FeIII catalyzed C-H amination

Obtaining mechanistic insight through structure-reactivity studies

Dieuwertje K. Modder, Dirk W. Zant, Jarl Ivar van der Vlugt
van’t Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands
dieuwertje.modder@student.uva.nl, d.w.zant@uva.nl, j.i.vandervlugt@uva.nl

Introduction

Nitrogen heterocycles crucial in medicine

Efficient synthesis: direct functionalization of C(sp^3)-H bonds, usually with Pd

Replace noble transition metal catalysts for base metals, e.g. Fe

Recent initial work

Investigate structure-reactivity relation

Kinetic studies:
- 0th order substrate
- 1st order catalyst
- 1st order Boc₂O

Research goal

- Understand activation mechanism of FeCl₃(NNO₅SO₄) by Boc₂O
- Elucidate structure of the active catalyst

Approach

1. Vary the monodentate ligands

2. Vary the redox-active ligand

3. Replace tridentate by bidentate ligand

Syntheses

1. Previously reported synthesis

Problem: formation of homoleptic [FeIII(NNO₅SO₄)]⁺ complex

Adapted synthesis

Works for X = Cl, Br based on MS and X-ray of FeCl₃(NNO₅SO₄)

2. FeCl₃(NNO₅SO₄) with different redox-active ligand

Coordination not yet achieved, potentially due to too strong base

Conclusions

- Successful synthesis of FeCl₃(NNO₅SO₄) and FeBr₃(NNO₅SO₄) complexes
- Fe(O Tf)₂ as starting material → only forms homoleptic [FeIII(NNO₅SO₄)]⁺ complex
- Successful synthesis of NNO' ligand
- Synthesis of FeCl₃(NNO') complex not yet achieved

Outlook

- Synthesize FeCl₃(NO)

- Optimize synthesis of FeCl₃(NNO')

- Explore synthesis of complexes with bidentate ligands
- Analyze catalytic activity of successfully synthesized new complexes

References