Introduction to Organometallic Chemistry
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Lecture - 28
Reactivity changes in coordinated ligands

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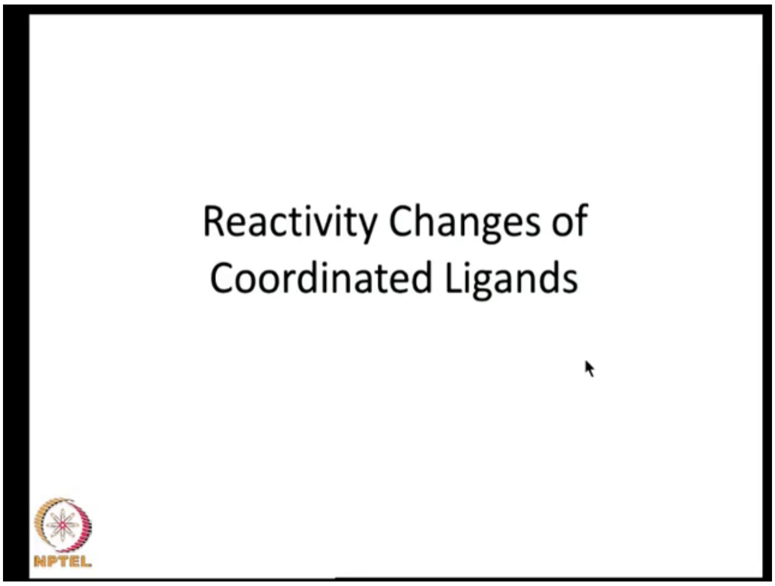

Reactivity Changes of
Coordinated Ligands

Organometallic chemistry primarily involves the chemistry of organic fragments, which are coordinated to the metal. When we are talking about the organic part of the organometallic compound, we noticed that there are often changes in the reactivity patterns of the organic ligand. Today, we would like to consider some of the changes, and see if we can understand the changes that have come about on the ligand, on the basis of the electronic structure of the molecules that we have considered so far. So, let us go through this.

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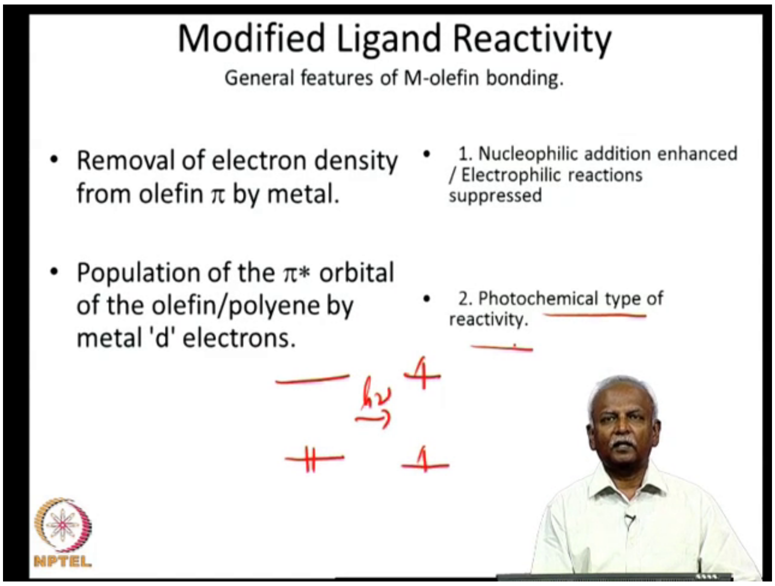

Modified Ligand Reactivity

General features of M-olefin bonding.

- Removal of electron density from olefin π by metal.
- Population of the $\pi*$ orbital of the olefin/polyene by metal 'd' electrons.

- 1. Nucleophilic addition enhanced / Electrophilic reactions suppressed
- 2. Photochemical type of reactivity.

We will give a few examples as we go along and see if we can glean some principles, which are behind these reactivity changes. In this first slide, I have shown you what happens or what the feature that we noticed when we considered a metal olefin complex. Primarily we have depletion of electron density in the pi bond. That weakening of the pi bond is seen by a lengthening of the carbon-carbon double bond distance. So, that implies that we have lost some electron density from the bonding orbital, and at the same time we have also populated the pi star orbital or the anti-bonding orbital of the olefin.

The result of these two factors should be what I have listed on the right side of the screen. Namely, you should have a nucleophilic addition of the double bond, nucleophilic additions on the double bond. If there were electrophilic reactions of the free ligand then these should be suppressed in the complex. In addition a combination of the two factors that we gave mentioned.

Namely, the promotion of electron density from the pi orbital to the pi star orbital should resemble the excitation of an olefin from its ground state to its first excited state. Although, we have not transferred one electron completely as in the case of photochemical excitation, it should be possible in the case of complex ligands. This helps us to see some type of photochemical reactivity. So, today we will take a look at some of these reactions and see how we can rationalize them on the basis of our expectations.

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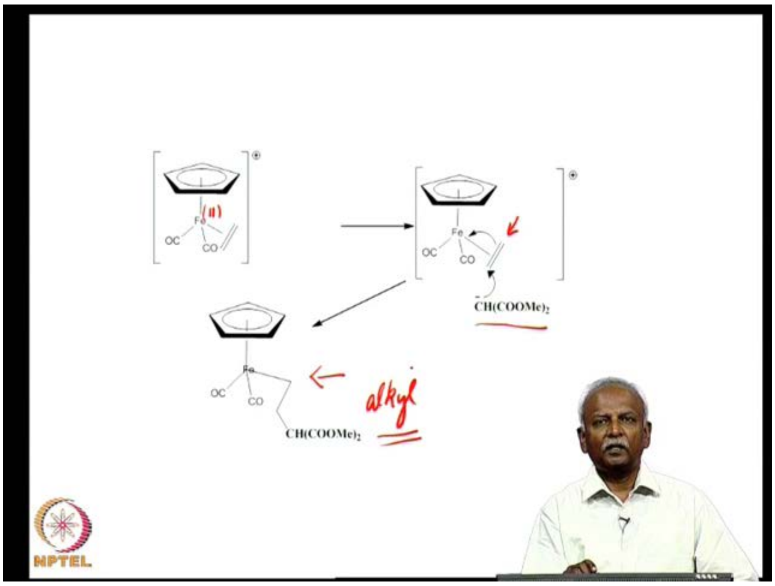

In the first example, I have shown you the generation of an olefin complex in which the olefin is complex to an iron two center. In this olefin complex you have the attack of a dimethyl malonate anion. The anion of dimethyl malonate attacks the double bond from the side opposite of the iron in such a way, that we transfer the two electrons which are present in the pi bond onto the iron directly.

Now, we have formed an alkyl complex because we started with a cationic system and then we attacked with an anion. The final product is a neutral product. There is no charge on the complex and we have started with an alkene complex and have ended with an alkyl complex. So, here is essentially a key step which is the attack of a nucleophile r minus on the double bond. This is exactly what we expected on the basis of the first effect that we saw namely, depletion of electron density from the pi orbital of the olefin.

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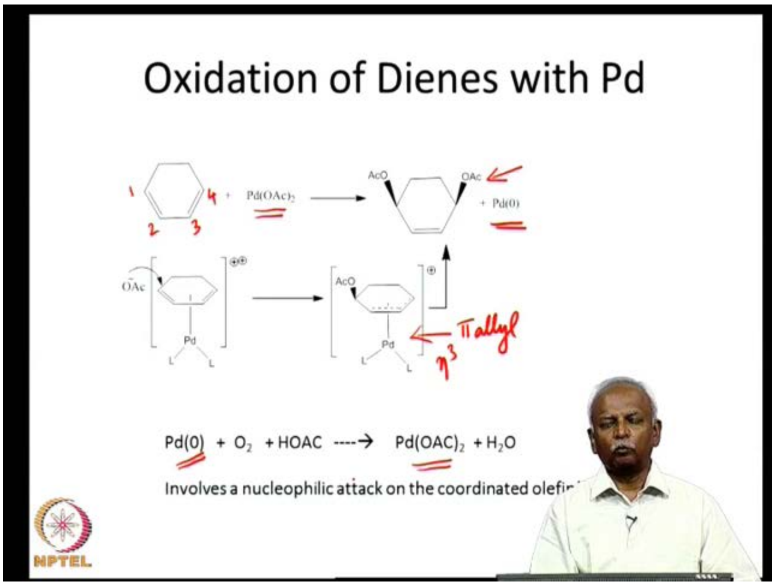

Oxidation of Dienes with Pd

$Pd(0) + O_2 + HOAC \dashrightarrow Pd(OAC)_2 + H_2O$

Involves a nucleophilic attack on the coordinated olefi

There are several reactions of dienes and olefins. These involve oxidation, net oxidation of the alkene which is complex to the metal. Here, I have shown for you a reaction of cyclo hexa diene which in the presence of palladium acetate gets oxidized to one four hexene acetoxy hexane. In this one four acetoxy compound, what we notice is that the net result is addition of acetoxy groups in the one and four positions of the diene. So, this molecule has in fact added 2 OAc minus groups.

Essentially it has added OAc minus groups at these two positions and palladium has been reduced from palladium, 2 plus 2 palladium 0. Now this type of a reduction, this type of a reduction of the palladium and oxidation of the olefin is the net reaction. The individual steps involved in a nucleophilic attack of the OAc minus on the palladium complex, which is coordinated to the diene. So, here I have pictured for you the individual steps, and individual steps indicate that a diene coordinated to palladium is attacked by the OAc minus.

The acetate anion generating pi allyl complex, this eta three pi allyl complex again undergoes reaction with an acetate anion and generates the diacetoxy compound. Here we can see that the important step or the key step involves the attack of a nucleophile on the coordinated double bond. If you notice the net reaction that is happening in this whole process is the oxidation. We can make this a catalytic process by bubbling oxygen through this reaction mixture because palladium 0 can be readily oxidized to palladium acetate can be oxidized to palladium acetate. This is done in the presence of oxygen. Very often, it is done with copper two plus as a catalyst and the presence of acetic acid to form palladium acetate again.

So, although this is an oxidation reaction the key step involves a nucleophilic attack on the coordinated diene. Here we see that the attack of an olefin, the attack of a nucleophile on an olefin is a process which is not favored when the metal is not present. But when the metal is present the depletion of electron density from the pi molecular orbitals enhances the possibility of the acetate attacking the double bond.

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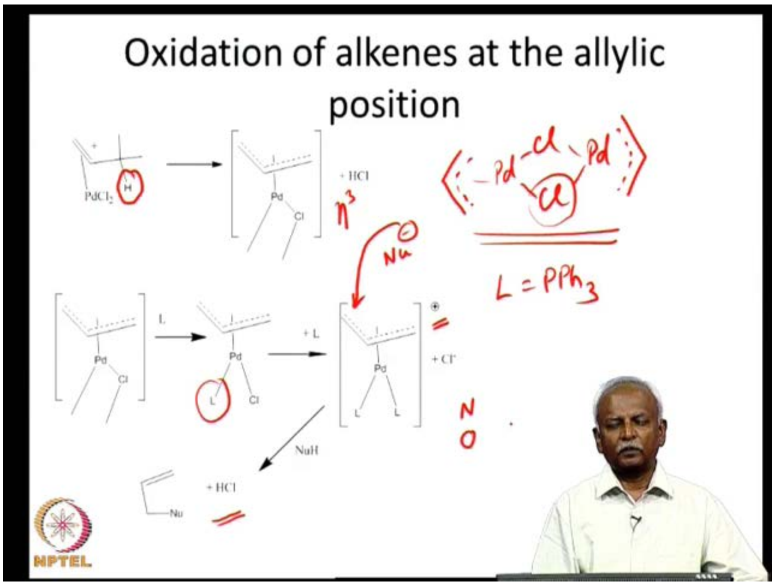

Oxidation of alkenes at the allylic position

Now, this type of an attack on a coordinated pi system happens in both neutral olefins dienes and also in allylic pi systems. Here I have shown you what happens when you have an alkene which has got an allylic hydrogen. So here is the allylic hydrogen that we are talking about, and in the course of interacting with the palladium chloride you can eliminate a molecule of hydrogen chloride. We went through this the various possible pathways by which this can happen in order to form a dinuclear eta three allyl complex.

Now this eta three allyl complex is pictured here, in fact it is something that could be written in this fashion. Also now you will notice that this allyl complex is capable of, is capable of undergoing a nucleophilic attack provided we make it more attractive for the nucleophile. How does one do that? Simply by replacing the chloride ion, the chloride ion is a negatively charged species, so it reduces the electron density requirement on the palladium. Hence, when you replace that with the neutral ligand very often this neutral ligand can be pph three or a phosphene and this results in the system becoming a neutral species.

Eventually if you add two equivalents of triphenyl phosphene it can even become a cationic species. This cationic species turns out to be more attractive for the nucleophile and the nucleophilic attack now takes place nu minus. This can attack one of the ns of the allyl group resulting in the formation of the nucleophile. This nucleophile is attached resulting in the formation of a substituted alkene.

Now, where the allylic position has been substituted the hydrogen has been substituted by a nucleophile. Very often the nucleophile has got a more electronegative atom like nitrogen or oxygen and that results in a net oxidation of the alkene in the allylic position. So, we have seen two examples here, where you can have a nucleophile, nucleophile attacking an alkene either on the double bond, or in the allylic position resulting in the formation of a new compound.

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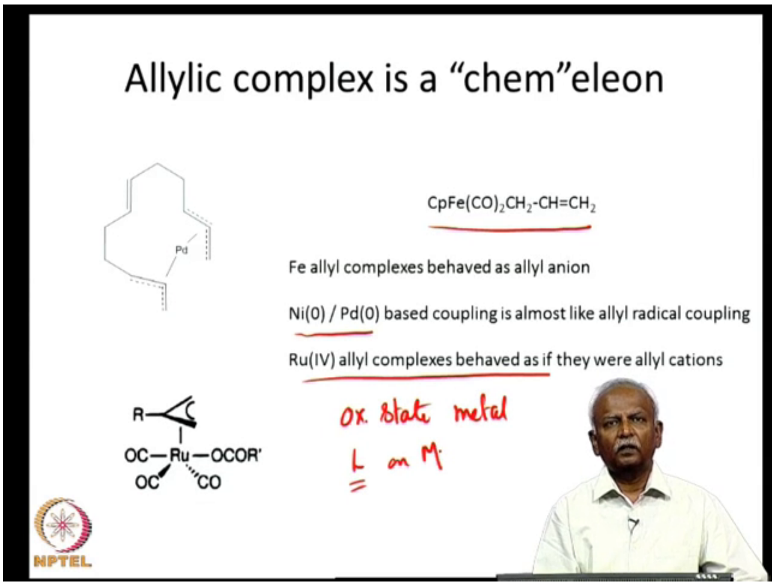

Allylic complex is a "chem"eleon

$CpFe(CO)_2CH_2$-$CH=CH_2$

Fe allyl complexes behaved as allyl anion

Ni(0) / Pd(0) based coupling is almost like allyl radical coupling

Ru(IV) allyl complexes behaved as if they were allyl cations

ox. state metal

L on M

Now, we also notice that, during the course of studying the allylic complexes those allylic complexes are in fact a chameleon. A chameleon changes color depending on the surroundings in which it is present. The allylic compound depending on the oxidation state of the metal which is coordinated to it can change its property from an allyl radical to either an allyl cation. It can also change itself to an allyl anion. In this a picture itself, the slide that is before you I have shown you three different examples palladium and nickel zero tend to enhance the property of allyl group to make it look like an allyl radical.

But the iron compound makes it look like an anion and the rhuthenium four species which is pictured here understandably makes it look like an allyl cation. Hence, it tends to be attracted by a nucleophile. This type of a changing in the reactivity of the allylic group is brought about by the ligand that is present. The metals oxidation state shows two things, the important oxidation state of oxidation state of metal, and also the ligand l that is present on the metal.

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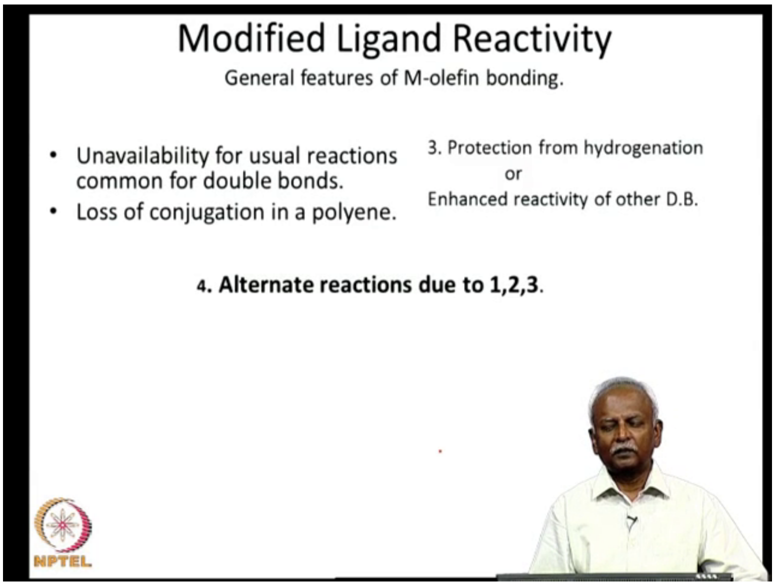

Modified Ligand Reactivity

General features of M-olefin bonding.

- Unavailability for usual reactions common for double bonds.
- Loss of conjugation in a polyene.

3. Protection from hydrogenation
or
Enhanced reactivity of other D.B.

4. Alternate reactions due to 1,2,3.

So, the modified ligand reactivity that we have seen here is a result of the general features of the metal olefin bonding. Now, we can also have additional reactions which are independent of the two factors that we have just considered. Consider for example, the protection of the double bond from the usual reactions of a double bond. Since, there must be the presence of an olefin the loss of conjugation with a polyene is also another possibility. Now we will see a few examples where these two aspects are probed.

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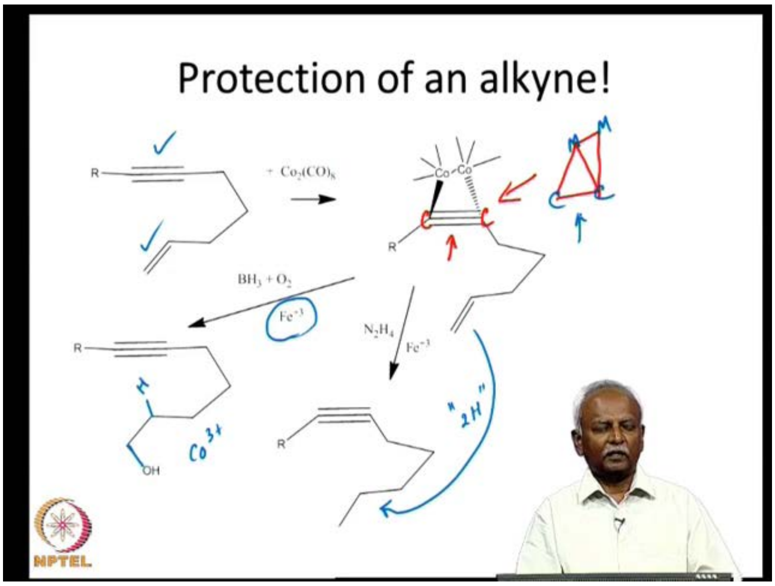

Protection of an alkyne!

A classic example is the interaction of dicobalt octacarbonyl with alkynes. This reaction is an extremely useful and valuable reaction. The formation of the dicobalt hexacarbonyl complex of an alkyne is extremely fragile. It takes place at a mild condition, under mild conditions. Secondly, the complex that is formed is reasonably stable and cannot be dislodged easily under normal circumstances. The double bond is the distance between the two carbon atoms which holds the triple bond. It is almost close to that of a double bond. We will also notice that the four atoms that form this unit turn out to be almost at the corners of a tetrahedrane.

So, it is almost like this, where let us just mark out the metal. The cobalt is in these two points in space and the two carbon atoms are in these two points on space in the tetrahedrane. So, this particular compound turns out to be a very useful way of protecting the triple bond from the normal reactions of the triple bond. If you have for example, as shown in this projection, that is there before you have a double bond and you have a triple bond. Now, if you want to carry out reactions on the double bond without affecting the triple bond, it is possible to just complex it with the dicobalt hexacarbonyl and then react it with the regions.

There are two extreme examples that are shown here. One is the oxidation the borohydride reduction BH 3 addition and oxygen oxidation. This results in the formation of the alcohol. So essentially, we have added in this case an OH group and a hydrogen to the double bond. But if you had left the triple bond unprotected it would have been, it would have also reacted with the BH 3.

Now, at the end of this reaction what one does is to add an oxidant like Fe 3 plus. The ferric ion is capable of oxidizing the dicobalt hexacarbonyl and cobalt 3 plus is generated. The carbon monoxide leaves the coordination sphere of the metal. Now we will notice that this is not really green chemistry. You end up destroying the protecting agent completely at the end of the reaction. But in cases where you do not have another option this might be the only way to go.

Here is another example, where the double bond is completely reduced to an alkene. We have added two hydrogen atoms, we have essentially added two hydrogen atoms to the double bond very conveniently in the presence of a more reactive triple bond. Once again the presence of this dicobalt hexacarbonyl moiety is extremely effective in protecting, the triple bond from any other reaction.

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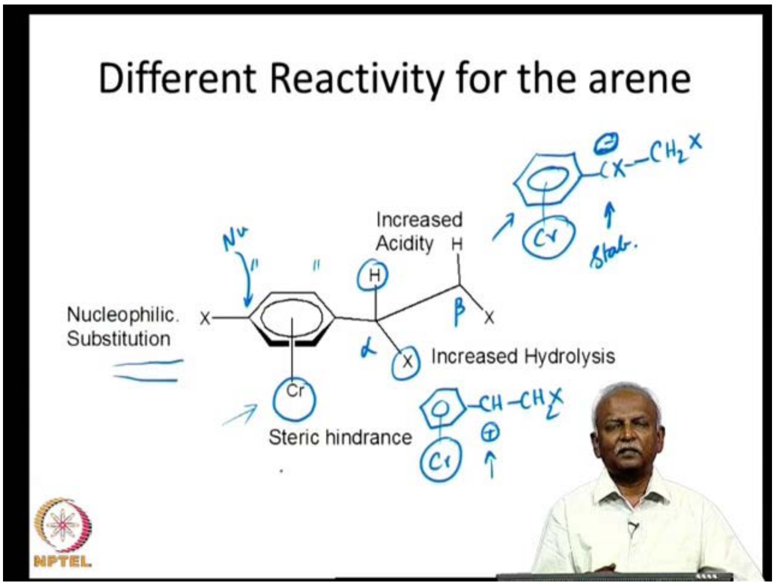

Different Reactivity for the arene

Nucleophilic Substitution

Increased Acidity

Increased Hydrolysis

Steric hindrance

Now, there are some other reactions which we will take up later, but now we will look at the reactivity changes that happen for an aromatic compound. When it is coordinated with the metal center we have considered the way in which a chromium atom reacts. It is one of the favorite metal atoms for interacting with an aromatic ring. We see how a chromium atom interacts with the benzene ring now although the reactivity of the benzene ring is well known in terms of its reactions with electrophiles for electrophilic aromatic substitution.

We noticed that during the lecture on the aromatic rings, on the aromatic compounds of chromium the bis-benzene sandwich complexes of chromium. The friedel crafts reactions are not favored when it comes to these compounds. This is because the easy oxidation of chromium to a chromium plus one and then chromium plus 3. During the course of this oxidation the benzene ring cannot coordinate any longer with chromium and essentially the complexes destroyed.

But there are other reactions which are enhanced in the presence of metal atom. Here I have shown you, about four types of reactions that we can consider. The first thing that we would like to consider is a fact, that you can do nucleophilic substitutions of a group that is present on the benzene ring. This is rather unusual because usually you do not have a nucleophile attacking the, attacking the aromatic ring this is definitely a no, a nono in terms of reactivity.

This is because the benzene ring pi system is extremely stable and it does not allow for it disruption of the benzene pi system, but when the chromium is attached to the benzene ring, the effect of the chromium is sufficient for the depletion of electron density from the aromatic ring. This is sufficient to allow for a nucleophilic attack. What is interesting is that there is an effect, not just the benzene ring which is present here but also in the benzilic position in the alpha and the beta positions of the substituents.

On the benzene ring you do have some changes; one of them is the increased acidity. By which we mean that the anion that is left behind, so essentially we are talking about this molecule right here or this fragment right here Cr minus. Essentially we are talking about this fragment being formed and this anion if it is stabilized. If this is stabilized, if this is stabilized then the activity of the acidity is increased for this molecule. This is how this anion is stabilized and this is something that we will look at in a moment.

You can also have increased hydrolysis, which means that if you have the same species let us just write the structure of that molecule. If you have CH plus and if this species is, if this species is stabilized to a greater extent than sn one type hydrolysis of this molecule would be favored. Surprisingly in both alpha and beta positions it is possible to have increased hydrolysis of x groups.

Also the increased acidity of these hydrogens, they seem rather contradictory, but if you look at the electronic structure of the bisbenzene chromium we will understand why lastly, we have a pi system. Usually the benzene ring has got two phases and both phases are equivalent. But when we coordinate a chromium atom to one side obviously we have changed the reactivity, and the protection of one side of the benzene ring from attacked by any reagent.

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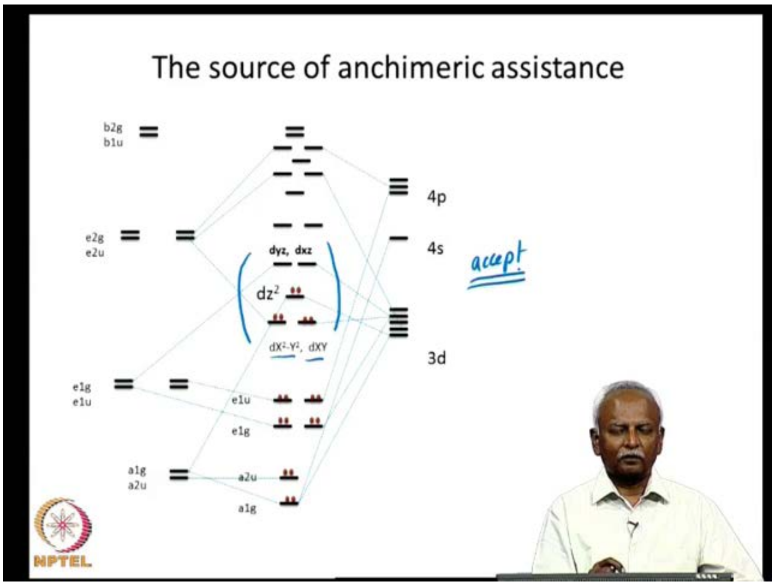
The source of anchimeric assistance

So, let us first look at the source of anchimeric assistance. We said that the valence orbitals on the bisbenzene chromium were mostly the set of d orbitals. Some of these have been stabilized or have been given electron density to the pi star orbitals on the benzene. So, it is slightly stabilized that is, the dx square minus y square and dxy. There was another group which was in fact interacting with the dyz and the dxz.

Now, because these groups of orbitals are the valence type that is those are the most easily accessible orbitals the dyz and dxz can accept electron density. Any type of electron density change on the ligand, can transfer electron density to dyz or dxz. Like the increased acidity that we just noticed. Where you have an anion generated in the alpha position that anion can be stabilized by partial overlap with the dyz or the dxz orbital.

Similarly, if you have a cation then that cation can accept some electron density from the dz squared orbital that we have. Here this type of anchimeric assistance is easily understood by looking at the molecular orbital picture. This suggests that the valence orbitals are readily capable of interacting with the anion or the cation that is formed in the alpha position.

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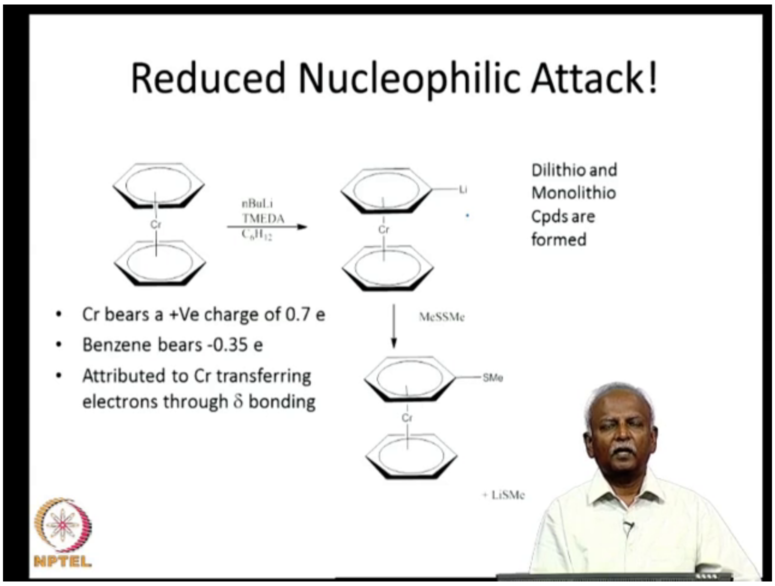

Reduced Nucleophilic Attack!

Dilithio and Monolithio Cpds are formed

- Cr bears a +Ve charge of 0.7 e
- Benzene bears -0.35 e
- Attributed to Cr transferring electrons through δ bonding

So, let us look at bisbenzene chromium itself. We noted for example, that the lithiation of the aromatic hydrogen is in fact not a favored reaction. You can, you can and you do lithiated, but then it is not as favorable as it is with pure benzene. This in fact is consistent with the electronic structure that we have looked at for the bisbenzene chromium.

The chromium itself bears a positive charge and a slight negative charge results on the benzene ring. This clearly suggests that you do have an increased electron density on the benzene ring. So, it is not likely that it will undergo a nucleophilic attack. That is true for an attack with n butyl lithium. Now, we will look at how we can change this scenario and make this benzene ring more reactive.

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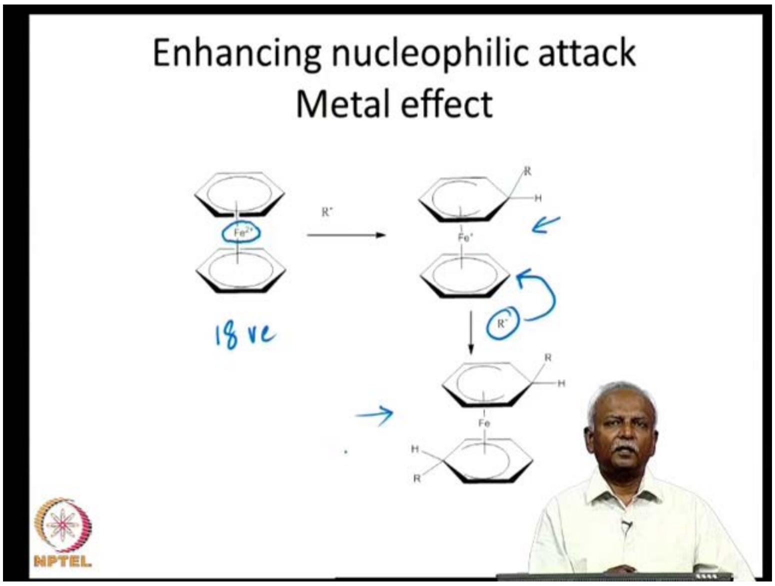
Enhancing nucleophilic attack
Metal effect

Let us consider two different pathways. Here, if we change the metal for example, in this projection that we have here in front of you. We have changed the iron to iron 2 plus. We have changed the metal from chromium to iron and so in order to make an 18 valence electron complex. We have oxidized iron to iron 2 plus so here is a complex which is iso electronic. The bisbenzene chromium is because the metal now has got a positive charge a plus 2 positive charge.

It now becomes easy to attack the benzene ring and form a complex where the r minus has in fact attacked the benzene ring. It destroys the aromaticity and you have a pentadienyl complex which is coordinated to the iron the net charge on the complexes now change from 2 plus to plus 1. What is interesting to note is that what bonds one ring is attacked. It becomes less reactive and the second r minus in fact attacks the second ring which was, which is still aromatic. That leads to a bispentadienyl complex which is shown here. It is clear that by modifying the metal system by enhancing, the electro philic nature of the metal, we can in fact change the nature of the benzene ring which is coordinated to the metal.

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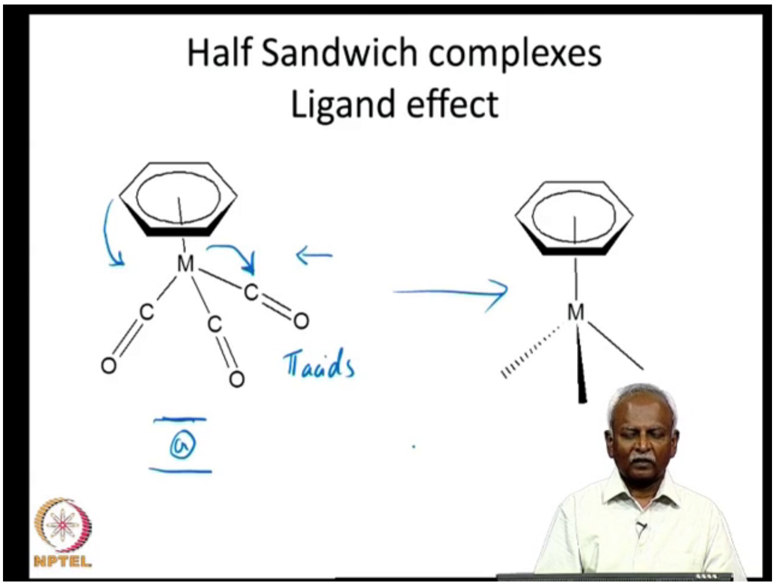

Half Sandwich complexes
Ligand effect

Now, we will move onto another way of enhancing the nucleophilic attack. That is by attaching very electron poor ligands as suppose to the benzene ring in the previous case. We had bisbezene chromium we have 2 benzene rings, which are attached to the chromium. Now, what we have done is we have converted the chromium benzene ring system to a chromium tricarbonyl ring, chromium tricarbonyl molecule. This as we know is a piano stool complex or a half sandwich complex because the three carbon monoxides are highly electron deficient they are capable of behaving as pi acids.

So, electron density flow is in the direction of the carbon monoxide. The electron density on the benzene ring is moved over to the metal to a greater extent. In the following slides we will approximate the mco three unit as m with three lines each. One of these lines has got a carbon monoxide attached to it. So this will make it simpler for us to draw these systems as we go along.

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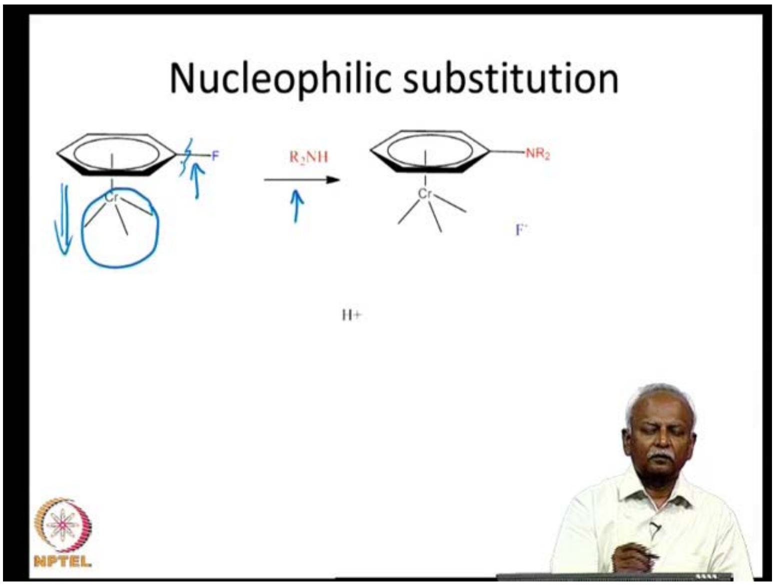

Nucleophilic substitution

Here is the first example of fluorobenzene which is coordinated to chromium tricarbonyl. Remember that each one of these lines represents a carbon monoxide. So, chromium tricarbonyl coordinated to fluorobenzene undergoes a nucleophilic attack with a second re amine. Surprisingly a carbon fluorine bond which is quite strong has now been broken and an amine has been attached to the benzene ring. This would be impossible in a simple aromatic system. We have been able to carry out a nucleophilic substitution reaction on a benzene ring using a simple secondary amine. This is purely because of the presence of this chromium tricarbonyl unit which withdraws electron density extremely well. As a result it is able to break the carbon fluorine bond.

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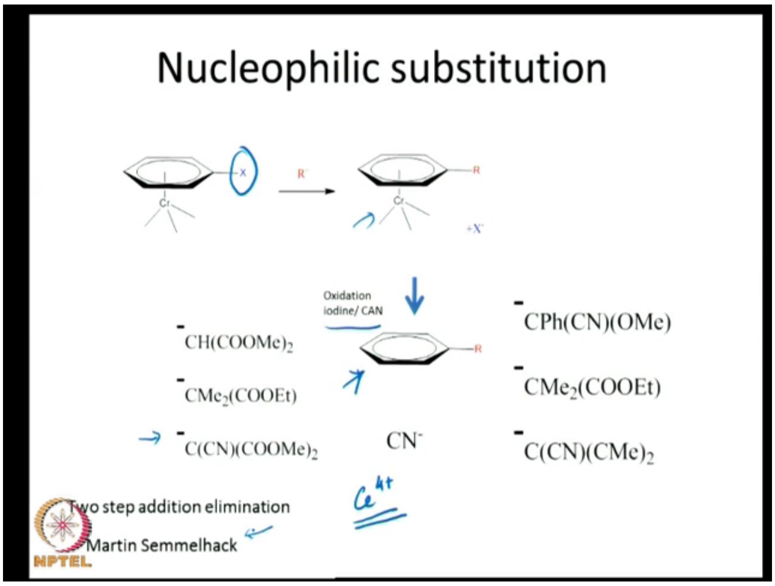

Nucleophilic substitution

$^-CH(COOMe)_2$

$^-CMe_2(COOEt)$

$^-C(CN)(COOMe)_2$

CN^-

$^-CPh(CN)(OMe)$

$^-CMe_2(COOEt)$

$^-C(CN)(CMe)_2$

Two step addition elimination

Martin Semmelhack

Through the intermediacy of course, of a sigma bonded intermediate complex we will come to that in a few minutes. This in fact turns out to be a general reaction you can have a variety of leaving groups and we have put a generic x. Here you can have a variety of leaving groups and these groups can be replaced by a series of carbon nucleophiles. All these carbon nucleophiles, many of them are pictured here have got at least one electron withdrawing substituent so that the negative charge on the carbon can be stabilized to start with so they are stabilized carbon nucleophiles. These nucleophiles now attack the aromatic ring very readily generating something like a meisenheimer complex.

Here you have the negatively charged species coordinated to the benzene ring forming a cyclopentadienyl intermediate. Then subsequently the x group or the leaving group is detached and you have the formation of the substituted product. At the end of this reaction again we have to oxidize. If you want the free aromatic compound one has to oxidize the chromium either with the iodine or ceric ammonium nitrate. Ceric ammonium nitrate is often abbreviated as CAN. This is cerium four plus which is now capable of oxidizing the chromium 0 to chromium plus 3 through one electron oxidations. This results in a convenient substitution reaction. It is a two step elimination addition elimination reaction that is happening. The r minus first attacks forms an intermediate, which is then undergoing an elimination process. The person who studied this extensively was Martin Semmelhack, who looked at how we can functionalize organic aromatic species by simply using a chromium tricarbonyl unit.

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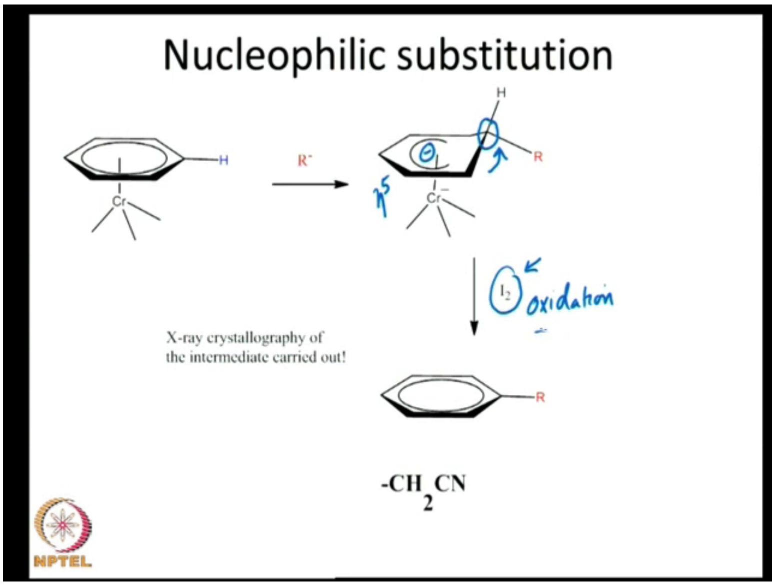

Nucleophilic substitution

X-ray crystallography of the intermediate carried out!

$-CH_2CN$

The intermediate as I told you has been even crysto graphically characterized. It is basically a cyclopentadienyl complex which now is an eta five mode. It is an eta five mode and the carbon that is undergoing substitution is lifted out of the plane. Of the 5 carbons which are coordinated to the chromium, the negative charge is present completely on these 5 carbons and that is coordinated to the transferring electron density to the chromium.

The subsequent oxidation can be carried out on this step which leads to the elimination of either a hydrogen or a x group. If a x group is present then one does not have to do the oxidation. At this stage you will just have elimination of the x group. Whereas, if you have, do not have an x group you can carry out nucleophilic substitution. Nucleophilic attack subsequently carry out an oxidation on the intermediate so, there are two different situations if you have an x group which can leave.

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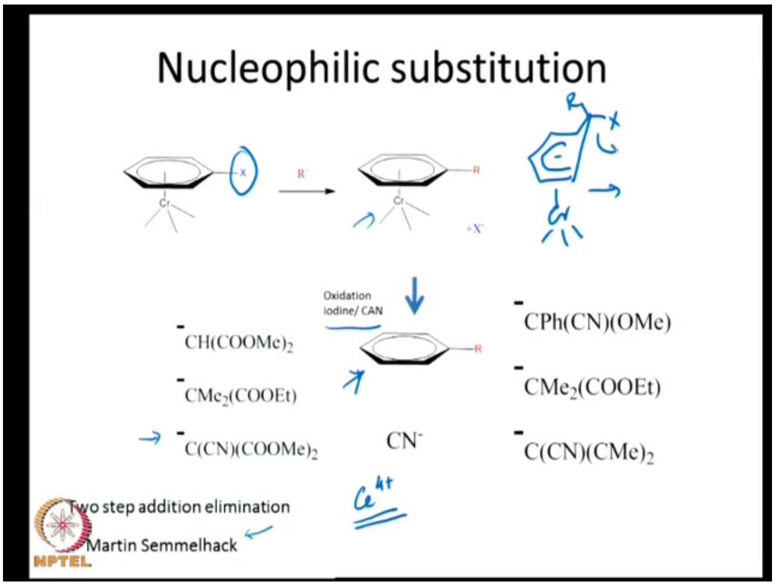

Nucleophilic substitution

$^-CH(COOMe)_2$

$^-CMe_2(COOEt)$

$^-C(CN)(COOMe)_2$

CN^-

$^-CPh(CN)(OMe)$

$^-CMe_2(COOEt)$

$^-C(CN)(CMe)_2$

Two step addition elimination

Martin Semmelhack

Then you have an intermediate which is present in this fashion. This molecule will lose a x minus, this is one possibility. The other possibility is that when you do not have a x group or a leaving group, still the aromatic ring is capable of undergoing a nucleophilic attack. The hydrogen can be released by subsequent oxidation step. That oxidation gives you the substituted aromatic ring and this is a very convenient way by which a variety of aromatic rings can undergo substitution reactions. But very often they have to be stabilized carbon anions in order for this reaction to occur.

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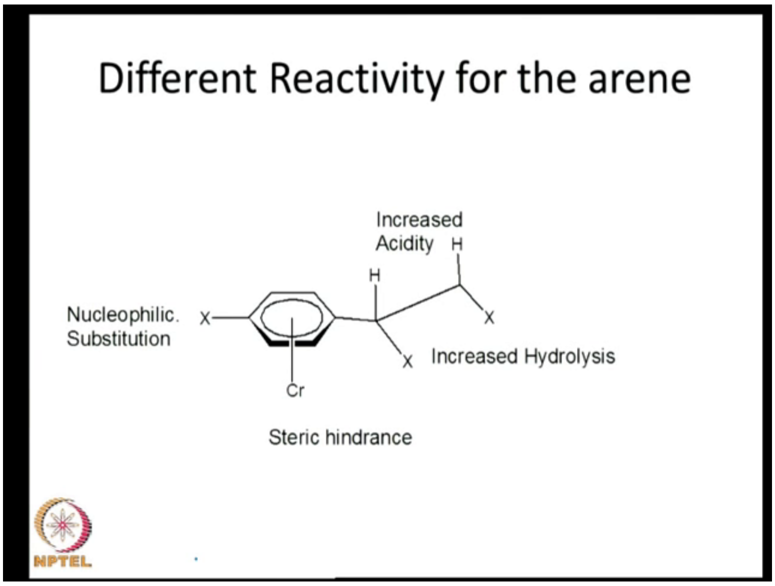

Different Reactivity for the arene

Increased Acidity

Nucleophilic Substitution

Increased Hydrolysis

Steric hindrance

So, we have looked at variety of reactions where you can have nucleophilic substitution.

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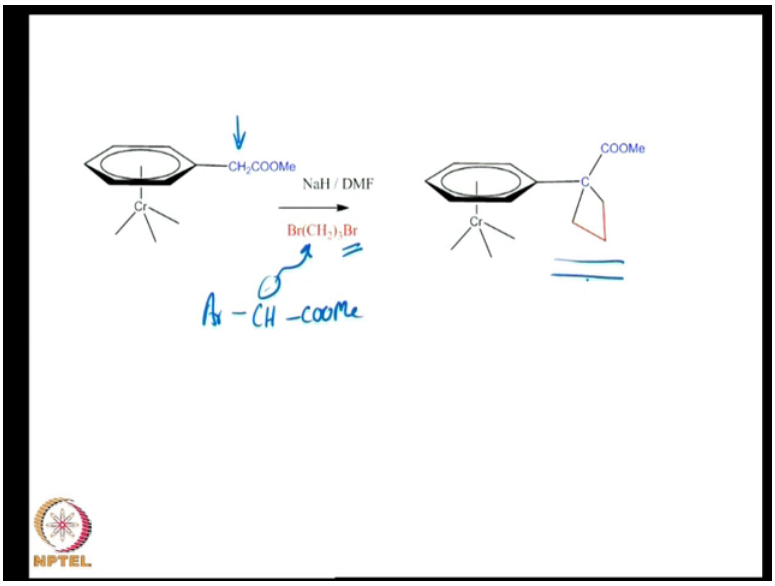

We will now look at the increased acidity of the carbon which is adjacent to the aromatic ring. Here I have shown for you the CH two group, the CH two group present adjacent to the benzene ring. If you treated it with sodium hydride it conveniently forms the anion and that anion undergoes a nucleophilic substitution. The CH minus conveniently undergoes substitution at the carbon leaving to a formation of an alkyl group.

This has another bromine at the third position so that comes again. One more hydrogen atom can be removed from this adjacent carbon because of this increased acidity. That leads to the formation the convenient formation of a four membered ring adjacent to the aromatic ring. This illustrates how you can have increased acidity of a carbon which is adjacent to an aromatic ring coordinated to CrCo 3.

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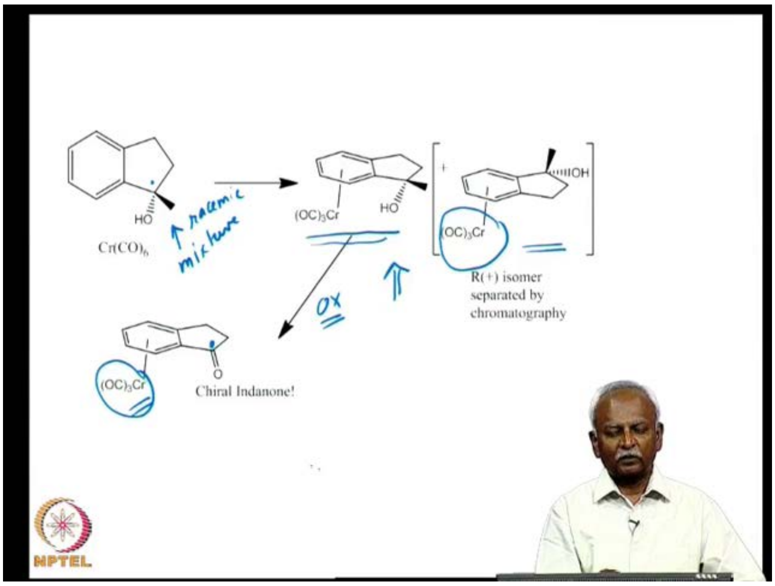

R(+) isomer
separated by
chromatography

Chiral Indanone!

Now, let us look at enhancing the hydrolytic reactions. Here I have a chromium tricarbonyl which is coordinated to an indenyl system. Indenyl saturated indene ype system where you have a hydroxy group. In the alpha position notice that this molecule, this molecule can form this CrCo 3 compound. This itself is not, is not a single isomer. You can have a mixture of two isomers; the carbon which is at this position is capable of being chiral, but we take the racemic mixture and it is interacted with CrCo 3.

We can form two different compounds, the two different compounds are the one where the hydroxy group is present in this orientation and the other is a second isomer where the hydroxy group is present with the same side of the CrCo 3. But by pointing away from the weaver, you will notice that these two are in fact capable of being separated because they can be separated either on a chiral column by chromatography, or with an another resolving agent.

But we has come about this type of separation, is come about because you have this large group this CrCo 3. It is coordinated to the benzene ring now you can also have another set of isomers where the OH group is coordinated away from the chromium. Now, the more favorable isomer is a one that we have shown. Here it is possible to easily separate out one chiral in indanone and that can be oxidized very easily to form a chiral indanone. Now, we will notice that an indanone is a flat molecule. There is no possibility for chirality, but when you have a CrCo 3 attached to it, it now turns out that it is chiral.

Now, you can understand this if you consider the fact that although the indanone carbon is flat it is a flat molecule, but on one side of this flat molecule you have a chromium tricarbonyl unit on the other side. There is no other group so although the indanone, the ketone is a sp 2 hybridized center it becomes a chiral center. This is purely because it is oriented with respect to another large group, which is coordinated to the adjacent benzene ring.

This is done in such a way that you have two different phases for the ketone. This is a convenient way of making molecule chiral although there is no chiral center at the point of reference, now it is possible to do the same thing with this isomer. Then you would get a different, the opposite enantiomer of this chiral indanone which is coordinated of course, to a CrCo 3 unit.

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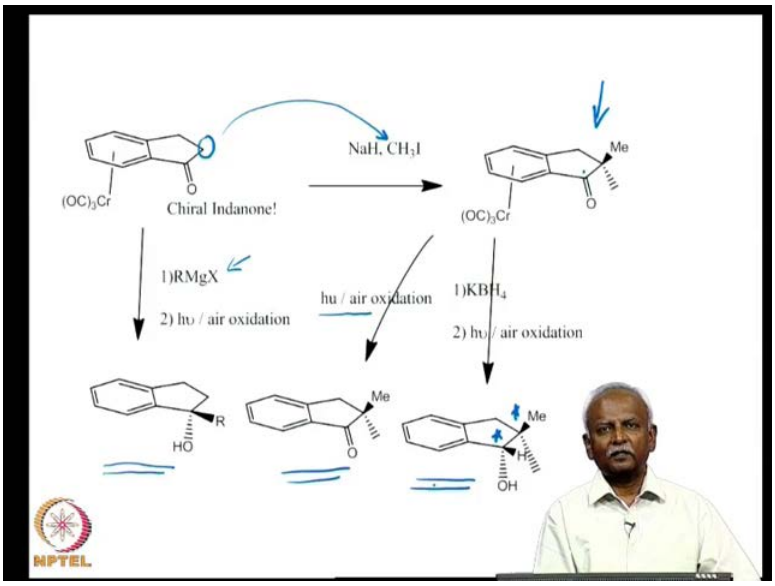

Now, what is more interesting is that if the chiral indanone was oxidized and the chromium tricarbonyl was released you would end up with a flat molecule, which is a chiral. But instead in this chiral version of this complex indanone, now you can carry out several reactions in a selective fashion. Here I have shown for you the abstraction of hydrogen from the beta position. As I have mentioned earlier even the beta position is capable of being stabilized by the chromium atom.

So, there is enhanced acidity at the beta position and once the anion is generated, this anion carries out a nucleophilic substitution on the methyl iodide resulting in the formation exclusive formation of one isomer. In a flat indanone you would not have been able to do this selective transformation. Here I have a second chiral center which is generated, but now the chiral center is generated selectively because the indanone carbon itself. The keto carbon in the indanone itself is chiral and it has handedness associated with it resulting in the formation of a single optically active form.

Now, you can carry out more reactions you just oxidize it with air in the presence of light you end up with this methyl substituted indanone. You can also reduce the chiral indanone, react it with chiral indanone itself with an alkyl magnesium bromide and then oxidize it. Then you get a chiral indanol which is again possible only because you have carried out the reaction in this circutus manner where you have isolated a chiral indanone.

Here there is yet another reaction where after doing the alkalation you have carried out reduction of the indanone to generate two chiral centers. So here is one chiral center and here is another chiral center and because we have started out with chromium which was inducing chirality. Then later removed it we have accomplished several reactions in a chiral fashion.

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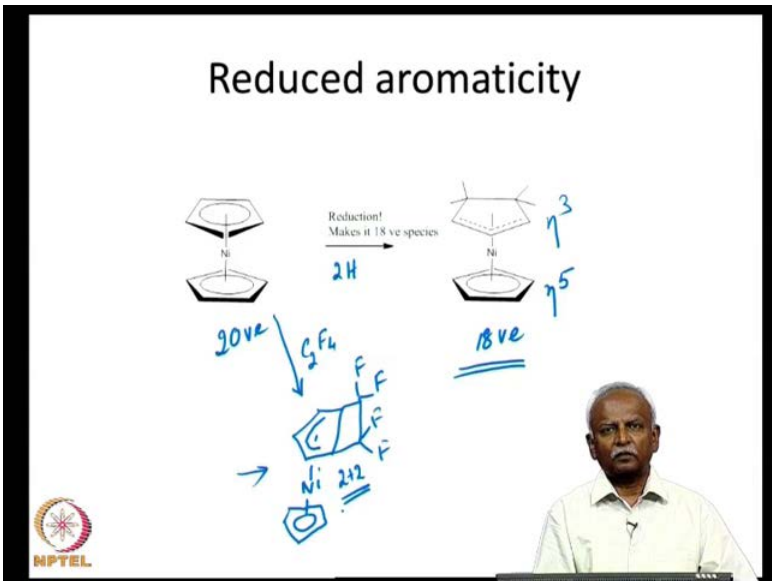

Reduced aromaticity

So, this set of reactions that we just talked about is because of the steric protection of the chromium tricarbonyl. Now, we will look at reduced aromaticity and the way in which protection of the double bond results in enhanced reactivity of other double, the other unsaturated bonds in the system. Nickelocene is a twenty valence electron system. So, if you want to reduce it with sodium and ethanol you can do. So, if you add two hydrogens. Two hydrogens easily with sodium and ethanol and those two hydrogens end up creating an eta 3 allyl nickel complex and eta 3 eta 5 eta 3 eta 5 system which is now, 18 valence electrons.

So, this turns out to be a case where the double bond which is not welcome to the metal is allowed to react with hydrogen easily. This forms the saturated carbon-carbon bond. It also generates the 18 valence electron species. Now this can also, this also reacts with C 2 f 4 which is which is understandable because now you have the formation, of you have the formation of eighteen valence electron system again. This is, this is an 18 valence electron system, which is formed as a result of reacting it.

Here again you can see that two carbons are isolated from the rest of the aromatic system. During the course of this reaction because the eta 3 eta 5 form of nickelocene is more stable than the 20 valence electron eta 5 eta 5 system. So, C 2 f 4 readily reacts in a 2 plus 2 reaction 2 plus 2 cyclo addition reaction resulting in the formation of a bicyclo compound. This is again an 18 valence electron stable nickel metal complex.

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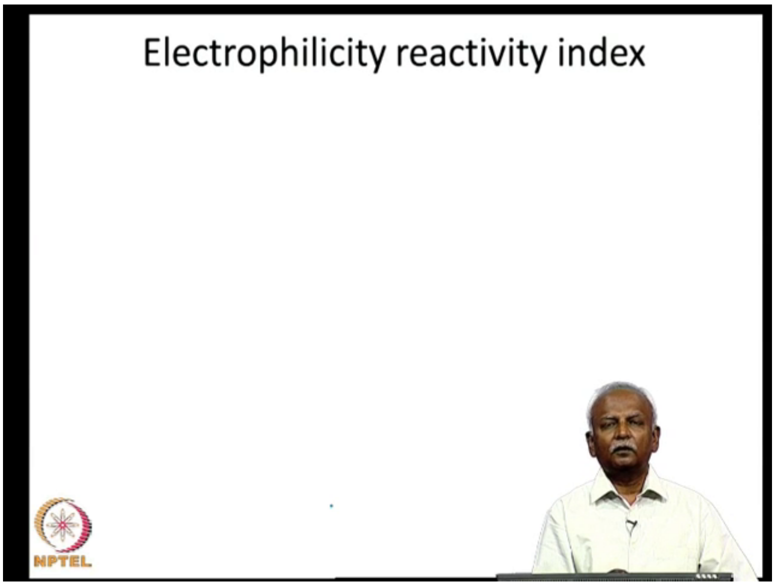

Electrophilicity reactivity index

Now, it is possible for us to rate the amount of electrophilicity that is present in these coordinated compounds.

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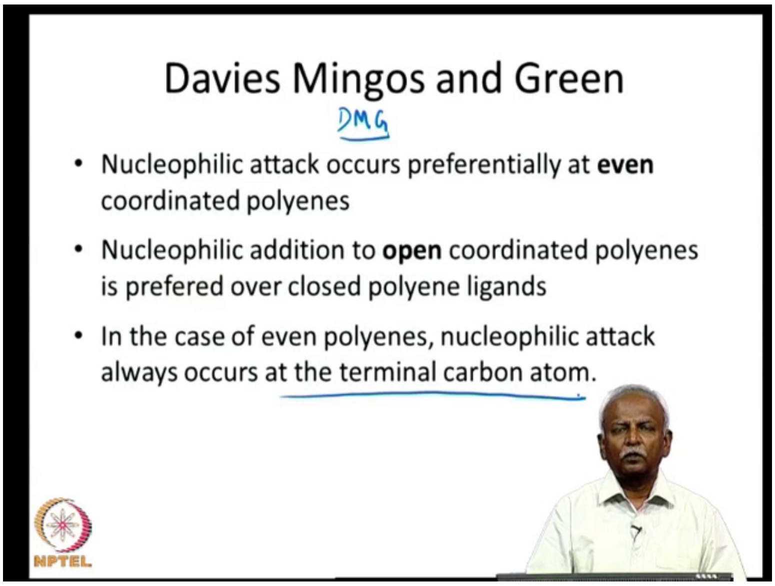

Davies Mingos and Green

DMG

- Nucleophilic attack occurs preferentially at **even** coordinated polyenes
- Nucleophilic addition to **open** coordinated polyenes is prefered over closed polyene ligands
- In the case of even polyenes, nucleophilic attack always occurs at the terminal carbon atom.

Davies, Mingos and Green formulated what is popularly called as a DMG rules. So the DMG rules comes from the three people who worked on understanding theoretically, as well as experimentally the reactivity of various coordinated groups. The question is if you have multiple coordinated organic compounds, which one would react first. The Davies Dingos Green rules are easy to understand as they suggest that a nucleophilic attack will happen preferentially at even electron compounds.

That means, if it is a C 2 or a C 4 then eta 4 or an eta 2 compound will react faster than an eta 3 compound. Secondly nucleophilic addition to open coordinated polyenes is preferred over closed polyene compounds. These are the two rules that can be readily understood and we will explain them in the following slides. Lastly we should say we can add that the even polyenes. The terminal carbon atom is the one which is most reactive. These can be readily understood from the molecular orbital picture, which is what they studied in order to arrive at these rules.

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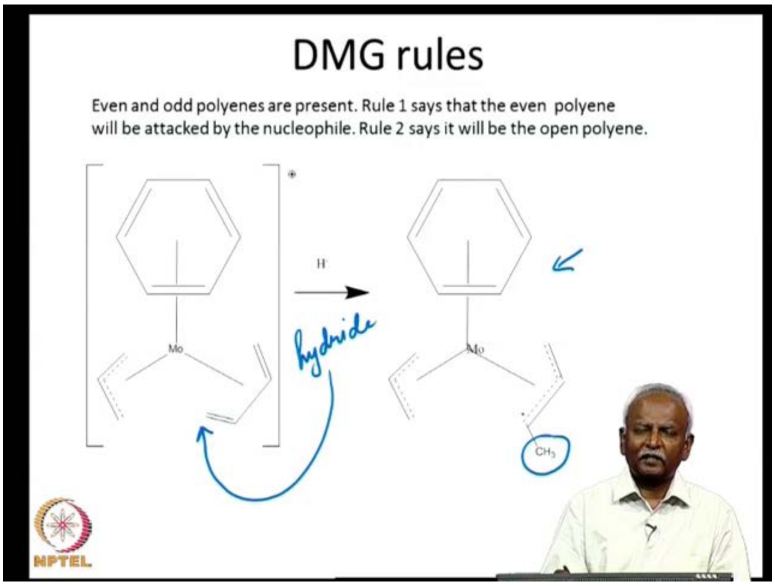

DMG rules

Even and odd polyenes are present. Rule 1 says that the even polyene will be attacked by the nucleophile. Rule 2 says it will be the open polyene.

So, here are three examples that are very popularly given in this example. I have a molybdenum complex with a net positive charge and a nucleophile in this case. A H minus a hydride, a hydride is attacking this molecule and the question is which one would it prefer. The aromatic ring as we have noticed does not lose its aromaticity significantly. The diene which is coordinated to the molybdenum is the second even electron system that is coordinated to the molybdenum.

That is the one that undergoes the attack and as we have said in the third rule. The terminal carbon atom is the one which undergoes attack. This can be seen from the fact that the lumo of the butadiene is the one the empty orbital on the butadiene is the one that will have a larger coefficient on the terminal carbon atom. As a result you have attack on the CH 2, which then becomes a CH 3 group. Now, you have a bisallyl complex and because you attacked it with an anionic group you end up with a bisallyl complex. This is neutral so the net charge on this complex is 0. One can see that the use of rules 1, 2 and 3 allow you to predict exactly the product that would be formed in this complex reaction.

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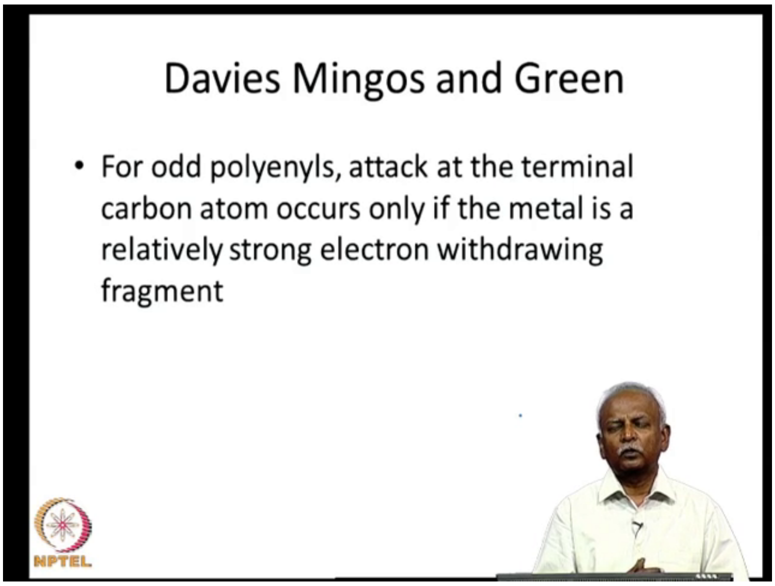

Davies Mingos and Green

- For odd polyenyls, attack at the terminal carbon atom occurs only if the metal is a relatively strong electron withdrawing fragment

For odd polyenyls attack at the terminal carbon atom is not the favored position. This might be surprising, but again based on the fact that you have in the lumo. If you have an allyl anion the lumo is a highest occupied the highest energy molecular orbital. That highest energy molecular orbital has got a large contribution from the central p orbital. As a result it is more likely to have an attack in the middle of the allyl group than in the terminal position. Whereas, if you deplete electron density from the allyl group and make it look like an allyl cation then a terminal attack is more favored. This is because the middle carbon atom now no longer contributes to the molecular orbital.

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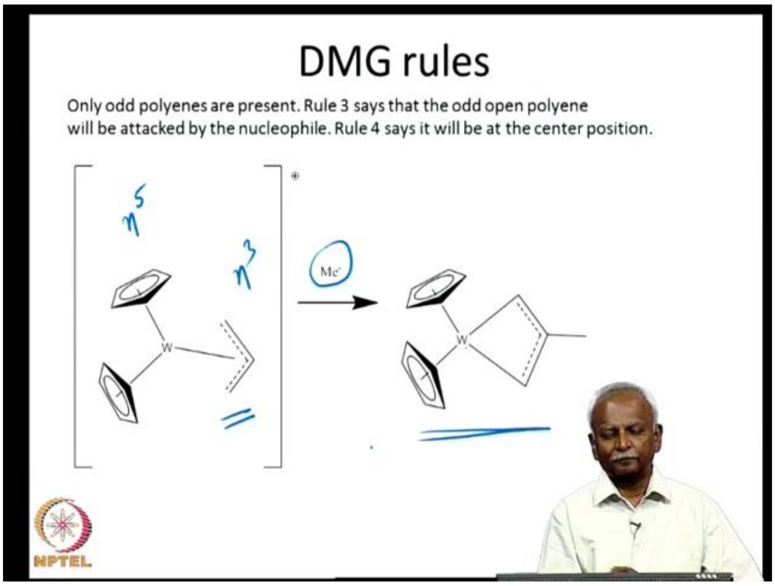

DMG rules

Only odd polyenes are present. Rule 3 says that the odd open polyene will be attacked by the nucleophile. Rule 4 says it will be at the center position.

So, here is an example where rule 3 and rule 4 are employed. You have the possibility of an e 2 odd systems and the closed polyenyl. This is eta 5 cyclopentadienyl unit or an eta 3, which is open center. It is the eta 3 open centers which will undergo reaction. We also note that the eta 3 centers will undergo attack in the middle position. Sure enough a methyl anion which attacks the allyl group attacks in the middle position. It then forms an allyl complex which is pictured here. Once again you have a cationic system which becomes a neutral molecule at the end of the reaction.

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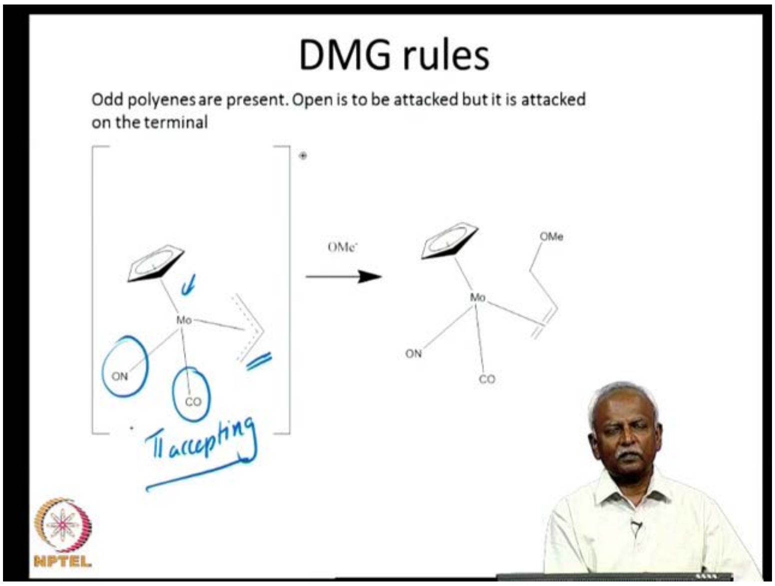

DMG rules

Odd polyenes are present. Open is to be attacked but it is attacked on the terminal

Now, odd polyenyls if they undergo reaction they undergo reaction at the terminal position. If you have very electron withdrawing groups on the metal atom so no plus, no plus and co are pi accepting ligands. They modify the reactivity, they modify the reactivity of the molybdenum so much so that now the methoxide attacks the terminal position. This is because the allyl has been depleted of electron density. This now behaves as if it is an allyl cation the previous example.

We also had a metal which is in the same group, but now we have a cationic system which does not have electron withdrawing substituents. Instead you had electron donating cyclopentadienyl anions. So the attack was in the middle carbon. Here I have two electron withdrawing substituents. A nitric NO and a CO and this turns out to be the electron depleting. Decreased electron density results in an attack at the terminal position.

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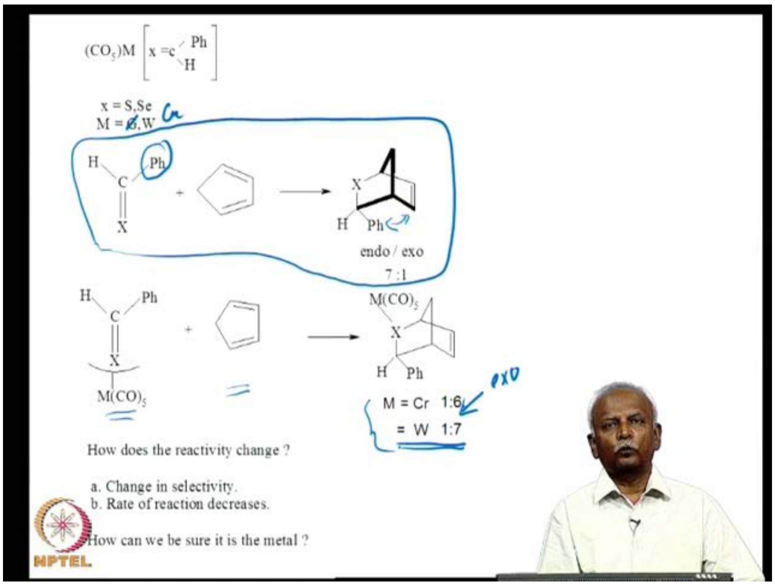

x = S,Se
M = ~~C~~,W Cr

M = Cr 1:6
= W 1:7

How does the reactivity change ?

a. Change in selectivity.
b. Rate of reaction decreases.

How can we be sure it is the metal ?

So, the altered reactivity of ligands is also seen in some other instances, where you have a diels alder reaction for example. The diels alder reaction that is happening here is happening between a hetero alkene and a cyclopentadiene. When you have a group like a Ph group then there is a possibility of having an endo and an exo product. The endo product, where the Ph group is close to the double bond would be favored. In fact if you carry out this reaction in the absence of any other reagent, if you carry out this reaction in the absence of any other reagent you get a seven is to one ratio of the endo versus exo.

This is in spite of the fact that the phenyl group would be sterically encumbering the nobonyl system. The electronic effects are secondary electronic effects which favor the endo product. They can be modulated if the x group is coordinated to a metal pentacarbonyl unit. You will note that these thiocarbonyls and the seleno carbonyls readily coordinate to a metal pentacarbonyl. When the coordinated thiocarbonyl reacts with the cyclopentadiene then it ends up with the same molecule. Except that the fact that the metal pentacarbonyl is attached to the x group.

Now, it turns out that the reactivity changes. How does it change? Now you have a greater amount of the exo product. You have a greater amount of the exo product compared to the endo product this change in reactivity has been brought about primarily because of the mco 5. Now the rate of the reaction also decreases but, how do we know that the metal is a cause for this?

So, I have already told you that it is possible to have this is chromium or tungsten. This is coordinated to the x group. If we change the tungsten, it gives you a ratio of one is to seven, where seven is a amount of exo. Seven times the exo product is formed. If you have chromium instead of tungsten then you have a change in this ratio a clear indicator of the fact the metal plays a role in modulating the reactivity of the hetero alkene, which is undergoing a diels alder reaction.

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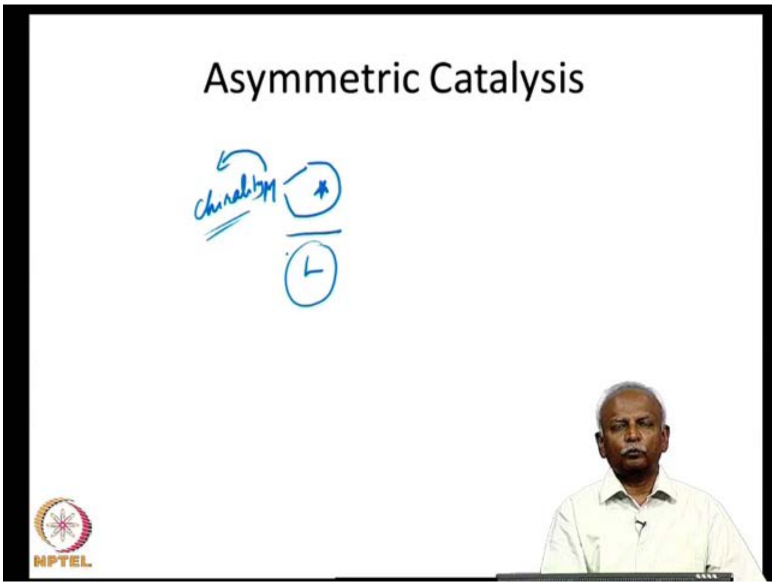

Asymmetric Catalysis

So, there is another large section where the catalyst which is carrying out the, or promoting the reaction has a chiral center. In which case, the metal is able to transfer this chirality. Transfer chirality onto the product even when the product and the reactant and the product are not having any chirality. It is possible to transfer chirality from the ligand. This is this turns out to be an extremely large chapter so we will consider them together in a separate talk.

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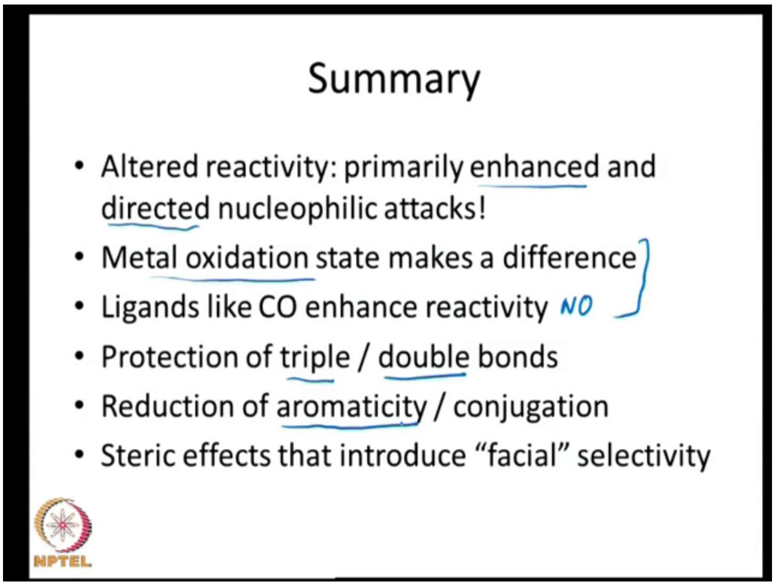

Summary

- Altered reactivity: primarily enhanced and directed nucleophilic attacks!
- Metal oxidation state makes a difference
- Ligands like CO enhance reactivity NO
- Protection of triple / double bonds
- Reduction of aromaticity / conjugation
- Steric effects that introduce "facial" selectivity

How about, let me just summarize, what we have discussed today? The presence of a metal on an unsaturated organic molecule alters its reactivity, and how it does so? Primarily you have an enhanced and directed nucleophilic attacks, we saw that not only there is enhancement; there is also directionality in the nucleophilic attack because of the presence of the metal atom, which protects one side of the pi system, and allows attack from the other side. We also noted that the oxidation state of the metal can enhance the nucleophilic attack, if it is more positively charged, then the nucleophilic attack is enhanced.

And ligands like CO and NO can also enhance the reactivity, because they withdraw electron density from the metal. So, these two factors are basically ones which are modulating the enhanced nucleophilic attack that we talked about in the first point. Now, if you have a double bond or a triple bond it is possible to protect it from further reaction by using a metal. This turns out to be useful especially for systems, where you have a triple bond. And further reduced aromaticity in a cyclopentadienyl system was observed when you have a twenty valence electron system.

This of course, is a special case, but it illustrates the principle nicely that you can have the reduced amount of reactivity, when you have a metal not just the enhancement of reactivity. Lastly we saw several examples, where there can be pi facial selectivity because of the presence of a metal atom. We also noted that the passing that a metal, the use of metal in carrying out this reactions. Although it turns out to be a useful way of doing it, it is not necessarily green chemistry that is going on.