

Designer Palladacycle Catalysts for Asymmetric P-H Addition Reactions

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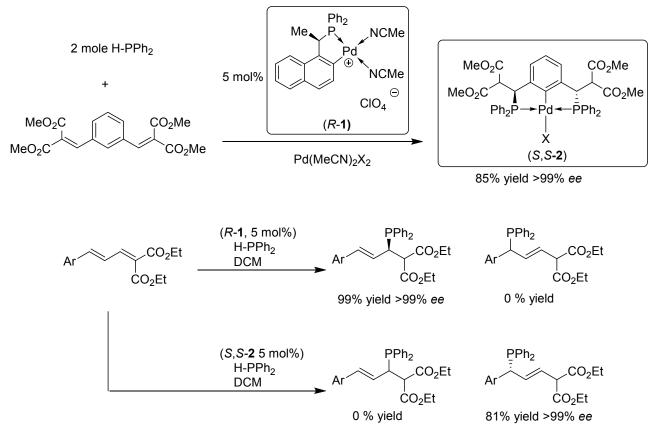
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The PC-cyclometalated complex (*R*-1) is an efficient catalyst for the asymmetric hydrophosphination reactions of achiral chalcones. For example, it facilitates the large scale synthesis of the stable PCP-pincer product (*S*,*S*-2) *via* a "double" 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.



R.J. Chew, P.-H. Leung, Chemical Records, 2016, 16, 141–158 (review).