Direct Cross-Coupling of Organoaluminum Reagents

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\text{R}_1 \text{AlMe}_2 \cdot \text{LiCl} \quad \begin{array}{c} \text{R}_2 \text{X} \\ \text{(2.5 equiv)} \end{array} \quad \text{THF, 110 °C, 24 h} \quad \text{R}_1 \text{R}_2 \quad \text{63–99% yield}
\]

R\text{\textsubscript{1}} = \text{Me}, \text{F}, \text{NMMe}_2, \text{OEt, CH}_2\text{OEt}
R\text{\textsubscript{2}} = \text{Ar, alkenyl, alkynyl}
X = \text{I, Br, Cl}

Significance: The authors report a direct cross-coupling of arylaluminum reagents and organic halides without an external catalyst. As the steric and electronic properties of functional groups on the aromatic ring had little influence of the reactivity, a variety of coupling products were obtained in high yields.

Comment: Interestingly, the reactions of aromatic iodides or bromides bearing a tosylate, triflate, or carbamate group did show high chemoselectivity, as the coupling only took place at the halide. Additionally, an ICP-MS analysis was performed to exclude traces of transition metals (level of 1 ppb).

Selected examples:

- \(\text{F} \quad 91\% \text{ yield} \quad X = \text{Br}\)
- \(\text{73\% yield} \quad X = \text{Cl}\) in THF–TMU (10:1), 130 °C
- \(\text{95\% yield} \quad X = \text{Br}\)
- \(\text{97\% yield} \quad X = \text{Br}\)

- \(\text{I} \quad 76\% \text{ yield} \quad X = \text{I}\)
- \(\text{Cl} \quad 68\% \text{ yield} \quad X = \text{Cl}\)
- \(\text{Cl} \quad 76\% \text{ yield} \quad X = \text{Cl}\)

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