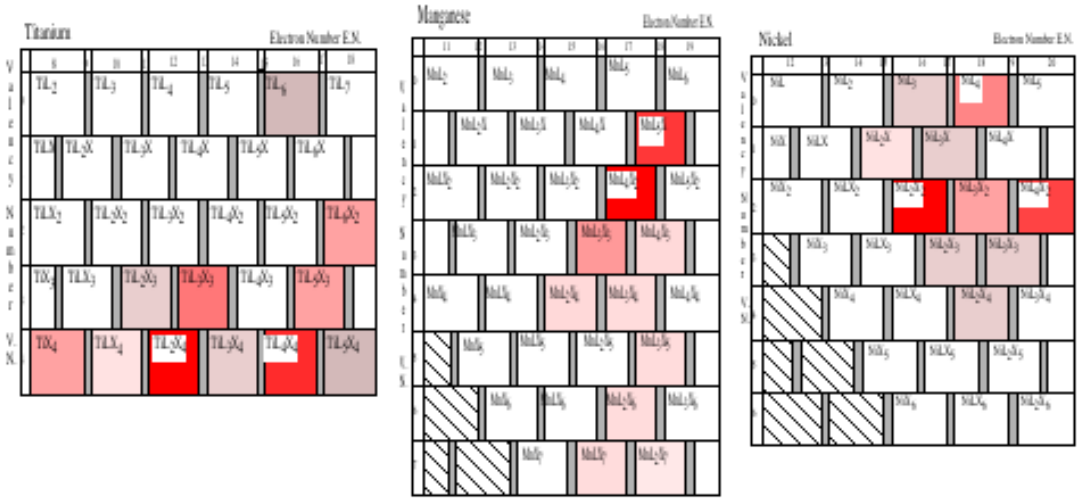
Annotated plots of Ti, Mn and Ni

MLX plots for Titanium, Manganese and Nickel



Rule 1) Filled orbitals (18 electrons): Only possible for Ti when there are very small or compact ligands since a further 14-electrons are required. E.g. $[TiCp_2(CO)_2]$. $TiCl_4$ is apparently an 8-electron compound but if the *symmetry allowed contributions from the Cl pπ-orbitals* are counted then there are an extra 10 electrons which gives the value for EN = 18-electrons!
For Mn, excellent for VN = 1 where also LBN = 6. but poor for VN = 3 and 5 since LNB = 7 or 8 respectively AND higher VN for Mn are rare since 3d orbitals are rapidly lowered in energy by the increasing patrial +ve change on the Mn centre.
For Ni, 18-electrons are found for NiL_4, NiL_3X_2 and (very rare) NiL_2X_4,. Higher VN's for Ni not found since increase effective nuclear charge at this end of the d-block TM's means the I.P.'s too high. The special stability of square-planer, 16-electron NiL_2X_2 is associated with the d^8 configuration.

Rule 2) Steric saturation: For Ti: unusually high LBN's (and high co-ordination nos) are commonly found, e.g. in 16-electron TiL_4X_4, LBN = 8. For Ni. low LBN's (3,4,5) are found since Ni already has 10 electrons and only requires 4 x L ligands to give 18e NiL_4 , e.g. $Ni(CO)_4$.

Rule 3) Electroneutrality rule: For Ti: since I.P.'s are low all 4 valency electrons are accessible to most ligands, e.g TiI_4.
For Mn, the increase of effective nuclear charge with increasing atomic number across the d-block elements means that the higher VN's are only obtainable with the first row elements as ligand atoms (since these for the strongest σ-bonds). Hence VN = 4 is found with F, O, N, and C ligands, e.g. MnR_4, R = CH_2SiMe_3. VN = 7 is known only for $[Mn(=X)_4]^-$, where X = O or NR, the electron donation from the appropriate symmetry combination of the pπ=orbitals of the X ligands and the negative charge resulting from the anion helps reduce the induced positive charge on the Mn centre. Nonetheless, the $[MnO_4]^-$ and Mn_2O_7 compounds are amongst the most oxidising known (in aqueous acid). which shows these Mn centres have exceptionally high partial +ve charges.