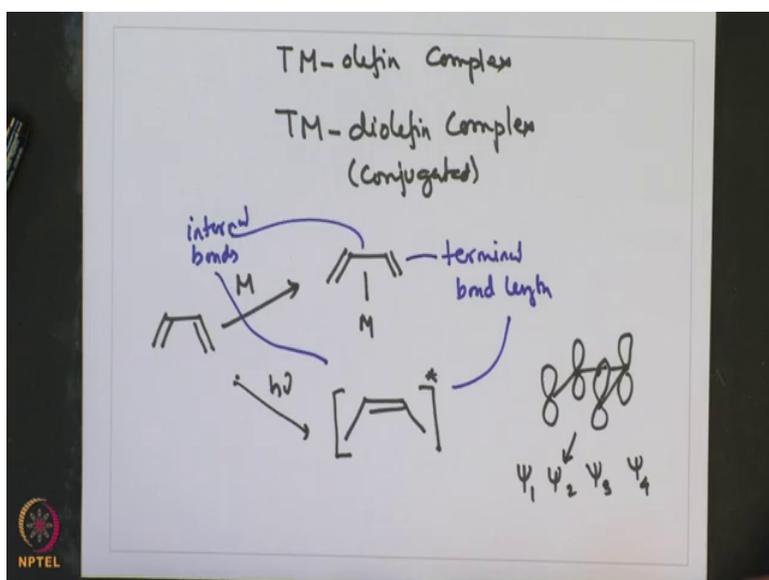


Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 12
Lecture - 56
Transition Metal Diolefin and Alkyne Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing an important type of organometallic compounds particularly the Transition Metal Diolefin Complexes.

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And we have been discussing this transition metal diolefin complex in the pretext of the transition metal olefin complex. And what we had seen that these transition metal diolefin complex differ significantly from the transition metal olefin complex when this diolefine is conjugated. And in terms of the only diolefine being conjugated they have delocalized molecular orbital's which results in lengthening or shortening of certain CC bonds of the diolefin moiety.

As an example what we had seen that for butadiene complex when butadiene is bound to the metal these there the change the change in the terminal as well as the terminal bonds. And the CC internal bonds change upon coordination to the metal and this can be sort of explained by the reaction that if there is a free butadiene, there is and when that reacts

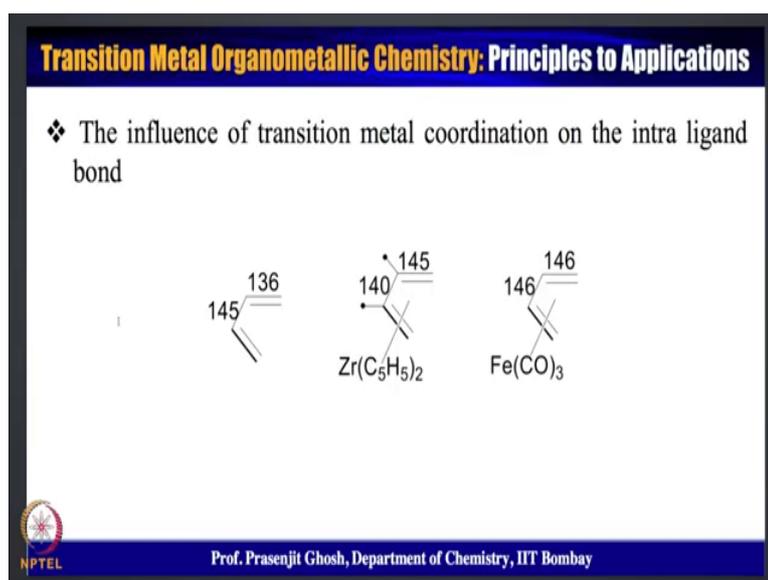
with a metal to give a metal coordinate butadiene the internal as well as the terminal bond lengths change.

And what we had discussed in the last lecture is that we see similar change when light is induced whereby the butadiene which is formed is excited one of the electron gets excited, and there also we saw that there is similar change in the CC internal as well as terminal bond lengths.

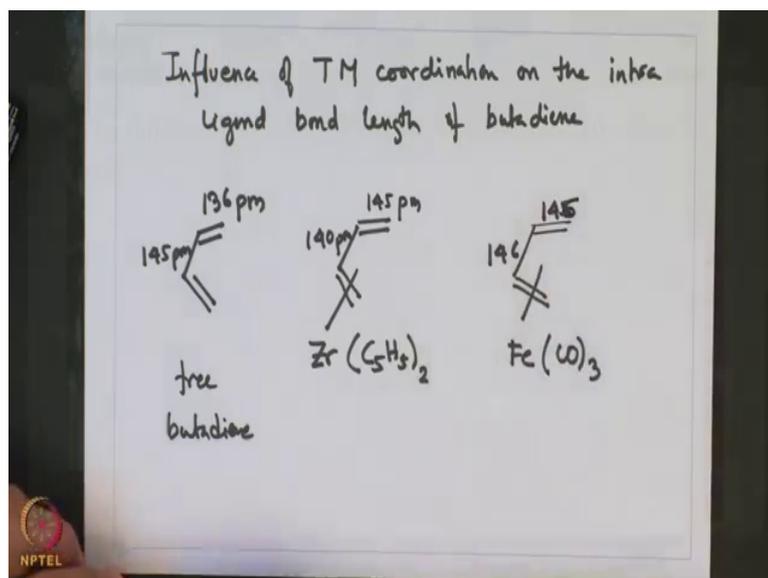
So, this is was an interesting phenomenon which was which we discussed and was explained by the butadiene molecular orbital form from the 4 pi type orbital's. So, what we have seen is that butadiene when it is activated by light or by metal show change in the bond lengths which can be the terminal and internal and these two changes are similar with regards to coordination to metal as well as by light excitation.

And all of these could be explained by the p orbital's p type orbital's or butadiene which are responsible for the various kind of molecular orbital's and that we have seen that these gives rise to psi 1, psi 2, psi 3, and psi 4 depending on the number of nodes that they combine to form after linearly linear combination. And that the population of one or the depopulation of other would result or explain this change in the internal as well as terminal bond length.

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Now, with that in mind let us take a look at some of the examples where similar change can be observed. For example, the influence of transition metal coordination on butadiene on the intra ligand bond length of butadiene can be seen this is a free butadiene.

The terminal bonds are 136 picometer, the internal is 145 picometer. So, internally is a longer bond terminal is a shorter bond, but when it coordinates to metal, particularly zirconium b c p then the terminal bond length depending on the population.

And depopulation the extent of forward sigma and pi by donation occur. The terminal bond has increased to about 145 picometer and the internal one has shortened to about 140 picometer and the same can be seen from iron coordination where butadiene when coordinated to F e CO 3 the terminal one is 146 and the internal one is 146.

So, there is a significant change the alkali bond length changes as the metal coordination occurs and also it depends on the nature of the metal for example, iron is more electron rich metal then zirconium and; obviously, the extent of the interactions in these two metals would be different.

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Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$, in the ^{13}C NMR spectra also gives evidence for change in bond order for η^4 -1,3-diene ligand

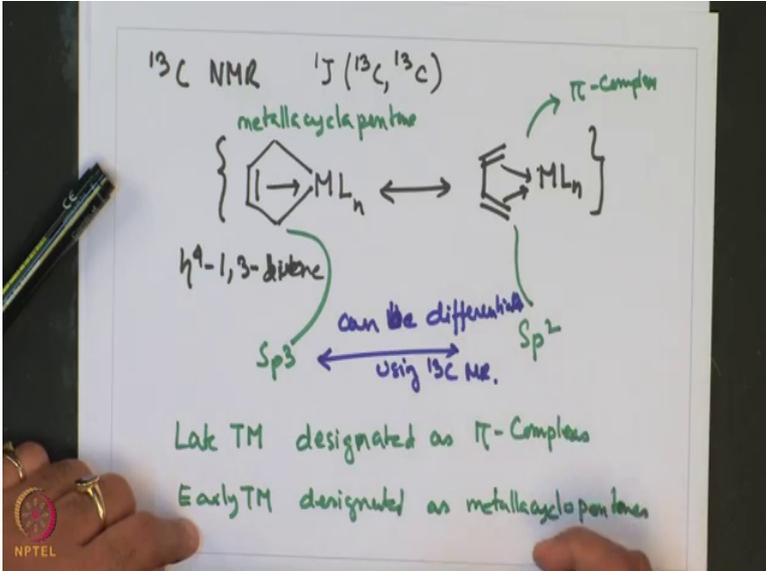


- ❖ The terminal carbon atoms having hybridization state of in-between sp^2 and sp^3 on the basis of coupling constants $^1J(^{13}\text{C}, ^1\text{H})$
- ❖ The late electron rich transition metals designated as π - complex whereas the corresponding compounds of early transition metals designated as metallacyclopentenes

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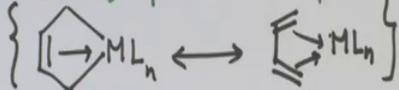
And these binding of butadiene to the metal can be characterized by various NMR techniques.

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^{13}C NMR $^1J(^{13}\text{C}, ^{13}\text{C})$

metallacyclopentene



η^4 -1,3-diene

can be differentiated using ^{13}C NMR.

sp^3 sp^2

Late TM designated as π -Complex

Early TM designated as metallacyclopentene

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For example, this can be done by carbon NMR provides a useful tool is suddenly useful for characterizing the binding of butadiene to the metal complexes and the carbon 13 coupling constant is far more useful in ascertaining this binding to the metal.

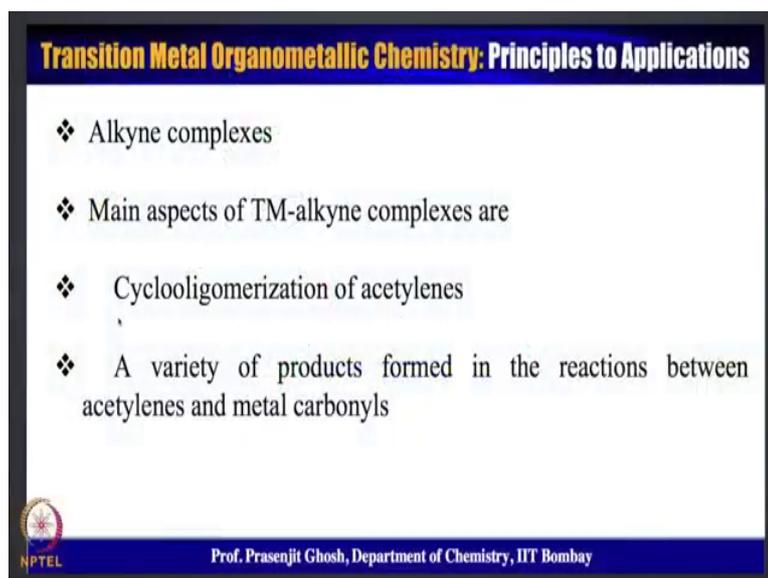
For example, in a η^4 1, 3 butadiene. So, this is a one type of binding. Now it has a canonical form which is where the olefinic bond is binding. Now if in these structure the

terminal bonds are sp^3 types and in these structure the terminal bond is sp^2 types and can be differentiated using ^{13}C NMR.

Also there is a the late transition metal designated as π complex whereas, the early transition metal designated as metallacyclopentane. So, this structure is called metallacyclopentene similar to the metallacyclo protein that we have seen. These are called metallacyclo pentene and this is just called simply π complex.

So, late transition metal designated as π complex whereas, early transition metal designated as metallacyclopentane. So, this is an interesting feature which can distinguish between these late transition metal type of chemical structures that exist with the late transition metal as well as the early transition metal and that dirotation of the ligand would change on going from this metallacyclopentene intermediate on to the simple π complex of the type shown.

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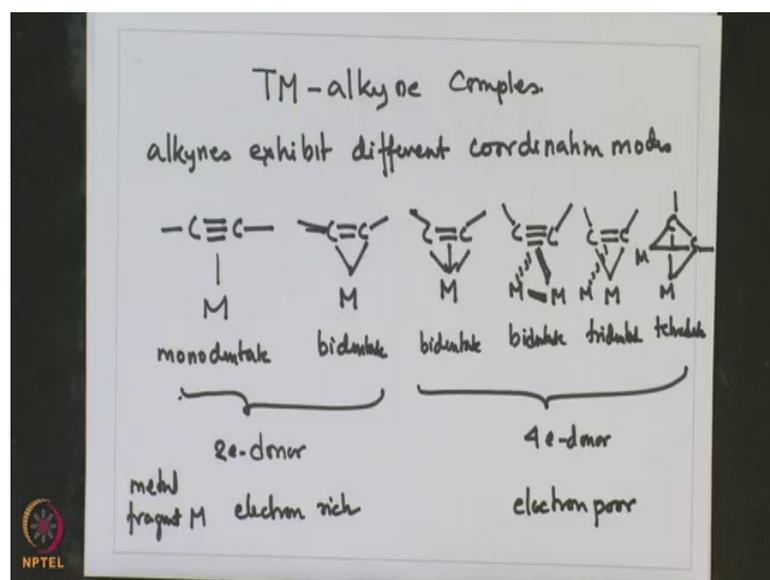


Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Alkyne complexes
- ❖ Main aspects of TM-alkyne complexes are
 - ❖ Cyclooligomerization of acetylenes
 - ❖ A variety of products formed in the reactions between acetylenes and metal carbonyls

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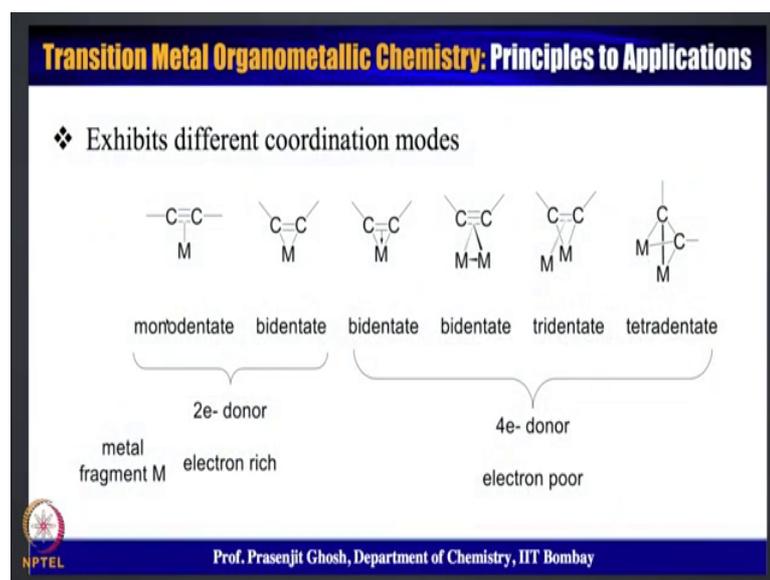
So, next we come to an interesting topic which are moving over from olefin complexes these are transition metal alkyne complexes. So, the main aspects of transition metal alkyne complexes are cyclooligomerization reactions of alkyne as well as a variety of products forms in the reaction between alkyne and the transition metal carbonyl complexes.

So, they are important in terms of their utility for kind of oligomerization reactions that go which are common for alkyne it is important for us to give these class of compounds special treatment particularly looking into the synthesis reactivity and the property as well as bonding studies of transition metal alkyne complexes.

Now, as per the transition metal alkynes to exhibit different coordination modes and this can be monodentate where the alkyne is bound to the metal so this is called monodentate. It can be bidentate, it can be bidentate with a pi bond, it can be bridging, it can be tridentate, or it can even be tetradentate.

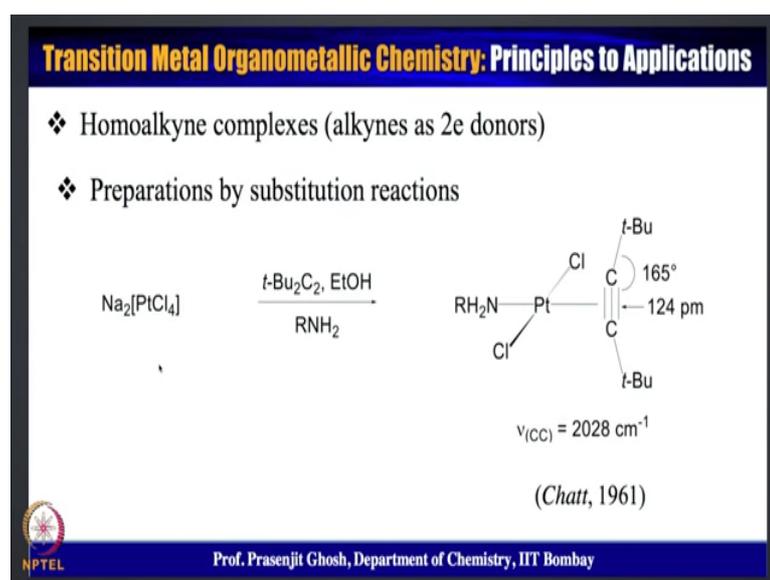
So, this is bidentate again bidentate tridentate and tetradentate of which these 2 are simple 2 electron donor and these are 4 electron donor. And when it binds as a 2 electron donors then the metal fragment m is electron rich and when it binds as 4 then the metal electron fragments is electron poor.

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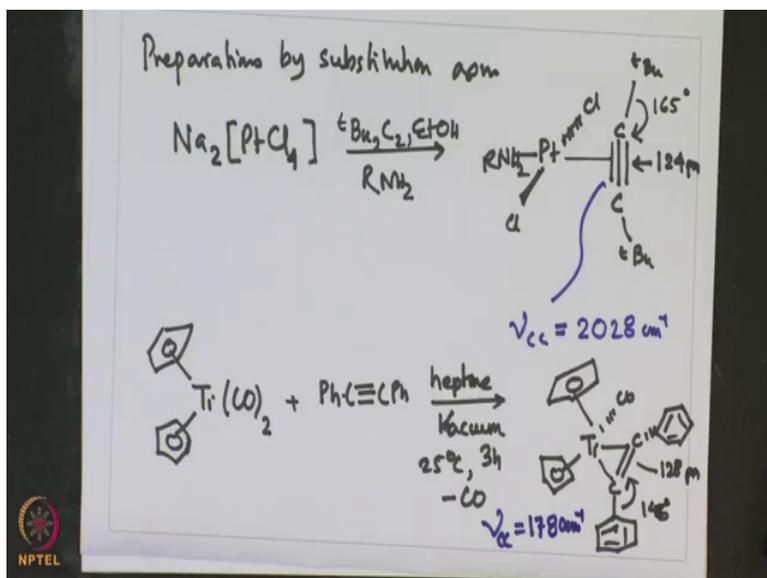
So, these slide throws very a good insight as to the versatility of the alkyne as a ligand. How does it bind on a side on fashion it can be mono dented by indented it has different modes of coordination to the metal it can bind to metal with a single metal double metal or a triple metal as well as it can give 2 electrons, and 4 electron donors depending on whether the metal is a electron rich or a electron deficient center.

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Now these being very important compounds in terms of their catalytic utility and also we have looked at the rich binding mode that it offers we are going to look at the preparations of some of these transition metal alkyne complexes, preparations.

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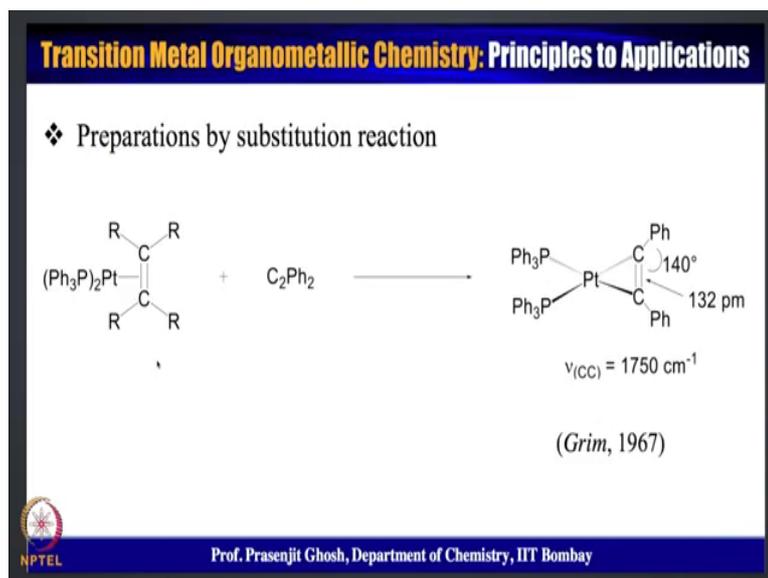


And the first and the foremost is preparation by substitution reaction. This is Na_2PtCl_4 reacting with $t\text{Bu}_2\text{C}_2$ in ethanol and RNH_2 provided this $\text{PtCl}_2\text{ClNH}_2\text{R}$ and acetylene $t\text{Bu}_2\text{C}_2$. Now this bond is 124 picometer and this angle is deviated from linearity and it is 165 degrees.

The C-C stretch new C-C as can also be characterized by IR and that is 2028 centimeter inverse. So, this is a method where the chlorides have been substituted by alkane providing these alkyne complex.

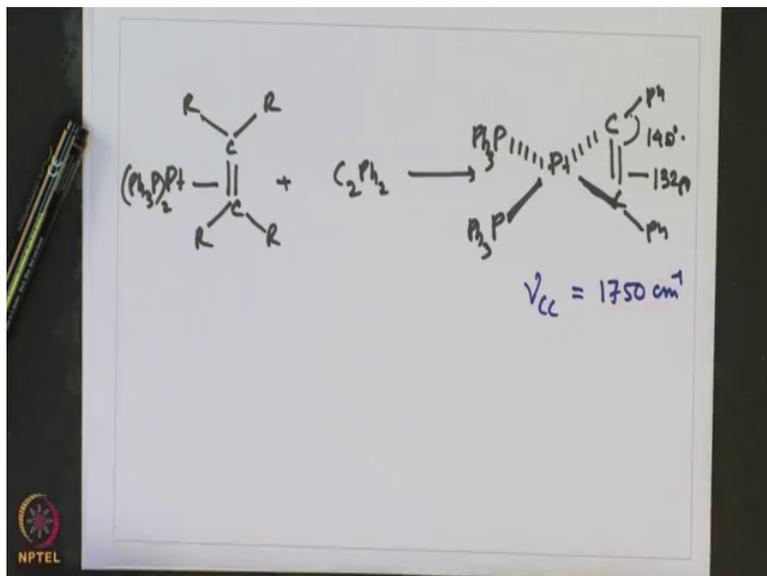
There are other examples of the substitution reactions for example, the reaction of $\text{Cp}_2\text{Ti}(\text{CO})_2$ titanium carbonyl compound plus alkyne in heptane under vacuum 25 degree centigrade 3 hour eliminate CO to give this $\text{Cp}_2\text{Ti}(\text{CO})\text{C}\equiv\text{CPh}$ compound where this angle now is more distorted to 146 degree and this distance is 128 picometer. So, this has also been characterized by IR where new series stretch is even 1780 centimeter inverse.

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Now, there is another preparation by substitution reaction.

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Triphenylphosphine giving these alkyne complex of with these phenyl and two of these triphenylic triphenylphosphine has a degree of 148° which is also different from linearity and 132 picometer . This has also been characterized by IR where it is $1750 \text{ centimeter inverse}$.

So, with that let me conclude the topics that has been discussed in this lecture we have looked into this transition metal diolefin complexes to begin with and looked at some of

the changes of the internal as well as terminal bond length so that happens when it they coordinate to transition metal and then we began the transition metal alkyne complexes.

We have looked we have also studied as to why these complexes are so important in organometallic chemistry. We have also looked at how these complexes bind to the transition metal in terms of their behaving as a monodentate, di bidentate. They show a versatile binding mode on going from mononuclear, binuclear, and as well as tetra nuclear they also in terms of electron donation.

They show 2 electron as well as 4 electron donating abilities depending on the electron richness of the metal and then we looked into a few synthetic methods that are available for preparing these transition metal alkyne complexes which mainly the ones that we have looked at are mainly by substitution reaction.

So, with that I am going to conclude today's lecture and I thank you for being with me in this lecture and I look forward to being with you in next lecture where we are going to take up these transition metal alkyne complexes in much more detail. With that let me conclude today's lecture and look forward to being with you in the next lecture till then.

Thank you and goodbye.