## $^1$H-NMR

The I value of proton is ½. The chemical shift value ranges from 0 to 10 ppm with respect to TMS. Due to spin-spin splitting of neighbouring atoms, more number of lines are observed. For n protons, (n+1) lines are observed. The peak area indicates the number of protons of same kind present in the molecule.

$SiH_3SiCl_2H$ - Doublet of quartet in the ratio of 3 : 1

$GeClH_2GeClH_2$ - only one line.

$PF_2H$ - wide doublet of triplet. Doublet due to $^{31}P$ (I = ½) splitting and triplet due to $^{19}F$ (I = ½) splittings.

**$SiH_3PH_2$**

For protons on Si, doublet of triplet, doublet due to $^{31}P$ and triplet due to H on P. For protons on P, doublet of quartets, doublet due to $^{31}P$ and quartet due to H on Si.

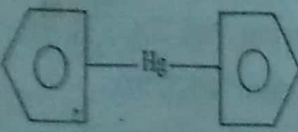
**$BH_4^-$**

$^{10}B$ and $^{11}B$ couplings.

$^{10}B$ I = 3, A septet of equal intensity is obtained.

$^{11}B$ I = 3/2, A quartet of equal intensity is obtained with 4 : 1 ratio.

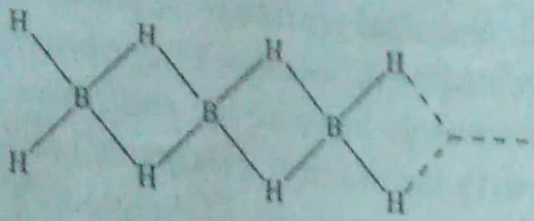
**$Hg(C_5H_5)_2$**



Three closely spaced lines-sandwitch structure. $\eta^5$-$C_5H_5$ ligands are attached with 3 kinds of protons; 3 lines are observed. No effect on increasing temperature and there is no fluxional behaviour.

**$M(BH_4)_n$**

Two broad groups of resonances of equal intensity. Each $BH_4$ group has two bridging and two terminal hydrogen atoms. These couple to one another and with the quadrupolar $^{11}B$ equally. On warming the protons exchange their positions by an intra molecular process. Therefore only a sharp peak is obtained.



At low temperature when $^{11}B$ is decoupled, triplet due to two bridging and two terminal protons are obtained.

**$HRh(CN)_5^{3-}$**

The pmr is a doublet. Protons attached to metal ions are very highly shielded. The resonance occurs at 5 - 15 ppm to the high field side of TMS. In some cases it may occur over 60 ppm upfield from TMS. The shifts may be due to paramagnetic shielding by the protons by the filled d orbital electrons of the metal.

In $HRh(CN)_5^{3-}$ the doublet occurs at 10.6 ppm. The splitting of proton by Rh (I = ½) and the shift to upfield establish the existence of a bond between Rhodium and hydrogen.

| | |
|---|---|
| HD | Proton resonance, a triplet of equal intensity.<br>Deuterium resonance, a doublet of equal intensity. |

**$H_2Fe(CO)_4$**

It has very high field NMR chemical shift. There is a metal hydrogen bond. It has large δ value in the up field ($\delta = -50$ ppm). It is consistent with an environment of high electron density. The proton is buried in the electron clouds of the metal. Therefore there is very high diamagnetic shielding effect of the metal on the protons.

## CARBON - 13 NMR SPECTROSCOPY

Like $^1H$, $^{13}C$ has a spin of ½. There is a huge amount of information on $^{13}C$ chemical shifts. In a 2.3 T field, the precession frequency of $^{13}C$ is 25 MHz while for $^1H$ it is 100 MHz. The magnetic moment of $^{13}C$ is about one quarter that of $^1H$ so that signals are very weak. The natural abundance of $^{13}C$ is 1.1% and therefore $^{13}C$-$^{13}C$ interaction is generally not possible.

The carbon chemical shifts are observed up to 400 ppm. For saturated carbon atoms δ is 0 - 100 ppm relative to TMS. Electronegative substituents increase the shift value. The $^{13}C$ chemical shifts associated with the methyl groups in compounds $CH_3X$ are directly related to the electonegativity of the group X and the number of lone pairs of electrons on the central atom of the group.

For three coordinate carbon atoms chemical shift is 80 - 240 ppm;

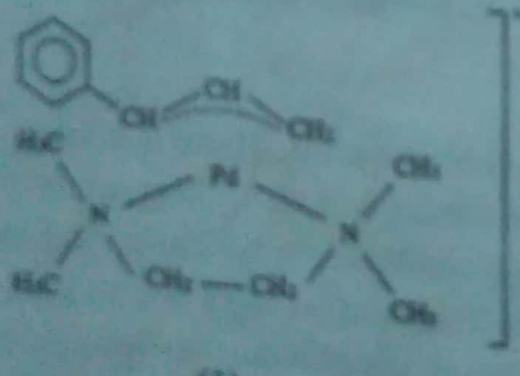
Alkyne shifts 20 - 110 ppm; Aromatic compounds 110 - 170 ppm.

In π-bonded metal alkene and arene complexes resonances are shifted up to 100 ppm to low frequency region. The shifts depend on the mode of coordination.

$Cl_4$ has a shift of - 293 ppm; For metal carbonyls 170 -29 ppm; For metal carbene complexes 250 -370 ppm.

It is difficult to record the $^{13}C$ spectra of metal carbonyls because the relaxation times for $^{13}C$ nuclei in these compounds are very large. Therefore paramagnetic relaxation agents are used to record the spectrum.

The $^{13}C$ nmr of organometallic compound 1 can be studied to understand its structure and nature of bonding.



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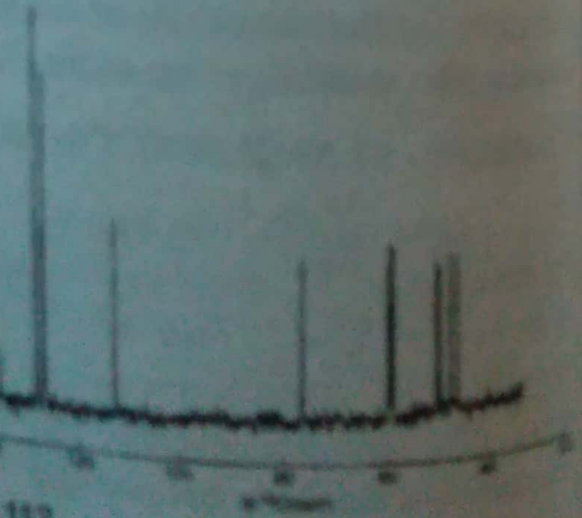
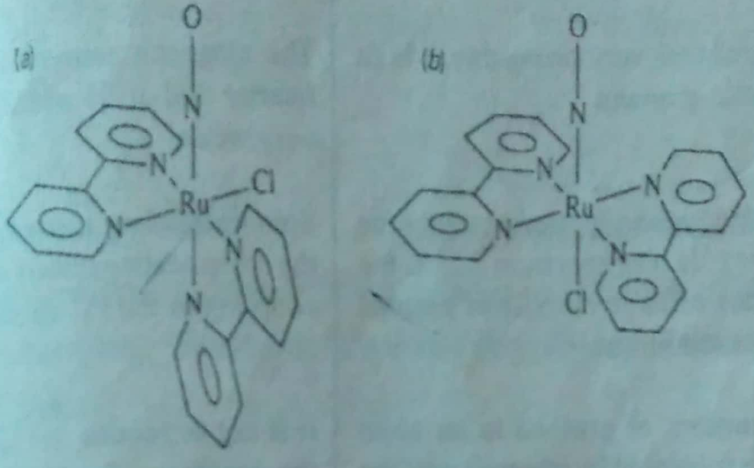


The tetramethylethylenediamine ligand has four non-equivalent types of methyl carbons and two distinct methylene carbons. The allyl ligand has a methylene, two methinyl and four chemically distinct aromatic sites. For all the groups 13 resonances are clearly seen.

For Trans-$[RuCl(NO)(bpy)_2]^+$ five resonances are seen in the $^{13}C$ spectrum while for the cis-compound 20 resonances are seen. In trans compound there are two planes of symmetries, so that each bpy ligand is bisected by the mirror plane and the two ligands are related by the second plane. There are five chemically distinct carbon atoms and so five resonances are seen in the $^{13}C$ spectrum.



In cis-$[RuCl(NO)(bpy)_2]^+$ there is no plane of symmetry. The carbon nuclei are all chemically distinct. Thus there are twenty resonances (20 carbon atoms). Four are due to quarternary carbons and are less intense than others. Each line in the spectrum of the trans isomer has become four lines and the chemical shift changes are small.

## COMPARISON OF $^1H$ AND $^{13}C$ NMR

| | $^1H$ NMR | $^{13}C$ NMR |
|---|---|---|
| 1. | The Nuclear spin angular momentum quantum number $I = ½$ | $I = ½$ |
| 2. | There is 100% natural abundance | There is 1.1% abundance |
| 3. | Tetramethylsilane is used as a reference standard | Tetramethylsilane is used as the reference standard. |
| 4. | In 2.3 T field the precession frequency is 100 MHz. | In 2.3 T field, the precession frequency is 25 MHz. |

| | | |
|---|---|---|
| 5. | The chemical shift value ranges from 0 to 10 ppm with respect to TMS | The chemical shift value ranges up to 400 ppm with respect to TMS. |
| 6. | Coupling between $^1$H – $^1$H is most abundant | Coupling between $^{13}$C – $^{13}$C is ignored as it is relatively unlikely that any one molecule will have more than one of the spin ½ nuclei. |
| 7. | The $^1$H spectrum has high intense lines with sharp peak | The intensity of $^{13}$C spectrum is very low and occurs as a satellite. The $^{13}$C spectral lines are immersed in the $^1$H spectral lines particularly in organic compounds where there are maximum number of protons. |
| 8. | $^1$H signals are very strong due to high magnetic moment. | The magnetic moment is about one quarter that of $^1$H and so signals are very weak. |
| 9. | Spin decoupling is used to study the complex $^1$H nmr spectrum due to the presence of large number of protons on adjacent atoms. | Spin decoupling is used to eliminate the complicating effects of the proton coupling in the $^{13}$C spectra. |
| 10. | The number of protons in an atom may be measured by integration of the peak area. | It is not so routine in $^{13}$C nmr due to the presence of nuclear overhauser effect and relaxation time. |
| 11. | Protons have longer relaxation time and hence sharp peaks are observed. | Protons bearing $^{13}$C have shorter relaxation time. Quarternary carbons tend to have long relaxation times. They show lowered intensity. |
| 12. | In pmr, local para and dia-magnetic terms are important. | The cmr spectra are dominated by the local paramagnetic term. |
| 13. | $^1$H spectrum is used to assign the molecule and the number of protons present on each site. | $^{13}$C spectrum is used as tracers to locate an atom in a molecule, reaction mechanism, nature of binding of carbon with other functional groups |