Introduction to Organometallic Chemistry
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Lecture - 10
Metal alkyl complexes

Today, we will talk about the metal carbon bond which is formed between a metal and an alkyl group. By an alkyl group, I wish to include aryl moieties. Alkyl moieties such as ethyl, methyl or propyl, and other systems like benzyls, and alyls and vinyls.

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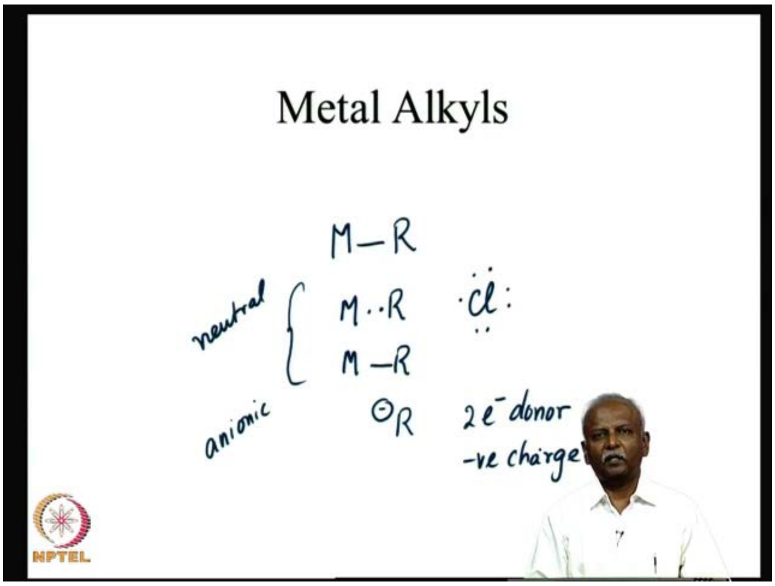

Metal Alkyls

$M-R$

neutral $M\cdot\cdot R$ $\cdot\ddot{\underset{\cdot\cdot}{Cl}}:$

$M-R$

anionic $^{\ominus}R$ $2e^-$ donor

-ve charge

So, we will group all of these group, all of these moieties together as alkyls. So, if you have an M R bond, what would be the chemistry of that bond, and how does it behave, These are the things that we are going to talk about today. First of all, we have to take care of the electron count. And in the neutral method that we talked about earlier, the R group is actually an radical. So, it is similar to what I would call as a chlorine radical. So, it is similar to the chlorine radical and it would be a one electron donor when it forms a metal alkyl bond. We actually take one electron from the metal and hence form the M R bond. So, this would be the neutral method.

In the anionic method, we actually consider the R as R minus. This is purely for convenience because carbon is in general more electronegative than the metal. So, we consider R as R minus and then it would be a two electron donor and it would have a negative charge. So, these two aspects needs need to be kept in my mind as we discuss the chemistry of the metal alkyl bond.

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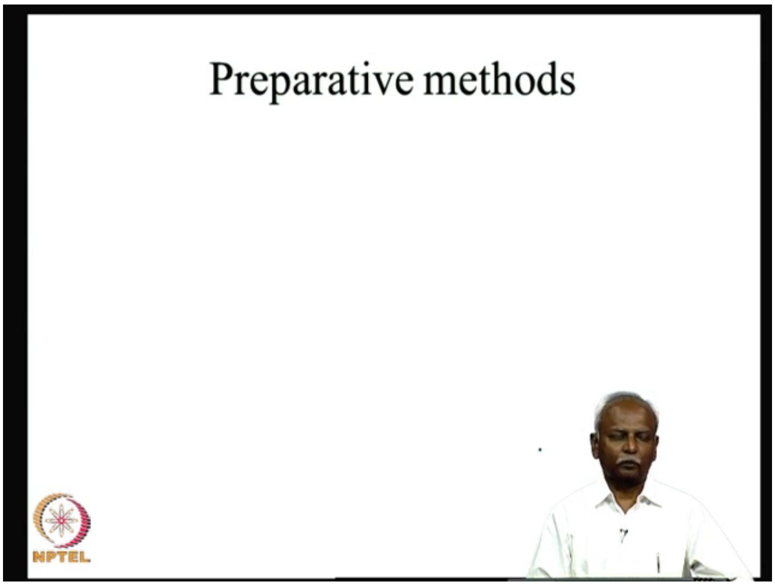

Preparative methods

And initially I wish to look at some of the preparative methods that are available for us to generate this metal alkyl bond.

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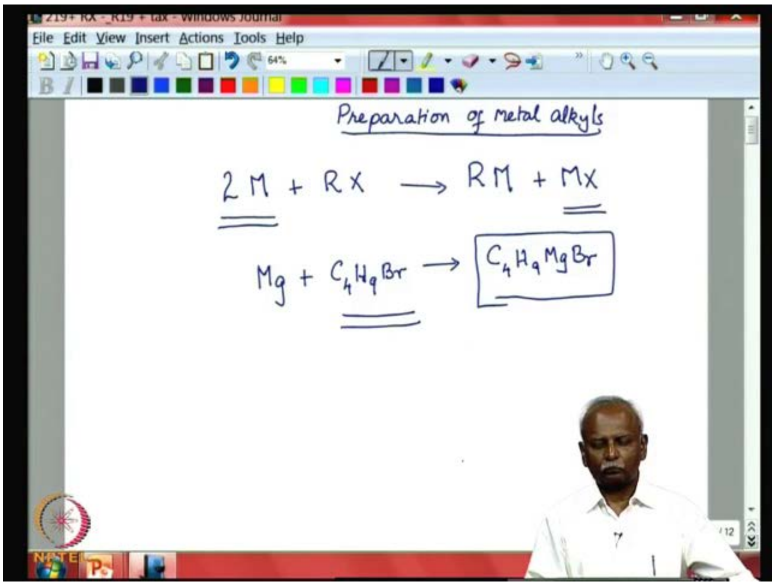

Preparation of metal alkyls

$$\underline{\underline{2M}} + RX \longrightarrow RM + \underline{\underline{MX}}$$

$$Mg + \underline{\underline{C_4H_9Br}} \longrightarrow \boxed{\underline{C_4H_9MgBr}}$$

When we talk about metal alkyls, it would be ideal if you look at some of the methods that permit us to make the metal alkyl bond or generate the metal alkyl bond directly from the organic compound. The most easy method is to use an organic halide. As I have pictured here and react it with a metal atom. Any metal atom which is reasonably reactive, by reactive I mean it has to be electropositive enough so that the M X which is formed has got a very stable bond. And the formation of M X actually drives this reaction from the left side to the right side.

So, if you take the reaction between alkyl bromide like butyl bromide, this is probably one of the most familiar and most common reagents that is used in organometallic chemistry. So, if you treat butyl bromide with magnesium one ends up with butyl magnesium bromide which is C 4 H 9 Mg Br. And this butyl magnesium bromide, although we write it in this particular fashion is not necessarily the same in solution. It is in equilibrium, as we shall see shortly with other species. But nevertheless it is convenient to talk about it as if it is butyl magnesium bromide.

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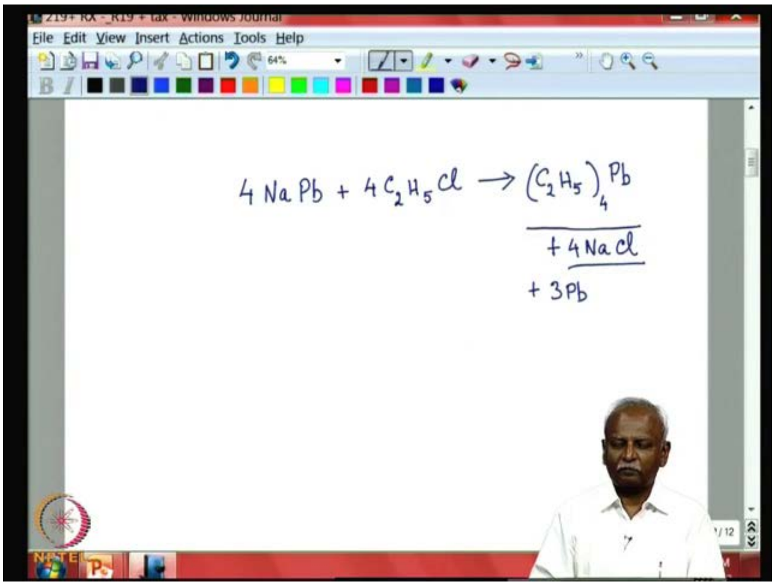

$$4\,NaPb + 4\,C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 4\,NaCl + 3\,Pb$$

In this fashion there is a different method that we can use in order to activate the metal. As I told you earlier it is important to use a very reactive metal. In the earlier instance we used magnesium and that is a very reactive metal. We can also use an alloy or a metal that will promote this reaction, but not itself participate in the reaction. One very good example is an alloy that is formed between sodium and lead.

So, sodium and lead form an alloy which is Na Pb and this Na Pb ligand. Na Pb alloy will react with ethyl chloride to form tetra ethyl lead. And this tetra ethyl lead when it is formed it also generated sodium chloride, since sodium chloride is a molecule which generates a lot of heat. It is a very stable molecule. This reaction goes from left to right and forms tetra ethyl lead. The bond between the ethyl group and the lead itself is not as strong as in the other case where we had magnesium and ethyl or magnesium and butyl forming a bond. But in spite of that this reaction is driven in the forward direction because of the formation of sodium chloride which is a very stable molecule.

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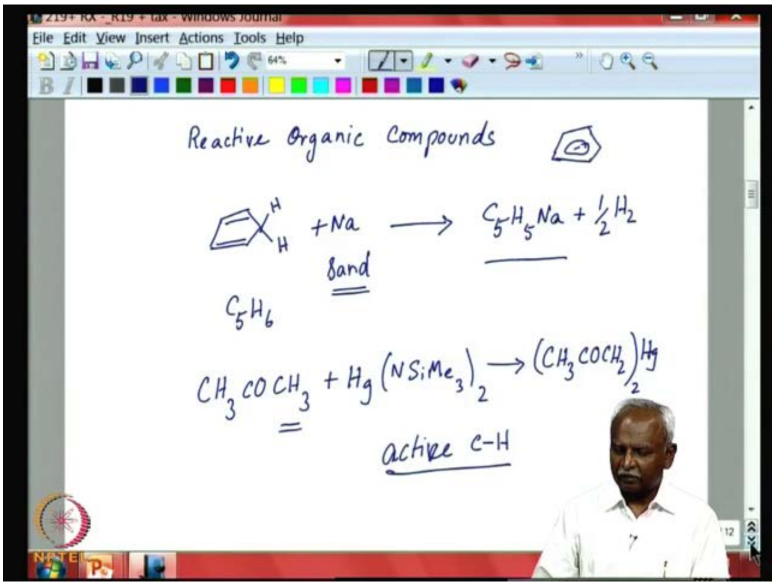

Reactive Organic Compounds

$+ Na \longrightarrow \underline{C_5H_5Na} + \frac{1}{2}H_2$

Sand

C_5H_6

$CH_3COCH_3 + Hg(NSiMe_3)_2 \longrightarrow (CH_3COCH_2)_2Hg$

active C-H

So, if you do not have a very reactive metal we should use a very reactive organic compound. An example for such a reactive organic compound I have taken cyclopentadiene. Now, you know that cyclopentadiene is easily ionized as H plus and C 5 H 5 minus. And that is because the C 5 H 5 minus ion is aromatic and could be written with a set of delocalized bonds in this fashion with a negative charge. So, that is a very stable system.

And so, the formation of this sodium organometallic which I have pictured here is very easy by directly reacting sodium with cyclopentadiene to make sodium more reactive. One normally converts it into sodium sand and this is purely a matter of convenience. One can heat the sodium and shake it up vigorously so that it forms fine droplets. And these fine droplets of molten sodium are extremely reactive and they react with C 5 H 6 and liberate hydrogen and form this organometallic compound C 5 H 5 Na.

At another method of making an organometallic compound starting with a reactive organic compound where there is a active CH. So, in all in both of these cases the presence of an active CH is presence of an active CH is what is important here. We have a CH group next to a ketone and that is enolizable. So, acetone an active CH bond next to the CO group and that is activated and it can be converted into an organometallic compound where there is a C Hg bond.

And one needs to use this trimetal cylil nitrogen compound. Tri methyl cylil compound which is attached to mercury and that is already a mercury 2 plus compound. But it exchanges with this active hydrogen in order to produce a carbon mercury bond. So, this is yet another way of making a metal alkyl bond fairly readily.

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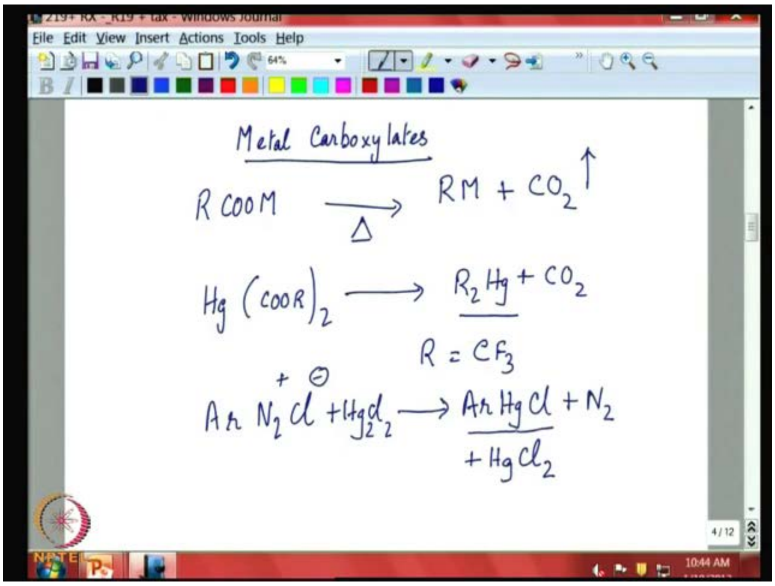

Metal Carboxylates

$$RCOOM \xrightarrow[\Delta]{} RM + CO_2\uparrow$$

$$Hg(COOR)_2 \longrightarrow \underline{R_2Hg} + CO_2$$

$$R = CF_3$$

$$Ar\overset{+}{N_2}\overset{\ominus}{Cl} + HgCl_2 \longrightarrow \underline{ArHgCl} + N_2 + HgCl_2$$

These examples illustrate that you have a tendency for a C minus interacting with a metal atom and that is the basis for forming these metal alkyl species. Here there is a variation in this particular projection that I am showing you. You can use a metal carboxylate. And if you heat the metal carboxylate, because of the elimination of carbon dioxide you will form a metal alkyl compound. And this is convenient because there are instances where you can generate metal alkyls which are otherwise difficult to make.

Here is a mercury compound with a tri fluoro methyl group attached to the mercury. So, it is this tri fluoro methyl that is formed and that is here. This tri fluoro methyl mercury with because of the liberation of carbon dioxide this reaction is again thermodynamically favourable. And it is driven to the right side and you have very good yields of a di alkyl mercury compound being formed.

The reactions that we have pictured in this projection are all driven from left to right because of elimination of a volatile molecule like carbon dioxide. Or in the last instance it is di nitrogen and di nitrogen elimination leads to the formation of a aryl mercury bond in this instance. And that is the elimination of nitrogen from arene dizonium salt. So, this Ar N 2 plus Cl minus and this molecule nearly is transferring an aryl group to the mercury. And you have the formation of a mercury 2 plus compound. So, during the process you also have an oxidation of the mercury from 1 plus to 2 plus.

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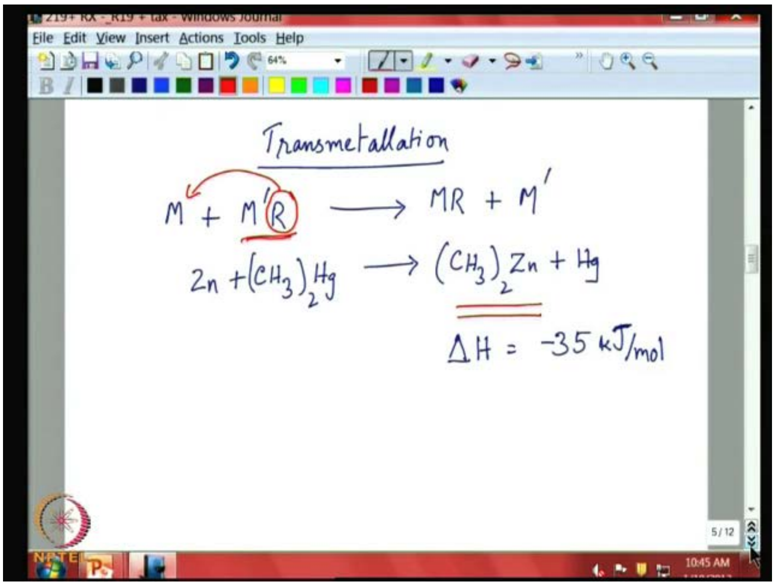

Transmetallation

$$M + M'R \longrightarrow MR + M'$$

$$Zn + (CH_3)_2Hg \longrightarrow (CH_3)_2Zn + Hg$$

$$\Delta H = -35 \text{ kJ/mol}$$

So, let us proceed further. The most common method of making organometallic compounds however is a reaction called a transmetallation. In this instance I have pictured a metal which is exchanging with position with another metal in a alkyl compound. So, you already have a metal alkyl bond and you are nearly transferring this R group form this position onto this other metal. And so, MR is formed and this M dash is liberated.

Once again for a transmetallation reaction you should have the thermodynamics right. And in the example that I have given here you are transferring the metal from mercury to zinc. And because zinc methyl bond is stronger, you have this reaction going from left to right and di methyl zinc is formed in this process. And mercury is usually eliminated as liquid mercury which comes out from the reaction and can be easily removed and you can have very pure di methyl zinc in this reaction.

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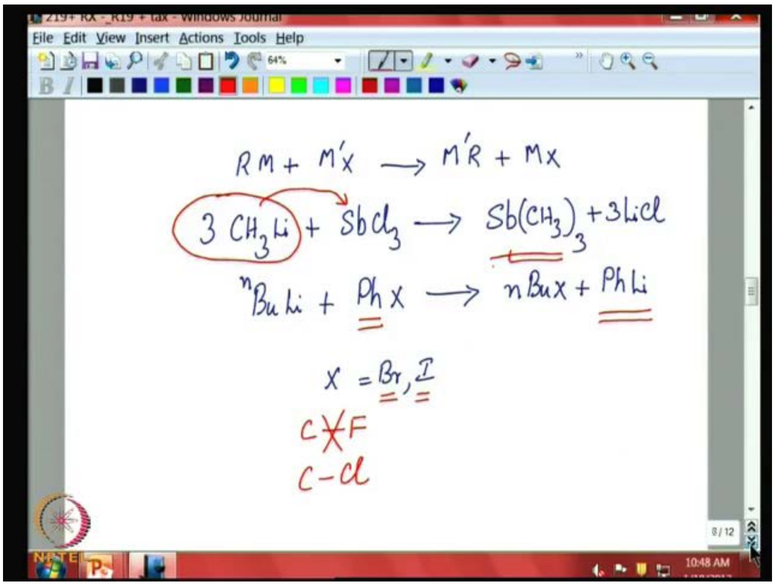

$$RM + M'X \longrightarrow M'R + MX$$

$$\boxed{3\,CH_3Li} + SbCl_3 \longrightarrow \underline{Sb(CH_3)_3} + 3LiCl$$

$$^{n}BuLi + \underline{\underline{Ph}}X \longrightarrow nBuX + \underline{\underline{PhLi}}$$

$$X = \underline{\underline{Br}}, \underline{\underline{I}}$$

$$C \cancel{-} F$$

$$C - Cl$$

Once again transmetallation is a process which you can use if you have a metal alkyl bond which is formed from a direct reaction. In this particular reaction or transparency that I am showing here, you react a methyl lithium. The methyl lithium is formed from methyl bromide and lithium. And then once you have this metal alkyl you can transfer it to a less electronegative, less electropositive element like antimony. And you form an organometallic compound which is not possible to. It is not possible to generate this antimony compound directly from a reaction of methyl bromide and antimony. But by this indirect method you first convert it to methyl lithium and then transfer the methyl group from the lithium onto the antimony atom.

Here is another example which is slightly different from what we have discussed earlier. And here I am going to transfer a butyl group. I am going to transfer the butyl group to a halogen. And a phenyl group to the lithium. And because the phenyl lithium is what has a better phenyl lithium interaction compared to the butyl. This reaction proceeds from left to right and you have elimination of butyl halide.

Now, it is very difficult to break carbon fluorine bonds. It is a very strong bond and it is not possible to break it. So, you would have to use either a bromine or an iodine in order for this reaction to proceed fairly readily. So, this reaction works if you have phenyl bromide or phenyl iodide, but it will not work with CF. And it will be very sluggish and if not impossible with carbon chlorine. Also chloro benzene and fluoro benzene are not good substrates. But bromo and iodo benzenes are good substrates for this particular transmetallation that we have carried out.

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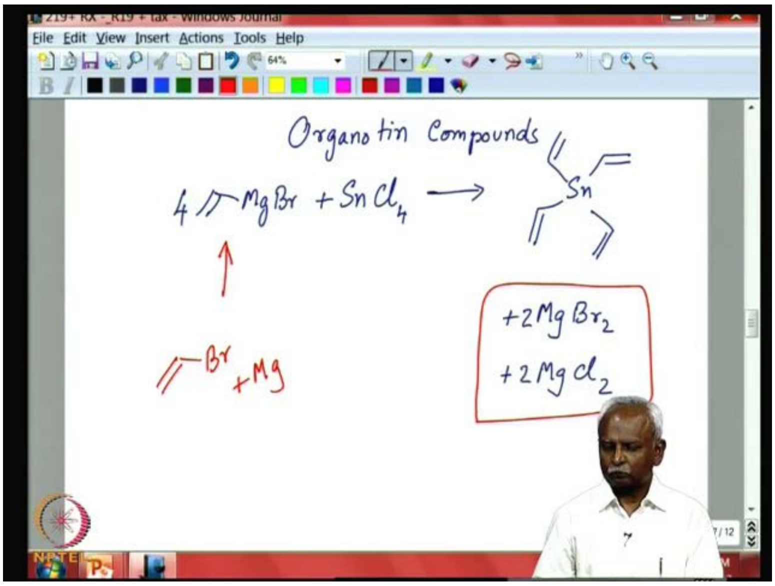

So, organo tin compounds are extremely important in the industry. It is also commonly used in the laboratory. And here is a transmetallation where we are carrying out a transmetallation between magnesium and tin. And the group that is transferred is vinyl. So, one would have to generate the species. One can generate this species from vinyl bromide and magnesium using the reaction that we talked about earlier.

You would end up with vinyl magnesium bromide which is again readily made in the laboratory and it can be transferred to the tin. So, the vinyl group is transferred to the tin and tetra vinyl tin is formed in this process. And you can eliminate because we are eliminating two very stable molecules or salts. In this process we have formation of this molecule tetra vinyl tin very readily.

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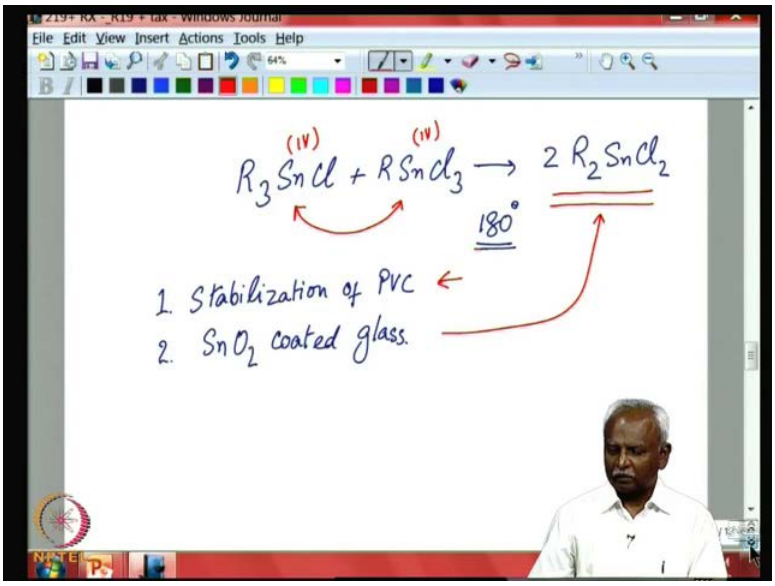

$$\overset{(IV)}{R_3SnCl} + \overset{(IV)}{RSnCl_3} \xrightarrow[180^\circ]{} \underline{\underline{2R_2SnCl_2}}$$

1. Stabilization of PVC ←
2. SnO_2 coated glass.

Tin is a special example because one can readily do transmetallation between one tin atom to the other. Here I have pictured for you a metathesis reaction. Metathesis purely means a change of place. Transmetallation is also a change of place where alkyl group changes place from one metal atom to the other. So, if you react R 3 Sn Cl with R Sn CL 3, both are tin four species and you are merely exchanging an R group from one tin to the other. That tells you that because you are not having a thermodynamic difference in the R Sn bond, this must be due to the fact that you are forming a set of compounds which are all of them are almost iso-energetic and probably its entropy.

The equilibrium is entropy driven and it is possible to carry out this reaction at a very good, with very good yields and with at a high temperature. And R 2 Sn Cl 2 is an important intermediate which is used in the stabilization of PVC. What happens is you can use tin chlorides, tin alkyls as molecules which will absorb hydrochloric H Cl that is evolved during the formation of making of PVC.

You can also use it, R 2 Sn Cl 2 is also used for the stabilization or the formation of Sn O 2 on glass. And tin oxide coated glass is a special glass which is very important in the industry as well. So, R 2 Sn Cl 2 and R 2 Sn are molecules which are reasonably accessible and fairly important in the literature. So, Mn 2 CO 10 is a molecule which we have already encountered in the carbonyl chemistry.

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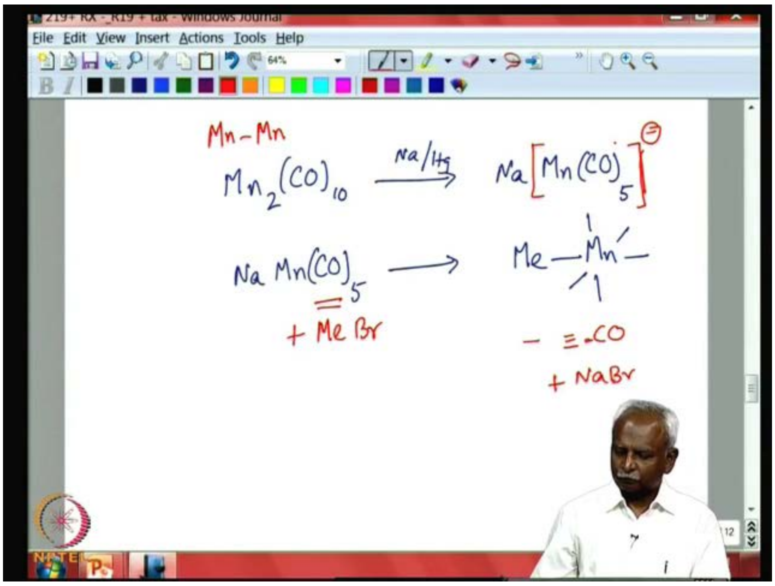

This is easily reduced, because you have a manganese manganese bond, Mn Mn bond. And this Mn Mn bond can be converted to anionic species. It can be broken and converted to anionic species which is also an eighteen electron species sodium salt of Mn CO 5. Mn CO 5 minus is readily formed in this process. And this Mn CO 5 minus is a nucleophyle and it can react with methyl bromide. It can react with methyl bromide and generate a Me Mn CO 5 species.

So, each one of these lines is equivalent to a carbon monoxide. So, that is actually equivalent to a carbon monoxide attached to the metal and we have a methyl manganese being methyl manganese bond being formed. And you also have in this process sodium bromide eliminated. So, this is a reaction which can be carried out if you have an anionic metal species. And it is not uncommon in organometallic chemistry to have anionic species because the negative charge is in fact stabilized by the five carbon monoxides which are present on the manganese. They can accept electron density and stabilize the negative charge on the metal.

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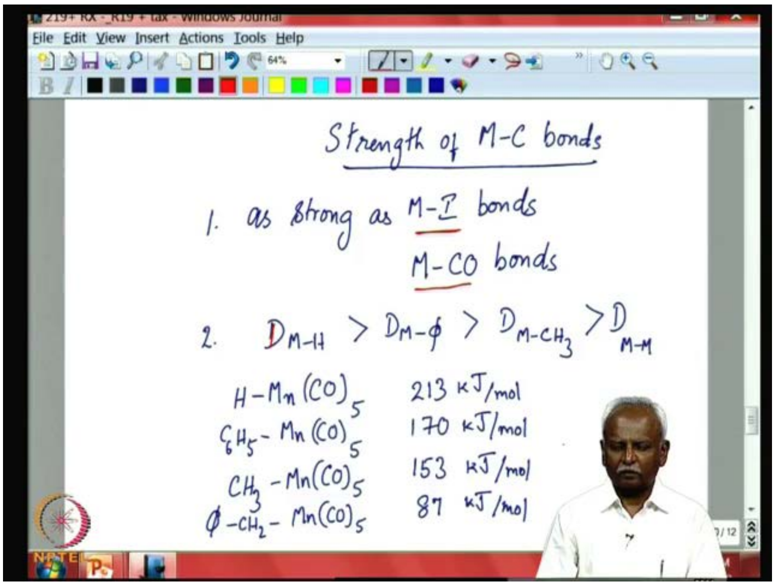

Strength of M–C bonds

1. as strong as M–I bonds
M–CO bonds

2. $D_{M-H} > D_{M-\phi} > D_{M-CH_3} > D_{M-M}$

$H-Mn(CO)_5$	213 kJ/mol
$C_6H_5-Mn(CO)_5$	170 kJ/mol
$CH_3-Mn(CO)_5$	153 kJ/mol
$\phi-CH_2-Mn(CO)_5$	87 kJ/mol

So, we have looked at a variety of preparative methods for the metal carbon bonds. Most of them are the main group compounds that we have considered. And many times it is convenient to make a main group organometallic metal carbon containing species and then transfer it to a transition metal. In general it is known that the metal carbon bond is as strong as an M I bond. A metal iodo bond is a good indicator. The strength of the metal iodo bond is a good indicator of how strong a metal metal bond would be.

That is also similar to what one encounters for the average metal carbonyl bond strength. So, the metal carbonyl bond strength, the metal iodo bond strength and the metal methyl bond strength all fall in the same range. However, in a particular metal system it is found that the metal hydride bond is much stronger. And that is what I have pictured here. The metal hydride bond is much stronger than the metal phenyl bond. So, if an aryl group is attached to the metal then that is more easily broken compared to the metal hydride and that in turn is stronger than a metal methyl and a metal metal bond.

So, this is the order in which you have bond strengths in a set of alkyl groups. So, if you vary the alkyl group you find that the metal aryl group is much stronger than a metal alkyl group. So, here I have given some representative values for the species that we just encountered and that is a H Mn CO 5 has got a bond strength of two 213 kilo joules per mole. Whereas, the methyl metal carbonyl species that we just encountered in the previous slide was about worth about 153 kilo joules per mole.

So, you have bond strengths that vary from 200 to 100 kilo joules per mole. So, the metal carbon chemistry is quite important. And it is often encountered in organometallic chemistry and it is probably the only group which has got purely sigma interactions between the metal and the alkyl group. We will discuss this in greater details in a later lecture.

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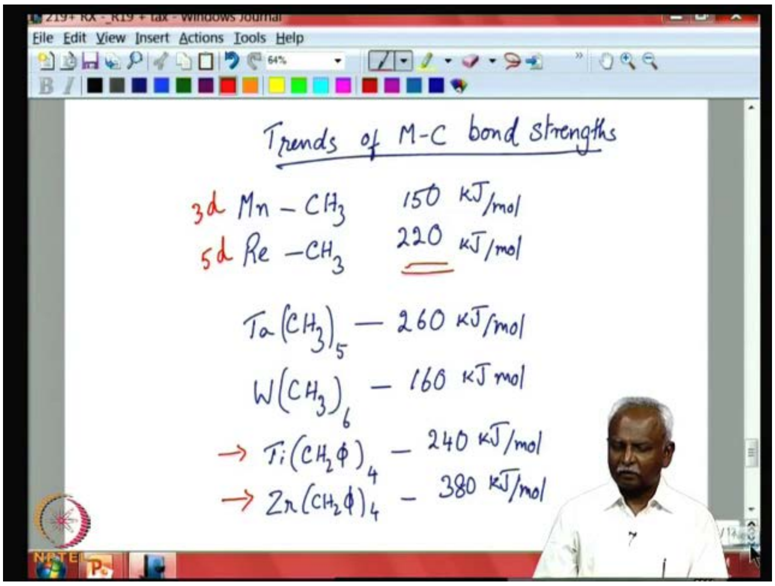

Trends of M-C bond strengths

3d $Mn - CH_3$ 150 kJ/mol
5d $Re - CH_3$ 220 kJ/mol

$Ta(CH_3)_5$ — 260 kJ/mol
$W(CH_3)_6$ — 160 kJ mol
→ $Ti(CH_2\phi)_4$ — 240 kJ/mol
→ $Zr(CH_2\phi)_4$ — 380 kJ/mol

We considered what happens when you change the alkyl group. In this particular transparency I have shown you what would happen if you change the metal. If you moved from a manganese methyl group to a rhenium methyl group, usually the bond strength increases. So, this is a 3 d element. And if you go down the group, manganese technetium and rhenium. So, you end up with a very strong very strong metal alkyl bond strength.

So, this seems to be a general phenomenon. If you go from titanium to zirconium once again you have a bond strength increase of nearly 50 percent. So, from 240 kilo joules per mole you end up with 380 kilo joules per mole. So, it is generally known that you have much stronger bond strengths when you go from one metal to another which is lower down the periodic table. So, the trends in metal carbon bond strengths at least in transition metals follow this order. It is interesting that the same order is not followed if you go to the main group chemistry.

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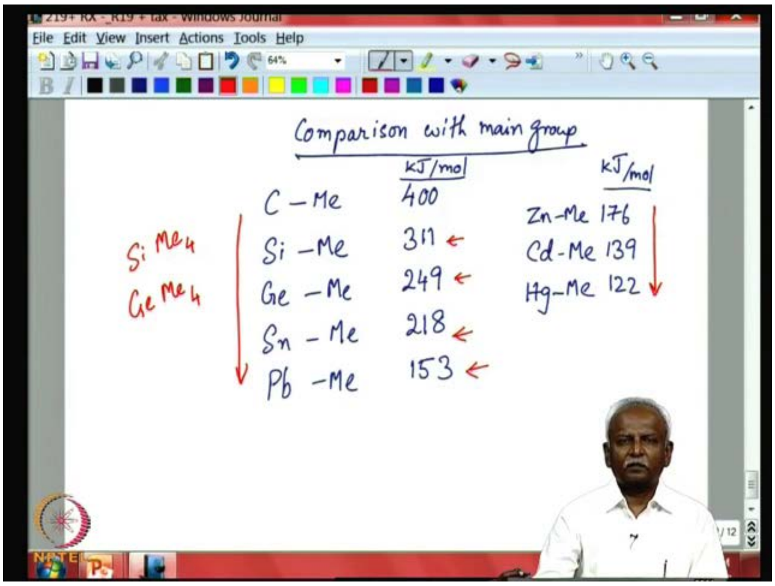

Comparison with main group

$SiMe_4$

$GeMe_4$

	kJ/mol
C – Me	400
Si – Me	311 ←
Ge – Me	249 ←
Sn – Me	218 ←
Pb – Me	153 ←

	kJ/mol
Zn-Me	176
Cd-Me	139
Hg-Me	122

So, in main group chemistry the metal carbon bond strength or the element carbon strentgth. If you want to call it that keeps decreasing as you go down the group. So, here are some examples that I have shown you. So, if you take silicon methyl bond it is about 300 kilo joules per mole. And if you make the corresponding germanium methyl bond it goes down to 200, and it goes down to 249 kilo joules per mole.

So, here we are talking about Ge Me 4 and Si Me 4. And we are talking about the average bond strength which is required for breaking the four methyl groups together. And then we take the average for all the four methyl germanium bonds and we get 249 kilo joules per mole. Similarly, tin goes down to 218. Tin goes down further and lead forms the weakest bond, which is 153 kilo joules per mole.

So, in general if you go down the group the bond strength seems to come down decreases. As we go down the group and this is uniformly observed for all compounds which are organometallic compounds of the main group. Here I have zinc cadmium and mercury and also falls in the same trend. As a same trend you have a decrease in the bond strength as you go down from zinc to mercury.

So, this difference between the main group and the transition metal chemistry is often observed in many properties including length changes, bond strength changes. And this is something that we have to look at from the theoretical point of view and see why is it that these bond strengths vary in the way they do.

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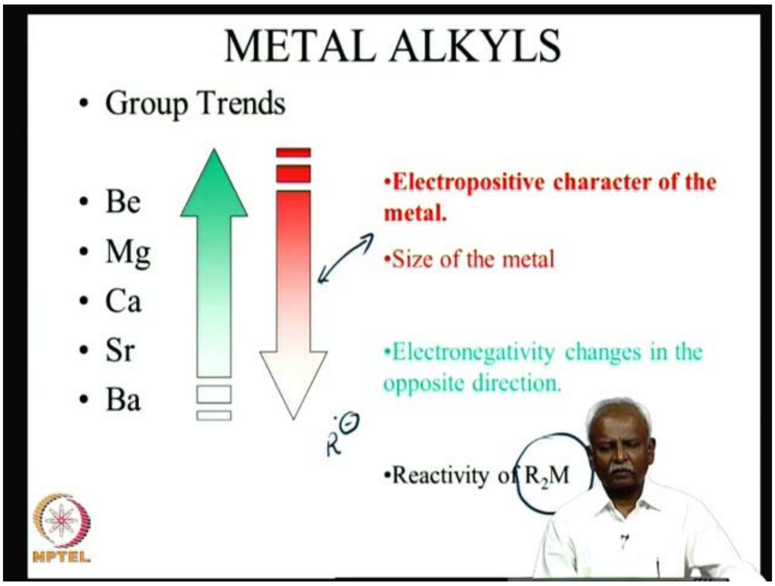
METAL ALKYLS

- Group Trends

- Be
- Mg
- Ca
- Sr
- Ba

•Electropositive character of the metal.

•Size of the metal

•Electronegativity changes in the opposite direction.

•Reactivity of R_2M

So, let me now proceed to some of the trends that we some of the properties of the alkyl metal bond. And we will discuss this, the main group chemistry a little bit. And before proceed to the transition metal chemistry, in general what we found that as we go down the group at least in main metal chemistry. The bond strength decreases and you also know that the electropositive character of the metal increases as you go down the group. So, the red arrow is connected to what we have shown here. The electropositive nature of the metal and that seems to increase as you go down the group. And the electro negativity of course changes in the opposite direction.

So, beryllium is the most electronegative species in this group of elements that I have pictured for you on the right side. And the reactivity of the metal alkyl species in this case R to M. The reactivity of R to M is such that it becomes more reactive as you go down the group. So, as you go down the group it behaves more and more like R minus. And because it is R minus the reactivity increases as you increase the electropositive character of the metal.

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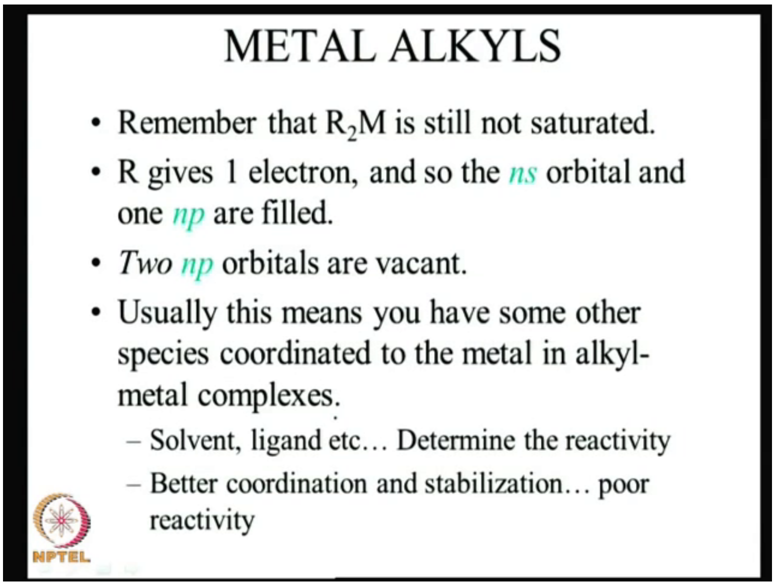

METAL ALKYLS

- Remember that R_2M is still not saturated.
- R gives 1 electron, and so the *ns* orbital and one *np* are filled.
- *Two np* orbitals are vacant.
- Usually this means you have some other species coordinated to the metal in alkyl-metal complexes.
  - Solvent, ligand etc… Determine the reactivity
  - Better coordination and stabilization… poor reactivity

So, remember that although we write the metal alkyl species as R 2 M, it is still not a saturated species. If you remember the electron counting that we did. R gives one electron in the neutral method. And so, if you have two of these you cannot have a totally filled set of orbitals. Because two n np orbitals will be vacant if it occupied. The s and the p orbitals with the two electrons that came from the R groups and the metal itself has got two electrons in the group two. So, you will only have total of four electrons and two p orbitals or two np orbitals will be vacant.

Usually this means that you need some other species to coordinate to the metal and stabilized the metal. And the stabilization is usually carried out with a solvent or an added ligand. The solvent is a solvent in which the species is formed initially. It has to be an ether or an amine in order to stabilize the insipiently formed metal alkyl species. If there is better coordination there is better stabilization, but then the reactivity of the metal alkyl species is poor. So, you have the familiar change between coordination stabilization and reactivity. The more reactive the species the poorer it is coordinated and vice versa.

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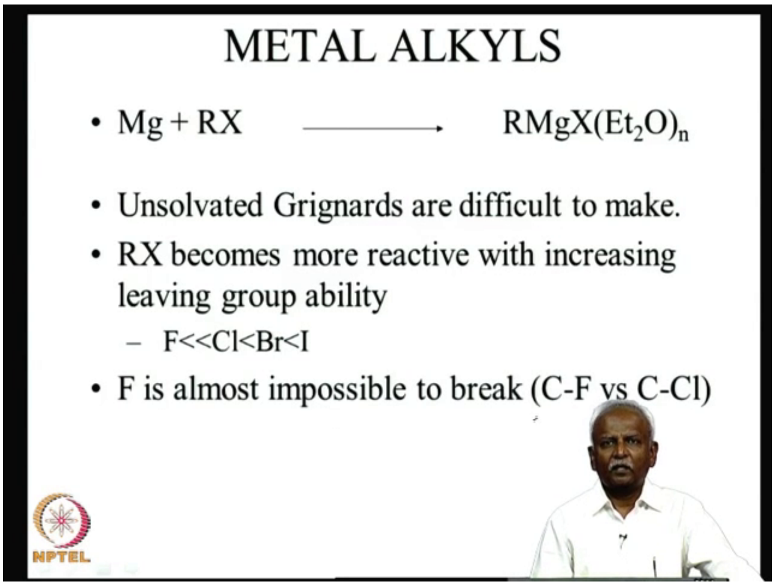

METAL ALKYLS

- Mg + RX $\longrightarrow$ $RMgX(Et_2O)_n$
- Unsolvated Grignards are difficult to make.
- RX becomes more reactive with increasing leaving group ability
  - F<<Cl<Br<I
- F is almost impossible to break (C-F vs C-Cl)

So, in general diethyl ether is a very convenient ligand. It is also is convenient solvent which is used in the preparation of grignards. And so, it is the R Mg X is usually coordinated with diethyl ether. And if you want to make unsolvated Grignard reagents these are extremely difficult to make. And the less you coordinate the Grignard, the more reactive it becomes. But there is also a trend in the R X group. When you make R I then the R X tends to be more reactive and the grignard is more readily formed.

So, here we are not talking about the reactivity of R Mg X. We are talking about the facility with which R Mg X is formed. For a fluoride it is very, very difficult to form a grignard reagent. Whereas, with an iodide it is very easy to form the grignard reagent. And with fluorine as I said it is almost impossible to break the C F bond. And that is the reason why it becomes so difficult to make the fluoro grignard.

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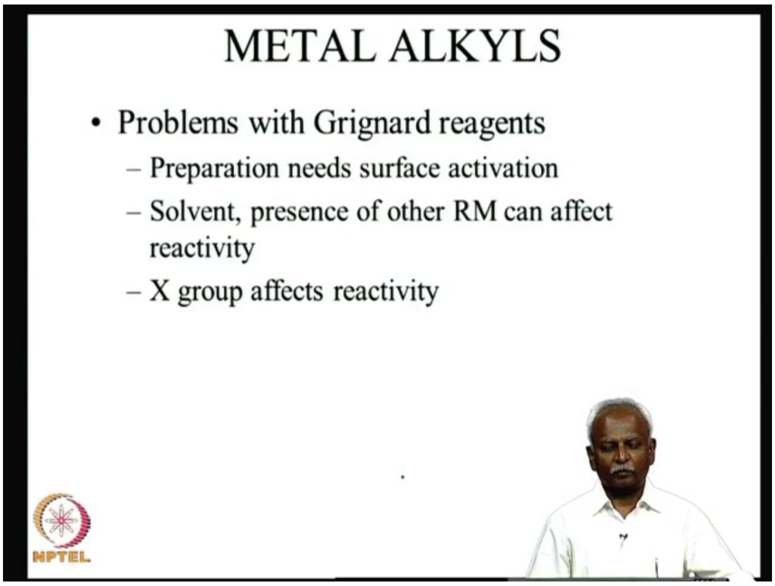

METAL ALKYLS

- Problems with Grignard reagents
  - Preparation needs surface activation
  - Solvent, presence of other RM can affect reactivity
  - X group affects reactivity

Now, let us take a look at a little about grignard reagents and the problems associated with grignard reagents. Usually the preparation is a bit difficult because you need very clear, very clean magnesium surface. And the surface is usually contaminated with an oxide layer. And you need to clean it up with an acid wash and then subsequently wash it with a solvent which will not oxidize and a solvent which will coordinate to the insipient grignard which is formed. As I have told you earlier the X group affects the reactivity of the grignard's reagent as well.

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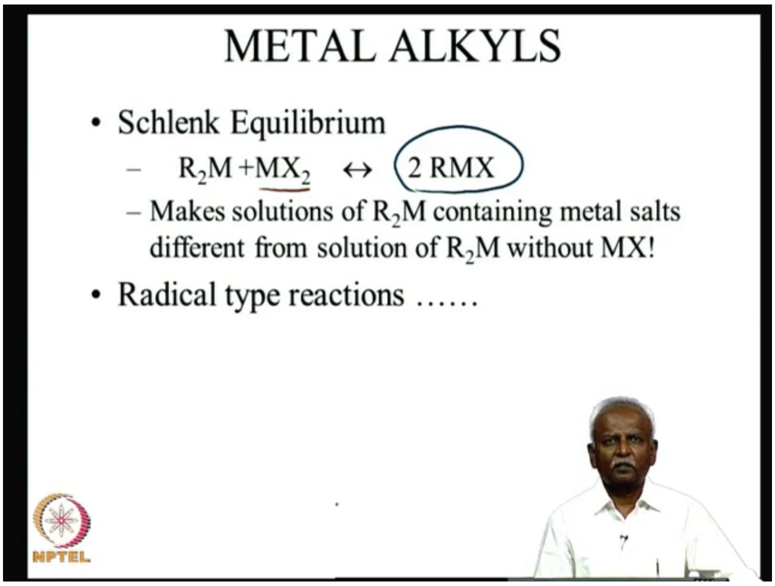

METAL ALKYLS

- Schlenk Equilibrium
  - $R_2M + \underline{MX_2} \leftrightarrow \boxed{2\ RMX}$
  - Makes solutions of R_2M containing metal salts different from solution of R_2M without MX!
- Radical type reactions ……

So, now let us look at the other problems which are associated with grignard's. I have mentioned this earlier but although we write R Mg X as the species which is there in solution. This is the species which we usually write as the species available in solution. But it is in equilibrium with R 2 M and M X 2. And this makes the reactivity of the species change in the presence of added M X 2. You can change the reactivity of the solution by adding some M X 2 to the solution. So, you can change this equilibrium position by adding one of these compounds. And you can change the reactivity of the species.

In many cases people try to remove the M X 2 from the solution so that more reactive species can be obtained. And although this is possible, it is possible to make a grignard reagent in an alkane solution where the M X 2 is precipitated out. It is in general more reactive and because it is more reactive it tends to decompose very readily. And so, its shelf life goes down as you remove the ether and replace it with an alkane. So, there is another complication that is associated with grignard reagent. And that is the fact that you can observe radical type reactions in grignard reactions sometimes.

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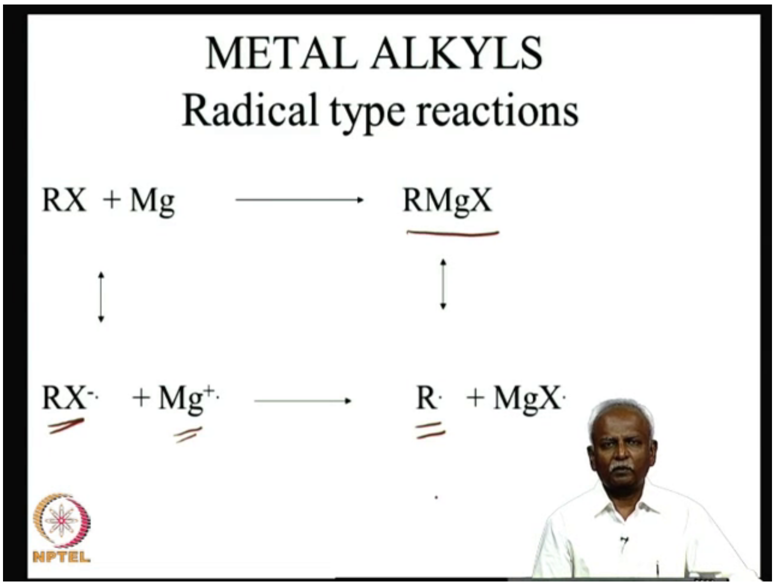

METAL ALKYLS

Radical type reactions

$$\begin{tikzcd} RX + Mg \arrow[r] \arrow[d, leftrightarrow] & \underline{RMgX} \arrow[d, leftrightarrow] \\ RX^{-\cdot} + Mg^{+\cdot} \arrow[r] & R\cdot + MgX\cdot \end{tikzcd}$$

And once again this is associated with the equilibrium that is present in solution. R Mg X is the usual species that we think about as being present. R Mg X is the species that is present but it can dissociate or be in equilibrium with a radical species R dot. So, this R dot can accept and electron from Mg X and from R X minus as well and Mg plus dot. So, a variety of species can be present in solution. This is in general. This is not a common occurrence.

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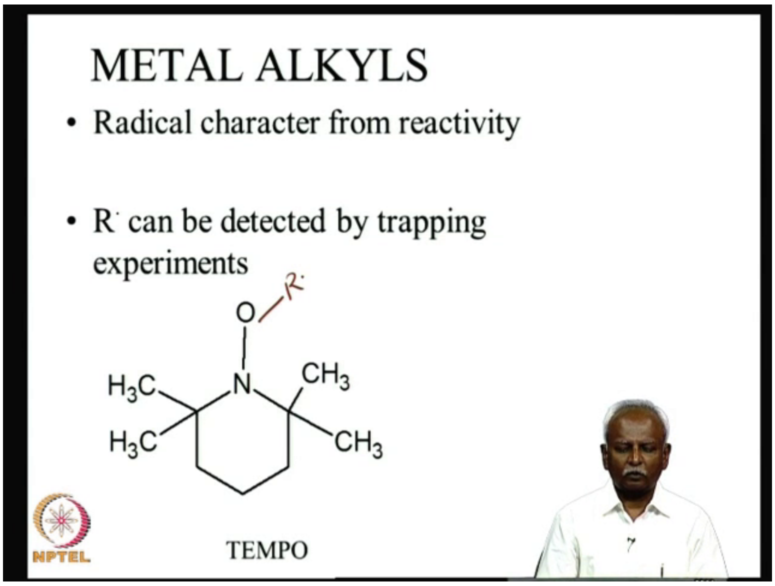

METAL ALKYLS

- Radical character from reactivity
- R· can be detected by trapping experiments

TEMPO

But it has been noticed that if you have radical species in solution, the radical character of the grignard reagent is enhanced. And you can in fact promote radical reactions by adding species like oxygen. Then you would induce radical like reactivity and the radical can be trapped. So, R dot is the radical that is generated in solution and can be trapped with a tempo and an O R bond is then formed. So, O R bond is formed because the R dot reacts with tempo to form this species.

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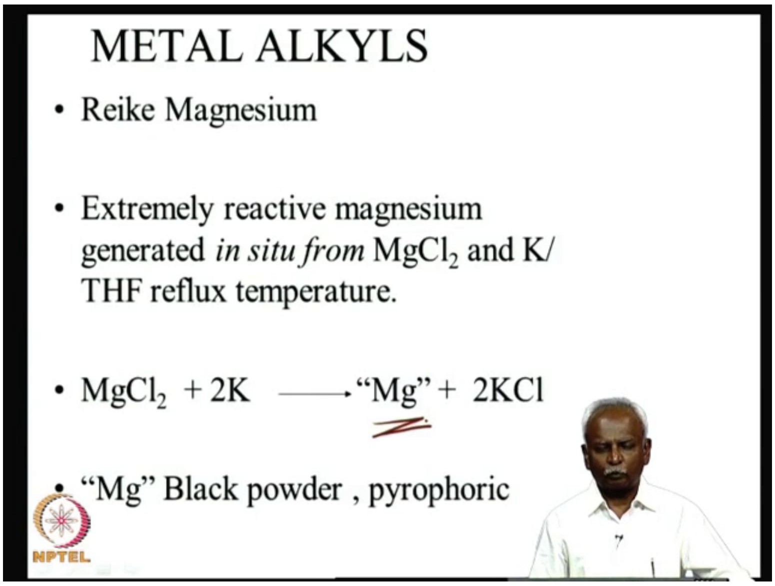

METAL ALKYLS

- Reike Magnesium
- Extremely reactive magnesium generated *in situ from* $MgCl_2$ and K/ THF reflux temperature.
- $MgCl_2 + 2K \longrightarrow \underline{\text{“Mg”}} + 2KCl$
- “Mg” Black powder , pyrophoric

So, let us proceed further. I talked about grignard reagents being one of the most common reagents and it is easy to make it in the laboratory. But some species are difficult, some alkyl bromides or halides are difficult to make. And so one has to start with a alkyl chloride or an alkyl fluoride. And in that case it is very difficult to make the grignard reagent.

So, it was discovered by reike that the magnesium which is usually used as a powder or magnesium is used as a metal ribbon. This magnesium can be activated further by a special process and this very reactive. Magnesium is generated in situ by reducing the magnesium chloride with potassium and THF. When the reflux temperature of THF potassium actually dissolves in or melts and forms metal globule and that metal globule reduces the magnesium chloride and forms a black magnesium powder.

And this black magnesium powder that is formed is extremely reactive. So, this is a pyrophoric powder that is formed by reduction of magnesium from magnesium 2 plus using very reactive potassium. So, this is called reike magnesium and it has some very interesting properties. Apart from the fact that it is not a shiny metal. But it is a black powder and it can catch fire when you expose it to air.

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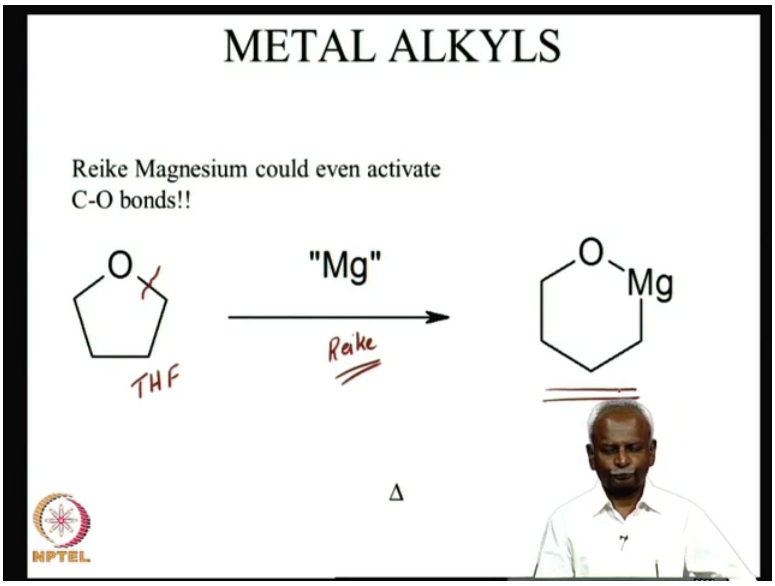

METAL ALKYLS

Reike Magnesium could even activate C-O bonds!!

It is so reactive that THF, tetra hydro furine which is a common solvent used when you make grignard’s can be cleaved. So, even the CO bond can be ruptured in the presence of reike magnesium. So, reike magnesium has a tendency to break the CO bond and form the six membered metallacycle. Some reactions of reike magnesium can be in fact disadvantageous if you have THF and you have to reflux the solution. Then you can end up with side products because of the formation of such a metallacycle.

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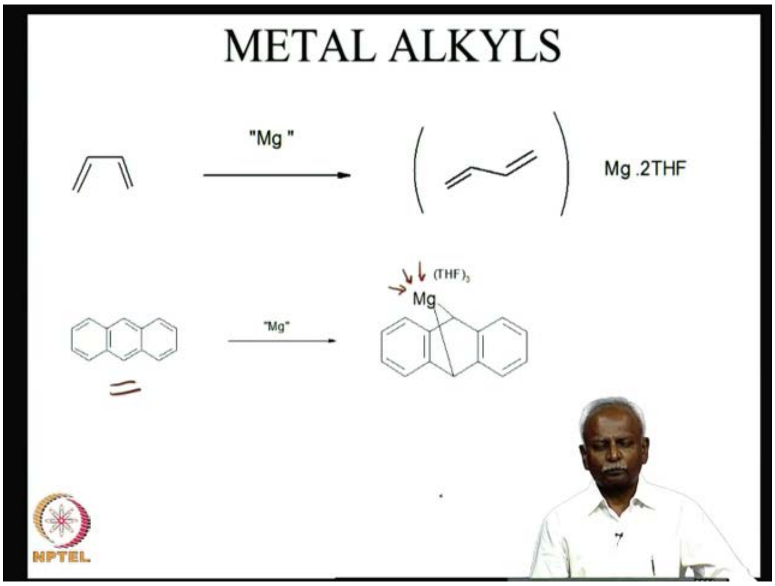

METAL ALKYLS

This reike magnesium is so reactive that it can complex to a double bond. Although, the structure of this species is not completely understood. It can form a complex species with magnesium in the case of anthracene. The central ring is less aromatic and so it can be complex to this reike magnesium in such a fashion that there are two carbon magnesium bonds formed in the process. And you can have 3 THF molecules which are coordinated to the magnesium and the oxygen of THF coordinates to the magnesium in such a fashion. And this coordination stabilizes this coordination, staibilizes the magnesium which is now complex to the naphthalene moiety.

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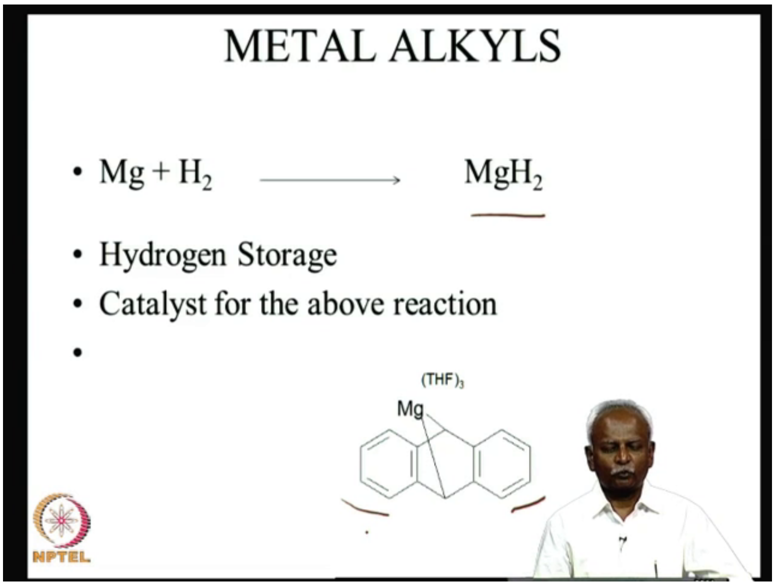

METAL ALKYLS

- $Mg + H_2 \xrightarrow{\quad} MgH_2$
- Hydrogen Storage
- Catalyst for the above reaction
-

So, this reactive magnesium can be used in a variety of ways. One very interesting use that has been proposed is the fact that it can be used as a catalyst for the storage of hydrogen. Magnesium itself can adsorb or chemisorb hydrogen and form a species Mg H 2. And this Mg H 2 formation is catalyzed by this anthracene complex of magnesium which I have pictured here. So, this is a catalyst for the formation of Mg H 2. So, these are some interesting applications of grignard reagents.

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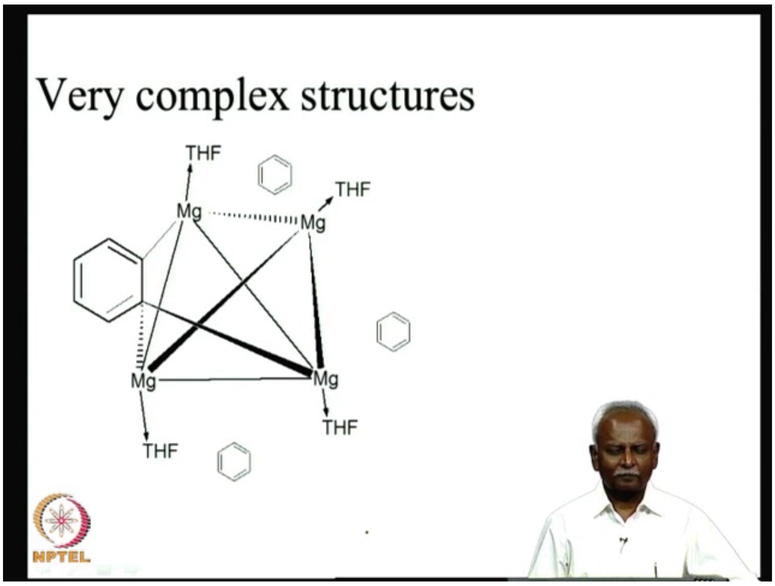

Very complex structures

Let me now move on a little bit towards the about the structures of metal alkyl complexes. They are in fact extremely complex and some of them have been crystographically characterized and I have pictured for you right here. The phenyl magnesium complex which is stabilized by THF. The magnesium is in fact in a tetrahedral array and it is coordinated with each phenyl group is coordinated with two magnesium atoms. And this complex structure needs a lot of explanation because you have a fairly difficult bonding situation here.

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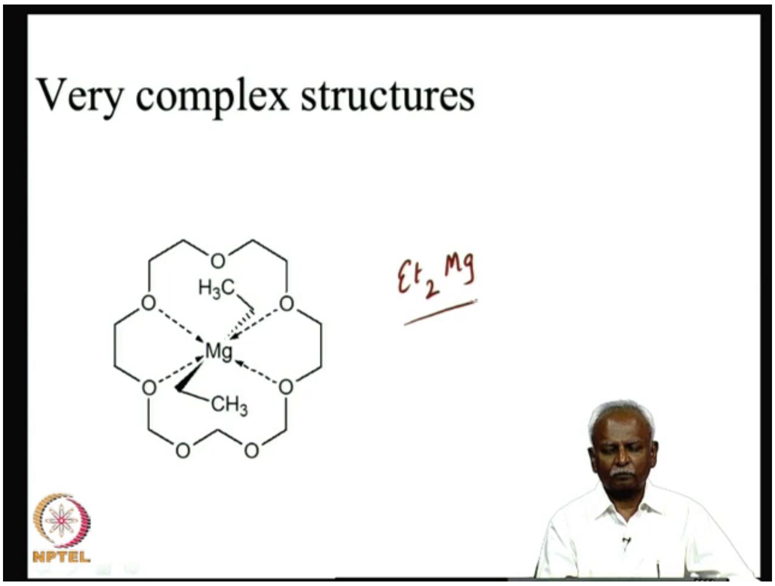

Very complex structures

Here is a simpler structure, you can understand this structure more readily. You have two ethyl groups which are coordinated to magnesium. So, it is very simply diethyl magnesium and the magnesium is coordinated to a crown ether here so that it forms a very stable complex. So, diethyl magnesium is coordinated to a crown ether and this structure has been crystographically characterized.

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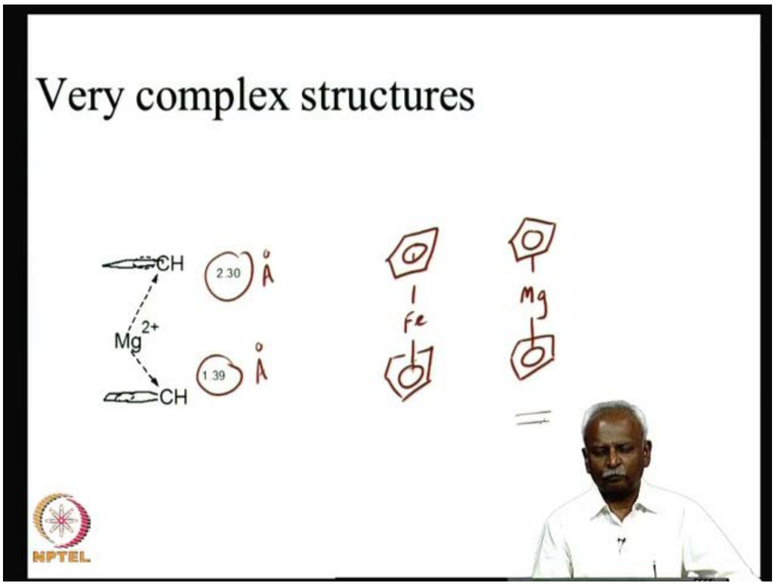

Very complex structures

So, here is a picture of a magnesium coordinated to two cyclopentadienyl groups. Most of us are familiar with the structure of ferrocene which has got two rings of cyclopentadienyl attached to two c p rings. So, this is a very familiar structure. Now, if try to make the analogous magnesium c p 2 species you find that it is no longer similar to ferrocene. But it has got an unsymmetrical coordination to the magnesium. On one side the ring has got a long metal carbon bond that is about 2.3 Angstroms.

And on other side it is only 1.39 Angstroms. And in this case also the bonding needs a little more explanation, but these structures are more fluxional and so they are having these unsymmetrical distances. Only in the solid state in solution they would equilibrate to have a more symmetrical structure as I have pictured here.

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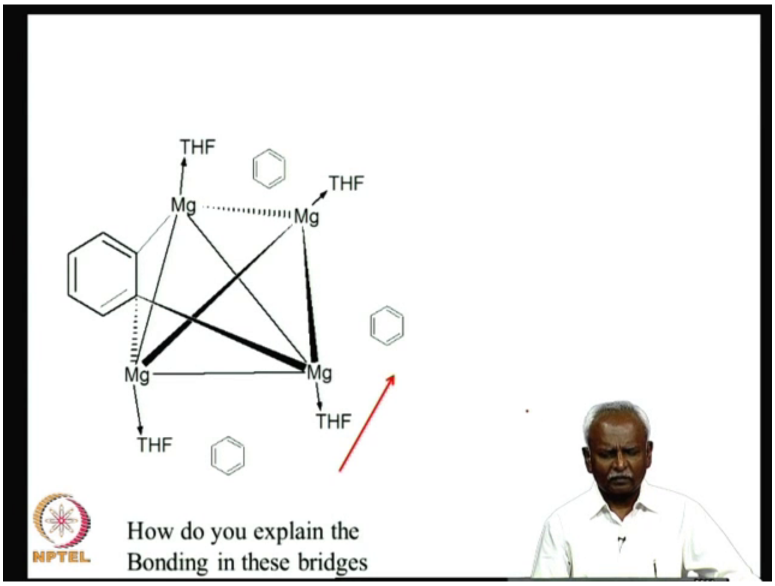

How do you explain the Bonding in these bridges

So, how do you explain this bridge structures that we talked about?

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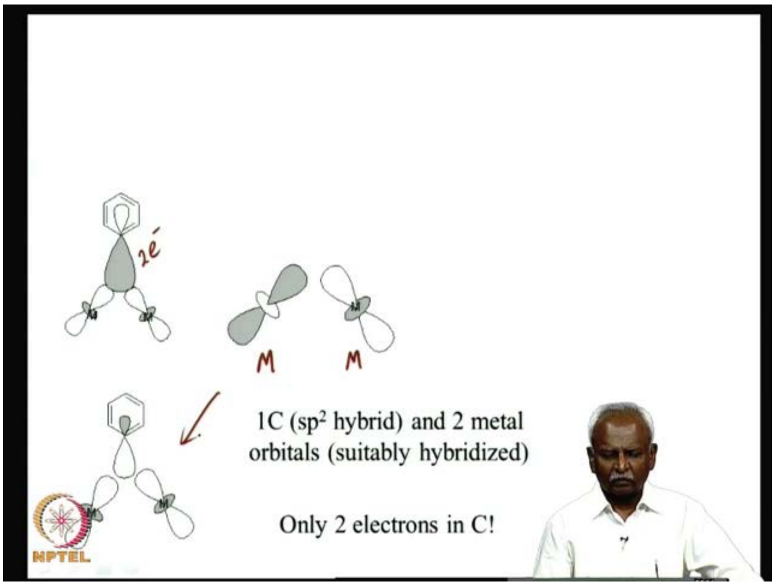

1C (sp^2 hybrid) and 2 metal orbitals (suitably hybridized)

Only 2 electrons in C!

In general it is possible to explain them using what is called three centred two electron bonding. Suffice it to say at this particular point that if you have phenyl group with two electrons and you have two empty orbitals, which are coming from the metal. These are the two empty orbitals from the metal. Then you will end up with a system which will have three orbitals and two electrons. And these three centre, two electron bonding interactions are very very popular or common in main group organometallic chemistry.

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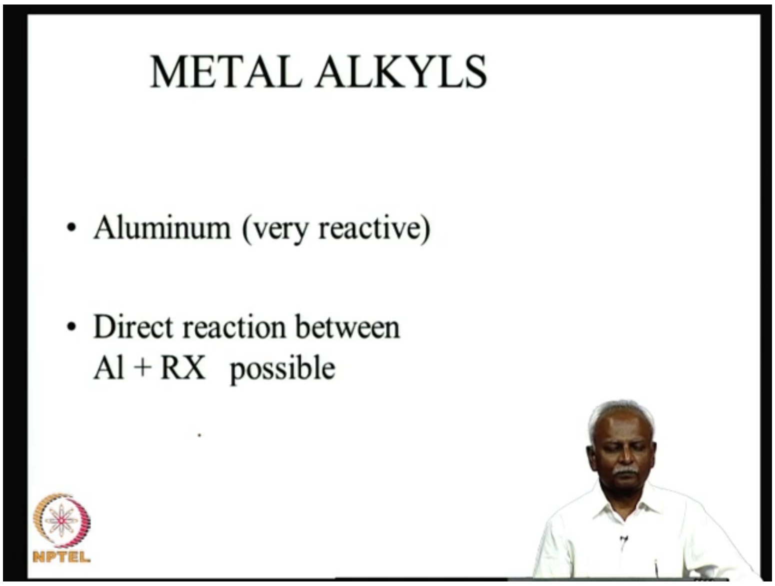

METAL ALKYLS

- Aluminum (very reactive)
- Direct reaction between Al + RX possible

So, there are only two electrons and three orbitals which are interacting. Let me now move on to some other species. It is possible in the case of aluminium to react. Aluminium and R X directly.

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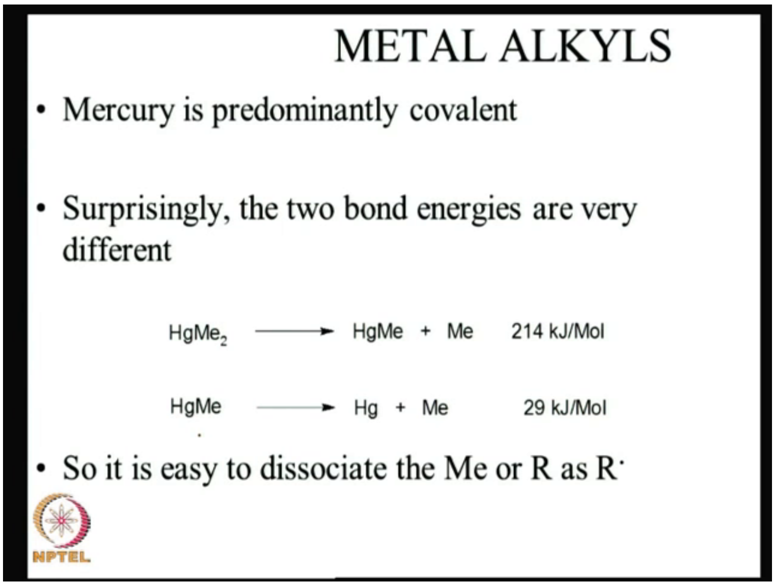

METAL ALKYLS

- Mercury is predominantly covalent
- Surprisingly, the two bond energies are very different

$HgMe_2 \longrightarrow HgMe + Me$ 214 kJ/Mol

$HgMe \longrightarrow Hg + Me$ 29 kJ/Mol

- So it is easy to dissociate the Me or R as $R^{\cdot}$

And in the case of mercury also it is possible to make these molecules with dimethyl mercury and so on.

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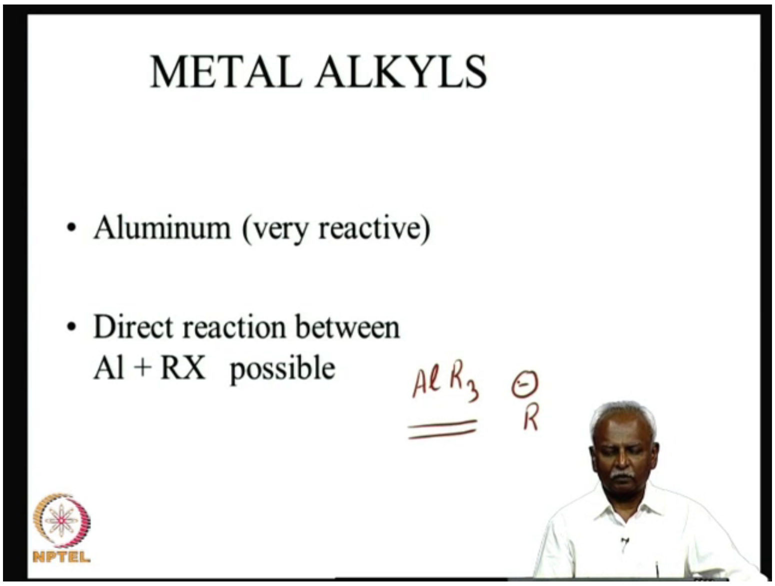

METAL ALKYLS

- Aluminum (very reactive)
- Direct reaction between Al + RX possible

$\underline{\underline{AlR_3}}$ $\overset{\ominus}{R}$

And it is interesting that where aluminium would form Al R 3 species which are bridged and appear to be reasonably covalent. You have most of the reactions of an alkyl. The alkyl group attached to the aluminium as if R is behaving as an R minus group. So, in many instances you can have R minus behaviour for the Al R 3 group.

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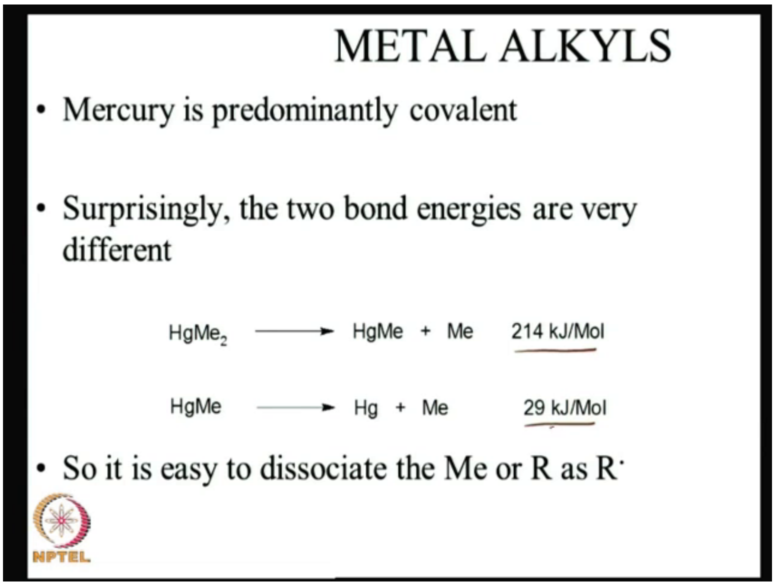

METAL ALKYLS

- Mercury is predominantly covalent
- Surprisingly, the two bond energies are very different

$$HgMe_2 \longrightarrow HgMe + Me \quad \underline{214\ kJ/Mol}$$

$$HgMe \longrightarrow Hg + Me \quad \underline{29\ kJ/Mol}$$

- So it is easy to dissociate the Me or R as $R^{\cdot}$

Whereas in the case of mercury the species is more or less covalent. And what is more surprising is the fact that they have a very large energy distance between the methyl mercury, methyl mercury bond. In the first dissociation it costs about 214 kilo joules per mole. Whereas, the second bond is only costing about 29 kilo joules per mole when we decompose Hg Me.

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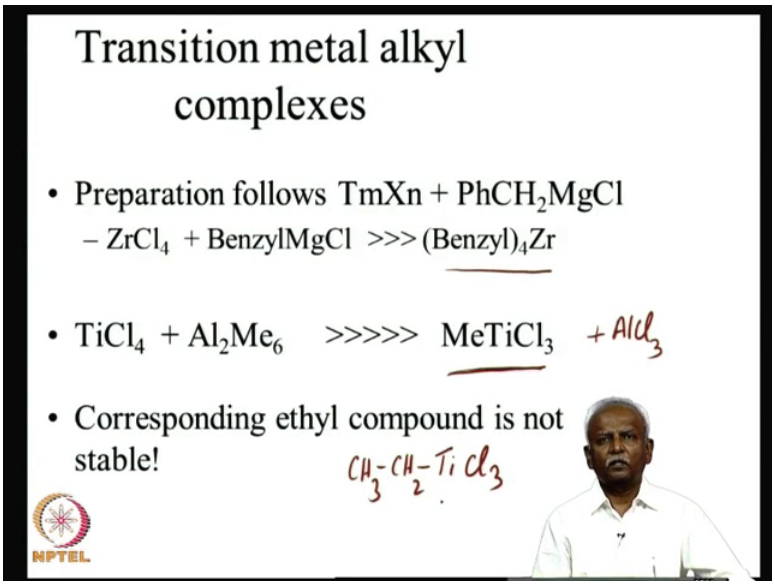

Transition metal alkyl complexes

- Preparation follows TmXn + $PhCH_2MgCl$
  - $ZrCl_4$ + BenzylMgCl >>> $(Benzyl)_4Zr$
- $TiCl_4$ + Al_2Me_6 >>>>> $MeTiCl_3$ $+ AlCl_3$
- Corresponding ethyl compound is not stable!

$CH_3-CH_2-TiCl_3$

Let me now proceed to transition metal alkyl compounds. Transition metal alkyl compounds are very often easily generated starting with an already made main group organometallic species. In this projection I have shown you a benzyl magnesium chloride reacting with zirconium tetra chloride and that makes tetra benzyl zirconium species. This tetrahedrally coordinated zirconium has got four benzyl groups around it. And it is quite stable.

And similarly, you can make the titanium species starting with a transmetallation reaction between aluminium and titanium since the aluminium chlorine bond is much much more stronger than the titanium chlorine bond. So aluminium chlorine bond is formed on this side. So, aluminium chlorine species is formed at the expense of generating a methyl titanium bond. So, if you mix appropriate amounts of Ti Cl 4 and Al 2 Me 6 you will end up with Me Ti Cl 3.

So while these compounds can be generated fairly easily they are quite stable. The corresponding ethyl compound is not stable at all. So, you cannot make using the same process Ti ethyl group attached to the titanium. This corresponding compound is not stable at all.

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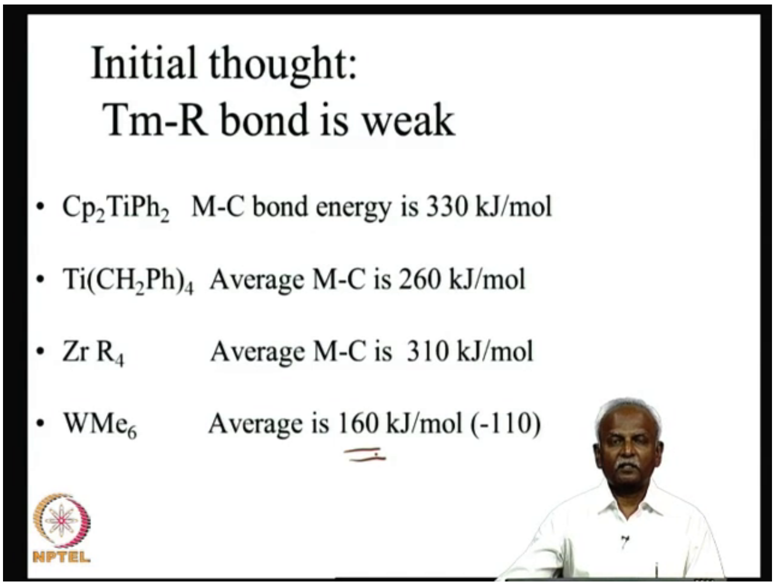

Initial thought:
Tm-R bond is weak

- Cp_2TiPh_2 M-C bond energy is 330 kJ/mol
- $Ti(CH_2Ph)_4$ Average M-C is 260 kJ/mol
- $Zr R_4$ Average M-C is 310 kJ/mol
- WMe_6 Average is 160 kJ/mol (-110)

So, this needs a little bit of thought because the initial understanding was that may be the titanium transition metal alkyl bonds are weak. And that it was only after the thermo chemistry was carried out it was realized that the metal carbon bond is not weak at all. In fact it is quite stable here. We have several bond energies pictured for us here. The metal carbon bond can be as high as 300 kilo joules per mole.

And as I have told you earlier if you go from titanium to zirconium you have an increase. And you have two groups here which are pictured. And in both cases the bond strength turns out to be quite large. Tungsten, hexa methyl tungsten is in fact a special case and we will discuss this little later if we have the chance to discuss the tungsten methyl hexa ethyl tungsten compound which has got a fairly unique structure.

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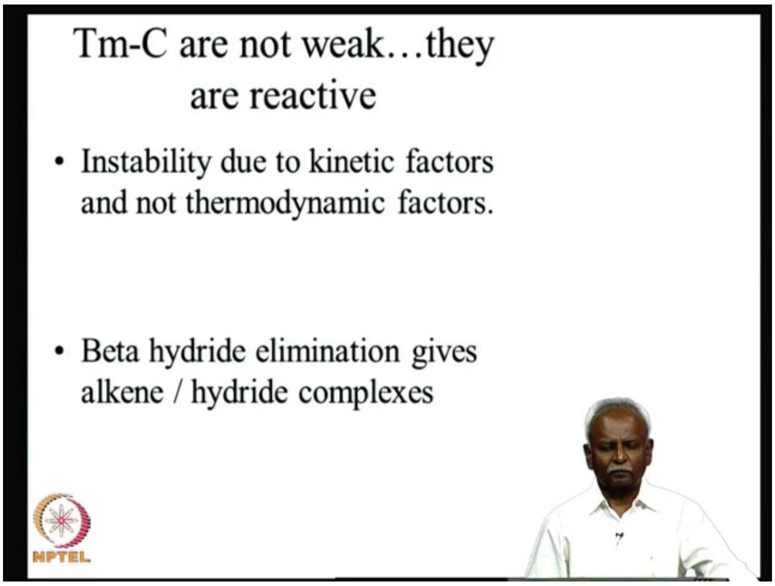

Tm-C are not weak…they are reactive

- Instability due to kinetic factors and not thermodynamic factors.
- Beta hydride elimination gives alkene / hydride complexes

So, the transition metal carbon bonds are not inherently weak. They are thermodynamically stable and the instability is really coming from some kinetic factors. They have a reaction channel which allows them to decompose very readily. Now, since we are going to discuss this reaction fairly extensively, later I will only mention here that as long as you have a beta hydrogen on the carbon attached to the transition metal you can have an elimination reaction that results in an alkene being formed.

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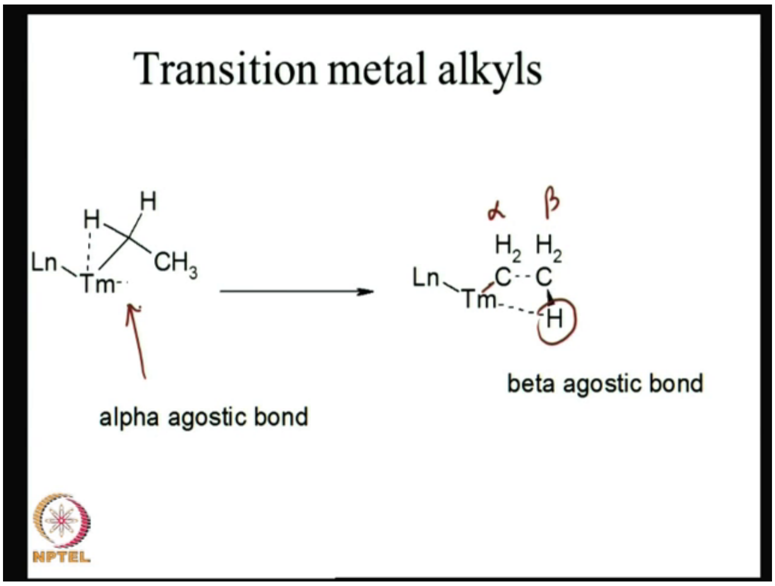

Transition metal alkyls

So, if you have a transition metal with an alkyl group which has got a beta hydrogen. So, this is the alpha hydrogen and this is this beta hydrogen. And this is a transition metal alkyl bond. If you have a beta hydrogen then this beta hydrogen has a tendency to interact with the transition metal. And this interaction has been called the beta agostic interaction. You can also have in a few cases an alpha agostic interaction as pictured here, but this is much rarer than the beta agostic interaction that is pictured here.

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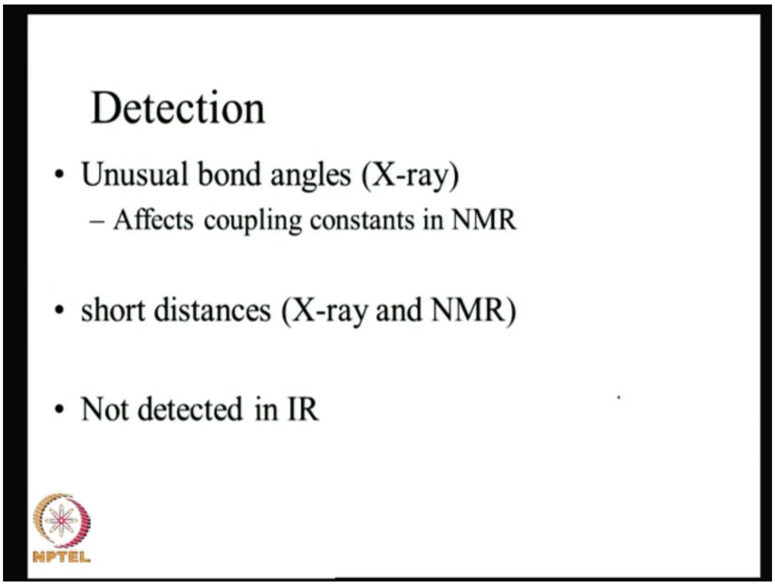

Detection

- Unusual bond angles (X-ray)
  - Affects coupling constants in NMR
- short distances (X-ray and NMR)
- Not detected in IR

So, it is possible for the beta agnostic interaction to lead to a decomposition reaction.

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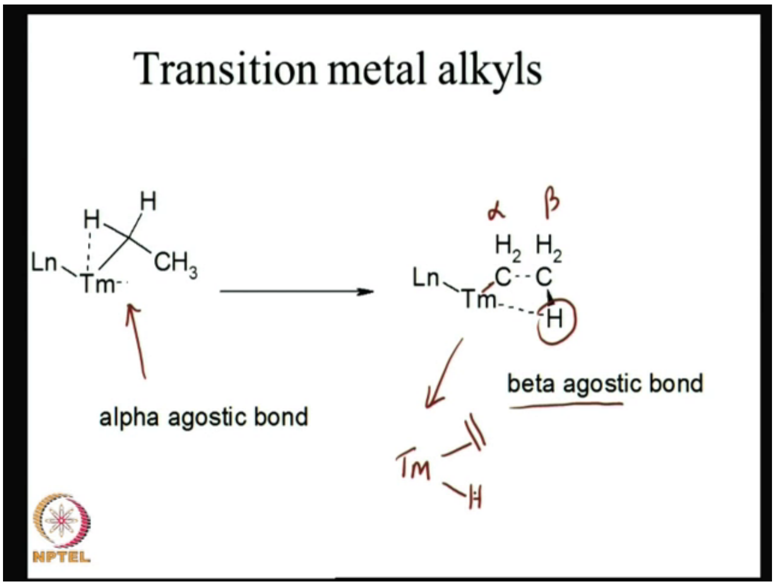

Transition metal alkyls

And this can lead to a decomposition reaction in which a transition metal forms a olefin and a hydrogen. This is a reaction which we are going to discuss much later.

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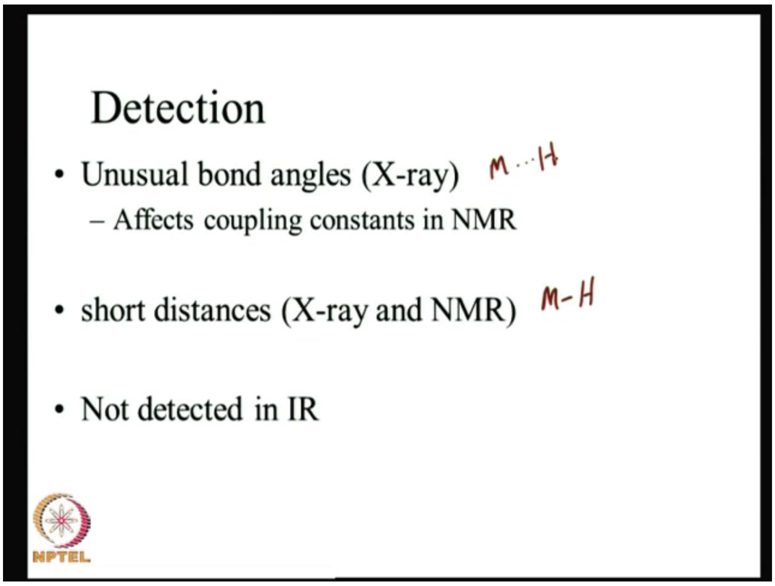

Detection

- Unusual bond angles (X-ray) M···H
  - – Affects coupling constants in NMR
- short distances (X-ray and NMR) M-H
- Not detected in IR

But how do you know that this weak interaction is present in these compounds? Usually you end up with unusual bond angles between carbon and hydrogen and these unusual bond angles have been consistent with the interaction that we just talked about. So, short distances between the metal and the hydrogen. So, metal hydrogen short distances can be responsible for or can be used as evidences for this weak interactions. You also have NMR. In NMR you can have this weak interaction can cause a different chemical shift. And it is also possible to have, if you have a crystal structure you can see that M H distance is shorter than what you would expect.

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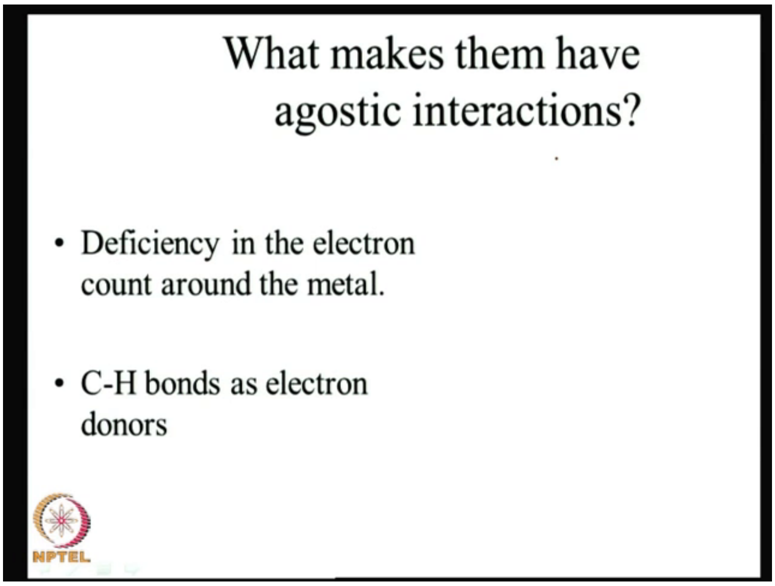

What makes them have agostic interactions?

- Deficiency in the electron count around the metal.
- C-H bonds as electron donors

So, what makes them have weak interactions or agostic interactions? It is usually the deficiency in the electron count around the metal. And the C H bond is actually functioning as an electron donor.

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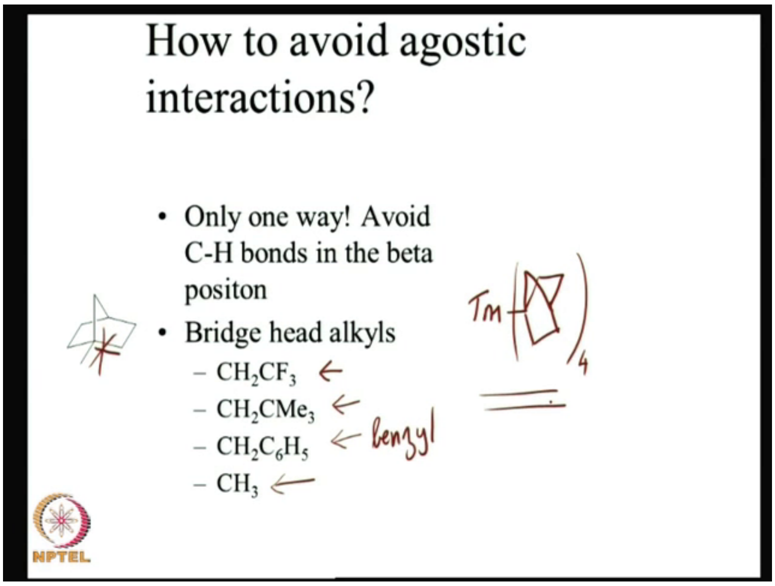

How to avoid agostic interactions?

- Only one way! Avoid C-H bonds in the beta positon
- Bridge head alkyls
  - CH_2CF_3 ←
  - CH_2CMe_3 ←
  - $CH_2C_6H_5$ ← benzyl
  - CH_3 ←

So, how do you avoid these agostic interactions? There seems to be only one way to avoid the agostic interactions and that is to avoid the beta hydrogen bond. And that is why very often one can form very strong metal alkyl complexes if you have no beta hydrogens. Some examples here it is not so difficult to generate them. You can have a C

H 2 C F 3. The C F bond is very very strong and cannot be broken. So, if you do not want a beta hydrogen you just replace them with fluorine or with methyl groups.

So, here is a instance where the beta hydrogens have been replaced with the methyl group. You can also replace the beta methyl group or the in the alpha position. You just replace the methyl group with a C 6 H 5 moiety. Then you also do not have a beta hydrogen that is a benzyl group. And you can also have just a methyl on the transition metal.

One very interesting way to avoid the beta hydrogen is to make it a bridge head. So, you can have a transition metal which is coordinated to a bridge head and that is what we have shown in this particular instance. So, you can have zirconium with four norbornyl groups and that forms a very stable moiety. And because you cannot form a double bond at a bridge head so you cannot form these bonds. It is difficult to form double bonds in the bridge head. Then it becomes unstable. So, transition metals complexes which have got a norbornyl group is quite, quite stable and you can observe them.

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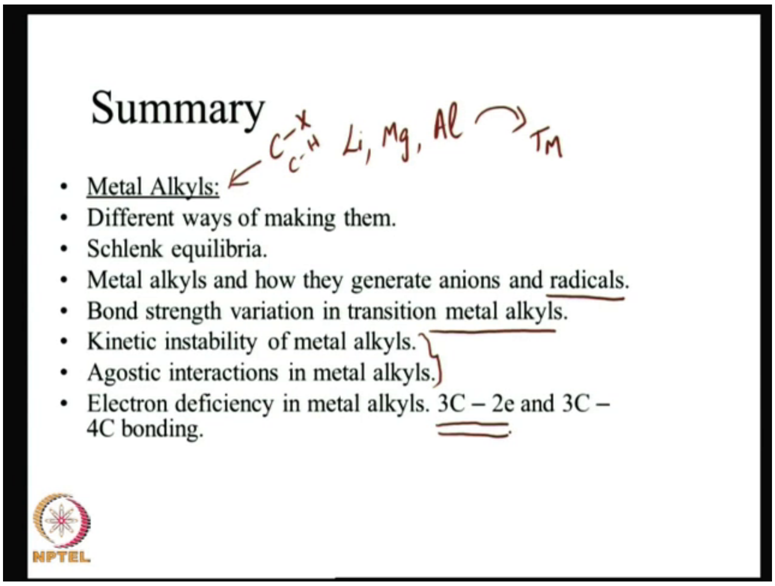

Summary

C–X
C–H
Li, Mg, Al → TM

- Metal Alkyls:
- Different ways of making them.
- Schlenk equilibria.
- Metal alkyls and how they generate anions and radicals.
- Bond strength variation in transition metal alkyls.
- Kinetic instability of metal alkyls.
- Agostic interactions in metal alkyls.
- Electron deficiency in metal alkyls. 3C – 2e and 3C – 4C bonding.

So, what we have seen in this lecture today is the fact that metal alkyls are in fact quite strong. And you can make them fairly readily directly from an active C H bond containing organic compound. Or you can use a C X bond to generate the metal alkyl species. Once you make the metal alkyl species using a very electro positive metal and this turns out to be in this case, lithium magnesium or aluminium.

So, if you have a very electropositive metal, you can use the C X bond or and active CH and generate a metal alkyl species and then you can transfer them to a transition metal. So, from these electropositive metals you can transfer the alkyl groups to the transition metal. And once you make them you realize that you can have a reactivity that is dependent on the type of species they form.

There are many instances where the species can be in what is called a Schlenk equilibrium. Specially, in the case of Grignard’s you can have a Schlenk equilibrium that changes the reactivity of the species. In general the metal alkyl species especially Grignard’s can be stabilized with coordination of an ether molecule or an amine. And that makes them quite stable and less reactive metal. Alkyls occasionally generate radicals. They occasionally generate radicals. And so, one has to watch out for radicals in solution because presence of radicals in turn initiates radical type reactions.

We also discussed the bond strength variations in main group chemistry. And in transition metal alkyls we found that for transition metal alkyls as you go down the group, the bond strength increases. Whereas, for main group elements, the bond strength of a metal alkyl moiety decreases. So, this anomalous behaviour has to be kept in mind when we look at the chemistry of metal alkyl species. In the case of transition elements and their alkyl compounds, we have kinetic instability; this kinetic instability is because you have a beta hydrogen. We can have agostic interactions of the beta hydrogen with the transition metal and that in turn leads to instability or decomposition pathways. And so, it is difficult to make transition metal alkyls with the beta hydrogen unless they are having saturated metal centre.

Lastly, we encountered this three centre two electron bonding in many situations. And you can also have three centre three centre or four centre two electron bonding as well. So, three-centre two electron bonding and other interactions complicated interactions tend to make the structures of metal alkyls fairly interesting from the theoretical stand point. So, metal alkyls are fundamental in organometallic chemistry and are used extensively. And we will look at some of the chemistry in future lectures.