Since the discovery of Nozaki and Hiyama in 1977, who found that Cr(II) ion promotes chemoselective C-C coupling in aprotic solvents, extensive studies have been devoted to organochromium(III) reagents. These compounds are prepared by oxidative insertion of CrCl₂ into allyl, alkenyl, alkynyl, propargyl and aryl halides or sulfonates which are well behaved nucleophiles for highly selective organic transformations.

Recently, Fürstner has demonstrated that these reactions could be performed with a catalytic amount of CrCl₂ or CrCl₃. Chromium chloride reagent is commercially available and can be used without further purification. It is very hygroscopic, stable in dry air but oxidizes rapidly in the presence of oxygen. Anhydrous chromous chloride could be prepared by the reduction of CrCl₃ with LiAlH₄ or other suitable reducing agents.

Abstracts

Highly stereoselective synthesis of homoallylic alcohols have been carried out by the use of Nozaki-Hiyama reaction in the presence of the (R,R)-N,N'-bis(3,5-di-tert-butyl-salicylidene)-1,2-cyclohexanediamine (salen).

This important reaction has recently been extended to halogenated allylic substrates. This reaction provides a new route for the preparation of quaternary halogenated carbons.

The reaction of haloform with an aldehyde mediated by CrCl₂ leads to the formation of an E-configured halogenated double bond (Takai reaction). A geminal organodichromium species is expected to be the reactive intermediate.

Besides C-C bond formation, CrCl₂ can also mediate efficiently the protection of a plethora of alcohols as their corresponding 2-tetrahydrofuranyl ethers.

References and Notes