

Hillhouse's Rules For Empirical Electron Counting

(Prof. Gregory Hillhouse of the University of Chicago)

1) Draw a legitimate Lewis structure consistent with the observed or hypothetical geometry of the ligand. If a non-linear geometry is observed, put a "lone pair" on the vertex atom. If a linear geometry is observed be sure to use the correct sp-hybridization. See rule 5 regarding the special case of bridging hydrogen and rule 6 for dimers and clusters.

2) Assign formal charges to each atom of the ligand, according to the usual convention. If necessary, consult a freshman chemistry text. In assigning the formal charge to the atom(s) of the ligand which connect to the central metal, the electrons involved in covalent bonds should be split equally. A dative interaction ($M \leftarrow L$) implies that both of the electrons should be included in the ligating atom's formal charge count.

Let the quantity μ be equal to the sum of the atomic formal charges over the entire ligand.

3) The number of electrons that any given ligand "donates" to the central atom's EAN (effective atomic number), defined as ν is given by:

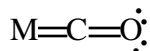
$$\nu = \mu + (\text{number of covalent } M-L \text{ bonds}) + 2(\text{number of dative } L \rightarrow M \text{ bonds})$$

note: the quantity ν can be, and often is, equal to zero.

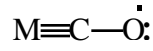
EXAMPLE A carbon monoxide ligand having the usual linear structure which is in accord with the octet requirements of O and C should be considered as shown:



$$\begin{aligned} &= \mu + 0 + 2(1) \\ &= 0 + 0 + 2 \\ &= 2e^- \end{aligned}$$



$$\begin{aligned} &= \mu + 2 + 2(0) \\ &= 0 + 2 + 0 \\ &= 2e^- \end{aligned}$$



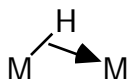
$$\begin{aligned} &= \mu + 3 + 2(0) \\ &= (-1) + 3 + 0 \\ &= 2e^- \end{aligned}$$

Note the absolute consistency of this method with regard to the number of donated electrons, regardless of the ridiculous electronic implications of the Lewis structure.

4) The EAN (total) of an atom is given by the following, for any number of ligands. Ligands are denoted as X.

$$\text{EAN} = \sum_{x=1}^x \text{EAN}(\text{X}) + (d^n \text{ count of zero-valent metal}) - (\text{complex's real charge})$$

5) Bridging hydrides should be considered in the manner pictured below.



Consider bridging hydrido ligands as 1 electron donors to one of the flanking centers, while donating in a dative sense (i.e. 2e-) to the other center. Metal-to-metal bonds should be ignored here unless they are explicitly demanded.

6) It is usually best to count each central atom individually when it is part of a dimer or a cluster. This is particularly necessary if said atoms are not symmetry related.