

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

- difference in reactivity toward diphenylvinylphosphine oxide-

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The P-H bond addition of Ph<sub>2</sub>P(O)H to Ph<sub>2</sub>P(O)CH=CH<sub>2</sub> was carried out using Cp<sub>2</sub>Zr(μ-OPPh<sub>2</sub>)<sub>2</sub>PdMe<sub>2</sub> as a catalyst precursor which had been reported to be transformed to H(PMePh<sub>2</sub>)Pd(μ-OPPh<sub>2</sub>)<sub>3</sub>Zr(μ-OPPh<sub>2</sub>)<sub>3</sub>PdH(PMePh<sub>2</sub>) by a reaction with the substrate Ph<sub>2</sub>P(O)H and a cocatalyst PMePh<sub>2</sub>. The addition proceeded quickly under mild conditions at 40 °C for 10 min to give Ph<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub> with 88% yield. To probe the interaction of the catalyst with Ph<sub>2</sub>P(O)CH=CH<sub>2</sub>, we prepared new Zr-Pd heterobinuclear complexes having two or three OPPh<sub>2</sub> bridges, 1 or 2 respectively, and examined the catalyst-substrate interaction using these complexes as catalyst models.

[Cp\*ZrCl<sub>2</sub>(μ-OPPh<sub>2</sub>)<sub>2</sub>PdCl<sub>2</sub>](HNEt<sub>3</sub>) (1) was characterized by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR, X-ray analysis, and elemental analysis,

while Cp\*Zr(μ-OPPh<sub>2</sub>)<sub>3</sub>PdPPh<sub>3</sub> (2) was identified by only <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra. The complex 1 having the two

OPPh<sub>2</sub> bridges was found to immediately react with Ph<sub>2</sub>P(O)CH=CH<sub>2</sub> to give new <sup>31</sup>P{<sup>1</sup>H} NMR signals of an

adduct formed. On the other hand, the complex 2 having the three OPPh<sub>2</sub> bridges did not show any interaction with

Ph<sub>2</sub>P(O)CH=CH<sub>2</sub>. 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<sub>2</sub>P(O)CH=CH<sub>2</sub> can not approach to the complex probably due to the substantial steric hindrance.

