Interpretative Spectroscopy

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Lecture 16

Multinuclear NMR Spectroscopy-5

Hello everyone, once again it is a pleasure to welcome you all to MSB lecture series on interpretative spectroscopy. In my previous lecture, I discussed about NMR spectra of various phosphorus containing compounds and also how to analyze, if you get more than one product in a reaction. For example, if you get cis and trans isomers or if you get some other isomers, we should be able to elucidate and understand the structures of those molecules by simply applying phosphorous NMR spectroscopy. So, let us continue from where I had stopped. Let me take another interesting reaction here. This reaction you can see, I have used two entities one is cyclopentadienyl bistrifenylphosphine chloro ruthenium 2 plus that is reacted with bistrifenylphosphine amine ligand.

So, that means in this reaction although we know that when you are mixing in a nose stoichiometry, we are supposed to get one product, but on the other hand due to some reactivity difference that we gauge, and that is what happens later, we end up getting more than one product. That means we may get a mixture of products as well. In that case, if we analyze by looking into the NMR spectrum of that reaction mixture that can give you lot more details and that can also guide you how to plan our reaction by altering reaction conditions. For example, in this one as I said, this ruthenium(II) compound was treated with this bisposphine in the above reaction, I have shown here; we are getting three products: four five and six in different stoichiometries.

Although the reaction is carried out in 1:1, the expected product is 4, but how other two compounds are formed, and how we got this information, one can see by simply looking into the ^{31}P NMR spectrum of the reaction mixture here. Several chemical shifts are there, but if you recall the first compound 4, where two triphenylphosphines are replaced by bisposphine.

Here both the phosphorous environments are identical, as a result, one can expect a single resonance here, that means this is assigned to the product 4. Now, let us look into other products. Let us go back to the reaction. In the product 6, one triphenylphosphine is there, and one bisposphine is there. Bisposphine chemical environments are identical and we have PPh_3.

So, by simple thumb rule, by looking into 2nI+1 rule, we can anticipate a triplet for triphenylphosphine and a doublet for bisposphine, because bisphosphine will be coupled with both of them together, whereas triphenylphosphine will be coupling with two equivalent phosphorous centers from bisposphine. So, we expect a triplet and a doublet for 6. So, you can see here: a doublet is there and a triplet is there. This is for triphenylphosphine and this is for chelated two phosphorous moeitis of bisphenylphosphine amine. So, then we have left with one here one here one here for product five. So, what is that product five? So, product five you see we have one dangling phosphine is there acting as a monodentate ligand.

So, this is different and this is different and these two are identical. That means, we are anticipating three signals and here this phosphine is further away from bisposphine. As a result, this can just couple with coordinated phosphorous to show a doublet. But on the other hand, the chelated phosphine also can couple with coordinated phosphorous from the monodentate ligand to show a doublet, whereas this one would show a triplet with this one and the triplet is further split into doublets from this one. That means, we are seeing a multiplet for monocoordinated phosphorous and a doublet for this coordinated or chelated compound and then again doublet for this one. So, let us see whether we have those things here, yes, we have a doublet with very small coupling constant value and also we have a multiplet here. It is a triplet of doublets.

So, we are seeing that one. That means this is giving some idea that three compounds are formed, but again looking into the integration, we can gauge how much quantity of each one is formed in what ratio and then looking into other two compounds, where ionic products are there, yes. That means probably instead of using, let us say, I have used dichloromethane here. Instead of using dichloromethane, if I use a polar solvent probably the formation of 4 can be diminished and formation of these two compounds can be enhanced and better yield. On the other hand, again by taking two equivalents of bisphosphine, probably enhance the possibility of formation of 5 even more.

So, this reaction was carried out, and this pure compound was obtained carrying out at low temperature and then by using two equivalents of bisphosphine in polar solvent resulted in this compound and then using a polar solvent, but one equivalent of bisphenylphosphine resulted in this compound. Of course, once after making this compound, if you bubble CO here, it can result in carbonyl compound. So, all these information come very nicely by analyzing the ^{31}P NMR spectrum of the reaction mixture. That means it is not just to analyze and understand what kind of compounds formed, it can certainly help us in altering our reaction conditions. So, that we can refine our methodology; later all these compounds were prepared in pure form and analyzed; you can see here. So, these compounds are formed and then this compound was again prepared in a separate reaction by getting that information from the reaction mixture and then this was obtained in pure form.

And now let us look into few more examples. Here I have given three examples here one is a bisphosphine with both the phosphorous oxidized by selenium that is bispelenide derivative here and then I have here analogous to vaska's compound both cis and trans chlorocarbonyl bisphenylphosphine, bisphenylphosphine rhodium and also the its cis analog and they differ significantly in their ^{31}P NMR spectra. First let us look into bisphosphine here of course, when we look into bisphosphine with the both the phosphorous oxidized by selenium, here ^{31}P NMR spectrum would show a singlet and then it is coupled to ^{77}Se and that shows satellites, here the separation is called phosphorous-selenium coupling constant. So, these are called satellite peaks, and then if you look into selenium NMR again, both the selenium centers are chemically and magnetically equivalent. As a result, they are equally coupled to phosphorus and we see just a doublet and then this whatever the separation is there here in case of selenium NMR should be same as what we obtained in case of ^{31}P NMR. That means coupling constants remain same, no matter which nuclei you are using. Now, let us look into trans compound; here in case of trans compound you can see, both the phosphorus atoms are identical by performing a C_2 axis of rotation passing through C1. As a result, you can see only one type of phosphorus and then you look into ^{31}P NMR, they are simply coupled to rhodium to give a doublet here. Very simple doublet is here and then this separation is called $^{1}J_{\mathrm{RhP}}$, but when you look into this one, here one triphenylphosphine moiety here. One triphenylphosphine is trans to CO, whereas the other one cis to CO. So, we cannot have C_2 axis of rotation, as a result two phosphorous atoms are chemically equivalent, but both are chemically and magnetically nonequivalent. As a result, it resembles AMX spin system.

So, P_a is coupled with rhodium and then coupled with phosphorous, and shows a doublet of doublet. In the same way, P_b is also coupled first with rhodium and each line is further coupled with phosphorus. So, first this is rhodium coupling. and then this is phosphorus coupling, whether you consider ${}^{\delta}P_a$ or ${}^{\delta}P_b$, they are very similar, but slight marginal difference is there in chemical shifts and coupling constants. So, this is rhodium- phosphorous coupling and then here it is ${}^{2}J_{PP}$ coupling. So, this is how we can distinguish cis and trans isomers in case if they are obtained in a reaction. Let us look into two more examples. Here we have a mixed ligand complex of platinum(0), a tetrahedral complex, where we have 2 trimethylphosphine and 2 diphenylphosphine.

So, that means platinum is in plus 2 state here. 2 trimethylphosphines are neutral ligands and here we have 2 diphenylphosphides; there they are anionic. So, platinum is in plus 2 state and it is a 16-electron complex. So, now, if you look into phosphorous NMR spectrum, we can anticipate two types of signals. So, these two are identical; they are coupled with these two to give a triplet. These two will couple with equally to this one to give a triplet and then these two will couple with this one to give a triplet. So, what we should get is a triplet something like this and then platinum coupling would come.

So, basically platinum coupling would come with platinum satellites because of ^{195}Pt is about 34 percent; NMR active and I equal to ½. So, as a result this is for ^{196}Pt which is I equal to 0. So, what we get is, this is split into a doublet here something like this, and then something like this. So, if you look into the spectrum, this distance is called ${}^{1}J_{PtP}$ coupling. This is similar for both of them, whether we consider a signal for trimethylphosphine or we look into that one they will be identical, but they will be having different chemical shifts. Here this one is for ^{196}Pt and then if you look into the integration this would account for 66 percent and then this would be 17 percent and then this is 17 percent.

So, this is how we can analyze the spectrum and you can ignore this spectrum and of course, you can also look into ^{1}H NMR spectrum here, because trimethyl group is there and this trimethyl group, what happens this is of course, here you can see both are identical. Both the trimethylphosphine groups and CH_3 first it will be coupled with phosphorus to give a doublet and then each doublet something will be there rhodium to hydrogen coupling and then we will see hydrogen to platinum coupling. So, this how the ^1H NMR spectrum would look like and most of the time by default when we are looking into phosphorus NMR, what we get is proton decoupled one, and of course, if we are interested in looking into phosphorus-hydrogen coupling, then we can go for coupled one. In that case, it should be represented something like this. The moment we write ^1H in flower bracket {} next to ^{31}P ($^{31}P\{^1H\}$) it indicates that ^1H is decoupled and that means interaction of protons in the magnetic field when we are measuring phosphorus NMR is nullified. So, now I have another interesting compound here. In this one, it is a dimetallic compound and two platinum atoms are there. They are held by two trimethylphosphine each and the middle we have diphenylphosphide ligands. So, both the platinum atoms, if it is symmetric will be +1, +1 or one side it is platinum(0) and one side it can be platinum(II).

So, now we shall look into the spectrum of this one here. How it looks? Let me write the structure again here. First, we can look into ^{195}Pt NMR, this is the structure. Now, if you see, these platinum atoms are both chemically and magnetically equivalent. Both the platinum atoms are coupled on either side by two different type of phosphorus units. So, here let us say first this is coupled with two phosphorus units and if you just look into 2nI + 1, it should be a triplet and then this separation is $^1J_{PtP}$. Each of these signals will be further split by two end trimethylphosphines. So, this is coupled with first these two and then these two. So, this separation is $^1J_{PtPMe3}$.

So, if it shows a triplet of triplet and if you look into the spectrum it should look like 1 : 2 : 1. So, this is the spectrum. So, this is how the ^{195}Pt NMR looks like, but on the other hand, when we look into phosphorus NMR, these two are identical and they are equally coupled to four trimethylphosphines. As a result, what would happen to $^{\delta}PPh_2$ let me write here; it will show first a quintet. So, it should show a quintet and then each quintet is further split into a doublet in the form of satellites. As a result, what would happen is we get something like this.

So, this is the spectrum and this is the $PPhH_2$. So, something like this again, this is for 66 percent and then this is 17 percent and this is 17 percent, and then distance from the middle one to middle one or first one to first one; this is called $^1J_{PtP}$ coupling and this spacing is called

PP-coupling. On the other hand, these two are identical with this one when they are coupled with this one we get simply a triplet. And then this triplet is split into another doublet because of platinum coupling. So, this would be something like this. This is $^1J_{PtP}$ coupling. So, this is how the spectrum can be analyzed.

So, now let us look into other applications. We have several applications. One very important application I am going to show you especially, those who are working with nano materials and working with carbon compounds such as fullerenes, graphines, graphene oxides and other things; very very important one. Measuring epoxide content of carbon nano materials. The presence of epoxide on nano materials such as carbon nano tubes and fullerenes can be readily monitored by reacting these nano materials with triphenyl phosphine. How it helps in understanding the presence of epoxide? So, this method involves the catalytic reaction of methyltrioxorhenium. So, an epoxide reacts with methyl trioxorhenium to form a five-membered ring and in the presence of triphenyl phosphine the catalyst is regenerated forming an alkene and then formation of triphenyl phosphine oxide. So, when we add triphenyl phosphine along with methyltrioxorhenium to nanomaterial containing epoxide, oxygen is abstracted by triphenyl phosphine to form triphenyl phosphine oxide by simply taking the known quantity of triphenyl phosphine and by monitoring the ^{31}P NMR spectra at regular intervals we can quantify the amount of epoxide present by looking into the amount of triphenyl phosphine is converted into triphenylphosphine oxide and how much is left at the end of the reaction.

So, this is the reaction for example, we have an epoxide here and epoxide when treated with ^{1}H it forms a cyclic system like this and when this cyclic system is treated with triphenyl phosphine, it abstracts oxygen from this oxo cyclic system to form triphenyl phosphine oxide and regenerating a methyltrioxorhenium through the formation of this olefin. So, now exactly this what happens. For example, we have on graphene we have epoxides. When this is treated with this one and then as I said here triphenyl phosphine abstracts, and this one is regenerated and then by simply looking into the reaction mixture NMR, we can conclude that the amount of PPh_3 used in the reaction is known, the relative amounts of triphenyl phosphine and triphenyl phosphine oxide can be determined simply by looking into the integration of ^{31}P signals in the spectrum and that in turn gives the amount of epoxide present on the nano tubes. So, this is very important and simple reaction one can analyze, and also one can also get rid of all these epoxides, if they are not read it. So, you can see here ^{31}P spectra before and after the reaction. Before the reaction PPh_3 is there and after the reaction, what happens partially PPh_3 is converted into triphenylphosphine oxide depending upon how many epoxide groups are present on nano material.

Then, if you just look into the integration now only 0.4 percent is left. Let us say if you have used two equivalents, 1.6 is converted into triphenyl phosphine oxide and now only 0.4 percent is left in the solution. So, that gives how much is there in it this is a very important method one can use effectively for determining epoxides present.

So, let me stop here and continue with more interesting examples in my next lecture until then have an excellent time reading spectroscopy. Thank you.