

■ Ruthenium Nanoparticles

N-Heterocyclic Carbene (NHC)-Stabilized Ru⁰ Nanoparticles: In Situ Generation of an Efficient Transfer Hydrogenation CatalystLakshay Kathuria, Noor U. Din Reshi, and Ashoka G. Samuelson^{*,[a]}

Abstract: Tethered and untethered ruthenium half-sandwich complexes were synthesized and characterized spectroscopically. X-ray crystallographic analysis of three untethered and two tethered Ru N-heterocyclic carbene (NHC) complexes were also carried out. These RuNHC complexes catalyze transfer hydrogenation of aromatic ketones in 2-propanol under reflux, optimally in the presence of (25 mol %) KOH. Under these conditions, the formation of 2–3 nm-sized Ru⁰ nanoparticles was detected by TEM measurements. A solid-state NMR investigation of the nanoparticles suggested that the NHC ligands were bound to the surface of the Ru nanoparticles (NPs). This base-promoted route to NHC-stabilized

ruthenium nanoparticles directly from arene-tethered ruthenium–NHC complexes and from untethered ruthenium–NHC complexes is more convenient than previously known routes to NHC-stabilized Ru nanocatalysts. Similar catalytically active RuNPs were also generated from the reaction of a mixture of [RuCl₂(*p*-cymene)]₂ and the NHC precursor with KOH in isopropanol under reflux. The transfer hydrogenation catalyzed by these NHC-stabilized RuNPs possess a high turnover number. The catalytic efficiency was significantly reduced if nanoparticles were exposed to air or allowed to aggregate and precipitate by cooling the reaction mixtures during the reaction.

Introduction

Catalysis by metal nanoparticles (MNPs) has drawn significant attention in recent years.^[1–3] The large surface area and the presence of numerous active sites make metal nanoparticles (MNPs) superior to bulk metals for catalysis. At the same time, they retain the advantages of heterogeneous catalysts in terms of high turnover number (TON), turnover frequency (TOF), and the easy separation of catalysts from products.^[4,5] Hence, nanoparticles are promising and high activity catalysts.^[6] Ru and Rh metal-based NPs are the most common nanocatalysts used for hydrogenation reactions.^[7–9] For example, Liu and co-workers reported hydrogenation of benzene by Ru nanoparticles immobilized on montmorillonite in ionic liquids.^[10] Song et al. have demonstrated the use of RuNPs for catalyzing the hydrogenation of nitroaromatic compounds and azo-dyes and showed that the catalytic activity was dependent on the size of the NPs.^[11] Similarly, Wang et al. reported highly efficient and recyclable polyethylene glycol (PEG)-stabilized RhNPs for hydrogenation of quinoline and its derivatives.^[12] More recently, flat and pristine face-centered cubic (fcc) RuNP-based catalysts have been reported to perform reductive amination of various carbonyl compounds for the synthesis of primary amines.^[13] Examples of transfer hydrogenation by Ru nanopar-

ticles are also known where the catalysts have been generated from metal complexes.^[14–16]

Most nanoparticulate catalysts are best stabilized by surfactants, solvents, or ligands, which provide stability by binding to the metal surface.^[10,17–20] As the catalytic properties of MNPs are strongly influenced by their surface state,^[21,22] many N, S, P, and C-based ligands have been used to control the size of NPs and tune the stereoelectronic properties of the surface. It is not surprising then, that N-heterocyclic carbenes (NHCs), which have emerged as ligands par excellence in organometallics,^[23] have found utility in stabilizing MNPs. Their good binding capacity to metals^[24–26] and their modular nature make them attractive.^[27,28] Glorius et al. have reported the stabilization effect of NHCs on various metal nanoparticle systems.^[29–31] Chaudret and co-workers utilized [Ru(cod)(cot)] as the metal precursor to prepare RuNPs^[25] in the presence of reducing dihydrogen and subsequently added externally generated NHC ligands to stabilize the nanoparticles and study their physical and catalytic properties.^[25,32,33] These NHC-stabilized RuNPs carry out a variety of reactions including hydrogenation of various unsaturated compounds such as olefins, ketones, and arenes.^[34] Chaudret and co-workers introduced a betaine adduct of NHC and a carbodiimide ligand to generate ultra-small ruthenium nanoparticles.^[35] Although catalytically active MNPs can be generated by using hydrogen gas and an organometallic complex,^[14,36,37] an easier approach to prepare NHC-stabilized MNPs would be welcome. Catalytically active ruthenium nanoparticles inadvertently generated from metal complexes have been found decorated with the ligands used in the precursor complexes.^[15,16] We report here our serendipitous discovery of a route to catalytically active NHC-stabilized RuNPs generated in situ from

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