Introduction to Organometallic Chemistry

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Lecture - 31
Quantifying Steric and Electronic Factors

Many of the organometallic reactions that we have looked at have some additional ligands that go along with the metal. And so when the reaction is studied, people have also found that the supporting ligand, which is present on the metal plays an important role.

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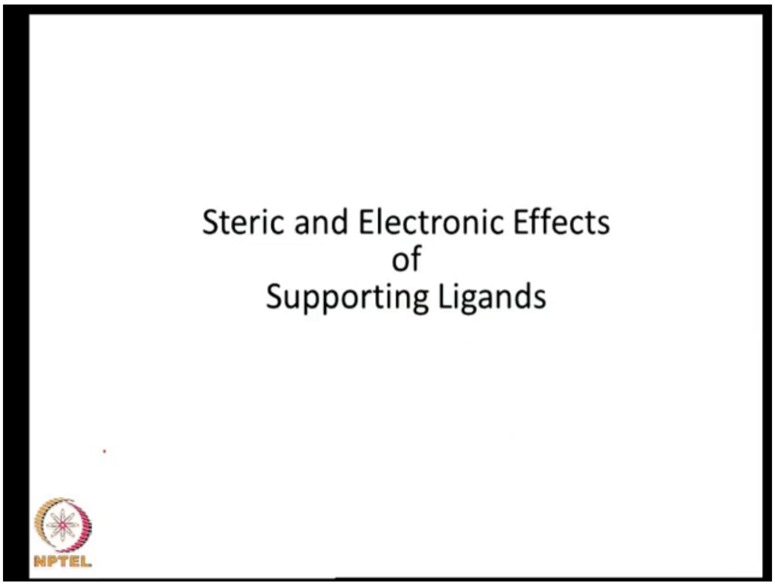

Steric and Electronic Effects
of
Supporting Ligands

One can notionally divided the effect ligand has into a steric effects and an electronic effect, though as we shall see in later slides that this division is partially artificial.

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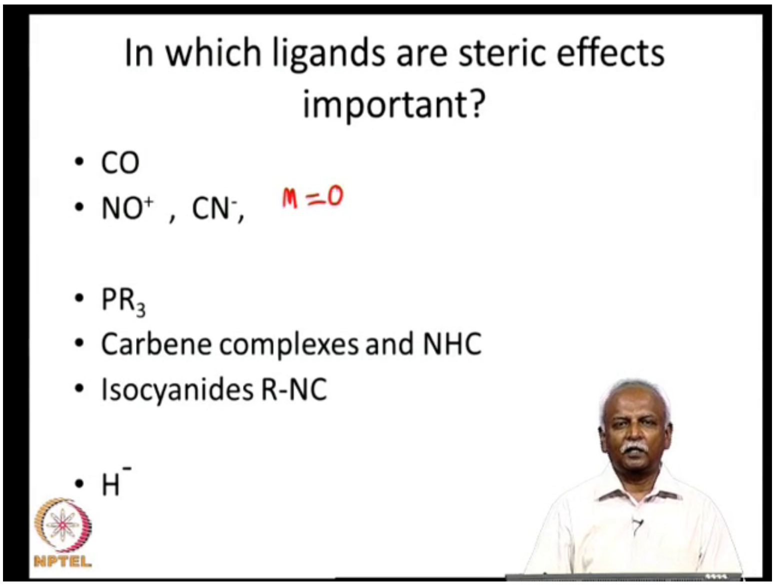

In which ligands are steric effects important?

- CO
- NO$^+$, CN$^-$, $M = O$
- PR$_3$
- Carbene complexes and NHC
- Isocyanides R-NC
- H$^-$

So, let us take a look at what ligands or which ligands would have any significant steric effects. If you recollect some other initial ligands that have looked at, have got carbon monoxide or cyanide or a nitric oxide on the metal atom. And these exert a very significant electronic effect. They are by accepting electron withdrawing and deplete the metal of electron density, but on the steric side, they do not appear to have any significant influence. So, I would group the ligands into three major categories. One is a group where you have a single atom like an oxo group and double bond O.

So, this would also belong to this particular category nitro cells, cyanide and carbon monoxide. And the next group of ligands are those like phosphine’s, carbene's, n-heterocyclicarbene’s which can exert a significant amount of steric influence through the presence of bulky R groups, which are located either in the phosphorus as in the case of phosphine’s or on the nitrogen atom as in the case of n-heterocyclic carbene's. So, the third group which really is consisting of only one ligand, which is the hydride is interesting, because it has some unique steric properties, which we shall discuss towards the end of this lecture.

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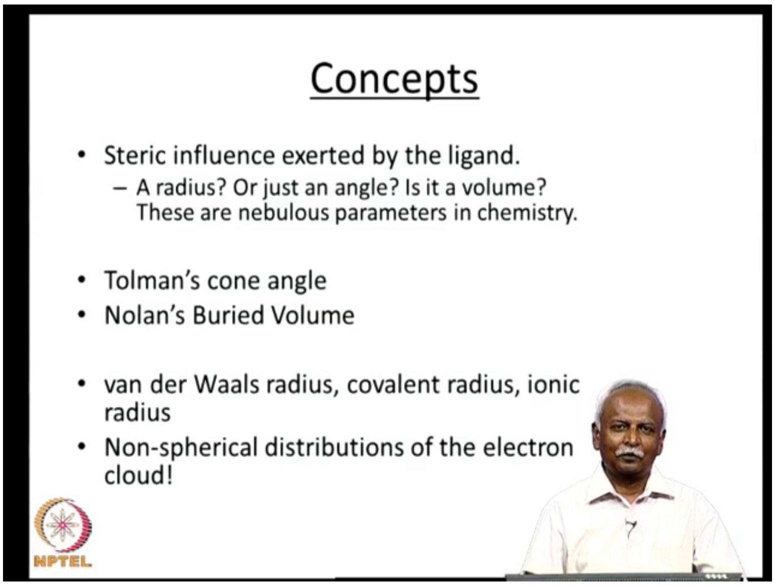

Concepts

- Steric influence exerted by the ligand.
  - A radius? Or just an angle? Is it a volume? These are nebulous parameters in chemistry.
- Tolman's cone angle
- Nolan's Buried Volume
- van der Waals radius, covalent radius, ionic radius
- Non-spherical distributions of the electron cloud!

So, now let us try and see how we can understand or quantify this stake affect. It seems to be fairly easy in many cases in inorganic chemistry week approximate annions to a sphere and get a radius for the annions. And use that as a measure of the steric influence of the anion. So, we might say pl six minus is a large annions whereas, chloride cl minus is a small annions and so on. So, can we used as radius for ligands or do we have to take a two-dimensional projection like an angle or do we have to use a three-dimensional property like a volume. These are as you can see each one of these has got some difficulties and so their nebulous parameters in chemistry.

And so introduce some amount of difficulty in this whole subject of quantification, but the initial work that was done was done with a angle-parameter so that was developed by Tolman to search called as Tolman's cone angle popularly it is referred to as Tolman's cone angle. And later on a buried volume has been estimated which is basically a three-dimensional solid cone that has been a used to model the ligand. Now, one should not think that this particular difficulty is unique to organometallic chemistry in fact this is a problem in inorganic chemistry. In general, even if you take a van de Waals radius which apparently is a simple concept should be easy to obtain for most of the elements.

It is in fact not available for many elements. The covalent radiation ionic radius have all got some problems associated with the type of measurements that we do in order to obtain them. Very often there are non-spherical distributions of the electron cloud and in the presence of a second annions or a second atom in the presence in with the close vicinity of a ion by change the shape and assume a very different distribution of the electron density around it. So, these are problems which are associated in general chemistry which make it both exciting and challenging and also complex.

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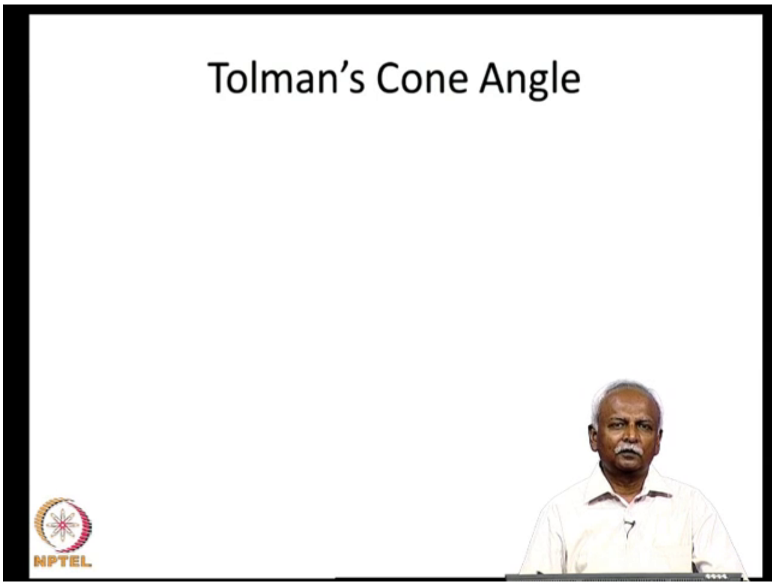

Tolman's Cone Angle

So, let us take a look at Tolman's cone angle and this is primarily developed the phoshines.

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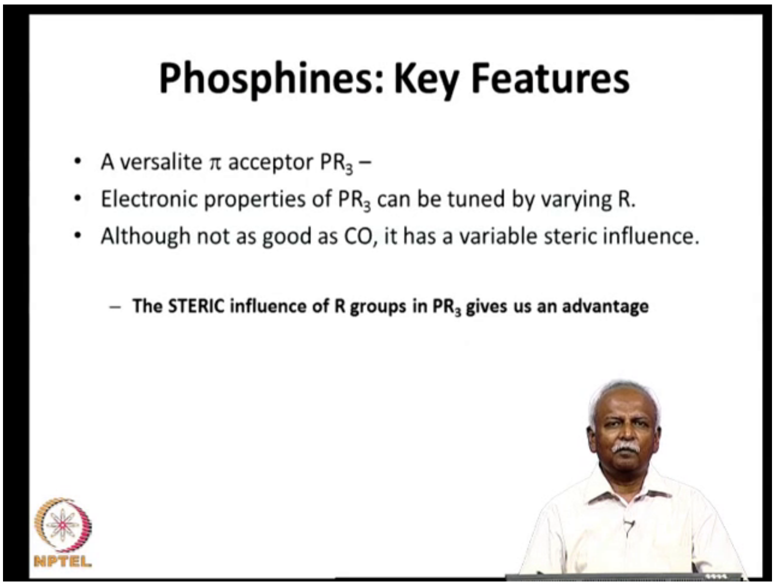

Phosphines: Key Features

- A versalite π acceptor PR_3 –
- Electronic properties of PR_3 can be tuned by varying R.
- Although not as good as CO, it has a variable steric influence.
  - **The STERIC influence of R groups in PR_3 gives us an advantage**

So, we noted in the initial lectures when we talked about tri-rail or tri alkyl phosphine is that this steric property of the phosphine and its electronic property can be buried because of the presence of different R groups on the phosphorus. Although, it is not as good as carbon monoxide the variability of the steric parameter gives it a significant advantage in chemistry. So, the scenic influence is something that we need to quantify if you have to use it with some predictive power.

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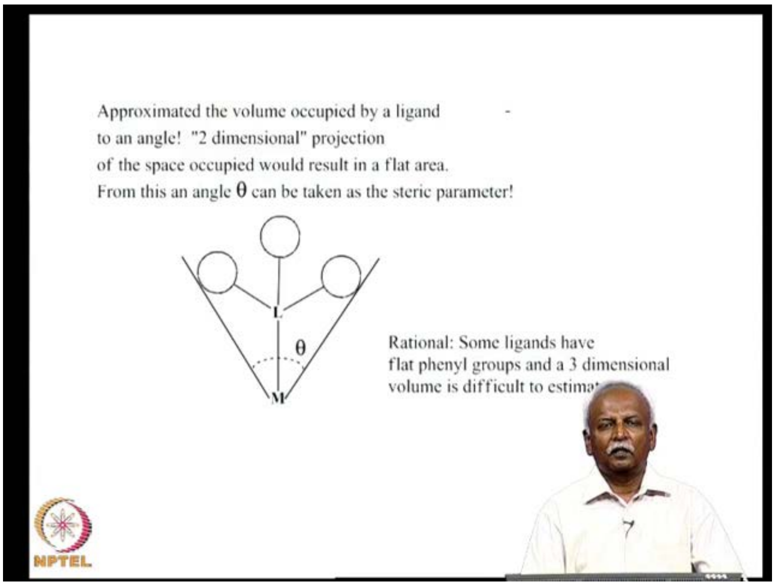

Approximated the volume occupied by a ligand
to an angle! "2 dimensional" projection
of the space occupied would result in a flat area.
From this an angle θ can be taken as the steric parameter!

Rational: Some ligands have
flat phenyl groups and a 3 dimensional
volume is difficult to estima

So, Tolman initially approximated it to this two-dimensional cone angle and the way he did it was as follows. He projected the ligand onto a flat surface and looked at the angle that would be substandard at the metal atom. So, this angle theta at the metal atom is a measure of the steric influence of the ligand. And this is very clear that you can in fact take the outermost points of the ligand and draw a line to the metal and measure this angle using a simple protractor. In fact he did it in a very simple way, he took made molecular models and measured it using a protractor.

Now, what is the rational behind this type of approximation. In fact it is difficult to estimate a in a very good fashion the volume that is occupied by a ligand. And that is because some of the ligands are flat like a try at a phosphine has got three phenyl groups of three hundred and aerial groups which are reasonably flat. And so the way you orient it could mean a big could change the volume that it is occupying. So, an approximation would be too projected on a surface using the best orientation that it would like to have.

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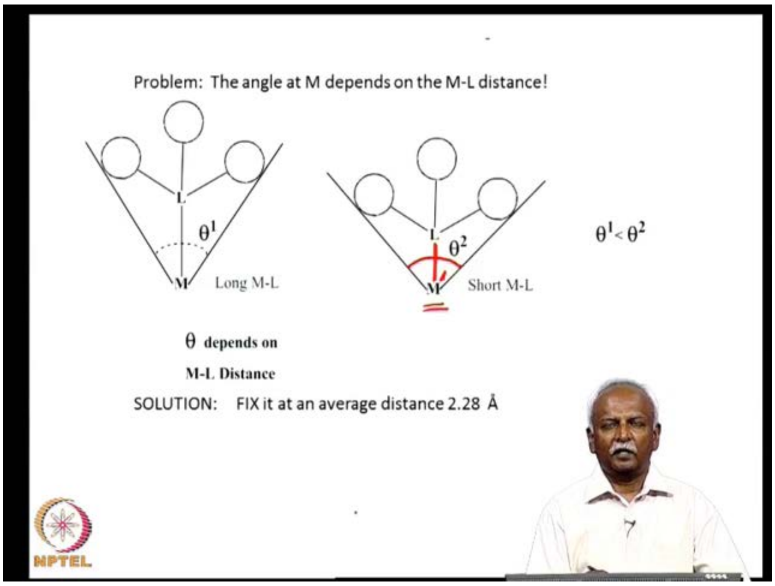

Problem: The angle at M depends on the M-L distance!

$\theta^1 < \theta^2$

θ depends on M-L Distance

SOLUTION: FIX it at an average distance 2.28 Å

So, the second difficulty that Tolman encountered was a following the angle that the subtended by the ligand at the metal can change. And how can I change, imagine the same ligand approaching the metal to in a close of fashion. If M and M dash, the two different metals and the one metal is a better bipolar than the phosphine might approach the metal atom to greater degree. When it comes closer this distance is shorter and this angle theta two becomes greater. So, this variability makes a big difference to the quadrangle theta cone angle is dependent on the metal and that is because it is dependent on the metal ligand distance.

So, this geometric dependence is quite obvious and it is easy to see and Tolman decided that this simple solution was to fix the distance for measuring the Tolman's cone angle he would fix the distance at 2.28 A. So, this was when he made a model he would keep it at a distance of 2.28 A or the of the appropriate distance and then he would measure the angle that the subtended at the metal atom.

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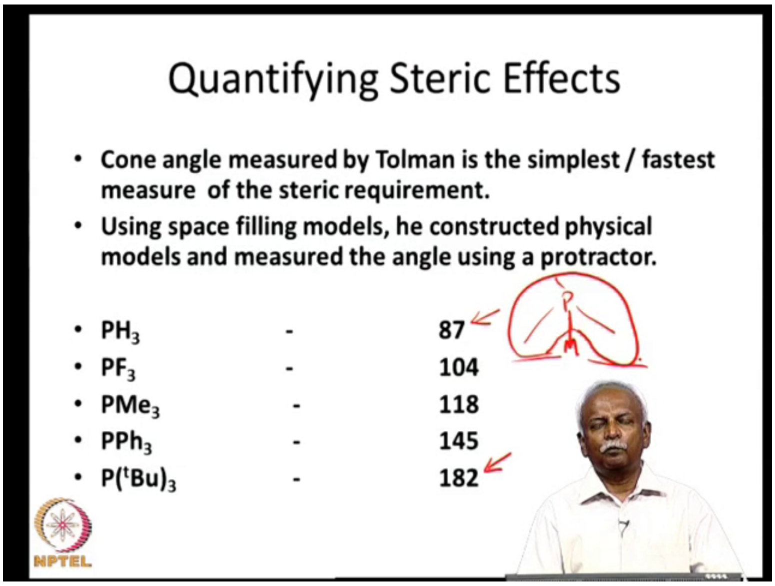

Quantifying Steric Effects

- Cone angle measured by Tolman is the simplest / fastest measure of the steric requirement.
- Using space filling models, he constructed physical models and measured the angle using a protractor.

- PH_3 - 87
- PF_3 - 104
- PMe_3 - 118
- PPh_3 - 145
- $P(^tBu)_3$ - 182

So, using this type of a model he measured various cone angles and these are listed here for you to see. It is obvious that the hydrogen if you have pph 3 pps 3 that is the ph 3 which has three hydrogen on the phosphorus will have the smallest cone angle and that is the least in this list. And you can see that as you increase the bulk of the R group the angle that you subtend at the metal becomes larger and larger. So, the largest in fact is an angle of 182 degrees. That is a angle measured from the tourists distribute any phosphine towards the main 182 degree.

It really means that on one side of the metal, if you have the phosphorus atom, one side of the metal is completely blocked by this large ligand that is present. So, even though the phosphorus is having three ligands which are apparently pointed away from the metal. The area that is the area that is occupied by this ligand when it is projected on the flat surface would indicate that about 182 degrees would be the cone angle of this particular ligand. So, this is in fact an interesting observation and you can see that many times it would be impossible to put more than two ligands around the metal.

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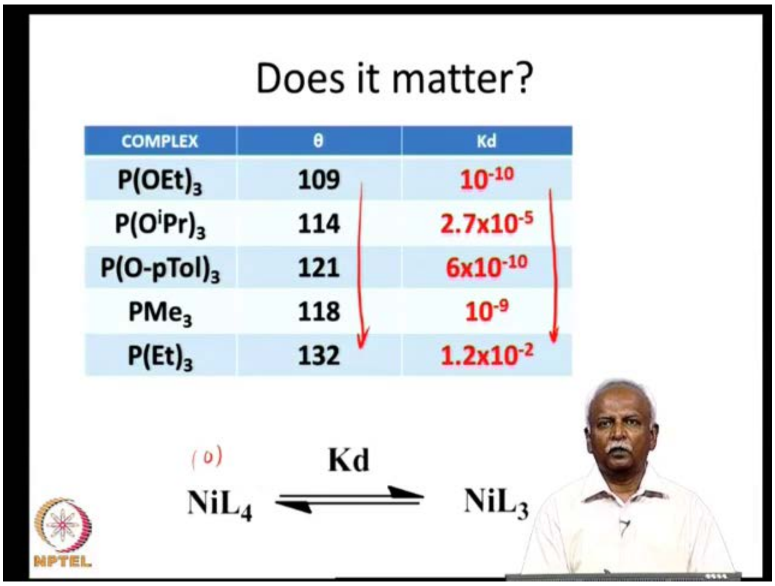

Does it matter?

COMPLEX	θ	Kd
$P(OEt)_3$	109	10^{-10}
$P(O^iPr)_3$	114	2.7×10^{-5}
$P(O\text{-}pTol)_3$	121	6×10^{-10}
PMe_3	118	10^{-9}
$P(Et)_3$	132	1.2×10^{-2}

(0)

$$NiL_4 \overset{Kd}{\rightleftharpoons} NiL_3$$

So, how does it matter, it is exactly the dissociation constants of the metal complexes that one is talking about here is a system where you have a series of four ligands connected to a nickel atom nickel zero. So, nickel would like to have four ligands in order to have an eighteen electron configuration, but because of the large cone angles that are present at the phosphorus it is not possible to pack four of them.

So, as you increase the size of the ligand one tends to dissociate one of the ligands easily. So, you end up dissociating one hell and this is shown here in this slide are dissociation constant is not. And so this increases as you increase the size the dissociation constant keeps increasing in this direction so as a bulk increases the dissociation constant also increases.

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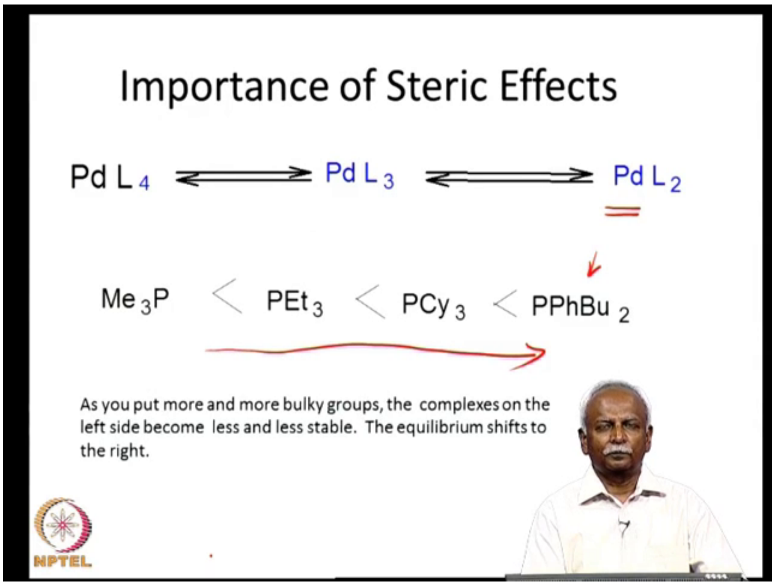
Importance of Steric Effects

$PdL_4 \rightleftharpoons PdL_3 \rightleftharpoons PdL_2$

$Me_3P < PEt_3 < PCy_3 < PPhBu_2$

As you put more and more bulky groups, the complexes on the left side become less and less stable. The equilibrium shifts to the right.

So, let us take a look at a larger metal does it make a difference. Surprisingly, in the case of nickel we noted that at the dissociation constant increases. In the case of palladium wears the metal is much larger the effect is still retained. So, in other words as you increase the size of the ligand which is attached to the metal atom you tend to form more and more of the dissociated complexes.

And in fact for this ligand the metal complex that is present in solution is a Pd L 2 system. So, although they are equilibrium the amount of the dissociated complex transferred to be more and more as you increase the size of the ligand. So, it makes a difference in chemistry if you want to do chemistry with the Pd L 2 complex then you would like to have more of the large ligands in solution.

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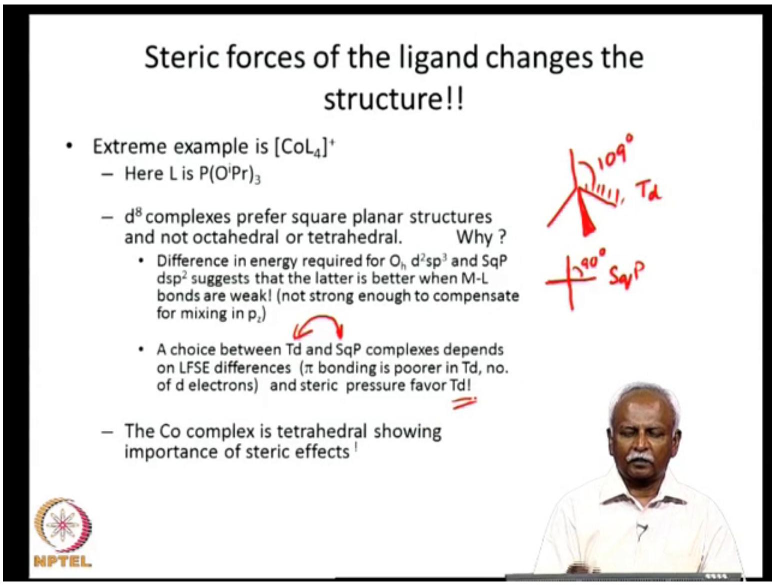

Steric forces of the ligand changes the structure!!

- Extreme example is $[CoL_4]^+$
  - Here L is $P(O^iPr)_3$
  - d^8 complexes prefer square planar structures and not octahedral or tetrahedral. Why ?
    - Difference in energy required for O_h d^2sp^3 and SqP dsp^2 suggests that the latter is better when M-L bonds are weak! (not strong enough to compensate for mixing in p_z)
    - A choice between Td and SqP complexes depends on LFSE differences (π bonding is poorer in Td, no. of d electrons) and steric pressure favor Td!
  - The Co complex is tetrahedral showing importance of steric effects !

So, any and that this turns out to be very crucial or very critical in the case of this cobalt complex which is an extreme example. Where you have four isopropoxy groups, four ligands where phosphorus has three isopropoxy groups around it. And the bulk of this isopropoxy group is so much that the cobalt would like to have which would like to have a square planar geometry tends to be tetrahedral in this case. So, why is it so first solid-state look at the d 8 complex which is cobalt want is a d 8 system and why does it prefer to have a square planar geometry and not an optimal complex.

And that refers to the difficulty of hybridizing the central metal atom to have d2sp3. If you want to have a nocturnal geometry you would have to makes 2 D's and 3 D's orbitals. And one so, but and that will give you the opportunity complex is if you only want to ligands you can manage with dsp2 to that release is one of the p orbitals from being involved in bonding and when you involve a high-energy p opportunity in these cases it is usually 3 d 4 s and 4 p which are talking about.

So, if you leave out one p orbital then you do not have to include the energy that is required for utilizing that high-energy orbital in bond formation. So, it is better for the molecule to remain in square planar geometry rather than assume this octahedral geometry. So, that is the reason why you would like to have a many d 8 complexes preferring square planar geometry rather than octahedral. Now, in this particular case the major difference that we are talking about is really not octahedral versus tetrahedral per square planar, but it is tetrahedral versus square planar. It is this difference that is very striking we know that the complex would like to have protected square planar geometry.

In this case it assumes the tetrahedral geometry because they are angle between the ligands when you have a tetrahedral geometry is 109 degree whereas, if you have a square planar geometry it would be 90 degree. So, this difference in the square planner geometry it is this the square planner geometry angle is 90 degree with a tetrahedral geometry is 109 degrees. And this larger angle is preferred by this cobalt ((Refer Slide time:16:24)) phosphine complex. And that is because of the large size of the ligand it would rather have a tetrahedral geometry with poor five bonding rather than a square planar geometry.

It is well-known that this scrap planar geometry has got very good pi interactions, where is the tetrahedral geometry has got weaker pi interactions. So, if you have a ligand like cyanide which would not require a larger area that it needs to occupy, then it would rather go for a square planar geometry. And in fact the large size of the ligand is what is forcing the complex to have the tetrahedral geometry in this case.

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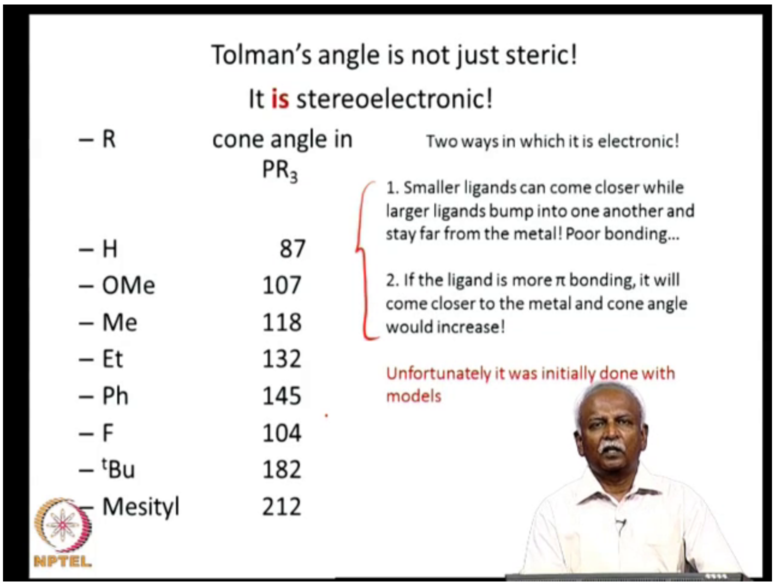

Tolman's angle is not just steric!

It **is** stereoelectronic!

– R	cone angle in PR_3
– H	87
– OMe	107
– Me	118
– Et	132
– Ph	145
– F	104
– ^{t}Bu	182
– Mesityl	212

Two ways in which it is electronic!

1. Smaller ligands can come closer while larger ligands bump into one another and stay far from the metal! Poor bonding...

2. If the ligand is more π bonding, it will come closer to the metal and cone angle would increase!

Unfortunately it was initially done with models

So, Tolman's cone angle is something that is very important, but very often it is important for us to realize that it has a stereo electronic influence. And there are two ways in which, we can call it a habit is something that has a subtle electronic influence first of all if you have four small ligands around the metal then, they can approach the metal much closer.

So, the metal ligand bond distance would be much better if you have smaller ligands. So, the cone angle at the same time this also has another effect with name that is the fact that the cone angle would automatically increase. So, if you have a small ligands then you can have a larger cone angle surprisingly, because the ligand approaches the metal to a greater degree.

So, and this is something which is quite obvious if you know the chemistry behind the ligands in know that there is pi bonding, you know that there is going to be a difference, but because of the complexity of the situation, one has to approximate to a fixed distance. And so the distance between the metal and ligand is always fixed at 2.28 angstrom and a cone angle measured using a protractor. So, unfortunately this is done with models to start with, but soon many crystallographic many crystal structures were available.

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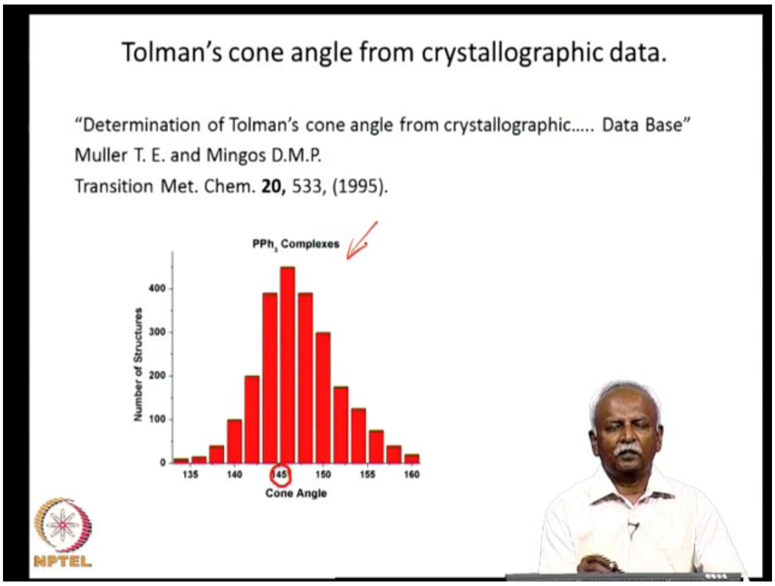

Tolman's cone angle from crystallographic data.

"Determination of Tolman's cone angle from crystallographic..... Data Base"
Muller T. E. and Mingos D.M.P.
Transition Met. Chem. **20,** 533, (1995).

And it was possible to derive the angle from crystallographic data. And are a very important and comprehensive paper Mingos showed that the distribution of various phosphorus ligands, around the metal atom can be studied using crystallography. You can derive the cone angle using crystallographic and when you plotted the complexes, the cone angle of the complexes and as a histogram he found that there were distribution of the cone angles. And the mean was approximately at the same place at in this particular instance it is close to 145 degree, which is what is assigned as a cone angle for triphinyle phosphine.

So, it is exactly what one would have a estimated using a simple protractor is as a simple model and what you get from crystallography is approximately is same. So, this tells you that the methodology used by the Tolman was more or less correct. And this gives you more accurate way of determining the cone angle, but this also brought to light the fact that that can be complications.

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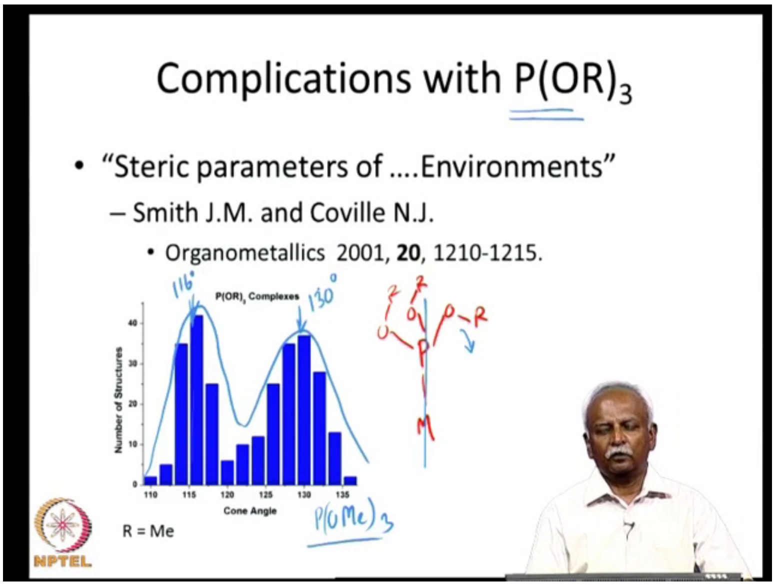

Complications with P(OR)$_3$

- "Steric parameters of ….Environments"
  - – Smith J.M. and Coville N.J.
    - Organometallics 2001, **20**, 1210-1215.

R = Me

The complications came in the Coville, studied the cone angles of for tri-alkyl phosphide. In this particular instance you have some variability in the R groups and the way in which the R groups are oriented. So, if you have two R groups which are oriented towards the metal ligand axis if this is the metal ligand axis and axis and market with a different color. So, that it is obvious so this is a metal ligand axis and paste the R groups are pointed towards the metal ligand axis then the angle would be smaller if the R groups are pointing away from the metal ligand axis then the angle would be larger. So, what he found was that if you use a ligand like POMe 3 this is particularly for the Me 3.

So, when you measure for POMe 3 you find that the two distributions which are quite obvious in this particular figure. So, in other words, you will end up with two cone angles for these ligands. One which is approximately 116 degree and other which is approximately 130 degree. So, this depends on the environment in which the ligand is present. And so it is possible to have two different angles for a single ligand. So, this is not possible when you have a measurement done using models you would assume the models you would assume a most favorable geometry or the maximum possible angle that the ligand can occupy.

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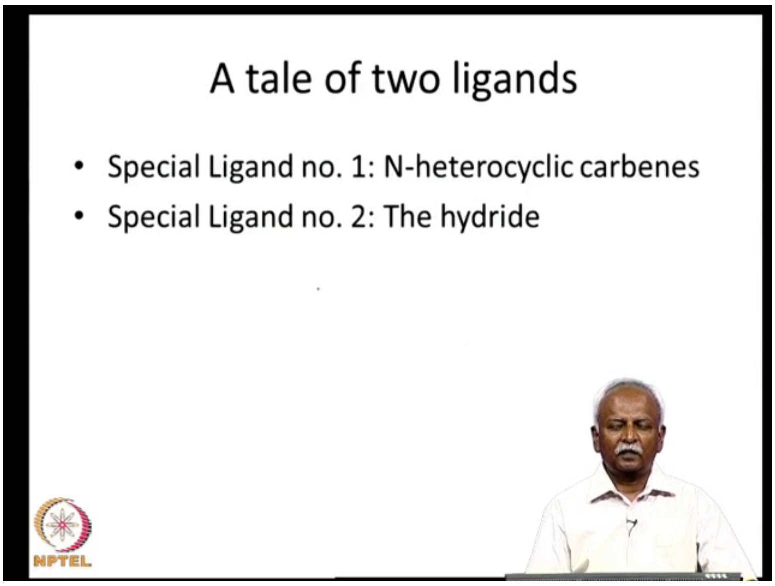

A tale of two ligands

- Special Ligand no. 1: N-heterocyclic carbenes
- Special Ligand no. 2: The hydride

Now, I want to move on to another topic and that is the utilization of not cone angles, but what was introduced by the Nolan as a very volume concept and this came about because they were studying about n- heterocyclic carbenes.

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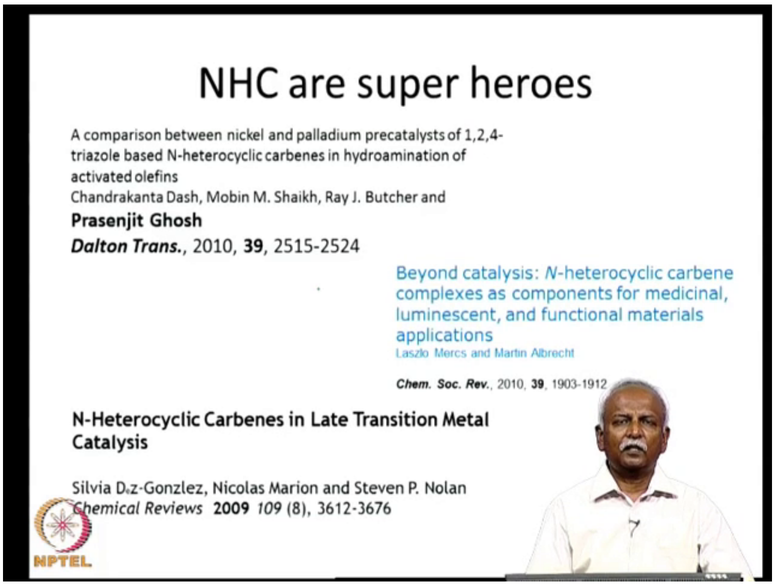

NHC are super heroes

A comparison between nickel and palladium precatalysts of 1,2,4-triazole based N-heterocyclic carbenes in hydroamination of activated olefins
Chandrakanta Dash, Mobin M. Shaikh, Ray J. Butcher and
Prasenjit Ghosh
Dalton Trans., 2010, **39**, 2515-2524

Beyond catalysis: *N*-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications
Laszlo Mercs and Martin Albrecht

Chem. Soc. Rev., 2010, **39**, 1903-1912

N-Heterocyclic Carbenes in Late Transition Metal Catalysis

Silvia D.z-Gonzlez, Nicolas Marion and Steven P. Nolan
Chemical Reviews **2009** *109* (8), 3612-3676

N-heterocyclic carbenes have become extremely popular because of the various reactions which they catalyze and the unique electronic properties that they have.

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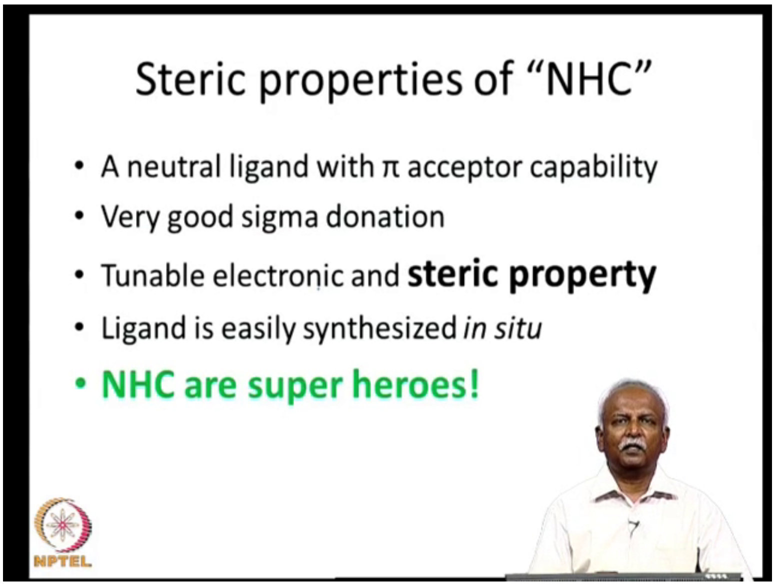

Steric properties of "NHC"

- A neutral ligand with π acceptor capability
- Very good sigma donation
- Tunable electronic and **steric property**
- Ligand is easily synthesized *in situ*
- **NHC are super heroes!**

So, the steric properties of n-heterocyclic carbenes have also captured the attention of people because the R group on the nitrogen makes a big difference on the reaction. So, in one short n-heterocyclic carbenes are having a significant electronic effect and steric effect. And NHC are called superheroes in the ligand field.

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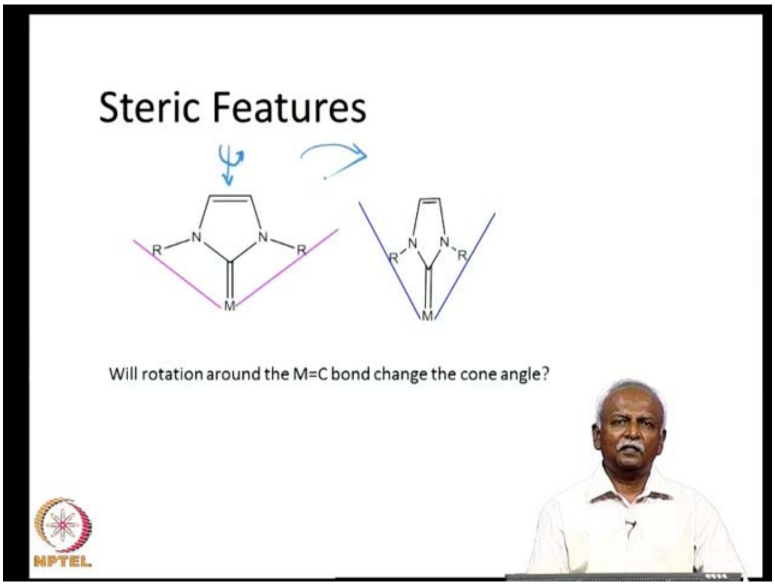
Steric Features

Will rotation around the M=C bond change the cone angle?

Now, let us take a look at the most popular n-heterocyclic carbenes. As pictured here is a imidazole based n-heterocyclic are being you can see that much of the ligand is reasonably flat. And if one rotates the ligand around this axis if one were rotates around this axis one would end up with a confirmation, which is indicated on my right side of the screen. So, it is obvious that is the angle Tolman's cone angle that you would obtain for this ligand would depend very much on how you will orient the ligand with respect to this axis.

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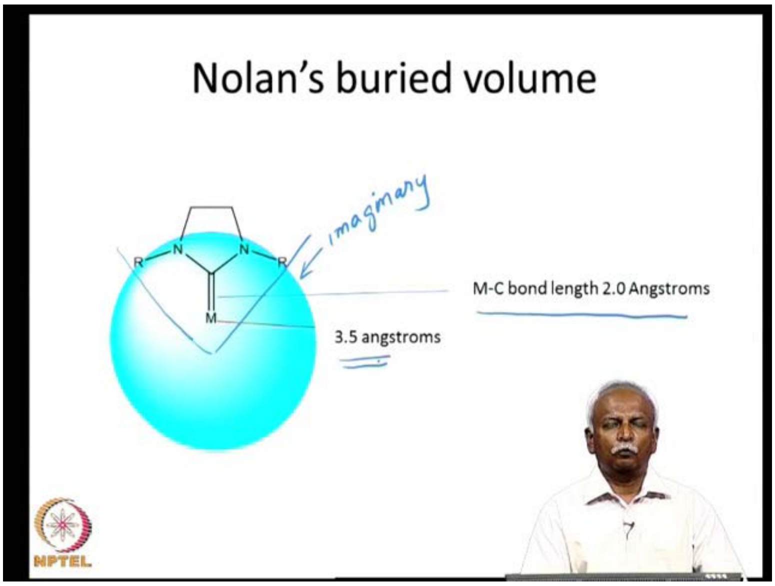
Nolan's buried volume

M-C bond length 2.0 Angstroms

3.5 angstroms

So, this does not make a lot of sense. And so Steve Nolan who was working on many n heterocyclic carbenes device to his very volume concept. What he did was to extend the Tolman's cone angle by assuming that you have a fixed metal carbon bond lengths and at this about 2 Angstroms. If fixed this bond length is 2 Angstroms. And he took a sphere which is 3.5 Angstroms. So, here is a sphere imaginary sphere this is an imaginary is sphere imaginary sphere around the metal atom. And on this imaginary sphere you position at carbene and you measure the volume that is occupied by this carbene

So, this is the volume that is occupied by the carbene. And that volume is actually a solid cone. And this volume you can estimate the percentage of the volume occupied by this ligand vis-a-vis. The total volume of this 3.5 angstroms cube sphere that is available around the metal so this percentage could be used as a measure of the of the size of the ligand.

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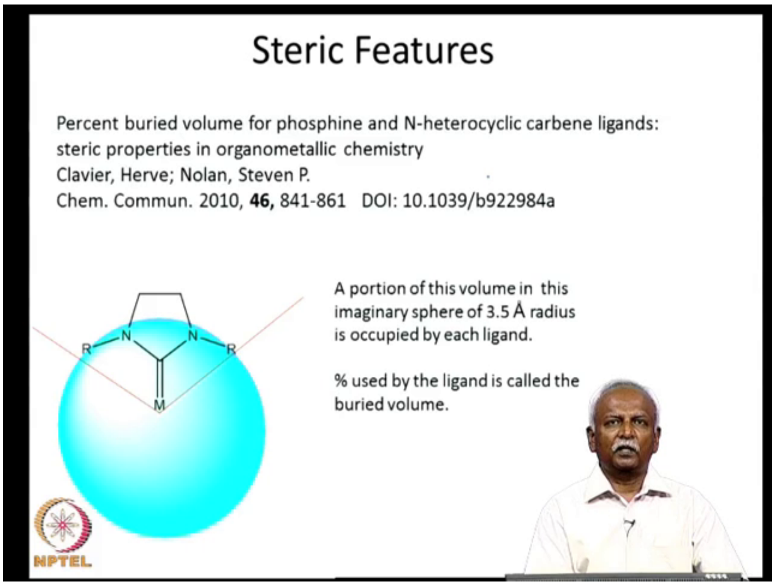

Steric Features

Percent buried volume for phosphine and N-heterocyclic carbene ligands: steric properties in organometallic chemistry
Clavier, Herve; Nolan, Steven P.
Chem. Commun. 2010, **46**, 841-861 DOI: 10.1039/b922984a

A portion of this volume in this imaginary sphere of 3.5 Å radius is occupied by each ligand.

% used by the ligand is called the buried volume.

So, this buried volume concept was introduced by Steve Nolan is quite interesting in that it now makes the two-dimensional cone angle introduced by a Tolman into a three-dimensional volume. Now, you can do this phosphine you can do it for any ligand that you can think of. You should estimate the volume that is occupied by ligand in an imaginary sphere of 3.5 Angstroms.

Now, it is obvious that this 3.5 and 2 Angstroms there is used by Nolan are two arbitrary parameters that have been introduced. And this is unavoidable because of the difficulty in quantifying the various metals that are involved and the various carbon metal distances that are present, but nevertheless it turns out to be useful feature and you can read this communication in order to get a greater insight into this particular concept.

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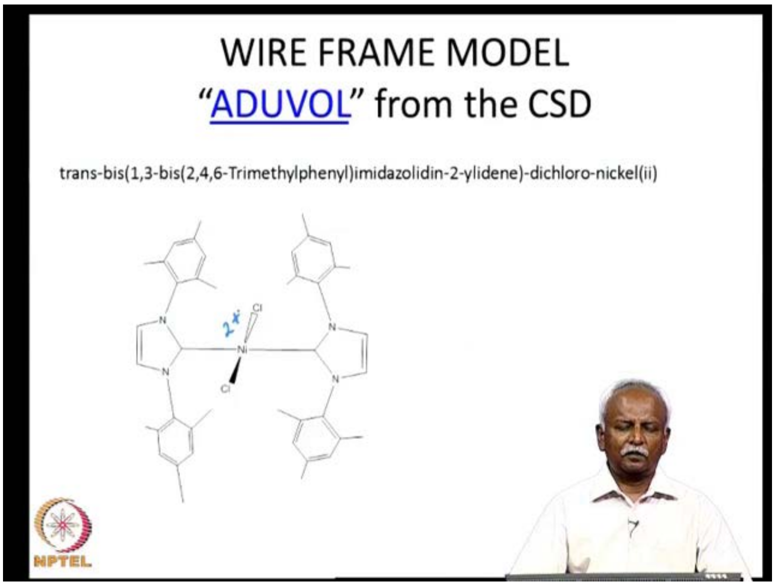

WIRE FRAME MODEL

“ADUVOL” from the CSD

trans-bis(1,3-bis(2,4,6-Trimethylphenyl)imidazolidin-2-ylidene)-dichloro-nickel(ii)

So, let us take a look at and real-life molecule here is a real-life molecule where you have two large groups which are attached to the nitrogen. If you look at two-dimensional picture of this molecule you might think that this is in fact a flat structure and this is a nickel two complex, nickel two plus complex. In which you have two carbenes in a square planar geometry and you notice that this is a system which might have a planar structure.

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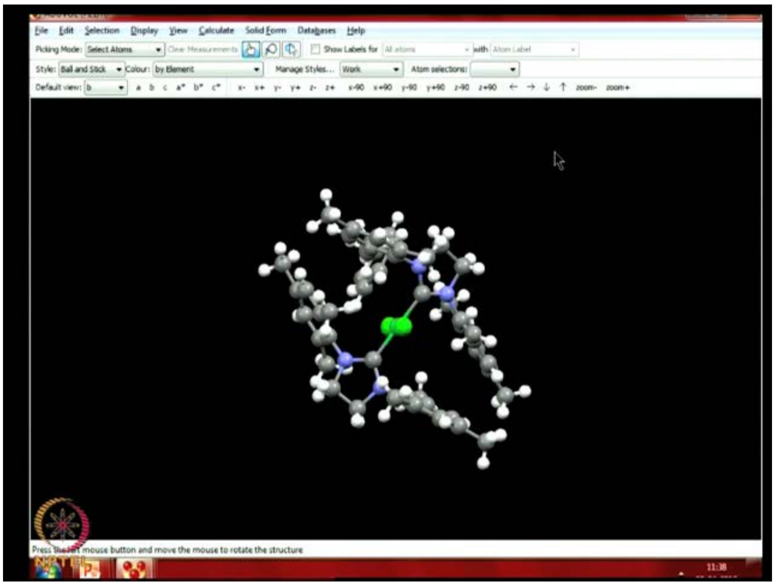

Picking Mode: Select Atoms

Style: Ball and Stick Colour: by Element Manage Styles... Work

Default view: b

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

Let us take a look at this molecule in three dimensions here is a molecule and you can see the two chlorine atoms are present and the chlorine atoms are green. And I have oriented the molecule in such a way that you are looking at a molecule through the nickel chloride axis. And you will notice that although this molecule is perfectly square planar the volume that is occupied by the ligand is significantly large. And in fact in a borrowed stick model you are able to see the nickel and the chlorine atoms very clearly, but if you use a different way at it.

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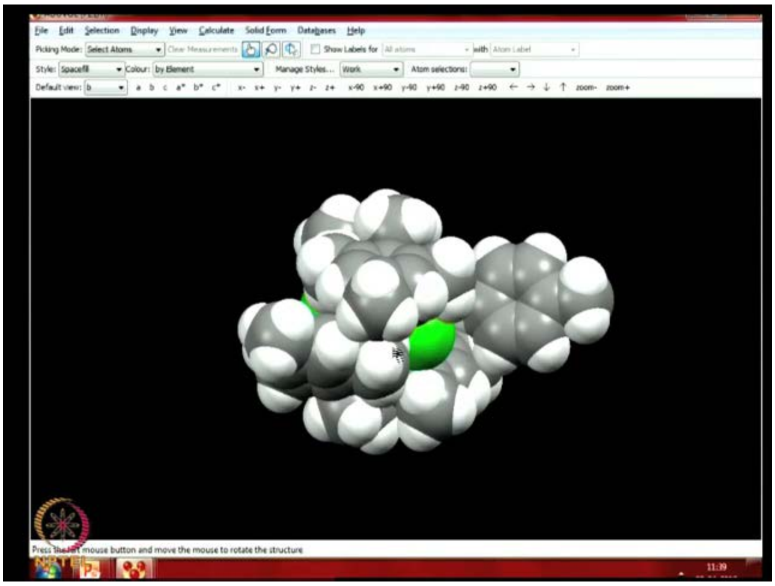

Picking Mode: Select Atoms

Style: Spacefill Colour: by Element Manage Styles... Work

Default view: b

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

Here is a space filling model of the same molecule. And you will notice that you can hardly see the nickel atoms inside this big blob of a molecule which is mostly showing only the two carbenes which are present. And you can see the chlorines at one particular point where you see it through the nickel chlorine bond. Let us go back to the two dimensional representation now. This is the molecule that we have just looked at 3 D of few seconds ago.

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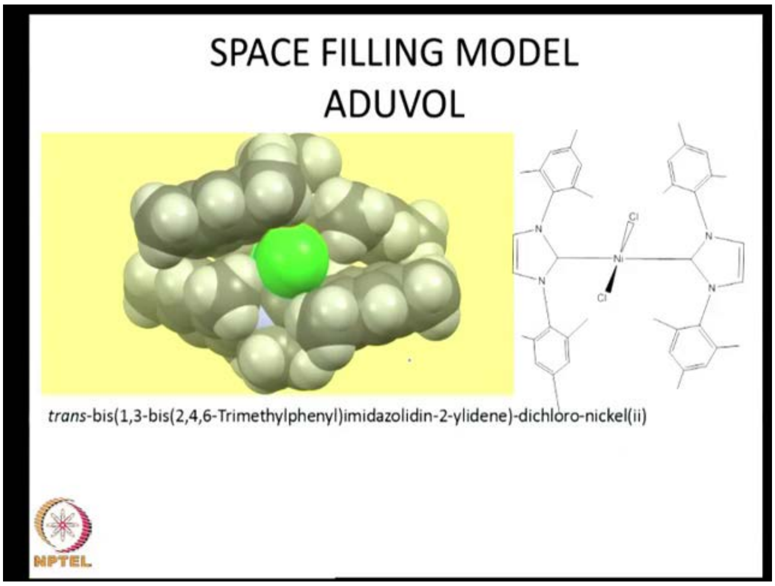

SPACE FILLING MODEL
ADUVOL

trans-bis(1,3-bis(2,4,6-Trimethylphenyl)imidazolidin-2-ylidene)-dichloro-nickel(ii)

And this is the picture that will looked at and you can see that the bulk of the ligand is extremely the volume that is occupied by the ligand is extremely large. And this is not conveyed by the two dimensional structure. So, is not possible to use a two-dimensional projection as the cone angle to get a proper idea of the volume that is used up by the ligand.

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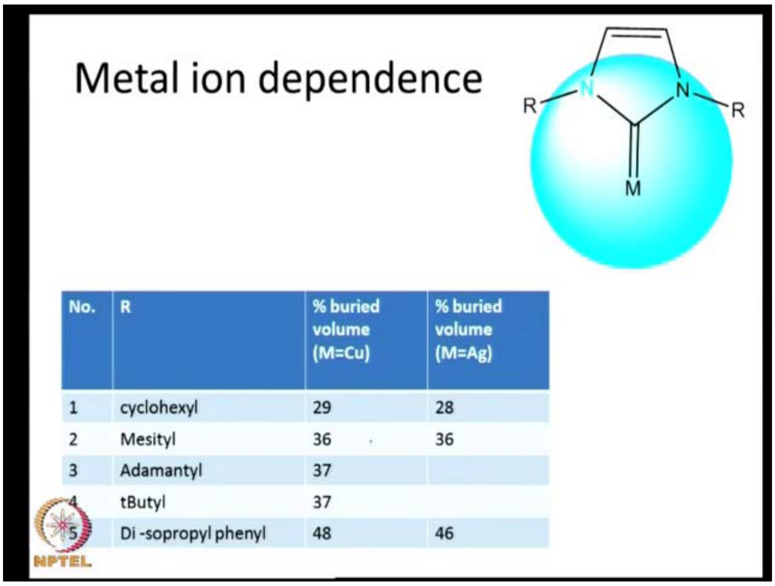

Metal ion dependence

No.	R	% buried volume (M=Cu)	% buried volume (M=Ag)
1	cyclohexyl	29	28
2	Mesityl	36	36
3	Adamantyl	37	
4	tButyl	37	
5	Di -sopropyl phenyl	48	46

So, the cone the solid cone and the volume that is occupied by the ligand is a better representation. And in fact here we have a few representative examples measured for copper and silver has shown a two different metals clearly to indicate, the fact that once again in the crystal structure. If you measure the actual buried volumes they do differ from metal to metal, but nevertheless the accepted the lead volume percentage is taken as the one where you have a fixed distance 2 Angstroms and a fixed imaginary sphere of 3.5 angstroms. So, the percentage buried volume for copper from crystallography here you have a list that is available for copper and silver. And you can see that there is a slight difference between the two.

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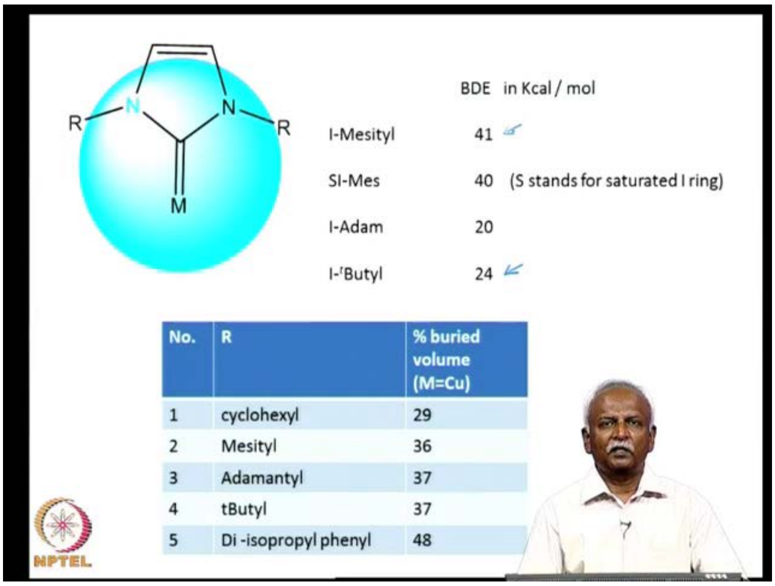

	BDE in Kcal / mol	
I-Mesityl	41	
SI-Mes	40	(S stands for saturated I ring)
I-Adam	20	
I-^{t}Butyl	24	

No.	R	% buried volume (M=Cu)
1	cyclohexyl	29
2	Mesityl	36
3	Adamantyl	37
4	tButyl	37
5	Di -isopropyl phenyl	48

Now, let us take a look at the influence of this buried volume and the influence it has chemistry. So here have a bond dissociation energy and you can see with the bond dissociation energy is related to the cone angle if you have a large buried volume percentage buried volume then the dissociation energy is small. When you have questionable time groups on the nitrogen and the buried volume turns out to be significantly smaller. And that is given here.

Whereas if you have a mesityl group because mesityl group is flat that occupies less space you can see that is got a larger bond dissociation energy indicating a better metal carbon bonds strength. So, the percentage buried volume is related to the cone angle and is a good measure of the steric parameter of the ligand.

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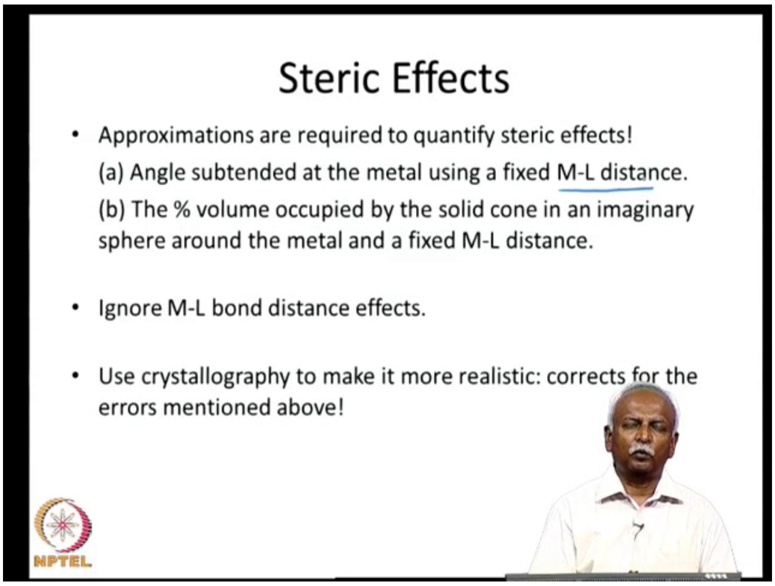

Steric Effects

- Approximations are required to quantify steric effects!
  (a) Angle subtended at the metal using a fixed M-L distance.
  (b) The % volume occupied by the solid cone in an imaginary sphere around the metal and a fixed M-L distance.
- Ignore M-L bond distance effects.
- Use crystallography to make it more realistic: corrects for the errors mentioned above!

So, at this point summarizes what we have been talking about. Approximations are required in order to quantify the steric effects. You seen both in the cone angle the dream that Tolman measured and in Nolan's buried volume concept there was an approximation made on theta approximation was to fix the metal ligand bond distance in order to get some consistency in the buried volumes.

And the cone angles that you report in the literature the percentage volume that is occupied by the ligand is a better estimate of the steric influence of the ligand. One can in fact use crystallography to if you have a large number of complexes, it would be easy to have a distribution of the cone angles or the buried volumes. And make an estimate a better estimate of the to the buried volume that you should use in order to calculate any property of the molecule.

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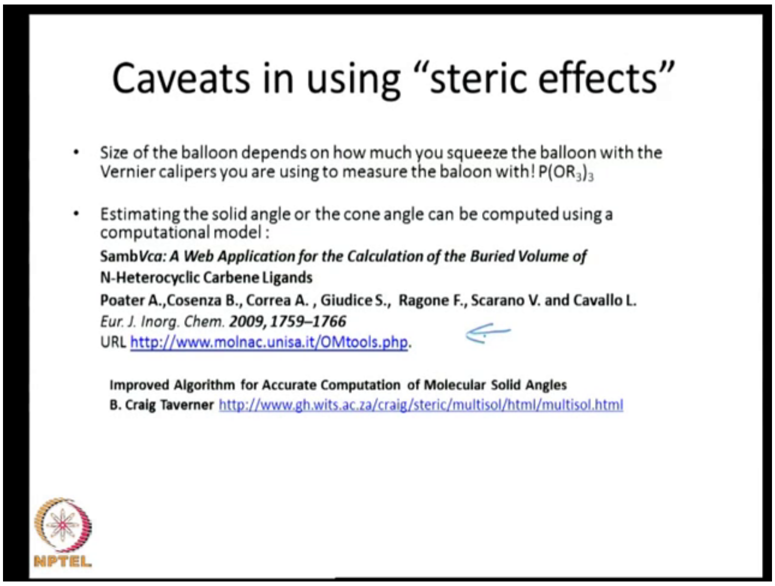

Caveats in using "steric effects"

- Size of the balloon depends on how much you squeeze the balloon with the Vernier calipers you are using to measure the baloon with! $P(OR_3)_3$
- Estimating the solid angle or the cone angle can be computed using a computational model :

Samb*Vca: A Web Application for the Calculation of the Buried Volume of*
N-Heterocyclic Carbene Ligands
Poater A.,Cosenza B., Correa A. , Giudice S., Ragone F., Scarano V. and Cavallo L.
Eur. J. Inorg. Chem. ***2009, 1759–1766***
URL http://www.molnac.unisa.it/OMtools.php.

Improved Algorithm for Accurate Computation of Molecular Solid Angles
B. Craig Taverner http://www.gh.wits.ac.za/craig/steric/multisol/html/multisol.html

So, we should also remember that there is a variation in the type of the volume that ligand occupies. And it really depends on the environment that is available for the ligand. So, the case of tris methoxy phosphide. The crystallography data clearly showed the third to cone angles that are possible for this particular ligand. This is very much akin to what we see with the balloon. If you want to measure to the one-year calipers and the size of the balloon depends on how much we squeeze the balloon with the calipers. So, one cannot have the unique size for the balloon when you measure it with calipers.

Similarly, the cone angle you can have it and have a similar situation and you can have variations in the cone angle also in the buried volume also read. In recent times it has been possible to estimate this cone angle or this volume using some computer programs and these are useful when you do not have a crystal structure. And when it is cumbersome to make a molecular model in order to estimate the cone angle. So, here are two references to papers where in fact you can use the web in order to estimate the work buried volume of ligand and this particular website. And you can also have a cone angles measured automatically.

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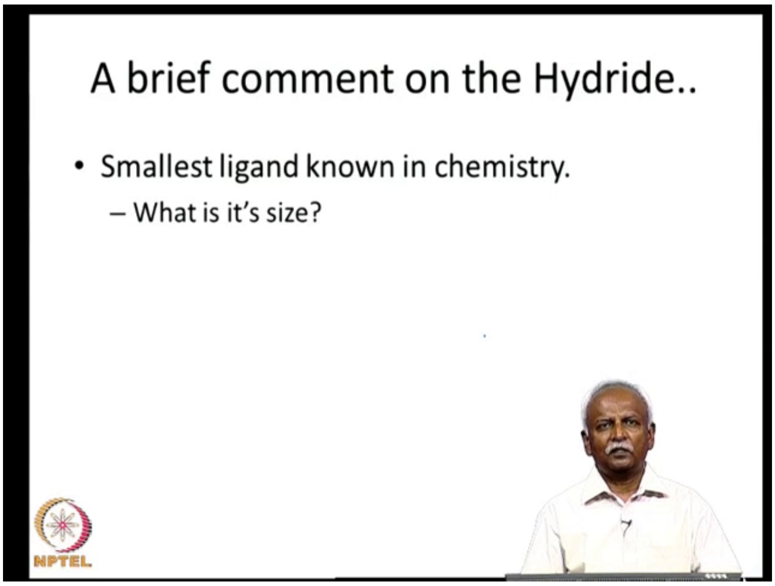

A brief comment on the Hydride..

- Smallest ligand known in chemistry.
  - What is it's size?

So, let us take a look at the hydride which I mentioned as the other unique situation in chemistry. Hydrogen is always poses a problem when you want to generalize some concepts hydrogen sticks out as a unique and her element. And in this particular case it is a unique ligand. If you asked the question what is the size it is difficult to give a proper answer for this question.

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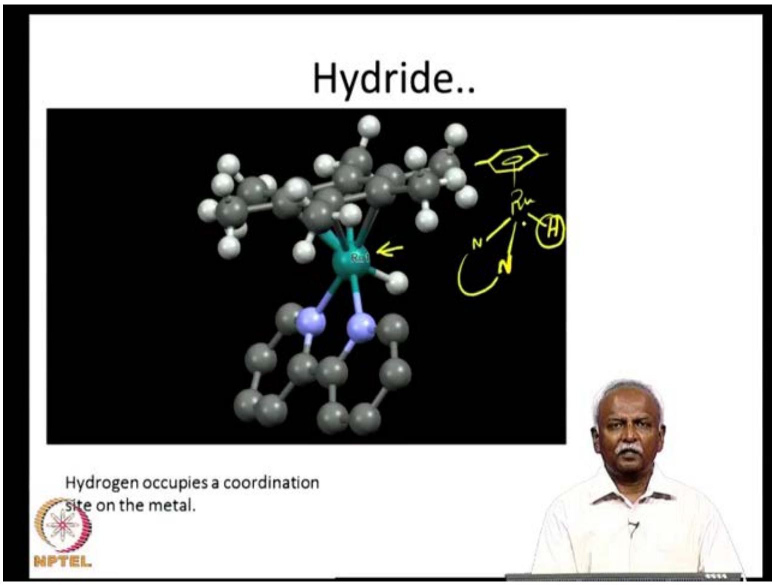

Hydride..

Hydrogen occupies a coordination site on the metal.

Here is a molecule which I have shown for you. The ruthenium atom which is pictured here images show you here is a ruthenium atom which is complex to an aromatic ring.

So, this is an aromatic ring system that is available for this metal to complex. This is the complex that we are talking about. You have two nitrogen and that is a directory and this ruthenium is coordinated to hydride. And you can see that this is a typical piano stool geometry that the ruthenium is an occupying. You have a situation where you have a flat stool which is sitting on three legs two nitrogen one hydrogen. And this hydrogen is occupying a reasonable amount of space next to the ruthenium. And here is another example.

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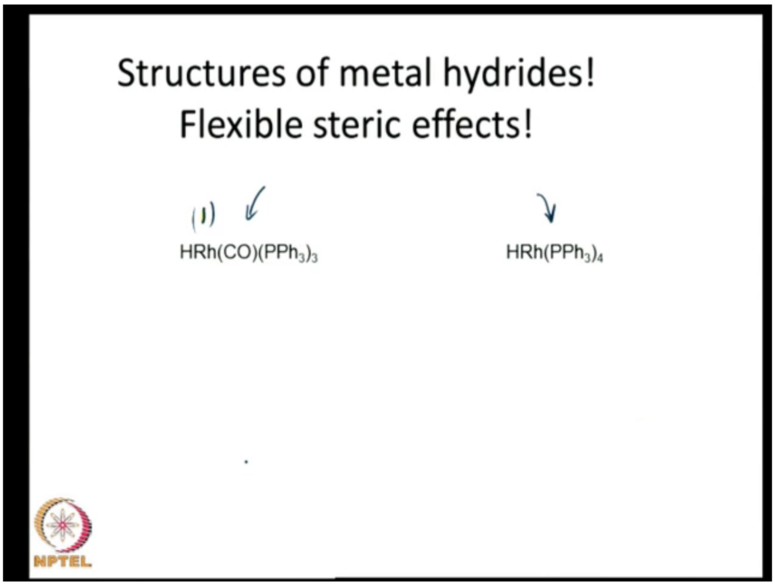

Structures of metal hydrides!
Flexible steric effects!

(1)

$HRh(CO)(PPh_3)_3$

$HRh(PPh_3)_4$

And this example I am going to choose rhodium complex. And rhodium complex we have tried several phosphine is attached to the rhodium. And because it is rhodium one you have a ligand which is a hydride. And in the two complexes differ in a very simple fashion. That is in one case you have resisted truckers trifle phosphine and this one has got three-crossings and the fourth ligand is in fact a carbon monoxide. So, let us take a look at the complex and 3 D and see how these complexes failed.

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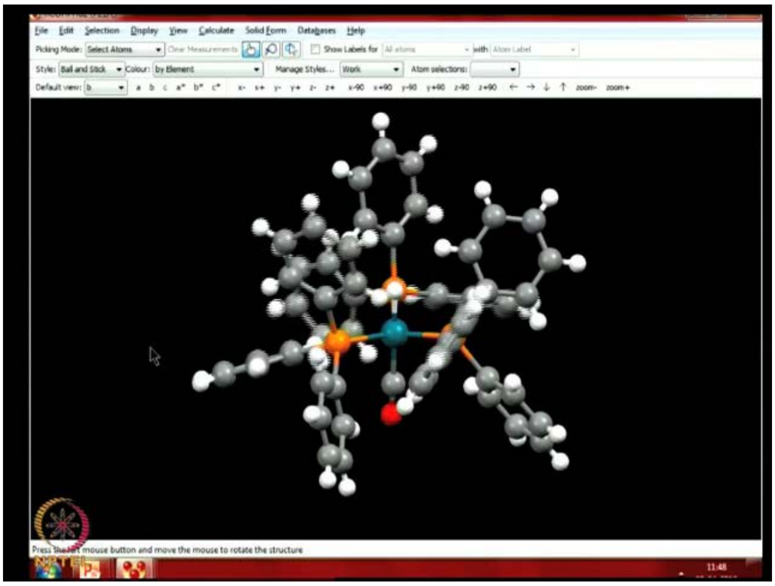

Press the left mouse button and move the mouse to rotate the structure

So, this is a complex which is the carbon monoxide complex. And you can see that you can see that the complexes got a hydrogen and carbon monoxide in an axial position in a tribunal by pyramidal geometry. And the three equal trial positions are occupied by the three trifle phosphine. So, this complexes in fact having five ligands and the filing lands occupied the five points of a tribunal by pyramid around the rhodium. And so this seems to be a very reasonable complex to just like the ruthenium complex as I showed you.

Now, if you measure the angles around the rhodium you can assist measure able angle here I have a phosphorus rhodium and a phosphorus and this angle turns out to be close to 115 degree or it should have been close to 120 degree. And here is the second angle and this is 116 degree. So, you can see that these angles of close to 120 degree. Now, let us move onto another complex which I have mentioned and this complexes got for trifle phosphine. And is for trifle phosphine is almost occupying the vertices of a tetrahedron. So, where is the hydrogen present the hydrogen is in fact on one of the faces of this tetrahedron.

And you can see it right here and can see the hydrogen that is sitting on the rhodium. And that is on the face of a tetrahedral tetrahedron that is formed by the four phosphorus atoms which are linked to the rhodium atom. So, you can see that the hydrogen is released theoretically accommodating and it is not demanding the fifth position in a five vertex geometry around the rhodium. So, it is almost as if the only four ligands around the rhodium and the hydrogen is occupying a small place on the surface or on the sphere of the rhodium atom.

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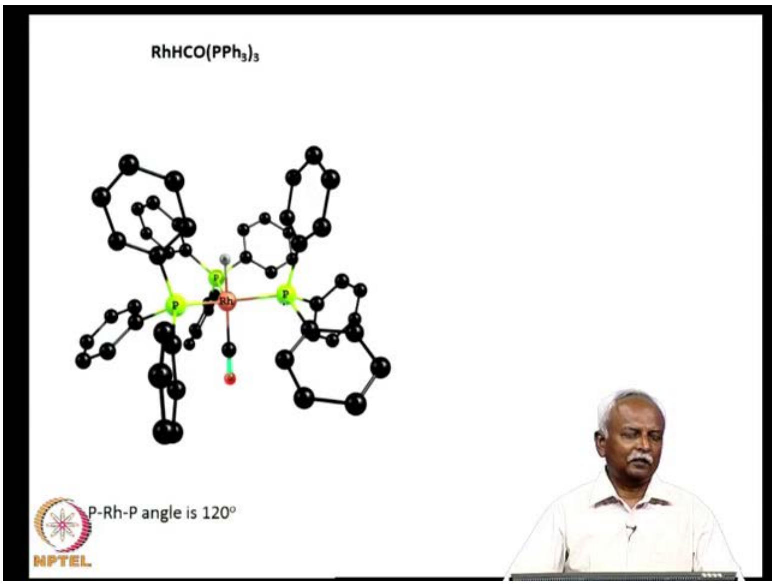

RhHCO(PPh$_3$)$_3$

P-Rh-P angle is 120°

So, let us proceed with this and let us take a look at the angles that I have was talking about. Here is the case where the rhodium has got one carbon monoxide and three phosphine. And the hydrogen is occupying a unique position that said that he typical position on the tbp geometry.

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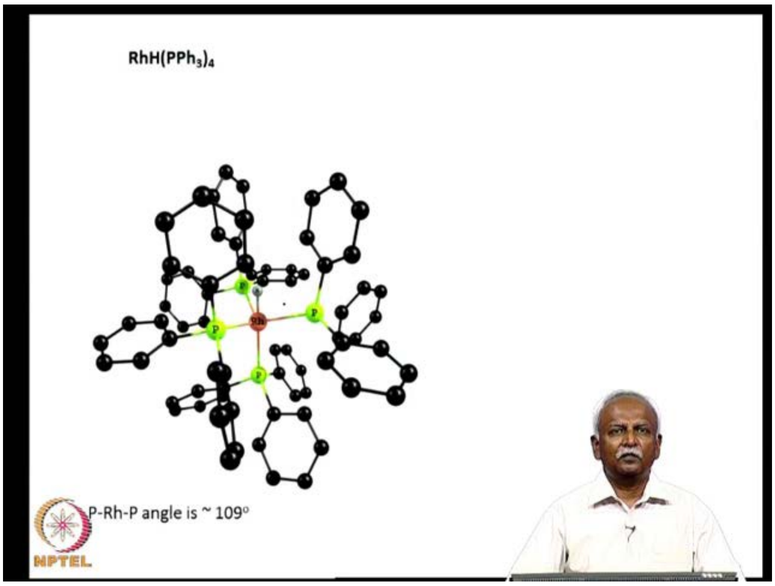

RhH(PPh$_3$)$_4$

P-Rh-P angle is ~ 109°

And in the case of the tetrahedron trifle phosphine complex. The hydrogen is occupying one of the faces of the tetrahedron and the four phosphorus ligand seemed to be occupying all the space around the rhodium.

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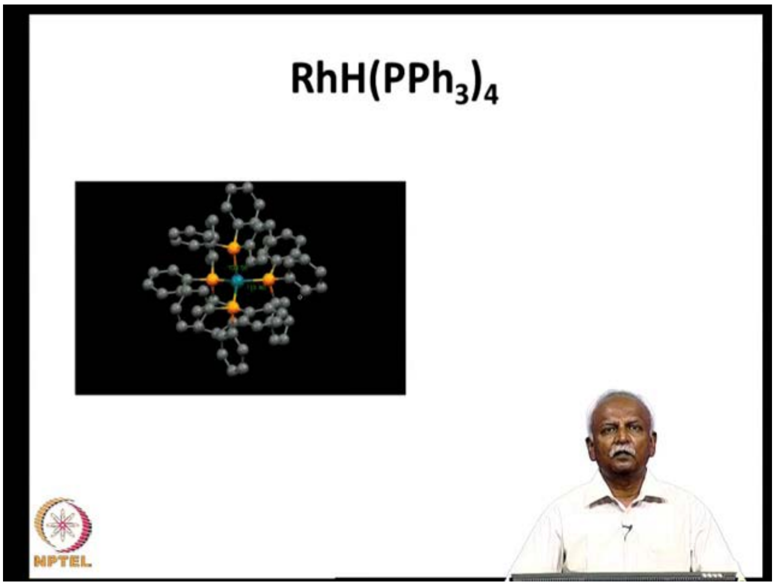

RhH(PPh$_3$)$_4$

So, the angle around the rhodium is almost close to phosphorus rhodium phosphorus angle is close to 109 degree. And if you see it closely this is both angles appear to be the two angle is close 209 degree

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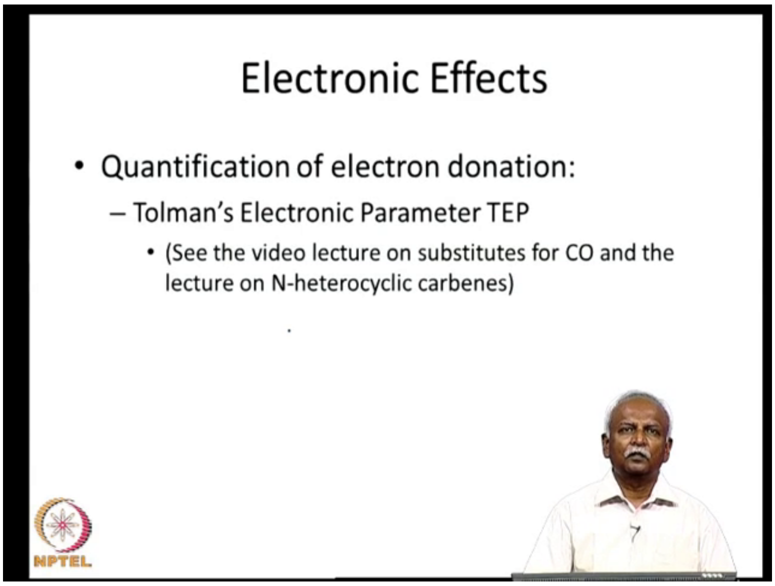

Electronic Effects

- Quantification of electron donation:
  - Tolman's Electronic Parameter TEP
    - (See the video lecture on substitutes for CO and the lecture on N-heterocyclic carbenes)

Now, in the remaining time I would like to discuss some of the electronic effects that the ligands exerts. And we have already discussed in the case of both n-heterocyclic carbenes and in the case of fostering. The type of electronic parameterization that can be done. In fact Tolman who devised the twelve months cone angry was the same person who devised Tolman’s electronic parameter.

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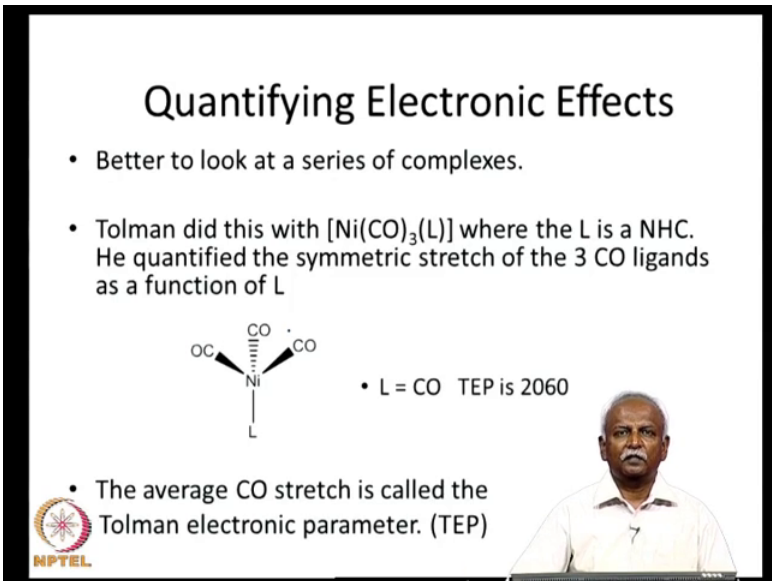

Quantifying Electronic Effects

- Better to look at a series of complexes.
- Tolman did this with $[Ni(CO)_3(L)]$ where the L is a NHC. He quantified the symmetric stretch of the 3 CO ligands as a function of L

- L = CO TEP is 2060
- The average CO stretch is called the Tolman electronic parameter. (TEP)

This is a quantification that is based on a simple spectroscopic measurement. If you take a nickel tetra carbonyl and substitute one of the carbon monoxides with a ligand, the ligand of choice that you want to measure the electronic parameter for then the three carbon monoxide there are on the other side of the nickel change CO stretching frequency. Depending on how much electron density is available on the nickel.

So, if you have a large amount of electron density on the nickel then the carbon monoxide stretching frequency goes down. So, electron density that is given to the metal is inversely proportional to the stretching frequency. Now, you will have two stretching frequencies of for the three carbon monoxide, if you have a C3V cemetery around metal. And so you would have to take the average of the CO stretch. And this is possible to use carbon 13 mr spectroscopy. And these two parameters what you measure what you have as the Tolman's electronic parameter.

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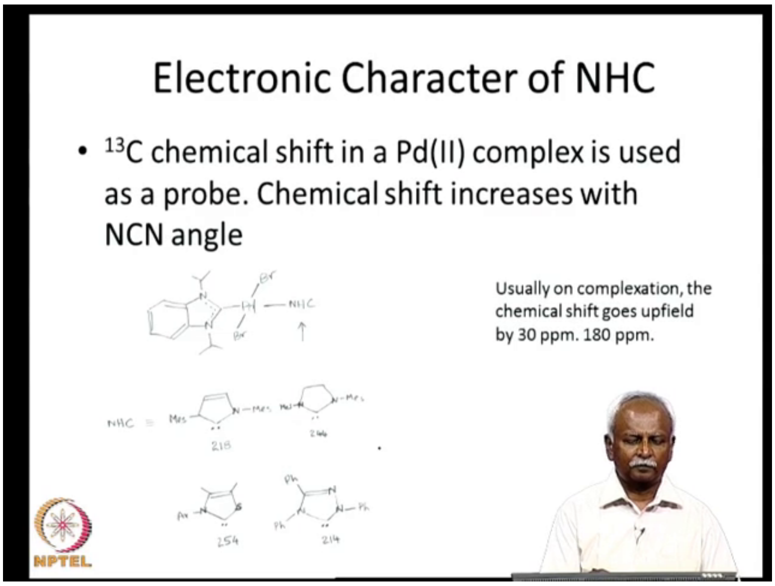

Electronic Character of NHC

- ^{13}C chemical shift in a Pd(II) complex is used as a probe. Chemical shift increases with NCN angle

Usually on complexation, the chemical shift goes upfield by 30 ppm. 180 ppm.

Now, it is also using Tolman's spectroscopic parameter carbon monoxide stretching frequency. And the carbon thirteen chemical shift could appear to be related and people have correlated the true and the founder of the same ligand. If you plot Tolman's electronic parameter and the carbon thirteen spectral data they correlate. Now, this carbon thirteen spectral data is very much dependent on the electron density around the carbon. And the carbenes carbon has got this in a chemical shift around 180 ppm. And that shifts to an up field region when it is coordinated to the metal.

And that the chemical shift video observed for the carbene carbon when it is attached to palladium the palladium two bromide complex is what is used as a standard for this carbon thirteen measure of the electronic parameter. So, here I have given before you were a couple of different n-heterocyclic car beans and electronic affect they exert. And you can see that the depends on the groups angle, and the both the angle and electron density that the carbon exerts.

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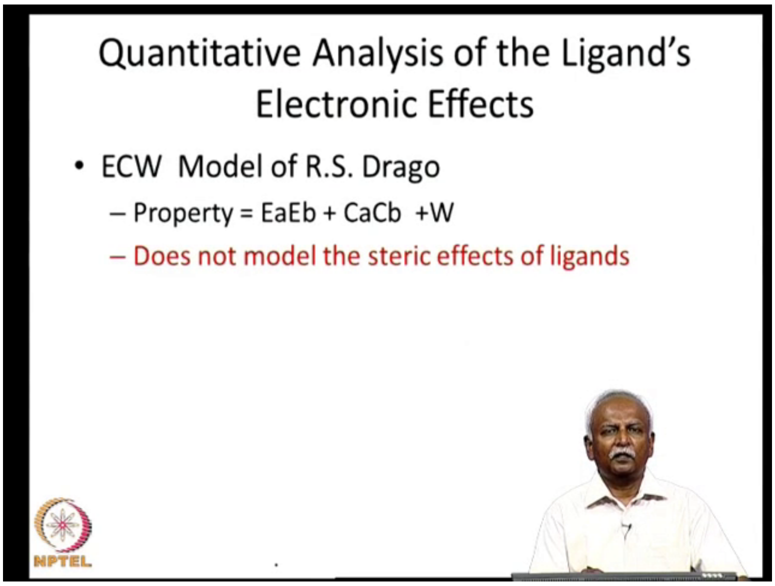

Quantitative Analysis of the Ligand's Electronic Effects

- ECW Model of R.S. Drago
  - Property = EaEb + CaCb +W
  - Does not model the steric effects of ligands

Now, the question comes up into a an estimate of any property for the metal complex using only electronic effects, because we mention that state parameters are in fact stereo electronic can we just use the electronic parameter to get an estimate of any particular property. Of these properties could be metal ligand bond distances, it could be a bond dissociation energy, or it could even be an kinetic parameter as the rate of reaction in which these ligand are present. Now, what we are what has been shown in the literature and is at this property tested electronic property is not sufficient to model any of the ligands influence completely.

So, in the case of the ECW model that is used by Drago. Drago modeled electronic influence of ligand using the electrostatic effect on covalent effect. And he described these parameters estimated these parameters for various ligands. And this does not quantitatively reproduce the property of a metal complex. Some properties are reproduced, but some are not. And this is primarily because there is no parameterization for the steric property. So, in this lecture we have actually dealt with two different parameters steric parameters and electronic parameters.

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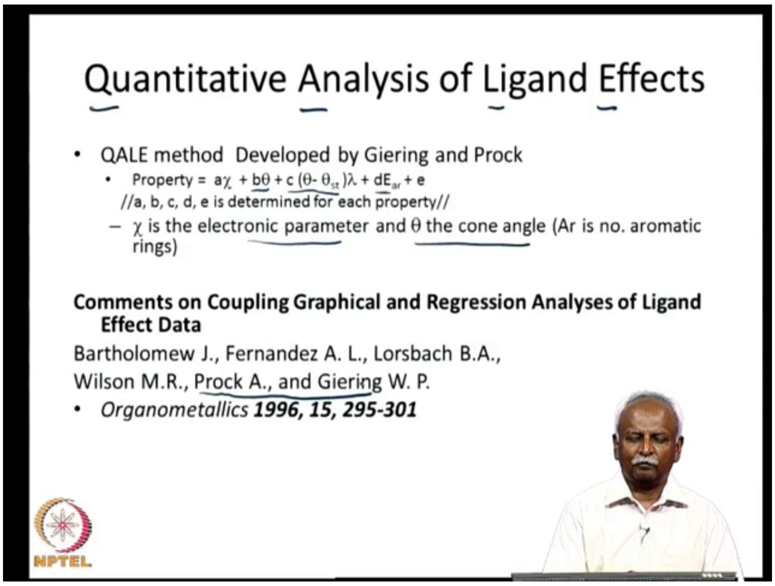

Quantitative Analysis of Ligand Effects

- QALE method Developed by Giering and Prock
  - Property = $a\chi + b\theta + c(\theta - \theta_{st})\lambda + dE_{ar} + e$

    //a, b, c, d, e is determined for each property//
  - χ is the electronic parameter and θ the cone angle (Ar is no. aromatic rings)

Comments on Coupling Graphical and Regression Analyses of Ligand Effect Data

Bartholomew J., Fernandez A. L., Lorsbach B.A., Wilson M.R., Prock A., and Giering W. P.

- *Organometallics* ***1996, 15, 295-301***

And it is quite obvious from this particular database shown you the electronic parameter alone is not sufficient to model the property of a molecule. Any property and the model that has been successful that has received reasonable amount of acclaimed, is what is known as a quantitative analysis of ligand affects, QALE is an acronym that is available for this particular method developed by Giering and Prock. These two people have developed a simple equation which relates at property any property of the molecule to the electronic and the steric parameters. Kylie is an electronic parameter that we need to plug in and theta is a cone angle, and registry.

You notice that theta appears twice in this equation. One is theta into b and another is the parameters c into theta st. Theta st refers to the limit of the angle, which is like the steric limit, after which there is some influence from the steric parameter. And it is the number of irael groups present on the ligand. And very often and aromatic parameter is required and in order to model the ligand properly, E is of course, a simple constant that is added to the property for the property and these parameters. Now, the last paper that was published in this a paper in 1996 by Prock and Giering. And this gives you a good summary of the many different nuances that are involved in utilizing this quantitative analysis of ligand fracture model.

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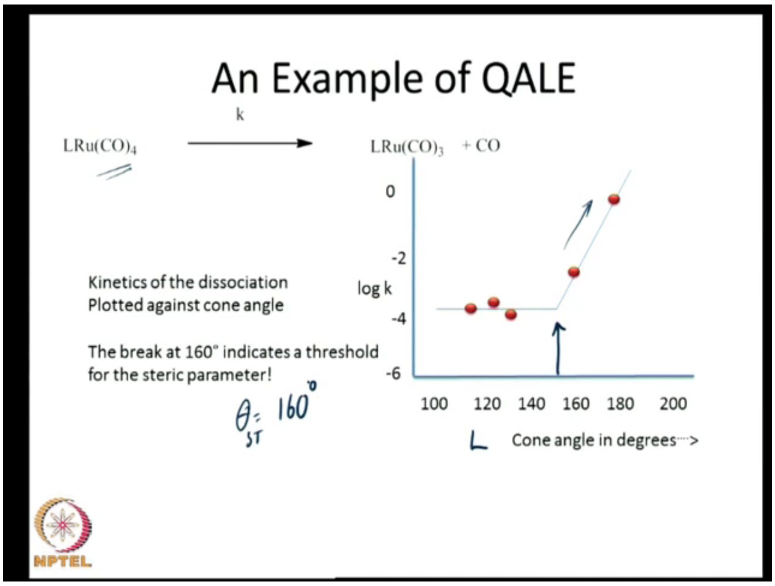

An Example of QALE

$LRu(CO)_4 \xrightarrow{k} LRu(CO)_3 + CO$

Kinetics of the dissociation
Plotted against cone angle

The break at 160° indicates a threshold for the steric parameter!

$\theta_{ST} = 160^{\circ}$

Now, all images illustrate how this grill can be used here is a plot of this dissociation energy the dissociation energy is a simple loss of carbon monoxide in this five coordinated complex. And this rate is dependent on the cone angle of the ligand l is plotted in this x-axis and the long tail is plotted along the y-axis. And you can see that up to 160 degree there is no influence of the cone angle on the rate of dissociation, but after 160 degree the larger the cone angle the faster the dissociation.

So, the dissociation becomes more easy as you have a bulkier L. And this is quite obvious that what is interesting is that the quail model incorporates a threshold cone angle. So, that you can in fact model this threshold steric parameter that is available for each reaction, also obvious that this is reaction dependent. And for this particular reaction theta ST be 160 degree in the equation that he just showed you earlier.

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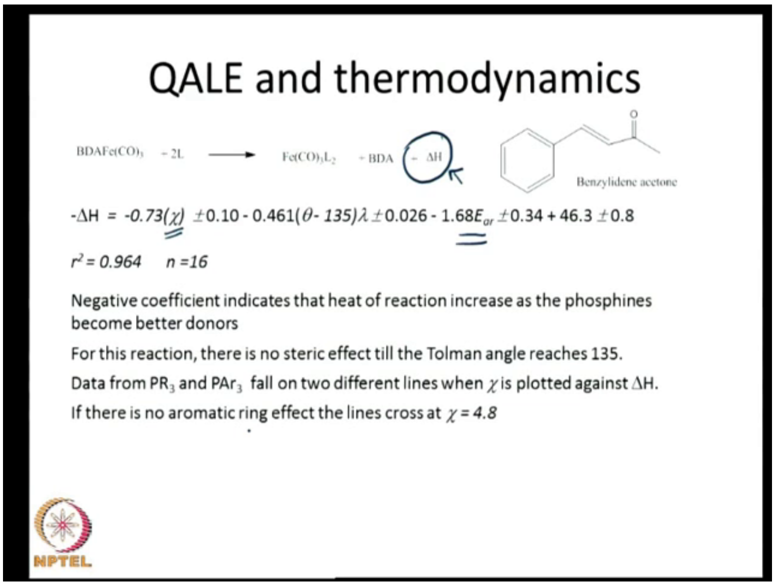

QALE and thermodynamics

$\mathrm{BDAFe(CO)_3} + 2\mathrm{L} \longrightarrow \mathrm{Fe(CO)_3L_2} + \mathrm{BDA} \; (-\Delta H)$

$-\Delta H = -0.73(\chi) \pm 0.10 - 0.461(\theta - 135)\lambda \pm 0.026 - 1.68E_{ar} \pm 0.34 + 46.3 \pm 0.8$

$r^2 = 0.964 \quad n = 16$

Negative coefficient indicates that heat of reaction increase as the phosphines become better donors

For this reaction, there is no steric effect till the Tolman angle reaches 135.

Data from PR_3 and PAr_3 fall on two different lines when χ is plotted against ΔH.

If there is no aromatic ring effect the lines cross at $\chi = 4.8$

So, here is the equation for a displacement reaction where when selecting acetone which is shown for you here and is replaced by two ligands. And the nature of these ligand is can affect this dissociation and the delegates for this particular reaction has been measured. The heat liberated when you replace a benzylidene acetone with these two ligands. And it is been shown that there is in fact an influence of the steric parameter and there is an influence of the electronic parameter and also the irael groups.

If you have irael groups on the ligand l then it turns out that that has got a better are the better largest dissociation. If you have an aerial group it has a different heat of reaction for this and particular exchange reaction. So, you can see that if you have a kyle which is indicated here Tolman's electronic parameter, then that has a significant influence on the delights. And the larger the kyle the larger the heat that is generated in this reaction. So, if you can measure various parameters like bond distances, bond energies and you can relate them with the steric parameter and the electronic parameter, it becomes a useful exercise when you want to design and new ligand in order to have an better reaction.

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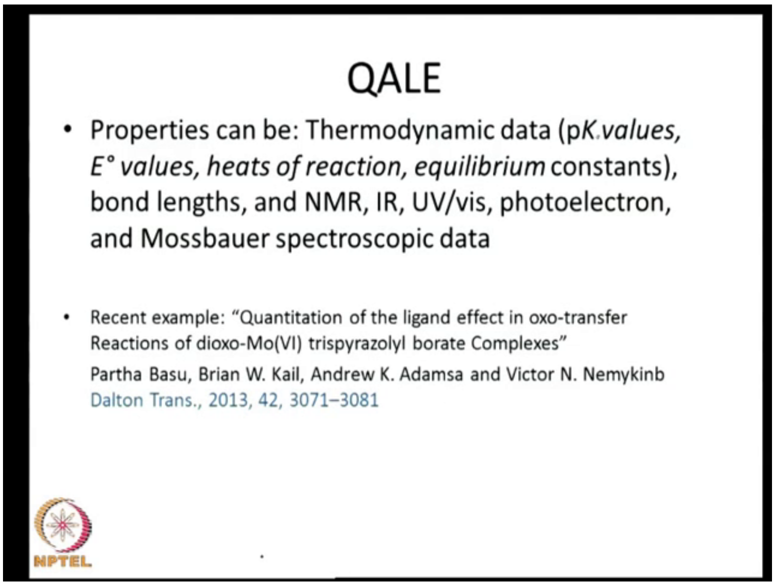

QALE

- Properties can be: Thermodynamic data (p*K values, E° values, heats of reaction, equilibrium* constants), bond lengths, and NMR, IR, UV/vis, photoelectron, and Mossbauer spectroscopic data
- Recent example: "Quantitation of the ligand effect in oxo-transfer Reactions of dioxo-Mo(VI) trispyrazolyl borate Complexes"
  Partha Basu, Brian W. Kail, Andrew K. Adamsa and Victor N. Nemykinb
  Dalton Trans., 2013, 42, 3071–3081

So, in fact in the literature is been has been shown that equilibrium constants pk values electrode potentials, all of them can be related to using QALE equation. In a recent paper it has been shown for the oxo transfer reaction in molybdenum 6 complex that you can quantitate the effect of the ligand using lifting quantitative effect of the ligand using QALE equation.

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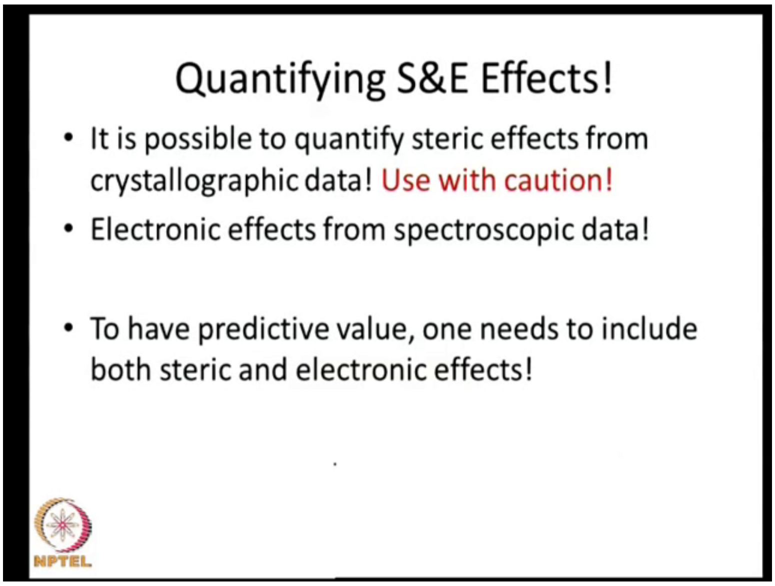

Quantifying S&E Effects!

- It is possible to quantify steric effects from crystallographic data! Use with caution!
- Electronic effects from spectroscopic data!
- To have predictive value, one needs to include both steric and electronic effects!

So, let me just conclude by talking about the difficulties that we have been steric quantifying, steric and electronic parameters. Steric parameters can be obtained in a reasonably good fashion using crystallographic data. This is in fact a great advantage, but you have to use it with caution. And secondly electronic effects are also measured very accurately using spectroscopic data, but if you want to have predictive value in chemistry turns out that you have to use both state and electronic effects.