

## 1

## Introduction

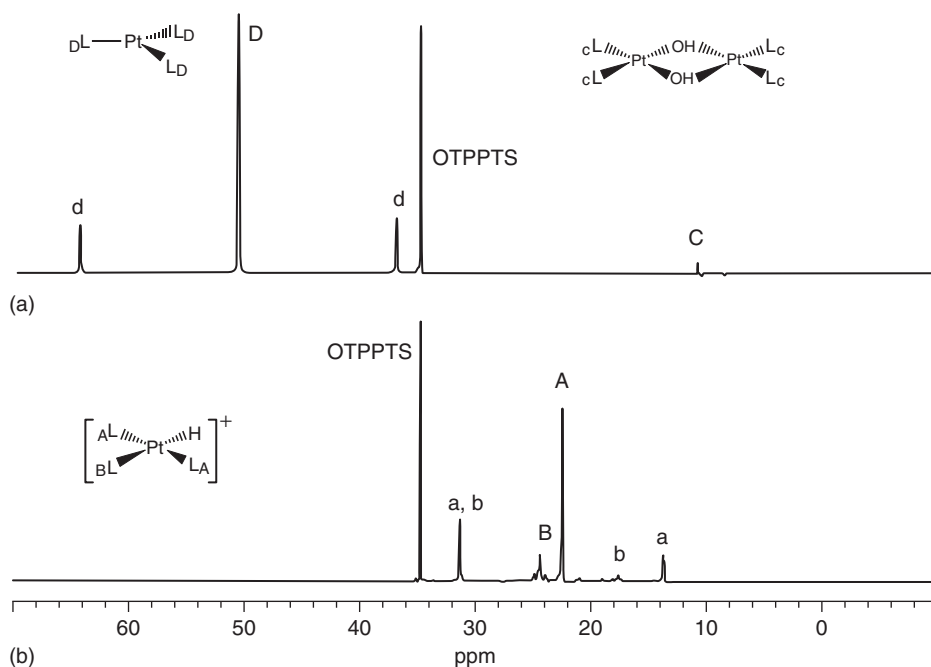
Just as in organic chemistry or biochemistry, it is now routine to measure  $^1\text{H}$ ,  $^{13}\text{C}$ , and, often,  $^{31}\text{P}$  NMR spectra of diamagnetic organometallic and coordination compounds. Many NMR spectra are measured simply to see if a reaction has taken place as this approach 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  $^{31}\text{P}$  NMR often represents one of the simplest analytical tools available as the spectra can be obtained quickly and do not normally contain many lines.

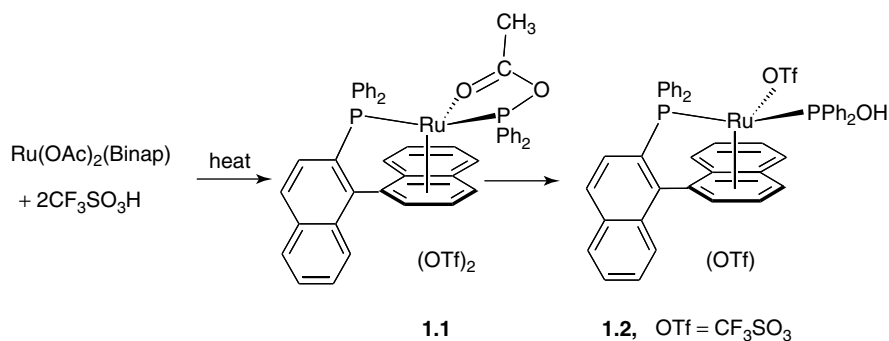
Figure 1.1 shows the  $^{31}\text{P}$  NMR spectra for aqueous solutions of the Pt(0) and Pt(II) complexes  $\text{Pt}(\text{TPPTS})_3$ , D, and  $\text{Pt}(\text{H})(\text{TPPTS})_3^+$ , A, respectively, as a function of pH (TPPTS is the water-soluble triphenyl phosphine derivative  $\text{P}(m\text{-NaSO}_3\text{C}_6\text{H}_4)_3$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

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| <p>1) Although not always specified, the <math>^{13}\text{C}</math> and <math>^{31}\text{P}</math> NMR spectra that follow throughout this text (and in the literature) are almost always measured with broad band <math>^1\text{H}</math> decoupling, so that <math>^nJ(^1\text{H}, \text{X})</math> coupling constants</p> | <p>are not present and this helps to simplify the spectra. Occasionally, this will be indicated as “<math>^{13}\text{C}\{^1\text{H}\}</math>” or “<math>^{31}\text{P}\{^1\text{H}\}</math>.” Unless otherwise specified, the reader should assume broad-band proton decoupling.</p> |
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**Figure 1.1**  $^{31}\text{P}$  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  $\text{H}_2\text{O}$  across a Binap P-C bond. But what is the water source? The

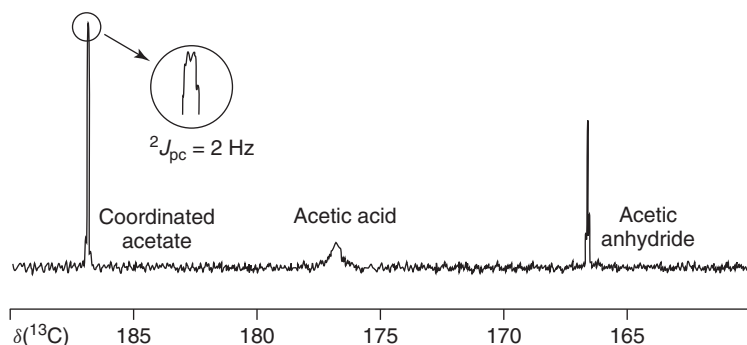
$^{13}\text{C}$  spectrum of the reaction solution, see Figure 1.2, reveals that acetic anhydride is produced (and thus water) from the two molecules of HOAc produced from the protonation. Further, the spectrum shows a  $\text{C}=\text{O}$  signal for the novel intermediate 1.1.

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

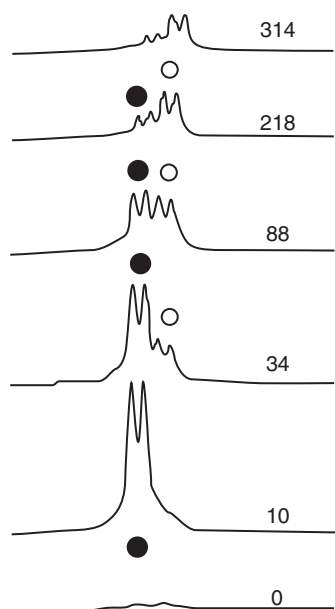
Figures 1.3 and 1.4 demonstrate point 3. The  $^1\text{H}$  NMR spectrum of the deuterated rhodium pyrazolylborate isonitrile complex,  $\text{RhD}(\text{CH}_3)(\text{Tp}')(\text{CNCH}_2\text{Bu}^t)$ , in the methyl region, slowly changes to reveal the isomer in which the deuterium atom is now incorporated 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  $^1\text{H}$  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  $^{33}\text{Cs}$  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).

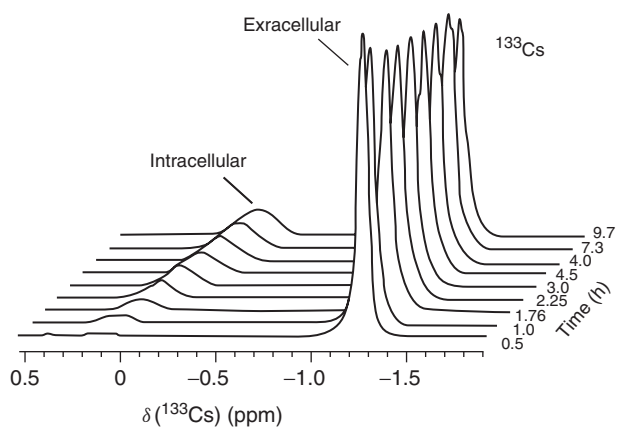
To be fair, a unique structural assignment cannot usually be made by counting the number of  $^1\text{H}$ ,  $^{13}\text{C}$ , or  $^{31}\text{P}$  signals and/or measuring their chemical shifts. X-ray crystallography remains the acknowledged ultimate structure proof. However, for monitoring reactions,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



**Figure 1.2** Section of the  $^{13}\text{C}$  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  $^1\text{H}$  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**  $^{133}\text{Cs}$  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  $^{31}\text{P}$ . In Figure 1.3, the  $^{103}\text{Rh}$  ( $I = 1/2$ , 100% natural abundance) couples to the  $^1\text{H}$  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

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