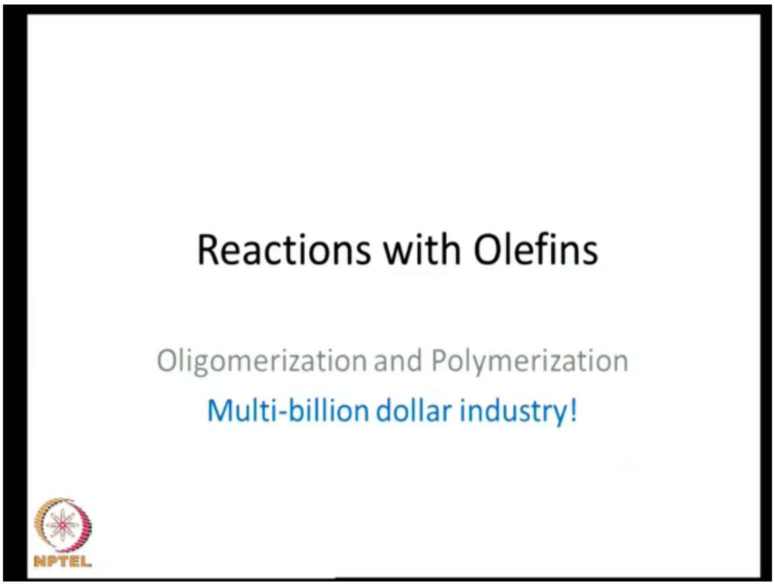
Introduction to Organometallic Chemistry
Prof. A. G. Samuelson
Department of Inorganic and Physical Chemistry
Indian Institute of Technology, Bombay

Lecture - 36
Organometallic polymerization

This lecture is regarding the reactions of olefins or the reactions, where olefins are the prime actors in the whole chain.

(Refer Slide Time: 00:21)



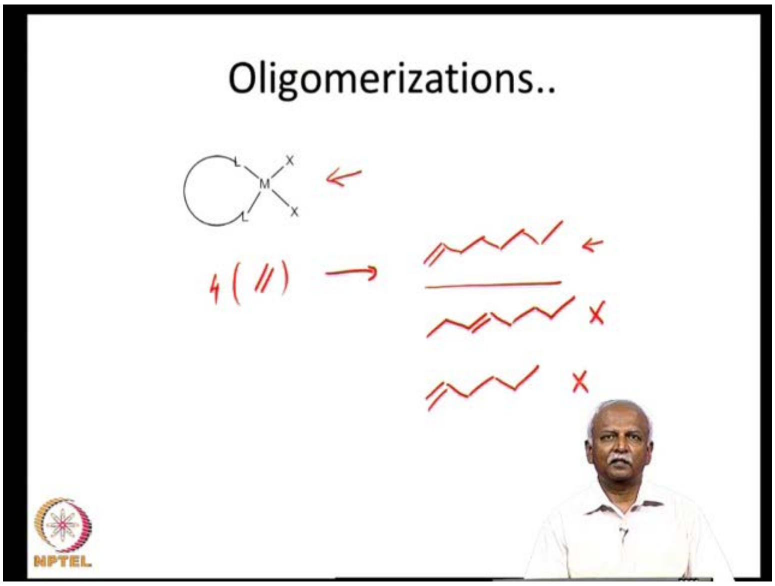
Reactions with Olefins

Oligomerization and Polymerization

Multi-billion dollar industry!

There are two major reactions that we are talking about. One is the oligomerization, the other is the polymerization of olefins. Both of them are probably multi-billion dollar industries. There is a large demand for products that are generated from simple olefins like ethylene and propylene. And so it is important that we look at the chemistry behind these systems.

(Refer Slide Time: 01:06)

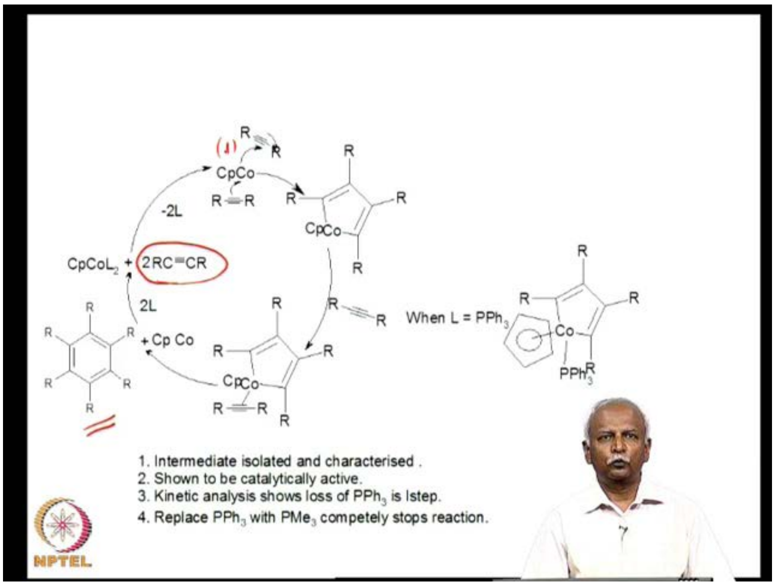


Oligomerizations..

Oligomerizations are basically talking about a systems where the molecule for example, you have an alkene, if you take something like a four alkenes and if you end up with this product. So, you have a system where you have oligomerized or combined together several of these olefins. Then it becomes a more useful product than ethylene itself which is useful. But not necessarily in the way a tetramer of the ethylene is useful. And so it is important to look at these molecules or the molecules the metal complexes which will carry out such oligomerizations.

A large number of molecules appear to do this and the challenge is to do it specifically. Meaning you want only the octane you want to only the one octane. So, you do not want this. And you also, want you do not want the molecule to proceed to hexene when you are trying to synthesize octene. So, this type of a specificity in the position of the double bond and in the oligomerization number that makes the whole chemistry challenging.

(Refer Slide Time: 02:53)

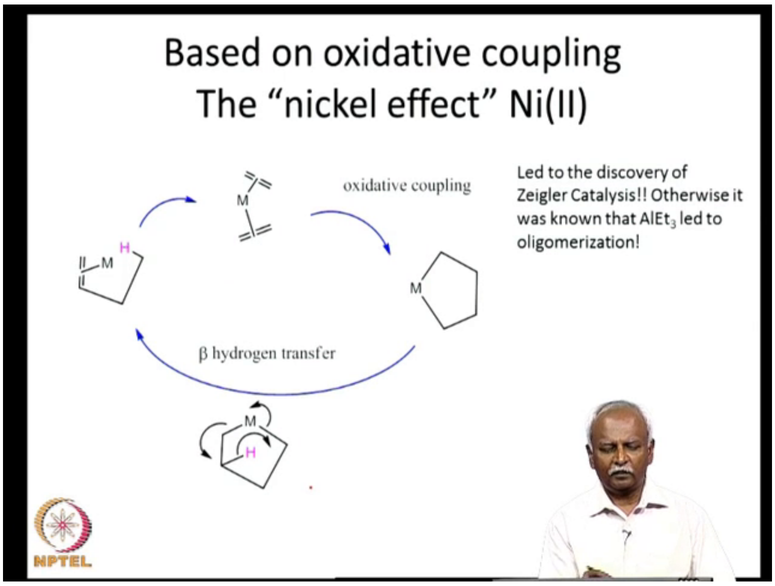


1. Intermediate isolated and characterised .
2. Shown to be catalytically active.
3. Kinetic analysis shows loss of PPh_3 is Istep.
4. Replace PPh_3 with PMe_3 competely stops reaction.

We have already looked at one type of chemistry where multiple alkynes were stitched together to generate different molecules. And the oligomerization that we discussed in detail just to remind you of what is possible was the cobalt catalyzed cyclotrimerization of acetylene to give you arenes. Arenes were the product simple alkynes were starting materials.

So, you stitched together three alkynes together to get an arene. This was done by an oxidative addition mechanism where the cobalt which is a cobalt one species oxidatively added, and at the same time coupled two carbon fragments. A similar reaction could be envisaged with alkenes. So, you can take alkenes, put two alkenes and then you would get a metallo cyclopentane. And that could be used to stitch together a variety of alkenes.

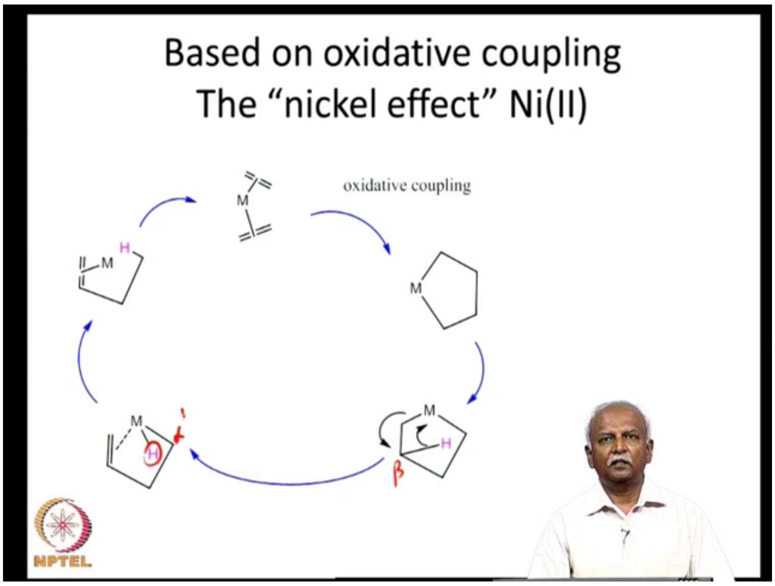
(Refer Slide Time: 04:04)


Based on oxidative coupling
The “nickel effect” Ni(II)

Led to the discovery of Zeigler Catalysis!! Otherwise it was known that $AlEt_3$ led to oligomerization!

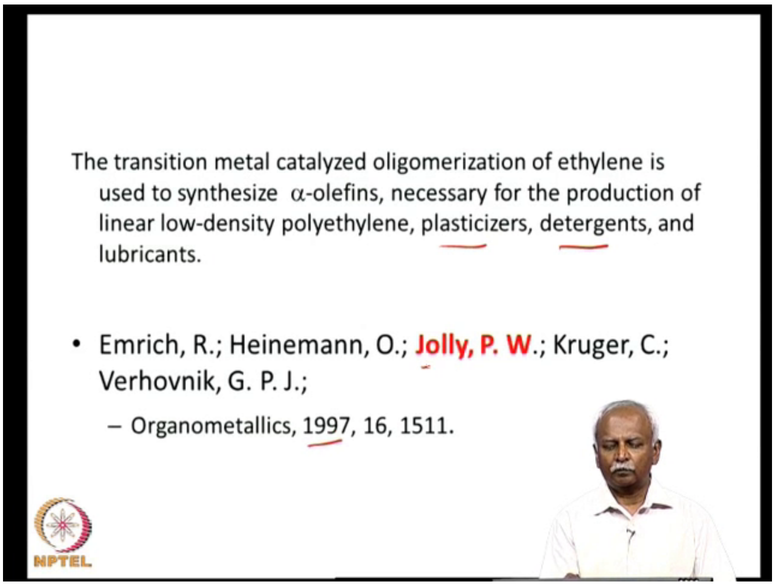
So, the two processes that can happen are one direct transfer of hydrogen from the beta position to the alpha dash carbon.

(Refer Slide Time: 04:17)


Based on oxidative coupling
The “nickel effect” Ni(II)

And the other is a transfer of hydrogen from the beta position, which is this position to the metal. And then a second reductive elimination to the alpha dash carbon. So, either mechanism it is the beta hydrogen which is transferred to the alpha dash carbon.

(Refer Slide Time: 04:41)

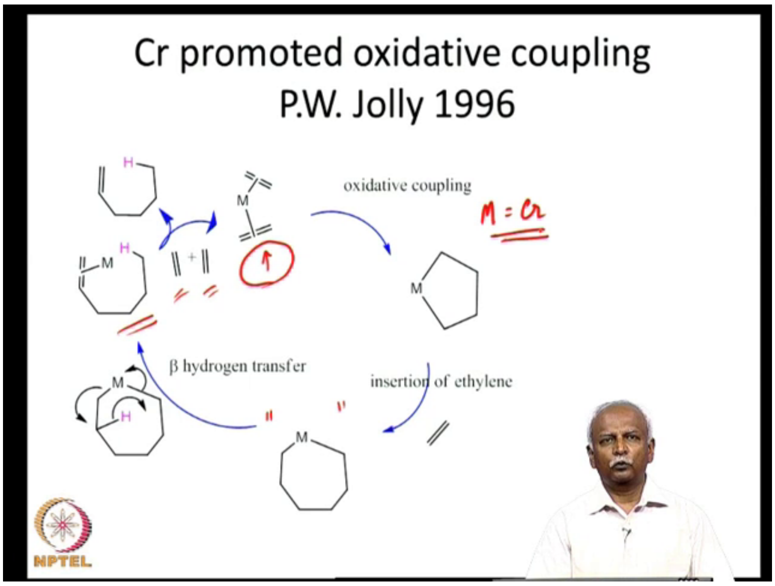


The transition metal catalyzed oligomerization of ethylene is used to synthesize α-olefins, necessary for the production of linear low-density polyethylene, plasticizers, detergents, and lubricants.

- Emrich, R.; Heinemann, O.; **Jolly, P. W.**; Kruger, C.; Verhovnik, G. P. J.;
  - Organometallics, 1997, 16, 1511.

Now, it turns out that butene is a useful molecule. But it would be valuable to have hexene as a product. So, that means you need to trimerize an olefin. And a synthesis of alpha olefins that means where the double bond is present in the alpha carbon is very important for the production of a variety of materials used in bulk quantities in the industry. And these are listed here, that is low density polyethylene, plasticizers, detergents and so on.

(Refer Slide Time: 05:34)



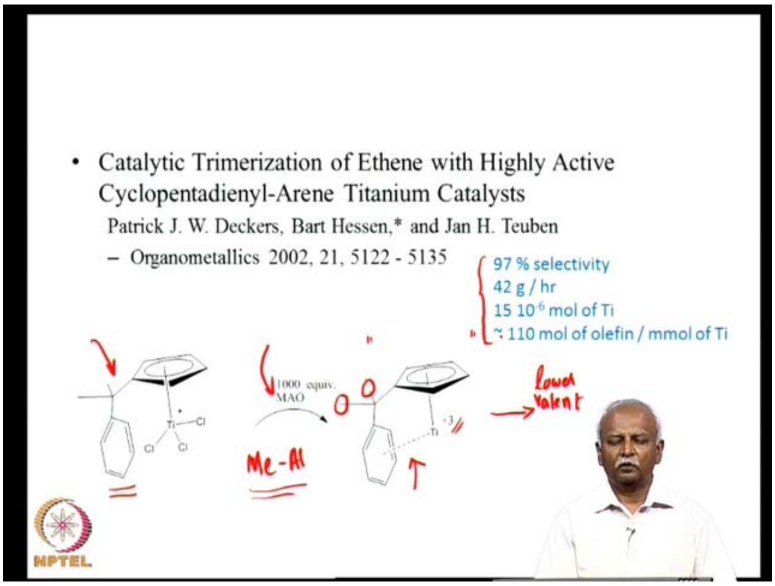
Cr promoted oxidative coupling
P.W. Jolly 1996

So, it was only recently in 1997 that a well cleaned catalyst was discovered by this person Jolly, who figured out that chromium is a suitable metal for carrying out this oxidative coupling of three ethylenes to produce hexane. The mechanism is very similar to what we had seen earlier.

You combine two alkenes. In this case two ethylenes as the most popular and the most cheaply available alkene that people use to synthesize a metallo cyclopentane insito. Insert another ethylene molecule to generate a metallo cycloheptane. Now, the generation of a metallo cycloheptane can result in the formation of an alkene which can which will be in the alpha position due to beta hydride hydrogen elimination. And this beta hydrogen transfers identical to what we had discussed earlier. It can happen directly or it can happen through a metal hydride intermediate and result in this olefin complex. Now, we know that substituted olefins are less stable than unsubstituted olefins.

So, referentially you would have exchange of this hexene with this ethylene molecules in order to generate this catalytically active species which is written here. In this particular case M equals chromium is the best option. And a variety of chromium complexes have been tested for this particular reaction. You will notice that in the case of nickel where you had a D eight system. You were able to couple two ethylene’s. In the case of a D six you are able to couple three alkenes. So, there seems to be a very strong electronic effect in the coupling of alkenes to generate the final product. You just keep this in mind as we go ahead with a discussion. So, the obvious extension for this would be to perceive to a D four system.

(Refer Slide Time: 07:46)



- Catalytic Trimerization of Ethene with Highly Active Cyclopentadienyl-Arene Titanium Catalysts
  Patrick J. W. Deckers, Bart Hessen,* and Jan H. Teuben
  - Organometallics 2002, 21, 5122 - 5135

97 % selectivity
42 g / hr
15 10^{-6} mol of Ti
∵ 110 mol of olefin / mmol of Ti

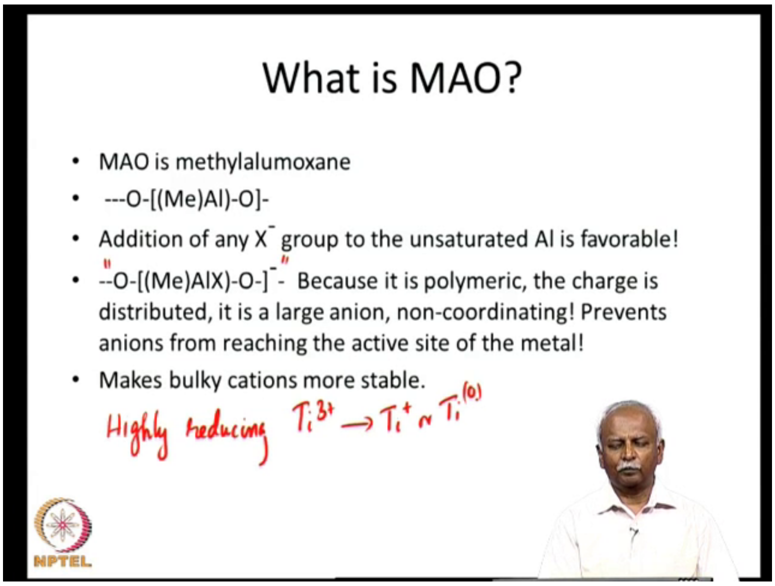
In fact if you use a D four system what you expect is a tetramerization. But it turns out as early as late as 2002. It was discovered that the tetramerization of titanium is tetramerization of ethylene is not what you observe but you end up with a trimerization. A very efficient trimerization of ethylene inorder to generate hexane. And in all these cases we are talking about the formation of one hexene which is a more useful product. Now, there are couple of more things that we need to emphasize this is not the only complex that has been tried.

I have picked up the examples which are most efficient and probably recent in the literature. And in this case the design involves several important factors. One of them is the presence of this benzene ring in a position suitable for having this weak interaction which is marked here with a dotted line. This stabilizes the catalytically active intermediate. Although it is a weak bond it is a titanium three plus complex that is involved. A weak bond but that interaction is responsible for the formation of a catalytically active species.

The other important point to note is that the bridge size here. The number of carbons and substituent’s present on this bridge play an important role. And the best catalyst was in fact with two methyl groups at this position. And also with a single carbon. So, that it is interaction is not too strong and it is not too weak either. I have to explain also what this particular molecule M A O is. M A O a mysterious aluminium oxide, it iss methyl alumina oxane.

And it is the polymeric compound which has been used extensively in the polymer industry and it has got a methyl aluminium bond. And this methyl aluminium bond is capable of carrying out a reduction of this titanium three species to a lower valent species. So, this lower valent species is presumably a responsible for this oxidative coupling reaction which leads to very high selectivity, very efficient selectivity for the trimerization of ethylene.

(Refer Slide Time: 10:51)



What is MAO?

- MAO is methylalumoxane
- ---O-[(Me)Al)-O]-
- Addition of any X^- group to the unsaturated Al is favorable!
- --O-[(Me)AlX)-O-]$^-$- Because it is polymeric, the charge is distributed, it is a large anion, non-coordinating! Prevents anions from reaching the active site of the metal!
- Makes bulky cations more stable.

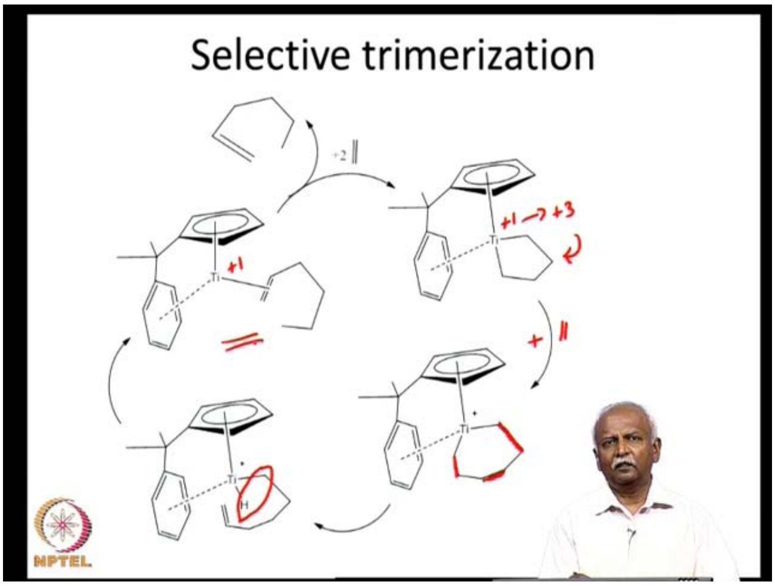
Highly reducing $Ti^{3+} \rightarrow Ti^{+}$ or $Ti^{(0)}$

Now, let us talk a little bit more about M A O. Because this is a molecule which we are going to talk about more extensively. And it is basically a polymeric species where you have a methyl aluminium bond. What does it do? It essentially removes an X minus group to the saturated aluminium which is coordinatively unsaturated and which can accept an X minus to form an anionic species. And here is the possible anionic species that would be formed if the aluminium picks up an X minus from the catalytically active species, but if it is just picking up an anionic species one would need only one aluminium per X group that you need to remove.

So, in the previous example we had three chloride groups which are present on the titanium. So, depending on the number of titanium and chloride bonds that you want to reduce you would need one methyl alumoxane. But you remember that number of methyl alumoxane molecules that are usually added to the catalytically active species is very large and this is a problem that chemists have been trying to solve and are struggling with the oligomerization and polymerization reaction. But let us continue with this species what else does it do? Because you can abstract an X group and form an anion it forms a very active species which is stabilized because the large anion the polymeric anion that is formed is non-coordinating.

It basically prevents other anions from reaching the titanium three plus site. And finally because of the methyl aluminium bond it is highly reducing. So, that is a point that has to be added. It is highly reducing so it would convert the titanium three plus to a titanium plus or titanium zero species. Even the presence of methyl alumoxane can reduce the titanium completely.

(Refer Slide Time: 13:38)



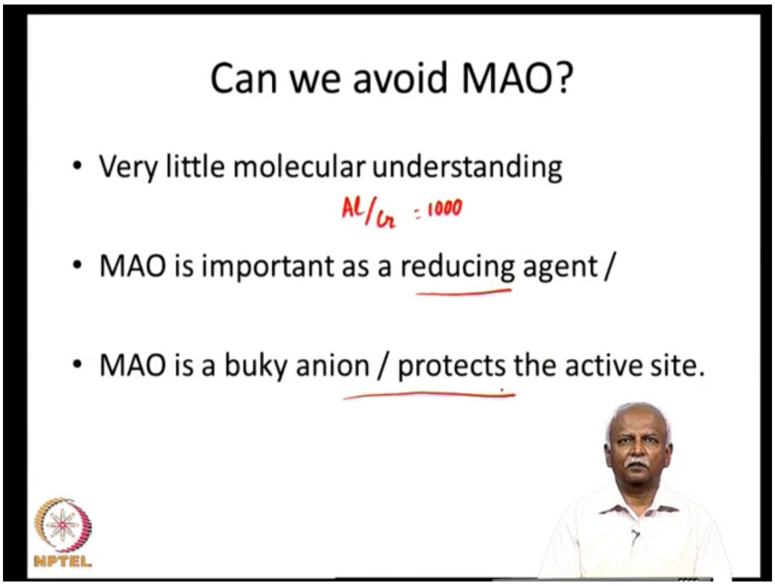
Selective trimerization

So, let us just take a minute and look at a possible catalytic cycle that would be involved in the selective trimerization of olefins. So, the mechanism that we have written here is using titanium. The titanium 1 plus species which we have indicated here as plus 1. The oxidation state is plus 1 here and we have reduced titanium from plus 3 to plus 1. After oxidative addition it becomes plus 3 and that is the plus 3 state that is involved in this reaction.

And then at the back end of this reaction it would come back to plus 1 and after oxidative addition becomes plus 3. So, if you add three alkenes so with every step you would add an ethylene molecule. You would end up with a metallo cycloheptane. And this metallo cycloheptane has got six carbons. Three ethylene's joined together and this is indicated by the three ethylene's which are coming together to form a metallo cycloheptane. And this can now by abstraction of the beta hydrogen.

The beta hydrogen elimination has been already explained. An identical reaction happens and now I have transferred it to the metal titanium here. And this species can undergo a reductive elimination of these three of these two units. And that gives you the olefin complex which is the titanium 1 complex and the titanium complex. Because it has got a hexene coordinated it prefers ethylene's exchanges for the ethylene and the catalytic cycle continues. So, the reaction apparently goes through this type of a catalytic cycle which is very similar to the one that we have noticed for chromium and nickel.

(Refer Slide Time: 15:52)



Can we avoid MAO?

- Very little molecular understanding

Al/Cr = 1000

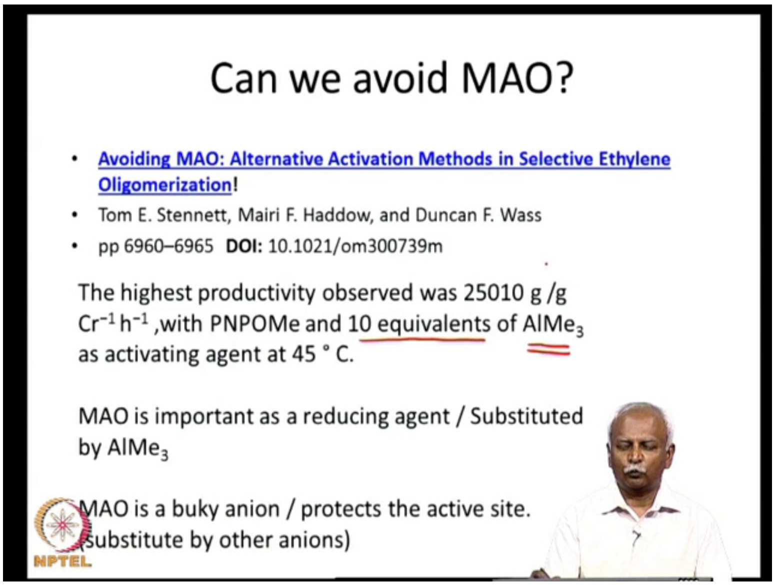
- MAO is important as a reducing agent /
- MAO is a buky anion / protects the active site.

Now, let us just take a brief minute to ask this question. Can we avoid the M A O or the M A O? The M A O is used in very large amounts. Usually it is used in the ratio 1:1000. If the catalytically active metal is chromium, the ratio of aluminium to chromium would be atleast thousand. So, this type of a excess use of M A O has been found to be a essential. So, that leads to very little molecular understanding.

Usually if you have, if you need a molecular understanding, one should have some stochiometric reaction of the two entities that are involved. Here chromium and aluminium are present in such a large ratio that a molecular understanding is avoided.

Now, the two important functions that we have just reviewed are that it is a good reducing agent and we have seen that it protects the active site.

(Refer Slide Time: 17:08)



Can we avoid MAO?

- **Avoiding MAO: Alternative Activation Methods in Selective Ethylene Oligomerization!**
- Tom E. Stennett, Mairi F. Haddow, and Duncan F. Wass
- pp 6960–6965 **DOI:** 10.1021/om300739m

The highest productivity observed was 25010 g /g $Cr^{-1} h^{-1}$,with PNPOMe and 10 equivalents of $AlMe_3$ as activating agent at 45 ° C.

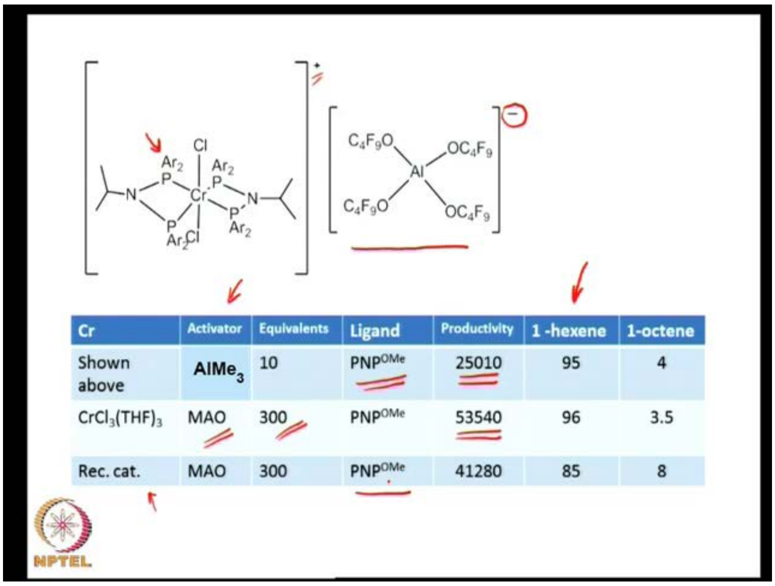
MAO is important as a reducing agent / Substituted by $AlMe_3$

MAO is a buky anion / protects the active site. (substitute by other anions)

So, recently it has been possible as is very recently it has been shown that M A O can be avoided. And it has been a substituted by two different strategies. One is to use aluminium, trimethyl aluminium as a reducing agent. The other was to use a very large bulky anion. We will show this in the next slide. But basically the use of a large very large amount of aluminium have been avoided.

And stochiometric amounts are close to stochiometric amounts of trimethyl aluminium are used in this whole reaction. And in this specific case about ten equivalents of trimethyl aluminium were added. And this is a far cry from the thousand equivalents which is usually used in order to achieve very large efficiencies of the order that is shown here. So, let us see what happens in this reaction.

(Refer Slide Time: 18:19)



Cr	Activator	Equivalents	Ligand	Productivity	1 -hexene	1-octene
Shown above	$AlMe_3$	10	PNP^{OMe}	25010	95	4
$CrCl_3(THF)_3$	MAO	300	PNP^{OMe}	53540	96	3.5
Rec. cat.	MAO	300	PNP^{OMe}	41280	85	8

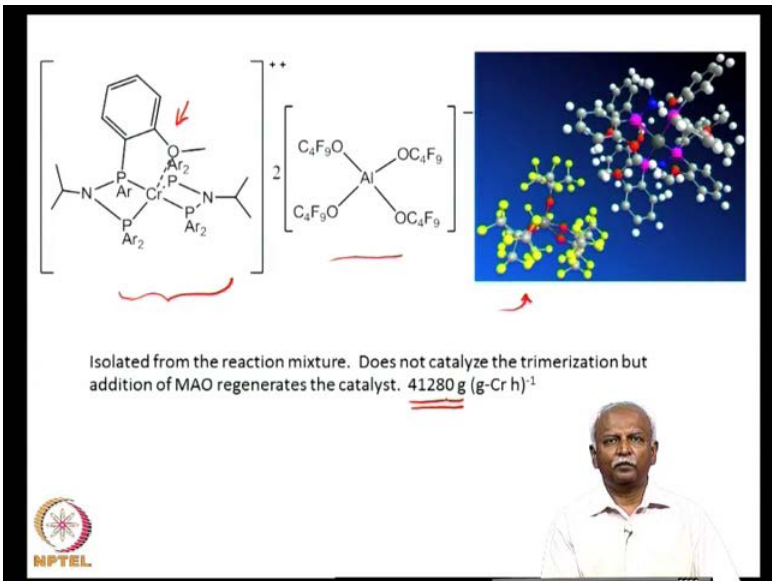
Here is the chromium complex that was used. It is a chromium dichloride. A dichloro complex of chromium with a net charge of plus 1. The net charge of plus 1 indicates that chromium is in the plus 3 oxidation state. The bulky anion that was used was this perflourinated butoxide ion. So, perfluorobutoxide anion or tetra perfluro butranyl is what you have here. Four of these coordinated to the aluminium so much so that the a single negative charge is there on the aluminium resulting in a very large bulky anion. And at the same time you have a chromium two plus species as a starting material. If it is treated with this activated which is aluminium trimethyl aluminium. This is a lower case here trimethyl aluminium.

Then ten equivalents were sufficient to bring about a substantial productivity. This is the grams of polyethylene, grams of the oligomerized ethylene, per gram of the chromium that is used. This is how the efficiency is measured. So, this is grams of ethylene oligomerized for each gram of chromium that is utilized in the reactions. So, the ligand that we have here we have not expanded it. But this is the special ligand which has got the methoxy group on the aryl moiety which is attached to the phosphorous.

This A r has got a O M e group and that turns out to be critical because it stabilizes the chromium after it is activated by the trimethyl aluminium. For the sake of comparison, the researchers have also carried out the same reaction in the with M A O. And they have noticed that you need close to 300 equivalents of M A O inorder to carry out the same reaction in the absence of this bulky anion and in the presence of the methyl alumoxen as a reducing agent.

But you will notice that the activity that we get with this bulky anion is not as good as what you would get with trimethyl alumoxane. But the selectivity for hexene which is group one of the important parameters is still retained. And you will also realize that we have moved from a chromium 3 plus complex to a chromium. Probably chromium zero species which is carrying out the actual reaction. One very important criterion in this whole process is that the recovered catalyst, the recovered catalyst can be used again and it has almost as good an activity when you use this ligand as the starting material itself.

(Refer Slide Time: 21:38)



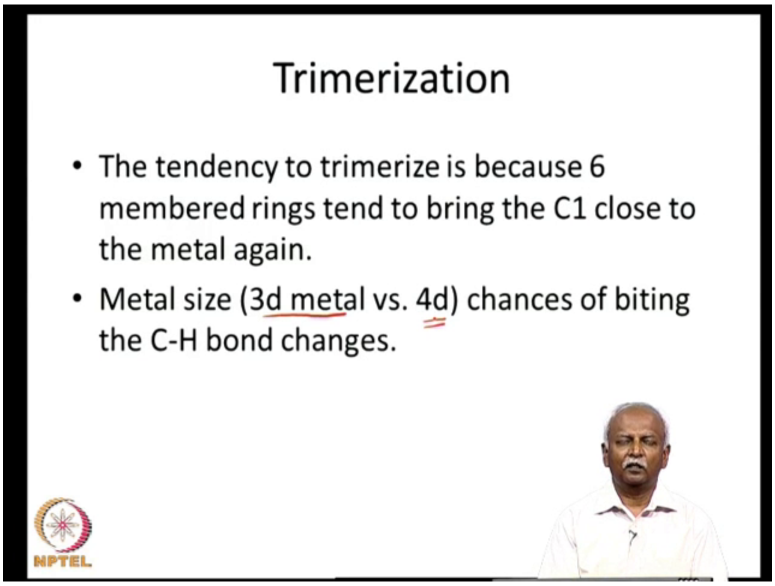
Isolated from the reaction mixture. Does not catalyze the trimerization but addition of MAO regenerates the catalyst. 41280 g (g-Cr h)$^{-1}$

So, let us take a look at the recovered catalyst that they have characterized which is I think a very significant. This is a very significant observation that they have made during the course of this reaction. They have shown that the chlorides have been removed and a coordinatively unsaturated species of chromium 2 plus is generated in the reaction medium and they have isolated a crystalline material which they have identified.

And I have shown the crystal structure here and you will notice that the anion that you have. That is the tetra alcoxy species. Aluminate species which is behaving as a anion is shown here. And the green fluorescent atoms are flourines and you can see that the whole aluminium is completely encapsulated by this fluoresce sphere. And so, it becomes a very large stabilizing anion and the chromium species is also covered by this very bulky phosphinoamine that we have used a ligand.

And this oxygen that is there in the ortho position of the aryl group is responsible for stabilizing the chromium in its coordinatively unsaturated state. If you look at the crystal structure which is freely available on the website of the journal you would be able to understand the interactions a little more. But I have shown you one interaction on the screen right here. And using this catalyst it was possible to catalyze the reaction very efficiently and generate one hexene in a very selective fashion.

(Refer Slide Time: 23:36)

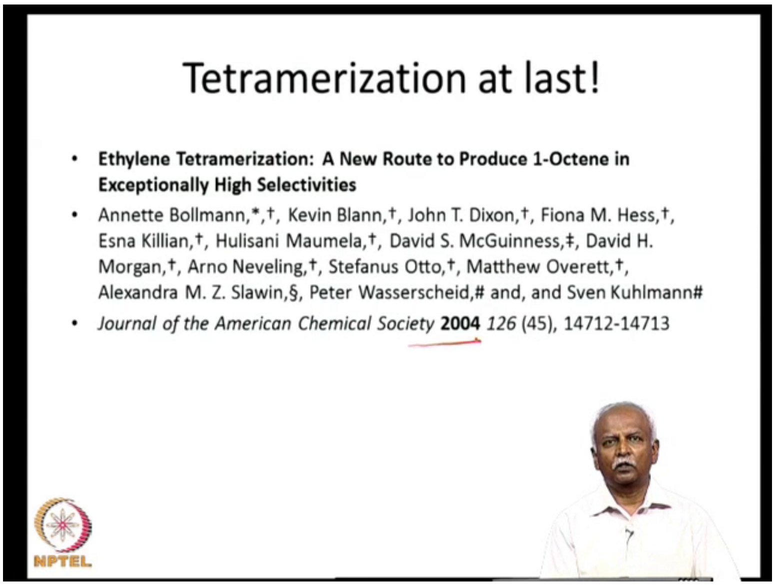


Trimerization

- The tendency to trimerize is because 6 membered rings tend to bring the C1 close to the metal again.
- Metal size (3d metal vs. 4d) chances of biting the C-H bond changes.

You will notice that the tendency to trimerize is fairly significant. And what it tells us is when the molecule oxidatively adds and inserts ethylene it tends to form a cycloheptane metallocycloheptane molecule and that has got a beta hydrogen extremely close to the metal. And bringing the C 1 close to the metal becomes more it becomes more favorable when you have this ring size. So, the metal size is also important. Most of these oligomerizations have been carried out with three D metal ions. Three D metal ions have been used for making the oligomers and it is not the four D. And we can see the chances of biting the C H bond changes when you have a three D versus a four D. So, the three D metal turns out to be good for making oligomers.

(Refer Slide Time: 24:43)

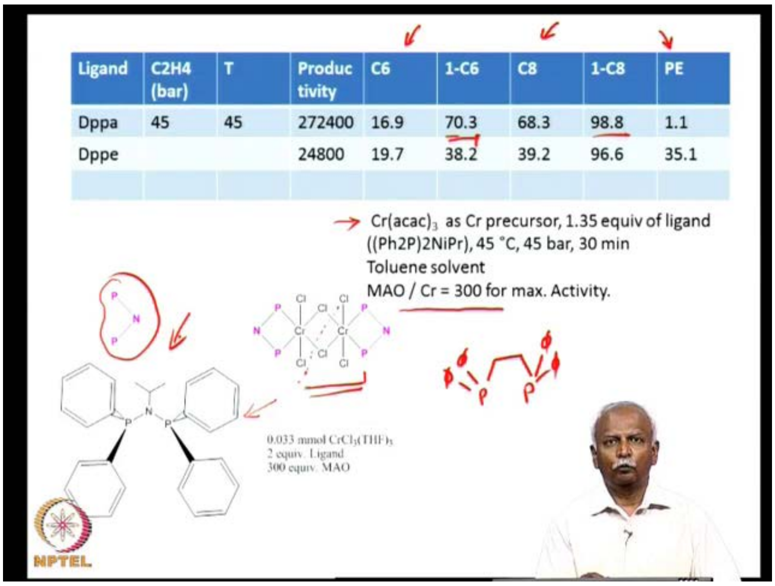


Tetramerization at last!

- **Ethylene Tetramerization: A New Route to Produce 1-Octene in Exceptionally High Selectivities**
- Annette Bollmann,*,†, Kevin Blann,†, John T. Dixon,†, Fiona M. Hess,†, Esna Killian,†, Hulisani Maumela,†, David S. McGuinness,‡, David H. Morgan,†, Arno Neveling,†, Stefanus Otto,†, Matthew Overett,†, Alexandra M. Z. Slawin,§, Peter Wasserscheid,# and, and Sven Kuhlmann#
- *Journal of the American Chemical Society* **2004** *126* (45), 14712-14713

Now, in all the cases that we have mentioned including the one on titanium where we expected a tetramerization, we saw only the trimerization of the ethylene. So, it is indeed a gratifying to note that eventually chemists have solved this puzzle and they have discovered a catalyst which can do tetramerization. That means if you tetramerize ethylene you get octane. And if you can make specifically one octene it would be an extremely good achievement. That is what the researchers have discovered and they have published this paper in the Journal of the American Chemical Society in 2004.

(Refer Slide Time: 25:27)



Ligand	C2H4 (bar)	T	Productivity	C6	1-C6	C8	1-C8	PE
Dppa	45	45	272400	16.9	70.3	68.3	98.8	1.1
Dppe			24800	19.7	38.2	39.2	96.6	35.1

Cr(acac)$_3$ as Cr precursor, 1.35 equiv of ligand ((Ph2P)2NiPr), 45 °C, 45 bar, 30 min
Toluene solvent
MAO / Cr = 300 for max. Activity.

0.033 mmol $CrCl_3(THF)_3$
2 equiv. Ligand
300 equiv. MAO

So, let us just take a look again. It is a phosphinoamine that has been used and in this particular instance they have used a very common ligand which is bisdiophenyl phosphino compound where you have an isopropyl group on the nitrogen. So, you just take isopropyl amine and treat it with P Ph 2 C l and you get this very easy to synthesize ligand. That ligand is abbreviated in this pink form here.

And the complex that they isolated and characterized was as shown here. And that is the complex that they used as the starting material. But in this case also a MAO was used as an activating agent. MAO was the best activating agent that has been used and they have used about 300 equivalents of MAO in a toluene solvent. In order to achieve this very high selectivity for tetramerization what is interesting is that, both C 6 and C 8 are formed in this reaction.

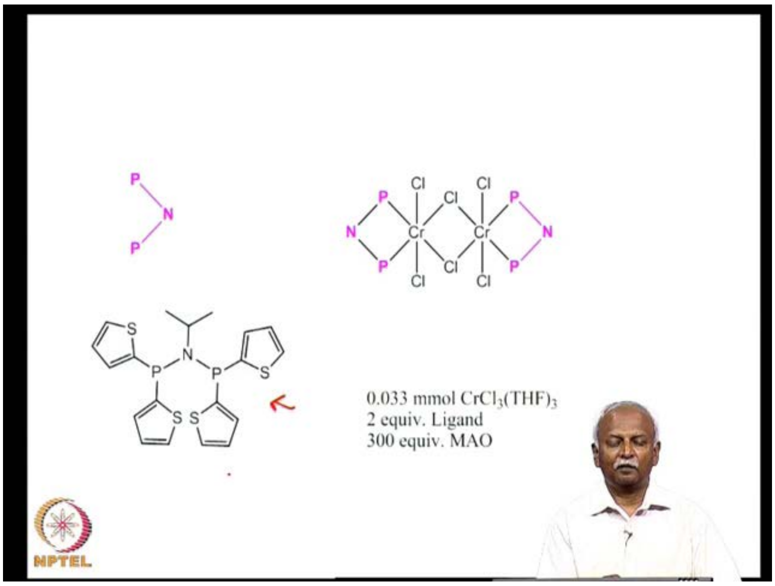
So, obviously that is tendency for the chromium to add another ethylene and form a cyclononane. And it is the cyclononane which has the right orientation inorder to do this C h abstraction. And you will notice that in the case of this ligand which they have this P N P ligand. It is possible to achieve very high selectivity for C 8. And what is written here is this C 6 selectivity. C 6 versus C 8 selectivity can be seen here. So, that is 17 percent versus 68 percent. C 6 versus C 8 in the case of Dppe.

And within that you will see that one hexene turns out to be about 70 percent. So, that means that the remaining 30 percent of the hexene are internal olefins. Similarly, out of 70 percent or 68 percent of the C 8 octene that is formed, 98 percent is one octane. So, that is excellent selectivity. The one octene which is what we really need in the industry. And if you look at the remaining amount it is mostly polyethylenes.

So, this is the polymeric species which is formed which is also formed in small amounts. So, we do not have to go through the catalytic cycle again. But sufficed to say that in the process of large amounts of methyl alumoxene. The chromium which is present here in the three plus state, if you draw a line here you will realize that a dimer has got three chlorines for each chromium. And so it is chromium in the plus 3 state. In the starting material is reduced in the presence of MAO to the chromium 1 plus or chromium 0 species which then carries out this catalytic function.

Now, it was also possible to use chromium acac directly as a precursor that makes the reaction fairly easy to handle in the laboratory. A very simple complex called Dppe diphenyl phospheno ethane which has got two phenyl groups on each phosphorous can also be used as a catalyst. And surprisingly that gives you a significantly less activity. But the C 8 selectivity is also poor. So, clearly the P N P ligand is a much better ligand if you want to synthesize the octane.

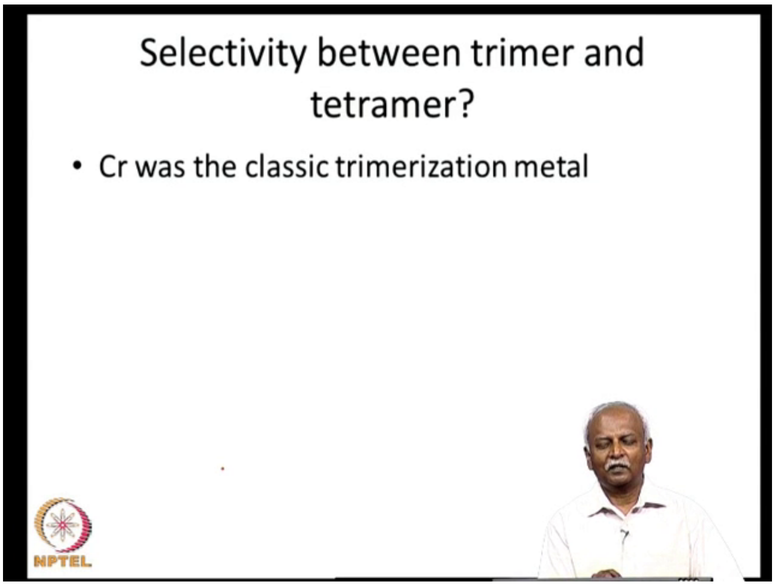
(Refer Slide Time: 29:50)



0.033 mmol $CrCl_3(THF)_3$
2 equiv. Ligand
300 equiv. MAO

Now, it is clear that the electronic effect of the P N P and also we shall see the steric effect is an important factor. Now, these researchers although I have only shown you two ligands. These researchers have tried a large library of P N P ligands as well some of them as exotic as a vinyl substituent on the phosphorous. But these are two ends. Although the one that is pictured for you here is sufficiently reactive. It is not necessary to use this exotic ligand. And the ligand that we saw earlier that this diphenyl phospheno amine is itself quite useful for carrying out selective octomeric tetramerization of the ethylene to produce octene.

(Refer Slide Time: 30:43)

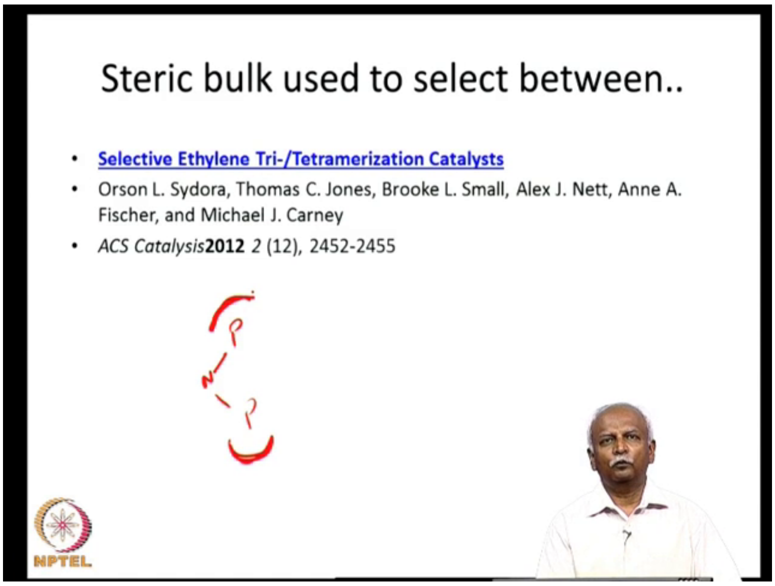


Selectivity between trimer and tetramer?

- Cr was the classic trimerization metal

So, now we have seen that chromium which we had originally touted as a main metal which would do trimerization is useful for tetramerization. So, chromium was a classic trimerization metal.

(Refer Slide Time: 31:01)

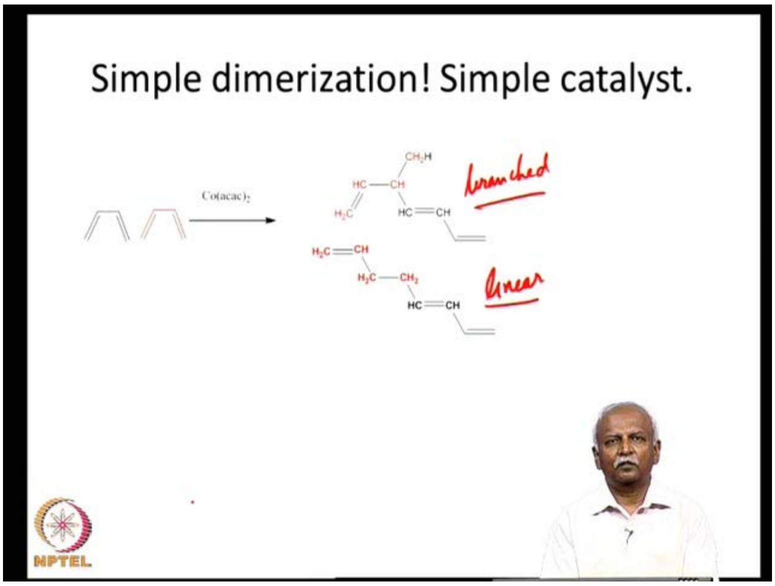


Steric bulk used to select between..

- Selective Ethylene Tri-/Tetramerization Catalysts
- Orson L. Sydora, Thomas C. Jones, Brooke L. Small, Alex J. Nett, Anne A. Fischer, and Michael J. Carney
- *ACS Catalysis* **2012** *2* (12), 2452-2455

So, how is it that we are able to do tetramerization? So, more research has gone on in this area and a very recent paper published American Chemical Society Journal called catalysis tells us about the selectivity between trimerization versus tetramerization. And what they have shown is that this steric bulk on the ligand which we use. So, the P N P ligand that you have this steric bulk on this ligand is responsible for the selectivity between trimerization and tetramerization. The more bulky the ligand it is likely that they give you the teramerizsation catalyst. So, not only electronic steric effects are also very important inorder to decide between the trimerization or the tetramerization.

(Refer Slide Time: 31:57)

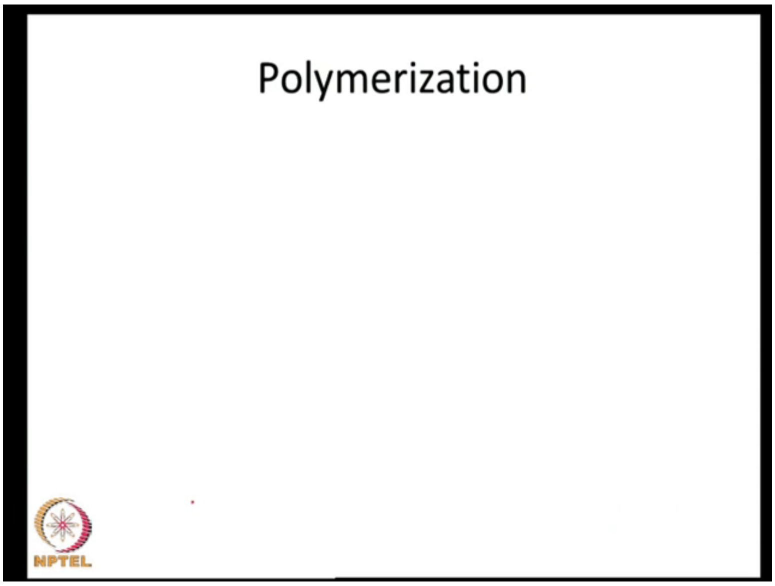


Simple dimerization! Simple catalyst.

So far we have talked about a trimerization, a tetramerization and so on. We can also do reactions with multiple yields which means dienes and trienes and a variety of reactions are known. But the principles are the same inorder to do a coupling reaction we would usually carry out an oxidative coupling reaction and that leads to the coupling of two dienes.

Here I have shown you two dienes which can couple in a linear fashion. This is a linear product and this is a branched product. So, these are these dienes are not so readily available as the ethylene is and so these reactions are less studied than the ethylene reactions that we have discussed. But sufficed to say that these reactions are also possible.

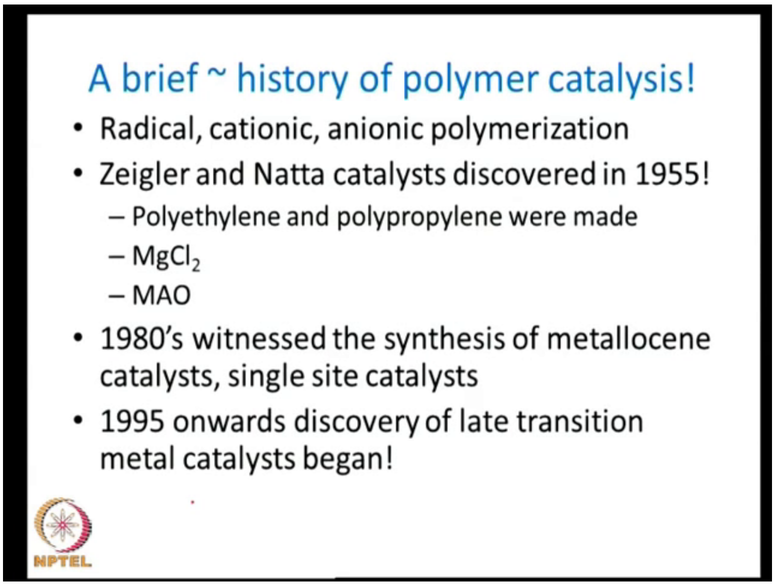
(Refer Slide Time: 33:01)



Polymerization

Now, let us take a look at polymerization. Why is polymerization so important? Because polymerization of ethylene to give you polyethylene is a very useful reaction. It polyethylene both low density polyethylene and high density polyethylene have got extensive industrial uses. And so it is important that we take some time and examine this particular process.

(Refer Slide Time: 33:33)



A brief ~ history of polymer catalysis!

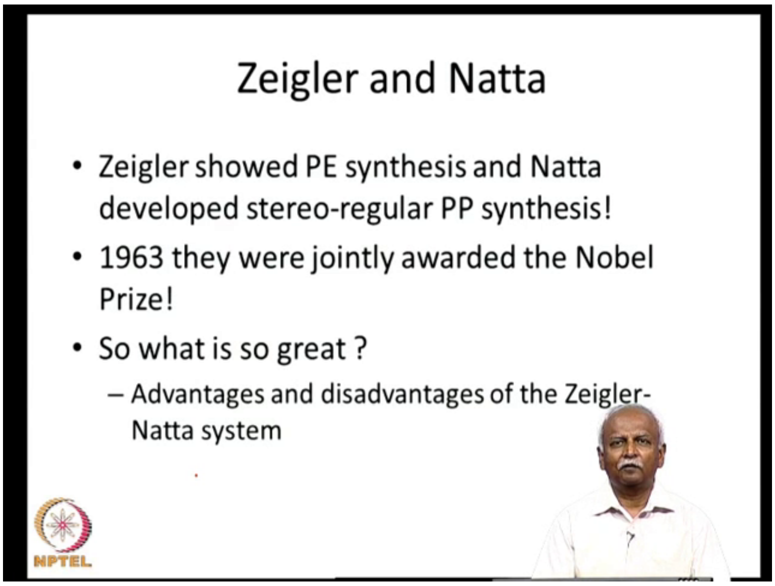
- Radical, cationic, anionic polymerization
- Zeigler and Natta catalysts discovered in 1955!
  - Polyethylene and polypropylene were made
  - $MgCl_2$
  - MAO
- 1980's witnessed the synthesis of metallocene catalysts, single site catalysts
- 1995 onwards discovery of late transition metal catalysts began!

Let me give you a brief history of the polymer catalysis. And I have listed here a series of events that are critical for the polymerization for understanding polymerization history. First of all the radical cationic and anionic polymerizations were known. But the molecular weights of the polymerized species were not as high as they were when Zeigler and Natta discovered metal catalysis in 1955.

So, polyethylene and polypropylene were first discovered and made popular. Essentially in the 1950s until then only polymers which were not having molecular weights were known and they were not reproducibly made. What Zeigler and Natta did is discovered was that not only are the metals titanium zirconium group metals are important. They also showed that the support on which these catalysts are kept in this particular case has shown you magnesium chloride and secondly the discovery of MAO. These things made a very big change in the catalysis industry.

So, in 1980s another very significant discovery was made and that was a fact that instead of using the group four transition metals, one can also use metallocenes which could perform a single side catalysis when you suspend the catalyst on or support the catalyst on magnesium chloride. The main feature of the catalyst is not very clear. However, metallocene catalysts are single side catalyst. Meaning they have a well characterized structure and there is only one type of an active species. We will see how this makes a difference a little bit later. Then more recently 1995 it was discovered that late transition metals can also do catalysis of ethylene.

(Refer Slide Time: 35:48)



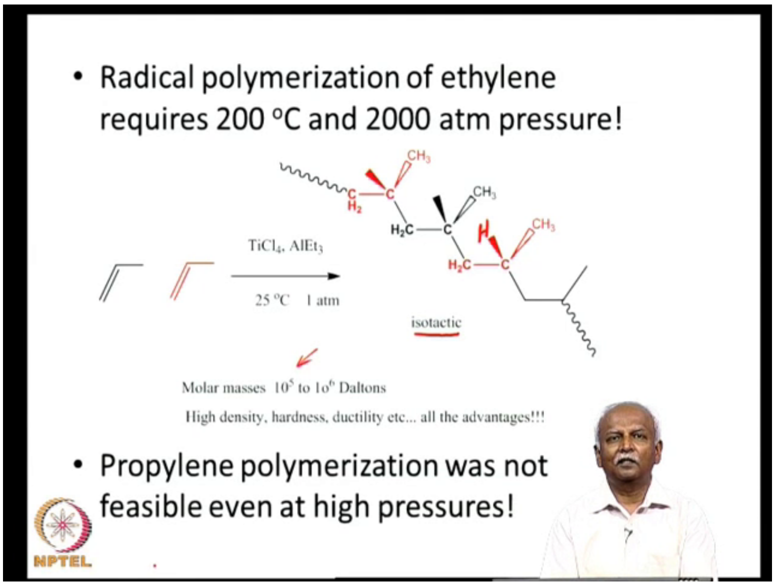
Zeigler and Natta

- Zeigler showed PE synthesis and Natta developed stereo-regular PP synthesis!
- 1963 they were jointly awarded the Nobel Prize!
- So what is so great ?
  - Advantages and disadvantages of the Zeigler-Natta system

So, let us proceed with Zeigler and Natta and we will not be talking about the properties of polymer, but essentially the mechanisms of polymerization and how the metals play a role important role in this polymer synthesis. So, Zeigler was the first one to show that polyethylene can be generated at very low pressures compared to what was done earlier at very low pressures.

They can be polymerized to generate useful polymeric materials. And it was Natta who extended it to polypropylene and that made a very big change in the polymer industry. As a result that 1955 discovery they were together the nobel prize in 1963. Now, we might be wondering what is so great about polymerization of ethylene or propylene and what are the advantages. There are significant advantages and disadvantages of the Zeigler Natta system and we will take a look at it in the following slides first of all.

(Refer Slide Time: 36:59)



- Radical polymerization of ethylene requires 200 °C and 2000 atm pressure!

Molar masses 10^5 to 10^6 Daltons

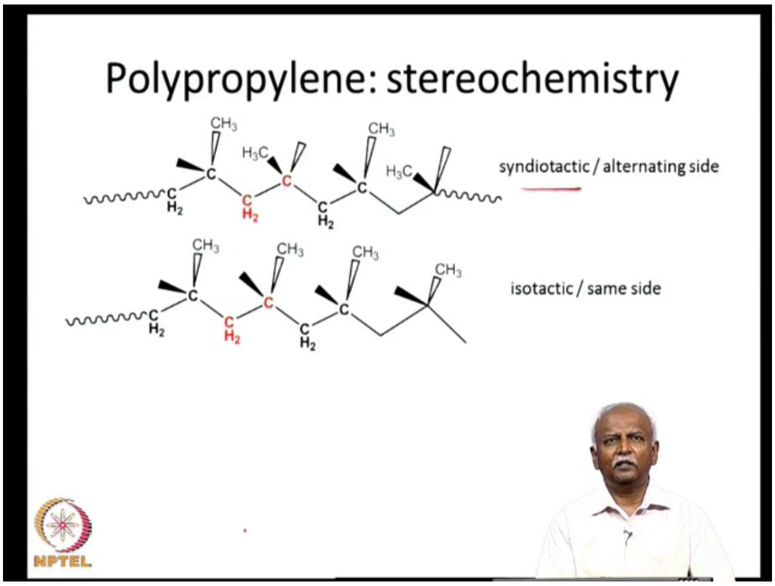
High density, hardness, ductility etc... all the advantages!!!

- Propylene polymerization was not feasible even at high pressures!

Radical polymerization as I mentioned earlier of ethylene requires a very high pressure of ethylene. And it also required a very high temperature and it led to significant amount of branching. And the polymers that were made using these procedures were not very useful. But one Natta polymerized propylene which is what is shown here he obtained what is called isotactic polymers. Isotactic polymers are those where the alkyl groups are organized in a same on the same side of the carbon in polymer chain. And I pictured for this for you here the a polymer chain which is as if it is in the plane of the screen. Then the methyl groups are going inside the screen. Whereas, the hydrogen which is present here is coming toward you.

So, if you keep all the carbons in a plane then the methyl groups are going away from you. And since all of them are going away from you it is called an isotactic polymer. Now, this turns out that the polymer characteristics are very important and these are dependent on the way in which these polymers act in the solid state. And the way they act depends on how these methyl groups are oriented. If they are isotactic they have excellent properties. So, not only that they are polymer molecular weights are very high it is about 10 power 5 to 10 power 6 dalton’s high density etcetera. And all of these are significant advantages.

(Refer Slide Time: 38:46)



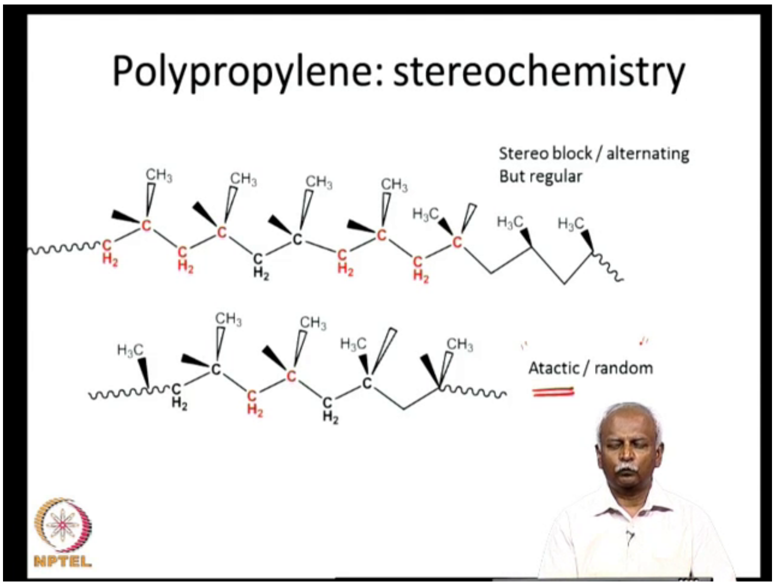
Polypropylene: stereochemistry

syndiotactic / alternating side

isotactic / same side

Propylene polymerization was not even possible. Although ethylene could be polymerized. Propylene was not polymerizable at all and even if was polymerized it generated a polymers with not so clear stereo chemistry.

(Refer Slide Time: 39:11)

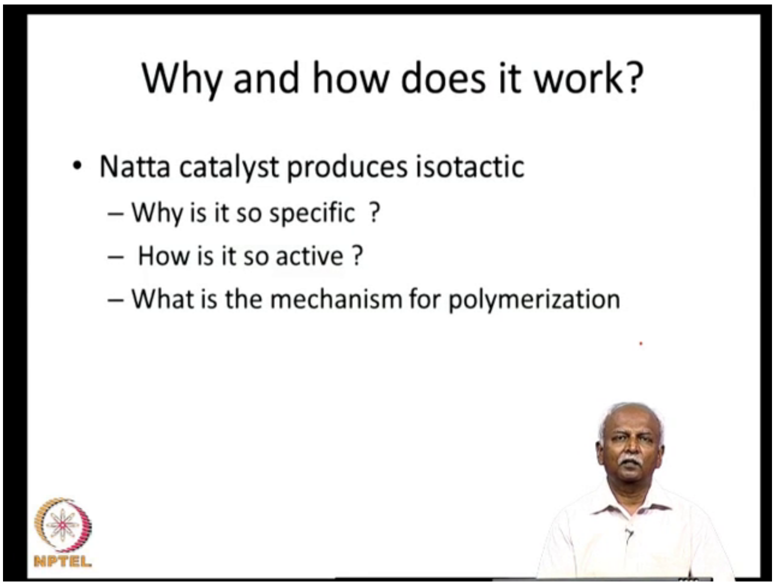

Polypropylene: stereochemistry

Stereo block / alternating
But regular

Atactic / random

It would either be a single tactic which means they alternate the methyl group alternate or they would be totally atactic. Which means they were randomly oriented along the polymer chain. Sometimes you can generate a metal complex which can give you stereo blocks. But alternating regular orientation of the metal blocks. All of these polymers may have different properties. And so they are useful in their own right except when you have a random orientation in which they case the usefulness decreases.

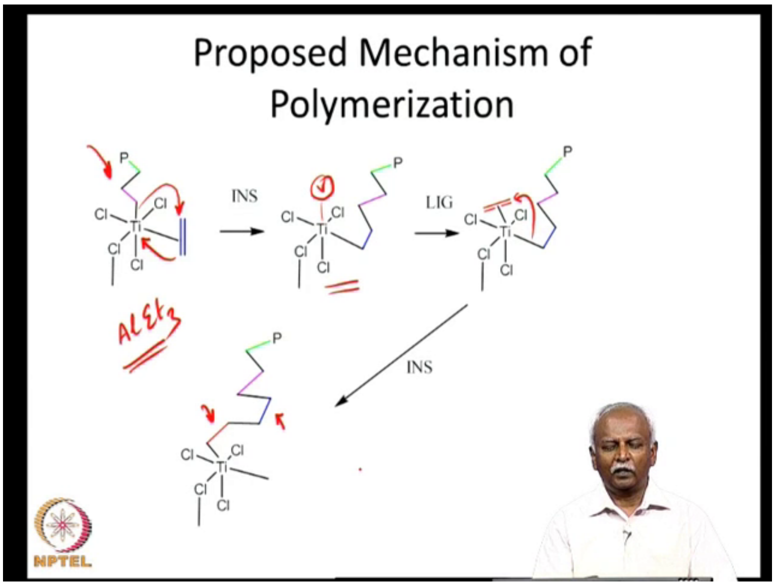
(Refer Slide Time: 39:43)


Why and how does it work?

- Natta catalyst produces isotactic
  - Why is it so specific ?
  - How is it so active ?
  - What is the mechanism for polymerization

So, this was the mist significant improvement that Natta made. And now we ask the question, why is the Natta catalyst so specific? And how is it so active? And at room temperature and low pressures how are we able to carry out polymerization so efficiently?

(Refer Slide Time: 40:02)



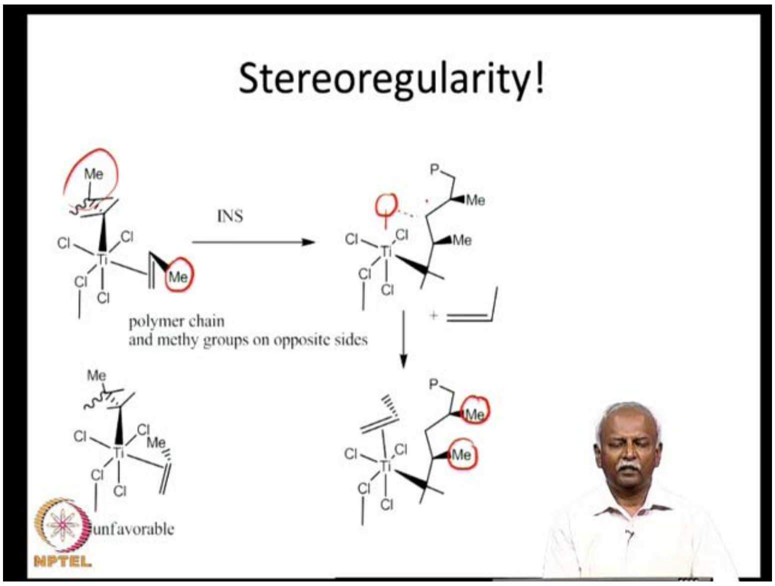
Proposed Mechanism of Polymerization

Let us first look at the basic mechanisms of polymerization. It involves an extremely simple insertion reaction as opposed to the oxidative coupling that they have been talking about. These are insertion reactions carried out on the titanium centre. Now, if you have a methyl group form the MAO or an alkyl group from the A L E T 3 which is usually used to activate the titanium. You will have an alkyl group on the titanium in the place where I have marked it with a growing polymer chain. So, in this position you will realize that you have this group which is attached to the titanium which can now undergo an insertion reaction. And we will mark this insertion reaction like this.

If this anionic group inserts into the ethylene and a new carbon titanium bond is formed you would get this particular product. And that product has got a vacant site. Here this is the vacant site. Here that we have marked at with v. And you have the growing polymer chain in the CIS position. Now, it is very easy to see that you can add an ethylene again into the vacant coordination site and the growing polymer chain can do another insertion reaction. This time between this carbon and the alkene carbon like this. And so the growing polymer chain now has got second ethylene attached to it. So, we started out with a magenta carbon being attached to the titanium and we have added a blue ethylene just for the sake of identification. I have color coded it. So, we have added a blue ethylene and a red ethylene to the titanium.

So, you can have a rapid polymerization. Thus ethylene notice that we are not changing the thermodynamics of this whole process. The thermodynamics is still a piece is still in the same way as in the uncatalyzed process. Carbon-carbon bond formation releases a lot of energy because you are converting a double bond to a single bond. But you will lose entropy. The net gain is the strong carbon-carbon bond which leads to a forward reaction. Polymerization is feasible in these cases.

(Refer Slide Time: 42:38)



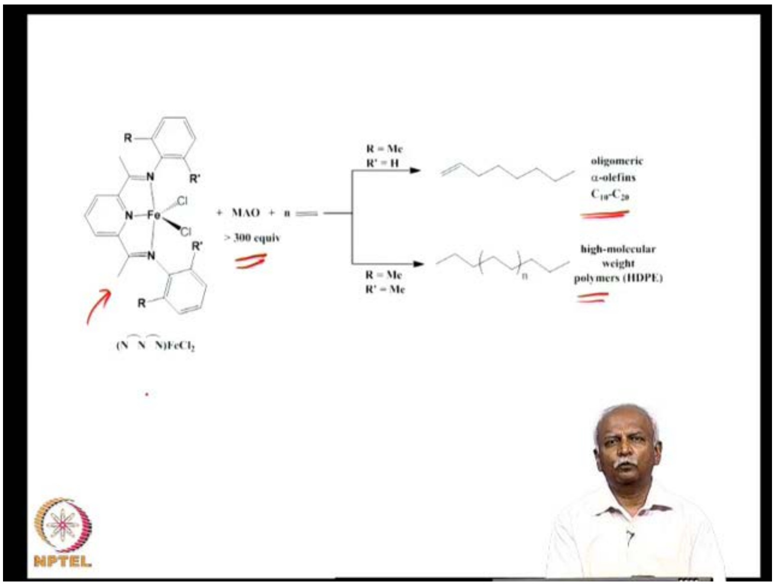
Stereoregularity!

Now, let us take a look now at stereo regularity. If you take propylene and if you look at a polymerization in the same catalytic cycle that we have just discussed. You will notice that because these two groups are oriented in a CIS position. It is important to orient them a way in such a way that the methyl group which is the bulky group on the propylene methyl group is a bulky group on the propylene.

The growing polymer chain is the bulky group on the alkyl chain which is attached to the titanium. Both of them will have to be oriented away from each other. And because of this requirement you will always end up with the chain inserting in such a way that the methyl groups end up in this same position or in the same direction along the polymer chain. Because you want to always orient the methyl group away from the growing polymer chain.

So, this very simple fact and the fact that in the resting state of the catalyst this vacant site has a beta hydrogen interaction. As in weak interaction with a beta hydrogen on the growing polymer chain you end up with a very strong stereo regularity in the polymerization process.

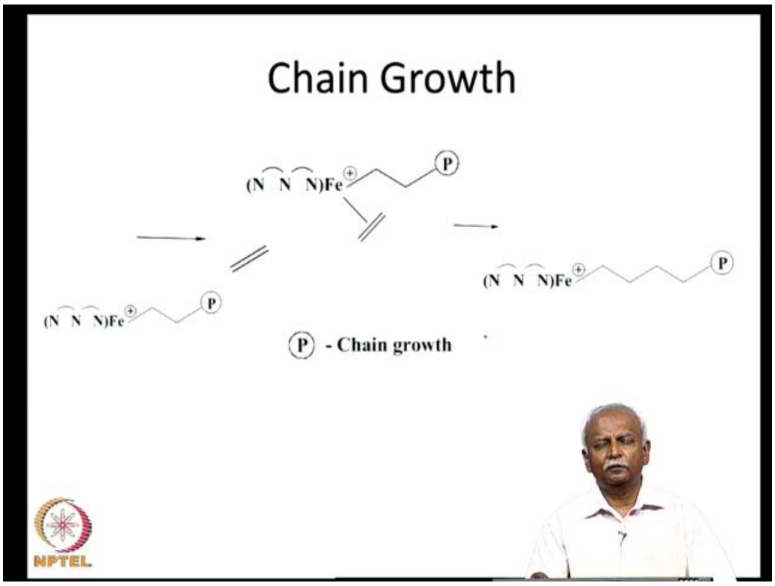
(Refer Slide Time: 44:11)



Now, it is been possible to have polymerization of ethylene with a variety of non-groups for metals. And this has led to a situation where you might call it the iron age of a polymerization, where even metals like iron have been activated using MAO. Again you need a reducing agent with a large anion so that ion is protected and only the ethylene is able to approach the metal center. And when you have ethylene coordinated to the iron. And you can have the insertion reaction. And you can have oligomeric oligomerization of olefins to give you alpha olefins or high molecular weight polymers like HDP when you use these catalysts.

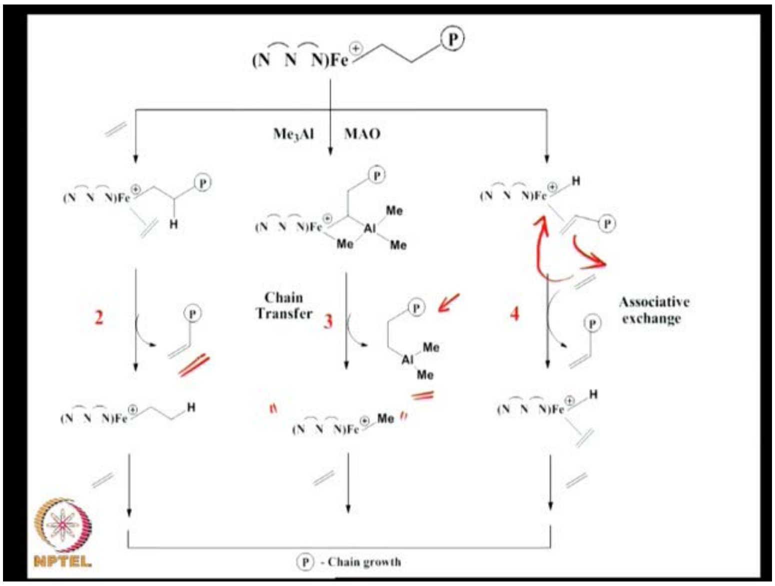
So, the mechanism of the reaction is assumed to be the same. And it is because of these bulky groups that are present on the ion that approach of other approach of other ions anions which would poison the catalyst are prevented. Especially water will be a serious poison for the catalyst. So, that is prevented by the presence of a large excess of MAO.

(Refer Slide Time: 45:43)


Chain Growth

Now, the chain growth is what it needs to be very efficient in order to generate a polymer. And this chain growth process as we have mentioned would be identical to what we showed on the titanium except that. Now, you have the iron which is in the plus 1 oxidation state and it is undergoing an insertion reaction with the ethylene.

(Refer Slide Time: 46:11)

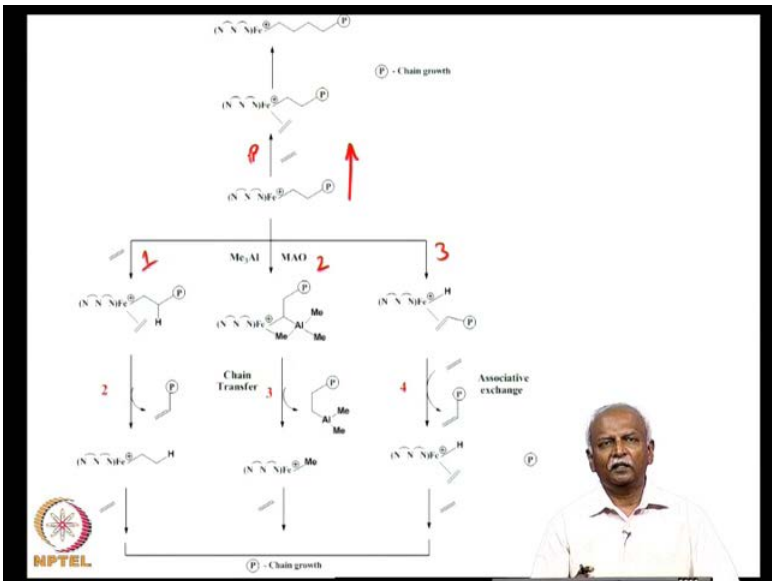


But at the same time it has to compete with other processes which in which will stop the chain from growing. What are these processes? Now you can see them in this slide they have pictured for you here. You have several processes. Instead of having a insertion reaction you can have an exchange with simple ethylene which would regenerate the catalyst instead of continuing the polymer growth. You can have an exchange reaction where ethylene comes in and the bulky polymer alpha olefin goes away.

So, that is called an exchange reaction. You can also have a reaction with trimethyl aluminium. If you have trimethyl aluminium as a reducing agent then it tends to have a chain transfer reaction where a methyl group is transferred to the growing chain and the reaction stops. And this is pictured here, where once again a methyl iron bond is formed.

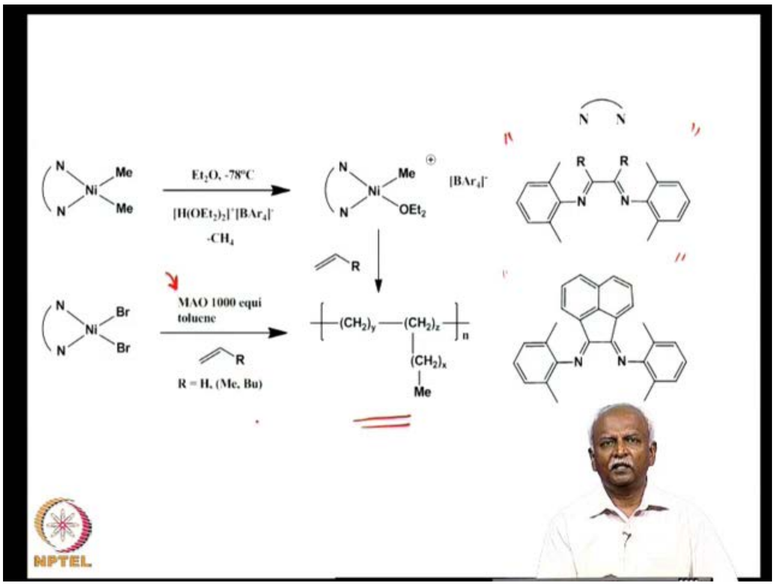
And the chain growth can continue. But nevertheless you stop the main chain from growing. At this particular chain a third possibility is that beta hydrogen abstraction becomes more favorable than the alkene insertion. Then of course, you would end up with the short polymer chain rather than a very long high molecular weight polymer in the whole reaction process.

(Refer Slide Time: 47:50)



So, any polymerization catalyst has to compete with being a two possibilities, three possibilities. So, this is the chain growth mechanism that would favor high molecular weight. And all these process is these three process is which I am labeling as 1, 2 and 3. These three have to compete with the polymerization process which is going on in the upward direction. So, this is usually favored by bulky groups on the metal atom which is a coordinating to the ethylene. And growth is wayward when you have unfavorable energetics for the beta hydrogen abstraction.

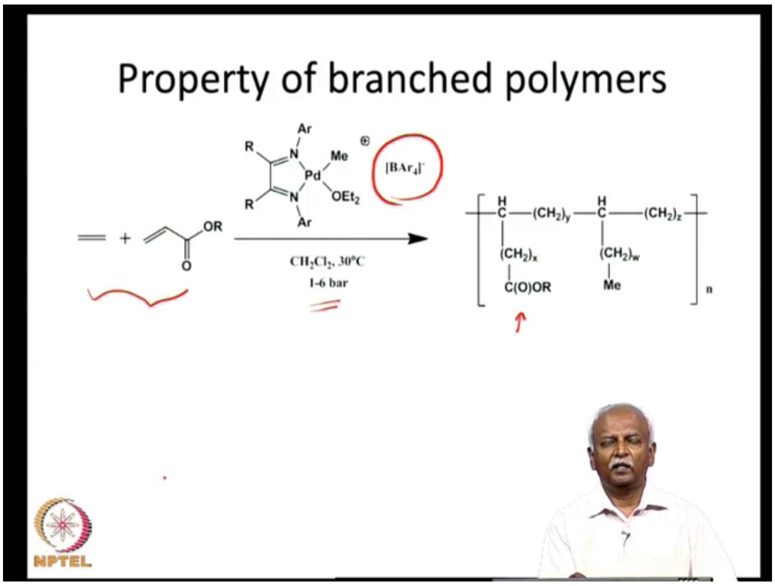
(Refer Slide Time: 48:42)



So, people have from the iron that I have described to you. It has also been possible to have nickel complexes. And here is a nickel complex that is pictures. Once again you have a bulky ligand, a key factor. And methyl alumoxane is again a key factor that is necessary for reducing nickel from the 2 plus state to the 0 plus state. And it is possible to generate a high molecular weight polymers using this particular catalyst as well.

So, you can see that the principles are very similar to what is happening on the titanium. Titanium is not unique you need a covalent metal center which can carry out the polymerization very effectively. But it needs to be prevented from anions attacking the metal center and stopping the reaction.

(Refer Slide Time: 49:44)

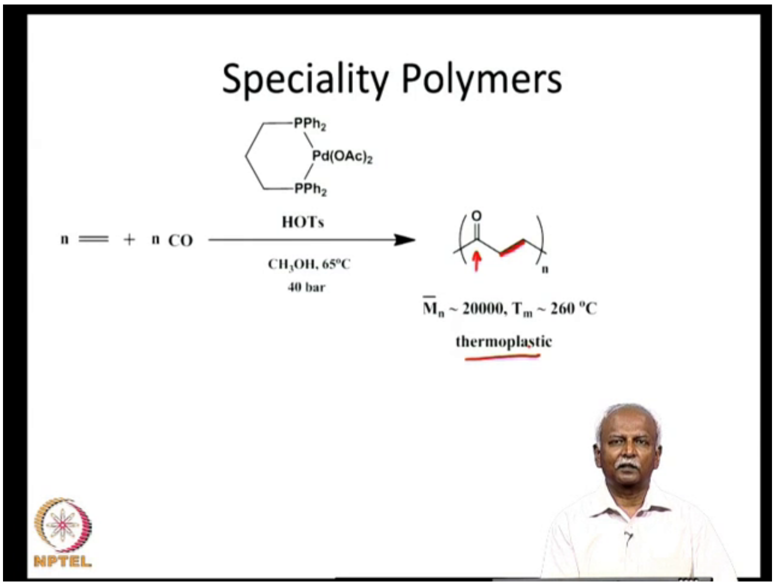


Property of branched polymers

It not only three D metals. Here it is an unusual example of a four D metal or a four D metal which is capable of carrying out this reaction. In this case a very large tetra aryl borate anion is being used as a stabilizing anion to carry out this polymerization process. And this polymerization is carried out at a not too high pressures. But the main the important difference that advantage is that they have co-polymerized two species in order to generate a very interesting polymer which is having this substituent on the polymer chain. And this allows for specialty polymers to be synthesized.

So, the polymer industry is in fact having a gamut of a transition metals and metal complexes available for it to make very interesting polymers. Here is one more example where a palladium center is being used for generating a alternating co-polymer of carbon monoxide and ethylene.

(Refer Slide Time: 50:47)



Speciality Polymers

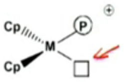
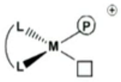
n ═ + n CO $\xrightarrow[\text{CH}_3\text{OH, 65°C, 40 bar}]{\text{HOTs}}$

$\overline{M}_n \sim 20000$, $T_m \sim 260\ °C$

thermoplastic

And so, this generates a polymer where the repeat unit has got the CO and ethylene. So, the ethylene has come from these two carbon centers and carbon monoxide was also a reactant. And so, you can make this high molecular weight thermoplastic using this palladium complex.

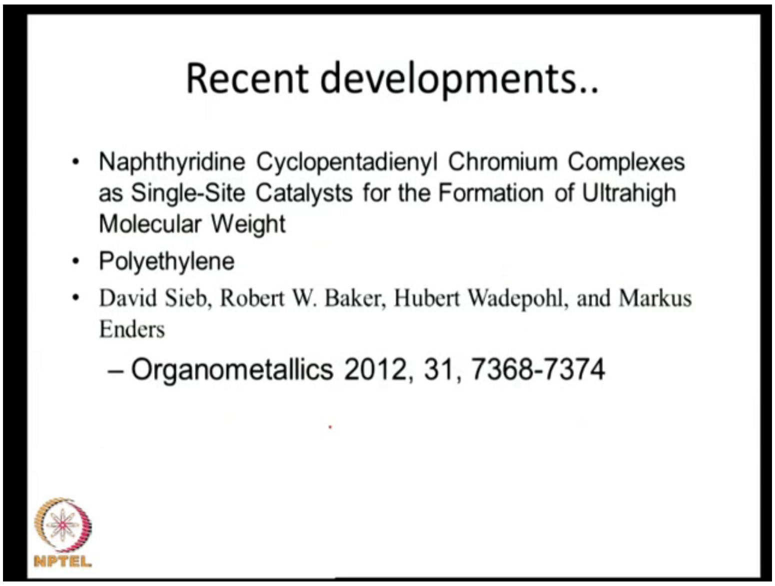
(Refer Slide Time: 51:20)

	"early"	"late"
central metal atom	Ti^{IV}, Zr^{IV}, Hf^{IV}, Ln^{III}	Fe^{II}, Ni^{II}, Pd^{II}
ligand in precatalyst	Cp$^-$, X$^-$	diphos, diimine, X$^-$
counteranion	noncoordinating	weakly or noncoordinating
coordination geometry	pseudotetrahedral	mostly square planar
active site		
tolerence of functional groups in monomer	no	yes

Finally, we look at some of the early and properties of the early and late transition metals and the type of catalyst that have been used. The important point is to generate an active site that would not be blocked by an anion. And in most cases MAO is used is the very large blocking anion that is very weakly interacting metal center. And so, you have a weakly or non-coordinating species that is important for both centers. You can have soft ligands in the case of late transition metals. But you need an oxo group or an X minus on the titanium and the vanadium and the early group early transition metals which have to be activated with MAO.

And usually the coordination geometry around the early transition metals are tetrahedral. Whereas, the late transition metals prefer a square planar intermediate. Now, the tolerance of functional groups is one place where the two vary differ very significantly in the case of late transition metals we can have a tolerance of functional groups where as in early transition metals only ethylene can be polymerized.

(Refer Slide Time: 52:46)



Recent developments..

- Naphthyridine Cyclopentadienyl Chromium Complexes as Single-Site Catalysts for the Formation of Ultrahigh Molecular Weight
- Polyethylene
- David Sieb, Robert W. Baker, Hubert Wadepohl, and Markus Enders
  - Organometallics 2012, 31, 7368-7374

Finally, I would end with a very recent example where a chromium catalyst has been used for synthesizing ultra high molecular weight polyethylene.