Development and Mechanistic Studies of Iridium-Catalyzed Oxidative C–H Arylation Reactions

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The high reactivity of half-sandwich iridium(III)-complexes toward C–H bond cleavage has attracted an intensive attention of chemists. As a result, a number of catalytic C–H functionalization strategies have been developed based on the iridium catalyst system. Despite this significant progress, however, the most of the reported catalytic procedures have been largely limited to C–N bond formation. In this regard, we have been focusing on the development of iridium(III)-catalyzed C–C bond forming reactions, especially, oxidative C–H arylation reactions. Specifically, we developed Cp*Ir(III)-catalyzed mild and external oxidant free $C(sp^2)$ –H arylation using aryldiazonium salts, which act as an aryl precursor and also as an oxidant via C–N₂ bond cleavage. Mechanistic studies revealed that the reaction proceeds via the formation of an Ir(V)-aryl intermediate. In addition, we also discovered Cp*Ir(III)-catalyzed oxidative C(sp²)–H arylation with arylsilanes. Mechanistic investigations, including CV, EPR, and DFT studies, disclosed that the catalytic cycle involves the generation of an Ir(IV)-aryl intermediate.



Reference

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