Organotransition metal compounds

Enormous variety of compounds, due to the availability of d orbitals (and electrons) for forming M-C bonds, which implies:

1. **Diverse coordination numbers and geometries** for each metal: hypervalent compounds, availability of free coordination sites, variability of the coordination number in situ (catalysis);

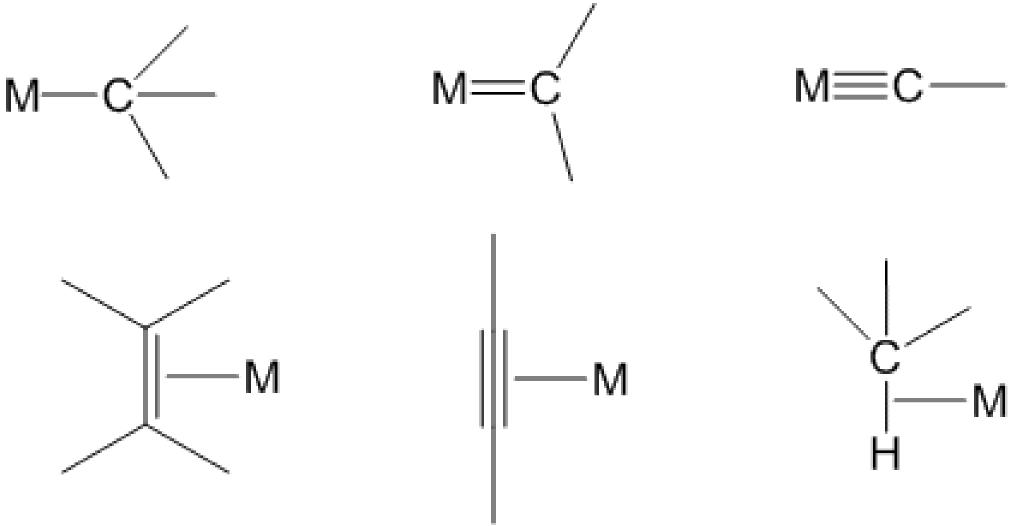
2. **Diverse stable formal oxidation states** for the metal;

3. Possibility to form **single or multiple M-M bonds**;

4. **Diverse types of M-C interactions**: apart from simple σ bonds, multiple M-C bonds, π bonds, bonds with σ donors.

Organotransition metal compounds

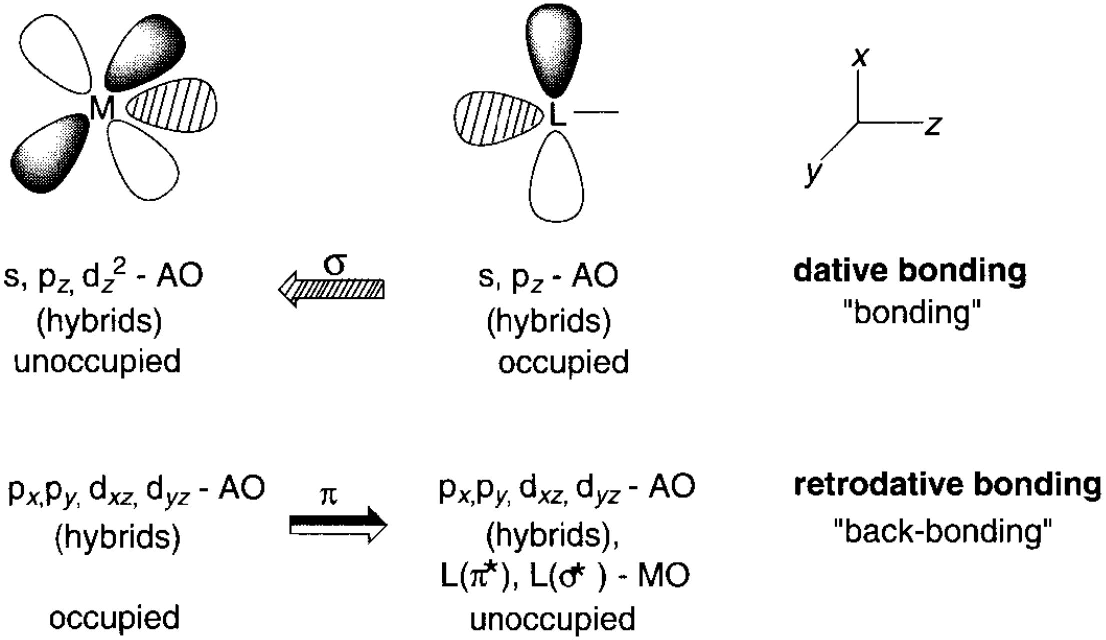
Contain diverse types of M-C bonds: σ M-C, multiple M-C, π M-C, agostic interactions, also in combination with one another:



Possibility to vary the **apticity** of a ligand (apticity η^n: no. of conjugated (C) atoms of the ligand which interact with M).

Donor-acceptor synergism

The organic ligand coordinated to the metal is often not only behaving 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>.



Extensive donor-acceptor synergism can be alternatively interpreted in terms of **multiple covalent bonding** between the metal and the organic moiety.

Donor-acceptor synergism

The donor-acceptor synergism is established when orbitals of suitable energy and simmetry are present on the ligand and metal.

It causes a redistribution of electron density between metal and ligand, which has consequences on the properties of the metal (e.g. stabilization of low oxidation states: $Fe(CO)_4^{2-}$) and of the ligand (e.g. olefin umpolung).

Donor and acceptor orbitals on the metal and especially on the ligand are different. Possibility of having an electron redistribution *within* the ligand as well.

Possibility of modulating the electron density redistribution acting on: a) charge of the complex; b) properties of other ligands; c) nature of the metal centre.

Descriptors for TM organometallic compounds

Parameters for the description of a generic organotransition metal compound:

First of all, a general formula for the compound of the type $[MX_aL_b]^{c+}$ is written, in which the ligands interacting with the metal are classified as **ligands L** or **ligands X** (Green convention):

Ligands L: Ligands which, once separated from the metal centre with their bonding electrons, are formally neutral;

Ligands X: Ligands which, once separated from the metal centre with their bonding electrons, are formally anionic;

Problem: sometimes it is not simple to define the type of ligand without structural data (diverse apticity, bridging CO, carbenes…)

Descriptors for TM organometallic compounds

Parameters for the description of a generic organotransition metal compound $[MX_aL_b]^{c+}$

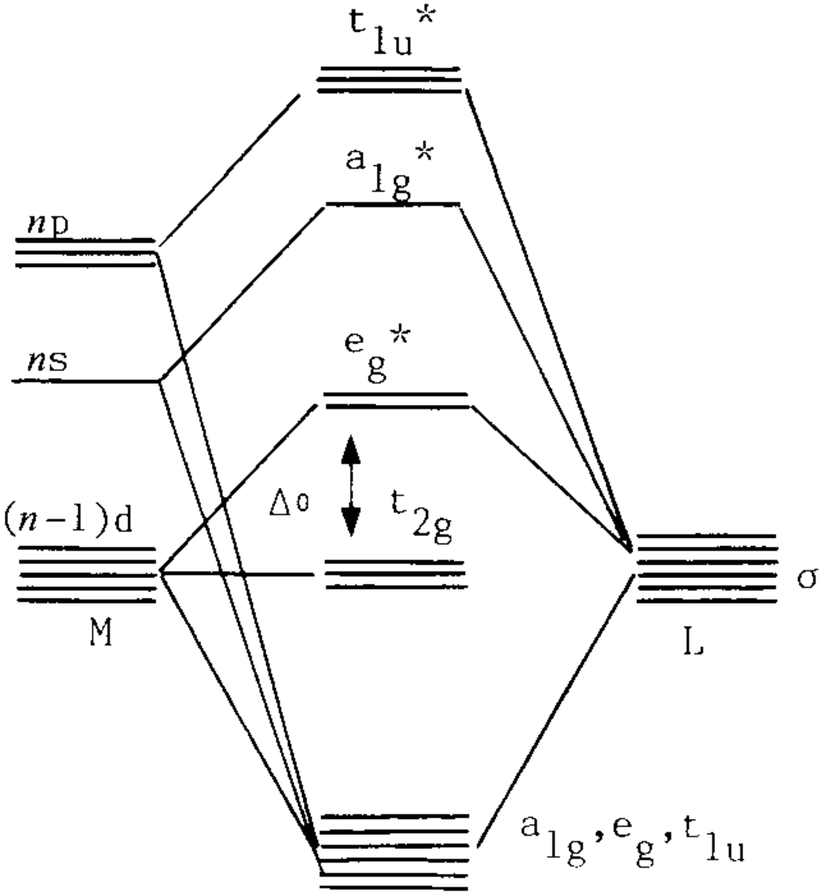
Number of electrons around the metal

no. $e^- = N + a + 2b - c$, N= group number of M

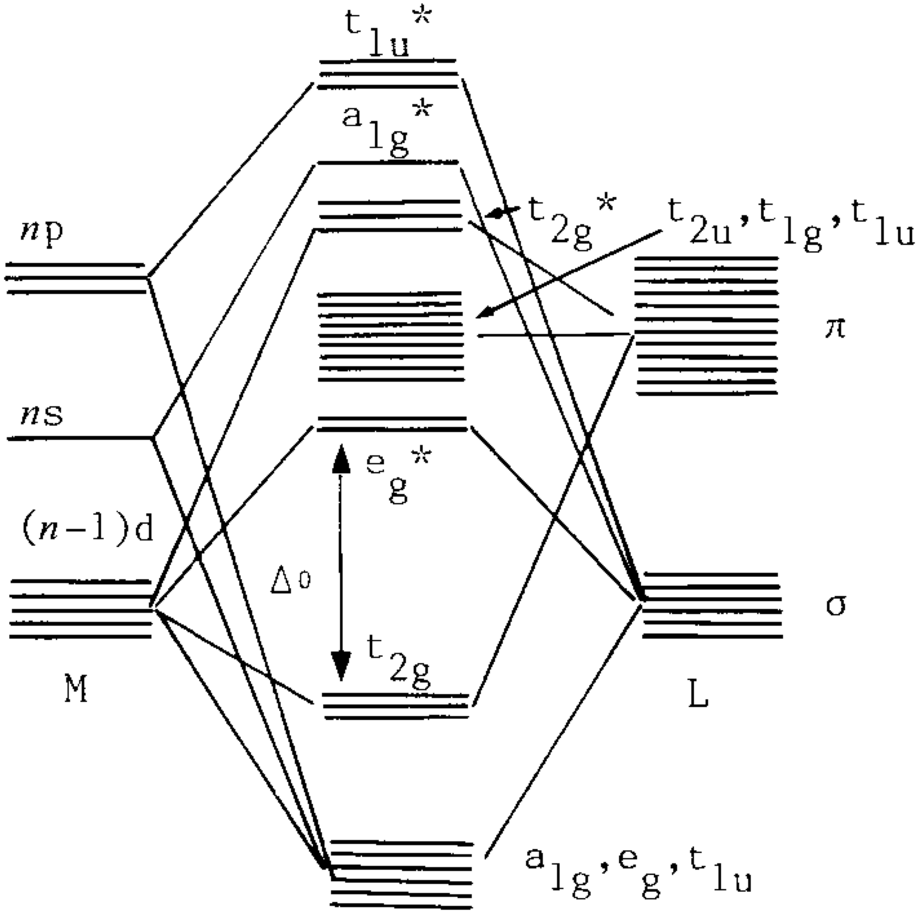
The 18-electron rule: the most stable organotransition metal compounds are obtained when the number of e- around the metal (electrons of the metal + bonding electrons with the coordinated ligands) reaches 18.

Intuitive explanation: since the metal provides 9 orbitals (1ns + 3np + 5(n-1)d), maximum occupancy is achieved with 18 e-…
A more rigorous explanation considers instead the molecular orbitals:

Descriptors for TM organometallic compounds



Molecular orbital diagram for an octahedral complex (simplified), σ bonding only



Molecular orbital diagram for an octahedral complex (simplified), σ and π bonding

Adapted from P. R. Mitchell, R. V. Parish, J. Chem. Ed. **1969**, *46*, 811.

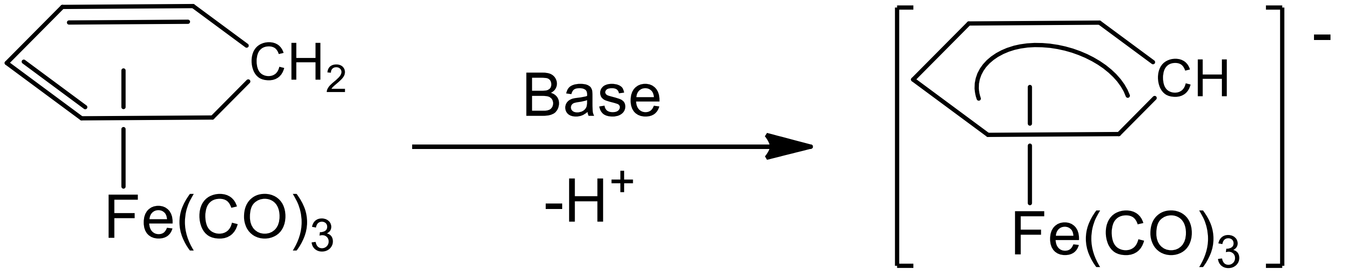
Descriptors for TM organometallic compounds

The 18 e- rule in organometallic chemistry is justified considering that ligands at carbon are generally high in the spectrochemical series.

The rule is extremely useful for predetermining stability/reactivity of organometallic compounds (e.g. Cp_2Fe, $[FeX_2L_4]$, 18 e^-; $[Fe(cyclohexadienil)(CO)_3]^+$ from $Fe(cyclohexadiene)(CO)_3$ upon hydride abstraction);

Exceptions to the 18 e^- rule: metal centres with few electrons at the beginning of the transition series, d^8 metal centres at the end of the transition series, compounds d^{10} of group 11, sterically encumbered compounds…

Descriptors for TM organometallic compounds

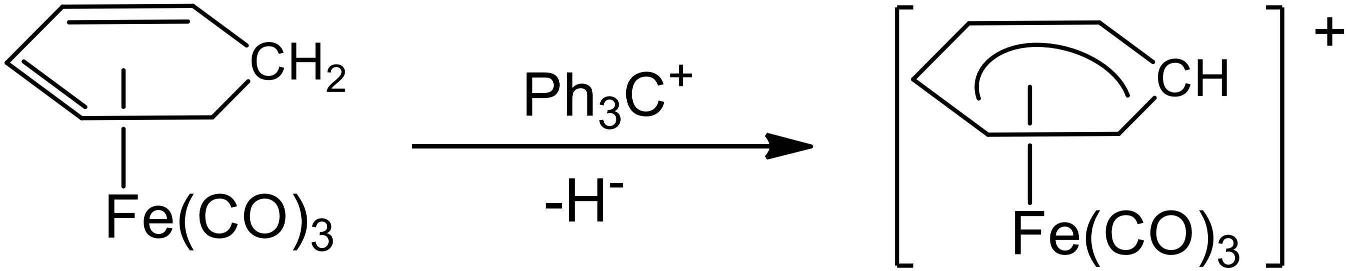


$[FeXL_5]^-$

$20e^-$

$[FeL_5]$

$18e^-$



$[FeXL_5]^+$

$18e^-$

Descriptors for TM organometallic compounds

Parameters for the description of a generic organotransition metal compound $[MX_aL_b]^{c+}$

Formal oxidation state of the metal

st. ox. = a + c

Less or equal than N (group number of M)

Electronic configuration of the metal (d^n)

n = N – (a + c)

These parameters, in particular the oxidation state, need to be considered **formalisms**, which, taken acritically, can determine the attribution to an organometallic compound of irrealistic chemical properties.

Descriptors for TM organometallic compounds

Parameters for the description of a generic organotransition metal compound $[MX_aL_b]^{c+}$

Coordination number and geometry

coord. no. = a + b, lower or equal to 9 (maximum number of available metal orbitals)

The determination of the coordination number can be nontrivial in organometallic chemistry (Cp_2Fe).

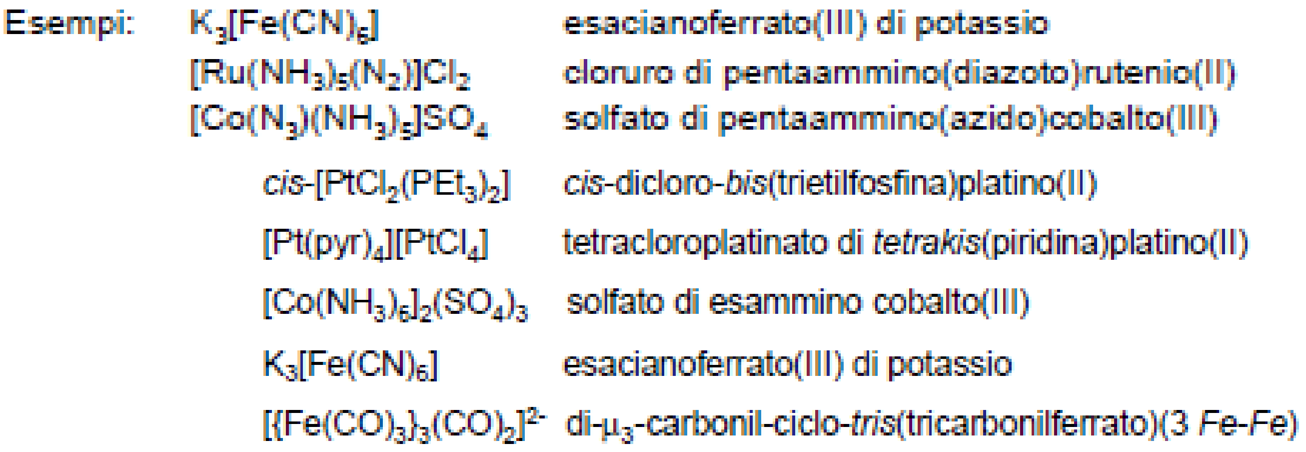
The coordination number can vary strongly with the steric bulk of the ligand.

The coordination geometry is influenced by steric and electronic effects (ligand field). VSEPR works only if the latter are absent (configuration d^0, d^5, d^{10}); electrons on M are not stereochemically active.

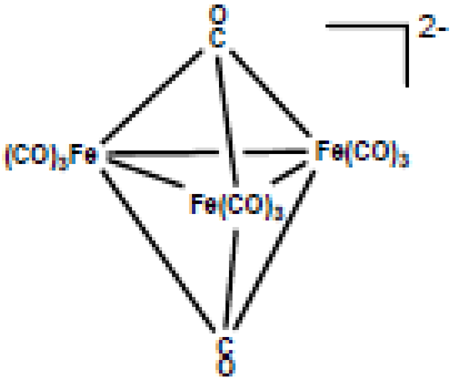
Nomenclature for TM organometallic compounds

$$[MX_aL_b]^{c+}$$

In the formula: in square brackets, metal centre, X ligands, L ligands (ligands in alphabetical order with the first letter of their formula; polyatomic ligands in brackets).
In the name: ligands X, ligands L (same order as above, with prefix when multiple), metal centre, suffix «ate» when anionic. Counteranions at the beginning (cations) / end (anions).



Esempi:	$K_3[Fe(CN)_6]$	esacianoferrato(III) di potassio
	$[Ru(NH_3)_5(N_2)]Cl_2$	cloruro di pentaammino(diazoto)rutenio(II)
	$[Co(N_3)(NH_3)_5]SO_4$	solfato di pentaammino(azido)cobalto(III)
	cis-$[PtCl_2(PEt_3)_2]$	*cis*-dicloro-*bis*(trietilfosfina)platino(II)
	$[Pt(pyr)_4][PtCl_4]$	tetracloroplatinato di *tetrakis*(piridina)platino(II)
	$[Co(NH_3)_6]_2(SO_4)_3$	solfato di esammino cobalto(III)
	$K_3[Fe(CN)_6]$	esacianoferrato(III) di potassio
	$[\{Fe(CO)_3\}_3(CO)_2]^{2-}$	di-μ_3-carbonil-ciclo-*tris*(tricarbonilferrato)(3 *Fe*-*Fe*)



Descriptors for TM organometallic compounds