

The Synthesis of Organoboronic Compounds by C-H Activation of Alkanes and Arenes

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Alkanes, although one of the most abundant chemical feedstocks, are relatively unreactive. A process that could directly convert alkanes into terminally functionalized compounds would be of great synthetic value. A series of ruthenium complexes has been found that selectively borylates alkanes terminally, yielding α -alkylboronic esters in excellent yields. It has been shown that these complexes will also borylate the least sterically hindered terminal methyl group both in branched alkanes and in substrates that contain heteroatoms, including ethers, fluoroalkanes, and amines.

Arene functionalization through C-H activation is more developed compared to the alkane borylation chemistry. Development of a mild, efficient, and regioselective iridium-catalyzed arene borylation system has allowed access to 3,5-disubstituted arylboronic esters in excellent yields starting from the corresponding arene. Other than Ir-catalyzed C-H activation methodologies, aryl boronic esters can be prepared by the dehydration of boronic acids and alcohols or through Pd-coupling chemistry. The Ir-catalyzed methodology has led to an alternative synthesis of 3,5-disubstituted arylboronic acids that does not rely on the production and subsequent quenching of a Grignard reagent with $B(OR)_3$, followed by hydrolysis to yield the desired boronic acid. Aryl trifluoroborates are usually produced from the corresponding aryl boronic acids. The borylation of arenes is synthetically valuable because arylboronic compounds are important synthetic reagents that participate in many transformations including etherifications, rhodium-catalyzed 1,2- and 1,4- additions to aldehydes, and Miyaura-Suzuki reactions. Aryl boronic acids and aryl trifluoroborates are more reactive towards addition and coupling reactions compared to the aryl boronic esters. Methodologies to convert arenes to either arylboronic acids or potassium aryl trifluoroborates using a one-pot synthesis have been developed and the scope of these transformations has been investigated.

