Labile or inert?

**Labile** – a compound that undergoes reactions with a relatively high rate of substitution

**Inert** – a compound that undergoes reactions with a slow rate of substitution

*Inert is a relative term, \( t_{1/2} > 1 \text{ min at } 25 \degree \text{C} \)*

3 main factors that affect the whether a complex is labile or inert:

1. Size: Smaller metal ions tend to be more inert as ligands are held more tightly.
2. Charge on Metal: The greater the charge on a metal ion in a complex, the greater the tendency towards the complex being inert
3. Number of d electrons and configuration
## Octahedral geometry d-electron configuration: labile or inert?

<table>
<thead>
<tr>
<th># of d-electrons / configuration</th>
<th>Reactivity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>Labile</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^2$</td>
<td>Labile</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^3$</td>
<td>Inert</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^4$ Low Spin</td>
<td>Inert</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^4$ High Spin</td>
<td>Labile</td>
<td>Especially labile as it is structurally distorted by the Jahn-Teller effect.</td>
</tr>
<tr>
<td>$d^5$ Low Spin</td>
<td>Inert</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^5$ High Spin</td>
<td>Labile</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^6$ Low Spin</td>
<td>Inert</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^6$ High Spin</td>
<td>Labile</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^7$ High Spin</td>
<td>Labile</td>
<td>N/A</td>
</tr>
<tr>
<td>$d^8$ Square Planar</td>
<td>Inert</td>
<td>For $d^8$ and above low spin is the same as high spin.</td>
</tr>
<tr>
<td>$d^8$</td>
<td>Intermediate</td>
<td>This configuration is intermediate, especially with weak field ligands.</td>
</tr>
<tr>
<td>$d^9$</td>
<td>Labile</td>
<td>Like $d^4$ H.S. this configuration is especially labile as it is distorted by Jahn-Teller effect.</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>Labile</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Trans-effect vs Trans-influence

**Trans-influence** – If “A” forms a very strong sigma-bond to the metal, it competes for the metal orbitals with the leaving group, “X,” thus weakening the M–X bond.

Trans-influence determined by sigma-donor strength (basicity):

\[
R_3\text{Si} \rightarrow H \rightarrow H_3\text{C} \rightarrow \text{NC} \rightarrow \text{olefin, CO} \rightarrow R_3\text{P} \rightarrow \text{NO}_2 \rightarrow I \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow H_3\text{N} \rightarrow \text{HO} \rightarrow \text{H}_2\text{O}
\]

**Trans-effect** – A strongly sigma-donating and/or pi-accepting group “A” will greatly increase the reaction rate relative to a weak sigma-donor/poor pi-acid “A.” Factors that dominate the trans-effect include:

1. Ground state weakening of M–X bond (trans-influence)
2. Stabilization of the presumed 5-coordinate intermediate

Taking into account BOTH trans-influence and pi-effects:

\[
\text{NO}^+ \rightarrow \text{CO} \rightarrow \text{CN} \rightarrow \text{PR}_3, H \rightarrow H_3\text{C} \rightarrow \text{Ph} \rightarrow \text{NO}_2, I \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow \text{py, H}_2\text{O, HO}, \text{NH}_3
\]
Inner Sphere Reactivity

**Metal Centered** – gain or loss of ligands
1. **Ligand substitution**
2. **Oxidative addition**
3. **Reductive elimination**
4. **Nucleophilic displacement**
5. **Transmetallation**

**Ligand Centered** – modification of ligands
1. **Migratory insertion**
   a) **Carbonyl insertion**
   b) **1,2–insertion**
2. **Hydride elimination**
3. **Abstraction**
Monsanto Acetic Acid Process
Olefin hydroformylation

At each step give:
1. Type of reaction
2. Oxidation state
3. d-electron count
4. Total electron count
Chauvin mechanism for olefin metathesis

At each step give type of reaction