Main Group Chemistry
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Lecture – 56
Organometallic compounds of Main Group Elements

I once again welcome you all to MSP lecture series on main group chemistry; this is 56th lecture in the series of 60 lectures of 30 minutes each. Today I am going to talk to you on organometallic compounds of main group elements; of course, by definition in organometallic compound should contain one or more metal to carbon bonds direct metal to carbon bonds.

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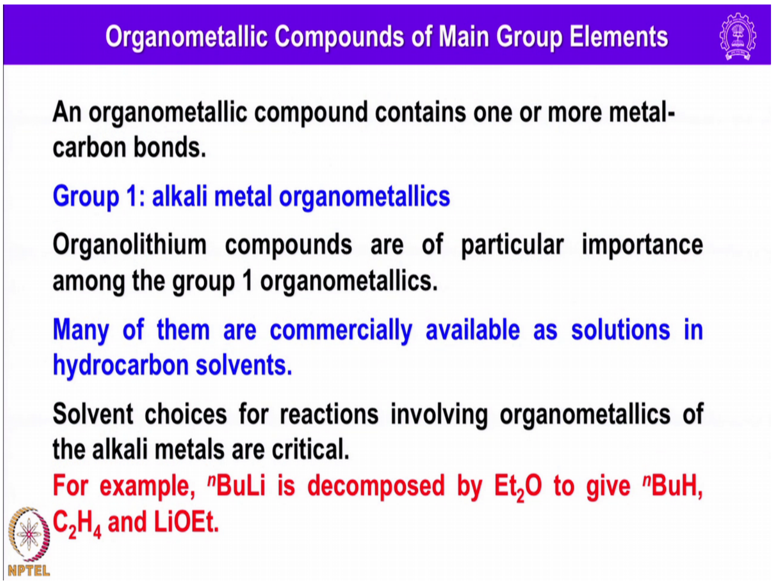

Organometallic Compounds of Main Group Elements

An organometallic compound contains one or more metal-carbon bonds.

Group 1: alkali metal organometallics

Organolithium compounds are of particular importance among the group 1 organometallics.

Many of them are commercially available as solutions in hydrocarbon solvents.

Solvent choices for reactions involving organometallics of the alkali metals are critical.
For example, ^{n}BuLi is decomposed by Et_2O to give ^{n}BuH, C_2H_4 and LiOEt.

So, let us look into the organometallic chemistry of main group elements group wise, group one organometallic compounds are of particular importance among the main group elements, because of their wide application in organic synthesis, many of them are commercially available as solutions in hydrocarbon solvents. Solvent choices for reactions involving organometallics of alkali metals are critical; one has to be very careful while choosing these solvents to perform reactions using the organometallic compounds of especially alkali and alkaline earth metals.

For example n Butyl lithium is decomposed by diethyl ether to give butane, ethylene and lithium with oxide. So, I will show you of course, here the culprit is beta hydrogen elimination. So, let us take n Butyl lithium ok.

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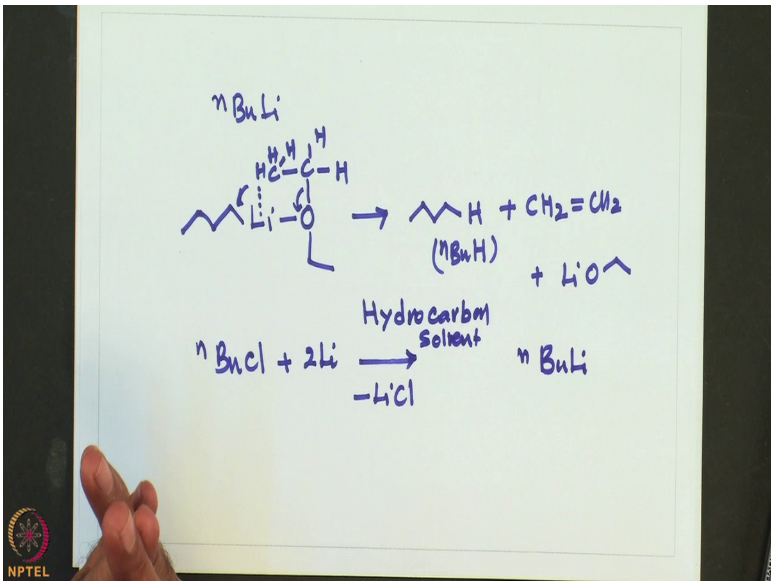

So, let me write n Butyl lithium in a different way, 1, 2, 3, 4 and now when that is say ether binds here, when you add ether what happens let me write ether in a little different way. So, now, it write to interact here of course, one another ethylene group is here. So, this essentially leads to the formation of this hydrogen is essential abstracted here, once this comes here this becomes double bond and in this process H comes that is n and plus ethylene comes, it comes out plus we have lithium with oxide.

So, this kind of reactions are quite common, as a result one has to be extremely careful while choosing the solvents in performing this reactions. Alkali metal organometallics are extremely reactive and must be handled in air and moisture free environments and also one should use very dry a solvents organic solvents.

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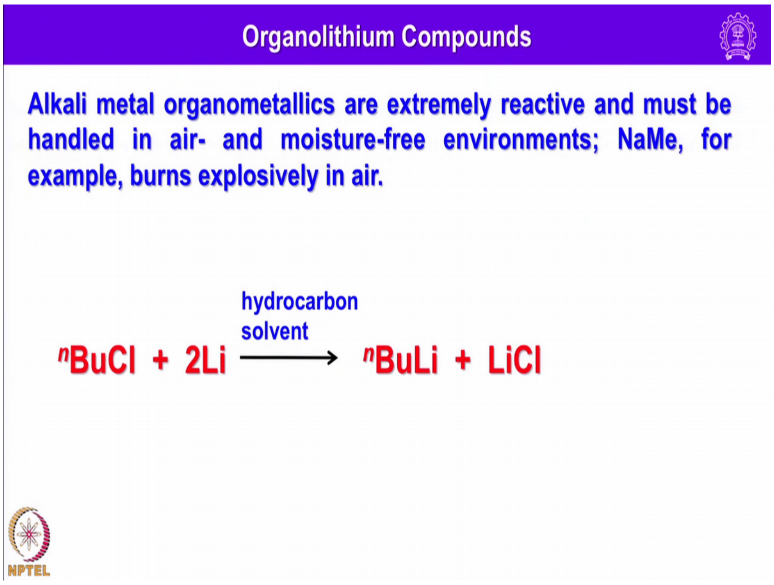

Organolithium Compounds

Alkali metal organometallics are extremely reactive and must be handled in air- and moisture-free environments; NaMe, for example, burns explosively in air.

$$^{n}\mathrm{BuCl} + 2\mathrm{Li} \xrightarrow[\text{solvent}]{\text{hydrocarbon}} {}^{n}\mathrm{BuLi} + \mathrm{LiCl}$$

For example, methyl sodium burns exclusively in air, and the preparation involves the treatment of alkyl or aryl chlorides with excess of lithium or 2 equivalents of lithium the typical reaction is you take for example, Butyl chloride and treat this one with 2 a equivalents of lithium, one to abstract lithium chloride it prosperous out and of course, here hydrocarbon solvent is important with gives n Butyl lithium. This is the typical synthetic procedure for the preparation of alkyl lithium reagents.

Lithium alkyls are polymeric both in solution and in the solid state, the structures of tertiary Butyl lithium and methyllithium or tetrameric in nature, and n Butyl lithium when mixed with tetramethyl ethylene diamine gives a polymeric chain. So, tetramethyl ethylene diamine is known as T M E D A or tmeda. This TMEDA link (Refer Time: 04:36) units together through the formation of lithium to nitrogen bonds. I would show you of a couple of slides the structures of this reagents, alkyl lithium compounds are soluble in organic solvents whereas, sodium and potassium salts are insoluble, but or solubilized by using chelating ligands such as TMEDA or in some cases dimethoxyethane. So, addition of tetramethylethylenediamine may break down the aggregate of lithium alkyls to give lower nuclearity complexes.

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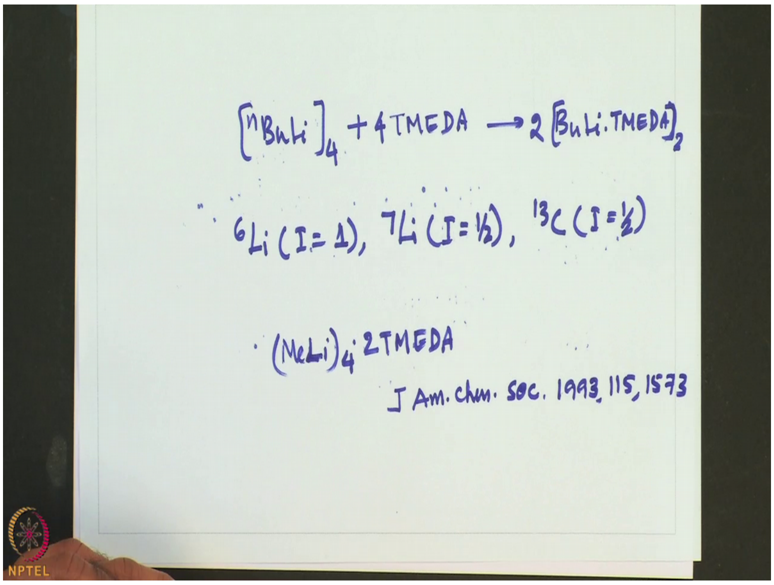

$[{}^{n}BuLi]_4 + 4TMEDA \rightarrow 2[BuLi \cdot TMEDA]_2$

${}^{6}Li\ (I = 1)$, ${}^{7}Li\ (I = 1/2)$, ${}^{13}C\ (I = 1/2)$

$(MeLi)_4 \cdot 2TMEDA$

J Am. chm. Soc. 1993, 115, 1573

For example n Butyl lithium to start with this will be tetrameric in nature. So, having cubane structure with alternate carbons being occupied by lithium and Butyl groups, and this one with TMEDA base this aggregate I have to give Butyl lithium TMEDA twice so; that means, you can write something like this here, this is what exactly happens. Of course, to characterize this compounds for assign the purity nuclear magnetic resonance is a very useful tool to understand the structure in solution, and we have here 2 isotopes of lithium 6 Li with nuclear spin I equals 1 and also 7 lithium with nuclear spin I equals half.

Of course, thirteen c abundance is only less than 1 percent that is I equals half. So, here NMR can be conveniently used to see whether lithium is there or not in a given compound.

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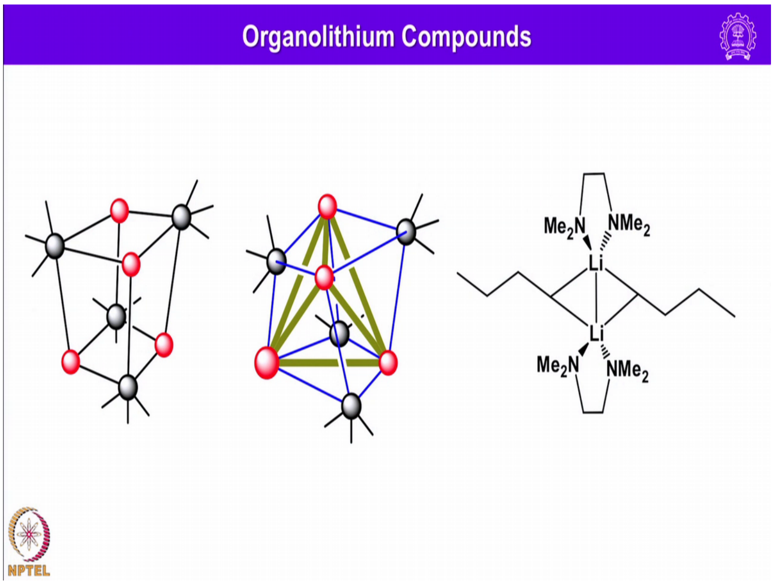
Organolithium Compounds

So, structures I have shown here tetrameric structure, and here this red one represents the lithium and this one represent organic fragment or carbon if it is methyl lithium it is CH 3 and of course, here you can assume the tetrahedral relationship between 4 lithium atoms here, and if you see each triangular face is occupied by methyl lithium. So, I will elaborate the structure later and of course, when you add TMEDA, it can break into this fashion through the creation of this bidentate ligand. So, detailed studies of organolithium reagents have revealed, that the system is far from simple; however, it is possible to isolate crystals of either n Butyl TMEDA at dimmer or tetramer of n butane lithium having TMEDA with information infinite structure.

In the case of methyl lithium tetramer, the addition of tetramethylethylenediamine does not lead to cluster breakdown and the x ray structure conforms the composition as MeLi 4; MeLi 4 times with 2 TMEDA. So, the presence of both tetramers and the amine molecules in the crystal lattice of course, if you want to see more information one can look into this article journal of American chemical society, 1993, 115, volume and page number 1573. So, lithium alkyls and aryls are very useful reagents in organic synthesis and also in making corresponding carbon compounds of main group elements. And lithium alkyls are important catalysts in synthetic rubber industry, for the stereo specific polymerization of alkenes.

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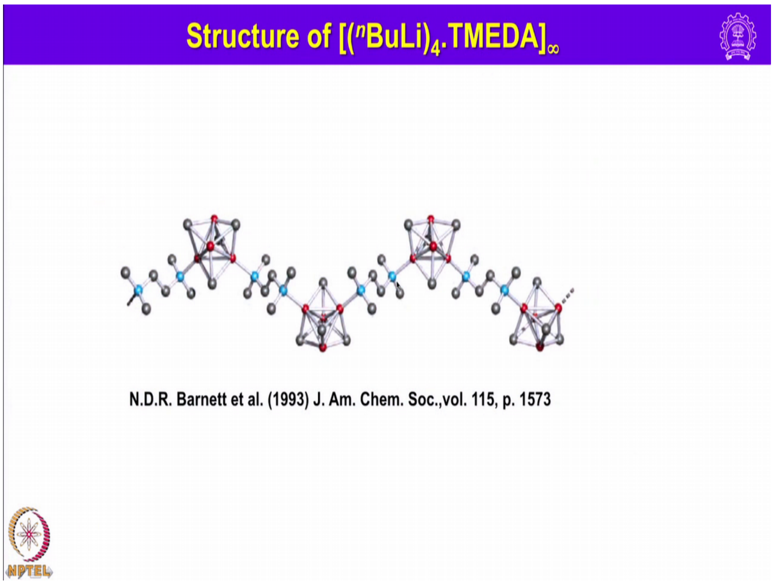

Structure of $[(^{n}BuLi)_4.TMEDA]_\infty$

N.D.R. Barnett et al. (1993) J. Am. Chem. Soc.,vol. 115, p. 1573

You can see addition of ethylenediamine to methyl lithium results in this polymeric structure, having tetramethylethylenediamine acting as a bridged bidentate ligand.

So, this is an infinite chain here, out of 4 lithiums 2 are coordinated by this nitrogen atoms of TMEDA. So, organic compounds such as a terminal alkynes which contain relatively acidic hydrogen atom form salts with alkali metals.

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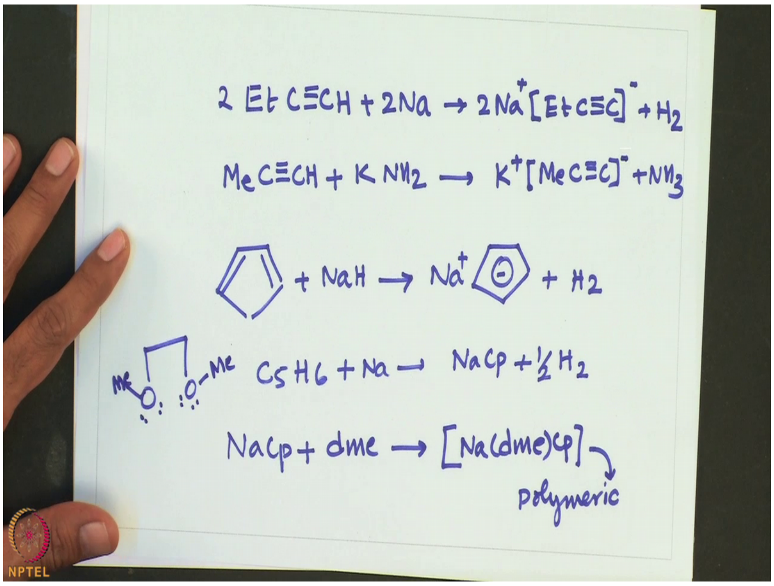

$2\,EtC\equiv CH + 2Na \rightarrow 2Na^+[EtC\equiv C]^- + H_2$

$MeC\equiv CH + KNH_2 \rightarrow K^+[MeC\equiv C]^- + NH_3$

$+ NaH \rightarrow Na^+ \quad + H_2$

$C_5H_6 + Na \rightarrow NaCp + \frac{1}{2}H_2$

$NaCp + dme \rightarrow [Na(dme)Cp]$

polymeric

For example if we take butane we treat with sodium it forms plus H 2, and if you take propane potassium amine it gives potassium salt. Of course, treating cyclopentadiene with sodium hydride leads to the formation of sodium Cp that is Na plus and Cp minus H 2 so; that means, essentially C 5 H 6 plus Na gives Na Cp plus half H 2. So, this is how one can prepare sodium and potassium organo metallic compounds.

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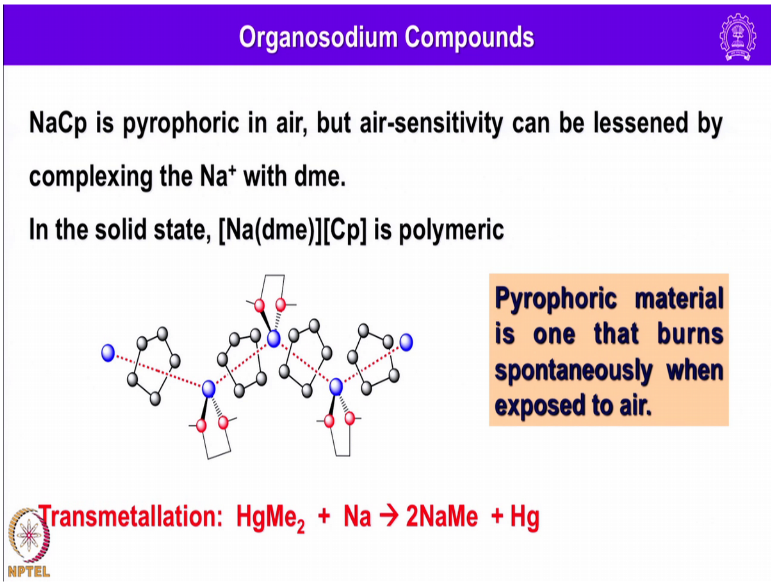

Organosodium Compounds

NaCp is pyrophoric in air, but air-sensitivity can be lessened by complexing the Na^+ with dme.

In the solid state, [Na(dme)][Cp] is polymeric

Pyrophoric material is one that burns spontaneously when exposed to air.

Transmetallation: $HgMe_2 + Na \rightarrow 2NaMe + Hg$

And sodium Cp is pyrophoric in air, but air sensitivity can be lessened by complex in the sodium with dme for example, if you take NaCp and if you add dimethoxy ethane, it forms a complex.

So, this is polymeric in nature. So, this how it looks like you can see this is a dimethoxy ethane alkyl. So, this (Refer Time: 12:03) ligand and you have this kind of polymeric structure one dimensional chain structure. And of course, another important method of preparation of methyl sodium is through transmetalation reaction, dimethyl mercury on treatment with sodium gives Na me plus mercury. So, one can use conveniently for obtaining pure compound of methyl sodium, one should use transmetalation method. Now what is pyrophoric? Pyrophoric material is one that burns spontaneously when exposed to air.

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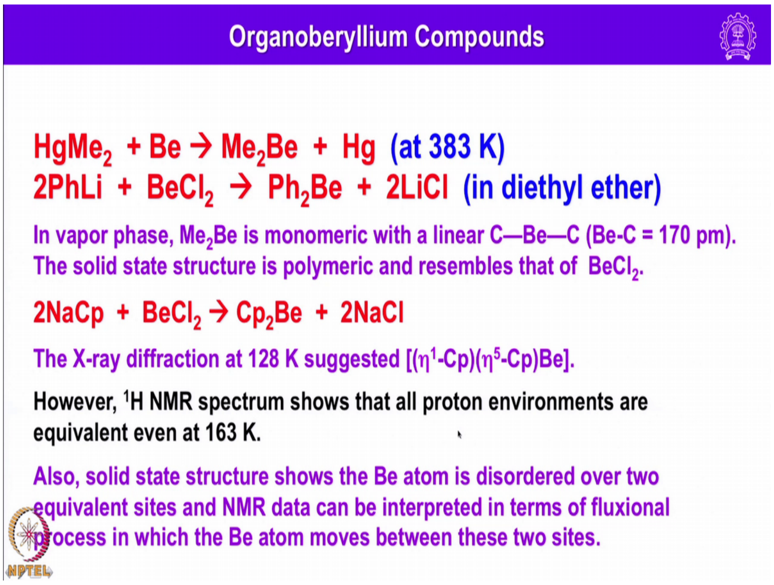

Organoberyllium Compounds

$HgMe_2 + Be \rightarrow Me_2Be + Hg$ (at 383 K)

$2PhLi + BeCl_2 \rightarrow Ph_2Be + 2LiCl$ (in diethyl ether)

In vapor phase, Me_2Be is monomeric with a linear C—Be—C (Be-C = 170 pm).
The solid state structure is polymeric and resembles that of $BeCl_2$.

$2NaCp + BeCl_2 \rightarrow Cp_2Be + 2NaCl$

The X-ray diffraction at 128 K suggested [(η^1-Cp)(η^5-Cp)Be].

However, ^{1}H NMR spectrum shows that all proton environments are equivalent even at 163 K.

Also, solid state structure shows the Be atom is disordered over two equivalent sites and NMR data can be interpreted in terms of fluxional process in which the Be atom moves between these two sites.

So, let us look into organoberyllium compounds; organoberyllium compounds also can be conveniently prepared using transmetallation method for example, I have shown here dimethyl mercury on treatment with beryllium gives dimethyl beryllium plus mercury.

This reaction has to be carried out at a temperature of 383 Kelvin and similarly phenyllithium on treatment with beryllium dichloride, gives diphenyl beryllium through the formation of 2 equivalents of lithium chloride and this reaction has to be carried out in diethyl ether. In vapor phase dimethyl beryllium is monomeric with a linear carbon beryllium carbon bond and with the bond angle is almost close to 180 and here beryllium to carbon bond distance is 170 picometer. The solid state structure is polymeic resembles that of BeCl 2 and of course, the treatment of sodium Cp with beryllium dichloride gives cyclopentadienyl beryllium a sandwich compound, similar to ferrocene through the formation of 2 equivalents of sodium chloride.

The x ray diffraction carried out at 128 k suggest that it has 2 different type of binding with Cp, one is eta 1 and another one is eta 5. You can see here eta 1 Cp where its mono coordinated whereas, here all the 5 carbon atoms are coordinated to beryllium hapticity is 5 and here hapticity is 1 and; however, 1 H NMR spectrum shows that all proton environments are equivalent even at 163 Kelvin that indicates; that means, there is a fractional process in which eta 1 is becoming eta 5, and eta 5 is becoming eta one. So, there is a process is there. So, also solid structure shows the beryllium atom is disordered over 2 equivalent sides and NMR data can be interpreted in terms of fractional process in which beryllium atoms moves between these 2 sides; that means, eta 1 and eta 5 beryllium atom is switching; that means, this if you designate Cp 1 and Cp 2.

So, Cp 2 acts as Cp eta 5 for a while, and then it becomes eta 1 and similarly Cp one acts as eta 1 for a while and becomes eta 5 for a while.

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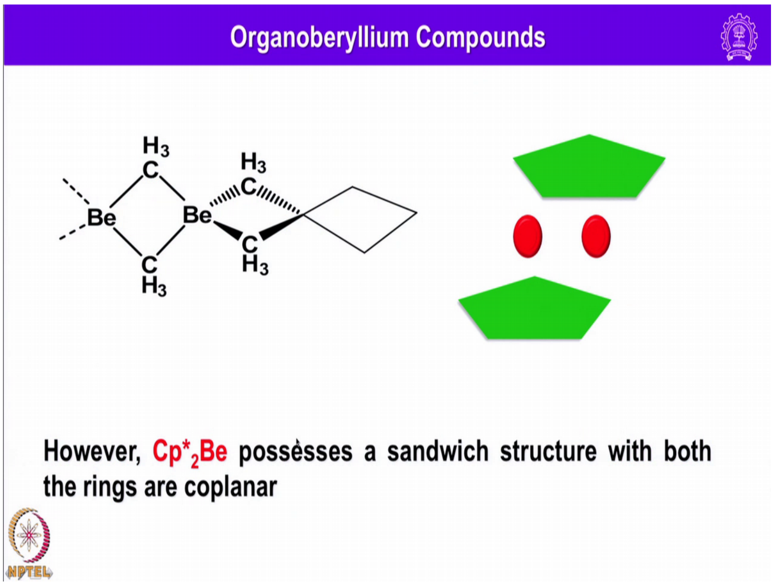

Organoberyllium Compounds

However, Cp^*_2Be possèsses a sandwich structure with both the rings are coplanar

You can see here beryllium structure here it is of course, it forms three centered 2 electron bond here similar to di boron and it extends through the chain, to give one dimensional polymer and this is very similar to beryllium chloride in solid state, and here you can see here 2 beryllium atoms; that means, it shows 2 positions of course, in this position if you consider this is eta 5 and this is eta 1 whereas, for this one in this position it is eta 5 and this is eta 1 so; however, if you go for a bulky cyclopentadienyl that is penta methyl cyclopentadienyl, here it possess a sandwich structure with both rings are coplanar very similar to ferrocene. Of course, one can understand in the better way this structure let me write this structure for you.

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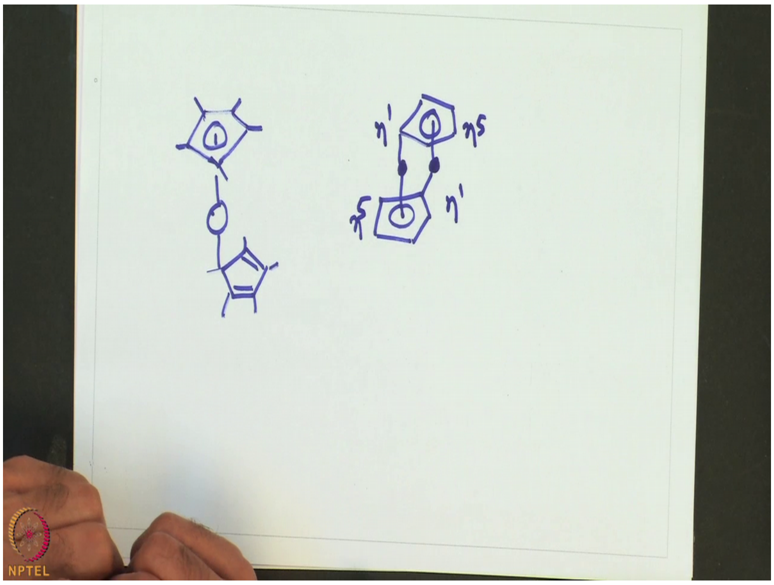

For example I can. So, here beryllium atom is there and now. So, something like this.

Of course here you have all and next in the structure what it shows is, one is something like this. So, here if I put one here. So, basically it is going like this whereas, if I put one here. So, here it now it is eta 1 and now this one eta 1 so; that means, eta 1 for this one and eta 5 whereas, here it is eta 5 for this one and it is eta 1. So, in this way what happens, its switches as a result it x ray depicts 2 positions here they started geometry with 2 positions are here, this is because of the fractional process in which there is a study exchange of eta 1 becoming eta 5 and eta 5 becoming eta 1. So, let us look into organomagnesium compounds.

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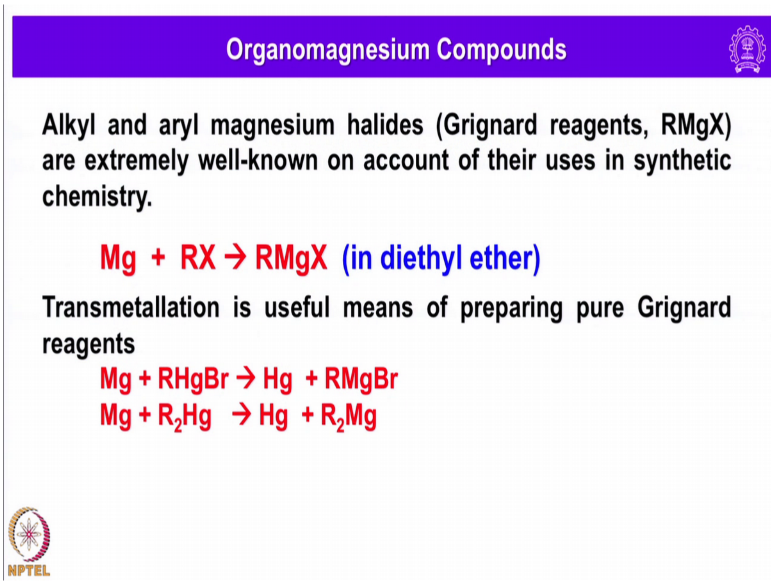

Organomagnesium Compounds

Alkyl and aryl magnesium halides (Grignard reagents, RMgX) are extremely well-known on account of their uses in synthetic chemistry.

$Mg + RX \rightarrow RMgX$ (in diethyl ether)

Transmetallation is useful means of preparing pure Grignard reagents

$Mg + RHgBr \rightarrow Hg + RMgBr$

$Mg + R_2Hg \rightarrow Hg + R_2Mg$

Of course alkyl and aryl magnesium halides are extremely well known on account of their use in synthetic chemistry, of course, Grignard reagents having general composition of RMgX is quite well known, and they can be readily prepared by treating activated magnesium with alkyl are aryl halides in the ether solvent such as diethyl ether, those transmettallation is useful means of preparing pure Grignard reagents. For example, if you take mercury and treat with alkyl mercury bromide, it gives mercury plus RMgX similarly magnesium (Refer Time: 18:13) stated with dialkyl mercury it gives dialkyl magnesium. So, 2 coordination at magnesium in all 2 mg is observed, only when they r groups are sufficiently bulky. In fact, it is very interesting to analyze the structure of RMgX. RMgX it appears like 2 coordinated it is not actually 2 coordinated, since the reactions are carried out in ether.

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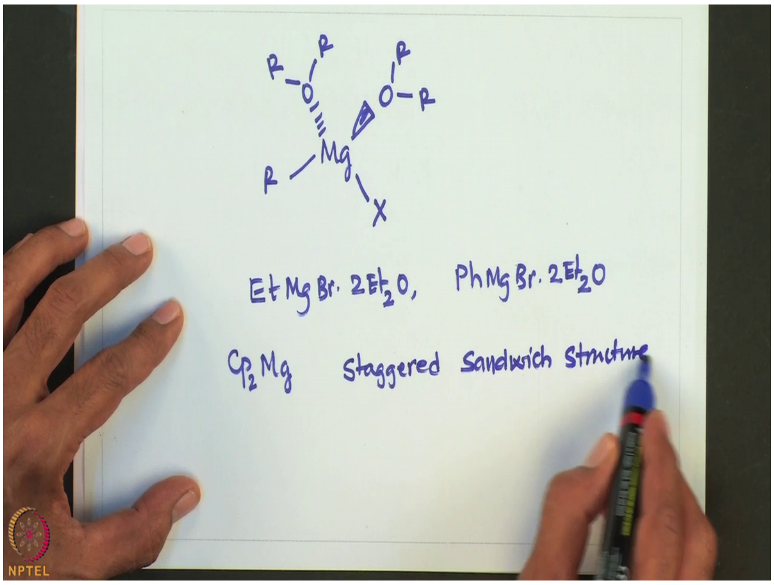

$EtMgBr \cdot 2Et_2O$, $PhMgBr \cdot 2Et_2O$

Cp_2Mg Staggered Sandwich Structure

It has a structure like this where here. So, in solution Grignard reagents have a tetrahydro geometry at magnesium with 2 coordination size being occupied by ethers, which essentially or hard basis; they interact with hard acid such as magnesium ok.

So, that is the reason in hundred stabilize RMgX, one has to use a solvent such as ether diethyl ether or tetrahydrofuran. That means, RMgX are essentially solvated and magnesium is typically tetrahedron. This is Et MgBr 2 Et 2 O, one can write or ph phenylmagnesium bromide 2 Et 2 O, and Cp 2 magnesium compounds are also known they have a straggled sandwich structure, one should be careful about handy Grignard's reagents because solutions of Grignard reagents may contain several species.

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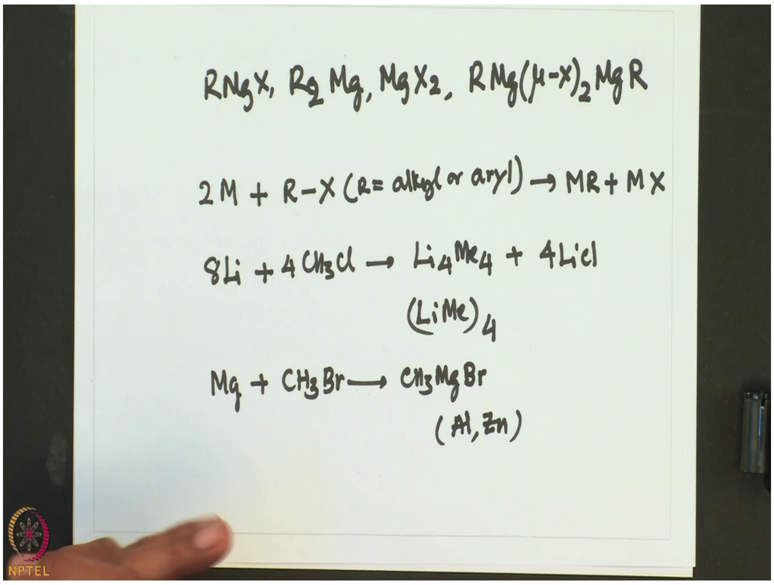

$RMgX$, R_2Mg, MgX_2, $RMg(\mu\text{-}X)_2MgR$

$2M + R-X$ (R= alkyl or aryl) $\rightarrow MR + MX$

$8Li + 4CH_3Cl \rightarrow Li_4Me_4 + 4LiCl$

$(LiMe)_4$

$Mg + CH_3Br \rightarrow CH_3MgBr$

(Al, Zn)

RMgX, R 2 Mg, MgX 2 also RMg with 2 bridging halides having a diametric structure of this type ok.

So, which are further complicated by salvation the position of equilibrium between these species are markedly dependent on concentration, temperature and the solvent employed in that particular reaction because strongly donating solvents favor monomeric species in which they coordinate to the metal center.

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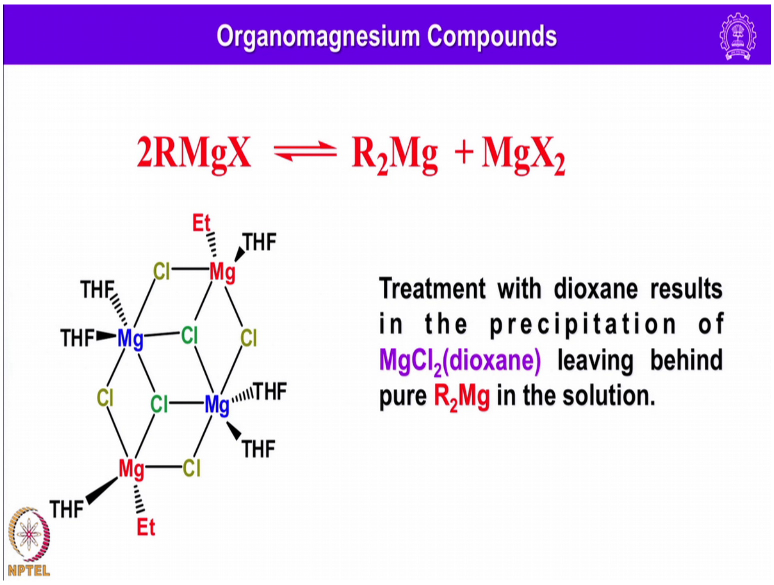

Organomagnesium Compounds

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

Treatment with dioxane results in the precipitation of $MgCl_2$(dioxane) leaving behind pure R_2Mg in the solution.

So, for example, this equilibrium is very very important, RMgX is always in equilibrium with R 2 Mg plus MgX 2. So, here this is the type of structure one can think of when it is in equilibrium. So, now, with the question is how to take out magnesium chloride from this one. So, that R 2 Mg can be used in organic synthesis. The best method one can look for is treatment of for this compound with dioxane, that results in the precipitation of magnesium chloride dioxide leaving behind pure dialkyl magnesium in the solution. So, that that can be filtered and taken for further reaction with other suitable organic reagents to do some coupling reactions or whatever the organic synthesis that is planned.

Although I wanted to tell the synthetic methodology in the beginning, I waited for a couple of compounds introduction; because without showing some of the precursors that are used in the scenes of organometallic compounds I thought its in inappropriate to start giving the methodologies for the preparation of organometallic compounds, but now if you can see alkali and alkaline earth metal organometallic reagents are extensively used in the organometallic preparation of almost transfer elements as well as p block elements, in view of this one first I spoke about the organometallic compounds of alkyl metals and alkaline earth metals. So, now, let us look into the synthetic rules that are available for the preparation of organometallic compounds of main group elements the most organometallic compounds can be synthesized by using.

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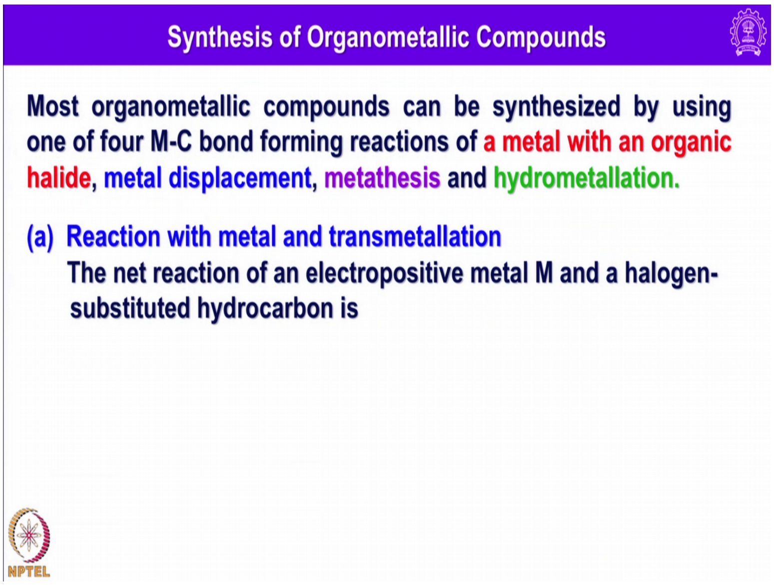

Synthesis of Organometallic Compounds

Most organometallic compounds can be synthesized by using one of four M-C bond forming reactions of a metal with an organic halide, metal displacement, metathesis and hydrometallation.

(a) Reaction with metal and transmetallation

The net reaction of an electropositive metal M and a halogen-substituted hydrocarbon is

One of the 4 metal to carbon bond forming reactions like a using a metal with an organic halide, metal displacement, metathesis and hydrometallation; that means, metal treatment of metal with an organic halide and metal and displacement or transmetallation metathesis and hydrometallation, these are the 4 important methods that are available for the preparation or synthesis of organometallic compounds of transfer elements or main group elements.

So, let us look into these methodologies one at a time, first let us look into the reaction with metal under transmetallation. So, here the net reaction of an electropositive metal m and a halogen substituted hydrocarbon. So, for example, here the general reaction can be written in this fashion 2M plus RX alkyl R aryl. So, this gives MR and MX. This is the typical reaction let me give a couple of examples here for example, lithium on treatment with methyl chloride gives methyl lithium of course, it is tetramer. So, let me write in this fashion or one can also write 4 times plus 4 LiCl. So, similarly magnesium when its treated with methyl bromide, it gives CH 3 Mg Br. So, organometal halide with mix up of course, this method can also be extended to aluminium, zinc as well.

So, similar to Grignard reagents here three mgBr one can mix a 3 AlBr r Ca 3, zinc ca three z and br of one metal atom takes the place of another one it is known as trans metal reaction or transmetallation reaction. Suppose if one metal takes the place of another it is known as transmetallation reaction, M plus MR gives M plus MR ok.

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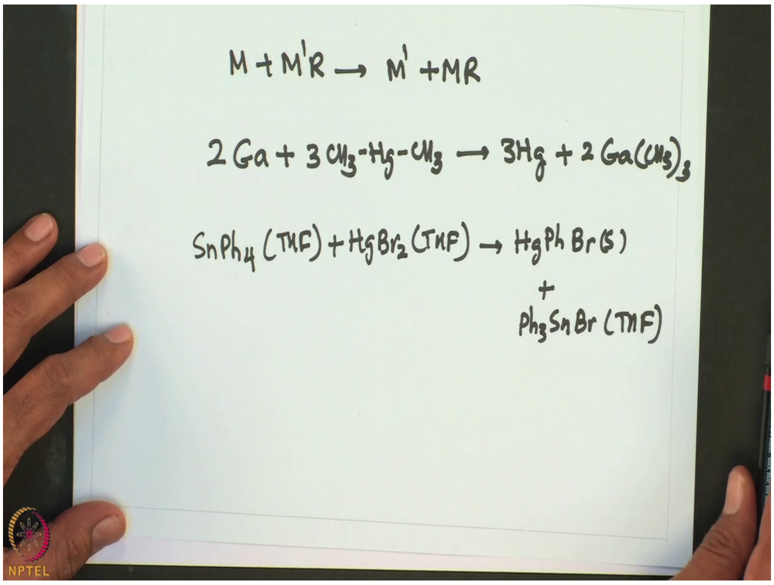

$$M + M'R \rightarrow M' + MR$$

$$2Ga + 3CH_3{-}Hg{-}CH_3 \rightarrow 3Hg + 2Ga(CH_3)_3$$

$$SnPh_4(THF) + HgBr_2(THF) \rightarrow HgPhBr(s) + Ph_3SnBr(THF)$$

So, this is a typical transmetallation reaction let us look into an example here, gallium is taken this is treated with dimethyl mercury of course, one can also write trimethylmercury in this fashion, it gives three mercury plus gallium comes below aluminium, trimethyl gallium. So, transmetallation is favorable when the displacing metal is higher in the electro chemical series then the displaced metal.

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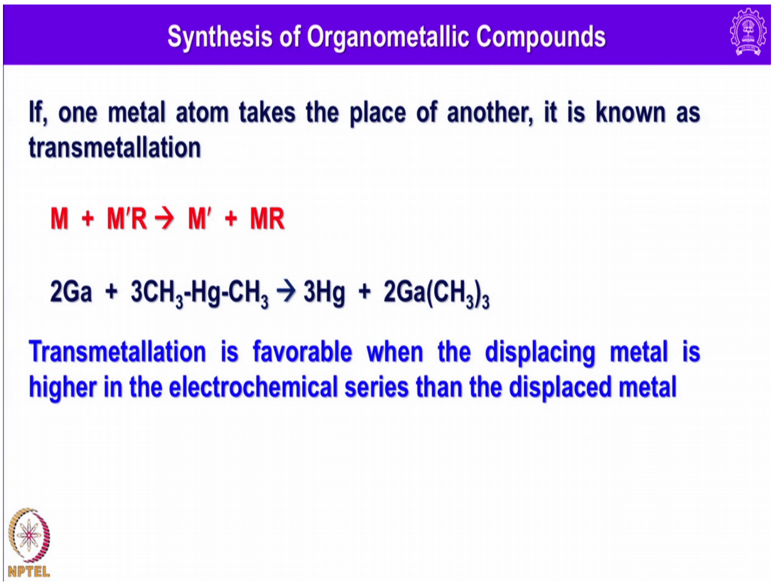

Synthesis of Organometallic Compounds

If, one metal atom takes the place of another, it is known as transmetallation

$M + M'R \rightarrow M' + MR$

$2Ga + 3CH_3\text{-}Hg\text{-}CH_3 \rightarrow 3Hg + 2Ga(CH_3)_3$

Transmetallation is favorable when the displacing metal is higher in the electrochemical series than the displaced metal

So, essentially in that case what happened stabilization of carbon anion takes place and as a result transmetallation is very smooth. So, let us look into the second method is metathesis, the metathesis of an organometallic compound MR.

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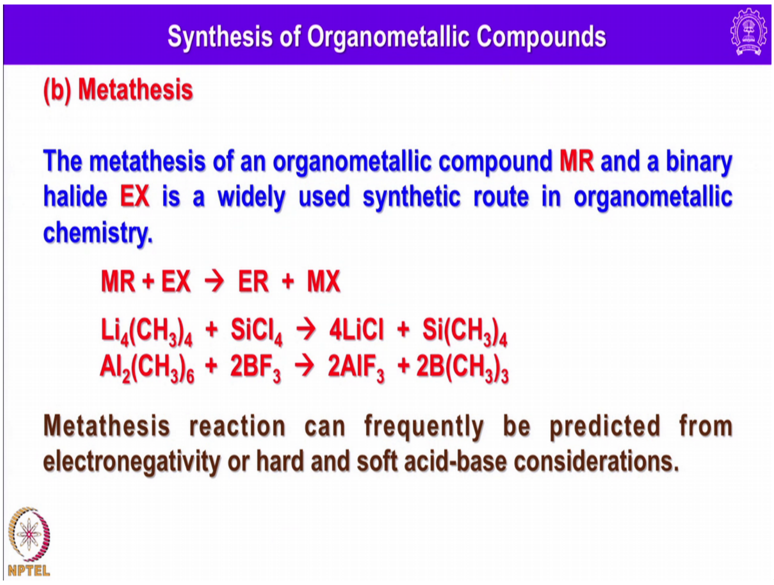

Synthesis of Organometallic Compounds

(b) Metathesis

The metathesis of an organometallic compound MR and a binary halide EX is a widely used synthetic route in organometallic chemistry.

$MR + EX \rightarrow ER + MX$

$Li_4(CH_3)_4 + SiCl_4 \rightarrow 4LiCl + Si(CH_3)_4$

$Al_2(CH_3)_6 + 2BF_3 \rightarrow 2AlF_3 + 2B(CH_3)_3$

Metathesis reaction can frequently be predicted from electronegativity or hard and soft acid-base considerations.

And a binary halide EX is a widely used synthetic route in organometallic chemistry, the typical reaction have shown here MR plus EX gives ER plus MX and here for example, if you take methyl lithium, and treat this one with SiCl 4, 4 equivalents of LiCl comes through the formation of 4 Si methyl bonds that is tetramethylsilane. Similarly trimethylaluminum when it started with boron trifluoride aluminium trifluoride is formed through the formation of trimethyl boron. So, these are the 2 examples, this method of treating a lithium alkyl reagent with halides of main group elements are transfer elements is termed as metathesis. Metathesis reaction can frequently be predicted from electro negativity are hard and soft acid base considerations.

So, this hydrocarbon groups tend to born to the more electronegative element. So, the horizon favors the formation of ionic compounds with more electropositive metal.

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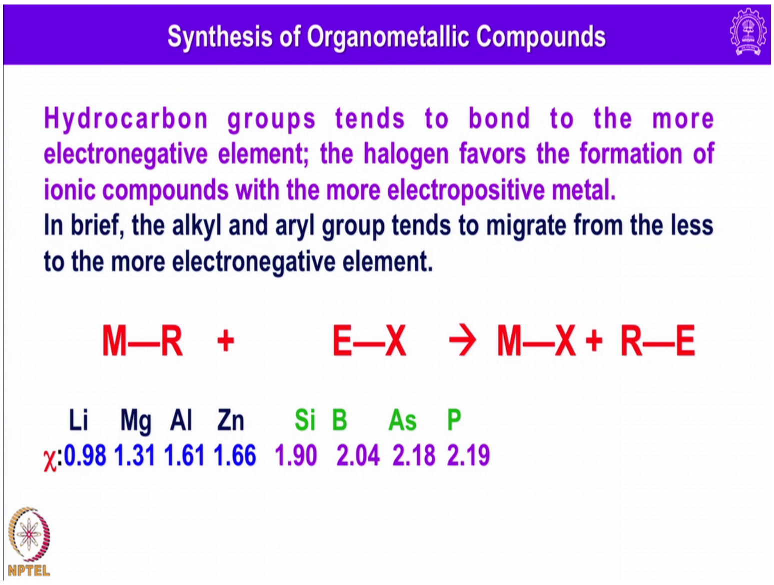

Synthesis of Organometallic Compounds

Hydrocarbon groups tends to bond to the more electronegative element; the halogen favors the formation of ionic compounds with the more electropositive metal.

In brief, the alkyl and aryl group tends to migrate from the less to the more electronegative element.

$$\mathrm{M{-}R} + \mathrm{E{-}X} \rightarrow \mathrm{M{-}X} + \mathrm{R{-}E}$$

	Li	Mg	Al	Zn	Si	B	As	P
χ:	0.98	1.31	1.61	1.66	1.90	2.04	2.18	2.19

So, in brief the alkyl and aryl groups tend to migrate from the less to the more electronegative element. So that means, in a typical metathesis reaction, one should look into the electro negativity difference between M and E. For example, here I have given. So, where MR is there, if M is lithium electronegatives 0.98 and in case of magnesium its 1.31 in the case of aluminium its 1.61 and in the case of zinc it is 1.66, now let us come to the main group element E silicon, boron, arsenic and phosphorus are given. In case of silicon it is 1.90, in case of boron its 2.04, in case of arsenic its 2.18 and in case of p 2 0.1 a; that means, carbon has a tendency to move from lower electronegative substrate to higher electronegative substrate. So, that the carbon and anion is more stabilized ok.

So, that it can get rid of its negative charge. So, this is the strategy in reaction involving metathesis route. So, when the electronegativities are similar the correct outcome may be predicted with care by considering the combination of software element with organic group and harder element with fluoride or chloride. That means, if the electronegative between the 2 metals between which this organic group has to be transferred are very similar, than one has to take care in identifying the soft element and the hard element and there tendencies. For example, I repeat again by considering the combination of software element with organic group and harder element with fluoride or chloride so; that means, an insoluble product or reaction may change the outcome.

So, for example, S n ph4, THF plus HgBr 2 in THF gives HgphBr solid plus ph 3 SnBr, it goes into the solution THF phenyl mercuric bromide is insoluble in THF so, that it prospirates out. So, once we have this kind of information choosing the right kind of reagents and performing the reaction would be very easy. So, that one can get the required organometallic compound in its pure form. So, with this I stop here in my next lecture I will continue to look into more organometallic chemistry of main group elements.

Thank you very much.