The 18 electron rule

For main group compounds we use the octet rule:
Valence orbitals: 1 × s and 3 × p

For TM compounds we use the **18 electron rule**, which states:

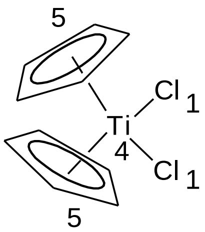
'18 electrons are required from the metal and its associated ligands to attain a noble gas configuration'.

The rule is derived from the fact that transition metals have nine valence atomic orbitals [5 × nd, 1 × (n+1)s and 3 × (n+1)p], which are used to accommodate either metal-ligand bonding or non-bonding electrons.

Breakdown of the 18-electron rule:

1. *Steric*: Metals at the left hand side of the transition series do not have many valance electrons so the ligands must provide more – there is not always enough space for all the ligands.

For example:

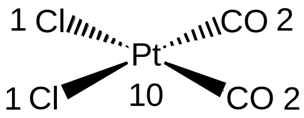


16 VE

2. *Electronic*: The 18-electron rule is nearly always obeyed by the elements near the centre of the transition series. Their conformity arises because the energies of the nd atomic orbitals are close in energy to those of the (n+1)s and (n+1)p atomic orbitals and hence they all make a full contribution to the bonding. Further to the right of the transition series, in Groups 10 and 11, the nd orbital energies become significantly lower in energy than those of the (n+1)s and (n+1)p orbital, due to the increase in effective nuclear charge that has the greatest effect on the d orbitals, and these orbitals no longer make a full contribution towards bonding giving rise to complexes with less than 18 VE.

3. *Special case*: square planar d^8 complexes – the $d_{x^2-y^2}$ orbital is very high in energy and is not used in bonding.

For example:



16 VE

Note: Cl 1-, CO neutral
Pt = Pt(II) = d^8

Counting electrons in transition metal complexes is very important and the simplest way to count electrons involves using the following set of rules:

i. Always consider the metal atom (and all the ligands) to have an oxidation state of zero.
ii. Add together the valence electrons of the metal atoms and the electrons donated by all the ligands.
iii. A metal-metal single bond provides one electron to each metal, a metal-metal double bond provides two electrons to each metal, a metal-metal triple bond provides three electron to each metal, etc.
iv. Account for any overall charge on the complex by adding (negative charge) or subtracting (positive charge) the appropriate number of electrons.

Oxidation states of organometallic complexes

Using the electron counting method does not provide the oxidation state of the metal and the 'real' number of d electrons present.

Transition metals have a number of easily assessable oxidation states, but in general organometallic complexes tend to contain metals in low oxidation states. The most noteworthy features of the accessible oxidation states are:

i. That while many are accessible only certain ones are commonly encountered. For example, rhodium compounds with oxidation states ranging from -1 – 6 are known, but the chemistry of rhodium is dominated by Rh(I) and Rh(III) complexes.
ii. The number of accessible oxidation states increases as the transition metal series (triad) is descended, i.e. first row transition metals typically exhibit fewer oxidation states than second row transition metals, and third row transition metals exhibit the largest range of accessible oxidation states.

The accessible oxidation states of the transition elements. Blue are less commonly observed oxidation states and yellow are those which dominate.

Les états d'oxydation accessibles des éléments de transition. Les cases bleues se rapportent aux degrés d’oxydation généralement les jaunes observés et les cases claires à ceux qui dominent.

Oxidation state	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Tc	Re	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au
-2							d^{8}	d^{8}	d^{8}	d^{9}			d^{10}	d^{10}	d^{10}									
-1	d^{5}			d^{6}	d^{6}	d^{6}	d^{7}		d^{7}	d^{8}	d^{8}	d^{8}	d^{9}			d^{10}	d^{10}	d^{10}	s^{1}			s^{2}		s^{2}
0	d^{4}	d^{4}		d^{5}			d^{6}	d^{6}	d^{6}	d^{7}	d^{7}	d^{7}	d^{8}	d^{8}	d^{8}	d^{9}	d^{9}	d^{9}	d^{10}	d^{10}	d^{10}	s^{1}		s^{1}
+1				d^{4}	d^{4}	d^{4}	d^{5}	d^{5}		d^{6}		d^{6}	d^{7}		d^{7}	d^{8}	d^{8}	d^{8}	d^{9}			d^{10}	d^{10}	d^{10}
+2	d^{2}	d^{2}	d^{2}	d^{3}	d^{3}	d^{3}	d^{4}	d^{4}	d^{4}	d^{5}		d^{5}	d^{6}	d^{6}	d^{6}	d^{7}	d^{7}		d^{8}	d^{8}	d^{8}	d^{9}	d^{9}	d^{9}
+3	d^{1}	d^{1}	d^{1}	d^{2}	d^{2}	d^{2}	d^{3}	d^{3}	d^{3}	d^{4}		d^{4}	d^{5}	d^{5}	d^{5}	d^{6}	d^{6}	d^{6}	d^{7}			d^{8}	d^{8}	d^{8}
+4	d^{0}	d^{0}	d^{0}	d^{1}	d^{1}	d^{1}	d^{2}	d^{2}	d^{2}	d^{3}	d^{3}	d^{3}	d^{4}	d^{4}	d^{4}	d^{5}	d^{5}	d^{5}	d^{6}	d^{6}	d^{6}	d^{7}		
+5				d^{0}	d^{0}	d^{0}	d^{1}	d^{1}	d^{1}	d^{2}	d^{2}	d^{2}		d^{3}	d^{3}		d^{4}	d^{4}			d^{5}			d^{6}
+6							d^{0}	d^{0}	d^{0}	d^{1}	d^{1}	d^{1}	d^{2}	d^{2}	d^{2}		d^{3}	d^{3}			d^{4}			
+7										d^{0}	d^{0}	d^{0}		d^{1}	d^{1}									d^{4}
+8														d^{0}	d^{0}									