

# Computational insights into the mechanisms of arene C-B and C-C bond forming reactions catalyzed by ruthenium pincer complexes bearing classical and nonclassical hydride centres

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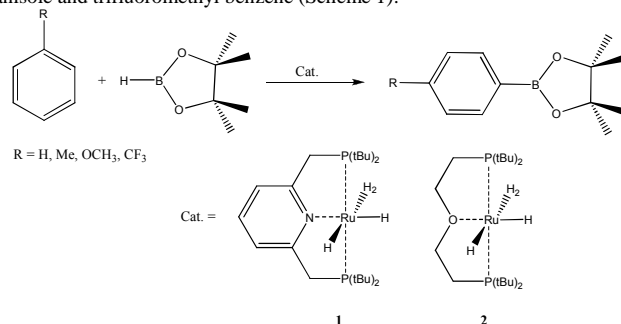
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## Introduction

Computational chemistry is an important tool for elucidating reaction mechanisms. Among the theoretical methods available density functional (DF) calculations are at the core of organometallic catalysis, as for this field they feature the most advantageous compromise between computational accuracy and computational cost. Nonclassical transition metal hydrides -first discovered by Kubas in 1984[1]- have shown in many cases interesting catalytic activities. Our group has an ongoing research interest in the synthesis, characterization and testing of new catalysts of this type[2-4]. We have a focus on group 8 pincer complexes with the general formula  $[M(H)_2(H_2)L]$  ( $M = Fe, Ru, Os$ ;  $L = PNP, PCP, POP$  pincer ligands) and aim at an understanding of their mechanism of action as catalysts i.e. in C-H activation and C-B, C-C, and C-N bond formation as well as in  $N_2$  activation. Furthermore these complexes are ideally suited to investigate computationally their potential as catalysts in hitherto unknown reactions. Here we report about recent developments in understanding mechanisms of important fundamental reactions such as C-B- (A) and C-C-bond formation (B).

## Results and Discussion

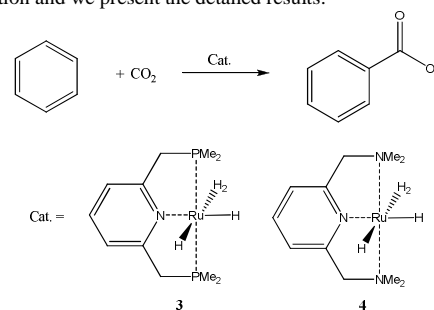
**A:** The direct catalytic functionalization of arenes is a highly desirable means to introduce functional groups to otherwise relatively unreactive aromatic compounds. We are currently exploring experimentally and computationally the performance of nonclassical ruthenium hydrides **1** and **2** in borylation reactions of differently substituted arenes such as benzene, toluene, anisole and trifluoromethyl benzene (Scheme 1).



Scheme 1. Borylation of arenes with pinacolborane and catalysts **1** and **2**.

This is the first time ruthenium pincer complexes of this kind were shown to be active in these reactions and interesting regioselectivities were obtained. We present different computationally derived reaction mechanisms that help explain the experimental results.

**B:** Carbon dioxide ( $CO_2$ ) is a highly abundant yet relatively unreactive molecule. Its activation and introduction into complex molecules is one of the important challenges in catalyses. The direct synthesis of benzoic acid from benzene and  $CO_2$  using an appropriate catalyst would be such a desired reaction (Scheme 2). As the formation of formic acid from  $H_2$  and  $CO_2$  is possible using ruthenium hydrides when bases are present,[5] we investigated computationally the behaviour of nonclassical ruthenium hydride pincer complexes as catalysts for the reaction of benzene and  $CO_2$ . We found closed catalytic cycles with surprisingly low activation barriers for C-C bond formation and we present the detailed results.



Scheme 2. Computationally investigated synthesis of benzoic acid with catalysts **3** and **4**.

## Computational details

Computations were carried out using the Gaussian03 or the Turbomole5.10 program series. Functionals employed were B3LYP, BP86 and PBE-D. Basis sets were of SDD or TZVP quality. All local minima and transition states were verified by frequency calculations and for most transition states IRC calculations were performed.

## References

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