Nickel-Catalyzed Kumada Vinylation of Enol Phosphates: A Comparative Mechanistic Study

Philippe-Alexandre Poisson, Gaël Tran, Céline Besnard, Cleément Mazet*

Department of Organic Chemistry, University of Geneva 30 Quai Ernest Ansermet, 1211 Geneva, Switzerland philippe.poisson@unige.ch

In 2018, our group reported a catalytic method for the synthesis of diversely 2-substituted 1,3-dienes. ¹⁻³ This methodology relies on the use of two complementary biphosphine-nickel complexes – $[(dppe)NiCl_2]$ and $[(dmpe)NiCl_2]$ – for the cross-coupling between vinyl Grignard reagents and enol phosphates.

Based on supporting stoichiometric organometallic syntheses, structural analyses, reaction monitoring, radical-clock experiments and kinetic investigations, a comparative mechanistic study between the two precatalysts has been conducted. We demonstrate that the two bisphosphine-nickel complexes operate via distinct Ni(0)/Ni(II) catalytic manifolds.

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