The Mechanism of the Enantioselective Tsuji Allylation Reaction

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Abstract

A proposed mechanism rationalizing the unique performance of the Tsuji-Allylation reaction with a non-prochiral allyl group was determined with density functional theory. Calculations suggest a distinct preference to an internal nucleophilic attack followed by interconversion from a 5-coodinate Pd complex to a 4-coordinate complex compared to non-enantioselective external nucleophilic attack. Non-rate determining reductive elimination proceeds in a non-traditional manner generating the formation of the product and a Pd$^0$ complex.

$$\Delta G^\ddagger = 3.3 \text{ kcal/mol in vacuum}$$
$$\Delta G^\ddagger = 3.0 \text{ kcal/mol in benzene}$$
$$\Delta G^\ddagger = 2.7 \text{ kcal/mol in THF}$$

$$\Delta G^\ddagger = 6.8 \text{ kcal/mol in vacuum}$$
$$\Delta G^\ddagger = 5.4 \text{ kcal/mol in benzene}$$
$$\Delta G^\ddagger = 4.2 \text{ kcal/mol in THF}$$