The Eighteen- (and Sixteen-) Electron Rule :Electron Counting

Methods for Electron Counting:

There are two methods for electron counting, the covalent (neutral) model and the ionic (charged) model. These are simply two different ways of accounting for the electrons and give the same answer. The former method has the advantage of completely avoiding the need for designating the formal oxidation state of the metal (remember the bonding is highly covalent), whereas the latter is more intuitive for electropositive metals, e.g. Cp^{-} Na^{+}.

The Covalent Model:

The major premise of this method is that we remove all the ligands from the metal, but rather than take them to a closed shell state, we do whatever is necessary to make them neutral.

In the covalent method, metals retain their full complement of d electrons because we never change the oxidation state from zero; e.g. Fe will always count for 8 electrons

Key Rule: for a transition metal the number of electrons the metal donates to the electron count is the same as its group number.

Electron Counting:

The Ionic Model:

The basic premise of this method is that we remove all of the ligands from the metal and, if necessary, add the proper number of electrons to each ligand to bring it to a closed valence shell state.

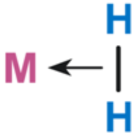
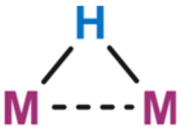
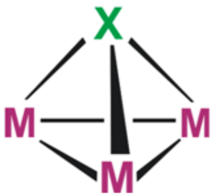
Notice that to keep charge neutrality we must then oxidise the metal by one electron per ligand (i.e. assign a positive charge to the metal). This, in turn, reduces the d-electron count of the metal centre by one.

Example: if we remove a methyl group from the metal and complete its octet, then we formally have CH_3^-. If we bond this methyl anion to the metal, the lone pair forms our metal-carbon bond and the methyl group acts as a two-electron donor ligand.

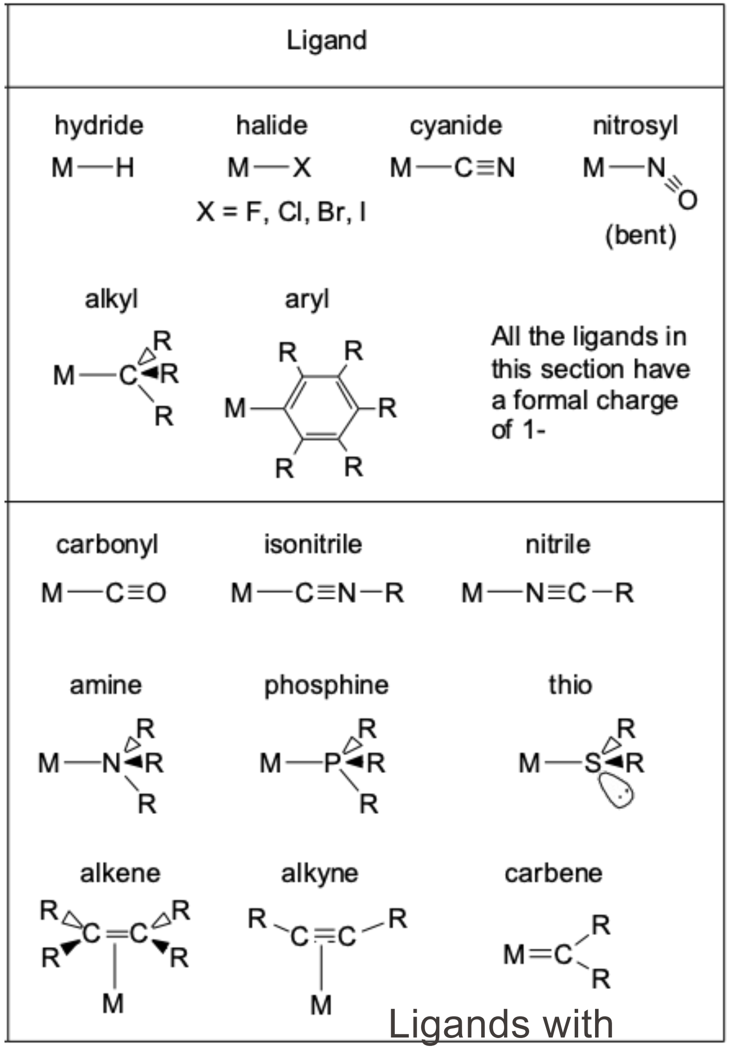
How to electron count:

- Work out which group the metal is in –the number of electrons it contributes = group number – O.S for the ionic method (or group number in covalent method).
- Decide which ligands are charged and which are neutral.
- Use the table to decide how many electrons each ligand contributes, remembering to account for bridging ligands if present (use the table according to the method).
- Adjust for the overall charge of the fragment.
- Consider whether metal-metal bonds may be present – adjust the number of valence electrons accordingly (one electron to each metal from each bond).
- Consider any extra π-interactions which may result from alkene and alkyne
- Consider whether alkoxide, amide, imide and oxo groups could donate extra electrons.
- Consider ring slippage by multi-hapto ligands, e.g. Cp $\eta^5 \rightarrow \eta^3$.
- Check the answer – does it make sense (18 or 16 VE for square planar) (exception exist).
- Both methods give the same number.

Ligands, Bonding Types, Charges, and Donor #'s

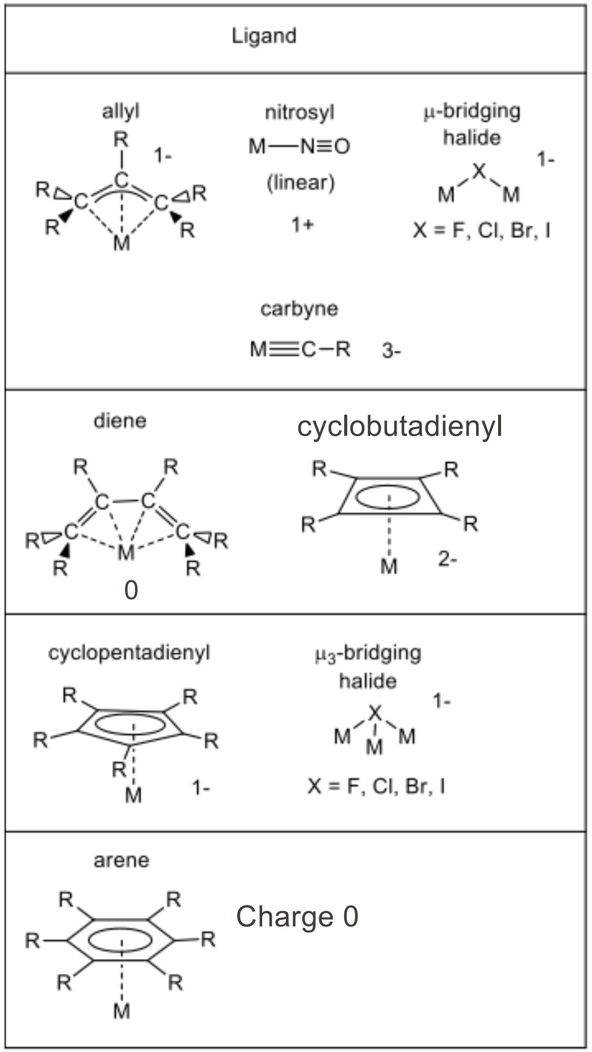
Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H_2		0	2
Hydride: H^-	M-H	-1	2
Hydride: H^-		-1	2
Halide: X^-	M-X	-1	2
Halide: X^- **μ bridging**		-1	4 (2 to each M)
Halide: X^- **μ_3 bridging**		-1	6 (2 to each M)

Common Ligands

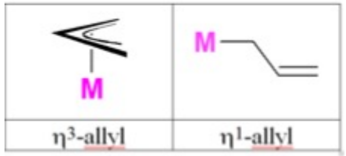


All the ligands in this section have a formal charge of 1-

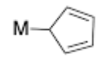
Ligands with Charge 0



Charge 0



η3-allyl η1-allyl



η^1-C_5H_5

monohaptocyclopentadienyl

(1-bonding C)

η^3-C_5H_5

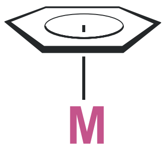
trihaptocyclopentadienyl

(3-bonding C)

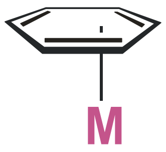
η^5-C_5H_5

pentahaptocyclopentadienyl

(5-bonding C)



η^6-C_6H_6



η^4-C_6H_6

	Ligand	Covalent (Neutral)	Ionic (Charged)
X	Alkyl, aryl, H, η^1-allyl, η^1-cyclopentadienyl (Cp), halide	1	2
X	NO (bent)	1	2
L	CO, N_2, PR_3, NR_3, OR_2, RNC, pyridine	2	2
	CR_2 (Fischer carbene)	2	2
L	Alkene, alkyne[b]	2 or 4 (alkyne only)	2 or 4
LX	η^3-allyl or η^3-Cp	3	4
	NO (linear)	3	2
	η^4-butadiene, η^4-C_6H_6, alkyne[b]	4	4
	η^5-Cp,	5	6
	η^6-arene, η^6-C_6H_8 (cycloheptatri<u>ene</u>)	6	6
	η^7-C_7H_7 (cycloheptatri<u>enyl</u>)	7	6 (as cation) 8 (as anion)
	η^8-C_8H_8 (cyclooctatetra<u>enyl</u>)	8	10
	Each metal–metal bond	1	1
	OR (alk- or aryl-oxide)	1 or 3	2 or 4
	NR_2 (amide)	1 or 3	2 or 4
	O (oxo) or NR (imido)	2 or 4	4 or 6

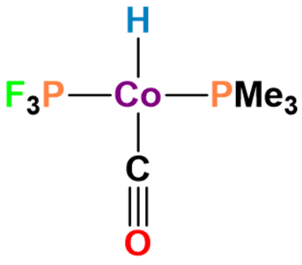
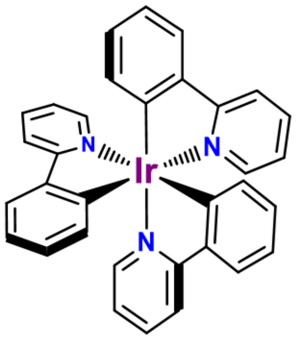
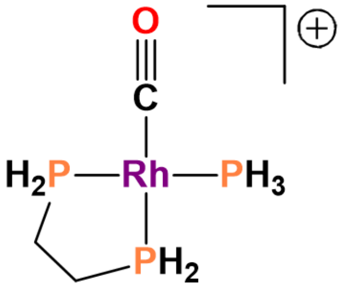
Ligands Nomenclature

L-type ligands are Lewis bases that donate two electrons to the metal center regardless of the electron counting method being used. These electrons can come from lone pairs, pi or sigma donors. Examples of this type of ligand include CO, PR_3, NH_3, H_2O, carbenes (=CRR'), and alkenes.

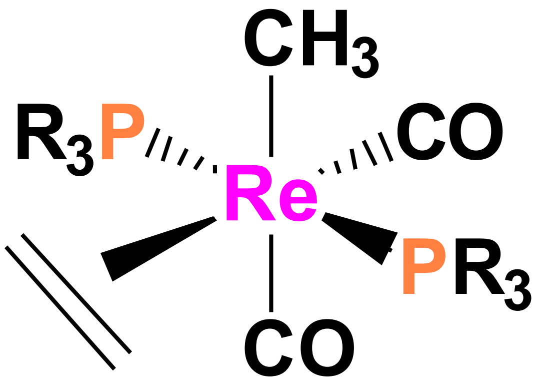
X-type ligands are those that donate one electron to the metal and accept one electron from the metal when using the neutral ligand method of electron counting, or donate two electrons to the metal when using the ionic method of electron counting. Regardless of whether it is considered neutral or anionic, these ligands yield normal covalent bonds. A few examples of this type of ligand are H, CH_3, halogens, and NO (bent).

Ligand Charges & Metal Oxidation States vs. DFT

Shown are three metal complexes with their formal charges and calculated Mullikan charges from DFT calculations on each:

Complex	Formal Charges	Calculated Charges
	Co(+1) = + 1.0 H^- = – 1.0 CO = 0 PMe_3 = 0 PF_3 = 0	Co(+1) = + 0.468 H^- = – 0.252 CO = – 0.332 PMe_3 = + 0.149 P only = + 0.266 PF_3 = + 0.023 P only = + 1.000
	Ir(+3) = + 3.0 3 C^- = – 1.0 3 N = 0	Ir(+3) = + 1.550 3 C^- = – 0.464 3 N = – 0.539 (only showing charges for the donor atoms coordinated to the Ir center)
	Rh(+1) = + 1.0 CO = 0 3 PH_3 = 0	Rh(+1) = – 0.419 CO = + 0.041 PH_3 = + 0.447 dhpe = + 0.929

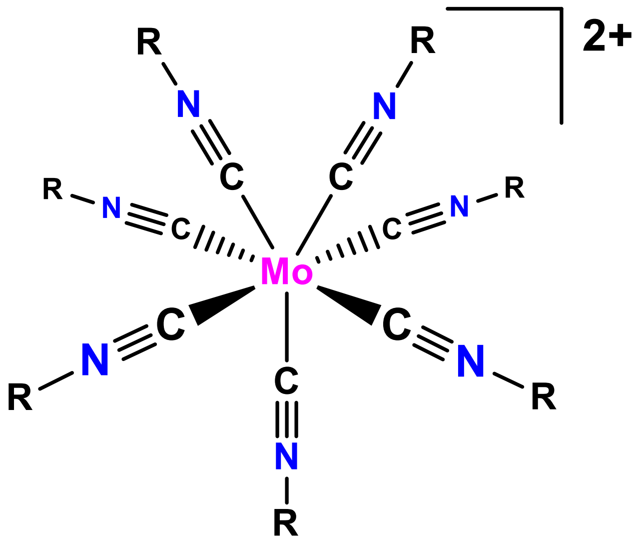
e-counting Examples: Simple



1) There is no overall charge on the complex
2) There is one anionic ligand (CH_3^-, methyl group)
3) The Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. So the Re is the in the +1 oxidation state. We denote this three different ways: Re(+1), Re^{+1}, Re(I), or Re^{I}.

Re(+1)	d^6
2 PR_3	4e-
2 CO	4e-
CH_3^-	2e-
$CH_2{=}CH_2$	2e-
Total:	18e-

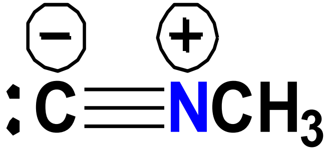
e-counting Examples: Simple *(but semi-unusual ligand)*



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

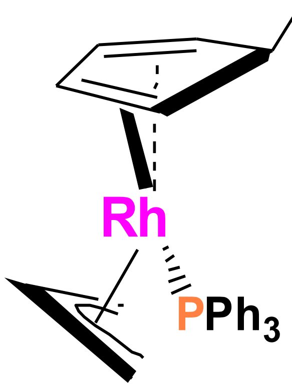
1) There is a +2 charge on the complex

2) The $CNCH_3$ (methyl isocyanide) ligand is neutral, but lets check the Lewis Dot structure to make sure that is correct:

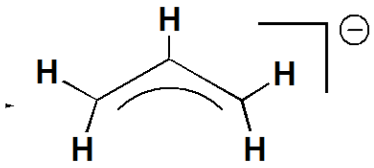


3) Because there is a +2 charge on the complex and all neutral ligands present, the Mo has a +2 charge & oxidation state.

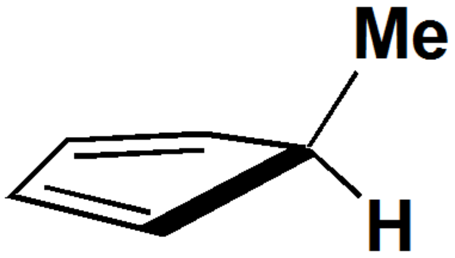
e-counting Examples: Tricky System

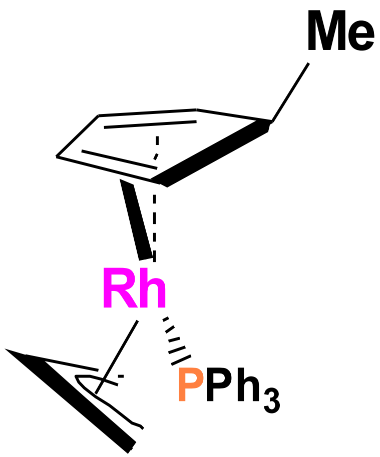


1) There is no overall charge on the complex
2) There is one anionic ligand ($C_3H_5^-$, allyl)



3) The top ligand is NOT a MeCp$^-$! It is a neutral diene that has a H attached to the methyl-substituted ring carbon. This is a neutral 4e- donor.

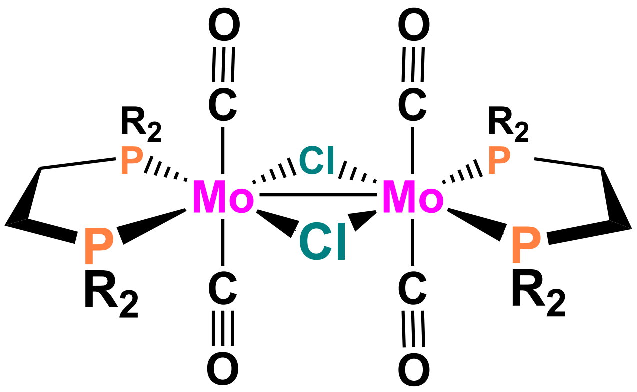




3) Because the complex is neutral and there is one anionic ligand present, the Rh atom must have a +1 charge to compensate for the one negatively charged ligand. So the Rh atom is in the +1 oxidation state.

Rh(+1)	d^8
PR_3	2e-
η^4-C_5H_5Me	4e-
η^3-$C_3H_5^-$	4e-
Total:	18e-

e-counting Examples: M-M Bonded System



Mo(+1)	d^5
2PR$_3$	4e-
2CO	4e-
2μ-Cl$^-$	4e-
Sub-total:	*17e-*
Mo-Mo	1e-
TOTAL:	18e-

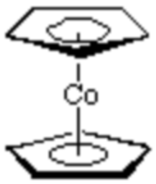
1) Generally treat metal-metal (M-M) bonds to be simple covalent bonds with each metal contributing 1e- to the bond. **If you have two metal atoms next to one another and each has an odd electron-count, pair the odd electrons to make a M-M bond.**

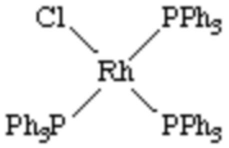
2) Bridging ligands, like halides, with at least 2 lone pairs almost always donate 2e- to each metal center.

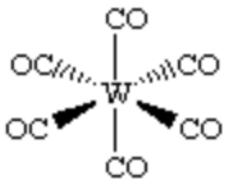
3) **Oxidation state determination:** Total of two anionic ligands for two metal centers (overall complex is neutral). Thus each metal center needs to have a +1 oxidation state to balance the anionic ligands.

Very Common Mistake: Students determining the oxidation state for complexes with 2 or more metal centers often add up all the anionic ligands and then figure out the oxidation state for only one of the metal centers based on this.

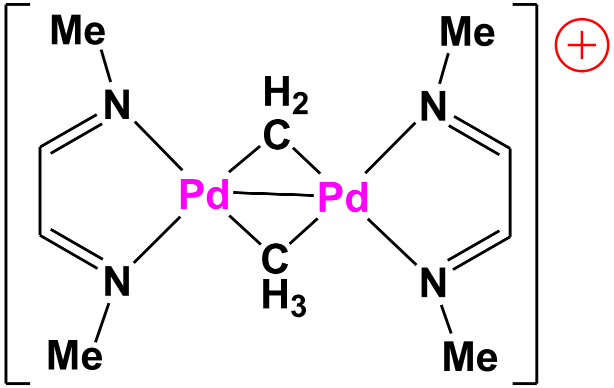
Problem: Find the valence electrons (EV) with bothe the ionic and covalent method







e-counting Examples: M-M Bonded System



e-counting Importance

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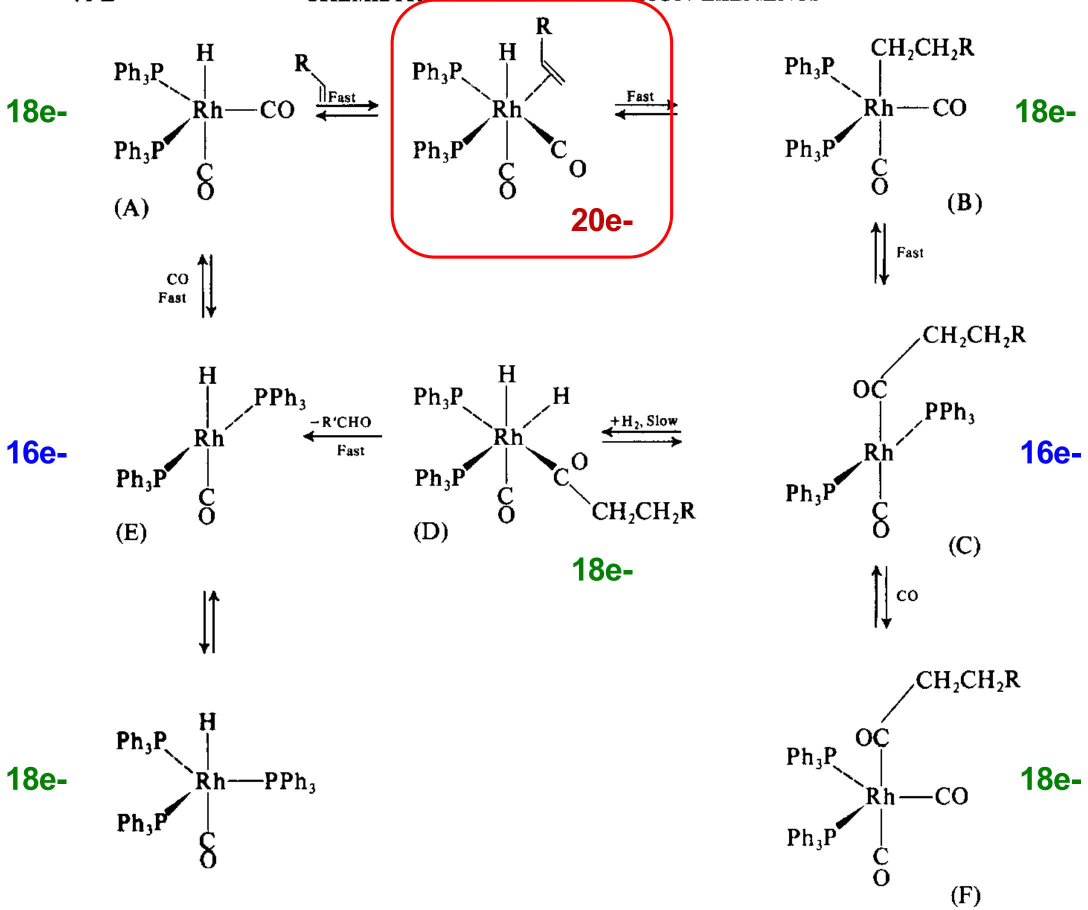

Fig. 24-B-2. Catalytic cycle for the hydroformylation of alkenes involving triphenylphosphine rhodium complex species. Note that the configurations of the complexes are not known with certainty.

e-counting Importance