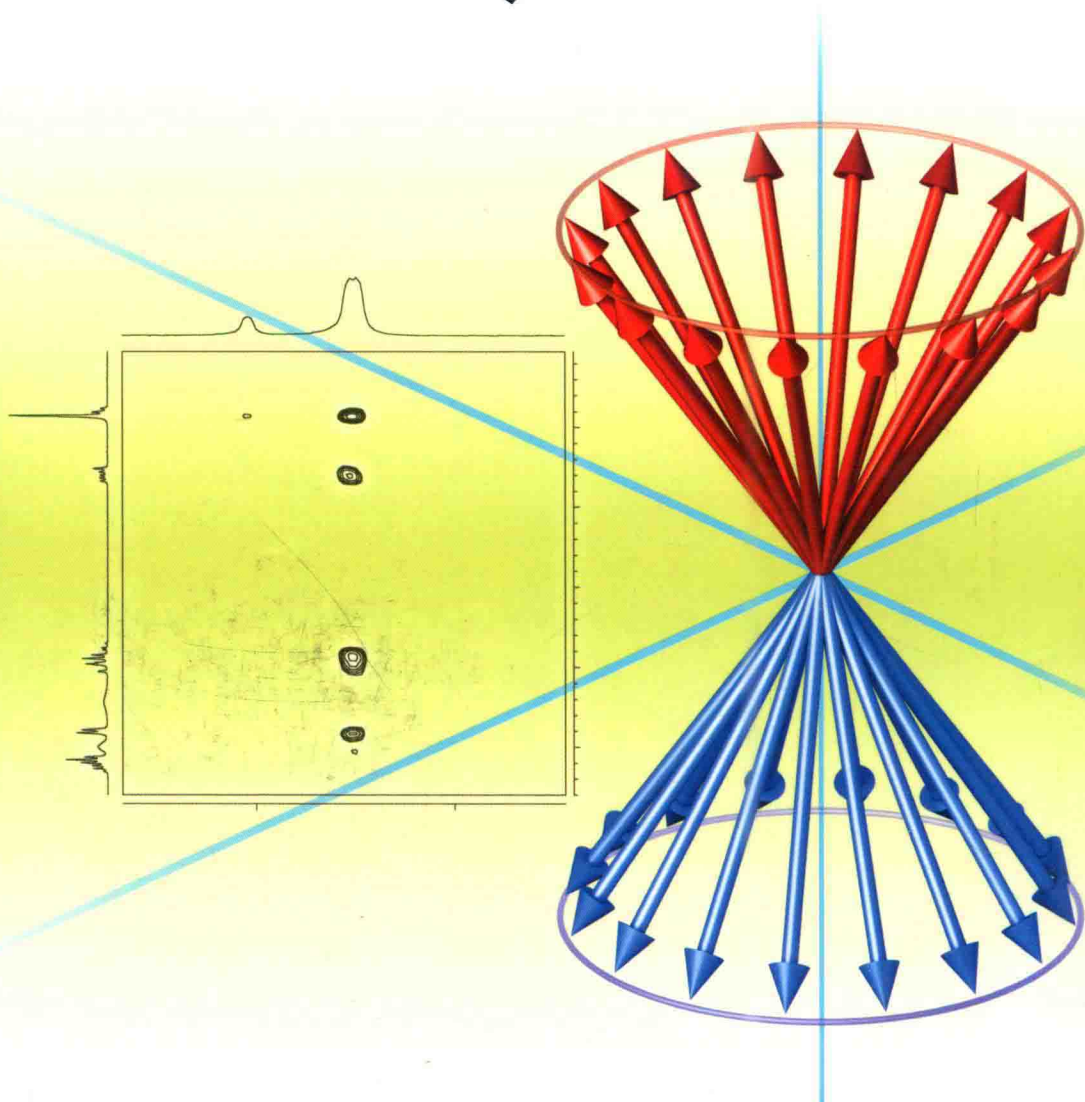


Paul S. Pregosin

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NMR in Organometallic Chemistry



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This book is dedicated, first and foremost, to my wife Carole-Joyce, without whose support and understanding, it would never have appeared and also to the memory of Prof. L. M. Venanzi.

Preface

Multinuclear NMR spectroscopy is without doubt a major contributor to elucidating molecular structure in solution. Coordination and organometallic chemists routinely measure hundreds (if not thousands) of NMR spectra every day. Nevertheless, there are very few books devoted to the NMR characteristics of these metal complexes. Further, although many of the NMR details connected with these measurements are closely related to those associated with the ^1H and ^{13}C characteristics of organic or biological molecules, there are some important and unique differences arising due to complexation of an organic molecule to a transition metal.

In this text, designed for PhD and postdoctoral chemistry students, I discuss many (but certainly not all) of the multinuclear NMR parameters that are most relevant for transition metal organometallic chemists. There will be a strong emphasis on routine measurements, that is, ^1H and ^{13}C NMR, but there are a number of readily measurable spin = 1/2 nuclei such as ^{15}N , ^{19}F or ^{31}P , that afford structurally valuable chemical shifts, plus diagnostic spin-spin coupling constants. Measurements on these nuclei are important since coordination chemists need to understand the immediate environment of the metal center, and ^1H and ^{13}C NMR alone may not be sufficient, as these probes can be somewhat remote from the metal. Frequently, ^{31}P and/or other spin $I = 1/2$ nuclei such as ^{29}Si , ^{103}Rh , $^{117,119}\text{Sn}$ or ^{195}Pt will prove to be a better choice. Some of the model transition metal compounds chosen for the chemical shift and coupling constant discussion will often be either directly involved with, or related to, some aspect of homogeneous and enantioselective catalysis. There will be an emphasis on metal phosphine and carbene complexes as these are fairly important ligands in this area.

Somewhere in an old cookbook I remember reading “the first thing one needs to do in order to make rabbit stew is to catch the rabbit”. First one needs to obtain the various spectra so that these NMR techniques make up the first part of the book. Although many young researchers measure NMR spectra, it is important to think not only about “routine measuring” but also a bit about how one might improve the quality of the spectra obtained. In my experience, we are a little spoiled, in that modern NMR spectrometers often deliver good quality spectra without much effort on the part of the user. Of course once the spectrum is present, there is the question of assignment. Since it may prove necessary to assign

modestly complicated spectra, a few words on current two-dimensional methods are appropriate. Some of these 2-D methods are fairly straightforward, whereas others require more effort on the part of the user. All of the NMR techniques presented are fairly standard (and available on all modern spectrometers) so that I will not review the theory associated with these methods.

A major part of this text, chapter 11, is devoted to solving structural and other NMR problems concerned with transition metal coordination and organometallic compounds. The reader will be shown a reaction followed by the kind of NMR data that one normally finds in a preparative experimental section. Using these chemical shifts and coupling constants one is asked to propose a structure. In chapter 12 the solutions to the problems will be provided, together with a literature citation and some subjective commentary.

In order to prepare the reader for these problems, a *schematic very brief* introduction to selected organometallic reaction mechanisms and the syntheses of several classes of metal complex will be given. This will hopefully direct the reader's thinking when confronted with the problems.

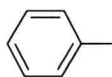
This text is *not* designed to be comprehensive, but rather to emphasize-as briefly as possible-what one needs to know in order to obtain the most useful spectra and then using the NMR data that one can derive from them, to solve routine research problems in coordination and organometallic chemistry.

August 2011

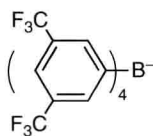
Paul S. Pregosin

Abbreviations

Me	methyl
Et	ethyl
<i>i</i> -Pr (or Pr ^{<i>i</i>})	iso-propyl
<i>t</i> -Bu (or Bu ^{<i>t</i>})	<i>tert</i> -butyl
Cy	cyclohexyl
<i>p</i> -Tol	<i>para</i> -methyl phenyl
Mes	2,4,6-trimethyl phenyl
Triflate	CF ₃ SO ₃ ⁻ anion
OA _c	acetate anion
acac	acetyl acetate anion
DFT	density functional theory
DMSO	dimethyl sulfoxide
DMF	dimethyl formamide

Ph = C₆H₅

py = pyridine

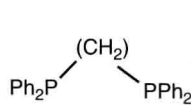
BArF⁻ η^5 -Cp η^5 -Cp* η^6 -arene



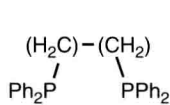
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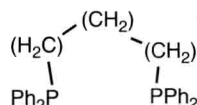
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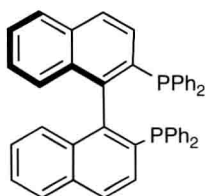
dppm



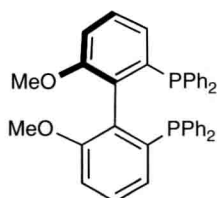
dppe = diphos



dppp



An enantiomer of Binap



An enantiomer of MeO-Biphep

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1

Introduction

Just as in organic chemistry or biochemistry, it is now routine to measure ^1H , ^{13}C , and, often, ^{31}P NMR spectra of diamagnetic organometallic and coordination compounds. Many NMR spectra are measured simply to see if a reaction has taken place as this approach can take sometimes take <5 min. Having determined that something has happened, the most common reasons for continuing to measure are usually associated with

- 1) Confirmation that a reaction has taken place and, by simply counting the signals, deciding how to proceed
- 2) The recognition of new and/or novel structural features via marked changes in chemical shifts and/or J -values, and
- 3) The need for a unique probe with sufficient “structural resolution” to follow the kinetics or the development of a reaction.

When a P atom is present, proton-decoupled ^{31}P NMR often represents one of the simplest analytical tools available as the spectra can be obtained quickly and do not normally contain many lines.

Figure 1.1 shows the ^{31}P NMR spectra for aqueous solutions of the Pt(0) and Pt(II) complexes $\text{Pt}(\text{TPPTS})_3$, D, and $\text{Pt}(\text{H})(\text{TPPTS})_3^+$, A, respectively, as a function of pH (TPPTS is the water-soluble triphenyl phosphine derivative $\text{P}(m\text{-NaSO}_3\text{C}_6\text{H}_4)_3$). At pH 13, the Pt(0) complex is stable, while at pH 4, the hydride cation is preferred. The lowercase letters indicate the ^{195}Pt satellites. One isotope of platinum, ^{195}Pt , has $I = 1/2$ and 33.7 natural abundance, and the separation of these satellite lines represents $^1J(^{95}\text{Pt}, ^{31}\text{P})$, another useful tool. Using ^{31}P rather than ^1H or ^{13}C provides a quick and easy overview of the changes in the chemistry and corresponds to point 1.¹⁾

1) Although not always specified, the ^{13}C and ^{31}P NMR spectra that follow throughout this text (and in the literature) are almost always measured with broad band ^1H decoupling, so that $^nJ(^1\text{H}, \text{X})$ coupling constants

are not present and this helps to simplify the spectra. Occasionally, this will be indicated as “ $^{13}\text{C}\{^1\text{H}\}$ ” or “ $^{31}\text{P}\{^1\text{H}\}$.” Unless otherwise specified, the reader should assume broad-band proton decoupling.

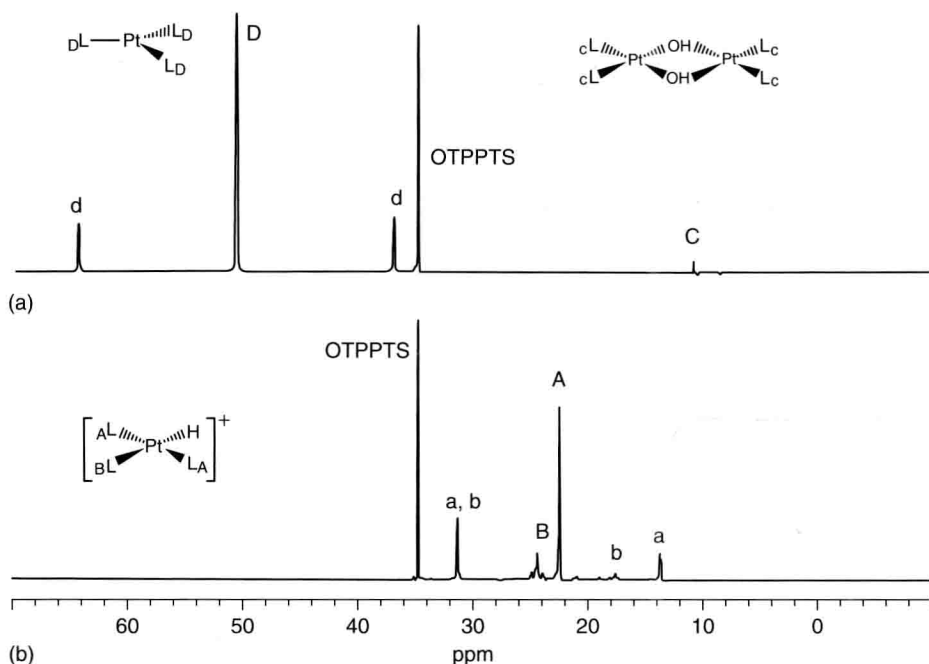
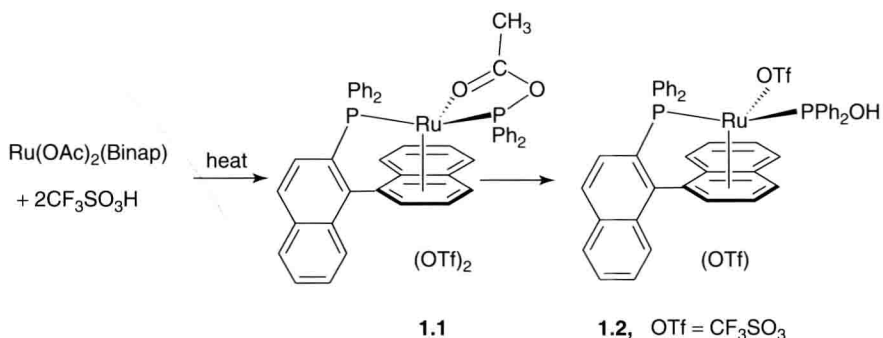


Figure 1.1 ^{31}P NMR spectra recorded on the same solution after 10 cycles between pH 4 and 13: (a) recorded at pH 13, showing the Pt(0) complex, D, Pt(TPPTS)₃, and (b) recorded at pH 4, showing Pt(H)(TPPTS)₃ cation, A. Traces of the hydroxide-bridged dinuclear complex, C, as well as the phosphine oxide, OTPPTS, are marked [1].

Apart from recognizing the number of different chemical environments, many times the important clue(s) with respect to the nature/and or source of the reaction products stem from specific chemical shifts.



Reaction of $\text{Ru}(\text{OAc})_2(\text{Binap})$ with 2 equivalents of the strong acid $\text{CF}_3\text{SO}_3\text{H}$ affords the product 1.2 in high yield. Superficially, complex 1.2 appears to arise as a result of the addition of H_2O across a Binap P-C bond. But what is the water source? The

^{13}C spectrum of the reaction solution, see Figure 1.2, reveals that acetic anhydride is produced (and thus water) from the two molecules of HOAc produced from the protonation. Further, the spectrum shows a $\text{C}=\text{O}$ signal for the novel intermediate 1.1.

This reaction represents an example of point 2, in that the product reveals an unexpected feature.

Figures 1.3 and 1.4 demonstrate point 3. The ^1H NMR spectrum of the deuterated rhodium pyrazolylborate isonitrile complex, $\text{RhD}(\text{CH}_3)(\text{Tp}')(\text{CNCH}_2\text{Bu}^t)$, in the methyl region, slowly changes to reveal the isomer in which the deuterium atom is now incorporated in the methyl group to afford $\text{RhH}(\text{CH}_2\text{D})(\text{Tp}')(\text{CNCH}_2\text{Bu}^t)$. In this chemistry, the deuterium isotope effect on the ^1H methyl chemical shift is sufficient to allow the resolution of the two slightly different methyl groups and thus allow the $^1\text{H}(^2\text{H})$ exchange to be followed.

Figure 1.4 shows the intracellular and extracellular exchange of cesium, via ^{33}Cs NMR ($I = 7/2$, 100% abundant), as a function of time. Although this subject does not involve transition metal chemistry, it does demonstrate how NMR can shed light on a potentially complicated biological subject. Both Figures 1.3 and 1.4 represent examples of the use of NMR to follow a slowly developing chemical transformation (point 3).

To be fair, a unique structural assignment cannot usually be made by counting the number of ^1H , ^{13}C , or ^{31}P signals and/or measuring their chemical shifts. X-ray crystallography remains the acknowledged ultimate structure proof. However, for monitoring reactions, identifying mixtures of products and detailed mechanistic studies involving varying structures, NMR has proven to be a flexible and unique methodology. Apart from ^1H , ^{13}C , ^{15}N , ^{19}F , or ^{31}P , already mentioned, there are many other possibilities, including ^2H , ^{29}Si , one of the Sn isotopes, and ^{195}Pt , to mention only a few.

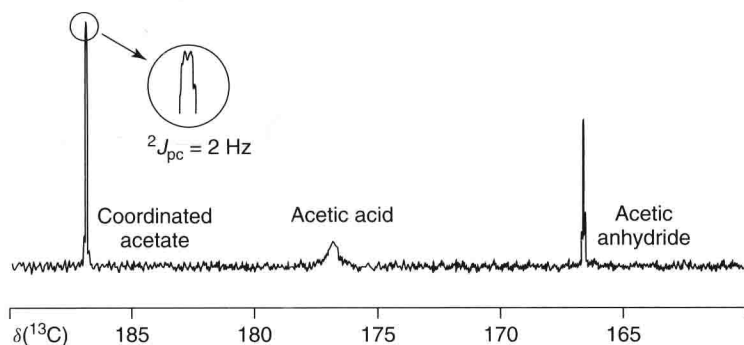


Figure 1.2 Section of the ^{13}C spectrum of the reaction solution after 30 min at 353 K with peaks for the acetate moiety of 1.1, acetic acid, and acetic anhydride. The expanded section shows the P C coupling, $^2J = 2 \text{ Hz}$ (75 MHz in 1,2-dichloroethane solution) [2].

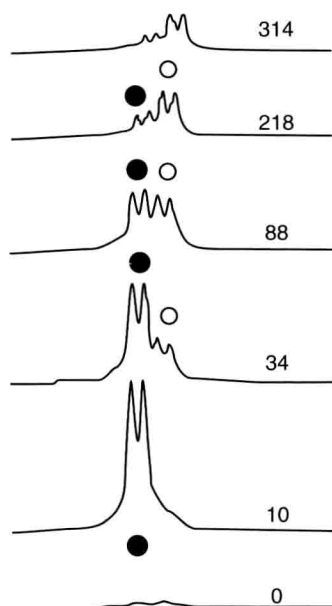


Figure 1.3 Methyl region as a function of time (minutes) of the ^1H NMR spectrum from the rearrangement of $\text{RhD}(\text{CH}_3)(\text{Tp}')(\text{CNCH}_2\text{Bu}^t)$, to $\text{RhH}(\text{CH}_2\text{D})(\text{Tp}')(\text{CNCH}_2\text{Bu}^t)$ in benzene- d_6 at 295 K [3].

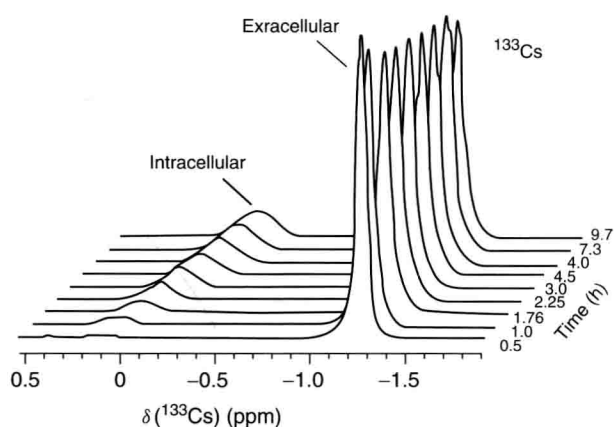


Figure 1.4 ^{133}Cs NMR spectra of human erythrocytes suspended in a buffer containing 140 mM NaCl and 10 mM CsCl. The origin of the chemical shift scale is arbitrary [4, 5].