

How Lewis Acids Catalyze Diels-Alder Reactions

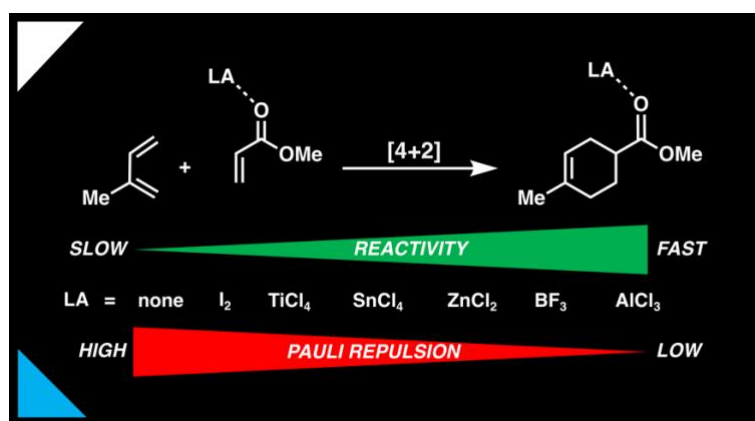
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Lewis acids (LA) are efficient catalysts of various organic reactions. Numerous studies have claimed that the origin of LA catalysis stems from the strong donor-acceptor interaction between the LA and one of the reactants, which, results in a significant stabilization of the LUMO of that reactant and, therefore, a smaller HOMO–LUMO energy gap.^[1] Recently, however, Hamlin *et al.* exhibited that LAs do not catalyze Michael addition reactions by decreasing the HOMO–LUMO energy gap, but, instead, by reducing the (steric) Pauli repulsion between the filled orbitals of the nucleophile and Michael acceptor.^[2] During this talk, it will become clear that this *Pauli repulsion-lowering catalysis* is not only restricted to the Michael addition reaction, but is actually a more general phenomenon.^[3] The textbook LA-catalyzed Diels-Alder reactions is one of the reactions that follow this electronic mechanism. Due to the presence of the catalytic LA, the (steric) Pauli repulsion between the diene and dienophile gets diminished, resulting in a lowering of the reaction barrier.



- [1] I. Fleming, *Molecular Orbitals and Organic Chemical Reactions*, Wiley, New Jersey, 2009.
[2] T. A. Hamlin, I. Fernández, F. M. Bickelhaupt, *Angew. Chem.* **2020**, *132*, 6260; *Angew. Chem. Int. Ed.* **2020**, *59*, 6201.
[3] a) P. Vermeeren, T. A. Hamlin, I. Fernández, F. M. Bickelhaupt, *Angew. Chem. Int. Ed.* **2020**, *59*, 6201. b) P. Vermeeren, T. A. Hamlin, I. Fernández, F. M. Bickelhaupt, *Chem. Sci.* **2020**, *11*, 8105. c) P. Vermeeren, F. Brinkhuis, T. A. Hamlin, F. M. Bickelhaupt, *Chem. Asian J.* **2020**, *15*, 1167. d) T. Hansen, P. Vermeeren, R. Yoshisada, D. V. Filippov, G. A. van der Marel, J. D. C. Codée, T. A. Hamlin, *J. Org. Chem.* **2021**, *86*, 3565.