



## Designer Palladacycle Catalysts for Asymmetric P-H Addition Reactions

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14/6/2016

### Научный семинар кафедры органической химии № 28 Преп. СХА 15-00

The PC-cyclometalated complex (**R-1**) is an efficient catalyst for the asymmetric hydrophosphination reactions of achiral chalcones. For example, it facilitates the large scale synthesis of the stable PCP-pincer product (**S,S-2**) via a “double” P-H addition reaction on the same substrate, as illustrated in the Scheme below. Subsequently (**S,S-2**) itself is also found to be an efficient catalyst for similar P-H addition reaction. However, the PC- and PCP-complexes show very different reactivity and selectivity. For example, when (**R-1**) was used as the catalyst, addition of the P-H bond to  $\alpha,\beta,\gamma,\delta$ -unsaturated malonate ester gave the 1,4-addition product exclusively. When the same reaction was catalysed by (**S,S-2**), only the 1,6-addition product was generated. Many similar examples have been observed when the two catalysts were applied for the same substrate. The catalyst-product specificity is due to the fact that the two catalysts operate via different reaction mechanisms. Catalyst (**R-1**) interacts with both reacting species simultaneously during the course of the intramolecular bond formation process. The pincer catalyst on the other hand operates via an inter-molecular mechanism by activating only the P-H moiety. The stereo-electronic features of (**R-1**) and (**S,S-2**) and their catalytic applications will be discussed in this seminar.

