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Synthesis of *N*-Aryl and *N*-Heteroaryl Hydroxylamines via Partial Reduction of Nitroarenes with Soluble Nanoparticle Catalysts

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ABSTRACT

Polystyrene-supported ruthenium nanoparticles enable the selective hydrazine-mediated reduction of nitroarenes to hydroxylamine products in high yield and selectivity. Key to obtaining the hydroxylamine product in good yield was the use of organic solvents capable of solubilizing the polystyrene-supported nanoparticle catalyst. *N*-Aryl and *N*-heteroaryl hydroxylamines are generated under exceptionally mild conditions and in the presence of a various easily reduced functional groups.

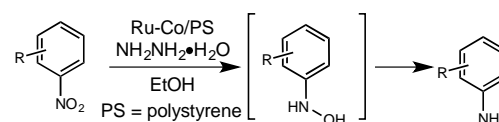
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Introduction

Nanoparticle catalysts represent a bridge between traditional heterogeneous and homogeneous transition metal catalysts because they possess catalytic properties inherent to both classes of catalysts.¹ Nanoparticle catalysts maintain the robustness inherent to heterogeneous catalysts and can often be recovered and recycled at the completion of a reaction.² In addition, the reactivity and selectivity of nanoparticles can be influenced by controlling the size and structure of the nanoparticle,³ or by varying the nature of the nanoparticle support.³ For example, the identity of solid supports, such as metal oxides or zeolites, can influence both the reactivity and selectivity of nanoparticle catalysts.⁴ In addition, varying the structure of surface-bound ligands or polymer supports has been shown to influence selectivity in organic transformations.^{1,5} Recent work by Kobayashi, Toste and others has demonstrated that chiral stabilizing ligands can enable the development of enantioselective transformations with nanoparticle catalysts.⁶ When supported on an organic polymer, a nanoparticle's solubility in organic solvents is dependent on the solubility of the polymer. The solubility of a nanoparticle has been shown to influence reactivity and can be optimized to control reaction dynamics.^{1b} In this report, we demonstrate that the selectivity of polystyrene-supported nanoparticle catalysts towards hydroxylamine formation in nitroarene reductions is highly dependent on the polarity of the solvent used and on the solubility of the nanoparticle catalyst.

During the course of our studies in nitroarene reductions with polystyrene-supported Ru/Co nanoparticles,^{5b} we observed that the partially reduced hydroxylamine was generated in high

concentrations at partial conversion to the aniline product (Scheme 1). We wondered whether the selective formation of the hydroxylamine product could be favored by careful optimization of our nanoparticle catalyst and reaction conditions. Aryl hydroxylamines are important intermediates en route to bioactive molecules⁷ and are commonly used as oxidants for C-N bond forming reactions,⁸ including with transition metal catalysts.⁹ Traditional routes to hydroxylamine products include the reduction of nitro compounds with stoichiometric metal reductants (Sn, Zn)¹⁰ or boron hydrides,¹¹ catalytic reductions with heterogeneous catalysts,¹² or through biocatalytic reductions/oxidations.¹³ The reduction of nitroaromatics with Pt nanoparticle catalysts under hydrogenation conditions has also been reported.¹⁴ Doris and coworkers also recently reported carbon nanotube-supported ruthenium nanoparticles for hydroxylamine formation.¹⁵ Herein we show that easily prepared (1 step from commercial materials) polystyrene-supported ruthenium nanoparticles selectively generate aryl hydroxylamines via partial reduction of readily available nitroarene substrates. Importantly, we demonstrate that the reduction reaction is highly chemoselective for hydroxylamine formation in the presence of various easily reduced functional groups and we expand the substrate scope of this important transformation to include *N*-heteroaryl hydroxylamines.



Scheme 1. Hydroxylamine synthesis via nitroarene reduction.

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