

Methoxycarbonylation of olefins catalyzed by palladium complexes bearing P,N-donor ligands

Aguirre, Pedro A.

Lagos, Carolina A.

Moya, Sergio A.

Zúñiga, César

Vera-Oyarce, Cristian

Sola, Eduardo

Peris, Gabriel

Bayón, J. Carles

The methoxycarbonylation of alkenes catalyzed by palladium(ii) complexes with P,N-donor ligands, 2-(diphenylphosphinoamino)pyridine (Ph₂PNHpy), 2-[(diphenylphosphino)methyl]pyridine (Ph₂PCH₂py), and 2-(diphenylphosphino)quinoline (Ph₂Pqn) has been investigated. The results show that the complex [PdCl(PPh₃)(Ph₂PNHpy)]Cl or an equimolar mixture of [PdCl₂(Ph₂PNHpy)] and PPh₃, in the presence of p-toluensulfonic acid (TsOH), is an efficient catalyst for this reaction. This catalytic system promotes the conversion of styrene into methyl 2-phenylpropanoate and methyl 3-phenylpropanoate with nearly complete chemoselectivity, 98% regioselectivity in the branched isomer, and high turnover frequency, even at alkene/Pd molar ratios of 1000. Best results were obtained in toluene-MeOH (3: 1) solvent. The Pd/Ph₂PNHpy catalyst is also efficient in the methoxycarbonylation of cyclohexene and 1-hexene, although with lower rates than with styrene. Related palladium complexes [PdCl(PPh₃)L]Cl (L = Ph₂