Interpretative Spectroscopy

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Lecture 15

Multinuclear NMR Spectroscopy-4

Hello everyone, once again I welcome you all to MSB lecture series on interpretative spectroscopy and I am sure you are all enjoying the interpretation of very interesting phosphorus compounds and also the metal complexes having several other NMR active nuclei. So, let me continue with some of the molecules that I showed you in my last lecture. I showed you in my last lecture this molecule, and then three spectra here, and the first one we concluded that it is due to ^{31}P NMR and the splitting pattern also I showed you. Now we have another set of signals here. In the second one, if you just see, 1, 2, 3, 4, 5, 6 are there, that means 4 multiplets of 6 lines each and again in the last one also we have 6 lines and 4 multiplets are there, each one having 6 lines, but the spacing are little bit different. That means they are not due to the same nuclei. They are due to the different nuclei. So, just let us look into them, now it is very clear that ^{31}P NMR spectrum can be interpreted in this way by writing this coupling tree here you can see first it is coupled with 3 fluorine atoms to give a triplet and then each line is coupled with ^{15}N to give a doublet here and then each line of this doublets again split into doublet because of two bond hydrogen coupling something like this, and then each line is coupled with 3 hydrogen atoms present on silicon to give quartet in 1:3:3:1 ratio, and if you count all of them, we have totally 48 lines and 48 line spectrum looks something like this. The original 1:2:1 ratio what we saw here is retained here and then again, if you see here, these doublets are 1:1:1 that is also maintained here.

So, now let us look into ^{19}F NMR spectrum. It looks little bit complicated, but it is not really. So, first of all, we have to analyze how each multiplet has 6 lines here. Before that, let us start looking into ^{19}F NMR. Assume it is ^{19}F NMR and at the end we can conclude about that one, and if you consider ^{19}F NMR, first that will be split into a doublet because of phosphorous coupling. So, this is the PF coupling here, and next this is coupled with two bond ^{15}N that is

again each one will be a doublet here. This is FN coupling here, this is FN coupling and then, signal of fluorine is coupled with hydrogen to give another doublet here. So, this is your $^{3}J_{FH}$ coupling due to hydrogen that is present on nitrogen. Now we have to look into 1 2 3 4 bond coupling here.

So, four bond coupling would be here. So, that would split each line into a quartet because of the smaller spacing of FH with the magnitude of that one is much smaller. What happens, first two lines of the second signal and last two lines will merge. As a result, what happen the intensity of this will go up and then same thing happens in case of all the four signals here, and you can see here, they are merging little bit because of closer spacing and very marginal difference in their chemical shifts, it can show now 1 2 3 4 5 6 are there, but intensity varies now. As a result, what happens, it appears like a sextet in each case and then if the spectrum is given, often we get confused why sextet is there, each line should have been a quartet very similar to what we saw in case of phosphorus, but here it is sextet because these two are merging here. So, as a result we get something like this is, a typical ^{19}F NMR spectrum shown here. Now let us look into ^{15}N NMR spectrum. Again, we have two options, whether NH coupling is larger or PN coupling is larger. Let us assume PN coupling is larger, getting some hint from the previous ^{31}P NMR spectrum, we shall look into it first: this N will be split into a doublet this is PN coupling, then this will be coupled with hydrogen. So, something like this. So, now if you just look into it, we have six lines; for each one, there is no individual splitting.

So, fluorine is also two bonds apart from ^{15}N and also silicon bound hydrogen atoms also two bonds apart from ^{15}N. That means totally, if you assume that coupling constant is of same magnitude in case of both FN coupling, as well as two bonds NH coupling, then we have to count together. So, we have 1 2 3 4 5 equivalent nuclei are there, then if you just use 2nI plus 1 rule (2nI + 1), of course, all of them are with spin half (I = ½) and we have five of them. Half plus 1 it, goes it gives 6 lines (2*5*1/2+1 = 6). So, each one should be a sextet so that means we have something like this 1 2 3 4 5 6 and the spacing are little bit different compared to what we saw in case of ^{19}F NMR. So, the spectrum should look something like this. Yes, now we have the spectrum. So, very easy, that means basically the three spectra given are for ^{19}F and ^{31}P and $^{1}5N$.

So, what is left is ^{1}H. So, ^{1}H NMR, I had left it for you people. So, you people try to sketch NMR spectrum after writing the coupling constant and splitting tree and then just see how it looks like and you can take hint from these three spectral data. Now, I have given another compound here. This is cyclodiphosphazane and cyclodiphosphazanes are 4-membered inorganic saturated ring system with alternate arrangement of phosphorus and nitrogen with phosphorus in trivalent state. They can exist in cis and trans forms. Cis is more stable, kinetically more stable isomeric form. And then the nitrogen is planar here because of the $N_{2P\pi}$ electrons interacting with the sigma star of phosphorus, that we call as 'negative hyper conjugation', as a result, what we have is $N_{2P\pi}$-σ*interaction. Because of that one, nitrogen lone pairs are delocalized here. As a result, the P—N has multiple bond character and hence this appears like a planar molecule having a sp^2 hybridized nitrogen.

So, when you react this one with appropriate metal reagents, either you can form binuclear bimetallic complexes or monometallic complexes, but it cannot chelate, because of the planar structure, but it can only act as a bridged bidentate ligand or if you use one equivalent, it can act as a monodate ligand leaving other phosphorus uncoordinated. We have one such case here [rhodium(chloro)(cod)] dimer $[RhCl(COD)]_2$. When it is reacted with two equivalents of cyclodiphosphazane, what we get is a mono coordinated compound of this type here. We have cod (cyclooctadiene) there. Now if you just look into it this is a typical AX spin system in case of ^{31}P and now if you see this P_X. P_x is directly attached to rhodium and first it will be split into a doublet, and then of course, each line can further split into a doublet because of PP coupling. In that case what happens, it will be very small, and it will appear something like this, whereas P_A is coupled with P_X to give a doublet, and then it does not show any rhodium coupling. Otherwise it would have split into a doublet of doublet. Here again, you can see here, that is, rhodium phosphorus coupling of 229 hertz and then see whatever the coupling we anticipated is not there, Since we have one free phosphorus, you can coordinate that one with another heteroatom for example, when it is treated with $AuClSMe_2$, SMe_2 is a very labile ligand and goes off, and then what you get is AuCl is bound, we have AX spin system both are coordinated earlier. We have one free uncoordinated phosphorus, now you can anticipate some sort of PP coupling, PP coupling is in the order of 30 hertz, that you can see here and also surprisingly now phosphorus is coordinated to gold, it also shows rhodium coupling that is $^{3}J_{RhP}$ coupling of 5.58 hertz and this one. What we see here is due to the complete

substitution of both the phosphorus atoms with gold that means basically when this compound is treated with $AuClSMe_2$, apart from forming heteronuclear compound, partly it has replaced rhodium also to form digold complex that is what it indicates. Here some of this vital information, you can extract when you look into NMR spectrum carefully so it gives much more than what you are looking for this is where the importance of spectral data comes into picture in understanding the reactivity and other things for example now if I start using excess of $AuClSMe_2$, probably I should be able to replace rhodium also to form a digold complex in fact we have done that one in our laboratory sometime back so interpretation is easy and also we came to know that suddenly phosphorus-phosphorus coupling is increased when both the phosphorus are coordinated and it is now very interesting to look into the electronic situation at both the phosphorus with some theoretical background or DFT calculation and other things that might tell you why now PP coupling is very intense compared to the compound where only one phosphorus is coordinated, one more interesting molecule is there again, this is rhodium chlorocarbonyl complex having a phosphineimine ligand. So one phosphorus is directly attached to rhodium and other nitrogen has phosphoryl azide is bound, so we have three phosphorus atoms. Now AMX spin system, and in this one in first case, where we have P. This phosphorus is directly attached to rhodium, so it can first couple to give a doublet and each line can be further split into a doublet, because of this two bond PP coupling, so this one you can assign for P here. This is rhodium coupling here, and this is $^2J_{PP}$ coupling and this is farther, so this is not showing any coupling with this one, now if you look into this one it is a doublet of doublet. This may be due to this one here, this first couples with this one and then this is coupled with this one also it's a doublet of doublet here so this phosphorus doesn't show rhodium coupling whereas this one shows now only this one is left now this one only coupled with this one so it gives a simple doublet so that means now very nicely interpret the data and also check whether the compound is formed or not. For example, this ligand is taken when it is treated with half equivalent of rhodium chlorocarbonyl $[Rh_2Cl_2(CO)_4]$ and this is a dimer so this is taken and then this is reacted with two equivalents, we had taken and then it gives the compound shown here. This compound is shown here, yes now we can conclude that this bond is broken and it is from a mono rhodium compound. In this case, now we have another interesting molecule here, this is a platinum compound of bisphosphine where it is a unsymmetrical bisphosphine one side it is $OPPH_2$ other side, it is $NPPH_2$ and then if you look into the ^{31}P NMR spectrum of this one it shows two signals without any PP coupling as they are one two, three, four, five bonds apart,

so that means, it does not show when we make a compound with this one, say platinum, now through metal they can interact. Because through metal they are only two bonds apart. So through the ligand framework, they are one, two, three, four, five bonds apart. When they are four or five bonds apart, it is less likely that they couple with each other, instead they will show a singlet, but on the other hand, when the complex is formed, what happens, they are coming closer through metal, you can anticipate through-metal coupling with this one. It is a very nice example, where the phosphorus-phosphorus coupling is absent in the free ligand, whereas when it forms a chelate complex, they are coming closer and show coupling. That means, it also gives some idea about when such molecules are there, how much the coupling one can anticipate? That information comes directly from this one. Initially this free ligand shows only two signals, singlets and then when you make a platinum complex, both the phosphorus are coupled, apart from coupling to platinum. I have shown here, PN bound one is shown here, whereas this is for PO bound one, and then they are also showing the satellites as expected, because this is for 66% ^{196}Pt *I* equal to 0, and then the corresponding one is here. One is here, this coupling is 3933 Hertz, and this is $^{1}J_{PtP}$ coupling, and in case of PO it is 4066 Hertz. The PP coupling is 13.3 Hertz here. This is again an interesting molecule. You can see the structure, it is a puckered chelate ring. You can see here. Now they are coupled through space one more example is there. Here just look into this molecule here, this is a cationic complex. We have three different types of phosphorus atoms. All of them are coupled with each other, because they are all two bond apart so now again interpretation is also easy here just it keeps you see here all are different so you have something like AMX spin system here this phosphorus couples with first this one trans and then it gives doublet of doublet and then similarly this one would couple with this one or this doublet of doublet and this also couples with doublet of doublet because all are in different chemical environment. You can see each one is showing a doublet of doublet, a typical AMX spin system. So, in case of AMX spin system, and also the field strength is very high, it does not show any second order splitting. Here second order splitting is invariably observed. In case of ^{1}H NMR, where we have two hydrogen atoms on same carbon, the geminal coupling will be seen. The carbon is substituted, with different groups on either side. So, now let us look into one interesting reaction here. This ruthenium compound is a tetrahedral molecule, with ruthenium in plus two state. You can also do electron counting for this one. If you do by neutral method this is eight plus five for CP group and this is for one and this is for two and this is for two this is an 18-electron complex, 14 plus 16 plus 18 and this is by neutral method. By ionic method ruthenium 8

means six are there and this is giving six electrons now and this is giving two electrons now and both of them are giving two electrons each this is an 18-electron system When it is reacted with this PNP ligand, what happens we are getting lot of different types of compounds. For example, you can see here, when it is reacted, it gives a mixture of compounds. One is a chelate compound replacing two triphenyl phosphine, whereas here it becomes a cationic complex here, Two PPh_3 and Cl also has come out and then one acting as a dangling monodentate ligand. In other one PPh_3 is there and so all these three are formed. How do we know that all the three are formed, simply by looking into the ^{31}P NMR spectrum of the reaction mixture? That also gives in what ratio these compounds are formed. Once we know that in what ratio these compounds are formed, whether it is possible to prepare those compounds in pure form by varying the stoichiometry and varying the reaction condition. For example if you take this compound here and then ruthenium to chlorine bond is ionized that means if we use a polar solvent and prolong the reaction it is likely that we can form a cationic compound, something like this or if we use excess of phosphine one can get like this, but by controlling the stoichiometry, if you use one is to one reaction in a polar solvent, you can get this one. That means this kind of vital information one can get simply by analyzing the spectrum of a reaction mixture again using very simple ^{31}P NMR spectroscopy. So, let me show you the spectrum for this molecule. In my next lecture, I will show you very interesting examples and also how we come to conclusion about a spectrum. Analyzing this particular set of multiples for this molecule, that of course, when we carried out individual reactions or separate reactions, and for isolated compounds we can confirm and in some cases, it is very simple, you should get a doublet and a triplet. Then in this case, you can get a singlet and so there is no scope for any confusion, but if there is any scope for confusion of having similar pattern for two or more molecules, then we have to separately make them and confirm their chemical shifts.

Okay, let me discuss more about this one in my next lecture, until then have an excellent time. Thank you so much you