

Hydrogenation and Borylation of Alkyl Chlorides using Zirconocene and Photoredox Catalysis

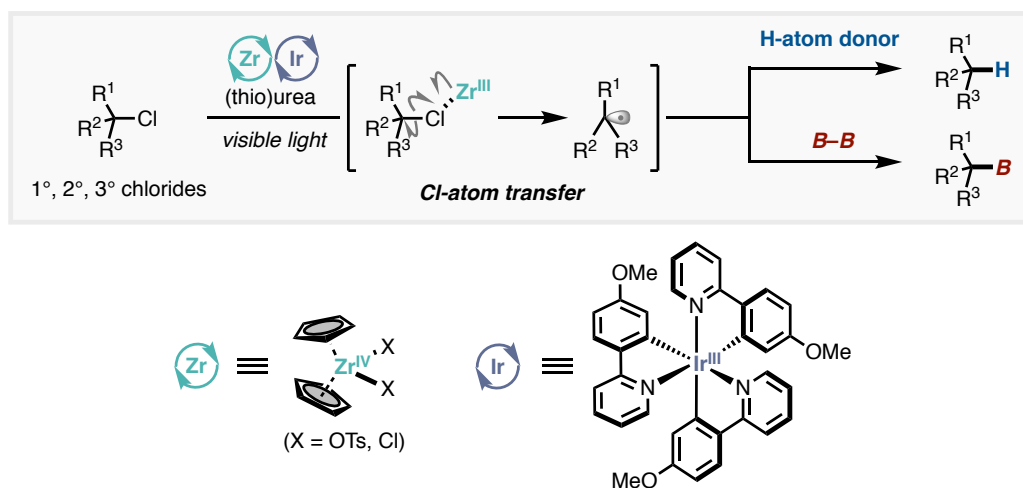
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Homolysis of C–Cl bond is one of the fundamental transformations generating alkyl radical intermediates from versatile and abundant alkyl chlorides. However, the C–Cl bond cleavage remains unexplored due to requirement of high negative potential and bond dissociation energy (BDE) compared with alkyl bromides and alkyl iodides. Although synthetically useful approaches utilizing stoichiometric metal reductants,^{1a} titanocene,^{1b} and photoredox catalyst^{1c,1d} can activate alkyl chlorides, some drawbacks remain such as requiring strong reductants, heating with high temperature, and lack of substrate generality.

Herein, we have developed a C–Cl bond cleavage of alkyl chlorides using zirconocene and photoredox catalysts. Catalytically generated zirconocene(III)² enabled chlorine atom transfer from an alkyl chloride to furnish a corresponding alkyl radical. The resulting radical successfully underwent hydrogenation or borylation by employing hydrogen atom donor or diboron as radical trapping agents. These reactions are facilitated by the addition of (thio)urea as a co-catalyst. This reaction has been applied to various alkyl chlorides including derivatives of natural products and medicinal agents under mild conditions.



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