Introduction to Organometallic Chemistry

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Lecture - 01

Hello, this course is about organometallic chemistry and my name is A.G. Samuelson and I work in the inorganic and physical chemistry department. And I have been there since 1983, I teach mostly organometallic chemistry and inorganic chemistry. This course is a result of my experience with the students in introducing them to organometallic chemistry.

So, organometallic chemistry is in fact a very complex field and it is a fascinating field. What this course does is to have a structured introduction to it, so that even if a person has not studied any organometallic chemistry. In the earlier days, he can boldly start reading the literature in organometallic chemistry after going through these few lectures. So, let us take a look at the slides one by one.

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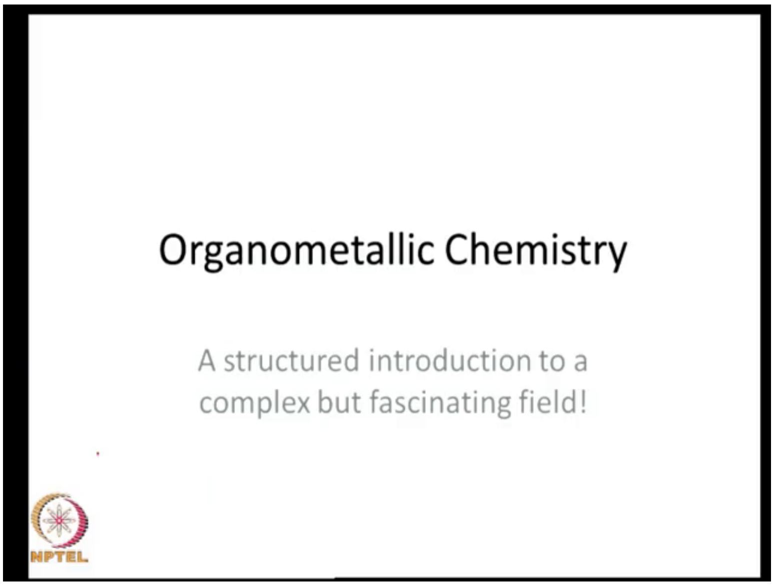

Organometallic Chemistry

A structured introduction to a complex but fascinating field!

We have structured introduction as I said, but it is definitely a very fascinating field.

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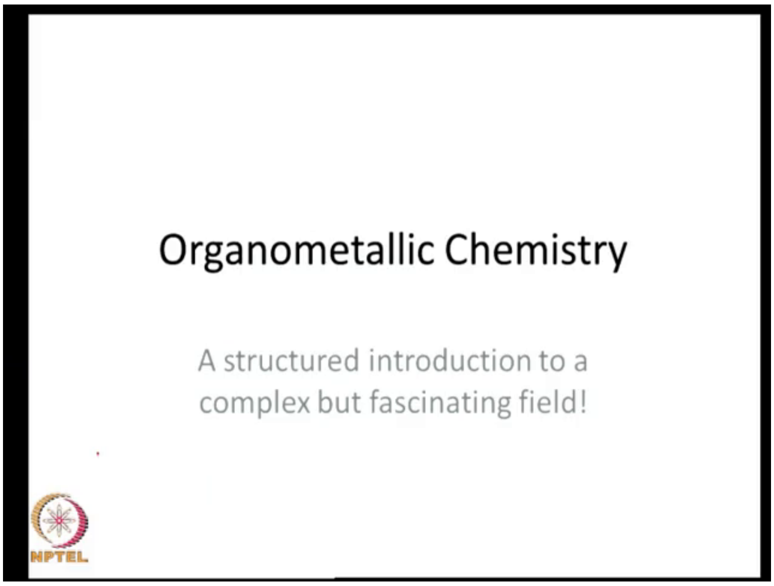

Organometallic Chemistry

A structured introduction to a
complex but fascinating field!

It was a late comer into the subject field of chemistry. It was only in 1956 that people realised that organometallic chemistry is a discipline. Sub-discipline of its own and it has a significant amount of material that would be of great interest, not just in the laboratories. But also in the industry the problem with organometallic chemistry is a the fact that suddenly the student is presented with a large number of new concepts, which were not available or necessary to understand organic chemistry or for that matter even inorganic coordination chemistry, classical coordination chemistry.

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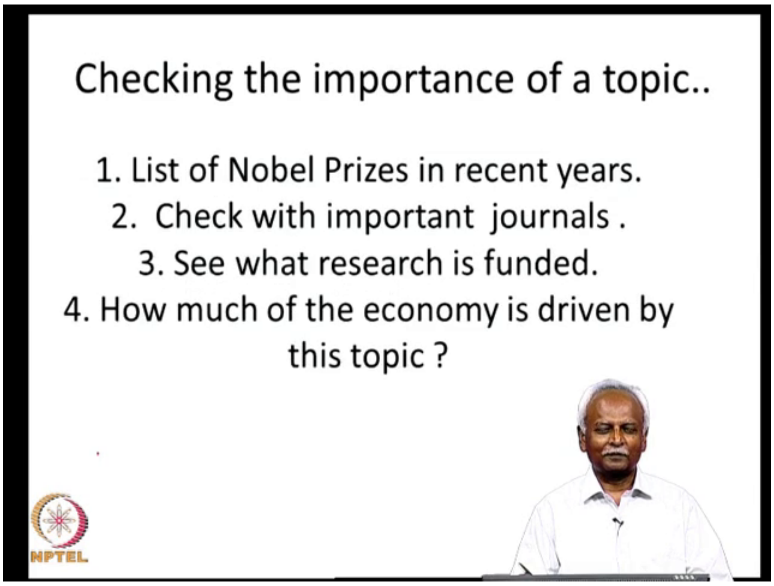

Checking the importance of a topic..

1. List of Nobel Prizes in recent years.
2. Check with important journals .
3. See what research is funded.
4. How much of the economy is driven by this topic ?

Now, we first answer the question, why study this particular field, if it is so complex. If it is interesting then it must be worth it. So, let us take a look at some reasons why we should study it. I have developed here a few questions that one should ask when you look at any new discipline and the first question that I ask is that, are there any significant discoveries in this field that has merited? For example, the award of a noble prize, now at least in the sciences it is well known that the noble prize is considered as one of the best prizes, or one of the top prizes that are given to a scientist, who has made a very important discovery, which would benefit mankind and, so we can ask this question.

Has organometallic chemistry really achieved that status, so that some people working in this field would receive the Nobel prize? Let us see what happens to that question. Then we ask the question, we look at some of the journals, which are of importance to all scientist working in the area of chemistry. Do we see any organometallic chemistry papers and what kinds of papers are they. Let us see what kind of research is funded and then finally, how much of the economy is really driven by this topic? So, each one of these questions will be briefly answered before we proceed to the subject itself.

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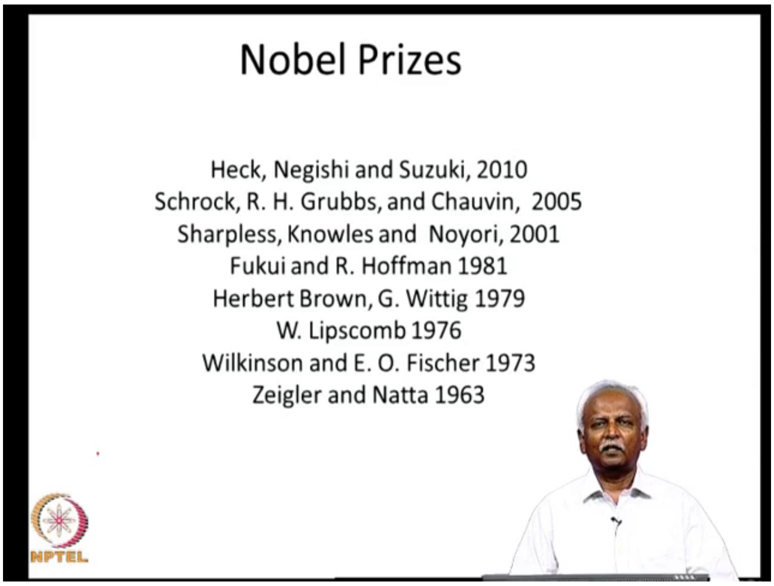

Nobel Prizes

Heck, Negishi and Suzuki, 2010
Schrock, R. H. Grubbs, and Chauvin, 2005
Sharpless, Knowles and Noyori, 2001
Fukui and R. Hoffman 1981
Herbert Brown, G. Wittig 1979
W. Lipscomb 1976
Wilkinson and E. O. Fischer 1973
Zeigler and Natta 1963

So, let us take a look at the Nobel prizes. Here I have listed for you some of the Nobel prizes that have been awarded in the general area of organometallic chemistry. As I said, the sub-discipline was recognised only in the late 1950's and surprisingly by 1963, Zeigler and Natta were awarded the Nobel prize for working in the area of titanium. And zirconium catylyst, catalyst which were capable of producing high molecular weight polymers.

Especially polyethylene and polypropylene, and polypropylene was made in a specific fashion, which resulted in very interesting and very valuable properties for polypropylene. This area continues in spite of the fact that the major discovery was made in 1963. Even today it continues to be an active area of research and through the series of lectures. We will see this, how this is quite important and what a fundamental reaction an organometallic chemistry is responsible for this particular discovery.

Next, let us take the Nobel prize that was awarded to Wilkinson and Fischer in 1973, that came just ten years after the first Nobel prize to Zeigler and Natta and Wilkinson. And Fischer were actually awarded the Nobel prize for their discovery of metallocenes. This discovery was in fact the key discovery that spurred people onto studying organometallic chemistry as a sub-discipline. By then it was very clear that it was this seminal discovery. The subsequent research work that was done in this area that was going to contribute significantly in chemistry.

I next talk about the discoveries made by Herbert Brown and Wittig and Lipscomb take these two Nobel prizes together, because it turns out that all of them contributed to the chemistry of elements on either side of carbon. Brown contributed to the chemistry of boron, Witting to the chemistry of phosphorous, which is on the next side and the right side of the periodic table, where carbon is there in the centre. So, Lipscomb and Brown contributed significantly to the understanding of the chemistry of boron and the structures. These are key discoveries in organometallic chemistry, because they helped one to understand some of the structures, which were not available in the literature in earlier days.

So, next comes the discovery or the Nobel prize to Fukui and Hoffman. Once again, Fukui and Hoffman were given the Nobel prize for their contribution to the structures of compounds and they used frontier molecular orbital theory, but Hoffman applied it completely to organometallic compounds. He was able to explain the structures of all the new compounds that were discovered in the 60’s and 70’s by researchers working in organometallic chemistry and also suggest a framework for understanding few structures that would be discovered in the future. So, that was a seminal contribution to the field of organometallic chemistry.

There was a long gap since, from 1981 to 2001, and in 2001 Sharp less Knowles and Noyori were awarded the Nobel prize for their contributions to asymmetric catalysis. And this was completely in the field of organometallic chemistry, where chiral ligands were used by these workers to generate chiral compounds, which were very important in the field of drug discovery.

So, Noyori, Knowles and Sharpless were recognised for this key contribution in 2001. This was rapidly followed by another two Nobel prizes in 2005 and 2010 and in 2005, Schrock, Grubbs and Chauvin were awarded the Nobel prize for their work on metathesis chemistry. Interestingly, this deals completely with carbon-carbon double bonds and double bond containing compounds and how they can be transformed from one to the other. It turns out that the new bonds that are formed were also double bonds and, so this turns out to be contribution that is not parallel in classical organic chemistry.

This was followed by Heck, Negishi and Suzuki who contributed significantly to the formation of a carbon-carbon single bond, these two discoveries in 2005 and 2010. These two Nobel prizes recognised the contribution of organometallic chemistry to the formation of carbon-carbon single bonds and carbon-carbon double bonds. If you look at the span of say fifty odd years from or sixty years from 1955 to the 2010.

You see that there are about eight Nobel prizes, that have been awarded to the field of organometallic chemistry. And even earlier the discoverer of Salvarsan, which is inorganic or organometallic drug that was given to treat syphilis was also Meone who received the Nobel prize for in the in the field of drug discovery, but then it was an organometallic compound.

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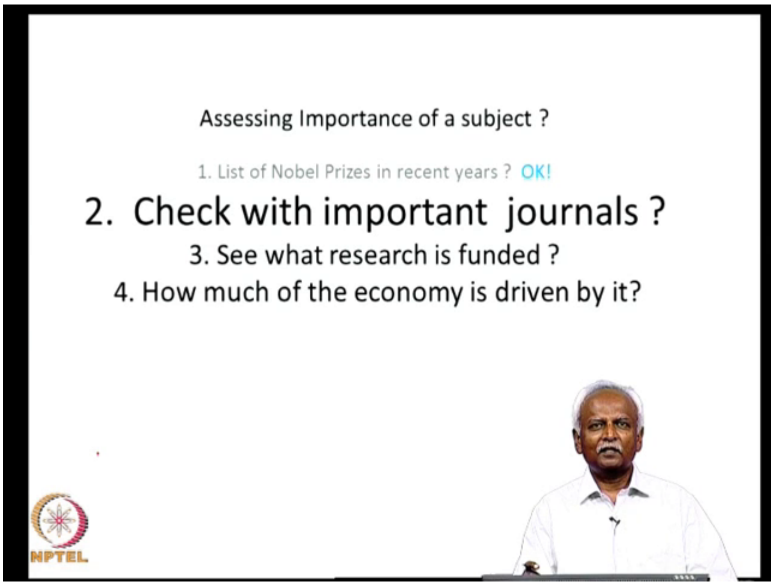

Assessing Importance of a subject ?

1. List of Nobel Prizes in recent years ? OK!

2. Check with important journals ?

3. See what research is funded ?

4. How much of the economy is driven by it?

So, you can see that several compound Nobel prizes have been given in this field. Now, we let us take a look at briefly at the journals and how they give importance to the subject of organometallic chemistry.

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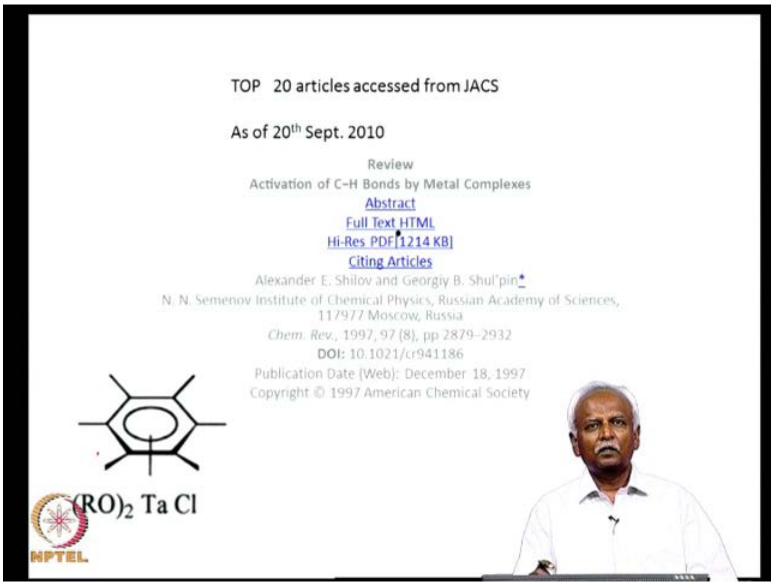

TOP 20 articles accessed from JACS

As of 20th Sept. 2010

Review
Activation of C–H Bonds by Metal Complexes
Abstract
Full Text HTML
Hi-Res PDF [1214 KB]
Citing Articles
Alexander E. Shilov and Georgiy B. Shul'pin*
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russia
Chem. Rev., 1997, 97 (8), pp 2879–2932
DOI: 10.1021/cr941186
Publication Date (Web): December 18, 1997
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$(RO)_2$ Ta Cl

Now, if you look at any one of these common journals, which are on the top of the list of any researcher like journal of American Chemical Society or Chemical Communications or the Ango Antichemy. These journals are journals which are publishing in the general area of chemistry and if you open any issue, you will find that there are at least two or three articles on organometallic chemistry. So, I have put for you to in this, in this projection here. Just one instance of article, written by Shilov and Shulpin about c h activation, this turns out to be a very important reaction, which has been made possible, because of organometallic compounds and organometallic chemistry.

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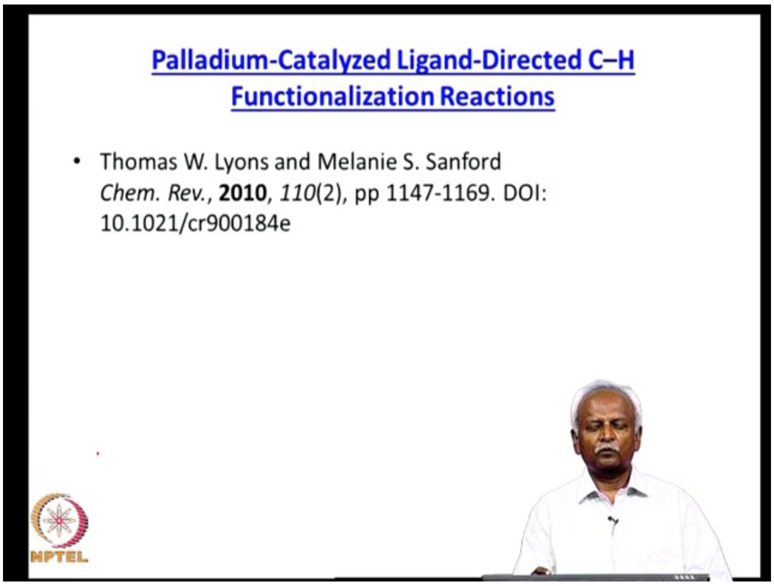

Palladium-Catalyzed Ligand-Directed C–H Functionalization Reactions

- Thomas W. Lyons and Melanie S. Sanford *Chem. Rev.*, **2010**, *110*(2), pp 1147-1169. DOI: 10.1021/cr900184e

So, you can see that once again, inorganic organometallic chemistry is extremely important in inorganic chemistry and chemistry in general once again early transition metals were shown to be good metals for transition metal c h activation. But recently it has been shown that even lead transition metals with appropriate set of ligands can carry out ligand directed c h activation reactions, and this work has been carried out by Melanie, Sanford and her co workers.

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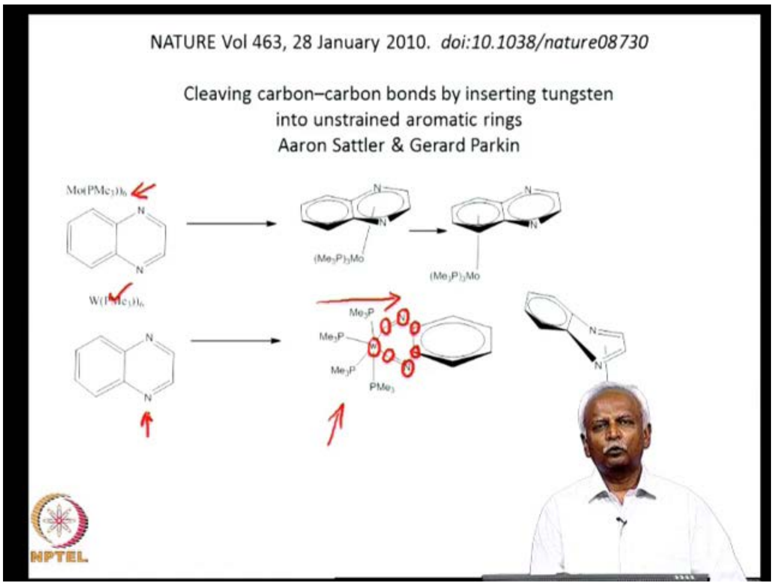

NATURE Vol 463, 28 January 2010. *doi:10.1038/nature08730*

Cleaving carbon–carbon bonds by inserting tungsten
into unstrained aromatic rings
Aaron Sattler & Gerard Parkin

If you look at the field of organic chemistry, it is not as if everything that needs to be discovered has been discovered. So, here I have a article which is appeared on the journal nature. You find that they have discovered something extraordinarily new, even in this last sixty years, what was not known has now been newly discovered. Here is an example of a reaction between a molybdenum complex, where molybdenum is in the 0 oxidation state and it has got 6 phosphorus ligands around it.

So, here is a ligand that we are here is a compound that we are talking about, when its reacted with this organic compound it forms a very interesting and novel complex, where the metal initially coordinates to the ring where there are 2 nitrogens. So, it is a phenazine ring that is having the nitrogen on the aromatic part of the ring, and then after some time if you heat it further. Then the molybdenum moves over to the ring which has got only the carbons.

So, here are some challenges about why this happens and what are the reasons which initially stabilise the nitrogen containing ring coordinated to the molybdenum. And later, what is the thermodynamic preference for the carbon containing ring. Interestingly, if you just move from molybdenum to tungsten, one would expect very similar reactivity, but surprisingly the same reaction which was carried out with tungsten, now suggests that the reactivity can be extremely different.

And you have extraordinarily novel compounds, where an aromatic ring system has been broken and the carbon-carbon ring has been broken, carbon-carbon bond has been broken and that to part of an aromatic ring and that forms a metallacycle. So, here is the set of atoms that we are talking about and that forms a ring and that ring turns out that ring is an aromatic ring. To start with, here is a ring and that has been broken by the tungsten. You can see that some extraordinarily novel complexes can be generated some things that challenge our understanding of chemistry in general and help us to think about what could be coming in the future.

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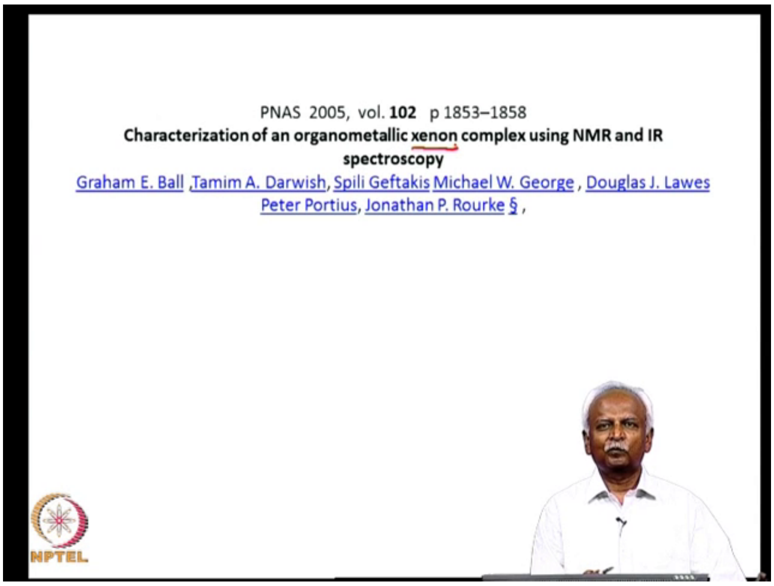

PNAS 2005, vol. **102** p 1853–1858

Characterization of an organometallic xenon complex using NMR and IR spectroscopy

Graham E. Ball ,Tamim A. Darwish, Spili Geftakis Michael W. George , Douglas J. Lawes
Peter Portius, Jonathan P. Rourke § ,

Here is another challenge that has come up very recently in 2005, Graham ball and co workers have shown that even xenon, which is 0 group element or an inert gas. What was originally considered as something that would not react with any other element, what was called inert gases or the 0 group that turns out to be a element, which can form an organometallic compound. Let us see what they have actually done.

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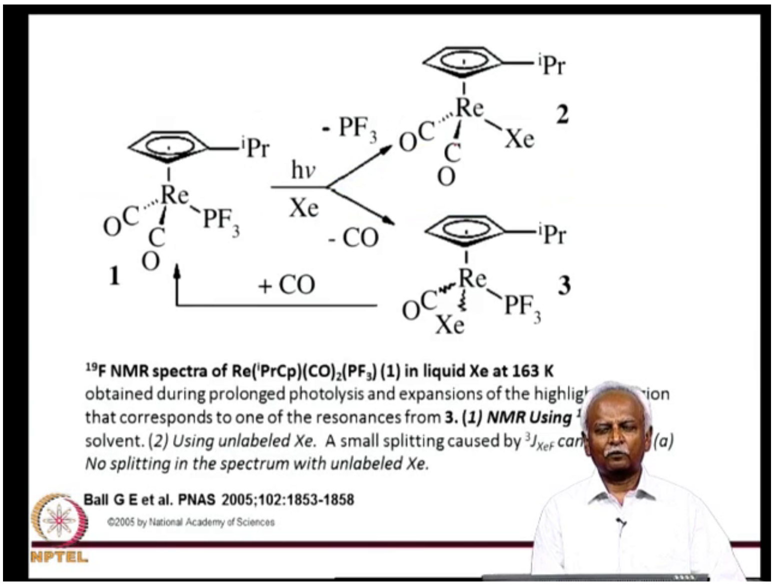

^{19}F NMR spectra of Re(^{i}PrCp)(CO)$_2$(PF$_3$) (1) in liquid Xe at 163 K obtained during prolonged photolysis and expansions of the highlig ion that corresponds to one of the resonances from **3.** ***(1) NMR Using*** solvent. *(2) Using unlabeled Xe.* A small splitting caused by $^{3}J_{XeF}$ *car* *(a) No splitting in the spectrum with unlabeled Xe.*

Ball G E et al. PNAS 2005;102:1853-1858

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Here is the reaction that they have carried out the rhenium complex, which was excited with a xenon flash lamp absorbs light and in the excited state loses one of the ligands if it loses the xenon. If it loses the carbon monoxide then this xenon appears to coordinate to the rhenium. In this particular state, it is possible to see the xenon phosphorus and xenon fluorine-coupling constant.

So, this was carried out by labelling the xenon, so they carried out a reaction in the presence of 128 xenon, which is NMR active and they were able to show that. In fact there is a covalent interaction between the xenon and the rhenium that is the only way in which, you can have this type of a weak coupling constant between the xenon and the fluorine.

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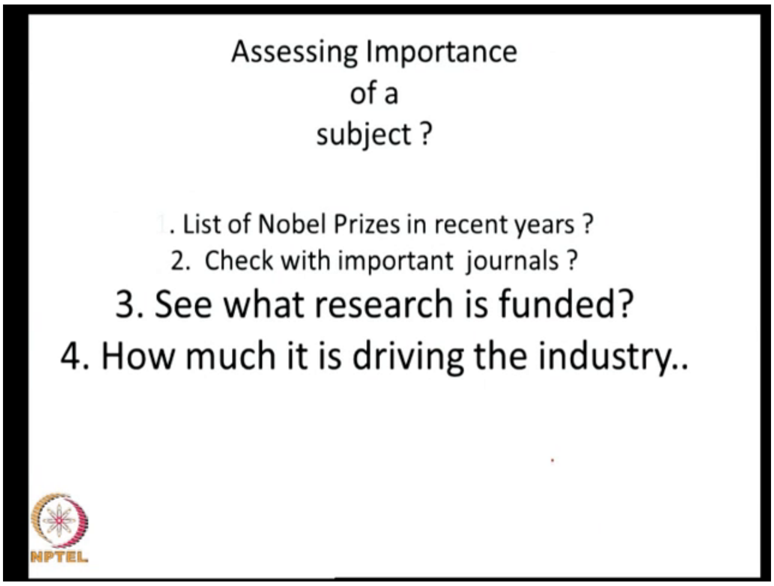

Assessing Importance
of a
subject ?

1. List of Nobel Prizes in recent years ?
2. Check with important journals ?
3. See what research is funded?
4. How much it is driving the industry..

So, you can see that there are surprises galore and there are challenges that have to be addressed in the field of organometallic chemistry. If you ask these two last questions, to see what research is funded, how much of it is driving the industry?

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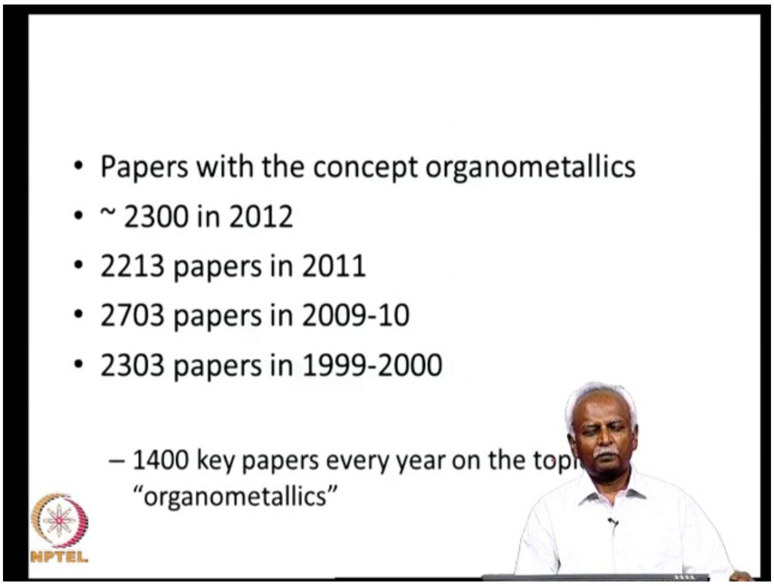

- Papers with the concept organometallics
- ~ 2300 in 2012
- 2213 papers in 2011
- 2703 papers in 2009-10
- 2303 papers in 1999-2000
  - 1400 key papers every year on the topi
    “organometallics”

Once again organometallic chemistry comes out on the top, you can take all the journals that publish organometallics. And you can see that the number of papers published are significantly large close to 2,400 papers have this concept of organometallic chemistry mentioned in their papers, or if you look at the key papers if you look at the topics that are mentioned. You see that organometallics are there in at least 1400 papers every year. So, it turns out that this is a very active field of research.

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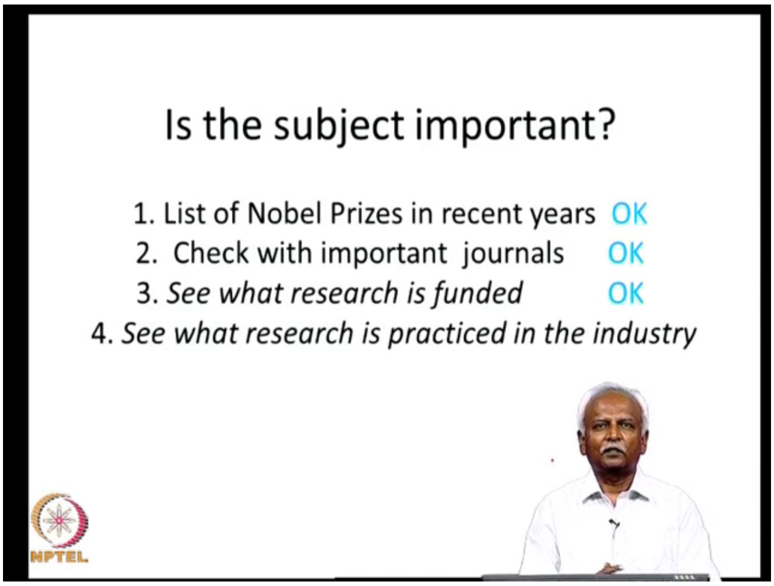

Is the subject important?

1. List of Nobel Prizes in recent years OK
2. Check with important journals OK
3. *See what research is funded* OK
4. *See what research is practiced in the industry*

And even if you look at the industry it looks as.

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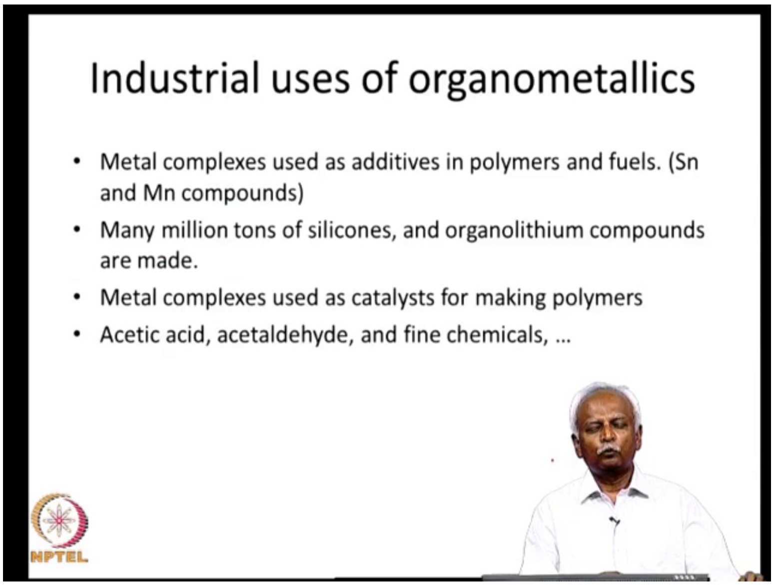

Industrial uses of organometallics

- Metal complexes used as additives in polymers and fuels. (Sn and Mn compounds)
- Many million tons of silicones, and organolithium compounds are made.
- Metal complexes used as catalysts for making polymers
- Acetic acid, acetaldehyde, and fine chemicals, …

If you have a large number of industries which employ organometallic compounds either as catalysts, or as additives and as part of the process which is there in the industry. So, here I have listed some of the silicones and organolithium compounds. Organolithium compounds are used significantly in fine chemical synthesis, silicones are used in various industrial applications and there elastomers and so on. Metal complexes are very commonly used for making polymers. Specially, poly propylene and poly ethylene which are made in tonnage quantities.

These molecules are made using organometallic catalysts which are basically the result of Zeigler, Natta’s work and then there are other small molecules like acetic acid acetaldehyde. Several other small molecules which are generated from carbon monoxide, hydrogen and readily available starting materials and this is again made possible by organometallic compounds. We will some of these reactions and how these are how these unique reactions are made possible, because of organometallic chemistry.

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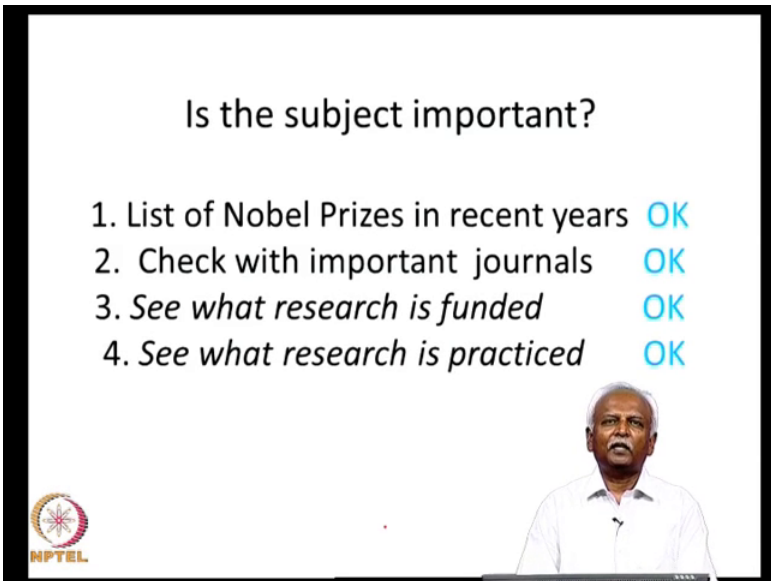

Is the subject important?

1. List of Nobel Prizes in recent years OK
2. Check with important journals OK
3. *See what research is funded* OK
4. *See what research is practiced* OK

So, we have looked at a variety of questions, are there Nobel prizes, are there important papers published in journals, is this research well funded and what is practised in the industry? In all these cases we have come up with positive answers for the field of organometallic chemistry.

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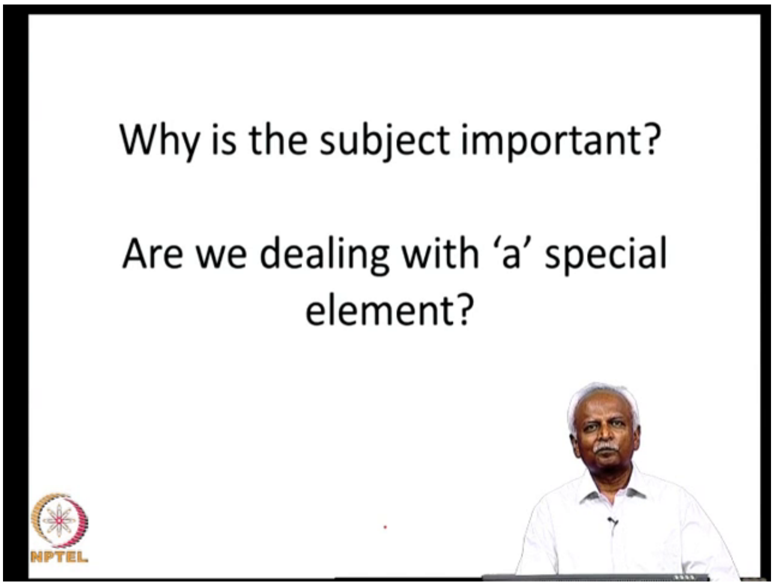

Why is the subject important?

Are we dealing with 'a' special element?

Now, we ask the question why is this subject so important? Are we dealing with a special element? Organic chemistry, for example deals with this very special element of carbon. What about organometallic chemistry, is it the same fact is it because of carbon?

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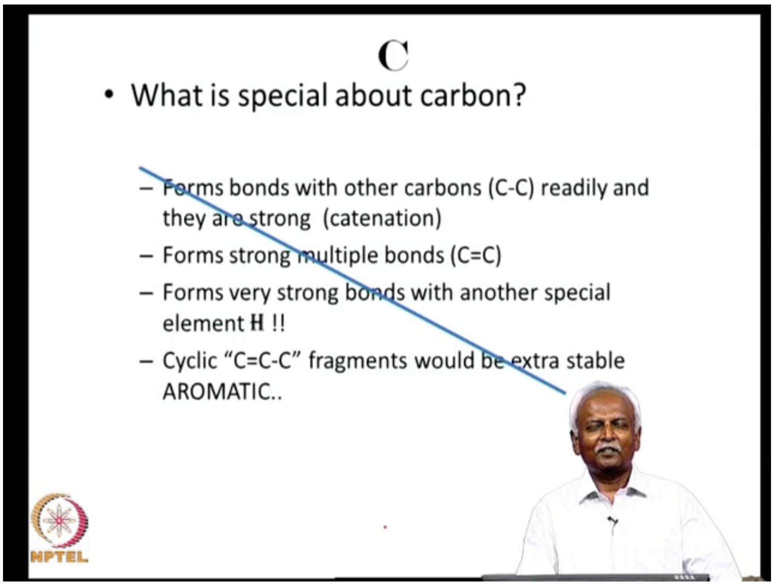

C

- What is special about carbon?
  - Forms bonds with other carbons (C-C) readily and they are strong (catenation)
  - Forms strong multiple bonds (C=C)
  - Forms very strong bonds with another special element **H** !!
  - Cyclic "C=C-C" fragments would be extra stable AROMATIC..

So, if I ask the question, what is special about carbon you would probably come up with these answers, which I have listed here carbon is unique because it forms bonds to other carbon. It forms strong multiple bonds and it forms strong multiple bonds to in a cyclic fashion, so that the molecules are called aromatic. So, if I list all these things I would still say this is not the reason why organometallic chemistry is so special?

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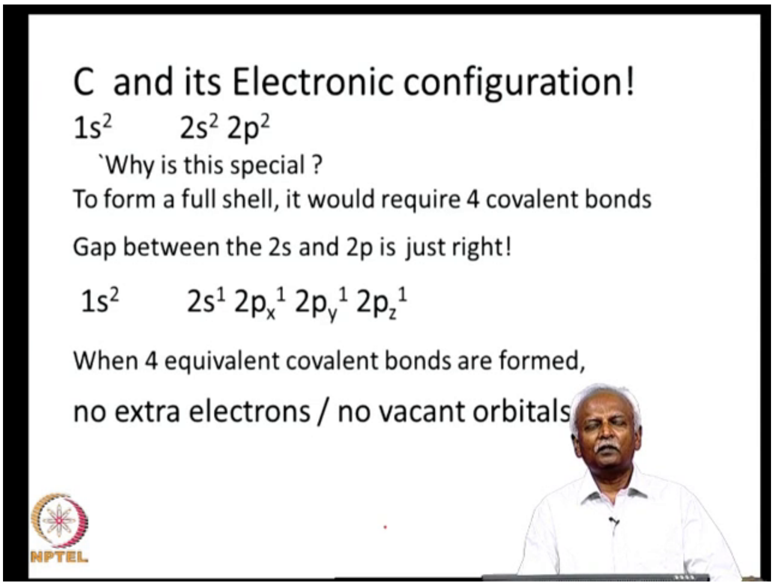

C and its Electronic configuration!

$1s^2$ $2s^2$ $2p^2$

`Why is this special ?

To form a full shell, it would require 4 covalent bonds

Gap between the 2s and 2p is just right!

$1s^2$ $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$

When 4 equivalent covalent bonds are formed,

no extra electrons / no vacant orbitals

Carbon has in fact, an electronic configuration of 1 s 2 2 s 2 and 2 p 2. This is in fact special, why the answer is that when it forms 4 covalent bonds, in order to generate the nobel gas configuration the molecule can do so by hybridising 2 s and 2 p. The gap between 2 s and 2 p orbitals are just right. So, the promotion of the electrons from the 2 s and 2 p orbitals are easy and 4 equivalent covalent bonds are formed. That leaves carbon with no extra electrons and no vacant orbitals, this is extremely important and this probably a fundamental fact which makes carbon a unique element.

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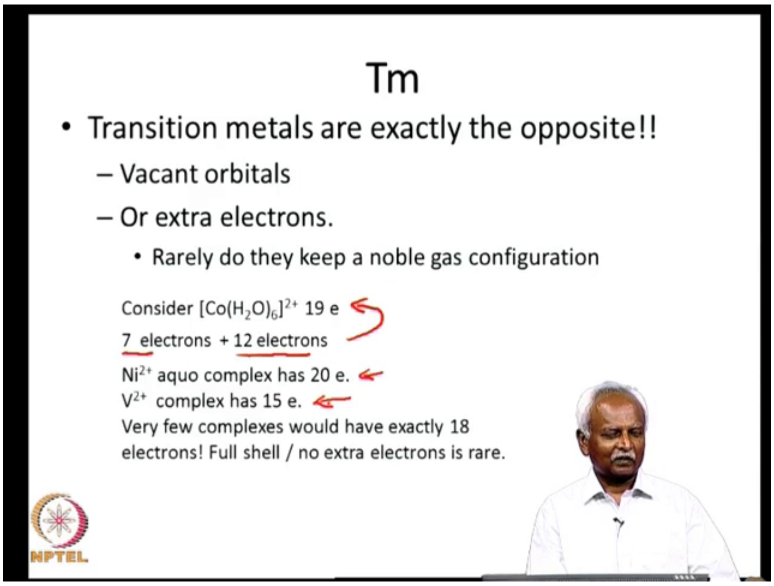

Tm

- Transition metals are exactly the opposite!!
  - Vacant orbitals
  - Or extra electrons.
    - Rarely do they keep a noble gas configuration

Consider $[Co(H_2O)_6]^{2+}$ 19 e

7 electrons + 12 electrons

Ni^{2+} aquo complex has 20 e.

V^{2+} complex has 15 e.

Very few complexes would have exactly 18 electrons! Full shell / no extra electrons is rare.

Now, when it comes to transition metals, you will notice that transition metals are exactly the opposite. They always have vacant orbitals almost always or they have extra electrons, rarely do they keep a Nobel gas configuration. In the case of transition metals the Nobel configuration would usually be an 18 electron configuration. Here I have shown for you some of the stable coordination compounds that are available in the literature most of them are octahedral complexes formed by the 3 d transition elements 3 d 2 plus ions or 4 d 2 plus ions or 3 plus ions. You will notice, that many of them or most of them are not 18 electron species to look at the valence electron count, you just count the number of valence electrons on the cobalt.

If it is cobalt 2 plus then you would have seven electrons and with 6 water molecules it each one of them would donate 2 electrons each. So, if you add up you would end up with a valence electron count of 19, so that is 1 more than 18. Similarly, for nickel it would be 20 for the vanadium aquo complex it would be 15, so very few complexes would really have 18 electrons. So, it neither has a full shell and it always many times it has less than 18 or more than 18.

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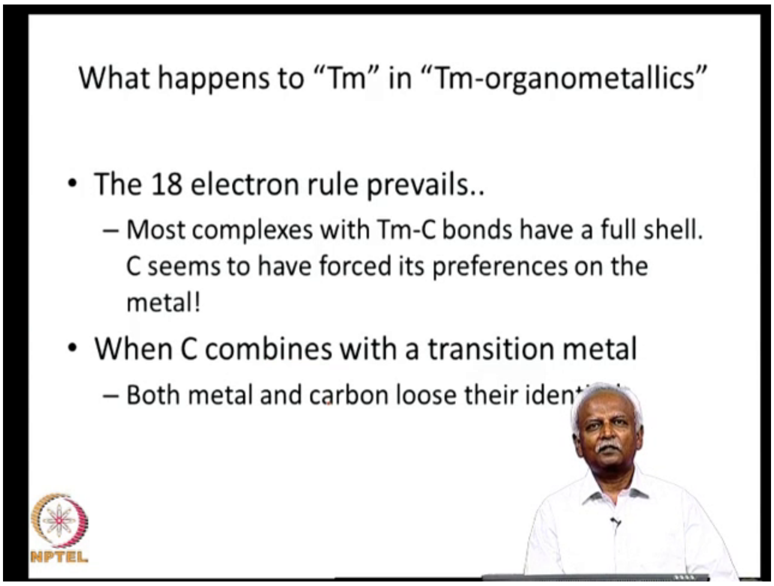

What happens to "Tm" in "Tm-organometallics"

- The 18 electron rule prevails..
  - Most complexes with Tm-C bonds have a full shell. C seems to have forced its preferences on the metal!
- When C combines with a transition metal
  - Both metal and carbon loose their ident

So, what happens in transition metals, to the transition metal, in transition metal organometallics? If you look at most of the compounds, they follow the 18 electron rule so much, so that it is important for us to look at this rule briefly, to see how this rule can be verified, when we write a structure to see if it would be a stable compound. Most complexes with transition metal carbon bonds force this preference, so they always have an 18 electron count. When carbon combines with the transition metal, both the metal and the carbon lose their identity. In what way has carbon lost its identity?

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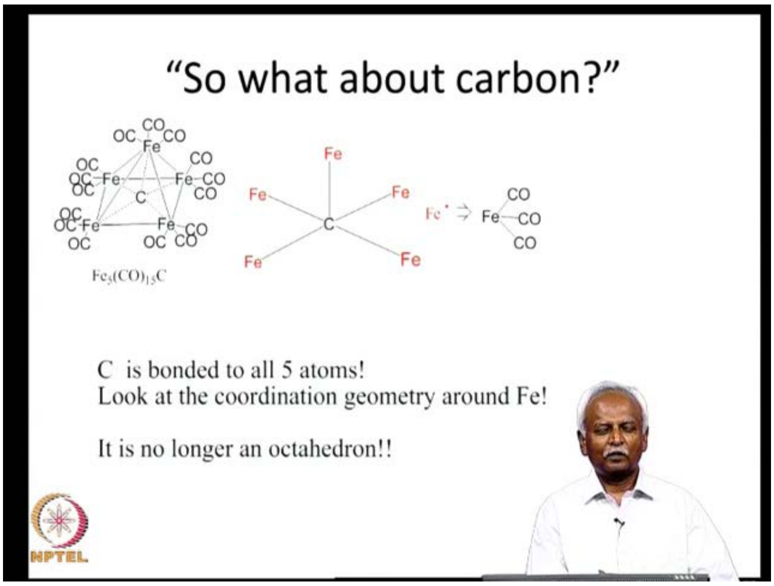

"So what about carbon?"

$Fe_5(CO)_{15}C$

C is bonded to all 5 atoms!
Look at the coordination geometry around Fe!

It is no longer an octahedron!!

So, here is the an organometallic compound that I want to show you for just illustration of the fact that carbon, in this molecule, is in a very strange environment very rarely would carbon or rather almost always, it would have a 4 coordinate geometry and that also it would be a tetrahedral geometry. If it has only single bonds, but here is a molecule where carbon is having 5 atoms around itself. Now, look at the coordination geometry around the iron that is no longer octahedral either, so that has got geometry, which is non octahedral and the carbon has got a geometry which is non tetrahedral.

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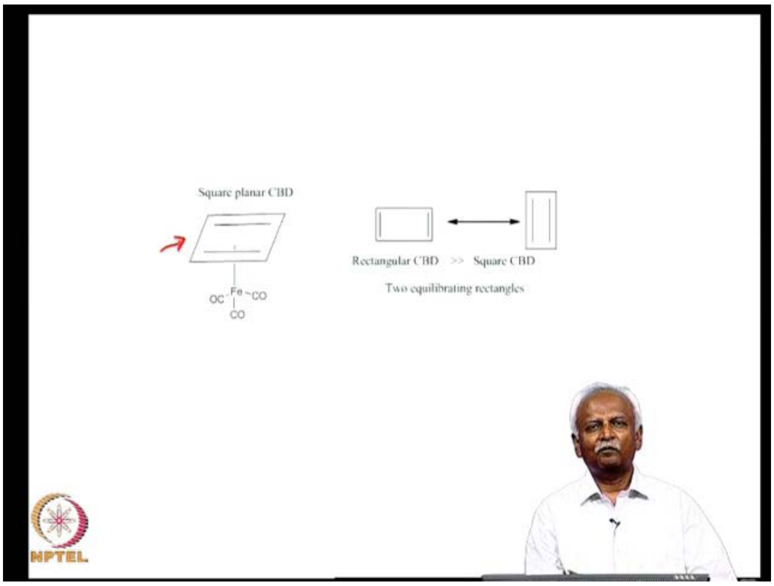

Square planar CBD

Rectangular CBD >> Square CBD

Two equilibrating rectangles

So, both carbon and the transition metal lose their identity. So, here is another example, we all know that cyclobutadiene is a rectangular molecule, because if it is square it would be anti aromatic. So, it turns out to be equilibrating between 2 rectangles structures and when it forms a iron carbonyl complex lone be hold it changes its character, it keeps a strictly square structure of 4 carbon atoms. So, you can see that now carbon has lost its character of being anti aromatic when it has got 5 n pi electrons.

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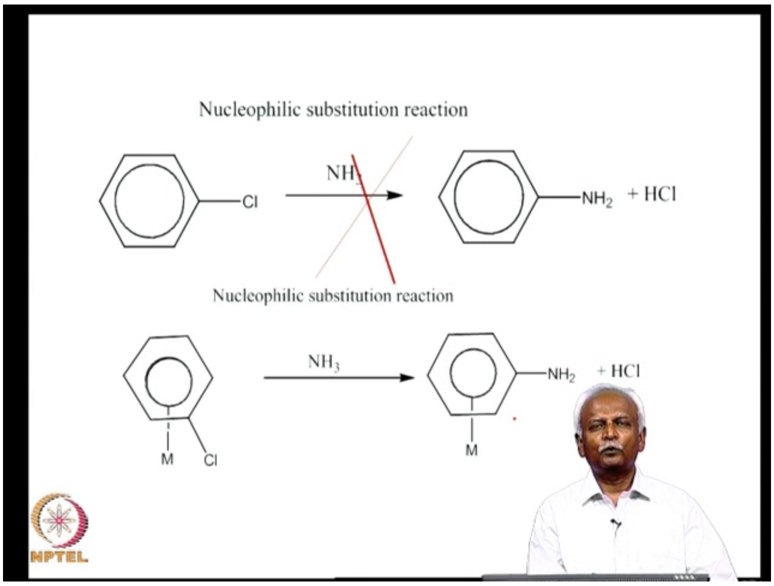

Nucleophilic substitution reaction

Nucleophilic substitution reaction

So, here is another example which is from an aromatic molecule like chlorobenzene, if you treat it with ammonia and heat it any amount, it will not carry out such a nucleophilic substitution. Nucleophilic substitution for an aromatic compound is not possible in classical organic chemistry, but if you do this with a transition metal attached to the aromatic ring, it is now possible to carry out this simple nucleophilic substitution. So, nucleophilic substitutions which were not possible in classical organic chemistry now becomes easy when you have a transition metal coordinated to the ring system.

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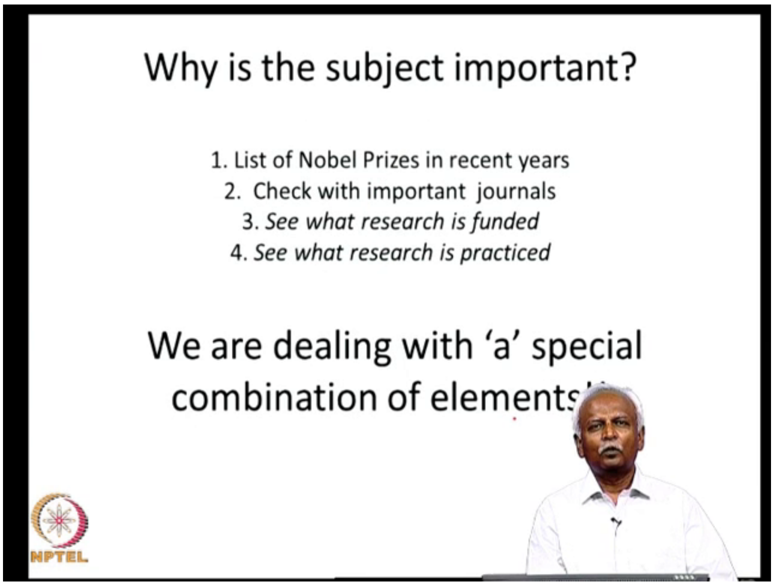

Why is the subject important?

1. List of Nobel Prizes in recent years
2. Check with important journals
3. *See what research is funded*
4. *See what research is practiced*

We are dealing with ‘a’ special combination of elements

So, are we dealing with a special element? The answer is probably no, we are dealing with a special combination of elements.

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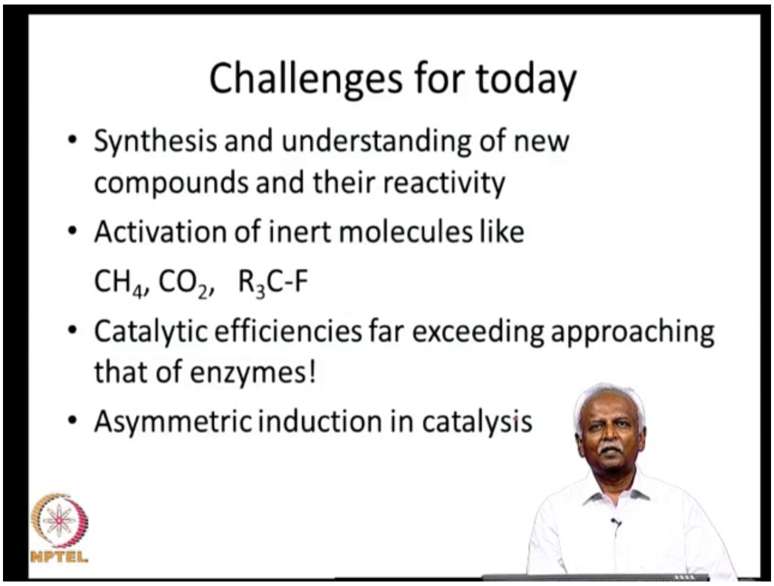

Challenges for today

- Synthesis and understanding of new compounds and their reactivity
- Activation of inert molecules like CH_4, CO_2, $R_3C\text{-}F$
- Catalytic efficiencies far exceeding approaching that of enzymes!
- Asymmetric induction in catalysis

The combination of transition metals and carbon. So, there are very interesting challenges which this combination throws at us. First of all, we can synthesise some new and interesting molecules, which have extraordinarily new interesting reactivity patterns, what was not possible with classical organic chemistry. Activation of inert molecules for example, methane or even carbon dioxide or the carbon fluorine bond, turn out to be challenges which are still being handled by organometallic chemists. There are other things also like catalysis.

Catalysis by organometallic chemistry is quite popular it is indeed feasible, but can we approach the efficiencies of enzymes? Can we use organometallic compounds to catalyse reactions at extremely fast rates? Finally, asymmetric induction and catalysis is also a major challenge and as I had mentioned just briefly, it was for this contribution that three people received the Nobel prize in 2005.

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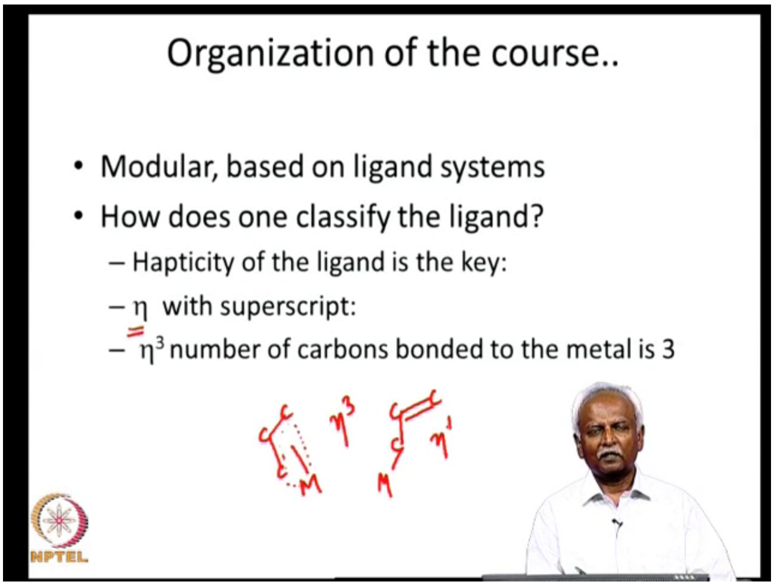

Organization of the course..

- Modular, based on ligand systems
- How does one classify the ligand?
  - Hapticity of the ligand is the key:
  - η with superscript:
  - η^3 number of carbons bonded to the metal is 3

I want introduce to you now to the organisation of this course as much as possible we have kept it modular based on the ligand systems. Now, so one would ask the question how are the ligands classified in organometallic chemistry? The ligands are classified according to the hapticity. Hapticity is indicated by the symbol eta and eta indicates the number of carbon bonds, number of carbon metal bonds that can be seen when you have a transition metal organometallic compound.

If I have a 3 carbon framework and if all 3 carbons are within bonding distance if all 3 carbons are within bonding distance to the metal. Then I would call this an eta 3 compound whereas, if the same compound is present in such a way that the metal is interacting with only 1 carbon. If it is interacting with only 1 carbon then I would call it a eta 1 compound. So, the hapticity of the ligand is really a key to understanding and unravelling organometallic compounds and many times the hapticity can change. This is called fluxional behaviour and this is something, which we deal with during the course of this particular set of lectures.

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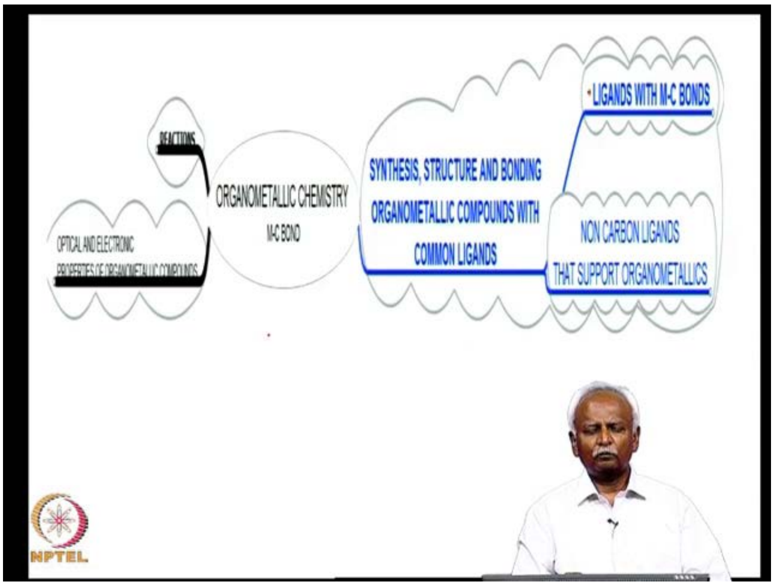

REACTIONS

OPTICAL AND ELECTRONIC
PROPERTIES OF ORGANOMETALLIC COMPOUNDS

ORGANOMETALLIC CHEMISTRY
M-C BOND

SYNTHESIS, STRUCTURE AND BONDING
ORGANOMETALLIC COMPOUNDS WITH
COMMON LIGANDS

- LIGANDS WITH M-C BONDS

NON CARBON LIGANDS
THAT SUPPORT ORGANOMETALLICS

Let me just now show you how we have organised the lectures. In many text books synthesis structure and bonding of organometallic compounds with common ligands are shown in initially and then we have reactions and we have properties. Now, in this course during the course of these lectures, we will not strictly follow this order, but let me introduce to you the way in which the ligands with metal carbon bonds are classified. Let us take a look at that first and then we will see how we have presented the topics in this particular course.

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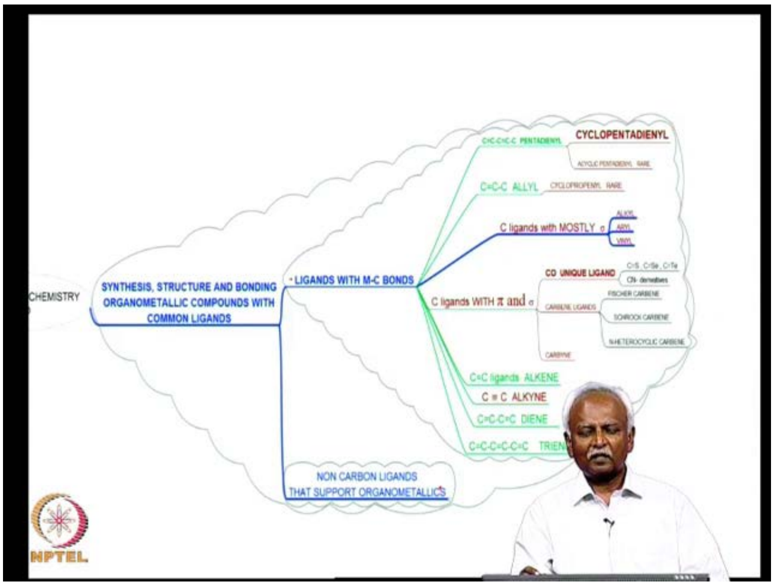

CHEMISTRY

SYNTHESIS, STRUCTURE AND BONDING
ORGANOMETALLIC COMPOUNDS WITH
COMMON LIGANDS

- LIGANDS WITH M-C BONDS

C=C-C=C-C PENTADIENYL
CYCLOPENTADIENYL
ACYCLIC PENTADIENYL RARE

C=C-C ALLYL
CYCLOPROPENYL RARE

C ligands with MOSTLY σ
ALKYL
ARYL
VINYL

C ligands WITH π and σ
CO UNIQUE LIGAND
C=S, C=Se, C=Te
CN- derivatives
CARBENE LIGANDS
FISCHER CARBENE
SCHROCK CARBENE
N-HETEROCYCLIC CARBENE
CARBYNE

C=C ligands ALKENE
C ≡ C ALKYNE
C=C-C=C DIENE
C=C-C=C-C=C TRIEN

NON CARBON LIGANDS
THAT SUPPORT ORGANOMETALLICS

Ligands with metal carbon bonds, if we only look at the metal carbon bonds, you have a very large number, but based on hapticity you can see that many of them or a large significant number of them have got a single carbon attached to the metal. These are all eta 1, eta 1 carbon ligands. So, they can be alkyl aryl or for that matter vinyl and you can also have small ligands like carbon monoxide and carbenes, carbon monoxide and carbenes are all single carbon bonded systems.

Then you have the odd number of carbons attached to the metal on the top, these are odd and then I have listed for you even number of carbons attached to the metal on the lower half. So, you will notice that the odd carbon attached metal complexes are usually indicated as anionic ligands and we will talk about the nature of this interaction in a few minutes. On, the other hand even carbon atoms that are linked to the metal are usually neutral ligands and many of them are known with transition metal, are interacting with them.

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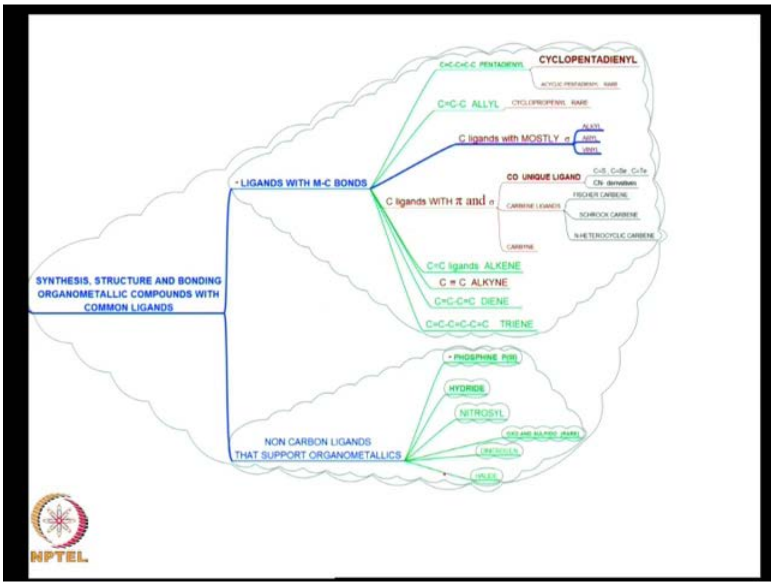
SYNTHESIS, STRUCTURE AND BONDING ORGANOMETALLIC COMPOUNDS WITH COMMON LIGANDS

• LIGANDS WITH M-C BONDS

C=C-C=C-C PENTADIENYL

CYCLOPENTADIENYL

ACYCLIC PENTADIENYL RARE

C=C-C ALLYL

CYCLOPROPENYL RARE

C ligands with MOSTLY σ

ALKYL

ARYL

VINYL

C ligands WITH π and σ

CO UNIQUE LIGAND

C=S, C=Se, C=Te

CN derivatives

CARBENE LIGANDS

FISCHER CARBENE

SCHROCK CARBENE

N-HETEROCYCLIC CARBENE

CARBYNE

C=C ligands ALKENE

C ≡ C ALKYNE

C=C-C=C DIENE

C=C-C=C-C=C TRIENE

NON CARBON LIGANDS THAT SUPPORT ORGANOMETALLICS

• PHOSPHINE P(III)

HYDRIDE

NITROSYL

Many of them are known where transition metals are interacting with even number of carbons and then there are non carbon ligands which support organometallic chemistry. This is the situation where there is 1 metal carbon bond, but the rest of the metal complex has got either a ligand with a phosphorous or a hydride or a nitrosyl. These do not have a metal carbon bond by themselves, but nevertheless they support organometallic chemistry or modify the properties of the organometallic chemistry, so much, so that we need to know a little bit about the chemistry of these molecules. If we have to understand organometallic chemistry. So, we are going to deal with these ligands as well.

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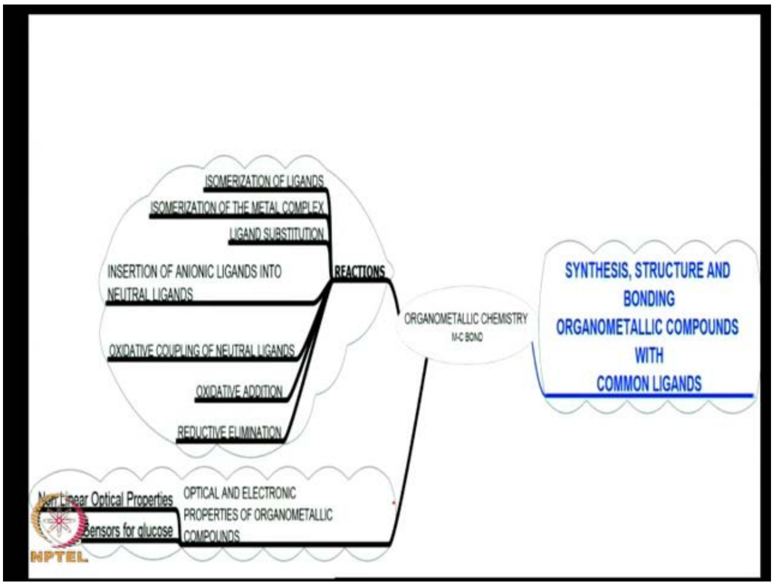

ISOMERIZATION OF LIGANDS
ISOMERIZATION OF THE METAL COMPLEX
LIGAND SUBSTITUTION
INSERTION OF ANIONIC LIGANDS INTO NEUTRAL LIGANDS
OXIDATIVE COUPLING OF NEUTRAL LIGANDS
OXIDATIVE ADDITION
REDUCTIVE ELIMINATION
REACTIONS
ORGANOMETALLIC CHEMISTRY
M-C BOND
SYNTHESIS, STRUCTURE AND BONDING ORGANOMETALLIC COMPOUNDS WITH COMMON LIGANDS
Non Linear Optical Properties
Sensors for glucose
OPTICAL AND ELECTRONIC PROPERTIES OF ORGANOMETALLIC COMPOUNDS

Now, if you look at the reactions once again we can go from the simple ligands. The reactions of the simple ligands to the more complex, but it is more convenient to classify them by the type of reactions that they undergo. The simplest of course is, substitution and isomerisation. These are listed for you on the top followed by what is unique to transition metal organometallic chemistry which is called insertion reaction. So, normally insertion of an anionic ligand occurs when the anionic ligand migrates to the neutral ligand.

We will look at these reactions and we will do that right after we talk about metal carbon containing compounds, where there is only a single carbon attached to the metal. Subsequently, we can also see that there can be an oxidation state change in the transition metal, when you have an organometallic compound. So, you have oxidative coupling of neutral ligands like a carbene and an olefin that is the basis for the famous metathesis reaction. Then you can also have oxidative additions of molecules like methyl iodide and elimination of such molecules including the elimination of two atoms of hydrogen. For example, on a metal that would result in reductive elimination.

Here there is a oxidation state change on the transition metal, so initially we will consider those reactions where there is no change in oxidation change, and then we will look at those where there is a change. If you look at the properties there are several properties which are very interesting for organometallic compounds, we will not be always dealing with these with with these examples. But towards end of the course we will deal with some cases, where organometallic chemistry has turned out to be an extremely important and valuable addition to the arsenal of the chemist.

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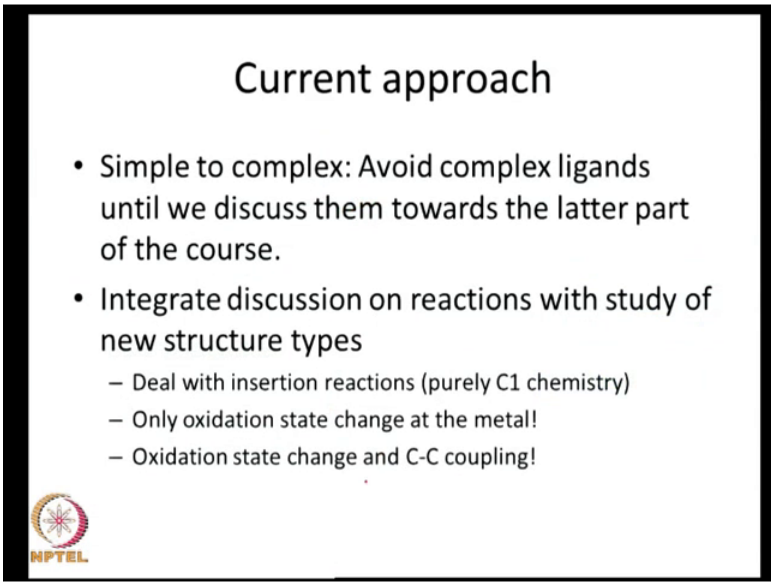

Current approach

- Simple to complex: Avoid complex ligands until we discuss them towards the latter part of the course.
- Integrate discussion on reactions with study of new structure types
  - Deal with insertion reactions (purely C1 chemistry)
  - Only oxidation state change at the metal!
  - Oxidation state change and C-C coupling!

So, in the current approach we will avoid, we will try to deal with these ligands in a systematic fashion going from the simple to the complex ligands until, we discuss the complex ligands, we will not introduce them as much as possible in the early part of the course. We will try to integrate the discussion on reactions with the new structure types. I found that this keeps the interest of the person studying this subject, so that first we do not deal with completely structures and then move completely over to reactions. So, there has been an integration done of the reactions and the structures, and you will see the value of doing that in a structured fashion.

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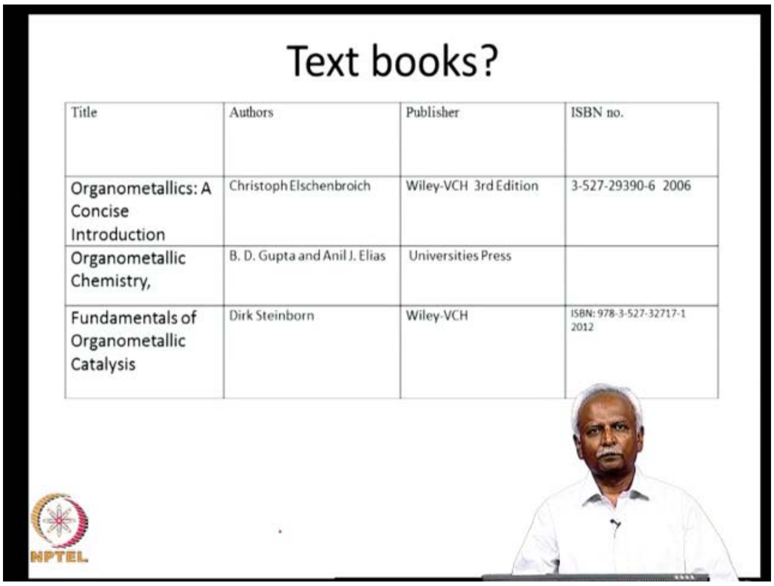

Text books?

Title	Authors	Publisher	ISBN no.
Organometallics: A Concise Introduction	Christoph Elschenbroich	Wiley-VCH 3rd Edition	3-527-29390-6 2006
Organometallic Chemistry,	B. D. Gupta and Anil J. Elias	Universities Press	
Fundamentals of Organometallic Catalysis	Dirk Steinborn	Wiley-VCH	ISBN: 978-3-527-32717-1 2012

So, when it comes to text books that are available in the literature, there are several new text books that have appeared, but I would strongly recommend that if you are a serious if you are a serious organometallic chemistry student. Serious chemistry student that you would have at least one book on organometallic chemistry and in recent times there is a book on organometallic chemistry that has been written by B D Gupta and Anil Elias, which has been published by Universities Press, which is quite affordable and available ready available for the chemist.

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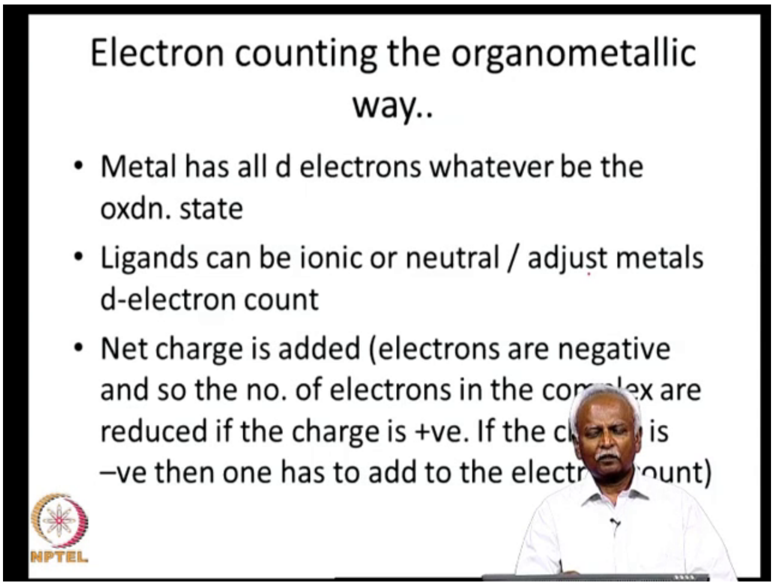

Electron counting the organometallic way..

- Metal has all d electrons whatever be the oxdn. state
- Ligands can be ionic or neutral / adjust metals d-electron count
- Net charge is added (electrons are negative and so the no. of electrons in the co lex are reduced if the charge is +ve. If the c is –ve then one has to add to the electr ount)

So, let us take a look at electron counting, the organometallic chemist way and unfortunately, as I had hinted earlier there are two ways in which the organometallic chemist or some organometallic chemist count the number of d electrons, which are accessible to the metal. So, let us take a look at some of these methods. First, we should mention that these counting rules are only to keep track of the number of electrons, they are not to be confused with the charge that is present on the metal or for example, on the ligand.

Nevertheless, we will talk about ligands as if they are ionic or as if they are neutral and this book keeping is important only for us to find out, if the molecule will be stable or will it undergo some reactions or will it undergo some redox reactions with other oxidants or reductants. When you want to look at a metal complex which has got a net charge, these electrons are usually, if you have excess electrons then they are added to the metal atom, so that you have a the total net charge of the species, which is inside the square bracket matches, the charge which is present outside the square bracket.

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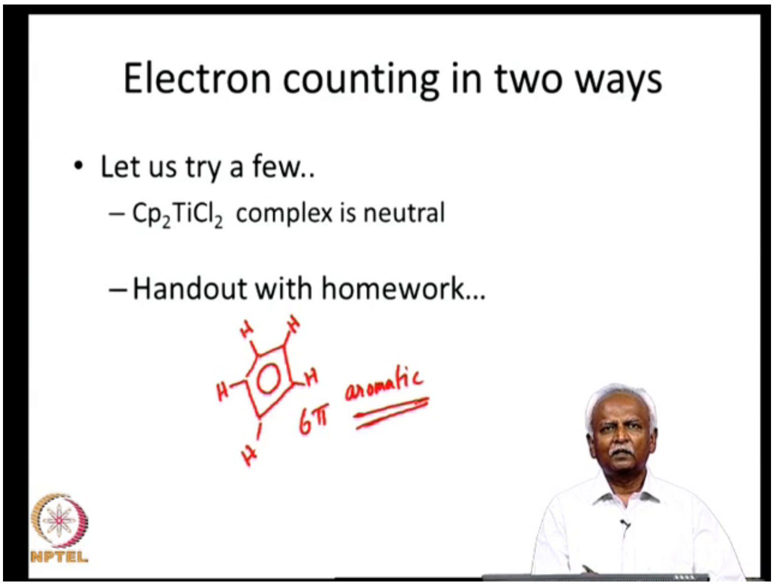

Electron counting in two ways

- Let us try a few..
  - Cp_2TiCl_2 complex is neutral
  - Handout with homework...

Let us take a few examples and then this would become fairly clear. If you take a simple complex like Cp 2 cI Cl 2 ((Refer Time 37:24)) Cp stands for the cyclopentadienyl ligand. So, cyclopentadienyl ligand is a system which has got 5 carbons and because it is c 5 h 5 minus, it is obvious see that this has got 6 pi electrons and if it has 6 pi electrons it is an aromatic ligand system. Now, it turns out that this aromatic ligand system will readily coordinate to a variety of metals and if it coordinate 2 of them coordinate to titanium you can have this complex Cp 2 Ti Cl 2.

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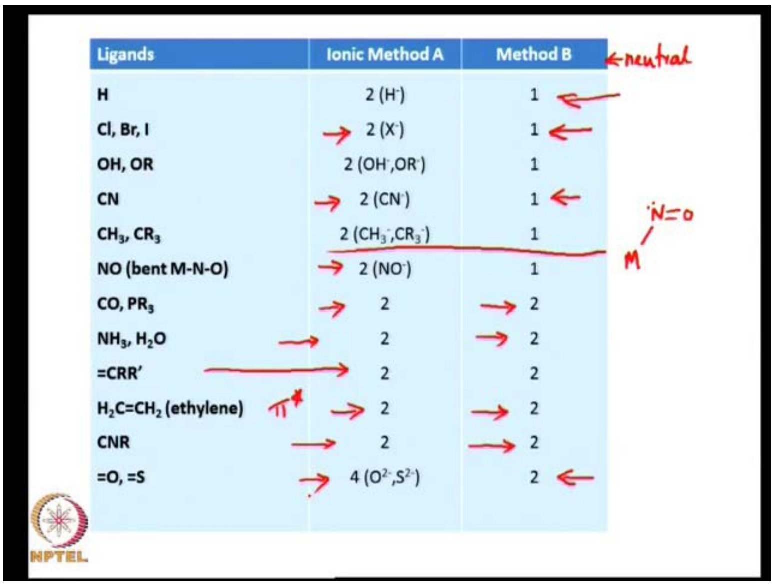

Ligands	Ionic Method A	Method B
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^-,OR^-)	1
CN	2 (CN^-)	1
CH_3, CR_3	2 (CH_3^-,CR_3^-)	1
NO (bent M-N-O)	2 (NO^-)	1
CO, PR_3	2	2
NH_3, H_2O	2	2
=CRR’	2	2
$H_2C{=}CH_2$ (ethylene)	2	2
CNR	2	2
=O, =S	4 (O^{2-},S^{2-})	2

Now, let us take look at the set of ligands where we have for us the two methods listed out. So, let us go from the simple ligands. If you have a ligand like hydrogen then in the ionic method you would assign it a charge of minus 1, if it has a charge of minus 1 hydrogen already has 1 electron around it and, so a minus 1 charge will necessarily mean that it has got 2 electrons, so this turns out to be a 2 electron donor.

Whereas, in the neutral method, this is the neutral method, you would only count the number of electrons which are there on the on the ligand to start with, you would not assume,you would not attribute a charge to the ligand if when it is not there. Here, for example, for hydrogen we would indicate that it is a 1 electron ligand. Now, you might wonder why do we confuse this issue by having h minus. Very often hydrogen is more electronegative than the metal, so when it is coordinated to the metal the assumption is that hydrogen acquires 1 electron from the metal. So, the metal becomes plus 1 and hydrogen becomes minus 1, so 1 electron is transferred from the metal to the hydrogen, so this turns out to be correct.

For example, in the next case when you have a halogen, it is very obvious that halogen is extremely electronegative and if so, when it coordinates to an electropositive element like a metal, then it will acquire a negative charge and it will become x minus. So, all halogens are indicated as 2 electron donors, but in the neutral method you still count it as a 1 electron ligand.

You can see that none of these methods either the ionic method or the neutral method is a perfect method both methods have their advantages and disadvantages, but what is interesting and what is important is that you use the methods consistently. You could not use the ionic method for some ligands in a metal complex and the neutral method, for some other ligands in the same complex, that would lead to a wrong result.

So, let us take a look at some of the other ligands which are listed here. Cyanide for example, is a electronegative group and it is it is indicated as CN minus and it is usually bonded through the carbon it is in the ion neutral method it is considered still as 1 electron ligand. Each of the metal radicals or any alkyl radicals it is indicted as an anionic species, this again turns out to be confusing at times, because carbon can be just as electronegative as a metal atom or sometimes it can even be less electronegative. But still we consider by convention carbon to be more electronegative and indicated as an anionic ligand.

All these species turn out to be simple species where you have a 1 electron donor and the neutral method and 2 electrons in the ionic method. Next comes carbon monoxide. Let us leave nitric oxide for the moment and deal with carbon monoxide. Carbon monoxide has got a lone pair on the carbon and of carbon monoxide and that means it donates 2 electrons. Here we have no confusion between the ionic method and the neutral method both of them suggest that 2 electrons are donated from the ligand to the metal.

Similar is the case for ammonia or water they are 2 electron donors, whether there are neutral or ionic it does not matter which method you use a carbene which is, what is indicated here carbene is also a 2 electron donor. So, you can imagine a carbene as a carbon containing a lone pair of electrons, that can donate 2 electrons in either method. Subsequently, we should look at isocyanides.

Here are isocyanides and isocyanides again have got a lone pair of electrons situated on the carbon. So, they are they are not confusing there will be 2 electron donors whether you consider them in method a which is ionic method or the method b which is the neutral method. So, ethylene is a molecule which is an unsaturated organic molecule, which has got a pair of electrons in the pi orbital and this can donate a pair of electrons.

So, we have a neutral species which is giving 2 electrons. Now, let us come back to nitric oxide.

Nitric oxide, because nitrogen is more electronegative, it can transfer an electron from the metal to the NO and then it will become NO minus. And this 1 electron that was sitting in the anti bonding orbital will now have another electron in the same orbital and these 2 electrons can be donated to the metal. So, NO, if it is specially if it is in a bent form. So, if the metal is having a bent NO then we end up calling it as a nitrosyl, bent nitrosyl which can donate 2 electrons and it is counted as a negative ligand.

In the ionic method in the neutral method of course, we will consider that only as a one electron donor oxo and sulphide oxido and sulphido ligands are rarely encountered in organometallic chemistry, but they are all 2 electron donors, when it comes to the neutral method and when it comes to the ionic method. Now, it will have to be considered as 4 electron donors. So, I guess this set of this classification helps you to follow the general trend, which is there in the literature.

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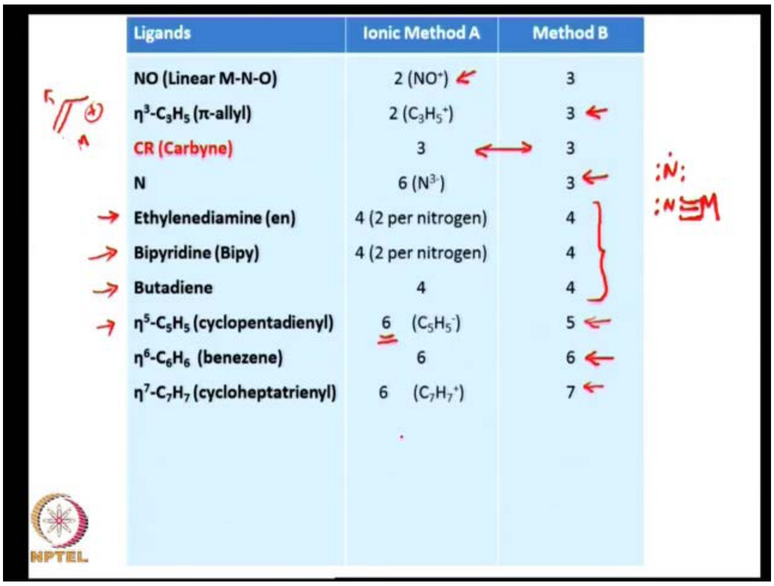

Ligands	Ionic Method A	Method B
NO (Linear M-N-O)	2 (NO^+)	3
η^3-C_3H_5 (π-allyl)	2 ($C_3H_5^+$)	3
CR (Carbyne)	3	3
N	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (Bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
η^5-C_5H_5 (cyclopentadienyl)	6 ($C_5H_5^-$)	5
η^6-C_6H_6 (benezene)	6	6
η^7-C_7H_7 (cycloheptatrienyl)	6 ($C_7H_7^+$)	7

They might either use the ionic method or the neutral method in order to assign the electron count. Now, in this next panel I have now for you a linear nitric oxide. A linear nitric oxide is a system where 1 electron from the nitric oxide anti bonding orbital is transferred from the ligand completely to the metal. Sometimes in the ionic, not sometimes, but always in the ionic method you will consider that as NO plus. So, this is a first example that we are considering where the ligand is positively charge.

Although, NO is more electronegative as a group than a metal atom. If it is a linear nitric oxide then it turns out that you can transfer the electron completely to the metal and you consider that as a 2 electron donor which is positively charged. Similarly, an allyl group can be considered as a 2 electron donor if it is positively charged and that is quite obvious, because you would have a double bond and then a positive charge at the allylic position, so it would have only 2 electrons which it can donate to the metal. Carbines are unusual we will leave them for the moment and look at other examples.

These are classical ligands ethylenediamine, bipyridine, butadiene is just an extension of ethylene. So, all of them will give 4 electrons each, whether they are in the ionic method or the neutral method. Similarly, benzene will give 6 pi electrons and that is again for the sake of electron count, it is not as if the electron is completely transferred to the metal. Where as in the case of C 5 H 5 minus, it is obvious that the metal will be positively charged and the ring system will be negatively charged. So, you have a 6 electron donor in the case of the cyclopentadienyl anion. In the neutral method they do a bit of violence to this concept and we say that it gives only 5 electrons.

Now, there are some advantages in using the neutral method, because it is easy to forget the fact that the metal is changing its role or the ligand is changing its role, we just count the number of atoms which are coordinated to the metal and keep that as a number of electrons that are donated to the metal. So, C 7 H 7 for example, we would not have to consider whether it is aromatic or not.

If all 7 carbon atoms are bonded to the metal then we consider that as a 7 electron donor. Now, let us come back to the nitride case. This is a example where in a simple minded fashion if you use a neutral method you would think that there are 3 electrons, which are donated to the metal. So, in other words there are totally 5 electrons which are there for the nitrogen.

This is the valence shell, but if you consider this as a nitrido ligand, then you would write it with a triple bond to the metal. So, here is a metal and it is forming a triple bond with these 3 electrons and you have only a lone pair on the nitrogen, which is present on the nitrogen side and so, you have a metal which is coordinated with a triple bond to the nitrogen, then in the neutral method, you take it as a 3 electron donor in the ionic method. You look at as if it is a N 3 3 minus. So, you would end up with a total of 6 electrons on the nitrogen. This is an unusual bonding situation, but that is the way we count it.

Surprisingly, for a carbine a similar situation should occur, but in terms of electron count people have always used a 3 electron count for the ionic and the neutral methods, so that is why I have marked it with a red colour. Since, that is an exception which is not following the convention that we have followed right through in this whole in this list of ligands.

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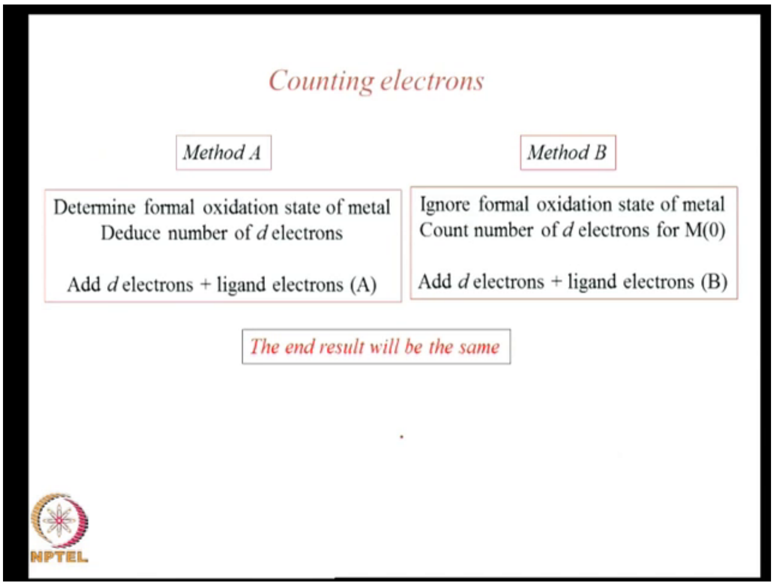

Counting electrons

Method A

Determine formal oxidation state of metal
Deduce number of *d* electrons

Add *d* electrons + ligand electrons (A)

Method B

Ignore formal oxidation state of metal
Count number of *d* electrons for M(0)

Add *d* electrons + ligand electrons (B)

The end result will be the same

So, when you count electrons you either should follow the method a, which would have charges on the ligands. When it is appropriate or you should stick to method b, where you would ignore the oxidation state of the metal you count the total number of d electrons for the metal as if it is in the 0 oxidation state. So, you just assume that it is in the 0 oxidation state, and you add the number of electrons that are coming from the ligand irrespective of what you might think is the charge on the ligand.

Let us take a few examples and then this will become easy to follow. And what is interesting or what is important is that with either method, we should end up with the same result. That is the most important fact and it is important that you practice with some of the compounds, so that you will understand what is going on.

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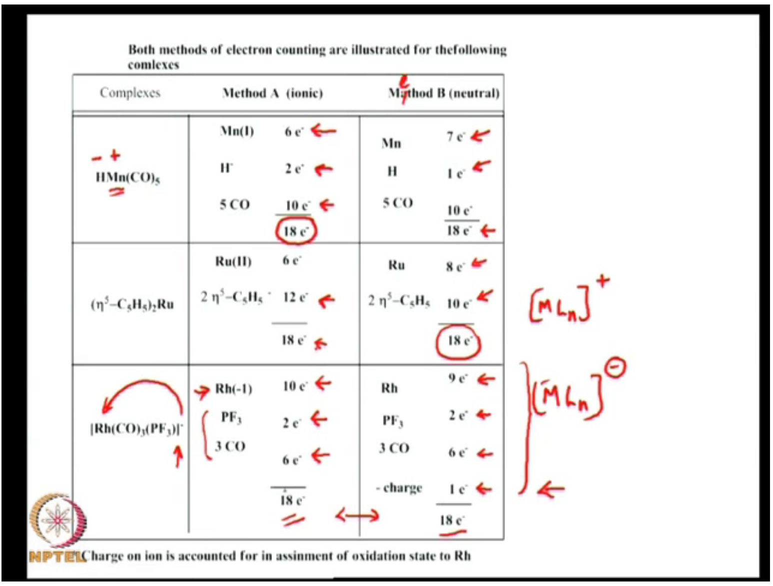

Both methods of electron counting are illustrated for thefollowing comlexes

Complexes	Method A (ionic)		Mathod B (neutral)	
$HMn(CO)_5$	Mn(I)	6 e^-	Mn	7 e^-
	H^-	2 e^-	H	1 e^-
	5 CO	10 e^-	5 CO	10 e^-
		18 e^-		18 e^-
$(\eta^5\text{-}C_5H_5)_2Ru$	Ru(II)	6 e^-	Ru	8 e^-
	2 $\eta^5\text{-}C_5H_5^-$	12 e^-	2 $\eta^5\text{-}C_5H_5$	10 e^-
		18 e^-		18 e^-
$[Rh(CO)_3(PF_3)]^-$	Rh(-1)	10 e^-	Rh	9 e^-
	PF_3	2 e^-	PF_3	2 e^-
	3 CO	6 e^-	3 CO	6 e^-
			- charge	1 e^-
		18 e^-		18 e^-

Charge on ion is accounted for in assinment of oxidation state to Rh

So, let us take a look at the first compound H MnCO5 that we are going to talk about HNnCO5 hydrogen, because as I mentioned to you in many cases it should be considered as a more electronegative element than the metal. And because we cannot figure it out the ionic method always takes it as H minus, and if it is H minus it is a 2 electron ligand. So, it is a 2 electron donor then if this is H minus and if the complex is having no charge that means something else in the metal complex should have a charge. So, if H is H minus then we have to put a plus charge on the manganese because we know that carbon monoxide is a neutral ligand.

So, 5 carbon monoxides give you 5 into 2, 10 electrons total and H minus is given 2 electrons and we have removed 1 electron from the manganese, we have removed 1 electron from the manganese and manganese had 7 electrons to begin with, so we end up adding 6 electrons as a contribution of manganese and the total turns out to be 18 electrons. We achieved this 18 electron rule by counting it in this particular fashion.

Now, let us take a look at the neutral method, so this is a typographical error, so this should be the neutral method. The neutral method, we have manganese as if it is in the 0 oxidation state, it has a electronic configuration of 3 d 5 4 s 2 which adds up to a total of 7 electrons. So, then you have hydrogen which we will now consider artificially as if it is H dot, so that will contribute only 1 electron and 5 carbon monoxides will give 10 electrons and the total will again be 18 electrons. So, you can see that whether you use the neutral method or the ionic method, you end up with a total of 18 valence electrons.

Now, let us take another example where there is a charge on the metal, because of the net charge on the complex. So, this is a complex which has got a net negative charge there is a charge on the complex, which is indicated as a charge after the square bracket. This charge adds to the total number of electrons that are present in the valence shell. So, carbon monoxide, 3 carbon monoxides are there, so we end up adding 6 electrons for the same PF 3 is like PR 3, it would donate 2 electrons, 2 valence electrons on the phosphorous will be donated to the metal.

Now, we have a net negative charge on the complex and neither of these 2 ligands systems are charged and so what we have to do is to add this extra electron on to the rhodium which is a metal. So, this negative charge is added on to the metal and that is why we consider rhodium as rhodium minus 1. Rhodium had 9 electrons to start with valence electrons and with 1 extra electron it becomes a 10 electron species. So, the total adds out to be 18 valence electrons.

Now, in a similar fashion in the neutral method, what we do is to take the rhodium which had 9 electrons in the valence shell, PF 3 2 electrons. And 3 carbon monoxides 6 electrons and because we had an extra charge on the whole complex that extra charge is added separately and as a result we would again end up with 18 electrons. Now, let us just think about this for the for a moment, if there was a net charge plus 1 indicated by a plus charge in a metal complex m, l, n. Then we would have to subtract 1 electron from the valence shell in the neutral method, in the neutral method we would have to subtract 1 electron. If there is a negative charge m, l, n, and then we have a negative charge then we end up adding this 1 electron.

So, you will it is important for us to note that both of them come at the same result as a result of this addition. So, once again ferrocene, the analog of ferrocene is ruthenocene that what we have here we have C 5 H 5, which would donate 5 electrons in the neutral method. So, 5 into 2, 10 and we have 18 electrons from ruthenium and it ends up with 18 valence electrons for the ruthenocene. Similarly, C 5 H 5 minus would be an anionic ligand. So, 6 electrons from each C 5 H 5 minus that gives us 12 plus 6 and that is 18 valence electrons. So, either method gives us the same number of valence electrons, but only thing that we have to remember is that we have to be consistent as we go through this electron counting.

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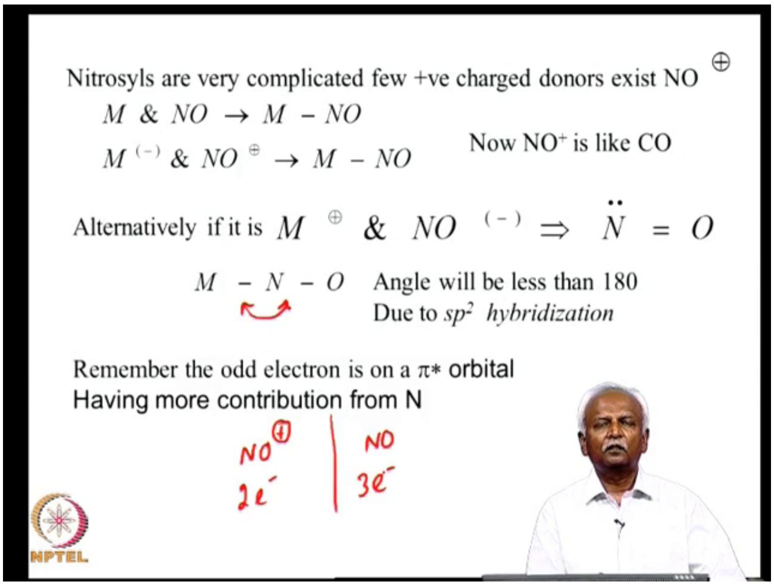

Nitrosyls are very complicated few +ve charged donors exist NO $^{\oplus}$

M & $NO \rightarrow M - NO$

$M^{(-)}$ & $NO^{\oplus} \rightarrow M - NO$

Now NO$^+$ is like CO

Alternatively if it is $M^{\oplus}$ & $NO^{(-)} \Rightarrow \ddot{N} = O$

$M - N - O$

Angle will be less than 180

Due to sp^2 *hybridization*

Remember the odd electron is on a $\pi*$ orbital

Having more contribution from N

$NO^{\oplus}$ | NO

$2e^-$ | $3e^-$

So, during the course of this series of lectures we will always be consistent and either use the neutral method or the anionic method. Nitrosyls are 1 example, where the situation is very complicated and one needs to know whether the nitrosyl is in a linear fashion or whether it is in a bent fashion. When it is in a linear fashion it is close to 180 degrees. The angle is 180 degrees. Then in the ionic method it is considered as a positive ligand NO is considered as NO plus and that is very important. Then it is considered as a 2 electron donor.

Whereas, in the case of the neutral method it is considered as NO and then it is considered as a 2 electron donor, but the net result would be the same. So, with this we end today’s lecture, where we were considered the classification of various ligands and how we look at them by their hapticity. The hapticity is a number of carbon atoms which are attached to the transition metal.

We have also seen that the number of electrons that are donated can either be based on the ionic method, which makes carbon hydrogen and nitrogen and halogens more electronegative. So, they are assigned negative charges, artificially given negative charges. In the case of the neutral method, we consider them as if they contribute 1 electron each. So, we will continue with this series of lectures where we will talk about one ligand after the other starting with carbon 1 containing systems.