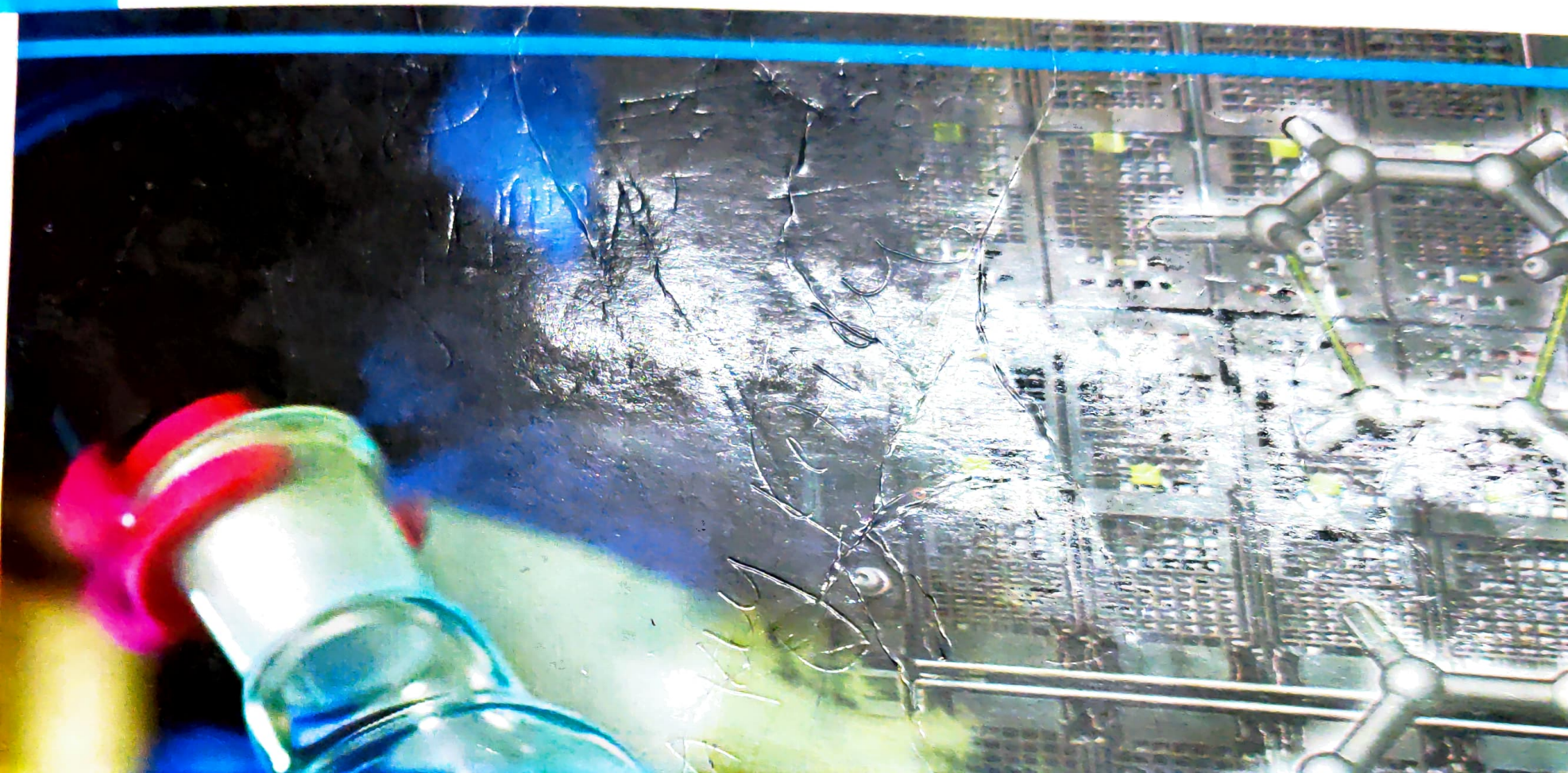
ORGANOMETALLIC COMPOUNDS



Chapter

8

FLUXIONAL ORGANOMETALLIC COMPOUNDS

8.1 INTRODUCTION

For most of the molecules, one stereochemical arrangement is much more stable than others. These molecules exist in a single most stable and well-defined nuclear configuration. The atoms execute approximately harmonic oscillations about their equilibrium positions but in other respects the structure may be considered rigid. Such molecules are called stereochemically rigid. These molecules usually have large HOMO-LUMO gap. However, there are some other molecules for which two or more structures have comparable stability. The molecular vibrations or intramolecular rearrangements transform such molecule from one nuclear configuration into another nuclear configuration. Such molecules change between or among these structures continuously even at ordinary temperature. These molecules are called stereochemically non-rigid. In some cases, two or more nuclear configurations are not equivalent chemically and the process of their interconversion is called tautomerisation or isomerisation, *e.g.*,

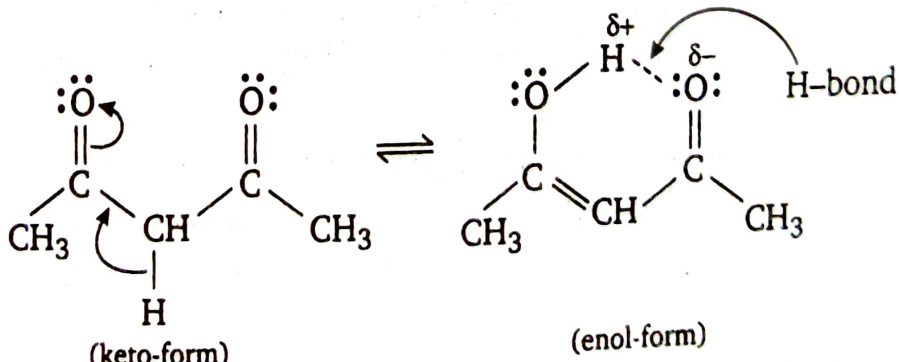


Fig. 8.1. Keto-enol tautomerisation of acetylacetone

On the other hand, in other cases two or more nuclear configurations are chemically equivalent. This type of stereochemical non-rigidity is called fluxionality and the molecules are called fluxional molecules. These molecules have small HOMO-LUMO gap and hence one configuration can be transformed into another configuration with low energy barrier to rotation.

Technique	Approximate time scale(s)
NMR spectroscopy	10^{-1} to 10^{-9}
NQR spectroscopy	10^{-1} to 10^{-8}
Mössbauer spectroscopy	10^{-7}
Experimental separation of isomers	$> 10^{2}$

Smaller the time scale, faster will be the process. It is obvious from the above table that the diffraction techniques have time scales of 10^{-18} to 10^{-20} s which is much faster than the frequency of molecular motions (10^{-11} s). Thus for a fluxional molecule whose all the configurations are equivalent there will be nothing in the observation to indicate the fluxional character. Like diffraction techniques, the spectroscopic methods using UV, visible or IR light are also much faster than molecular vibrations and interconversions. All these techniques reflect the weighted averages of the species present.

The NMR techniques are the most suitable for the investigation of stereochemical non-rigidity of fluxional molecules because at low temperatures, time scales for rotations and vibrations leading to change in the nuclear configuration are often greater, *i. e.*, the process is slower than the scale for nuclear spin transitions. But at higher temperatures, they are often smaller. Let us illustrate it taking example of $BrCl_2CCBrF_2$. At 273 K, the thermal energy (kT) available is greater than the energy barrier to rotation of $BrCl_2CCBrF_2$ molecule about the C—C bond. Therefore, $BrCl_2CCBrF_2$ molecule rotates freely about the C—C bond. Thus, there is a dynamic equilibrium between the enantiomers *A* and *C* of $BrCl_2CCBrF_2$ as shown in fig. 8.5.

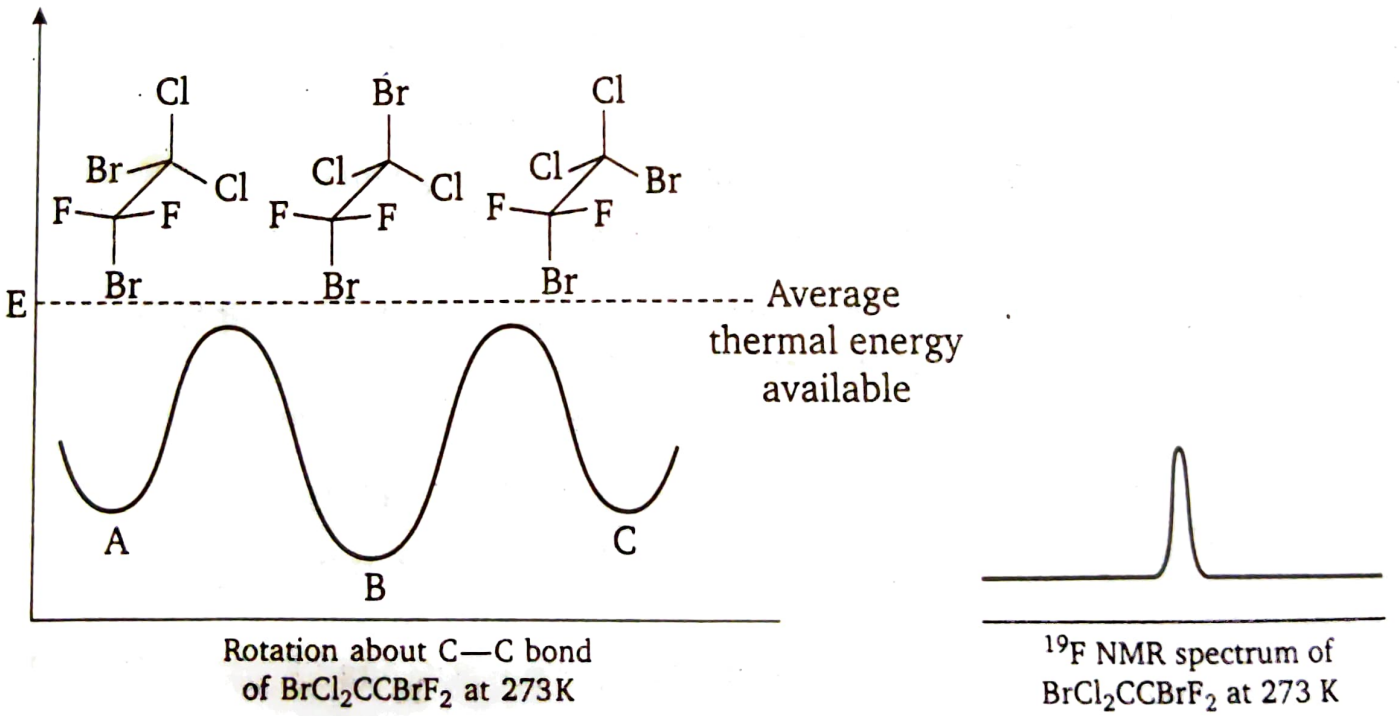


Fig. 8.5. Interconversion of enantomers of $BrCl_2CCBrF_2$ and their ^{19}F NMR spectrum at 273 K.

The frequency of this rotation is so high that the time scale for it smaller than the time scale for NMR spectrum. As a result, the F atoms experience an average environment over the time required for scanning the NMR spectrum and only one signal is obtained in the ^{19}F NMR spectrum.

But on lowering the temperature upto 193 K, the thermal energy available is less than the energy barrier to rotation of $BrCl_2CCBrF_2$ molecule about the C—C bond. Therefore, the internal rotation of molecule is slowed down. The time scale for this rotation becomes greater than the time scale for the NMR spectrum. Thus, NMR spectrum becomes able to detect the presence of rotational isomers *A* and *C* (enantiomers) in chiral solvent as shown in fig. 8.6.

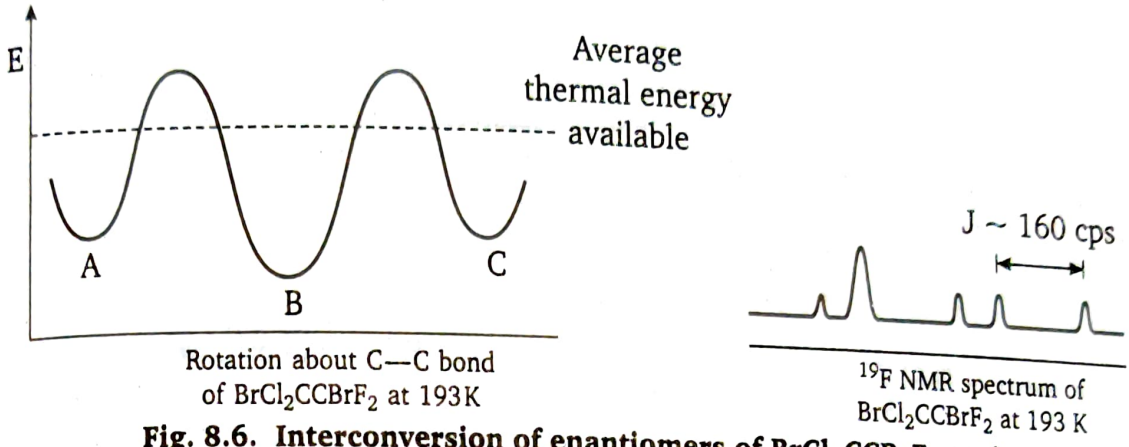


Fig. 8.6. Interconversion of enantiomers of $BrCl_2CCBrF_2$ and their ^{19}F NMR spectrum of 193 K.

8.3 RATE OF FLUXIONALITY

The rate of fluxionality of a stereochemically non-rigid molecule can be calculated by the careful and judicious analysis of changes in the NMR signal shapes that occur with variation in temperature.

Let us consider the simplest dynamic process involving only two molecular configurations *A* and *B* of equal probability. Let the interconversion of configurations takes place at a rate comparable with the NMR time scale. We can slow the exchange down by cooling the sample to such a lower temperature that the rate of interconversion of configurations becomes slower than the NMR time scale. In this situation, two separate sets of equal-intensity resonances, one for each configuration, will be observed in the NMR spectrum at ν_A and ν_B. It is called static NMR spectrum in the low-temperature limit. If we warm the sample, the rate of interconversion may rise to such an extent that it may become faster than NMR time scale. As a result, the fully averaged single set of signal will be obtained at the mid-point of two sets observed at low-temperature limit, *i.e.*, at $\frac{\nu_A + \nu_B}{2}$. At this high temperature limit, two configuration of molecule interconvert so rapidly that NMR cannot distinguish between two separate molecular configurations *A* and *B*. It is called dynamic NMR spectrum. In between above two extremes, *i.e.*, at intermediate interconversion rates, broadened resonances are usually observed as shown in fig. 8.7.

The maximum broadening of spectral lines occurs when the life time (δt) of a configuration gives rise to a line-width that is comparable to difference of resonance frequencies, $\delta\nu$, and both broadened lines blend together in a very broad line as in fig. 8.7(c). Thus, the greatest broadening occurs when

$$\delta t = \frac{1}{2\pi\delta\nu}$$

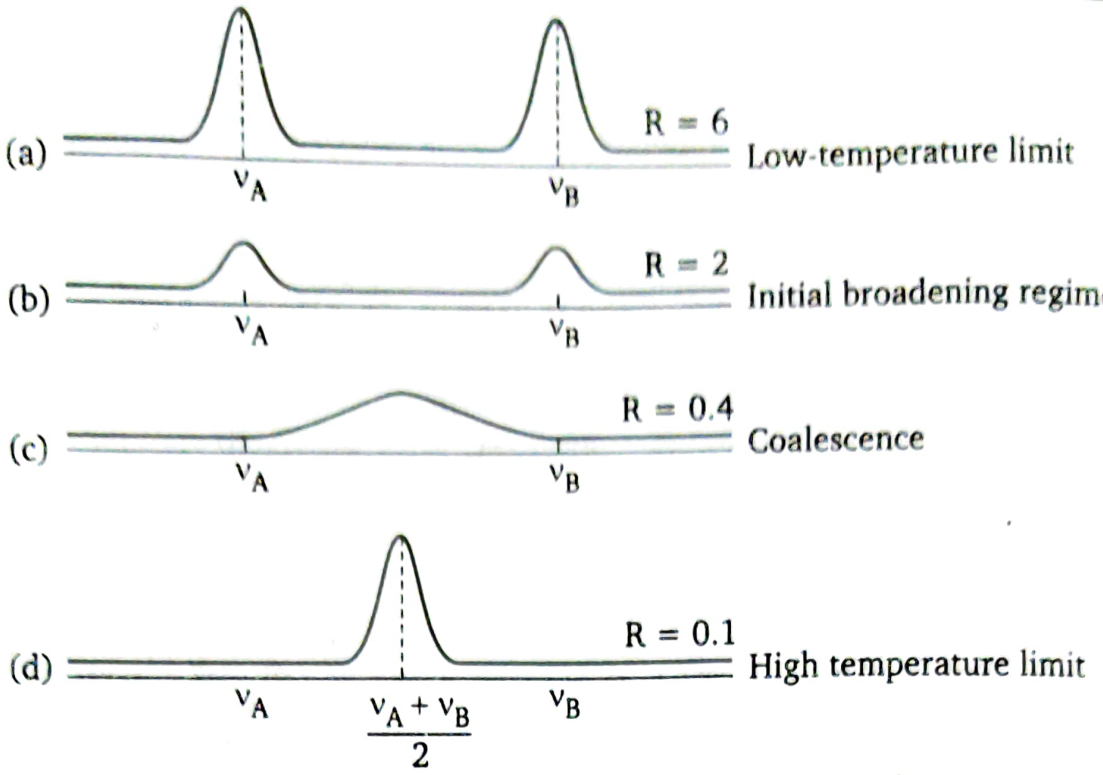


Fig. 8.7. Changes in the NMR spectra of a two-site system with variation in temperature.

where, δt = life-time of configurations *A* and *B*

$\delta\nu = |\nu_A - \nu_B|$

For example, if the chemical shifts differ by 100 Hz, then the spectrum collapses into a single line when the configuration life time is less than 1.6×10^{-3} s.

$$\delta t = \frac{1}{2\pi \times \delta\nu} = \frac{1}{2 \times 3.14 \times 100\ s^{-1}} = 1.6 \times 10^{-3}\ s$$

It is generally convenient to discuss the NMR spectra of such dynamic systems in terms of the ratio *R* which is defined as

$$R = \frac{\text{Chemical shift differences of } A \text{ and } B \text{ without interconversion}}{\text{rate of exchange or interconversion}}$$

$$= \frac{\Delta}{k}, \quad \text{Here, } \Delta = |\nu_A - \nu_B|$$

R decreases with increase in the rate of interconversion. It is obvious from fig. 8.7 that the NMR signals become increasingly broader with decrease in the value of *R*, *i.e.*, increase in the rate of interconversion of configuration with increase in temperature. If the chemical shift difference, Δ, for no interconversion can be measured independently by lowering temperature to freeze interconversion, the rate constant of the interconversion of configuration can be calculated from

$$k = \frac{\Delta}{R}$$

The position of the averaged signal at the high temperature limit is simply the weighted average of the resonance positions at low-temperature limits. For example, if n_1 nuclei resonate at δ_1 and n_2 nuclei resonate at δ_2, the resonance position will be given by

$$\delta_{av} = \frac{n_1\delta_1 + n_2\delta_2}{n_1 + n_2}$$

8.4 FLUXIONALITY IN TRIGONAL BIPYRAMIDAL COMPLEXES

The trigonal bipyramidal organometallic compound, $Fe(CO)_5$, exhibits fluxionality. Its ^{13}C NMR spectrum exhibits only one resonance signal instead of two in the ratio of 3 : 2. This was explained by R.S. Berry in 1960 by saying that the axial and equatorial carbonyl groups interchange their positions more rapidly than NMR time scale. This process was termed pseudorotation. The mechanism proposed for this process is shown in fig. 8.8. The trigonal bipyramidal (TBP) and square pyramidal (SP) configurations of an AB_5 molecule differ only little in energy. At the same time, they can be interconverted by relatively small and simple angle deformation motions.

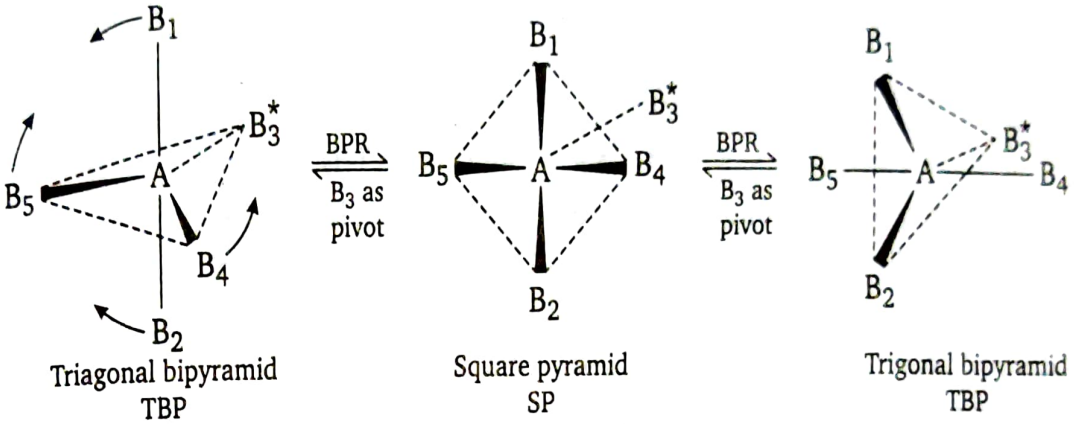


Fig. 8.8. Interchange of axial and equatorial positions of AB_5 molecule by Berry pseudorotation (BPR)

As a result of this TBP–SP–TBP interconversion, the axial and equatorial vertices of TBP are interchanged rapidly and all the five CO groups of $Fe(CO)_5$ become equivalent. This is why, $Fe(CO)_5$ exhibits only one signal in its ^{13}C NMR spectrum.

8.5 FLUXIONALITY IN η^3 ALLYL COMPLEXES

The η^3-allyl complexes generally exhibit fluxionality at room temperature or slightly above it. The fluxionality of η^3-allyl complexes has been studied extensively by ^1H NMR spectroscopy. The η^3-allyl group (C_3H_5) has three types of H atoms as shown in fig. 8.9.

(i) One H_c : It is present on the central carbon atom, *i.e.*, at C_2.

(ii) Two H_s : These syn H atoms are present on terminal carbon atoms (C_1 and C_3). These are towards the metal atom.

(iii) Two H_a : These anti H atoms are present on terminal carbon atoms. These are away from the metal atom.

Therefore, the coordinated η^3-allyl group exhibits three signals in the ^1H NMR spectrum at very low temperature as follows :

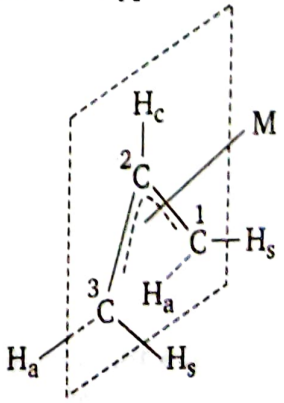


Fig. 8.9. Different environments of H atoms in the coordinated η^3-allyl group

$$\delta H_a = 5 \text{ to } 2.5 \text{ (doublet)}$$
$$\delta H_s = 3 \text{ to } 1 \text{ (doublet)}$$
$$\delta H_c = 6.5 \text{ to } 4 \text{ (multiplet)}$$
$$J_{H_aH_c} \sim 7 \text{ Hz}$$
$$J_{H_sH_c} \sim 11 \text{ Hz}$$
$$J_{H_aH_s} = 0 \text{ Hz}$$

The NMR signals due to H_a and H_s atoms split up into doublet due to spin-spin interaction with H_c. It is called static NMR spectrum. For example, $[Mn(CO)_4(\eta^3 - C_3H_5)]$ exhibits three signals in the ratio 2 : 2 : 1 in its ^1H NMR spectrum at low temperatures at

$$\delta H_s = 1.8 \text{ (doublet) (2H)}$$
$$\delta H_a = 2.8 \text{ (doublet) (2H)}$$
$$\delta H_c = 4.7 \text{ (multiplet) (1H)}$$

But at room temperature or elevated temperatures, $[Mn(CO)_4(\eta^3 - C_3H_5)]$ exhibits only two signals in the ratio 4 : 1 in its ^1H NMR spectrum at

$$\delta H_s, \delta H_a = 2.3 \text{ (doublet) (4H)}$$
$$\delta H_c = 4.7 \text{ (multiplet) (1H)}$$

It is called dynamic NMR spectrum. This is due to the fact that at higher temperatures, the syn and anti H atoms interchange their positions rapidly probably via a short-lived η^1 – allyl-metal intermediate as shown in fig. 8.10. The rate of this interchange is faster than the NMR time scale. As a result, the NMR spectrum becomes unable to distinguish between syn and anti H atoms and all the four H atoms present on terminal carbon atoms (C_1 and C_3) give rise to a single NMR signal (doublet) at $\delta = 2.3$ which is the weighted mean of $\delta H_a = 2.8$ and $\delta H_s = 1.8$ in low-temperature limit NMR spectrum.

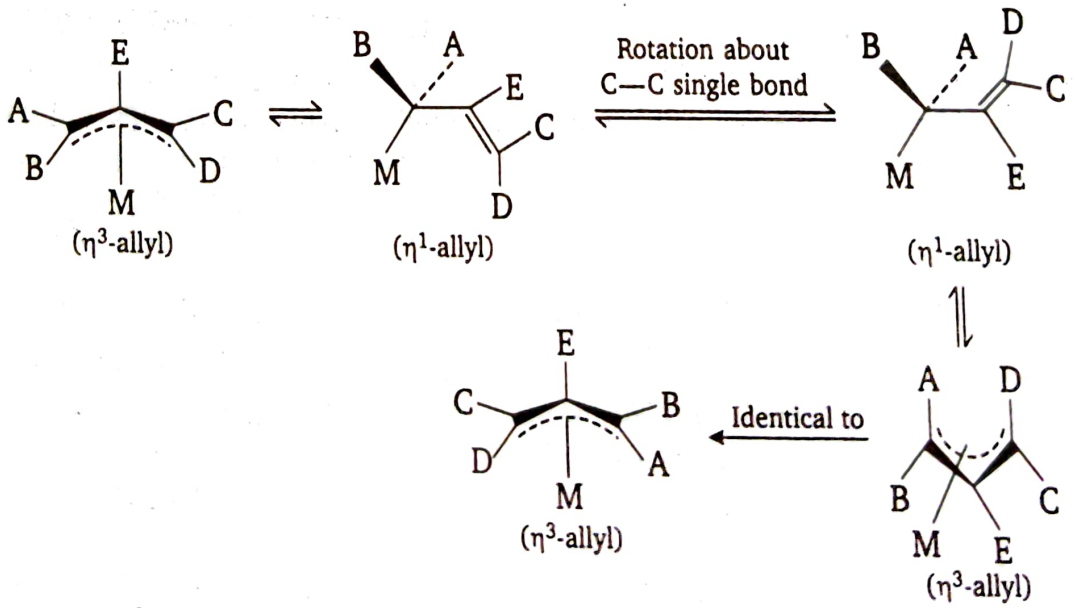


Fig. 8.10. Interchange of position of syn and anti H atoms of η^3-allyl group via η^3-η^1-η^3 process.

First of all the coordinated η^3 – allyl group is transformed into a short-lived η^1-allyl species which undergoes rotation about C—C single bond producting a

spectrum of this organometallic compound exhibits only one singlet signal. This is due to a dynamic process in which the monohapto-C_5H_5 and pentahepto -C_5H_5 (i.e., σ-bonded C_5H_5 and π-bonded C_5H_5) rings interchange their roles rapidly. At the same time, the point of attachment of each of the monothapto C_5H_5 rings to the Ti atom changes continuously between 5 carbon atoms of the ring as shown in fig. 8.12.

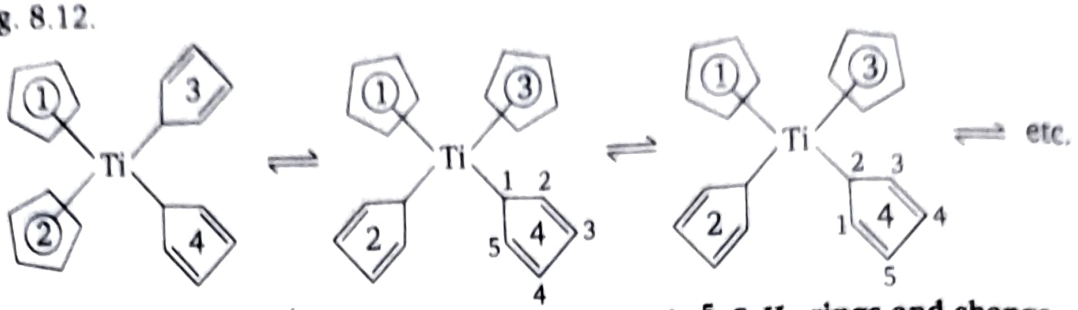


Fig. 8.12. Interchange of roles of η^1-C_5H_5 and η^5-C_5H_5 rings and change in point of attachment of η^1-C_5H_5 ring to the Ti atom.

As a result of these time averaging processes, all the four C_5H_5 ligands become equivalent and all the 20 H atoms of $(\eta^1 - C_5H_5)_2Ti$ $(\eta^5 - C_5H_5)_2$ become indistinguishable and they give rise to a single singlet signal in the ^1H NMR spectrum at $\delta = 4.45$ at 62°C. As the temperature is lowered, this signal is broadened

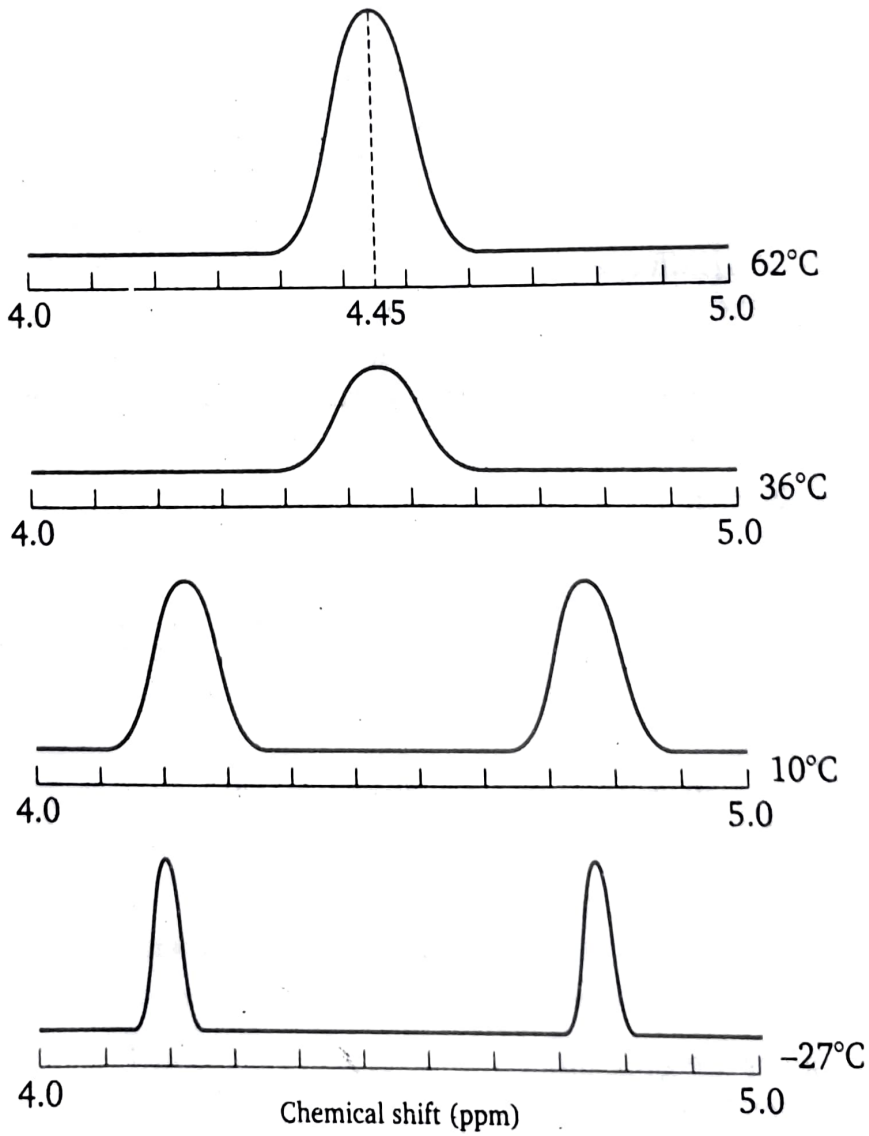


Fig. 8.13. ^1H NMR spectra of $(\eta^1$-$C_5H_5)_2$ Ti$(\eta^5$-$C_5H_5)_2$ at different temperatures from +62°C to -27°C

and gradually splits up into two lines which sharpen into equal intensity singlets at -27°C as shown in fig. 8.13. At this point, the interconversion of monohapto and pentahapto-C_5H_5 rings is slower than NMR time scale and both the configurations-η^5-C_5H_5 and η^1 $-C_5H_5$ are observed in the ^{1}H NMR spectrum. However, even at -27°C, the monohapto-C_5H_5 rings are involved in a dynamic process (ring-whizzing) which averages the signals for the three types of ring-protons. Therefore, a single fairly sharp line is obtained instead of separate resonances in a 2 : 2 : 1 ratio for the η^1 $-C_5H_5$ ring.