Transition metal carbonyl compounds

Enormous number and variety of compounds prepared during the long history of this class of complexes (from the second half of the XIX century), which pertains to coordination chemistry beside organometallic chemistry.

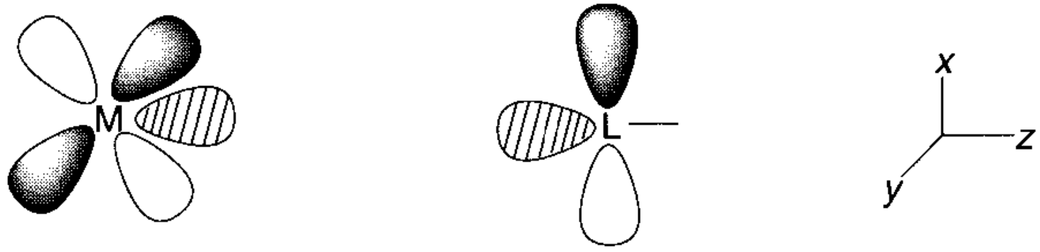
CO is able to form stable bonds with all transition metals, often acting as bridging ligand, supporting M-M bonds and favouring the generation of polynuclear complexes reaching a high degree of complexity (metallocarbonyl clusters).

Whereas free CO is chemically inert, coordinated CO shows electrophilic reactivity at C; this enables numerous synthetic applications which use CO as a “C1 building block”.

Prototypical σ-donating/π-accepting ligand

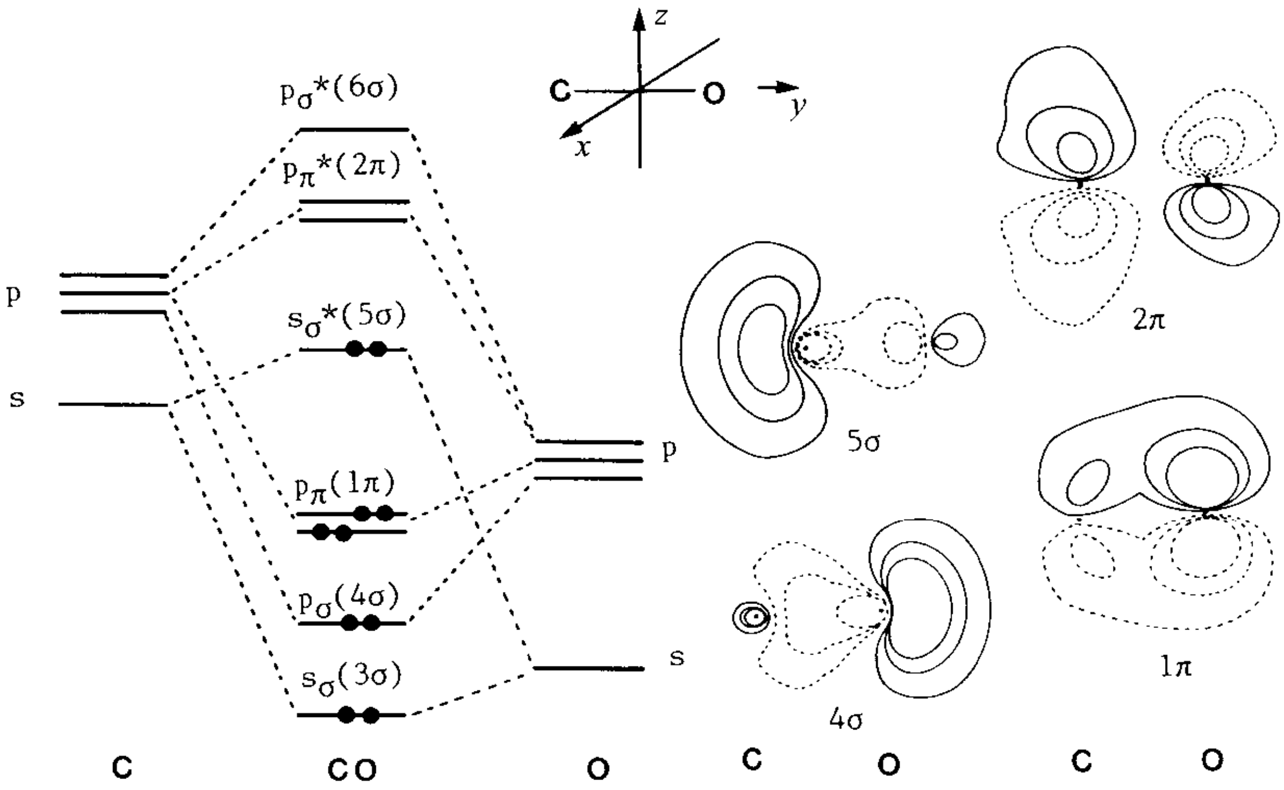
Transition metal carbonyl compounds

Donor-acceptor synergism: the organic ligand coordinated to the metal is not behaving only as a donor of electron density towards the metal, but also accepts electron density from the metal; <u>both these electron density transfers contribute in a synergistic way to the M-C bond</u>.



s, p_z, d_{z^2} - AO (hybrids) unoccupied	$\xleftarrow{\sigma}$	s, p_z - AO (hybrids) occupied	**dative bonding** "bonding"
p_x,p_y, d_{xz}, d_{yz} - AO (hybrids) occupied	$\xrightarrow{\pi}$	p_x,p_y, d_{xz}, d_{yz} - AO (hybrids), L(π^*), L(σ^*) - MO unoccupied	**retrodative bonding** "back-bonding"

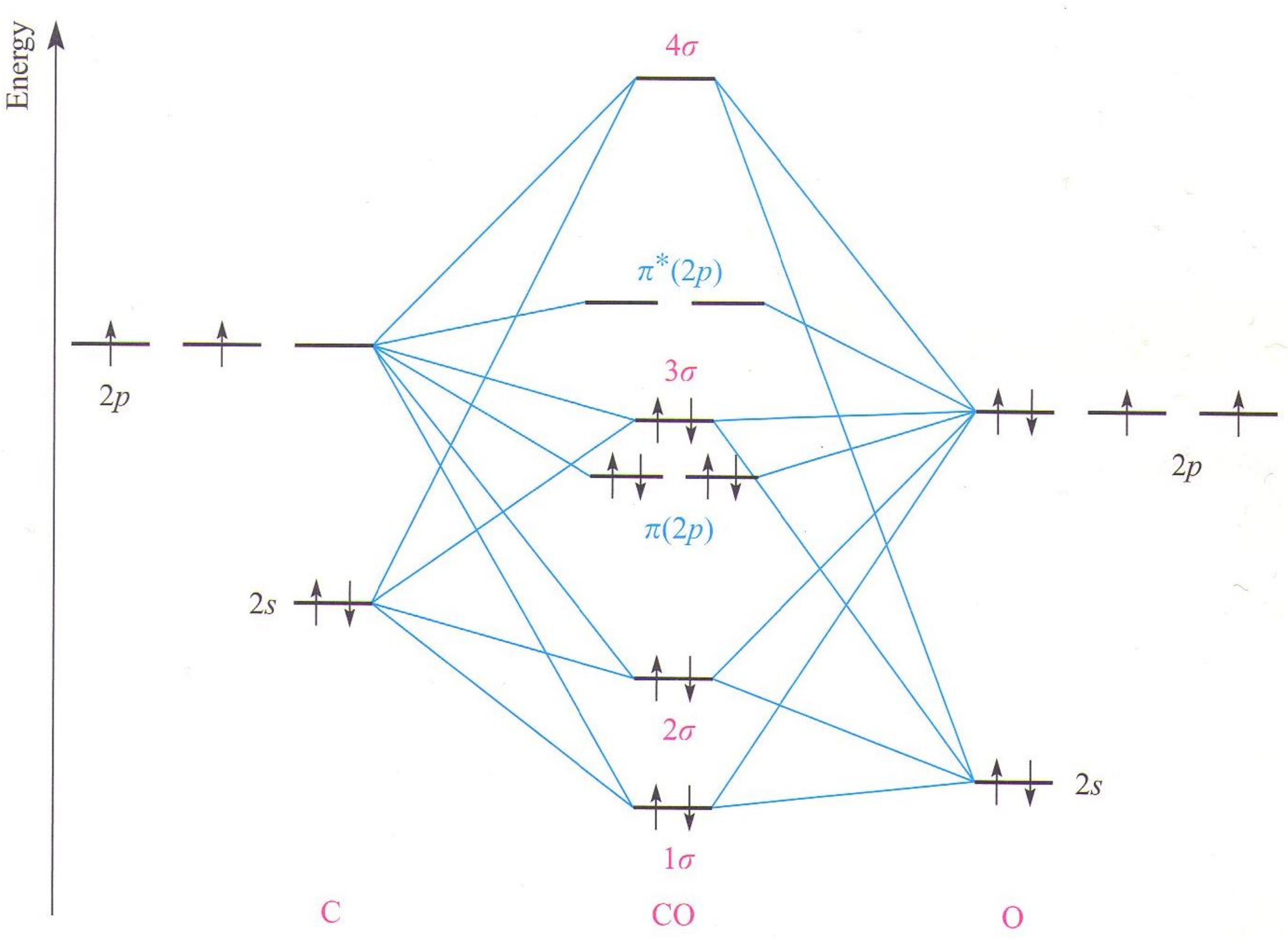
CO molecular orbitals



This rudimentary **energy-level diagram for CO** can be refined by inclusion of s,p_y mixing. The symbols in brackets refer to the sequence of the orbitals that results when all electrons (including C(1s) and O(1s)) are considered. Crucial to the discussions on M–CO bonding properties are the frontier orbitals 1π, 5σ, and 2π. Weak antibonding character is generally attributed to the 5σ MO, even though clear experimental evidence to this effect is lacking.

Contour line diagrams for the frontier orbitals of free CO can be drawn on the basis of quantum-chemical calculations. They portray the shape of the ligand molecular orbitals that are relevant for M–C–O bonding. Solid and broken lines indicate opposite phases with absolute values of 0.3, 0.2, and 0.1.

CO molecular orbitals



C. E. Housecroft, A. G. Sharpe, **Inorganic Chemistry**, 2nd Ed., Pearson, 2005

CO coordination and its consequences

In a simple diatomic molecule such as CO, coordination will have immediate consequences on the C-O bond strength, which can be directly measured from the position of the C-O bond stretching band in the IR spectrum of the complex:

νCO = 2143 cm^{-1}

Simple σ donation can be assimilated to CO ionization:

νCO^+ = 2184 cm^{-1}

The wavenumber of the stretching band increases, hence the C-O bond strengthens (weakly antibonding character of the HOMO, electrostatic contribution…). Such an increase is observed also in complexes in which CO exclusively acts as s donor:

$\nu H_3B–CO$ = 2164 cm^{-1}

CO coordination and its consequences

When donor-acceptor synergism is established, electron density is withdrawn from the HOMO of coordinated CO by M and pumped into the LUMO. This event can be mimicked as the promotion of one electron from the HOMO into the LUMO:

νCO* = 1489 cm^{-1} (singlet)
1715 cm^{-1} (triplet)

The LUMO is clearly strongly antibonding in character.

Since the donor-acceptor synergism in coordinated CO shifts electrons from a weakly antibonding orbital (HOMO) into a more markedly antibonding one (LUMO), this translates into a net weakening of the CO bond, hence into a decrease in the CO stretching wavenumber.

CO coordination and its consequences

It is important to remark that **the two CO orbitals involved in donor-acceptor synergysm have a different distribution on the CO molecule**: the HOMO is much more localized on C, hence C loses electron density and becomes electrophilic, whereas O becomes nucleophilic.

CO complexes can form even with metal centres in which back donation is negligible or even absent. In these complexes, though, the wavenumber of the CO stretching will be higher than in free CO (nonclassical metal carbonyls). The M-CO bond in these cases is weaker, but still useful for applications;

$$Cu^+/NH_4OH + CO \leftrightarrows [Cu(CO)(NH_3)_2]^+$$

Reaction employed for the removal of CO traces from gaseous effluents.

Stability of transition metals metallocarbonyls

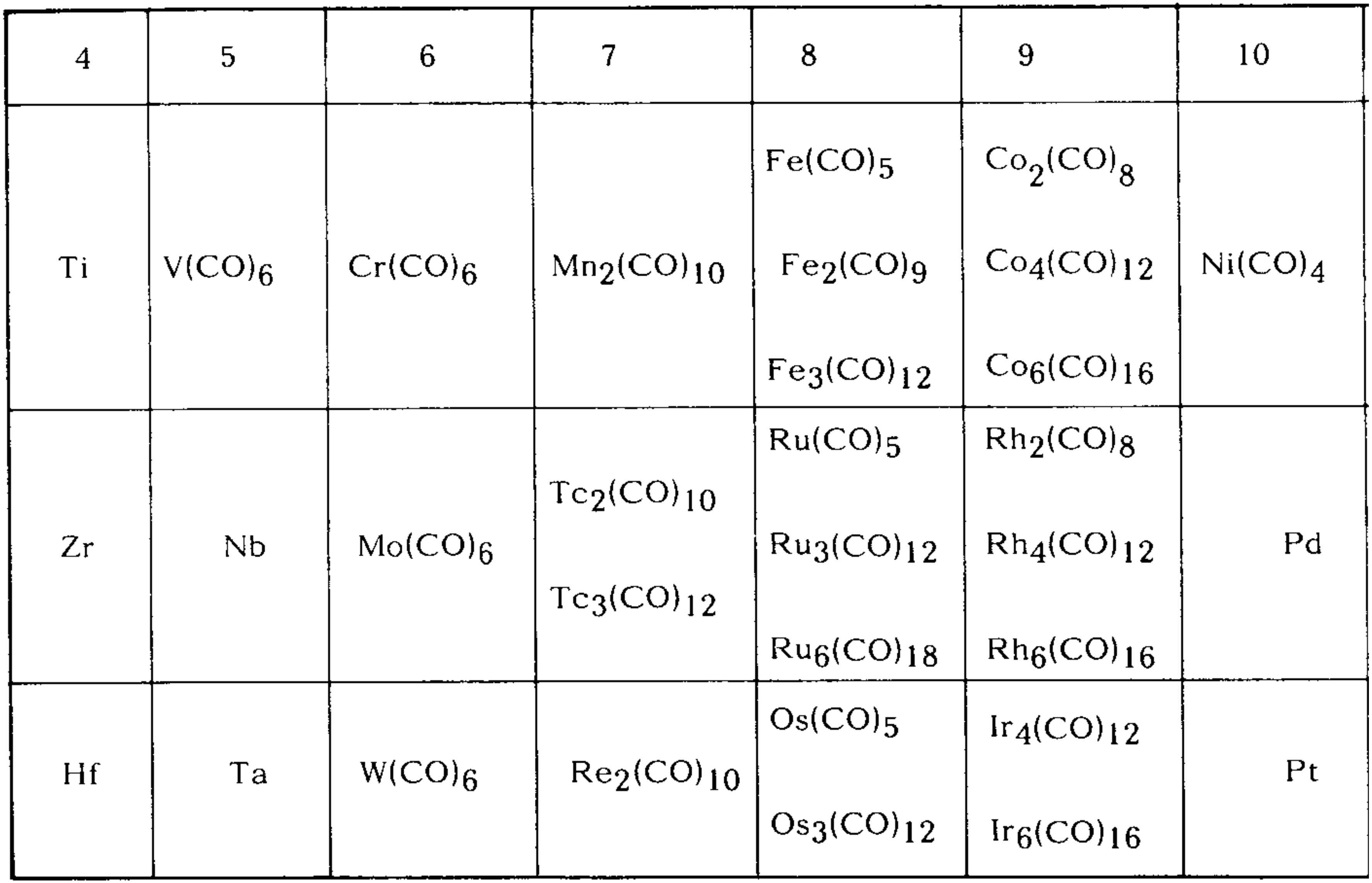
CO forms neutral homoleptic complexes (metal in oxidation state 0) with ALL transition metals of groups 6-9, plus V (group 5) and Ni (group 10).

- Back donation stabilizes low oxidation states, which are otherwise very reactive (oxidation, oxidative addition, aggregation…);

- Back donation makes out the main contribution to the stability of the M-CO interaction (d electrons are necessary!);

- The extent of back donation depends on the availability of electrons in the metal d orbitals, but also on the energy of these orbitals!

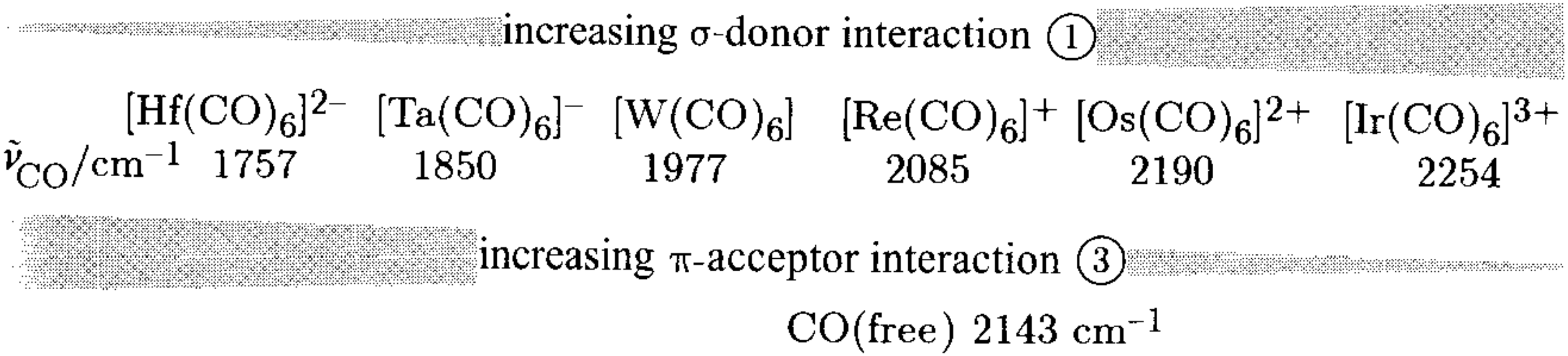
Stability of transition metals metallocarbonyls



4	5	6	7	8	9	10
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$ $Co_6(CO)_{16}$	$Ni(CO)_4$
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$ $Tc_3(CO)_{12}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$ $Ru_6(CO)_{18}$	$Rh_2(CO)_8$ $Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$ $Ir_6(CO)_{16}$	Pt

Stability of transition metals metallocarbonyls

Going from left to right in the periodic table, <u>the number of d electrons on the metal increases</u>, favouring back donation. At the same time, though, <u>the energy of the d orbitals decreases</u> (increase of effective nuclear charge) and consequently the d electrons are less available for back donation.
The <u>charge on the metal</u> also has a marked effect: a positive charge stabilizes the d orbitals making them less available for back donation, whereas a negative charge favours it.



increasing σ-donor interaction ①

	$[Hf(CO)_6]^{2-}$	$[Ta(CO)_6]^{-}$	$[W(CO)_6]$	$[Re(CO)_6]^{+}$	$[Os(CO)_6]^{2+}$	$[Ir(CO)_6]^{3+}$
$\tilde{\nu}_{CO}/cm^{-1}$	1757	1850	1977	2085	2190	2254

increasing π-acceptor interaction ③

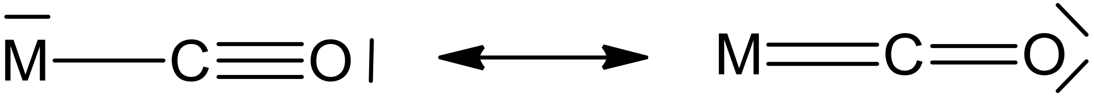
CO(free) 2143 cm^{-1}

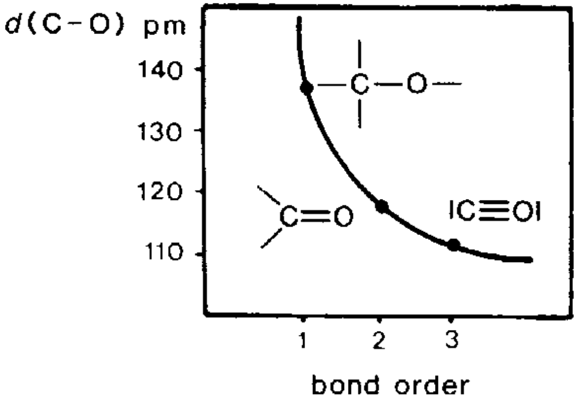
Stability of transition metals metallocarbonyls

In the M-CO interaction, with varying M the contribution of back donation to the bond varies, and consequently....

- The wavenumber of C-O stretching varies;

- The length of the C-O bond varies (only little; small differences between triple and double C-O bond);

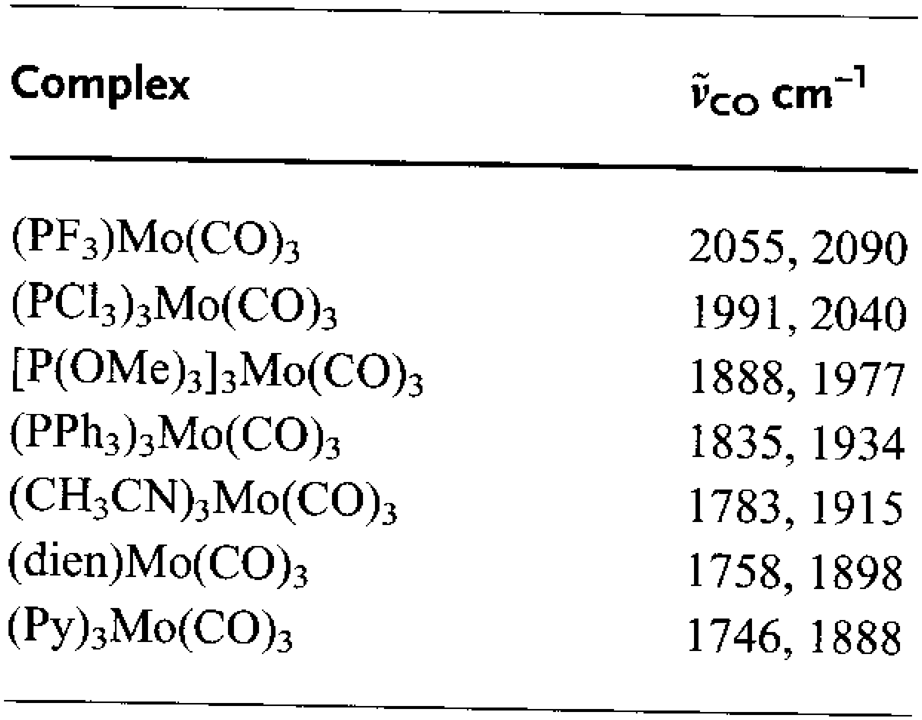




- The length of the M-C bond, which increases with increasing back donation (partial double bond character); it is however difficult to compare this length with that of single M-C bonds…

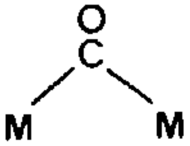
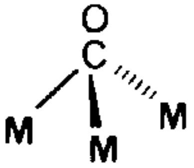
Effect of the other ligands

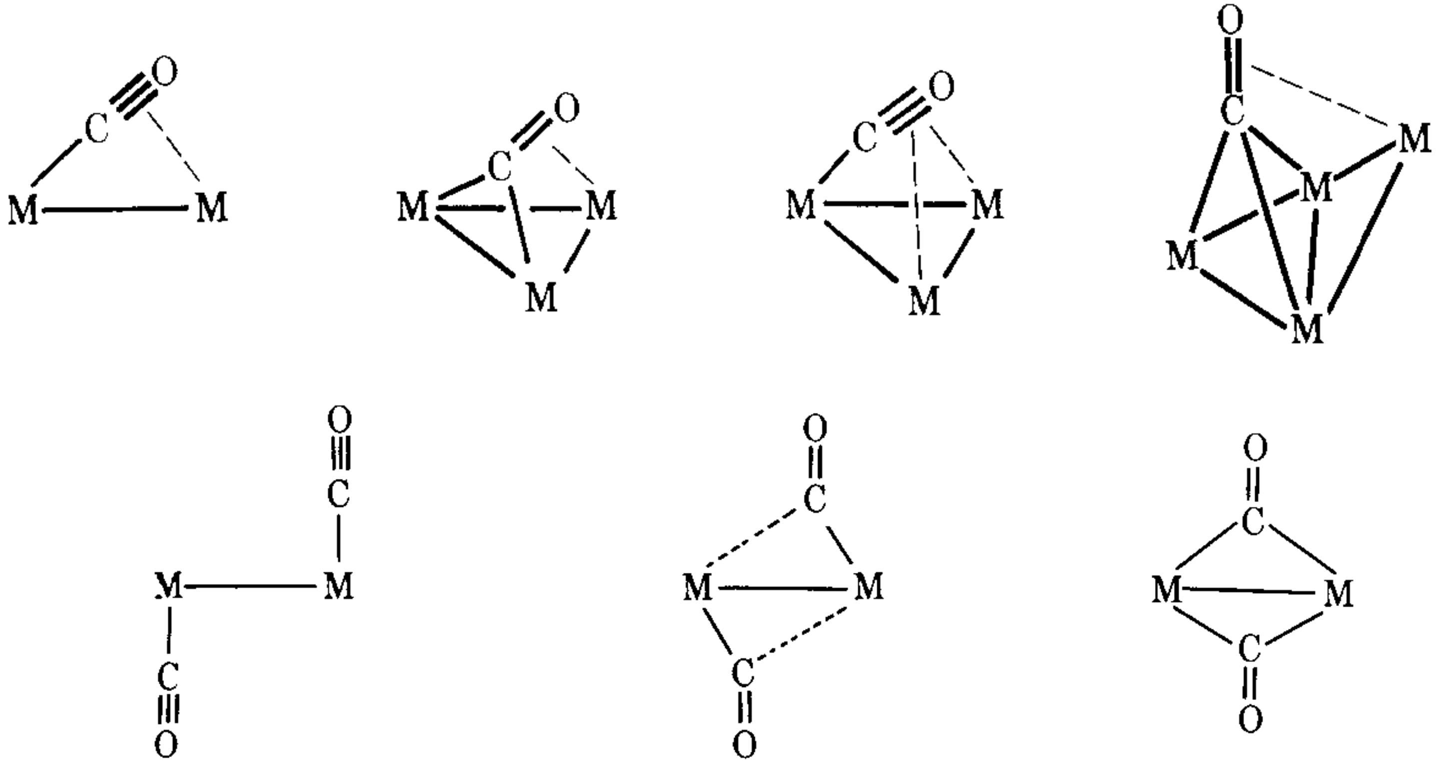
In the presence of other π-accepting ligands, these compete with CO for the electron density on the metal. This allows tro measure, through the stretching wavenumber of CO in L-M(CO)$_n$ σ-donating (and π-accepting) ability of L (Tolman Electronic Parameter, TEP).
M(CO)$_n$ = strong "soft" Lewis acid



Complex	$\tilde{\nu}_{CO}$ cm^{-1}
$(PF_3)Mo(CO)_3$	2055, 2090
$(PCl_3)_3Mo(CO)_3$	1991, 2040
$[P(OMe)_3]_3Mo(CO)_3$	1888, 1977
$(PPh_3)_3Mo(CO)_3$	1835, 1934
$(CH_3CN)_3Mo(CO)_3$	1783, 1915
(dien)$Mo(CO)_3$	1758, 1898
$(Py)_3Mo(CO)_3$	1746, 1888

Bridging CO

	Free	Terminal	μ_2-CO	μ_3-CO
				
$\tilde{\nu}_{CO}$ (cm^{-1})	2143	1850–2120	1750–1850	1620–1730



Synthesis of transition metal carbonyls

CO easily binds to TM centres, occupying free coordination sites or substituting other ligands. Often it is enough to place the starting complex in an atmosphere of CO. CO complexes can be prepared also by decarbonylation of metal acyls (see below).

The synthesis of homoleptic metallocarbonyls can follow two routes:

- Direct synthesis:

$Ni + 4CO \rightarrow Ni(CO)_4$ at room T and 1 bar CO

$Fe + 5CO \rightarrow Fe(CO)_5$ at 150 °C and 100 bar CO

- Metal salt + reducing agent + CO:

$WCl_6 + 2AlEt_3 + 6CO \rightarrow W(CO)_6 + 3C_4H_{10}$

As reducing agent, metals (group 1 metals, Al…), organometallic compounds of the main groups, or even CO itself are employed.

Reactivity of transition metals carbonyls
CO substitution

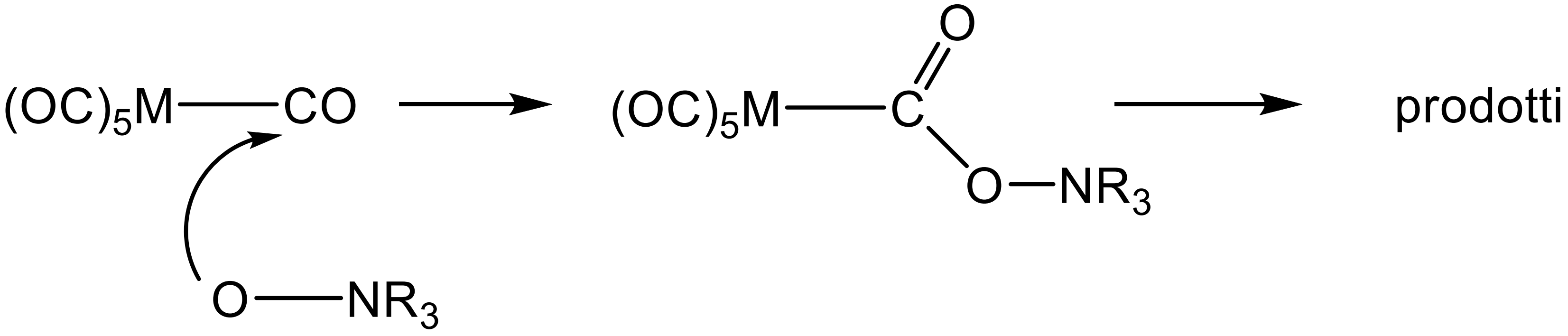
Generally, the substitution of CO with another ligand is not a facile reaction, given the small size of CO and the strength of the M-CO bond. The substitution rate is usually highest for the second metal in each group.

Homoleptic metallocarbonyls are generally 18 e^- complexes. Consequently, they give substitution reactions with a dissociative mechanism. The activation energy almost coincides with the M-CO boind energy. The substitution becomes increasingly difficult the more CO molecules are removed (the availability of electron density on the metal for back donation increases).

The dissociation can be promoted thermally, photochemically, chemically (using nucleophilic reagents) or catalytically (electron transfer catalysis).

Chemically promoted substitution

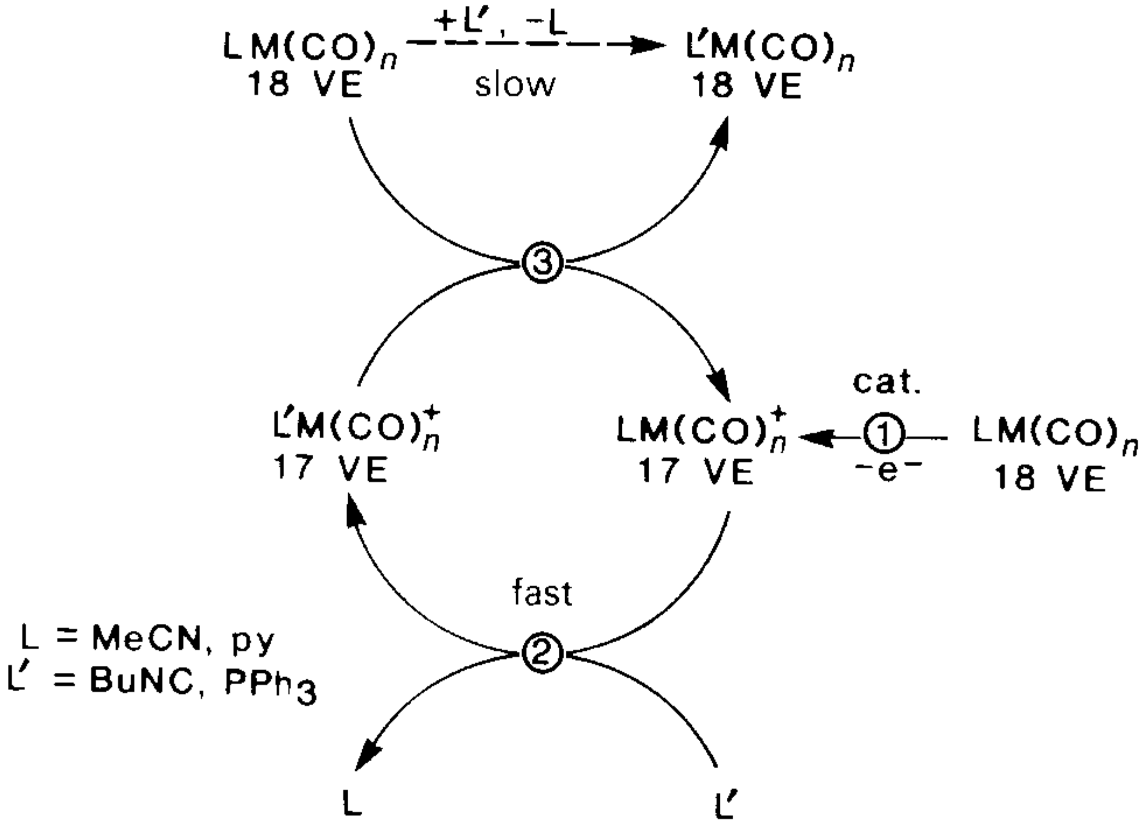
$M(CO)_n + O\text{-}NR_3 + L \rightarrow M(CO)_{n-1}L + CO_2 + NR_3$



Nucleophilic attack of the tertiary amine oxide formally oxidizes the coordinated CO; subsequent fast decomposition of the resulting intermediate liberates a coordination site on the metal for the incoming ligand L.

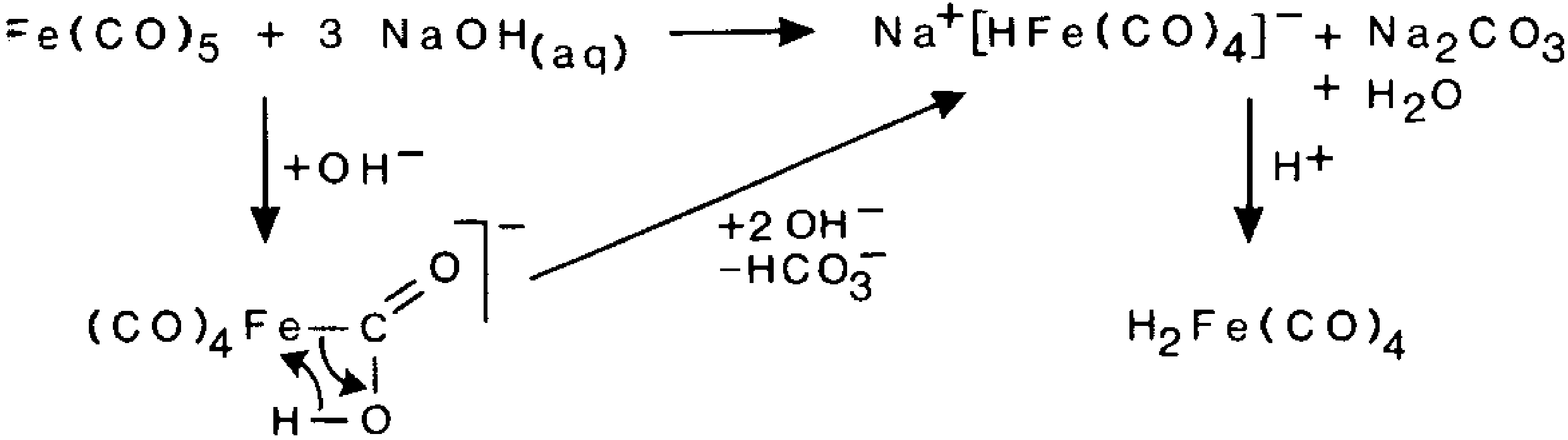
Substitution via electron transfer catalysis

The process is initiated by a reversible monoelectronic **oxidation**/reduction. 17 e$^-$ complexes generally react much faster than 18 e$^-$ complexes (e.g. $V(CO)_6$ reacts 10^{10} times faster than $Cr(CO)_6$



Reactivity of transition metal carbonyls
Nucleophilic attack on CO

Coordinated CO becomes electrophilic, hence it can be attacked by nucleophiles, via **external nucleophilic attack** or via **intramolecular migratory insertion** of a precoordinated nucleophile on CO. The former reaction is typical for homoleptic metallocarbonyls (requires strong nucleophiles, stoichiometric reactions). For example, upon treating with aqueous bases, carbonyl hydrides can be prepared:



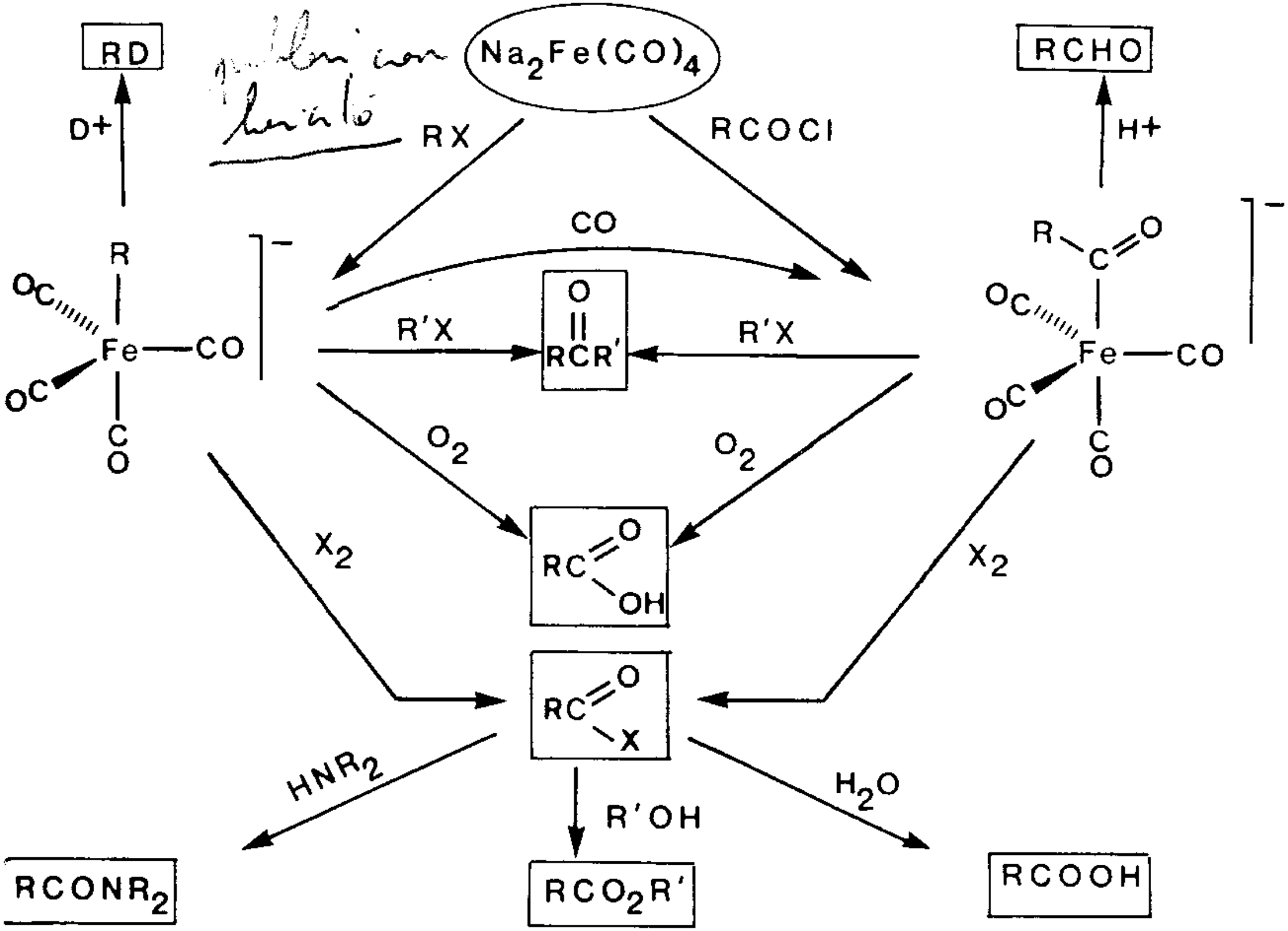
Transition metal carbonyl hydrides

The chemical behaviour of metal-bound hydrogen in metal carbonyl hydrides varies considerably depending on the nature of the metal, of other ligands present etc. Even if it shows some typically hydridic properties (e.g. it is commonly found at negative values of δ in the ^{1}H-NMR spectrum), it often behaves as an acid:

$HCo(CO)_4$	pK_a 1	(in water)
$H_2Fe(CO)_4$	pK_a 4.7	(in water)
$HMn(CO)_5$	pK_a 7	(in water)
$HCo(CO)_4$	pK_a 8.4	(in acetonitrile)
$HCo(CO)_3P(OPh)_3$	pK_a 11.4	(in acetonitrile)
$HCo(CO)_3PPh_3$	pK_a 15.4	(in acetonitrile)

Deprotonated carbonyl hydrides (carbonylate anions) can be conveniently employed as nucleophiles at the metal.

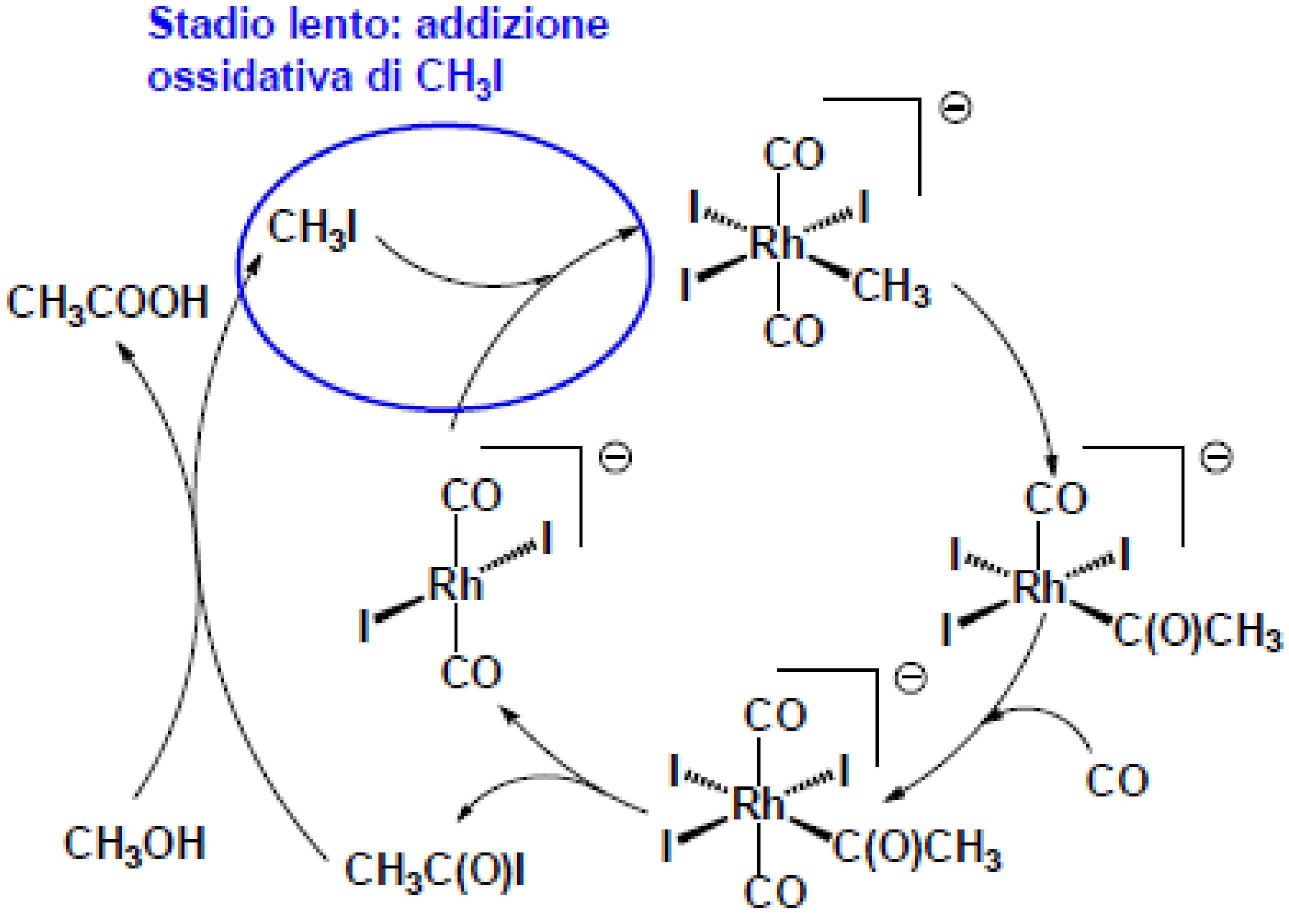
Carobonyl metallates: the Collman reagent



<u>Catalytic</u> R-X carbonylation reactions

R-X + CO + HNu → R-CO-Nu + HX

<u>Monsanto process (MeOH, 180 °C, 30-40 atm)</u>



<u>Catalytic</u> R-X carbonylation reactions

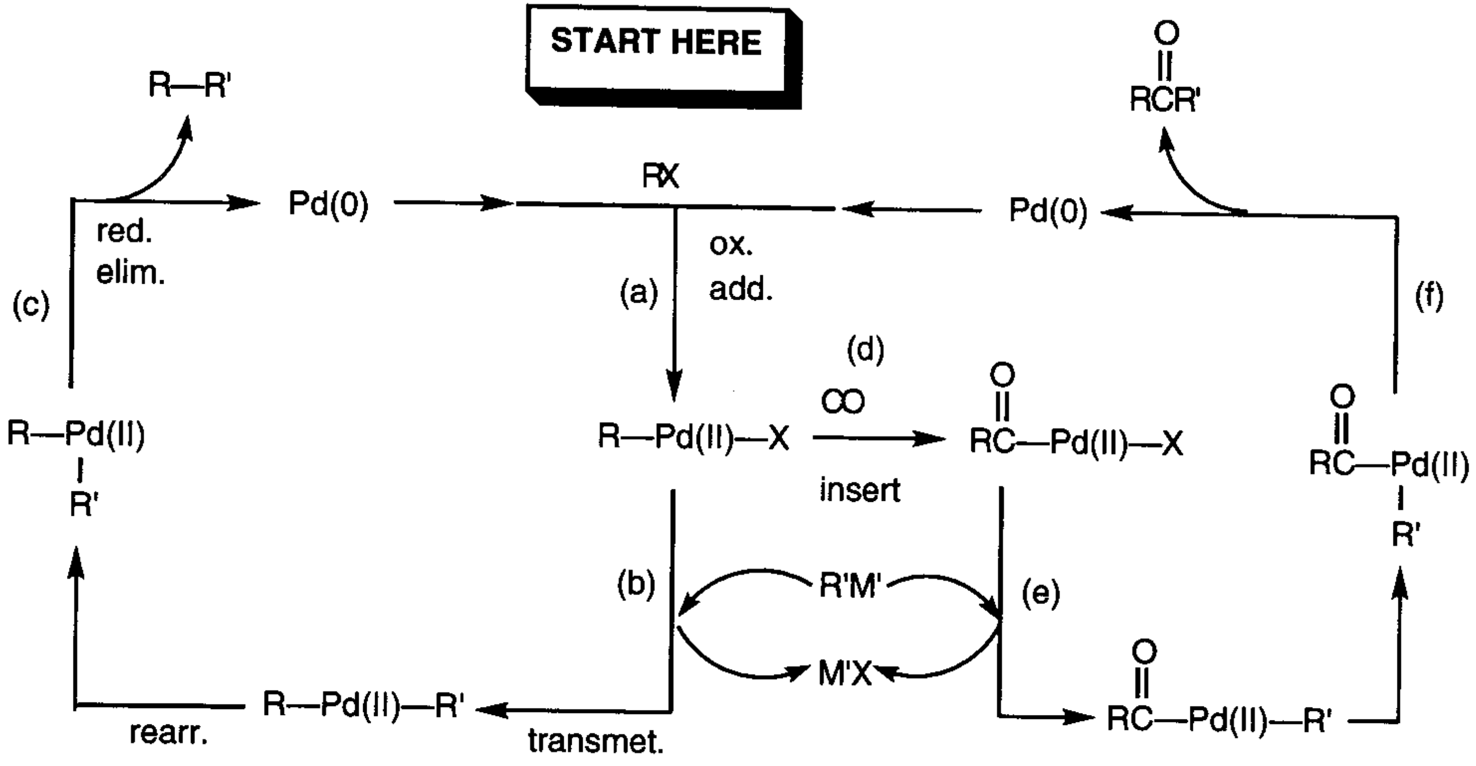
Carbonylation reactions can be performed with several metal centres as catalysts; apart from the Rh(I)/Rh(III) system, employed in the Monsanto process, Ir(I)/Ir(III) (Cativa process), Pd(0)/Pd(II), Ni(0)/Ni(II) etc. have been used.

The rate determining step of these processes is most commonly the oxidative addition of RX, since CO coordination inhibits it by coordinating to the metal in low oxidation state and withdrawing electron density from it. Consequently, it is necessary to use reactive RX and to optimize the reaction conditions, the charge of the complex etc.

The final reductive elimination can proceed through a <u>concerted mechanism</u> or through an <u>S_N2 mechanism</u> (external nucleophilic attack on the coordinated acyl, usually by a solvent molecule).

Carbonylative cross coupling reactions

Cross coupling reactions can be performed introducing an intermediate CO insertion stage, resulting in ketones as reaction products.



M = Mg, Zr, **Zn**, Sn, B, Al, Si, Cu

Aldehyde decarbonylation reactions

Stoichiometric reaction (catalytic above 200 °C), useful since it proceeds under mild conditions with retention of configuration on R. As catalyst, $RhCl(PPh_3)_3$ is employed.
Use of acyl halides as reagents for decarbonylation is possible but problematic (slow reaction, loss of stereoselectivity, competition with the β-elimination reaction).

Eq. 5.26