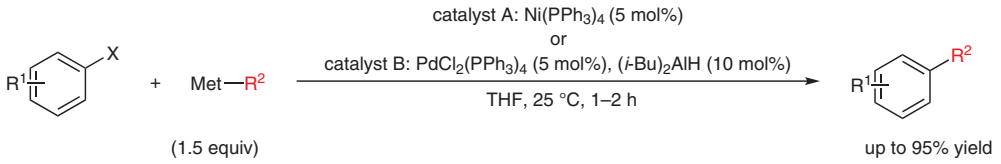
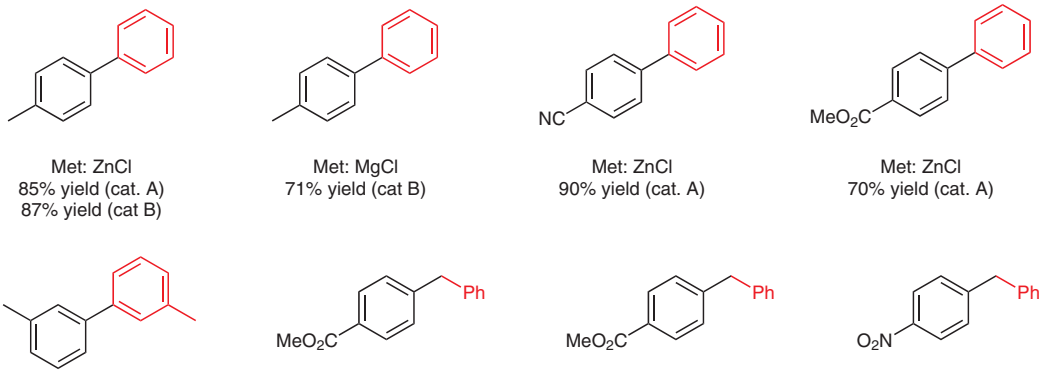
E. NEGISHI*, A. O. KING, N. OKUKADO (PURDUE UNIVERSITY, WEST LAFAYETTE, USA)
Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 3. A Highly Selective Synthesis of Unsymmetrical Biaryls and Diarylmethanes by the Nickel- or Palladium-Catalyzed Reaction of Aryl- and Benzylzinc Derivatives with Aryl Halides
J. Org. Chem. **1977**, *42*, 1821–1823.

The First Csp^2–Csp^2 Cross-Coupling Using Organozinc Reagents



R^1 = various functional moieties
R^2 = Ar, Bn
X = I, Br
Met = Zn, Mg, Al

Selected examples:



Met: ZnCl
85% yield (cat. A)
87% yield (cat B)

Met: MgCl
71% yield (cat B)

Met: ZnCl
90% yield (cat. A)

Met: ZnCl
70% yield (cat. A)

Met: ZnCl
95% yield (cat. A)

Met: ZnCl
85% yield (cat. A)

Met: MgCl
12% yield (cat. A)

Met: ZnCl
88% yield (cat. B)

Significance: In 1977, Negishi and co-workers described the first transition-metal-catalyzed cross-coupling using aryl- and benzylzinc reagents with substituted aryl halides. Two catalytic systems using either nickel or palladium salts in combination with PPh_3 were developed leading to the coupling products in high yields.

Comment: In comparison to the corresponding magnesium-based organometallics, the use of organozinc species enables the coupling of aryl halides bearing sensitive functional moieties, such as ester, nitrile, or even nitro groups. Due to the low toxicity of organozinc reagents, and the mild conditions required for the cross-coupling, their application in academic and industrial research remains a growing field.

Review: D. Haas, J. M. Hammann, R. Greiner, P. Knochel *ACS Catal.* **2016**, *6*, 1540–1552.

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