

ORGANIC SEMINAR

Dicobalt-catalyzed N=N coupling reactions of tertiary alkyl azides to form azoalkanes

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Abstract: Azoalkanes can serve as radical precursors for various catalytic and stoichiometric C–C bond-forming reactions. However, their use in these processes is hampered by the complexity of their synthesis, which often requires multiple steps and strong oxidants. Here, we report a direct denitrogenative dimerization of tertiary alkyl azides to form tertiary azoalkanes. The reaction uses a dicobalt catalyst, which is uniquely effective at performing this transformation relative to analogous monocobalt catalysts and an isostructural dinickel catalyst. Critical to the N=N coupling reactivity is the formation of a dicobalt imido intermediate that is resistant to undergoing competing H-atom abstraction. The catalytic N=N coupling provides access to a broad scope of tertiary azoalkanes, and the resulting products can be used to form hindered C–C bonds between quaternary carbons.



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