Supporting Information

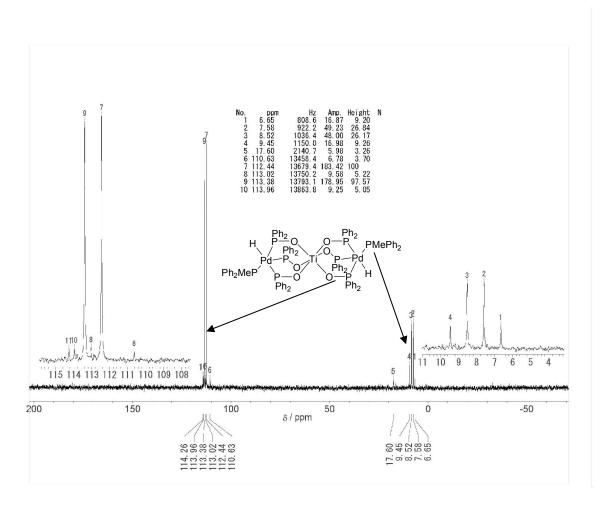
Bi- and Tri-nuclear Complexes of Group 4 Metal and Pd Bridged by OPPh<sub>2</sub> Groups: Synthesis and High Catalytic Activities in Double Hydrophosphinylation of 1-Octyne

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Miyoshi

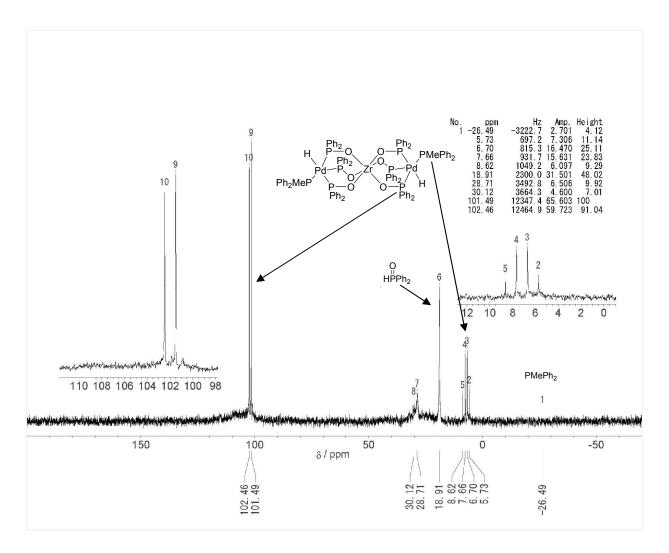
Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan, fax: +81-82-424-0729, E-mail: mizuta@sci.hiroshima-u.ac.jp

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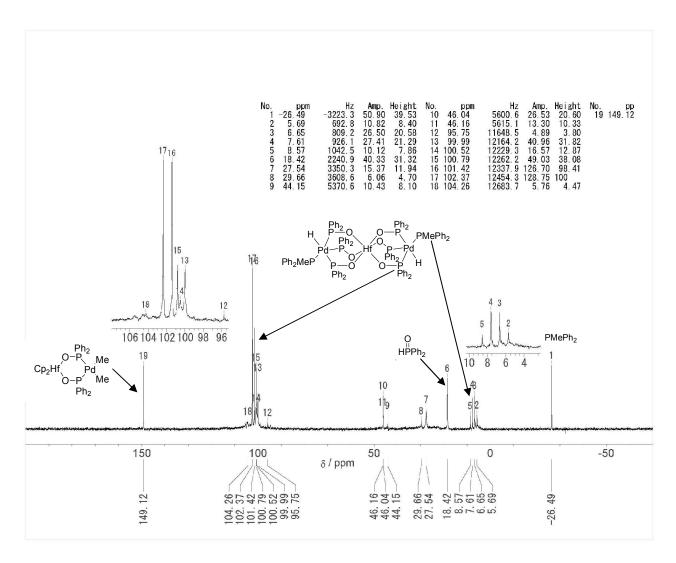
Figures S1-S5.



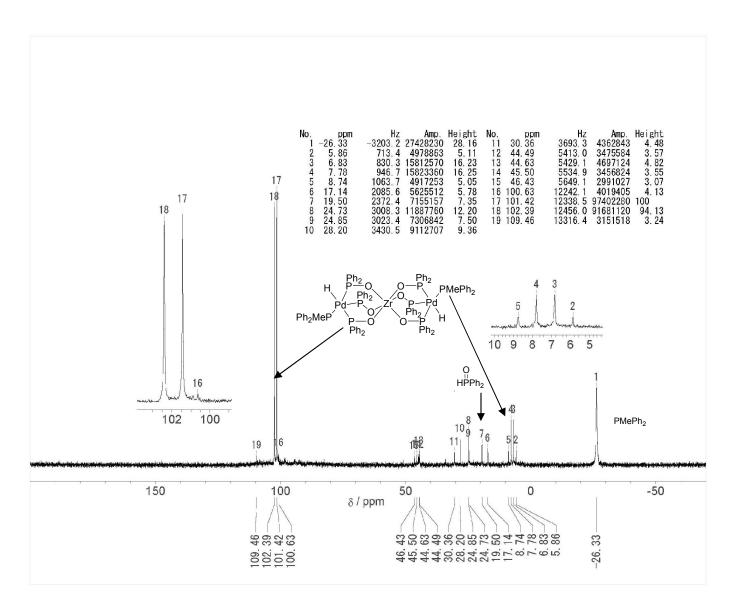
**Figure S1**. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the Pd-Ti-Pd complex **6**.



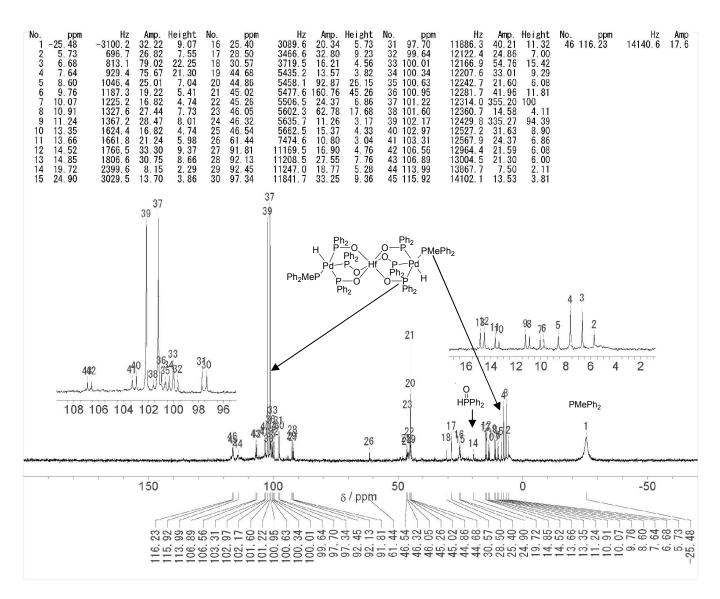
**Figure S2**. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture obtained by the treatment of the Zr-Pd complex **2** with HP(O)Ph<sub>2</sub> and PMePh<sub>2</sub>.



**Figure S3**. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture obtained by the treatment of the Hf-Pd complex **3** with HP(O)Ph<sub>2</sub> and PMePh<sub>2</sub>.



**Figure S4**.  ${}^{31}P\{{}^{1}H\}$  NMR spectrum of the reaction mixture obtained by the treatment of the  $Cp_2ZrCl_2$  and  $PdMe_2(tmeda)$  with  $HP(O)Ph_2$  and  $PMePh_2$ .



**Figure S5**.  ${}^{31}P\{{}^{1}H\}$  NMR spectrum of the reaction mixture obtained by the treatment of the  $Cp_2HfCl_2$  and  $PdMe_2(tmeda)$  with  $HP(O)Ph_2$  and  $PMePh_2$ .