

Computational Analysis of the Mechanism for C-H activation by a Fe(dmpe)₂ Complex

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C-H activation refers to the cleavage of hydrogen from a C-H bond followed by the formation of a bond between the carbon atom and a new functional group. C-H activation's ability to alter specific bonds to modify entire molecules provides an opportunity to streamline functionalization for chemical synthesis. However, low polarity, large bond strength, and low site selectivity due to the ubiquitous nature of C-H bonds can make activation difficult to achieve. Many early examples of C-H activation use precious noble metal catalysts due to predictable reactivities and single-spin surfaces. However, these metals are often too expensive or wasteful for widespread use. Earth-abundant transition metals such as Iron can provide a cheaper and less toxic alternative to precious noble metal catalysts. However, they are more difficult to study than their noble metal counterparts due to their many oxidation states and multiple spin surfaces. In turn, computational research can provide a valuable analytical tool for C-H activation using transition metal complexes to expand their use and efficacy.

This research analyzed a proposed mechanism involving an Fe(dmpe)₂ [dmpe = 1, 2-bis(dimethylphosphino)ethane] intermediate in a synthetically characterized C-H activation reaction. The proposed mechanism for this reaction begins with an Fe(II) dihydride reactant undergoing photolysis to form the proposed coordinatively unsaturated Fe(0) intermediate with a ground triplet state. When in a cyclopentene substrate, the intermediate then undergoes spin crossover (SCO) to enter a singlet excited state before undergoing the process of oxidative addition, in which C-H activation of the complex occurs to form the reactions cis product, which later isomerizes to the trans product while remaining in the singlet state (1). Computational methods including density functional theory and coupled cluster calculations were used to model the transition from the proposed intermediate to the cis-product, particularly the SCO step from the high spin ground state to an excited singlet state, as the short lifespan of the reaction's transition state means it can not be characterized synthetically.

Via the computational calculations of the proposed intermediate's electronic structure, this research found a predicted triplet to singlet energy gap of the proposed Fe intermediate, providing insight into the reactivity and thermal accessibility of the proposed mechanism as SCO must proceed for C-H activation to occur. With DLPNO-CCSD(T) as the computational methodology, it was found that the singlet to triplet energy gap of the intermediate is 14.40 kcal/mol. This result closely aligns with experimental data where the spin state gap was 14.80 kcal/mol, with the slight discrepancy between the two likely due to the benchmark data not including solvation effects (done in the gas phase) in its computation (1). This result is significant as it provides further evidence supporting the studied reaction's proposed mechanism by confirming that spin crossover is accessible and the proceeding C-H activation step may occur. Future work on this project includes characterizing the transition state geometry and energy of this mechanism to produce a complete reaction coordinate diagram. From there, this mechanism can be further investigated by comparing other possible substrates used in the reaction, such as benzene, as well as other possible mechanisms to most accurately describe the process of this reaction.

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References

1. Harvey, Jeremy N., and Rinaldo Poli. "Computational Study of the Spin-Forbidden H₂ Oxidative Addition to 16-Electron Fe(0) Complexes." *Dalton Transactions*, no. 21, Oct. 2003, pp. 4100-06. pubs.rsc.org, <https://doi.org/10.1039/B302916F>.