Advanced Transition Metal Organometallic Chemistry
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Lecture – 26
Transition Metal Arene Carbonyl Complexes: Reactivity

Welcome to this course on advanced tension metal organometallic chemistry we have been discussing half sandwich complexes of the type transition metal arene carbonyl complexes and their reactivity in the last lecture. And with that perspective we have seen that these transition metal arene metal carbonyl complexes are quite significant in number we had seen various of them which exists and then we have looked into their prepare procedures as well.

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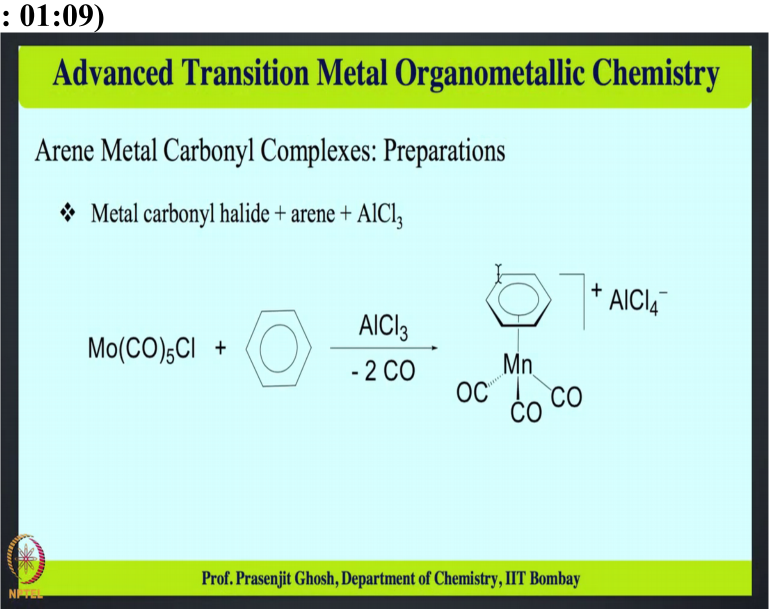

Advanced Transition Metal Organometallic Chemistry

Arene Metal Carbonyl Complexes: Preparations

- Metal carbonyl halide + arene + $AlCl_3$

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One of the most common procedures which often are used for making these half-sandwich transition metal arene carbonyl complexes is the carbonyl substitution reaction of metal carbonyls with arenes at high elevated temperatures. So, this is by far the most direct method for synthesizing these arene metal carbonyl complexes and continuing upon that discussion we are going to take a look at few other methods which are available for synthesizing these transition metal arene carbonyl complexes.

And the next reaction that comes to the mind with regard to preparation of these complexes is the direct reaction of metal carbonyl halides with arene's in presence of AlCl3.

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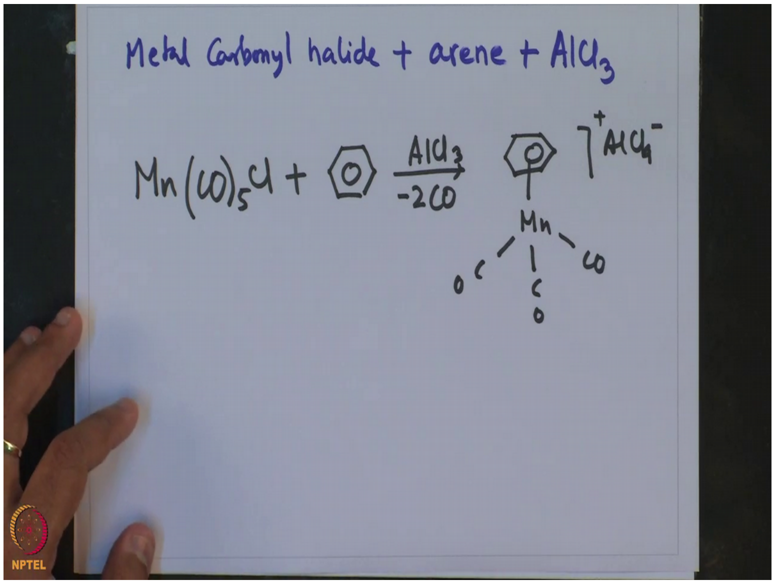
Metal Carbonyl halide + arene + $AlCl_3$

So, metal carbonyl halide + arene + Al Cl 3 Mn CO 5 Cl + benzene in presence of AlCl3 gives 2 carbonyl to give this benzene amen CO CO CO and Al Cl 4 - anion here this AlCl3 can be perceived as something which is abstracting a chloride to creating a vacant site and then two other carbonyl gives away gives way to this incoming arene which is 6 electron donor resulting in this benzene manganese tricarbonyl cation with AlCl 4 anion.

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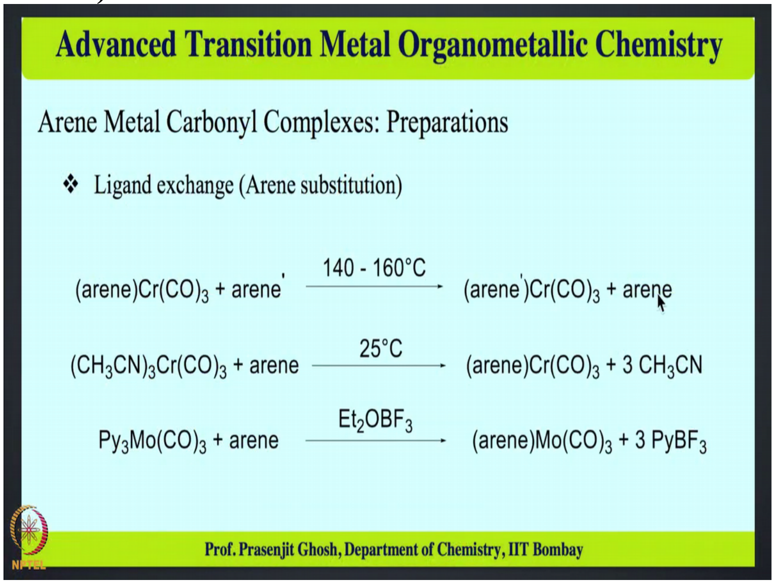

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Arene Metal Carbonyl Complexes: Preparations

- Ligand exchange (Arene substitution)

$$(arene)Cr(CO)_3 + arene' \xrightarrow{140 - 160°C} (arene')Cr(CO)_3 + arene$$

$$(CH_3CN)_3Cr(CO)_3 + arene \xrightarrow{25°C} (arene)Cr(CO)_3 + 3\ CH_3CN$$

$$Py_3Mo(CO)_3 + arene \xrightarrow{Et_2OBF_3} (arene)Mo(CO)_3 + 3\ PyBF_3$$

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The next, of course comes these arene substitution reactions or the ligand exchange reaction.

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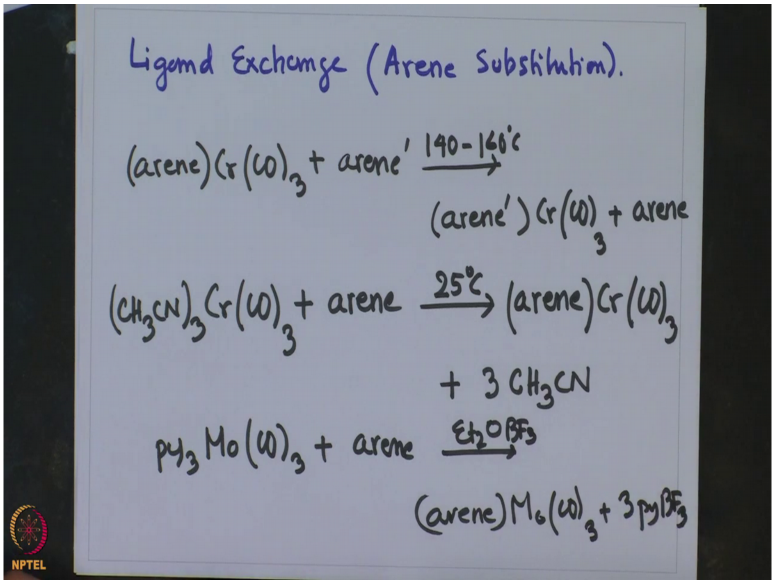

Ligand Exchange (Arene Substitution).

$$(\text{arene})\text{Cr}(\text{CO})_3 + \text{arene}' \xrightarrow{140-160^\circ\text{C}} (\text{arene}')\text{Cr}(\text{CO})_3 + \text{arene}$$

$$(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3 + \text{arene} \xrightarrow{25^\circ\text{C}} (\text{arene})\text{Cr}(\text{CO})_3 + 3\,\text{CH}_3\text{CN}$$

$$\text{py}_3\text{Mo}(\text{CO})_3 + \text{arene} \xrightarrow{\text{Et}_2\text{O BF}_3} (\text{arene})\text{Mo}(\text{CO})_3 + 3\,\text{pyBF}_3$$

Or the substitution the reaction is illustrated by a few examples given over here. This is the direct reaction of arene chromium tricarbonyl + another arene which is given by having dust at 140 to 160 degree centigrade giving ring dust chromium tricarbonyl + arene. The next reaction is Ch3 Cn whole 3 chromium tricarbonyl + arene at 25 degree centigrade giving arene chromium tricarbonyl + 3 CH 3 CN.

And the last one is tripyridine Py 3, molybdenum tri carbonyl + arene in presence of Et 2 BF3 salt giving arene molybdenum tri carbonyl + 3 Py BF3. So, this seems like quite a more general reaction in the sense that there can be direct substitution of an arene with another arene or it can even be a substitution of coordinated asymethyl arene or it can also be substitution of pyridine with arene by treatment with BF3 threat.

so these adding substitution reactions seems more like a general reaction now regarding the structure of these arene metal carbonyl complexes it is important to note that quite a wide variety of structures have been reported for these kind of complexes by what wide variety I mean that these arene in metal carbonyl complexes have been found to be coordinated in a eta 6 fashion or even eta 2 fashion to two different to two different metal center or even eta 3 fashion eta 2 fashion to 3 different so, metal centers giving rise to dinuclear as well as tri nuclear complexes.

I am going to talk about some of the interesting ones that have been structurally characterized as a representative example of the same.

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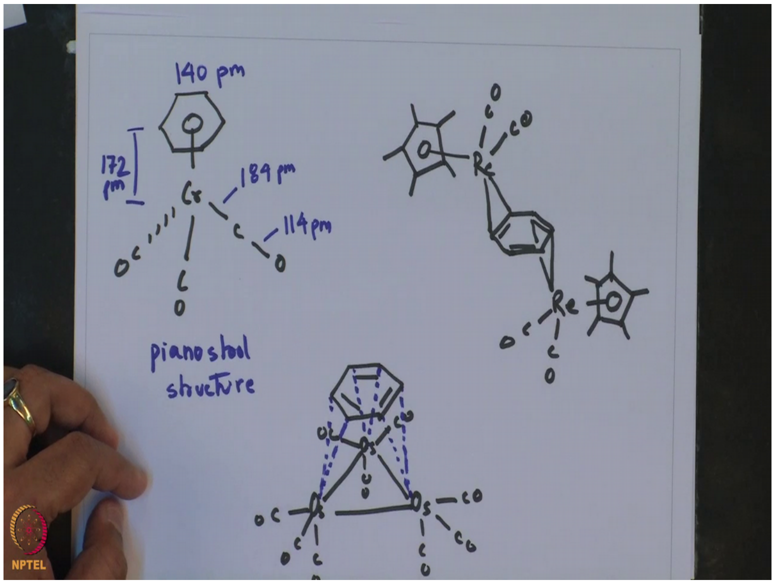

For example this benzene tri carbonyl chromium which is 140 picometer is the carbon-carbon and this distance between the benzene and the chromium is 172 picometer chromium-carbon distance is 184 picometer and carbon-oxygen is one 114 picometer. Here is a another; so this is like a piano stool structure another dinuclear compound is this rhenium dinuclear compound with two arene rings where one of arene rings is eta 6 coordinated the other arene ring is eta 2 coordinated and this is a beautiful structure.

As we will be saying this is with pentamethyl CP rhenium carbonyl with one of the benzene ring being hit at tuber coordinated and the other benzene ring be also in a eta 2 coordination fashion bound to all this Penta methyl cyclopentadienyl ligand and then two carbonyls. You know so here we see a diversified a new kind of binding where this arene moiety is bound in an additive fashion to one central rhenium and additive fashion to another rhenium so, giving these dinuclear structure.

Here is also a tri nuclear structure this is also a very interesting example in which the rhenium is bound to three osmium centers in a tri nuclear fashion okay. And the binding is shown in blue which is shown over here. So, this is a very interesting example where this rhenium is bound in an additive fashion to two different metal center. Now what is interesting about these examples is the fact that there is a wide diversity of binding of this arene ring to the metal in these arene transition metal carbonyl complexes.

And it can vary from the more conventional eta 2, 6 x 6 type adding complexes to dinuclear to a tattoo tri nuclear metal carbonyl complex as is shown over here. Now you know then comes the interesting aspects for these complexes and it is the fact that these reactivity pattern of these metal carbonyl complexes.

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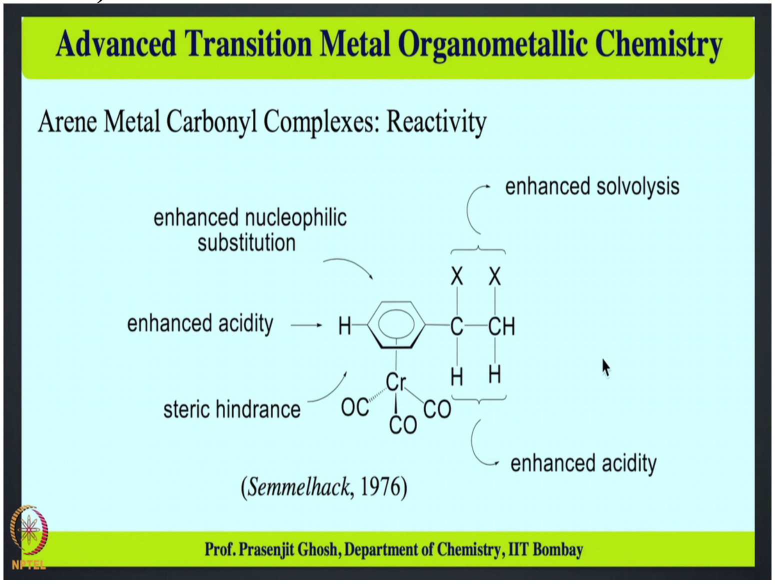

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Arene Metal Carbonyl Complexes: Reactivity

enhanced solvolysis

enhanced nucleophilic substitution

enhanced acidity

steric hindrance

enhanced acidity

(*Semmelhack*, 1976)

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So, we are going to discuss this in bit more details by looking at the structure and there has been convergence on the type of reactivity these arene metal carbonyl complexes. So, depending on the part of the culture they arene ring which is one looking at.

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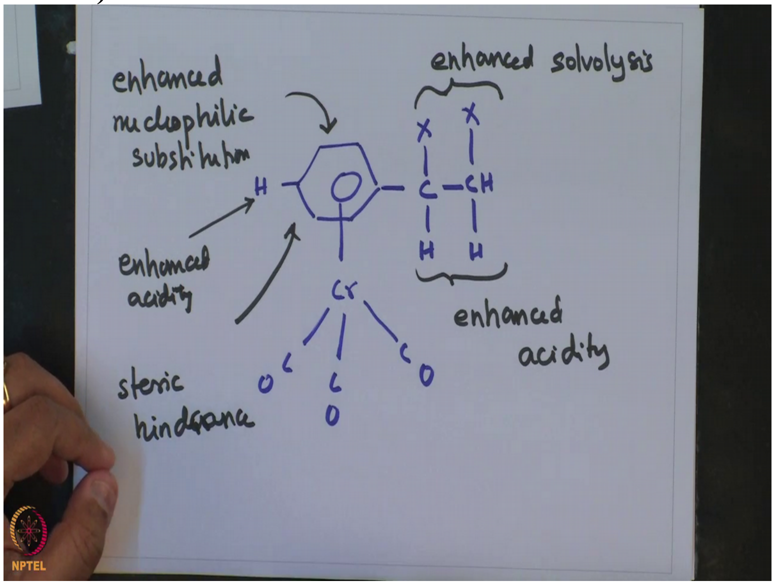

So, I will illustrate this with this beautiful example for example this arene CH XCH XH these kind of structure bound to chromium tricarbonyl. So, the; these halides the position in Alpha and the beta position they undergo ready solvolysis or these are the regions which shows enhanced solvolysis. Similarly the protons over here show enhanced acidity these benzene ring shows enhanced nucleophilic substitution.

So, this ring undergoes nucleophilic substitution reaction this proton shows enhanced acidity and these underneath he benzene ring and that metal tricarbonly may undergo enhanced steric hindrance. So, as a consequence of this enhanced steric hindrance one sees in many occasions the attack happening from the exo phase of the arene ring as opposed to the interface of the arene ring. So, with these reactivity scheme put in place let us take a look at some of the reactions which these arene chromium tricarbonyl complexes that exhibit.

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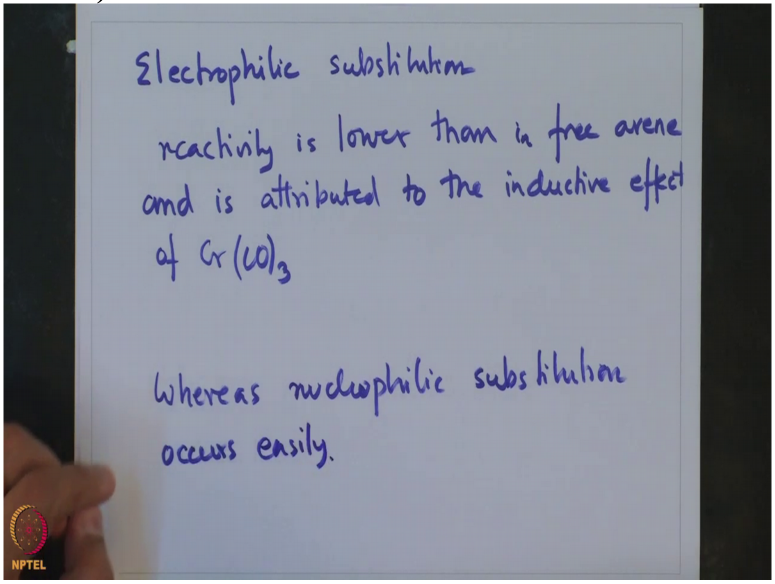

Electrophilic substitution

reactivity is lower than in free arene
and is attributed to the inductive effect
of $Cr(CO)_3$

Whereas nucleophilic substitution
occurs easily.

So, the first and foremost is the electrophilic substitution, now this electrophilic substitution in adding metal carbonyl complexes is lowered in reactive reactivity than that of free benzene the activity is lower than in free benzene free arene and is attributed to the inductive effect of chromium tricarbonyl unit. Now, these so that means that electrophilic reaction sort of occurs but occurs very slowly. And that is because of the inductive effect of the chromium draconian unit whereas nucleophilic substitution occurs readily. And this is best explained by and this is best explained by the slide shown over here.

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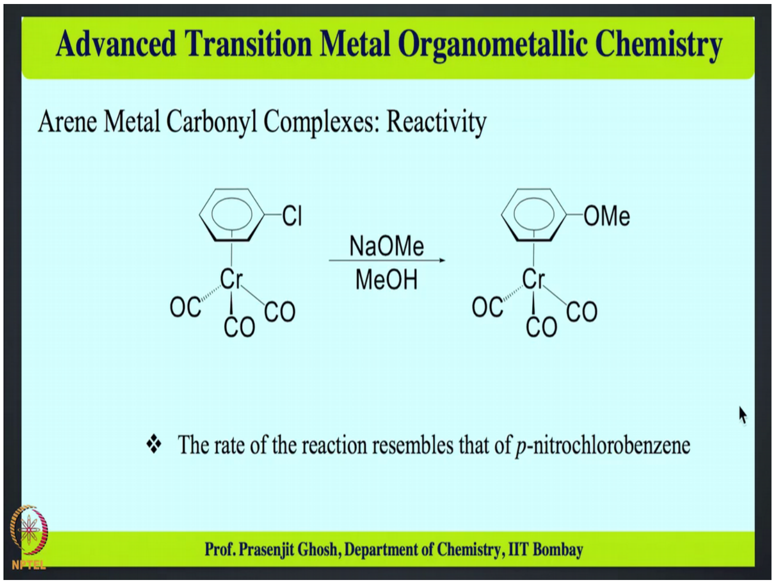

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Arene Metal Carbonyl Complexes: Reactivity

- The rate of the reaction resembles that of *p*-nitrochlorobenzene

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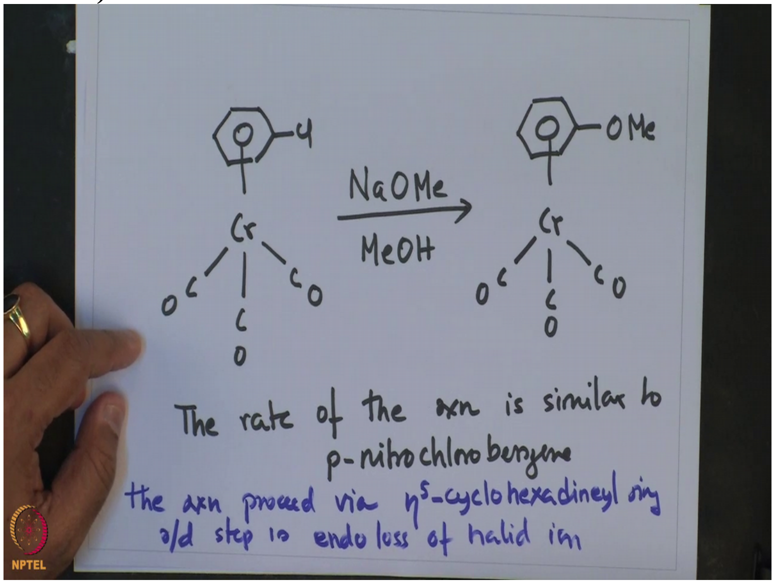

The rate of the rxn is similar to p-nitrochlorobenzene

the rxn proceed via η5-cyclohexadienyl ring r/d step is endo loss of halid ion

Where one sees that chlorinated benzene with chromium tricarbonyl and sodium methoxide and ethanol giving OMe in presence of the halide methoxy benzene chromium tricarbonyl and the weight of the reaction is similar to that of para nitro benzene rite of the reaction is similar to para nitrobenzene para nitro chlorobenzene. Another interesting thing is that the play determining step is the endow loss of halide ion.

The reaction proceeds via eta 5 cyclo hexa dienyl ring which means that nucleophilic attacks over here and in spirit becomes dyene in and aromaticity is lost and the r/d step is in the endow loss of the halide ion. So, that sort of suggests that when the nucleophile attacks have over here there are armocity loss and it just becomes a hexa diene with way Me on the top and the chlorine and the bottom face and the loss of the chlorine resulting in the gaining of the aromaticity and methoxy a occurs by uploading being lost from the bottom face of the endow face which is sort of the most slowest step of the reaction and hence is the rate determining step of this reaction.

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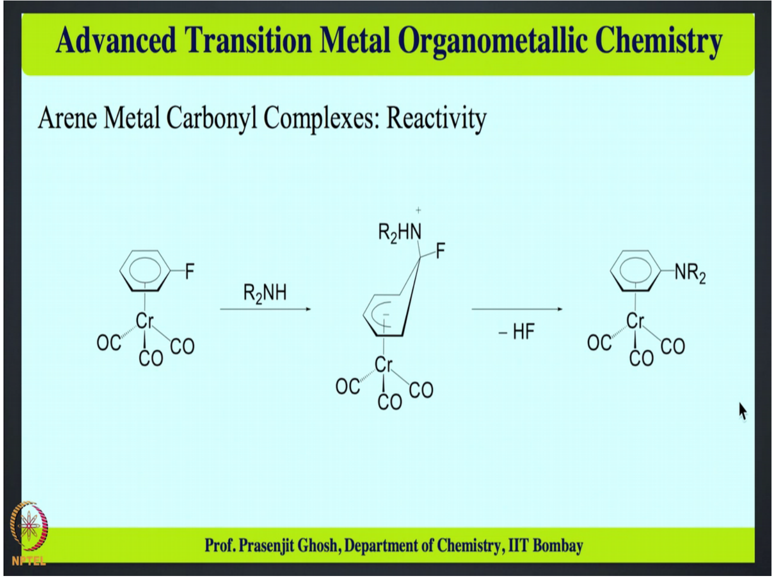

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Similarly a another example of this nucleophilic substitution reaction is shown over here with this amine on these fluorobenzene derivative our 2n h plus this is a nine chromium which loses HF to give this di alkyl aniline, di alkyl amin bound chromium tricarbonyl another example in this reaction is the treatment of lithium CH 2 CN to this O-methoxydy, O-methoxy complex. This is explained in this beautiful example.

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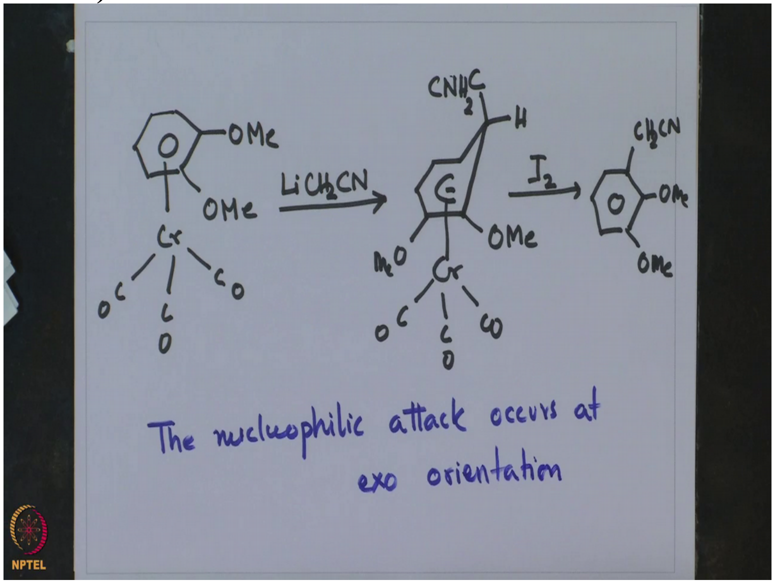

The nucleophilic attack occurs at exo orientation

Arene OMe OMe chromium CO CO CO that reacting with Li CH2 CN giving this nucleophilic attack occurring on HC CNH2 OMe OMe chromium CO CO CO which in presence of iodine gives this trisubstituted derivative of benzene with CH 2 CN OMe OMe and if one looks at it is kind of obvious that the nucleophilic attack occurs and the exo orientation. The nucleophilic attack occurs at exo orientation.

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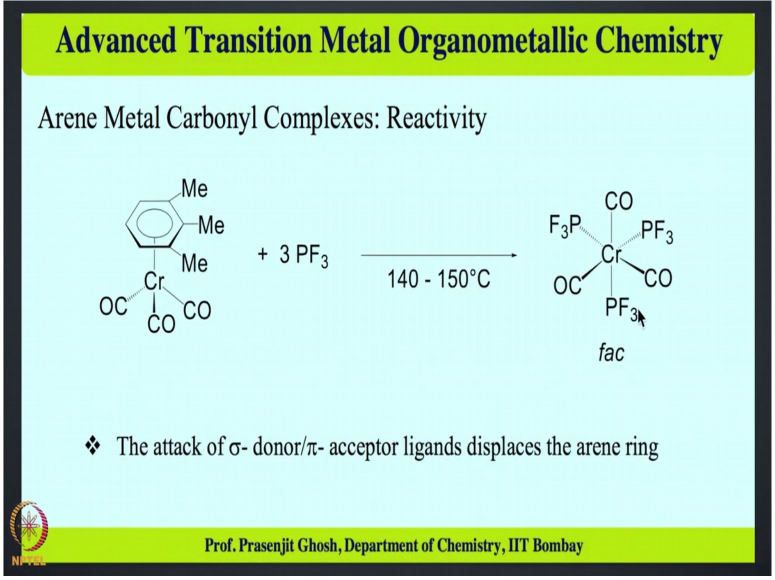

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Arene Metal Carbonyl Complexes: Reactivity

❖ The attack of σ- donor/π- acceptor ligands displaces the arene ring

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Another interesting example involves the reaction of tri methoxy benzene with chromium tricarbonyl and the beauty about this reaction is that the attack of Sigma Pi except Sigma donor pi acceptor ligands displaces are in range.

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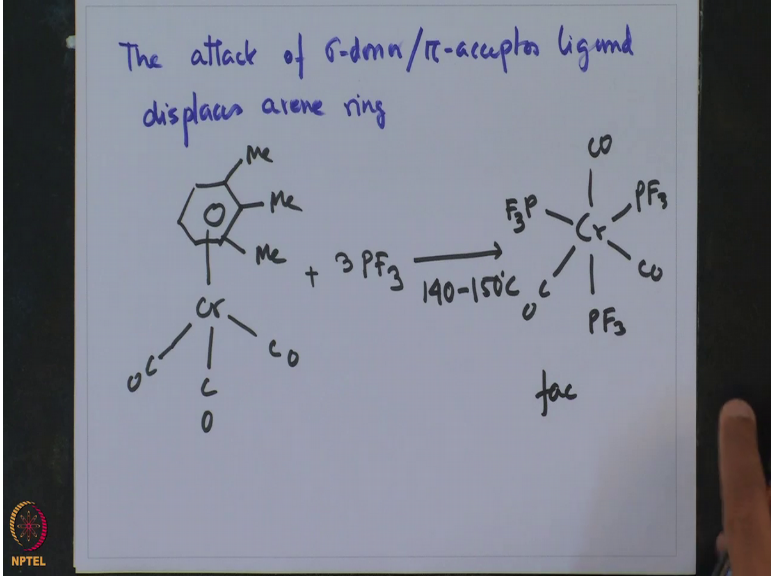

The attack of σ-donor/π-acceptor ligand displaces arene ring

So, this is kind of an interesting reaction in which the attack of Sigma donor PI acceptor ligand displaces arene ring usually we have we see this other way round and that arene rings displaces sigma Pi donor ligands. For example metal carbonyl by reaction with artene gives arenen metal carbonyl complexes but here this is the other way around then what we usually see. So, we have tri methoxy benzene 1 2 3 tri methyl benzene chromium carbonyl carbonyl carbonyl + 3 PF 3 at elevated temperature 140 to 150 degree centigrade giving chromium tricarbonyl PF 3 PF 3 PF 3 facial isomer is obtained in this case.

So, with this I am going to conclude today's lecture in which we have begin began by discussing the propriety methods available for preparation of these areneg metal carbonyl complexes. To begin with we had seen two other new methods for preparing these arene metal carbonyl complexes. And one such method involved the direct reaction of metal carbonyl halide with arrene in presence of AlCl 3 and the other was simple arene exchange reactions.

In addition to that we have looked into the structure of various metal adding carbonyl complexes and what we had seen is that a large diversity is observed from the most common eta 6 bound complexes to eta 2 bound nuclear as well as eta 2 bound tri nuclear complexes have been discussed. In addition to that we have also looked into the reactivity of arene metal carbonyl complexes and we saw that depending on the part of the ring the reactivity differs.

And to begin with what we saw that electrophilic substitution reactions no possible are kind of slower or less facility in that of the fluorines however nucleophilic substitution are considerably more facile and this nucleophilic substitution occur from the exo phase resulting in the loss of aromaticity of the ring followed by a gain of aromaticity and the loss of the group. We have to take a look at several examples of is nucleophilic substitution reaction.

And then to end with today's talk we have also seen that Sigma PI donor can also displace arraign from arene metal carbonyl complexes which is usually the other way round that we have studied so far at elevated temperatures. So, with this I conclude today's lecture some more discussion still remains on this metal arene metal carbonyl complexes which you are going to take up in the next lecture.

Until then I thank you again for patiently being with me for this lecture and I look forward to take the next lecture discussing on more of these arene metal carbonyl complexes and other topics till then good bye and thank you.