Nickel-Catalyzed Cyclopropanation of Unactivated Olefins

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Cyclopropanes have always been an appealing synthetic building block for any organic chemist. New Cyclopropanation methods have been investigated intensely through the last decades in order to avoid inorganic waste (Simmons-Smith reaction) and/or highly toxic chemicals (diazo-compounds)[1-6].
Our group proposed a Nickel-catalyzed cyclopropanation method of unactivated olefins using tetramethylammonium triflate as the methylene donor[7]. Compared to other catalytic systems (Pd/Pt, Zn, diazo-compounds) this proposed method makes use of cheap and abundant materials, making it safer and more atom economic. Good yields have been achieved by means of thorough mechanistic studies and reaction optimization, achieving now up to 75% yield for highly unactivated olefin (cyclooctene). It has been shown that the reaction can be performed using bench-stable reagents including the catalyst (excluding *n*-BuLi) giving similar yields than more cumbersome oxygen/temperature-sensitive Ni(0) sources.
Mechanistic studies showed that the catalyst retains its catalytic activity for several days after full consumption of tetramethylammonium triflate. Side reactions still seem to be a major problem in the reaction, consuming the methylene donor in a competitive reaction. Ongoing studies in order to reduce the side reaction (homocoupling) are taking place as well as parametrization efforts.

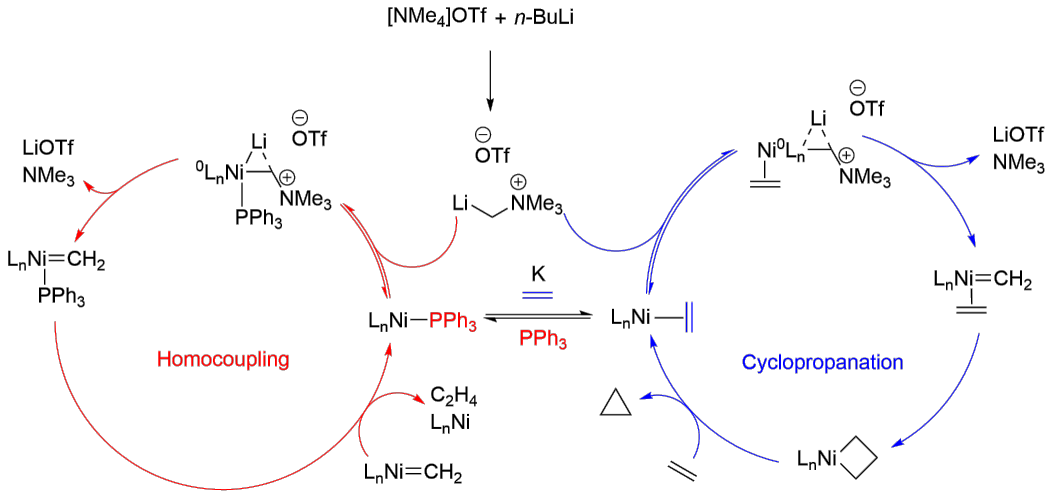


Figure 1: Cyclopropanation proposed catalytic cycle, involving Cyclopropanation (blue) and side reaction homocoupling (red).

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