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A mechanistic study of transfer hydrogenation catalyzed by cyclometallated ruthenium half-sandwich complexes

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ABSTRACT

Transfer hydrogenation of aromatic ketones catalyzed by eight cyclometallated ruthenium half-sandwich complexes, including three new complexes, was examined. The catalytic process was studied using different ratios of substrate to base and base to catalyst and using a deuterated reductant. Optimum conditions for catalysis were shown to be in the presence of higher amounts of base in refluxing isopropanol. Under these conditions, the complexes were reduced *in situ* to give Ru(0) nanoparticles invisible to the naked eye. The nanoparticles were characterized by TEM, DLS and XPS. The catalytic transfer hydrogenation, under conditions in which nanoparticles were generated, was found to be far greater than the transfer hydrogenation by the molecular catalyst. Complete characterization of the three new complexes, including the X-ray crystallographic characterization of these complexes was carried out.

1. Introduction

Transfer hydrogenation, an attractive alternative for direct hydrogenation, is a commonly used organic transformation catalyzed by many transition metal complexes [1]. The mechanism of catalytic transfer hydrogenation varies with the nature of transition metals, ligands, donors, bases, reaction media, and substrates. The reaction pathways include a simple direct hydrogen transfer, a monohydride pathway, a dihydride mechanism and the more complex ligand assisted or bifunctional mechanism proposed by Noyori [2]. To add to these possibilities, transition metal catalyzed transfer hydrogenation can be accompanied by conversion of the transition metal complex to uncharacterized elusive species of an unknown structure or nature. Complexes of late-transition-metals, which are often used as catalysts in the transfer hydrogenation, are susceptible to reduction to form catalytically active heterogeneous species like bulk metals and metal colloids under the reducing conditions employed for transfer hydrogenation [3,4]. Not too long ago, Morris and co-workers pointed out that even chelated iron complexes of the type *trans*-$[Fe(NCMe)CO(PPh_2C_6H_4CH{=}NCHR\text{-})_2][BF_4]_2$; (R = H, Ph) are reduced to give catalytically active Fe(0) nanoparticles under the transfer hydrogenation conditions [5]. Although the formation of heterogeneous catalysts during the use of homogeneous catalysts has been known for a long time [4,6–14], the problem remains largely underappreciated particularly in transfer hydrogenation. It is very difficult to detect the formation of nanoclusters by simple methods. The mercury poisoning test for example can be misleading for metals such as Ru, Ir, and Rh which do not form amalgams [4].

One way to prevent the formation of a heterogeneous species is to use more robust systems which do not decompose easily. Lewis used cyclometallated Ru complexes for olefin hydrogenation and found that these complexes resist the irreversible decomposition to metal colloids [15]. Since then, cyclometallated complexes have been extensively used in catalysis [16] particularly in hydrogenation [15,17–20] and transfer hydrogenation [21–34]. The true catalyst is usually presumed to be a homogeneous metal-complex catalyst due to the robustness of these complexes which is a result of the additional stability offered to the metal carbon bond through chelation [35]. We report here our studies on the transfer hydrogenation of aromatic ketones catalyzed by cyclometallated Ru half sandwich complexes. Based on a few key observations, the formation of heterogeneous catalysts was suspected. Detailed investigations confirmed that these presumably robust cyclometallated complexes can also be reduced *in situ* to form Ru(0) nanoparticles which are more catalytically active in the transfer

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