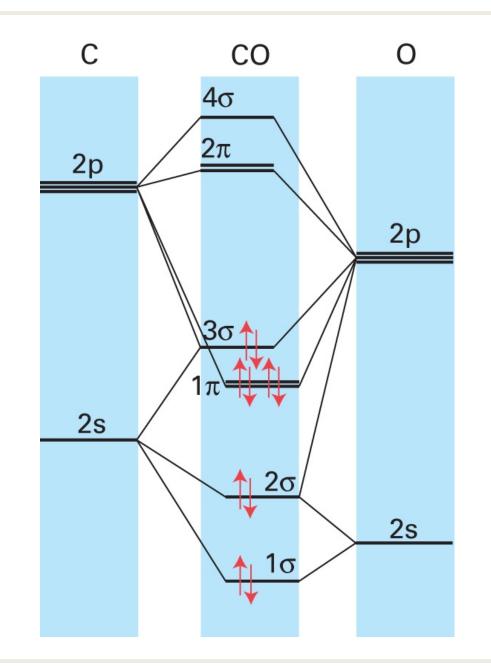
Metal Carbonyls

Inorganic Chemistry Chapter 1: Figure 22.3

W. H. Freeman



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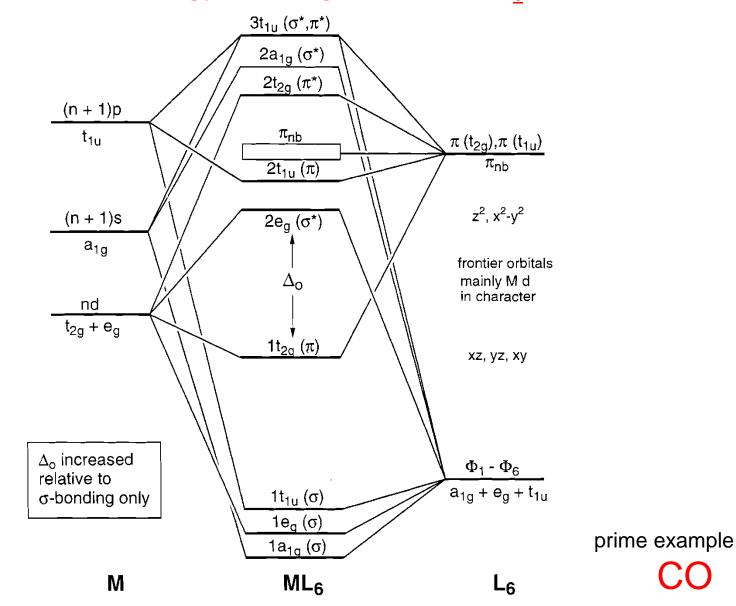
Homoleptic (binary) Metal Carbonyls of 1st Row Transition Metals

Group formula		Valence electrons		Structure
6	Cr(CO) ₆	Cr 6(CO) Total	6 12 18	
7	Mn ₂ (CO) ₁₀	Mn 5(CO) M—M Total	7 10 1 18	OC CO OC CO
8	Fe(CO) ₅	Fe 5(CO) Total	8 10 18	
9	Co ₂ (CO) ₈	Co 4(CO) M—M Total	9 8 1 18	
8	Ni(CO) ₄	Ni 4(CO) Total	10 8 18	

 Table 22.5
 Formulas and electron count for some 3d-series carbonyls

<u>Case 2</u>. L π orbitals vacant and less stable than d π orbitals (L is a π -acceptor)

<u>A more accurate MO energy level diagram for $Cr(CO)_{6}$.</u>



Metal Carbonyls Report on Electron Density at Metal by CO Stretching "frequencies" (actually wavenumber, $E \propto 1/\lambda$)

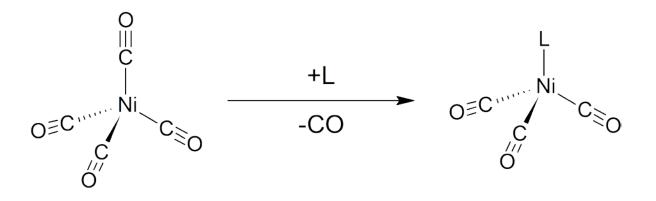
Complex	v(CO), cm⁻¹
[V(CO) ₆] ⁻	1858
[Cr(CO) ₆]	2000
[Mn(CO) ₆]⁺	2095
(Free CO	2143

Complex	v(CO), cm-1
[W(CO) ₆]	1977
[Re(CO) ₆] ⁺	2085
[Os(CO) ₆] ²⁺	2190
[Ir(CO) ₆] ³⁺	2254

Metal Carbonyls are "Reporter Ligands"

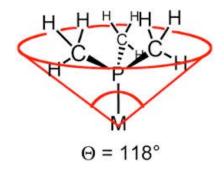
Classifying Ligand Properties: Chad Tolman



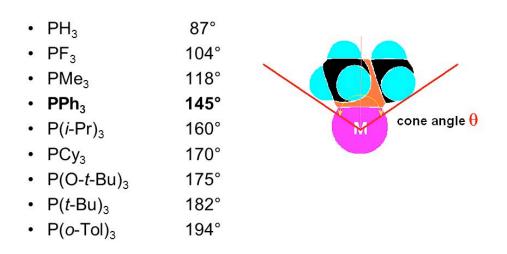


Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis

Chadwick A. Tolman Chem. Rev., 1977, 77 (3), pp 313–348 DOI: 10.1021/cr60307a002

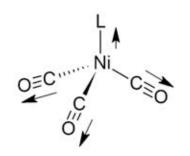


Tolman cone angle



Tolman Electronic Parameter

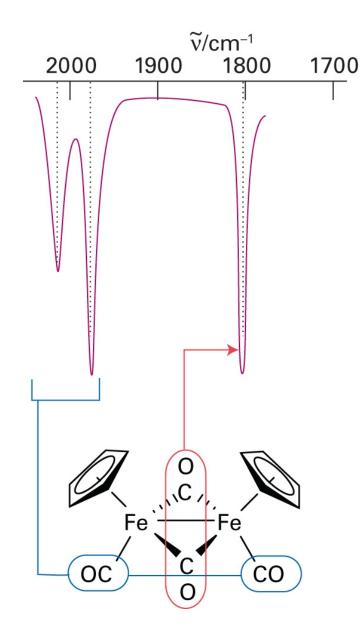
TEP for selected phosphines



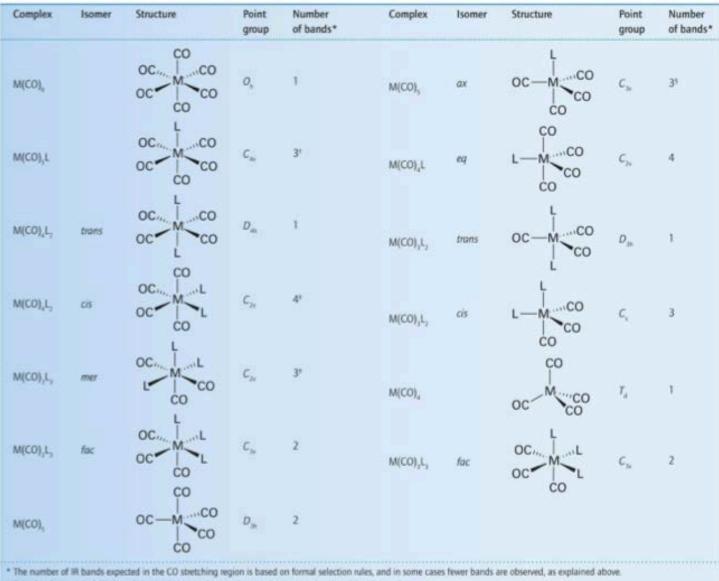
L	v(CO) cm ⁻¹
P(t-Bu) ₃	2056.1
PMe ₃	2064.1
PPh ₃	2068.9
P(OEt) ₃	2076.3
PCl ₃	2097.0
PF ₃	2110.8

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Infrared spectra report on types of CO groups in the organometallic.



Infrared spectra report on symmetry of substitution products.



If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.

* If the trons-CO ligands are nearly collinear, one fewer band will be observed.

If the threefold array of CO ligands is nearly planar, only two bands will be observed.

<u>SOME FACTS</u> Typical stretching frequencies:

- •Uncoordinated or "free" CO: 2143 cm⁻¹
- •Terminal M-CO: 2125 to 1850 cm⁻¹
- •Doubly bridging (μ -2): 1850 to 1750 cm⁻¹
- •Triply bridging (μ -3): 1675 to 1600 cm⁻¹
- •Semibridging: somewhere between terminal and μ -2.

Trends observed in the IR spectra of carbonyl complexes that are consistent with the concept of π -backbonding:

- 1. With each charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm⁻¹.
- 2. The better the sigma-donating capability (or worse the pi-acceptor ability) of the other ligands on the metal, the lower the CO stretching frequency.
- 3. For simple carbonyl complexes, counting the number of IR and Raman CO stretching frequencies will often permit one to make a structural assignment. The number of CO stretches expected for possible geometries/isomers can be predicted using group theory and the calculated results compared to the experimental data.

4. In the ¹³C NMR spectrum, coordinated carbonyl ligands typically appear in the range of 180 to 250 ppm. Isotopically enriched carbonyl complexes are often prepared to simplify mechanistic investigations or to facilitate the collection of the spectrum. In addition, the coupling of a ¹³C-enriched complex to other spin active nuclei such as ¹⁰³Rh or ³¹P, can aid in structural assignments.

All geometries are seen for Metal Carbonyls

Octahedral : M(CO)₆

Trigonal Bipyramidal : Fe(CO)₅

Square planar Don't know of any

Tetrahedral Ni(CO)₄

Trigonal planar

Linear $Cu^{I}(CO)_{2}^{+}$, $Ag^{I}(CO)_{2}^{+}$