# Metal Mediated Synthesis - I
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## Lecture – 2
## Transition metal carbenes Fischer and Schrock carbenes

Hello, welcome everyone. Today for Metal Mediated Synthesis we will discuss transition metal carbenes as you all know carbenes are divalent carbon centers with 2 atoms attached to with it. Transition metal carbenes are the one where metal is associated with the carbon center and the carbon is attached with 2 different atoms. Today we will discuss the transition metal carbenes how they are synthesized, how their names have appeared and also their reactivity pattern. Let us look at the transition metal carbene what are those actually.

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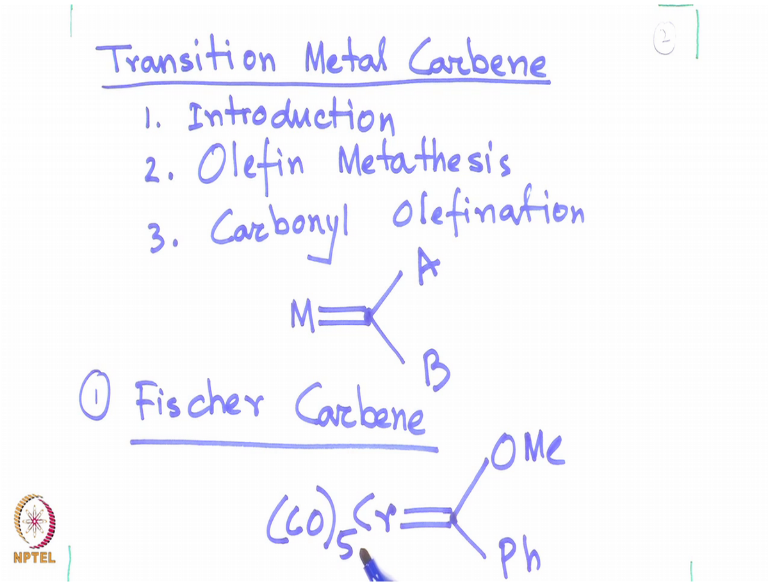

Transition Metal Carbene

1. Introduction
2. Olefin Metathesis
3. Carbonyl Olefination

① Fischer Carbene

So, transition metal carbenes are the one where metal is doubly coordinated with a carbon center and the carbon center is attached with A and B 2 different atoms. Now general classes typically features 2 types of carbene as you know Fischer carbene and the Schrock carbine. These 2 type of carbene we have very distinct features Fischer carbenes are electrophilic at the carbon center and the Schrock carbene are Nucleophilic at the carbon center. In addition there are a number of characteristic features that differentiate the

Fischer carbene from the Schrock carbine. Let us look at one example of Fischer carbene and point out the characteristic of such carbon compound subsequently.

We will discuss the Schrock carbene with 1 example and their characteristic features let us try to look at Fischer carbene. So, Fischer carbene all first of all the a it is easier if we try to remember one example of the Fischer carbene and one example of the Schrock carbene. So, with one example we will try to discuss their inherent properties and the type of ligand that I is associated with the metal center one example that you might want to remember for the Fischer carbene is the one where you have the chromium complex.

Let us look at the characteristic features. So, the chromium complex is associated with the carbene center with 2 atoms associated with the carbon center and this is a Penta carbonyl species. Now if you look at this chromium complex very carefully the chromium center is attached with some ligand and the carbon center is also attached with some substituent. Now let us look at each of these features quite carefully the chromium center as you have seen is associated with carbon monoxide. Now these are the ones which are going to be your you know pi acceptor type of ligand on the other hand the carbon center is electrophilic in nature as you see in the chromium complex let us look at the characteristics one more time and carefully.

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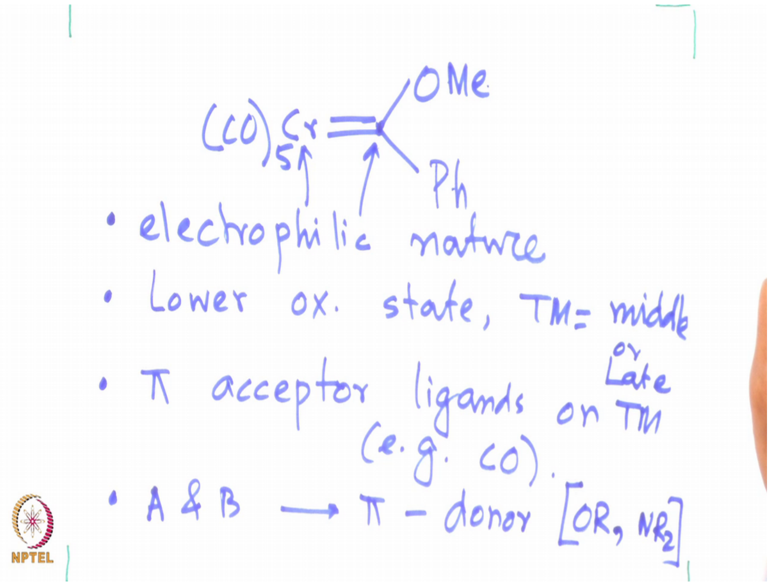

- electrophilic nature
- Lower ox. state, TM = middle or Late
- π acceptor ligands on TM (e.g. CO).
- A & B → π - donor [OR, $NR_2$]

So, you have chromium complex with penta carbonyl associated with it the carbon center over here that is electrophilic in nature this is electrophilic in nature, in a moment we will see the Schrock carbene is nucleophilic in nature. Usually the metal center that is associated over here is the middle or late transition metal and these are having lower oxidation state. So, lower oxidation state and transition metals are late or middle these are the characteristics of your Fischer carbine most importantly you have pi acceptor ligands these are the one the carbon monoxide or the one associated with the metal center directly, which are pi acceptor in nature on pi acceptor ligands on transition metals that is for example, you have carbon monoxide in this particular case.

And the 2 atom that is associated with the carbon center they are often a pi donor A and B are often pi donor. So, these are of 2 different types usually we can get alkoxide or NR 2 types. So, as you have seen with the Fischer carbene this is an example of an Fischer carbene of a Fischer carbene where you have chromium complex of penta carbeneyl species and the methoxide and phenyl is attached with the carbon carbene center.

Now chromium is directly associated with a pi acceptor ligand the carbon center, the carbene carbon center is associated with and the A the l type ligand which is the pi donor ligand; that means, the methoxy you have or NR 2 anything you can have these are going to be electron donating in nature and therefore, the carbine carbon centers is electrophilic in nature.

You can you can draw a conjugation between the lone pair of the methoxy and to that of the carbene double bond. So, the carbon center at carbene is electrophilic in nature that is most important feature of the Fischer carbine. You have chromium complex over here you can have other middle or late transition metal complexes. Once again the main features you need to look at a whether carbene carbon is electrophilic or nucleophilic in nature. If it is electrophilic in nature it is going to be Fischer carbine the atoms 2 atoms that are associated with the carbon carbene center that is going to be at least l type of donor that is it is the lone pair he is there on those hetero atoms let us look at one example of the Fischer carbene. So, Fischer carbine, we have looked at now look at the Schrock carbine.

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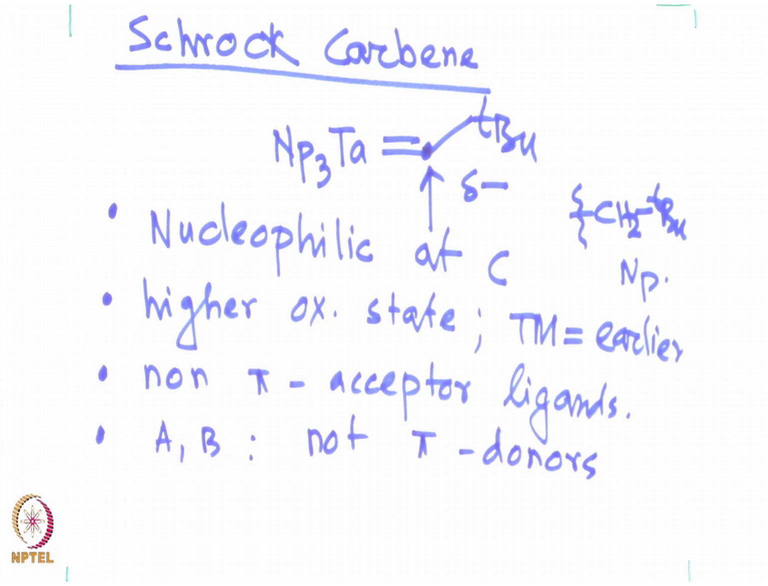

Schrock Carbene

$Np_3Ta=$ tBu

$\delta-$

- Nucleophilic at C

$\{CH_2-tBu$

Np.

- higher ox. state ; TM = earlier
- non $\pi$ - acceptor ligands.
- A, B : not $\pi$ - donors

These are the ones also alkylidene type of molecules ok. We can have a tantalum complex with neopentyl 3 and the classical this carbon center with the carbine. Now this carbene as you will see this is delta negative neopentyl are the one where you have CH 2 that butyl group associated with it this is your neo pentyl group. Now this compound if you look at we have a higher oxidation state for the transition metal in case of Fischer carbene this one work was a lower oxidation state for the metal, now you have a higher oxidation state of the metal in this particular case this is tantalum 5 plus the carbon center the carbene carbon center is nucleophilic in nature.

So, the most importantly it is going to be nucleophilic as opposed to the electrophilic Fischer carbon center nucleophilic at carbon and you have higher oxidation state tantalum as you can see over here it is plus 5 oxidation state. So, higher oxidation state as opposed to fisher carbene where usually it is a lower or middle oxidation state transition metal, in this schrock carbine these are earlier transition metal in nature and most importantly you see the metal center is not associated with something which are pi acceptor in nature this is not a pi acceptor ligand unlike carbon monoxide.

So, on acceptor ligand is directly attached with the metal center non pi acceptor ligand this is very characteristics of your Schrock carbene and the 2 atoms that is attached with this carbon center the carbene carbon center they are not also pi donor. So, non pi acceptor non pi donor type of complex will give you the Schrock carbine, that A and B are not pi donors usually these are the ones which are X 2 type of ligand.

So, these 2 carbenes, we have discussed with one example is are very characteristic and their synthesis pattern is also very different, Fischer carbene and Schrock carbene are the 2 different type of carbine, you can expect. Therefore, the reactivity of these 2 carbenes are also vary for Fischer carbine, we have seen the carbon center is electrophilic in nature or the carbon you can think of delta plus for the Schrock carbene we have delta minus at the carbon center, for the Fischer carbine the metal centers are the one which are middle or late transition metal.

The metal center is also associated with a pi acceptor type ligand, the carbon center of the Fischer carbene is attached to it 2 different atom if it is A and N Nano or both of them or at least one of them should be pi donor in nature. This leaves the carbon center electrophilic in their characteristic on, the other hand for the Schrock carbine, you have the carbon carbene center, nucleophilic in nature that is delta negative most importantly A and B that is associated with the carbon center are not a pi donor. The other ligand that is associated with the metal centers center is also not pi acceptor type. Therefore, as you can see the metal center that is associated for Schrock carbene is the earlier transition metal ones and their oxidation state is relatively high compared to the Fischer carbine. Ones all right now let us look at the synthesis of these 2 different types of carbene namely Fischer carbene and the Schrock carbene.

First we will discuss the synthesis of Fischer carbine.

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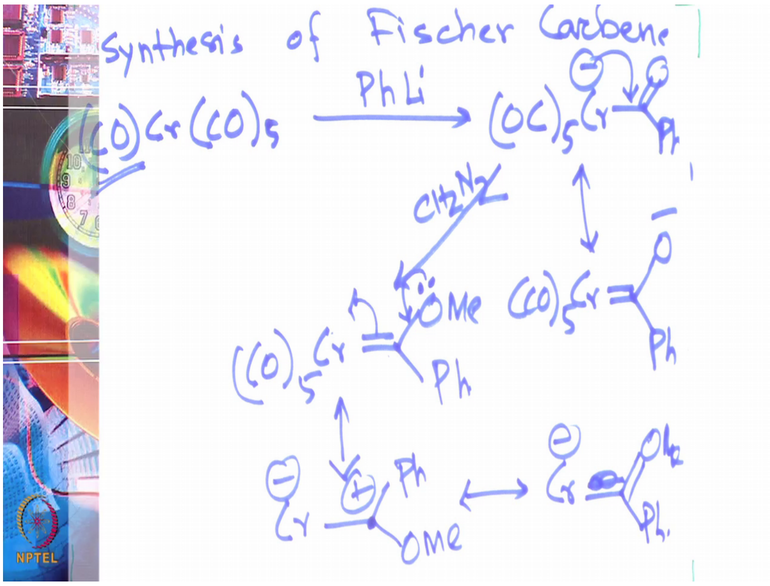

So, we can start with a chromium hexacarbonyl species we have let us say one carbon monoxide we are putting on outside. Now the phenyl lithium will react with one of those carbeneyl center to give you co 5 chromium phenyl species right from there on we can have. So, this is the species which is the usual carbene you can think of chromium double bond and all minus phenyl species right from their own if we have reacted with let us say for example, (Refer Time: 14:00) methane we will get chromium this usual Fischer carbene complex where you we have a pi donor type of ligand and penta carbonyl is associated with the chromium species most importantly this compound you can write down in an canonical form, where you have minus and plus center are the carbon carbon in the carbene center overall you can write down as if the chromium is minus and OMe is you know OMe is plus in nature ok.

So, as you have in this synthesis what we have did done is simply we have taken hexa chrome cobalto sorry hexa carbonyl chromium complex and reacted it with the organo lithium reagent Ph li in this particular case. Now this organo lithium reagent has reacted with one of the carbon monoxide center to give rise to an intermediate from which you can react with diajomethane to get the your Fischer carbene species. This is a very easy synthesis and of course, you need to handle it little carefully, but overall it is relatively easier synthesis. So, that is one of the syntheses for the Fischer carbene.

Now, we will look at the one of the synthesis of Schrock carbene. So, Schrock carbene was not really a planned synthesis it was Richard Schrock when he was at DuPont, he was trying to synthesize a different complex will come in a moment, but accidentally he has discovered and very interesting complex which then later came to fame and known as Schrock carbine, it is the tantalum complex that was studied at that point at DuPont by Richard Schrock where we will see the accidental synthesis that has revolutionized this area of organo metallic complexes and subsequent chemistry to give the metathesis reactions.

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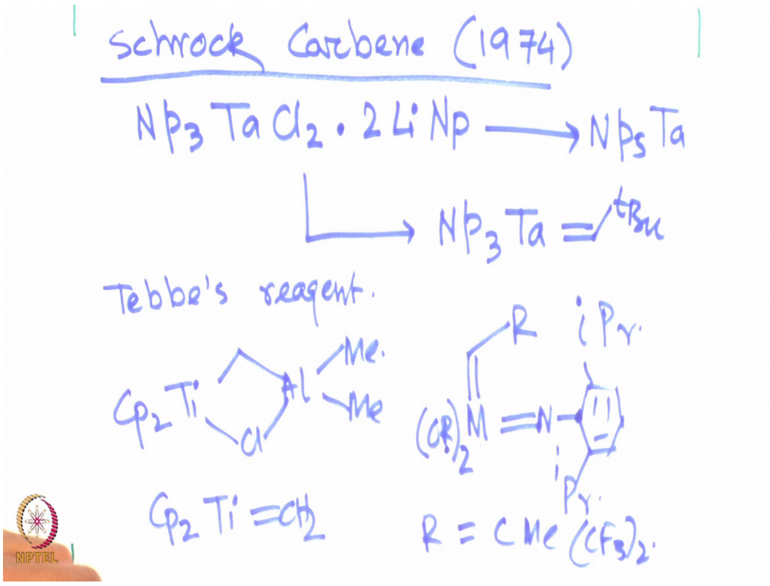

Now Schrock carbine it was discovered in 1974 once again little shock was at that point at DuPont scientist later on he moved to of course, as right now he is at MIT, before that he was at DuPont. So, neopentane neopentyl 3 tantalum chloride complex, he was studying and he was interested in reacting with lithium neopentanyl complex the idea was to get NP 5 Tantalum complex.

Instead what he actually got is a history and that is neopentyl ta 3 instead of penta neopentyl tantalum complex he got thistreece neopentyl tantalum complex with the carbene center attached with the tantalum of course, tantalum is in 5 oxidation state. Similarly agent one can think of that can have this type of behavior or similar behavior at Schrock carbene could be your (Refer Time: 17:54) where this C P 2 titanium can be attached with aluminum and overall you can have a reaction where this is C P 2 titanium double bond or carbene center. Most often nowadays the 1 carbene or Schrock carbene that mostly familiar people familiar with are the one with the molybdenum complex where this molybdenum is in plus 6 oxidation state and alkylating we have this counterpart where this isopropyl and 2 ISO profiles are associated with the with this I mean center and your metal is associated with 2 alcoxide, where R this alcoxide R is CMe CF 3 2.

So, this this is the modern days Schrock catalyst where Schrocked carbene and you see was first discovered although accidentally in 1974 at DuPont, where penta neopentyl title tantalum complex was planned to synthesize starting from the trees neopentyl tantalum dichloride species by reacting with neopentyl chloride unfortunately or I would say rather fortunately, we did not see the synthesis of or we did not get that trees it from the trees neopentyl species to pentyl neopentyl tantalum species instead, what we ended up getting is the one of the neopantile of the neopentyle lithium reacting with the tantalum dichloride to give the tantalum 4 neopentyl species the fifth neopentyl one obstruct from the alpha carbon Ch bond to give the neopentyl 3 of them on the tantalum and the other one is now associated with the tantalum center in double bond or so called Schrock carbene fashion.

Now, this was the initial discovery till then numerous progress has been made the one with which we are mostly familiar with as a Schrock carbine are the one we have molybdenum complex molybdenum is in plus 6 oxidation state as you have seen we have the nitrogen associated with the molybdenum and these 2 di ISO profiles are bulky substituent on this on this amine and we have the carbene center right over here where this is nucleophilic in nature and the as you have seen there is no pi acceptor or pi donor ligand in the whole complex we have the alcoxide complex, where R is a again a bulky one tertiary carbon center with CMe CF 3 2 another carbine, which you are often familiar with is the one we have which is most popular I would say at this point that is the Grubbs one as you look at the when Grubbs started out his career he did not have his carbene to start with the reactivity.

He was initially working with the Schrock carbene later on he came up with a very modified and versatile version of the carbene which came to fame as the Grubbs catalyst, as you know it and they are at different generation of the Grubbs catalyst that we have in the market.

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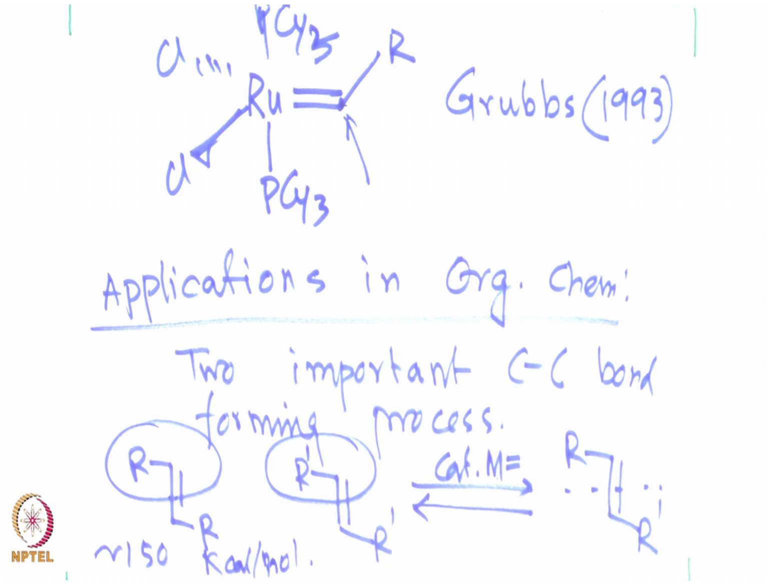

Grubbs (1993)

Applications in Org. Chem:

Two important C–C bond forming process.

Now the one in the Grubbs catalyst we need to discuss that is the one which is most popular we have this ruthenium complex, once again this is of Schrock carbine type where you have ruthenium attached with the carbon center this is again a nucleophilic in nature and you have PC y 3 dichloride species attached with it and 2 of them sorry PC y 3.

So, this is the one which is known as Grubbs and this was first discovered in 1993 and you have you have of course, different other ligands are also used for this for this Grubbs catalyst is.

Now, as you know this is the Schrock carbine covers also the Grubbs this catalyst because this carbon center is nucleophilic in nature as you have seen first example was in 1974 and lateral on Grubbs comes at 1993 to come up with his own modified and the very reactive version of the Schrock carbine, which is known to the literature as Grubbs catalyst or Grubbs different generation of catalyst. Blatron as you know both of them came and the came and developed this field quite beautifully to give the field the prominence and nowadays the organic synthesis or even any synthetic chemist cannot think of doing a complicated molecule synthesis, without use utilizing the great nature or great behavior of these 2 carbene complexes.

Will, now look at little bit at the their reactivity pattern. So, will look at the application of this specifically you know the Fischer carbene and the Schrock carbene first we will discuss the one where we have the metathesis reactions. So, we will have 2 important 2 important carbon carbon bond formation process that will go on for the metathesis reaction, if you start with one olefin where 2 different substituents are there let us say R and R and you have another olefin where once again 2 different substituents are there R prime and R prime.

Now if you react it with the Schrock carbene or so to speak nowadays Grubbs catalyst or Schrock catalyst or Schrock carbene usually you will get in exchange of partner, where one half of the olefin will be exchanged with the another half to give you the mixture of this compound the final compound where one half is associated with the double bond of one carbon or all of one olefin the other half is associated with the other olefin.

Now this metal is used as a catalyst and often it is done under thermal reaction control of course, it can be reversible in nature these carbon carbon double bond as you know these are 150 kcal per mole. And doing this reaction breaking and do doing this reactions are quite interesting because you are breaking a 150 kcal per mole that those co compounds with the double bond in in there and you are exchanging the exchanging the partners at room temperature, how these reactions are possible at room temperature has caught the imagination of the whole suns whole chemistry community this is because the very reactive nature of the carbene that helps them to undergo A 2 plus 2 reaction fast we will see when a the later, next class where 2 plus 2 reaction fast and then a retro 2 plus 2 eventually gives an intermediate which leads to the final product.

So, for this class what we have seen. So, far is the 2 most prominent are the 2 known classes of carbene namely Fischer carbene and Schrock carbene with one example is we have tried to show the characteristic feature of both these carbenes Fischer carbene and the Schrock carbene. As you have seen Fischer carbene carbon center is electrophilic in nature and Schrock carbene carbon center is nucleophilic in nature their synthesis you have seen also are of different in nature you have chromi chromium hexa carbonyl species for example, to start with which was reacted with phenyl lithium to give you the Fischer carbene on the other hand Schrock carbene, which was discovered rather accidentally at the beginning which you have seen the earlier transition metal such as tantalum in a very high oxidation state starting from a tantalum dichloride trice neopentyl species.

We have seen lithium neopentyl gives you the corresponding Schrock carbene parcel. This Schrock carbene once again is nucleophilic in nature. Most importantly Schrock carbene also covers that is Grubbs known as the Grubbs catalyst where we have both the Schrock carbene the original Schrock version and the subsequent modified version, which is nowadays are very popular in molybdenum in 6 plus oxidation state.

This molybdenum catalyst as well as Grubbs ruthenium based catalyst most often are widely used and there are certain benefits of each of these 2 different types of Schrock carbene, I would say both the fish the both the Grubbs version and the Schrock old version we do see the reactivity difference in in quite a lot of cases. We will discuss this reactivity of those Fischer and the Schrock catalysts and we will get into the 2 plus 2 and retro 2 plus 2 and subsequent transformation to give the value added product synthesis in the next class.

Alright till then keep reading will get back soon and will discuss the reactivity pattern of these carbenes mainly the Schrock carbenes and the Fischer carbenes and most importantly we will discuss also the reactivity of the Grubbs catalyst till then, bye-bye.