Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 19

^{6}Li and ^{7}Li NMR Spectroscopy

So, hello everyone. I once again welcome you all to MSB lecture series on interpretative spectroscopy. In the last couple of lectures, I was discussing about multi nuclear NMR. In the beginning, I gave more emphasis for ^{31}P NMR and also in between I brought other nucleus such as ^{14}N, ^{15}N, ^{19}N. So, let me continue from where I had stopped. Let us look into another interesting example.

So, we will look into the problem shown here. So, let us look at the spectrum below for the compound. Methyl group is there, platinum, ethylene is there and two dimethyl phenyl phosphine ligands are there. So, justify all splitting, cis or trans isomer, and the data given is ^{31}P is 100 percent abundant, I equal to half (I = ½), and of course, ^{195}Pt is NMR active with I equals half (I = ½), and 34 percent abundance is there, and then ^{196}Pt is 66 percent and it is NMR inactive; I equal to 0 (I = 0).

With this information, the information is not given about the spectrum shown here, which spectrum. So, by looking into the spectrum and also by writing all possible isomers for this compound, we should decide whether it is cis or trans. If that is the case which NMR this spectrum represents. So, let me first write this one. So, platinum I can write $PPhMe_2$, this is ethylene.

Other two possibilities are there, and if you consider this trans isomer, both the phosphorous environments are identical because one can perform C2 axis of rotation in this direction along with ethylene platinum CH_3 axis, whereas here I do not think we can perform C2 axis of rotation in this direction or in this direction and to make two phosphorous moieties equivalent. If you consider this one, and now we have to see what

nuclei NMR this figure given here represents. Now, if you look into phosphorous, whether we take this one or we have two take cis, if yes, we should have PP coupling.

So, it should appear as a doublet of doublet. That is not there; the pattern does not look like it belongs to this kind of spectrum. If it is phosphorous NMR and if it is platinum NMR again and this will be first a doublet and then a doublet of doublet and there is a possibility of long range or two bond platinum to hydrogen coupling. Then that would be some sort of satellites or if you take platinum then it should be doublet of doublet of triplets or quartets. So, that is not there. The other option left now is ^{1}H NMR. if we consider ^{1}H NMR, we can identify three different type of environments, apart from phenyl region. One is methyl groups here and then we have CH_3 and then CH_2 is there, and if we exclude phenyl region then we will come across three different type of environments one is for ethylene protons one is for methyl and the other one is for methyl groups present on phosphorus. If you just see that, ^{1}H NMR spectrum if you take and this would couple this ethylene protons equally with two phosphorus atoms to give a triplet, and then each triplet will have satellites and appear like doublet of triplet of doublets and that is the case.

For example, if it splits into a triplet, this I am writing for ethylene protons and then because of platinum coupling we will see something like this. If you look into CH_3 protons, again same case; CH_3 protons will be split by two identical phosphorous into a triplet and then they are further split by platinum showing platinum satellites. It is also identical to what I have drawn here, and when we look into these six protons, they are quite similar. As a result, these twelve protons are there so they split by again phosphorous into triplet and then again platinum is split them into doublet that means we can anticipate, three sets of individual separate triplets in this case. If it is ^{1}H NMR and then they will be having corresponding platinum satellites that is what the spectrum looks like now and you can see that expanded version here one is at -1.10 ppm and other one is -41.2 ppm and other one is 0.083 ppm. So that means without any problem, we can say, this is for CH_3 and this is for methyl groups on phosphorus and this is for ethylene hydrogen atoms. We can say that this is ^{1}H NMR spectrum of this trans phosphorous, ethylene, methyl group containing

platinum compound. Whatever we see here, these are all platinum to hydrogen couplings they come as satellites. So, this is ^{1}H NMR spectrum and it shows for ethylene a triplet and satellites, for methyl group a triplet because of two equivalent phosphorous splitting that into triplet with satellites, and again methyl groups with satellites. So, no doubt, this is ^{1}H NMR spectrum. How one can analyze and interpret the data.

Let us move on to another example here. Let us come back to lithium, we have two isotopes ^{6}Li with I equal to one (I = 1), 7.4 percent abundance, and then other one is ^{7}Li with I equal to 3/2 (I = 3/2) and natural abundance is 92.6 percent. One should remember the fact that those nuclei with I greater than half are quadrupolar and since ^{6}Li has lower quadrupolar moment and yields sharp signals but has low sensitivity. However, in case of ^{7}Li, is highly sensitive but has a higher quadrupolar moment so its signals are always broader and then when we look into chemical shift range, whether you consider seven lithium NMR or six lithium NMR, the range is very similar for both the nuclei. You can see here for lithium amide in ammonia. It comes in this range and then external paratropic contact ions will be in this range and aqueous lithium plus would be around zero and for solvent separated aryl ions also come in the same range. External diatropic aromatic contact ions would also come here, and alkyl lithium would come around here and sandwich diatropic aromatic contact ions would come anywhere between -10 to 15 and also lithium plus ion in ammonia comes around -10. I have given here for LiCl taken in D_2O with natural abundance. In case of six lithium, it comes here as expected as a singlet. Similarly, one can also plot seven lithium NMR for LiCl in D_2O; this also is sharp singlet, you can see here. Here I equal to 3/2 (I = 3/2) but it doesn't matter. This would come only when we are seeing lithium is coupled to other NMR active nuclei. You can see here, spectrum given is for six lithium and then these are not simple lithium compounds that deuterium induced isotropic fingerprints in six lithium NMR spectra of partially deuterated organolithium aggregates that is the reason they look not simple phenyl lithium monomer because of interaction of pi (π) electrons of the carbon that is bound to lithium. They will be having a dimeric structure, something like this, and of course when you take methyl lithium or any alkyl lithium such as tributyl lithium or methyl lithium they will be having cubane type structure with this relationship would be like tetrahedral and in this one each methyl group, lithium is coupled with CH_3 protons to give a 1 : 3 : 3 : 1 triplet, and here they are coupled with methylene protons,

here of course it is not easy to interpret. It looks like it is coupled to two hydrogen atoms. As a result, it is showing a triplet, because these are all partially deuterated, you never know how many CH_2 are there, whether it is CHD and all those things, but from spectrum, it appears that it is coupled with two equivalent hydrogen atoms. As a result, it shows 1 : 2 : 1 triplet, whereas here it is very clear, methyl hydrogen atoms are coupled with lithium to show quartet (1 : 3 : 3 : 1) and here one such lithium reaction is shown here. This was carried out in our group here. What happens, lithiation is very sensitive to temperature and also if other acidic protons are there you can expect the possibility of lithium exchange. Although we replace with halogen exchange process, for example, this bromo compound is taken and when it is treated with n-butyl lithium -78°C and then at the same temperature if you add chloro-diphenylphosphine after lithiation, exocyclic ortho position, here PPh_2 is added and it gives a compound like this. But on the other hand, after adding n-butyl lithium -78°C, it initially form this one, and in case if it is warmed to room temperature for the addition of chloro-diphenylphosphine ($ClPPh_2$), what happens, the moment it is warmed above -78°C , that means when it starts warming up and attain 0 °C or coming to room temperature, lithium exchange takes place with this one and then lithium will move here and H will move here and then if we add chloro-diphenylphosphine ($ClPPh_2$), it goes to trizolic carbon. That means one has to be extremely careful while doing lithium reactions. They are very very sensitive to temperature and if you have some acidic protons nearby, where lithium is on the carbon atom, there can be exchange process and this is one such example where temperature assisted lithium hydrogen exchange takes place. Is it possible to monitor this one? Yes, it can be monitored by looking into ^7Li NMR spectrum. We carried out time dependent ^7Li NMR spectra and series of spectra shown here. Immediately after the addition of n-butyl lithium, what happens it goes through halogen exchange to ortho carbon and with time, you can see here after 6 minutes what happens, another signal is developing towards the right side that means lithium-hydrogen exchange has started and by the time, it attains 1 hour 15 minutes complete exchange takes place and lithium is no longer present on phenyl ortho position; it has moved to trizolic carbon. So, this indicates, sometime this kind of variable temperature assists in understanding, how this process is taking place and why? We expected phosphination at ortho position, whereas we got phosphination on triazolic carbon. So, all this vital information, one can extract

from doing variable temperature NMR studies, not necessarily with lithium, but with any other NMR active nuclei provided it gives a clue about such reactions. Now let us look into another interesting aspect: isomerization. If you just look into this compound here, it is a multidentate ligand and of course the most favored is PP chelation, but on the other hand, we also have this triazolic nitrogen atoms with a pair of electrons on each one so they can also coordinate. When this compound is treated with tetra carbonyl, this pipyridine tungsten compound at room temperature, initially PN coordination takes place and on keeping this in solution for 72 hours, it undergoes isomerization from PN coordination to PP coordination. On the other hand, if you take the same bisphosphine and add molybdenum, here whether it is molybdenum or tungsten in both the cases, the isomerization happens, but in case of tungsten it takes 72 hours, whereas in case of molybdenum within 2 minutes PN bonded compound forms and on storing for 2 hours isomerization completes and it becomes PP coordinated compound. That means again here, whether it is possible to monitor isomerization process, the ligand being PN coordinated initially, to become PP coordinated, isomerization of PN coordination to PP coordination on molybdenum and if you take it initially you can see, 2 signals are there 2 signals can be seen for both uncoordinated phosphorous atoms. since this compound here both the phosphorous atoms are chemically and magnetically non-equivalent and they are farther from each other as a result, you are not seeing any PP coupling, nevertheless they show 2 chemical shifts, that you can see here. Once after adding molybdenum complex to this one, coordination starts immediately, you can see only one chemical shift is there other one is coming somewhere here coordinated. That means one of the phosphorous is left uncoordinated, whereas one of the phosphorous is coordinating. So, you can see here that means here we have a complex where we have PN coordination. Since PN coordination is there, other phosphorous and triazolic carbon are left uncoordinated and only in the uncoordinated region little bit shift is there compared to this one. With time you can see another signal is developing here these 2 are for PP coordinated compound, with time it is increasing and you can after 2 hours within 120 minutes, this isomerization is completed and this is disappearing. Uncoordinated present is disappearing and after 2 hours you can see completely PP coordinated product. We do not have any trace of PN coordinated compound. That means we know now isomerization from PN to PP takes roughly 2 hours,

whereas in case of tungsten it is taking little more time so you can see here to begin with again very similar to molybdenum complex it's uncoordinated both are here within 1 hour what happens one of the triazolic carbon remains uncoordinated where the other one is getting coordinated as a result what happens the PP coordinated and PN coordinated compounds are there and then with the time what happens this is decreasing and then it nearly takes 72 hours for the completion of isomerization from PN to PP. Another advantage with tungsten compound is we can see here the tungsten satellites. Tungsten is also NMR active, and we have very trace quantity here and we are seeing the tungsten satellites and tungsten to phosphorus ^{1}J coupling can vary between 200 to 350 hertz. This also we can see very nicely, the satellites are coming here so that means in case of molybdenum it took 2 hours, whereas in case of tungsten it took 72 hours and that can be clearly seen from this time dependent ^{31}P NMR spectra for the isomerization.

So, let me stop here and continue in my next lecture more interesting examples with emphasis on boron, mercury and even including ^{19}F NMR spectra of some of these mixed NMR nuclei compounds. Until then have an excellent time and enjoy the rest of the lectures. Thank you.