Transition Metal Organometallic Chemistry : Principles to Applications
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Week – 10
Lecture – 46
Transition Metal Carbonyls: Reactivities

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing a very important class of compounds in the last few lectures and these are transition metal carbonyl complexes. And we in the last lecture we have looked into the reactivity of transition metal carbonyl complexes and as well as they are binding mode.

Now, with regard to the binding mode of transition metal carbonyl complexes what we have seen that the binding mode can vary as for being from being bridging to terminal and with regard to bridging it can bridge against 2 metal center or 3 metal centers; And depending on how it bridges to metal or how does it bind even in terminal fashion to metal. The new shear stretching frequency is a good marker about the extent of interaction that takes place between the transition metal and the carbon almighty.

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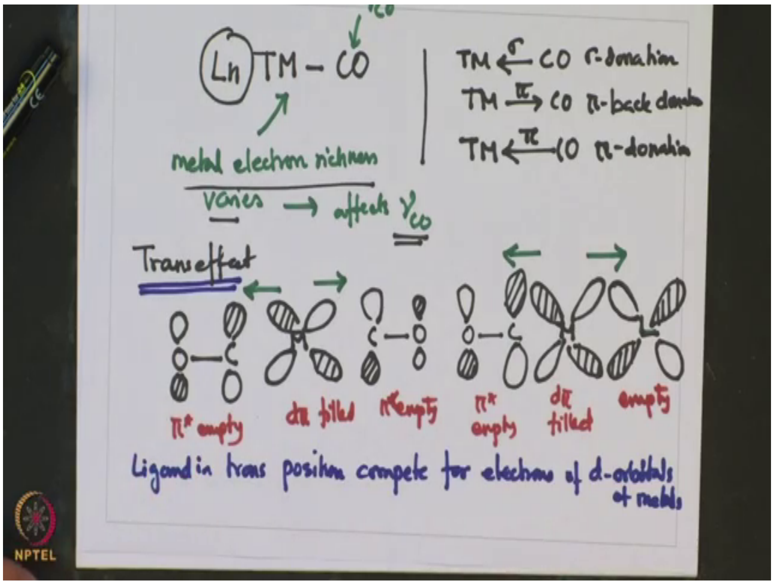

So, what we saw that there are two kinds of interaction: one is CO to transition metal sigma interaction; as well as transition metal to CO pi interaction, this is called sigma donation and this is called pi back donation. And we had also discussed particular mode which is not that observed, but this is CO to Transition Metal pi, pi donation which is often neglected, but is observed in sigma breathing kind of binding modes of transition metal carbonyl compounds.

Now, of these interactions what we saw that because of these interactions the electron density at transition metal varies; electron richness varies and which affects the mu CO bond. Now, this is the stretching frequency of CO.

Now, as the electron richness of the transition metal varies because of this kind of interaction which can either be donating electron to the transition metal or it can be taking away from the electrons from the transition metal because of various factors which can be charges which also can be because of the ligand fragments, which is associated with transition metal, how they would affect the transition metal electron den richness and as that electron richness is varies this new (Refer Time: 03:14) stretching frequencies also varies.

And we had taken a couple of examples in this regard, and now with that interplay of this forward sigma, forward pi as well as backward pi donation we are going to look at a very important part of the reactivity today which is the trans effect.

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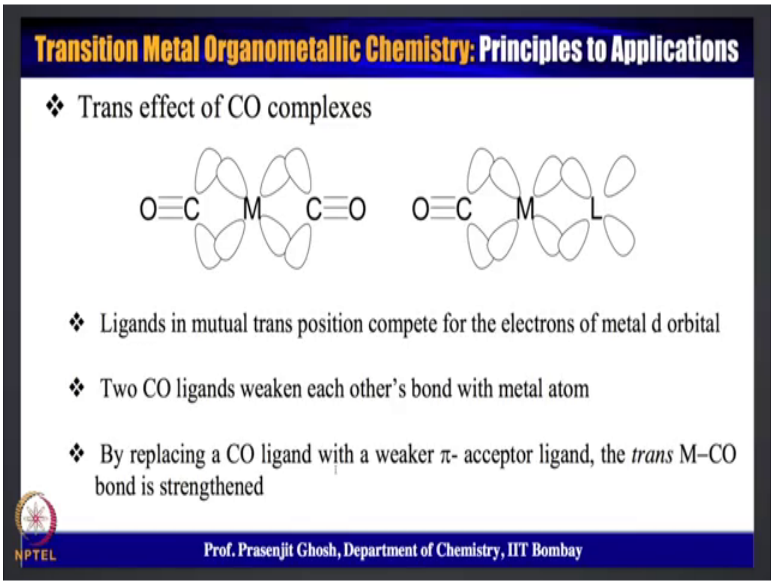

Transition Metal Organometallic Chemistry: Principles to Applications

- Trans effect of CO complexes

- Ligands in mutual trans position compete for the electrons of metal d orbital
- Two CO ligands weaken each other’s bond with metal atom
- By replacing a CO ligand with a weaker π- acceptor ligand, the *trans* M–CO bond is strengthened

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So, trans effect is the trans ligand particularly with respect to CO gets promptly substituted because of the strong binding of CO. Now, trans effect we are going to trying to understand a trans effect by thinking that metal d type orbital interacting with the pi star CO; the way it is drawn over here.

Now, usually this is a empty the pi star pi star orbital is empty, and this is d pi filled and the electron donation happens from metal to the ligand. Now, in the trans effect scenario there can we can imagine that there is another competing carbon monoxide ligand, which can also suck up for this electron density; which is also a pi star empty CO orbital can also compete with the central metal atom and suck up the electron density from the metal. So, there may be competition in the ligand occupying the transposition for this metal filled orbital which contains electrons.

So, ligands in transposition compete for electrons of the orbitals of metals. So, electrons the transmission compete for it. Now and that is sort of effects or sort of explains that trans effector that is where the trans effect arises from.

Now, one can imagine that this trans ligand instead of b being a CO it can be another ligand which can compete for the electron density of that metal bound trans to the carbonyl moiety and this is explained through this diagram CO.

So, in this case this is a d pi filled and this is the pi star empty and the electron donation happens in this direction. Now, imagine a ligand with a empty orbital of appropriate pi symmetry which is empty; and would also like to compete for this electron of the d orbital of the central metal atom.

As a result these because of the competition one ligand would try to we can the trans ligand in terms of bond strength. Because it would do so, by sucking away all the electron density onto itself as a result back donation would not happen at the trans ligand and thereby it becomes weakened. So, replacing carbon monoxide by ligand which is a weak pi acceptor these trans metal CO bond is strengthened.

So, if a CO is replaced by a weak pi acceptor then the CO itself will suck away most of the electron density from the metal to itself as a result the metal CO bond will be strengthened and the that would be reflecting in lowering of the CO stretching frequency.

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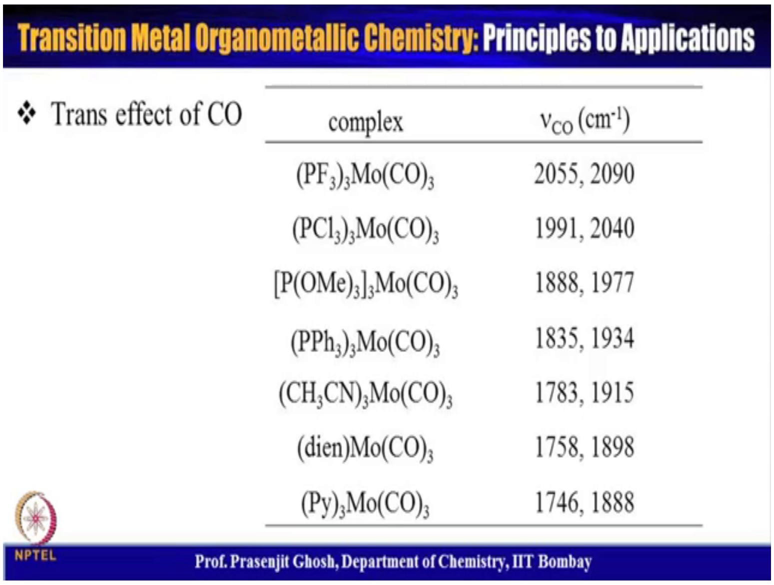

Transition Metal Organometallic Chemistry: Principles to Applications

- Trans effect of CO

complex	ν_{CO} (cm^{-1})
$(PF_3)_3Mo(CO)_3$	2055, 2090
$(PCl_3)_3Mo(CO)_3$	1991, 2040
$[P(OMe)_3]_3Mo(CO)_3$	1888, 1977
$(PPh_3)_3Mo(CO)_3$	1835, 1934
$(CH_3CN)_3Mo(CO)_3$	1783, 1915
$(dien)Mo(CO)_3$	1758, 1898
$(Py)_3Mo(CO)_3$	1746, 1888

NPTEL

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Now, this is very nice illustrated in this series of examples where we saw that replacing carbon monoxide by weak pi ligands lead to decreasing in the mu CO stretching frequency.

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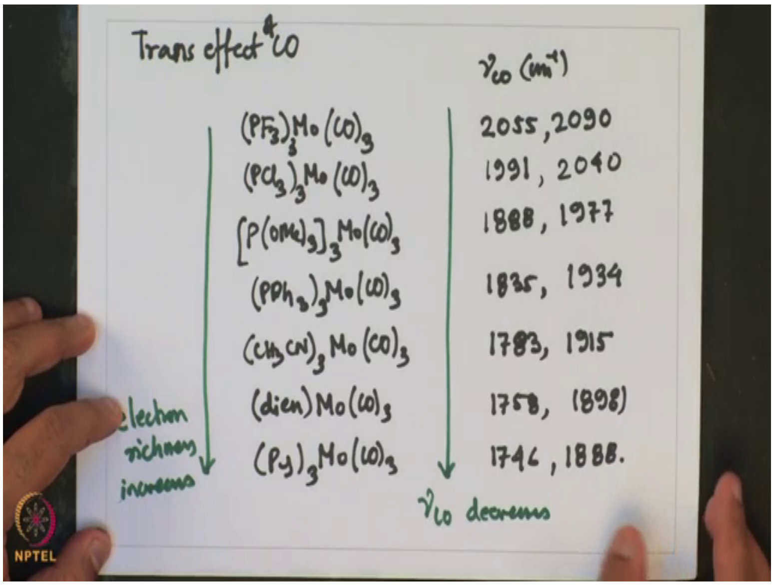

Trans effect of CO

	ν_{CO} (cm^{-1})
$(PF_3)_3Mo(CO)_3$	2055, 2090
$(PCl_3)_3Mo(CO)_3$	1991, 2040
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$(dien)Mo(CO)_3$	1758, (1898)
$(Py)_3Mo(CO)_3$	1746, 1888.

electron richness increases

ν_{CO} decreases

NPTEL

So, here, one example of some complexes, showing this trans effect of CO. For example, in P F 3 Mo CO 3 3 mu CO centimeter inverse is 2055, 2090; that means, that PF 3 fluorine being highly electro negative atom is sucking away some electron density from molybdenum on towards itself as a result CO cannot engage in too much of back bonding from molybdenum d orbital.

As a result the CO stretch in this complex is quite high. Now, if one goes from PF 3 to PCl 3. Now, fluorine has been replaced by less electro negative CL; that means, the molybdenum center would be more electron rich and hence the molybdenum would donate back donate more to carbon monoxide as a result CO stretch would decrease; and indeed it decreases significantly to 1991 and 2040. Now, this 1991 is the CO which are trans and these are the 2 modes depending on the combinations of the COs. Now, if one goes from PCl 3 to PO Me 3 whole 3 Mo CO 3 which is more electron rich and sort of it goes to 1888, 1977.

Some more examples, like PPh 3 Mo CO 3 1835, 1934 CH 3 CN the nitrogen is coordinated of acid nitrile mighty on to molybdenum CO 3 even further 1783, 1915 dien molybdenum CO 3 1758, 1898 to Py 3 pyridine molybdenum CO 3 1746 to 1888. So, what we see that ongoing down as the electron density of molybdenum increases richness increases that leads to enhanced molybdenum to CO pi back donation; as a result CO stretching frequency decreases.

So, these gives us quantitative or semi quantitative fill for the extent of electro pi back donation that may arise by substitution of pi acidic ligand CO by more electron donating ligands and that will be reflected in the new shear stretching frequency; as is shown over here.

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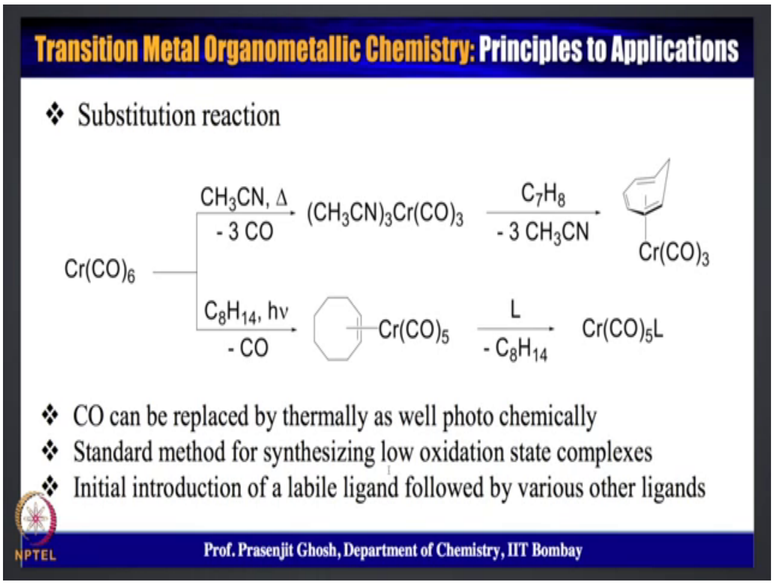

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Substitution reaction

- ❖ CO can be replaced by thermally as well photo chemically
- ❖ Standard method for synthesizing low oxidation state complexes
- ❖ Initial introduction of a labile ligand followed by various other ligands

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Now, let us move to the reactivity of transition metal carbonyl complexes and the primarily these are mainly of substitution reaction well CO undergoes substitution reaction.

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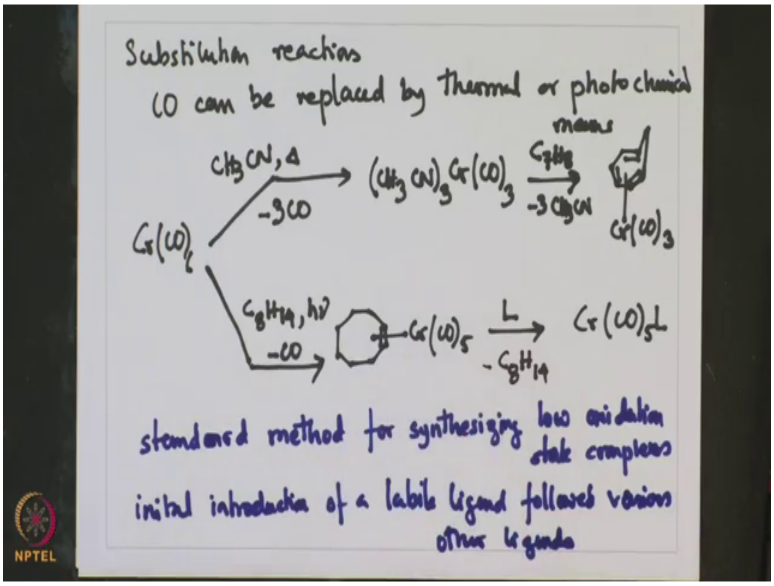

Substitution reactions

CO can be replaced by thermal or photochemical means

standard method for synthesizing low oxidation state complexes

initial introduction of a labile ligand followed various other ligands

Now, COs can be replaced by thermally or photo chemically; replaced by thermal or photochemical method means for example, Cr CO 6. When heated in acetonitrile, eliminates 3 molecules of CO to gives CH 3 CN whole 3 Cr CO 3; and when that is treated with another olefin cyclic olefin C 7 H 8 it eliminates 3 molecules of CH 3 CN to give Cr CO 3.

Now, the way the substitution happened is that CO is first replaced by a liable ligand followed by the addition of the second ligand. Now, this is a standard method for synthesizing low oxygen state carbonyl complexes. Now, this was done thermally, the same strategy can be used photo chemically. For example, reaction of this with C 8 H 14 in h mu eliminates CO to give this here CO 5 and then it this labile ligand is replaced by the ligand for which the substitution reaction is being tried to give Cr CO 5 l.

So, this method of photo chemically as well as thermally substituting CO, but initially by replacing it by a labile ligand followed by other ligand this is a standard method, standard method for synthesizing low oxygen state complexes and this is done by initial introduction of a labile ligand; followed by various other ligands.

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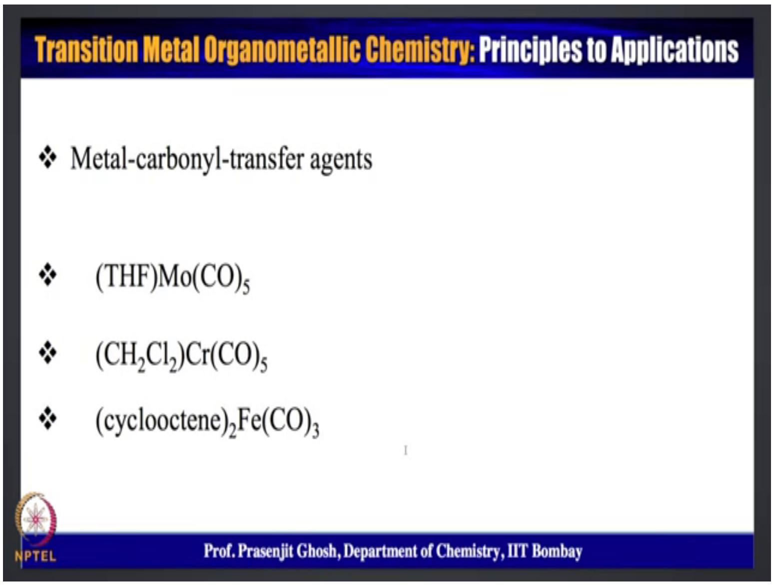

Transition Metal Organometallic Chemistry: Principles to Applications

- Metal-carbonyl-transfer agents

- $(THF)Mo(CO)_5$
- $(CH_2Cl_2)Cr(CO)_5$
- $(cyclooctene)_2Fe(CO)_3$

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Now, these complexes where COs have been partially replaced by a labile ligand these are called carbonyl Metal carbonyl transfer agents. Because they can be used for synthesizing low oxidation state carbonyl hetero elliptic complexes. So, these are called Metal carbonyl transfer agents.

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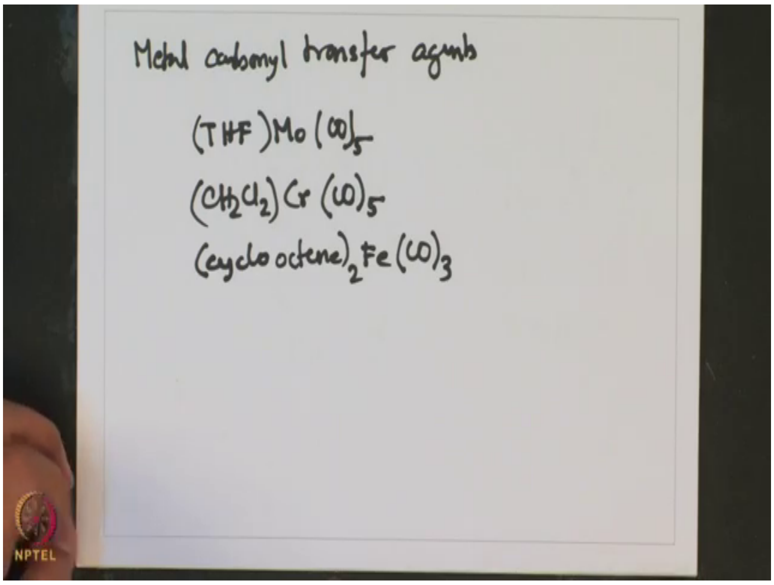

Metal carbonyl transfer agents

$(THF)Mo(CO)_5$

$(CH_2Cl_2)Cr(CO)_5$

$(cyclooctene)_2Fe(CO)_3$

The examples include THF molybdenum penta carbonyl CH 2 Cl 2 chromium penta carbonyl and cyclooctene whole 2 Fe tri carbonyl. So, these are designated as methyl transfer agent. Usually, these carbonyl substitution reaction occur at 18 electron valence complexes and follows dissociative pathway.

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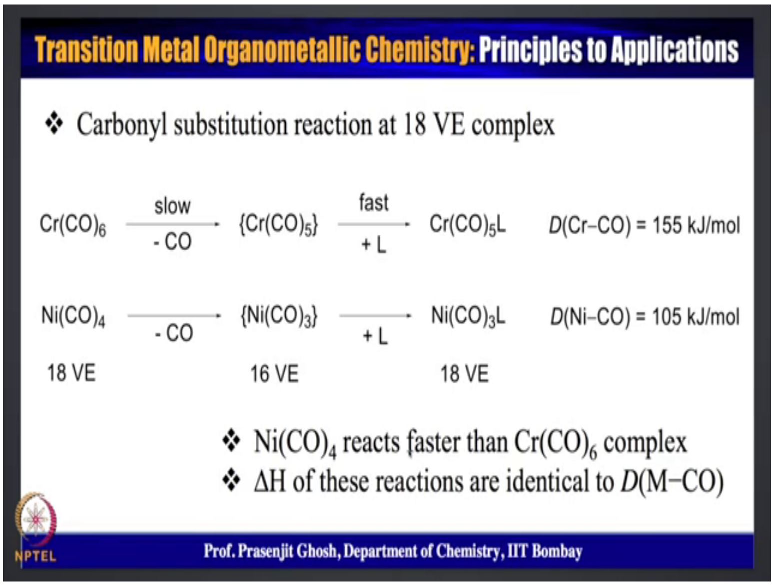

Transition Metal Organometallic Chemistry: Principles to Applications

- Carbonyl substitution reaction at 18 VE complex

$$Cr(CO)_6 \xrightarrow[-\,CO]{slow} \{Cr(CO)_5\} \xrightarrow[+\,L]{fast} Cr(CO)_5L \qquad D(Cr\text{–}CO) = 155\ kJ/mol$$

$$Ni(CO)_4 \xrightarrow[-\,CO]{} \{Ni(CO)_3\} \xrightarrow[+\,L]{} Ni(CO)_3L \qquad D(Ni\text{–}CO) = 105\ kJ/mol$$

18 VE 16 VE 18 VE

- $Ni(CO)_4$ reacts faster than $Cr(CO)_6$ complex
- ΔH of these reactions are identical to $D(M\text{–}CO)$

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This is illustrated by the following examples shown below

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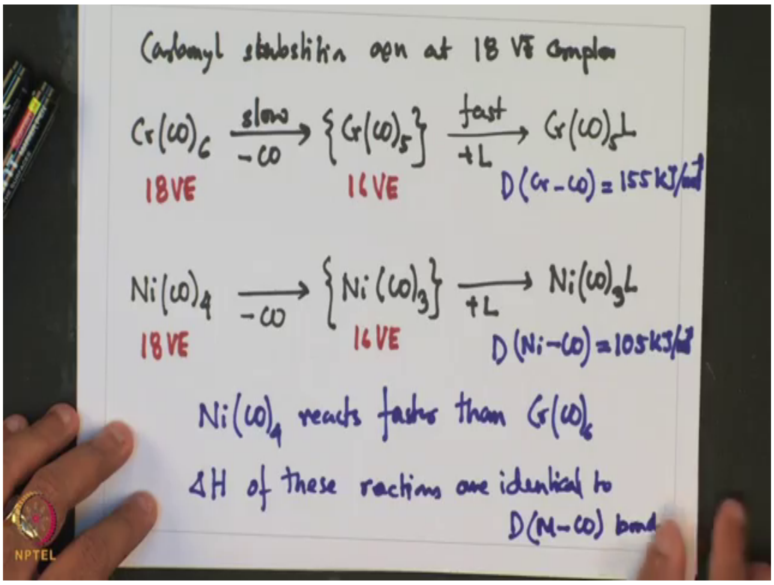

Carbonyl substitution rxn at 18 VE Complex

$Cr(CO)_6 \xrightarrow[-CO]{slow} \{Cr(CO)_5\} \xrightarrow[+L]{fast} Cr(CO)_5L$

18VE 16VE

$D(Cr-CO) = 155\ kJ/mol$

$Ni(CO)_4 \xrightarrow[-CO]{} \{Ni(CO)_3\} \xrightarrow[+L]{} Ni(CO)_3L$

18VE 16VE

$D(Ni-CO) = 105\ kJ/mol$

$Ni(CO)_4$ reacts faster than $Cr(CO)_6$

ΔH of these reactions are identical to $D(M-CO)$ bond

Carbonyl substitution reaction at 18 VE complex Cr CO 6 slow because this is already 18 VE complex and what it means that this is quite stable. So, no wonder it is slow to dissociate a carbon monoxide to give chromium penta carbonyl which is a 16 valence electron complex and this is very fast in reacting with the ligand of choice to give Cr CO 5 l.

Now, this reaction is governed by dissociation energy of chromium carbonyl and d Cr CO bond of chromium carbonyl bond is about 155 Kilo Joules per mole. Where else if 1 were 2 look at the same reaction for nickel tetra carbonyl Ni CO four which also is the 18 valence electron complex; it eliminates CO to give nickel tri carbonyl which is 16 valence electron complex and that reacts with l to give nickel tri carbonyl l.

Now, with regard to nickel carbonyl bond dissociation energy nickel carbonyl bond is much weaker than the above mentioned chromium carbonyl bond and this bond energy is about 105 Kilo Joule per mole. And the reason that nickel reacts faster is because this has much weaker this nickel carbonyl bond and as a result that nickel CO 4 reacts faster than Cr CO 6, because the bond dissociation then energy of nickel carbonyl is much weaker than that of chromium carbonyl.

Now, one thing which is evident by comparing the reactivity for these two pairs of reaction is the fact that delta H enthalpy change of these reactions are identical to or depends on the bond energy of the M CO bond. So, as we saw that nickel carbonyl bond was much weaker than the chromium carbonyl hence the reactivity of nickel tetra carbonyl was much higher or nickel tetra carbonyl substitution occurred much faster than that of the chromium tetra carbonyl.

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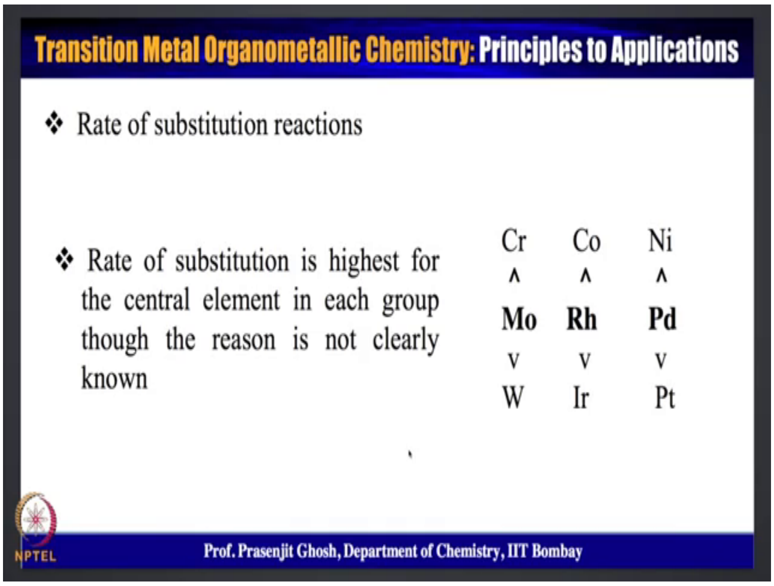

Transition Metal Organometallic Chemistry: Principles to Applications

- Rate of substitution reactions

- Rate of substitution is highest for the central element in each group though the reason is not clearly known

Cr Co Ni
∧ ∧ ∧
Mo Rh Pd
v v v
W Ir Pt

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This rate of substitution which was found that is highest for the central element was highest for the second row element transition metal, though the reason is not clearly understood.

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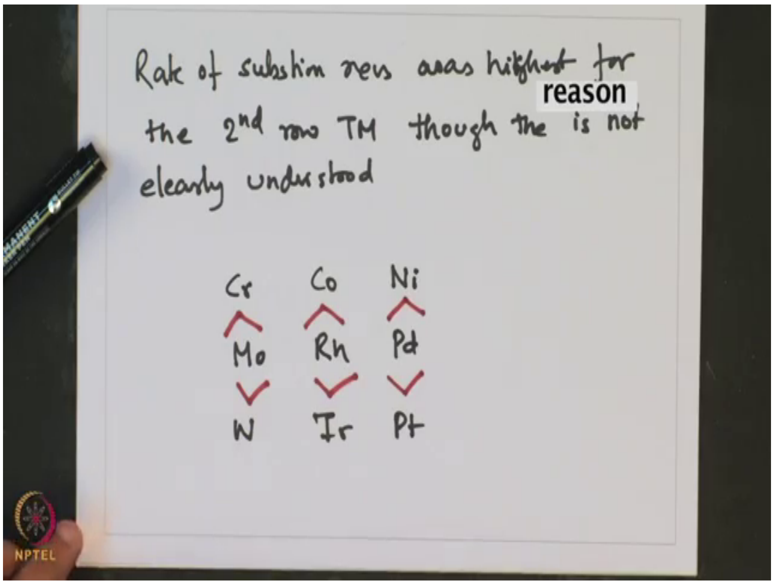

Rate of substn rens was highest for the 2^{nd} row TM though the reason is not clearly understood

Cr Co Ni
∧ ∧ ∧
Mo Rh Pd
v v v
W Ir Pt

For example, for chromium molybdenum tungsten molybdenum showed higher reactivity then chromium and tungsten, for cobalt rhodium iridium rhodium should higher the activity for cobalt and iridium and for palladium nickel and platinum palladium should higher reactivity over nickel.

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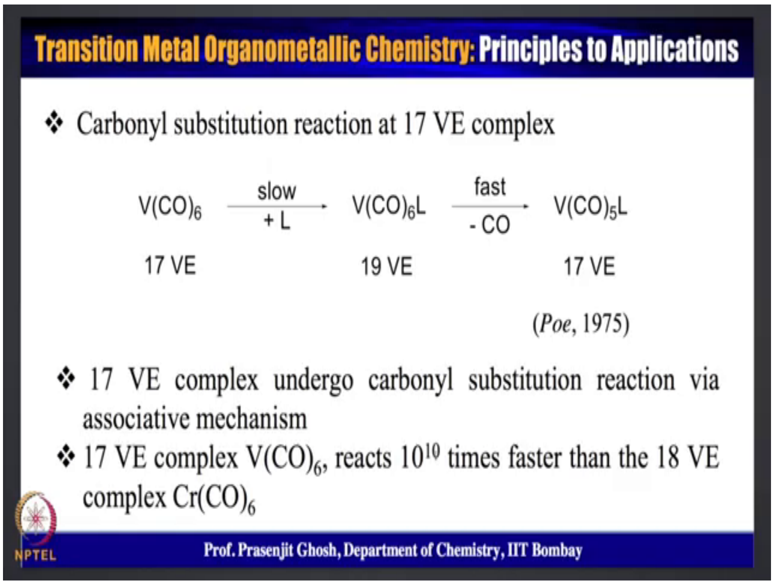

Transition Metal Organometallic Chemistry: Principles to Applications

- Carbonyl substitution reaction at 17 VE complex

$$\underset{17\ \mathrm{VE}}{V(CO)_6} \xrightarrow[+\,L]{\text{slow}} \underset{19\ \mathrm{VE}}{V(CO)_6L} \xrightarrow[-\,CO]{\text{fast}} \underset{17\ \mathrm{VE}}{V(CO)_5L}$$

(*Poe*, 1975)

- 17 VE complex undergo carbonyl substitution reaction via associative mechanism
- 17 VE complex $V(CO)_6$, reacts 10^{10} times faster than the 18 VE complex $Cr(CO)_6$

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So, this substitution reaction also for 17 electron species is slightly different because for the 18 electron species what we have seen that it underwent substitution in a dissociative fashion whereas, the 17 electron species the substitution reaction is formed by associative react mechanism.

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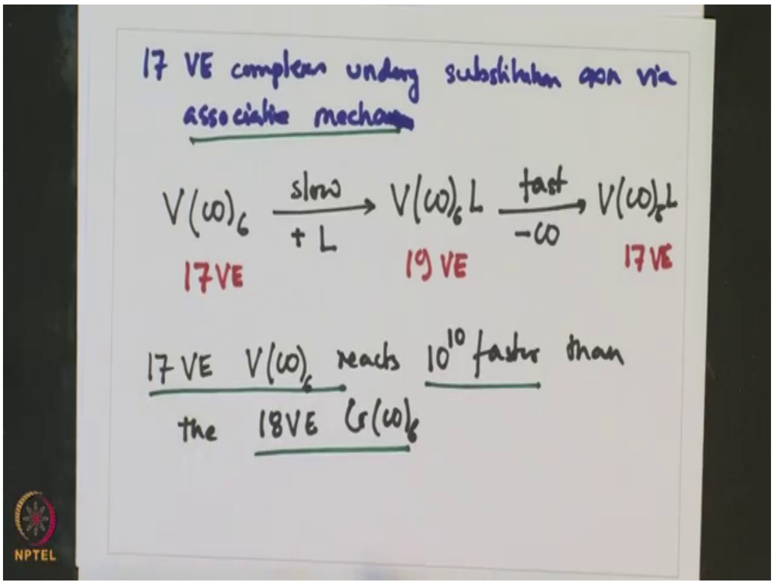

17 VE complexes undergo substitution rxn via associative mechanism

$$\underset{17\,VE}{V(CO)_6} \xrightarrow[+L]{slow} \underset{19\,VE}{V(CO)_6L} \xrightarrow[-CO]{fast} \underset{17\,VE}{V(CO)_5L}$$

17 VE $V(CO)_6$ reacts 10^{10} faster than the 18VE $Cr(CO)_6$

So, 17 VE complex undergo substitution reaction via associative mechanism. And this is shown by the example given. So, V CO 6 this is the 17 valence electron species it is slow to add this electron which is V CO 6 l.

Now, it has become a 19 valence electron species which is highly unstable as a result it rapidly eliminates carbon monoxide to give V CO 5 l which again is a 17 valence electron species.

Now, it is interesting to note that, 17 VE valence electron vanadium carbonyl species reacts 10 to the power 10 times faster than the 18 VE Cr CO 6 which is 18 valence electron species.

So, this is an interesting observation which shows that unlike the 18 VE species which undergoes dissociative mechanism 17 VE species undergoes associative mechanism and that 17 VE species reacts 10 to the power 10 times faster than the 18 valence electron species.

So, with that I would like to conclude today's lecture. And would like to summarize the points that we have develop today particularly with respect to the reactivity of transition metal carbonyl complexes. And to begin with we have started looking at several transition metal carbonyl complexes and we had seen how the variation of the electron density at the metal affected the new shear stretching frequencies. And this we have looked at particularly with respect to the trans effect where the ligand trans to the carbonyl ligand competes with the electron density of the central metal atom and because of its weak pi accepting nature leads to strong metal carbon carbonyl bond and thereby weakening the metal trans other ligand bond and which can readily be substituted.

Now, the effect of the trans effect was observed in substitution reactions where 18 valence electron complexes under photochemical conditions or like thermal conditions eliminated carbon monoxides and then were replaced in turn by labile ligands which then were substituted by other ligands.

So, these in this set a series of heterolytic labile ligand metal carbonyl complexes were designed. And these are known as turbulent transfer agents. We have also looked at the mechanism of substitution that occur for metal carbonyl complexes. And what we had seen that there is a distinct mechanistic pathway that is observed for the 18 electron species as well as that of the 17 electron species.

It was noted that 18 electron species undergo dissociative pathway, whereas 17 electron species undergo associative pathway. And lastly it was shown that for vanadium hexa carbonyl complexes the 17 electron species was found to undergo the substitution reaction at a tremendously rapid pace of about 10 to power 10 times faster than the corresponding 18 electron chromium hexa carbonyl complex.

So with these, I will have to conclude this lecture on the reactivity of transition metal carbonyl complexes for today and we are going to discuss and take up some more of the reactions of transition metal carbonyl complexes in the next lecture. Until that, I thank you for being with me in this lecture and look forward to being with you in the next lecture where you are going to look up the reactivity of transition metal carbonyl complexes in bit more details, till then goodbye.

Thank you.