Advanced Transition Metal Organometallic Chemistry
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Lecture – 17
Transition Metal Cyclopentadienyl Nitrosyl Complexes

Welcome to today's lecture on advanced transition metal organometallic chemistry, we have been discussing half sandwich complexes of transition metals in the last few lectures. And in this figure we have discussed about transition metal cyclo pentadienyl carbonyl complexes and transition metal cyclo pentadienyl nitro cell complexes. These nitrosyl complexes are the ones that we had just started towards the end of the last lecture where we looked at the electron donating abilities of microsil as a ligand.

Now nitrosyl are Eno's can bind to ligand or with 1 electron or it can bind to ligand using 3 electrons. Now depending on how it binds to the transition metal it can exhibit a linear geometry or a bent geometry now we have looked into these nitrosyl ligands electronically as equivalent to carbonyl ligands for example 3 carbonyls can be substituted by 2 nitrosyl or 1 carbonyl can be substituted by one nitrosyl but having a positive charge.

And all of these can be correlated to the total valence electrons of each of these ligands, now continuing further in today's lecture we are going to discuss on transient metal nitrosyl complexes in more details particularly from the point of view of their preparations and reactivity.

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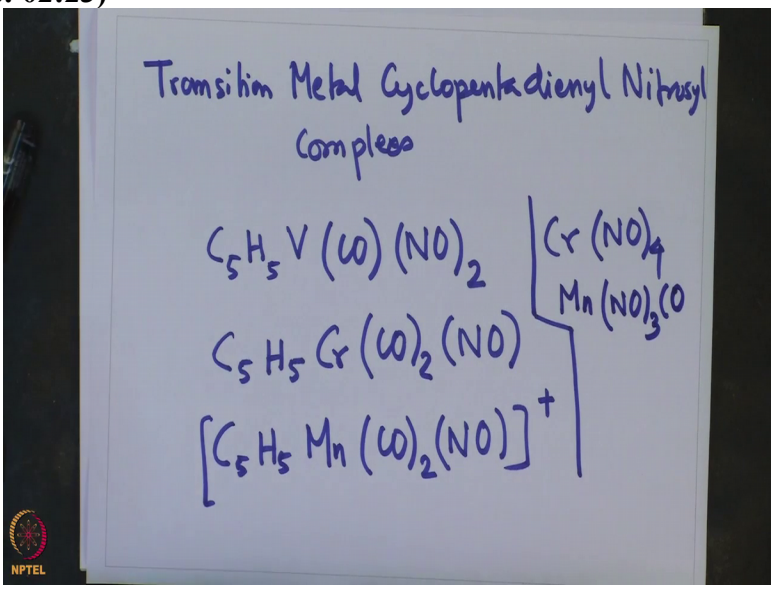

So, today we are going to be talking about so various examples of transition metal cyclopentadienyl nitrosyl complexes that exists are cyclopentadienyl vanadium karbolyn di nitrosyl or CO2 NO or plus. So, these there are a variety of nitrosyl complexes which contains cyclopentadienyl as well as carbonyl and nitrosyl almighty's there are complexes which are exclusively a binary nitrosyl compounds for example chromium NO4, so this is a binary nitrosyl compound and not a half-sandwich compounds like the ones which are shown over here.

For example also there are nitrosyl carbonyl compounds like, so what we see is the fact that there are several combinations of different ligands which including that of nitrosyl which can make transition metal complexes this can be half sandwich complexes where you have cyclopentadienyl ligand carbon ligand nitrosyl ligand making this kind of complexes or it can be just among manganese tri nitrosyl mono carbonyl complex where there is no cyclopentadienyl ligand or it can be even simple binary nitrosyl compounds for example as in chromium tetra nitrosyl okay.

So, having seen this what comes to the fore next is that 1 should find a ways and means for preparing these complexes and the preparative pathway is quite intuitive and simple in the sense that these nitrosyl complexes can be prepared from of their cycle or cyclopentadienyl transition metal complexes by direct treatment with NO for example in our in the previous case where we had seen preparation of half-sandwich cyclopentadienyl transition metal carbonyl complexes one of the effective method was just taking metellocene and adding CO gas to make this kind of option which complexes.

Analogous to that strategy a similar strategy is in a place for preparing this carbon cyclopentadienyl metal nitrosyl complexes where the metellocene’s are directly treated with a NO gas to get these complexes.

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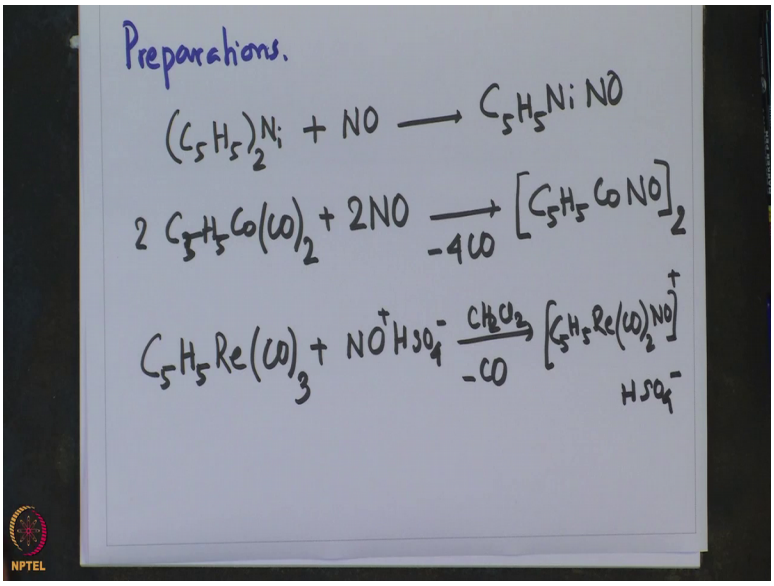

Let us will illustrate these with a few examples; for example for example here we have nikelocene giving C5H5 Ni NO or 1 can take 2 C5 H5 CO CO2 plus twice NO giving 4 carbon monoxide and H5 CO NO dimer as well as C5 H5 rhenium tri carbonyl plus a source of NO NO +8 SO4- in dichloromethane eliminates a CO2 give C5 H5 rhenium CO2 NO+ and HSO4- now all of this reaction has a commonality and commonality is that these are either binary metal cyclopentadienyl complexes or half-sandwich metal cyclo pentadienyl carbonyl complexes by reaction with NO giving these cyclo pentadienyl tri transition metal nitrosyl complexes.

Now that is a similarity over here another similarity for the last 2 reaction is the fact that carbonyl moieties are getting replaced by NO in each of this reaction. For example in this reaction the 2 carbonyl gets replaced by NO whereas over here 1 of the carbonyl gets again replaced by NO. So, what does that indicate that it indicates probably is that NO can successfully place a carbonyl in a sense that probably binds more strongly than carbonyl and also so these kind of is very informative in the sense that we have this belief that CO binds quite strongly to transition metal.

So, from that perspective if something we are displace even CO bound to transition metal there only indicates that we know probably binds more strongly to CO so that it can successfully place already tightly-bound metal bound CO for making these CP transition metal nitrosyl complexes. So, having seen the preparation there is not much variety in terms of synthesis of the cyclopentadienyl transition metal nitrosyl complexes given the fact that there is only 1 kind of

preparation that involves these metal cyclopentadienyl complexes we can know as is shown over here for preparing this transition metal cyclo pentadinyl and nitrosyl complexes.

So, this indicates that there are not many a route available for preparing these complexes other than the 1 which are shown over here. So, next we move on to some important aspect of these nitrosyl binding to transition metal particularly the structure and bonding of these nitrosyl ligand.

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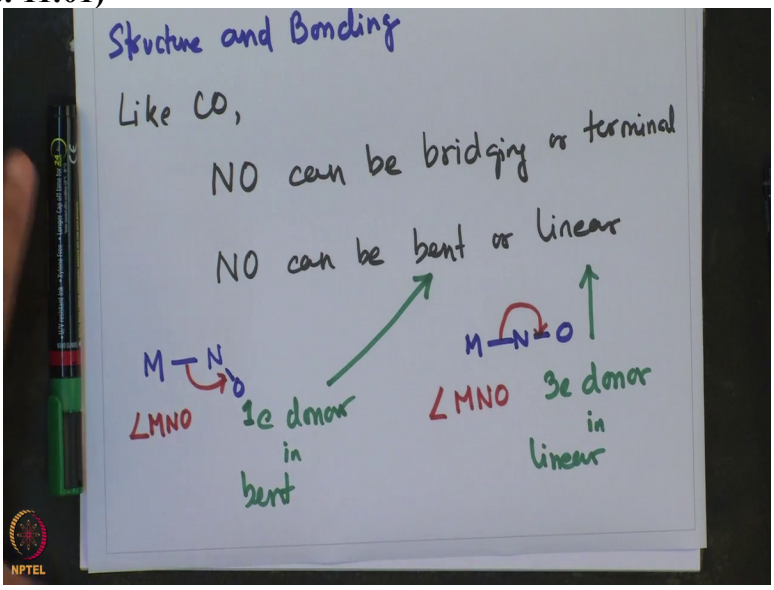

Now nitrosyl like a CO oh oh can also be a be reading as well as a terminal but it also has another dimension that it can be bent or linear. So, like CO carbon monoxide NO can be it can be bridging or terminal and also the second variable is NO can be bent or linear upon binding to transition metal and these is coded to oh the type of bonding a binding that the NO exhibits with a transition metal.

For example in a linear binding NO is a 3 electron donor 3 donor in linear binding and it is 1 electron donor in bent binding so, to illustrate this further metal bound bent a more NO would look like something like this whereas linear NO is something like that and this binding of the bent or the linear form can be characterized by this angle or angle MNO which is around 180 degree for the linear ones and the same angle the angle MN O would be significantly a shorter are smaller than 180 degree if it were to be bent binding.

Now these can be bent or the linear form of binding can be easily discerned from the extra strophic express single crystal experiment whereby one can measure the angle at nitrogen in the bent and the linear form of transition metal MNO metal nitrosyl complexes.

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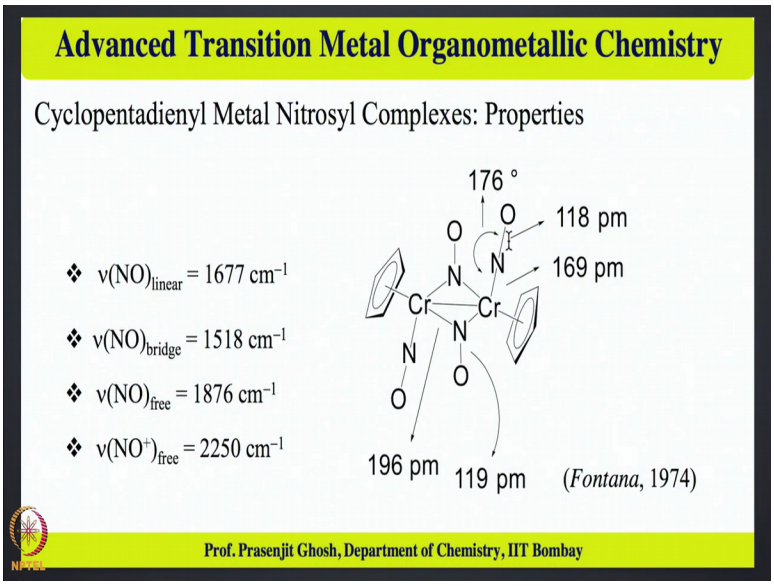

Let us now look at some of the cyclopentadienyl nitrosyl complexes which have been structurally characterized and look at the binding frequencies other frequencies of this metal nitrogen interaction bond to sort of a look to sort of get some insight as to the type of binding they exhibit.

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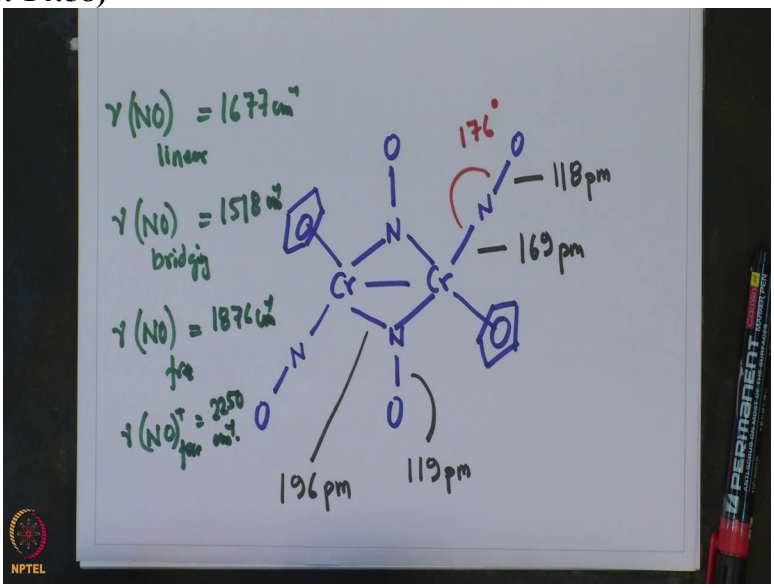

For example this di chromium nitrosyl complex cyclopentadienyl nitrogen complex as is shown over here, so here the markers are the chromium nitrogen bond is about 169 picometer the nitrogen oxygen bond 118 picometer and did this bridging nitrogen oxygen bond is 119 picometer then this chromium nitrogen bridging chromium nitrogen a nitrogen bond is 196 picometer.

So, one can see that the bridging chromium nitrogen and the nitrogen oxygen bonds are longer then the terminal chromium nitrogen bond which is 169 vs 196, 196 vs 169 and NO sort of remains almost the same with 119 picometer as was to 218 picometer. Whereas these angle at the linear one is quite close to the angle that the linear one is quite close to 180 degree which is about 176 degree.

So, this molecule has several Mu stretches for example Nu NO linear is Nu a nonlinear is 1677 Nu NO bridging is 1518 whereas Nu NO free is 1876 centimeter and Nu NO+ free is 20 to 50 centimeter inverse. So, here is a molecule in which both the bridging as well as the terminal a NO's can be a same these there are 2 bleaching and 2 terminal not only a that the terminal ones are in a linear form that means these terminal NO's are being bound as a 3 electron donor.

In this molecule however there is no bent terminal NO's observed over here there are only 2 types 1 is bridging and the linear and they can be characterized by different frequencies. For example the bridging NO's appear at a lower wave number then the terminal NO's.

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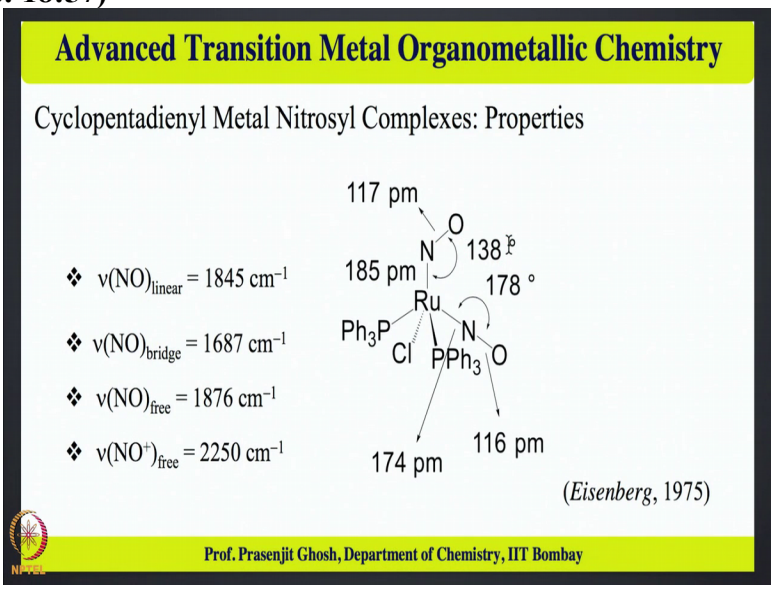

Now we will take a look at a few such examples which will clarify the point for example these ruthenium another ruthenium complex which has no bridging nitrosyl but 2 terminal nitrocine however 1 of the terminal nitrosyl is linear whereas the other 1 is bent.

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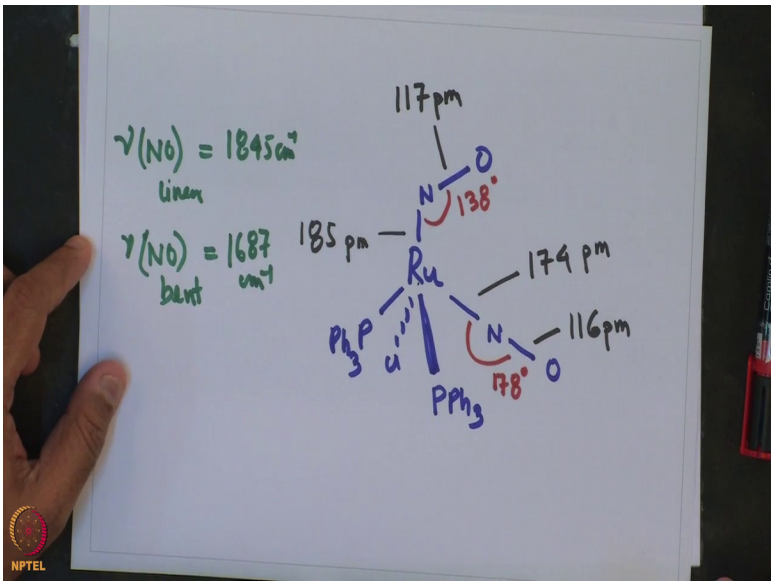

So, we will see that here we have a ruthenium complex which has a bent terminal NO and their linear terminal NO and it has 1 chlorine and 1 phosphine the metrical data are as follows. So, the NO bond as expected is around 117 picometer in ruthenium metal ruthenium bond ruthenium nitrogen bond is about 185 picometer and for the bent NO's where as it is 174 picometer for the linear NO and nitrogen oxide NO our distance is 116 picometer.

This ruthenium nitrogen oxygen angle is 178 degrees whereas in the bent 1 it is 138 degrees. Now what is interesting is the fact that one can sort of correlate these bond distances with the electron donor ability of this NO ligand. For example a linear NO is a 3 electron donor and hence it forms a stronger bond with ruthenium as opposed to the bent NO which is a 1 electron donor and result what we see is that with ruthenium nitrogen bond in a linear terminal NO is indeed shorter at 174 Picometer than that of 185 picometer which in bent NO which is a 1 electron donor.

So, this sort of this external data sort of verifies is the nature of bonding are corroborates the natural bonding which sort of suggests that a linear NO would be at the electron donor making a stronger bond resulting in a shorter metal nitrogen distance in comparison to that of a bent NO which is a 1 electron donor and then that would be a longer ruthenium nitrogen distance.

So, for example let us look at the infrared frequencies over here to Nu NO linear is 1845 centimeter inverse so there this stretching is 1845 centimeter inverse whereas Nu NO bent is 1687 centimeter inverse, so one can really see in this case as well that the bent one is of a longer bond length 1 electron donor and hence a weaker bond so a lower energy is required for the

stretching of this bond which is 1687 whereas the linear NO is a stronger of the 2 NO interactions and involves 3 electrons it has a much shorter ruthenium nitrogen bond distance and as a result it has a higher 1845 centimeter inverse as the stretching frequency.

So, what we see over here is a nice demonstration of IR as well as x-ray a corroborating each other and sort of indicating the type of interactions these metal nitrosyl compounds are showing. So, we are going to look at some more of these examples that will further highlight this point of infrared spectroscopy and IR spectroscopy corroborating each other in the characterization of metal nitrosyl interaction is very in various half-sandwich transition metal nitrosyl complexes.

So, here we have another nickel cyclopentadienyl i nitrosyl complex which contains only 1 type of linear metal nitrosyl bond.

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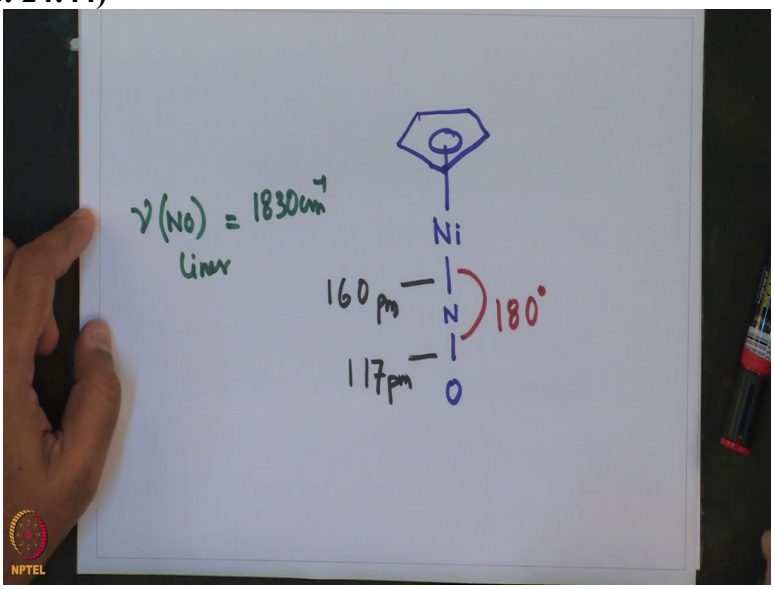

I am drawing the complex over here so these has a linear metal nitrogen bond the nitrogen oxygen 1 distance is 117 Picometer which we have seen and nickel nitrogen is 160 picometer this angle is linear so it is about 180 degrees degrees and the correspondingly the stretching frequencies are as Nu NO linear is 1830 centimetre inverse. So, this is quite higher energy indicating that this is the 3 electron interaction.

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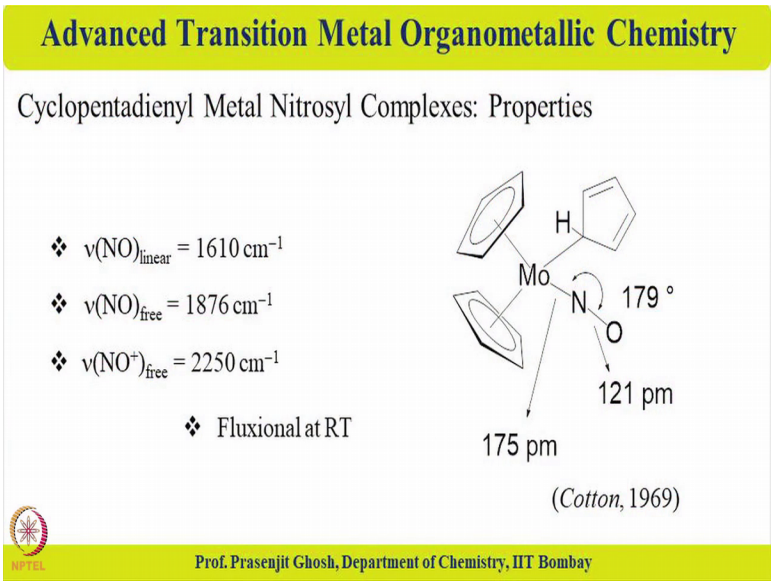

Now we are going to take up another example containing 2 cyclopentadienyl ligand bound to molybdenum eta 5 fashion and eta 1 bound cyclopentadienyl ligand bound to molybdenum and the 4th ligand being NO ligand and bound in a linear fashion.

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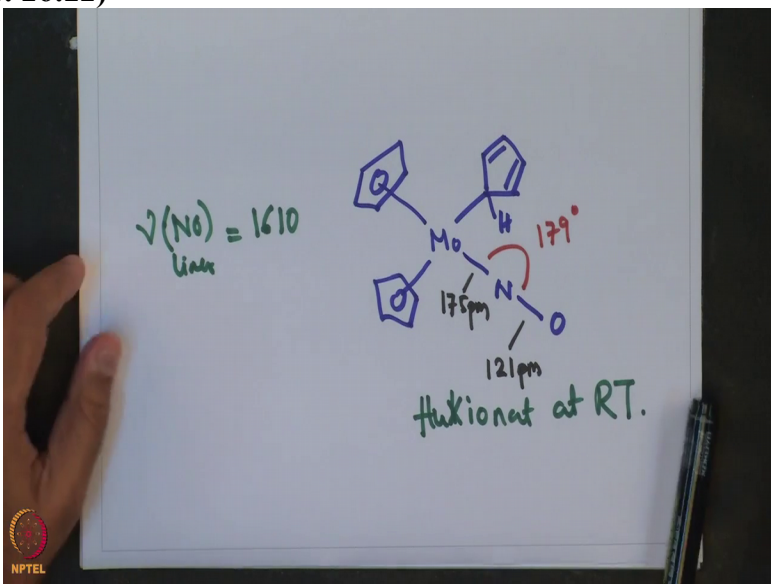

So, let me just draw this complex over here so CP molybdenum CP NO H, now this these NO distance in this complex is 121 picometer and molecule nitrogen is 175 picometer whereas this angle is close to being linear 179 degrees so the corresponding the frequency is Nu NO linear is 1610 centimeter inverse and this molecule is highly a fluxional at room temperature. So, with this I would like to conclude today's lecture.

In this lecture we had been looking into half sandwich complexes of cyclopentadienyl transition metal nitrosyl complexes particularly with respect to their synthesis these come as well as

structure and bonding. These complexes are usually prepared by mainly 1 type of method that involve cyclopentadienyl transition metal complexes by by reaction with NO gas or NO source giving the cyclopentadienyl transition metal nitrosyl complexes.

We have also looked into the binding of these nitrosyl complexes and what we found that these nitrosyl began similar to what had been observed for carbon monoxide can bind in both bridging as well as terminal forms and also in between there is another additional versatility of these NO binding is that within its terminal binding it can exhibit a linear or bent form. Now linear form arises due to 3 electron donation of a NO to the metal whereas the bent 1 arises due to 1 electron donation of the anode to the metal.

And as a result of these the number of electron that is being donated to that metal the bond becomes stronger in case of the 3 electron donor and that is reflected in a shorter metal nitrogen bond in the metal in moities and that also reflects in a relatively higher MNO stretch a nitrogen stretching frequency for these complexes. Whereas in the bent 1 since it is a 1 electron donor metal nitrogen bonds are relatively longer and as a result the new stretching frequencies for the bent terminal nitrosyls are occur at lower wave numbers.

So, with these I would like to conclude today's discussion or metal nitrogen complexes at cyclopentadiene nitrosyl complexes, we are going to be discussing some more on these transition metal nitrosyl cyclopentadienyl nitrousyl complexes into the beginning of the next lecture and then move on to another new type of some half sandwich complexes which are cyclo pentadiene transition metal hydride complexes in the next lecture.

So, I thank you for patiently listening to these today's lecture and I look forward to being with you in the next lecture, till then good bye.