

**Validation of a novel composite DFT-based approach for describing electronic and steric effects in the oxidative addition step of the Suzuki–Miyaura reaction****Научный руководитель – Соловьев Ярослав Владимирович****Чистякова Екатерина Андреевна***E-mail: ktyachistiakova.05@mail.ru*

The Suzuki–Miyaura reaction is a widely used cross-coupling process, where the oxidative addition step plays a crucial role in determining reaction efficiency and selectivity. Recent studies have shown that different catalysts exhibit distinct behaviours during this reaction. For instance, bidentate ligands often rearrange to form monodentate species to facilitate oxidative addition, as described for various phosphine ligands [1] and amino acid ligands [2]. The ligand environment significantly impacts this step; both steric and electronic effects can shift the equilibrium from the bidentate to the monodentate catalyst form. Moreover, the preliminary adsorption of PhBr onto Pd catalysts lowers the activation barrier and impacts reaction kinetics, which is substantial for Pd nanoparticles [3]. These findings highlight the necessity of accurate computational models to describe the varied oxidative addition mechanisms under different ligand environments.

In our study, we examined the ability of a composite DFT-based approach to reproduce kinetic constants obtained from in vitro experiments [4]. Geometry optimization was performed using the B97-3c method, followed by an electronic energy correction using the wB97X-V functional. The results show that the designed computational approach accurately describes Pd–ligand interactions, supporting experimental findings. We described the ligand dissociation process observed experimentally for certain types of Pd ligands. The discrepancy between theoretical and experimental kinetic constants was less than one order of magnitude.

However, for sterically hindered ligands, the theoretical constants were consistently lower than the experimental values by approximately 1.5 to 2 orders of magnitude. This distinction may be due to the suboptimal conformation of the obtained transition-state geometry and an extended conformational screening could yield a more optimal geometry. Thus, we conclude that while novel DFT functionals can accurately reproduce the main electronic effects of the oxidative addition, for more sterically hindered systems, complete conformational sampling is essential.

**References**

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