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# Synthesis of Group 4 transition-metal complexes bearing a secondary phosphine pendant cyclopentadienyl ligand

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**Abstract**

Reactions of some chlorides of the Group 4 transition metals were examined with secondary phosphine pendant cyclopentadienyl derivatives, $XC_5H_4CH_2CH_2PHR$ (X = Li, $SiMe_3$, Sn(*n*-Bu)$_3$; R = 2,4,6-trimethylphenyl (Mes), 2,4,6-tri-*i*-propylphenyl (Tip), 2,4,6-tri-*t*-buthylphenyl (Mes*)). Although reactions of $MCl_4$ (M = Zr, Hf) did not yield $(C_5H_4CH_2CH_2PHR)MCl_3$, reactions of $MCl_4(SR''_2)_2$ ($SR''_2 = SMe_2$, tetrahydrothiophene) gave $(C_5H_4CH_2CH_2PHR)MCl_3(SR''_2)_n$ ($n = 1$, 2). The steric bulkiness of the substituent (R) on the secondary phosphine affects the coordination mode of the phosphine moiety in solution. When R is Mes, the phosphine-coordinated species is stable, when R is Tip, the phosphine-coordinated and -dissociated species are in equilibrium, and when R is Mes*, only the phosphine-dissociated species is observed. © 2002 Published by Elsevier Science B.V.

*Keywords:* Secondary phosphine; Phosphine pendant cyclopentadienyl ligand; Sulfide complex; Group 4 transition metal

## 1. Introduction

In organometallic chemistry an $\eta^5$-cyclopentadienyl group (Cp) is an excellent ancillary ligand because it normally binds very strongly to a transition metal center and its steric and electronic properties can readily be modified by variation of the organic substituents on the Cp ring. Phosphines also represent a prominent class of ancillary ligands like a Cp ligand but have different properties. Since bidentate ligands have proven important in a variety of complexes and are invaluable in a number of catalytic processes, the chemistry of complexes with a bidentate ligand in which a Cp and a phosphine are connected to one another by an alkyl chain or a similar spacer has attracted considerable attention [1]. Many such complexes have been prepared. They, however, have all tertiary phosphine derivatives in the sidearm, and no secondary phosphine-substituted Cp complexes have been reported to date. Since a P–H bond is known to be readily activated [2,3], transition-metal Cp complexes bearing a sidearm with a PHR group are potentially convertible into another type of phosphorus functionalized Cp complexes, such as a phosphide-substituted Cp complex.

In this paper, we report the synthesis of secondary phosphine pendant cyclopentadienyl derivatives, in which cyclopentadienyl and PHR groups (R = 2,4,6-trimethylphenyl (Mes), 2,4,6-tri-*i*-propylphenyl (Tip), 2,4,6-tri-*t*-butylphenyl (Mes*)) are connected by a $CH_2CH_2$ spacer, and their complexation with Zr and Hf.

## 2. Results and discussion

### 2.1. Preparation of cyclopentadienyl derivatives bearing secondary phosphine in the side chain

Lithium cyclopentadienide is the most widely used direct precursor for introduction of a Cp ligand into transition metals. Another convenient precursor of $CpMCl_3$ is a trimethylsilyl- or a tri-*n*-buthylstannyl-substituted Cp derivative [4]. So we planned to prepare $LiC_5H_4CH_2CH_2PHR$ and $R'_3EC_5H_4CH_2CH_2PHR$ ($R'_3E = Me_3Si$, *n*-$Bu_3Sn$). Several synthetic routes for tertiary phosphine pendant cyclopentadienyl derivatives

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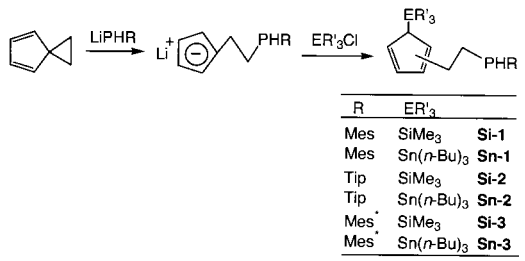
have been summarized [1]. The most convenient one for $LiC_5H_4CH_2CH_2PR_2$ is the reaction of the appropriate lithium phosphide with spiro-[2.4]hepta-4,6-diene [5–7]. We applied the method for obtaining lithium cyclopentadienide bearing a secondary phosphine pendant. $R'_3EC_5H_4CH_2CH_2PHR$ was obtained in the reaction of $LiC_5H_4CH_2CH_2PHR$ with an appropriate chloride ($Me_3SiCl$, $n$-$Bu_3SnCl$) according to the literature methods [5,6] (Scheme 1).

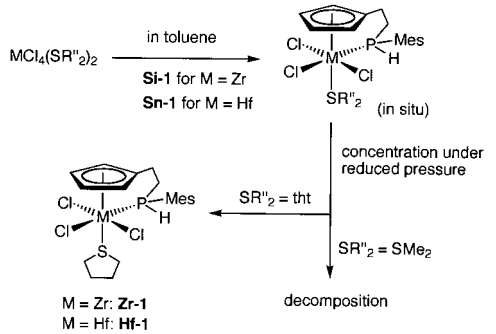
### 2.2. Consideration of the starting transition metal complex in the reaction with $XC_5H_4CH_2CH_2PHR$

First, the reactions of $MCl_4$ (M = Zr, Hf) with $LiC_5H_4CH_2CH_2PHR$ were examined, but complexes of the $(C_5H_4CH_2CH_2PHR)MCl_3$ type were not obtained. Next, the reaction of $MCl_4$ with $R'_3EC_5H_4CH_2CH_2PHR$ was examined. The reaction in toluene was not clean and yielded several unidentified products. We supposed that the complication might arise from the initial coordination of the phosphorus lone pair electrons in the secondary phosphine to $MCl_4$ prior to the Cp group coordination, followed by the P–H bond activation due to the strong acidity of the metal center. Initial coordination of the $PPh_2$ group in $Me_3SiC_5H_4CH_2CH_2PPh_2$ to $ZrCl_4$ has been proposed [5a]. Therefore, reducing the acidity of the starting $MCl_4$ is considered to lead to the formation of the desired $(C_5H_4CH_2CH_2PHR)MCl_3$. On the basis of this consideration, we next attempted to use $MCl_4(SMe_2)_2$ as a starting complex in place of $MCl_4$, because $ZrCl_4(SMe_2)_2$ is reported to be a nice starting complex for preparing $CpZrCl_3(SMe_2)_2$ in the reaction with $Me_3SiCp$ [8]. In addition, it is also reported that silyl- and stannyl-substituted Cp derivatives are suitable for the preparation of Zr and Hf complexes, respectively [8]. Therefore, we employed **Si-1**, **Si-2**, and **Si-3** for Zr complexes and **Sn-1**, **Sn-2**, and **Sn-3** for Hf complexes.




| R | ER'3 | |
|---|---|---|
| Mes | $SiMe_3$ | **Si-1** |
| Mes | $Sn(n\text{-}Bu)_3$ | **Sn-1** |
| Tip | $SiMe_3$ | **Si-2** |
| Tip | $Sn(n\text{-}Bu)_3$ | **Sn-2** |
| Mes* | $SiMe_3$ | **Si-3** |
| Mes* | $Sn(n\text{-}Bu)_3$ | **Sn-3** |

Scheme 1.



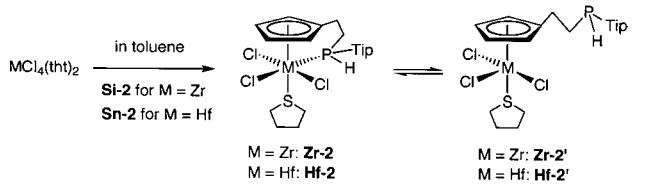

Scheme 2.

### 2.3. Preparation of Zr and Hf complexes with $C_5H_4CH_2CH_2PHMes$

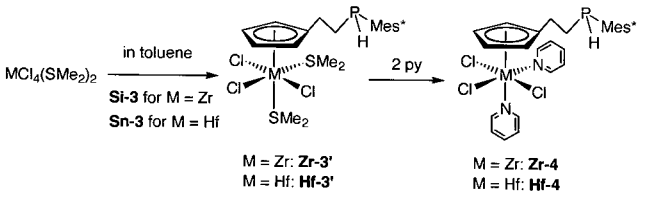
The reaction of $ZrCl_4(SMe_2)_2$ with **Si-1** was examined in toluene. The $^{31}$P-NMR spectrum without proton irradiation of the reaction mixture showed two doublets at $-22.60$ ppm ($J_{PH} = 329.3$ Hz) and $-22.93$ ppm ($J_{PH} = 329.3$ Hz) with almost the same intensity. The chemical shifts are at more than 50 ppm lower magnetic field than those for metal-free **Si-1** (ca. $-85$ ppm), and the coupling constants are more than 100 Hz greater than those for **Si-1** (ca. 217 Hz). Therefore, the products are expected to be phosphine-coordinated complexes (Scheme 2). In order to isolate the products, the solvent was removed under reduced pressure, which led to decomposition of the products. The reaction of $HfCl_4(SMe_2)_2$ with **Sn-1** showed similar results.

Next we examined the reaction of $MCl_4(tht)_2$ (tht stands for tetrahydrothiophene) with **Si-1** and **Sn-1**, because tht has a higher boiling point and higher donor ability than $SMe_2$. After work up, a white powder was isolated. The spectroscopic data show that the product is $[\eta^5{:}\eta^1\text{-}(C_5H_4CH_2CH_2PHMes)MCl_3(tht)]$ (**Zr-1**, 84% yield; **Hf-1**, 88% yield) (see Scheme 2). With **Zr-1**, the $^{31}$P-NMR spectrum exhibits two resonances at $-22.60$ and $-22.93$ ppm with $J_{PH} = 329.3$ Hz (vide infra). These $^{31}$P-NMR data indicate the coordination of the secondary phosphine to the Zr center. The X-ray structures of a tertiary phosphine pendant Cp complex and its tetramethyl-Cp derivative, $[\eta^5{:}\eta^1\text{-}(C_5R_4CH_2CH_2PPh_2)ZrCl_3(thf)]$ (R = H, Me), have been reported [5]. For each complex, the Zr atom possesses a distorted octahedral coordination assuming that the Cp ligand occupies one site, and the Cp ring and thf molecule lie in the mutually *trans* positions. Therefore, it is highly likely that **Zr-1** with secondary phosphine has the same alignment around the Zr as depicted in Scheme 2.

It should be noted here that the P–H moiety in **Zr-1** shows two resonances with almost the same chemical shifts and coupling constants in both the $^{31}$P- and $^1$H-NMR spectra. Since the $^1$H- and $^{13}$C-NMR spectra show that there is only one kind of tht, it is clear that the two resonances do not arise from two different geometrical isomers around the Zr. We tentatively concluded that the rotation along the P–Zr bond involving the puckering of the $CH_2CH_2$ bridge is prohibited due to the bulky Mes group, resulting in the existence of inconvertible two rotational isomers. Complex **Hf-1** also was isolated and characterized as **Zr-1** was.




Scheme 3.




Scheme 4.

### 2.4. Preparation of Zr and Hf complexes with $C_5H_4CH_2CH_2PHTip$

The reaction of $ZrCl_4(tht)_2$ with **Si-2** bearing a 2,4,6-tri-*i*-propylphenyl group (Tip) on the phosphorus, and that of $HfCl_4(tht)_2$ with **Sn-2** yielded $[\eta^5{:}\eta^1$-$(C_5H_4CH_2CH_2PHTip)MCl_3(tht)]$ (M = Zr, 72% yield; M = Hf, 79% yield) (Scheme 3). The spectroscopic data indicate that these Tip derivatives exist in solution as an equilibrium mixture of the phosphine-coordinated and -dissociated species. With the Zr complex, for example, the $^{31}$P-NMR spectrum without proton irradiation of the reaction mixture showed three doublets at $-22.71$ ppm ($J_{PH} = 319$ Hz), $-23.02$ ppm ($J_{PH} = 319.5$ Hz), and $-92.46$ ppm ($J_{PH} = 206.6$ Hz). The first two chemical shifts and the coupling constants are close to those for **Zr-1**, indicating the formation of a phosphine-coordinated complex, **Zr-2**, shown in Scheme 3. In contrast, the signal at $-92.46$ ppm ($J_{PH} = 206.6$ Hz) is close to that for **Si-2** and **Sn-2**, indicating the presence of a phosphine-dissociated complex, **Zr-2′**. Although a phosphine-dissociated structure is simply depicted as **Zr-2′** in Scheme 3, it is likely that the vacant site is occupied by the solvent or another tht, or alternatively the complex dimerizes with Cl bridges [5a]. The ratio of **Zr-2** and **Zr-2′** at room temperature was approximately 3:1 in benzene and toluene, whereas the ratio was about 4:1 in $CH_2Cl_2$. Therefore, it can be said that **Zr-2** is in equilibrium with **Zr-2′**, presumably due to a bulkier Tip group rather than a Mes group. The corresponding hafnium complex showed the same behavior; **Hf-2** and **Hf-2′** are in equilibrium in solution.

### 2.5. Preparation of Zr and Hf complexes with $C_5H_4CH_2CH_2PHMes^*$

Finally, the reaction of $MCl_4(SMe_2)_2$ with **Si-3** or **Sn-3**, having a bulky 2,4,6-tri-*t*-butylphenyl substituent (Mes*) on the phosphorus was examined. The $^{31}$P-NMR spectrum without proton irradiation of the reaction mixture of $ZrCl_4(SMe_2)_2$ with **Si-3** in toluene showed only one doublet at $-71.71$ ppm ($J_{PH} = 217.5$ Hz). The chemical shift is at about 50 ppm higher magnetic field than those for **Zr-1** and **Zr-2**, but is close to that for **Si-3**. The coupling constant is also close to that for **Si-3**. These data suggest that the product is only a phosphine-dissociated complex, $[\eta^5$-$(C_5H_4CH_2$-$CH_2PHMes^*)ZrCl_3(SMe_2)_2]$ (**Zr-3′**), but $[\eta^5{:}\eta^1$-$(C_5H_4CH_2CH_2PHMes^*)ZrCl_3(SMe_2)]$ corresponding to **Zr-1** and **Zr-2** is not formed (Scheme 4). Removal of the solvent from the reaction mixture gave a white powder. The powder is sparingly soluble in most organic solvents. The $^{31}$P-NMR spectrum in $C_6D_6$ shows a broad doublet at $-72.89$ ppm ($J_{PH} = 229.6$ Hz) with some other signals. The removal of the solvent may result in oligomerization of **Zr-3′** by bridging Cl. A similar product ($[\eta^5$-$(C_5H_4CH_2CH_2PHMes^*)ZrCl_3$-$(tht)_2]$) was obtained in the reaction of $ZrCl_4(tht)_2$ with **Si-3**.

In order to convert **Zr-3′** into an isolable complex, 2 equimolar amounts of pyridine (py) were added to a solution containing **Zr-3′**. After work up, a white powder was obtained. The $^1$H- and $^{13}$C-NMR spectra show that the complex has two py ligands in total. The $^{31}$P-NMR spectrum shows that the phosphine moiety does not coordinate to the Zr center. These data indicate the formation of $[\eta^5$-$(C_5H_4CH_2CH_2PHMes^*)$-$MCl_3(py)_2]$ (**Zr-4**) (Scheme 4). The variable temperature NMR measurements of the complex did not show the formation of the phosphine-associated species.

Similar results were obtained for the hafnium systems: $HfCl_4(SMe_2)_2$ and $HfCl_4(tht)_2$ react with **Sn-3** to give the phosphine-dissociated complexes, $[\eta^5$-$(C_5H_4CH_2CH_2PHMes^*)HfCl_3(SMe_2)_2]$ (**Hf-3′**) and $[\eta^5$-$(C_5H_4CH_2CH_2PHMes^*)HfCl_3(tht)_2]$, respectively, both of which are converted into an isolable complex (**Hf-4**) by the reaction with py.

## 3. Concluding remarks

Syntheses of secondary phosphine pendant cyclopentadienyl complexes of Zr and Hf have been reported. Although $[\eta^5{:}\eta^1$-$(C_5R_4CH_2CH_2PPh_2)ZrCl_3]$ has been reported to be prepared by the reaction of $ZrCl_4$ with $Me_3SiC_5H_4CH_2CH_2PPh_2$, the reaction of $ZrCl_4$ with $Me_3SiC_5H_4CH_2CH_2PHR$ did not yield the corresponding $[\eta^5{:}\eta^1$-$(C_5R_4CH_2CH_2PHR)ZrCl_3]$, presumably due to the P–H bond activation by the strong Lewis acidity of the transition metal center. The use of $ZrCl_4(SR''_2)_2$ as a starting complex solved the problem. Secondary phosphine pendant Cp complexes could be obtained, and it was found that the selection of the kind of the $SR''_2$ was important. $ZrCl_4(SMe_2)_2$ reacts with

$Me_3SiC_5H_4CH_2CH_2PHMes$ to give [$\eta^5$:$\eta^1$-($C_5H_4CH_2CH_2PHMes$)$ZrCl_3(SMe_2)$] in situ, but the complex decomposes when the solvent is removed, whereas the reaction of $ZrCl_4(tht)_2$ gives an isolable [$\eta^5$:$\eta^1$-($C_5H_4CH_2CH_2PHMes$)$ZrCl_3(tht)$]. The same results were obtained for the hafnium system.

The bulkiness of the substituent (R) on the secondary phosphine strongly affects the coordination mode of the phosphine moiety in solution. When R is 2,4,6-trimethylphenyl (Mes), the phosphine-coordinated species is stable, when R is 2,4,6-tri-*i*-propyl (Tip), the phosphine-coordinated and -dissociated species are in equilibrium, and when R is 2,4,6-tri-*t*-butylpheyl (Mes*), the phosphine-coordinated species is not observed.

The conversion of these secondary phosphine pendant Cp complexes into phosphide pendant Cp complex by the P–H bond activation is now under investigation.

## 4. Experimental

### 4.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk tube and glove box techniques. All solvents were rigorously dried with an appropriate drying agent. Spiro-[2.4]hepta-4,6-diene [9], $PH_2Mes$ [10], $PH_2Tip$ [11], and $PH_2Mes^*$ [12] were prepared by the literature procedures.

A JEOL LA-300 multinuclear spectrometer was used to obtain $^1$H-, $^{13}$C-, and $^{31}$P-NMR spectra. $^1$H- and $^{13}$C-NMR data were referred to $Si(CH_3)_4$ as an internal standard. $^{31}$P-NMR data were referred to 85% $H_3PO_4$ as an external standard. Elemental analysis data were obtained on a Perkin–Elmer 2400 CHN elemental analyzer. Correct elemental analysis data could not be obtained only for **Zr-4** due to its instability toward air and moisture, but satisfactory spectroscopic data were obtained.

### 4.2. Preparation of $R'_3EC_5H_4CH_2CH_2PHR$ ($R'_3E = Me_3Si$, $R = Mes$ (**Si-1**); $R'_3E = n\text{-}Bu_3Sn$, $R = Mes$ (**Sn-1**); $R'_3E = Me_3Si$, $R = Tip$ (**Si-2**); $R'_3E = n\text{-}Bu_3Sn$, $R = Tip$ (**Sn-2**); $R'_3E = Me_3Si$, $R = Mes^*$ (**Si-3**); $R'_3E = n\text{-}Bu_3Sn$, $R = Mes^*$ (**Sn-3**))

Spiro-[2.4]hepta-4,6-diene (0.51 ml, 5.54 mmol) was added to a solution of LiPHMes (4.98 mmol, prepared from $PH_2Mes$ (4.98 mmol) and *n*-BuLi (4.98 mmol)) in THF (10 ml) at room temperature (r.t.). After stirring overnight, the solution was cooled to −78 °C and treated with TMSCl (0.8 ml, 6.30 mmol). The reaction mixture was allowed to attain to r.t. and stirred for 2 h. The solvent was removed in vacuo, and the residue was extracted with hexane and filtered through Celite. Removal of the solvent afforded a pale brown oil of **Si-1** (1.40 g, 4.93 mmol, 99%). This is an equilibrium mixture of isomers in terms of the $Me_3Si$ and the $CH_2CH_2PHMes$ groups in allylic and vinilic positions. $^1$H-NMR ($\delta$, in $CDCl_3$): 6.91 (s, 2H, *m*-H in Mes), 6.44 (s, 2H, Cp), 6.09 (s, 1H, Cp), 4.31 (dm, $J_{PH} = 218.5$ Hz, 1H, PH), 3.26 (s, 1H, Cp), 2.56 (s, 2H, $CpCH_2$ or $PCH_2$), 2.46 (s, 6H, *o*-Me in Mes), 2.27 (s, 3H, *p*-Me in Mes), 2.02–1.85 (m, 2H, $CpCH_2$ or $PCH_2$), −0.04, −0.05 (s, 9H, $SiMe_3$). $^{31}$P-NMR ($\delta$, in $CDCl_3$) −85.69 (d, $J_{PH} = 217.5$ Hz), −85.97 (d, $J_{PH} = 217.3$ Hz).

A treatment of spiro-[2.4]hepta-4,6-diene (29.67 mmol), LiPHMes (25.80 mmol) in 60 ml of THF, and $Sn(n\text{-}Bu)_3Cl$ (25.80 mmol) in a manner similar to that for **Si-1** resulted in the formation of a pale brown oil of **Sn-1** (13.20 g, 24.77 mmol, 96%). $^1$H-NMR ($\delta$, in $CDCl_3$): 6.90 (s, 2H, *m*-H in Mes), 6.01 (s, 2H, Cp), 5.49 (s, 2H, Cp), 4.33 (dm, $J_{PH} = 218.7$ Hz, 1H, PH), 2.56 (s, 2H, $CpCH_2$ or $PCH_2$), 2.48 (s, 6H, *o*-Me in Mes), 2.27 (s, 3H, *p*-Me in Mes), 2.05–1.86 (m, 2H, $CpCH_2$ or $PCH_2$), 1.49–0.71 (m, 27H, $Sn(n\text{-}Bu_3)$). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −85.13 (d, $J_{PH} = 217.5$ Hz), −85.19 (d, $J_{PH} = 219.9$ Hz).

A treatment of spiro-[2.4]hepta-4,6-diene (90.30 mmol), LiPHTip (60.20 mmol) in 150 ml of THF, and TMSCl (88.20 mmol) in a manner similar to that for **Si-1** resulted in the formation of a colorless oil of **Si-2** (22.59 g, 56.59 mmol, 94%). $^1$H-NMR ($\delta$, in $CDCl_3$): 7.08 (d, $J_{PH} = 2.0$ Hz, 2H, *m*-H in Tip), 6.49–6.15 (br m, 3H, Cp), 4.34 (dm, $J_{PH} = 216.0$ Hz, 1H, PH), 3.71 (m, 2H, *o*-C*H*$Me_2$ in Tip), 3.31 (s, 1H Cp), 2.92 (m, 1H, *p*-C*H*$Me_2$ in Tip), 2.65 (br s, 2H, $CpCH_2$ or $PCH_2$), 2.11–1.89 (m, 2H, $CpCH_2$ or $PCH_2$), 1.35–1.26 (m, 18H, $CH(CH_3)_2$ in Tip), 0.00 (s, 9H, TMS). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −92.39 (d, $J_{PH} = 215.1$ Hz), −92.78 (d, $J_{PH} = 213.8$ Hz), −93.31 (d, $J_{PH} = 213.8$ Hz), −93.72 (d, $J_{PH} = 222.3$ Hz).

A treatment of spiro-[2.4]hepta-4,6-diene (94.80 mmol), LiPHTip (63.20 mmol) in 150 ml of THF, and $Sn(n\text{-}Bu)_3Cl$ (63.20 mmol) in a manner similar to that for **Si-1** resulted in the formation of a yellow oil of **Sn-2** (38.00 g, 61.30 mmol, 97%). $^1$H-NMR ($\delta$, in $CDCl_3$): 7.04 (d, $J_{PH} = 2.0$ Hz, 2H, *m*-H in Tip), 6.06 (m, 2H, Cp), 5.48 (m, 2H, Cp), 4.32 (dm, $J_{PH} = 216.3$ Hz, 1H, PH), 3.69 (m, 2H, *o*-C*H*$Me_2$ in Tip), 2.88 (m, 1H, *p*-C*H*$Me_2$ in Tip), 2.65 (m, 2H, $CpCH_2$ or $PCH_2$), 2.08–1.87 (m, 2H, $CpCH_2$ or $PCH_2$), 1.55–0.74 (m, 45H, $Sn(n\text{-}Bu)_3$ and $CH(CH_3)_2$ in Tip). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −92.09 (d, $J_{PH} = 216.3$ Hz), −92.96 (d, $J_{PH} = 219.9$ Hz), −93.43 (d, $J_{PH} = 216.3$ Hz).

A treatment of spiro-[2.4]hepta-4,6-diene (3.95 mmol), LiPHMes* (2.67 mmol) in 10 ml of THF, and TMSCl (3.95 mmol) in a manner similar to that for **Si-1** resulted in the formation of a pale yellow oil of **Si-3** (1.07 g, 2.59 mmol, 97%). $^1$H-NMR ($\delta$, in $CDCl_3$): 7.37

(m, 2H, *m*-H in Mes*), 6.39–6.04 (m, 3H, Cp), 4.83 (dm, $J_{PH} = 221.4$ Hz, 1H, PH), 3.21 (s, 1H Cp), 2.65–2.47 (m, 2H, $CpCH_2$ or $PCH_2$), 2.10–1.87 (m, 2H, $CpCH_2$ or $PCH_2$), 1.35, 1.34, 1.31, 1.29 (s, 27H, $C(CH_3)_3$ in Mes*), −0.06, −0.07 (s, 9H, $Si(CH_3)_3$). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −72.16 (d, $J_{PH} = 220.0$ Hz), −72.59 (d, $J_{PH} = 219.9$ Hz), −73.06 (d, $J_{PH} = 217.5$ Hz).

A treatment of spiro-[2.4]hepta-4,6-diene (46.50 mmol), LiPHMes* (31.00 mmol) in 100 ml of THF, and $Sn(n\text{-}Bu)_3Cl$ (31.00 mmol) in a manner similar to that for **Si-1** resulted in the formation of an orange oil of **Sn-3** (19.02 g, 28.83 mmol, 93%). $^1$H-NMR ($\delta$, in $CDCl_3$): 7.36 (m, 2H, *m*-H in Mes*), 5.98 (m, 2H, Cp), 5.42 (m, 2H, Cp), 4.84 (dm, $J_{PH} = 221.3$ Hz, 1H, PH), 2.61–2.38 (m, 2H, $CpCH_2$ or $PCH_2$), 1.84–1.55 (m, 2H, $CpCH_2$ or $PCH_2$), 1.58, 1.34, 1.29 (s, 27H, $C(CH_3)_3$ in Mes*), 1.44–0.69 (m, 27H, $Sn(n\text{-}Bu)_3$). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −71.95 (d, $J_{PH} = 219.9$ Hz), −72.55 (d, $J_{PH} = 217.5$).

### 4.3. Preparation of [$\eta^5$:$\eta^1$-($C_5H_4CH_2CH_2PHMes$)-$MCl_3(tht)$] (M = Zr (**Zr-1**), Hf (**Hf-1**))

THT (0.199 g, 2.258 mmol) was added to a suspension of $ZrCl_4$ (0.263 g, 1.129 mmol) in 5 ml of toluene at r.t. The reaction mixture was immediately changed into a clear solution, and then treated with **Si-1** (0.357 g, 1.129 mmol) in 3 ml of toluene. After stirring overnight at 80 °C to complete the reaction, the reaction mixture was concentrated in vacuo. The white residue was washed with hexane–toluene = 1/2, and dried in vacuo to give a white powder of **Zr-1** (0.947 g, 0.95 mmol, 84%). $^1$H-NMR ($\delta$, in $C_6D_6$): 6.68 (s, 2H, *m*-H in Mes), 6.63 (s, 1H, Cp), 6.54 (s, 1H, Cp), 6.42 (s, 1H, Cp), 6.34 (s, 1H, Cp), 5.05 (d, $J_{PH} = 325.2$ Hz, 0.5H, PH), 5.01 (d, $J_{PH} = 324.5$ Hz, 0.5H, PH), 3.03 (m, 4H, tht), 2.60 (m, 2H, $CpCH_2$ or $PCH_2$), 2.47 (s, 6H, *o*-$CH_3$ in Mes), 2.02 (s, 3H, *p*-$CH_3$ in Mes), 1.95 (m, 2H, $CpCH_2$ or $PCH_2$), 1.50 (m, 4H, tht). $^{13}$C-NMR ($\delta$, in $C_6D_6$): 141.86 (d, $J_{PC} = 8.7$ Hz, *ipso*-C or *p*-C in Mes or 1-C in Cp), 139.96 (s, *o*-C in Mes), 130.10 (d, $J_{PC} = 6.9$ Hz, *m*-C in Mes), 128.10 (s, *ipso*-C or *p*-C in Mes or 1-C in Cp), 127.79 (s, *ipso*-C or *p*-C in Mes or 1-C in Cp), 123.15 (s, Cp), 120.11 (s, Cp), 117.60 (s, Cp), 115.70 (s, Cp), 36.24 (s, tht), 30.46 (s, tht), 27.60 (d, $J_{PC} = 17.4$ Hz, $CpCH_2$ or $PCH_2$), 25.76 (d, $J_{PC} = 11.8$ Hz, $CpCH_2$ or $PCH_2$), 24.06 (m, *o*-$CH_3$ in Mes), 20.84 (s, *p*-$CH_3$ in Mes). $^{31}$P-NMR ($\delta$, in $C_6D_6$): −22.60 (d, $J_{PH} = 329.3$ Hz), −22.93 (d, $J_{PH} = 329.3$ Hz).

A treatment of $HfCl_4$ (0.475 g, 1.483 mmol) in 10 ml of toluene, THT (0.262 g, 2.966 mmol), and **Sn-1** (0.791 g, 1.483 mmol) in 3 ml of toluene in a manner similar to that for **Zr-1** resulted in the formation of a white powder of **Hf-1** (0.802 g, 1.30 mmol, 88%). Anal. Found: C, 38.75; H, 4.70. Calc. for $C_{20}H_{28}Cl_3HfPS$: C, 38.98; H, 4.58%. $^1$H-NMR ($\delta$, in $C_6D_6$): 6.67 (s, 2H, *m*-H in Mes), 6.51 (s, 1H, Cp), 6.38 (s, 1H, Cp), 6.25 (s, 1H, Cp), 6.20 (s, 1H, Cp), 5.06 (dm, $J_{PH} = 324.4$ Hz, 0.5H, PH), 5.02 (dm, $J_{PH} = 327.4$ Hz, 0.5H, PH), 2.99 (m, 4H, tht), 2.60 (m, 2H, $CpCH_2$ or $PCH_2$), 2.47 (s, 6H, *o*-$CH_3$ in Mes), 2.02 (s, 3H, *p*-$CH_3$ in Mes), 1.90 (m, 2H, $CpCH_2$ or $PCH_2$), 1.48 (m, 4H, tht). $^{13}$C-NMR ($\delta$, in $C_6D_6$): 141.95 (d, $J_{PC} = 8.1$ Hz, *ipso*-C or *p*-C in Mes or 1-C in Cp), 140.07 (s, *o*-C in Mes), 130.16 (m, *m*-C in Mes), 128.11 (s, *ipso*-C or *p*-C in Mes or 1-C in Cp), 127.78 (s, *ipso*-C or *p*-C in Mes or 1-C in Cp), 120.45 (s, Cp), 117.52 (s, Cp), 116.02 (s, Cp), 113.57 (s, Cp), 35.30 (s, tht), 30.57 (s, tht), 27.38 (d, $J_{PC} = 19.2$ Hz, $CpCH_2$ or $PCH_2$), 25.33 (d, $J_{PC} = 10.6$ Hz, $CpCH_2$ or $PCH_2$), 24.04 (m, *o*-$CH_3$ in Mes), 20.80 (s, *p*-$CH_3$ in Mes). $^{31}$P-NMR ($\delta$, in $C_6D_6$): −18.75 (d, $J_{PH} = 332.9$ Hz), −19.05 (d, $J_{PH} = 329.3$ Hz).

### 4.4. Preparation of [$\eta^5$:$\eta^1$-($C_5H_4CH_2CH_2PHTip$)-$MCl_3(tht)$] (M = Zr (**Zr-2**), Hf (**Hf-2**))

A treatment of $ZrCl_4$ (1.32 mmol), THT (2.64 mmol) in 9 ml of toluene, and **Si-2** (1.32 mmol) in 3 ml of toluene in a manner similar to that for **Zr-1** resulted in the formation of a white powder of **Zr-2** (0.58 g, 0.95 mmol, 72%). Anal. Found: C, 51.12; H, 6.47. Calc. for $C_{26}H_{40}Cl_3PSZr$: C, 50.92; H, 6.57%. $^1$H-NMR ($\delta$, in $C_6D_6$): 7.15 (d, $J_{PH} = 2.9$ Hz, 2H, *m*-H in Tip), 6.62 (s, 1H, Cp), 6.49 (s, 1H, Cp), 6.39 (s, 2H, Cp), 5.16 (dm, $J_{PH} = 320.7$ Hz, 1H, PH), 3.51 (m, 2H, *o*-$CH(CH_3)_2$ in Tip), 3.04 (m, 4H, tht), 2.69 (m, 1H, *p*-$CH(CH_3)_2$ in Tip), 2.60 (m, 2H, $CpCH_2$ or $PCH_2$), 2.03 (m, 2H, $CpCH_2$ or $PCH_2$), 1.51 (m, 4H, tht), 1.43–1.27 (m, 12H, *o*-$CH(CH_3)_2$ in Tip), 1.12 (d, $J_{HH} = 6.8$ Hz, 6H, *p*-$CH(CH_3)_2$ in Tip). $^{31}$P-NMR ($\delta$, in $C_6D_6$): −22.71 (d, $J_{PH} = 319.5$ Hz), −23.02 (d, $J_{PH} = 319.5$ Hz).

A treatment of $HfCl_4$ (2.08 mmol), THT (4.16 mmol) in 15 ml of toluene, and **Sn-2** (2.08 mmol) in 3 ml of toluene in a manner similar to that for **Hf-1** resulted in the formation of a white powder of **Hf-2** (1.15 g, 1.64 mmol, 79%). Anal. Found: C, 44.72; H, 5.53. Calc. for $C_{26}H_{40}Cl_3HfPS$: C, 44.58; H, 5.76%. $^1$H-NMR ($\delta$, in $C_6D_6$): 7.15 (d, $J_{PH} = 2.4$ Hz, 2H, *m*-H in Tip), 6.53 (s, 1H, Cp), 6.39 (s, 1H, Cp), 6.31 (s, 2H, Cp), 5.14 (d, $J_{PH} = 318.6$ Hz, 1H, PH), 3.52 (br, 2H, *o*-$CH(CH_3)_2$ in Tip), 3.01 (m, 4H, tht), 2.69 (m, 1H, *p*-$CH(CH_3)_2$ in Tip), 2.62 (br, 2H, $CpCH_2$ or $PCH_2$), 2.15 (br, 2H, $CpCH_2$ or $PCH_2$), 1.49 (m, 4H, tht), 1.36 (br, 12H, *o*-$CH(CH_3)_2$ in Tip), 1.13 (d, $J_{HH} = 7.0$ Hz, 6H, *p*-$CH(CH_3)_2$ in Tip). $^{31}$P-NMR ($\delta$, in $C_6D_6$): −19.51 (d, $J_{PH} = 330.5$ Hz).

### 4.5. Preparation of [$\eta^5$-($C_5H_4CH_2CH_2PHMes^*$)-$MCl_3py_2$] (M = Zr (**Zr-4**), Hf (**Hf-4**))

$SMe_2$ (1.231 g, 19.82 mmol) was added to a suspension of $ZrCl_4$ (2.309 g, 9.91 mmol) in 70 ml of toluene

at r.t., and then **Si-3** (4.39 g, 9.91 mmol) in 3 ml of toluene was added. After the reaction mixture was stirred overnight at 80 °C to complete the reaction, pyridine (3.14 g, 39.64 mmol) was added at r.t. and the solution was stirred for 1 h. The solvent was removed in vacuo to give a white residue, which then was washed with hexane–toluene = 4/1, followed by dying in vacuo to yield a white powder of **Zr-4** (6.54 g, 9.02 mmol, 91%). Anal. Found: C, 57.84; H, 6.49; N, 4.01. Calc. for $C_{35}H_{48}Cl_3N_2PZr$: C, 57.96; H, 6.67; N, 3.86%. $^1$H-NMR ($\delta$, in $CDCl_3$): 8.98 (br, 4H, py), 7.79 (br, 2H, py), 7.36 (s, 2H, *m*-H in Mes*), 7.26 (br, 4H, py), 6.45 (s, 2H, Cp), 6.37 (s, 2H, Cp), 4.81 (dm, $J_{PH} = 221.1$ Hz, 1H, PH), 2.95–2.85 (m, 2H, $CpCH_2$ or $PCH_2$), 1.93–1.64 (m, 2H, $CpCH_2$ or $PCH_2$), 1.55 (s, 18H, *o*-$C(CH_3)_3$ in Mes*), 1.30 (s, 9H, *p*-$C(CH_3)_3$ in Mes*). $^{13}$C-NMR ($\delta$, in $CDCl_3$): 154.36 (d, $J_{PC} = 7.5$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 152.04 (s, py), 148.94 (s, *o*-C in Mes*), 138.49 (br, py), 134.92 (d, $J_{PC} = 11.8$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 132.97 (d, $J_{PC} = 29.2$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 124.01 (br, py), 121.97 (d, $J_{PC} = 3.7$ Hz, *m*-C in Mes*), 119.65 (s, Cp), 119.56 (s, Cp), 38.30 (s, $CpCH_2$ or $PCH_2$), 34.85 (s, *o*-$C(CH_3)_3$ in Mes*), 33.57, 33.47 (s, *o*-$C(CH_3)_3$ in Mes*), 31.54 (s, *p*-$C(CH_3)_3$ in Mes*), 31.26 (s, *p*-$C(CH_3)_3$ in Mes*), 29.40–28.85 (m, $CpCH_2$ or $PCH_2$). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −73.46 (d, $J_{PH} = 219.9$ Hz).

A treatment of $HfCl_4$ (8.88 mmol), $SMe_2$ (17.76 mmol) in 70 ml of toluene, and **Sn-3** (8.88 mmol) in 3 ml of toluene in a manner similar to that for **Zr-4** resulted in the formation of a white powder of **Hf-4** (6.42 g, 7.90 mmol, 89%). Anal. Found: C, 52.01; H, 6.12; N, 3.47. Calc. for $C_{35}H_{48}Cl_3HfN_2P$: C, 51.73; H, 5.95; N, 3.45%. $^1$H-NMR ($\delta$, in $CDCl_3$): 9.18–8.89 (br, 4H, py), 7.83 (br, 2H, py), 7.38 (br, 4H, py), 7.36 (s, 2H, *m*-H in Mes*), 6.26 (s, 2H, Cp), 6.19 (s, 2H, Cp), 4.81 (dm, $J_{PH} = 220.2$ Hz, 1H, PH), 3.01–2.83 (m, 2H, $CpCH_2$ or $PCH_2$), 1.89–1.71 (m, 2H, $CpCH_2$ or $PCH_2$), 1.55 (s, 18H, *o*-$C(CH_3)_3$ in Mes*), 1.29 (s, 9H, *p*-$C(CH_3)_3$ in Mes*). $^{13}$C-NMR ($\delta$, in $CDCl_3$): 154.29 (d, $J_{PC} = 7.4$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 152.18 (br, py), 148.96 (br, py), 148.86 (s, *o*-C in Mes*), 139.48 (s, py), 133.04 (d, $J_{PC} = 28.5$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 132.06 (d, $J_{PC} = 11.1$ Hz, *ipso*-C or *p*-C in Mes* or 1-C in Cp), 124.31 (br, py), 121.92 (d, $J_{PC} = 3.1$ Hz, *m*-C in Mes*), 117.49 (s, Cp), 117.25 (s, Cp), 38.27 (s, $CpCH_2$ or $PCH_2$), 34.81 (s, *o*-$C(CH_3)_3$ in Mes*), 33.54 (s, *o*-$C(CH_3)_3$ in Mes*), 33.45 (s, *o*-$C(CH_3)_3$ in Mes*), 31.51 (s, *p*-$C(CH_3)_3$ in Mes*), 31.24 (s, *p*-$C(CH_3)_3$ in Mes*), 29.61–28.60 (m, $CpCH_2$ or $PCH_2$). $^{31}$P-NMR ($\delta$, in $CDCl_3$): −73.36 (d, $J_{PH} = 221.1$ Hz).

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## References

[1] H. Butenschön, Chem. Rev. 100 (2000) 1527.
[2] L.J. Farrugia, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Pergamon, 1995 Chapter 4.
[3] (a) W. Malisch, U.-A. Hirth, K. Grün, M. Schmeußer, J. Organomet. Chem. 572 (1999) 207;
(b) W. Malisch, N. Gunzelmann, K. Thirase, M. Neumayer, J. Organomet. Chem. 571 (1998) 215.
[4] (a) C.H. Winter, X.X. Zhou, D.A. Dobbs, M.J. Heeg, Organometallics 10 (1991) 210;
(b) A. Martin, M. Mena, F. Paracios, J. Organomet. Chem. 480 (1994) C10.
[5] (a) D.P. Krut'ko, M.V. Borzov, E.N. Veksler, A.V. Churakov, J.A.K. Howard, Polyhedron 17 (1998) 3889;
(b) D.P. Krut'ko, M.V. Borzov, E.N. Veksler, R.S. Kirsanov, A.V. Churakov, Eur. J. Inorg. Chem. (1999) 1973.
[6] T. Koch, E. Hey-Hawkins, Polyhedron 18 (1999) 2113.
[7] A. Döhring, V.R. Jensen, P.W. Jolly, W. Thiel, J.C. Weber, Organometallics 20 (2001) 2234.
[8] E.C. Lund, T. Livinghouse, Organometallics 9 (1990) 2426.
[9] C.F. Wilcox Jr., R.R. Craig, J. Am. Chem. Soc. 83 (1961) 3866.
[10] T.C. Jempty, K.A.Z. Gogins, Y. Mazur, L.L. Miller, J. Org. Chem. 46 (1981) 4545.
[11] Y. Winkel, H.M.M. Bastiaans, F. Bickelhaupt, J. Organomet. Chem. 405 (1991) 183.
[12] A.H. Clowley, N.C. Norman, M. Pakulski, G. Becker, M. Layh, E. Kirchner, M. Schmidt, Inorg. Synth. 27 (1990) 235.