

Role of Acid Additives in the C–H Bond Activation by Palladium(II) Acetate

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Palladium-mediated carbon–hydrogen (C–H) bond activation is a well-established transformation that plays a central role in metal-catalyzed functionalization of organic compounds, both in solution and in the solid state [1]. Studies suggest that acids promote the activation by palladium(II) acetate ($\text{Pd}(\text{OAc})_2$) *via* activating the $\text{Pd}(\text{OAc})_2$ trimer and facilitating anion exchange at the palladium center [2]. Since our group reported the first solid-state C–H bond activation in 2014 [3], our research was expanded to the solid-state functionalization of organic molecules and the effects of different palladium sources, as well as the roles of basic and acidic additives, on the reaction course in the solid state [4].

Here, we present a computational rationalization of the influence of acidic additives on azobenzene C–H bond activation by $\text{Pd}(\text{OAc})_2$. By combining experimental and computational approaches, we correlate the pK_a values of the employed acids (Figure 1) with the reaction outcome, highlighting the critical role of acid strength in promoting $\text{Pd}(\text{OAc})_2$ trimer dissociation and accelerating C–H bond cleavage.

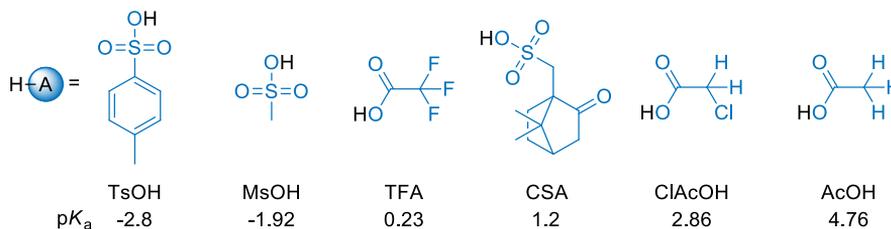


Figure 1. Acids used as additives in azobenzene C–H bond activation by $\text{Pd}(\text{OAc})_2$

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