Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture – 30
Transition Metal Alkyne / Carbene Complexes

Welcome to this lecture on transition metal organometallic chemistry from principals to applications. In our previous lecture, we were talking about transition metal alkyne complexes and these complexes have transition metal bonded to C carbon containing S p hybridized or can be referred to as C S p in terms of hybridization.

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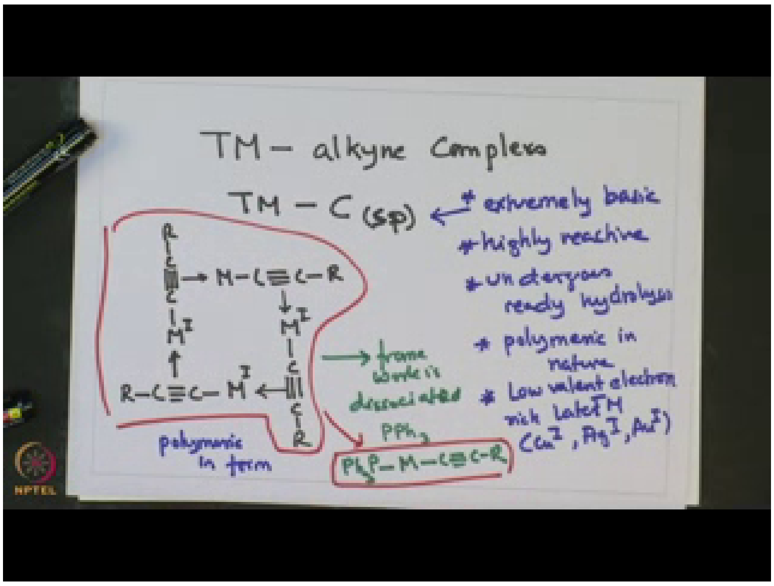

As a result, this complexes are very basic highly reactive, undergoes hydrolysis and also polymeric in nature and this mainly are observed for low valent electron. Rich late transition metals like; copper one, silver one, and gold one, in terms of their polymeric nature, they attain stabilization, because of this polymerization and that can be illustrated as below. For example, if it is a metallatesatellite, then that metal can interact with another metal through is pi cloud.

Now, these pi cloud can interact with another metallatesatellite moiety that can also interact with another metallatesatellite moiety and that in term can inter like with the metal. So, this is how they acquire polymeric nature and this framework is dissociated when treated when treated with ligands like P P h 3 giving compounds like C R type from this polymeric nature by treatment with P P h 3. So, with that in the background, we are going to discuss some more on the stability and reactivity of these transition metal alkyne complexes and also look into some of the preparative methods available for preparing these transition metal alkyne complexes in today's lecture.

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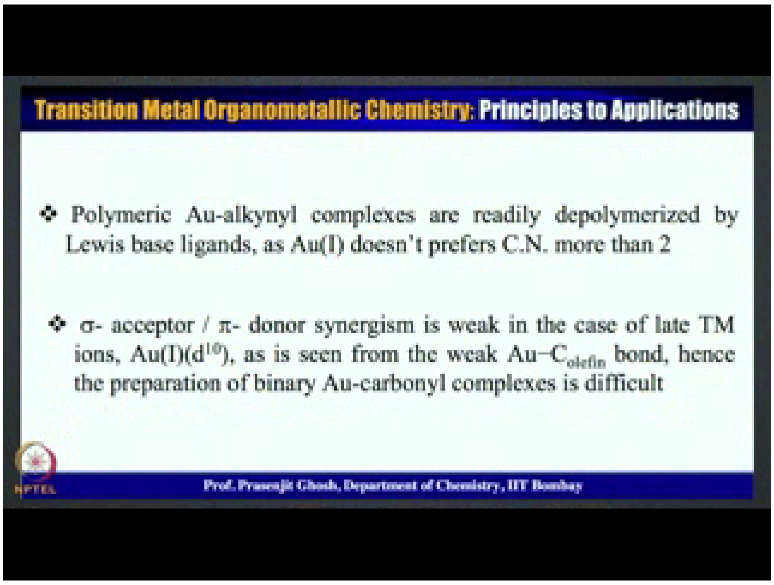

Transition Metal Organometallic Chemistry: Principles to Applications

- Polymeric Au-alkynyl complexes are readily depolymerized by Lewis base ligands, as Au(I) doesn't prefers C.N. more than 2
- σ- acceptor / π- donor synergism is weak in the case of late TM ions, Au(I)(d^{10}), as is seen from the weak Au–C_{olefin} bond, hence the preparation of binary Au-carbonyl complexes is difficult

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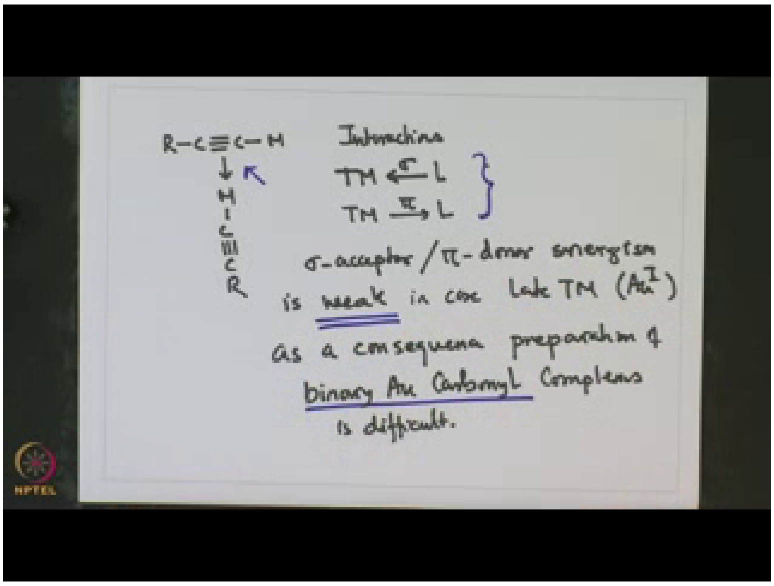

σ-acceptor / π-donor synergism is weak in case late TM (Au^I)

as a consequence preparation of binary Au Carbonyl Complexes is difficult.

So, with regard to this kind of interactions that we have been talking about, one was the interactions with metals being ligand to transition metal sigma interaction as well as transition metal to ligand pi interactions and this kind of sigma acceptor and pi donor synergism is weak in case of late transition metals like gold one, copper one, silver one, and as a consequence preparation of binary gold, carbonyl complexes is difficult.

So, what it shows that, these synergism is required for stabilizing this type of complexes, but they are not too strong, they are weak to the extent, that this synergy, synergism failed to stabilize binary gold carbonyl complexes. This is very interesting observation in the fact that they split transition metal like gold can stabilize acetylate moiety, but find it difficult to stabilize carbonyl moiety, because of the fact that these synergism pi acceptor and sigma donor synergism that stabilize this kind of interaction is kind of weak in nature for late transition metal, gold one complexes.

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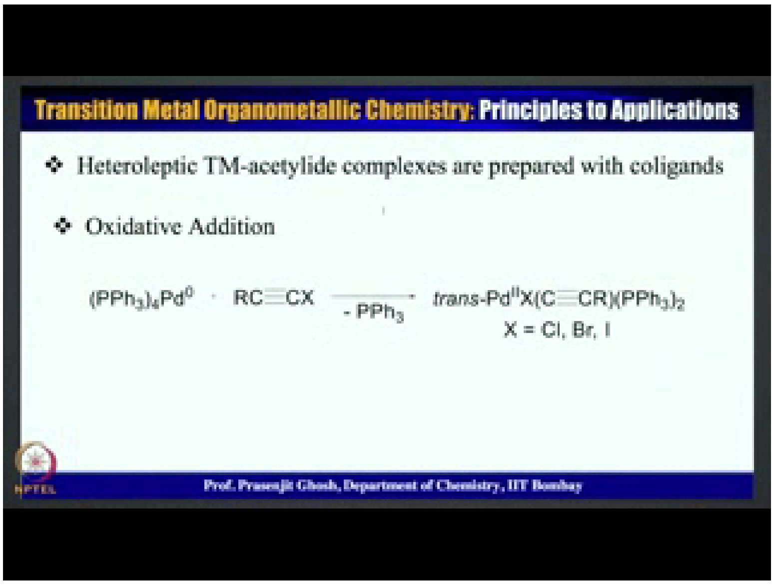

Transition Metal Organometallic Chemistry: Principles to Applications

- Heteroleptic TM-acetylide complexes are prepared with coligands
- Oxidative Addition

$$(PPh_3)_4Pd^0 + RC{\equiv}CX \xrightarrow[-\,PPh_3]{} \textit{trans}\text{-}Pd^{II}X(C{\equiv}CR)(PPh_3)_2$$

X = Cl, Br, I

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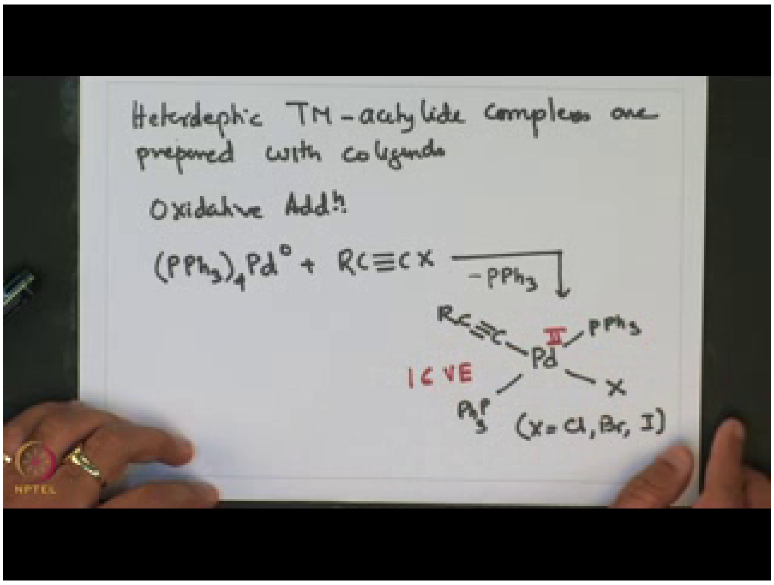

Heteroleptic TM-acetylide complexes are prepared with coligands

Oxidative Add^{n}

$(PPh_3)_4Pd^0 + RC\equiv CX \xrightarrow{-PPh_3}$

Hence, this transition metal acetylate complexes are usually prepared as heteroleptic; heteroleptic complexes using other coligands and one of the most common method is the one, that uses oxidative addition of an acetylate halide bond on a globalent metal centre. For example, the reaction of palladium tetra, first in palladium 0 complex plus C X, where the C X bond is O X datively added on the palladium 0 centre, eliminating triphenylphosphine, to give this trans complex, where X equals chlorine, bromine iodine here, the oxygen state of palladium after oxidative addition has gone on to become palladium 2 and this being a square planar complex, this is a 16 valence electron complex of palladium and this reaction is a convenient way of preparing heteroleptic palladium acetylate complex, where the palladium acetylate moiety has been stabilized along with other coligands in making a monomeric complex of the type shown over here.

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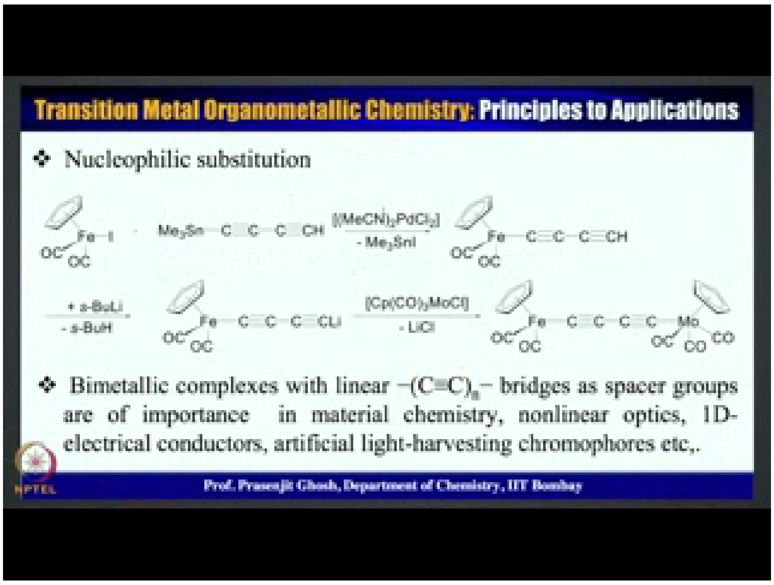

Transition Metal Organometallic Chemistry: Principles to Applications

- Nucleophilic substitution

- Bimetallic complexes with linear $-(C{\equiv}C)_n-$ bridges as spacer groups are of importance in material chemistry, nonlinear optics, 1D-electrical conductors, artificial light-harvesting chromophores etc,.

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Apart from oxidative addition, nucleophilic substitution also can be successfully used for preparing the acetylate type of complexes.

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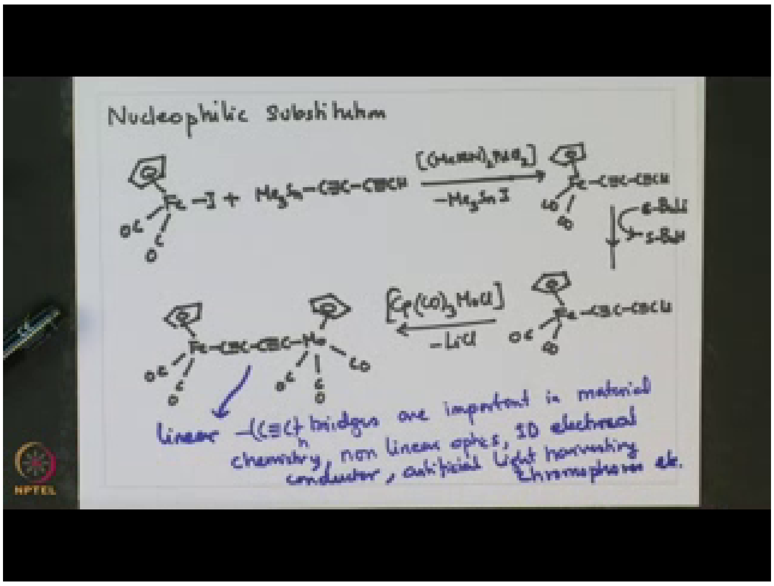

Nucleophilic Substitution

linear $-(C{\equiv}C)_n$ bridges are important in material chemistry, non linear optics, 1D electrical conductor, artificial light harvesting chromophores etc.

For example, the reaction of C P iron dicarbonyl iodide plus tri methyl acetylate of the type shown over here, reacting in presence of these acetonitrile palladium chloride and eliminating tri methyl, tri iodide, results in this iron acetylate complex that in presence of butyl lithium eliminates butane giving, this lithiated complex, which here the hydrogen has been replaced by lithium by treatment with butyl lithium.

Now, this lithiated complex reacts with C P tricarbonyl molybdenum chloride eliminating lithium chloride to give this hetero bimetallic complex and this kind hetero bimetallic complexes containing linear bridges as special, are important in material chemistry, non-linear optics applications 1 d electrical conductor, artificial light harvesting chromophorse and explain etcetera.

So, what we see that this is a very powerful technique, for making non-linear compounds, for non-linear optics, activations for electrical conductor artificial light harvesting chromophorse. So, on and so forth, by using this nucleophilic substitution reaction, when iron dicarbonyl was reacted with this acetylate compound of tin for, is making the iron acetylate complex, which was then deprotonated butyl lithium and then lithiatedanalogue reacting with molybdenum complex, to give these hetero by metallic a complexes, continuing linear acetylate bridge, which has so such important applications. So, with this we will draw conclusion on our discussion of transition metal alkyne complexes, which was transition metal bound to a carbon centre having S p hybridized and then we move onto a very exciting chemistry, which is transition metal carbene complexes.

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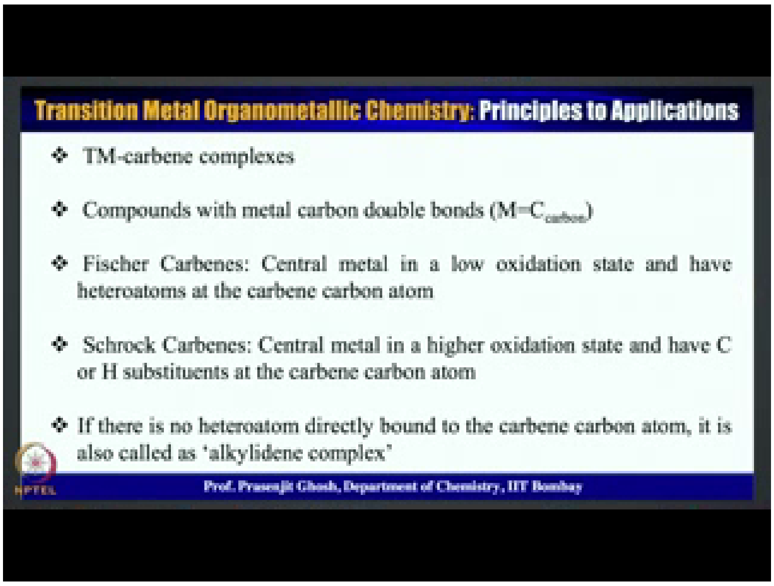

Transition Metal Organometallic Chemistry: Principles to Applications

- TM-carbene complexes
- Compounds with metal carbon double bonds ($M=C_{carbon}$)
- Fischer Carbenes: Central metal in a low oxidation state and have heteroatoms at the carbene carbon atom
- Schrock Carbenes: Central metal in a higher oxidation state and have C or H substituents at the carbene carbon atom
- If there is no heteroatom directly bound to the carbene carbon atom, it is also called as 'alkylidene complex'

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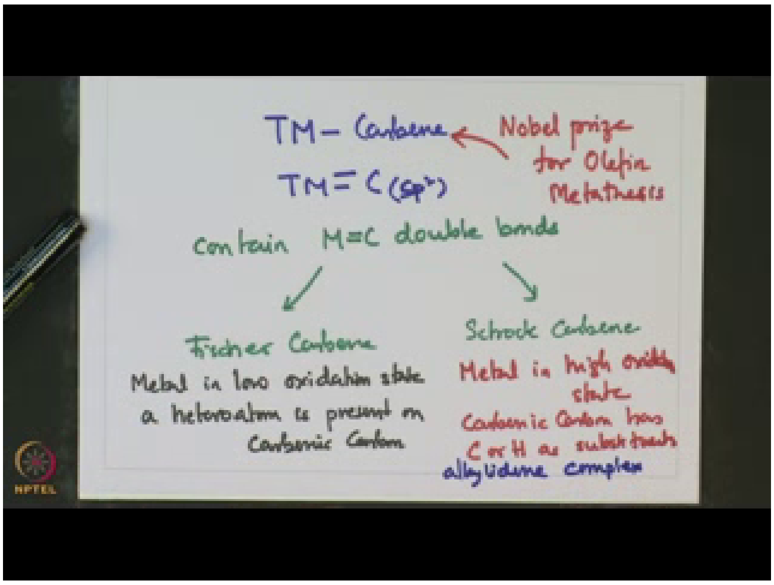

TM – Carbene ← Nobel prize for Olefin Metathesis

TM = C (sp^2)

contain M=C double bonds

Fischer Carbene

Metal in low oxidation state
a heteroatom is present on Carbenic Carbon

Schrock Carbene

Metal in high oxidation state
Carbenic Carbon has C or H as substituents
alkylidene complex

Transition metal carbene complexes are of interest in the contemporary times, where transition metal is bound to S p 2 centre and also is multiply bonded with the carbon. So, these contain two kinds of bonds, the transition metal mix with the S p 2 carbon in transition metal ariel complexes. There was no multiple bonding occurring between transition metal and the C S p 2 centre of the transition metal ariel, but in the carbenic case, there is a metal ligand, multiple bonding occurring in transition metal are in carbene complexes and hence, there of importance.

So, this transition metal carbene complexes contain metal carbon double bonds and they can be classified into two types; one is Fischer Carbene and the other is Schrock carbine, it is important to note that these chemistry is extremely important and also is a contemporary interest, with the last Nobel prize even in olefin metathesis as less as 2010 olefin meta metathesis was given conferred, Nobel prize in 2010 which involves this transition, metal carbene chemistry which relates to this chemistry and this was given very recently.

Now, between the types of carbine complexes that one encounters, one is call Fischer Carbene and the other is called Schrock Carbene. The difference being that in Fischer Carbene, the metal centre is in low oxidation state and the carbon has a heteroatom atom is present on carbenic carbon. Now, with regard to the Schrock Carbene, the metal is in high oxidation state and there is no heteroatom. So, carbon have carbonic, carbon have has carbon or hydrogen as substituents and when there is no heteroatom daily, directly, bound to the carbonic carbon these are called alkylating complex, in this case these are called alkylidine.

Now, this carbon cam chemistry is important from the fact that carbene by itself are very unstable molecules and hence, there highly reactive and very difficult to isolate synthesise are utilised for any chemical reaction. Now, it turns out that way carbine, when buying to metal, in terms of transition metal carbene complexes, which can be Fischer type, as well as Schrock types. They become organometallic species and when they are organometallic in nature and this organometallic compound have very high reactivity to and have very different catalytic applications and these are unique, for this kind of complexes and have been exploited to it's fullest code. So, from the catalysis point of view, this metal carbine complexes are very prominent and they are being investigated and studied in great detail and from where their importance or significance arise.

So, let me now discuss in more details about these two carbene compounds, beginning with the preparation of these complexes.

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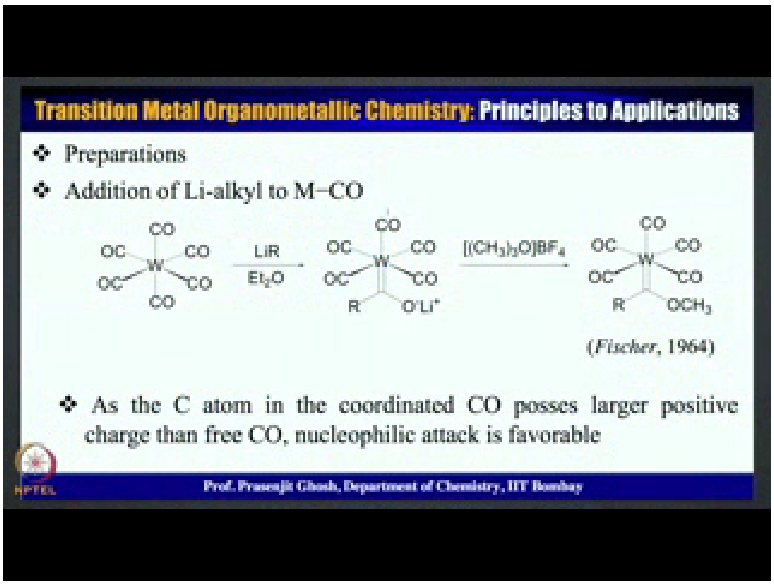

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Preparations
- ❖ Addition of Li-alkyl to M–CO

(*Fischer*, 1964)

- ❖ As the C atom in the coordinated CO posses larger positive charge than free CO, nucleophilic attack is favorable

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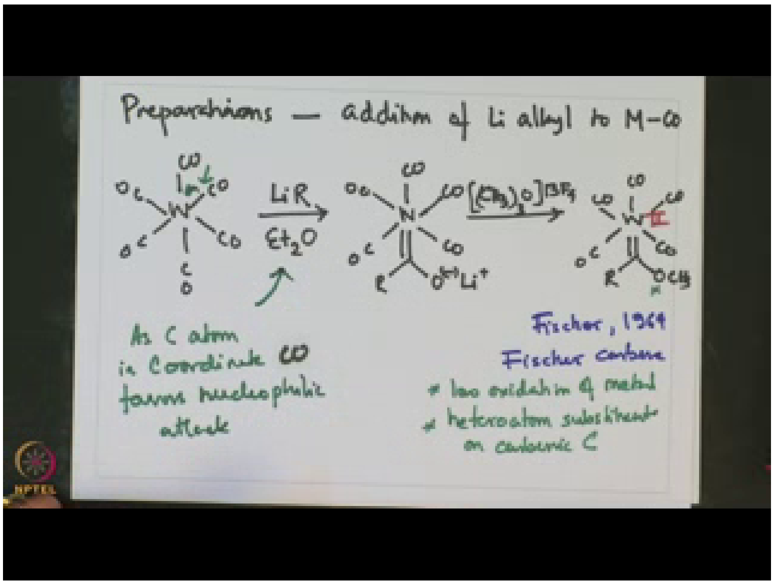

Preparations — addition of Li alkyl to M–CO

As C atom in Coordinate CO favors nucleophilic attack

Fischer, 1964
Fischer carbene
* low oxidation of metal
* heteroatom substituent on carbenic C

The first carbine was prepared by Fischer; obviously, then this is the Fischer carbine and was obtained by lethal additional of lethal alkyls to metal carbonyl bond, specifically reaction of transient hexacarbenyl with lithium alkyl in diethyl lethal cave, the following compound and which when treated with C h 3 whole 3 O B F 4, these are agent that produces methyl cation, calculate this oxygen, gave the following carbine compound. Since, this carbine was prepared by Fischer, we back in 1964; this is called Fischer Carbene or this kind of compound. The hallmark of Fischer Carbene is the low oxidation state of metal and heteroatom substituent on carbenic carbon. So, were here this is the heteroatom substituent carbenic carbon.

Now, these strategy exploits the fact that when the car, the carbonyl is bound to tungsten, a metal, the way it is shown over here, the carbon centre becomes slightly activated in terms of becomes positively charged and favouring a nucleophilic attack in coordinated C O favours nucleophilic attack, which has been achieved in this. So, with this I would draw the conclusion for today, is main points that have been discussed. The lecture we have started off with transition metal alkyne complexes, looked into various synthetic methods, available for transition metal alkyne complexes, particularly that of oxidative addition to lower and compounds as well as nucleophilic substitution, where by hetero by metallic transition, metal alkyne complexes well prepared this transition. Metal alkyne complexes are complexes of transition metal with carbon, which is a S p hybridized and these compounds have lot of applications, particularly the linear change a acetylate moieties in various kind of electronic devices, optic electronic purposes and with that we conclude without discussion on transition metal. Alkyne complexes in the laster check, lecture and then moved on to transition metal carbine complex. These are transition metal bound to S p 2 carbon and we have looked into various kinds of transition metal, carbine complexes that occur, mainly the Fischer and Schrock type carbene complexes. This carbine complex, signify metal ligand bonding present between the metal and the carbenic centre for Fischer Carbenes, the hallmark is the Fi, the metal should be in the low oxidation state and there be a heteroatom substituents on the cabenic centre.

Whereas for that of the Schrock Carbenes, the metal centre is on higher, high oxidation states and there is no heteroatom substituents on the carbonic carbon, it has only carbon and another hydrogen as a substituents with that, we have looked into the first method available for preparation of Fischer Carbene in this lecture and that was the reaction of nucleophilic attack by lithium reagent, lithel alkyne reagent on to transitions tungsten hexacorbenyl compound, where the nucleophile attacks on to the coordinated carbonyl compound, followed by treatment with methyl plus source, which results in the Fischer Carbene complex of tungsten. So, with that we conclude that today's lecture and I look forward to being in the next lecture, where we are going to discuss transition metal carbine complexes in more details for particularly from the point of their synthesis reactivity and property type applications, till then thank you for being with me in this lecture and I look forward to being with you in the next lecture. Goodbye.