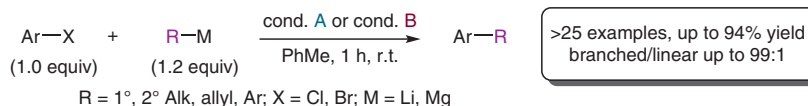


T. SCHERPF, H. STEINERT, A. GROßJOHANN, K. DILCHERT, J. TAPPEN, I. RODSTEIN, V. H. GESSNER* (RUHR-UNIVERSITÄT BOCHUM, GERMANY)
Efficient Pd-Catalyzed Direct Coupling of Aryl Chlorides with Alkylolithium Reagents
Angew. Chem. Int. Ed. **2020**, DOI: 10.1002/anie.202008866.

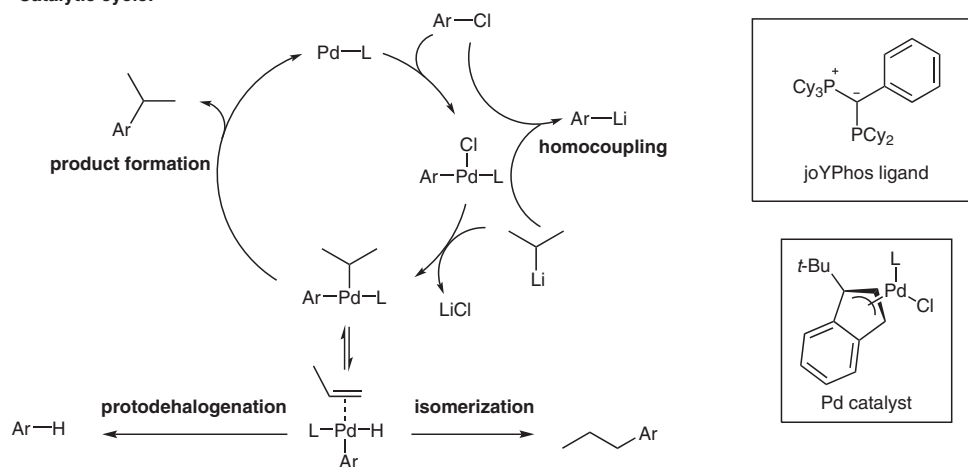
Palladium-Catalyzed Cross-Couplings of Alkylolithiums with Aryl Chlorides



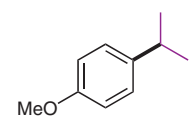
>25 examples, up to 94% yield
branched/linear up to 99:1

cond. A: joYPhos ligand (3 mol%), Pd₂(dba)₃·dba (1.5 mol%) or cond. B: joYPhos ligand and Pd catalyst (3 mol%)

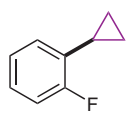
Catalytic cycle:



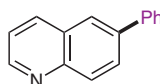
Selected examples:



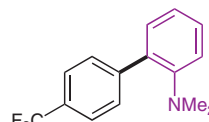
cond. A
71% yield (br/li = 95:5)
X = Cl, M = Li



cond. B
88% yield
X = Cl, M = Li



cond. A
81% yield
X = Cl, M = Li



cond. B
91% yield
X = Cl, M = Li

Significance: Gessner and co-workers report the palladium-catalyzed cross-coupling of aryl chlorides with alkylolithium reagents under mild conditions in good to excellent yields. Furthermore, gram-scale reactions were performed, demonstrating the scalability of this protocol.

Comment: The authors performed extensive screening and discovered a suitable catalyst based on ylide-substituted phosphines which gave good selectivities combined with high yields, preventing several undesired side-reactions such as homocoupling, isomerization or protodehalogenation. In addition, the catalyst proved to be successful for Kumada type cross-couplings.

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