

2P126

イリジウム触媒を用いる 2-アルキルピリジンの位置選択的 C(sp³)-H 結合ホウ素化反応の機構解析

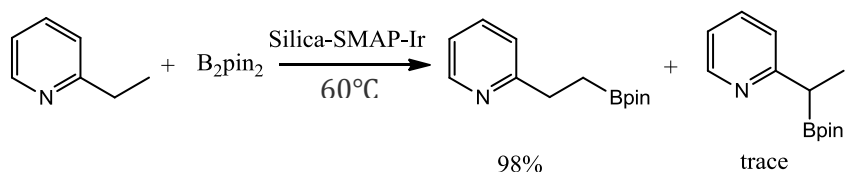
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Theoretical study on the mechanism of Ir catalyzed site-selective borylation of a C(sp³)-H bond in 2-alkylpyridines

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Introduction

The borylation reaction catalyzed by transition metal complex has attracted lots of interest because the organoboron compounds act as useful intermediates and reagents in organic synthesis. Recently, Sawamura and coworkers reported that a silica-supported monophosphine (Silica-SMAP)-Ir catalyst showed high site-selectivity in the C(sp³)-H borylation of substituted pyridines [1]. In this reaction, the C(sp³)-H borylation occurred selectively at the position γ to the N atom in substituted pyridines as shown in Scheme 1. In this study, we examine the detailed mechanism of this reaction to clarify the reaction pathways leading to the two different products and discuss the reason for the high site-selectivity.



Scheme 1. Silica-SMAP-Ir catalyzed site-selective borylation of 2-ethylpyridine [1].

Computational Method

In the present study, all the reaction pathways were obtained by using the artificial force induced reaction (AFIR) method [2, 3] which use the gradient and Hessian calculated by Gaussian 09 programs. We carried out calculations using the ONIOM (BP86:PM6) method for the initial search. Then, all obtained geometries were reoptimized with the DFT method using the M06L functional. The effective core potential ECP60MWB given by the Stuttgart/Bonn group was used in describing Ir atom where 5s² 5p⁶ 5d⁷ 6s² are considered as the valence electrons with the VDZ basis set from the same group, whereas the cc-pVDZ basis set was used for all the other atoms. Frequency calculations at the same level of theory have also been performed to identify the stationary points as minima or transition states.

Results and Discussion

In Silica-SMAP, phosphine is supported by the Silica surface, and this allows generation of 1 : 1 complexes between the phosphine and Ir. In other words, only one phosphine ligand can coordinate to the

Ir atom due to the silica support. This allows coordination of the N atom in substituted pyridines to Ir, and gives reasonable interpretation on the high site-selectivity [1]. Therefore, we started calculations from the coordination step of 2-ethylpyridine to a four coordinated P-Ir(III)-(Bpin)₃ complex giving six coordinated complexes. It should be noted that the silica surface is not included in our calculation model, because it does not have significant effects on the reaction center of given complexes. According to our calculation results, the reaction occurs via the following steps: (1) coordination of the N atom in 2-ethylpyridine to the Ir atom; (2) oxidative addition of a C-H bond to the Ir atom to form a seven coordinated intermediate; (3) dissociation of H-Bpin with small barrier; (4) reductive elimination of the borylated product; (5) oxidative addition of (Bpin)₂ to the Ir atom to get back the catalyst. This catalytic cycle is very similar to that obtained in a previous work with two-point ligand coordination [4]. Details of the catalytic cycle will be reported in the poster session.

We studied the effect of N coordination in 2-ethylpyridine and compared energy barriers for the C-H activation at the β and γ positions. The coordination of N atom plays an important role in the catalytic cycle especially in the step (2). Barriers for the oxidative addition without N coordination were found to be too high to occur, no matter in the case of the β or γ C-H bonds. The high selectivity is achieved at the transition state in the step (2). The β position C-H and the γ position C-H can undergo the oxidative addition through five- and six-membered-ring transition states, respectively. As seen in Fig. 1, the barrier for the C-H activation at the β position through the five-membered-ring transition state is much higher in energy than that for the γ position. This is due to the geometrical strain to form the five-membered-ring transition state. The strain energy will be analyzed by using the energy decomposition analysis and discussed in the poster presentation.

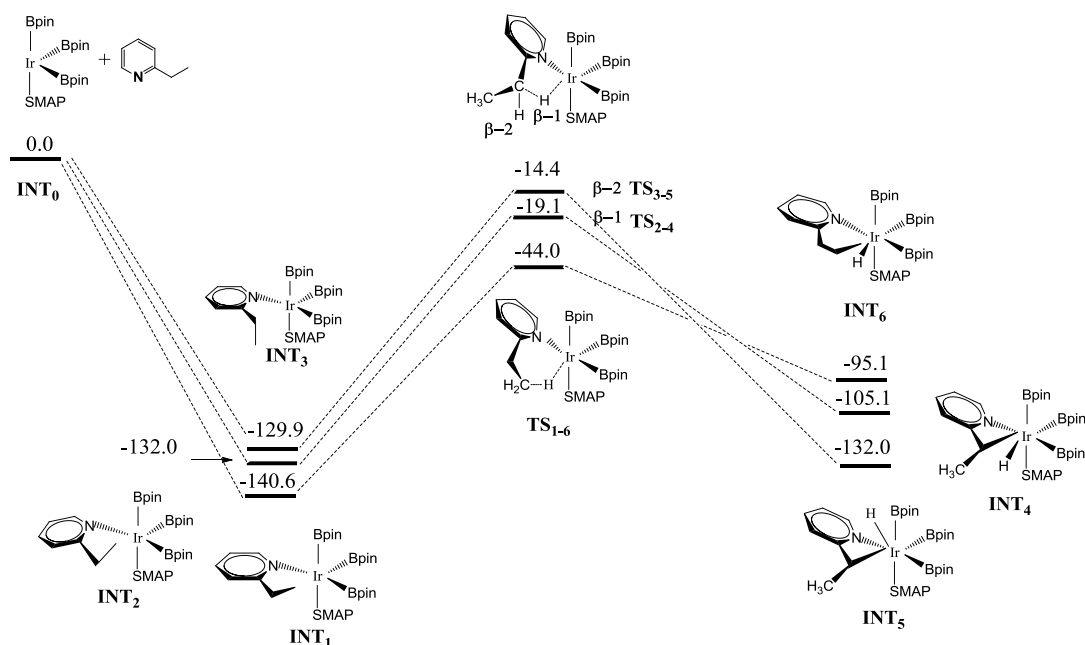


Figure 1. Energy profile (in kJ/mol) for the C-H activation step calculated with M06L functional.

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