Transition Metal Organometallic Chemistry : Principles to Applications
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Week – 11
Lecture - 52
Transition Metal Olefin Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We had been discussing a very important class of transition metal organom organometallic compound. These are Transition Metal Olefin Complexes and they are they have tremendous applications in various catalytic transformations, which we have discussed in the previous lecture.

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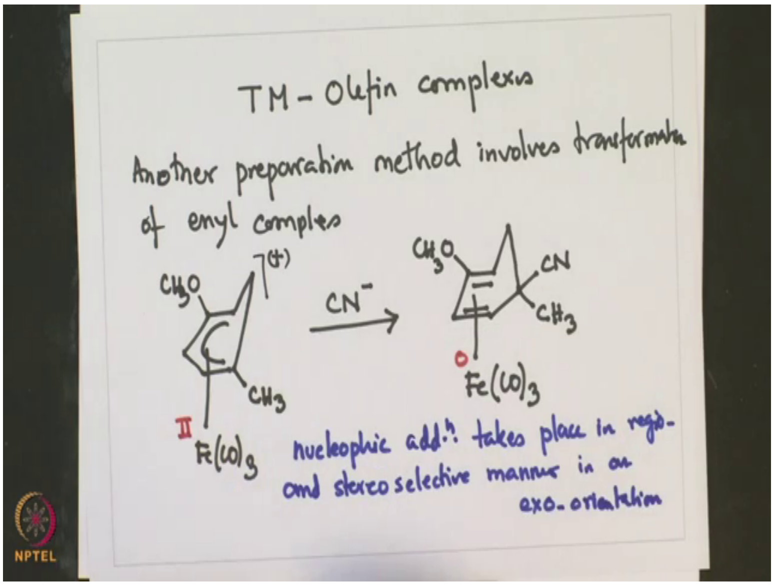

TM - Olefin complexes

Another preparation method involves transformation of enyl complexes

nucleophilic addn. takes place in regio- and stereo selective manner in an exo-orientation

These complexes are important catalytically and also these complexes were among the first to be synthesized, starting with the Zeise's salt way back in 1827 and subsequently some more transition metal olefin complexes were synthesized. In that perspective we have looked into various synthetic procedures available for synthesizing this transition metal olefin complexes in the past lecture. Particularly with respect to the reactions that involved for preparing these namely; for example, like transition metal halides with olefin in presence of a reducing agent and various other new methods which are available for preparing these transition metal olefin complexes.

In today’s lecture, we are going to see some more new methods which are available for preparation of these transition metal olefin complexes. And then look into the bonding and characterization and property studies of these transition metal olefin complexes.

So, for example, another method for preparation, involves transformation of an enyl complexes and this is explained or shown by this reaction where this mono anionic ligand containing O CH 3 moiety and this is mono anionic in nature with one methyl substituents in 1. And iron tricarbonyl reacting with cyanide molecule to give this di olefinic complex with OCH 3 CH 3 CN Fe CO 3.

So, this is a interesting reaction in which this cyanide acts like nucleophile and this nucleophilic addition. This is a cationic complex of overall unit positive charge; that means, that the iron is in plus 2 oxidation state and the nucleophilic attack instead of happening at the metal happens at this olefinic in ionic the ligand moiety ok. Enyl complex happens with the ligand.

So, nucleophilic addition takes place in regio and stereo selective manner in an exo orientation. As a result what happens is that the cyanide is formed on the outside of the ring and the diolefinic compound is formed to the metal. So, because of this nucleophilic attack the metal then gets reduced to 0; oxygen state as opposed to this was 18 electron cationic. So, this was a plus 2 oxidation state.

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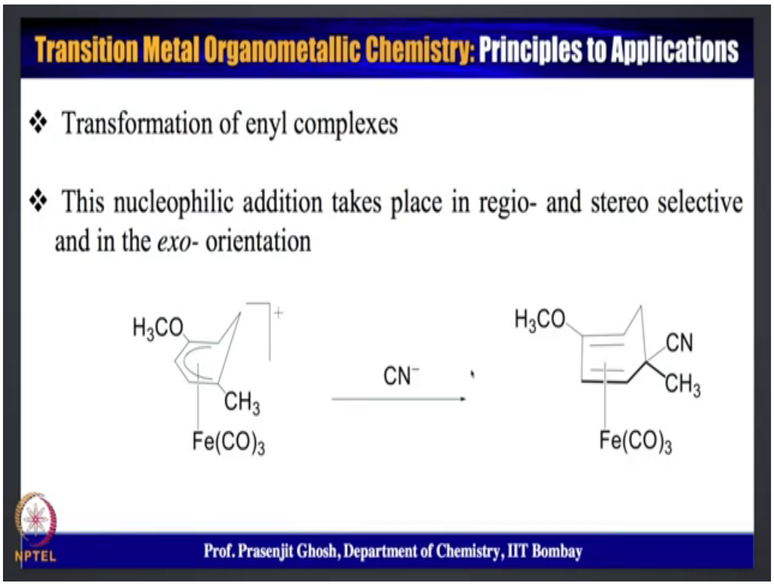

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- Transformation of enyl complexes
- This nucleophilic addition takes place in regio- and stereo selective and in the *exo*- orientation

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So, because of this nucleophilic attack and resulting in the new compound which happens in a regio and stereo selective fashion, the iron has gotten reduced from plus 2 oxidation state on to a iron 0 of olefinic complex as is shown over here. So, this is an interesting reaction whereby a metal olefin complex is obtained a by a nucleophilic attack of cyanine and falls among the unusual way of obtaining such kind of complexes.

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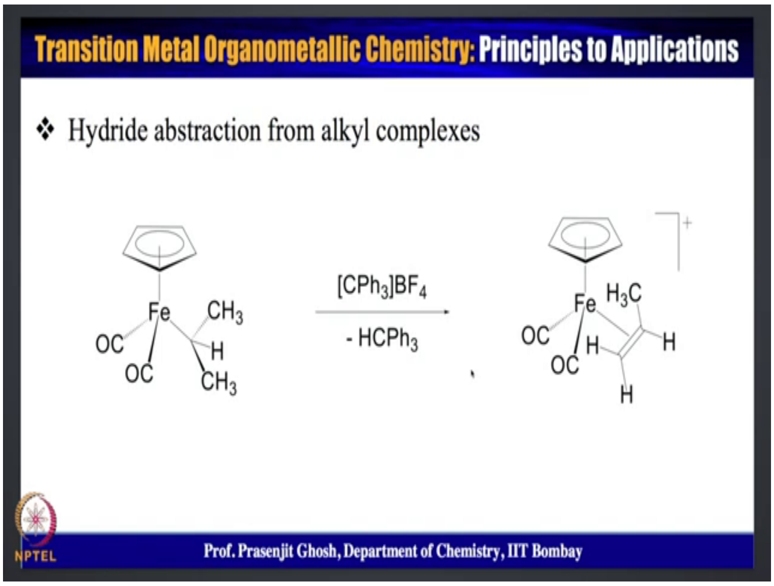

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- Hydride abstraction from alkyl complexes

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Hydride abstraction also provides a useful method for synthesizing these olefin complexes from alkyl metal alkyl complexes. So, hydride abstraction from alkyl complexes leads to the transition metal olefin complex. So, the alkyl is a isopropyl moiety with 2 methyl and as a as a isopropyl iron alkyl complex. And the hydride is abstracted with CPh 3 trityl cation BF 4 minus which gives CH Ph 3 and the corresponding cationic olefinic complex; Fe CO CO CH 3 H H H cation.

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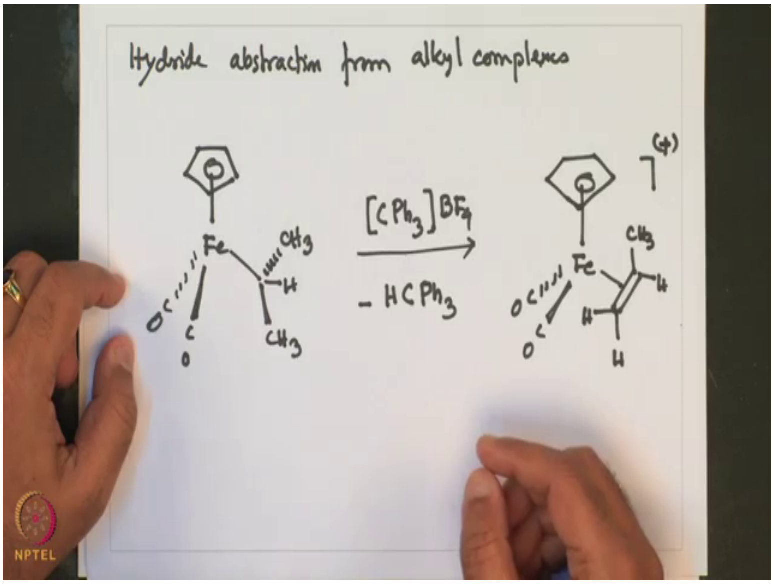

So, we see that hydride abstractions can lead to olefinic complex as over here and this is an interesting reaction whereby transient metal olefin complex is formed. Now, in this context I should also mention that we had discussed this hydride abstraction in the context of making carbene carbene complexes; where similar instances of hydride abstracted from the alpha carbon atom leading to the formation of transition metal carbene complexes for very early transition metal.

Whereas, in this particular ligand system; in a metal alkyl if a hydride is abstracted then one can also form the olefin complex and not the carbene complex, the way in the present scenario unlike that of the metal carbon complexes discussed in the earlier example.

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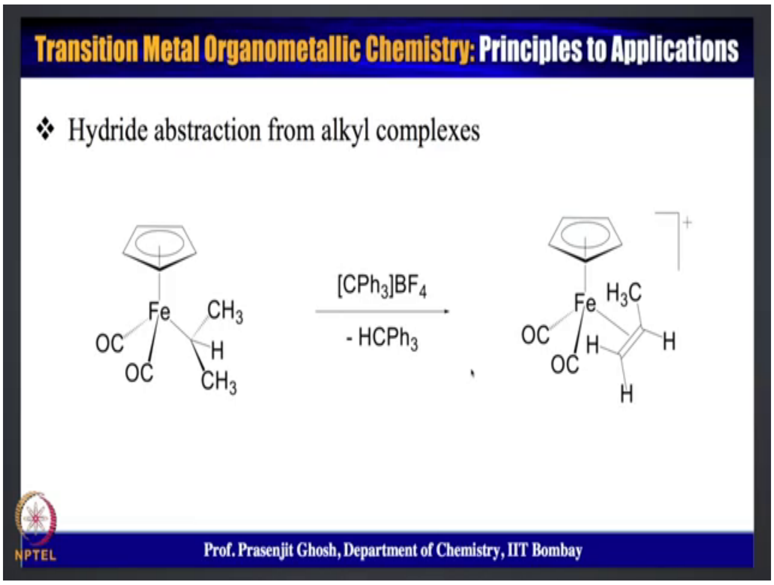

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- ❖ Hydride abstraction from alkyl complexes

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Now, with that we come to the end of now discussing various synthetic protocols available for preparing at this transition metal olefin complexes. And then we are going to look into something which is far more interesting particularly a provide on providing insight as to how these olefinic comfort conferences; olefins are stabilized by transition metal in these transition metal olefin complexes.

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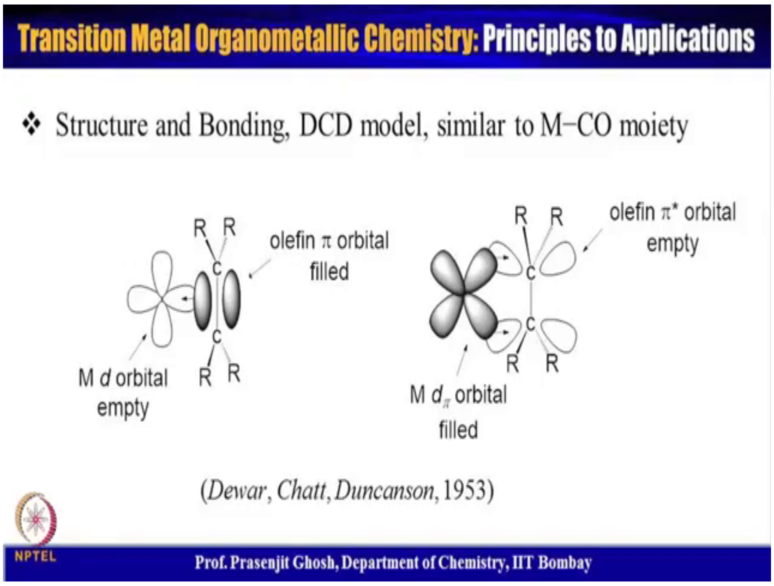

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Structure and Bonding, DCD model, similar to M–CO moiety

(Dewar, Chatt, Duncanson, 1953)

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And from this viewpoint one needs to understand the bonding scenario prevalent or look between this olefin and transition metal, particularly looking at the interactions which occur between the ligand frontier orbitals with the transition metal frontier orbitals.

Now, there is a historical perspective to this bonding theory. In the sense that the first transition metal olefin complex was synthesized way back in 1827 with the report of this ethylene complex of platinum in the form of Zeise's salt. Whereas, the theory of understanding of how does an olefin is stabilized by a transition metal came much later about a century or 120 years later to be more precise in 1950s; when Dewar, Chatt and Duncanson proposed this model for olefin binding to transition metal.

A model which is a similar to that of the transition metal carbonyl interactions; where, however, the interacting orbital ligand orbital's are different in case of the olefin as opposed to their of the transition metal carbonyl carbon orbital's. So, with that I am going to spend few more times right now, in speaking about structure and bonding of transition metal olefin complex. Particularly with respect to Dewar, Chatt and Duncanson model; which was developed at 1953; this is called DCD model.

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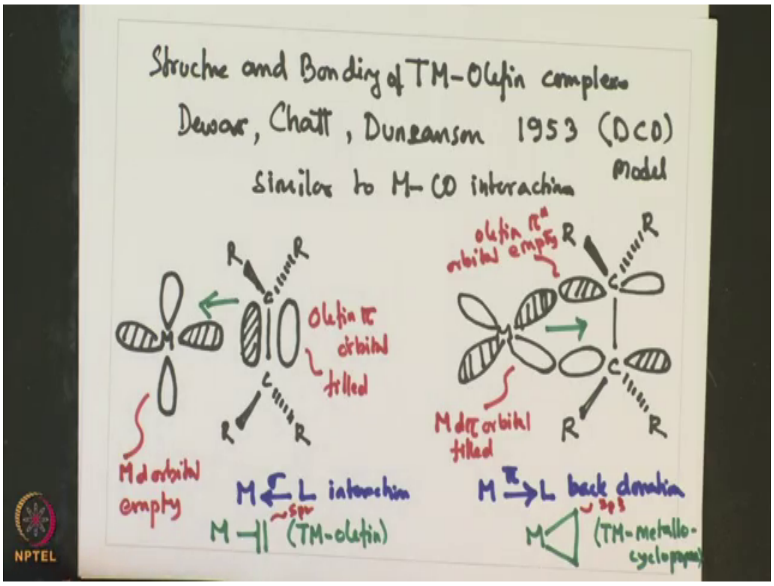

Structure and Bonding of TM-Olefin complexes

Dewar, Chatt, Duncanson 1953 (DCD) Model

Similar to M-CO interaction

And this model was developed similar to the metal carbonyl moiety; however, the to that of metal CO interaction. But changing but changing the elegant orbital I going from CO to an olefin.

Now, to start with this also the ligand or olefin interacts with metal with two kinds of interaction; one is the forward sigma donation, the other is the backward pi back donation. And let me explain that; for example, for the olefin CR R C R R. Now, olefin has pi electrons, because of the pi bond. And usually this will have opposite symmetry and this is a filled orbital which is that would interact with an empty metal sigma type orbital of appropriate symmetry. And this is an empty orbital which is empty.

As a result the donation would happen from filled orbital to the metal. And this is olefin pi orbital donating to the metal. So, this is often referred to as ligand sigma interaction. Sigma, because the electron density resides in the bonding internuclear distance. And this is the forward sigma donation; followed by pi back donation which happens from the field metal orbital onto the pi star ligand orbital which is given over here.

Now, this is a pi star orbital which is empty. So, they would have opposite face. And this is olefin pi star orbital and these are empty. Now, this empty pi star olefin orbital would receive electron density from the metal orbital of appropriate symmetry. The way it is done and these are metal d pi orbital; and these are filled orbital.

So, back donation happens from metal to ligand and these interactions are called metal to ligand pi back donation. So, these two interactions are synergic in nature; means interaction of one will reinstate the other. So, that is why they are synergic interaction. Now, this was developed by the Dewar, Chatt and Duncanson and then hence the name DCD.

Now, point to note over here is that when I am olefin interacts with the transition metal; it can either be purely olefinic or purely a metallo cyclopropane interaction. So, and each of these as to where the olefin resides in these two form of interaction is reflected in the kind of geometry they would form and that can be characterized by a spectroscopic techniques.

So, for example, these two interactions were ligand to metal sigma donation is predominant and the pi back donation is negligible. So, such kind of olefinic complexes are called or can be represented by these. These are transition metal olefin complex; whereas, interactions where pi back donation is predominant and that significant amount of back donation happens. As a result the pi star orbitals are cleaved and those are sort of leads to the formation of metallo cyclopropane and these are called transition metal metallo cyclopropane intermediate metallocyclo propane.

Now, based on the type of structures that exist because over here; the hybridization of carbon is Sp 2; whereas, over here it has become Sp 3. So, that bares a signature spectroscopic signature which can be characterized accordingly and some information as to what extent this forward donation or back donation occurred in transition metal olefin complex can be obtained not only by NMR but also characterization techniques.

And we are going to dwell more on it as we come to discuss about the reactivity pattern of transition metal olefin complex based on these interplay of these two kind of interactions. So, I will discuss this in bit more details when we talk about the reactivity of this transition metal olefinic complexes.

Now, what came out from the earlier discussion is that the transition metal olefin complex formation is dependent on sigma, etcetera and pi donor properties of the metal.

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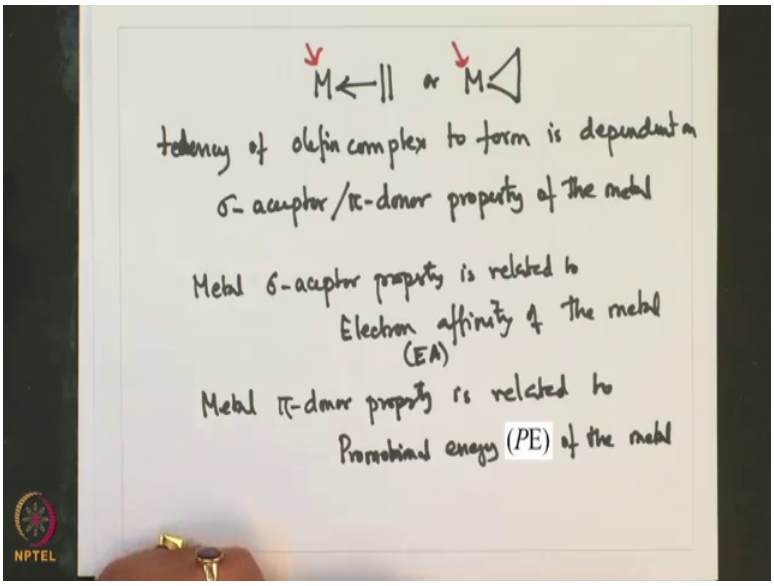

M←|| or M◁

tedency of olefin complex to form is dependant on σ-acceptor/π-donor property of the metal

Metal σ-acceptor property is related to Electron affinity of the metal (EA)

Metal π-donor property is related to Promotional energy (PE) of the metal

So, for example, a structure like this when the olefin is formed or when the back donation is maximum and metal cyclo butane is formed; which of these or two what extent they would; these are the tendency of olefin complex to form is dependent on sigma acceptor or pi donor property of the metal.

And so, this is sort of trying to get or have an idea as to how this complex is formed by looking at the metal. And from the metals perspective there are sigma acceptor property is related to electron affinity of the metal. So, which means that how strongly is the metal need to take the additional electron.

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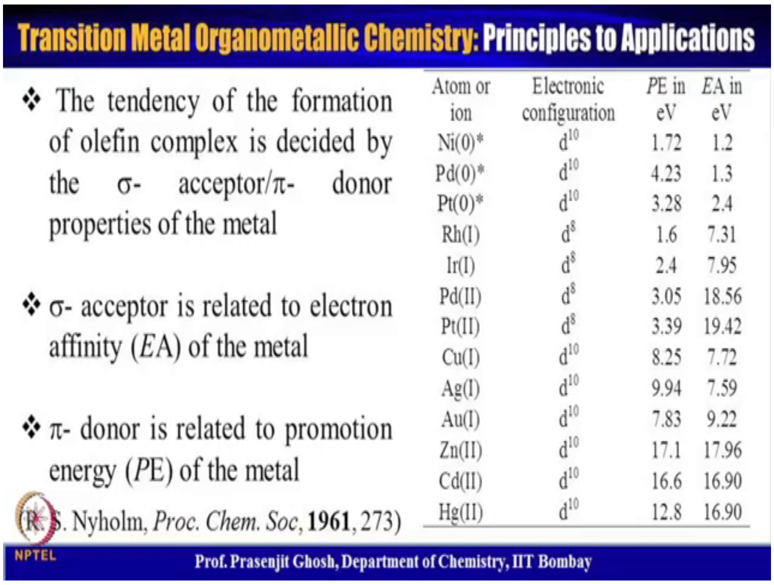

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- The tendency of the formation of olefin complex is decided by the σ- acceptor/π- donor properties of the metal
- σ- acceptor is related to electron affinity (*E*A) of the metal
- π- donor is related to promotion energy (*P*E) of the metal

(R. S. Nyholm, *Proc. Chem. Soc*, **1961**, 273)

Atom or ion	Electronic configuration	*P*E in eV	*E*A in eV
Ni(0)*	d^{10}	1.72	1.2
Pd(0)*	d^{10}	4.23	1.3
Pt(0)*	d^{10}	3.28	2.4
Rh(I)	d^{8}	1.6	7.31
Ir(I)	d^{8}	2.4	7.95
Pd(II)	d^{8}	3.05	18.56
Pt(II)	d^{8}	3.39	19.42
Cu(I)	d^{10}	8.25	7.72
Ag(I)	d^{10}	9.94	7.59
Au(I)	d^{10}	7.83	9.22
Zn(II)	d^{10}	17.1	17.96
Cd(II)	d^{10}	16.6	16.90
Hg(II)	d^{10}	12.8	16.90

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Similarly, metal pi donor property is related to term called the promotional energy; energy of the metal. So, promotional energy is energy required for taking the valence electron of the metal and putting it in the next higher energy orbital. So, how difficulty or how easily will the metal be able to promote its valence electron to the next available empty orbital; that is called promotional energy.

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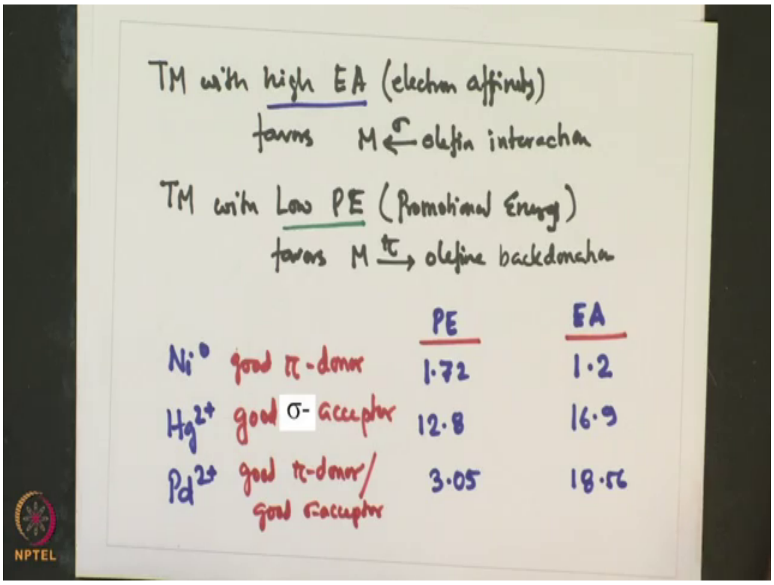

TM with high EA (electron affinity)
favors $M \xleftarrow{\sigma}$ olefin interaction

TM with Low PE (Promotional Energy)
favors $M \xrightarrow{\pi}$ olefine backdonation

		PE	EA
Ni^0	good π-donor	1.72	1.2
Hg^{2+}	good σ-acceptor	12.8	16.9
Pd^{2+}	good π-donor/ good σ-acceptor	3.05	18.56

Now, these two properties significantly affect this forward sigma donation as well as the pi back donation of the elements. For example, a transition metal with high electron affinity; means high electro affinity favors olefin to metal sigma interaction. So, that means that is the metal has a high electron affinity, then it would prefer a very strong intensive interaction or the olefin; that means, that the first coordination is very strong. Similarly, transition metal conversely with low promotional energy favors metal to olefin pi back donation.

So, the metals which have no promotional energy they should be able to back donate easily. For example, let us take a look at some of the values. For example, these are promotional energy and electron affinity. So, let us say, for nickel 0; the promotional energy is 1.72 and electron affinity is 1.2.

Now, it says high electron affinity means favors forward sigma donation , electron affinity is very low, so, sigma donation is not strong but it says a low promotional energy means favors back donation. So, the nickel 0 is indeed have a low promotional energy. So, this is a good pi donor; pi donor. So, nickel as a metal is a very good pi donor.

For example, let us now move to mercury Hg 2 plus; the corresponding promotional energy value is now 12.8 and the electron affinity value is a 16.9. So, what we have is very high promotional energy. So, that means that, for backward back donation is very minimal for mercury; whereas, it has very high electron affinity. So, that means, that it will be favoring olefin to metal sigma donation and hence mercury is a good sigma acceptor.

And similarly, let us take a look at palladium Pd 2 plus has quite low promotional energy of 3.05 and extremely. So, it has low promotion energy means good back donation and extremely high electron affinity of 18.56; that means, palladium 2 plus is a good a pi donor and also a good sigma acceptor because of very high electron affinity.

So, with that what one can see is that the extent of forward donation and backward donation from the metal perspective depends on these two parameters which is electron affinity and promotional energy. And with that from the quantitative values of this electron affinity and promotion energy one can have an idea as to sigma donating ability as well as sigma pi accepting donating abilities of these metal ions towards the ligand.

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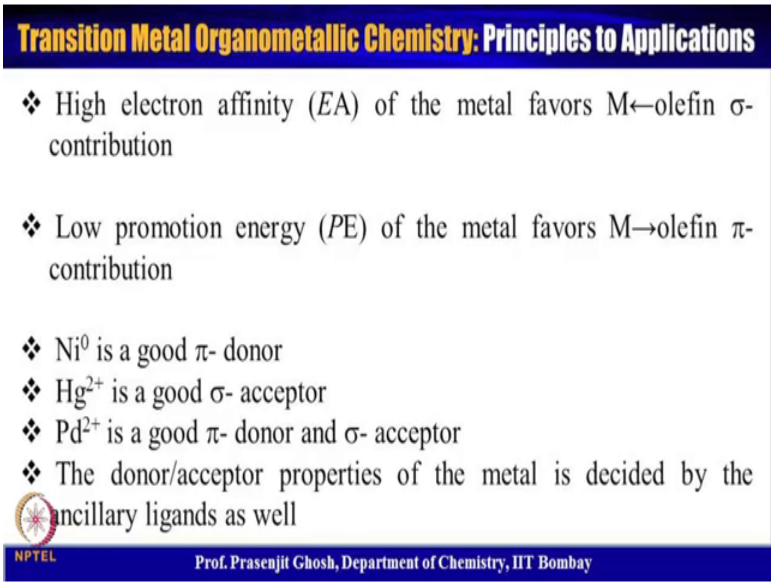

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- High electron affinity (*EA*) of the metal favors $M \leftarrow$olefin σ-contribution
- Low promotion energy (*PE*) of the metal favors $M \rightarrow$olefin π-contribution
- Ni^0 is a good π- donor
- Hg^{2+} is a good σ- acceptor
- Pd^{2+} is a good π- donor and σ- acceptor
- The donor/acceptor properties of the metal is decided by the ancillary ligands as well

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So, with that I would like to conclude today's discussion which had mainly been in looking at various synthetic methods available for making transition olefin complexes. We have also looked into detail the bonding interaction that occurs between an olefin with the transition metal particularly with respect to the Dewar, Chatt and Duncanson theory, he which has been developed and explaining this olefin transition metal interaction. And this theory is sort of in line with the transition metal carbonyl interaction which has been discussed in the earlier lectures.

And what we had seen is transient metal olefin interaction depends on the extent of sigma donation and pi back donation and the olefinic moiety can lie in the reaction trajectory; in any of the in various any of the coordinates depending on what extent the forward sigma donation or a backward pi back donation; were in place. We have also looked from the metal perspective, the properties of the metal that will affect is sigma acceptance and pi back dona pi donation ability and what we had co-related this term is with electron affinity and promotional energy of the metal.

So, with that I would like to conclude today's lecture which was on synthesis and binding properties of transition metal olefin complexes. And in the subsequent lecture we are going to look at some of the characterization methods available for these transition metal olefin complexes and their corresponding reactivity and property studies.

Until that time I thank you for patiently being with me in this lecture and going through all these concepts and I look forward to have an interesting lecture in the next one where, we are going to discuss the properties as well as these some of the applications; properties and reactivities of transition metal. Olefin complexes which indeed are very interesting compounds not only from their catalytic potential but also from the their interaction with transition metal in terms of understanding the frontier molecular orbital interaction that occurs from the ligand perspective to that of the transition metal.

So, with that let me thank you once again for patiently being with me in this lecture and look forward to being with you in the next lecture, till then goodbye.