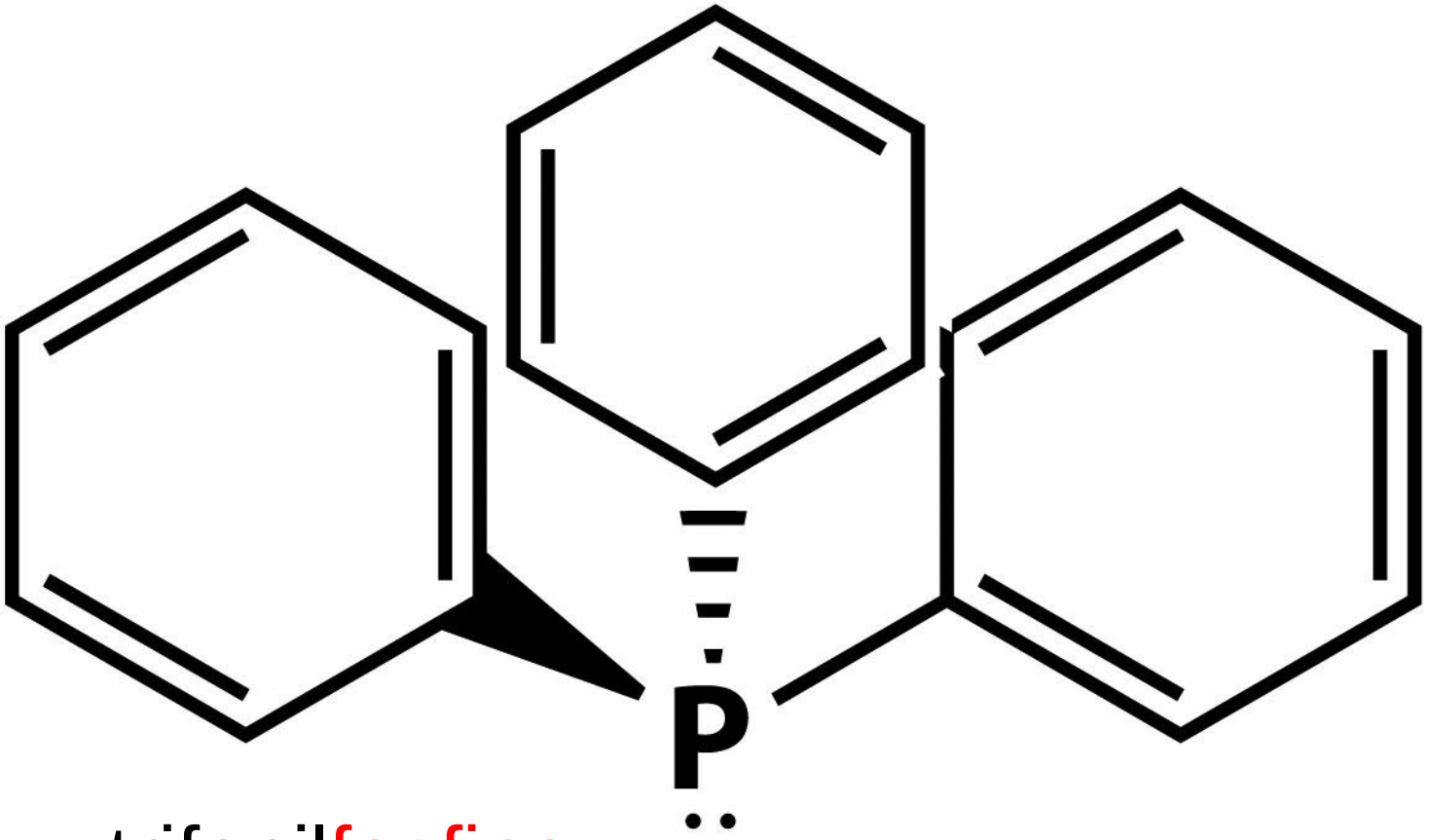
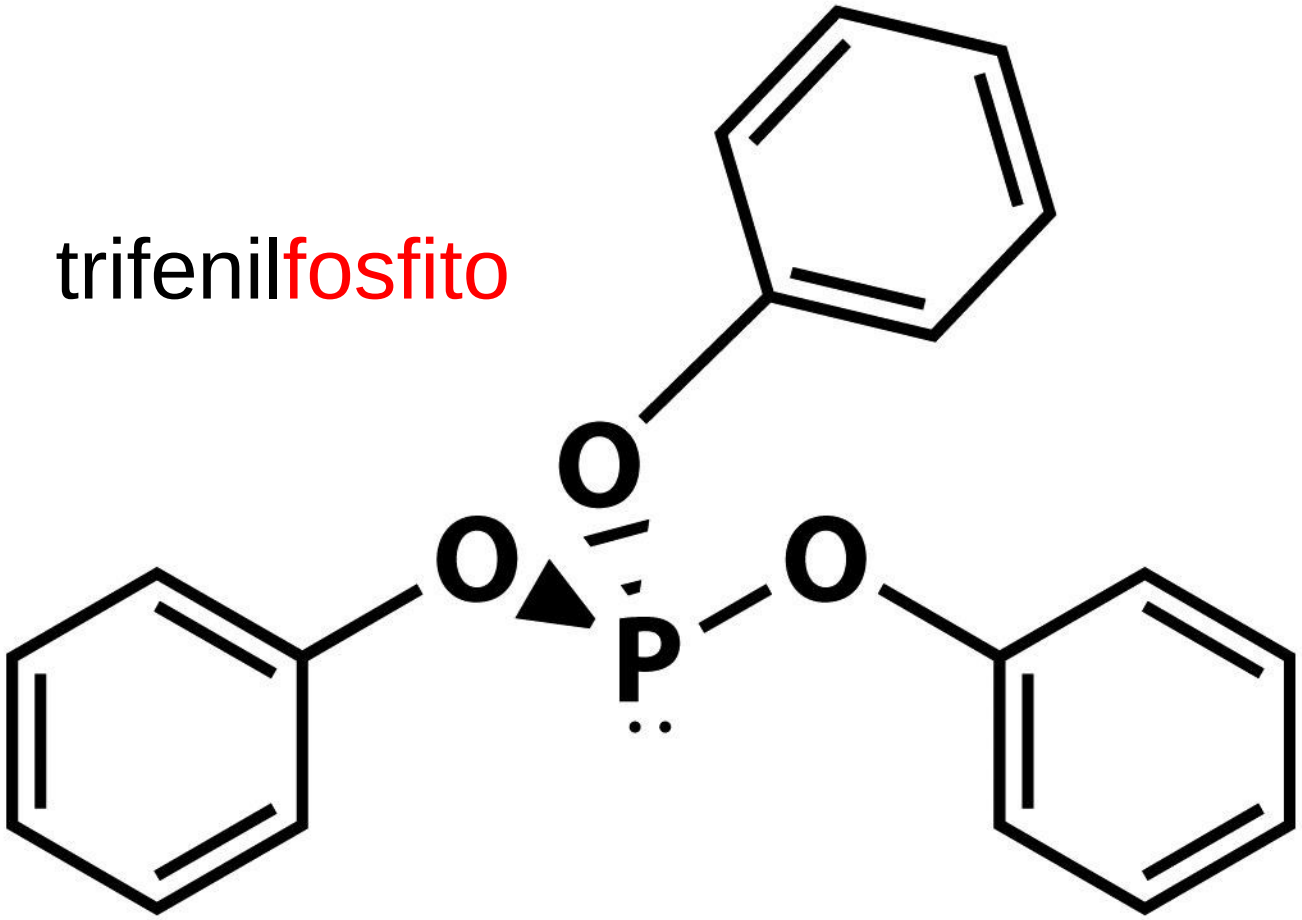


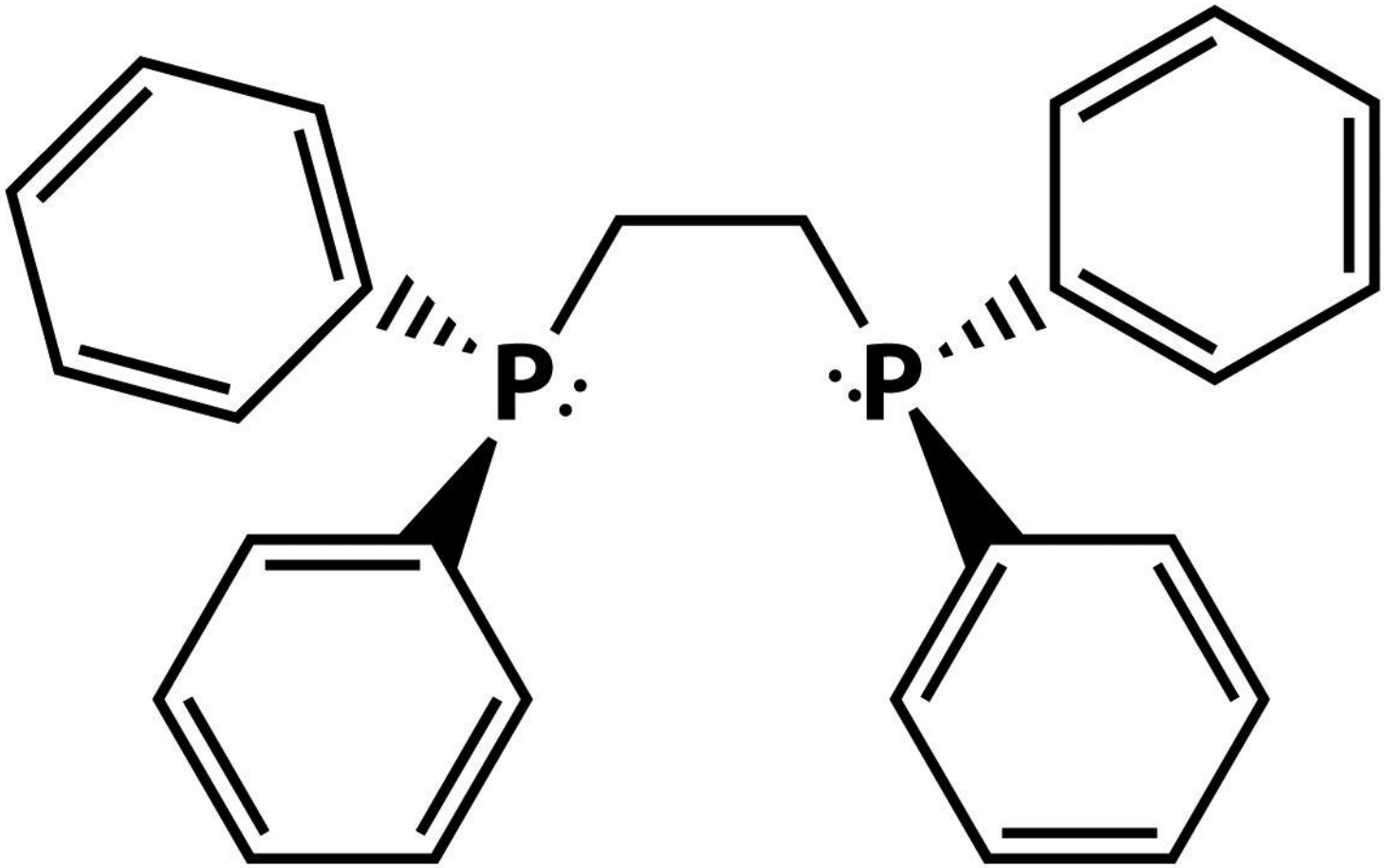
trifenilfosfina

PPh_3

trifenilfosfito

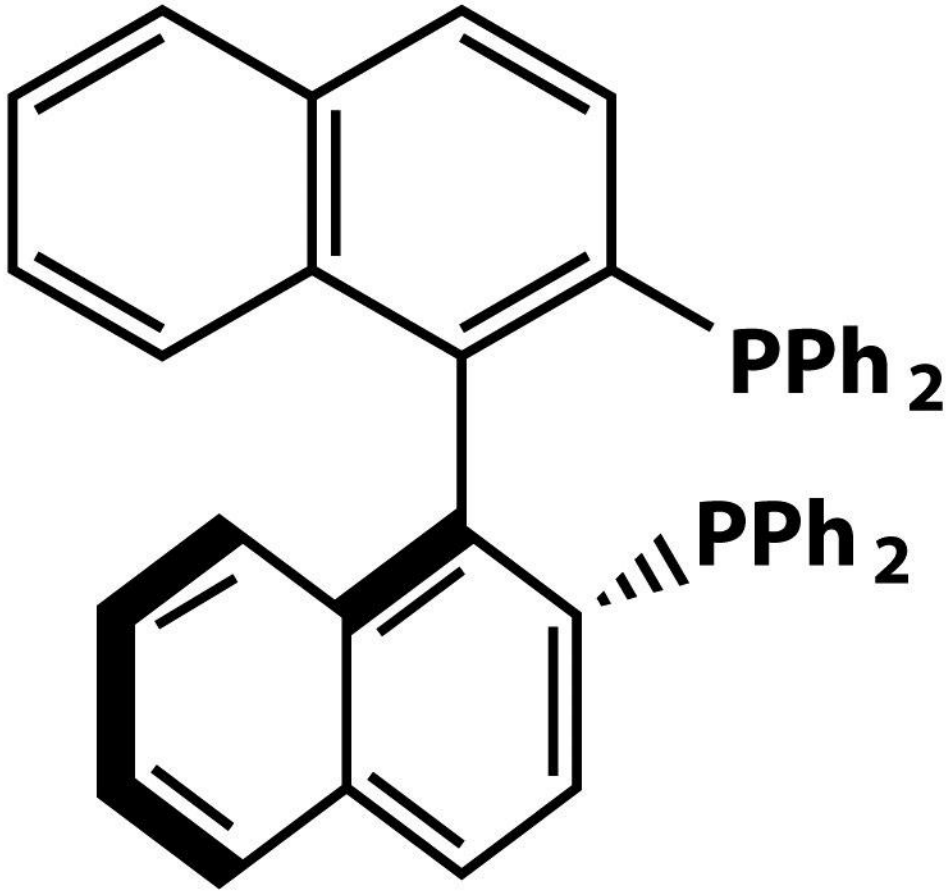


$P(OPh)_3$

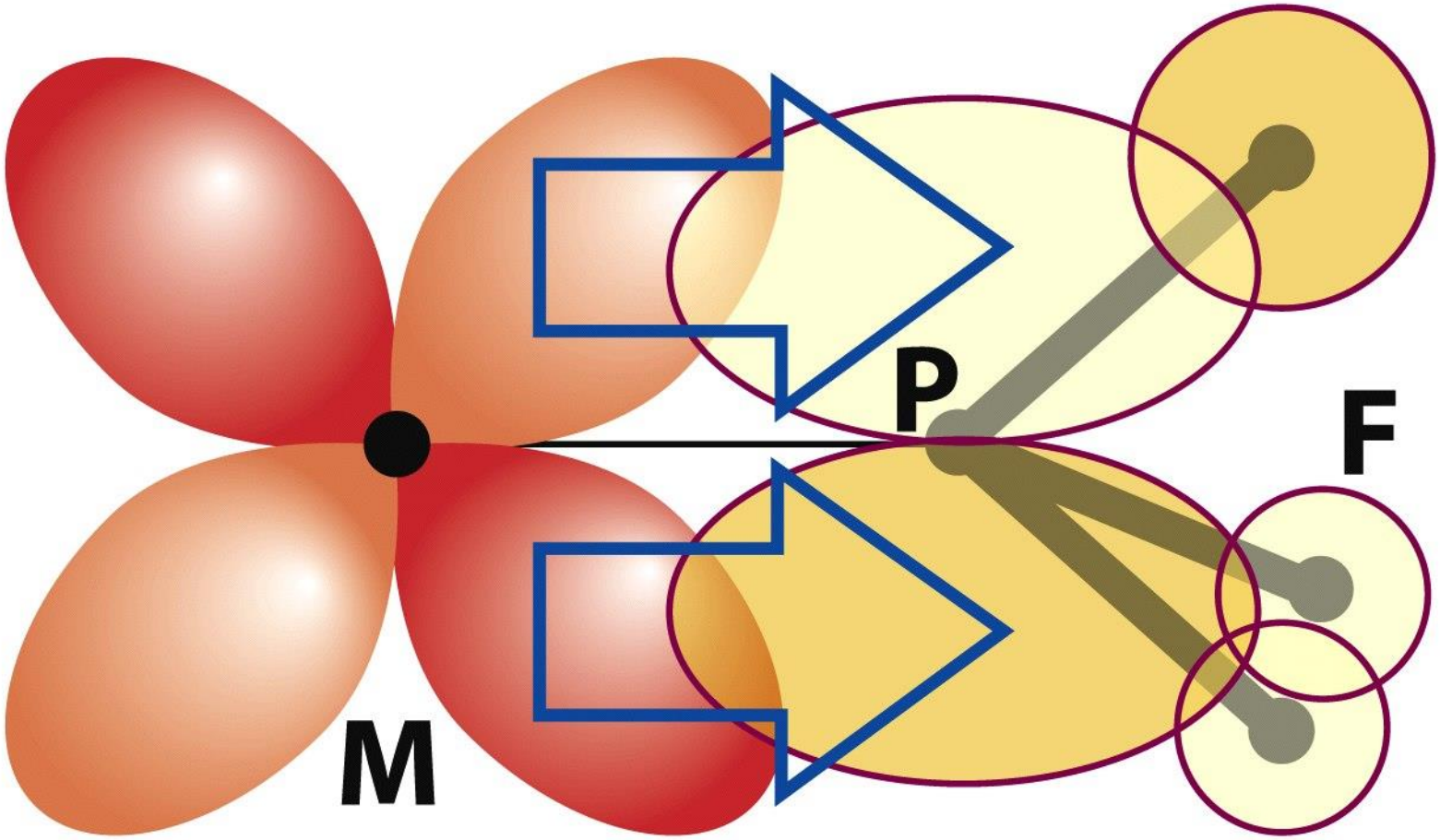


$Ph_2PCH_2CH_2PPh_2$, dppe

difenilfosfinoetano



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



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

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	$\Delta\nu$
$P(p\text{-Tol})_3$	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	

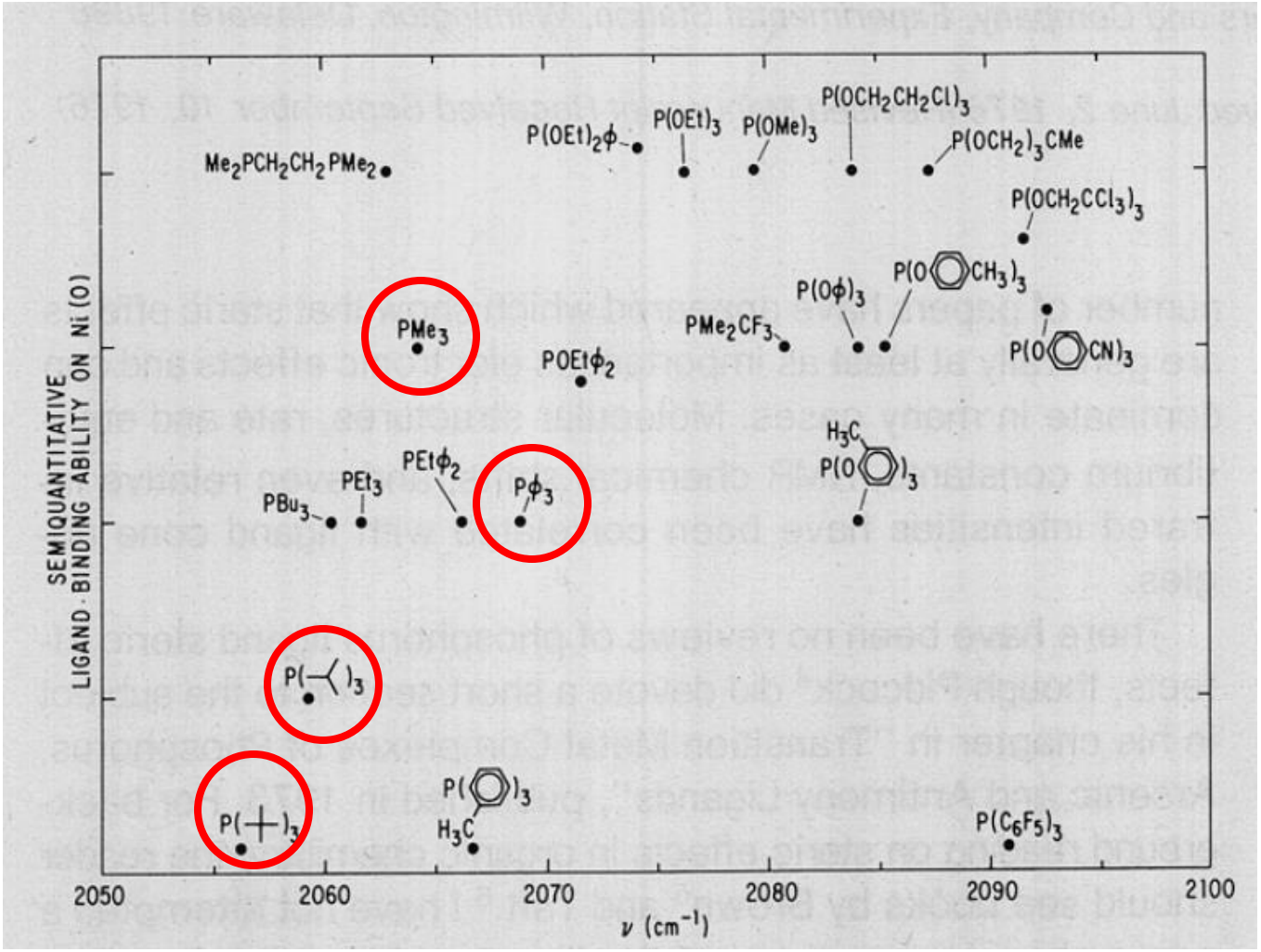
Basicità di Lewis delle fosfine

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

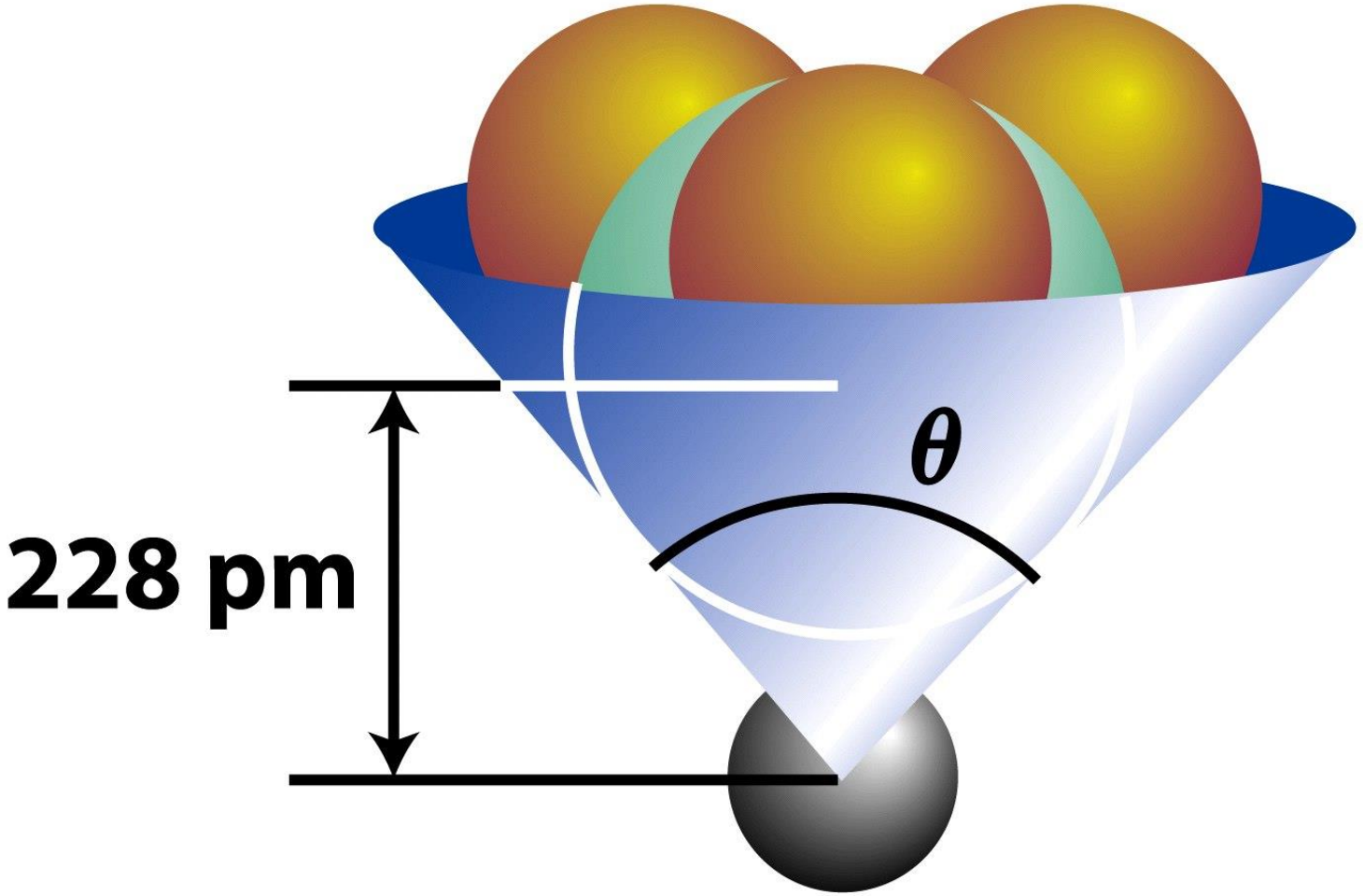
$[Cr(CO)_5(PEt_3)]$ *vs* $[Cr(CO)_5(PPh_3)]$

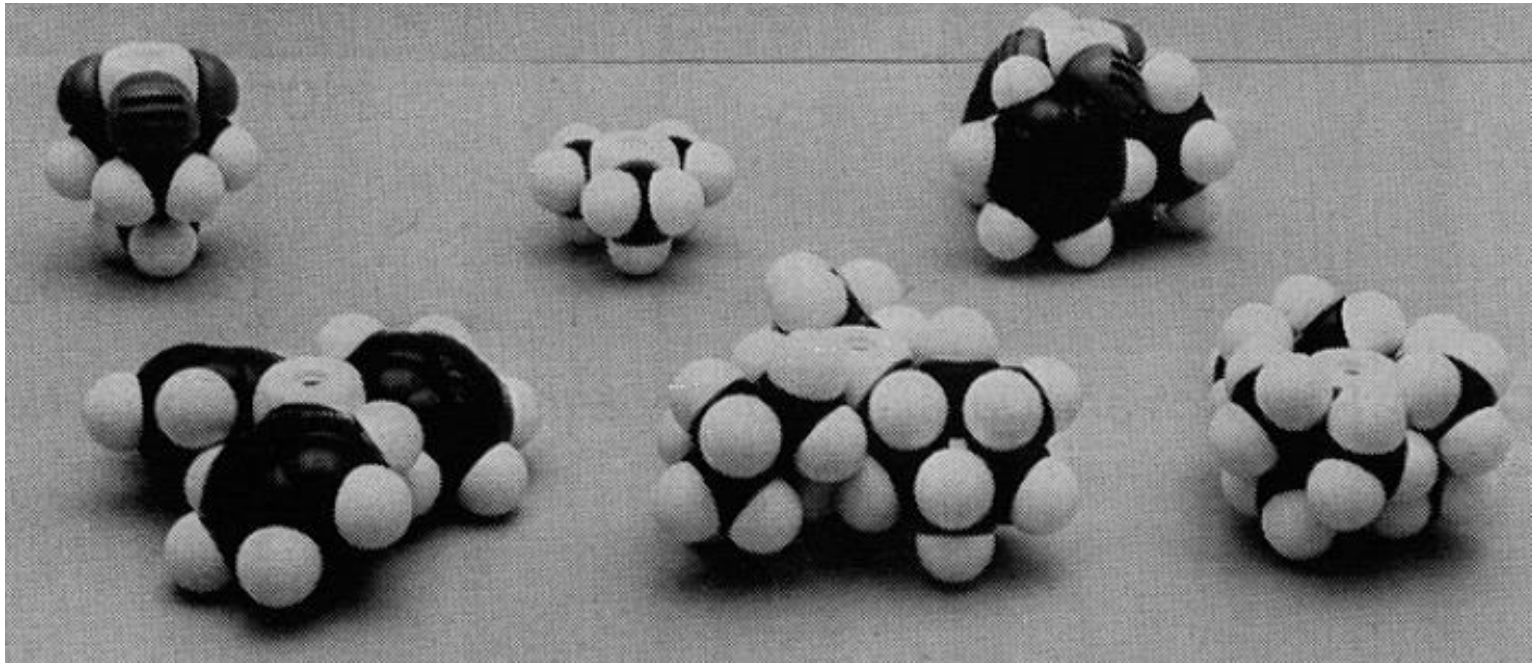
$Fe(CO)_5$ *vs* $[Fe(CO)_4(PEt_3)]$

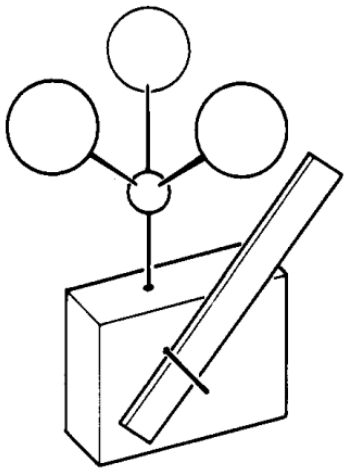
Necessità di introdurre un parametro sterico



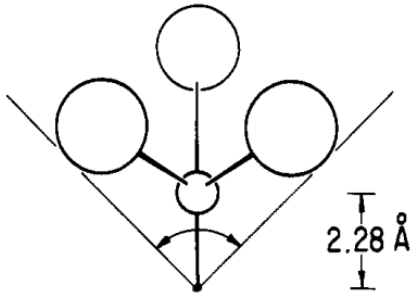
Angolo di cono di Tolman in $Ni(CO)_3L$







(a)



(b)

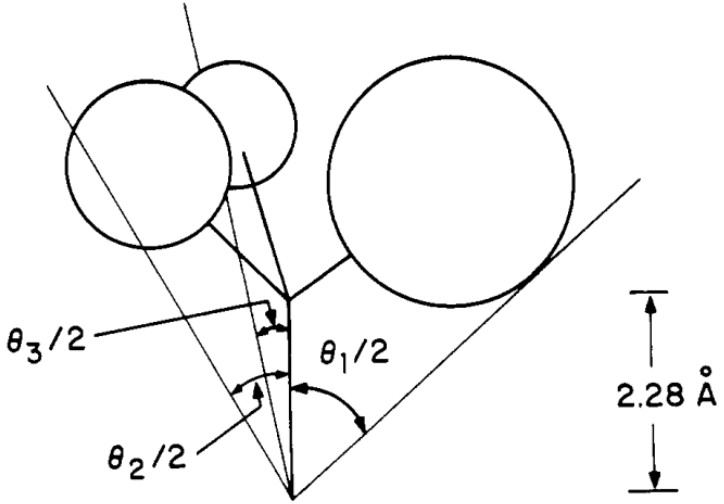


Table 21.4 Tolman cone angles (in degrees) for selected phosphines

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^tBu_3	182
$P(o\text{-tol})_3$	193

TEP *vs* cone angle

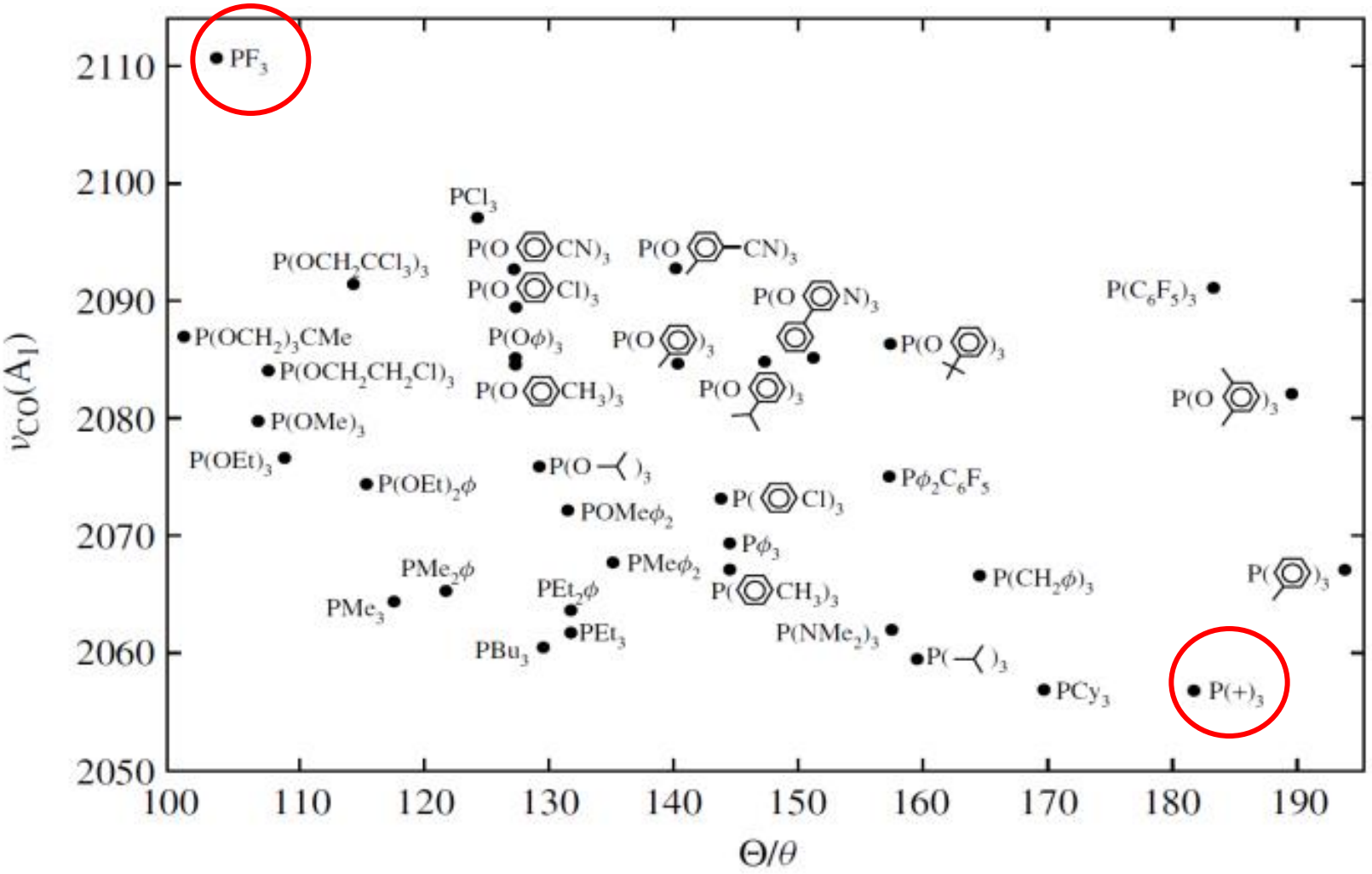


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1}, θ in degrees).

Idruri (1931)

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

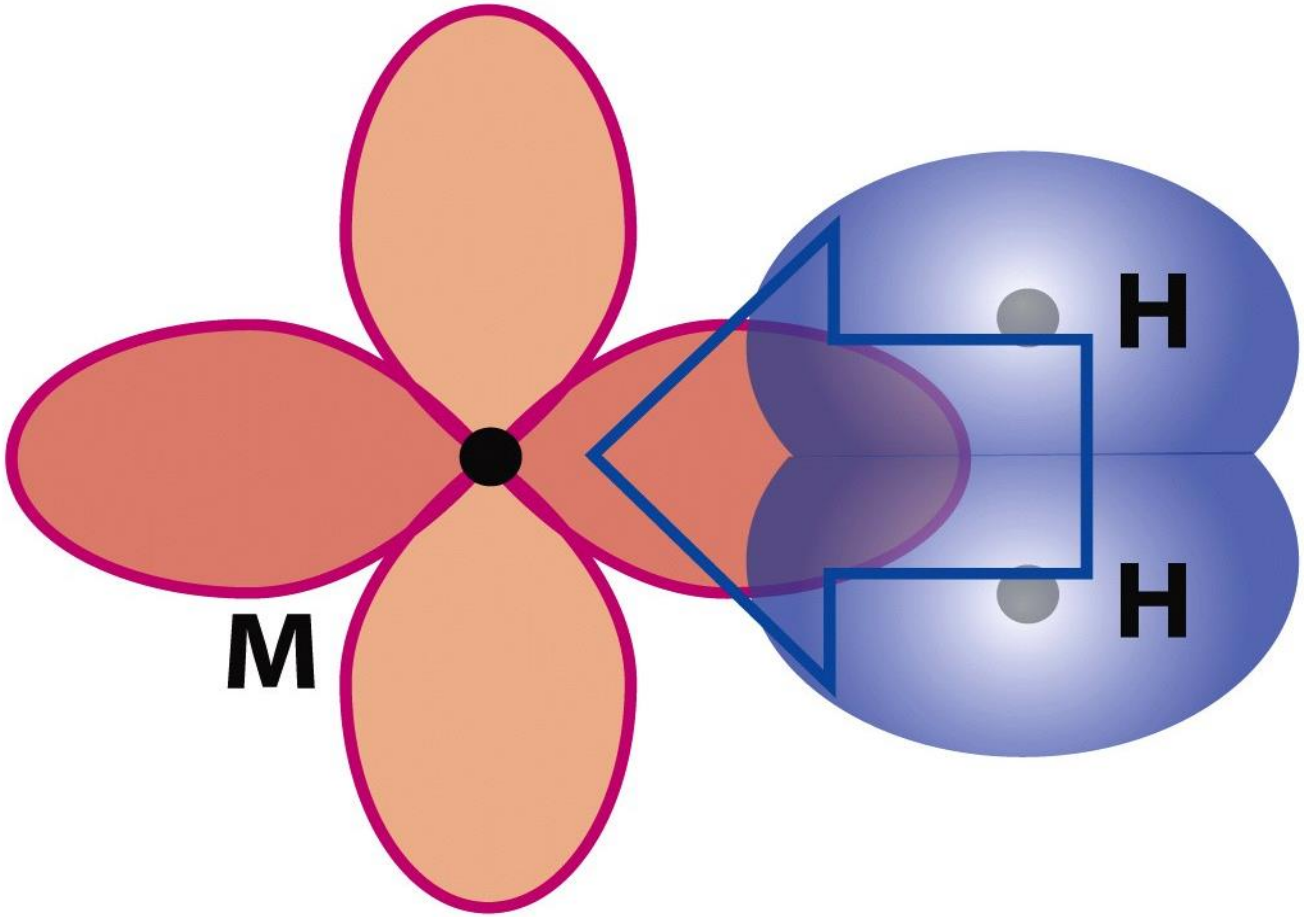
$pK_a = 8.3$

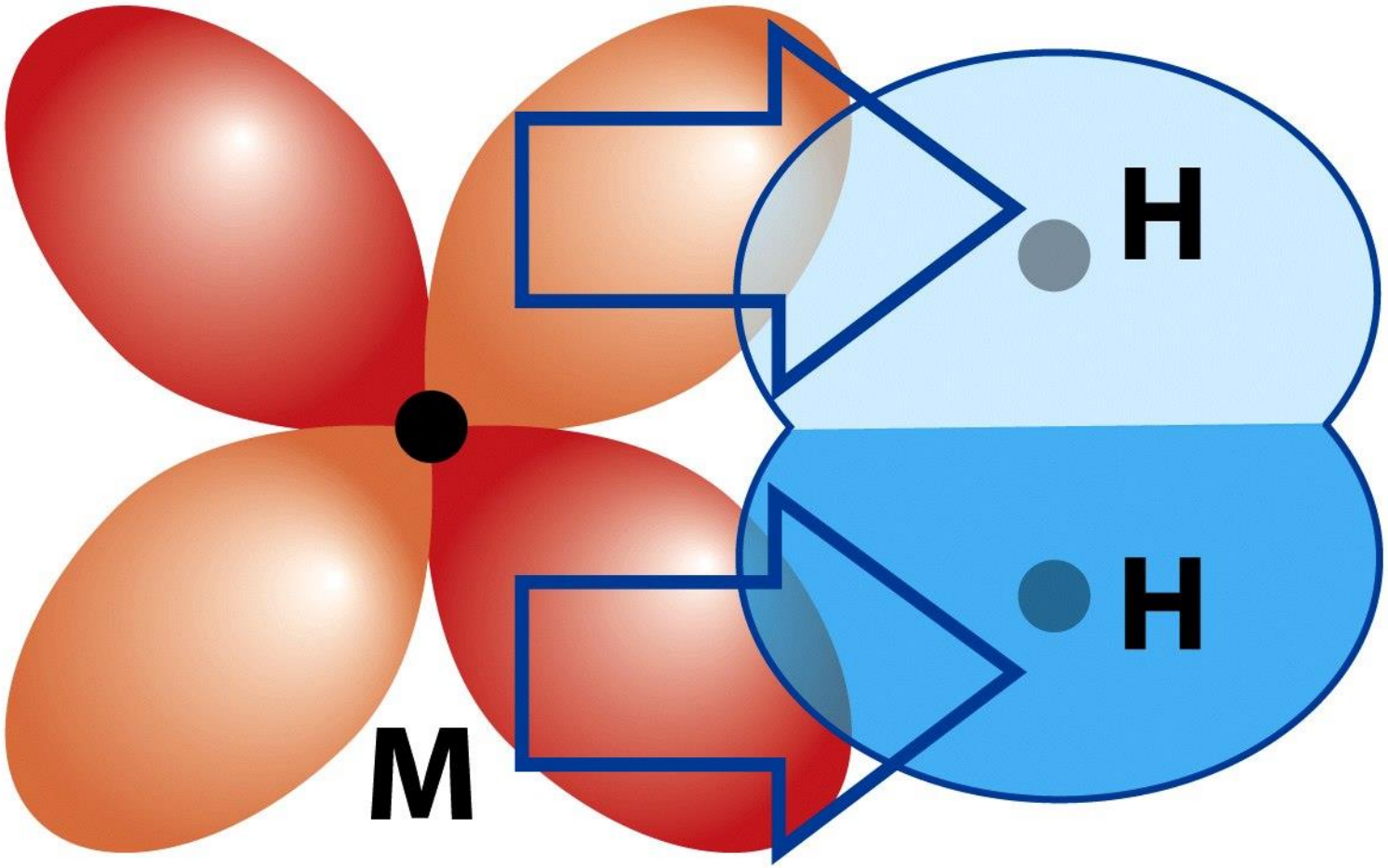
^1H NMR: $-50 < \delta < 0$

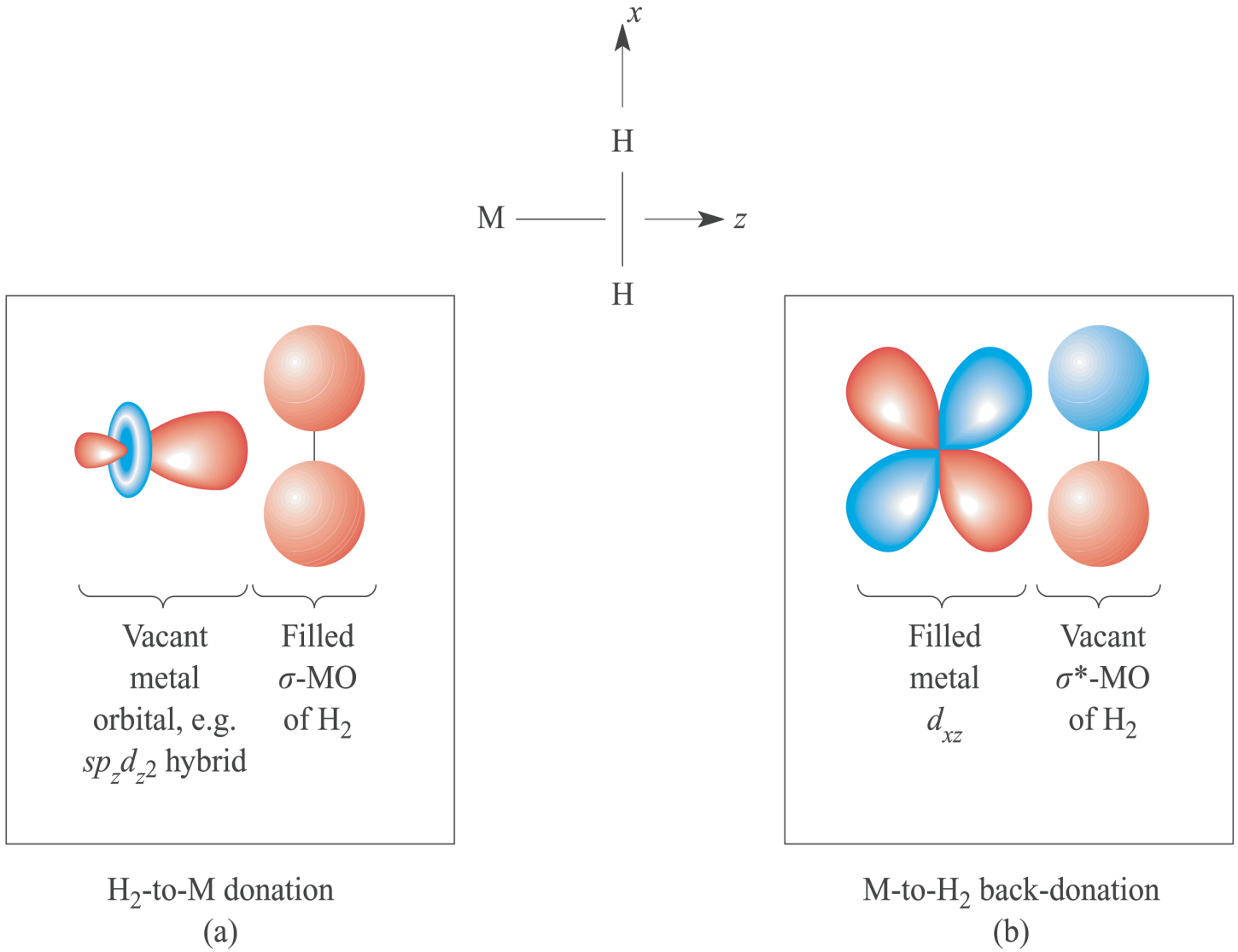
IR: 2250 – 1500 cm^{-1}

Diffrazione di neutroni (struttura)

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



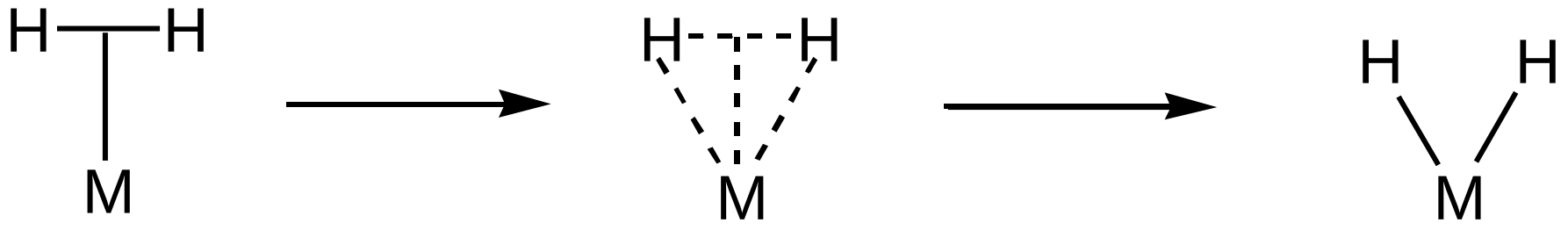

H
H
M



H_2-to-M donation
(a)

M-to-H_2 back-donation
(b)

Addizione ossidativa



NMR: $-10 < \delta < 0$

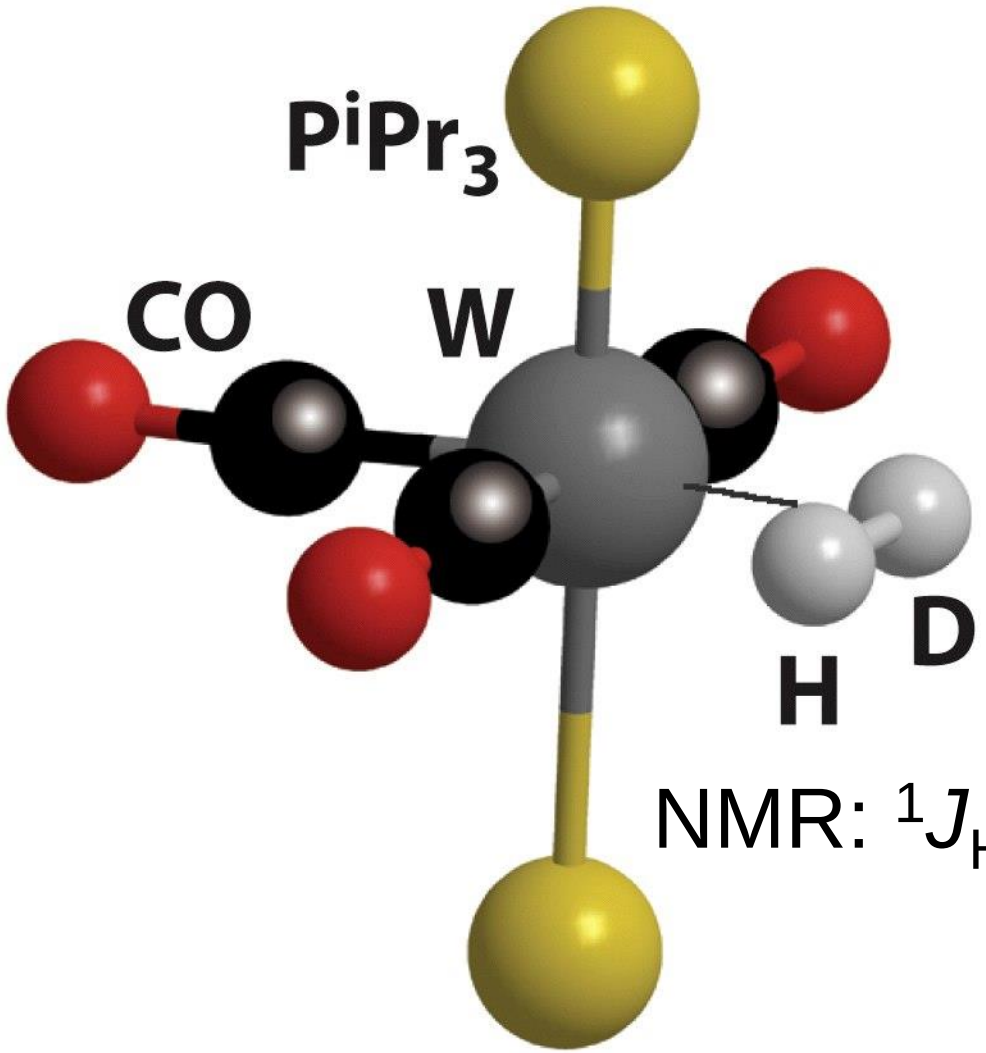
$^{1}J_{HD}$ = 20 – 34 Hz

IR: H–H 2900 – 2300 cm^{-1}

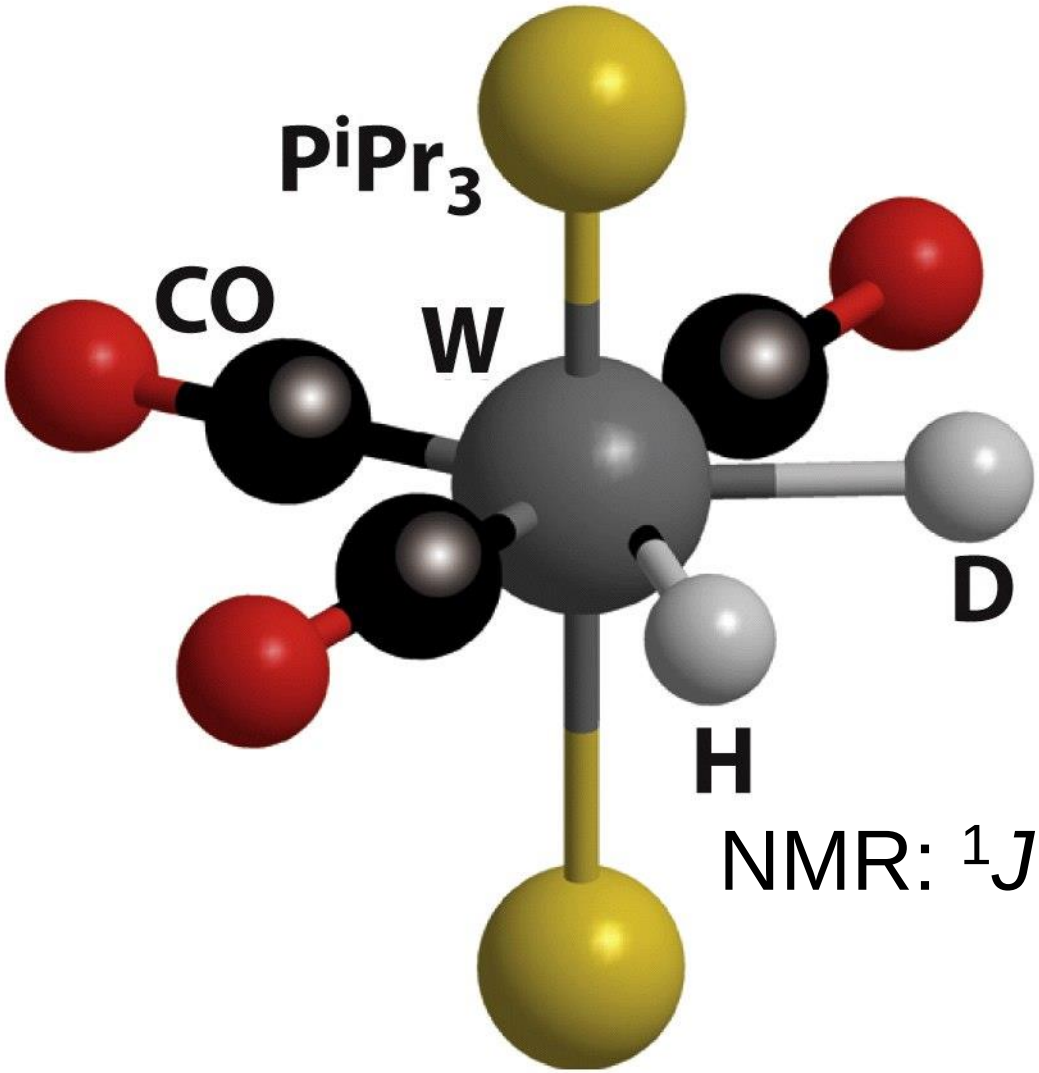
NMR: $-50 < \delta < 0$

$^{1}J_{HD}$ = ~1Hz

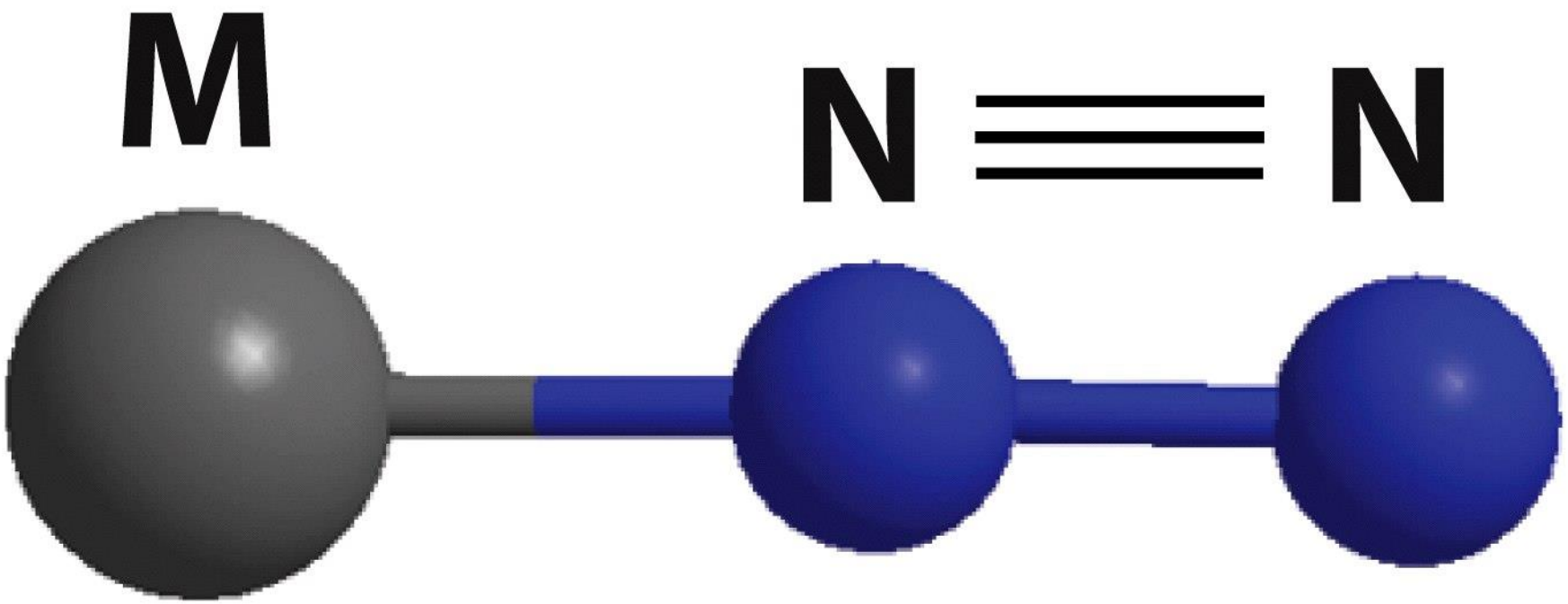
IR: M–H 2200 – 1500 cm^{-1}



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

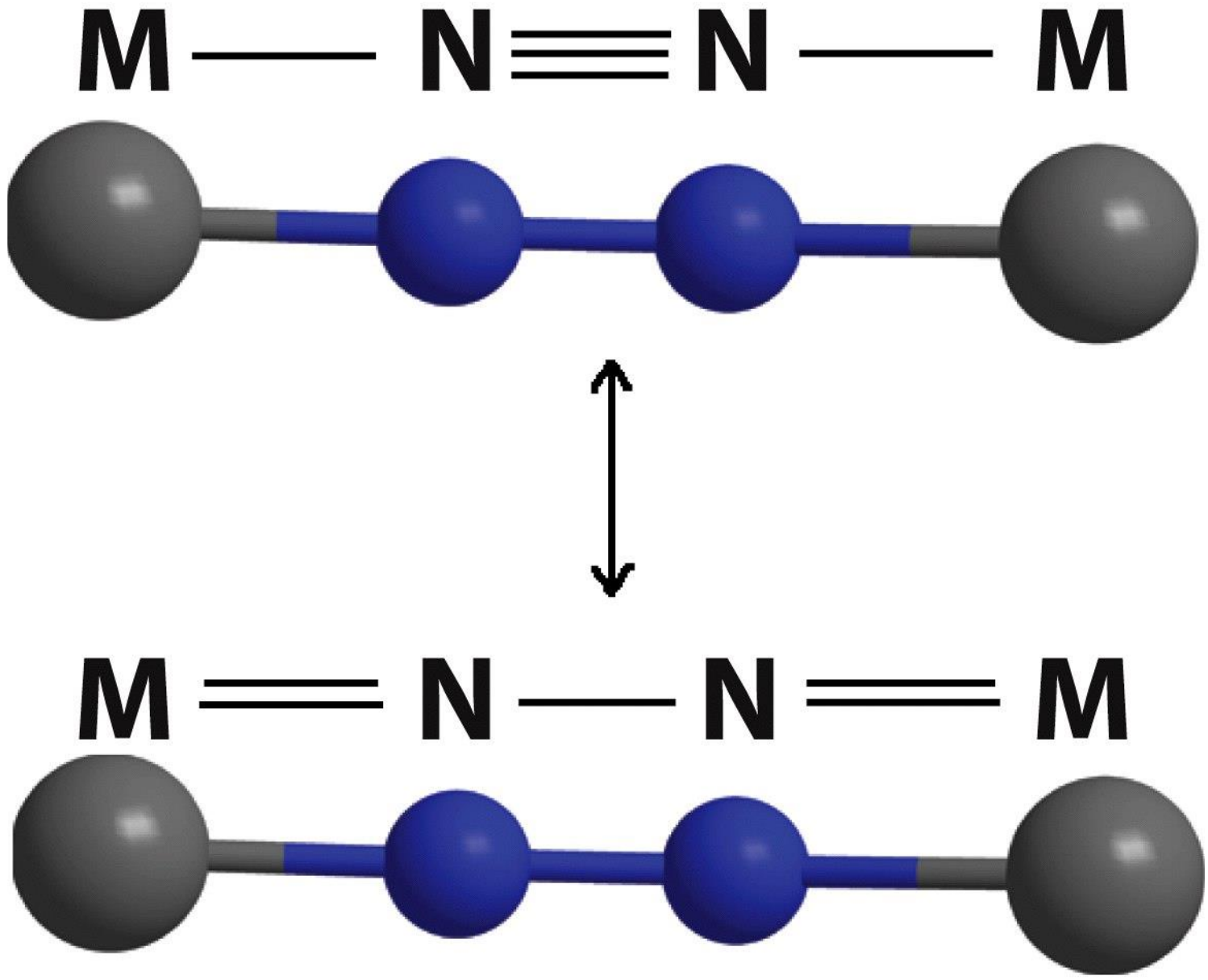


NMR: $^{1}J_{HD} < 2$ Hz

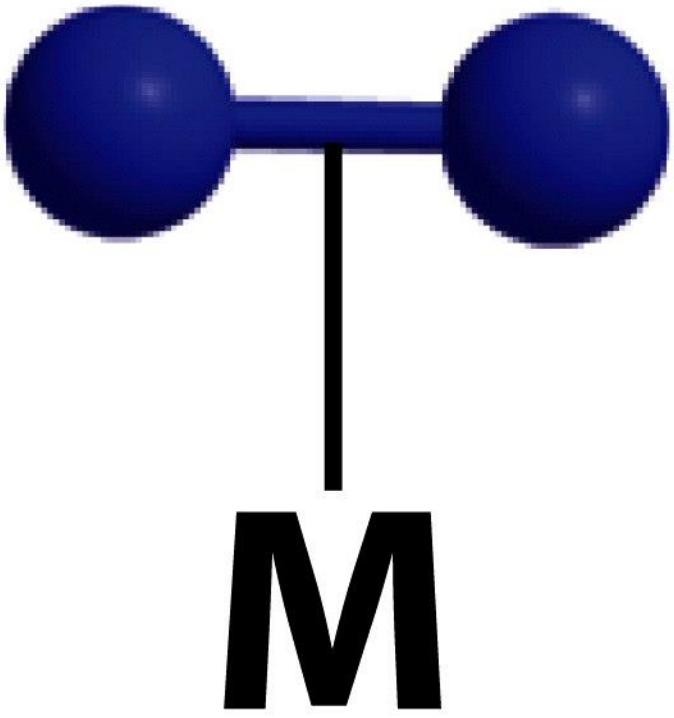


End-on (η^1)
(più comune)

IR: N–N 2150 – 1900 cm^{-1}

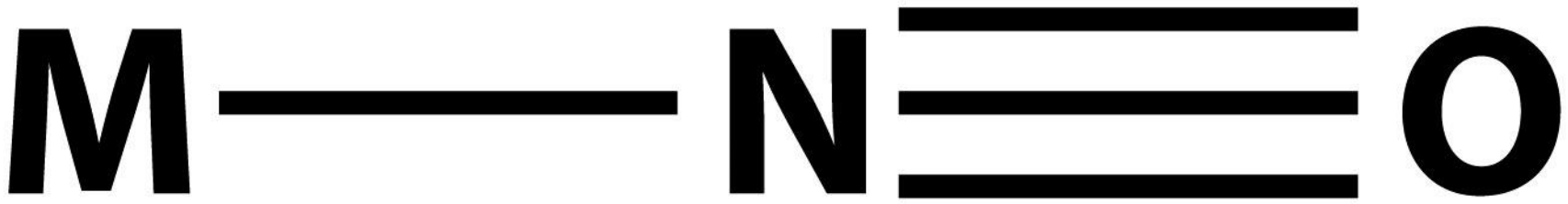


«idrazina»



Side-on (η^2)
(più raro)

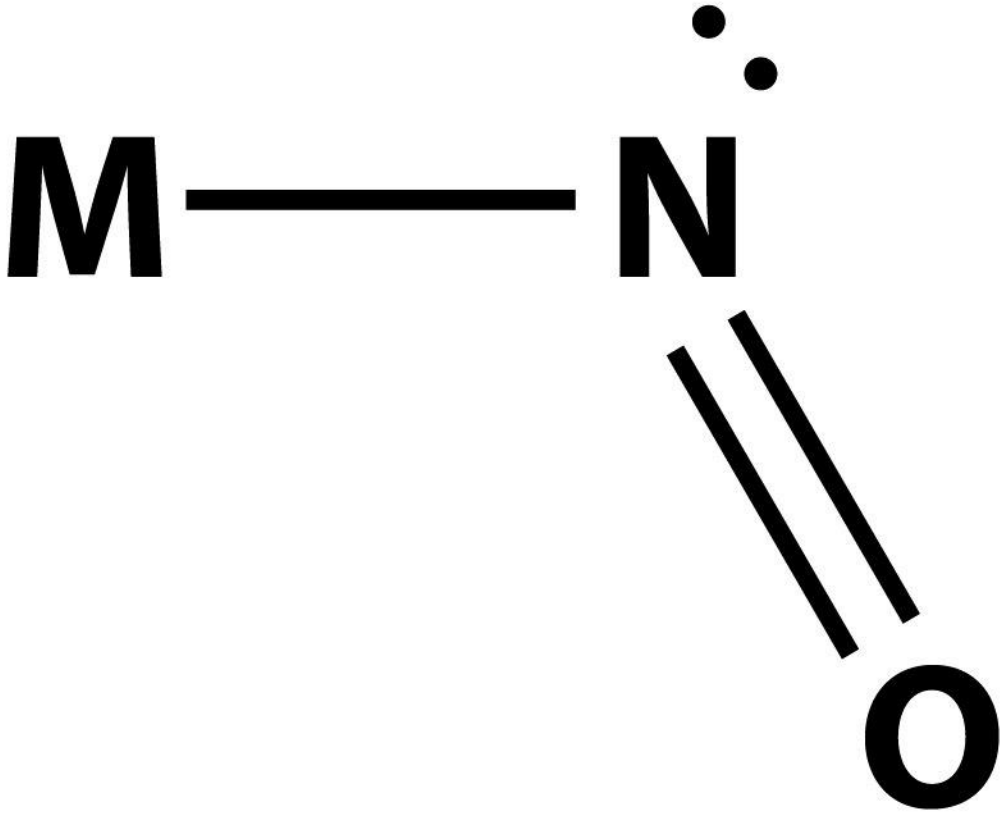
Nitrosile



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