1.19: Electron Counting and the 18 Electron Rule

The 18 Electron Rule is a useful tool to predict the structure and reactivity of organometallic complexes. It describes the tendency of the central metal to achieve the noble gas configuration in its valence shell, and is somewhat analogous to the octet rule in a simplified rationale. Exceptions to this rule exist, depending on the energy and character of atomic and molecular orbitals.[1]

The 18 Electron Rule

The General Rule

Atoms tend to have all its valence orbitals occupied by paired electrons. For transition metals, the valence orbitals consist of ns, 3 np and 5 (n-1)d orbitals, leading to its tendency of being surrounded by 18 electrons. This is somewhat analogous to the octet and Lewis structure rules of main group elements in a simplified rationale.

Structures that satisfy this preferred electron structure are described as electron-precise. Transition metal complexes with 18 electrons are also referred to as saturated, and there will be no other empty low-lying orbitals available for extra ligand coordination. Complexes with less than 18 electron counts are unsaturated and can electronically bind to additional ligands.

Exceptions to The Rule

The 18 electron rule is usually followed in metal complexes with strong field ligands that are good σ donors and π acceptors (for example, CO ligands). The energy difference (Δ_0) between t_{2g} and e_g* orbitals is very large, and in this case the three t_{2g} orbitals become bonding and are always filled, while the two e_g* orbitals are strongly antibonding and are always empty.

However, when Δ_0 between t_{2g} and e_g* orbitals are small, for example, in the case of first row transition metals with weaker field ligands, the antibonding character of e_g* orbitals weakens, and the complex can have up to 22 electrons.

On the other hand, less than 18 electrons may be observed in complexes of 4th and 5th row transition metals with high oxidation states. In this case, Δ_0 is relatively large due to increased repulsion between d orbitals of metals and the ligands. The e_g* orbitals are strongly antibonding and remains empty, while t_{2g} orbitals are non-bonding, and may be occupied by 0-6 electrons. [2]

Still, generally, the types of ligands in a complex determine if the complex would follow the 18 electron rule or not.

A few common examples of exceptions to 18 electron rules include:[3]

- 16-electron complexes: The metal center is usually low-spin and is in d^8 configuration. These complexes adopt square planar structure, such as Rh(I), Ni(II), Pd(II), and Pt(II) complexes. In a lot of catalytic reactions, the organometallic catalysts convert back and forth between 18 and 16 electron configurations, and thus completes a catalytic cycle.
- Bulky ligands may hinder the completion of 18 electron rule. Examples include complexes with agostic interaction. [4] [5]
- Complexes with ligands of strong π-donating characters often violate 18 electron rule. Examples of this kind of ligands include F^-, O^{2-}, RO^- and RN^{2-}.

Electron Counting Methods

There are two widely used methods for electron counting of complexes - covalent method and ionic ligand method. Both of the two methods are applicable to all organometallic complexes, and should give the same electron count.

Covalent Method

In this method, all metal-ligand bonds are considered covalent. Ligands are considered neutral in charge, and may donate either 2, 1 or zero electrons to the bond. For example, ligands such as CO and NH_3 are considered to have filled valence and contribute 2 electrons. Halide and hydroxo groups, however, do not have octet structure in neutral state, and contribute 1 electron to the bonding. Ligands such as BF_3 do not have any free electron available, and the two electrons for bonding would come from the metal center.

Steps for covalent counting method:

1. Identify the group number of the metal center.
2. Identify the number of electrons contributed by the ligands.
3. Identify the overall charge of the metal-ligand complex.
4. At the presence of metal-metal bond, one electron is counted towards each metal center in a bond.

5. Add up the group number of the metal center and the e⁻ count of the ligands, then take into consider the overall charge of the complex to obtain the final electron count.

Ionic Method

The ionic method always assigns filled valences to the ligands. For example, H group is now considered H⁻, as well as other groups such as halide, hydroxyl and methyl groups. These groups now contribute one more electron than they do in covalent method, and oxidize the metal center when a bond is formed. Groups with neutral charge in octet structure, such as CO and NH_3, behaves the same as in valence methods.

Steps for ionic counting method:

1. Determine the overall charge of the metal complex.
2. Identify the charges of the ligands, and the numbers of e⁻s they donate.
3. Determine the number of valence electrons of the metal center, so that the oxidation state of the metal and charges of the ligands balance the overall charge of the complex. (E⁻ count of metal center = Metal atom group number + $\sum$(charges of ionic ligands) – overall charge of the complex)
4. If metal-metal bond is present, one bond counts for one electron for each metal atom.
5. Add up the electron count of the metal center and the ligands.

Electron Counts of Some Common Ligands [6]

Ligand	Covalent	Ionic	Charge
H	1	2 (H⁻)	-1
Cl, Br, I	1	2 (X⁻)	-1
OH, OR	1	2 (OH⁻,OR⁻)	-1
CN	1	2 (CN⁻)	-1
CH_3, CR_3	1	2 (CH_3^-,CR_3^-)	-1
NO (bent M-N-O)	1	2 (NO⁻)	-1
NO (linear M-N-O)	3	2 (NO^+)	+1
CO, PR_3	2	2	0
NH_3, H_2O	2	2	0
=CRR' (carbene)	2	2	0
$H_2C=CH_2$ (ethylene)	2	2	0
CNR	2	2	0
=O, =S	2	4 (O^{2-}, S^{2-})	-2
η^3-C_3H_5 (π-allyl)	3	2 ($C_3H_5^+$)	+1
≡CR (carbyne)	3	3	0
≡N	3	6 (N^{3-})	-3
en (Ethylenediamine)	4	4	0
bipy (Bipyridine)	4	4	0
butadiene	4	4	0
η^5-C_5H_5 (cyclopentadienyl)	5	6 ($C_5H_5^-$)	-1
η^6-C_6H_6 (benzene)	6	6	0
η^7-C_7H_7 (cycloheptatrienyl)	7	6 ($C_7H_7^+$)	+1

Examples

Examples of Electron Counting of Some Organometallic Complexes[7]

Complexes	Covalent Method	Ionic Method	Total Number of Electrons
$(\eta^5$-$C_5H_5)_2$Fe	• Fe gives 8e⁻	• Fe(II) gives 6e⁻	18

	• 2 η^5-C$_5$H$_5$ give 2×5e$^-$ • Complex Charge is 0	• 2 η^5-C$_5$H$_5^-$ give 2×6e$^-$	
[V(CO)$_7$]$^+$	• V gives 5e$^-$ • 7 CO give 7×2e$^-$ • Complex Charge is +1 (-1e$^-$)	• V(I) gives 4e$^-$ • 7 CO give 7×2e$^-$	18
[Re(CO)$_5$(PF$_3$)]$^+$	• Re gives 7e$^-$ • 5 CO give 5×2e$^-$ • PF$_3$ gives 2e$^-$ • Complex Charge is +1 (-1e$^-$)	• Re(I) gives 6e$^-$ • 2 CO give 5×2e$^-$ • PF$_3$ gives 2e$^-$	18

References

1. "18 electron rule" - Wikipedia, 18 May 2019.
2. ↑ Libretexts 24.3-The 18 electron rule
https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/24%3A_Organometallic_chemistry%3A_d-block_elements/24.03%3A_The_18-electron_Rule
3. ↑ "18 electron rule" - Wikipedia, 18 May 2019.
4. ↑ "Agostic Interaction" - Wikipedia, 9 November 2018.
5. ↑ International Union of Pure and Applied Chemistry. "agostic interaction". *Compendium of Chemical Terminology* Internet edition.
6. ↑ Miessler, G.; Tarr, D. (1998). Inorganic Chemistry. New Jersey: Prentice-Hall. pp. 430.
7. ↑ Miessler, G.; Tarr, D. (1998). Inorganic Chemistry. New Jersey: Prentice-Hall. pp. 430.