Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 06
Lecture – 27
Transition Metal Alkenyl/Aryl Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In our previous lecture we have been talking about a special type of transition metal sigma alkyl complexes and these are called transition metal perfluoroalkyl complexes and they are represented by TM R F type complexes.

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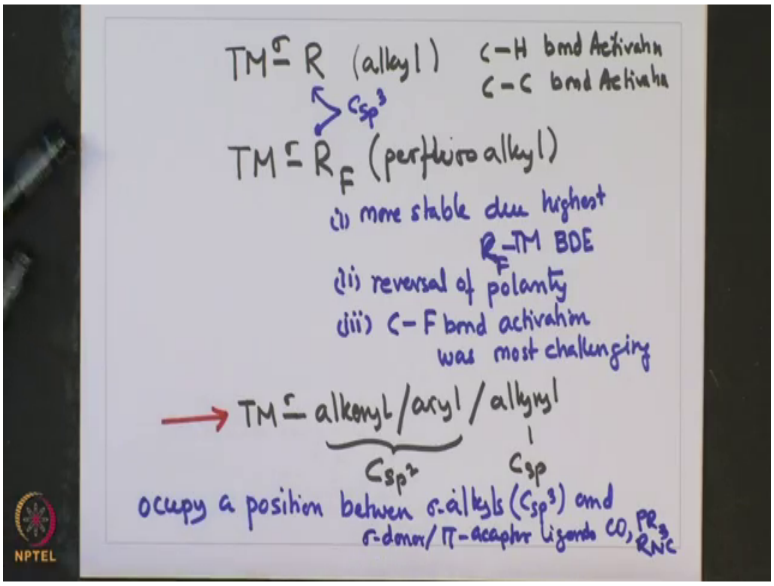

$TM \overset{\sigma}{-} R$ (alkyl) C–H bond Activation
C–C bond Activation

C_{sp^3}

$TM \overset{\sigma}{-} R_F$ (perfluoroalkyl)

(i) more stable due highest R_F–TM BDE

(ii) reversal of polarity

(iii) C–F bond activation was most challenging

→ $TM \overset{\sigma}{-}$ alkenyl/aryl/alkynyl

C_{sp^2} C_{sp}

occupy a position between σ-alkyls (C_{sp^3}) and σ-donor/π-acceptor ligands CO, PR_3, RNC

And these transition metal sigma perfluoroalkyl type complexes are very stable, as opposed to transition metal sigma alkyl complexes which we have also discussed prior to discussing this transition metals perfluoro sigma alkyl complexes. These are alkyl and these are perfluoroalkyl. One of the attributes of transition metal perfluoroalkyl complexes is that they are more stable due to high or probably the highest bond energy more stable. Also we had seen that these compounds show unique reactivity which are absent in their transition metals in the alkyl counterpart that arises due to reversal of polarity.

And lastly we had seen that of all the type of activations bond activations for example, in this case C-H bond activation or C-C bond activation. In case of transition metal perfluoroalkyl C-F bond activation was most challenging. And we had also seen in our previous lecture some of the examples pertaining to C-F bond activation not only in a stoichiometric fashion, but also in catalytic fashion using a rhodium catalyst. In today's lecture we are going to look into something along this line and these are transition metal sigma alkenyl aryl or alkynyl type complexes.

So, these are transition metal complexes with C SP 2 type hybridization and for this one it will C SP type hybridization whereas, for the ones that we had studied so far these had C SP 3 type of hybridization. So, these ligand C SP 2 and C SP type this alkynyl are alkenyl legands they occupy a position between alkyne sigma alkyles that is C SP 3 type and sigma donor pi acceptor ligands like carbon monoxide, P R 3, R N C etc. So, today's lecture will focus along this line looking into various types of transition metal sigma alkenyl, aryl and alkynyl complexes.

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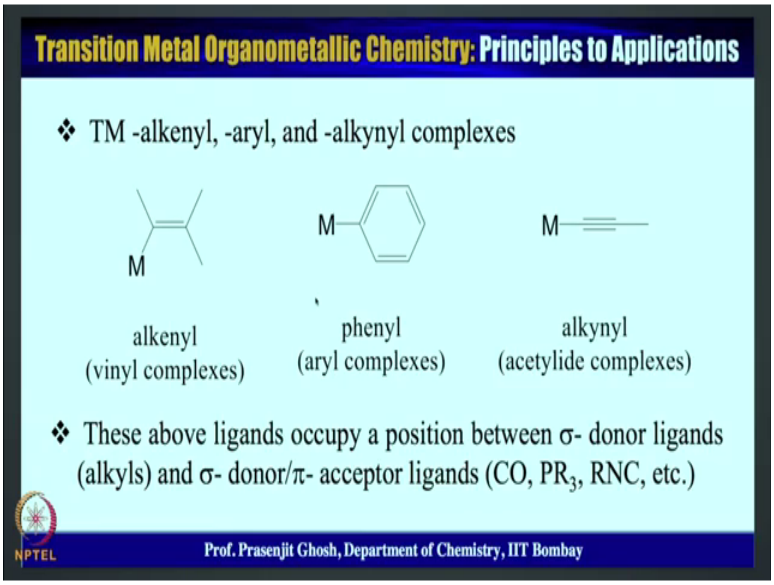

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- TM -alkenyl, -aryl, and -alkynyl complexes

alkenyl (vinyl complexes)

phenyl (aryl complexes)

alkynyl (acetylide complexes)

- These above ligands occupy a position between σ- donor ligands (alkyls) and σ- donor/π- acceptor ligands (CO, PR_3, RNC, etc.)

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Now, in terms of transition metal sigma alkynyl complexes they can bind in both bridging and terminal fashion as can be seen here. This is a terminal binding or it can be a bridging type of something of this which can be bridging.

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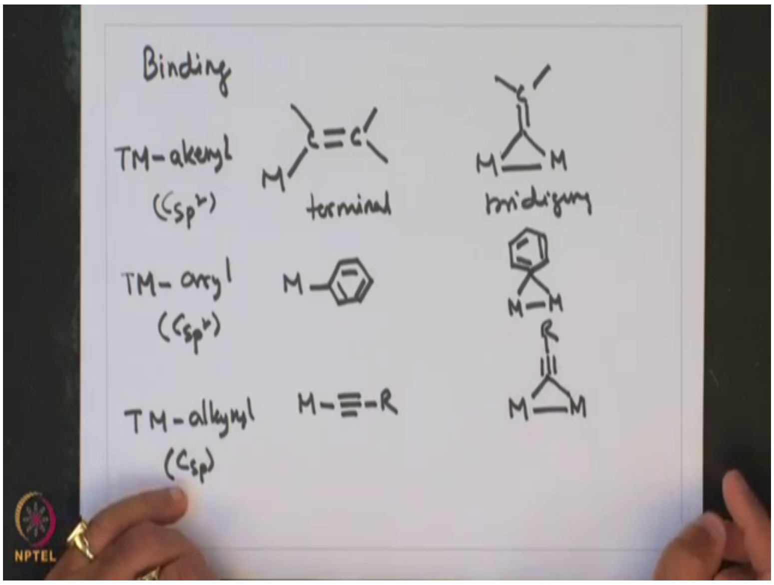

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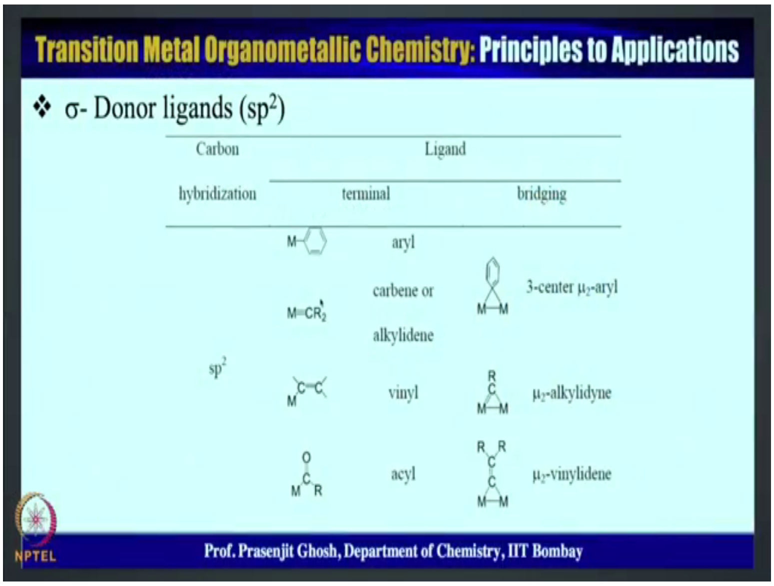

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- σ- Donor ligands (sp^2)

Carbon hybridization	Ligand			
	terminal		bridging	
sp^2		aryl		3-center μ_2-aryl
	$M{=}CR'_2$	carbene or alkylidene		
		vinyl		μ_2-alkylidyne
		acyl		μ_2-vinylidene

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So, this is transition metal alkynyl type of moiety transition metal aryl can also display similar terminal as well as bridging binding the terminal is shown over here and the bridging can be of this type. And lastly so this is C SP 2 this one also is a C SP 2 type and lastly for transition metal alkynyl which is C SP it can be as well terminal as well as bridging the way as shown over here.

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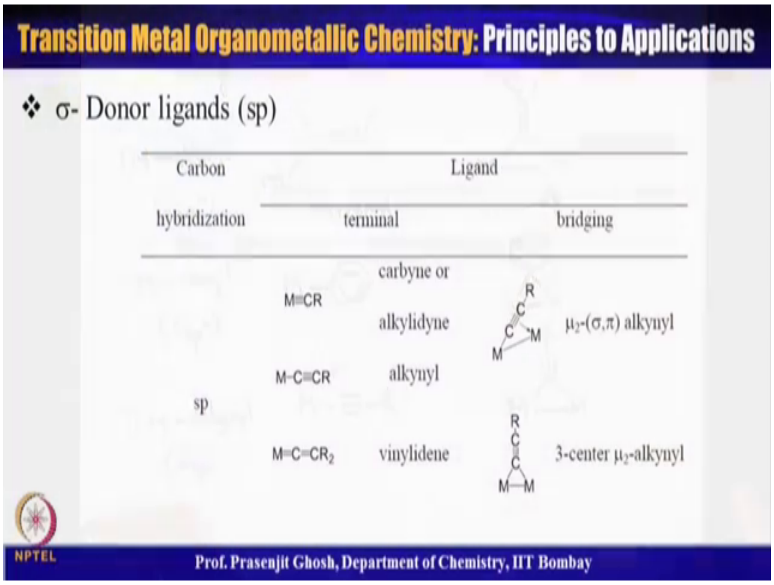

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- σ- Donor ligands (sp)

Carbon hybridization	Ligand terminal		bridging	
sp	M≡CR	carbyne or alkylidyne		μ_2-(σ,π) alkynyl
	M–C≡CR	alkynyl		
	M=C=CR$_2$	vinylidene		3-center μ_2-alkynyl

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So, these 3 types of compounds that show different additional bridging moves as supposed to simple the terminal ones would be the ones that we are going to be discussing in this next series of lectures and they are primarily focused on transition metal C SP 2 or transition metal C SP type of functionality.

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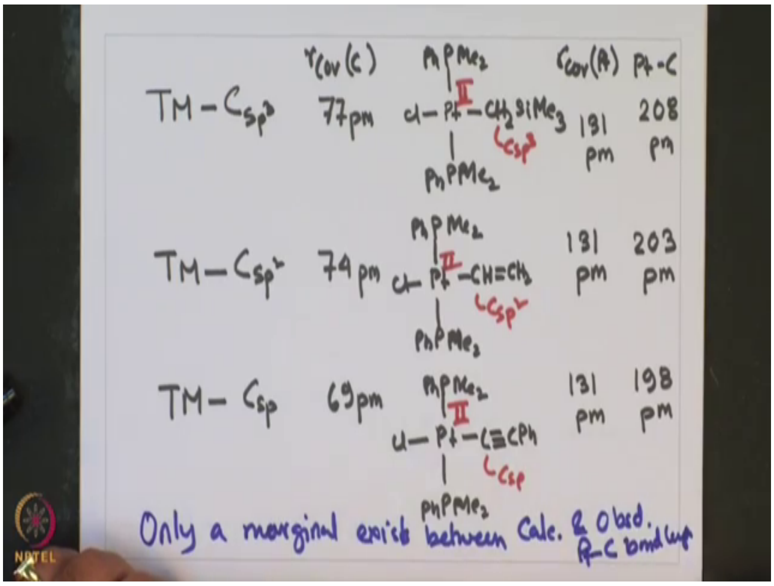

	r_{cov}(C)	r_{cov}(Pt)	Pt-C
TM – C_{sp^3}	77 pm	131 pm	208 pm
TM – C_{sp^2}	74 pm	131 pm	203 pm
TM – C_{sp}	69 pm	131 pm	198 pm

Only a marginal exists between Calc. & Obsd. Pt–C bond length

Now, one interesting thing that one moves from as one moves from transition metal C SP 3 two transition metal C SP 2 to transition metal C SP the covalent radius of carbon changes and with the increase in s character its covalent radii decreases. For example, for

SP 3 it is 77 picometer whereas, in SP 2 as the S character increased because of that the radius of carbon has shrunk to 74 picometer to C SP it has come down to 69 by now there is more as s character picometer.

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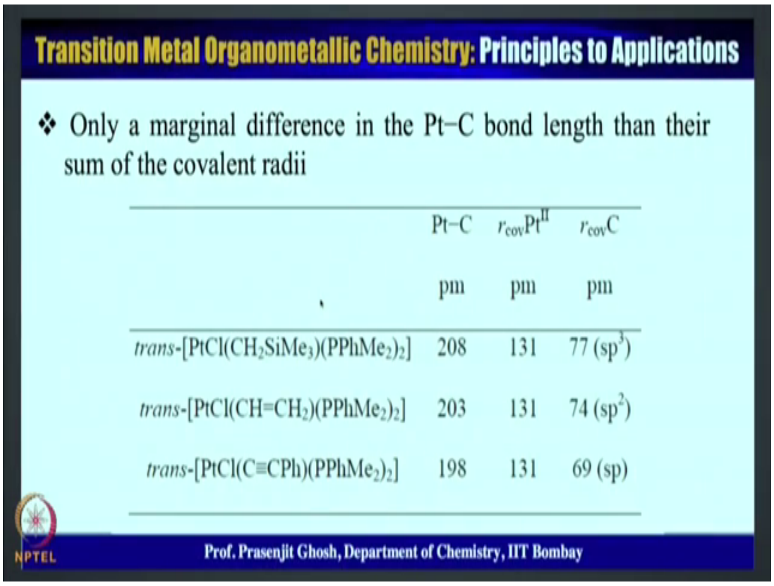

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- ❖ Only a marginal difference in the Pt–C bond length than their sum of the covalent radii

	Pt–C pm	$r_{cov}Pt^{II}$ pm	$r_{cov}C$ pm
trans-[$PtCl(CH_2SiMe_3)(PPhMe_2)_2$]	208	131	77 (sp^3)
trans-[$PtCl(CH{=}CH_2)(PPhMe_2)_2$]	203	131	74 (sp^2)
trans-[$PtCl(C{\equiv}CPh)(PPhMe_2)_2$]	198	131	69 (sp)

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So, as a result this transition metal if these 3 carbon 3 hybridized carbon binds to the same transition metal then their bond length is suppose to shrink. If that transition metal remains the remains the same and if it binds to 3 different hybridized carbon the overall transitional carbon distance is supposed to decrease as the covalent radii of carbon would decrease from SP 3 to SP 2 SP SP whereas, the covalent radii of the transition metal would remain the same. And this can be seen in this particular example where this platinum is bound to P Ph Me 2 P Ph Me 2 chlorine and C-H 2 Si Me 3.

So, this has a SP 3 carbon and it has a platinum 2 center platinum to covalent radii is 131 picometer and in this case the platinum carbon bond distance thus would be 208 picometer. And what is the observed as well as the calculated one which can be done by adding the covalent radii of SP 3 carbon and platinum they match up very nicely. Now, in another related complex similarly when platinum is bound to two first phosphorous Ph Me 2, P P Me 2, Ph chloride and C-H double bond C-H 2 where the carbon is now C SP 2 center. The platinum radii this being platinum 2 would remain the same as 131 picometer so that would predict this platinum carbon bond to be 131 plus 74 picometer.

And the observed bond distance is almost close and found to be very close to be 203 picometer.

Now, when one goes to the third SP type of example where this analog where platinum is bound to P Ph Me 2, P Me 2 Ph chlorine and now there is a SP center bound to platinum. So, hybridization over here is C SP platinum N plus 2. So, it is a covalent ionic radius would remain the same and that would predict this to be 200 picometer, but the distance is even smaller and found to be 198 picometer. So, only marginal difference exists between the Pt-C bond length only a marginal difference exists between calculated and observed platinum carbon bond length. These shows that how the change in hybridization would result in variation in the bond and that would end up being the bonding getting shortened with the (Refer Time: 15:04) s character.

We are going to now discuss some of the methods available for preparation of this transition metal alkynyl complexes.

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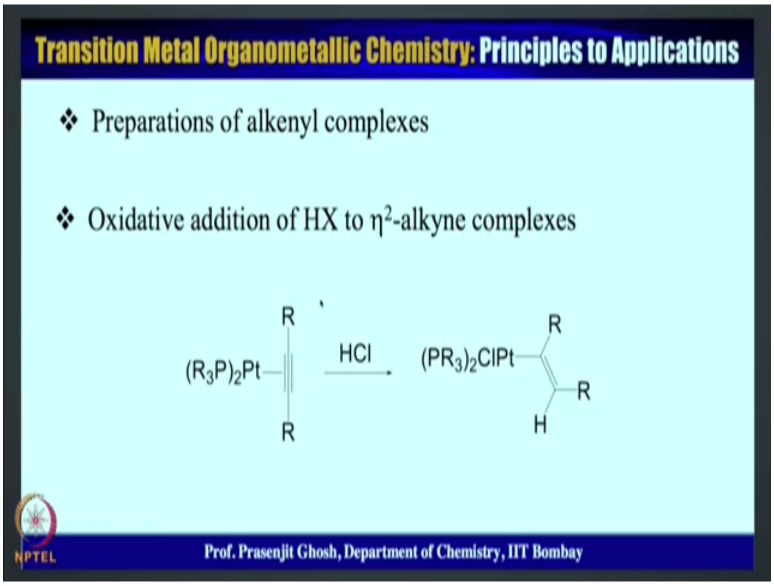

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- ❖ Preparations of alkenyl complexes
- ❖ Oxidative addition of HX to η^2-alkyne complexes

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The foremost method is oxidative addition of HX of HX to an activated eta 2 alkyne complex.

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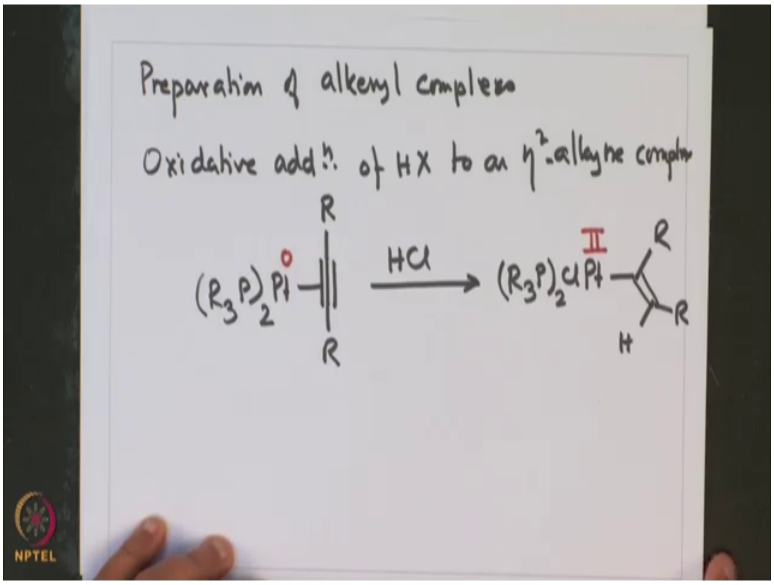

Preparation of alkenyl complexes

Oxidative addn. of HX to an η^2-alkyne complex

This is best represented by R 3 P whole 2 Pt having an alkyne bound to it results in reacting with HCL moiety and HCL protonating the alkyne and platinum getting chlorinated giving the R 3 P whole 2 chloride Pt R H R as a result of oxidative addition whereas, to begin within this (Refer Time: 16:50) alkyne complex the platinum 0 which result resulted in oxydative variation. It must be noted that 0 valent platinum or electron rich platinum was crucial to having this alkyne adapt where the alkyne adapt was stabilized by electron donation from platinum on to the alkyne portion.

Another method in synthesis of alkynyl complexes also involved reaction of similar eta two alkyne complex with a nucleophile.

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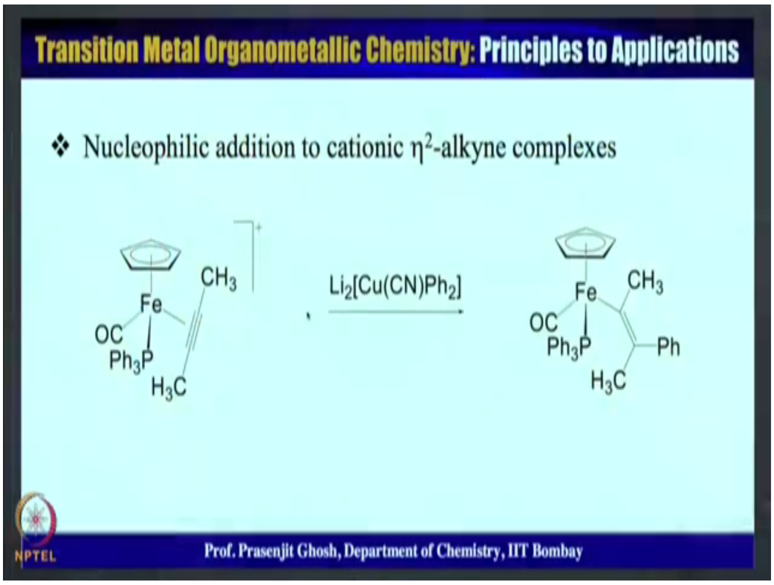

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- Nucleophilic addition to cationic η^2-alkyne complexes

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The first one was eta 2 alkyne complex undergoing oxidative addition in this method this is a slight variation as to having a nucleophilic addition to a cationic alkyne era to complex.

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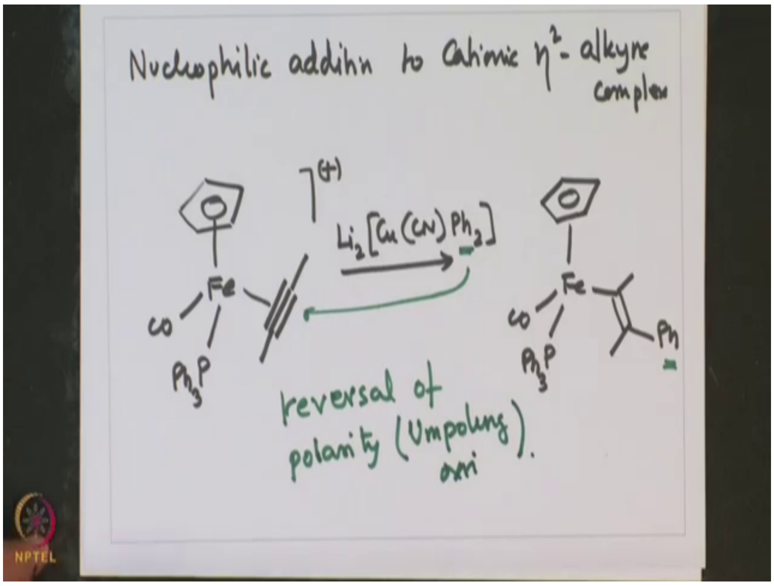

Nucleophilic addition to Cationic η^2- alkyne complex

reversal of polarity (Umpolung).
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The second method thus involves nucleophilic addition to cationic eta 2 alkyne complex. So, for example, this iron alkyne complex which is catanionic nature reacted with a Li 2 Cu CN Ph 2, where Ph minus is the nucleophile that attacks at the olefin giving this alkynyl complex of iron as shown here. So, what we see is this nucleophilic attack on this alkyne resulting in a phenyl over here.

So, it must be noted that nucleophilic attack to an alkyne is counterintuitive because nucleophile as well as alkyne both are electron rich. However when alkyne or alkyne gets coordinated to the metal center in the coordinated state it becomes amenable to nucleophilic at attack and such is called if the umpolung nature or reversal of polarity of alkyne or alkyne or it is called umpolung reaction. So, here is another example whereby this umpolung nature of alkyne and alkyne upon coordination to iron has been utilized in synthesizing these iron alkenyl complex.

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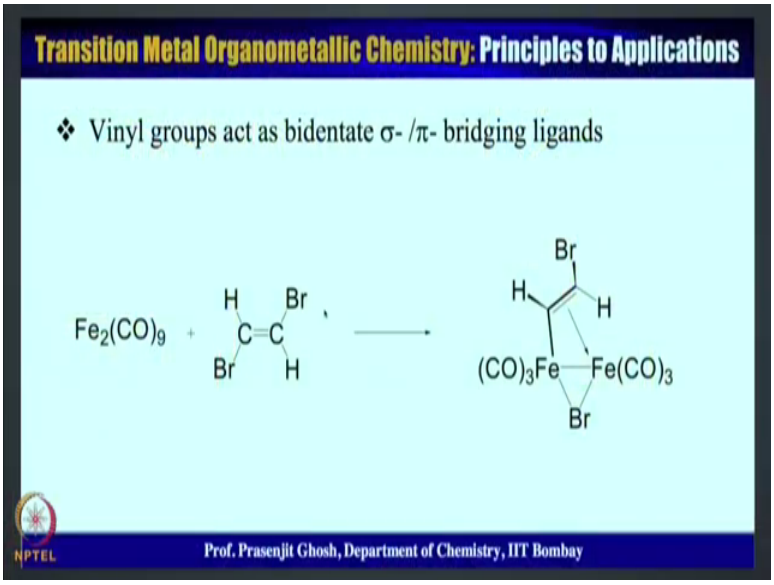

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❖ Vinyl groups act as bidentate σ- /π- bridging ligands

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Another example involves this vinyl group acting as a bridging sigma pi bridging type of ligand and this is obtained by C Br addition to iron carbonyl compound.

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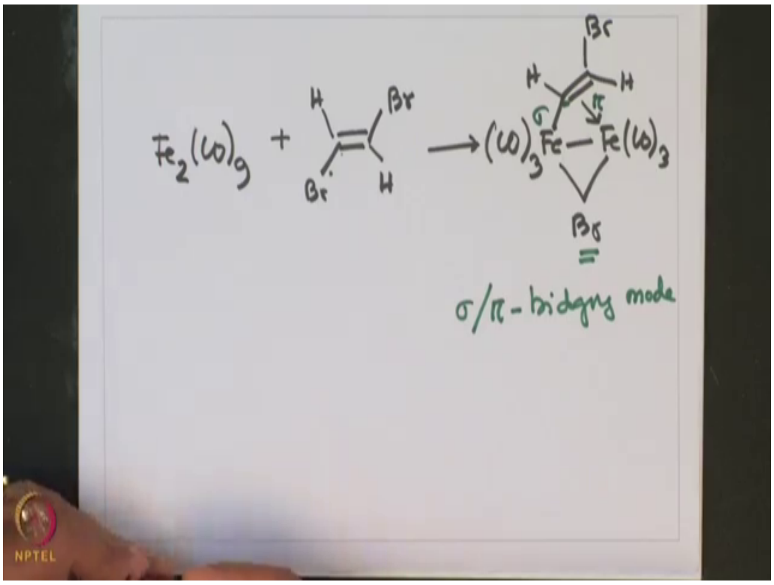

So, this method involves low valent iron di-carbonyl reacting with one two di-bromo ethane where the C Br at insertion happens resulting in the following iron compound and alkynyl compound.

So, one note that these bromide and these carbon there is a activation that has happened over here resulting in this kind of sigma pi bridging ligand, sigma type of bridging mode. This is an interesting binding mode where this is the sigma and is the pi type binding that this compound is displaying. Now, one interesting thing as opposed to with regard to this metal alkynyl complex is that that most of the preparation has been achieved by the reaction of coordinated alkyne onto a metal centered followed by oxidative variation or by nucleophilic attack. From this perspective this particular method of synthesizing iron or metal alkynyl complexes where there is a C Br activation occurring on a low valent iron complex becomes useful.

So, with this let me summarize what has been discussed in this lecture which were on metal SP 2 type interaction. In the beginning of this lecture we have covered various kinds of ligand displaying metal SP 2 as well as SP 3 type of interactions. For SP 2 this includes metal alkenyl metal aryl and for SP type of interaction this included metal alkynyl type of complexes. We have also looked at the binding mode of this metal alkenyl aryl as well as alkynyl type of complexes we have looked into various synthetic methods which are available for metal alkenyl complexes which primarily involved the reaction of eta 2 coordinated alkyne onto a metal center followed by oxidative addition or nucleophilic attack as well as by C Br activation of a alkane onto a metal low valent metal carbonyl compound. It must be noted that the second method where, which that involved nucleophilic attack on a metal coordinate alkenyl system involved the umpolung reactivity or the reversal of polarity that arises because of alkyne coordination to the metal.

So, with this we looked into various synthetic methods available for preparation of metal alkenyl complexes and now we conclude today's lecture and in next lecture we are going to look into more details at metal aryl as well as metal alkynyl type of complexes. I thank you for being with me in this lecture and look forward to being with you in the next lecture. Till then good bye and see you in the next lecture.

Thank you.