

D NMR spectroscopy and dynamic processes

1 Chemical shift norms in organometallic systems

^1H 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

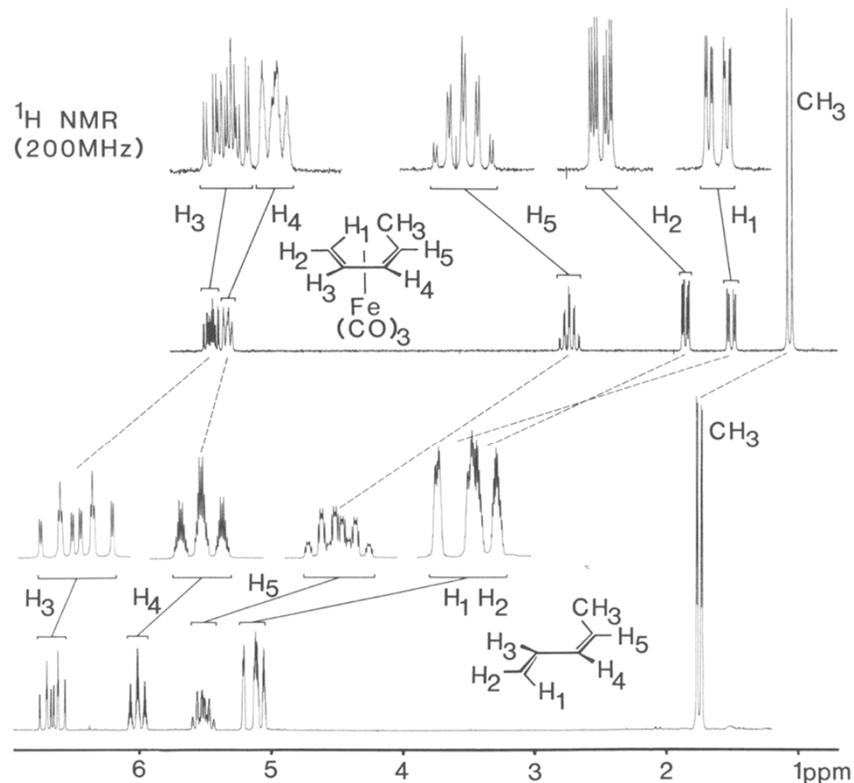
	δ (ppm)		δ (ppm)
$(\text{CO})_5\text{MnH}$	-7.5	Cp_2MoH_2	-8.8
$(\text{CO})_5\text{ReH}$	-5.7	$\text{Cp}_2\text{MoH}_3^+$	-6.1
$(\text{CO})_4\text{FeH}_2$	-11.1	$\text{CpCr}(\text{CO})_3\text{H}$	-5.5
$(\text{CO})_4\text{RuH}_2$	-7.6	$\text{CpMo}(\text{CO})_3\text{H}$	-5.5
$(\text{CO})_4\text{OsH}_2$	-8.7	$\text{CpW}(\text{CO})_3\text{H}$	-7.3
$(\text{CO})_4\text{CoH}$	-10.7	Cp_2FeH^+	-2.1
<i>trans</i> - $(\text{Et}_3\text{P})_2\text{ClPtH}$	-16.8	Cp_2RuH^+	-7.2
$(\text{CO})_{10}\text{Cr}_2\text{H}^-$	-19.5 (<i>bridging</i>)		
$(\text{CO})_{24}\text{Rh}_{13}\text{H}_3^{2-}$	-29.3 (<i>bridging</i>)		
$[\text{HCo}_6(\text{CO})_{15}]^-$	+23.2 (<i>encapsulated</i>)		

- **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)



¹H-NMR spectra of (η⁴-cis-1,3-pentadiene)Fe(CO)₃ and of free 1,3-pentadiene in CDCl₃ at 200 MHz.

$\Delta\delta$ ¹H decreases in the order terminal, endo (H₁) > terminal, exo (H_{2,5}) > central (H_{3,4})

- **Chemical shift trends can be useful but they are not always intuitive (see Chart D-1):**

$\delta(\text{Cp})$ Cp_2Os (4.71) > Cp_2Ru (4.42) > Cp_2Fe (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)

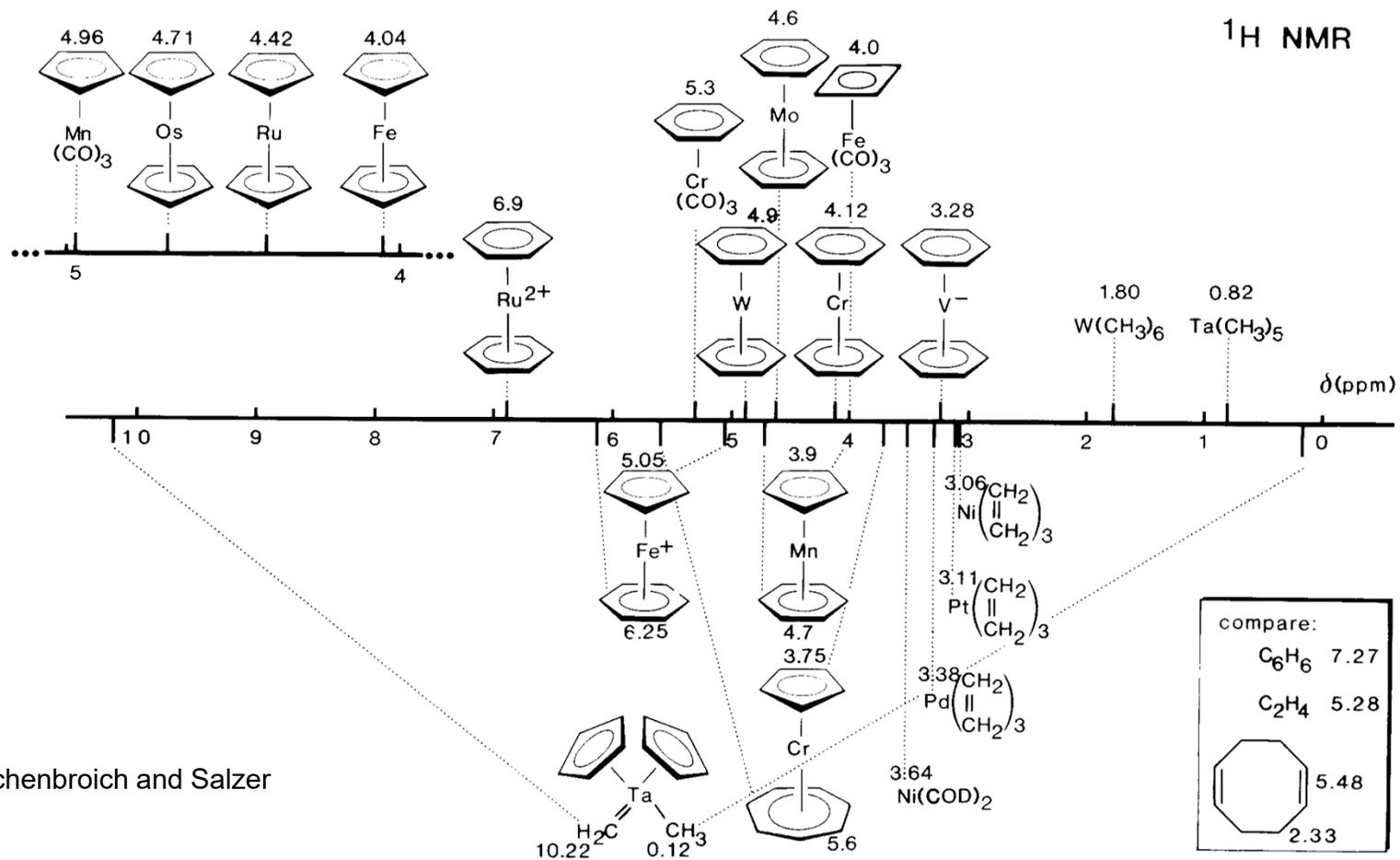
$\delta(\text{Cp}/\text{C}_6\text{H}_6)$ $\text{CpFe}(\text{C}_6\text{H}_6)^+$ (5.05/6.25) > $\text{CpMn}(\text{C}_6\text{H}_6)$ (3.9/4.7)

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 δ value? Also note that the mixed Cp/C₆H₆ complexes of Fe and Mn also go against this trend.

- ***H bonded to remote carbons (M-C-C_n-H)***

- not surprisingly, remote protons show very small $\Delta\delta$ values: typically ± 0.5 ppm or less
- these can be positive or negative (governed by conformation)

Chart D-1 ¹H Values in diamagnetic organometallic complexes

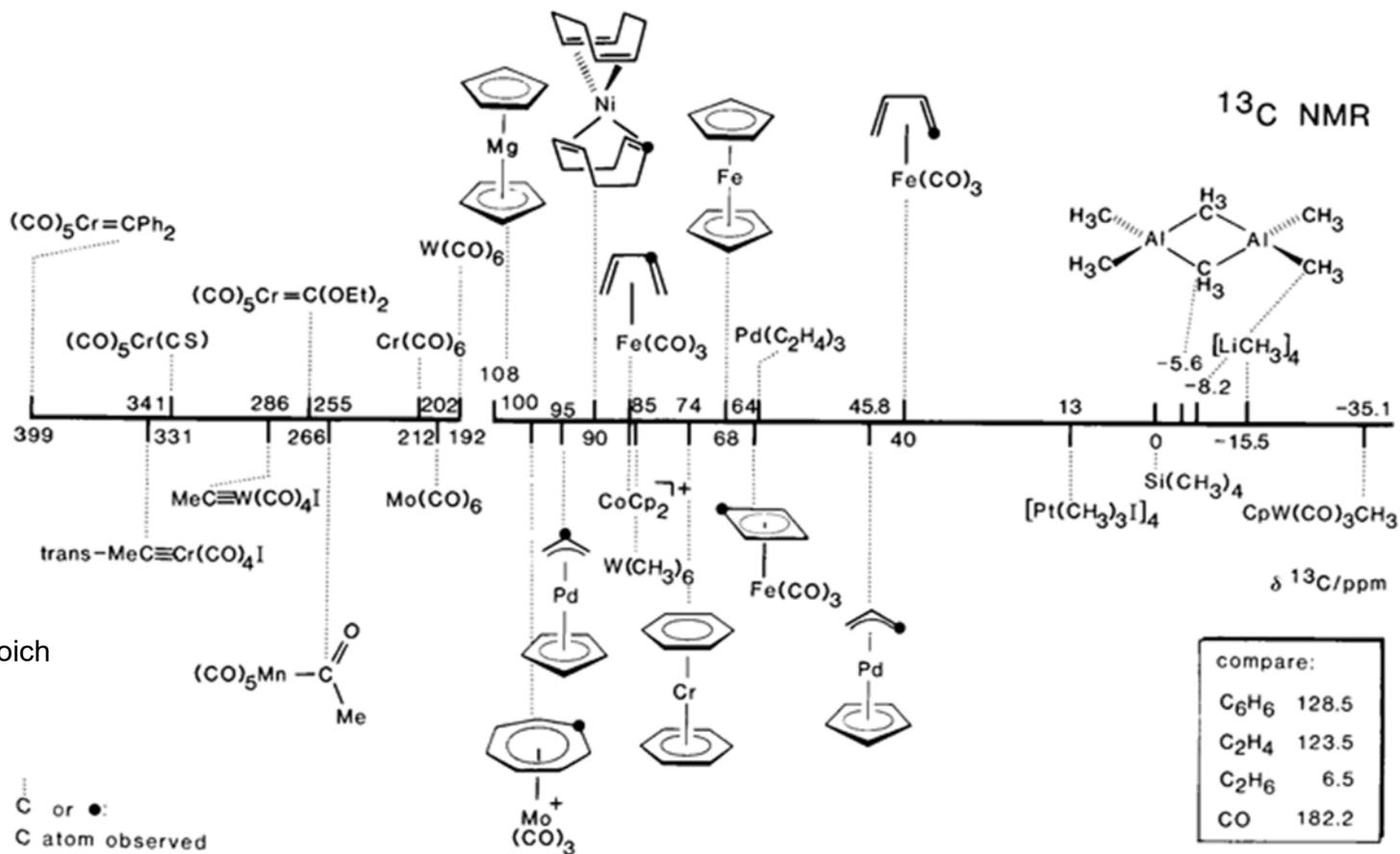


From Elschenbroich and Salzer

^{13}C NMR spectroscopy (see Chart D-2)

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

Chart D-2: $\delta^{13}\text{C}$ 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

δ (Me) ^{13}C : WMe_6 (85 ppm) $\text{CpW}(\text{CO})_3\text{Me}$ (-35.1)

- for most metals the α -C shows a negative $\Delta\delta$ value (but note the exception in WMe_6)
however, Grp 4 and 5 metals usually show positive $\Delta\delta$ values:

$\text{Zr}[\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}(\text{C}_6\text{F}_5)]_2(\text{CH}_2\text{Ph})_2$ δ (ZrCH₂) 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: δ 150-220 ppm** **bridge: δ 230-280 ppm**
- decreases down a triad for the same type of complex:

$\text{Cr}(\text{CO})_6$ (212 ppm)

$\text{Mo}(\text{CO})_6$ (202)

$\text{W}(\text{CO})_6$ (192)

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

- typical alkylidene and alkylidyne: **δ 200-400 ppm**
- similar to carbocations: Ph_3C^+ (212 ppm) Me_3C^+ (336 ppm)
- hetero-substituted carbenes/carbynes fall in a similar range but for a given class of compounds they resonate at higher field:

$(\text{CO})_5\text{Cr}=\text{C}(\text{NMe}_2)\text{H}$ (246)

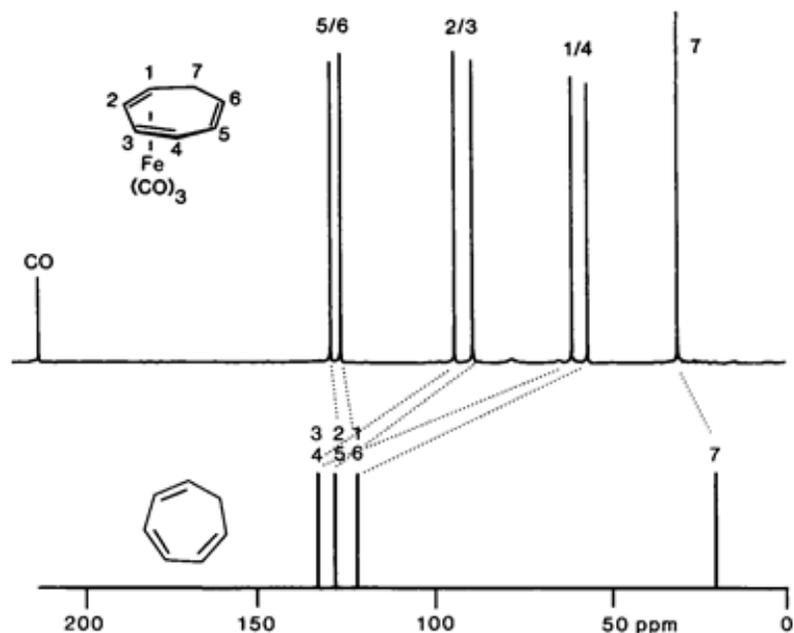
$(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Ph}$ (351)

$(\text{CO})_5\text{Cr}=\text{CPh}_2$ (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 η^3 -allyls and η^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 $(\eta^4\text{-C}_7\text{H}_8)\text{Fe}(\text{CO})_3$
and free cycloheptatriene



2 Heteronuclear NMR

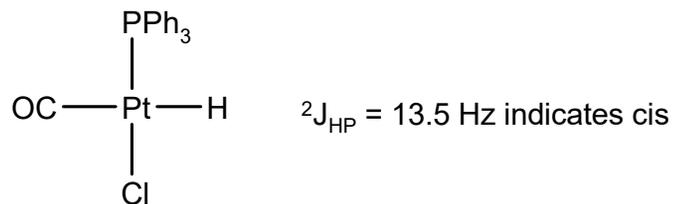
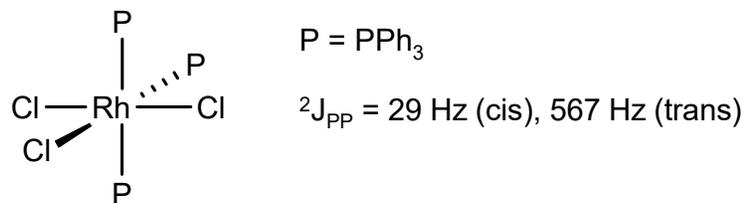
- ^{31}P ($I = \frac{1}{2}$, 100%) and ^{29}Si ($I = \frac{1}{2}$, 4.7 %) in ancillary ligands are commonly studied
- ^{31}P especially important because of very high receptivity and importance of phosphines (+40 to -100 ppm vs. H_3PO_4 reference) and phosphine oxides (+25 to +90 ppm) as ancillary ligands
- phosphines usually show positive $\Delta\delta$ values from +5 to +60 ppm

cis- $\text{PtCl}_2(\text{PPh}_3)_2$ $\delta_{\text{P}} = +10.5$ ppm

free PPh_3 $\delta_{\text{P}} = -5.5$ ppm

$\Delta\delta = +16$ 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:



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. $^1J_{\text{Pt-P}} = 1000\text{-}4000$ Hz) that are sensitive to the structure of the complex and metal oxidation state

- ^{103}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 Rh^+ complexes have $^{103}\text{Rh-X}$ coupling constants that are 1.5 times larger than those in octahedral Rh^{3+} compounds.

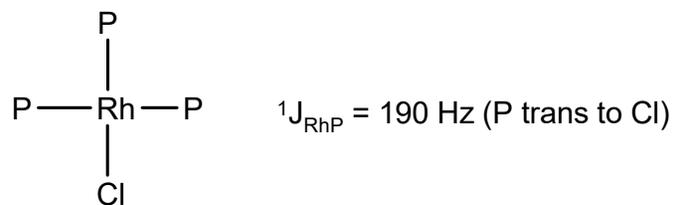
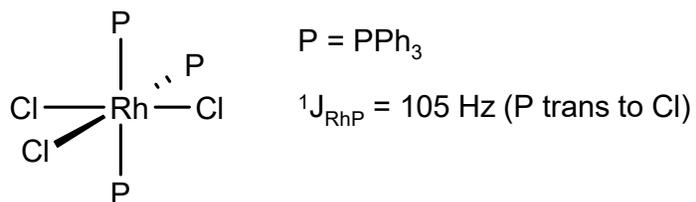


Table D-1 Metal isotopes suitable for NMR spectroscopy

Isotope	I	Nat. Abund. (%)	NMR Freq. (MHz) ^a	Receptivity ^b
⁶ Li	1	7.4	44.146	0.00851
⁷ Li	3/2	92.6	116.950	0.294
²⁷ Al	5/2	100	78.172	0.207
⁴⁵ Sc	7/2	100	72.882	0.3
⁵¹ V	7/2	100	78.864	0.383
⁵⁹ Co	7/2	100	70.842	0.281
⁶⁵ Cu	3/2	30.9	85.183	0.116
⁸⁷ Rb	3/2	27.2	98.163	0.177
⁸⁹ Y	1/2	100	14.697	0.000117
¹⁰³ Rh	1/2	100	9.442	0.0000312
¹⁰⁷ Ag	1/2	51.4	12.139	0.0000669
¹⁰⁹ Ag	1/2	48.7	13.956	0.000101
¹¹¹ Cd	1/2	12.9	63.616	0.00954
¹¹³ Cd	1/2	12.3	66.548	0.0109
¹¹⁷ Sn	1/2	7.7	106.875	0.0453
¹¹⁹ Sn	1/2	8.7	111.817	0.0518
¹²⁵ Te	1/2	7.0	94.790	0.0316
¹⁷¹ Yb	1/2	14.3	52.8	0.0055
¹⁸³ W	1/2	14.3	12.48	0.000720
¹⁸⁷ Os	1/2	1.6	23.276	0.0000007
¹⁹⁵ Pt	1/2	33.7	64.447	0.00994
¹⁹⁷ Au	3/2	100	5.138	0.0000214
¹⁹⁹ Hg	1/2	16.9	53.481	0.00572
²⁰³ Tl	1/2	29.5	171.448	0.187
²⁰⁵ Tl	1/2	70.5	173.124	0.192
²⁰⁷ Pb	1/2	21.1	62.765	0.00913

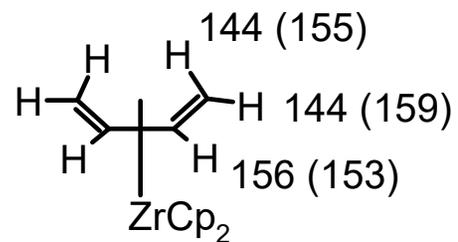
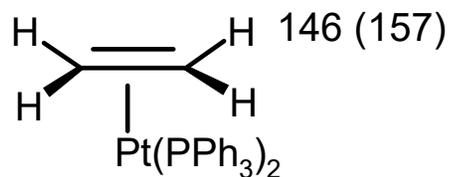
^a at a field such that ¹H resonates at 300 MHz ^b relative to ¹H receptivity = 1
(¹³C receptivity = 0.0159)

3 Coupling constants

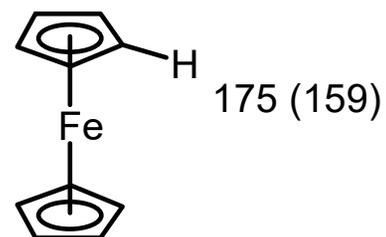
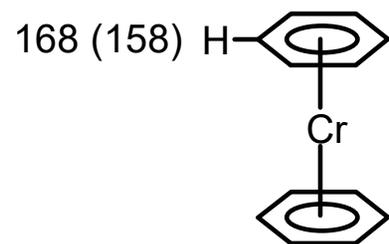
$^1J_{\text{CH}}$ values correlated with s character in the C-H bond:

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

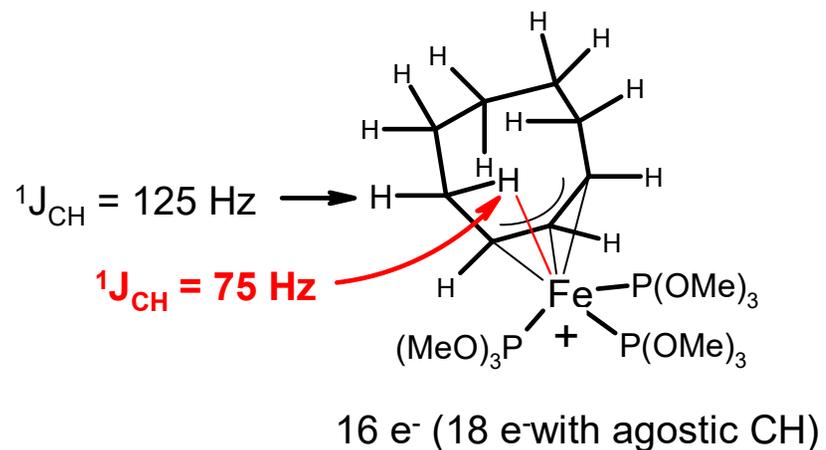
- decrease in $^1J_{\text{CH}}$ observed in alkene complexes is attributed (mainly) to a decrease in s character in the terminal M-C bond:



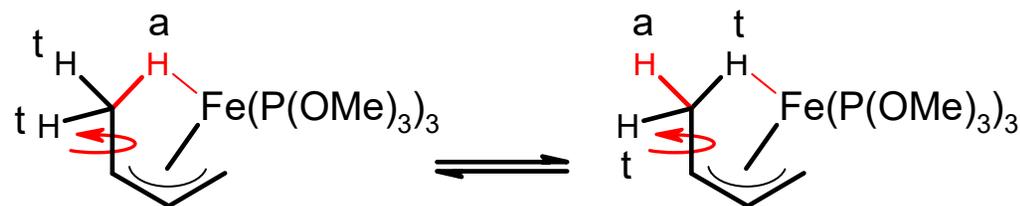
- $\eta^5\text{-Cp}$ and $\eta^6\text{-arenes}$ show an **increase in $^1J_{\text{CH}}$** but no convincing explanation has been forwarded to explain this:



- **agostic** complexes show a **pronounced reduction in the $^1J_{CH}$** 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

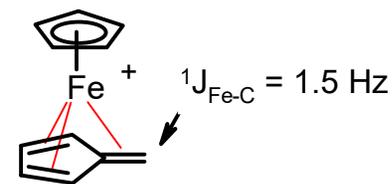
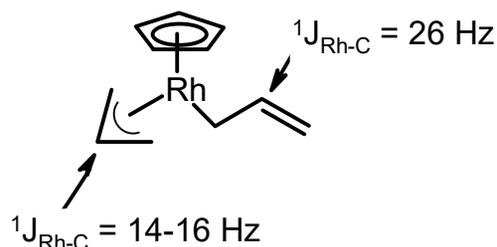


- the analogous complex with $\eta^3\text{-C}_4\text{H}_7$ (1-methylallyl) has a $^1J_{CH}$ value of 106 Hz due to fast rotation of the agostic methyl:



$^1J_{MC}$ values

- larger for M-C σ -bonds than for π -bonds; varies with amount of s character at C (ie. hybridization):



^{57}Fe enriched

$$^1J_{Fe-C} = 9 \text{ Hz for Fe-C } \sigma$$

$$^1J_{Fe-C} = 1.5-4.5 \text{ Hz for Fe-C } \pi$$

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

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

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

$$J_{MC} = h(\gamma_M\gamma_C)K_{MC}/(4\pi^2)$$

where h is Planck's constant, γ_M and γ_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.

$^2J_{CX}$ (geminal) coupling

- useful in providing stereochemical information

