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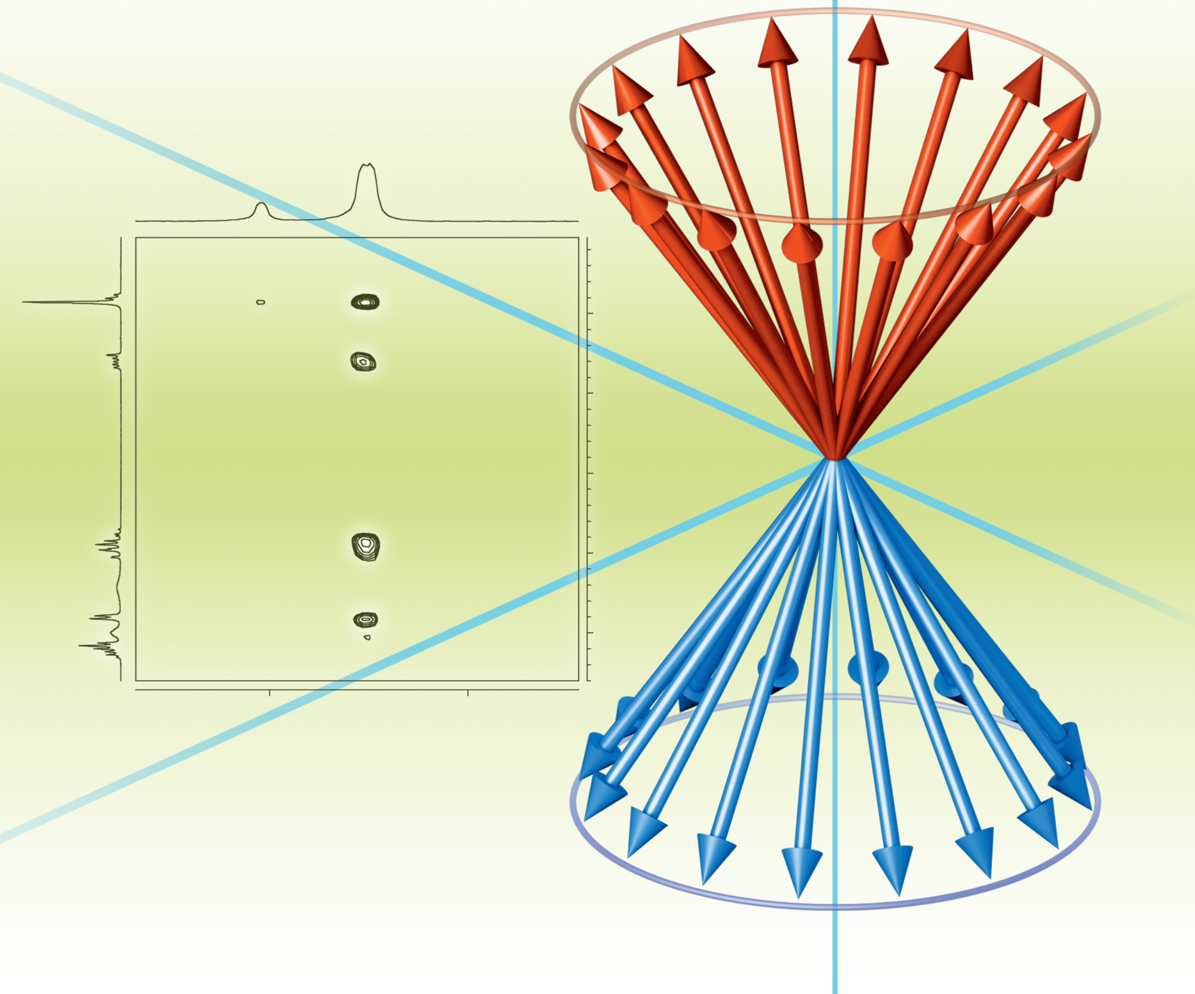
NMR in Organometallic Chemistry



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Paul S. Pregosin

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.

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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 ^{1}H 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, ^{1}H 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 ^{1}H 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}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.

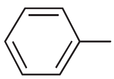
In order to prepare the reader for these problems, a schematic *very brief* introduction to selected organometallic reaction mechanisms and the syntheses of several classes of metal complex will be given. This will hopefully direct the reader's thinking when confronted with the problems.

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.

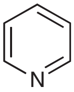
August 2011 *Paul S. Pregosin*

Abbreviations

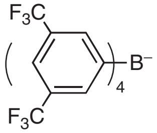
Me	methyl
Et	ethyl
i-Pr (or Pr^i)	iso-propyl
t-Bu (or Bu^t)	*tert*-butyl
Cy	cyclohexyl
p-Tol	*para*-methyl phenyl
Mes	2,4,6-trimethyl phenyl
Triflate	$CF_3SO_3^-$ anion
OAc	acetate anion
acac	acetyl acetonate anion
DFT	density functional theory
DMSO	dimethyl sulfoxide
DMF	dimethyl formamide



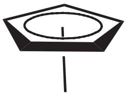
Ph = C_6H_5



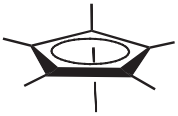
py = pyridine



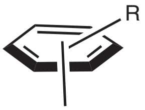
$BArF^-$



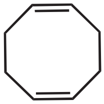
η⁵-Cp



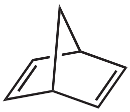
η⁵-Cp*



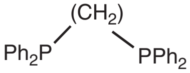
η⁶-arene



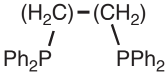
1,5-COD



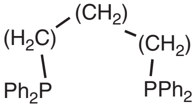
NBD


(CH2)
Ph2P
PPh2

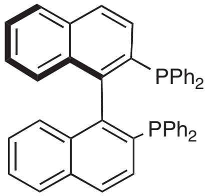
dppm


(H2C)
(CH2)
Ph2P
PPh2

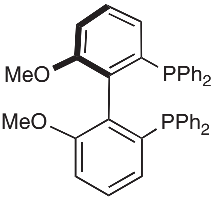
dppe = diphos


(CH2)
(H2C)
(CH2)
Ph2P
PPh2

dppp



An enantiomer of Binap


MeO
PPh2
MeO
PPh2

An enantiomer of MeO-Biphep

1
Introduction

Just as in organic chemistry or biochemistry, it is now routine to measure ^{1}H, ^{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 $Pt(TPPTS)_3$, D, and $Pt(H)(TPPTS)_3{}^+$, A, respectively, as a function of pH (TPPTS is the water-soluble triphenyl phosphine derivative $P(m\text{-}NaSO_3C_6H_4)_3$). 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 ^{1}H 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 ^{1}H decoupling, so that $^nJ(^1H,X)$ coupling constants are not present and this helps to simplify the spectra. Occasionally, this will be indicated as ‘‘$^{13}C(^1H)$’’ or ‘‘$^{31}P\{^1H\}$.’’ Unless otherwise specified, the reader should assume broad-band proton decoupling.

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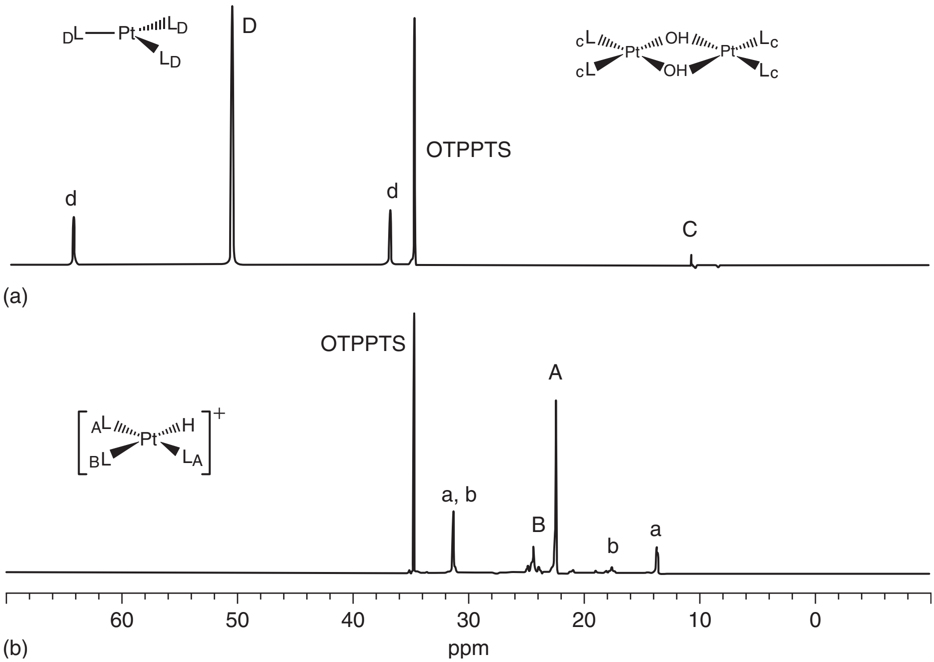
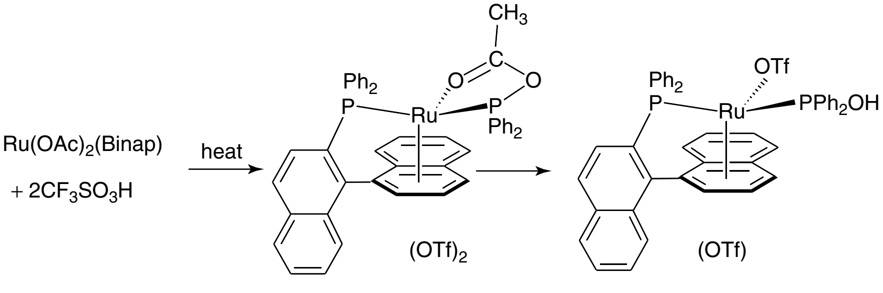


Figure 1.1 ^{31}P NMR spectra recorded on the same solution after 10 cycles between pH 4 and 13: (a) recorded at pH 13, showing the Pt(0) complex, D, Pt(TPPTS)$_3$, and (b) recorded at pH 4, showing Pt(H)(TPPTS)$_3$ cation, A. Traces of the hydroxide-bridged dinuclear complex, C, as well as the phosphine 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.



1.1 **1.2,** OTf = CF_3SO_3

Reaction of Ru(OAc)$_2$(Binap) with 2 equivalents of the strong acid CF_3SO_3H 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 C=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 ^{1}H NMR spectrum of the deuterated rhodium pyrazolylborate isonitrile complex, RhD(CH$_3$)(Tp′)(CNCH$_2$Bu^t), in the methyl region, slowly changes to reveal the isomer in which the deuterium atom in now incorporated in the methyl group to afford RhH(CH$_2$D)(Tp′)(CNCH$_2$Bu^t). In this chemistry, the deuterium isotope effect on the ^{1}H methyl chemical shift is sufficient to allow the resolution of the two slightly different methyl groups and thus allow the ^{1}H(^{2}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 ^{1}H, ^{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 ^{1}H, ^{13}C, ^{15}N, ^{19}F, or ^{31}P, already mentioned, there are many other possibilities, including ^{2}H, ^{29}Si, one of the Sn isotopes, and ^{195}Pt, to mention only a few.

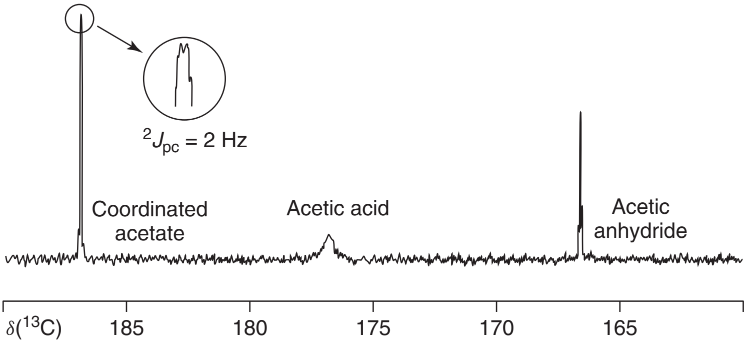


Figure 1.2 Section of the ^{13}C spectrum of the reaction solution after 30 min at 353 K with peaks for the acetate moiety of **1.1**, acetic acid, and acetic anhydride. The expanded section shows the P C coupling, $^2J = 2$ Hz (75 MHz in 1,2-dichloroethane solution) [2].

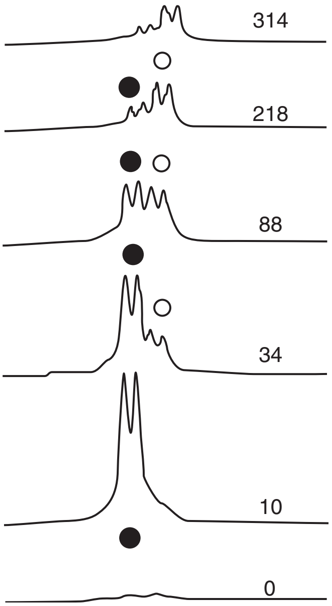


Figure 1.3 Methyl region as a function of time (minutes) of the ^{1}H NMR spectrum from the rearrangement of $RhD(CH_3)(Tp')(CNCH_2Bu^t)$, to $RhH(CH_2D)(Tp')(CNCH_2Bu^t)$ in benzene-d_6 at 295 K [3].

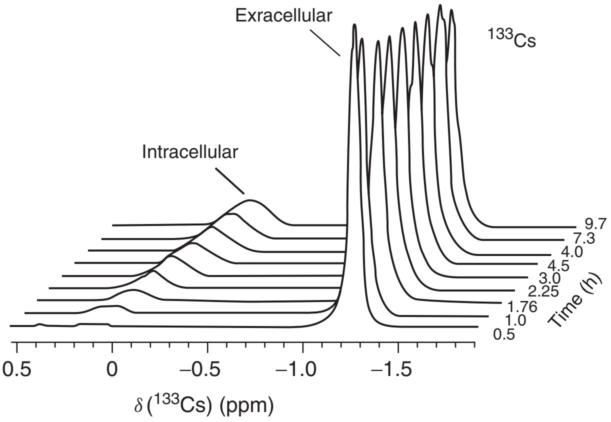


Figure 1.4 ^{133}Cs NMR spectra of human erythrocytes suspended in a buffer containing 140 mM NaCl and 10 mM CsCl. The origin of the chemical shift scale is arbitrary [4, 5].

In addition to chemical shifts, the observed signal multiplicity (as in Figures 1.2 and 1.3) can be useful, as the observation of a coupling constant (*J*-value) can help to confirm that a fragment is within the coordination sphere. In Figure 1.2, an acetate carbon is coupled to the ^{31}P. In Figure 1.3, the ^{103}Rh ($I = 1/2$, 100% natural abundance) couples to the ^{1}H of the methyl group. Apart from these routine parameters, organometallic chemists need to occasionally use slightly more specialized NMR tools. Spin–lattice relaxation times, T_1's, for example, are now used to characterize metal molecular hydrogen complexes. All these, and others, together with the ability to detect and measure solution dynamics over several orders of magnitude, contribute to making NMR an indispensable technique. However, modern NMR spectrometers are not always simple to use and obtaining good quality NMR spectra can require some effort.

References

1. Helfer, D.S. and Atwood, J.D. (2002) *Organometallics*, **21**, 250.
2. Geldbach, T.J., den Reijer, C.J., Worle, M., and Pregosin, P.S. (2002) *Inorg. Chim. Acta*, **330**, 155.
3. Wick, D.D., Reynolds, K.A., and Jones, W.D. (1999) *J. Am. Chem. Soc.*, **121**, 3974.
4. Davis, D.G., Murphy, E., and London, R.E. (1988) *Biochemistry*, **27**, 3547.
5. Ronconi, L. and Sadler, P.J. (2008) *Coord. Chem. Rev.*, **252**, 2239.

2
Routine Measuring and Relaxation

2.1
Getting Started

Preparing the sample may not be trivial (many organometallic complexes are air and water sensitive); but assuming that one has prepared circa 0.7 ml of a clear solution containing 5–10 mg of sample,1) in the usual 5 mm NMR tube, one is ready to measure a spectrum.

Most beginning researchers place the sample in the magnet, stabilize the magnetic field via a ^{2}H lock (frequently no longer necessary), call up a simple measuring program, and type, ''go.'' For a standard one-dimensional proton ^{1}H NMR measurement, a few minutes (or less) of accumulation time are often sufficient to obtain a ^{1}H free induction decay (FID) that, after Fourier transformation, affords a spectrum with sufficient signal-to-noise (S/N) ratio. After a phase correction, the spectrum is plotted.2)

Typically, these operations are followed by an integration procedure to determine the relative number of protons in the various groupings of resonances, and this may be where a problem arises. The integration obtained may indicate that, instead of, for example, a 2 : 1 ratio, one finds a 1.7 : 1 ratio or 2.3 : 1 ratio. There may be a structural reason for the observed results, but sometimes, the problem is simply one of ''relaxation.''

The NMR program may already contain a ''recommended'' ^{1}H pulse length (or it may simply be what the last researcher found to be optimal for his or her chemistry). If the chosen pulse length and/or the acquisition time (the time used by the computer to collect the FID) have not been properly considered, the integrals may not (and usually do not) correctly reflect the relative populations. Moreover, the S/N ratio may not be optimal.

---

1) The amount necessary to obtain excellent signal-to-noise in a short period of time, will depend on the molecular weight and of course the nucleus to be measured amongst other parameters.

2) No longer carried out at the NMR console, but rather at some remote PC station so that others can efficiently utilize the machine time.

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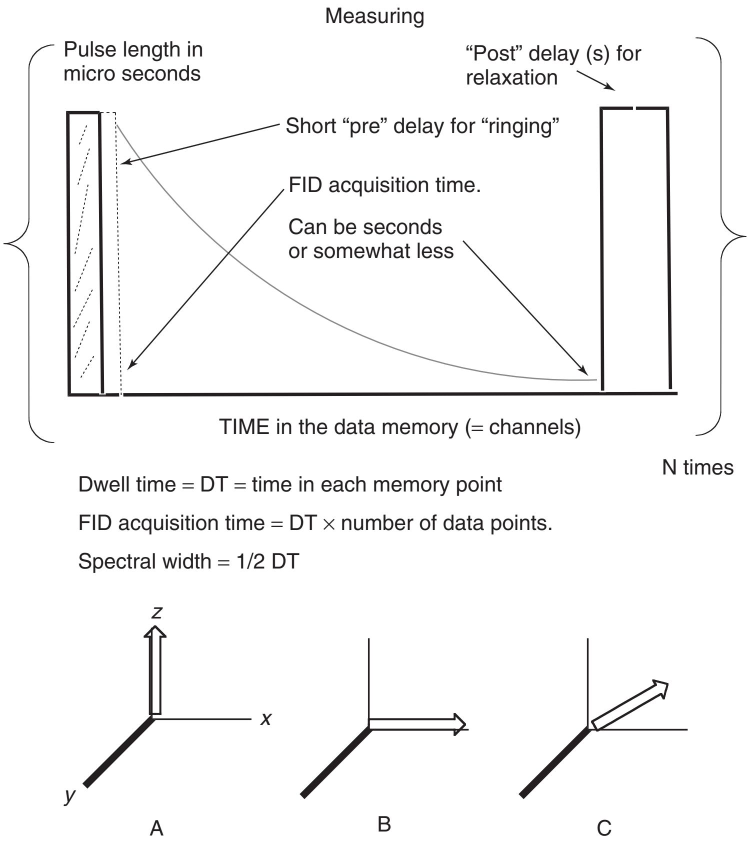
Measuring
Pulse length in micro seconds
"Post" delay (s) for relaxation
Short "pre" delay for "ringing"
FID acquisition time.
Can be seconds or somewhat less
TIME in the data memory (= channels)
N times
Dwell time = DT = time in each memory point
FID acquisition time = DT × number of data points.
Spectral width = 1/2 DT
z
x
y
A
B
C

Scheme 2.1

Scheme 2.1 shows a cartoon of a routine measurement (note that the horizontal axis is not to scale). We will assume that the pulse length chosen (in microseconds) corresponds to a 90° pulse. A 90° pulse is defined as that pulse length that tips the magnetization vector 90° from its equilibrium position on the *z*-axis (A) and affords the maximum signal after one pulse (B). Less than 90° will afford a vector whose projection on (for example) the *x*-axis, will not be quite so large (C).

After the excitation via the 90° radio frequency pulse, an FID is collected in the chosen number of memory points. If there is no relaxation (post) delay, the experiment is repeated "*N*" times until sufficient signal is obtained. The acquisition time is determined by the number of data points in the FID (chosen by the operator), multiplied by the time the computer "resides" in each channel (the dwell time, DT). The value of DT is set by the computer and is related to the selected spectral width. The simple relation is spectral width = 1/2(DT)[3], so that for large spectral widths the computer spends less time in each data point. Since the spectral width chosen is normally much larger for ^{13}C or ^{31}P, than for ^{1}H, for the same number of data points, the DT will normally be much shorter for these nuclei relative to ^{1}H. Since, as we will learn in the chemical shift section, the range of ^{1}H and ^{13}C shifts in organometallic species is larger than for routine organic compounds, there is a tendency to ''play it safe'' and choose a relatively large spectral width. As we will see, this is acceptable provided that one adjusts the acquisition time accordingly.

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[3] For Bruker instruments.

Before discussing relaxation phenomena, it is useful to think, briefly, about the subject of spectral resolution and especially the accuracy of measured coupling constants. If one selects, for example, a spectral width of 20 000 Hz and places the spectrum (after transformation of the FID) into 32 K data points, the resolution cannot be better than circa 0.62 Hz. If we assume that an error of ±1 channel is reasonable, rather than just 1 channel, then the *J*-values will not be better than about 1.2 Hz. Of course, one can use 64 K points, but this will still not allow the *J*-values to be determined to ±0.1 Hz. The student might keep this in mind when reading the literature.

2.2
Relaxation

Returning to relaxation, what happens after the first 90° pulse? It is often the case that the various protons (or carbons) to be measured have not had sufficient time to completely relax to their equilibrium positions during the acquisition time chosen. Consequently, in a multipulse experiment, the amount of signal obtained for each of the individual protons of the molecules under consideration will vary with their ^{1}H relaxation characteristics. It is sufficient to note that, to obtain a spectrum with the correct relative integrals, one either reduces the length of the pulse and/or one adds a relaxation delay at the end of the FID accumulation. An alternative to a relaxation delay involves the use of more data points during the accumulation of the FID. This adds more time in the gathering of the data (not always desirable) and improves the spectral resolution. It is not normally necessary to add a paramagnetic relaxation reagent.

Usually, a smaller pulse angle, perhaps, between 30° and 45°, will most likely afford correct integrals. But how do we know whether 30° or 45° corresponds to the correct choice?4) Generally speaking, if one plans to work on a given set of molecules for a prolonged period (for example, for the length of a Ph.D. research project), it is advisable to measure the spin lattice relaxation times, T_1 for the protons of the class of compounds to be studied, and then to set up the experiment with a suitable acquisition time and/or postdelay.

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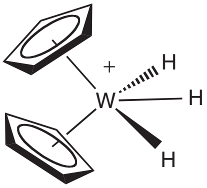
4) This problem has been studied at length. The optimum angle (the so-called Ernst angle) depends on T_1. For T_1 values between 0.4 and 4.0 s this angle changes from 53° to 86° assuming an acquisition time of 1 s.

Measuring T_1, for example, via the inversion-recovery sequence (Eq. (2.1)):

$$180^\circ \text{ pulse} - \tau(\text{waiting time}) - 90^\circ \text{ pulse} - (\text{collect the FID and transform}) \quad (2.1)$$

is a straightforward process and affords a series of spectra as a function of the different waiting times, τ. The 180° pulse inverts the magnetization. After short τ values, the magnetization is still inverted and, after the 90° pulse, transformation of the FID affords a "negative" signal. As the waiting time τ increases, the spins relax more and more toward their original equilibrium positions and the 90° pulse results in a "positive" signal.

Figure 2.1a shows an inversion-recovery T_1 measurement for the two types of hydride ligand in $WH_3(Cp)_2^+$ (**2.1**). Note that with a τ value of 2000 ms, the central proton is "positive" whereas the outer two hydride signals have close to zero intensity. For the two separate ^{195}Pt measurements on Pt{P(*t*-Bu)$_3$}$_2$ at 310 K, given in Figure 2.1b, one sees the effect on the signal intensities of altering the waiting time and of changing the magnetic field strength and we shall come back to this field dependence shortly. The T_1 values can be calculated from the experimental data via a well-known regression analysis. The waiting time that corresponds to "zero" signal is circa $T_1(\ln 2)$ and although this may prove a useful relation for estimating T_1 it is not usually very accurate.



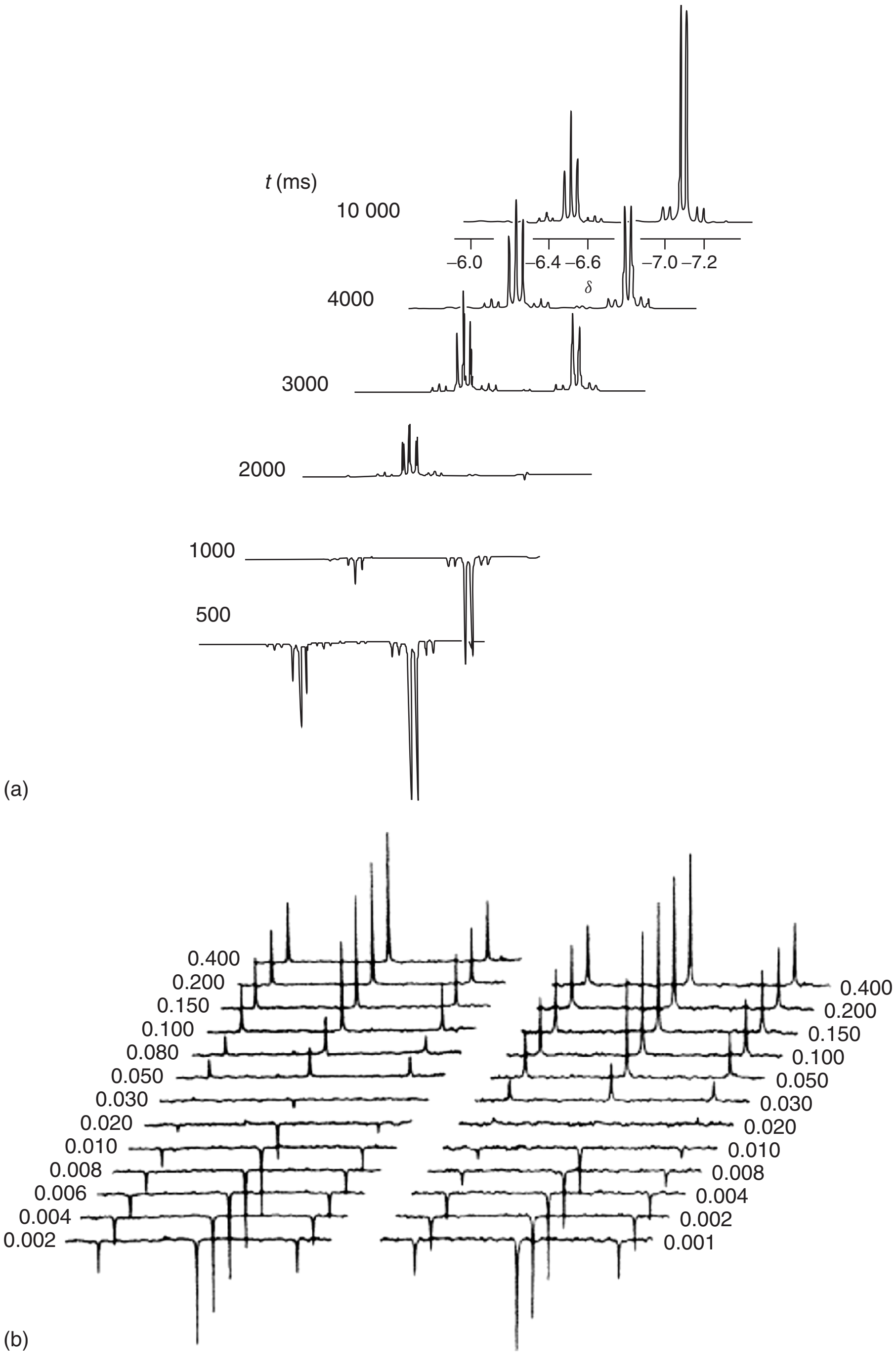
2.1

An understanding of the factors affecting the spin–lattice relaxation times, T_1's, will help to solve the ^{1}H integration problem, and also can be of value in connection with optimizing S/N ratios and/or mixing times in 2-D ^{1}H,^{1}H nuclear Ovehauser effect (NOE) experiments. Moreover, there are some subtle problems concerned with integrals and intensities for ^{13}C and ^{31}P, involving T_1 so that a brief discussion on NMR relaxation is useful.

One can summarize the longitudinal relaxation rate of a nucleus, $R_1(= 1/T_1)$, as resulting from the sum of a number of contributions and these are shown in Eq. (2.2).

$$R_1 = R_1^{DD} + R_1^{CSA} + R_1^{SR} + R^{sc} + R_1^{EN} \quad (2.2)$$

Figure 2.1 (a) Inversion-recovery experiments to determine the relaxation times of the hydride ligands for $WH_3(Cp)_2^+$ in CF_3CO_2H at 298 K. The waiting times are in milliseconds. The weak resonances surrounding the main bands stem from ^{183}W [1]. (b) ^{195}Pt T_1 measurements on Pt{P(*t*-Bu)$_3$}$_2$ at 310 K at 7.0 T (left) and 9.4 T (right) using the inversion-recovery pulse sequence. The variable delays between the 90″ and 180″ pulses were varied between 0.001 and 0.4 s. The spectral width corresponds to 12 000 Hz [2].


t (ms)
10 000
4000
3000
2000
1000
500
−6.0
−6.4
−6.6
−7.0
−7.2
δ
(a)
0.400
0.200
0.150
0.100
0.080
0.050
0.030
0.020
0.010
0.008
0.006
0.004
0.002
0.400
0.200
0.150
0.100
0.050
0.030
0.020
0.010
0.008
0.004
0.002
0.001
(b)

The various contributions [3] to the overall relaxation rate are defined as follows: DD, dipole–dipole; CSA, chemical shift anisotropy; SR, spin rotation; SC, scalar coupling; Q, quadrupole; and EN, electron–nuclear. For our purposes, it is useful to discuss only two of these contributions, R_1^{DD} and R_1^{CSA}.

2.2.1
Dipole–Dipole Relaxation

Dipole–dipole relaxation, in which one of the two dipoles is ^{1}H, represents an important (and usually dominating) contributor to the relaxation of the two

$$R = 1/T_1 = 4\gamma_H^2\gamma_{\mathrm{A}}^2 \mathrm{h} S(S+1)\tau/3r_{\mathrm{H,A}}^6 \tag{2.3}$$

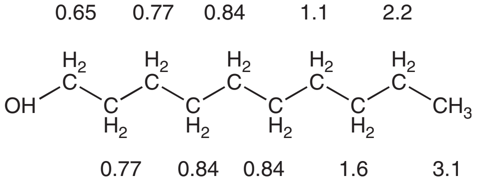
important nuclei ^{1}H, ^{13}C, and occasionally for ^{15}N and ^{31}P. In the equation above, γ is the gyromagnetic ratio and is directly proportional to the magnitude of the magnetic moment of the nuclei A and ^{1}H, S is the spin quantum number, h is Planck's constant, τ is a molecular correlation time, and r is the distance between the two dipoles. Often, a number of proximate dipoles (for example, a set of protons in an aliphatic chain and/or the protons of an aromatic moiety) will contribute to the relaxation of a given ^{13}C, ^{15}N, or (sometimes) ^{31}P. The values of τ and r represent two very important factors that vary with molecular structure. Large molecules move slowly (large τ) and some ^{13}C or ^{15}N spins have the protons directly bonded (short r-values).

Specifically for ^{13}C

$$R = 1/T_1 \text{ is proportional to } N\gamma^2{}_{13\mathrm{C}}{}^2\gamma_{1\mathrm{H}}{}^2\tau/r_{\mathrm{C-H}}^6 \tag{2.4}$$

where N in Eq. (2.4) represents the number of protons attached to the carbon in question. Clearly, a short r-value (e.g., a hydrogen atom directly bound to the ^{13}C in question) will afford a shorter T_1. However, the τ value can be quite important. Anything that changes molecular motions (different solvents, via their viscosities, variable temperature experiments – again through a change in viscosity –, large vs small molecular size, or perhaps steric crowding) can affect τ and thus T_1.

The ^{13}C T_1 values given below (in seconds) for 1-decanol, represent a classical example of how τ can be important for relaxation



^{13}C T_1 values for 1-decanol (s).

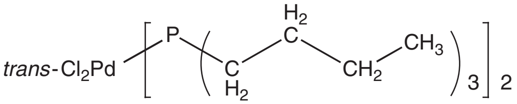
The OH group provides a molecular anchor in that there is H-bonding to another alcohol (or solvent). This leads to different local τ-values along the chain with more freedom for movement (shorter τ-values) as one moves down the chain away

Table 2.1 ^{31}P T_I for PPh_3 and some phosphine complexes in $CDCl_3$.

***trans*-IrCl(CO)(P(*p*-X-C_6H_4)$_3$)^a**		***trans*-$PdCl_2(PR_3)_2$^{b}**	
X	**T_1 (s)**	**R**	**T_1 (s)**
H	8.7–9.0[c]	Et	9.5
F	8.1	*n*-Pr	6.3
Cl	6.8	*n*-Bu	4.3
CH_3	6.2	Cy	3.6
OCH_3	4.4		
AuCl(P(*p*-X-C_6H_4)$_3$)^a			
H	16.0		
OCH_3	11.3		
PPh_3 (free ligand)	26.0		

[a] R_1^{DD} is not the only contributor to the P-relaxation [4a].
[b] Ref. [4b].
[c] Measured several times. All values in seconds.

from the OH group. A very similar effect is found for the ^{13}C T_1's in P(*n*-Bu)$_3$ complexes of palladium such as *trans*-$PdCl_2L_2$, L = P(*n*-Bu)$_3$. Here, the metal and its halogen and phosphine ligands function as the anchor, and once again, the ^{13}C T_1's increase as one moves down the phosphine chain [4b].



^{13}C T_1 values for *trans*-$PdCl_2L_2$ (s) 0.36 0.55 1.10 2.45

Changing nucleus, Table 2.1 shows some ^{31}P T_I values for P(Aryl)$_3$ complexes of iridium and gold, plus T_1's for several alkyl phosphine complexes of palladium, in $CDCl_3$ solution. The T_I values for the Ir and Au complexes decrease as the molecular weight of the P(Aryl)$_3$ increases due to the differing τ-values. Note that PPh_3 itself (not complexed, and thus presumably with a shorter τ-value(5)) has a relatively long T_1, 26.0 seconds. The same trend for the ^{31}P T_I's is found when the R group of the *trans*-$PdCl_2(PR_3)_2$ is made larger by increasing the chain length. Since dipole–dipole relaxation is important for these alkyl phosphines (the methylene protons on the adjacent carbon are not too far away), the observed changes in the T_I's are reminiscent of what we have seen for the ^{13}C T_1 values shown above, for *trans*-$PdCl_2L_2$, that is, an increasing correlation time leading to a shorter ^{13}C T_1.

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5) Dipole–dipole is not the only relaxation mechanism for PPh_3.

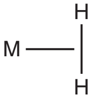
Where dipole–dipole relaxation is important (as in ^{1}H and ^{13}C NMR), NOEs, that develop due to relaxation effects, can result in signal enhancement. The theoretical maximum is 50% for ^{1}H and almost a factor of 2 for ^{13}C. Although not widely recognized, *there is a dipole–dipole contribution to the* ^{31}P *relaxation in metal phosphine complexes, and especially in alkyl phosphine complexes.* Indeed, the dipole–dipole contribution can amount to between 70 and 100% of the relaxation [5]. Since a substantial dipole–dipole contribution exists, Overhauser effects between ^{31}P and ^{1}H can have a marked effect on the ^{31}P signal intensity when the phosphorus spectrum is measured with ^{1}H decoupling.

Assume that one is interested in studying a reaction involving P-donor exchange

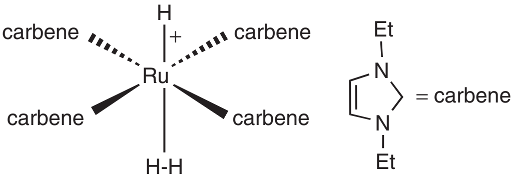
$$L,M(P^{1}R_{3}) + P^{2}R_{3} \longrightarrow M(P^{2}R_{3}) + P^{1}R_{3} \tag{2.5}$$

such as that indicated in Eq. (2.5). Simple integration of the ^{31}P spectra will most likely *not* lead to the correct relative populations, unless both T_1's and NOE's have been considered. Measuring and using integrals in ^{31}P spectra can be quite challenging!

Although technically important, there are not too many areas of organometallic chemistry where measuring T_I's is necessary to understand the chemistry. However, in the discussion of the NMR parameters of molecular hydrogen complexes, to follow later on, ^{1}H T_1 data for both the hydrogen and hydride ligands are suggested to afford a diagnostic tool for these complexes in solution. The short H–H distance in the complexed η^2-H_2 ligand (short *r*-values) results in extremely short ^{1}H T_1 values, (usually <20 ms) relative to those T_1's for terminal hydrides (often several hundred milliseconds). A review by Morris [6] includes more than 100 representative examples of these very short T^1's.



An example is illustrative. At 198 K, the proton NMR spectrum of the Ru-carbene complex **2.2**, exhibited two low-frequency signals in a 2 : 1 ratio. One finds a broad singlet for the η^2-H_2 hydrogen ligand at $\delta = -4.1$ and a much sharper singlet for the classical hydride at $\delta = -8.7$. The T_1 value measured for the η^2-H_2 resonance was found [5] to be much shorter (36 ms: 223 K) than the value found for the terminal hydride signal (241 ms: 253 K).



2.2 The anion is BArF.