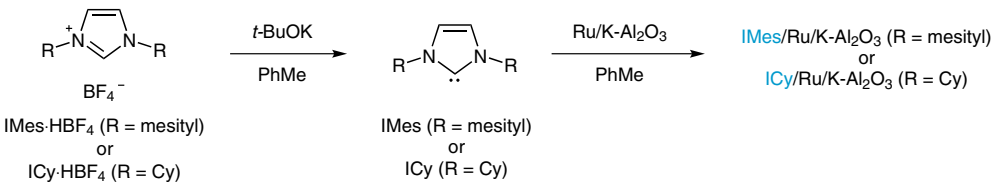
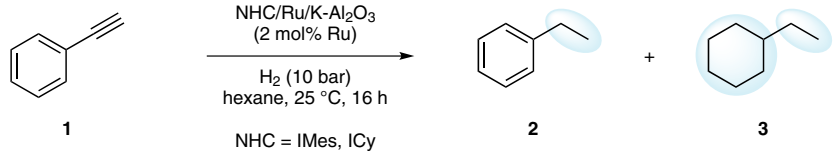
J. B. ERNST, S. MURATSUGU,* F. WANG, M. TADA, F. GLORIUS* (WESTFÄLISCHE WILHELMS-UNIVERSITÄT MÜNSTER, GERMANY AND NAGOYA UNIVERSITY, JAPAN)
Tunable Heterogeneous Catalysis: N-Heterocyclic Carbenes as Ligands for Supported Heterogeneous Ru/K-Al_2O_3 Catalysts to Tune Reactivity and Selectivity
J. Am. Chem. Soc. **2016**, *138*, 10718–10721.

Hydrogenation on NHC-Modified Ru/K-Al_2O_3 Catalysts

Preparation:



Selected examples:



2 (%)/**3** (%) = 0:95 (Ru/K-Al_2O_3)
89:0 (IMes/Ru/K-Al_2O_3)
92:0 (ICy/Ru/K-Al_2O_3)

Significance: A surface-modification method was developed for tuning the catalytic performance of ruthenium nanoparticles supported on K-doped alumina (Ru/K-Al_2O_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_2O_3 gave ethylcyclohexane (**3**) as the sole product in 95% yield, whereas the use of IMes/Ru/K-Al_2O_3 or ICy/Ru/K-Al_2O_3 (2 mol% ruthenium, NHC-modified Ru/K-Al_2O_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.

SYNFACTS Contributors: Yasuhiro Uozumi, Takuma Sato
Synfacts 2016, 12(12), 1313 Published online: 17.11.2016
DOI: 10.1055/s-0036-1589442; **Reg-No.:** Y15616SF

Category
Polymer-Supported Synthesis

Key words
N-heterocyclic carbenes
ruthenium catalysis
hydrogenation
heterogeneous catalysis
ligands