

New rhodium systems for biphasic hydrogenation and hydroformylation of 1-hexene.

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Streszczenie

The catalytic activity of rhodium complexes formed in reactions of catalyst precursor, $[\text{Rh}(\text{acac})(\text{CO})_2]$ with water soluble phosphines: $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{Li}$ (**PNS**), $\text{Ph}_2\text{PCH}_2\text{CH}(\text{COOLi})(\text{CH}_2\text{COOLi})$ (**PC**), $\text{Ph}_2\text{PCH}_2\text{CH}(\text{CH}_3)(\text{COOH})$ (**PH**) or $\text{Ph}_2\text{PCH}_2\text{CH}(\text{CH}_3)(\text{COONa})$ (**PNa**) in hydrogenation and hydroformylation of 1-hexene in mono- and biphasic systems have been studied. The yield of aldehydes obtained in hydroformylation of 1-hexene in the system $[\text{Rh}(\text{acac})(\text{CO})_2]+\text{PNS}$ strongly depends on the kind of solvent: 24% in toluene, 53–86% (*n*/*iso* 2.9–4.6) in the toluene–water–ethanol mixture and 77–94% (*n*/*iso* 2.5–3.8) in water–ethanol solution. The mixture of water–ethanol as a solvent was also found to be the best for hydrogenation of 1-hexene (96% of hexane) with $[\text{Rh}(\text{acac})(\text{CO})_2]+\text{PNS}$ system. Application of PH phosphine (in hydrogen form) produces ca. 2% of aldehydes in both solvents, toluene only and toluene–water mixture. However, conversion of PH phosphine into its sodium salt, PNa, increased the catalytic activity of rhodium catalyst up to 85% yield of aldehydes in toluene, 92% in toluene–water and 94% in toluene–water–ethanol mixture. Spectroscopic studies of the reaction mixture in situ (IR, -, -NMR) allowed to identify following rhodium complexes existing in hydroformylation reaction conditions in the system $[\text{Rh}(\text{acac})(\text{CO})_2]+\text{PH}/\text{PNa}$: $[\text{Rh}(\text{acac})(\text{CO})(\text{PH})]$, $[\text{Rh}(\text{OH})(\text{CO})(\text{PH})_2]$, $[\text{HRh}(\text{CO})(\text{PNa})_3]$, $[\text{Rh}_4(\text{CO})_{12-x}(\text{PH})_x]$. $[\text{HRh}(\text{CO})(\text{PNa})_3]$ was found to be stable only when sodium hydroxide was introduced to the system.

Słowa kluczowe

Rhodium, Hydrogenation, Hydroformylation, Biphasic system, Water soluble phosphines

Adres publiczny

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