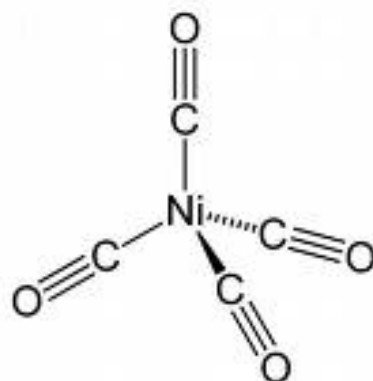


Transition Metal Carbonyls



Tetrahedral !
Electron count?
CO = 2e donor

- In **1884** Ludwig Mond found his nickel valves were being eaten away by CO. An experiment was designed where he deliberately heated Ni powder in a CO stream thus forming the volatile compound, $\text{Ni}(\text{CO})_4$, the first metal carbonyl. It was also found that upon further heating $\text{Ni}(\text{CO})_4$ decomposes to give pure nickel. This Ni refining process still used today is known as the Mond process.
- Having no net dipole moment, intermolecular forces are relatively weak, allowing $\text{Ni}(\text{CO})_4$ to be liquid at room temperature.

- CO groups have a high **tendency to stabilize M–M bonds**; not only are CO ligands relatively small but they also leave the metal atom with a net charge similar to that in its elemental form (*electroneutrality principle*).

“Stable complexes are those with structures such that each atom has only a small electric charge. Stable M-L bond formation generally reduces the positive charge on the metal as well as the negative charge and/or e- density on the ligand. The result is that the actual charge on the metal is not accurately reflected in its formal oxidation state”

- **Pauling**; *The Nature of the Chemical Bond, 3rd Ed.*;1960, pg. 172.

- CO also has the **ability to stabilize polyanionic species** by acting as a strong π acceptor and delocalizing the negative charge over the CO oxygens.
- $\text{Na}_4[\text{Cr}(\text{CO})_4]$ has the extraordinarily low $\nu(\text{CO})$ of 1462 cm^{-1} , the extremely high anionic charge on the complex, and ion pairing of Na^+ to the carbonyl oxygen contribute to the reduced CO bond order by favoring the $\text{M}\equiv\text{C}-\text{ONa}$ resonance form.
- As the CO ligand is small and strongly bound, many will usually bind as are required to achieve coordinative saturation, e.g. $\text{V}(\text{CO})_7$
- Metal carbonyls, in common with metal hydrides, show a strong preference for the 18e configuration.

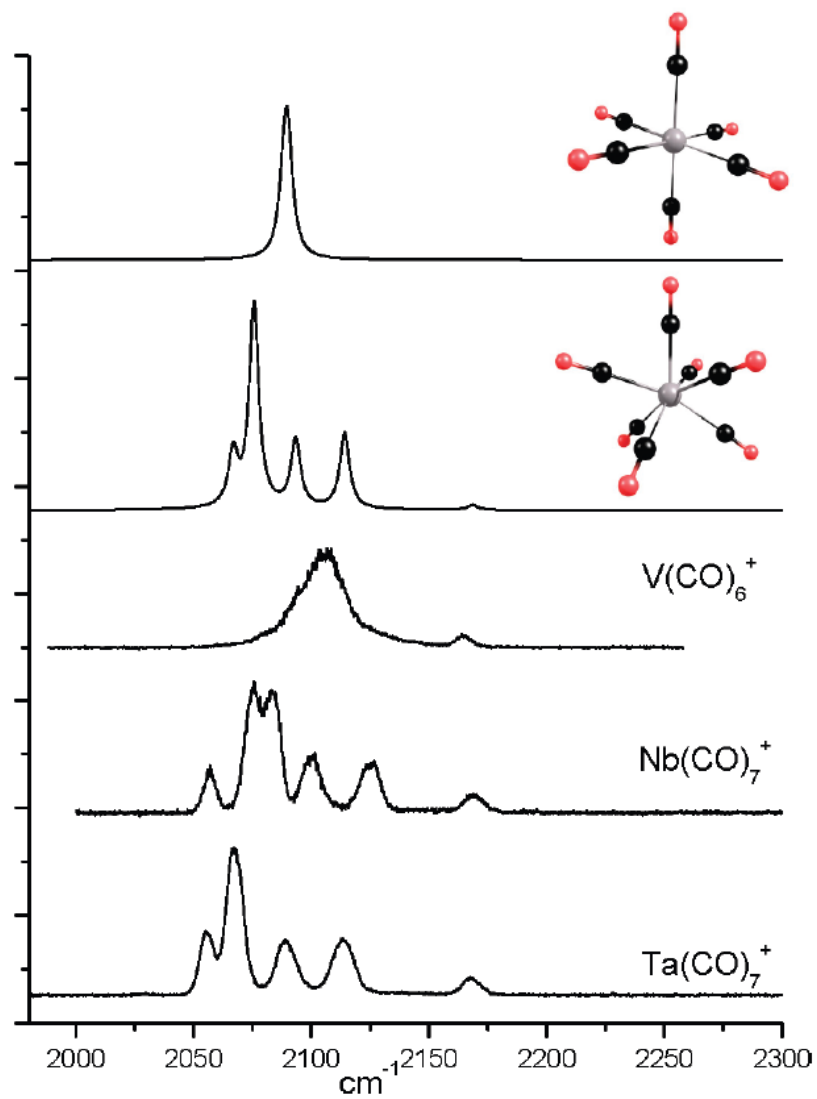
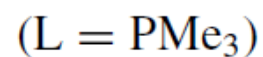
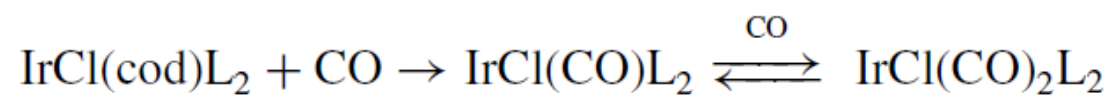
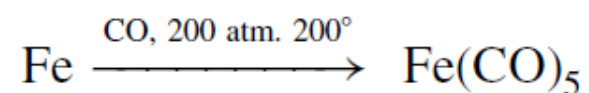


Figure 2. Calculated IR spectra of 6C $\text{Ni}(\text{CO})_2^+$ and 7C $\text{Ni}(\text{CO})_3^+$ complexes and experimental spectra of 6C $\text{V}(\text{CO})_6^+$, 7C $\text{Nb}(\text{CO})_7^+$, and 7C $\text{Ta}(\text{CO})_7^+$. Computed frequencies were scaled by 0.94, and bands were given a 5 cm^{-1} fwhm Lorentzian line shape.

Synthesis of Metal Carbonyls

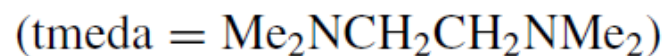
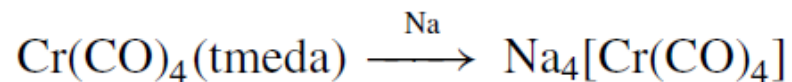
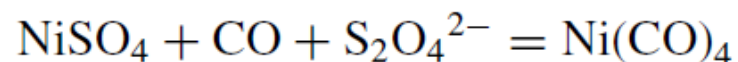
1. From CO gas:



- This method requires that the metal already be in a reduced state because only π -basic metals can bind CO.

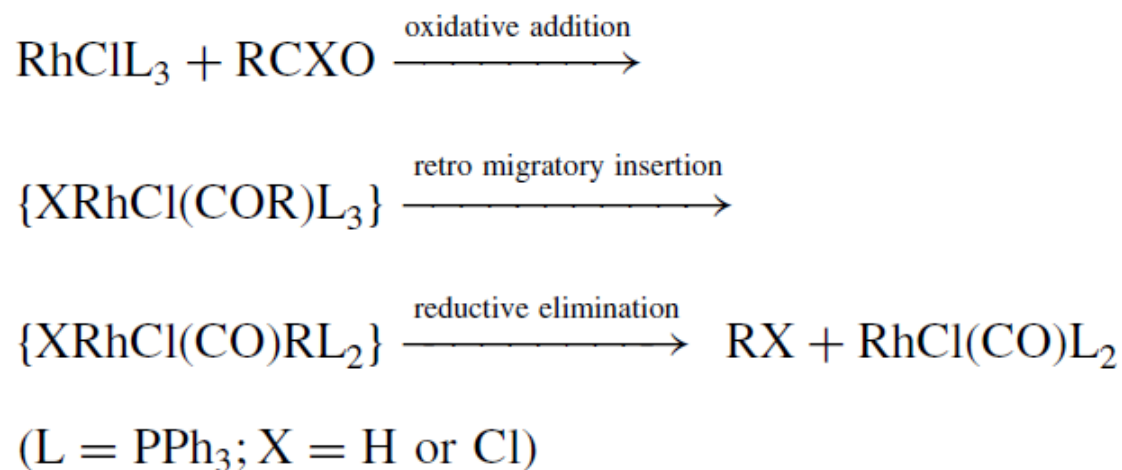
- If a high-oxidation-state complex is the starting material, we need to reduce it first :

2. Reductive carbonylation (reducing agent plus CO gas):



3. From an organic carbonyl:

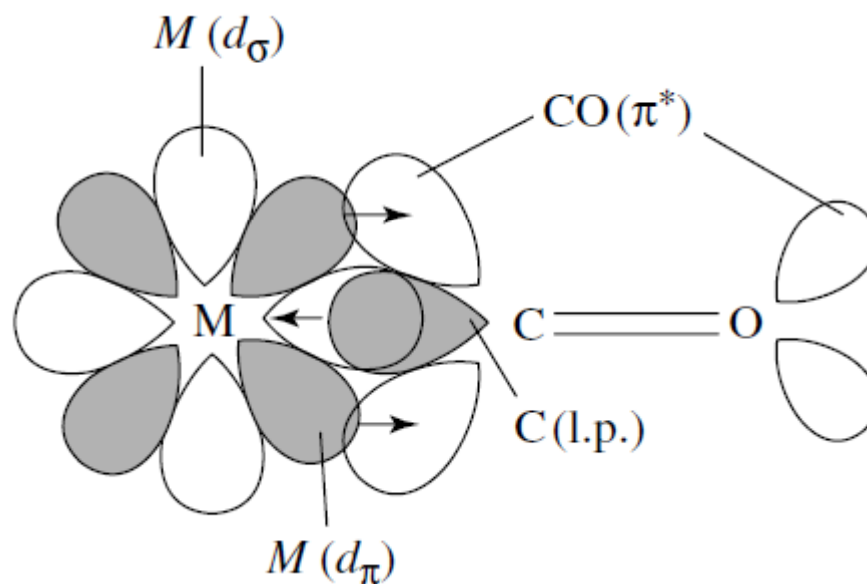
- **This can happen for aldehydes, alcohols**



- In this example the reaction requires three steps; the second step is the reverse of migratory insertion. The success of the reaction in any given instance relies in part on the thermodynamic stability of the final metal carbonyl product, which is greater for a low-valent metal.
- Note that the first step in the case of an aldehyde is oxidative addition of the aldehyde C–H bond. It is much more difficult for the metal to break into a C–C bond so ketones, R_2CO , are usually resistant to this reaction.

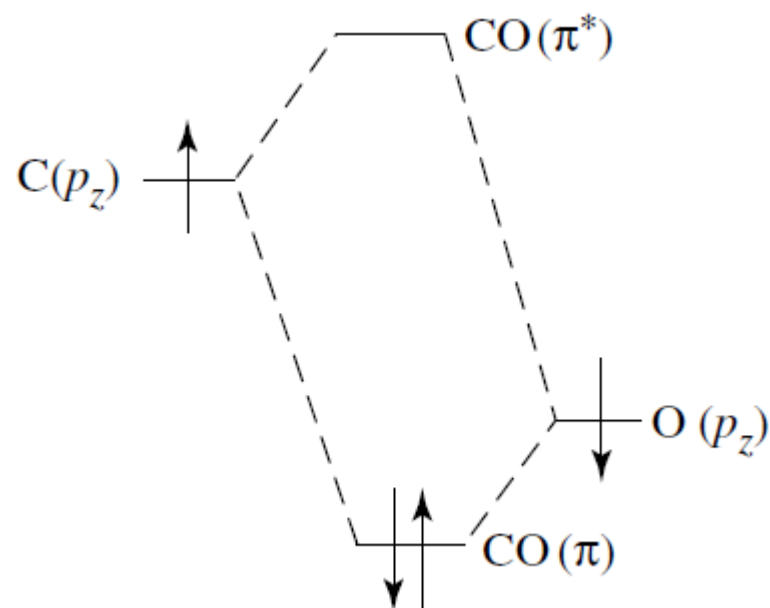
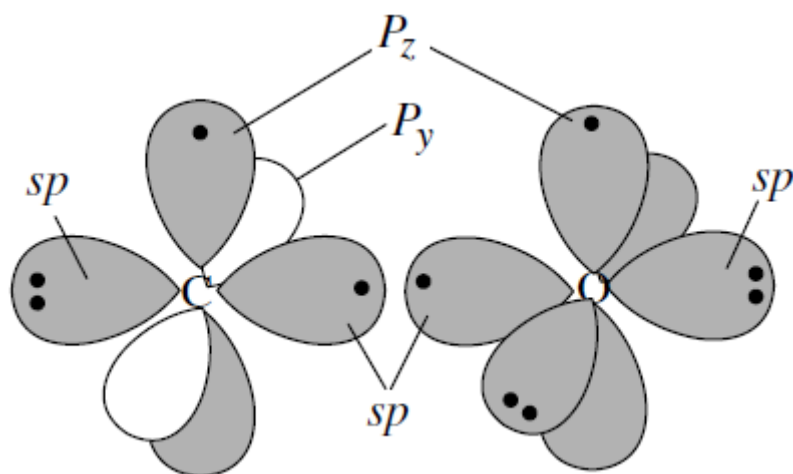
Metal Carbonyls: Structure and Bonding

- CO is an unsaturated ligand, by virtue of the $\text{C}\equiv\text{O}$ multiple bond.
- CO is classed as a **soft ligand** because it is capable of accepting metal $d\pi$ electrons by back bonding, i.e. it is a σ -donor π -acceptor ligand.



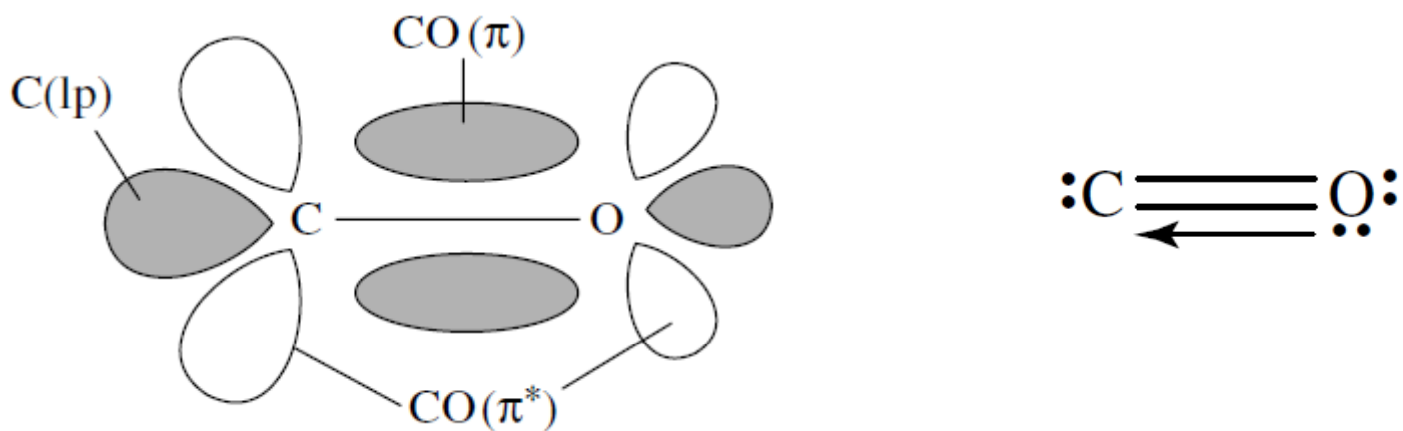
- This contrasts to **hard ligands, which are σ donors, and often π donors**, too.
- CO can act as a **spectator or an actor ligand**.

- In the CO molecule both the C and the O atoms are *sp hybridized*.
- The singly occupied sp and p_z orbitals on each atom form a σ and a π bond, respectively.

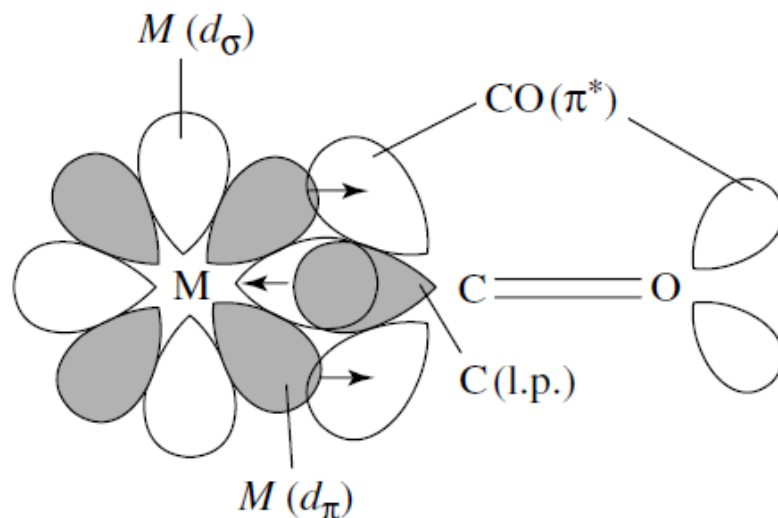


Frontier orbitals of free CO showing the polarization of the π_z orbital.

- This leaves the C p_y orbital empty, and the O p_y orbital doubly occupied, and so the second π bond is formed only after we have formed a **dative bond** by transfer of the lone pair of O p_y electrons into the empty C p_y orbital.

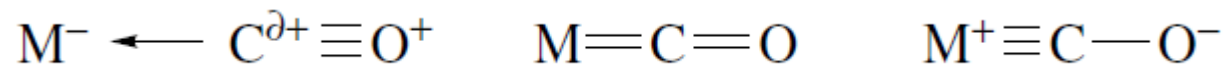


- This transfer leads to a $C^{\delta-}-O^{\delta+}$ polarization of the molecule, which is almost exactly canceled out by a partial $C^{\delta+}-O^{\delta-}$ polarization of all three bonding orbitals because of the higher electronegativity of oxygen.
- The free CO molecule therefore has a net dipole moment very close to zero.



- The metal e_g orbital forms a σ bond with HOMO orbital of CO.
- The HOMO is a σ orbital based on C (due to the higher electronegativity of O its orbitals have lower energy).
- The metal t_{2g} orbitals form a π bond with the CO π^* LUMO (again polarized toward C)
- The metal HOMO, the filled M $d\pi$ orbital, back donates to the CO LUMO increasing electron density at both C and O because CO π^* has both C and O character.
- The result is that C becomes more positive on coordination, and O becomes more negative. This translates into a polarization of the CO on binding.

- This metal-induced polarization chemically **activates the CO ligand**.
- It makes the **carbon more sensitive to nucleophilic** and the **oxygen more sensitive to electrophilic** attack.
- The polarization will be modulated by the effect of the other ligands on the metal and by the net charge on the complex.
- In $\text{LnM}(\text{CO})$, the CO carbon becomes particularly δ^+ in character if the L groups are good π acids or if the complex is cationic, e.g. $\text{Mo}(\text{CO})_6$ or $[\text{Mn}(\text{CO})_6]^+$, because the CO-to-metal σ -donor electron transfer will be enhanced at the expense of the metal to CO back donation.
- If the L groups are good donors or the complex is anionic, e.g. $\text{Cp}_2\text{W}(\text{CO})$ or $[\text{W}(\text{CO})_5]^{2-}$, back donation will be encouraged, the CO carbon will lose its pronounced δ^+ charge, but the CO oxygen will become significantly δ^- .



- The range can be represented in valence bond terms the extreme in which CO acts as a pure σ donor, through to the extreme in which both the π_x^* and π_y^* are both fully engaged in back bonding.

- Neither extreme is reached in practice, but each can be considered to contribute differently to the real structure according to the circumstances.
- We can tell the ***bond order of the CO ligand*** by recording the M-CO IR spectrum.
- The normal range of the M-CO stretching frequency, $\nu(\text{CO})$ is **1820–2150 cm⁻¹**.

As the metal to CO π^* back bonding becomes more important, we populate an orbital that is antibonding with respect to the C=O bond, and so we lengthen and weaken the CO bond, i.e. the M–C π bond is made at the expense of the C=O π bond.

- The high intensity of the CO stretching bands (***a result of polarization on binding***) means that IR spectroscopy is extremely useful.
- From the band position, we can tell how good the metal is as a π base.
- From the number and pattern of the bands, we can tell the number and stereochemistry of the CO's present.

- Strong σ donor co-ligands or a negative charge on the metal result in CO stretches at lower frequency. **Why?**

	$\nu(\text{CO}) \text{ cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{V}(\text{CO})_6]^-$	1859
$\text{Cr}(\text{CO})_6$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2204

- The greater the ability of a metal to donate electrons to the π^* orbitals of CO, the lower the energy of the C-O stretching vibration.

- Carbonyls bound to very **poor π -donor metals** have very **high frequency $\nu(\text{CO})$** bands as a result of **weak back donation**.
- When these appear to high energy of the 2143 cm^{-1} band of free CO, the complexes are sometimes called ***non-classical carbonyls***.
- Even d^0 species can bind CO, for example, the nonclassical, formally d^0 Zr(IV) carbonyl complexes, $[\text{Cp}^*_2\text{Zr}(\kappa^2\text{-S}_2)(\text{CO})]$ has a $\nu(\text{CO})$ stretching frequency of 2057 cm^{-1} .
- The highest oxidation state carbonyl known is *trans*- $[\text{OsO}_2(\text{CO})_4]^{2+}$ with $\nu(\text{CO}) = 2253 \text{ cm}^{-1}$. Carbonyls with exceptionally low $\nu(\text{CO})$ frequencies are found for negative oxidation states (e.g., $[\text{Ti}(\text{CO})_6]^{2-}$; $\nu(\text{CO}) = 1747 \text{ cm}^{-1}$) or where a single CO is accompanied by non π -acceptor ligands (e.g., $[\text{ReCl}(\text{CO})(\text{PMe}_3)_4]$; $\nu(\text{CO}) = 1820 \text{ cm}^{-1}$); these show short M–C and long C–O bonds.

Table 1. Vibrational spectra ($\tilde{\nu}_{\text{CO}}$ region), force constants f_{CO} , and ^{13}C chemical shifts for homoleptic, isoelectronic, and octahedral $[\text{M}(\text{CO})_6]$ species of the 5d block metals.

	$[\text{Hf}(\text{CO})_6]^{2-}$	$[\text{Ta}(\text{CO})_6]^{-}$	$[\text{W}(\text{CO})_6]$	$[\text{Re}(\text{CO})_6]^+$	$[\text{Os}(\text{CO})_6]^{2+}$	$[\text{Ir}(\text{CO})_6]^{3+}$
$\tilde{\nu}(a_{1g})/\text{cm}^{-1}$			2115 [e]	2197 [g]	2259 [i]	2295
$\tilde{\nu}(e_g)/\text{cm}^{-1}$			1998 [e]	2122 [g]	2218 [i]	2276
$\tilde{\nu}(f_{1u})/\text{cm}^{-1}$	1757 [a]	1850 [c]	1977 [e]	2085 [g]	2190 [i]	2254
$f_{\text{CO}}/\times 10^2 \text{ Nm}^{-1}$			17.0 [f]	18.1 [f]	19.8 [f]	20.8 [f]
$\delta(^{13}\text{C})$	244 [b]	211 [d]	192 [d]	171 [h]	147 [i]	121

- One of the most extreme weak π -donor examples is $[\text{Ir}(\text{CO})_6]^{3+}$ with $\nu(\text{CO})$ bands at 2254, 2276, and 2295 cm^{-1} .
- The X-ray structure of the related complex $[\text{IrCl}(\text{CO})_5]^{2+}$ shows the long M–C [2.02(2) \AA] and short C–O [1.08(2) \AA] distances expected.

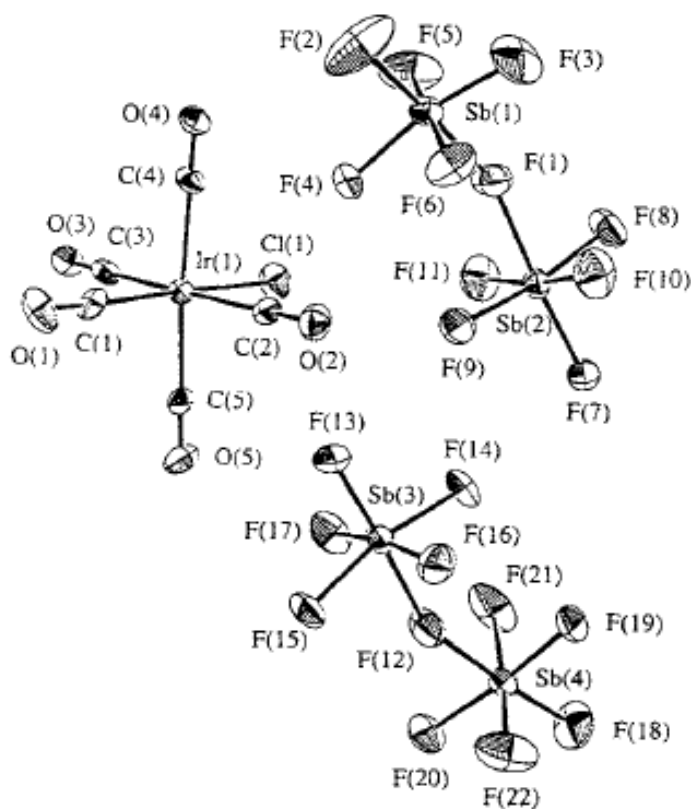
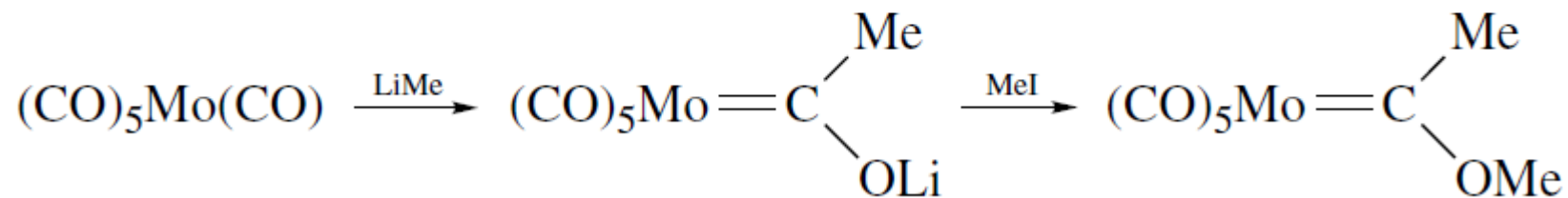
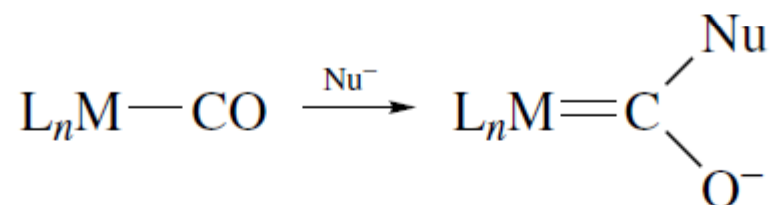


Fig. 1. Molecular structure of $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ (50% probability thermal ellipsoids are shown).

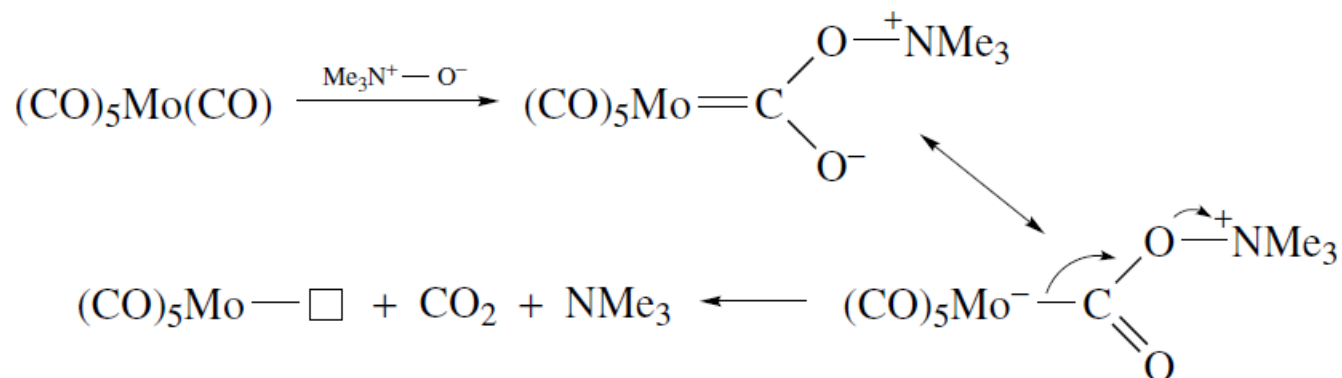
Reactions of Metal Carbonyls

- All reactions of the CO ligand depend on the polarization of the CO upon binding, and so change in importance as the coligands and net charge change.

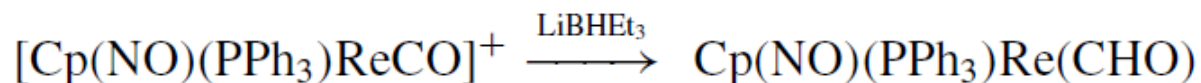
1. Nucleophilic attack at carbon:



1. Nucleophilic attack at carbon (contd):

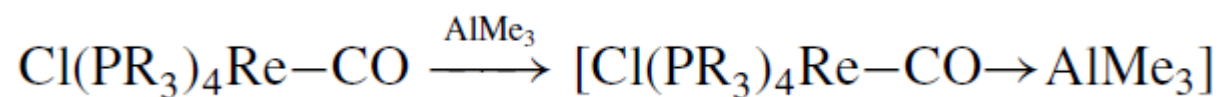


- This reaction is particularly important because it is one of the rare ways in which the tightly bound CO can be replaced by a ligand less basic than CO itself.

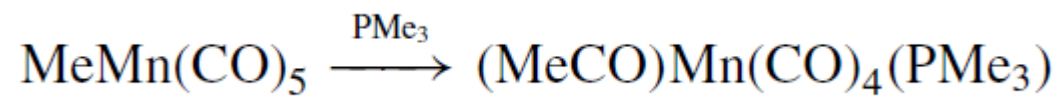


- Hydride attack at the C atom of CO here produces the unusual formyl ligand, which *is important in CO reduction to MeOH*.
- It is stable in this case because the final 18e complex provides no empty site for rearrangement to a hydridocarbonyl complex (α -elimination).

2. Electrophilic attack at oxygen:

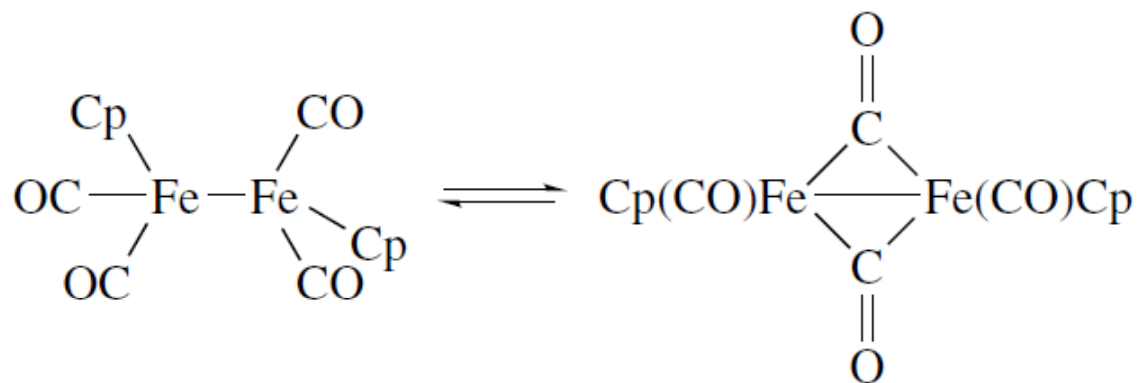


3. Migratory Insertion:



Bridging modes of the CO ligand

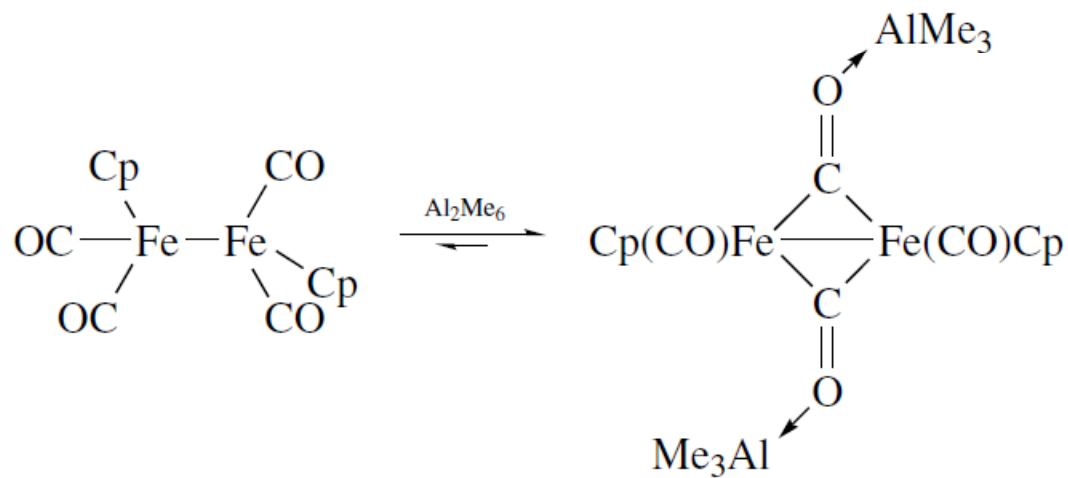
- CO has a high tendency to bridge two metals (μ^2 -CO)
- Electron count here is unchanged either side of equilibrium



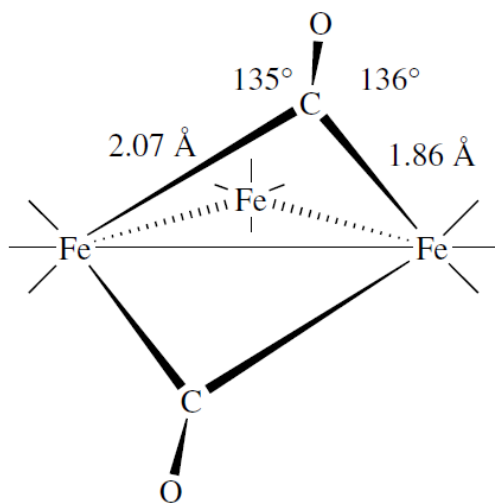
- In most cases the M–M bond accompanies the CO bridging group.
- The CO stretching frequency in the IR spectrum falls to 1720–1850 cm^{-1} on bridging.

<u>Type of CO</u>	<u>$\nu(\text{CO}) \text{ cm}^{-1}$</u>
Free CO	2143
terminal M-CO	1850-2120
bridging CO	1700-1850

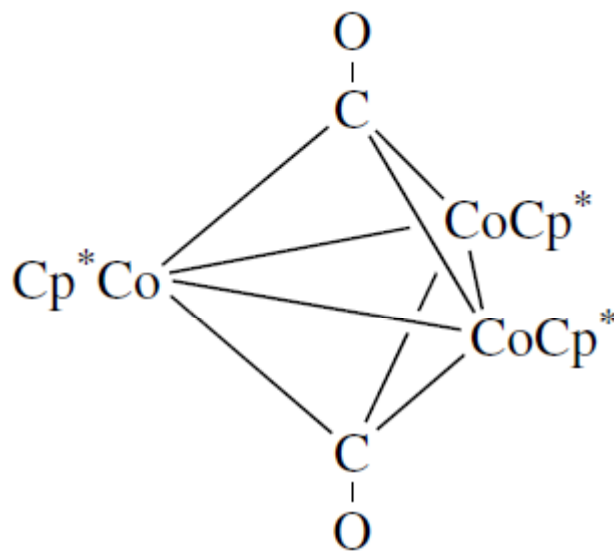
- Consistent with the idea of a nucleophilic attack by a second metal, ***a bridging CO is more basic at O than the terminal ligand.***
- Thus a bridging CO ligand will bind a Lewis acid more strongly than a terminal CO ligand.
- Equilibrium can therefore be shifted in the previous reaction scheme.



- There also exists the *semi-bridging carbonyl* in which the CO is neither fully terminal nor fully bridging but intermediate between the two.
- This is one of the many cases in organometallic chemistry where a stable species is intermediate in character between two bonding types.
- Below each semi-bridging CO is bending in response to the second metal atom being close by.

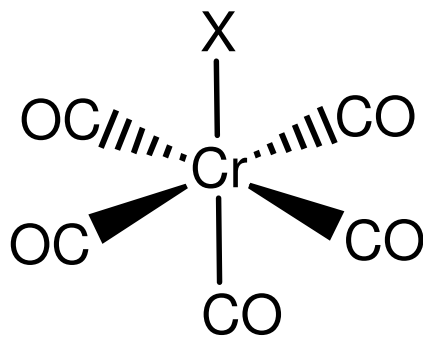


- **Triply and even quadruply bridging CO groups** are also known in metal cluster compounds.
- For example, $(\text{Cp}^*\text{Co})_3(\mu^3\text{-CO})_2$



- These have CO stretching frequencies in the range of $1600\text{--}1730\text{ cm}^{-1}$.

- The number of $\nu(\text{CO})$ can also tell us the shape of the molecule.

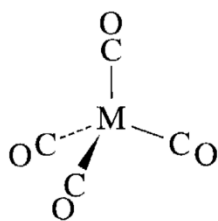


X = pyridine or tri-phenylphosphine

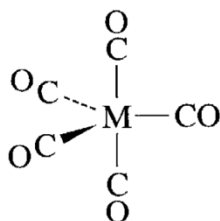
How can we predict the number of infrared stretches?

- Rule of thumb....
 - **Each unique CO has 1 $\nu(\text{CO})$**
 - **Each set of equivalent CO's have 2 $\nu(\text{CO})$**
(symmetric and antisymmetric)
- Therefore $(\text{CO})_5\text{CrX}$ has 3 $\nu(\text{CO})$
- How many $\nu(\text{CO})$ will $\text{Cr}(\text{CO})_6$ have?
 - All carbonyl ligands are equivalent.
 - For highly symmetric molecules such as octahedral or tetrahedral, the symmetric stretch does not result in a dipole change and therefore is not IR active.

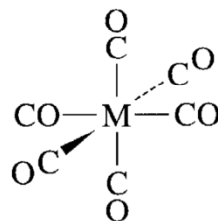
Mononuclear [M(CO)_x]



M = Ni, Pd

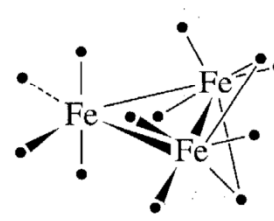


M = Fe, Ru, Os

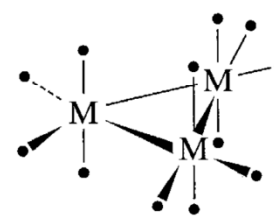


M = V, Cr, Mo, W

Polynuclear (CO represented by • for clarity)

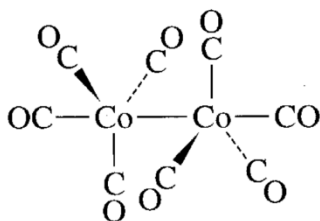


Fe₃(CO)₁₂

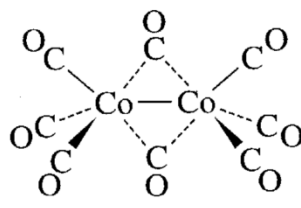


M₃(CO)₁₂
M = Ru, Os

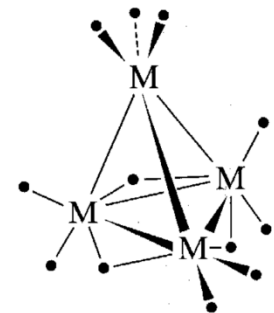
Binuclear [M₂(CO)_x]



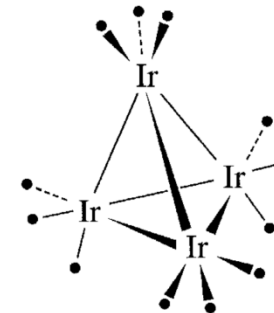
Co₂(CO)₈ (solution)



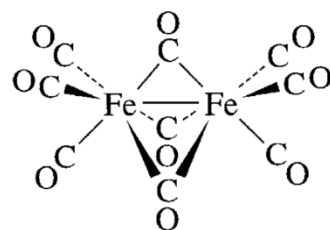
Co₂(CO)₈ (solid)



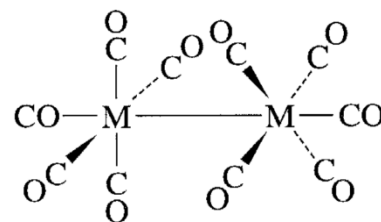
M₃(CO)₁₂
M = Co, Rh



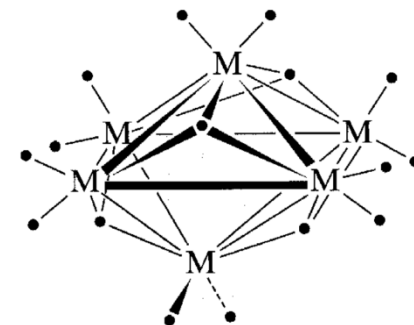
Ir₄(CO)₁₂



Fe₂(CO)₉



M₂(CO)₁₀
M = Mn, Tc, Re



M₆(CO)₁₆
M = Co, Rh

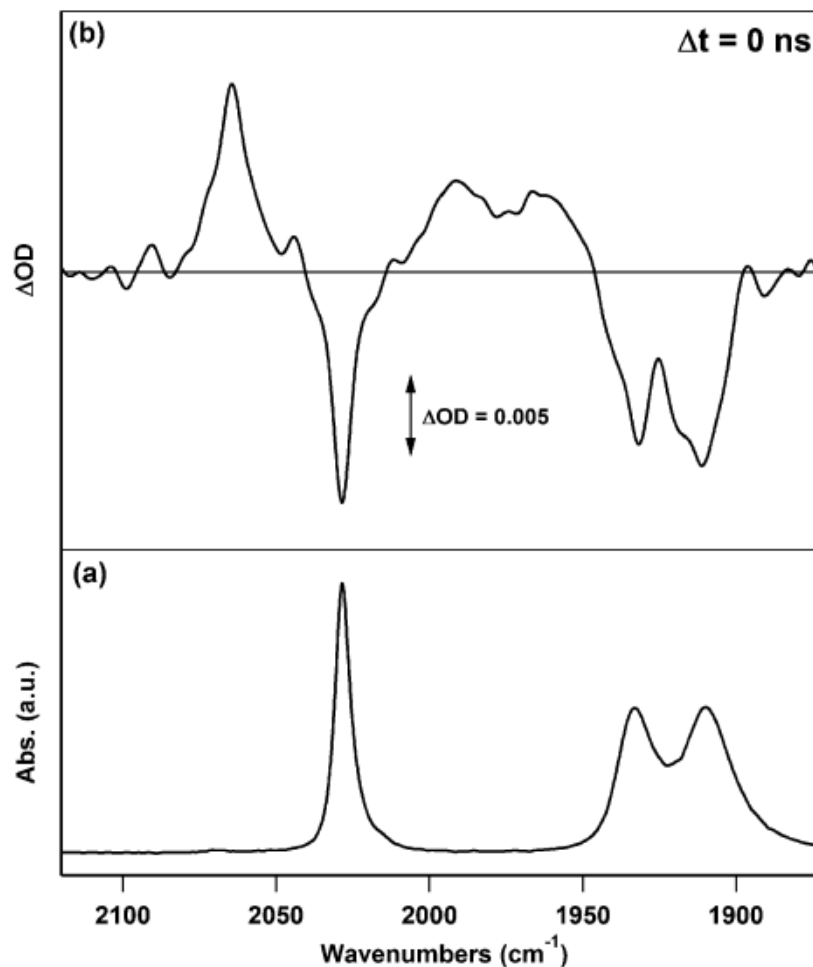
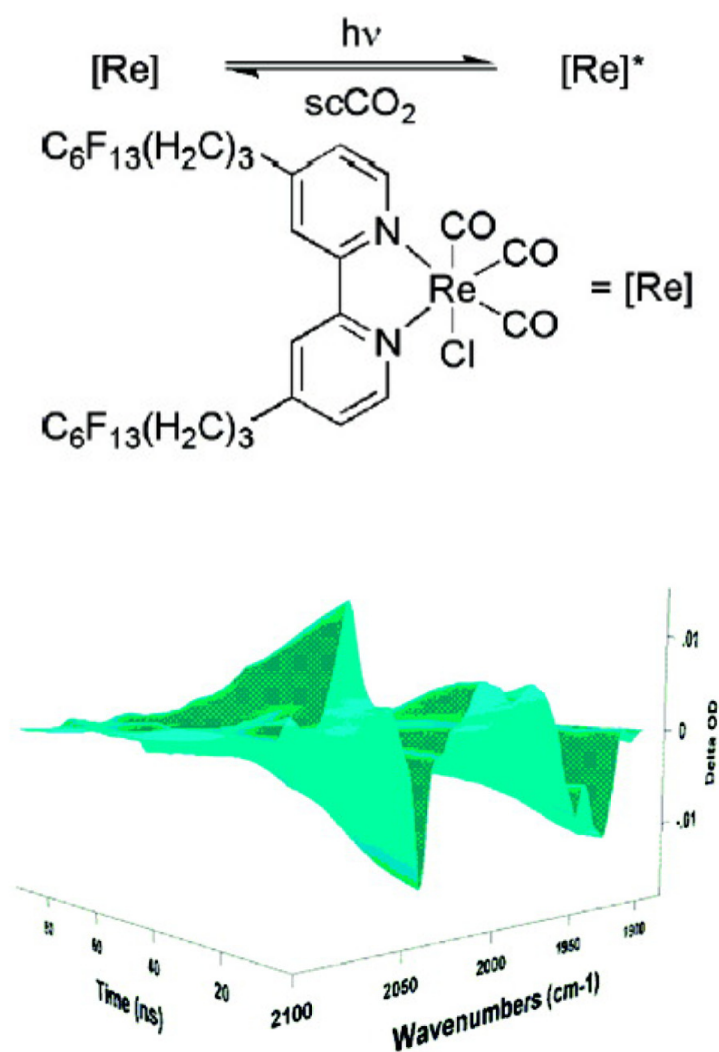


Figure 1. (a) Fourier transform IR (FTIR) spectrum of **2a** in scCO_2 (vs scCO_2 background; 35°C , 13.8 MPa). (b) Time-resolved step-scan FTIR spectrum recorded immediately after 410 nm laser excitation of this solution. Positive bands represent the excited-state species, while negative bands represent the ground-state bleach.

Phosphine Ligands

- Tertiary phosphines, PR_3 , are important because they constitute one of the few series of ligands in which *electronic and steric properties can be altered in a systematic and predictable way* over a very wide range by varying R.
- They also *stabilize an exceptionally wide variety of ligands* of interest to the organometallic chemist as their phosphine complexes $(\text{R}_3\text{P})_n\text{M-L}$.
- Phosphines are more commonly *spectator* than actor ligands.

PH_3
phosphine

PMe_3
trimethylphosphine

PPh_3
triphenylphosphine

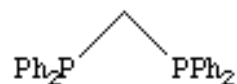
PPh_2Me
methyldiphenylphosphine

PF_3
trifluorophosphine

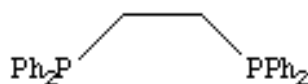
P(OMe)_3
trimethylphosphite

P(OPh)_3
triphenylphosphite

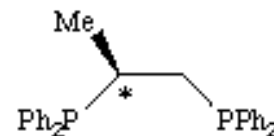
PCy_3
tricyclohexylphosphine



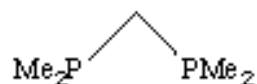
diphenylphosphinomethane
(dppm)



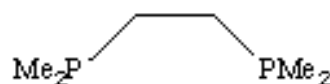
diphenylphosphinoethane
(dppe; also called diphos)



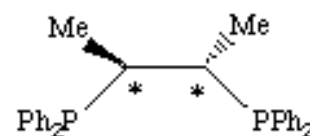
PROPHOS



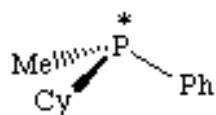
dimethylphosphinomethane
(dmppm)



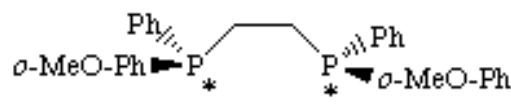
dimethylphosphinoethane
(dmpe; also called diphos)



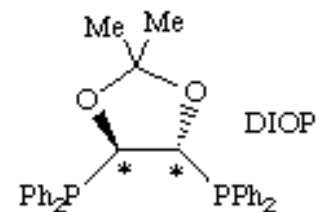
S,S-chiraphos



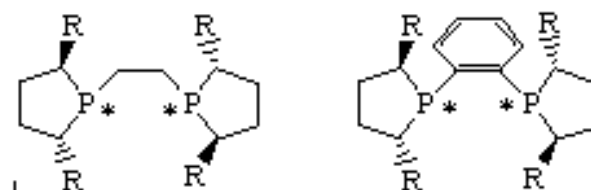
PAMP



DIPAMP



DIOP



DuPHOS

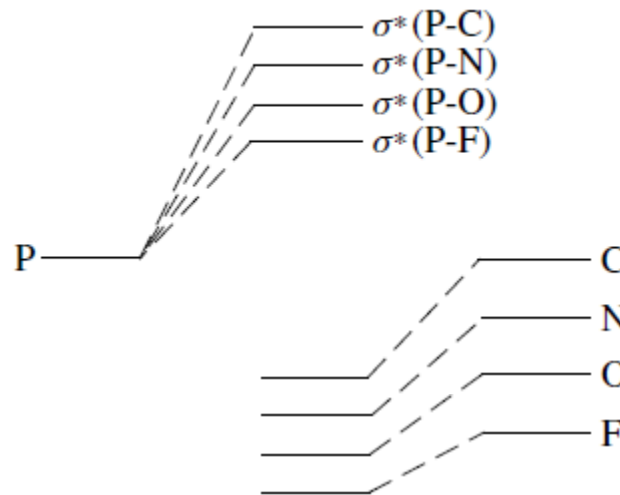
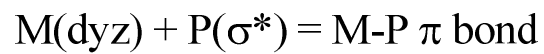
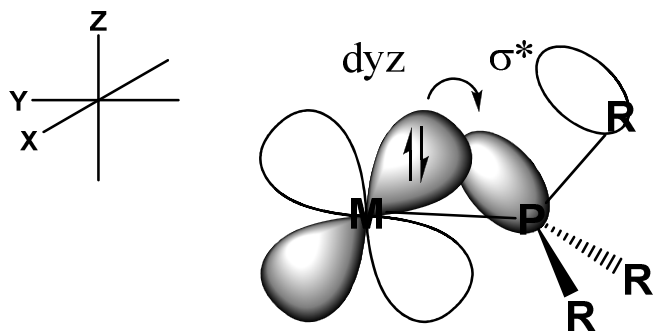
- Like NR_3 , phosphines have a lone pair on the central atom that can be donated to a metal.
- Unlike NR_3 , they are also *π -acids*, to an extent that depends on the nature of the R groups present on the PR_3 ligand.
- For alkyl phosphines, the π acidity is weak; aryl, dialkylamino, and alkoxy groups are successively more effective in promoting π acidity.
- In the extreme case of PF_3 , the π acidity becomes as great as that found for CO!

In the case of CO the π^* orbital accepts electrons from the metal.

The σ^* orbitals of the P–R bonds play the role of acceptor in PR_3 .

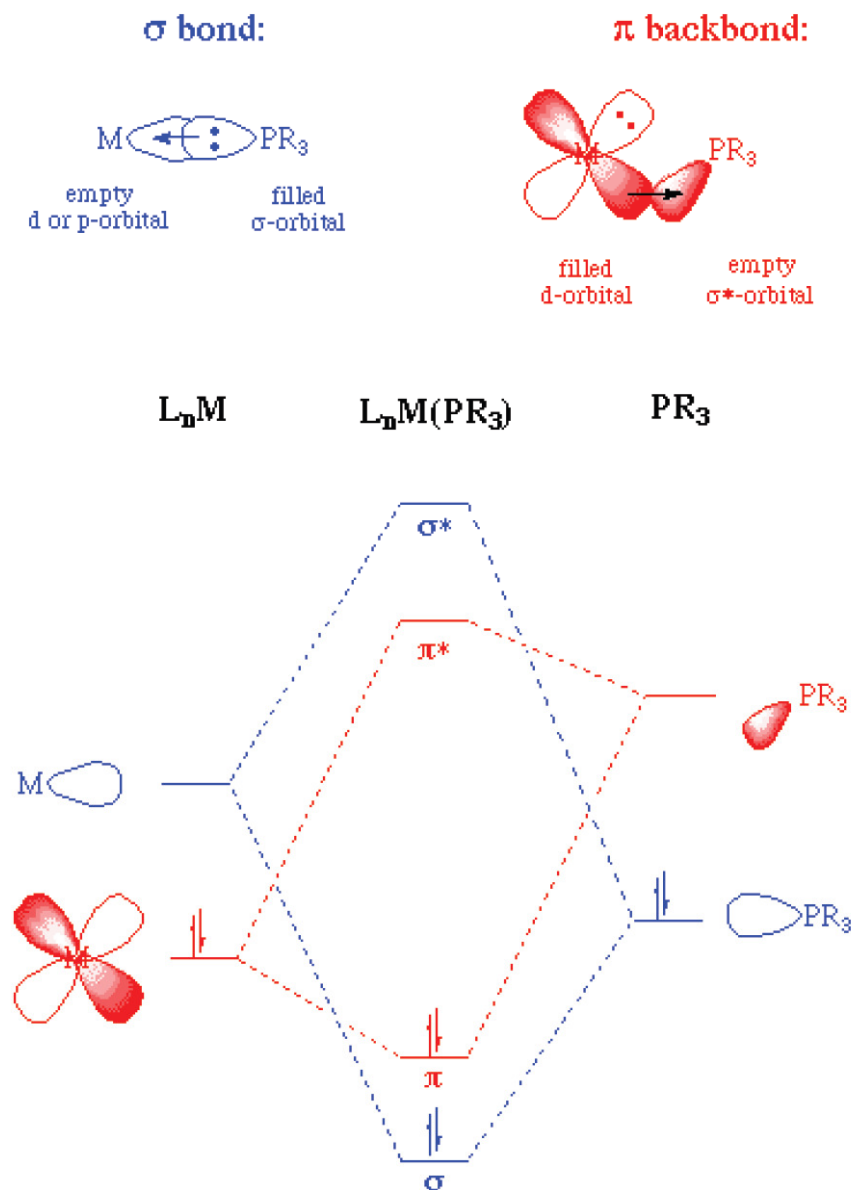
- Whenever the R group becomes more electronegative, the orbital that the R fragment uses to bond to phosphorus becomes more stable (lower in energy).
- This implies that the σ^* orbital of the P–R bond also becomes more stable.
- At the same time, the phosphorus contribution to σ^* orbital increases, and so the size of the σ^* lobe that points toward the metal increases
- Both of these factors make the empty σ^* more accessible for back donation.
- The final order of increasing π -acid character is





- The empty P–R σ^* orbital plays the role of acceptor in metal complexes of PR_3 .
- As the atom attached to the P atom becomes more electronegative, the empty P–X σ^* orbital becomes more stable (lower in energy) making it a better acceptor of electron density from the metal centre.

- Occupation of the P–R σ^* orbital by back donation from the metal also implies that ***the P–R bonds should lengthen slightly on binding.***
- In practice, this is ***masked by a simultaneous shortening of the P–R bond*** due to donation of the P lone pair to the metal, and the consequent decrease in P(lone pair)–R(bonding pair) repulsions.
- Once again, as in the case of CO, the M–L π bond is made at the expense of a bond in the ligand, but this time it is a σ , not a π , bond.

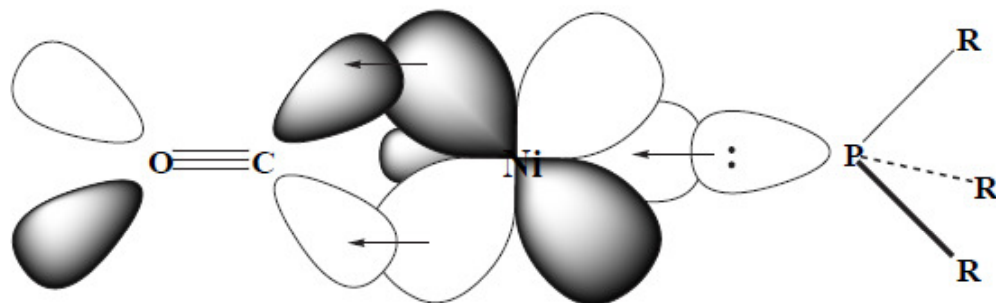


Tolman Electronic Parameter

Phosphorus Ligand (L)	CO ν , cm^{-1}
P(<i>t</i> -Bu) ₃	2056
PCy ₃	
P(<i>i</i> -Pr) ₃	2059
P(NMe ₂) ₃	2062
PMe ₃	2064
PPhMe ₂	2065
PBz ₃	2066
PPh ₂ Me	2067
PPh ₃	2069
PPh ₂ (OEt)	2072
P(<i>p</i> -C ₆ H ₄ Cl) ₃	2073
PPh(OEt) ₂	2074
P(OEt) ₃	2077
PH ₃	2083
PCl ₃	2097
PF ₃	2111

CO stretching frequencies measured for Ni(CO)₃L where L are PR₃ ligands of different σ -donor abilities. [$\nu(\text{CO}) = 2143 \text{ cm}^{-1}$]

The electronic effect of various PR₃ ligands can be adjusted by changing the R group as, quantified by Tolman, who compared the $\nu(\text{CO})$ frequencies of a series of complexes of the type LNi(CO)₃, containing different PR₃ ligands.



The increase in electron density at the nickel from PR₃ σ -donation is dispersed through the M-L π system *via* π -backbonding. Much of the electron density is passed onto the CO π^* and is reflected in decreased $\nu(\text{CO})$ stretching frequencies which corresponds to weaker CO bonds.

$$\nu = \frac{1}{2\pi c} \left[\frac{f}{(M_x M_y)/(M_x + M_y)} \right]^{1/2}$$

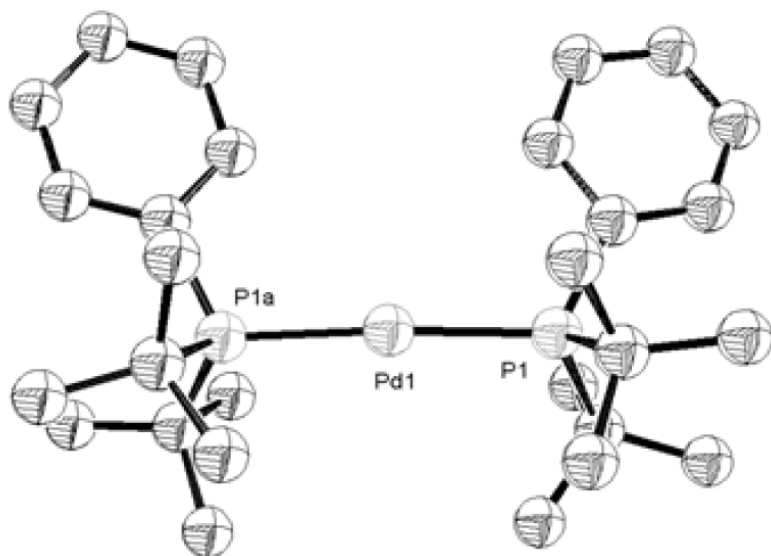
Tolman Cone Angle

- The second important feature of PR_3 as a ligand is the **variable steric size**, which can be adjusted by changing R.
- CO is so small that as many can bind as are needed to achieve 18e. In contrast, the same is rarely true for phosphines, where **only a certain number of phosphines can fit around the metal**.
- This can be a great advantage in that by using bulky PR_3 ligands, we can favor forming low-coordinate metals or we can leave room for small but weakly binding ligands,
- The usual maximum number of phosphines that can bind to a single metal is
 - two for PCy_3 or $\text{P}(i\text{-Pr})_3$
 - three or four for PPh_3
 - four for PMe_2Ph
 - five or six for PMe_3

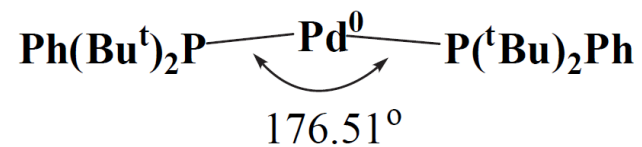
- **Coordination Number (CN) – the number of bonding groups at metal centre**

- **Low CN favored by:**

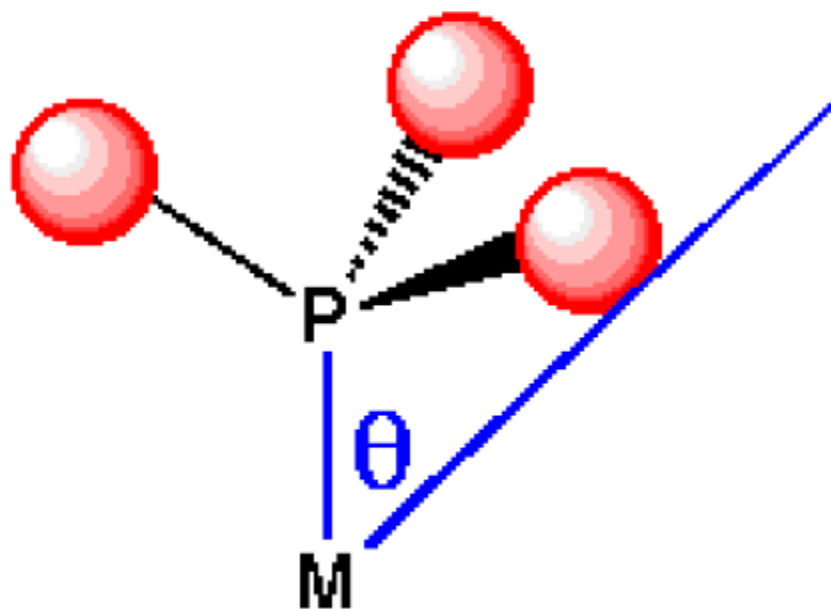
1. Low oxidation state (e^- rich) metals.
2. Large, bulky ligands.



Although $\text{Pd}(\text{P}(\text{tBu})_2\text{Ph})_2$ is *coordinatively unsaturated electronically*, the steric bulk of both $\text{P}(\text{tBu})_2\text{Ph}$ ligands prevents additional ligands from coordinating to the metal.



- The cone angle is obtained by taking a space-filling model of the $M(PR_3)$ group, folding back the R substituents as far as they will go, and measuring the angle of the cone that will just contain all of the ligand, when the apex of the cone is at the metal.
- Although the procedure may look rather approximate, the angles obtained have been very successful in rationalizing the behavior of a wide variety of complexes.



Tolman Plot of Electronic Parameter and Cone Angle

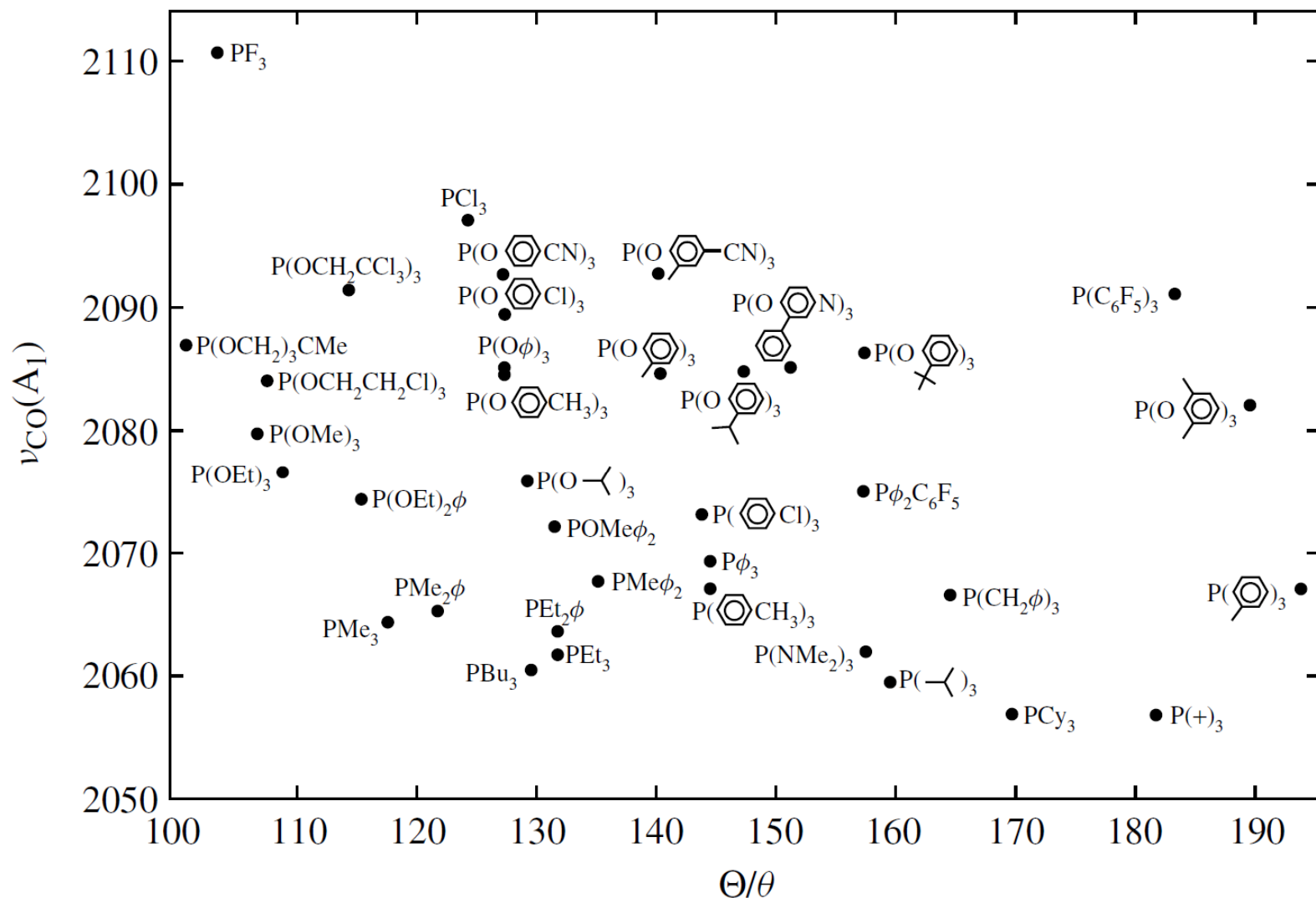


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1} , θ in degrees).

- An important part of organometallic chemistry consists in **varying the steric and electronic nature of the ligand environment of a complex** to promote whatever properties are desired: activity or selectivity in homogeneous catalysis, reversible binding of a ligand, facile decomposition, or high stability.
- Using the Tolman plot we can relatively easily change electronic effects without changing steric effects
 - e.g., by moving from PBU_3 to P(OiPr)_3
- Also, we can relatively easily change steric effects without changing electronic effects
 - e.g., by moving from PMe_3 to P(o-tolyl)_3