

Abstract

In the present thesis, the catalytic behavior of iron(III) triflimide, $\text{Fe}(\text{NTf}_2)_3$ where ($\text{Tf} = \text{SO}_2\text{CF}_3$), have been studied for different hydroaddition reactions to alkenes and alkynes. This metal salt composed of a hard Lewis acid cation (Fe^{3+}) together with a weakly-coordinating and low nucleophile anion Tf_2N^- has displayed an excellent catalytic activity for the hydroaddition of C-C multiple bonds (alkenes and alkynes). In all these reactions the regioselectivity observed is good towards the benzylic positions (internal position of double bond in styrenes and of triple bond in phenylacetylenes).

The $\text{Fe}(\text{NTf}_2)_3$ synthesis is simple and straightforward, from the metathesis reaction between AgNTf_2 and FeCl_3 in 1,4-dioxane, and its formation and chemical nature was evaluated by ^{19}F and ^{15}N NMR spectroscopy studies, cyclic voltammetry experiments and UV-VIS and EPR spectroscopies. In principle, the presence of triflimide anions produces the iron LUMO stabilization (3d orbitals), which confers a higher electropositive character to Fe(III), thereby increasing Lewis acidity. Additionally, iron(III) triflimide presents a high-spin d^5 Fe(III) configuration having a semi-full 3d level. The studied reactions where iron(III) triflimide has been found as an active and selective catalyst are: 1) head-to-tail dimerisation of olefins for substituted styrenes, 2) regioselective Markovnikov hidrotiolación of styrenes for the synthesis of benzyl thioethers, and 3) regioselective Markovnikov hydration of alkynes to obtain ketones.

Iron(III) in the form of $\text{Fe}(\text{NTf}_2)_3$ can act as a catalytic substitute of gold(I) complex $\text{PPh}_3\text{AuNTf}_2$ without the requirement of an auxiliary ligand, for various regioselective hydroaddition reactions to alkenes and alkynes. *In situ* ^{19}F , ^{15}N and ^{31}P NMR spectroscopy show that, under specific reaction conditions (suitable temperature, reagents and solvents), the $\text{PPh}_3\text{AuNTf}_2$ complex is unstable and suffers a partial or total hydrolysis with the corresponding generation of triflimidic acid (HNTf_2) while $\text{Fe}(\text{NTf}_2)_3$ remains stable.