NMR spectroscopy and dynamic processes

1 Chemical shift norms in organometallic systems

$^1$H NMR: chemical shift range 25 to –40 ppm

- **direct M-H bonds (hydrides)**
  - hydrides generally experience a strong *shielding* effect: resonances far upfield of 0 ppm are diagnostic for M-H
  - more electron rich metal center = more upfield (shielded) hydride resonance
  - bridging hydrides are more shielded
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (ppm)</th>
<th>Compound</th>
<th>$\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CO})_5\text{MnH}$</td>
<td>-7.5</td>
<td>$\text{Cp}_2\text{MoH}_2$</td>
<td>-8.8</td>
</tr>
<tr>
<td>$(\text{CO})_5\text{ReH}$</td>
<td>-5.7</td>
<td>$\text{Cp}_2\text{MoH}_3^+$</td>
<td>-6.1</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{FeH}_2$</td>
<td>-11.1</td>
<td>$\text{CpCr(CO)}_3\text{H}$</td>
<td>-5.5</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{RuH}_2$</td>
<td>-7.6</td>
<td>$\text{CpMo(CO)}_3\text{H}$</td>
<td>-5.5</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{OsH}_2$</td>
<td>-8.7</td>
<td>$\text{CpW(CO)}_3\text{H}$</td>
<td>-7.3</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{CoH}$</td>
<td>-10.7</td>
<td>$\text{Cp}_2\text{FeH}^+$</td>
<td>-2.1</td>
</tr>
<tr>
<td>$\text{trans-}(\text{Et}_3\text{P})_2\text{ClPtH}$</td>
<td>-16.8</td>
<td>$\text{Cp}_2\text{RuH}^+$</td>
<td>-7.2</td>
</tr>
<tr>
<td>$(\text{CO})_{10}\text{Cr}_2\text{H}^+$</td>
<td>-19.5 (bridging)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CO})<em>{24}\text{Rh}</em>{13}\text{H}_3^{2-}$</td>
<td>-29.3 (bridging)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{HCo}<em>6(\text{CO})</em>{15}]^-$</td>
<td>+23.2 (encapsulated)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
- **H bonded to η-carbon (M-C-H)**
  - much smaller $\Delta \delta$ *(coordination chemical shift)*
    - range: typically $\Delta \delta = -1$ to $-4$ ppm *(upfield)*
  - effects depend on many factors and are not easily predictable:
    - local effects at carbon (partial charge, rehybridization)
    - non-local effects (magnetic anisotropy of metal, perturbation of ring currents on coordination)
Chemical shift trends can be useful but they are not always intuitive (see Chart D-1):

- \( \delta(\text{Cp}) \):
  - \( \text{Cp}_2\text{Os} \) (4.71) > \( \text{Cp}_2\text{Ru} \) (4.42) > \( \text{Cp}_2\text{Fe} \) (4.04)

- \( \delta(\text{C}_6\text{H}_6) \):
  - \( \text{W}(\text{C}_6\text{H}_6)_2 \) (4.90) > \( \text{Mo}(\text{C}_6\text{H}_6)_2 \) (4.60) > \( \text{Cr}(\text{C}_6\text{H}_6)_2 \) (4.12)
  - but > \( \text{V}(\text{C}_6\text{H}_6)_2^- \) (3.28)

- \( \delta(\text{Cp}/\text{C}_6\text{H}_6) \):
  - \( \text{CpFe}(\text{C}_6\text{H}_6)^+ \) (5.05/6.25) > \( \text{CpMn}(\text{C}_6\text{H}_6) \) (3.9/4.7)

It would be tempting to argue that these shifts reflect the electron richness of the rings: since the electronegativity drops down a group, the rings become more electron rich down a group and hence the ring current increases (primary deshielding effect). However, if this is so then why does the anionic V analog, which must certainly have the most electron rich rings, have the lowest \( \delta \) value? Also note that the mixed Cp/C\(_6\)H\(_6\) complexes of Fe and Mn also go against this trend.

- \textit{H bonded to remote carbons (M-C-C\(_n\)-H)}
  - not surprisingly, remote protons show very small \( \Delta\delta \) values: typically \( \pm 0.5 \) ppm or less
  - these can be positive or negative (governed by conformation)
Chart D-1 $^1$H Values in diamagnetic organometallic complexes

From Elschenbroich and Salzer
$^{13}\text{C NMR spectroscopy}$ (see Chart D-2)

- despite low abundance and receptivity, $^{13}\text{C}$ NMR is very valuable as a characterization tool:
  - chemical shift range (dispersion) is 5 times $^1\text{H}$ NMR
  - $^1\text{H}$-decoupled spectra usually consist of sharp singlets
  - allows study of faster dynamic processes (discussed in section D-4)
  - $^{13}\text{C}$-$^1\text{H}$ and $^{13}\text{C}$-Metal ($I\neq 0$) coupling constants directly indicate C hybridization and indicate likely structure (see section D-3)
Chart D-2: $\delta^{13}C$ values for the metal-coordinated carbons in various organometallic compounds

From Elschenbroich and Salzer
**σ-Bonded ligands**

**alkyls**

- $^{13}$C values are strongly dependent on the metal and the ancillary ligands bonded to it
  
  $\delta$ (Me) $^{13}$C: 
  
  $\text{WMe}_6$ (85 ppm)  
  
  $\text{CpW(CO)}_3\text{Me}$ (-35.1)

- for most metals the α-C shows a negative $\Delta\delta$ value (but note the exception in $\text{WMe}_6$) however, Grp 4 and 5 metals usually show positive $\Delta\delta$ values:

  $\text{Zr[CH}_2\text{OCH}_2\text{CH}_2\text{N(C}_6\text{F}_5\text{)]}_2(\text{CH}_2\text{Ph})_2}$ 
  
  $\delta$ (ZrCH$_2$) 72.7 ($\Delta\delta = +47$ ppm)

- $\Delta\delta$ drops off rapidly with distance:  
  
  β-C (0 to +10 ppm)  
  
  γ-C (0 to –2.5 ppm)
Carbonyls

- difficult to observe (quaternary, long $T_1$)
- **terminal:** $\delta$ 150-220 ppm  **bridge:** $\delta$ 230-280 ppm
- decreases down a triad for the same type of complex:
  - $\text{Cr(CO)}_6$ (212 ppm)  $\text{Mo(CO)}_6$ (202)  $\text{W(CO)}_6$ (192)

Alkylidenes $\text{M}=$CR$_2$ (carbenes $\text{M}=$CR(ER)) and alkylidyynes $\text{M}=$CR (carbynes $\text{M}=$CER)

- typical alkylidene and alkylidyne: $\delta$ 200-400 ppm
- similar to carbocations:  $\text{Ph}_3\text{C}^+$ (212 ppm)  $\text{Me}_3\text{C}^+$ (336 ppm)
- hetero-substituted carbenes/carbynes fall in a similar range but for a given class of compounds they resonate at higher field:
  - $(\text{CO})_5\text{Cr}=\text{C(NMe}_2\text{)H}$ (246)  $(\text{CO})_5\text{Cr}=\text{C(OMe)Ph}$ (351)  $(\text{CO})_5\text{Cr}=\text{CPh}_2$ (399)
π-Bonded ligands

- generally show large negative $\Delta\delta$ for coordinated carbons
- adjacent, non-bonded C centers usually show a small positive $\Delta\delta$
- internal C in $\eta^3$-allyls and $\eta^4$-dienes show smaller $\Delta\delta$ than do the terminal C (hybridization arguments)
- influenced by many factors: partial charges, C-C bond order, hybridization and metal anisotropy effects

Eg. $^{13}\text{C}^{1\text{H}}$ NMR for ($\eta^4$-C$_7$H$_8$)Fe(CO)$_3$

and free cycloheptatriene
Heteronuclear NMR

- $^{31}$P (I = ½, 100%) and $^{29}$Si (I = ½, 4.7 %) in ancillary ligands are commonly studied

- $^{31}$P especially important because of very high receptivity and importance of phosphines (+40 to –100 ppm vs. H$_3$PO$_4$ reference) and phosphine oxides (+25 to +90 ppm) as ancillary ligands

- phosphines usually show positive $\Delta\delta$ values from +5 to +60 ppm

\[
\text{cis-PtCl}_2(\text{PPh}_3)_2 \quad \delta_P = +10.5 \text{ ppm}
\]
\[
\text{free PPh}_3 \quad \delta_P = -5.5 \text{ ppm}
\]
\[
\Delta\delta = +16 \text{ ppm}
\]
coupling to other ligands and to C or H of organic groups is extremely useful in determining structure because these values are strongly influenced by complex geometry:

\[
P = \text{PPh}_3
\]

\[
\begin{align*}
\text{Cl} - &\text{Rh} - \text{Cl} \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]

\[{^2}J_{pp} = 29 \text{ Hz (cis), 567 Hz (trans)}\]

\[
\begin{align*}
\text{PPh}_3 &\quad \text{OC} - \text{Pt} - \text{H} \\
\text{Cl} &
\end{align*}
\]

\[{^2}J_{hp} = 13.5 \text{ Hz indicates cis}\]
Direct observation of metal NMR

- this can be done for some metals, especially those with $I = \frac{1}{2}$ (Table D-1)

- most useful for $^{103}$Rh and $^{195}$Pt:
  - observation of M-L coupling can provide information about bond order
  - loss or retention of coupling during fluxional processes can provide information about certain mechanistic possibilities (eg. phosphine dissociation)

- $^{195}$Pt has a huge chemical shift range (13,000 ppm) and exhibits very large Pt-L coupling constants (eg. $^1J_{Pt-P} = 1000-4000$ Hz) that are sensitive to the structure of the complex and metal oxidation state
- $^{103}\text{Rh}$ has nearly as large a chemical shift range (9000 ppm) and also shows a strong relationship between the metal oxidation state and $^{103}\text{Rh}$-X coupling constants. Typically square planar $\text{Rh}^+$ complexes have $^{103}\text{Rh}$-X coupling constants that are 1.5 times larger than those in octahedral $\text{Rh}^{3+}$ compounds.

![Diagram](image_url)

- $^{103}\text{Rh}$ P = PPh$_3$
  
  - $^1J_{\text{RhP}} = 105$ Hz (P trans to Cl)

- $^{103}\text{Rh}$ P = PPh$_3$
  
  - $^1J_{\text{RhP}} = 190$ Hz (P trans to Cl)
### Table D-1 Metal isotopes suitable for NMR spectroscopy

<table>
<thead>
<tr>
<th>Isotope</th>
<th>I</th>
<th>Nat. Abund. (%)</th>
<th>NMR Freq. (MHz)</th>
<th>Receptivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li</td>
<td>1</td>
<td>7.4</td>
<td>44.146</td>
<td>0.00851</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>3/2</td>
<td>92.6</td>
<td>116.950</td>
<td>0.294</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>5/2</td>
<td>100</td>
<td>78.172</td>
<td>0.207</td>
</tr>
<tr>
<td>$^{45}$Sc</td>
<td>7/2</td>
<td>100</td>
<td>72.882</td>
<td>0.3</td>
</tr>
<tr>
<td>$^{51}$V</td>
<td>7/2</td>
<td>100</td>
<td>78.864</td>
<td>0.383</td>
</tr>
<tr>
<td>$^{59}$Co</td>
<td>7/2</td>
<td>100</td>
<td>70.842</td>
<td>0.281</td>
</tr>
<tr>
<td>$^{65}$Cu</td>
<td>3/2</td>
<td>30.9</td>
<td>85.183</td>
<td>0.116</td>
</tr>
<tr>
<td>$^{87}$Rb</td>
<td>3/2</td>
<td>27.2</td>
<td>98.163</td>
<td>0.177</td>
</tr>
<tr>
<td>$^{89}$Y</td>
<td>1/2</td>
<td>100</td>
<td>14.697</td>
<td>0.000117</td>
</tr>
<tr>
<td>$^{103}$Rh</td>
<td>1/2</td>
<td>100</td>
<td>9.442</td>
<td>0.0000312</td>
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<tr>
<td>$^{107}$Ag</td>
<td>1/2</td>
<td>51.4</td>
<td>12.139</td>
<td>0.0000669</td>
</tr>
<tr>
<td>$^{111}$Cd</td>
<td>1/2</td>
<td>12.9</td>
<td>63.616</td>
<td>0.00954</td>
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<tr>
<td>$^{113}$Cd</td>
<td>1/2</td>
<td>12.3</td>
<td>66.548</td>
<td>0.0109</td>
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<tr>
<td>$^{117}$Sn</td>
<td>1/2</td>
<td>7.7</td>
<td>106.875</td>
<td>0.0453</td>
</tr>
<tr>
<td>$^{119}$Sn</td>
<td>1/2</td>
<td>8.7</td>
<td>111.817</td>
<td>0.0518</td>
</tr>
<tr>
<td>$^{125}$Te</td>
<td>1/2</td>
<td>7.0</td>
<td>94.790</td>
<td>0.0316</td>
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<tr>
<td>$^{171}$Yb</td>
<td>1/2</td>
<td>14.3</td>
<td>52.8</td>
<td>0.0055</td>
</tr>
<tr>
<td>$^{183}$W</td>
<td>1/2</td>
<td>14.3</td>
<td>12.48</td>
<td>0.000720</td>
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<tr>
<td>$^{187}$Os</td>
<td>1/2</td>
<td>1.6</td>
<td>23.276</td>
<td>0.0000007</td>
</tr>
<tr>
<td>$^{195}$Pt</td>
<td>1/2</td>
<td>33.7</td>
<td>64.447</td>
<td>0.00994</td>
</tr>
<tr>
<td>$^{197}$Au</td>
<td>3/2</td>
<td>100</td>
<td>5.138</td>
<td>0.0000214</td>
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<tr>
<td>$^{199}$Hg</td>
<td>1/2</td>
<td>16.9</td>
<td>53.481</td>
<td>0.00572</td>
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<tr>
<td>$^{203}$Tl</td>
<td>1/2</td>
<td>29.5</td>
<td>171.448</td>
<td>0.187</td>
</tr>
<tr>
<td>$^{205}$Tl</td>
<td>1/2</td>
<td>70.5</td>
<td>173.124</td>
<td>0.192</td>
</tr>
<tr>
<td>$^{207}$Pb</td>
<td>1/2</td>
<td>21.1</td>
<td>62.765</td>
<td>0.00913</td>
</tr>
</tbody>
</table>

a at a field such that $^1$H resonates at 300 MHz  

b relative to $^1$H receptivity = 1 

($^{13}$C receptivity = 0.0159)
3 Coupling constants

$^1J_{CH}$ values correlated with s character in the C-H bond:

rule of thumb is $^1J_{CH} = 500 \times \text{(fraction s)}$ $sp^3 = 125 \text{ Hz}$, $sp^2 = 167 \text{ Hz}$ and $sp = 250 \text{ Hz}$

- decrease in $^1J_{CH}$ observed in alkene complexes is attributed (mainly) to a decrease in s character in the terminal M-C bond:

\[
\begin{align*}
\text{H} & \quad \text{H} & 146 (157) \\
\text{H} & \quad \text{H} & \text{H} \\
\text{H} & \quad \text{Pt(PPh}_3\text{)} & \text{2} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & 144 (155) \\
\text{H} & \quad \text{H} & \text{H} \\
\text{ZrCp}_2 & \quad \text{H} & \text{156 (153)}
\end{align*}
\]
• \( \eta^5\text{-Cp} \) and \( \eta^6\text{-arenes} \) show an increase in \( ^1J_{\text{CH}} \) but no convincing explanation has been forwarded to explain this:
• **agostic** complexes show a **pronounced reduction in the** $^{1}J_{CH}$ **value although in most case the effect is averaged at room temperature due to interchange of the H involved in the C-H···M interaction**

\[
^{1}J_{CH} = 125 \text{ Hz} \quad \text{and} \quad ^{1}J_{CH} = 75 \text{ Hz}
\]

\[
16 \text{ e}^{-} \quad \text{(18 e}^{-} \text{with agostic CH)}
\]

• the analogous complex with $\eta^{3}$-$C_{4}H_{7}$ (1-methylallyl) has a $^{1}J_{CH}$ value of 106 Hz due to fast rotation of the agostic methyl:
$^{1}J_{MC}$ values

- larger for M-C $\sigma$-bonds than for $\pi$-bonds; varies with amount of s character at C (ie. hybridization):

\[
\begin{align*}
^{1}J_{Rh-C} & = 26 \text{ Hz} \\
^{1}J_{Rh-C} & = 14-16 \text{ Hz} \\
^{1}J_{Fe-C} & = 1.5 \text{ Hz} \\
^{1}J_{Fe-C} & = 1.5-4.5 \text{ Hz for Fe-C } \pi \\
^{57}Fe \text{ enriched} \\
^{1}J_{Fe-C} & = 9 \text{ Hz for Fe-C } \sigma \\
\end{align*}
\]

$^{183}W$  
$^{1}J_{WC} = 43 \text{ Hz (WMe}_6) \quad ^{1}J_{WC} = 126 \text{ Hz (W(CO)}_6)$

$^{195}Pt$  
$^{1}J_{PtC} = 568 \text{ Hz (Me), 2013 Hz (CO) in cis-PtCl}_2(CO)Me^-$

Specific values of $^{1}J_{MC}$ vary tremendously from metal to metal depending on the magnetogyric ratio $\gamma$ (a constant for each isotope) according to the formula below:

\[
J_{MC} = \frac{h(\gamma_M\gamma_C)K_{MC}}{(4\pi^2)}
\]

where $h$ is Planck’s constant, $\gamma_M$ and $\gamma_C$ are the magnetogyric ratios of the metal isotope involved and $^{13}C$ respectively, and $K_{MC}$ is the ‘reduced’ coupling constant. The reduced coupling constant is therefore independent of the specific identity of the coupling isotopes but depends on a number of electronic interaction terms between the nuclei in question.
$^{2}J_{CX}$ (geminal) coupling

- useful in providing stereochemical information

$^{2}J_{PC} = 9$ Hz

$^{2}J_{PC} = 104$ Hz