

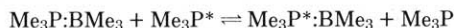
A Change in the Sign of an NMR Coupling Constant

An advanced undergraduate experiment

An understanding of the phenomenon that nmr coupling constants have a sign associated with them is an integral part of understanding the nuclear magnetic resonance experiment. However, normally the sign of a coupling constant is manifest only either in certain decoupling experiments or in second-order spectra, both of which are rather abstract to the beginning student. The experiment described herein graphically demonstrates a change in the sign of the P—C—H coupling constant, $^2J_{P-H}$, between trivalent phosphorus and tetra-valent phosphorus. The samples yield first-order 1H spectra that are recorded at ambient spectrometer temperature with no decoupling.

Discussion

The exchange reaction of the Lewis acid-base complex $Me_3P:BMe_3$ with excess Me_3P



has been shown to proceed by a dissociative mechanism (1, 2). At ambient temperature these exchange reactions are rapid on the nmr time scale. Thus the 1H nmr spectrum of the complex plus excess Me_3P does not yield separate phosphorus methyl proton peaks for both the complexed and the free Me_3P , but rather a single doublet is observed that is an average of the quantity of complexed and free Me_3P . The doublet arises from spin-spin coupling between the protons and the phosphorus nucleus (for ^{31}P , $I = 1/2$, 100% natural abundance). Additionally, and of integral importance to the experiment, the coupling between the phosphorus methyl protons and the phosphorus nucleus is also a weighted average between $^2J_{P-H}$ in $Me_3P:BMe_3$ and $^2J_{P-H}$ for free Me_3P . The coupling $^2J_{P-H}$ in trivalent phosphorus compounds such as Me_3P has been shown to be positive (2, 3), while $^2J_{P-H}$ for tetravalent phosphorus compounds is of opposite sign, i.e. negative. Thus the average $^2J_{P-H}$ in the system $Me_3P:BMe_3 + Me_3P$ involves both positive and negative coupling constants.

Figure 1a is an 1H nmr spectrum at ambient temperature of Me_3P in cyclohexane, showing the doublet (2.8 Hz) for $^2J_{P-H}$. Figure 1b shows the spectrum of Me_3P and BMe_3 in a mole ratio of 1/2.5, which can also be considered to be $Me_3P:BMe_3$ and PMe_3 in a mole ratio of 1/1.5. Only a single doublet is observed for the protons of Me_3P due to the rapid averaging of the free and complexed forms. The resonance is shifted downfield due to the deshielding of the protons as the phosphorus atom coordinates to the Lewis acid BMe_3 . (The methyl protons of BMe_3 are upfield and are broadened by the quadrupolar boron nucleus.) Not only are the protons of the phosphorus methyls chemical shift averaged between the amount of free Me_3P and $Me_3P:BMe_3$, but also the coupling constant $^2J_{P-H}$ is averaged. Since $^2J_{P-H}$ undergoes a sign change between three coordinate phosphorus in Me_3P and four coordinate phosphorus in $Me_3P:BMe_3$, then at an appropriate stoichiometry when Me_3P and $Me_3P:BMe_3$ are undergoing rapid exchange, the average coupling constant will be zero. An average coupling constant $^2J_{P-H}$ will be zero at a BMe_3/PMe_3 mole ratio of about 1/4 (since $^2J_{P-H}$ in $Me_3P = +2.8$ Hz and $^2J_{P-H}$ in $Me_3P:BMe_3 = -9.0$ Hz). When the mole ratio exceeds 1/4, then the average coupling constant will be again manifest. Figure 2 shows the changes that occur in the appearance of the protons of the phosphorus methyl groups with progressive addition of BMe_3 to Me_3P . Figure 2g

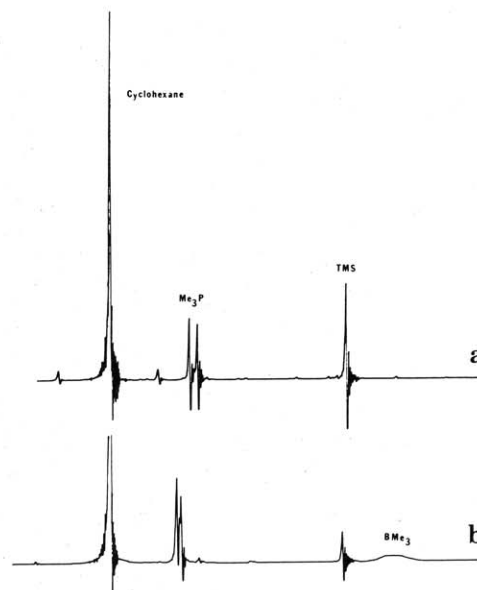


Figure 1. (a) 1H nmr of 1.7 M Me_3P in cyclohexane solvent. (b) 1H nmr spectrum of BMe_3 and Me_3P in a mole ratio of 1/2.5 ($BMe_3 \sim 0.80$ M). Sweep width 500 Hz.

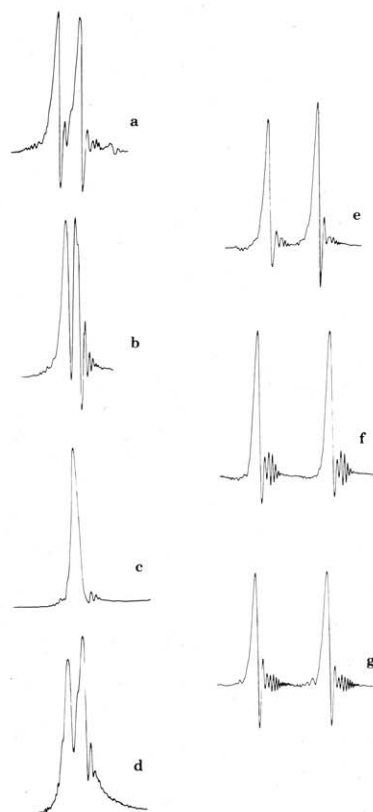


Figure 2. 1H nmr resonance of Me_3P in the system $BMe_3 + PMe_3$ with: (a) BMe_3/Me_3P , 0.100; (b) BMe_3/Me_3P , 0.12/1.00; (c) BMe_3/Me_3P , 0.24/1.00; (d) BMe_3/Me_3P , 0.40/1.00; (e) BMe_3/Me_3P , 0.77/1.00; (f) BMe_3/Me_3P , 1.00/1.00; (g) BMe_3/Me_3P , 2.00/1.00.

represents total complexation of Me_3P with BMe_3 with a full mole ratio excess of Me_3B , i.e. a 2/1 mole ratio of BMe_3 to Me_3P . Figure 3a is a plot of the coupling constant $^2J_{\text{P-H}}$ versus the mole ratio of Me_3B to Me_3P . It is clear that the average coupling constant progresses from +2.8 Hz for free Me_3P , to zero for a 1/4 mole ratio and finally to -9.0 Hz for the totally complexed Me_3P . The chemical shift (from internal cyclohexane solvent) also undergoes a linear change as the Me_3P is complexed (Fig. 3b). It should be noted also that the protons of the boron methyl groups in $\text{Me}_3\text{P}:\text{BMe}_3$ are shifted upfield from free BMe_3 due to the extra shielding provided by the phosphorus lone pair of electrons. However, when there is more BMe_3 than Me_3P , as in Figure 2g, the boron methyl resonance will be shifted downfield because the resonance will be a weighted average of the chemical shifts of free and complexed BMe_3 .

Experimental

Trimethylborane, BMe_3 (4), and trimethylphosphine, Me_3P (5), can be either synthesized or purchased. (CAUTION: Trimethylborane and trimethylphosphine are pyrophoric and toxic. They should be used only on a standard high vacuum line.) The compound BMe_3 and Me_3P are introduced into an accurately calibrated high vacuum line using standard techniques (6), very similar to the experiment in Angelici's text describing the preparation of the Lewis acid-base complex $\text{Me}_3\text{N}:\text{BF}_3$ (7). The appropriate quantities of Me_3P and BMe_3 are measured using the ideal gas law and are transferred by condensation with liquid N_2 into an nmr tube that is attached to the vacuum line. Appropriate quantities of Me_3P and BMe_3 that will yield high resolution spectra in a medium wall nmr tube are: tube 1, 0.50 mmole Me_3P ; tube 2, 0.08 mmole BMe_3 and 0.67 mmole Me_3P ; tube 3, 0.16 mmole BMe_3 and 0.67 mmole Me_3P ; tube 4, 0.27 mmole BMe_3 and 0.67 mmole Me_3P ; tube 5, 0.52 mmole BMe_3 and 0.67 mmole Me_3P ; tube 6, 0.67 mmole BMe_3 and 0.67 mmole Me_3P ; and tube 7, 0.80 mmole BMe_3 and 0.40 mmole Me_3P . Sufficient solvent should be condensed into each nmr tube to yield solutions that are 1.0–2.0 M: in our samples, we used 0.33 ml of purified cyclohexane. Cyclohexane is an ideal inert solvent because of high solubility of the acid, base, and complex, and because it provides a good internal standard for chemical shift measurements. Chlorinated hydrocarbon solvents have been shown to react with Me_3P , and benzene often causes anisotropic chemical shifts. Sealed nmr tubes prepared as described are stable indefinitely. Other Lewis acids besides BMe_3 that undergo rapid exchange in solution with Me_3P can be used also, such as other boranes or organoaluminums (8). However, BMe_3 is ideal because it is convenient to use on the vacuum line, and it has no ^1H nmr resonances that interfere with the Me_3P resonance.

Each nmr sample should be recorded on two scales, one of which allows for accurate measurement of the chemical shift of the Me_3P resonance relative to the internal standard cyclohexane, e.g. 500 Hz, and one of which allows for accurate measurement of the Me_3P coupling constant, e.g. 100 Hz. A plot similar to Figure 3 should be made using the data collected.

Conclusion

This experiment demonstrates the very important phenomena in nmr spectroscopy of the sign of coupling constants. No decoupling or variable temperature accessories are re-

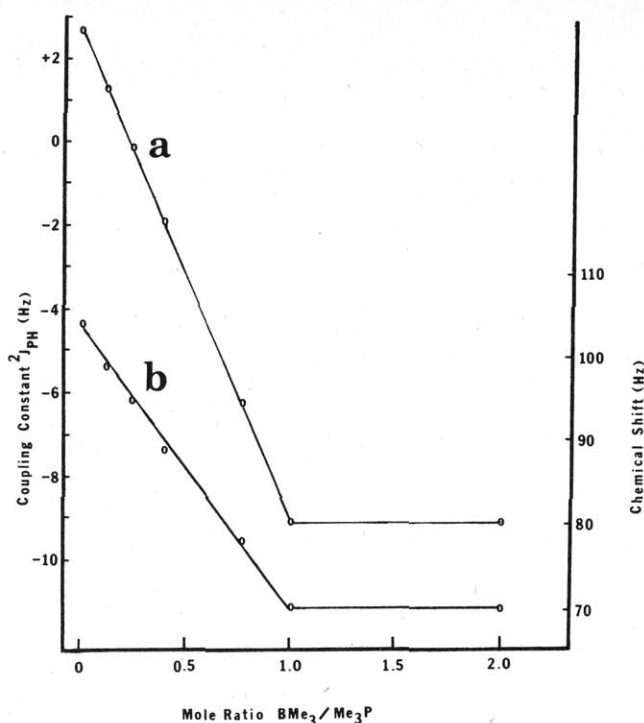


Figure 3. (a) Plot of $^2J_{\text{P-H}}$ (Hz) and (b) Chemical shift (Hz) from cyclohexane solvent versus mole ratio $\text{BMe}_3/\text{Me}_3\text{P}$ in the system $\text{BMe}_3 + \text{Me}_3\text{P}$.

quired. The nmr experiment can be performed in conjunction with high vacuum line preparations, or the samples can be prepared in advance in sealed nmr tubes and stored indefinitely, requiring the student simply to record the spectra and graph the results.

Acknowledgment

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