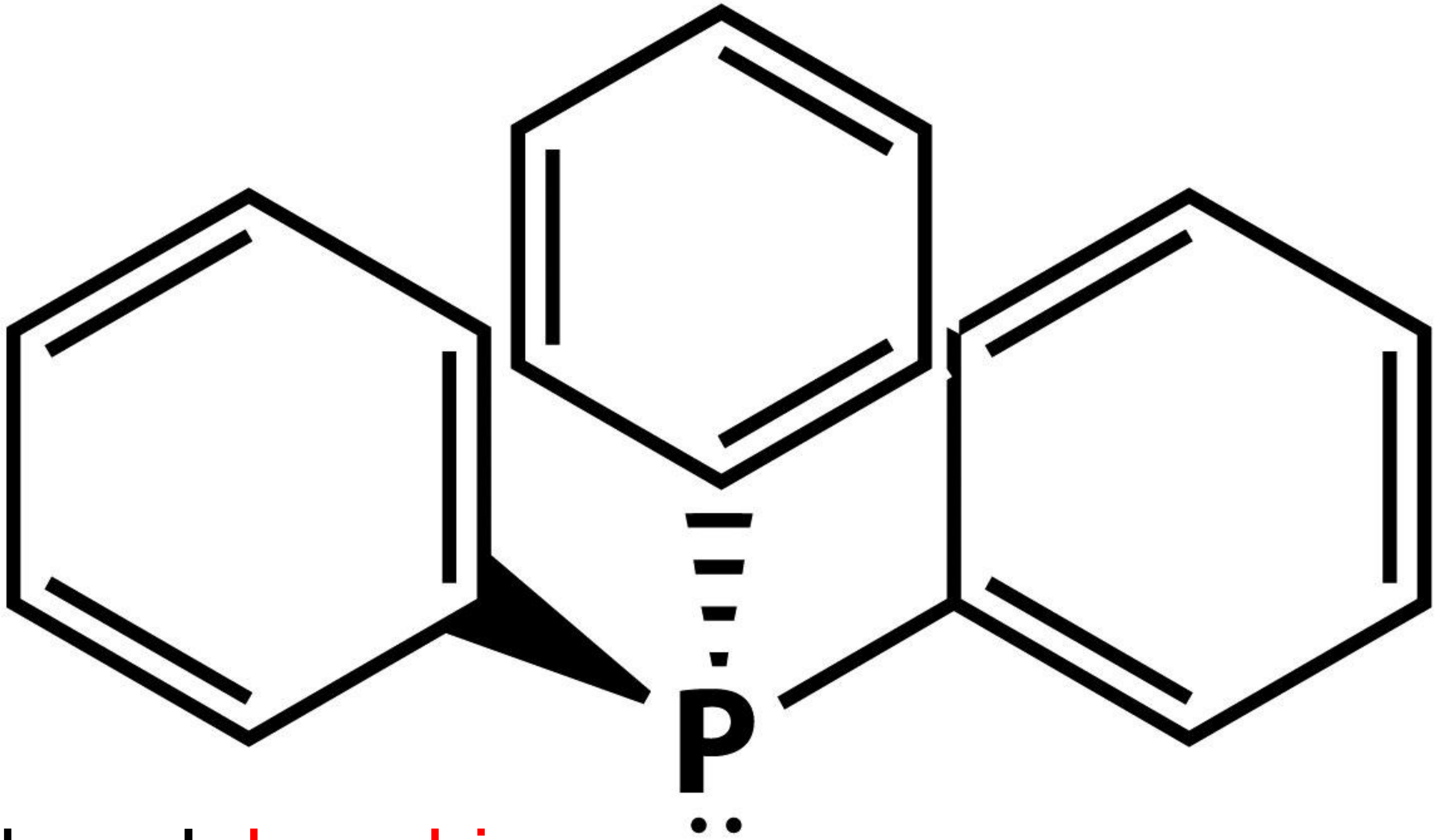
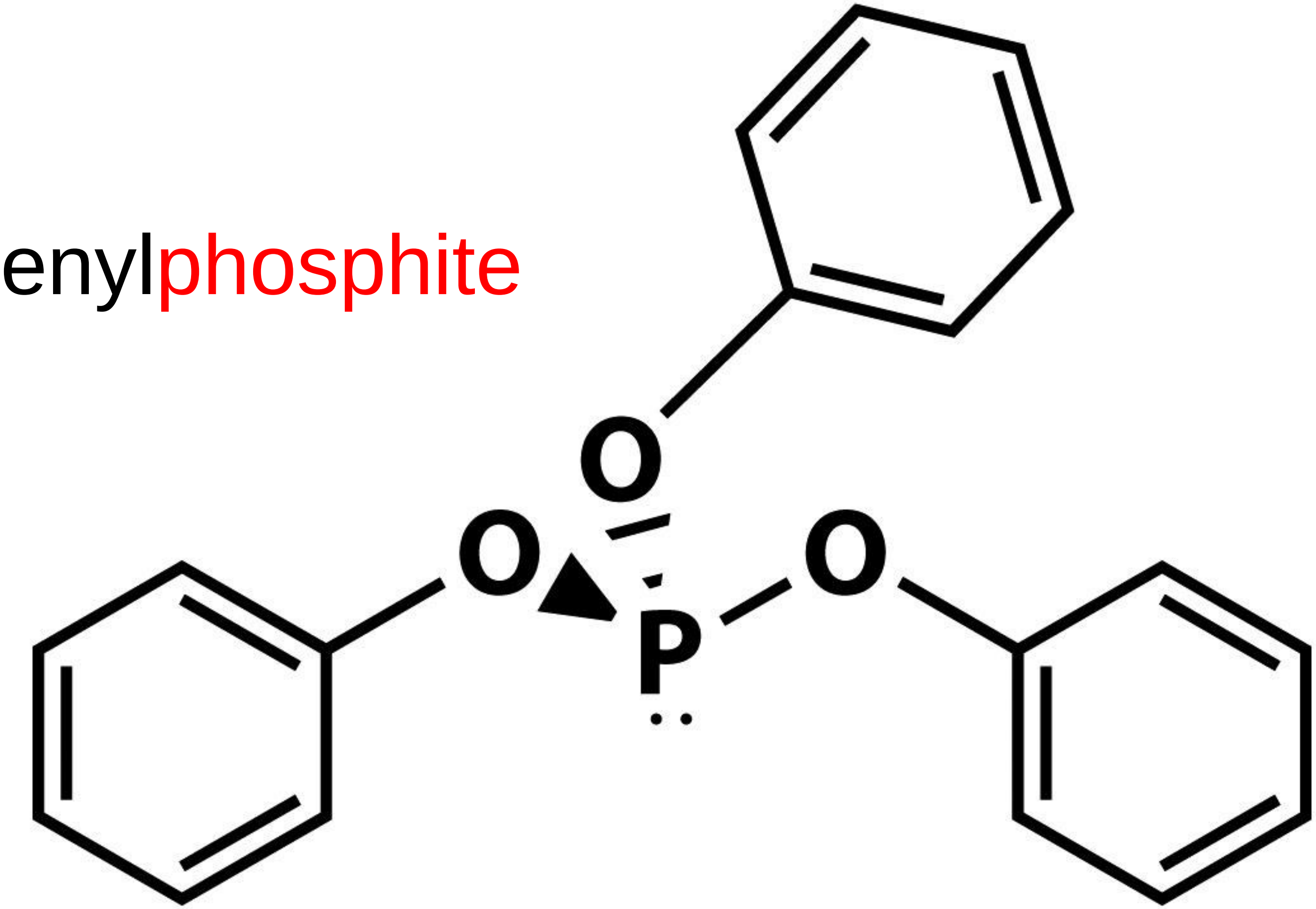


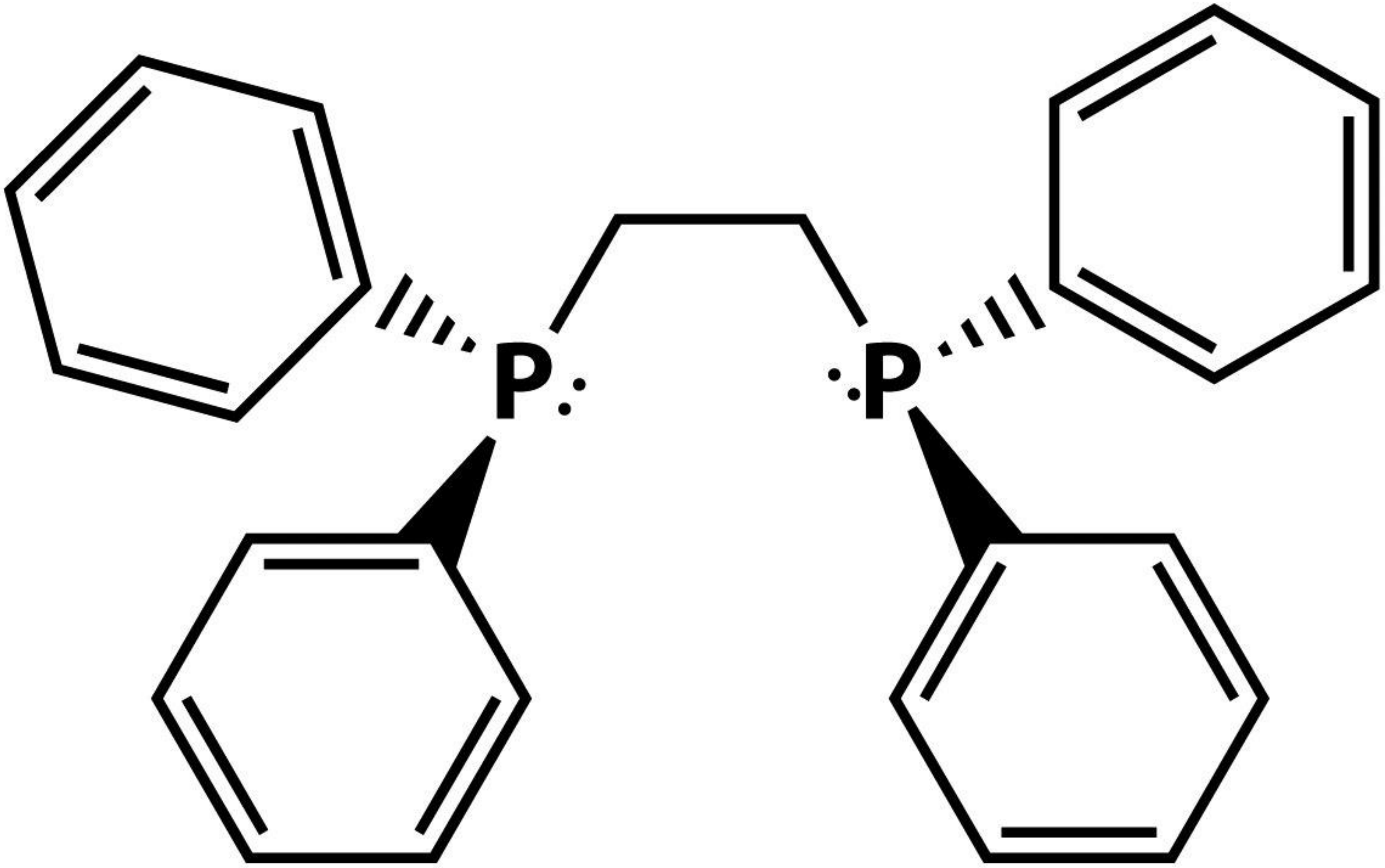
triphenylphosphine

PPh_3

triphenylphosphite

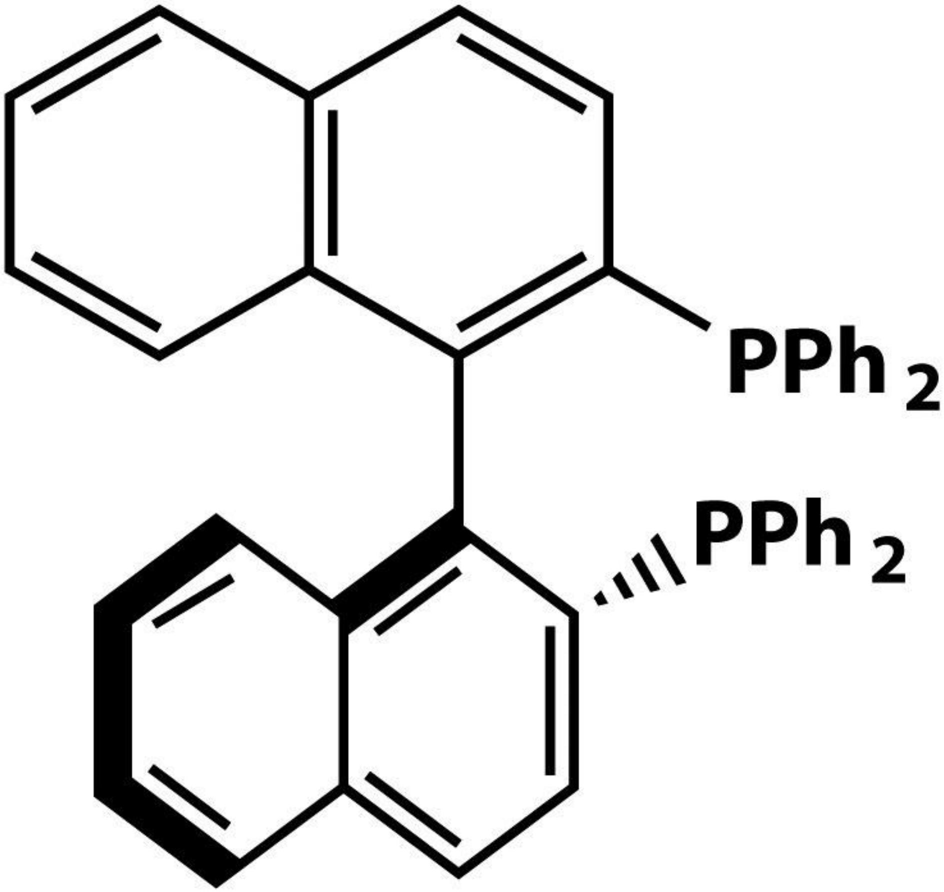


$P(OPh)_3$

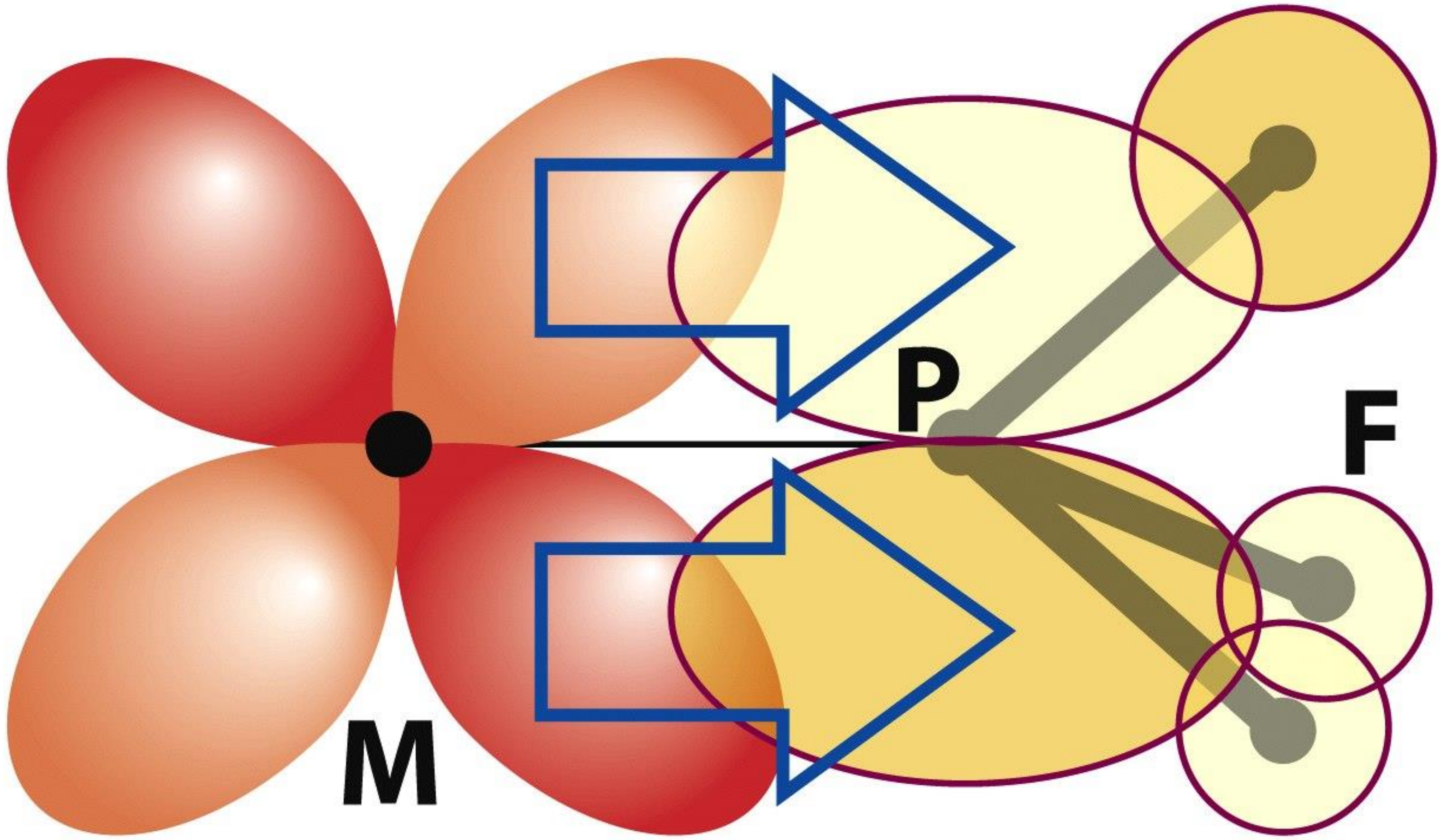


$Ph_2PCH_2CH_2PPh_2$, dppe

diphenylphosphinoethane



**2,2′-bis(diphenylphosphino)-
1,1′-binaphthyl, BINAP**



For Phosphines the σ-donor and the π-acceptor characters are inversely proportional

TEP = Tolman Electronic Parameter for phosphines

For $PX_1X_2X_3$ in $Ni(CO)_3L$

$$\nu = 2056.1 + \sum_{i=1}^{3} \chi$$

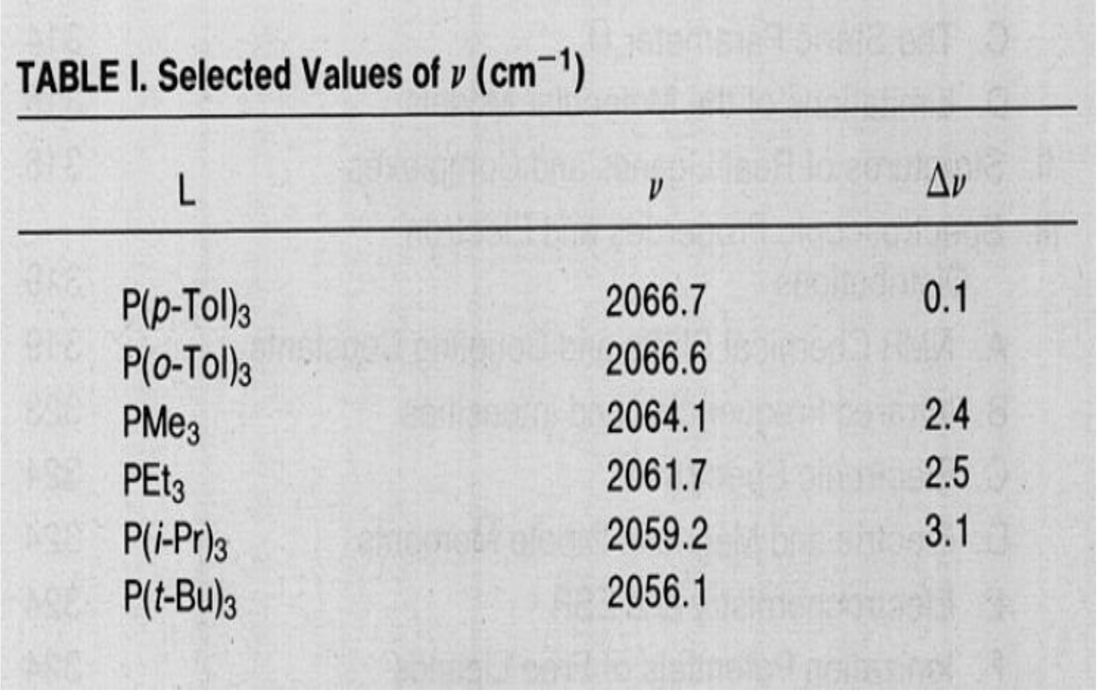


TABLE I. Selected Values of ν (cm^{-1})

L	ν	$\Delta\nu$
$P(p\text{-Tol})_3$	2066.7	0.1
$P(o\text{-Tol})_3$	2066.6	
PMe_3	2064.1	2.4
PEt_3	2061.7	2.5
$P(i\text{-Pr})_3$	2059.2	3.1
$P(t\text{-Bu})_3$	2056.1	

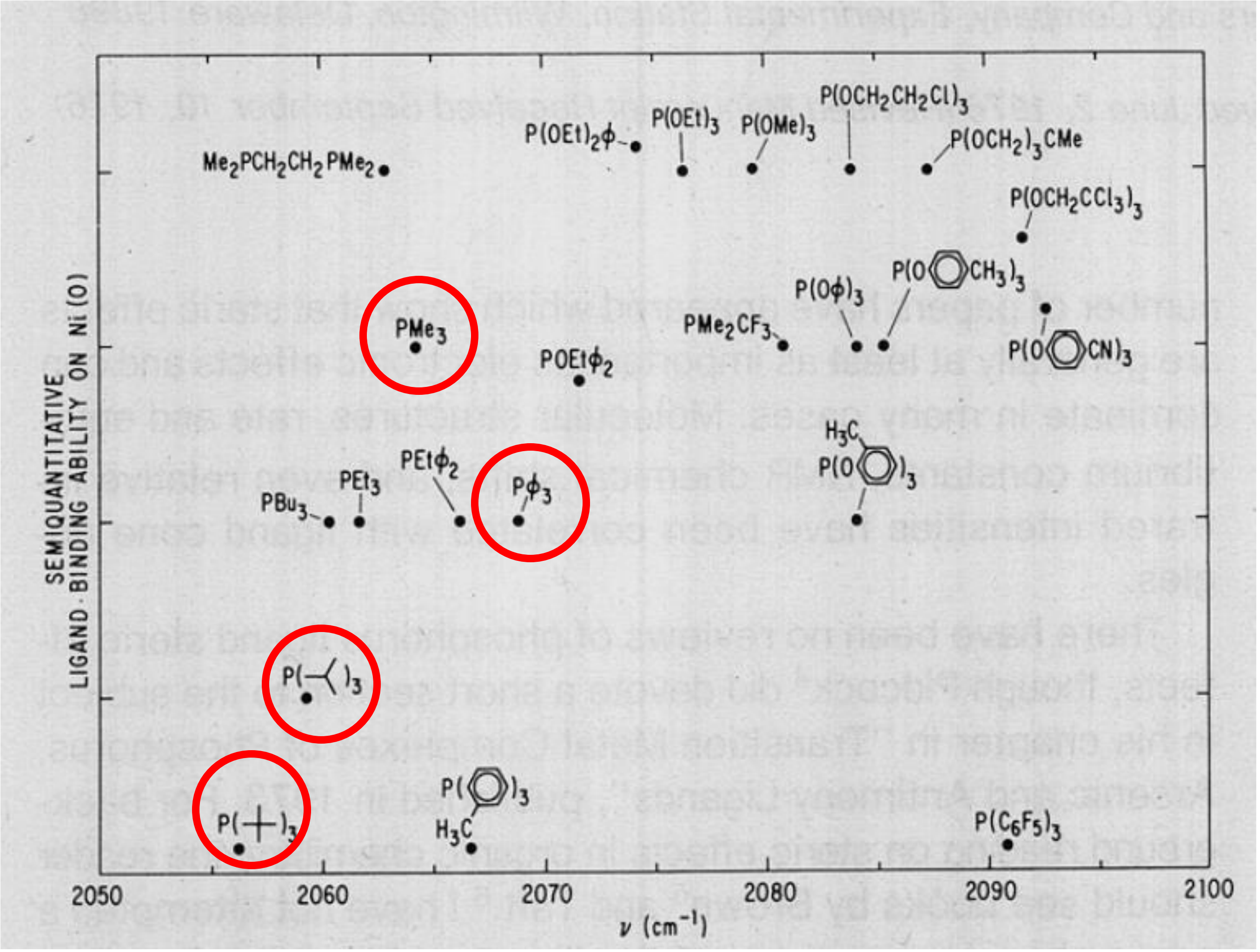
Lewis basicity of phosphines

$PCy_3 > PEt_3 > PMe_3 > PPh_3 > P(OMe)_3 >$
$P(OPh)_3 > PCl_3 > PF_3$

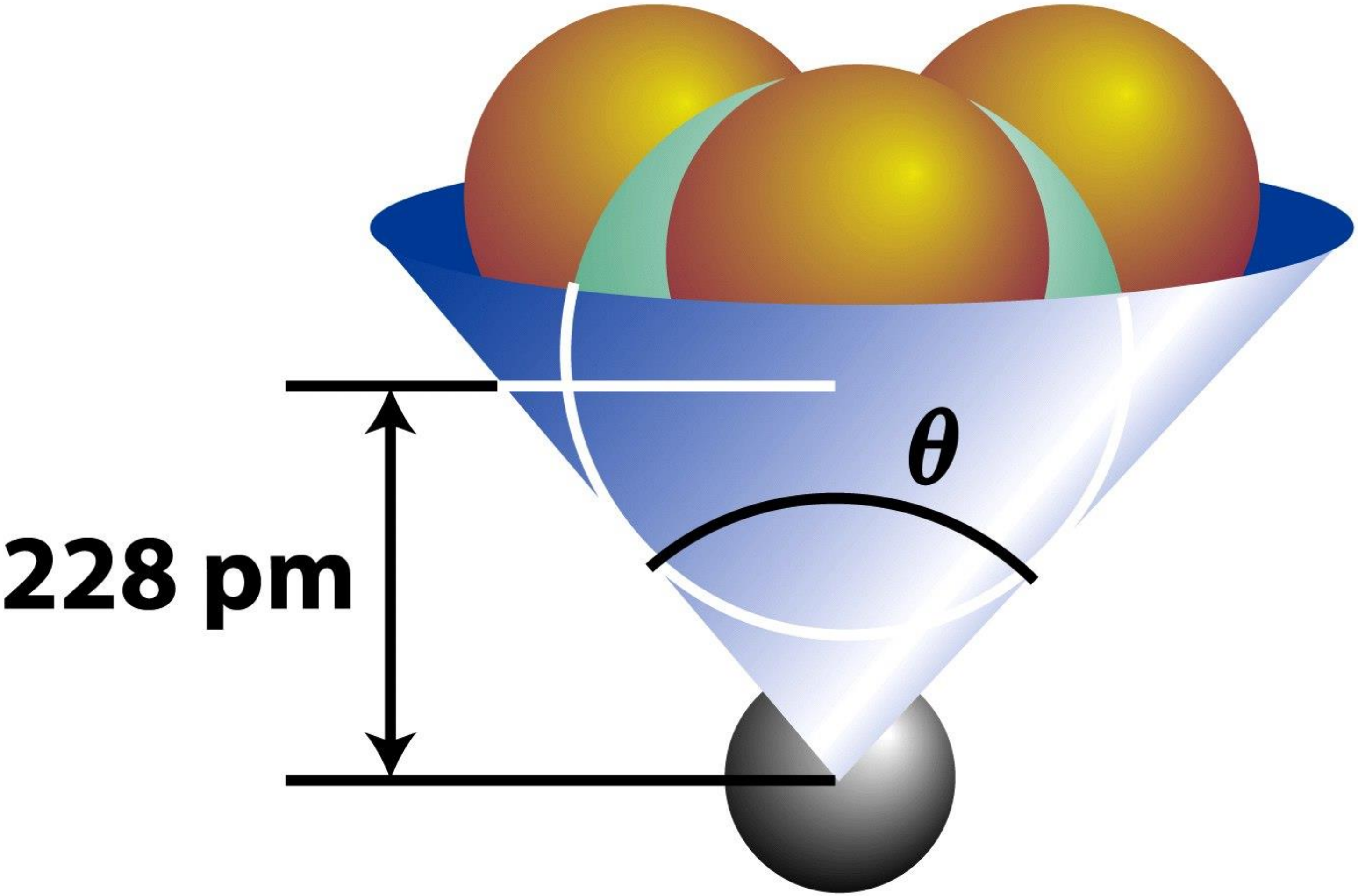
$[Cr(CO)_5(PEt_3)]$ *vs* $[Cr(CO)_5(PPh_3)]$

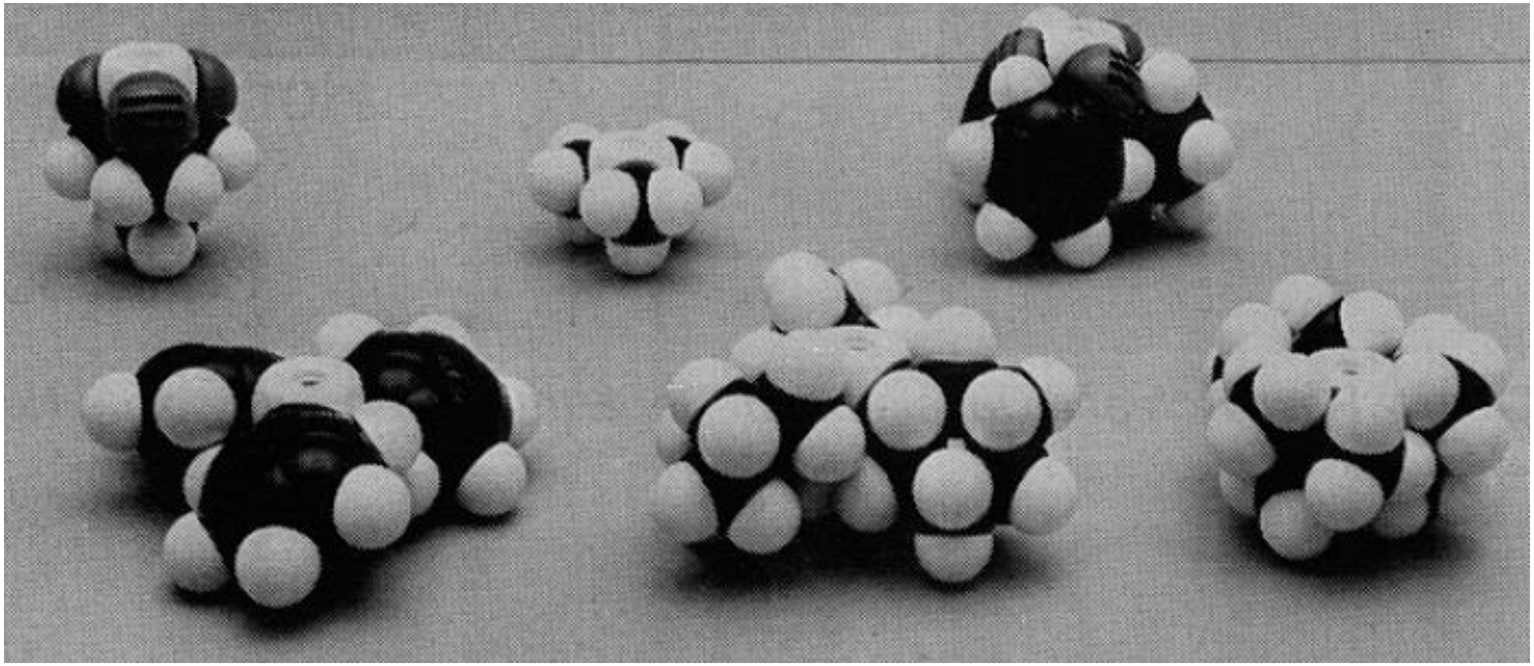
$Fe(CO)_5$ *vs* $[Fe(CO)_4(PEt_3)]$

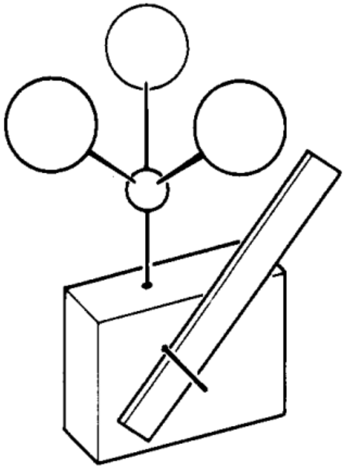
Need to introduce the steric parameter



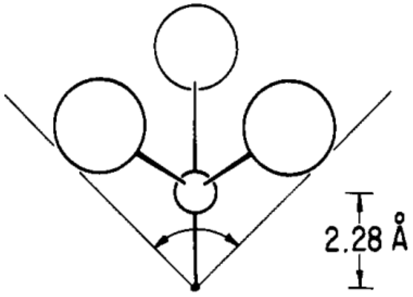
Tolman cone angle in $Ni(CO)_3L$



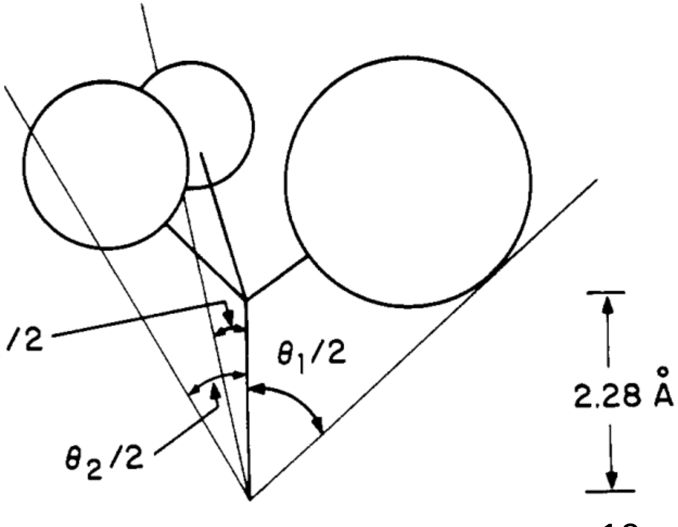




(a)



(b)



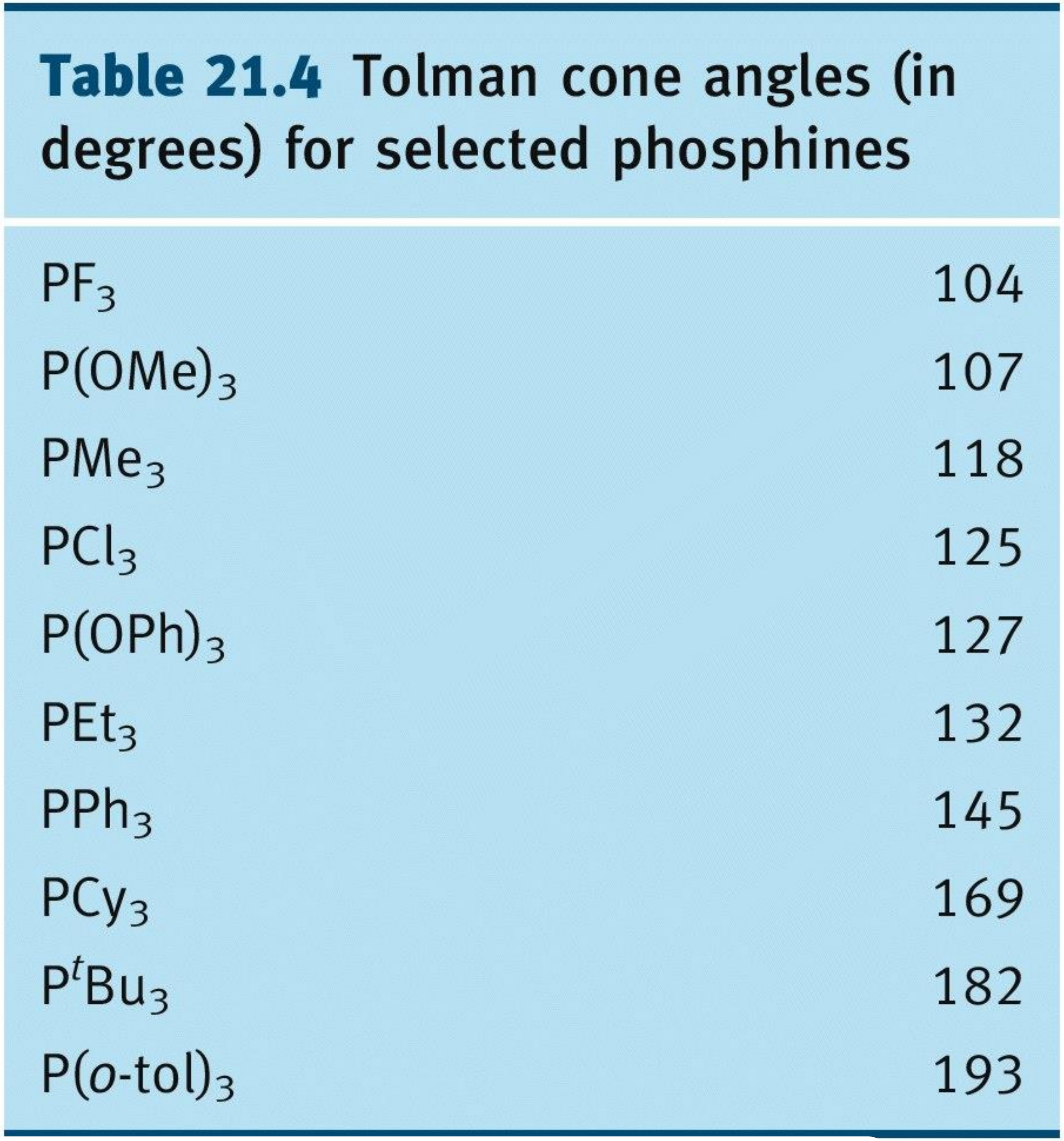


Table 21.4 Tolman cone angles (in degrees) for selected phosphines

PF_3	104
$P(OMe)_3$	107
PMe_3	118
PCl_3	125
$P(OPh)_3$	127
PEt_3	132
PPh_3	145
PCy_3	169
$P^{t}Bu_3$	182
$P(o\text{-tol})_3$	193

TEP *vs* cone angle

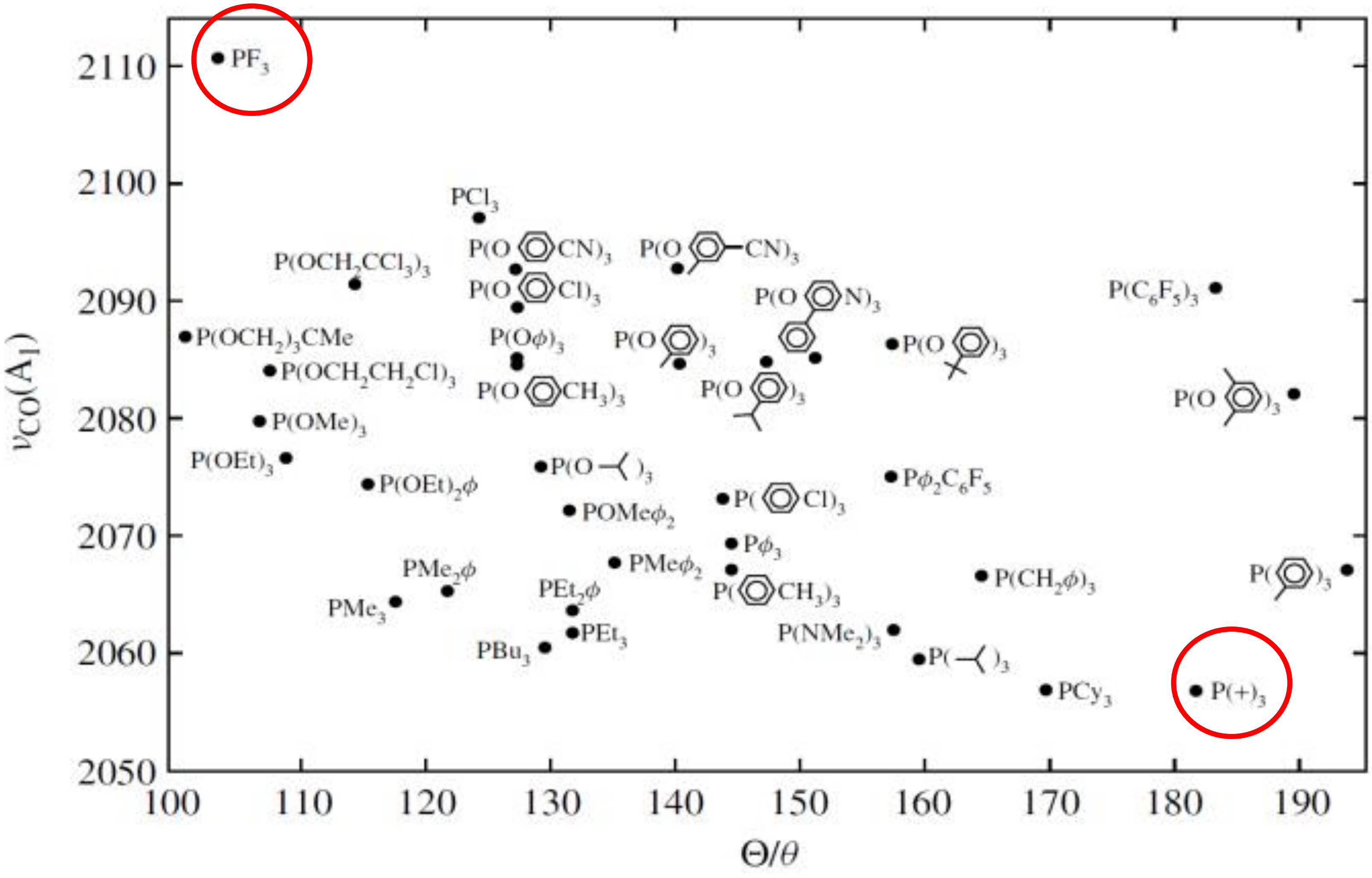


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1}, θ in degrees).

Hydrides (1931)

$[CoH(PMe_3)_4]$ *vs* $[CoH(CO)_4]$

$pK_a = 8.3$

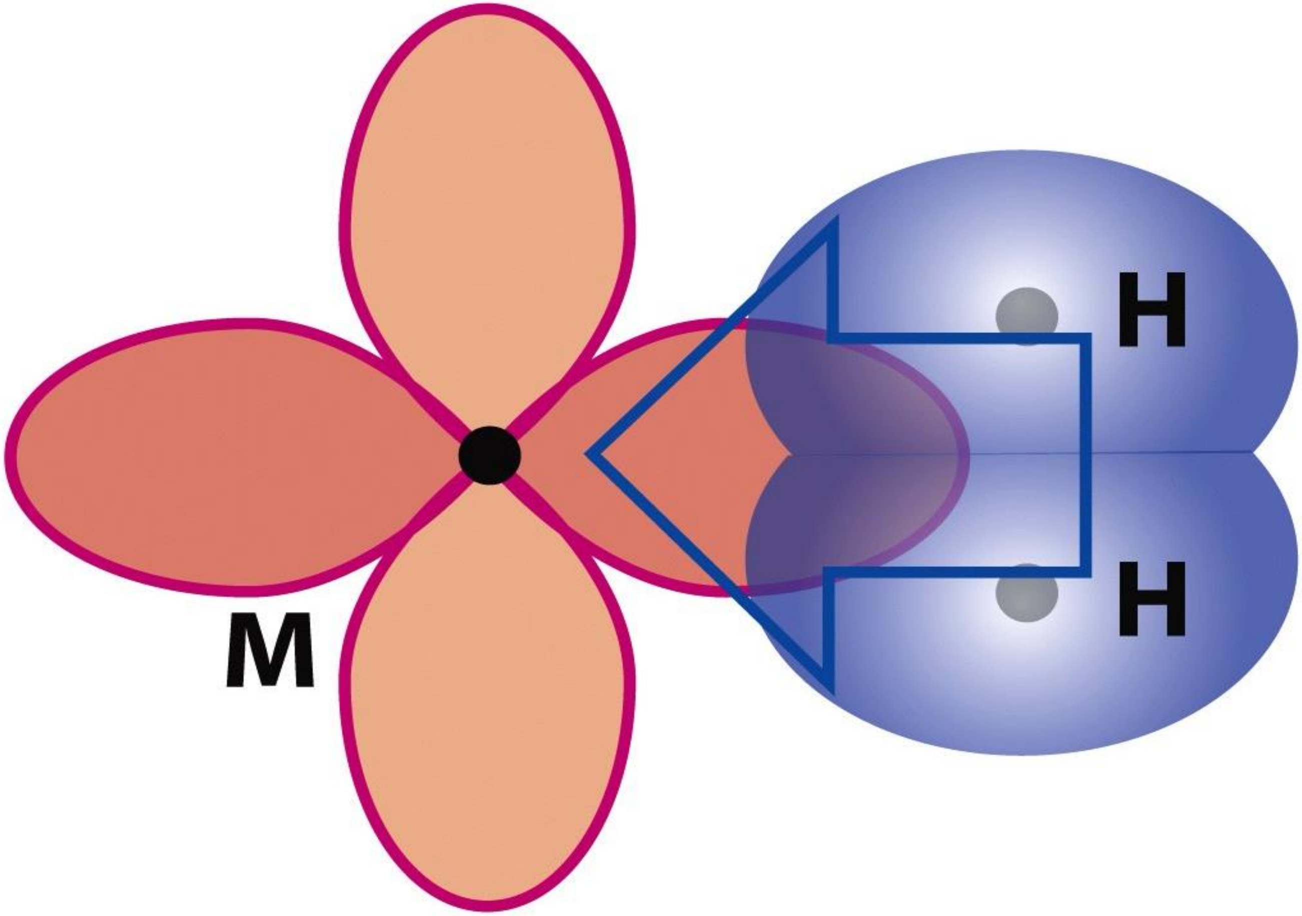
^1H NMR: $-50 < \delta < 0$

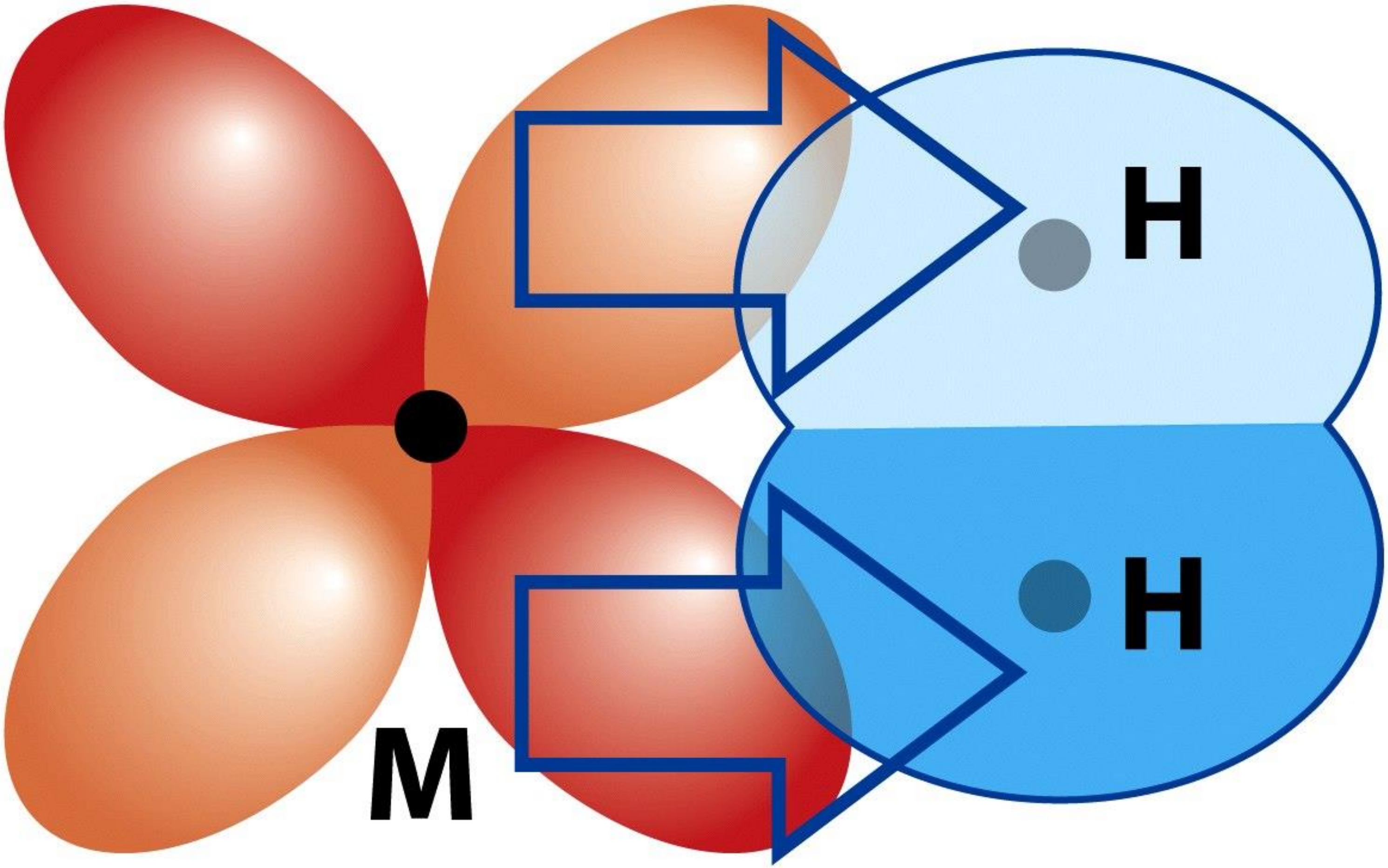
IR: 2250 – 1500 cm^{-1}

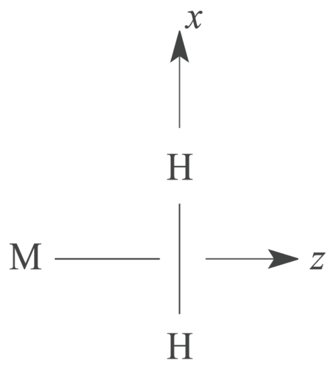
Neutron Diffraction (structure)

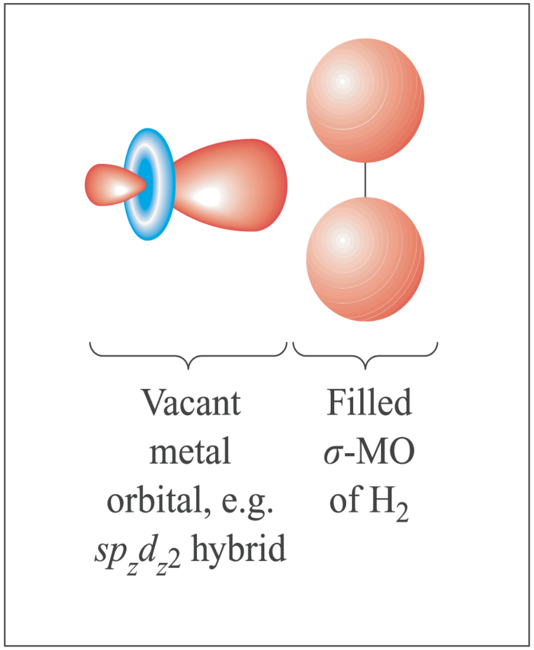
H_2 coordination (1984): *side-on*

(typically in d^6 low-spin compounds)

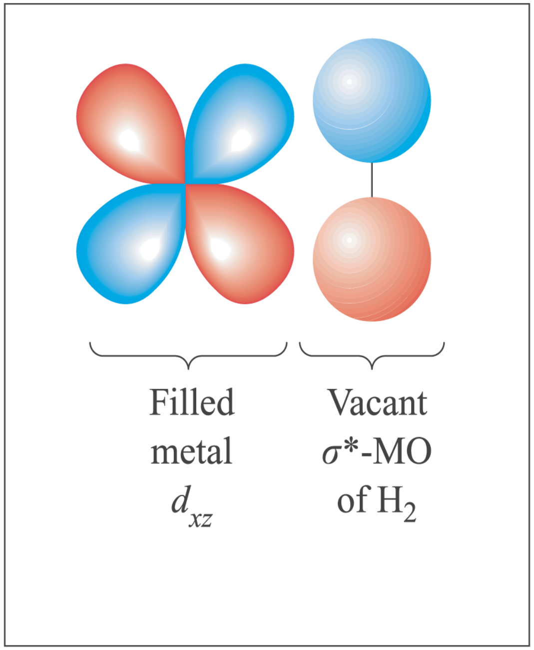



H
H
M

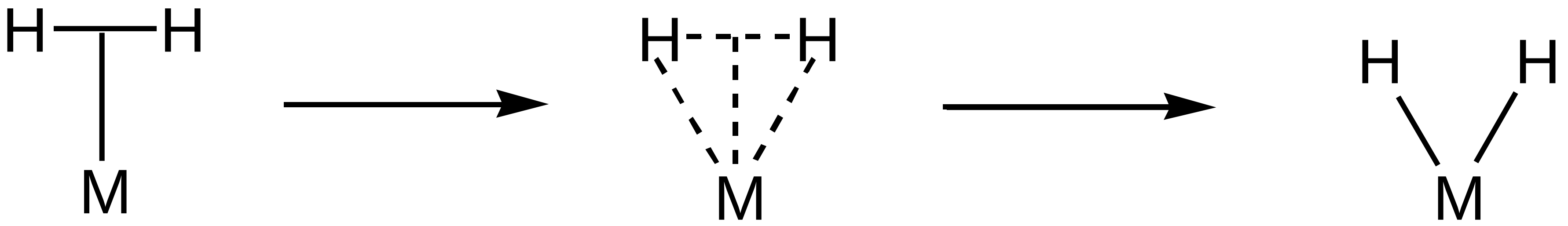




H_2-to-M donation
(a)

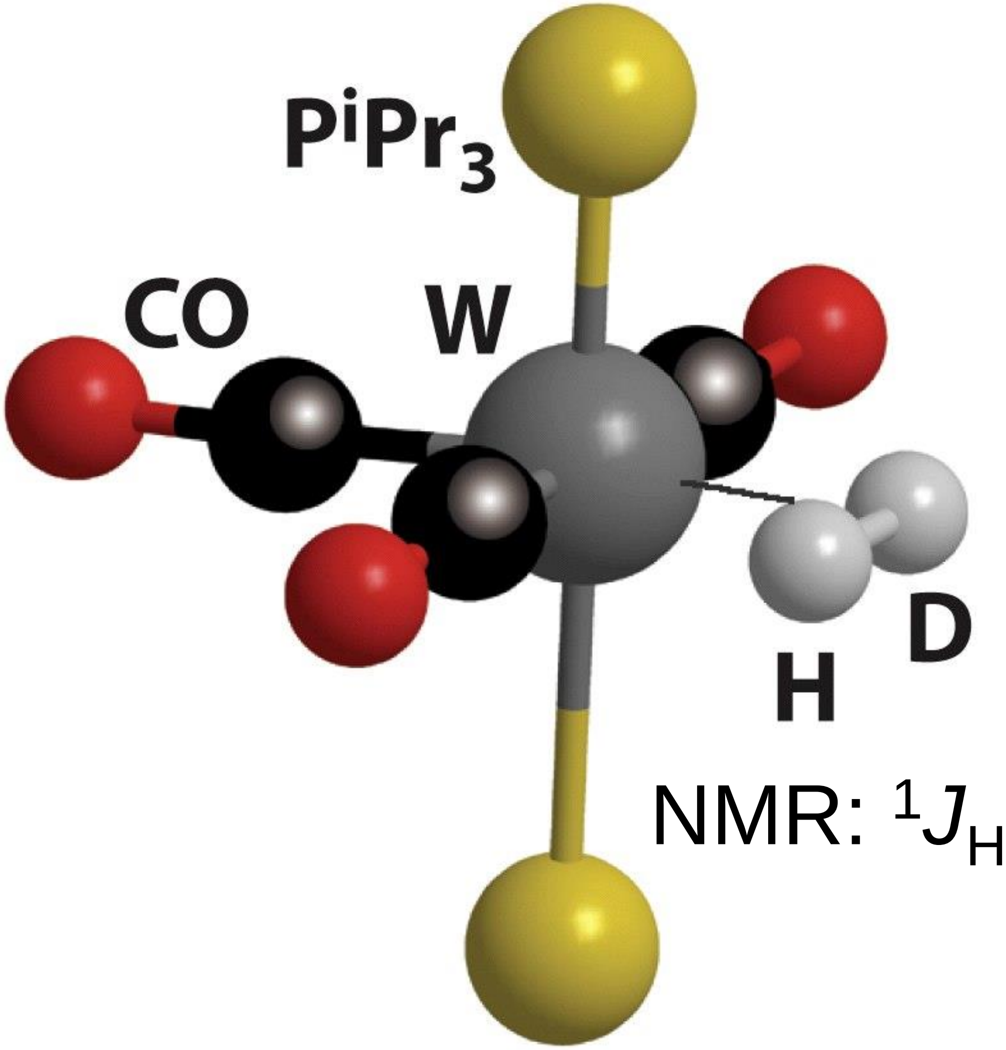


M-to-H_2 back-donation
(b)

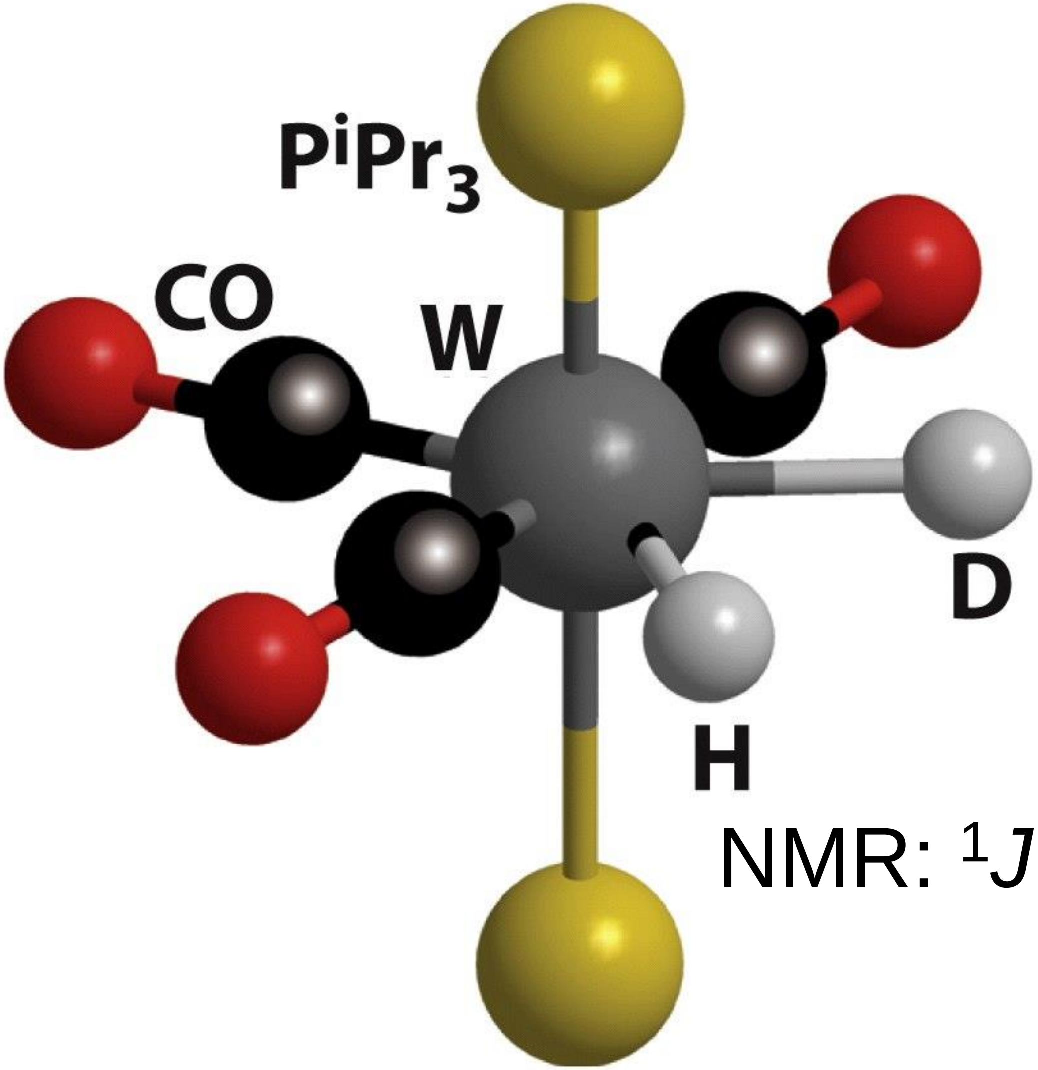

Oxidative Addition

NMR: $-10 < \delta < 0$
$^{1}J_{HD} = 20 - 34$ Hz
IR: H–H 2900 – 2300 cm^{-1}

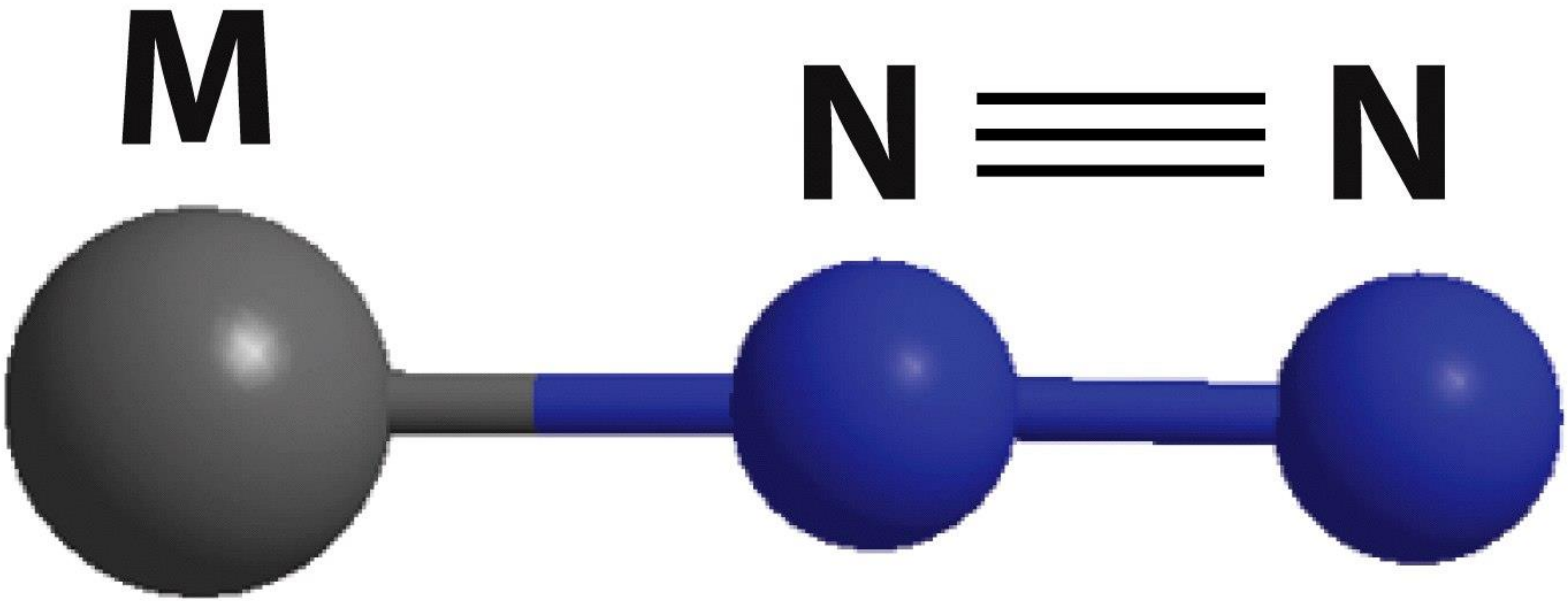
NMR: $-50 < \delta < 0$
$^{1}J_{HD} = \sim 1$Hz
IR: M–H 2200 – 1500 cm^{-1}



NMR: $^1J_{HD}$ = 34 Hz



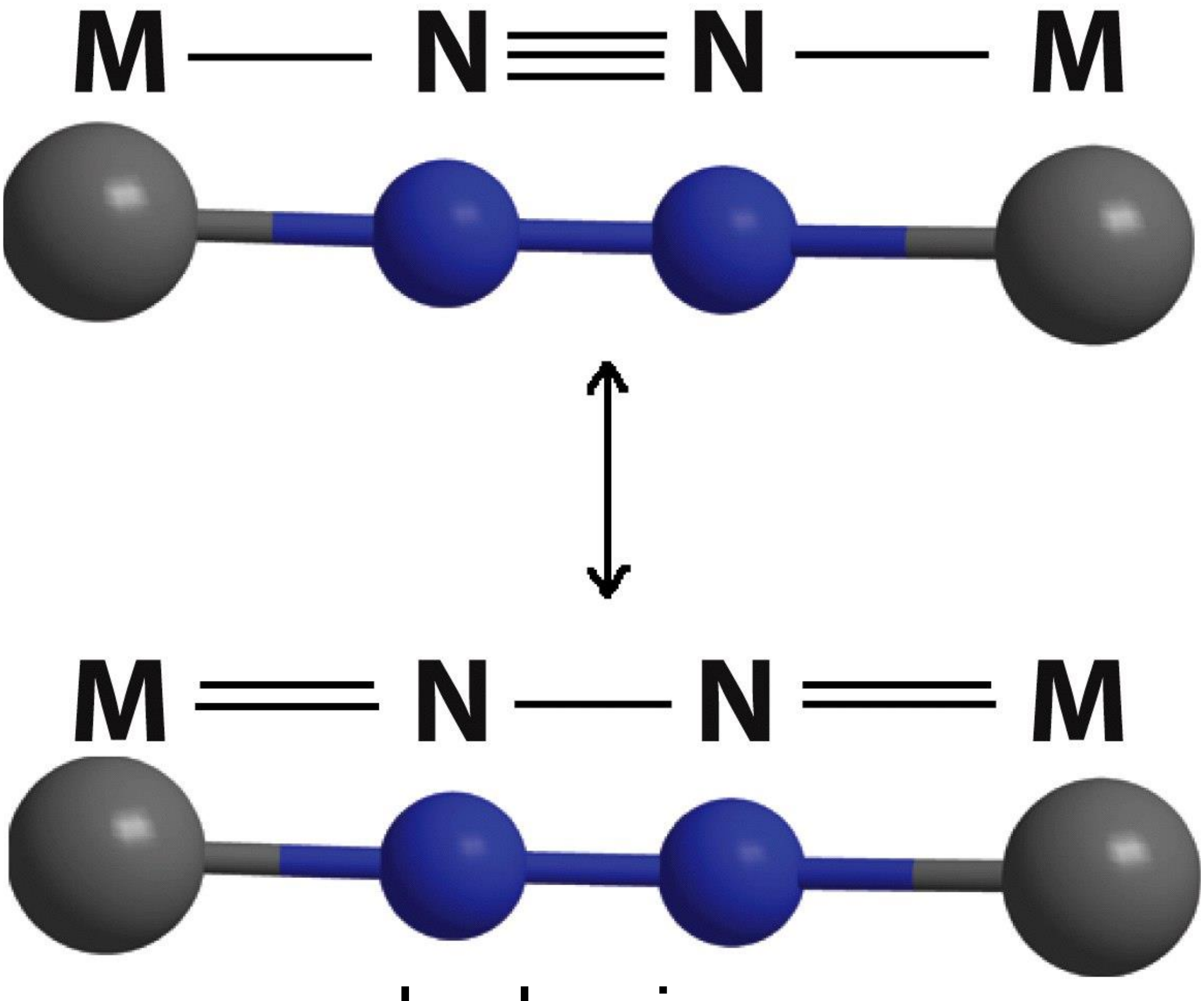
NMR: ${}^1J_{HD} < 2$ Hz



End-on (η^1)

(most common)

IR: N–N 2150 – 1900 cm^{-1}

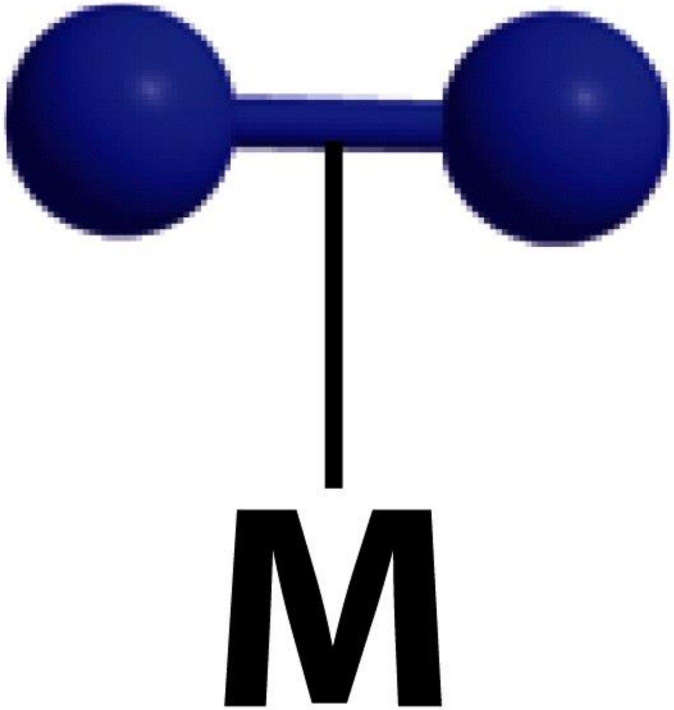


$$\mathrm{M} - \mathrm{N} \equiv \mathrm{N} - \mathrm{M}$$

$$\updownarrow$$

$$\mathrm{M} = \mathrm{N} - \mathrm{N} = \mathrm{M}$$

«hydrazine»



Side-on (η^2)
(more rare)

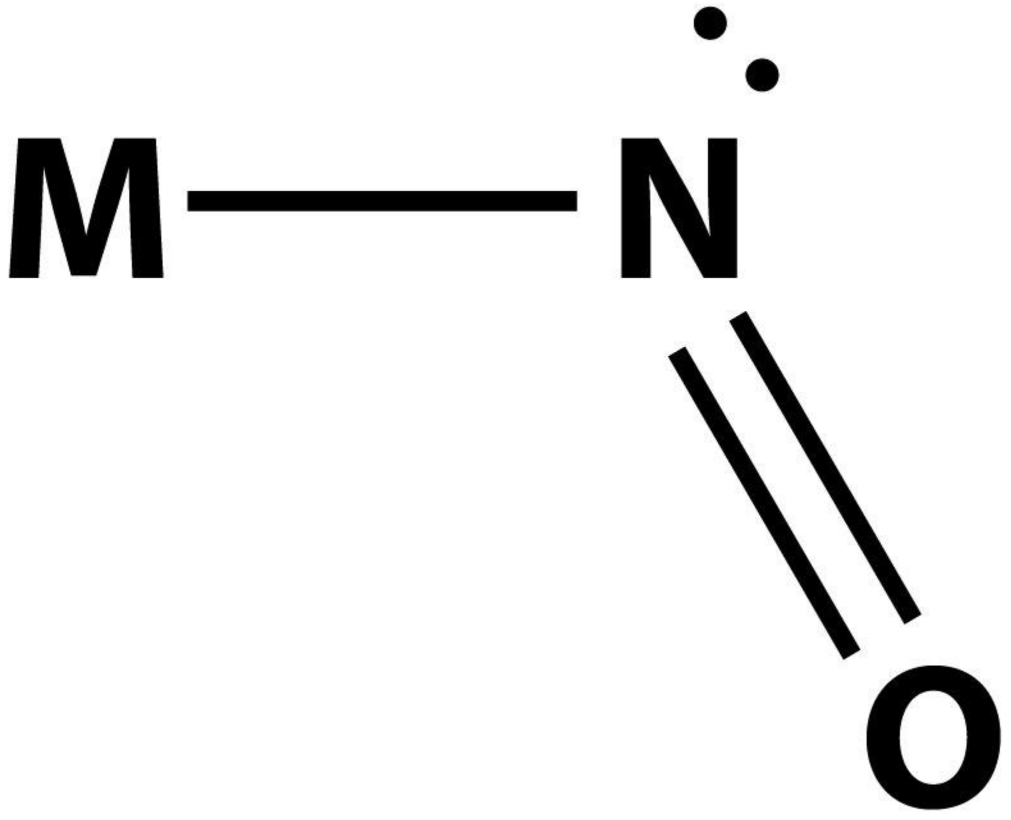
Nitrosyl

$$\mathbf{M}-\mathbf{N}\equiv\mathbf{O}$$

Linear: formally NO^+

Iso-electronic to CO

2e^- donor, strong π-acceptor



Bent: formally NO$^-$

2e$^-$ donor, σ-donor only

Swithching from NO$^+$ to NO$^-$: formal loss of two electrons