**Electron Counting**

Description of a transition metal

1) Formal Oxidation State
2) d Electron Configuration
3) Total Electron Count at the Metal
4) Coordination Number

Consider Wilkinson’s Catalyst:

\[
\begin{align*}
\text{Ph}_3\text{P} & \stackrel{\text{Rh}}{\text{Cl}} \quad \text{Ph}_3\text{P} \stackrel{\text{Rh}}{\text{PPh}_3}
\end{align*}
\]

**Assignment of Oxidation State**

a) Remove ligands in closed shell configuration
b) The charge on the metal is the oxidation state [Rh(I)]

\[
\begin{align*}
\text{Ph}_3\text{P} & \stackrel{\text{Rh}}{\text{Cl}} \quad \text{Ph}_3\text{P} \stackrel{\text{Rh}}{\text{PPh}_3}
\end{align*}
\]

\[d^-\text{Electron count} (d^8)\]

\[n = \text{Valence of neutral metal – charge on the metal}\]
\[\text{Rh(0)} \text{ has 9 valence electrons, so Rh(I) has (9-1= 8)}\]
\[\text{Rh(I) has 8 d-electrons and is said to be } d^8\]

**Total electron count**

The total electron count at the metal is given by:
(metal electrons + ligand electrons). In this case:
the phosphines and chloride are all 2 e- donors so,
Total e- = 8 + 2 + 2 + 2 + 2 = 16 e-

**Coordination number**

\[\text{CN} = (\# \text{ of monodentate}) + 2(\# \text{ of bidentate}) + \ldots\]

In the example Rh is 4-coordinate. Other cases may be less obvious.

**Common Ligands**

- **Anionic Ligands**
  - Monodentate (2 e-)
  - Bidentate (4 e-)
  - Tridentate (6 e-)

- **Neutral Ligands**
  - Monodentate (2 e-)
  - Bidentate (4 e-)
  - Tridentate (6 e-)

**Variable coordination modes**

- \(d^6, 6\text{ coordinate metal} = \text{octahedral}\)
- \(d^8, 3\text{-coordinate} = \text{T-shaped}\)
- \(d^8, 4\text{-coordinate metal} = \text{square planar}\)
- \(d^8, 5\text{-coordinate metal} = \text{square pyramidal or trigonal bipyramidal}\)
- \(d^{10}, 3\text{-coordinate metal} = \text{trigonal planar}\)
- \(d^{10}, 4\text{-coordinate metal} = \text{tetrahedral}\)

**Coordination mode and electron count affect reactivity**

\(d^6, 6\text{ coordinate metal is substitutionally inert}\)
Practice

Where "formal" oxidation state fails


Consider WMe₆: the calculated charge on W is +0.4 not +6.

On the 18 e- “rule”:

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The 18 e- rule works well for groups 6-8, but in general you should regard 18 e- as a maximum (not as you view the octet rule).
Where do the electrons go?

Approximate d-orbital MO’s for common coordination geometries.

\[ \begin{align*}
\text{dx}_z & \quad \text{dy}_z \\
\text{dz}_2 & \\
\text{dxy} & \\
\text{dx}^2-y^2 & \\
\end{align*} \]

\[ \begin{align*}
\text{dx}_z & \quad \text{dy}_z \\
\text{dz}_2 & \\
\text{dxy} & \\
\text{dx}^2-y^2 & \\
\end{align*} \]

\[ \begin{align*}
\text{dx}_z & \quad \text{dy}_z \\
\text{dz}_2 & \\
\text{dxy} & \\
\text{dx}^2-y^2 & \\
\end{align*} \]

\[ \begin{align*}
\text{dx}_z & \quad \text{dy}_z \\
\text{dz}_2 & \\
\text{dxy} & \\
\text{dx}^2-y^2 & \\
\end{align*} \]

Note: Metals have lone pairs that are often not shown

These lone pairs can be involved in \( \pi \)-backbonding

Backbonding in metal alkene complexes

1) lengthens the C-C bond
2) makes carbons more tetrahedral
3) formally oxidizes the metal by 2 e-

Consequence of backbonding: HCo(CO)\(_4\) is as acidic as HCl!

Phosphines and phosphites can be \( \pi \)-acceptors

\[ \begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{CO} & \quad \text{cm}^{-1} \\
\text{complex} & \\
\text{H}_3\text{C} & \quad 2299 \\
\text{CO} & \quad 2143 \\
\text{Ni(CO)} & \quad 2060 \\
\text{Ni(CO)} & \quad 2068, 1990 \\
\text{Ni(CO)} & \quad 2056, 1971 \\
\text{Ni(CO)} & \quad 2049, 1965 \\
\text{Ni(CO)} & \quad 1890 \\
\text{Ni(CO)} & \quad 1770 \\
\text{(O}_3\text{C})\text{Ni} & \quad 2049, 1965 \\
\text{PPh}_3 & \quad 1990 \\
\text{PMe}_3 & \quad 2068, 1990 \\
\text{P(NR}_2\text{)} & \quad 2056, 1971 \\
\text{CO} & \quad 2049, 1965 \\
\end{align*} \]
What type of ligand would be best for the following reaction?

\[
\begin{array}{c}
M \equiv \text{Nu} \rightarrow \text{Nu} \quad \text{Nu}
\end{array}
\]

Other ligand effects

The size of a ligand can dramatically influence substitution reactions at the metal. One convenient measure of ligand size is its Cone Angle. The cone angle is essentially the area that is blocked by the ligand. See Tolman, C. A. Chem. Rev. 1977, 313.

<table>
<thead>
<tr>
<th>L</th>
<th>Cone Angle</th>
<th>(K_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe_3</td>
<td>118</td>
<td>&lt;10^{-9}</td>
</tr>
<tr>
<td>P(O-iPr)_3</td>
<td>130</td>
<td>2.7 \times 10^{-5}</td>
</tr>
<tr>
<td>PPh_3</td>
<td>145</td>
<td>no NiL_3</td>
</tr>
<tr>
<td>P(tBu)_3</td>
<td>170</td>
<td>-</td>
</tr>
</tbody>
</table>

Bite Angle: The angle produced when a chelating ligand binds to a metal center. van Leeuwen, P. W. N. M. Dalton 2003, 1890.


Bond Strengths

Note: In the d-block bond strengths increase by row. This is due to better overlap with the larger d-orbitals. 3rd row > 2nd row > 1st row

\[
\begin{array}{ccc}
\text{M(CO)}_3 & + \text{CO} & \text{M(BDE(kcal/mol))} \\
\text{Cr} & 46 & \\
\text{Mo} & 67 & \\
\text{W} & 80 & \\
\end{array}
\]

Calibration: \(\text{BDE(CH}_3\text{-I)} = 58 \text{ kcal/mol}\)

Mn: Skinner, Orgmet 1982, 1166
Ir: Blake et. al. JACS 1979, 74; JACS 1981, 5768

\[
\begin{array}{ccc}
(\text{OC})_4\text{Fe} & \text{Fe(CO)}_4 & (\text{OC})_3\text{Fe} \\
\Delta H \approx 24 \text{ kcal/mol} & \text{BDE} \approx 50 \text{ kcal/mol} & \Delta H \approx 5 \text{ kcal/mol}
\end{array}
\]
While BDE’s decrease going down a row in the d-block, Atomic size does not.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic radius</th>
<th>Ionic radius (IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1.40 Å</td>
<td>0.56 Å</td>
</tr>
<tr>
<td>Zr</td>
<td>1.55 Å</td>
<td>0.73 Å</td>
</tr>
<tr>
<td>Hf</td>
<td>1.55 Å</td>
<td>0.72 Å</td>
</tr>
<tr>
<td>Ni</td>
<td>1.35 Å</td>
<td>0.62 Å</td>
</tr>
<tr>
<td>Pd</td>
<td>1.40 Å</td>
<td>0.76 Å</td>
</tr>
<tr>
<td>Pt</td>
<td>1.35 Å</td>
<td>0.76 Å</td>
</tr>
</tbody>
</table>

d-orbitals do not shield the nuclear charge well, so elements decrease in size going to the right.

**Lanthanide contraction:** electrons in f-orbitals shield the nucleus more poorly than d-orbitals, so many of the 3rd row d-block elements are smaller than their 2nd row analogs.