Main Group Chemistry
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Lecture – 57
Organometallic compounds of Main Group Elements

Welcome to MSP lecture series on main group chemistry, in my last lecture I initiated discussion on organometallic chemistry of main group elements and while discussing the synthetic methodologies that are available, for the preparation of organometallic compounds, I did mention about metathesis and transmetallation reaction or reaction of metal with halide sources. So, let me continue from where I had stopped, this metathesis reaction involving the same central element or often referred to as redistribution reactions.

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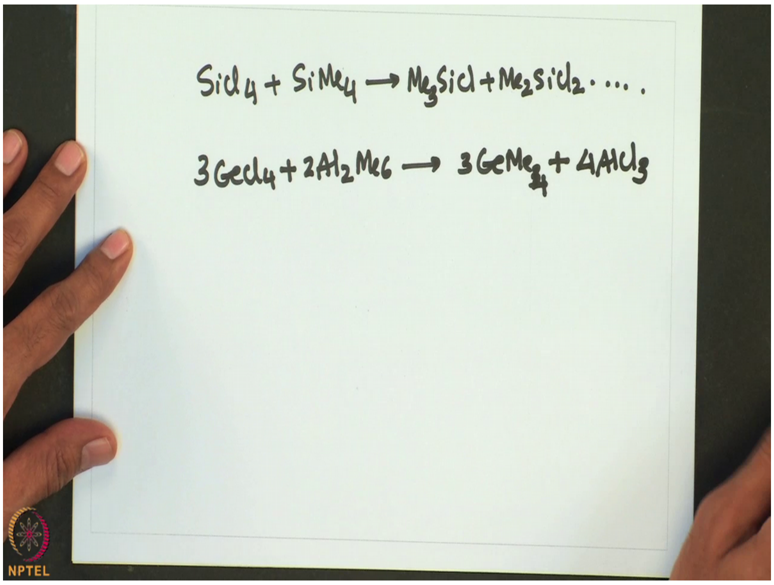

For example Sicl 4 when it is treated with tetramethylsilane. So, redistribution occurs to give a mixture of a products such as Me3Sicl plus Me 2 Sicl 2, etcetera.

So, this is called redistribution reaction, similarly treatment of germanium tetrachloride with trimethylaluminum, it gives trimethylgermanium plus 4 Alcl 3. So, aluminium is more electro positive than the germanium. So, this reaction occurs as it is thermodynamically favorable. Because here there stability of trichloro aluminium is much more stable compared to trimethylaluminium, because trimethylaluminium is more electro deficient whereas, aluminium (Refer Time: 02:29) not really electron deficient, but it forms a dimmer utilizing the chlorine (Refer Time: 02:34) here. So, here despite aluminium having more electropositive than germanium, this reaction occurs as it is thermodynamically favourable. So, now, let us look into another method or route called hydro methylation ok.

So, the reaction is driven by the high strength of EC bond relative to that of most E H bonds.

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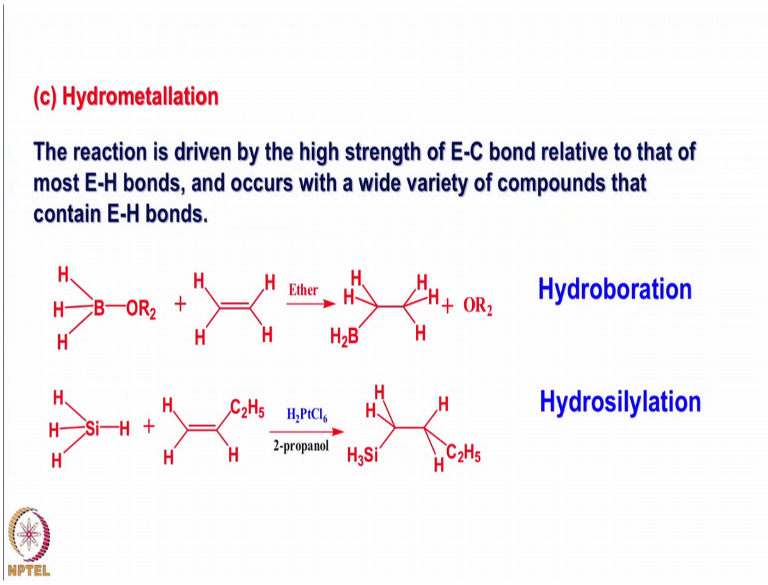

And occurs with a wide variety of compounds that contain E-H bonds well E is a main group element. For example, we can say hydroboration reaction I have shown here if you take this (Refer Time: 03:13) of boron trihydrate treat with alky in ether. So, hydroboration occurs through the elimination of war 2 similarly one can also perform this hydrosilylation reaction, but this requires a catalyst preferably a transmitter get its such as platonic acid here H 2 PtCl 6, this reaction is carried out in 2 propanol and here SIH bond is added across this carbon; carbon double bond. So, this is called hydrosilylation reaction. The slight differences that arises between aromatic compounds and binary hydrogen compounds is mainly due to the tendency of alkyl groups to avoid ionic bonding.

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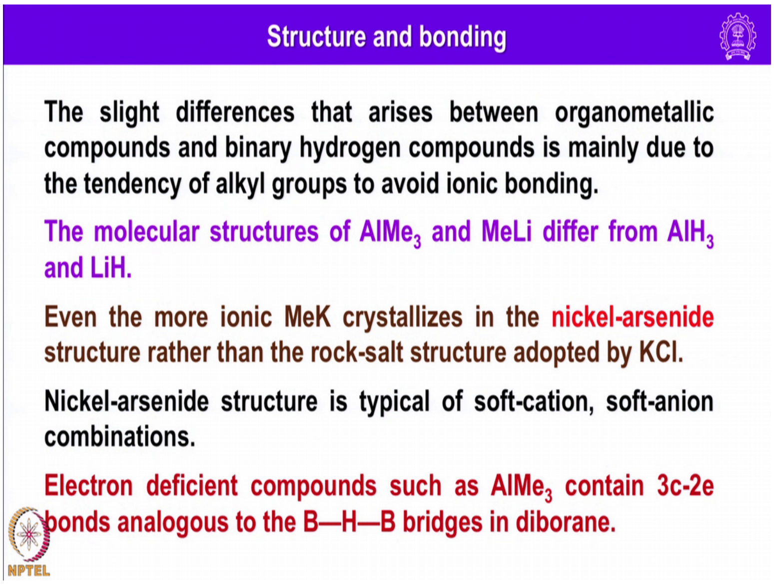

For example, the molecular structure of trimethylaluminium and methyl lithium, differ from aluminium trihydrate and lithium hydride.

Even the more ionic methyl potassium crystallizes in the nickel arsenide structure rather than rock salt structure adopted by KCl so; that means, nickel arsenide structure is typical of soft cation, soft anion combination. So, electron deficient compound such as trimethylaluminum contain three centered to electron bonds similar to B-H-B bond we come across in case of diborane. So, we can see here nickel arsenide structure ok.

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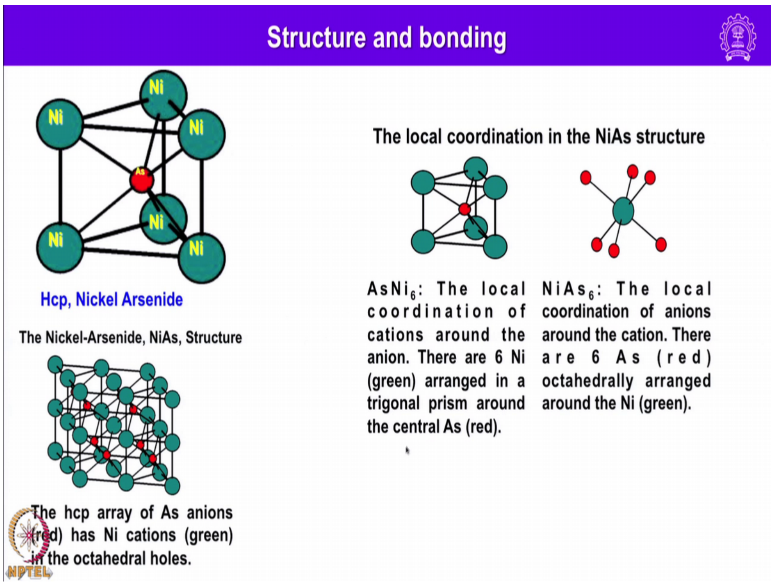

And of course, in the lattice this is how the arrangement of nickel and arsenide anions are shown here. The local coordination cation around the anion need shown in this one the first one. There are 6 nickel arranged in a trigonal prism around this central arsenic; arsenic is central here and here in case of nickel a s 6, here the local coordination of anion around the cation is shown here it is octahedrally surrounded by 6 arsenide ions. So, both are hexa coordinated ok.

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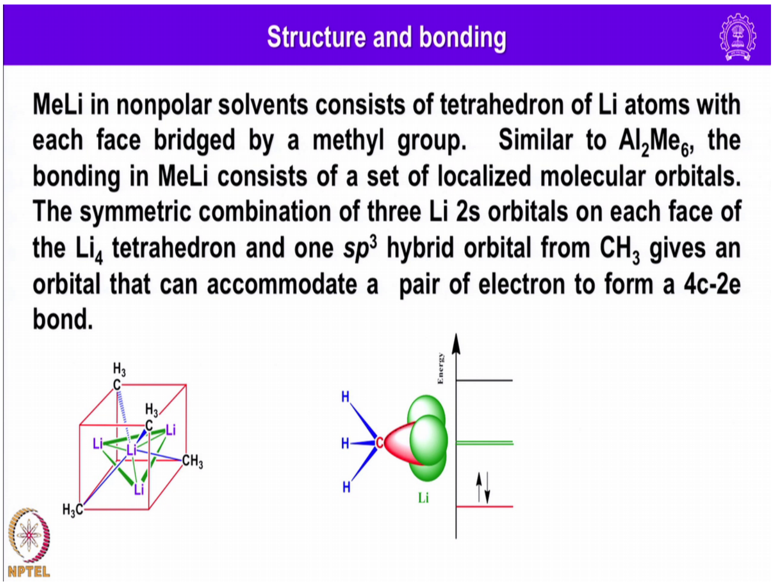

So, it is let us look into the structure of methyl lithium, methyl lithium in non-polar solvents consists of a tetrahedron of lithium atoms which each face bridged by methyl group. So that means, in a simple way one can write although this is referred to as a cubic structure having alternate corners occupied by methyl and lithium and let me just consider a tetrahedron of lithium atoms here.

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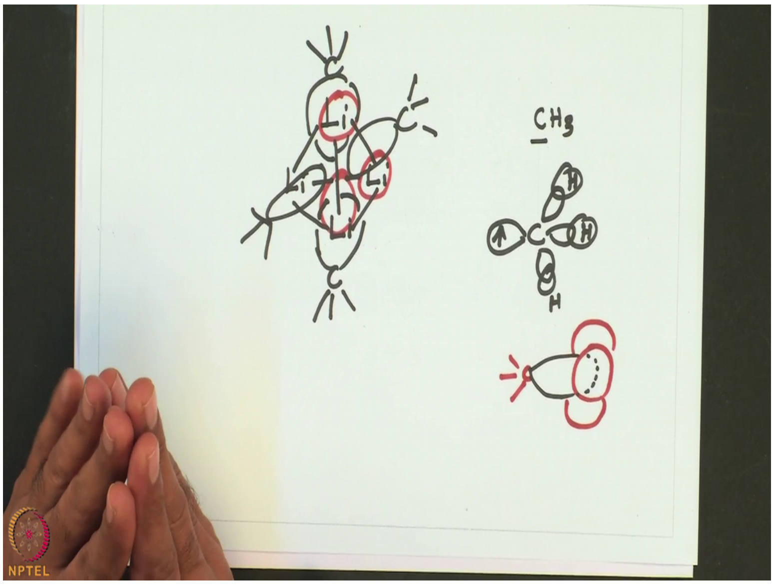

So, now we have 4 equilateral triangle faces, consists of three lithium atoms. So, here essentially if you assume in case of CH 3 the fragment we have here, carbon has undergone SP 3 hybridization having 4 SP 3 with one electron each, here something like this and having here H-H-H and now we have one with one electron is there and out of this one electron will be available. So, essential this one comes here and sits here you know one thing faces. So, something like this can each face something like this and here, so on to here. So, something like this. So, this eventually gives a tetrahedron structure that is what I have shown here, here you can see here and of course, this can also be simply shown in this fashion and if I put here.

So, you can see here now three are they are and this one is coming and of course, one can show in this fashion your SP 3 is coming here. So, another 2 lithium short terms will be blanking from the other position this is how exactly it shows here. So, you have methyl group. So, this give some idea about essentially it shows having 4 centered to electron bonds each lithium has one electron and each methyl group has one electron. So, that we have essentially 4 electrons from methyl groups and 4 electrons from lithium that forms a covalent bond, and remaining lithium atoms are not contributing anything and as a result what we have is 4 centered three lithium and one carbon constitute 4 centered, but we have 2 electron. So, here we have 4 centered 2 electron bond ok.

So, you can see that one and of course, one can also write in this way. This is bonding orbital and these 2 are nonbonding orbital and this is antibonding orbital. So, through mo diagram also one can represent this involves three lithium 2 S1 orbitals and 1SP 3. So, here we have 4 orbital says initially, that constitute one bonding orbital where this 2 electron recite and we have 2 nonbonding and one anti bonding. So, this is how one can explain the bonding in methyl lithium ok.

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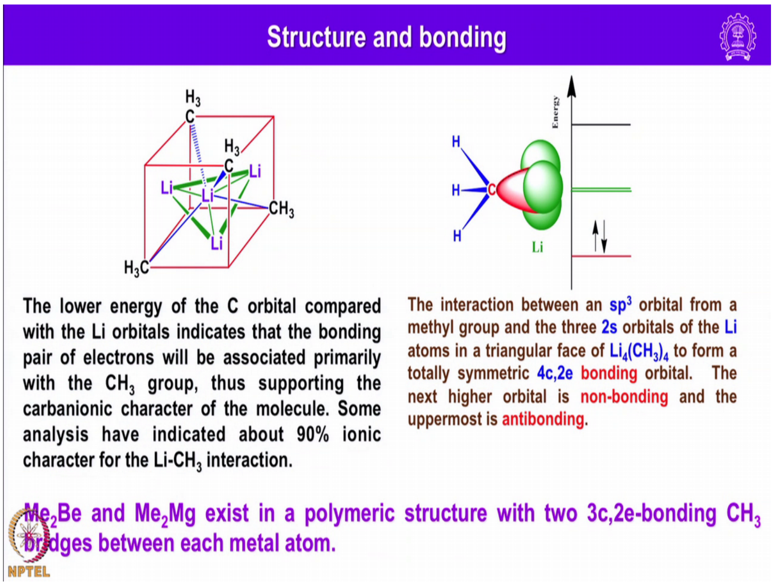

So, the lower energy of the carbon orbital compared with the lithium, orbital indicates that the bonding pair of electrons will be associated primarily with the CH 3 group, the supporting the carbanionic character of molecule. Since the carbon is much more electronegative the shared electron. So, essentially resides and carbon making it more electronegative. So, that that is increasing its carbanionic character, as a result what happens this is much more reactive. Similarly dimethyl beryllium and magnesium existing polymeric structure with 2 3sent to electron bonding; that means, CH 3 bridges between each metal atom that already I showed you in my previous lecture ok.

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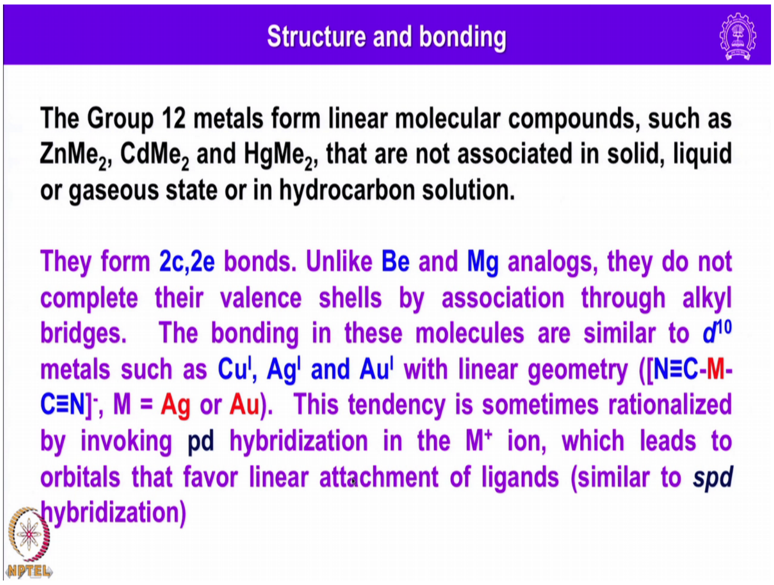

So, the group twelve metals form linear molecular compounds, such as dimethyl zinc, dimethyl cadmium, and dimethyl mercury that are not associated in solid liquid are gaseous state or in hydrocarbon solutions. So, they form 2 centered to electron bonds unlike beryllium and magnesium analogs they do not complete their valence shells by association through alkyl bridges, the bonding in these molecules are very similar to d ten metals such as copper one, silver one and gold one having linear geometry. This a tendency sometimes rationalized by invoking pd habitation in M plus ion which leads to orbitals that favor linear attachment of ligands similar to spd hybridization. So, this is something unusual usually when 2 orbits are mixed it gives 2 hybrid orbits whereas, here 3 orbits are mixing to give 2 hybrid orbitals.

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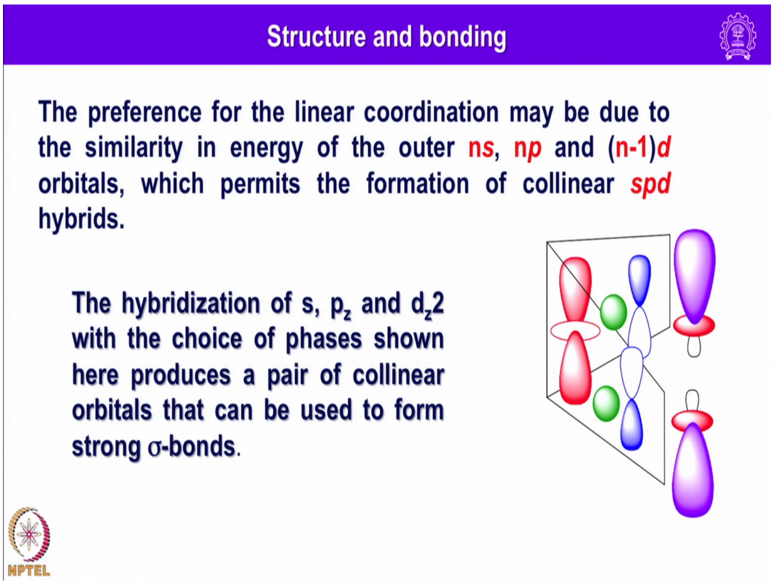

So, something like this is are the preference for the linear coordination may be due to the similarity in the energy of the outer ns, np and n minus one d orbitals, which permits the formation of collinear spd hybrids, I am going to show you how this spd hybrid orbits look like.

So, this is how it looks like here this is a desert square and this is s and this is p z orbital. So, they combined together to form to spd hybrid orbitals so; that means, here the hybridization of s pz and dz square with the choice of phases shown here produces a pair of collinear orbitals that can be used to form string sigma bonds. Now these 2 spd hybrid orbitals combine with carbon SP 3 have been electron to form linear compound like dimethyl a mercury or dimethyl zinc or dimethyl cadmium.

So, let us look into the reaction patterns; the reactions of organometallic compounds of electro positive elements are essentially dominated by factors such as the carbon ion character of the organic moiety, and the availability of a coordination sight on the central metal atom. So, carbon present on most electropositive metals, are essentially very reactive reagents. So, let us look into these reactive patterns by considering oxidation first.

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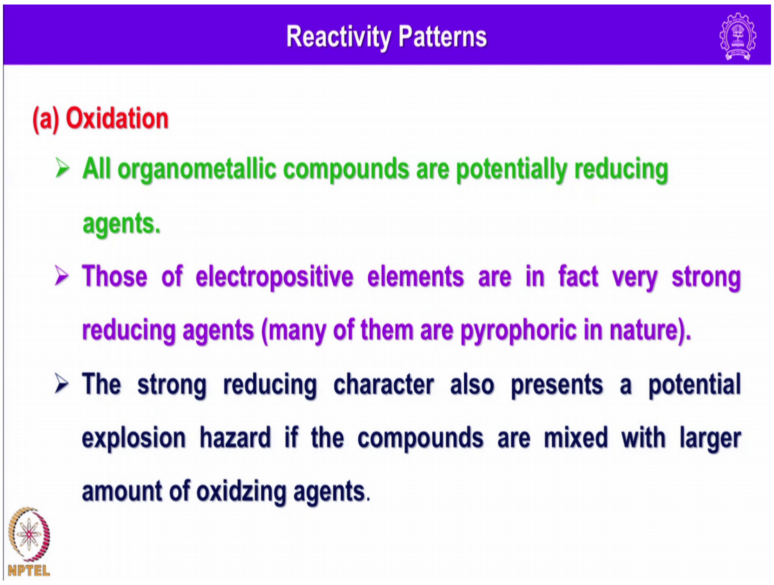

All organometallic compounds are potentially reducing agents, those of electropositive elements are in fact, very strong reducing agents and many of them are highly pyrophoric in nature. The strong reducing character also presents a potentially explosion hazard its compounds are mixed with larger amount of oxidizing agents; one has to be very careful and one should understand the nature of the reagents that are used in such reactions. So, that any such explosion or any unwanted accidental reactions can be avoided.

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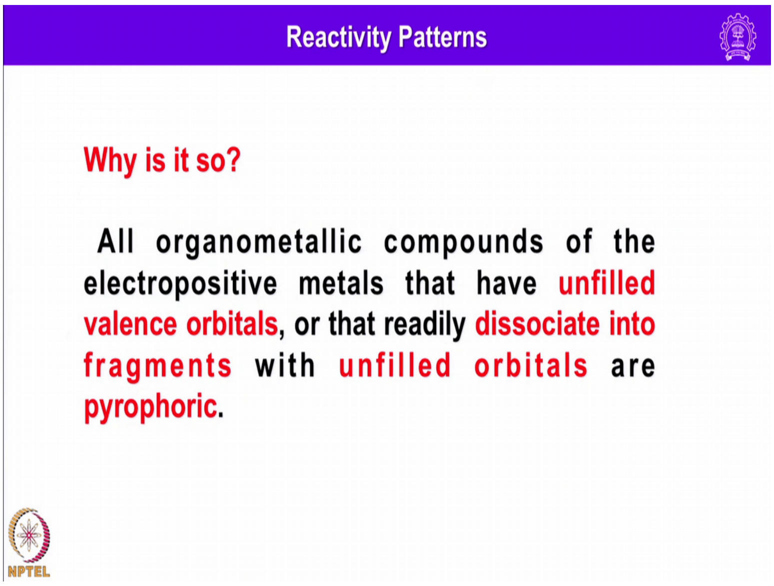

So, why this compounds are very reactive? All organometallic compounds of the electropositive metals that have unfilled valence orbitals or that readily dissociate into fragments with unfilled orbitals are pyrophoric. So, that is the reason most of this organometallic compounds if you consider, they have unfilled valence orbitals or they have a tendency to dissociate into fragments with unfilled orbitals, as a result they become highly pyrophoric in nature.

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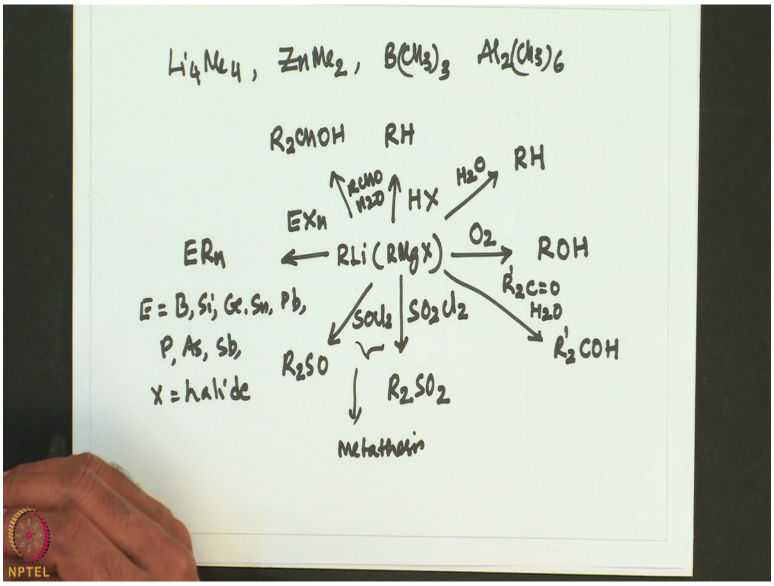

So, let us consider these examples methyl lithium. So, Li4 M e 4 or zinc dimethyl zinc or trimethylboron or al 2 CH 3 6 times trimethylaluminum. So, they are all volatile pyrophoric compounds for example, bch 3price dimethyl boron may be handled in vacuum line and inert atmosphere techniques are used for less volatile, but al sensitive compounds. Compound such as tetramethyl silicon and tetramethyl tin which do not have low lying empty orbitals, and if you consider silicon and tin there 3 d and 5 d orbitals are very high in energy. So, as a result what happens they cannot really increase their coordination number from 4 to 5 or 6 as a result what happens at to room temperature they do not react readily, they require elevated temperature to initiate combustion so that they can be handled in al. The combustion of many organometallic compounds takes place by a radical chain mechanism.

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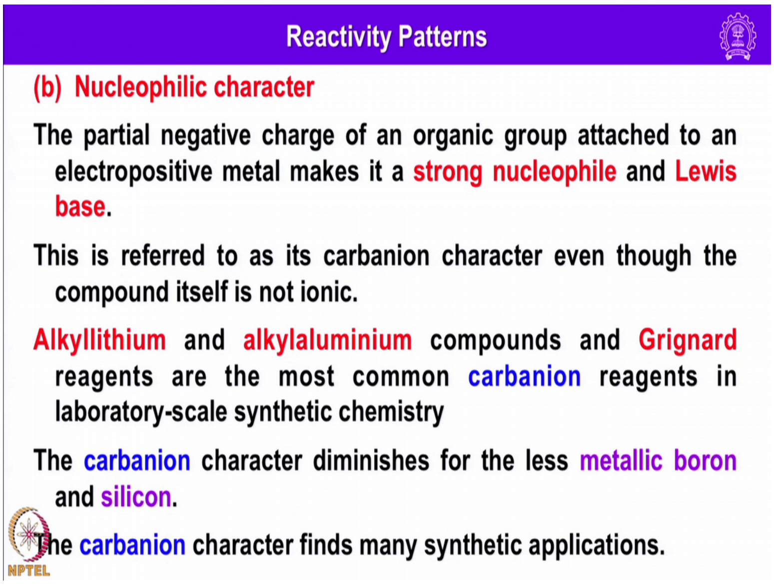

So, let us look into the nucleophilic character of some of these reagents. The partial negative charge of an organic group attached to an electropositive metal makes it a strong nucleophile and Lewis base. So, this is referred to as carbon and ion character even though compound itself is not ionic.

That means alkyllithium and alkylaluminium compounds and also Grignard reagents are the most carbon, carbon and reagents in laboratory scale synthetic chemistry the carbon ion character diminishes for the less metallic boron and silicon. And the carbon and character finds many synthetic applications let me write some of those things for you let us consider lithium alkyl lithium or Grignard reagents their applications are essentially similar.

For example, if it is treated with O 2 that means, oxidation that leads to the formation of ROH. And if is treated with h x it leads to the formation of R H so that lix will come out and if it is treated with water hydrolysis. So, it gives again RH and treatment of this one with sulfuryl chloride So 2 cl 2 is to the formation of R 2 SO 2 similarly treatment of RLI or RMgx with thionyl chloride is to R 2S 4 and if we treat this one with appropriate reagent EXn, one can get E R n here E can be boron silicon germanium tin pb or arsenic antimony or even phosphorus ok.

Of course, x is a typical halide. So, what would happen if you treat this one with a aldehyde and water forward by addition of water. So, with aldehyde and water, it gives R

2 CH OH if you take a key tone and water, it gives tertiary alcohol. So, this are some of the reactions these are all very important reactions in organic synthesis to generate a variety of useful compounds and of course, these 2 reactions are essentially called as metathesis reactions, and this is oxidation reaction this is hydrolysis reaction and one can you several other reactions ah and they come very handy in synthetic organic chemistry and also in earlier chemistry.

So, I have shown here the same slide here (Refer Time: 19:07) see.

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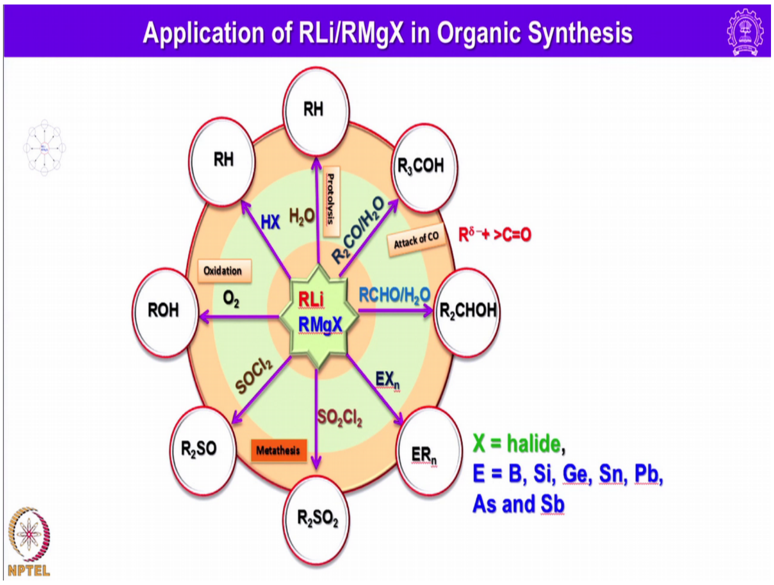

Its use let us continue the reactivity patterns of some of these organometallic reagents for example, trimethylaluminium when it is treated with ethanol, it forms triethoxidealuminium through the elimination of 6 equivalents of methane. So, how that happens is shown here.

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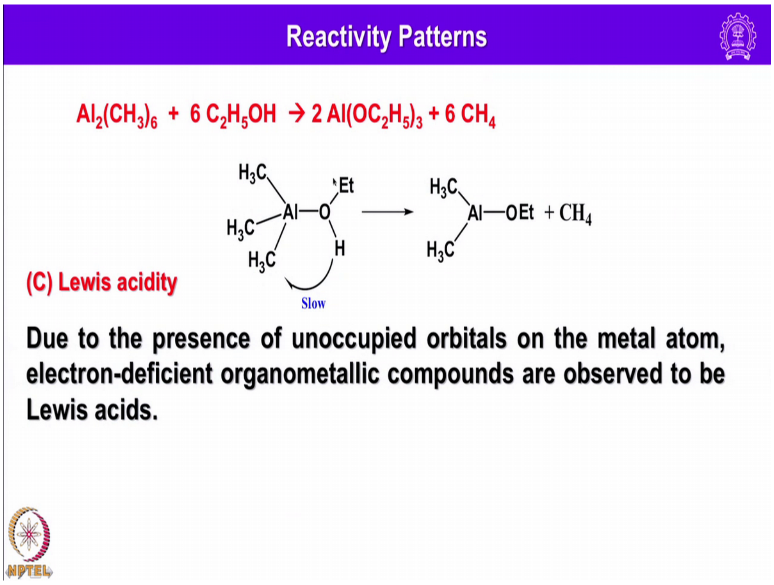

Since here this dimmer breaks as a result one coordination site is vacant, that is occupied by auction lone pair and then this H most words this one in the slow step, to form dimethylaluminium ethoxide through the formation of CH 4. This continues with if another equivalent of ethanol comes eventually it replaces OEt ethoxide groups replace all methyl groups and they come out as methane. So, another one is Lewis acidic nature of organometallic compounds due to the presence of unoccupied orbitals on the metal atom electron deficient organometallic compounds are observed to be Lewis acidic in nature are they performer as Lewis acids.

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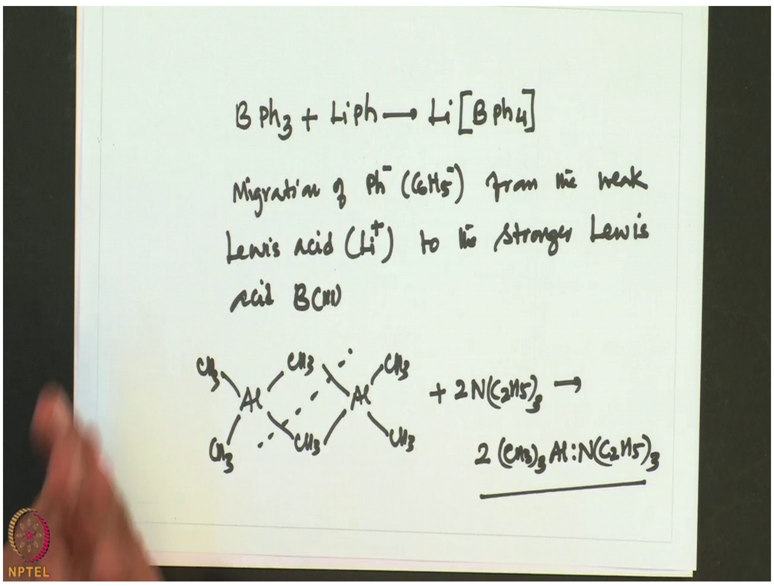

So, let us look into the Lewis acidity of this compounds for example, if I take triphenylboron, if it is treated with phenyl lithium it forms lithium tetraphenylborate. So, this reaction may be viewed as the transfer of the strong phenyl from the weak Lewis acid to the weak Lewis acid is lithium plus to the stronger acid b there so; that means, migration of Ph minus r C 6 H5 minus from the weak Lewis acid that is Li plus to the stronger Lewis acid B 3 ok.

So; that means, there is always some driving force for this kind of reactions, organometallic species that are bridged by organic groups can also serve as Lewis acids and in this process bridge cleavage can takes place readily. For example, I have shown here trimethylaluminium is a diametric compound something like this. So, bridge break as takes place across and if here addition of 2 equivalents of triethylamine say, it leads to the formation of two. So, this is how adopt is formed here. So, electron deficient organometallic species are essentially perform as Lewis acids. Now let us look into the ionic and electron deficient components of group 1 2 as well as group 12.

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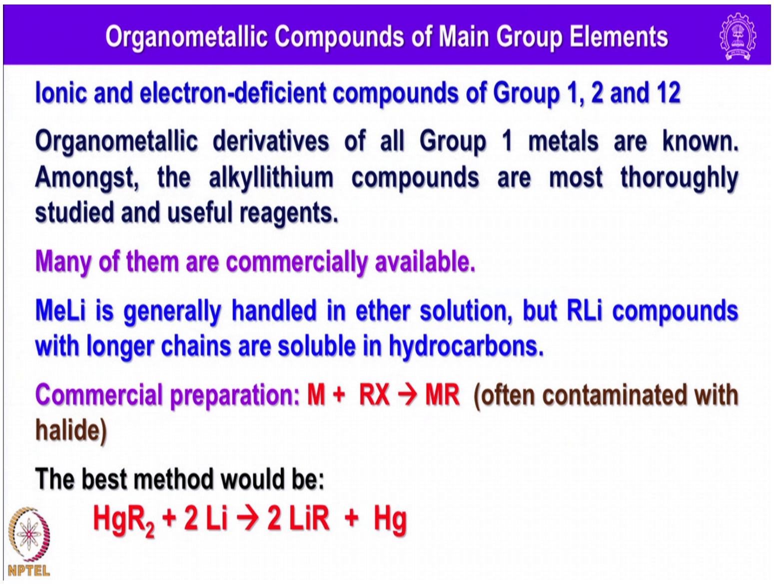

So, organometallic derivatives of all group one metals are known amongst the alkyllithium compounds are most thoroughly studied and useful reagents, many of them are commercially available. So, even be tell lithium, phenyllithium (Refer Time: 23:14) a lithium all those things in different concentrations in mostly in hexane or pentane one molar solution 1.6 molar solution are 2.5 molar solution in 100 ml or 500 ml or in 1000 ml containers. So, methyl lithium is generally handled in ether solution, but all li compounds with longest chin or soluble in hydrocarbons.

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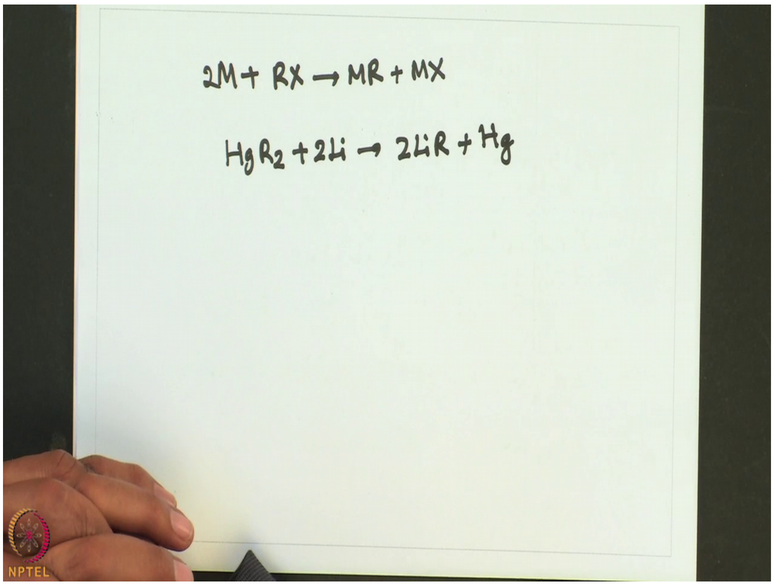

So, commercial preparation as I mentioned it can also involve M plus Rx gives MR. They often contaminated with halides in this method basically what happens you have taken 2 equivalents of M and MR and Mx comes this is the commercial method of preparation of ah methyl lithium or ethyl lithium or (Refer Time: 24:23) lithium, but the best method for the preparation of this compound which are free from contaminated halide is to go for transmetallation method for example, dimethylmercury or dialkylmercury when is treated with 2 equivalents of lithium, it gives 2 LiR and mercury comes out ok.

So, this is the best method of course, one also should be careful about the contamination of this compounds with mercury, methyl lithium exists as a tetrahedral cluster in the solid state and in solution that is already clear.

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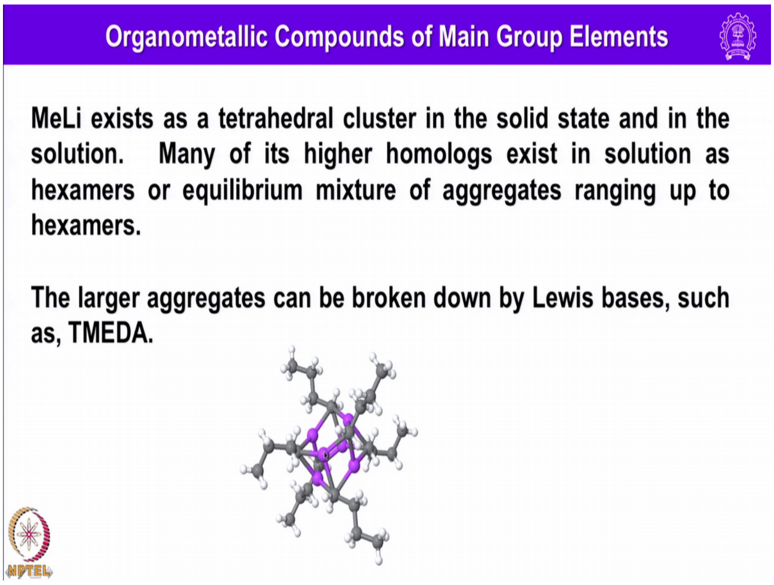

Many of its higher homologs exist in solution as hexamers or equilibrium mixtures of aggregates ranging of to hexamers. The larger aggregates can be broken down by Lewis bases such as TMEDA, that is tetramethylethylenediamine you can see here it can also exists in hexametric form something like this here, you know 6 lithium atoms are there and 6 alkyl groups are there.

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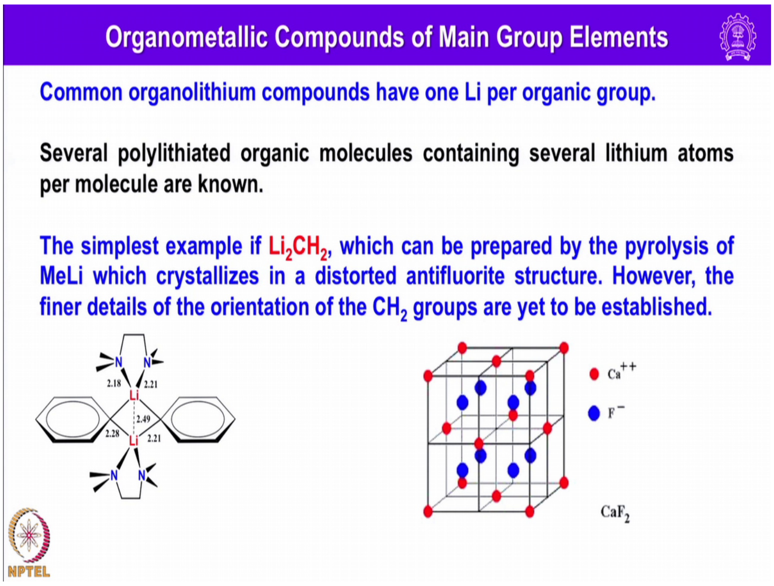

So, common organolithium compounds have normally only lithium per organic group like methyl lithium phenyllithium, n butyllithium, thricely butyllithium, secondary butyllithium like that, but several polylithiated organo molecules containing several lithium atoms per molecular also known the simplest example is Li 2 CH 2 which can be prepared by the pyrolysis of methyl lithium which crystallizes in a distorted antifluorite structure.

However the final details of the orientation of CH 2 groups are yet to be established because of its high reactivity and less stability. Here in case of phenyllithium one can see this how the structure looks like here its phenyllithium with tetramethylethylene di m unit form say dimmer and of course, here it is getting stabilized because it utilizes this pi electrons of benzene to stabilize or overcome some of the electron deficiency of lithium here. And this is the structure for Li 2 CH 2 similar to fluorite structure there is calcium fluoride structure sodium naphthalene is an example of when organmetallic salt with a d localized radical anion C 10 H 8 minus.

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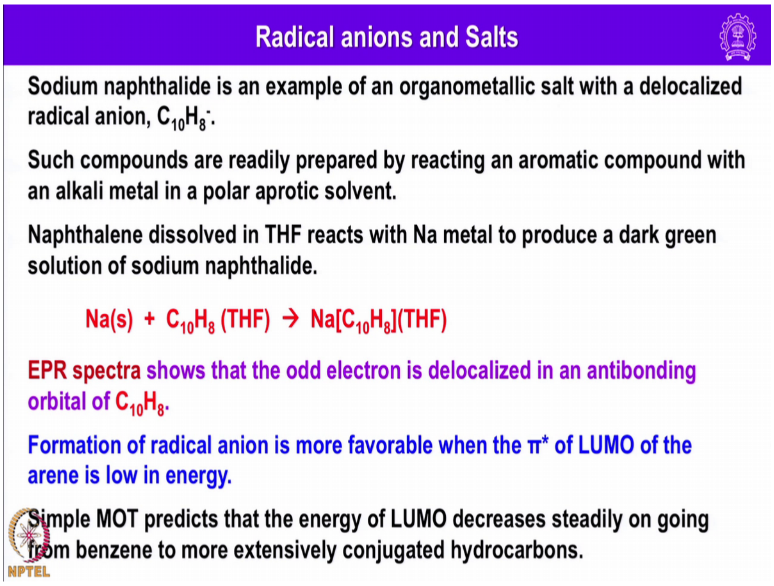

Such compounds are readily prepared by reacting an in organmetallic compound with an alkali metal, in a polar aprotic solvent usually tetrahydrofuran is used. So, naphthalene dissolved in tetrahydrofuran reacts with sodium metal to produce a dark green solution of sodium naphthalene so; that means, you can see here sodium solid when it is added to naphthalene THF it forms this sodium naphthalene, this dissolves in solution and which is green in color.

So, EPR spectrum shows that the odd electron is d localizing and anti-bonding orbital of C 10 H 6. So, formation of radical anion is more favourable when the pi star of lowest unoccupied molecular orbital of the iron is low in energy. So, simple molecular orbital theory predicts that the energy of lumo lowest and occupied molecular orbital decreases steadily on going from benzene to more extensively carbonated hydrocarbons, as a result they have a tendency to form some of these kind of stable sodium salts which come very handy in organic synthesis. So, why sodium naphthalide is very important in organic synthesis is, sodium naphthalide and similar compounds are highly reactive reducing agents. So, there preferred to sodium metal because unlike sodium there readily soluble in ether another problem is wearing accurate amount of sodium is very difficult, because on even slightest exposure the surface will be coated with sodium oxide and we lose a certain quantity of sodium.

So, in this case what happens in the stoichiometry of the sodium salt is very critical then using sodium metal is not a good idea. So, instead one can you sodium naphthalide where exact quantity of sodium can be taken in solution by finding out the molarity of the sodium naphthalide solution, and taking the right amount of sodium naphthalide.

So, the resulting homogenous reaction is generally faster and easier to control than a heterogeneous reaction between one reagent in solution, and pieces of sodium metal which are often coated with unreactive sodium oxide or with insoluble reaction products. In this context the utility of sodium naphthalene comes into the picture in organic synthesis where the stoichiometry is very very critical.

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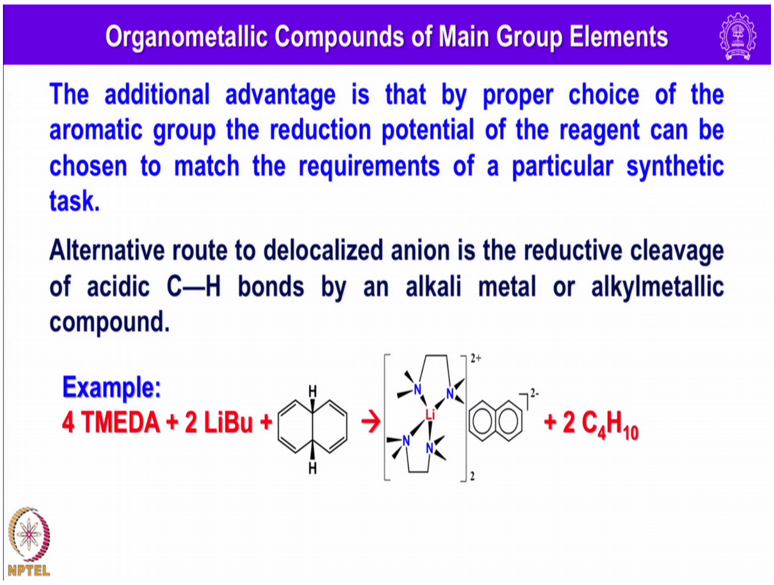

The additional advantage is that by proper choice of the aromatic group, the reduction potential of the reagent can be chosen to match the requirement of a particular synthetic task.

So; that means, weather one has to carry out and compiled condition or and ambient condition by knowing that one, one can choose a right kind of aromatic group, so that its reduction potential can be a match the requirement of a particular synthetic scheme that is planned. So, alternate route to delocalized anion is the reductive cleavage of acidic C H bonds by an alkali metal or alkylmetallic compound ok. So, here you can see here. So, in butyllithium instead with 4 equivalents of TMEDA in fronts of it forms naphthalide it forms a compound of this type.

So, one can also conveniently use this one as a source of lithium, and sodium and potassium also form intensely colored salts with many aromatic compounds. In the reaction such as this that I showed you the oxidation of the alkali metal involves the transfer of one electron to the aromatic system producing a paramagnetic radical anion. So, let me stop here and continue in my next class the remaining organmetallic chemistry of main group elements.

Thank you very much.