Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 11
Lecture - 53
Transition Metal Olefin Complexes: Reactivity

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing Transition Metal Olefin Complexes over the last few lectures, particularly in the last lecture we have looked at various kinds of reactivity and bonding of transition metal olefin complexes.

In particular we have looked at how the bonding effects the reactivity of this kind of a complexes and these as has been mentioned earlier they are very important intermediates in many catalytic cycles, for example, hydrogenation, metathesis, polymerization reactions, oligomerization reactions and so on and so forth, isomerization reactions and hence, it is important to study the chemistry of transition metal olefin complexes.

So, with that in this lecture we are going to look at the reactivity of transition metal olefin complexes in more details.

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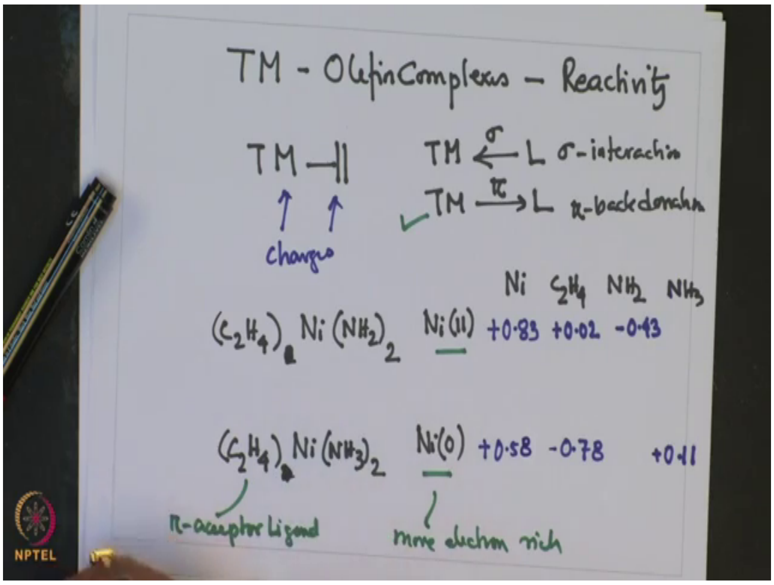

Now these olefins when they bind to transition metals undergoes 2 kinds of interaction.

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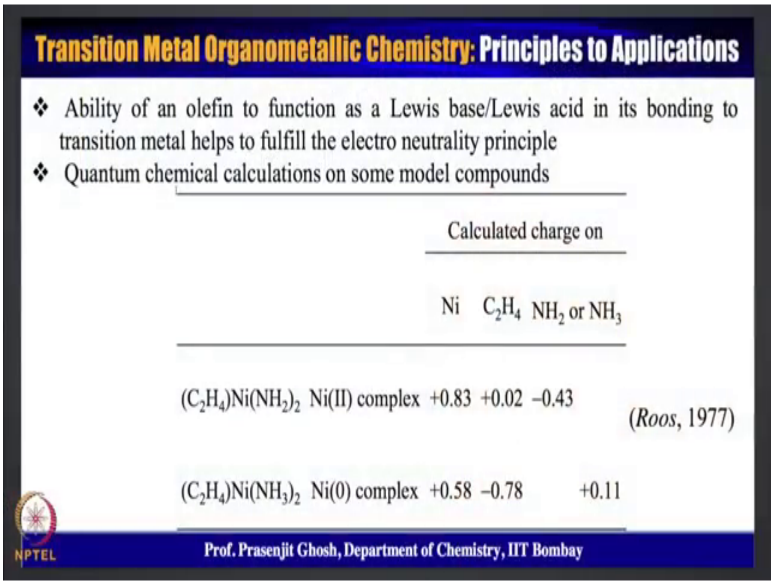

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- ❖ Ability of an olefin to function as a Lewis base/Lewis acid in its bonding to transition metal helps to fulfill the electro neutrality principle
- ❖ Quantum chemical calculations on some model compounds

		Calculated charge on		
		Ni	C_2H_4	NH_2 or NH_3
$(C_2H_4)Ni(NH_2)_2$	Ni(II) complex	+0.83	+0.02	−0.43
$(C_2H_4)Ni(NH_3)_2$	Ni(0) complex	+0.58	−0.78	+0.11

(*Roos*, 1977)

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One is ligand to metal sigma interaction as well as a transition metal to ligand pi back donation. And this we have discussed in the previous lecture.

But what happens is as a result of these dynamics of these 2 interactions the charges at that transition metal as well as the ligand carbons gives a vital clue as to the nature of this interaction. For example, if there is a predominance of sigma donation then the transition metal would be less positively charged and the ligand would be more positively charged because there is a loss of electron density and there is a gain on the electron density of the transition metal.

And for example, if there is a predominance of pi back donation and then the ligand electron density would increase whereas, the electron density on metal would decrease and thus by looking at the calculated atomic charges one can guess an in idea as to the nature of this forward sigma donation and backward pi donation that occur in these complexes.

And this can be computed using the quantum chemical calculations using simple DFT methods where one can have an idea as to the charges atomic charges on each of these fragments and moieties. So, for example, these bs alkane nickel b 7 n complex, NH 2 twice the oxygen state of the nickel is in plus 2 state ok.

The charges on nickel alkane and a moiety molecule which is a negative N H 2 minus; the computed charges are nickel being plus 2, it is not really plus 2, it is plus 0.83 and for the alkene, since it is sigma donating there is a loss of a electron density from the alkene and it is almost 0.02 and for the amide which is the mono anionic ligand this is not really minus 1 it is minus 0.43.

So, what one sees that the computed charges at the atom are less than what the calculated charges based on the oxygen state would lead to and that is understandable in the sense that oxidation state is a formal concept where complete charge separation of the bonded electron is assumed when calculating the oxygen state of the metal. So, even though nickel is formally a plus 2 ox is in plus 2 oxidation state in this complex the real charge or computed charged in the nickel is only plus 1 or 0.83.

And similarly the amide ligand which is supposedly minus 1, but the computed one is even half less than half than that in it is minus 43 and for alkene this is 0.02. So, now if one goes from nickel 2 complex to a nickel 0 complex. For example, instead of this amido if there is this alkene this amine C 2 H 4 hold C 2 H 4 nickel NH 3 whole 2.

So, now there is 2 ammonia instead of 2 amido then the charge on the nickel this is the nickel 0 complex, the charge on the nickel is plus 0.58. So, it is not really 0 that means, that a considerable amount of back donation has happened on nickel and the pi accepting ligand is since the pi acceptor ligand is alkene.

Then the alkene sort of got this electron density from metal so; that means, the predominance of this transition metal to ligand pi interaction that happens as a result the alkene has become negative now and the metal has become positive. So, it is no longer 0, but it is 0.58. Because now electron density has moved from transition metal on to this alkene, ligand which itself has become negative and ammonia moiety which is NH 3 has slightly positive because of just sigma donation from ammonia to the ligand and it is it stands at plus 0.11.

So, what one can see that if one were to compare nickel 2 and nickel 0, nickel 0 is more electron rich. And hence nickel 0 has greater transition metal to alkene by back donation as a result alkene moiety in, nickel 0 complex is more negatively charged at minus 0.78 whereas, in case of nickel 2 the metal center is electron rich. As a result nickel to alkane back donation occurs not much and hence this alkene is no longer negative and it is slightly positively charged probably in that case the back donation is almost negligible or does not occur at all.

So, these charges gives a nice view or insight about the extent of ligand to metal sigma donation and metal to ligand pi back donation. As elucidated by these related complexes which contain alkane nickel (Refer Time: 08:35) amido where nickel is in plus 2 oxidation state and alkane nickel (Refer Time: 08:40) amino where nickel is in 0 oxidation state.

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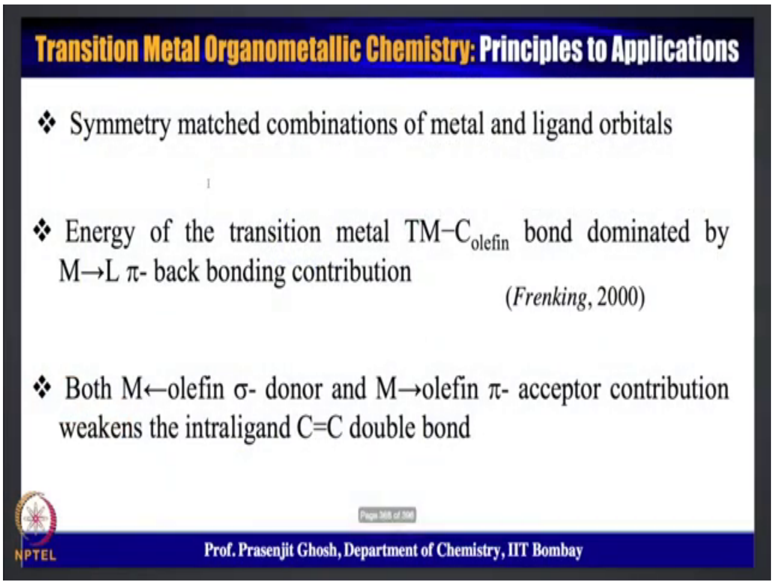

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- Symmetry matched combinations of metal and ligand orbitals
- Energy of the transition metal TM–C_{olefin} bond dominated by M→L π- back bonding contribution (*Frenking*, 2000)
- Both M←olefin σ- donor and M→olefin π- acceptor contribution weakens the intraligand C=C double bond

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So, now we are going to sort of look at these metal ligand and ligand to metal interaction in olefin complexes in much more details as we discuss a few more examples in this particular regard.

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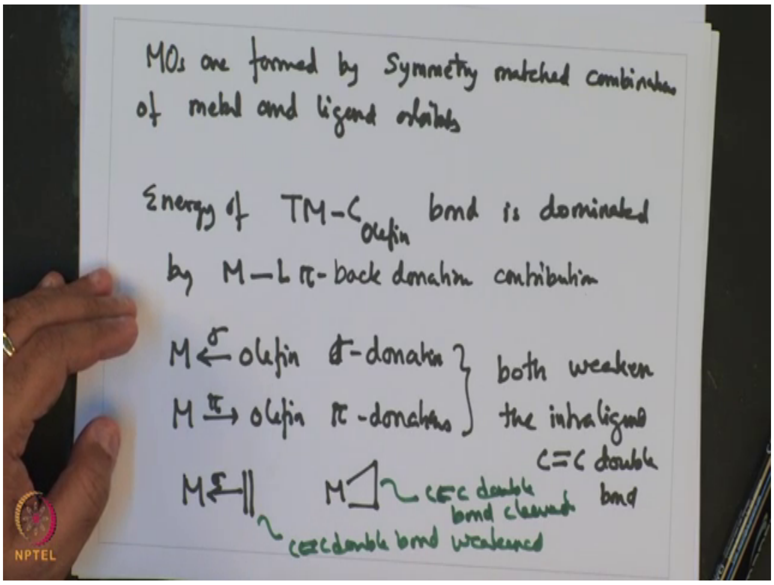

MOs are formed by Symmetry matched combination of metal and ligand orbitals

Energy of TM-C_{olefin} bond is dominated by M—L π-back donation contribution

$M \xleftarrow{\sigma}$ olefin σ-donation
$M \xrightarrow{\pi}$ olefin π-donation
} both weaken the intraligand C=C double bond

$M \xleftarrow{\sigma} \|$ ~ C=C double bond weakened

M◁ ~ C=C double bond cleaved

Now, the molecular orbital’s are originating from the interaction of the olefin with the metal is constructed by symmetry matched MOs are formed by symmetry matched combinations of metal and ligand orbital. So, the energy of the transition metal olefin bond is dominated by of TM bond is dominated by metal to ligand pi back donation contribution.

Now, this is an important statement given the fact that these settle to ligand pi back donation results in multiple bonding character of the transition metal olefin bond. Because now over and above the sigma bond that is formed the back donation gives the multiple bond in a pi bond in addition to the sigma bond and as a result the energy of the transition metal olefin bond increases. So, the energy of this transition metal olefin bond dissociation energy is dominated by metal to ligand pi back donation and that is a very crucial information.

Because then one can look at the transition metal olefin bond dissociation energy and have an insight as to the extent of forward donation forward sigma donation and backward pi back donation that is occurring in these complexes. And also the another important aspect of these 2 forward sigma donation and pi back donation is the fact that olefin to metal sigma donation and metal to olefin pi back donation both weakens the intra ligand CC double bond. The reason being that in the first case, where the pi electron is donated to the transition metal then the CC double bond is weakened.

Now in the next case when there is back donation then obvious as the donation happens on the pi star orbital then that sort of tries to give the cyclopropane due to intermediate where this double bond has weakened or even cleaved. So, what it says that both the interaction the forward as well as the backward ah donations significantly weakens the carbon-carbon double bond.

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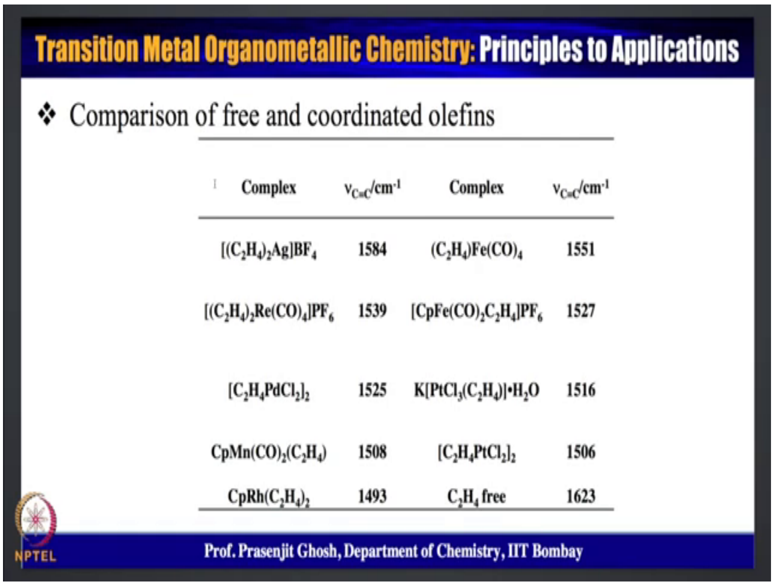

Transition Metal Organometallic Chemistry: Principles to Applications

- Comparison of free and coordinated olefins

Complex	$\nu_{C=C}/cm^{-1}$	Complex	$\nu_{C=C}/cm^{-1}$
$[(C_2H_4)_2Ag]BF_4$	1584	$(C_2H_4)Fe(CO)_4$	1551
$[(C_2H_4)_2Re(CO)_4]PF_6$	1539	$[CpFe(CO)_2C_2H_4]PF_6$	1527
$[C_2H_4PdCl_2]_2$	1525	$K[PtCl_3(C_2H_4)]\cdot H_2O$	1516
$CpMn(CO)_2(C_2H_4)$	1508	$[C_2H_4PtCl_2]_2$	1506
$CpRh(C_2H_4)_2$	1493	C_2H_4 free	1623

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Now, let us take a example of how these really effects and what we saw that in both cases the CC double bond is weakened and let us take a look at some of the experimental examples for the same. For example, let us say if it is free C 2 H 4.

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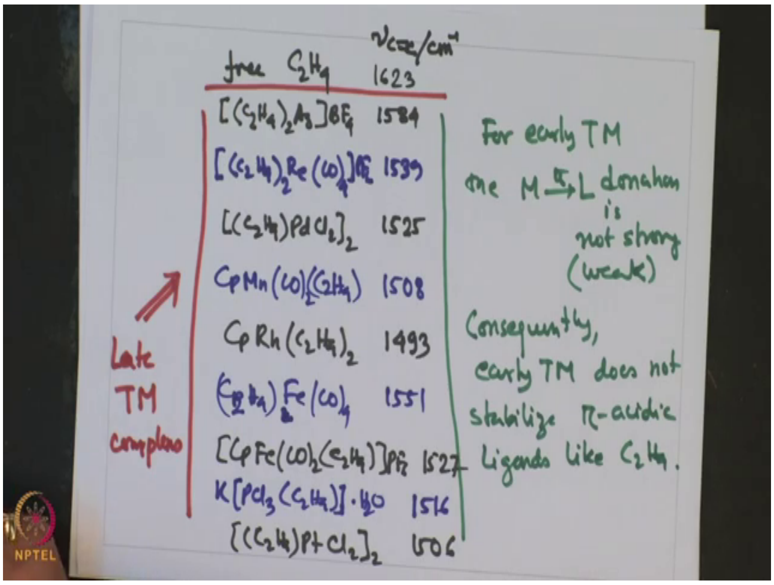

	$\nu_{C=C}/cm^{-1}$
free C_2H_4	1623
$[(C_2H_4)_2Ag]BF_4$	1584
$[(C_2H_4)_2Re(CO)_4]PF_6$	1539
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$CpRh(C_2H_4)_2$	1493
$(C_2H_4)Fe(CO)_4$	1551
$[CpFe(CO)_2(C_2H_4)]PF_6$	1527
$K[PCl_3(C_2H_4)]\cdot H_2O$	1516
$[(C_2H_4)PtCl_2]_2$	1506

Late TM complexes

For early TM the $M \xrightarrow{\pi} L$ donation is not strong (weak)

Consequently, early TM does not stabilize π-acidic Ligands like C_2H_4.

Then a new CC C double bond C centimeter inverse is 1623 and let us say if it is this alkane C 2 H 4 whole 2 A g B F 4 then because of both of these interaction it is 1584.

Let us say then another complex C 2 H 4 whole 2 rhenium C O 4 P F 6, this is 1539. Then C 2 H 4 P d cl 2 dimmer is 1525, C p M n is C O 2 C 2 H 4 is 1508, C p rhodium C 2 H 4 whole 2 is 1493, C 2 H 4 F e C O 4 is 1551, then C P F e C O 2 C 2 H 4 PF 6 is 1527 and the one that is Zeise's salt K PCl 3 C 2 H 4 H2O is a 1516 and the last one is C 2 H 4 Pt Cl 2 is 1506.

Now, what we see is that all of these are startly at lower energy than that of this free alkane which is way much at higher energy so; that means, that CC C double bond C is more strong for free alkene then when it is bound to transition metal complexes.

Now another instance which sort of comes out by looking at the table is all of these are late transition metal complexes. Now, that sort of a makes sense in the sense that that sort of indicates that the are for early transition metal the metal to ligand back donation is not a very strong that makes sense because for early transition metal the metal to ligand pi back donation is not strong or weak.

And as a result early transition metal does not consequently early metal does not stabilize pi acidic ligands like C 2 H 4. So, that is a very interesting observation in the sense that in the absence of the metal to ligand back donation it is very difficult to have a transition metal olefinic complex.

So, just simple sigma donation for the ligand to transition metal is not sufficient enough to stabilize olefinic complexes and that metal should be electron rich enough to participate in metal to lingand pi back donation otherwise the olefinic complex is would not be stable that is the second observation.

So, in all cases what it seems that both of these forward donation and back donation significantly weakens the CC double bond intra ligand CC double bond resulting in the CC frequency appearing at lower energy.

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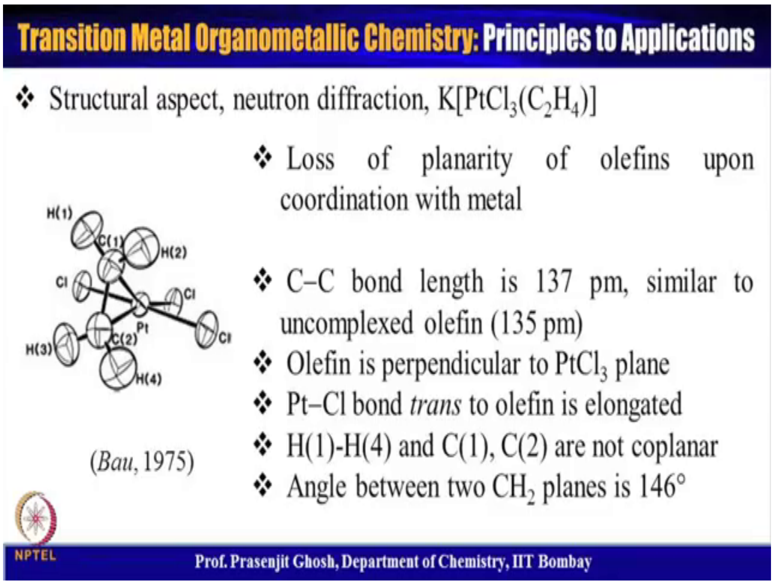

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- Structural aspect, neutron diffraction, K[$PtCl_3(C_2H_4)$]
  - Loss of planarity of olefins upon coordination with metal
  - C–C bond length is 137 pm, similar to uncomplexed olefin (135 pm)
  - Olefin is perpendicular to $PtCl_3$ plane
  - Pt–Cl bond *trans* to olefin is elongated
  - H(1)-H(4) and C(1), C(2) are not coplanar
  - Angle between two CH_2 planes is 146°

(*Bau*, 1975)

NPTEL

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Now, these complexes have been characterized structurally not only by proton x-ray diffractions, but also using the neutron diffractions and hence more accurate data thought of exists.

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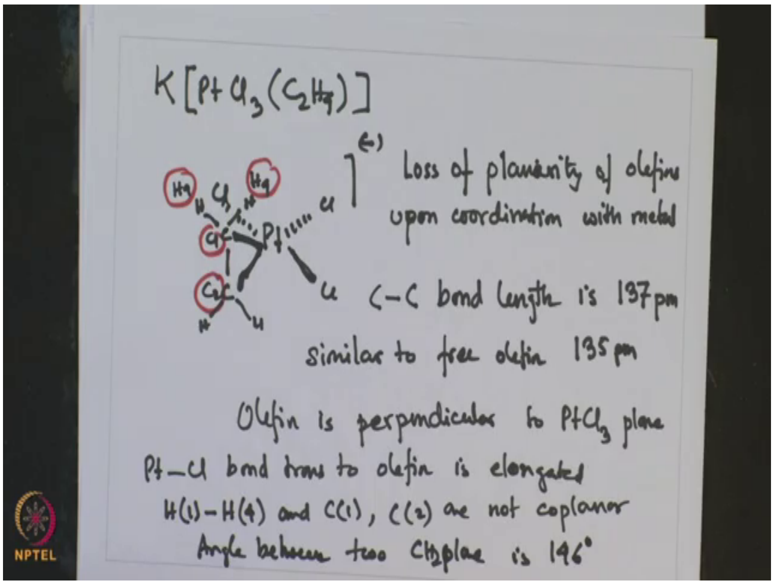

$K[PtCl_3(C_2H_4)]$

Loss of planarity of olefins upon coordination with metal

C–C bond length is 137 pm similar to free olefin 135 pm

Olefin is perpendicular to $PtCl_3$ plane

Pt–Cl bond trans to olefin is elongated

H(1)–H(4) and C(1), C(2) are not coplanar

Angle between two CH_2 plane is 146°

So, to begin with we are going to take up some examples of this. To begin with let us take a look at this zeisel salt which is K P t Cl 3. So, the structure is P t Cl Cl Cl and this is a anion. Now what is observed is that there is lot loss of penalty of olefins upon coordination with metal and the CC bond length is 137 picometer similar to uncomplexed free olefin which is 135 picometer.

Now, what it means is that this is a very wicked act of the olefin bound to the transition metal. Olefin the structure also says that olefin is perpendicular to P t Cl3 plane and because of this trans effect the P t Cl bond trans to olefin is elongated and H 1 H 4 and maybe highlight this H 1 H 4 and C 1 and this one is C 2 are not coplanar and the angle between two C H 2 planes is 146 degrees.

So, here is a nice example where one can look at the structural parameters of the olefin after it binds to the metal center and this has been done in by the structural characterization of the zeisel salt where we saw that there is a loss of penalty of olefin upon binding, CC bond length has slightly increased from 135 picometer to 137, olefinic CC bond is perpendicular to the P t Cl 3 plane and lastly is that the chlorine which is trans to the olefin is slightly elongated as a result of the trans influence.

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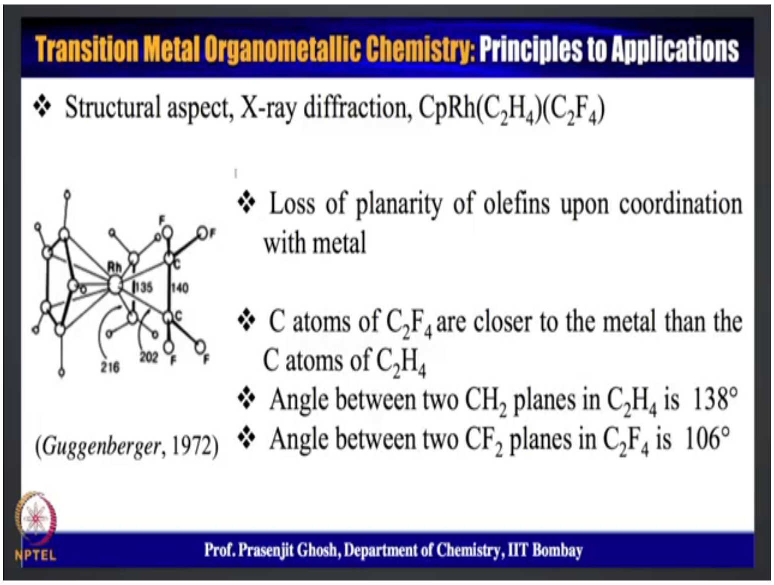

Transition Metal Organometallic Chemistry: Principles to Applications

- Structural aspect, X-ray diffraction, $CpRh(C_2H_4)(C_2F_4)$

(Guggenberger, 1972)

- Loss of planarity of olefins upon coordination with metal
- C atoms of C_2F_4 are closer to the metal than the C atoms of C_2H_4
- Angle between two CH_2 planes in C_2H_4 is 138°
- Angle between two CF_2 planes in C_2F_4 is 106°

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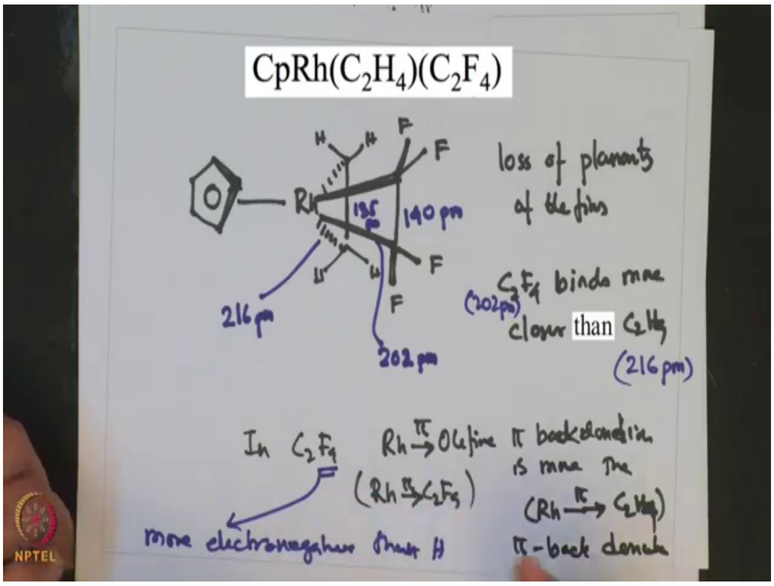

$CpRh(C_2H_4)(C_2F_4)$

loss of planarity of the olefins

C_2F_4 binds more (202 pm) closer than C_2H_4 (216 pm)

In C_2F_4 $Rh \xrightarrow{\pi} Olefine$ π backbonding ($Rh \xrightarrow{\pi} C_2F_4$) is more than ($Rh \xrightarrow{\pi} C_2H_4$) π-back donation

F more electronegative than H

Similarly, to look at another example this is for C p rhodium C 2 H 4 and C 2 F 4. So, here there are two olefins be bound; one is a only C 2 F 4, the other one is C 2 F 4. So, here is this rhodium bound to 4 fluorines and these are olefin containing 2 hydrogens.

So, CC bond between the 2 hydrogen is 135 picometer and for the rhodium fluorine 1 this is 140 picometer. So, there is elongation that happens in the CC bond rhodium CC bond length containing 2 hydrogen’s is 216 picometer rhodium CC bond length containing 2 fluorine is 202 picometer.

So, what it says that there is loss of penalty of olefins and C 2 F 4 binds more closer than C 2 H 4; C 2 F 4 distance is 202 picometer and C 2 H 4 is from rhodium. So, this is about 216 picometer and this is a 202 picometer.

Now reason that C 2 F 4 is more tightly held because in C 2 F 4 this rhodium to olefin pi back donation is more and this interaction can be represented as C 2 F 4 pi is more than the rhodium to C 2 H 4 H 4 pi back donation and that is because fluorine is more electronegative more electro negative than hydrogen ok.

So, what we have seen over here is that fluorine being more electronegative the metal to ligand pi back donation is more accurate in the C 2 F 4. As a results C 2 F 4 is more tightly bound closer to rhodium about 202 and because of the mode back donation the CC bond is almost like a signal broad character at 140 picometer and because of the less back donation the CC bond is shorter for the C 2 H 4 moiety.

So, this is not only reflected in the proximity, but also lifted in the CC double bond and a very nice example were competing olefin one more electronegative than the other compete for electron density and the more literal deficient olefin ah takes one more back donation from the metal as a result it is bound more tightly than the corresponding hydrogen counterpart.

So, with that I would like to conclude the discussion that we have had in today's lecture where we have looked into the reactivity of transition metal olefin complexes particularly with respect to the sigma donation and pi back donations which are reflected in the atomic charges as well as the characterization that are involved by IR where one can look at the CC double bond. And from the extent of the decrease in CC bond are gone to the lower energy one can sort of guess to what extent these forward sigma donation or pi back donation has happened one.

We had also seen that these olefin complexes are sort of stabilized by late transition metal which are capable of undergoing metal to ligand pi back donation and for early transition metal which does not have much electron density olefinic complexes are very difficult to make. And then we have seen structural characterization of 2 important olefin complexes one is a pellet platinum contains complex containing olefin which is the initials zeisel salt where we saw that olefin loses planarity upon coordination and also we have looked at the bond lengths and bond distances.

And the next one is a very interesting example of a rhodium where the rhodium is a bound to two olefins one very electron rich, another electron poor and what we saw that the electron poor olefin has a competes for the electron density and because of the electron negativity of fluorine substituent it grabs more electron density in from a more ligand pi back donation and as a result it is more tightly held or more closely held towards the by the metal. And also it is reflected in the CC double CC bond length which it has more like a single bond character.

So, with that I would like to conclude today's lecture which was on transition metal olefin complexes and its reactivity and we are going to discuss more on it particularly the reactivity aspect in the next lecture, till that time goodbye.

Thank you.