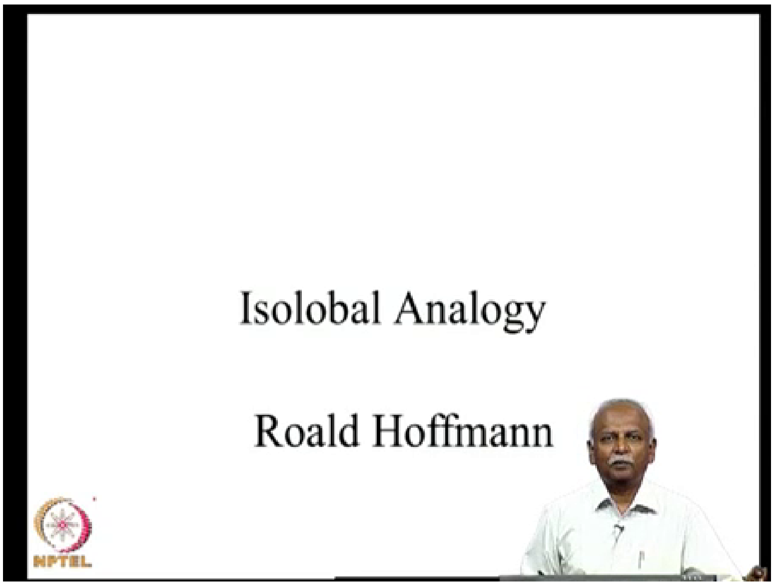
**Course Title – Introduction to organometallic Chemistry**
**Prof. A. G. Samuelson**
**Department of Inorganic and Physical Chemistry**
**Indian Institute of Science, Bangalore**

## Lecture - 29
## The Isolobal Analogy

Today, we will discuss the concept of Isolobal analogy. The problem that we have in organometallic chemistry or even inorganic chemistry is the fact that we do not have the same systematization, that is available in organic chemistry.

(Refer Slide Time: 00:35)

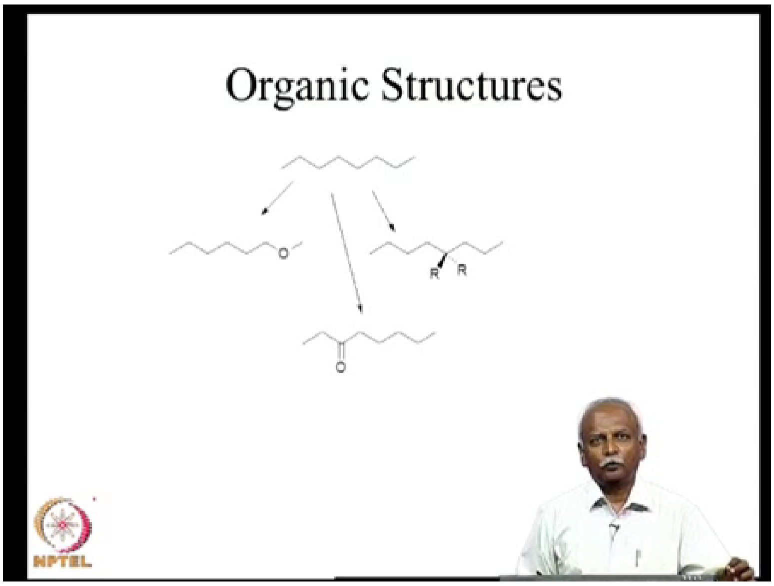


Isolobal Analogy

Roald Hoffmann

So, a concept of isolobal analogy was introduced by professor Roald Hoffman and this analogy allows one to understand the variety of organometallic compounds, structures, and sometimes the reactivity. Primarily the structures are explained extremely well using the isolobal analogy. So, let us just develop this concept in the following few slides.

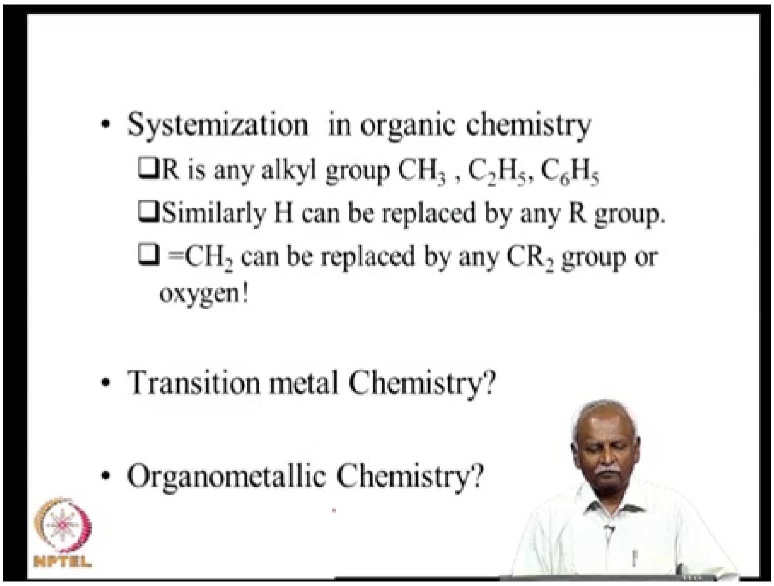
(Refer Slide Time: 01:01)



Organic Structures

If you look at organic structures, you notice that there are different functional groups, these functional groups can be transformed in a fairly systematic manner in a wide range of compounds. So, you could think of for example, a ketone which is present in an organic structure which can be present in a very different scenario in a cyclic molecule. It would behave very similar to the ketone, which is present here in this linear acyclic form and these groups are replaceable in a systematic fashion. If I have 2 hydrogens which are present on this carbon, each one of them can be replaced by any R group which is a univalent radical. Similarly, a C H 2 group can be replaced by an oxygen and so on.

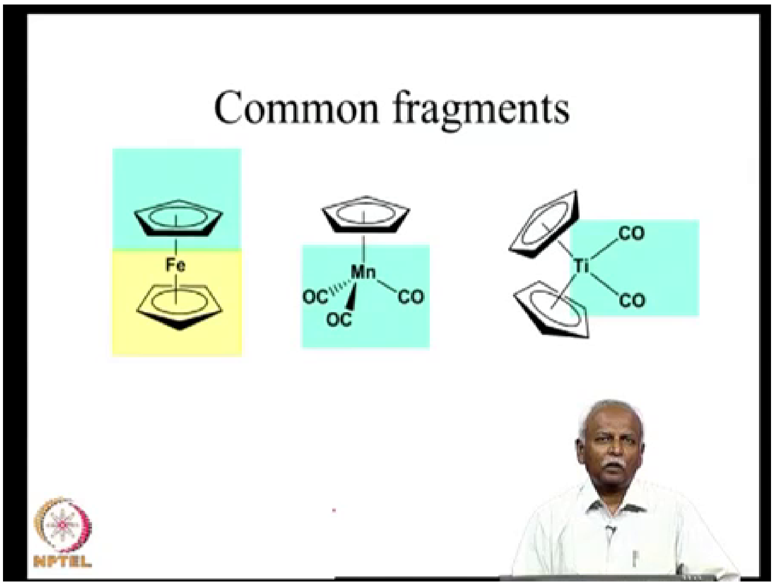
(Refer Slide Time: 02:09)



- Systemization in organic chemistry
  - ❑R is any alkyl group $CH_3$ , $C_2H_5$, $C_6H_5$
  - ❑Similarly H can be replaced by any R group.
  - ❑ $=CH_2$ can be replaced by any $CR_2$ group or oxygen!
- Transition metal Chemistry?
- Organometallic Chemistry?

So, this type of systematization is unfortunately not available in inorganic chemistry whereas, in organic chemistry you have a systematic replacement that can easily explain wide range of compounds. It would be nice if we can do it for transition metal chemistry and organometallic chemistry. So, that is really the goal and we will see how far we can succeed in this particular venture.

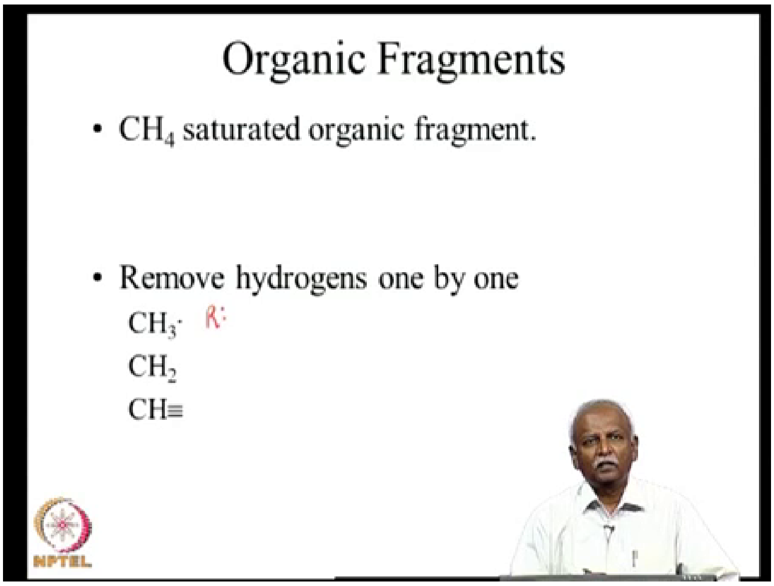
(Refer Slide Time: 02:41)



Common fragments

There are indeed common fragments if you look at organometallic compounds. In general, you find that there are common fragments like the cyclopentadienyl fragment which is highlighted for you or for example, the F e ion cyclopentadienyl group that is pictured here in yellow. You can have these groups such as Mn C O 3 or M C O 3, a metal with 3 Ca H 3 carbonyl groups, so these are recurring fragments.

(Refer Slide Time: 03:14)



## Organic Fragments

- $CH_4$ saturated organic fragment.
- Remove hydrogens one by one

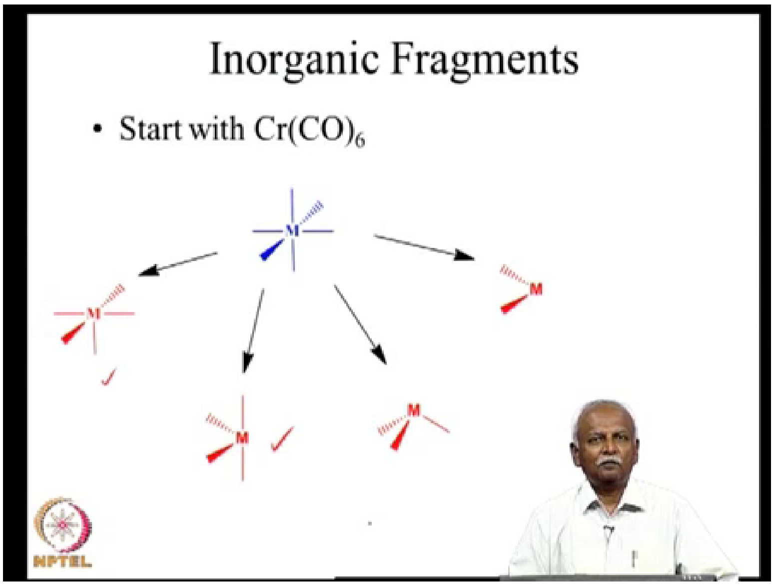
$CH_3\cdot$ R:

$CH_2$

$CH\equiv$

So, if one can in a systematic way replace them in different molecules just like we can do it in organic fragments, it would be nice. Now, how did we form the organic fragments, if you really want to go back to how one can think of fragments, you are normally looking at the C 1 fragment and the saturated variety at that. So, that is methane and we systematically remove hydrogens one by one in order to generate a variety of molecules for fragments which can be used as groups that can be plugged in a molecule. So, you have the alkyl group, which is the methyl radical here and you can also have the methylene group and the methane group and so on.

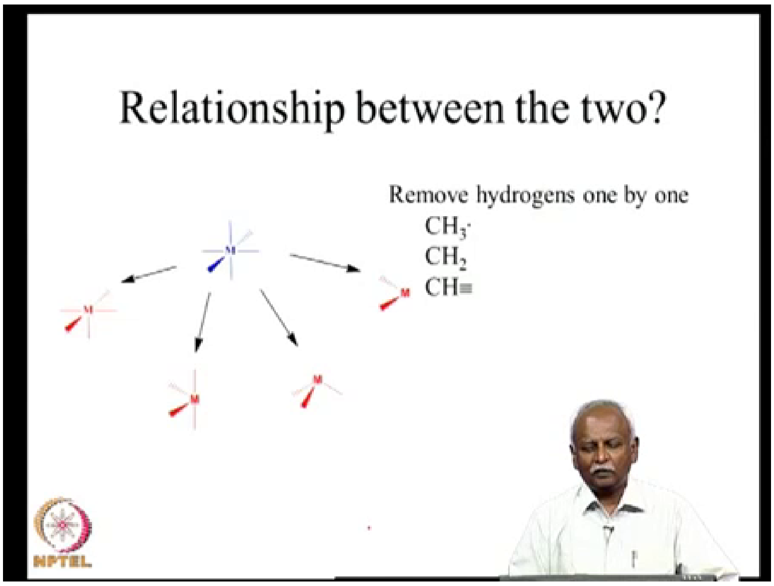
(Refer Slide Time: 04:08)


Inorganic Fragments

- Start with $Cr(CO)_6$

So, let us take a look at the inorganic fragment and see if we can do such plucking of groups so that we can arrive at different fragments. So, let us take hexacarbonyl chromium and that is like typical octahedral fragment available in inorganic chemistry and organometallic variety of the inorganic icon and octahedral metal complex. Let us remove one by one and then we get these various fragments, a 5 coordinated metal atom a 4 coordinated metal atom and so on. When it comes to 3 and 2 or even 4, we tend to have or we can have a variety of geometries, but nevertheless these fragments can they be used as a fragments that we encounter in organic chemistry.

(Refer Slide Time: 05:07)


Relationship between the two?

Remove hydrogens one by one

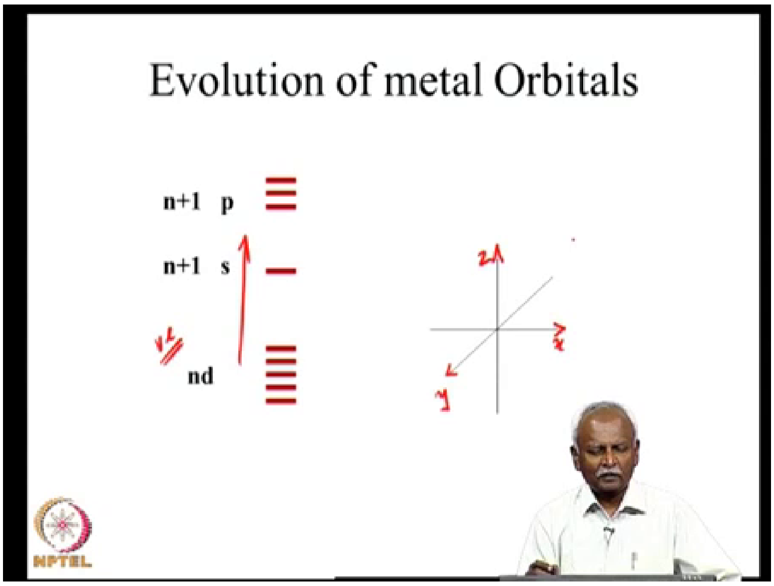
$CH_3\cdot$

$CH_2$

CH≡

Can we have a kind of a mapping of one to one? That is the question we are asking really.

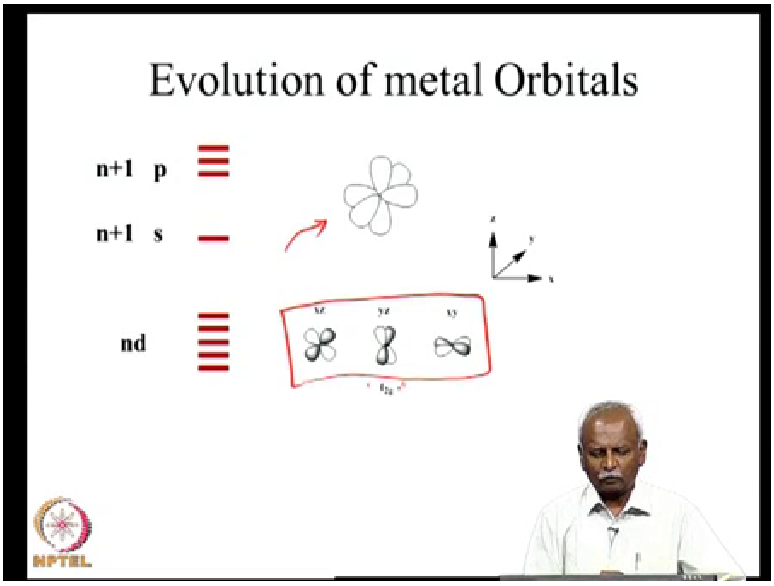
(Refer Slide Time: 05:16)



Evolution of metal Orbitals

So, in order to do that let us take a look at electronic structure of these molecules because that would give us a key that would give us a way to systematically understand these molecules. So, as we are described earlier in octahedral fragment which is pictured here, we are to define our axis. So, we will use the usual axis that we the convention the z axis will be the one which is going up and down on the screen, and the x axis is the one which is going from left to right. The y axis is the axis which is projecting into the screen, so you have three axes defined and in these axes, you have a bunch of orbitals valence orbitals. In the case of transition metal systems, we normally talk about n d and the n d n plus 1 s and n plus 1 p which are pictured, here the energy ordering is in this fashion. Now, if you want to form an octahedral complex, we have to choose the right set of atomic orbitals that will form a combination of molecular orbitals with the six ligands, which are coming in the plus x minus x plus y minus y and the plus z minus z directions.

(Refer Slide Time: 06:51)

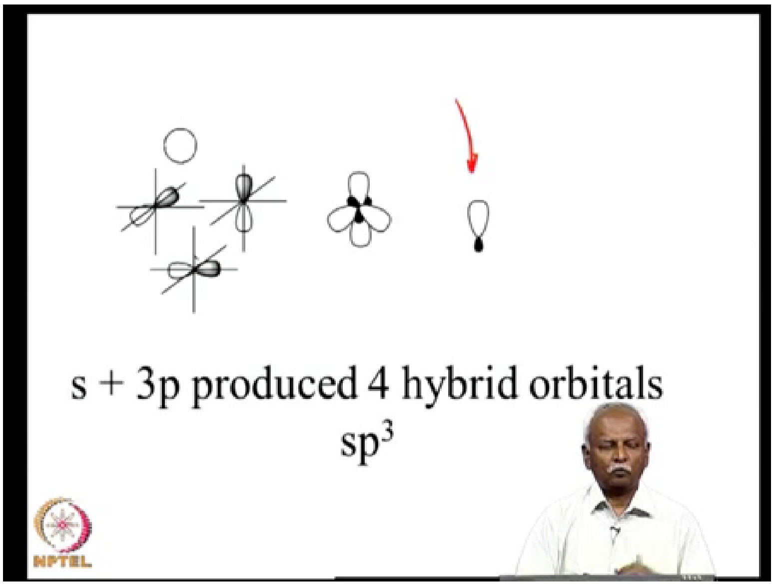


Evolution of metal Orbitals

So, if you want of form a set of molecular orbitals, we normally end up taking the d 2sp 3. We take 2 d orbitals 1 s and 3 p orbitals, so that we can combine them and form a combination of molecular orbitals, which will be pointed along the x y and z directions. We are in fact mixing two methodologies, the valence bond formulism and the molecular orbital formulism. Here in the molecular orbital formulism, we normally do not talk about hybridization of the d 2 sp 3, but if you look carefully at the ligand group orbitals that have the right symmetry to interact with six ligands coming in the x y and z directions.

The molecular orbitals are in fact those which are formed by mixing the same set of orbitals which we have used in the valence bond formulism. So, this type of mixing of these two theories gives us an easy way of explaining the fragments molecular orbital that we are going to obtain. So, here I have for you pictured the d 2 s p 3 hybrids which are oriented in the right way to interact with the ligands coming along the cartesian coordinates. So, the three orbitals that are left behind they are not going to interact with any orbitals along the axis because they are pointed in between the axis or the x z y z and the x y orbitals. These are in the crystal field formulism encountered even in the molecular orbital formulism; we would call them the t 2 g set.

(Refer Slide Time: 08:39)

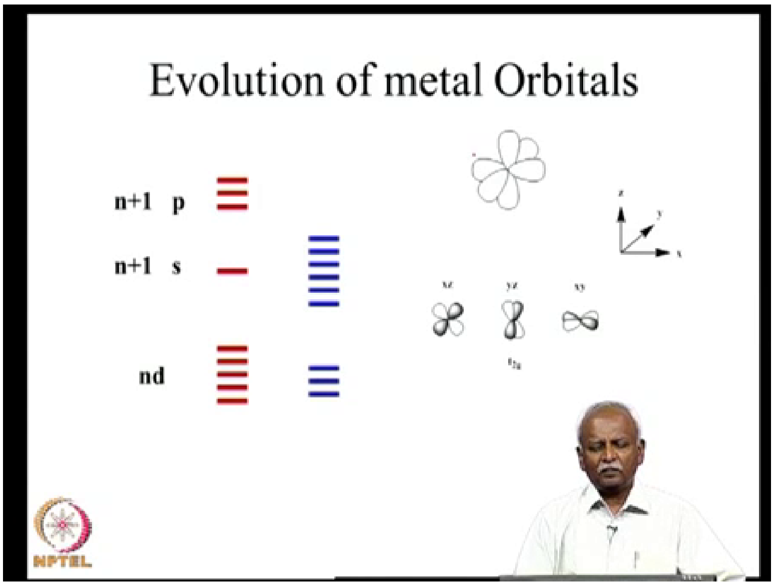


s + 3p produced 4 hybrid orbitals

$sp^3$

So, the situation is a chin to what we encountered in organic chemistry when we in fact hybridize s and 3 p orbitals in the carbon to generate 4 hybrid orbitals which we call as a sp3 hybrid. So, these hybrids are now pointed along the 4 vertices of the tetrahedron and you are familiar with this and each one of these lobes would look in a in this fashion. So, each one of these lobes, which are formed by combining the s and the 3 p's would look approximately like that and are pointed along the vertices of a tetrahedron.

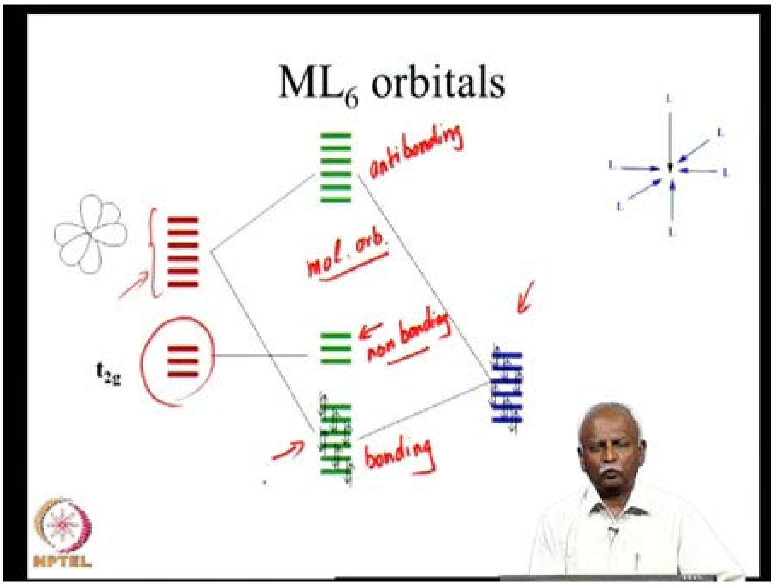
(Refer Slide Time: 09:26)



Evolution of metal Orbitals

So, let us now look, go back to the metal fragment and if you look at it you get a exactly similar picture.

(Refer Slide Time: 09:36)

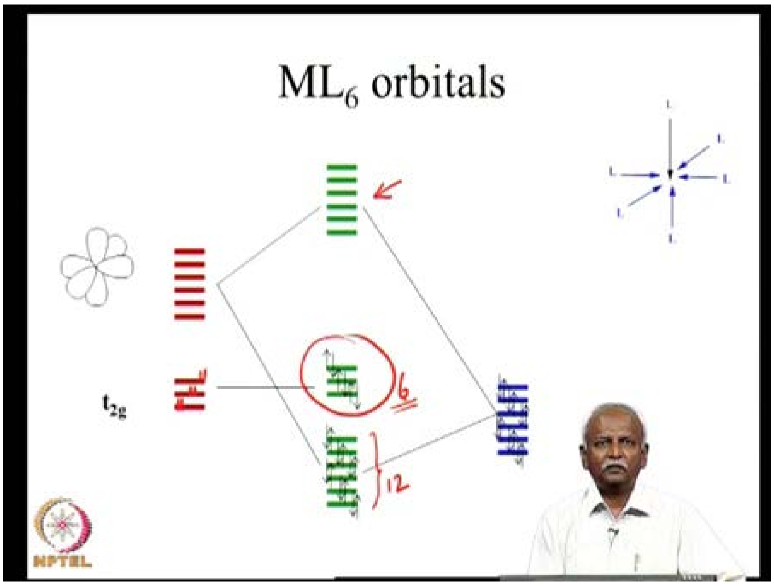


ML$_6$ orbitals

You have a set of orbitals which are pointed along the x y and z axis and if a metal complex is formed by combining six ligands each with a pair of electrons. They come towards the metal atom, we are hypothetically using a metal which neither has d electrons or the no valence electrons basically. So, we have the set of t 2 g orbitals which are empty. The six ligand group orbitals which we formed metal group orbitals, which are suitable for interacting with the ligand group orbitals are mixed and they would have an average energy corresponding to the weighted average of the d 2sp 3 orbitals.

So, here we can interact with the ligand group orbitals which presumably are filled and are usually at a lower energy level. So, they would combine together or mix to form molecular orbitals, so these are our molecular orbitals. So, these are our molecular orbitals which are formed where you have a set of bonding orbitals this is our bonding group and this is our anti-bonding orbitals. In our approximate picture we are not worried about the individual levels or energy levels, but approximately you would have a bonding and an anti-bonding group and this would be essentially the non bonding group. Now, let us take a closer look at this picture, we have the ligand which has come in with 12 electrons 6 into 2 12 electrons and these are filled nicely in the bonding set of orbitals.

(Refer Slide Time: 11:28)

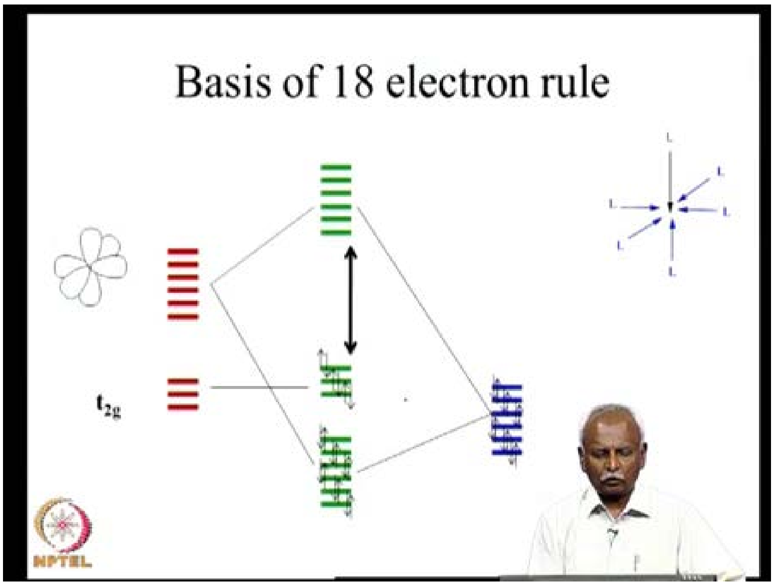


ML$_6$ orbitals

Now, if you have in addition to the electrons that are there in the ligand group, suppose I have a maximum of 6 electrons on the metal. So, I have 6 electrons which are sitting here and these 6 electrons would only fill up the t 2 g set of electron set which is in the middle. It is the non bonding group, you will notice that we had 6 into 2 12 electrons here and 6 electrons here. So, we have a total of 18 electrons and this is roughly the origin of the 18 electron rule. When you have more than 18 electrons, you tend to form electrons tend to form complexes where you are populating the anti-bonding orbitals that are located here.

Since you populate anti bonding orbitals, you will have weaker metal ligand bonds. Essentially, what we are saying is these 6 electrons which are present on the metal, go into non bonding orbitals do not contribute really to the bonding situation here. Even if you have less than 6 bonding electrons, so instead of 18 if you have 16 or 14, you would still have a reasonably good bonding situation between the metal and the ligand. Now, let us proceed further.

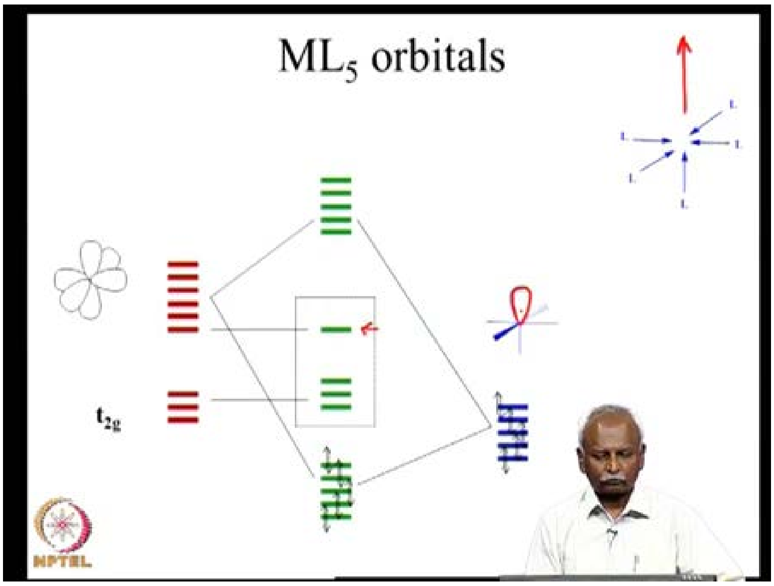
(Refer Slide Time: 12:59)



Basis of 18 electron rule

Let us take a look at what would happen if you are to remove one of these ligands, but before we do so we must emphasize the fact this energy gap between the bonding and non bonding group of orbital is prohibitive as compared to energy gap that is existing. As a result usually one does not fill in these anti bonding orbitals at all, in most cases you would stop at 18. So, although 18 electron rule is touted as the most stable configuration, you could have less than 18 electrons and still have stable configurations without difficulty.

(Refer Slide Time: 13:47)

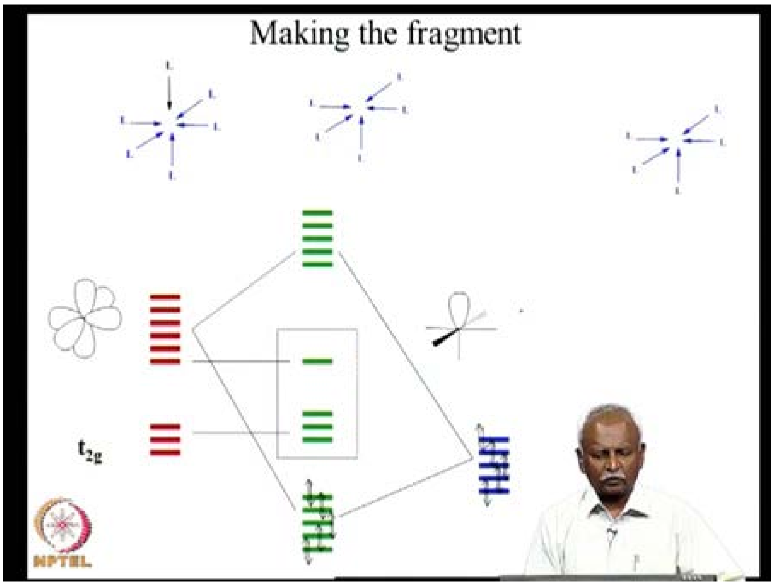


ML$_5$ orbitals

So, if you remove one of the electrons, one of the ligands that have come in with the pair of electrons and these ligands are let us say you remove these ligands by just pulling them out from the top the plus z direction, we just removed one electron. Now, what would happen is the following, let us say we prepared the metal in order to interact with six ligands. So, one of these orbitals metal group orbitals which are suitable for interacting with the ligand is now left without an appropriate combination to form the bonding and the anti bonding orbitals.

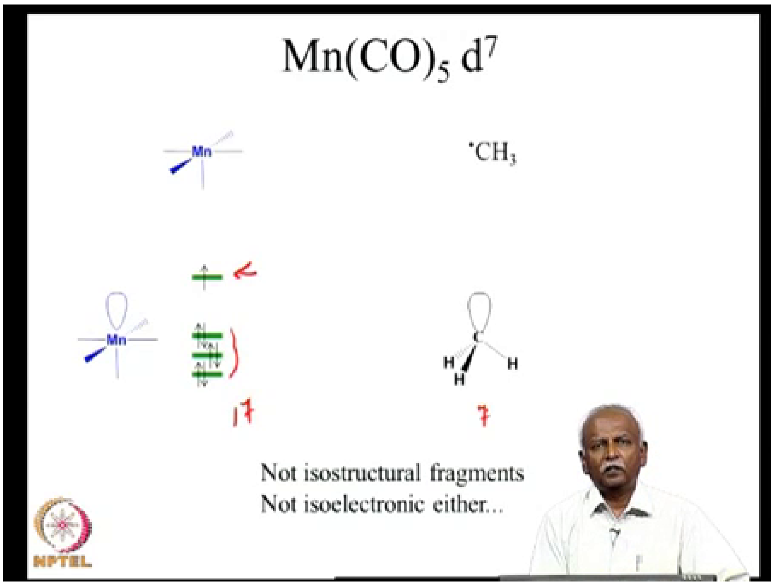
So, it would approximately be at a level where it had in where it had mixed, so this is approximately the d 2 weighted average of the d 2 and sp3 orbitals. It will be at a slightly higher energy compared to the t 2 g set. So, you have 1 electron here and what we are going to find is that this leaves an empty orbital, which is present on the metal atom in the place where the ligand should have been. So, you have an M L 5 complex and you have an empty orbital which is present on the metal.

(Refer Slide Time: 15:14)


Making the fragment

Let us go further and think about what would happen what would happen if we fill in some electrons into the metal.

(Refer Slide Time: 15:26)



$Mn(CO)_5$ $d^7$

$^{\bullet}CH_3$

Not isostructural fragments
Not isoelectronic either...

If you have the approximate appropriate number of electrons, let us consider Mn C O 5 manganese pentacarbonyl is a fragment that is formed when you break Mn 2 C O 10. If you break Mn 2 C O 10, if you split it in half you would end up with Mn C O 5 species which would have exactly the same structure as what we have drawn here. This fragment Mn C O 5 fragment would have 7 d electrons, you remember that the electronic configuration of manganese, which is usually written has has d 5 s 2 and in the free state.

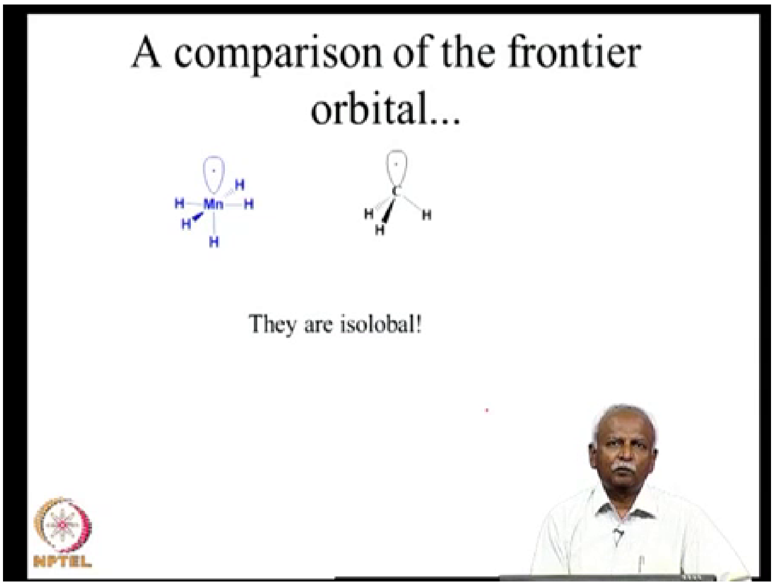
In fact in a chemically significant environment would switch over to d 7 and you would end up with the arrangement of filling in the t 2 g set with 6 electrons. The empty orbital that was available for the ligand had it been there is now sitting in this one orbital, which is at a slightly higher energy level. Notice that when you form Mn 2 C O 10 we would have simply combined this one electron, which is present on this Mn 2 C O 5 fragment with the other Mn 2 C O 5 fragment to form Mn 2 C O 10. Now, we have these 7 electrons and you have a single electron on the manganese fragment.

Consider the situation you have when you remove one ligand from methane. If you remove 1 ligand 1 hydrogen atom from methane you end up with a C H 3 radical and the C H 3 radical has a s p 3 hybrid present on the carbon. The s p 3 hybrid has a single electron present in it and that single electron, which is present on the metal group can be compared with the Mn 2 C O 5 fragment which also has a single electron. Notice some more similarities which are present between the two groups, what you have on the right hand side is the methyl group.

The methyl group has got a single lobe and the manganese Mn C O penta carbonyl has also got a single lobe which is a s p 2 s p 3d 2 hybrid. Now, the forms are reasonably similar, now these are schematic diagrams what about the actual diagrams. We should let us take a look at them, also before we do that we should tell ourselves that these are not iso structural fragments. The manganese has got 5 groups carbon has got only 3, neither are they isoelectronic the carbon has has got only 7 electrons. Now, the manganese has got only 7 valence electrons and there are more electrons on the manganese, and so the carbon and the manganese cannot be considered as isoelectronic fragments.

Nevertheless, the total valence electrons that are present if you consider the carbon and manganese they appear to be similar. What we have forgotten is that there are 5 bonding electrons which we have omitted and here we have 6 bonding electrons, which we have counted. So, the total number of electrons on manganese should be really be 17 and this one should be 7, so we are not talking about iso-electronic fragments.

(Refer Slide Time: 19:12)

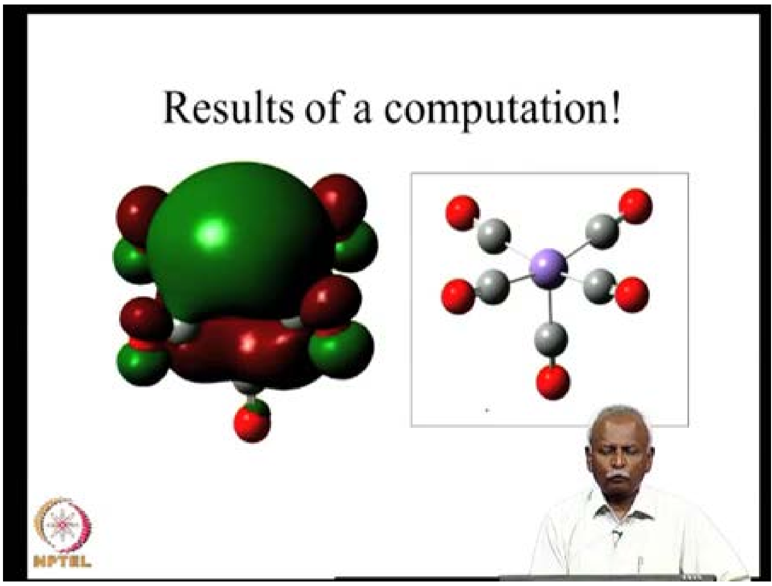


A comparison of the frontier orbital...

They are isolobal!

The comparison of the frontier orbital tells us now that the two have a similar form they have a similar lobe.

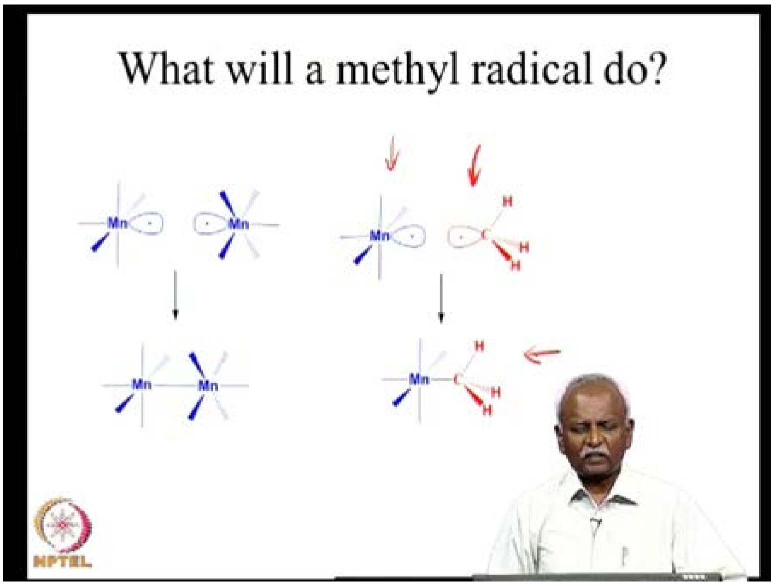
(Refer Slide Time: 19:23)



Results of a computation!

If you look at the results of a computation, you really find that there is a large lobe on the manganese, which as if you think of a C O of the fragment as a being oriented in this fashion, here you have contributions from all the carbonyls also to a small extent. So, the highest occupied molecular orbital which was having the single electron in fact looks as if it is got a large lobe which is pointed away from the Mn 2 C O 5 fragment, but it is very similar to what you have on the methyl group which also had a single lobe. Only difference seems to be small contributions from the carbon monoxides as well.

(Refer Slide Time: 20:15)

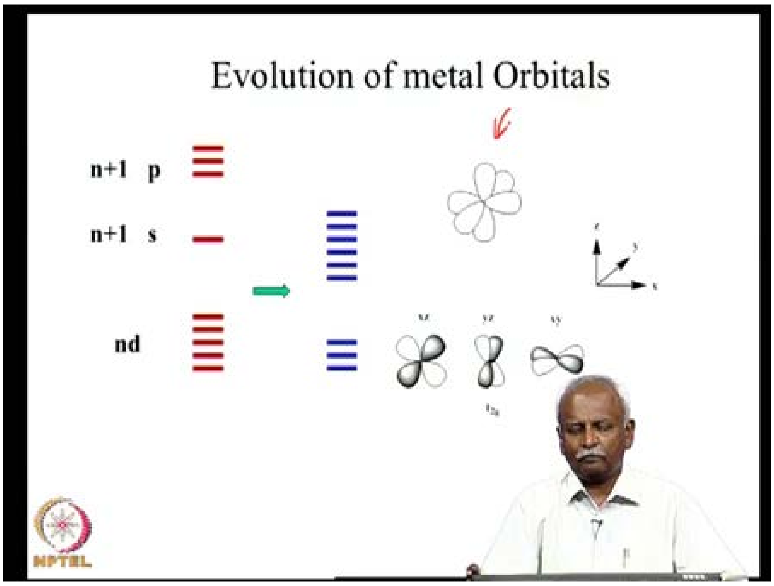


What will a methyl radical do?

So, if you look at the methyl radical if you look at the methyl radical we can ask the question since the lobes are similar would they have similar reactivity. Here, we have the methyl group, what does it do? It combines with another methyl radical and forms ethane and a very similar situation happens with Mn 2 C O 10. You take 2 Mn 2 C O 5 fragments; both of them have got 1 electron each on the highest occupied molecular orbitals. They can form a manganese manganese bond here on the organic side you form a carbon carbon bond.

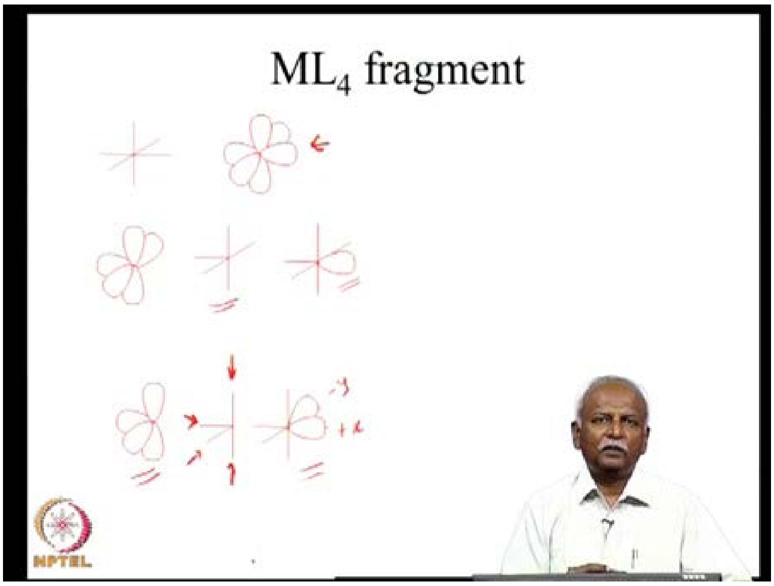
Their two similarities seem to be fairly striking, now we can also ask the question: can we combine the metal instead of combining with another metal can it combine with a can the metal combine with the metal? So, the answer is yes and we have this familiar molecule Mn 2 C O 5 which we used for looking at the insertion reactions. So, metal pentacarbonyl manganese is a perfectly stable molecule which is formed by combining these two radicals. The organic fragment which is on your right and metal fragment on the left, you can combine these two just like 2 methyl radicals would combine, and form Me Mn 2 C O 5. So, you can see that there is a lot of similarity between the two in terms of reactivity in terms of the behavior.

(Refer Slide Time: 21:56)


Evolution of metal Orbitals

We can in fact go ahead and look at them as isolobal fragments which have similar reactivity. Now, if we if we do this further let us push analogy a little further. Let us go back to our drawing board and look at the fragments that would be formed, if you would remove two ligands from the octahedral complex. So, here is the bunch of orbitals which is generated for the six metal group orbitals as if six ligands are going to come in.

(Refer Slide Time: 22:35)

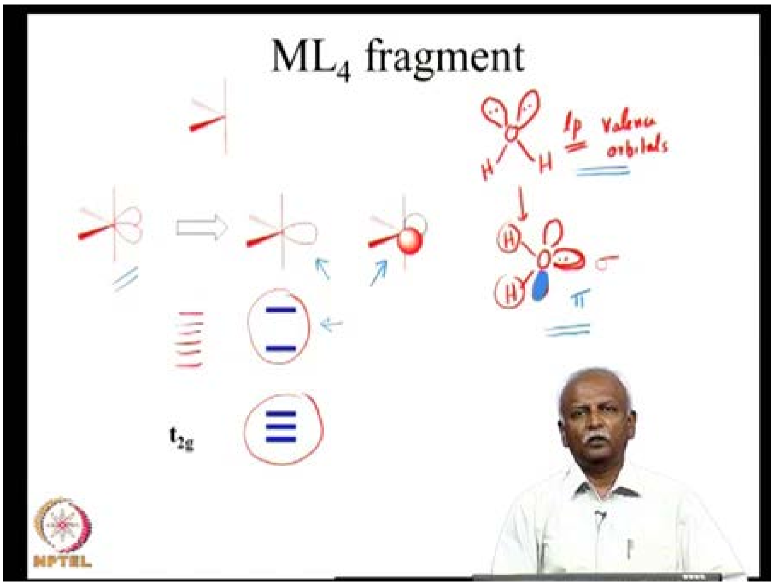


ML$_4$ fragment

Now, if we remove two of them, if we bring only 4 ligands and these 4 ligands, we are going to bring in on along this axis along this axis. So, we do not bring in one which is away from you on the y axis and 1 on the right side of x axis. So, the plus x axis and the minus y axis do not have ligands now. So, what will happen is that the four orbitals, initially there were six orbitals and these are pictured here, and then we looked at the fragment which will be formed.

When we removed one ligand and that is the fragment here we are left with an orbital which does not have a suitable competition. Now, we are having 2 orbitals along the minus y axis and the plus x axis. They do not have a suitable partner to interact with, and as a result there will be 4 ligand group orbitals interacting at the 4 metal group orbitals which are pictured here, but two metal orbitals are left without partner to interact with. They form molecular orbitals, so again they will be left in the state where they have no bonding or anti bonding, they will be similar to the nonbonding orbitals which are formed by the t 2 g set.

(Refer Slide Time: 24:10)



ML$_4$ fragment

So, here we have the familiar t 2 g set which is left in the nonbonding state and we had six metal group orbitals an out of which 4 of them have now bonding orbitals and anti bonding orbitals, but two are still left in a non bonded state. Now, before we proceed further the 2 orbitals which are in the non bonded state have in fact they are in fact equienergetic. If they are hybridized together, but in the molecular orbital formulas you will note that even in the case of water, where we are used to writing two fragment 2 M O's or 2 lone pairs, sorry two lone pairs on the oxygen which as identical.

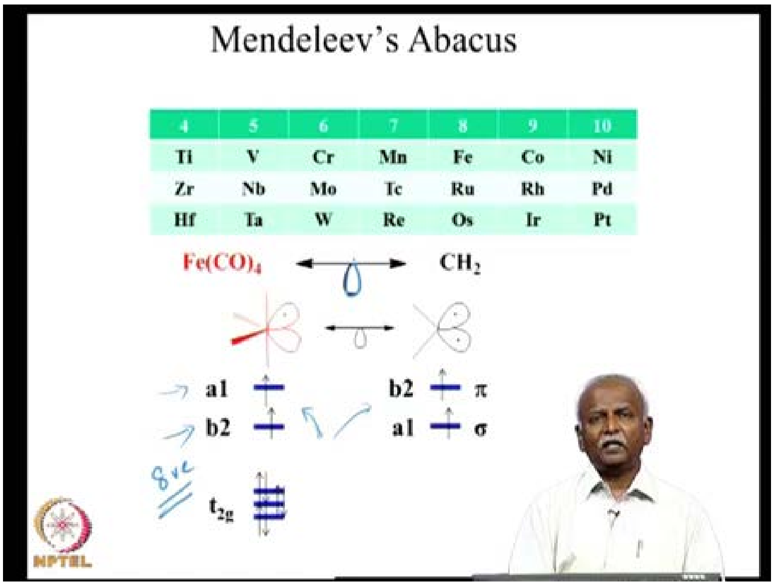
We call them the rabbit ear lone pairs, these lone pairs are called rabbit ear lone pairs and they are from the valence formalism. These are the valence orbitals which have two pairs of electrons which are pointed in the tetrahedral direction, but if you look at the M O formalism we will end up with a sigma pair of electrons. Let me write it for convenience in this fashion, I write it on the plane of the screen. So, that I have 2 hydrogens in the plane of the screen and the third orbital, which is called the sigma lone pair is present on the lone on the plane of the screen as well.

Now, perpendicular to the plane of the screen I will have an another lone pair which is going in and out of the plane of the screen. Now, I would have p type orbital or pi type lone pair, so here are two types of lone pairs one is the sigma type lone pair and another is the pi type lone pair. So, the molecular orbital formulism in fact distinguishes these 2 electron pairs and it suggests that there would be 2 different energy levels for them. One would be lower than another. In fact if you do spectroscopy electron spectroscopy on a water molecule, you would find out that in fact there are 2 different energy levels for the non bonded lone pairs.

So, although the valence bond formalism which we have used to derive the rabbit ear lone pairs on water are very common and very familiar to us. The actual situation in an isolated water molecule is that there are 2 different lone pairs one is a sigma lone pair and the other is a pi lone pair. So, a very similar situation happens when you look at the two other rabbit ear valence orbitals, which are present in M L 4 system, the M L 4 system has got a rabbit ear group of orbitals, which have to be split in to a sigma and a pi set of orbitals.

So, these are the sigma and pi set of orbitals and that is the reason why they have different energies and these different energies come out they are very slightly different in energy but both are empty. Now, you see that the M L 4 fragment should have some analogy with a fragment, which is present in the groups that we formed after removing hydrogens from methane.

(Refer Slide Time: 28:22)



Mendeleev’s Abacus

| 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|
| Ti | V | Cr | Mn | Fe | Co | Ni |
| Zr | Nb | Mo | Tc | Ru | Rh | Pd |
| Hf | Ta | W | Re | Os | Ir | Pt |

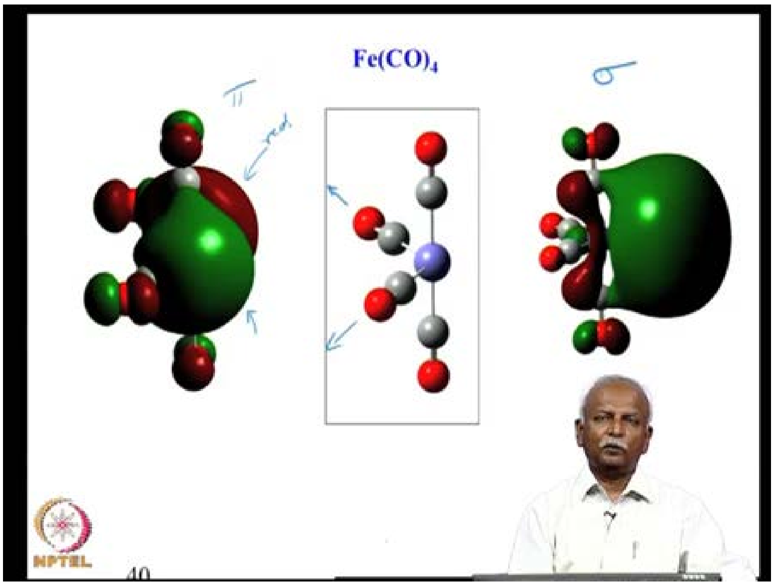
So, let us take a look at the Mendeleev’s abacus and see what would be similar to the methylene group that is formed by removing 2 hydrogens on the methane. You remove 2 carbon monoxides on the M L 6 fragment and if you want to have 2 electrons on the 2 orbitals which are the valence orbitals. Now, for the iron carbonyl fragment you would need 8 valence electrons, and we know that the metal which has got 8 valence electrons is actually iron tetra carbonyl.

You would have iron has got the 8 configuration so that t 2 g set would be filled with 6 electrons. And 1 electron would be available for the 2 molecular orbitals, which are the two molecular orbitals which are present and which have the symmetry of a1 and b2. So, you have the same and or a similar situation for the C H 2, the methylene fragment except that the energy of the sigma lone pair is lower in the case of the C H 2 fragment whereas in the Fe C O 4 fragment.

You have the pi the pi type the p type orbital which is lower in energy nevertheless because these two orbitals are reasonably close in energy, you end up with the electronic configuration that is very similar for the two fragments. So, the two lobes which we derived for C H 2 and Fe C O 4 in the valence bond formalism would have two rabbit ear type lone pairs or two rabbit ear type orbitals which are a filled with one electron each.

In the molecular orbital formalism we would have to split them as sigma and pi type and they have the symmetry of a1 and b2, and this is the way in which they are filled with one electron each. So, these two fragments also appear to be similar and the C H 2 methylene fragment is now considered to be isolobal with the iron tetra carbonyl. So, notice the symbol that professor Hoffmann has suggested for these two groups they are it is a double headed arrow with an orbital lobe below the double headed arrow. So, this a double headed arrow, which we have and the orbital lobe is attached to the lower half of the double headed arrow suggesting that the two fragments have got similar lobes in the valence orbitals of course.

(Refer Slide Time: 31:09)

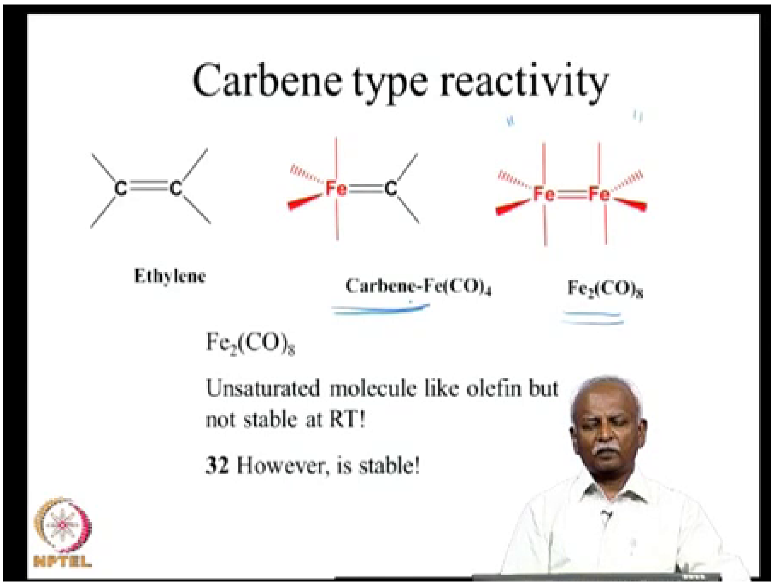


Fe(CO)$_4$

So, let us take a look at the iron tetra carbonyl species and the type of molecular orbitals they have here I have shown for you the valence orbitals ,which are available for Fe C O 4. Now, this has got a very large lobe which is the sigma lobe which corresponds to sigma type interaction on the iron, and that is pointed exactly midway between the two carbon monoxides units, which are like this one coming towards you. The other is going away from you and two carbon monoxides are up and down on the plane of the screen and this lobe is in the plane of the screen also, but it is a large lobe which has got only one phase.

So, it is a sigma type orbital this is a sigma type orbital, whereas the other orbital which we have has got a nodal plane which is passing in between the along the 2 carbon monoxides which are along on the plus z and minus z axis. So, you have a nodal plane passing along the x z plane, so you have 2 lobes, one is shaded green and the other is shaded red. So, this one is red, so they are the two M O's that are present on the Fe C O 4 fragment. Now, this is very similar to the p-orbital that would have been present on the carbon and the s p 2 hybrid which would be present on the carbon in a sigma type orbital.

(Refer Slide Time: 32:56)



Carbene type reactivity

Ethylene

Carbene-Fe(CO)$_4$

Fe$_2$(CO)$_8$

Fe$_2$(CO)$_8$

Unsaturated molecule like olefin but not stable at RT!

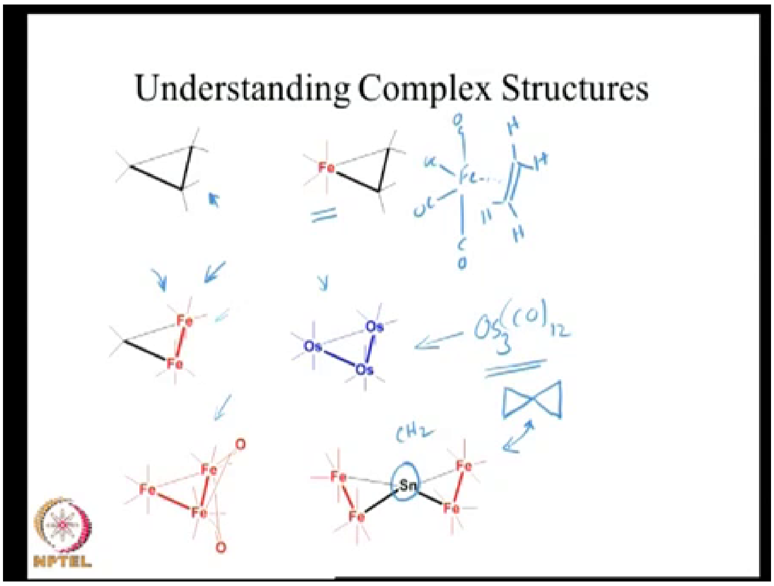
**32** However, is stable!

So, the Fe C O 4 fragment and the methylene fragment are very similar. Now, let us take a look at the reactivity if you take 2 methylene, they would combine together they would combine together to form ethylene. Now, it turns out that ethylene is quite stable a similar situation happens when you take the iron tetra carbonyl. It can form di iron octa carbonyl, but unfortunately this species which has the iron-iron double bond is not as stable as the one which has a carbon carbon double bond. Now, you know that in most systems when you have a heavy metal or a heavy atom other than the first row atom, it do not form strong multiple bonds.

So, also the iron iron bond is weaker and it is not as stable as ethylene itself, but nevertheless this is the reactant intermediate that is formed in the reaction of Fe 2 C O 9 which is the stable molecule. It can in fact react with a methylene carbene fragment and that is what is pictured for you in the center of the screen, you have a carbene complex of Fe C O 4. That is the simplest carbene complex that you can form with a C H 2 group and a iron tetra carbonyl unit.

So, there are differences between the two although the two are supposedly isolobal, you do have some similarities. You can combine them together to form the organic fragment and the inorganic fragment together to form an iron tetra carbonyl complex, which is complex to ch2 which is prototypical carbene and the Fe2CO8. The unsaturated molecule is more reactive than ethylene itself, now it is possible for us to have apart from this reactivity it is possible to have more fragments which can be compared.

(Refer Slide Time: 35:08)



Understanding Complex Structures

I have for you in this screen a series of molecules, which can be compared to the organic fragment. Suppose, you take 3 carbenes and put them together, you would form a cyclopropane that is a saturated cyclopropane that we are talking about. Now, if you replace one of the methylene units with an FeCO4 units, then you end up with a iron iron tetra carbonyl olefin complex.

Notice that it is although written in this fashion what we are really talking about is the olefin complex of iron tetra carbonyl. So, this is the complex this is the way we normally write an iron tetra carbonyl species. You have where each of these lines is caped with a carbon monoxide and we normally write it with to the centre of the carbon-carbon bond. If you rotate as if the two carbons are directly bonded to the iron, which in fact is the way in which they are interacting, then you would end up with the form where a cyclopropane has been formed by an isolobal replacement.

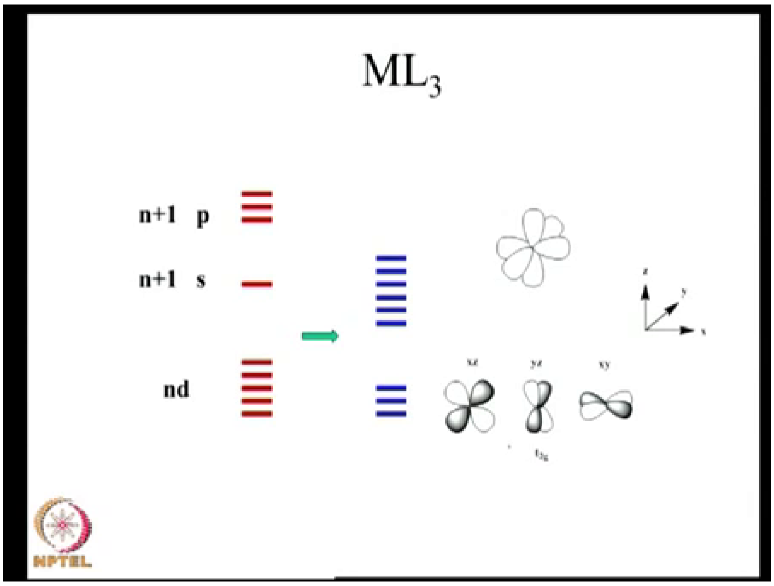
So, there is yet a another way in which we can go from inorganic side let us take Fe2CO8, and treat it with a carbene then we end up with a carbene complex where a methylene group is bridging a Fe 2 C O 8 unit. This is exactly the same thing that we have done except it is the exactly the same type of replacement we have done. Now, instead of replacing 2 instead of replacing 1 Fe C O 4 unit, we have replaced 2 Fe C O 4 unit from the cyclopropane.

So, from cyclopropane, we have added 2 iron tetra carbonyl units and we have obtained the olefin complex, or the methylene carbene complex. Now, we have a replacement of all the three carbons on the cyclopropane with Fe C O 4 unit and then you would obtain Fe 3 C O 12. Unfortunately, Fe 3 C O 12 has got this structure where there are bridge carbon monoxides. So, it looks different, but however remember you can just replace iron with ruthenium and ruthenium with osmium. If you do that, you get Os 3 C O 12, Os 3 C O 12 is extremely similar to the cyclopropene unit, so we have gone from one metal cyclopropane.

This an organic cyclopropane from that you have gone to a one metal cyclopropane to a two metal cyclopropane, and then we have gone to completely inorganic cyclopropane system. So, the analogy can even be extended further you can replace a methylene group with a simple replace 2 hydrogens of methylene group with another molecule. So, here I have for you a tin atom which is in fact bridging 2 C, 2 Fe 2 C O 8 unit on the either side. So, imagine this to be a C H 2 group initially and then the 2 hydrogens have been replaced with a ethylene molecule the inorganic part of the ethylene molecule. So, you would end up with Fe 2 C O 8 unit interacting with this carbon, the central carbon .

Since carbon can be replaced with tin, silicon and then subsequently tin and then replaced by lead, you have here an inorganic analog of the spiro compound which we would have found if we just combine two cyclopropanes together. So, this a spiro compound that we are the organic analog, and this is inorganic spiro compound formed by replacing the central carbon, which we have here with the tin atom.

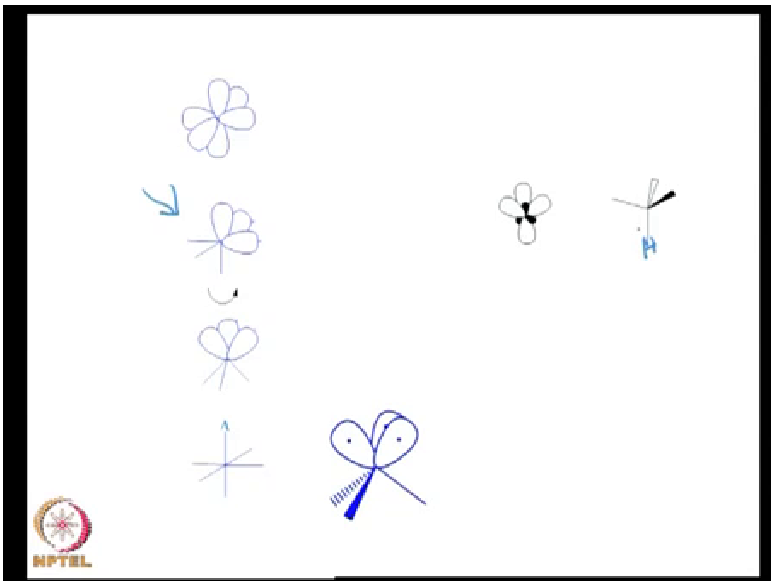
(Refer Slide Time: 39:37)



ML$_3$

Now, let us go on to the M L 3 fragment the M L 3 fragment could be formed by simply removing 3 ligands from the M L 6 fragment that we are familiar with now.

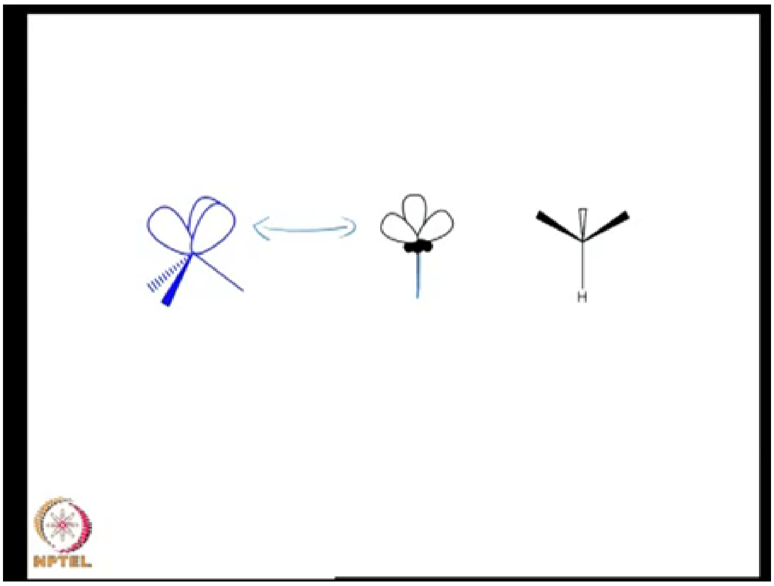
(Refer Slide Time: 39:49)



So, let us remove them and let us take them out from plus z, plus x and the minus y axis. So, we would have to fragment that is pictured for you on the top here and this fragment can be rotated in such a way that it has a c 3 axis, which is now pointed along the z z plus z of the cartesian frame work. So, this we wanted it to be pointed it in such a way that we will have C 3 axis passing through the plus z axis.

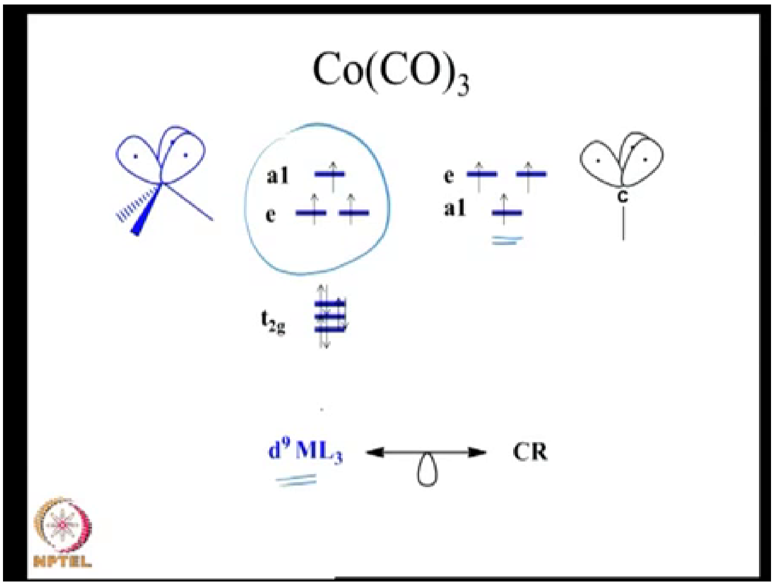
Usually, the plus z axis is considered the principle axis and so we rotate it and so that we have a proper orientation of the M L 3 fragment. Now, if we have 3 electrons present in them, we would have a C H fragment something equivalent to a C H fragment. So, here is the organic analog and I have hydrogen here. So, this hydrogen has got 3, 3 lobes which are pointed along the places, where the other 3 hydrogens would have been in methane.

(Refer Slide Time: 41:06)



These two turn out to be looking very similar except for one striking difference the methane fragment the C H fragment, which was formed from methane has got 3 lobes. It has got a single hydrogen which is pointed downward. Whereas, the 3 carbonyl fragment that we have here has got 3 legs and 3 orbitals pointed upward, but the 3 lobes seem to be looking very similar.

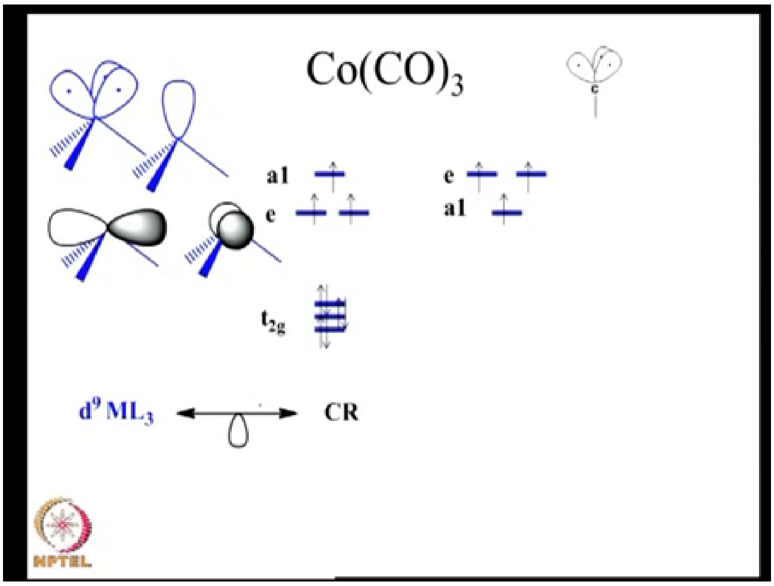
(Refer Slide Time: 41:41)


$Co(CO)_3$

Let us see what would happen if we if we want to form the analogous fragment for the carbyne. So, this C H or the C R unit which is has got 3 electrons. So, we want one electron for each one of these orbitals, and if you remember the t 2 g set has to be filled with 6 electrons. We want 3 electrons on the 3 valence orbitals which are available for the M L 3 fragment. If we have to fill up with 9 electrons, it has to be a d 9 system so a d 9 ml 3 would be tri cobalt octa carbonyl tri carbonyl cobalt, so Co C O 3 is the right fragment which would have 3 electrons available for interacting with other fragments.

So, just as we explained in the previous instance, we had the inversion of the symmetric orbital and the unsymmetrical orbital. Here also the degenerate set of orbitals which we have on the carbon frame work will be higher in energy where 2 p orbitals and this is the hybridized orbital which we have at a slightly lower energy. Similarly, here also you would have to split them into a a and a e set of orbitals and these orbitals would have the form, that I have shown here for you.

(Refer Slide Time: 43:07)



Co(CO)$_3$

a1

e

$t_{2g}$

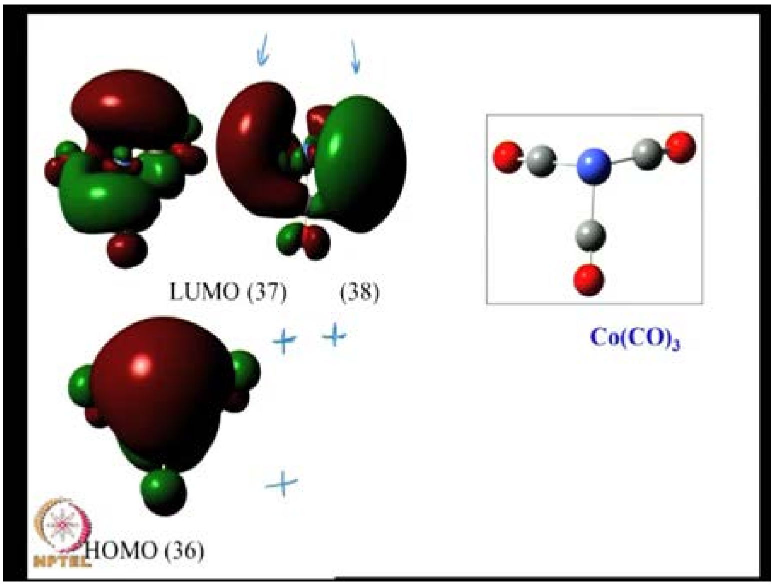
e

a1

$d^9$ ML$_3$ ⟷ CR

Here is the form of the metals orbitals you will if you were orienting the Co CO 3 unit such that one of these carbon monoxides fall on the except then the nature of these orbitals would look somewhat like the p orbitals on the cobalt. So, this is what you would have a symmetric orbital, which is pointed along z axis and p y and p x set of orbitals. So, very similar situtation happens in the C H also the C H fragment, so the d 9 M L 3 fragment and the C R group turn out to be very similar.

(Refer Slide Time: 44:03)



LUMO (37) (38)

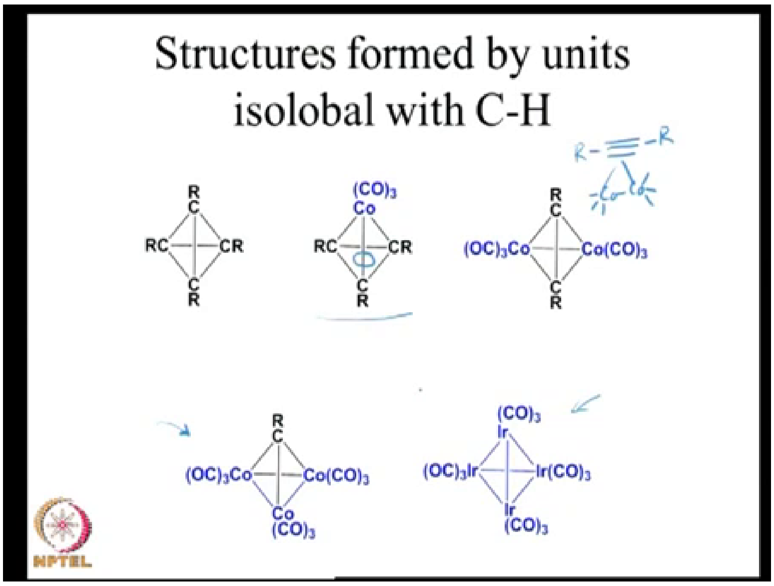
HOMO (36)

Co(CO)$_3$

So, let us take a look at the C at the actual molecular orbitals which have been computed for tri carbonyl cobalt. Here are the 3 orbitals which are present, the carbon monoxide; the 3 carbon monoxides are oriented in a slightly tilted fashion. So, that you can see the lobes a little better there are 2 p type orbitals on the cobalt, and they are marked lomon lumo and homo, but in fact the 3 orbitals are filled in this fashion. This depends on the electron count that we have used for doing the calculation.

So, here I have for you the lowest energy orbital has got the single lobe, which is symmetric and pointed along the z axis and that is rotated in such a way, so that we can see it fully. It has got only one phase in the whole sign that is pointing towards you and you have 2 p type orbitals, where you have a red lobe or a green lobe and a red lobe. So, these 2 whether it is pointed whether they are oriented in such a way that you have a nodal plane. So, they are degenerate and they have pi type symmetry for interaction with other fragments, so just like you have in the case of carbon, the carbine unit.

(Refer Slide Time: 45:50)



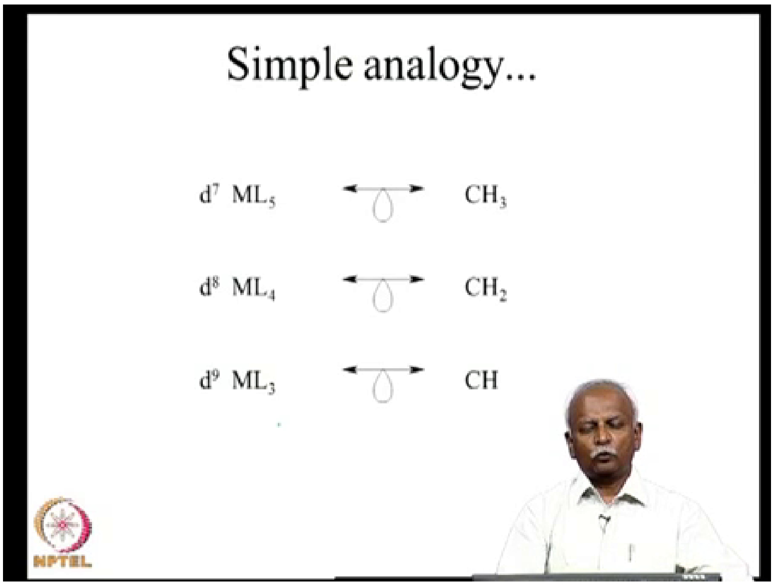
Structures formed by units isolobal with C-H

You have a system which has got sigma and pi type interactions, now let us take a look at tetra hydrine which would be the fragment that has formed by combining 4 carbine units C H fragments and that is tetra hydrine. You can replace each one of these fragments with a tri carbonyl cobalt unit that is a inorganic analog of C H. So, you have a cyclopropenyl unit compound and that can be complexed with cobalt tricarbonyl. So, Co C O 3 is a piano stool complex which has been inverted, so the piano stool is at the bottom now and the Co C O 3 units are on the top. I can replace two of them and this is my alkyne complex, so this is my alkyne complex where I have C O 2.

So, here I have a CO2CO6 unit interacting with an alkyne and the axis of the alkyne is perpendicular to the axis of cobalt cobalt bond. So, here is an alkyne complex here is a cyclopropenyl complex, which is a 3 carbon fragment that is interacting with a cobalt. Now, we have made it in an inverted stool structure and you can also have 3 cobalt atoms that is a tri cobalt non carbonyl complex which is caped with a carbine. So, here you have 3 cobalt units, which are caped with a carbine and the finally completely inorganic analog of tetra hydrine is the Ir4CO12 unit that is pictured here.

So, you can see very clearly that each one of these fragments, each one of these carbine fragments, which are present in tetra hydrine has already been replaced in organometallic chemistry and equivalent structures have been made and characterized. So, it is possible to understand some of these complex structures as simple combinations of isolobal fragments.

(Refer Slide Time: 48:32)



Simple analogy...

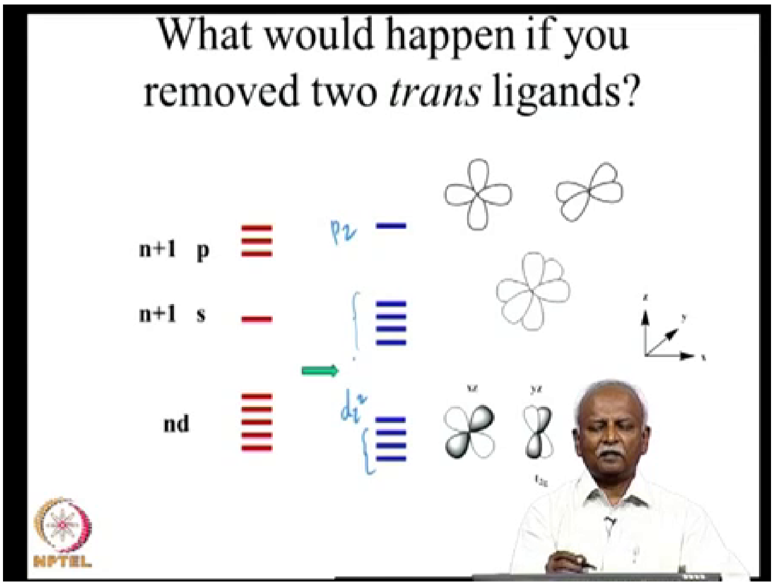
$d^7\ ML_5 \longleftrightarrow CH_3$

$d^8\ ML_4 \longleftrightarrow CH_2$

$d^9\ ML_3 \longleftrightarrow CH$

So, we have seen that the C H 3 fragment can be equated to a d 7 M L 5 you can equate the d 8 M L 4 with the C H 2 and d 9 M L 9 with a C H fragment. So, each one of these is an isolobal replacement.

(Refer Slide Time: 48:52)

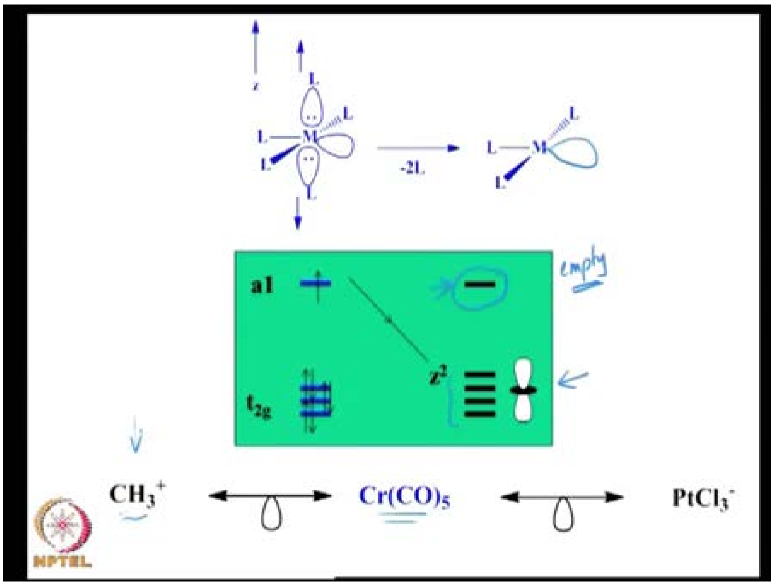


What would happen if you removed two *trans* ligands?

Now, if you removed other, if you would generate other geometries you would end up with different structures and these also have isolobals equivalents. Now, we are going to a look at least 2 examples where we can have such replacements. Now, imagine the scenario where we have 2 ligands in the trans plus z and minus z axis which are removed simultaneously, you will recall that a octahedral complex is sometime destabilized. It becomes a square planar system and that is exactly what we are talking about, here let us remove 2 of the ligands in the trans position.

So, what would happen is the 2 ligands which are involved which is the pz and the dz squared the dz squared are not going to interact. So, instead of you of having a t 2 g set instead of having the simple t 2 g set you have in addition the dz squared which is not interacting. Similarly, the p z which was mixing with lower energy s and forming a combination of metal all group orbitals, you are only having four groups of orbitals and the p z is left non interacting.

(Refer Slide Time: 50:23)

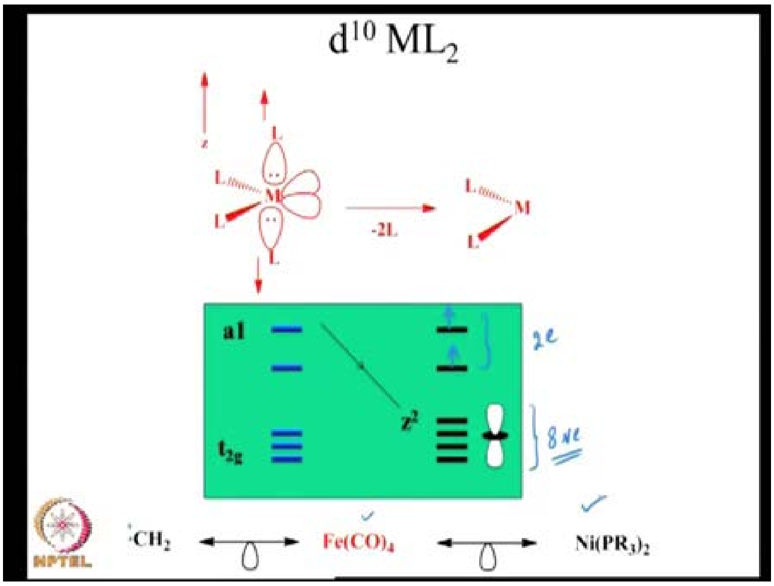


Now, let us take a look at what would happen if you removed 1 ligand along the plus x axis. So, notice that you have in this picture first of all the modified set of orbitals that is dz squared has been relegated to the level of the t 2 g set. So, you have 4 orbitals, which are available for the metal at the lower energy level and I have only 1 orbital, which has been removed or which has no suitable partner ligand. So, it is left non interacting or the ligand or the metal group orbital level.

So, that gives you an empty orbital and here I have if I if I have a d 8 system, as I have in the case of platinum I would end up filling up all these or all these orbitals, so that I have only 1 empty orbital and that is at the higher energy level. So, Pt Cl 3 minus, for example, is a fragment that is formed by removing 1 ligand, which is present along the plus x axis and that leaves behind a hybridized orbital. A hybridized orbital which is present on the metal and it is pointed along the plus x axis, you have a lobe which is pointed in this direction and this empty lobe will make it look as if it is a C H 3 plus.

So, now here we have as in the case of Cr C O 5 where we have 5 ligands and 1 empty orbital and you have Pt Cl 3 minus which is formed from the four M L 4 fragments. You have a species which has got an empty orbital very similar to C H 3 plus. So, that will also have an empty orbital, so you have the possibility for forming other geometries and other fragments which are isolobal. So, we have seen here what would happen if you formed from the M L 4 fragment, a M L 3 fragment in a t shaped geometry.

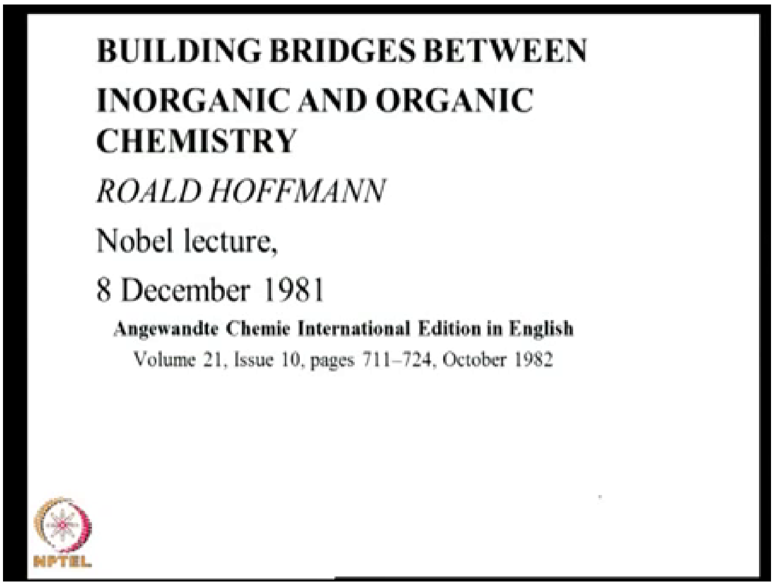
(Refer Slide Time: 52:53)


$d^{10}$ $ML_2$

Now, let us take a look at what would happen if you removed 2 ligands along the minus y axis and the plus x axis. In this particular case you remove 2 ligands, you end up with 2 orbitals which are hybridized and left empty. The 2 orbitals on the metal are hybridized and left empty and I have a total of 4 metal orbitals, which have not interacted at all. As a result if I take a d 10 system I would fill up 8 here, 8 valence electrons here.

I would have 2 valence electrons 1 here 1 one here, so that is looks similar to what we have in C H 2 fragment. So, a M L 2 system on a d 10 metal would look like Fe C O 4, except that now we will have a different geometry on the metal, it will have a v shaped geometry and it would similar to my carbene which is a C H 2 di radical. So, a C H 2 di radical is isolobal with iron penta, iron tetra carbonyl and the iron tetra carbonyl is isolobal with my Ni L 2 or Ni P R 3 2 unit.

(Refer Slide Time: 54:22)



**BUILDING BRIDGES BETWEEN INORGANIC AND ORGANIC CHEMISTRY**

*ROALD HOFFMANN*

Nobel lecture,

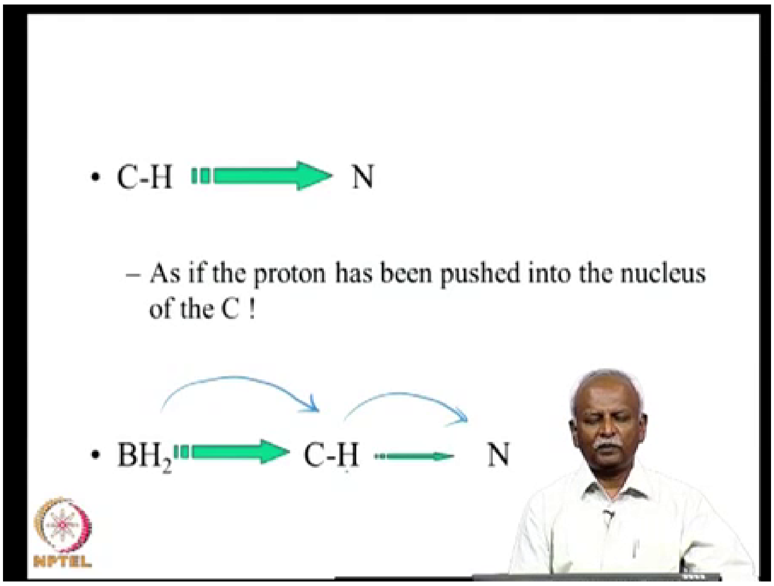
8 December 1981

**Angewandte Chemie International Edition in English**

Volume 21, Issue 10, pages 711–724, October 1982

So, for this lecture I have given is described beautifully by Professor Hoffman himself in his Nobel lecture, which has been introduce in Angewandte Chemie international edition and that reference is given here for you to go through in detail.

(Refer Slide Time: 54:42)

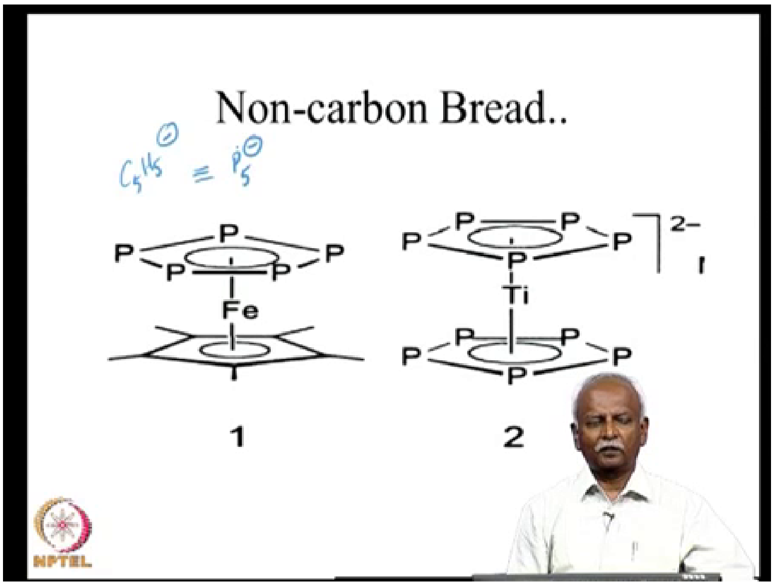


- C-H → N
  - As if the proton has been pushed into the nucleus of the C !
- $BH_2$ → C-H → N

Now, what we can do is to extend this analogy and also talk about isoelectronic systems. If you have a C H the C H group can be converted into nitrogen as if the proton is pushed in to the nucleus of carbon. In a similar fashion in a B H 2 unit can be thought of as a C

H unit and that in turn can be converted into nitrogen. So, we can make replacements of C H groups in by nitrogen.

(Refer Slide Time: 55:17)



Non-carbon Bread..

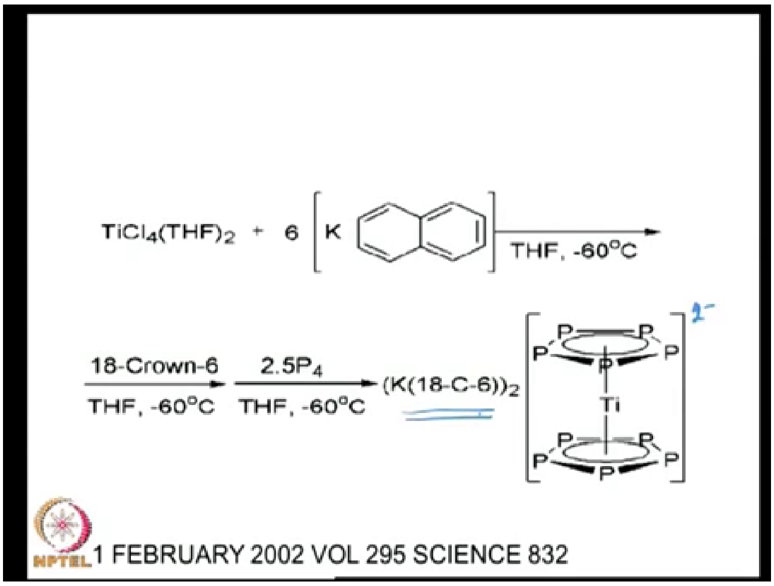
$C_5H_5^{\ominus} \equiv P_5^{\ominus}$

1

2

Even a B H 2 unit with a C H and a nitrogen and we talked about sandwich complexes earlier and here is an iron sandwich, which has on one side cyclopentadienyl unit and on the other side a p 5 minus the p 5 minus is isoelectronic with C 5 H 5 minus. So, C 5 H 5 minus is identical to a p 5 minus, this is similar to a p 5 minus group. So, notice that each C H unit has been replaced with a phosphorus and these molecules have been well characterized. And structurally have been well characterized both spectroscopically and structurally. In the solid state and both of this molecules which I am showing for on the screen have a well defined crystal structures. So, this a interesting system where you have an iron 2 plus with an inorganic sandwich on inorganic sandwich one side, and an organic sandwich on the other side. So, the titanium molecule of course is completely inorganic.

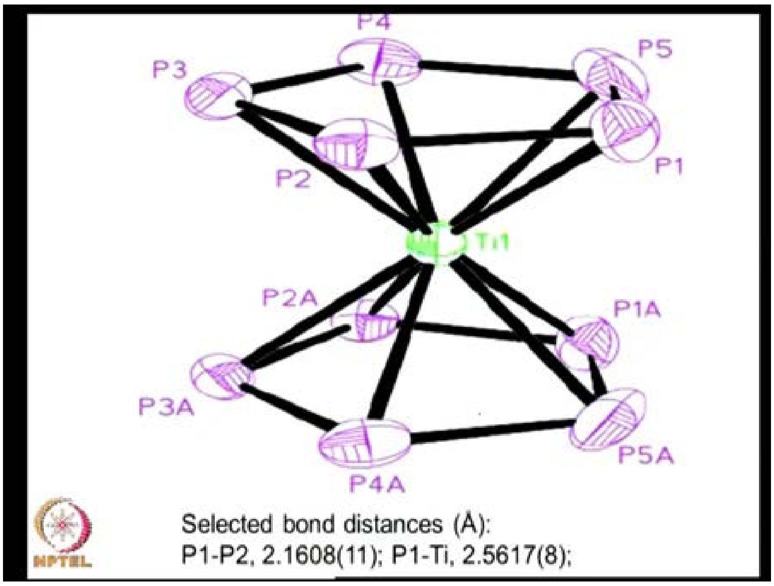
(Refer Slide Time: 56:33)



1 FEBRUARY 2002 VOL 295 SCIENCE 832

Let us move on and this is the synthesis of a titanium sandwich molecule this was recently published in 2002 in a science paper, and it has got the titanium sandwich between two P 5 units. So, you can see very clearly that this has got a 2, it is a 2 minus charge, it is a di anion. And it is stabilized by a 18 crown 6 coordinated to potassium plus and you have as table system being formed.

(Refer Slide Time: 57:10)



Selected bond distances (Å):
P1-P2, 2.1608(11); P1-Ti, 2.5617(8);

So, here is the crystal structure of the molecule with one distance indicating that you have a very stable structure and something that can be well characterized both spectroscopically and crystallographically. So, with this we end this discussion about ioslobal analogies, what we find is that isolobal and isoelectronic replacements can be done? These replacements allow you to make a wide range of molecules with very interesting properties, and understand the type of interactions that are present between the molecules, especially the inorganic fragments because of the type of lobes or the valance electrons. The lobes that they have in their valence shell, and using a combination of valance bond theory and molecular orbital theory. You can readily explain the type of molecular obtains that are available for these fragments to interact with other fragments.