Advanced Transition Metal Chemistry – Classification of Ligands
Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 27
Classification of Ligands - Hydrogen

Hello everyone. I welcome you once again to MSB lecture series on transition metal chemistry. In my previous two lectures, I gave the method of preparation of important compounds useful in doing substitution reactions in coordination chemistry and also their utility in organic transformation as homogeneous catalysts or precursors. So, let me now try to do the classification of ligands.

As you know, ligands can be classified in several ways. The simplest way of classifying all ligands into two categories is classical or simple donor ligands, and nonclassical ligands or pi bonding and pi acceptor ligands. So, what are the difference between classical or simple donor ligands and nonclassical ligands, besides having sigma donor capability, they also can be pi donors or pi acceptors.

So, these classical or simple donor ligands act as electron pair donors to acceptor ions or molecules and form complexes with all types of Lewis acids, metal ions or molecules including main group elements. Now how about nonclassical ligands? They are also called as pi-bonding or pi acid ligands. They form largely with the transition metal atoms and we will come across a special interaction between the metal and the ligands under nonclassical ligands.

And these ligands act as both sigma donors and pi acceptors due to the availability of empty orbitals of suitable symmetry and energy, comparable to those of metal nonbonding orbitals. For example, if you consider octahedral complexes, here t_{2g} remains as nonbonding and t_{2g} orbitals you know already that they are d_{xy}, d_{xz} and d_{yz} and they have pi symmetry and they can interact with suitable pi acceptor orbitals of ligands and back bonding takes place.

For example, consider a tertiary phosphine and ammonia, both can act as bases towards H^+ but phosphorus differs from N because in teritiary phosphines, we come across low energy sigma star (σ^*) orbitals essentially of antibonding in nature, whereas N does not have such orbitals for back bonding. So, that means sigma star orbitals of tertiary phosphines can interact with the t_{2g} or nonbonding orbitals of the metal complex and accept electrons which are not utilized in metal to ligand bond formation and hence it can reinforce the metal to phosphorus bond that is what we call it as back bonding.

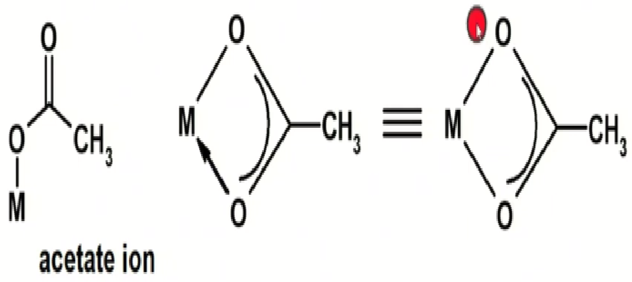
Let us consider carbon monoxide that do not have measurable basicity to protons, yet readily reacts with metals like nickel that have high heats of formation or high heats of atomization to give compounds such as nickel tetracarbonyl.

Ligands may also be classified electronically depending upon how many electrons that they contribute to a central atom. That means apart from classifying them into classical, nonclassical, one can also classify ligands depending upon how many electrons they are in a position to donate or contribute to the central atom. For example, if a ligand is capable of giving only 2 electrons that is called monodentate ligand.

Or if it has 2 donor atoms with each one a pair of electrons is called bidentate ligand or it can be tridentate ligand, tetradentate or it can be a polydentate. So, atoms or groups that can form a single covalent bond, one electron donors. For example, if you take F^-, SH^-, CH_3^- consider they are one electron donors, Cl also for that matter. Of course, I had already discussed it and classified them in my previous lectures. Any compound with an electron pair or 2 electron donors, For example, ammonia, water, tertiary phosphine, carbon monoxide, etc.

(Refer Slide Time: 04:34)

Groups that can form a single bond and at the same time donate an electron pair are called three electron donors.



And groups that can form a single bond at the same time donate an electron pair are called 3 electron donors. We also come across many. An ideal and classical example is acetate here. Acetate you can see, if you take acetic acid and remove one hydrogen it forms anionic and now it forms a covalent bond here and then this carbon monoxide, this oxygen also has a pair of electrons, two pairs of electrons are there.

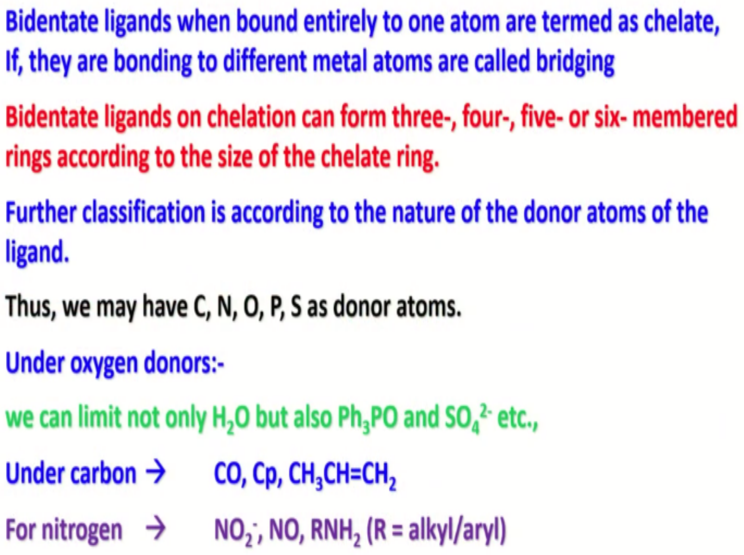
One of that when can rotate in this fashion that it can give, since here it shows two resonance structures we represent acetate in this fashion having electron distribution or this pair of electrons are delocalized and it becomes a monoanionic and this is a 3 electron donor in the neutral method, whereas in this one it is a 4 electron donor because O^- is there and CO, so this is essentially 4 electron donor, according to ionic method.

In neutral method it is 3 electron donor, just dot will represent here unless it takes a negative charge it is not a 4 electron donor. So, now, we also come across two donor atoms in a molecule, they are called bidentate ligands. Bidentate ligands when they bond entirely to one metal atom are termed as chelate, and if they are bonding to two different metal atoms, they are called bridging.

Of course, we are also using the terms kappa (κ) for chelate and mu (μ) we are using for bridging that already I told you in the beginning. Bidentate ligands on chelation can form 3, 4, 5 or even 5 membered rings according to the size of the chelate ring and further classification is according to the nature of donor atoms of the ligand. So, that means if you take any species and if you identify that donor atom, then we can classify according to that donor atom.

That means we may classify them as carbon, nitrogen, oxygen, phosphorus, sulfur or hydrogen donor atoms. So, under oxygen, we come across several, the simplest one being water. But also, if you take triphenylphosphine oxide, here phosphorus no longer has a pair of electron because phosphorus is in +5 state; oxygen has a pair of electrons so that triphenylphosphine oxide is also an oxygen donor, of course when we go for hard acids and hard base concepts, we come across sulfate, acetate, carboxylate, all those things come.

(Refer Slide Time: 06:49)



Bidentate ligands when bound entirely to one atom are termed as chelate,
If, they are bonding to different metal atoms are called bridging

Bidentate ligands on chelation can form three-, four-, five- or six- membered rings according to the size of the chelate ring.

Further classification is according to the nature of the donor atoms of the ligand.

Thus, we may have C, N, O, P, S as donor atoms.

Under oxygen donors:-

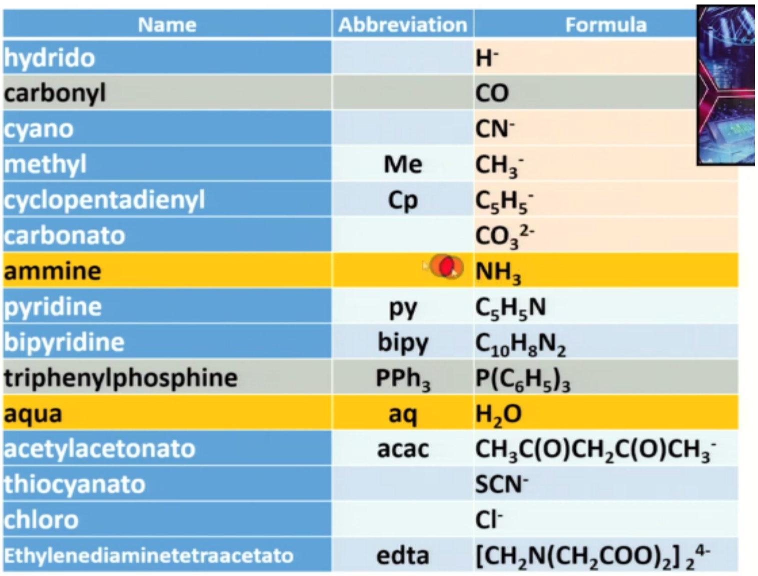
we can limit not only H_2O but also Ph_3PO and SO_4^{2-} etc.,

Under carbon → CO, Cp, $CH_3CH=CH_2$

For nitrogen → NO_2^-, NO, RNH_2 (R = alkyl/aryl)

Under carbon, we come across a variety of ligands, a few I have shown here. Cyclopentadienyl, like allyl group or carbon monoxide and also neutral ligand such as benzene, etc. For nitrogen nitrate, is there, nitrosyl is there. Primary, secondary and tertiary amines are there and we have plenty of pyridine ligands besides that we have several macrocycles having nitrogen as donor atoms.

(Refer Slide Time: 07:14)



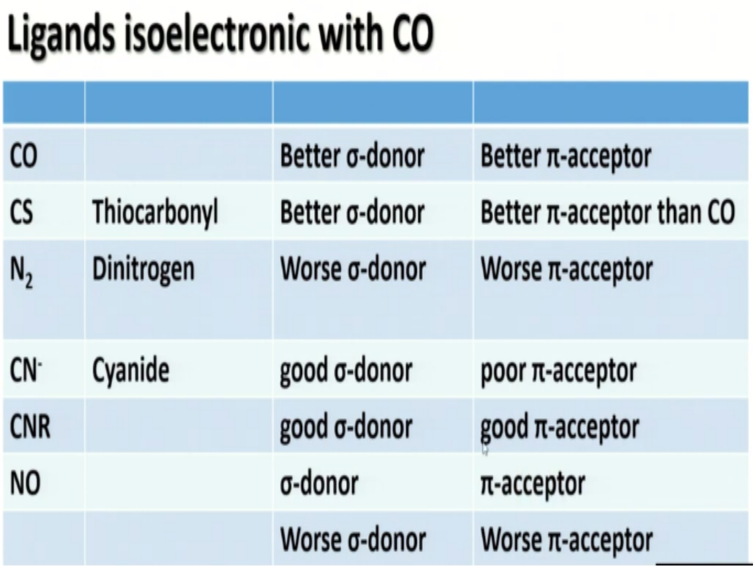
Name	Abbreviation	Formula
hydrido		H^-
carbonyl		CO
cyano		CN^-
methyl	Me	CH_3^-
cyclopentadienyl	Cp	$C_5H_5^-$
carbonato		CO_3^{2-}
ammine		NH_3
pyridine	py	C_5H_5N
bipyridine	bipy	$C_{10}H_8N_2$
triphenylphosphine	PPh_3	$P(C_6H_5)_3$
aqua	aq	H_2O
acetylacetonato	acac	$CH_3C(O)CH_2C(O)CH_3^-$
thiocyanato		SCN^-
chloro		Cl^-
Ethylenediaminetetraacetato	edta	$[CH_2N(CH_2COO)_2]_2^{4-}$

So, here I have listed some important compounds with their abbreviation and formula to make you familiar. I must have shown this one in my previous lecture. However, let me continue telling something about these things as well, now before I take up the classification of ligands by donor atoms. So, hydrido we call is H. Of course carbonyl CO, cyano we call CN–, methyl CH_3^- and cyclopentadienyl Cp^- or C5H5$^-$.

Carbonato is there $[CO_3]^{2-}$and ammine we call ammonia NH_3 and pyridine is there and then bipyridine is there. Of course, in case of bipyridine we come across two types of bipyridines, one is 2,2’-bipyridine and another one is 4,4’- bipyridine. 4,4’- Bipyridine can only act as a bridging ligand whereas 2, 2’-bipyridine can comfortably chelate to a metal centre.

And triphenylphosphine is there and of course under here we come across several phosphorus compounds, I shall elaborate more when we go to phosphorus as donor atom. And aqua we call water and acetylacetonato is also there. it is anionic similar to acetate and thiocyanato and chloro and edta is a hexadentate ligand.

(Refer Slide Time: 08:31)



Ligands isoelectronic with CO

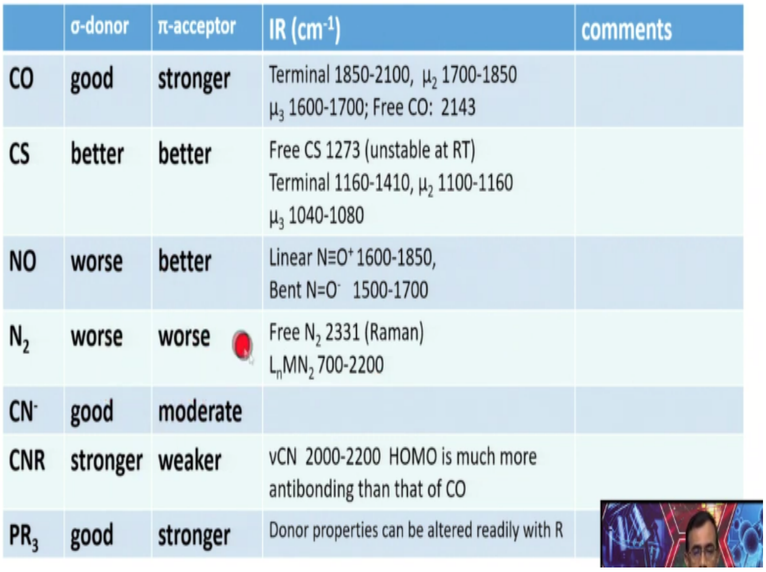
CO		Better σ-donor	Better π-acceptor
CS	Thiocarbonyl	Better σ-donor	Better π-acceptor than CO
N_2	Dinitrogen	Worse σ-donor	Worse π-acceptor
CN^-	Cyanide	good σ-donor	poor π-acceptor
CNR		good σ-donor	good π-acceptor
NO		σ-donor	π-acceptor
		Worse σ-donor	Worse π-acceptor

And then let us compare the donor and acceptor capability of several ligands with respect to carbon monoxide. Many of these ligands are isoelectronic with carbon monoxide. Of course, we all know that carbon monoxide is a better sigma donor and also a better pi acceptor. Thiocarbonyl does not have an independent existence. However, this can be generated in situ starting from appropriate precursors or starting materials to establish a metal to CS bond.

And when you make this one, this is a better sigma donor and it is a better acceptor than even CO. And N_2, dinitrogen we come across many dinitrogen complexes, I shall discuss more about that one under nitrogen. And of course, we all know that this is very inert molecule, as a result is a worse sigma donor and is a worse pi acceptor and it is very challenging to coordinate N_2 to metal complexes.

And cyanide, very good sigma donor, but it is a poor pi acceptor. I shall tell you why it is a poor pi acceptor, it is already negatively charged, as a result, what happens, it is a poor pi acceptor. CNR is a good sigma donor and also good pi acceptor and nitrosyl good sigma donor and good pi acceptor.

(Refer Slide Time: 09:45)



	σ-donor	π-acceptor	IR (cm^{-1})	comments
CO	good	stronger	Terminal 1850-2100, μ_2 1700-1850 μ_3 1600-1700; Free CO: 2143	
CS	better	better	Free CS 1273 (unstable at RT) Terminal 1160-1410, μ_2 1100-1160 μ_3 1040-1080	
NO	worse	better	Linear $N{\equiv}O^+$ 1600-1850, Bent $N{=}O^-$ 1500-1700	
N_2	worse	worse	Free N_2 2331 (Raman) L_nMN_2 700-2200	
CN^-	good	moderate		
CNR	stronger	weaker	vCN 2000-2200 HOMO is much more antibonding than that of CO	
PR_3	good	stronger	Donor properties can be altered readily with R	

And then as I mentioned carbon monoxide is good sigma donor and a very strong pi acceptor. Then how to distinguish, to what extent a carbon monoxide has taken electrons from metal to its antibonding orbital. So that can be readily monitored using IR spectroscopy by looking into the CO stretching frequencies. If you have terminal carbonyl groups, in that case what happens depending upon how many carbon monoxides are there and what is the geometry, the stretching frequency can range from 1850 to 2100 cm^{-1}.

And when they are bridging what happens it will be having double bond character as a result stretching frequency drops significantly to be in the range of 1700 to 1850 cm^{-1}. And when it is bridging three metal centres, it further drops and one can observe stretching frequency between 1600 to 1700 cm^{-1}. And of course, one should know that free CO has stretching frequency of 2143 cm^{-1}. And as I mentioned CS is a better sigma donor and also a better pi acceptor and free CS is very unstable.

But at low temperature if you monitor, it shows a stretching frequency of 1273 cm^{-1} and the terminal CS will be having stretching frequency between 1160 to 1410 cm^{-1}. And when it is bridging, the same stretching frequency will drop to 1100 to 1160 cm^{-1}. And then when it is bridging three metal centres it further drops and appears in the range of 1040 to 1080 cm^{-1}. And NO is a worse sigma donor and it is a better pi acceptor.

And of course, again it can show two different types of binding, one is linear, one is bent. When it's linear it is a 3 electron donor, when it is a bent it is 1 electron donor. So here when it is linear and whether it is linear or bent, one can also analyse by simply doing electron count. On the other hand, the experimental one can also know by simply taking IR spectrum of that complex. For linear NO, stretching frequency appears around 1600 to 1850 cm^{-1}, for bent it comes around 1500 to 1700 cm^{-1}.

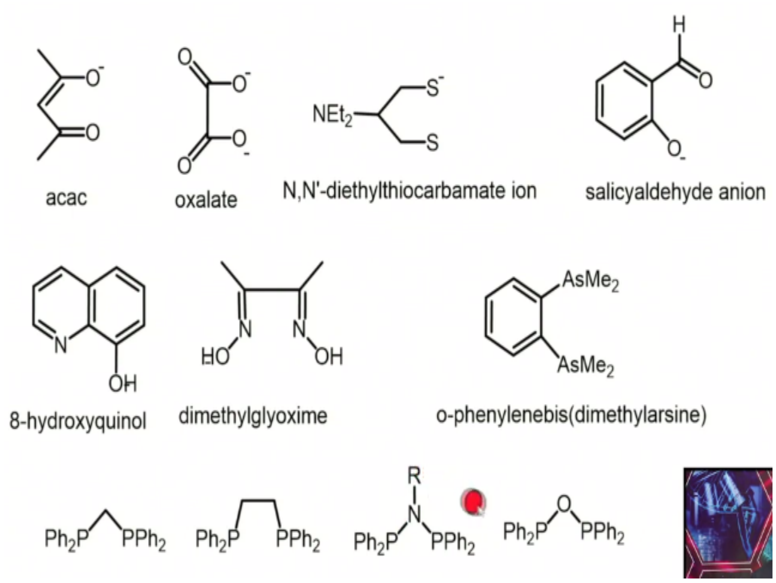
That means characterizing these compounds and identifying the nature of coordination should not be a problem because IR comes very handy in these cases. N_2 as I mentioned is a worse sigma donor and worse pi acceptor and it is very challenging to make these complexes, nevertheless I will show you preparation of these compounds and what kind of metals one should look for to make dinitrogen complexes.

And free N_2 has Raman active band at 2331 cm^{-1}. And of course, when it is binding terminally with one nitrogen donating this lone pair to metal, the stretching frequency will be 700 to 2200 cm^{-1}. And CN^- is a good to moderate and of course here also one can look at stretching frequency, there should not be a problem. And CNR (isocyanide) is a stronger sigma donor, but weak pi acceptor. And in this case, the stretching frequency comes around 2000 to 2200 cm^{-1}.

Here HOMO highest occupied molecular orbital is much more antibonding than that of CO, one should remember when we look into the activity. And teritiary phosphine is a good sigma donor and stronger pi acceptor. And of course, it is very interesting to compare the donor and acceptor ability of carbon monoxide and phosphine. Let me do it at appropriate juncture as we progress with this one.

It is very interesting and we can always say why teritiary phosphine is a better ligand compared to carbon monoxide, we can discuss those things in length, let me do it at later stage.

(Refer Slide Time: 13:32)

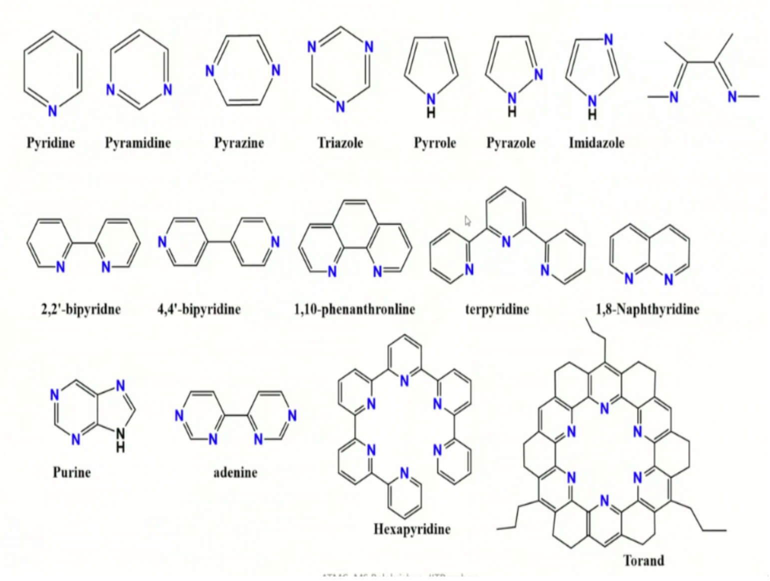


So, now let me show you a few examples of all types of ligands we come across before I take up the classification of ligands by donor atom starting with hydrogen ligands. This acac you can see here because of tautomerism what happens, it becomes a double bond shifted here and it becomes O^- and again O^- can be here or here, so again, the negative charge is delocalized and it acts as a monoanionic ligand.

And also, it is a 4 electron donor in this fashion. Similarly, oxalate is dianionic and then one can also go for diethylthiocarbamate ion here and salicylaldehyde anion again is very similar to acetate and 8-hydroxyquinol O^- anionic and neutral it can be. And then dimethylglyoxime also can be anionic and phenylenebis(dimethylarsine) this is 1,2-substituted one is a very nice bidentate ligand.

And also, we have several bidentate ligands phosphines, this is dppm, and diphenylphosphinomethane, it is 1,2-bis(diphenylphosphino)methane and this is diphenylphosphinoamine and of course here R can be H or any other alkyl or aryl group. This is also another interesting oxygen bridged ligand.

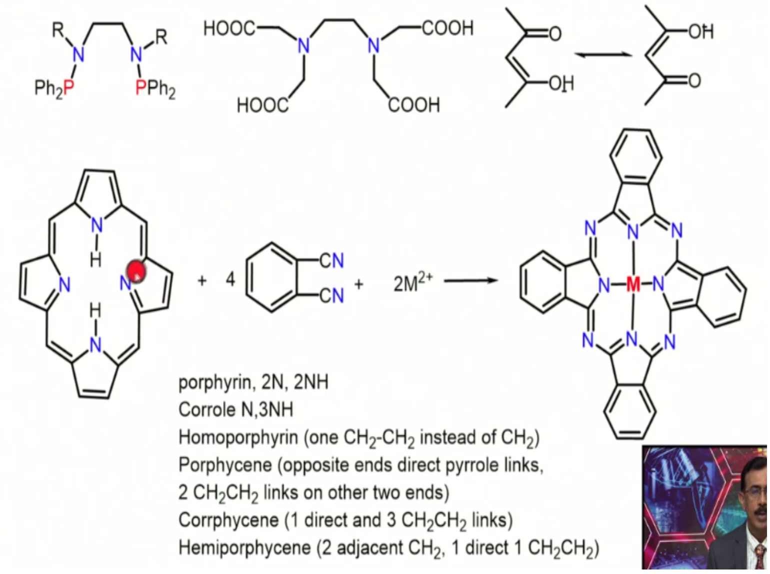
(Refer Slide Time: 14:53)



And of course, as I mentioned, we have plenty of nitrogen based cyclic and acyclic ligands. So, there are numerous examples of cyclic ligands of nitrogen, the simplest one being pyridine, pyrimidine, pyrazine, triazole, pyrrole of course it can be an ionic and pyrazole, imidazole is there. And then 2,2'-bipyridine a chelating ligand, 4,4'-bipyridine ideal for bridging and also we have 1,10-phenanthroline.

This is another interesting ligand, terpyridine and this is naphthyridine and this is purine, adenine and also this is hexapyridine and also it is a torand. So, we have plenty of nitrogen donor ligands. Apart from this, we also have classical macrocyclic ligands which are widely seen among biologically active molecules.

(Refer Slide Time: 15:48)



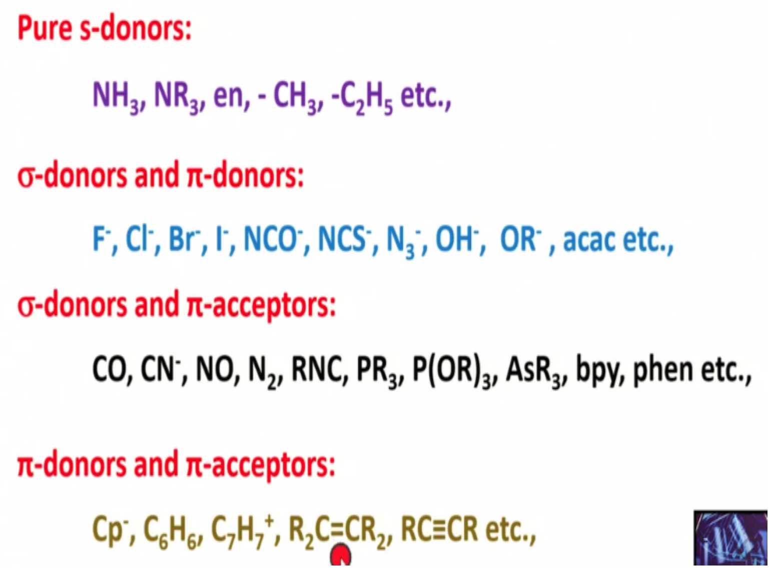
porphyrin, 2N, 2NH
Corrole N,3NH
Homoporphyrin (one CH_2-CH_2 instead of CH_2)
Porphycene (opposite ends direct pyrrole links,
2 CH_2CH_2 links on other two ends)
Corrphycene (1 direct and 3 CH_2CH_2 links)
Hemiporphycene (2 adjacent CH_2, 1 direct 1 CH_2CH_2)

For example, this one is also ethylene diamine derived bisphosphine and this is the famous EDTA, ethylene diamine tetra acetic acid and then it can form readily anionic, as a result it can be tetra anionic and then this will be hexadentate ligand. And then we have this acac we have. And then as I mentioned several nitrogen macrocycles are there, this is one such compound, this is phthalocyanine and this one can be prepared only in situ and this also called encapsulating ligand, one can make something like this here.

And then porphyrin, if you want to know the difference between several macrocyclic ligands if you simply look into the porphyrin it has two N and two NH one opposite sides, that means it can be dianionic and it can stabilize metal in +2 to state and corrole will be having one nitrogen and three NH will be there trianion, and homoporphyrin if you take, one CH_2CH_2 bridge will be there instead of one CH_2 here that is called homoporphyrin. And porphycene opposite ends have pyrrole links.

I have given the information about those, one can look into the structures of some of these nitro macrocycles in standard textbooks. So, in this porphycene opposite ends have direct pyrrole links and two CH_2CH_2 links on other two ends. And also we have corrphycene in that one direct and $3CH_2CH_2$ links will be there. And in case of hemiporphycene we have 2 adjacent CH_2 and one direct CH_2CH_2 links will be there. The links I am talking about is these things that separates pyrrole groups.

(Refer Slide Time: 17:31)



Pure s-donors:

NH_3, NR_3, en, - CH_3, -C_2H_5 etc.,

σ-donors and π-donors:

F^-, Cl^-, Br^-, I^-, NCO^-, NCS^-, N_3^-, OH^-, OR^-, acac etc.,

σ-donors and π-acceptors:

CO, CN^-, NO, N_2, RNC, PR_3, $P(OR)_3$, AsR_3, bpy, phen etc.,

π-donors and π-acceptors:

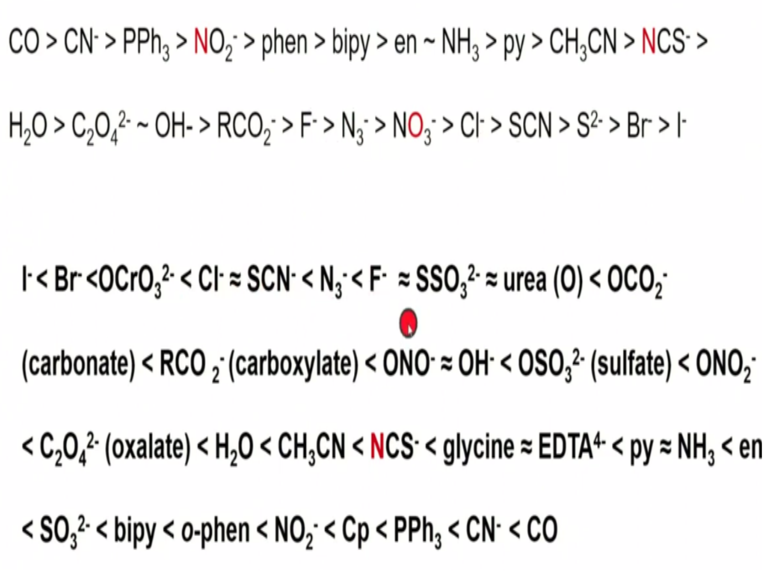
Cp^-, C_6H_6, $C_7H_7^+$, $R_2C{=}CR_2$, $RC{\equiv}CR$ etc.,

And this I have done it again, I shall just tell you about pure sigma donors. These are pure sigma donors, they do not have pi acceptor or pi donor capabilities. And then we have sigma donors and pi donors, all these halogens and NCO, NCS, N^{3-}, OH^-, OR, acac, etc. They are sigma donors as well as pi donors.

We have sigma donors and pi acceptors, very important ligand system, they are also called as nonclassical, unfortunately. They are carbon monoxide, cyano, NO, N_2, RNC, PR_3 and one can also write a spectrochemical series for these things by looking into their donor and acceptor capabilities. Similarly, among pi donors and pi acceptors, we have several carbon donor ligands such as Cp^-, C6H6**,** $C_7H_7^+$ and ethylene and acetylene. They are called pi donors and pi acceptors because these pi electrons are going to the metal as sigma that is the reason they are called pi donors.

One of the bonds in a double bond will be donated to the metal in the form of 2 electrons that is the reason they are called pi donors and pi acceptors, but however this pi bond whatever that is established is sigma in nature.

(Refer Slide Time: 18:53)



$CO > CN^- > PPh_3 > NO_2^- >$ phen $>$ bipy $>$ en $\sim NH_3 >$ py $> CH_3CN > NCS^- >$

$H_2O > C_2O_4^{2-} \sim OH- > RCO_2^- > F^- > N_3^- > NO_3^- > Cl^- > SCN > S^{2-} > Br^- > I^-$

$I^- < Br^- < OCrO_3^{2-} < Cl^- \approx SCN^- < N_3^- < F^- \approx SSO_3^{2-} \approx$ urea (O) $< OCO_2^-$

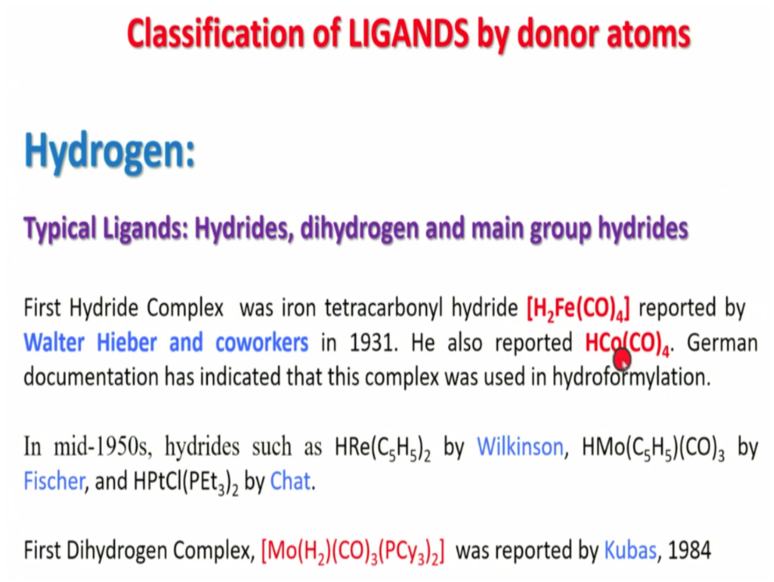
(carbonate) $< RCO_2^-$ (carboxylate) $< ONO^- \approx OH^- < OSO_3^{2-}$ (sulfate) $< ONO_2^-$

$< C_2O_4^{2-}$ (oxalate) $< H_2O < CH_3CN < NCS^- <$ glycine $\approx EDTA^{4-} <$ py $\approx NH_3 <$ en

$< SO_3^{2-} <$ bipy $<$ o-phen $< NO_2^- <$ Cp $< PPh_3 < CN^- < CO$

Let me give an extended spectrochemical series also, before I begin the discussion. It is very difficult to remember the relative positions, nevertheless by looking into the nature of ligands we should be able to tell whether a given ligand is a strong field ligand or a weak field ligand, relatively we should be able to tell. We should be familiar with the nature of the ligands.

(Refer Slide Time: 19:17)



Classification of LIGANDS by donor atoms

Hydrogen:

Typical Ligands: Hydrides, dihydrogen and main group hydrides

First Hydride Complex was iron tetracarbonyl hydride **$[H_2Fe(CO)_4]$** reported by **Walter Hieber and coworkers** in 1931. He also reported **$HCo(CO)_4$**. German documentation has indicated that this complex was used in hydroformylation.

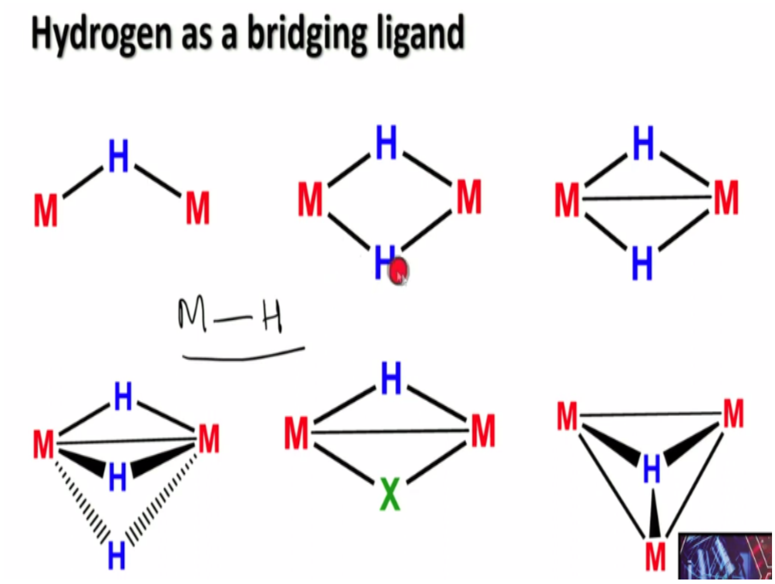
In mid-1950s, hydrides such as $HRe(C_5H_5)_2$ by Wilkinson, $HMo(C_5H_5)(CO)_3$ by Fischer, and $HPtCl(PEt_3)_2$ by Chat.

First Dihydrogen Complex, $[Mo(H_2)(CO)_3(PCy_3)_2]$ was reported by Kubas, 1984

So, now let us start the classification of ligands by donor atoms. To begin with, let us consider hydrogen, the simplest donor atom. Typical ligands of hydrogen donor are hydrides, dihydrogen and also several main group hydrides. For example, BH_4^-, AlH_4^-, etc. First hydride complex was iron tetracarbonyl hydride and then this was reported by Walter Hieber and coworker in 1931. He also reported this cobalt hydride having 4 carbon monoxide.

So German documentation has indicated that this complex was used in hydroformylation much earlier. In mid 50s, hydrides such as rhenium hydride by Wilkinson and also this was made by Fischer and also this one platinum hydride was made by Chat. So, all these hydrides of rhenium, molybdenum and platinum were made in 1950s by these respective chemists. First dihydrogen complex is $MoH_2(CO)_3(PCy_3)_2]$ was reported by Kubas in 1984.

(Refer Slide Time: 20:29)

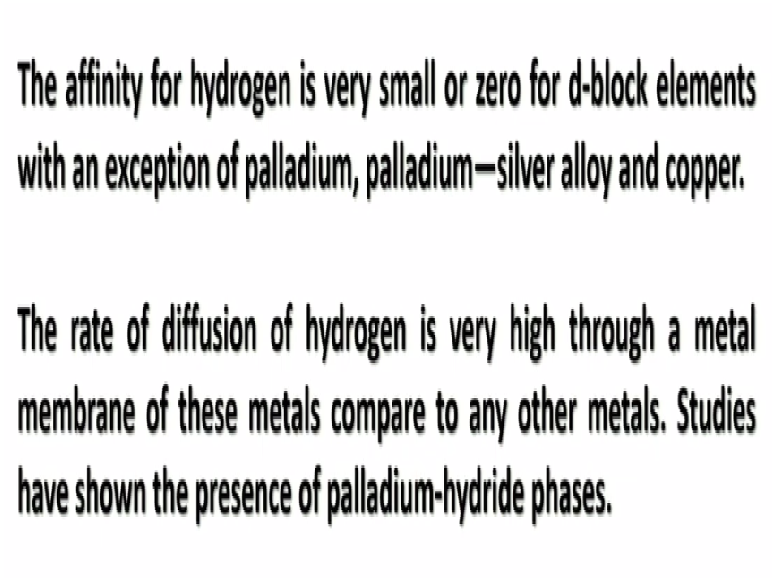


Hydrogen as a bridging ligand

So, let us look into the coordination modes of hydrogen. There can be terminal hydrogen also something like this, so this is terminal. Apart from this terminal and standard, we can also see hydrogen bridging two metal centres and of course you can recall the structure of borane where we form three-centre two-electron bond, in the same way here also it establishes a three-centre two-electron bond, this one binds with suitable orbitals of both the metal centres.

And of course, you can also have two bridging hydrides in this fashion without metal-metal bond or with metal-metal bond. And three hydrides linking or bridging two metal centres are also known. And also we can have mixed bridging ligands such as halides and also hydrogen. And we can also have something like this hydrogen bridging three metal centres. These are some common coordination modes or binding modes of hydrogen among metal hydride complexes.

(Refer Slide Time: 21:37)

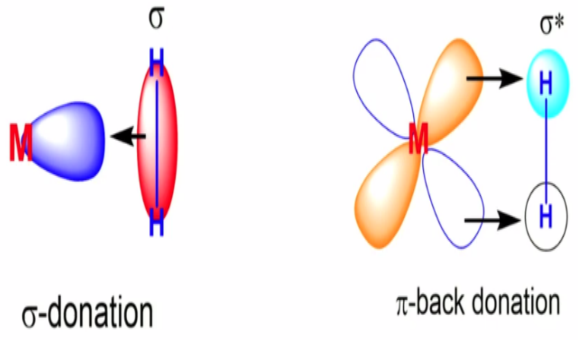


The affinity for hydrogen is very small or zero for d-block elements with an exception of palladium, palladium—silver alloy and copper.

The rate of diffusion of hydrogen is very high through a metal membrane of these metals compare to any other metals. Studies have shown the presence of palladium-hydride phases.

The affinity for hydrogen is very small or zero for d-block elements with an exception of palladium and also palladium silver alloy and copper complex. So, the rate of diffusion of hydrogen is very high through the metal membrane of these metals compared to any other metals among transition element series. Studies have shown the presence of palladium-hydride phases. That is the reason palladium on carbon is widely used in hydrogenation reactions.

(Refer Slide Time: 22:08)



More details will be provided while considering oxidative addition of H_2 to a square planar complex.

So, now let us look into the binding modes of hydrogen. And of course, when you look into H_2 molecule, we have a pair of electron that establishes H-H bond, that pair of electron can be readily donated to M through sigma donation, very similar to olefines, and this is pi donation. On the other hand, this sigma star is empty, the sigma star of H_2 can be comparable to the sigma star of PR_3.

So, that means the sigma star can also interact with suitable metal pi symmetry orbitals such as d_{xy}, d_{xz} and d_{yz} to establish back bonding, that is from metal to hydrogen antibonding. That means, hydrogen can act as a sigma donor as well as a pi acceptor. More details will be provided while considering oxidative addition of H_2 to a square planar complex.

When I go to oxidative addition reductive elimination reaction, I shall elaborate more about how one can manipulate hydrogen coordination to metal centre for the purpose of hydrogenation of olefins and other unsaturated organic compounds, that you cannot do conventionally, even at a very high temperature. So, let me stop at this juncture and continue discussing more about hydrogen as donor atom with examples and method of preparation and properties and bonding, etc., in my next lecture. Until then, have an excellent time reading chemistry.