

Transition Metal Organometallic Chemistry : Principles to Applications

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Week - 10

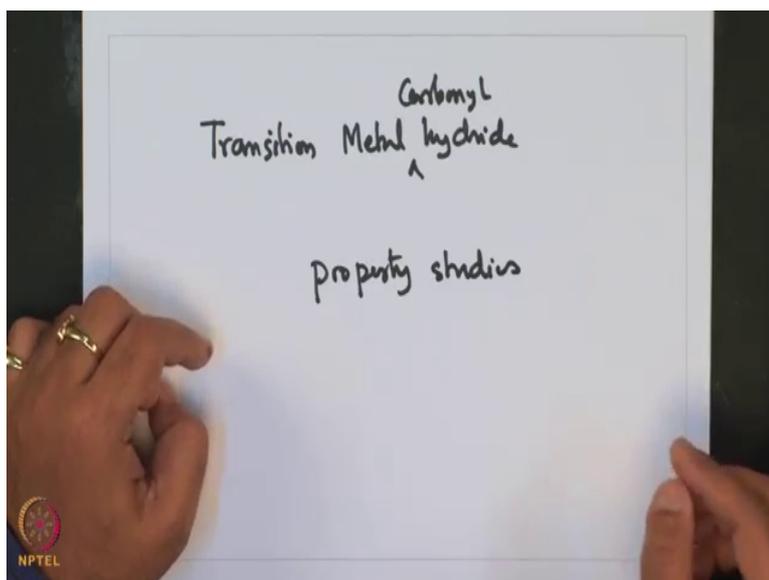
Lecture - 48

Transition Metal Carbonyl Hydrides

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing in the last few lectures a very important class of compound; these are transition metal carbonyl compounds and in that we have looked into the various kinds of transition metal carbonyl compounds that are there; particularly with respect to their synthesis, reactivity, property studies. As well as they are binding to transition metals; the various binding modes that they exhibit.

We also looked into related transition metal carbonyl metallate complexes and as well as in the last lecture we have looked into new type of transition metal carbonyl hydride complexes. Now, in regard to transition metal carbonyl hydride complexes, we have looked into the synthesis of these transition metal hydride complexes in the previous lectures.

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Now, these transition metal, this transition metal carbonyl hydride complexes are interesting because they also are active intermediates in many catalytic cycles particularly that of hydroformylation reactions.

So, now we have looked into various synthetic strategies available for synthesizing these transition metal carbonyl hydride complexes in the past lecture. And we are going to look at the property studies; property studies of these complexes in this lecture.

Now, with that in the backdrop we are going to sort of look at how these hydrolytic moiety when bound to metal in a metal transition metal carbonyl compounds, behave with regard to various chemical reactivity as a function of metal as well as a function of the ligand.

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❖ Properties of metal carbonyl hydrides

complex	M.Pt. °C	Decomp. °C	IR ν_{M-H}	1H NMR δ (ppm)	pK_a	comparable acidity
$HCo(CO)_4$	-26	-26	1934	-10	1	H_2SO_4
$H_2Fe(CO)_4$	-70	-10	,	-11.1	4.7	CH_3COOH
$[HFe(CO)_4]^-$					14	H_2O
$HMn(CO)_5$	-25	stab. RT	1783	-7.5	7	H_2S

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So, with that let us take a look at some of the examples of transition metal carbonyl; hydride complexes. For example, we start with the famous hydride cobalt tetra carbonyl complex; which is $HCo(CO)_4$. It has a melting point of minus 26 degree centigrade and it also is highly unstable. So, it has a decomposition temperature of similar minus 26 degree centigrade. This hydride moiety is characterized by in the IR by new metal hydride bonds which comes at 1934, centimeter inverse in the proton NMR. This del chemical shift of this hydride is highly up field shifted like any other metal hydrides and come as minus 10 ppm.

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Complex	Mp	Decomp temp	IR ν_{M-H}	1H NMR δ (ppm)	pKa	Comparable acidity
$HCo(CO)_4$	-26°C	-26°C	1939	-10	1	H_2SO_4
$H_2Fe(CO)_4$	-70°C	-10°C		-11.1	4.7	CH_3CO_2H
$[HFe(CO)_4]^-$					14	H_2O
$HMn(CO)_5$	-25°C	stable	1783	-7.5	7	H_2S

for π acidic ligand CO

for σ donating ligand

$L_n M - H$

$\delta^- \quad \delta^+$

$\delta^+ \quad \delta^-$

acidic hydrogen

hydridic hydrogen

Now, because, of the presence of 4 very pi acidic carbonyl ligand; this hydride moiety is very much acidic and has a pKa of nearly 1; which is comparable to sulfuric acid. So, what we see that this hydride moiety bound to cobalt is very much acidic in nature. So, and that is comparable to that of sulfuric acid. So, this is kind of very interesting in observation.

Now, if you move from cobalt to this complex which is dihydrate iron CO 4. Now this also is a very unstable compound melting point minus 70 degree centigrade, decomposition temperature minus 10 degree centigrade, the metal hydride moiety has not been characterized by IR, but in NMR it comes at minus 11.1 ppm. Now, this because is bit less acidic than this hydridic moiety and has a pKa of 4.7; which is comparable to let us say acetic acid.

Now, when this acidity is further gone down when goes to the metallate form of these complexes which is $HFe(CO)_4^-$ this is a metallate and here this the acidity has gone down substantially and pKa is 14; so, which is comparable to water.

Now, one can look at these manganese complex, $HMn(CO)_5$ melting point minus 25 degree centigrade; stable at room temperature and this MH moiety has been characterized by IR; where it comes with 1783. This proton is also characterized by proton NMR where it comes at a field minus 7.5 ppm; pKa is about 7; which is comparable to H_2S .

Now, what is interesting to note over here that this metal hydrogen moiety has different properties and that depends on the Ln. For example, when this Ln is highly a pi acidic for pi acidic ligand like carbon monoxide, this metal is highly electron deficient. And as a result it pulls the image bonded electron very much towards itself resulting in the polarization in δ^- and H plus.

So, these results in acidic hydrogen. Whereas, if the metal has electron donating ligands and because the hydrogen is more electronegative than the metal, then this image bond would be polarized as H minus and δ^+ , which sort of makes these proton hydridic.

So, that is a very interesting observation. That these proton, the character of the proton would very much depend on what kind of metal which is bound to, as well as what kind of ligand the metal is substituting substituted by. And as a result consequence of these metal and the ligand it is bound by the the hydrogen can have a character which is highly acidic to something which is highly basic or hydrolytic in natures. And a large variation of this acidic character of hydrogen is shown in these four complexes that have been discussed in the beginning of this table.

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- ❖ The term hydride is based on the assignment of formal oxidation states
- ❖ As the properties of the transition metal hydrides vary considerably, it can not be related with reactivity
- ❖ The transition metal hydrides behavior range from hydridic through neutral to protic in character

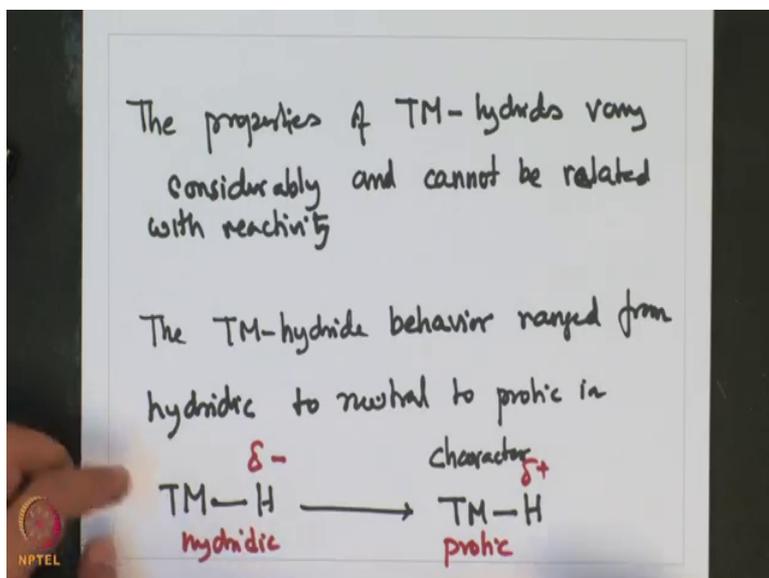


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So, with that in mind so one should realize that a hydride depends on the assignment of the formal oxidation state and the properties of transition metal hydrides vary considerably. One must realize that the property of transition metal hydride vary considerably and cannot be related with reactivity; related with reactivity.

Furthermore, from our discussion on the nature of this hydride to the transition metal, what we saw the transition metal hydride behavior; behavior ranged from hydridic to neutral to protic in character.

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So, what does it say is that transition metal hydride varied from δ^- which is hydridic to δ^+ which is protic in nature. So, this is an interesting observation and there as well as was commented upon in the previous slide by looking at the various transition metal carbonyl hydride complexes; that the nature of the hydrogen changed from something very protic, very acidic to something very basic which is hydridic and that all dependent on what kind of transition metal it is bonded to and also on what kind of ligand substituent's this transition metal bond. So, these two are important criteria which sort of dictates the property of transition metal carbonyl hydride.

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Transition Metal Organometallic Chemistry: Principles to Applications

❖ M-H functions as hydride donor

$$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H} + \text{HCl} \longrightarrow \text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl} + \text{H}_2$$

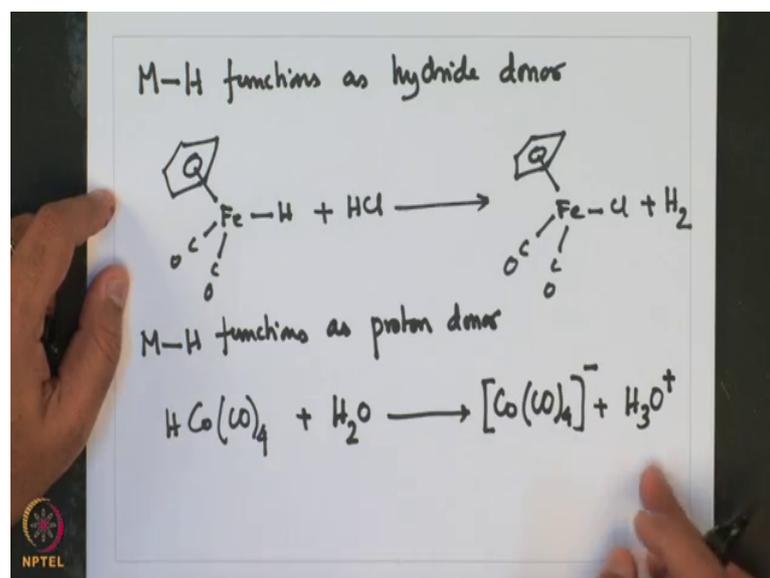
❖ M-H functions as proton donor

$$\text{HCo}(\text{CO})_4 + \text{H}_2\text{O} \longrightarrow [\text{Co}(\text{CO})_4]^- + \text{H}_3\text{O}^+$$

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So, let us illustrate this hydridic or acidic property through some chemical reactivity. For example, the function of transition metal image bond as a hydrolytic donor is illustrated below: MH functions as hydride donor. For this complex Cp Fe tricarbonyl hydride plus HCl giving Cp Fe CO CO Cl plus H 2. Now, this H 2 contains H plus from HCl and H minus from this iron hydride complex. So, here the hydrogen is acting as a hydride donor.

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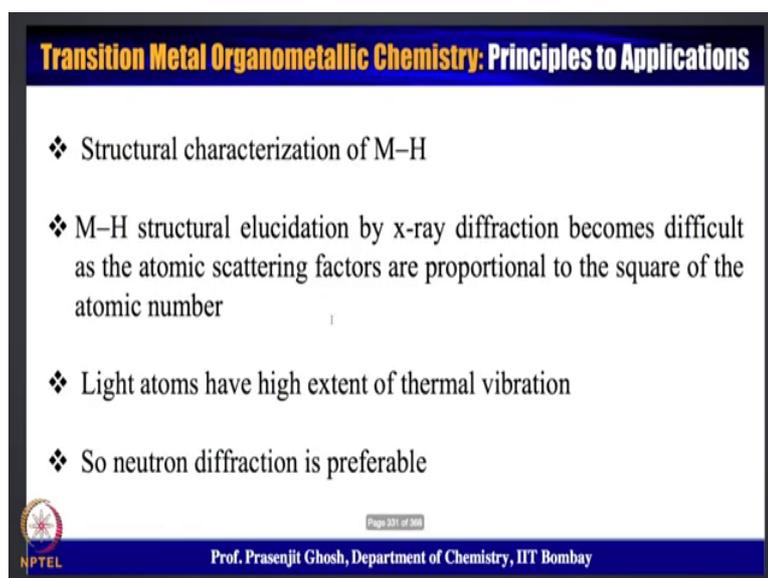


Now, take a let us take a look at another example where MH functions as a proton donor. For example, HCo CO 4 and we had seen for this particular complex that this hydrogen is very much acidic like that of sulfuric acid and should be able to protonate water H 2 O

giving the conjugate base which is the cobalt metallate; carbonyl metallate plus H_3O^+ plus.

So, here this hydrogen is acting as a protic proton donor. So, indeed as we see that depending on the ligand environment as well as the metal; this property of the metal hydride can vary a lot. In some cases it and it can act as a hydrate donor, in some cases it can also act as a proton donor.

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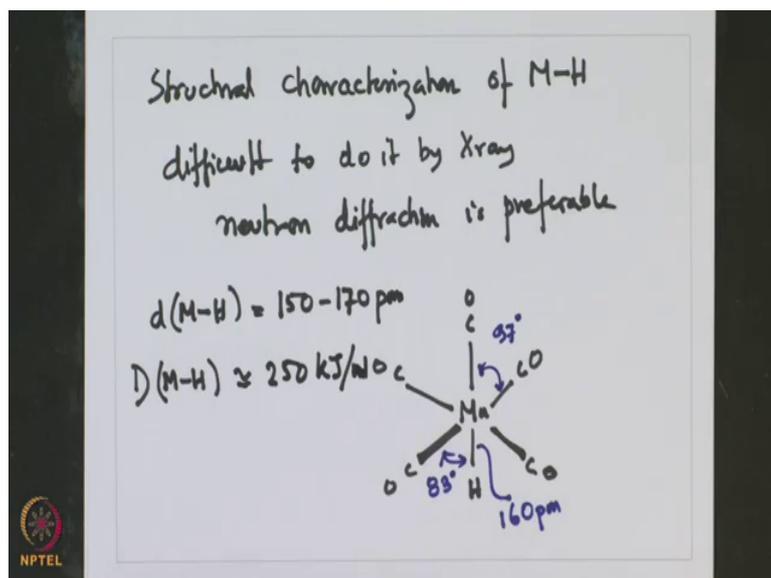
- ❖ Structural characterization of M–H
- ❖ M–H structural elucidation by x-ray diffraction becomes difficult as the atomic scattering factors are proportional to the square of the atomic number
- ❖ Light atoms have high extent of thermal vibration
- ❖ So neutron diffraction is preferable

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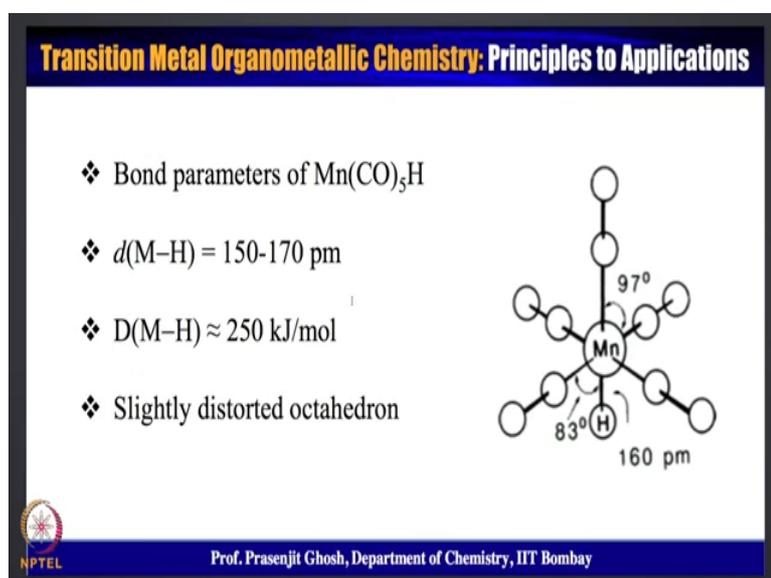
Now, in terms of characterizations, this transition metal hydride moieties have been characterized by various spectroscopic techniques including that of x ray diffraction studies. So, structural characterization has been done of metal hydride moiety and it is difficult to do to do it by by x ray. Because of heavy atom present two are very small, hydrogen which scatters very less. And then, neutron diffraction is more favorable, is preferable for characterization of the MH moiety.

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So, here is an example of manganese hydride complex. And these distance manganese hydride distance is about 160 picometer and these angles are around 90 degree; 83 to be more precise. This one instead of 90 is sort of 97 degrees. So, for the general characterization is that d metal hydride bonds can vary from 150 to 170 picometer and as far as the strength of this bond concerned, the bond dissociation energy of metal hydride are about 250 Kilo Joules per mole. So that means, they are quite strong; if not as strong as transition metal carbon bonds but they are also quite strong about 250 Kilo Joules per mole.

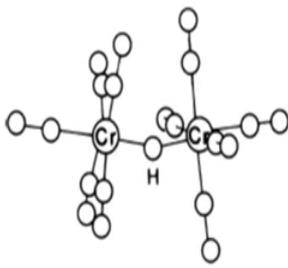
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Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Bond parameters of $[\text{Et}_4\text{N}]^+[\text{HCr}_2(\text{CO})_{10}]^-$
- ❖ The localization of a bridging M-H-M becomes more difficult because of the proximity of two strong scattering metal atoms
- ❖ Structural elucidation done by neutron diffraction



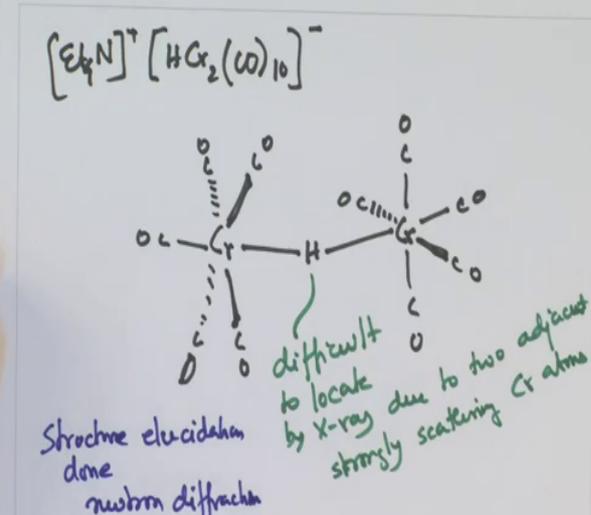
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Another example of these characterizations, where there is a bridging hydride, has been done in this $[\text{Et}_4\text{N}]^+[\text{HCr}_2(\text{CO})_{10}]^-$; where this hydrogen is a bridging. And here the structure is as follows: chromium is bridged by a hydrogen atom and it has 5 carbonyls and the bridging hydride and CO CO.

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$[\text{Et}_4\text{N}]^+[\text{HCr}_2(\text{CO})_{10}]^-$

Structure elucidation done by neutron diffraction

difficult to locate by X-ray due to two adjacent strongly scattering Cr atoms

Now, because location of becomes difficult, it is difficult to locate this hydrogen because of the two strongly scattering metal; difficult to locate by x-ray due to two adjacent,

strongly scattering chromium atoms. And hence the structure elucidation done by neutron diffraction.

So, the new as far as sort of the locating or this hydrogen atom neutron diffraction is more efficient and effective in that of the x-ray diffraction techniques.

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Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ ^1H NMR characterization of M-H units
- ❖ M-H (hydride) chemical shifts between 0 and -50 ppm (resonates at large up field shifts)
- ❖ More reliable indication is by the coupling constants

$$^1J(^{103}\text{Rh}, ^1\text{H}) = 15\text{-}30 \text{ Hz}$$
$$^1J(^{183}\text{W}, ^1\text{H}) = 28\text{-}80 \text{ Hz}$$
$$^1J(^{195}\text{Pt}, ^1\text{H}) = 700\text{-}1300 \text{ Hz}$$

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So, other apart from the structural characterization, this has of this can also be done, using proton NMR which is a useful tool for characterizing this metal hydrogen moiety.

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^1H NMR characterization of M-H units

M-H chemical shifts vary between 0 and -50 ppm
(large upfield shifts)

More reliable indication is by coupling constants

$$^1J(^{103}\text{Rh}, ^1\text{H}) = 15\text{-}30 \text{ Hz}$$
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Now, these as was observed in the examples of transition metal carbonyl hydride that we had discussed at the beginning of this lecture, this metal hydride chemical shift is highly upfield shifted and can vary from between 0 to minus 50. So, MH chemical shifts vary between 0 to minus 50 ppm; large upfield shifts. And apart from the chemical shift which is highly upfield shifted, coupling constants are also useful indication or reliable marker for this for the characterization of MH units.

So, more reliable indication is by coupling constants. And this is given by 1J ; let us say if it is rhodium 1H , if the hydrogen H is bound to a rhodium; then the 1J bond coupling is about 15 to 30 Hertz. If the metal is a tungsten then 1J tungsten 1H is about 28 to 80 Hertz and if the 1J is platinum, when the metal is bound to platinum; then this coupling is even further; so, 700 to 1300 Hertz.

So, proton NMR provides a very useful characterization for this metal hydride moiety. Not only by chemical shift because it is highly up field shifted and it appears, it can appear from between 0 to minus 50 ppm. And the best part of these upfield shifted chemicals shift is that that there is no other resonances which come so much upfield shifted because most of the the resonances for diamagnetic compounds come between 0 and plus 10 ppm. So, the window from 0 to minus 50 is almost empty for almost all of the compounds and from that perspective, it is very easy and useful place to detect this transitional metal hydride chemical shift which is upfield shifted in between from 0 to minus 50 ppm.

Another major reliable indication of this MH moiety is that of the coupling constant of the hydrogen atom which metal is bound to and that can varies in 10s like in rhodium or tungsten to even 100s and 1000 in case of platinum. So, these are proton NMR also in provides a very useful measure of characterization of this transition metal carbonyl hydride moieties.

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Transition Metal Organometallic Chemistry: Principles to Applications

❖ Alkylation reaction of carbonyl metallates



❖ Silylation reaction of carbonyl metallates

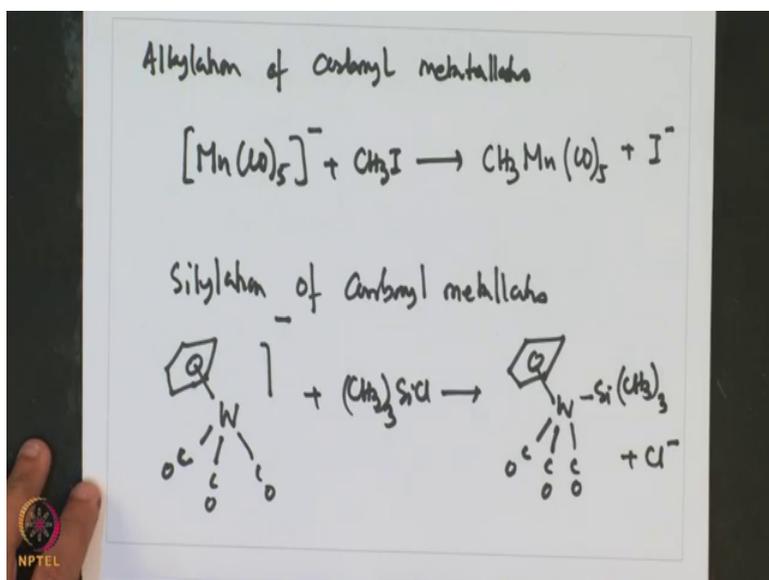


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Now, we have looked at the properties. Let us sort of look at some of the reactivity studies. The alkylation reaction of carbonyl metallates: For example, $\text{Mn}(\text{CO})_5^-$ plus CH_3I giving $\text{CH}_3\text{Mn}(\text{CO})_5$ plus I^- .

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And another example is silylation of carbonyl metallates. An example of that is Cp^- tungsten tetragon minus plus CH_3 whole 3 S i Cl gives Cp^- tungsten carbonyl Si Me 3 plus Cl^- .

Now, with that I would like to conclude what has been discussed in today's lecture. Today, we start off by looking at properties of transition metal carbonyl hydride complexes. And what we had seen that the transition metal hydride complexes can vary from hydridic to protic types depending on the metal as well as the ligand substituted around the metal in these complexes. So, they can be highly acidic to something which they can also be highly basic.

And this transition metal hydride complexes show their property when they carry out reactions with electrophiles and nucleophiles. We have also looked at the characterization methods available for transition metal hydride complexes. And what we found that even though some of the complexes have been characterized as x-ray diffraction studies but because of the small size and pores scattering ability of hydrogen with respect to the metallate is bound to which is much larger in size and hence a bigger scatter of x-rays. The x-ray diffraction is not the preferable technique for characterizing transition metal hydride complexes.

Instead neutron diffraction studies can be more effectively used in determining or characterizing transition metal hydride complexes. We have also seen in the discussion that proton NMR provides a reliable characterization of transition metal hydride complexes. As this metal hydrogen resonances appear highly upfield shifted from between 0 to minus 50; in a region where no other peaks arise and hence this is a very useful technique, to characterize this transition metal hydride complexes; because there is no interference from any other resonances in this particular region.

Another unique property of transition metal hydride complexes is the $1J$ coupling constant of the hydride moiety with the metal in which it is bound to. And what we saw that these are very specific to the metal it is binding to and can varies from 10s and 100s or even 1000s depending on what kind of metal it is bound to.

Lastly, we have looked into some of the reactions of transition metal carbonyl metallates and from that perspective we have looked into silylation and alkylation reactions of these metallates giving rise to transition metal or silylated or alkylated compounds. And we are going to look at much more of the reactivity in when we take up the topic in the next lecture. Until the time I thank you for being with me and look forward to being with you in the subsequent lecture goodbye.