

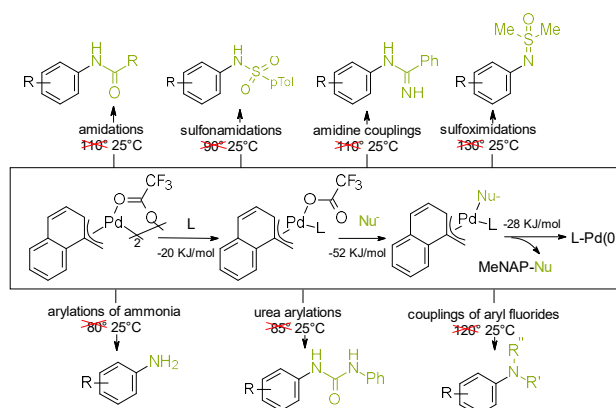
MeNAP Dimers as Versatile Precatalysts for Palladium Catalyzed Cross-Coupling Reactions

Prof. Dr. Lukas J. Gooßen*¹

¹Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Universitätsstr. 150,
44801 Bochum, Germany

E-mail: lukas.goossen@rub.de

Palladium-catalyzed cross-coupling reactions are indispensable tools in modern synthetic chemistry.¹ However, the continuously increasing steric demand of contemporary ligand architectures has created a growing mismatch with traditional palladium precursors, making catalyst activation a decisive yet often overlooked limitation. Here, we present halogen- and trifluoroacetate-bridged methylnaphthyl (MeNAP) palladium dimers as highly effective precatalysts.² These bench-stable, highly soluble complexes rapidly react with phosphine or carbene ligands with formation of monoligated palladium species, regardless of the ligand bulk. Upon treatment with nucleophiles, active Pd(0) species are cleanly formed within minutes by reductively eliminating inert naphthalene derivatives. Catalysts generated in situ from MeNAP precursors exhibit excellent performance across numerous C–C, C–N, and C–O bond-forming reactions and are particularly effective in couplings of weak nucleophiles.^[3]



They promote couplings of aryl chlorides with amides, sulfoximines, carbamates, sulfonamides, amidines, ureas, cyclopropylamines, trifluoroethylamines and many other substrate classes at record-setting low temperatures. The mild conditions improve functional-group tolerance and compatibility with coordinating heterocycles. MeNAP systems even promote catalytic couplings of aryl fluorides at room temperature.^{4,5} Their air and water stability, combined with high solubility, make MeNAP dimers ideal palladium sources for numerous applications ranging from automated microscale screenings to industrial syntheses.

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