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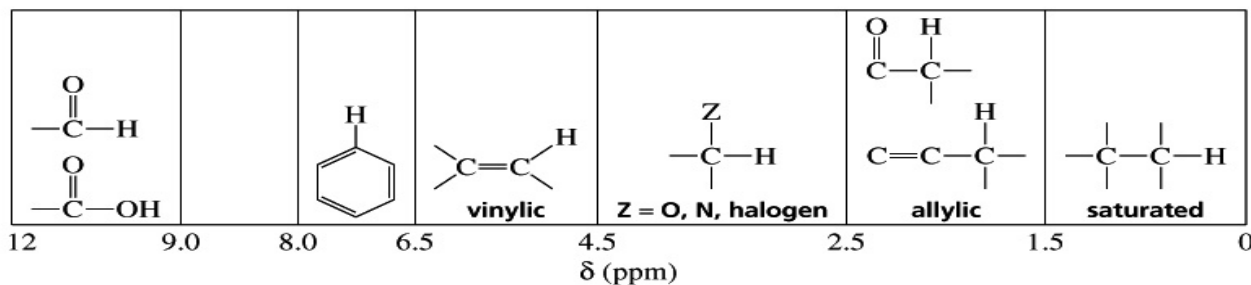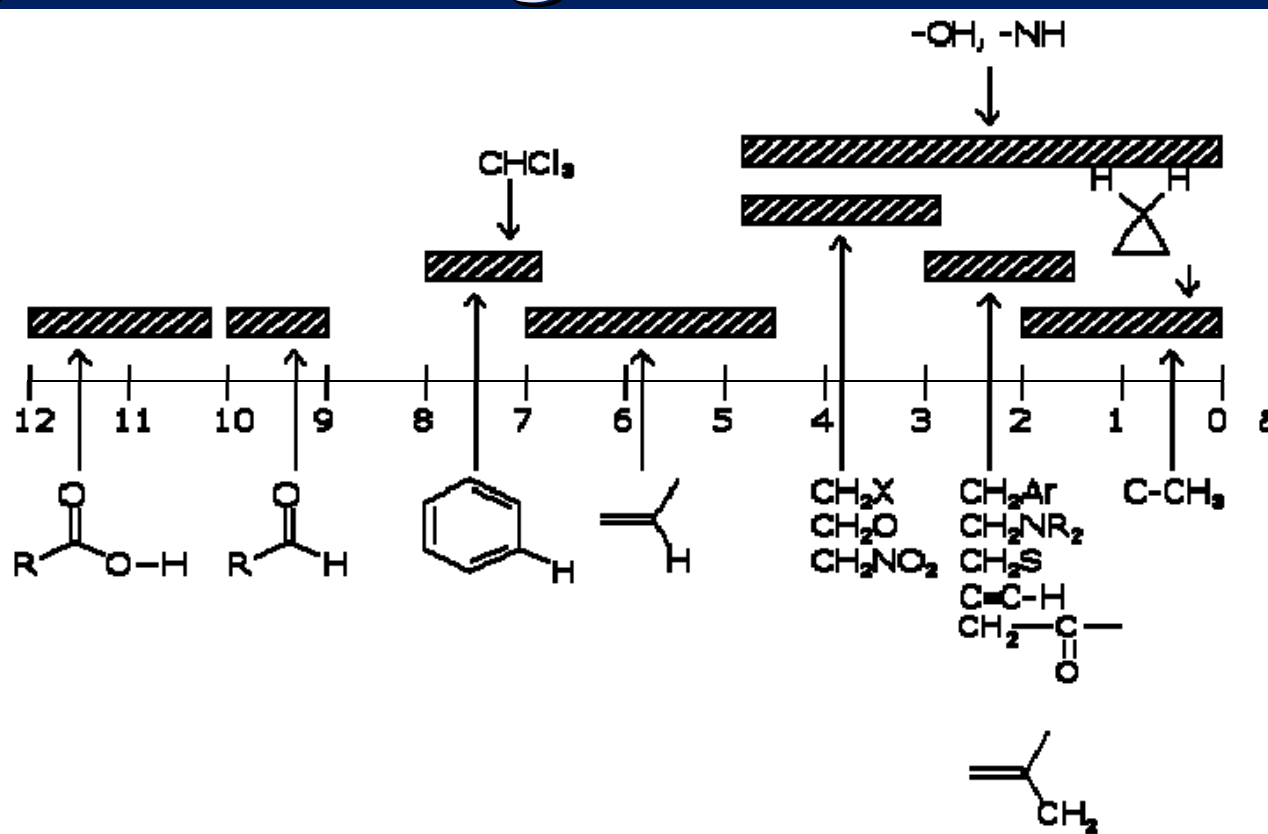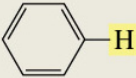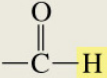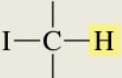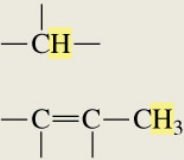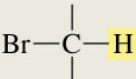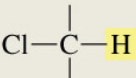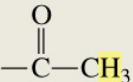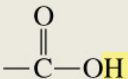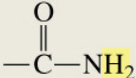
Table 14.1 Approximate Values of Chemical Shifts for ^1H NMR[a]

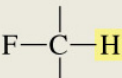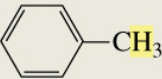| Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C₆H₅—H (phenyl—H)	6.5–8
—CH_3	0.9	$-\overset{\overset{O}{\|\|}}{C}-H$	9.0–10
—CH_2—	1.3	$I-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
—CH—	1.4	$Br-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
—C=C—CH_3	1.7	$Cl-\overset{\|}{\underset{\|}{C}}-H$	3–4
$-\overset{\overset{O}{\|\|}}{C}-CH_3$	2.1	$F-\overset{\|}{\underset{\|}{C}}-H$	4–4.5
C₆H₅—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 below)	4.7	$-\overset{\overset{O}{\|\|}}{C}-OH$	Variable, 10–12
R—C=C—H (R, R below)	5.3	$-\overset{\overset{O}{\|\|}}{C}-NH_2$	Variable, 5–8

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

^{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
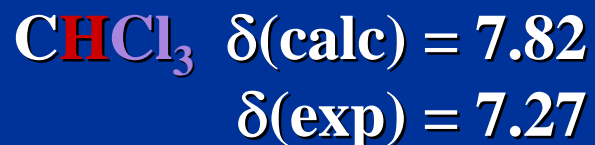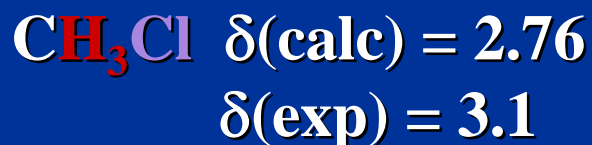
Table 4.3 Substituent constants, $S(\delta)$, for proton resonances in substituted methanes
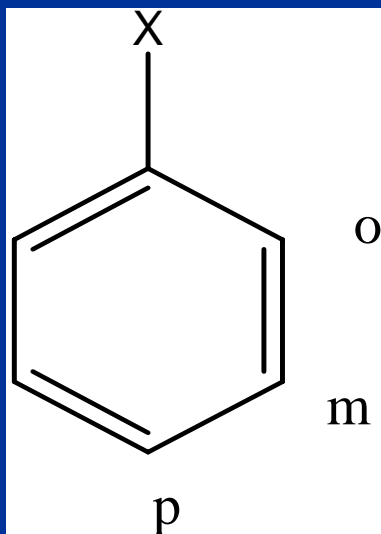
Substituent	$S(\delta)$ (ppm)
Cl	2.53
Br	2.33
I	1.82
NRR′	1.57
OR	2.36
SR	1.64
CR=O	1.70
CR=CR′R′	1.32
C≡CH	1.44
C≡N	1.70
CH$_3$	0.47
Phenyl	1.85
OH	2.56
OCOR	3.13
COOR	1.55
CF$_3$	1.14

^{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_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
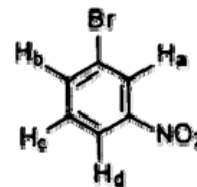
$\delta(H_a) = 7.27 + 0.22 + 0.95 = 8.44$

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

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

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

^{1}H NMR Chemical Shift Increments

Olefinic compounds

Ethylene

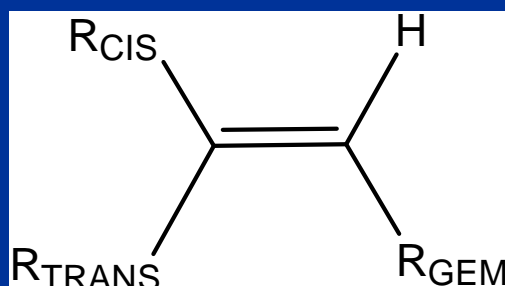$\delta(^1H) = 5.28$ ppm

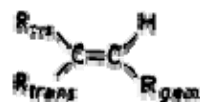$\delta = 5.28 + \Sigma\, S_i\,(\delta)$

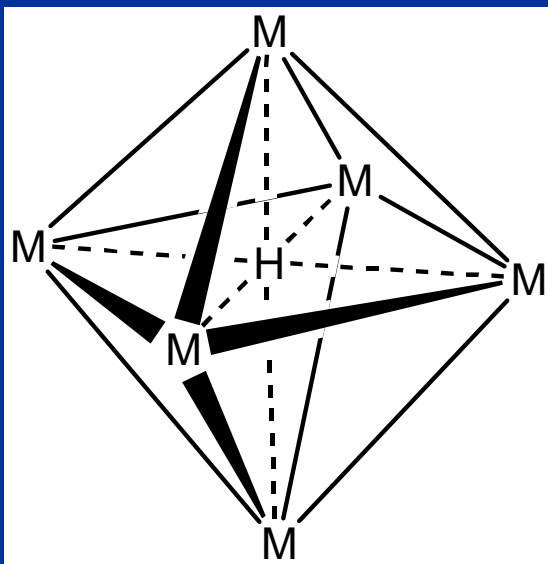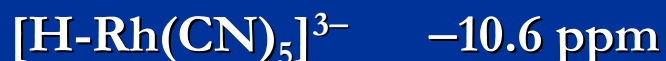**Table 4.7** $S(\delta)$ values for substituted ethylenes (after Ref. 10)

Substituent R*	S(δ)(ppm)			Substituent R*	S(δ)(ppm)		
	gem	cis	trans		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 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				
—COOR (conj.)	0.68	1.02	0.33	—N (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.
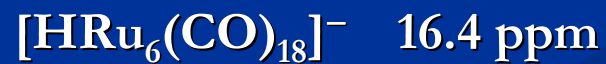
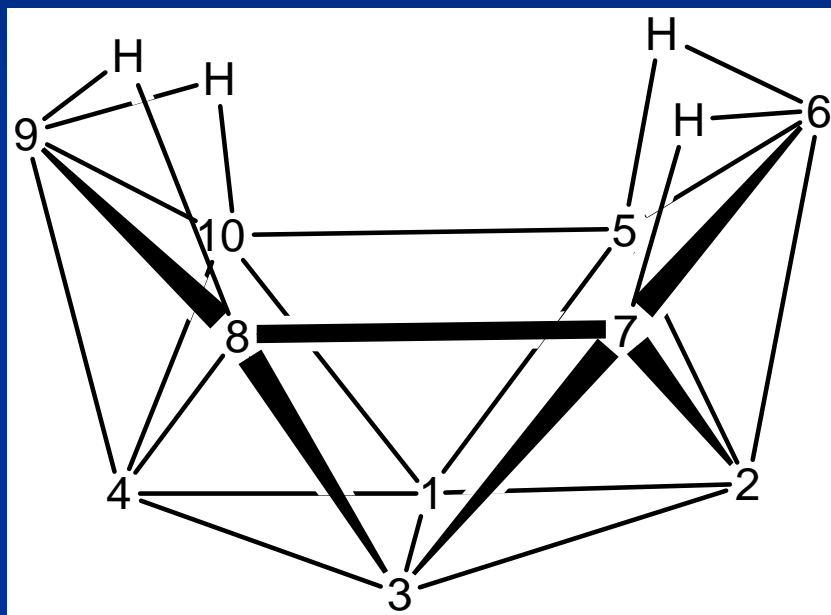# Regions of Inorganic Proton Shifts

Organometallic hydrides

Highly shielded   −5 to −60 ppm

$[H\text{-}Rh(CN)_5]^{3-}$ −10.6 ppm

Highly deshielded

$[HRu_6(CO)_{18}]^-$ 16.4 ppm
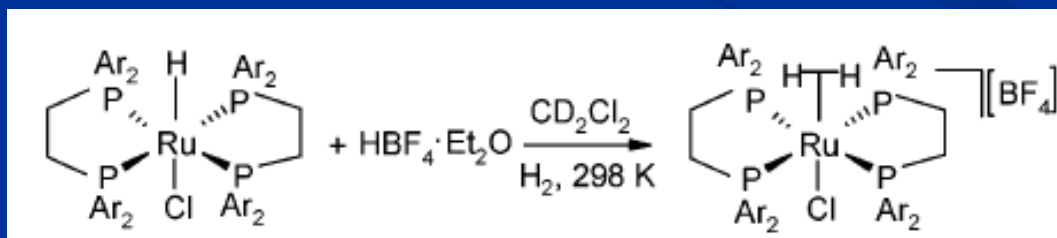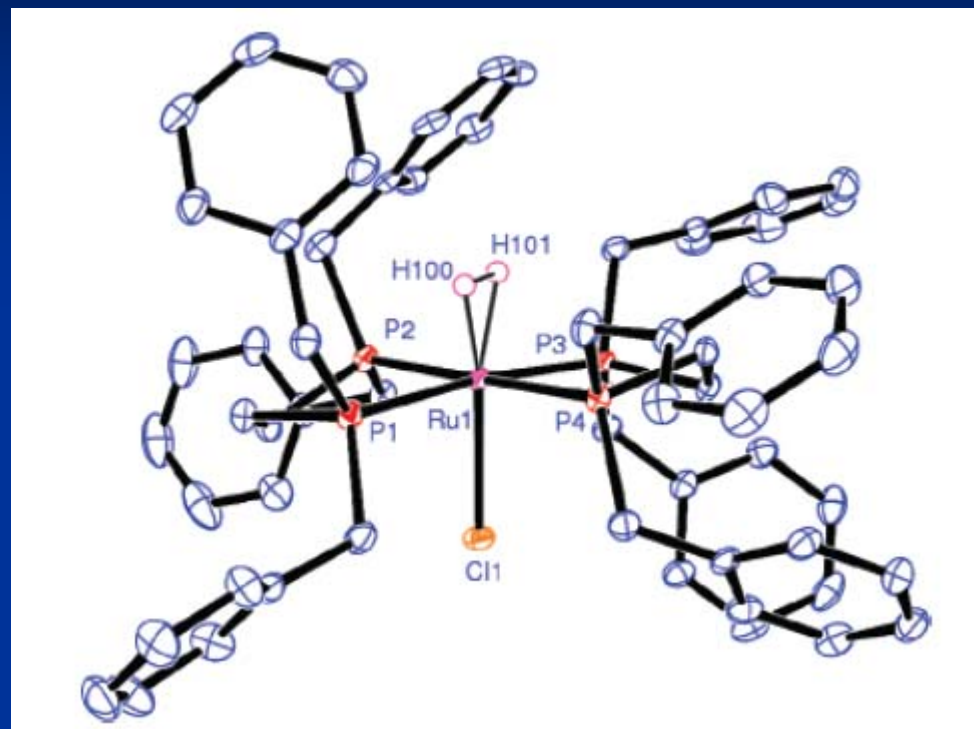
$[HCo_6(CO)_{15}]^-$ 23.2 ppm

6

^{1}H NMR of Boranes

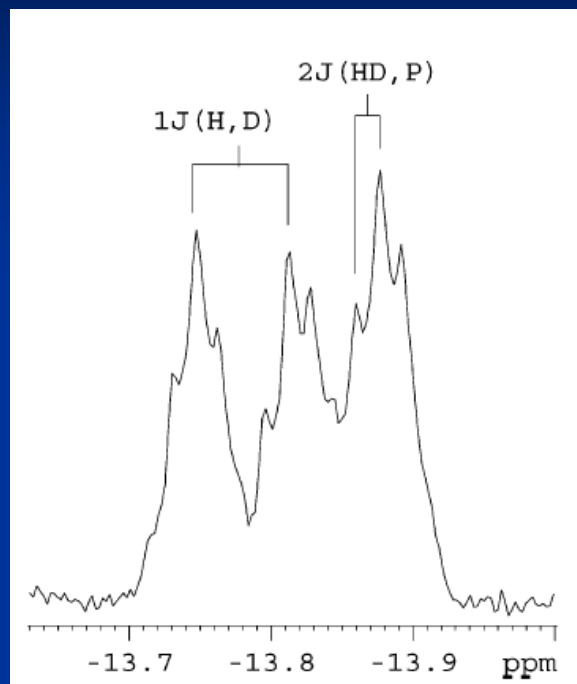*nido*-Decaborane(14)

bridging B_2H −2.12 ppm

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

¹H NMR Organometallic Hydrides
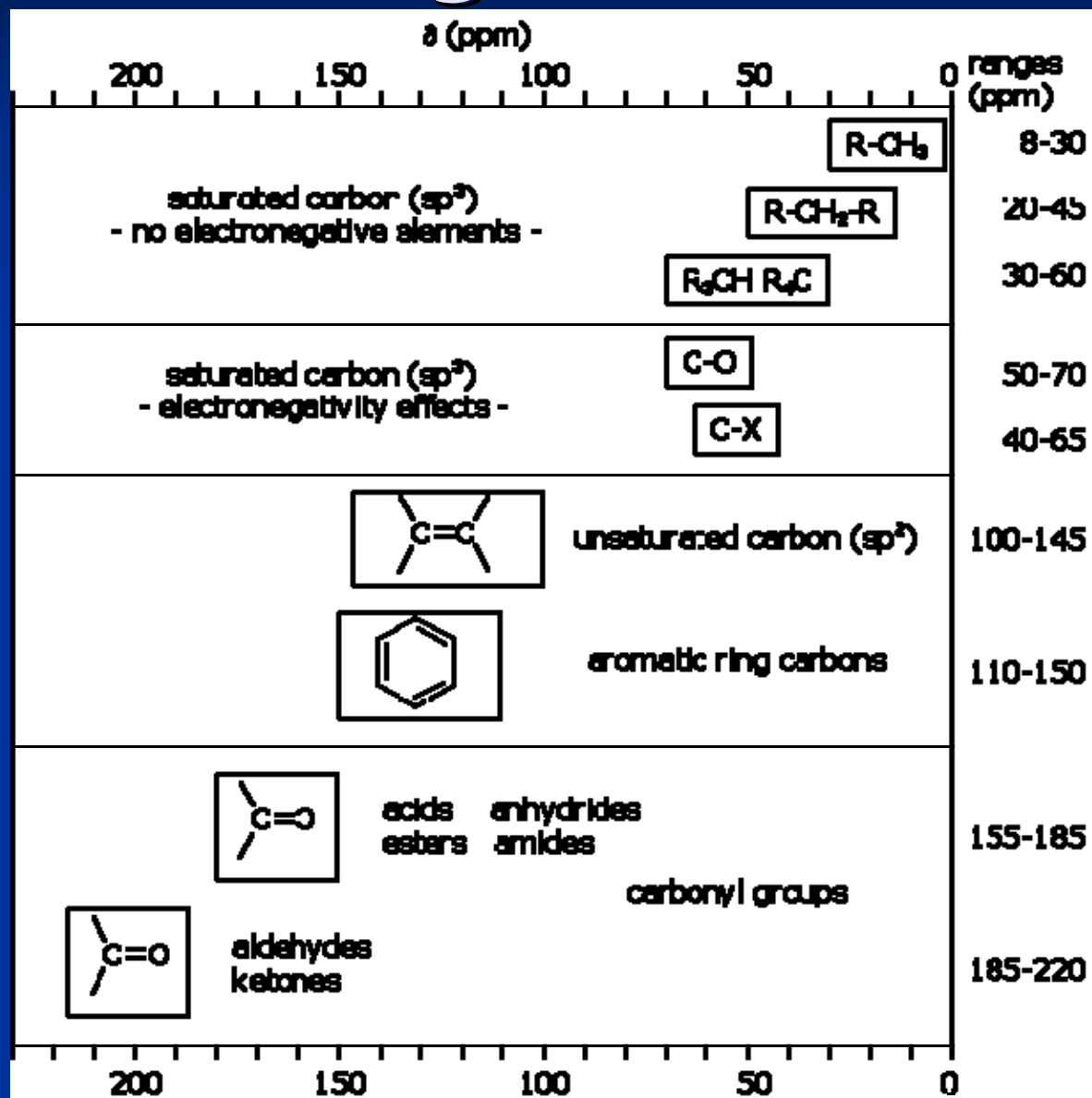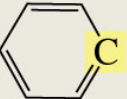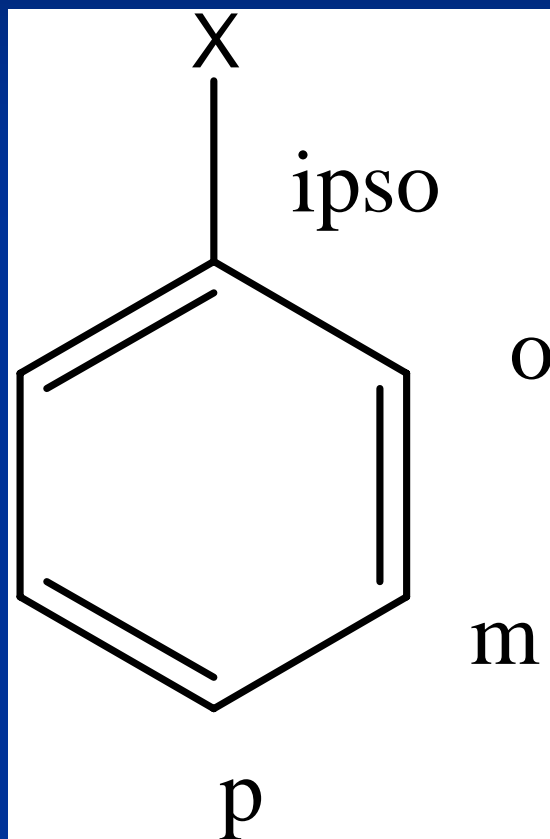
Regions of Organic Carbon Shifts

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)	20–60	R, C=O, —N (amide)	165–175
R—C—R (with R, R)	30–40	R, C=O, RO (ester)	165–175
≡C	65–85	R, C=O, HO (acid)	175–185
=C	100–150	R, C=O, H (aldehyde)	190–200
benzene C	110–170	R, C=O, R (ketone)	205–220

^{13}C NMR Chemical Shift Increments
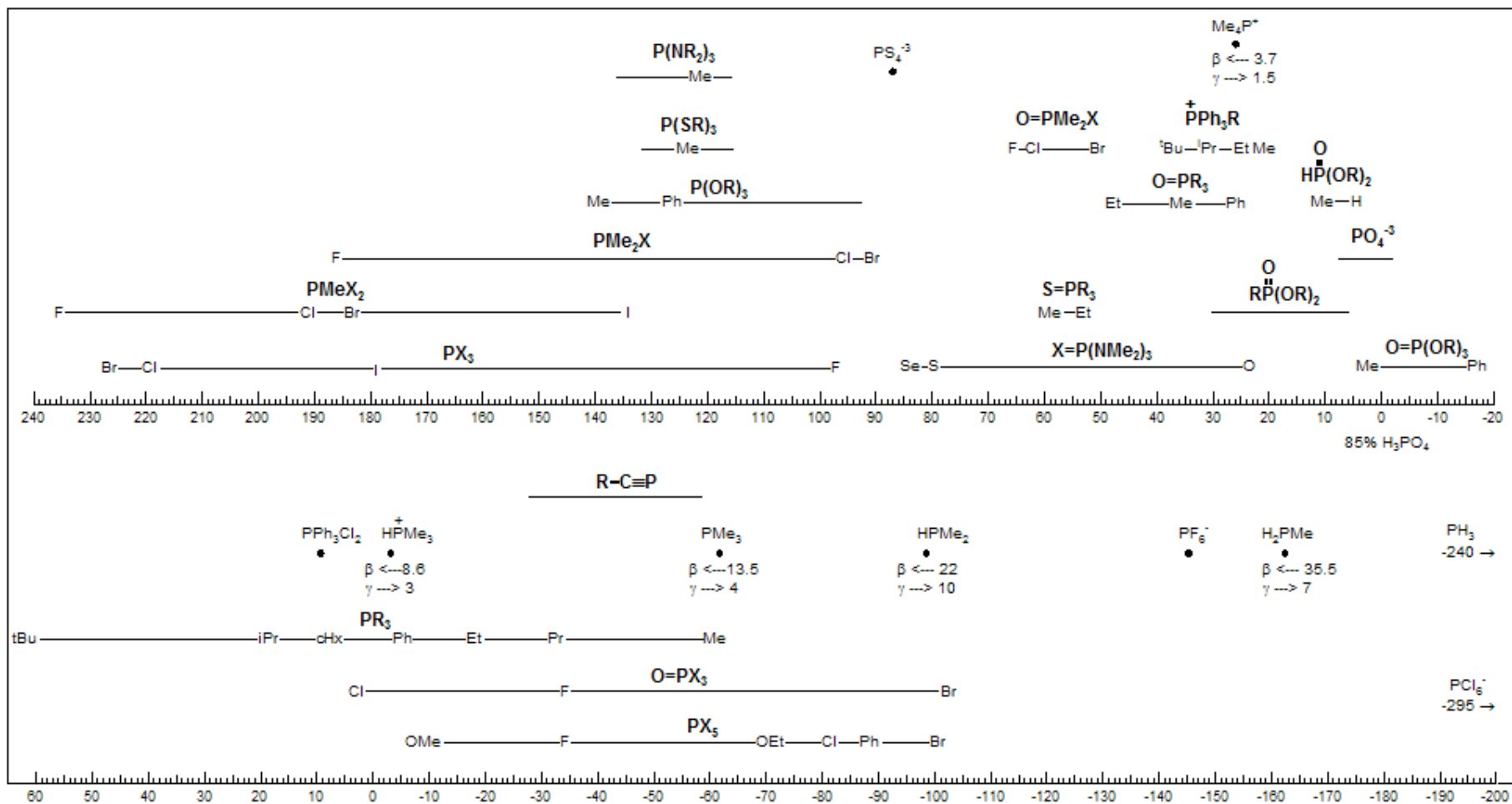

$\delta(^{13}C) = 128.5$ ppm

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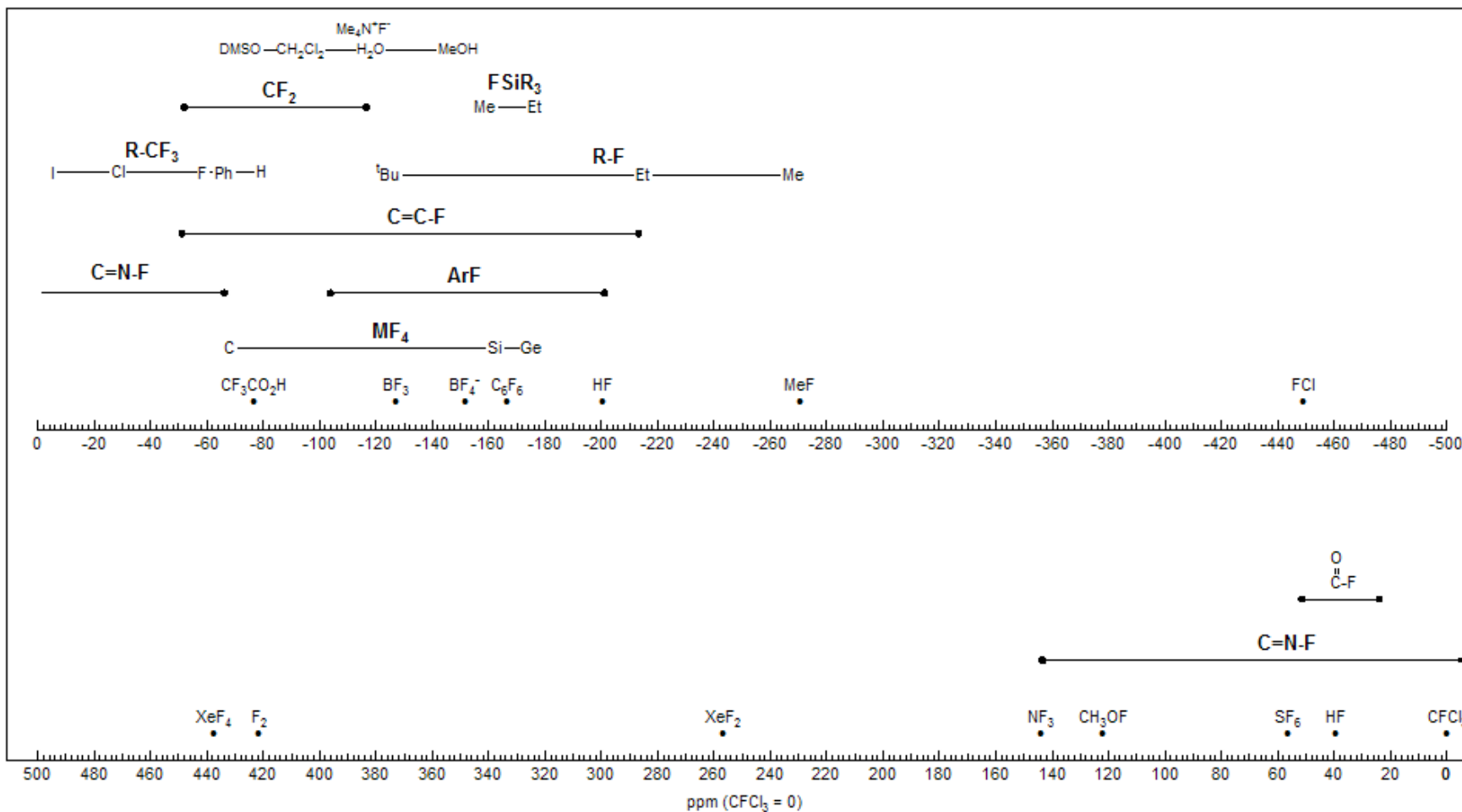for each carbon (ipso, o, m, p)

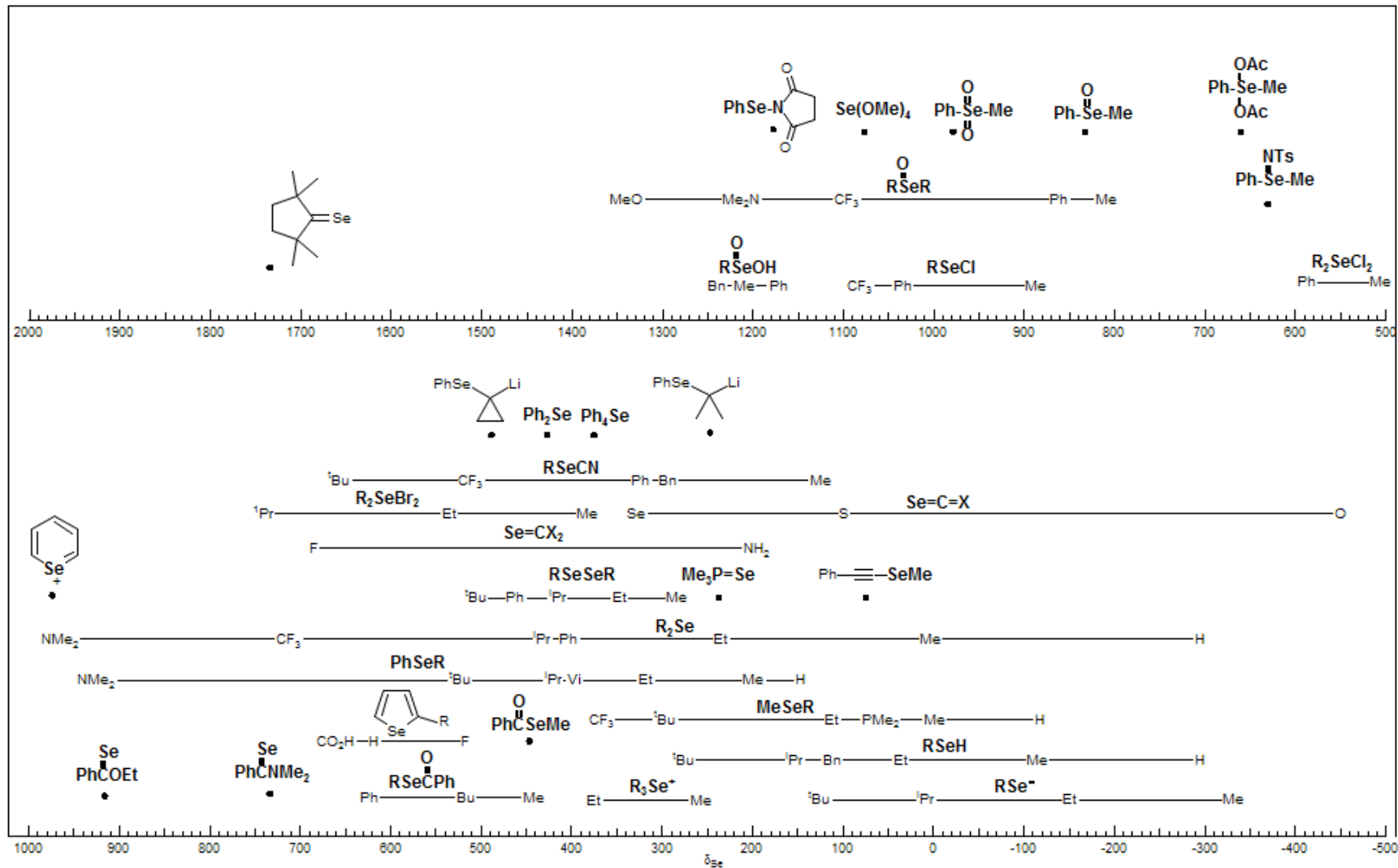# Regions of ^{31}P NMR Shifts

- Phosphorus Shifts Overview

Regions of ^{19}F NMR Shifts

- Fluorine Shifts Overview

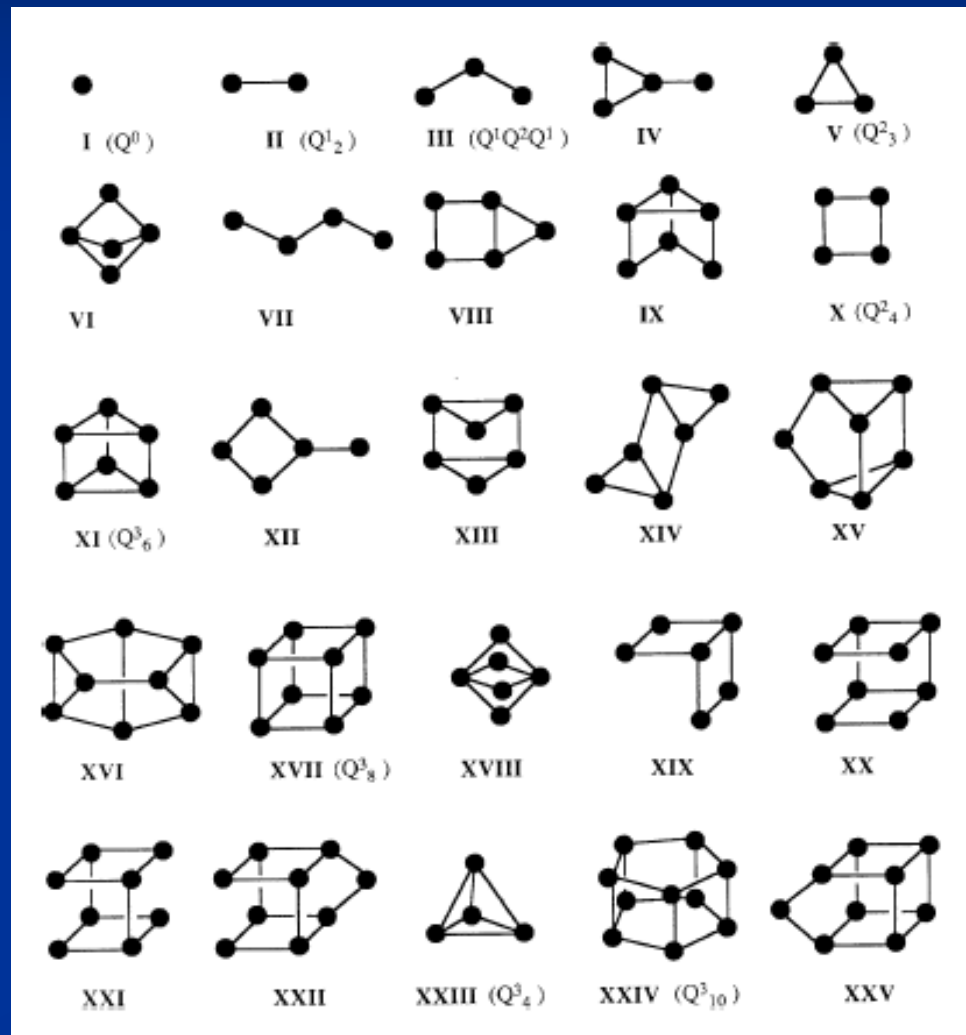# Regions of ^{77}Se NMR Shifts
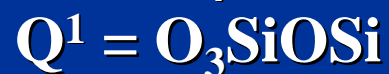

- Selenium Shifts Overview

Regions of ^{29}Si NMR Shifts

^{29}Si NMR chemical shift ranges for various silyl groups
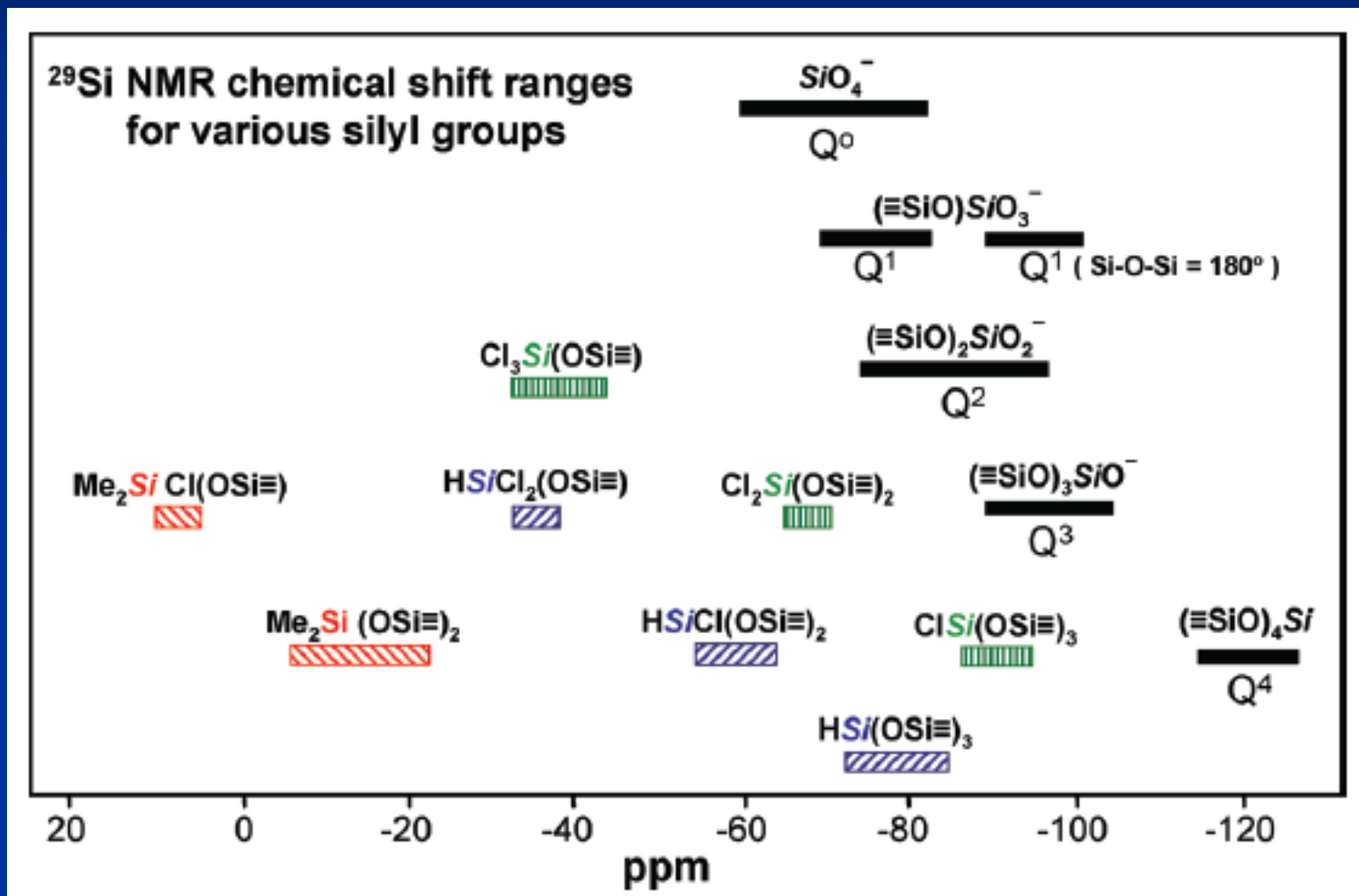
Silicate Anions in Aqueous Alkaline Media Detected by ^{29}Si-NMR

$M = OSiR_3$

$D = O_2SiR_2$

$T = O_3SiR$

$Q = O_4Si$

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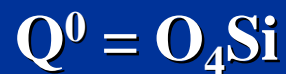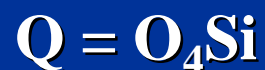
Regions of ^{17}O MAS NMR
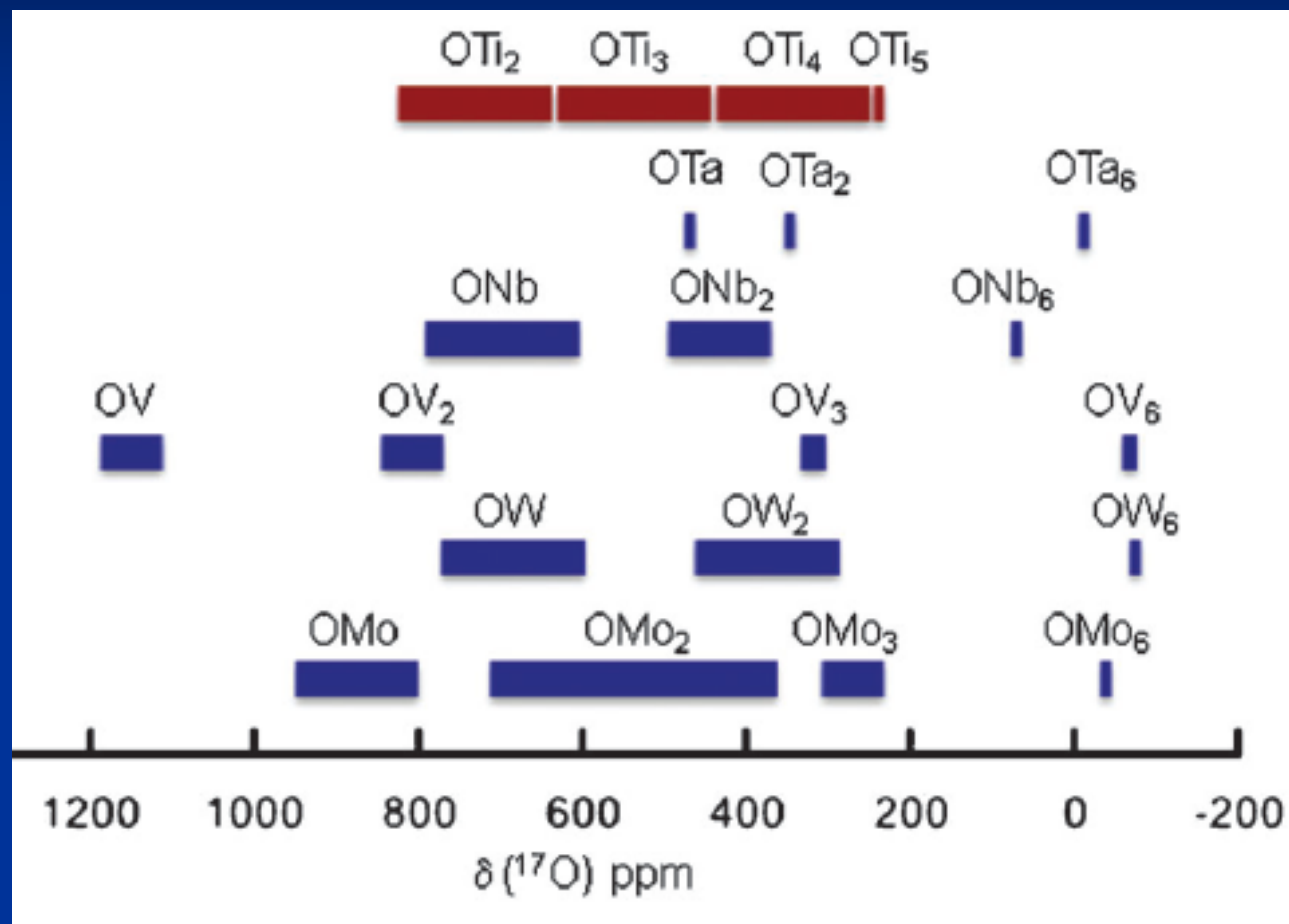
Octahedral Metal Clusters

Halogen or chalcogen

Cr, Mo or W

Six axial ligands (L) coordinate to the metal atoms
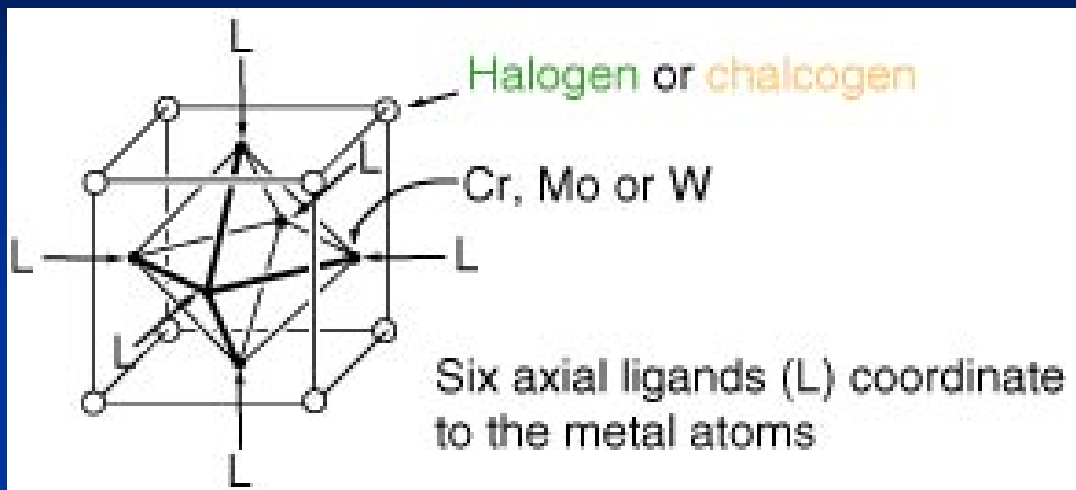
How many derivatives and isomers for

2 different L

?????????????
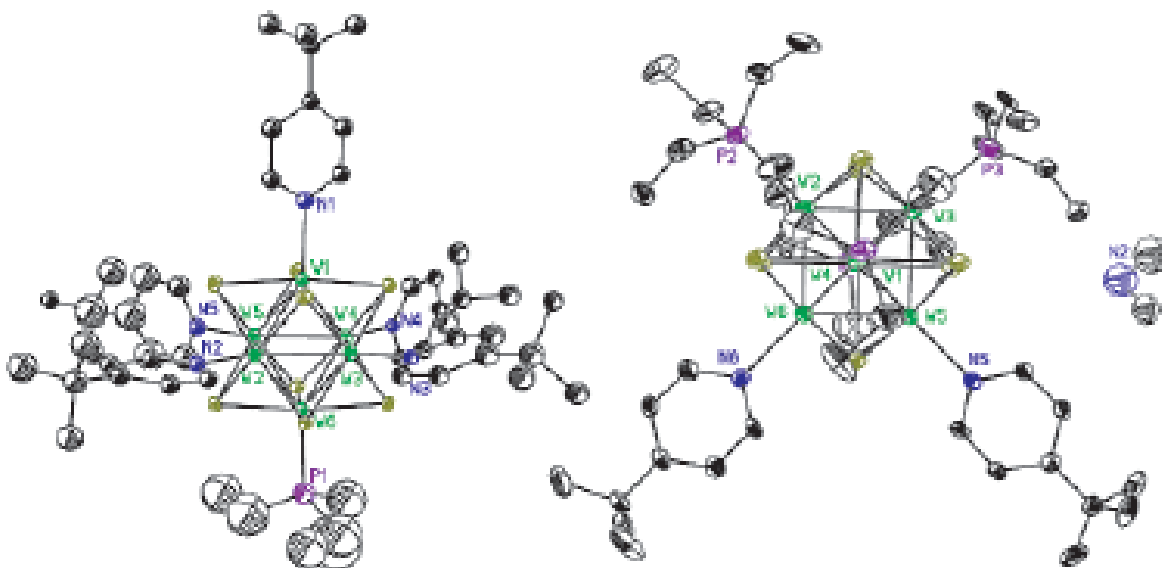
W_6S_8(4-tbp)$_5$(PEt$_3$)

cis-W_6S_8(4-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 ???

$W_6S_8(P^nBu_3)_6$

$W_6S_8(MeNH_2)_6$

$W_6S_8(PPh_3)_6$

$W_6S_8(morpholine)_6$

$W_6S_8(tBuNC)_6$

$W_6S_8(t\text{-}butylamine)_6$
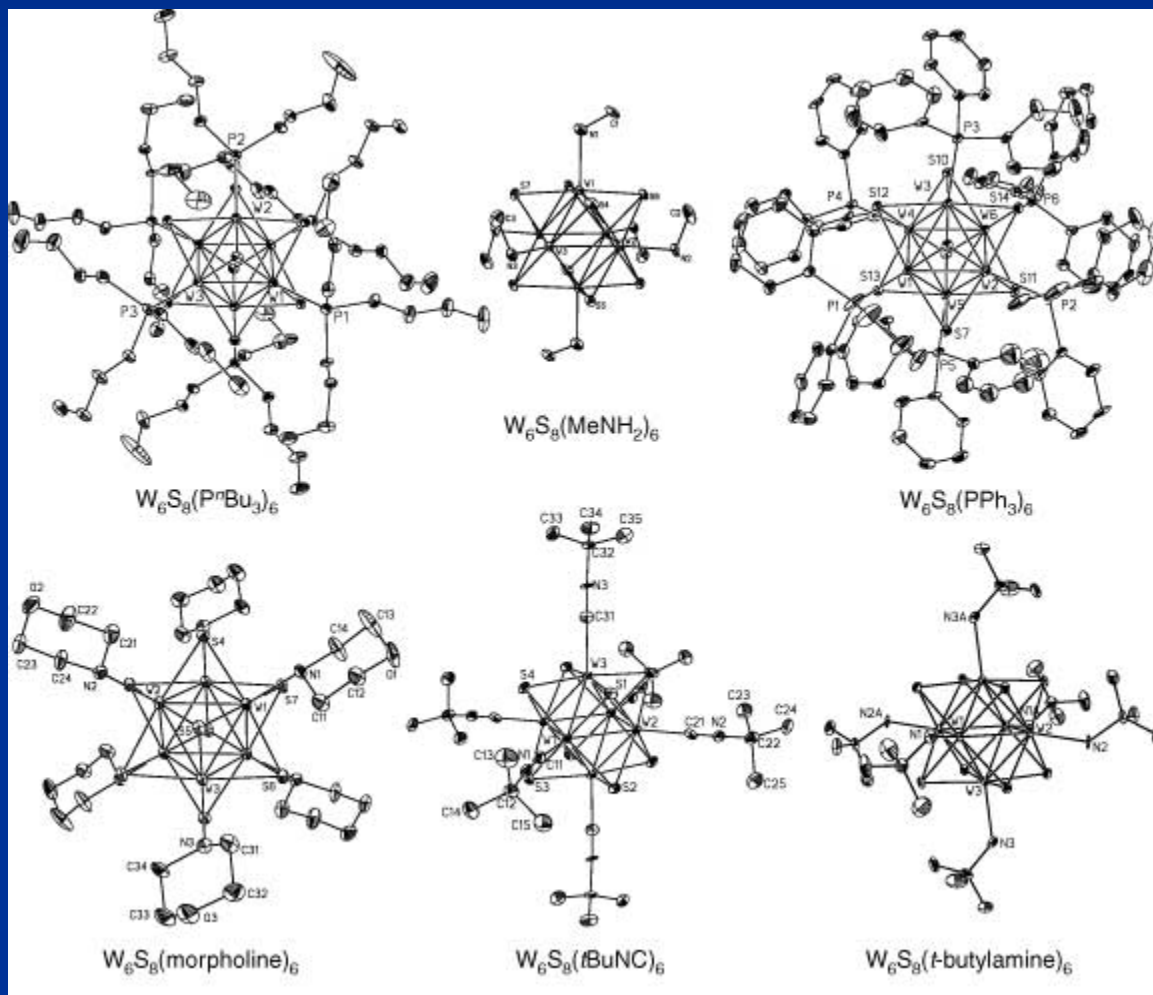
NMR Identification of the Clusters

Series of 200 complexes

(A)

-8 -9 -10 -11 -12 -13 -14 -15 -16 ppm
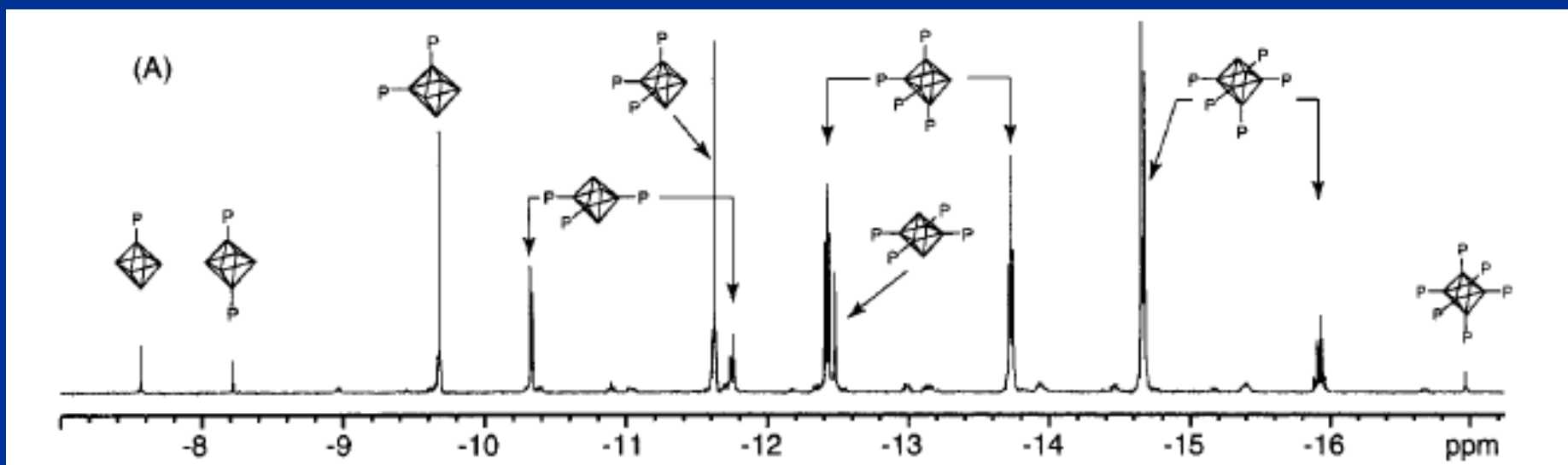
12 Signals in ^{31}P NMR

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

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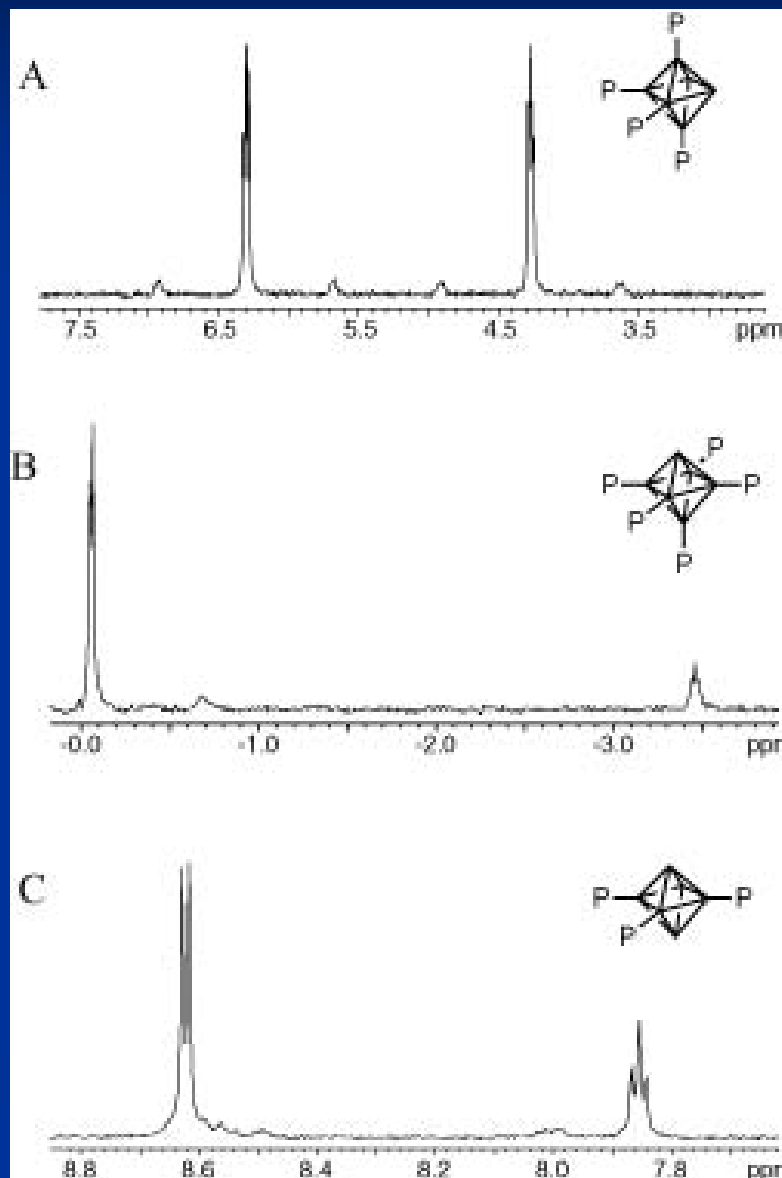
^{183}W (I=1/2)
the satellite peaks
flanking the main P
peaks

NMR Identification of the Clusters

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

Dean-Evans relation

a two-parameter linear relation

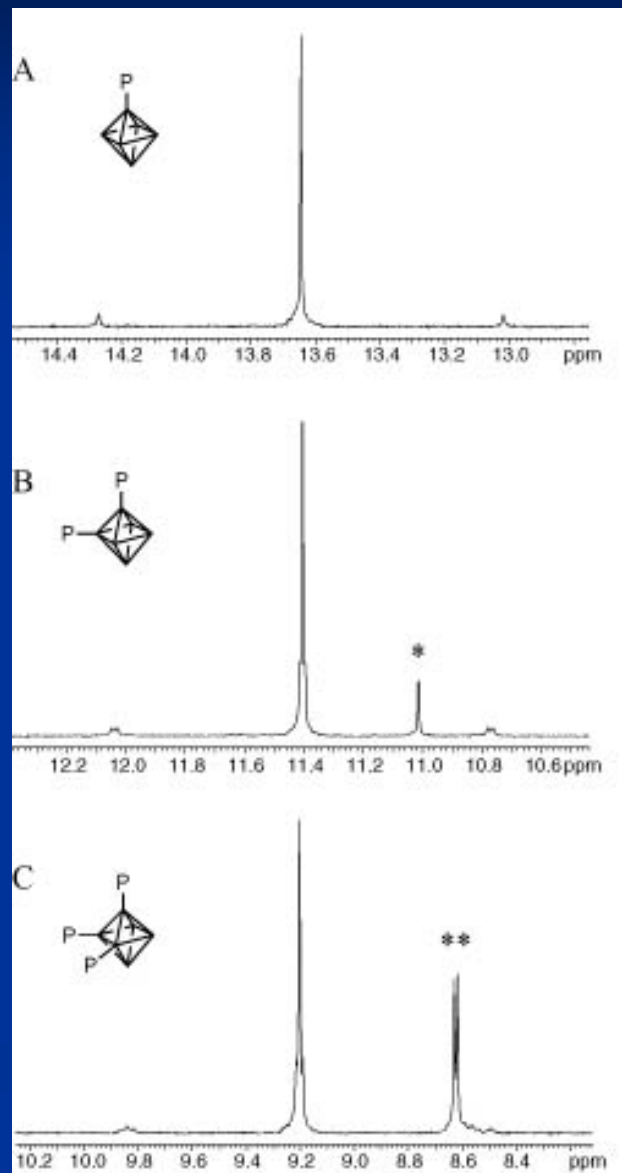Dean-Evans Relation of $\delta(^{31}P)$ for $W_6S_8(PEt_3)_n(tbp)_{6-n}$ Cluster Complexes

n (number of phosphine ligands)

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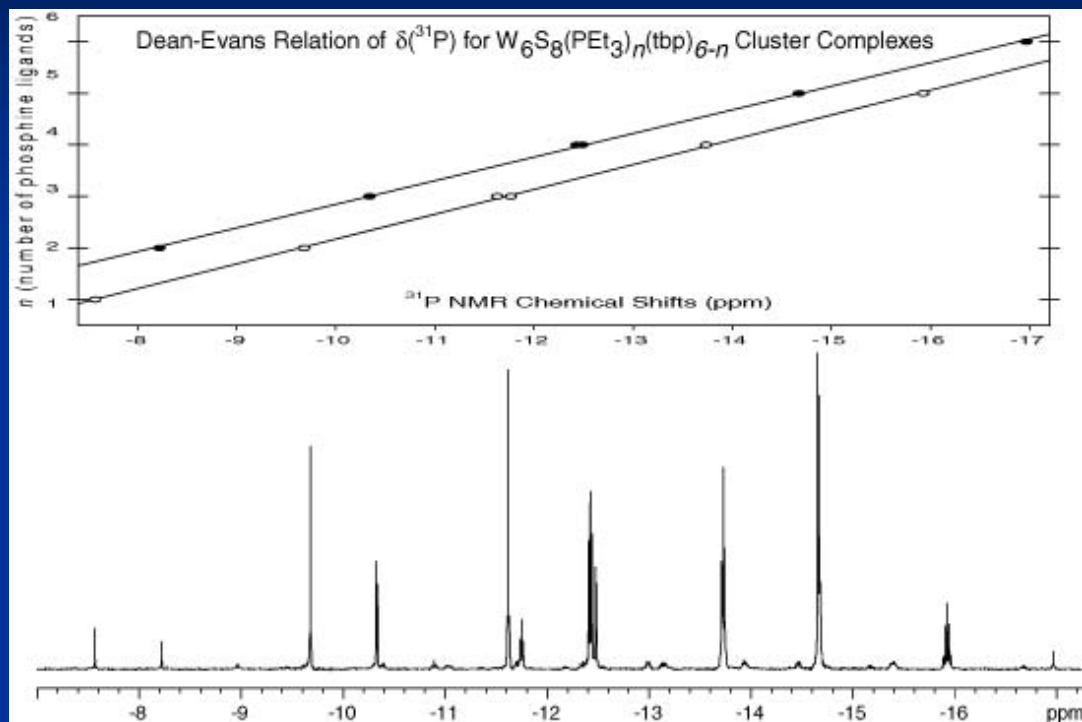
Dean-Evans Relation in $\delta(^{31}P)$ of $W_6S_8L_{6-n}(PR_3)_n$ Cluster Complexes

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

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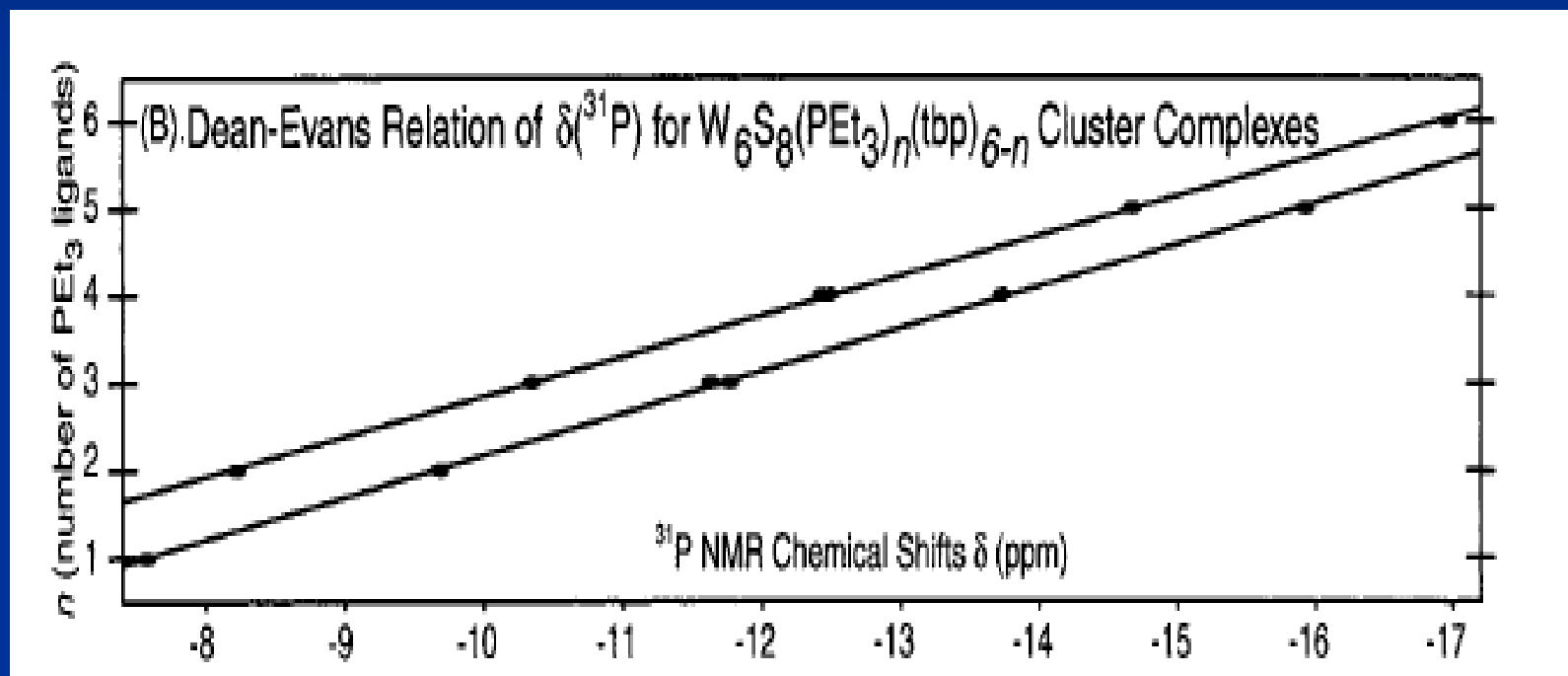
$$\delta(^{31}P) = \delta_{ref} + pC + qT$$

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)

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