Advanced Transition Metal Organometallic Chemistry
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Lecture – 05
Types of Transition Metal Sandwich Complexes:

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. In today's lecture we will to be discussing interesting class of compounds, which has immense historical importance, particularly with respect to the understanding of transition metal organometallic compound in general, these compound, that I would be talking of are called the sandwich complexes, these sandwich complexes actually refer to homoleptic or heteroleptic organometallic compounds.

These transition metal compounds contains cyclo pentadienyl or other kind of cyclic ligands that sandwiches or binds the metal or transition metal. These sandwich complex sort of originates from ferrocene or has its genesis in ferrocene and has aroused tremendous interest right from its synthesis to isolation, to understanding the interaction, that occurs between transition metal and ligand in sandwich complexes in general and that of ferrocene in particular.

A tremendous amount of enthusiasm surrounded this sandwich complex. Now in our earlier discussion we have seen how the sandwich complex can be very general that it is not only limited to or restricted to cyclopentadiene and ligands that it can vary from a wide bunch of ligands which can be cyclopropane nyle cation or cyclobutane cyclpen cyclopentane six-membered, seven member, eight member rings.

And we have also seen in our last discussion that sandwich complexes are again no longer limited to a restricted to iron, it can go all across the period starting from titanium, chromium, iron, nickel, cobalt, so on and so forth. So, as a result, of this larger interest on these kind of sandwich complexes there has been a tremendous growth in information available about them and we are going to discuss today the variety of sand, transition metals sandwich complexes that exist.

Now having said that even though there is a large body of compounds which fall in the category of sandwich complexes, there are also, another interesting subclass of compound which aroused beside the sandwich complexes and these are called half sandwich complexes.

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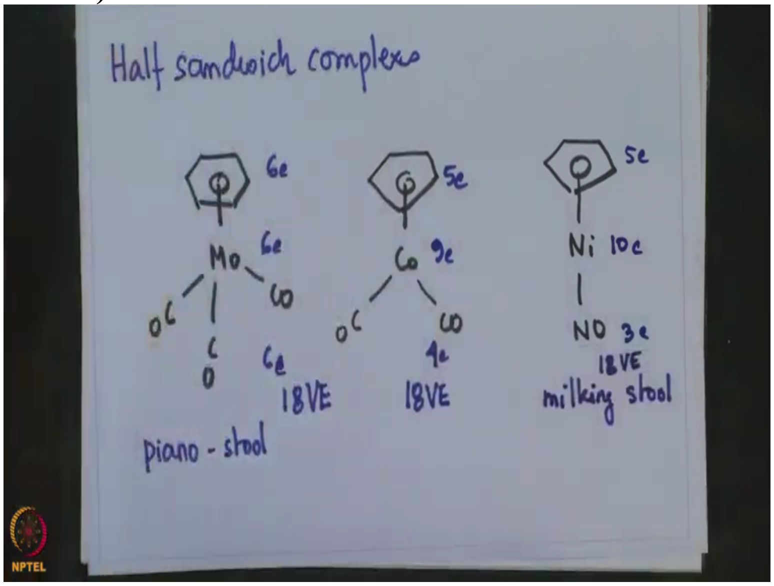

As the name suggests that it contained only one cyclic ring and the other half of the metal is bare and bound to other kind of ligands. So, here we have a six membered cyclic ring bound to molybdenum in this half-sandwich compound, and then the molybdenum in turn is bound to three carbon carbonyl groups, so these kind of complexes are called pianos to structure. As the name suggests that these resembles most likely the piano stool where the six membered ring sort of represents the flat seat of the piano stool, and the CO groups represents the legs of the piano stool.

These also or if is a stable compound as you can see that this is a 18 valence electron compound six from the benzene ring six from molybdenum and 3 Cos means six giving a total of 18 valence electron count. One can have the cobalt version of it, which contains RCP cobalt and two COs, so this is 18 electron complex so five electron from CP, 9 from cobalt, and 4 from CO again this is a 18 valence electron compound. Now as one goes from molybdenum to cobalt to nickel again with a CP ring this is called a milking stool configuration and this also is a 18 valence electron compounds.

So, one sort of sees in the pretext of the sandwich complexes that, half-sandwich complexes can also have possibility not only in structure but also in the metals which exhibit them. So, it also can span according to across the periodic table, there are various kinds of rings as that can be get involved in formation of the sub sandwich complexes and also there exist various kinds of ligands which also can be part of half-sandwich complexes.

Similar to what we had observed in case of sandwich complexes that there is also a similarity in the case that most of these complexes are electronically saturated, because they are also 18 valence electron compounds similar to that what we had observed in case of half sandwich complexes. There is another interesting compound which is even an extension or further extension of sandwich complexes and these are called multidecker sandwich complexes.

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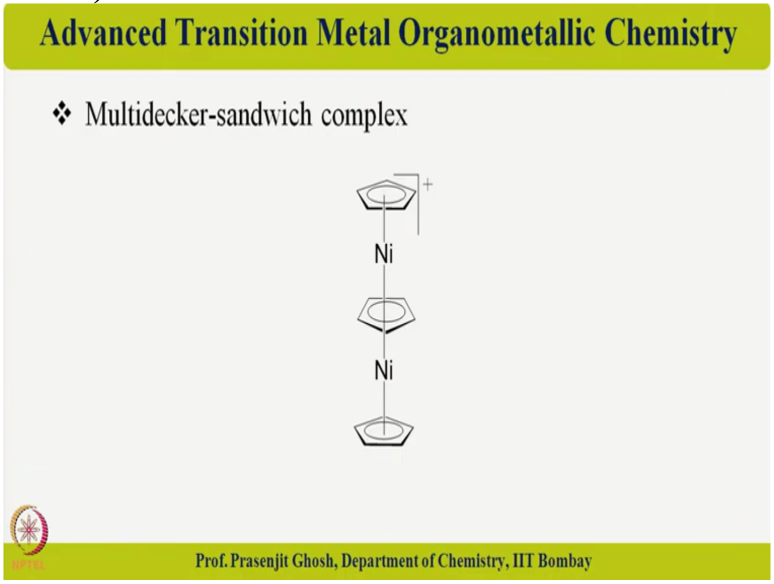

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❖ Multidecker-sandwich complex

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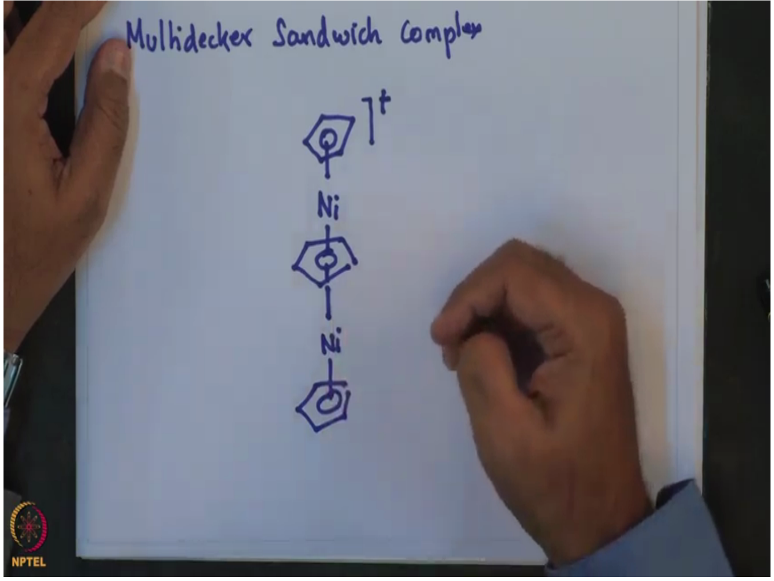

So, here it is a CP, nickel CP, and again nickel, the CP and it is a cationic nature. So what is interesting over here is that, these the central cyclo pentadienyl anion binds to two nickel on both of its sides or not both of its phases so that is an interesting aspect of the cyclopentadienyl ligand in a triple decker sandwich because this also exists or exhibits the property that CP not only can bind to metal on one of its side but in certain cases the CP ligand can also bind to two metal centers across both of its sides of the cyclopentadienyl anion.

So that is a very interesting observation which comes out of it, also, please note the fact, that this overall compound is mono cationic that means that both of the nickel are 2+ divalent cationic so which gives to 4 positive charge, and there are three anionic CPs which is 3 negatives, so 4 positive, 3 negatives, so there is overall a positive charge to the overall triple decker sandwich complex. So, this is just a vertical growth of the sandwich complex across the Z direction in which one can conceive these triple decker complex as being a nickel oozing getting extended by another nickel CP unit on one of the face of the cyclopentadienyl ligand.

So, that makes this compound compound kind of very interesting. The most of the geometry that we have been considering about sandwich complexes is the fact that it seemed that the sandwich complexes are kind of linear with two planar cyclopentadienyl ring completely a engulfing the transition metal from above and below. However as the portfolio of sandwich complexes are expanded.

Our interesting observation further came into being, is the fact that, there are lot of sandwich complexes which was even tilted in nature and that these two CP rings are no longer planar. So these particular kind of ligands are called tilted sandwich complexes.

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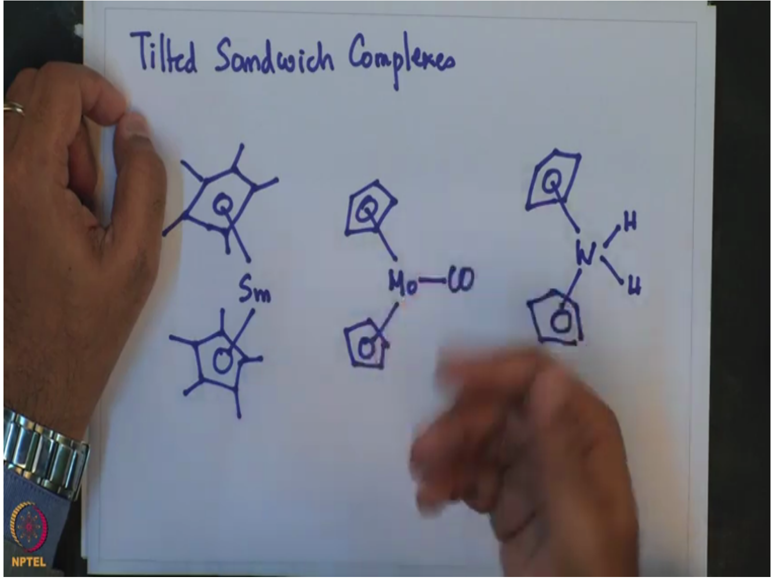

So, here is the example of penta methyl CP, samarium or CP this CP molybdenum carbonyl or this CP tungsten dihydride. So, these are interesting variation of sandwich complexes as one can see that these two CP rings are not parallel to each other and they are tilted across the middle. Another interesting observation comes from the fact that these most, at least the one, the examples that we have discussed all of them had second row or third row transition metals which are more bigger and bulkier than the first row transition metal which most likely would show our normal sandwich structure.

Whereas the second row and third row, these are bigger atoms, where as a result the CP cannot fully engulf the metal center and as a result they can tilt over and accommodate a third or the fourth ligand to make up for the increased white space that arise because of the bigger nature of the central metal atom. There is another interesting class of compounds, which contains, more than 2 CN HN ligands or 2 types of CN HN ligand, these are really very interesting compounds and we will illustrate this with example.

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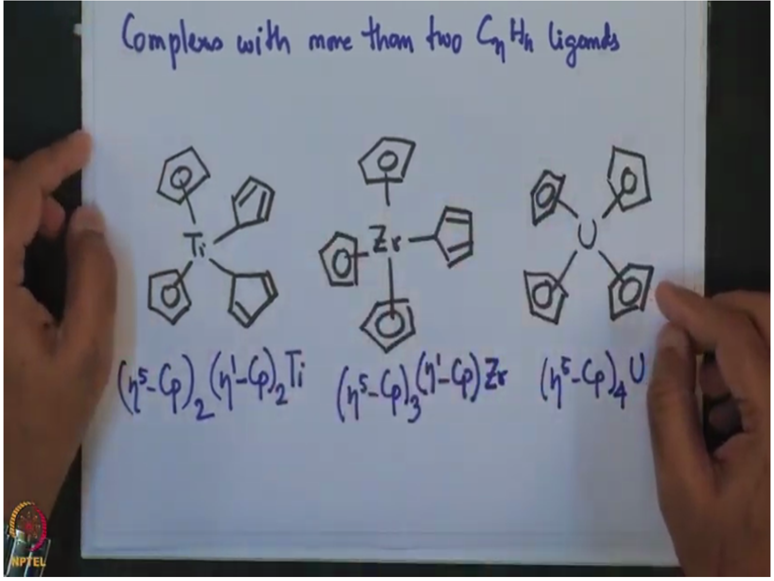

Complexes with more than two C_nH_n ligands

$(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})_2\text{Ti}$ $(\eta^5\text{-Cp})_3(\eta^1\text{-Cp})\text{Zr}$ $(\eta^5\text{-Cp})_4\text{U}$

So, we have CP titanium, so this is a eta 5 CP2 titanium eta 5 CP2, eta 1 CP2 titanium so, the formula is eta 5 CP2, eta 1 CP2 titanium. So, here we see that 4 cyclopentadienyl ligands are engulfing the transition metal however, all 4 are not bound in the same fashion, they are actually bound in two different kinds of fashions, one is at eta 5 another is eta 1, the reason primarily probably, is because of the fact that titanium being for very small, all 4 cannot bind in a eta 5 fashion.

It would be too crowded to do so and so, two are bound in eta 5 one and two are bound in a eta 1 fashion. Similarly with zirconium there are 4 CP ligands similar to what we have seen for titanium, but what is interesting is the fact that zirconium being a second row metal is probably slightly more bulkier than titanium and as a result we see here is enough room for 3 CP ligands to bind in a eta 5 fashion and one in a eta 1 fashion.

So, unlike in titanium where they were in eta 5 CP2 , in this case what we have is a eta 5 CP3 and instead of 2 eta 1CP you have one eta 1CP a zirconium. Now, if one go down further to more bulkier elements, one can sort of see that one can even have ligands, which have 4 eta 5 bound CP, for example in these uranium complex. So, this has four eta 5 bound CP, so apart from the fact that as one goes down the group, the propensity of having larger number of eta 5 bound CP, increases.

The other interesting aspect which these series of 3 complexes highlight is the fact that CP can bind in more than one ways it can bind in eta 5 as well as eta 1 fashion there are also certain reports that we had seen in our earlier class where we had seen that hydrogenation of a nickelosin complex led to formation of a eta 5 bound CP and eta 3 bound CP, to nickel.

The binding of CP to metal is very much dependent on the size and the electron richness of the metal and also the number in which the number of CPS would bind in a eta 5 fashion or eta 1 fashion is also dependent on these criteria. We are going to now take a look in some of the very interesting class of rings which are C3 R3 or cyclopropyl ring based ligands.

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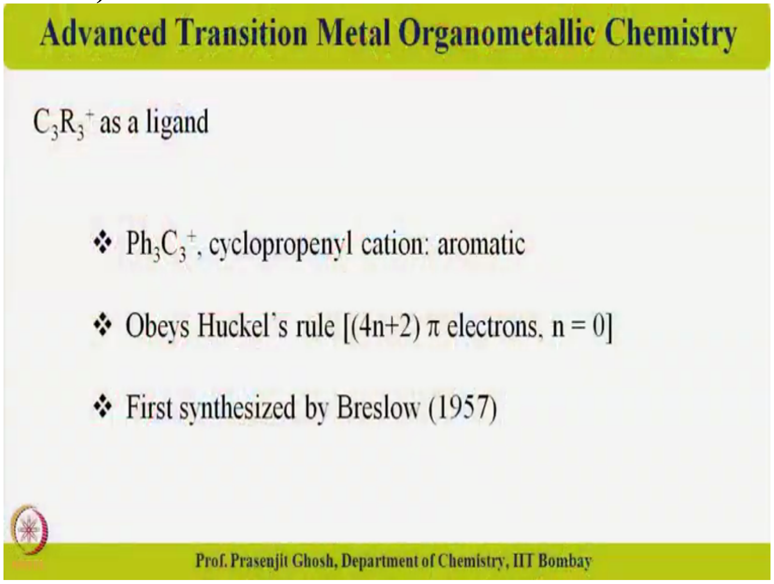

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$C_3R_3^+$ as a ligand

- ❖ $Ph_3C_3^+$, cyclopropenyl cation: aromatic
- ❖ Obeys Huckel's rule [(4n+2) π electrons, n = 0]
- ❖ First synthesized by Breslow (1957)

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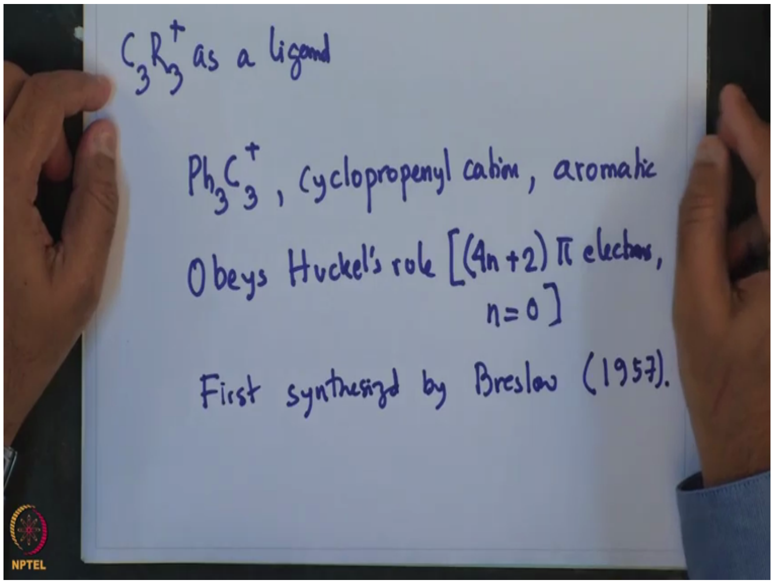

$C_3R_3^+$ as a ligand

$Ph_3C_3^+$, cyclopropenyl cation, aromatic

Obeys Huckel's rule [$(4n+2)\pi$ electrons, $n=0$]

First synthesizd by Breslow (1957).

These for example Ph3 C3+ cyclopropenyl cation are important class of ligands which are aromatic, these obeys Huckel's rule, what is Huckel's rule? Huckel's rule says that if it has 4n + 2 Pi electrons then they are aromatic, and in the present C3 R3+ , n = 0, so they have 2Pi electrons and these kind of C3 R3+ cation compounds were first synthesized by Professor Ronald Breslow in 1957. At that point it was a very interesting example ah, of a aromatic compound having only 2 Pi electron.

And that the experimental proof validation of that was provided by Professor Ron Breslow with that in 1957 and hence this discovery is considered very important not only then even now from a historical perspective. We are going to take a look at some of the reactions which are involved in preparing these eta 3 cyclopropenyl complexes.

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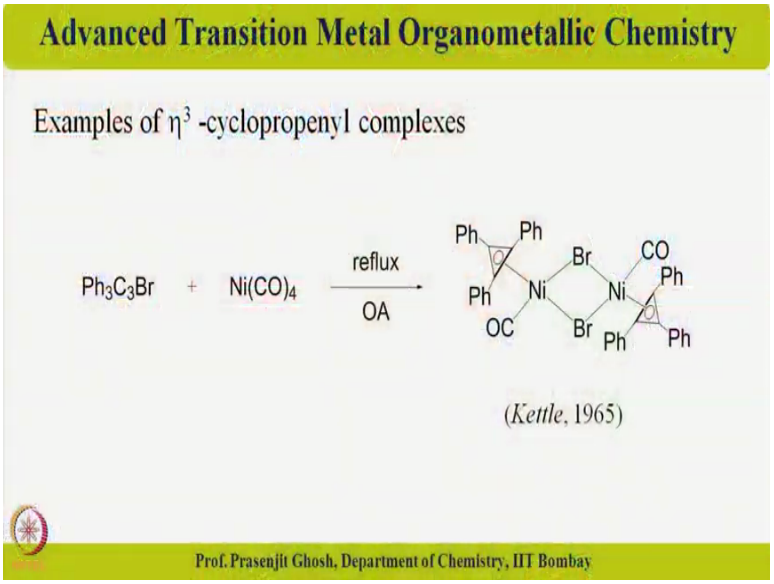

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Examples of η³ -cyclopropenyl complexes

$Ph_3C_3Br + Ni(CO)_4 \xrightarrow[OA]{reflux}$

(*Kettle*, 1965)

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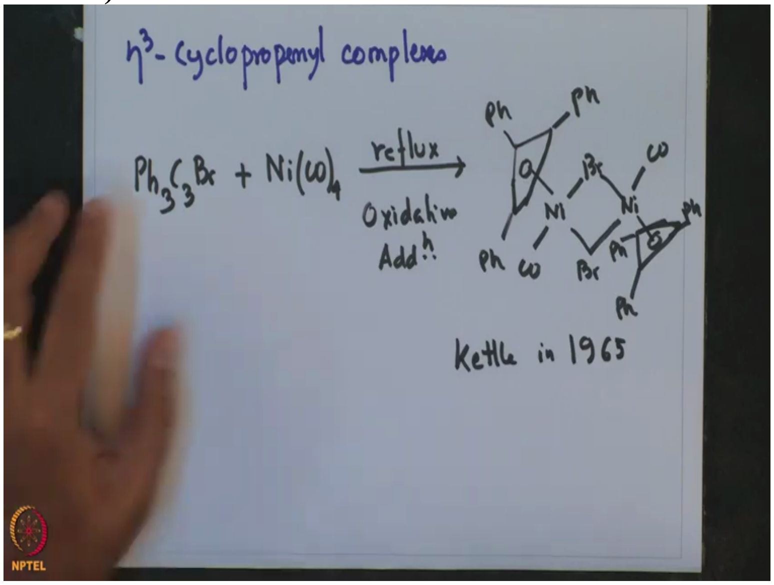

η³- cyclopropenyl complexes

$Ph_3C_3Br + Ni(CO)_4 \xrightarrow[\text{Oxidative Add}^n]{reflux}$

Kettle in 1965

For example the reaction with Ph3 C3 Br + nickel tetracarbonyl under reflux conditions oxidative addition occurs between on nickel which is in a zero complex states, and this C3 Ph3 C3 Br, cyclopropenyl cation, giving rise to this beautiful cyclopropyl cation, phenol, phenol, phenol, nickel, bromide, which is bridging nickel, carbonyl, carbonyl bromide and this compound. This was synthesized way back by Kettle in 1965.

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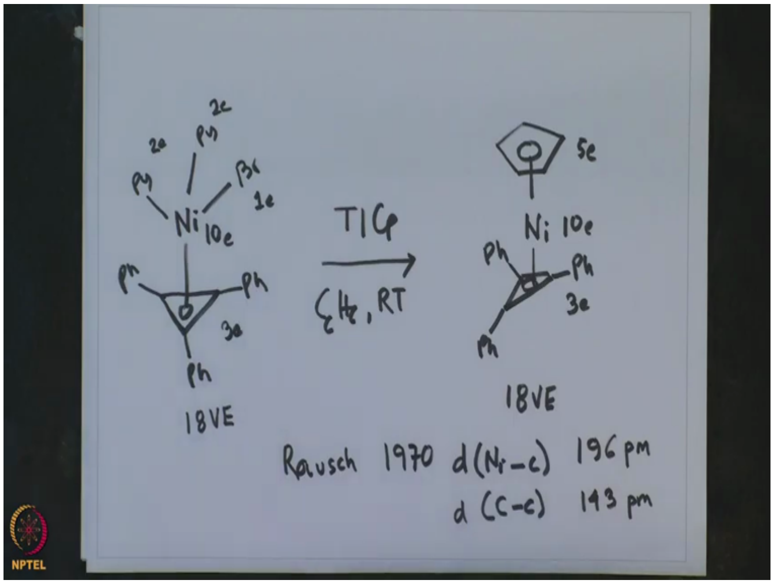

Another interesting example involved the reaction of a nickel C3 Ph3 compound of nickel having bromide pyridine, pyridine with thallium CP, in benzene at room temperature, giving CP nickel C3 Ph3 cation, this also is an 8 electron compound 5 3 and 10, 18 valence electron compound. So, kind of stable and this one also is 3, 10, 1, 2 and 2, 5, 15, 3, 18 valence electron compound. So the distance between nickel carbon is 196 Pico meter and distance between CC is 143 Pico meter this was synthesized by Rousch in 1970.

So, with that I would like to summarize what we have been discussing in today's class mainly we have looked into various kinds of sandwich complexes that exists not only the sandwich complexes, we have looked into, what are the type of half sandwich complexes, that exist which contains one cyclopentadienyl or one cyclic ring apart from other ligands. We have also looked into various kind of sandwich complexes which sort of originated from CP whether they are home elliptic and heterolytic or the kind of variations they show we along the rings as well as along the ah, metal center metal across the periodic table.

One thing for certain or which most of this sandwich as well as the half sandwich complexes that exhibit is the fact that most of them are almost all of them are 18 valence electron compounds, so that means they are kind of stable once formed. We have also looked at various variations of half sandwich complexes that of sandwich complexes we have seen, this can be 2 CP ring, cyclic ring, being planar, which are normal sandwich complexes or they can be tilted simply sandwich complexes or bend sandwich complexes.

There are compounds which contains, more than 2 CP rings and the nature of the CP binding to the metal can vary from eta 5 to eta 1 as we have seen in this discussion we had also seen eta 3 bound CP in our last lecture, and also we saw that as one goes down the group to a bigger and heavier transition metals or lanthanides, then one can see that, these more number of CP is being bound to the metal in a eta 5 fashion.

We have also seen that how these compounds are synthesized the first of its kind was synthesized by Professor Breslow way back in 1957 and then the Kettle synthesized using oxidative addition root which are discussed by reaction of Ph3 C3 bromide with nickel 0 tetra carbonyl compound using oxidative addition step. And then a very elegant example in 1970 by Rousch which involved reaction of a cyclopropane and nickel compound with thallium CP giving this sandwich compound, which also is a 18 valence electron compound.

Now with this I would conclude today's lecture we are able to look into the sandwich complexes their reactivity synthesis and the variation in a bit more detail in the next lecture, which is following up on this, and thank you for being with me in this lecture and also look forward to the next lecture where we are going to take up the sandwich complexes in a bit more detail. Till then good bye and thank you.