Nuclear Magnetic Resonance is a powerful tool, especially for the identification of hitherto unknown organic compounds. $^1$H- and $^{13}$C-NMR spectroscopy is known and applied by virtually every synthetically working Organic Chemist. Consequently, the factors governing the differences in chemical shift values, based on chemical environment, bonding, temperature, solvent, pH, etc., are well understood, and specialty methods developed for almost every conceivable structural challenge. Proton and carbon NMR spectroscopy is part of most bachelors degree courses, with advanced methods integrated into masters degree and other graduate courses.

In view of this universal knowledge about proton and carbon NMR spectroscopy within the chemical community, it is remarkable that heteronuclear NMR is still looked upon as something of a curiosity. Admittedly, most organic compounds contain only nitrogen, oxygen, and sulfur atoms, as well as the obligatory hydrogen and carbon atoms, elements that have an unfavourable isotope distribution when it comes to NMR spectroscopy. Each of these three elements has a dominant isotope: $^{14}$N (99.63% natural abundance), $^{16}$O (99.76%), and $^{32}$S (95.02%), with $^{16}$O, $^{32}$S, and $^{34}$S (4.21%) NMR silent. $^{14}$N has a nuclear moment $I=1$ and a sizeable quadrupolar moment that makes the NMR signals usually very broad and difficult to analyse.

There are quite a few less common heteronuclei, particularly in Elementorganic Chemistry, with highly important applications in catalysis, C—C and C—N bond forming reactions, Medicinal Chemistry, Pharmacy, Green Chemistry and natural product synthesis, to name a few, that would make studying their NMR spectroscopy highly beneficial to that part of the chemical community that occupies itself with the research, production, and distribution of these chemicals.

In particular, $^{31}$P (100%), $^{19}$F (100%), $^{11}$B (80.42%), and, to a lesser extent, $^{27}$Al (100%), $^{29}$Si (4.70%), and $^{195}$Pt (33.8%) are arguably the most important heteronuclei in NMR spectroscopy. There are excellent books and reviews available that deal with some regions of the chemical shift range of these heteronuclei, together with a plethora of highly theoretical books and reviews on all aspects of instrumentation, algorithms, Hamiltonians, pulse sequences, etc., which may be very beneficial to the technician or the NMR specialist, but which are almost meaningless to the Synthetic Chemist. The Synthetic Chemist is interested in the identification of a compound, and thus uses the chemical shifts as a means to establish a link to the heteronucleus contained in the compound, and needs a
means of identifying a chemical shift value that bears the structural aspects of his/her proposed compound.

Heteronuclear NMR is highly useful in this context, since a given compound normally contains only very few atoms of this nucleus, making the spectrum relatively simple, especially when compared to carbon or proton NMR.

Simplicity is needed in explaining the very complex field of phosphorus NMR to the non-specialist, and the Synthetic Chemist in particular. Simplicity is also the main shortcoming of this book; complex explanations are sometimes deliberately and necessarily oversimplified to keep the book in perspective and the intended reader in sight. I am far from apologetic in this regard, since I believe that it is better to teach 99 students to be right most of the time than just one to be completely right all of the time.

It is the primary aim of this book to enable the reader to identify the main factors governing the phosphorus chemical shift values in the $^{31}$P-NMR spectrum, and to make an educated guess as to where the phosphorus resonance(s) of a given target compound can be expected. It is not within the scope of this book to enable one to predict a phosphorus chemical shift precisely, or even within a reasonable margin of error, with a few notable exceptions.

Whereas proton and carbon NMR spectroscopy is largely governed by $\sigma$-bonding contributions or well-defined $\pi$-bonded units, the influence of $\pi$-bonding interactions (hyperconjugation, negative hyperconjugation, and $\pi$-donor bonds) on the phosphorus chemical shifts is much more frequent and larger in magnitude. There are frequently no simple empirical formulae to describe the chemical environment of phosphorus atoms, making a quantitative calculation very complex and impractical. In fact, most theoretical computations of phosphorus chemical shifts take days, if not weeks, and plenty of financial and instrumental resources to produce the same (or worse) results as the educated guess of a seasoned researcher in the field.

The further intent of this book is to assist the reader in determining important issues, such as bond order, $\pi$-bonding contributions from substituents, the existence or non-existence of metalla cycles, etc.; in short, to make structural assignments without the aid of X-ray crystal structure determinations or theoretical chemists, and to explain structural differences in solution and the solid state where appropriate.

I regret that the book requires a good knowledge of organometallic chemistry for those chapters dealing with phosphorus ligands and substituents bonded to metal atoms. Those whose research takes them into the realm of metal coordinated phosphorus compounds undoubtedly already possess this knowledge. For those who read on out of curiosity, my best advice to them is to peruse one of the many excellent textbooks available in that field.
Phosphorus-31 NMR Spectroscopy
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