

Title: Coupling of Coordinated 2-Iminophosphorano-1-phosphaallyl leading to Bridged-Iminophosphoranato Complexes of Zirconium and Hafnium

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Synthesis of complexes **3-5**

Synthesis of complex **3**: To a stirred solution of **1** ($n = 1.5$) (3.44 g, 7.23 mmol) in 40 mL of Et₂O was added ZrCl₄ (0.85 g, 3.64 mmol) at $-80\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and stirred for 15 h. The mixture was filtered and the filtrate was concentrated *in vacuo*. Pale yellow crystals were obtained after 3 days. Yield: 1.29 g (33.8 %). m.p. $>300\text{ }^{\circ}\text{C}$. Slow decomposition of this compound in the course of crystallization prevented us from obtaining satisfactory elemental analysis.

Synthesis of complex **4**: To a stirred solution of **1** ($n = 1.5$) (1.19 g, 2.50 mmol) in 30 mL of Et₂O at $-80\text{ }^{\circ}\text{C}$ was added HfCl₄ (0.41 g, 1.28 mmol). The reaction mixture was allowed to reach room temperature and stirred for 15 h. Volatiles were removed *in vacuo*. The residue was extracted with CH₂Cl₂ and filtered. Crystallization at room temperature afforded 0.32 g of **4**·CH₂Cl₂ as pale yellow crystals. Further concentration of the mother liquor and keeping at $-20\text{ }^{\circ}\text{C}$ gave again 0.35 g of product, yield: 51.1 %. m.p. $246\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd for C₃₉H₅₄Cl₄N₂P₄Si₂Hf: C, 44.56; H, 5.18; N, 2.66. Found: C, 44.28; H, 5.41; N, 2.98.

Synthesis of complex **5**: To a solution of **2** ($n = 2$) (1.59 g, 2.54 mmol) in 30 mL of Et₂O at $-80\text{ }^{\circ}\text{C}$ was added ZrCl₄ (0.26 g, 1.12 mmol) with stirring. The reaction mixture was warmed to room temperature and stirred for 15 h, resulting in a deep red solution. Volatiles were removed *in vacuo*, and the residue was extracted with CH₂Cl₂ and filtered. The filtrate was concentrated to about 3 mL and then about 3 mL of Et₂O was added. Concentration of the mixture gave 0.22 g of deep red crystals of complex **5**·Et₂O·0.6CH₂Cl₂. The mother liquor was kept at $-20\text{ }^{\circ}\text{C}$ to give further 0.21 g of product, yield: 31.1 %. m.p.: $222\text{--}224\text{ }^{\circ}\text{C}$. Anal. Calcd for C₅₀H₈₀Cl₂N₂P₄Si₄Zr·0.6CH₂Cl₂: C, 52.46; H, 7.07; N, 2.42. Found: C, 52.38; H, 6.97; N, 2.40.