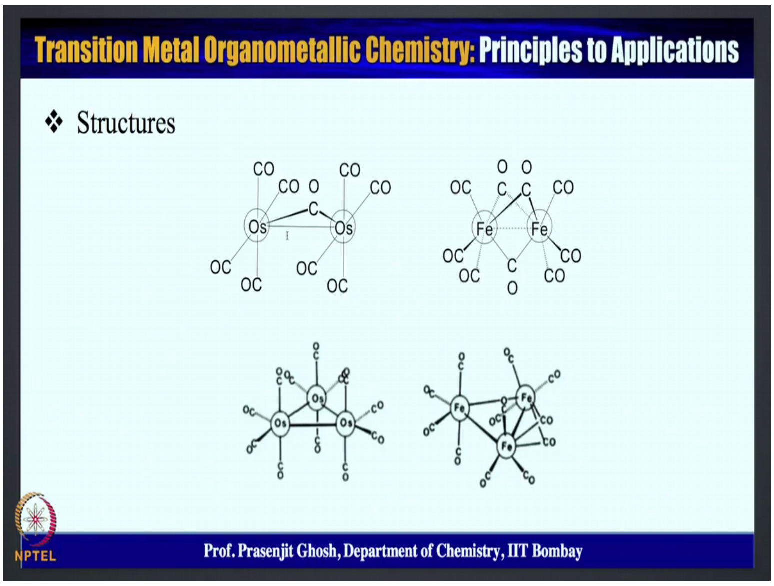
Transition Metal Organometallic Chemistry
Principles to Applications
Prof. Prasenjit Ghosh
Department of Chemistry

Indian Institute of Technology Bombay
Week - 09
Lecture - 43
Transition Metal Carbonyls

Welcome to this lecture on transition metal organometallic chemistry from principles to applications, we have been discussing an very important an interesting topic over the last few lectures and this is on transition metal carbonyl complexes.

(Refer Slide Time: 00:31)



Transition Metal Organometallic Chemistry: Principles to Applications

❖ Structures

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

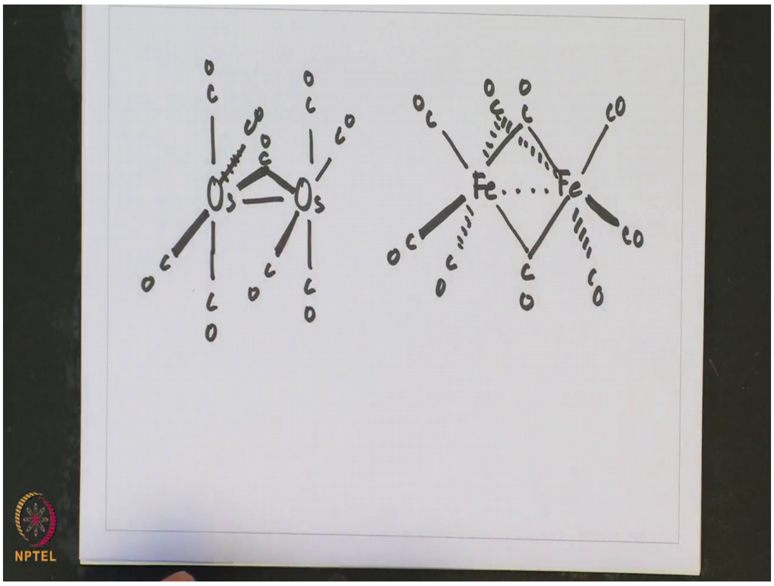
Transition metal carbonyl complexes are important with regard to their applications in chemical catalysis, as well as in understanding other ligands in terms of their electron donating ability; this transition metal carbonyl complexes have been used. We have spoken about this application of transition metal carbonyl complexes in details in our previous lecture.

Now, this in the last lecture we have also looked at the synthesis of transition metal carbonyl complexes and look also at the structure of this transition metal carbonyl complexes. Now as far as synthesis is concerned for transition metal carbonyl complexes, what we had seen that several strategies are use particularly of the ones that involve direct reaction of zero metal in it is zero oxidation state with carbon monoxide making this transition metal carbonyl complexes, the other method involves reducing transition metal solves by a reducing agent in presence of COs to produce transition metal carbonyl complexes.

We also looked at some of the structures of transition metal carbonyl complexes and what we saw that there is a white diversity of structures that are seen for binary transition metal carbonyl complexes and with that discussion we are going to start today by looking at some of the structural features of this transition metal carbonyl complexes.

Now, what we had seen that transition metal carbonyl complexes, for example in disodium 9 carbonyl there is single bridging carbonyl.

(Refer Slide Time: 02:21)

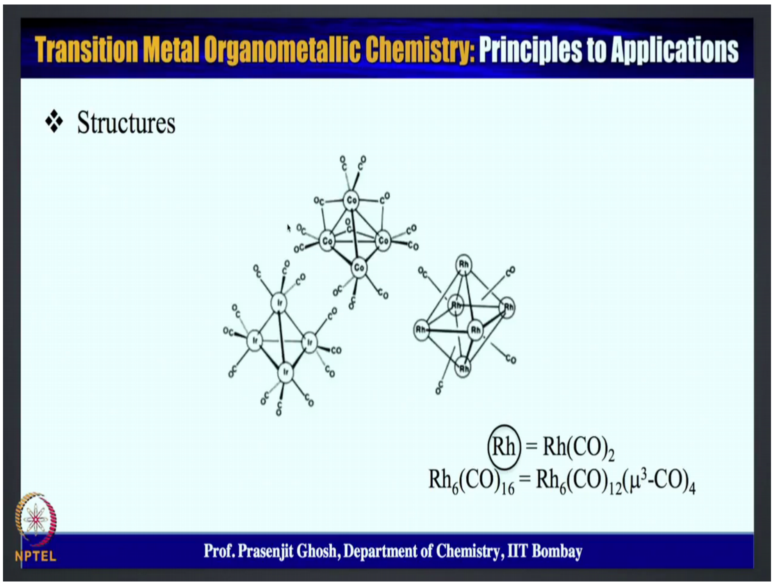


Whereas, the same for the iron there are 3 bridging carbonyl moieties and this were ascribed big to the small size of iron as opposed to the osmium leading to this, the different number of bridging carbonyl moieties. So, as far as the iron is concerned iron contains 3 bridging carbonyls and osmium contains a singly a bridged carbonyls.

So, reason for lesser number of bridging carbonyls in osmium has been attributed to the bigger size of osmium as opposed to iron. So, what we saw in osmium in our previous discussion that this as a single bridging carbonyl, whereas the iron has 3 and that has been ascribed to the bigger size of osmium to that of iron.

Now, continuing this discussion further we are going to take a look at some interesting more binary carbonyl complexes.

(Refer Slide Time: 04:09)



Transition Metal Organometallic Chemistry: Principles to Applications

❖ Structures

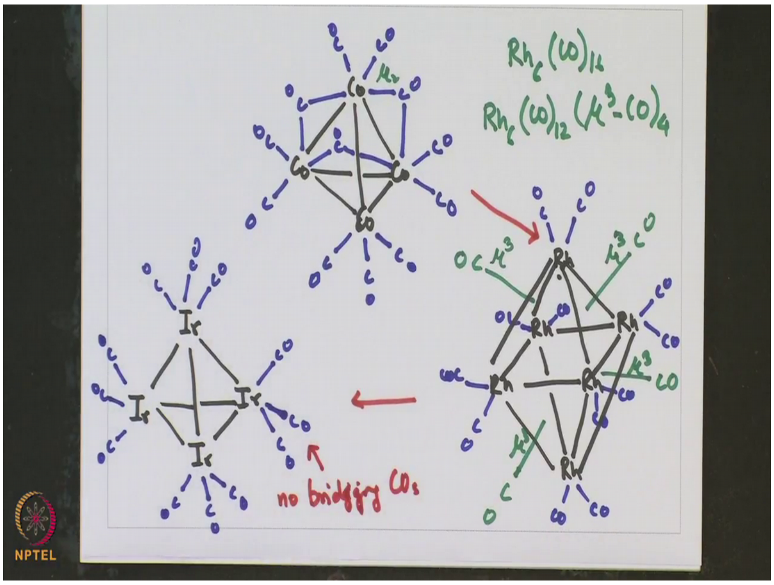
$\text{(Rh)} = Rh(CO)_2$

$Rh_6(CO)_{16} = Rh_6(CO)_{12}(\mu^3\text{-}CO)_4$

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Which shows different modes of binding for example, cobalt being first row transition metal forms this cluster with Co4 of tetra cobalt carbonyl cluster and each of these are cobalt has 2 terminal carbonyls and the bottom 1 has 3 terminal carbonyls and then there are 3 bridging carbonyls 1 2 3.

(Refer Slide Time: 04:15)



Now, this is example of carbonyl bridging between 2 metal centre, now if 1 moves from cobalt to rhodium and here is this rhodium 6 cluster of rhodium is cluster each rhodium contains 2 terminal carbonyl and there are 4 triply bridging carbonyls which happens at this face, which has a triply bridging carbonyl this face and the back face of triply bridging carbonyl and this front face of triply bridging carbonyl and this.

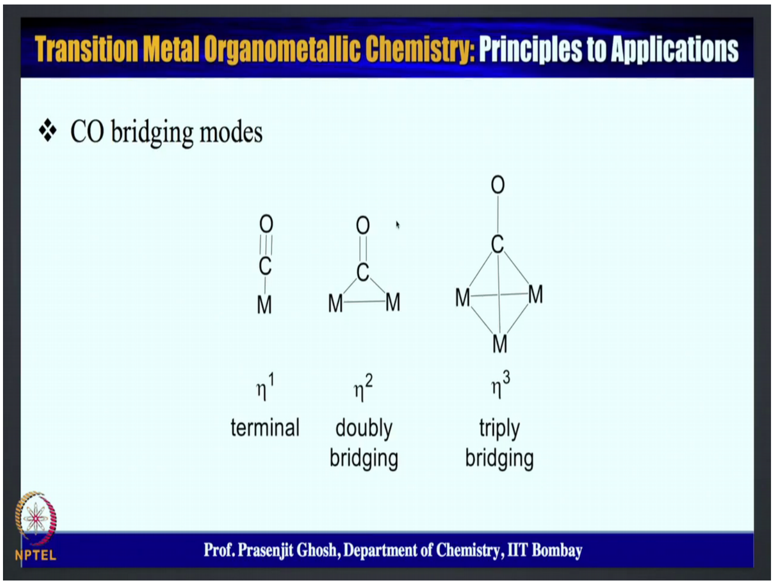
So, this compound is a interesting one which contains carbonyl which are bridged to 3 rhodium and they are designated as Rh6 Co16 and this sort of represents Rh6 Co12 with mu 3 Co 4 and these are mu 3 carbonyls. So, we see a complex structure whereby there are terminal carbonyls and mu 3 bridging, these are mu 2 types and terminal carbonyl.

Now, when 1 goes from cobalt to rhodium which is bigger in size, then from rhodium 1 goes to iridium which is even bigger in size, we see that the formation of bridging carbonyl is completely in inhabited.

So, here is iridium 4 cluster and each of the there is no bridging carbonyl at all and each of the iridium is bound to 3 a carbonyl moieties as shown over here. So, the taken message is that as size increases the bridging tendency of carbonyl to bridge decreases iridium complex, iridium in bigger in size no bridging carbonyls in this.

So, this is an interesting example where you can see that as the size increase the number of bridging carbonyl decreases and also these example afford the different kind of bridging carbonyls that are possible which is mu 2 type and also it can go from mu 2 to mu 3 type.

(Refer Slide Time: 10:53)



Transition Metal Organometallic Chemistry: Principles to Applications

- CO bridging modes

η^1 terminal

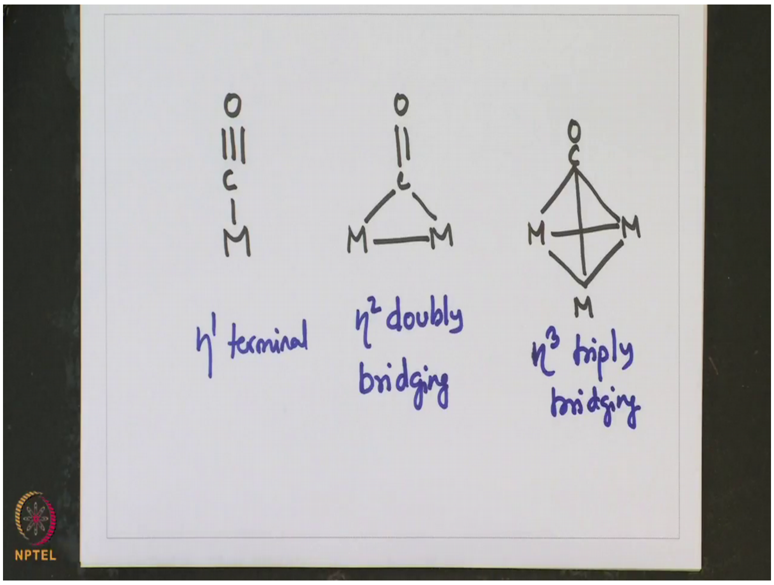
η^2 doubly bridging

η^3 triply bridging

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

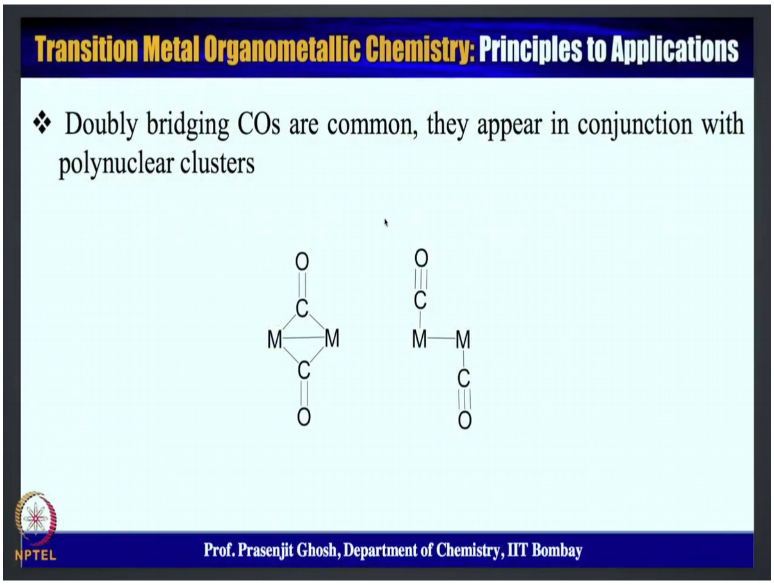
So, that the bridging modes as seen in that compound is that you can.

(Refer Slide Time: 11:01)



One can have a terminal carbonyl which is eta 1 terminal one can have mu 2 doubly bridging or eta 2 and one can even have the mu 3 triply bridging, where as we saw in the rhodium carbonyl cluster that this triply bridging carbonyls was also seen. Now, these also sort of exposes the kind of versatility that this carbonyl compounds that they show furthermore.

(Refer Slide Time: 12:34)



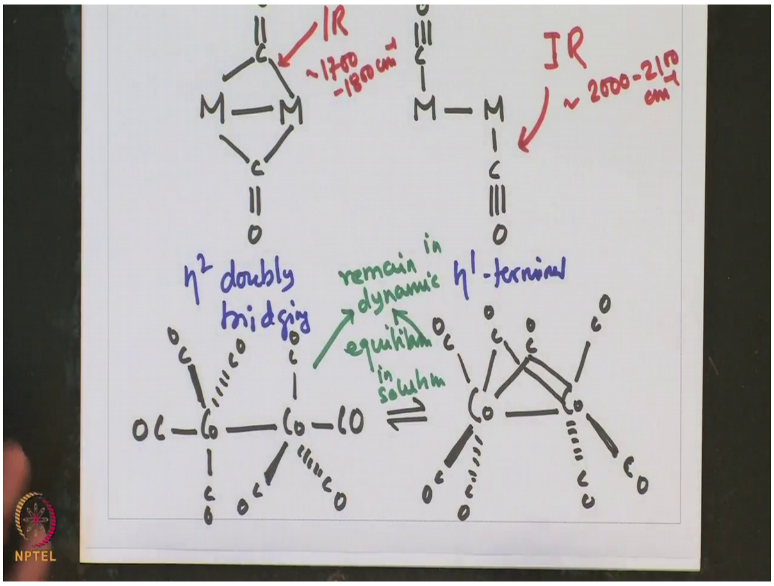
Transition Metal Organometallic Chemistry: Principles to Applications

- Doubly bridging COs are common, they appear in conjunction with polynuclear clusters

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

There is another interesting feature that this doubly bridging carbonyl can sort of exist as a equilibrium between the terminal clusters. So, the equilibrium between the doubly bridging carbonyl as is drawn over here.

(Refer Slide Time: 12:47)

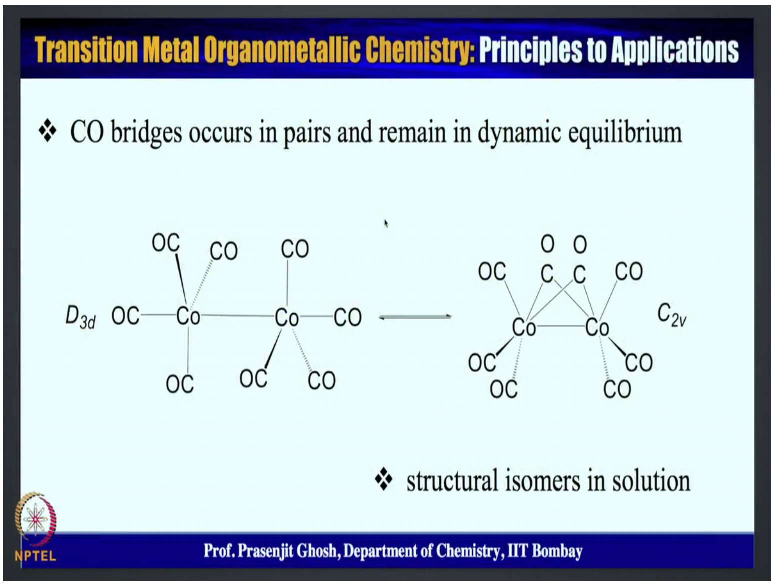


So, that can sort of the M conjunction with this or in equilibrium with this terminal carbonyl compound as well, this is doubly bridging and eta one terminal and the perfect example of this is in this dicobalt complex which sort of exhibits, which shows both kind of bridging in dynamic equilibrium in solution and that can be seen over here, where all the terminal carbonyls; the structure containing terminal carbonyl is in equilibrium with the structure containing the bridging carbonyls as is shown over here.

Now, the these 2 structure are in dynamic remains in dynamic equilibrium installation, now one and hence one can see the presence of both of the structure; now infrared spectroscopic is a excellent tool for monitoring or characterising these modes of vibration and they would be different for these the terminal ones as opposed to the bridging once.

So, the bridging ones as well as the terminal ones they appear at distinct region this one comes around 2000 to 2100 centimetre inverse, whereas this would come somewhere around 1700 to 1800 centimetre inverse. So, there are distinct region where this bridging and terminal carbonyl might disappear and from looking at the Co stretching frequencies is for this bond, one can ascertain how many kinds of bridging.

(Refer Slide Time: 16:46)



Transition Metal Organometallic Chemistry: Principles to Applications

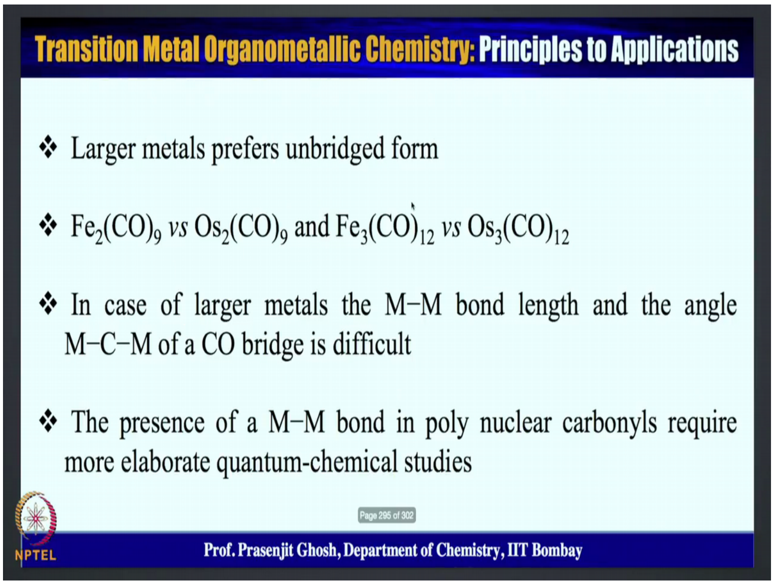
- CO bridges occurs in pairs and remain in dynamic equilibrium

- structural isomers in solution

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Or how many terminal carbonyls are associated with the structure concerned.

(Refer Slide Time: 16:51)



Transition Metal Organometallic Chemistry: Principles to Applications

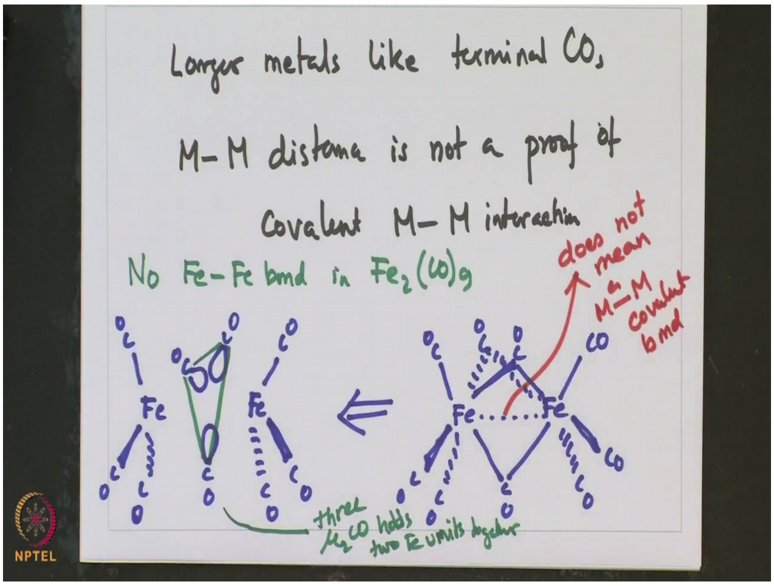
- Larger metals prefers unbridged form
- $Fe_2(CO)_9$ *vs* $Os_2(CO)_9$ and $Fe_3(CO)_{12}$ *vs* $Os_3(CO)_{12}$
- In case of larger metals the M–M bond length and the angle M–C–M of a CO bridge is difficult
- The presence of a M–M bond in poly nuclear carbonyls require more elaborate quantum-chemical studies

Page 295 of 302

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So, the taken message is the larger preferred larger size metals preferred on bridge form a terminal carbonyl.

(Refer Slide Time: 17:02)



Larger metals like terminal CO,

M–M distance is not a proof of covalent M–M interaction

does not mean M–M covalent bond

No Fe–Fe bond in $Fe_2(CO)_9$

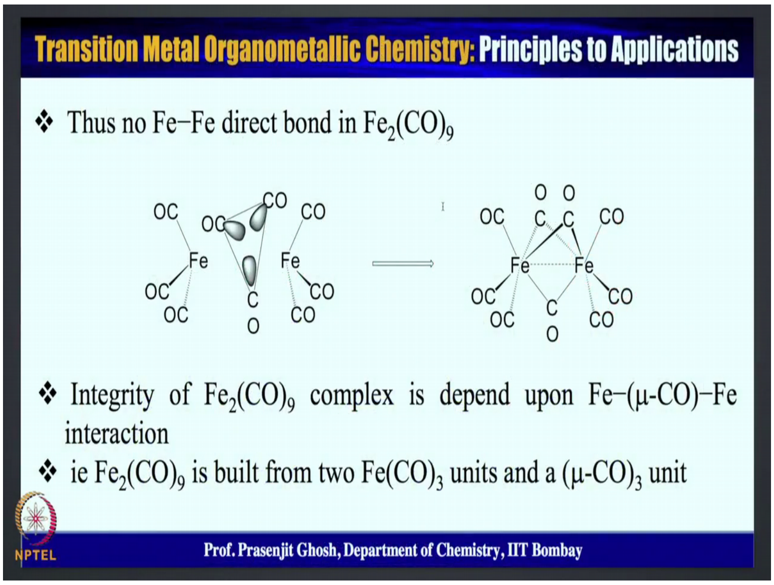
three μ_2 CO holds two Fe units together

Larger metals like terminal COs and in case of larger metals this Co difficult to form and sometimes the present presence of metal bond cannot be ascertained just by proximity; metal distance is not a proof of covalent metal interaction and that you is just maybe a constrained put in by bridging carbonyls and for example, there is no metal bond no Fe Fe bond in Fe 2 Co 9 and this is based described by this bridging carbonyl, holding this 2

Fe unit and this sort of can be perceived as 2 Fe Co units, held by 3 2 Fe units held by this 3 uh Co bridging ligands. So, these 3 mu 2 Co holds 2 Fe units together.

So, these the carbonyl distances the Fe 2 Co 9 dimmer is held by these 3 bridging carbonyl and here the metal distance M-M distance does not mean M-M covalent bond.

(Refer Slide Time: 20:57)



Transition Metal Organometallic Chemistry: Principles to Applications

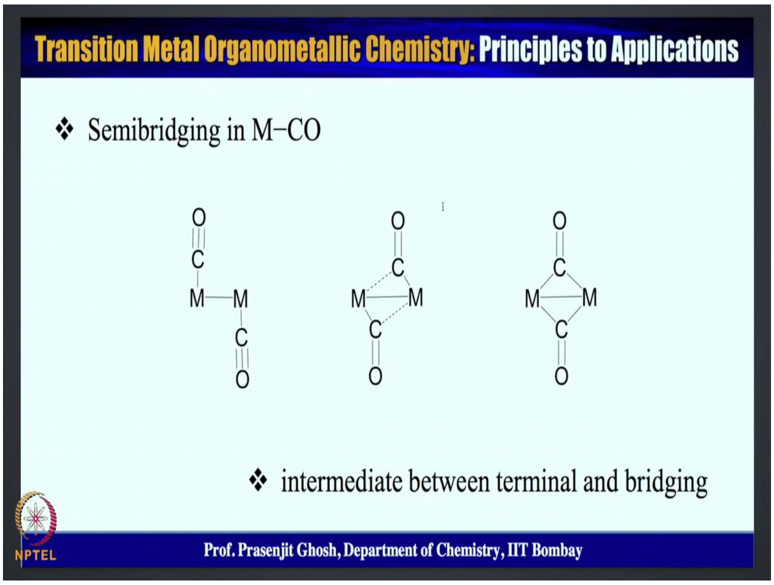
- Thus no Fe–Fe direct bond in $Fe_2(CO)_9$

- Integrity of $Fe_2(CO)_9$ complex is depend upon Fe–(μ-CO)–Fe interaction
- ie $Fe_2(CO)_9$ is built from two $Fe(CO)_3$ units and a $(\mu\text{-}CO)_3$ unit

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So this is an interesting observation because, in most of the cases bond can bond is ascertained by the distance or proximity of the distance, but here we find example in particularly in Fe 2 CO 9, where the distance is not a reflection of the presence of a bond, but just an artefact because of the presence of the 3 bridging carbonyl.

(Refer Slide Time: 21:19)



Transition Metal Organometallic Chemistry: Principles to Applications

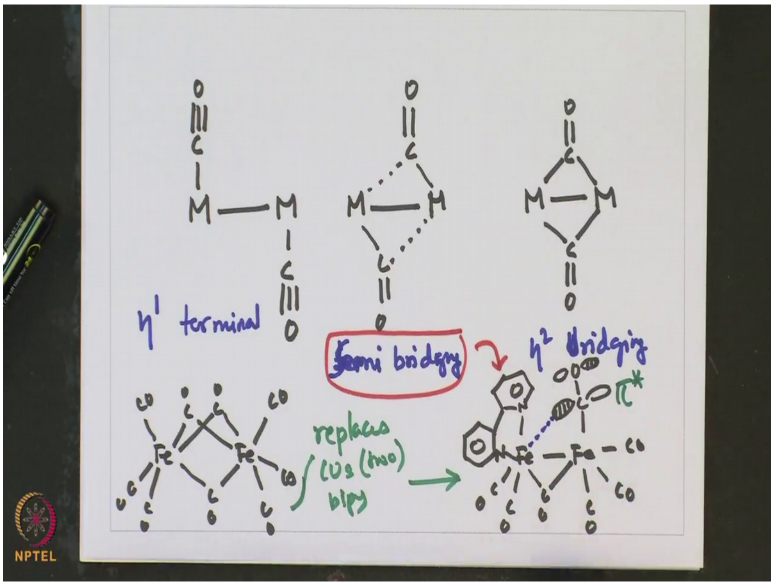
- ❖ Semibridging in M–CO

- ❖ intermediate between terminal and bridging

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, as far as the bridging is concerned the extent of the bridging can also vary. So, what we had seen in last example is that terminal carbonyl may remain in equilibrium with bridging.

(Refer Slide Time: 21:37)



So we have seen that terminal carbonyl remain in equilibrium with 2 bridging carbonyls as we had seen. So, we have seen that this is in dynamic equilibrium in the cobalt carbonyl compound and this is terminal called eta one terminal and this is eta 2 bridging.

Now, there is a structure which is intermediate between the 2 and that is called semi bridging and semi bridging structure means that, carbonyl is not halfway through bridging between the 2 metal centre, it is interacting more strongly with one centre as opposed to other centre this is semi bridging.

Now, these semi bridging systems are of interest and what is what 1 finds for Fe Co 9, if one replaces 2 of the carbonyls with bp let us say replaces COs 2 of them with bipyridine ligand and then the complex that result would have the following structure, where iron is now coordinated to bipyridine ligand.

So, there are instead of 9 carbonyls there are 7 carbonyls 1 2 3 4 5 6 7 and what it happens is under these conditions? this carbonyl becomes semi bridged because, this iron is seen to interact with the pi star orbital of this Co, leading to the formation leading to this semi bridging carbonyl in this bipyridine complex. So, what really happens is that bipyridine become because, of it is extremely good sigma donor ability makes iron more electron rich and these 2 iron centre become disproportionately unsymmetrical and some of the electron density of the iron is removed by interaction with the vacant pi star orbital of the Co, leading it 2 bridge under unsymmetrical way in a semi bridging fashion.

So, with these let me summarize the developments of today's lecture, what we have done is we have looked at the several kinds of bonding exhibited by metal carbonyl complexes and particularly with respect to terminal and bridging carbonyl, we have looked into situations which will sort of tend to facilitate metal clusters with terminal carbonyls and then the ones where there would be conditions were to see the bridging, the bridging terminal can bridge between 2 centres it is called doubly bridging.

We have also looked at examples, where the carbonyl is bridging between 3 centre that is called triply bridging and then lastly we have looked into some examples where carbonyl can be a semi bridging 2 metal centres, that is it is more strongly bond to one metal centre as opposed to other and that we saw in the latest example where of the 2 metal sites one is electron rich by putting strong sigma donor ligand like by pyridine as a result, the iron centre becomes more electron rich and then being more electron rich; if siphons of some of the electron density onto the pi star of the bridging carbonyl making the carbonyls unsymmetrical or semi bridging in binding.

So, with that I would like to oh conclude today's lecture that is on transition metal carbonyl complexes and where we have looked into various binding modes of the metal carbonyl kind of clusters that they form and with that we are going to conclude today's lecture and we are going to take up some more of transition metal carbonyl complexes there reactivity so on and so for.

In the next lecture I thank you for being with me in this lecture and looking forward to being with you in the next lecture, where we are going to study bit more details about transition metal carbonyl complexes and some of the other relevant complexes which we will take up in the subsequent lecture till then.

Thank you and goodbye.