Advanced Transition Metal Organometallic Chemistry

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Lecture – 25
Transition Metal Arene Complexes: Reactivity

Welcome to this 25th lecture of the course entitled advance transition metal organ metal chemistry. In the last lecture we have been talking about the reactivity of transition metal arene complexes. We have looked into the different reactivity patterns of these bis-arene transition metal complexes and compare them to that of their cyclo pentadienyl counterparts and what we had seen that these bis-arene transition metal complexes are more air and moisture sensitive as compared to the metallocene counterparts.

Furthermore we had also seen in our last lecture that these transition metal bis-arene complexes are more vulnerable to oxidation. We are also observed that these transition metal bis-arene complexes are kind of kinetically inert towards ligand exchange if it were simple Bis benzene type complexes however for condensed and in complexes the ligand exchange reactions are quite favored. And we had observed the formation of mixed benzene naphthalene dinuclear complex of chromium through this taking advantage of this ligand exchange reaction of condensed bis-arene transition metal complexes.

Also another sharp difference between bis-arene transition metal complexes particularly with respect to the these cyclo pentadienyl transitional bis-arene complexes is the fact that these bis-arene transition metal complexes does not undergo electrophilic aromatic substitution reactions similar to the ones that you had observed for cyclo pentadienyl cyclo pentadienyl transition metal complexes.

In fact what we what we observed in case of bis-arene transition metal complexes is that the electrophile instead of undergoing electrophilic substitution reaction at the arenering ends up oxidizing the central metal atom and does not participate in the electrophilic substitution reaction. Continuing further on these the reactivity pattern of bis-arene transition metal complexes we are going to take up another interesting reaction on this topic and this is called the methylation reaction.

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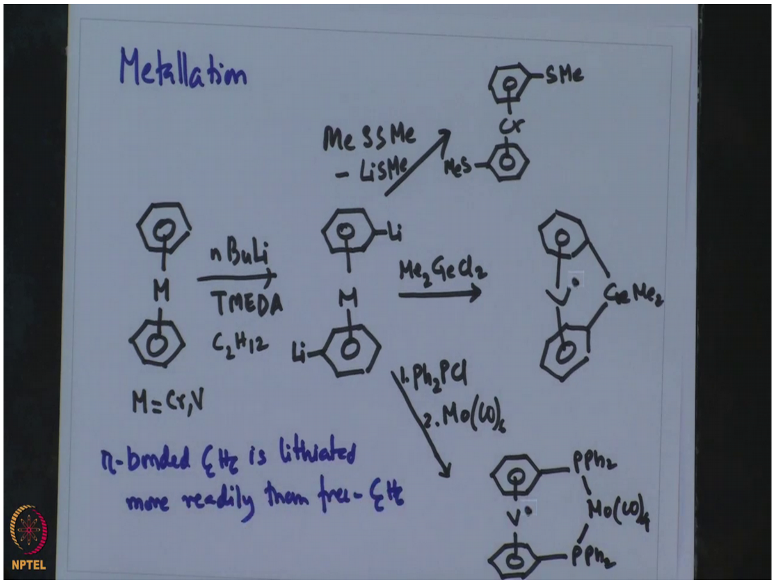

Metallation

π-bonded C_6H_6 is lithiated more readily than free-C_6H_6

What in contrast to what we had observed for cyclopentadienyl transition metal complexes particularly with that of ferrocene what we had seen that in presence of lithium reagents multiple litheiation was a problem and there was sort of not a simple strategy to get monolith eiated or dy selectively litheiated or selectively mono litheiated or di litheiated pattern for this kind of cyclo pentadienyl transition metal complexes.

Unlike that in case of transition metal bis-arene complexes selective delineation can be effected by performing the reaction in presence of TM EDA as is shown over here gives this dilated product with litheiation occurring in each of the two rings. Now it must be noted that these Pi bonded benzene is methylated more readily than free benzene, free benzene. The another interesting thing is that this dilated product with litheiation in each of the ring was indeed observed even for metallocenes again in presence of TM EDA.

So, this method of obtaining time dilatation is not only a same not only is similar to what is observed for bis-arene transition metal complexes but also was observed for cyclopentadienyl transition metal complexes. Now this is a useful intermediate which can be converted to many other interesting reagents leading to substitution on the ring as is a shown over here. So, reactions with Me S S Me - Li S Me give the substitution of S Me on the ring or reactions of Me2 Ge Cl 2.

Now this is a method whereby answer system with breeding dimethyl zirconium can be created of the formula somewhat like this M = 2 vanadium radical and third one is P Ph2 PCl and then reaction with molybdenum hexacarbonyl giving this beautiful di nuclear complex of Bis benzene vanadium radical with PPh2 molybdenum CO4. So, what we had seen that though electrophilic aromatic substitution was kind of hindrance or not very a common for Bis-arene complexes however these double litheiation or litheiation in presence of TM EDA provides route for putting different kind of substitutes on the benzene ring and examples of three different reactions are shown over here.

So, in one for chromium substitution leads to the SMe 3 on the ring for vanadium like answer type complex of germanium dimethyl or dinuclear vanadium molybdenum complex so that one with substituent on the link can be achieved as is shown over here.

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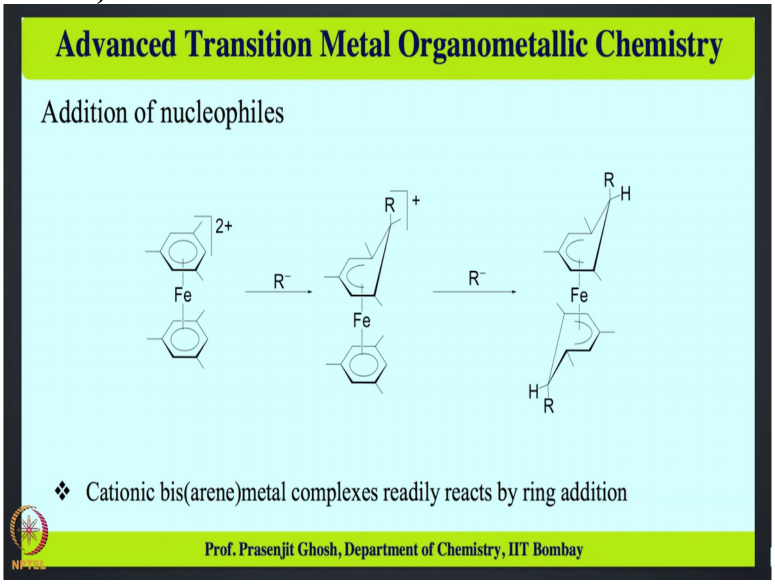

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Addition of nucleophiles

- Cationic bis(arene)metal complexes readily reacts by ring addition

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So, the addition of the electrophile nucleophiles that is an interesting reactions which sort of lead to the addition on the ring of nucleophiles cationic bis-arene metal complexes.

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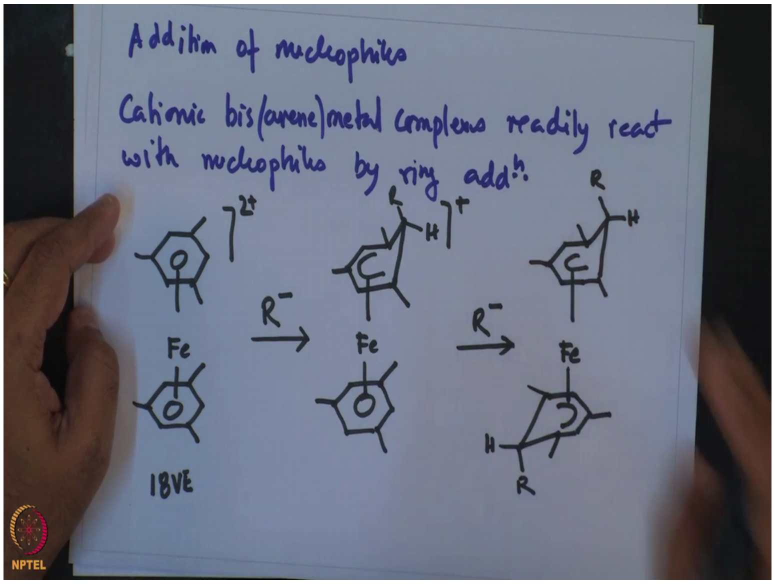

Addition of nucleophiles

Cationic bis(arene)metal complexes readily react with nucleophiles by ring add^n.

Readily react with nucleophiles by ring addition. So, this is illustrated by this nice example of tri methyl 246 tri methyl benzene this is a diatonic complex, so, diatonic electron so 6 + 6, 12; 12 +8; 20, 20 + 2 gives you 18 valence electron compound that when reacts with nucleophile like r- the nucleophile does not attack the metal center but instead attacks the ring and the ring loses its aromaticity iron Fe and the other ring still remains intact.

And overall this becomes a monocatonic complex which can react with a second nucleophile to give this neutral compound. And so where we see the nucleophile attacking both of the rings with the first ring getting attacked and again the ring does not regain its aromaticity and just the cationic complex by addition of the nucleophile just two of them becomes a neutral one. Similar addition has also observed been observed on the ruthenium complex as well as is shown over here.

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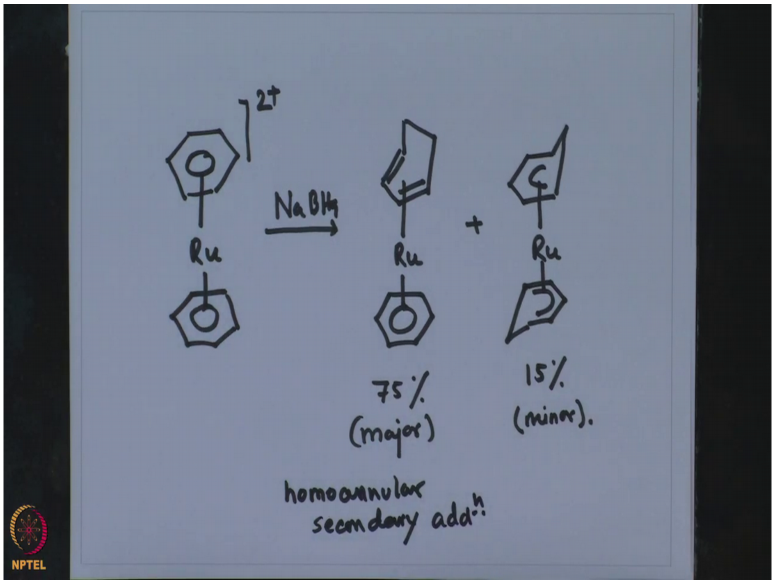

2+ with sodium borohydride gives this has the major product 75% plus the expected duration that is the minor product on; so, the difference is that in this case the nucleophile acts on the two different rings but in the ruthenium this homo annular secondary addition that both the nucleophiles act ad on the same ring. So, in this case homo annular secondly addition is more predominant and the reason given for this so more on the secondary addition in case of ruthenium is just that the thermodynamics favors.

So, here we had seen a nice addition of nucleophiles where the nucleophile leads to the addition on the ring for cationic bis-arene complexes in case of iron what we see is that the nucleophile going on on to two different rings giving the neutral compounds. Whereas in case of ruthenium what is seen that this nucleophile both of the nucleophile attacking the same benzene ring. So, homonuclear secondary addition is predominant as giving like to the product corresponding product in 75% as opposed to the nucleophile attacking each of the 2 rings separately.

And that is only a minor product in case of the ruthenium and the explanation given is just the thermodynamics governs the control of these two different type of reactivity observed okay.

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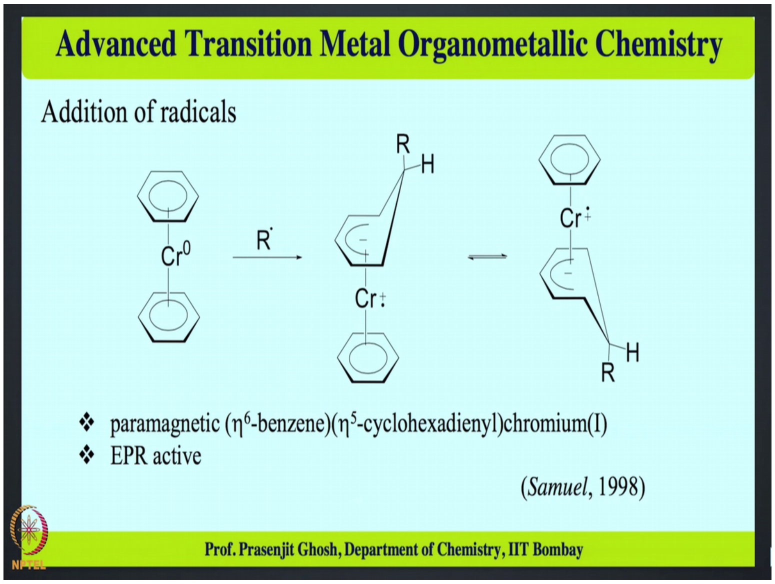

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Addition of radicals

- paramagnetic (η^6-benzene)(η^5-cyclohexadienyl)chromium(I)
- EPR active

(*Samuel*, 1998)

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So, the next after addition of nucleophiles the another interesting reaction is addition of radicals.

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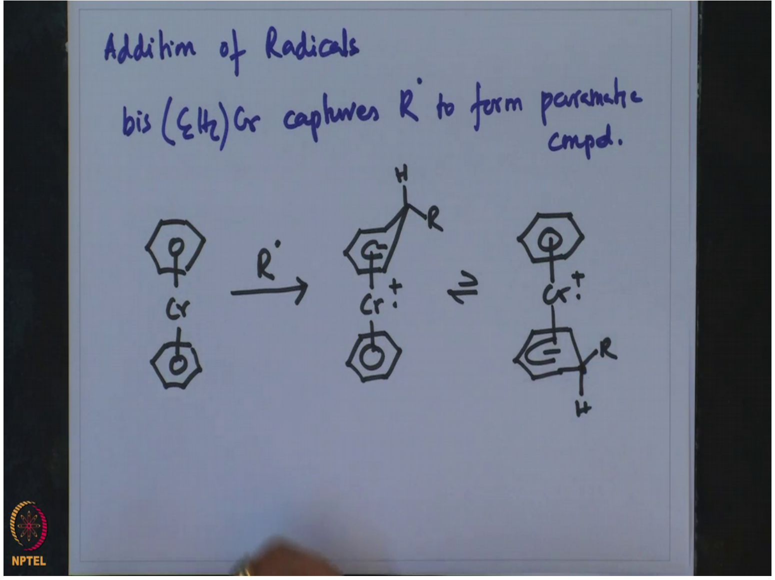

Addition of Radicals

bis $(C_6H_6)Cr$ captures $R^{\cdot}$ to form paramagnetic cmpd.

Now this addition of radical there leads to formation of paramagnetic compounds bis benzene chromium captures radical to form paramagnetic compound and this is illustrated as shown over here. Bis benzene chromium reaction with R dot H-R chromium and this is a radical cation which stays in equilibrium with chromium. So, overall this is a radical species because the chromium is in has a overall charge of +1 and the anionic ring has a -1 so they cancels out.

As a result that these species to form he is radical in nature and being radical in nature this compound is EPR active. So, what we had seen in terms of the reactivity is that the addition of the electrophilic substitution reaction does not occur but in state litigation can be affected in peace are in transition metal complexes and litigation can leads to a various kind of substitution reaction we had seen that other than that one can also see addition of nucleophile which sort of results in cationic complexes giving to the attack on the ring.

And the attack on the ring can be happening or can happen for on the same ring or on two different rings. And we have also seen the addition of the radicals occurring for base benzene chromium complexes giving to paramagnetic species and with that we come to end on end of our discussion of bis-arene complexes of transition metal and then we are going to discuss in line with of the half-sandwich type complexes.

Particularly we are going to be talking about arene metal carbonyl complexes so these are metal with an arene and carbonyl complexes similar to the half sandwich complexes of cyclopentadienyl metal carbonyl complexes that we had spoken about.

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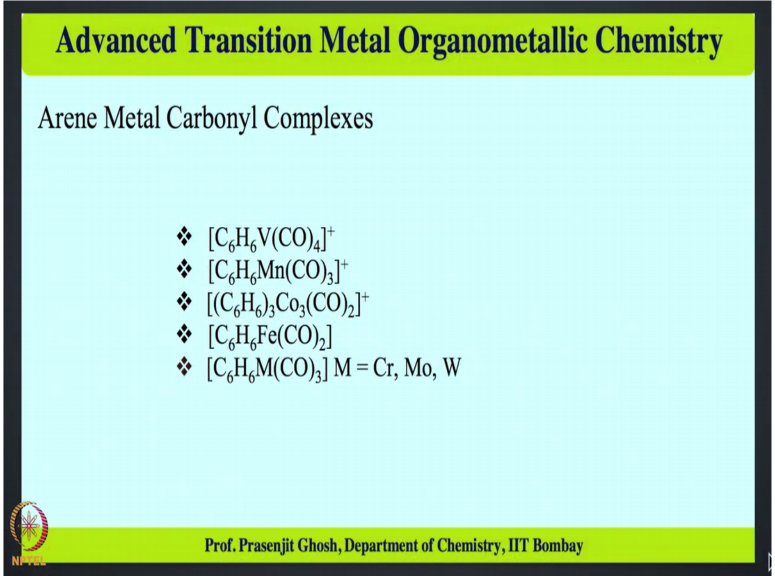

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Arene Metal Carbonyl Complexes

- $[C_6H_6V(CO)_4]^+$
- $[C_6H_6Mn(CO)_3]^+$
- $[(C_6H_6)_3Co_3(CO)_2]^+$
- $[C_6H_6Fe(CO)_2]$
- $[C_6H_6M(CO)_3]$ M = Cr, Mo, W

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So, the next few minutes of this lecture would be dedicated towards picking up these arraign metal complexes.

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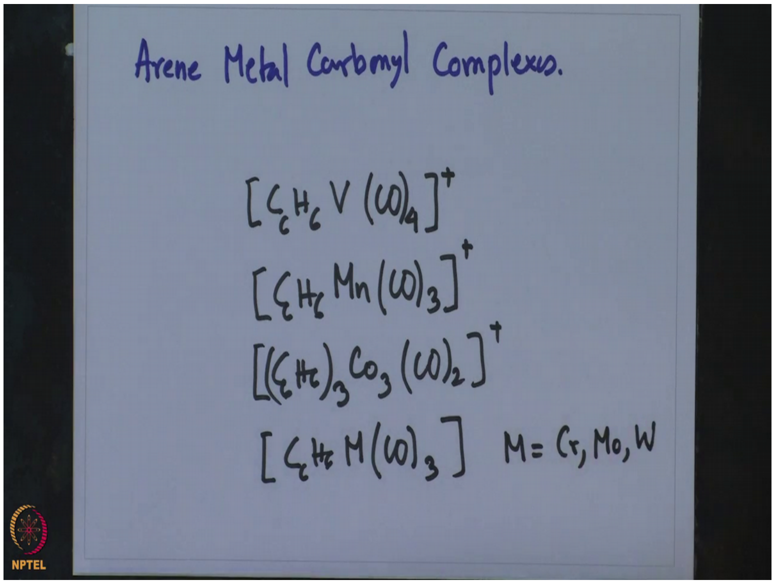

Arene Metal Carbonyl Complexes.

$[C_6H_6V(CO)_4]^+$

$[C_6H_6Mn(CO)_3]^+$

$[(C_6H_6)_3Co_3(CO)_2]^+$

$[C_6H_6M(CO)_3]$ M = Cr, Mo, W

So, there are several examples of these some of them are given over here C 6 H 6 V CO 4 + C 6 H 6 Mn CO 3 + C 6 H 6 whole 3 CO 3 CO 2 + C 6 H 6 M CO 3 where M can be chromium molybdenum tungsten. So, what we see is in like with that cyclo pentadienyl transition metal carbonyl complexes there are a whole range of corresponding benzene transition metal carbonyl complexes and they to the extent that they can be treated as a class of their own and we are going to focus now on the synthesis aspects of this benzene transition metal carbonyl complexes.

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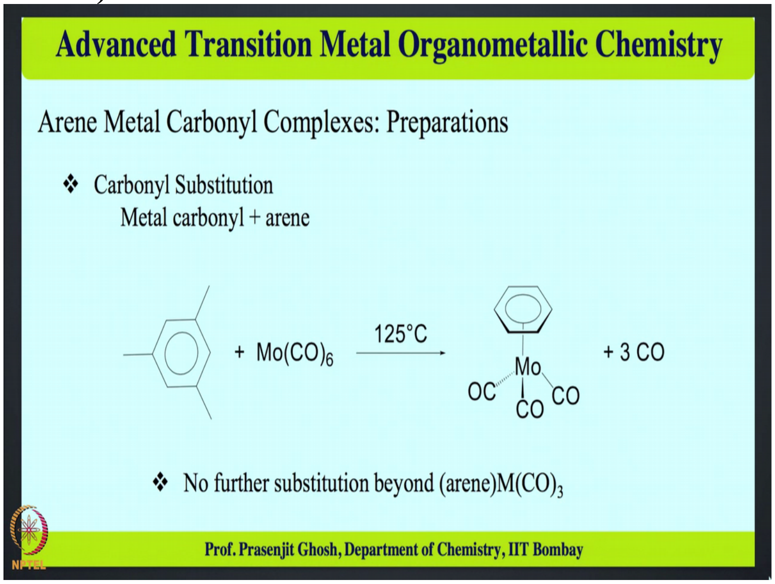

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Arene Metal Carbonyl Complexes: Preparations

- Carbonyl Substitution
  Metal carbonyl + arene

- No further substitution beyond (arene)$M(CO)_3$

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So, one of the common methods of preparing these complexes involve metal carbonyl.

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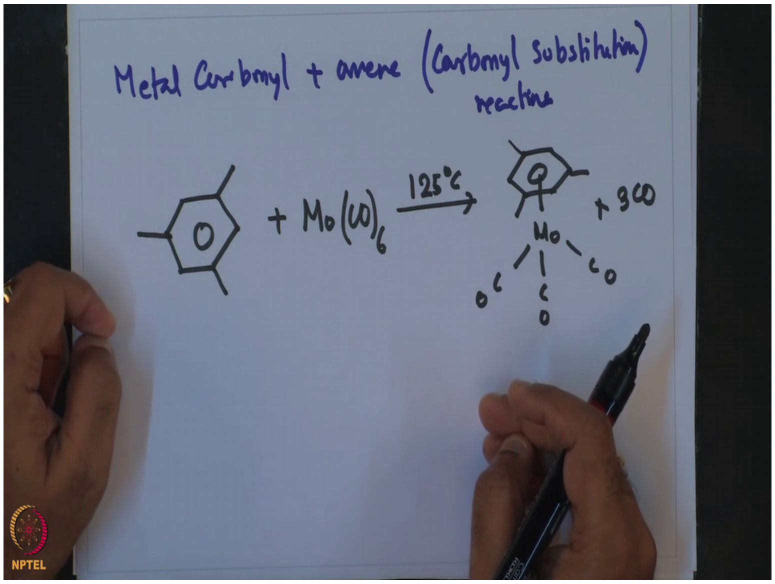

And reaction of metal carbonyl an arene + arene and these are called carbonyl substitution reactions and this is given as tri methyl benzene + molybdenum hexacarbonyl 125 degree centigrade giving add in molybdenum tri carbonyl complexes + 3 CO. Now this is a very simple method and kind of a very intuitive as well because the target compound is a lean metal carbonyls. So, a very good way would be to start with metal carbonyls with arene and by simple heat now if arene each of their in is a 6 electron donor and it kind of replaces 3 carbonyls in return.

Now, one can synthesize chiral complexes using these compounds and this is illustrated by this beautiful example in which the diastereomers are formed depending on the types of the arena used.

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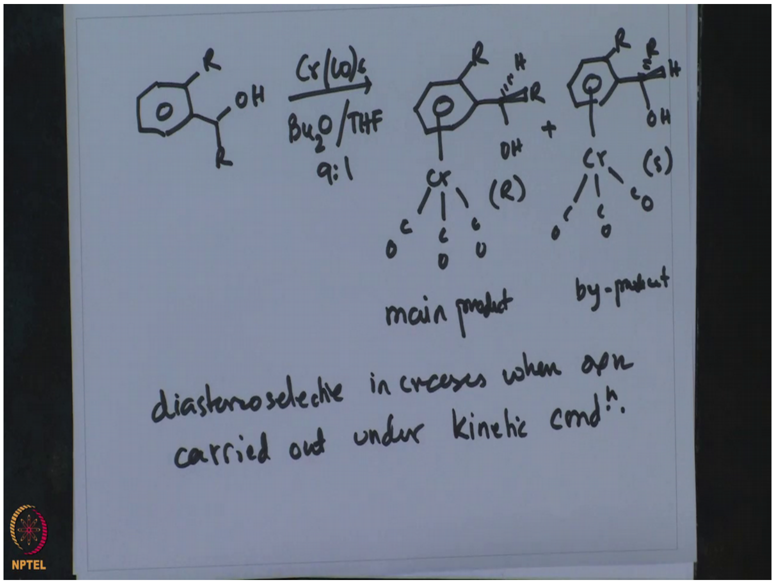

And the example given over here is benzene R OH in presence of chromium hexacarbonyl in Bu 2 O THF 9:1 then what one gets is this substituent C 8 ROH 8 which is the R confirmation rate chromium tricarbonyl + the corresponding our RH OH the S confirmation with chromium tricarbonyl and this is the main product and this is the byproduct and these they can be separated and diasterioselective increases when reaction carried out in under kinetically kinetic conditions okay.

So, with these I would like to conclude today's discussion today we have mainly looked at the reactivity of transition metal bis-arene complexes. This was in continuation with our earlier discussion on the same topic and what we had discussed today in particular was that these compounds can undergo selective methylation particularly dilatation in presence of TM EDA and the diliethiated compounds can be further sub transformed to other compounds depending on various reagents.

We have also looked at the reactivity in terms of addition of nucleophiles and what we had seen that nucleophilic addition indeed take place on the ring leading to loss of reactivity in case of transition a cationic transition metal bis-arene complexes in some cases the nucleophiles add on the different ring losing leading to loss of aromaticity in both of the arene rings, both of the two rings of the bis-arene transition metal complexes.

And in some other cases that it both of the nucleophile attacked on to the same ring where the other aromaticity of the other thing remained intact parallel to this reaction. We have also looked at how the radicals attack these bis-arene transition metal complexes. And here also the radical do attack to the ring leading to the loss of aromaticity of the ring and resulting in these cationic complexes. So, with this we finished off with our discussion on BCA reactivity of bis-arene transition metal complexes and then moved on to transition metal a arene carbonyl complex which is similar to the half sandwich complexes we have discussed for the CP counterpart.

And we had seen that there are very many examples of that and we have also taken up a preparatory method for adding transition metal carbonyl complexes and this method is quite simple that it involves static reaction of transition metal carbonyls with arene's at highly very temperature resulting in transition metal arene tri carbonyl complexes. One must note that each ring is a 6 electron donor.

So, the substitution leads to elimination of 3 carbonyls and the substitution does not go further than that. So, with this I would like to draw a conclusion and today's lecture and we are going to be discussing more on these arene transition metal carbonyl complexes particularly with respect to their synthesis structure and reactivity in the next class till then goodbye. And thank you Anna lip and I look forward to take up this topic with you in the next class goodbye.