



Developing azole-based ambient condition Pd(II) catalysts for C-C coupling: trends and study of electronic / rigidity features of 2-(thiophen-2-yl)-1H-imidazoles on catalyst activity

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Abstract:

Palladium catalysed carbon- coupling reactions have provided seamless solutions and invaluable to otherwise difficult or impossible organic synthetic challenges [1-4]. Furthermore, it is also a common practice to add a palladium salt and a prescribed ligand into reaction mixtures during application of C-C catalytic coupling strategies [5,6]. However, studies of catalytic behaviours for varying possible catalyst or pre-catalyst species self-assembled during in-situ generation of catalyst are scarce. In particular, comparative study of effects of pre-catalyst molecular variations such as cis- or trans-coordination disposition, donor systems variation, etc. on catalytic outcomes is generally scarce [7].

A series of monodentate 2-(thiophen-2-yl)-1H-imidazole ligands (L1 - L8), 2,4,5-triphenyloxazole (L9) and 2-(1H-imidazol-2-yl)pyridines L10 - L11 were prepared in search for improved azole-based palladium coupling catalysts as well as for systematic study of molecular variation effects on catalytic efficiencies of their palladium complexes. These phosphine-free ligands formed diverse dichloropalladium complexes in three coordination forms, which are chloro-bridged dimers (PdL)₂, mono-ligand species with trans-solvent coordination PdL-solvent and trans-bis-ligand complexes PdL₂. The triphenylphosphine complex PdI₂(PPh₃)₂ was also studied for comparative purposes. Ligand pK_a estimations and palladium complex single crystal data were analysed and correlations were observed between ligand donor strengths, x-ray structural properties and catalytic efficiencies.

The synthetic design paid off by affording very attractive ambient condition Suzuki-Miyaura coupling efficiencies with catalytic activities at as low as 40 °C, 0.2 mol % catalyst loading, high yields within minutes and tolerance for substrate variation. These catalytic results represent a very significant advancement relative to known imidazole-based precatalysts [8,9], which are often dependent on high temperature and / or requiring very long durations. Furthermore, complexes bearing the weakly-donating and more rigid phenanthrenyl-substituted ligands L1 - L5 displayed superior catalyst activities over complexes of the



strongly-donating and more flexible 4,5-diphenyl-substituted ligands L6 - L11. Very poor catalyst activities were observed for trans-bis-ligand precatalyst analogues Pd₈₂, Pd₁₁₂ and PdI₂(PPh₃)₂ at ambient temperatures, which is ascribed to lack of sufficient ligand-ligand repulsion resulting from non-rigidity coupled with stronger ligand donor strengths. To the best of our knowledge, results obtained in this study represent the best performance for palladium catalyst precursors bearing only simple phosphine-free imidazole ligands.

Biography:

Abiodun O. Eseola currently works at the Department of Chemical Sciences, Redeemer's University. Abiodun does research in Inorganic Chemistry, Materials Chemistry and Organometallic Chemistry. Their current project is 'Developing simpler palladium catalysts for C-C Coupling'.

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