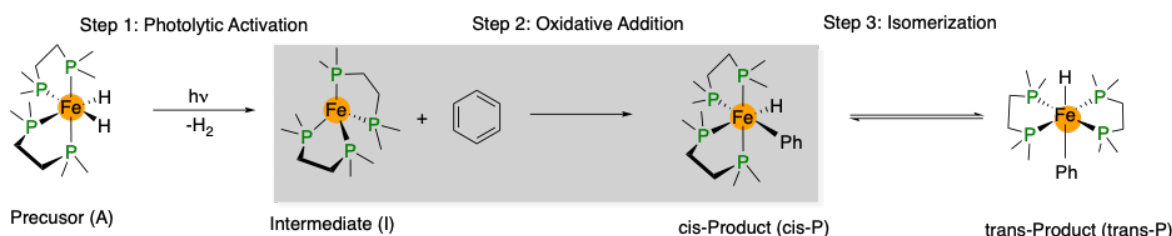


## Computational Investigation of C–H Activation by Fe(dmpe)<sub>2</sub> Dana Zhao, Class of 2026

C–H activation is considered a “Holy Grail” in chemistry<sup>1</sup>. It allows for a direct and efficient way to functionalize C–H bonds in comparison to traditional methods. Traditional methods may require the use of pre-activated/pre-functionalized starting materials, making the process of modifying a molecule less step-economical and more waste-heavy<sup>1</sup>. C–H activation offers a way for sustainable chemistry.

C–H bonds are nonpolar, covalent bonds, with a large bond dissociation free energy<sup>1</sup>. The strong, non-polar nature of a C–H bond results in low reactivity. Therefore, the activation of C–H bonds often requires reactive species or catalytic systems to facilitate bond cleavage. Typically, transition metal complexes, such as the Fe(dmpe)<sub>2</sub> complex we are studying, are used as the reactive species to facilitate C–H bond activation.



The reaction we are studying is first proposed by Field et al<sup>2,3</sup>, who were able to synthetically characterize some aspects of the reaction, namely the precursor (A) and product (cis-P and trans-P). They have not been able to use experimental techniques such as NMR spectroscopy to characterize the intermediate because of the intermediate’s short lifespan and the rate the oxidative addition step of the reaction can rapidly occur. Due to experimental limitations, we employed computational methods to gain insight and explore the potential mechanisms for C–H activation for these complexes.

In our computational study, we used three DFT (Density Functional Theory) functionals, TPSS, PW6B95, and TPSSh, along with the wavefunction method DLPNO-CCSD(T), to perform various calculations on the oxidative addition step of Fe(dmpe)<sub>2</sub> intermediate and benzene substrate to cis-product reaction. The results were benchmarked with Harvey et al<sup>4</sup> results.

Functionals	Spin State Energy Gap	Minimum Energy Crossing Point	Sigma Complex Energy	Transition State Energy	Cis-Product Energy
TPSS	6.55	5.37	6.52	18.29	-10.08
PW6B95	9.91	17.69	–	–	-0.99
TPSSh	12.28	10.96	12.12	24.98	-6.65
CCSD(T)	14.35	14.97	16.22	31.39	-6.15

Figure 1: Energies in kcal/mol computed by using TPSS, PW6B95, TPSSh, and CCSD(T) functionals.

**Faculty Mentor: Sean Lutz**

**Funded by the Littlefield Summer Research Fellowship**

### References

- (1) Roudesly, F.; Oble, J.; Poli, G. Metal-Catalyzed CH Activation/Functionalization: The Fundamentals. *J. Mol. Catal. Chem.* 2017, *426*, 275–296. <https://doi.org/10.1016/j.molcata.2016.06.020>.
- (2) Baker, M. V.; Field, L. D. Reaction of Ethylene with a Coordinatively Unsaturated Iron Complex Fe(DEPE)<sub>2</sub>: Sp<sup>2</sup> Carbon-Hydrogen Bond Activation without Prior Formation of a  $\pi$ -Complex. *J. Am. Chem. Soc.* 1986, *108* (23), 7436–7438. <https://doi.org/10.1021/ja00283a065>.
- (3) Whittlesey, M. K.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Field, L. D.; Wilkinson, M. P.; George, M. W. Transient and Matrix Photochemistry of Fe(Dmpe)<sub>2</sub>H<sub>2</sub> (Dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>): Dynamics of C-H and H-H Activation. *J. Am. Chem. Soc.* 1993, *115* (19), 8627–8637. <https://doi.org/10.1021/ja00072a016>.
- (4) Harvey, J. N.; Poli, R. Computational Study of the Spin-Forbidden H<sub>2</sub> Oxidative Addition to 16-Electron Fe(0) Complexes. *Dalton Trans.* 2003, No. 21, 4100–4106. <https://doi.org/10.1039/B302916F>.