Introduction to Organometallic Chemistry

Prof. A. G. Samuelson

Department of Inorganic and Physical Chemistry

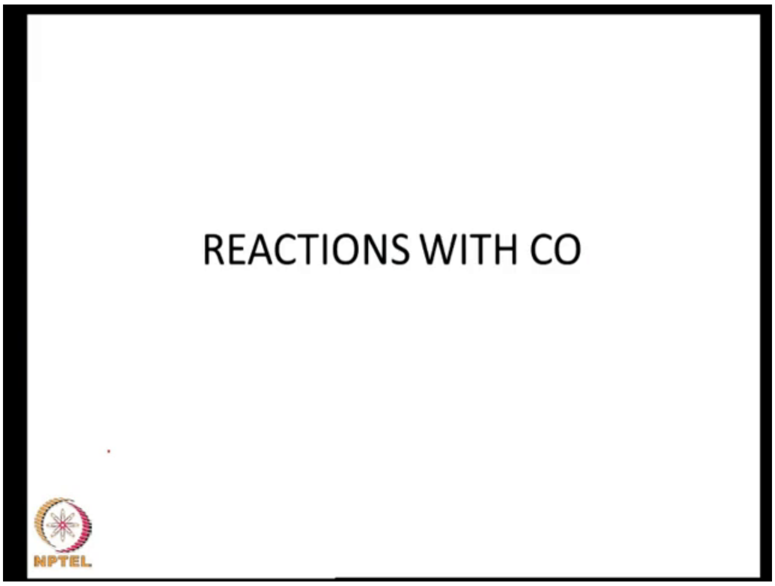
Indian Institute of Science, Bangalore

Lecture - 34

Reactions with CO Insertion

In this lecture, we will discuss some of the important organometallic reactions, which deal with carbon monoxide.

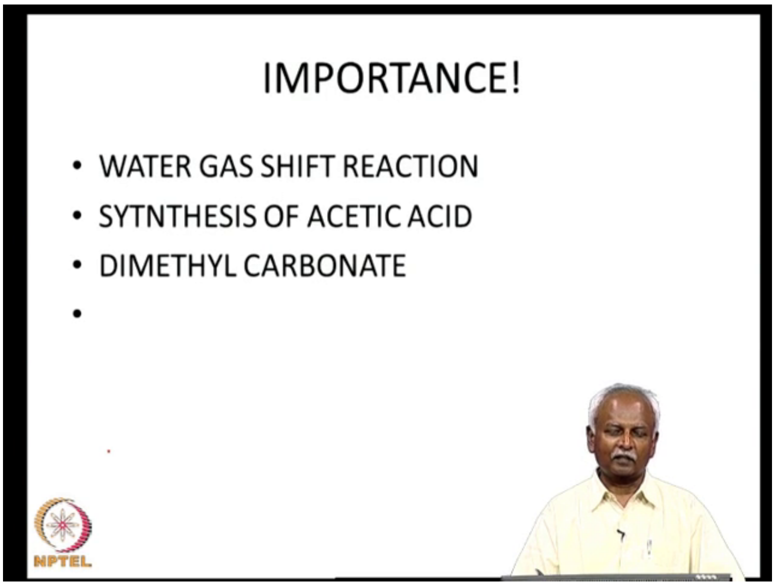
(Refer Slide Time: 00:22)



REACTIONS WITH CO

Carbon monoxide is probably one of the most important raw materials that are available to the chemist. It is important that we have some means of converting it into useful chemicals because of the small polarity of carbon monoxide. It is not possible to carry out reactions with carbon monoxide, which you can do with carbon dioxide.

(Refer Slide Time: 00:54)

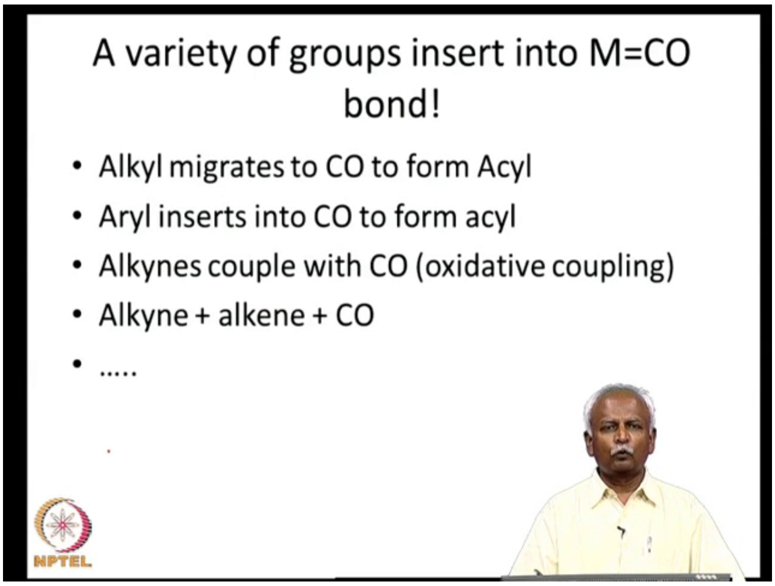


IMPORTANCE!

- WATER GAS SHIFT REACTION
- SYTNTHESIS OF ACETIC ACID
- DIMETHYL CARBONATE
-

So, how is carbon monoxide, which is unreactive, activated? If you look at the industrial scene, it is clear that there are several reactions such as the water gas shift reaction, the synthesis of acetic acid or even dimethyl carbonate which are extensively used in CDs, in the manufacture of CDs. For example, all of these utilize carbon monoxide as a raw material. So, how exactly does organometallic chemistry succeed in inactive or deactivating? How exactly does organometallic chemistry succeed in activating this unreactive molecule?

(Refer Slide Time: 01:35)



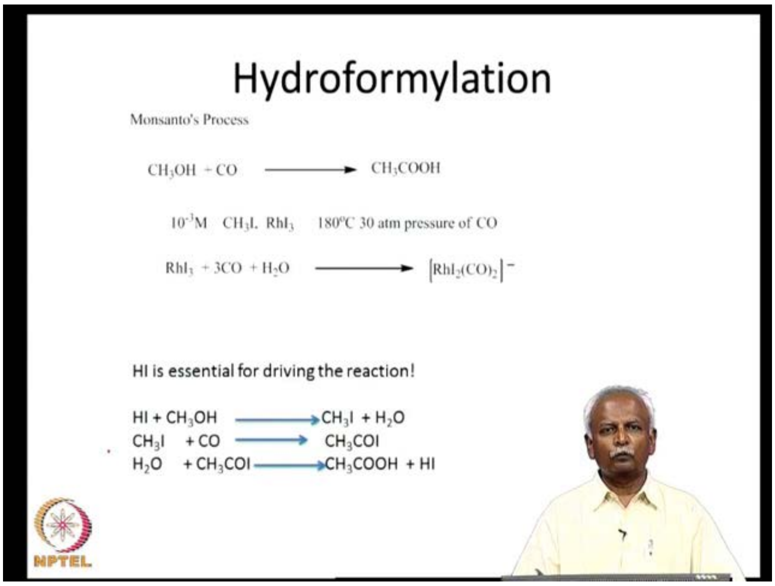
A variety of groups insert into M=CO bond!

- Alkyl migrates to CO to form Acyl
- Aryl inserts into CO to form acyl
- Alkynes couple with CO (oxidative coupling)
- Alkyne + alkene + CO
- .....

If you look at the chemistry that has been developed, you will realize that carbon monoxide has an extensive chemistry that includes alkyl groups, aryl groups, alkynes, alkenes and a combination of all of these groups to form useful materials. So, we will consider each one of these initially separately. Then, we will look at some complicated reactions where multiple groups are involved.

So, in all of these reactions, carbon monoxide is activated. It is being possible for a reaction between unreactive carbon monoxide, which is now coordinated to the metal and alkyl group or an aryl group or a vinyl or allyl group.

(Refer Slide Time: 02:29)



Hydroformylation

Monsanto's Process

$$CH_3OH + CO \longrightarrow CH_3COOH$$

10^{-3}M CH_3I, RhI_3 180°C 30 atm pressure of CO

$$RhI_3 + 3CO + H_2O \longrightarrow [RhI_2(CO)_2]^-$$

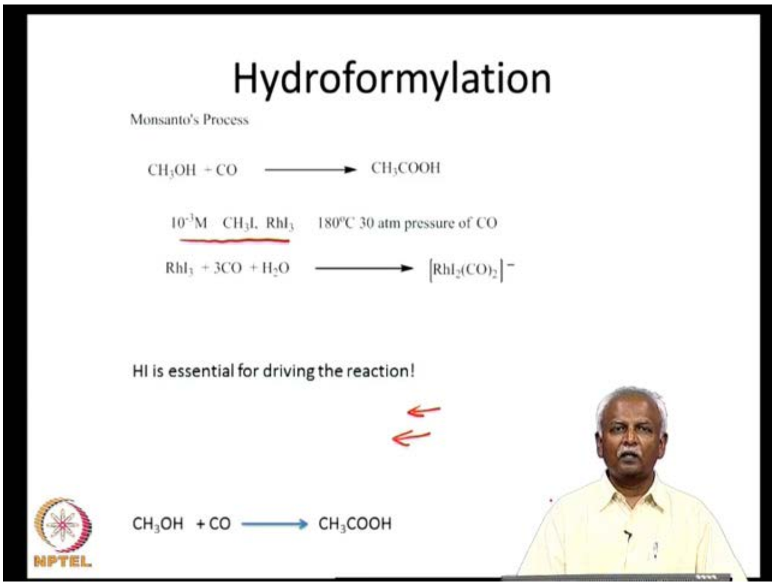
HI is essential for driving the reaction!

$$HI + CH_3OH \longrightarrow CH_3I + H_2O$$
$$CH_3I + CO \longrightarrow CH_3COI$$
$$H_2O + CH_3COI \longrightarrow CH_3COOH + HI$$

So, let us take up the first reaction, which is possibly one of the simplest reactions that are available in this series of chemistry. That belongs to the carbonylation of methanol. This chemistry is that of the carbonylation of methanol where methanol is reacted with carbon monoxide to generate acetic acid. Now, it turns out that if you heat the 2 under very high pressure, you will not get acetic acid by any means. The presence of rhodium iodide and methyl iodide as a catalyst, these 2 are used in catalytic quantities. That is the molar ratios in which you have to do the reaction.

So, it is extremely small amounts of rhodium iodide, methyl iodide that are necessary to push the reaction from the left to the right. Why use rhodium iodide? Can we not use rhodium chloride or the bromide? The answer is no. Actually, it has been shown that HI is essential for driving the reaction from the left to the right. Now, this is strange till you consider the fact that HI actually converts methanol into methyl iodide. That is this reaction that we are talking about right here. It undergoes a simple insertion reaction of methyl iodide with carbon monoxide to give you acetyl iodide.

(Refer Slide Time: 04:25)



Hydroformylation

Monsanto's Process

$CH_3OH + CO \longrightarrow CH_3COOH$

10^{-3}M CH_3I, RhI_3 180°C 30 atm pressure of CO

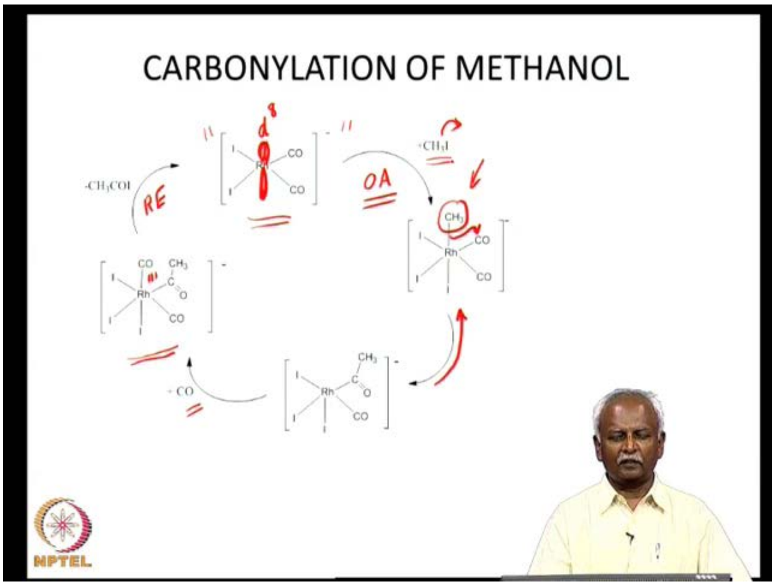
$RhI_3 + 3CO + H_2O \longrightarrow [RhI_2(CO)_2]^-$

HI is essential for driving the reaction!

$CH_3OH + CO \longrightarrow CH_3COOH$

If you add up all 3 reactions, the hydrolysis of acetyl iodide gives you acetic acid and the 2 reactions that we just talked about, you will come to the conclusion that you just need to add methanol and carbon monoxide to get acetic acid. So, it turns out when although you need methyl iodide in catalytic quantities and rhodium iodide also, this reaction is an extremely profitable reaction. You have taken 2 rather unreactive species and converted them into acetic acid, which is such a useful raw material in the industry.

(Refer Slide Time: 04:53)



CARBONYLATION OF METHANOL

Now, let us take a look at the science behind this whole process. Why do we need methyl iodide? Methyl iodide is the one which will undergo this first step in this reaction where the rhodium di iodo rhodium carbonylate species, which I am marking for you right here, is the one that undergoes oxidative addition. You will notice that is d 8 species. It is a nice full d orbital that is in the d z squared along the z axis in the d z quad orbital. That is perpendicular to the plane in which the ligands are kept.

Now, that carries out a nucleophilic substitution reaction on methyl iodide. So, you need fairly good leaving group for the iodo groups to leave from the methyl species. So, you can achieve this 6 coordinated compound, which are now d 6. It is octahedral in nature. You have a rhodium 1 compound being converted to rhodium 3 because you have undergone oxidative addition. This is an oxidative addition reaction. It is now set up to carry out the next step, which is the insertion of carbon monoxide.

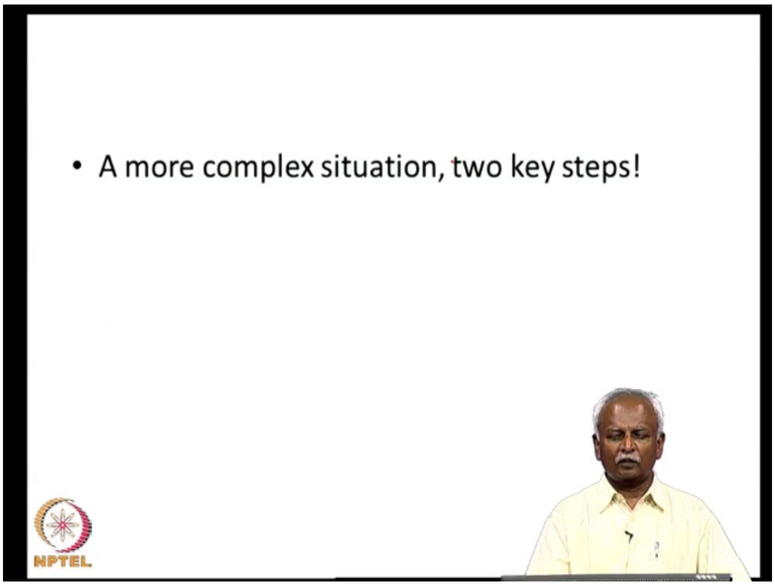
Now, as we mentioned in the studies in insertion reactions, it is the methyl group which migrates to the carbon monoxide. So, the methyl group migrates to the carbon monoxide, so that you have an acetyl group coordinated to the rhodium. Now, this full step is in fact an equilibrium process. This keeps oscillating back and forth.

If you have excess pressure of carbon monoxide, you can drive the reaction to the left side of this catalytic cycle so much, so that you will end up with this compound in solution, which now reductively eliminates. So, it undergoes a reductive elimination.

This is a rhodium 3 species and that undergoes reductive elimination to give you the catalytically active R HI2 CO2 minus species, which is the resting state of the catalyst. This is the resting state of the catalyst. Acetyl iodide is eliminated in the reductive elimination step.

So, as we saw earlier, acetyl iodide will now be converted to hydroiodic acid and acetic acid. The hydroiodic acid is capable of converting the methanol to methyl iodide, which we have fixed here. So, essentially we have converted methanol to acetic acid. So, this is the step that we have just considered in the catalytic cycle. We have just considered the simplest of the carbonylation reactions that we would consider today. There is only one oxidative addition and there is an insertion process and the reductive elimination. So, this is an extremely simple catalytic cycle.

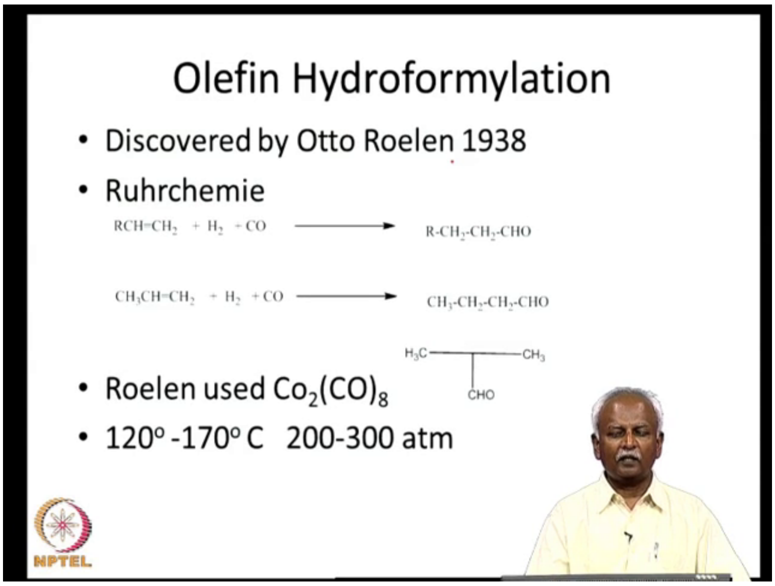
(Refer Slide Time: 08:14)



- A more complex situation, two key steps!

Now, we will consider a more complex situation where there are 2 key steps in the whole reaction.

(Refer Slide Time: 08:21)



Olefin Hydroformylation

- Discovered by Otto Roelen 1938
- Ruhrchemie

$RCH{=}CH_2 + H_2 + CO \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CHO$

$CH_3CH{=}CH_2 + H_2 + CO \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$

$H_3C\text{—}\underset{CHO}{\underset{|}{C}}H\text{—}CH_3$

- Roelen used $Co_2(CO)_8$
- 120° -170° C 200-300 atm

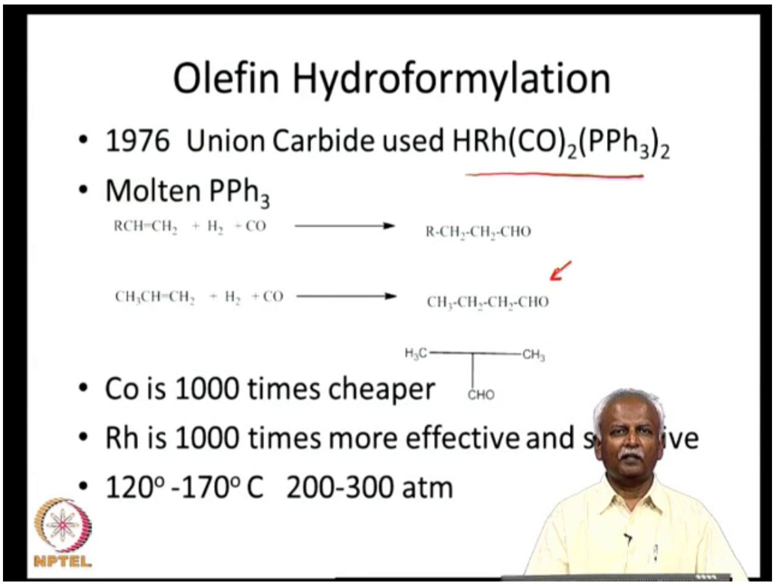
That is in the hydroformylation reaction. You will realize that the previous reaction that we discussed was primarily developed by this company Santo. Now, we are talking about another chemical company called Ruhrchemie, which developed the hydro formulation reaction.

The person who was primarily responsible for this famous discovery was Otto Roelen. He did this as early as 1938. So, you can see that this is long before the renaissance that took place before in organometallic chemistry. The discovery of kerosene happened in 1956. This reaction is an extremely useful reaction because it converts alkenes in the presence of hydrogen and carbon monoxide to very useful aldehydes. Now, it is possible for this reaction to give you an isomer. We have illustrated this in the second equation that we have written.

We have written the hydro formulation of propylene with hydrogen and carbon monoxide gives you the normal aldehyde that is the butyl aldehyde and the isobutyl aldehyde, which is an isomer. This should be formed of the hydrogen adds on to the terminal carbon. That becomes CH3 and this terminal CH2 becomes CH3. The CHO group, the carbon monoxide is added to the middle carbon in the propene. So, this turns out to be a complication.

In fact, the main advantages or the main improvements that have been done in this reaction are the improvement in the selectivity of this whole process. Now, roelen used di cobalt octa carbonyl as a catalyst. It turns out to be a very efficient catalyst if we may use it at these high temperatures 120 and 170 degrees, with fairly high pressure of carbon monoxide and hydrogen. So, you will realize that in many of these chemistries that we have talked about today, you have to use high pressure of carbon monoxide in order to drive the equilibrium to the right and make the whole situation very favorable and fast.

(Refer Slide Time: 10:54)



Olefin Hydroformylation

- 1976 Union Carbide used $HRh(CO)_2(PPh_3)_2$
- Molten PPh_3

$$RCH{=}CH_2 + H_2 + CO \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CHO$$

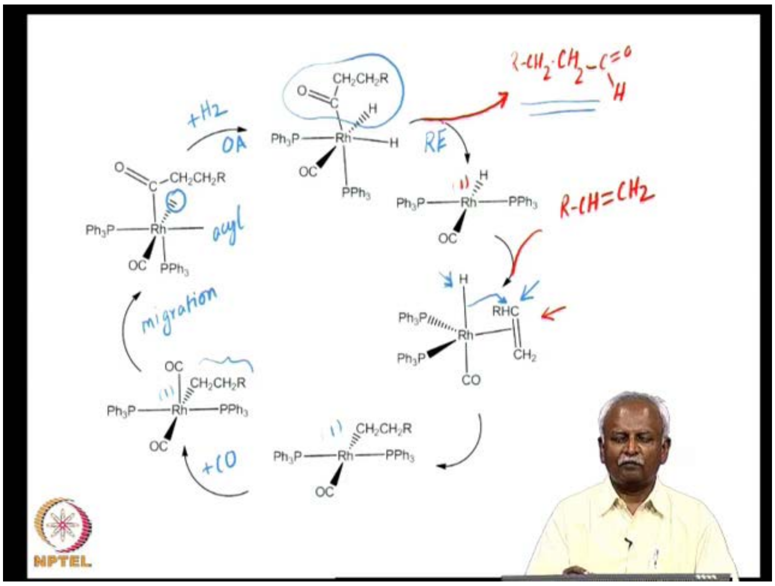
$$CH_3CH{=}CH_2 + H_2 + CO \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$$

- Co is 1000 times cheaper
- Rh is 1000 times more effective and s ive
- 120° -170° C 200-300 atm

Now, it turns out that this olefin hydro formulation reaction underwent a significant improvement in 1976. That is the time when union carbide introduced a catalyst, which was based on rhodium. The catalyst that was used by Otto Roelen was on cobalt. That would have given an edge COCO4. So, the catalyst that was used by him was identical to this species except for the ligands and the metal has been changed. The oxidation state and the electron count are the same for these 2 complexes. So, HRhHCO2, which we have seen twice, was a catalyst that was used by union carbide. In fact, they used molten PPh3. PPh3 above the melting point of the compound was found in the reaction medium.

They found that they could convert the propene to normal butyl aldehyde in very good yield. Now, we know that cobalt is 1000 times cheaper. So, one has to ask the question why would you use rhodium, which is so much more expensive? The answer is of course that fact that rhodium is 1000 times more effective. So, it turns out to be more economical in the long run to use rhodium rather than cobalt. The temperatures and pressures are again very high. They have to be kept high in order to drive the reaction to the right.

(Refer Slide Time: 12:38)



We will write a catalytic cycle now, which is based on rhodium, but has analogous reaction with cobalt. It can be very easily written. The resting state is again a rhodium 1 compound. Here, we have written a rhodium 1 species as the resting state of the catalyst. The reaction starts with the coordination of an olefin to this d 8 species. Now, form a coordinative saturated d 10 alkene complex. That is a d 8 alkene complex.

Now, you have a hydrogen cyst next right next to alkene. The alkene would coordinate in such a way that the bulky group will indicate that. So, the bulky group in fact coordinates closer to the hydrogen. So, that would be the preferred way of coordinating the alkene. The alkene now undergoes an insertion reaction. The negatively charged or the formerly negatively charged species migrates on to the neutral ligand in such a way that you have an alkyl rhodium 1 complement.

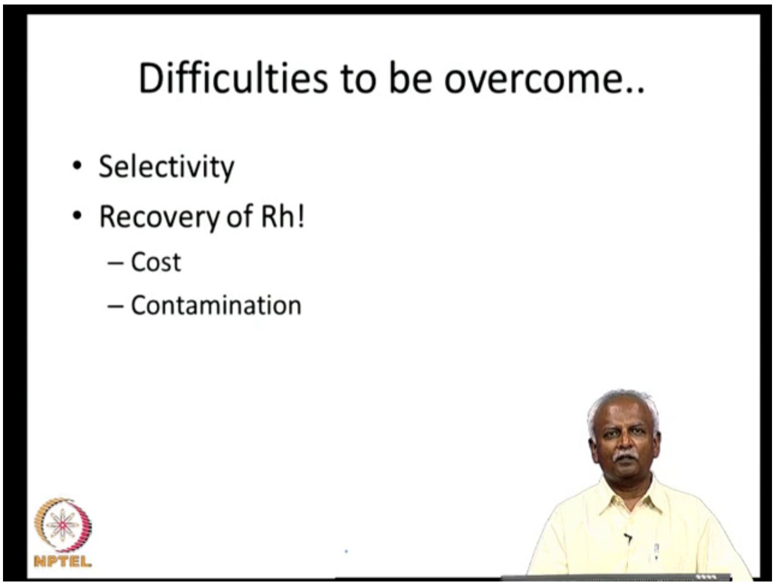
So, you had hydrido alkene complex. After the migration of the hydride, you now have an alkyl complex. This gain is a rhodium 1 species. So, we have just carried out during the course of this 1 step a migration reaction, which does not change the oxidation state of rhodium. Now, you can in the next step carry out a carbonylation reaction. So, we can add a carbon monoxide to the species to this rhodium 1 alkyl molecule.

We can add a carbon monoxide. That gives us a penta coordinate rhodium 1 species, which can undergo migratory insertion reaction again. Now, the anionic group is this alkyl group here. So, this alkyl group migrates on to the carbon monoxide. As a result of this migration, you have an acyl complex. So, you have an acyl complex with a vacant coordination site right here, a vacant coordination site right here. We also have as a result of this migration, we have and acyl group. This can add on hydrogen to have an oxidative addition reaction.

So, this is the oxidative addition reaction that happens right here with an oxidative addition of hydrogen. You would end up adding 2 groups in a cis position. This results in the formation of a dihydride. That is the final step in this catalytic cycle. You have a dihydride and an acyl moiety. This acyl moiety is cis to the hydrogen. Now, you can eliminate this aldehyde. This aldehyde can be eliminated. This is what is coming out in the catalytic cycle like that to regenerate the catalytically active species. It is the rhodium 1 complex.

So, this is the reductive elimination step. So, very often, the reductive elimination step is the final step in the reaction where your catalytically active species is regenerated after the regeneration of the catalyst. You may have either an oxidation or a simple substitution reaction in this catalytic cycle. The oxidative addition and the reductive elimination have happened in the very last 2 steps. So, a similar catalytic cycle can be written for cobalt. Only difference would be that HCOCO4 would be the catalyst instead of the hydrido rhodium species that we have written right here, otherwise all the steps would be extremely similar.

(Refer Slide Time: 17:26)



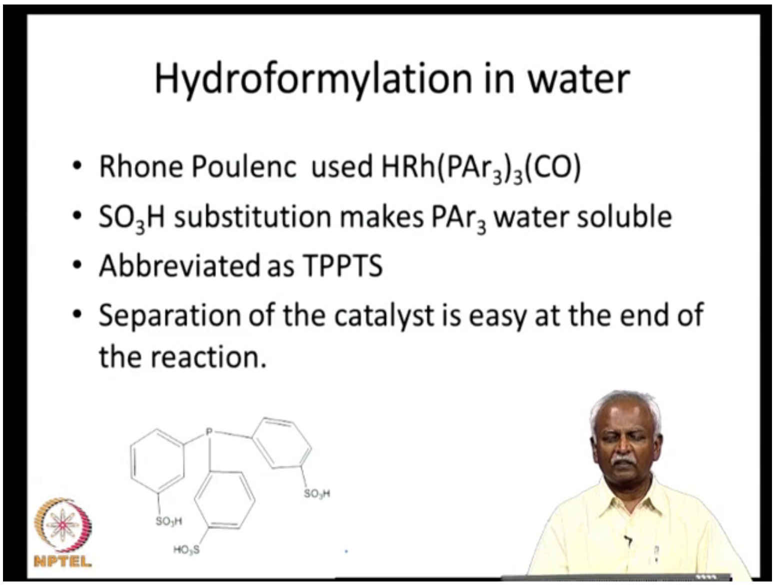
Difficulties to be overcome..

- Selectivity
- Recovery of Rh!
  - Cost
  - Contamination

Now, the hydroformylation reaction is something, which is being actively pursued because it gives us a convenient entry into aldehydes. This has to be done very selectively. Also, one should note that rhodium is a very expensive metal. So, one normally recovers, the rhodium 1 tries to recover the rhodium after the reaction.

This turns out to be an expensive process. Also, we should also avoid the contamination of the product with the catalyst; in this case, rhodium. It has been that in some of the expensive catalyst being used the early process is so inefficient that the concentration of the catalyst in the metal was greater than the concentration of metal in the ore from which it was initially synthesized. So, this has to be prevented. One has to have efficient means of recovering the catalyst.

(Refer Slide Time: 18:32)



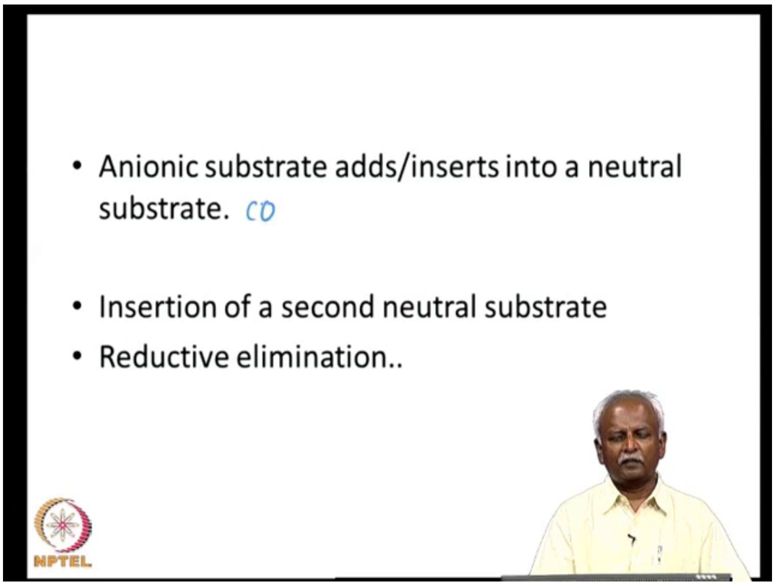
Hydroformylation in water

- Rhone Poulenc used $HRh(PAr_3)_3(CO)$
- SO_3H substitution makes PAr_3 water soluble
- Abbreviated as TPPTS
- Separation of the catalyst is easy at the end of the reaction.

So, hydroformylation in water was one possible solution to this whole difficulty. A company Rhone Poulenc was the French company, which discovered water soluble rhodium catalyst. Once again, the catalyst was the rhodium 1 species, the d 8 species, which has been discussed earlier. So, the mechanism of the reaction would be identical except the introduction of the SO3H group. The SO3 group makes the phosphene water soluble. In turn, the phosphene coordinated to the rhodium makes the catalyst water soluble.

There is a catalyst that is quite popular and has been abbreviated as TPPTS. It splits out here. It has got 3 SOH3 groups, which make the compound extremely water soluble. It is usually kept as a sodium salt. The separation of a catalyst is easy because one has to remove only the aldehyde, which is usually an organic compound soluble in organic solvents. So, it can be extracted and the water containing the catalyst can be recycled. So, hydro formulation in water is one of the means by which one can carry out the reaction efficiently and at the same time save the catalyst and use it for the next step of the reaction.

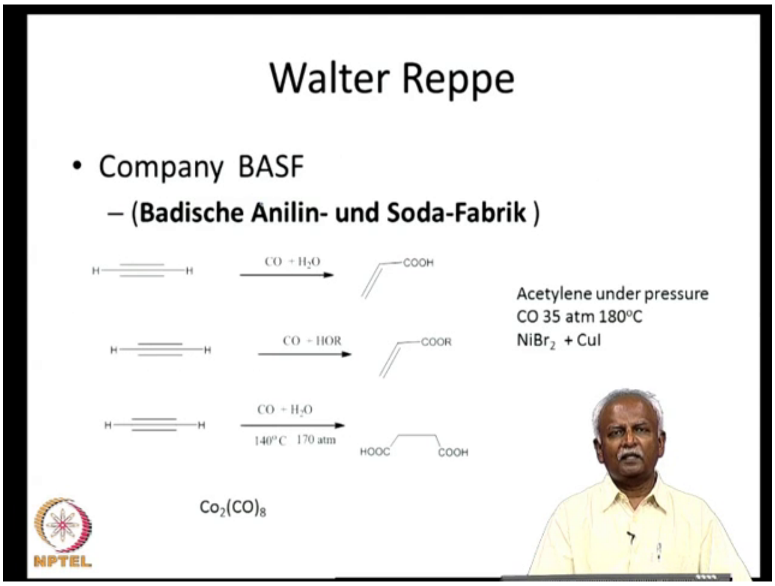
(Refer Slide Time: 20:12)



- Anionic substrate adds/inserts into a neutral substrate. CO
- Insertion of a second neutral substrate
- Reductive elimination..

So, in all these cases, you notice that the anionic substrate is the one that add on to the neutral substrate. In this case, the neutral substrate is carbon monoxide. It is also possible to carry out the reaction in such a way that the second neutral substrate is also added. Then, subsequently a reductive elimination is carried out. So, multiple insertions can happen in the catalytic cycle.

(Refer Slide Time: 20:45)



Walter Reppe

- Company BASF
  - (**Badische Anilin- und Soda-Fabrik**)

Acetylene under pressure
CO 35 atm 180°C
$NiBr_2$ + CuI

$Co_2(CO)_8$

An example of such a reaction is the reppe reaction, Walter reppe reaction. Walter reppe again was working in German company called BASF, which is still around and is an extremely old company. It used to manufacture aniline and soda, soda ash. These chemicals are bulk chemicals, which are used in the chemical industry in very large amounts.

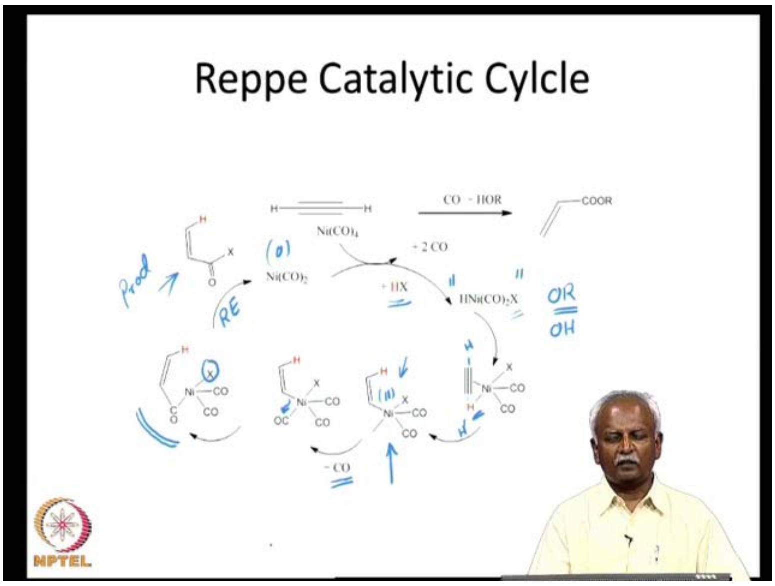
They discovered some very interesting chemistry, which went a long way acetylene carbon monoxide and water. You will notice that essentially a molecule of water and carbon monoxide has been added to acetylene in order to generate this very useful acid. So, the reaction was carried out again at high pressure of carbon monoxide. Notice because you are using acetylene, this reaction was a great technical challenge to counter acetylene without an explosion. It was in fact a difficult task to accomplish.

It is to credit of Walter reppe who discovered ways and means of handling acetylene, so that it would not explode even when it was pressurized and used in this particular reaction. So, he used it at high temperature at 180 degrees in the presence of nickel bromide as catalyst. He was able to convert acetylene to acrylic acid in the presence of an alcohol instead of water. You can directly convert it into the ester.

So, you can either make an ester or an acid depending upon whether you use water or an alcohol. So, these reactions were primarily carried out with nickel as a catalyst and copper iodide was just a promoter that was added. If you do the reaction at a higher pressure of carbon monoxide, slightly higher pressure of carbon monoxide, then the same reaction would undergo a second addition of a carbon monoxide and water to this acrylic acid and generate this saturated dye acid.

So, you can see that the reaction can be an extremely versatile and extremely useful reaction where you can convert acetylene. This is again available in bulk quantities to useful organic compounds, which were required in the industry for the synthesis of drugs and pharmaceuticals and dye stuffs and so on.

(Refer Slide Time: 23:39)



Reppe Catalytic Cylcle

So, how exactly does this reaction work? Here is a possible scheme that we have written with nickel. A same reaction scheme can be written for the second step also. Only the first step is shown here and that too with nickel tetra carbonyl. Nickel tetra carbonyl can lose 2 molecules of carbon monoxide and undergo oxidative addition to give you this nickel 2 complex. Here, nickel is in oxidation state of plus 2. You have a hydrido nickel compound, which has got this X group. This is a group that has to be added. In this particular case, you would have to have OR excess OR. It could be OH, if you are using water in the reaction medium.

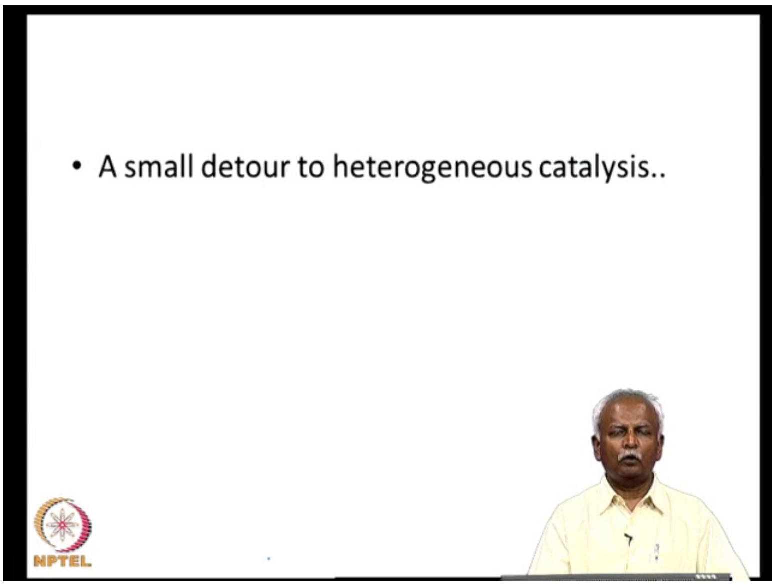
So, if you end up having this nickel 2 plus complex, it can then coordinate to acetylene. The next step is of course, the coordination of an acetylene molecule. This is what we have here. So, you have an acetylene molecule coordinated to a nickel. You have hydrogen next to the nickel next to the acetylene. You can have an insertion reaction.

This insertion reaction would give you a vinyl nickel species. That is shown here a vinyl nickel species. The hydrogen in the cis position has migrated on to the acetylene. That gives you again a nickel 2 species. Now, the nickel 2 species can have carbon monoxide, which it can migrate to. So, you have a migration of this vinyl group. The vinyl group migrates on to the carbon monoxide, which is in the cis position. That gives you the acyl moiety, which is pictured here. The acyl moiety can now do a reductive elimination of the 2 groups; the X group and the acyl moiety to give you the product.

So, this is your product. This step is your reductive elimination that gives you that nickel 0, which has only got only 2 carbon monoxides. If it oxidatively adds HX, which in this particular case, it would be the ROH. So, if you start with nickel bromide, you can also think of adding the B r. In the final step, you would have a hydrolysis reaction or an alcoholysis reaction.

So, because you would have nickel, tetra carbonyl is generated from nickel bromide. In the catalytic cycle, you need only nickel carbonyl, but you can generate it from nickel di bromide and carbon monoxide. So, the Reppe catalytic cycle involves an oxidative addition and insertions, 2 insertions in fact an insertion of carbon monoxide, insertion of acetylene. That gives you the required acrylic acid and water is used in the reaction again.

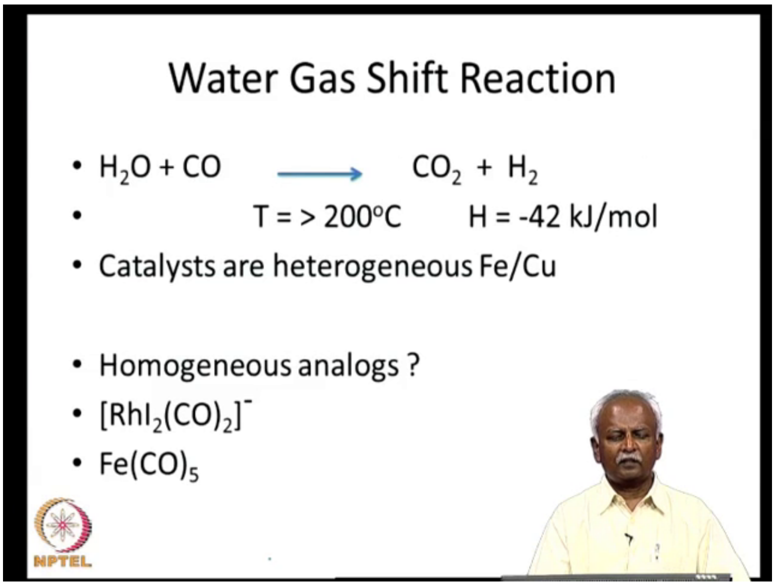
(Refer Slide Time: 27:24)



- A small detour to heterogeneous catalysis..

Now, let us take a small detour to heterogeneous catalysis and mention 2 important industrially important reactions, which have got a lot of relevance to organometallic chemistry we are studying.

(Refer Slide Time: 27:39)



Water Gas Shift Reaction

- $H_2O + CO \longrightarrow CO_2 + H_2$
- T = > 200°C H = -42 kJ/mol
- Catalysts are heterogeneous Fe/Cu

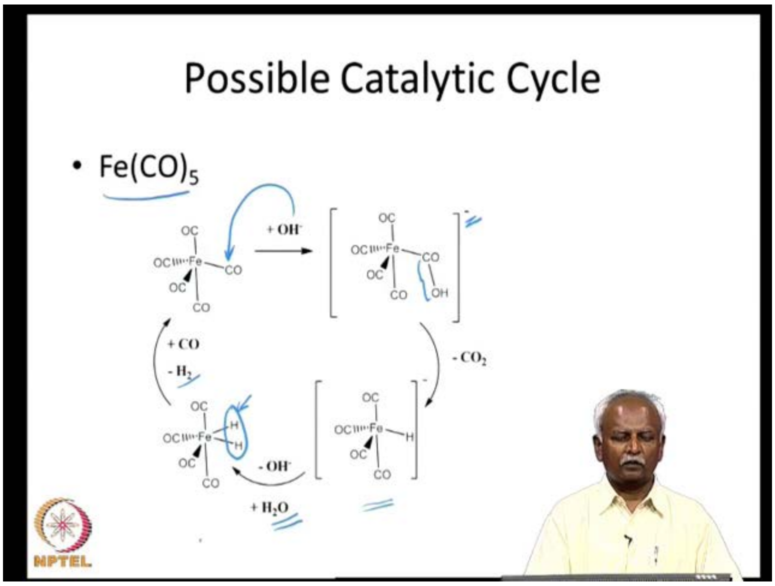
- Homogeneous analogs ?
- $[RhI_2(CO)_2]^-$
- $Fe(CO)_5$

This reaction is actually the water gas shift reaction where water and carbon monoxide is converted to carbon dioxide. The extremely useful energy rich species is hydrogen. Now, this reaction is normally carried out in heterogeneous conditions. You have a catalyst, which is mostly iron supported on a copper. These reactions are surprisingly difficult to carry out in homogeneous conditions.

So, there are practically no homogeneous analogs for these heterogeneous reactions. Yet catalysts like the species that I have indicated here have been used to show that these reactions can be done at least on a small scale. Even if they are inefficient, they show that such chemistry is in fact feasible.

So, the reason why I have chosen these examples is because even though these heterogeneous reactions are really like blank books, we do not know what is going on. But, still sufficient organometallic chemistry must be going on. That is sufficient organometallic chemistry that is available, which shows that these reactions can be mimicked in the homogeneous scale also.

(Refer Slide Time: 29:20)



Possible Catalytic Cycle

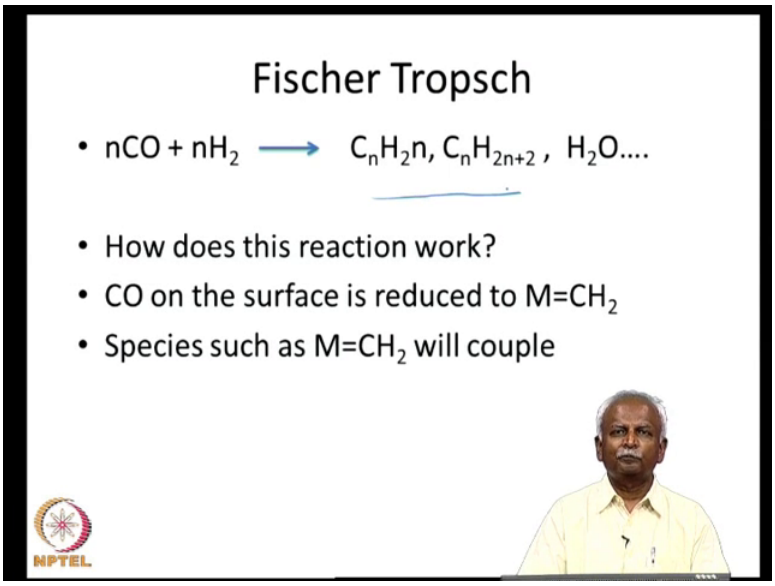
- $Fe(CO)_5$

So, let me give you a catalytic cycle that is possible written with iron pentacarbonyl. Here, if you have iron pentacarbonyl and you have water reacting with it, let us consider it in 2 steps with OH minus attacking the carbon monoxide. You can have this OH minus attacking this carbon monoxide to give you COOH coordinated. It is acyl, a carboxylated anion which is coordinated to the iron and that will have a negative charge. This is because we have added a negatively charged species.

We can eliminate from this species CO2 because you have the right groups with the right connectivity. If you eliminate CO2 and if the hydrogen moves on to the iron, so that would be just like beta hydride elimination. So, you would get an iron hydrido species. This iron hydrido species that we have written here can react with water. If it donates a proton here essentially, this water is for donating a proton, and then you get a di hydride. This is a dihydride that we have here with the iron, which can eliminate dihydrogen to give you iron pentacarbonyl back.

So, this is a simple catalytic cycle that demonstrates a water gas shift reaction. Although on an industrial case scale, this is not efficient, still people use heterogeneous catalyst for this reaction; although there is a homogenous analog, which is available although inefficient. So, what we have done is we have done a reverse of the process. You have done an insertion on the carbon monoxide, which has given a hydrido species. That hydrido species gets protonated in this step with water. Dihydrogen is eliminated in order to get you the iron pentacarbonyl back.

(Refer Slide Time: 31:55)



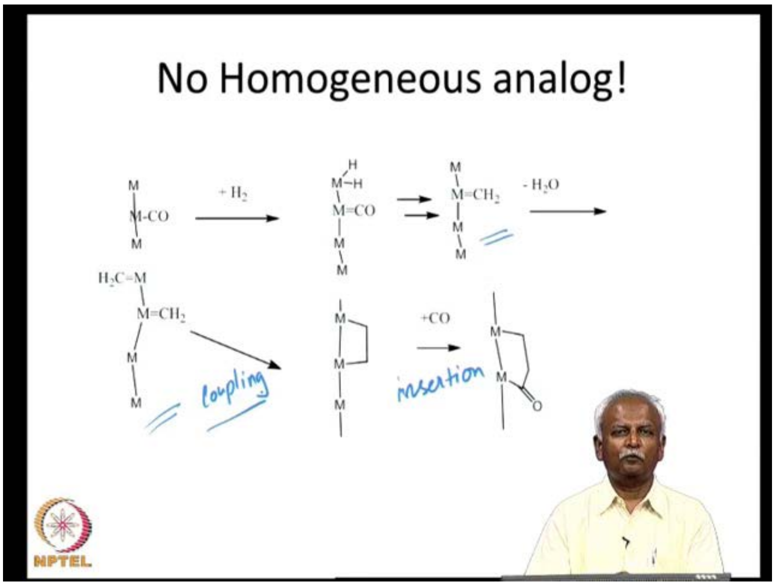
Fischer Tropsch

- $nCO + nH_2 \longrightarrow C_nH_2n, C_nH_{2n+2}, H_2O....$
- How does this reaction work?
- CO on the surface is reduced to $M{=}CH_2$
- Species such as $M{=}CH_2$ will couple

So, the next reaction that I want to discuss is a Fischer Tropsch process, which is again an extremely important process. It is in fact the key energy source for certain countries especially South Africa. There is a plant called the Sasol plant, which converts the carbon monoxide and hydrogen to alkenes to products, which are like petroleum products. They are alkanes and alkenes. Sometimes, some oxygenated products are also there like alcohol, some aldehydes.

Now, the question is how this reaction works. Now, carbon monoxide is reacted in the presence of a metal surface. So, it is easy to imagine the metal surface as reacting with carbon monoxide to generate metal carbonyl species. This can be reacted with hydrogen. It might get converted to a methylene species. These species can couple.

(Refer Slide Time: 33:02)

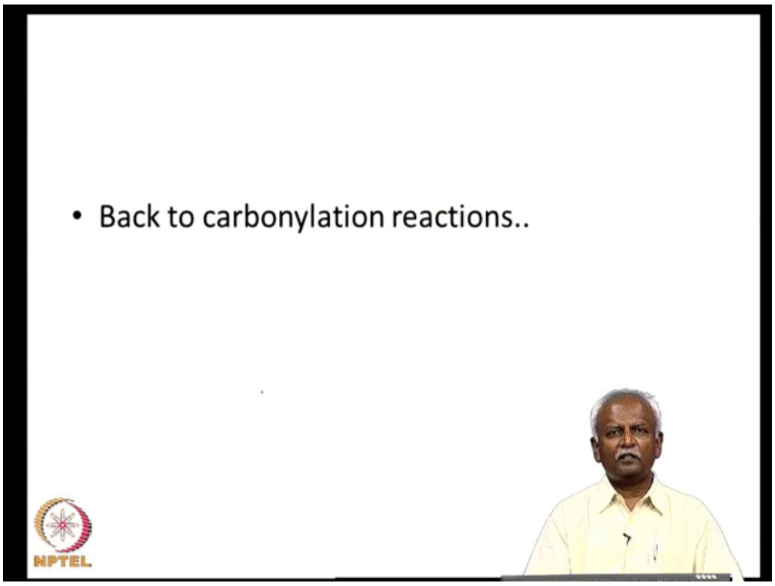


No Homogeneous analog!

So, this is shown here in a pictorial fashion, but essentially what we have seen is that the metal carbonyl can undergo heterogenation reactions. The activated hydrogen, which is like a hydride can undergo migration reactions and eventually generate metal carbenes. These carbenes can couple as we have shown here. If you 2 carbenes are close together, then they can couple. The coupled product can undergo an insertion reaction. Here is an insertion reaction and here is a coupling reaction. These are steps, which we are repeatedly encountering in carbon monoxide chemistry.

This is the kind of chemistry that must be going on the surface of the heterogeneous catalyst. This heterogeneous catalyst is the one that is efficient in generating the petroleum products. So, it suffices to say heterogeneous catalysis is very efficient. It cannot be supplemented by organometallic chemistry completely. There is sufficient enlightenment in what is going on inside the heterogeneous catalyst by studying in organometallic chemistry.

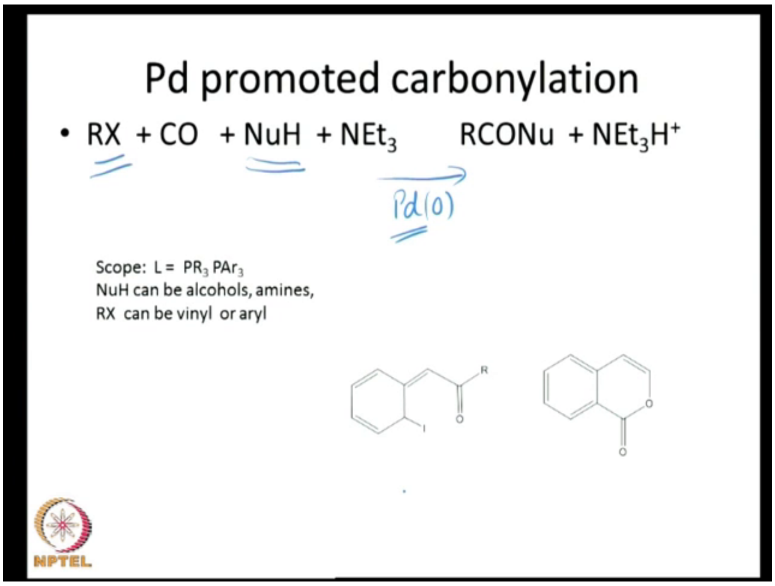
(Refer Slide Time: 34:26)



- Back to carbonylation reactions..

Now, let us go back to the carbonylation reactions that we were discussing.

(Refer Slide Time: 34:32)



Pd promoted carbonylation

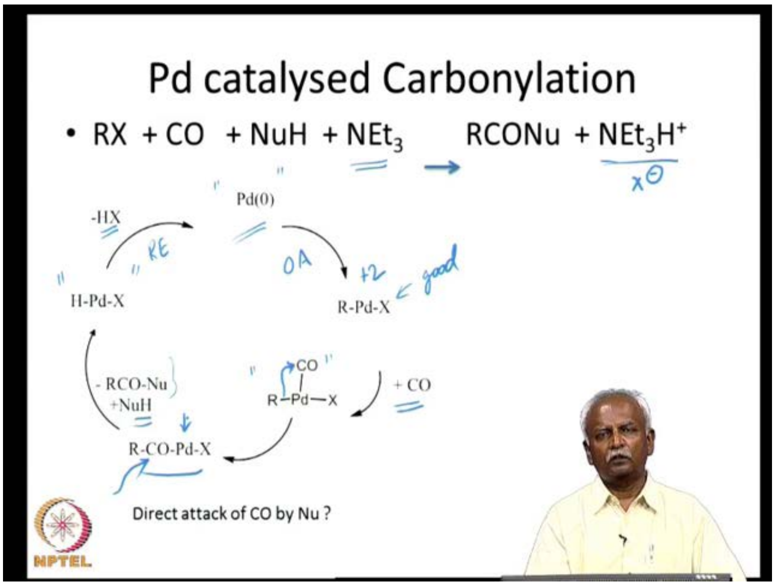
- $RX + CO + NuH + NEt_3 \xrightarrow[Pd(0)]{} RCONu + NEt_3H^+$

Scope: L = PR_3 PAr_3
NuH can be alcohols, amines,
RX can be vinyl or aryl

Now, we will talk about a palladium promoted carbonylation reaction. Now, these are extremely useful in the laboratory. I have shown for you a reaction, which generates a cumorine and cumorines. Isocumorines are synthesized very efficiently in the laboratory using this palladium promoted. This is catalyzed by palladium and usually palladium in the 0 oxidation state. That is usually the resting state of the catalyst. It is generally in the presence of carbon monoxide.

Carbon monoxide efficiently reduces palladium 2 to palladium 0. So, palladium 0 is the actual resting state of the catalyst. It is interesting that a variety of nucleophiles can be used. What you have written as N u H can be anything from alcohols or amines. This RX could be a variety of groups. It could be vinyl aryl and insertion reactions can happen very efficiently with even complicated molecules as the one that is shown here. Let us write the catalytic cycle.

(Refer Slide Time: 35:52)



Pd catalysed Carbonylation

- RX + CO + NuH + NEt_3 → RCONu + NEt_3H^+

Direct attack of CO by Nu ?

Now, exactly this reaction can proceed. So, here is a reaction where you have palladium 0 as the resting state of the catalyst. That can readily do an oxidative addition reaction. So, palladium goes to palladium plus 2. This is palladium 2 plus t the formal oxidation state. It has got the R and the X groups attached to the palladium, which can now undergo an insertion reaction.

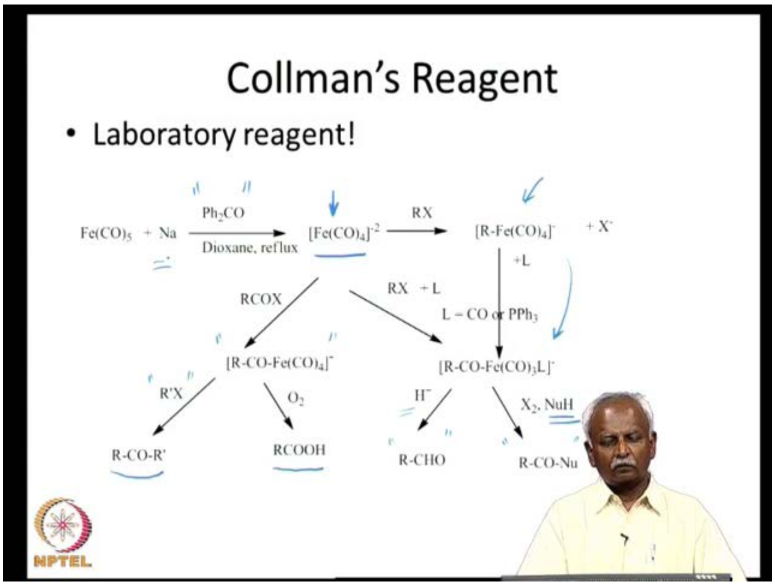
So, migratory insertion reaction happens initially. Add a carbon monoxide ligand and generate this species this active species where the R group migrates on to the carbon monoxide. Once the R group migrates on to the carbon monoxide, you have an acyl moiety. This acyl moiety is attached to the attached to the X group, which came from the RX.

Now, instead of doing a reductive elimination, we can have an attack by the nucleophile, which we want to react RX with. So, if the nucleophile attacks the carbon monoxide, the CO group of the acyl moiety, so that is the co group. If the nucleophile attacks here, you can end up with RCO in you. Any edge will give the proton to the palladium. So, this ends up generating a species which has got a hydrido palladium X group. This can eliminate HX and you regenerate palladium 0.

So, this reaction is a simple reaction. Also it involves an oxidative addition. So, that is this step an oxidative addition and a reductive elimination in the last step. So, the oxidative addition in fact happens between R and X. so, X has to be a good leaving group. This has to be a good leaving group and nucleophile has to be a better nucleophile than the H group, which is coming out as HX. So, as long as these conditions are satisfied, this condition is satisfied for a variety of nucleophiles. If you have a halide and amine, which is coming in, then you have no problem.

The tri ethylamine is basically a base which maps the HX that is generated. So, at the end of the reaction, you could see NE t 3. H plus is liberated or rather the H plus that is liberated is taken has converted into this NE t3 H plus salt, X minus salt. That is removed from the reaction sphere. So, you could have a direct attack of the acyl group with the nucleophile. The nucleophile can also coordinate prior to the reaction to the palladium before the attack on the acyl group. So, these 2 possibilities are there.

(Refer Slide Time: 39:24)



Collman's Reagent

- Laboratory reagent!

Another reagent which is useful in the laboratory is called a collman's reagent because collman developed it to great extent.

This is nothing but the reaction of iron pentacarbonyl with sodium. Sodium by itself does not react with iron penta carbonyl. If you react it in the presence of benzophenone, benzophenone is like a catalyst because it generates the ketyl radical anion. This radical anion is capable of transferring the electron to ion that results in the tetra carbonylate di anion iron tetra carbonylate di anion. This is called collman's reagent. So, this is the collman's reagent that we are talking about. Its chemistry has been extensively studied.

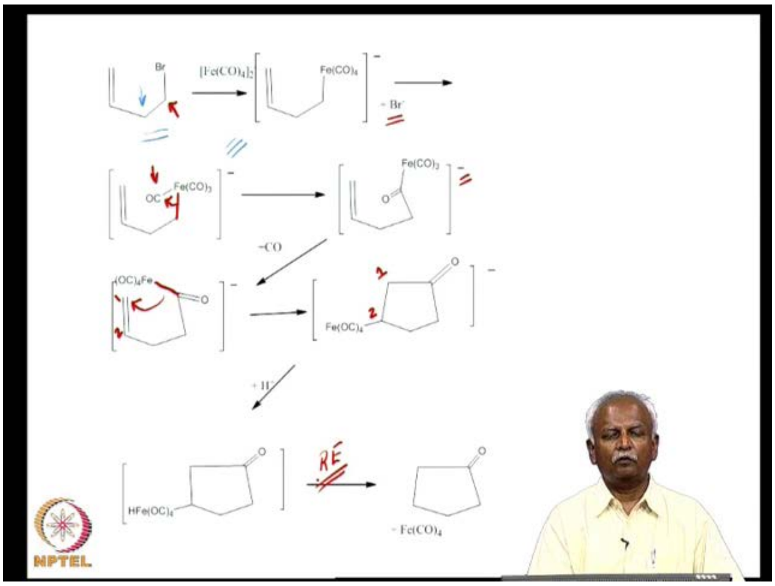
This is because it is such a nucleophilic species. It has got a lot if electron density on the iron. It can carry out nucleophilic attacks on many electrophilic organic compounds, which are electrophiles. Here, we have shown 2 possibilities. One is RX. That will give you an alkyl ferrite carbonylate species alkyl iron carbonylate species or an acyl carbonylate species.

So, it is also possible to convert this alkyl carbonylate species with addition of either a ligand of PPh3 or carbon monoxide itself to the acyl carbonylate species. So, you can generate this acyl carbonylate species very efficiently. This carbonylate species which is nothing but the R group with an added carbon monoxide can undergo another reaction with another electrophile. Here, we have shown the reaction with RX that gives you a ketone. That gives you a ketone starting with RX. You have converted to a ketone or to an acid with reaction with oxygen.

In that case, iron carbonylate anion is decomposed directly. Now, you can also treat it with an acid. If you treat it with an acid, you generate an aldehyde. As in the previous case, you can also react it with a good nucleophile to generate R CO N u. So, you notice along with addition of a nucleophile, you have managed to introduce a carbon monoxide into the molecule. So, collman's reagent turns out to be a useful reagent for synthesizing laboratory scale chemicals easily.

I emphasize the fact it is a laboratory reagent, not an industrial reagent because one has to use a very expensive material in order to generate the collman's reagent. So, you have to use sodium and the fluxing dioxide in order to generate the collman's reagent.

(Refer Slide Time: 43:06)



Now, let us take a look at an example where we converted organic bromide into a cyclic molecule using collman’s reagent just to illustrate the chemistry that is behind this reaction. Suppose that you take this homoallylic bromide. If the bromide is here, we would have called it an allylic bromide. But, here homoallylic bromide you have an extra CH2 group, if you tear that with the iron carbonylate species, you end up with this molecule. This is identical to this compound although we have written an arrow here. So, these 2 things are identical.

I have written the carbon monoxide separately and indicated. I have indicated the carbon monoxide. I have indicated an extra carbon monoxide separately.

We are now going to do a migratory insertion reaction now. This is because it is a super nucleophile. It did a simple s n 2 substitution on this carbon. So, first we did s n 2 substitutions on this carbon, got iron attached to this organic moiety and anionic alkyl group, which is going to do a migration on to the carbon monoxide. So, if it does a migration to the carbon monoxide, we end up with an acyl species.

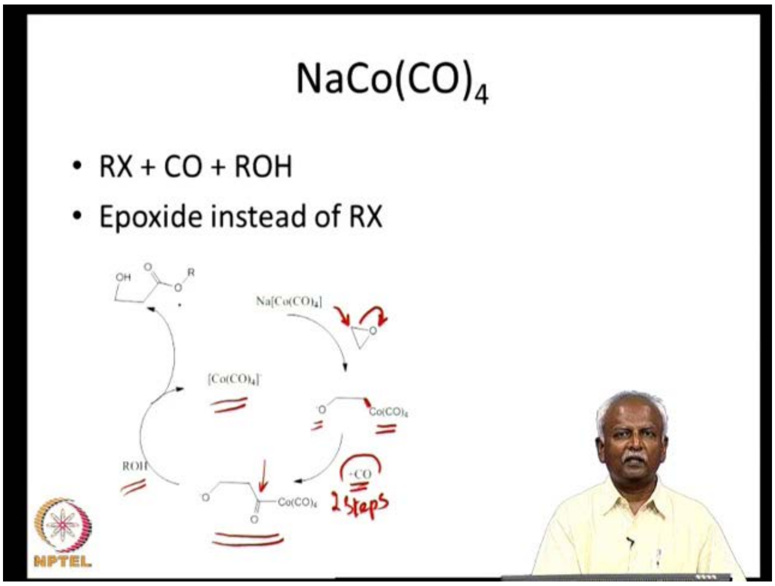
This acyl species has also an anion. Remember, we started out with a di anion CCO4, 2 minus. and we eliminated bromide. So, we are left with a mono anion that can still undergo addition of a carbon monoxide. This gives us back an iron tetra carbonyl acyl species.

Now, notice that this species has got an acyl group. This is a negatively charged group that is there, which I have colored in red. That can undergo a migratory insertion. This time the migratory insertion happens on to an olefin. Earlier, we are doing these insertion reactions on carbon monoxides or in some cases; we have done it on an alkyne. Now, here we are doing it on an alkene.

As a result, the iron will be attached to the second carbon atom. So, this is carbon atom 1. This is carbon atom 2. The iron will be found on the second carbon atom. The migrating group is found on the first carbon atom of the alkene. So, this species which is a carbonylate anion can in fact get attached to proton and then undergo a reductive elimination step.

So, this is the last step. It is in fact a reductive elimination, which will give you in this particular case a fairly simple molecule. But, you can imagine. Since, this is of a more complex structure where a pentanone is needed. That can be constructed with this chemistry with the collman's reagent. So, you have a series of migrations and insertion reaction of a carbon monoxide in order to generate this cyclic structure.

(Refer Slide Time: 46:53)



$NaCo(CO)_4$

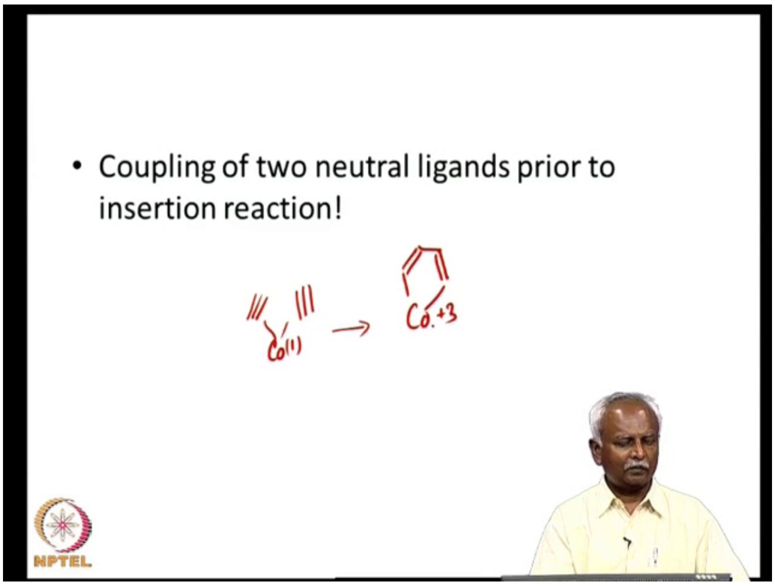
- $RX + CO + ROH$
- Epoxide instead of RX

That reaction can also be done with instead of having an alkyl bromide; it can also be done on an epoxide. Now, here I have shown you another metal, which is capable of carrying out this kind of chemistry. Instead of the cobalt, instead of the iron di anion, we have a sodium cobalt 8, a tetra carbonyl sodium 8. This is going to carry out this nucleophilic attraction at this position and that opens up the ring. It is an anion and is an O minus species here.

In this reaction, you have this neutral group carbon monoxide and an alkyl species, which I have marked in red for you. This alkyl species can migrate to one of the carbon monoxides, which is present on the cobalt. If it does that and adds on a carbon monoxide, we have put, we have included 2 steps here. One is the migration of the alkyl group and the other is the addition of carbon monoxide.

So, addition of carbon monoxide and migration gives you this new compound, which has got O minus attached to an acyl moiety. It is attached to the cobalt. Now, we can do an alcoholysis using out OH, which means you will have the ROH attacking in this position and liberation of COCO4 minus. This of course, gives you directly an ester and an alcohol directly. So, this tells you how useful this reaction can be. You have an attack of nucleophilic organometallic agents on epoxides, halides and esters and so on.

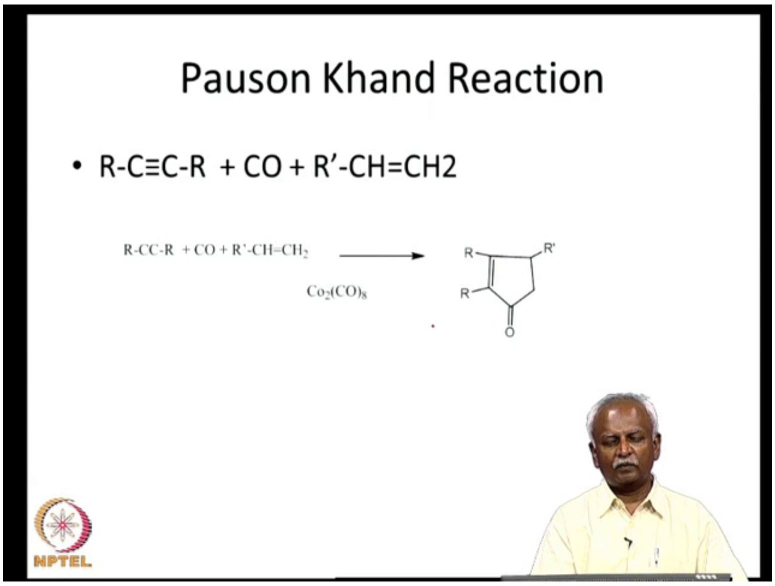
(Refer Slide Time: 49:01)



- Coupling of two neutral ligands prior to insertion reaction!

So, up to now, we have not considered the coupling of 2 neutral ligands. In the subsequent reactions, we are going to look how 2 neutral ligands can be coupled in an oxidative fashion. Now, just to remind you, this reaction is not something new. We have discussed the coupling of 2 acetylene fragments on a cobalt system, cobalt 1 to give us cobalt 3, oxidatively coupled cobalt 3 species. So, this is going to be a very similar reaction. So, what we have is an oxidative coupling reaction.

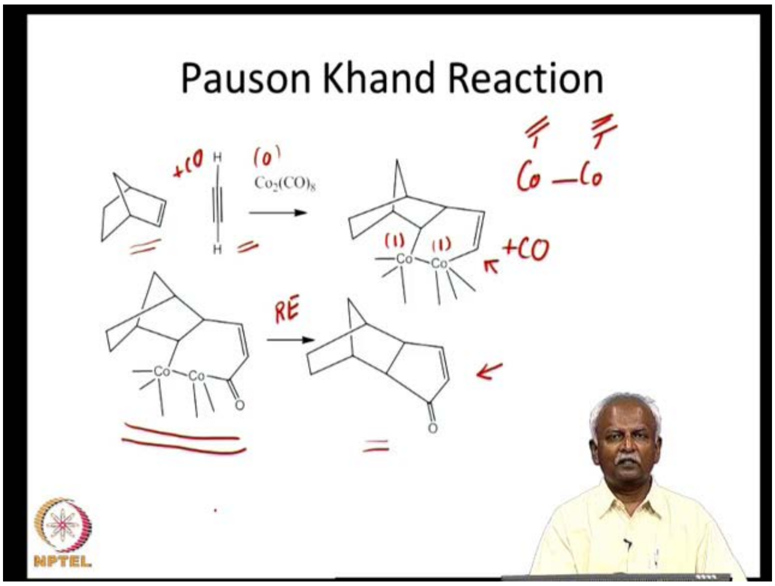
(Refer Slide Time: 49:52)


Pauson Khand Reaction

- R-C≡C-R + CO + R'-CH=CH2

Here is a reaction, which is called the pauson khand reaction where an acetylene and alkene and carbon monoxide are mixed together to generate a cyclopentinone. In the previous reaction, in one of the previous reaction, we considered. Then, reaction of pentanone and here the saturated form here, it is a cyclopentinone that is generated in this reaction.

(Refer Slide Time: 50:18)

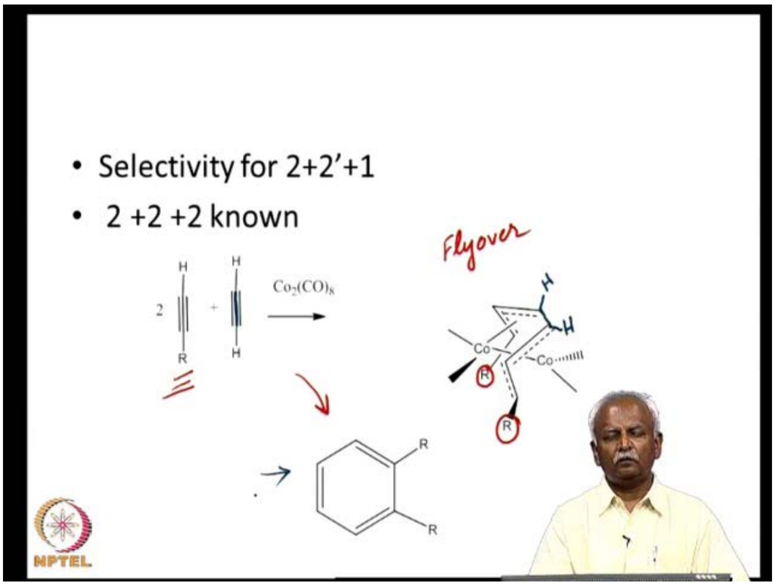

Pauson Khand Reaction

The important thing is that it is a single one spot reaction that is carried out with carbon monoxide di cobalt of the carbonyl and 2 or organic compounds. One is an alkene. The other is an alkyne. You end up converting all 3 species in 1 step into a cyclic pentinone. That is what we have here. In order to just show you how the reaction can be done with more complex molecules, I have shown you Narbonne as an alkene.

So, because it is a di nucleus species, we can imagine the di nucleus species CO2CO8 losing 2 carbon monoxides and complexing with the alkene and the alkyne. 1cobalt is complexing to an alkene, the other complexing to an alkyne. If you do an oxidative coupling, you have a cobalt 0 species to start with. After the oxidative coupling, each of these metal centers would increase the oxidation state by 1. You would get cobalt 1, a cluster where 2 cobalt 1 centers are adjacent to one another. This di metalo cyclohexene, which we have here can introduce or insert a carbon monoxide.

So, this can insert a carbon monoxide plus CO that can give you a new species, which is actually a heptanone and di metalo heptanone, which can reductively eliminate. Now, reductive elimination gives us this complex structure, which has been stitched together in the coordination sphere of the metal. So, you can see how fairly complex reactions can be carried out in a one spot reaction. Now, it has been possible to carry out this reaction only because the metal is capable of changing its oxidation state to plus 1 and also because the metals are close enough together to stitch together these 2 dissimilar fragments.

(Refer Slide Time: 52:53)



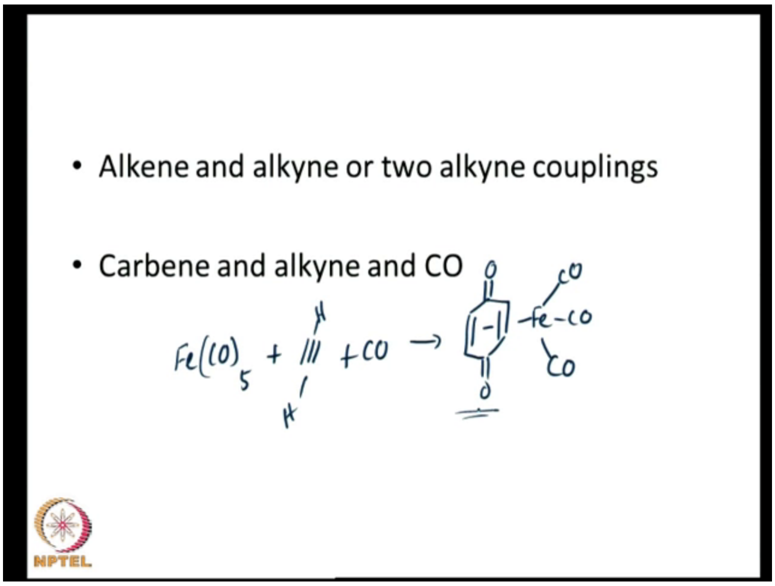
- Selectivity for 2+2'+1
- 2 +2 +2 known

Now, it has been shown in the case of acetylenes, which are substituted with only one atom on one side. They can be combined with simple acetylene to give you an aromatic ring. So, this aromatic ring can also be generated in the presence of cobalt di carbonyl. In this case, if people have to isolate and characterize the intermediate that is being formed, this is called a fly over complex.

This fly over complex is basically having the 3 acetylene moieties attached together on the di cobalt species. The di cobalt species is coordinated to 3 allylic fragments, 2 allylic fragments with 3 carbons each. You can see that this R group. This R group is coming from the 2 acetylenes, which we have used.

This central acetylene, we will mark it here with a different color, so that you can see it. So, this is the central acetylene that is being added. That is the central acetylkene that we have added. The 2 other substituted acetylenes are bearing the R groups. They are attached in such a way that they are as far away as possible from the central cobalt cluster. So, they will not be sterically congested, but reductive elimination from this diallyl unit generates the selectivity.

(Refer Slide Time: 55:01)

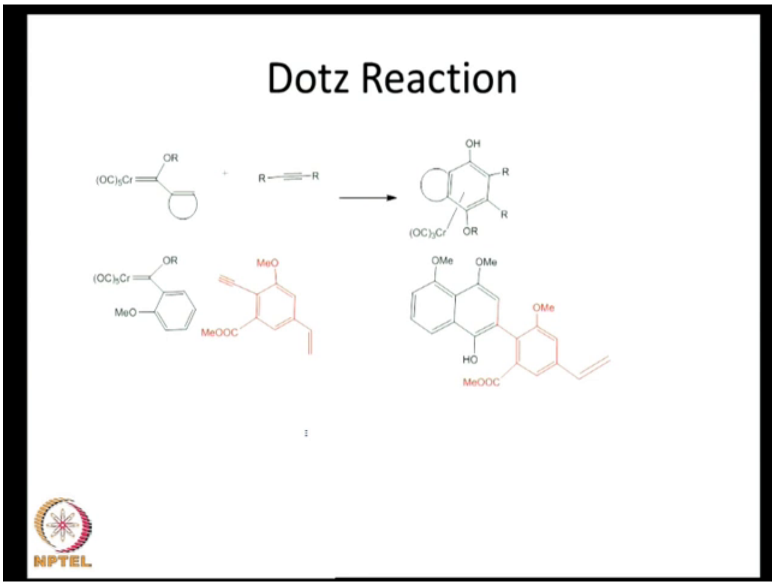


- Alkene and alkyne or two alkyne couplings
- Carbene and alkyne and CO

So, you can combine alkenes, alkynes or 2 alkynes together along with carbon monoxide. In fact, if you treat iron penta carbonyl with acetylene with simple acetylene and carbon monoxide, it is possible to achieve the synthesis of a quinone, which is now coordinated to iron tri carbonyl.

So, you can generate this molecule in the coordination spheres simply by stitching 2 acetylenes and carbon monoxides, 2 insertions, oxidative coupling of 2 acetylenes together. Sequential insertions of carbon monoxides will give you this quinone. it is coordinated to iron tri-carbonyl.

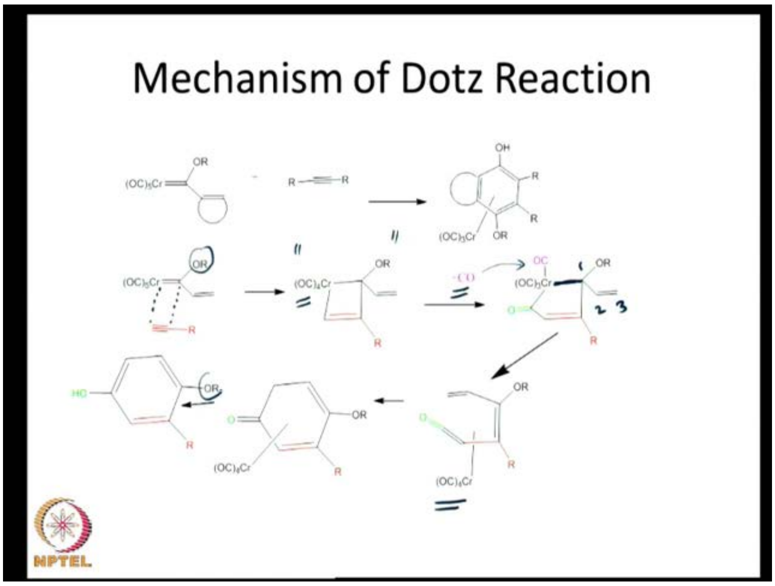
(Refer Slide Time: 56:05)



Dotz Reaction

So, we will end with this last example, which is the dotz reaction. The dotz reaction involves the combination of a vinyl carbene and an acetylene vinyl. Carbene acetylene can be combined together along with carbon monoxide to give you this fairly complicated ring structure. This is a good example, which tells you that very complex chemistries can be carried out in the coordination sphere of the metal atom. So, we have a mechanism of the dotz reaction, which is described here.

(Refer Slide Time: 56:46)

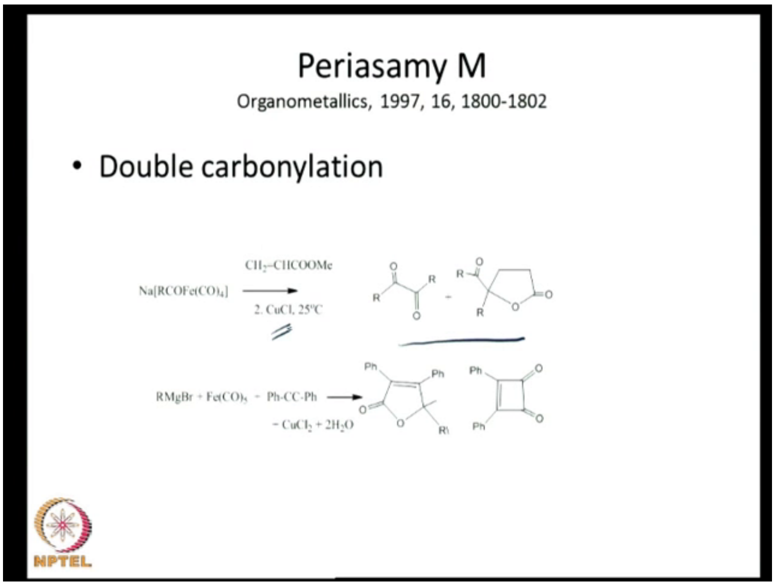


Mechanism of Dotz Reaction

We have acetylene, which is coordinated to the chromium in such a fashion that you end up with a reaction, which is very similar to what happened in the metal carbene metathesis chemistry. So, you have the formation of cyclobutene where this chromium is on the cyclobutene ring. This now inserts carbon monoxide and adds a key step. As indicated in green here, the inserted carbon monoxide comes from the coordination sphere of the metal.

The added carbon monoxide just fills in vacant coordination sphere. Subsequently, we can do an allylic shift of this group, which is attached here. It is allylic position. So, you can see this 1, 2 and 3. So, that will give you this chromium tetra carbonyl compound, which will result in the formation of this diphenol. On one side, you would have ether because you started out with ether here. So, that is a group, which is present here.

(Refer Slide Time: 57:54)



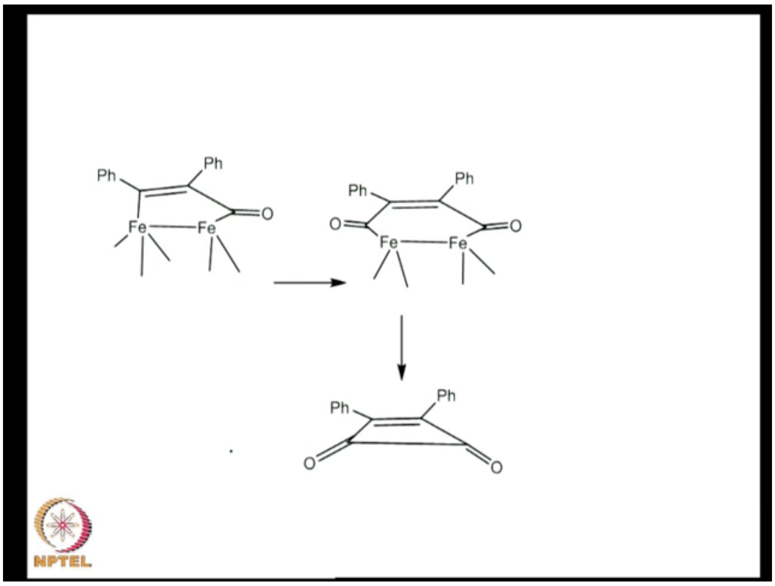
Periasamy M

Organometallics, 1997, 16, 1800-1802

- Double carbonylation

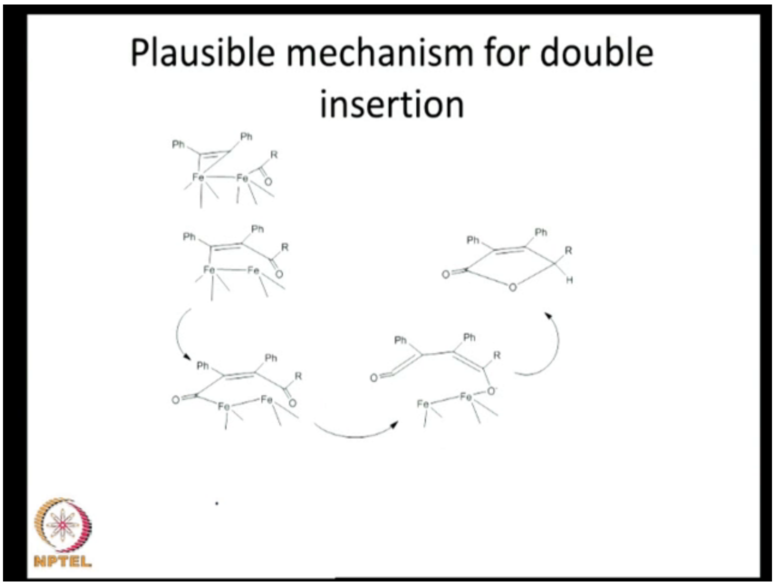
So, these are extremely useful reactions and with a dicarbonylation which was discovered by Periasamy. That is again with iron. That can also lead to very interesting molecules, which are fixed here, cyclobutene dions and so on. The double carbonylation is a reaction, which has rarely been observed. It is very unique reaction that has been discovered with the use of simple iron tetra carbonyl and cuprous chloride as a catalyst. The reaction can be modified to give a variety of substrates that are fixed here.

(Refer Slide Time: 58:40)



One example, one possible intermediate is what I have shown you in this particular screen because iron too can dimerise. It can give you these very interesting species where 2 iron centers can be coordinated to the acetylene and sequentially insert carbon monoxide.

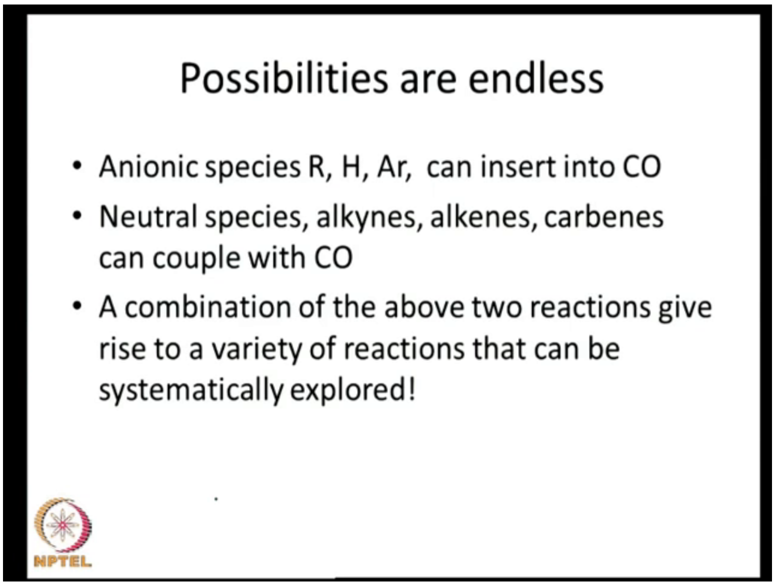
(Refer Slide Time: 59:01)



Plausible mechanism for double insertion

So, a possible insertion mechanism for the double carbonylation is shown here in the last slide.

(Refer Slide Time: 59:08)



Possibilities are endless

- Anionic species R, H, Ar, can insert into CO
- Neutral species, alkynes, alkenes, carbenes can couple with CO
- A combination of the above two reactions give rise to a variety of reactions that can be systematically explored!

So, the possibilities are endless and anionic species like R, H and A r can insert carbon monoxide. You can have a huge library of reactions built on the insertion of carbon monoxide.