**Transition Metal Organometallic Chemistry: Principles to Application**

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**Lecture- 03**
**Week – 01**
**Reactivity of Organometallic Compounds**

Welcome to this lecture on organometallic chemistry. Today we are going to touch upon something which is very interesting. And as to finding out, what are the important attributes of organometallic compounds. And what we saw in our previous lecture, that the uniqueness of organometallic compounds arises from their reactivity. And the reactivity of these compounds arises from the polarity of the metal carbon bond. So, the fact that these compounds are extremely reactive depends on the polarity of these metal carbon bonds.

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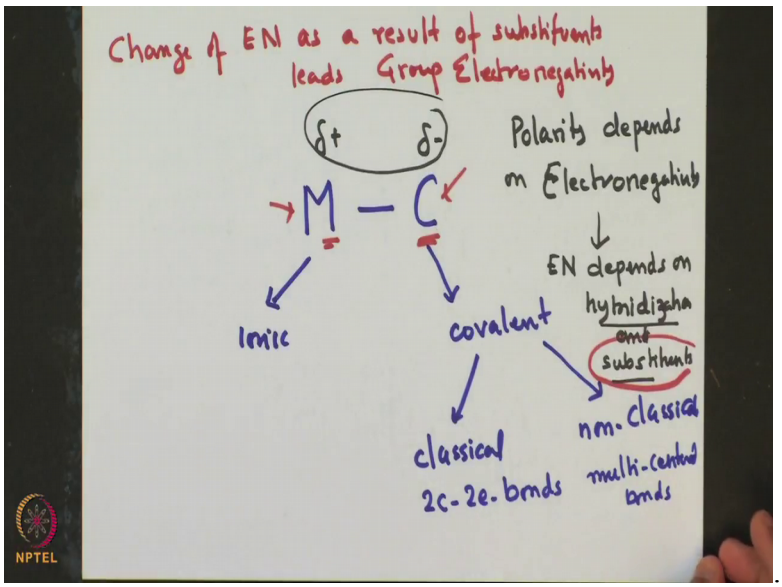


Metal carbon bonds can be ionic, can be covalent, can be classical, 2 centered, 2 electron bonds. Can be non-classical, multi centered bonds. What we saw that the polarity depends on electronegativity. The electronegativity in terms, electronegativity and that can be of metal, and can be of carbon, and of metal. The electronegativity depends on hybridization and substituents.

So, the polarity what this bond is, would depend on, what is the hybridization of the metal, what is the hybridization of carbon, as well as the metal, as well as what kind of substituents are present on the metal of the carbon. So, what we saw for carbon, it could change significantly, and same thing for the metal. And these gives rise, the change of electronegativity as a result of substituents, leads to group electronegativity. So, what we saw, is that the going from cf 3 to ch 3, this polarity change a lot. As well as the substituents in the metal would also lead to change of polarity. For example, in 83 Ge H and in Cl 3 Ge H.

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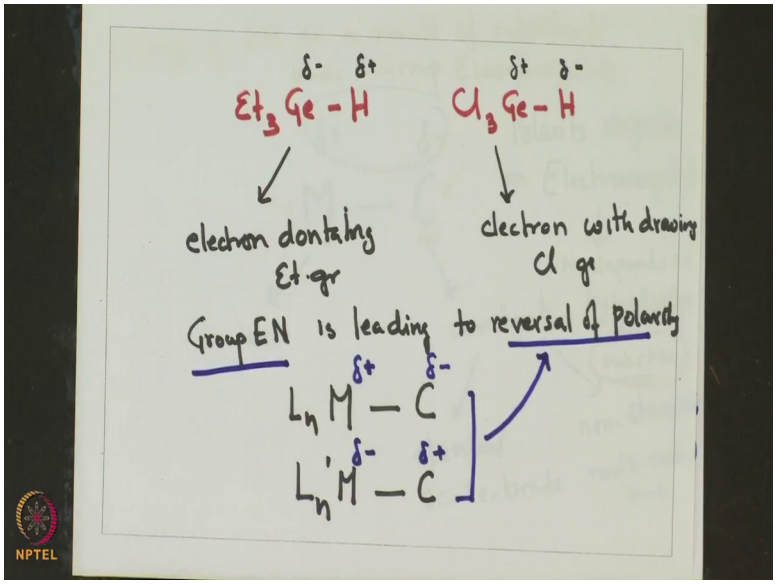


Because of change in substituents, from electron donating ethyl groups, to electron withdrawing chlorine groups. There is a reversal of polarity in the bond, in which this is del plus del minus. This is del minus del plus. Please note that the substituents is affecting the polarity of the germanium hydride bond, and group electronegativity is leading to reversal of polarity. This is very significant. So, if I have a metal carbon bond with certain group, let us say Ln, I have a polarity something like this.

Now, if I go to have a different substituents, I can in principle go from this to this. So, what we see is, reversal of polarity which arises due to group electronegativity.

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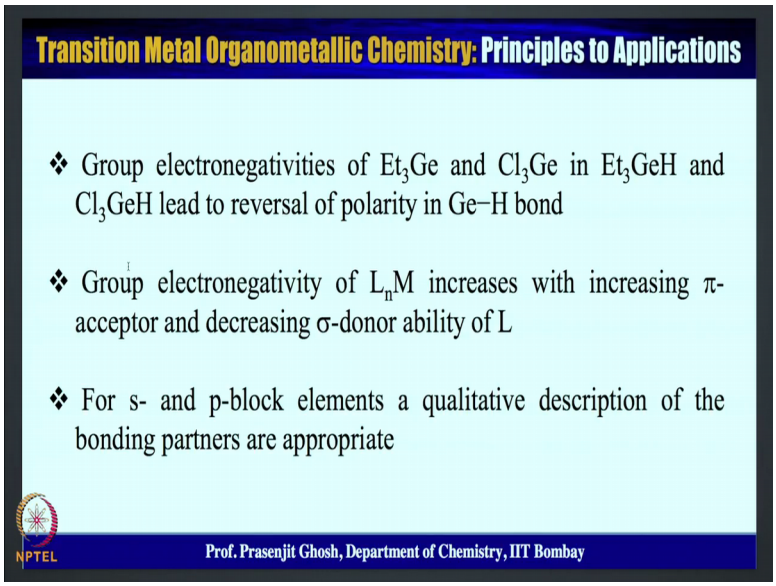


So, group electronegativity plays an important role in changing the group probability. What we are seeing that depending on what is the substituent on metal.

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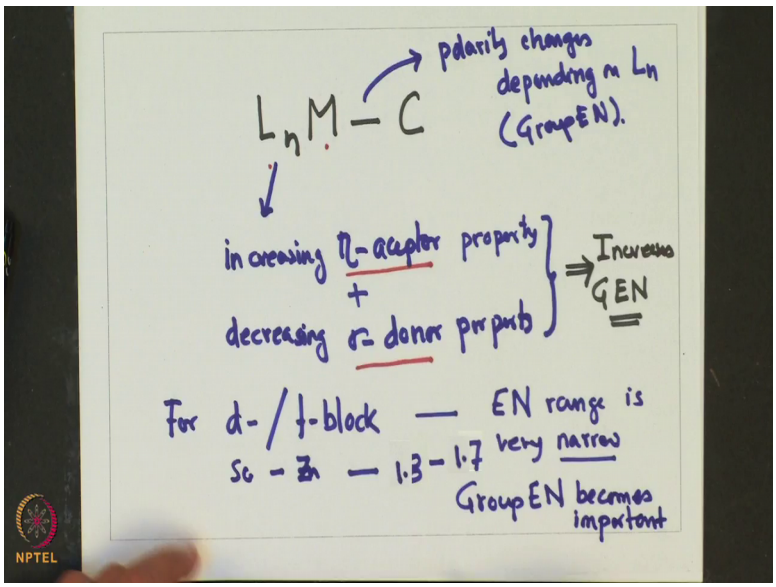


Let us say Ln the polarity of this bond changes L n, and this is called group electron negativity. Now the group electronegativity of L n depends upon the pi acceptor, properties of the ligand. This means that increasing pi acceptor property, and decreasing sigma donor property, increases group electronegativity. This makes is very important that how does this sigma donor and pi acceptor interaction happen between the metal and

the ligand, and that is why the bonding the interaction in transition metal complexes becomes all the more important.

The ability for metal to engage with a ligand depends on the placement in the periodic table. For example, for s and p block elements interact differently than that of our transition metal. For d and f block elements, and f block elements, their electronegativity range is very narrow; that is why the group electronegativity becomes important. Electronegativity range is very narrow from scandium to zinc. So, this range of change in electronegativity across the period is very narrow, and hence group electronegativity becomes important. And group electronegativity depends on what kind of substances plates on the metal n.

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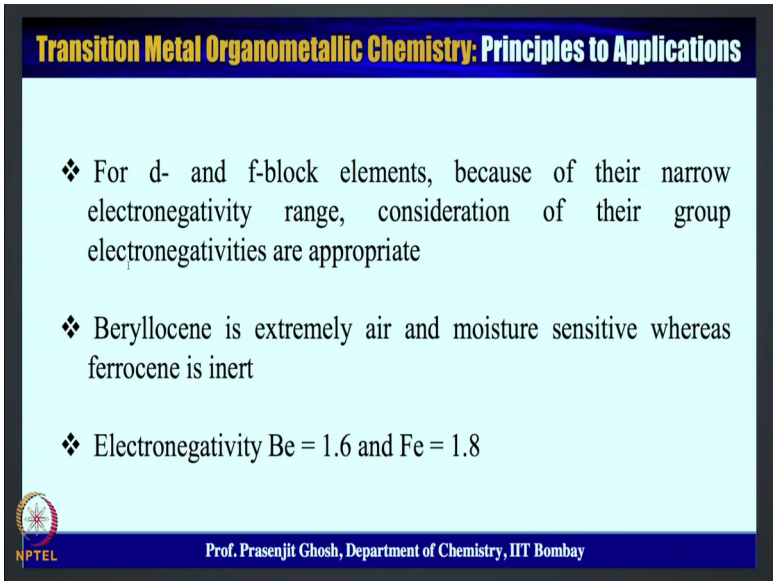


For example let us take a look at some important compounds. Let us say we take a look at this Beryllocene.

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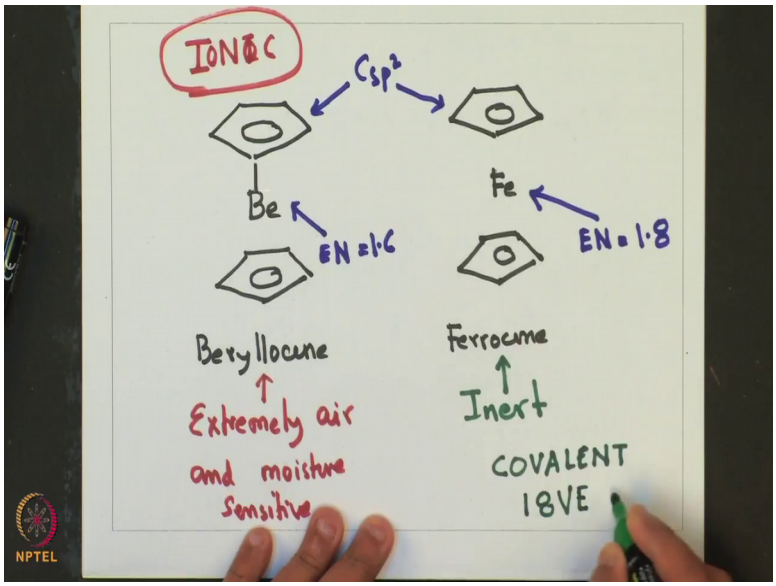


Beryllocene is a sandwich compound of 2 cyclopentadienyl anion with beryllium. And similarly a structural analog of this is ferrocene. Ferrocene is just a structural analog of beryllocene, and it also has two cyclopentadienyl anion ligand flanked by iron; iron flanked by 2 cyclopentadienyl anion ligand returning ligand. Now you if you were to explain the reactivity of it, it seems very confusing, because the carbon is same hybridization over here as well as over there. Hence the electronegativity of the carbon would not change much. As for the electronegativity of beryllium, it is 1.6, and electronegativity of iron, it is 1.8.

So, if one were to look at the electronegativity difference between the metal and the ligand, they would almost be the same, but the interesting aspect is that beryloceneis extremely, highly reactive and extremely air and moisture sensitive. Whereas, ferrocene is inert. So, this is an interesting example where we see the type of bonding, or type of interaction dictate the property. The interaction between metal carbon interaction in beryllocene is very ionic, completely ionic. Whereas, the inertness in ferrocene arises from their 18 electron covalent. This is covalent interaction, and also they obey the inert 18 electron rule.

So, what we see, is the apart from electronegativity, the polarity, there are certain important concepts; like the nature of bonding, ionic or covalent, also whether it is

obeying the inert, it electron balance electron rule or not, that governs the reactivity. So, that brings us to a very important point in this discussion.

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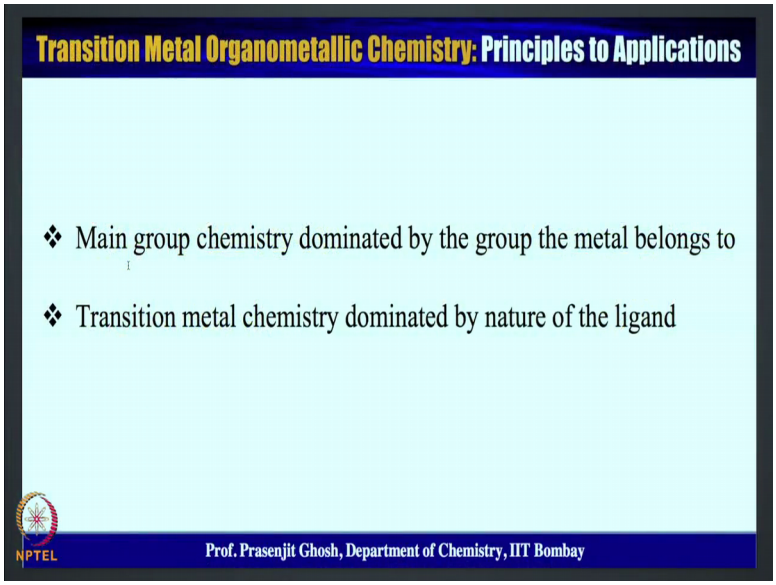


Similarly, for metal carbon, main group interaction, is dominated by what kind of, which position of ligand the metal belongs to.

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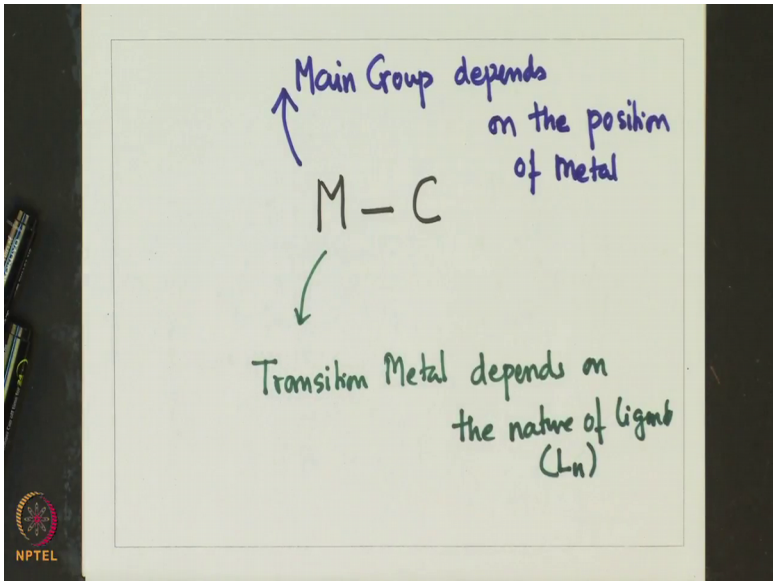


So, metal carbon interaction for main group elements depends on their position in periodic table metal. On the other hand, for transition elements, the reactivity as well as. The reactivity and there, the nature of interaction depends on the type of ligand it is

substituted with, present on it. So, here we see a very important concept merging out, that not only the electronegativity, but there are factors which goes beyond electronegativity in explaining the reactivity of these complexes.

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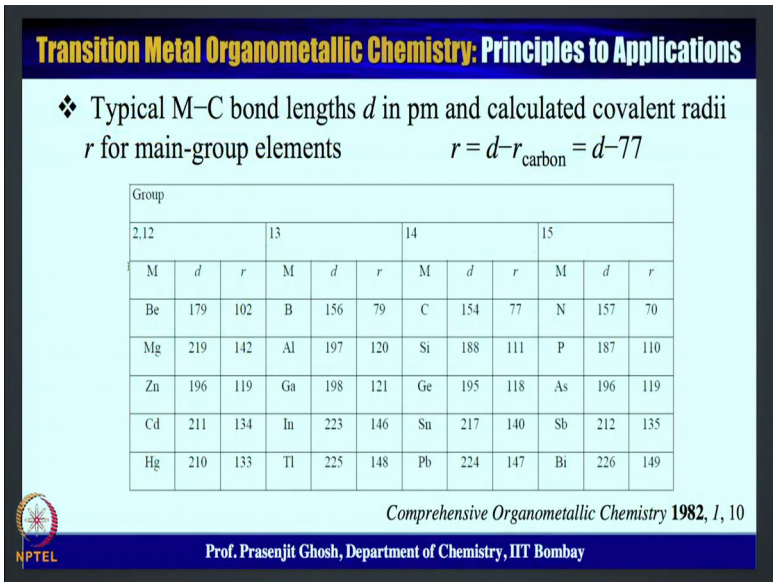


Also important in this, is the knowledge about metal carbon bond distances.

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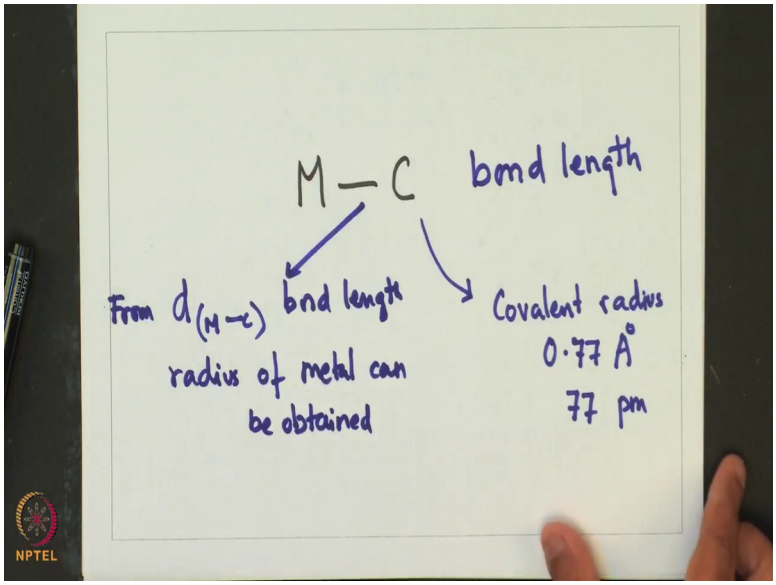


Now, for a covalent bond, carbon covalent radii says 77 angstrom, or 77 picometer, and from the total metal carbon distance, one can get calculate the radius of the metal. From this metal carbon bond length, radius of metal can be obtained. And using this large

number the Ca covalent and radii of, a large number of metals have been obtained. For example, magnesium had a radius of 102 picometer beryllium, magnesium 142, zinc 119 so on and so forth, depending on their place in the periodic table.

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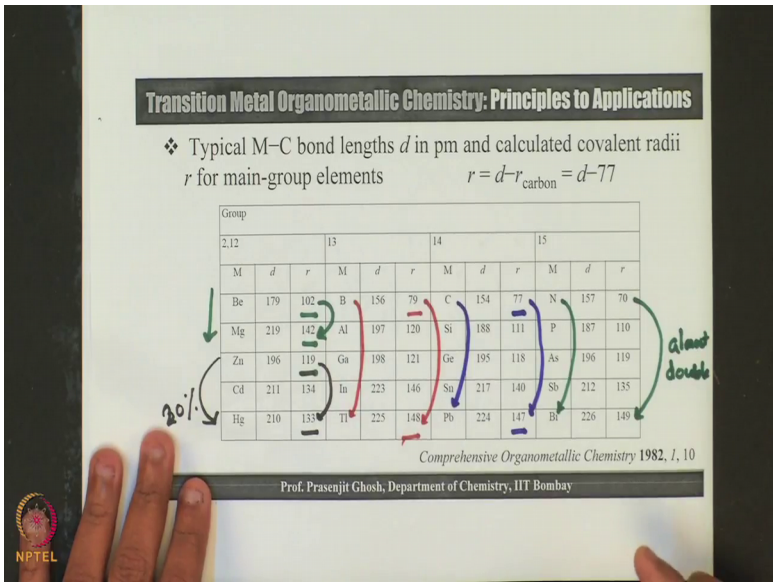


Now as we see that if one goes down the table, let us say from beryllium to magnesium. There is an increase in bond length from 104 to 142 similarly if one goes down from zinc to mercury, the bond length increases from 119 to 133. So, that is about 30 percent increase in bond length 20 percent increase in bond length; however, for the main group elements, let us say if one goes from boron all the way to thallium, the bond length almost doubles 79, becoming 150. There is a huge increase if we look at group 14, and we look at the trend from carbon to lead. We also see from 77, it goes to 147 from, if we go beyond to the next one from nitrogen to bismuth, it also goes from 70 to 140. So, these are almost double, as we go down the group and these also impacts the reactivity of the metal carbon bonds.

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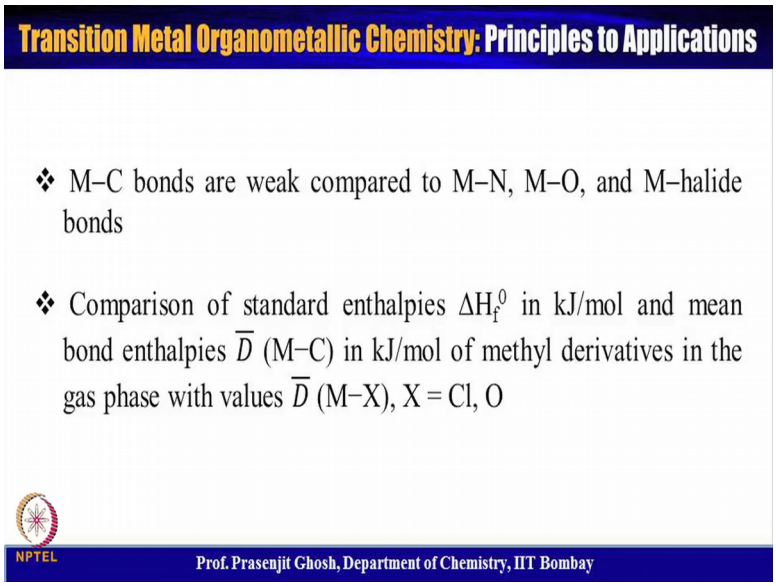


Now, from a very conventional method, the bonds which are longer, are bonds which are weaker.

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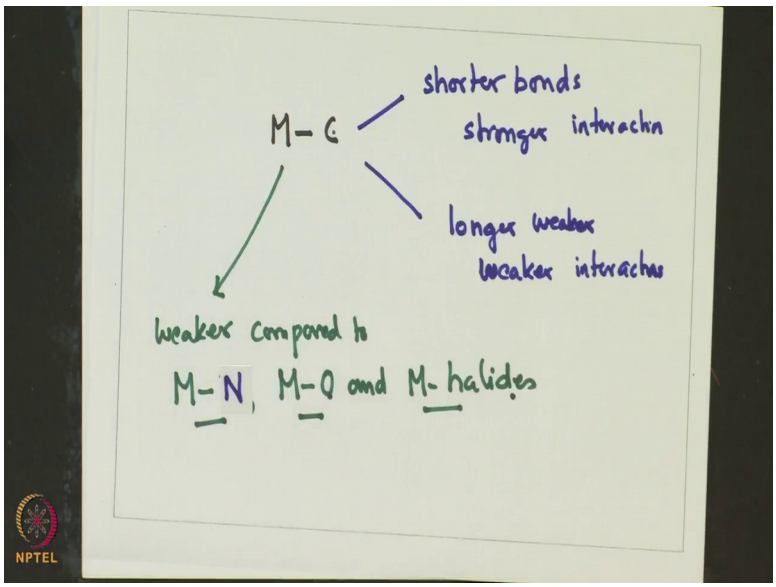


What we know is, shorter bonds. Shorter bonds stronger interaction and longer bonds weaker interaction. So, what turns out that a very important concept, is emerging from the bond variation in bond lengths. Like we saw the variation in polarity arose from electronegativity, and could explain reactivity. Similarly if you look at the bond length, and if you look at the variation in bond lengths, it tells us about the strength of the bond,

and that in principle could also give an input about how, what would be the reactivity. A stronger bond means lesser of a reactivity. A weaker bond means more of reactivity. Metal carbon bonds are weaker compared to the metal nitrogen, metal nitrogen, metal oxides and metal halide bonds.

Now these bonds are weaker between. These are weaker, because these are more polar than that of metal carbon bond. So, enhance polarity in metal nitrogen, metal oxygen, metal halides, as the nitrogen oxygen halides are more electronegative than carbon. So, these are more polar, and hence they form strong bonds. And the discussion on the strength of the bond arising due to the variation in the bond distance, as well as the strength of the bond arising due to the polarity of the bond, brings us to the very important concept of bond energies of metal carbon bonds. So, one need to know that how much does an metal carbon bond worth. How does this metal carbon bond compared with that of metal nitrogen, metal oxygen, or metal halide bonds.

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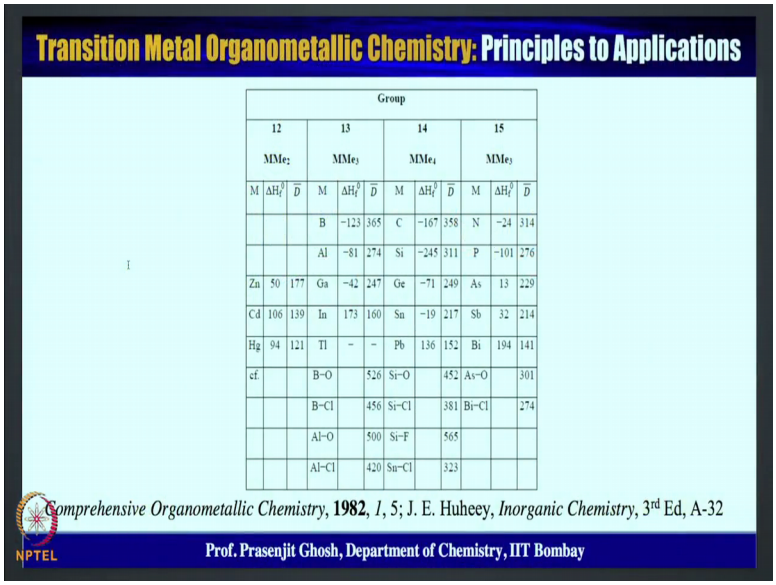


So, here we have a interesting table, that sort of compares the metal carbon bonds, as well as metal heteroatom bonds. For example, if we look at boron.

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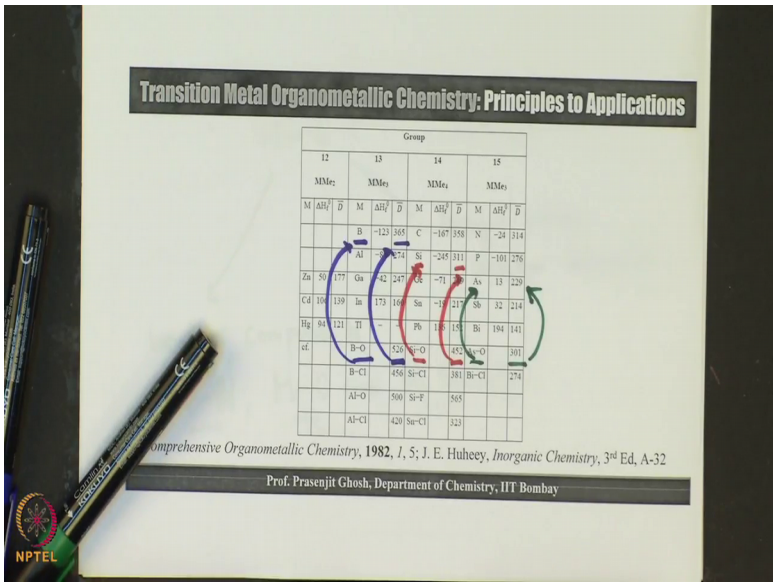


So, boron oxygen bond is very high about 526 kilojoules per mole, and corresponding boron carbon bond is much lower. So, if you go from boron oxygen which is here, to boron carbon which is here. We see that there is a decrease. Similarly if we look at; for example, silicon oxygen bond which is of 452, and then we look at the silicon carbon bonds, which is 311. Then here also we see that there is a decrease. Same thing for arsenic, arsenica, arsenic oxygen is 300 think one. Whereas, arsenic carbon is 229. Here also we see there is a decrease.

So, that sort of tells us how inherently weak the metal carbon bonds are, with respect to metal heteroatom bonds, and this bond enthalpy becomes more important, when we look at organometallic compounds for example. Here we come to another concept of how strong are these metal alkyl bonds.

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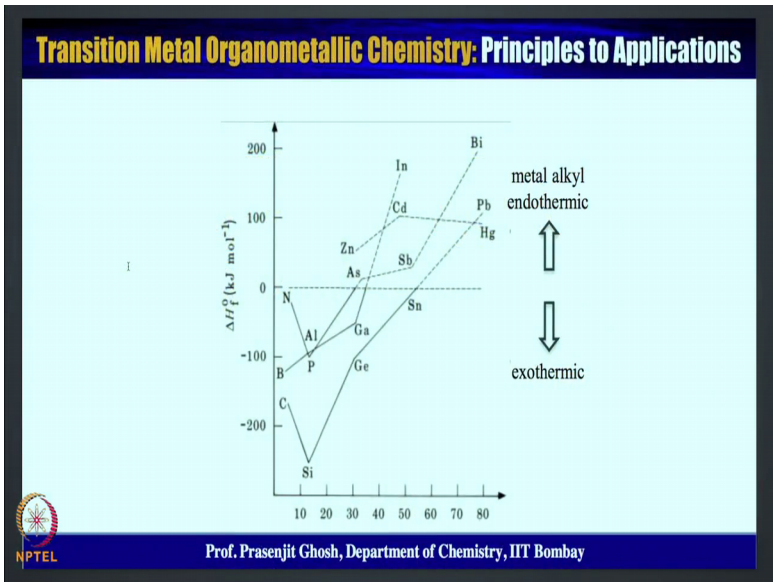


And we have a plot which has on its Y axis, says the delta H of formation of bonds along particular group.

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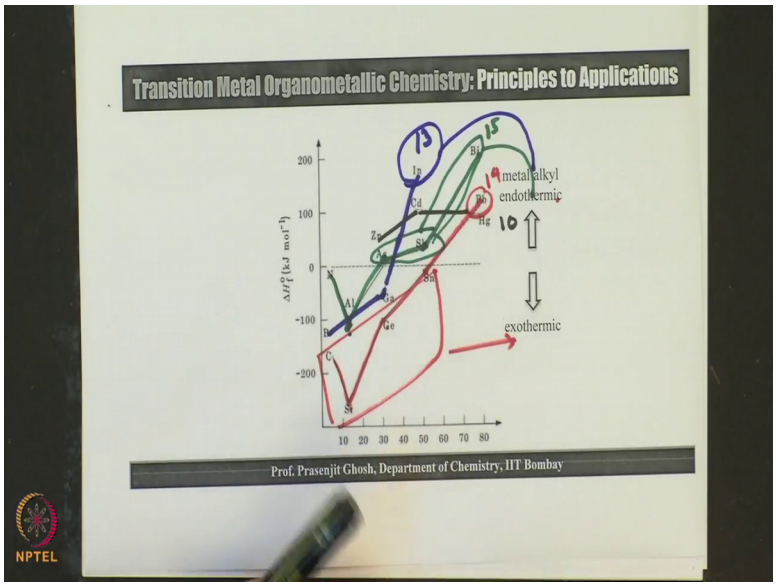


So, this, the bottom one goes from carbon to silicon, to germanium, to tin, to lead hm. This is group 14. We have the data for group 13. So, what we see the group 13 bonds are less endothermic then group 14. So, we have boron, aluminum, gallium and then we have all the way to indium. So, this is 13. This was 14. So, we have group 15 nitrogen phosphorus, arsenic antimony bismuth 15, and we have the group 10 with zinc cadmium

mercury. So, what we see interesting trend emerging out. It says that most of the group 14, which is carbon, silicon, germanium, tin. They are all exothermic; that means, they are favored. Whereas, the lead is endothermic.

So that tells us lead is not as stable as the other one. If we go to group 15 what we see is, only nitrogen and phosphorusare stable, arsenic silicon and bismuth, they are all endothermic. And similarly if we go to group 13, we see from indium onwards. It is also endothermic, and as for the group 10, it is all zinc cadmium mercury. All are endothermic; that means, that ones which are endothermic are less stable than the ones which are exothermic. And if they are so, then they may easily decompose.

So, today let me summarize. We have gone over the reactivity of organometallic compounds, and what we found that not only the polarity a influences the reactivity, and the polarity can arise from the electronegativity difference, as well as the reactivity can also be dependent on the strength, strength of the bond. Strength of the bond can be gauged by the bond distances. Shorter bonds mean stronger bonds, longer bonds means weaker bonds, and the strength of the bond can also be ascertain from the bond energies.

If something is endothermic, then it is less stable as compared to something which are exothermic, and this gives a valuable input as to how this organometallic compounds react, and what are the factors which are responsible for this. So, as we have seen these concepts. In the last few lectures we have seen; what are the historical background. We have seen how the polarity influences the reactivity. We have seen how the bond energy influences the reactivity, and then we move on to a very important topic which is on the classification of this compounds, and that would be the subject of the next lecture.

I hope you really understood assimilate, as well as enjoyed this series of lecture. And I hope that this generate some interest in you in the area, which is really fascinating, and I think you have slowly started to realize; why is it. So, with that I would conclude todays lecture. I look forward to seeing you in the next lecture where we will discuss something very important, as to classification of this compound based on their stability. And with that I thank you for going through all these lecture.

Thank you.