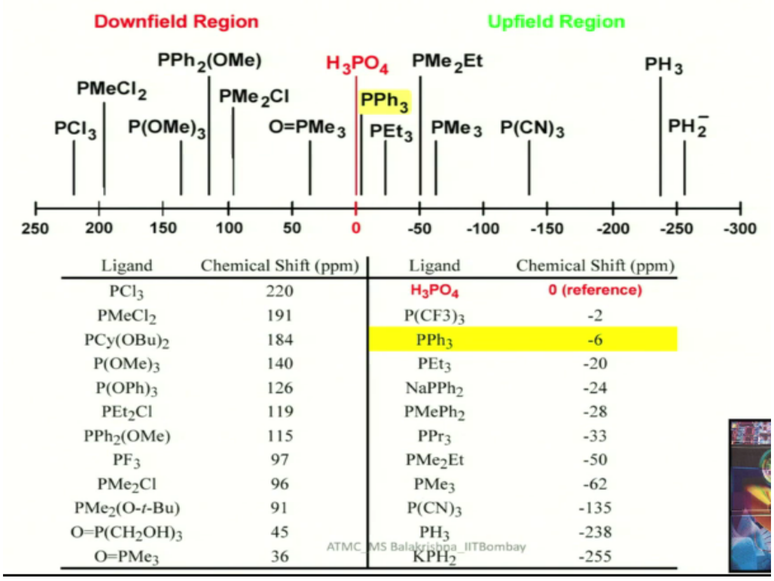

Ligand	Chemical Shift (ppm)	Ligand	Chemical Shift (ppm)
PCl_3	220	H_3PO_4	0 (reference)
$PMeCl_2$	191	$P(CF3)_3$	-2
$PCy(OBu)_2$	184	PPh_3	-6
$P(OMe)_3$	140	PEt_3	-20
$P(OPh)_3$	126	$NaPPh_2$	-24
PEt_2Cl	119	$PMePh_2$	-28
$PPh_2(OMe)$	115	PPr_3	-33
PF_3	97	PMe_2Et	-50
PMe_2Cl	96	PMe_3	-62
$PMe_2(O\text{-}t\text{-}Bu)$	91	$P(CN)_3$	-135
$O{=}P(CH_2OH)_3$	45	PH_3	-238
$O{=}PMe_3$	36	KPH_2	-255

Another advantage with phosphines is ^{31}P NMR. NMR spectroscopy comes very handy in diagnosing the complexes and nature of the complexes and also reactivity of the complexes because, phosphorus depending upon what kind of groups we have and also what is the oxidation state, whether trivalent phosphorus or pentavalent phosphorus they have very distinct chemical shifts that vary, that range from +250 to –300 ppm in general or it can go from plus +600 to –600 ppm or in some cases it can also go from +800 to –800 ppm.

And here ^{31}P NMR, P nuclear spin is half and it is 100% abundant. As a result carrying out or performing phosphorus NMR will be very easy and here we are using 85% phosphoric acid as a reference and that chemical shift is considered as 0. Whatever comes on the left is called downfield region, on right region is called upfield region or this is shielded and that is deshielded and low frequency shift and high frequency shift; we also call.

If time permits, I shall introduce interpreting NMR spectroscopy to make you familiar to interpret spectral data while characterizing metal complexes when you have nuclear active species in it. I shall try to do that at the end. When you have different substituents, they have very distinct chemical shifts. For example, trichlorophosphorus or phosphorus trichloride appears at 220 ppm.

When you start replacing chlorides what happens it will be more shielded and when it comes here, it is more shielded and it appears at 36. And as I mentioned phosphoric acid 0 reference, then when you have this one –2 is there, triphenylphosphine –6 ppm. They have distinct chemical shifts. When you react a metal complex with phosphine, whether the metal complex has formed or not or if we have any unreacted phosphine or whether it is decomposed, where it is oxidized.

All this information comes simply by looking into ^{31}P NMR of the species. So, this is where it comes very handy in diagnosing the reactions and reaction sequences and also sometimes one can also perform kinetics using ^{31}P NMR spectroscopy.

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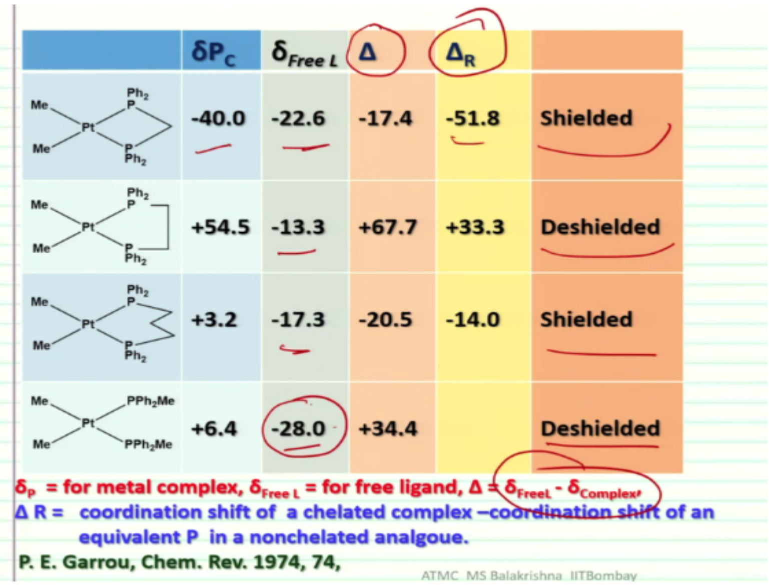

	δP_C	$\delta_{Free\ L}$	Δ	Δ_R	
	-40.0	-22.6	-17.4	-51.8	Shielded
	+54.5	-13.3	+67.7	+33.3	Deshielded
	+3.2	-17.3	-20.5	-14.0	Shielded
	+6.4	-28.0	+34.4		Deshielded

δ_P = for metal complex, $\delta_{Free\ L}$ = for free ligand, $\Delta = \delta_{FreeL} - \delta_{Complex}$,
Δ R = coordination shift of a chelated complex –coordination shift of an equivalent P in a nonchelated analgoue.
P. E. Garrou, Chem. Rev. 1974, 74,

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So, now I will show you very interesting feature here. For example, when we have four membered ring, this is a bisphosphine having one methylene group there and it is dppm, we have, bis(diphenylphosphino)ethane. We have, bis(diphenylphosphino)propane. So all of them are forming four membered or five member or six membered rings and then again chelate ring size also has influence on chemical shift.

That means electron density on the phosphorus can also vary with ring size. That also sometimes assist us in understanding the reaction sequence and also how much electron density resides on phosphorus and all those things. For example, now if you look into this chelate complex and let us say in case of dppm if you want to imagine two simple monodentate ligands, the best would be having; so we have methylene group there.

So the best monodentate ligands that come very close to the property of bidentate ligand or methyl diphenylphosphino, for example it is here, this one is more or less comparable to two donor atoms present in these three chelate rings. And now what I have done here is to show you chemical shift for these metal complexes here and then plus or minus charge indicates shielded or deshielded, so this is for the complex and this is for the free ligand dppm.

Similarly this is for dppe and this is for dppp and this is for the free ligand here. And then the difference, what is this? This is called coordination shift. Coordinates shift is nothing but the difference in the chemical shift between the free ligand and the complex. So, that one is given here. What is this one? This is called coordination shift of a chelate complex. So, here this value also gives you some information. This is taken by considering this value from this one.

For example, if you take this value here and then the difference would come here in the ligand chemical shift and this one should give you this one, now we can see dppm is more shielded and dppa deshielded and again this is shielded and this one is deshielded. So, that information we can effectively use in analysing some of these reactions and also to understand the nature of donor properties and also the stability and all those things. Let us try to do these things as and when we get such opportunities.

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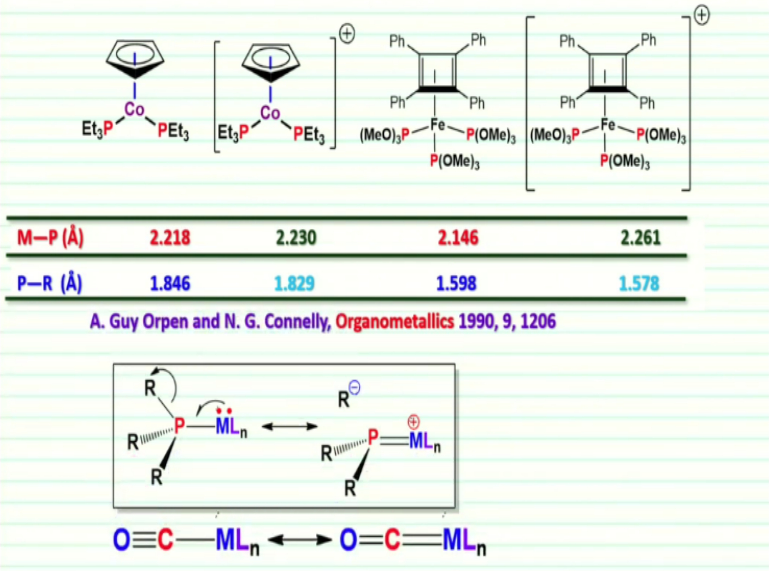

M–P (Å)	2.218	2.230	2.146	2.261
P–R (Å)	1.846	1.829	1.598	1.578

A. Guy Orpen and N. G. Connelly, Organometallics 1990, 9, 1206

$$O{\equiv}C{-}ML_n \longleftrightarrow O{=}C{=}ML_n$$

Now, just I would show you the donor and acceptor properties of phosphines, how one can analyse or how they can impact the bond parameters. I have taken two examples here with cobalt heaving one Cp group cyclopentadienyl and two triethylphosphines, one is positive and one is neutral. So, that means here we have taken a cobalt(I) and here we have taken a cobalt(II).

Similarly in iron case also we have taken one neutral and then one cation, so that means a positive one and a neutral, that means in this one electron density is less and here electron density is more. Now let us look into the Co—P and P—R bonds. Cobalt to phosphorus bond distance is 2.218 Å here in this one, whereas in this one it is 2.230 Å. That means the bond is a little bit elongated. Why is it elongated?

There is less back bonding from cobalt to phosphorus, because it is already electron deficient. So, that means this one certainly gives you a hint that yes back bonding is there and back bonding can strengthen metal to phosphorus bond, the way we see in case of metal carbonyls where excessive back bonding from metal to carbon monoxide increases the strength of metal to carbon bond and decreases its length and also CO bond length is increased, it is elongated.

In the same context, you can also compare here. In this one bond is little shorter whereas here a little longer because Co is not a very good donor here because of positive charge, same thing one can see here in iron compound 2.146 and 2.261 Å. So, that means, again here iron because of one electron less it is a weak pi donor. And then how that impacts? Of course, here what happens if back bonding is more metal to phosphorus bond is strengthened, on the other hand, what would happen to phosphorus to carbon bond, you can see here.

In this one it is 1.846 Å, so that means bond is getting elongated, P-C bond is getting elongated, of course that should happen, I will show you later. And then here not much back bonding is there, as a result what happens the bond P-C bond is little stronger here, 1.829 Å . So, that means the impact has not only alters metal to phosphorus bond, but also dramatically it alters metal to carbon bond also, that can be seen here.

In extreme cases, what happens? One can think of cleaving P-C bone, this is what exactly happens I showed you in my previous slide. So, same thing, analysis you can make. That means if we have careful analytical observation, we can see all those things and we can understand the properties in a much better way, you can get like this. For example, we take when the excessive back bonding is there and that means more and more electrons goes to the sigma star.

As result what happens this R group can come out as a carbanion and then it will carry a positive charge. If that happens, whether we can use this moiety in a catalytic manner as an alkylating agent, yes we can do it, no one has done so far, but if you want to do it, we have to see how again we can bring back another alkyl group here. If we can catalytically using a suitable reagent, if you can furnish again formation of PR bond, yes we can use this one very interestingly as an alkylating agent.

Let me stop at this juncture and continue talking, discussing interesting phosphorus chemistry in my next lecture. Until then enjoy reading phosphorus chemistry.