



# Rhodium catalyzed hydroamination of C<sub>2</sub>H<sub>4</sub> with NH<sub>3</sub> with pincer derived PE(CH<sub>2</sub>CH<sub>2</sub>X)P ligands – Fighting the energy span



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## ABSTRACT

Density functional theory (DFT) calculations were carried out on a variety of rhodium complexes with a variety of pincer derived PE(CH<sub>2</sub>CH<sub>2</sub>X)P ligands (E = B, C, N; X = O, NH, CH<sub>2</sub>, PH, SiH<sub>2</sub>) to answer the question if computationally a catalyst for the as yet unresolved hydroamination of ethylene with ammonia can be designed. The influence of the different side arm donor groups X was studied with the central pincer backbone element E being carbon. Additionally to rhodium as the metal center cobalt and iridium were studied. Furthermore, the influence of solvation for four solvents (toluene, dichloromethane, tetrahydrofuran, acetonitrile) was investigated on an optimized system. While the majority of the study focuses on neutral catalysts the influence of the complex charge was also studied briefly. Anionic complexes generated by exchanging the backbone carbon E from C to B were studied as well as cationic complexes which were generated by replacing C with N. The variation of the calculated energy spans is large with many systems yielding spans of ca. 40 kcal/mol or above. The lowest energy span ( $\Delta G = 28.7$  kcal/mol) was identified for a neutral rhodium catalyst with E = C and X = NH in dichloromethane or tetrahydrofuran solution yielding a predicted TOF of 90 h<sup>-1</sup> at 130 °C. Outer sphere mechanisms were studied briefly and cannot compete energetically with inner sphere mechanisms.

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## 1. Introduction

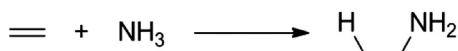
Amines are compounds of profound importance in all kinds of chemical product classes ranging from bulk to fine chemistry [1]. The hydroamination of olefines – i.e. the direct addition of amines and ammonia to C–C double [2] and triple bond [3] systems – has developed into an important tool for generating selectively a large variety of amines and imines, respectively. However, the seemingly simplest case, the direct addition of ammonia to ethylene is an open research target for which the development of efficient catalysts has remained a challenge (Scheme 1).

The groups of Hartwig and Turculet have independently studied different kinds of [Ir(PEP)] pincer complexes (E = C, Si) and were able to oxidatively add NH<sub>3</sub> to complexes [Ir(PCP)] (PCP = [ $\kappa^3$ -(tBu<sub>2</sub>P-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>CH]<sup>-</sup>) [4] and [Ir(PSiP)] (PSiP = [ $\kappa^3$ -(2-Cy<sub>2</sub>P-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMe]<sup>-</sup>), respectively [5]. Furthermore, the group of Hwang has shown in a very brief computational investigation that the replacement of silicon by carbon in the PSiP-type pincer complexes might be beneficial for achieving lower activation barriers in N–H

bond cleavage [6]. Combining these facts it is interesting to investigate catalysts in which the PEP pincer motif is retained in general, however with some important modifications. (a) The backbone element E of the PEP pincer ligand is chosen to be carbon (for other variations of E vide infra), (b) the fourth valence of this carbon atom is used for adding an ethyl side arm to the pincer ligand which finalizes in a donor group X. (c) The group X occupies one of the vacant coordination sites at the metal and binds to it. In this way the coordination site is blocked which can prevent undesired reactions at this site. Furthermore it will help preventing the pincer ligand to adopt another than the meridional coordinating structure, as it was shown repeatedly that different coordination modes for pincer ligands are possible. Finally, an increased thermal stability of the catalyst complex is assumed, which will most likely be beneficial in experimental work, as a high reaction temperature can be expected. With regard to the metal we have shown previously, that it depends crucially on the ligand if rhodium is more beneficial than iridium with regard to barrier heights and complete energy spans [7]. The focus in this study is on rhodium although a few iridium and cobalt catalysts will be studied for reasons of comparison (vide infra). Therefore, to start the computational design process we arrive at catalyst lead structure **1** which is a group 9 metal(III) amide. The three most important questions that will be

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**Scheme 1.** Hydroamination of ethylene with ammonia.

addressed in this study are: (1) Can a catalyst be designed which has an appreciably low energetic span? [8]. (2) Which side reactions are possible? (3) Are there low energy pathways to the respective side products and do they contain low energy minima, which increase the energetic span? Fig. 1

It can be expected that the group X has a large influence on the catalytic performance of **1** as it influences directly the electronic properties of the metal center. Accordingly, we included a variety of plausible elements to make up for X in this study (X = O, NH, CH<sub>2</sub>, PH, SiH<sub>2</sub>). In further investigations for one particular ligand iridium and cobalt complexes were added to the study to obtain a coherent view on complexes of all group 9 metals. To obtain an impression on the influence of a positive or a negative charge on the catalytic performance we selected one rhodium catalyst and repeated the calculations with the backbone donor element E being exchanged to be boron or nitrogen yielding an anionic and a cationic catalyst system, respectively. Furthermore modifications in the periphery of the ligand were introduced for one rhodium catalyst and finally the influence of solvation was studied. For the optimized catalyst system side reactions were investigated to conclude the study.

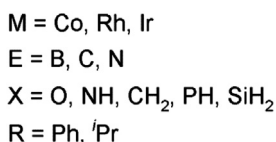
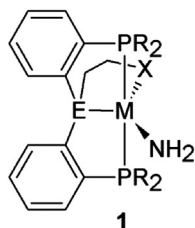
## 2. Results and discussion

For the sake of readability this work is subdivided in seven parts: (1) General description of the calculated catalytic cycles and influence of the donor group X studied in the parent rhodium catalyst system with E = C. (2) Influence of the metal. (3) Influence of the complex charge. (4) Influence of the solvent. (5) Influence of substitutions in the periphery of the ligand backbone. (6) Side reactions. (7) Outer sphere mechanism. Some minima and transition states did not require to be calculated, which is noted in the respective tables (n.d. = not determined).

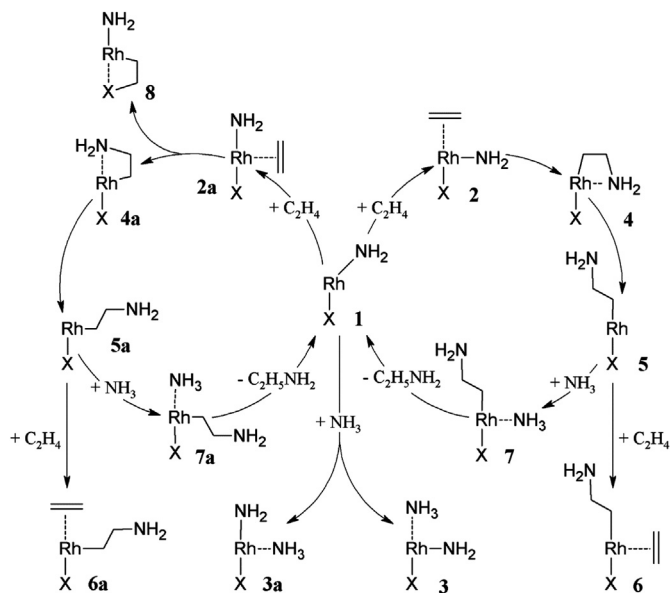
### 2.1. General description of the calculated catalytic cycles and influence of the donor group X

The parent complex **1** (M = Rh, E = C, X = O, NH, CH<sub>2</sub>, SiH<sub>2</sub>, R = Ph) allows for the generation of a complex reaction scenario which is shown in Scheme 2. Reactions following an inner sphere mechanism are considered in detail in the main text, while outer sphere reactions were studied briefly (vide infra).

The addition of either olefin or ammonia to **1** is possible generating complexes **2** and **3**, respectively. Depending on the side



**Fig. 1.** Catalyst lead structure investigated in this study.



**Scheme 2.** Calculated catalytic cycles and dead ends starting from **1**.

of the attack of olefin or ammonia the amido group of **1** will either move to the site *cis* or *trans* to the group X. Accordingly, isomers **2** and **2a** are possible as well as **3** and **3a**. Both isomers of **3** are considered to be dead ends, as there is no plausible reaction to follow. Instead, **2** and **2a** will react by passing via transition states TS(**2**–**4**) and TS(**2a**–**4a**), respectively, leading to C–N bond formation and resulting in complexes **4** and **4a**, in which the amino group is coordinating to the metal center. Breaking this coordination by dissociation and rotating around the C–C bond leads to complexes **5** and **5a** with a vacant coordination site at the metal, which can be occupied either by olefin (**6**, **6a**) or by ammonia (**7**, **7a**). Complexes **6** and **6a** in general are the entry to oligomerization processes, which were not investigated in this study. From **7** and **7a** the reaction proceeds toward the formation of ethylamine, via transition states TS(**7**–**1**), TS(**7a**–**1**) in a  $\sigma$ -bond-type metathesis reaction. The product then dissociates from the complex and in this way regenerates the catalytically active starting species **1**. There is an alternative reaction for compound **2a**: The coordinated ethylene molecule can insert to the M–X bond yielding compound **8**. Depending on the height of the transition state TS(**2a**–**8**) and of **8** on the hyper surface this reaction will either be a dead end when the barrier is low enough to be passed and when **8** is a very stable product. However, in case the stability of **8** is not very pronounced and the barrier for the reaction back to **2a** is not too high, this reaction path would not hamper product formation as **8** would react back to **2a**. Further side reactions will be discussed later for an optimized catalyst system.

### 2.2. Influence of X

Calculations were initially carried out for five catalysts **1** with E being carbon, R being phenyl and M being Rh in all cases and with X = O, NH, CH<sub>2</sub>, PH and SiH<sub>2</sub>. For all five catalysts investigated it was possible to locate a representative number of stationary points including the most relevant local minima and transition states. The relative Gibbs free energies obtained in gas phase calculations on M06L/def2-TZVP//M06L-def2-SVP are listed in Table 1 together with the energetic span obtained from these values.

The addition of ethylene to **1** is endergonic in all cases. Generally the energy uptake increases in going from the most electronegative

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