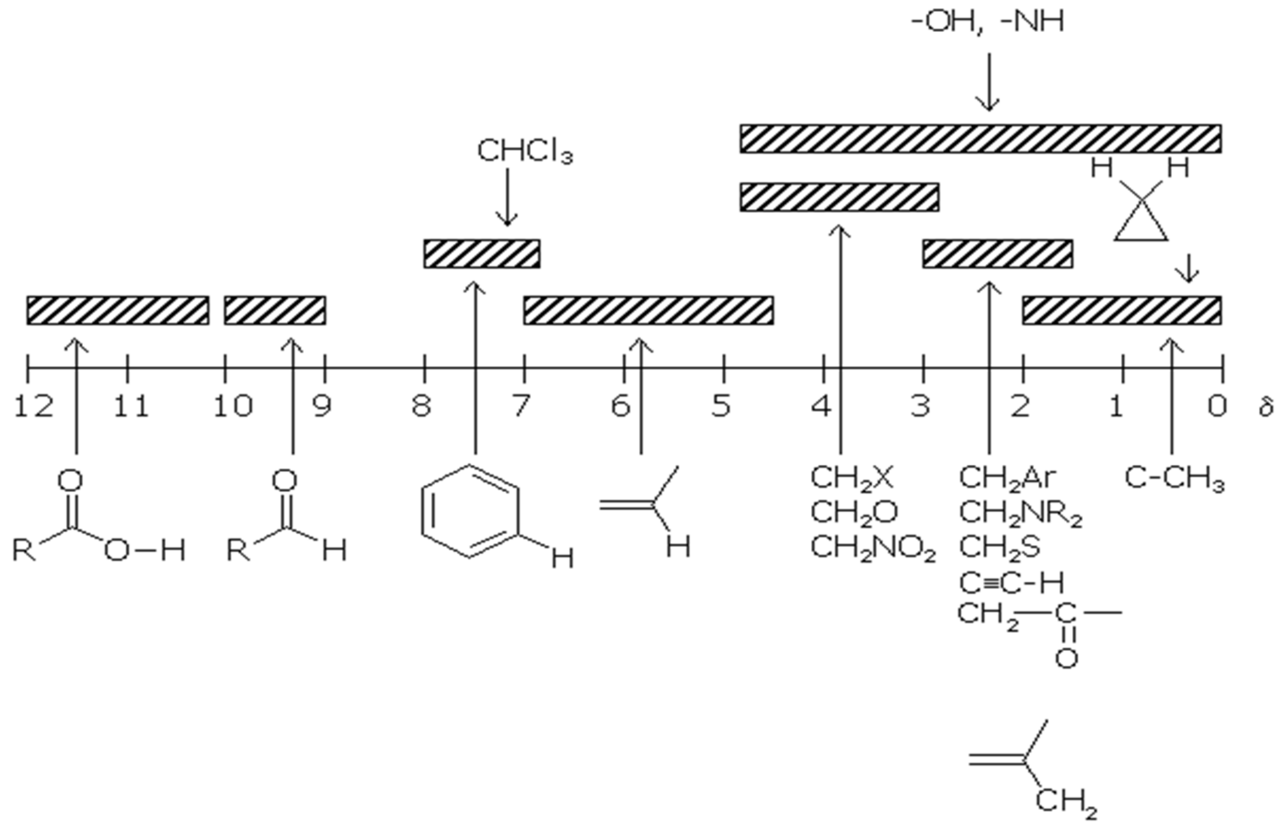
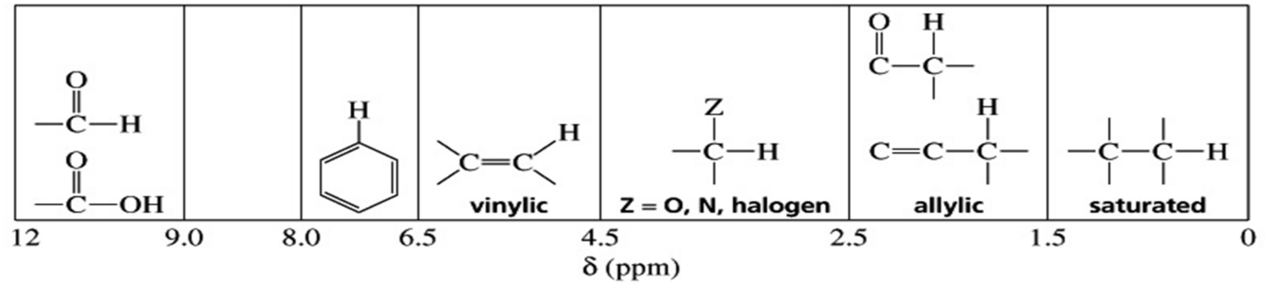
Regions of Organic Proton Shifts





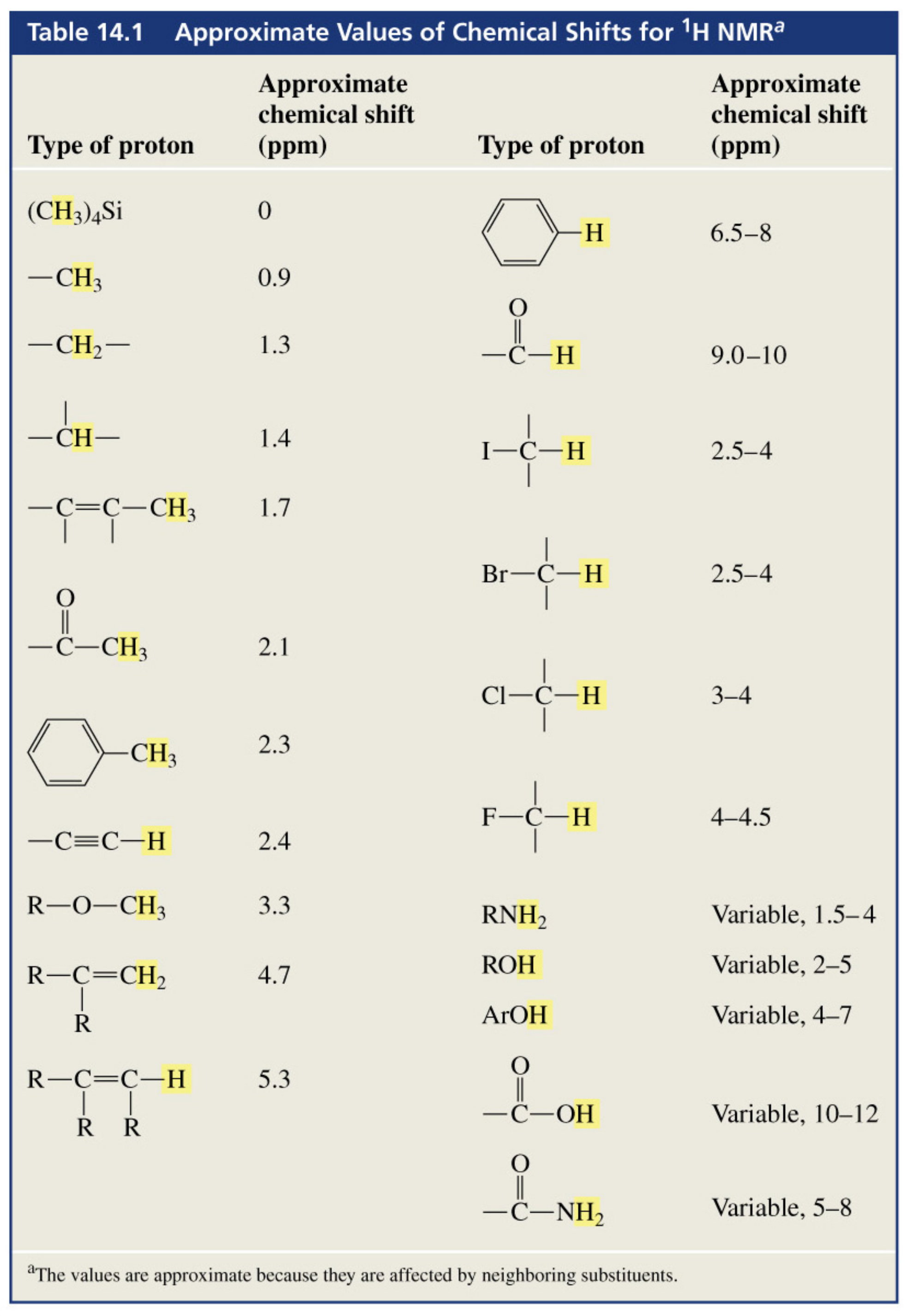


Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	⌬—H	6.5–8
$-CH_3$	0.9	$-\overset{O}{\overset{\|}{C}}-H$	9.0–10
$-CH_2-$	1.3	$I-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
$-\overset{\|}{C}H-$	1.4	$Br-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
$-\underset{\|}{C}=\underset{\|}{C}-CH_3$	1.7	$Cl-\overset{\|}{\underset{\|}{C}}-H$	3–4
$-\overset{O}{\overset{\|}{C}}-CH_3$	2.1	$F-\overset{\|}{\underset{\|}{C}}-H$	4–4.5
⌬—CH_3	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	$ArOH$	Variable, 4–7
$R-\underset{R}{\underset{\|}{C}}=CH_2$	4.7	$-\overset{O}{\overset{\|}{C}}-OH$	Variable, 10–12
$R-\underset{R}{\underset{\|}{C}}=\underset{R}{\underset{\|}{C}}-H$	5.3	$-\overset{O}{\overset{\|}{C}}-NH_2$	Variable, 5–8

[a] The values are approximate because they are affected by neighboring substituents.

Shoolery Chemical Shift Rules

- The different effects on chemical shifts have been tabulated.
- Most of the effects are additive, meaning that if we can estimate the different effects on the chemical shift from different groups and bonds, we can estimate chemical shift by adding all the effects together.
- There are several empirical rules, derived mostly by Shoolery in the late 50s/early 60s.

- In order to use them, we first have to identify the type of proton we have, such as aliphatic CH_3, CH_2, CH, olefinic CH_2 or C_H, aromatic, α or β to a ketone or alcohol, belonging to an a α,β-unsaturated system, etc. They will have a base value.
- Then we look up the contributions from different groups attached to carbons in the surrounding of our system, and add them up to obtain the estimated chemical shift.

^{1}H NMR Chemical Shift Increments

Aliphatic compounds

Methane $\delta(^1H) = 0.23$ ppm

$$\delta = 0.23 + \Sigma\, S_i\,(\delta)$$

CH_3Cl $\delta(\text{calc}) = 2.76$
$\delta(\text{exp}) = 3.1$

CH_2Cl_2 $\delta(\text{calc}) = 5.29$
$\delta(\text{exp}) = 5.3$

$CHCl_3$ $\delta(\text{calc}) = 7.82$
$\delta(\text{exp}) = 7.27$

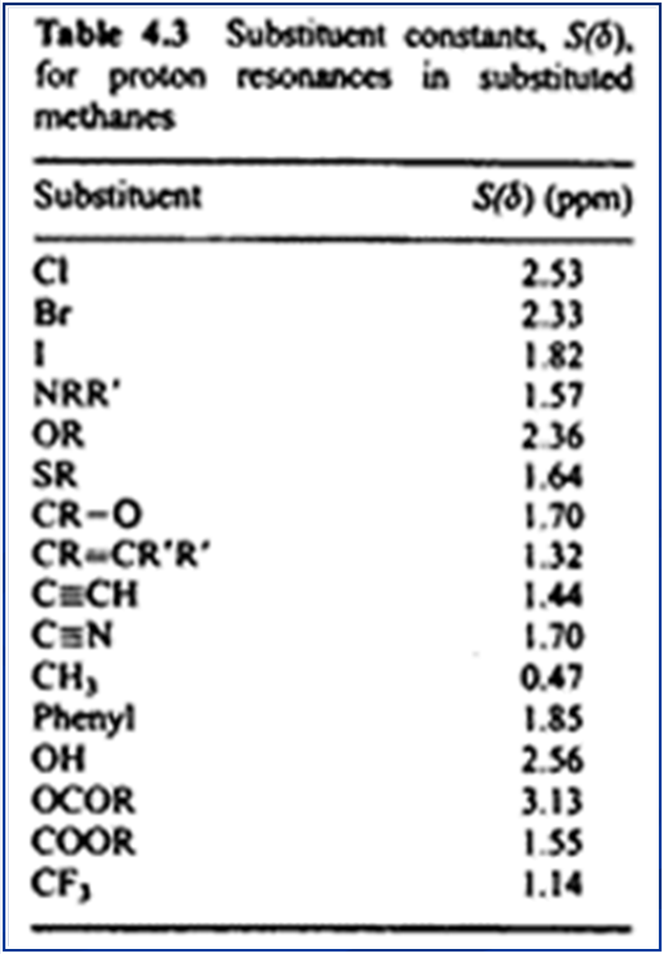


Table 4.3 Substituent constants, *S*(δ), for proton resonances in substituted methanes

Substituent	*S*(δ) (ppm)
Cl	2.53
Br	2.33
I	1.82
NRR'	1.57
OR	2.36
SR	1.64
CR=O	1.70
CR=CR'R'	1.32
C≡CH	1.44
C≡N	1.70
CH_3	0.47
Phenyl	1.85
OH	2.56
OCOR	3.13
COOR	1.55
CF_3	1.14

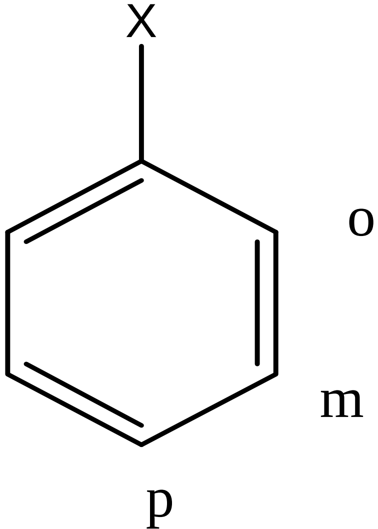
Shoolery chemical shift rules

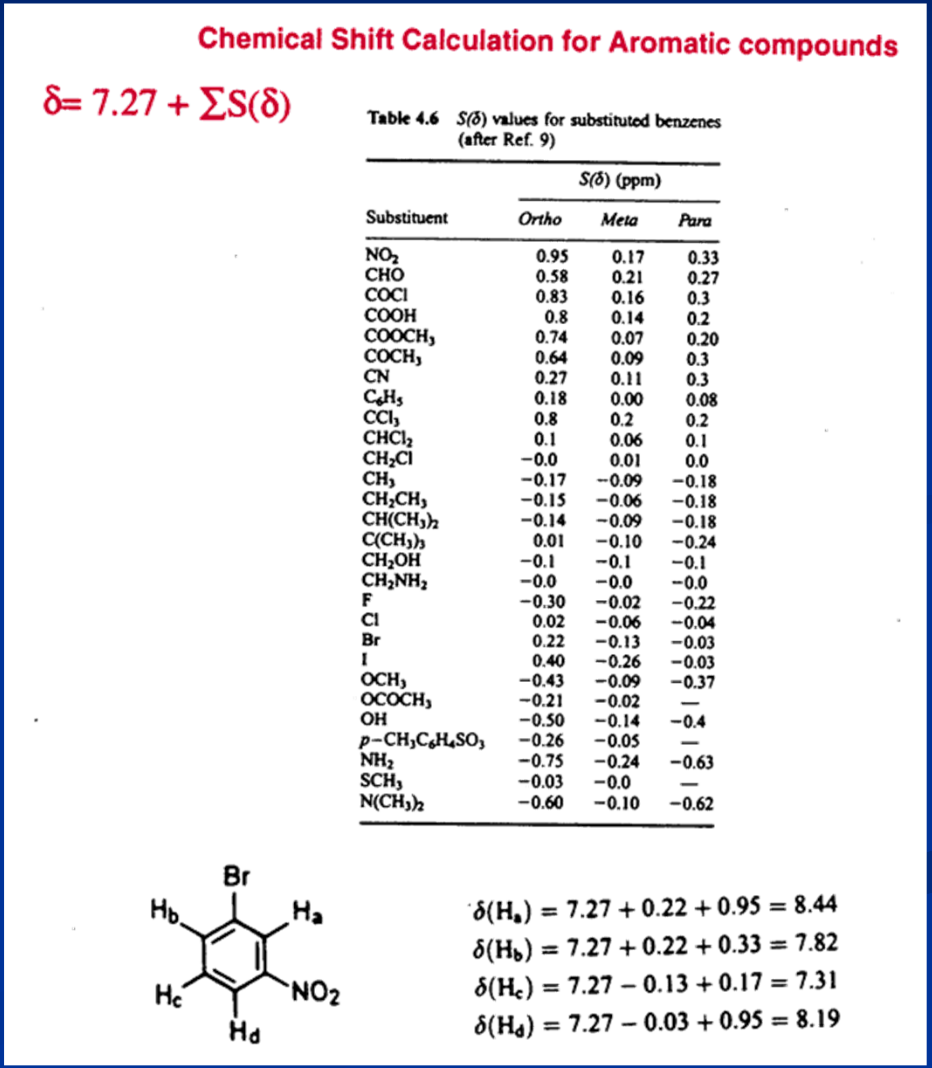
^{1}H NMR Chemical Shift Increments

Aromatic compounds

Benzene $\delta(^1H) = 7.27$ ppm

$$\delta = 7.27 + \Sigma S_i(\delta)$$





Chemical Shift Calculation for Aromatic compounds

$$\delta = 7.27 + \Sigma S(\delta)$$

Table 4.6 *S*(δ) values for substituted benzenes (after Ref. 9)

Substituent	*S*(δ) (ppm) *Ortho*	 *Meta*	 *Para*
NO_2	0.95	0.17	0.33
CHO	0.58	0.21	0.27
COCl	0.83	0.16	0.3
COOH	0.8	0.14	0.2
$COOCH_3$	0.74	0.07	0.20
$COCH_3$	0.64	0.09	0.3
CN	0.27	0.11	0.3
C_6H_5	0.18	0.00	0.08
CCl_3	0.8	0.2	0.2
$CHCl_2$	0.1	0.06	0.1
CH_2Cl	−0.0	0.01	0.0
CH_3	−0.17	−0.09	−0.18
CH_2CH_3	−0.15	−0.06	−0.18
$CH(CH_3)_2$	−0.14	−0.09	−0.18
$C(CH_3)_3$	0.01	−0.10	−0.24
CH_2OH	−0.1	−0.1	−0.1
CH_2NH_2	−0.0	−0.0	−0.0
F	−0.30	−0.02	−0.22
Cl	0.02	−0.06	−0.04
Br	0.22	−0.13	−0.03
I	0.40	−0.26	−0.03
OCH_3	−0.43	−0.09	−0.37
$OCOCH_3$	−0.21	−0.02	—
OH	−0.50	−0.14	−0.4
p-$CH_3C_6H_4SO_3$	−0.26	−0.05	—
NH_2	−0.75	−0.24	−0.63
SCH_3	−0.03	−0.0	—
$N(CH_3)_2$	−0.60	−0.10	−0.62

$$\delta(H_a) = 7.27 + 0.22 + 0.95 = 8.44$$
$$\delta(H_b) = 7.27 + 0.22 + 0.33 = 7.82$$
$$\delta(H_c) = 7.27 - 0.13 + 0.17 = 7.31$$
$$\delta(H_d) = 7.27 - 0.03 + 0.95 = 8.19$$

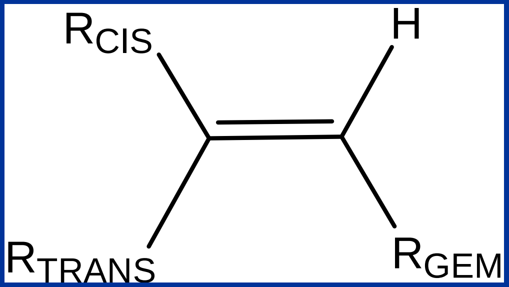
^{1}H NMR Chemical Shift Increments

Olefinic compounds

Ethylene

$\delta(^1H) = 5.28$ ppm

$$\delta = 5.28 + \Sigma S_i(\delta)$$



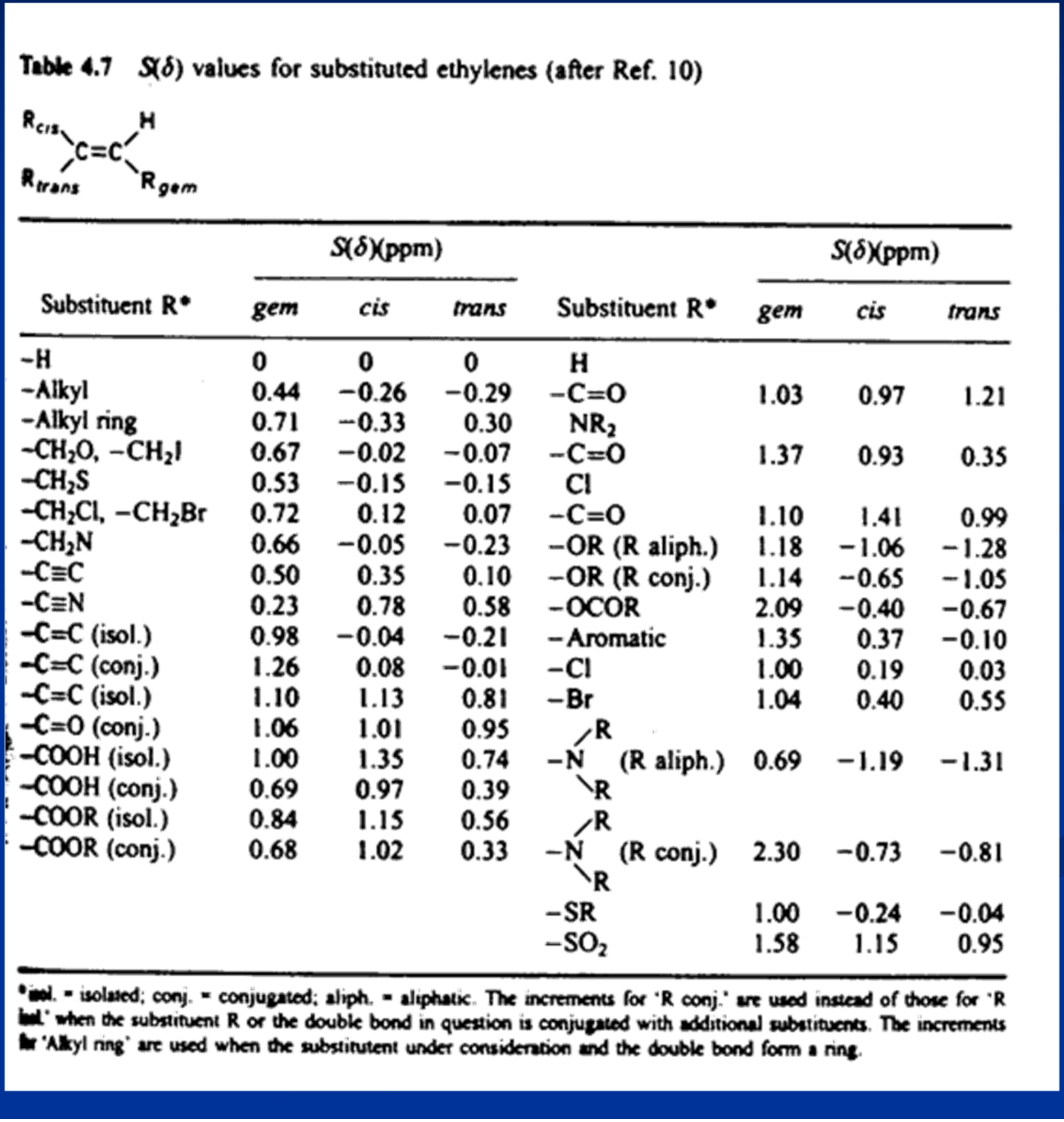


Table 4.7 $S(\delta)$ values for substituted ethylenes (after Ref. 10)

Substituent R*	$S(\delta)$(ppm) *gem*	*cis*	*trans*
$-H$	0	0	0
–Alkyl	0.44	−0.26	−0.29
–Alkyl ring	0.71	−0.33	0.30
$-CH_2O$, $-CH_2I$	0.67	−0.02	−0.07
$-CH_2S$	0.53	−0.15	−0.15
$-CH_2Cl$, $-CH_2Br$	0.72	0.12	0.07
$-CH_2N$	0.66	−0.05	−0.23
$-C{\equiv}C$	0.50	0.35	0.10
$-C{\equiv}N$	0.23	0.78	0.58
$-C{=}C$ (isol.)	0.98	−0.04	−0.21
$-C{=}C$ (conj.)	1.26	0.08	−0.01
$-C{=}C$ (isol.)	1.10	1.13	0.81
$-C{=}O$ (conj.)	1.06	1.01	0.95
–COOH (isol.)	1.00	1.35	0.74
–COOH (conj.)	0.69	0.97	0.39
–COOR (isol.)	0.84	1.15	0.56
–COOR (conj.)	0.68	1.02	0.33
$-\overset{H}{C}{=}O$	1.03	0.97	1.21
$-\overset{NR_2}{C}{=}O$	1.37	0.93	0.35
$-\overset{Cl}{C}{=}O$	1.10	1.41	0.99
–OR (R aliph.)	1.18	−1.06	−1.28
–OR (R conj.)	1.14	−0.65	−1.05
–OCOR	2.09	−0.40	−0.67
–Aromatic	1.35	0.37	−0.10
–Cl	1.00	0.19	0.03
–Br	1.04	0.40	0.55
$-N\genfrac{}{}{0pt}{}{/R}{\backslash R}$ (R aliph.)	0.69	−1.19	−1.31
$-N\genfrac{}{}{0pt}{}{/R}{\backslash R}$ (R conj.)	2.30	−0.73	−0.81
–SR	1.00	−0.24	−0.04
$-SO_2$	1.58	1.15	0.95

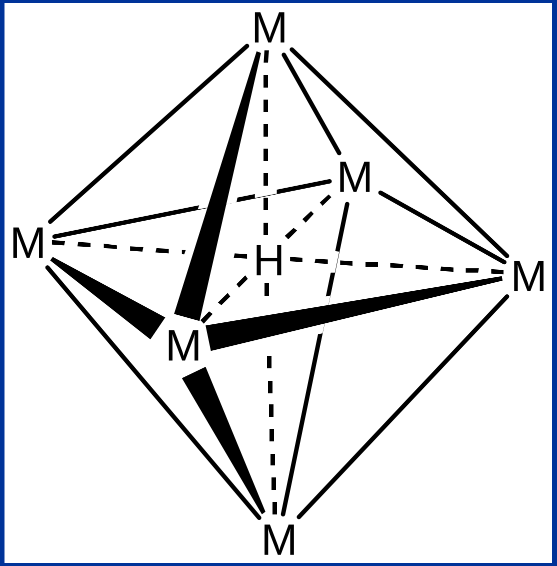
*isol. = isolated; conj. = conjugated; aliph. = aliphatic. The increments for 'R conj.' are used instead of those for 'R isol.' when the substituent R or the double bond in question is conjugated with additional substituents. The increments for 'Alkyl ring' are used when the substituent under consideration and the double bond form a ring.

Regions of Inorganic Proton Shifts

Organometallic hydrides

Highly shielded –5 to –60 ppm

$[H\text{-}Rh(CN)_5]^{3-}$ –10.6 ppm multiplet? unpaired electrons ?

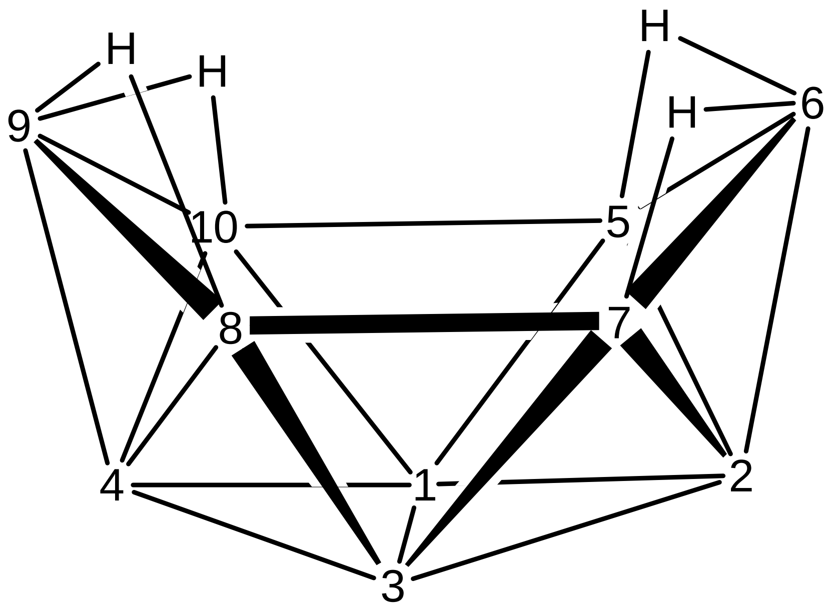


Highly deshielded

$[HRu_6(CO)_{18}]^-$ 16.4 ppm

$[HCo_6(CO)_{15}]^-$ 23.2 ppm

^{1}H NMR of Boranes



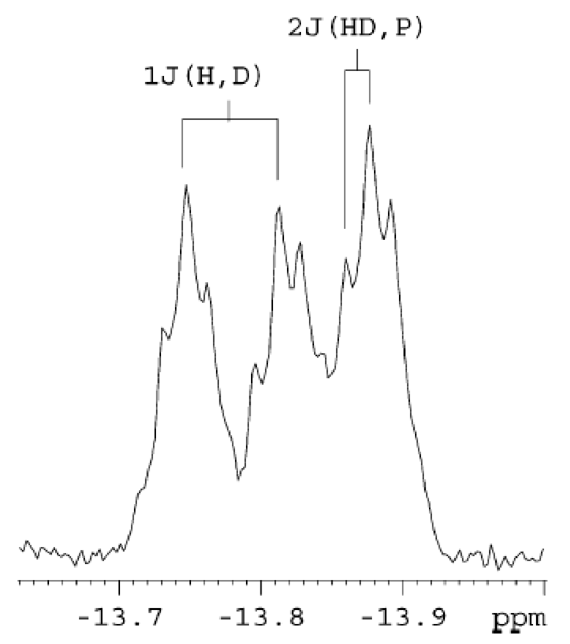
nido-Decaborane(14)

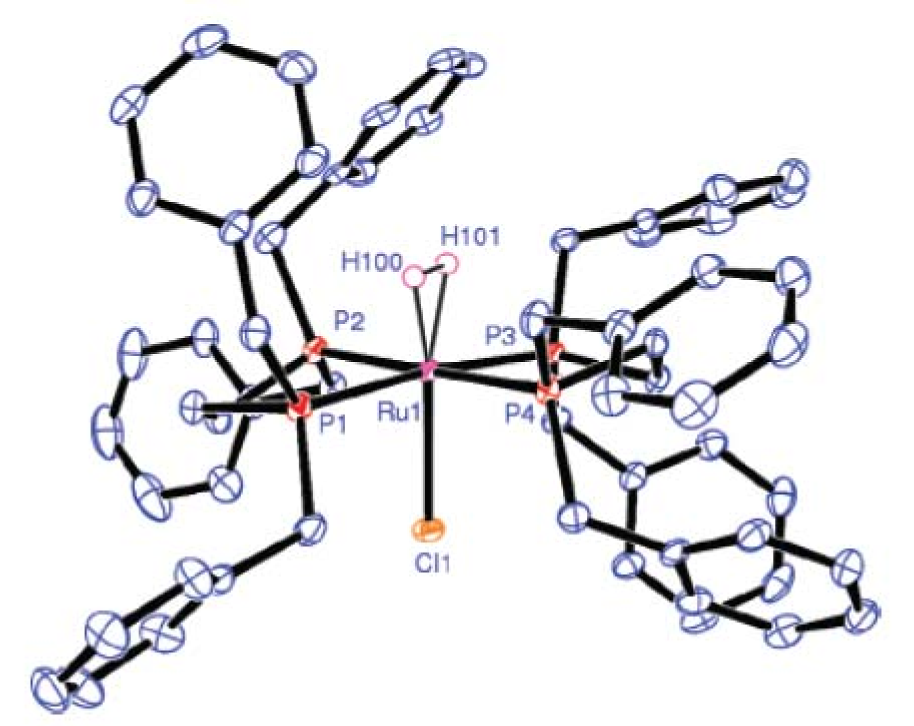
bridging B_2H –2.12 ppm

terminal BH

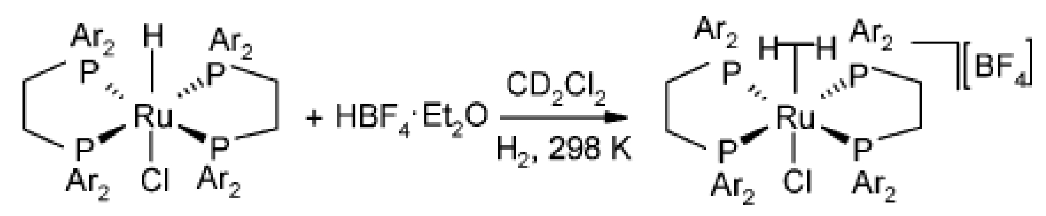
(2,4)	0.62
(5,7,8,10)	3.13
(1,3)	3.63
(6,9)	3.90

^{1}H NMR Organometallic Hydrides

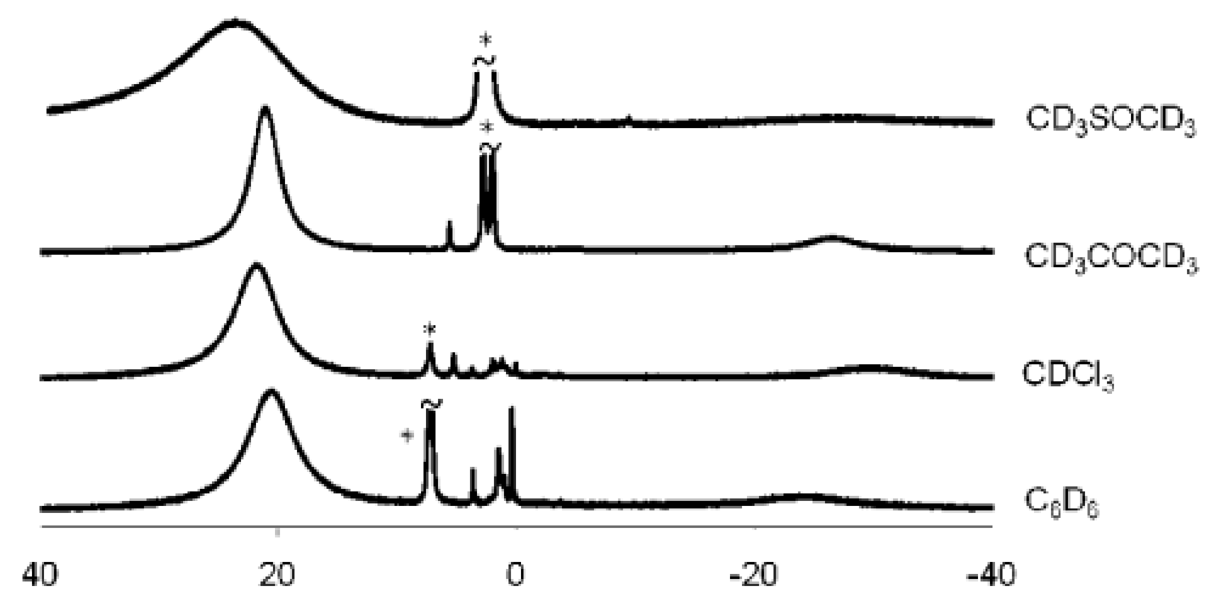




unpaired electrons ?



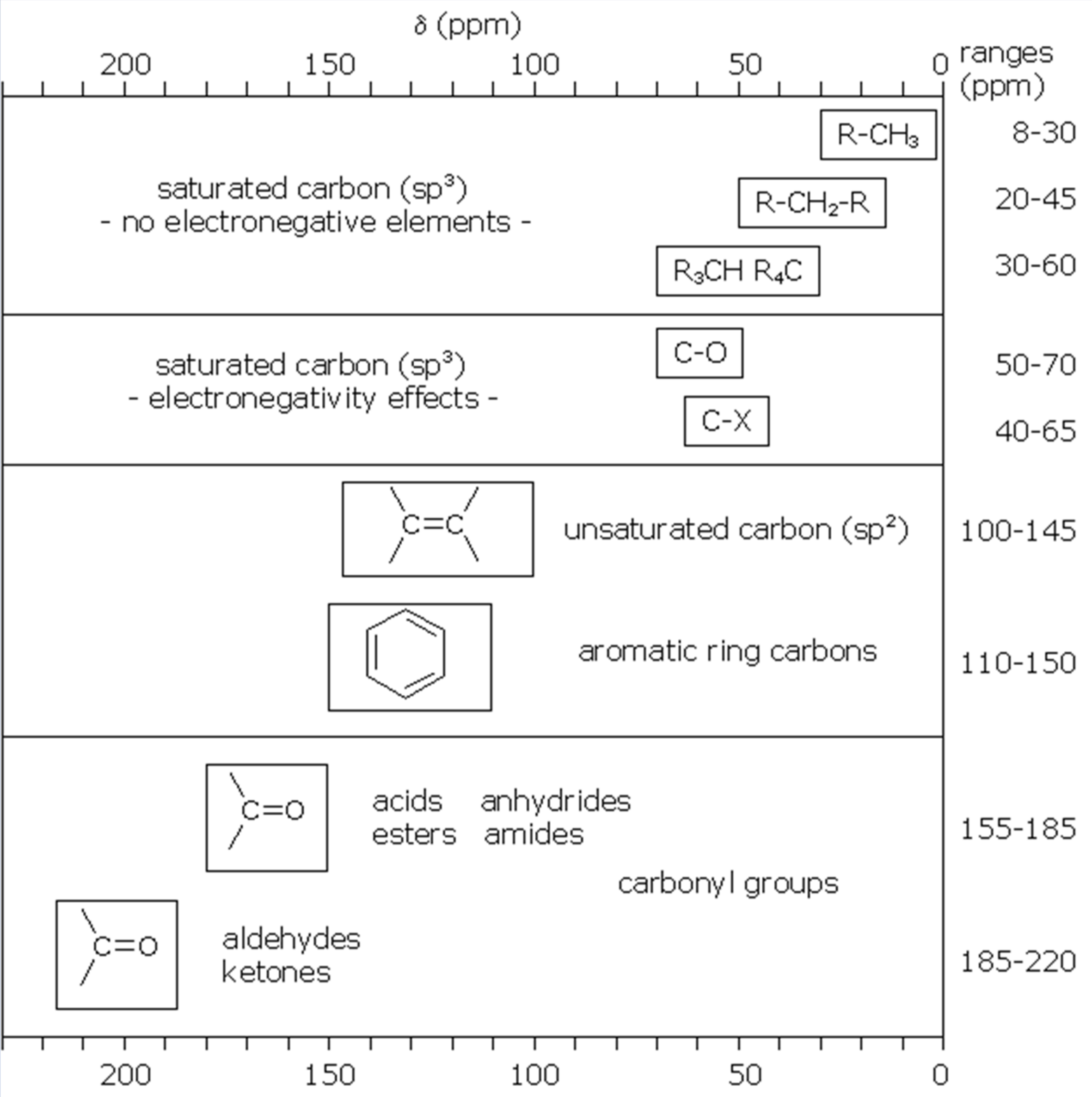
^{1}H NMR of Paramagnetic Compounds



^{1}H NMR spectra of Fe(acac)$_3$

CH$_3$ **CH**

Regions of Organic Carbon Shifts



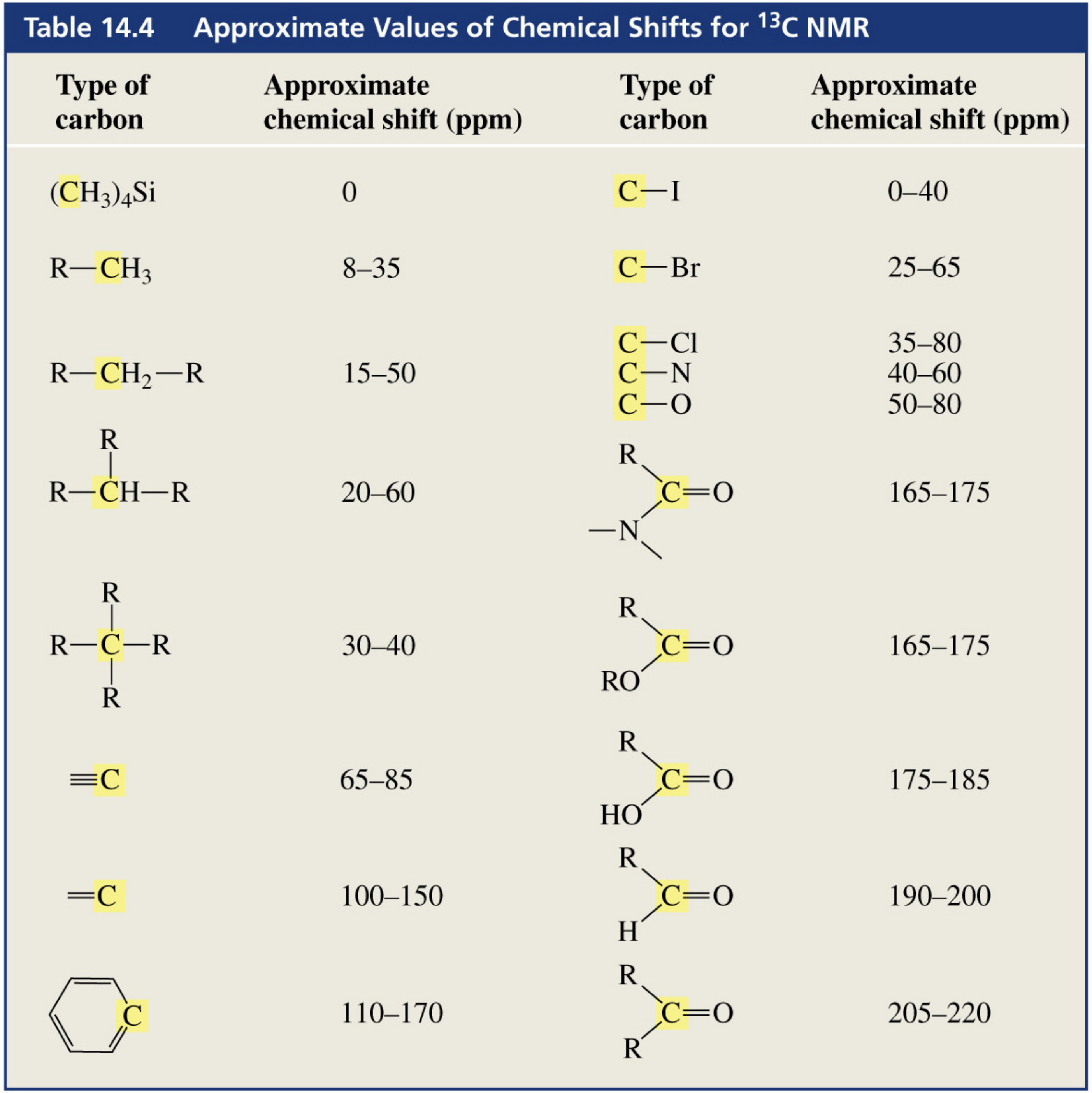
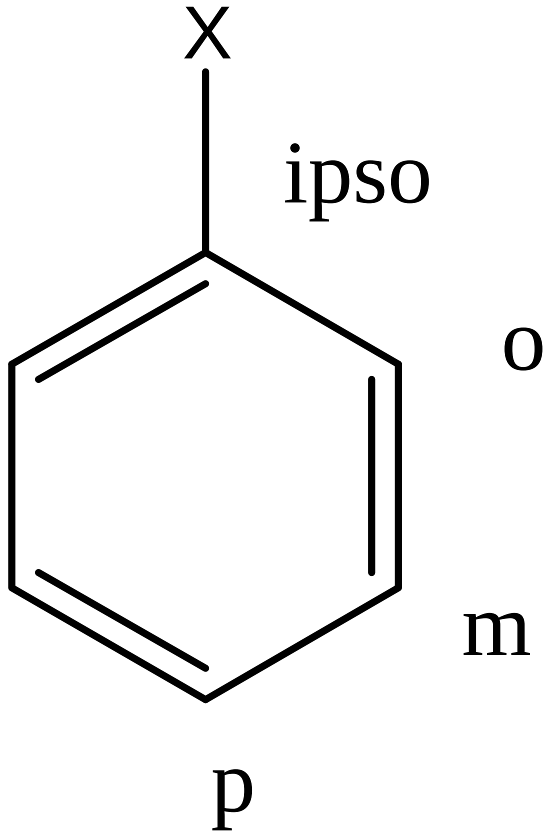


Table 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
$R-CH(R)-R$	20–60	$R-C(=O)-N<$	165–175
$R-C(R)(R)-R$	30–40	$R-C(=O)-OR$	165–175
$\equiv C$	65–85	$R-C(=O)-OH$	175–185
$=C$	100–150	$R-C(=O)-H$	190–200
C	110–170	$R-C(=O)-R$	205–220

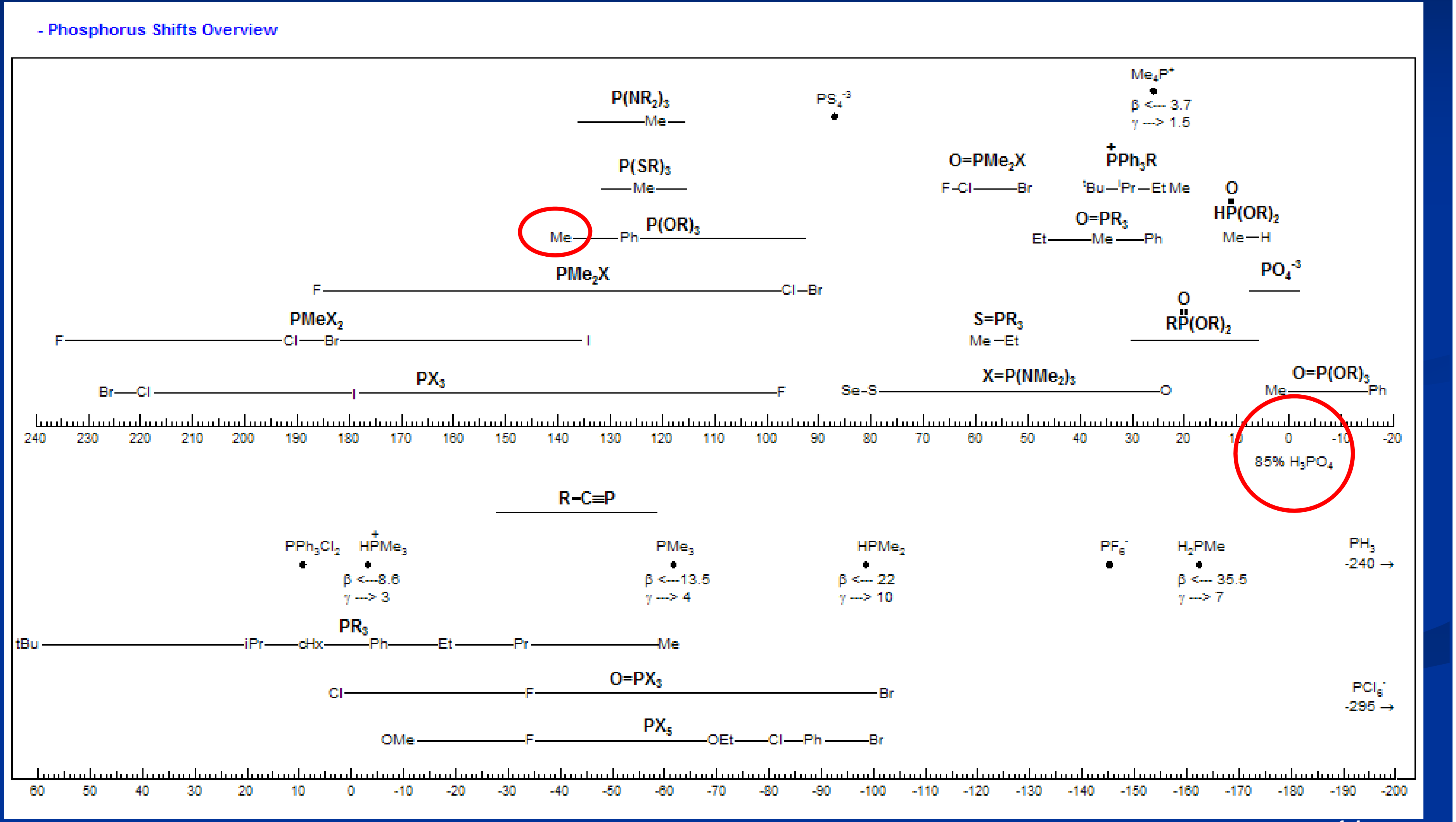
^{13}C NMR Chemical Shift Increments



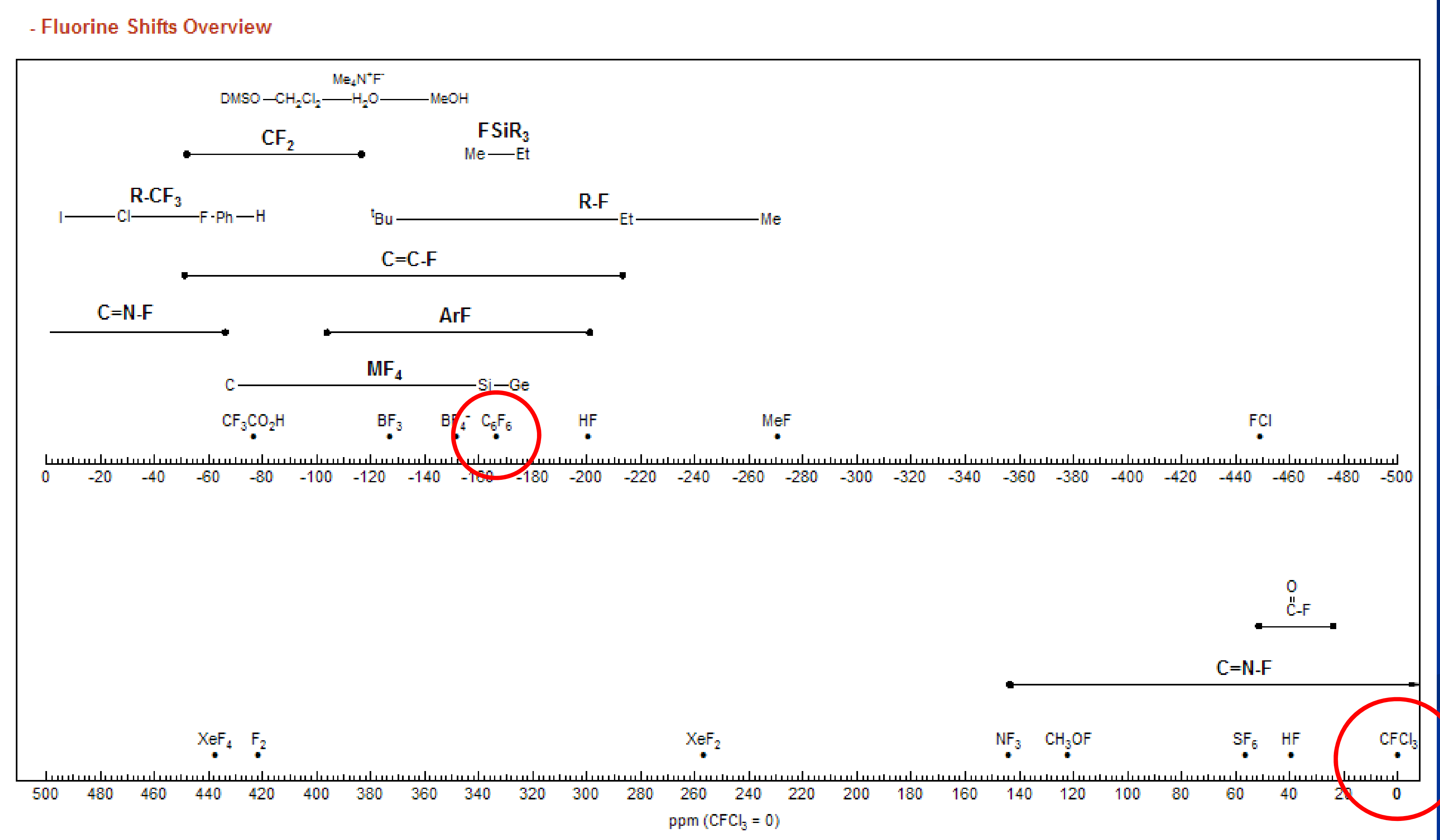
$\delta(^{13}C) = 128.5$ ppm

+/- substituent X increments
for each carbon (ipso, o, m, p)

Regions of ^{31}P NMR Shifts

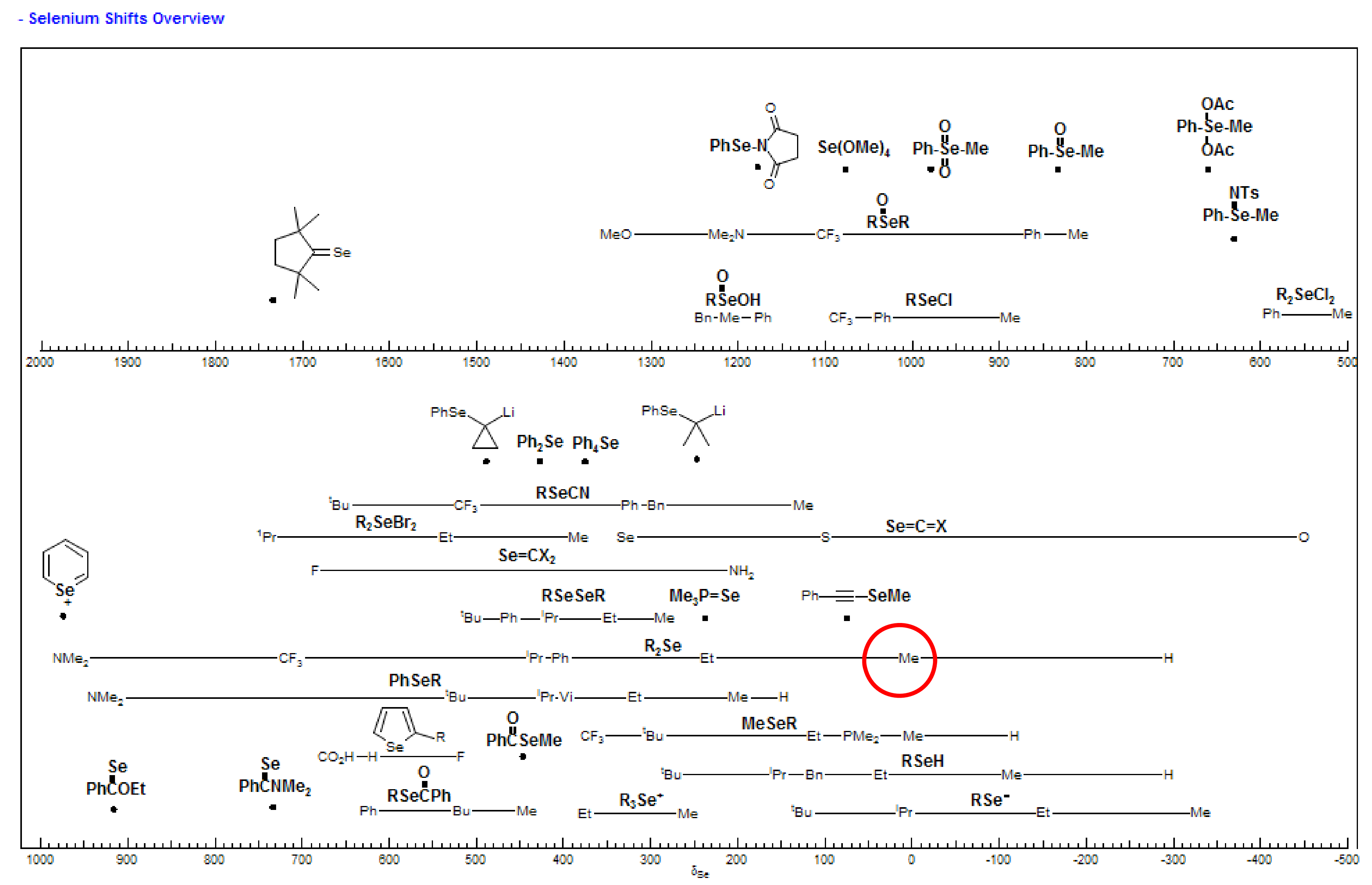

- Phosphorus Shifts Overview

Regions of ^{19}F NMR Shifts

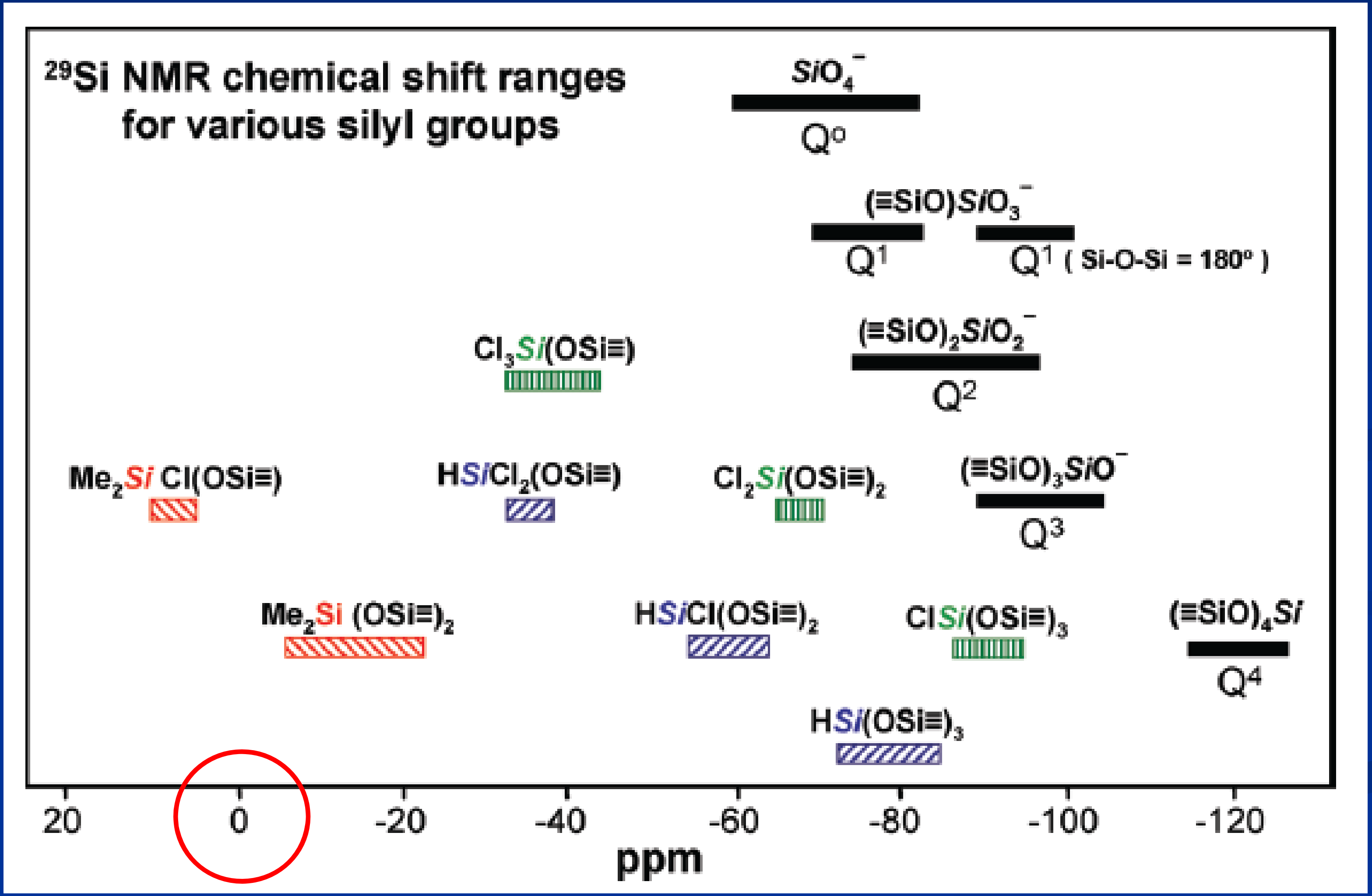


- Fluorine Shifts Overview

Regions of ^{77}Se NMR Shifts



Regions of ^{29}Si NMR Shifts



SiO_6

–200 ppm

Silicate Anions in Aqueous Alkaline Media Detected by ^{29}Si-NMR

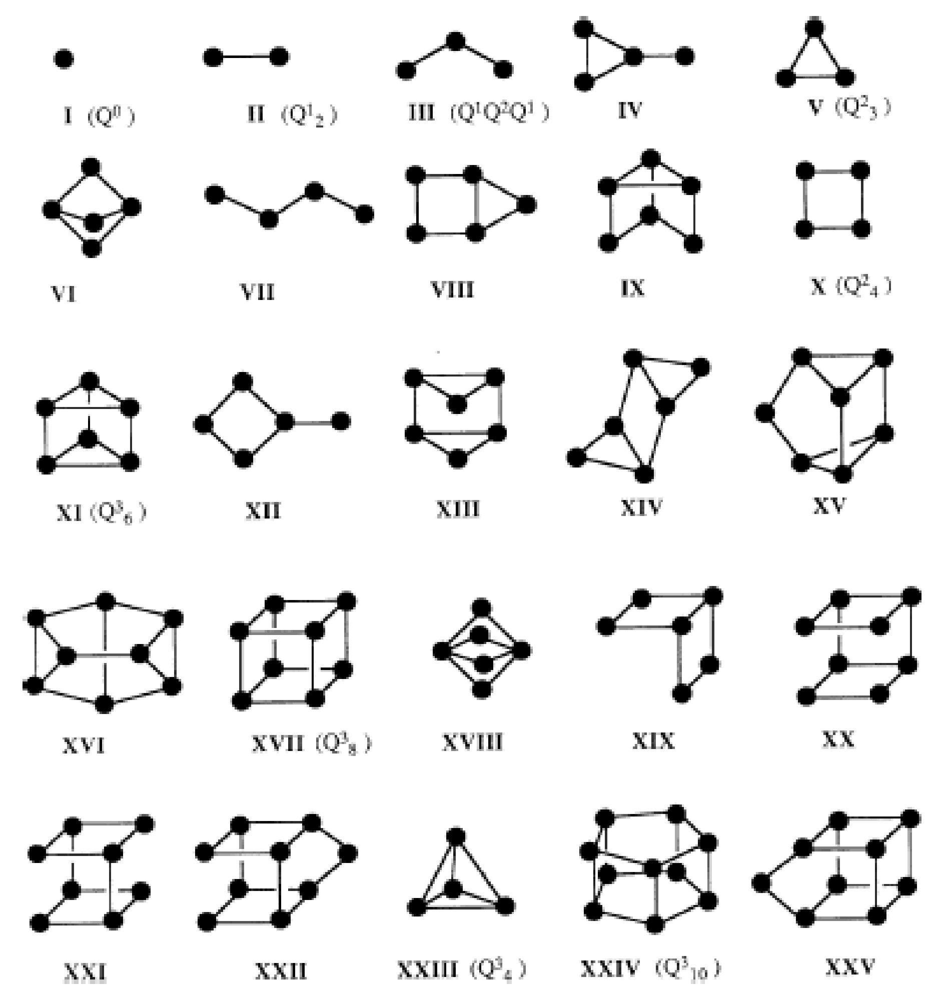
$M = OSiR_3$

$D = O_2SiR_2$

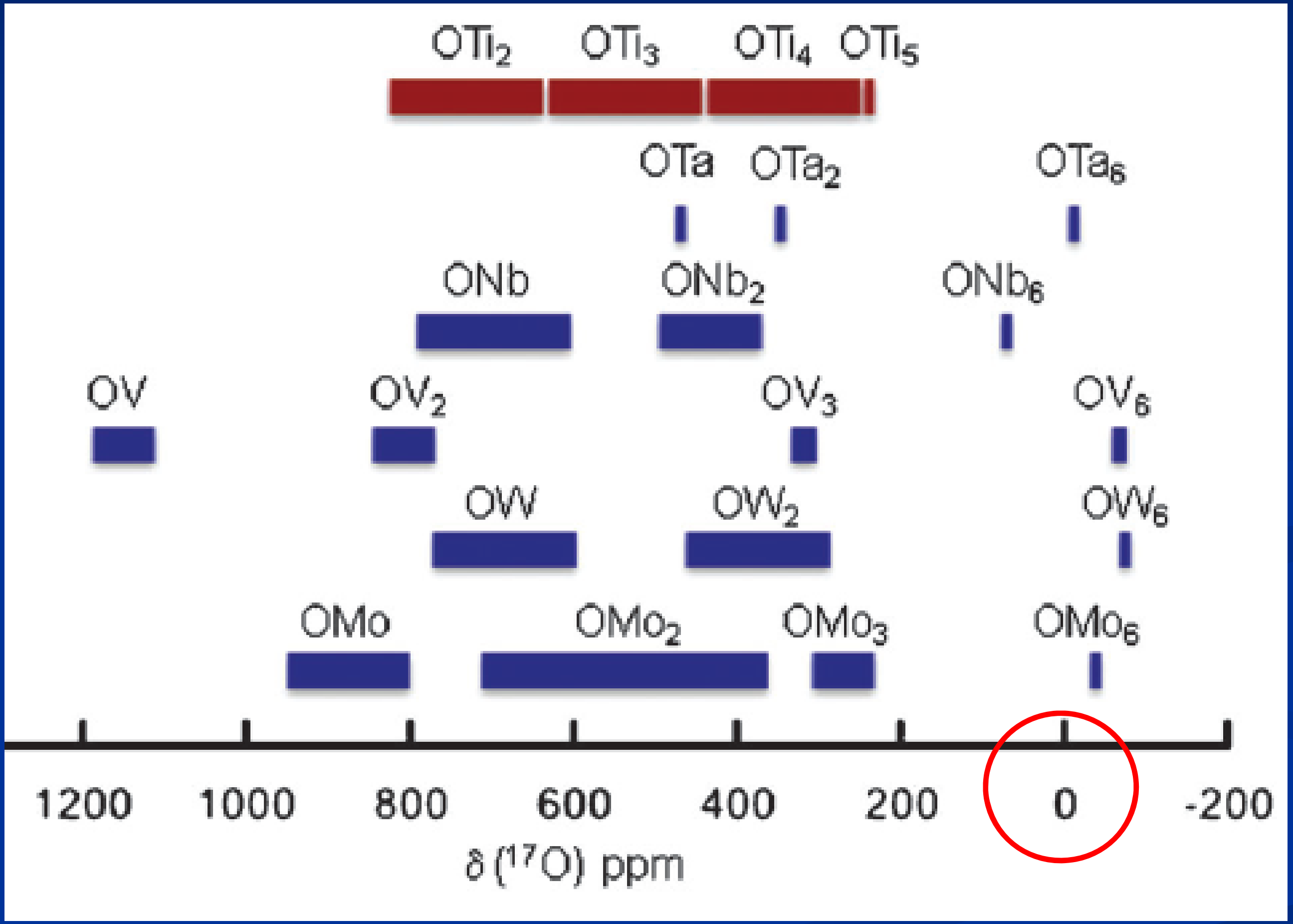
$T = O_3SiR$

$Q = O_4Si$

$Q^0 = O_4Si$
$Q^1 = O_3SiOSi$
$Q^2 = O_2Si(OSi)_2$
$Q^3 = OSi(OSi)_3$
$Q^4 = Si(OSi)_4$

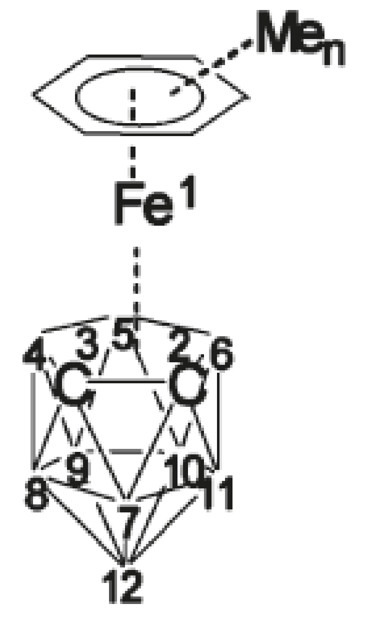


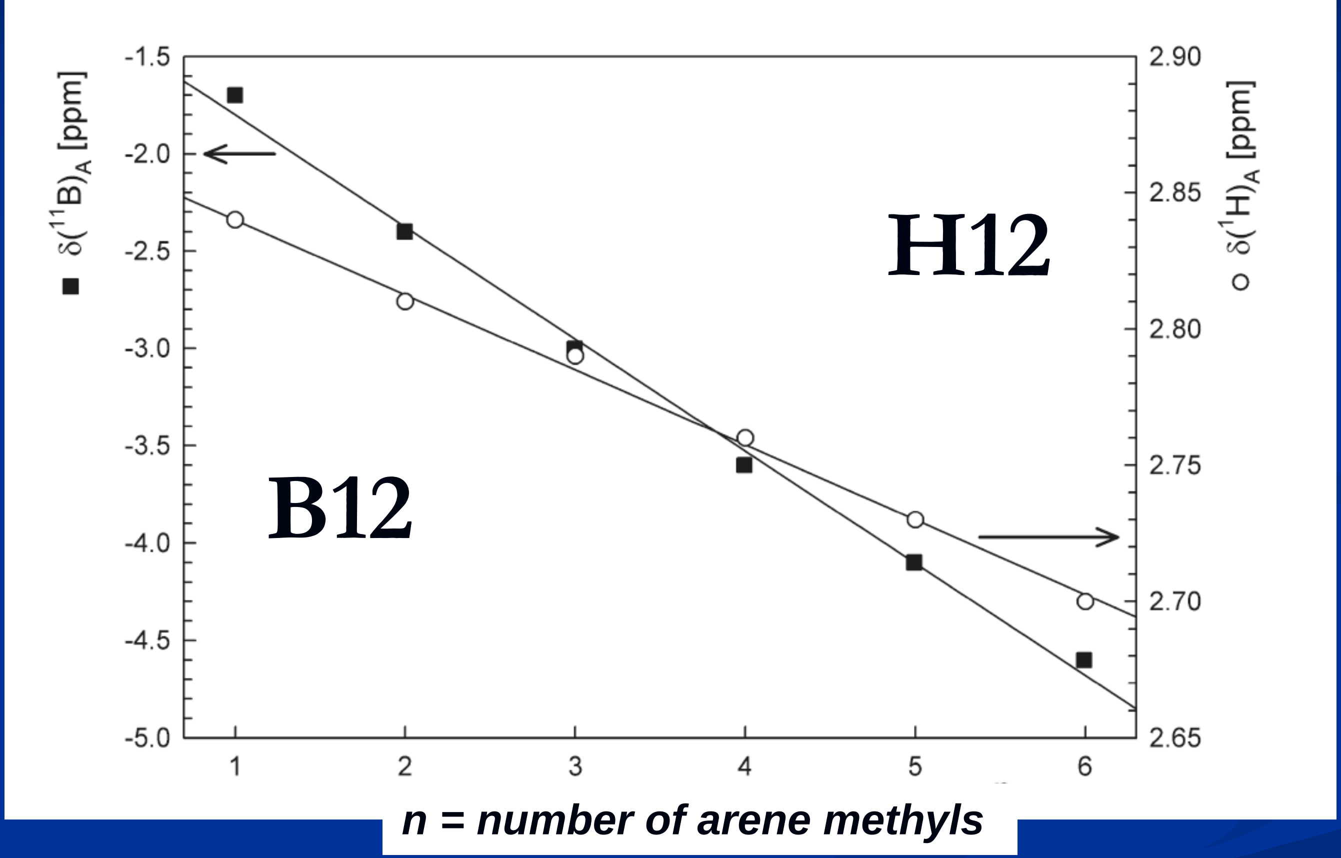
Regions of ^{17}O MAS NMR



$H_2{}^{17}O$

Linear Correlations of the NMR Parameters with the Number of Arene Methyls

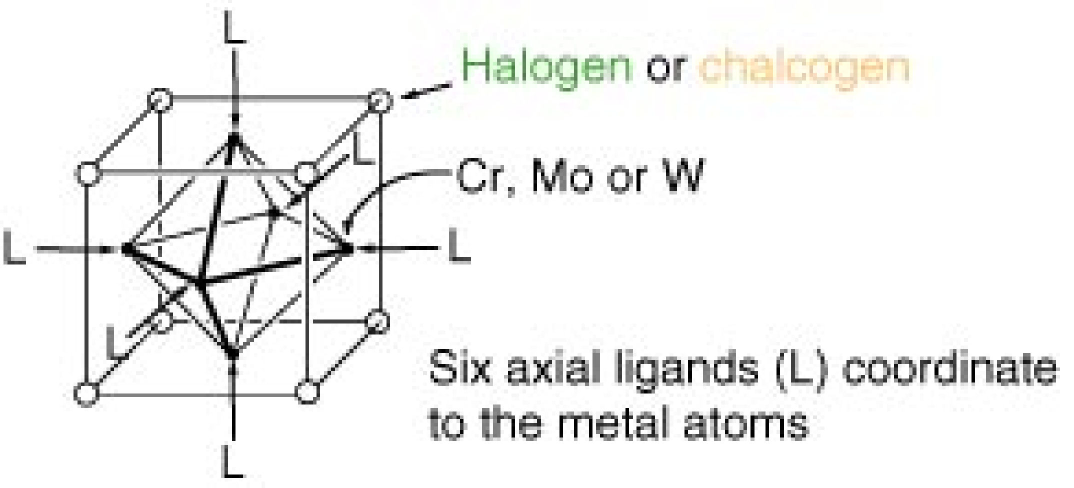




Is diamagnetic or paramagnetic shielding affected?

B. Stibr, M. Bakardjiev, J. Holub, A. Ruzicka, Z. Padelkova, P. Stepnicka Inorg. Chem. 2011, 50, 3097–3102

Octahedral Metal Clusters



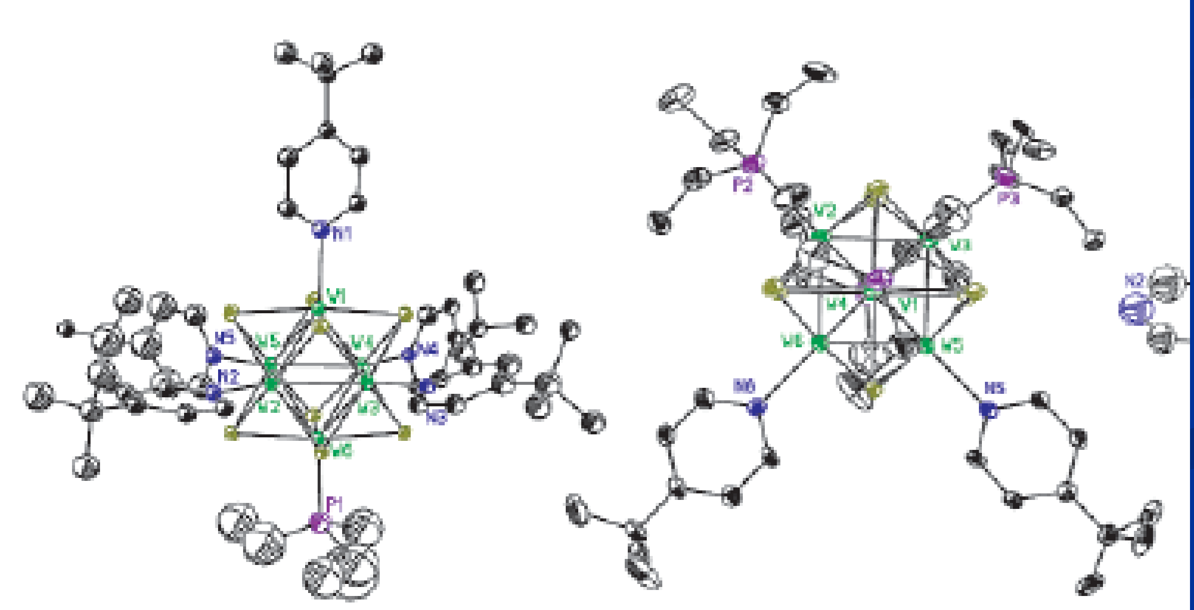
Six axial ligands (L) coordinate to the metal atoms

Song Jin, Jennifer Adamchuk, Bosong Xiang, and Francis J. DiSalvo* J. AM. CHEM. SOC. 2002, 124, 9229-9240

How many derivatives and isomers for

2 different L

???????????????



$W_6S_8(4\text{-tbp})_5(PEt_3)$ $\quad$ *cis*-$W_6S_8(4\text{-tbp})_2(PEt_3)_4$

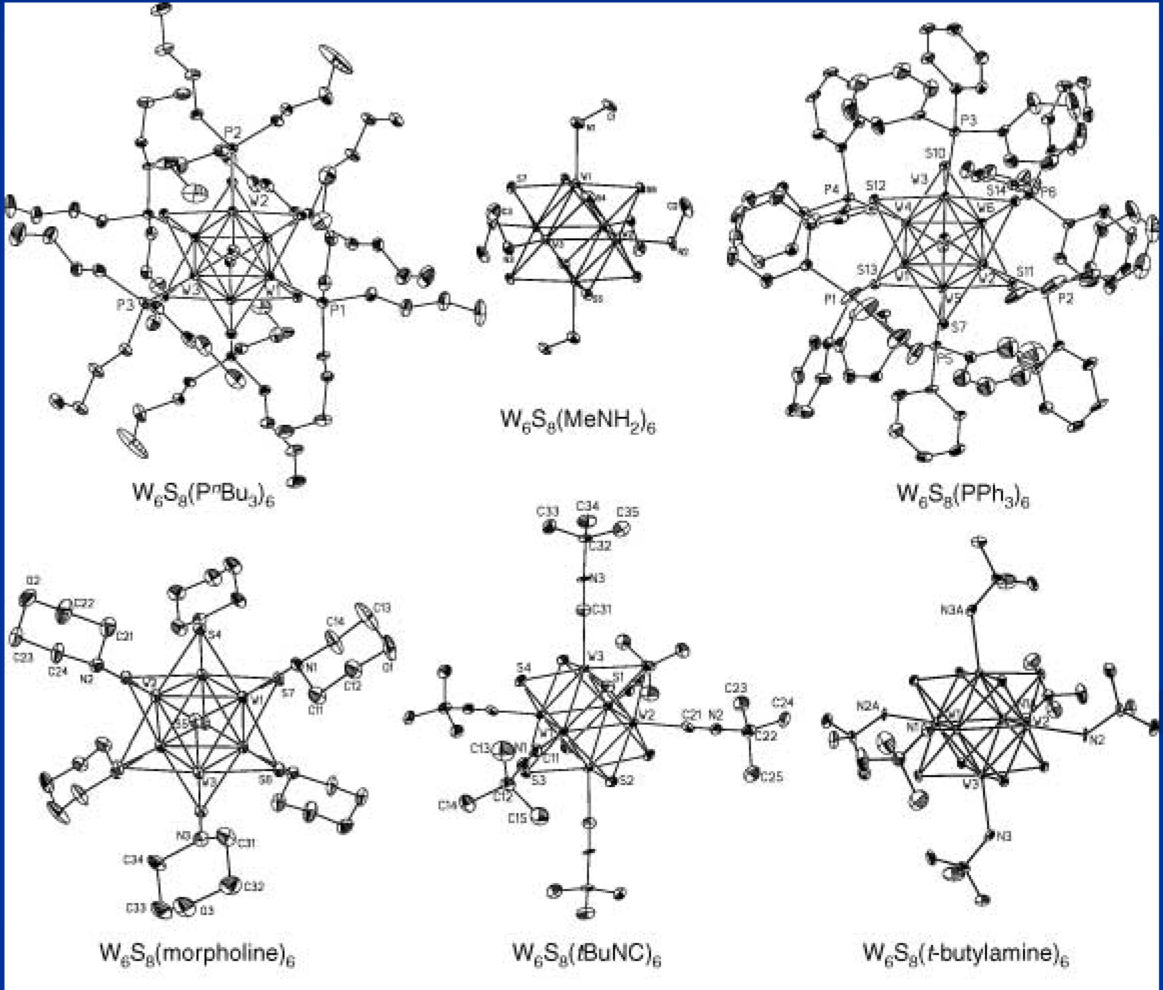
NMR Identification of the Clusters

$W_6S_8L_nL'_{6-n}$

For 2 different L, L´

there are
10 complexes

How many signals
in ^{31}P NMR
if L´ = PR_3 ???



$W_6S_8(P^nBu_3)_6$

$W_6S_8(MeNH_2)_6$

$W_6S_8(PPh_3)_6$

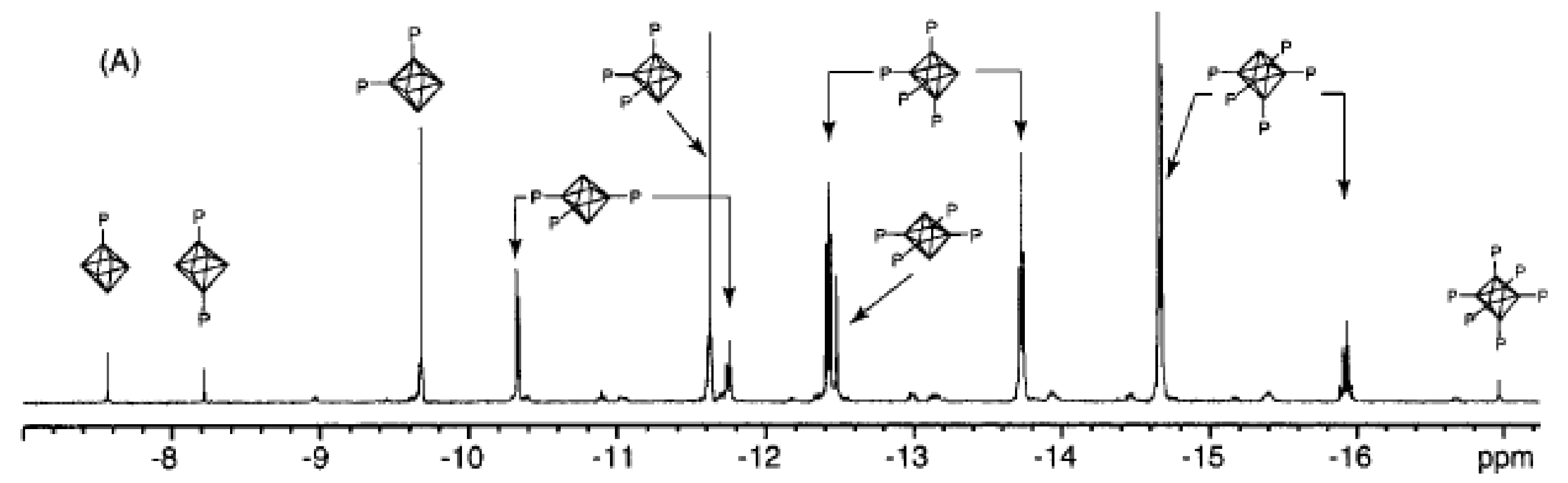
W_6S_8(morpholine)$_6$

W_6S_8(*t*BuNC)$_6$

W_6S_8(*t*-butylamine)$_6$

NMR Identification of the Clusters

Series of 200 complexes

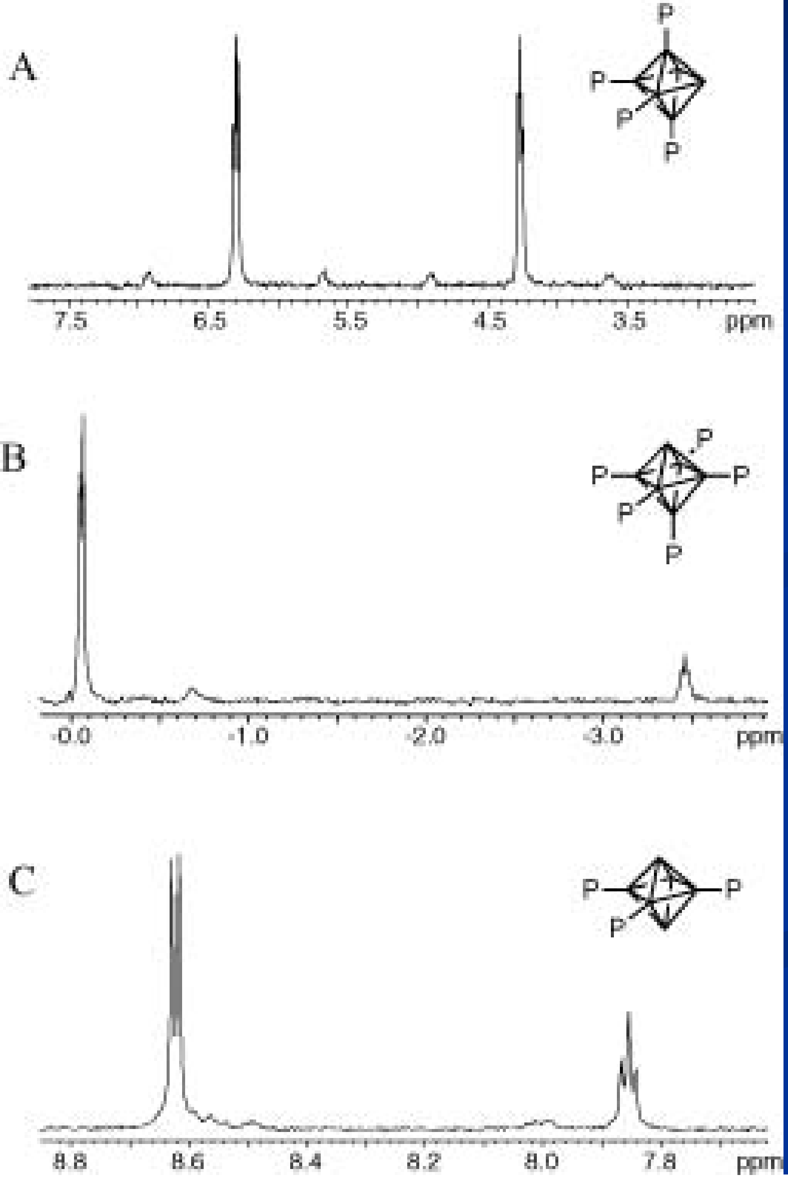


12 Signals in ^{31}P NMR

NMR Identification of the Clusters

$W_6S_8(PR_3)_n(L)_{6-n}$

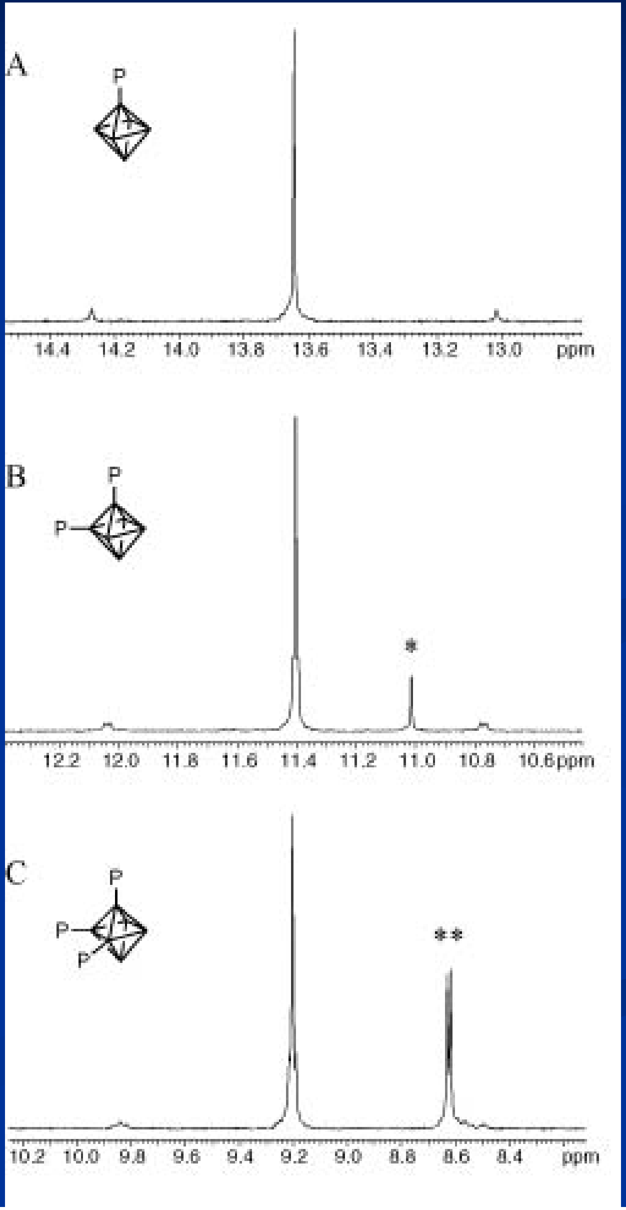
P-W-W-P coupling through the cluster core in the $^{31}P\{^1H\}$ NMR spectra



NMR Identification of the Clusters

$W_6S_8(PR_3)_n(L)_{6-n}$

^{183}W (I=1/2)
the satellite peaks flanking the main P peaks

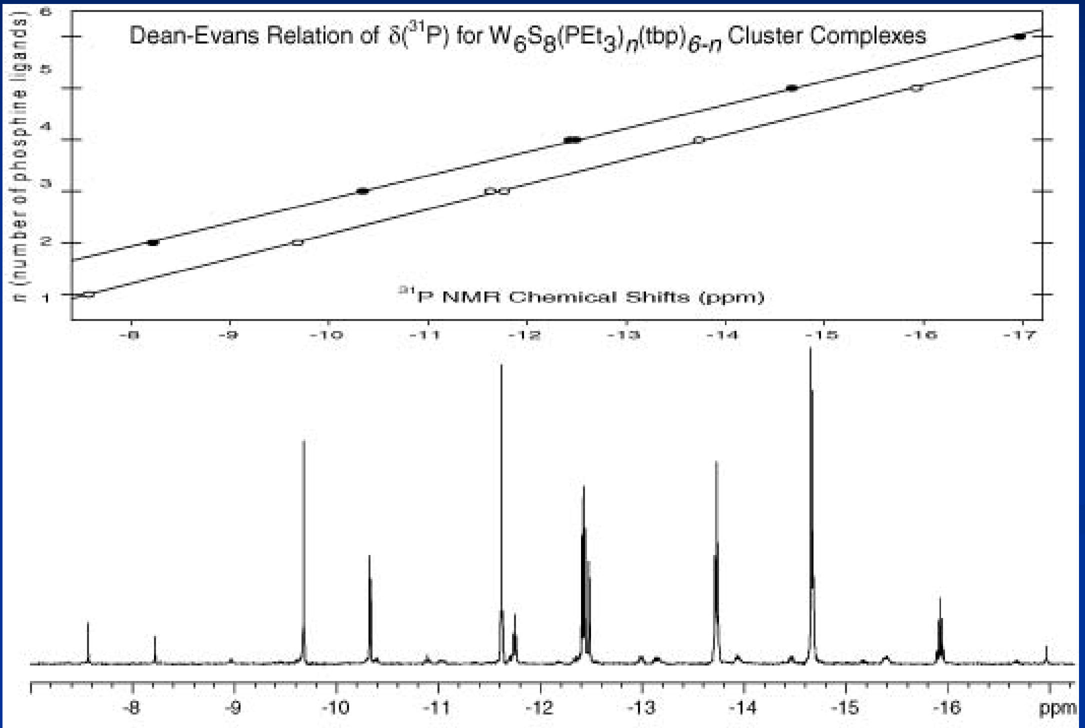


NMR Identification of the Clusters

$W_6S_8(PR_3)_n(L)_{6-n}$

Dean-Evans relation

a two-parameter linear relation



Dean-Evans Relation in $\delta(^{31}P)$ of $W_6S_8L_{6-n}(PR_3)_n$ Cluster Complexes

$$\delta(^{31}P) = \delta_{ref} + pC + qT$$

$\delta(^{31}P)$	chemical shift of the P atom under consideration
δ_{ref}	reference chemical shift
p	number of ligand L in *cis* position to P (0-4)
q	number of ligand L in *trans* position to P (0,1)
C and T	empirical increments of chemical shifts corresponding to *cis* and *trans*

NMR Identification of the Clusters

Dean-Evans relation = a two-parameter linear relation

$\delta(^{31}P) = \delta_{ref} + pC + qT$

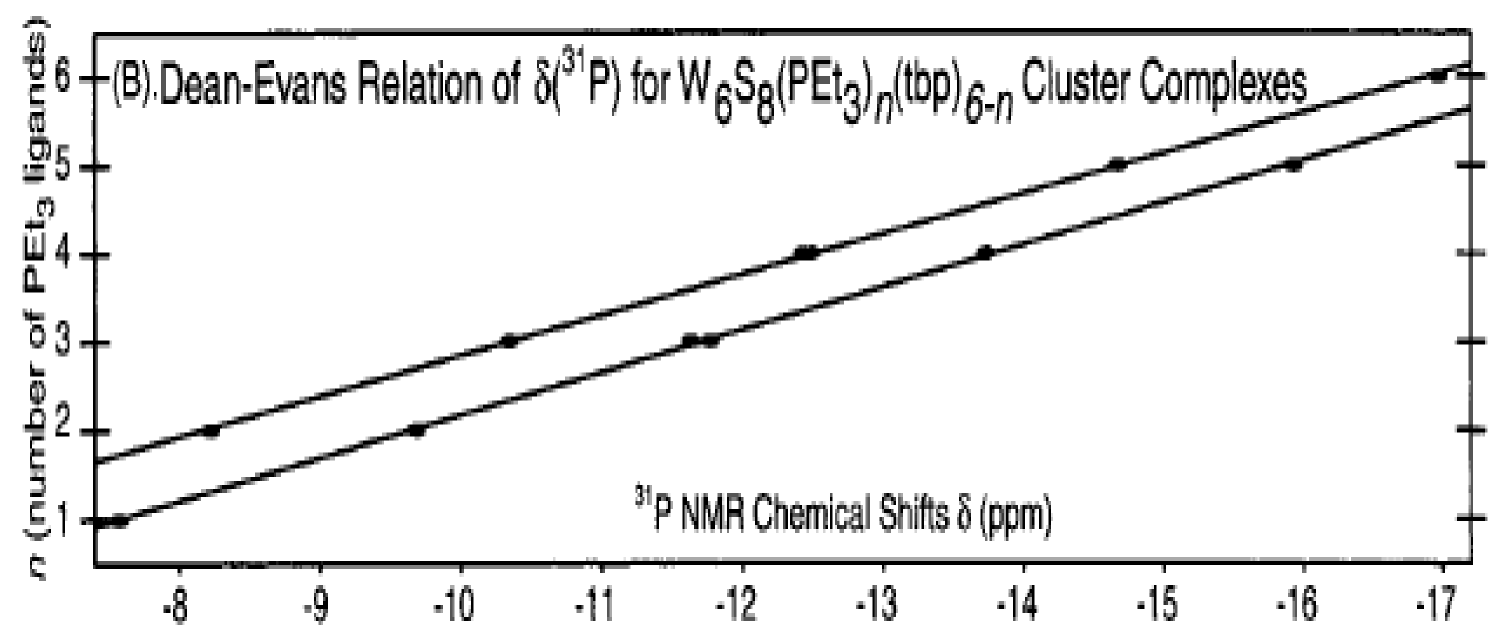
δ_{ref}

two variables (p and q, the number of ligands L in the cis or trans position to PR_3, respectively)

two constants (C and T, characteristic of a given ligand L)

NMR Identification of the Clusters

Dean-Evans relation = a two-parameter linear relation



$$\delta(^{31}\mathrm{P}) = \delta_{\mathrm{ref}} + pC + qT$$