



β -Boration of α,β -unsaturated carbonyl compounds in ethanol and methanol catalyzed by CCC-NHC pincer Rh complexes



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ABSTRACT

Quantitative β -boration of α,β -unsaturated carbonyl compounds was achieved utilizing the eco-friendly solvent EtOH along with MeOH at room temperature in 1 h, by a CCC-NHC pincer Rh complex mixture. Substrates with β -substituents were successfully converted yielding challenging, quaternary C–B bonds. The air- and water-stable pre-catalyst **A**, identified as a mixture of iodo and chloro CCC-NHC pincer Rh amine complexes, was evaluated for catalytic activity. This report is the first example of a pincer Rh complex demonstrating catalytic activity in a 1,4-addition at room temperature.

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1. Introduction

Organoborane compounds are highly sought after intermediates in organic synthesis. The facile transformation of the C–B bond into other functional groups such as alcohols, amines, and alkenes allows direct access to a wide range of organic molecules [1–4]. In 1997, a Pt catalyst was utilized in the first report of β -boration of α,β -unsaturated carbonyl compounds using a diboron reagent [5]. To date, the boration of α,β -unsaturated carbonyl compounds has been catalyzed with Pt [5–8], Pd [9,10], Rh [11–14], Cu [15–41], Ni [10,42,43], Fe [44], metal-free phosphines [45–47], and N-heterocyclic carbenes (NHCs) [48–51]. Subsequently, β -boration of α,β -unsaturated carbonyl compounds has become very useful due to the additional carbonyl contained in the product [6,11,17–22,42,44,52,53]. Oxidation of the product provides access to β -hydroxy compounds as an alternative to the aldol reaction or reduction of β -keto carbonyl compounds. β -Hydroxy carbonyl compounds are found widely in natural products and pharmaceuticals [54,55]. Additionally, β -boro-carbonyl compounds have been reported as being effective therapeutic agents in cancer treatment [56,57].

Cu systems have been the most commonly applied catalysts for β -boration of α,β -unsaturated carbonyl compounds. Noteworthy examples have been reported using strictly protic solvents such as MeOH [26] and H₂O [36,37,58–61]. In 2009, Santos reported the synthesis of an innovative sp^2 – sp^3 diboron reagent and demonstrated its application in a Cu catalyzed β -boration of acyclic substrates [32]. In 2008, the first asymmetric catalysis for β -boration of acyclic compounds was reported using a chiral Cu phosphine complex [15], opening the path for innovative work such as asymmetric β -borations conducted in water [37,58–60] and the development of chiral β -tetrasubstituted carbon centers using β,β -substituted substrates [62–64]. Subsequently, other examples of asymmetric catalysis have been reported with Ni [10], Pd [10], Rh [11,12,14], and Cu [18,21,22,27–30,33–35,39,40,61,65,66]. Metal free-catalysis has also been developed, including asymmetric variants [47,49], such as a chiral NHC salt reported by Hoveyda [49,50,67].

Despite many reports utilizing various transition metals, base additives or high temperatures have been required for efficient rates, and limitations to acyclic α,β -unsaturated carbonyl substrates have been noted. In addition, very few cyclic products with boron-substituted quaternary carbon centers have been reported [48]. A catalyst that provides cyclic β -boro-carbonyl compounds containing quaternary carbon centers and can operate at room temperature without the need for an exogenous base provides a straight-

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forward methodology in the formation of C–B bonds as well as β -hydroxy carbonyl compound derived thereof.

Previously, we reported a mixture of the CCC-NHC pincer Rh complexes **1/2** (Scheme 1) that efficiently catalyzed 1,4-addition of aryl boronic acids to electron-deficient alkenes [68]. CCC-NHC pincer Rh complexes **1/2** (Scheme 1), along with added NHMe_2 , produced excellent yields (>90%) with various Michael acceptors and arylboronic acids in protic solvents [68]. In looking toward the preparation of chiral variants, further attempts to optimize the synthesis of **1** led to a crude isolate (**A**) that was orange in color and was obtained reproducibly. We report herein, the characterization of mixture **A**, separate isolation and screening of the components and material **A** in the β -boration of cyclic and acyclic, α,β -unsaturated, electron-deficient alkenes. Furthermore, this report is among the few examples [69,70] in the literature of a pincer complex catalyzing 1,4-addition reactions at room temperature.

2. Results and discussion

2.1. Characterization of catalytically-active material **A**

The previously reported methodology for the synthesis of the CCC-NHC pincer Rh complexes was modified by switching the solvent to THF (Scheme 1) and using a careful work up procedure as detailed in the experimental procedure. This sequence reproducibly yielded an orange microcrystalline to powdery solid **A** that was highly catalytically active. Spectroscopic data indicated the orange mixture **A** consisted of two CCC-NHC pincer Rh complexes evidenced by two sets of diastereotopic, overlapping methylene signals (Fig. 1 and ESI) in the ^1H NMR spectrum and two carbene carbon signals coupled to Rh in the ^{13}C NMR spectra (Fig. 2 and ESI). Two $\text{Rh}-\text{C}_{\text{aromatic}}$ and $\text{Rh}-\text{C}_{\text{carbene}}$ doublets (Fig. 2) are observed in the ^{13}C NMR spectrum with identical $\text{Rh}-\text{C}_{\text{carbene}}$ and $\text{Rh}-\text{C}_{\text{aromatic}}$ doublet coupling values ($^1J = 39$ Hz and $^1J = 29$ Hz, respectively) observed for **A**. These data indicated that the complexes were similar.

A dark orange solid was isolated from mixture **A** using silica gel chromatography. Spectroscopic data analysis of the isolated material lead to the assignment of axial amine adduct **1** as the structure [71], which has NMR peaks coincident with the major component of mixture **A**. Additionally, an orange X-ray quality crystal of **1** was grown by vapor diffusion (toluene/DCM) from mixture **A** (Fig. 3) [72]. The molecular structure was observed to be a distorted octahedron with the amine ligand in an axial position. The metric data (bond distances and angles) are typical for the CCC-NHC pincer ligand system Rh complexes.

Further analysis of the exact mass ESI-TOF spectrum of **A** contained a peak at m/z 537.0942 ($[\text{M} - 2\text{H}]^+$, corresponding to a theoretical mass for $\text{C}_{22}\text{H}_{30}\text{N}_5\text{Cl}_2\text{Rh}$ 537.0928) indicating a chloro

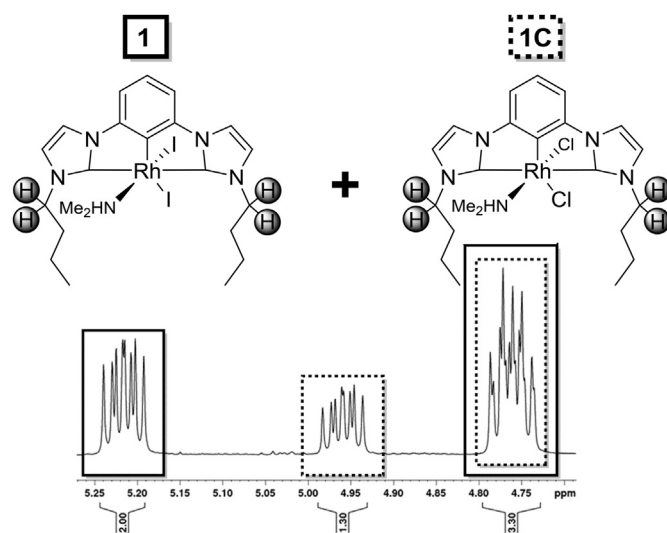


Fig. 1. Two sets of diastereotopic methylene peaks indicating a mixture of CCC-NHC pincer Rh complexes **1** and **1C** in **A**. The signal at 4.75 ppm is overlapping from both complexes.

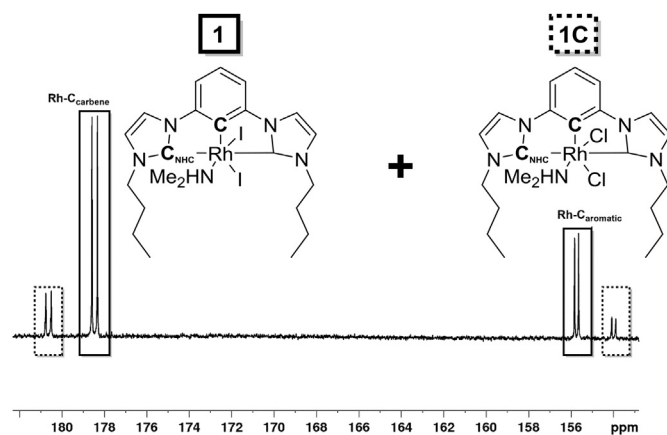
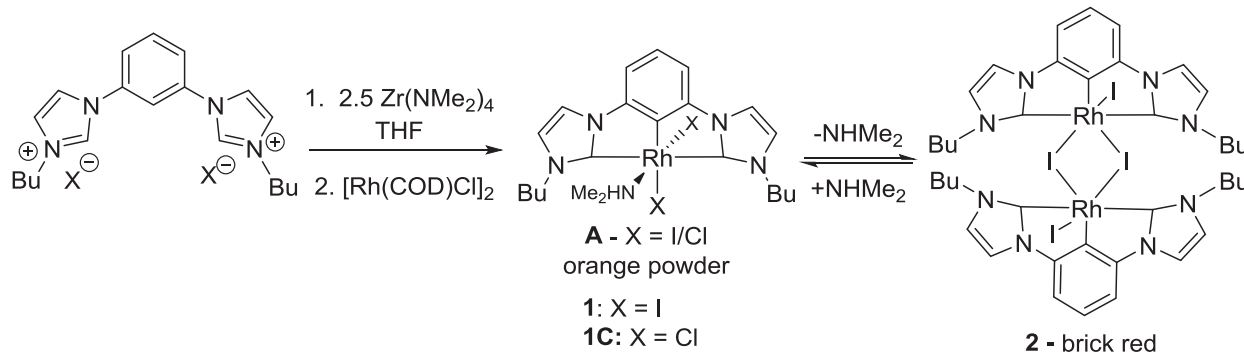


Fig. 2. Two $\text{Rh}-\text{C}_{\text{aromatic}}$ and $\text{Rh}-\text{C}_{\text{carbene}}$ doublets are observed in the ^{13}C NMR spectrum of **A**.

variant (**1C**). Spectroscopic data from the ^{13}C NMR also supported the assignment and similarities of the two species. Complex **1C** was then prepared independently by starting with the chloroimidazolium salt ($\text{X} = \text{Cl}$, Scheme 1). It was analyzed to determine if the ^1H and ^{13}C NMR signals of this complex corresponded to



Scheme 1. Equilibrium of amine adduct and iodo-bridged dimer.

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