

Methoxycarbonylation of iodobenzene in ionic liquids. A case of inhibiting effect of imidazolium halides.

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The palladium(II) complexes, $\text{PdCl}_2(\text{cod})$ (**1**), $\text{PdCl}_2[\text{P}(\text{OPh})_3]_2$ (**2**), $[\text{bmim}]_2[\text{PdCl}_4]$ (**3**), and $[\text{bmpy}]_2[\text{PdCl}_4]$ (**4**) (bmim =1-butyl-3-methylimidazolium cation, bmpy =1-butyl-4-methylpyridinium cation), were found to be active catalysts for the methoxycarbonylation of iodobenzene in ionic liquid (IL) media. The best results were obtained in pyridinium salts, $[\text{bmpy}]\text{X}$ ($\text{X}=\text{Cl}$, Br , BF_4 , PF_6) (76–100 % yield). In methoxycarbonylation reactions carried out in imidazolium salts, $[\text{bmim}]\text{BF}_4$ and $[\text{bmim}]\text{PF}_6$, the yield of benzoic acid methyl ester was slightly lower (50–78 % yield), whereas in $[\text{bmim}]\text{X}$ ($\text{X}=\text{Cl}$, Br) the reaction was totally retarded. The inhibiting effect was not observed when a Me group was present at C-2 (instead of a proton) on the imidazole ring. A palladium-carbene complex, $\text{Pd}(\text{bmimy})_2\text{Br}_2$ (**5**), obtained in the reaction of a palladium catalyst precursor with $[\text{bmim}]\text{Cl}$, presented much lower activity than precursors **1–4**. Its formation may explain the observed inhibition of methoxycarbonylation in a $[\text{bmim}]\text{Cl}$ medium.

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