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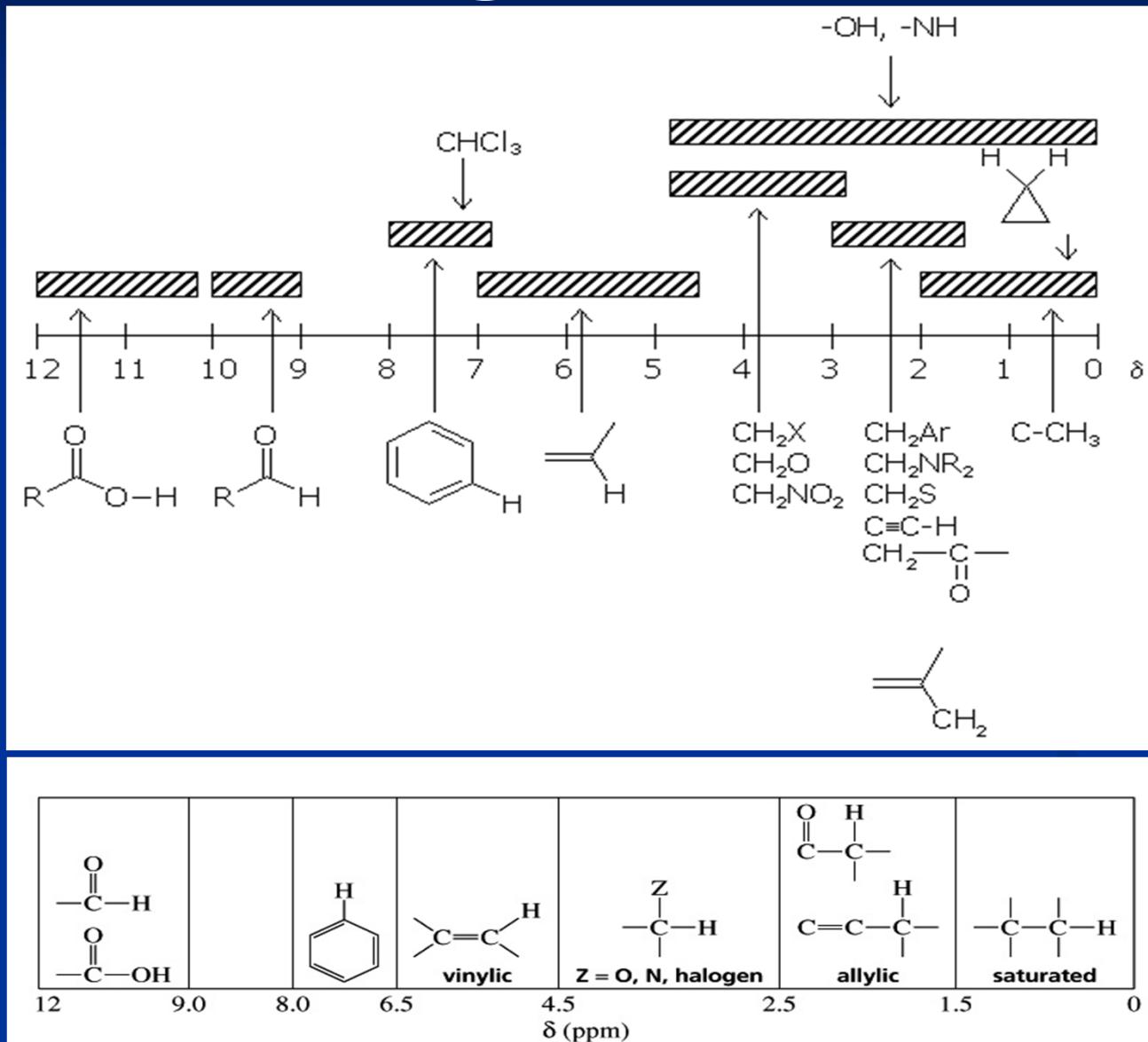
Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C$_6$H$_5$—H	6.5–8
—CH_3	0.9	—C(=O)—H	9.0–10
—CH_2—	1.3	I—C—H	2.5–4
—CH—	1.4	Br—C—H	2.5–4
—C=C—CH_3	1.7	Cl—C—H	3–4
—C(=O)—CH_3	2.1	F—C—H	4–4.5
C$_6$H$_5$—CH_3	2.3	RNH_2	Variable, 1.5–4
—C≡C—H	2.4	ROH	Variable, 2–5
R—O—CH_3	3.3	ArOH	Variable, 4–7
R—C=CH_2 (R)	4.7	—C(=O)—OH	Variable, 10–12
R—C=C—H (R R)	5.3	—C(=O)—NH_2	Variable, 5–8

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

2

^{1}H NMR Chemical Shift Increments

Aliphatic compounds

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

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

C**H$_3$**Cl δ(calc) = 2.76
          δ(exp) = 3.1

C**H$_2$**Cl$_2$ δ(calc) = 5.29
          δ(exp) = 5.3

C**H**Cl$_3$ δ(calc) = 7.82
          δ(exp) = 7.27

Shoolery chemical shift rules

Table 4.3 Substituent constants, $S(\delta)$, for proton resonances in substituted methanes

Substituent	$S(\delta)$ (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

^{1}H NMR Chemical Shift Increments

Aromatic compounds

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

$$\delta = 7.27 + \Sigma\, S_i\,(\delta)$$
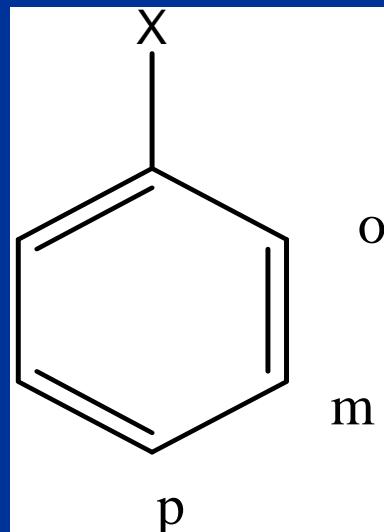
Chemical Shift Calculation for Aromatic compounds

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

Table 4.6 $S(\delta)$ values for substituted benzenes (after Ref. 9)

Substituent	$S(\delta)$ (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$_6$H$_5$	0.18	0.00	0.08
CCl$_3$	0.8	0.2	0.2
CHCl$_2$	0.1	0.06	0.1
CH$_2$Cl	−0.0	0.01	0.0
CH$_3$	−0.17	−0.09	−0.18
CH$_2$CH$_3$	−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$_2$OH	−0.1	−0.1	−0.1
CH$_2$NH$_2$	−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$_3$C$_6$H$_4$SO$_3$	−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
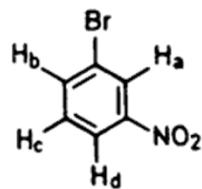
$\delta(H_a) = 7.27 + 0.22 + 0.95 = 8.44$

$\delta(H_b) = 7.27 + 0.22 + 0.33 = 7.82$

$\delta(H_c) = 7.27 − 0.13 + 0.17 = 7.31$

$\delta(H_d) = 7.27 − 0.03 + 0.95 = 8.19$

4

^{1}H NMR Chemical Shift Increments

Olefinic compounds

Ethylene

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

$\delta = 5.28 + \Sigma\, S_i\,(\delta)$
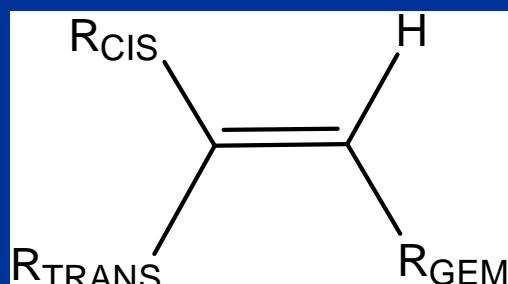
Table 4.7 $S(\delta)$ values for substituted ethylenes (after Ref. 10)
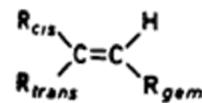
| Substituent R*	$S(\delta)$(ppm) gem	cis	trans	Substituent R*	$S(\delta)$(ppm) gem	cis	trans
−H	0	0	0	H			
−Alkyl	0.44	−0.26	−0.29	−C=O	1.03	0.97	1.21
−Alkyl ring	0.71	−0.33	0.30	NR$_2$			
−CH$_2$O, −CH$_2$I	0.67	−0.02	−0.07	−C=O	1.37	0.93	0.35
−CH$_2$S	0.53	−0.15	−0.15	Cl			
−CH$_2$Cl, −CH$_2$Br	0.72	0.12	0.07	−C=O	1.10	1.41	0.99
−CH$_2$N	0.66	−0.05	−0.23	−OR (R aliph.)	1.18	−1.06	−1.28
−C≡C	0.50	0.35	0.10	−OR (R conj.)	1.14	−0.65	−1.05
−C≡N	0.23	0.78	0.58	−OCOR	2.09	−0.40	−0.67
−C=C (isol.)	0.98	−0.04	−0.21	−Aromatic	1.35	0.37	−0.10
−C=C (conj.)	1.26	0.08	−0.01	−Cl	1.00	0.19	0.03
−C=C (isol.)	1.10	1.13	0.81	−Br	1.04	0.40	0.55
−C=O (conj.)	1.06	1.01	0.95	−N ⟨R,R⟩ (R aliph.)	0.69	−1.19	−1.31
−COOH (isol.)	1.00	1.35	0.74				
−COOH (conj.)	0.69	0.97	0.39				
−COOR (isol.)	0.84	1.15	0.56	−N ⟨R,R⟩ (R conj.)	2.30	−0.73	−0.81
−COOR (conj.)	0.68	1.02	0.33				
				−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
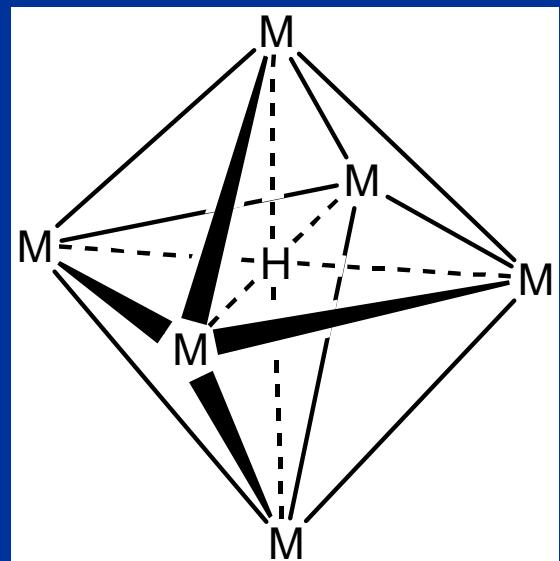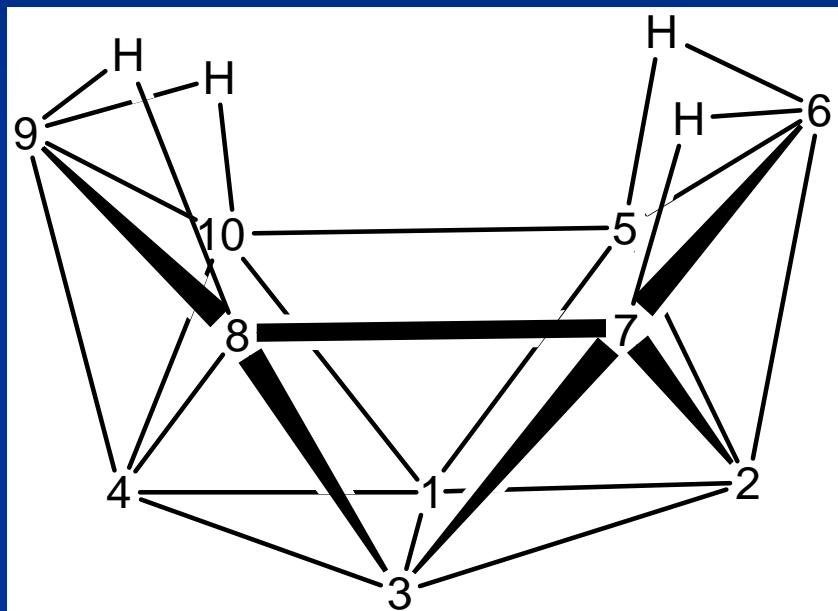
^{1}H NMR of Boranes


nido-Decaborane(14)

bridging B$_2$H   −2.12 ppm

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

¹H NMR Organometallic Hydrides
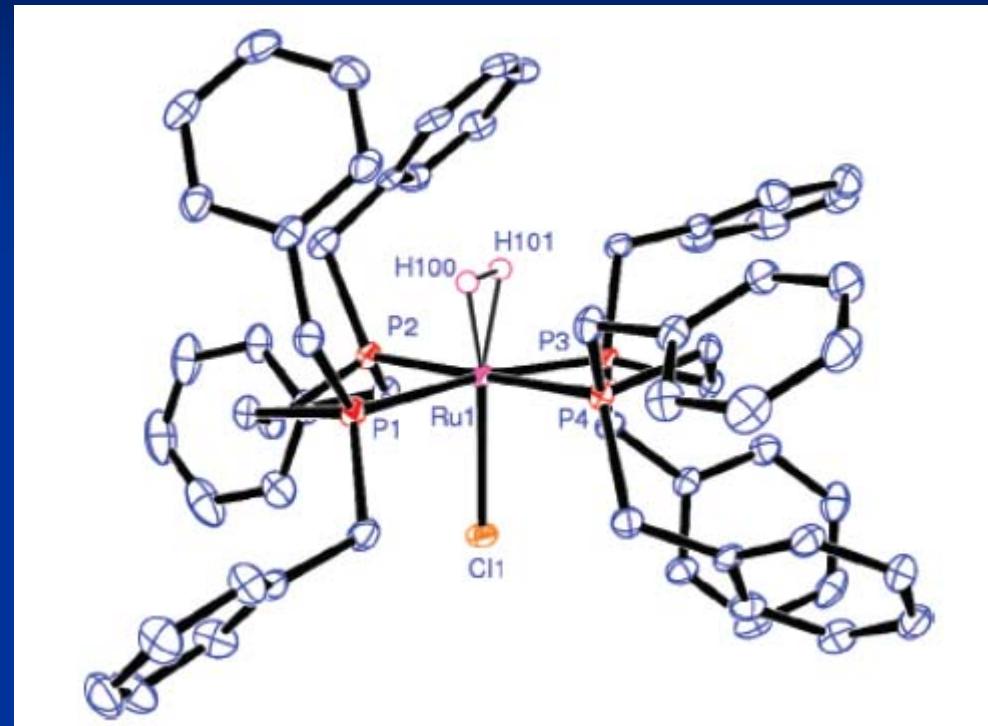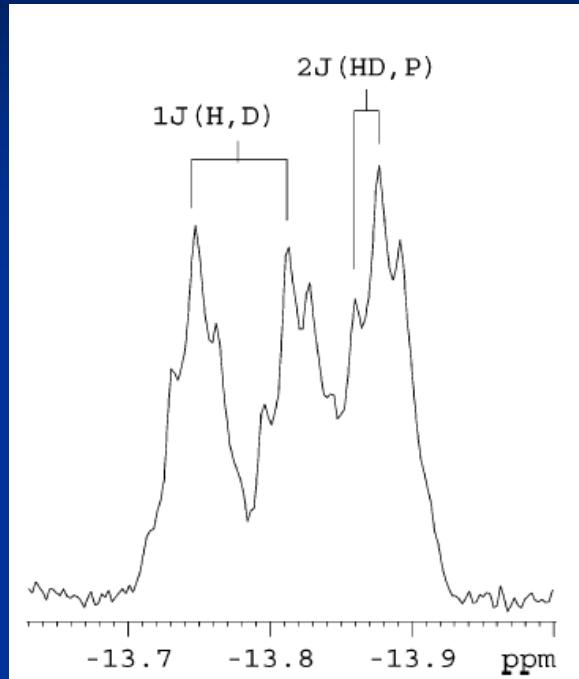
unpaired electrons ?
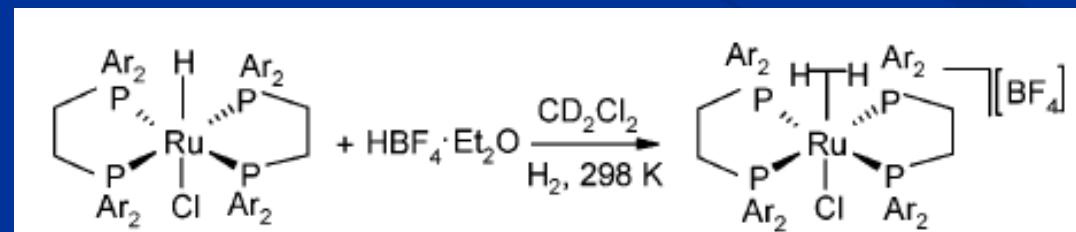
^{1}H NMR of Paramagnetic Compounds
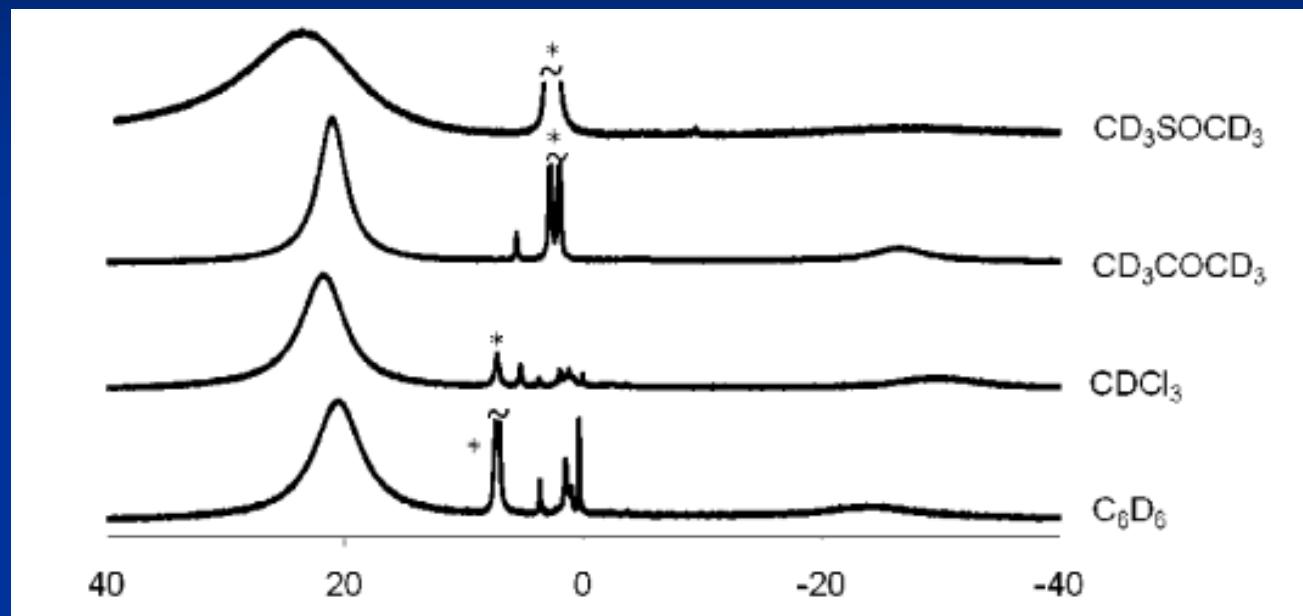
^{1}H NMR spectra of Fe(acac)$_3$

CH$_3$ CH

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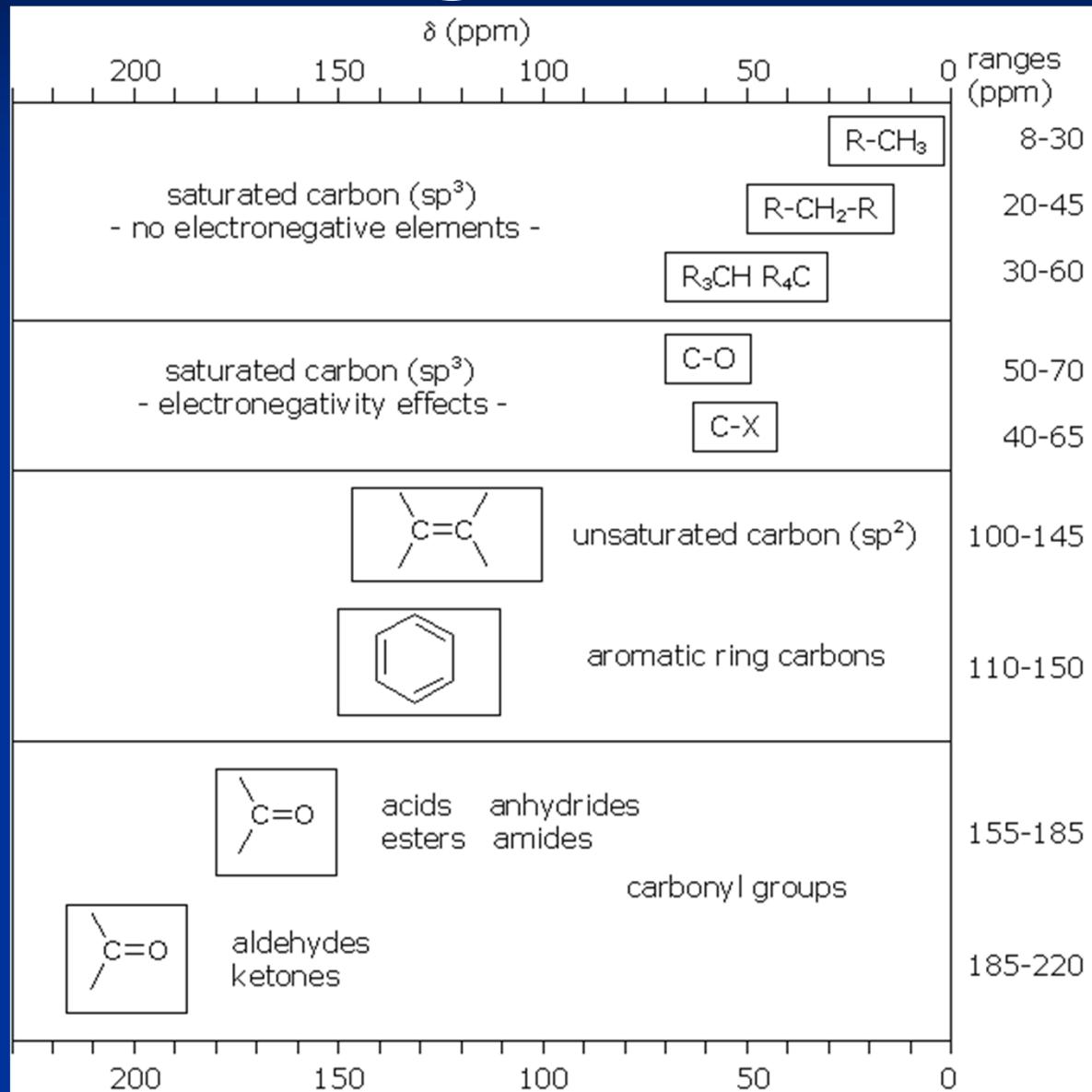
Table 14.4   Approximate Values of Chemical Shifts for ^{13}C NMR

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 (with R branch)	20–60	R, —N \ C=O	165–175
R—C—R (with R branches)	30–40	R, RO \ C=O	165–175
≡C	65–85	R, HO \ C=O	175–185
=C	100–150	R, H \ C=O	190–200
(aromatic)—C	110–170	R, R \ C=O	205–220

11
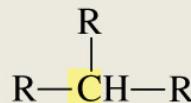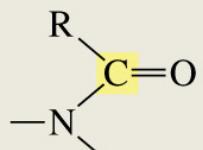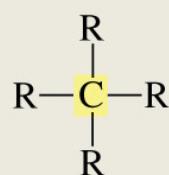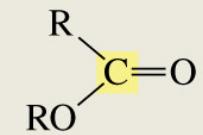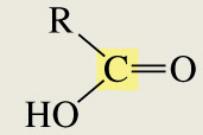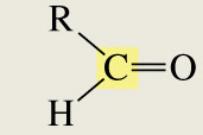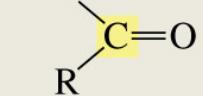
^{13}C NMR Chemical Shift Increments


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

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

Regions of ³¹P NMR Shifts
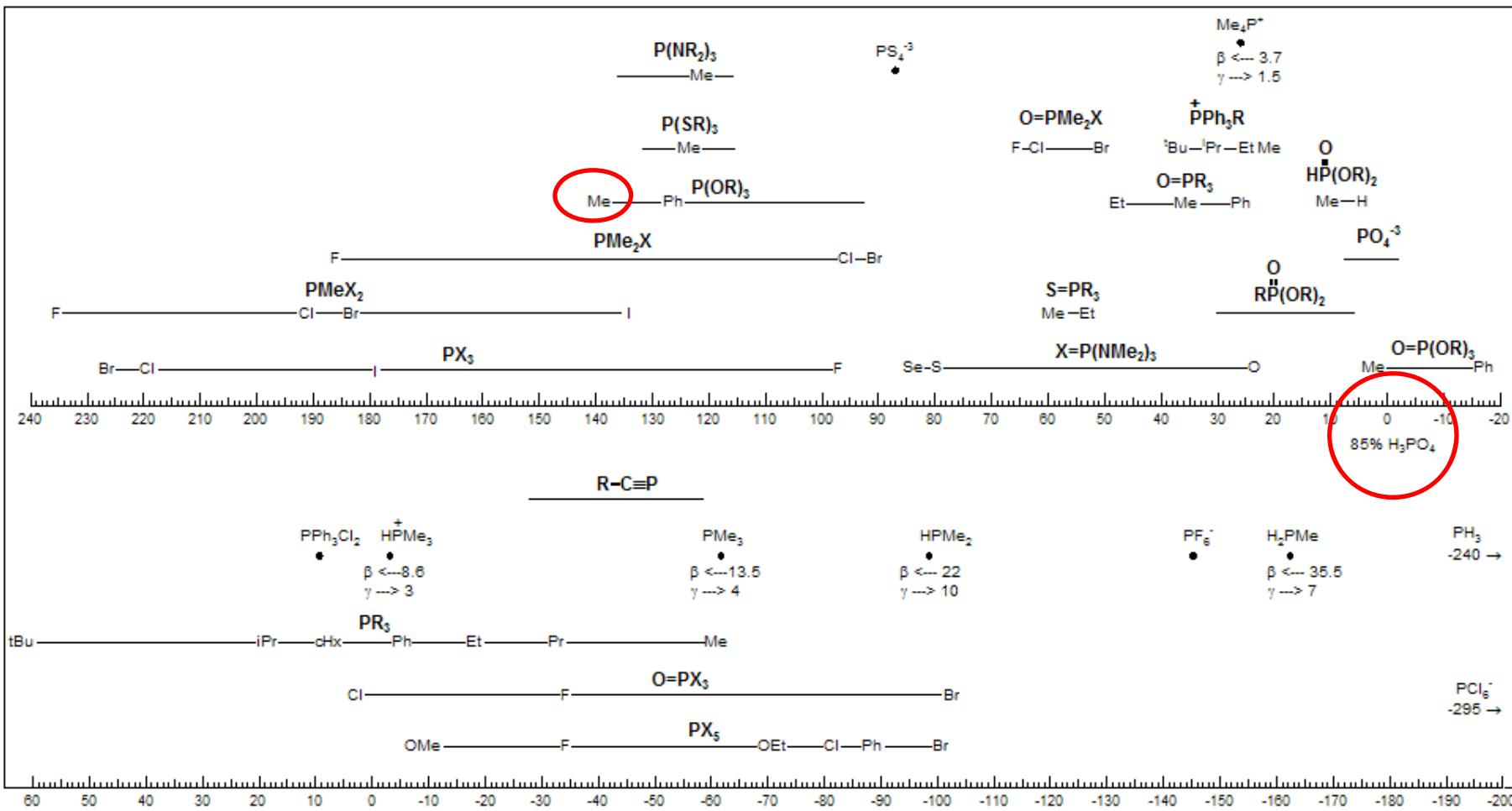
Regions of ¹⁹F NMR Shifts

- Fluorine Shifts Overview
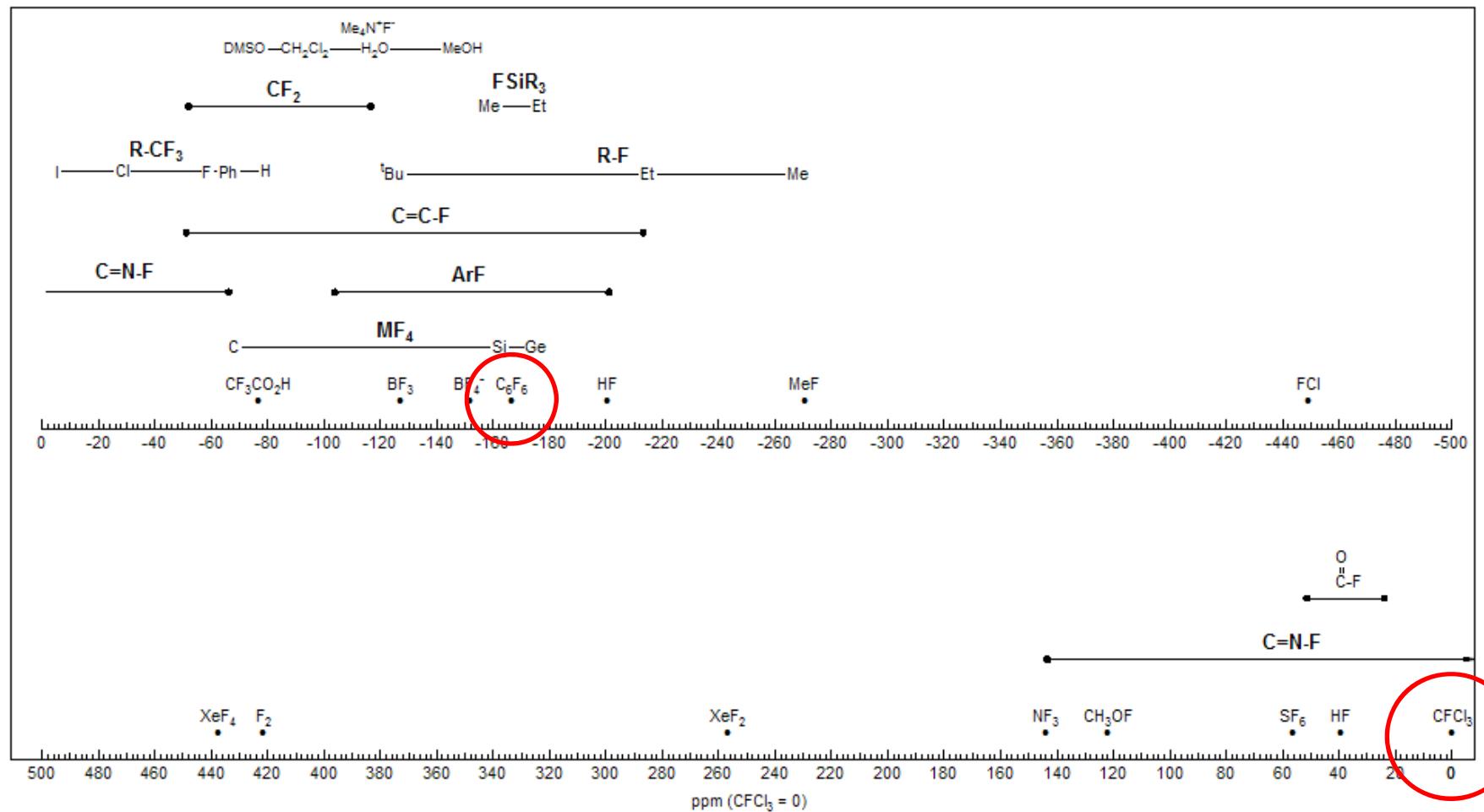
Regions of ^{77}Se NMR Shifts

- Selenium Shifts Overview
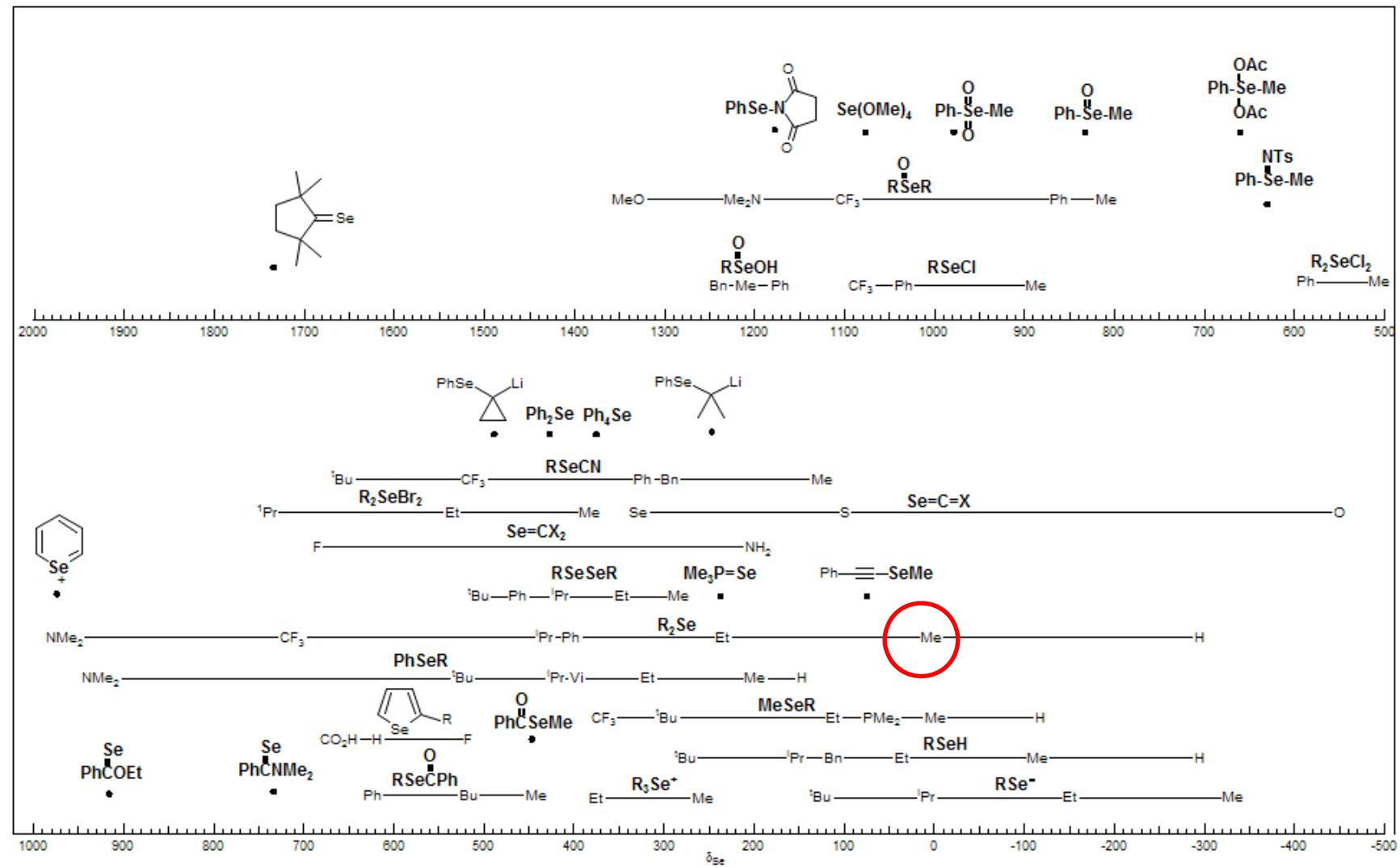
Regions of ^{29}Si NMR Shifts

^{29}Si NMR chemical shift ranges for various silyl groups

SiO_4^- — Q^0

$(\equiv SiO)SiO_3^-$ — Q^1

$(\equiv SiO)SiO_3^-$ — Q^1 (Si-O-Si = 180°)

$Cl_3Si(OSi\equiv)$

$(\equiv SiO)_2SiO_2^-$ — Q^2

$Me_2SiCl(OSi\equiv)$

$HSiCl_2(OSi\equiv)$

$Cl_2Si(OSi\equiv)_2$

$(\equiv SiO)_3SiO^-$ — Q^3

$Me_2Si(OSi\equiv)_2$

$HSiCl(OSi\equiv)_2$

$ClSi(OSi\equiv)_3$

$(\equiv SiO)_4Si$ — Q^4

$HSi(OSi\equiv)_3$

20   0   -20   -40   -60   -80   -100   -120

ppm

SiO_6
−200 ppm

16
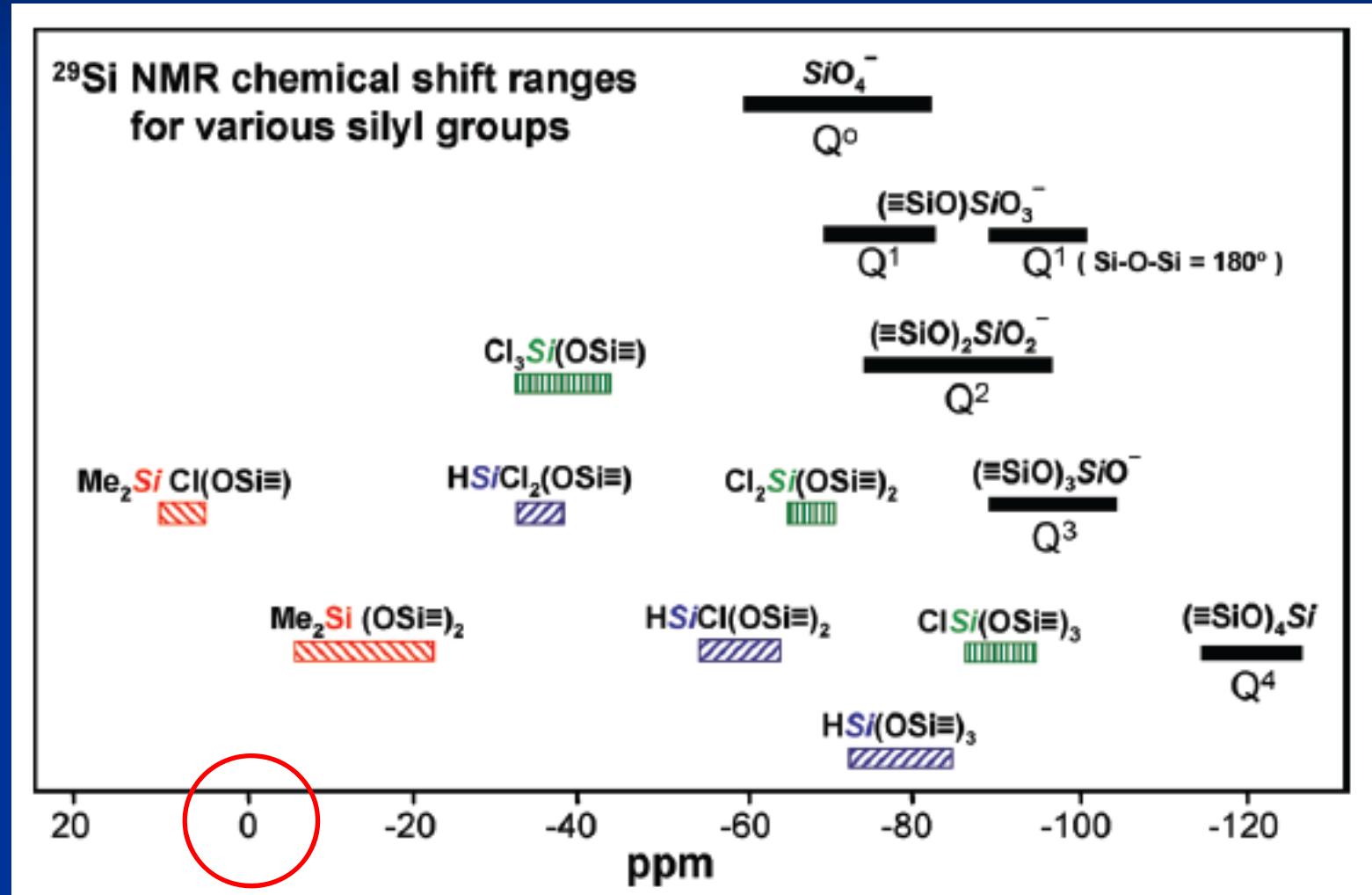
Silicate Anions in Aqueous Alkaline Media Detected by ^{29}Si-NMR

$M = OSiR_3$

$D = O_2SiR_2$

$T = O_3SiR$

$Q = O_4Si$

$Q^0 = O_4Si$
$Q^1 = O_3SiOSi$
$Q^2 = O_2Si(OSi)_2$
$Q^3 = OSi(OSi)_3$
$Q^4 = Si(OSi)_4$
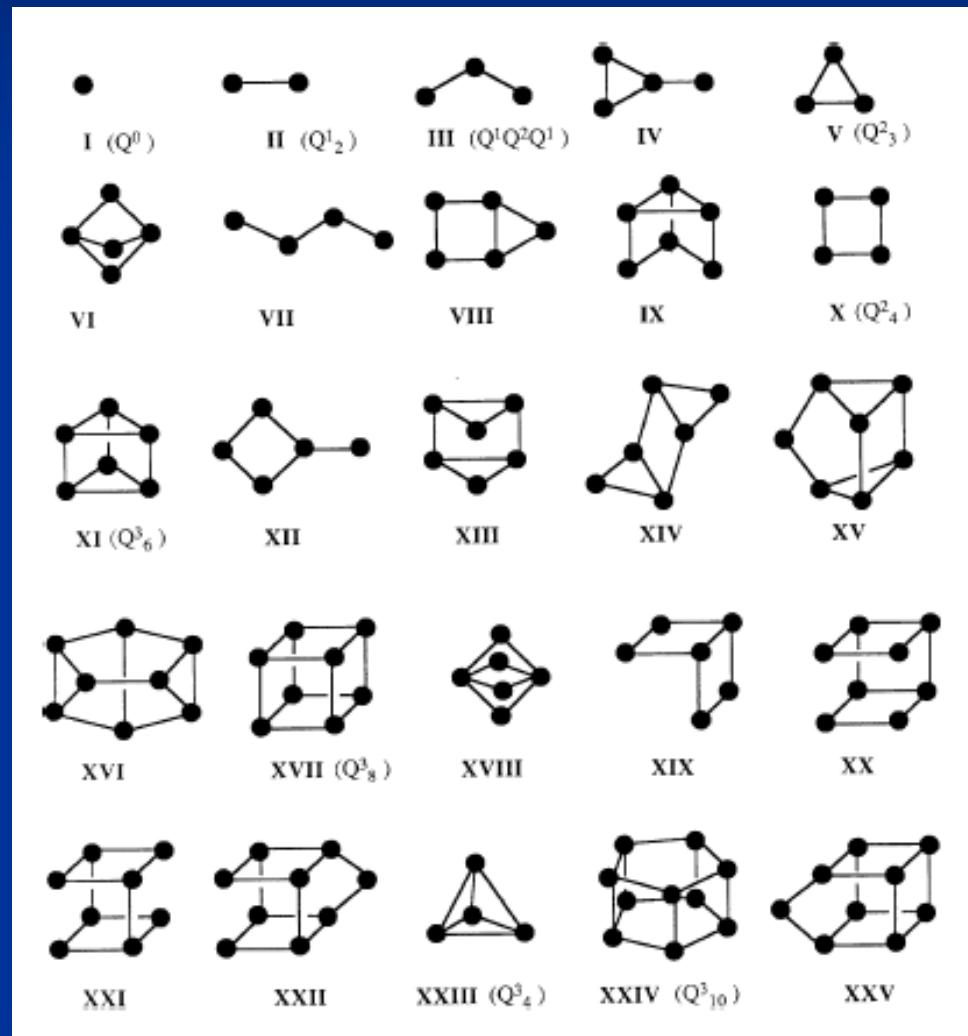
Regions of ^{17}O MAS NMR
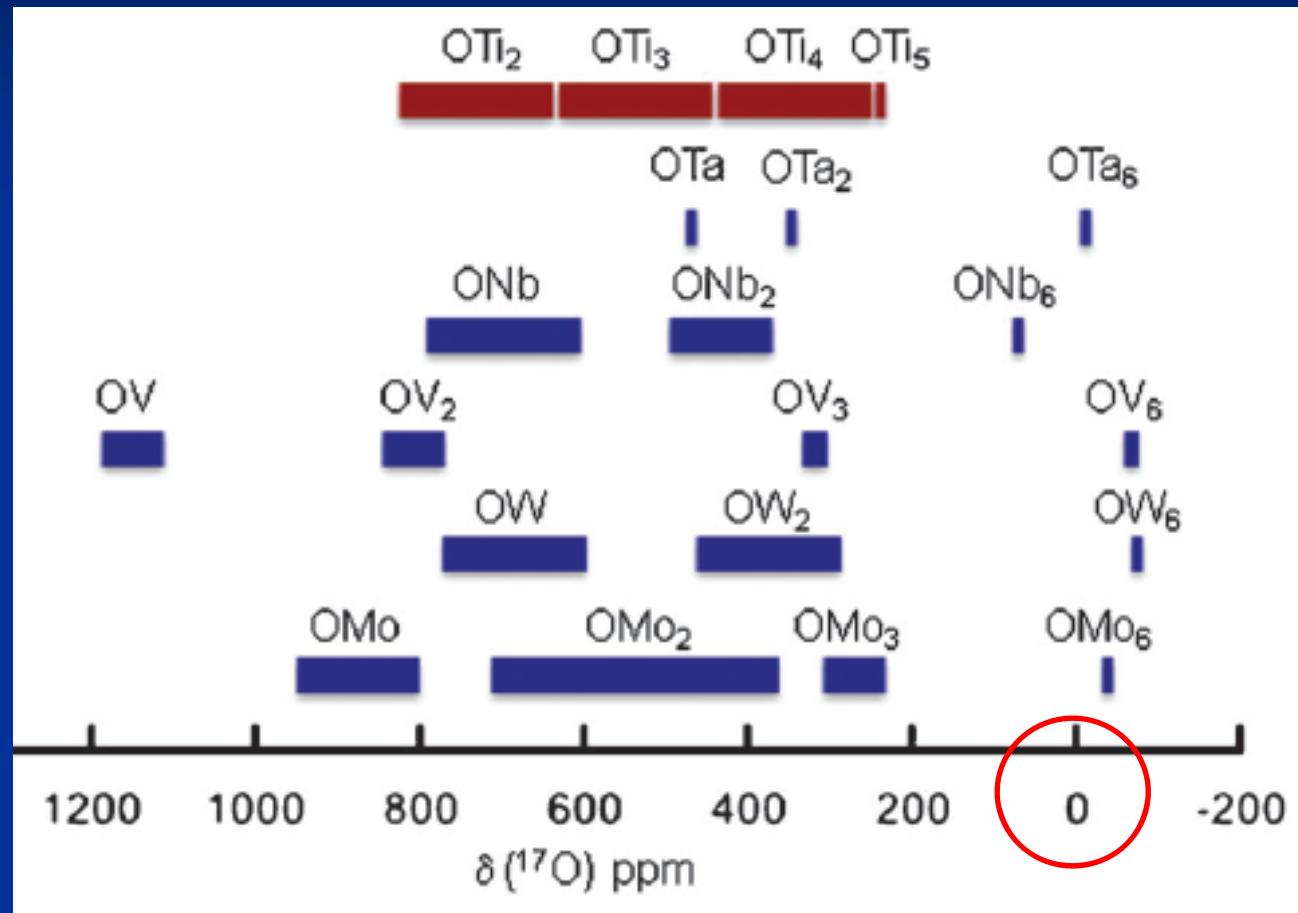
$H_2{}^{17}O$

Linear Correlations of the NMR Parameters with the Number of Arene Methyls
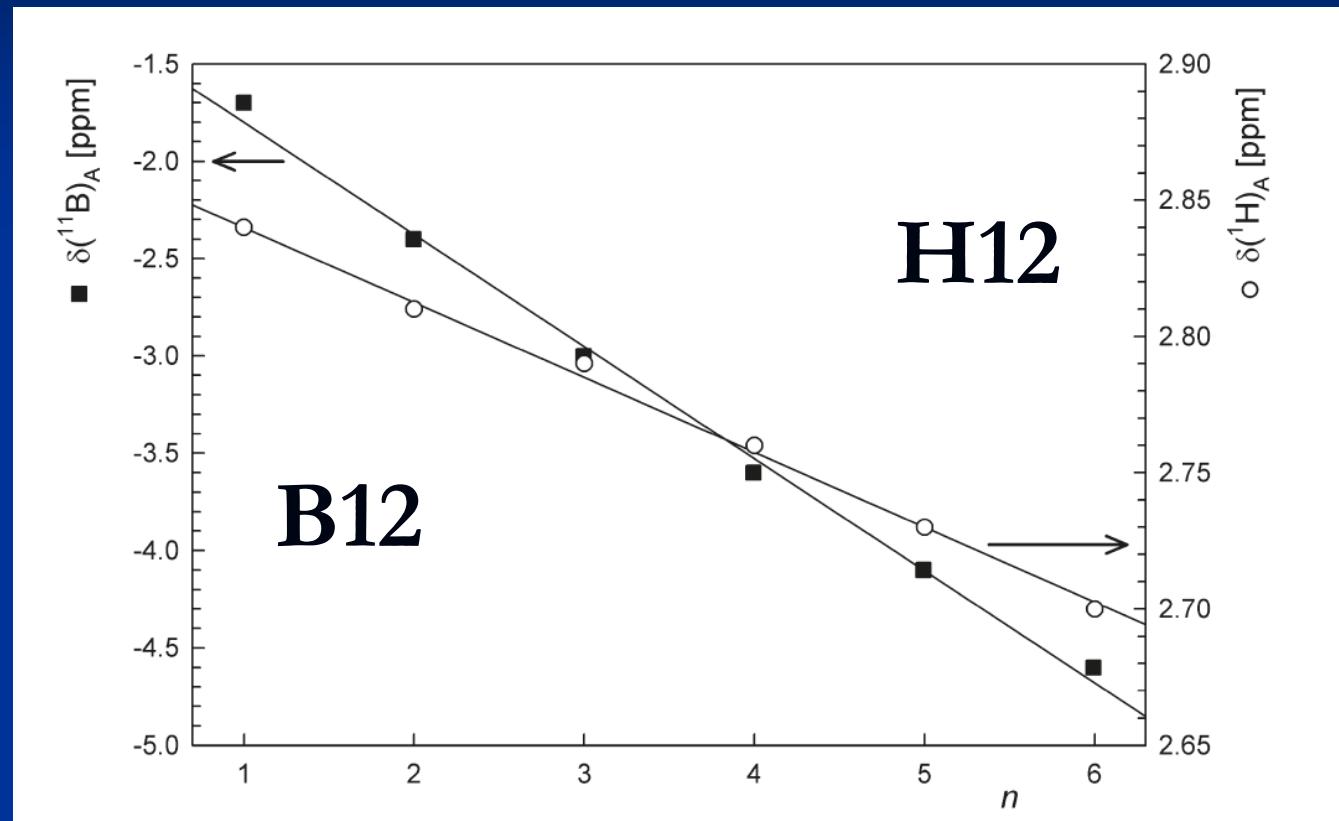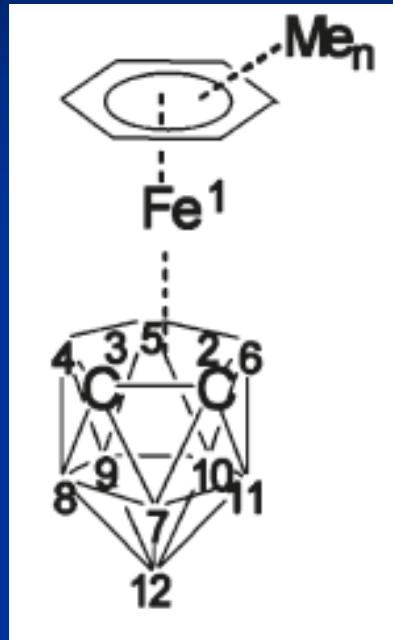
Is diamagnetic or paramagnetic shielding affected?

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

Octahedral Metal Clusters

Halogen or chalcogen

Cr, Mo or W

Six axial ligands (L) coordinate to the metal atoms
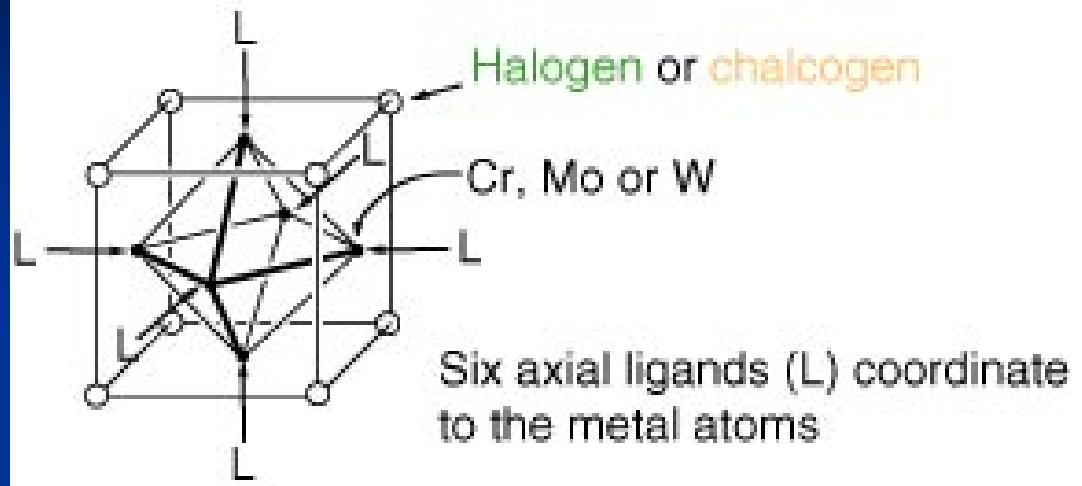
Song Jin, Jennifer Adamchuk, Bosong Xiang, and Francis J. DiSalvo* J. AM. CHEM. SOC. 2002, 124, 9229-9240

How many derivatives and isomers for

2 different L

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

$W_6S_8(4\text{-tbp})_5(PEt_3)$

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

NMR Identification of the Clusters

$$W_6S_8L_nL'_{6-n}$$
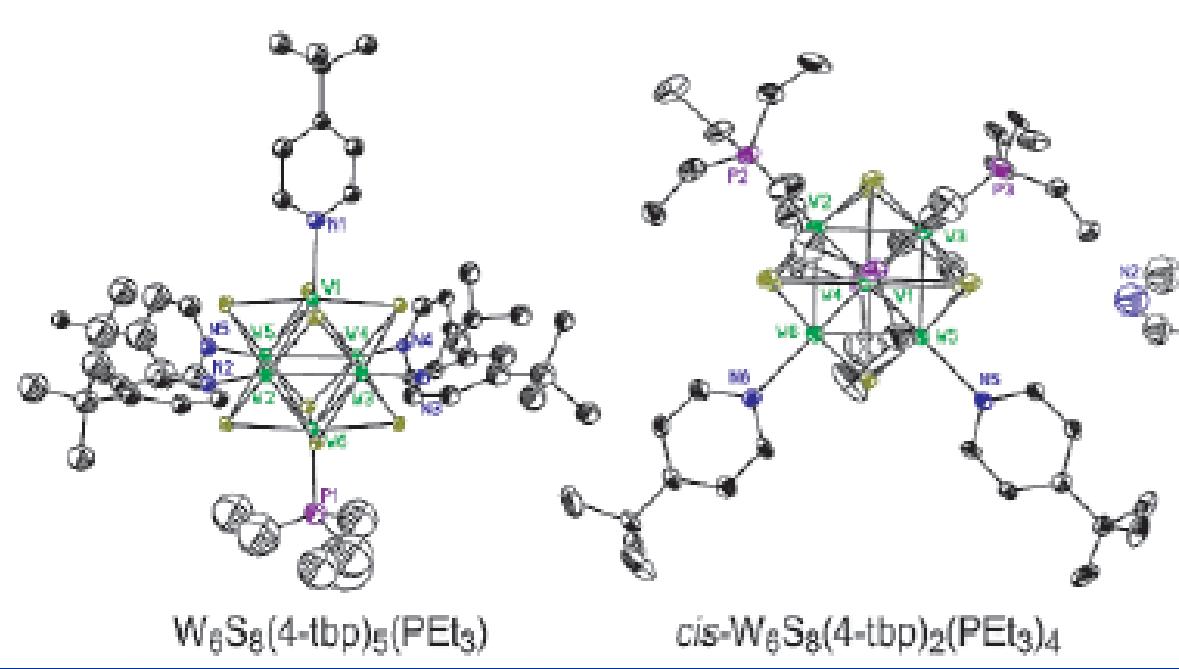
For 2 different L, L′

there are
10 complexes

How many signals
in ^{31}P NMR
if L′ = PR$_3$???

W$_6$S$_8$(P^{n}Bu$_3$)$_6$

W$_6$S$_8$(MeNH$_2$)$_6$

W$_6$S$_8$(PPh$_3$)$_6$

W$_6$S$_8$(morpholine)$_6$

W$_6$S$_8$(tBuNC)$_6$

W$_6$S$_8$(t-butylamine)$_6$
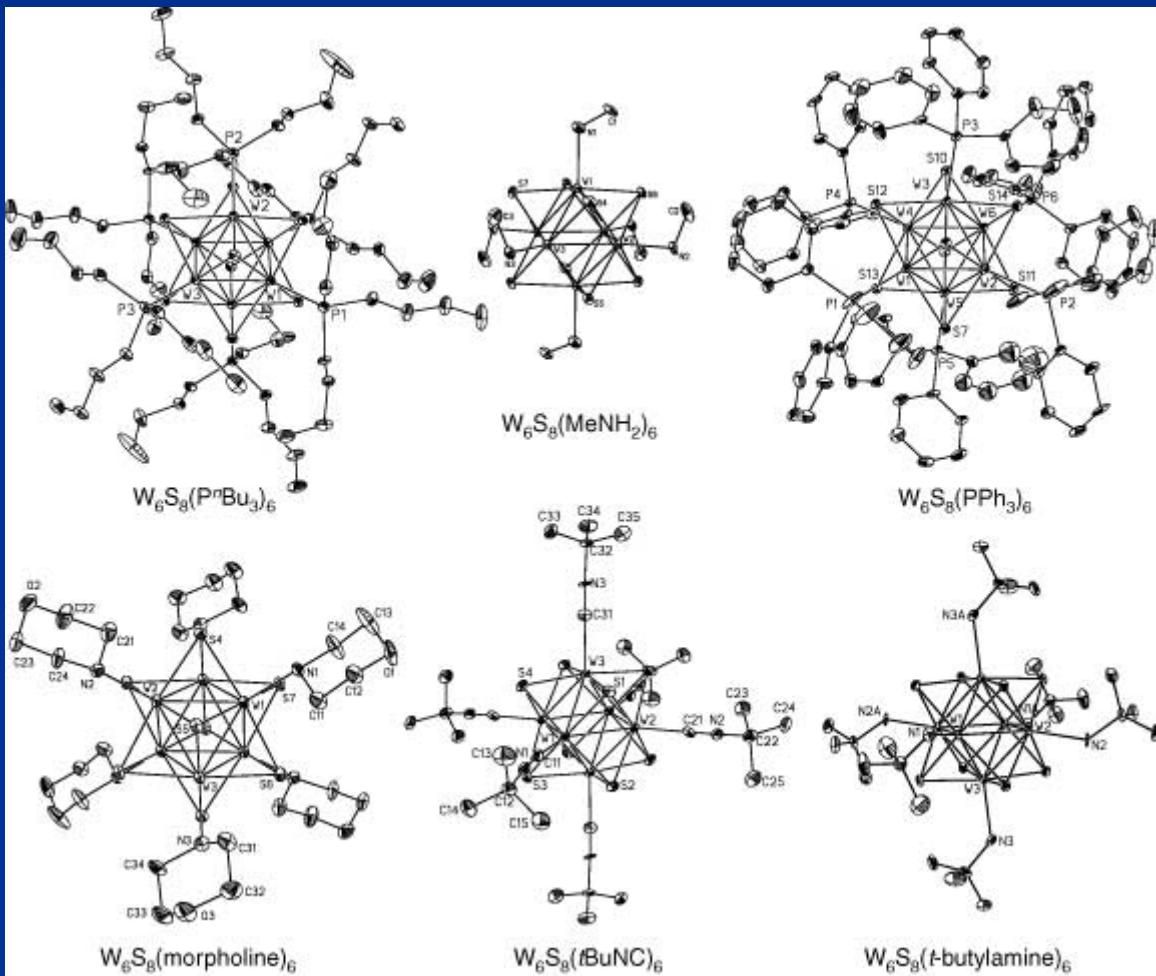
NMR Identification of the Clusters

Series of 200 complexes
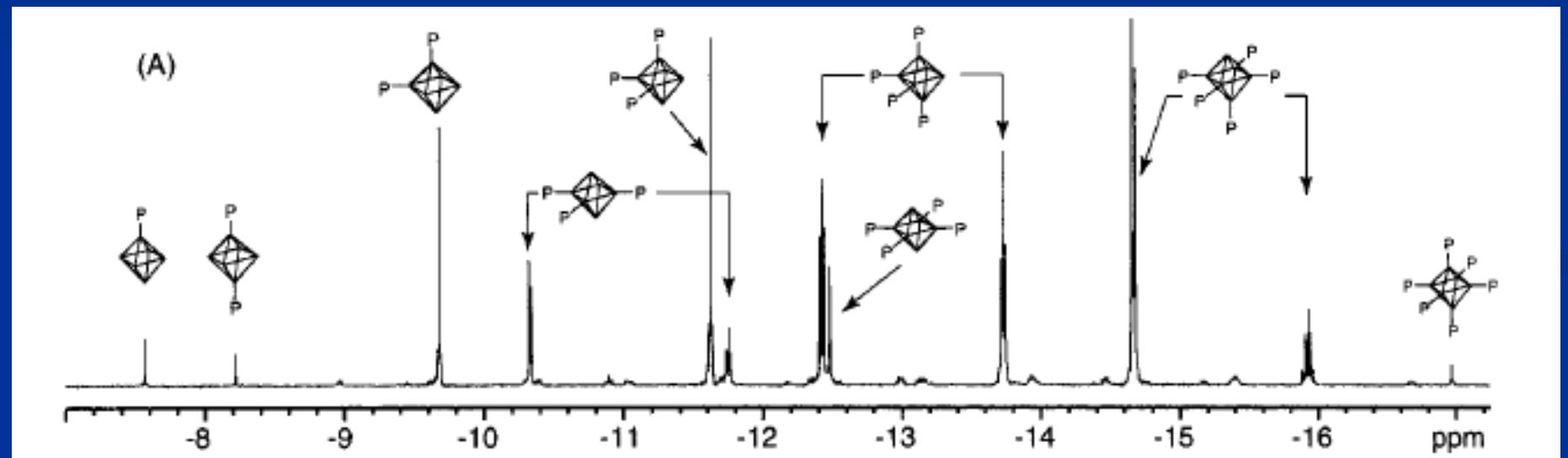
12 Signals in ^{31}P NMR

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

23

NMR Identification of the Clusters

$$W_6S_8(PR_3)_n(L)_{6-n}$$
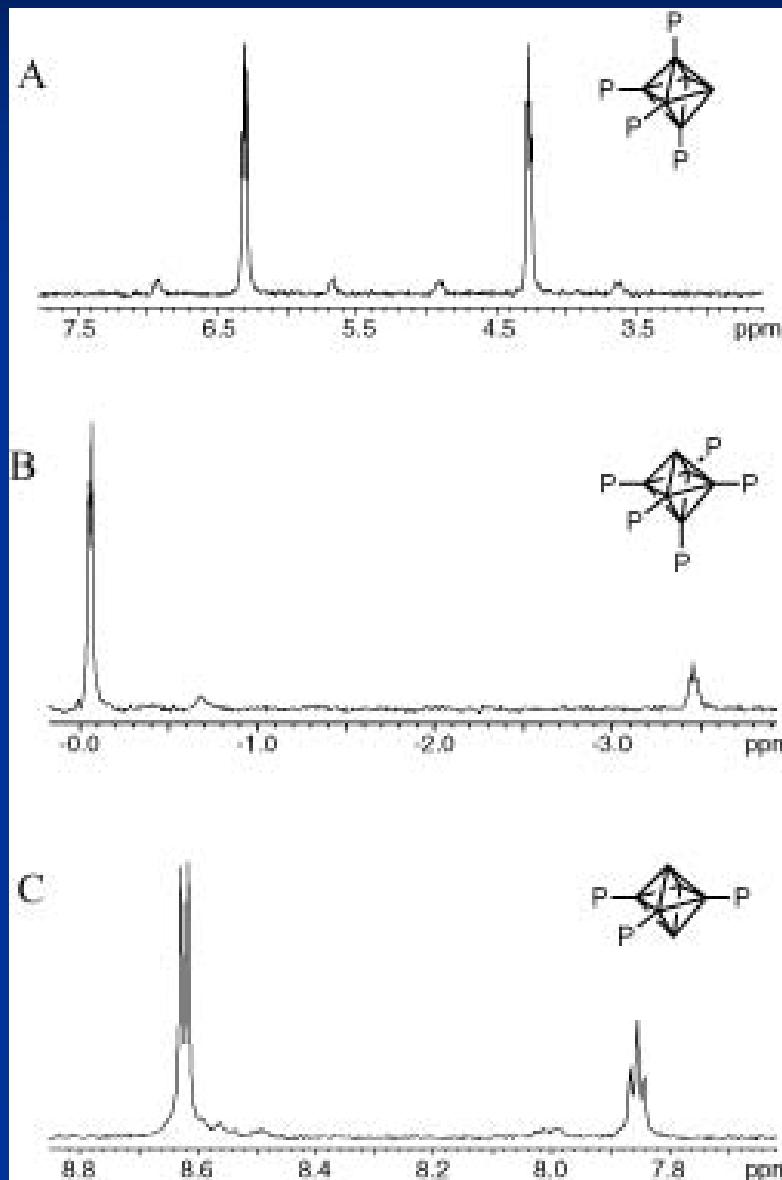
^{183}W (I=1/2)
the satellite peaks
flanking the main P
peaks
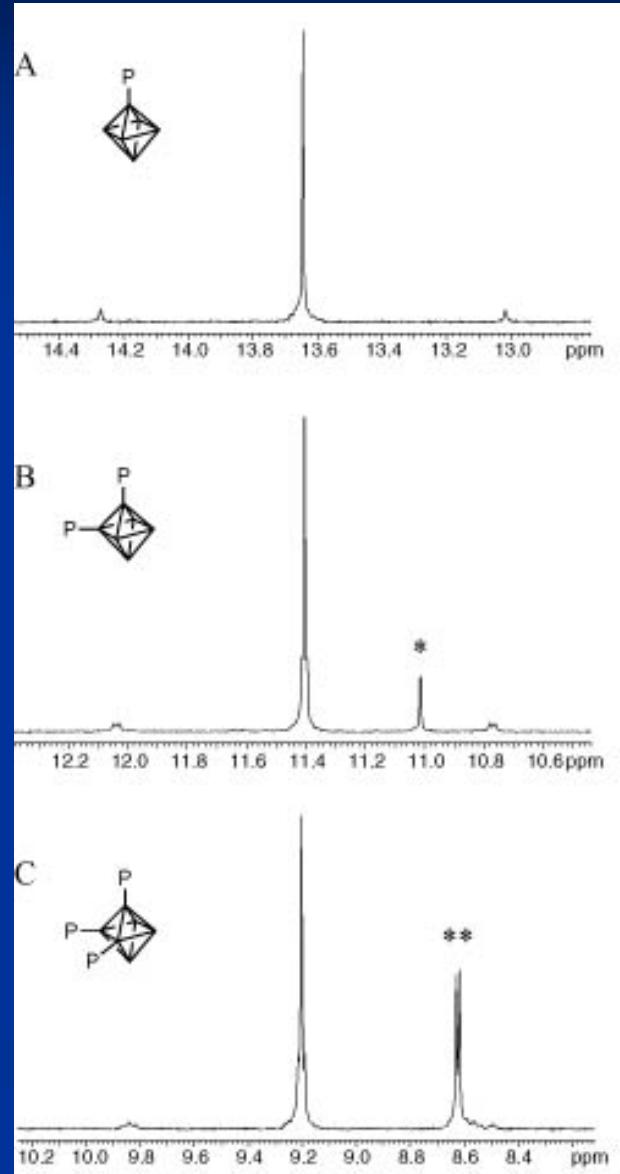
NMR Identification of the Clusters

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

Dean-Evans relation

a two-parameter linear relation


Dean-Evans Relation of $\delta(^{31}P)$ for $W_6S_8(PEt_3)_n(tbp)_{6-n}$ Cluster Complexes

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*
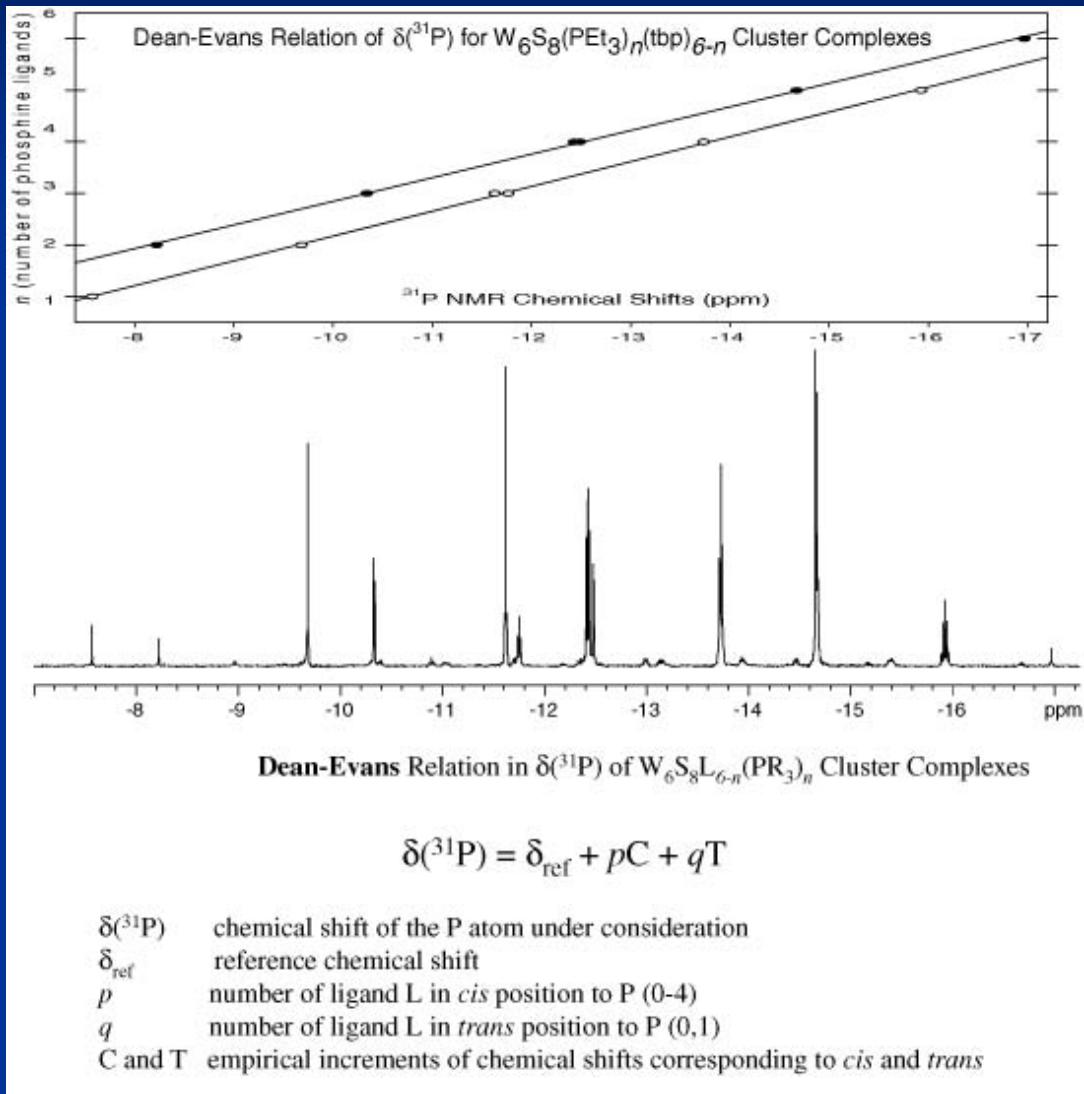
NMR Identification of the Clusters

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

(B) Dean-Evans Relation of $\delta(^{31}P)$ for $W_6S_8(PEt_3)_n(tbp)_{6-n}$ Cluster Complexes

^{31}P NMR Chemical Shifts δ (ppm)

n (number of PEt_3 ligands)

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