

Interpretative Spectroscopy
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Lecture 14
Multinuclear NMR Spectroscopy-3

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy and now let me continue again discussing more interesting examples of phosphorus compounds, and then see how easy it is to interpret the data obtained from ^{31}P NMR spectra of various very interesting phosphorus compounds. So, in my previous lecture I showed these three molecules here and then I could show you how to interpret or how to sketch NMR spectrum of both ^{195}Pt as well as ^{31}P phosphorus in case of platinum compounds.

Let me now discuss the splitting pattern and also sketch NMR spectrum corresponding to rhodium complex here. First let me look into ^{31}P NMR spectrum of this rhodium complex. As I said earlier ^{103}Rh isotope is 100% abundant with I equal to half. So, it couples equally and then we have phosphorus and the moment you look into the molecule you should be able to tell that there are two different types of phosphorus atoms. One is directly attached to rhodium with two fluorine atoms on it and, one oxygen, whereas the second phosphorus is doubly bound to sulphur and then it is not directly connected to rhodium. So, we have two phosphorus atoms and fluorine can also couple with both the phosphorus atoms, and rhodium can also couple with both the phosphorus atoms and rhodium phosphorus coupling constant is in the order of 180, it can go up to 300 or 350 hertz (Hz).

Now let me go to the spectrum of rhodium complex here. In rhodium I have labeled as P_a and P_b here, and of course I can also label them as A and X. This is a typical AMX spin system but we are looking into A and X signals because rhodium is a heteronucleus here. So now first if you look into P_a it is first coupled with rhodium, because rhodium to phosphorus coupling is larger than phosphorus to fluorine so it first couples with rhodium to give a doublet here and this is $^1J_{\text{RhP}}$ coupling. Now it is coupled with fluorine, since two fluorine atoms are there

and each of the doublet lines are split further into triplet; something like this and this is $^1J_{PF}$ coupling, and next we have is two bonds apart, P_b . P_b also couples with P_a to give a doublet, so each one is split. This one here, it is $^2J_{PP}$ coupling.

So now the spectrum should look like a doublet of triplets of doublets, a doublet of triplets of doublets. So, this is how we have to pronounce. So initially start from doublet of triplets of doublets so this is how we can pronounce the multiplet related to P_a signal. And now let us look into P_b . When we look into P_b , first it will couple with phosphorus because that $^2J_{PP}$ (phosphorus to phosphorus) coupling is little larger; it couples with $^2J_{PP}$ and then each line will be split by rhodium that is two bonds apart. So, this is rhodium coupling. This also $^2J_{RbP}$ coupling. Now we have 1, 2, 3 so three bonds apart, two fluorine atoms are there so they are also likely to show some coupling, long range coupling of three bonds coupling. So each line here will be split into triplet here due to the presence of two equivalent fluorine atoms. So, this spacing is $^3J_{PF}$ coupling. So that means basically what we have is a doublet of doublets of triplets, doublet of doublets of triplets and this is how the spectrum would look like. So this is about ^{31}P NMR spectrum and you can try to sketch ^{19}F NMR spectrum for this molecule and also you should try to write ^{103}Rh . Try it is very simple to sketch ^{19}F NMR spectrum for this molecule and also try to sketch ^{103}Rh spectrum also for this molecule. I shall tell you in case of ^{19}F fluorine NMR what happens is first it splits into a doublet due to PF coupling and then each line will be split into another doublet because of fluorine to rhodium coupling and then each line will be split into again a doublet because of three bond PF coupling. So, I have already given you hint you can do in the case of rhodium. ^{103}Rh is exactly very similar. First it will be coupled with phosphorus 1J to give a doublet and then each line will be split by fluorine to give a triplet and then each line in the triplet will be further split into doublet because of P_b .

Now you try to sketch the NMR spectrum of both ^{19}F as well as ^{103}Rh . If you have any difficulties, let me know so that I can provide you later. So now let us look into this molecule here this molecule we have three cases as I mentioned and when spectrum is not given. If somebody ask you to sketch the ^{14}N NMR spectrum of this molecule, here this is called bis(diphenylphosphino)amine ($C_{24}H_{21}NP_2$) and then you have to look into all the three cases. i) one is NH coupling is larger than NP coupling, ii) NP coupling is larger than NH coupling

and iii) third one is NP coupling is equivalent to NH coupling. Because all of them are one bond apart. So first let us look into PN coupling is larger than ^1H coupling: Since we have two phosphorus atoms, what happens? first it would be split into a triplet and each line will be split into a doublet something like this. So, we have doublet of triplets. Next when we look into $^1J_{\text{PN}}$ is less than $^1J_{\text{NH}}$ coupling, in that case what happens, first it splits into a doublet and then each line will be split into a triplet because of two equivalent phosphorus atoms. This is how it looks like in this case. So, it is simply something like this. Here it would be something like this, and then in this case, the last one, where PN coupling is equivalent to NH coupling. Then we are identifying three nuclei equally coupled to nitrogen in that case what happens it would be a quartet. When we have a quartet, it would be something like this. So all the three cases we should draw. If we plot ^{14}N NMR and it should correspond to one of these so this how you should be able to sketch and compare and analyze and interpret the data. It is not really complicated! right? Now we have another interesting problem. Here consider all possible isomers that could be obtained for the 8 membered ring compound $\text{P}_4\text{N}_4\text{Cl}_6\text{F}_2$ and indicate the ideal ^{31}P and the ^{19}F resonance spectrum expected for each. Of course, the moment you look into this one, it is already stated that this is an 8 membered ring. We have alternate phosphorus and nitrogen with alternate P—N single and P=N double bonds. They are called cyclophosphazanes. This is cyclotetraphosphazane, and each phosphorus having two halogens that is the reason each P is pentavalent and tetra coordinated. So, we have each one has two nitrogen bonds one is double bond one is single bond and it has a combination of or it can have 2 chlorine atoms or a chlorine and a fluorine. So now what we should do is, try to sketch all possible isomers and then we should speculate or we should try to sketch the ^{31}P NMR spectrum and also ^{19}F NMR spectrum for each isomer. I have already written all possible isomers. Totally 5 isomeric structures are possible for this composition of $\text{N}_4\text{P}_4\text{Cl}_4\text{Ph}_4$. I have taken a different molecule here and the problem, I showed you is $\text{P}_4\text{N}_4\text{Cl}_6\text{F}_2$, whereas here I have taken a different example to make it little simple. I have considered 4 chlorine atoms and phenyl groups. May be in my next lecture I can sketch all possible isomers for Cl_6 and F_2 combination and then sketch NMR spectrum for each case.

So now let us look into this simple one. In this one, we are looking into only coupling between non-equivalent phosphorus atoms and that is the reason, I thought to begin with a simple one. Now this is one isomer, you can see in isomer one, we have two different types of phosphorus. Two of them on opposite sides are doubly substituted with phenyl, whereas the

other two with chlorine and is very symmetric molecule. We have two different types of that means basically we have A_2X_2 type spin system and then again, we have identical ones. If we just look into it, we can have a axis of rotation, it looks identical from one portion here so these two and these two again it is A_2X_2 type system and then if you go for the third molecule, here we have three different types of phosphorus atoms, one having two phenyl groups, two phosphorus having one each of chlorine and phenyl group and other one having two chlorine groups. That means here we have some sort of AMX spin system and in this one it is a very symmetric, we can anticipate a single resonance for this molecule. There is one more possibility and then here also we have four different types of phosphorus atoms, here one two three four and we can also see here each one is having of course one two three four couplings. How they are going to look like, we can look into it. I have shown here first one: as I said it is an A_2X_2 spin system, we get these two in blue color, would couple with two red colored phosphorus to give a triplet and same thing is true for the other set, so we get two triplets, we are getting here and of course in case of two also it is identical we can get two triplets A_2X_2 again in case of 3, what we have is AMX spin system. So, basically what we have is this one is coupled with this one; two triplets and each triplet is split into a doublet so we get this one and then these two will be coupled with this one first gives a doublet and then this splits further so that we get doublet of doublet for this one and then this is a triplet and this is a triplet here. So, you can see, this is given here and then the 4) all phosphorus atoms are identical, we are getting a signal here and in case of 5 as I said, we have one, two, three, four signals; all of them are separate. We are getting, well further coupling is not possible, one, two, three, four coupling is not possible only they are coupled to two. As a result, what happens? each one will show a doublet of doublet here. So, all four of them will be showing different ones and with color code I have given. This color corresponds to the color given for the phosphorus atoms so that the understanding would be rather easy. Thus, we get four quartets, whereas in case of 5 because all four are identical and they are coupling with only the nearby ones, the fourth one is further away so that they are not coupling so P shows coupling with only these two P (red and pink) and similarly this one will couple with blue and green, and this one will couple with red and pink. It goes like that, so four of them will be showing each one a doublet of doublets. So now I have listed compounds I have given the molecular formula. Also, I have given the corresponding chemical shifts. I have given if you recall the extensive list, I gave you in one of my previous lectures. If you compare from that one where exactly the chemical shift falls based on that one whether it is down field or up

field shifted. You have to rate the spectrum for example, if you just look into the molecule given here, one signal is there, means only one phosphorus is there. obviously and then we have $C_3H_9O_3$ so that means basically you can assume this may be $P(OCH_3)_3$, CH_3 three times, so this will be having composition like I have shown here in the same way you identify the type of molecule here and then try to write the structure in the blank given here. If you have any difficult, try it is very interesting. It covers most phosphorus compounds, we come across and also the extensive. The list I gave you in one of my lectures; you can use that one and write the structures for all of them. Once you write the structure, it is very easy to understand and of course here only this one is missing. Further information is also giving how each signal would look like the multiplet. We have ten lines why it is ten lines because nine equivalent protons are coupled with phosphorus to give ten lines one two three four five five six seven eight nine ten. Looks something like this and then next one is septate is given if the septate is given and J_{PF} is eighty point six hertz then you should be able to analyze and then write the spectrum here and also write the structure so make an attempt for all of this molecule is very simple because all the data is given it is almost like providing ^{31}P NMR spectrum here and you have two molecular formula is given you should be able to write appropriate structure for in each case you can see here chemical should 159 and then you know we have 144 and then 2.3, -27, 11., 20.7 -2.8, 9, -66.4 and 53 and -45 and -144. I have very interesting molecule here. You can see here. This molecule has a silicon and three hydrogen atoms on silicon and then nitrogen fifteen enriched molecule. H is there and phosphorus is there that means it is a very interesting molecule you can sketch NMR for almost all nuclei here you have ^{19}F , two, three, four and five, five different types of NMR active nuclei are there. Of course, silicon abundance is very less, ^{29}Si , but nevertheless you can. When you are looking into fluorine NMR, phosphorus NMR, 1H NMR and ^{15}N NMR you can ignore the coupling due to silicon, and of course in case of silicon NMR, you can consider all other couplings.

So, let us try to do one at a time here. First let us look into ^{31}P NMR. Herein ^{31}P NMR, you can see two fluorine atoms and you know the magnitude of J_{PF} , that is $^1J_{PF}$ coupling is much larger. So, what you can do is first this splits into a triplet. This is your $^1J_{PF}$ coupling, so next it is coupled with the nitrogen here. This is $^1J_{PN}$ coupling. Next, we have $^2J_{PH}$ coupling. Each line will be split, So this is $^2J_{PH}$ coupling. So next we have one two three three bond coupling with silicon bound hydrogen atoms. We have three equivalent hydrogen atoms. Each line will be split into a quartet here. So this many lines will be there if you count one two three four five six seven eight nine ten eleven twelve. Twelve x four = forty-eight ($12 \times 4 = 48$) lines will be

there in it, and then the intensity should be maintained. 1:3, overall intensity should be 1:3 and here. It is 1:3:3:1. It is 1:1, 1:1, 1:2:1, so when we sketch spectrum looking into this coupling tree, we should ensure that the intensity, whatever is there, that is maintained here. So now with this one, you can interpret which spectrum it is, it is not mentioned but by sketching say ^{31}P NMR, ^{19}F , ^1H NMR or ^{15}N . You should be able to tell which spectrum is for which NMR nuclei we are talking about, so this one should be phosphorus NMR. So, this one if you just see, it looks like this here. Yes, this is for ^{31}P . So let me show you in the next slide. Here I have taken ^{31}P NMR. You can see here. Whatever the coupling I showed you here, it is there. You can see, first phosphorus is coupled you know split by three fluorine atoms into triplet and then each line in the triplet is split into a doublet because of $^1J_{\text{PN}}$ coupling, doublet and then each line is further split by $^2J_{\text{PH}}$ coupling with nitrogen bound hydrogen here. And each one is a doublet here, one two three four five six and then each line is split by H on silicon. Three hydrogen atoms to a quartet something like this. Now we have something like this here. We have forty-eight lines. So, this is how you can show and then the corresponding spectrum would look like. This is very interesting molecule right, and also spectrum looks wonderful, is that right. So very nice one it is. As I said, once you understand, once you write clear structure, even if the molecular formula is given or structural formula is given, try to write the full structure showing all the bonds and then start analyzing all NMR active nuclei, how far they are from the one we are looking into and then with little bit of information you are having about the magnitude of the couplings, of course no matter what happens 1J coupling is always larger than the 2J coupling then the 3J coupling. Then you see, you start analyzing and due to some reason if we have two different nuclei, which are same number of bonds apart, then it is likely that they are coupling equally. So, there is another possibility so that also one should look into. We saw in case of bis(diphenylphosphino)amine, where we saw two phosphorus and one hydrogen were coupled equally to nitrogen. One should look into all those things and analyze. It becomes very easy for interpretation. So, one that I looked into is ^{31}P NMR. For this molecule, in my next lecture I shall discuss about other two spectra that is yet to be analyzed that I shall do it in my next lecture until then have an excellent time. Thank you.