Main Group Chemistry
Prof. M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture – 58
Organometallic compounds of Main Group Elements

Welcome to MSP lecture series on main group chemistry. In my last lecture, I began in discussion on the organometallic chemistry of main group elements. So, let me continue from where I had stopped, I was discussing about the Lewis acid properties of organometallic compounds of especially group 13 elements like tryalkylaluminium and tryalkylarylboron compounds. Here tryalkyl and triboron compounds are mild Lewis acids. So, when they react with strong carbonate reagent that leads to anions of the type b are 4 minus that is.

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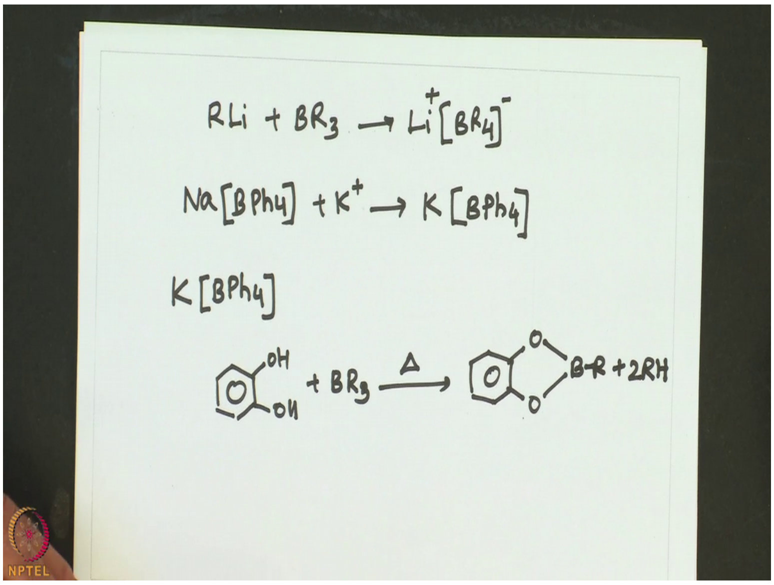

So example one can consider sodium salt of for tetraphenylborate. The bulky anion here hydrolyses very slowly in neutral or basic water and is used for the preparation of large positive cations. In fact, in coordination chemistry this large anions are very essential to stabilize and crystallize larger positive ions or larger cations. If you treat this one with potassium one can conveniently make the potassium salt as well. This potassium salt of tetraphenylborate is insoluble used for the gravimetric estimation of potassium, in example of the low solubility of large cation and large anion salts in water.

This Lewis acidic boron compounds organoboron compound such as tryalkylarylboron can also react with catacal. So, this kind of compounds are one can anticipate. Organohalogen compounds are organo hollow boron compounds are more reactive than simple tryalkylboron compounds. So, let us look into the preparation of this organo hollow boron compounds, because these compounds are very useful in further the utilization of main group or transfer elements. Let us look into the preparation of this organo hollow boron compounds treatment of Bc l 3 with trialkylaluminium leads to be alkyl boron chloride.

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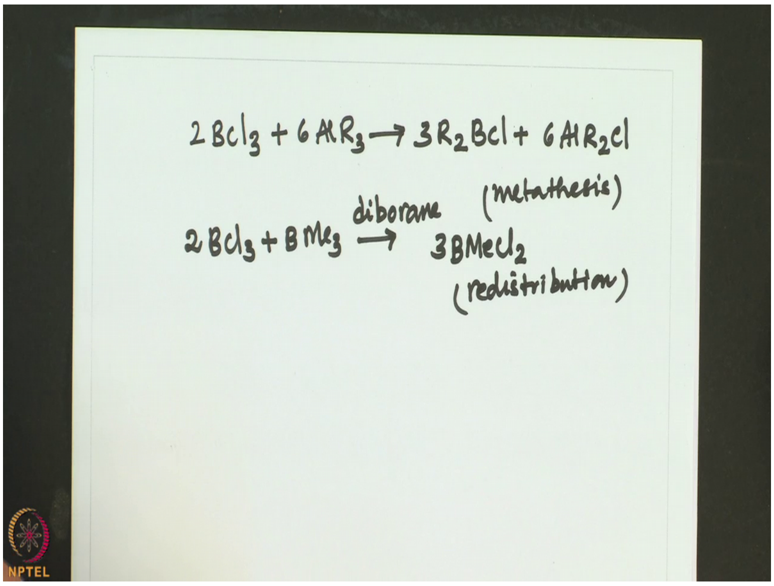

Of course this reaction can also be termed as metathesis reaction or one can also go for a redistribution reaction for example, treatment of Bc l 3 with trimethylboron leads to the redistribution of course, this reaction has to be carried out in diborane B 2 h 6 at least to the formation of B Mecl 2 this is redistribution reaction. Of course, this organo hollow boron compounds having very reactive Bcl bonds can undergo nucleophilic substitution reaction to give a variety of other derivatives. For example, they can react with alcohols and amines and other reagents; let me give a couple of examples here ok.

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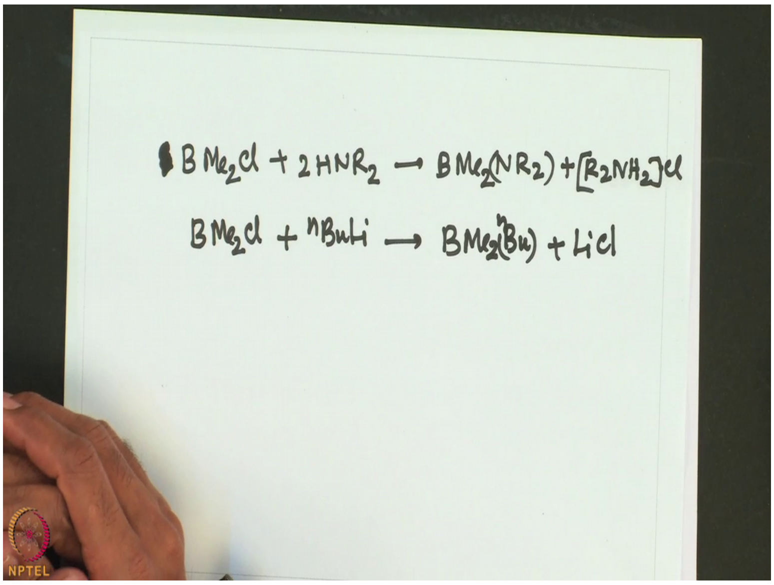

So, here with 3 B Mecl 2 or one can also perform this reaction standing from n butyl lithium. So, these are some of the reactions, once you have some Bcl are bond one can look into a variety of other reagents.

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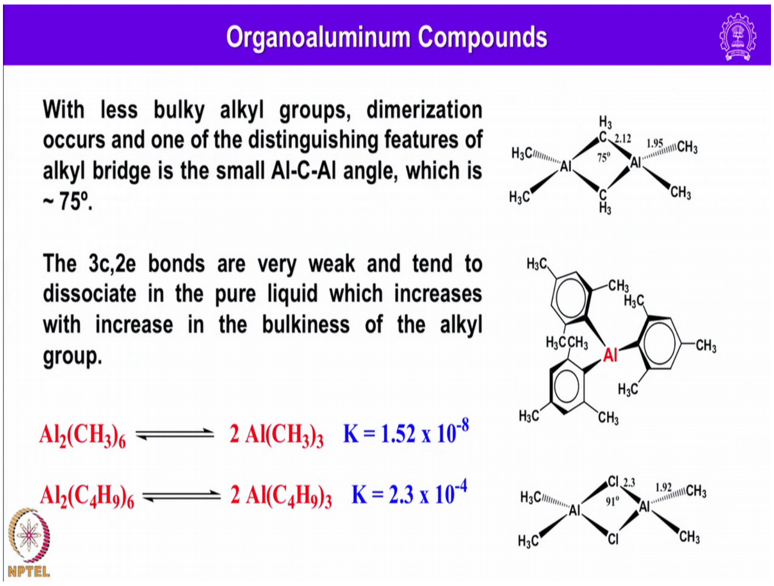

Let us look into organo aluminum compounds with less bulky alky groups dimerization occurs, and one of the distinguishing feature of alkyl bridge is the small A- C-Al angle which is 75 degree here it is unusual of course, carbon is tetrahedral; however, the angle is very small because 2 smaller aluminium ions in their plus 3 state become very close to each other as a result this angle shrinks to as low as 75 degree. These 3 centered 2 electron bonds are very weak, and tend to dissociate in the pure liquid which increases with increase in the bulkiness of the alkyl groups.

For example if you use very bulky groups and aluminium, it is possible to stabilize in monomeric state. Some examples are given here you can see here 2 4 6 trimethylphenyl groups one can have simple Al r 3 in the monomeric form. Whereas, in case of less bulky groups it undergoes dimerization similar to Al 2 Cl 6. Of course, here one can see the dissociation constant here Al 2 CH 3 6 when it dissociate into 2 monomeric species, K equals 1.5, 2 into 10 to the power minus 8 whereas, when you have C 4 H 9; this is 2.3 into 10 to the power of minus 4 ok.

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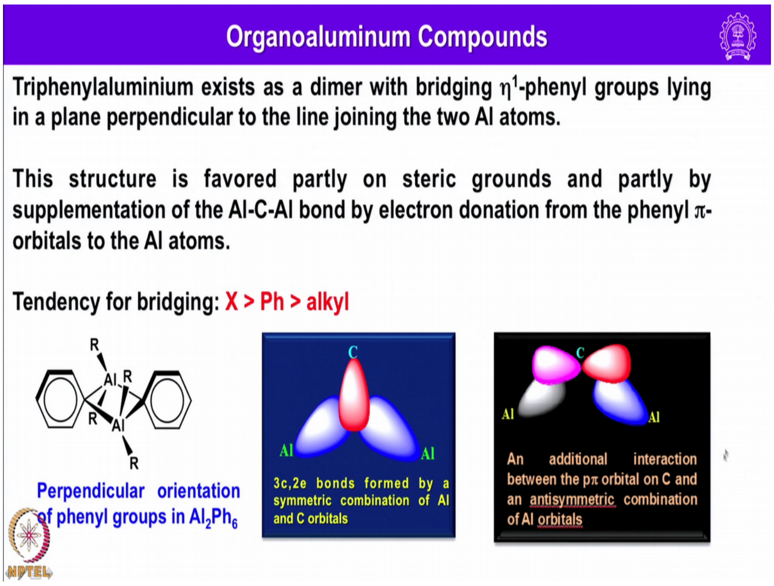

This triphenyl aluminium exists as a dimer with bridging eta one phenyl group lying in a plane, perpendicular to the line joining the 2 aluminium atoms, if the 2 aluminium atoms are like this and essentially aromatic group is a perpendicular to it.

This structure is favored partly on steric grounds and partly by supplementation of AlCl Al-C-Al bond by electron donation from the phenyl pi orbitals to the aluminium atom. So, tendency for bridging if you look into it for example, if you look into AlCl 3 and al ph 3 and al me 3 or al et 3 the tendency for bridging is more in case of halides and next is phenyl and the least one is for alkyl groups; that means.

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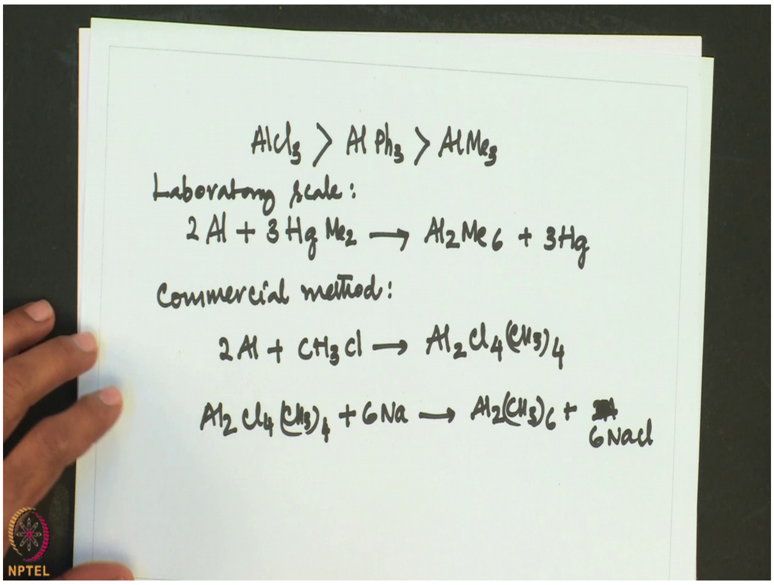

If you just consider Alcl 3 more tendencies therefore, bridging because chlorine has a lone pair, next one will be Al ph 3 and next one will be Al Me 3. Here essentially it becomes 3 centered to electron more electron deficient here pi electron can be utilized to strengthen the bridging unit or 3 centered to electron bond, and here it is no longer a 3 centered to electron bond as chlorine is readily giving a pair of electrons, that will go to the mt sp 3 orbital on aluminium.

To aluminium if you assume or in the plane, this is a perpendicular something like this. With this kind of arrangement, the over lapping of pi cloud with aluminium will be much more efficient mt sp 3 with orbital will be more efficient. That has shown here you can see here to aluminium of course, one has one electron other one has no electron similar to diboron type, these 2 will interact with carbon sp 2 of phenyl and then of course, with now this is along the plane and now we have this p orbits that are perpendicular to this one. So, the essentially interact with aluminium orbitals that is one is sp 3 with the pair; another one is antibonding one additional interaction between the p pi orbital on carbon, and an antisymmetric combination of aluminium orbital.

This essentially strengthens the aluminium carbon aluminium bond, and hence they are little more stable compared to the analogous alkyl compounds.

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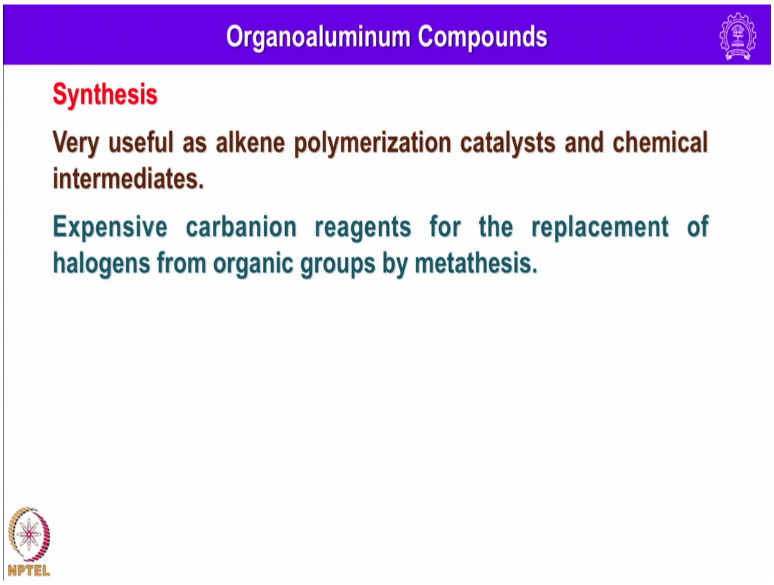

So, let us look into the synthesis of these aluminum organoalumiium compounds very useful as alkene polymerization catalysts and chemical intermediates and of course, they are expensive carbon and reagents for the replacement of halogens from organic groups by metathesis. Let me give the laboratory synthesis of trimethyl aluminium; in laboratory synthesis they react directly dimethylmercury with aluminium metal. This gives Al 2 Me 6 plus; commercial method involves the treatment of aluminium with methyl chloride this is laboratory scale preparation.

Commercial method here aluminium is directed treated with methylchloride, that leads to the formation of initially dichloro tetramethyl dialuminium Al 2 Cl 4 CH 3 4 times means Al 2 Cl 4, CH 3 4 times when it is reacted with 6 equivalence of sodium, Al 2 CH 3 6 times. So, trimethylaluminium be formed plus 2 Al, 6 Nacl. Of course, this equations I have not balanced one should be able to write the balanced equation in this case.

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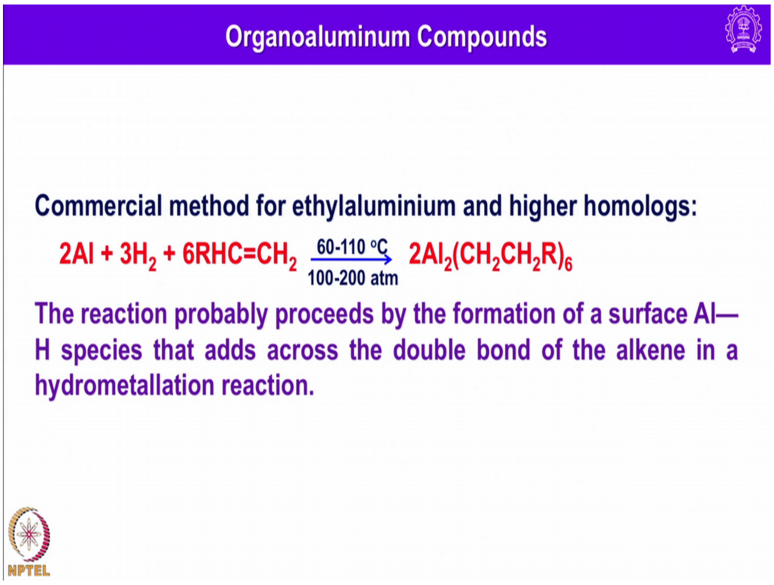

Another important method is there for the preparation of ethyl aluminium, which finds application in polymerization reactions, and in this case the reaction that is used is hydro-metallation reaction.

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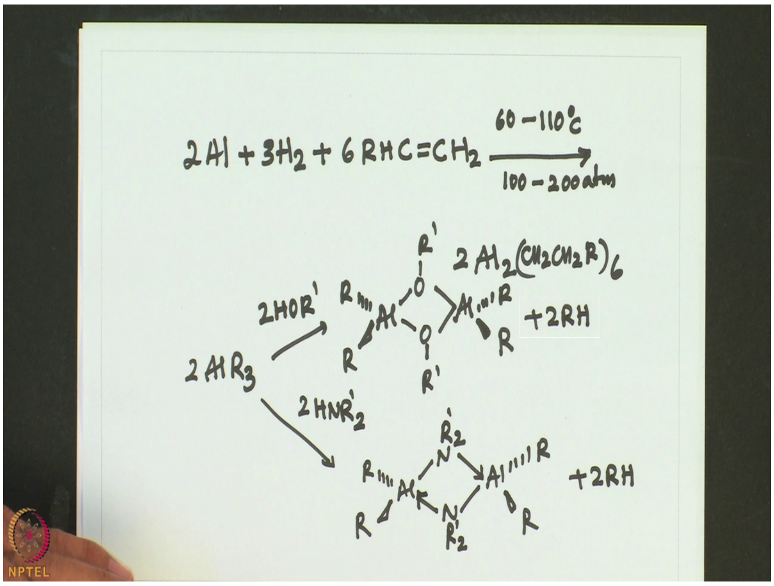

For example aluminium when its treated with hydrogen gas and ethylene or alkene in; of course, temperature maintained is 110 and the pressure is 100 to 200 at atmosphere, this leads to the formation of Al 2, CH 2, CH 2, R 6 times. This is quite opposite to beta hydrogen elimination reaction; the reaction probably proceeds by the formation of a surface aluminium hydride species that adds across the double bond of the alkane in a hydro metallization reaction.

Essentially it is a hydrogenation reaction in which h 2 is broken and sits on aluminium to form aluminium hydrogen bond, and then addition of alkynetakes place and it is getting hydrogenated lead in to the formation of this trialkyl aluminium compound. And of course, these trialkyl aluminium compounds can undergo reactions with alcohols and amines, that me write a couple of examples here if you take 2 Al R 3, treat this one with alcohol similarly it can undergo reaction with secondary amine. Of course, plus 2 RH will come, should remember one of this will be a coordinate bond something like this. So, alkyl aluminium compounds are mild Lewis acids and form complexes with ethers, amines and anions when heated often beta hydrogen elimination is responsible for the decomposition of ethyl and higher alkyl aluminium compounds.

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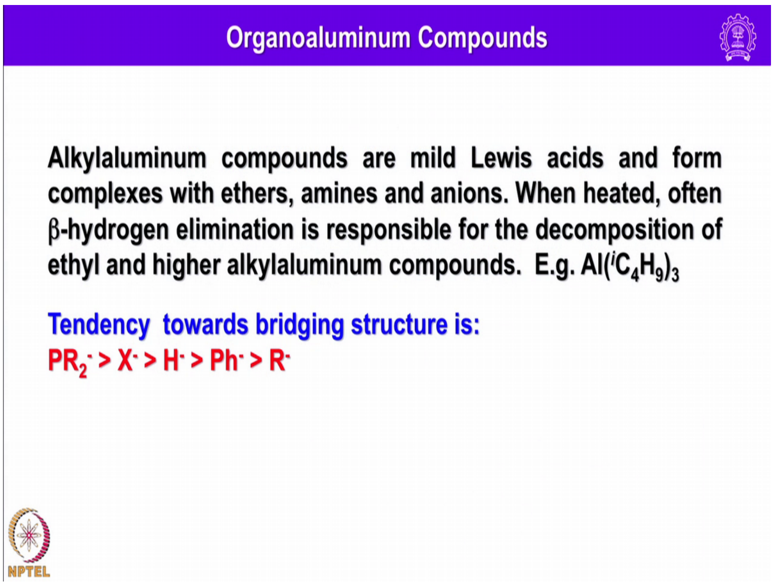

So, tendency towards bridging structure I have shown here. So, this is the sequence they follow.

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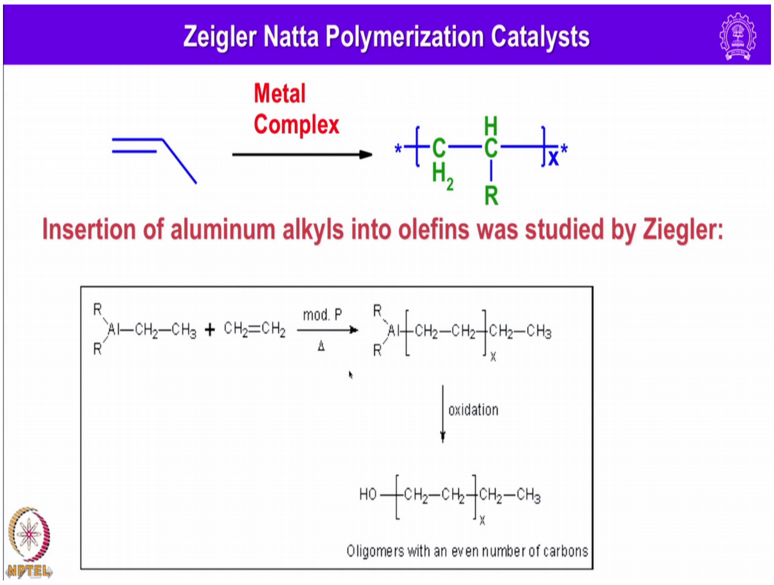

So, let us look into zeigler natta polymerization catalysis, where aluminium alkyls plays major role. Of course, here you take care a olefin here and metal complex, and it undergoes polymerization to give in this fashion. Insertion of aluminium alkyls into olefin was essentially studied by ziegler and if you take here a simple ethyl aluminium compound is shown here, when ethylene is added under moderate pressure on heating, it this is the group that keep on adding and then it undergoes oxidation and then we get the corresponding polymer.

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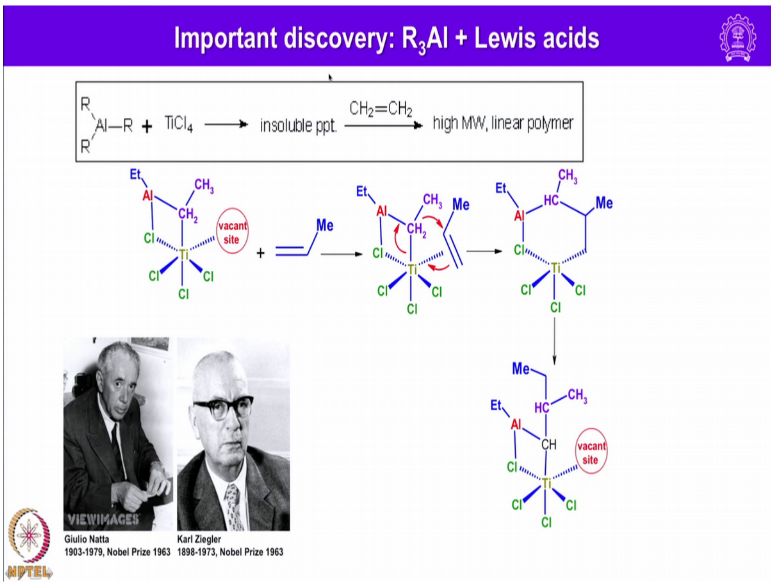

So, here and of course, here initially this triaklylaluminium is stated with TiCl 4 radius and insoluble prosperite, and to this one and adding ethylene, high molecular weight linear polymer is will be obtained. So, this essentially here it involves both aluminium as well as titanium, the sequence of reactions and also the direction of bond breakage and bond formation are shown here in this one, it goes like this. So, these 2 people Natta and Ziegler were given Nobel Prize in 1963 for this important discovery.

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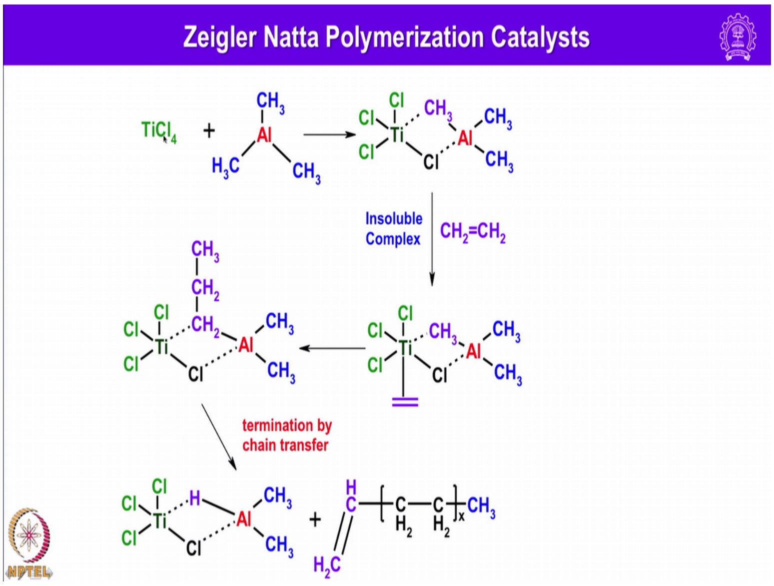

So, TiCl 4 on treatment with tri methyl aluminium, it initially forms a di metallic compound of this type in volume one chlorine and one methyl bridges, and this is an insoluble complex on treatment with ethylene, it adds ethylene to titanium and then rearrangement takes place, and this is more on to the bridging CH 2, CH 3 group, and then termination by chain transfer happens and eventually we get this polymer and this keep on adding until everything is hydrogenated here ok.

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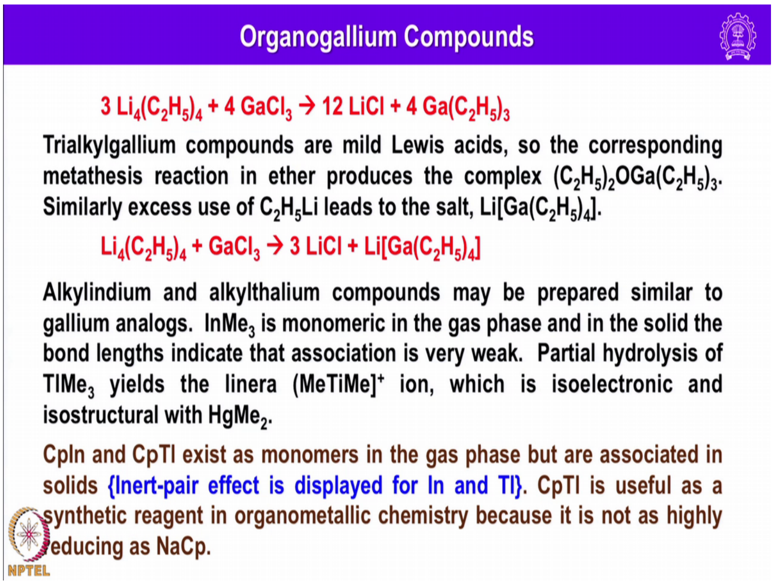

So, let us look into organogallium compounds. Organogallium compounds one method have shown here essentially are alkyl lithium components are used. So, appropriate alkyl lithium reagents when they are treated with gallium trichloride, one can get trialkylgallium compounds. So, this trialkylgallium compounds are also mild lewis acid. So, the corresponding metathesis reaction in ether produces the complex of this type. So, ether add it. Similarly excess of ethyl lithium leads to the salt of this type of course, if you take triethyl or trialkylgallium and if you take another lithium alkyl lithium, it can for a ionic spaces it is shown here. For example, you you take gallium trichloride and treat this only 4 equivalents. So, what we get is 3 equivalents of lithium chloride plus lithium salt of gallium tetra ethyl.

Alkylindium and alkylthalium compounds may be prepared similar to gallium analogs, trimethylindium is monomeric in the gas phase and in the solid the bond length indicate that association is very weak, partial hydrolysis of thallium tri methyl thallium yields the linear dimethyl thallium plus ion, which is iso electronic and iso structural with dimethyl mercury both cp indium and cp thallium exists as monomers in the gas phase, but are associated in solid solids. So, they display inert pair effect, Cp thallium is useful as a synthetic reagent in organometallic chemistry, because it is not as highly reducing as NaCp. So, wherever NaCp has to be used one can conveniently use Cp thallium ok.

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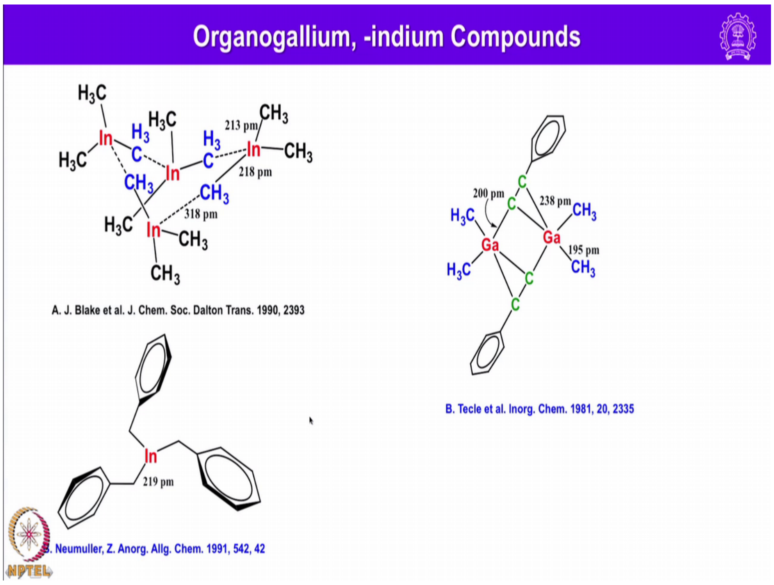

So, this indium compound is shown here, it is tetrameric in the solid state having 3 center to electron bonds, and this one with benzyl try benzyl indium, this is monomeric in nature and this one has a dimeric structure here.

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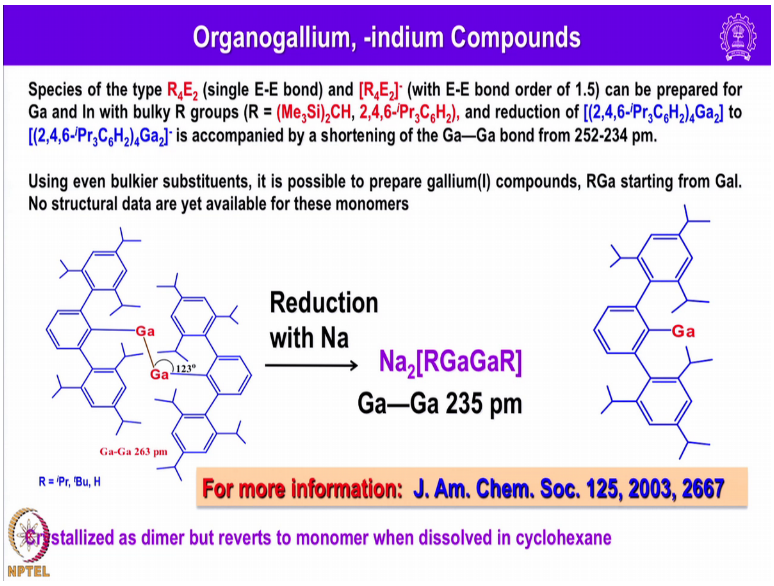

So, organogallium and organo indium compounds can also be made and impact low coordinated compounds can also be made provided are groups are very bulky. Species of this type R 2 E 2 having single bond and R 4 E 2 with EE bond order upon 0.5 can be prepared for both gallium and indium with very bulky R groups like this tri (Refer Time:

21:52) methyl R 246 tries a propylene phenyl group, and reduction of this one is essentially this gallium compound is accompanied by a shortening of the gallium, gallium bond from 250 to 234 pickometer; that means, a normal gallium gallium single bond distance is 252 and if it changes to 234 indicates the multiple bond character in this one. So, using you one bulkier substituents, it is even possible to prepare gallium one compound having one coordination like RGA starting from gallium iodide.

No structural data are yet available for this monomer I have shown here. So, if you use a sufficiently very bulky groups like this, it should be able to make a alkyl gallium having alkyl to gallium one is to one. So, this one undergoes dimeration, and this one on treatment with sodium undergoes reduction to form a gallium gallium double bonded compound. Here gallium gallium distance is 235; this is an indication of the multiple bond character between gallium and gallium. Of course, for more information one can look into this paper appeared in jocks in 2003. So, this crystallized as dimer, but reverse to monomer when dissolved in cyclohexane.

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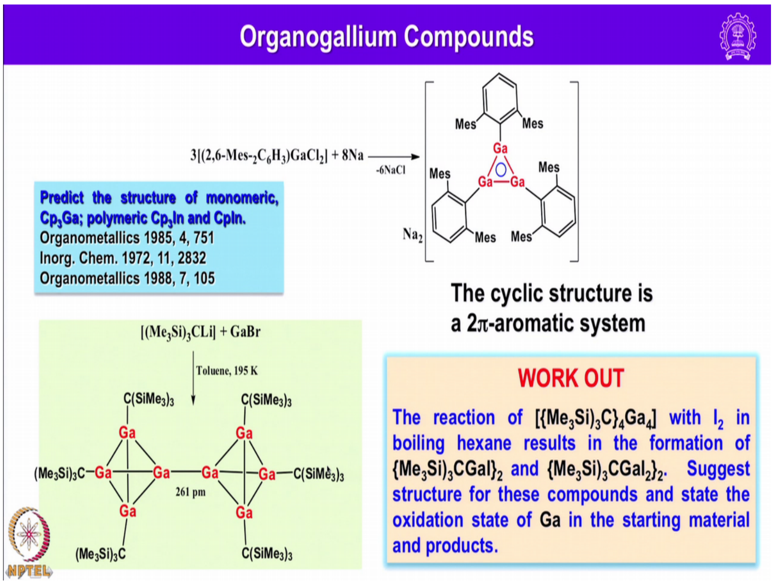

There a few more examples of organogallium compounds of course, if we take this mono r aryl gallium dichloride and reduces with sodium, that leads to the formation of a cyclic structure having 2 pi aromatic system here and of course, once when you take this tri (Refer Time: 23:36) methyl lithium and treat with gallium bromide, one can make a a dimeric species of this type ah.

Of course I have given a example, the reaction of this compound with iodine in boiling hexane results in the formation of a compound of this composition, along with this composition suggest structure for these compounds and state the oxidation state of gallium in the starting material and product. So, this is a easy product by deving clue through from this one as well as this one, you should be able to work out, this problem given even here.

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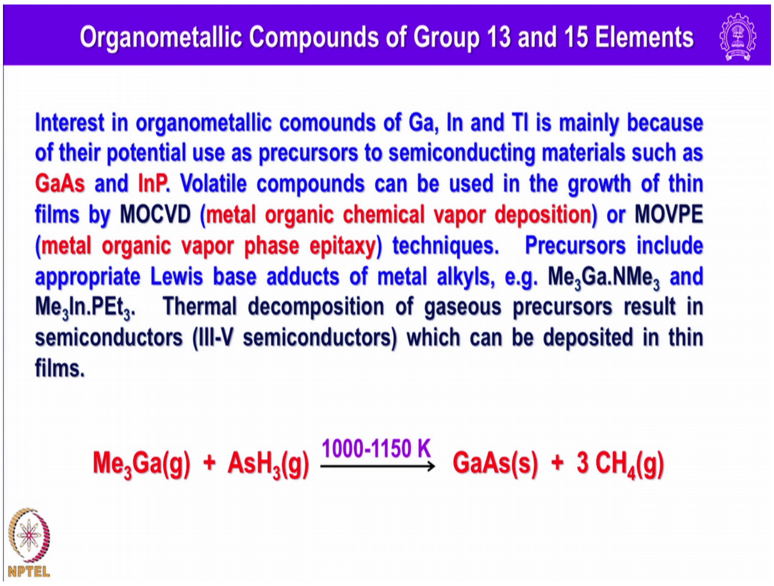

So, interesting organometallic compounds of gallium, indium and thallium is mainly because of their potential use as precursors to semiconducting materials, such as gallium arsenide and the indium phosphide. So, volatile compounds can be used in the growth of thin films by MOCVD. MOCVD is nothing, but metal organic chemical vapor deposition or MOVPE metal organic vapor phase epitaxy techniques.

So, precursors include appropriate Lewis base adducts of metal alkyls example if you take methyl, gallium adduct of trimethylamine or methyl, trimethyl indium adduct of triethylphosphine you should see here. So, trimethyl gallium is highly volatile, and trimethylamine is volatile similarly here trimethyl indium is volatile and triethylphosphine is volatile. So, preferably volatile compound should be taken in this metal organic chemical vapor composition. So, thermal decomposition of gaseous precursors results in the semiconductor 3 and 5 semiconductors, which can be deposited in thin films. A typical method I have shown here trimethyl gallium at high temperature.

So, gaseous trimethylgallium when it stated with arsine heated to1000 to 1150 kelvin, gallium arsenide is formed along with the liberation of only methyl here.

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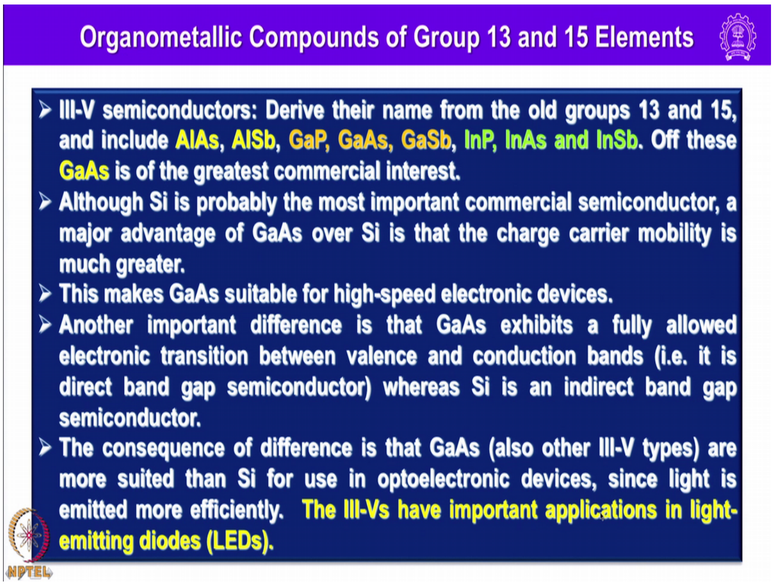

So, 3 5 semiconductors derive their name from the old groups 13 and 15, and include aluminium arsenide, aluminium (Refer Time: 26:09) sb, and gallium phosphide, gallium arsenide and also antimonite. indium password in a indium arsenide. and indium antimonite of these gallium arsenide is of the greatest commercial interest. All those silicon is probably the most important commercial semi conductor, a major advantage of gallium arsenide over silicon is that the charge carrier mobility is much greater this makes gallium arsenide suitable for high speed electronic devices. So, another important difference is that gallium arsenide exhibits a fully allowed electronic transition between valence and conduction bands, that is it is a direct band gap semiconductor whereas, silicon is an indirect band gap semiconductor. So, one should know the difference between these 2, the consequence of difference is that gallium arsenide also other 3 and 5 types are more suited then silicone for use in optoelectronic devices, since light is emitted more efficiently. So, this 3-5 types have important application in light emitting diodes as well. So, LEDs. So, let me stop here in my next lecture I will conclude the organometallic chemistry of main group elements.

Thank you very much.