Understanding the Origin of the LZ → X$_2$ Rule

An important component of the CBC method is to reduce the $[ML_lX_xZ_z]^{Q\pm}$ assignment to its "equivalent neutral class" (ENC), which is essentially the classification that would be obtained if the $Q\pm$ charge were to be localized on the ligand rather than the metal center. By performing such a transformation, it is then possible to compare the nature of metal centers in compounds with differing charges.

Localization of the charge on a ligand changes its classification and some of the more common transformations are summarized in Figure 1.
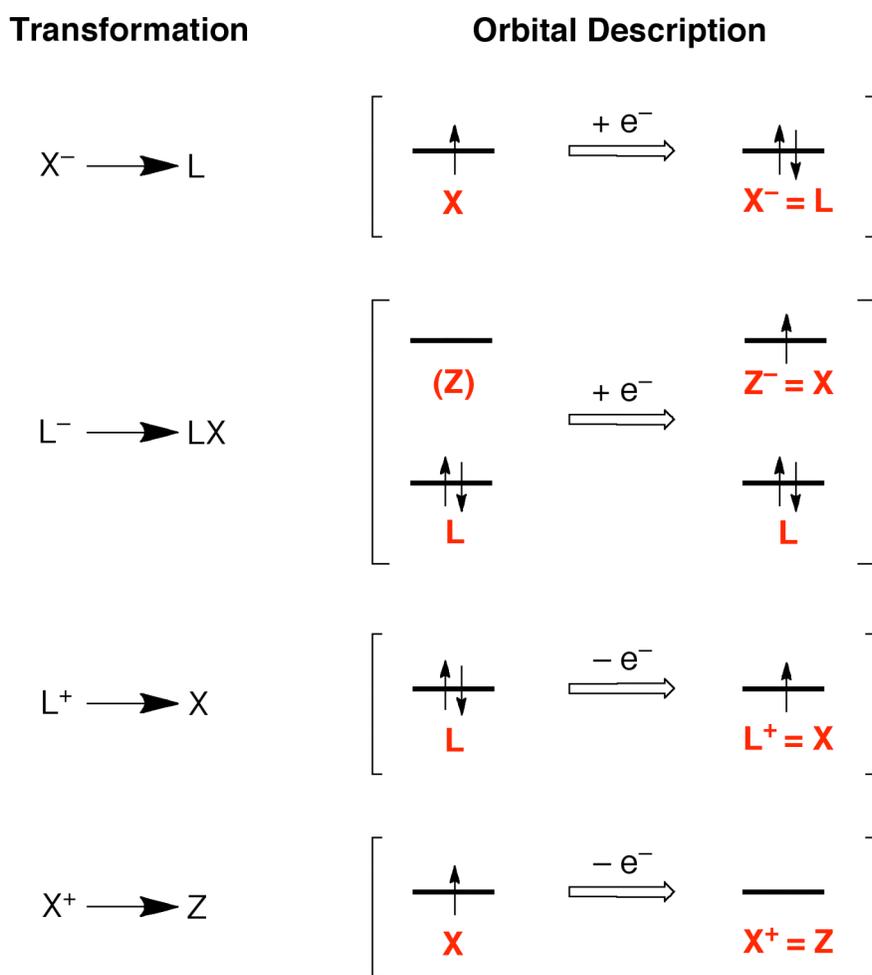
Figure 1. Orbital explanation of rules to derive the Equivalent Neutral Class.

For cations, the transformations are: *(i)* $L^+ \rightarrow X$, *i.e.* a cationic 2-electron donor is equivalent to a neutral 1-electron donor, and *(ii)* $X^+ \rightarrow Z$, *i.e.* a cationic 1-electron ligand is equivalent to a neutral 0–electron ligand. While at one level the logic behind these transformations can be viewed as mathematical, it is more instructive to realize that this has a basis with respect to the construction of molecular orbital diagrams. For example, an L ligand function is characterized by a pair of electrons in a single orbital and so removal of one of these electrons to create L^+ results in a singly occupied ligand function orbital, which is equivalent to an X function. Correspondingly, removal of an electron from an X function orbital to give X^+ results in an empty orbital that is equivalent to a Z function.

For anions, the most commonly encountered transformations are: *(i)* $X^- \rightarrow L$, *i.e.* an anionic 1-electron donor is equivalent to a neutral 2-electron donor and *(ii)* $L^- \rightarrow LX$, *i.e.* an anionic 2-electron donor is equivalent to a 3-electron donor. From an orbital perspective, addition of an electron to a singly occupied X function to give X^- gives a filled orbital that is equivalent to an L function. Since it is not possible to add another electron to an occupied L function orbital, the extra electron in L^- must enter a nascent Z orbital, which becomes a singly occupied X orbital. Thus, the transformation is $L^- \rightarrow LX$. Since the added electron must enter an unoccupied orbital, this rule is only applied if the compound is of the type $[ML_n]^{x-}$ and there is no X ligand available to accept the charge; otherwise, if an X ligand is present, the transformation $X^- \rightarrow L$ takes priority. Furthermore, it is evident that compounds of the type $[ML_n]^{x-}$ are only likely to be feasible if the ligand has an empty orbital of sufficiently low energy. Thus, CO, which has low energy π–acceptor orbitals available, is much more likely to afford anionic $[ML_n]^{x-}$ derivatives than would PMe_3.

After appropriately localizing the charges on the ligands, a final transformation to obtain the equivalent neutral class is $LZ \rightarrow X_2$. The logic behind this transformation is

that both an LZ combination and an X_2 combination combine with two metal orbitals to give two fully occupied bonding molecular orbitals (Figure 2).
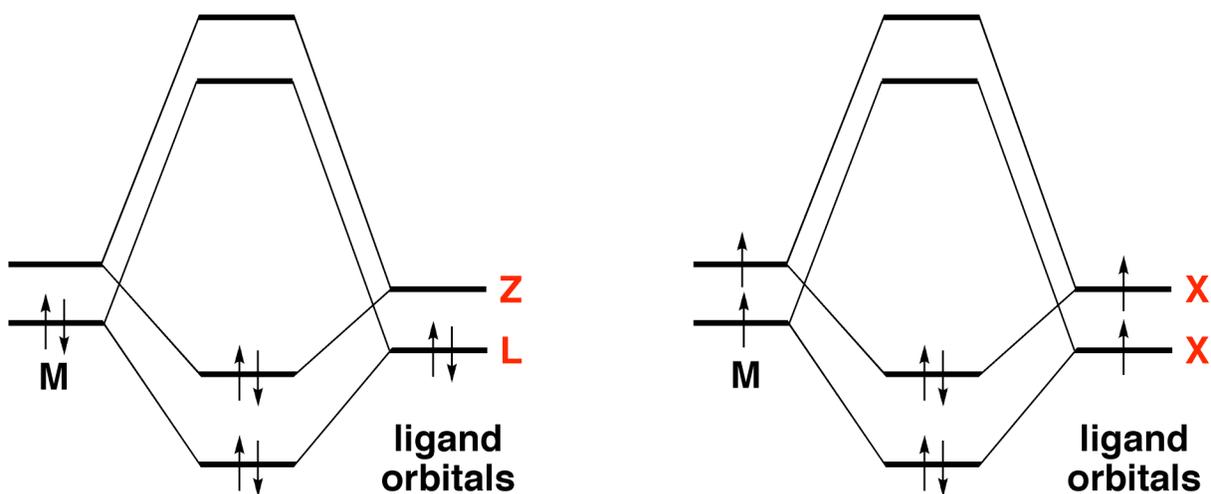
Figure 2. Molecular orbital illustration of the equivalence between LZ and X_2 ligand combinations.

Thus, if the ligand contains both accessible L and Z functions (*i.e.* the donor orbital is not too low in energy and the acceptor orbital is not too high in energy), the combination behaves, in a molecular orbital sense, as if it were two X functions.

Another simple rationalization of the LZ → X_2 rule is provided by consideration of the hypothetical transformation involving the heterolytic addition of H_2 to a mixed amide-boryl derivative, $M(NH_2)(BH_2)$, converting it to the ammonia-borane complex $M(NH_3)(BH_3)$ (Figure 3). This transformation entails addition of H^+ to the Lewis basic nitrogen atom and addition of H^- to the Lewis acidic boron atom and does not formally involve a reaction at the metal center; as such, the metal center in the product, $M(NH_3)(BH_3)$, is still classified as MX_2. However, $M(NH_3)(BH_3)$ can also be identified as a compound that features ammonia (L) and borane (Z) ligands and so it becomes evident that an LZ combination is equivalent to X_2.
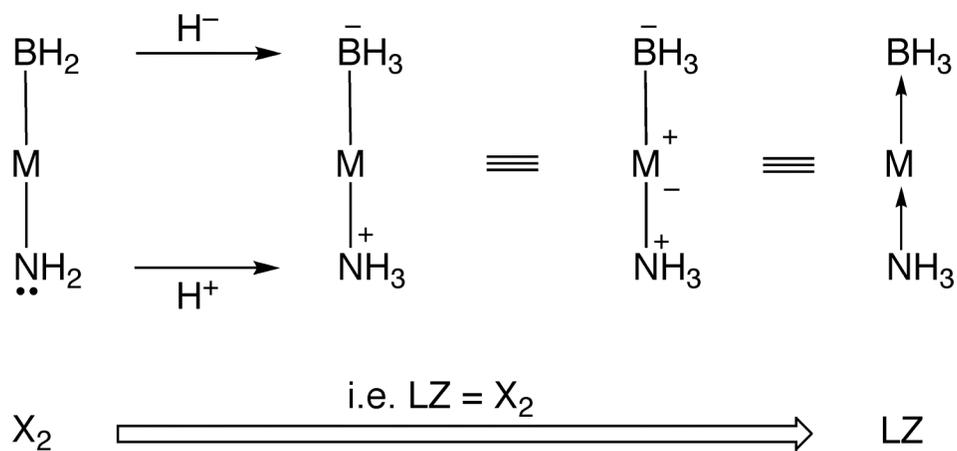
Figure 3. Illustration of the LZ → X_2 rule. Addition of H^+ to N and H^- yields a product that has a pair of L (NH_3) and Z (BH_3) ligands, but since there is no direct reaction with the metal center, it is evident that the class of the molecule remains MX_2.