

Introduction

Phosphorus nuclear magnetic resonance (^{31}P NMR) is conceptually the same as proton (^1H) NMR. The ^{31}P nucleus is useful in NMR spectroscopy due to its relatively high gyromagnetic ratio, 17.235 MHz T^{-1} , and a 100% isotopic abundance. Like the ^1H nucleus, the ^{31}P nucleus has a nuclear spin of $\frac{1}{2}$ which makes spectra relatively easy to interpret. ^{31}P NMR is an excellent technique for studying phosphorus containing compounds, such as organic compounds and metal coordination complexes.

Differences Between ^1H and ^{31}P NMR

There are certain significant differences between ^1H and ^{31}P NMR. While ^1H NMR spectra is referenced to tetramethylsilane, the chemical shifts in ^{31}P NMR are typically reported relative to 85% phosphoric acid, which is used as an external standard due to its reactivity.

As in ^1H NMR, positive chemical shifts correspond to a downfield shift from the standard. However, prior to the mid-1970s, the convention was reversed. As a result, older texts and papers report shifts using the opposite sign.

Chemical shifts in ^{31}P NMR commonly depend on the concentration of the sample, the solvent used, and the presence of other compounds. This is true because the external standard does not take into account the bulk properties of the sample. As a result, reported chemical shifts for the same compound could vary by 1 ppm or more, especially for phosphate groups ($\text{P}=\text{O}$).

^{31}P NMR spectra are often recorded with all proton signals decoupled, as is done with ^{13}C NMR. This gives rise to single, sharp signals per unique ^{31}P nucleus. In this chapter, we will consider both coupled and decoupled spectra.

Interpreting Spectra

As in ^1H NMR, phosphorus signals occur at different frequencies depending on the electron environment of each phosphorus nucleus (Table 1). In this section we will study a few examples of phosphorus compounds with varying chemical shifts and coupling to other nuclei.

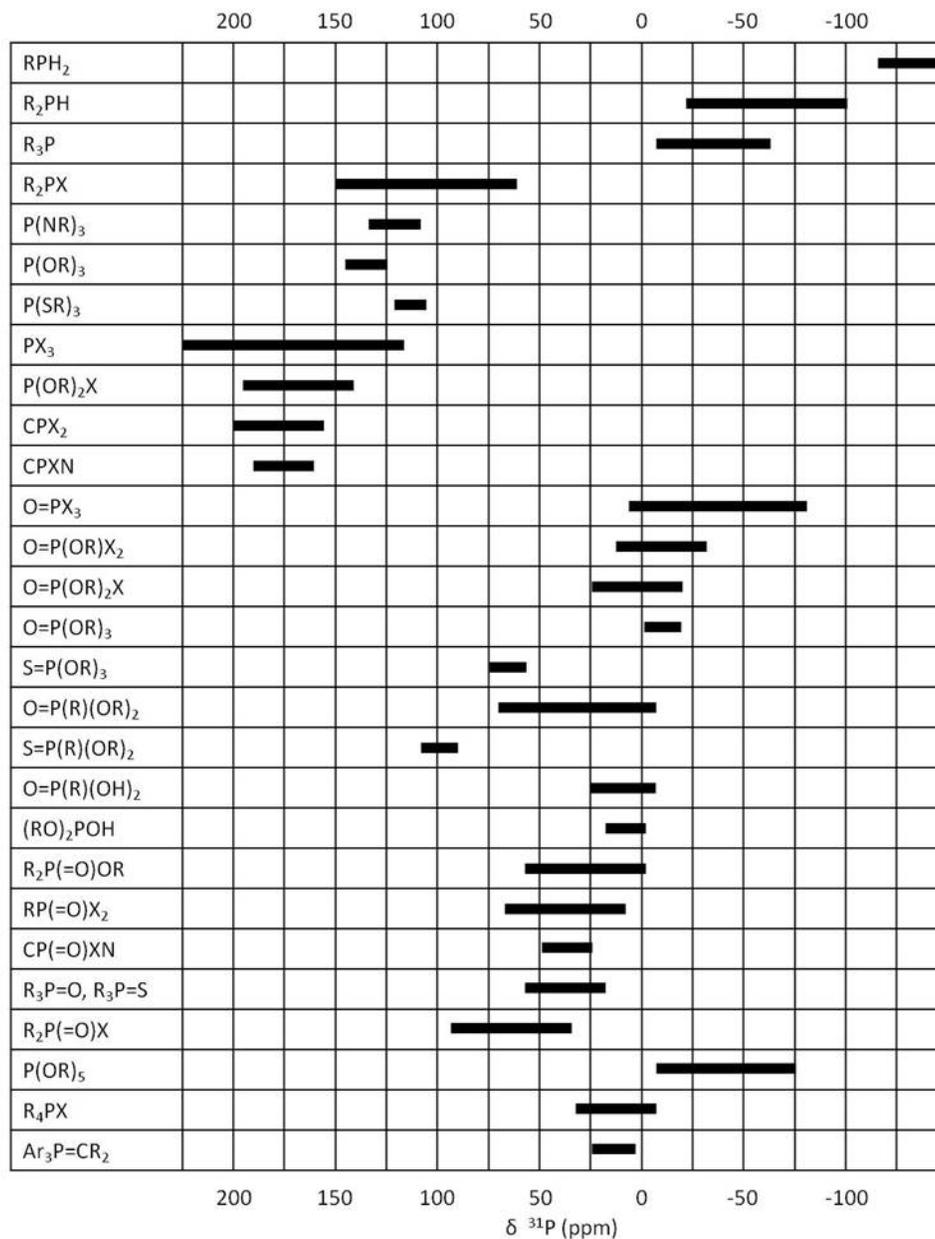


Table 1. Chemical shift ranges for different types of phosphorus compounds.

Example 1 – Different P environments and coupling to ¹H

Consider the structure of 2,6,7-trioxa-1,4-diphospha-bicyclo[2.2.2]octane (P_α(OCH₂)₃P_β) shown in Figure 1. The subscripts α and β are simply used to differentiate the two phosphorus nuclei. According to Table 1, we expect the shift of P_α to be downfield of the standard, roughly around 125 ppm to 140 ppm and the shift of P_β to be upfield of the standard, between -5 ppm and -70 ppm. In the decoupled spectrum shown in Figure 1, we can assign the phosphorus shift at 90.0 ppm to P_α and the shift at -67.0 ppm to P_β.

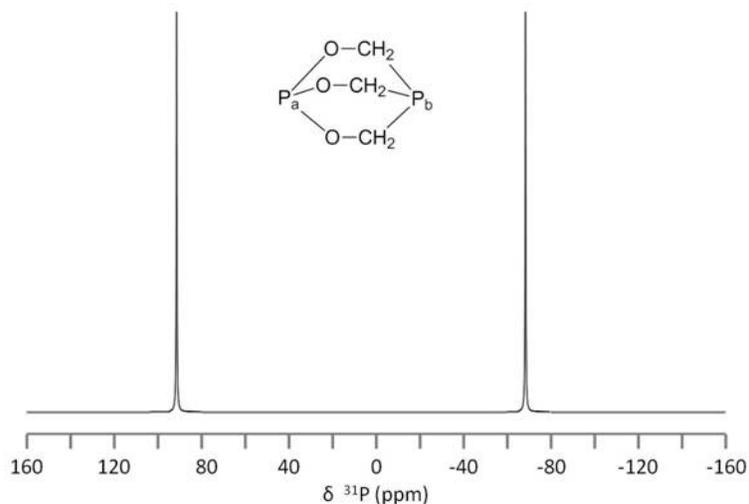


Figure 1. Structure and decoupled ^{31}P spectrum of $\text{P}_\alpha(\text{OCH}_2)_3\text{P}_\beta$.

Figure 2 below shows the coupling of the phosphorus signals to the proton. We expect a stronger coupling for P_β because there are only two bonds separating P_β from H, whereas three bonds separate P_α from H ($J_{\text{PCH}} > J_{\text{POCH}}$). Indeed, $J_{\text{PCH}} = 8.9 \text{ Hz}$ and $J_{\text{POCH}} = 2.6 \text{ Hz}$, corroborating our peak assignments above.

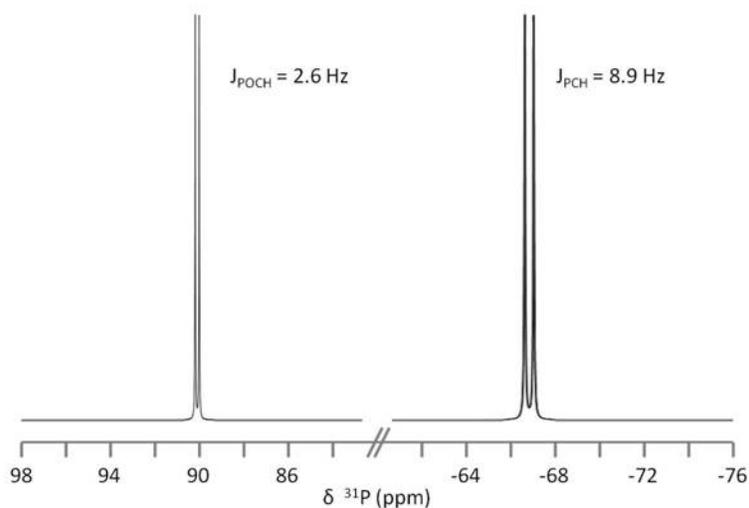


Figure 2. Spin coupling in $\text{P}(\text{OCH}_2)_3\text{P}$

Finally, Figure 3 below is the ^1H spectrum of $\text{P}(\text{OCH}_2)_3\text{P}$, which shows a doublet of doublets for the proton signal due to coupling to the two phosphorus nuclei.

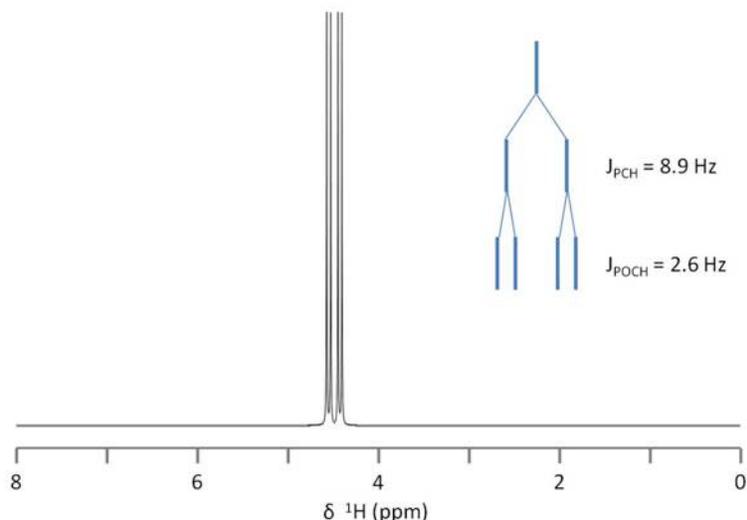


Figure 3. ^1H spectrum of $\text{P}(\text{OCH}_2)_3\text{P}$ and proton splitting pattern due to phosphorus.

As suggested by Table 1 above, we can predict and observe changes in phosphorus chemical shift by changing the coordination of P. Figure 4 shows a variable structure of the compound studied above. Table 2 shows the different chemical shifts corresponding to different phosphorus compounds.

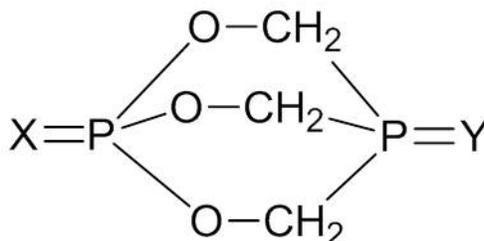


Figure 4. Structure of $\text{XP}_\alpha(\text{OCH}_2)_3\text{P}_\beta\text{Y}$ where X and Y may be O, S, or nothing.

X	Y	P_α chemical shift (ppm)	P_β chemical shift (ppm)
nothing	nothing	90.0	-67.0
O	O	-18.1	6.4
S	nothing	51.8	-70.6

Table 2. ^{31}P chemical shifts for variable coordination of $\text{XP}_\alpha(\text{OCH}_2)_3\text{P}_\beta\text{Y}$ (K. J. Coskran and J. G. Verkade, *Inorg. Chem.*, 1965, **4**, 1655.)

Example 2 – Coupling to F

^{19}F NMR is very similar to ^{31}P NMR in that ^{19}F has spin $\frac{1}{2}$ and is a 100% abundant isotope. As a result, ^{19}F NMR is a great technique for fluorine-containing compounds and allows observance of P-F coupling. The coupled ^{31}P and ^{19}F NMR spectra of

ethoxybis(trifluoromethyl)phosphine, $\text{P}(\text{CF}_3)_2(\text{OCH}_2\text{CH}_3)$, are shown below. Note the splitting due to $J_{\text{PCF}} = 86.6$.

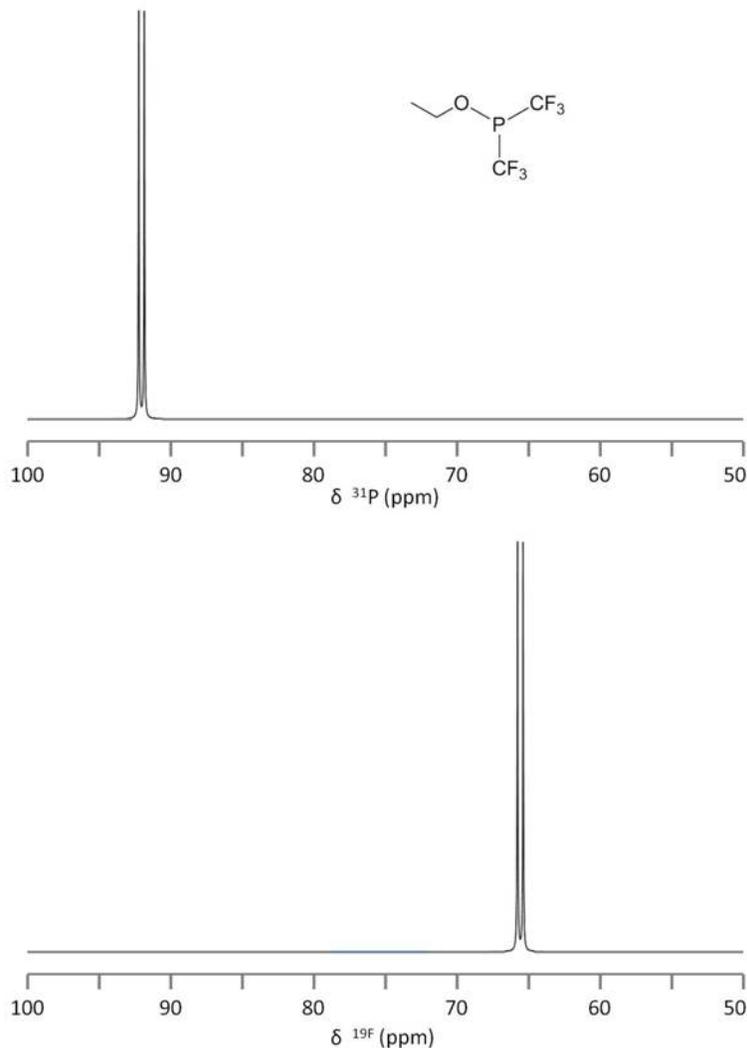


Figure 5. Structure, ^{31}P spectrum (top), and ^{19}F spectrum (bottom) of $\text{P}(\text{CF}_3)_2(\text{OCH}_2\text{CH}_3)$. (K. J. Packer, *J. Chem. Soc.*, **1963**, 960.)

Example 3 – PH coupling

Finally, consider the structure of dimethyl phosphonate, $\text{OPH}(\text{OCH}_3)_2$, shown in Figure 6. Because the phosphorus nucleus is coupled to a hydrogen nucleus bound directly to it – that is, a coupling separated by a single bond – we expect J_{PH} to be very high. Indeed, the separation is so large that one could easily mistake the split peak for two peaks corresponding to two phosphorus nuclei.

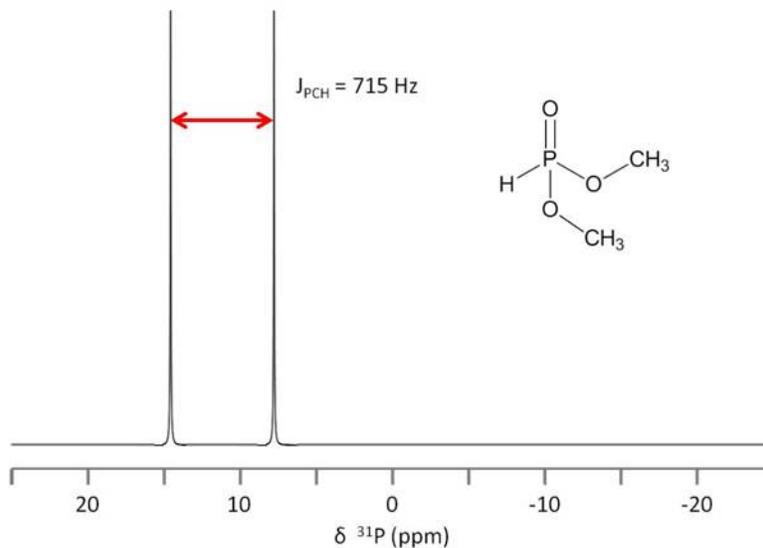


Figure 6. Structure and ^{31}P NMR spectrum of $\text{OPH}(\text{OCH}_3)_2$.

This strong coupling could also lead us astray when we consider the ^1H NMR spectrum of dimethyl phosphonate (Figure 7). Here we observe two very small peaks corresponding to the phosphine proton. The peaks are separated by such a large distance and are so small relative to the methoxy doublet (ratio of 1:1:12), that it would be easy to confuse them for an impurity. To assign the small doublet, we could decouple the phosphorus signal at 11 ppm, which will cause this peak to collapse into a singlet.

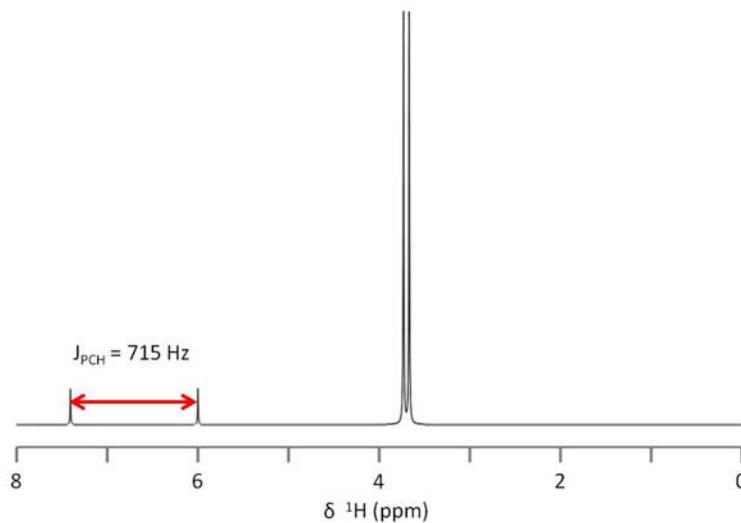


Figure 7. ^1H spectrum of $\text{OPH}(\text{OCH}_3)_2$. (K. Moedritzer, *J. Inorg. Nucl. Chem.*, 1961, **22**, 19).

Obtaining ^{31}P Spectra

Sample Preparation

Unlike ^{13}C NMR, which requires high sample concentrations due to the low isotopic abundance of ^{13}C , ^{31}P sample preparation is very similar to ^1H sample preparation. As in

other NMR experiments, a ^{31}P NMR sample must be free of particulate matter. A reasonable concentration is 2-10 mg of sample dissolved in 0.6-1.0 mL of solvent. If needed, a solution can be filtered through a small glass fiber. Note that the solid will not be analyzed in the NMR experiment.

Unlike ^1H NMR, however, the sample need **not** be dissolved in deuterated solvent since solvents do not have ^{31}P nuclei to contribute to spectra. This is true, of course, only if a ^1H NMR spectrum is not to be obtained from this sample. Being able to use nondeuterated solvents offers many advantages to ^{31}P NMR, such as the simplicity of assaying purity and monitoring reactions, which will be discussed later.

Instrument Operation

Instrument operation will vary according to instrumentation and software available. However, there are a few important aspects to instrument operation relevant to ^{31}P NMR.

The instrument probe, which excites nuclear spins and detects chemical shifts, must be set up appropriately for a ^{31}P NMR experiment. For an instrument with a multinuclear probe, it is a simple matter to access the NMR software and make the switch to a ^{31}P experiment. This will select the appropriate frequency for ^{31}P . For an instrument which has separate probes for different nuclei, it is imperative that one be trained by an expert user in changing the probes on the spectrometer.

Before running the NMR experiment, consider whether the ^{31}P spectrum should include coupling to protons. Note that ^{31}P spectra are typically reported with all protons decoupled. This is typically the default setting for a ^{31}P NMR experiment. To change the coupling setting, follow the instructions specific to your NMR instrument software.

As mentioned previously, chemical shifts in ^{31}P NMR are reported relative to 85% phosphoric acid. This must be an external standard due to the high reactivity of phosphoric acid. One method for standardizing an experiment uses a coaxial tube inserted into the sample NMR tube (Figure 8). The 85% H_3PO_4 signal will appear as part of the sample NMR spectrum and can thus be set to 0 ppm.

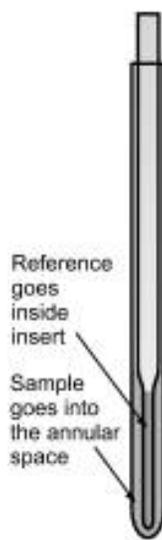


Figure 8. Diagram of NMR tube with inserted coaxial reference insert.

Another way to reference an NMR spectrum is to use a 85% H_3PO_5 standard sample. These can be prepared in the laboratory or purchased commercially. To allow for long term use, these samples are typically vacuum sealed, as opposed to capped the way NMR samples typically are. The procedure for using a separate reference is as follows.

1. Insert NMR sample tube into spectrometer.
2. Tune the ^{31}P probe and shim the magnetic field according to your individual instrument procedure.
3. Remove NMR sample tube and insert H_3PO_4 reference tube into spectrometer.
4. Begin NMR experiment. As scans proceed, perform a fourier transform and set the phosphorus signal to 0 ppm. Continue to reference spectrum until the shift stops changing.
5. Stop experiment.
6. Remove H_3PO_4 reference tube and insert NMR sample into spectrometer.
7. Run NMR experiment without changing the referencing of the spectrum.

^{31}P NMR Applications

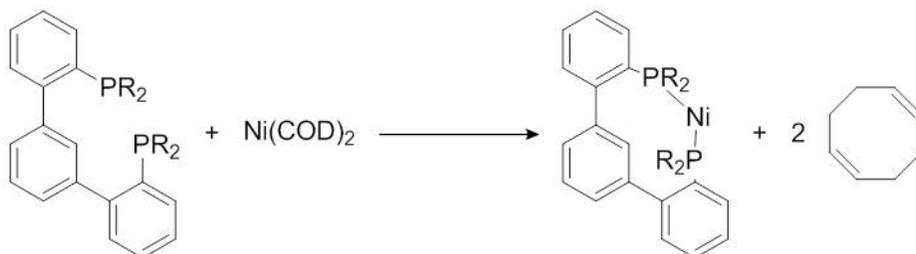
Assaying Sample Purity

^{31}P NMR spectroscopy gives rise to single sharp peaks that facilitate differentiating phosphorus-containing species, such as starting materials from products. For this reason, ^{31}P NMR is a quick and simple technique for assaying sample purity. Beware, however, that a “clean” ^{31}P spectrum does not necessarily suggest a pure compound, only a mixture free of phosphorus-containing contaminants.

^{31}P NMR can also be used to determine the optical purity of a chiral sample. Adding an enantiomer to the chiral mixture to form two different diastereomers will give rise to two unique chemical shifts in the ^{31}P spectrum. The ratio of these peaks can then be compared to determine optical purity.

Monitoring Reactions

As suggested in the previous section, ^{31}P NMR can be used to monitor a reaction involving phosphorus compounds. Consider the reaction between a slight excess of organic diphosphine ligand and a nickel(0)biscyclooctadiene (Scheme 1).



Scheme 1. Reaction between terphenyl diphosphine ligand and nickel(0)biscyclooctadiene to form a nickel diphosphine complex and free cyclooctadiene.

The reaction can be followed by ^{31}P NMR by simply taking a small aliquot from the reaction mixture and adding it to an NMR tube, filtering as needed. The sample is then used to acquire a ^{31}P NMR spectrum and the procedure can be repeated at different reaction times. The data acquired for these experiments is found in Figure 9.

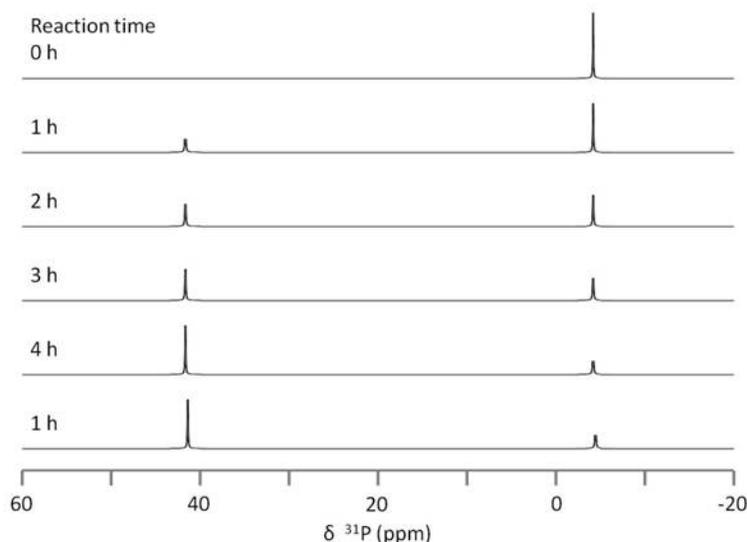


Figure 9. NMR spectra of the reaction of diphosphine ligand with nickel(0)biscyclooctadiene to make a diphosphine nickel complex over time.

The changing in ^{31}P peak intensity can be used to monitor the reaction, which begins with a single signal at -4.40 ppm corresponding to the free diphosphine ligand. After an hour, a new signal appears at 41.05 ppm, corresponding to the diphosphine nickel complex. The downfield peak grows as the reaction proceeds relative to the upfield peak. No change is observed between four and five hours, suggesting the conclusion of the reaction.

There are a number of advantages for using ^{31}P for reaction monitoring when available as compared to ^1H NMR:

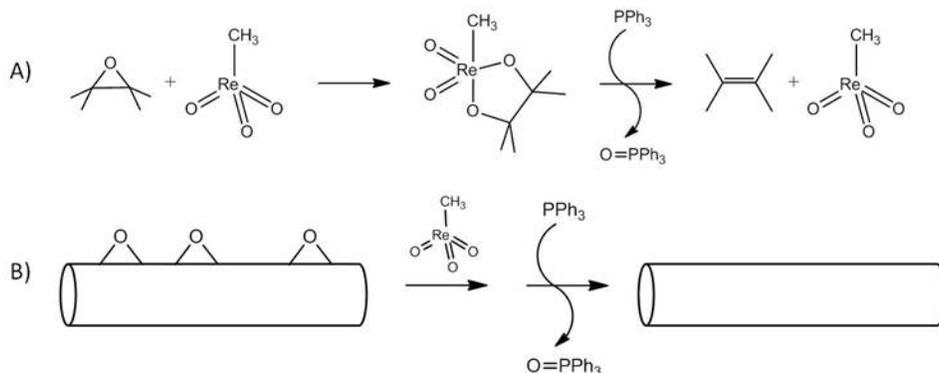
- There is no need for a deuterated solvent, which simplifies sample preparation and saves time and resources.
- The ^{31}P spectrum is simple and can be analyzed quickly. The corresponding ^1H NMR spectra for the above reaction would include a number of overlapping peaks for the two phosphorus species as well as peaks for both free and bound cyclooctadiene ligand.
- Purification of product is also easily assayed.

^{31}P NMR does not eliminate the need for ^1H NMR characterization, as impurities lacking phosphorus will not appear in a ^{31}P experiment. However, at the completion of the reaction, both the crude and purified products can be easily analyzed by both ^1H and ^{31}P NMR spectroscopy.

Measuring Epoxide content of nanomaterials.

One can measure the amount of epoxide on nanomaterials such as carbon nanotubes and fullerenes by monitoring a reaction involving phosphorus compounds as shown above.

This technique uses the catalytic reaction of methyltrioxorhenium (Scheme 2A). An epoxide reacts with methyltrioxorhenium to form a five membered ring. In the presence of triphenylphosphine (PPh_3), the catalyst is regenerated, forming an alkene and triphenylphosphine oxide (OPPh_3).



Scheme 2. A) Reaction of an epoxide with methyltrioxorhenium in the presence of triphenylphosphine. B) Schematic showing the process of quantification of epoxide on a carbon nanotube. (Adapted from A. R. Barron lecture, February 2013)

The same reaction can be applied to carbon nanostructures and used to quantify the amount of epoxide on the nanomaterial (Scheme 2B). Because the amount of initial PPh_3 used in the reaction is known, the relative amounts of PPh_3 and OPPh_3 can be used to stoichiometrically determine the amount of epoxide. ^{31}P NMR spectroscopy is used to determine the relative amounts of PPh_3 and OPPh_3 (Figure 10).

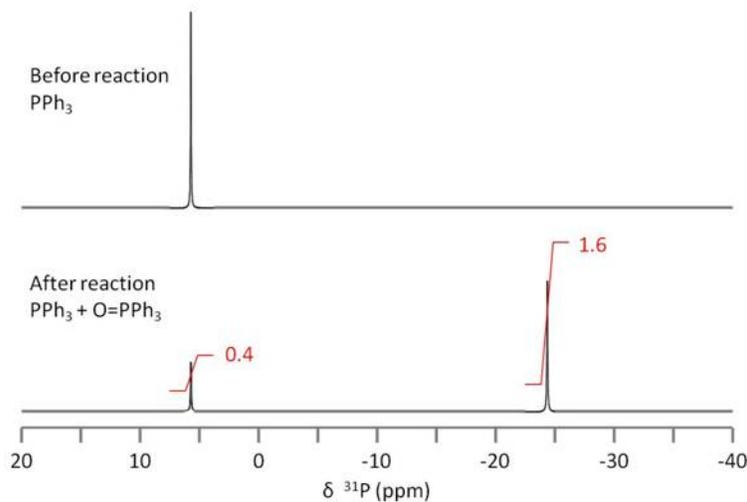


Figure 10. ^{31}P spectrum of experiment before addition of Re complex (top) and at the completion of experiment (bottom).

The integration of the two ^{31}P signals is used to quantify the amount of epoxide on the nanotube according to the following equation:

$$\text{moles of epoxide} = \frac{\text{area of OPPh}_3 \text{ peak}}{\text{area of PPh}_3 \text{ peak}} \times \text{moles of PPh}_3$$

Thus, from a known quantity of PPh_3 , one can find the amount of OPPh_3 formed and relate it stoichiometrically to the amount of epoxide on the nanotube. Not only does this experiment allow for such quantification, it is also unaffected by the presence of the many different species present in the experiment. This is because the compounds of interest, PPh_3 and OPPh_3 , are the only ones that are characterized by ^{31}P NMR spectroscopy.

Conclusion

^{31}P NMR spectroscopy is a simple technique that can be used alongside ^1H NMR to characterize phosphorus-containing compounds. When used on its own, the biggest difference from ^1H NMR is that there is no need to utilize deuterated solvents. This advantage leads to many different applications of ^{31}P NMR, such as assaying purity and monitoring reactions.

References

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