Transition Metals: located in the middle of the periodic table.

We would expect metals in the same column to behave similarly, but we see that this isn't always the case. For example, the following reaction works well with Pd but not with Pt:

\[
\begin{align*}
\text{H}_3\text{P} & \quad \text{Pd} \quad \text{CH}_3 \\
\text{H}_3\text{P} & \quad \text{CH}_3
\end{align*}
\to
\begin{align*}
\text{PH}_3 \\
\text{Pd} & \quad + \quad \text{CH}_3\text{-CH}_3 \\
\text{Pd} & \quad + \quad \text{PH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{P} & \quad \text{Pt} \quad \text{CH}_3 \\
\text{H}_3\text{P} & \quad \text{CH}_3
\end{align*}
\to
\begin{align*}
\text{PH}_3 \\
\text{Pt} & \quad + \quad \text{CH}_3\text{-CH}_3 \\
\text{Pt} & \quad + \quad \text{PH}_3
\end{align*} \quad \text{NOT OBSERVED.}
\]

We will see that these are consequences of the electronic ground states of Pd and Pt.

What are the ground states of these atoms?

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s'\ d^9) (ground state)</td>
<td>(d^{10}) (ground state)</td>
<td>(s'\ d^9) (ground state)</td>
<td></td>
</tr>
<tr>
<td>(s^2\ d^8\ (+0.7 \text{ kcal/mol}))</td>
<td>(s'\ d^9\ (+21.9 \text{ kcal/mol}))</td>
<td>(d^{10}\ (+11 \text{ kcal/mol}))</td>
<td></td>
</tr>
<tr>
<td>(d^{10}\ (+40 \text{ kcal/mol}))</td>
<td>(s^2\ d^8\ (+56 \text{ kcal/mol}))</td>
<td>(s^2\ d^8\ (+14.7 \text{ kcal/mol}))</td>
<td></td>
</tr>
</tbody>
</table>

Their different ground state and the drastically different energies of the available states.
affect the chemistry (reactivity) and also the promotion energy costs that must take place in the course of chemical reactions.

Another factor that is important is the hybridization of d-orbitals with s-orbitals:

\[
\begin{align*}
&\text{d-orbital} \\
&\to \\
&\text{s-orbital}
\end{align*}
\]

we will now consider what are the causes of the different reactivity of Pt and Pd (as shown above).

Before doing that we clarify a misconception in the way these reactions are named

\[
\begin{align*}
\text{CH}_3-\text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Pt}^\circ & \to \text{Pt}^{\text{II}}
\end{align*}
\]

This is incorrectly called oxidative addition (the C-Pt bonds are covalent, so no oxidation is taking place).

Similarly

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3 & \quad \text{CH}_3-\text{CH}_3 \\
\text{Pt}^{\text{II}} & \to \text{Pt}^\circ
\end{align*}
\]

This is called reductive elimination but no reduction of Pt is taking place.

This isn't critical, but it is something worth noting.

Now let's look at the reactions with C=H, H and C=H

\[
\begin{align*}
\text{H}_3\text{P} & \quad \text{H} \\
\text{Pt}^\circ & \to \text{H}_3\text{P} + \text{H}_2 \\
\text{H}_3\text{P} & \quad \text{PH}_3
\end{align*}
\]

\[
\text{H-H coupling:} \\
\Delta H_R = +12.3 \text{ kcal/mol} \\
\text{(Worst } \Delta H_R\text{)}
\]
\[ \begin{align*} \text{H}_3\text{P} & \quad \text{Pt} \quad \text{H} \quad \text{PH}_3 \\ \text{H}_3\text{P} & \quad \text{Pt} \quad \text{CH}_3 \quad \text{Pt} + \text{CH}_4 \quad \Delta H_R = -5.9 \text{ kcal/mol} \\ \text{H}_3\text{P} & \quad \text{Pt} \quad \text{CH}_3 \quad \text{Pt} + \text{CH}_3\text{-CH}_3 \\ \text{H}_3\text{P} & \quad \text{Pt} \quad \text{CH}_3 \quad \text{Pt} + \text{PH}_3 \quad \Delta H_R = -11.3 \text{ kcal/mol} \end{align*} \]

Experiments show that C-C coupling is the worst, so the difference must not be in the $\Delta H_R$ but in the reaction barrier.

\[ \begin{align*} \text{H-H coupling} & \quad \text{VIRTUALLY NO BARRIER} \\ \text{C-H coupling} & \quad \text{MODERATE BARRIER} \\ \text{C-C coupling} & \quad \text{HIGH $\Delta H_R$} \end{align*} \]

Analysis of the orbitals in the transition state helps us explain these barriers. Consider how well the wave functions of the species can overlap:

Round Hydrogen orbitals overlap well with another hydrogen and with Pt simultaneously.

directional orbitals in CH₃ can only overlap either with Pt or with another CH₃ (they must rotate to do so).
This shows why the reaction doesn't proceed with Pt (why the barriers are different) but it doesn't explain why palladium works. For palladium the reaction barrier during C-C coupling is four times smaller. Let's look at the products:

Pt or Pd

\( \text{PH}_3 \) is an electron donor. In order to bond with the metal it pushes the metal's orbitals to the side (this works best if all the metal's electrons are in d orbitals (lobes) and not in s orbitals. So the addition of 2 \( \text{PH}_3 \) forces the metal to prefer a \( d^{10} \) state.

Pt is \( s^2d^8 \) in its ground state, so during the reaction it needs to change to \( d^{10} \), which costs 11 kcal/mol (see table above). Pd is already a \( d^{10} \), which is 21.9 kcal/mol better than \( s^2d^9 \), so going to \( d^{10} \) gives it additional energy gain, which favors the reaction and also lowers the energy barrier (the atom naturally tends towards this state and this gives a 'push' to the reaction while it is occurring).

Note the following oxidation states of Pt:

<table>
<thead>
<tr>
<th>Pt(^0)</th>
<th>Pt(^{\text{II}})</th>
<th>Pt(^{\text{IV}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d^{10} ) (full)</td>
<td>( s^1d^9 ) (can form one bond to s and one bond to d)</td>
<td>( s^2d^8 )</td>
</tr>
<tr>
<td></td>
<td>( d^8 )</td>
<td>( d^6 )</td>
</tr>
</tbody>
</table>
Consider now

\[ \text{Cl}_2 \text{ Ti} \quad \text{H} \quad \ldots \quad \text{H} \quad \text{H} \quad \text{Cl} \]

Normally we would expect the Ti-H bond to have ionic character due to being so electropositive, but since the Cl has already taken so much of its electronic density, it is much harder for the hydrogens to take more of it. As a result, Ti and H share the electrons in a covalent bond:

\[ \text{Cl} \quad \text{H} \quad \text{Ti} \quad \text{H} \quad \text{Cl} \]