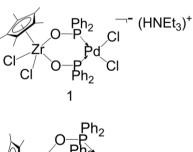
## Syntheses of Zr-Pd heterobinuclear complexes having two or three OPPh<sub>2</sub> bridges

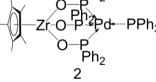
- difference in reactivity toward diphenylvinylphosphine oxide-

○<u>Yoshihisa Koro</u>, Tsutomu Mizuta Graduate School of Science, Hiroshima University

The P-H bond addition of  $Ph_2P(O)H$  to  $Ph_2P(O)CH=CH_2$  was carried out using  $Cp_2Zr(\mu-OPPh_2)_2PdMe_2$  as a catalyst precursor which had been reported to be transformed to  $H(PMePh_2)Pd(\mu-OPPh_2)_3Zr(\mu-OPPh_2)_3PdH(PMePh_2)$  by a reaction with the substrate  $Ph_2P(O)H$  and a cocatalyst PMePh\_2. The addition proceeded quickly under mild conditions at 40 °C for 10 min to give  $Ph_2P(O)CH_2CH_2P(O)Ph_2$  with 88% yield. To probe the interaction of the catalyst with  $Ph_2P(O)CH=CH_2$ , we prepared new Zr-Pd heterobinuclear complexes having two or three  $OPPh_2$  bridges, 1 or 2 respectively, and examined the catalyst-substrate interaction using these complexes as catalyst models.

 $[Cp*ZrCl_2(\mu-OPPh_2)_2PdCl_2]HNEt_3 (1)$  was characterized by  ${}^{31}P{}^{1}H$  and  ${}^{1}HNMR$ , X-ray analysis, and elemental analysis, while  $Cp*Zr(\mu-OPPh_2)_3PdPPh_3$  (2) was identified by only  ${}^{31}P{}^{1}H$  and  ${}^{1}HNMR$  spectra. The complex 1 having the two  $OPPh_2$  bridges was found to immediately react with  $Ph_2P(O)CH=CH_2$  to give new  ${}^{31}P{}^{1}H$ NMR signals of an adduct formed. On the other hand, the complex 2 having the three  $OPPh_2$  bridges did not show any interaction with





 $Ph_2P(O)CH=CH_2$ . The results indicate the number of the bridge plays a critical role in the catalyst-substrate interaction. In the case of the three-OPPh<sub>2</sub>-bridge complex 2,  $Ph_2P(O)CH=CH_2$  can not approach to the complex probably due to the substantial steric hindrance.