Pd-PEPPSI-IPent\textsuperscript{Cl} – Selective Coupling of Secondary Organozinc Nucleophiles

**Significance:** The authors report the new catalyst Pd-PEPPSI-IPent\textsuperscript{Cl}, 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 cross-coupling 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.

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**Selected examples:**

- **99% yield**
  - n/r > 99:1
  - \(\text{Ar} = \text{Ar, O- and N-HetAr}\)
  - \(\text{R}_1^1 + \text{R}_2^2 = \text{Boc-protected piperidine}\)
  - \(\text{X} = \text{Br, Cl, OTf}\)

- **85% yield**
  - n/r = 49:1
  - \(\text{Ar} = \text{Ar, O- and N-HetAr}\)
  - \(\text{R}_1^1 + \text{R}_2^2 = \text{Boc-protected piperidine}\)
  - \(\text{X} = \text{Br, Cl, OTf}\)

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  - \(\text{Ar} = \text{Ar, O- and N-HetAr}\)
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- **84% yield**
  - n/r > 99:1
  - \(\text{Ar} = \text{Ar, O- and N-HetAr}\)
  - \(\text{R}_1^1 + \text{R}_2^2 = \text{Boc-protected piperidine}\)
  - \(\text{X} = \text{Br, Cl, OTf}\)