Advanced Transition Metal Organometallic Chemistry
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Lecture – 16
Transition Metal Cyclopentadienyl Carbonyl Complexes: Reactivity

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. Today we are going to be discussing transition metal cyclopentadienyl carbonyl complexes and their reactivity. So, these transition metal cyclopentadienyl carbonyl complexes are more popularlycalled as half sandwich complexes, the name derives from their metallocene counterpart, which contains cyclopentadienyl metal complexes and referred to as sandwich complexe,s whereas these compounds, transition metal cyclopentane carbonyl complexes are referred to as half sandwich complexes.

So, in our last class, we have looked into various methodsavailable for preparation of these half sandwich transition metal cyclo pentadienyl carbonyl complexesand also we have looked into their reactivity. Primarily of the synthetic routes that are available for preparation of these complexes involved, direct reactions of metal carbonyl withcyclo pentadiene ligands or the reactions involved metal carbonylmethylates with cyclopentadienyl reagentsin presence of oxidizing agents.

Also involves the reaction of cyclopentadienyl transition metal complexeswith the carbonyl compounds in presence of reducing agents or direct reactions of metallocenes with carbonylcompounds or but just simplyheating metallocenes with carbonyl compounds would yield these half-sandwich transition metal carbonyl complexes. We have also looked into the reactivity of these compounds.

And what we found that the reactivity of these compounds dependson the nature of the carbonyl moiety, the carbonyl moiety can act as a bridging ligand or also act as a terminal again and it turns out that for di-nuclear complexes of 3d metals which are smaller in sizeboth the bridging and terminal carbonyls are observed, whereas for trans, trans, such complexes of 4d and 5d which are morebigger in size only terminal carbonyls complexes are same.

So, with that, today continuing further on this discussion, we are going to be talking aboutthe reactivity of transition metal cyclopentadienyl carbonyl complexes.

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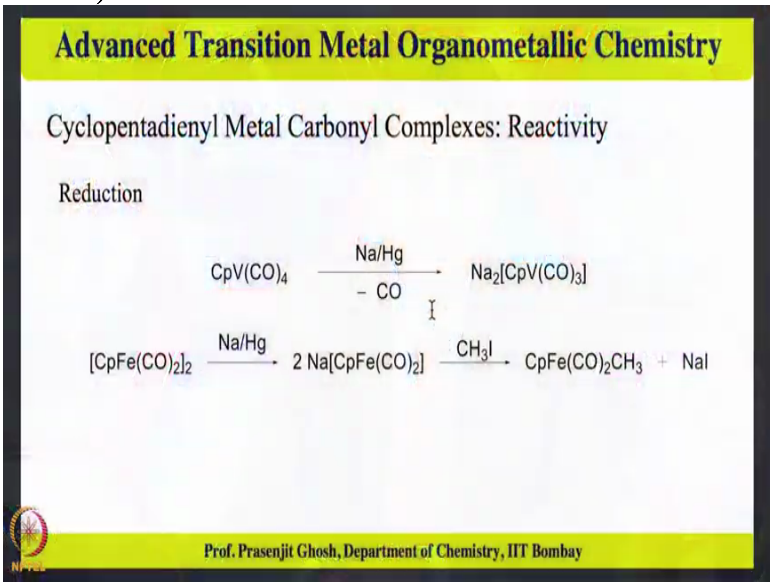

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Cyclopentadienyl Metal Carbonyl Complexes: Reactivity

Reduction

$$CpV(CO)_4 \xrightarrow[-\ CO]{Na/Hg} Na_2[CpV(CO)_3]$$

$$[CpFe(CO)_2]_2 \xrightarrow{Na/Hg} 2\ Na[CpFe(CO)_2] \xrightarrow{CH_3I} CpFe(CO)_2CH_3 + NaI$$

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So one ofthe,main thing is the reduction of such complexes.

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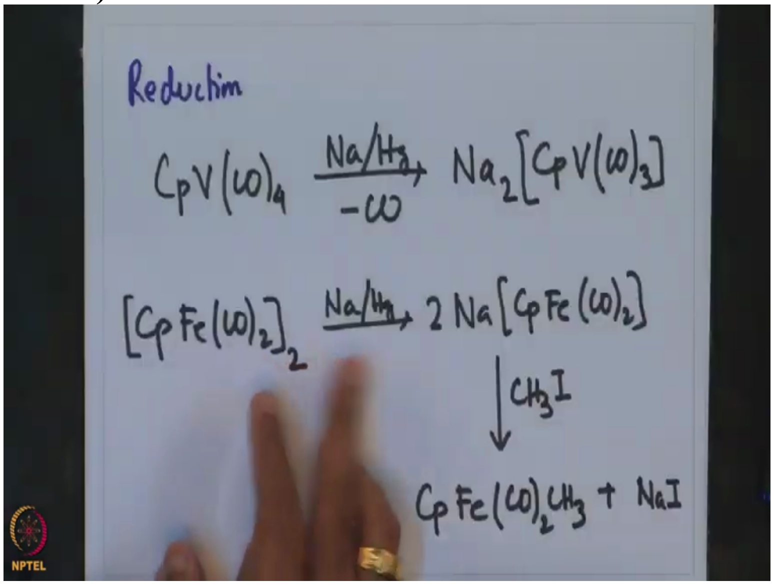

Reduction

$$CpV(CO)_4 \xrightarrow[-CO]{Na/Hg} Na_2[CpV(CO)_3]$$

$$[CpFe(CO)_2]_2 \xrightarrow{Na/Hg} 2\ Na[CpFe(CO)_2]$$

$$\downarrow CH_3I$$

$$CpFe(CO)_2CH_3 + NaI$$

Example is CP vanadium tetra carbonyl in presence of sodium mercury eliminates CO to give disodium CP V CO3, furthermore the reaction of CP, Fe dicarbonyl dimer, againthe reduction with sodium mercury gives the metallate sodium CP Fe CO2, now that upon reaction with methyl iodide, gives the methyl derivative CP Fe CO2 CH3 along with the formation of sodium iodide. Sothis is an interesting reaction, in which the dimer is, CP iron dicarbonyl dimer, is reduced to give this metallate,which then furthermore is alkylated to give to make the methyl derivative which is cyclopentadienyl iron dicarbonyl methyl, along with the formation of sodium iodide. So certainly a reduction is an important reaction for cyclopentadienyl metal tri carbonyl complexes.

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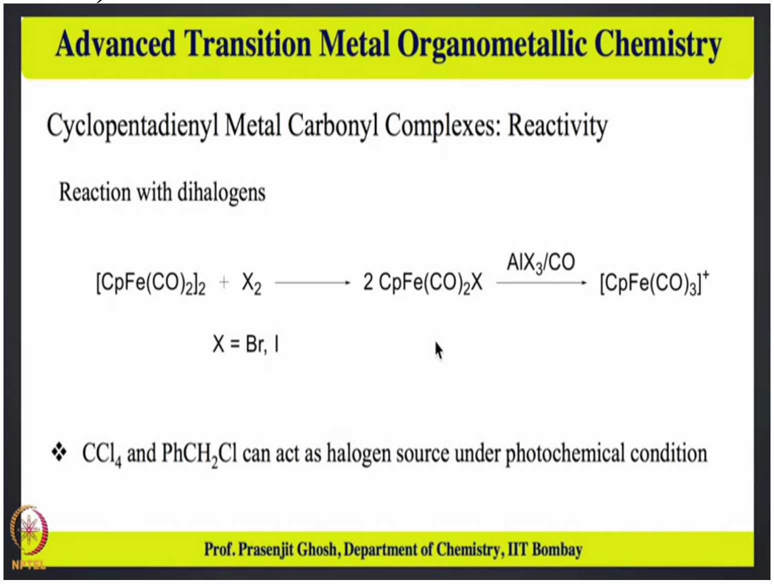

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Cyclopentadienyl Metal Carbonyl Complexes: Reactivity

Reaction with dihalogens

$$[CpFe(CO)_2]_2 + X_2 \longrightarrow 2\ CpFe(CO)_2X \xrightarrow{AlX_3/CO} [CpFe(CO)_3]^+$$

X = Br, I

❖ CCl_4 and $PhCH_2Cl$ can act as halogen source under photochemical condition

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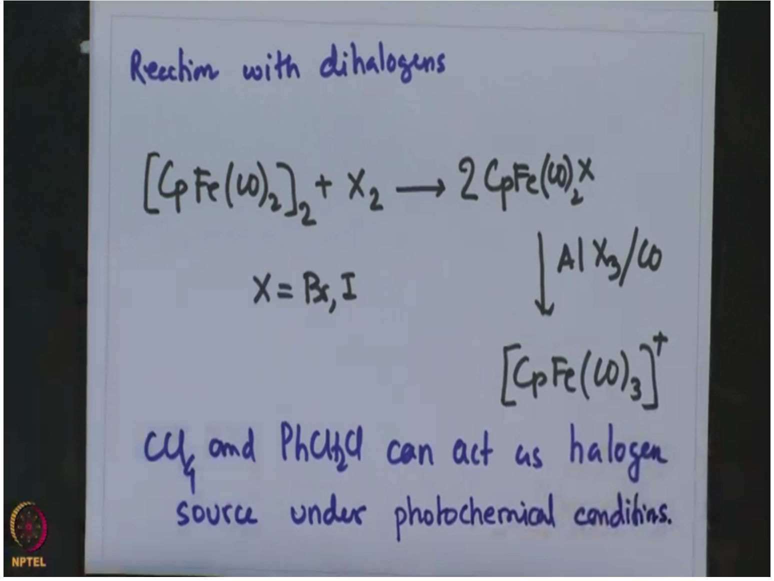

Reaction with dihalogens

$$[CpFe(CO)_2]_2 + X_2 \longrightarrow 2\ CpFe(CO)_2X \xrightarrow{Al\,X_3/CO} [CpFe(CO)_3]^+$$

X = Br, I

CCl_4 and $PhCH_2Cl$ can act as halogen source under photochemical conditions.

Similarly the reactionwithdihalogens makes the iodide complexes gives the halide derivative. This is illustrated by the reaction over here. CP Fe dicarbonyl dimer + X2, X equals bromine iodine giving 2 CP Fe CO2 X, that reacting with Al X3 CO gives CP Fe CO3 X. Now what we see over hereis the formation of the halide and subsequent abstraction of thehalide to give this CP Fe tricarbonyl cation and the vacant site so generated by the abstraction of the halide is occupied by the carbonyl. So many of these times even CCL 4 and benzyl chloride and PH CH 2 CL can act as halogen source under photochemicalconditions.

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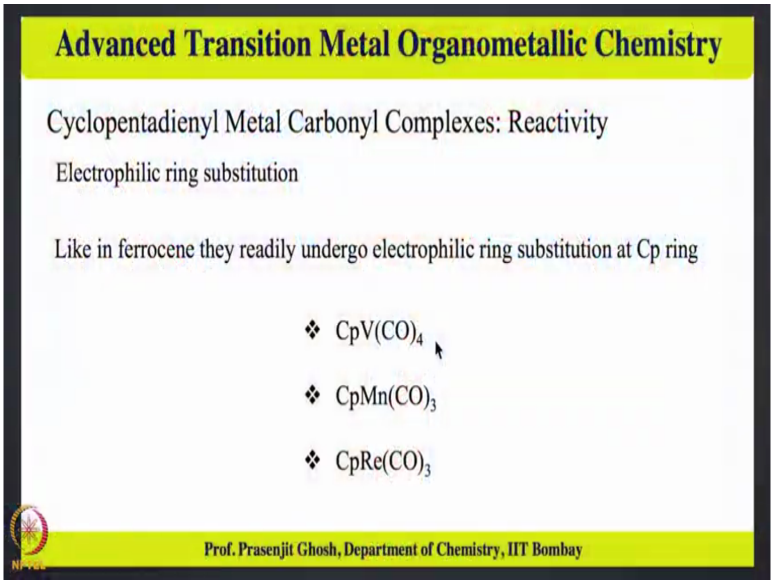

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Cyclopentadienyl Metal Carbonyl Complexes: Reactivity

Electrophilic ring substitution

Like in ferrocene they readily undergo electrophilic ring substitution at Cp ring

- $CpV(CO)_4$
- $CpMn(CO)_3$
- $CpRe(CO)_3$

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The other obvious reaction for this half-sandwich cyclopentadienyl metal tricarbonyl complexes are the electrophilic ring substitutions.

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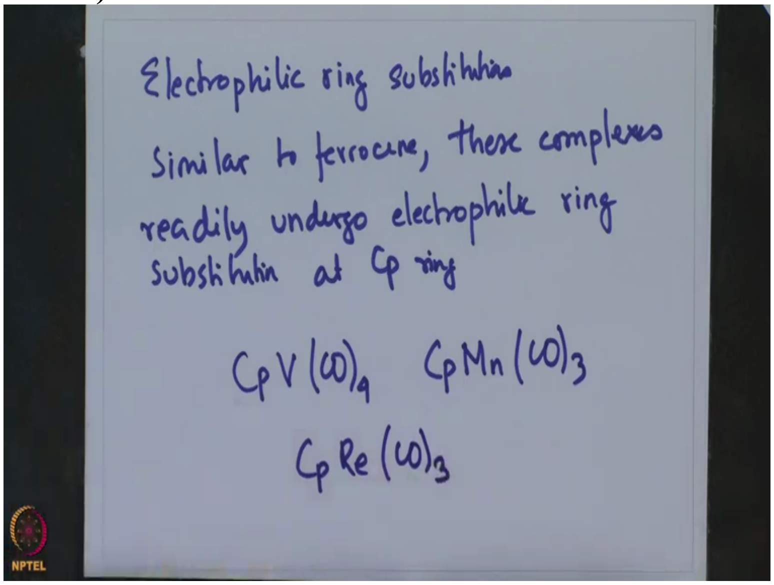

Electrophilic ring substitution

Similar to ferrocene, these complexes readily undergo electrophilic ring substitution at Cp ring

$CpV(CO)_4$ $CpMn(CO)_3$

$CpRe(CO)_3$

So, like in ferrocene, similar to ferrocene, these complexes readily undergo electrophilic linked substitution at CP ring and the examples of this are CP V CO 4, CP Mn CO3, CP Re CO3. So, this is something which parallels the reactivity seen in ferrocenyl complexes where two electrophilic substitution was facile at the cyclopentadienyl ring and even in half-sandwich, cyclo pentadienyl metal carbonyl complexes we see the same trend happening that the electrophilic substitution at the cyclopentane ring is also facile.

Now obviously the reason behind the same is also similar given the fact that cyclopentadienyl anion is electron rich carbon ionic and has partial negative charge. Hence it is no wonder that this ligand undergo electrophilic substitution reactions similar to that observed for ferrocene or other metalocene complexes. Now having said that one should also think that whatever restrictions which held good for electrophilic substitution for ferrocene should also be holding good over here.

And that is that the electrophile cannot be acting as an oxidizing agent or somehow oxidize the metal center of the sub sandwich complexes obviously, in that case the literal agreeing substitution might not occur.

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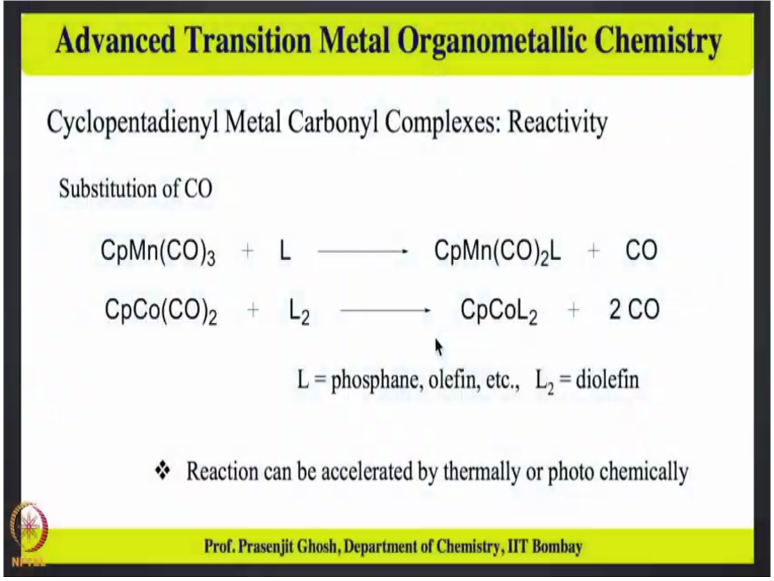

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Cyclopentadienyl Metal Carbonyl Complexes: Reactivity

Substitution of CO

$$CpMn(CO)_3 + L \longrightarrow CpMn(CO)_2L + CO$$

$$CpCo(CO)_2 + L_2 \longrightarrow CpCoL_2 + 2\,CO$$

L = phosphane, olefin, etc., L_2 = diolefin

- Reaction can be accelerated by thermally or photo chemically

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Soas far as the substitutions are concerned actually there are two kinds of substitution that might happen in such kind of complexes which are CP M Con;

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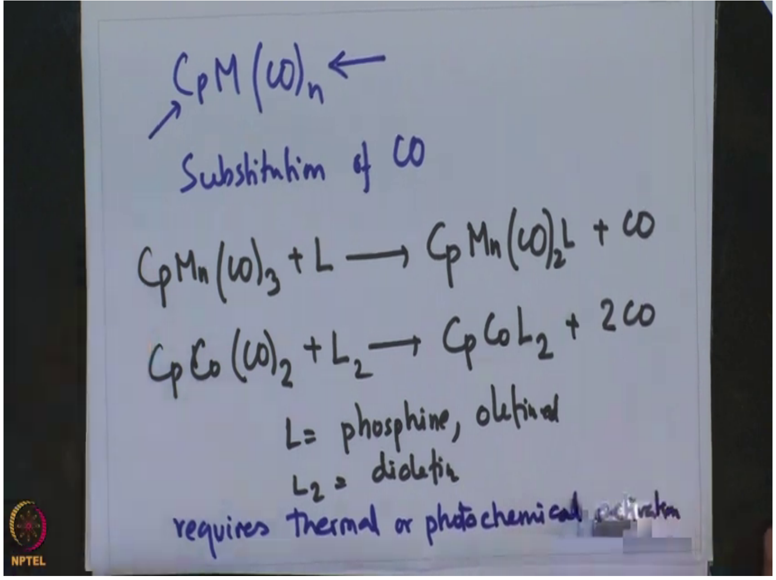

$CpM(CO)_n$

Substitution of CO

$$CpMn(CO)_3 + L \longrightarrow CpMn(CO)_2L + CO$$

$$CpCo(CO)_2 + L_2 \longrightarrow CpCoL_2 + 2CO$$

L= phosphine, olefin

L_2 = diolefin

requires thermal or photochemical activation

The substitution can happen at the CP ring which was we are just talking about electrophilic linked substitution, the other possibility is substitution occurring at the CO and we are going to see how that effects. So, substitution, this is illustrated by this example of manganese which is CP MN CO3 reacting with L giving CP MN CO to L + CO similarly CP cobalt CO2 reacting with L giving CP CO L2 + 2 CO, L can be phosphine, polythene. L2 can be diolefin, okay and this reaction generally is exploited by thermally orphotochemically so requires thermal or photochemical activation.

So, we see that this CP manganese is carbonyl complex is being heterolytic in nature substitution not only at the CP ring can be invoked but also substitution of the carbon ligands can also be done, and this is by replacing the carbonyl with other dative ligands like phosphenes, olefins or diolefins, and the process would require temperatureor photochemical activation. Now,we had spoken about oxidative dimerizationin our previous class that spoke about how compound was dimerizedas a result of oxidation by using an oxidizing agent.

Here today we are going to look at another such reactions or related reactions which are which is oxidative decarbonisation.

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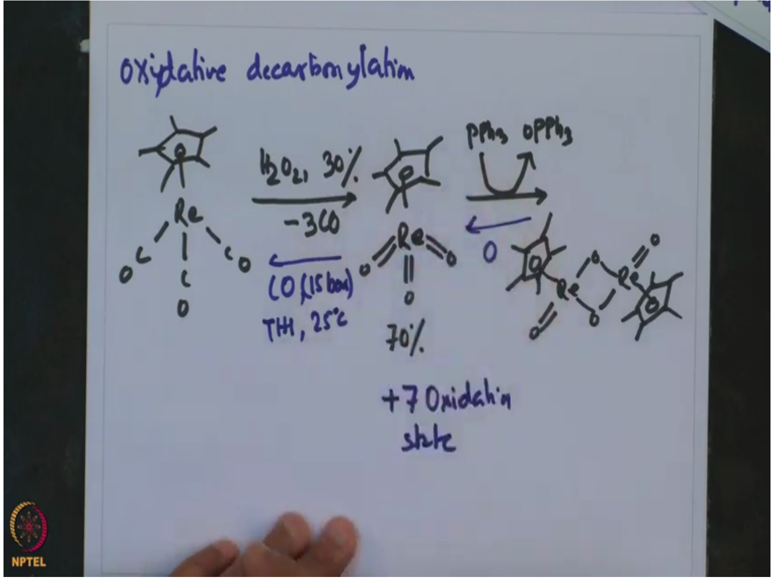

So, the reaction involves, the reaction of CP star rhenium tri carbonyl, reacting with hydrogen peroxide 3% leading to elimination of 3 carbonyls to give CP star rhenium, tri oxo compound in 70% yield which in presence of phosphine gives corresponding phosphine oxidesto give this dimer. To give this dimer the opposing reactions if we takethe dimer, and react thatwith oxygen, give this rhenium CP star tri-oxo compound, whichin presence of high CO pressure in THF at 25 degree centigrade would give back this rhenium tri carbonyl compound.

So,this is an interesting compound in which the rhenium is in +7 oxidation state and it alsoprovesthe fact thatthese cyclopentadienyl rheniumcomplexes also occur for higher oxidation states of the transition metal. Usually the CP complexes by and large that one encounters occur for low oxidation stateof the transition metal, but here we have, this rhenium compound tri carbonyl CP star rhenium when oxidized with hydrogen peroxide produces a sinister complex of rhenium containing three trioxo species, in which the metal center is in +7 oxidation state and that iskind of interesting.

Subsequent reaction of this trioxo CP star compound with triphenylphosphine would give this, rhenium oxo, bleaching oxo, as well as terminal oxo, rhenium CP star, dinickel compound shown over here. So with this we sort ofcovered the topic ofCP star transition metal carbonyl complexes and will move onto look at another interesting topic which are CP startransition metal nitrosyl complexes.

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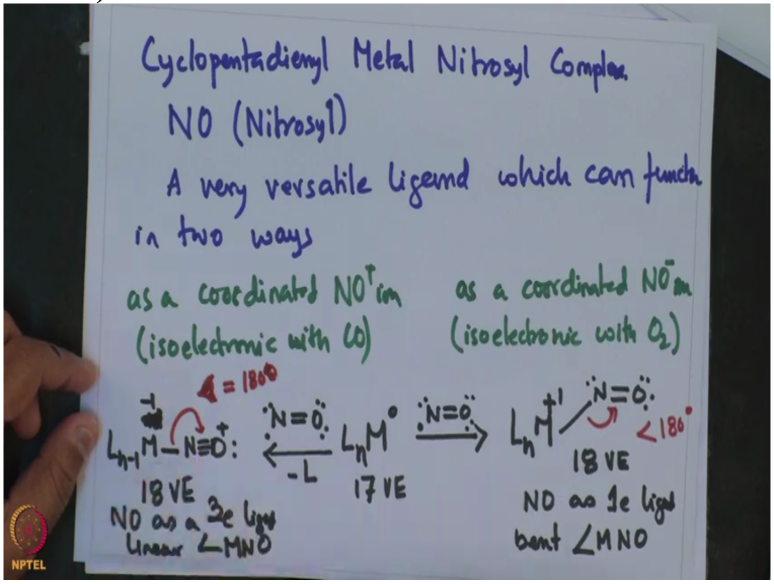

Cyclopentadienyl Metal Nitrosyl Complex

NO (Nitrosyl)

A very versatile ligand which can function in two ways

as a coordinated NO^+ ion (isoelectronic with CO)

as a coordinated NO^- ion (isoelectronic with O_2)

So, instead of carbonyl complexes, that we have been talking about now we are going to be talking about cyclo pentadienyl metal nitrosyl complexes. Now nitrosyls are usually called a NO ligands and the nitrosyls are a versatile ligand because it functions in two ways, a very versatile ligand, which can function in two ways. What are the two ways? One is as coordinated NO plus cation, ascoordinated NO plus ion, this, in this state, it is isoelectronic with CO or as a coordinated in O minus ion, in this case it is isoelectronic with O2.

Now interesting thing about NO is, NO can bindin a linear fashion as well as in a bent fashion and this is illustrated over here. For example, Ln metal M, if this is a 17 valence electron species, can bind with, NO to give Ln n +1 and so this is NO as one electron ligand and bent angle MNO and so the metal complexover here become 18 valence electron by virtue of getting this one electron from the NO.

Similarly, NO can also bind as a three electron donor in that case it loses an L and the resultant n -1 M the oxidation state becomes -1 NO+ so it will have a confirmation of this type. This is -1 and this is plus so overall it is a neutral molecule and then it also has 18 valence electron configuration, NO has3 electron ligand, and linear, linear angle of MNO, so what we see is that NO can bind in two ways to metal, it can form a one electron bent where the angle is a bent less than 180 degrees, whereas it can be linear, this angle will be equal to 180 degrees.

So, this isthe linear binding, and when it is the linear binding it is a 3 electron donor, as a result one of the dative ligand bound to the metal is lost and that is replaced by the electrons from the NO. So basicallywhat it proves is the versatile nature of the NO, the way it canbind to the metal structure.

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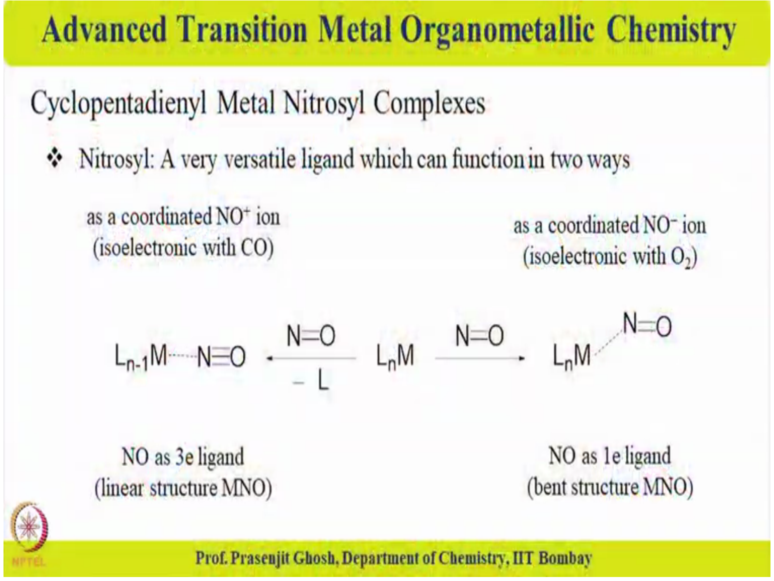

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Cyclopentadienyl Metal Nitrosyl Complexes

- Nitrosyl: A very versatile ligand which can function in two ways

as a coordinated NO^+ ion
(isoelectronic with CO)

as a coordinated NO^- ion
(isoelectronic with O_2)

$$L_{n-1}M\cdots N{\equiv}O \xleftarrow[-\,L]{N{=}O} L_nM \xrightarrow{N{=}O} L_nM\cdots N{=}O$$

NO as 3e ligand
(linear structure MNO)

NO as 1e ligand
(bent structure MNO)

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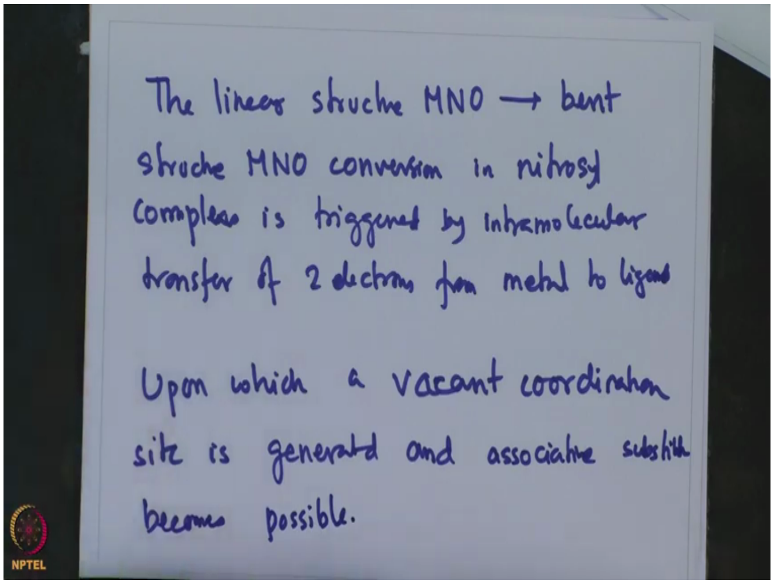

The linear structure MNO → bent structure MNO conversion in nitrosyl complexes is triggered by intramolecular transfer of 2 electrons from metal to ligand

Upon which a vacant coordination site is generated and associative substitution becomes possible.

Now with respect to the linear to bent structures, triggered by 2 electron transfer from the metal, the linearstructure MNO to bent structure MNO, conversion in nitrosyl complexes, is triggered by intra-moleculartransfer of two electrons from metal to ligand. Well, also, as a result of these a vacuum site is generated, and that results in associative substitution. So, upon which, a vacant coordination site is generated and associative substitution becomes possible. So, becausenitrosyl ligands can be a 3 electron donor as well as1 electron donor,because depending on the way it binds.

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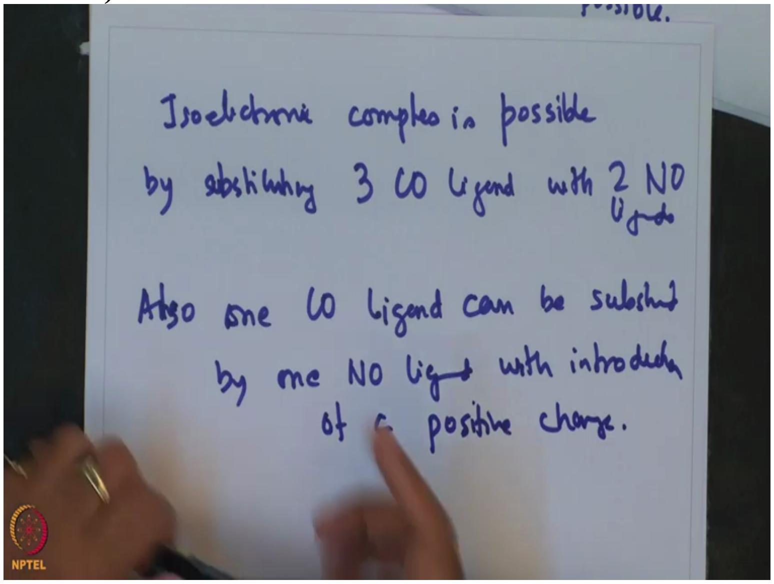

Isoelectronic complex is possible by substituting 3 CO ligand with 2 NO ligands

Also one CO ligand can be substituted by one NO ligand with introduction of a positive charge.

So, isoelectronic complexes, complexes is possible by substituting 3 CO ligands with 2 NO ligands. Also 1 CO ligand can be substituted by one NO ligand with intro duction of a positive charge. So, with this I would like to bring upon the conclusion of today's lecture, now today we have spoken about two different kinds of half sandwich complexes these are transition metal carbonyl complexes as well as transition metal nitrosyl complexes.

With regard to transition metal carbonyl complexes we have looked into various synthetic methods available for preparation of these complexes, also we have looked into the structurewhich are observed for transition metal carbonyl complexes in the beginning of our lecture and what we had seen that this carbonyl moiety can act as a bridging and terminal ligand depending on which kind of metal center they are binding to.

And this is very much observed in di-nuclear complexes where bridging and terminal modes for the carbonyl moiety or observed for smaller 3d metals whereas terminal carbon moites are observed for dinuclear 4d and 5d metals. So, as far as the other half sandwich complexes are concerned these are traditional metal nitrosyl complexes,we have seen that the nitrosyl ligand as a versatile form of ligand because they can bind both in as a 1 electron donor as well as a 3 electron donor.

And depending on their types of binding, for example, if it is a three electron donor they show linear binding whereas if there is one electron donor, they bind in a bell fashion, also what we have learned in today's classis the fact that,in isoelectronic complexes one can sort of envision to substitute CO’s with NO’s, and if they want to do that, they have to keep track of the electron counts, for example,3 CO’s which will have 6 electron can be substituted by 2 NO’s, it will have 3 electronsfor each other NO, so eventually they would be isoelectronic.

Similarly one can substitute 1 CO by 1 NO, but with the introduction of a positive charge. So, here by what we see is that these ligands for the nitrosylic species or the CO counterpart or the corresponding NO counter part can be equally possible to synthesize, based on the electron count alone. So, we will to continue furtherour discussion on these transition metal nitrosyl complexes, particularly looking at various preparatory methods, the structural bonding, and also their reactivity in the next class. So, till then good bye to you oh, and I hope to see you in the next class thank you.