Transition Metal Organometallic Chemistry: Principles to Applications

Prof. Prasenjit Ghosh

Department of Chemistry

Indian Institute of Technology, Bombay

(Week 09)

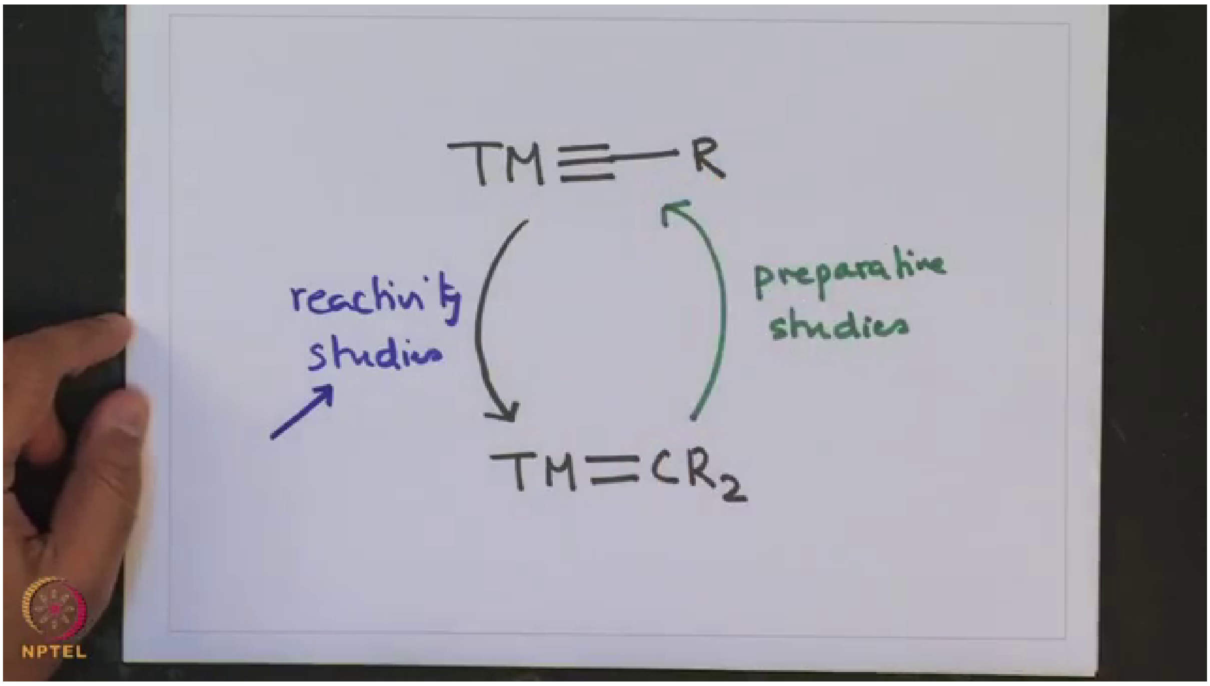
Lecture - 41

Properties of Transition Metal Carbynes and Transition Metal Carbonyls

[noise]

Welcome to this lecture on [vocalized-noise] transition metal organometallic chemistry from principles to applications. We have been discussing about transition metal carbyne complexes and ah we have looked into the reactivity of ah this transition metal carbyne complexes ah in the last lecture, and what we had seen that ah this transition metal ah carbyne complexes had ah 2 nucleophiles, and ah undergo some other kind of ah reaction reactions for example, deductive coupling and so on so forth and ah they do all ah all these as a part of the reactivity study uh.

(Refer Slide Time: 00:54)



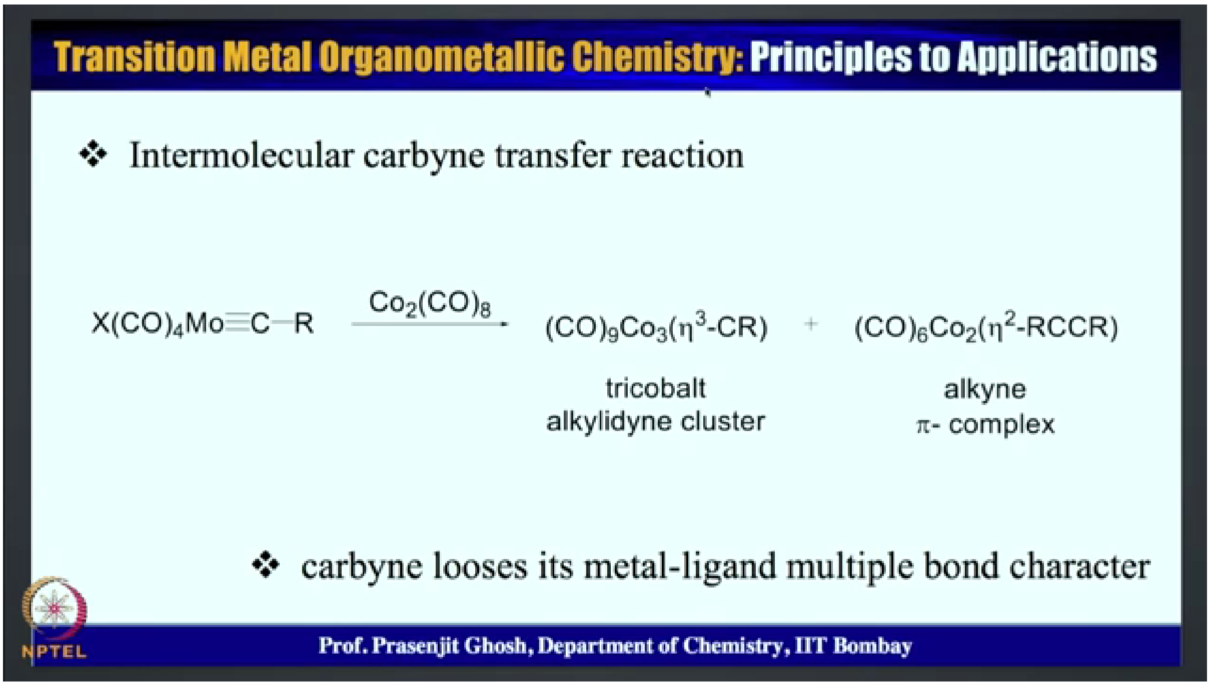
And [noise] what one ends up is the formation of transition metal [noise] carbene complexes [noise]. So, oh these ah where part of the reactivity [noise] studies, that we had seen [noise] ah the in our previous lecture.

Now, at this I would like to note that the formation of carbene complexes ah from the reactivity ah of the studies is akin to ah the going in the reverse direction, where we have prepared [noise] the transition metal ah carbyne complexes [noise] ah through various method ah ah from the corresponding ah transition metal carbyne complexes. So, these were ah preparative [noise] [noise] studies of [vocalized-noise] transition metal carbyne complexes.

So, we see [noise] a a that the cycle ah completes itself, when we look at the preparative studies and reactivity studies or transition metal carbyne complexes ah by the time mean that this transition metal carbyne complexes, can be prepared from transition metal carbene complexes by number of synthetic procedures that exists, and the when the reactivity studies of this transition metal carbyne complexes ah are carried out they can also ah be converted that to the transition metal carbene complexes, through much of the reactivity studies that we have discussed in our ah ah last lecture.

Now, today ah in this lecture, I am going to focus some more [vocalized-noise] on this reactivity studies ah that ah ah can be done with transition metal carbyne complexes.

(Refer Slide Time: 02:48)



Transition Metal Organometallic Chemistry: Principles to Applications

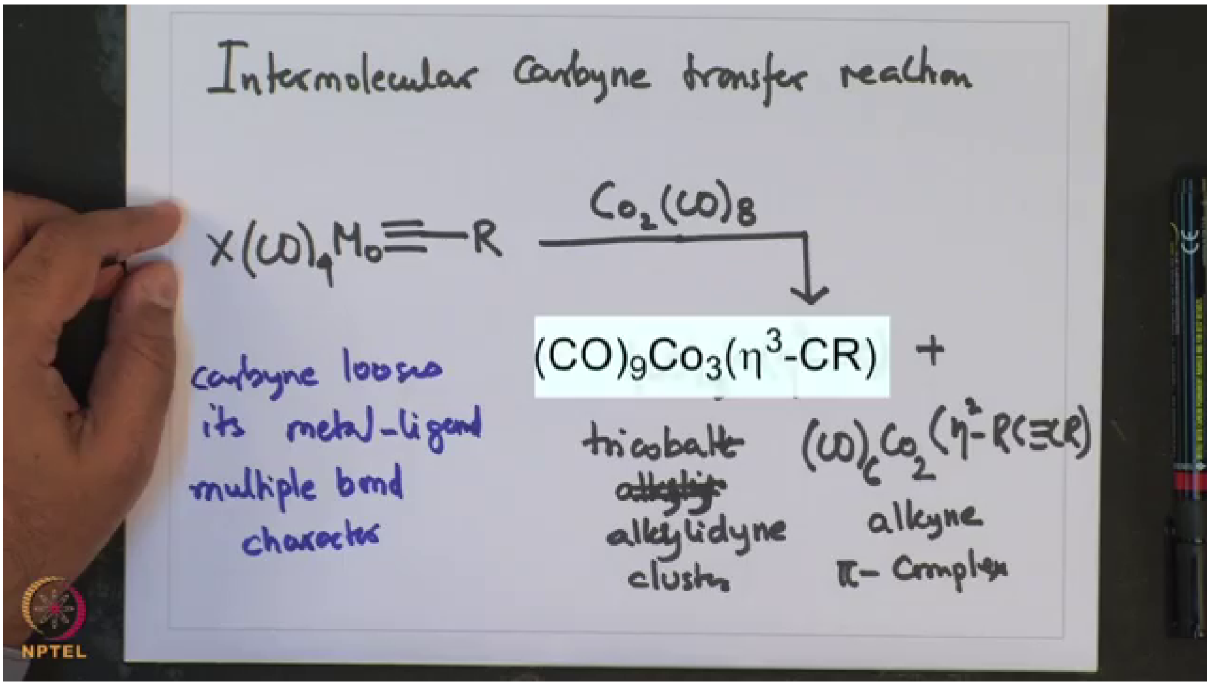
- Intermolecular carbyne transfer reaction

$$X(CO)_4Mo{\equiv}C{-}R \xrightarrow{Co_2(CO)_8} (CO)_9Co_3(\eta^3\text{-}CR) + (CO)_6Co_2(\eta^2\text{-}RCCR)$$

- carbyne looses its metal-ligand multiple bond character

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 02:57)



Intermolecular Carbyne transfer reaction

$$X(CO)_4Mo{\equiv}{-}R \xrightarrow{Co_2(CO)_8} (CO)_9Co_3(\eta^3\text{-}CR) + (CO)_6Co_2(\eta^2\text{-}RC{\equiv}CR)$$

carbyne looses its metal-ligand multiple bond character

And one important reaction in this regard is transition ah intermolecular carbon transfer reaction [noise].

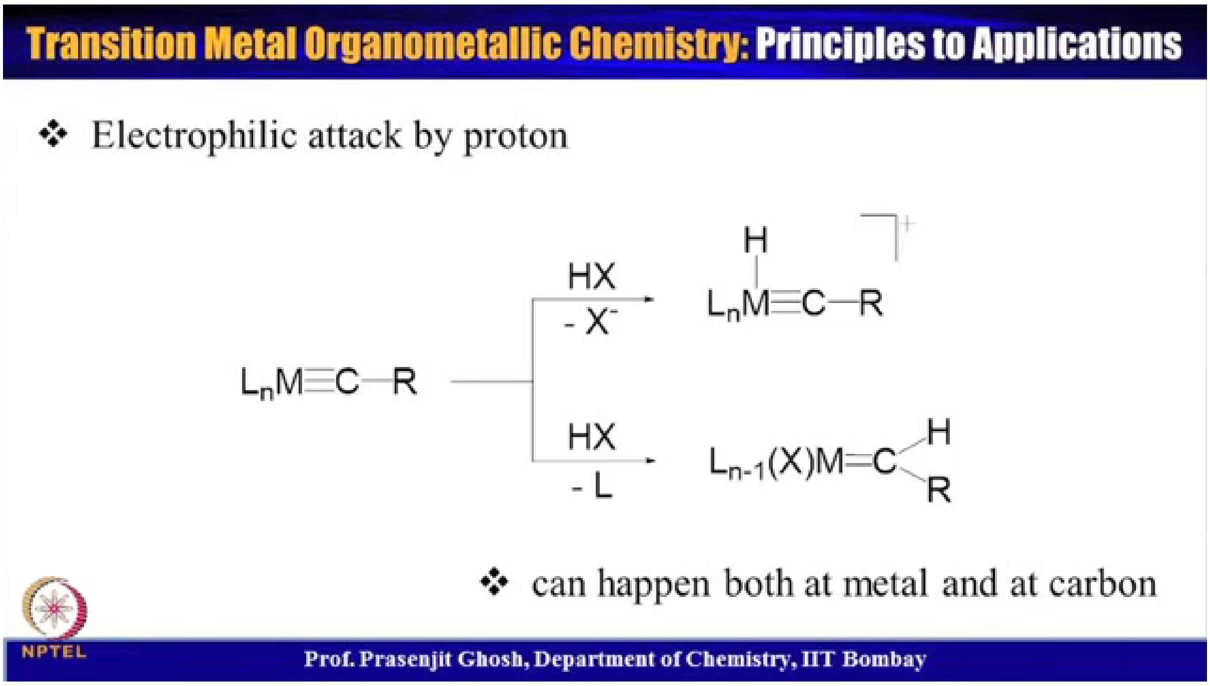
Now, ah let me mention ah this in context of the transition metal carbene chemistry, that we have discussed the transition metal carbene ah ah regions are not to good ah [vocalized-noise] source for transition metal carbene transfer reactions, and that that the chances of obtaining free carbenes from transition metal carbene complexes were ah rare and there were few examples, which are known for ah reacts transition metal ah carbene transfer reactions were the carbonic moiety has been transferred onto some organic substrates particularly uh olefins leading to formation of cyclopropanes, and this were achieved both chirally as well as achiral [vocalized-noise] as well as in achiral fashion.

Now, with respect to carbyne getting transferred, there are not too many examples where ah this transition metal carbyne complexes exist [vocalized-noise] as [vocalized-noise] carbon transfer agents; ah and here I discuss one earlier example of intermolecular carbyne transfer reactions, in which the carbonic moiety get transferred [vocalized-noise] in the course of the reaction um. [noise] And [vocalized-noise] this is for the complex X CO 4 [noise] molybdenum [noise] CR carbyne moiety when treated [noise] with [noise] cobalt dicobalt octacarbonyl [noise] gives [noise] CO 9 cobalt [noise] eta 3 CR. This is tri-cobalt [noise] alkylidyne [noise] cluster along with [noise] CO 6 cobalt 2 [noise] eta 2 RC [noise] CR complex, this is alkyne [noise] pi complex [noise].

So, what can be seen over here that in this molecule there is a intermolecular carbyne transfer reaction happening, leading to formation of a tri-cobalt alkylidyne ah cluster where the ah metal ligand multiple bond bonding character is lost, [noise] where the carbon loses its metal ligand [vocalized-noise] multiple bond character and as a ah similar to what we had seen ah in metathesis reactions that formation of ah pi complex with a metal ah is also observed.

Now, this ah ah may [vocalized-noise] kind of metathesis type reaction was also ah noted for ah the corresponding carbene ah counterpart, where ah olefin was formed from this kind of [vocalized-noise] reaction. So, we do see that there is a parallel reactivity of transition metal carbyne and transition metal carbene kind of complexes for ah this kind of carbyne transfer or carbene transfer reactions.

(Refer Slide Time: 07:17)



Transition Metal Organometallic Chemistry: Principles to Applications

- Electrophilic attack by proton

$$L_nM\equiv C-R \xrightarrow[-X^-]{HX} \left[\overset{H}{\overset{|}{L_nM}}\equiv C-R\right]^+$$

$$L_nM\equiv C-R \xrightarrow[-L]{HX} L_{n-1}(X)M=C\begin{smallmatrix}H\\R\end{smallmatrix}$$

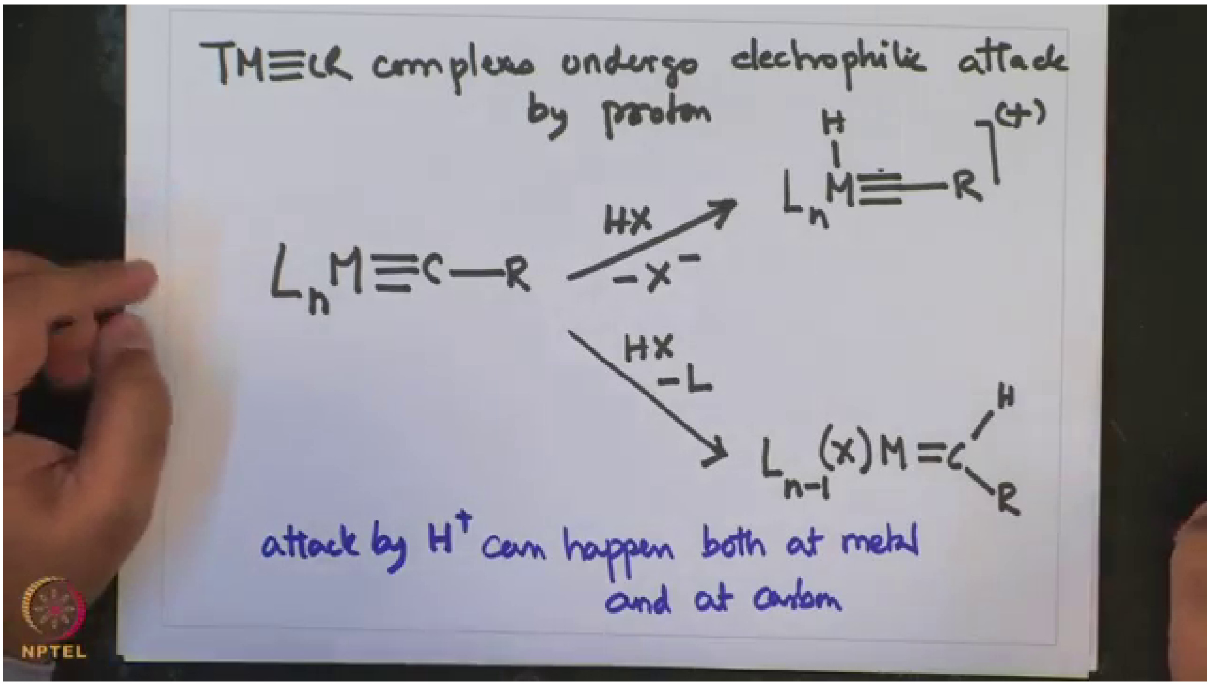
- can happen both at metal and at carbon

NPTEL

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, this transition ah ah metal carbyne complexes also undergo electrophilic attack by proton [noise].

(Refer Slide Time: 07:25)



TM≡CR complexes undergo electrophilic attack by proton

$$L_nM\equiv C-R \xrightarrow[-X^-]{HX} \left[\overset{H}{\overset{|}{L_nM}}\equiv -R\right]^{(+)}$$

$$L_nM\equiv C-R \xrightarrow[-L]{HX} L_{n-1}(X)M=C\begin{smallmatrix}H\\R\end{smallmatrix}$$

attack by H^+ can happen both at metal and at carbon

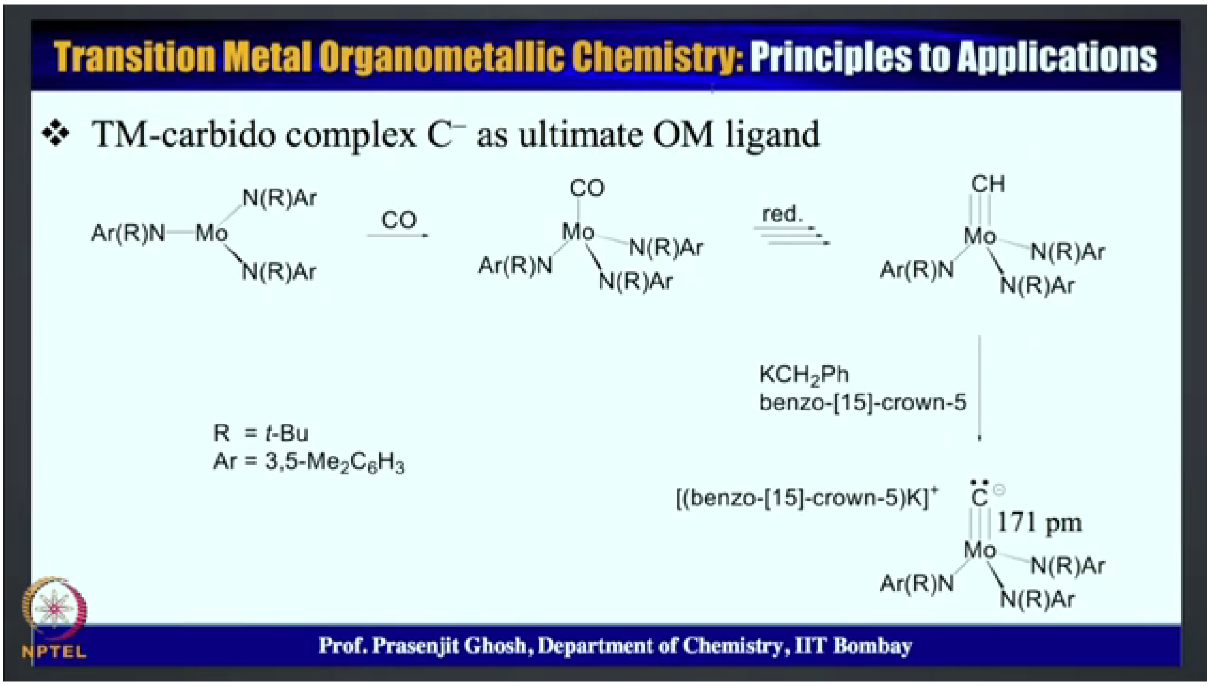
NPTEL

And this can be explained [noise] by this reaction L n M [noise] C R. Now the attack can happen at carbon or at metal. So, [noise] when it reacts with H X, [noise] that leads to elimination of X minus. So, giving the proton and then proton attacks the pi cloud, resulting in formation of [noise] this cationic species or [noise] results can also happen at carbon [noise] giving this [noise] L n minus 1 [noise] X M [noise] H R. So, depending on the metal and depending on the ah ligand, one can see [noise] attack by proton [noise] can happen [noise] both at metal [noise] and at carbon [noise].

So, oh here ah we see an interesting ah reactivity [vocalized-noise] proton towards carbonic centre, where ah the proton can go and attack the metal. As well as it can attack at the carbon and an undergo violation of H X to give a a transition metal carbene complex.

So, what we see that ah ah there is ah differential ah reactivity has to [vocalized-noise] which attack may [vocalized-noise] take place, and that all depends on what kind of ah ligand is surrounding at the metal and what kind of metal ah is ah forming this carbyne bond depending on the [vocalized-noise] these ah these one of the other ah modes of ah attack would be favoured.

(Refer Slide Time: 10:46)



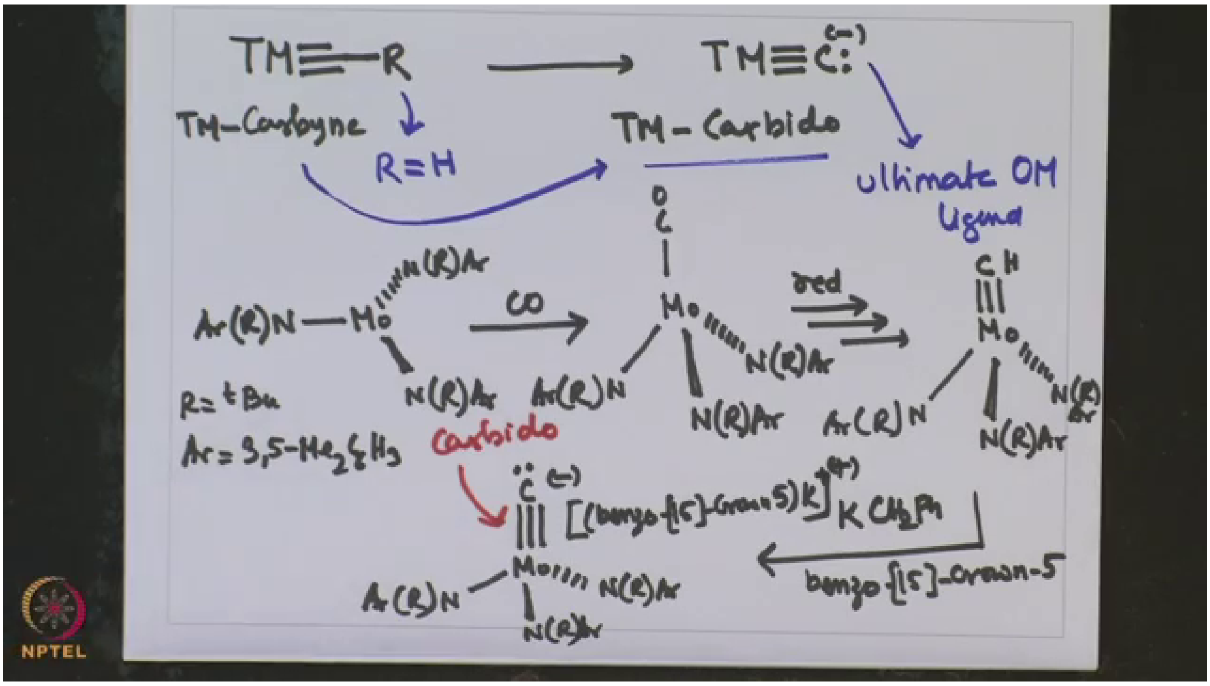
Transition Metal Organometallic Chemistry: Principles to Applications

- TM-carbido complex C^- as ultimate OM ligand

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Another interesting ah example is ah that of conversion of the carbyne complexes to C minus as ultimate organometallic ah ligand. So, this is an ah interesting example where transition metal.

(Refer Slide Time: 11:02)



Carbyne complex [noise] is combine this is a carbyne complex [noise] is converted to [noise] carbido [noise] TM carbyne complex converted to a carbido complex. Now this carbido is a very interesting ligand this is ultimate [noise] organometallic ligand [noise] because there is fully carbon and there is no other substance on the carbon, and this is the C minus ah kind of ah species; and these ah ah to be obtained from transition metal carbyne complexes, but this only occurs when there is a special ah criteria of r equal to being hydrogen ok.

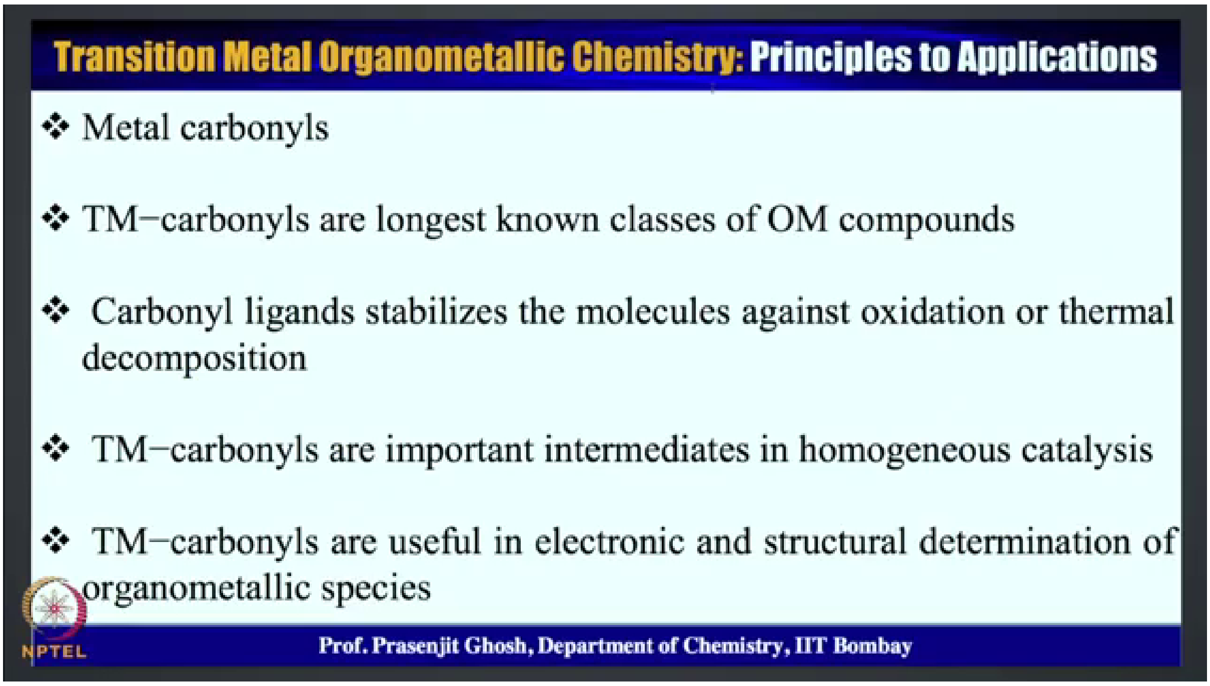
So, ah when ah the carbyne complexes having R equals hydrogen ah is obtained that can be converted to the ultimate organometallic ligand, where this carbonic moiety is converted to ah carbido moiety [noise] [vocalized-noise] as seen over here. A nice example of this ah is [noise] discussed here where [noise] Ar R N. R equals t [noise] butyl, A r is a bulky ligand [noise] 3,5 dimethyl C 6 H 3 [noise] molybdenum [noise] N R A r [noise] N [noise] R A r [noise] reacts with carbon monoxide [noise] to give [noise] co N [noise]R A r [noise] N R [noise] A r [noise] N R A r.

Now, this undergoes [noise] reduction to give the carbyne species which is [noise] N R A r, [noise] N R A r, N R A r [noise]. So, that [noise] when treated with k potassium CH 2 p h n benzo 15 crown its a crown 5 ether, then one gets this carbido complex C [noise] minus molybdenum [noise] N R A r, [noise] N R A r, [noise] N R A r [noise] and this being a minus it has counter an ion is [noise] benzo [noise] 15 [noise] crown 5 potassium [noise] plus.

So, this is an interesting example where a carbyne moiety is efficiently converted to oh ah [vocalized-noise] carbido moiety, a a where there is a [noise] this ah no substituent in the [vocalized-noise] carbon and it is their carbon found to metal this is the ultimate organometallic ligand and ah these are called carbido o ligand, and they can be prepared for transition metal carbyne complexes where R R is ah only ah hydrogen ah. This is the nice example of how ah this reactivity has been achieved and this is something which is unique to carbyne complexes and there is no such parallel ah ah ah that is known for the carbene complexes in terms of they been converted to carbido ligand.

Now, with these ah we come to ah [vocalized-noise] our end of the ah the discussion on transition metal carbyne complexes.

(Refer Slide Time: 17:16)



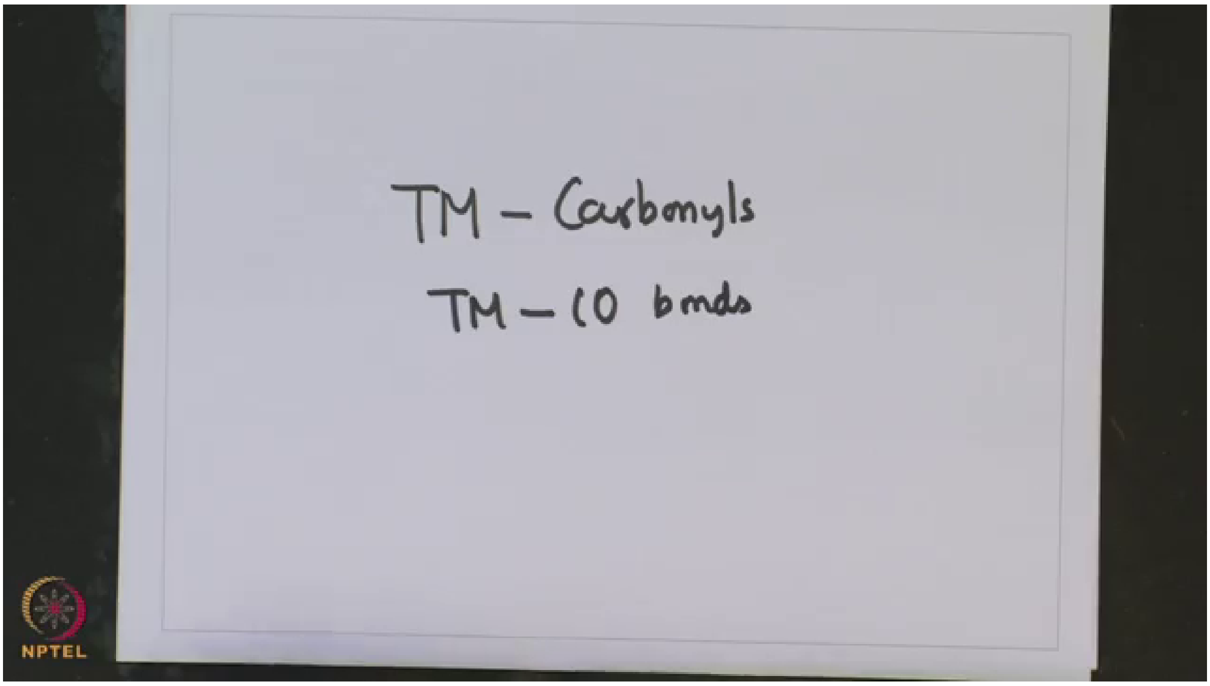
Transition Metal Organometallic Chemistry: Principles to Applications

- Metal carbonyls
- TM−carbonyls are longest known classes of OM compounds
- Carbonyl ligands stabilizes the molecules against oxidation or thermal decomposition
- TM−carbonyls are important intermediates in homogeneous catalysis
- TM−carbonyls are useful in electronic and structural determination of organometallic species

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

And we are going to now move on to one important ah top class of compounds which are transition metal carbonyl compounds ah these are very important class of compounds, in the sense that a large number of studies have been carried out ah with these ligands these are one of the compounds which are long known ah ah have been studied a lot over ah hundr[ed]- [vocalized-noise] ah over probably a couple of centuries ah. So, the chemistry of these ah ah compounds are well developed and ah also extremely in ah interesting ah in terms of their ah structural bonding and synthetic ah details.

(Refer Slide Time: 17:55)



TM – Carbonyls

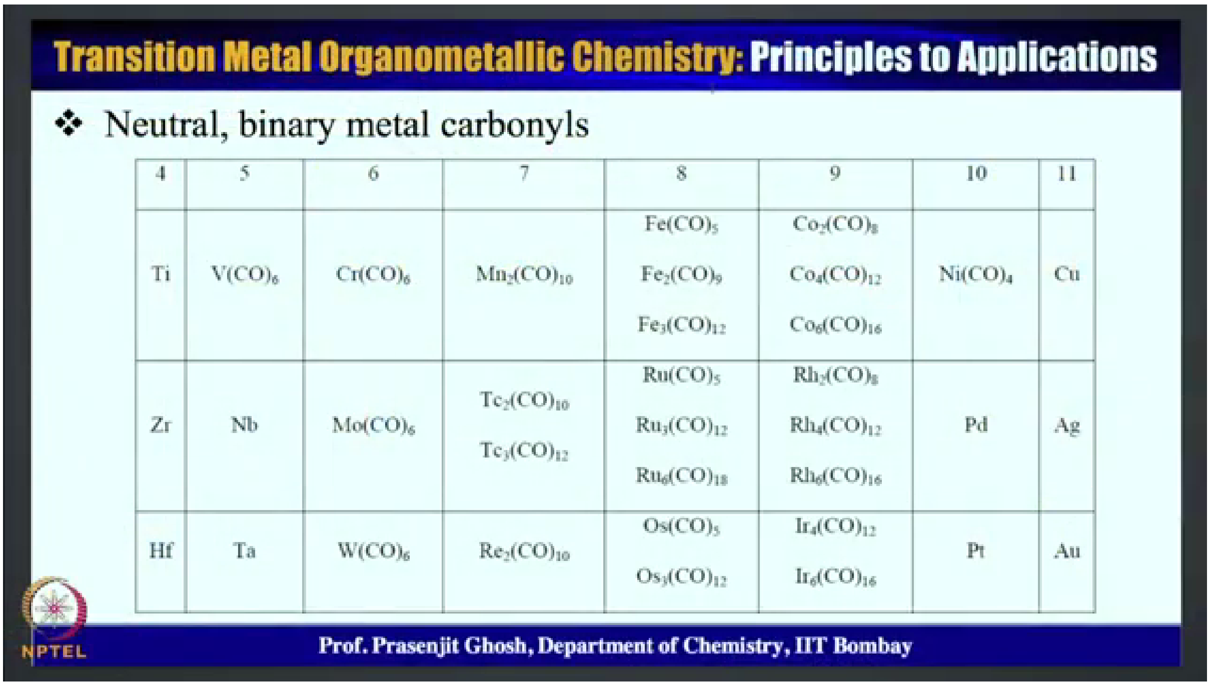
TM – CO bonds

Ah [noise]. So, we are going to move on to an interesting ah compounds or these are called transition metal carbonyls [noise] [noise] and ah these ah compounds containing [vocalized-noise] contain transition metal ah CO bonds, [noise] ah and these ah can be monitored both by NMR as well as ah IR ah spectroscopies. ah These transition metal carbonyls compounds are also important intermediate in many homogeneous catalytic reactions as well as ah these servers useful tool in electronic and structural determination of organometallic species.

So, ah carbonyl ah compounds have ah really play the crucial role ah in quantifying ah ah in the ligand strength or ah the electronic nature particularly of ah that is electron donating and [vocalized-noise] ah electron withdrawing ability of ligands, ah ah ah in quantifying ah this ligands in the field of organometallic chemistry, [vocalized-noise] transition metal carbonyl compounds have ah played a long role and have also been studied ah ah a lot.

So, with that pre-test ah I am going to talk about ah ah various kinds of ah transition metal carbonyls that have been developed, and we are going to see a that ah like how these carbonyl compounds ah have ah has involved around ah these [vocalized-noise] class of other organometallic ah ah compounds that we have just discussed.

(Refer Slide Time: 19:32)



Transition Metal Organometallic Chemistry: Principles to Applications

- Neutral, binary metal carbonyls

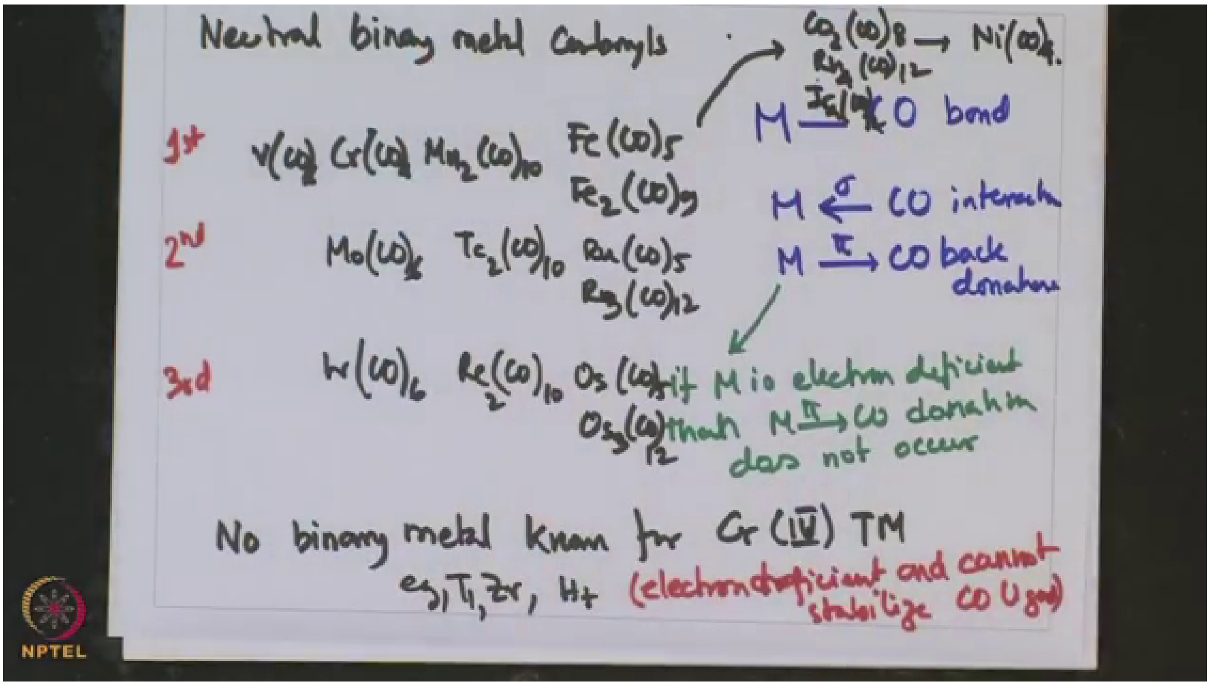
4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$ $Co_6(CO)_{16}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$ $Tc_3(CO)_{12}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$ $Ru_6(CO)_{18}$	$Rh_2(CO)_8$ $Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$ $Ir_6(CO)_{16}$	Pt	Au

NPTEL

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, ah [vocalized-noise] with these ah ah ah with these interaction, let me just say that a transition metal carbonyl compounds ah ah usually [vocalized-noise] many of them are known for to be ah the binary compounds or a binary metal carbonyl, where there is uh these are homiletic complexes ah where ah there is no other cool ligands present ah with transition metal ah carbonyl compounds.

(Refer Slide Time: 20:07)



Neutral binary metal Carbonyls

1st $V(CO)_6$ $Cr(CO)_6$ $Mn_2(CO)_{10}$ $Fe(CO)_5$ $Fe_2(CO)_9$

2nd $Mo(CO)_6$ $Tc_2(CO)_{10}$ $Ru(CO)_5$ $Ru_3(CO)_{12}$

3rd $W(CO)_6$ $Re_2(CO)_{10}$ $Os(CO)_5$ $Os_3(CO)_{12}$

$Co_2(CO)_8 \rightarrow Ni(CO)_4$.

$Rh_4(CO)_{12}$

M — CO bond

$M \xleftarrow{\sigma} CO$ interaction

$M \xrightarrow{\pi} CO$ back donation

if M is electron deficient then $M \xrightarrow{\pi} CO$ donation does not occur

No binary metal known for Gr (IV) TM

eg, Ti, Zr, Hf (electron deficient and cannot stabilize CO ligand)

And these among some of the examples of these ah neutral [noise] are that of ah [vocalized-noise] iron [noise] iron, ah pentacarbonyl or diiron nonacarbonyl ok.

Ah similarly uh there are ah examples of manganese [noise] CO 10 or ah from ah chromium C r [noise] CO 6 [noise] or [noise] vanadium CO 6. [noise] Now one must ah note t that there is nothing no binary carbonyl known for group 4 no [noise] binary [noise] metal carbonyls [noise] known for group 4[noise] transition metal ah for example, [noise] ah titanium, ah [noise] zirconium and hafnium.

Now, reason being that these ah group 4 transition metals are ah electron deficient, these are [noise] electron deficient and cannot and cannot [noise] stabilise [noise] CO ligand. Now this is an important observation from the perspective of the fact that, ah the metal carbonyl [noise] ah ah bond has 2 kinds of interaction ah for example, [noise] metal to carbonyl sigma ah donation [noise] as well as ah metal to carbonyl pi back donation.

Now, as group four transition metals ah if the metal is electron [vocalized-noise] deficient, if a metal is electron [noise] deficient [noise] then metal C pi CO back donation do not occur [noise] [noise] as a result ah the metal carbonyl bond is not stabilised ok. So, [noise] that is why [vocalized-noise] these ah group four transition transition metals like chromium, zirconium, hafnium which are extremely electron deficient they cannot participate in metal to [vocalized-noise] ah carbonyl pi back donation as a result ah their carbonyl complexes as binary neutral metal carbonyls are not known.

On the other hand ah the electron ah ah among electron rich materials, this is quite common and not only its common for ah the first row [noise] ah first row transition metal, but also the same ah can be seen for ah second row and third row [noise] ah ah with the corresponding ah ah with the corresponding ah the chromium ah molybdenum counterpart, [noise] Mo CO 6 as well as tungsten CO 6 or manganese ah one like technetium Tc 2 CO 10 or Ret c CO 10 being known similarly for ruthenium R u CO 5 or R u 3 CO 12 ah is known and similarly for osmium Os ah CO 5 or ah os 3 CO 12 are all known.

Now, um not only its offset carbon, it can go over to cobalt ah with cobalt ah ah ah cobalt [vocalized-noise] which can move over to let us say cobalt CO 2 CO 8 being known ah and all the way a one can go to uh rhodium [noise] [noise] Rh a ah 4 CO ah 12 or iridium I R 4 CO 12 is also known and finally, to nickel tetracarbonyl is also known.

Ah. So, what is ah seen though over here that the centre of the periodic table from group ah ah 6 to group 9 almost for all the ah ah transition metals in first row, second row, third row a lot of binary metal carbonyl complexes are known and that is because these ah from group ah 6 to [vocalized-noise] group 9 ah that these are electron rich metal centres, and that the metal is ah has enough electron density to participate in metal to ligand pi back donation as a result the binary compounds are ah stable.

So, with these ah let me conclude what have been discussed in today's lecture, we started off by looking at transition ah metal carbyne complexes we looked at their reactivity from the perspective of how they were synthesised, and what we have observed that the much of the reactivity of transition metal carbyne complexes lead to the formation of transition metal carbene complexes and this is ah similar to that we had ah [vocalized-noise] seen earlier, where transition metal ah carbene complexes ah under suitable manipulation ah gave the transition metal carbyne complexes.

we have ah ah looked at the reactivity of transition metal carbyne complexes in this regard, with respect to the addition of the ah protons ah ah ah where it can add to the metal or it can add ah to the carbon ah as ah the situations ah ah would demand based on the ligand and the metal environment. We have also seen an excellent example where transition metal carbyne ah complex for carbyne carbon where the hydrogen substituted on it could be uh converted to a the ultimate organometallic [vocalized-noise] ligand which is transition metal carbido complex, this was an excellent example and the ah final complex was also structural characterised using and uh this complexes first was indeed stabilized using by bulky ligand and then there was [vocalized-noise] succeeded in [vocalized-noise] structurally characterising it.

We have ah with that ah we have looked into some other reactivity of transition metal carbyne complexes and then moved on to another ah pi acidic ligand which are metal carbonyls metal carbonyls are long known ah compounds in the area for organometallic [vocalized-noise] ah chemistry. Unlike the transition metal carbene or carbyne complexes which we are discussed which were only uh known since last 20 or 30 years whereas, metal carbonyls in organometallic chemistry had existence over ah centuries ah may be 2 over 2 centuries.

So, this [vocalized-noise] compounds have been studied about and they have been [vocalized-noise] used successfully in quantifying ah the electronic nature of many other organometallic ligands, and ah that was ah ah one of the utility of transition metal carbonyl complexes which is matched merged out ah also transition metal carbonyl complexes are important intermediates for many ah catalytic reactions particularly hydro formalization done with cobalt carbonyl ah or rhodium carbonyl compounds.

And then we [vocalized-noise] moved on to ah the binary transition metal carbonyl compounds; and what we saw that this binary [vocalized-noise] transition metal carbonyl compound compounds are mainly uh dominant in the middle of the periodic table from group 6 to group 9, where ah these complexes exist ah for all the ah metals ah [vocalized-noise] ah from first row to second row to third row, and that is because that this carbonyls are stabilized electron rich metal centres which can not only can ah accept electron by sigma donation, but also can back donate electron from the metal to the ligand.

And this back donation is very critical in stabilising transition metal carbonyl complexes; is evident from the fact that [vocalized-noise] for the electron deficient ah ah group four metals like titanium zirconium hafnium no binary [vocalized-noise] carbonyl complexes ah are known or an idea to be stabilised.

So, with that I would like to conclude todays lecture, and we are going to be a discussing bit more details ah ah this metal carbonyl chemistry this exciting [vocalized-noise] (Refer Time: 29:30) of chemistry, and we would see how this compounds [vocalized-noise] have been ah developed ah in the area for organometallic chemistry right from their synthesis to properties, and their application studies and that would be the ah subject ah ah topic of next lecture.

So, ah thank you for being with me in this lecture, I am look forward to being with you where we going to be discussing in the metal carbonyl chemistry in detail in the next lecture till then goodbye [noise].