Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture – 33
Transition Metal Carbene Complexes: Reactivities

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. Over the last few lectures, we have been discussing very important topic, particularly about an important class of organometallic compounds. These are transition metal Carbene complexes. Transition metal Carbene complexes are important, because they are important intermediates in many catalytic cycles, they serve as catalysis catalysts for many catalytic reactions and that is why they become very important.

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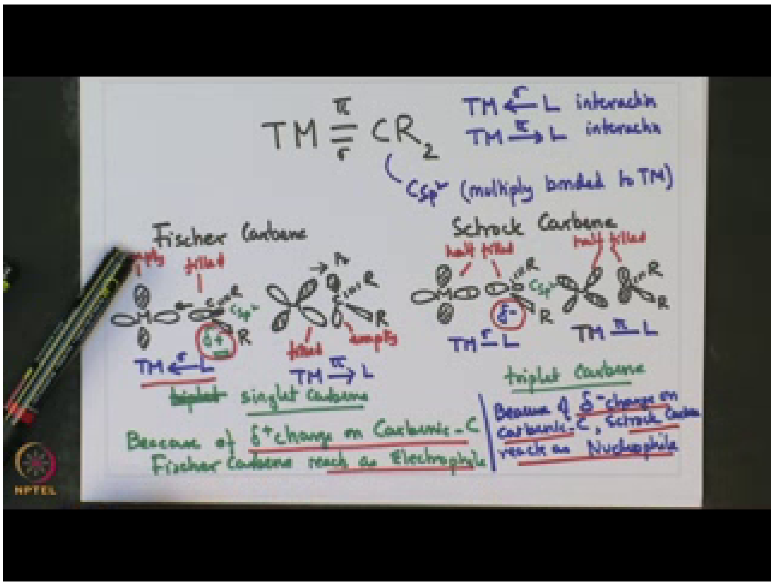

Because of δ^+ charge on Carbenic-C Fischer Carbene react as Electrophile

Because of δ^- charge on carbenic-C, Schrock Carbene react as Nucleophile

Now, these transition metal Carbene complexes are usually designated as one transition metal bonded to a carbonic moiety, which has a sigma bond as well as pi bond and this carbon is having a Sp 2 centre, Sp 2 hybridized carbon, which is multiply bonded with the transition, where metal we have also seen that these transition metal complexes having this transition, metal carbonic moiety have two kinds of interactions, prevalent one is ligand to metal sigma interaction and the other is transition metal to ligand pi interaction.

Now, in our last class we have seen that these kind of transition metal Carbene complexes can be classified into two types; one is Fischer Carbene and the other is Schrock Carbene. Now, each of these Carbenes, this has a CR to moiety, being bound to the transition metal and each of these Carbenes does show these two type of interaction, one is legend to metal and the other is metal to ligand it. Now, as for the Fischer Carbene, we have looked into the reactivity or we have looked into the bonding in terms of the molecular orbital into responsible for this kind of Fischer Carbene complexes. We have looked into the orbital interaction of CR 2 fragments, with that of the orbitals of the transition metal and what we saw that this is comprised of two interactions; one is ligand to metal sigma bonding interactions that involved metal d type orbital, which is empty interacting with a ligand Sp 2 carbonic moiety. So, here this is filled and this is empty and the ligand is donating electron, on to the empty metal orbital and this is represented by TM ligand to metal sigma interaction.

We had also seen that the second component of this transition metal to ligand pi interaction consists of metal d orbital, interacting with an empty p z orbital of the ligand and this time around, this one is filled and this one is empty and the electron donation happens from the metal to the d a p z orbital p z orbital at the carbonyl centre. So, this is designated by TM to ligand pi type interaction.

Now, in our last discussion what we had seen that, in this kind of interaction the Carbene centre is in singlet spin state that is, because that there is that Sp 2. Hybridized Carbene centre is occupied by 2 electrons and the p z orbitals remains empty. So, Fischer Carbene represents singlet Carbene and then there are two kinds of donation happening, one from the Carbene lone pair, donating to waken metal d orbital and then a metal full filled metal d orbital, donating to vacant p z orbital and that comprises these two kind of bonding.

Now, if we analyze this interaction bit more closely, what can be seen that, because of the sigma donation that happens from the Carbene lone pair on to the transition metal and that, because of the back donation is not as prominent as that of the sigma donation. There is a partial positive charge at the Fischer Carbene. So, over here there is a partial positive charge at the Fischer Carbene and hence, Fischer Carbene reacts as an electrophile or undergoes nucleophilic attacks. So, Fischer Carbenes, our singlet Carbenes and, because of del positive charge on Carbene carbonic carbon, Fischer Carbene reacts as electro electrophile. This is a significant property of Fischer Carbene and that arises, because of predominant. Predominance of this ligand to transition metal sigma donation, which is not fully replenished by the transition metal to ligand pi back donation, as a result there is this partial positive charge on the carbonic centre and which transform Fischer Carbene to react as an electrophile.

Now, let us take a look at how the scenario develops in case of the Schrock Carbene. Similarly, we have two interaction; one involves metal to ligand as well as the other involves ligand to the metal. Now, in this case of Schrock Carbene, the Carbene is in triplet state; that means, that Sp 2 as well as the p z orbital, each are occupied by 1 electron, each and they covalently interact with singly filled orbitals. So, in case of Schrock Carbene, the analogous orbital diagram can be a, is drawn over here. For example, metal orbital interacting with a carbon Sp 2 type orbital and each having one electron. So, this conveys, this transition metal to ligand sigma interaction. Now, this is a pure covalent interaction, one electron being shared by each of the metal as well as the car, the Carbene Sp 2 hybridized orbital and both are partially 4 half filled or partially half filled, both of the metal and the ligand orbitals are half filled.

Now, as far as the transition metal to ligand, pi interaction is our observed. Similar scenario exists, where the metal d orbital interacts with p z of the carbine, where each of these are half filled. So, this also is a Sp 2 orbital and the metals as well as the ligand orbitals are half filled and they undergo a covalent interaction of the type; pi type and unlike in Fischer Carbene, which had been a dative interaction over here. We have two bonds being formed simple by a covalent interaction transition metal ligand sigma bond as well as transition metal ligand pi bonds as a result, because of this Schrock Carbonic centre being triplet in nature and that 1 electron resides in the C Sp 2 O orbital as well as 1 electron in the p z orbital and they interact with partially filled metal orbitals, all appropriate symmetry giving transition metal, ligand sigma bond as well as transition metal ligand pi bond. Thus, as a result of these, as the electronegative Carbene is more electronegative than the transition metal. The carbonic centre has a del minus charge always and hence, the Schrock Carbene reacts as a nucleophile. So, because of del minus charge on carbonic carbon, Schrock Carbene reacts as nucleophiles.

So, here we see that interesting correlation emerges out that as the carbonic carbons are more electronegative then the metal centre in this case, because of pure covalent bond being formed sigma as well as pi type the Carbene centre is del negative, the carbonic centre is delta negative and as a result Schrock Carbene X reacts as and nucleophile.

So, here we see that even though that to difference, different reactivity emerges, because of the nature of bonding that takes place between the Carbene moiety and the transition metal and what is seen that in Fischer Carbene, which is a singlet Carbene 2, coordinate bonds form and these two coordinates bond or ligand to metal sigma coordinate bond as well as transition metal to ligands pi coordinate bond and as the extent of pi coordinate bond is not as effective, as that of ligand to metal sigma coordinate bond. There is a partial positive charge on the carbinic centre of the Fischer Carbene resulting in the Fischer Carbene, behaving like an electrophile.

On the other hand, for the Schrock Carbene, which is in triplet state, the carbine Sp 2 orbital as well as the empty p z orbital, they are partially, we feel that each is occupied by 1 electron, as a result this carbonic moiety interact with the partially filled metal orbitals, result in transition metal league ma sigma bond and this will as transition metal ligand pi bonds and going to the greater electro negativity of this carbon, then that of the transition metal, the two bonds, two covalent bonds that are formed, are polarized towards carbon, resulting in carbon being del minus or partially negative and, because of this del minus charge and the carbinic carbon Schrock carbine reacts as an nucleophile.

So, we see two different kind of reactivity, emerging out the type of bonding that is present between the carbonic moiety and the transition metal and the commonality between these bonding is that, this bonding has two components, each of them have two components, that is ligand to metal sigma donation as well as metal to ligand pi pack donation as well, but they pan out differently to give different kind of reactivities as discussed here, we are going to who now, probe these differential reactivity of Carbene moieties in bit more details and looking at examples of such differential reactivity. So, as a result one can to understand the reactivity, one can look up or draw various reasoning structures that are possible for Carbene complexes.

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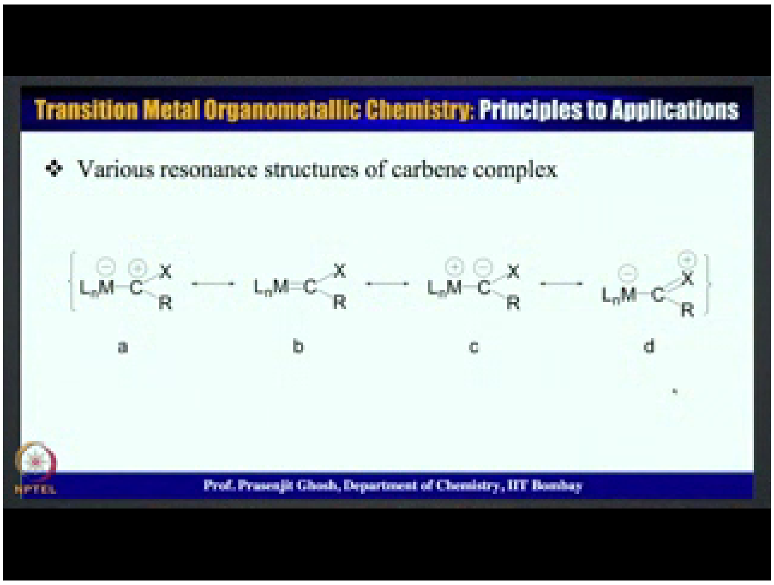

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- Various resonance structures of carbene complex

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And some of these resonances as forms drawn here and these resonance forms which can either represent the Schrock Carbene or a Fischer Carbene would explain the kind of reactivity, the carbonic centre would show.

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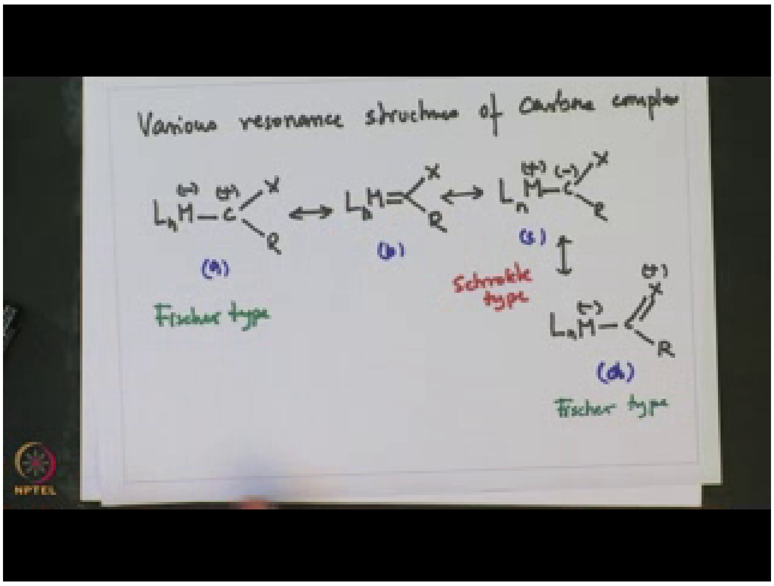

Various resonance structures of carbone complex

So, I am going to illustrate the various resonance forms that are prevalent for metal carbine moiety and down below for example, one can conceive as L minus c plus X R or it can exist as L n M double bond X R that can also be sort of exists as L n M class c minus X R and that can also exist as L n M minus X plus c hard and let us designate this as some structures as a b c and d.

So, what one finds that the structure a and b e sort of a predominantly represents Fischer type carbine, well carbine centre is positively charged and acts as an electrophile. So, this representation is more of Fischer type. Similarly, one can say that the representation c is more of Schrock type as the carbonic centre is dell negative and that it can act as a nucleophile; reacts as nucleophile and this structure d is high extension of a Fischer type compound which follows from a Fischer type canonical structure. So, this also is a canonical form that represents the Fischer type and this is a neutral.

So, what one can see is that the different canonical structures that exist for metal Carbene moiety can vary from the metal centre, being positively charged to metal centre being negatively charged and similarly, the carbon centre being positively charged to carbon centre, being negatively charged and sudden and each of some of each of these canonical structure in term represents the type of reactivity associated with particular classes of Carbenes, that is for example, a the canonical structure a and canonical structure d is more of a Fischer type whereas, canonical structure as c d presents are more of a Schrock type and the kind of reactivity, it is Carbene complexes exhibit.

So, these Carbene complexes being important intermediates, which are very unstable otherwise and somehow, I have been stabilized by forming metal Carbene bond, have been characterized by various spectroscopic methods and of these the most powerful one; obviously, is the X ray single crystal crystallography, where both the examples of Schrock and Fischer type Carbenes have been structurally characterized and we are going to look at some of the structures of these structurally characterized metal Carbene complexes and see how their structure sort of represents, the kind of carbine they are classified into.

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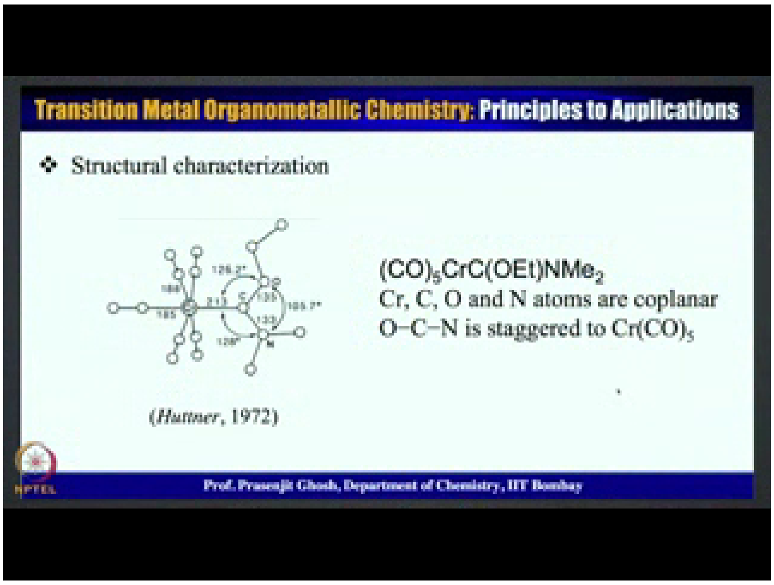
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- ❖ Structural characterization

(CO)$_5$CrC(OEt)NMe$_2$
Cr, C, O and N atoms are coplanar
O–C–N is staggered to Cr(CO)$_5$

(*Huttner*, 1972)

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So, in the next few minutes, we are going to look at some of the classical examples of Fischer and Schrock Carbene complexes that have been structurally characterized.

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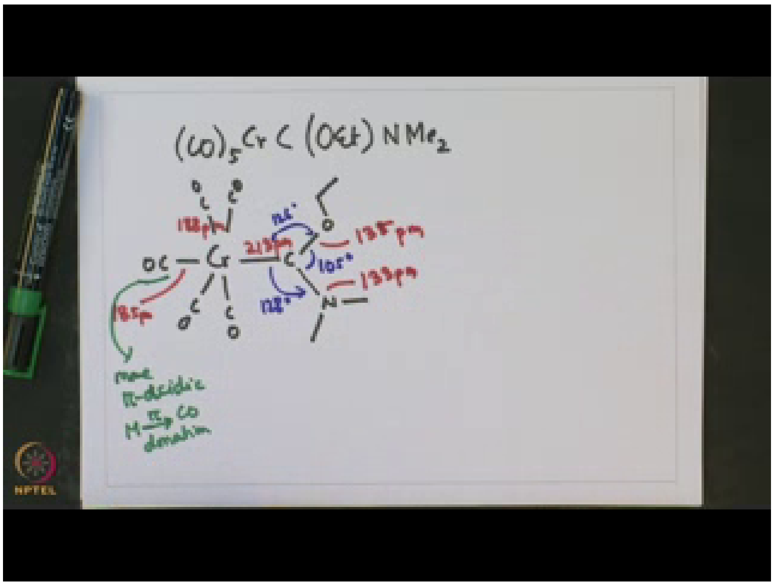

So, for example, this chromium penta carbonyl complex C o e t N M e 2 and structure, it exhibits, it is chromium. So, chromium is surrounded by five carbonyls and then is bound to a Carbene with oxygen and corresponding ethyl group and then nitrogen with two methyl group.

Now, these the metal Carbene bonds, what we see is slightly different, that these all five carbonyl compounds are not equivalent, the four of them being equivalent and the fifth one being slightly long different and what we see is that these four of these has a bond distance of 188 picometer; whereas, this one is slightly shorter of 185 picometer whereas, the metal Carbene bond is; however, much longer at 2 1 3 picometer. So, this is a metal carbon bond, this also is a metal carbon bond that, this is more shorter; that means, that carbonyl, the carbonyl moiety is more pi acidic; that means, that C o C o is more pi acidic as a result, that there is metal to ligand back donation metal to C o pi. Back donation is more prominent as opposed to metal to Carbene and back donation. So, this has sort of more stronger, double bond character, resulting in much shorter bond whereas, direction density of the chromium is not back donated much on to carbon, as a result we see a longer chromium carbon bond also the angle at carbine. A carbonic carbon is somewhat between 1 of 5, this is 1 0 5 degrees, 1 0 5 day and whereas, this is 128 and 126 degrees from here to here.

So, what it shows that this Sp 2 carbon has been pushed back from 120 to somewhat 128 and 126 on both sides and this O C N bond has been become smaller as a result of these two bond, expanding from there 120 values and this has contracted from 120 to 1 of 5, the Carbene oxygen bond lengths and carbine nitrogen bond lengths are 135 and 133 picometer.

So, these clearly demonstrates the structural characterization of Fischer Carbene complexes, where chromium pentacarbonyl is bound to a Carbene moiety that contain hetero atoms like O and the nitrogen adjacent to the carbonyl centre and also what it can be seen from here, that there is a competition between metal chromium carbonyl metal ligand bonding, as well as chromium Carbene metal ligand bonding and what we saw is the pi back bonding from metal to carbonyl is much more stronger than that of the pi back bonding from chromium to carbine, as a result the bond distance between carbonyl carbon and chromium is much shorter 185 picometer as compared to 2 1 3 picometer from chromium to Carbene as a result, this shows that carbon monoxide is a more acidic ligand than Carbene.

So with that, let me conclude what we have discussed in today’s lecture. We have looked into a very important topic in today’s lecture, particularly looked at the differential reactivity of two classes of metal Carbene complexes. These are mainly trend Fischer

Carbene and Schrock Carbene and what we saw that, these two classes Carbene complexes display nearly, opposite reactivity in a sense that one reacts as a nucleophile and one other reacts as electrophile and what we saw that their differential reactivity arises from the type of interactions.

They show while making the bond carbonic bond with the metal Fischer Carbene being singlet in nature, undergoes two ligand to metal to ligand interaction, but these are of coordinate coordinative bond type coordination bond type and as a result the carbonic centre is positively charged and reacts as an electrophile whereas, in the Schrock case, the carbonic centre is in triplet spin state and as a result it does interact with the metal forming two bond; metal ligand sigma bond and metal ligand pi bond, but these interactions are more covalent in nature, where it engages itself. We partially filled metal orbitals as a result of greater electronegativity of carbonic carbon, the Schrock Carbenes are more electron rich and has a del minus delta negative character on it, that makes it behave like or makes it reacts like an nucleophile.

So, that is a very interesting observation that we had seen, that can be explained by the kind of bonding interaction that this carbine, the show with the transition metal.

We have also looked in this lecture at structural characterization of various Carbene complexes particularly with respect to X-ray diffraction and for this chromium petrica penta carbonyl Carbene complex, with that I conclude today’s lecture and we are going to be discussing more on these properties reactivities of Carbene complexes, their characterization techniques that have been used to improve these complexes, in the next lecture.

Till then goodbye and thank you.