LITTLE FLOWER COLLEGE

DEPARTMENT OF CHEMISTRY

TOPIC : 18 ELECTRON RULE

PRESENTED BY
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A. **Organometallic Mechanisms**

Oxidation State: The oxidation state of a metal is defined as the charge left on the metal after all ligands have been removed in their natural, closed-shell configuration. This is a formalism and not a physical property!

d-Electron Configuration: position in the periodic table *minus* oxidation state.

18-Electron Rule: In mononuclear, diamagnetic complexes, the total number of electrons never exceeds 18 (noble gas configuration). The total number of electrons is equal to the sum of d-electrons *plus* those contributed by the ligands.

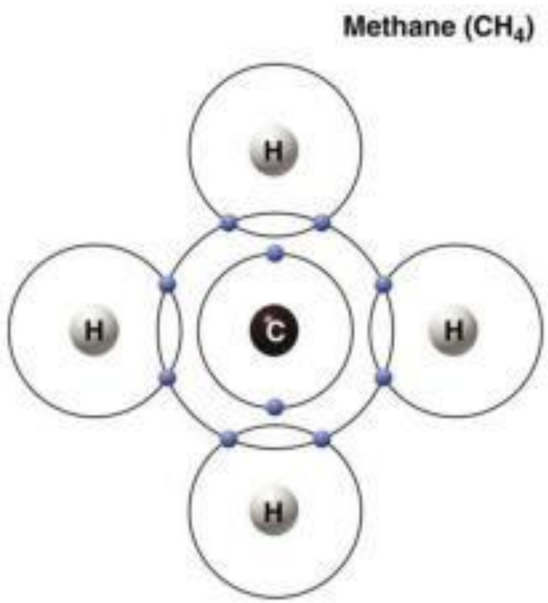
18 electrons = coordinatively saturated

< 18 electrons = coordinatively unsaturated.

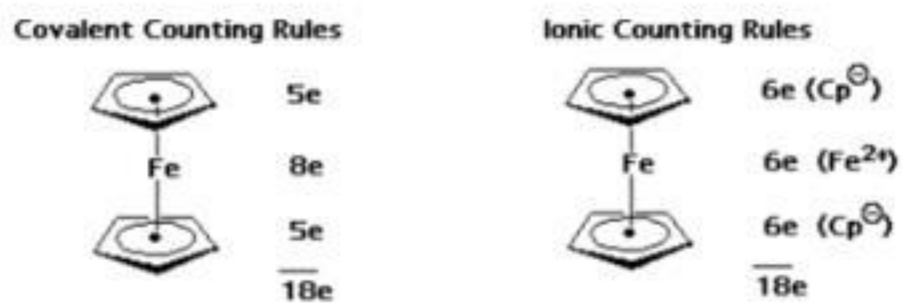
THE 18-ELECTRON RULE

In main group chemistry, we have encountered the octet rule, in which the electronic structures of many main group compounds can be rationalized on the basis of a valence shell requirement of 8 electrons.

In organometallic chemistry, the electronic structures of many compounds are based on a total valence electron count of 18 on the center metal atom.



Main group



Organometallic compound

THE 18-ELECTRON RULE

HOW to count ?

Method A : Donor Pair Method

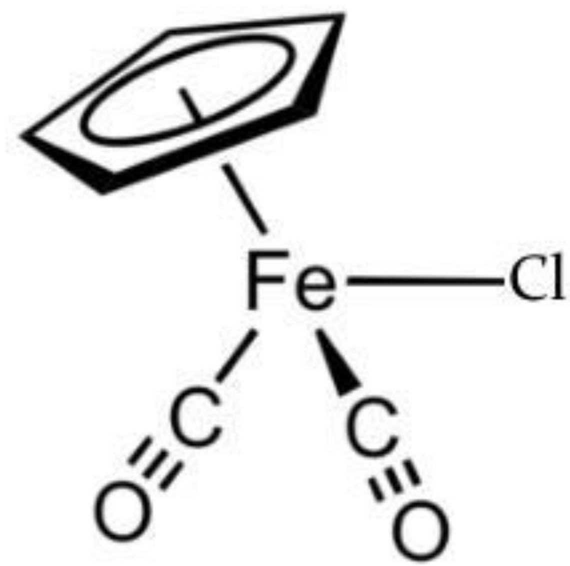
This method considers ligands to donate electron pairs to the metal. To determine the total electron count, we must take into account the charge on each ligand and determine the formal oxidation state of the metal.

THE 18-ELECTRON RULE

HOW to count ?

Method A : Donor Pair Method

Example> (η-C_5H_5)Fe(CO)$_2$Cl



Fe(Ⅱ)	6 electrons
η^5-$C_5H_5^-$	6 electrons
2 (CO)	4 electrons
Cl^-	2 electrons
Total =	18 electrons

THE 18-ELECTRON RULE

HOW to count ?

Method B : Neutral-Ligand Method

This method uses the number of electrons that would be donated by ligands of they were neutral. For simple inorganic ligands, this usually means that ligands are considered to donate the number of electrons equal to their negative charge as free ions.

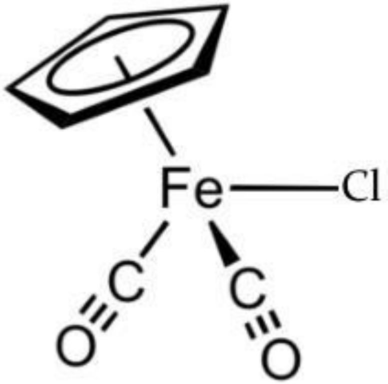
Cl is a 1-electron donor (charge on free ion = -1)
O is a 2-electron donor (charge on free ion = -2)

THE 18-ELECTRON RULE

HOW to count ?

Method B : Neutral-Ligand Method

Example> $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$



Fe atom	8 electrons
$\eta^5\text{-}C_5H_5$	5 electrons
2 (CO)	4 electrons
Cl	1 electron
Total =	18 electrons

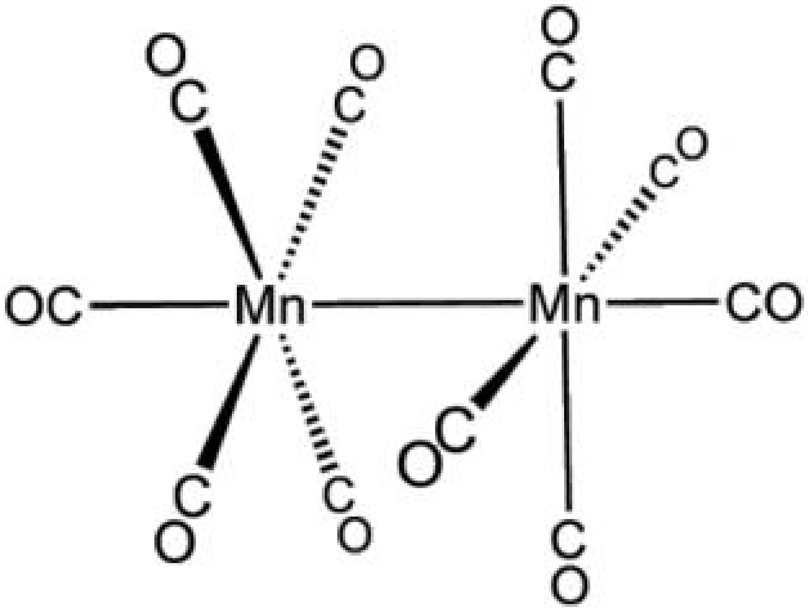
THE 18-ELECTRON RULE

HOW to count ?

Metal – Metal single bond counts as one electron per metal, a double bond counts as two electrons per metal, and so forth.

Example> $(CO)_5Mn - Mn(CO)_5$

Mn	7electrons
5 (CO)	10electrons
Mn – Mn	1 electron
Total =	18electrons



THE 18-ELECTRON RULE

HOW to count ?

Ligand	*Method A*	*Method B*
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^-, OR^-)	1
CN	2 (CN^-)	1
CH_3, CR_3	2 (CH_3^-, CR_3^-)	1
NO (bent M—N—O)	2 (NO^-)	1
NO (linear M—N—O)	2 (NO^+)	3
CO, PR_3	2	2
NH_3, H_2O	2	2
=CRR′ (carbene)	2	2
$H_2C{=}CH_2$ (ethylene)	2	2
CNR	2	2
=O, =S	4 (O^{2-}, S^{2-})	2
η^3-C_3H_5 (π-allyl)	2 ($C_3H_5^+$)	3
≡CR (carbyne)	3	3
≡N	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
η^5-C_5H_5 (cyclopentadienyl)	6 ($C_5H_5^-$)	5
η^6-C_6H_6 (benzene)	6	6
η^7-C_7H_7 (cycloheptatrienyl)	6 ($C_7H_7^+$)	7

THE 18-ELECTRON RULE

HOW to count ?

	Method A		Method B	
$ClMn(CO)_5$	Mn(I)	6 e^-	Mn	7 e^-
	Cl^-	2 e^-	Cl	1 e^-
	5 CO	10 e^-	5 CO	10 e^-
		18 e^-		18 e^-
$(\eta^5\text{-}C_5H_5)_2Fe$	Fe(II)	6 e^-	Fe	8 e^-
(Ferrocene)	2 $\eta^5\text{-}C_5H_5^-$	12 e^-	2 $\eta^5\text{-}C_5H_5$	10 e^-
		18 e^-		18 e^-
$[Re(CO)_5(PF_3)]^+$	Re(I)	6 e^-	Re	7 e^-
	5 CO	10 e^-	5 CO	10 e^-
	PF_3	2 e^-	PF_3	2 e^-
	+ charge	*	+ charge	−1 e^-
		18 e^-		18 e^-

THE 18-ELECTRON RULE

WHY 18 Electrons ?

If the octet represents a complete valence electron shell configuration (s^2p^6), then the number 18 represents a filled valence shell for a transition metal ($s^2p^6d^{10}$).

$Cr(CO)_6$ – a Cr atom has 6 electrons outside its noble gas core. CO is considered to act as a donor of 2 electrons.

Cr	6 electrons
6(CO)	12 electrons
Total =	18 electrons

-> 18-electron complex. It is stable. On the other hand, $Cr(CO)_5$ (16 electrons) and $Cr(CO)_7$ (20 electrons) are much less stable and known only as transient species.

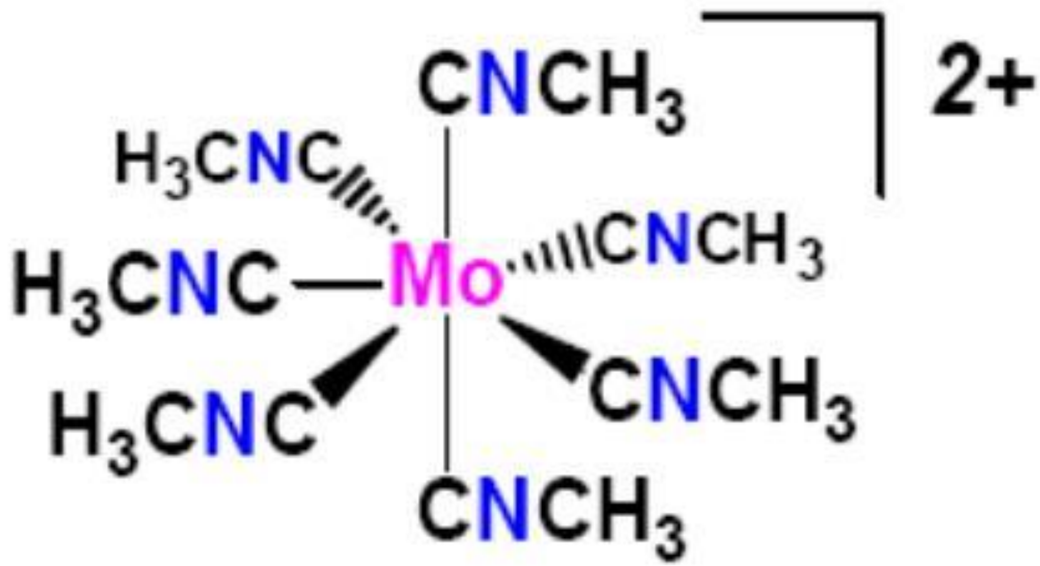
THE 18-ELECTRON RULE

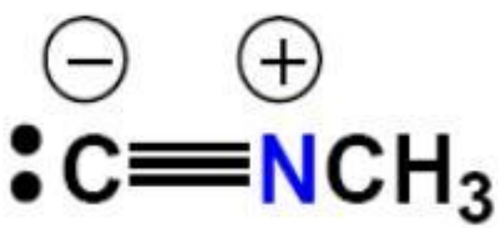
Example I

Mo(+1)	d^5
$2PR_3$	4e-
2CO	4e-
2μ-Cl^-	4e-
Sub-total:	*17e-*
Mo-Mo	1e-
TOTAL:	18e-

THE 18-ELECTRON RULE

Example II

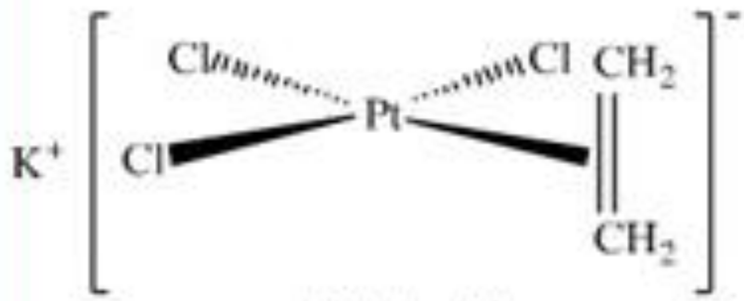




Mo(+2)	d^4
7 $CNCH_3$	14e-
Total:	18e-

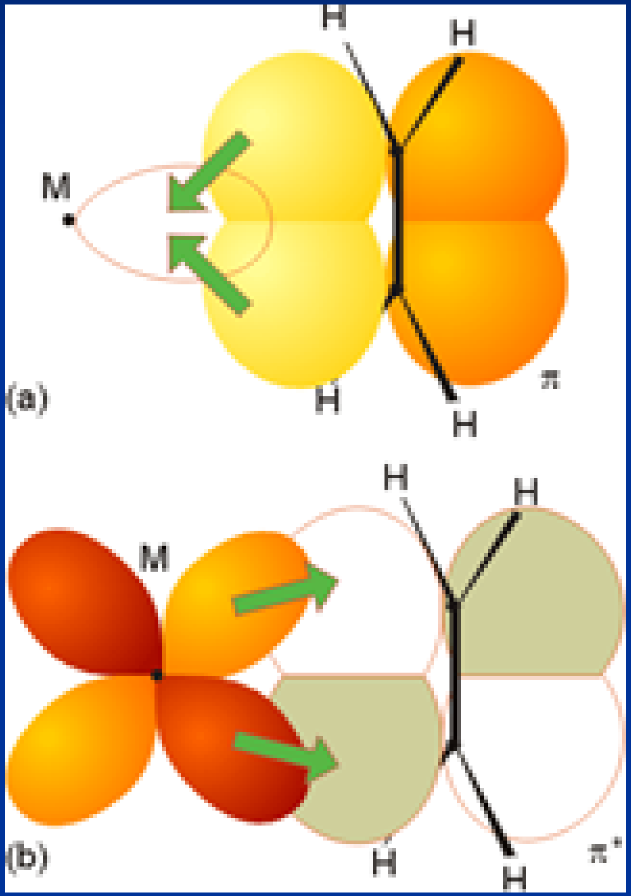
M_T Organometallics

One of the earliest compounds, known as Zeise's salt, was prepared in 1827. It contains an ethylene molecule π bonded to platinum (II).



Zeise's Salt
Potassium trichloro(ethylene)platinate(II)

Zeise's Salt



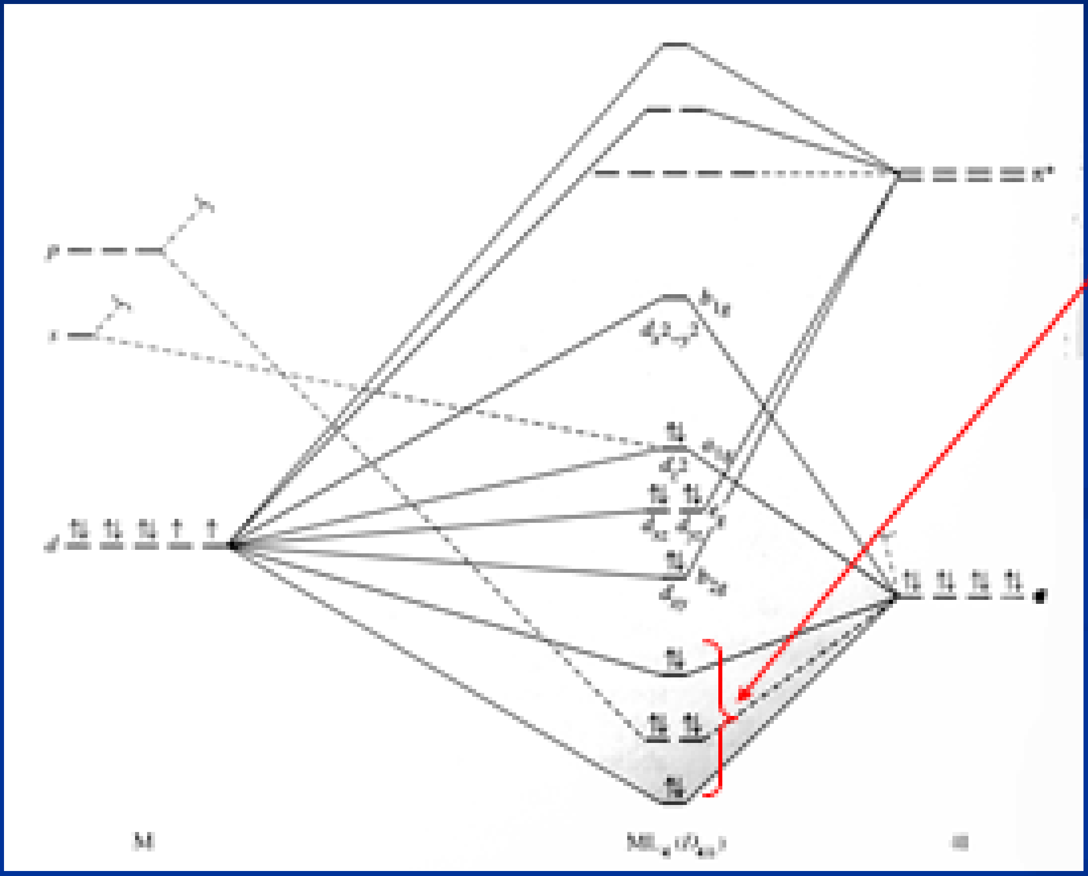
The bonding orbital of ethene donates electrons to the metal. The filled d orbitals (d_{xz} or d_{yz}) donate electrons to the antibonding orbital of ethene.

Square Planar Complexes

The complexes of platinum(II), palladium(II), rhodium(I) and iridium(I) usually have 4-coordinate square planar geometry. These complexes also typically contain 16 electrons, rather than 18.

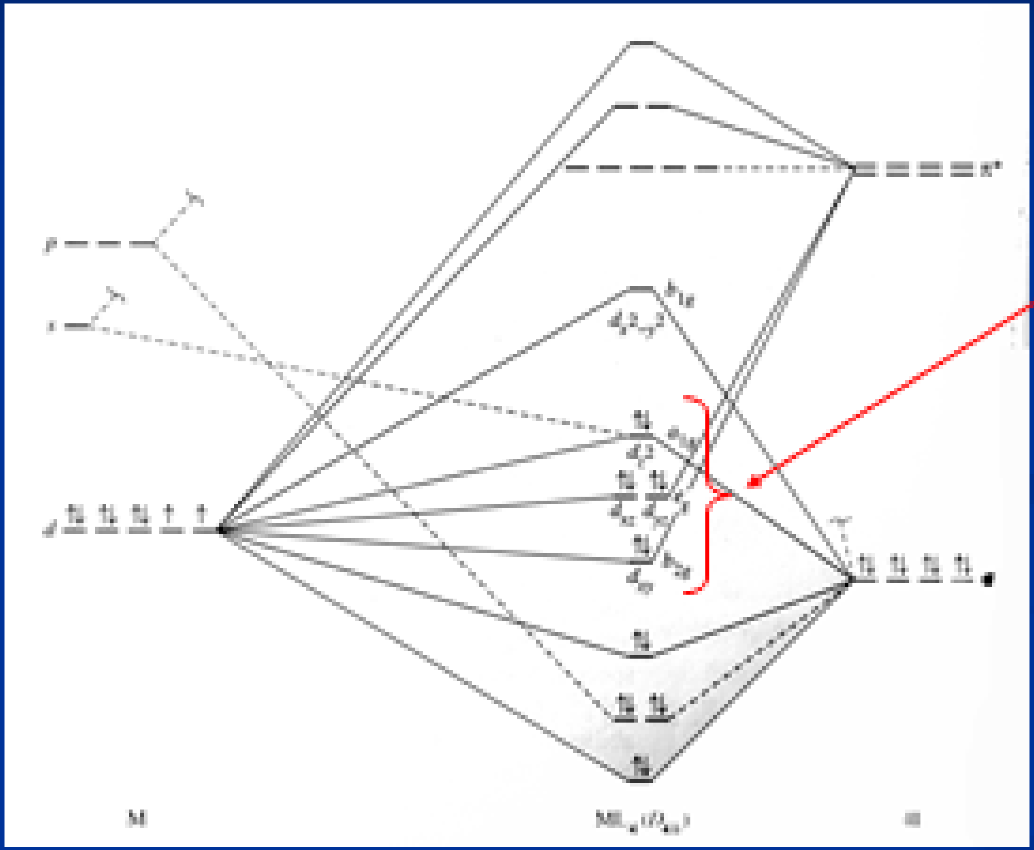
The stability of 16 electron complexes, especially with σ-donor π-acceptor ligands, can be understood by examining a MO diagram.

Square Planar Complexes



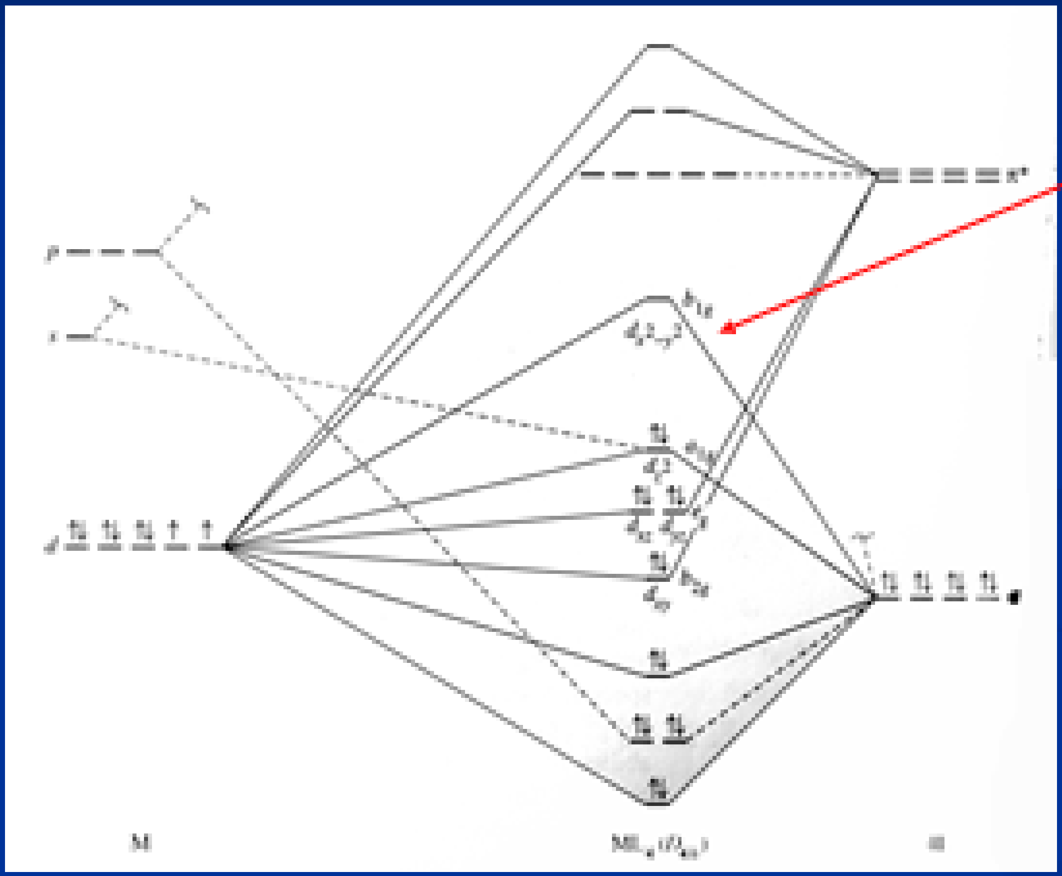
The electron pairs from the 4 ligands used in σ bonding occupy the bonding orbitals.

Square Planar Complexes



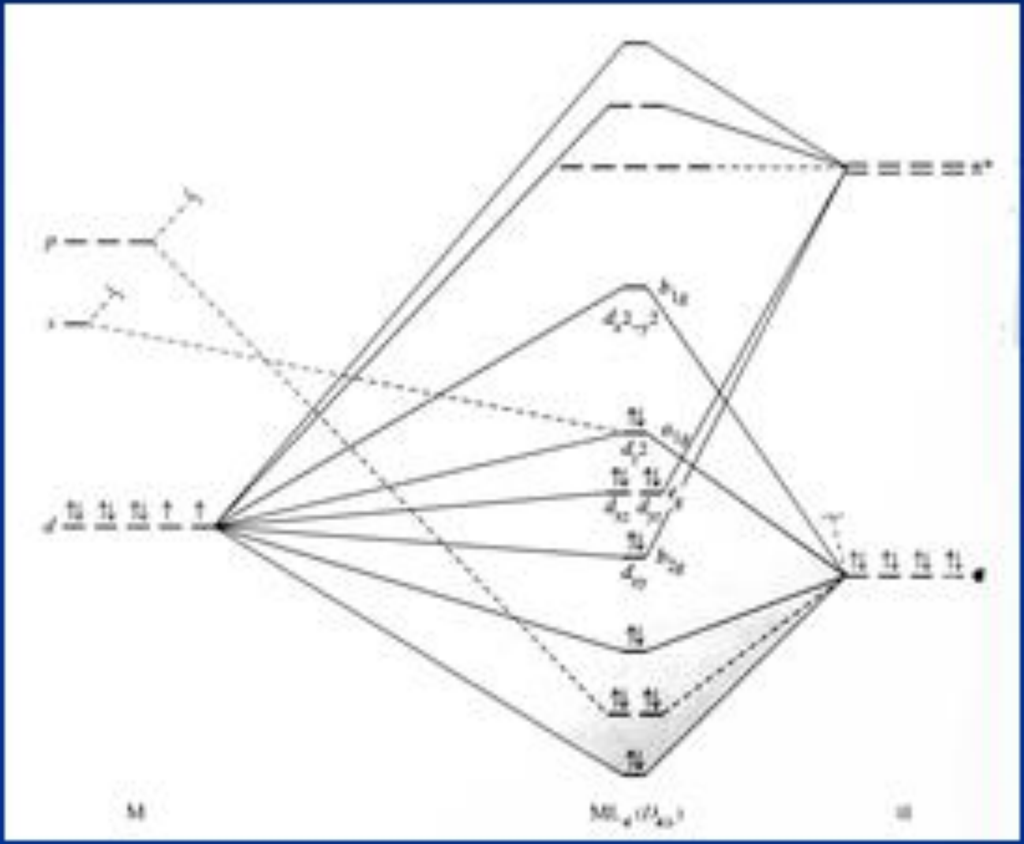
The d_{xy}, d_{xz}, d_{yz} and d_{z^2} orbitals are either weakly bonding, non-bonding, or weakly antibonding.

Square Planar Complexes



The $d_{x^2-y^2}$ orbital is anti-bonding, and if filled, will weaken the σ bonds with the ligands.

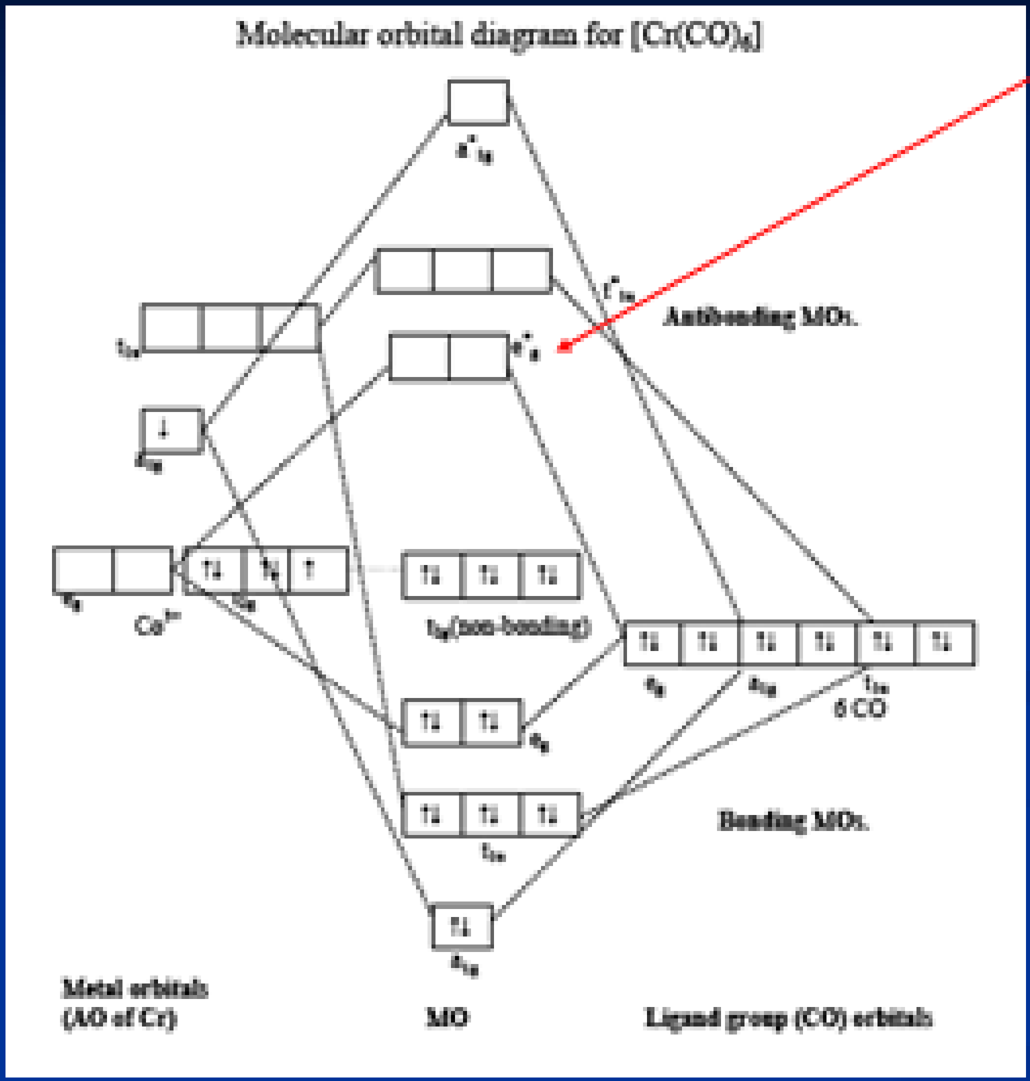
Square Planar Complexes



As a result, 16 electrons will produce a stable complex.

The 18 Electron Rule

Many transition metal carbonyl compounds obey the 18-electron rule. The reason for this can be readily seen from the molecular orbital diagram of $Cr(CO)_6$. The σ donor and π acceptor nature of CO as a ligand results in an MO diagram with greatest stability at 18 electrons.



The e_g* orbitals are destabilizing to the complex. Since the 12 bonding orbitals are filled with electrons from the CO molecules, 6 electrons from the metal will produce a stable complex.

THANK YOU…..