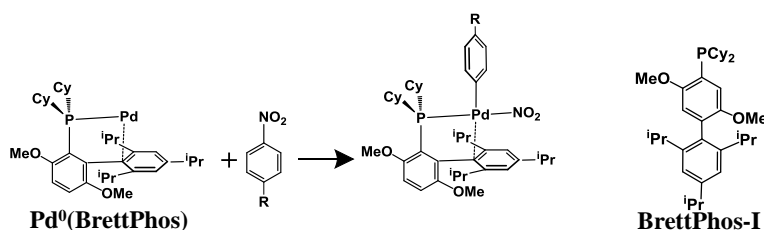


Oxidative Addition of Nitrobenzene to Palladium(0) Complex: Theoretical Analysis of Unexpected Ligand Effect

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[Abstract] The oxidative addition of nitrobenzene to palladium(0) complex was difficult for long time but it has been succeeded recently. In this reaction, usual phosphines such as PPh₃ and PMe₃ are not useful but a unique BrettPhos is effective. We theoretically investigated the oxidative addition of nitrobenzene to Pd⁰(BrettPhos) using DFT method and found that the oxidative addition of nitrobenzene to this complex occurs more easily than that to Pd⁰(PMe₃)₂ because Pd⁰(BrettPhos) has a good d_π MO at a higher energy even in equilibrium geometry than Pd⁰(PMe₃)₂ and it stabilizes reactant adduct, transition state, and product. BrettPhos-I that has a phenyl group at a different position from that in BrettPhos cannot provide such d_π MO at higher energy because the phenyl group of this ligand cannot interact with Pd(0). Thus this is not favorable for charge transfer from Pd(0) to nitrobenzene in transition state and the oxidative addition becomes difficult.

[Introduction] The Suzuki–Miyaura cross-coupling reaction with nitroarenes has been succeeded recently.^[1] The use of nitroarenes instead of haloarenes is potentially useful for synthesis of biaryls because nitroarenes can be synthesized more easily from arenes than haloarenes. Up to now, the fundamental understanding of the aryl-NO₂ bond activation has not been presented yet. In this study, we wish to report the characteristic features of the oxidative addition of nitrobenzene to Pd⁰(BrettPhos) (see scheme 1) and elucidate crucial role(s) of BrettPhos in comparison with different ligands including PMe₃ and BrettPhos-I (see Scheme 1).



Scheme 1. Oxidative addition of 1-methoxy-4-nitrobenzene to Pd⁰(BrettPhos) and the structure of BrettPhos isomer (BrettPhos-I).

[Methods]

All geometry optimizations were performed by ω B97XD functional, where the Stuttgart-Dresden-Bonn basis set was employed for Pd with the effective core potentials for core electron of Pd and the 6-31G(d) basis sets for other atoms. Single-point calculations were performed, using better basis set system, in which two f polarization functions were added to Pd and 6-311G(d) basis sets were used for other atoms and a set of diffuse functions was added to anionic N and O atom of NO₂ group. All discussions were presented based on the Gibbs energy, where the translation entropy in solution was corrected by the method of Whiteside et al.^[2]

[Results and Discussion]

The oxidative addition of nitrobenzene to $\text{Pd}^0(\text{BrettPhos})$ occurs with the Gibbs activation energy (ΔG^{\ddagger}) of 30.3 kcal/mol and the Gibbs reaction energy (ΔG°) of -2.1 kcal/mol, as shown in Figure 1, indicating that the oxidative addition of nitrobenzene is moderately exergonic that needs large Gibbs activation energy. In the transition state of this reaction, charge transfer (CT) occurs from the d_π MO of $\text{Pd}^0(\text{BrettPhos})$ to the $\sigma^*+\pi^*$ mixing MO (LUMO) of nitrobenzene. In the case of $\text{Pd}^0(\text{PMe}_3)_2$, the oxidative addition of nitrobenzene is also exergonic, while the adduct, transition state, and product are less stable than those of $\text{Pd}^0(\text{BrettPhos})$ because $\text{Pd}(\text{PMe}_3)_2$ distorts very much in the adduct, transition state, and product to give rise to very large destabilization energy compare to $\text{Pd}^0(\text{BrettPhos})$. As a results, the TSc is much more unstable than the sum of reactants ($\text{Pd}(\text{PMe}_3)_2$ and nitrobenzene), which is not favorable for the reaction because the dissociation of nitrobenzene occurs more easily than the oxidative addition. In the case of $\text{Pd}^0(\text{BrettPhos-I})$, the reaction is endergonic, because the d_π orbital of $\text{Pd}^0(\text{BrettPhos-I})$ is at a lower energy than that of $\text{Pd}^0(\text{BrettPhos})$ and the CT from Pd to nitrobenzene becomes weaker. These results indicate that BrettPhos is a good ligand for the Ph-NO₂ bond activation $\text{Pd}^0(\text{BrettPhos})$ has a d_π orbital at high energy to form good CT to nitrobenzene.

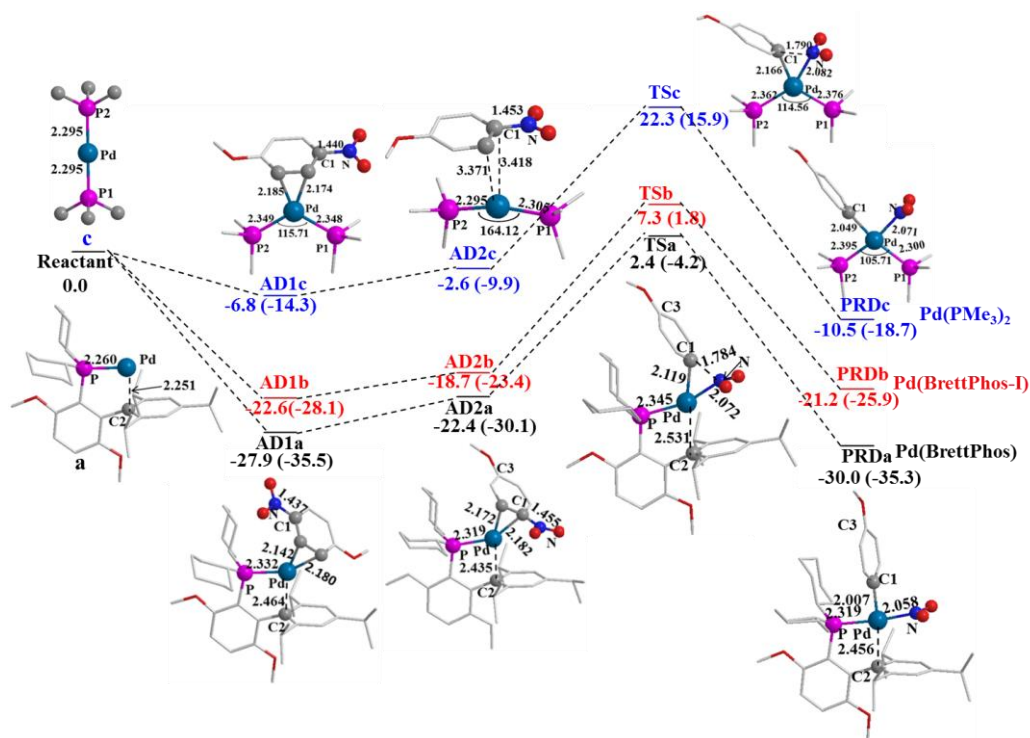


Figure 1. Geometry and energy change in the oxidative addition of nitrobenzene to $\text{Pd}^0(\text{BrettPhos})$, $\text{Pd}^0(\text{PMe}_3)_2$, and $\text{Pd}^0(\text{BrettPhos-I})$.

[References]

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