Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

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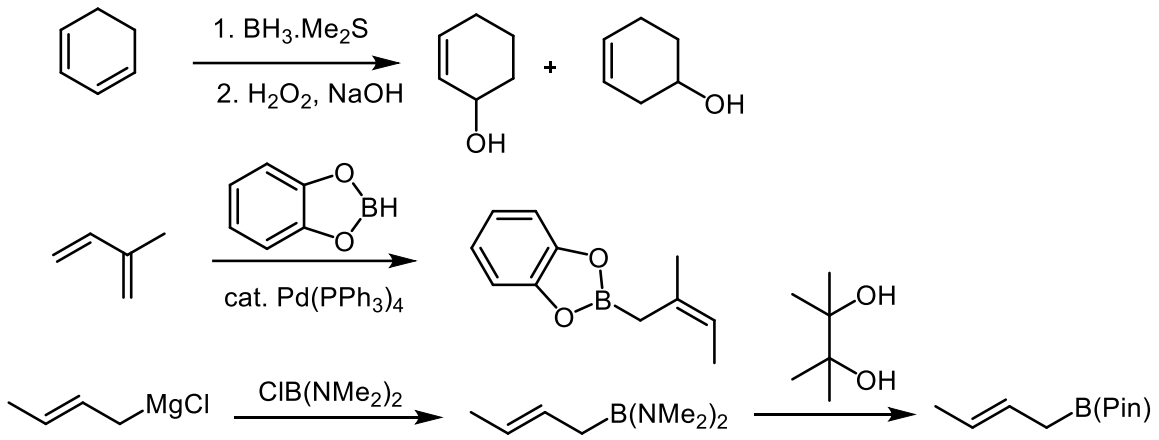
Lecture 45: Organoboron

Welcome back to this NPTEL online certification course in molecular arrangement and in reactive intermediates. In the last couple of classes, I was talking about organoboron chemistry. So, I started about different reaction of organoboron compounds, I talk about hydroboration reactions then you have seen about the hydroboration oxidation and then you have seen different type of chemistry asymmetric hydroboration and then selective hydroboration. In the today's class I learned one of the important things. I have covered if you must go back and go through that lecture which reducing agent like boron based reducing agent like sodium borohydride, zinc borohydride. So, these are all already discussed.

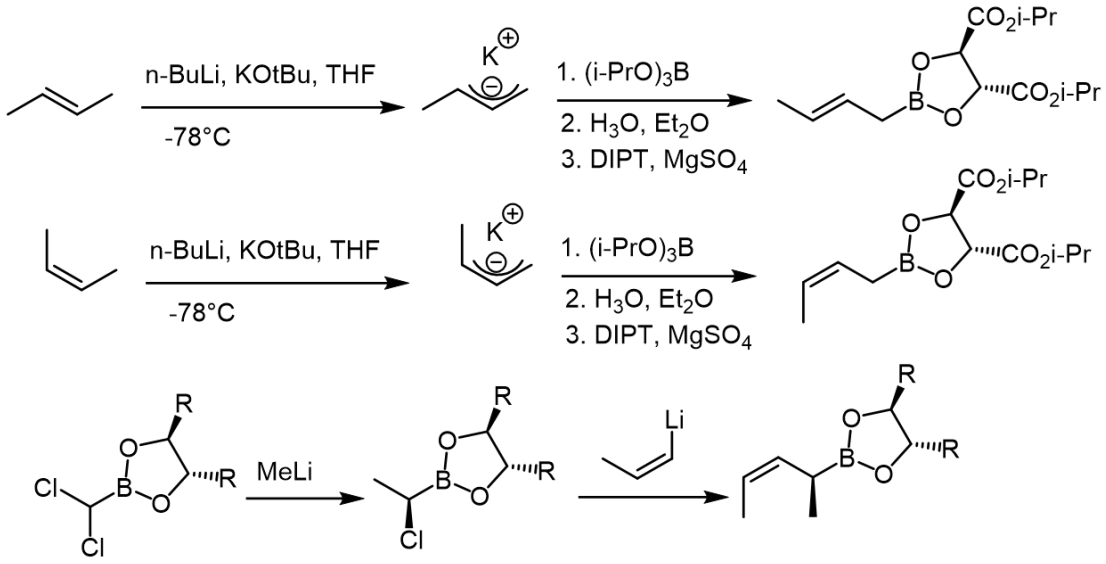
In the today's class my plan is to come back and talk about another very important chemistry is the allyl boron chemistry and then talk about the Suzuki coupling and some other important reaction using organoboron agent. So, let us start with the allyl boron chemistry. So, first I will talk about the allyl boron agents and then I will talk about the Suzuki coupling, as I mentioned chan Lam coupling, then the Boron-Wittig reactions. and then some of the conversion of organoboron compounds to other functional group. So, let us start with the allyl boron chemistry. So, if I talk about the allyl boron chemistry before that you have to understand the hydroboration. So, you have already seen that if you have a single double bond then after the hydroboration you can introduce the boron there and then you can able to do the oxidation using H_2O to NaOH. and then go to the corresponding alcohol but now if you have a scenario like a cyclohexadiene you have a two olefin here now if one of the double bond going to convert to the organoboron compounds and then you can able to oxidize to the corresponding alcohol you end up getting to the allylic alcohol but the important thing to understand that when you are doing the hydroboration in this compound where you are going to convert to the corresponding alcohol. what is happening here you can see you have a double bond here and you have done a hydroboration here correct once you have done a hydroboration here you have two different double bonds here now if you are doing a selectively one of this hydroboration ok then what is going to happen you can end up introducing a boron here

so that can if the boron is adding in this position then what is going to happen it can end up giving you a species where you have a boron here of course, this will be trialkyl.

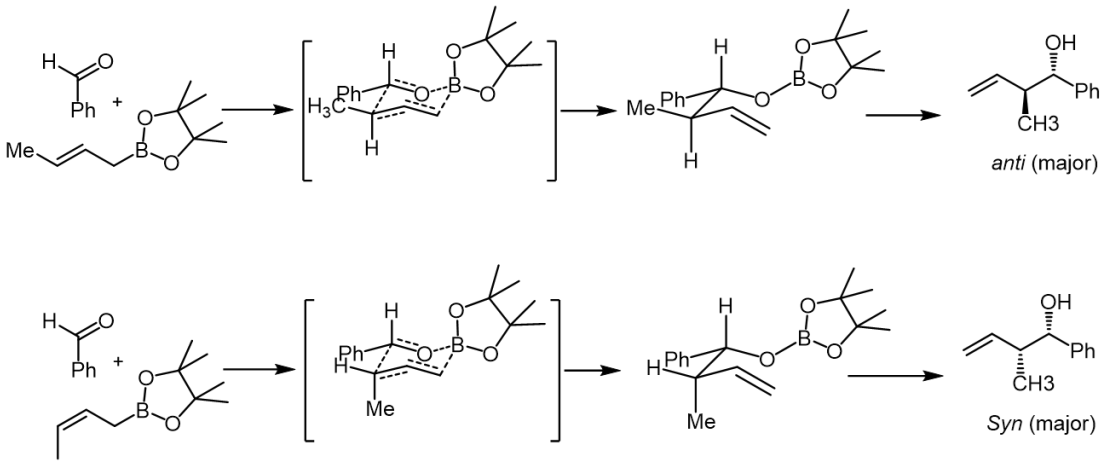


So, you can add up thinking about that you are making this compound ok after the hydroboration because here you have a H here you have a boron and then you will be ending up making this compound correct. Now, if you think about this is a functional group where you have a allyl group here and you have a boron here. So, this is called a allyl boron compound ok. So, it is actually forming a allyl boron compound as a intermediate at the after the hydroboration and then once you oxidize using H_2O to NaOH it is given to the corresponding allylic alcohol. Now you can we can make so there are different type of allyl boron compound. So, let me try to write in about them if you have to know about allyl bromide correct. Now we are talking about allyl boron. So, here you have a boron now it could be a different type of protecting group it you could have just $(-OMe)_2$ dimethoxy or it could be a pinacol boron that means you have a pinacol as a protecting group So, you can see these are the compound called allyl boron compounds. You can see these are esters of boronic ester ok. Now, you have another class of compounds where you can have a methyl group here. So, instead of finishing here in the terminal poison if you have then these are called crotyl boron compounds ok. So, now you can see that you are going to come to in a minute that once you have this substitution like here methyl or any other group here that can also allow you to generate another extra stereocenter here ok. Now before I go to the reaction, I am going to talk about some of the synthesis how do you make them suppose you have this dye in here now what is going to happen this if you see here one is here is this if you try to compare these two one then here this is a disubstituted one here this is a monosubstituted one. So, after the hydroboration using palladium catalyst using catechol borane you can able to do

hydroboration selectively here and then the there will be isomerization as well you will be end up making this compound ok. So, again you can see if you think about this particular type of a allyl boron region you can see.



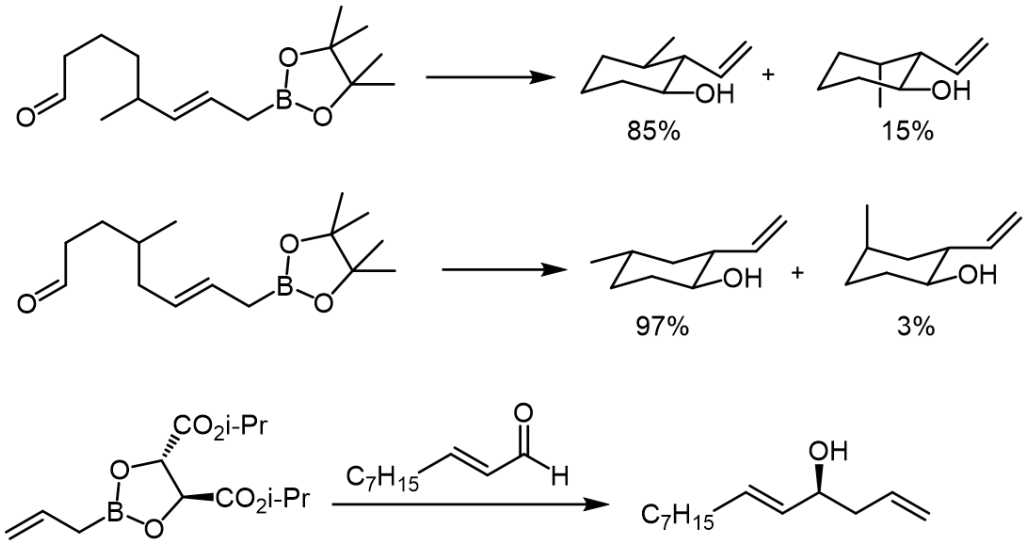
So, this will be if you give them name as 1, then it will be a 2 methyl-butanyl boron compounds. Again if you have this type of Grignard agent that could be this one or if you have start from allyl bromide and put some magnesium here that can also generate you allyl Grignard all these reagent once you treat with this reagent that can generate these compounds where it will be eliminating Cl. Now, if you put a protecting group like a pinnacle that can remove this the dimethylamine and able to make this corresponding crotyl boronic esters. There are several other methods also developed. You can see using a very strong base, using N-butyllithium and potassium tert-butoxide, you can able to take this allylic proton, you can after this allylic proton here, and you can generate this allylic anion, which can react with this- try iso-propoxide boron compound which can remove one of this iso-propoxide group and then what is going to happen once you treat with the H_3O plus there it can convert to the boronic acid. Now you can use a chiral diol ok. So, you can see here this will be a isopropyl group here. So, it is a di-isopropyl you can use this one to do a protection. So, now, you are generating a crotyl boron compound. So, this will be a E crotyl boron compound, where you have a chiral diol here.



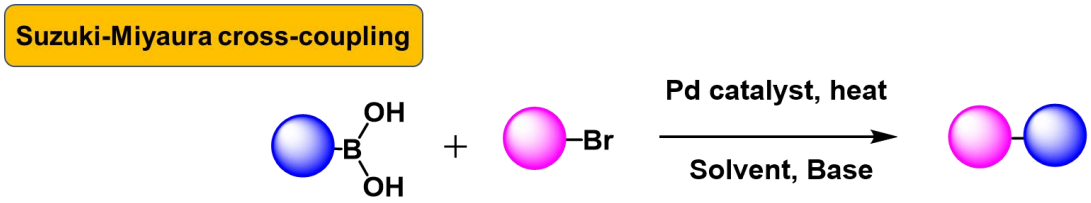
You can also able to make the corresponding Z here, where you can start with the corresponding Z olefin of this. So, you have this olefin you started from which is Z now you treat with the again N-butyl lithium potassium tert-butoxide this stronger base can abstract this allylic proton and then this negative charge can again you have you are generating this anionic species which can react with this isobutoxide boron compound and then you treat with H_3O plus and again you do it you need a production of this boronic acid to get to the boron ester now you are generating a chiral Z-cortyl boron ester. there is other methods you can use a very important reaction here called the medicine homologation what is happening here if you start from this alpha dichloro boronic esters react with methyl lithium then what is going to happen the methyl lithium react with this boron to make this. now there will be a 1,2 migration going to happen to get rid of this corresponding Cl species to generate this corresponding alpha chloro and now as you have this chiral center here I am going to come back to talk about this reaction about this medicine in homologation reaction how this chirality is getting control I am going to talk about in all of this but once you get to this alpha chloro species now once you have this vinyl lithium if you can take this vinyl lithium and add here you can now understand the vinyl lithium which is very similarly going to add here ok and then it is going to transfer a there will be 1,2 shift going to happen now it will be B minus it will go for a 1,2 shift to get it of chlorine to form this corresponding product. So you have a 2 methyl again a crotyl species, but you have a 2 methyl So, now we have learned about different type of allyl and crotyl boron compounds now what are the different reaction we can use them. One of the reaction is you can take the allyl boron compound you can take aldehyde it can react them to form this corresponding product here.

Now the question comes how you are able to control this stereochemistry here because you can see we are getting a anti product here measure once we start from this E-crotyl

boron compounds we get the anti as a major and once we start from the Z-crotyl boron compounds we got syn product as a major product ok. Now, we are trying to understand how this how this type of allyl boron compound is reacting. So, one of the important reactive parameter about this type of allyl boron species. That once you take the boronic ester or the the the methoxy boron compound as soon as you put a Lewis base can give a lone pair of electron or give some electron density or if you can have a base which can give electron density here. Suppose you can I can consider as a B which can give a electron density here making a minus once you make this minus this become a labile. So, it can now for react with a electrophile. So, that is how the the allyl group can be transferred. So, here what is happening your oxygen will have the lone pair which can be given to the corresponding the boronic ester. So, once this lone pair is given to the boronic ester through this 6 member transition state it is going to give it to the corresponding product. Now if you look into the 6 member transition state one of the important thing once you are trying to draw it you have to understand this is a E geometry. So, your methyl and this will be trans which is can you can see which is drawn here. and then this oxygen going to coordinate with the boron this is a very important because that is how the boron is getting activated for this allylation to be take place and once it is happening this bond is so there is a formation of a double bond here because and then you can see this bond is getting broken so this bond is going to form and again this carbon oxygen development is getting broken. So, that is how you are end up generating this compound here finally, this oxygen boron bond is going to get cleaved and that is going to form the corresponding product here. And you can see here in if you see your methyl and your oxygen is actually in the anti. So, that is how it is forming this product, but once you short form Z then you can see in the corresponding tangent state we have to draw the methyl down because the methyl will be in the axial position because that can able to now you can that can allow to draw the corresponding tangent state because now this is a Z conformation here and again you have this the carbonyl group here where the oxygen is coordinating with the boron.



So, again this very similar thing going to happen there will be new bond going to form this bond going to break and going to form this product. Now, if you see here your methyl is also down and your oxygen is this bond with the oxygen and between this bond is also down after the cleaving of the burning ester you can get to the corresponding product and this methyl and the oxygen will be in the same side. So, going to the corresponding syn product. Again there are several other reactions of this allyl boron compound it can react with a imine and you will find you know in a very similar reactivity where your nitrogen at the time will have a lone pair that can give it to the



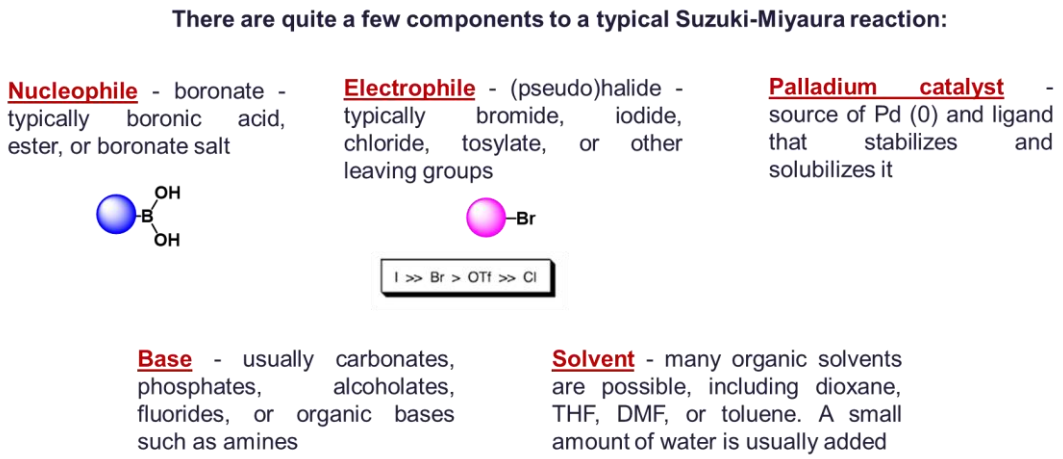
Suzuki-Miyaura cross-coupling is palladium catalyzed reaction. During the reaction, the carbon skelets of nucleophile and electrophile are coupled together, creating a new C-C bond.

Its development originated in the 1980s by Akira Suzuki, and in 2010 he was awarded the Nobel Prize in chemistry

boron and very similarly this allyl group will be transferred to the corresponding imine to generate the corresponding amines. this type of reaction could be intramolecular correct this reaction with this the aldehyde and this allyl boron species so you have allyl boron species reactive species you have aldehyde so again once this oxygen going to so once they are going to coordinate they are going to react and going to form the corresponding product now if you look into the product you can clearly understand how this is forming you must have aldehyde here and that is how this is getting attacked. and you can clearly understand this methyl group will be in the equatorial position not in the axial position because that will be generating the steric. So, that will be higher energy transition state. So, the reaction will follow the lower energy transition state to giving this product as a major product and this will be your minor product.

Again if you come to this example here if you see the changes happen here previously this methyl group is the in the next carbon of this double bond now you moved in one more carbon If you do that that is still the still the in reaction will be similar this allyl

boron species is going to react with your aldehyde and in the transition state also you can see this methyl is going to be in the equatorial position not in the axial position because even the axial position this will go through a higher energy transition state going to give the so that will be the only 3% your major fluid will form where the methyl will be in the equatorial position. and now if you use this reaction with a aldehyde because now you have a this chiral entity here what is the point of putting this chiral group here because

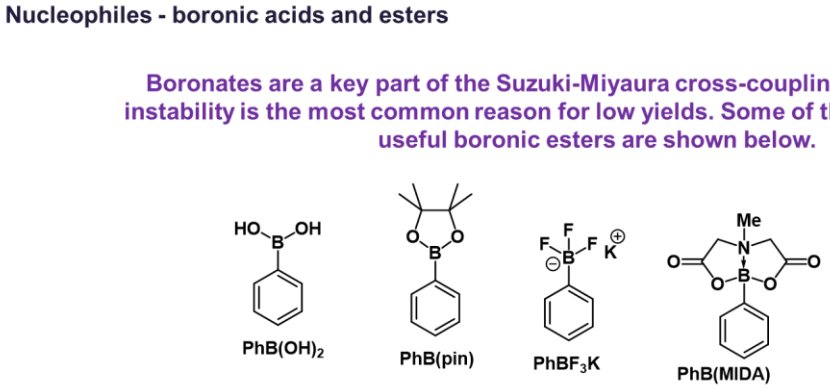


once you have this chiral group here this can control the enantioselectivity of this new stereocenter ok so now using this you can able to achieve up to 87 percent of enantioselectivity once you react this allyl bond species with the aldehyde so that is all about this allyl boron compounds again if someone wants to know about more about allyl boron compound there are some references given you can go through them i am moving to the Suzuki-Miyaura cross coupling reaction so this is a very important cross coupling reaction it actually change the way we think about how to make the bi-aryl systems so this reaction was discovered in 1980s by professor Akira Suzuki so he was in awarded in Nobel prize in chemistry. so if you look into the reaction this is a reaction of a aryl boronic acid so if you think at the beginning you can say these are and you can see these are aryl bromide let us think about that way or it could be a vinyl so aryl or vinyl ok so in those boronic acid or the organoboron compound it is not always has to be a boronic acid it could be a boronic ester also and if you use a aryl bromide or different type of oxidating addition partner. In case of palladium catalyst heat and solvent and base it can able to form the corresponding bi aryl if both of they are aryl.

If it is a vinyl then it can make a substituted vinyl compound. So, let us try to understand the different component of this reaction. One thing is nucleophile. So, there is a nucleophilic coupling partner and there is a electrophilic coupling partner. The nucleophilic coupling partner is your organoboron compound, it could be a boronate or a boronic acid, boronic ester or a boronate salt. In case of electrophile as I said it could be

aryl bromide. So, you have aryl group now it could be a bromo, iodo, chloro, it could be -OTs, it could be -OTf. So, there are lot of other groups. which can participate in oxidative addition in the presence of palladium catalyst and then of course you need a palladium(0) catalyst of course and then the ligand which can stabilize this palladium catalyst then base has a very important role I am going to show you in the mechanism so usually the carbonate phosphate or different alkoxide the Cesium fluoride or could be organic base used for this reaction Of course various different solvents are known, but usually you will see the dioxane, THF, DMF and toluene the very common solvent for this coupling. And you will always find there will be small amount of water usually needed for this reaction ok.

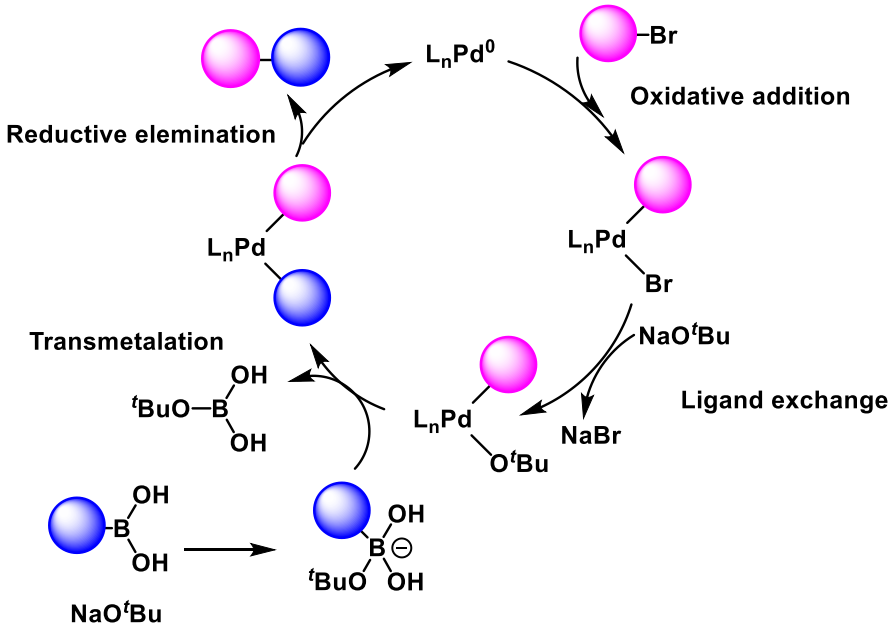
You can add some water and I am going to explain why you have to add water for some of the cases. and then if you talk about the boronic component just now I said you can use the boronic ester the boronic acid the thing is there are different type of the protecting group for the boron it could be simple boronic acid could be a boronic esters or could be the salt this is a tri-fluoro boron salt. or could be a meda boron compound if you think about this meda boron compounds one of the important thing is this nitrogen is giving electron density. So, this can stabilize this boronic acid much more compared to boronic acid. so why this type of MIDA boronic ester protecting groups was developed because lot of the times if you have a hetero atom like if you have a pyridine or if you have indole or if you have a different type of heterocyclic boronic acid those are not stable in the cross coupling reaction there they can decompose so stop the decomposition the different different protecting group was developed and MIDA protecting group is one of the best of them. because what is going to happen if you use this type of protecting group and a base the MIDA protection can be slowly deprotected and from the boronic acid in the



reaction, but the process will be slower. So, throughout your reaction you do not have a higher concentration of boronic acid. So, that is why the amount of boronic acid which going to form is going to participate in the cross coupling to get to the corresponding product.

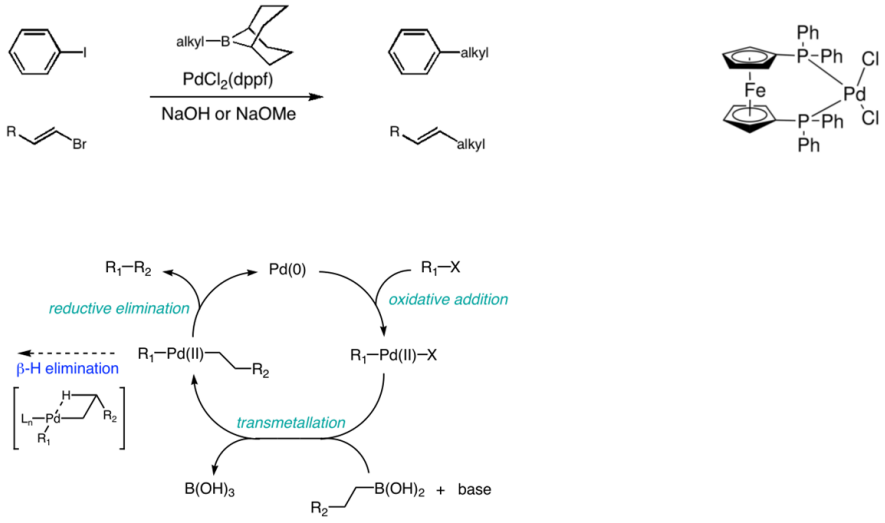
So now we will try to understand the mechanism of this reaction of course as I mentioned you have palladium(0) catalyst of course the palladium (0) can be formed in the different ways if you go through organometallic chemistry book I think you will be able to find them. Now once you have a palladium (0) it can participate the reaction called oxidative addition because here the oxidation state of palladium is becoming 2 from palladium 0. So, there is a addition and there is a oxidation together we can tell them oxidative addition. So, palladium is becoming here, after the oxidative addition this aryl group is here, the bromo is here. Now, you have to go for a ligand exchange what is going to happen the bromo will be exchange if you have this base and then still you keeping the palladium 2 and then the most important step going to happen called transmetalation.

So, what is happening in the transmetalation step if you using a boronic acid. If you are using boronic acid lot of the times people use some water and some base like a potassium



hydroxide what is going to happen that can generate this OH minus can attack on the

boron can make this boronate species. So, you are generating this boronate species. So, once you generate them now this R group can are eligible for because once you generate the boron species the bond between this aryl group and the boron become weaker. So, now this aryl group can participate in a transmetalation reaction to get to this sort of intermediate from there after reductive elimination you will be able to get to the corresponding bi-aryl. I hope you understand this the mechanism of the Suzuki coupling.



Now the question comes that is it this reaction only work with aryl boron compounds or the reaction also going to work with alkyl boron compounds. Of course, it was later on developed that yes the alkyl boron compound also can take part. So 9 BBN compounds can be used. So that can also synthesize from the hydroboration from the olefin using the 9 BBNH. So that compound can react with a aryl halide or with a vinyl bromide or vinyl halide in place of palladium catalyst, but there is a important you can see in this palladium catalyst you have to use a bidentate ligands. So, this bidentate ligand has a very important role in this reaction. because in this when use a alkyl boron compounds for this cross coupling the major problem was not this step not the oxidative addition because oxidative addition is still fine because you are using the aryl iodide or vinyl iodide or vinyl bromides and then the problem i think the transmetalation is still ok but the problem was after this step the reductive elimination. After that the beta hydride elimination is a very common problem and that is how you are not able to get to this

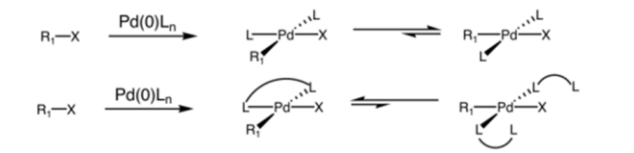
corresponding that the desired product, but instead of that you can end up forming corresponding styrene. So, to stop that this type of bident and ligand plays an important role to stop the beta hydride elimination to get to the corresponding product.

As you can see the competition experiments when also explain that the order of the reaction the iodo reacting the oxidative addition going to be faster compared to bromo, triflate and of course, compared to chloro and that also depends on the bond dissociation energy of these bonds. Then again the bidental ligands keep a cis complex ok. So, that make a huge factor of facilitating the reactive elimination and preventing the beta hydro elimination. So that means after this step the so the bidental ligands which play very important role to make sure that make a cis complex here with the palladium correct once you have a bidental ligand you are forming this cis complex correct. So once you have this cis complex formation happen that can allow once you have this cis complex happen

Competition experiments determines the order of reactivity of Oxidative addition.

I >> Br > OTf >> Cl

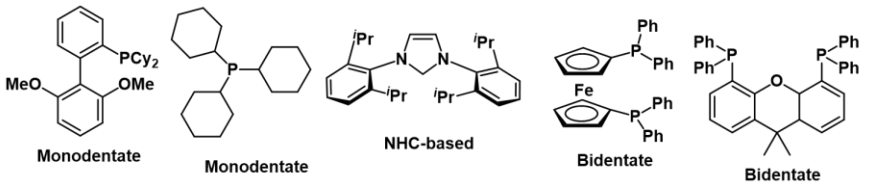
Bidentate Ligands keep a cis Complex (also a huge factor in facilitating reductive elimination and thus preventing of Beta-H-elimination of Alkyl-M Complexes).



so that can facilitate the corresponding reductive elimination once you after the transmetalation step instead of the beta hydrate elimination. You can see there are several different type of bidental ligand was developed. You can see different class of ligands here. There are also a NHC based ligands are developed also they are sterically hindered. So, the palladium cannot take part this side reaction which can also the stabilize the palladium catalyst. Also there are monodentate ligand which was developed by the Buchwald group these are also very useful ligand for the palladium catalysis.

Common ligands and their properties

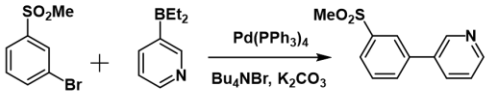
Palladium ligands are a key component in most cross-coupling reactions. They fulfil many roles, including solubilizing and stabilizing the Pd(0) species, preventing the formation of palladium black, and modulating the electronic and steric properties of the reactive palladium center.



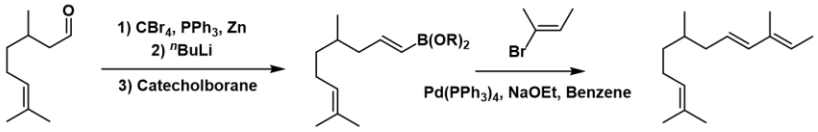
These are very reactive catalysis and then also you have seen some ligands were using a bulky phosphine it could be a phosphorus also this tertbutyl ok. So, this type of different ligand also used for this cross coupling reaction ok. Now, I am going to show some of the application of this Suzuki-Miyaura cross coupling reaction this is done in a industry for synthesis of different type of marketed drugs and a bioactive compound you can see this reaction was done in 278 kilograms just look into this number. if you see in a lot of this blockbuster drug synthesis you will find the suzuki coupling is used. You can see here using this palladium catalyst and you can able to couple these two where you have this aryl bromide and you have this organoboron compounds which is in this heterocyclic ring can able to get to this corresponding product corresponding by aryl product ok.

Applications **This reaction has a wide application for the bioactive molecule synthesis and various APIs.**

The coupling of 3-pyridylborane and 1-bromo-3-(methylsulfonyl)benzene that formed an intermediate that was used in the synthesis of a potential central nervous system agent.
The coupling reaction to form the intermediate produced 278 kilograms in a 92.5% yield

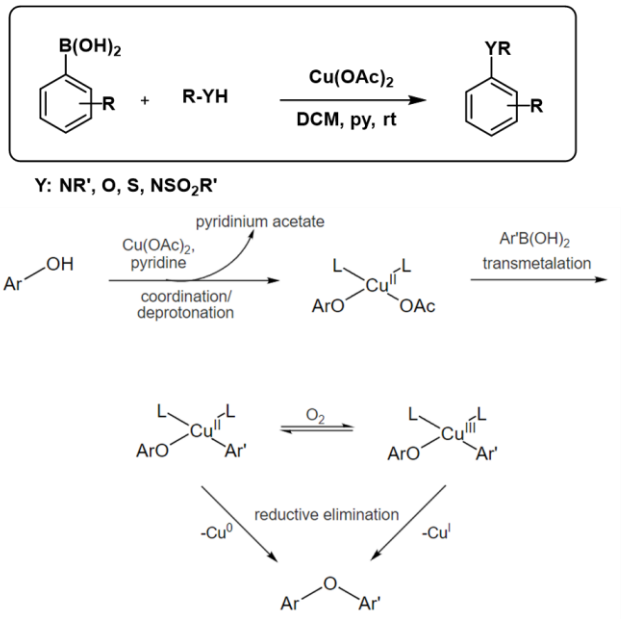


The Suzuki coupling has been used on a citronellal derivative for the synthesis of caparratriene, a natural product that is highly active against leukemia



There is another application here the suzuki coupling also used for the the the citronellal derivative synthesis for a you can see here also which is a natural product which is highly active against the leukemia. So, for synthesis of very important compound we also use a suzuki coupling here because once you have synthesized this vinyl boron compounds starting from this corresponding aldehyde now you can have this vinyl bromide it can take part in the suzuki coupling to get to this corresponding product.

So, the other important reactions I already talk about suzuki coupling the other important reaction using a transition metal catalyst and organoboron reagent is a Chan-Lam coupling. So this is a very important reaction because you can see in a lot of the marketed drugs you will find have amine functional group. So this reaction can allow you to take a amine, if you take a secondary amine here and if you react with a organoboron compound, a boronic acid, you will be able to end up making to the corresponding, so here you can introduce, you can make an aniline derivatives.



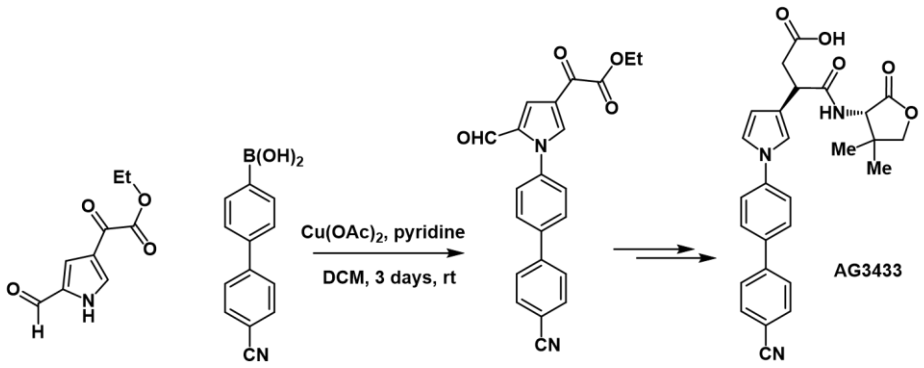
The **Chan–Lam coupling** reaction – also known as the **Chan–Evans–Lam coupling** is a cross-coupling reaction between an aryl boronic acid and an alcohol or an amine to form the corresponding secondary aryl amines or aryl ethers, respectively

If you start with a a phenol instead of this amine if you start with a phenol or alcohol you can also able to get to this corresponding product here. So, this boronic acid this aryl group will be transferred from the boron to this corresponding alcohol or corresponding amine. So, you can see here this is the alcohol or amine to form the corresponding secondary amine or secondary aryl ether. So, you can also use the primary amine and alcohol as well. So, what is happening here if you start with this phenol let us think about if you started with phenol and the and the aryl boronic acid what is this reaction.

So, still if you find in the literature there are lot of publication coming on the Chan-Lam coupling. So, if you see copper acetate, pyridine is acting as a ligand here with the copper. and then it is going to form this species here you can see these two ligands so first is the complex formation with the copper now the important thing is transmetalation with the aryl boronic acid so that is actually bringing you to in this species here this copper 2 species. Now there is two possibility it can go for a reactive elimination forming a copper (0) get to the corresponding product or it can oxidize to copper (3) from there it

can go for a reactive elimination to generate a copper (1) species and it can go back to the catalytic cycle again.

An example of the Chan–Lam coupling to synthesize biologically active compounds

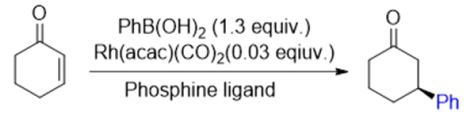


Again the Chan-lam coupling again used for the synthesis of biologically important compounds biologically active compounds here you have this boronic acid. And you can see you have this pyrrole, so you can understand this can allow the cross coupling between this pyrrole NH and the boronic acid using copper acetate very simple reagent and pyridine. In the DCM in 3 days in the room temperature you can able to get to this product which can convert to this bioactive compound. So, the other reactions is important reaction using this organoboron compound and transition metal.

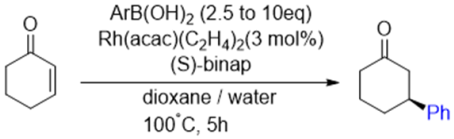
So, now I think we talk about the palladium which is the suzuki coupling, the copper I talk about the Chan-Lam coupling, now I come to another important transition metal called rhodium. So, if you use the phenyl boronic acid in place of rhodium catalyst using a phosphine ligand you can end up doing a 1,4 addition of this aryl group here. So, you have learned about this 1,4 addition chemistry correct. I am sure you guys have gone to I think I have already gone through organocopper chemistry, the Gilman reagent you have seen that Me_2CuLi I think I you have seen that you can able to put this methyl group here correct. And then if you remember I also talk about that you can also make this center chiral if you use a chiral ligand. at the time and so now what I am talking here in so there is a problem in that reaction it will be difficult for you to introduce a aryl group here. So, but in this method we can use a aryl boroninc acid so you can see this is a very complementary method here you are using aryl boroninc acid here and now this can allow you to introduce the aryl group one for addition product.

So now the question come as you are generating a stereocenter here with rhodium catalyst if you use a chiral ligand which can bind with the rhodium catalyst then you can able to control the stereochemistry of this to get to a particular enantiomers. So here you can see by using this rhodium catalyst so in place of the rhodium catalyst and the boronic

a) *Miyaura* (1998):

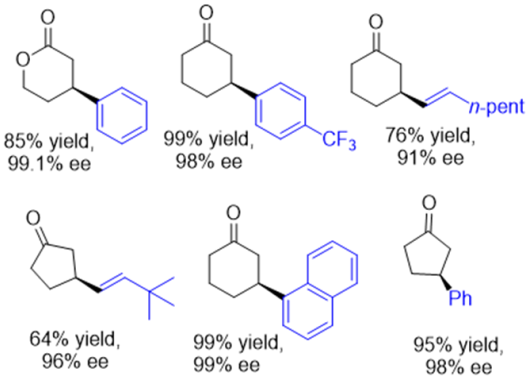


b) *Miyaura* (2002):



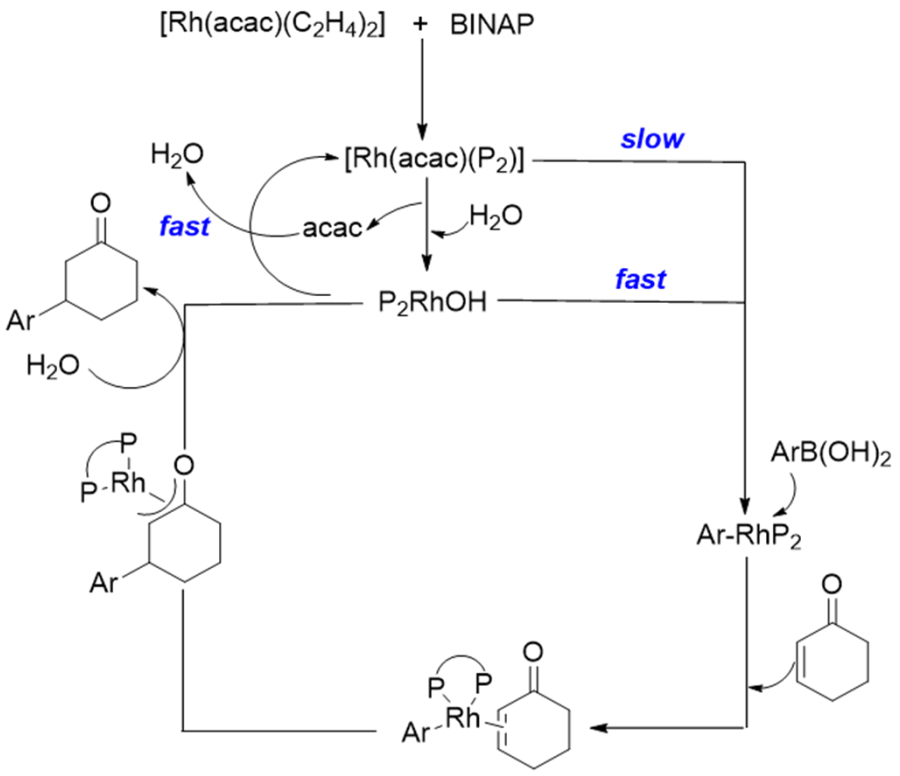
Entry	Rh complex	$PhB(OH)_2$	yield	ee
1	$[Rh(acac)(CO)_2)]$	1.4	15	43
2	$[Rh(acac)(C_2H_4)_2]$	1.4	64	97
3	$[Rh(acac)(C_2H_4)_2]$	2.5	93	97
4	[Rh(acac)(S)-BINAP	1.4	64	97

Substrate scope



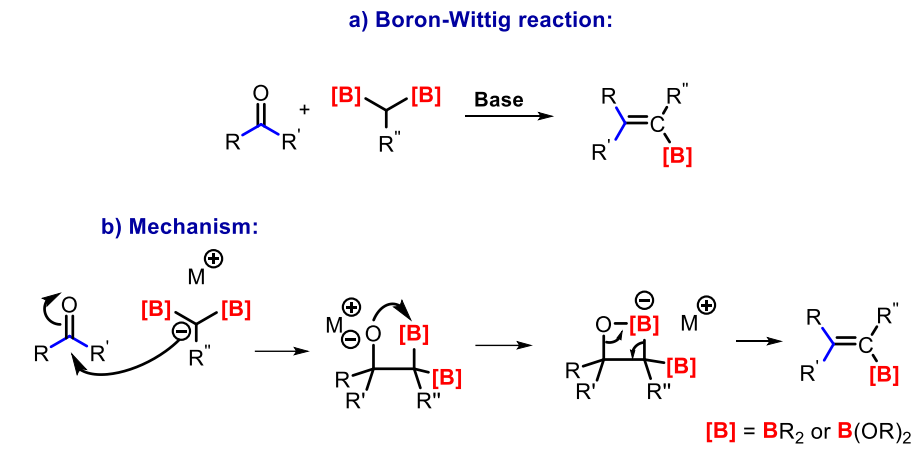
acid makes a important role using a 2.5 equivalent of boronic acid you can able to get to 93 % yield and 97% of ee. So, here you can see the BINAP was used as a catalyst with the rhodium. So, you can see this so rhodium actually forms some sort of bidentate because you have the phosphorus here in the BINAP which can forms a bidentate complex with the rhodium. So, I am not drawing the the entire BINAP here, but here you can have the other ligand where here you have a check all these other ligands can be bound here which can allow the substrate to come in and participate in the reaction. You can see different type of substrates can take part and they are giving very good yield and very good ee in every single cases ok.

So, now what you are going to see we are going to try to understand the mechanism of this reaction how this reaction mechanism is going on. So, in place of the rhodium this complex BINAP first forms a complex with the BINAP. As I said the BINAP the two of this phosphine can chelate with this rhodium but now there is important thing once you have use a water in the reaction that can also form this rhodium hydroxyl species here. or if it can start the reaction from this species I think this will be so from the kinetic data where the high acid group have published they have seen this is a much more reactive species compared to this one so this can react fast with the boroninc acid once you have this species it can react fast with the boroninc acid so first thing is there is a transmetalation happening to generate this aryl rhodium species so this is a aryl rhodium species is generating So, once this process is generating then the next thing is there will be this allyl rhodium species now going to interact with this olefin here ok of this alpha beta unsaturated carbon compound and there will be insertion. So, this allyl group will be inserted here and then the rhodium will be inserted here, but that will go for a O-allyl

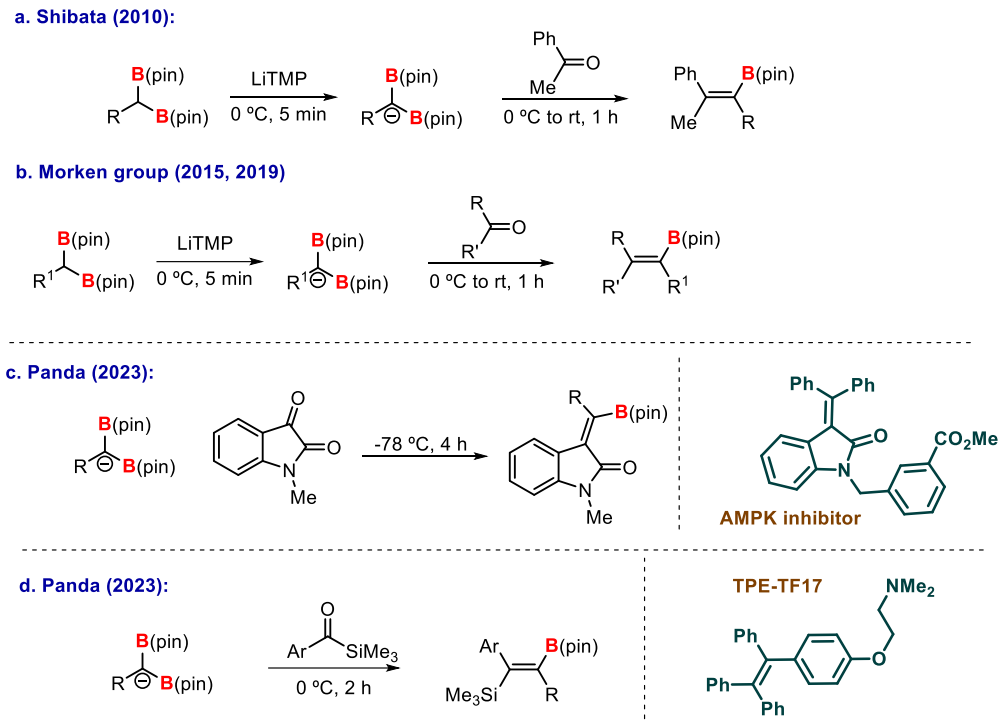


rhodium compound. So, there is a oxo allyl rhodium species going to generate here and then once either there is a water that can get the compound, get back to the hydroxyl species of the rhodium and you can get to the corresponding desired product. So, the important role of water is show you that is why in this reaction Hayashi coupling you always find some equivalent water was used that can help you first to form this active catalyst which is much more reactive compared to this one and also helping you in the final step from these species to get to the corresponding product and getting back to this corresponding the rhodium hydroxyl species ok. And as you can see, once you have this chiral ligand, chiral BINAP ligand that can control, so the chirality actually build up in this particular step. So based on the chirality on the ligand that can transfer, that can allow you to add this aryl in the particular phase of this double bond to get to the corresponding chiral product.

So we have talked about a lot about the transition metal catalyst organoboron reaction. Now I'm going to talk about some of the transition metal free reaction. So one of the important reaction I'm going to talk about today So, this reaction called Boron-Wittig reaction. So, we all know about the Wittig reaction I think if you remember in this reaction you can generate this phosphorous ylide correct. So then it can react with this corresponding aldehyde if you have this R here and R dash CHO then you can able to form this corresponding olefin correct. So, here we are talking about a boron based ylide. So how we are forming this boron based ylide because once you have this geminal di



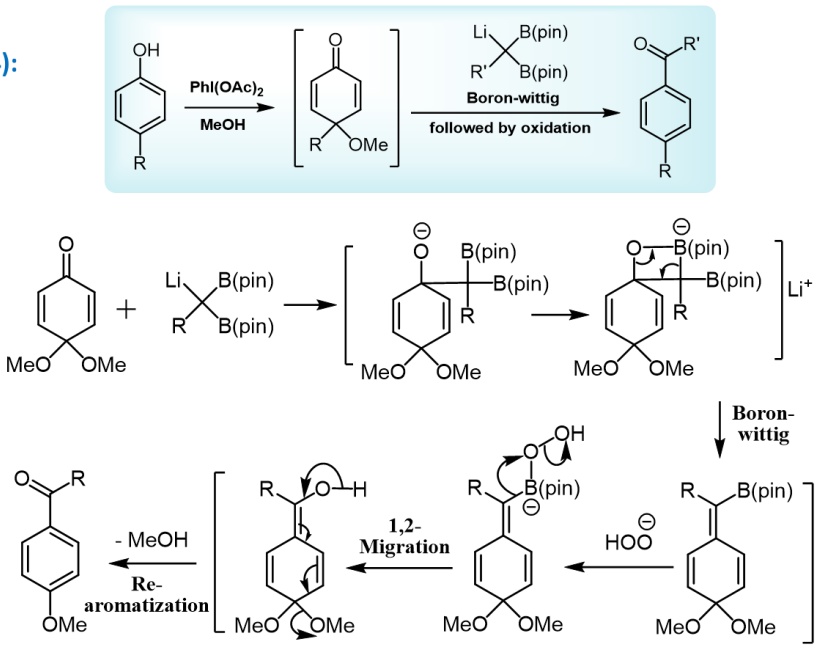
bipin compound that means your carbon has 2 boronic esters. So, if you have that scenario that you have 2 Bipin or any other projecting group on the same carbon and this carbon has some other functional group let us take in R and this H then this proton can be deprotonated very easily using LiTMP. which is a very strong base can able to allow you deprotonation to generate this species called ok. So, you generate this carbon species on the boron. So, it you can think about this species as a very similar to this wittig ylide of the phosphorus this could be a very similar to a boron forming a ylide because this negative charge can be donated to the boron and you can think about a boron based ylide. So, this can react with a carbon group here and after the reaction what is going to happen this O minus going to form a bond with the boron from this four membered specie then there is a boron oxygen bond formation happening here and cleavage of this carbon boron bond to form this double bond to form the vinyl boron compounds after the elimination of this boron and oxygen. So, you started with the two different boron compounds using a base you can make the vinyl boron compound stereo selectively. So, the reaction originated in the in 1975 by Matteson group here if you react this compound with methyl lithium then that can cleave this bond to generate a carbanion here. So, this is again generating a boron ylide which can react with a carbonyl compound to form this vinyl boron compounds. Once you treat with H_2O to NaOH this boronic ester can generate a -OH which can convert to the corresponding aldehyde ok. So, now his chemistry become very popular the Shibata group apply this chemistry using acetophenone and other ketones. So, what he has done, he is allow this synthesis of tetra substituted vinyl boron compounds ok. So very very important that this reaction comes with very high stereoselectivity ok. Then Morken group in they have two different publications on this



topic and they also solve several problems the reaction with aldehyde. When you are try to make a tri substituted compounds there are some problem with the stereoselectivity that can be solved by adding some extra base as additives. Our group also recently published very important discovery on this area where we have shown that you can take isartin here and once in this cases what is going to have you have two different carbonyl group here. one is next to the nitrogen this could be more reactive one. So, here you can react with this corresponding the boron ylide and then that can able to form this vinyl boron compound. So, now you can see you are making some of this vinyl oxy indole species because this vinyl oxy indole species are difficult to make using other methods as you can see these compounds are present in a biological active compounds and in the natural products. So, you can able to make this using the boronotic reaction. we have shown that not only using just like a alkyl aryl ketone, you can put a trimethyl sillyl group here in the carbonyl group. These are called acyl sillen. If you use that, then the important thing is now you have two different functional group in this tetra substitute of boron compound. So, what is the important of boron compounds in this? Because once you introduce a boron compound and a silicon, you can functionalize them using a suzuki coupling or other cross coupling reaction. We have recently shown another important application of this chemistry to one-pot conversion of phenol to carbonyl compound.

So, it was a very difficult transformation to achieve without transition metal. What we have shown that you can use a phenyl iodo acetate that can oxidize this corresponding

Panda (2024):



phenol to the corresponding quintal ketone. And now once you use this boronotic reaction this corresponding lithium can add here to this carbonyl because this can consider like a carbonyl group here very similar to the boronotic reaction. will form the vinyl boron compounds. Now, once you oxidize using H_2O to NaOH, what is going to happen? This boron will be converted to the OH. Now, the after the, re-aromatization, it will form the corresponding carbon compound. So, you can see in the one pot, we have done all these transformations to get to this corresponding product. these are the references and I hope you have learned about some of this allyl boron chemistry, Suzuki coupling, the Hayachi coupling, the Chan-Lamp coupling, and the boronotic reaction. Thank you so much.