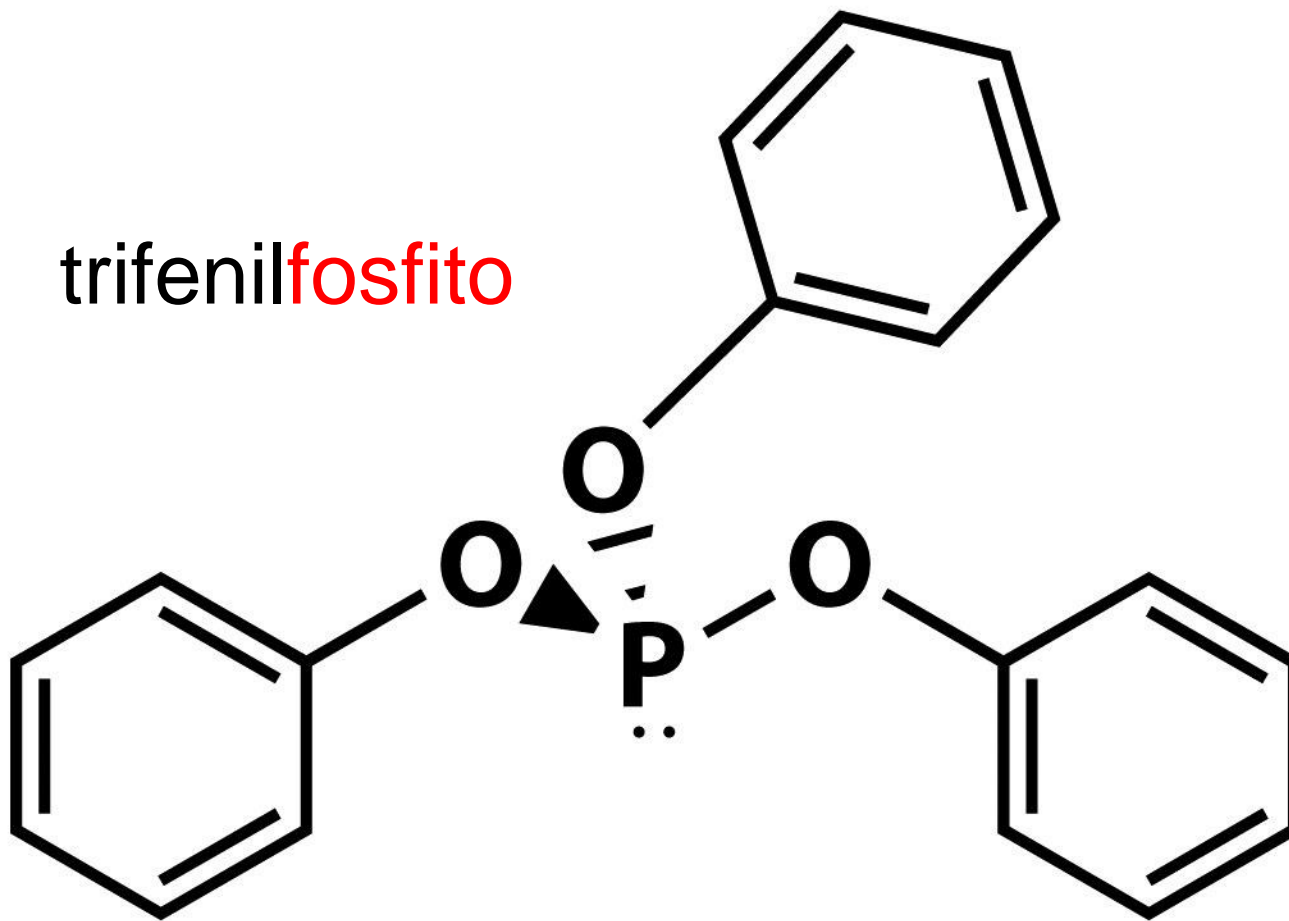


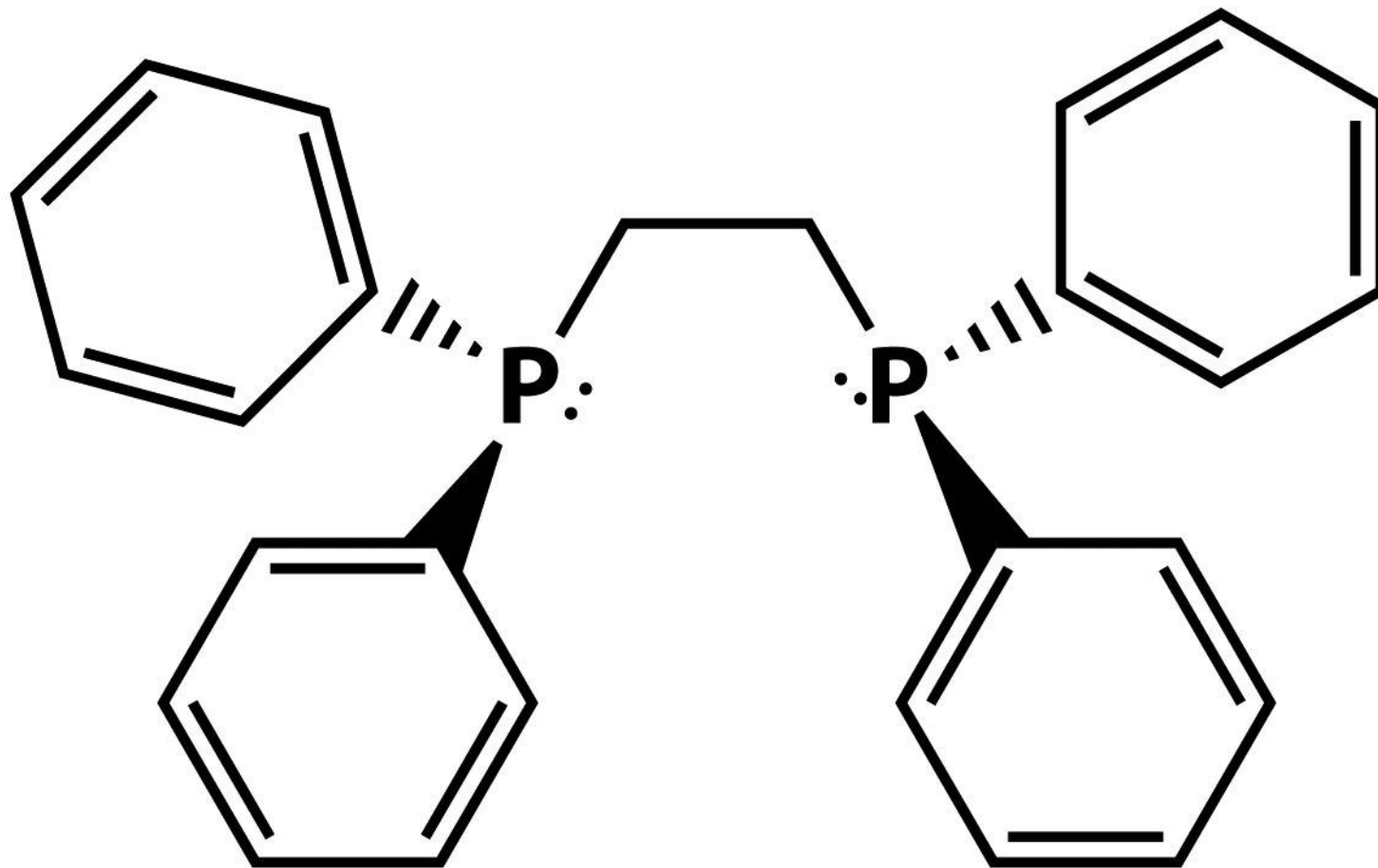
trifenilfosfina

PPh₃

trifenilfosfito

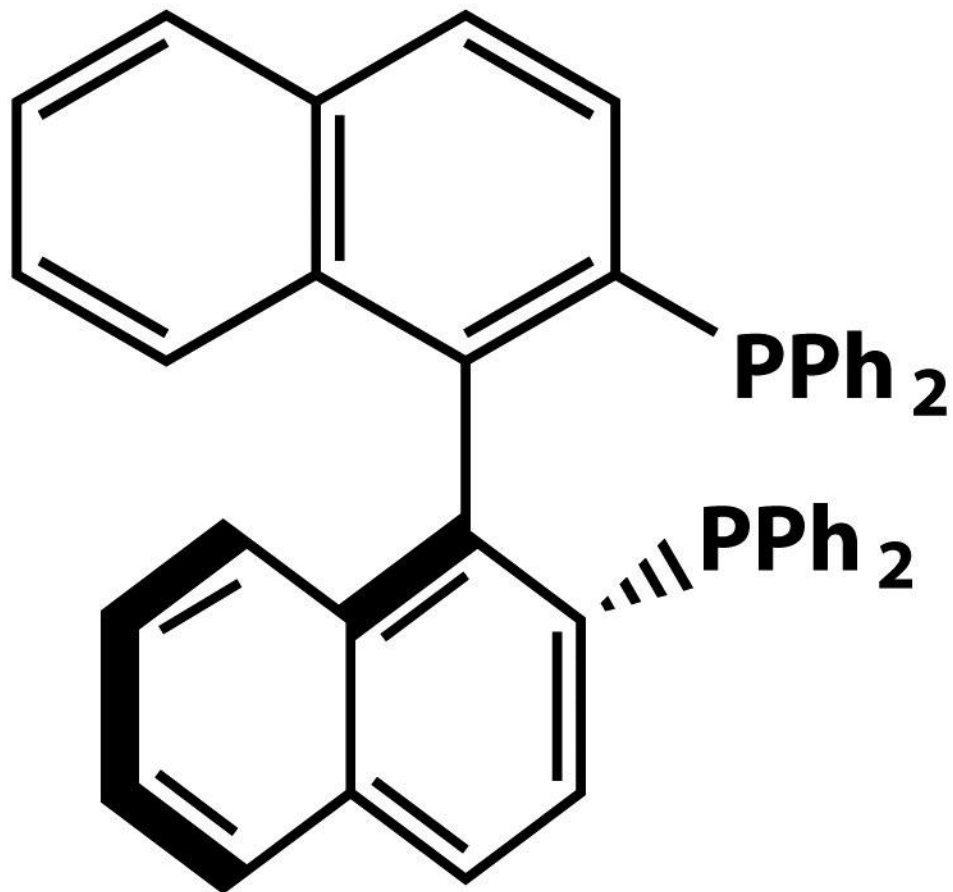


$P(\text{OPh})_3$

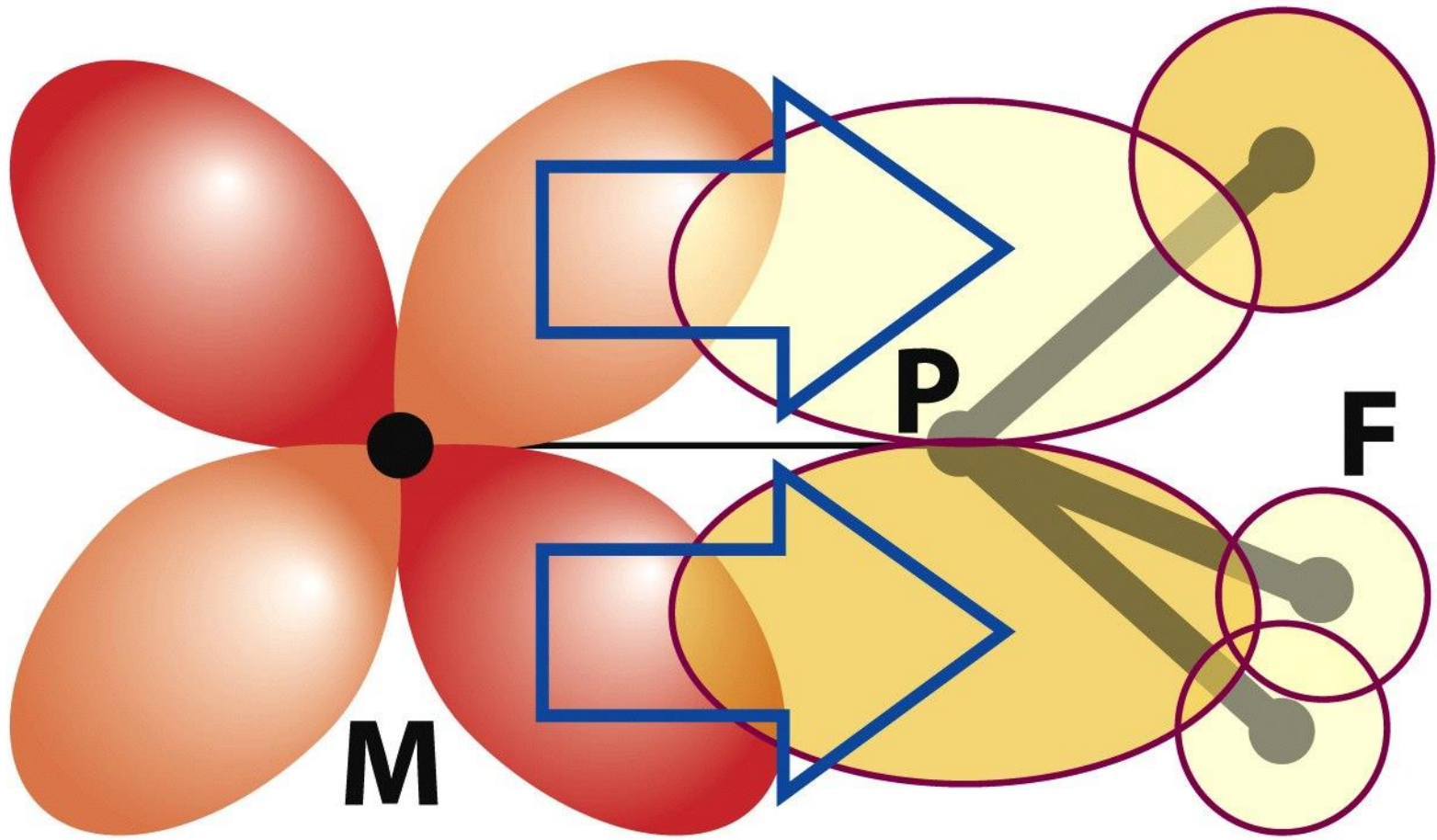


$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, dppe

difenilfosfinoetano



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



Nelle fosfine il contributo σ -donatore e quello π -accettore sono fra loro inversamente proporzionali

TEP = Tolman Electronic Parameter per le fosfine

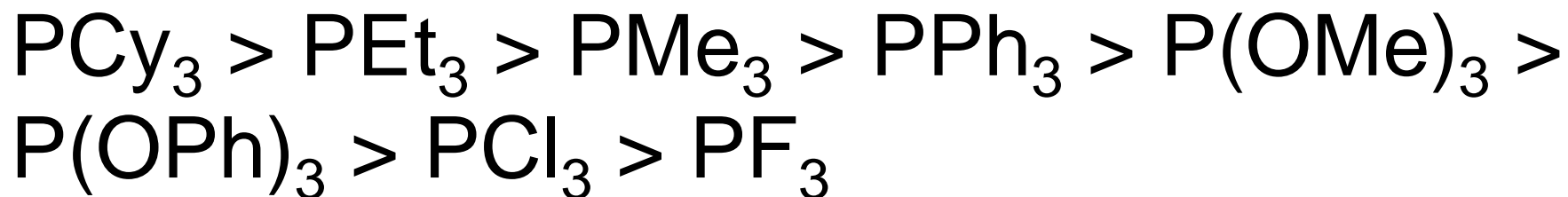
Per $PX_1X_2X_3$ in $Ni(CO)_3L$

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

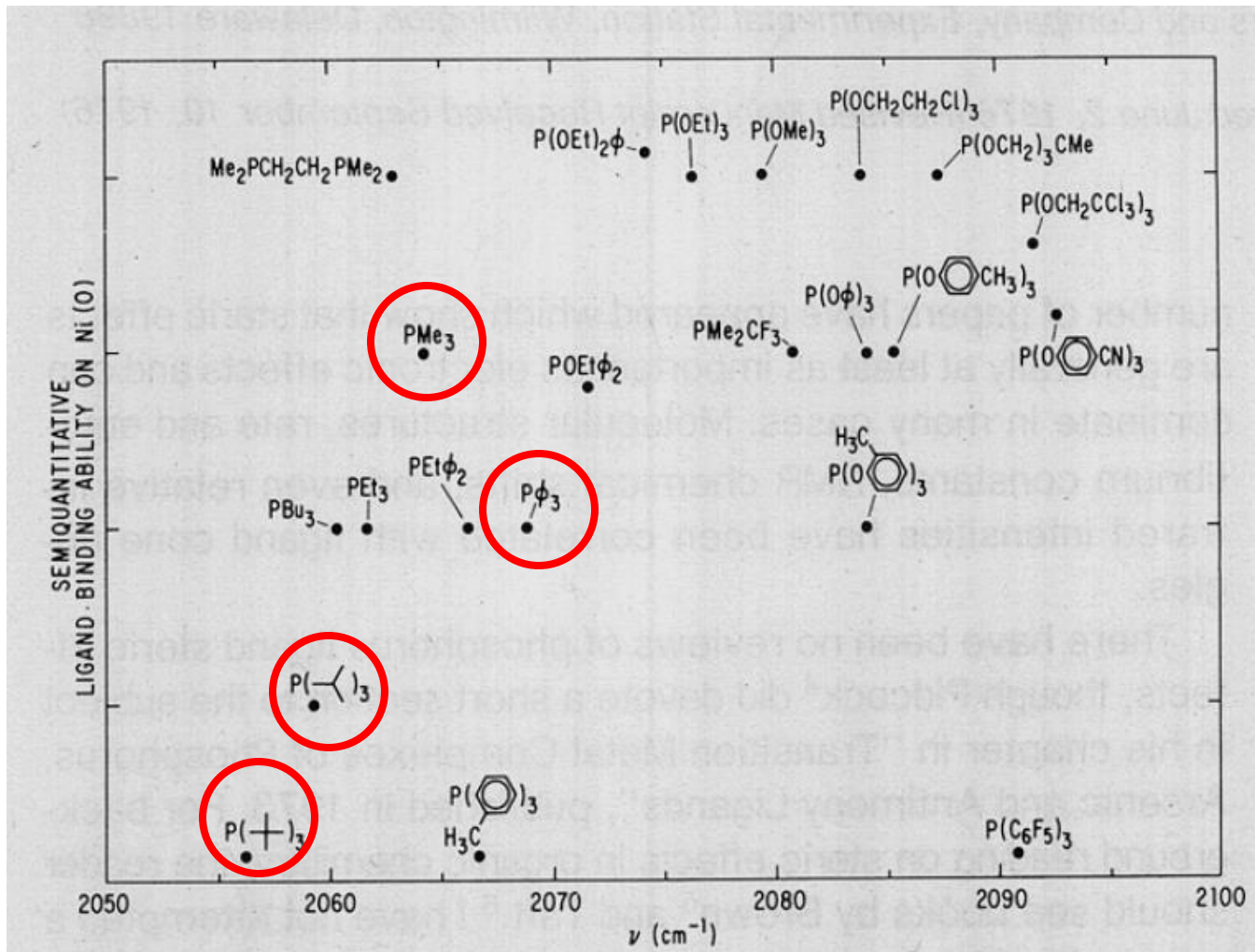
TABLE I. Selected Values of ν (cm^{-1})

L	ν	$\Delta\nu$
P(<i>p</i> -Tol) ₃	2066.7	0.1
P(<i>o</i> -Tol) ₃	2066.6	
PMe ₃	2064.1	2.4
PEt ₃	2061.7	2.5
P(<i>i</i> -Pr) ₃	2059.2	3.1
P(<i>t</i> -Bu) ₃	2056.1	

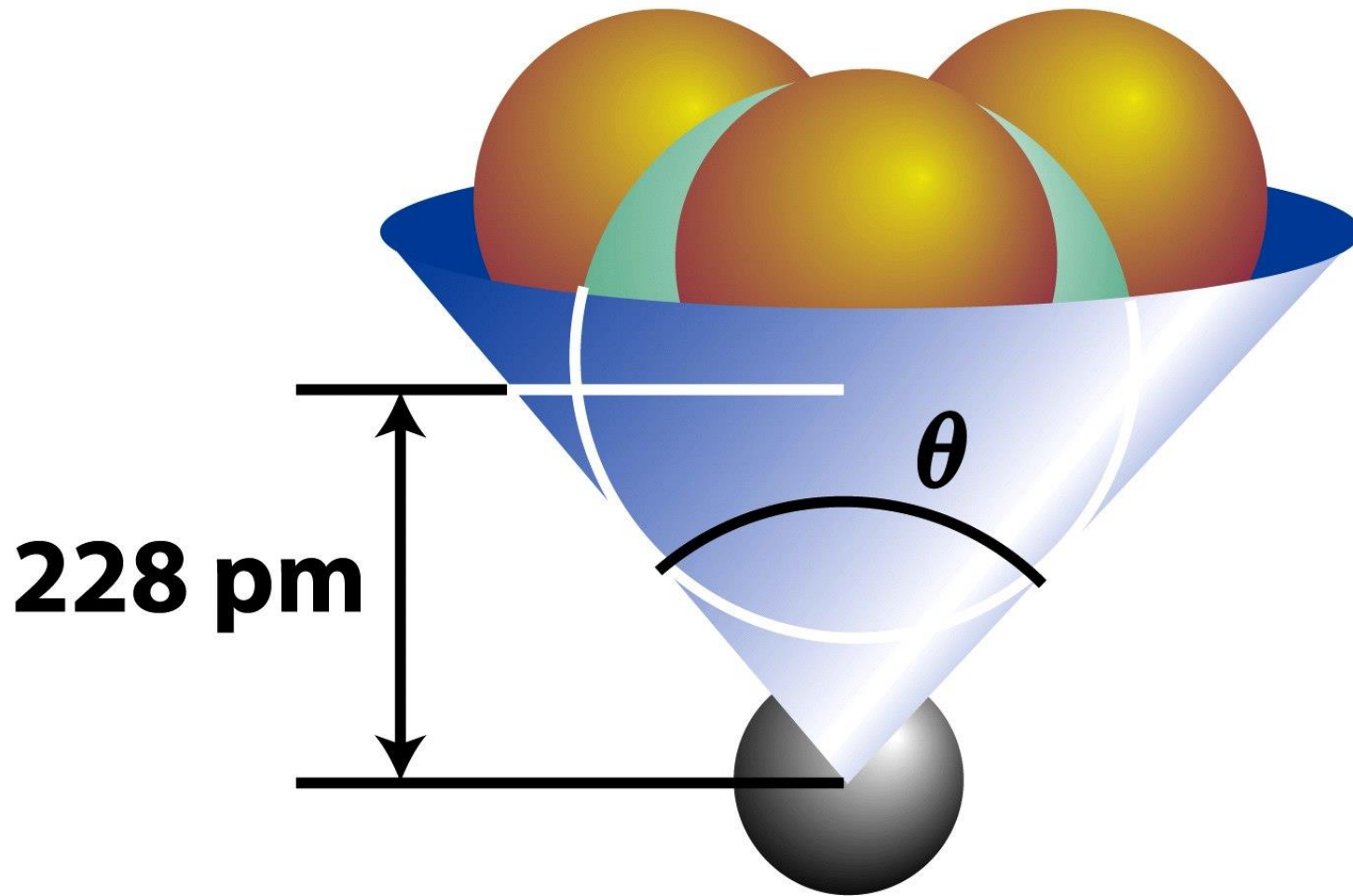
Basicità di Lewis delle fosfine

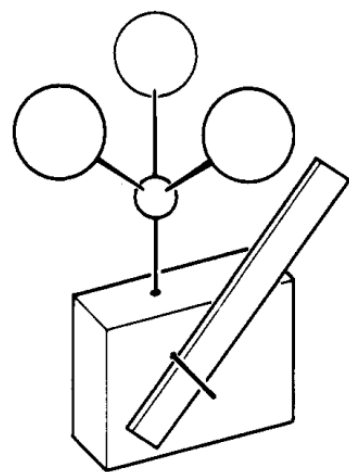
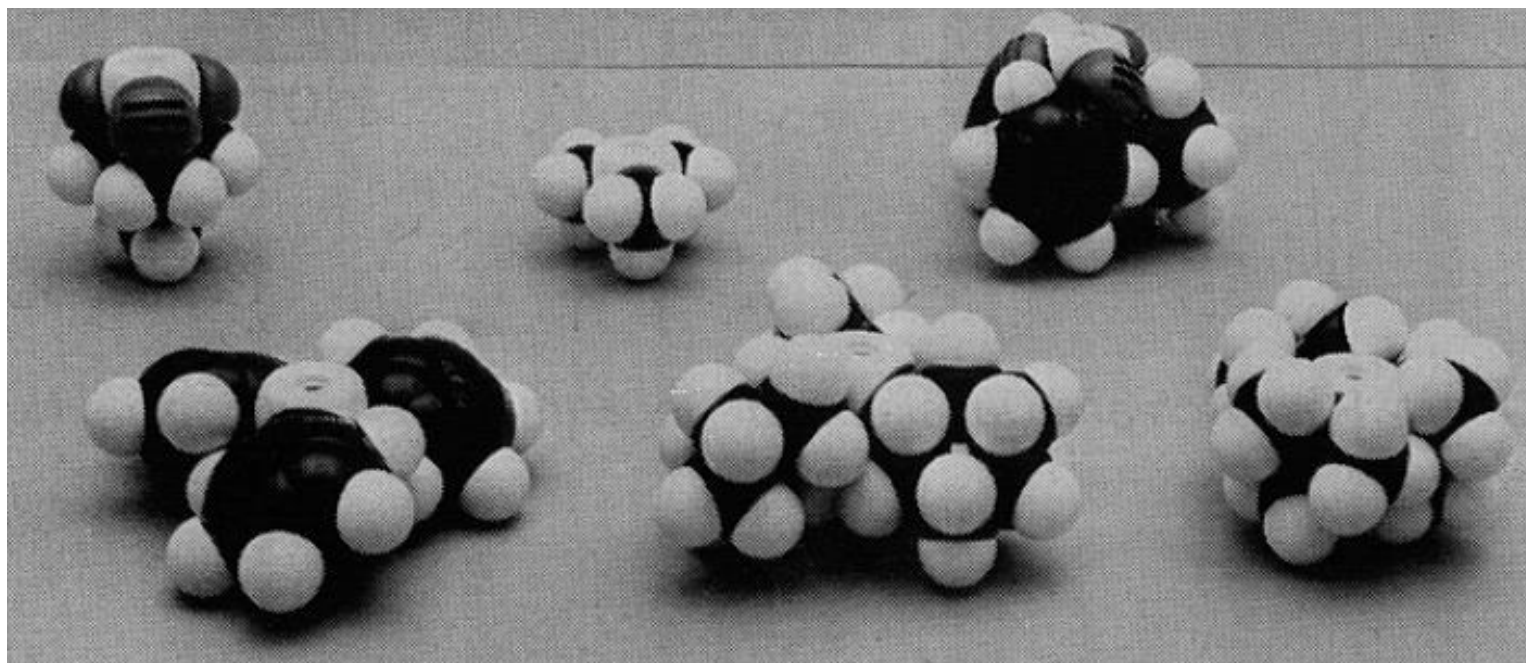


Necessità di introdurre un parametro sterico

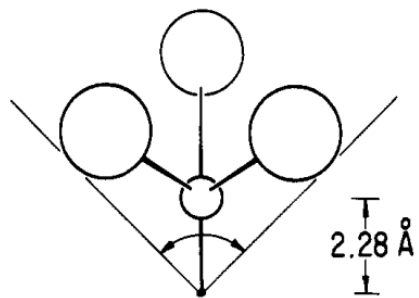


Angolo di cono di Tolman in $\text{Ni}(\text{CO})_3\text{L}$





(a)



(b)

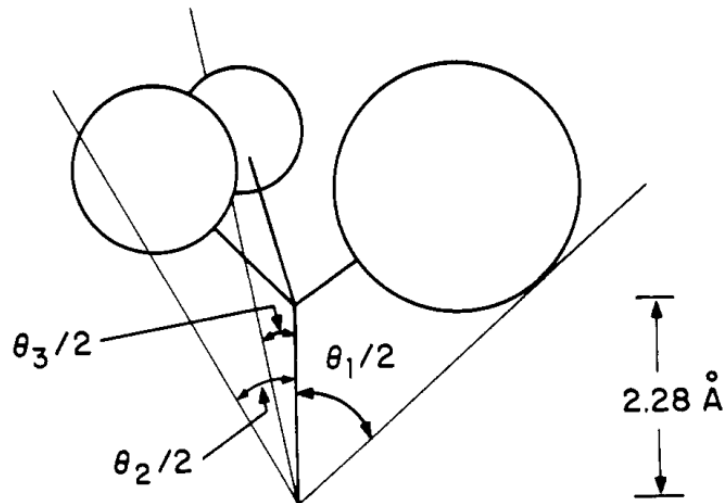


Table 21.4 Tolman cone angles (in degrees) for selected phosphines

PF_3	104
$\text{P}(\text{OMe})_3$	107
PMe_3	118
PCl_3	125
$\text{P}(\text{OPh})_3$	127
PEt_3	132
PPh_3	145
PCy_3	169
P^tBu_3	182
$\text{P}(o\text{-tol})_3$	193

TEP vs cone angle

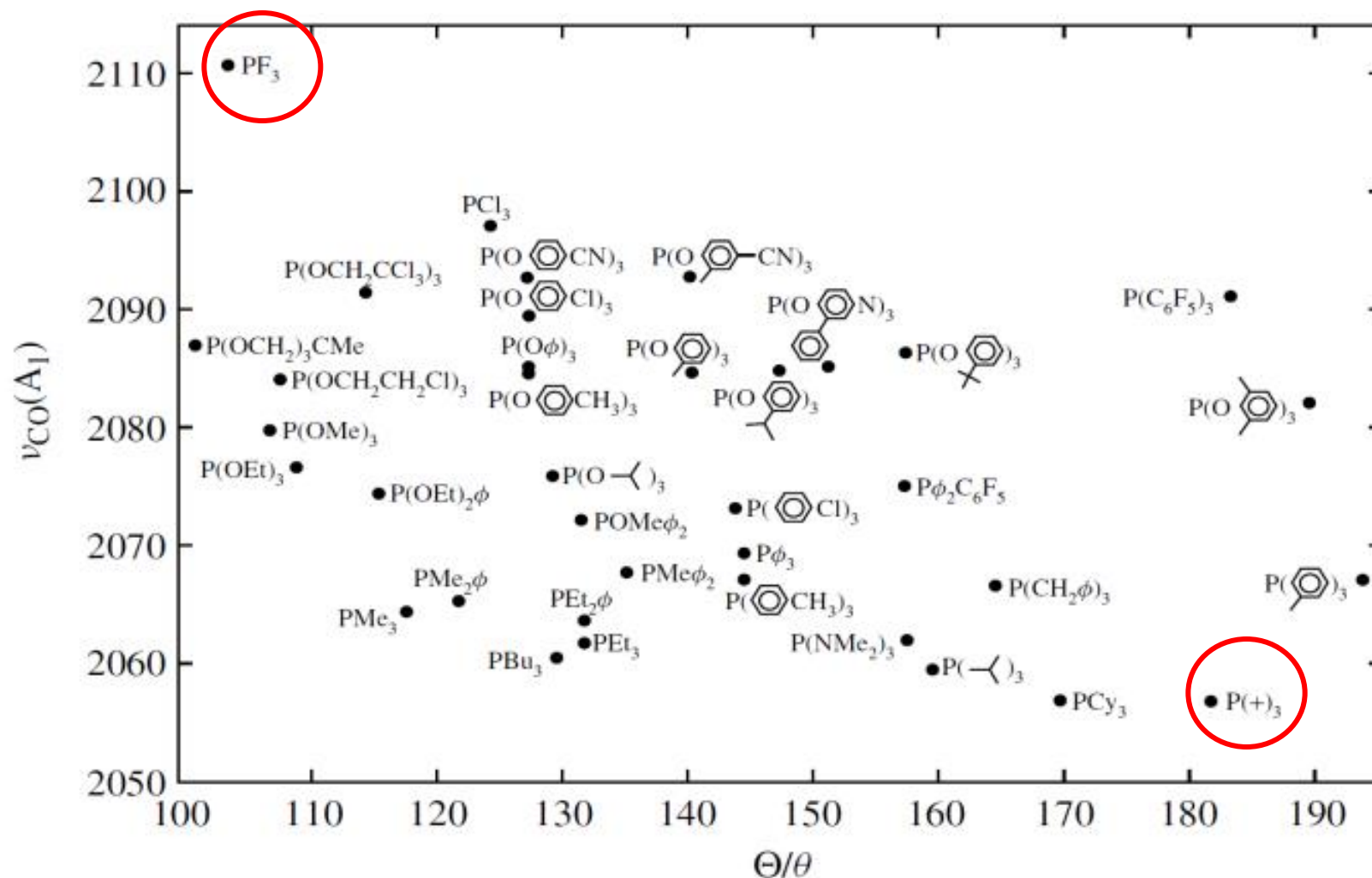


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1} , θ in degrees).

Idruri (1931)



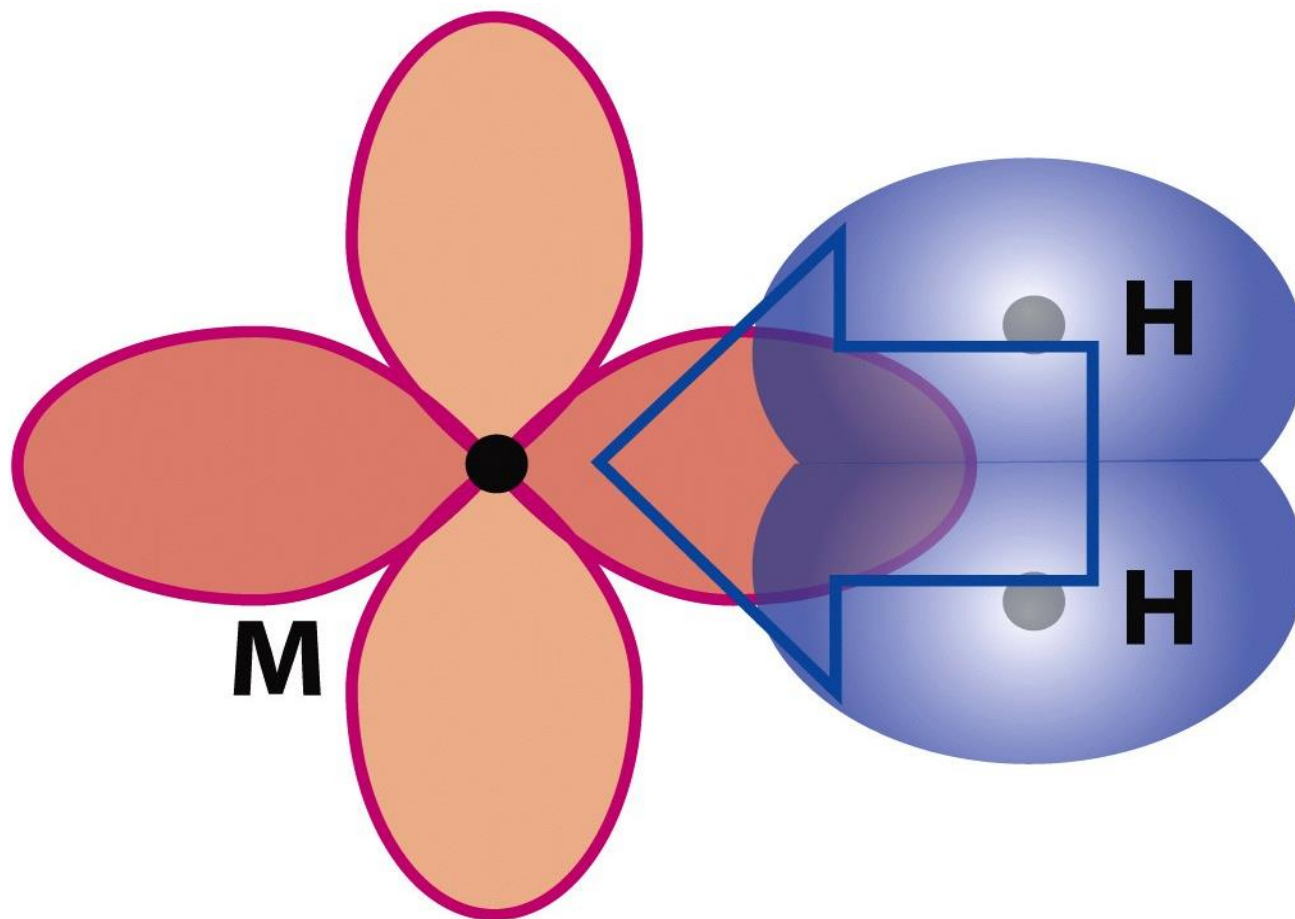
$$\text{pK}_a = 8.3$$

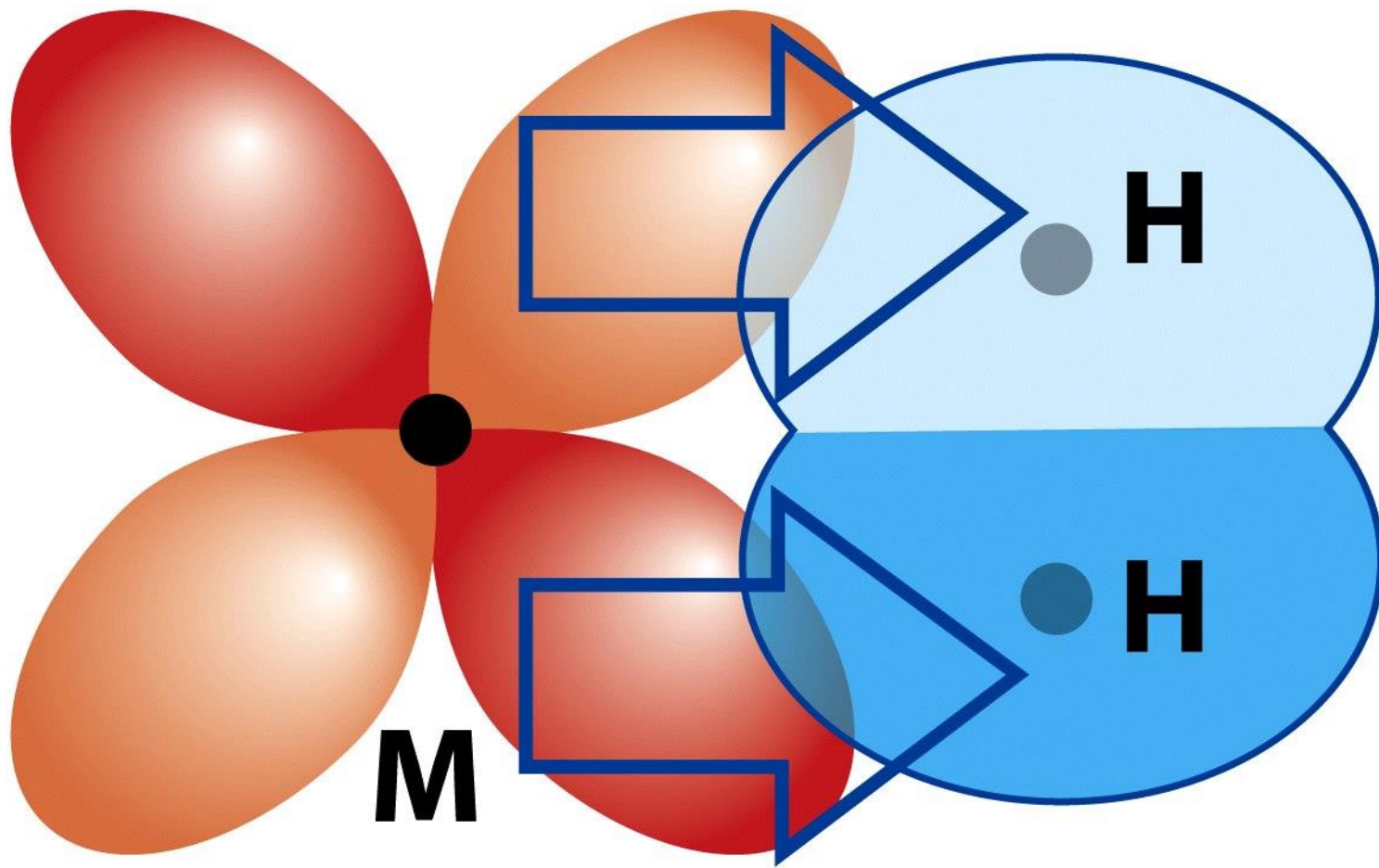
^1H NMR: $-50 < \delta < 0$

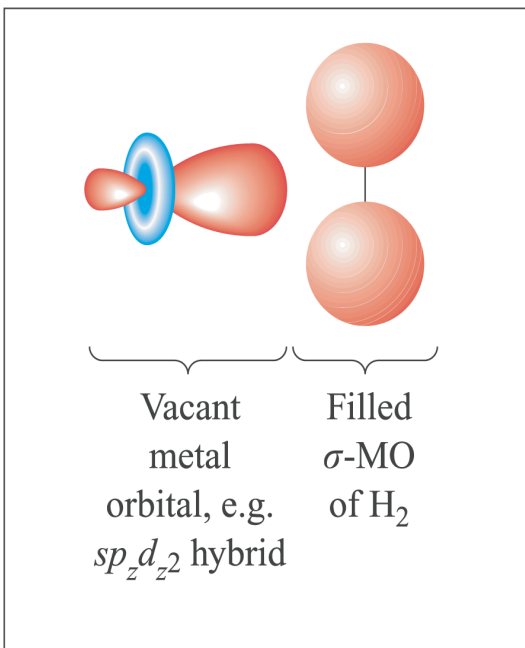
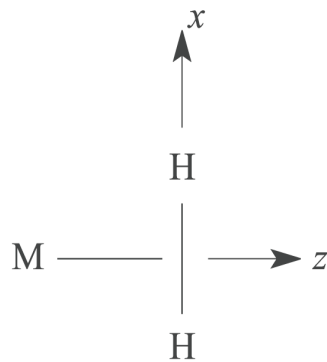
IR: $2250 - 1500 \text{ cm}^{-1}$

Diffrazione di neutroni (struttura)

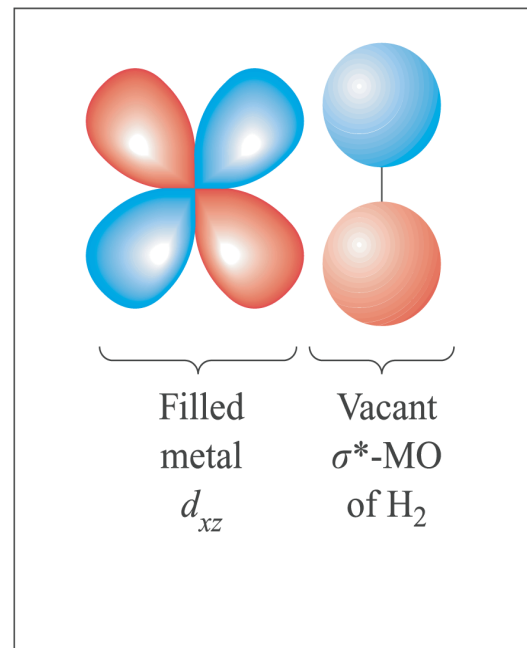
Coordinazione H_2 (1984): *side-on* (tipicamente su ioni d^6 basso-spin)



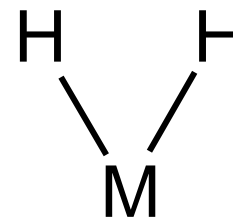
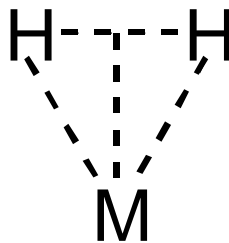
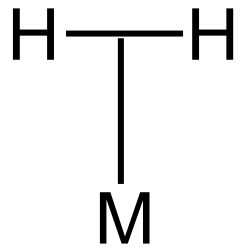




H_2 -to-M donation
(a)



M-to- H_2 back-donation
(b)



Addizione ossidativa

NMR: $-10 < \delta < 0$

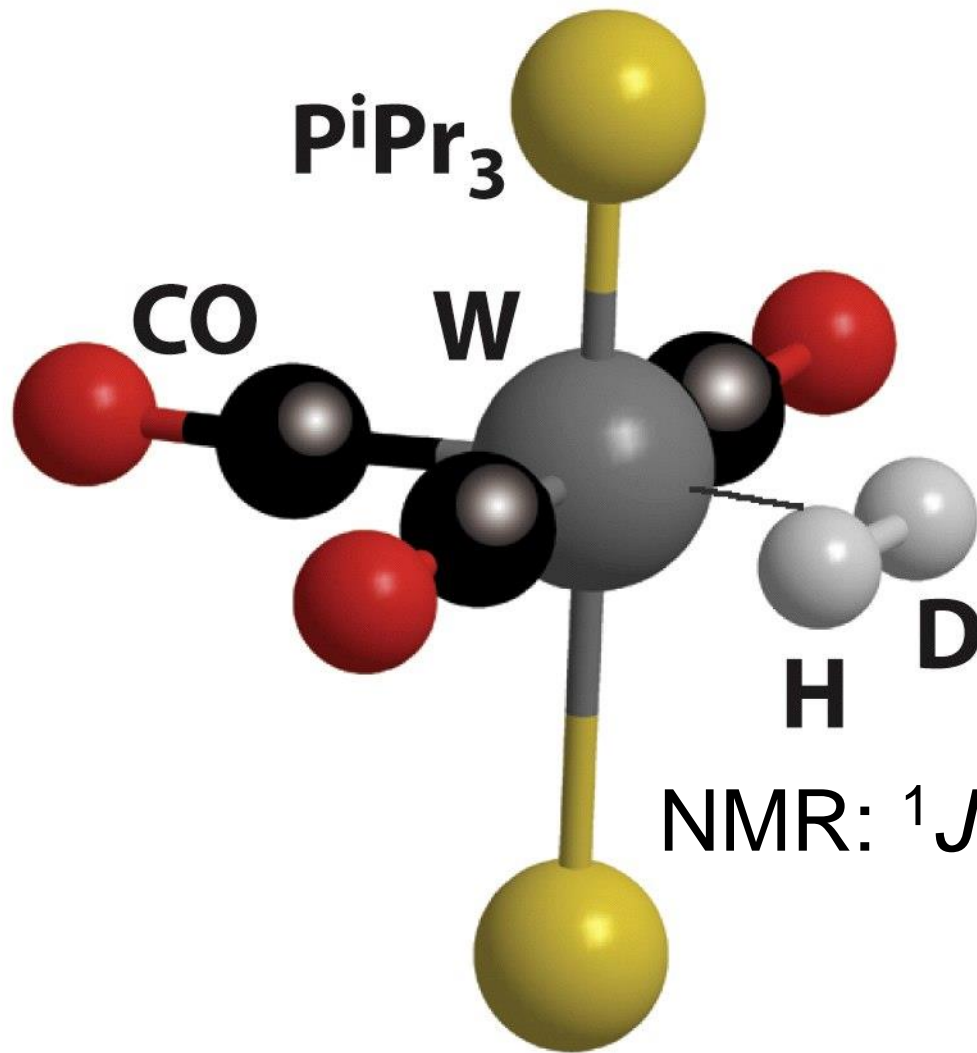
$^1J_{\text{HD}} = 20 - 34 \text{ Hz}$

IR: H-H $2900 - 2300 \text{ cm}^{-1}$

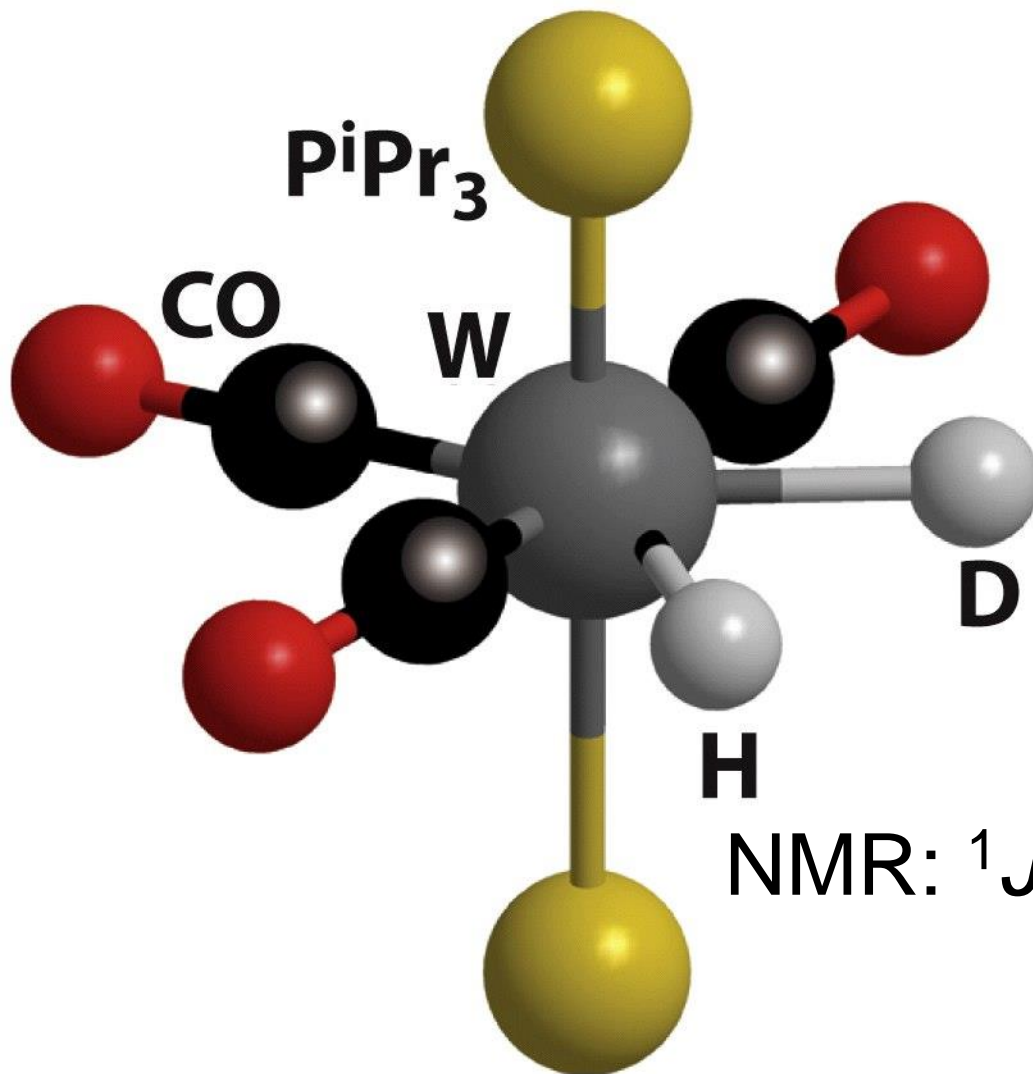
NMR: $-50 < \delta < 0$

$^1J_{\text{HD}} = \sim 1 \text{ Hz}$

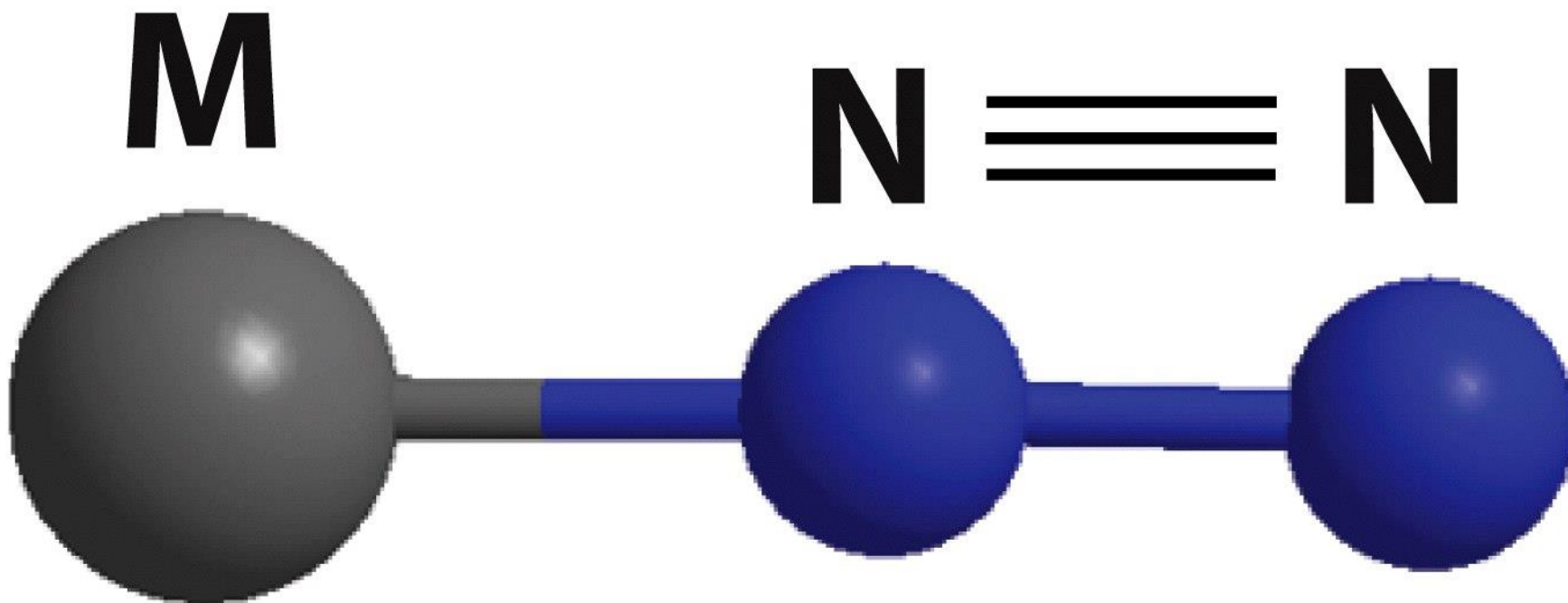
IR: M-H $2200 - 1500 \text{ cm}^{-1}$



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

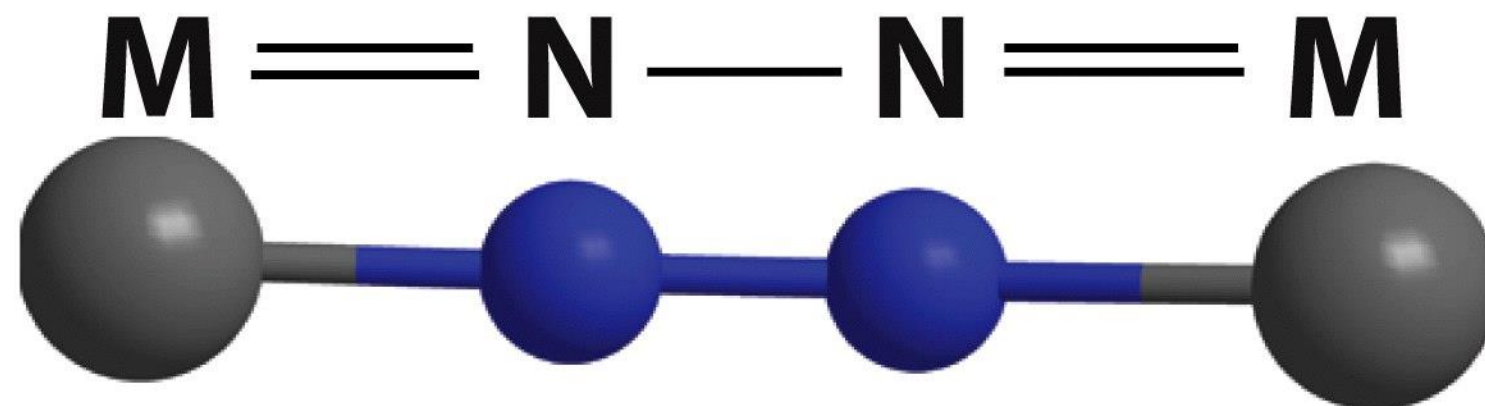
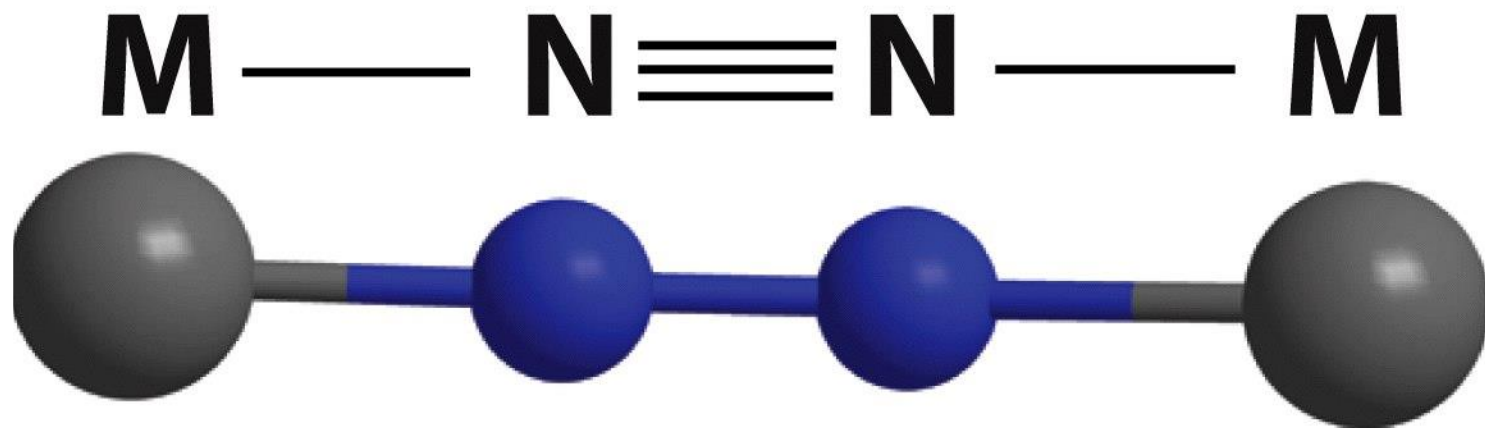


NMR: $^1J_{\text{HD}} < 2 \text{ Hz}$

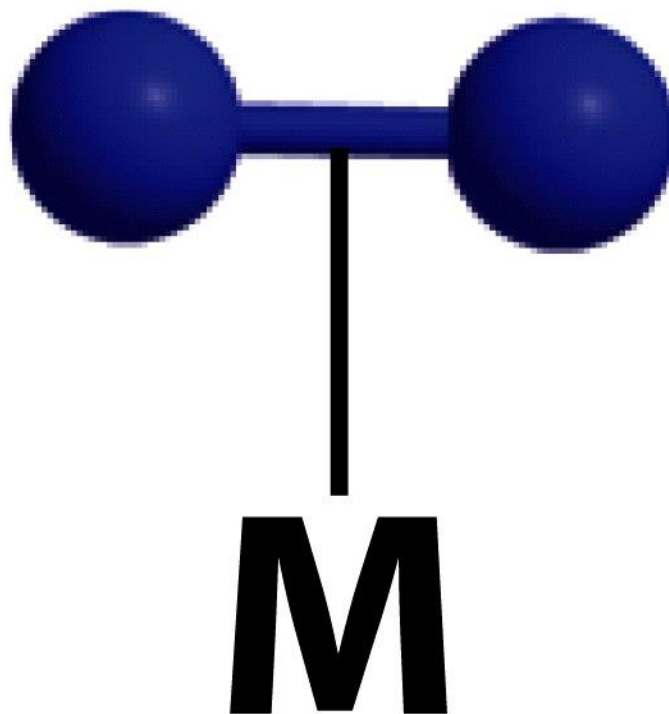


End-on (η^1)
(più comune)

IR: N–N 2150 – 1900 cm^{-1}

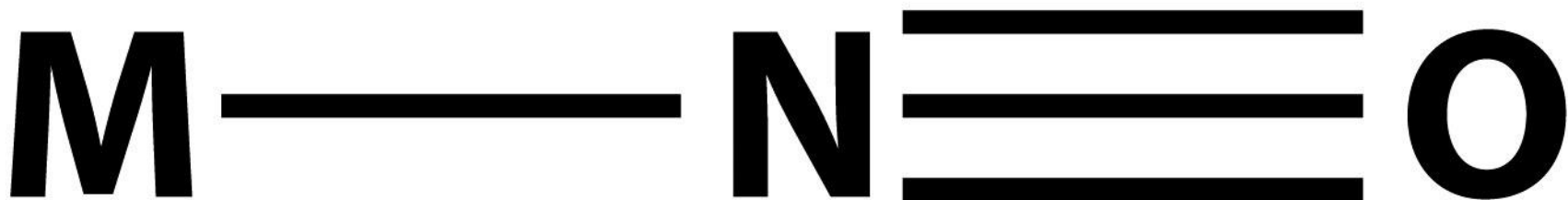


«idrazina»



Side-on (η^2)
(più raro)

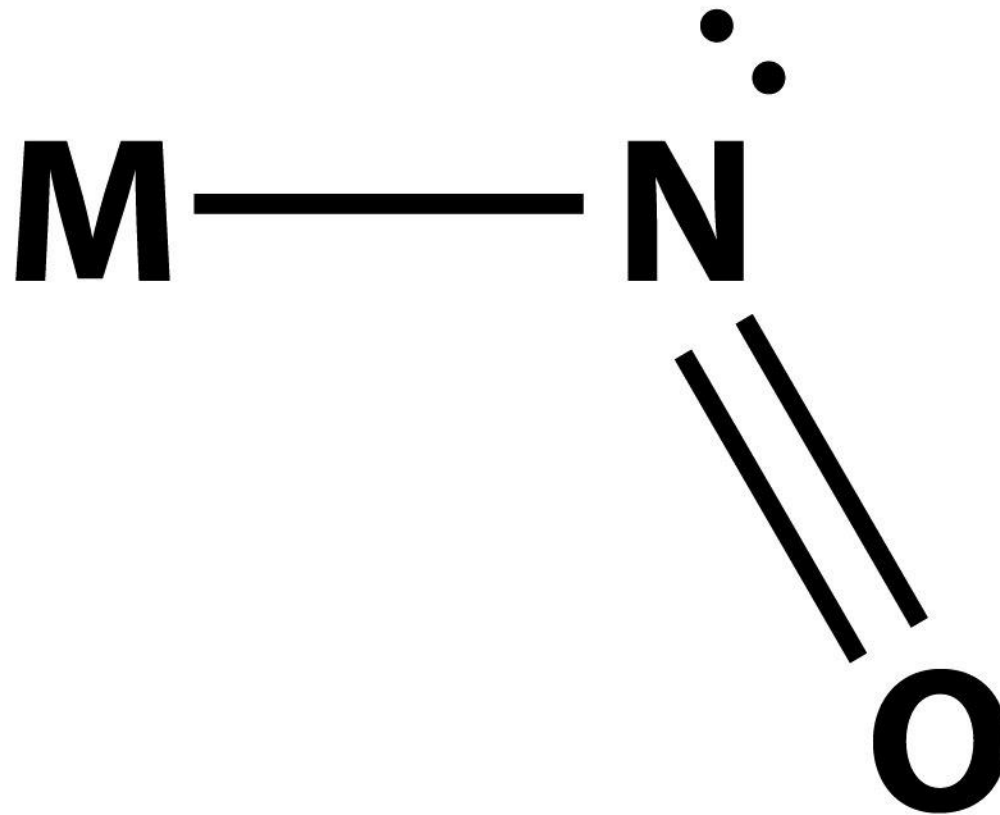
Nitrosile



Lineare: formalmente NO^+

Isoelettronico a CO

Donatore di $2e^-$, forte π -accettore



Piegato: formalmente NO^-
Donatore di $2e^-$, solo σ -donatore

Passando da NO^+ a NO^- , il metallo coordinato perde formalmente 2 elettroni