Abstract

Iron plays a pivotal role in metabolism and transport processes in nature but can also be used to accomplish important chemical transformations on the bench top; recently, iron(II) salts have been shown to catalyze direct Suzuki–Miyaura coupling of N-heterocyclic compounds and arylboronic acid derivatives in the presence of oxygen. Presented herein are three tetra-aza macrocyclic iron(III) complexes: [L1FeClO]4+, [L2Fe]2+ (L2Fe), and [L3Fe]3+ (L3Fe) which we expected to be capable of coupling pyrrole and phenylboronic acid. Following the synthesis and reactivity studies, investigation into the oxidative state of the iron center throughout the catalytic cycle was explored. The results of this work to date will be presented, and will facilitate the understanding of the challenging chemical reactions catalyzed using inexpensive earth abundant metal salts such as iron.

Introduction

Nature is capable of transforming unreactive alkynes and alkenes under mild conditions, but comparable laboratory transformations require multiple steps that include expensive and/or toxic metals such as palladium, protecting groups, and strong oxidants. The development of highly efficient, catalytic reactions to modify organic bonds continues to be a formidable synthetic challenge to chemists. Due to the large abundance and low toxicity of iron, it has received attention as a catalyst for the synthesis of fine organic materials. Many studies have focused on developing mononuclear iron catalysts based on chelating motifs seen in nature. These complexes are then studied to determine their catalytic profile, based on the modification of directing groups, steric effects, and electronic characteristics of the substrates. In many cases less emphasis is given to the spin state of the iron center. Although it is necessary to identify the key properties the catalyst based on substrate scope, it is also important to determine the properties of the metal center that allow catalytic processes to occur. Identification of necessary metal properties will allow for rational design of future iron catalysts.

Catalyst Design and Properties

Hypothesis: Structural changes to ligands will impact the donor ability and iron coordination chemistry.

Conclusion: 1) The complexes take on a cis-folded octahedral geometry, in which the iron center is high-spin. 2) The donor ability of the ligands does not affect the stability of the iron(III) center.

Comparison of Catalytic Reactivity

Hypothesis: The high-spin iron(III) complexes are capable of coupling pyrrole and phenylboronic acid.

Conclusion: [L1FeClO]4+ catalyzes the reaction to the greatest extent followed by [L2Fe]2+ then [L3Fe]3+.

Radical Scavenging Ability and Its Effect on Catalytic Yield

Hypothesis: The difference in the catalytic ability of the complexes is caused by the radical scavenging ability of the complexes themselves.

Conclusion: The coupling of pyrrole and phenylboronic acid is not a radical process.

Catalyst and Mechanistic Investigation of Three Tetra-aza Macrocyclic Iron(III) Complexes

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References