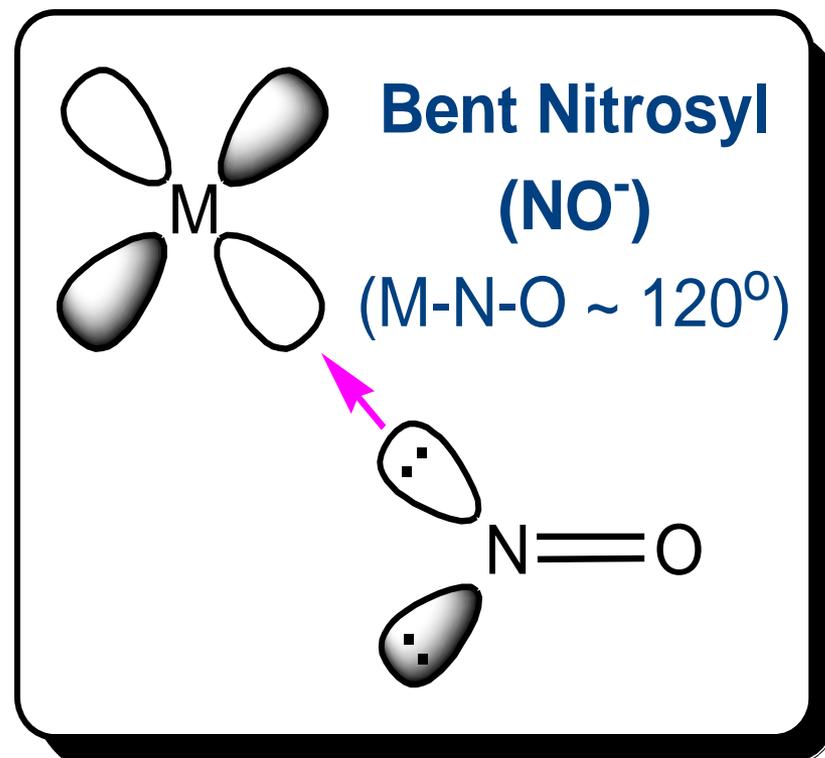
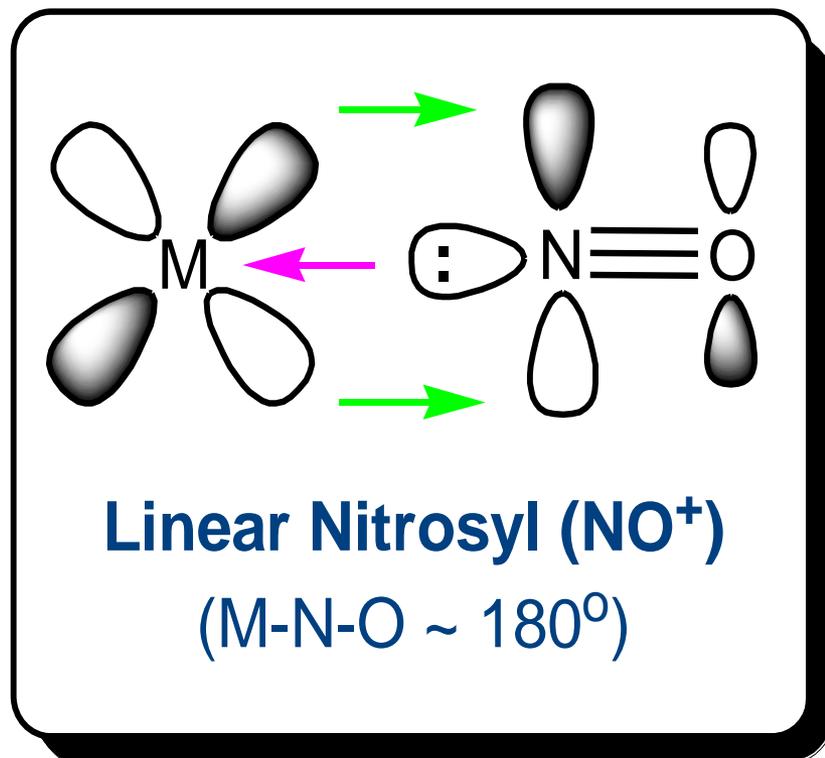


Ligands Isoelectronic With CO

- CS (thiocarbonyl) → better σ -donor and better π -acceptor than CO.
- N₂ → a poor ligand (much worse σ -donor and π -acceptor) – typically reduced in its complexes
- CN⁻ → good σ -donor, OK π -acceptor – more similar to a halide than CO.
- CNR (isocyanide or isonitrile) → similar to CO but can tune the steric and electronic properties. More reactive for insertion chemistry.

Ligands Isoelectronic With CO

- NO and NNR \rightarrow redox active ligands (linear NO^+ or bent NO^-) can change the total electron count of a complex (what would you expect for $[\text{Cr}(\text{NO})_4]$?).



Ligands Isoelectronic With CO

CO	<ul style="list-style-type: none"> • Carbonyl: σ-donor, strong π-acceptor. • Terminal ($1850\text{-}2100\text{ cm}^{-1}$), μ_2-bridging ($1700\text{-}1850\text{ cm}^{-1}$) or μ_3-bridging ($1600\text{-}1700\text{ cm}^{-1}$). For free CO, $\nu(\text{CO}) = 2143\text{ cm}^{-1}$.
CS	<ul style="list-style-type: none"> ▪ Thiocarbonyl: better σ-donor and better π-acceptor than CO. ▪ Terminal ($1160\text{-}1410\text{ cm}^{-1}$), μ_2-bridging ($1100\text{-}1160\text{ cm}^{-1}$) or μ_3-bridging ($1040\text{-}1080\text{ cm}^{-1}$). ▪ For free CS (not stable at room temperature), $\nu(\text{CS}) = 1273\text{ cm}^{-1}$. ▪ Synthesis of thiocarbonyl complexes from $\text{ML}_x + \text{CS}_2/\text{PR}_3$ or $\text{ML}_x^{2-} + \text{Cl}_2\text{C}=\text{S}$.
NO	<ul style="list-style-type: none"> ▪ Nitrosyl: redox active \rightarrow linear $\text{N}\equiv\text{O}^+$ ($1600\text{-}1850\text{ cm}^{-1}$) or bent $\text{N}=\text{O}^-$ ($1500\text{-}1700\text{ cm}^{-1}$) ▪ NO^+ is isoelectronic with CO: worse σ-donor, better π-acceptor. ▪ Nitrosyls can be terminal or bridging. ● Synthesis from NO gas, $\text{NO}^+ \text{PF}_6^-$ or ClNO. ▪ A related pair of redox active ligands are $\text{R}-\text{N}\equiv\text{N}^+$ (diazonium) and $\text{R}-\text{N}=\text{N}^-$ (diazenide)
N₂	<ul style="list-style-type: none"> ▪ Dinitrogen: isoelectronic with CO ● Worse σ-donor and much worse π-acceptor than CO. ▪ A poor ligand, and very unreactive due to extremely strong $\text{N}\equiv\text{N}$ triple bond. N-N bond dissociation energies: $\text{N}\equiv\text{N}$ (946 kJmol^{-1}), $\text{HN}=\text{NH}$ (414 kJmol^{-1}), $\text{H}_2\text{N}-\text{NH}_2$ (159 kJmol^{-1}). ▪ $\nu(\text{N}_2)$ for free $\text{N}_2 = 2331\text{ cm}^{-1}$ (Raman). $\nu(\text{N}_2)$ for $\text{L}_x\text{M}(\text{N}_2) = 700\text{-}2200\text{ cm}^{-1}$. ▪ In complexes – N_2 often reduced to N_2^{2-} or N_2^{4-} - use low valent early TM, lanthanide or actinide complexes {<i>e.g.</i> '$(\text{R}_2\text{N})_3\text{Nb}^{\text{III}}$', $\text{R}_2\text{Ti}^{\text{IV}}\text{Cl}_2 + \text{Na}/\text{Hg}$, $\text{Cp}^*_2\text{Sm}^{\text{II}}$ or $(\text{R}_2\text{N})_3\text{U}^{\text{III}}(\text{THF})$}. ▪ Huge interest in converting N_2 to useful N-containing compounds <i>e.g.</i> NH_3. Plants do this at RT and 1 atm pressure. Haber-Bosch process (120 million Tonnes <i>p.a.</i>) Ru/C cat., $400\text{ }^\circ\text{C}$, 200 atm.

Ligands Isoelectronic With CO

CN⁻	<ul style="list-style-type: none"> ▪ Cyanide: isoelectronic with CO, but in some ways more like a halide than CO. ▪ Good σ-donor, only a moderate π-acceptor. ● $\nu(\text{CN})$ for $\text{L}_x\text{M}(\text{CN})$ useful. ▪ Better at stabilizing metals in high oxidation states than those in low oxidation states.
CNR	<ul style="list-style-type: none"> ▪ Isonitrile or Isocyanide (Stench !): isoelectronic with CO but much larger dipole moment. ▪ $\text{M}-\text{C}\equiv\text{N}-\text{R}$ almost always linear. ● Generally a stronger σ-donor and a weaker π-acceptor than CO (depends on R), but more able to adjust to suit the metal than CO. ▪ Unlike CO, metal coordination can either raise or lower $\nu(\text{CN})$ ($2000\text{-}2200\text{ cm}^{-1}$) \rightarrow because the HOMO of CNR is much more antibonding than that of CO.
PR₃	<ul style="list-style-type: none"> ▪ Phosphines – σ-donors and π-acceptors. ▪ No useful IR handle, but ^{31}P-NMR is almost as easy to run as ^1H NMR. ▪ Huge variety of phosphines available - Can just pick one with the desired steric and electronic properties. C. A. Tolman, <i>Chem. Rev.</i>, 1977, 313. ▪ Related ligands: $\text{P}(\text{OR})_3$ = phosphites (worse σ-donors, better π-acceptors), AsR_3 = arsine (slightly worse ligands, lone pair not as available for bonding as in PR_3) ▪ Other related ligands: Arduengo carbenes = stable $:\text{C}(\text{NR}_2)_2$ (see later)