Hydrosilylation of Acetophenone with Diphenylsilane in the Presence of Rhodium(I) Complexes with Chiral Amines

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Abstract—New chiral rhodium complexes *cis*-[Rh(CO)$_2$(RNH$_2$)Cl] [RNH$_2$ = (*R*)-(–)-*cis*-MyrtNH$_2$, (*R*)-(–)-MenthylNH$_2$, (*R*)-(+)-BornylNH$_2$] were synthesized and their catalytic properties in reactions of hydrosilylation of acetophenone with diphenylsilane were studied. It was shown that the reaction products were diphenyl-1-phenylethoxysilane, diphenyl-1-phenylvinyloxysilane and 1,1,3,3-tetraphenyldisiloxane. The best catalytic activity displayed (–)-*cis*-[Rh(CO)$_2$(MenthNH$_2$)Cl]. The hydrosilylation of acetophenone with diphenylsilane in the presence of [Rh(CO)$_2$(μ-Cl)]$_2$ and [Rh(cod)Cl]$_2$ and amines *in situ* was studied. The best ratio amine:complex = 5:1 was established. With the catalytic systems based on [Rh(cod)Cl]$_2$ or [Rh(CO)$_2$(μ-Cl)]$_2$ the activity increased in the series of amines: (*R*)-(–)-*cis*-MyrtNH$_2$ < (*R*)-(–)-MenthylNH$_2$ ≈ (*R*)-(+)-BornylNH$_2$, and (*R*)-(–)-MenthylNH$_2$ < (*R*)-(+)-BornylNH$_2$ < (*R*)-(–)-*cis*-MyrtNH$_2$, respectively. The chemoselectivity maximum was observed in the presence of [Rh(cod)Cl]$_2$ with (*R*)-(–)-MenthylNH$_2$ and [Rh (CO)$_2$(μ-Cl)]$_2$ with (*R*)-(+)-BornylNH$_2$; maximum asymmetric induction was 43.5% *ee* at the use of [Rh(CO)$_2$ (μ-Cl)]$_2$ and (*R*)-(+)-BornylNH$_2$.

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