

DINICKEL OXIDATIVE ADDITION COMPLEXES IN C–O CLEAVAGE: RELEVANCE IN CATALYTIC C–Si BOND-FORMATION

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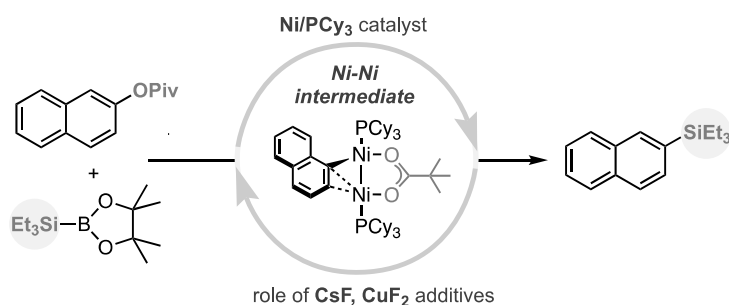
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Nickel catalysis has been key to the development of phenol-derived compounds into widely available substrates for cross-coupling, hydrogenolysis, and carbon-heteroatom bond-forming reactions.[1] However, the mechanisms of many Csp^2 -O functionalization reactions remain unclear, particularly those with monodentate phosphines such as the Ni-catalyzed silylation of C–OPiv bonds reported by Martin.[2]

Herein, we report an experimental and computational investigation into the mechanism of the nickel-catalyzed silylation of aryl pivalates with monodentate PCy_3 . [3] Specifically, we have found that oxidative addition of Ni(0)/ PCy_3 to C–OPiv bonds forms complexes with a Ni–Ni bond, and that these dinickel complexes release the active monometallic species by disproportionation. Additionally, we have unraveled the effect of the fluoride-containing additives on the transformation.



[1] a) J. Cornella, C. Zarate, R. Martin, *Chem. Soc. Rev.* **2014**, 8081-8097. b) M. Tobisu, N. Chatani, *Acc. Chem. Res.* **2015**, 1717-1726.

[2] C. Zarate, R. Martin, *J. Am. Chem. Soc.* **2014**, 2236-2239.

[3] R. J. Somerville, L. V. A. Hale, E. Gómez-Bengoña, J. Burés, R. Martín, *J. Am. Chem. Soc.*, **2018**, 8771–8780.