Oxidative Coupling Reactions of Grignard Reagents with Nitrous Oxide *Angew. Chem. Int. Ed.* **2013**, *52*, 6302–6305.

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Fe-, Co- and Cu-Catalyzed Coupling Reactions Using N₂O

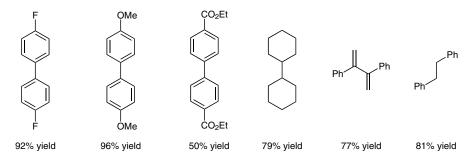
Oxidative homo-coupling of aryl, alkenyl and alkyl Grignard reagents:

$$\begin{array}{c} \text{metal salt (<1 mol\%)} \\ \text{N}_2\text{O} \\ \hline \text{2} \quad \text{R-MgX} \\ \hline \\ \text{THF, r.t.} \\ \text{up to 99\% yield} \end{array}$$

R = aryl, alkenyl and alkyl groups metal salt = for aryl and alkenyl coupling partners: $Fe(acac)_3$ or $CoCl_2$ for alkyl coupling partners: Li_2CuCl_4 X = Cl. Br

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Selected examples:



Example for the oxidative cross-coupling of Grignard reagents:

Significance: For the first time, N_2O ('laughing gas') is reported to undergo oxidative homo-coupling reactions of Grignard reagents in the presence of metal catalysts under mild reaction conditions. Whereas less than 1 mol% of Fe(acac)₃ and $CoCl_2$ showed to be superior in the homo-coupling reactions of arylmagnesium reagents, also alkyl Grignard reagents undergo oxidative homo-coupling reactions in the presence of Li_2CuCl_4 .

Comment: The authors applied this new protocol also to oxidative cross-coupling reactions between sp²- and sp³-hybridized Grignard reagents. Therefore, PhMgCl and various primary and secondary alkyl Grignard reagents furnish the desired aryl–alkyl cross-coupling products in 59–83% yield.

SYNFACTS Contributors: Paul Knochel, Andreas K. Steib Synfacts 2013, 9(9), 0991 Published online: 19.08.2013 **DOI:** 10.1055/s-0033-1339561; **Reg-No.:** P09413SF