PALLADIUM-CATALYZED ARYLATION AND AMINATION OF POLYCHLOROARENES

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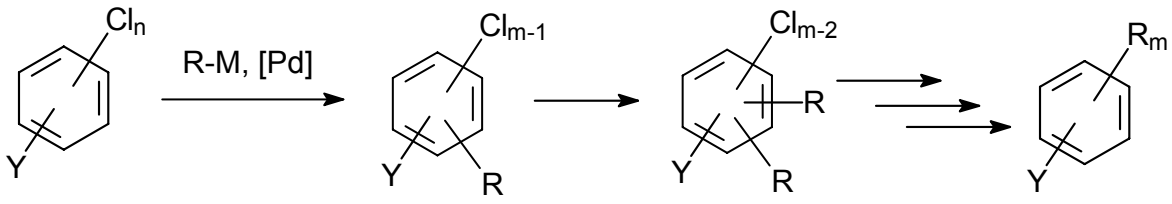
Polychloroarenes (PCA) are ecologically dangerous materials. Development of methods for the substitution of C-C and C-heteroatom for poorly reactive C-Cl bonds can allow transformation of PCA into practically useful aromatic compounds [1]. Catalytic cross-coupling of PCA has been scarcely studied so far.

We have demonstrated that highly-chlorinated PCA, *viz.*, hexachlorobenzene, do not react with arylboronic acids under conditions typical of bromo- and iodoarenes. For their successful processing special catalytic systems based on palladium source combined with sterically hindered electron-rich phosphines [2] or imidazolium salts [3] are required. For example, di-, tri- and tetrachlorobenzenes afforded products of full substitution of all chlorine atoms in 80-100% yields in $Pd(OAc)_2$ – 2-dicyclohexylphosphino-2'-dimethylaminobiphenyl – K_3PO_4 – toluene system at 90 °C [1]. Catalysts based on imidazolium salts [4a,b] and ligand-free systems [4c] were less efficient.



n = 2-6; m = n or n-1; RM = $ArB(OH)_2$, ArZnCl, PhC≡CZnCl, R^1R^2NH; Y = H, Cl, C(O)Me, OMe

Reaction of PCA with highly nucleophilic organozinc compounds proceed readily under the action of conventional $Pd(PPh_3)_4$ [4b].

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