

Spin-Forbidden Reactions and Iron Complexes.

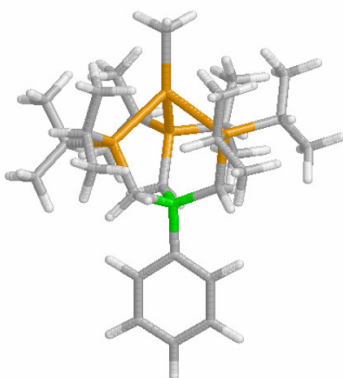
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The reactions named Spin-Forbidden are those in which a change in spin state takes place during the reaction. A typical case of spin forbidden reaction involves a reactant with one spin state and a product with another. The study of this type of reaction requires accurate calculations on the different spin state potential energy surfaces, and localization of the crossing points between them.¹

[Fe]-CH₃ ([Fe]= [PhB(CH₂PⁱPr₂)₃]Fe) has been shown to be a pre-catalyst for the room-temperature hydrogenation of unsaturated hydrocarbons.² Experiments suggested that the corresponding [Fe]-H species was the active catalyst.

The computational work presented here is aimed at the understanding catalyst [Fe]-H formation from the pre-catalyst [Fe]-CH₃. Both species have quintet ground states. However, the intermediates formed from addition of H₂ to [Fe]-CH₃ have triplet ground states, so that catalyst formation is a doubly spin-forbidden process, in which the reactants and products have one spin-state, while the intermediates have another.



This study has been challenging due to the size of the system (the pre-catalyst is shown above), and the need to explore three different potential surfaces, singlet, triplet and quintet. Also, the accuracy of the computational DFT approach used to characterize the potential energy surfaces required extensive calibration.

References

1. Harvey, J. N. *Phys. Chem. Chem. Phys.* **2007**, 9(3), 331-343.
2. Daida, E. J.; Peters, C. P. *Inorg. Chem.* **2004**, 43, 7474-7485.

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