Is Your Mechanism Correct?
Insights into Hydrogenation and Carboxylation Reactions

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Computational methods are increasingly applied to investigate reaction pathways. However, the proposed mechanisms are not always sufficiently validated. I will discuss the state-of-the-art in DFT modelling of metal-catalyzed reactions and show approaches to validate computationally proposed pathways.[1,2] Examples from two areas of organometallic catalysis are included: 1) **Hydrogenation**. In particular, recent insights into Co-catalyzed hydrogenation are discussed, where a mechanism proposed by us explains the experimental substrate preferences,[2] and 2) **CO_2 incorporation**. C-CO_2 bond formations with late transition metal complexes (e.g. Rh, Ni, Pd, and Cu) are discussed,[3,5] alongside a novel base-mediated reaction developed in our laboratory.[4] Based on our computational work, we propose trends as to when metal-CO_2 interactions should be expected during C-CO_2 bond formation.

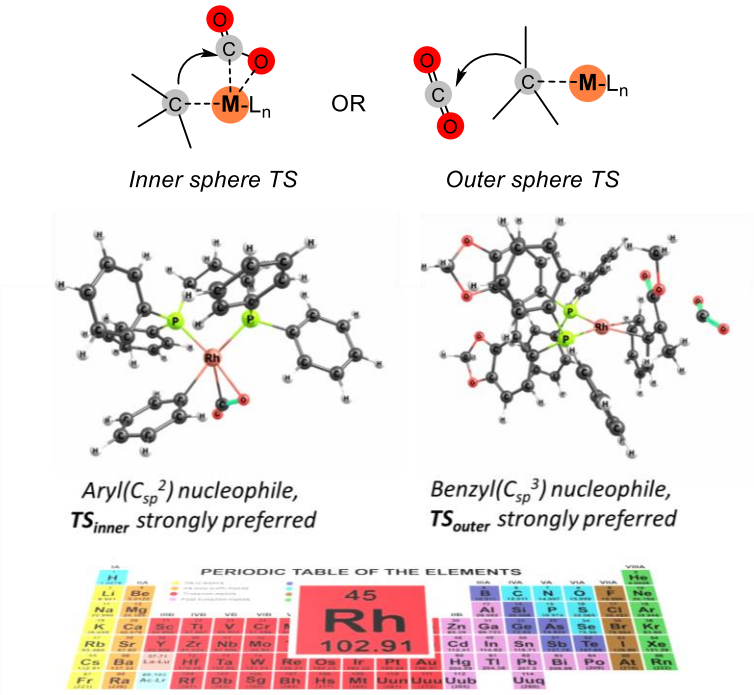

Figure 1. ***To bind or not to bind:*** *we present trends as to when metal-CO_2 interactions should be expected for C-CO_2 bond formation.*[3-5]

[1] Morello, G. R.; Hopmann, K. H. *A dihydride mechanism can explain the intriguing substrate selectivity of iron-PNP-mediated hydrogenation*, *ACS Catal.* **2017**, *7*, 5847.
[2] Morello, G. R.; Zhong, H.; Chirik, P. J.; Hopmann, K. H., *Cobalt-catalysed alkene hydrogenation: A metallacycle can explain the hydroxyl activating effect and the diastereoselectivity*, *Chem. Sci.* **2018**, *9*, 4977.
[3] Pavlovic, L.; Vaitla, J.; Bayer, A.; Hopmann, K.H. *Rhodium-catalyzed hydrocarboxylation: Mechanistic analysis reveals unusual transition state for C-C bond formation*, *Organometallics* **2018**, *37*, 941.
[4] Gevorgyan, A.; Obst, M. F.; Maseras, F.; Hopmann, K. H., Bayer, A., *Transition metal-free hydrocarboxylation of olefins: Scope and mechanistic insights*, *Submitted* **2019**.
[5] Garcia-Lopez, D.; Obst, M. F.; Pavlovic, Lj.; Nova, A.; Cascella, M.; Hopmann, K. H. *In preparation*.