Transition Metal Organometallic Chemistry: Principles to Applications

Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture – 08
Week – 02
σ - Donor ligands

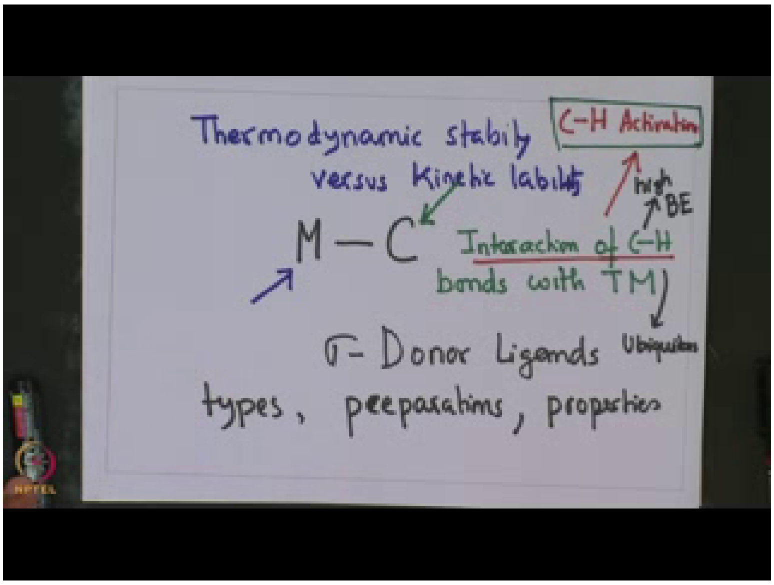
Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In our previous lecture we had seen the implications of 18 valence electron rules, we had also observed the classification that various organometallic compounds show based on this 18 valence electron rule, and also we had looked at the complexes that deviate from the 18 valence selection rules.

We have studied these rules in the perspective of molecular orbital theory, particularly looking at the frontier orbital interactions of the metal with the ligand. In our discussion on understanding the molecular orbital correlation diagram representing each of the classes of organometallic compounds that is of class one type class two type, and class three types.

What came to the 4 was the fact that organometallic compounds generally exhibit 2 kinds of interaction, 1 is a sigma type interaction which occurs between the ligands or atomic orbitals with that of the metal, orbitals of similar symmetry. And the other thing that came emerged out which is something very special for organometallic compounds is the pi interaction that also occurs between metal atomic orbitals with the pi type ligand orbitals of appropriate symmetry.

Now, these two features are very unique to transition metal organometallic compounds, and these arise because of partial occupancy of the inner d orbitals at the metal center. Now in our last few lectures looking at the valence electron rule and their deviations as well as their classifications what we had focused on was on the metal center of the metal carbon bond. So, the last few lectures had focused on the metal and the requirement electronic as well as cleric requirement of the metal centre that affects the metal centre bond.

(Refer Slide Time: 03:10)



Thermodynamic stabily
versus Kinetic labilit

C-H Activation

high
BE

M — C

Interaction of C-H
bonds with TM

Ubiquitous

σ- Donor Ligands

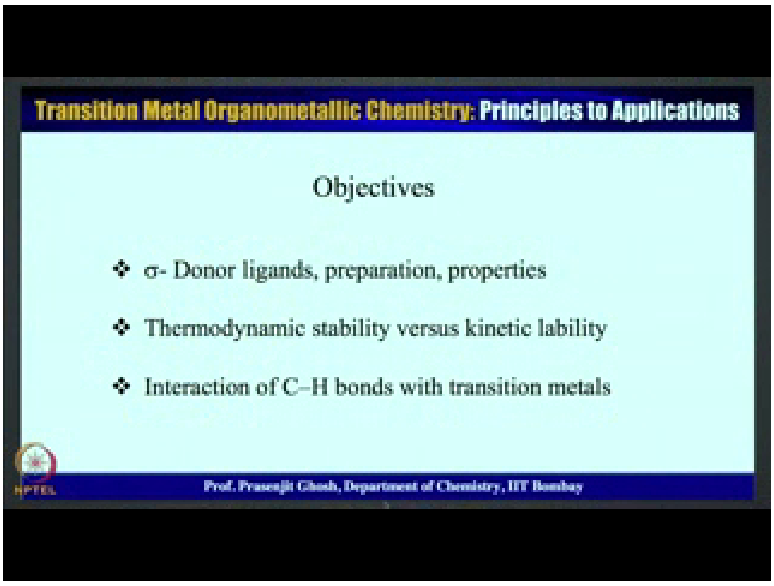
types, peeparations, properties

Now, in next few series of lectures we are going to look at the ligand requirement in terms of what kind of bonds they make with the metal center, that affect the organometallic compounds and they are called classifications. So, to start with in this lecture we would be discussing the our most basic of the ligands of the organometallic compounds, and these are sigma Donor ligands what does this mean is that these ligands have sigma orbitals which involved in bonding with the metal center.

So, the focus in this lecture would be on the various types of sigma Donor ligands, that they come along how they are prepared preparations of organometallic compounds having sigma donor ligands. And then we would look on the properties of sigma donor ligands, transition metal complexes of sigma donor ligands this will bring us to an important topic that is very sensitive to organometallic compound that is their stability.

So, we would also discuss in this lecture the thermodynamic stability of these compounds versus, their kinetic lability what I must mention over here that the carbonately compounds being extremely sensitive to air, and moisture difficult to hand them handle there is a false perception. That these compounds are largely unstable thermodynamically, but in reality what has been found out that these compounds thermodynamically are stable, but their reactivity or high reactivity are of kinetic origin and we will try to look at organometallic compounds from this perspective, and understand their high reactivity that arises from their kinetic lability. Lastly we are going to touch upon a very interesting topic which is of contemporary activation contemporary interest that is the interaction of C-H bond with transition metals.

(Refer Slide Time: 06:53)



Transition Metal Organometallic Chemistry: Principles to Applications

Objectives

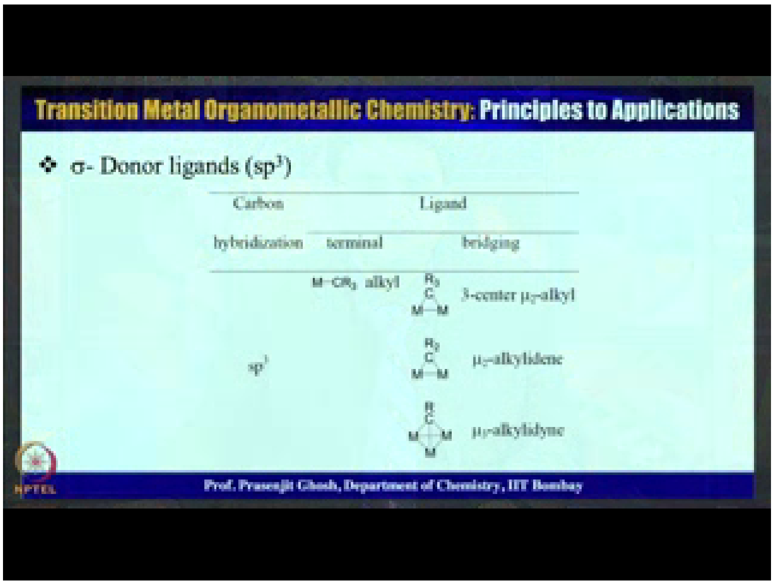
- σ- Donor ligands, preparation, properties
- Thermodynamic stability versus kinetic lability
- Interaction of C–H bonds with transition metals

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

We would look at this topic with very closely based on the fact that this is an important area of contemporary research currently this area is called as C-H activation this is a challenging area as C-H bond strength is very high bond energy, and C-H bonds are ubiquitous. So, they are very common they are very stable bonds and they are very common. And hence the selectivity in activating them becomes very challenging.

And as a result C-H activation is an important area which can result in selective functionalization of the C-H bond, and can make valuated chemicals. So, C-H activation initiates with the C- H interaction with transition metal compounds and we are going to look at how does a C-H interact with the transition metal during this course of this lecture.

(Refer Slide Time: 09:06)



Transition Metal Organometallic Chemistry: Principles to Applications

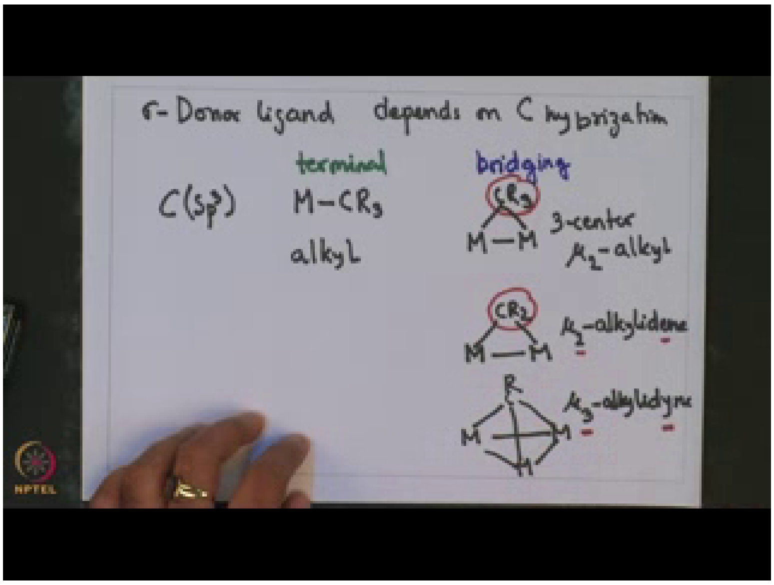
- σ- Donor ligands (sp^3)

Carbon	Ligand	
hybridization	terminal	bridging
sp^3	M–CR_3 alkyl	3-center μ_2-alkyl
		μ_2-alkylidene
		μ_3-alkylidyne

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, with that prelude let us take a look at how many types of sigma donor ligands are there.

(Refer Slide Time: 09:17)



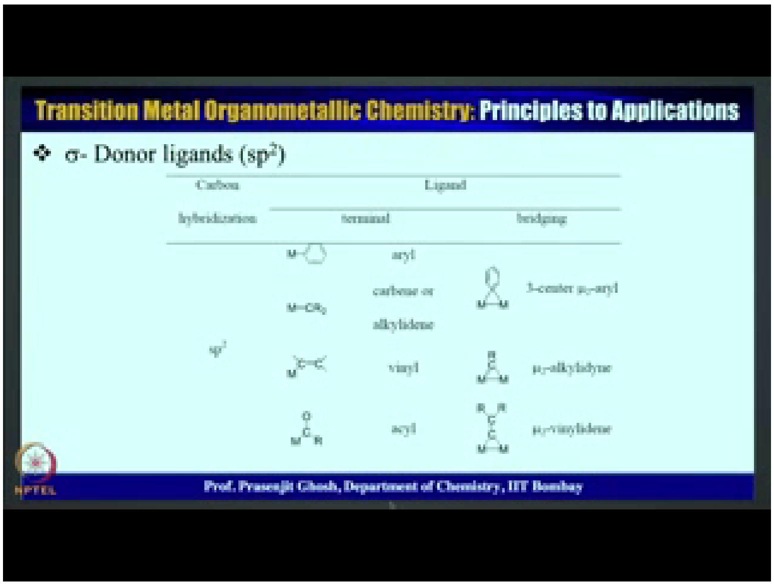
Now the sigma donor ligand depends on hybridization of the carbon center hybridization. So, for sp 3 carbon one can have compounds which are of this type metal bound to CR 3 these are called alkyl complexes or metal alkyls. Now, when the compound is in this way the one the way it is drawn, then this kind of binding is called terminal binding.

So, ligand is a terminal ligand, this alkyl ligand is the terminal ligand, alkyl ligand can also bridge and become a bridging system. If it bridges between 2 metal centre then that can be represented as shown over here so, alkyl bridging between 2 metal center and these are designated as 3 center mu 2 alkyl mu represents bridging between 2 metal centres that is why it is mu 2.

Now, instead of CR 3 bridging between 2 metal center it can also be alkyl moiety of the type CR 2 bridging analogously between the 2 metal centres, and these are called mu 2 again mu is bridging 2 means between the 2 metal center alkylidene, and it can be such that instead of CR 2 one can have a alkyl moiety of the type CR bridging between 3 metal centres and this likewise would be called mu 3.

Now, that there are 3 metal centres alkylidyne. So, the difference being we have a dy versus den rest and mu 2 versus mu 3 rest all remaining the same. So, what we saw is that sp 3 carbon which will represent a metal alkyl ligand can act as a terminal ligand, where metal is directly bound to the alkyl, and alkyl is bound to only one metal center the alkyl can even bind to more than one metal center. When it is bound to 2 metal centres it is called mu 2, and it can bind as a CR 3, when it is mu 2 alkyl it can bind to 2 metal center as CR 2 it is called mu 2 alkylidene. And when it is buying bound to 3 metal center its called mu 3 and since CR is being bound it is called mu 3 alkylidyne.

(Refer Slide Time: 14:40)



Transition Metal Organometallic Chemistry: Principles to Applications

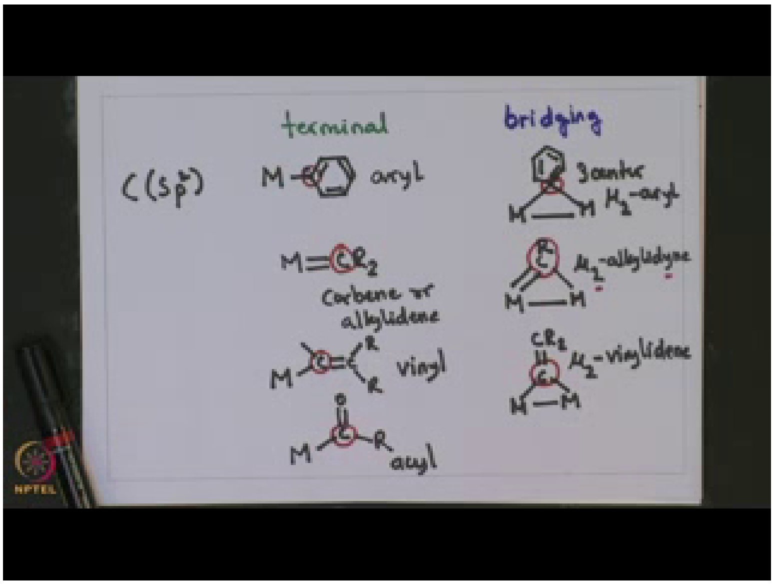
- σ- Donor ligands (sp^2)

Carbon hybridization	Ligand terminal		Ligand bridging	
sp^2		aryl		
	$M{=}CR_2$	carbene or alkylidene		3-center μ_2-aryl
		vinyl		μ_2-alkylidyne
		acyl		μ_2-vinylidene

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Similarly, there is a lot of diversity observed in binding.

(Refer Slide Time: 14:48)



When it is sp 2 like the sp 3 center see sp 2 also has a rich type of binding which is can be as metal bound to an aryl group, where this center is an sp 2 center carbon binding to the metal, and these are called aryl this being a terminal binding it can be classified as terminal ligand. Similarly this aryl group can also bridge, and become show a bridging binding the way it is shown here. Similar to what we had observed for the alkyl binding this is designated as 3 center mu 2 aryl, there can be a direct carbene ligand having sp 2 hybridization bound to the metal and that can be designated as R 2.

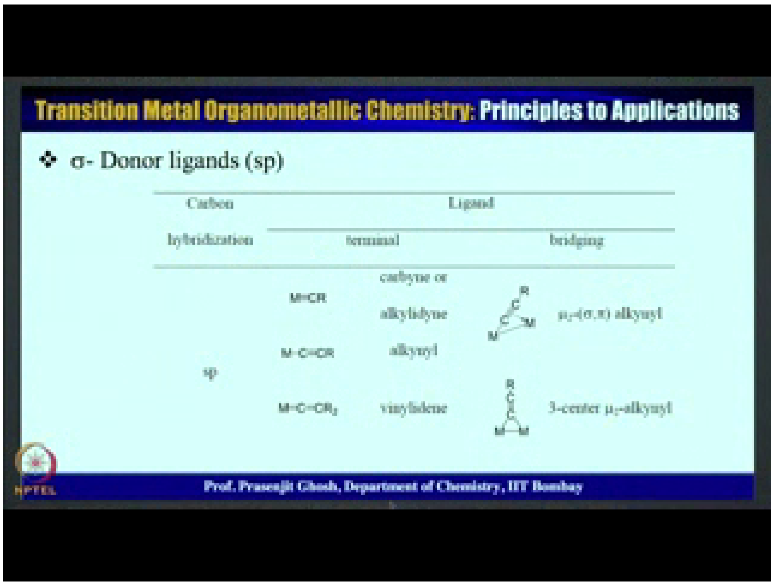
So, these are called carbene or alkylidene this is a terminal carbene bound to the metal center. Similarly sp 2 carbon in the form of carbene can bind in a bridging fashion with CR 2 being a CR moiety the way it is shown here. And then it is called mu 2 alkylidyne with d y and mu 2. C 2 fragment can also bind in a terminal fashion as shown this is called a vinyl ligand. The terminal vinyl binding is shown here likewise there is a mode which also show a bridging binding, bridging vinyl binding.

Now, based on the previous way of naming this bridging modes a bridging vinyl thus would be written as mu 2 vinylidene, there can also instead of olefin there can also be a carbonyl moiety having sp 2 center binding to a metal center. The way its shown over here and these are called acyl ligands. So, what we see that sp 2 centres of various organic moieties as shown over here as well as over here.

That bind to metal center in 2 types mainly bridging as well as terminal also what comes to the fore by looking at various kinds of bridging and binding, terminal bindings for the sp 2 center, and then comparing the same with the earlier discussed sp 3 ones. Then it becomes obvious that the sp 2 center has a rich diversity of binding modes, that is something which is important to remember and many of these sp 2 carbon binding are important intermediate in many catalytic cycles.

For example in olefin metathesis, hydrogenation, polymerization reactions, many of which have gone on to be hydroformylations many of which have gone to become blockbuster industrial processes, that has millions or probably billion dollars of turnover annually throughout the globe. So, from these it is can be gauged that these compounds are extremely important from the catalysis point of view.

(Refer Slide Time: 22:41)



Transition Metal Organometallic Chemistry: Principles to Applications

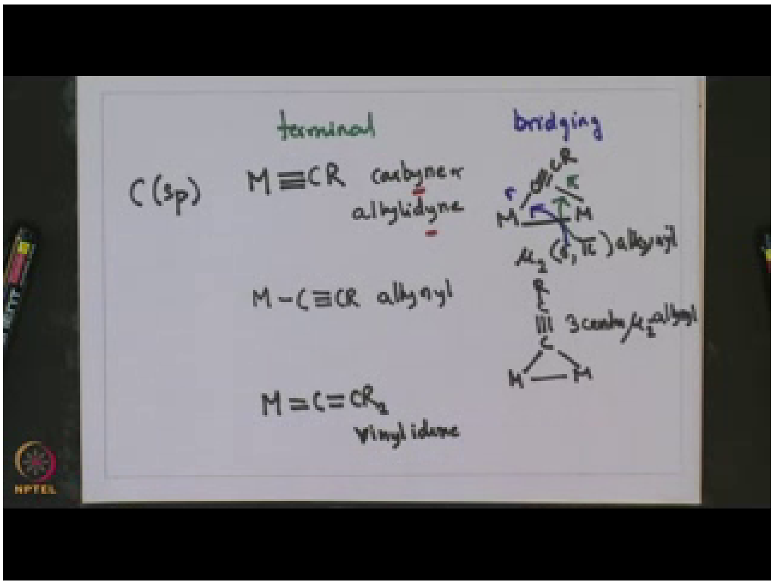
❖ σ- Donor ligands (sp)

Carbon hybridization	Ligand			
	terminal		bridging	
sp	$M\equiv CR$	carbyne or alkylidyne		μ_2-(σ,π) alkynyl
	$M-C\equiv CR$	alkynyl		
	$M=C=CR_2$	vinylidene		3-center μ_2-alkynyl

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, let us look at the 3rd type of sigma donor ligands which are carbon having sp hybridization.

(Refer Slide Time: 22:52)



Now here one can have a CR moiety bonded multiply to a metal center, these are very interesting compounds and are called carbenes, carbynes or alkylidynes, which is unlike with that of CR 2 where it had been carbene in carbyne the B is replaced with y. And alkylidyne is replaced with y the carbyne can also bind in a bridging fashion. So, this is terminal type the carbyne can also bind in a bridging fashion, which can be shown as like this. And these is called mu 2 sigma pi alkynyl. So, this sigma is this bond designates this bond and this pi designates this bond.

So, the alkyne moiety bridges between 2 metal center by two kinds of interaction this is very unique and kind of very special, one type is a sigma type, another type is a pi type. Like metal alkynyl there can be another type of C CR, and these are called alkynyl; metal alkynyl, can also be terminal as shown over here, and can also be bridging as is shown over here. So, this is again 3 center mu 2 alkynyl and lastly of sp type there can be terminal bonds like this and these are called vinylidene.

So, to summarize today's lecture what we had see seen is we have seen through the various binding modes of carbon ligands sigma, donor ligands and what we saw that are rich diversity of binding can be observed depending on the hybridization of at the carbon what can range from sp 3, to sp 2, to sp and most of these bindings can be classified into two types terminal and bridging, and of the 3 had hybridized centres the sp 2 probably shows a rich diversity in binding.

And lastly I must note that these binding are extremely important in understanding the crucial interactions that happen between the metal and ligand, in this compound as this compound play a significant role in chemical catalysis. And hence their reactivity can be understand by understanding their binding, so with these I would conclude todays lecture look forward to taking up the next lecture which involves synthesis preparation property and stability of this kind of sigma alkyl complexes.

So, a lot more to learn about what kind of reactivity the sigma alkyl complexes displayed by virtue of their binding to metal, how they can be prepared what are their uses, and so on, and so forth. So, I look forward to being with you in the next lecture and with that thank you for being with me in this lecture.