Introduction to Organometallic Chemistry

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Lecture - 8
Non-Carbon Ancillary ligands

In this lecture, we are going to talk about some ligands, which are based on phosphorous in the oxidation state 3.

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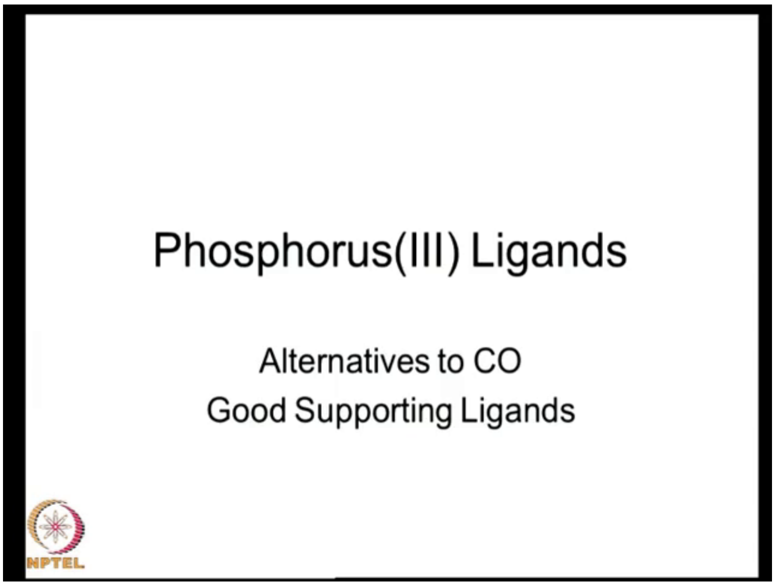

Phosphorus(III) Ligands

Alternatives to CO
Good Supporting Ligands

We talk about it as phosphorous 3 ligands in many instances.

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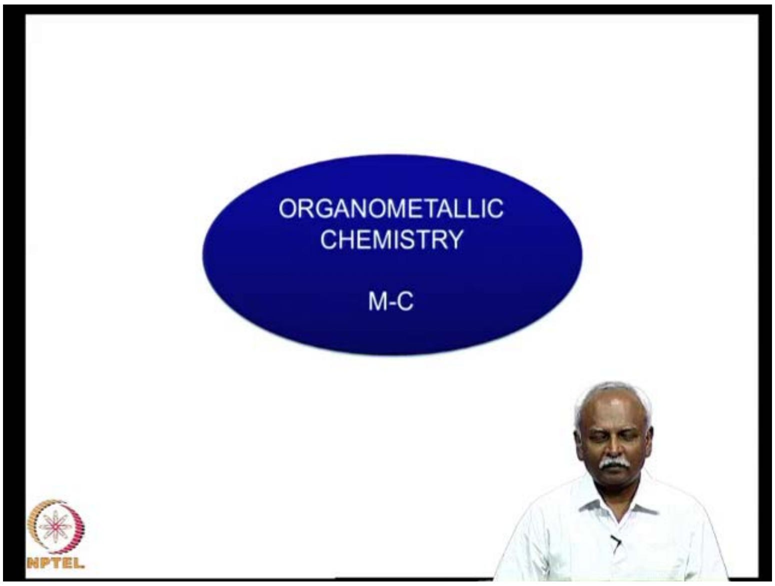

ORGANOMETALLIC CHEMISTRY

M-C

Organometallic chemistry is associated with a metal carbon bond and that is correct. You also need some other ligands to support the metal carbon chemistry that is going on.

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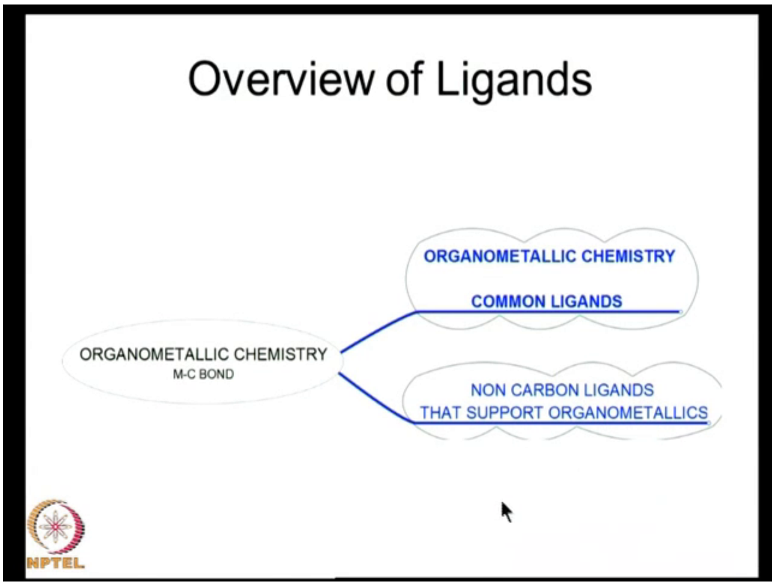

Overview of Ligands

ORGANOMETALLIC CHEMISTRY
M-C BOND

ORGANOMETALLIC CHEMISTRY

COMMON LIGANDS

NON CARBON LIGANDS
THAT SUPPORT ORGANOMETALLICS

In general there are a variety of ligands which are useful in organometallic chemistry. The most common ligands of course, are the ones

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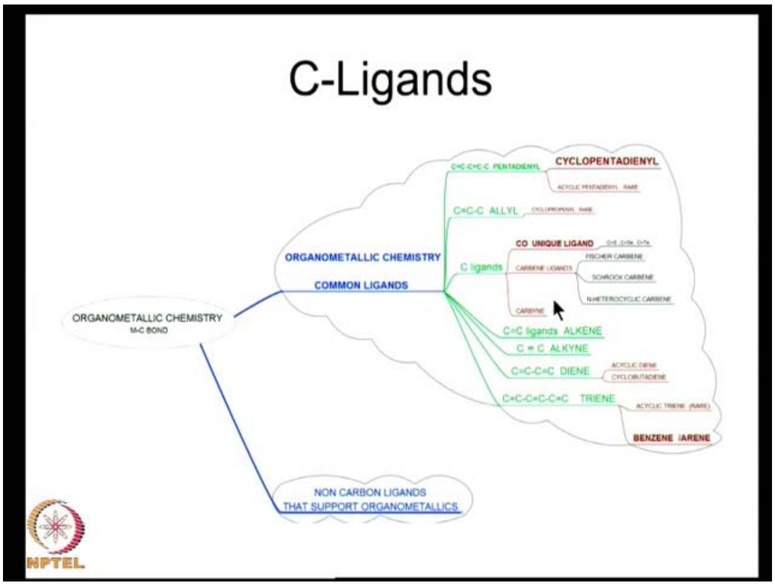

C-Ligands

ORGANOMETALLIC CHEMISTRY
M-C BOND

ORGANOMETALLIC CHEMISTRY
COMMON LIGANDS

C=C-C=C-C PENTADIENYL
CYCLOPENTADIENYL
ACYCLIC PENTADIENYL RARE
C=C-C ALLYL
CYCLOPROPENYL RARE
C ligands
CO UNIQUE LIGAND
C=S, C=Se, C=Te
CARBENE LIGANDS
FISCHER CARBENE
SCHROCK CARBENE
N-HETEROCYCLIC CARBENE
CARBYNE
C=C ligands ALKENE
C ≡ C ALKYNE
C=C-C=C DIENE
ACYCLIC DIENE
CYCLOBUTADIENE
C=C-C=C-C=C TRIENE
ACYCLIC TRIENE (RARE)
BENZENE /ARENE

NON CARBON LIGANDS
THAT SUPPORT ORGANOMETALLICS

which have the carbon metal bond. That can be carbon monoxide which is what we have already discussed. We can also talk about carbene ligands and carbyne ligands. These are all having a single carbon attached to the metal center. On the other hand, there are several ancillary ligands which also support organometallic chemistry. These do not have a metal carbon bond.

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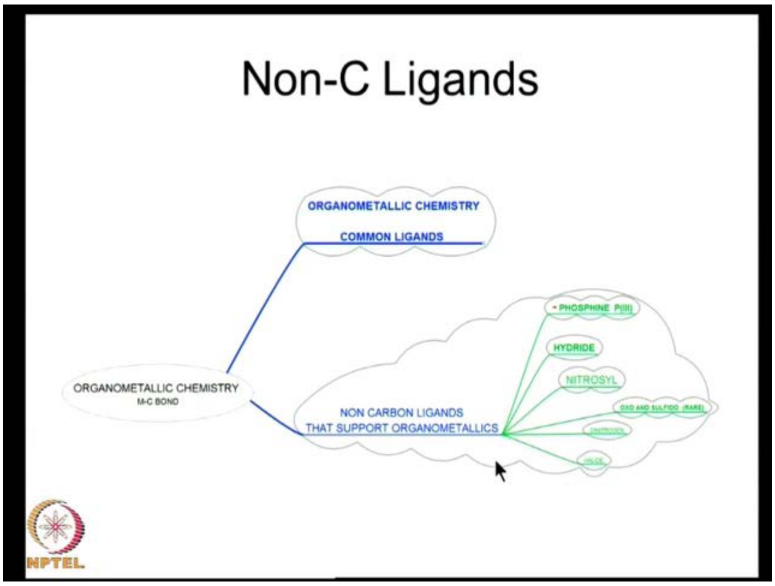

Non-C Ligands

ORGANOMETALLIC CHEMISTRY
COMMON LIGANDS

ORGANOMETALLIC CHEMISTRY
M-C BOND

NON CARBON LIGANDS
THAT SUPPORT ORGANOMETALLICS

PHOSPHINE P(III)
HYDRIDE
NITROSYL
OXO AND SULFIDO (RARE)
DINITROGEN
HALIDE

Today we are going to talk about one such ligand. That is the phosphorous 3 chemistry metal hydride, chemistry metal nitrosyls. Metal dinitrogen chemistry and metal halides are all important in organometallic chemistry. Although the chemistry may not happen at the metal carbon center these are good supporting ligands. So, I am calling it as those ligands that support organometallics. So, today we will talk about phosphorous 3 ligands.

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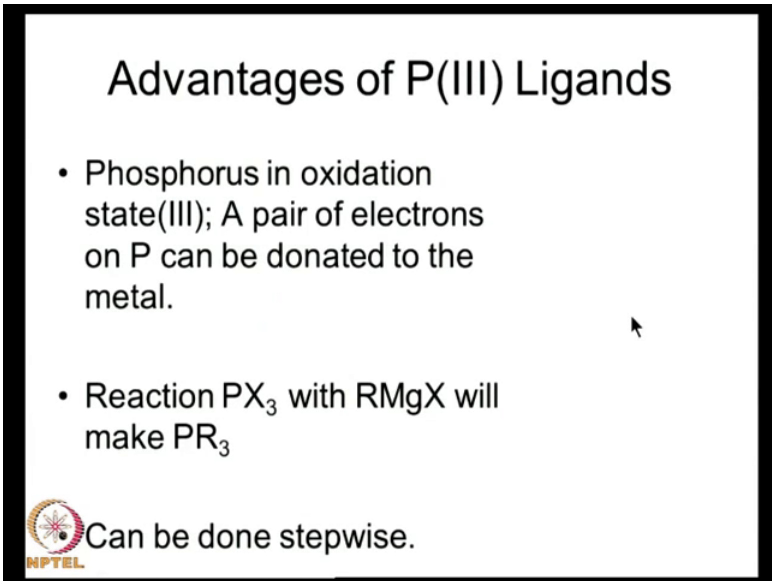

Advantages of P(III) Ligands

- Phosphorus in oxidation state(III); A pair of electrons on P can be donated to the metal.
- Reaction PX_3 with RMgX will make PR_3

Can be done stepwise.

There are some distinct advantages to phosphorous 3 ligands. We will consider them one by one. First of all it is a good sigma donating ligand because phosphorous is in the oxidation state 3 a pair of electrons on phosphorous. This can be donated to the metal. The phosphorous 3 ligands can be varied extensively contrary to carbon monoxide, where carbon monoxide cannot be changed. You can only change the oxygen to sulphur or to selenium, but in the case of P 3 ligands you can change the R group which is attached to the phosphorous extensively.

So you can react this molecule PX three usually it is the halogen. This is usually the effects, stands for halogen. You can change the halogen to an R group using a reaction with grignard reagent, you can make the PR 3 molecules, these PR 3 molecules. It can also be varied; you can change the R group to R1, R2, and R3. This synthesis is relatively easy. This has been shown in a stepwise fashion.

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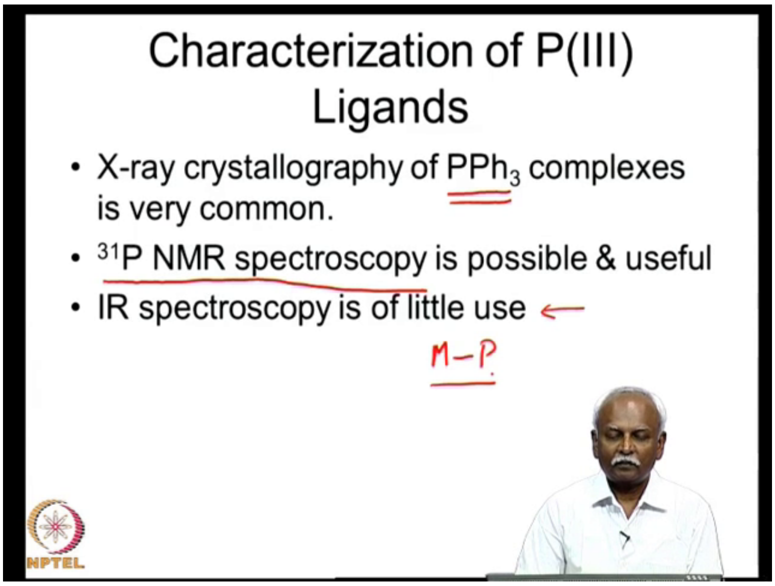

Characterization of P(III) Ligands

- X-ray crystallography of PPh_3 complexes is very common.
- ^{31}P NMR spectroscopy is possible & useful
- IR spectroscopy is of little use ←

M–P

The other great advantage of phosphorous 3 ligands is a fact that x-rays crystallography of especially PPh 3, PPh 3 complexes becomes very easy. This is because of some super molecular interactions that are there in triphenyl phosphene. So, whenever you have PPh 3 as an ancillary ligand, the orgaometallic complex is easy to crystallize. If it crystallizes as a single crystal one can do the crystallography of this molecule and study the solid state structure very readily and extremely accurately. It can also carry out phosphorous 31 MNR spectroscopy.

This is again a very useful technique because no other element in the molecule might interfere in this spectrum. Only the ligand is visible in the NMR spectrum. So this becomes an extremely useful tool because of non interference. Only the active species is visible infrared spectroscopy. Unfortunately, this is of not much value in this instance. This is because of the metal phosphorus bonds, metal phosphorus bonds are single bonds. They are possible; it is possible to absorb them in the infrared spectrum in the very low energy regions like 300 to 400 centimeter minus 1. This region is 300 to 400 and is quite crowded. It is very often not useful as a tool to analyze the phosphorous 3 organometallic chemistry that goes on.

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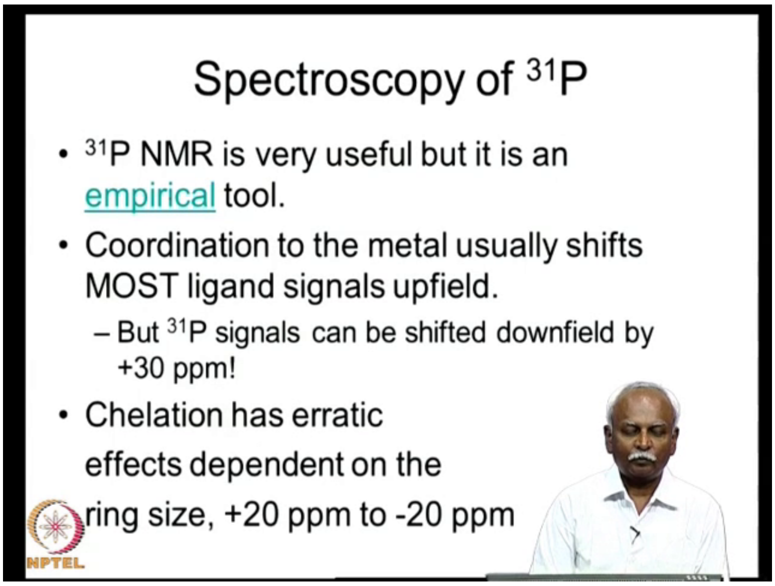

Spectroscopy of ^{31}P

- ^{31}P NMR is very useful but it is an empirical tool.
- Coordination to the metal usually shifts MOST ligand signals upfield.
  - But ^{31}P signals can be shifted downfield by +30 ppm!
- Chelation has erratic effects dependent on the ring size, +20 ppm to -20 ppm

Let me say a few words about 31 P NMR. It is an extremely useful technique, but unfortunately it is an empirical tool. When you call it an empirical tool it only means that it is based on prior evidence that you have. You can in fact use this empirical tool based on prior evidence. If you have a crystallographically characterized molecule one can use the 31 P NMR usefully. As one assumes the solid state structure and the solution NMR have to be related

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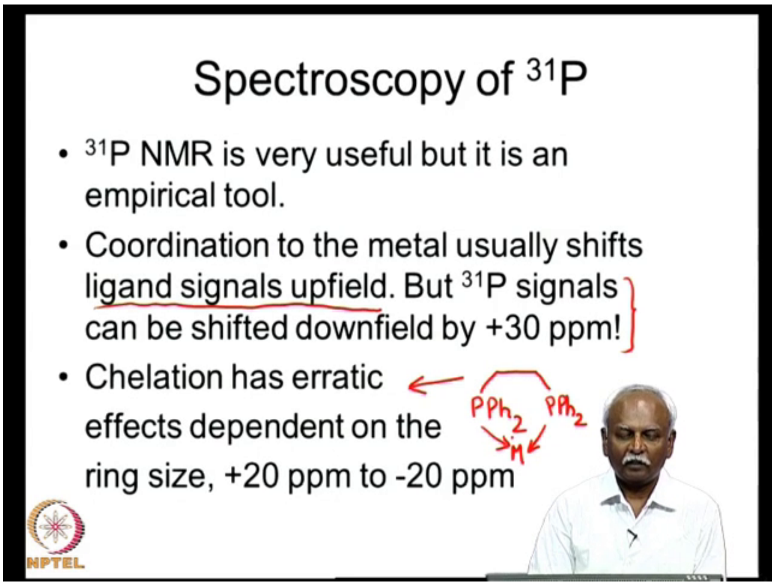

Spectroscopy of ^{31}P

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- Coordination to the metal usually shifts ligand signals upfield. But ^{31}P signals can be shifted downfield by +30 ppm!
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coordination to the metal. This usually shifts the ligand signals up-field. Now this is what happens, the coordination of the metal. It shifts the ligand signals up-field. But the 31 P signals can also be shifted down-field by up to 30 NMR.

The usefulness of this tool is significantly affected because of this empirical nature. The fact that the signals are in unusual regions with respect to the free ligands, there is another erratic behavior of phosphorous 31 signals. That is the fact, that if you have a chelated molecule. Let me write down a chelate, an example of a chelate molecule. If you have bisdiphenyl phosphene of ethane which is this ligand, now this ligand is capable of coordinating to the metal through 2 phosphorous centers.

So, a chelate ring will be formed depending on the chelate ring in this particular case. What I have written is a 5 membered ring 1, 2, 3, 4 and 5. This 5 membered ring is formed and then the shift can be a plus 20 PPM. If you have a single carbon then the shift is minus 20 PPM because of this erratic behavior of the chemical shift sometimes it becomes difficult to interpret the NMR spectrum of these phosphorous metal complexes. But otherwise if you have prior knowledge about the way the chemical shift changes on chelation it turns out to be an extremely useful tool.

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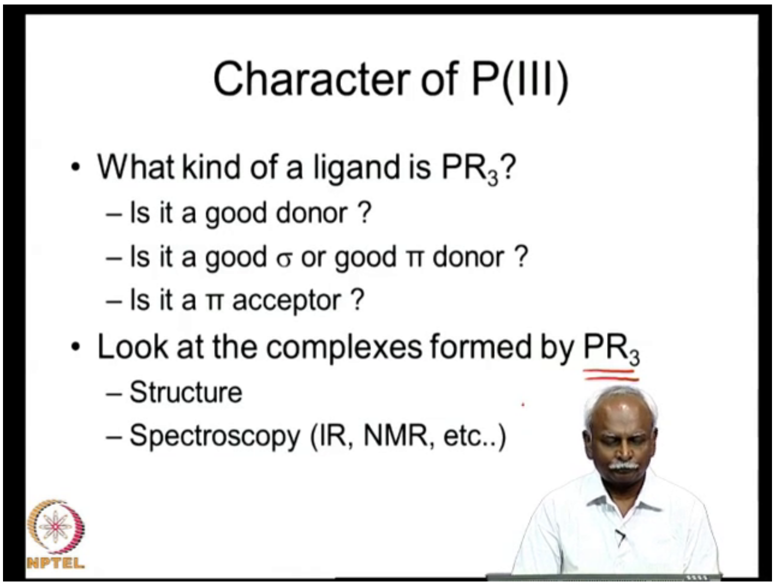

Character of P(III)

- What kind of a ligand is PR_3?
  - Is it a good donor ?
  - Is it a good σ or good π donor ?
  - Is it a π acceptor ?
- Look at the complexes formed by PR_3
  - Structure
  - Spectroscopy (IR, NMR, etc..)

Based on these, based on the information that we have so far we can see that phosphorous 3 ligands can be readily synthesized. They can be synthesized in a variety of R groups having variety of R groups. Now the question arises that what kind of a ligand is this PR three. The PR 3 group is a good donor. It is a good sigma donor or is it a pi donor. One can also ask the question if it is a pi acceptor. If you look at the complexes formed by triphenyl phosphine or trialkyl phosphines then one can understand based on the structure and the spectroscopy. We do, we can figure out what kind of a donor we are dealing with. So let us take a look at a little bit of the chemistry that is there in this molecules.

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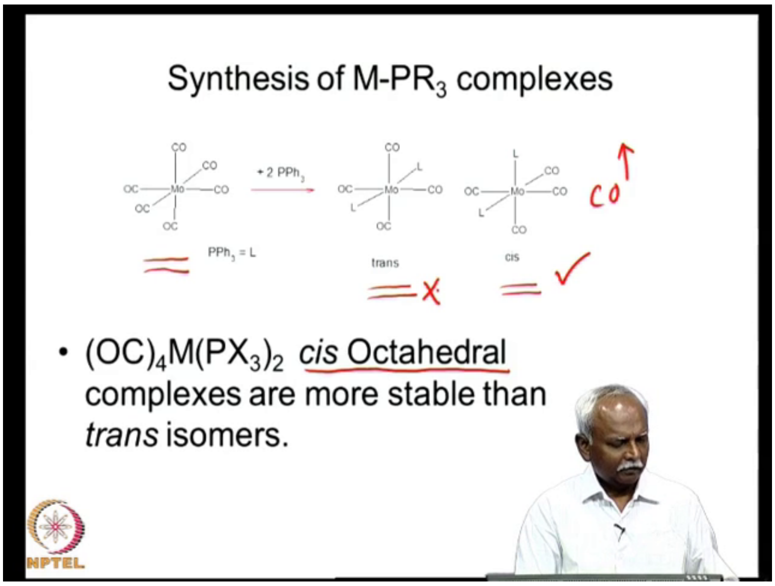

Synthesis of M-PR_3 complexes

- $(OC)_4M(PX_3)_2$ *cis* Octahedral complexes are more stable than *trans* isomers.

First let me give you an example on how one can synthesize these triphenyl phosphine complexes. This will illustrate the chemistry that I am talking about. Let us take a molybdenum hexacarbonyl complex. This is a molybdenum hexacarbonyl complex I treat that with 2 equivalents of triphenyl phosphene. This appears to be a general way of synthesizing phosphorous containing molecules. You can take any labile ligand in this particular case carbon monoxide and transfer it to be useful. This is because carbon monoxide will escape into the reaction medium, away from the reaction medium and you will be left with a complex.

You would expect the treatment of moco 6 with 2 equivalents of triphenyl phosphene will result in the formation of a trans complex. It can also result in the formation of a cis complex. It turns out that exclusively the cis octahedral complex is formed. Only the cis octahedral complex isolated from this reaction mixture. If you look at the complex it, itself you can very easily see that carbon monoxide has no great steric influence. It is only the phosphorous containing ligand which has got some steric influence.

So, if you want to pack 2 ligands 2 phosphorous containing ligands around the molybdenum it would be best to have the trans geometry. This is because the 2 l groups are far away from each other but, surprisingly it is the sis ligand which is sis complex which is formed. The trans complex is not formed so there must be an electronic reason for this particular preference. Very often

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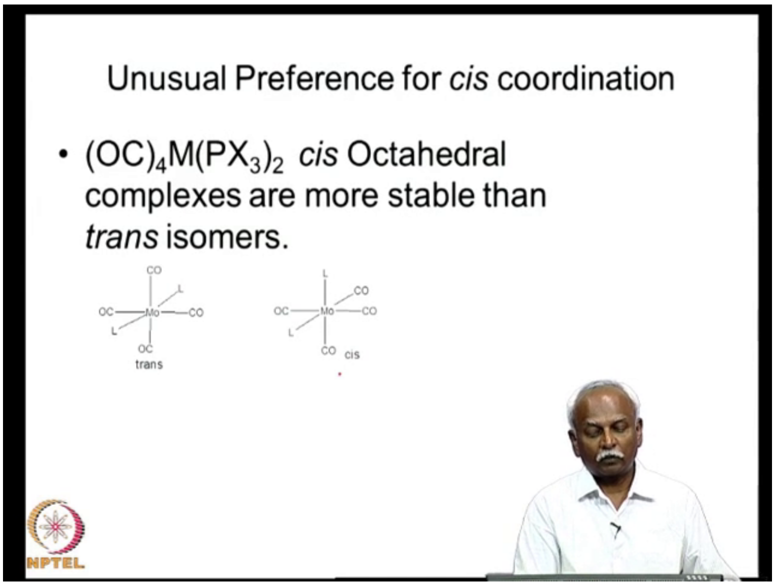

Unusual Preference for *cis* coordination

- $(OC)_4M(PX_3)_2$ *cis* Octahedral complexes are more stable than *trans* isomers.

it is good to form a particular opinion by looking at a variety of complexes. This has been done in the case of phosphene complexes both trans and a cis. These have been attempted preparations of these, have been attempted and almost always the cis complex is what is observed. In many metals and with many carbon monoxide geometries one forms only the cis complex.

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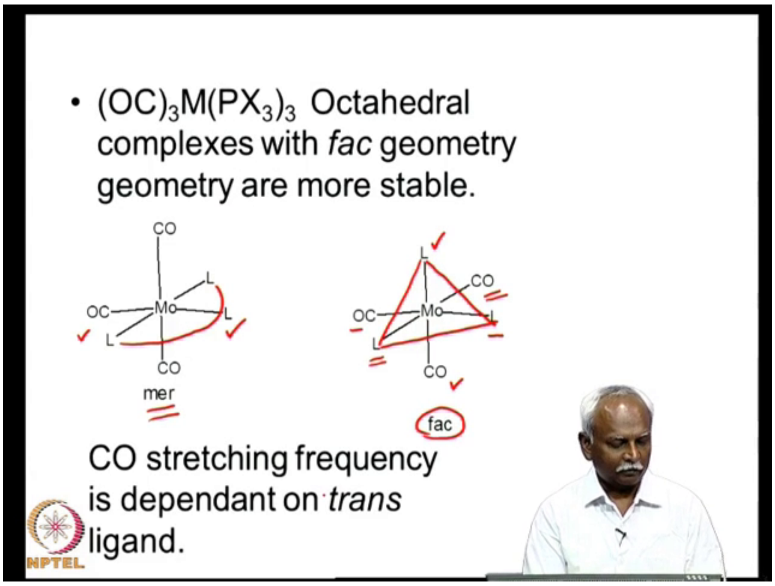

- $(OC)_3M(PX_3)_3$ Octahedral complexes with *fac* geometry geometry are more stable.

CO stretching frequency is dependant on *trans* ligand.

Now, one can also make the tris coordinated complex the tris tri alkyl phosphene complexes. They have been synthesized and here again you can have 2 particular geometries. One is called the mer geometry where the 3 ligands are placed in a meridonal plane. The 3 ligands are placed in a meridonal plane then it is called a mer complex. Then you can also have a fac complex, and a fac complex. You have a facial geometry so one face of the octahedron is occupied by the 3 ligands which are the phosphorous three ligands. So between these two geometries you will notice that the fac complex always has one l trans to a carbon monoxide.

You have 1 carbon monoxide trans to an l group so all 3 l groups have got a trans carbon monoxide. You will notice that each of these l groups has got a trans carbon monoxide, but in the meridonal geometry you do not have that particular situation. In one case which is this particular l group you do have a trans carbon monoxide but, the other 2 l groups do not have a carbon monoxide opposite them. Now, it turns out that you can distinguish these two species very easily using the carbon monoxide stretching frequency.

This is because that depends on the trans ligand so based on carbon monoxide stretching frequency. Hence, you can find out that it is only the fac isomer which is formed and their mer isomer is not formed. So we have two situations now both in the disubstituted case and in the trisubstituted case. We can see a clear preference for the ligand l to be trans to a carbon monoxide. This electronic preference is to be explained in order for us to understand why exactly l prefers this geometry and what the electronic reason is for the same.

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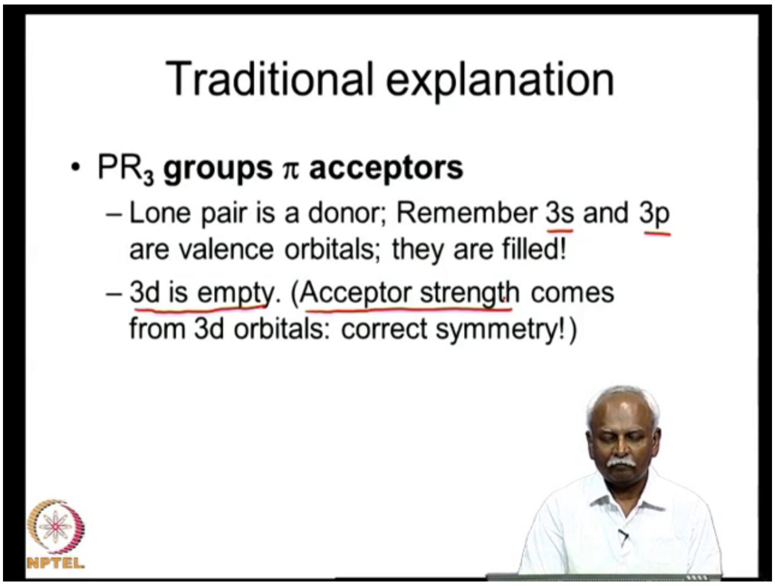

Traditional explanation

- PR_3 **groups π acceptors**
  - Lone pair is a donor; Remember 3s and 3p are valence orbitals; they are filled!
  - 3d is empty. (Acceptor strength comes from 3d orbitals: correct symmetry!)

Let us now look at the traditional explanation which was available. Until the mid nineteen eighties people normally gave this explanation. We will discuss this first because; it illustrates an important scientific principle. Whenever there is an argument or a discussion regarding a concept one achieves a better explanation at the end of the discussion. Here is the explanation that was given originally. People thought that PR 3 groups are pi acceptors and this pi accepting property arose from the 3 d orbital.

This is empty because the phosphorous is a element which has got the valence electrons in the three s and three p. So remember 3 s and three p are the valence electrons. These are the ones which are having the 5 electrons which are there on phosphorous and the 3 d is usually empty. As the 3 d is empty, people thought that the acceptor strength, the acceptor strength of the PR 3 group comes from the 3 d orbitals. As they have the right symmetry to overlap with metal orbitals.

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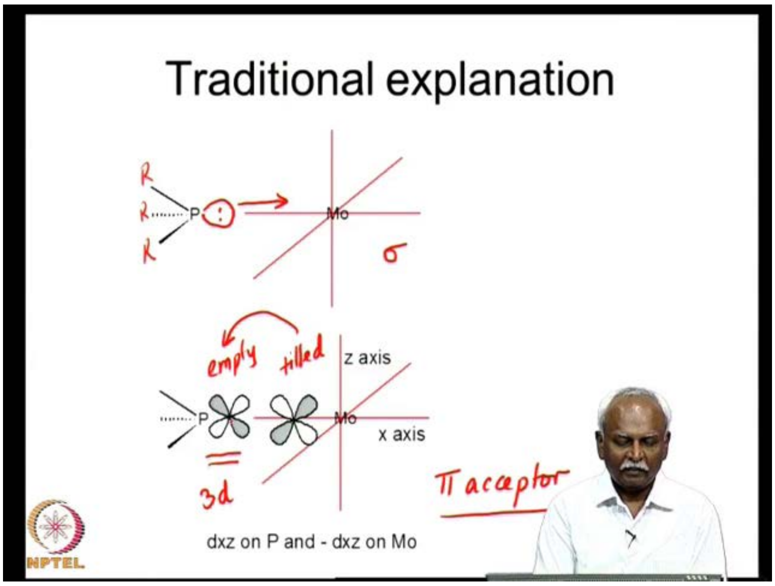

Traditional explanation

dxz on P and - dxz on Mo

So, let us take a look at what we are discussing here. Here is the molybdenum centre interacting with the phosphorous 3 molecules. The 3 molecules, the 3 arms of the phosphorous where the R groups are present will be distributed just like ammonia. This is done in an umbrella like fashion. The lone pair on the phosphorous is now pointed towards the metal atom. It has got 2 electrons and this lone pair is going to be donated to the metal.

So, this is the electron density flow in the sigma orbital that we are talking about. If the phosphorous atom has got a 3 d orbital, it has got a 3 d orbital then the 3 d orbital can interact with the metals 3 d orbital, if this is empty and if this is filled. So, you have a filled metal orbital and you have an empty p orbital phosphorous orbital which is a 3 d system then you have electron density flowing in this direction. This kind of an electron density flow will result in a pi acceptor behavior. People thought that phosphorous ligands are good pi acceptors. This is because electron density flow going from the metal d orbital into the empty d orbital on the phosphorous.

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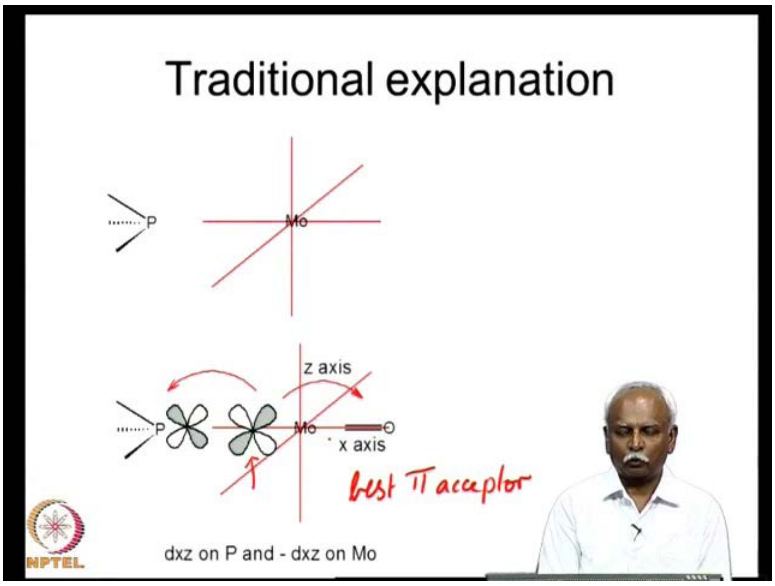

Traditional explanation

dxz on P and - dxz on Mo

How does this help us to explain the geometrical preferences that we observed earlier? As the carbon monoxide is an excellent pi acceptor, carbon monoxide is one of the best pi acceptors that we know of. This is a best pi acceptor that we know it is natural that carbon monoxide would like to have a poor pi acceptor in the trans position. Now, you might ask why is this situation, why should it be in the trans position. That is because this d orbital that is there on the molybdenum centre. This is the d orbital that is there on the molybdenum centre.

I have drawn it slightly pushed away from the centre so that you can understand the overlaps. You can see that the d orbital that is involved in this d pi d pi d pi interaction. This interaction that we are talking about is on the same axis as this carbon monoxide in the trans position. It is the same orbital which will have to donate electron density in both directions. It will have to donate electron density from the metal d to the phosphorous d. It will have to give electron density from the metal d to the pi star of the carbon monoxide.

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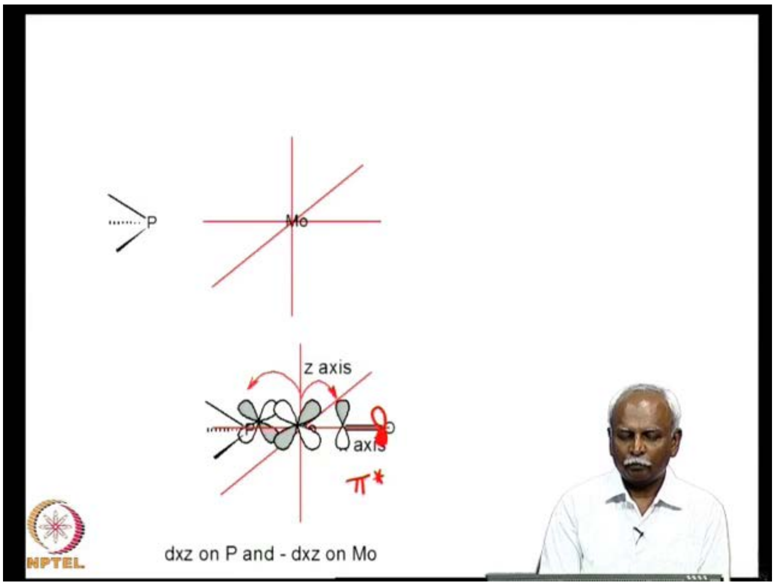

dxz on P and - dxz on Mo

This is the interaction that we are talking about. There is a competition between the phosphorous empty d and the carbon monoxide pi star. This is the pi star and you can draw the second set of orbitals. Also this would be shared and this would be empty. This is the pi star orbital and the electron density has to flow into the pi star of the carbon monoxide. That is what usually one observes in all the complexes. So, because carbon monoxide is such a good pi acceptor the phosphorous is a poorer pi acceptor, so by putting 3 phosphorous ligands trans to carbon monoxide the carbon monoxide ligands are kept happy.

They will have enough electron density moving in this direction. If you have the phosphorous ligands all in the meridonal position or in the trans position. You will notice that the carbon monoxides also have to be trans if the carbon monoxide is trans 1 carbon monoxide. It competes with another carbon monoxide for the same d orbital. That is an unhappy situation for the metal. It does not prefer that situation. It likes to have a phosphorous which is a poor pi acceptor opposite carbon monoxide which is a strong pi acceptor.

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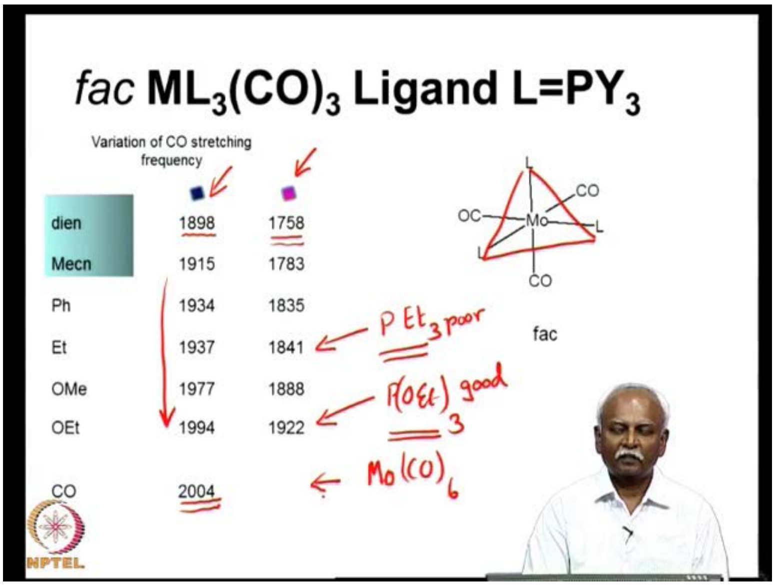

fac $ML_3(CO)_3$ Ligand $L=PY_3$

Variation of CO stretching frequency

	■	■
dien	1898	1758
Mecn	1915	1783
Ph	1934	1835
Et	1937	1841
OMe	1977	1888
OEt	1994	1922
CO	2004	

PEt_3 poor

$P(OEt)_3$ good

$Mo(CO)_6$

Now, how do we know that whatever we have said so far is true? Look at carbon monoxide stretching frequencies in the fac complexes. Here is a fac complex that I have. We are talking about this is a fac complex because the 3 ligands, the substituents are in the facial position of an octahedron. Then the carbon monoxides are on the opposite face. You can look at the symmetric stretching this is a symmetric stretching. The anti-symmetric stretching of the carbon monoxide, you will find that if you have a very good donor, on the face or on this face. For example, if you have a very good donor then the carbon monoxide stretching frequency reduces quite significantly.

You will notice that in moco 6 that is a molybdenum hexacarbonyls where carbon monoxide is trans to another carbon monoxide always. So, this is the observation for moco 6. Then you have a stretching frequency of 2004 centimeter minus 1 adding a ligand like dien. This has got 3 nitrogen donors in the facial position. This results in a very low stretching frequency for the carbon monoxide ligands. This is because electron density flows from the nitrogen to the metal. It then flows from the metal to the carbon monoxide very effectively.

This stretching frequency goes down the moment you start adding a ligand which can compete with the carbon monoxide for electron density. Then the frequency of the carbon monoxide slowly keeps going up. You have triethyl phosphite for example. In this case, it is poet thrice if you have, poet thrice then the triethyl phosphite happens to be a better pi acceptor than triethyl phosphates, a triethyl phosphene pet 3. This is a poor pi acceptor, so poor pi acceptor. This is a good pi acceptor. If you have a good pi acceptor trans to the carbon monoxide then the stretching frequency is higher.

You can see that as this stretching frequency of the 3 carbonyl ligands go up. You can see that the electron density on the metal has gone down. This is because the phosphorous atom is also competing for the electron density. That is the reason why you have this competition between the d pi d pi interaction between the phosphorous and the metal. The d pi pi star interaction on the carbon monoxide. These two compete with one another. It is better to have the phosphorous ligands in the trans position.

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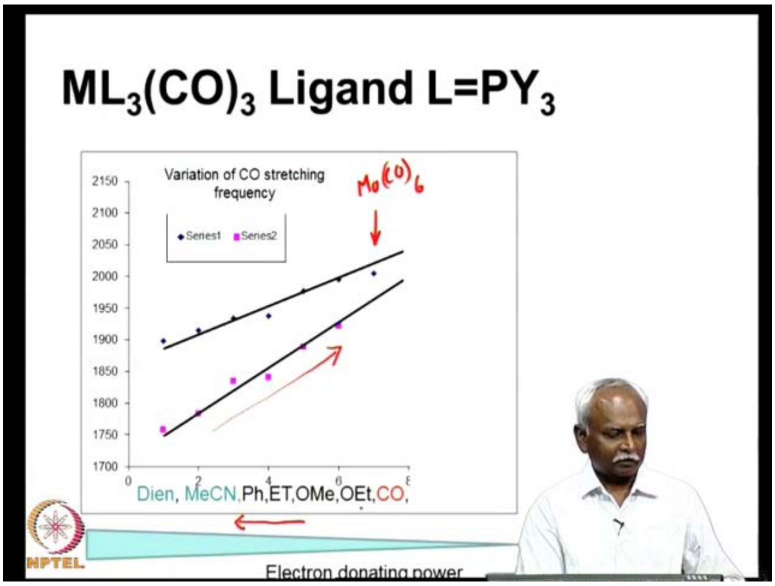

$ML_3(CO)_3$ Ligand L=PY_3

One can look at this graphically, to understand it and appreciate it better. Here is an example, where you have the 3 carbon monoxide ligands having two stretches in a symmetric stretch. An asymmetric stretch both of them are plotted in a series. You find that the metal carbonyl complex the pure metal carbonyl complex. This is marked here as moco 6. It has got the higher stretching frequency, but if you put good donors on the trans position, the best donor that is the nitrogen donor has a very low stretching frequency.

As you increase the pi accepting nature of the phosphorous ligand the stretching frequency keeps increasing. The electron donating power of the trans ligand keeps increasing in this direction. It keeps increasing in this direction and the trans carbon monoxide. The stretching frequency keeps increasing in the opposite direction. This is a very clear indication of the fact that the trans ligand competes for the same d orbital for d electron density for pi donations.

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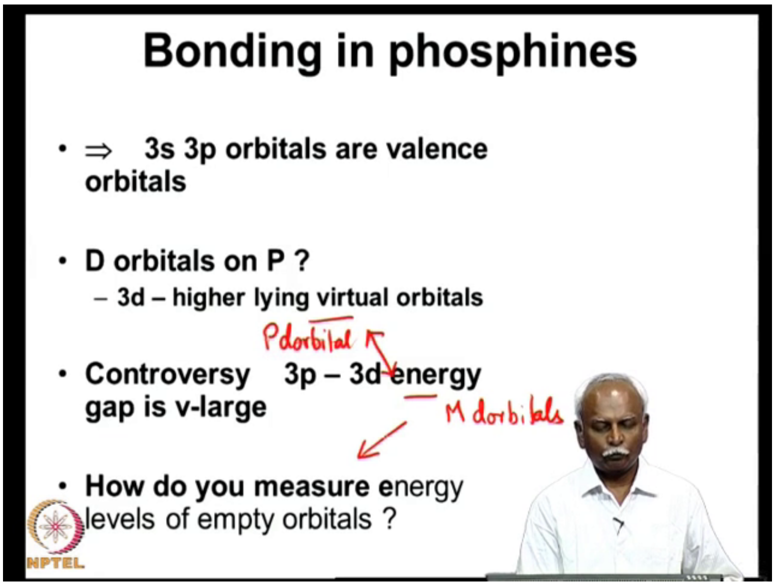

Bonding in phosphines

- ⇒ 3s 3p orbitals are valence orbitals
- D orbitals on P ?
  - 3d – higher lying virtual orbitals
- Controversy 3p – 3d energy gap is v-large
- How do you measure energy levels of empty orbitals ?

P d orbital

M d orbitals

This explanation, this traditional explanation was quite satisfactory. It was used in the text books for a very long time. In more recent text books you might find that it is being disputed. People found by computational methods that 3 d orbitals are actually not available or accessible for the metal d orbitals. The metal d orbitals are in one particular energy level. The 3 d orbitals are much higher in energy. So if one has to represent this graphically, one can say that these are the metal d orbitals and the phosphorous d orbitals are much higher in energy. The interaction between these 2 orbitals will be very poor because the energy matching is important for forming em bonding and anti bonding molecular orbital.

Hence, because of this controversy people have abandoned this explanation that the d orbitals on phosphorous are actually involved in d pi d pi pi interactions. This gap that is large has resulted in abandoning of this explanation. One also notes the fact that you cannot measure the energy of empty orbitals. So it is difficult to disprove or prove this particular point that we are talking about as a result.

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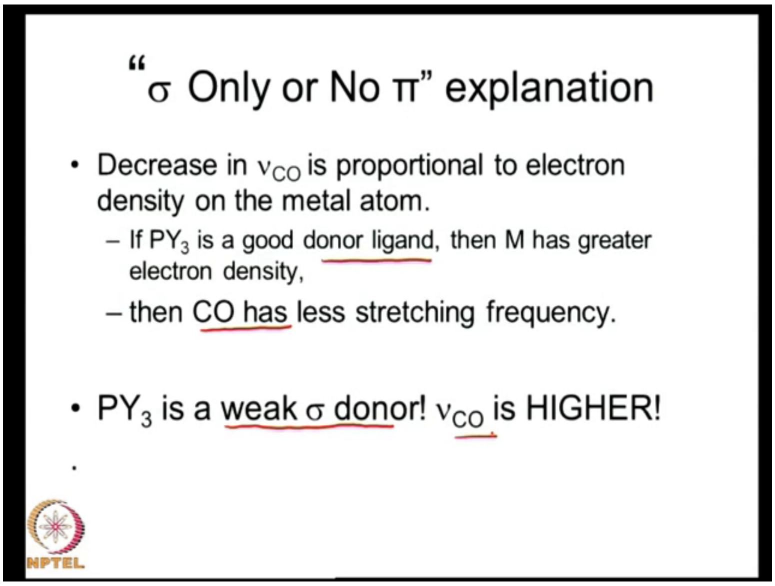

“σ Only or No π” explanation

- Decrease in ν_{CO} is proportional to electron density on the metal atom.
  - If PY_3 is a good donor ligand, then M has greater electron density,
  - then CO has less stretching frequency.
- PY_3 is a weak σ donor! ν_{CO} is HIGHER!

There was an alternative explanation that was built around what is called a sigma only theory. That means, phosphorous ligands are only good sigma donors. There is no pi interaction that is present. This particular theory was able to explain a few of the observations that are present. Let us just take a look at some of the explanations that could be made using the sigma only theory, or the no pi bond theory.

The decrease in the Mu CO is proportional to the electron density on the metal atom if the PY 3 ligand is a good donor. If PY 3 is a good donor then metal has got greater electron density. If the metal has greater electron density CO has less stretching frequency. The pi star orbitals are populated to a better extent. If PY 3 is a weak or it is a weak sigma donor then the Mu CO is higher this explanation also seem to be.

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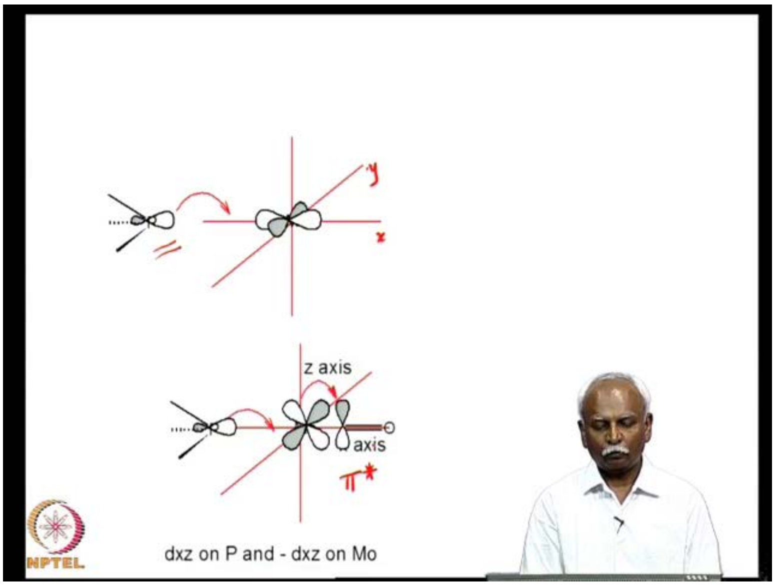

dxz on P and - dxz on Mo

The type of electron donation that we are talking about is an electron donation from the 3 sp hybrid on the phosphorous to the metal. This is the d if this is x and this is y this is dx squared minus y squared accepts electron density from the phosphorous. It is the dxz on the phosphorous on the metal which is interacting with the pi star on the carbon monoxide. So, this type of an interaction would be sufficient to explain the type of electron density changes that are happening on the carbon monoxide, subsequently the carbon monoxide stretching its frequencies.

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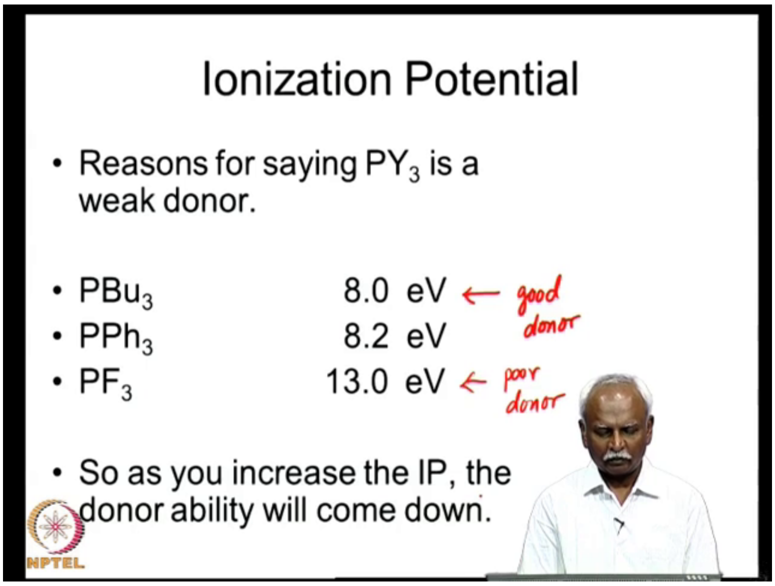

Ionization Potential

- Reasons for saying PY_3 is a weak donor.

- PBu_3 8.0 eV ← good donor
- PPh_3 8.2 eV
- PF_3 13.0 eV ← poor donor

- So as you increase the IP, the donor ability will come down.

One way in which people tried to explain these changes, is to look at the ionization potential of the phosphorous atom. The electron density that is being donated from the phosphorous is on the hybrid orbital. The lone pair on the phosphorous, if you do ionization of the phosphene the electron is coming out from the phosphorous hybrid orbital. The extent to which the phosphorous is able to donate a pair of electrons to the metal must depend on the ionization potential. If the ionization potential is low then this is a good donor. If the ionization potential is very poor, as in the case of PF 3, this would be a poor donor. As you increase the ionization potential, the donor ability of the phosphorous will come down.

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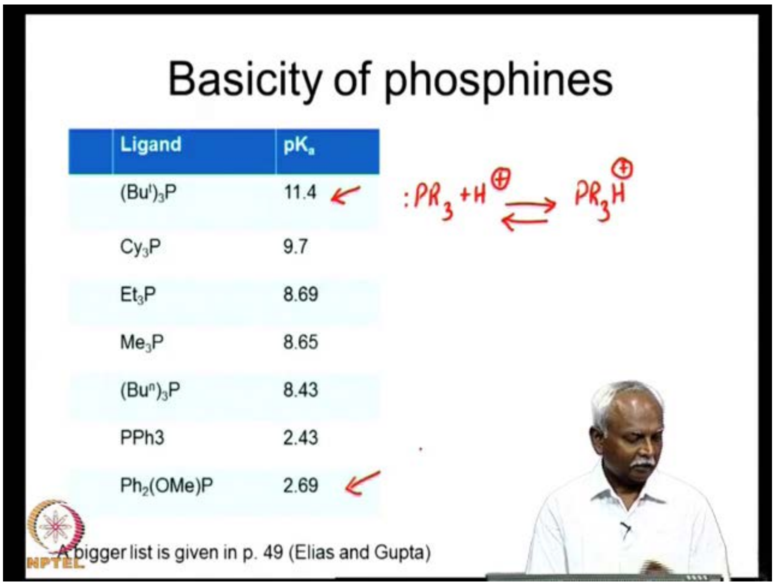

Basicity of phosphines

Ligand	pK_a
$(Bu^t)_3P$	11.4
Cy_3P	9.7
Et_3P	8.69
Me_3P	8.65
$(Bu^n)_3P$	8.43
PPh3	2.43
$Ph_2(OMe)P$	2.69

$$:PR_3 + H^{\oplus} \rightleftarrows PR_3H^{\oplus}$$

A bigger list is given in p. 49 (Elias and Gupta)

A second way to look at this is to also look at the ligand. The PKA means the easiness with which you can remove a proton from the protonated phosphene. The extent to which you can give the electron density on the phosphorous to the proton is dependent on this particular equation. This is obviously equilibrium. If you have a very high value of PKA, then that means that the proton is not easily dissociated.

That means, that this is a good donor of electron density. If you have a very small value as in the case of PPh 2 ome then this is a poor electron donor. This can also be correlated with the stretching frequencies. It was indeed possible to analyze the type of changes that you have with electron density donation. This is done from the phosphene to the metal and the frequency changes that are there in fac complexes.

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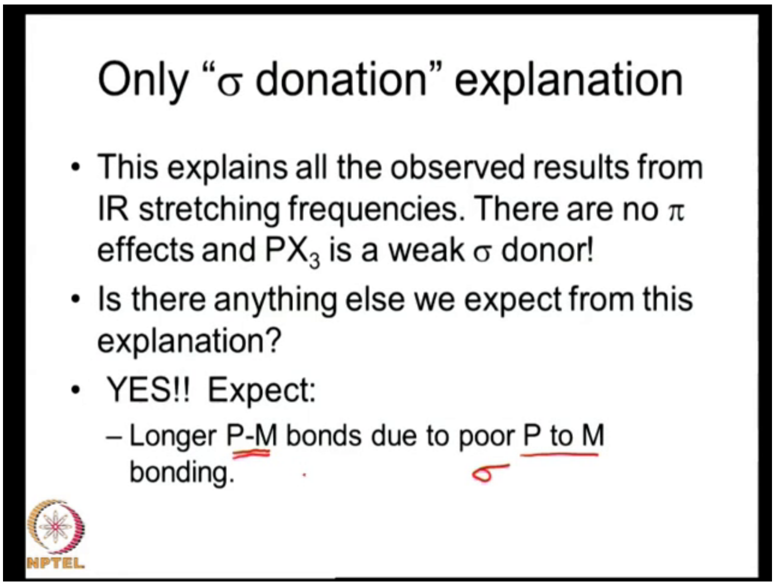

Only "σ donation" explanation

- This explains all the observed results from IR stretching frequencies. There are no π effects and PX_3 is a weak σ donor!
- Is there anything else we expect from this explanation?
- YES!! Expect:
  - Longer P-M bonds due to poor P to M bonding.

So, this explains all the observed results from the infra red stretching frequencies. One can almost confidently say that there were no pi effects in the interaction of PX 3 with the metal atom. PX 3 is a sigma donor. There is no pi interaction at all. However, it is possible for us to explain the stretching frequencies, but not the bond distances. Look at the bond distances that are there between the phosphorous and the metal.

One can see that you would one can expect longer phosphorous metal bonds due to poor phosphorous to metal bonding in the sigma manifold. If you have electron donation from the phosphorous to the metal, you have a poor sigma donor. You should have longer bonds. If you have a strong sigma donation you should expect stronger or shorter bonds. This is what you can expect.

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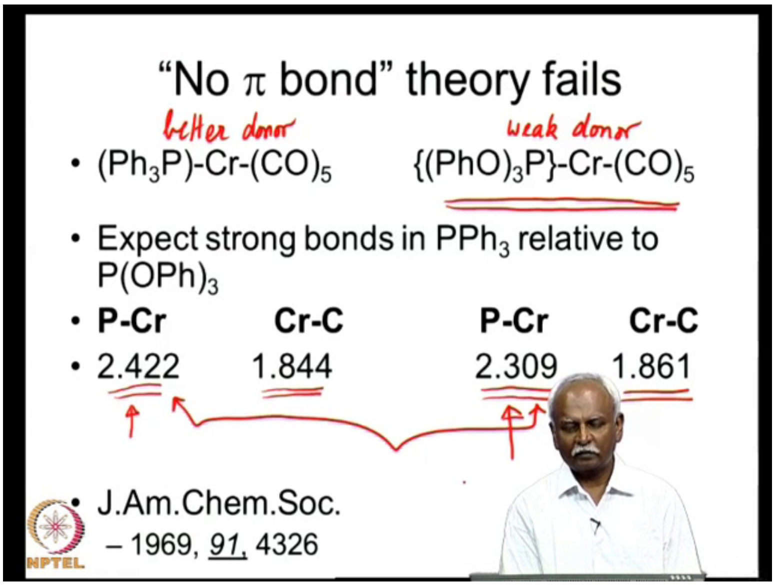

"No π bond" theory fails

better donor   weak donor

- $(Ph_3P)\text{-}Cr\text{-}(CO)_5$ $\{(PhO)_3P\}\text{-}Cr\text{-}(CO)_5$
- Expect strong bonds in PPh_3 relative to $P(OPh)_3$
- **P-Cr   Cr-C   P-Cr   Cr-C**
- 2.422   1.844   2.309   1.861
- J.Am.Chem.Soc.
  - 1969, *91*, 4326

But what is observed is something else here is where the no pi bond theory fails. Let us take two examples. One example is the case of PPs 3 with Cr CO 5. Here we have a mono substituted carbon carbon new complex. You have Cr CO 6, where only 1 phosphorous ligand has been added. You can also compare it with the triphenyl phosphite complex which is given. We can now look at the phosphorous chromium bond distances that are there in these metal complexes.

Suppose, you have a P-Cr distance of two point four two two angstroms, this is in the case of the triphenyl phospene complex. This is an instance where the POPh complex will have less electron density to donate. You would expect a longer bond distance for this particular complex where you have a weak donor. So, POPh thrice is a weak donor. This is a weak donor, this is a better. So, the better donor should have the shorter distance, but we find that this is exactly the opposite of what you would expect. You have a shorter bond distance for the triphenyl phosphite complex.

What is interesting is that you would expect for the same reasons that we have discussed. If you have good sigma donation the trans carbonyl should have the longer bond distance. This is also in the opposite direction. So, it is very clear that the no pi bond theory or the sigma bond only theory is not sufficient to explain all the data that we have in terms of crystallography. Hence, you expect something else other than the sigma bonds to explain these bonding interactions.

One of course, knows that POPs 3 if it, if because it is a better electron withdrawing groups this would form better pi bonds between the phosphorous and the chromium. If this forms better bonds between phosphorous and chromium the pi bonding is there then this is exactly what one would expect. The phosphorous chromium bonding would be short. The phosphorous chromium bonding in this case where there is poorer pi interaction would be longer. The pi bond theory is able to explain the bond distance changes in these cases. Whereas, the sigma bond only theory is not able to explain this changes.

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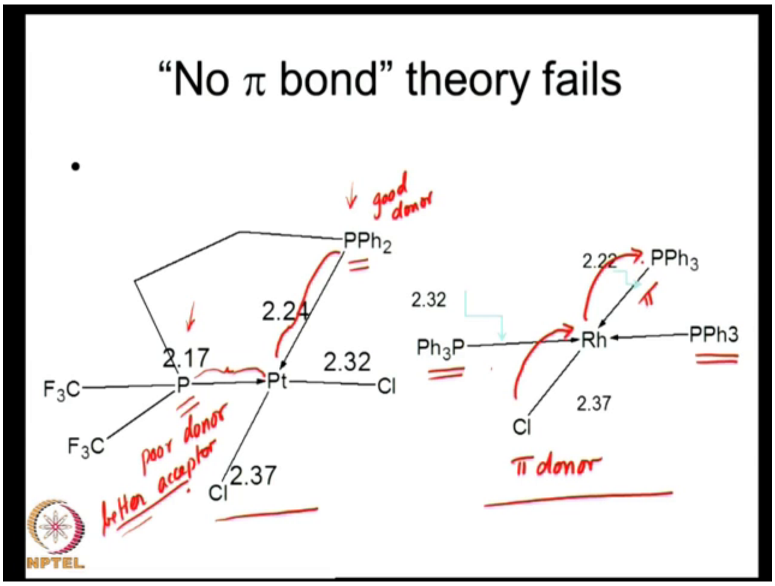

"No π bond" theory fails

I will give you one more example, where this has been conclusively shown. If I take an example where the two phosphorous metal distances are in the same complex. This is always a good way to make comparisons because there are many factors that go into a metal ligand bond distance. Here is a case where you have PPh 2 which is a good electron donor compared to P-Cf 3. Cf 3 is an electron withdrawing group. This would be a poor donor and a better acceptor.

This is a good donor relative to this phosphorous, relative to this phosphorous. One can see that this phosphorous is a better donor. If this is a better donor one would have expected based on sigma bond only theory this should have a short distance. Whereas, we find that this distance is longer. So, clearly there are some pi effects in the x plane.

This shows the need for this, in order to explain the short bond distance that is observed 2.17 for this phosphorous platinum bond. This bond distance is 2.24 Angstroms.

So, one can explain these bond distance changes using the pi effects. This is a better pi acceptor. You have multiple bonding between the phosphorous and the platinum. You have multiple bonding. So, this bond distance is reduced from what you expect. A similar explanation can be offered for these complexes when you put 2 triphenyl phosphines trans to each other. You are competing for the same d orbital electron density.

When you have a chloride trans to a triphenyl phosphine then you have a pi donor trans to the triphenyl phosphene. If there is a pi effect then the electron density can flow from the chlorine to the rhodium and from the rhodium to the triphenyl phosphene. As the pi bonding is reinforced the pi bond in the phosphorous trans to the chlorine is reinforced by electron density being donated from the chlorine to the rhodium. From the rhodium to the phosphorous this pi bond is in fact making this bond distance shorter. It is 2.22 angstroms about 0.1 Angstroms less than, what you expect for this triphenyl phosphene.

This is present in this complex. You have a same complex two complexes that are being compared in both complexes. You compare the bond distances within them we are not comparing the 2.24. Here with the 2.32 here rather we compare it within this system. Within the platinum complex you compare two phosphorous platinum distances. Within the rhodium complex, you compare this phosphorous rhodium distance with the rhodium phosphorous distance which is along this direction.

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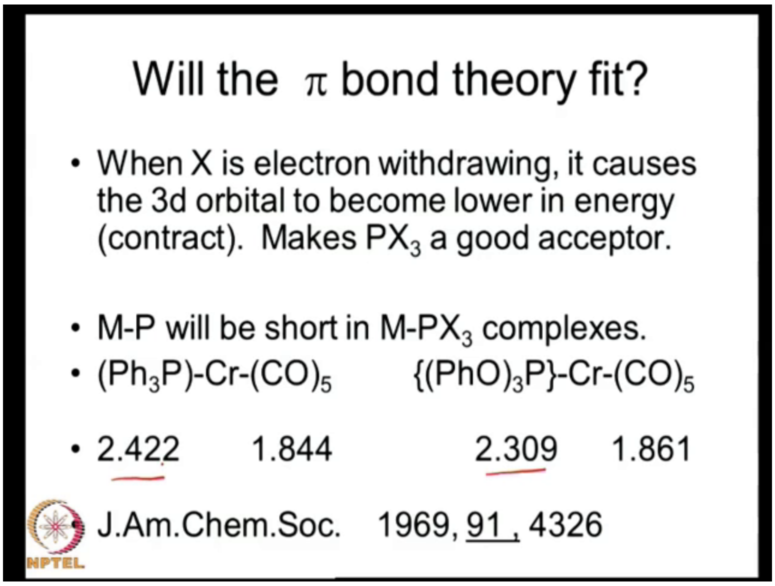

Will the π bond theory fit?

- When X is electron withdrawing, it causes the 3d orbital to become lower in energy (contract). Makes PX_3 a good acceptor.
- M-P will be short in M-PX_3 complexes.
- (Ph_3P)-Cr-$(CO)_5$ $\{(PhO)_3P\}$-Cr-$(CO)_5$
- 2.422 1.844 2.309 1.861

J.Am.Chem.Soc. 1969, 91 , 4326

The pi bond theory is able to explain why the triphenyl phosphite has got a short distance. 2.309 This is the triphenyl phosphine which has got the longer distance. That is because of the pi bond which is there between the phosphorous and chromium. This is more effective in the case of the electron withdrawing phosphite which is present here.

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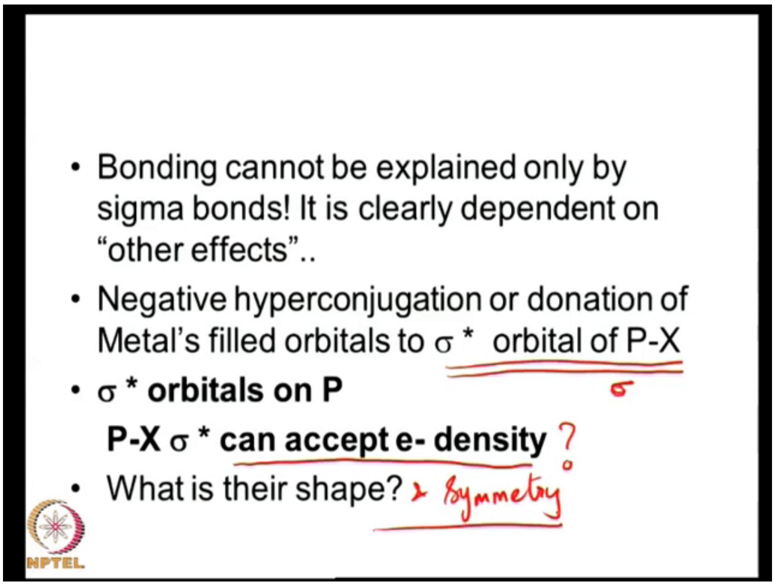

- Bonding cannot be explained only by sigma bonds! It is clearly dependent on “other effects”..
- Negative hyperconjugation or donation of Metal’s filled orbitals to σ * orbital of P-X

  σ
- **σ * orbitals on P**

  P-X σ * can accept e- density ?
- What is their shape? → Symmetry

Now, if we cannot explain the pi bonding using the d orbitals, how can we explain the pi bonding? To do this, the theory the computational chemists came up with the idea. You can have what is called negative hyper conjugation. Negative hyper conjugation or donation of metals filled d orbitals to the sigma star orbitals of the PX group. So, if you have a PX bond and the PX will have a sigma bond or a sigma orbital corresponding to the sigma bond and a sigma star orbital.

The sigma star orbital on the phosphorous is capable of accepting electron density. Then one can say that there is negative hyper conjugation from the metal to the phosphorous PX sigma star. Now, can these PX sigma star orbitals accept electron density? Can they accept electron density, and if so what is their shape and symmetry? So, depending on this shape and symmetry you can expect them to behave as good pi acceptors. This is what we are going to see in the next section.

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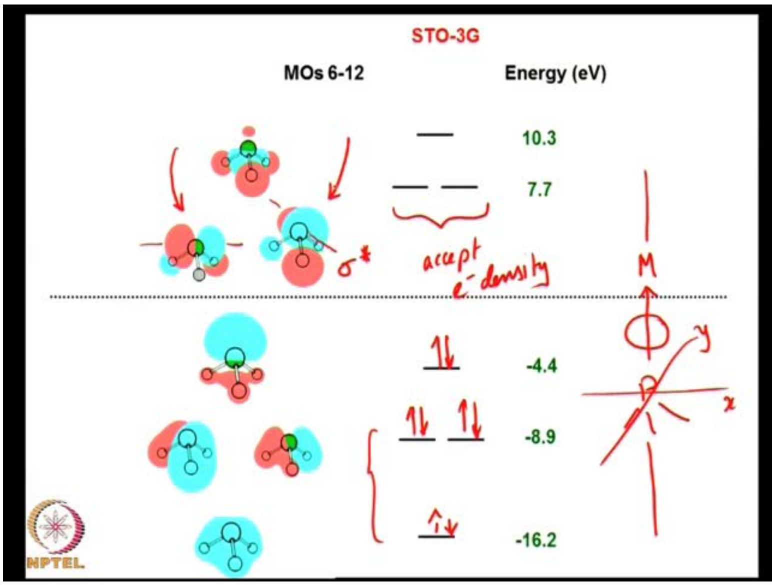

STO-3G

MOs 6-12

Energy (eV)

Here I have for you the molecular orbitals of a hypothetical phosphine which is Ph 3. Ph 3 is arranged according to the energy. Look at the 3, the 3 sigma bonds or the Ph sigma bonds. They form a set of molecular orbitals bonding molecular orbitals. All of these are filled these are filled molecular orbitals. These are filled molecular orbitals and then there we have the traditional lone pair which is sitting on the phosphorous.

This is pointed away from the three groups which are there on the phosphorous. This is if you want to talk about the metal interacting with the phosphorous. Then this would be the direction in which we are orienting the phosphorous ligand. The phosphorous has got a large lone pair which is sitting on the face opposite the 3 hydrogens. It is pointed in such a way that can be now donated to the metal atom that is your sigma bond between the phosphorous and the metal.

Now, the pi acceptor orbitals are actually coming from the sigma star orbitals which are the sigma star orbitals of the Ph bonds. The sigma star orbitals are primarily phosphorous Px and Py if this is the z axis. If this is my z axis then the Px and the Py x and y. This Px and Py orbitals are what you see here. This is my Px and this is a perpendicular Py direction. The Px and the Py orbitals are the empty orbitals.

These are empty and they can accept electron density. This is how the phosphorous atom is able to accept electron density from the metal, from the metal. Electron density flows into the sigma star orbitals of the phosphorous x bond the Px sigma star. It is capable of accepting electron density. It turns out that it has the same shape and the right symmetry to overlap with the metal orbital.

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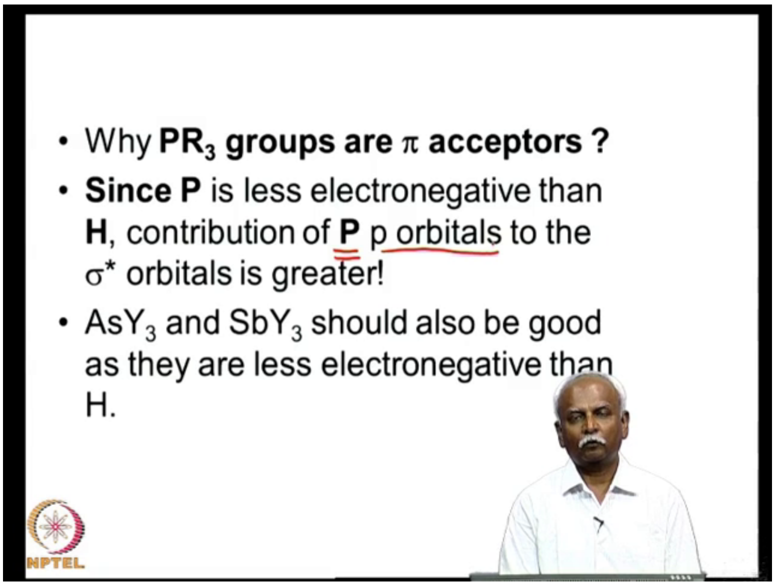

- Why **PR_3 groups are π acceptors ?**
- **Since P** is less electronegative than **H**, contribution of **P** p orbitals to the σ^* orbitals is greater!
- AsY_3 and SbY_3 should also be good as they are less electronegative than H.

So, phosphorous is a good pi acceptor not because of the empty d orbital, but because you have the sigma star orbital. That sigma star orbital has got greater contribution from the phosphorous, greater contribution from the phosphorous. It is primarily the P orbitals which are present on phosphorous. They contribute maximum to the sigma star orbital. It is able to accept electron density from the filled orbital of the metal arsenic x 3 arsenic, arsenic y 3 and antimony y 3 groups. These should also be good as they are also less electronegative than r groups. They have a good option of accepting electron density into the sigma star orbitals.

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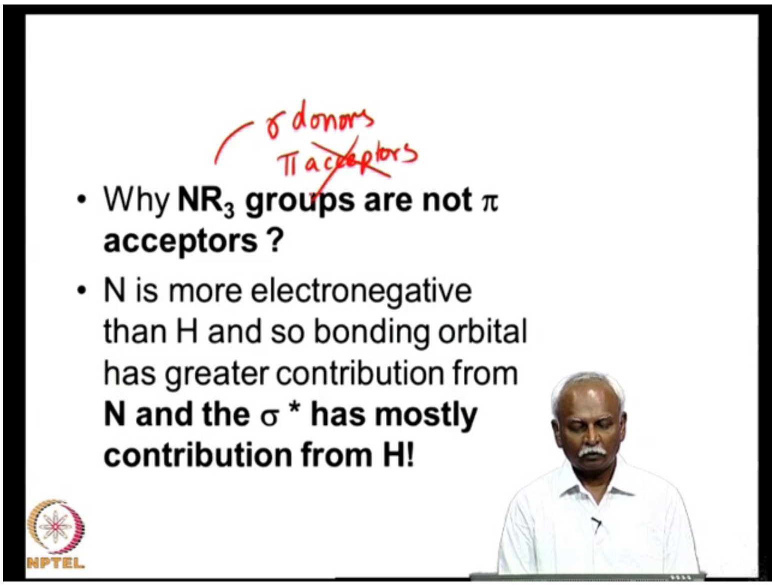

σ donors
π acceptors

- Why **NR_3 groups are not π acceptors ?**
- N is more electronegative than H and so bonding orbital has greater contribution from **N and the σ * has mostly contribution from H!**

One can also ask the question, why it is that amines or NR 3 groups are not good pi acceptors? This is surprising because in the same periodic, in the periodic table we find in the same group NR 3 is only a sigma donor. These are only sigma donors and not pi acceptors. One can in fact categorically say that these are not pi acceptors. So, why is it that they are good sigma donors and not pi acceptors nitrogen? This is in fact more electronegative than other groups. In the case of ammonia for example, it is definitely more electro nitrogen is more electronegative than hydrogen. So nitrogen has got good contribution to the bonding molecular orbital, but the sigma star has most of the contribution from hydrogen.

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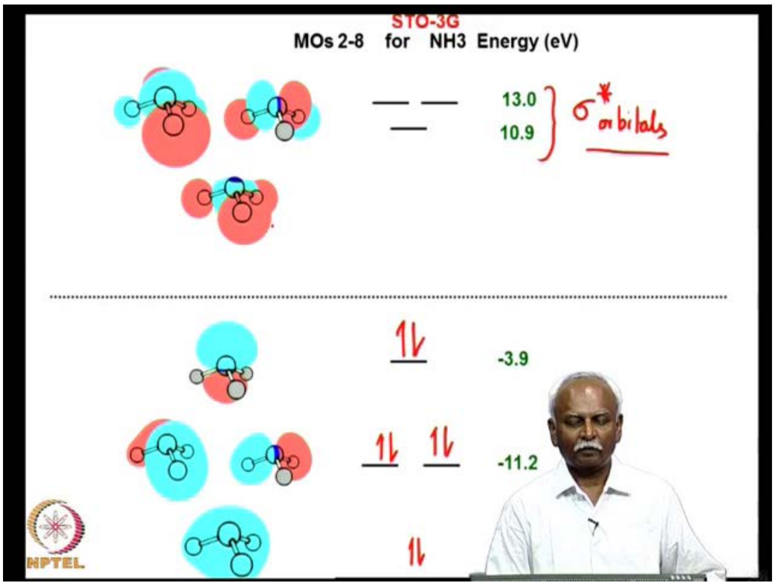
STO-3G

MOs 2-8 for NH3 Energy (eV)

I will show you the molecular orbitals of NH 3 as an example. Here you can see that the nitrogen contribution to the bonding molecular orbitals is significant. These are all filled. Now you have filled molecular orbitals here. This is the lone pair and so that again it is a good donor orbital. You can see that the sigma star orbitals where you have this 3 sigma star orbitals. These are the sigma star orbitals. You can see that the contribution of hydrogen is significantly greater compared to what you had in the case of triphenyl or trialkyl phosphines. Here phosphorous, because of it is lesser electro negativity compared to nitrogen contributes more to the sigma star orbital.

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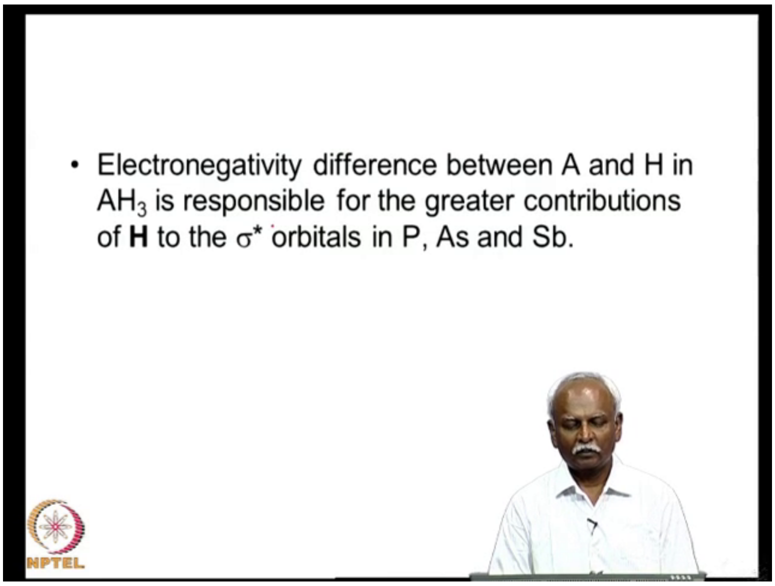
- Electronegativity difference between A and H in AH_3 is responsible for the greater contributions of **H** to the σ^* orbitals in P, As and Sb.

So, one can say that the electro negativity between A and H in 3. It is responsible for the sigma star orbital being capable of accepting electron density, if A is less electro electronegative.

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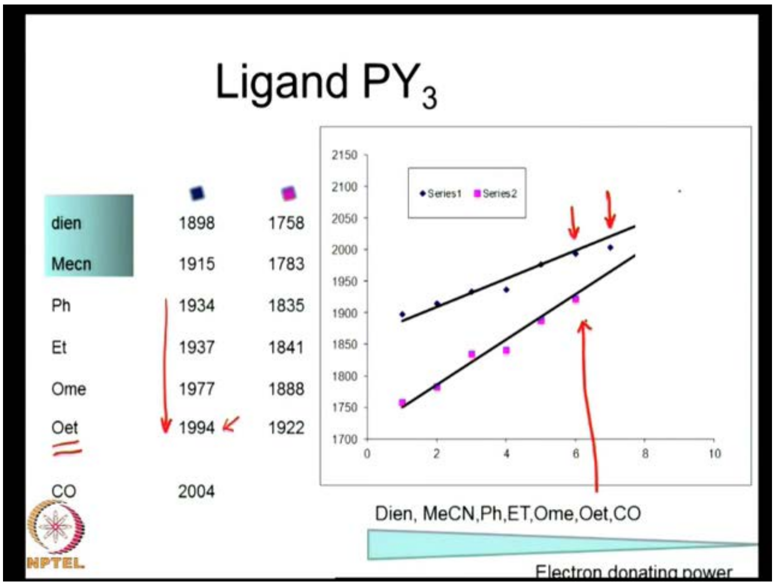

Ligand PY_3

	🟦	🟪
dien	1898	1758
Mecn	1915	1783
Ph	1934	1835
Et	1937	1841
Ome	1977	1888
Oet	1994	1922
CO	2004	

Dien, MeCN,Ph,ET,Ome,Oet,CO

Electron donating power

Then it will be a good sigma star pi accepting ligand. In the case of phosphorous arsenic and antimony their good sigma star orbitals capable of accepting electron density. Now we can go back to this figure and see if the pi donation to the sigma star orbitals is capable of explaining the carbon monoxide stretching frequencies that you have observed.

First let us take a look at what we saw earlier. If you have Oet groups, which is strongly electron withdrawing. We find that the frequency of the trans carbon monoxide is in fact higher. So the frequency is in fact increasing in this direction when, a when the group was a phenyl group. Then it was not as good a pi acceptor, but when we have Oet it is a very good pi acceptor. You find that relative to moco 6 which was listed here. The Oet has got the trans carbon monoxide stretching frequencies closest to moco 6. So, poet thrice is a very good pi accepting ligand, so poet thrice is a very good pi accepting ligand.

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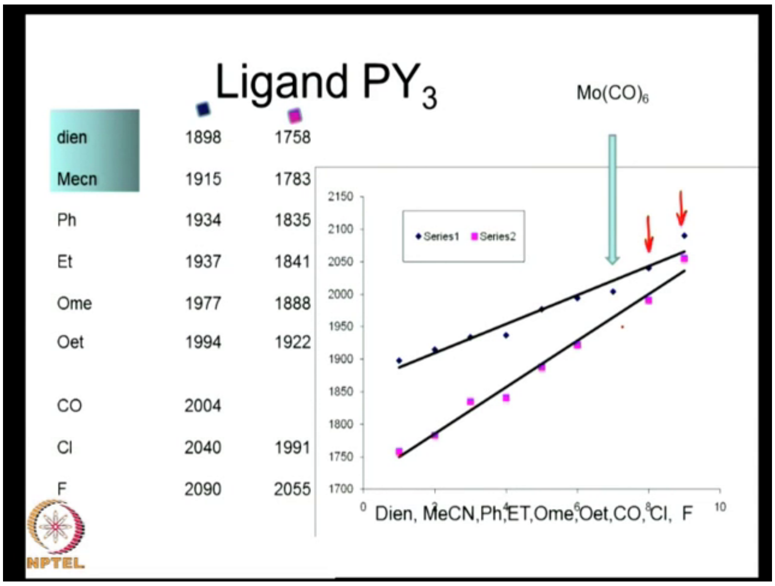

Ligand PY_3

$Mo(CO)_6$

	■	■
dien	1898	1758
Mecn	1915	1783
Ph	1934	1835
Et	1937	1841
Ome	1977	1888
Oet	1994	1922
CO	2004	
Cl	2040	1991
F	2090	2055

Let us now look forward. We see that suppose we had chlorine and phosphorous in the previous diagram. We did not have the PCl 3. The PF 3 ligands suppose we add the PCl 3 and the PF 3 ligands. We find that these complexes have got stretching frequencies which are even higher than what you expect for PR 3 groups. Here we go moco 6, had the stretching frequency 2004 centimeter minus 1. In the case of PCl 3 and PF 3 the stretching frequencies are even higher they are at 2040 and 2090 centimeter minus 1.

So, clearly you have a situation where the trans ligand is capable of attracting pi electron density as much as carbon monoxide PCl 3 and PF 3. They are able to compete with the trans carbon monoxide for pi electron density. So, the trans carbon monoxide stretching frequency has increased beyond what you have for moco 6. This explanation is again something that could not have been given by the sigma only theory.

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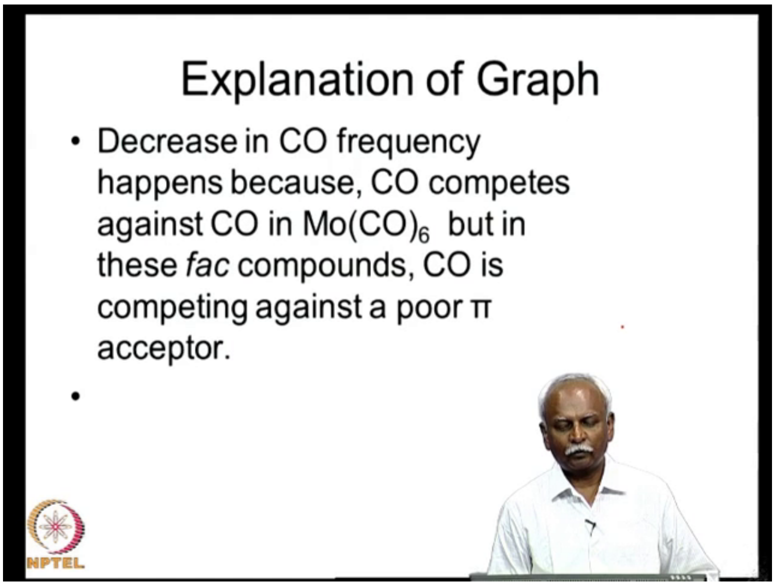

Explanation of Graph

- Decrease in CO frequency happens because, CO competes against CO in $Mo(CO)_6$ but in these *fac* compounds, CO is competing against a poor π acceptor.
-

In fac compounds carbon monoxide is competing against the poor pi acceptor. That is why it is a situation which leads to greater stability. So, fac compounds are more stable than mer isomers. It is also true that the carbon monoxide stretching frequency is changing in the way in which changes for a series of complexes based on the trans ligand.

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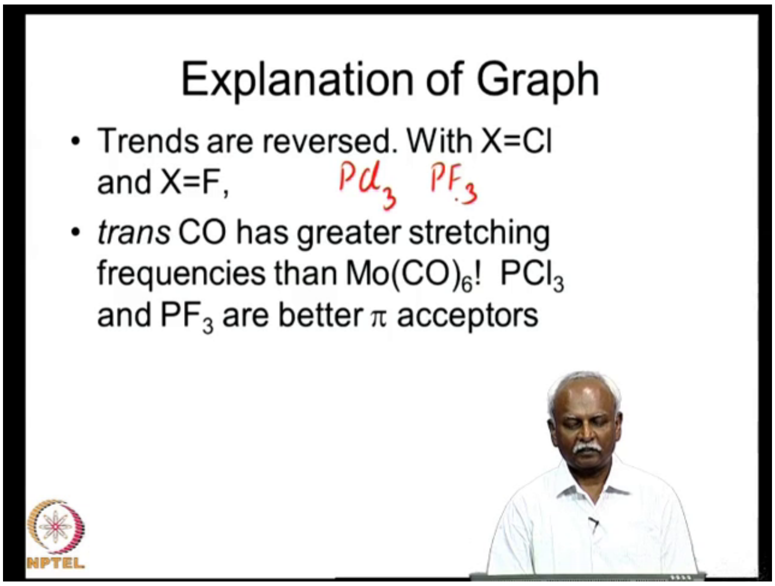

Explanation of Graph

- Trends are reversed. With X=Cl and X=F, Pcl_3 PF_3
- *trans* CO has greater stretching frequencies than $Mo(CO)_6$! PCl_3 and PF_3 are better π acceptors

The trends are reversed in the case of PCl 3 and PF 3. When you have PCl 3 and PF 3 you have a situation where the trans carbon monoxide has greater stretching frequencies than moco 6 where the trans ligand is carbon monoxide.

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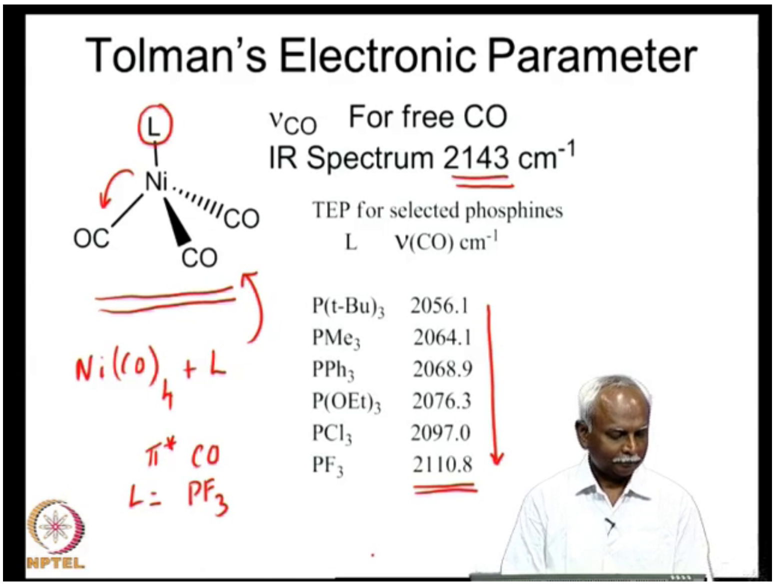

Tolman's Electronic Parameter

ν_{CO} For free CO

IR Spectrum 2143 cm^{-1}

TEP for selected phosphines

L	ν(CO) cm^{-1}
$P(t\text{-}Bu)_3$	2056.1
PMe_3	2064.1
PPh_3	2068.9
$P(OEt)_3$	2076.3
PCl_3	2097.0
PF_3	2110.8

$Ni(CO)_4 + L$

π^* CO

$L = PF_3$

Now, based on these factors Tolman in fact devised what is called Tolmans electronic parameter. Tolmans electronic parameter measures the extent to which the complex nico 3 l has two stretching frequencies for the system. This is pictured here. The reason for choosing this nickel complex is a fact that you can readily make it by reacting nico 4. You can make react nico 4 with any ligand. It will readily form nico 3 l. You can readily measure the infrared spectrum.

You can see that as you substitute a good carbon monoxide with a phosphorous ligand the stretching frequency of the trans carbon monoxides are lower than, what you expect for nico 4. But, as you substitute the trans ligand you tend to have an increase in the stretching frequency. It increases so much that in the case of PF 3, the stretching frequency is close to that of free carbon monoxide. In other words there is very little pi star electron density on the carbon monoxide.

When you substitute the ligand with l equals PF 3. There is very little electron density that flows into the carbon monoxide ligands the pi star orbital. The stretching frequency is close to what you expect for free carbon monoxide. This is the reason why you end up with a good pi acceptor in the trans position. It is always competing for the carbon monoxide electron density. So, you have poor pi acceptors in the trans positions. If you have a good pi acceptor like PF 3, then the stretching frequency of carbon monoxide is close to the free carbon monoxide stretching frequency.

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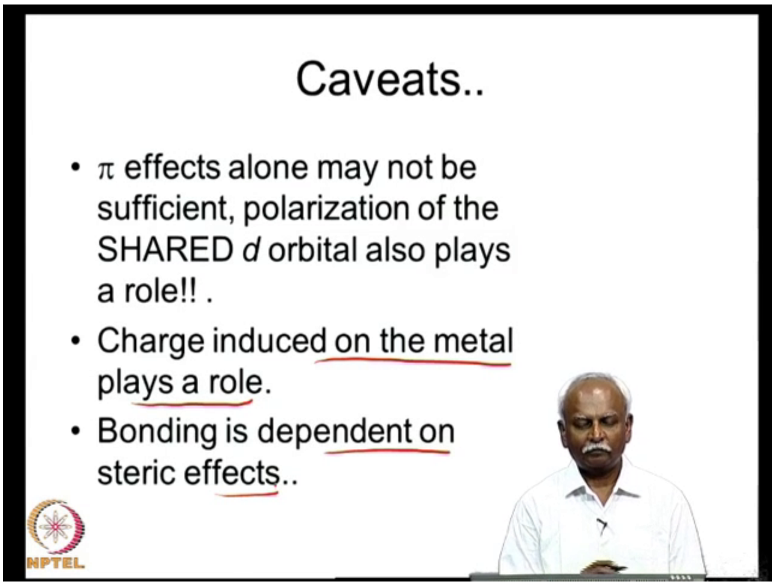

Caveats..

- π effects alone may not be sufficient, polarization of the SHARED *d* orbital also plays a role!! .
- Charge induced on the metal plays a role.
- Bonding is dependent on steric effects..

So, pi effects alone may not be sufficient to explain many of the interactions that we have described. The charge induced on the metal also plays a role. This is something which we have not discussed in this lecture, but we will discuss it in a lecture on carbon monoxide. One should also remember that bonding is dependent on steric effects. This is again a factor which we will explain in a future lecture. Now, discussed so far, what we are going to do is to look at a diagram.

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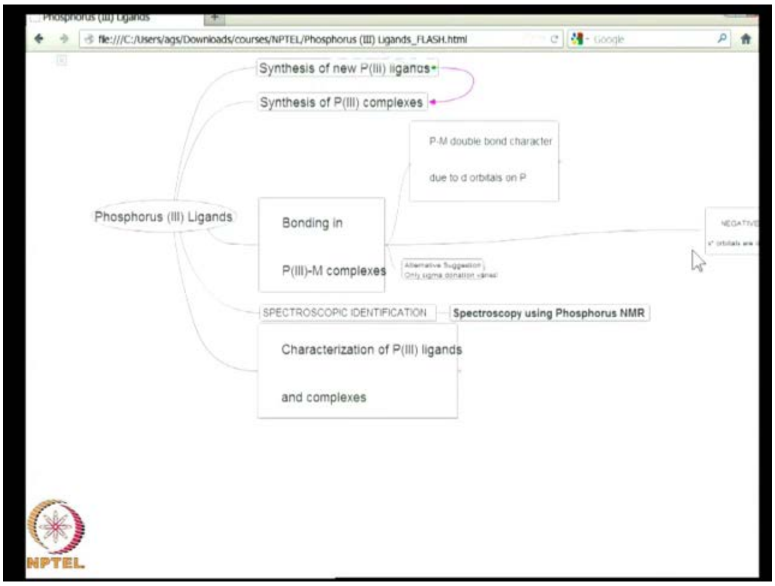

This which will tell us what we have discussed so far in a diagrammatic fashion. We first looked at phosphorous ligands. We looked at P 3 ligands and how it is easy to synthesize P 3 ligands. We can make this in a stepwise fashion. We are able to make PR 2 x, PR x 2, and PR 3. Through stepwise formation is possible. We can make ligands which are got three different ligands or three different r groups on the phosphorous. This is a very useful tool because if three R groups that are present. The phosphorous becomes a chiral species.

After we looked at synthesis of phosphorous 3 ligands we also looked at how one can make phosphorous 3 complexes. This is done by a simple substitution reaction. Having looked at these complexes we looked at some of the spectroscopic factors that are useful in these systems. One noted that the fact, one noted the fact that phosphorous 31 NMR is extremely useful. It is an empirical tool.

It is an empirical tool because phosphorous 31 signals are readily absorbed in these complexes. It is possible to use them effectively. Then we looked at phosphorous bonding to the metals. Initially people thought that there was a double bond character. This is due to the presence of d orbitals on the phosphorous. Then it was realized that it was not just the d orbitals on phosphorous.

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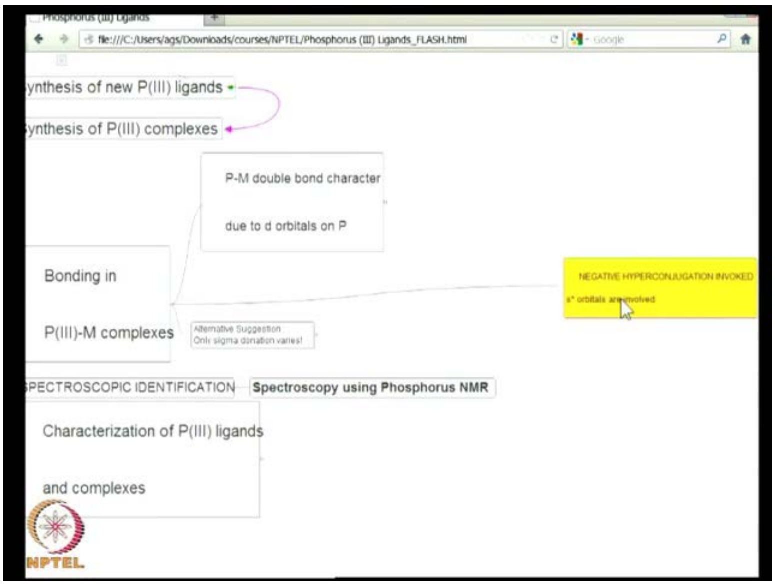

ynthesis of new P(III) ligands

ynthesis of P(III) complexes

P-M double bond character

due to d orbitals on P

Bonding in

P(III)-M complexes

NEGATIVE HYPERCONJUGATION INVOKED

σ* orbitals are involved

Alternative Suggestion
Only sigma donation varies!

PECTROSCOPIC IDENTIFICATION

Spectroscopy using Phosphorus NMR

Characterization of P(III) ligands

and complexes

It is possible to have electron donation. The electron donation to the sigma star orbitals on the phosphorous is due to negative hyper conjugation. The alternative suggestion is that electron densities flowing into the PX sigma star. It is quite sufficient to explain all the factors which we have observed in the case of metal phosphorous bonding.

Finally, we looked at characterization of phosphorous 3 ligands. We looked at the Tolmans electronic parameter. The Tolmans electronic parameter is extremely useful, extremely useful to understand the type of bonding that is there between the metal and the phosphorous ligand. In future classes, we will look at Tolmans cone angle and the buried volume concept.

These are also useful for explaining the phosphorous metal bonding. So, if you look at the range of complexes that are formed by phosphorous ligands interacting with metals, one finds that it is truly a remarkable range. One can use a variety of R groups. One can use a variety of R groups. One can use a variety of metals and a truly amazing number of molecules can be made using phosphorous chemistry. This turns out to be a very rich field which is being actively pursued even today.