Hydrogenation on NHC-Modified Ru/K-Al₂O₃ Catalysts

**Preparation:**

\[
\text{IMes HBF₄ (R = mesityl)} \quad \text{or} \quad \text{ICy HBF₄ (R = Cy)}
\]

**Significance:** A surface-modification method was developed for tuning the catalytic performance of ruthenium nanoparticles supported on K-doped alumina (Ru/K-Al₂O₃) by using N-heterocyclic carbene (NHC) ligands. For example, the hydrogenation of ethynylbenzene (1) under hydrogen in the presence of unmodified Ru/K-Al₂O₃ gave ethylcyclohexane (3) as the sole product in 95% yield, whereas the use of IMes/Ru/K-Al₂O₃ or ICy/Ru/K-Al₂O₃ (2 mol% ruthenium, NHC-modified Ru/K-Al₂O₃, 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 ¹³C 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, ¹³C NMR spectroscopy confirmed that the carbene carbon was directly attached to the ruthenium nanoparticles.