Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture- 04
Week - 1
Reactivity of Organometallic Compounds

Welcome to this lecture on organometallics chemistry. Today's topic is very interesting one. It is about reactivity of organometallic compounds. Now reactivity is something which or distinguishes organometallic compounds from other compounds, because they are extremely reactive with air and moistures. And they often are synthesized in the exclusion of air and moisture. They are extremely unstable under ordinary aerobic conditions. So, detail know-how is required in handling this compound.

Now in the beginning it was thought that the extreme reactivity of organometallic compounds, are probably of thermodynamic origin; that is they are unstable compounds, and that they tend to degrade quickly, but later it was found that they are, their degradation is not due to thermodynamic instability or rather of kinetic origin, and that can be gauged by looking at the bond energy of organometallic compounds.

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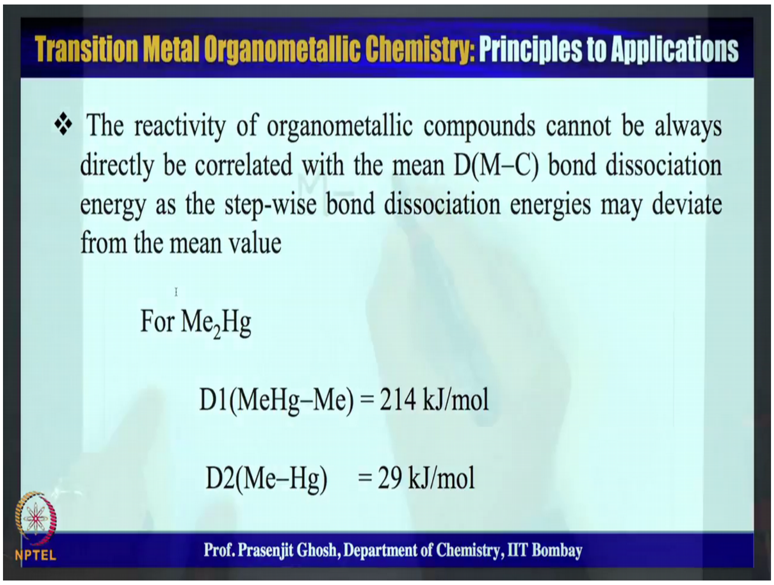

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- The reactivity of organometallic compounds cannot be always directly be correlated with the mean D(M–C) bond dissociation energy as the step-wise bond dissociation energies may deviate from the mean value

For Me_2Hg

$$D1(MeHg{-}Me) = 214\ kJ/mol$$

$$D2(Me{-}Hg) = 29\ kJ/mol$$

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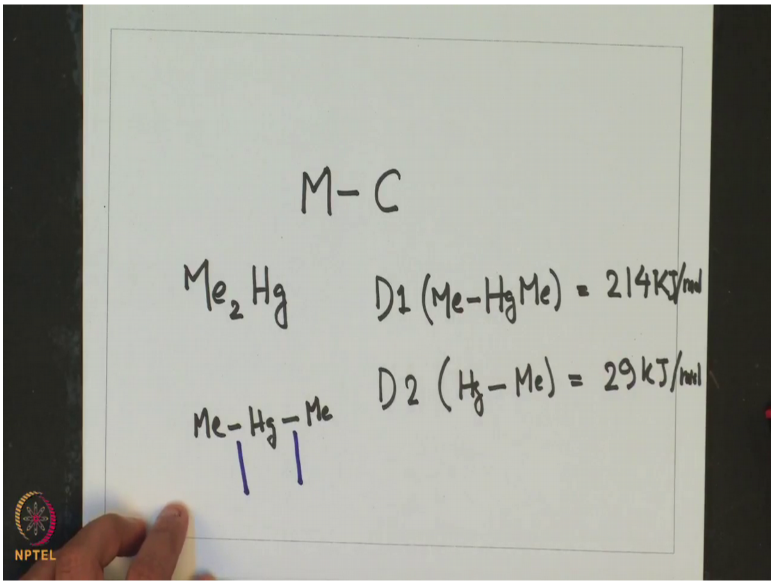

M-C

Me_2Hg D1 (Me-HgMe) = 214 kJ/mol

Me-Hg-Me D2 (Hg-Me) = 29 kJ/mol

The bond energy of the organometallic compounds depends on the strength of the metal carbon bonds and metal carbon bonds are sort of weaker than that of the metal oxygen, metal nitrogen or metal halide or metal, other metal heteroatom bonds. Now furthermore it was seen that when you have a multiple ligand attached to metal that their bond dissociation energy may not directly correlate a, for each bond dissociation. For example, for dimethyl mercury, the first bond dissociation of methyl mercury, methyl bond is about 214 kilo joule per mole, and the second bond dissociation of mercury methyl is much lower ,about 29 kilo joule per mole.

So, what it tells that the two bonds of mercury, as they dissociate by themselves, they are bond dissociation energy varies, and that depends on the intermediate species which is formed after the dissociation of the first bond.

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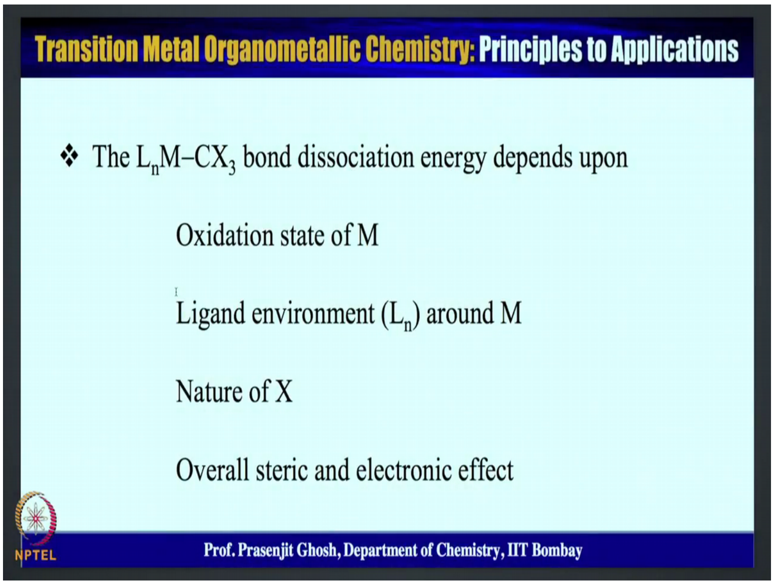

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- The $L_nM–CX_3$ bond dissociation energy depends upon

  Oxidation state of M

  Ligand environment (L_n) around M

  Nature of X

  Overall steric and electronic effect

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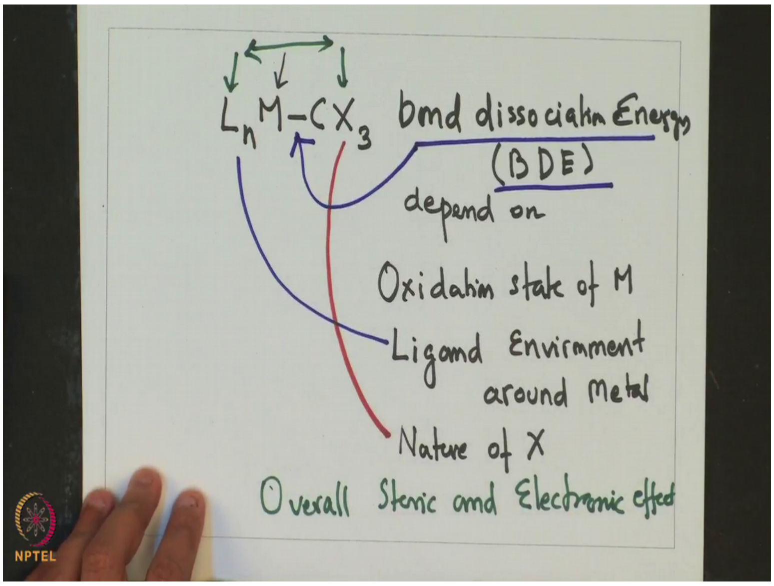

$L_nM–CX_3$ bond dissociation Energy (BDE)

depend on

Oxidation state of M

Ligand Environment around Metal

Nature of X

Overall Steric and Electronic effect

Thus in overall the L and M CX 3, where we have a metal, and then the ligand substituents on the metal, and we have X substituents on the carbon. Its bond dissociation energy, or this is commonly referred to as B D E, depends on the oxidation state of the metal, which is this ligand environment around metal, which is this. Then nature of X which is this. And in addition to all of these, overall steric and electronic effect, which is kind of very interesting that, and electronic effect. This overall steric and electronic effect arise, because of the presence of the substituents L N and X, and their mutual interaction among each other. So all of these influences the bond dissociation energy influences the bond dissociation energy of the metal x bond, and that is why; it becomes very interesting.

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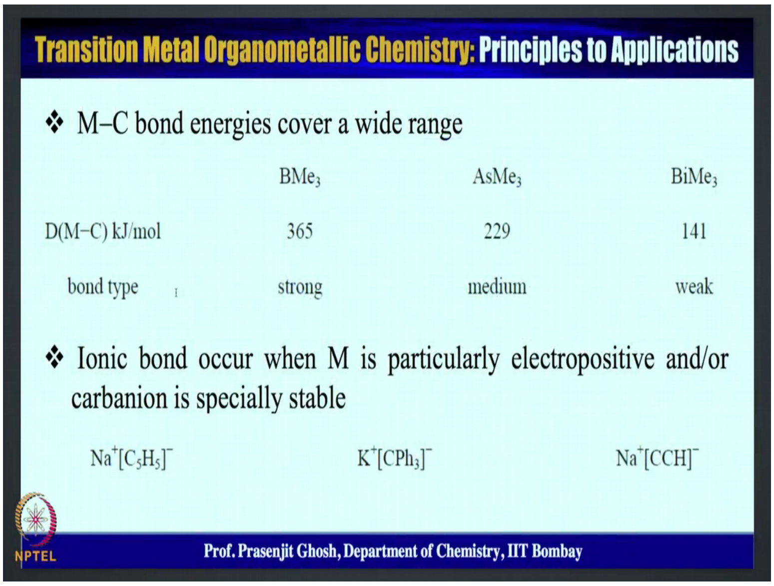

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- ❖ M–C bond energies cover a wide range

	BMe_3	$AsMe_3$	$BiMe_3$
D(M–C) kJ/mol	365	229	141
bond type	strong	medium	weak

- ❖ Ionic bond occur when M is particularly electropositive and/or carbanion is specially stable

$Na^+[C_5H_5]^-$ $K^+[CPh_3]^-$ $Na^+[CCH]^-$

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Now, let us take a look at this bond dissociation energy, and sort of classify them where how the bond stands.

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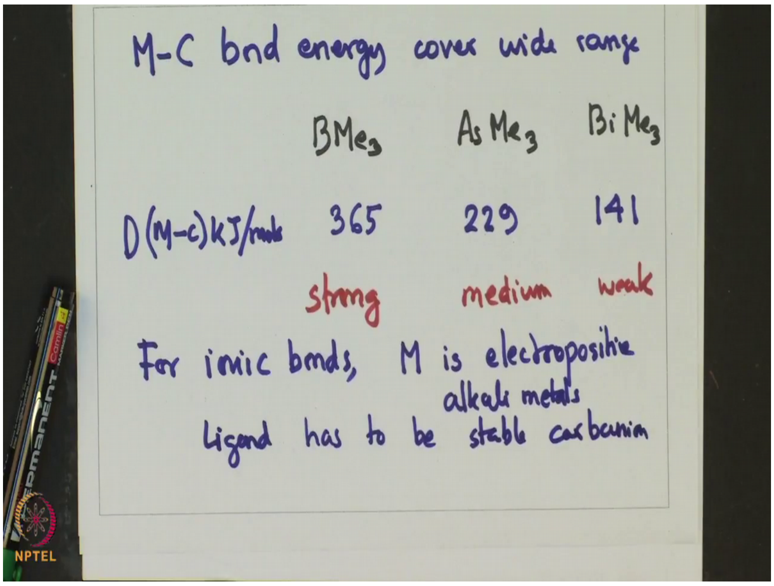

M-C bond energy covers wide range

	BMe_3	$AsMe_3$	$BiMe_3$
D(M-C) kJ/mole	365	229	141
	strong	medium	weak

For ionic bonds, M is electropositive
alkali metals
Ligand has to be stable carbanion

For example, this bond, metal carbon bond energy can vary a wide range, covers wide range. Let us say for B M e 3, and arsenic M e 3, and bismuth Me 3. The metal carbon bond dissociation energy in kilojoules per mole stands at 365 to arsenic. This is much lower in the periodic table to 229, do this one, being the lowest as 141 kilojoules per mole. And what it signifies that 365 this to be a very strong bond, strong bond, this being medium, this being a weak bond. So, the range in which a covalent metal carbon bond arrives can vary a lot, from being very strong to very weak. And for nonmetals that depends on the location of the metal in its periodic table. Now for the other kinds of bonds, which are mainly ionic bonds. For ionic bonds, the bond energy depends on the type of the metal, and the metal has to be electro positive one, when the aim is electro positive. So, these are mainly alkali metals, and the ligand has to be a carbanion. Ligand has to be a stable carbanion.

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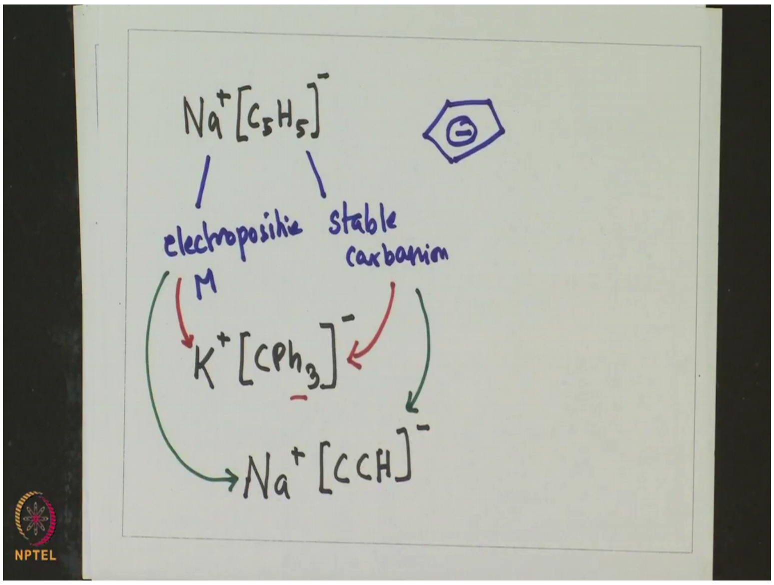

So, examples of this include various ionic compounds. For example, we have; so, here we see a very electro positive alkali metal, and here is a stable carbanion. Structure of this anion, is this conjugated cyclopentadienyl anion, which is very stable. Similarly if we take a look at the other ionic compounds. For example, potassium C P h 3 minus. Here the metal is again a electropositive metal, potassium alkali metal, and anion also is a stable carbon ion. So, the carbon, negative charge on the carbon is stabilized over 3 phenyl rings. So, what we see that. For a ionic compounds the metal has to be electro positive ion, and then anion a stable one. Another example is the sodium acetylide, where this sodium is again electropositive metal, and this acetylide moiety is also a stable carbon ion. Where then iron is stabilized over a S P carbon atom. So, there are cases where multicenter non classical bonds are formed. These MC bonds.

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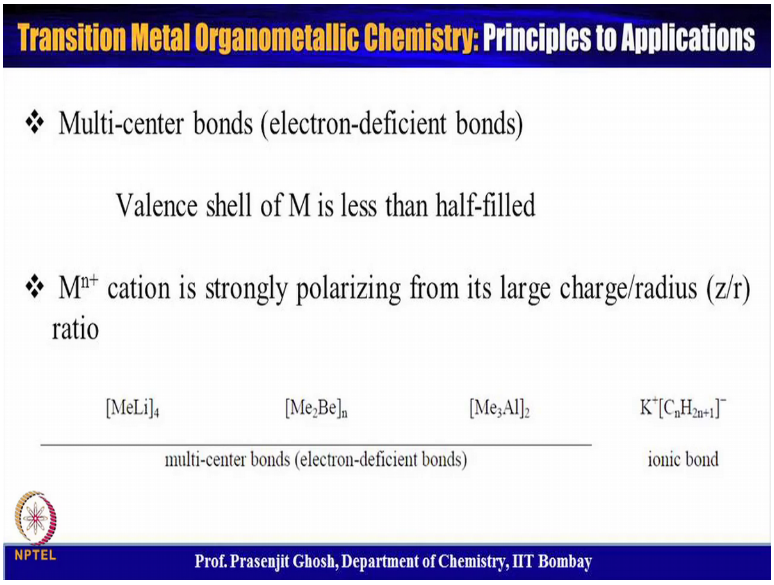

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- Multi-center bonds (electron-deficient bonds)

  Valence shell of M is less than half-filled

- M^{n+} cation is strongly polarizing from its large charge/radius (z/r) ratio

$[MeLi]_4$	$[Me_2Be]_n$	$[Me_3Al]_2$	$K^+[C_nH_{2n+1}]^-$
multi-center bonds (electron-deficient bonds)			ionic bond

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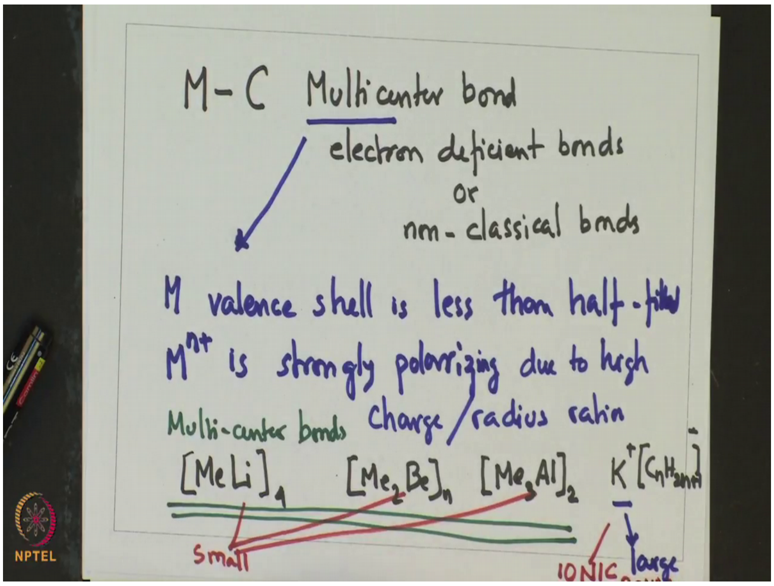

M – C Multicenter bond

electron deficient bonds
or
non-classical bonds

M valence shell is less than half-filled

M^{n+} is strongly polarizing due to high charge/radius ratio

Multi-center bonds

$[MeLi]_4$ $[Me_2Be]_n$ $[Me_3Al]_2$ $K^+[C_nH_{2n+1}]^-$

Small

IONIC

large

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Bonds generally forms of atoms like boron, electron deficient atoms like borons, aluminums. And these are generally referred to as electron deficient bonds, or non classical bonds, because they do not follow the conventional view of two bond, two center two electron covalent bonds.

Now, in this case, where non self classical bonds are forms, multicenter non classical bonds are formed, the valence shell of L is usually less than half filled; M valence shell, is less than half filled, and M is the polarizing, strongly polarizing a cation, is strongly polarizing due to high charged to radius ratio. So; that means, that these cations are very small, and hence we see the examples of this class includes methyl lithium, dimethyl beryllium, tri methyl aluminum, which is a dimer as opposed to potassium 2 M H n plus 2 n plus 1 anion.

Now what we see over here; that except for potassium which is large, other metals are very small. There is very small. And hence the cations which are polarizable they have less than half filled, they conveniently formed multicenter bonds. So all of these forms multicenter bonds, electron deficient bonds. Whereas, when the metal is large, and it is not as polarizable as the other one; then, this is forming ionic bonds. So, what we see, is that depending on the size and the polarizable ability, polarizability of the cation, the organometallic compound can have non classical, electron deficient, multicenter bonds, or it can also be truly ionic ones, and hence the reactivity of this species would also vary accordingly.

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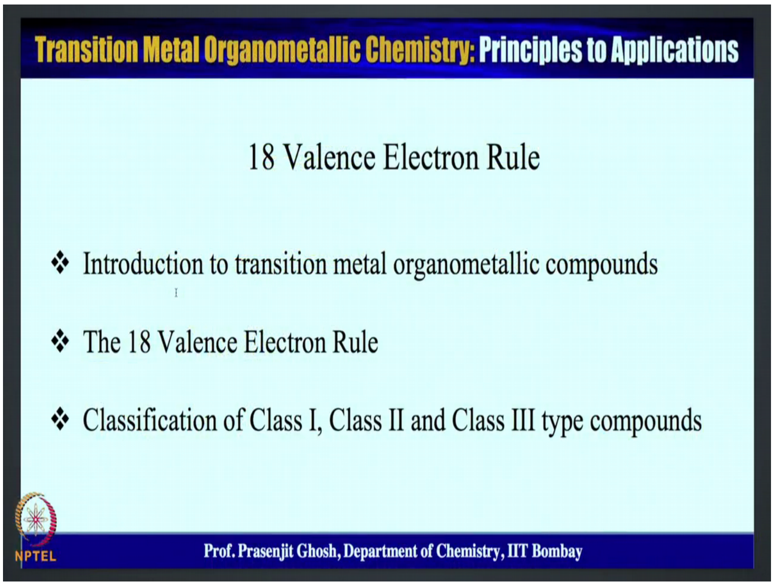

Transition Metal Organometallic Chemistry: Principles to Applications

18 Valence Electron Rule

- Introduction to transition metal organometallic compounds
- The 18 Valence Electron Rule
- Classification of Class I, Class II and Class III type compounds

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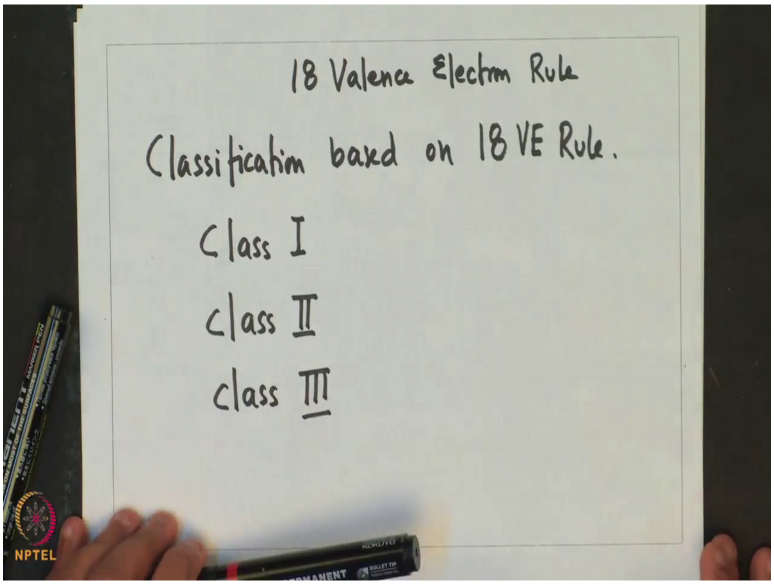

18 Valence Electron Rule

Classification based on 18 VE Rule.

Class I

Class II

Class III

Now, another important concept involving organometallic compounds is its 18 valence electron rule. So, this is the important rule that says, that transition metal complexes one which are stable ones, should have 18 electron in its valence orbitals. And this rule have often be used conveniently in stating that certain compounds could be prepared, because they would meet the 18 valence electron rules, and sometimes erroneously it is said that compounds which cannot have 18 valence electron rule, be unstable, and hence cannot be prepared or dealt with.

However, as lot of organometallic compounds were synthesized and their structures and interactions were looked into, then it was found that there are compounds which obey 18 valence electron rules, and there are compounds which does not obey 18 valence electron rule. So, first of all, we would take a look at 18 valence electron rule, and see a; what are the compounds which will obey them, and when the 18 valance electron rule is not obeyed. And gradually, we move on to the classification based of these kind of organometallic compounds. And usually it is found that there are three types of compounds; class 1, class 2 and class 3.

So, let us see and analyze what is 18 valence electron rule, and what are the different classes of 18 valence electron rule that we just has described. Now in order to understand the origin of 18 valence electron rule, we should understand what leads to the concept of 18 valence electron rule. And that stems from the fact, that these rule is primarily applicable for transition metal complexes. The reason being that transition metal complexes have d orbital which leads to larger number of valence electron. For example, our main group element uses.

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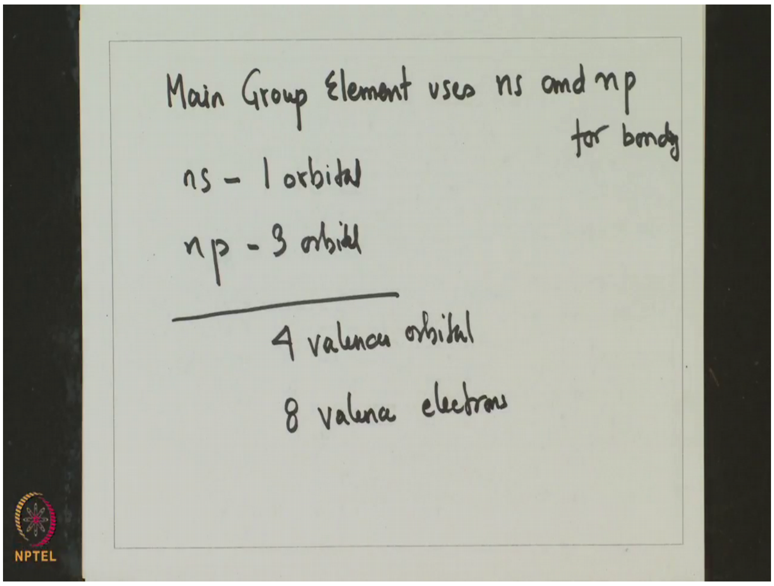

Main Group Element uses ns and np for bonding

ns - 1 orbital

np - 3 orbital

4 valence orbital

8 valence electrons

Only n s and n p orbitals for chemical bonding, for bonding. So, the number of orbitals used is n s has 1 orbital, and n p has 3 orbital, leading to 4 valence orbital, which can have 8 valence electron. So, main group elements primarily would follow that 8 electron rule for its stability. Similarly for transition metals, they have inner d orbitals.

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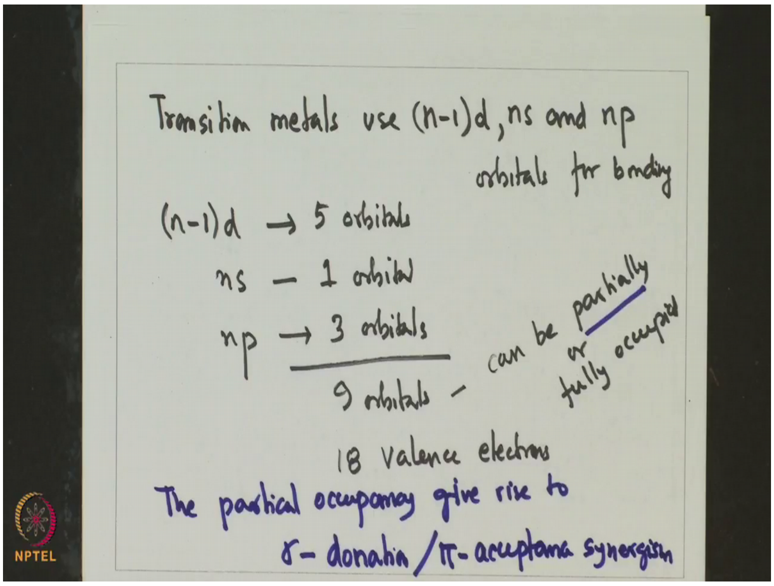

Transition metals use (n-1)d, ns and np orbitals for bonding

(n-1)d → 5 orbitals

ns — 1 orbital

np → 3 orbitals

9 orbitals - can be partially or fully occupied

18 valence electrons

The partial occupancy give rise to σ- donation / π- acceptance synergism

They use n minus 1 d n s and n p orbitals for bonding. So, it has providing 5 orbitals, n s providing 1 orbital, and in p providing 3 orbital, giving a total of 9 orbitals, which can accommodate 18 valence electrons.

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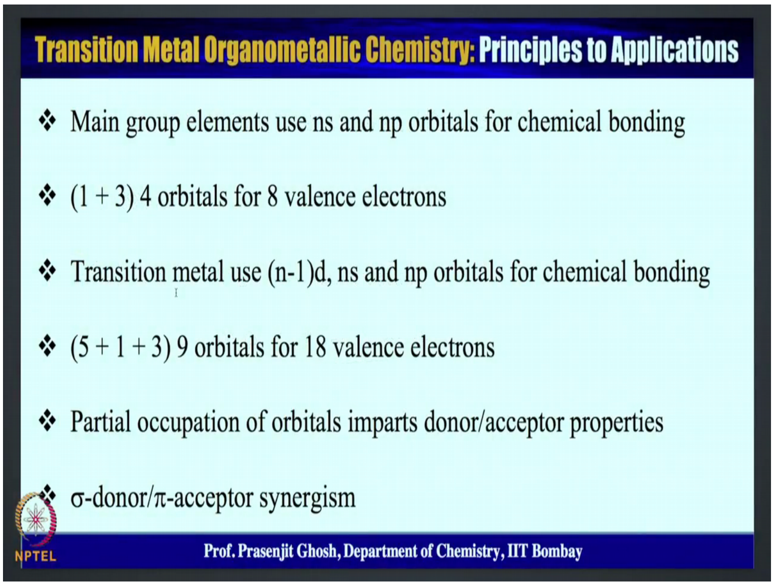

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- Main group elements use ns and np orbitals for chemical bonding
- (1 + 3) 4 orbitals for 8 valence electrons
- Transition metal use (n-1)d, ns and np orbitals for chemical bonding
- (5 + 1 + 3) 9 orbitals for 18 valence electrons
- Partial occupation of orbitals imparts donor/acceptor properties
- σ-donor/π-acceptor synergism

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Now, the question arise that for a transition metal complexes are all these nine of orbitals fully occupied or not. Now it turns out that these orbital need not be fully occupied, and they can be partially a filled, can be partially or fully occupied. Now this is a very interesting concept. The concept of partial occupancy of this orbital, because if it is, these orbitals are partially occupied, then they can accept electron, and if it is fully, as well as they can donate electron. And this is a unique characteristics of the transition metals which has d orbitals. And these partial occupancy gives rise to very interesting interaction that manifests when it binds to the ligand in the form of sigma donation, as well as pi acceptance synergism. The partial occupancy to sigma donation and pi acceptance synergism.

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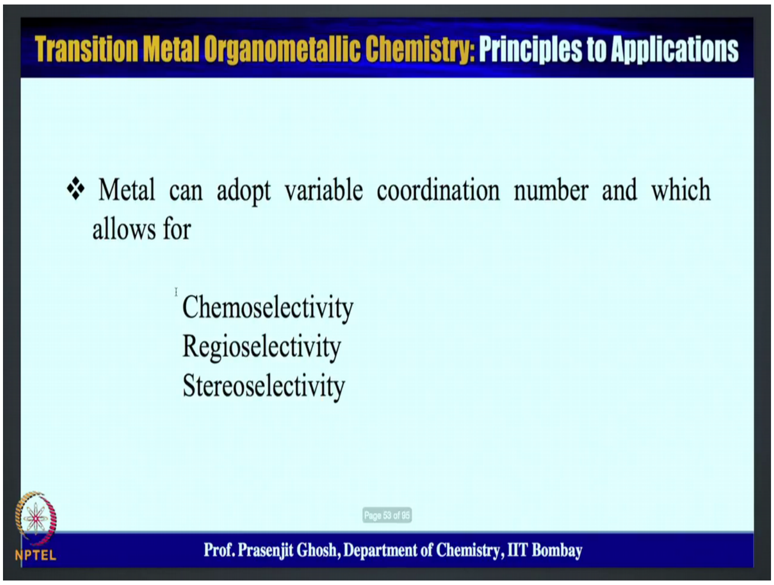

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❖ Metal can adopt variable coordination number and which allows for

Chemoselectivity
Regioselectivity
Stereoselectivity

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So, this sigma donation pi acceptance gives rights to various reactivity attributes. For example, this partial occupancy leading to sigma donation or pi acceptance, can give rise to variation in coordination number.

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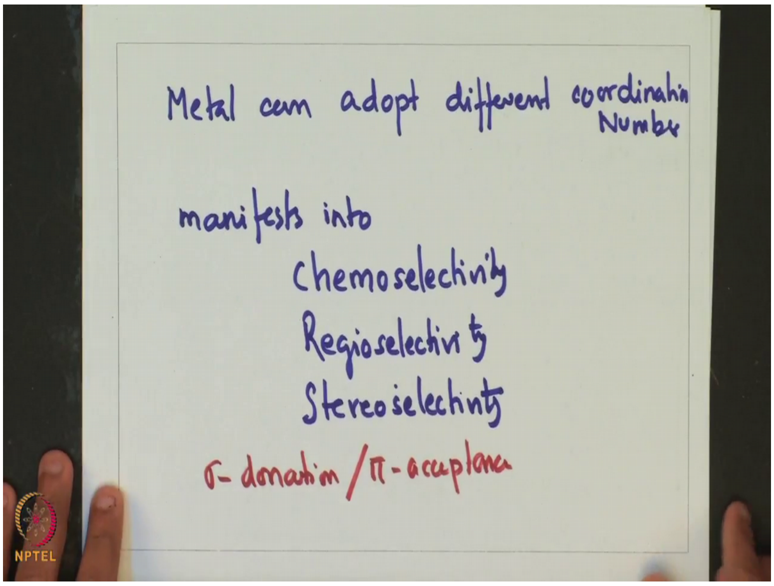

Metal can adopt different coordination Number

manifests into
Chemoselectivity
Regioselectivity
Stereoselectivity

σ- donation / π- acceptance

And in terms of reactivity what it means, that as the coordination number is changed, our variation of it is allowed. Then the middle compound can show chemo selectivity, manifests into chemoselectivity, regioselectivity and stereoselectivity. So, this is indeed a wonderful reactivity pattern that arises out of this or variability in coordination number of transition metal, and which in turn arises from sigma on its ability to undergo sigma donation, and pi acceptance, same property of its orbital, the valence orbital.

So, what we came to know today is that, that there is a significant amount of interactions, which arises due to partial occupancy of the metal d orbital, and these leads to such kind of sigma bonding and pi bonding. Now sigma donation of metal.

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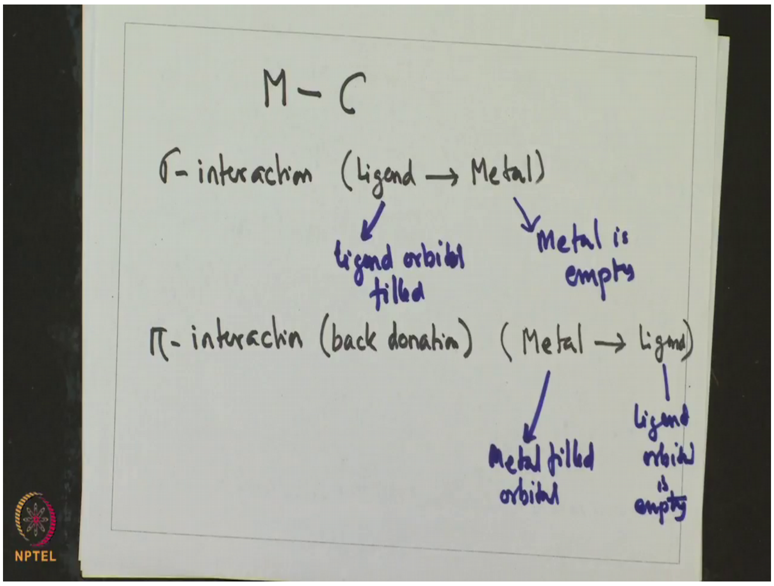

Let us say we have a metal carbon bond. It can have an interactions like sigma interactions, as well as pi interactions. The sigma interaction is usually from ligand to metal, and whereas, the pi interaction usually called back donation, occurs between metal to ligand. So, what does that mean that the ligand orbital, in sigma interaction ligand orbital is filled, and metal orbital is empty. Whereas, in pi interaction, the metal orbital is filled and ligand orbital is empty. So, what happens over here is two opposing electron donation that happens between the metal and the carbon. In the first one is the sigma interaction, where field ligand orbital donates; it is all this electron to the metal, and in return the metal gets its electron reach, and through its pie back donation orbital, field metal orbital, then donates on to the ligand orbital.

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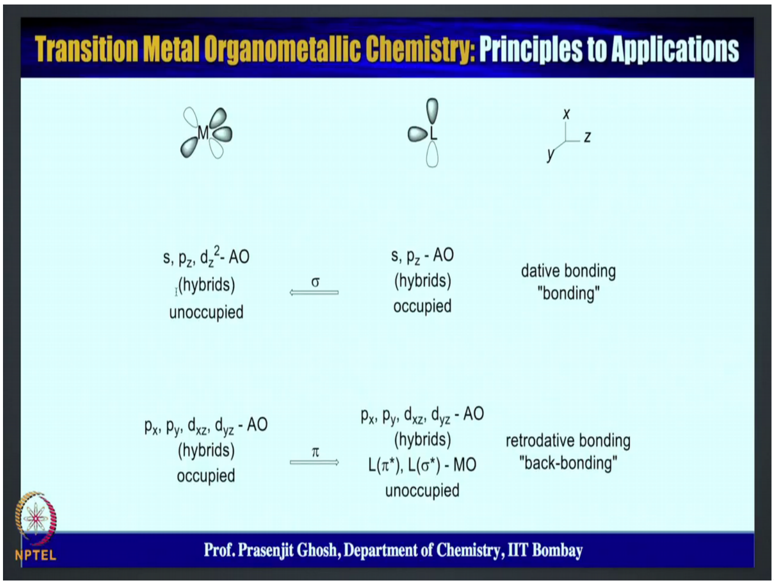

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s, p_z, d_{z^2} - AO (hybrids) unoccupied	$\xleftarrow{\sigma}$	s, p_z - AO (hybrids) occupied	dative bonding "bonding"
p_x, p_y, d_{xz}, d_{yz} - AO (hybrids) occupied	$\xrightarrow{\pi}$	p_x, p_y, d_{xz}, d_{yz} - AO (hybrids) L(π^*), L(σ^*) - MO unoccupied	retrodative bonding "back-bonding"

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And these two forward donation and backward donation are symbiotic in nature, they sort of reinforce each other. As a result they make the bond, all the more stronger.

I must say that this sigma donation and pi back donation synergy is a feature, which is unique to transition metal complexes, and hence something which is unique to organometallic chemistry. Usually such a sigma donation and pi back donation are rare for nonmetals, or as well as for alkali and alkaline earth metal. So, these makes transition metal complexes unique, and as well as they exhibit several properties in various important transformations.

So, with this I would briefly summarize todays, the highlights of today's lectures in which we have looked into the reactivity. We have also looked into the metal ligand interaction, we have looked into the directions in which the electrons flow from the metal to the ligand, and the ligand to the metal. And we have also looked at the reasons, which leads to such synergism that happens between metal ligand interaction, leading to sigma donation, and pi back donation. Now with this foundation in place, we are going to take a look at another important principles that in the next lecture; that is about the compounds or classification of the compound, based on the 18 valence electron rules that we have learned today.

We have also learned the origin of this 18 valence electron rule, and how they come about in transition metal complexes. So, with this, I hope you enjoy today's lecture, and let us look forward to the next lecture, where we are going to look at the classifications of 18 valence electron rule based principles in various organic compounds.

Thank you.