Advanced Transition Metal Organometallic Chemistry
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Lecture – 31
Transition Metal C 7 H 7 Complexes: Reactivity

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. As a part of various types of transition metal orgonometallic complexes particularly from the perspective of different ligands that exists, we have been talking about a transition metal C 7 H 7 complexes and in that discussion in the last class we have looked into various methods which are available for preparation of these transition metal C 7 H 7 complexes.

Now what had come to the fore, in the discussion that there are about 2 to 3 types of reactions which can eventually lead to the preparation of transition metal C 7 H 7 complexes, and the first of its kind being, the substitution reactions in which metal carbonyls or metal arenes are substituted by treatment with C 7 H 7 ligands. The other method involved reductive coupling in which metal halides are treated with C 7 H 7 R C 7 H 7 ligands in presence of our reducing agent.

We have also seen that photochemically or chemically induced sigma pi rearrangement leading to the formation of these kind of complexes and lastly we have seen that metal vapour to co-condensation methods can also be used for preparation of this transition metal C 7 H 7 complexes. Now today mainly what we are going to be starting off with is particularly look at the reactivity of transition metal C 7 H 7 complexes. Now of these what comes to the fore is the redox processes of these transition metal C 7 H 7 complexes.

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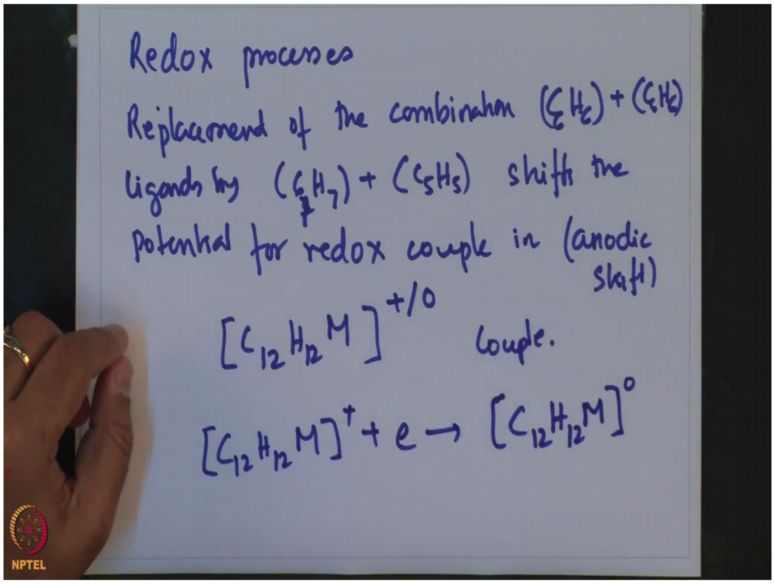

Redox processes

Replacement of the combination $(C_6H_6)+(C_6H_6)$ ligands by $(C_7H_7)+(C_5H_5)$ shifts the potential for redox couple in (anodic shift)

$[C_{12}H_{12}M]^{+/0}$ couple.

$[C_{12}H_{12}M]^{+} + e \rightarrow [C_{12}H_{12}M]^{0}$

Now what comes to the fore is that replacement of the combination of C 6 H 6 of 2 arene ligands which can be C 6 H 6 + C 6 H 6 ligands by C 7 H 7 + C 5 H 5 like shifts the potential for the redox couple in the anodic region so the shift is anodic shift. So, the couple is C12 so overall this can be written as C 12 H 12 M +10 couple. So this means that these can be used for the reaction C 12 H 12 M ++ e giving C 12 H 12 M 0 reaction, and we have values which have been measured for certain complexes are to be mentioned over here will explain our give some insight on the reactivity of these ligands.

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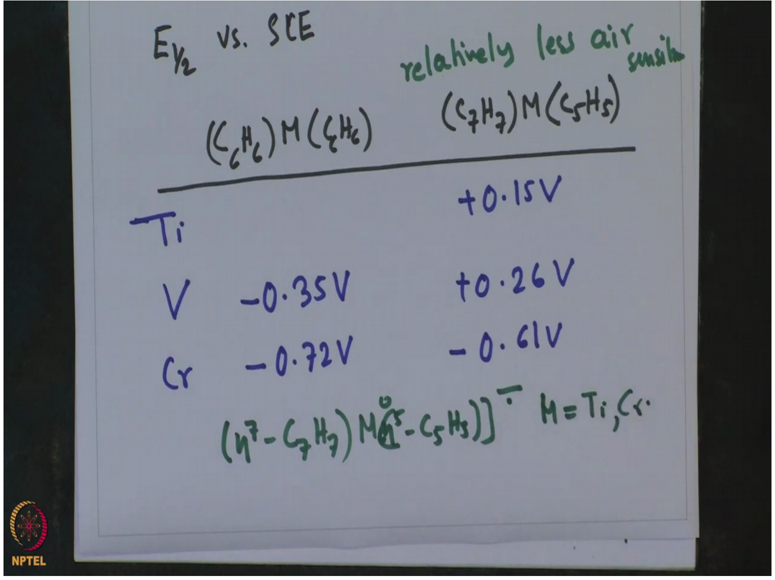

$E_{1/2}$ vs. SCE

relatively less air sensitive

	$(C_6H_6)M(C_6H_6)$	$(C_7H_7)M(C_5H_5)$
Ti		+0.15V
V	−0.35V	+0.26V
Cr	−0.72V	−0.61V

$(\eta^7-C_7H_7)\overset{0}{M}(\eta^5-C_5H_5))]^{-\bullet}$ M = Ti, Cr.

So for example, the E 1/2 values, versus standard calomel electrode SCE for different complexes of the type C 6 H 6 M C 6 H 6 as opposed to C 7 H 7 M C 5 H 5, so if one were to look at these E 1/2 values, for titanium this is about 0.15 volts which the positive value meaning that these reduction from +1 to by accepting a electron to become the neutral is favorable, so that is positive so that means this compound is formed favorably as opposed to existing in its cationic form.

For example for vanadium these complex has a for this complex the 0+ 1 + 1 0 E 1/2 value is about -0.35 whereas that shifts towards becoming +0.26 volts and for chromium, so this is more towards the anodic shift, more towards the positive region for chromium it is -0.72 volt again shifting making anodic shift to -0.61 volt. So, what this sort of tells grossly is the fact that these benzene complexes C 6 H 6 complexes are more air or moisture step stable, more unstable, as opposed to the C 7 H 7 M C 5 H 5.

So they are relatively less air sensitive and that can be easily gauged from this potential values which says that the formation of these neutral complexes from its cationic state is favored for these C 7 H 7 M C 5 combination because this E values are mainly positive with respect to C 6 H 6 metal complexes where formation of these neutral complexes from its cationic state is less favored because now they have very high negative E values which sort of indicates that these are less and what all of these translates to prove is the fact that these compounds are less relatively or less air sensitive.

Now because of these C 7 H 7 MC 5 H 5 complexes being less sensitive, they are like radical cation, anions can also be studied or eyes observed. For example for this complex, eta 7 C 7 H 7 molybdenum M0 eta 5 C 5 H 5 radical anion, has been observed for M equals titanium and chromium. So these can further these complexes can further be reduced to the radical anion because they are 0, no neutral state is quite stable.

So then, now this is an interesting information that we get about the air sensitivity of these C 7 H 7 metal complexes, what we see the combination of C 7 H 7 metal C 5 H 5 which is equivalent to the combination of 2C 6 H 6 complexes of the metal and what we see that C 6 H 6 complexes of the metal are less or more air sensitive as opposed to C 7 H 7 M C 5 H 5 complexes which are less air sensitive and that is primarily because the e values for our formation of the neutral complex from its cationic form has positive E0 values.

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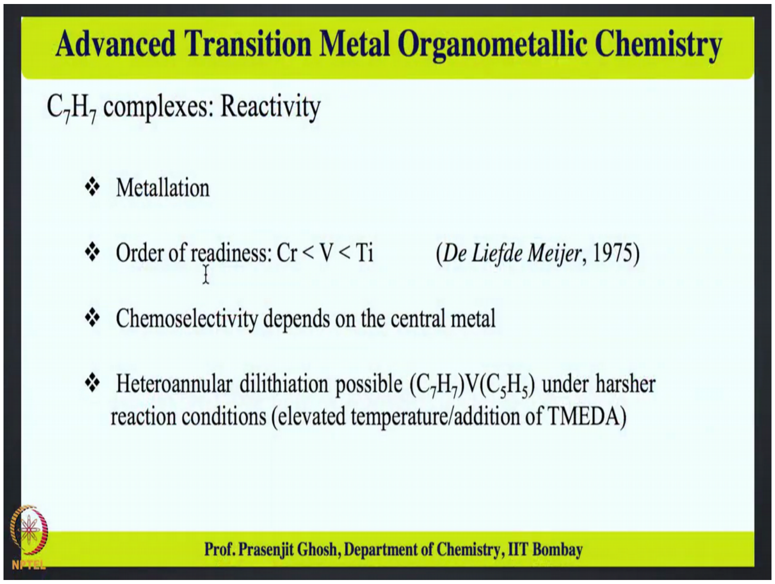

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C_7H_7 complexes: Reactivity

- Metallation
- Order of readiness: Cr < V < Ti (*De Liefde Meijer*, 1975)
- Chemoselectivity depends on the central metal
- Heteroannular dilithiation possible $(C_7H_7)V(C_5H_5)$ under harsher reaction conditions (elevated temperature/addition of TMEDA)

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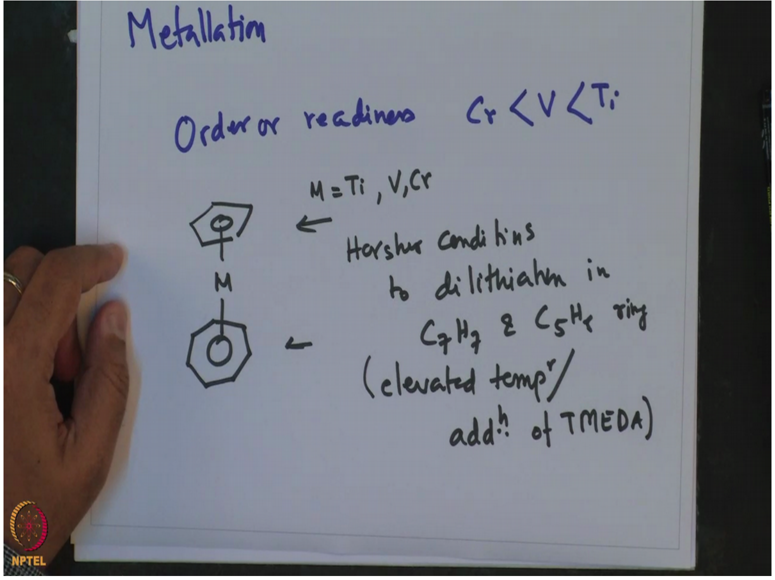

Metallation

Order or readiness $Cr < V < Ti$

$M = Ti, V, Cr$

Harsher conditions to dilithiation in C_7H_7 & C_5H_5 ring (elevated temp^r/ add^n of TMEDA)

So we are going to take a look at the metallation part of these C 7 H 7 complexes and metallation is an interesting reaction that this C 7 H 7 transition metal complexes exhibit and the order of readiness is given by a chromium becoming less than vanadium becoming less than a titanium. So order of readiness chromium vanadium titanium and for this mixed CP a C 7 H 7 type complexes, like the one shown over here the middle can be titanium vanadium chromium the lithiation can happen in both of the rings but requires harsher conditions.

For di lithiation in both C 7 H 7 and C 5 H 5 ring so harsher conditions means elevated temperature and our addition of TMEDA. So these are sort of the conditions in which the metallation can be achieved, so we are going to take this up with some interesting examples where we are going to follow up these metallation which are possible and one thing that emerges out that metallation happens at different rings depending on different metal and that is beautifully illustrated by the example which is given over here.

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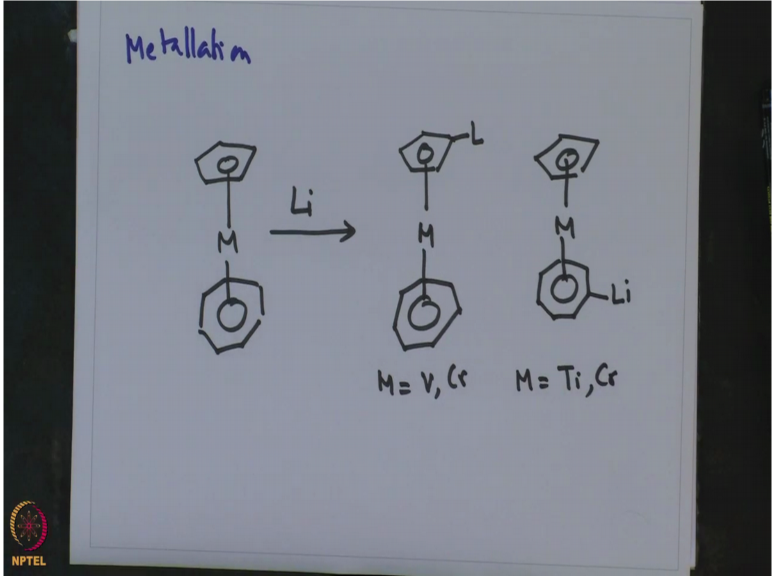

For example for this compound the lithiation in the CP ring occurs for vanadium and chromium where as the lithiation on the C 7 H 7 rings occurs for titanium and chromium, for titanium and chromium. So we are going to spend some more time looking at various chemical reactivity that arises from this variation in the lithiation. And how that leads to generation of conversion of these lithiated derivatives to many useful other compounds.

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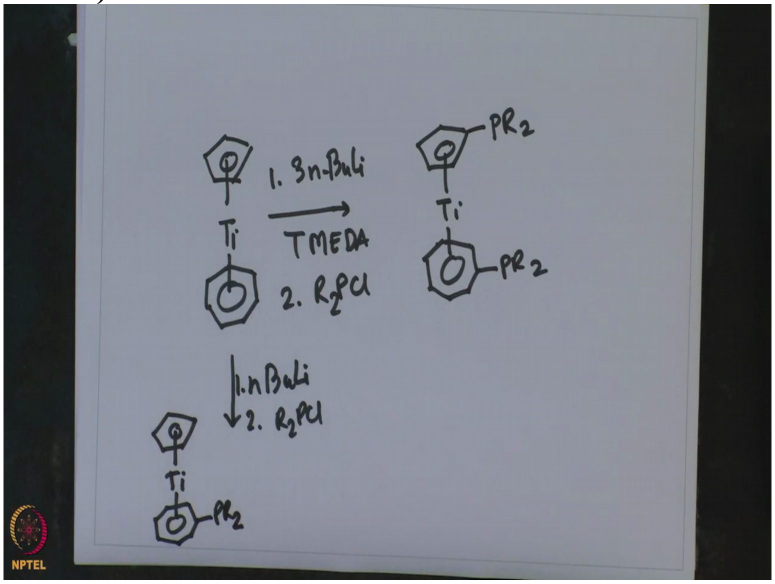

Similarly a di lithiation of the ring can be achieved in presence of TMEDA as was discussed earlier and we are going to see it in this example 3n Bu lithium TMEDA and second is R2 PCl giving this di lithiated product where the phosphination which arises after lithiation happens in 2 different rings whereas if one does the reaction in absence of TMEDA which is taking n butyllithium and second is R2PCl, then one sees that lithiation happening on the cyclopentadienyl ring.

So, the difference lies in this harsher conditions which is TMEDA that leads to dilithiations resulting subsequently resulting in di fastination of both of the rings and in the absence of TMEDA, if one gives the same reagent, one sees the lithiation happening but happening at one of the ring and this ring not being the C 7 H 7 ring but not of the on this is C 5 H 5 cyclopentadienyl ring ok.

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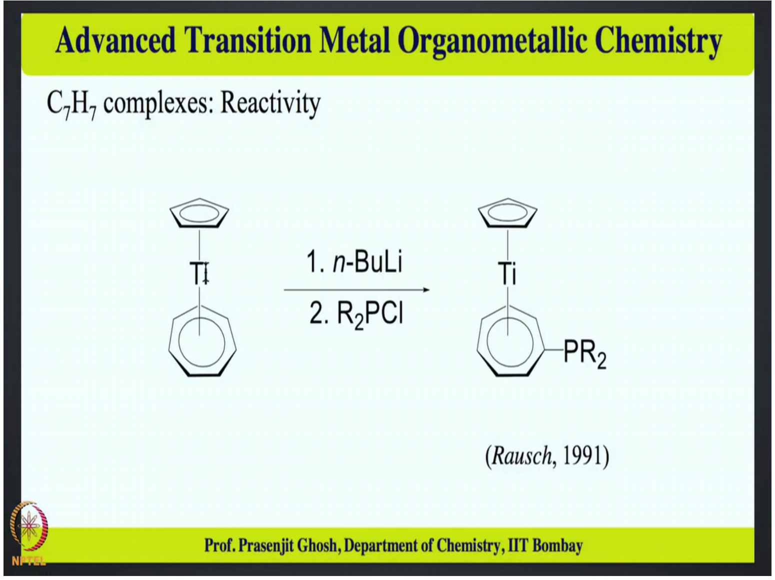

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C_7H_7 complexes: Reactivity

(*Rausch*, 1991)

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Now another nice example of lithiation, this lithiation chemistry on the CP ring is shown over here and in this case there is iodination reaction which has been achieved for the compounds using C 4 C 2 F 4 I 2 reagent and we are going to be discussing this over here.

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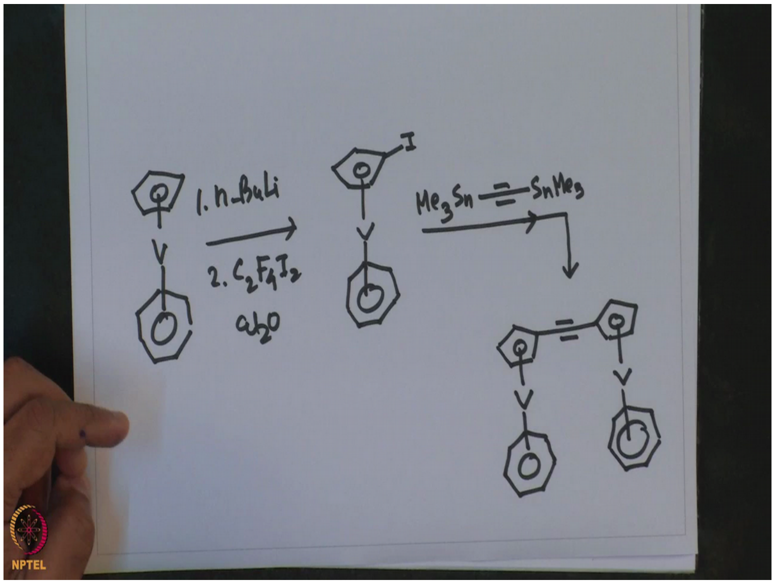

So, this is CP vanadium C 7 H 7 in presence of n butyl lithium and the secondary agent is C2 F4 I2 in ether giving this iodination and in this case the addition happens at the CP ring and that with Me 3 Sn Sn Me 3 would give this dinuclear complex beautiful dinuclear complex where the CP is joined by an alkyne linker and each of the CP is bound to vanadium, so thus 2 CP binding to 2 vanadium and then subsequently, each of the vanadium is bound to C 7 H 7 ring as is shown over here so this is a beautiful work of synthetic chemistry where one can form these dinuclear complexes by sort of achieving lithiation on selectively on the CP ring.

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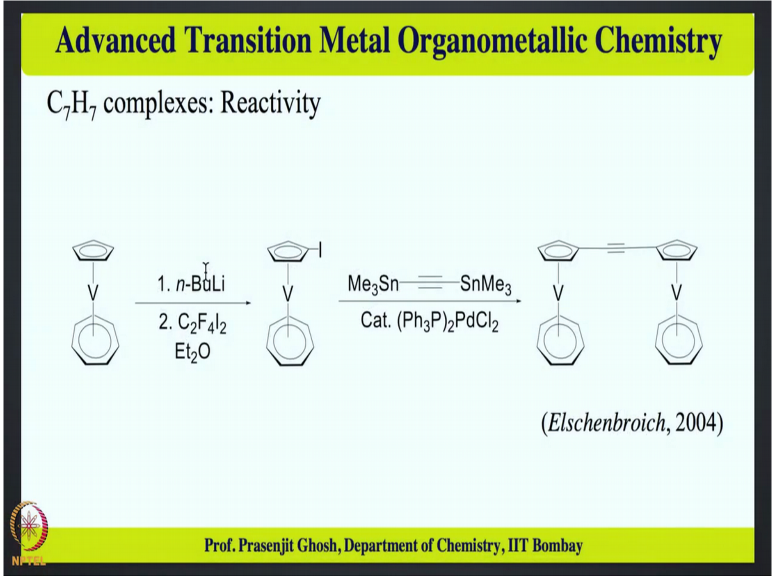

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C_7H_7 complexes: Reactivity

(*Elschenbroich*, 2004)

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So actually lithiation is a powerful reaction which is used as an useful tool for synthesizing various kinds of metal complexes and we see a nice demonstration of this fact in these four or five different examples which we discussed right now under lithiation, which showed that different types of chemical entities can be synthesized by the selective mono or di lithiation using mild or harsh conditions.

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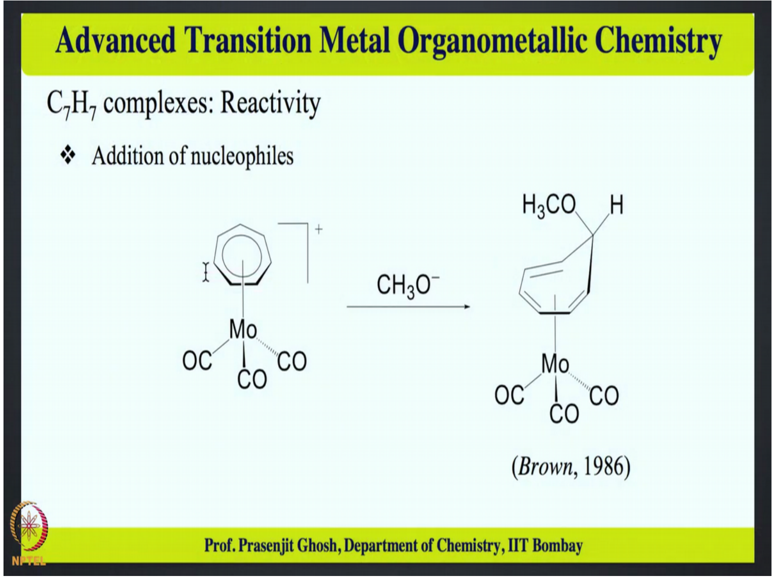

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C_7H_7 complexes: Reactivity

- ❖ Addition of nucleophiles

(*Brown*, 1986)

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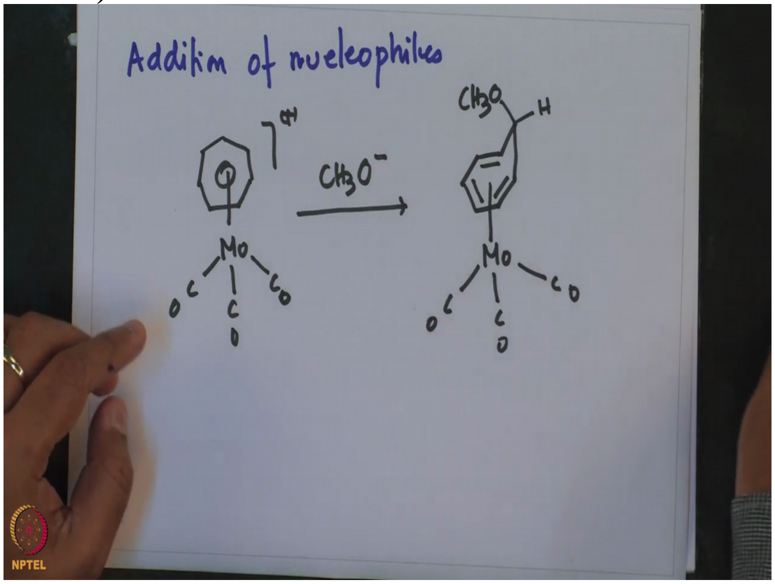

Addition of nucleophiles

So now we are going to take a look at another interesting reactions which are addition of nucleophiles now in these, this is the cationic C 7 H 7 MO CO 3+ complex which reacts with methoxide CH3 O- giving this CH3 O, so CH3 O attacking the ring molybdenum and what is interesting thing over here that this nucleophile does not go and attack molybdenum but instead attacks this C 7 H 7 ring and then as a result this mm, cyclo cycloheptatriene is formed. And this attack as discussed over here as well as another compound is exo attack which attacks from the outer periphery of the ring.

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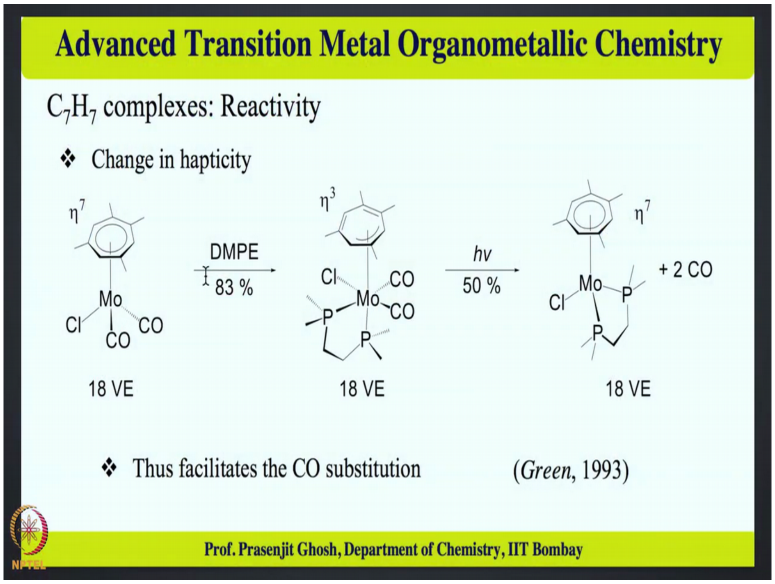

Advanced Transition Metal Organometallic Chemistry

C_7H_7 complexes: Reactivity

- Change in hapticity

- Thus facilitates the CO substitution

(*Green*, 1993)

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Now another example of change of hapticity is observed over here this is also elegant reactivity in which diversified chemistry is sin. So this is a nice illustration in which the hapticity of C 7 H 7 ring changes.

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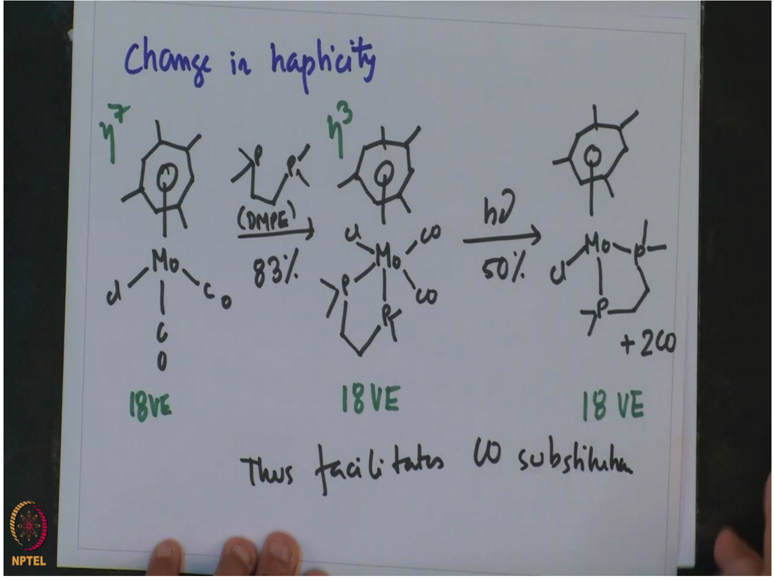

So for these substituted molybdenum chloride CO this is eta 7 compound and 18 valence electron in presence of dimethyl phosphino methyl or DMPE gives this DMPE coordinated compound, Team B coordinate compound which also is a eta 3 bound 18 valence electron species, which eliminates carbon monoxide and this forward reaction is very high yielding formed in 83% eliminates carbon monoxide to give the eta 7 bound molybdenum phosphate chloride +2 CO and that also is a 18 valence electron compound and these reaction facilitates thus facilitates CO substitution.

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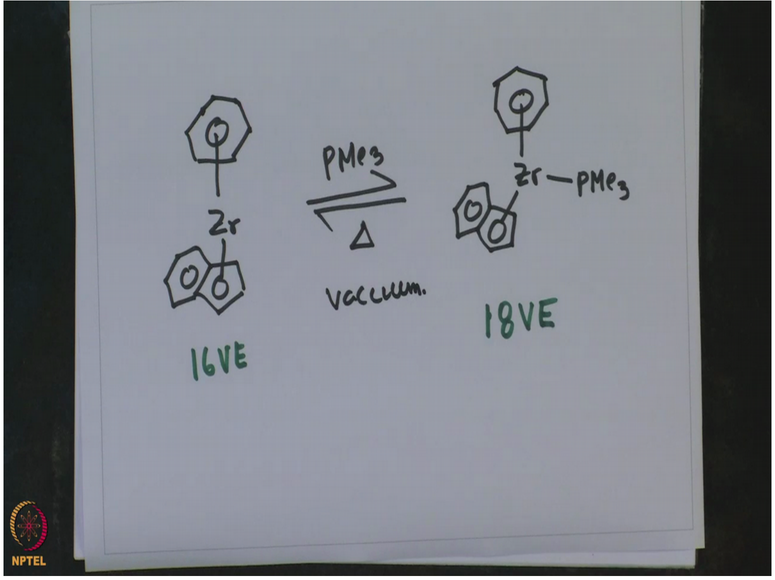

So in this we are going to see another nice example in which a 16 electron compound becomes an 18 electron species by coordination and this is illustrated in this mixed ligand compound zirconium PMe 3. So this is a 16 valance electron species easily coordinates with the PMe 3 giving zirconium PMe 3 adduct, of this complex which also is a 18 valence electron species and under vacuum these goes back and gives back the 16 electron species.

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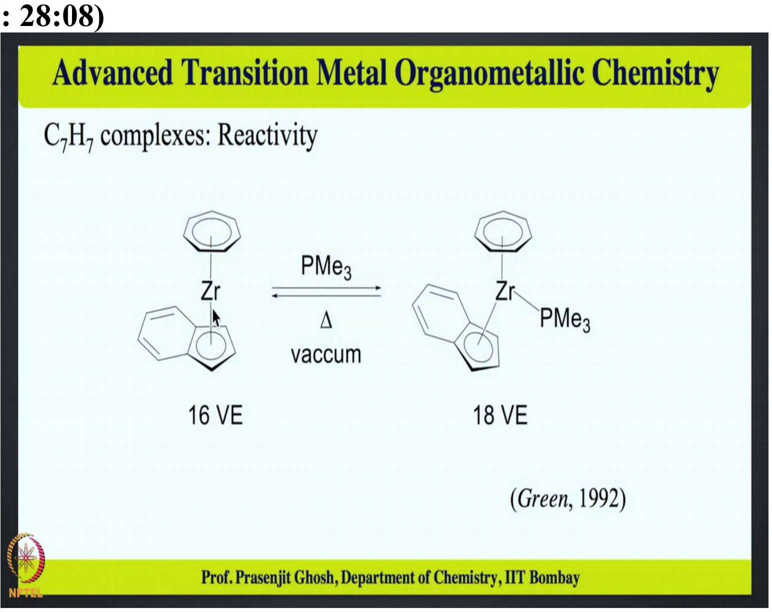

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C_7H_7 complexes: Reactivity

(*Green*, 1992)

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So with these we come to an end of our discussion on C 7 H 7 complexes for in today's class and what we had seen is that we are spoken about reactivity of the C 7 H 7 complexes particularly looking at the various redox processes, for present for these C 7 H 7 type complexes and what we had seen that mixed C 7 H 7 metal, C 5 H 5 complexes are slightly less air sensitive as opposed to be C 6 H 6 metal complexes, and also we had seen that these C 7 H 7 complexes, translate to many other, can be converted to many other, type of compounds by lithiation and lithiation can be selectively achieved in each of the ring or in both the ring depending on the conditions in which the lithiations are tried.

We have also looked at the nucleophilic attacks and what we had seen that nucleophilic attacks occur on to the ring instead of the metals and we have also seen examples, where one can see the change of hapticity occurring in these complexes. So, with these I would like to conclude our today's discussion on C 7 H 7 complexes particularly on the reactivity a little bit more is left on the reactivity of C 7 H 7 complexes which would be taken up in the next lecture and in the next lecture we would also be taking up a new ligand which is C 8 H 8 ligand and look into their reactivity synthesis reactivity and property studies.

I thank you for being with me in this lecture and patiently listening to all that has been taught in today's lecture and I very much look forward to being with you in the next lecture when we finish off with C 7 H 7 ligands and take up C 8 H 8 ligands of transition metal complexes. Thank you and good bye.