Kinetics and Mechanism of the Insertion of Olefins into Transition-Metal-Hydride Bonds

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Outline

• Synthesis of olefin hydride niobium complex

• The kinetics and mechanism study of the insertion

• Conclusion
Synthesis and characterization

• Synthesis

Method 1

Method 2

N.Doherty; J Bercaw. J.Am.Chem.SOC. 1985, 107, 2670-2682
• NMR spectrum is consistent with the product

$^1$H-NMR: a singlet (1.63); two triplets (0.65, -0.23); one broad singlet (-3.04)

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Ethylene hydride configuration

“Agostic” configuration

N.Doherty; J Bercaw. J.Am.Chem.SOC. 1985, 107, 2670-2682
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Endo and Exo isomers in Cp complexes:

In the case of Cp* complex, only endo product could be obtained

• The $^1$H-NMR spectrums for the olefin part of other olefin compounds are similar to the ethylene compound

• However, the signals of the methyl groups on Cp* split into two singlets

• Ligand promoted olefin insertion

\[
\begin{align*}
\text{Cp}^*_{2}\text{Nb} + \text{CHR} + \text{CO} &\rightarrow \text{Cp}^*_{2}\text{Nb} + \text{CH}_2\text{CH}_2\text{R} \\
\text{Cp}^*_{2}\text{Nb} + \text{CHR} + \text{CNMe} &\rightarrow \text{Cp}^*_{2}\text{Nb} + \text{CH}_2\text{CH}_2\text{R}
\end{align*}
\]

R = H, Me, C_6H_4X

• IR frequency for either CO or CNMe is much lower than the free ligand

• Attempts to trap the olefin insertion product of $\text{Cp}^*\text{Nb}(\text{ole-fin})(\text{H})$ with other donor ligands ($\text{PMe}_3$, $\text{P(OMe)}_3$, $\text{CH}_2=\text{CH}_2$, $\text{MeC}=\text{N}$, solvent) were not successful
Kinetic study and mechanism

Figure 1. Variable-temperature $^1$H NMR spectra for Cp$_2$Nb(CH$_2$=CH$_2$)(H) (2) in toluene-$d_8$. 

N.Doherty; J Bercaw. J.Am.Chem.SOC. 1985, 107, 2670-2682
“Due to the complex coupling pattern and the observation of decomposition at temperatures just above coalescence, line-shape analysis from these data was not attempted. Rather, magnetization-transfer experiments were undertaken to obtain the forward rate”
Magnetization transfer from \( \text{Cp}^*_2\text{Nb}(\text{CH}_2) \) to \( \text{Cp}^*_2\text{Nb}(\text{CH}_2) \) at \( T = 59^\circ \text{C} \) in \( \text{C}_6\text{D}_6 \).

\[
k_{\text{exchange}} = \frac{2}{3} k_1
\]

\[
k_1 = 5.0 \pm 0.6 \text{ s}^{-1}
\]

**Figure 2.** Magnetization transfer experiment for \( \text{Cp}^*_2\text{Nb}(\text{CH}_2=\text{CH}_2)(\text{H}) \).
Figure 3. Arrhenius plot for the hydride-olefin insertion reaction for Cp*₂Nb(CH₂═CH₂)(H).
Measurement of the insertion rate during chemical trapping experiments

\[-\frac{d[A]}{dt} = k_{\text{obsd}}[A] = \frac{k_1 k_2[L]}{k_{-1} + k_2[L]}[A]\]

\[
\begin{align*}
\text{Cp}^*_2\text{Nb} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad + \text{CNMe} \\
\text{Cp}^*_2\text{Nb} & \quad \text{CH}_2\text{CH}_3 \\
\text{CNMe} & \quad \text{CNMe}
\end{align*}
\]
• The overall rate shows a first-order dependence on the [CNMe].
• The kinetics of this reaction are best described by a rapid preequilibrium insertion followed by slow, rate-limiting trapping.
• Consequently, in this temperature and concentration regime, it is not possible to obtain $k_1$ from ligand-trapping kinetics.
Ground state effects of olefin coordination on the insertion barrier

\[
\text{Cp}^*_2\text{Nb} + \text{CH}_2=\text{CHR} + \text{CH}_2=\text{CHR} + \text{CH}_2=\text{CH}_2
\]
### Table VII. Equilibrium Data for Competitive Binding of Ethylene, Propene and Styrene (Eq 11) (25 °C, Benzene-\textit{d}_6)

<table>
<thead>
<tr>
<th>(R)</th>
<th>(K_{eq})</th>
<th>(\Delta G^\circ, \text{kcal mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Me</td>
<td>0.0069 (17)</td>
<td>2.9 (2)</td>
</tr>
<tr>
<td>Ph</td>
<td>0.047 (4)</td>
<td>1.8 (1)</td>
</tr>
<tr>
<td>(p)-Me_2N–C(_6)H(_4)</td>
<td>0.032 (3)</td>
<td>2.0 (1)</td>
</tr>
<tr>
<td>(p)-MeO–C(_6)H(_4)</td>
<td>0.041 (3)</td>
<td>1.9 (1)</td>
</tr>
<tr>
<td>(p)-Me–C(_6)H(_4)</td>
<td>0.039 (4)</td>
<td>1.9 (1)</td>
</tr>
<tr>
<td>(p)-CF(_3)–C(_6)H(_4)</td>
<td>0.040 (3)</td>
<td>1.9 (1)</td>
</tr>
</tbody>
</table>
Table VIII. Free Energy Data for Olefins (25 °C, Gas)\textsuperscript{a}

<table>
<thead>
<tr>
<th>R</th>
<th>$\Delta G^\circ$ \textsuperscript{f} (CH$_2$=CHR)</th>
<th>$\Delta G^\circ$ \textsuperscript{f} (CH$_3$CH$_2$R)</th>
<th>$\Delta G^\circ_{\text{hydrog}}$</th>
<th>$\Delta \cdot (\Delta G^\circ_{\text{hydrog}})$ \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>16.282</td>
<td>-7.860</td>
<td>-24.142</td>
<td>0</td>
</tr>
<tr>
<td>Me</td>
<td>14.990</td>
<td>-5.614</td>
<td>-20.604</td>
<td>-3.54</td>
</tr>
<tr>
<td>Ph</td>
<td>51.10</td>
<td>31.208</td>
<td>-19.892</td>
<td>-4.25</td>
</tr>
<tr>
<td>$p$-MeC$_6$H$_4$</td>
<td>50.24</td>
<td>30.281</td>
<td>-19.959</td>
<td>-4.18</td>
</tr>
</tbody>
</table>

\textsuperscript{a} From ref 34. Values are given in kcal mol$^{-1}$. \textsuperscript{b} Relative to ethylene.

Table IX. Relative Binding Energies for Ethylene, Propene, and Styrene Complexes, Cp$_2$Nb(CH$_2$=CHR)(H) (2, 4, 5a, 6d)

<table>
<thead>
<tr>
<th>R</th>
<th>$\Delta G^\circ$ (eq 12)</th>
<th>$0.5\Delta \cdot (\Delta G^\circ_{\text{hydrog}})$</th>
<th>rel G.S. E. for olefin complex\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Me</td>
<td>2.9 (2)</td>
<td>-1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Ph</td>
<td>1.8 (1)</td>
<td>-2.1</td>
<td>-0.3</td>
</tr>
<tr>
<td>$p$-MeC$_6$H$_4$</td>
<td>1.9 (1)</td>
<td>-2.1</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

N.Doherty; J Bercaw. J.Am.Chem.SOC. 1985, 107, 2670-2682
**Figure 6.** Partial free-energy surfaces for insertion of styrenes into the niobium-hydride bond.

**Figure 7.** Partial free-energy surfaces for insertion of ethylene, propene, and styrene into the niobium-hydride bond.
• As can be seen from these data, ethylene has a more readily reduced double bond than propene, styrene, or p-methylstyrene.

• Consequently, the position of equilibrium, which favors the ethylene complex in all cases, is partly due to the fact that free ethylene has a less stable double bond than the other free, substituted olefins.

N.Doherty; J Bercaw. J.Am.Chem.SOC. 1985, 107, 2670-2682
Mechanism

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• The transition state ordering $R = H > Ph > Me$ for $\text{CH}_2=\text{CHR}$ insertion reflects the electronic properties of these substituents:

Both phenyl and methyl stabilize the developing positive charge at the p carbon in the transition state.

Conclusion

- Study of the kinetics and mechanism of olefin insertion into the niobium hydride bond of \( \text{Cp}^* \text{Nb(olefin)(H)} \) support the generally proposed picture for olefin insertion and \( \beta \)-H elimination.

Thank you