Amide Synthesis from Alcohols and Amines Catalyzed by Ruthenium N-Heterocyclic Carbene Complexes

The direct synthesis of amides from alcohols and amines is described with the simultaneous liberation of dihydrogen. The reaction does not require any stoichiometric additives or hydrogen acceptors and is catalyzed by ruthenium N-heterocyclic carbene complexes. Three different catalyst systems are presented that all employ 1,3-diisopropylimidazol-2-ylidene (IiPr) as the carbene ligand. In addition, potassium tert-butoxide and a tricycloalkylphosphine are required for the amidation to proceed. In the first system, the active catalyst is generated in situ from \([\text{RuCl}_2(\text{cod})]\) (cod = 1,5-cyclooctadiene), 1,3-diisopropylimidazolium chloride, tricyclopentylphosphonium tetrafluoroborate, and base. The second system uses the complex \([\text{RuCl}_2(\text{IiPr})(p\text{-cymene})]\) together with tricyclohexylphosphine and base, whereas the third system employs the Hoveyda-Grubbs 1st-generation metathesis catalyst together with 1,3-diisopropylimidazolium chloride and base. A range of different primary alcohols and amines have been coupled in the presence of the three catalyst systems to afford the corresponding amides in moderate to excellent yields. The best results are obtained with sterically unhindered alcohols and amines. The three catalyst systems do not show any significant differences in reactivity, which indicates that the same catalytically active species is operating. The reaction is believed to proceed by initial dehydrogenation of the primary alcohol to the aldehyde that stays coordinated to ruthenium and is not released into the reaction mixture. Addition of the amine forms the hemiaminal that undergoes dehydrogenation to the amide. A catalytic cycle is proposed with the \((\text{IiPr})\text{Ru-II}) species as the catalytically active components.

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