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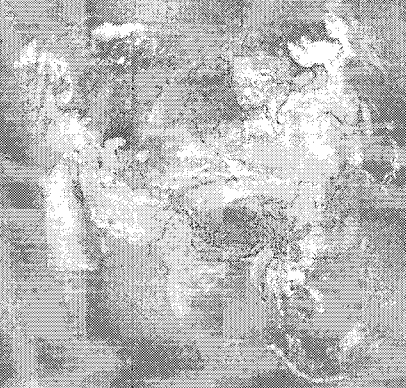

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Palladium(II)-catalyzed Suzuki–Miyaura Reactions of Arylboronic Acid with Aryl Halide in the Presence of Aryl-Ferrocenyl-Phosphines

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Abstract

This study examined investigation of catalytic activity of aryl-ferrocenyl-phosphine (2-methoxyphenyl diferrocenyl phosphine (cat. 1), 2-tert-butyloxyphenyl diferrocenyl phosphine (cat. 2), 2-methoxynaphtyl diferrocenyl phosphine (cat. 3), 1,1'-bis(diphenylphosphino) ferrocene (cat. 4), phenyl diferrocenyl phosphine (cat. 5)) ligands with palladium salts as precursors in Suzuki–Miyaura reaction. Suzuki–Miyaura reaction is one of the important cross-coupling reactions and extremely powerful in forming C–C bonds. Aryl-ferrocenyl-phosphine ligands confer unprecedented activity for these processes, allowing reactions to be performed at low catalyst levels, to prepare extremely hindered biaryls and to be carried out, in general, also for reactions of aryl chlorides by temperature 100 °C and pressure 1 atm. Sterically demanding and strongly Lewis-basic ferrocene-based phosphines are water- and oxygen-resistant. The Suzuki–Miyaura reaction is also an important reaction in the ground and fine organic synthesis, in the production of drugs and intermediates. To analyze the conversion of halogen aryl compounds the ^{1}H NMR spectroscopy was used. The advantage of Suzuki–Miyaura reaction in comparison with other cross-coupling reactions (Kumada-, Heck-, Heck-Carbonylation-, Murahashi-, Sonogashira-, Negishi-, Stille-reaktion, etc.) is in the usage of low toxic, water- and oxygen-insensitive thermostable organoboron compounds. As boronic acid was used phenylboronic acid and as weak base – potassium phosphate. Catalyst, precursor and weak base were dissolved in toluene. All reactions were performed under an atmosphere of nitrogen or argon. The catalytic cycle of Suzuki–Miyaura reaction typically includes three main steps: oxidative addition of the haloaromatic to catalytic active palladium (0) species, transmetalation, and reductive elimination of the product under back formation of catalytically active species. All used catalysts showed good activity with aryl bromides and weak activity with aryl chlorides.

Keywords: ferrocene, palladium catalysts, C,C-cross-coupling reactions, Suzuki–Miyaura reaction, homogeneous catalyses.

Introduction

Recently palladium catalysts and C,C-cross-coupling reactions find application in synthesis of various chemicals in pharmaceutical and electronic industry, in petrochemistry, in generation of liquid crystals [1], solar cells [2], etc. An example of such application is large–scale production of 2-cyano-4-methylbiphenyl [3] – an intermediate in the synthesis of antagonist angiotensin II [4], synthesis of liquid–crystal compounds [5], antibiotics, for instance vancomycin [6]. With these catalysts it is possible to construct large molecules from small. 2010 specialists from pharmaceutical company GlaxoSmithKline (GSK) published a work, where they calculated, that 17% of all "medical" reactions are catalyzed by palladium catalysts [7]. It should be noted that not only heterogeneous catalysts are widely used in the chemical and petroleum industries, but also homogeneous metal complex catalysts. They characterized by high selectivity and enable to create cost-effective and environmentally friendly processes. In several cases homogeneous metal complex catalysts have significant advantages over homogeneous catalysts.

Among diverse C,C-cross-coupling reactions it is necessary to single out Suzuki–Miyara reaction, representing a combination of aryl- or vinyl boronate

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