Ligand-Controlled Selectivity in Palladium(0)-Catalyzed Barbier-Negishi Cross-Couplings of Secondary Alkyl Bromides

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Palladium-catalyzed C(sp²)-C(sp³) cross-coupling reactions are particularly valuable tools in synthetic chemistry and hence a great deal of interests has emerged in this area.[1] Although great progress has been made over the last decades, important challenges still exist, such as the preformation of organometallic species prior to the cross-coupling step and the control of the coupling site-selectivity due to competing β-H elimination.[2,3] Herein, an operationally simple and mild Barbier-Negishi coupling of secondary alkyl bromides is described. Whereas the newly developed sterically hindered phosphine ligands favour the direct cross-coupling, more flexible phosphine ligands induce migrative couplings through a β-H elimination/rotation/reinsertion sequence.[4]


