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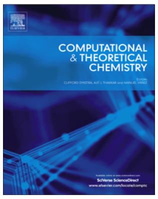

# The substituent effect of the pentafluorophenyl groups on ruthenium-porphyrin-catalyzed intramolecular amidation of sulfamate ester: A DFT study

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ABSTRACT

The substituent effect of the pentafluorophenyl ($PhF_5$) groups on the Ru-porphyrin complex-catalyzed intramolecular reaction was investigated with density function theory calculations. The interested reaction steps are the unsubstituted and substituted Ru-porphyrin complexes-mediated nitrene insertion into one of the C—H bonds on a certain sulfamate ester. For both of the unsubstituted and substituted reactant complexes, the singlet state has a close energy to the triplet state. The substitution of the $PhF_5$ groups leads to a lowered reaction barrier on both of the singlet and triplet potential energy surfaces (PESs). The barrier lowering corresponds to an increased reaction rate by 2 orders of magnitude on both PESs. The singlet PES has a predominant contribution to the overall reaction rate compared to the triplet one for both of the unsubstituted and substituted cases. The results from the natural bond orbital analysis show that the $PhF_5$ groups are highly negative in charge, and the group substituting leads to an increased electron deficiency of the nitrene N atom. This increase can account for the increase of the reaction rate on both of the singlet and triplet PESs.

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## 1. Introduction

The chemistry of transition metal catalyzed amidation of C—H bonds and aziridination of alkenes using imino phenyliodinane (PhI=N—Y, where Y = R, $SO_2R$, $SO_3R$, COOR…) or organic azides (Y—N=N=N) as a nitrogen source has grown dramatically over the past few decades. These types of catalytic reactions are increasingly attractive as a route to synthetic amines [1–9], aziridines [1,10–14]. Similar reactions also can be used to synthesize epoxides [12,15,16], as well as new mimics of natural products [13,16]. This type of reaction is also a green synthetic method, since nearly all reactants go to products. Tunable steric hindrance of the N—Y substrates and the diverse ligand scaffolds on the catalyst may lead to controllable stereo or regioselectivities of the products. It will be very appealing to synthetic chemists if the product selectivities can be predicted by computation for a given N—Y group and a catalyst ligand. Such predictions can help save great works in synthesizing a lot of ligands and/or reactants, and doing extensive searches experimentally.

However, compared to the amount of synthetic reports using this method, the theoretical studies are much fewer in number [7,17–21] in the literature. The detail mechanisms as well as how different factors influence the reaction behaviors not well understood. The actual intermediate(s) directly responsible for the nitrene insertion into the C—H bonds remains elusive in the literature. In particular, the "metal-nitrene" complex and the "metal-imino phenyliodinane" complex are generally believed to be possible intermediate(s) responsible for the C—N bond formation. The papers published in the recent years show theoretically the "metal-nitrene" is a more plausible candidate compared to the "metal-imino phenyliodinane" complex for the reaction systems using Ru or Rh based catalysts [17–19]. However, to our knowledge, there is no report seeking for understanding the substituent effect on the scaffold of the ligand with first-principle calculations. This is undoubtedly an interesting issue since synthetic chemists often try to tailor their catalysts by tuning substituent close to the reaction center.

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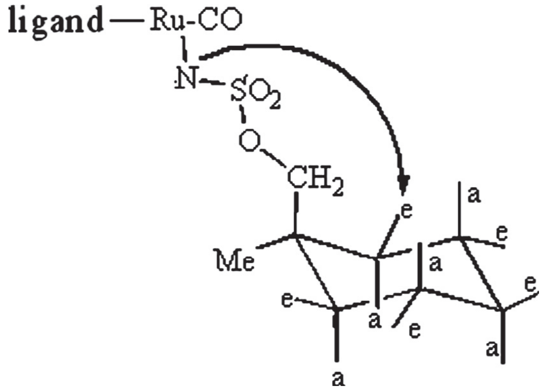
We have previously performed a computational study [18] on the reaction as indicated in Scheme 1, the intramolecular amidation of a C—H bond in a cyclohexane ring to form a diastereoselective amide (**3** in Scheme 1) with two chirality centers [22]. The Ru(por)(CO) complex, **4b** (por represents the porphyrin ligand) was used to model the real catalyst of Ru($F_{20}$-TPP)(CO) complex, **4a** ($F_{20}$-TPP represents the tetrapentafluorophenyl porphyrin ligand). The imino phenyliodinane, **5**, can be in situ generated from the initial reaction system (**1 + 2**) [18,22], and the starting materials can be treated as **4b + 5** in a catalytic cycle. The "metal-nitrene" intermediate in this reaction, Ru(por)(CO)—$SO_3R^1$ (**7b**, $R^1$ represents 1-methylclohexlmethyl) was found to be highly favorable to generate on the basis of free energy profile from the reaction of the starting materials. Ru(por)(CO)—$SO_3R^1$ **7b** is more favorable than the "metal-imino phenyliodinane" intermediate, Ru(por)(CO)—(Ph—I)=$NSO_3R^1$, **6b**. The singlet and triplet state of **7b** are close in energy. In each state, six possible C—H bond amidation pathways were characterized structurally and energetically. One of these six reaction pathways that results in the (5R,6S) diastereomer, indicated in Scheme 2 here, contributes predominantly compared to other five. Based on the calculated relative reaction rates the calculated product selectivity of the (5R,6S) diastereomer for **3** is 98% with a gas-phase model and 81% with a solution-phase model. The predicted diastereoselectivities agree well with the reported experimental results [22].

However in Ref. [18] the model catalyst used is Ru(por)(CO), **4b**, which is not the real catalyst of Ru($F_{20}$-TPP)(CO), **4a**. In this context it is interesting to understand the substituent effect of the four pentafluorophenyl ($PhF_5$) groups that are connected with the porphyrin ring. In this paper we aim at providing insight to this issue, emphasizing on the effect of the $PhF_5$ groups on the reaction rate. To this end only one reaction pathway starting from **7a** and **7b** as shown in Scheme 2 was investigated in this work. This pathway is the most favorable one in free energy among the possible six examined in Ref. [18]. The substituent effect of the charge distributions will also be discussed.

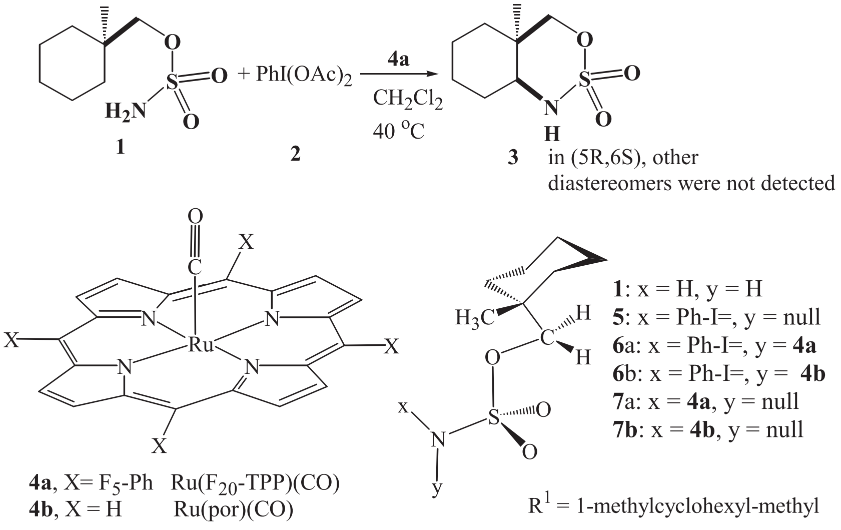
## 2. Computational details

The potential energy surfaces (PES) of the Ru-catalyzed intramolecular amidation were investigated by locating the structures with the energy minimum (for reactant complexes and product complexes) and the first-order saddle point (for transition states). Geometry optimization, frequency analysis and natural bond orbital (NBO) analysis were performed using density functional theory (DFT) with the Gaussian 09 suite of programs (B.01 version) [23]. The temperature for frequency analysis and then for free energy calculation is 313.15 K [22]. Becke's 1988 exchange [24] in conjunction with the PW91 [25] correlation functionals (BPW91) were used for the DFT calculations. Benchmark calculation reported previously [17] shows BPW91 provides good description on the singlet–triplet energy split compared to the result from the CCSD(T) level of theory. The SDD basis set was used for the Ru atom [26], and the 6-31G* bas set was employed for all of the C, H, O, N, S, and F atoms. This combined basis sets are denoted as BS1 in this paper. The product selectivity of several similar reactions was well explained by the BPW91/BS1 calculation [17,18]. Intrinsic reaction coordinate (IRC) calculations were performed to confirm the transition states connected to the appropriate reactants and products [27].



**7a**, where ligand = **$F_{20}$-TPP**
**7b**, where ligand = **por**

**Scheme 2.** A simple schematic diagram for the reaction pathway of amidation via "metal-nitrene" investigated in this paper. The nitrene N atom as indicated inserts into the indicated C—H bond and the amide **3** is formed. The notations "a" and "e" represent "axial" and "equatorial" H atoms on the cyclohexane ring. "Por" represents unsubstituted porphyrin and $F_{20}$-TPP represents the tetrapentafluorophenyl porphyrin. According to the definition in Section 2 below, **7a** is the same as **RC-sub**, **7b** is the same as **RC-uns**.



**Scheme 1.** Ru-porphyrin complexes-catalyzed intramolecular amidation of a sulfamate ester [18].

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