Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture - 09
Week - 02
Preparation of σ – alkyl compounds

Welcome to this lecture on transition metal organometallic chemistry from principles to applications now over the last lecture we are going through an exciting topic which is based on the ligand properties and not on the usually center in organometallic chemistry that is the metal part and from the ligand perspective we are discussing sigma alkyl complexes or sigma donor ligands and what we have seen that these ligands show a variety of binding modes to the metal center displaying a rich diversity in binding which eventually will translate into a rich unique chemistry that are attributes of organometallic compounds in our previous lecture we have seen how the sigma donor ligands depending upon the hybridization of the carbon center bound to

The metal display such diverse binding modes this binding can be classified into two types mainly the terminal binding modes and the bridging binding modes and a variety of organic moieties depending on their hybridized state bind to the metal center in bridging as well as terminal forms as mentioned earlier that sigma alkyl complexes are very important many of them are important intermediate in many catalytic processes and hence it is important to have a full understanding of them to get a proper understanding of the metal sigma alkyl complexes it is important that one be able to prepare them

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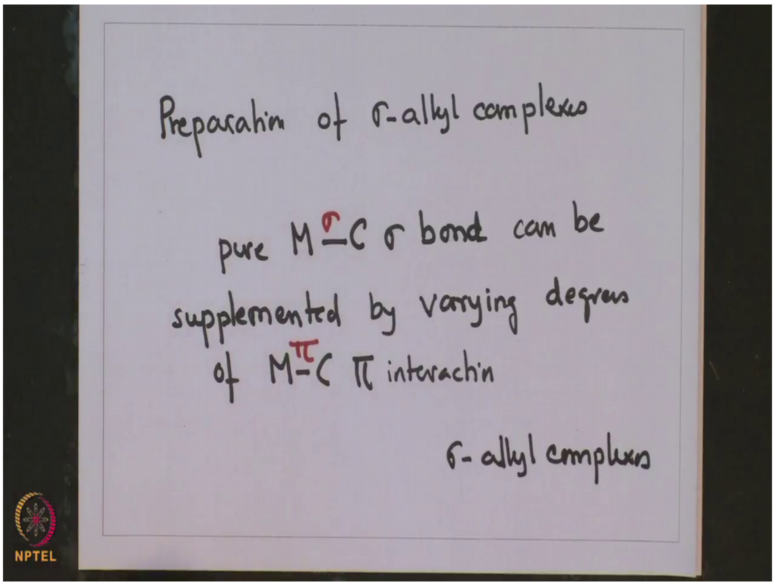

Preparation of σ-alkyl complexes

pure $M \overset{\sigma}{-} C$ σ bond can be supplemented by varying degrees of $M \overset{\pi}{-} C$ π interaction

σ-alkyl complexes

So, preparation of sigma alkyl complexes is a very important topic as far as these kind of organometallic complexes are concerned and this lecture looks into the various methods that have been developed for preparing these sigma alkyl complexes another unique feature about these complexes is that depending upon the ligands ability pure metal carbon sigma bond can be supplemented by varying degrees of of metal carbon pi interaction this is an important attribute of transition metal organometallic compounds.

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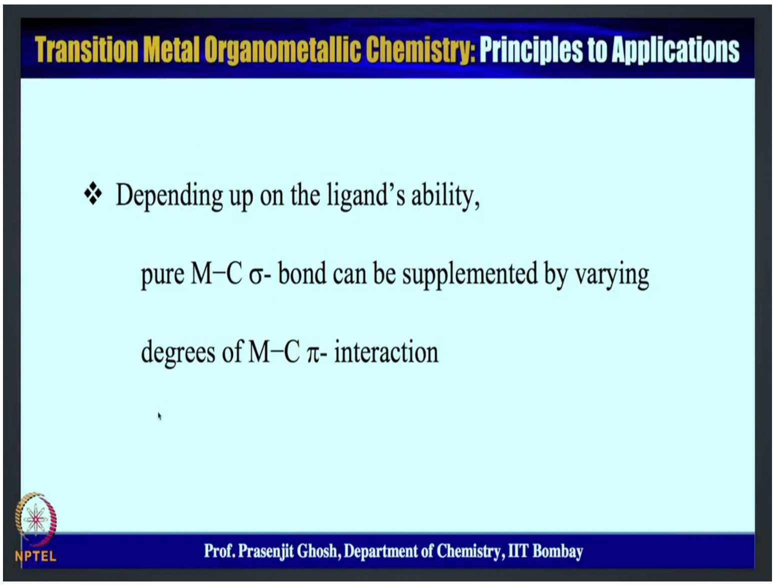

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- Depending up on the ligand's ability,

  pure M–C σ- bond can be supplemented by varying

  degrees of M–C π- interaction

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And this synergism is possible because of the partial occupancy of the inner d orbitals and also is seen manifested in many sigma donor complexes

So, let us take a look at different methods there are used for preparing them.

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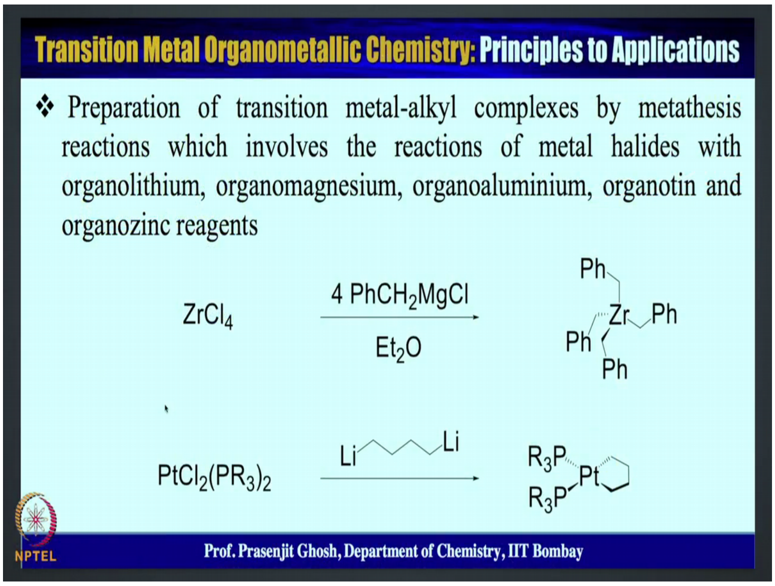

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- Preparation of transition metal-alkyl complexes by metathesis reactions which involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents

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The first and the foremost is a method called metathesis reactions that involves reaction between metal halides.

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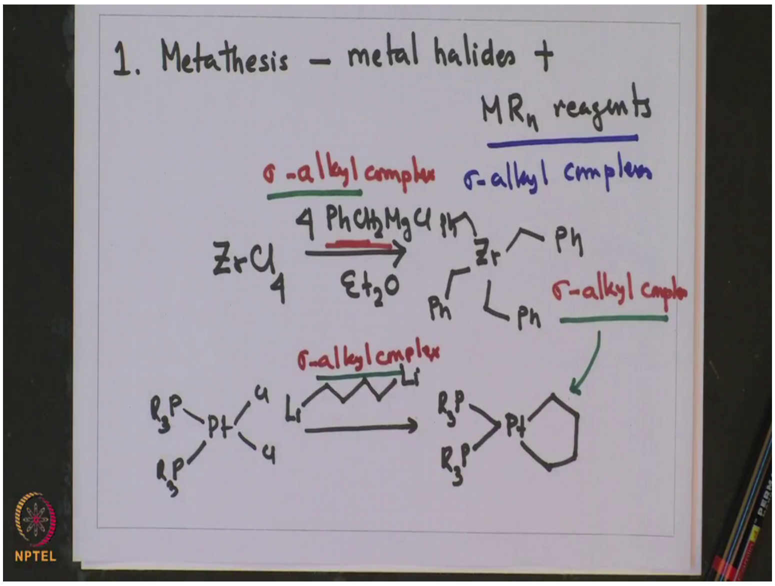

1. Metathesis – metal halides + MR_n reagents

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Plus organolithium organo magn magnesium organoaluminum and organozinc reagents. So, these organozinc organomagnesium organotin are all sigma alkyl complexes let us see an example for example, reaction with zirconium tetrachloride with four equivalents of benzylmagnesium chloride in ether gives zirconium tetrabenzyl

Now, what is interesting thing is that the product is a sigma alkyl complex and one of the reagent also is a sigma alkyl complex. So, the interesting bit is that if one were to synthesize this sinthe sigma alkyl complex by this method then one needs a stratification which also is a sigma alkyl complex. So, one of the reagent has to be a sigma alkyl complex reacting with the metal halide to give another sigma alkyl complex

Let us take a look at another example platinum dichloride diphosphate reacting with this organolithium compounds gives the following chelated compound here too the product is a sigma alkyl complex the way it had been discussed earlier in the earlier example and one of the reagent too also is a sigma alkyl complex having said that this is a very useful method metathesis is a very useful method for.

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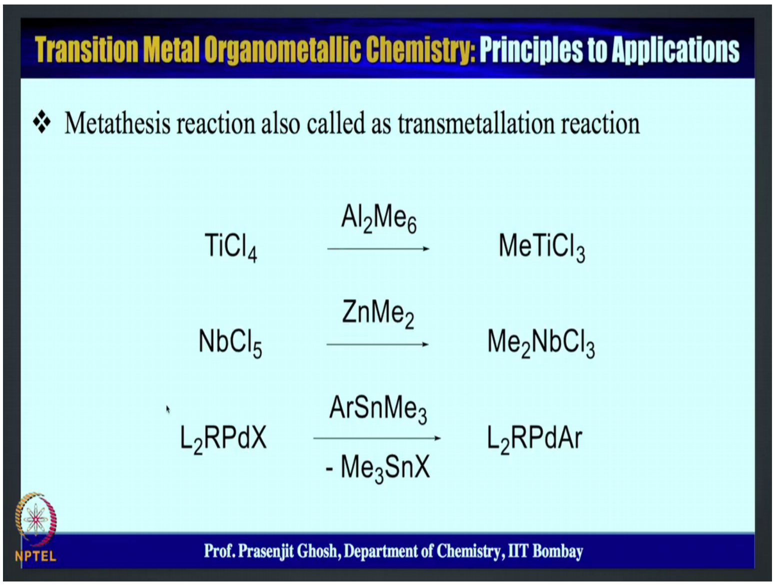

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- Metathesis reaction also called as transmetallation reaction

$$TiCl_4 \xrightarrow{Al_2Me_6} MeTiCl_3$$

$$NbCl_5 \xrightarrow{ZnMe_2} Me_2NbCl_3$$

$$L_2RPdX \xrightarrow[-\ Me_3SnX]{ArSnMe_3} L_2RPdAr$$

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And very common method for preparing transition metal organometallic sigma bonded complexes metathesis is also.

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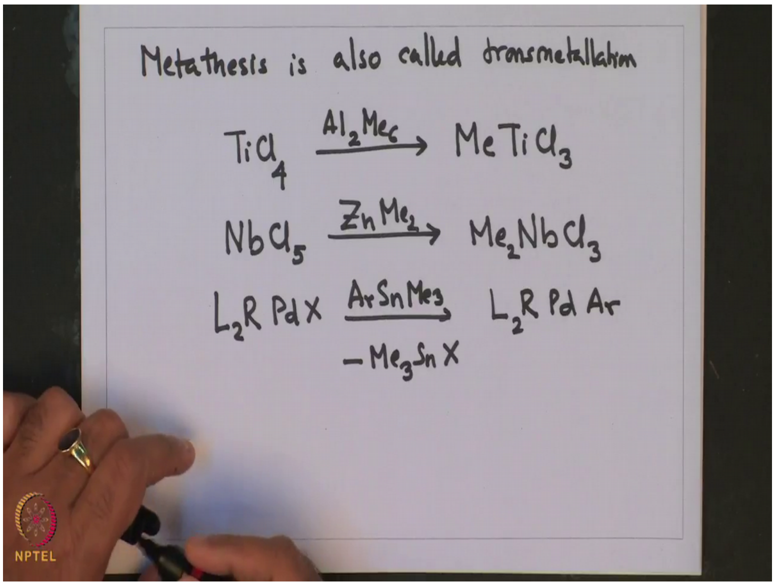

Metathesis is also called transmetallation

$$TiCl_4 \xrightarrow{Al_2Me_6} MeTiCl_3$$

$$NbCl_5 \xrightarrow{ZnMe_2} Me_2NbCl_3$$

$$L_2R\,PdX \xrightarrow[-Me_3SnX]{ArSnMe_3} L_2R\,PdAr$$

Commonly referred to as transmetallation reaction transmetallation reaction and several examples of this include reaction of t i c l four with aluminium alkyls a l two m e c gives m e t i c l three in this case partial transmetallation of one of the chloride has taken place n b c l five reacting with dimethyl zinc giving m e two n b c l three l two r p d x with a r tin m e three giving m e three s n x and l two r p d a r

So, these reagents which are used in metathesis or transmetallation reactions are called transmetalating reagents after this common method of preparing sigma alkyl complexes another interesting method involves alkene insertion or hydrometallation reaction hydrometallation reaction.

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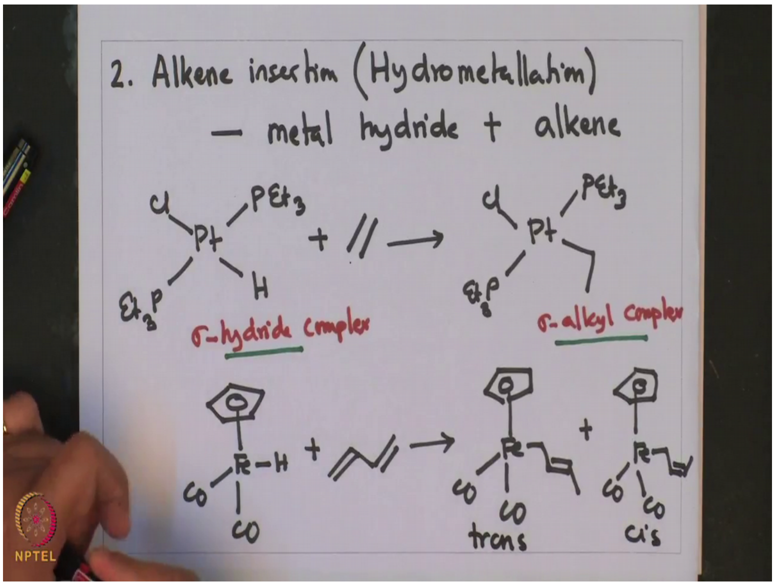

2. Alkene insertion (Hydrometallation)
— metal hydride + alkene

And this involves reaction between a metal hydride and an alkene as the name suggests this reaction would involve insertion of alkene into a metal hydride bond

Let us see that with an example for example, in this platinum hydride complex, but there is a platinum hydrogen bond the reaction of that with an alkene ethylene is showing over here leads to insertion of alkene into the platinum hydride bond giving ethyl moiety. So, this is c two h four plus one hydrogen from here it gives you c two h five a ethyl moiety here too the product is a sigma alkyl complex that is what we want to make and the reactant unlike in the metathesis reaction stage where the reagent was also a sigma alkyl complex over here it is a sigma hydride complex

So, what we see that a sigma hydride complex is required to get to a sigma alkyl complex.

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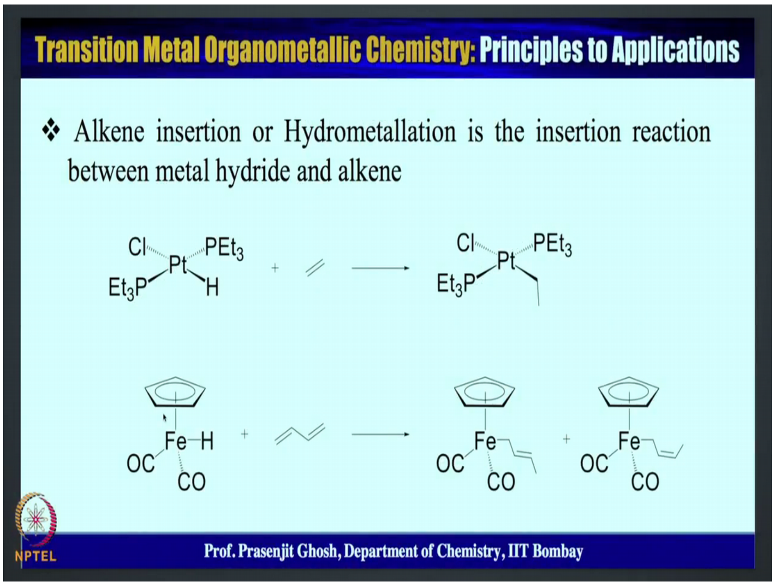

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- Alkene insertion or Hydrometallation is the insertion reaction between metal hydride and alkene

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And if we compare this reaction with our earlier metathesis reaction what we can observe that in that case a sigma alkyl complex was required to pro produce another sigma alkyl complex in this case a sigma hydride complex is required produce a sigma alkyl complex we will illustrate this with another example in which iron hydride dicarbonyl hydride bound to one cyclopentadienyl ring. So, this also is a sigma hydride complex reacting with butadiene which is an alkene a conjugated alkene giving one four inserted products and also the geometric isomer will illustrate this with an example where a metal hydride complex

Similar to the earlier example a sigma hydride complex reacting with butadiene or conjugated diene to give a iron sigma alkyl complex with one four insertion and producing both the cis and the trans geometric isomers here too as one can see the product is a sigma alkyl complex and one of the reagent is also a sigma hydride complex a close variant of alkyne insertion is the carbene insertion reactions here.

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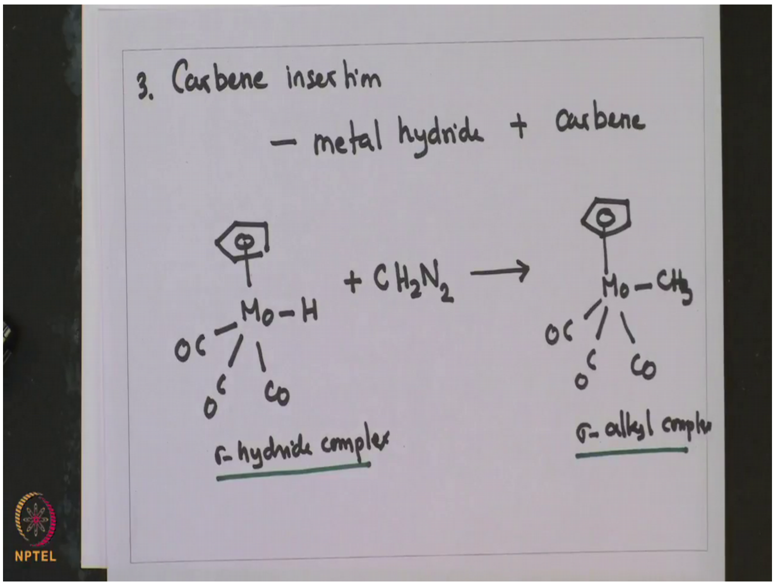

3. Carbene insertion

– metal hydride + carbene

The reaction involves again a metal hydride and a carbene for example, the reaction of cyclo pentadienyl molybdenum hydride tri carbonyl compound with diazomethane

Now, diazomethane is nothing, but a carbene precursor and similar to that of alkene insertion into metal hydride here too we get the carbene inserted molybdenum compound leading to a molybdenum methyl c h three. So, the three hydrogens of c h three comes from c two hydrogens of c h two and one hydrogen of molybdenum hydride producing molybdenum methyl cyclopentadienyl tri carbonyl compound as shown below this compound too is a sigma alkyl complex and also one of the starting reagent is a sigma hydride complex here too we see the same analogy what we had observed in the carbene insertion into metal hydride reaction

So, far we had looked into metathesis followed by two variation of insertion reaction into metal hydride one being alkene insertion the other being carbene insertion.

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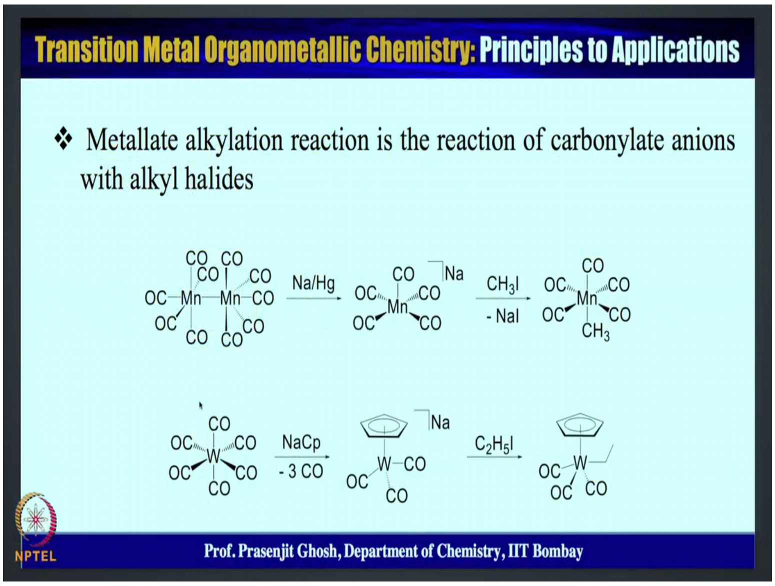

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- Metallate alkylation reaction is the reaction of carbonylate anions with alkyl halides

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And now we are going to look at a very unique reaction for preparation of this organometallic sigma alkyl complexes this particular reaction is extremely difficult to perform as the intermediate species is highly reactive to air and moisture.

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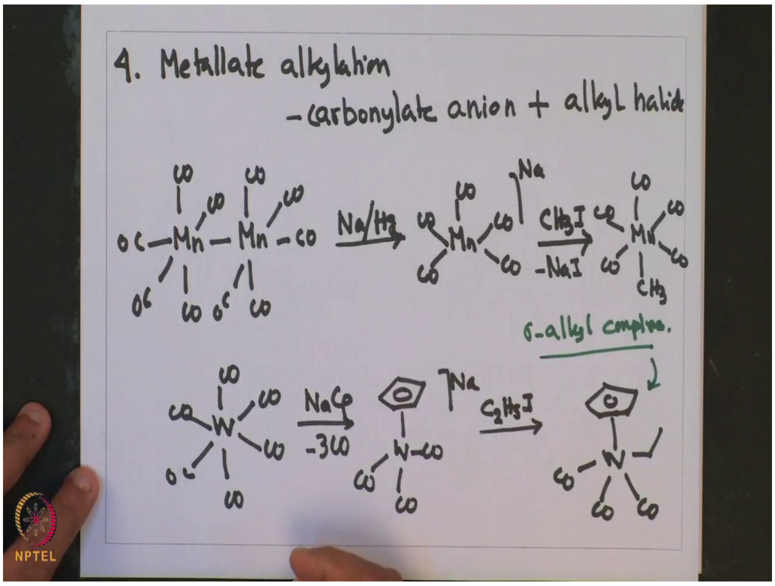

4. Metallate alkylation

– carbonylate anion + alkyl halide

And hence a very challenging method this method is called metallate alkylation and involves reaction between a carbonylate anion with an alkyl halide an example of this is given here we have a manganese pentacarbonyl dimer which has manganese in zero oxidation state which is further reduced by sodium mercury amalgam to make a very electron rich metal species called metallate where the metal center is very electron rich and then that is reacted with methyl iodide where the carbon center is electron deficient iodine is partially negative and this is partially positive. So, a rich metal center metal center then attacks the methyl eliminating sodium iodide to produce this methyl compound

Now, this is a sigma alkyl complex , but none of the reagents where a sigma alkyl complex or a sigma hydride complex like the other methods. So, in that quail from that perspective this method is also very useful this is a successfully applied to another tungsten hexacarbonyl compound which also has a tungsten in its zero valance state reacting with sodium c p with elimination of three molecules of carbon monoxide giving tungsten tri carbonyl metallate compound in this case to the metal center is highly electron rich and when reacted with ethyl iodide it produ produces the corresponding tungsten ethyl derivative

So, here too the final product is a sigma alkyl complex, but none of the reagents used where a sigma alkyl compound or a sigma hydride compound. So, from this perspective metallate alkylation reaction is a very unique approach of making this metal sigma alkyl complexes. So, with this i would like to summarize the various preparative methods that we have discussed in todays lecture in particular we have looked at four preparative methods the first one involved metathesis reaction between a metal sigma alkyl complexes with a metal halide giving another metal sigma alkyl complexes this reaction is commonly called as transmetallation reaction next one was alkyl internal insertion into metal hydride complexes and following that the third type was also an carbene insertion in a metal hydride complexes

So, we had seen two varieties of insertion reactions for making metal sigma alkyl complexes one was that of alkyne insertion and the other of carbene insertion into metal hydride complexes and the fourth one being a unique method called metallate alkylation where low valent metal were reduced further to their metallate anions and which were then reacted with alkyl halides producing metal sigma alkyl complexes

So, with these we have looked into some of the preparative methods for making this very important metal sigma alkyl complexes we are not done yet there are a few other very interesting methods that remains to be discussed and their properties and their stabilities which will be the topic of the subsequent lecture i will hope you are enjoying this exciting chemistry of organometallic compounds that are being discussed well and i hope that this would generate further interest in you in the topic with this i thank you for being with me in this lecture and i look forward to being with you in the next lecture which would discuss few more preparative details along with their properties and reactivities of this metal sigma alkyl complexes.

Thank you.