Synthesis of Amines from Alcohols and Urea with Ru(OH)$_x$/TiO$_2$

R–OH + H$_2$NCONH$_2$ \[\rightarrow\] Ru(OH)$_y$/TiO$_2$ (6–8 mol% Ru) \[\rightarrow\] R$_2$NH or R$_3$NH

Significance: TiO$_2$-supported ruthenium hydroxide (Ru(OH)$_x$/TiO$_2$) catalyzed the reaction of alcohols 1 with urea in mesitylene under Ar atmosphere to give the corresponding tertiary amines 2 or secondary amines 3 in 76–98% yield (13 examples). The catalyst was recovered by simple filtration and reused without significant loss of catalytic performance for formation of 3k (reuse: 90% yield). No leaching of ruthenium was observed by ICP-AES analysis after the reaction.

Comment: The authors have previously reported the preparation of Ru(OH)$_x$/TiO$_2$ and its application to the hydrogen transfer reactions (Chem. Eur. J. 2008, 14, 11480). The catalytic activity of Ru(OH)$_y$/TiO$_2$ was superior to that of the other supported ruthenium catalysts for the formation of 2a [Ru(OH)$_y$/Al$_2$O$_3$: 47% yield, RuCl$_x$/TiO$_2$: 0% yield, RuHAP: 0% yield, Ru/C: 18% yield].