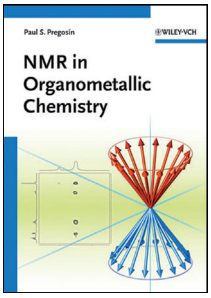
NMR in Organometallic Chemistry

This book is a comprehensive guide to applications of NMR spectroscopy in organometallic chemistry, written by Paul Pregosin, a recognized expert in both fields. NMR spectroscopy is a central analytical technique of organometallic chemistry. Nevertheless, among beginners in its use, a lack of proper understanding of the underlying principles is rather common. Consequently, NMR techniques are not always used to their full potential, and the spectroscopic features are not always fully understood. With this publication, Pregosin has produced a unique resource to address the needs of many researchers working with metal complexes.

After a brief introduction, the book provides several chapters dealing with the main topics: the fundamentals (Chapter 2), 2D correlation spectroscopy (Chapter 3), NOE spectroscopy (Chapter 4), diffusion measurements (Chapter 5), chemical shifts (Chapter 6), coupling constants (Chapter 7), and analysis of dynamic phenomena (Chapter 8). At the end of the book, the reader finds a useful summary of standard organometallic transformations, followed by more than 50 spectroscopic problems based on real-life examples of organometallic compounds and their reactions.

The introduction is written as a conventional overview describing the general approach taken by chemists when applying NMR spectroscopy to organometallic problems. Strangely, Pregosin voices a somewhat defeatist opinion here, by saying that "a unique structural assignment cannot usually [!] be made" on the basis of NMR data. The "most common reasons" for NMR measurements are given as 1) monitoring/studying reactions, and 2) recognizing new structural features of the products. Without disagreeing with the latter, the former statement is questionable. I believe that, in the hands of an experienced user, NMR spectroscopy is the prime method of structural elucidation of organometallic compounds, usually providing conclusive structural evidence.

Chapter 2 of the book discusses chiefly (and quite appropriately) NMR relaxation. Magnetic relaxation is at the heart of NMR spectroscopy, as the NMR spectra are emissions from relaxing nuclear spins, which are routinely collected in the form of the FIDs (free induction decay signals). The neglect (or poor understanding) of the relaxation phenomena is widespread, and Pregosin fills the gap by providing here a concise account of magnetic relaxation, nicely illustrated by carefully chosen examples.



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Chapter 2 might have been more logically followed by Chapters 4 and 5, since they are largely devoted to applications of relaxation phenomena: NOE (nuclear Overhauser effect) and PGSE (pulsed gradient spin-echo) studies. Both Chapters 4 and 5 contain focused, yet informative, theoretical introductions, followed by insightful examples and practical comments.

Chapter 3 deals with the applications of 2D correlation experiments. 2D techniques are arguably less important in organometallic chemistry than in organic chemistry or biochemistry. Pregosin rightly notes that for "a simple complex" it is often sufficient to inspect the chemical shifts, integrals, and couplings. Chapter 3 outlines the strategy for dealing with "complicated problems"; it introduces the COSY and HMQC pulse sequences and explains some of the technical aspects of 2D NMR. As is general throughout the book, this chapter is well illustrated by relevant organometallic examples, mostly dealing with the uses of HMQC and HMBC experiments.

Chapters 6 and 7, devoted to chemical shifts and coupling constants respectively, are the central parts of the book and occupy 55 % of it. The theory of chemical shifts is briefly discussed, with due emphasis placed on the paramagnetic contribution as the dominant part of the screening (shielding) constant for nuclear spins of main group and metal elements. Pregosin appropriately warns the reader against trying "to interpret ^{13}C, ^{15}N, or ^{31}P, etc., chemical shifts using concepts such as local electron density". The discussion of Chapter 6 is naturally subdivided into sections according to spin species: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and metals. The characteristic shifts are discussed thoroughly, also providing a wealth of reference information for typical examples of coordination compounds. For example, the discussion of ^{1}H shifts includes hydrides and dihydrogen ligands, and the protons of alkyls, η^2-olefins, η^6-arenes, allyls, and cyclopentadienyl and carbene ligands. The sections on chemical shifts of Main Group elements and metals are similarly comprehensive and rich in experimental details.

Chapter 7 first addresses the theory of one-bond spin–spin interactions and gives examples of chemical applications of ^{1}J couplings. The topics discussed include the variation of one-bond couplings between different spins encountered in organometallic compounds, and the factors affecting the magnitude of ^{1}J. Structurally important examples of one-bond couplings include ^{1}J(H,D) in dihydrogen complexes and ^{1}J(C/Si,H) in compounds with C−H and Si−H agostic interactions. Also discussed in this part is the relationship between the *trans* influence and the one-bond coupling to the central metal nucleus in square-planar and octahedral complexes of Rh and Pt. The rest of Chapter 7 is devoted to two- and three-bond couplings, with much attention given to the angular dependence of such couplings as diagnostic of the ligand arrangement and complex stereochemistry.

Chapter 8 on dynamics concludes the main material of the book. This chapter provides concise but well-illustrated introductions to the line shape analysis of variable-temperature NMR spectra, magnetization transfer techniques, and the use of the 2D NOESY experiment for studying chemical exchange. At the end of the book, the reader finds a beautiful collection of spectroscopic problems (with solutions), which should provide hours of entertainment for the enthusiast of organometallic NMR, as well as many instructive opportunities to apply the information presented throughout the book to solving real-life spectroscopic problems of organometallic chemistry.

While reading the book, I noticed a relatively large number of technical problems. These ranged from many typographical errors (e.g., occasional appearance of T_I instead of T_1, σ-H instead of *o*-H in Figure 3.17, Pl instead of Pt in Figure 3.18, and NCy_2 instead of PCy_2 in Compound 7.43, etc.) to more serious problems, such as the missing of the irradiated spectra from Figure 4.1. The adoption by Pregosin of the IUPAC-recommended term "high-frequency shift" for a downfield shift makes me uncomfortable. On another point, several references to ligands with a strong *trans* influence as "strong donors" instead of strong ligands (e.g., "the hydride is a relatively strong donor" on page 232) are potentially confusing, if understood literally as references to the electron-donor properties of the ligands.

In summary, I would encourage all organometallic chemists to explore the new book. In the preface, the author presents his work as "designed for PhD and postdoctoral chemistry students". In fact, I am confident that all generations of experimental chemists working with coordination compounds—from the beginners to experts in the field—will find reading the new book useful, instructive, and entertaining.

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