Novel rhodium(I) complexes with (2-hydroxyphenyl)diphenylphosphine ligand: catalytic properties and X-ray structures of $Rh(OC_6H_4PPh_2)(CO)(PPh_3)$ and $Rh(OC_6H_4PPh_2)\{P(OPh)_3\}_2\ 0.5C_6H_6$.

Autorzy

Anna M. Trzeciak

Józef J. Ziółkowski

Tadeusz Lis

R. Choukroun

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Streszczenie

The novel rhodium complexes with the bidentate PO ligand ($PO=OC_6H_4PPh_2^-$) of the form $Rh(PO)(CO)L$ (L^a=POH=$HOC_6H_4PPh_2$ (**1**), PPh_3 (**2**), $P(NC_4H_4)_3$ (**4**), $PPh_2(NC_4H_4)$ (**6**)) and $Rh(PO)L_2$ ($L^b=P(OPh)_3$ (**3**), $P(NC_4H_4)_3$ (**5**)) were obtained by ligand exchange in Rh(β-diketone)$(CO)_2$, Rh(β-diketone)(CO)L and Rh(β-diketone)L_2 complexes. All complexes of the $Rh(PO)(CO)L^a$ type exist in solution as isomers with both phosphorus atoms in the *trans* position as was shown by $^{31}P\{^1H\}$-NMR. The *trans* influence of the phosphorus atom of a bidentate PO ligand is stronger than that of oxygen atom, which is manifested by the differences of Rh–P bonds in (**2**) (2.283(1) and 2.327(1) Å) and of Rh–P (phosphite) bonds in (**3**) (2.233(2) and 2.139(2) Å). The complexes (**1**) and (**2**) used alone or with an excess of free phosphine (POH, PPh_3, $P(NC_4H_4)_3$) are not active in hexen-1-e hydroformylation at 1 MPa $CO/H_2=1$ and at 353 K. The lack of catalytic activity is explained by the extremely high stability of the chelate (PO) ring which does not allow the formation of the active form of the catalyst. In contrast, the complex (**3**) used alone as the catalyst precursor produces 54 and 72.9% of aldehydes when used with a six-fold excess of $P(OPh)_3$. Complex (**1**) modified with $P(OPh)_3$ catalyses hexen-1-e hydroformylation with a 73.6–84.6% yield of aldehydes. Under hydroformylation reaction conditions, the PO ligand is removed from the coordination sphere of (**1**) and complexes of the form $HRh(CO)\{P(OPh)_3\}_3$ and $HRh\{P(OPh)_3\}_4$ are formed.

Słowa kluczowe

Rhodium complexes, Phosphines, Catalysis, X-ray structure

Adres publiczny

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