Introduction to Organometallic Chemistry

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Lecture - 5
Substitutes for carbonyl ligands

Carbon monoxide is a fairly unique ligand and in the previous lectures, we have seen how carbon monoxide is occupying a very special place in organometallic chemistry. In fact one might say that, the R group which is used in organic chemistry, as a representation for all alkyl moieties. Therefore the organic chemist, so the carbon monoxide is there for the organometallic chemist to plug in at any place and use as a ligand. It turns out that, carbon monoxide however has some very unique properties and some of the unique properties are what I want toemphasize.

First, before we look at alternatives to carbon monoxide, any chemist wants to have some variation in the molecules that he is making so that, new properties can be studied new reactivities can be studied. So, people have been looking for alternatives to carbon monoxide, which is sucha unique ligand and occupying a special place in organometallic chemistry. So, let us look first at the uniqueness of carbon monoxide. Let us just rise that.

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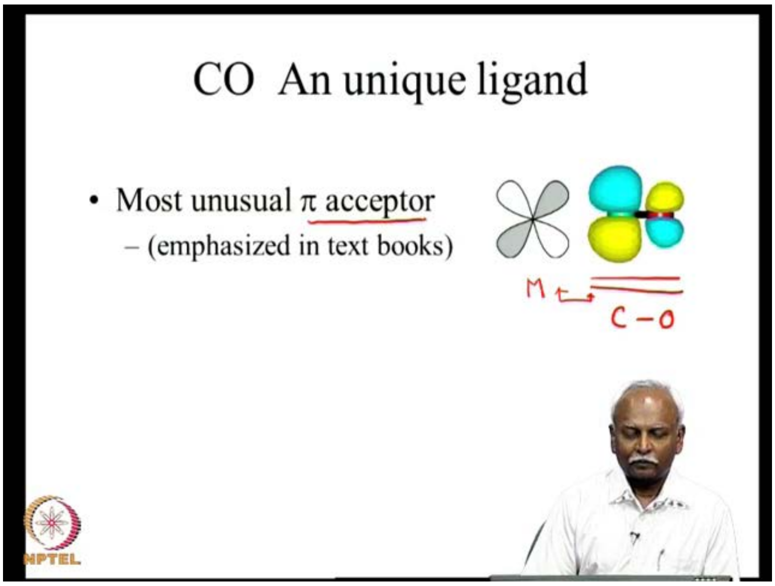

CO An unique ligand

- Most unusual π acceptor
  - (emphasized in text books)

The aspect that is emphasized most often, in organometallic chemistry is the fact that, carbon monoxide is a pi acceptor ligand. Carbon monoxide has gotpi acceptor orbital and we can see this pi acceptor orbital, whichis denoted here. It has got a very large lobe on the carbon side, this is the carbon side and this is the oxygen side. So, you have a very large lobe on the carbon side and a smaller lobe on the oxygen side. So, the pi acceptor orbital can overlap very effectively with the filled orbital of the metal. So this is the metal and the metal is interacting with carbon monoxide and this interaction becomes very effective, and carbon monoxide occupies this unique place because of its pi acceptor property.

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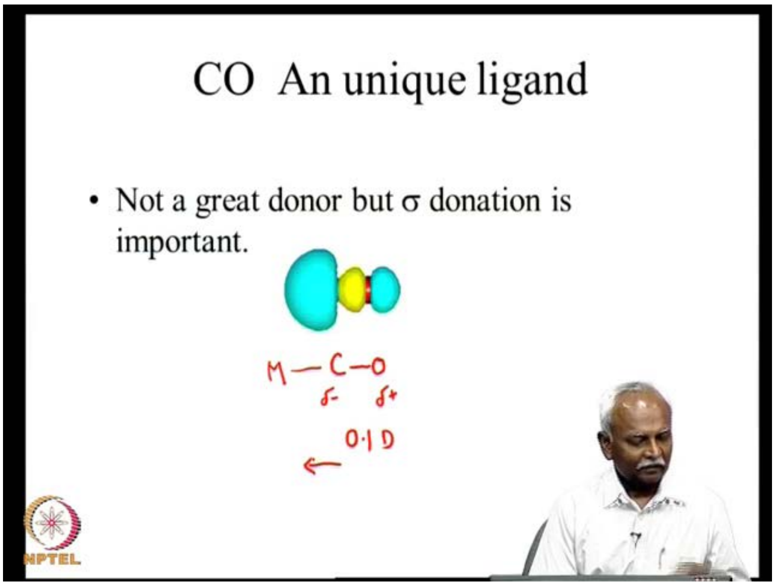

CO An unique ligand

- Not a great donor but σ donation is important.

However, what we tend to ignore more often than not, is the fact that carbon monoxide is also a good donor and this donation comes from the sigma orbital of carbon monoxide. And the sigma orbital is also located, primarily onthe carbon. So, the carbon end of carbon monoxide turns out to be the negative end, the negative end of the dipole in carbon monoxide. Carbon monoxide occupies a special place, because of this unique property that carbon end is a negative end and it has a very small dipole moment. Point one ((Refer Time: 3:23)) units. So, 0.1 ((Refer Time: 3:27)) units of the dipole is concentrated on the carbon end of the carbon monoxide and this carbon end is now, attached to the metal centre.

So, there are some unique features that result from this sigma donation, from the carbon monoxide to the metal. And then, from the metal, the electron density flows back into the carbon monoxide, into the pi star orbital of the carbon monoxide. So you can see that, these two aspects of carbon monoxide make it a very unique ligand and make it a synergistic ligand. This synergism is what is called as a unique property of carbon monoxide.

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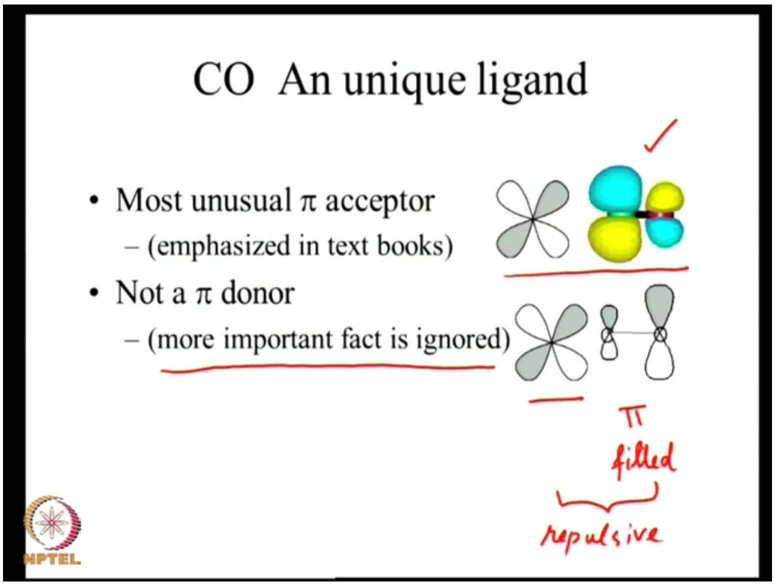

CO An unique ligand

- Most unusual π acceptor
  - (emphasized in text books)
- Not a π donor
  - (more important fact is ignored)

What is not emphasized in most of the text books is the fact that, carbon monoxide is not a pi donor, is not an effective pi donor. And that happens because the pi orbital on this ligand, which is a filled orbital, this is a filled orbital on carbon monoxide and this filled orbital on carbon monoxide can also interact with the filled metal D orbital. So, this interaction turns out to be a repulsive interaction, this interaction is a repulsive interaction and this repulsive interaction has to be minimised and this stabilising interaction has to be emphasized, or it has to be better than, the repulsive interaction.

And so, the repulsive interaction is minimised, because the overlap between the carbon monoxide and the filled metal D orbital is less because of the small size of the lobe, on the carbon in the pi orbital of carbon monoxide. So, it is a combination of these three factors, the fact that you have a good pi acceptor, the fact that you have sigma donation from the carbon end. And the fact that you have pi accepting property and pi donation property, which is minimised. The pi accepting property is maximised and the pi donating property is minimised and this three factors tend to make carbon monoxide a very unique ligand. Now, if you want to make an alternative for carbon monoxide how do we go about doing it.

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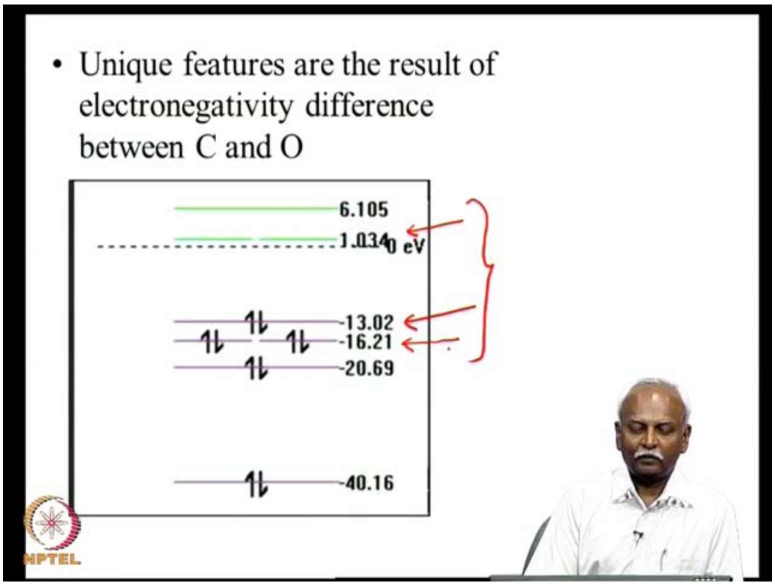

- Unique features are the result of electronegativity difference between C and O

The chemist usually ends up going back to the periodic table. And if you go to the periodic table, you realise that the electronegativity difference between carbon and oxygen is one of the reasons, why you have all these unique features for carbon monoxide. The sigma donation from the highest occupied molecular orbital of carbon monoxide, is happening from this orbital which is having an ionisation potential of 13.02 electronvolts. And this is the sigma orbital and the pi accepting orbitals are located here, they are virtual orbitals are denoted in green. And these virtual orbitals are the ones, which are going to accept electron density from the metal.

So, you have sigma donation from here and pi acceptingproperty of carbon monoxide arising from this orbital. And this is the orbital which is the filledpi orbital on carbon monoxide and that is the one which is going to be a repulsive interaction, but because of poor overlap it does not repel too much, and that makes carbon monoxide very unique. And these three factors, are all the result of the electronegativity difference between carbon and oxygen.

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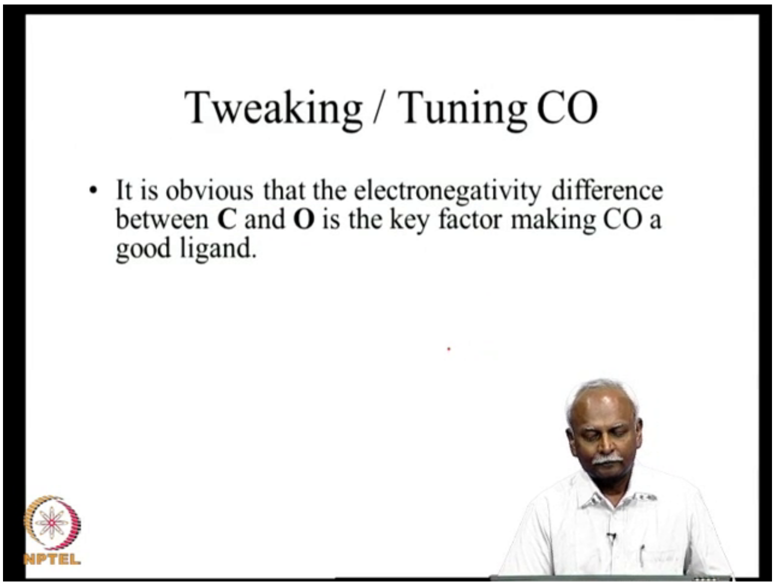

Tweaking / Tuning CO

- It is obvious that the electronegativity difference between **C** and **O** is the key factor making CO a good ligand.

So, if you go to the periodic table we see that, the electronegativity difference has to be maintained as much as possible.

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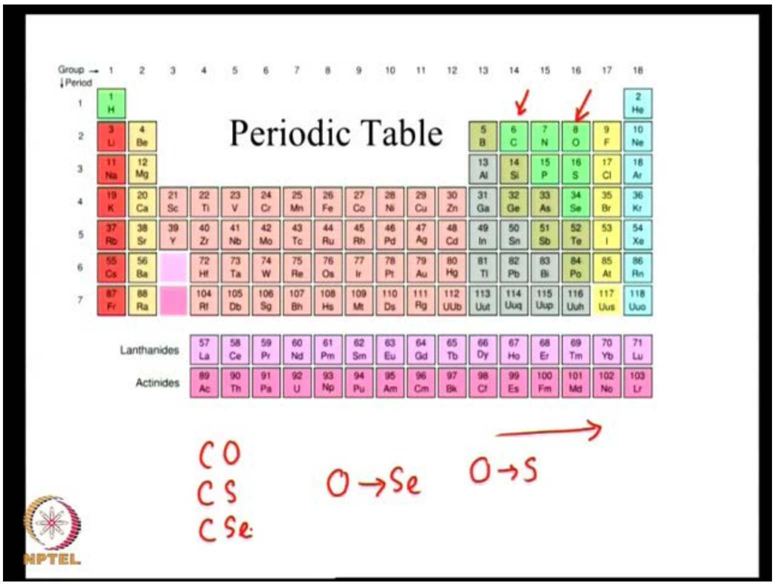

Periodic Table

Group → ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 UUb	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

CO
CS
CSe

$O \rightarrow Se$

$O \rightarrow S$

So here is the periodic table, carbon is right here, carbon is here and oxygen is here. And you can see that, the electronegativity difference will keep increasing in this direction as we go from left to right in the periodic table. The electronegativity difference will keep increasing. So, if you substitute as chemists often do by an element which is lower in the periodic table, with respect to the element that we are substituting. So, one would replace oxygen by sulphur then, what would happen is that, we would lose out on the electronegativity difference between carbon and oxygen.

Carbon and sulphur would have lesser electronegativity difference, if we go further below, if we replace oxygen with a selenium that, electronegativity difference will even be less. So, if we make carbon monoxide it is a good ligand, if we make carbon monosulphide it is expected to be a poorer ligand, carbon monoselenide should even be a poorer ligand, based on the electronegativity difference. However, we will now see what happens when we make it C Sand CSe.

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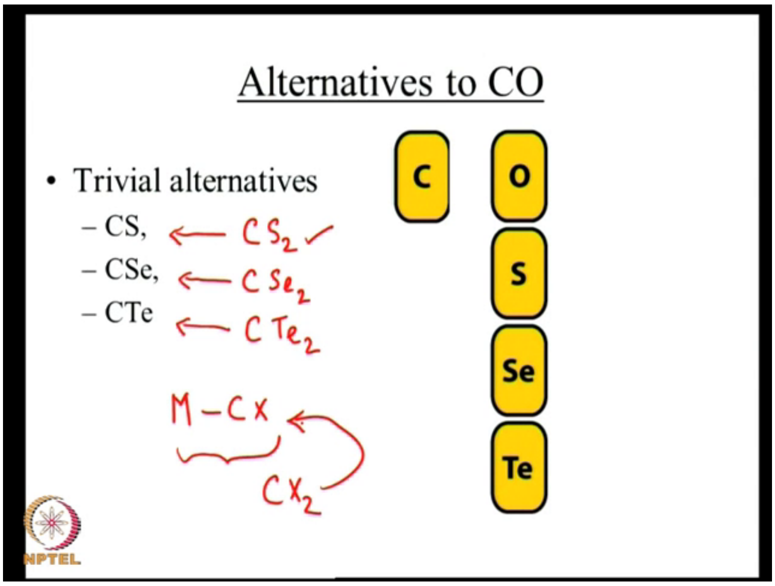

Alternatives to CO

- Trivial alternatives
  - CS, ← CS_2 ✓
  - CSe, ← CSe_2
  - CTe ← CTe_2

$\underbrace{M-C}X \leftarrow CX_2$

So, these are trivial alternatives that we have, we can makecarbon monosulphide, carbon monoselenide and carbon monotelluride. It turns out, that carbon monosulphide is not a stable molecule by itself. So, if one has to make carbon monoselenide, one has to start with CSe2. And similarly, if we have to make CS1 has to start from CS2 and CTe2 is available, but it is still not an extremely stable molecule and it is even more difficult to convert CS2 to CS and CSe2 to CSe and CTe 2 to CTe. So, these are transformations which have to be carried out in the presence of the metal complex, which has to form the MCx complex.

So, if you want to make Cx combine with metal then, you have to use the CS 2 you have to start with carbon disulphide, react with metal in the presence of this molecule. So usually, this is not a great difficulty for the chemist because there are reagents, which will remove one of the x atoms from Cx 2 and generate Cx in the coordination sphere of the metal.

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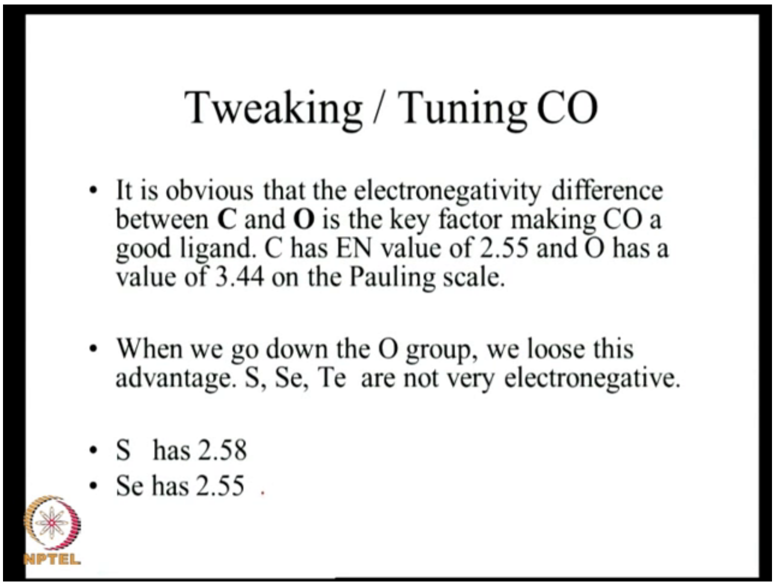

Tweaking / Tuning CO

- It is obvious that the electronegativity difference between **C** and **O** is the key factor making CO a good ligand. C has EN value of 2.55 and O has a value of 3.44 on the Pauling scale.
- When we go down the O group, we loose this advantage. S, Se, Te are not very electronegative.
- S has 2.58
- Se has 2.55

So, what we have just seen is that, we can in fact make an alternative to carbon monoxide. We can make a alternative molecule for carbon monoxide, butthe electronegativity difference between carbon and oxygen is something which is lost. Carbon has a electronegativity value of 2.55 and oxygen has a value of 3.44. So, you can see that, this is a big difference whichbased on the Pauling scale, this big difference is advantageous for making carbon monoxide a very unique ligand.

When we go down the group, the oxygen group we lose this advantage CSe Se and CTe are not great molecules. They are not very stable, butin spite of the lower electro negativity difference, you can still make these molecules in the coordination sphere of the metal. Sulphur has in fact an electro negativity value of 2.58 and selenium has electro negativity value, which is almost identical to that of carbon. Which is also 2.55.

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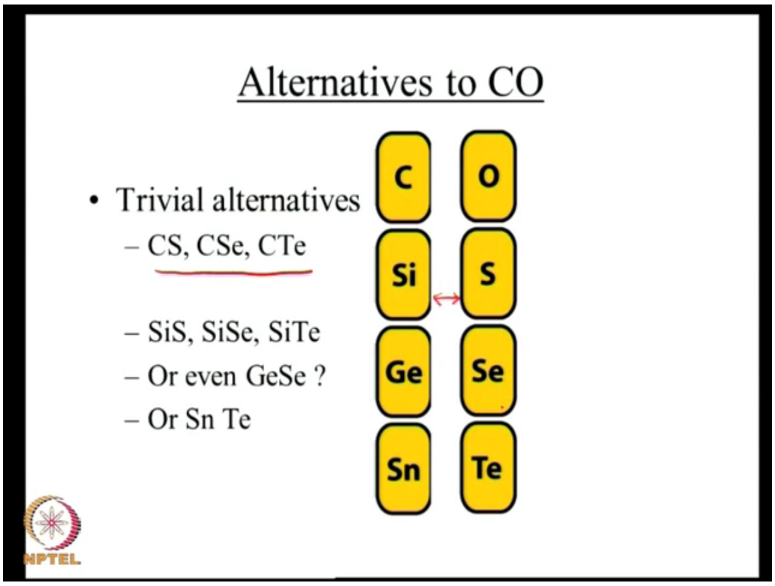

Alternatives to CO

- Trivial alternatives
  - CS, CSe, CTe
  - SiS, SiSe, SiTe
  - Or even GeSe ?
  - Or Sn Te

So you can see that,this is not going to be a great source of help, butstill CS, CSe and CTe are the best alternatives that, we have. If you try to make, an alternative molecule starting with siliconand you can make silicon sulphide. You would expect that, the electronegativity difference would again be good, but that is not the case. Moreover, it is not possible to make stable molecules because the tendency of silicon to form double bonds with sulphur is very small. It does not form stable molecules, with the oxygen group. So, germanium is even worse and tin is even worse than, germanium. So you cannot make alternatives to carbon mono sulphide or carbon monoselenide using thissubstitution. However, we can substitute oxygen by sulphur, selenium, tellurium.

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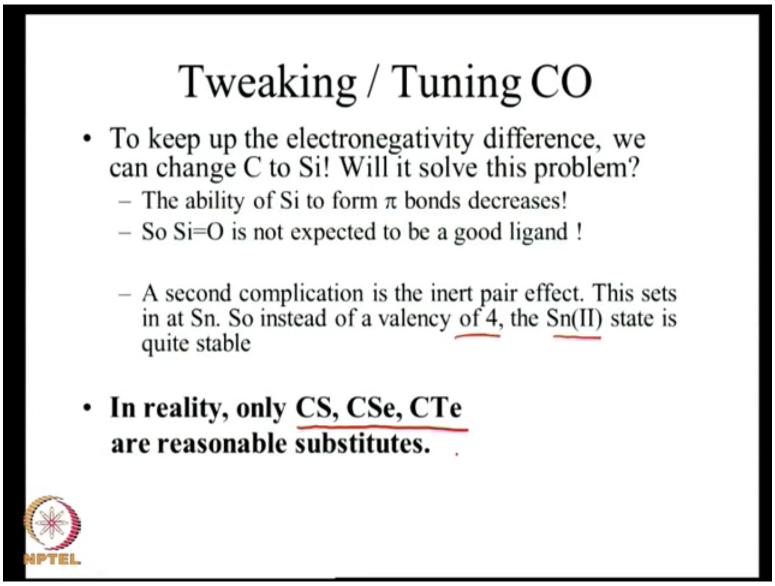

Tweaking / Tuning CO

- To keep up the electronegativity difference, we can change C to Si! Will it solve this problem?
  - The ability of Si to form π bonds decreases!
  - So Si=O is not expected to be a good ligand !
  - A second complication is the inert pair effect. This sets in at Sn. So instead of a valency of 4, the Sn(II) state is quite stable
- **In reality, only CS, CSe, CTe are reasonable substitutes.**

So, what we have seen is that, changing from carbon to silicon is not going to solve the problem of the electro negativity difference because pi bonds are not readily formed by silicon, a second complication is the fact that, you have the inert pair effect. The inert pair effect, which sets in at tin makes the valency of tin plus 2 rather than, plus 4. So tin likes to be in a stable oxidation state of plus 2rather than plus 4. And so, the tendency of this molecule to form a ligand is very poor. In reality than to summarize this section, what we find is that CS, CSe and CTe are good ligands for a transition metal. But the other possibilities, which arise from combining silicon or tin with sulphur, selenium, tellurium are not good possibilities.

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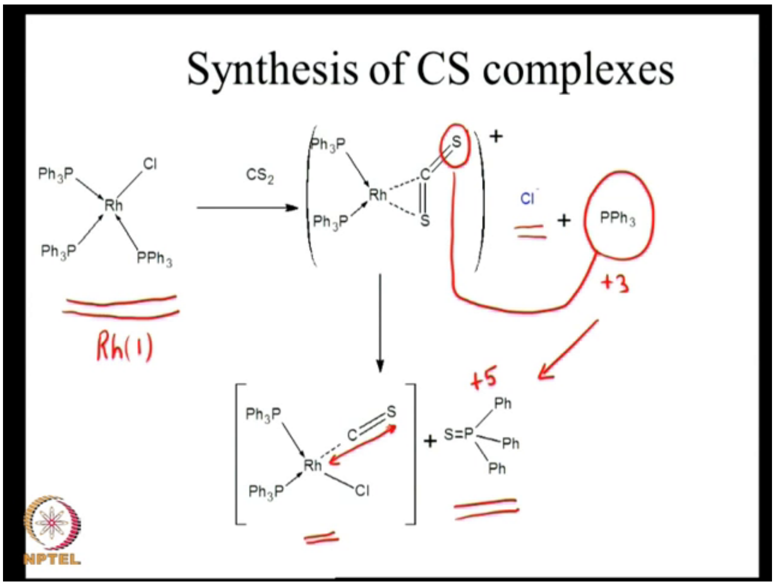

Synthesis of CS complexes

So, let us move on to the synthesis of some of these molecules. As I told youearlier in this lecture,it is possible to use a molecule which will remove one of the sulphur atoms in the carbon disulphide. So, what we do is, to start with the rhodium complex which has got a triphenylphosphine, which is coordinated to the rhodium and this is a rhodium one species.

You will notice that this is a rhodium one species, it has got one uninegative ligand and three phosphine molecules. Which are coordinating a pair of electrons, to the rhodium. Now, when this molecule is reacted with carbon disulphide, it likes to form a carbon disulphide coordinated rhodium complex, which is an intermediate in which the chloride has been ejected from the coordination sphere.

So, Cl minus is a species, which leaves the coordination sphere along with a PPH3, this might occur in two steps, but the intermediate that is formed has got a carbon disulphide coordinated to rhodium and this is a rhodium one complex, which has got three neutral ligands. Now, in this intermediate the PPH3 molecule that was ejected from the coordination sphere of rhodium, reacts with the PPH3 and eliminates one sulphur atom. One sulphur atom from this coordinated molecule, leaves with this PPH3 to form PPH3 double bond S and this is a phosphorous five species. So, phosphorous has got oxidised from plus 3 to plus 5 here.

So, you have an oxidation of the phosphorous to a P 5 compound and a carbon mono sulphide complex of rhodium, one has been formed. Now, this rhodium one complex that hasbeen formed here, has got CS bonded just like carbon monoxide, but it is in a linear fashion. And this CS molecule is quite stable now, in the coordination sphere of rhodium. It would not have been possible, to isolate carbon mono sulphide as a neutral molecule except, in a metrics which is kept at a very cold temperature. So, the metal is in fact stabilising an very unstable molecule carbon monosulphide, in the coordination sphere of the metal. It is stabilising the unstable molecule carbon monosulphide.

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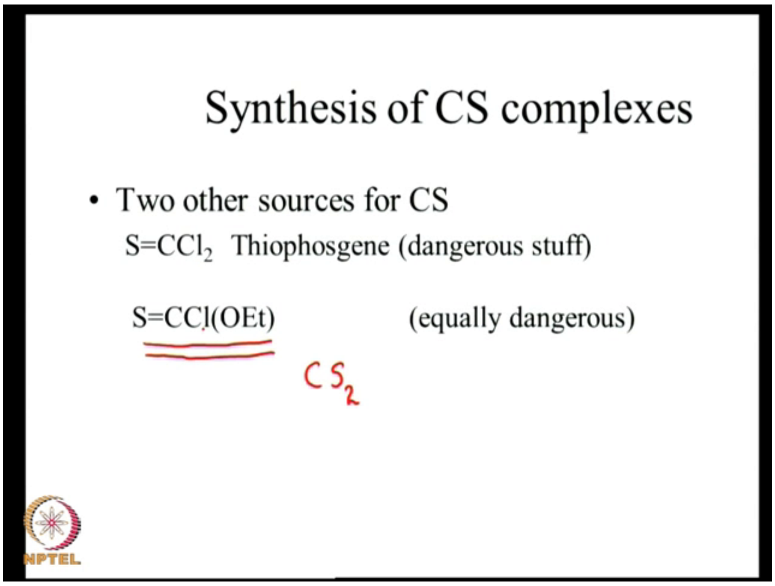

Synthesis of CS complexes

- Two other sources for CS

$S{=}CCl_2$ Thiophosgene (dangerous stuff)

$\underline{S{=}CCl(OEt)}$ (equally dangerous)

CS_2

So, what are the disadvantages of carbon monosulphide in spite of the fact that, it is possible to get carbon disulphide very readily. One should note that carbon disulphide is in fact a very poisonous chemical. So, it was difficult to generate carbon monosulphide in the lab very easily without taking adequate precautions. There are alternatives for carbon disulphide, but they are even equally dangerous. Consider for example, CS Cl 2 this is thiophosgene, phosgene as you know is a very dangerous chemical itself and thiophosphene, phosgene is also very unstable.

And it is also dangerous, it decomposes readily in the presence of moisture, but thiophosgene can be used in fact if you are careful enough. You can use it as an alternative for, carbon disulphide so, instead of CS 2, we can in fact substitute it with thiophosgene or ethoxythiochloroformate is another option. It is also dangerous, but it is easier to handle than thiophosgene. So, we will look at some of the molecules that can be generated using, these two alternatives to carbon disulphide.

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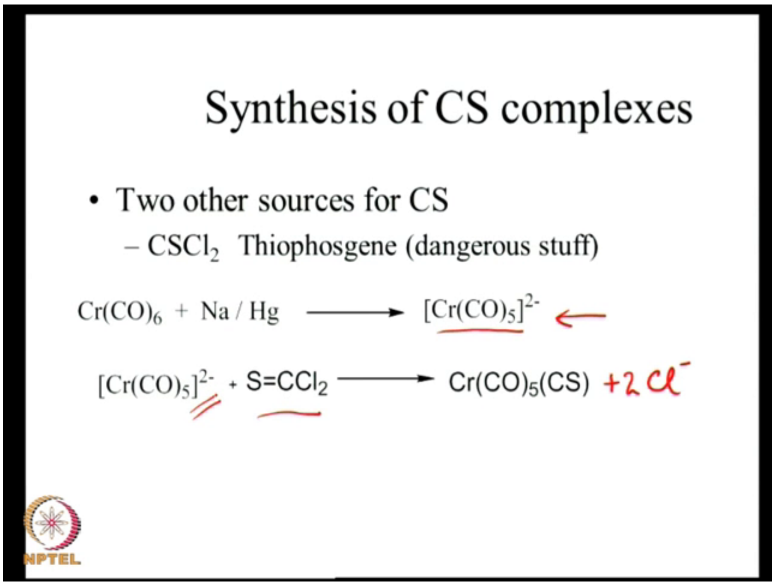

Synthesis of CS complexes

- Two other sources for CS
  - $CSCl_2$ Thiophosgene (dangerous stuff)

$$Cr(CO)_6 + Na/Hg \longrightarrow \underline{[Cr(CO)_5]^{2-}} \leftarrow$$

$$[Cr(CO)_5]^{2-} + \underline{S{=}CCl_2} \longrightarrow Cr(CO)_5(CS) + 2Cl^-$$

As I told you, these two molecules have to be used very carefully. Let us now look, at how one can use thiophosgene as a source for a carbon mono sulphide complexes. Chromium hexa carbonyl is a molecule, that we have seen extensively in previous lectures. Now, this molecule which is a stable 18 electron species can be reduced in the presence of sodium and mercury. So, if you take sodium which is a metal, dissolved in mercury it forms amalgam and this amalgam very readily gives out electrons. These electrons will reduce the chromium hexa carbonyl to a dianionic species, which has got two electrons more than CrCO6.

And it has got one carbon monoxide less so, this species CrcO5 2 minus can be reacted with thiophosgene and in that case you have the formation of CrcO5CS. This of course, will result in the formation of 2 Cl minus molecules or ions. As a result of displacement of Cl minus from the CSCl2 and the electrons are coming from the chromium di anion, that we generated using sodium amalgam.

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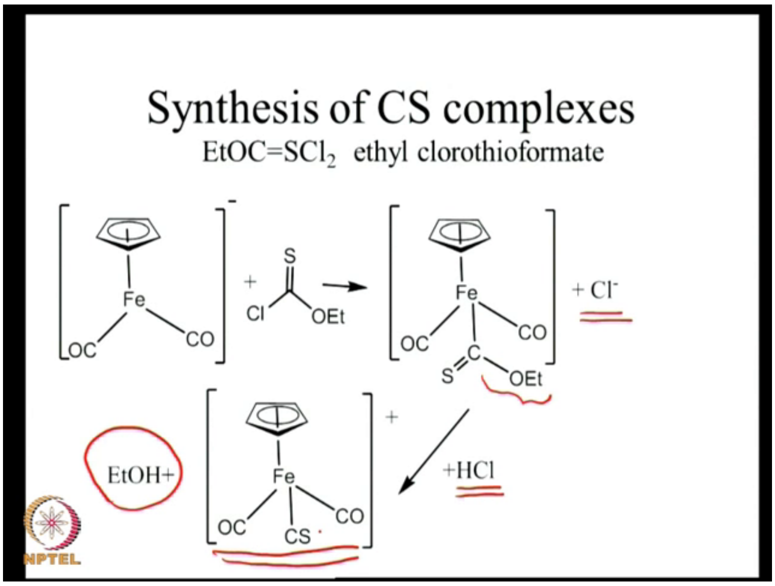

Synthesis of CS complexes

EtOC=SCl$_2$ ethyl clorothioformate

Now, I told you that, ethylchlorothioformate can also be used as a source and in this case also I am going to start making this molecule from an anionic carbonyl complex. Anionic carbonyl complexesare reasonably stable and the reason for this stability comes from the fact that, the negative charge can be delocalised on the carbon monoxide. It turns out that, the carbon monoxide can accept this electron density into the pi star orbitals of the carbon monoxide very readily. And form extremely stable complexes, in the presence of anionic metal ions.

So, here is the system where you have a negatively charged species on the iron, iron has got a negative charge and that charge is delocalised on this two carbon monoxides. We react that now, with this ethyl chlorothioformate. Ethyl chlorothioformate reacts with this anion and ejects one Cl minus and that gives us a iron thiocarbonyl complex, ethoxy thio carbonyl complex, which ishaving an iron carbon bond. And it will also having this fragment CS attached to it. Now, how do we get rid of we want to make CS complexes. So, how do we get rid of this ethoxy group.

Surprisingly, if you treat this system with hydrochloric acid one normally thinks that, acids and organometallic chemistry will not go together, but here is a very surprising example, you can treat this ethoxy thio carbonyl complex with hydrochloric acid and what happens is that, it protonates this ethoxy group. And ethanol is removed from this system so, ethanol is removed from this system, as a result of protonating this ethoxy group with this proton here. And because we are adding a proton and removing a neutral molecule this complex, which is formed must be charged and it is positively charged.

And this positively charged molecule, is now having a carbon mono sulphide coordinated to the ion. So, this is the carbon mono sulphide that has been formed and this carbon mono sulphide is coordinated to a18 electron species, which is a ion cyclopentadienyl ((Refer Time: 22:22)) with two other carbonyls. Now, this is a very good example because it allows us to compare the efficiency of carbon mono sulphide and carbon monoxide attached to the same metal atom. How, will these two species compare in terms of bonding. So, these are examples which are very useful for us to look at the bonding efficiency of carbon mono sulphide ((Refer Time: 22:50)) carbon monoxide.

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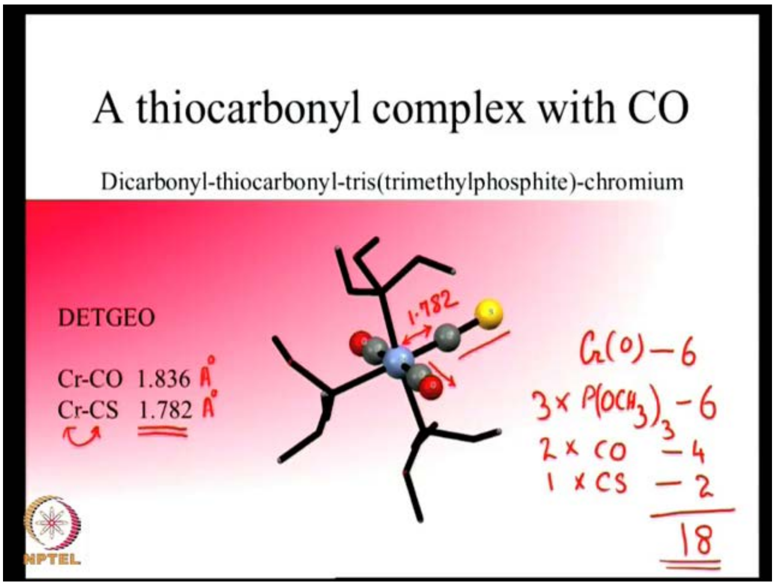

A thiocarbonyl complex with CO

Dicarbonyl-thiocarbonyl-tris(trimethylphosphite)-chromium

DETGEO

Cr-CO 1.836 Å

Cr-CS 1.782 Å

$Cr(0) - 6$

$3 \times P(OCH_3)_3 - 6$

$2 \times CO - 4$

$1 \times CS - 2$

$\underline{\underline{18}}$

So, here is the molecule that,I havedrawnfor you from using a structure drain program called mercury. And this gives us another example where, you have both carbon mono sulphide that is, right here CS. And carbon monoxide which is bonded here so, both of them are attached to a single metal atom which is, chromium. Now, this molecule of chromium is again a chromium 0 complex. So, it contributes 6 electrons, 6 valence electrons and then you have 3 phosphite molecules. So, you have, 3 phosphite molecules, 3 of them attached to the chromium. Each one of them will give twoelectrons each and so that, accounts for 6 electrons. And then we have also, 2 carbon monoxide units so, 2 carbon monoxide units give 4 electrons and one carbon monosulphide molecule.

And so we have 2 electrons coming from here so, this molecule turns out to be a nice 18 electron species. Where, you have a chromium 0 species donating 6 electrons to trimethylphosphite units, giving 6 electrons and 3 of them, are there. So, three of them giving 6 electrons, 2 electrons each, 2 carbon monoxides giving 4 electrons and one carbon monosulphide giving, 2 electrons making a total 18 which is a very stable system. So, in this molecule we have, the advantage of comparing the carbon monoxide with a carbon monosulphide in the same species. And it turns out that the chromium carbon bond, this is the distance that we are talking about, the chromium carbon bond.

The chromium carbon bond, in carbon monoxide that is here, is 1.836 angstroms. So, 1.836 angstroms is the distance between the chromium and the carbon and in the carbon monosulphide, this distance turns out to be 1.782. So we have 1.782, which is a shorter distance between the chromium and this carbon, in carbon mono sulphide compared to the chromium and the carbon, in carbon monoxide which is 1.836. So, what does this tell us, if you remember the distance between the metal and the carbon is shortened from whatis expected for a single bond.

Distance between the chromium and the carbon because of pi interactions, these pi interactions. Or these back bonding interactions, as they are called in some text books or pi accepting character of carbon monoxide, makes the carbon monoxide, carbon chromium bond shorter than what you would expect. So, when it comes to carbon monosulphide, there also the distance appears to be shorter than what you expect for a chromium carbon single bond. So, clearly there is a very strong interaction between carbon monosulphide and the chromium.

So, the back donation from the chromium to the carbon monosulphide must be very strong indeed. This is probably one indication that you have a very strong interaction between the chromium and carbon mono sulphide. So, carbon mono sulphide is in fact a very good pi accepting ligand. It has got very strong interactions between the metal and the ligand, both in terms of sigma donation from the carbon monosulphide, and also the pi accepting character from the chromium to the carbon mono sulphide.

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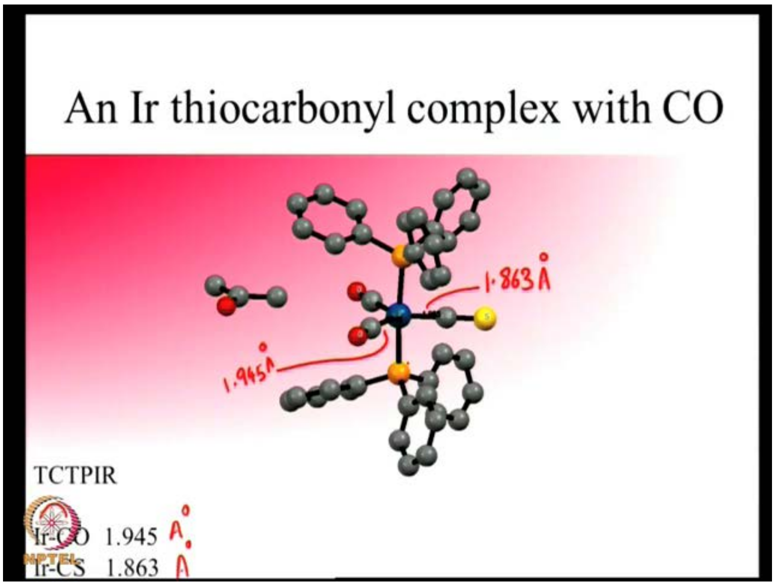

An Ir thiocarbonyl complex with CO

TCTPIR

Ir-CO 1.945 Å

Ir-CS 1.863 Å

So, let us just proceed a little further, look at another complex, in this complex we have a iridium complex which, has got again two triphenylphosphines. Here, we have two triphenyl phosphines and these triphenylphosphines are coordinated to the iridium. And in the same way, you have a carbon monoxide ligand and a carbon mono sulphide ligand. Once again you see that, the carbon iridium distance, the carbon iridium distance is in fact much longer thanthe iridium carbon distance which is there, for carbon mono sulphide.

So, you can see that, this distance is 1.863 angstroms, 1.863 angstroms and this distance which is the iridium carbon monoxide carbon distance, that is 1.954 angstroms. What is interesting is the fact that, you now have two examples where, the carbon metal distance is always shorter than the, carbon metal distance in carbon monoxide. This is clearly indicative of the fact that, it is a general phenomenon carbon monosulphide is in fact, a much better ligand compared to carbon monoxide, when it comes to pi accepting character.

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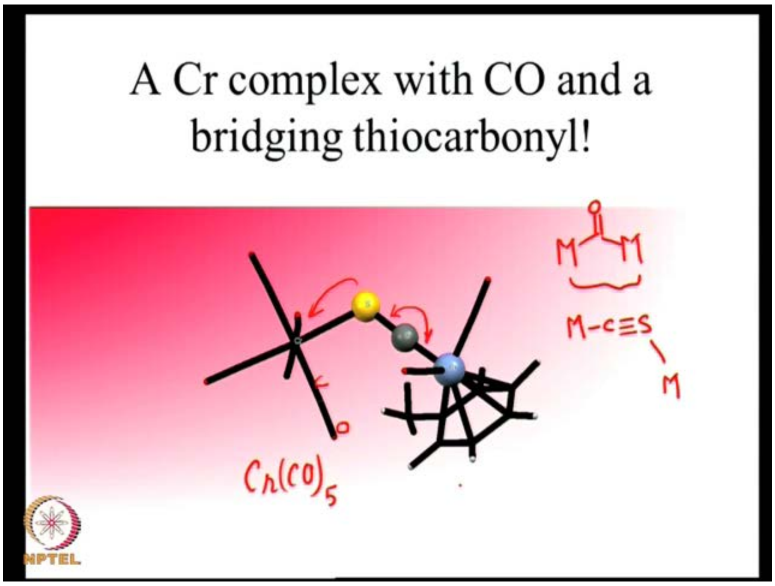

A Cr complex with CO and a bridging thiocarbonyl!

So, are there any differences between carbon monoxide and carbon monosulphide. Carbon monosulphide in fact has this tendency, to have, to form a bridge between the carbon monosulphide which is bonded to the chromium. So, here is a system where, you have chromium carbonsuphide and so it is a chromium CS complex where you have, the expected 180 degreeangle between the chromium carbon and the sulphur, but then this sulphur is using its lone pairs, to interact with another chromium atom. This chromium atom is also CRCO5. So, this is CRCO5 and although we have notindicated the atoms here, there is a carbon here and there is an oxygen here.

And so to make this structure fairly easy to understand, we have not put all the atoms in place, buteach one of these lines represent a carbon monoxide molecule. So, you have a CS coordinated to a chromium and that is in fact forming a bridge to the other chromium through the lone pair on the sulphur. So, this turns out to be, a fairly interesting way in which carbon mono sulphide can act, carbon monoxide is not known to act in this particular fashion. In fact bridging carbon monoxide complexes are very rare and when they do bridge, they do bridge to the carbon end.

So, you have systems where, the metal is interacting or bridging a carbon monoxide is present in this fashionand you have, a bridging carbon monoxide between two metal atoms. Here, the bridge seems to be formed between MC triple bond S and then there is a second metal here. So you can see that, there is a significant difference between the way a carbon monoxide behaves and a carbon monosulphide behaves. This is a probably one unique difference between carbon monoxide and thio carbonyl. In fact it would be interesting for us to see, this molecule in three dimensions so, what I am going to do is to show you this molecule in three dimensions.

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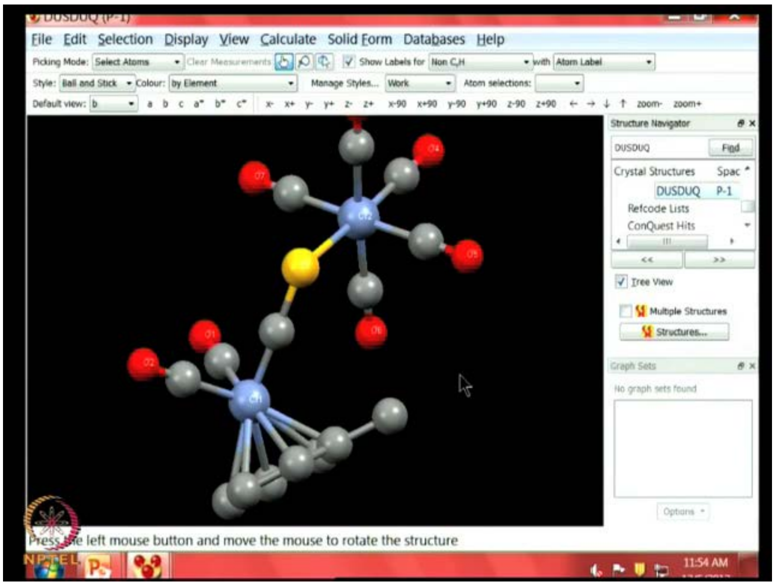

Press the left mouse button and move the mouse to rotate the structure

I will take this example where, you have a chromium which is interacting with the sulphur which is in fact coming from a carbonyl sulphide. This is a carbonyl atomwhich is present, this carbonyl atom is thiocarybonyl atom is present on this chromium atom. And this first chromium atom which is labelled as Cr1 is having a CS which is used as, a ligand and the CS ligand is in fact bridging a second chromium atom, which has got 5 carbon monoxides attached to it. So, this is different from the complex that I have showed you a little earlier, but the system is similar.

You have a carbon monosulphide, which is capable of bridging, which is coordinated to one metal atom and it is capable of bridging the other metal atom. So, you can see this, molecule as I rotate it you can see that it is, in fact a species where, the sulphur is a very nice bridge between the two chromium atoms.The first chromium atom has got a benzene ring, in which you have a 6 carbon atoms of the benzene ring coordinated to the chromium. And then, it has got a CS bonded to it and this CS is bridging the second chromium atom.

Whereas, the carbon monoxides which are also coordinated to the chromium 1 are independent, they are not interacting with any other metal. Neither are these carbon monoxides bonded to any other species, so CS has a tendency to bridge which is rather unique to the metal atom. So, let us proceed further we have now seen an example where, you can have a bridging carbon monosulphide.

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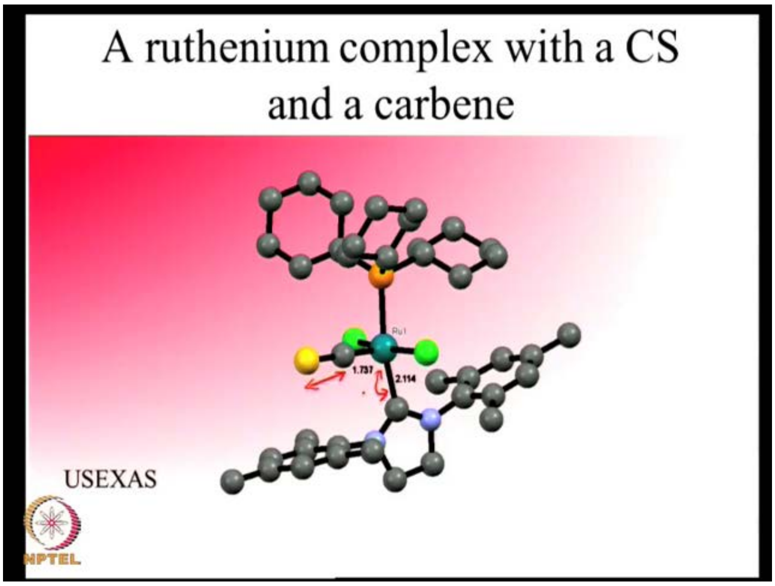

A ruthenium complex with a CS
and a carbene

USEXAS

And this is different from the example where you, have carbon mono, monoxide which is not a bridging molecule. So, I have here ruthenium complex now I, which is a carbene complex. I have shown this example only to indicate the fact that, you have a carbene which is capable of pi accepting electrons, from the metal onto the carbene. And so, this is an example where, you have a pi accepting going on between the metal. Here it is ruthenium and the carbene and in the same complex you have, a CS complex. So you have, a CS coordinated to the ruthenium and again you can see that, the carbene has a carbon ruthenium distance of 2.11 angstroms that is almost like, a single bond distance betweenruthenium and carbon.

And the distance between the carbon, on carbon mono sulphide and ruthenium that is almost 1.737 angstroms. So, the distance between, carbon mono sulphide and ruthenium is much much smaller, than the distance between ruthenium and carbine, which is a very poor pi acceptor, but a very good sigma donor. So, you can see from all these examples that, carbon mono sulphide is in fact an excellent ligand. It has a great tendency, to form pi bonds with the metal and itconsistently forms very strong bonds with the metal because, of its pi accepting character. So, even compared to examples like carbon monoxide, or in fact carbene here, you can see that in the same molecule carbon monosulphidecompetes with carbon monoxide for pi accepting.

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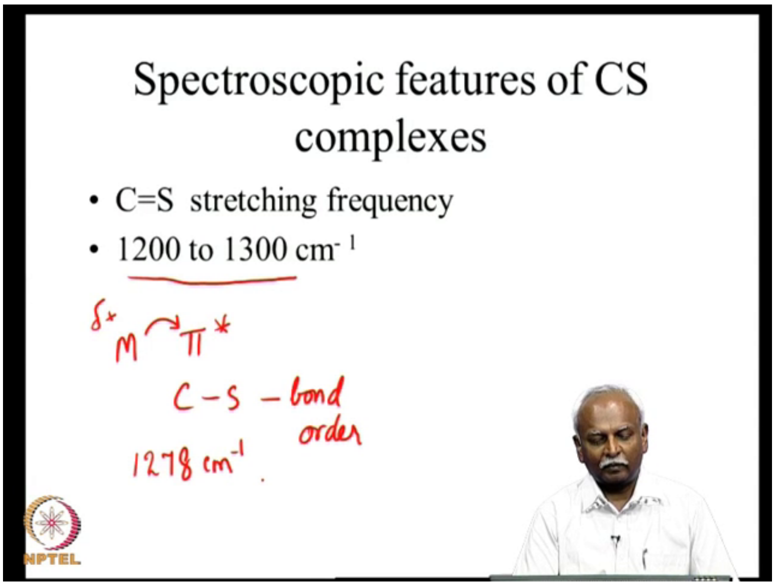

Spectroscopic features of CS complexes

- C=S stretching frequency
- 1200 to 1300 cm^{-1}

$\overset{\delta+}{M} \curvearrowright \pi^*$

C – S – bond order

1278 cm^{-1}

Normally, apart from the bond distance between the metal and carbon monoxide it is also possible, to use the stretching frequency between the two atoms which are bonded to the metal. In this case, carbon and sulphur we can look at the stretching frequency, CS stretching frequency how it is affected, on coordination to the metal. It is surprising that, once you coordinate a carbon monoxide, the stretching frequency between the carbon and the oxygen goes down by 100 to 200 centimetres minus 1. In the case of carbon mono sulphide, the reduction in the stretching frequency is not very significant, but it is also about 70 centimetres minus 1.

So, the CS stretching frequency in metal complex is ranges from 1200 to 1300 centimetres minus 1 and it, the frequency of carbon mono sulphide has been measured, only in the metrics. Which is a metrics, very cold metrics of liquid nitrogen and in that, the carbon monosulphide has been trapped and that stretching frequency is around 1270 centimetres minus 1. So, you can see that, the stretching frequency just like in carbon monoxide, it ranges from 1200 centimetre minus 1to 1300 centimetre minus 1. But it is lower than, what is observed for the free molecule, as I mentioned before the free molecule is not stable and so, it has to be, this spectroscopic features have to be measured under special conditions called metric isolation spectroscopy.

So, the reduction in the stretching frequency is clearly indicative of the factthat, you have electron donation from the metal onto the carbon mono sulphide. And this transfer of electron density into the pi star orbitals of carbon mono sulphide so, there are pi star orbitals of carbon mono sulphide. And these pi star orbitals are accepting electron density, from the metal. And as a result, the carbon sulphur bond order, this bond order, this bond order is reduced. So, the reduction in bond order is responsible for the stretching frequency going down from 1200 centimetre minus 1,1270 centimetre minus 1 to,1200 centimetre minus 1.

In a few cases the stretching frequency, in fact increases from 1270 centimetre minus 1 to, a slightly higher value. And this increase is, normally present only in positively charged systems or when you have a slight delta plus on the metal atoms. If you have a slight positive charge on the metal atom then, the frequency of the carbon mono sulphide is not reduced from the 1278 centimetre minus 1 that you have. It is in factincreased to, a slightly higher value and that is around 1300 centimetre minus 1.

So, both from spectroscopic and from x ray evidence we can see very clearly that, there is a strong pi bond which is formed between the metal and the carbon mono sulphide. And not only that this strong pi bond is weakened spectroscopically it is observable that, the pi bond is weakened because of the electron density coming from the metal.

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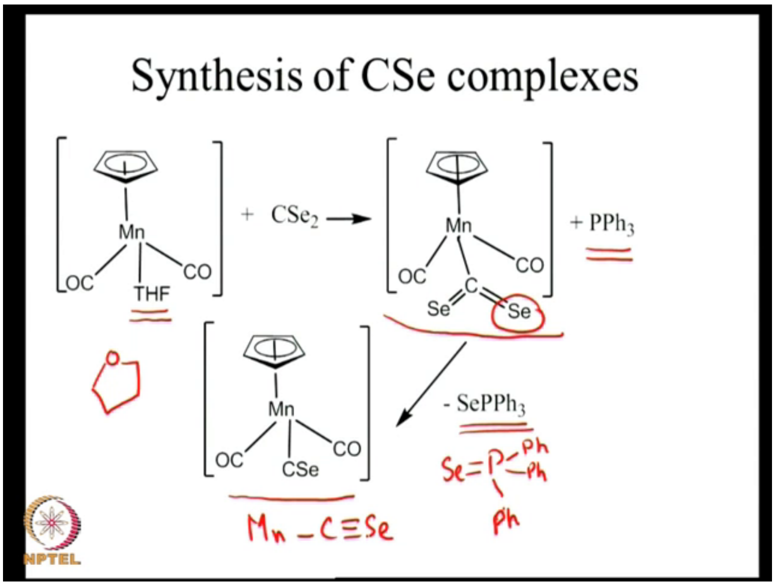
Synthesis of CSe complexes

So, let us now go to carbon monoselenide, carbon monoselenide can be made in a very similar fashion compared to carbon monosulphide, what one has to do is to start with CSe2 now. CSe2 is less stable than, carbon disulphide, but nevertheless it is accessible. One can make carbon diselenide and that can be treated with a carbon monoxide complex. In order to make these complexes what one normally does is, the following you start with the complex, which has got a labile ligand. So, here is an example where you have a metal THF complex, THF which is tetra hydro furan this is, tetra hydro furan is a weak ligand. And that weak ligand if, it is coordinated to the manganese then, one can use that as a precursor for making a CSe2 complex.

This CSe2 complex is, not a stable system and it is not being isolated and characterised. But if you treat this intermediate after, treating this molecule with carbon diselenide, if you treat it with triphenylphosphine what happens is the following. Once again, there is elimination of one of the selenium atoms, one of the selenium atoms is captured by triphenylphosphene. And you form a P5 molecule, which is phosphorous in the plus 5 oxidation state with a P double bond Se formed in the process. So, this molecule is formed as a result of interacting withthis carbon diselenide, which is coordinated to the manganese. And now you have, a carbon monoselenide which is coordinated to the manganese.

So, once again we have a system, where you have carbon monoxide coordinated to the metal and carbon mono selenide which is coordinated to the metal. So, we can examine both in terms of spectroscopy and in terms of bond distances. And in this particular instance, we will also look at the carbon monoselenide complex in three dimensions using this program. We can look at these molecules in three dimensions and we can see how the carbon monoselenide is also interacting with manganese just like, carbon monosulphide. There is a linear metal manganese CSe bond and the CSe bond, since its r in fact indicative of a pi back donation from the manganese to the CSe. And you can see that, this is now weaker as we had expected.

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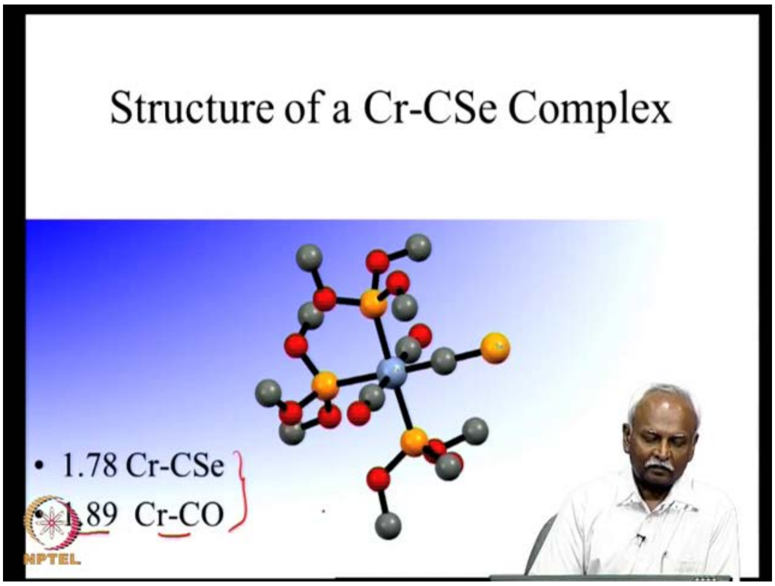

Structure of a Cr-CSe Complex

- 1.78 Cr-CSe
- 1.89 Cr-CO

This is now weaker and we have poorer pi accepting character compared to carbon mono sulphide, but nevertheless it still seems to be much better than, carbon monoxide because if you look at the bond distance that you have in this chromium complex, here is a chromium complex which is coordinated to carbon monoselenide. And you find that, the bond distance between chromium and carbon in this complex is 1.78 angstroms. And this is shorter than the distance that, you observe in the same complex that is 1.89 angstroms between the chromium and the carbon monoxide.

So, chromium and carbon monoxide seem to form longer chromium carbon bonds, compared to chromium and carbon monoselenide. Which is much shorter 1.78 about, 0.1 angstroms shorter, but nevertheless and since we are comparing the two systems in a same environment that means, the remaining ligands are the same. All of them have got, the same type of ligands attached to the chromium CSe and CO attached to the same chromium. And we can now compare, the two bond distances and it is clear that CSe is a good pi accepting ligand just like carbon monoxide.

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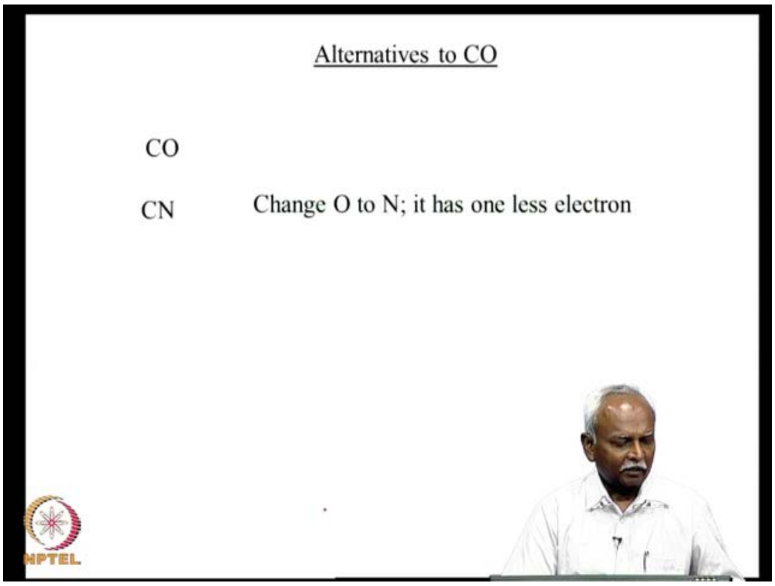

Alternatives to CO

CO

CN Change O to N; it has one less electron

So, this is in fact a surprising phenomenon what we have learned is that carbon monosulphide and carbon monoselenide can form equally good metal carbon pi bonds. Although, we did not expect this in the first place based on electronegativity differences. So, the pi accepting character of CS and CSe are reasonably good. The disadvantage however is the fact that, you do not have easy access to CS and CSe molecules. Carbon monoxide is a very stable molecule by itself, it is known as a gas that can be bottled and stored and kept under high pressure as long as you do not keep it in an nickel cylinder, which it will react with.

You can, you can keep carbon monoxide safely in the laboratory whereas, carbon mono selenide and carbon mono sulphide are molecules that you cannot store. You have to generate it, in the coordination sphere of the metal. Now, let us take a look at, what are some other tricks that a chemist can use in order to generate alternative molecules to carbon monoxide.

Because of the difficulty that we have, in identifying or making carbon monosulphide onecan think of an alternative way of making a ligand, which will be just as good as carbon monoxide, instead of changing the oxygen to sulphur, let us change oxygen to nitrogen. Now, if you change oxygen to nitrogen, there is one electron less in this atom compared to carbon monoxide. So, CN has got one electron less, it is got 13 electrons instead of 14 electrons which carbon monoxide.

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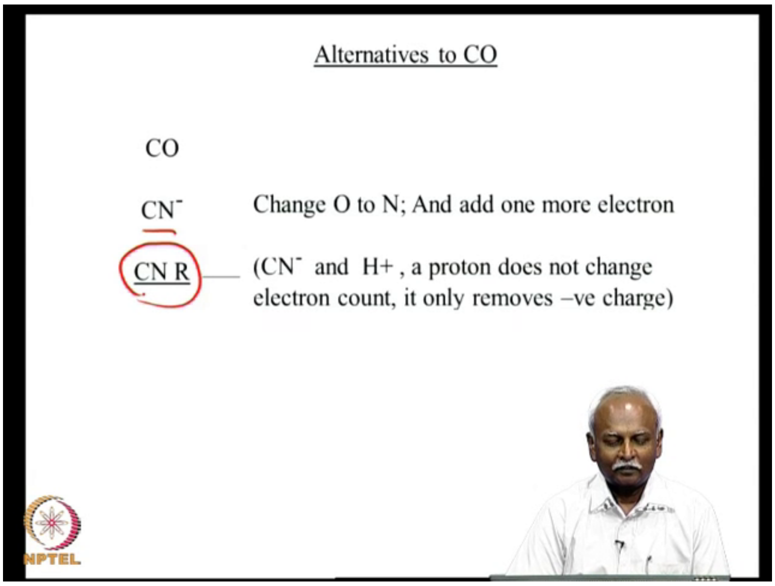

Alternatives to CO

CO

CN^- Change O to N; And add one more electron

$CN\,R$ (CN⁻ and H+ , a proton does not change electron count, it only removes –ve charge)

We can add this electron to form an ion. So, let us just add this electron, you add this electron and form the cyanide ion. The cyanide ion, as you might already be familiar with is quite a stable molecule. It forms a variety of complexes and it is isoelectronic with carbon monoxide. So, can it notbe a good alternative to carbon monoxide, the answer is yes. In fact carbon, alkyl isocyanides are good ligands as well where you have, protonated the CN minus with a H plus.

That is you react CN minus with a proton and then you can have RNC. So, this molecule an alkyl isocyanide can be a good replacement for carbon monoxide. So, there are alternative ways to make a ligand which is as good as carbon monoxide, by converting the oxygen to a nitrogen, adding an electron and then protonating it. These are tricks which a chemist uses, little bit of alchemy in order to generate new ligands.

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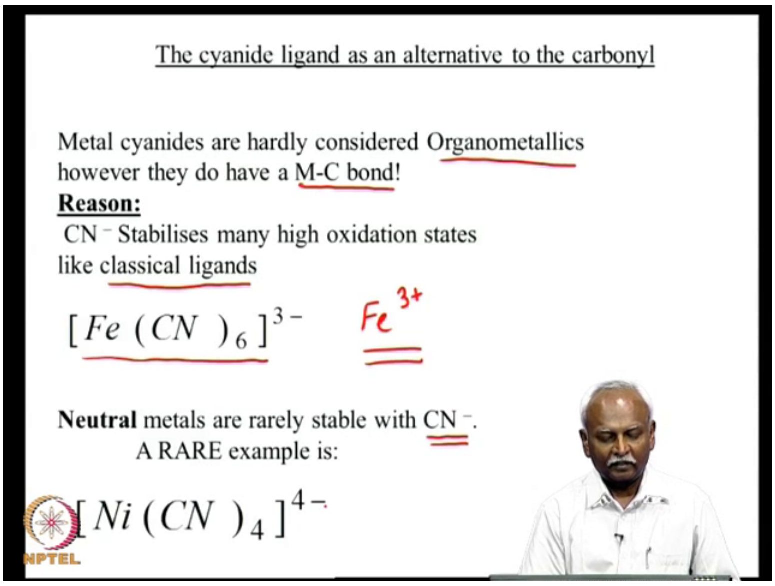

The cyanide ligand as an alternative to the carbonyl

Metal cyanides are hardly considered Organometallics however they do have a M-C bond!

Reason:

CN^- Stabilises many high oxidation states like classical ligands

$[Fe(CN)_6]^{3-}$ Fe^{3+}

Neutral metals are rarely stable with CN^-.

A RARE example is:

$[Ni(CN)_4]^{4-}$

So,what are the type of ligand, what are the type of complexes that the cyanide ligand forms. Metal cyanides are not considered as organometallics, based on tradition because, although they have a metal carbon bond, it is very often found that the cyanide is in fact coordinated to high oxidation state metals. So, here is an example where, you have iron coordinated to cyanide, butiron is present in the plus 3 oxidation state. So, if iron is plus 3 then, you find that the other organometallic molecules or ligands which are found inorganometallic chemistry are not coordinated to, are not stabilised by iron 3. So cyanide has a ability to, stabilise highoxidation states.

So, this is considered as classical behaviour or cyanide is grouped under classical ligands. So although, you have a molecule which has a metal carbon bond, you have a metal carbon bond and that qualifies for calling it an organometallic species. You normally, do not call it an organometallic molecule. So, here is a system where, you have iron coordinated to six cyanide ligands just like, you have 6 carbon monoxide ligands coordinated to chromium, but this molecule is normally considered under coordination chemistry.

Neutral metals are rarely stable with CN minus and the reason for this is that, as you add a cyanide, you also add a negative charge and when you add a negative charge then the excess electron density has to be pushed into the ligand. And cyanide is not as gooda pi accepting ligand, as carbon monoxide. So, one normally does not have many organometallic examples where, carbon monoxide, cyanide and other organic ligands are coordinated to the metal.

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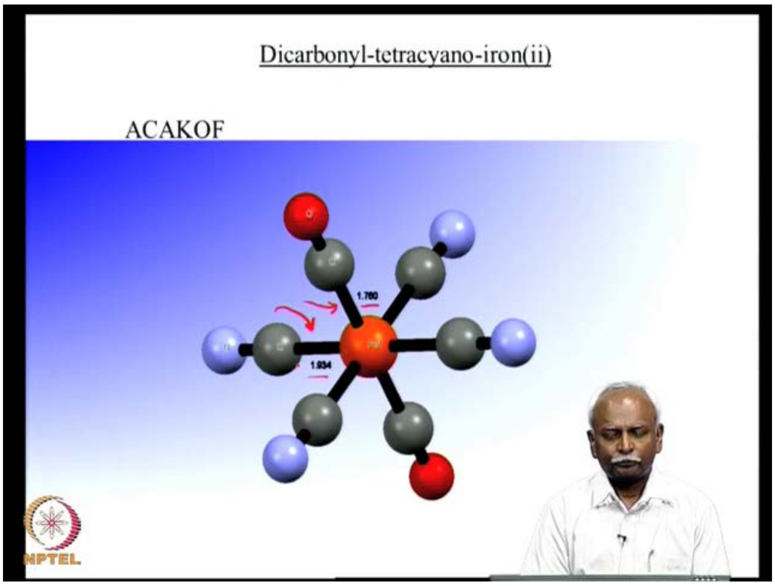

Dicarbonyl-tetracyano-iron(ii)

ACAKOF

Here is a unique example, this is in fact a iron 2 species that means, iron is in the plus 2 oxidation state. But you have both carbon monoxide and cyanide coordinated to the metal. I have chosen all examplesin such a way that, we can compare the ligands the new ligands that we are talking about with an old ligand carbon monoxide that we have studied earlier. So, in this particular case, you can see that the distance between cyanide is in fact longer.

It is 1.93 angstroms compared to, 1.76 angstroms which is the distance between carbon and iron and in this species. So, this bond distance is shorter, this bond distance is shorter and the cyanide bond distance, the carbon iron distance is much longer. So, you can immediately guess that the pi accepting character of cyanide, so the pi bond between the cyanide ligand and the iron is much poorer than the pi bond between carbon monoxide and the iron atom.

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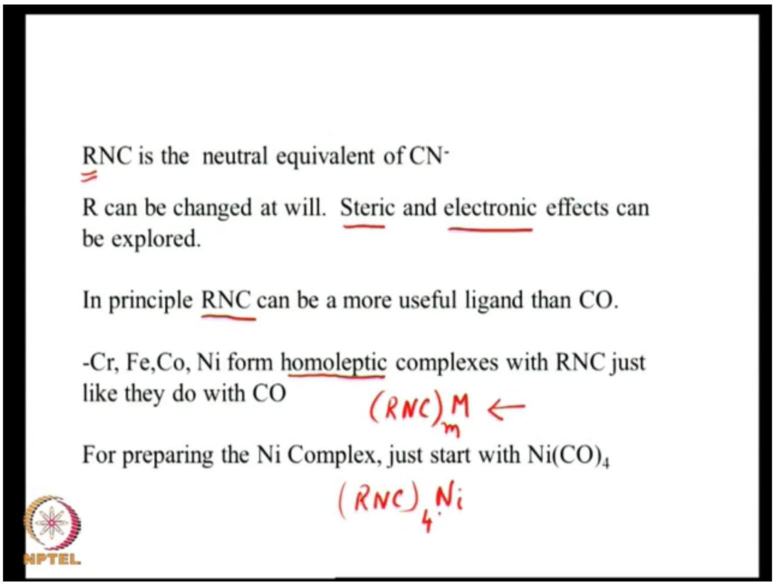

RNC is the neutral equivalent of CN$^-$

R can be changed at will. Steric and electronic effects can be explored.

In principle RNC can be a more useful ligand than CO.

-Cr, Fe,Co, Ni form homoleptic complexes with RNC just like they do with CO

$(RNC)_m M \leftarrow$

For preparing the Ni Complex, just start with $Ni(CO)_4$

$(RNC)_4 Ni$

So, you can understand how the negative charge on the cyanide is not a great help and so one has toreplace the cyanide negative charge with a proton. So that you can form a neutral molecule, which will be a better pi accepting molecule. Since R, the R group or the proton can bereplaced with, any R group we can have, alkyl isocyanides and this alkyl isocyanides can in fact be changed. To represent a wide variety of molecules, it can be, R can be an aryl group, it can be methyl, ethyl or propyl and this changes the steric effect. And it can also affect the electronic influence, the ligand influence, ligand places on the metal.

So, in principle, RNC or an alkyl isocyanide can be a more useful ligand than, carbon monoxide, but in practice RNC is not a great molecule, for the reasons that we will study in the following lectures, but sufficed to say that chromium, iron, cobalt, nickel can all form homolypticcomplexes with RNC. Which means RNC is the only ligand, which is coordinated to the metal.

So, a metal is coordinated to M units of RNC and this molecule is stable. For preparing the nickel complex, where nickel will have 4 units of RNC attached to it. So, you will have 4 RNC molecules with nickel, one has to just start with nickel tetra carbonyl, you treat nickel tetra carbonyl with RNC and you will form this isoelectronic species, which has got 4 alkyl isocyanides coordinated to the nickel.

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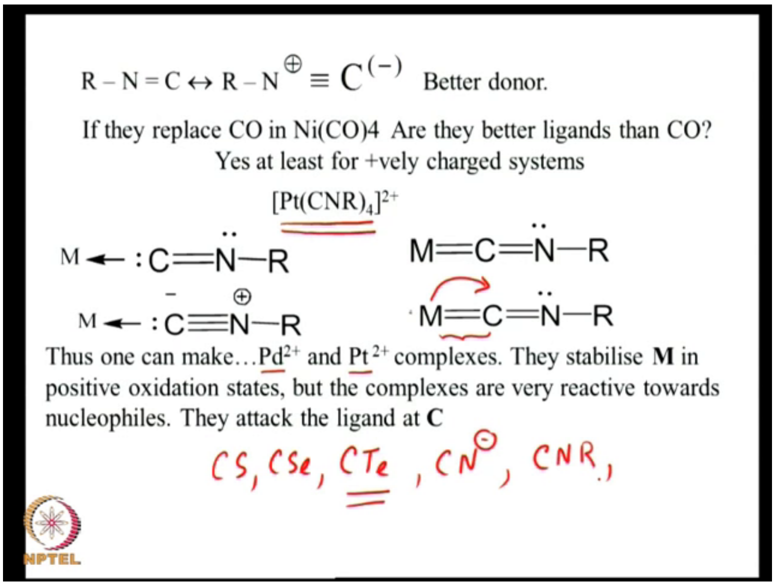

$R-N=C \leftrightarrow R-N^{\oplus} \equiv C^{(-)}$ Better donor.

If they replace CO in Ni(CO)4 Are they better ligands than CO?

Yes at least for +vely charged systems

$[Pt(CNR)_4]^{2+}$

Thus one can make…Pd^{2+} and Pt^{2+} complexes. They stabilise **M** in positive oxidation states, but the complexes are very reactive towards nucleophiles. They attack the ligand at **C**

CS, CSe, CTe, $CN^{\ominus}$, CNR,

So, let us just quickly take a look at the Se structural properties because RNC has got this valence bond structure where, you have a negative charge on the carbon. Here is the valence bond structure, written on the top of the screen. You have RN triple bond C minus, as one of the resonant structures. So, you have a very large negative dipole on the carbon and it becomes a much better donor. And so, it is in fact a better sigma donor than, carbon monoxide and it will replace carbon monoxide in nickel tetra carbonyl and form a complex.

And this can be done because, you have a negative charge you can also form complexes with a positively charged metal systems just like, cyanide, but this time the molecule is exactly similar to the carbon monoxide complex, you have a neutral ligand, not a negatively charged ligand, a neutral ligand which is coordinated to the metal centre. And thatalso, is quite stable so, you have,you can have complexes with palladium.

You can have complexes with platinum and both of these are positively charged and they from nice complexes with alkyl isocyanides. And it is this, resonant structures which make it avery good ligand, you have a negative end on the carbon and that makes it a much better donor and the metal can pump electron density back into the pi star orbitals, of the cyanide alkyl isocyanide.

And that can make this, metal carbon pi bond a very stable system. So, what we have seen today is that, there are in fact alternative ligands for carbon monoxide. What one uses is, a little bit of alchemy and the periodic table to generate a new set of ligands and the ligands that we have seen are CS, CSe and CTe. Although we have not seen examples of this ligand, this can also be made and then CN minus and CN minus can also be protonated so that, you have CNR that is alkyl isocyanide. And that can also be, a good ligand for the metal atom. So, with this, we conclude this lecture on alkylisocyanide, cyanides, carbon monotellurides, carbon monoselenides. And carbon monosulphides and these are good alternatives for carbon monoxide in organometallic chemistry.