Advanced Transition Metal Chemistry – Metal-Metal Multiple Bonding
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Lecture – 26
Preparation of Important and Useful Metal Complexes

Hello everyone. I once again welcome you all to MSB lecture series on transition metal chemistry. In my previous lecture, I started discussing about the preparation of important and very useful coordination compounds and also organometallic compounds having labile ligands so that you can do substitution reaction to make desired complexes of your choice for whatever the desired application.

So, let me continue from where I have stopped. In my previous lecture, I wrote the preparation of rhodium chloro cod dimer and that is a very useful compound. So, let me write few more complexes to make you familiar with the preparatory methods. Let me give the preparation of another important compound of rhodium that is rhodium chlorocarbonyl dimer.

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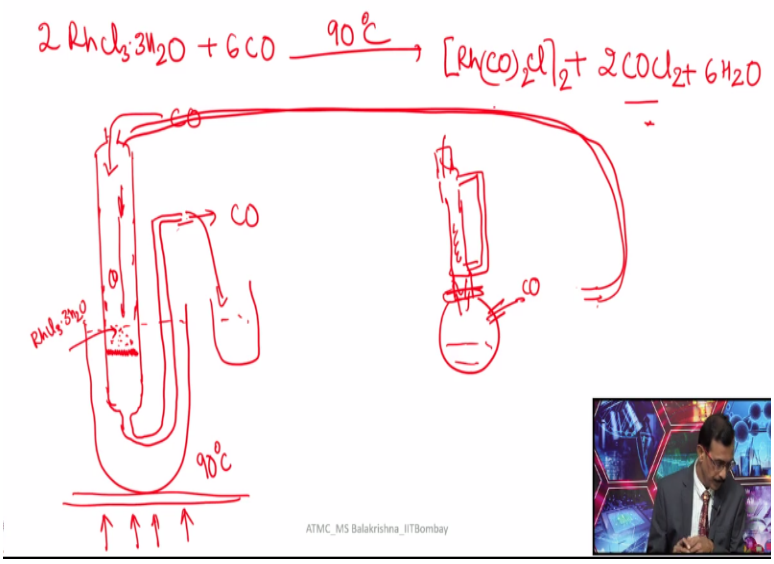

$$2\,RhCl_3{\cdot}3H_2O + 6CO \xrightarrow{90^\circ C} [Rh(CO)_2Cl]_2 + 2\,COCl_2 + 6H_2O$$

This is the component I am talking about. This is a dimer having symmetric chloro bridges. This is very interesting. This is a solid state reaction. Take rhodium trichloride trihydride and pass carbon monoxide at 90 to 95 ºC, so you get this compound. So, in this one what are other products we are going to get? We are going to get, so later try to see whether this reaction is balanced or not.

In this reaction, we are getting this phosgene. Now, one has to be very careful and this reaction has to be carried out in a well-ventilated hood. So, how to do this reaction? As I mentioned in this case, we are not using any solvent. For this one it is very simple. You have to choose an apparatus like this, have a frit here and then you should have a side tube like this and put here, CO should be bubbled.

Of course, the flow of carbon monoxide can be monitored by passing carbon monoxide through a paraffin bubbler so that you know how much it is coming. You have to bubble about couple of bubbles per second, very slow to minimize wastage of carbon monoxide, it is also very poisonous. Then what happens? It will keep on coming like this because of positive pressure and it touches here, it will start moving carbon monoxide and this entire place up to here, it should be immersed in liquid paraffin and heated to 90 to 95 ^{o}C.

It should not exceed beyond 95 ^{o}C, in that case what happens? It may lose this water in that case it becomes anhydrous and that is not reactive, so you will not get the product. And here of course this is an outlet for CO. So, in this reaction when you are doing this the CO will react with $RhCl_3.3H_2O$ to form rhodium chlorocarbonyl dimer and phosgene will be coming out and water will be coming out and then water vapours also will be condensing somewhere here.

And then very nice crystals of this dimer will start subliming and it will come here and you have some greyish colour rhodium trichloride trihydride. You can visually monitor the disappearance of starting compounds that indicates formation of rhodium chlorocarbonyl dimer, and it is almost 100% pure. And in case if you find some dust and other things due to the impurity present in rhodium chloride trihydrate what you can do is you take the product later.

Of course the frit is there you can add here hexane and then you apply pressure so that you can collect it from the side, and solution on cooling to zero degree temperature you can see very orange crystals of rhodium chlorocarbonyl dimer formation and it is moderately stable. One can use it for further substitution reactions with various phosphines and other ligands.

And in case carbon monoxide cylinders are not there, carbon monoxide can be generated in the laboratory by using formic acid and sulfuric acid. What you can do is you can take formic acid in a flask and then add using a dropping funnel sulfuric acid dropwise and when the carbon monoxide is liberated, because of dehydration process, CO is formed and this CO will try to come out something like this.

So, when you add from here sulfuric acid, using pressure equalizing dropping funnel, you can see the better picture in any of these books. So, here you pass, here you have sulfuric acid, when adding dropwise here, to the formic acid and CO will come and this CO may carry moisture. So, it has to be passed through again sulfuric acid and bubbling through sulfuric acid and collect it here and then this can be used here.

And of course, once the reaction is complete, you can cut off the addition of sulfuric acid and you will stop it and this reaction has to be carried out in a well-ventilated fume hood because of we are handling carbon monoxide.

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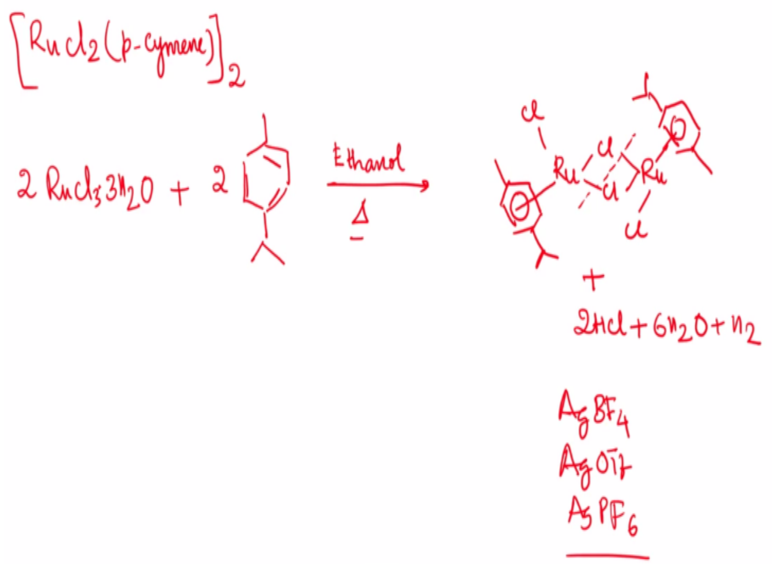

Now let us go to another important component of ruthenium, ruthenium dichlorocymene dimer. I shall write the structure later, first I will give you the preparation. Take ruthenium trichloride trihydrate as usual and treat with two equivalents or slightly excess of cymene. Cymene is this aromatic compound having these kinds of para substituents and take this reaction mixture in ethanol and reflux it, to indicate reflux in a chemical reaction, we use the symbol, Δ. We get the desired dimer in quantitative yield.

So, this is how the dimer looks like and plus what we get is, so this is a very useful compound in many catalytic reactions in homogeneous catalysis and of course this also once again when you perform some reactions with phosphines and other ligands, this breaks symmetrically here and it generates a vacant coordinate site so there you can place desired ligand. And of course, once you do this reaction in polar solvent, you can also knock out one of the chlorines and again put another phosphine or use a bidentate ligand. And for removal of halogens from metal, the best method is to use salts such as silver tetrafluoroborate or silver triflate or silver acetate, silver triflate you can use or one can also use $AgPF_6$. Plenty of such salts are available having larger anion. The advantage with larger anion is if the anions are larger the compounds readily crystallizes and isolation in pure crystalline form and also looking into the structure would be very easy.

And one can also use corresponding potassium salts also if the compounds are more reactive, otherwise ideal ways to use some of the silver salts and silver halide will precipitate out and that can be separated and you have anionic compounds, cationic complexes with these larger anions.

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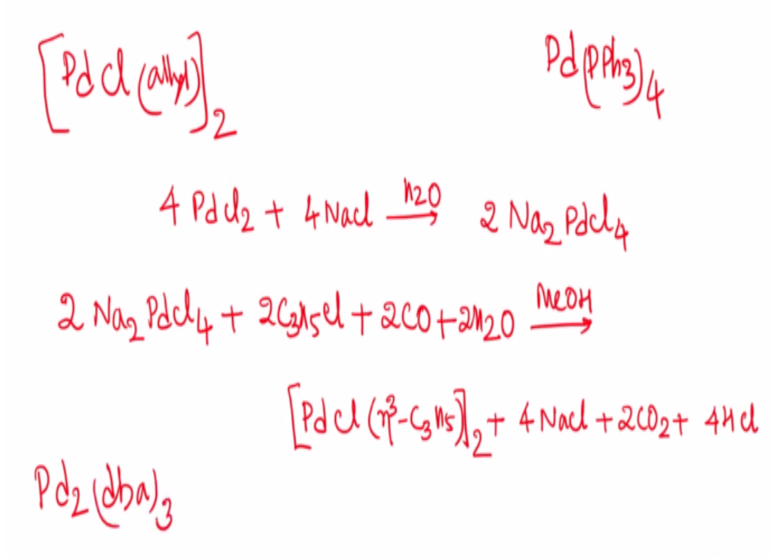

$[PdCl(allyl)]_2$

$Pd(PPh_3)_4$

$$4\,PdCl_2 + 4\,NaCl \xrightarrow{H_2O} 2\,Na_2PdCl_4$$

$$2\,Na_2PdCl_4 + 2\,C_3H_5Cl + 2\,CO + 2\,H_2O \xrightarrow{MeOH} [PdCl(\eta^3\text{-}C_3H_5)]_2 + 4\,NaCl + 2\,CO_2 + 4\,HCl$$

$Pd_2(dba)_3$

Now, let me give the preparation of another important component palladium allyl dimer. So, for the preparation of this one, one has to begin with, if you do not have potassium or sodium palladate, one has to make that one, that is very simple. Take palladium chloride and treat that one with sodium chloride or potassium chloride in water, you can get the corresponding palladate. Once after making this one, take this sodium tetra palladate, treat this one with the allyl chloride.

So, this is the method used for preparation of palladium chloro allyl dimer, it has a hapticity η^3, Another important component is $Pd_2(dba)_3$. So, of course I showed you the other day preparation of palladium and platinum tetrakistriphenylphosphine, a very useful compound. After that one another important compound that is widely used in catalysis as a starting zero valent palladium complex is $Pd_2(dba)_3$.

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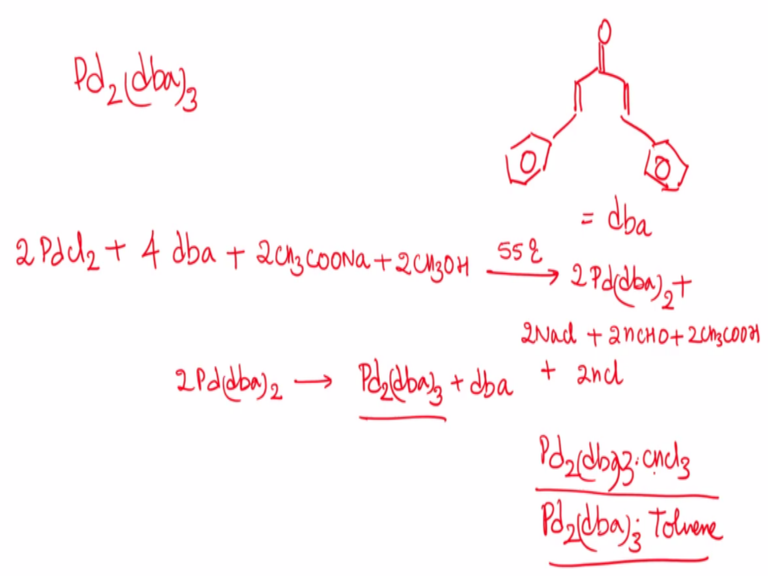

So, let me give you the preparation of this one. So, what is dba, dibenzylideneacetone. So, this can be prepared very easily starting from benzaldehyde and acetone. One can prepare this compound in large quantities, enormous quantitative yield, few hours reaction, this is simple condensation reaction. Once you have this one, bright yellow colour stuff, one can treat this one with palladium chloride using a reducing agent such as sodium acetate. This is called dba.

This should be heated to strictly 55 °C. One should not go beyond that one. If you exceed this temperature, it may lead to some other product or some reduction of palladium to palladium(0) and that becomes useless and also that reduces yield of the product. Initially, $Pd(dba)_2$ is formed. So, this is a balanced chemical equation for the preparation of $Pd(dba)_2$ starting from palladium chloride. This $Pd_2(dba)_3$ will be in equilibrium.

What it does is in solution it forms this one, just dba comes out. So, 1 gram of palladium chloride can give you as much as 3.5 grams of $Pd_2(dba)_3$ and of course once after making $Pd_2(dba)_3$ if you dissolve in chloroform and if you crystallize, it comes as solvated with chloroform something like this. And if you crystallize this one in toluene, it will be solvated with toluene or if you crystallize in dichloromethane, one mole of dichloromethane will be this.

And if you want to use this compound which is free from any chlorinated solvents and if you think this chlorine will affect your reaction, better to go for toluene solvated one. Otherwise, for most of the purposes one can go for this one. It gives excellent yield and also this compound very nicely crystallizes and handling would be very easy.

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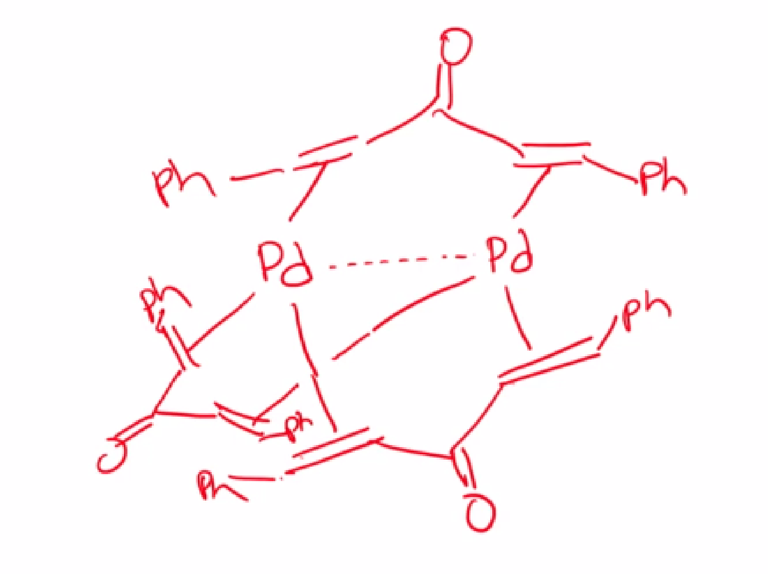

How this is binding? I will show you here. It is $Pd_2(dba)_3$, so you may be wondering what is the geometry, so something like this. These double bonds will be binding and of course here you have phenyl groups there. So, another one will also bind like this and then you have about 3.2 Å separation between two palladium atoms. So, this is how it binds and palladium has trigonal planar geometry, having weak palladium-palladium interaction. Let me give you the preparation of some metal carbonyl complexes.

Of course, when I go to classification of ligands and discuss about carbon as a donor atom or ligands containing carbon as donor atom, I shall give you more information. Nevertheless, when we have homolyptic metal carbonyls, there are three ways we can activate CO bonds for further substitution reaction. One is thermal reaction. So, taking metal carbonyl and heating in presence of desired ligand using aliphatic or aromatic solvents.

One has to be careful with aromatic solvents because aromatic solvent itself can bind in η^6 fashion and to form, for example: if you take molybdenum hexacarbonyl and treat with benzene or reflux in benzene it may form η^6 arene coordinated tricarbonyl complex like $[\eta^6\text{-}C_6H_6)Mo(CO)_3]$. So, in order to prevent the formation of aromatic complexes, one should use solvents such as heptane or methylcyclohexane.

And heating to about 100 degrees centigrade can give you thermally activated where you can eliminate one or two carbon monoxide and in its place you can bring desired phosphines or some other ligands. And then another method is photochemical reaction. And you do perform photochemical reaction using THF or something. Initially what happens carbon monoxide comes out, and in its place loosely held THF coordination will be there and later when you add a better sigma donor ligand such as phosphine that can replace.

And of course, the advantage with photochemical reaction you can monitor the reaction using IR and IR can tell you by just looking into how many absorptions we are getting, stretching frequencies you can observe whether it is forming η^5, η^4 or η^3 that also depends on the type of ligands you are using. And sometimes, we also end up with getting a mixture of compounds and you should be able to know how to separate them.

If not best is to go for tetracarbonyl complexes having two labile ligands so that you can do it very easily in substitution reactions. So, those things also I will tell you. And another one is you can also use mild reagents to replace carbon monoxide at room temperature and carbon monoxide comes out in the form of very inert gas and in its place, now the site that is vacated by carbon monoxide can be substituted by phosphines and other ligands. So, you can use 3 methods according to the convenience.

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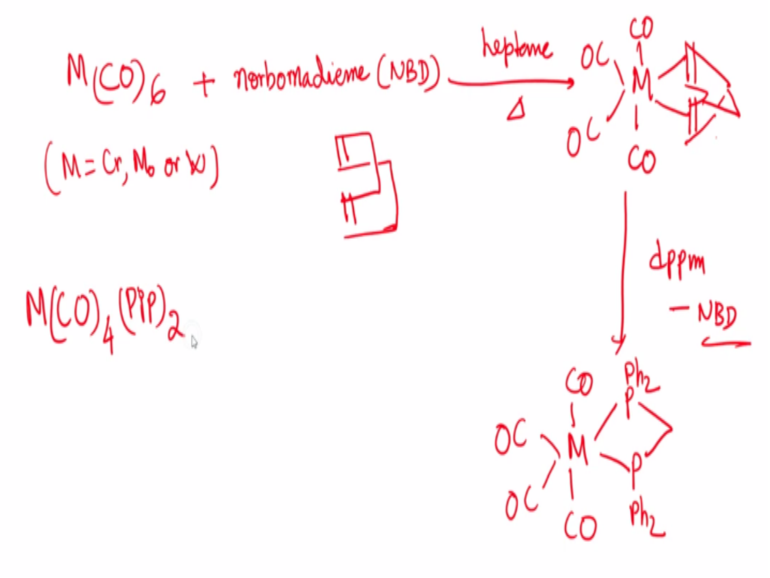

To begin with let me show you how to make some of these $[Mo(CO)_4L_2]$ compounds having C_{2V} symmetry, for example if you take $M(CO)_6$ where M = Cr, Mo or W) and treat this one with norbornadiene, it is also called NBD, taken in heptane, take this with $Mo(CO)_6$ or $M(CO)_6$ with slight excess of norbornadiene and heat it in heptane. What you can get is a compound of this type having four carbonyl groups.

This is called bicycloheptadiene, it is also called norbornadiene. And here the advantage with this one is you can see this is a very strained chelating ligand because of this strain, what happens you can readily substitute this one with a bidentate ligand. For example, you take this one, treat with dppm, perhaps you know what is dppm already, we discussed several times. It can readily form this type of compounds in almost quantitative yield, NBD comes out here.

And some time if there is a problem of separating NBD what you can do the same reaction in refluxing in hexane. In that case what happens at that temperature when NBD comes out it undergoes some sort of polymerization to form insoluble stuff and that will stick to the walls inside and as a result this compound is dissolved in hexane and comes out very easily and separation will be very easy.

So, that is the advantage. Some time, if performed this reaction with slightly higher temperature, NBD gets polymerised, some time it also forms cyclic polymers, one can use these compounds for further reactions. Of course, in case of chromium, molybdenum, tungsten, temperature little varies and also yields are little different. One can get good yield in case of molybdenum and yields are much lower in case of chromium and tungsten. And in place of norbornadiene one can use cyclooctadiene also. This also one can use.

This compound is slightly more stable compared to norbornadiene complexes and again they have very characteristic smell. Once when they are replaced with appropriate ligands, you can also the smell the liberated one near the reaction that also indicates that, yes, your reaction is complete or substitution is going on or is completed you should be able to see. So, another couple of important components of molybdenum, tungsten are having four carbon monoxide groups are these piperazine complexes.

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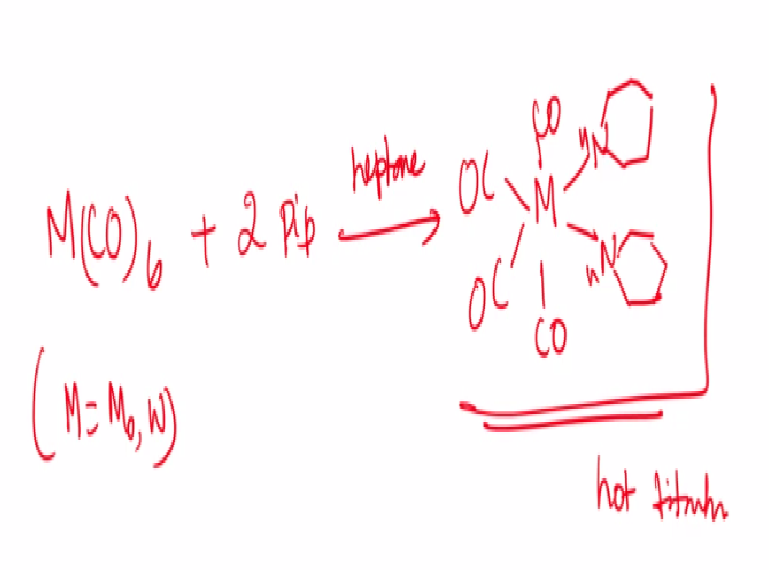

And this can also be made starting for $Mo(CO)_6$, $M(CO)_6$ here, only in case of molybdenum and tungsten one can make this compound. These piperidines will be binding here and take these two and reflux in heptane, within about 2 hours bright yellow precipitate is formed, one has to do hot filtration. You have to do hot filtration. Hot filtration will ensure that unreacted $Mo(CO)_6$ or $W(CO)_6$ comes out.

And after hot filtration whatever remains on the filter paper, insoluble material, that is this compound. Of course, in heptane it is insoluble whereas this component is highly soluble in dichloromethane. And at room temperature if you add any other phosphines, 2 equivalents of monophosphines or bisphosphine, you can readily knock off and make $M(CO)_4L_2$ complexes in almost quantitative yield.

Why I am telling all these compounds is, you can further use these compounds to make molybdenum(II), tungsten(II) complexes that are very widely used in olefin metathesis and ring opening polymerization reactions and other reactions in organic chemistry. From that point of view, these are very important reactions. Let me continue giving the preparation of several other interesting compounds as we go through the classification of ligands.

That means, I will stop at this juncture and in my next lecture, let me talk about the classification of ligands. And there are several ways to do the classification. Let me do the classification by choosing the donor atoms. So, that way, I can cover almost all ligands we come across under one donor atom. For example, hydrogen donor atom, nitrogen donor atom or oxygen donor atom or carbon donor atoms; all important ligands coming under those donor atoms would be discussed in detail. So, until then have an excellent time reading chemistry.