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Synthesis of Group 4 Transition Metal Complexes Bearing a Phosphine Pendant Cyclopentadienyl Ligand

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SYNTHESIS OF GROUP 4 TRANSITION METAL COMPLEXES BEARING A PHOSPHINE PENDANT CYCLOPENTADIENYL LIGAND

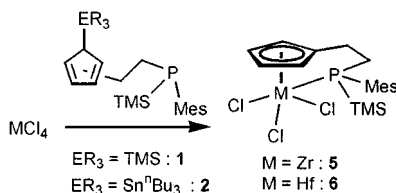
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Synthesis and spectroscopic properties of Piano-stool type Zr and Hf complexes bearing a PRMes (R = SiMe₃, H) pendant cyclopentadienyl ligand are described.

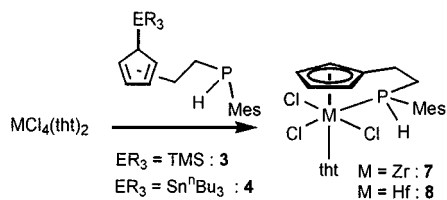
Keywords: Hf; phosphine pendant ligand; sulfide complex; Zr

Many transition metal complexes bearing a cyclopentadienyl (Cp) ligand with a Lewis base as a pendant have been reported. However, complexes bearing a phosphorus pendant Cp ligand, especially for early transition metals, have hardly been investigated. We here report the synthesis of Zr and Hf complexes with a phosphine pendant Cp ligand. The pendant phosphine has Mes (C₆H₂Me₃) and either TMS (SiMe₃) or H substituents. The reaction of MCl₄ (M = Zr, Hf) with **1** and **2** in toluene yielded **5** and **6**, respectively (Scheme 1). In contrast, the reaction with **3** and **4** bearing a P–H bond gave several unidentified products. However, it was found that the treatment of MCl₄(tht)₂ (tht = tetrahydrothiophene) with **3** and **4** yielded **7** and **8**, respectively (Scheme 2).



SCHEME 1

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**SCHEME 2**