CHIRAL CYCLOOCTADIENE LIGANDS FOR RHODIUM CATALYSIS

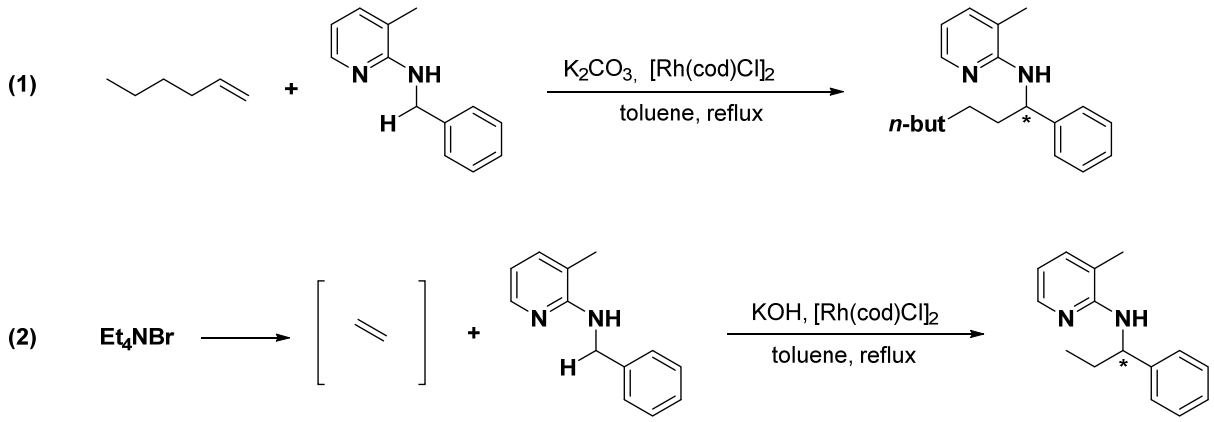
Charlie Lim[a], Manuel Spettel[a], Robert Pollice[b], Michael Schnürch[a]

[a]E163 - Institute of Applied Synthetic Chemistry
[b]ETH Zürich, Zürich, Switzerland

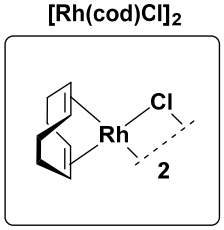
INTRODUCTION

The scaffold of organic molecules is dominated by the presence of carbon-hydrogen (C-H) and carbon-carbon (C-C) bonds. Considering this dominance of carbon atoms, it is only natural that carbon-carbon bond forming transformations are of fundamental interest for organic chemists. Numerous approaches towards C-C bond forming reactions have been realized – including the highly useful transition-metal catalysed cross-coupling reactions. However, the major drawback with such transformations is the need for at least one pre-functionalized coupling partner. This is where C-H functionalization proves to be superior. The selective C-H functionalization, an uprising and promising field within the plethora of C-C transformations, allows the direct coupling of non-pre-functionalized substrates and results in a more atom- and step-efficient synthesis of complex molecules.

Our group has previously reported the direct alkylation of benzylic amines *via* C-H functionalization by utilizing terminal olefins as alkylating agents.[1] Additionally, the introduction of the gaseous short-chain olefins was reported by *in-situ* generation of the olefins *via* Hoffmann-elimination from the corresponding tetraalkylammonium salts.[2]



Scheme 1: (1) Direct alkylation of benzylic amines via C-H functionalization with terminal olefins (2) Utilizing alkylammonium salts as olefin source *via* Hoffmann-elimination



So far, the potentially enantioselectivity of this reaction was of less attention. Within this project, we are aiming for chiral modification of the cyclooctadiene ligand on the rhodium catalyst (Scheme 2).

Scheme 2: Rhodium catalyst used in the reaction

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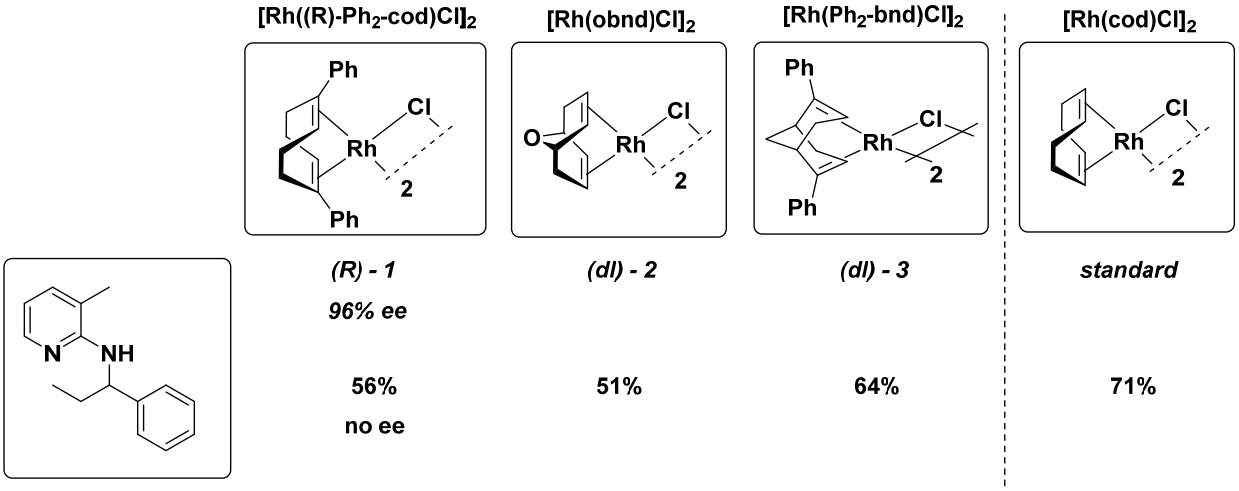
We have synthesized three different cyclooctadiene derivatives (Scheme 3) for the investigation of the enantioselective induction. The ligands were synthesized and coordinated onto the rhodium as racemic mixture.[3] According to the Grützmacher method, the enantiomerically pure **(*R*)-1** was obtained by optical resolution *via* fractional crystallization of the diastereomers [Rh((*R*)-Ph_2-cod(*R*)-DABN)]BF_4 and [Rh((*S*)-Ph_2-cod(*R*)-DABN)]BF_4.[4] The optical resolution of **(*dl*)-2** and **(*dl*)-3** *via* the Grützmacher method is currently pending.



Scheme 3: Overview of synthesized catalysts bearing modified cod-ligands

RESULTS AND DISCUSSION

All of the racemic catalysts were tested in the Hoffmann-approach (reaction (2) in Scheme 1) and showed general catalytic activity (Scheme 3). In case of the enantiomerically pure catalyst **(*R*)-1**, the product was obtained as a racemic mixture. The absence of any ee indicates the racemization of the catalyst. This may be caused by dissociation of the diene ligand and re-coordination with the other face.

CONCLUSIO

To avoid the racemization by the proposed dissociation/re-coordination process, we are currently investigating cod-derivatives **(*dl*)-2** and **(*dl*)-3** bearing a bridge-moiety in their backbone. This bridge-moiety would trap the conformation and thus prevent racemization.

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