Low-pressure carbonylation of benzyl bromide with palladium complexes modified with PNS (PNS=$Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$) or $P(OPh)_3$. Structural identification of palladium-catalyst intermediate.

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The catalytic activities of two palladium complexes with water soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$) (I) and phosphite $P(OPh)_3$ (II) were tested in the carbonylation of benzyl bromide in methanol at 40–50°C and 1 atm of CO. The first catalyst, (I), was formed *in situ* from $PdCl_2$(cod) and PNS, the second one, (II), was based on the $PdCl_2(P(OPh)_3)_2$ complex. At the ratio of $[NEt_3]$:$[PhCH_2Br]$ equal to 2.5 the yields of phenylacetic acid methyl ester were 83–86% in the carbonylation with PNS and 100% in the carbonylation with $P(OPh)_3$. The palladium catalyst with $P(OPh)_3$ produced under the same conditions 70% of phenylacetic acid methyl ester in the carbonylation of benzyl chloride and 60% of 2-methylphenylacetic acid methyl ester in the carbonylation of 1-bromoethylbenzene. The lower rate of carbonylation of 1-bromoethylbenzyl bromide in comparison to that of benzyl bromide was explained by the lower rate of the substrate oxidative addition step leading to palladium benzyl complexes. Two palladium benzyl complexes, *cis*-$PdBr(PhCH_2)(P(OPh)_3)_2$ and *trans*-$PdBr(PhCH(Me))(P(OPh)_3)_2$ have been isolated and characterized (X-ray, ^{31}P and ^{1}H NMR).

Słowa kluczowe

carbonylation, benzyl bromide, palladium catalyst, water soluble phosphine

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