Hydrogenation on NHC-Modified Ru/K-Al$_2$O$_3$ Catalysts

**Preparation:**

\[
\begin{align*}
\text{IMes HBF}_4 \ (R = \text{mesityl}) \quad \text{or} \quad \text{ICy HBF}_4 \ (R = \text{Cy}) \\
\quad \quad \quad \quad \Downarrow \text{Hexane, 25 °C, 16 h} \\
\text{Ru/K-Al}_2\text{O}_3 \end{align*}
\]

\[
\text{IMes/Ru/K-Al}_2\text{O}_3 \ (R = \text{mesityl}) \quad \text{or} \quad \text{ICy/Ru/K-Al}_2\text{O}_3 \ (R = \text{Cy})
\]

**Selected examples:**

\[
\begin{align*}
\text{PhMe} & \quad \text{NHC/Ru/K-Al}_2\text{O}_3 \\
\text{H}_2 \ (10 \text{ bar}) & \quad \text{hexane, 25 °C, 16 h}
\end{align*}
\]

**Significance:** A surface-modification method was developed for tuning the catalytic performance of ruthenium nanoparticles supported on K-doped alumina (Ru/K-Al$_2$O$_3$) by using N-heterocyclic carbene (NHC) ligands. For example, the hydrogenation of ethynylbenzene (1) under hydrogen in the presence of unmodified Ru/K-Al$_2$O$_3$ gave ethylcyclohexane (3) as the sole product in 95% yield, whereas the use of IMes/Ru/K-Al$_2$O$_3$ or ICy/Ru/K-Al$_2$O$_3$ (2 mol% ruthenium, NHC-modified Ru/K-Al$_2$O$_3$, 3.0 equiv of the NHC based on surface ruthenium) as a catalyst under similar conditions gave ethylbenzene (2) as the sole product in 89% and 92% yield, respectively.

**Comment:** The catalysts were characterized by means of $^{13}$C solid-state NMR, Ru 3p XPS, Ru K-edge EXAFS, and TEM. The particle size of ruthenium (TEM), the oxidation state of ruthenium (XPS), and the Ru–Ru coordination number (EXAFS) remained unchanged after the surface modification. In addition, $^{13}$C NMR spectroscopy confirmed that the carbene carbon was directly attached to the ruthenium nanoparticles.