

The nature of active palladium species in the Suzuki-Miyaura reaction with aryl chlorides using "ligandless" catalytic systems

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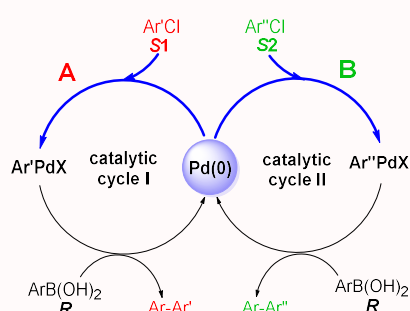
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The Suzuki–Miyaura cross-coupling represents one of the most powerful and widely used methods for the constructing of a new C–C bond between organohalide and organoboron reagents using Pd catalytic systems in both academia and industry. In spite of progress in the development of effective catalytic systems for Suzuki–Miyaura coupling, some common problems exist for the reaction with aryl chlorides. Aryl chlorides are less expensive, less toxic, and less wasteful substrates than aryl bromides and iodides. However, aryl bromides and iodides in the Suzuki–Miyaura coupling reaction work better, while their chloride analogues are less reactive, require harsher conditions and longer reaction times and give the coupling products in lower yields. It is known, that salts dissolved in solutions as additives can accelerate some organic reactions. The results of a kinetic study of the influence of halide salt on the differential selectivity of the Suzuki – Miyaura reaction with aryl chlorides are presented here.

Method of investigation

Differential selectivity (DS) of Competing Reactions

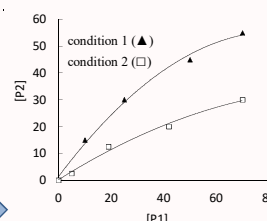
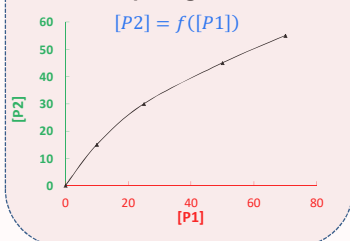


$$Sel_{dif} = \frac{r_{P1}}{r_{P1} + r_{P2}} = \frac{1}{1 + r_{P2}/r_{P1}}$$

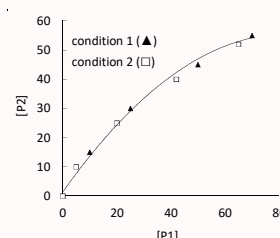
$$\frac{d[P2]/dt}{r_{P1}} = \frac{d[P2]/dt}{d[P1]/dt} = \frac{1 - Sel_{dif}}{Sel_{dif}}$$

$$\frac{r_{P2}}{r_{P1}} = \frac{d[P2]}{d[P1]} = tg\alpha$$

Phase Trajectories of Competing Reactions

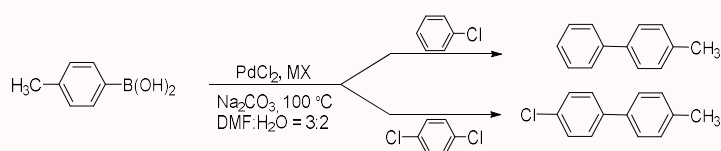


Not the same phase trajectories => noncoincidence of DS => The nature of the active species **changed** with varying reaction conditions.

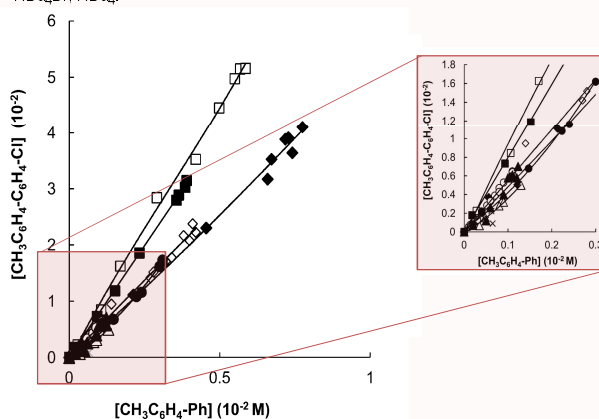


The same phase trajectories => the coincidence of DS => The nature of the active species **remained the same** with varying reaction conditions.

Results

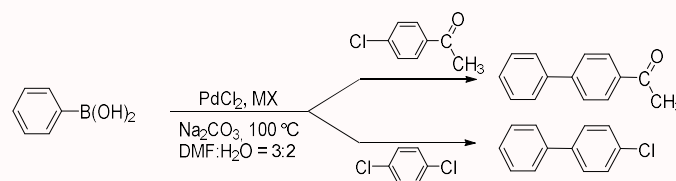


MX = LiCl, LiBr, KBr, KI, NaBr, NaI, NBu₄Br, NBu₄I

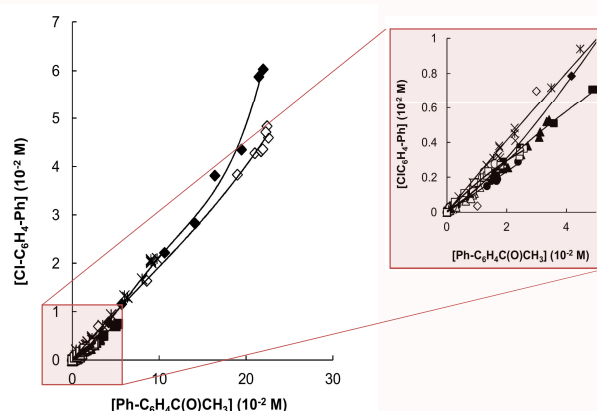


NBu₄Br (□), NaI (×), NaBr (●), without salt additive (◆), NBu₄I (■), LiBr (○), LiCl (▲), KBr (◇), KI (△).

Comparative study of the catalytic systems with and without various halide salt additives demonstrated that differential selectivity of the reaction with competing chlorobenzene and 1,4-dichlorobenzene was sensitive to the added ammonium salt.



MX = LiCl, LiBr, KBr, KI, NaBr, NaI, NBu₄Br, NBu₄I, NBu₄Cl



NBu₄Br (◆), NaI (○), NaBr (●), without salt additive (◇), NBu₄I (×), LiBr (△), NBu₄Cl (*), LiCl (■), KBr (▲), KI (□).

Comparative study of the catalytic systems with and without various halide salt additives demonstrated that differential selectivity of the reaction with competing 4-chloroacetophenone and 1,4-dichlorobenzene was more sensitive to the nature of inorganic salts, than to the nature of ammonium salts.

Differential selectivity in the series of competitive experiments with both pairs of competing aryl chlorides has been found to depend on the nature of anion of a salt used as an additive in catalytic system. This fact indicates that such anions presenting in the system are involved in active anionic Pd(0) species reacting with aryl chlorides in oxidative addition step.