Advanced Transition Metal Organometallic Chemistry

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Lecture no. 7

Transition Metal Cyclobutadiene Complexes: Preparations

Welcome to the seventh lecture of the course, titled Advanced Transition Metal Organometallic Chemistry. In our previous lectures, we have been discussing very important topic, which is cyclobutadiene as a ligand, for transition metals in organometallic chemistry. In this context, in the last class, we have looked at the structure and bonding of this cyclobutadiene ligand.

And what are the issues that concerns the nature of cyclobutadiene ligand, how does it bind to transition metal, what kind of structure would it exist, what kind of reactivity would it exhibit, all of these we tried to understand, with respect to its molecular orbital diagram, and these molecular orbital diagrams were constructed from atomic orbital's of cyclobutadiene ligands.

And then we had seen, these fragment molecular orbital's, or FMOS, constructed from the atomic orbitals represents diradical nature of cyclobutadiene, in its neutral form and square geometry which sort of mixing, extremely reactive. However, often complexation to transition metal this cyclobutadiene accept two more electrons from its metal orbital resulting in aromatic configuration of six Pi electron, and then getting stabilised in its transition metal complexes.

So, these molecular orbital diagram that we have looked at, we have not only looked at for cyclopentadiene, cyclobutadiene but also has compared it with just butadiene as well as allyl radicals that we have discussed in our earlier classes. Towards the end of last lecture we have also looked at various preparatory methods available for preparation of transition metals cyclobutadiene complexes and today in this lecture we would be continuing upon these various synthetic schemes that are available for preparing the metal cyclobu, cyclobutadiene complexes.

First method, that we had looked at involves the reaction of cyclobutadiene with two halogens di halogenenated cyclobutadiene, and looked into dehalogenetion by reaction with nickel carbonyl, resulting in nickel chloride and the half sandwich transition metal cyclobutadiene complex as we had seen earlier. Now in this class we will see another example of along the same thing in which iron complex of cyclobutadiene was prepared along the same lines.

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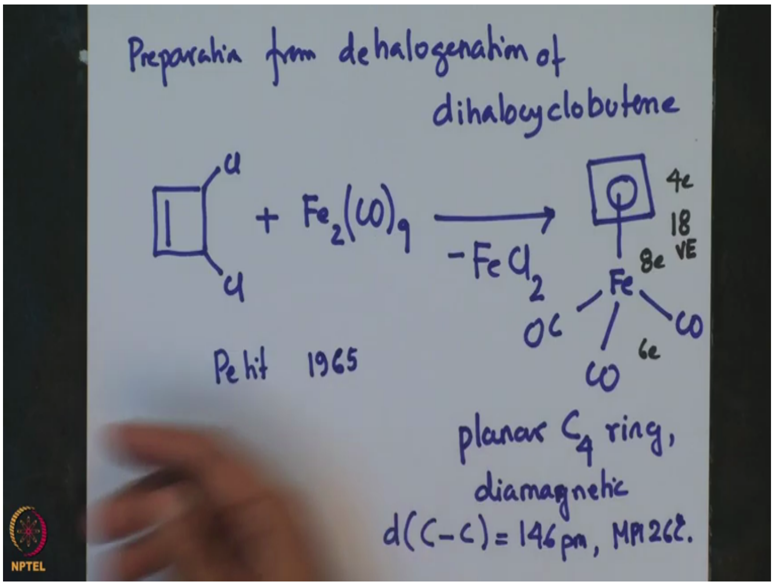

Preparation from dehalogenation of dihalocyclobutene

Petit 1965

planar C_4 ring,
diamagnetic
$d(C-C) = 146$ pm, MP 26°C.

So this preparation is about preparation from dehalogenation of dihalocyclobutane. So this is a dihalocyclobutane reacting with iron zero precursor Fe2 CO9 and also eliminates FeCl2 giving cyclobutane Fe cyclobutane and this is again a planar structure ring diamagnetic this has 18 valence electrons so 4 , 8, 12 and 6 from three COs this is a 18 valence electron compound and hence very stable. It has a CC bond distance of 146 picometer and melting point of 26 degree centigrade.

This was synthesized by Petit in 1965. So this method is similar to the nickel carbonyl method and also follows the same strategy of preparing this cyclobutadiene transition metal complex from this dihalocyclobutene by reaction of with by dehalogenation with nickel carbon precursor.

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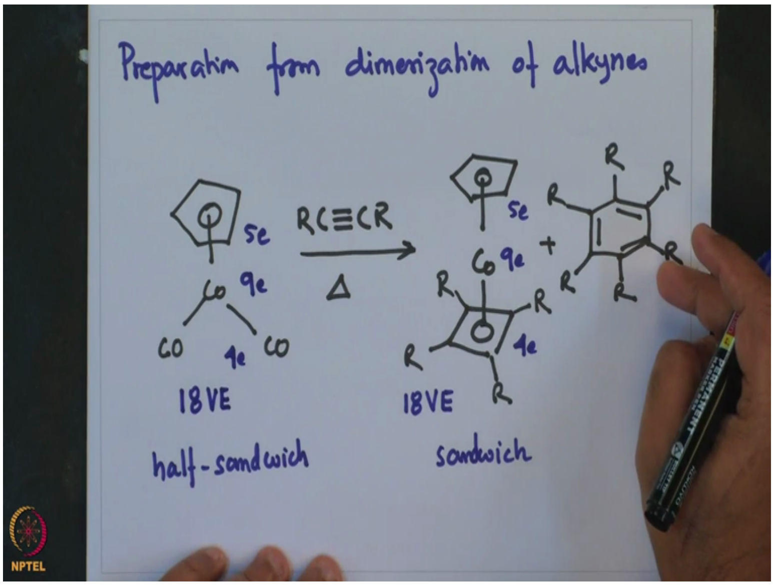
Preparation from dimerization of alkynes

The second method involves preparation from that uses dimerization of alkynes the reaction of CP, this is a half sandwich complex CP CO carbonyl reacting with alkyne and in presence of heat giving a sandwich compound along with trimerization dimerization will give cyclobutene of this alkyne and trimerisation will give benzene.

So what we see that we want to synthesize a sandwich compound a sandwich complex the classification that we had spoken about from a half sandwich cobalt complex, in that classification, both are also electron rich species this is 5, 9, and 4 so this is 18 valence electron species as well as the cobalt precursor is also 18 valence electron species 5, 9, and 2 carbonyls 4 so this also is a 18 valence electron species along with the formation of benzene.

So this is nice example what we saw that dimerization or trimerisation of alkene leading to the synthesis of cyclobutene and that is stabilized by complexation with cp carbonyl fragment with the results of elimination of two carbonyl molecule giving this heteroleptic sandwich complex the same route is used in another preparation that also involves dimerization of alkynes.

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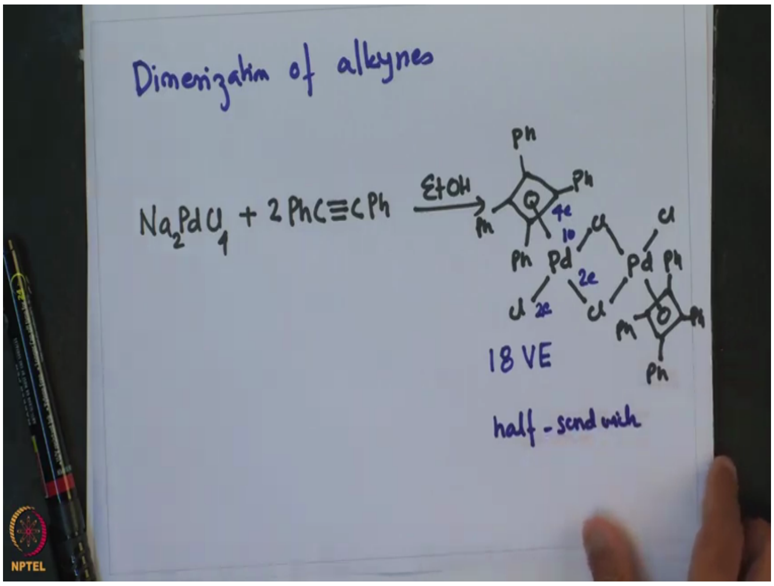

Dimerization of alkynes

So here, the reaction of Na2 Pd Cl4 + 2 alkynes in ethanol gives this tetra phenyl cyclobutadiene complex of palladium chloride, and these also 18 electron compound, 4 + 10, 14 and 2 chloride 21 bond is so this is one electron age to together 16, and then one dating plus 2 so this also is a 18 valence electron compound. And hence on the classification that we have been studying is for the category of half sandwich complex.

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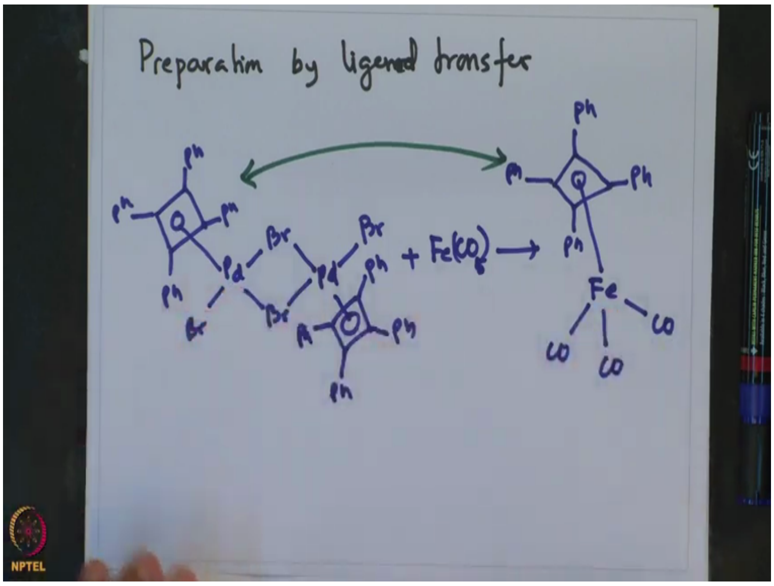

Preparation by ligand transfer

Cyclobutadiene complex can also be prepared by ligand transfer reactions. For example, the reaction of the palladium tetra phenyl cyclobutadiene with Fe CO5 gives the corresponding cyclobutadiene complex of iron. So, here we see a lateral ligand transfer, a lateral ligand transfer from palladium to iron and these arise that, these are lateral gliding transfer of cyclobutadiene ligand from one metal palladium on to another metal which is iron.

So, this is sort of can be perceived as the ligand exchange reaction and also a very useful method for producing this metal cyclobutadiene complexes. So the, another method is preparation of cyclobutadiene from metalla cyclopentine, cyclopentadiene complexes. This is a very interesting example where cyclobutadiene is constructed from metalla cyclopentadiene complexes.

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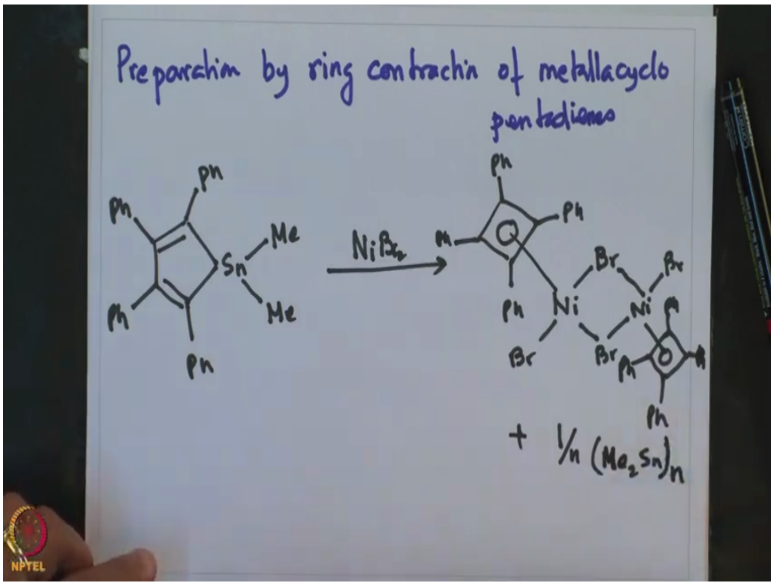
Preparation by ring contraction of metallacyclo pentadienes

And this preparation occurs by ring contraction. Example is a triene metalla cyclopentadiene complex, giving rise to this nickel bromide plus Me2 Sn polymer. So this ring contraction is kind of and very elegant way where a metalla cyclopentadiene, this is white is metalla cyclopentadiene which is there is a cyclopentadiene ring 5 member ring containing one of the what is this a metal, so it is a metalla cyclopentadiene, and then it has been dying, dying because there is two double bond.

So the method uses the concepts of extracting the metals out so resulting in cyclopentadiene, and then coordinating that form cyclopentadiene by extraction of the triene to nickel bromide giving rise to this structure. So this is a, in terms of synthetic aesthetics, this is a very elegant way of synthesizing this cyclobutadiene ring and as we progress in the field of organometallic chemistry, look at different strategies people have been implied in creating this complexes.

One cannot but stand back and appreciate the beauty and the aesthetic and the complexity of the synthesis people have undertaken in order to reach their destination and in this particular example is one such very elegant example, where ring contraction of metalla cyclopentadiene having a team have been performed to get to the cyclobutadiene ring. I must also mention that this cyclo metalla cyclopentadiene having a team or any other metal in one of its verses itself is a very exotic organometallic compound, and also requires lot of synthetic skills and challenges in trying to synthesize them.

So this is a very nice example of beautiful chemistry that is been cleared out in the field of organometallic chemistry. We are into take a look at another such elegant example along the same lines that involves contraction, ring contraction by metalla cyclopentadiene and in this case, is this with aluminium.

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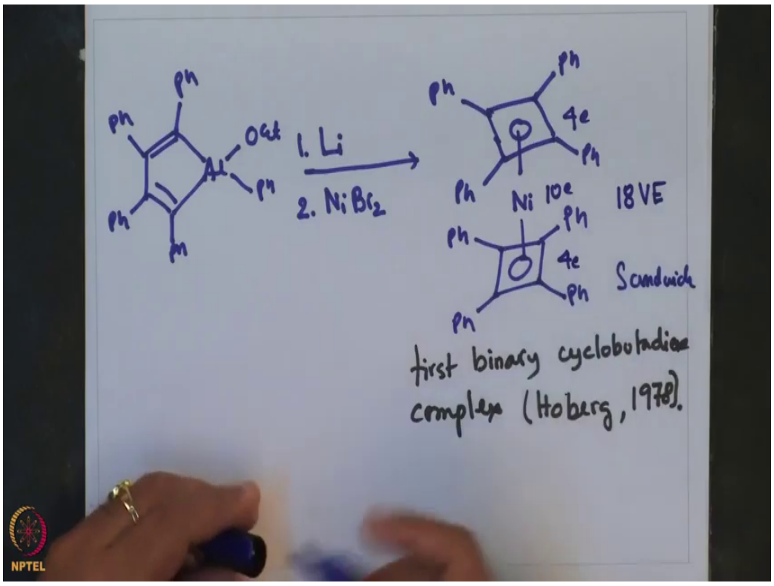

This gives over here this aluminium based metalla cyclopentadiene undergoes slots of aluminium and then resulting in cyclobutadiene ring, that when coordinates to nickel, to give this binary cyclobutadiene complex. A beautiful example, so this is the first binary complex, first binary cyclobutadienal complex, and was synthesized by Hoberg, in 1978, so this again in the nomenclature would be sandwich complex and this also is a 18 valence electron compound, 4e, 10e, 4e is 18 valence electron compound.

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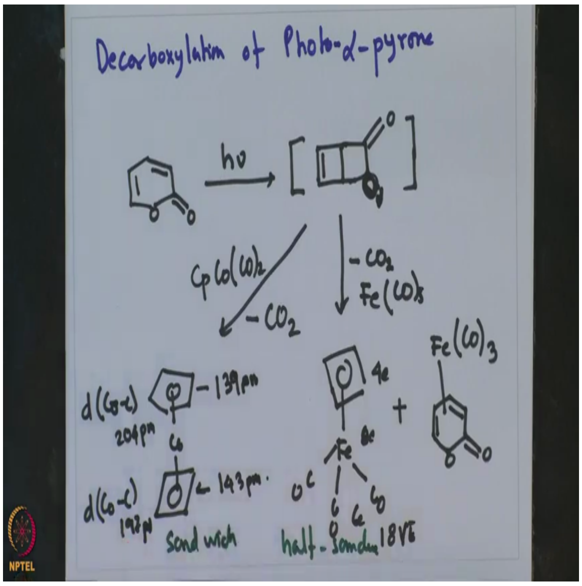

Another method is the decarboxylation of photo alpha pyrone. So this is also an elegant chemistry, as is outlined over here, in presence of light, it gives this intermediate, and that loses carbon dioxide, in presence of Fe CO5, so this moiety , this carbondioxide moiety is lost, and as a result one gets this cyclobutadiene, so this is lost, and there is a bond over here, with Fe CO3 and reaction also goes little bit backwards, and one also isolates this alpha pyrone compound of iron carbonyl as well, both of these are 18 electron compounds, so 4 electron and this iron is 8 electron and this is 6, so these are 18 VE compounds.

And this intermediate can also reacts with CP cobalt bicarbonyl, in this case eliminates carbon dioxide, resulting in cyclopentadienal cobalt cyclobutadiene. So, cobalt carbon distance is 204 picometer and for this cyclopetadiene cobalt carbon distance is 197 picometer the CC bond is 139 picometer and this one is 143 picometer. So this also is a very interesting example where by using light, one generates this very highly unstable intermediate, and that releases carbon dioxide, with the generation of cyclobutadiene.

And that can be complexed with iron carbonyl to give this half sandwich compound, half sandwich compound and can also react with CP cobalt dicarbonyl to give the sandwich compound. So with this, I would like to come to the end of today's class in which we have looked at various preparative methods that is available for preparation of transition metal cyclobutadiene complexes to reiterate that we have come across in a very elegant examples.

In which one can see the ring contraction relating to this, one can also use organic molecules like alpha pyrones and use light and then subsequent trapping with metal carbonyls and to make this cyclobutadiene transition metal complexes, one also use this strategy of simple ligand transfer from one metal to another metal for preparing this cyclobutadiene transition metal complexes.

And further we are also seen the use of the dehalogenations of dihalo cyclobutadiene for preparation of this complexes, so with these we come to the end on our discussion on various methods used for preparing this cyclobutadiene transition metal complexes and in the next class we would be discussing about various reactivity that this transition metal cyclobutadiene complexes exhibit, it is interesting class of compounds and lead to very interesting reactivity, that we will see in next lecture, till then good bye and thank you.