## Category

Metal-Mediated Synthesis

## Key words

palladium

zinc

PEPPSI

organcozinc reagents M. POMPEO, R. D. J. FROESE, N. HADEI, M. G. ORGAN\* (YORK UNIVERSITY, TORONTO, CANADA)

Pd-PEPPSI-IPent<sup>Cl</sup>: A Highly Effective Catalyst for the Selective Cross-Coupling of Secondary Organozinc Reagents *Angew. Chem. Int. Ed.* **2012**, *51*, 11354–11357.

## Pd-PEPPSI-IPent<sup>Cl</sup> – Selective Coupling of Secondary Organozinc Nucleophiles

Ar = Ar, O- and N-HetAr

 $R^1$  = Me, Et

 $R^2$  = Et, alkenyl, *n*-Pr

 $R^1 + R^2 = Boc-protected piperidine$ 

X = Br, Cl, OTf

## Selected examples:

**Significance:** The authors report the new catalyst Pd-PEPPSI-IPent<sup>Cl</sup>, which highly efficiently couples secondary alkylzinc reagents to (hetero)aryl bromides, chlorides and triflates. The corresponding alkylated aromatics are obtained in excellent yield and with high regioselectivity.

Comment:  $\beta$ -Hydride elimination (BHE) constitutes one of the main drawbacks for the crosscoupling of secondary alkyl reagents, especially if they react with electron-rich coupling partners. These problems are overcome by the new palladium-catalyst, which bears bulkier substituents and additionally, is characterized by a decreased electron density, thus favoring reductive elimination instead of BHE. Density functional theory (DFT) calculations support the theoretical selectivities.

up to >99:1 n/r (normal to rearranged product)

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