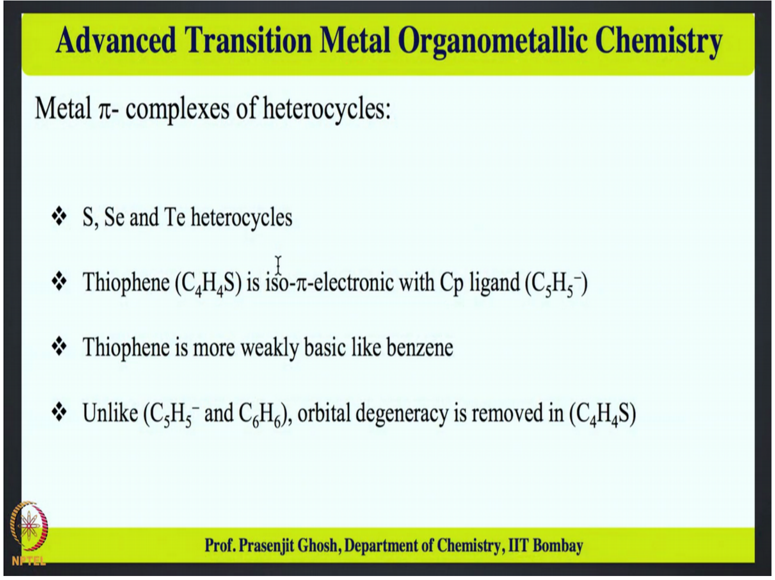
Advanced Transition Metal Organometallic Chemistry
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture – 34
Transition Metal PI- complexes of heterocycles

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. In our foray into looking into various kinds of transition metal complexes of different ligands, mainly of Sigma and PI type, we have looked into a wide variety of such ligands starting from cyclopropenyl to butadiene to cyclobutadiene cyclopentane benzene C 6 cyclo heptadiene as well as cyclo heptatriene type of ligands, and in that backdrop we are going to take up a new topic today which is transition metal complexes of another type of ligands these are hetero cycles.

So, these are heterocycles containing nitrogen, phosphorus, oxygen or sulfur. So these heterocycles also can form PI type complexes, with transition metals and we are going to take up these transition metal pi complexes of heterocycles in the context of our studies, which were done with transition metal complexes of other cyclic ligands. So to begin with we are going to take up the heterocycles of sulfur, selenium and tellurium complexes of metals.

(Refer Slide Time: 01:50)



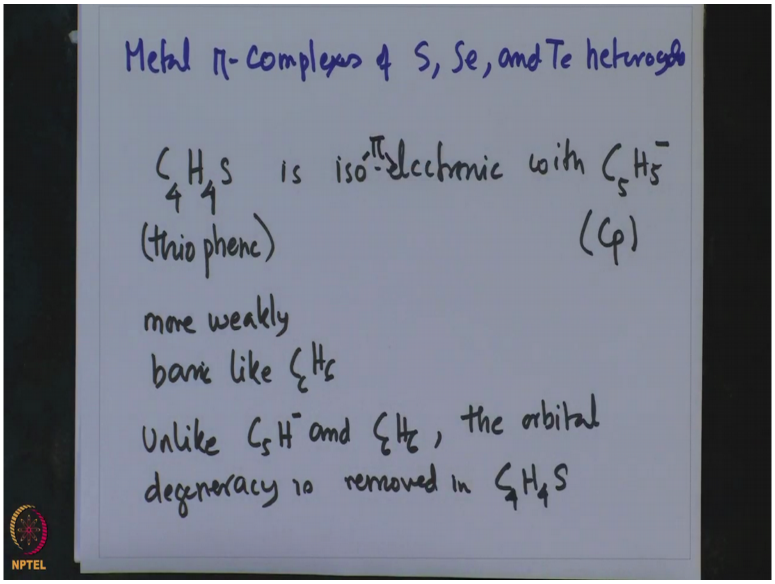
Advanced Transition Metal Organometallic Chemistry

Metal π- complexes of heterocycles:

- S, Se and Te heterocycles
- Thiophene (C_4H_4S) is iso-π-electronic with Cp ligand ($C_5H_5^-$)
- Thiophene is more weakly basic like benzene
- Unlike ($C_5H_5^-$ and C_6H_6), orbital degeneracy is removed in (C_4H_4S)

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 01:58)



Metal π-complexes of S, Se, and Te heterocycles

C_4H_4S is iso-π-electronic with $C_5H_5^-$

(thiophene) (Cp)

more weakly basic like C_6H_6

Unlike C_5H^- and C_6H_6, the orbital degeneracy is removed in C_4H_4S

So, we are going to be talking about metal PI complexes of of sulfur, selenium and tellurium heterocycles. Though you know thiophene is isoelectronic with C 5 H 5- but it behaves more weakly basic like that of benzene. So, this is an interesting consideration though thiophene C 4 H 4 S or thiophene which is what it is popularly called is isoelectronic with, with C 5 H 5- ligand or rather cyclopentadienyl ligand, CP ligand, thiophene is more weakly basic but behaves, as if, as more weakly basic, like benzene.

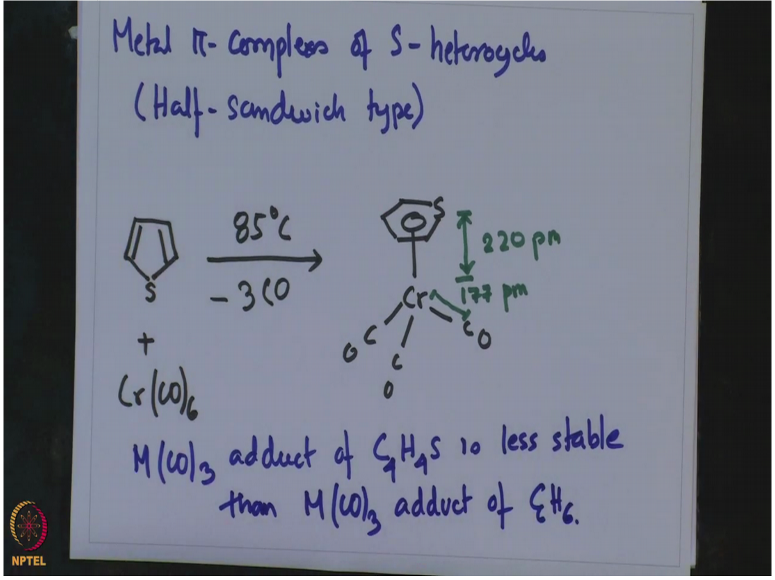
So, this behaves as more weakly basic like benzene and that is kind of understandable because CP being anionic is much more basic whereas thiophene being neutral, is certainly less basic than what CP would be and hence a neutral thiophene ligand also, is kind of similar to that of benzene which itself also is a neutral molecule. Now thiophene if one were to look at the molecular orbital involving the PI orbital which are there in the aromatic ring.

One would see that the orbital degeneracy which is present because of various symmetry elements present in the C 5 H 5- or C 6 H 6 ring, get lost the symmetry elements are no longer presents, and hence the orbital degeneracy is removed, in thiophene C 4 H 4. So, unlike C 5 H 5 minus and C 6 H 6, the orbital degeneracy, degeneracy is removed in C 4 H 4 S. So, there is, there are, certain distinctions between C 5 H 5- the commonly called cyclopentadienyl anion and the thiophene C 4 H 4 S.

Though they are isoelectronic in terms of the PI electrons are concerned. So these are ISO PI electronic to be more precise this can be called as ISO PI electronic, that is what it is more appropriately be called as, and these distinctions arises from their lack of charge in thiophene as opposed to be a C 5 H 5- being an ionic in nature, which is what it is more basic thiophene is less basic, thiophene is neutral, C 5 H 5- is anionic and thiophene PI orbitals does not have any degeneracy the degeneracy is lifted or removed, lost, whereas in C 5 H 5-, there indeed the orbital degeneracy is present, because of the presence of the symmetry elements.

So, then we are going to see some of the methods of preparation of these sulfur based heterocycles and the first example involves the preparation of half sandwich complex from thiophene.

(Refer Slide Time: 06:46)



Metal π- complexes of S- heterocycles
(Half- sandwich type)

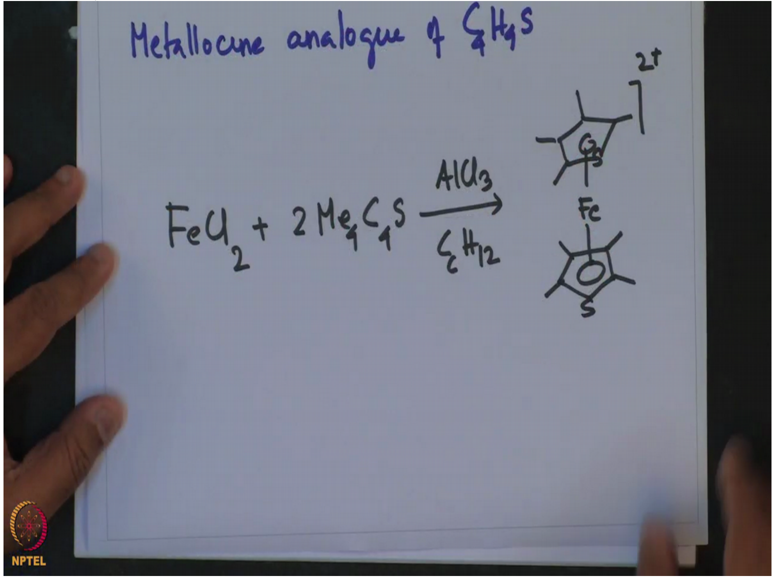
M(CO)$_3$ adduct of C$_4$H$_4$S is less stable than M(CO)$_3$ adduct of C$_6$H$_6$.

So, we are going to be talking about preparation of metal PI complexes of sulfur heterocycle and the first preparation involves of half sandwich complex and the reaction involves is thiophene at 85 degrees centigrade -3CO and this reacts with chromium hexacarbonyl giving the thiophene half sandwich complex of chromium. Now, this distance of chromium to thiophene, this is about 220 picometer where as this distance of chromium to carbonyl is much shorter at 177 picometer and that sort of indicates that there is a considerable amount of back bonding which happens from chromium on to the acidic carbo CO carbonyl ligands and thiophene being less basic so it is not acidic.

So, thiophene donate electron density on to the chromium and that electron density is further set in metal to ligand PI bonding, by these 3 carbon atoms which results in the observation of much shorter chromium carbonyl distance in thiophene chromium tricarbonyl complex. Now these chromium tricarbonyl adapt of thiophene, however even is less stable than that of benzene. So, even though it, thiophene sort of behaves similar to that of the benzene in terms of coordination to metal carbonyls, but that is not exactly the same but it turns out that CO 3 adapt of thiophene is less stable than MCO 3 adduct of benzene.

So, the metallocene, interesting example metallocene analog of these can also be prepared Fairfield and the reaction is direct reaction from tetramethyl thiophene with Fe Cl2 we are able to be discussing that in details.

(Refer Slide Time: 11:00)

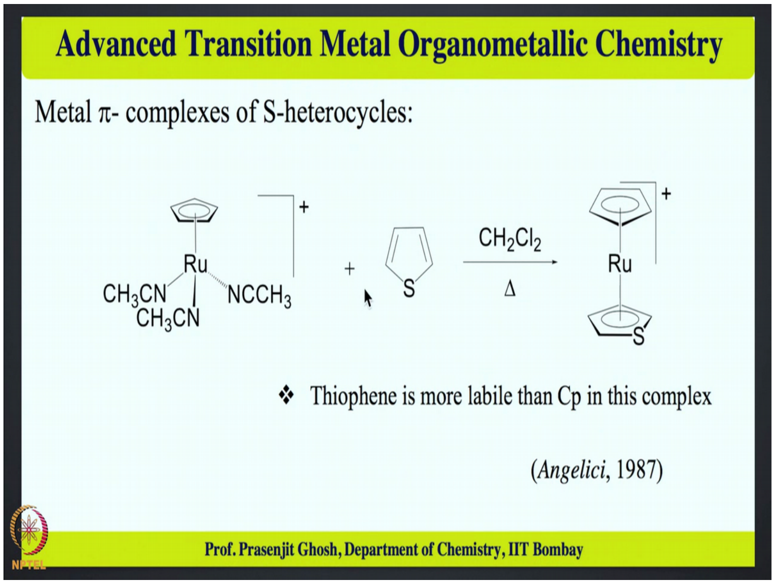


Metallocene analogue of C_4H_4S

$FeCl_2 + 2Me_4C_4S \xrightarrow[C_6H_{12}]{AlCl_3}$

So, this interesting example which is metallocene analog of C 4 H 4 S can be obtained by treatment of Fe Cl 2 + tetramethyl thiophene, which is 2 twice of the Me 4 C4 S, in presence of Al Cl 3 in cyclohexane C 6 H 12 gives this tetra methyl thiophene, metallocene complex of iron and these to be neutral ligands. So, overall there is a tri cationic charge and so this is a nice demonstration where the metals in analog can be prepared for the thiophene are substituted thiophene by direct reaction involving Fe Cl 2 and Me 4 C4 S.

(Refer Slide Time: 12:41)



Advanced Transition Metal Organometallic Chemistry

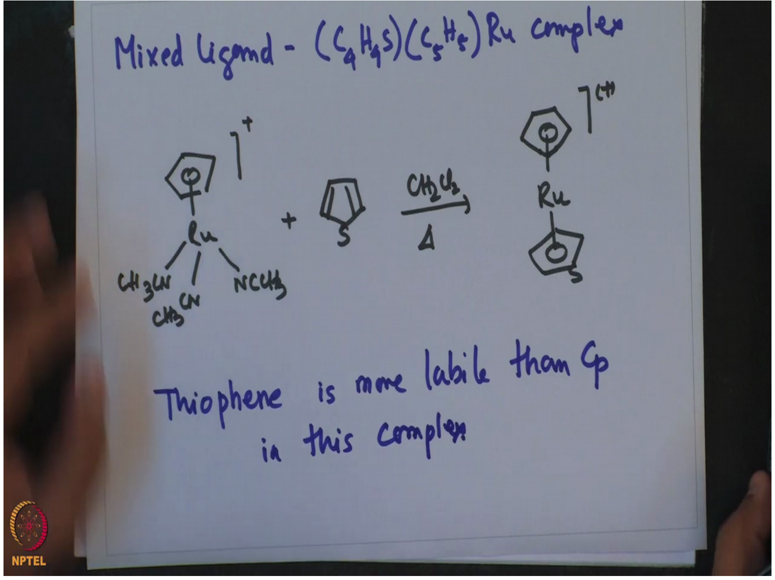
Metal π- complexes of S-heterocycles:

- Thiophene is more labile than Cp in this complex

(*Angelici*, 1987)

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 12:54)



Mixed Ligand - $(C_4H_4S)(C_5H_5)$Ru complex

Thiophene is more labile than Cp in this complex

Similarly mixed thiophene cyclo pentadienyl ligand can also be obtained from the from a ruthenium complex, this is also an interesting reaction that eventually gives rise to mixed ligand C 4 H 4 S, C 5 H 5, ruthenium complex and the starting precursor is this cyclo pentadienyl ruthenium twist acetonitrile species, when treated with thiophene in dichloromethane and heat gives this CP ruthenium thiophene cationic complex.

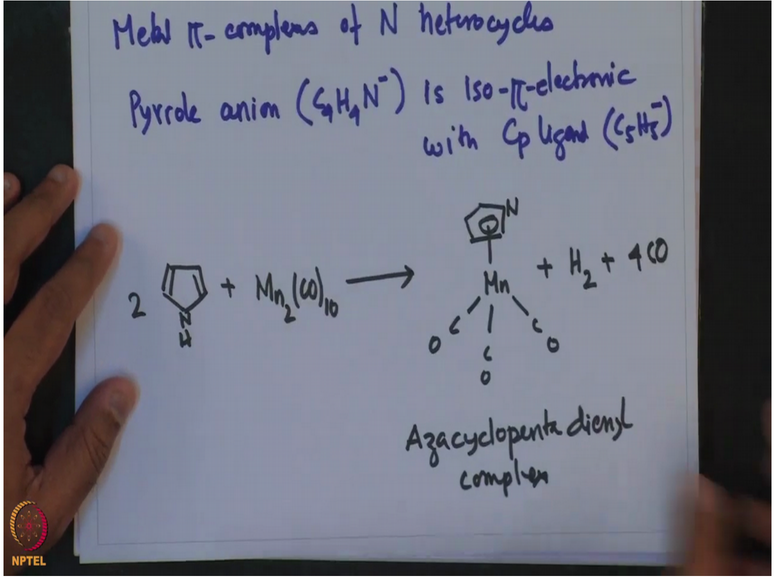
Now, you know, it is of this 2 mixed ligand CP's and ionic ruthenium bound to thiophene is neutral, and hence it is quite logical that neutral ligand like thiophene bound to ruthenium is more labile than the CP in this complex, because CP being anionic everything m is in + 2 oxidation step, state, so this is more tightly bound, whereas this is less compared to this, this is relatively less tightly bound and then this thiophene ligand is more labile than the CP ligand in this complex.

So that is an observation which sort of, can be rationalized quite easily by looking at this mixed ligand complex and then taking into account, the neutral or the anionic nuture, nature of the individual ligands. So thiophene is more labile than CP in this complex. So, this is a brief discussion on the sulfur based heterocycle by complexes of transition metals and then we are going to look into ooh the nitrogen counterparts of these heterocycles.

So, in the sulphur, before I proceed, in the sulfur, petrol base it recycles of transition metal what we had seen is that the sulfur base heterocycles are, the neutral less basic and they have their orbital degeneracy lifted and that are even they are adduct of metal carbonyls that even weaker than that of, of the benzene adduct of metal carbonyls and also they can they can be used to prepare half sandwich complexes or that of even the sandwich metallocene counterpart or even the mixed ligand type of complexes.

So, they are quite versatile in the preparation of all the three types of complexes. Now with that we finish our discussion on these sulfur based heterocycle and then start on with the transition metal complexes by complexes of nitrogen based heterocycles.

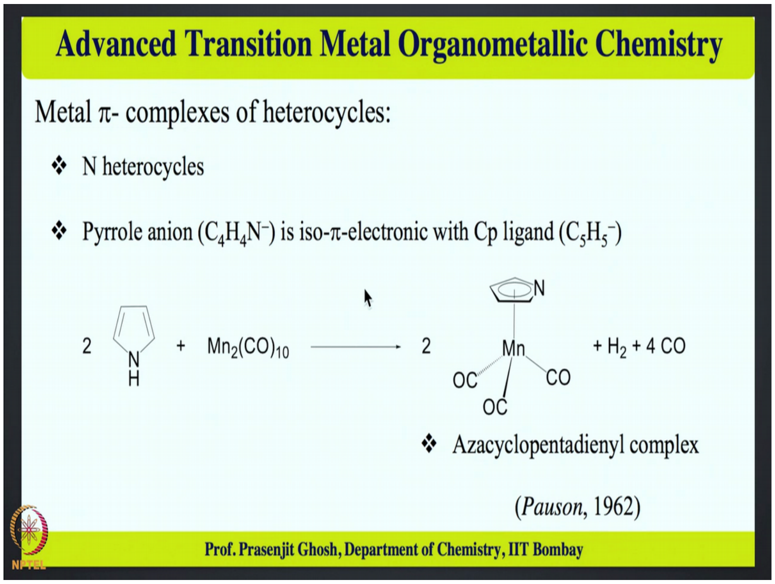
(Refer Slide Time: 17:06)



Metal π- complexes of N heterocycles

Pyrrole anion ($C_4H_4N^-$) is Iso-π-electronic with Cp ligand ($C_5H_5^-$)

(Refer Slide Time: 17:25)



Advanced Transition Metal Organometallic Chemistry

Metal π- complexes of heterocycles:

- N heterocycles
- Pyrrole anion ($C_4H_4N^-$) is iso-π-electronic with Cp ligand ($C_5H_5^-$)

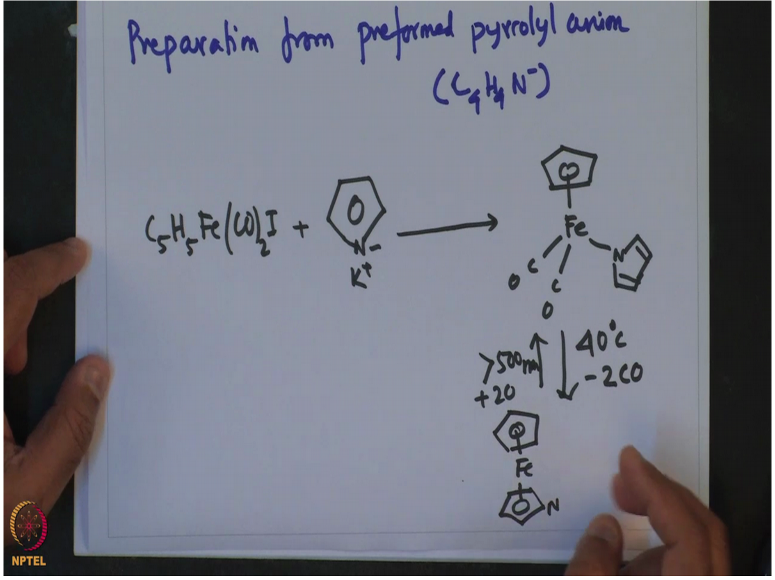
- Azacyclopentadienyl complex

(*Pauson*, 1962)

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So, these are prepared from pyrrole anion. So, in this case the nitrogen based heterocycles, one has to remember that the pyrrole anion is isophile electronic with CP ligand, to remember okay and this is given in this, by this reaction where the manganese half sandwich complex has been prepared by direct reaction of pyrrole, with Mn 2 CO 10, giving, pyrrole bound manganese complex + H2 + 4CO, and this is commonly referred to as, Azacyclopentadienyl complex. So, this ligand is commonly referred to as Azacyclopentadienyl ligand or so this can be directly prepared from the pyrrole or even from this pyrrole and iron, from iron precursor.

(Refer Slide Time: 20:11)



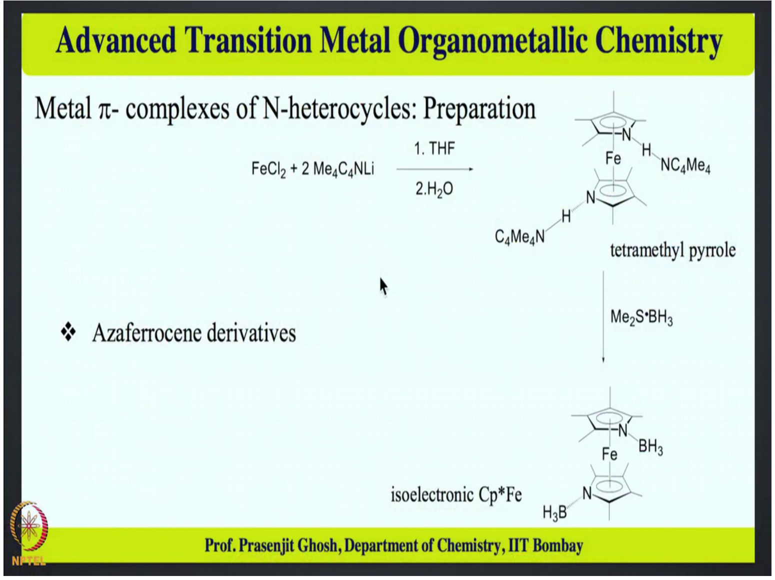
So, the first synthesis that we have seen involve direct reaction of pyrrole with manganese chloride, the other synthesis involved synthesis from preformed preparation from preformed pyrrole anion, or C4 H4 N-. The synthesis is a very simple reaction between CP C 5 H 5 Fe CO

2I + sodium salt of pyrrole anion giving eta 1 bound iron carbonyl pyrrole which at 40 degree centigrade loses to carbon monoxide to give this mixed ligand complex of iron CP pyrrole anion, and this compound in plight greater than 500 nanometer and carbonyl gives back this eta bound pyrrole.

So, this is a nice compound which mixed, mixed ligand compound which can be formed from CP iron I carbonyl iodide which preformed pyrrole anion and giving a eta 1 bound CP iron dicarbonyl pyrrole which on heating eliminates the two carbon CO molecules and give this mixed as a cyclo pentadienyl iron mix CP as a cyclo pentadienyl iron complex which is a mixed pyrrole CP iron complex.

It is a neutral complex and kind of similar to that of the metallocenes that we had spoken about but only the fact that these 2 ligands of the metallocenes are 2 different ligands.

(Refer Slide Time: 23:20)



Advanced Transition Metal Organometallic Chemistry

Metal π- complexes of N-heterocycles: Preparation

$FeCl_2 + 2\ Me_4C_4NLi \xrightarrow[2.\ H_2O]{1.\ THF}$

tetramethyl pyrrole

$Me_2S{\cdot}BH_3$

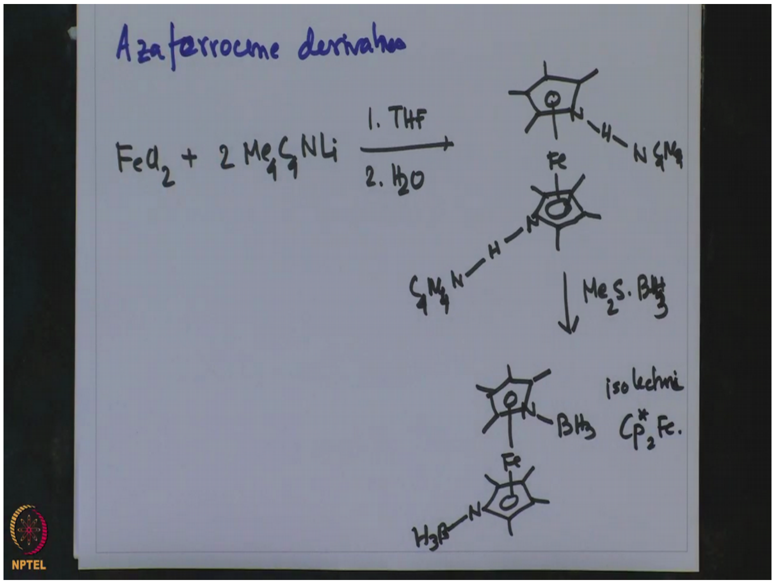
- Azaferrocene derivatives

isoelectronic Cp*Fe

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

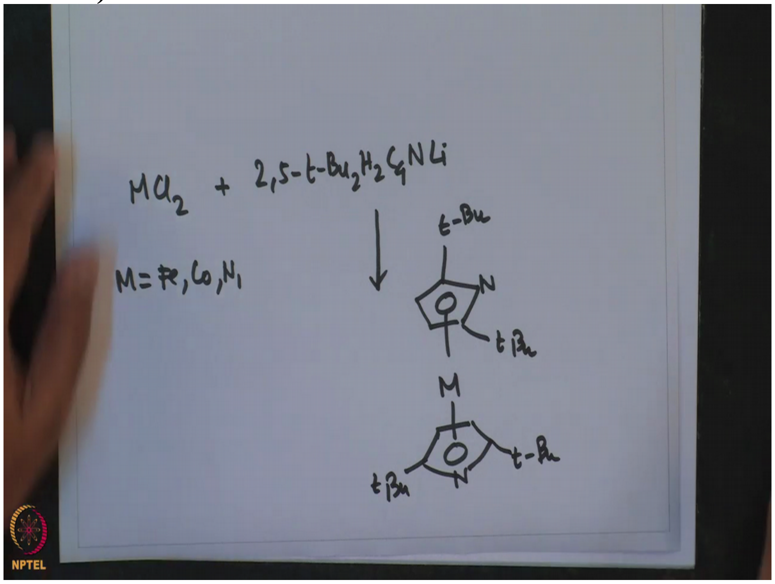
So, another interesting example are these tetra azaferrocenes. So, in the previous example what we had seen that it is a sandwich complex where one ligand was CP, the other one was azapyrrole azapyrrole, one was CP and in other words a pyrrole ring. So, now the next reaction that you are going to be talking about is about the preparation of azaferrocenes, by that what it means that both the ligands of these sandwich complexes are pyrrole based heterocycles. So, this is produced by an interesting sequence of reactions which shall be a talking about.

(Refer Slide Time: 24:04)



So, we are going to be look at preparations of azaferrocenes and the preparations starts from Fe Cl 2 reacting with tetramethyl pyrrole from pyrrole and iron, so 2Me 4 C4 N Li similar to that tetramethyl thiophene, that we had seen, for in case of the PI complexes of thiophene, in THF and second, water, giving this, tetramethyl in hydrogen-bonded NC 4 Me 4 so these are tetramethyl pyrroles semi 4 and then this when treated with Me 2 S BH 3 gives this as a ferrocene and this one is isoelectronic with, with CP star 2 Fe.

(Refer Slide Time: 27:02)



So, here is a synthesis of azaferrocene where both are heterocycle formed sandwich complex of with, iron and one another interesting reaction of the same thing was made with the substituted more sterically reminding substituted pyrroles and that the reaction involves M Cl 2, M equals iron, cobalt and nickel + 2 5 t butyl H2 C4 N Li, the preformed lithium salt, that would give this t butyl N and t-butyl M as a ferrocene with t-butyl and t-butyl there substituents.

Now it is important to see that unlike the previous example where the nitrogen lone pair had to be protected by extended binding 2BH 3 this acid agrees 2BH 3, in this case, because of the presence of two to that t bulky t-butyl group flanking the nitrogen lone pair on that pyrrole ring, such protection is not required and thus this as a ferrocinal derivative of this substituted pyrrole can be obtained.

So, with this I would like to draw conclusion on today's lecture, we have looked into two different kinds of metal PI complexes of heterocycles, containing sulfur and nitrogen and what we had seen that these the sulfur which is that of thiophene they are PI isoelectronic with C 5 H 5 -, but being neutral they are less basic and also have their orbital degeneracy lifted and then they form weaker attacks even as compared to that of benzene and these thiophene complexes can be used to make half sandwich complex or their tetra methyl substituted thiophene can be used to make the corresponding metallocene derivative as well as we had taken an example where one made the CP thiophene mixed complex of ruthenium.

Along the same lines we have also taken up these nitrogen heterocycles or pyrrole base systems and what we had seen that they can be pyrroles can directly can be used in metal carbonyls to produce this half sandwich type complexes, metal carbonyl pyrrole or they can be used in this preformed anionic state that is potassium salt of the pyrrole and then treated with iron to give this mixed iron CP pyrrole compounds as a ferrocene type molecules for the less on that pyrroles, tetra methyl substituted pyrrole could be prepared;

However the nitrogen lone pair had to be protected with BH 3 and if one proceeds further and put more bulkier t-butyl substitute and substituent's flanking the nitrogen lone pair on the pyrrole ring then one can even make this as a ferrocene without this stabilization of the lone pair using BH 3. So this is a nice demonstration of various chemical concepts that we see, we have been studying and what we saw that if one can enhance the statics around the lone pair the reactivity of the lone pair of the pyrrole link could be lessened, such that the stabilization can be isolated without any reagent.

So, with this I conclude today's discussion on transition metal PI complexes of heterocycles of sulfur and nitrogen and I thank you again for patiently listening to me in this lecture and we are going to be taking up interesting application of transition metal organometallic chemistry particularly a Nobel prize-winning application with in the form of CC cross coupling reaction in the next lecture until then mm, I thank you again and I look forward to taking up this new topic in the new class in the next lecture. Goodbye.