

Advanced Transition Metal Organometallic Chemistry
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Lecture – 22

Transition Metal Arene Complexes: Preparation, Structure and Bonding

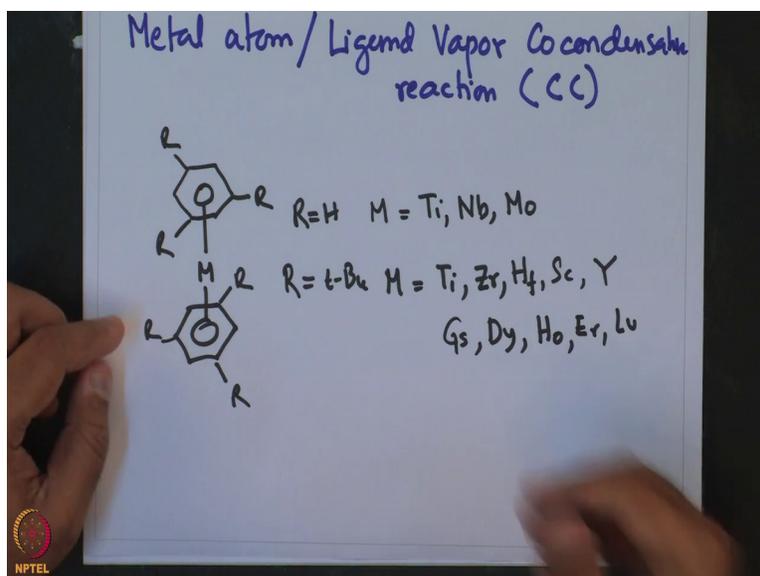
Welcome to today's lecture on advanced transition metal organometallic chemistry we have been discussing transition metal arene complexes in the in the last few lectures and in particular we have spoken about various synthetic methods that are available for synthesizing these transition metal arene complexes. In our last lecture to start with we have discussed Fisher-Hafner synthesis which involved reaction of metal tri chloride with aluminum in presence of arene.

And these gives this transition metal added binary complexes these this method is quite general in the sense that many transition metals can be used for synthesizing arene complexes using Fisher-Hafner synthesis. The other method that we discussed these cyclo trimerization of arene in these reactions trimerization of alkynes occurs in presence of some metal template resulting in transition metal arene complexes.

And then we have also discussed the third method which is a reductive complexation this is an interesting method in the sense that the method involves ligand which could form radical anion and then the reaction of the radical anion solves with transition metal halides giving these binary transition metal arene complexes. So, these are very interesting methods for preparing these binary transition metal arene complexes and we are going to continue this discussion further by looking into some more examples of these transition metal arene complexes in this lecture today.

So, one such important method is this metal atom ligand to condensation reactions.

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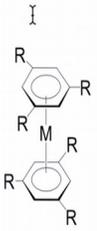
These are called metal atom ligand, vapor, co-condensation reactions are better known as CC reactions actually in this method metal atom in his vaporized state is directly reacted with ligand vapor and then cooled to very low temperature in which all combinations of compound that can possibly form results. And then after workup each of these compounds are isolated and characterized. This method however is very useful for producing a variety of be arene complexes which otherwise would be extremely difficult to synthesise.

(Refer Slide Time: 03:45)

Advanced Transition Metal Organometallic Chemistry

Bis(arene) Metal Complexes: Preparation

- ❖ Metal atom/Ligand vapor Cocondensation (CC)
- ❖ This method provides a variety of bis(arene) complexes



$R=H \quad M = Ti, Nb, Mo$ (Green, 1973, 1978)

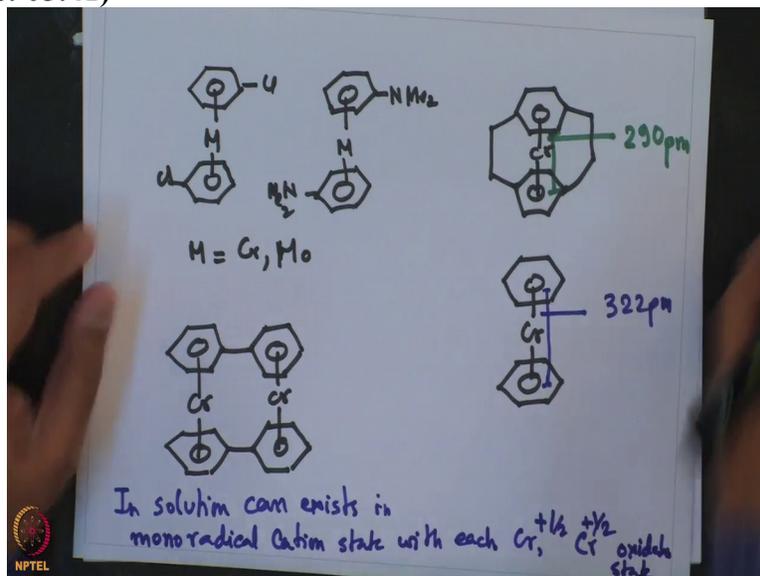
$R = t-Bu \quad M = Ti, Zr, Hf, Sc, Y, Gs, Dy, Ho, Er, Lu$ (Cloke, 1993)

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And we are going to take a look at some of the interesting compounds which utilizes this method to produce certain Bis arene complexes which otherwise would have been very difficult to synthesise. Now this method was sort of propagated or developed and propagated by and large by a professor Malcolm Green and Geoffrey Cloak and so they have done a significant

advancement in developing this method and popularizing this method. So, for example complexes like this our tools hydrogen then metal equals titanium, niobium, molybdenum and R equals t-butyl then metal equals titanium, zirconium, hafnium, scandium, terbium Gs, Dy, Ho, Er, Lu. So, these are a large variety of these these arene complexes which are synthesized by this method.

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We are going to take a look at some more interesting examples that have been synthesized using this method. For example the halide complexes like this or the amide complexes like this you; here metal is chromium and molybdenum similarly sandwich cyclopentadienyl type compounds this distance chromium are in distance is 290 picometer whereas the same which is much smaller, then the chromium arene distance is this benzene compound.

In this case where this is about 322 picometer this distance that 290 picometer is the distance between the two limbs two rings and over here this 322 picometer is the distance between the two rings. So, what one says that there is a compression arising from the presence of this ethylenic bridge in the cyclopentadienyl ligand. Now there is another interesting systems system which is a biphenyl ring where both of the rings are directly a methylated giving some structure like this.

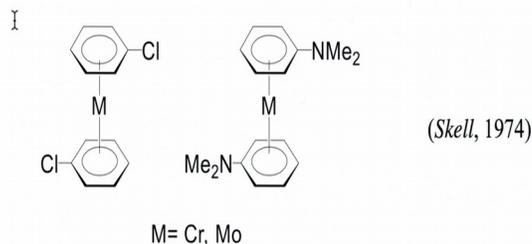
And one interesting thing about this compound is that these compound in solution can exist in mono radical cation state in solution can exist in mono radical cation state with each chromium +1/2 and chromium ++ 1/2 oxidation state.

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Advanced Transition Metal Organometallic Chemistry

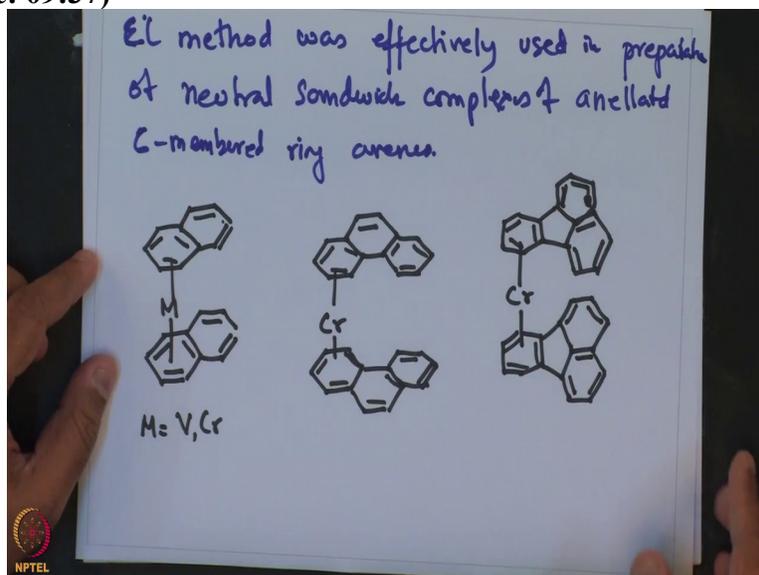
Bis(arene) Metal Complexes: Preparation

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So, this is interesting and complexes also this method was effectively used for preparing neutrals and sandwich complexes of annihilated first 6 membered rings.
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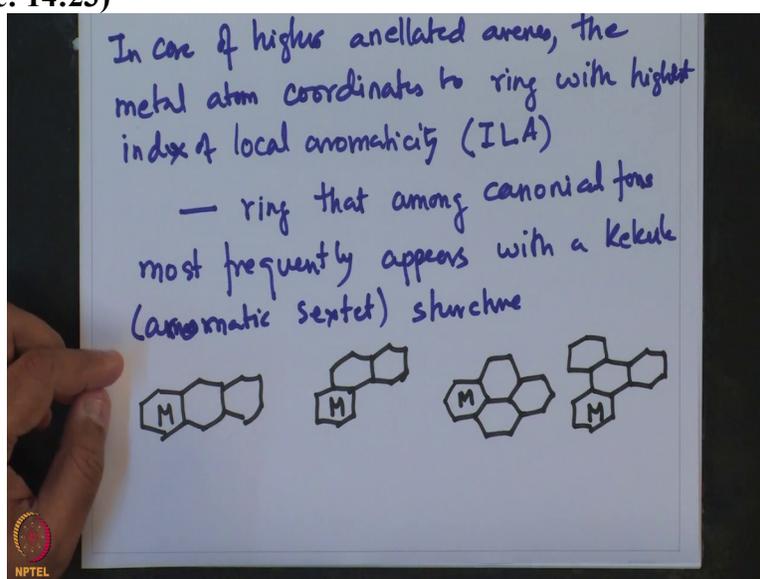


Effectively used CC method was effectively used in preparation of neutral sandwich, sandwich complexes of annihilated 6 membered arene's. So, let me just give some examples of these types these are really there are really some interesting examples so M = vanadium chromium one can even extend it further through three rings. Now here the complex formed is of this type as well as another interesting example include chromium okay.

Now of these are very interesting complexes where we have these annihilated 6 membered ring complexes of various arene. Now while these complexes are synthesized and characterized the way it is shown. The interesting thing about it is that in higher annihilated arene which of the

rings if there are more than as 1, 6 membered rings are present which of the ring would really be a coordinating to the metal.

So, the question primarily over here is that let us say for example in these there are 2 arene rings for these there are 3 arene rings there, for these there are 4 arene rings the question is that which particular one would be forming these are in complexes of with chromium and is there is this just by coincidence of which there any rule which governs them. And in fact this has been studied extensively and the reason which has been given out is the ring which has the maximum highest index of local aromaticity that being results in formation of this Bis arene complexes. (Refer Slide Time: 14:23)



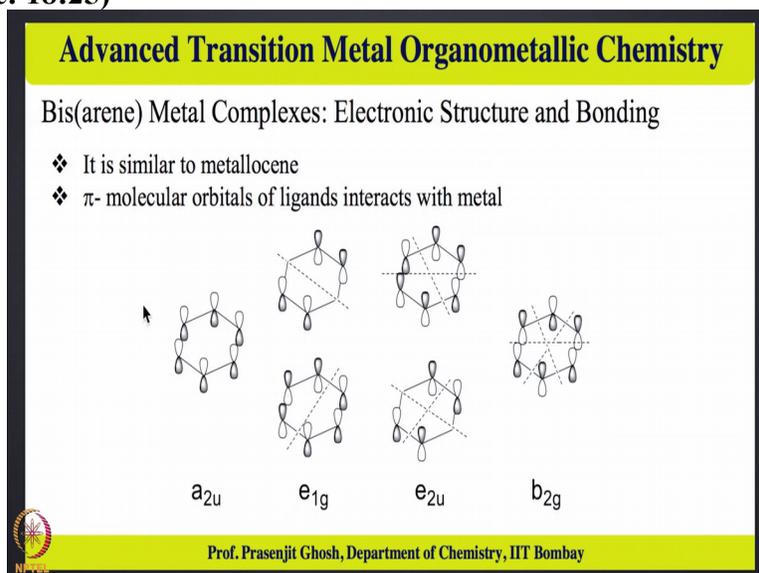
So, let me just illustrate this in bit more details in case of higher annelated arenes the metal atom coordinates to ring with highest index of local aromaticity and this is a ILA index of local aromaticity and this is explained as the ring that among canonical forms most frequently appears with a kekule a that means aromatics sextet structure. So, this is an interesting observation what it says that when you have annelated rings where there are multiple 6 membered arene links conjoined together then the question is which of this ring the metal would coordinate to?

And the answer to that is the metal prefers to bind to the aromatic ring which will have highest index of local aromaticity or rather which is every barely known as ILA. And ILA means that the ring when you draw the canonical structures of this whole conjugated system that the ring which will have which will most frequently appear in the calculus aromatic structure that is the ring which would ultimately end up binding to the metal.

So, let me just show some structure and their preferential binding for example if this is 3, 6 membered conjugated ring then M link M is the one which one the side as side on ring that it be the one which would be binding to the metal. Similarly for structures like this the metal would bind to the first side one or when the structure is like 4 rings like this the middle would bind to this one and if it is something like this the metal would bind to this one.

So, this is an interesting observation which explains a variety of structures that arise by this kekule insertion method. This method obviously is a very useful method where one can significantly get access to very interesting compounds which otherwise using propriety chemistry may be extremely difficult to synthesize. With these let me just move on to the structure and bonding in these Bis arene complexes.

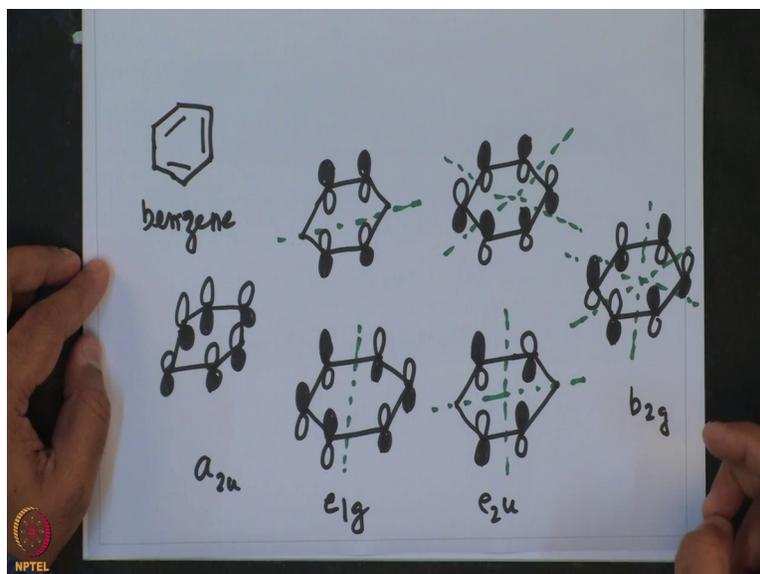
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And these we are going to be looking at the structure and bonding with respect to its molecular orbital diagram and so in the beginning ladies sort of look at how these atomic orbitals combine to form this fragment atomic orbitals for the atom rings and then move on to system which is more complicated like Bis-arene interacting with the metal and then look at the interaction at the middle level.

Now as far as the bees are in complexes structure and bonding this also is similar somewhat similar to the cyclopentadienyl ligand where the PI orbitals engage in bonding and let us sort of take a look at the different combinations of PI orbital that can result in various fmos and then see how they orient and themselves prior to their binding to metal.

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So, you know for the benzene and we were the simplest constructions that we would do is for benzene we are going to draw the structures of different molecular orbital and the first obviously is the all bonding orbital which is a $2u$ and in this all there is zero all the nodes are at the bottom the way it is shown. Similarly the first degenerate pair is $e1g$ and here one has two orbitals.

The first one has molecular orbital of this type where and the corresponding the nodal plane is shown over here and the other form is somewhat like this and the corresponding nodal plane is given as this. The next is $e2u$ this also have to degenerate fmos and the first one is something like this so this has two nodal planes one around this and another along this and the other one is this and this also is degenerate to the top one and has two nodal planes one along this the other one there.

And the the last orbital is some what like this it has alternate lobes of opposite phases and has three nodal planes and this one is called $b2g$. Now these gives a feel for how this individual Pi orbitals are oriented based on their energy and before they stack up with this benzene or Bis arene prior to they finally interacting with the metal orbital. Now if you look at this benzene atomic orbitals you see there are 6 PI orbitals.

So, there should be overall 6 fragment molecular orbital in combination and we do have 6 over here 1, 2, 3, 4, 5, and 6 and of the six the distribution is the first one is fully a bonding with zero nodal plane, the second one is a degenerate 2 orbitals with singular nodal plane and third one is

also a degenerate doubly degenerate orbitals with two nodal plane and the third one and the fourth one is the most high energy a orbit anti-bonding orbital having three a nodal planes.

So, we have seen how these PI orbitals sort of combine themselves to give six fragment molecular orbitals. This is somewhat similar to what we had seen for cyclopentadienyl anion where it was e 1 and e 2 combinations. So, that was just the sixth orbital which is present over here was missing for the cyclopentadienyl ligand. So, with these I am going to conclude today's lecture we have been discussing on the synthetic methods available for synthesizing these Bis-arene complexes.

And particularly to begin with we have looked into this fancy method which is called metal atom ligand vapour co-condenses in method or CC method in general. This method is a very useful method for producing preparing a wide variety of besides in complexes we have looked into some of the examples of this method and had seen that how this method was successfully used in preparing these complexes also we had observed that in case of at large higher annihilated ring systems it is the and the 6 membered ring which has highest local aromaticity index ILA that world that ring was particularly found preferably coordinated to the metal in the bis-arene and in systems.

We have also looked at the structure and bonding of these basurin systems and to start with we have looked into how the P orbitals of benzene orient themselves to form the fragment molecular orbitals which are a 2u, e 1g, e 2u and v 1Ga containing 6 set of orbitals depending on the nodal plane that arises out of their combination. So, with this we are going to stop in today's lecture we are going to take up this structure bonding in much more detail where we now look at the concepts which are developed over here.

And now see that how this 2u 1 GE to U and B to D finally interact with the metal and study its correlation diagram which eventually we will construct using this fragment molecular orbital. So, we are in the midst of a very interesting discussion on bis-arene complexes its structure and bonding and we are going to be continuing this in the next lecture where we develop or construct this molecular orbital diagram using these fragment molecular orbitals that we have developed over here.

So, till then I really thank you for being with me in this lecture and hope to see you in the next lecture where we are going to be discussing structure and bonding of piece array metal places in greater details thank you