

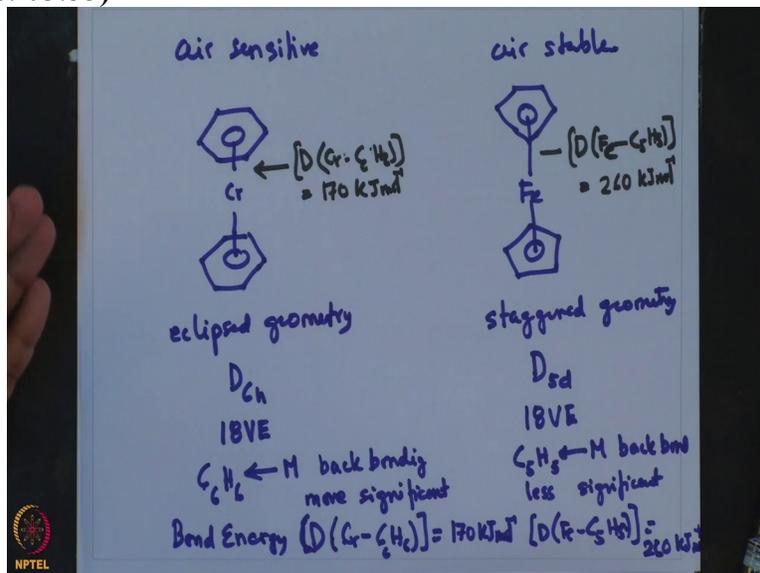
And we had seen that the several ligand based orbital remains nonbonding in the sense that they do not engage in any atomic orbital on the metal side. And these nonbonding orbitals are a 2g as shown over here in green and then e 2u seen over here in green and these to b 1u and d 2g remains nonbonding in the sense that they do not interact with anything. So, these are the benzene bis benzene atomic orbitals which remains nonbonding and does not interact with the ligand orbitals.

Similarly from the metal counterpart the a 1g metal d orbital remains nonbonding as can be seen over here also the p orbital a 2u one of the p orbital remains nonbonding. So, the orbitals which remains nonbonding are show over here and the rest of the orbitals they engage in bonding the 18 valence electron that compounds have goes up to a 1g filling that is the Sigma. So, that 18 goes around 2, 4 this is 8, 12, 2, 4, 6, 8, 10, 12, 14, 16, 18.

So, this is how the 18 orbitals are filled and one last thing about previous discussion is the fact that the time of kind of interaction one exists this e 2g, e 2u engage in delta type interaction a 1g engaged in Sigma interaction and e 1g star engaged in Pi type interactions. So, these are the three interactions Sigma, Delta, Pi type which are prevalent in these benzene chromium of d 6 symmetry.

Now I would sort of dwell upon little bit on the differences as well as similarities of these B's benzene as well chromium as well as this cyclopentadienyl iron complexes.

(Refer Slide Time: 05:33)



For example, chromium is in Eclipsed geometry and this is by far the most stable one has seen from the x-ray structure whereas this cyclopentadienyl iron is in a staggered geometry these are again the probably the more, more stable conformation. The point group over here is D_{6h} over here it is D_{5d} and then the similarity is that both are 18 valence electron compounds, both are 18 valence electron compounds.

As far as the metal to ligand bonding is concerned metal to ligand Δ bonding is more predominant in this as well as compared to the this iron complexes. So, C_6H_6 back bonding more, more significant as compared to comparatively this is more compared as to this this kind of makes sense or kind of quite intuitive given the fact that benzene is a neutral ligand. So, electron donation from metal onto a neutral ligand is probably more feasible as opposed to cyclopentadienyl anion where it is already an ionic in nature and hence the back bonding of electron donation from metal to already electron anion is kind of going to be a less prominent.

So, that is a significant difference also the bond energy the benzene chromium bond energy $D_{CR C_6H_6}$ is less 170 kilo Joule per mole whereas in ferrocene $D_{Fe C_5H_5}$ the bond energy is 260 kilo joule per mole. So, now this CP this is more strongly bound the $Fe C_5H_5$ is 260 whereas $D_{CR C_6H_6}$ equals 170. So, what on the face what we see is that this is a weaker bond as compared to this cyclopentadienyl ferrocene and that also is quite intuitive given the fact that cyclopentadienyl anion is a negative anionic ligand and hence it binds more strongly to the electron deficient cationic iron species giving rise to more stronger bond having higher bond dissociation energy.

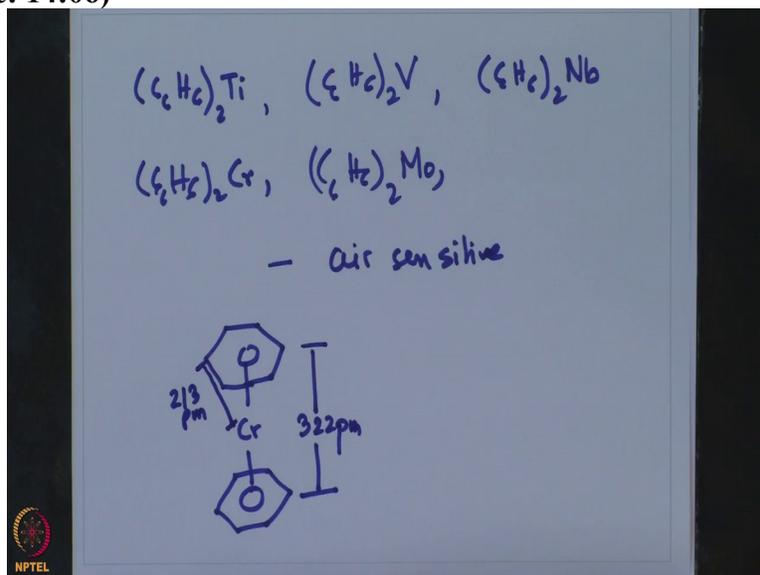
Whereas arene's being neutral ligand they bind less tightly to cationic metals and as a result this bond dissociation energy is quite low. And another important thing about this Bis-arene complexes in general is that these bis-arene complexes are quite air sensitive whereas the metallocene most of them are air stable. So, for example over here this chromium is air sensitive whereas the corresponding the metallocene counterpart this iron is air stable.

So, we had made a sharp parallel compare and contrast between the this one representative example of these arene complexes in the form of this 18 electron bis benzene chromium with that of another 18 electron Bis cyclopentadienyl iron complexes and what we found that there are certain similarities for them as well as there are certain differences. The similarities being that they both are 18 valence electron compounds.

The differences being that the chromium bis benzene is air sensitive iron bis cyclopentadiene in the air stable the chromium bis benzene exist in eclipsed geometry which is the most stable conformation whereas iron the cyclopentadienyl compound exist in staggered geometry. Also the back bonding is more predominant in bis benzene chromium as compared to the back bonding or Delta interaction in iron bis cyclopentadienyl complex.

And lastly the bond energy of arene metal bond energy is less as compared to the cyclopentadienyl metal bond energy in the metallocene. So, here is a sharp compare and contrast between a representative example of a bis-arene transition metal complex and that of these bis cyclopentadienyl iron transition metal complexes. Not only the bis-arene the chromium air sensitive almost all of the known transition metal base benzene complexes are air sensitive.

(Refer Slide Time: 14:06)

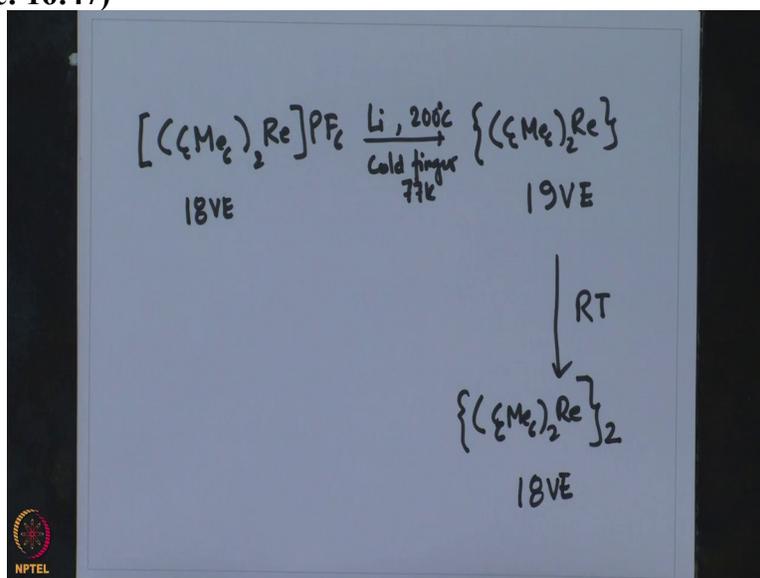


The example being C_6H_6 whole 2 titanium C_6H_6 whole 2 vanadium C_6H_6 whole 2 niobium C_6H_6 whole 2 chromium C_6H_6 whole 2 molybdenum so on and so forth. So, these, all of these are almost extremely air year sensitive to great extent okay. Now another spectral feature of these bis-arene complexes involves the structural characterization of bis-arene complexes and which has shown that the ligand to ligand distance in X eclipsed this chromium compound is 322 picometer and chromium to the edge of the ring is 213 picometer.

Also there is an interesting example in which 19 electron bis exomethyl benzene derivative of rhenium can be prepared from the 18 electron counterpart there is a nice example in which bis benzene rhenium a 19 electron unstable compound can be prepared from the bis benzene

rhenium 18 electron counterpart and being unstable it dissociates immediately to form a diamagnetic compound.

(Refer Slide Time: 16:47)



The equation is given over here so this is C₆Me₆ hexamethyl benzene 2 rhenium PF₆ this is 18 valence electron complex in presence of lithium at 200 degree centigrade and then the depositing in the cold finger at 77 Kelvin these very intriguing 19 electron complex C₆Me₆ whole 2 rhenium is isolated. Now this is a 19 valence electron compound which is isolated at very low temperature of 77 Kelvin and then at room temperature it decomposes to give this dimer C₆Me₆ whole 2 re which again is a 18 valence electron compound okay.

So, another interesting feature about these bis-arene complexes are their reactivity and one important aspect is that they are very air sensitive.

(Refer Slide Time: 18:31)

Advanced Transition Metal Organometallic Chemistry

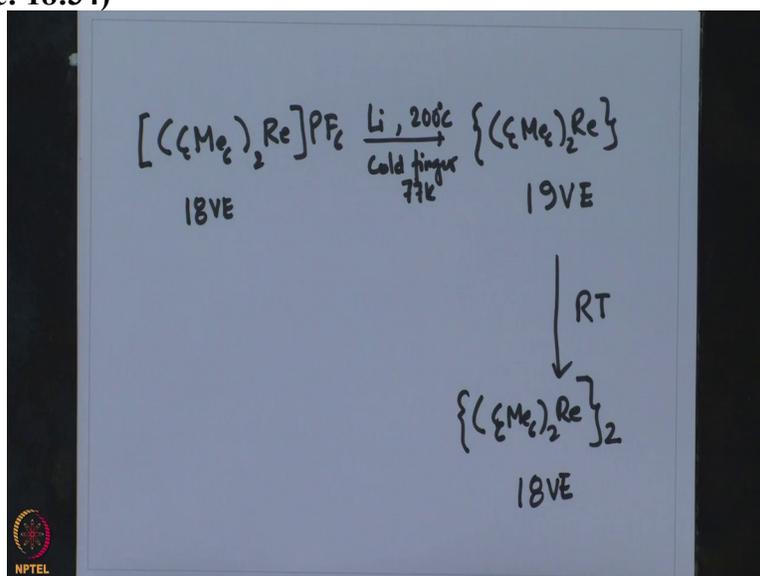
Bis(arene) Metal Complexes: Reactivity

- ❖ Oxidation
- ❖ The complexes with pure hydrocarbon ligands in bis(arene) complexes are air sensitive
- ❖ This can be overcome by the replacement of hydrogens with electron withdrawing groups
- ❖ eg, $(\eta^6\text{-C}_6\text{H}_5\text{Cl})_2\text{Cr}$ is air stable



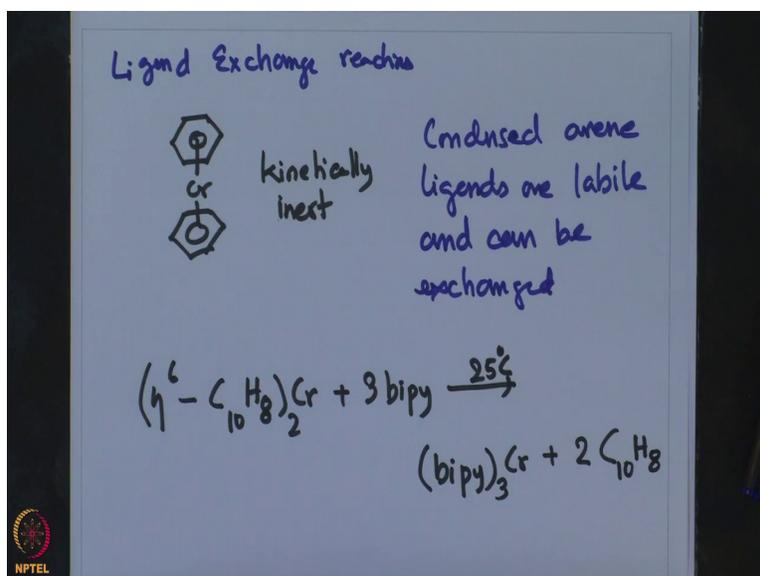
Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 18:34)



And prone to oxidation so all neutral bis-arene metal complexes are air sensitive and vulnerable to oxidation and so this is something which is sharp quite sharp in contrast to that of ferrocene or the metallocene complexes. Many 18 electron metallocene complexes are quite stable in here in moisture and not as much susceptible to oxidation as the current bis-arene complexes are and these tendency to overcome oxidation is achieved by replacement of hydrogen's with electron withdrawing group can overcome vulnerability towards oxidation example eta 6 C 6 H 5 Cl whole 2 chromium is air stable.

(Refer Slide Time: 21:01)



The next important reactions are these ligand exchange reactions and in the ligand exchange reactions just simple bis-arene transition metal complexes are kinetically inert towards ligand exchange whereas condensed means which has multiple cyclic arene rings fused together they are more labile towards ligand exchange reactions and can be exchanged. So, this is an interesting observation. For example this benzene chromium is kinetically inert whereas condensed condensed arene ligands are labile and can be exchanged.

For example as it shown over here whole 2 chromium +3 bi pyridine at 25 degree centigrade keeps chromium +2C₁₀H₈.

(Refer Slide Time: 23:39)

Advanced Transition Metal Organometallic Chemistry

Bis(arene) Metal Complexes: Reactivity

- ❖ Ligand exchange
- ❖ The condensed arene ligands are labile and can be exchanged

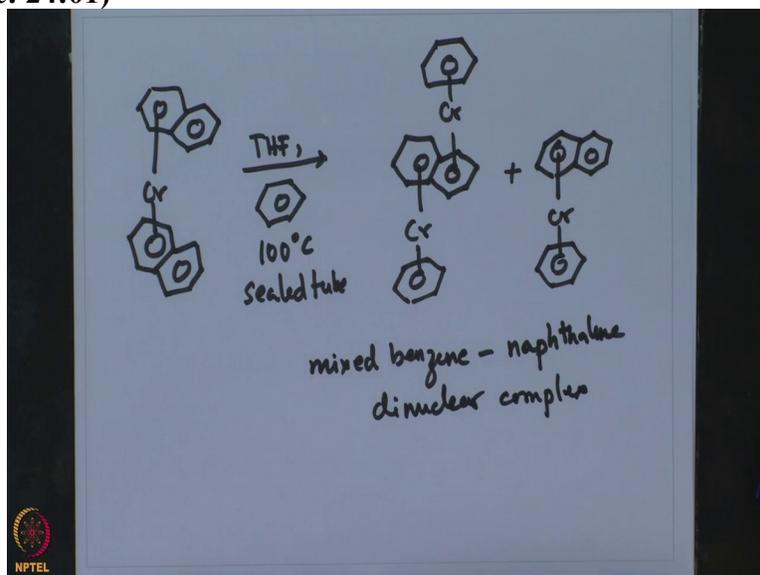
$$(\eta^6\text{-C}_{10}\text{H}_8)_2\text{Cr} + 3 \text{bipy} \xrightarrow{25^\circ\text{C}} (\text{bipy})_3\text{Cr} + 2 \text{C}_{10}\text{H}_8$$

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay



Another interesting example of this is shown over here and has been successfully used for synthesizing mixed benzene ethylene dimethyl metal complex.

(Refer Slide Time: 24:01)



I will illustrate this with this beautiful example in which this benzene naphthalene chromium complex in THF in presence of benzene at 100 degree centigrade in a sealed tube gives this beautiful mixed benzene naphthalene di nuclear complex and naphthalene dinuclear complex and this exploits this ligand exchange ability of condensed arene chromium complex. So, this is the nice work in which this mixed benzene ethylene dinuclear complex can be observed.

Another interesting feature about these arene complexes is that unlike the metallocene counterparts the bis-arene complexes does not undergo a electrophilic aromatic substitution reaction. So, this also is a prominent deviation from the chemistry that we had observed for bis-arene cyclopentadienyl transition metal complexes.

(Refer Slide Time: 27:10)

Bis(arene) metal complexes do not undergo Electrophilic Aromatic Substitution
reactions similar to metallocenes.

- As attacking electrophiles oxidizes the central metal atom.

The fact is that these are in metal complexes do not undergo electrophilic aromatic substitution reactions substitution reactions similar to metallocene's and as a as attacking electrophiles oxidizes the central metal atom. So, this is a interesting deviation for bis-arene complexes in terms of chemical reactivity with regard to that of Bis-arene cyclopentadienyl transition metal complexes.

So, with this I would like to draw conclusion on today's lecture in this lecture we have started off by looking at the electronic structure of this benzene chromium complex particularly with regard to the molecular orbitals that are engaged in the overall molecular structure resulting in their electronic structure. We had also seen how these electronics molecular orbital filling led to their lead to their chemical reactivity and property.

We have also drawn a parallel for Bis-arene transition metal arene complexes with regard to be cyclopentadienyl transition metal complexes in terms of their total valence electron counts reactivity a then bond energy in terms of the extent of metal to ligand back donation occurring in these complexes. We have looked into some of the key features that arises out of this electronic structure of these bis-arene complexes.

And we have looked into reactions like oxidations then ligand exchange as well as electrophilic substitution aromatic substitution reactions for these are in transition metal complexes. So, with this I would like to close today's discussion on the reactivity of transition metal Bis-arene complexes some more discussion still remains on this reactivity talk that we are discussing and would like to conclude that in the next lecture like, so I would like to again thank you for being with me in this lecture.

And I look forward again to initiate this discussion in the subsequent lecture when you take out the reactivity of bis-arene transition metal complexes in bit more detail till then goodbye and thank you.