Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture- 02
Week - 01
Polarity and Reactivity of M-C bonds

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the previous lecture, we have seen a brief overview of the development of compounds in the realm of organometallic chemistry, we have seen the utility of these compounds how these compounds were synthesized over times, and what are the reactions that were used for making these complexes. We have also seen that the significance of these compounds were realized over time as many of these compounds were recognized with Nobel Prizes going to the inventors of them. Today, in this lecture, we are going to touch upon something very interesting. We try to find out why are these compounds so special what are the properties responsible for making these compounds extremely good in catalysis.

Now, as I mentioned in my previous lecture that organometallic compounds are extremely air and moisture sensitive; and hence it may seem to one that they would be an reasons to handle or deal with it and that one should stay away from it. But on the other hand it can be seen as a great advantage of these compounds. These compounds being extremely reactive by virtue of the ability to react with air and moisture a very unstable these compounds are extremely reactive and sensitive. And hence they can do reactions which otherwise other compounds the stabler ones could not do, and then these compounds impart a different reactivity and dimension to what all compounds can do. And as I said in my previous lecture that one of the main attributes of organometallic chemistry is their ability to carry out homogeneous catalysis. Hence, in this lecture, we are going to look for what are the causes of the reactivity for these compounds. As I mentioned that organometallic compounds are compounds with metal carbon bonds, and they are extremely reactive and the reactivity arises from the polarity of the metal carbon bond.

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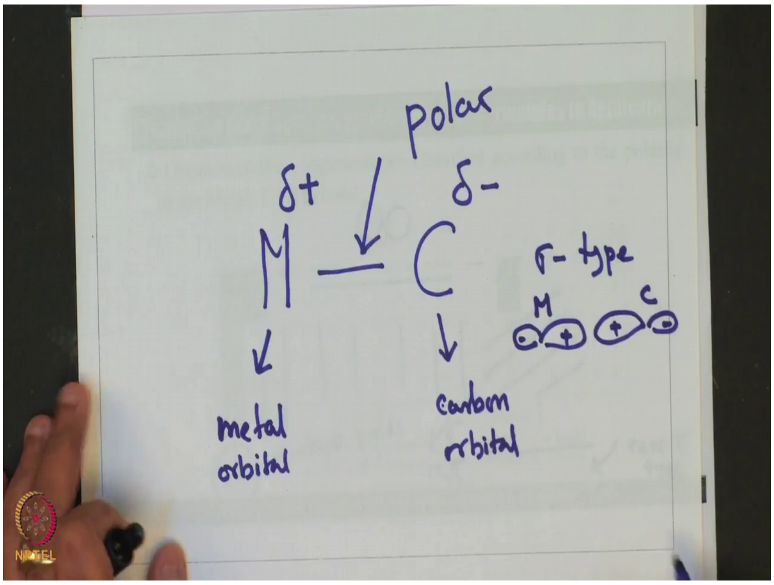

That means that the metal and the carbon bond is polar. As a result they have sort of a kind of dipole with metal being partially positively charged and carbon being negatively charged. And sometimes this polarity leads to the higher reactivity of these compounds. Now, let us take a look at what kind of reactivity this compound show depending on the kind of polarity they have.

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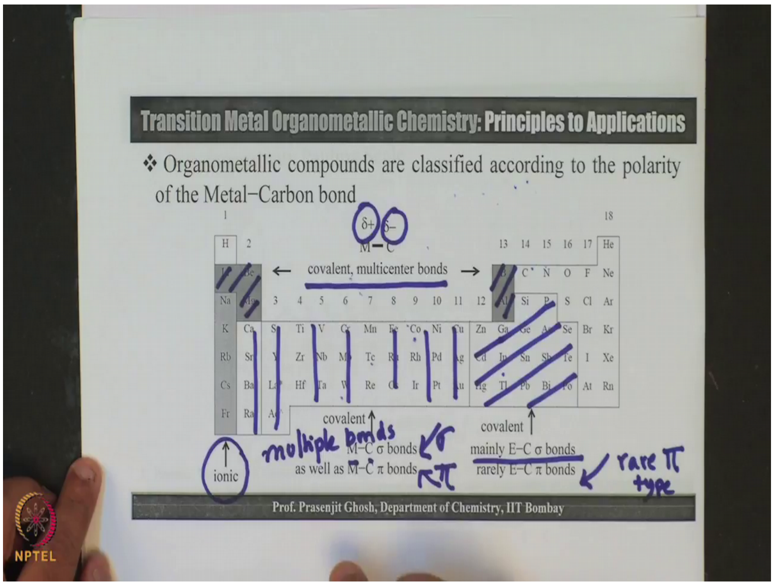

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- Organometallic compounds are classified according to the polarity of the Metal–Carbon bond

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The best way to start off is to look at the periodic table. Here we have periodic table and we see that various elements form polar bonds with carbon, so where the metal is positively charged and carbon is negatively charged. Now, in periodic table, we have first group which is alkali then we have alkaline earth metal, then we have a series of transition metals, then we have metalloids and then we have non-metals and then the finally, the noble gases. So, what has been observed very interestingly that the metal carbon bonds of this elements show a particular trend, and the trend is that organometallic compounds of lithium, beryllium, magnesium, boron, aluminum in this region, they show covalent multicenter bonds.

Now, these are very interesting kind of bonds. There is a covalent bonds means there is a overlap between a metal and ligand which is carbon centered orbitals, they are covalent, but they are non classical in nature. A non-classical bond means that it is not a conventional two center two-electron bonds; so they are multi centered many centered many electron bonds. So, these are special kind of non-classical bonds that these regions of this part of elements in the regions of this part of periodic table make.

Now, as per the extremely electro positive ones like sodium, potassium, rubidium, cesium and francium, they are extremely electro positive and they make ionic bonds. So, the metal is completely in the ionic state and the ligand is also in the anionic state. So, there is no overlap as far as the metal and the ligand concerned. So, these are extremely ionic compounds which is formed by elements from sodium to francium. Now, as for this region mainly the transition metal and part of the alkaline earth metals, they make covalent bonds. A covalent bond means that there is a overlap between a metal and the carbon orbital; and this overlap can be of sigma types, where there is a sigma bond as well as it can be of pi type where there is a pi bonds.

So, many of these compounds they not only make over covalent overlap, but they are able to form multiple bonds that is kind of a specialty of this kind of complexes. These bonds unlike the multi centered ones are classical two center two electron bonds; that means, two nuclei share two bonded electrons. Now, as for this region from silicon, phosphorus, zinc, selenium, cadmium till all the way to lead they also make covalent bonds, but these columns are mainly sigma type and very rarely pi type.

So, what it says are the metal carbon interaction is dependent very much on the placement of metal in which the carbon is bonding too and that can vary a lot it can be ionic. Well it is completely a anion versus cation type of electrostatic interaction, it can be covalent, covalent can be a classical type two center two electron types or it can be a non classical type which is covalent, but multi centered multi electron bonds.

As well further more between the covalent type interactions which are prevalent over here as well as in this block, there is also a subtle difference by the fact that in the transition metal bonds they are equally possible between a metal carbon sigma bonds as well as formation of a metal carbon pi bonds. But on this region they are mainly metal carbon sigma bonds and very rarely a metal carbon pi bonds. So, what it says that organometallic chemistry provides a very interesting approach for studying the interaction of metal with carbon, and they are not all the same, and they differ based on their placement in periodic table.

Now, let us look at the middle carbon interaction. So, we have metal orbital interacting with a carbon orbital. These interaction can be sigma type which means that the metal carbon orbital would be interacting with a carbon sigma type orbital of same symmetry. And hence there is no nodal plane between the internal clear axis, the interaction can also be pi type.

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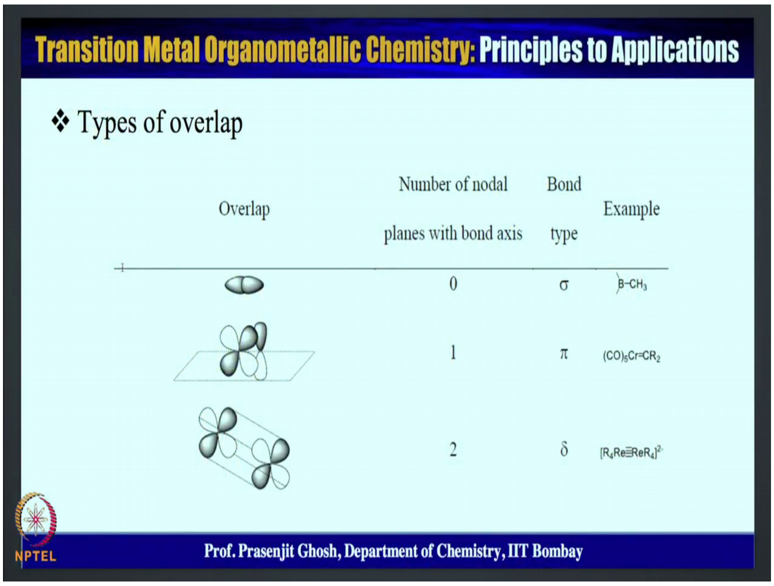

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- Types of overlap

Overlap	Number of nodal planes with bond axis	Bond type	Example
	0	σ	$\rangle B{-}CH_3$
	1	π	$(CO)_5Cr{=}CR_2$
	2	δ	$[R_4Re{\equiv}ReR_4]^{2-}$

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The next kind of interaction between metal carbon bond is of a pi type.

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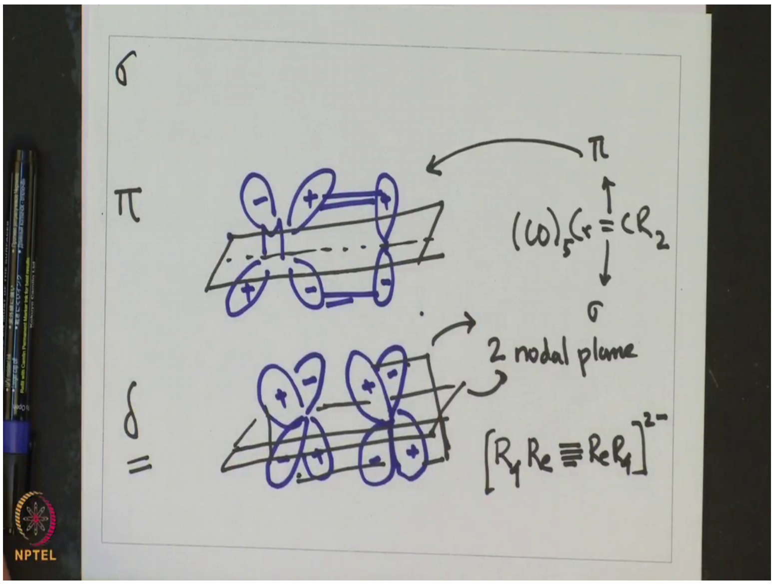

Where metal d orbital can interact with a p type orbital of the ligand. So, these being a p type interaction there is a nodal plane along the intern nuclear axis. So, the kind of compounds which shows such interaction is a carbene type which is of this formulation. So, here we have a sigma bond as well as a pi type interaction, and this pi type interaction is shown over here.

The next comes very interesting interaction which is very unique for transition metals and these are called delta type interaction. So, this was pi type interaction, now there is a delta type interaction. Delta type interaction occurs from side and overlap of 2D orbitals and the best way to depict them is given over here. So, there are two kinds of nodal plane over here, one is between this, the other is across the inter nuclear axis. So, there are two nodal planes. As mentioned that this kind of delta interaction is very special and occurs in only metal-metal interaction in various transition metal complexes.

So, an example of a compound having delta interaction is ok, now one I must say that these interaction sigma pi and delta are not independent of each other. Sigma for a pi interaction to happen sigma has to be present; and for delta two happen sigma and pi has to be present. So, one of the interaction reinforces the other ones. Pi cannot happen independently of sigma; and similarly delta cannot have occurred independent of pi and sigma.

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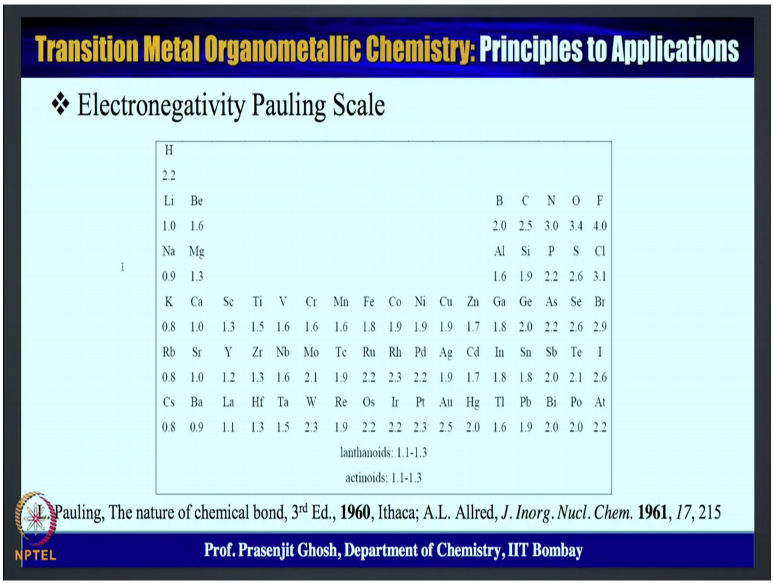

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❖ Electronegativity Pauling Scale

H																
2.2																
Li	Be											B	C	N	O	F
1.0	1.6											2.0	2.5	3.0	3.4	4.0
Na	Mg											Al	Si	P	S	Cl
0.9	1.3											1.6	1.9	2.2	2.6	3.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.6	1.8	1.9	1.9	1.9	1.7	1.8	2.0	2.2	2.6	2.9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.3	1.6	2.1	1.9	2.2	2.3	2.2	1.9	1.7	1.8	1.8	2.0	2.1	2.6
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.8	0.9	1.1	1.3	1.5	2.3	1.9	2.2	2.2	2.3	2.5	2.0	1.6	1.9	2.0	2.0	2.2

lanthanoids: 1.1-1.3

actinoids: 1.1-1.3

L. Pauling, The nature of chemical bond, 3rd Ed., **1960**, Ithaca; A.L. Allred, *J. Inorg. Nucl. Chem.* **1961**, *17*, 215

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Now, another important feature one is to consider when they look at the reactivity of transition metal complexes is the electronegativity. Electronegativity is defined as the property by which the bonded pair of electrons is attracted by each of the nuclei. Now, this is a very interesting feature which results in polarity and polarity results in reactivity. Now, a seminal work in this area has been done by Pauling in providing a table for all the elements in periodic table.

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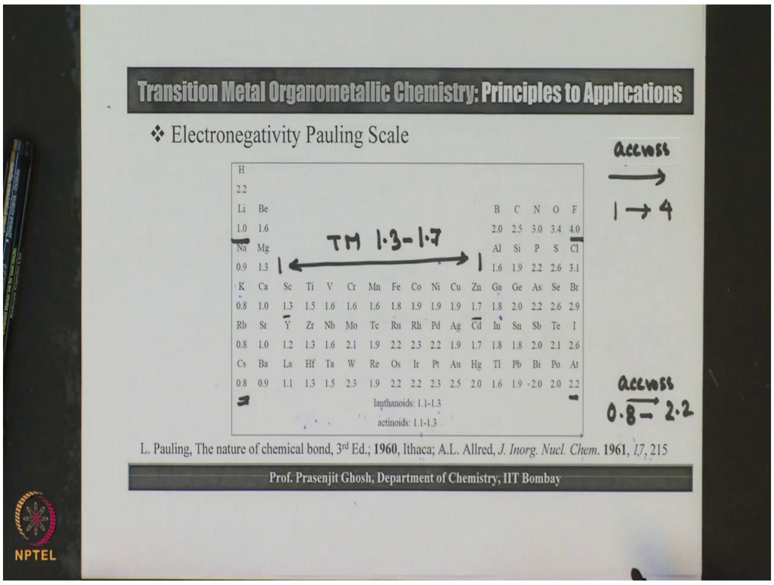

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Electronegativity Pauling Scale

H																
2.2																
Li	Be											B	C	N	O	F
1.0	1.6											2.0	2.5	3.0	3.4	4.0
Na	Mg											Al	Si	P	S	Cl
0.9	1.3											1.6	1.9	2.2	2.6	3.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.6	1.8	1.9	1.9	1.9	1.7	1.8	2.0	2.2	2.6	2.9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.3	1.6	2.1	1.9	2.2	2.3	2.2	1.9	1.7	1.8	1.8	2.0	2.1	2.6
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.8	0.9	1.1	1.3	1.5	2.3	1.9	2.2	2.2	2.3	2.5	2.0	1.6	1.9	2.0	2.0	2.2

lanthanoids: 1.1-1.3

actinoids: 1.1-1.3

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TM 1.3-1.7

across

1 → 4

across

0.8 – 2.2

And it starts giving electronegativity with hydrogen 2.2 and maximum being fluorine for 4. Lanthanides have the range from 1.1 to 1.3; actinides from 1.1 to 1.3. So, we see that the electronegativity difference for the whole of the lanthanide and actinide series is very less. Whereas, if one goes from left hand side of the periodic table to the right hand side of the periodic table, one can see that the range is huge. Lithium is 1; fluorine is 4. So, if you go across the periodic table, the change is 1 to 4. Whereas, if you go across the periodic table at the bottom then the change is less pronounced, it is from 0.8 to 2.2. Also one can see that if you go across the so that means, that if you go down the group the change in electronegativity becomes less pronounced.

Another interesting feature to note that for transition metal, the change is also for transition metal the change is also not to significant from 1.3 to 1.7 from scandium to zinc. And hence we need to see that how these change in electronegativity affect the reactivity of transition metal carbene compounds. Another interesting feature about electronegativity is that of a metal or element change with the hybridization.

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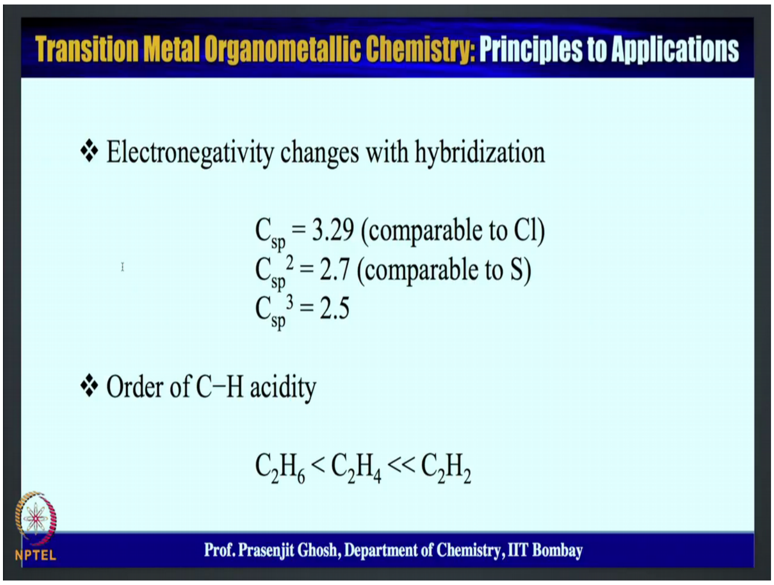

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- Electronegativity changes with hybridization

$C_{sp} = 3.29$ (comparable to Cl)
$C_{sp^2} = 2.7$ (comparable to S)
$C_{sp^3} = 2.5$

- Order of C–H acidity

$C_2H_6 < C_2H_4 << C_2H_2$

NPTEL

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For example carbon has a electronegativity of 2.5 in the Pauling electronegativity scale, but what really turns out that this value of 2.5 on carbon is something which is variable which is very much dependent on type of hybridization that carbon has.

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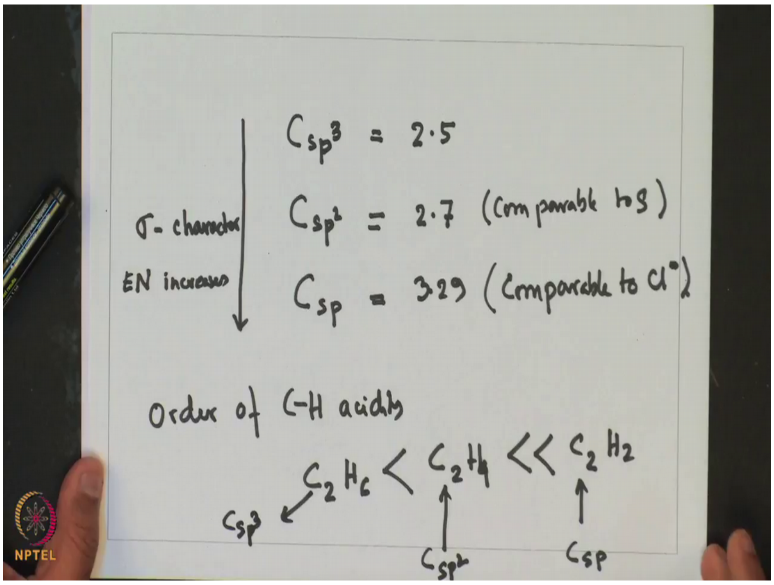

σ- character

EN increases

$C_{sp^3} = 2.5$

$C_{sp^2} = 2.7$ (comparable to S)

$C_{sp} = 3.29$ (comparable to Cl°)

Order of C-H acidity

$C_2H_6 < C_2H_4 << C_2H_2$

C_{sp^3}

C_{sp^2}

C_{sp}

For example when carbon is sp 3 then its electronegativity is 2.5; when it is sp 2, it becomes 2.7. And when it is carbon become sp, then, it becomes 3.29. So, what happens is that the s character increases as one goes from sp 3 to sp 2 and electronegativity increases so 2.5 which is a commonly electronegativity of a commonly occurring carbon at sp 3 hybridization becomes 3.29 and which is comparable chlorine. Sp 2 value of 2.7 is comparable to sulfur. So, what it shows is that as the hybridization changes the electronegativity of carbon can significantly change from 2.5 to 3.29; this is much higher than what has been observed for transition metal where it could change by only 0.5 electronegativity you need.

Thus the order of C-H acidity becomes C 2 H 6 less than C 2 H 4 very, very less then C 2 H 2. This carbon is C sp; in the ethylene, it is C sp 2; and in ethane, it is c sp 3. Now these become all the more important when one considers to explain the reactivity. So, what one sees that the reactivity of transition metal compounds would thus depend on the polarity and the polarity would eventually depend on the electronegativity of carbon in further would depend on what kind of hybridization the carbon was in. So, we see sequence of chain of causes that can lead to different reactivity. Now, this is at the carbon end.

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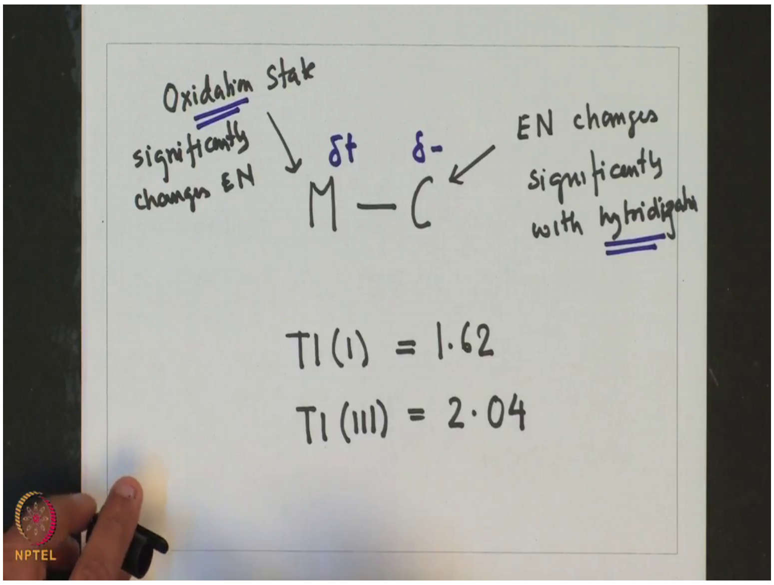

Oxidation State
significantly changes EN

$\delta+$ $\delta-$
M — C

EN changes significantly with hybridization

Tl (I) = 1.62

Tl (III) = 2.04

So, here we have metal carbon bond, and what we saw that electronegativity changes significantly with hybridization. Similarly, what are the factors that would change the on metal; and it turns out that oxidation state, state of the metal significantly changes its electronegativity. To illustrate this point, let us take a look at thallium in it is plus 1 state its electronegativity is 1.62. Whereas, for thallium if it is in plus 3 state, the electronegativity changes to 2.04. So, we see that the polarity of this metal carbon bonds is very much dependent on the hybridization of the carbon as well as the oxygen state of the metal.

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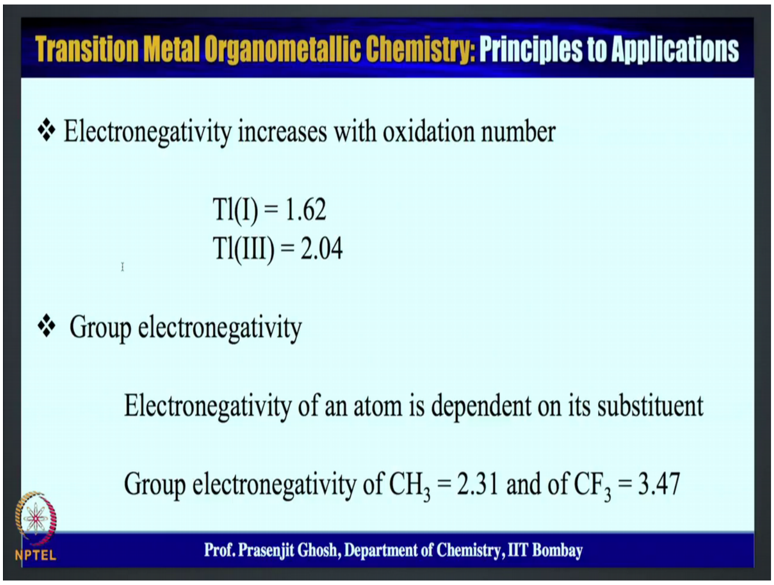

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❖ Electronegativity increases with oxidation number

Tl(I) = 1.62
Tl(III) = 2.04

❖ Group electronegativity

Electronegativity of an atom is dependent on its substituent

Group electronegativity of CH_3 = 2.31 and of CF_3 = 3.47

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Now, comes another important concept which also leads to change of the bond polarity of metal and carbon and that is called group electronegativity

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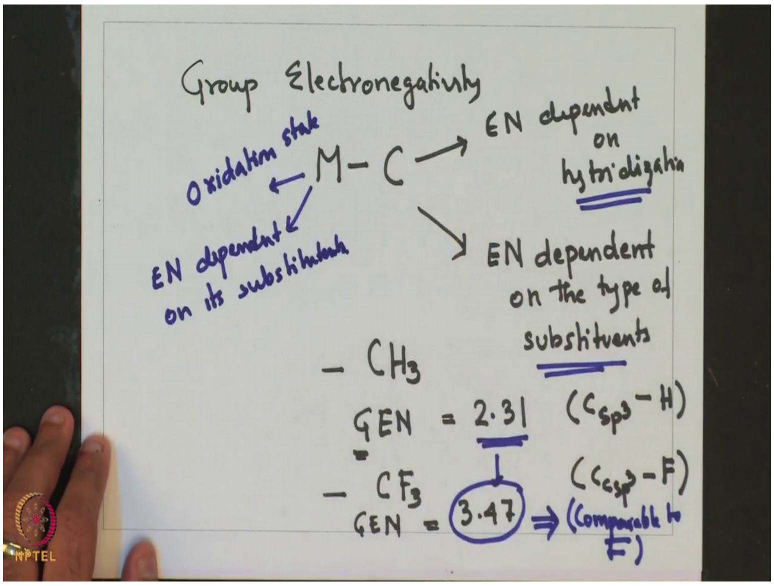

Remember for the metal carbon bond, we said that electronegativity dependent on hybridization. The next thing that is said is the group that the electronegativity of the carbon is also dependent on the type of substituent. To give an example, for example, if I have a methyl group the group electronegativity is 2.31. So, what it is, here it is sp 3 carbon C sp 3 carbon bound to hydrogen atoms it is 2.31. On the other hand, if we go to C F 3 which is carbon again as carbon C sp 3 carbon bound to three fluorine atoms because of the electron with drawing effect of the fluorine the group electronegativity of C F 3 goes up higher. So, it increases from 231 to 3.47 and which is almost comparable to fluorine which is 4.

So, what we see that the polarity of the metal carbon bond can affect the reactivity; and the polarity is dependent not only on the hybridization of the carbon, but also on the type of substituent's on the carbon as well as on the metal front it is dependent on the oxidation state. Let us try to look at what else does it depend upon. The way the carbon is dependent on the substituents; similarly group metal can also be dependent on its substituents. So, what we are saying that these bond being polar, the polarity depends on many other factors other than electronegativity.

So, in this lecture, I have given you a brief overview as to what are the reasons behind the extremely reactivity that is observed for transition metal organometallic compounds or metal organometallic compounds and what are the factors that are affecting it. So, with this, I conclude today’s lecture; and in the next lecture, we are going to prove this a bit more in details, and also look at what are the rules that are governing the reactivity of these compounds. We would also look at is there any classification that can be made on type of complexes they are formed the way we had seen in this lecture that they make different kinds of compound with metals depending on their location in periodic table. So, I look forward to seeing you again in the next lecture where we look at what kind of classifications, what kind of formulation, formalizations can be made of these compounds I hope you found today’s lecture beneficial.

Thank you.