Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 12
Lecture - 57
Transition Metal Alkyne Complexes

Well welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing transition metal alkyne complexes over the last few lectures these are very important compounds which has a lot of applications in homogeneous catalysis.

Now transition metal alkyne complexes as we have discussed in the last lecture we spoke about various synthetic strategies available for preparing these complexes. We have also looked at the characterization of these complexes particularly with respect to x ray diffraction studies that are available for characterizing these transition metal complexes.

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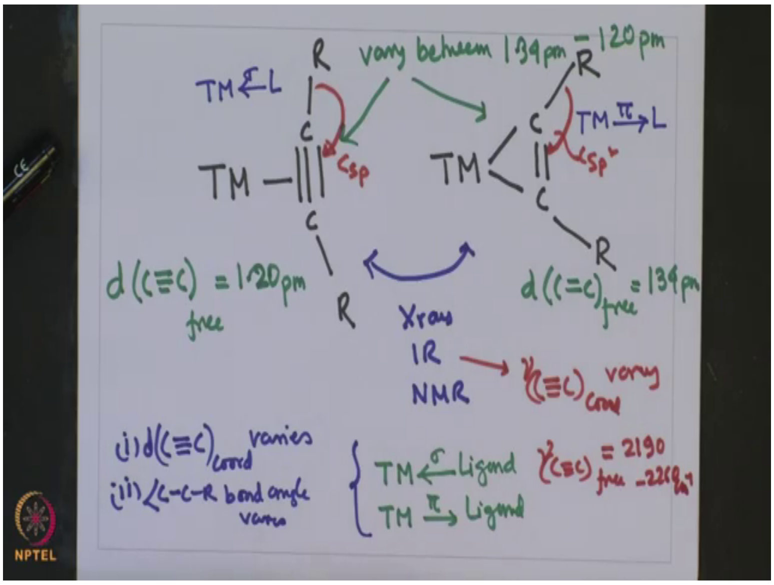

And what we had seen that these transition metal alkyne complexes can be designated as something of this type or something of that type. So, this is metalo cyclo propane kind of intermediate or binding of alkyne to the transition metal and this is the acetylenic bound transition metal type of complex.

Now these two structure can be distinguished by various characterization techniques like X-ray, IR, NMR so on and so forth.

And once they are distinguished they can be used to understand the big angle transition metal sigma interaction as well as transition metal to ligand pi back donation. So, these 2 interactions can be well understood if one takes a look at each of these 2 structures and see which one is predominating based on X-ray, IR and NMR studies.

Now, in our last lecture we are spoken about characterization of transition metal alkyne complexes based on x ray diffractions. We have taken 2 examples where we have seen how the alkyne moiety was characterized using X-ray diffraction studies by looking at the bond length and in this discussion we are going to elaborate for few more instances of how one can distinguish between these 2 canonical structures in transition metal alkyne complexes and have some insight about the big angle transition metal sigma interaction as well as transition metal to ligand pi interactions that are prevalent in this transition metal alkyne complexes.

Now one can see that in these 2 structures where the acetylene is purely sigma donating versus the one which is a cyclo propane kind of intermediate so this has more C triple bond C character and whereas, this has more double bond character and to compare the bond lengths for example, in free acetylene it is 120 picometer.

Whereas for free ethylene the distance is 134 picometer so these distance the C C distance of transition metal alkyne complexes vary vary between 134 picometer to 120 picometer. So, depending on the kind of interaction which is the forward sigma donation and the pi back donation these can vary. So, one can see that these structure where the acetylene triple bound is sort of retained that can be viewed as big and tool transition metal sigma interaction and where the other canonical form where the C C double bond structure is retained.

So, there is significant amount of pi back donation these sort of indicates transition metal to ligand pi in predominance of transitional metal to ligand pi interactions.

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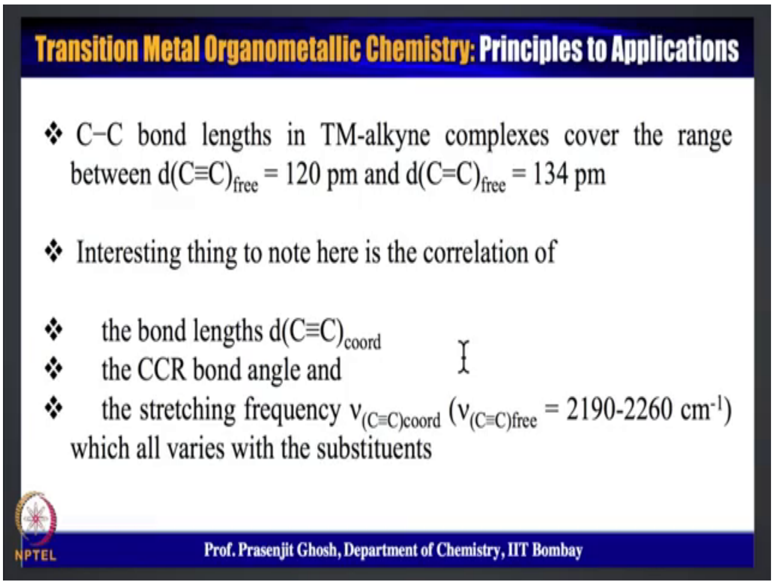

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- C–C bond lengths in TM-alkyne complexes cover the range between $d(C{\equiv}C)_{free} = 120$ pm and $d(C{=}C)_{free} = 134$ pm
- Interesting thing to note here is the correlation of
- the bond lengths $d(C{\equiv}C)_{coord}$
- the CCR bond angle and
- the stretching frequency $\nu_{(C\equiv C)coord}$ ($\nu_{(C\equiv C)free} = 2190\text{-}2260\ cm^{-1}$) which all varies with the substituents

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So, another artifact of these power donation and sigma donation is not only that this C is C triple bond C bond length coordinated bond length varies going to the interplay of these 2 interactions. The other artifact of these fall out of this is that C C R bond angle angle varies. Now that occurs because in the acetylic form this is more to us C s p kind of hybridization whereas, in the ethylene C double bond C this is more towards C S p 2 type hybridization.

So, there is this variation of the angle this angle varies as a result of these forward donation and back donation and the variation is much more from linearity in case of these complexes. So, in the cyclo propane intermediate where there is extensive metal to ligand pi back donation in such case this C C R angle is varied significantly from that of linearity. Now as far as the I R is concerned the seed these can be very well monitored by I R spectroscopy where this new C triple bond C coordination coordinated once vary to lower frequency with respect to nu C triple bond C free a a which comes around 2190 to 2260 centimeter inverse.

So, as a result of these 2 structure in for spectroscopy one can see that this seed of triple bond C stretch to be significantly reduced compared to the stretch of the free acetylenic moiety and coordinate acetylenic moiety which comes around 2190 to 2260. So, one can look at these I R, NMR, and X-ray assignments and one can distinguish between these 2 forms of the alkyne compounds depending on the change in the bond length, bond angle which results from interplay of these 2 interaction leading it to change in the hybridization of the carbon.

Now in this regard I must note that similar characterization of ethylene as well as cyclo propane moiety in transition metal alkyne complexes has also been discussed and the and there is a analogy in terms of being able to assign these 2 forms of the canonical forms of the acetylene and as well as ethylene bound transition metal complexes with the aid of NMR, I R, and X-ray studies leading to this change in bond energy and C C bond frequencies.

So, this is exactly similar to what we had discussed for the ethylene complex transition gentle bond ethylene and complex and similar characterizations are possible. So, with that let us take a look at some of the reactions available for synthesizing this alkyne complex, and the first and foremost is preparation by substitution reaction.

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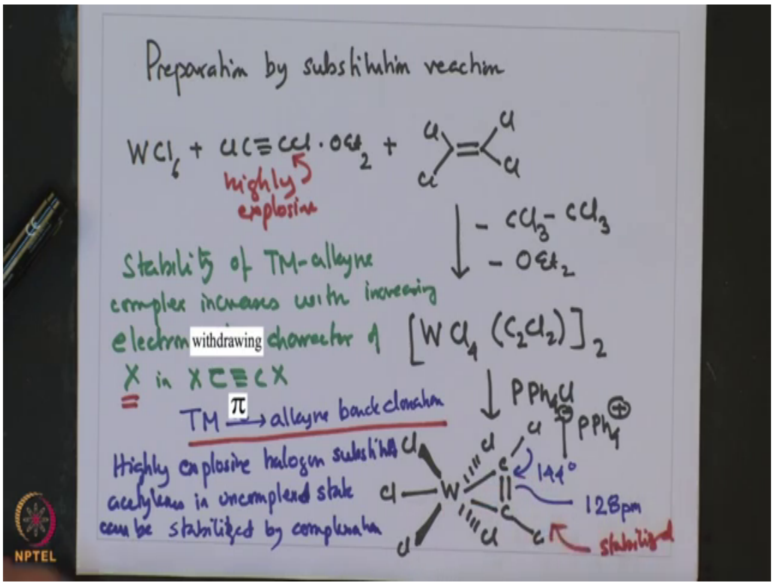

Preparation by substitution reaction

$WCl_6 + ClC{\equiv}CCl \cdot OEt_2 + Cl_2C{=}CCl_2 \xrightarrow[-\,OEt_2]{-\,CCl_3-CCl_3} [WCl_4(C_2Cl_2)]_2 \xrightarrow{PPh_4Cl}$

highly explosive

Stability of TM-alkyne complex increases with increasing electron withdrawing character of X in $XC{\equiv}CX$

TM $\xrightarrow{\pi}$ alkyne back donation

Highly explosive halogen substituted acetylenes in uncomplexed state can be stabilized by complexation

So, the reaction of W C l 6 plus C l C C C l iterate complex plus C l, C l, C l, C l, gives minus C C l 3 C C l 3 minus O 82 to give W C l 4 C 2 C l 2 dimmer which when treated with P P h 4 C l gives the compound C l C l alkyne compound with chlorine chlorine and P P h 4 plus.

So, this is a an any kind of compound now of interest is this double bond which is at 128 picometer, and this angle which is 144 degree, a very much deviated from the linearity.

Now, one thing interesting to note is that the stability of these alkyne complexes increases with the electron withdrawing character of this substituted alkyne that is because the more of eight favours turns same to alkyne by donation and that results in the cyclo metal or cyclo propane structure.

So, stability of T M alkyne complex increases with increasing electron withdrawing character withdrawing character of x in C x acetylene. So, more electronic withdrawing character of x so that would that would resolves in transition metal to alkyne pi back donation resulting stabilization of the metal cyclo propane type of intermediate.

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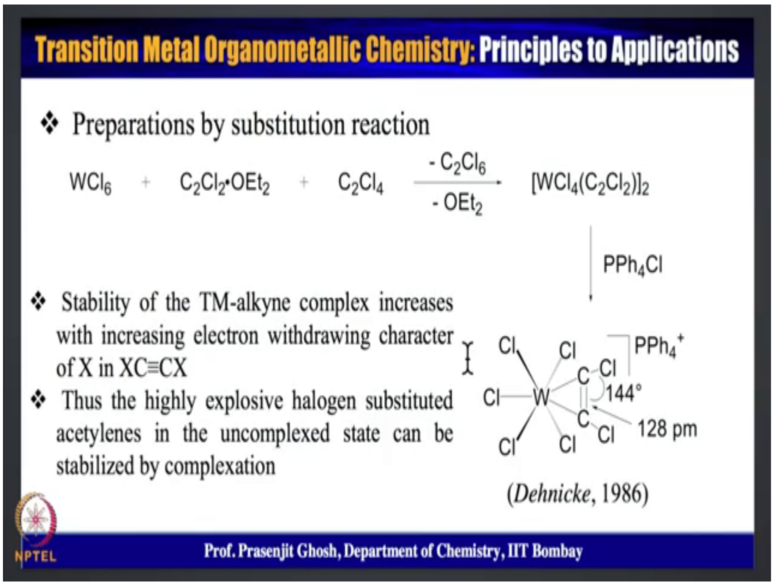

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- Preparations by substitution reaction

$$WCl_6 + C_2Cl_2{\cdot}OEt_2 + C_2Cl_4 \xrightarrow[-\,OEt_2]{-\,C_2Cl_6} [WCl_4(C_2Cl_2)]_2$$

$$\downarrow PPh_4Cl$$

- Stability of the TM-alkyne complex increases with increasing electron withdrawing character of X in XC≡CX
- Thus the highly explosive halogen substituted acetylenes in the uncomplexed state can be stabilized by complexation

(*Dehnicke*, 1986)

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And as a result the fall out is that highly explosive halogen substituted acetylenes are in un complex state can be stabilized by complexation. Thus highly explosive halogen substituted acetylenes in uncomplexed state can be stabilized by complexation. So; that means, these alkyne by itself is a highly explosive in nature highly explosive at this alkyne and when it is a stabilized in the complex state the alkyne is stabilized in the complex state so that is a kind of a very interesting.

And this extra stabilization arise because of the electron withdrawing nature of this x where chlorine over here results resulting in transition metal to alkyne pi back donation pi pi back donation which results in this formation of the metal cyclo propane kind of intermediate.

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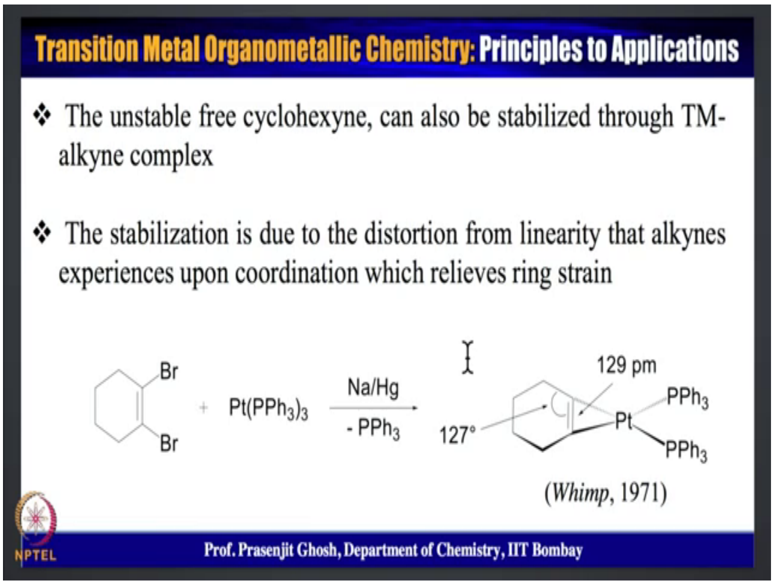

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- The unstable free cyclohexyne, can also be stabilized through TM-alkyne complex
- The stabilization is due to the distortion from linearity that alkynes experiences upon coordination which relieves ring strain

(*Whimp*, 1971)

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Now these forward sigma donation has a important applications and for example, unstable cyclohexyne can be stabilized through complexation with transition metal.

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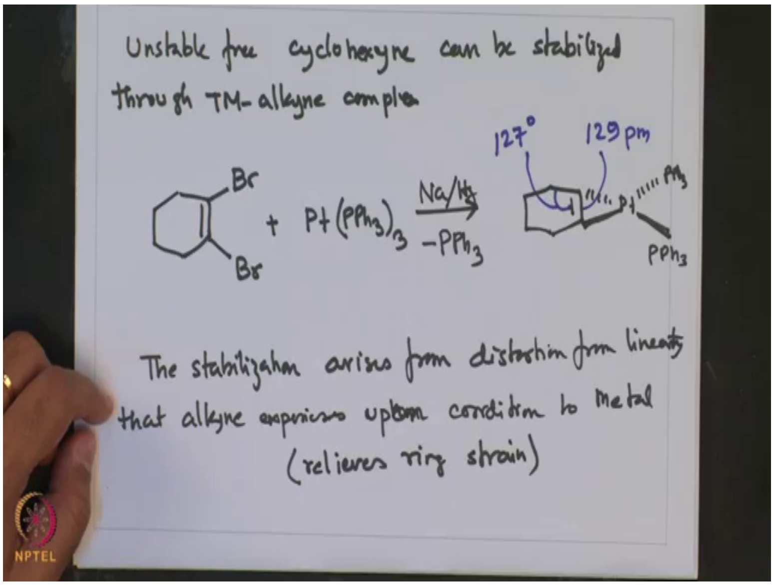

Unstable free cyclohexyne can be stabilized through TM-alkyne complex

The stabilization arises from distortion from linearity that alkyne experiences upon coordination to metal (relieves ring strain)

So, thus unstable free cyclohexyne can be through transition metal alkyne complex, and example of these can be seen over here actually it is so unstable that one can not directly use a cyclohexyne alkyne.

But generates it from the cyclohexyne alkyne want to diebromide complex reacting that with P t P P h 3 whole 3 in presence of sodium mercury which allows elimination of P P H 3 to give this cyclohexyne compound of platinum P P H 3 and these distance.

Now is 129 picometer and this angle is 127 degrees. So, the stabilization one can see that the stabilization is arises from distortion from linearity, that alkyne experiences upon coordination to metal and this can be sort of relieves ring strain. So, this highly unstable cyclohexyne which is a cyclohexyne then with alkyne is highly strained and unstable because of the increased ring strain can be stabilized when it is bond to metal and destabilization arises from the distortion from linearity a upon coordination to metal leading to release of ring strain.

So, here we see a 2 important applications of this transition metal complexes upon coordination one is that you can stabiler one can stabilize unstable alkynes in form of cyclohexyne or one can even stabilized explosive alkynes like hello substituted alkynes upon coordination to transition metals.

So, these 2 are very important applications of transition metal alkyne complexes hm. We are going to take a look at some more reactions applications along this thing. For example, along the stabilization of cyclohexyne alkyne similarly coordination of benzyne which is also not stable in the free state can be a stabilized through transition metal alkyne complex.

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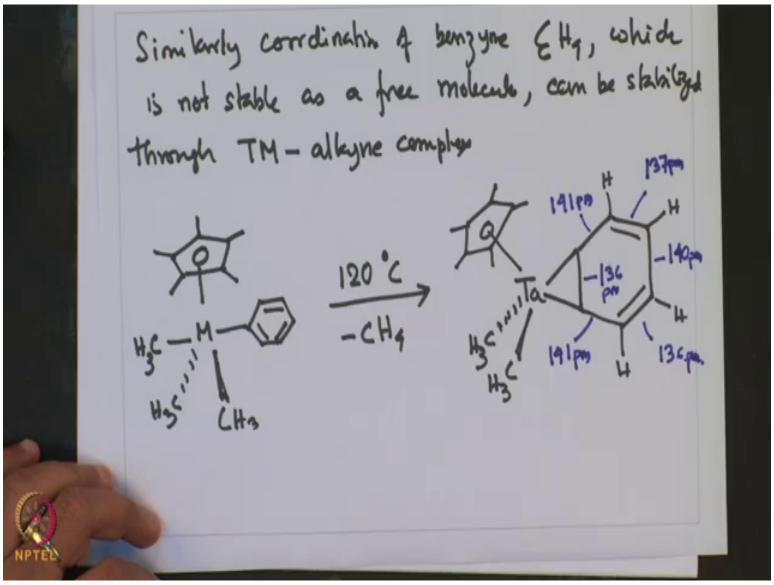

Similarly corrdination of benzyne C_6H_4, which is not stable as a free molecule, can be stabilized through TM – alkyne complexes

Similarly coordination of benzyne C 6 h 4 which also is not stable. As a free molecule can be stabilized through transition metal alkyne complex. And these can be observed in this very nice reaction for nabhiem and tantalum C p star metal C h 3, C h 3, C H 3 p h at 120 degree centigrade, eliminates methane to give the tantalum C H 3 H 3 benzyne complex H, H, H, H. This is 136 picometer, this 1 141 picometer, this one also 141 picometer. This is a double bond this is 137 picometer 140 picometer and this one 136 picometer.

So, there is alternative C double bond single bond and this is as a multiple bonded character approximately equal to double bond because this also is about 136 picometer and these 2 sides are having a single bond is slightly higher it is at 141 picometer.

So, what we saw that these can be characterized by a various spectroscopic method. We have also seen that how unstable complexes can be a stabilized in comes of cyclohexyne as well as benzyne and also we had seen how the binding in the transition metal alkyne complexes take place.

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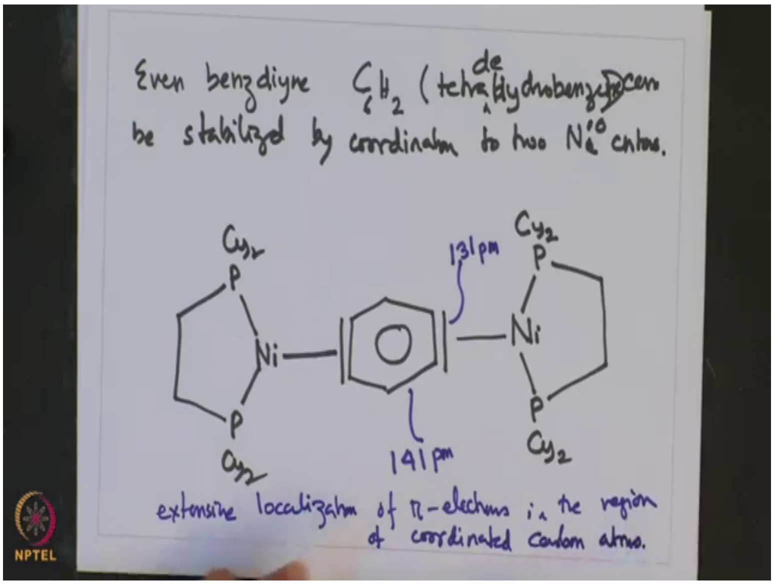

Even benzdiyne C_6H_2 (tetradehydrobenzene) can be stabilized by coordination to two Ni^0 centres.

extensive localization of π-electrons in the region of coordinated carbon atoms.

Now one can ago further and even tetra benz benzidine co extend further from benzene to even benzidine. So, where this is C 6 H 2 or and this is called tetra d hydro benzene can be stabilized by coordination 2 2 nickel 0 centers d hydro benzene two nickel 0 centers.

So what does what is the tetra dehydro benzene. So, it is like a benzyne molecule on the both side with 2 alkyne, highly unstable intermediate but they are stabilized by coordinating to nickel 0 containing P cyclohexyl 2 P C y 2, nickel P C y 2 P C y 2.

Now, this bond distance on the side which is more of a single protractor is 141 picometer whereas, the benzene is 131 picometer. And these complex shows extensive localization of pi electrons in the region of coordinated carbon atoms. Now of these then what we had seen is that these transition metal complexes let me summarize what we have talked about?

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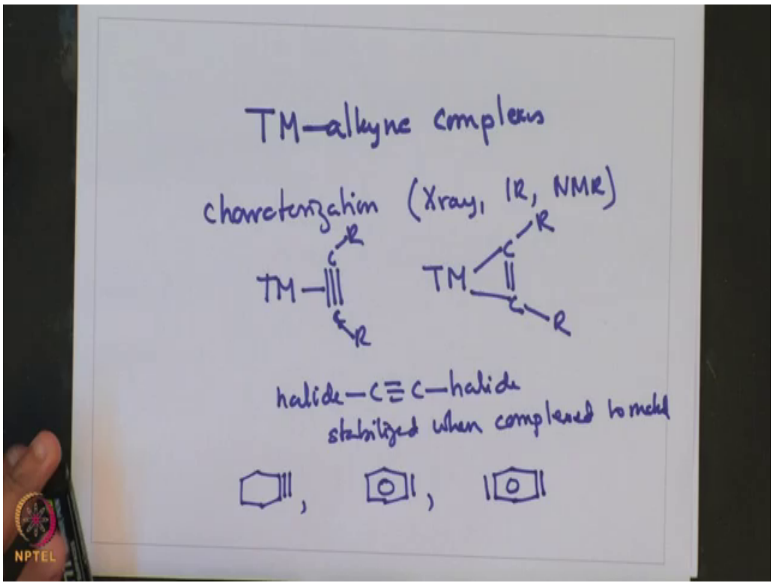

TM–alkyne complexes

characterization (Xray, IR, NMR)

halide–C≡C–halide

stabilized when complexed to metal

These transition metal alkyne complexes in this particular lecture we have looked at the characterization aspect of this transition metal alkyne complexes; particularly with respect to the X-ray, I R, and NMR data, characterization of these alkyne complexes with regard to X-ray, IR and NMR.

Spectroscopy and one what one see is that this transition metal alkyne complexes can exist in two forms of structures. One is the acetylenic one which is a carbon carbon triple bond the other is the the metallocyclo propane one, which has a carbon carbon double bond and between these 2 structure the C C a bond distance would vary from going from a shorter or to a longer one depending on the extent of the metal to ligand pi a back donation.

We have also know seen apart from this characterization these transition metal alkyne complexes have great application particularly a in stabilization of a halides substituted acetylenes. Now halides are substituted acetylenes are extremely explosive in nature in their free state, but when complex to transition metal they form stable cyclo propane kind of intermediate and then these complexes become less reactive or less explosive.

So, we saw an important application in the through this transition metal alkyne complexes which sort of stabilizes unstable compounds particularly halide substituted acetylenes stabilized when complex to metal. You know this discussion we have also seen the stabilization of unstable alkynes like cyclohexyne which were stabilized upon coordination to metal, or benzine for that matter which also are highly unstable molecule, but got stabilized when complex to metal as well as benze tyene which is benzine sort of benzine as acetylic moiety and both the ends and this was also stabilized by coordination to metal.

So, with these let me just summarize these transition metal alkyne complexes are very important compound in particularly in organometallic chemistry, particularly with regard to their ability to stabilize otherwise unstable alkynes which through coordination to transition metals.

Some of these alkynes like benzyne bins di in our cyclohexyne alkyne they are stabilized in when coordinate to metal and they are stabilizes arises from the release of ring strain because the acetylic moiety itself is highly unstable. Because of the ring strain arising from this deviation from linearity as a part of their cyclic ring that they are attached to. So, these release of ring strain when complex to metal stabilizes this alkyne intermediate.

Now, with that let me conclude today’s lecture on transition metal alkyne particularly their characterization aspect and also we looked at various utility of this transition metal alkyne complexes particularly with regard to stabilization of unstable alkynes. And now we move on to something more interesting in the next lecture which are which is about reactivity of transition metal alkyne complexes.

So, I thank you for being with me in this lecture and I look forward to being with you in the next lecture where we are going to dig up the reactivity of transition metal alkyne complexes in more details. Until then goodbye and see you in the next lecture.

Thank you.