Chemistry of palladium phosphinite ($PPh_2(OR)$) and phosphonite ($P(OPh)_2(OH)$) complexes: catalytic activity in methoxycarbonylation and Heck coupling reactions.

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The new phosphinite and phosphonite complexes (**1–8**) are very efficient catalysts for the methoxycarbonylation of iodobenzene and Heck cross-coupling of bromobenzene with butyl acrylate. High catalytic activity of these complexes can be explained by their *in situ* transformations during the reaction, stimulated by the presence of water, acid (HCl) or base (NEt_3). Hydrolysis of phosphinite palladium complexes of the form *trans*-$PdCl_2[PPh_2(OR)]_2$ (R = C_6F_5 **2**, ^{t}Bu **3**, or O-menthyl **4**) results in the formation of the dimeric complex $[\mu\text{-}ClPd(PPh_2OH)(PPh_2O)]_2$ **5**, which is deprotonated by NEt_3, producing a polymeric complex of formula $[Pd(P(O)PPh_2)_2]_n$ **8**. The reverse reaction, protonolysis of **8** with HCl, leads back to **5** and the monomeric complex **5a**. The phosphinite complex $PdCl_2[PPh_2(OBu)]_2$ **1** with a more lipophilic ligand, $PPh_2(OBu)$, does not undergo hydrolysis under the same conditions. In the reaction of $PdCl_2(cod)$ with $P(OPh)_2(OH)$, the new dimer $[\mu\text{-}ClPd(P(OPh)_2OH)(P(OPh)_2O)]_2$ **6** was obtained, whereas reaction of $Pd(OAc)_2$ with $P(OPh)_2(OH)$ leads to the polymeric complex $[Pd[P(O)(OPh)_2]_2]_n$ **7**. Protonolysis of **7** with HCl results in the formation of **6**.

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