

## 12.1: Characterization of Organometallic Complexes

### Learning Objectives

In this lecture you will learn the following

- The characterization techniques of organometallic compounds.
- The NMR analysis of these compounds.
- The IR analysis of these compounds.
- The X-ray single crystal diffraction studies of these compounds.

The characterization of an organometallic complex involves obtaining a complete understanding of the same right from its identification to the assessment of its purity content, to even elucidation of its stereochemical features. Detailed structural understanding of the organometallic compounds is critical for obtaining an insight on its properties and which is achieved based on the structure-property paradigm.

### Synthesis and isolation

Synthesis and isolation are two very important experimental protocols in the overall scheme of things of organometallic chemistry and thus these needs to be performed carefully. The isolation of the organometallic compounds is essential for their characterization and reactivity studies. Fortunately, many of the methods of organic chemistry can be used in organometallic chemistry as the organometallic compounds are mostly nonvolatile crystalline solids at room temperature and atmospheric pressure though a few examples of these compounds are known to exist in the liquid  $[(\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3]$  and even in the vapor  $[\text{Ni}(\text{CO})_4]$  states. The organometallic compounds are comparatively more sensitive to aerial oxygen and moisture, and because of which the manipulation of these compounds requires stringent experimental skills to constantly provide them with anaerobic environment for their protection. All of these necessities led to the development of the so-called special Schlenk techniques, requiring special glasswares and which in conjunction with a high vacuum line and a dry box allow the lab bench-top manipulation of these compounds. Successful isolation of organometallic compounds naturally points to the need for various spectroscopic techniques for their characterizations and some of the important ones are discussed below.

### $^1\text{H}$ NMR spectroscopy

The  $^1\text{H}$  NMR spectroscopy is among the extensively used techniques for the characterization of organometallic compounds. Of particular interest is the application of  $^1\text{H}$  NMR spectroscopy in the characterization of the metal hydride complexes, for which the metal hydride moiety appear at a distinct chemical shift range between 0 ppm to  $-40$  ppm to the high field of tetramethyl silane (TMS). This upfield shift of the metal hydride moiety is attributed to a shielding by metal  $d$ -electrons and the extent of the upfield shift increases with higher the  $d^n$  configuration. Chemical shifts, peak intensities as well as coupling constants from the through-bond couplings between adjacent nuclei like that of the observation of  $J_{\text{P-H}}$ , if a phosphorous nucleus is present within the coupling range of a proton nucleus, are often used for the analysis of these compounds. The  $^1\text{H}$  NMR spectroscopy is often successfully employed in studying more complex issues like fluxionality and diastereotopy in organometallic molecules (Figure 12.1.1).

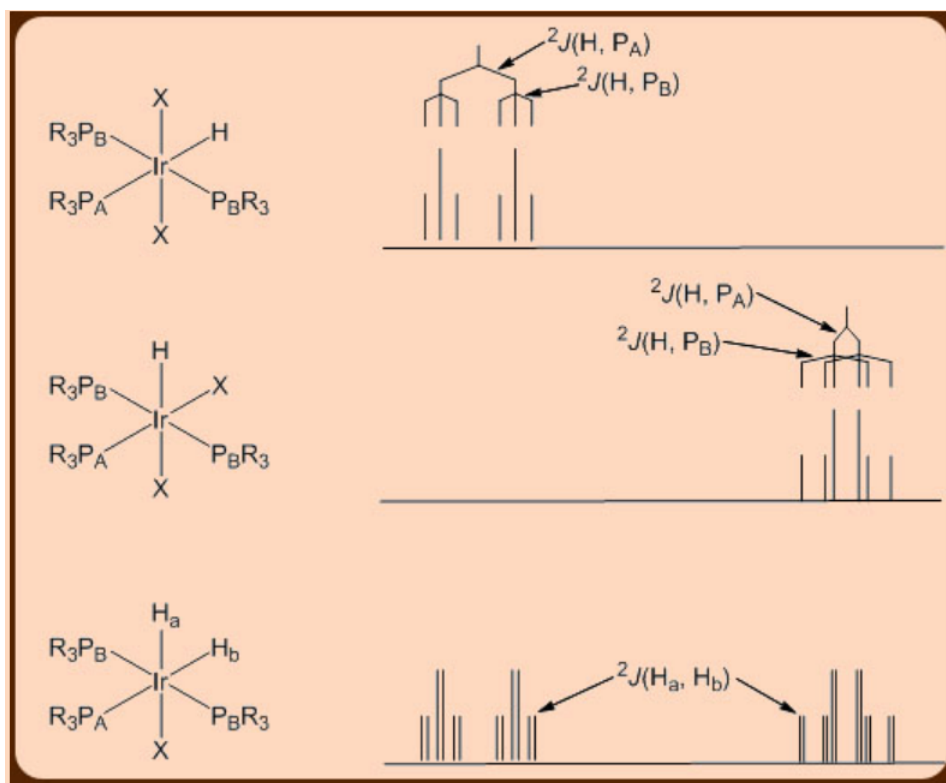


Figure 12.1.1: Different phosphorous-proton coupling patterns in various iridium hydride complexes.

The paramagnetic organometallic complexes show a large range of chemical shifts, for example,  $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$  exhibits proton resonances that extend even up to 290 ppm.

### **13C NMR spectroscopy**

Although the natural abundance of NMR active  $^{13}\text{C}$  ( $I = \frac{1}{2}$ ) nuclei is only 1 %, it is possible to obtain a proton decoupled  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for most of the organometallic complexes. In addition, the off-resonance  $^1\text{H}$  decoupled  $^{13}\text{C}$  experiments yield  $^1J_{\text{C-H}}$  coupling constants, which contain vital structural information, and hence are very critical to the  $^{13}\text{C}$  NMR spectral analysis. For example, the  $^1J_{\text{C-H}}$  coupling constants directly correlate with the hybridization of the C-H bonds with  $sp$  center exhibiting a  $^1J_{\text{C-H}}$  coupling constant of  $\sim 250$  Hz, a  $sp^2$  center of 160 Hz and a  $sp^3$  center of 125 Hz. Similar to what is seen in  $^1\text{H}$  NMR, a phosphorous-carbon coupling is also observed in a  $^{13}\text{C}$  NMR spectrum with the *trans* coupling ( $\sim 100$  Hz) being larger than the *cis* coupling ( $\sim 10$  Hz).

### **$^{31}\text{P}$ NMR spectroscopy**

The  $^{31}\text{P}$  NMR spectroscopy, which in conjunction with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, is a useful technique in studying the phosphine containing organometallic complexes. The  $^{31}\text{P}$  NMR experiments are routinely run under  $^1\text{H}$  decoupled conditions for simplification of the spectral features that allow convenience in spectral analysis. Thus, for this very reason, many mechanistic studies on catalytic cycle are conveniently undertaken by  $^{31}\text{P}$  NMR spectroscopy whenever applicable.

### **IR spectroscopy**

Qualitative to semi-quantitative analysis of organometallic compounds using IR spectroscopy are performed whenever possible. In general the signature stretching vibrations for chemical bonds are more conveniently looked at in these studies. The frequency ( $\nu$ ) of a stretching vibration of a covalent bond is directly proportional to the strength of the bond, usually given by the force constant ( $k$ ) and inversely proportional to the reduced mass of the system, which relates to the masses of the individual atoms.

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{k}{m_r}}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

The organometallic compounds containing carbonyl groups are regularly studied using IR spectroscopy, and in which the CO peaks appear in the range between 2100–1700 cm<sup>-1</sup> as distinctly intense peaks.

## Crystallography

The solid state structure elucidation using single crystal diffraction studies are extremely useful techniques for the characterization of the organometallic compounds and for which the X-ray diffraction and neutron diffraction studies are often undertaken. As these methods give a three dimensional structural rendition at a molecular level, they are of significant importance among the various available characterization methods. The X-ray diffraction technique is founded on Bragg's law that explains the diffraction pattern arising out of a repetitive arrangement of the atoms located at the crystal lattices.

$$2d \sin \theta = n\lambda$$

A major limitation of the X-ray diffraction is that the technique is not sensitive enough to detect the hydrogen atoms, which appear as weak peaks as opposed to intense peaks arising out of the more electron rich metal atoms, and hence are not very useful for metal hydride compounds. Neutron diffraction studies can detect hydrogens more accurately and thus are good for the analysis of the metal hydride complexes.

## Summary

Along with the synthesis, the isolation and the characterization protocols are also integral part of the experimental organometallic chemistry. Because of their air and moisture sensitivities, specialized experimental techniques that succeed in performing the synthesis, isolation and storage of these compounds in an air and moisture-free environment are often used. The organometallic compounds are characterized by various spectroscopic techniques including the <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectroscopies and the X-ray and the neutron diffraction studies.

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