Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

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Lecture – 39

Classification of Ligands – Phosphorus, Halogens

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. We have been discussing in length about the classification of ligands by donor atoms, in the middle of discussion about phosphorus donor ligands, I did mention about how phosphines can be tuned both electronically and sterically to make ideal candidates for the application of the complexes in coordination chemistry, organometallic chemistry and catalysis.

So, when we talk about ligands, they are the most important components of chemistry, especially coordination chemistry, organometallic chemistry and their ultimate use in catalysis. All ligands, we know how to classify them as classical and nonclassical. So, these nonclassical type of ligands stand out as most important class of ancillary ligands or silent ligands or supporting ligands compared to any other donor systems.

Essentially because of their remarkable flexibility in tuning their electronic and steric properties and also the remarkable flexibility in the ligand design process. So, from that point of view, especially phosphines offer a great deal of flexibility in designing several types of phosphines, that goes with our imagination. One can make monodentate to polydentate with different linkers.

Linkers can be alkyl groups, aryl groups or any other heterodonor atoms or any other heteroatoms for that matter. And another important thing I am highlighting here is about steric and electronic properties, they can be easily tuned and once when you tune and use them, they offer remarkable flexibility to the geometries around central metal atoms. And another advantage with phosphines is ^{31}P phosphorus is 100% abundant and has nuclear spin $I = \frac{1}{2}$, very easy to analyse and record spectra.

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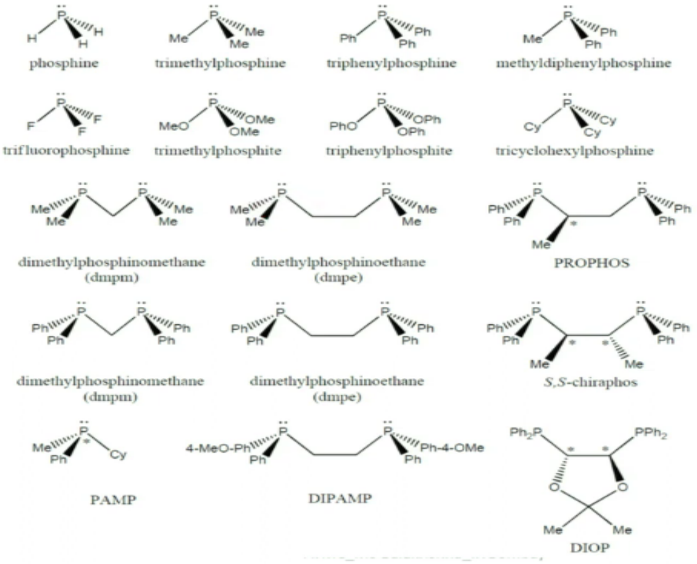

With this, let us talk a little bit more about phosphines. This is a simple phosphine, it is very similar to ammonia we have and once when you start replacing these hydrogen atoms with alkyl groups, aryl groups, we will be having secondary phosphines and eventually tertiary phosphines. These are all with carbon linkers you can see here, one carbon is there, two carbons are there and even chiral is there. As I mentioned it goes with our imagination, we have several starting compounds at our disposal to hook on these phosphorus moieties.

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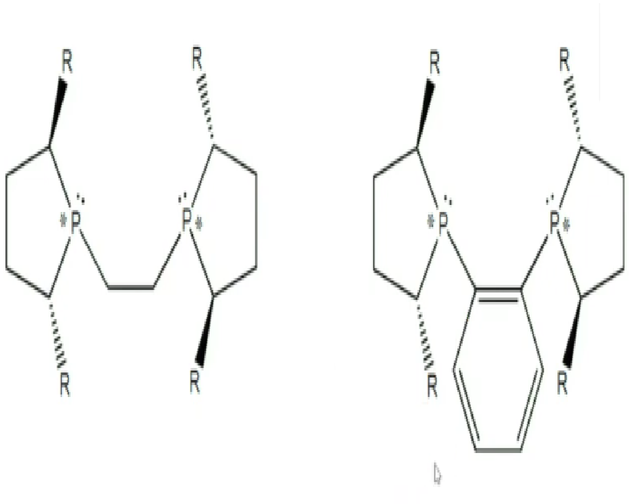

DuPHOS

So, this is an interesting chiral phosphorus ligand called DuPHOS.

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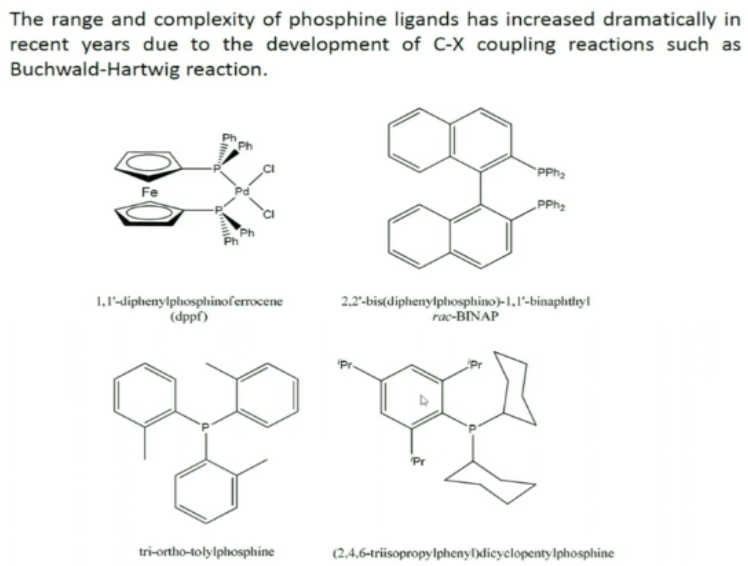

The range and complexity of phosphine ligands has increased dramatically in recent years due to the development of C-X coupling reactions such as Buchwald-Hartwig reaction.

1,1'-diphenylphosphinoferrocene (dppf)

2,2'-bis(diphenylphosphino)-1,1'-binaphthyl *rac*-BINAP

tri-ortho-tolylphosphine

(2,4,6-triisopropylphenyl)dicyclopentylphosphine

And of course, this is quite well known, this is called dppf, bis(diphenylphosphino)ferrocene and widely used in catalysis. I have shown one palladium complex of this one. This is a stereogenic complex here BINAP. And of course, one can also have bulky groups at ortho position and also one can have cyclohexyl groups on phosphorus and also a bulky group here so that we can stabilize with low coordination number.

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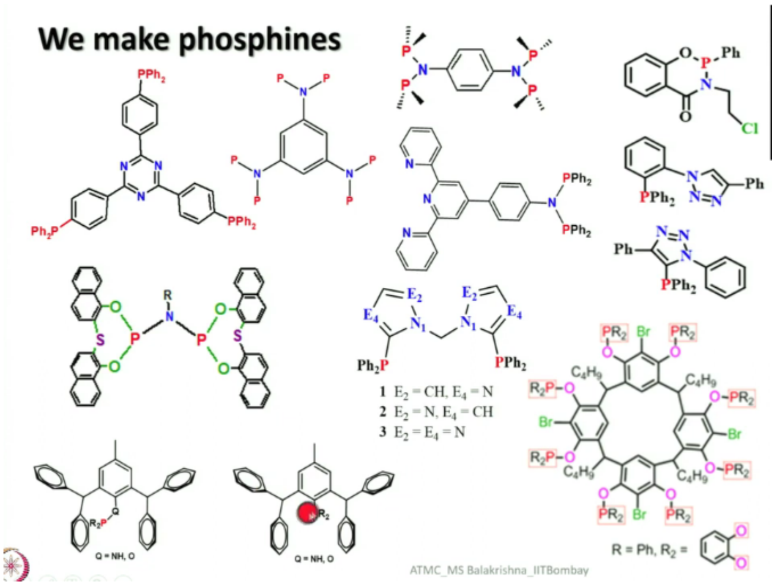

We make phosphines

And these are some of the phosphines that we made in our group. We have been working with phosphorus chemistry since 25 years. We have been focused on making a variety of phosphines with an intention of using them in catalysis. You can see, we have made also octaphos and also we have other donor atoms are there like triazole or you can have some other oxygen donors and we can also make very bulky phosphines here. They show interesting properties.

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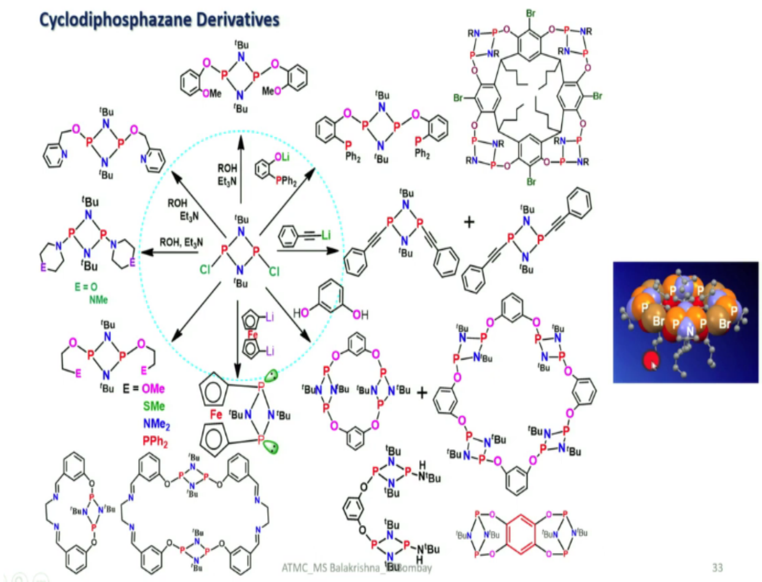

Cyclodiphosphazane Derivatives

These are some of very interesting phosphines generated from this cyclodiphosphazane. You can see having different structural features, some of them are macrocycles. We have as many as 8 phosphorus atoms here. This is ferrocene based one, shows very interesting chemistry. And this is the one I have shown here, so this has something like this structure.

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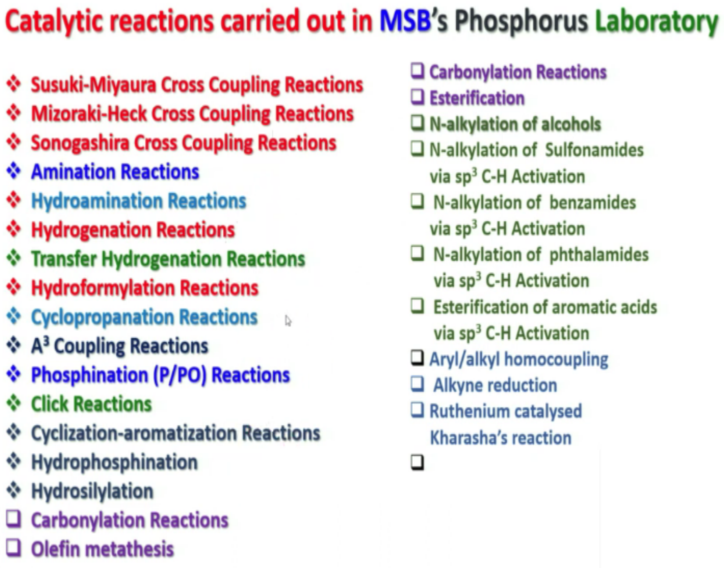

Catalytic reactions carried out in MSB's Phosphorus Laboratory

❖ Susuki-Miyaura Cross Coupling Reactions
❖ Mizoraki-Heck Cross Coupling Reactions
❖ Sonogashira Cross Coupling Reactions
❖ Amination Reactions
❖ Hydroamination Reactions
❖ Hydrogenation Reactions
❖ Transfer Hydrogenation Reactions
❖ Hydroformylation Reactions
❖ Cyclopropanation Reactions
❖ A^3 Coupling Reactions
❖ Phosphination (P/PO) Reactions
❖ Click Reactions
❖ Cyclization-aromatization Reactions
❖ Hydrophosphination
❖ Hydrosilylation
❑ Carbonylation Reactions
❑ Olefin metathesis

❑ Carbonylation Reactions
❑ Esterification
❑ N-alkylation of alcohols
❑ N-alkylation of Sulfonamides via sp^3 C-H Activation
❑ N-alkylation of benzamides via sp^3 C-H Activation
❑ N-alkylation of phthalamides via sp^3 C-H Activation
❑ Esterification of aromatic acids via sp^3 C-H Activation
❑ Aryl/alkyl homocoupling
❑ Alkyne reduction
❑ Ruthenium catalysed Kharasha's reaction
❑

And using these phosphines, we have been carrying out lot of catalytic reactions. Most of the catalytic reactions we perform are listed here. You can go through it if you are interested in whenever you get time.

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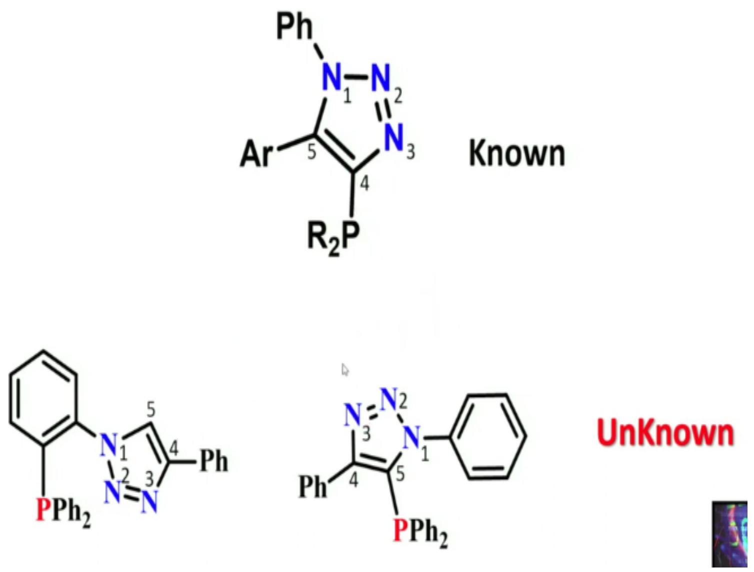
Known

UnKnown

When we started again making phosphines, we also looked into adding some of these functional groups with the donor atoms. As I mentioned earlier, they have a very totally different and interesting chemistry and only this one was known having a phosphine on one of the triazolic carbons, but these two were not known.

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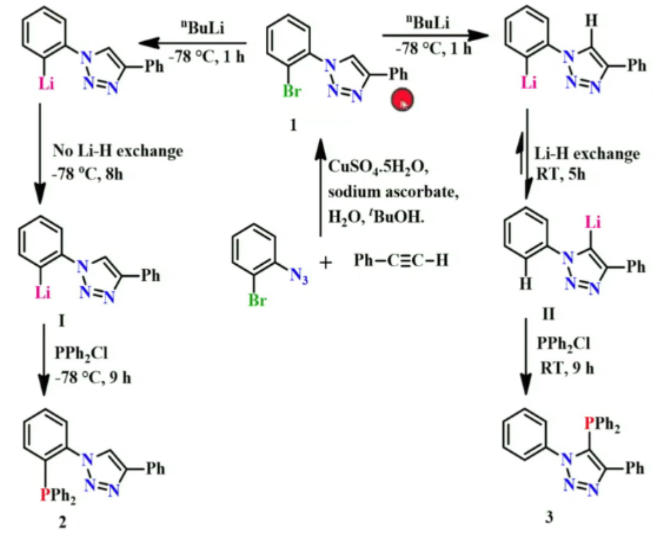

Bimba, Radhakrishna, Balakrishna Inorg. Chem. 2016, 55, 8514-8526

So, then when we started digging, we understood the synthetic problems people came across. For example, the best way to put a phosphorus moiety on a carbon is by lithiation and then replacing that lithium with chlorophosphines. For example, when this bromo derivative was taken and treated with N-butyl lithium at –78 ºC, lithium goes here through halogen exchange.

And then at –78 ºC, maintained for a couple of hours or even 8 hours and then add chlorodiphenylphosphine, it gives this one as expected. In contrast after lithiation, if the solution was warmed to room temperature and added chlorodiphenylphosphine, it does not go to ortho position of phenyl ring, instead it goes to triazolic carbon. That means when you warm it, what happens lithium hydrogen exchange takes place.

This requires small energy for the C-N rotation and it should come here, it should interact and then lithium exchange takes place. As a result, when you add later chlorodiphenylphosphine, phosphine goes to triazolic carbon. So, these things we came to know when one of my students was working on the system and eventually we investigated in detail using spectroscopic means and other kinetics and we concluded that yes, this is very temperature dependent reaction.

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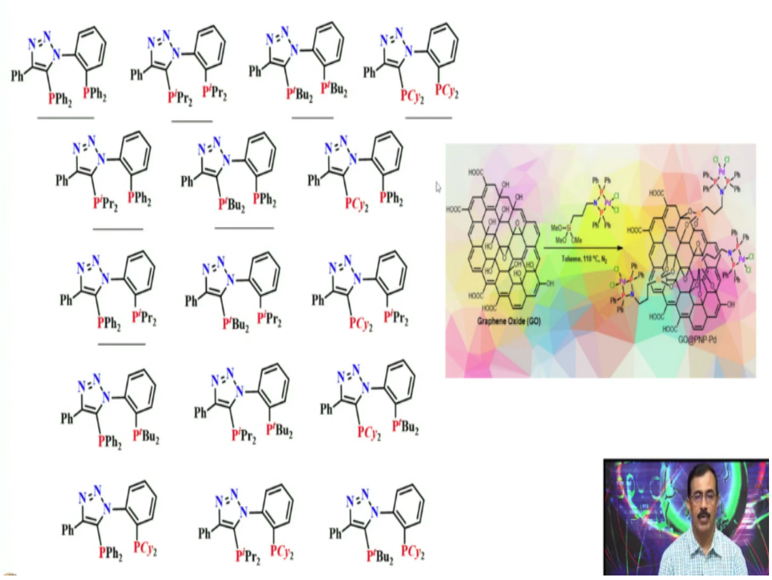

Once we did this one, we generated a series of phosphines here and we also immobilized on a heterogeneous surface such as graphene oxide. So, now it is very easy to perform catalysis here. This system can be called as homogenised heterogenous surface, that means homogenised heterogenous system. So, in this case, what happens, this portion of course graphene oxide is insoluble in any organic solvent, but when you attach these things like here and here put a metal and now this entire moiety is soluble in organic solvents.

That means if you just soak it in organic solvent, what happens this will remain, but on the other hand this goes into the solution. If it goes into the solution, you can carry out homogeneous catalysis and the interesting thing is once the product is formed, if you just do filtration, along with this heterogeneous surface it comes out, so that means contamination of organic product with complex and tedious job of separation does not exist here that is the advantage.

So, one can conveniently fix some of these organic soluble ligand systems especially bisphosphine and then compensation you can do with whatever the metals of your choice and in a particular oxidation state and then one can perform homogeneous catalysis. This is the advantage of homogenizing heterogeneous surface by phosphines or any other ligands for that matter.

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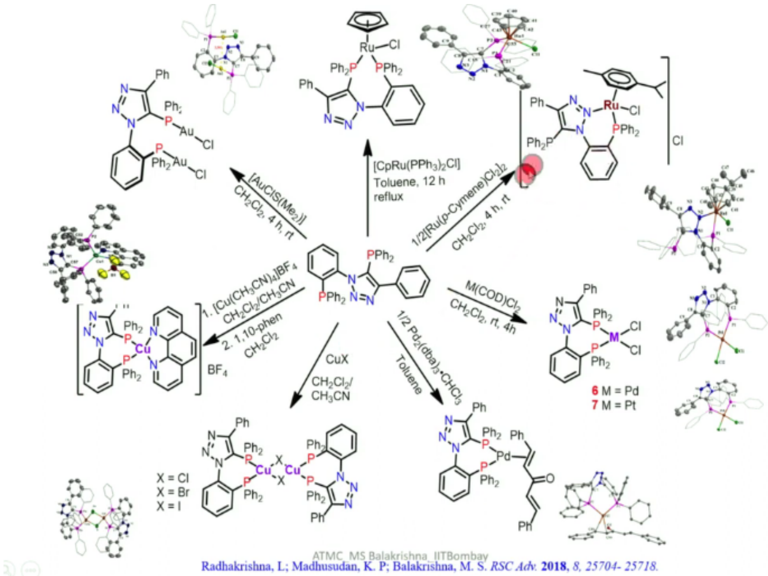

Radhakrishna, L.; Madhusudan, K. P.; Balakrishna, M. S. *RSC Adv.* **2018**, *8*, 25704- 25718.

So, now, with this one you can see the versatility of these kinds of ligands, bisphosphines are there. Besides that, we also have at least two nitrogen atoms that can coordinate to metals and these are also called hemilabile ligands because what happens either phosphorus and nitrogen can coordinate or with CN rotation both the P can come on to the same side to form P-P coordination. You can see all these things are happening here and also isomerization also happens in case of molybdenum and tungsten complexes.

You can see P-N coordination is there, whereas here P-P coordination is there and in this one, again P coordination is there and here P-P coordination is there along with another phenanthroline ligand. P-P coordination. This is an interesting 16 electron species in palladium(0) state, this is a wonderful catalyst for a lot of organic reactions. So, that means as I mentioned, it goes with your imagination.

If you know the basics, very nicely these factors like electronic and steric property should be imbibed into the design so that you can make desired phosphines and attach to right kind of transition metals to explore their catalytic activities.

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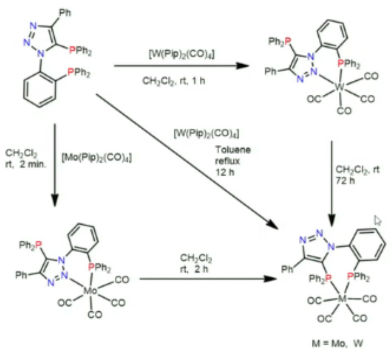
Synthesis of Mo(0) and W(0) Complexes



Compound	P1 in ppm	P2 in ppm	Coupling constant (Hz)
W[PN]	23(s)	-23.9(s)	$^{1}J_{WP}$=239.2
Mo[PP]	35.6(d)	23.7(d)	$^{2}J_{PP}$=18.7
W[PP]	18.9(d)	6.9(d)	$^{2}J_{PP}$=18.7 $^{1}J_{WP}$=238.3 and 247.3
W[PN]Au-P	22.9(s)	12.8(s)	$^{1}J_{WP}$=237.5
	P1 = Ar-P, P2 = Triazole-P		

Compound	ν_{CO} (cm^{-1})
W[PN]	2013, 1887 and 1850
Mo[PP]	2023, 1927 and 1901
W[PP]	2018 and 1892
W[PN]Au-P	2010, 1901, 1888 and 1857

And as I mentioned here, you can see initially if you take this bisphosphine and treat with tungsten tetracarbonyl with two labile ligands such as piperidine they can be readily replaced at room temperature in dichloromethane to initially form a P-N compound. On standing this one in solution for 72 hours, it undergoes isomerization to form P-P compound. Whereas in case of molybdenum, also same thing happens.

But this P-N coordinated compound is relatively unstable compared to tungsten complex and on keeping in solution after the completion of the reaction within 2 hours get isomerization from P-N to P-P compound, whereas here it takes 72 hours. So, why that happens? One can also do DFT calculations to understand the energy profile to conclude that why molybdenum is much faster, whereas in case of tungsten it takes longer time.

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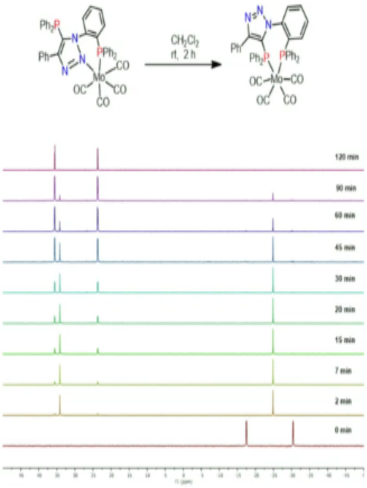
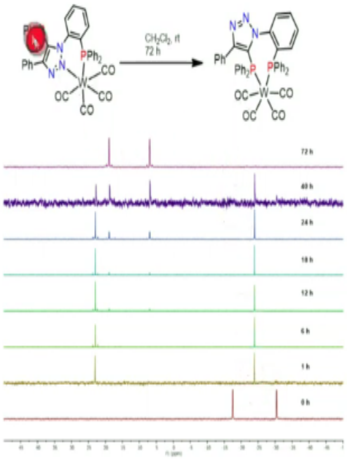


Time dependent $^{31}P\{^{1}H\}$ NMR spectra for the isomerization of **Mo** complex



Time dependent $^{31}P\{^{1}H\}$ NMR spectra for the isomerization of complex **W** complex

You can see here this conversion was monitored using phosphorus NMR. As I mentioned, phosphorus NMR comes very handy in characterizing the compound and also in understanding the reaction sequence. For example, your take here before the reaction started, we have two distinct chemical shifts for two phosphorus atoms which are very different, they are chemically and magnetically non-equivalent.

I shall tell you a little bit more about NMR, then you will understand these terms magnetically and chemically non-equivalent and all those things, if you have already studied it is very easy. So, once you add a metal immediately what happens, one of the phosphorus is coordinated that is shifted here, other one is uncoordinated, it does not change, very few ppm change is expected. And with the time what happens?

This one would start diminishing, here you can see this, the chemical shift due to uncoordinated is diminishing because simultaneously formation of this set has started here. At the end of 2 hours in case of molybdenum, everything is converted into bisphosphine from P-N coordination to P-P coordination. Same experiment was also carried out with tungsten compounds, whereas here it takes 72 hours.

You can see after 72 hours, we have these two. These two corresponds to both coordinated one, whereas here this corresponds to one coordinated that is shifted, another one is not shifted, it is still in the free ligand region that is for this one. So, that means you can see know how important phosphorus NMR in diagnosing the reaction sequence in coordination chemistry.

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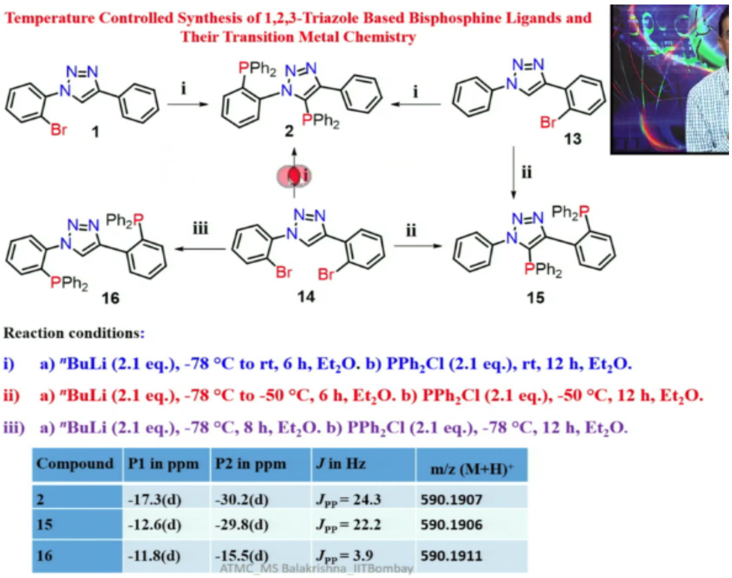

Temperature Controlled Synthesis of 1,2,3-Triazole Based Bisphosphine Ligands and Their Transition Metal Chemistry

Reaction conditions:

i) a) ^{n}BuLi (2.1 eq.), -78 °C to rt, 6 h, Et_2O. b) PPh_2Cl (2.1 eq.), rt, 12 h, Et_2O.

ii) a) ^{n}BuLi (2.1 eq.), -78 °C to -50 °C, 6 h, Et_2O. b) PPh_2Cl (2.1 eq.), -50 °C, 12 h, Et_2O.

iii) a) ^{n}BuLi (2.1 eq.), -78 °C, 8 h, Et_2O. b) PPh_2Cl (2.1 eq.), -78 °C, 12 h, Et_2O.

Compound	P1 in ppm	P2 in ppm	J in Hz	m/z $(M+H)^+$
2	-17.3(d)	-30.2(d)	J_{PP} = 24.3	590.1907
15	-12.6(d)	-29.8(d)	J_{PP} = 22.2	590.1906
16	-11.8(d)	-15.5(d)	J_{PP} = 3.9	590.1911

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And of course, as I mentioned since we know the strategy of performing reactions, we can conveniently carry out and make all kinds of phosphines here. And of course, temperature is very critical, you can see here at what temperature, what is added and what you get at the end. Go through these sequences of reactions to get to know about the synthetic strategies usually planned by people who design ligands.

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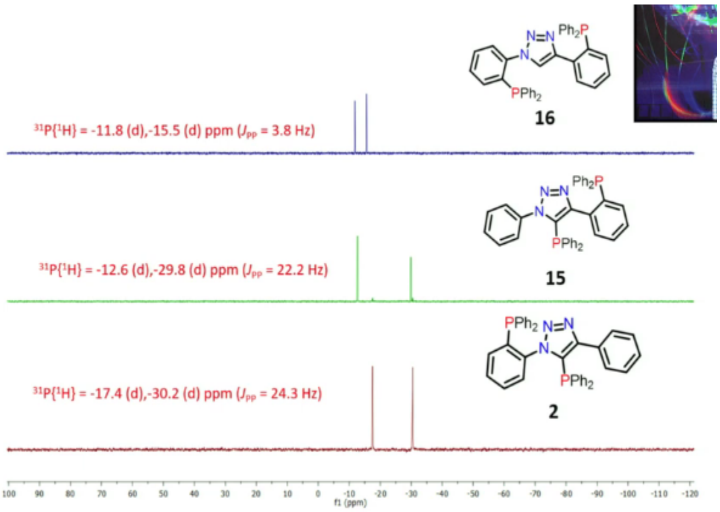

$^{31}P\{^1H\}$ spectra of bisphosphines (**2**, **15** and **16**)

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And again, when you perform this reaction, you never know which product is formed. But however, when you just look into the ^{31}P NMR, it can guide you, yes the nature of product that is formed in a particular reaction. Even if all these three are formed in a reaction in various proportions, again by looking into the intensity, you should be able to tell the percentage of formation of these compounds. I shall show you more interesting reactions that were monitored using phosphorus NMR, when I go to the interpretive part after completing all aspects of coordination chemistry.

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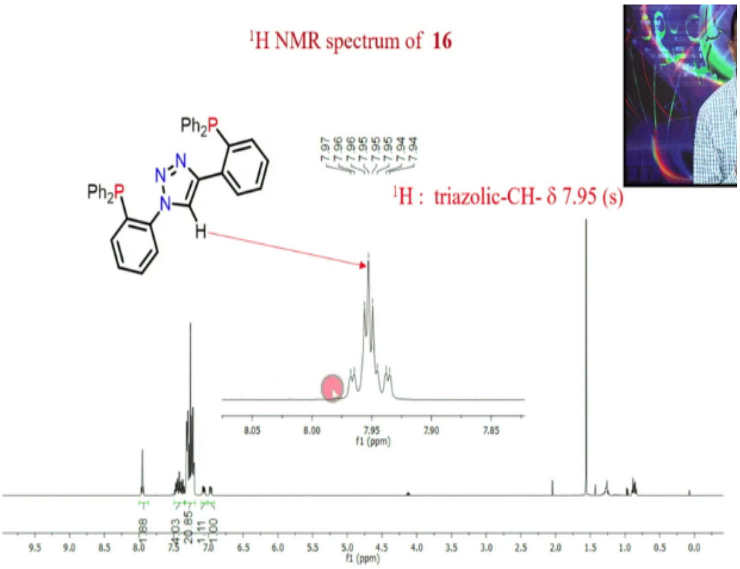

^{1}H NMR spectrum of **16**

^{1}H : triazolic-CH- δ 7.95 (s)

So, you can see here, this is a triazolic hydrogen coupled with two phosphorus atoms, as a result, it shows a triplet that can also be seen here. Also once if it is replaced and a metal comes here through CH activation, disappearance of this hydrogen can also be seen in ^{1}H NMR. So that concludes that yes, this hydrogen has been replaced and probably this ligand is acting as a tridentate ligand where we have a carbon to metal covalent bond.

And when we have carbon to metal covalent bond, the chemical shift of carbon in its ^{13}C NMR spectrum will also vary. So, that means NMR is an important tool in characterizing metal complexes or organometallic compounds we make.

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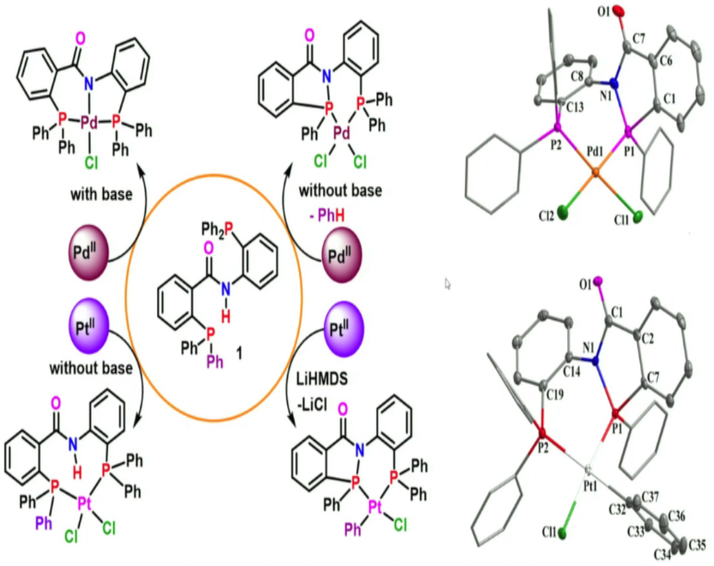

So, this is another interesting reaction. I was just telling you about phosphorus to carbon bond activation on a coordinated phosphine in my last lecture, so this one we observed in our own reaction. For example, this is a very interesting ligand prepared by one of my students and when it was treated with palladium and platinum you can see what happens. If you take this one and treat in presence of a base, forms a compound like this, pincer compound it is called.

Because N-H is there, H is gone, HCl is eliminated because we started with palladium chloride having some labile ligand such as COD, that is COD with base. And whereas in this case, even without base, it forms a compound and then with base usually this HCl is eliminated and you can see this ligand acting as a tridentate ligand. Another interesting feature of this ligand system is; this one you can see here, in this one without base when you add palladium(II) complex to this one, a P-C bond is broken here.

And P-C bond is broken, that phenyl fragment has abstracted H from N to come out as benzene, and then that resulted in the formation of a five membered azaphospholine ring and now phosphorus is still trivalent, this lone pair comes to palladium. So, now we have some sort of unsymmetrical phosphine, very rarely seen, probably this the first example we have reported. And then in this case, what happens this phenyl group comes out, it binds to the metal, very interesting.

Whether we can use this in alkylation arylation reaction, yes, there is an answer, still our group is working on to see whether we can see a catalytic reaction emerging out of it. One interesting thing is all compounds can be nicely crystallized and assessed while performing single crystal x-ray analysis, most of the complexes we make, we always try to crystallize and look into single crystal structure to understand the bonding features.

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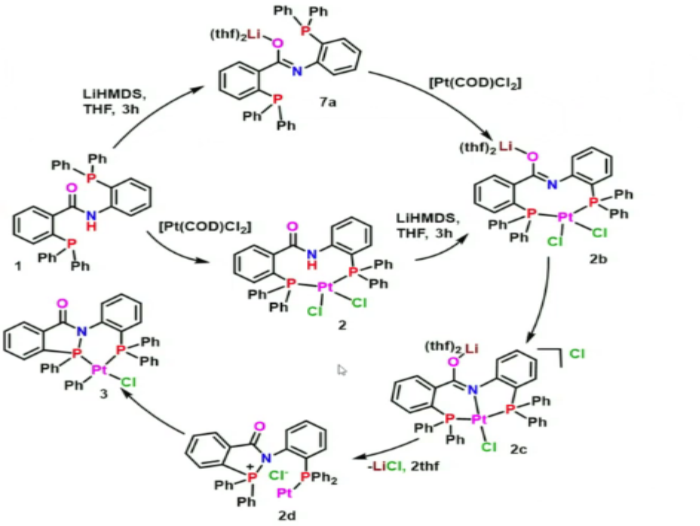

Kunchur, H. S.; Balakrishna, M. S. *Inorg. Chem.* **2021**, *00*, 0000.

And how the reactions were carried out systematically is shown through this reaction sequence here. Of course, I am not going to elaborate all those things, when you get time just look into it and try to understand how these intermediates have been formed and what is the reason. The another interesting thing is here, you can see now platinum is just a 12 electron species, platinum(0).

It is a 12 electron species formed as a transient species and then this phosphonium salt what happens, one of the phenyl groups is now added oxidatively to platinum to form this kind of compound here and then Pt—Cl bond is established here. So, now it comes back from platinum(0) to platinum(II), some sort of oxidative addition. Of course, I shall elaborate more about oxidative addition after the completion of this topic I am discussing at present.

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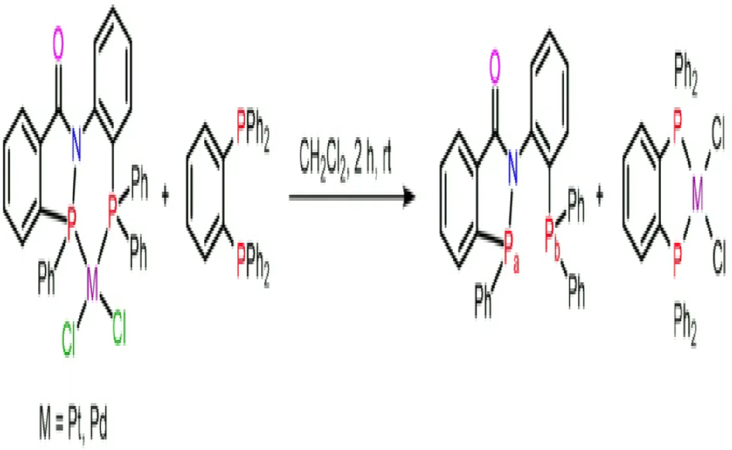

Once after making this one, initially we did not have this kind of ligand, N-H was there and we have PPh_2, but during this time azaphospholine ring formation took place, whether we can get free ligand that is the next step, of course one can do it by treating with bis(diphenyl phosphino)benzene. This has more affinity to palladium to chelate. As a result, this is chelated and this was freed from the metal. This is some sort of electrophilic substitution, you can see this ligand is free. So, that means a very interesting chemistry one can carry out with phosphine ligands.

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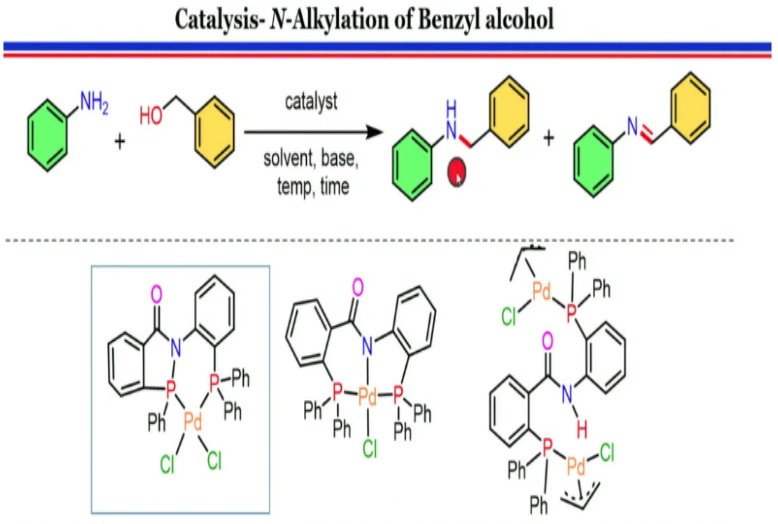
Catalysis- *N*-Alkylation of Benzyl alcohol

And why we make? As I mentioned we are using several catalytic reactions, once such reaction I have shown here, this is called N-alkylation of benzyl alcohol. Here, these three compounds were used. We found this compound is much more superior in terms of its catalytic activity in forming both of these compounds and initially both the compounds are formed and then again this H can go as H_2 and then that can also give this one. That means, we can control the formation of either this one or this one by changing the reaction conditions.

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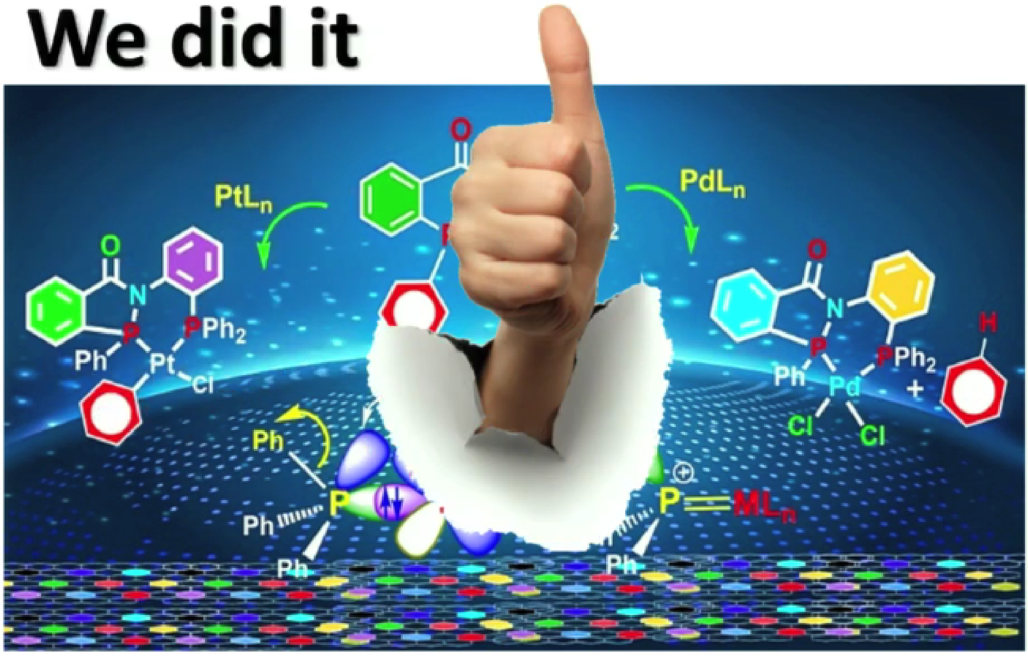

We did it

H. S. Kunchur, L. Radhakrishna, M. K. Pandey, M. S. Balakrishna, *Chem. Commun.* **2021**, 57, 4835-4838.
Kunchur, M. S. Balakrishna, *Inorg. Chem.* **2022**, 61, 857-868.

And this is a consolidation I have shown. This is very interesting result. One is breaking of P-C bond and then formation of this P-N bond. In fact, P-N bond is much more reactive, but however P-C bond is less reactive and more stable, but it is against that one. So, P-C bond is broken and less stable P-N bond is formed. So, always unusual and interesting chemistry emerges that you can see here.

That means R can be taken out and then whatever the R^- comes out as carbanion, it binds to the metal, migration takes place, so very interesting result this is. With this, we shall move on to classification of ligands by donor atoms, so now we shall move on to halogen-based ligands. So, far we completed and this is the last ligand series, the halogens, group 16 elements.

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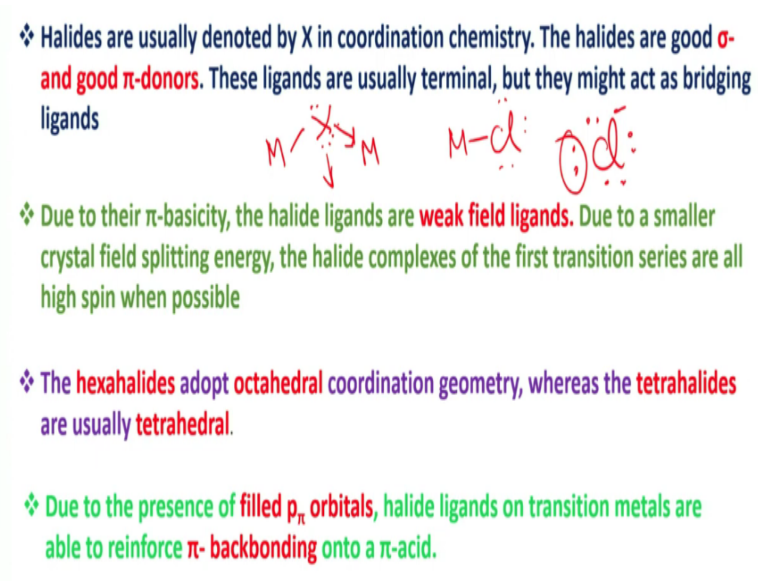

- Halides are usually denoted by X in coordination chemistry. The halides are good σ- and good π-donors. These ligands are usually terminal, but they might act as bridging ligands

- Due to their π-basicity, the halide ligands are **weak field ligands.** Due to a smaller crystal field splitting energy, the halide complexes of the first transition series are all high spin when possible
- The **hexahalides** adopt **octahedral** coordination geometry, whereas the **tetrahalides** are usually **tetrahedral**.
- Due to the presence of **filled p_{π} orbitals**, halide ligands on transition metals are able to reinforce **π- backbonding** onto a π-acid.

So, when we talk about group 16 elements, usually they are denoted by term X in coordination chemistry. And we know that halides are very good sigma donors and very good pi donors because they have low energy field sigma orbitals and low energy field pi orbitals. When they interact with the metal, especially when the metals are there in high valence state, metals are electron deficient.

In that case what happens these ligands not only perform as sigma donors, they can also perform as pi donors because pi orbitals on metals are empty and they can readily pass on electrons from halogens to metal orbitals. So, these ligands are usually terminal, but often they can act as bridging ligands. When they act as bridging ligands, they can bridge two metal centres, they can bridge three metal centres. Interestingly, they can also bridge four metal centres.

We have several examples in our own laboratory, I shall show you later. Due to their pi basicity, the halide ligands are weak field ligands. Of course, when you look into spectrochemical series, you know where these halides stand among rest of the ligands. If you just look into spectrochemical series, it can be broadly classified into again three categories. In the beginning what we have is pure sigma donor and pi donor ligands.

And later we have only sigma donor ligands, at the end were strong field ligands, sigma donor and pi acceptor ligands. Due to a small crystal field splitting energy, I have shown clearly in the MO diagram how that crystal field splitting energy decreases, shrinks when we have halogens because of their donor properties. And as a result, what happens halide complexes are very labile.

In most of the reactions, we use anhydrous halogen complexes for performing substitution reaction to generate other coordination compounds and also organometallic compounds. Most of the halide complexes are high spin complexes. Hexahalides, that means homoleptic halides are also known with most of the metals and when you have 6 halogen atoms or 6 halides are there, they adopt preferably octahedral geometry.

Whereas for coordination they prefer tetrahedral geometries, but in some cases especially with the platinum metals, they still form square planar complexes. And due to the presence of filled pπ-orbitals, halide ligand on transition metals are able to reinforce pi back bonding onto pi acid. That means those metals which are oxophilic and oxohallic, we call them especially early metals in their high valence state, high oxidation state, they are electron deficient.

In that case what happens, metals conveniently drift electrons from halogens. Of course, if you take any halogen, for example if Cl^- we know that we have 8 electrons, and out of 8 electrons, two electrons go for making a covalent bond, still we are left with, strictly speaking still it can coordinate all lone pairs, but most common ones are something like this. Just I have taken chloride, it can also be in general it can also be X so that any halide, so this is the one.

Now, basically if this is covalent bond, you should remember this is a coordinate bond, this lone pair is coming. If another is there, this can also come like this. Always if it is triple A bridging, one is called covalent bond, other two are coordinate bonds. So let me stop at this and may be continue discussing more interesting chemistry of halogens in my next lecture. Until then have an excellent time.