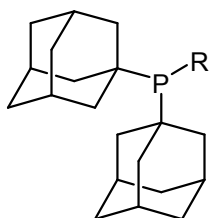


cataCXium: NEW HIGHLY EFFICIENT LIGANDS FOR C-X-COUPLING REACTIONS

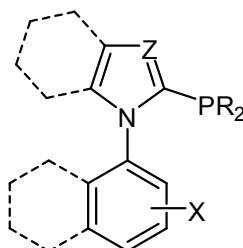
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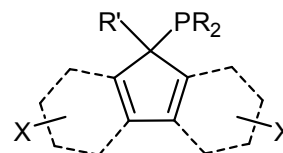
Organic coupling reactions are an important tool to form carbon-carbon and carbon-heteroatom bonds. The popularity of coupling reactions is partly due to their tolerance against the presence of functional groups. This characteristic allows the use of coupling reactions in the synthesis of very complex molecules and thus, coupling reactions are widely used in the chemical and pharmaceutical industry, e.g. for the preparation of agricultural chemicals, pharmaceuticals, and dyestuffs, and, if vinyl compounds are coupled, to prepare monomers for polymerization reactions. Almost all of these modern catalytic reactions require ligands to stabilize and activate the central metal atom, and to tune the selectivity of the desired transformation. Clearly, until to date phosphines constitute the most important class of ligands for cross coupling reactions.



CataCXium A



CataCXium P



CataCXium F

Since the first introducing in 2000 the di-1-adamantylalkylphosphines (cataCXium A) as sterically demanding and electron rich ligands has proven successful for aryl halide activation. More specifically they become apparent as excellent ligands for Heck and Suzuki coupling reactions, for Buchwald-Hartwig aminations⁸ and α -arylation reactions of ketones. Recently, another class of basic, sterically hindered phosphines has been developed. Inspired by Buchwald's biarylphosphine motif CataCXium P ligands are characterized by an N-aryl heterocyclic backbone, which is substituted by a bulky dialkylphosphino group. An important feature of the ligands is their easy preparation in one or two steps, even on a large scale, by

selective deprotonation of the N-aryl heterocycle and quenching with the corresponding chlorophosphine..

Due to their basicity and steric bulkiness, they constitute excellent ligands for palladium-catalyzed coupling reactions. For example, an in situ mixture of palladium acetate and ligand 7 catalyzes the Suzuki reactions of both electron rich and electron deficient aryl chlorides with TONs of up to 10 000 at 60 uC. These type ligands also work excellently in the amination of aryl chlorides.

More recently a new class of cyclopentadiene, indenylidene and fluorine based highly modular ligands (CataCXium F) was introduced in the praxis of cross coupling reactions. The in-situ formed palladium-phosphine complexes showed high performance in the Sonogashira, Suzuki and Buchwald-Hartwig reactions of aryl chlorides.

The presentation will summarize our recent developments in the field of cross coupling reactions and discuss some latest results on the performance of several new members' cataCXium ligands. New fields of applications of our ligands will be highlighted. Particularly, very recently established a very productive C-O coupling using cataCXium P and a protocol for the reductive carbonylation of aryl halides with cataCXium A will be discussed.