Transition Metal Organometallic Chemistry
Principles to Applications
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Lecture - 07
Week - 02
Reactivity and types of Organometallic compounds

Welcome to this lecture on reactivity and classes of organometallic compounds. This is in continuation with our earlier lecture, where we have looked at various type of organometallic compounds. The classes in which they belong to, which are mainly class 1, class two and class 3, depending upon the famous 18 valence electron rule.

Class 1 types are the ones which does not obey valence 18 valence electron rules. Class 2 types are the ones which does not exceed 18 valence electron rules, and class 3 are the ones which always obey the 18 valence electron rules. What we had seen in the earlier lecture, that there are specific requirements for belonging to each of the classes. For example, for class 1, mainly 3 d transition, metals fall in this category.

So, organometallic compounds of 3 d transition metal belong to class 1 type complexes, as for the class 2 types. They primarily are of 4 d and 5 d mention metals, and their complexes. And lastly for the class 3 types ligand becomes important, and the pi acidic nature of the ligand is crucial for complex, is to exhibit class 3 type of properties. And today we are going to look into this 18 valence electron rule from a critical standpoint. Particularly from the complexes which shows deviations from these for example for late transition metal compounds.

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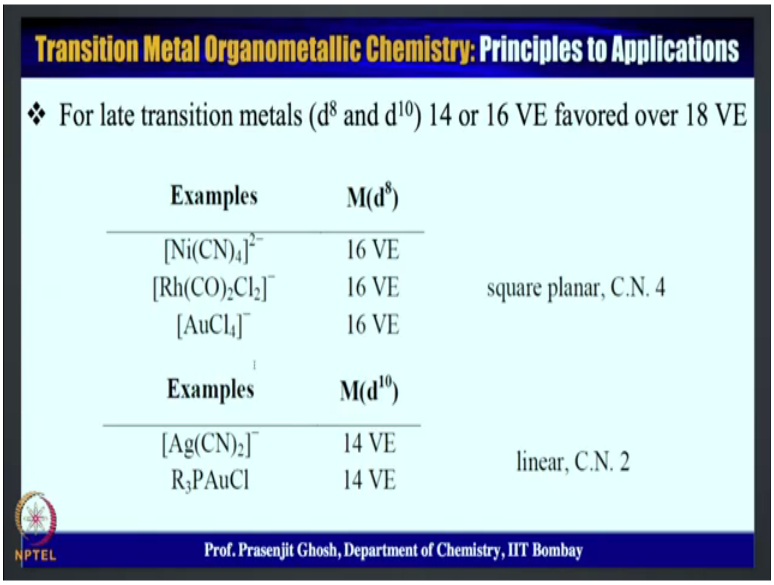

Transition Metal Organometallic Chemistry: Principles to Applications

- For late transition metals (d^8 and d^{10}) 14 or 16 VE favored over 18 VE

Examples	M(d^8)	
$[Ni(CN)_4]^{2-}$	16 VE	square planar, C.N. 4
$[Rh(CO)_2Cl_2]^-$	16 VE	
$[AuCl_4]^-$	16 VE	

Examples	M(d^{10})	
$[Ag(CN)_2]^-$	14 VE	linear, C.N. 2
R_3PAuCl	14 VE	

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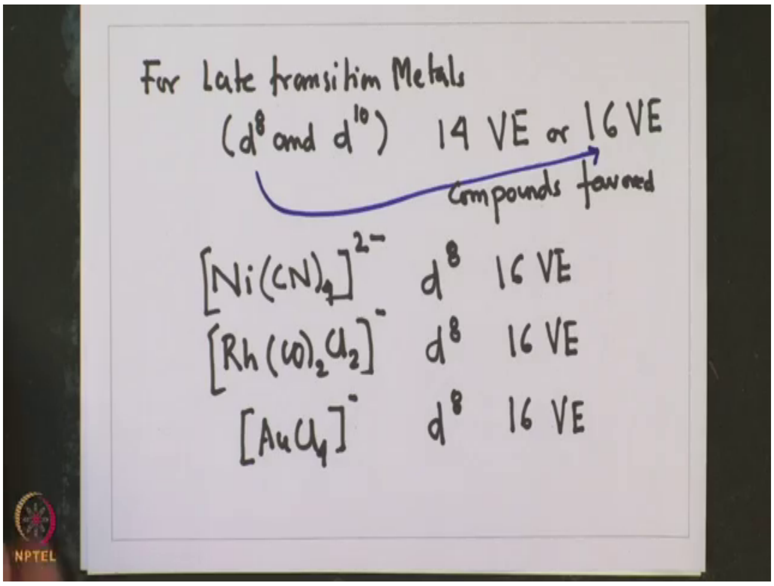

For late transition Metals
(d^8 and d^{10}) 14 VE or 16 VE
compounds favored

$[Ni(CN)_4]^{2-}$ d^8 16 VE
$[Rh(CO)_2Cl_2]^-$ d^8 16 VE
$[AuCl_4]^-$ d^8 16 VE

Particularly d 8 and d 10 ones 14 or 16 14 valence electron or 16 valence electron compounds favoured for example, for nickel tetracyanide 2 minus, it is in d 8 system, and has 16 valence electron. For example, rhodium dicarbonyl chloride dichloride minus is also a d 8 system, having 16 valence electron A u C l 4 minus, similarly is a d 8 16 valence electron.

So, what is emerging is configurations like d 8 prefers to have 16 valence electron over the conventional 18 valence electron for other complexes. Let us take a look at d 10 systems for example.

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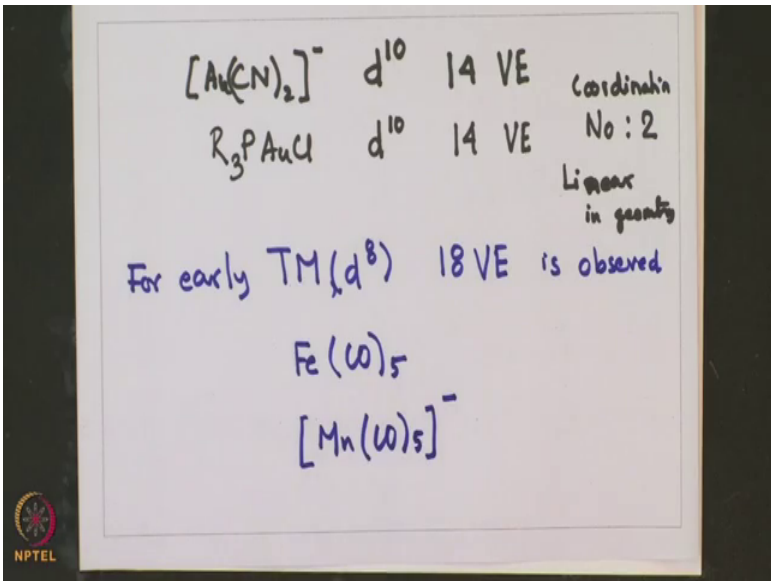

$[Au(CN)_2]^-$ d^{10} 14 VE

R_3PAuCl d^{10} 14 VE

Coordination No : 2

Linear in geometry

For early TM (d^8) 18 VE is observed

$Fe(CO)_5$

$[Mn(CO)_5]^-$

A u C N whole 2 minus is a d 10 system having 14 valence electrons. This is way too different significantly the different from the 18 valence electron, which conventional system show. Similarly with R 3 P A u C l, that also is a d 10 system having 14 valence electrons. This system has exhibit a coordination number of two and a linear in geometry, on the other hand for early transition metals.

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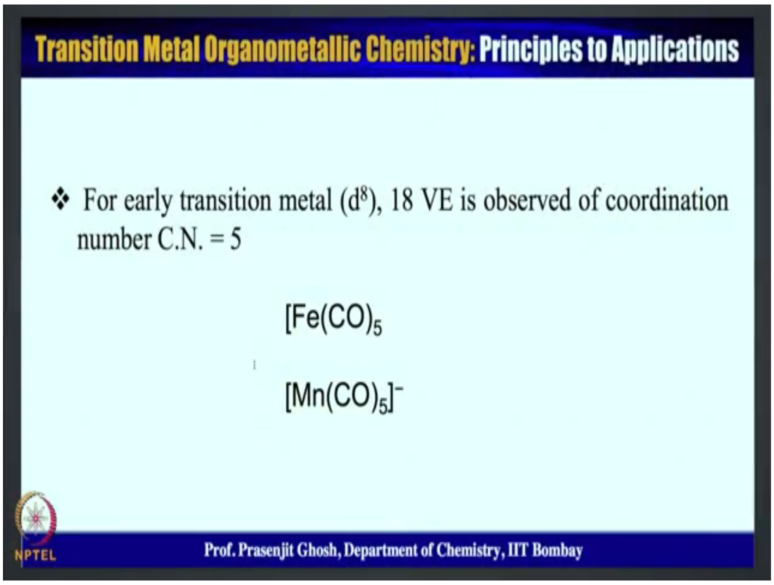

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❖ For early transition metal (d^8), 18 VE is observed of coordination number C.N. = 5

$[Fe(CO)_5]$

$[Mn(CO)_5]^-$

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Having d 8 configuration 18 valence electron is observed, examples is F e C O 5 M n C O 5 minus. So, this discussion is emerging into something very interesting, if I have a transition metal.

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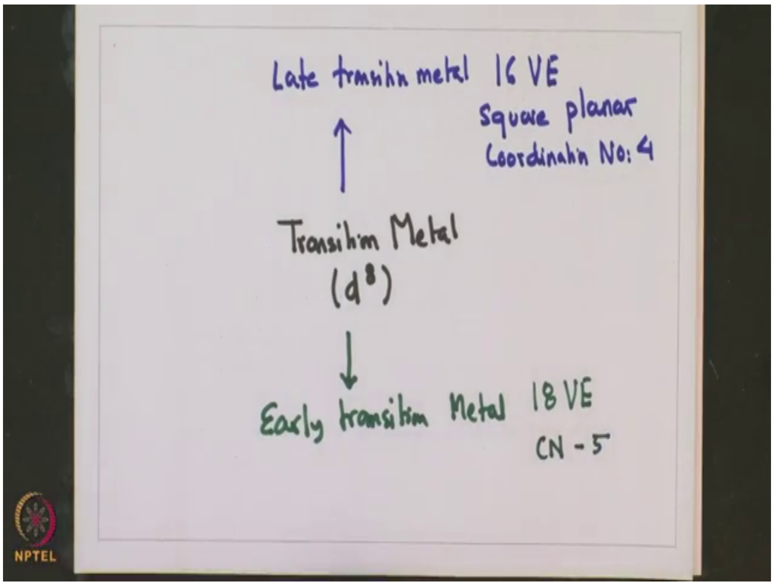

Late transition metal 16 VE
Square planar
Coordination No: 4

Transition Metal
(d^8)

Early transition Metal 18 VE
CN - 5

Having d 8 configuration. Then if it is a late transition metal, then 16 valence electron is there in its valence. Shell is does not obey 18 valence electron rule. It exhibits square planar geometry, and has a coordination number 4. On the other hand, if this transition metal happens to be an early transition metal, then 18 valence electron rule is valid; coordination number is 5 for the examples covered.

Let us look this in an example, with respect to their placement in periodic table.

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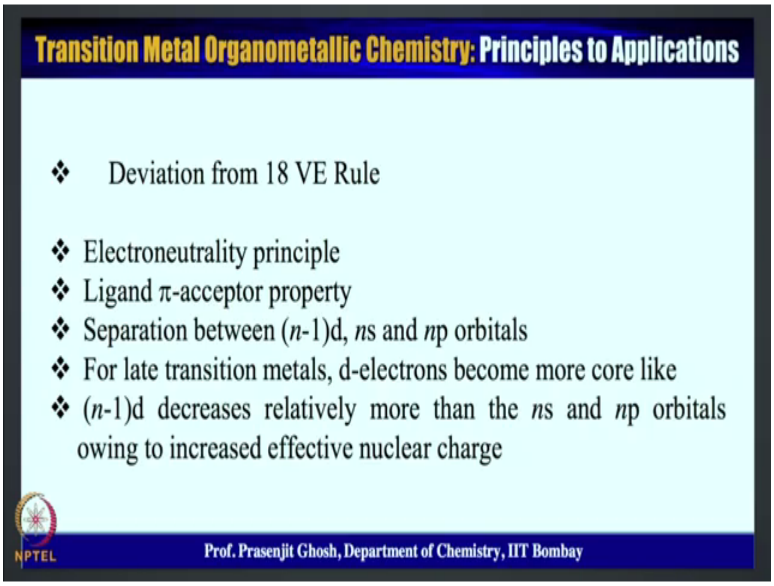

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- ❖ Deviation from 18 VE Rule
- ❖ Electroneutrality principle
- ❖ Ligand π-acceptor property
- ❖ Separation between $(n-1)$d, ns and np orbitals
- ❖ For late transition metals, d-electrons become more core like
- ❖ $(n-1)$d decreases relatively more than the ns and np orbitals owing to increased effective nuclear charge

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So, compounds like.

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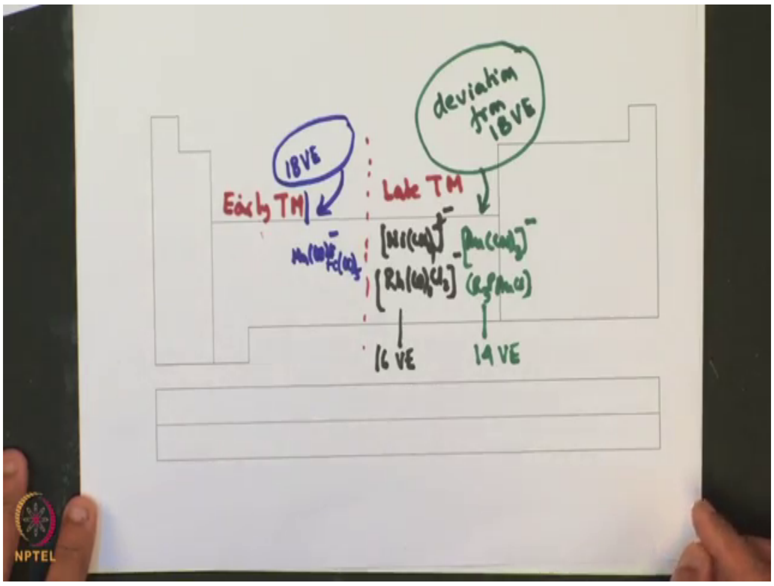

F e c of 5 M n c of 5 minus for them 18 V E rule holds, whereas compounds like N I C n 4 2 minus minus 16 V E rule holds and compounds like A u C n 2 minus R 3 P A u C l 14 valence electron rule holds. So, what is emerging is that the, this part belongs to early transition metal and the other part is late transition metal. So, thing that is emerging is 18 valence electron rule is more valid or more appropriate in this region, and deviation from 18 valence electron rule, is more in the regime of late transition metal compounds; that is a very important observation and a qualitative interpretation for this deviation from 18 valence electron rule is provided from the following. First is electron neutrality principle.

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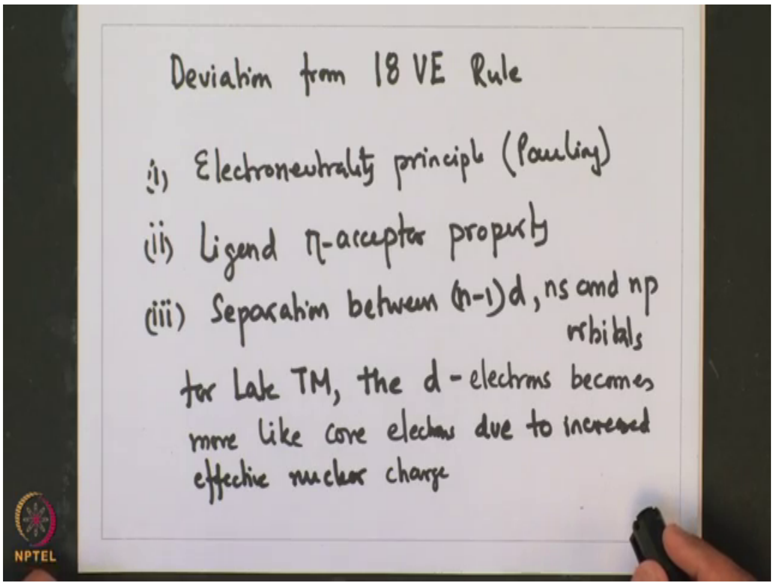

Deviation from 18 VE Rule

(i) Electroneutrality principle (Pauling)

(ii) Ligand π-acceptor property

(iii) Separation between (n-1)d, ns and np orbitals

for Late TM, the d-electrons becomes more like core electrons due to increased effective nuclear charge

So, this was first proposed by Pauling, **a**nd it says in a sense that if a atom metal in our case receives too much electron density, by (Refer Time: 13:16) to ligand, should also find a way to give back the electron density on to the ligand. And hence the electron utility of the atom is maintained, and the factors which lead to metal donating back the excess electron density on to the ligand, it is bound to gives rise to the important concept of ligand pi acceptor ability. This ligand pi acceptor property follows from the electroneutrality principle discussed above and would help in explaining deviations from the 18 valence electron rule. Another important factor which comes into play at the separation of between the n minus 1 d n s and n p orbitals.

Now, as 1 moves across a period towards the late transition metal, the d electrons becomes more core, like more, like core electrons due to increased effective nuclear charge, with increase in atomic number. The other important aspect is the gap between these orbital increases. Let me illustrate this with the following graph for example.

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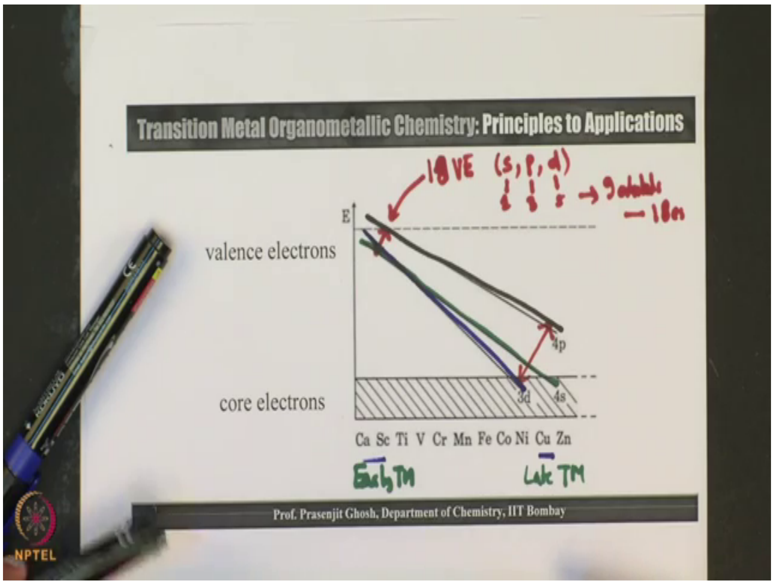

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Here we have the energy, the bottom part or the shaded region shows the energy corresponding to the core electrons, and the top part indicates energy of the valence electrons. As we move from calcium, all the way to the zinc. All the orbitals 3 d 4 s 4 p, they become stabilized. Further going to the increase in effective nuclear charge what is more important, though is the relative stability of these orbitals, as we move across the period. For example, let us take a look at the d orbital which moves from here all the way to there, and in the region of calcium and scandium d 3, d is above 4 s. Where as in the region of copper and zinc, which is the late transition metal 3 d is now lower in energy than 4 s and 4 p.

Similarly, let us look at 4 s orbitals in the early transition metal region domain 4 s is lower than 3 d, and in the late transition metal domain 4 s has become higher than 3 d, and the 4 s decreases as such. Now as for the 4 p there has been a decrease shown by this line, but what is striking though is, that for early transition metal the relative difference between the orbitals, is much smaller than for the play transition metals, where the differences has become bigger as a result orbital participation of all of this orbital for late transition metal becomes more difficult. And I must note that for 18 valence electron rule to hold participation of all s p and d orbitals are required to, because there is 1 s 3, p 5 d having 9 orbitals leading to 18 electrons.

So, that is more possible in the early transition metal domain, where as in the late transition metal domain, because of these large energy gap, such participation of orbitals becomes difficult, and d orbitals become more core like, and inert in nature relative to the s and p. And hence it accounts for lower valence electron coordination complexes.

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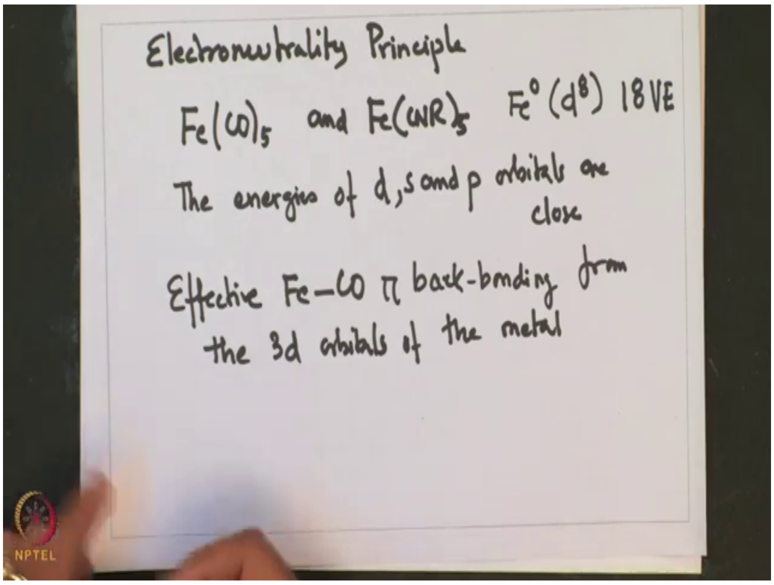

Electroneutrality Principle

$Fe(CO)_5$ and $Fe(CNR)_5$ Fe^0 (d^8) 18VE

The energies of d, s and p orbitals are close

Effective Fe–CO π back-bonding from the 3d orbitals of the metal

For example, for iron system like F e C O 5 and F e C N R 5 the application of electroneutrality principle becomes prominent. These both complexes are F e zero d 8 system, and have 18 valence electron count this being a late transition metal. The energies of d s and p orbitals are close, and as a result of metal center being electron rich going to coordination to all of these ligands. The metal with the availability of all these orbitals, close in energy is such is capable enough to perform effective iron to carbonyl pi back bonding from the 3 d orbitals of the metal.

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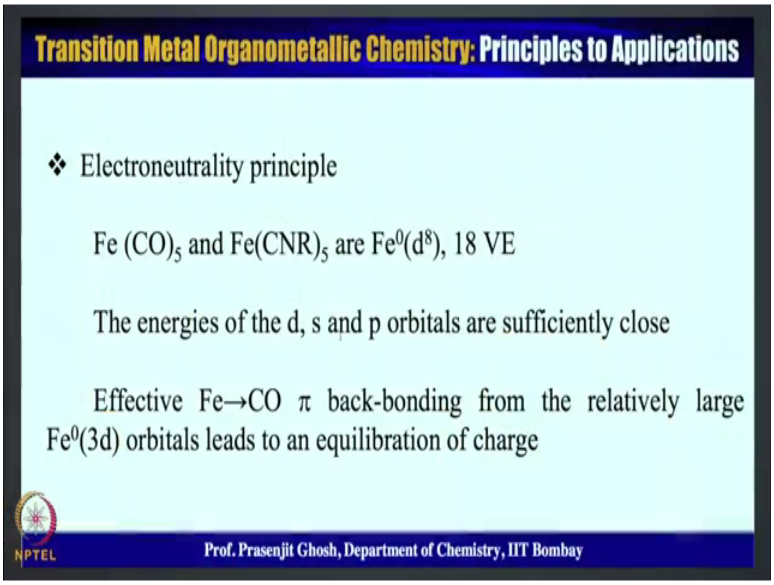

Transition Metal Organometallic Chemistry: Principles to Applications

- Electroneutrality principle

Fe $(CO)_5$ and $Fe(CNR)_5$ are $Fe^0(d^8)$, 18 VE

The energies of the d, s and p orbitals are sufficiently close

Effective Fe→CO π back-bonding from the relatively large $Fe^0(3d)$ orbitals leads to an equilibration of charge

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So, the electroneutrality principle is a fail. So, there is a synergism in which the metal, which accepts electron from the ligand is able to maintain its electroneutrality by a mechanism, where by it donates back some of the electron density to its ligand by virtue of the ligands pi acidic nature for example, for another complex.

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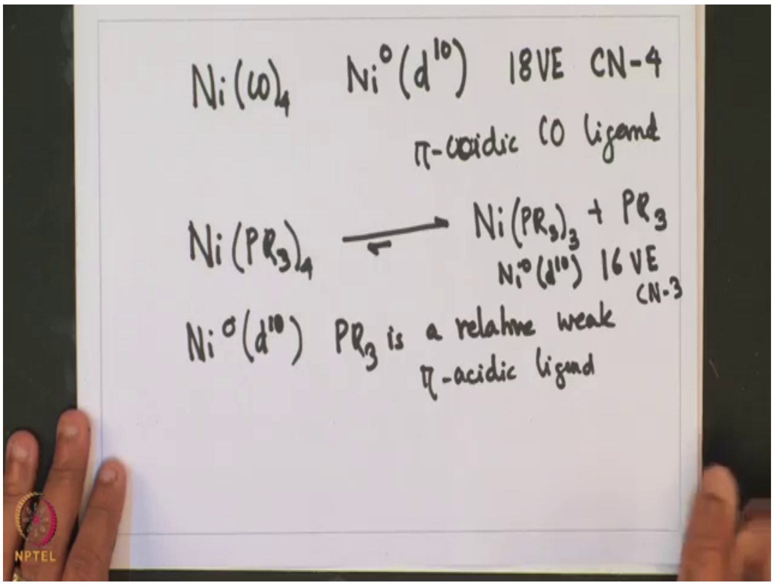

$Ni(CO)_4$ $Ni^0(d^{10})$ 18VE CN-4

π-acidic CO ligand

$Ni(PR_3)_4 \rightleftharpoons Ni(PR_3)_3 + PR_3$

$Ni^0(d^{10})$ 16 VE CN-3

$Ni^0(d^{10})$ PR_3 is a relative weak π-acidic ligand

Let say nickel tetracarbonyl here too nickel is in zero oxidation state, having detail configuration exhibiting 18 valence electron with coordination number 4. What happens, when and nickel is bound to a pi acidic C O C O ligand nickel is bound to a pi acidic C O ligand and whereby nickel can give back electron density on to the ligand. On the other hand in the complex, which is nickel tetra phosphine.

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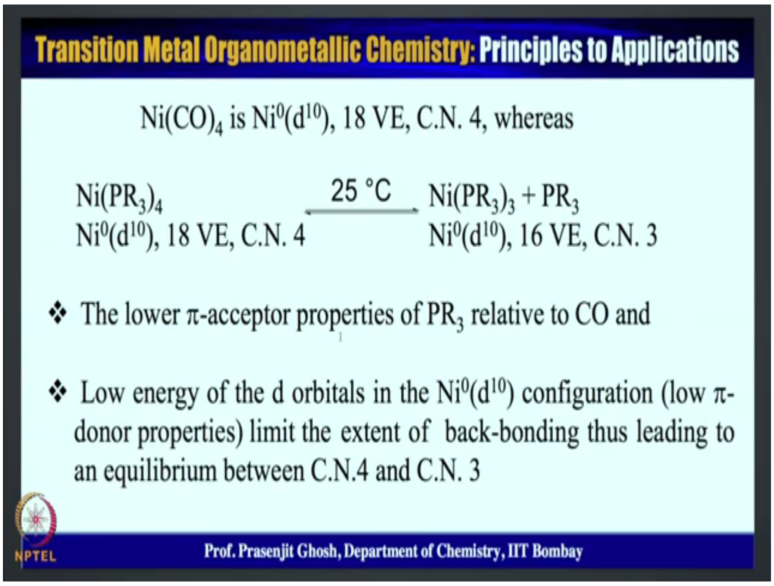

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$Ni(CO)_4$ is $Ni^0(d^{10})$, 18 VE, C.N. 4, whereas

$$\underset{Ni^0(d^{10}),\ 18\ VE,\ C.N.\ 4}{Ni(PR_3)_4} \xrightleftharpoons{25\ ^{\circ}C} \underset{Ni^0(d^{10}),\ 16\ VE,\ C.N.\ 3}{Ni(PR_3)_3 + PR_3}$$

- The lower π-acceptor properties of PR_3 relative to CO and
- Low energy of the d orbitals in the $Ni^0(d^{10})$ configuration (low π-donor properties) limit the extent of back-bonding thus leading to an equilibrium between C.N.4 and C.N. 3

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Here also nickel is a zero oxygen state, having d 10 configuration, but P R 3 is a relatively weak pi acidic ligand as a consequence, because of the lack of the back bonding, this complex sort of stays in equilibrium favouring. A different complex where by N R P R 3 3 and losing a P R 3 ligand here too nickel is in zero, and d 10 system, but 16 valence electron count having coordination number 3.

So, what we saw in this lecture is that, the late transition metals show deviations or has a tendency to show deviation from the. So, called 18 valence electron rule, and this late transition metal particularly of d 8 and d 10 configuration are more common in showing this deviation from 18 valence electron rule.

The deviation from this 18 valence electron rule for late transition metal has been explained by electroneutrality pi acidic nature of the ligand, and also the relative stabilization of N N minus 1 D N S N P orbitals, in which as we go across the periodic table to late transition metal domain, the d electrons become more core, like and they sort of resist is from engaging in balance a bonding.

So, with this, we have come into. We have concluded a series of lectures on the properties classifications of organometallic compounds, and then we going to take up something more interesting in the next lecture, that will be on the classification of the middle conjugate, or rather the ligand part are, and their reactivity. So, thank you for being with me in this lecture. And I look forward to being with you in the next lecture, which will look at various kinds of ligands available for binding two metals in the organometallic compounds.

Thank you.