Metal Carbonyls Lecture 3 462
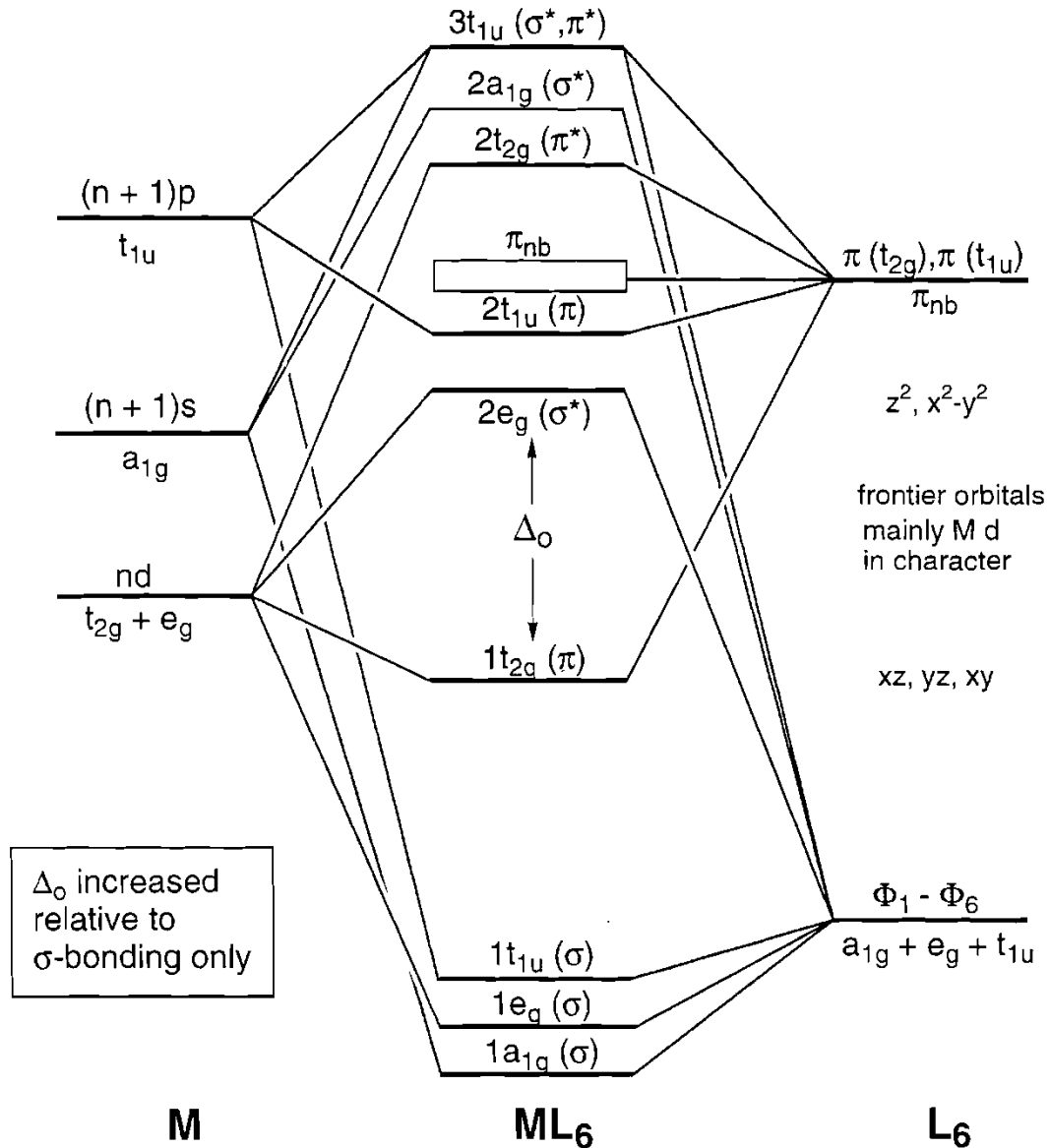
Actors and Spectators

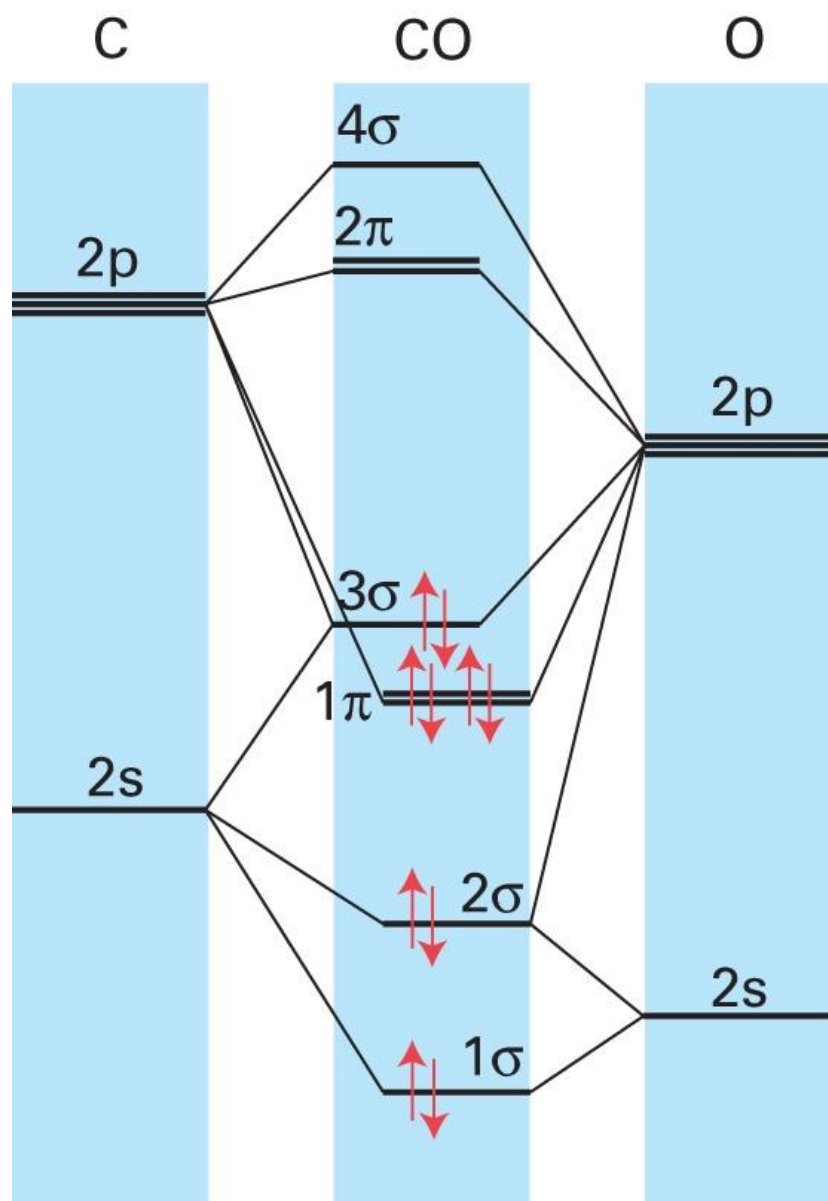Non-innocent ligands

Redox active ligands

Case 2. Lπ orbitals vacant and less stable than dπ orbitals
(L is a π-acceptor)

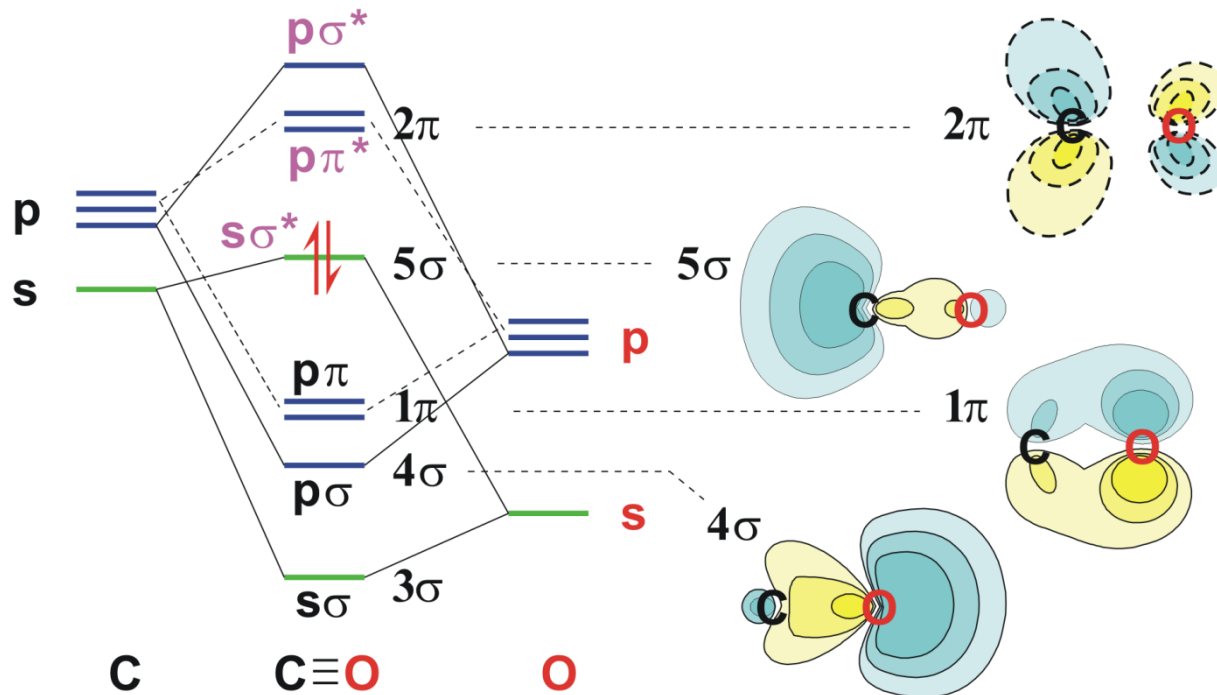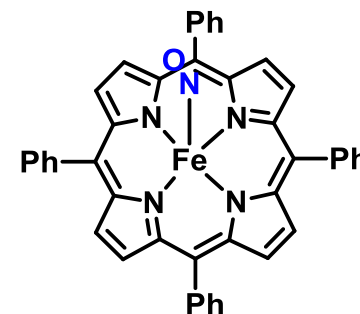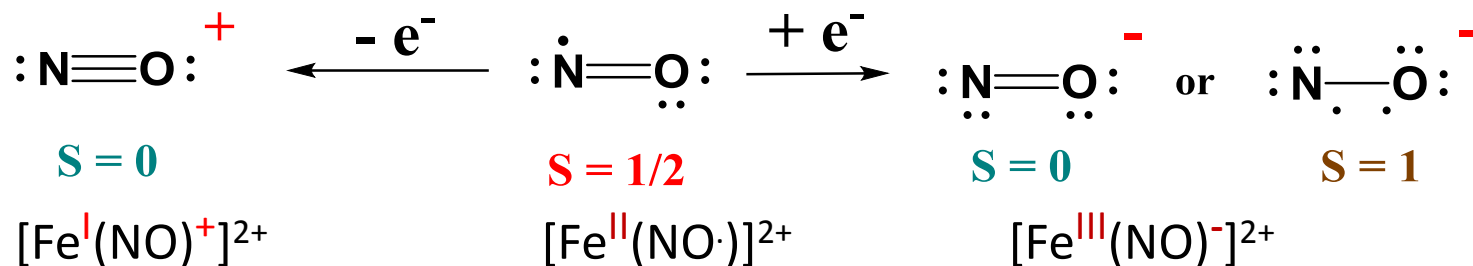## A more accurate MO energy level diagram for $Cr(CO)_6$.

$3t_{1u}$ (σ^*, π^*)

$2a_{1g}$ (σ^*)

$2t_{2g}$ (π^*)

π_{nb}

$2t_{1u}$ (π)

$2e_g$ (σ^*)

Δ_o

$1t_{2g}$ (π)

$1t_{1u}$ (σ)

$1e_g$ (σ)

$1a_{1g}$ (σ)

$(n + 1)p$

t_{1u}

$(n + 1)s$

a_{1g}

nd

$t_{2g} + e_g$

π (t_{2g}), π (t_{1u})

π_{nb}

z^2, x^2-y^2

frontier orbitals
mainly M d
in character

xz, yz, xy

Φ_1 - Φ_6

$a_{1g} + e_g + t_{1u}$

Δ_o increased
relative to
σ-bonding only

M

ML$_6$

L$_6$

prime example

CO

Carbon Monoxide or Carbonyl:
HOMO (5σ) and LUMO (2π)

Non-Innocent Ligands: Paradigm: NO and Dioxygen

$:N{\equiv}O:^{+}$ $\xleftarrow{-\ e^{-}}$ $:\dot{N}{=}\ddot{O}:$ $\xrightarrow{+\ e^{-}}$ $:\ddot{N}{=}\ddot{O}:^{-}$ or $:\ddot{N}{-}\ddot{O}:^{-}$

S = 0　　　　　　　S = 1/2　　　　　　S = 0　　　　　S = 1

$[Fe^{I}(NO)^{+}]^{2+}$　　　$[Fe^{II}(NO\cdot)]^{2+}$　　　$[Fe^{III}(NO)^{-}]^{2+}$

Enemark-Feltham Notation

$\{M(NO)_{x}\}^{n}$　n = # metal d electrons + # electrons in NO π^{*}

$\{Fe^{I}(NO)^{+}\}^{7}$　　　$\{Fe^{II}(NO\cdot)\}^{7}$　　　$\{Fe^{III}(NO)^{-}\}^{7}$

	$N{\equiv}O\cdot$	$\underset{Mn}{\overset{O}{\underset{\|}{\|\|\|}N}}$	$\underset{Fe}{\overset{O}{\underset{\|}{N^{140}}}}$	$\underset{Co}{\overset{O}{\underset{\|}{N^{120}}}}$
$v(N{-}O)$:	$1860\ cm^{-1}$	$1740\ cm^{-1}$	$1625\ cm^{-1}$	$1689\ cm^{-1}$

O$_2$: the most famous actor/non-innocent ligand of all
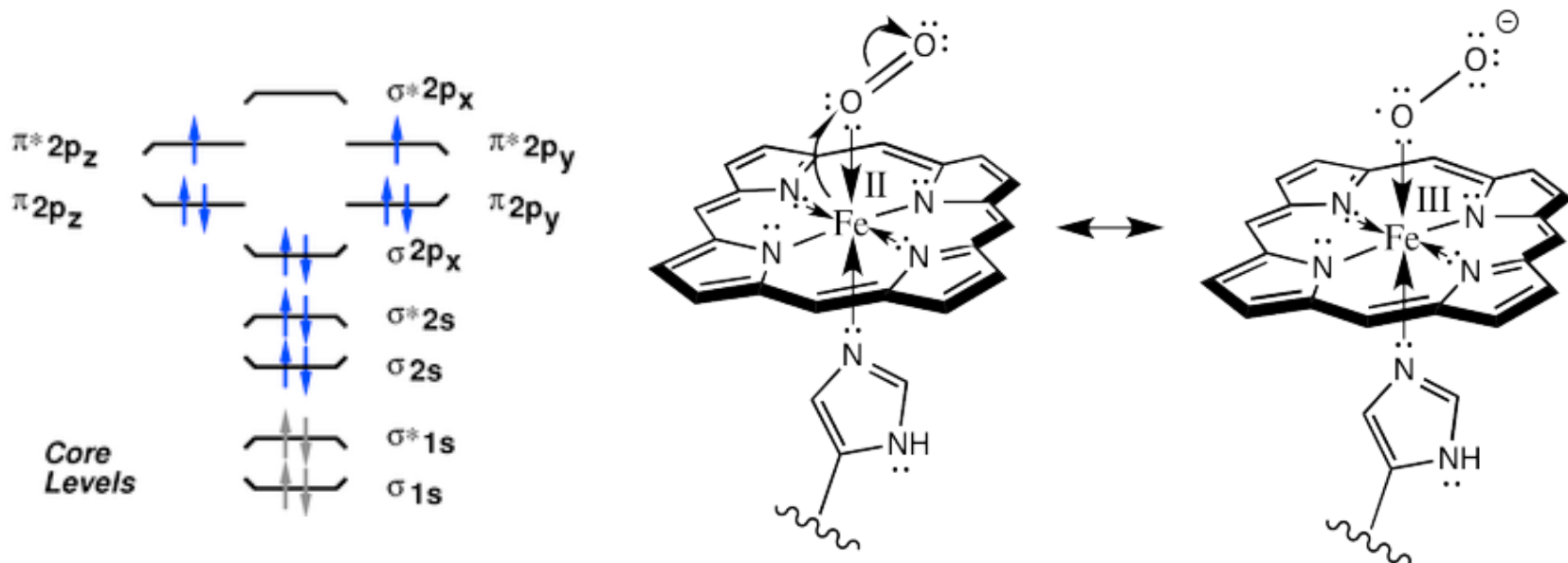
Dithiolenes
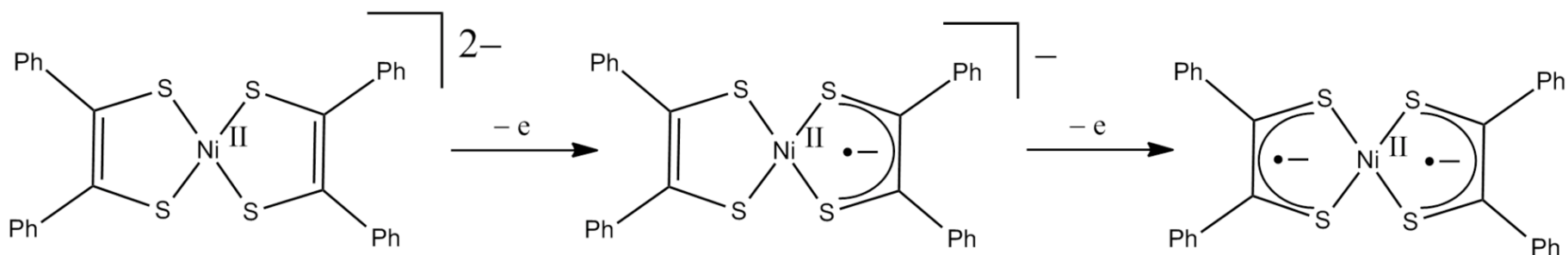
$E = hc/\lambda$

Hooke's Law

Energy is absorbed in molecular vibrations.

$$\frac{1}{\lambda} = \bar{v} = k\sqrt{f\frac{(m_1 + m_2)}{m_1 m_2}}$$

$\frac{1}{\lambda} = \bar{v}$ = vibrational frequency

f = force constant

m_1 = mass of atom 1

m_2 = mass of atom 2

Calculating stretching frequencies

Hooke's law :

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$: Frequency in cm^{-1}

c   : Velocity of light => $3 * 10^{10}$ cm/s

K   : Force constant => dynes /cm

μ : masses of atoms in grams

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{M_1 M_2}{M_1 + M_2 (6.02 * 10^{23})}$$
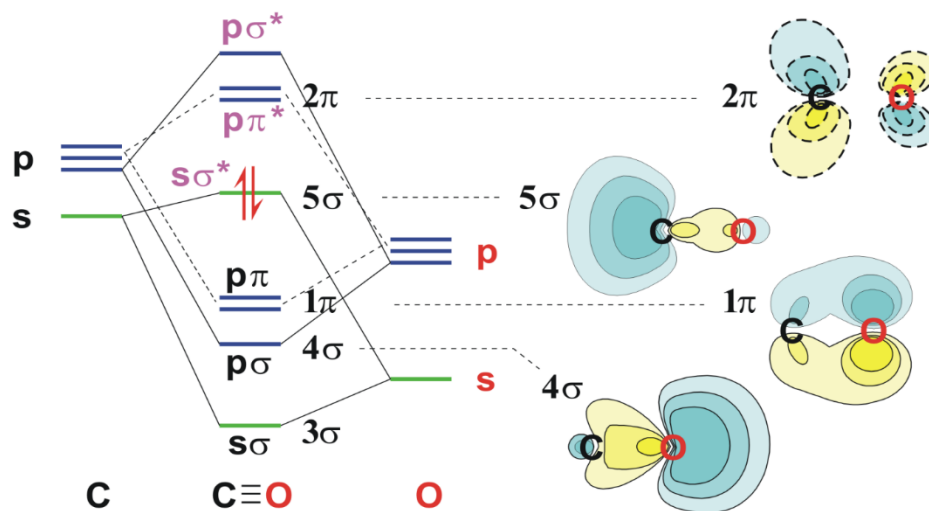
$$\bar{\nu} = 4.12 \sqrt{\frac{K}{\mu}}$$

C—C	$K = 5 * 10^5$ dynes/cm
C=C	$K = 10 * 10^5$ dynes/cm
C≡C	$K = 15 * 10^5$ dynes/cm

How do we know?


Experimental Data Supporting Nature of MO's in CO

Species	Config	C-O Å	ν_{CO} cm^{-1}	Comment
CO	$(5\sigma)^2$	1.13	2143	
CO$^+$	$(5\sigma)^1$	1.11	2184	5σ MO is weakly antibonding
CO*	$(5\sigma)^1(2\pi)^1$	S 1.24	1489	2π MO is strongly antibonding
		T 1.21	1715	

Metal Carbonyls Report on Electron Density at Metal by CO Stretching "frequencies" (actually wavenumber, $E \propto 1/\lambda$)
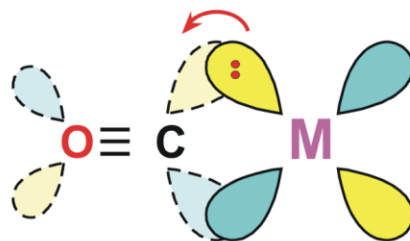
Complex	$\nu(CO)$, cm^{-1}
$[V(CO)_6]^-$	1858
$[Cr(CO)_6]$	2000
$[Mn(CO)_6]^+$	2095
(Free CO	2143

Complex	$\nu(CO)$, cm^{-1}
$[W(CO)_6]$	1977
$[Re(CO)_6]^+$	2085
$[Os(CO)_6]^{2+}$	2190
$[Ir(CO)_6]^{3+}$	2254

The M-C bond in Metal Carbonyls
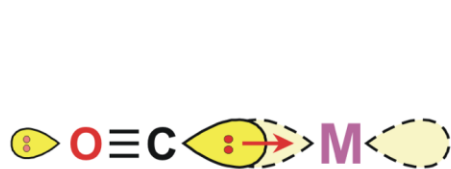
|	CO-M sigma bond	M to CO pi backbonding	CO to M pi bonding (rare)
M-C bond:	increases	increases	increases
C-O bond:	increases	decreases	decreases
ν_{CO} freq:	increases	decreases	decreases
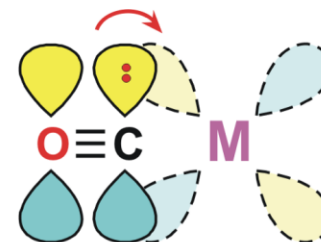
Carbonyl IR Stretching Frequencies

- The **position** of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being π-backbonded to the CO.

- The **number** (and intensity) of the carbonyl bands one observes depends on the number of CO ligands present and the symmetry of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.

Metal Carbonyls are "Reporter Ligands"

Classifying Ligand Properties: Chad Tolman
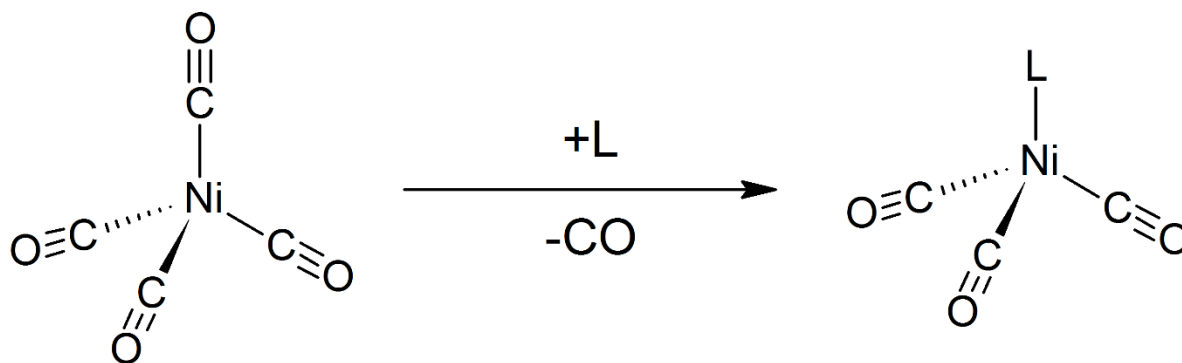
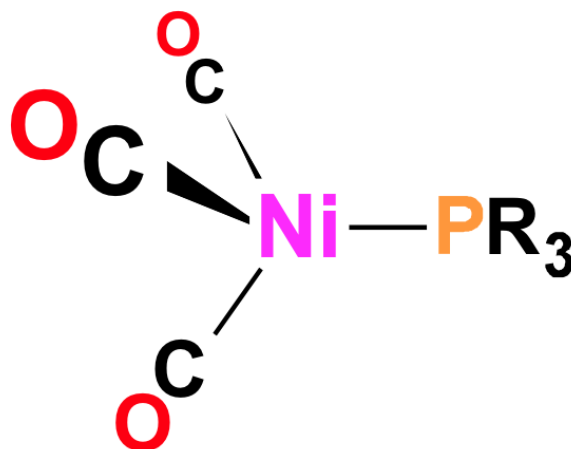Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis

Tolman Electronic Parameter for Ligand Donor Ability

Lowest CO stretching frequency:
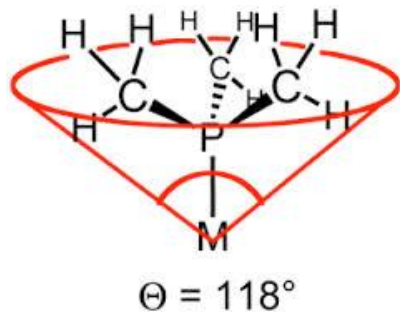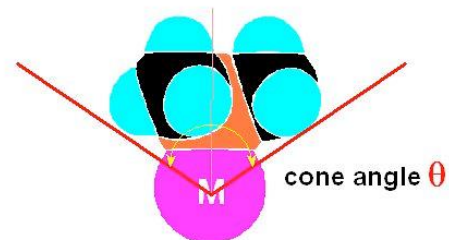
most donating phosphine

Highest CO stretching frequency:

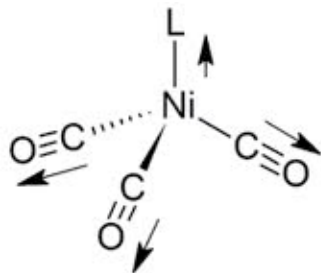*least donating phosphine*

(best π-acceptor)

Tolman cone angle

Θ = 118°

- PH$_3$ 87°
- PF$_3$ 104°
- PMe$_3$ 118°
- **PPh$_3$**   **145°**
- P(*i*-Pr)$_3$ 160°
- PCy$_3$ 170°
- P(O-*t*-Bu)$_3$ 175°
- P(*t*-Bu)$_3$ 182°
- P(*o*-Tol)$_3$ 194°

cone angle θ

49

Tolman Electronic Parameter

TEP for selected phosphines

L	v(CO) cm^{-1}
P(t-Bu)$_3$	2056.1
PMe$_3$	2064.1
PPh$_3$	2068.9
P(OEt)$_3$	2076.3
PCl$_3$	2097.0
PF$_3$	2110.8

Commonly Used Polydentate Phosphines:

Ph₂P ——— **PPh₂**
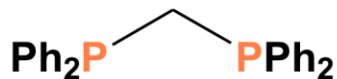
dppm (121°)
diphenylphosphinomethane
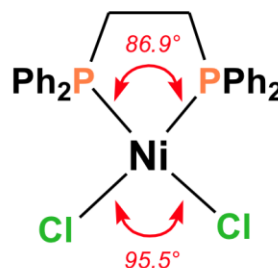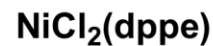bis(diphenyl)phosphinomethane
bridging ligand
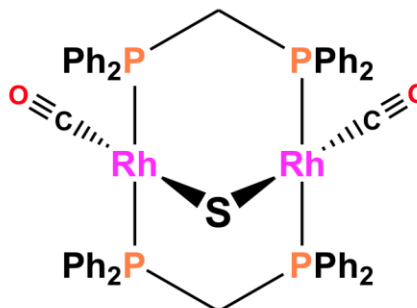
A-Frame bimetallic

Rh₂(μ-S)(CO)₂(dppm)₂

Kubiak & Eisenberg
JACS, **1977,** *99,* 6129

Ph₂P, O≡C, Rh, S, Rh, C≡O, PPh₂, Ph₂P, PPh₂

Ph₂P ——— **PPh₂**
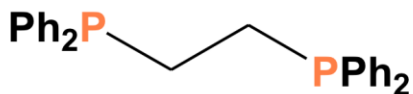
dppe (125°)
diphenylphosphinoethane
bis(diphenyl)phosphinoethane
chelating ligand

86.9°
Ph₂P, PPh₂
Ni
Cl, Cl
95.5°

typical P-M-P angle for a 5-membered chelate ring 82-87°

NiCl₂(dppe)

van Koten, et al
Acta Crys. C, **1987,** *43,* 1878

Me₂P ——— **PMe₂**
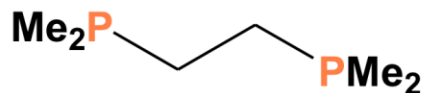
dmpe (107°)
dimethylphosphinoethane
bis(dimethyl)phosphinoethane
chelating ligand
electron-rich, strong donor

Ph₂P ——— **PPh₂**
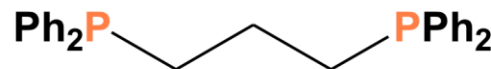
dppp (127°)
diphenylphosphinopropane
bis(diphenyl)phosphinopropane
chelating ligand
forms 6-membered rings

typical P-M-P angle for a 6-membered chelate ring 88-92°

All geometries are seen for Metal Carbonyls

Octahedral : $M(CO)_6$

Trigonal Bipyramidal : $Fe(CO)_5$

Square planar Don't know of any

Tetrahedral $Ni(CO)_4$

Trigonal planar

Linear $Cu^I(CO)_2{}^+$, $Ag^I(CO)_2{}^+$

Homoleptic (binary) Metal Carbonyls of 1st Row Transition Metals

Table 22.5 Formulas and electron count for some 3d-series carbonyls

Group	formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr	6	
		6(CO)	12	
		Total	18	
7	$Mn_2(CO)_{10}$	Mn	7	
		5(CO)	10	
		M–M	1	
		Total	18	
8	$Fe(CO)_5$	Fe	8	
		5(CO)	10	
		Total	18	
9	$Co_2(CO)_8$	Co	9	
		4(CO)	8	
		M–M	1	
		Total	18	
8	$Ni(CO)_4$	Ni	10	
		4(CO)	8	
		Total	18	

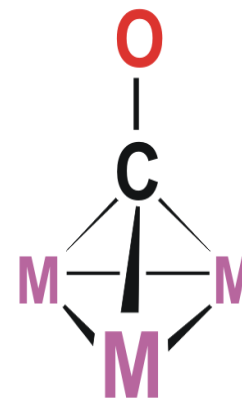## Standard Bonding Modes:

$:O\equiv C: \rightarrow M$

terminal mode

2e⁻ neutral donor
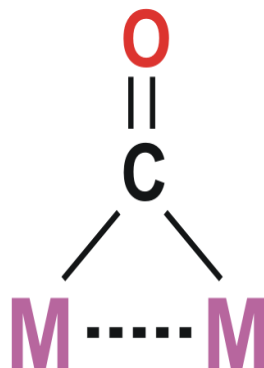
μ_2- **bridging mode**

2e⁻ neutral donor

μ_3- **bridging mode**

3e⁻ neutral donor

From Stanley, Ch. 3; VIPeR

Metal carbonyls form one of the oldest (and important) classes of organometallic complexes. Most metal carbonyls are *toxic*!

Examples of *neutral*, binary metal carbonyls:

4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	Pt	Au

Note: Early Transition Metals may form Carbonyls, but only with Anionic donors to "soften" the metals: e.g., $Cp_2Ti(CO)_2$

Physical Properties of Selected Metal Carbonyls

	Color	mp °C	Sym	IR ν_{CO} cm^{-1}	Misc
$V(CO)_6$	blue-black	70(d)	O_h	1976	paramagnetic, S = 1/2
$Cr(CO)_6$	white	subl	O_h	2000	Cr-CO = 1.91 Å, air-stable
$Mo(CO)_6$	white	subl	O_h	2004	Mo-CO = 2.06 Å, air-stable
$W(CO)_6$	white	subl	O_h	1998	W-CO = 2.06 Å, air-stable in solid state.
$Mn_2(CO)_{10}$	yellow	154	D_{4d}	2044, 2013, 1983	Mn-Mn = 2.89 Å, bond is easily broken.
$Tc_2(CO)_{10}$	white	160	D_{4d}	2065, 2017, 1984	Tc-Tc = 3.03 Å
$Re_2(CO)_{10}$	white	177	D_{4d}	2070, 2014, 1976	Re-Re = 3.04 Å
$Fe(CO)_5$	yellow	-20	D_{3h}	2034, 2013	bp = 103°C, *toxic*, Fe-CO (ax) = 1.81 Å, Fe-CO (eq) = 1.83 Å, hv produces $Fe_2(CO)_9$
$Fe_2(CO)_9$	gold plates	d	D_{3h}	2082, 2019, 1829	Fe-Fe = 2.46 Å, insoluble in most solvents except for THF where is dissociates to produce $Fe(CO)_4$ + $Fe(CO)_5$
$Fe_3(CO)_{12}$	green	d	low	complex	
$Ru(CO)_5$	colorless	-16	D_{3h}	2035, 1999	unstable, forms $Ru_3(CO)_{12}$
$Ru_3(CO)_{12}$	orange	150(d)	D_{3h}		
$Os(CO)_5$	colorless	2	D_{3h}	2034, 1991	v. unstable, forms $Os_3(CO)_{12}$
$Os_3(CO)_{12}$	yellow		D_{3h}		
$Co_2(CO)_8$	orange-red	51(d)	D_{3d}	2107, 2069, 2042, 2031, 2023, 1991	solid state structure has 2 μ-CO's (1886, 1857 cm^{-1}). Solution structure is unbridged. Co-Co = 2.54 Å in solid-state.
$Rh_4(CO)_{12}$	red		C_{3v}		3 μ-CO's around one triangular Rh_3 face.
$Ni(CO)_4$	colorless	-25	T_d	2057	bp 34°C, *highly toxic*, CO's quite labile, Ni-CO = 1.84Å

SOME FACTS   Typical stretching frequencies:

- Uncoordinated or "free" CO: 2143 cm^{-1}

- Terminal M-CO: 2125 to 1850 cm^{-1}

- Doubly bridging (μ-2): 1850 to 1750 cm^{-1}

- Triply bridging (μ-3): 1675 to 1600 cm^{-1}

- Semibridging: somewhere between terminal and μ-2.

Infrared spectra report on types of CO groups in the organometallic.
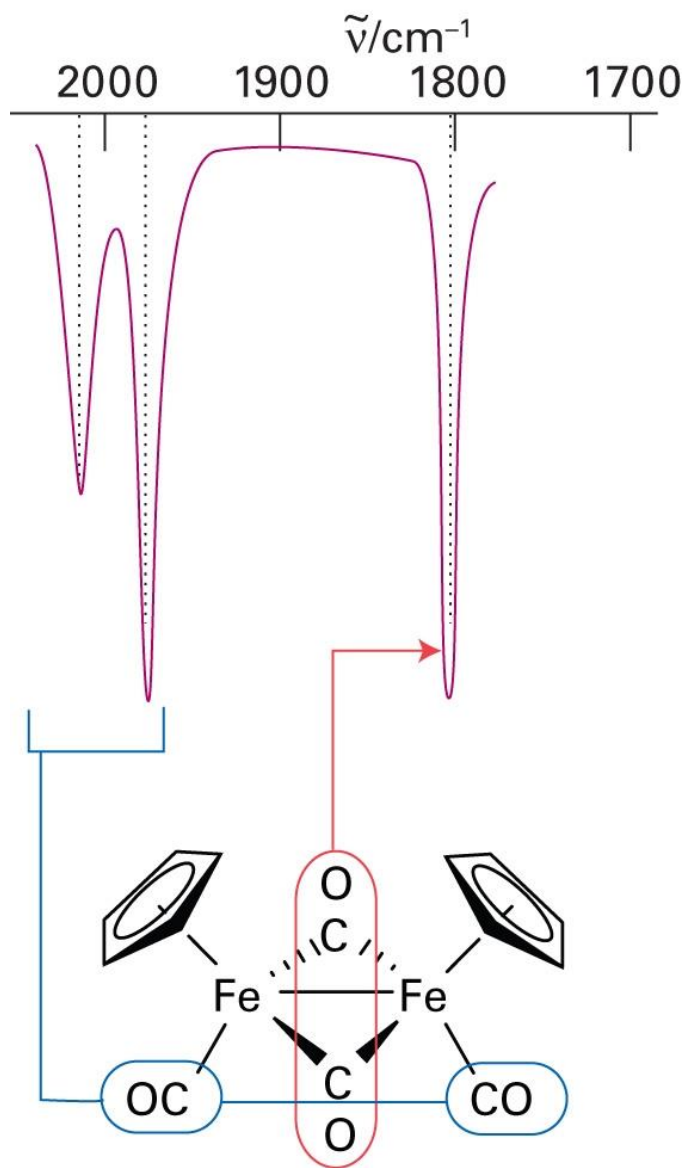
Infrared spectra report on symmetry of substitution products.

Complex	Isomer	Structure	Point group	Number of bands*	Complex	Isomer	Structure	Point group	Number of bands*
M(CO)₆			O_h	1	M(CO)₅	ax		C_{4v}	3[§]
M(CO)₅L			C_{4v}	3[†]	M(CO)₄L	eq		C_{2v}	4
M(CO)₄L₂	trans		D_{4h}	1	M(CO)₃L₂	trans		D_{3h}	1
M(CO)₄L₂	cis		C_{2v}	4[†]	M(CO)₃L₂	cis		C_s	3
M(CO)₃L₃	mer		C_{2v}	3[†]	M(CO)₄			T_d	1
M(CO)₃L₃	fac		C_{3v}	2	M(CO)₃L₃	fac		C_{3v}	2
M(CO)₅			D_{3h}	2					

* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained above.
† If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.
‡ If the trans-CO ligands are nearly collinear, one fewer band will be observed.
§ If the threefold array of CO ligands is nearly planar, only two bands will be observed.

Trends observed in the IR spectra of carbonyl complexes that are consistent with the concept of π-backbonding:

1. With each charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm^{-1}.

2. The better the sigma-donating capability (or worse the pi-acceptor ability) of the other ligands on the metal, the lower the CO stretching frequency.

3. For simple carbonyl complexes, counting the number of IR and Raman CO stretching frequencies will often permit one to make a structural assignment. The number of CO stretches expected for possible geometries/isomers can be predicted using group theory and the calculated results compared to the experimental data.

4. In the ^{13}C NMR spectrum, coordinated carbonyl ligands typically appear in the range of 180 to 250 ppm. Isotopically enriched carbonyl complexes are often prepared to simplify mechanistic investigations or to facilitate the collection of the spectrum. In addition, the coupling of a ^{13}C-enriched complex to other spin active nuclei such as ^{103}Rh or ^{31}P, can aid in structural assignments.

Molecular Orbitals Help Understand:
Ligands of Organometallic Chemistry. Homoleptic complexes from CO and PR_3.
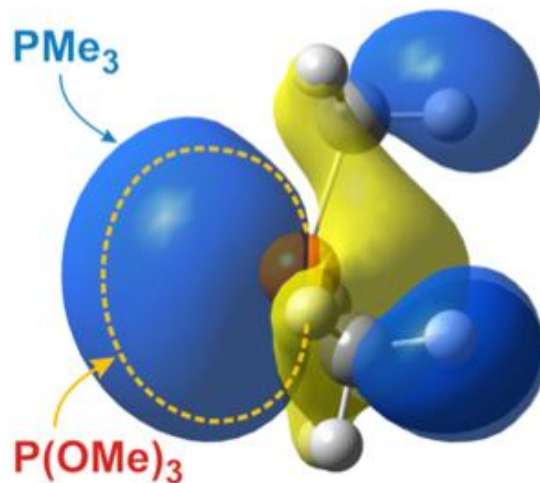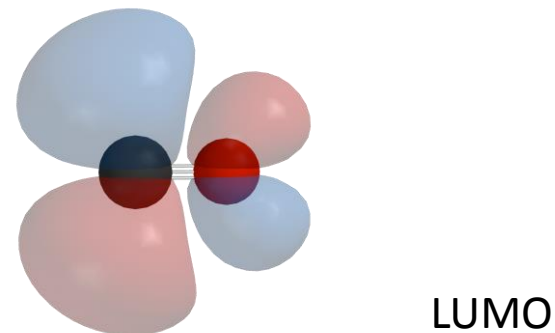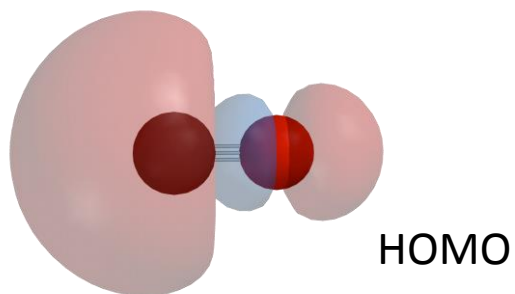
HOMO

LUMO

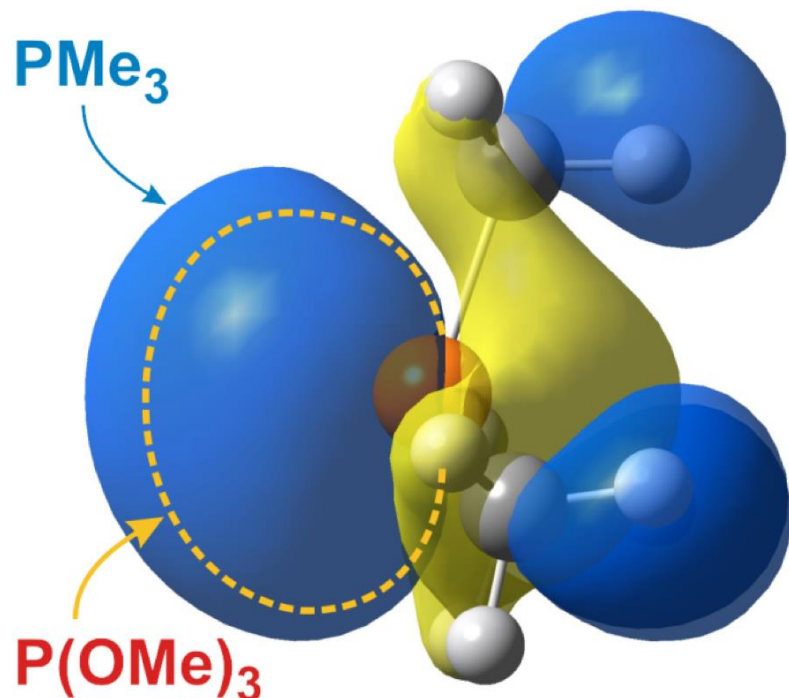PMe$_3$

P(OMe)$_3$

PMe$_3$
HOMO = −5.03 eV
Charge on P = +0.22

P(OMe)$_3$
HOMO = −7.40 eV
Charge on P = +0.75

MO plot of the lone pair orbital (HOMO) for PMe$_3$. Dashed outline
indicates the spatial extent of the lone pair for P(OMe)$_3$.

Donor Ability of Phosphines vs. Phosphites:

PMe$_3$
HOMO = −5.03 eV
Charge on P = +0.22

P(OMe)$_3$
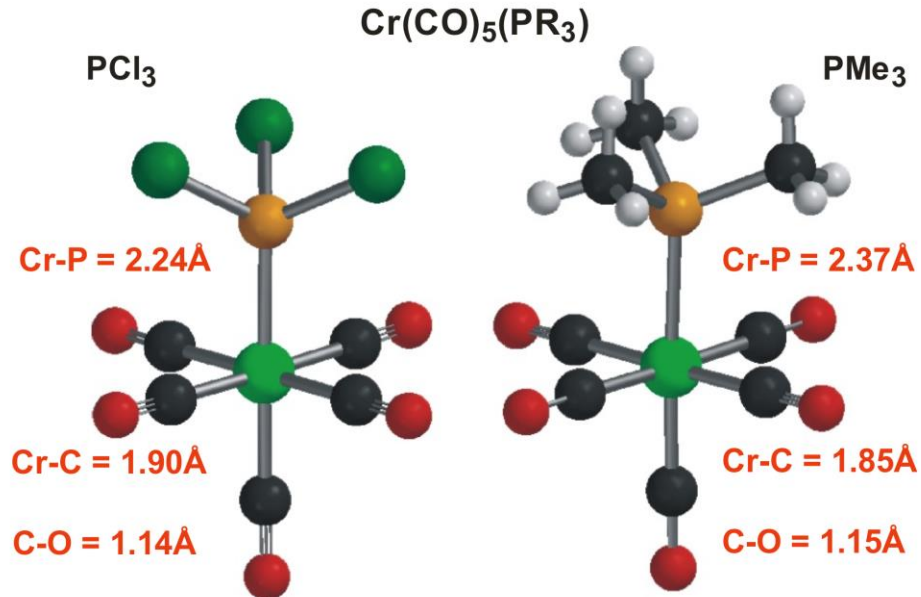HOMO = −7.40 eV
Charge on P = +0.75

MO plot of the lone pair orbital (HOMO) for PMe$_3$. Dashed outline indicates the spatial extent of the lone pair for P(OMe)$_3$.

therefore, stronger than the $Cr-PMe_3$ bond.

$Cr(CO)_5(PR_3)$

PCl_3

PMe_3

Cr-P = 2.24Å

Cr-P = 2.37Å

Cr-C = 1.90Å

Cr-C = 1.85Å

C-O = 1.14Å

C-O = 1.15Å

Let's compare the P lone pair orbital for free PCl_3 and PMe_3 ligand, which is the highest occupied molecular orbital (HOMO):

PCl_3

PMe_3

HOMO energy = −8.36 eV   −6.23 eV
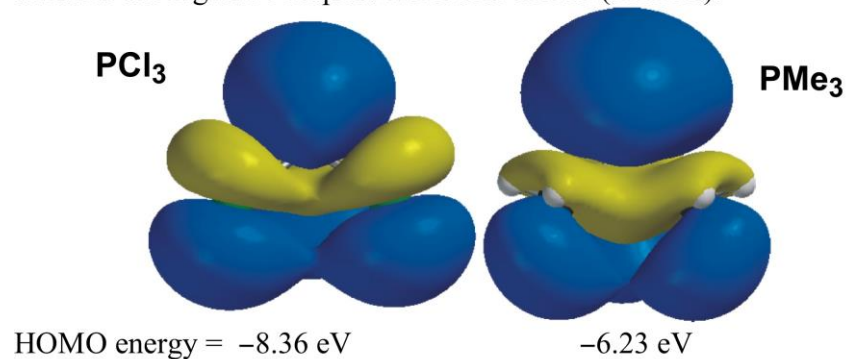
P-31 100% natural abundance; nuclear spin = 1/2
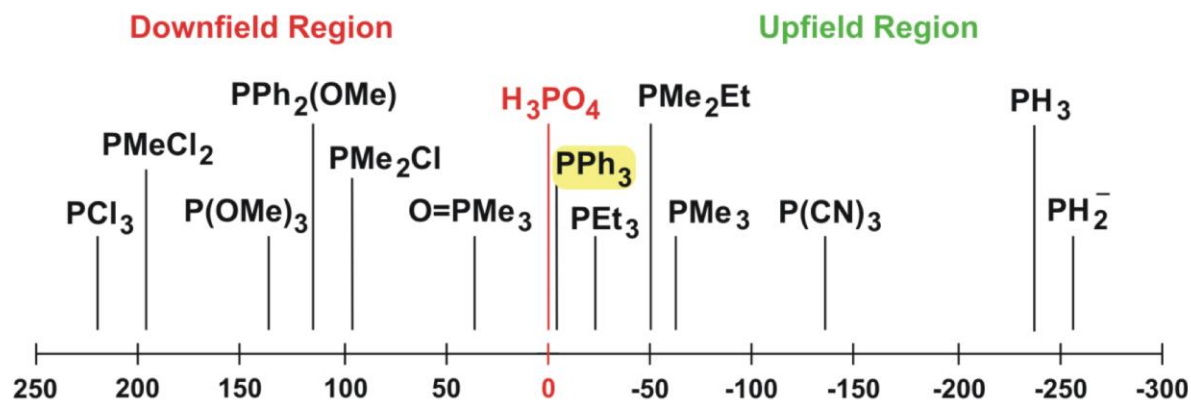
Ligand	Chemical Shift (ppm)	Ligand	Chemical Shift (ppm)
PCl$_3$	220	H$_3$PO$_4$	0 (reference)
PMeCl$_2$	191	P(CF3)$_3$	-2
PCy(OBu)$_2$	184	PPh$_3$	-6
P(OMe)$_3$	140	PEt$_3$	-20
P(OPh)$_3$	126	NaPPh$_2$	-24
PEt$_2$Cl	119	PMePh$_2$	-28
PPh$_2$(OMe)	115	PPr$_3$	-33
PF$_3$	97	PMe$_2$Et	-50
PMe$_2$Cl	96	PMe$_3$	-62
PMe$_2$(O-t-Bu)	91	P(CN)$_3$	-135
O=P(CH$_2$OH)$_3$	45	PH$_3$	-238
O=PMe$_3$	36	KPH$_2$	-255