Synthesis and Characterization of Some Zirconium and Hafnium Complexes with a Phosphide-Pendant Cyclopentadienyl Ligand

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Synthesis of some Zr and Hf complexes with a phosphide-pendant cyclopentadienyl ligand was attempted via alkylation (tribenzylation, triallylation, or monotritylation) of the secondary phosphine-pendant trichloride complex [{η^5-$C_5H_4(CH_2)_2$P(H)Mes-κP}MCl_3(tht)] (**Zr-1**, **Hf-1**; Mes = 2,4,6-trimethylphenyl; tht = tetrahydrothiophene). The phosphide-pendant dibenzyl complex [{η^5-$C_5H_4(CH_2)_2$PMes-κP}$M(CH_2Ph)_2$] (**Zr-5**, **Hf-5**) and the phosphide-pendant diallyl complex [{η^5-$C_5H_4(CH_2)_2$PMes-κP}M(allyl)$_2$] (**Zr-7**, **Hf-7**) were successfully prepared through tribenzylation followed by thermolysis and through triallylation, respectively, of **Zr-1** or **Hf-1**. The phosphide-pendant dichloride complex [{η^5-$C_5H_4(CH_2)_2$PMes-κP}MCl_2(*N*-methylimidazole)$_2$] (**Zr-13**, **Hf-13**) was also obtained through monotritylation of **Zr-1** or **Hf-1** followed by the treatment with *N*-methylimidazole, and the X-ray crystal structure of **Zr-13** was determined. In addition, the allyl-chloride exchange reaction between 1 equiv of **Hf-1** and 2 equiv of **Hf-7** gave the unstable phosphide-pendant monoallyl monochloride Hf complex [{η^5-$C_5H_4(CH_2)_2$PMes-κP}HfCl(allyl)] (**Hf-8**), which was characterized as its derivatives [{η^5-$C_5H_4(CH_2)_2$PMes-κP}Hf(Y)(allyl)] (Y = C_6F_5, **Hf-14**; Y = NPh_2, **Hf-15**; Y = NEt_2, **Hf-16**). It is proposed that the η^3-alkyl-like ligand (benzyl, allyl, or trityl) in the secondary phosphine-pendant complex serves as an effective H-abstracting group to generate the corresponding phosphide-pendant complex with liberation of the alkyl-H coupling product.

Introduction

The chemistry of transition metal (M) compounds having covalent bonds with heteroatom ligands (E) is an interesting subject, since they have the potential to exhibit novel reactivities which arise from their unique M−E bonds.[1] Additionally, such heteroatom ligands often play a subtle role as an ancillary ligand to control the reactivities, in particular for the early transition metal complexes, which often survive as a less-than-18 electron species. Most of the early transition metal complexes reported so far have covalent bonds to hard heteroligands such as alkoxy and dialkylamide groups. They obey the HSAB principle, are relatively stable, and so are amenable to detailed studies. In contrast, less common are early transition metal complexes with soft ligands, especially phosphide ligands, which are phosphorus analogues of hard amide ligands.[2−5] These complexes are antagonistic to the HSAB principle, often have difficulties in preparation, and so have not yet been studied fully. Recently, there has been a growing interest in the phosphide analogues (**A**,[3f,h] **B**,[3f−h] and **C**[4d]) of the amide-pendant cyclopentadienyl complexes [(η^5-$C_5Me_4SiMe_2N^tBu$-κN)TiL_2] (L = Cl, alkyl group) called constrained-geometry catalysts (CGC)[6] (**D**), which are effective in olefin copolymerization (Chart 1), be-

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(1) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*; Wiley-VCH: Weinheim, 1998; Vol. 2.

(2) For reviews and examples of phosphide group 4 metallocene complexes: (a) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661, and references therein. (b) Hey-Hawkins, E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 4, pp 501−542. (c) Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 314. (d) Issleib, K.; Häckert, H. *Z. Naturforsch. Teil B* **1966**, *21*, 519. (e) Chiang, M. Y.; Gambarotta, S.; Bolhuis, F. *Organometallics* **1988**, *7*, 1864. (f) Ho, J.; Stephan, D. W. *Organometallics* **1991**, *10*, 3001. (g) Nielsen-Marsh, S.; Crowte, R. J.; Edwards, P. G. *J. Chem. Soc., Chem. Commun.* **1992**, 699. (h) Ho, J.; Stephan, D. W. *Organometallics* **1992**, *11*, 1014. (i) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145. (j) Köpf, H.; Richtering, V. *J. Organomet. Chem.* **1988**, *346*, 355. (k) Hey, E. *J. Organomet. Chem.* **1989**, *378*, 375. (l) Vaughan, G. A.; Hillhouse G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760. (m) Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 994. (n) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *Polyhedron* **1988**, *7*, 2083.

(3) For examples of phosphide group 4 nonmetallocene complexes: (a) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (b) Danopoulos, A. A.; Edwards, P. G.; Harman, M.; Hursthouse, M. B.; Parry, J. S. *J. Chem. Soc., Dalton Trans.* **1994**, 977. (c) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. (d) Frenzel, C.; Hey-Hawkins, E.; Müller, U.; Strenger, I. *Z. Anorg. Allg. Chem.* **1997**, *623*, 277. (e) Firth, A. V.; Stephan, D. W. *Inorg. Chem.* **1998**, *37*, 4732. (f) Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181. (g) Schottek, J.; Erker, G.; Kunz, K.; Doering, S. PCT Int. Appl. 2001, p 69. (h) Altenhoff, G.; Bredeau, S.; Erker, G.; Kehr, G.; Kataeva, O.; Fröhlich, R. *Organometallics* **2002**, *21*, 4084. (i) Driess, M.; Aust, J.; Merz, K. *Eur. J. Inorg. Chem.* **2002**, 2961.

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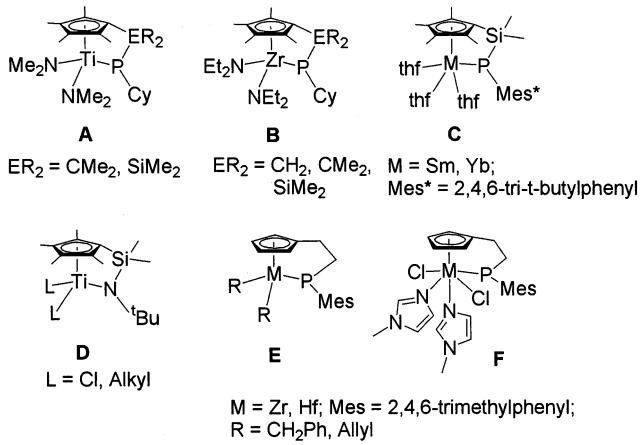
Chart 1

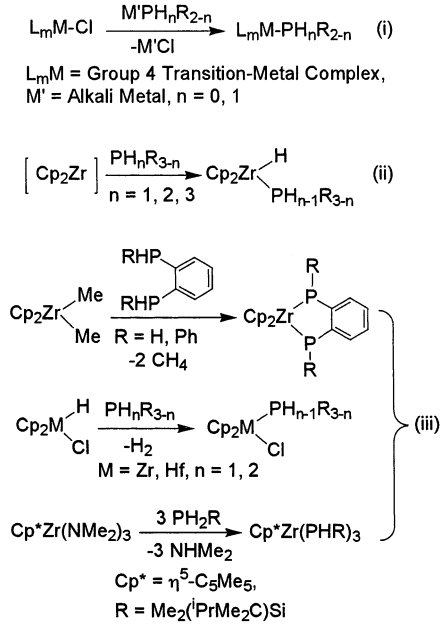


cause such phosphide complexes are expected to have unique reactivities based on the M−P covalent bonds. We report here the synthesis and the characterization of the dialkyl (benzyl and allyl) (**E**) and dichloride (**F**) complexes of Zr and Hf with an ethylene-linked phosphide-cyclopentadienyl ligand and some related complexes.

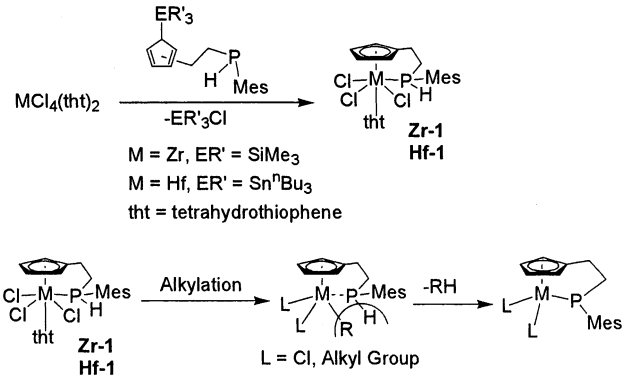
Results and Discussion

Although the first phosphide complex of a group 4 transition metal has been reported by Issleib et al. in 1966,[2d] the synthetic methods have not yet been established enough to obtain various phosphide complexes for the purpose. Most of the phosphide complexes reported for group 4 transition metals are limited to bis(cyclopentadienyl) compounds,[2] and there are only a few reports on nonmetallocene type phosphide complexes.[3] Most of the synthetic methods reported are classified into three groups;[2a−c] (Scheme 1) (i) the salt-elimination reaction of a group 4 transition metal chloride complex (L_mMCl) with an alkali-metal phosphide ($M'PH_nR_{2-n}$, $n = 0, 1$), (ii) the oxidative addition of a P−H-functionalized phosphine PH_nR_{3-n} ($n = 1, 2, 3$) to a divalent metallocene complex,[2e−i] and (iii) the reaction of a metallocene dialkyl complex with a P−H-functionalized diphosphine (1,2-$(PHPh)_2C_6H_4$ or 1,2-$(PH_2)_2C_6H_4$)[2j−k] or the similar reaction of a hydride or an amide complex with a P−H-functionalized phosphine.[2i,l,3i] The phosphide complexes have been prepared almost exclusively by the first salt-elimination reaction (i). So, we at first applied the conventional method (i) to the preparation of the desired phosphide-pendant cyclopentadienyl complex. However, the reaction of MCl_4 (M = Zr, Hf) with the dilithio ligand $Li_2C_5H_4(CH_2)_2PMes$ (Mes = 2,4,6-trimethylphenyl) did not give any products of the [{η^5-$C_5H_4(CH_2)_2$PMes-κP}MCl_2] type, in accordance with the results obtained recently by Hey-Hawkins et al. and Erker et al. in the similar reactions of $ZrCl_4$ with $Li_2C_5Me_4SiMe_2PR$ (R = Mes, Cy).[3h,7d]

Scheme 1



Scheme 2



Next, we focused on method (iii), since the starting alkyl complexes were readily available. The synthetic route adopted consists of two steps (Scheme 2), i.e., preparation of a trichloride complex with a secondary phosphine-pendant cyclopentadienyl ligand[7] and its subsequent alkylation leading to the desired phosphide complex with liberation of a coupling product RH. The synthesis of the secondary phosphine-pendant trichloride complexes [{η^5-$C_5H_4(CH_2)_2$P(H)Mes-κP}MCl_3(tht)] (**Zr-1**, **Hf-1**; tht = tetrahydrothiophene) has been reported in our previous paper.[7e]

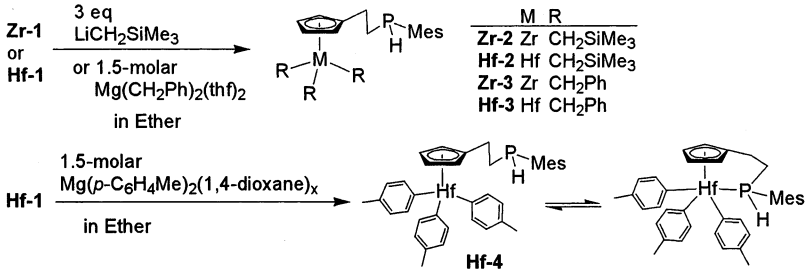
(4) For examples of phosphide group 3 transition metal complexes: (a) Cendrowski-Guillaume, S. M.; Ephritikhine, M. *J. Organomet. Chem.* **1999**, *577*, 161. (b) Clegg, W.; Izod, K.; Liddle, S. T. *J. Organomet. Chem.* **2000**, *613*, 128. (c) Clegg, W.; Izod, K.; Liddle, S. T.; O'Shaughnessy, P.; Sheffield, J. M. *Organometallics* **2000**, *19*, 2090. (d) Tardif, O.; Hou, Z.; Nishiura, M.; Koizumi, T.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 4565.

(5) For examples of phosphide group 5 transition metal complexes: (a) Domaille, P. J.; Foxman, B. M.; McNeese, T. J.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4114. (b) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830. (c) Alcalde, M. I.; Mata, J.; Gòmez, M.; Royo, P.; Sánchez, F. *J. Organomet. Chem.* **1995**, *492*, 151. (d) Nikonov, G. I.; Kuzmina, L. G.; Mountford, P.; Lemenovskii, D. A. *Organometallics* **1995**, *14*, 3588. (e) Hadi, G. A. A.; Fromm, K.; Blaurock, S.; Jelonek, S.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 721.

(6) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587, and references therein.

(7) For examples of related complexes having phosphine-pendant cyclopentadienyl ligands: (a) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527, and references therein. (b) Krut'ko, D. P.; Borzov, M. V.; Veksler, E. N.; Churakov, A. V.; Howard, J. A. K. *Polyhedron* **1998**, *17*, 3889. (c) Koch, T.; Hey-Hawkins, E. *Polyhedron* **1999**, *18*, 2113. (d) Koch, T.; Blaurock, S.; Somoza, F. B., Jr.; Voigt, A.; Kirmse, R.; Hey-Hawkins, E. *Organometallics* **2000**, *19*, 2556. (e) Ishiyama, T.; Nakazawa, H.; Miyoshi, K. *J. Organomet. Chem.* **2002**, *648*, 231. (f) Höcher, T.; Blaurock, S.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2002**, 1174.

Scheme 3

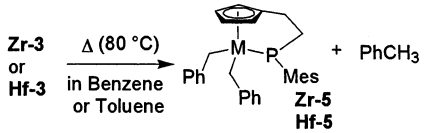


Trialkylation of the Secondary Phosphine Trichloride Complex. The secondary phosphine-pendant trichloride complex (**Zr-1**, **Hf-1**) was subjected to trialkylation and triarylation. First, **Zr-1** or **Hf-1** was allowed to react with 1.5 M $MgMe_2$ or $MgEt_2$ in ether, but some complicated reactions took place to give intractable products. Next, we used bulkier alkylation and arylation reagents such as $LiCH_2SiMe_3$, $Mg(CH_2Ph)_2(thf)_2$, and $Mg(p\text{-}C_6H_4Me)_2(1,4\text{-dioxane})_x$ (Scheme 3). The reaction with 3 equiv of $LiCH_2SiMe_3$ or 1.5 M $Mg(CH_2Ph)_2(thf)_2$ proceeded cleanly, in contrast with that with $MgMe_2$ or $MgEt_2$, to give a brown, oily complex. In the ^{31}P NMR spectra without proton irradiation, the four products commonly showed a doublet at −86 to −87 ppm (J_{PH} = 215−218 Hz), which is close in chemical shift to that of the metal-free secondary phosphine-pendant cyclopentadienyl compound $Me_3SiC_5H_4(CH_2)_2P(H)Mes$ (−85.7 ppm (J_{PH} = 218 Hz), −86.0 ppm (J_{PH} = 217 Hz)).[7e] This suggests that the secondary phosphine-pendant is not coordinated to the metal center in any of the four products. On the basis of the ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra, the products were identified as tris(trimethylsilylmethyl) complexes (**Zr-2**, **Hf-2**) and tribenzyl complexes (**Zr-3**, **Hf-3**), with the secondary phosphine-pendant freed from the metal center. The tribenzyl complex (**Zr-3**, **Hf-3**) decomposed slowly in solution when it was concentrated at room temperature, to afford intractable complexes.

The triarylation reaction of **Hf-1** with 1.5 M $Mg(p\text{-}C_6H_4Me)_2(1,4\text{-dioxane})_x$ (Scheme 3) gave a yellow powder, which was identified by the ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra as the corresponding secondary phosphine-pendant tri(p-C_6H_4Me) Hf complex (**Hf-4**). In contrast, the similar triarylation of **Zr-1** led to complicated reactions, giving no desired tri(p-C_6H_4Me) Zr complex. In the ^{31}P NMR spectrum under off-resonance conditions, **Hf-4** showed a broad doublet at −67.9 ppm (J_{PH} = 243 Hz) at 25 °C in toluene. With lowering the temperature, the signal became split; at −80 °C, **Hf-4** showed two broad doublets at −21.0 ppm (J_{PH} = 314 Hz) and −84.6 ppm (J_{PH} = 211 Hz). The former is close in chemical shift to that of **Hf-1**, having a definite Hf−P−H bond (−18.8 ppm (J_{PH} = 333 Hz), −19.1 ppm (J_{PH} = 329 Hz)), and the latter is close to that of the free secondary phosphine ligand (vide supra).[7e] The variable-temperature ^{31}P NMR spectra suggest that **Hf-4** exists as a dynamic mixture of the secondary phosphine-coordinated and -uncoordinated species in toluene.

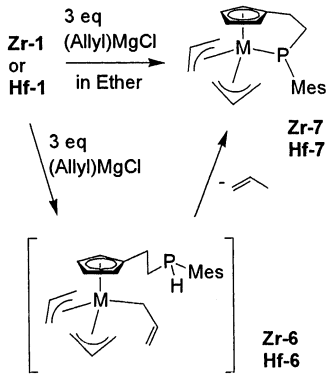
Next, we attempted to convert the trialkyl complexes thus obtained (**Zr-2**, **Hf-2**, **Zr-3**, **Hf-3**) into the corresponding phosphide complexes by thermolysis. The tris(trimethylsilylmethyl) complex (**Zr-2**, **Hf-2**) was heated at 80 °C for several days in toluene. However, any reaction except decomposition did not occur, probably because the bulky trimethylsilylmethyl groups prevented the secondary phosphine from approaching the metal center. In contrast, the tribenzyl complex (**Zr-3**, **Hf-3**) successfully afforded the dibenzyl phosphide complex (**Zr-5**, **Hf-5**) with liberation of $PhCH_3$ in benzene or toluene at 80 °C (Scheme 4). The thermolysis in C_6D_6 was monitored by the ^{31}P and ^1H NMR spectra. In the ^{31}P NMR spectrum without proton irradiation, a singlet at 126.0 ppm for **Zr-5** and at 111.2 ppm for **Hf-5** newly appeared at the expense of a doublet due to the starting complex (−86.9 ppm (J_{PH} = 215 Hz) for **Zr-3** and −86.8 ppm (J_{PH} = 215 Hz) for **Hf-3**). The spectral change for the Zr complex was completed within 20 min, and that for the Hf complex was accomplished after 4 h. These ^{31}P NMR data indicate the formation of the M−P covalent bond with the P−H bond instead lost. In the ^1H NMR spectrum, a doublet of multiplets due to the P−H proton of the starting complex (4.45 ppm for **Zr-3** and 4.39 ppm for **Hf-3**) disappeared and signals assignable to toluene appeared (7.13−7.04 ppm (5H) and 2.16 ppm (3H)). The methylene protons of the benzyl groups, which had appeared as a singlet at 1.63 ppm (6H) for **Zr-3** and at 1.72 ppm (6H) for **Hf-3**, shifted to 2.23 ppm (4H) for **Zr-5** and to 2.35 ppm (4H) for **Hf-5**. These ^1H NMR data are consistent with nearly quantitative formation of the dibenzyl phosphide complex (**Zr-5**, **Hf-5**) together with an equimolar amount of toluene. **Zr-5** and **Hf-5** decomposed slowly in solution and could not be isolated as a solid. The thermolysis of the tri(p-C_6H_4Me) Hf complex (**Hf-4**) was also examined in toluene, but it led only to decomposition even at 40 °C.

Scheme 4



The above results prompted us to seek other trialkylation reagents to afford isolable phosphide complexes, and it was found that triallylation was particularly effective (Scheme 5). The reaction of **Zr-1** or **Hf-1** with 3 equiv of (allyl)MgCl in ether/THF at room temperature resulted in direct and almost quantitative formation of the isolable diallyl phosphide complex [{η^5-$C_5H_4(CH_2)_2$-PMes-κP}M(allyl)$_2$] (**Zr-7**, 79%; **Hf-7**, 89%). In this reaction, the triallyl secondary phosphine-pendant complex [{η^5-$C_5H_4(CH_2)_2P(H)Mes$}M(allyl)$_3$] (**Zr-6**, **Hf-6**) corresponding to **Zr-3** or **Hf-3** in Scheme 4 was probably once formed, but it was immediately converted into the diallyl phosphide complex with elimination of propene even at room temperature. The ^1H, $^{13}C\{^1H\}$, and ^{31}P

Scheme 5



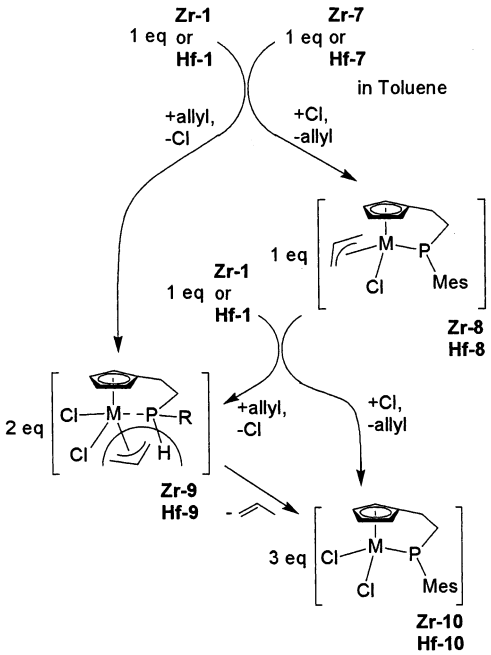
NMR spectra observed are all consistent with the formation of the diallyl phosphide complex. The ^{31}P NMR spectrum without proton irradiation showed a singlet at 147.4 ppm for **Zr-7** and at 118.8 ppm for **Hf-7**, which is in a reasonable range as judged from that of the dibenzyl phosphide complex (**Zr-5**, **Hf-5**) (vide supra). In the ^{1}H NMR spectrum, the two allyl groups were observed as a multiplet due to the CH group (5.37−5.29 ppm for **Zr-7** and 5.47−5.35 ppm for **Hf-7**) and as two doublets due to the CH_2 group (2.85 ppm (J_{HH} = 12.6 Hz) and 2.84 ppm (J_{HH} = 12.3 Hz) for **Zr-7**, and 2.76 ppm (J_{HH} = 12.5 Hz) and 2.75 ppm (J_{HH} = 12.3 Hz) for **Hf-7**), indicating that the allyl groups are coordinated to the metal center with an η^3-mode on the NMR time scale.[8,9a,b] Unfortunately, these diallyl complexes did not grow to be crystals suitable for single-crystal X-ray analysis. **Zr-7** and **Hf-7** (and **Zr-5** and **Hf-5** as well, though unstable and characterized by the ^{1}H and ^{31}P NMR spectra only) are rare examples of half-sandwich type phosphide complexes of group 4 transition metals.[3c−i]

Monoallylation of the Secondary Phosphine Trichloride Complex. It was found above that the allyl group present in the precursor secondary phosphine-pendant complex (**Zr-6**, **Hf-6**) was effectively eliminated as propene to leave the corresponding phosphide complex (**Zr-7**, **Hf-7**). However, the complex **Zr-7** or **Hf-7** thus obtained has two extra allyl groups indifferent to the elimination. So, our synthetic interest prompted us to prepare the dichloride phosphide complex via the monoallyl dichloride complex having a PHMes moiety as a pendant, since the dichloride phosphide complex is expected to be a useful precursor of several kinds of related phosphide derivatives.

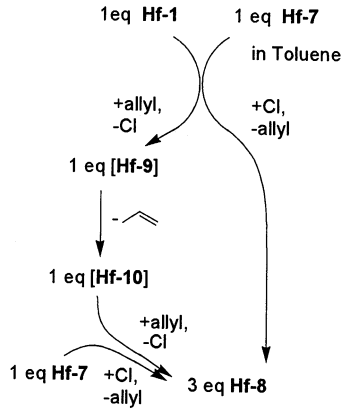
To prepare the monoallyl dichloride secondary phosphine-pendant complex, we took two synthetic routes, one of which was the cross reaction,[9a,c] i.e., the ligand exchange between 2 equiv of the trichloride secondary phosphine complex (**Zr-1**, **Hf-1**) and 1 equiv of the diallyl phosphide complex (**Zr-7**, **Hf-7**) (Scheme 6), and the other of which was the reaction of the secondary phosphine trichloride complex (**Zr-1**, **Hf-1**) with 1 equiv of (allyl)MgCl.

First, the exchange reaction was conducted in toluene, but neither the desired dichloride phosphide complex (**Zr-10**, **Hf-10**) nor its precursor complex (**Zr-9**, **Hf-9**) predicted in Scheme 6, which was tentatively presumed, was obtained with only intractable products formed, probably because **Zr-10** or **Hf-10** was too labile to isolate. Then, we altered the target complex to the monoallyl monochloride phosphide complex (**Zr-8**, **Hf-8**), which might be isolated because the corresponding diallyl complex (**Zr-7**, **Hf-7**) was stable enough. For this purpose, the mixing ratio of the starting complexes was changed to **M-1**:**M-7** = 1:2 (M = Zr, Hf) so as to enhance the formation of the target complex (**Zr-8**, **Hf-8**) (Scheme 7). Under these conditions, the exchange reaction with the Zr complexes, however, led to intractable products again. On the other hand, the similar reaction with the Hf complexes did yield the target complex **Hf-8** quantitatively, though fairly unstable. In the ^{31}P NMR spectrum without proton irradiation, the reaction mixture showed a singlet at 151.0 ppm due to **Hf-8** at the expense of the signals due to the starting complexes **Hf-1** and **Hf-7** (vide supra). We propose the mechanism of this reaction as shown in Scheme 7; the reaction involves not only the direct formation of **Hf-8** but also

Scheme 6. Presumed Allyl-Chloride Exchange Reaction between 2 equiv of M-1 and 1 equiv of M-7 (M = Zr, Hf)



Scheme 7. Allyl-Chloride Exchange Reaction between 1 equiv of Hf-1 and 2 equiv of Hf-7



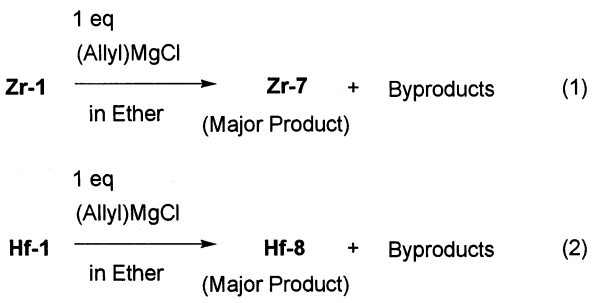
(8) Becconsall, J. K.; Job, B. E.; O'Brien, S. *J. Chem. Soc. (A)* **1967**, 423.

(9) (a) Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383. (b) Erker, G.; Berg, K.; Angerrmund, K.; Kunz, K. *Organometallics* **1987**, *6*, 2620. (c) Hessen, B.; Heijden, H. *J. Organomet. Chem.* **1997**, *534*, 237.

the formation of **Hf-10** via **Hf-9**, both as a spectroscopically undetectable intermediate, followed by the ligand exchange between **Hf-10** and **Hf-7** to form **Hf-8**. The complex **Hf-8** slowly decomposed in solution at room temperature and was isolated as a crude product, which was characterized narrowly by the ^{1}H and ^{31}P NMR spectra, but some related complexes could be derived from **Hf-8** (vide infra).

Similar allyl-chloride exchange reactions were conducted in ether or THF in place of toluene, with the view of stabilizing the chloride phosphide complexes (**Zr-8**, **Hf-8**, **Zr-10**, and **Hf-10**) by solvation with ether or THF, but no practical improvement was attained.

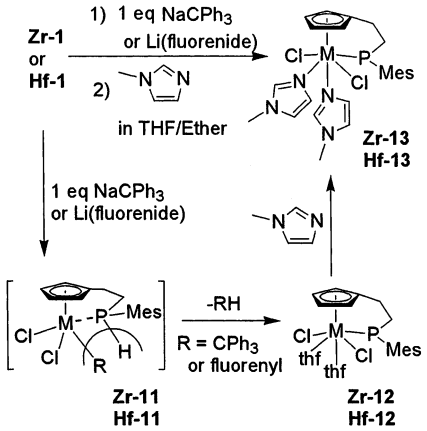
Next, we examined the other synthetic route to **Zr-10** or **Hf-10**, i.e., the monoallylation reaction of **Zr-1** or **Hf-1** with 1 equiv of (allyl)MgCl in ether, which, however, gave a few kinds of unexpected products. The ^{31}P NMR spectrum of the reaction mixture indicated that the major product in the Zr case was the diallyl phosphide complex **Zr-7** with a part of the starting complex **Zr-1** left (eq 1). In the Hf case, the major product was the monoallyl monochloride phosphide complex **Hf-8** (eq 2). These results and those of the above exchange reactions indicate that the present phosphide complexes gain some stability when they have electron-donating allyl group(s) as an ancillary ligand.



In addition to the above monoallylation which led eventually to the multiallylation, monobenzylation, monomethylation, and mono-*p*-tolylation of **Zr-1** or **Hf-1** were examined in ether, but the formation of any phosphide complexes was not discerned in the ^{31}P NMR spectra. This observation is also in favor of the view that the allyl group(s) present as an ancillary ligand stabilize the present phosphide complexes.

Monotritylation and Monofluorenylation of the Secondary Phosphine Trichloride Complex. On the basis of the above monoallylation reaction (eqs 1 and 2), it is necessary to suppress the multisubstitution so as to obtain the desired dichloride phosphide complex, though it does not have enough stability as it is. For this purpose a bulky allyl analogue such as CPh_3 and fluorenyl groups are chosen, because both are expected not only to control the reaction sterically but also to coordinate to the metal center with an η^3- or η^1-mode to behave like the allyl group in the elimination process. Furthermore, it is also necessary more or less to stabilize the unstable dichloride phosphide complex, for example, by solvation. So, we examined the reaction of **Zr-1** or **Hf-1** with 1 equiv of $NaCPh_3$ or Li(fluorenide) in THF/ether solution (Scheme 8). In the reaction with $NaCPh_3$, the ^{31}P NMR spectrum without proton irradiation showed a singlet (236.2 ppm for **Zr-12** and 176.9 ppm for **Hf-12**) at the expense of the doublets due to the starting complex. The spectral change suggests that the P−H bond has been converted into the M−P covalent bond. It is probable that this reaction proceeds via the trityl complex (**Zr-11**, **Hf-11**) as an undetectable intermediate, which affords immediately and quantitatively the dichloride phosphide complex (**Zr-12**, **Hf-12**) with liberation of $CHPh_3$, formation of which was confirmed by the ^{1}H NMR spectrum. The dichloride complex must be stabilized by solvation with one or more THF molecules, because the corresponding solvation-free **Zr-10** or **Hf-10**, if formed in Scheme 6, is too labile to detect. However, the dichloride complex (**Zr-12**, **Hf-12**) solvated by THF could not be isolated owing to its very high and similar solubility to that of $CHPh_3$. To convert it into an isolable derivative, moderately electron-donating *N*-methylimidazole was added to result in narrow isolation of the highly air- and moisture-sensitive dichloride bis(*N*-methylimidazole) phosphide complex (**Zr-13**, 40%; **Hf-13**, 39%). The product was identified by the ^{1}H, ^{13}C{^{1}H}, and ^{31}P NMR spectra. The complexes **Zr-13** and **Hf-13** together with **Zr-7** and **Hf-7** provide rare examples of isolable nonmetallocene type phosphide complexes of group 4 transition metals.[3]

Scheme 8



The similar reaction with 1 equiv of Li(fluorenide) in place of $NaCPh_3$ and then with *N*-methylimidazole gave the same dichloride phosphide complex (**Zr-13**, **Hf-13**) with liberation of fluorene, but it could not be isolated in a pure form due to the contamination of several byproducts.

It should be noted here that the direct reaction dehydrochlorination of **Zr-1** or **Hf-1** with a base such as triethylamine, 1,8-diazabicyclo[5,4,0]undec-7-ene (dbu), *N*-methylimidazole, etc., did not give the corresponding dichloride phosphide complex at all, but led to release of the secondary phosphine moiety from the metal center.

A single-crystal X-ray structural analysis was performed on **Zr-13**, the ORTEP drawing of which is shown in Figure 1. An asymmetric unit contains a pair of the enantiomers (**Zr-13(i)**, **Zr-13(ii)**) represented schematically in Figure 2 and one disordered solvent THF molecule. The Zr center has a distorted octahedral coordination geometry which has two chloride groups in trans positions. The selected bond distances and angles are summarized in Table 1. The Zr−P distance (2.600 and 2.597 Å) is smaller than that in the analogous phosphine-pendant Zr complex [{η^5-$C_5H_4(CH_2)_2$-

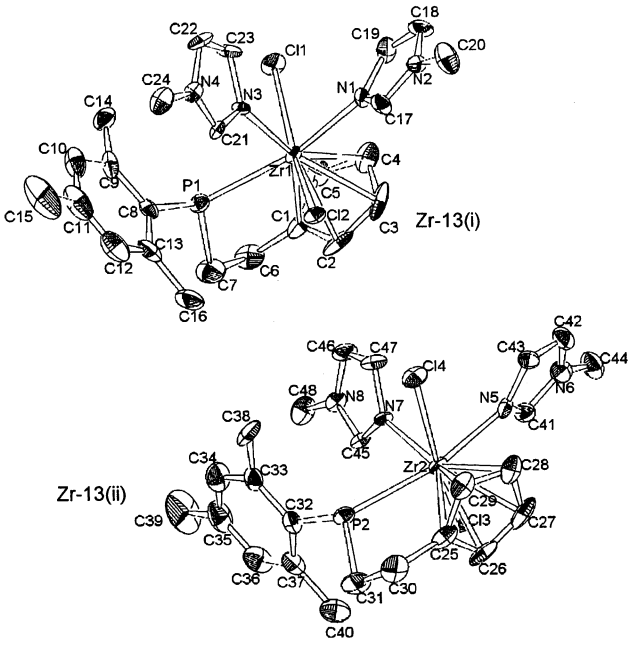


Figure 1. ORTEP drawing of **Zr-13**. Ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

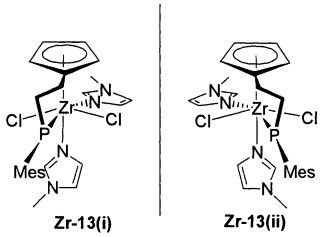


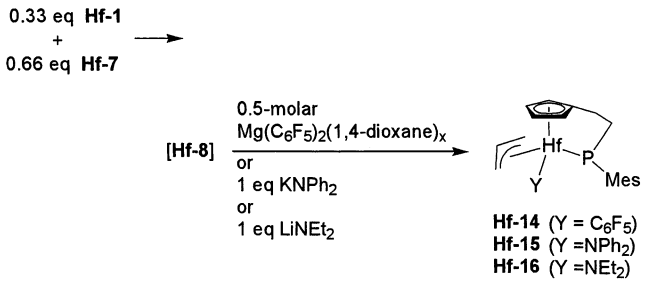
Figure 2. Enantiomeric isomers of **Zr-13**.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Zr-13

Zr-13(i)		Zr-13(ii)	
Zr1−P1	2.600(2)	Zr2−P2	2.597(2)
Zr1−C11	2.537(2)	Zr2−C13	2.567(2)
Zr1−C12	2.563(2)	Zr2−C14	2.537(2)
Zr1−N1	2.429(5)	Zr2−N5	2.413(6)
Zr1−N3	2.366(5)	Zr2−N7	2.376(5)
Zr1−C1	2.589(7)	Zr1−C25	2.589(7)
Zr1−C2	2.533(6)	Zr1−C26	2.538(7)
Zr1−C3	2.475(7)	Zr1−C27	2.490(7)
Zr1−C4	2.483(7)	Zr1−C28	2.498(7)
Zr1−C5	2.549(7)	Zr1−C29	2.556(7)
Zr1−P1−C7	110.3(3)	Zr2−P2−C31	110.4(3)
Zr1−P1−C8	119.4(2)	Zr2−P2−C32	120.8(2)
C7−P1−C8	111.9(3)	C31−P2−C32	111.1(4)
Σ of angles around P	341.6(8)		342.3(9)

PPh_2-κP}$ZrCl_3$(thf)] (2.847 Å),[7b] showing that the Zr−P bond in **Zr-13** bears a considerable double-bond character. The phosphorus atom has a distorted trigonal-planar geometry with the sum of bond angles around it being 341.7° or 342.4°, indicating that the phosphide phosphorus has some sp^2-hybridization character.[2a] The low-field ^{31}P NMR resonance (162.8 ppm, (s), in C_6D_6) for **Zr-13** also points to the considerable Zr−P π-interaction.[2a] The structural comparison with the diamide phosphide-pendant Zr complex [(η^5-$C_5Me_4SiMe_2PCy$-κP)$Zr(NEt_2)_2$] reported recently by Erker et al. (Zr−P = 2.648 Å, sum of bond angles around P = 321.2°)[3h] suggests that the phosphide ligand interacts with the Zr center more strongly in the present dichloride complex **Zr-13** than in the diamide complex, which is attributed probably to the higher σ/π-donor ability of the NEt_2 group than that of the chloride group (vide infra).

Scheme 9



The present structural data are comparable also to those for other monophosphide Zr metallocene complexes reported so far: [Cp_2{$P(SiMe_3)$(2,4,6-$^tBu_3C_6H_2$)}-ZrCl] (Zr−P = 2.541 Å, sum of bond angles around P = 359.5°),[2m] [Cp_2{$P(SiMe_3)_2$}ZrCl] (Zr−P = 2.548 Å, sum of bond angles around P = 344.4°),[2n] and [Cp_2{$P(SiMe_3)_2$}ZrMe] (Zr−P = 2.629 Å, sum of bond angles around P = 349.2°).[2a,n]

The spectroscopic and/or X-ray structural characterization of **Zr-13** and **Hf-13** thus derived support, though indirectly, that **Zr-12** and **Hf-12** are the desired dichloride phosphide complexes which are probably solvated with two THF molecules, judging from the X-ray structure of **Zr-13**. The higher-field ^{31}P NMR resonances in **Zr-13** and **Hf-13** (162.8 and 98.4 ppm, respectively) than in **Zr-12** and **Hf-12** (236.2 and 176.9 ppm, respectively) suggest that the P-to-M donation is weaker in the bis(*N*-methylimidazole) complex (**Zr-13**, **Hf-13**), consistent with the usual expectation that the P-to-M donation is less significant when the ancillary ligands have higher donor ability like *N*-methylimidazole, and vice versa.[2a]

As described above, all of the tribenzyl (**Zr-3**, **Hf-3**), triallyl (**Zr-6**, **Hf-6**), and monotrityl/monofluorenyl (**Zr-11**, **Hf-11**) complexes having a PHMes-pendant serve as an effective precursor of the phosphide-pendant complexes. A common characteristic of these ligands is that they are able to coordinate to the metal center with an η^3-mode. Therefore, it is highly probable that the π-electrons on the α-carbon of these ligands enhance the electrophilic attack of the P−H moiety to facilitate the ligand−H coupling, leading to subsequent formation of the phosphide complex.

Derivation from Monoallyl Monochloride Phosphide Complex Hf-8. Of the phosphide complexes formed in Schemes 6 and 7, the only monoallyl monochloride complex **Hf-8** had a relatively long lifetime, and so some of its derivatives were prepared as shown in Scheme 9. Isolable derivatives [{η^5-$C_5H_4(CH_2)_2$PMes-κP}Hf(Y)(allyl)] (Y = C_6F_5, **Hf-14**; Y = NPh_2, **Hf-15**; Y = NEt_2, **Hf-16**) were obtained in the reaction of **Hf-8** formed in situ (Scheme 7) with 0.5 M $Mg(C_6F_5)_2$(1,4-dioxane)$_x$, 1 equiv of $KNPh_2$, and 1 equiv of $LiNEt_2$, respectively. They were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P NMR spectra. The ^{31}P NMR spectra are summarized in Table 2, where the chemical shifts of **Hf-7** and **Hf-8** are also given for comparison. It can be seen there that when Y is an electron-withdrawing group

Table 2. ^{31}P NMR Spectra of [η^5:η^1-{$C_5H_4(CH_2)_2$PMes}Hf(Y)(allyl)]

Y	^{31}P NMR (δ, in C_6D_6)
Hf-14 C_6F_5	230.1
Hf-8 Cl	151.0
Hf-7 allyl	118.8
Hf-15 NPh_2	114.9
Hf-16 NEt_2	42.7

such as C_6F_5 and Cl, the ^{31}P NMR signal is observed at a considerably low magnetic field, while when Y is an electron-donating group such as NEt_2, the signal appears at a high magnetic field. These ^{31}P NMR data indicate that the phosphide ligand acts as a stronger donor when the complex bears weaker donor(s) as ancillary ligand(s), and vice versa.

If the phosphide phosphorus has a trigonal-planar geometry, it should be achiral. In contrast, if it does not, in other words, if it takes a pyramidal geometry, the phosphorus becomes a chiral center. If so for **Hf-8**, **Hf-14**, **Hf-15**, and **Hf-16** in which the Hf atom is also a chiral center, these complexes may consist of diastereomers giving rise to two sets of resonances in the ^{31}P NMR spectra. The ^{31}P NMR spectra of these complexes show one signal, which indicates either a planar geometry of the phosphorus or rapid inversion between enantiomeric trigonal geometries. The real reason is not clear at present.

Catalytic activities in olefin polymerization are now under investigation for the phosphide complexes isolated in the present study.

Consideration of the Pendant Effect. Finally, we examined if the secondary phosphine-pendant ligand is a requisite in the present synthetic methods we exploited. Namely, the reaction of readily available $CpMCl_3(tht)_2$ (**Zr-17**, **Hf-17**) with 3 equiv of (allyl)MgCl or 1 equiv of $NaCPh_3$ in the presence of nonpendant PHMeMes in ether was conducted. In the reaction with (allyl)MgCl (cf. Scheme 5), formation of a phosphide complex such as $CpM(allyl)_2$PMeMes was not detected at all by the ^{31}P NMR spectrum, but the reaction gave only $CpM(allyl)_3$ with the added PHMeMes ligand intact. $CpZr(allyl)_3$ thus formed was so unstable that it decomposed immediately even at room temperature.[9a,b] Likewise, the similar reaction with 1 equiv of $NaCPh_3$ (cf. Scheme 8) did not afford any phosphide complex. These results suggest that the formation of the present phosphide complexes requires the secondary phosphine to be located close to the coordination sphere of the metal by the pendant effect.

Conclusions

The tribenzyl, triallyl, monotrityl, and monofluorenyl complexes of Zr and Hf carrying a secondary phosphine-pendant are converted into their phosphide-pendant derivatives with liberation of a ligand−H coupling product, wherein these alkyl-like ligands coordinated with an η^3- or η^1-mode act as an effective leaving group. In addition, the formation of the present phosphide complexes requires the secondary phosphine to be situated close to the metal center by the pendant effect. The ^{31}P NMR spectra of the phosphide complexes indicate that the phosphide ligand acts as a better donor when the complex has poorer donors as ancillary ligands, and vice versa. It is expected that the present synthetic method can be applied widely to the preparation of a variety of high oxidation state transition metal phosphide complexes.

Experimental Section

All experiments were performed under nitrogen atmosphere using Schlenk, glovebox, and vacuum line techniques. All solvents used were dried over Na/K alloy and distilled before use. Tetrahydrothiophene and *N*-methylimidazole were distilled from CaH_2. The compounds [η^5-{$C_5H_4(CH_2)_2$PHMes-κP}-$MCl_3(tht)$] (**Zr-1**, **Hf-1**),[7e] MgR_2 (R = Me,[10] R = Et[11]), $Mg(CH_2Ph)_2(thf)_2$,[12] $Mg(p\text{-}C_6H_4Me)_2$(1,4-dioxane)$_x$,[13] and $NaCPh_3$[14] were prepared by published procedures. The arylation activities of $Mg(p\text{-}C_6H_4Me)_2$(1,4-dioxane)$_x$ and $Mg(C_6F_5)_2$(1,4-dioxane)$_x$ were determined before use by HCl titration of the solutions treated individually with H_2O and $PhCH_2Cl$. (Allyl)MgCl and $LiCH_2SiMe_3$ were obtained from common commercial sources and used without further purification. ^{1}H, ^{13}C{^{1}H}, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were recorded on a JEOL LA-300 multinuclear spectrometer. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si NMR data were referenced to $SiMe_4$, and ^{19}F and ^{31}P NMR data were referenced to $CFCl_3$ and 85% H_3PO_4, respectively. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer, but satisfactory results could not be accessible for some complexes because of their high air- and moisture-sensitivities and/or intrinsic instabilities.

Synthesis of $Li_2C_5H_4(CH_2)_2$PMes. The procedure applied is a modification of that for $Li_2C_5H_4(CH)_2$PPh.[7c] BuLi (0.31 mL of BuLi, 1.65 M hexane solution, 0.51 mmol) in 0.31 mL of hexane was added to $LiC_5H_4(CH_2)_2$P(H)Mes[7e] (0.51 mmol) in 15 mL of THF at −78 °C. The reaction mixture was warmed to room temperature and stirred for 10 min. $Li_2C_5H_4(CH_2)_2$-PMes thus formed quantitatively in THF/hexane was used directly. ^{31}P NMR (121.5 MHz, THF/hexane): δ −92.1 (s).

Synthesis of [{η^5-$C_5H_4(CH_2)_2$P(H)Mes}Zr(CH_2SiMe_3)$_3$] (Zr-2). A pentane solution of $LiCH_2TMS$ (1.30 mmol) was added to a suspension of **Zr-1** (0.23 g, 0.43 mmol) in 15 mL of ether at room temperature. The reaction mixture was stirred overnight and then filtered. The filtrate was reduced in volume in vacuo to give a brown oil of **Zr-2** (0.23 g, 89%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.80 (s, 2H, *m*-H in Mes), 6.06 (m, 2H, Cp), 6.00 (m, 2H, Cp), 4.37 (dm, J_{PH} = 214.1 Hz, 1H, PH), 2.60−2.40 (m, 2H, CpCH_2), 2.44 (s, 6H, *o*-Me in Mes), 2.14 (s, 3H, *p*-Me in Mes), 2.05−1.75 (m, 2H, PCH_2), 0.55 (s, 6H, CH_2-$SiMe_3$), 0.16 (s, 27H, $SiMe_3$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 141.8 (d, J_{PC} = 11.2 Hz, aromatic-C in Mes), 138.0 (s, aromatic-C in Mes), 131.2 (d, J_{PC} = 7.4 Hz, aromatic-C in Mes), 130.3 (s, 1-C in Cp), 129.4 (d, J_{PC} = 2.5 Hz, aromatic-C in Mes), 110.1 (s, Cp), 109.2 (s, Cp), 63.3 (s, CH_2SiMe$_3$), 29.2 (d, J_{PC} = 8.1 Hz, CpCH_2), 23.6 (d, J_{PC} = 15.5 Hz, PCH_2), 23.2 (d, J_{PC} = 11.2 Hz, *o*-Me in Mes), 21.0 (s, *p*-Me in Mes), 2.90 (s, $SiMe_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −6.95 (s). ^{31}P NMR (121.5 MHz, C_6D_6): δ −87.0 (d, J_{PH} = 218 Hz).

Synthesis of [{η^5-$C_5H_4(CH_2)_2$P(H)Mes}Hf(CH_2SiMe_3)$_3$] (Hf-2). Treatment of **Hf-1** (0.25 g, 0.41 mmol) in 15 mL of ether with $LiCH_2SiMe_3$ (1.30 mmol) in a manner similar to that for **Zr-2** resulted in formation of a brown oil of **Hf-2** (0.25 g, 89%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.80 (s, 2H, *m*-H in Mes), 5.98 (m, 2H, Cp), 5.93 (m, 2H, Cp), 4.37 (dm, J_{PH} = 214.8 Hz, 1H, PH), 2.61−2.44 (m, 2H, CpCH_2), 2.44 (s, 6H, *o*-Me in Mes), 2.14 (s, 3H, *p*-Me in Mes), 2.03−1.74 (m, 2H, PCH_2), 0.25 (s, 6H, CH_2SiMe$_3$), 0.17 (s, 27H, $SiMe_3$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 141.8 (d, J_{PC} = 11.2 Hz, aromatic-C in Mes), 138.0 (s, aromatic-C in Mes), 130.4 (d, J_{PC} = 7.5 Hz, aromatic-C in

(10) Ashby, E. C.; Arnott, R. C. *J. Organomet. Chem.* **1968**, *14*, 1.
(11) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118.
(12) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209.
(13) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2583.
(14) Renfrow, W. B., Jr.; Hauser, C. R. *Org. Synth., II* **1943**, 603.

Mes), 129.9 (s, 1-C in Cp), 129.4 (d, J_{PC} = 3.0 Hz, aromatic-C in Mes), 110.1 (s, Cp), 109.7 (s, Cp), 69.7 (s, CH_2SiMe_3), 29.2 (d, J_{PC} = 8.1 Hz, CpCH_2), 23.8 (d, J_{PC} = 15.5 Hz, PCH_2), 23.2 (d, J_{PC} = 11.2 Hz, *o*-Me in Mes), 21.0 (s, *p*-Me in Mes), 3.2 (s, $SiMe_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −5.15 (s). ^{31}P NMR (121.5 MHz, C_6D_6): δ −87.1 (d, J_{PH} = 216 Hz). Anal. Calcd for $C_{28}H_{53}HfPSi_3$: C, 49.21; H, 7.82. Found: C, 49.06; H, 7.89.

Synthesis of [{η^5-$C_5H_4(CH_2)_2P(H)Mes$}$Zr(CH_2Ph)_3$] (Zr-3). A solution of $Mg(CH_2Ph)_2(thf)_2$ (1.09 g, 3.11 mmol) in 10 mL of ether was added slowly to a suspension of **Zr-1** (1.10 g, 2.07 mmol) in 70 mL of ether at room temperature. The reaction mixture was stirred for 1 h and then filtered. The filtrate was reduced in volume in vacuo to give a brown oil of **Zr-3** (1.11 g, 88%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.29−7.04 (m, 9H, Ph), 6.91 (s, 2H, *m*-H in Mes), 6.59 (m, 6H, Ph), 5.63 (m, 2H, Cp), 5.50 (m, 2H, Cp), 4.45 (dm, J_{PH} = 214.8 Hz, 1H, PH), 2.54 (s, 6H, *o*-Me in Mes), 2.52−2.44 (m, 2H, CpCH_2), 2.22 (s, 3H, *p*-Me in Mes), 2.00−1.83 (m, 2H, PCH_2), 1.63 (s, 6H, CH_2Ph). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 143.7 (s, Ph), 141.9 (d, J_{PC} = 11.8 Hz, aromatic-C in Mes), 138.1 (s, aromatic-C in Mes), 130.0 (d, J_{PC} = 6.9 Hz, aromatic-C Mes), 130.0 (s, Ph), 129.4 (s, 1-C in Cp), 129.3 (s, aromatic-C Mes), 127.6 (s, Ph), 123.5 (s, Ph), 111.6 (s, 2,5- or 3,4-C in Cp), 111.5 (s, 2,5- or 3,4-C in Cp), 66.2 (s, CH_2Ph), 29.0 (d, J_{PC} = 8.8 Hz, CpCH_2), 23.3 (d, J_{PC} = 16.1 Hz, PCH_2), 23.2 (d, J_{PC} = 11.8 Hz, *o*-Me in Mes), 21.0 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ −86.9 (d, J_{PH} = 215 Hz). Anal. Calcd for $C_{37}H_{41}PZr$: C, 73.10; H, 6.80. Found: C, 72.84; H, 6.62.

Synthesis of [{η^5-$C_5H_4(CH_2)_2P(H)Mes$}$Hf(CH_2Ph)_3$] (Hf-3). Treatment of **Hf-1** (1.54 g, 2.50 mmol) in 70 mL of ether with $Mg(CH_2Ph)_2(thf)_2$ (1.32 g, 3.76 mmol) in 10 mL of ether in a manner similar to that for **Zr-3** resulted in formation of a brown oil of **Hf-3** (1.59 g, 91%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.29−7.02 (m, 9H, Ph), 6.91 (s, 2H, *m*-H in Mes), 6.76 (m, 6H, Ph), 5.59 (m, 2H, Cp), 5.53 (m, 2H, Cp), 4.39 (dm, J_{PH} = 215.0 Hz, 1H, PH), 2.52 (s, 6H, *o*-Me in Mes), 2.52−2.40 (m, 2H, CpCH_2), 2.22 (s, 3H, *p*-Me in Mes), 1.93−1.89 (m, 2H, PCH_2), 1.72 (s, 6H, CH_2Ph). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 144.3 (s, Ph), 141.8 (d, J_{PC} = 11.8 Hz, aromatic-C in Mes), 138.1 (s, aromatic-C in Mes), 131.3 (d, J_{PC} = 8.1 Hz, aromatic-C in Mes), 130.0 (s, 1-C in Cp), 129.4 (d, J_{PC} = 3.2 Hz, aromatic-C in Mes), 129.2 (s, Ph), 127.7 (s, Ph), 123.2 (s, Ph), 112.7 (s, Cp), 112.0 (s, Cp), 78.0 (s, CH_2Ph), 28.5 (d, J_{PC} = 8.7 Hz, CpCH_2), 23.2 (d, J_{PC} = 11.8 Hz, *o*-Me in Mes), 23.2 (d, J_{PC} = 14.9 Hz, PCH_2), 21.0 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ −86.8 (d, J_{PH} = 215 Hz). Anal. Calcd for $C_{37}H_{41}HfP$: C, 63.92; H, 5.94. Found: C, 64.21; H, 5.70.

Synthesis of [{η^5-$C_5H_4(CH_2)_2P(H)Mes$}$Hf(p\text{-}tolyl)_3$] (Hf-4). A suspension of Mg(*p*-$C_6H_4Me)_2$(1,4-dioxane)$_x$ (1.48 mmol) in 10 mL of ether was added to a suspension of **Hf-1** (0.61 g, 0.99 mmol) in 30 mL of ether at room temperature. The reaction mixture was stirred overnight and then filtered. The filtrate was reduced in volume in vacuo to give a yellow powder of **Hf-4** (0.56 g, 82%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.76 (d, J_{HH} = 7.5 Hz, 6H, tolyl), 7.13 (d, J_{HH} = 7.5 Hz, 6H, tolyl), 6.70 (s, 2H, *m*-H in Mes), 6.34 (m, 1H, Cp), 6.29 (m, 1H, Cp), 6.18 (m, 2H, Cp), 4.27 (dm, J_{PH} = 245.3 Hz, 1H, PH), 2.58−2.33 (m, 2H, CpCH_2), 2.18 (s, 15H, *p*-Me in tolyl and *o*-Me in Mes), 2.10 (s, 3H, *p*-Me in Mes), 1.93−1.89 (m, 2H, PCH_2). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 200.3 (d, J_{PC} = 1.9 Hz, aromatic-C in tolyl), 141.8 (d, J_{PC} = 10.6 Hz, aromatic-C in Mes), 138.1 (s, aromatic-C in Mes), 137.6 (s, aromatic-C in tolyl), 136.3 (s, aromatic-C in tolyl), 132.6 (s, 1-C in Cp), 129.3 (s, aromatic-C in Mes), 128.3 (s, aromatic-C in tolyl), 127.2 (s, aromatic-C in Mes), 113.6 (s, Cp), 113.1 (s, Cp), 112.3 (s, Cp), 111.2 (s, Cp), 28.3 (d, J_{PC} = 8.7 Hz, CpCH_2), 24.1 (d, J_{PC} = 6.0 Hz, *o*-Me in Mes), 22.8 (d, J_{PC} = 9.3 Hz, PCH_2), 21.6 (s, *p*-Me in tolyl), 20.9 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ −66.2 (br d, J_{PH} = 243 Hz).

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$Zr(CH_2Ph)_2$] (Zr-5). A solution of **Zr-3** (0.025 g, 0.041 mmol) in 0.4 mL of C_6D_6 was sealed into an NMR glass tube. The tube was kept at 80 °C, and the thermolysis resulted in quantitative formation of **Zr-5**, which was monitored by the NMR measurements. **Zr-5** decomposed slowly in solution, which interfered with the ^{13}C-{^{1}H} NMR measurement. ^{1}H NMR (300 MHz, C_6D_6): δ 7.20−6.52 (m, 10H, Ph), 6.93 (s, 2H, *m*-H in Mes), 5.65 (m, 2H, Cp), 5.55 (m, 2H, Cp), 2.91−2.45 (m, 4H, CH_2CH_2), 2.48 (s, 6H, *o*-Me in Mes), 2.23 (s, 4H, CH_2Ph), 2.15 (s, 3H, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 126.0 (s).

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$Hf(CH_2Ph)_2$] (Hf-5). A solution of **Hf-3** (0.030 g, 0.043 mmol) in 0.4 mL of C_6D_6 was kept at 80 °C in a manner similar to that for **Zr-5**. The thermolysis for 4 h resulted in quantitative formation of **Hf-5**. **Hf-5** decomposed slowly in solution, which interfered with the ^{13}C{^{1}H} NMR measurement. ^{1}H NMR (300 MHz, C_6D_6): δ 7.28−6.82 (m, 10H, Ph), 7.05 (s, 2H, *m*-H in Mes), 5.77 (m, 2H, Cp), 5.58 (m, 2H, Cp), 3.16−2.35 (m, 4H, CH_2CH_2), 2.64 (s, 6H, *o*-Me in Mes), 2.35 (s, 4H, CH_2Ph), 2.22 (s, 3H, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 111.2 (s).

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$Zr(allyl)_2$] (Zr-7). A solution of (allyl)MgCl (26.90 mmol) in 12 mL of THF was added to a suspension of **Zr-1** (4.74 g, 8.97 mmol) in 80 mL of ether at room temperature. After stirring overnight, the volatiles were evaporated in vacuo. The orange residue obtained was extracted with ether/hexane (2:1) and then filtered. Removal of the solvents gave a brown powder of **Zr-7** (2.95 g, 79%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.92 (s, 2H, *m*-H in Mes), 5.37−5.29 (m, 6H, Cp and 2-H in allyl), 2.90 (m, 2H, CpCH_2), 2.85 (d, J_{HH} = 12.6 Hz, 4H, 1,3-H in allyl), 2.84 (d, J_{HH} = 12.3 Hz, 4H, 1,3-H in allyl), 2.63 (s, 6H, *o*-Me in Mes), 2.62 (m, 2H, PCH_2), 2.19 (s, 3H, *p*-Me in Mes). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 142.4 (d, J_{PC} = 4.3 Hz, aromatic-C in Mes), 137.6 (s, aromatic-C in Mes), 131.2 (s, aromatic-C in Mes), 130.9 (d, J_{PC} = 3.8 Hz, 2-C in allyl), 129.4 (s, 1-C in Cp), 128.8 (d, J_{PC} = 5.0 Hz, aromatic-C in Mes), 103.8 (s, 2,5- or 3,4-C in Cp), 101.9 (s, 2,5- or 3,4-C in Cp), 64.4 (s, 1,3-C in allyl), 37.3 (s, CpCH_2), 27.5 (d, J_{PC} = 16.1 Hz, PCH_2), 23.7 (d, J_{PC} = 8.7 Hz, *o*-Me in Mes), 21.1 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 147.4 (s). Anal. Calcd for $C_{22}H_{29}PZr$: C, 63.57; H, 7.03. Found: C, 63.51; H, 6.97.

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$Hf(allyl)_2$] (Hf-7). Treatment of **Hf-1** (5.95 g, 9.65 mmol) in 100 mL of ether with (allyl)MgCl (28.95 mmol) in a manner similar to that for **Zr-7** resulted in formation of a brown powder of **Hf-7** (4.34 g, 89%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.92 (s, 2H, *m*-H in Mes), 5.47−5.35 (m, 2H, 2-H in allyl), 5.42 (m, 2H, Cp), 5.35 (m, 2H, Cp), 2.96 (m, 2H, CpCH_2), 2.76 (d, J_{HH} = 12.5 Hz, 4H, 1,3-H in allyl), 2.76 (m, 2H, PCH_2), 2.75 (d, J_{HH} = 12.3 Hz, 4H, 1,3-H in allyl), 2.62 (s, 6H, *o*-Me in Mes), 2.20 (s, 3H, *p*-Me in Mes). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 142.9 (d, J_{PC} = 4.9 Hz, aromatic-C in Mes), 137.5 (s, aromatic-C in Mes), 132.1 (d, J_{PC} = 3.1 Hz, 2-C in allyl), 130.9 (s, 1-C in Cp), 130.4 (s, aromatic-C in Mes), 128.8 (d, J_{PC} = 5.6 Hz, aromatic-C in Mes), 103.9 (s, 2,5- or 3,4-C in Cp), 101.9 (s, 2,5- or 3,4-C in Cp), 64.3 (s, 1,3-C in allyl), 36.5 (s, CpCH_2), 27.1 (d, J_{PC} = 16.1 Hz, PCH_2), 23.9 (d, J_{PC} = 8.7 Hz, *o*-Me in Mes), 21.0 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 118.8 (s). Anal. Calcd for $C_{22}H_{29}HfP$: C, 52.54; H, 5.81. Found: C, 52.18; H, 6.33.

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$HfCl(allyl)$] (Hf-8). The mixture of **Hf-1** (0.061 g 0.10 mmol) and **Hf-7** (0.10 g, 0.20 mmol) was dissolved in 10 mL of toluene with stirring at room temperature. After 30 min, **Hf-8** was quantitatively formed. The compound decomposed slowly in solution, so that it was isolated as a crude brown product with difficulty. ^{1}H NMR (300 MHz, C_6D_6): δ 6.93 (s, 2H, *m*-H in Mes), 6.27 (m, 1H, Cp), 6.13 (m, 1H, Cp), 5.95 (m, 1H, Cp), 5.35−5.18 (m, 1H, 2-H in allyl), 4.75 (m, 1H, Cp), 3.33−2.40 (m, 8H, CH_2-CH_2 and 1,3-H in allyl), 2.57 (s, 6H, *o*-Me in Mes), 2.21 (s, 3H, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 151.0 (s).

Synthesis of [{η^5-$C_5H_4(CH_2)_2PMes$-κP}$ZrCl_2$(*N*-methylimidazole)$_2$] (Zr-13). A solution of $NaCPh_3$, generated in

situ (0.35 mmol) in 20 mL of ether, was slowly added to a solution of **Zr-1** (0.19 g, 0.35 mmol) in 25 mL of THF at room temperature. The reaction mixture was stirred for 30 min, and then the solvents were removed in vacuo. The residue was dissolved in 20 mL of toluene, and the solution was filtered. To the filtrate was slowly added a solution of *N*-methylimidazole (0.039 g, 0.47 mmol) in 10 mL of THF (addition of 2 equiv or more of *N*-methylimidazole gave rise to decomposition of the product). After stirring for 10 min, the solution was reduced in volume in vacuo, and then the residue was washed with ether, followed by drying it in vacuo to yield a red powder of **Zr-13** (40% based on **Zr-1**, 0.080 g). ^{1}H NMR (300 MHz, C_6D_6): δ 8.33 (s, 1H, imidazole), 8.23 (s, 1H, imidazole), 8.10 (s, 1H, imidazole), 8.00 (s, 1H, imidazole), 6.74 (s, 2H, *m*-H in Mes or Cp), 6.67 (s, 2H, *m*-H in Mes or Cp), 6.17 (s, 2H, Cp), 5.84 (s, 1H, imidazole), 5.69 (s, 1H, imidazole), 3.41 (m, 2H, CpCH_2), 3.21−3.08 (m, 2H, PCH_2), 2.70 (s, 6H, *o*-Me in Mes), 2.15 (s, 6H, MeN), 2.08 (s, 3H, *p*-Me in Mes). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 144.0 (s, imidazole), 143.3 (s, imidazole), 143.2 (s, imidazole), 141.3 (s, imidazole), 139.9 (d, J_{PC} = 3.7 Hz, aromatic-C in Mes), 138.1 (s, 1-C in Cp), 136.0 (d, J_{PC} = 1.9 Hz, aromatic-C in Mes), 131.5 (br s, aromatic-C in Mes), 129.9 (s, aromatic-C in Mes), 119.0 (s, imidazole or 2,5- or 3,4-C in Cp), 117.4 (s, imidazole or 2,5- or 3,4-C in Cp), 116.0 (s, imidazole or 2,5- or 3,4-C in Cp), 112.1 (s, imidazole or 2,5- or 3,4-C in Cp), 37.5 (s, CpCH_2), 32.5 (s, MeN), 32.4 (s, MeN), 27.7 (d, J_{PC} = 19.8 Hz, PCH_2), 24.0 (d, J_{PC} = 9.9 Hz, *o*-Me in Mes), 20.9 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 162.8 (s).

Synthesis of [{η^5-$C_5H_4(CH_2)_2$PMes-κP}$HfCl_2$(*N*-methylimidazole)$_2$] (Hf-13). Treatment of **Hf-1** (0.17 g, 0.28 mmol) in 25 mL of THF with $NaCPh_3$ (0.28 mmol) in 20 mL of ether and then with *N*-methylimidazole (0.032 g, 0.39 mmol) in 10 mL of THF in a manner similar to that for **Zr-13** resulted in formation of an orange powder of **Hf-13** (39% based on **Hf-1**, 0.071 g). ^{1}H NMR (300 MHz, C_6D_6): δ 8.20 (s, 2H, imidazole), 7.94 (s, 2H, imidazole), 6.71 (s, 4H, *m*-H in Mes & Cp), 6.02 (s, 2H, Cp), 5.81 (s, 1H, imidazole), 5.69 (s, 1H, imidazole), 3.66 (m, 2H, CpCH_2), 3.31−3.19 (m, 2H, PCH_2), 2.74 (s, 6H, *o*-Me in Mes), 2.17 (s, 3H, *p*-Me in Mes), 2.14 (s, 6H, MeN). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 144.6 (s, imidazole), 143.7 (s, imidazole), 143.6 (s, imidazole), 141.5 (s, imidazole), 141.4 (d, J_{PC} = 5.1 Hz, aromatic-C in Mes), 136.8 (s, 1-C in Cp), 134.9 (d, J_{PC} = 1.9 Hz, aromatic-C in Mes), 131.4 (br-s, aromatic-C in Mes), 129.3 (s, aromatic-C in Mes), 119.3 (s, imidazole or 2,5- or 3,4-C in Cp), 117.3 (s, imidazole or 2,5- or 3,4-C in Cp), 116.4 (s, imidazole or 2,5- or 3,4-C in Cp), 111.1 (s, imidazole or 2,5- or 3,4-C in Cp), 36.0 (s, CpCH_2), 32.6 (s, MeN), 32.5 (s, MeN), 27.2 (d, J_{PC} = 22.9 Hz, PCH_2), 24.5 (d, J_{PC} = 11.8 Hz, *o*-Me in Mes), 20.8 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 98.4 (s).

Synthesis of $Mg(C_6F_5)_2$(1,4-dioxane)$_x$. The procedure applied is a modification of that for Mg(*p*-$C_6H_4Me)_2$(1,4-dioxane)$_x$.[13] To a 500 mL ether solution of $(C_6F_5)MgBr$[15] (0.056 mol) was added slowly 1,4-dioxane (4.77 mL, 0.056 mol). The white slurry formed was stirred overnight and then centrifuged. The supernatant was filtered and concentrated to ca. 250 mL in vacuo. To the solution was added slowly 1,4-dioxane again (4.77 mL, 0.056 mol) to give a white suspension. After stirring for 4 h, the solvent was removed in vacuo. A white residue obtained was washed with hexane, followed by drying it in vacuo to yield a white powder of $Mg(C_6F_5)_2$(1,4-dioxane)$_x$ (6.39 g).

Synthesis of [{η^5-$C_5H_4(CH_2)_2$PMes-κP}Hf(C_6F_5)(allyl)] (Hf-14). A mixture of **Hf-1** (0.061 g, 0.10 mmol) and **Hf-7** (0.10 g, 0.20 mmol) was dissolved in 10 mL of toluene with stirring. After 30 min, to the toluene solution containing **Hf-8** formed in situ was added slowly $Mg(C_6F_5)_2$(1,4-dioxane)$_x$ (0.30 mmol) dissolved in 5 mL of THF at room temperature. The reaction mixture was stirred for 1 h, and then the solvents were removed in vacuo. The residue was extracted with toluene, and the extract was filtered. The filtrate was concentrated in vacuo to give a brown powder of **Hf-14** (0.16 g, 85%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.86 (s, 2H, *m*-H in Mes), 6.07 (m, 1H, Cp), 6.02 (m, 1H, Cp), 5.64−5.48 (m, 1H, 2-H in allyl), 5.53 (m, 1H, Cp), 5.37 (m, 1H, Cp), 3.35−2.00 (m, 14H, CH_2CH_2, 1,3-H in allyl, and *o*-Me in Mes), 2.15 (s, 3H, *p*-Me in Mes). ^{19}F NMR (282.7 MHz, C_6D_6): δ −115.0 (m, 2F), −157.0 (m, 1F), −162.1 (m, 2F). ^{31}P NMR (121.5 MHz, C_6D_6): δ 230.1 (m). Anal. Calcd for $C_{25}H_{24}F_5HfP$: C, 47.74; H, 3.85. Found: C, 47.45; H, 3.89.

Synthesis of [{η^5-$C_5H_4(CH_2)_2$PMes-κP}Hf(NPh_2)(allyl)] (Hf-15). The synthetic procedure was similar to that for **Hf-14**, using **Hf-1** (0.061 g, 0.10 mmol), **Hf-7** (0.10 g, 0.20 mmol), and $KNPh_2$ (0.30 mmol) prepared by the reaction of $NHPh_2$ (0.051 g, 0.30 mmol) with KH (0.012 g, 0.30 mmol) in 10 mL of THF. A brown powder of **Hf-15** was obtained (0.17 g, 89%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.36−6.71 (m, 12H, Ph and *m*-H in Mes), 5.93 (m, 1H, Cp), 5.48 (m, 1H, Cp), 5.40−5.32 (m, 2H, Cp and 2-H in allyl), 5.14 (m, 1H, Cp), 3.33−2.65 (m, 8H, CH_2-CH_2, 1,3-H in allyl), 2.40 (s, 6H, *o*-Me in Mes) 2.19 (s, 3H, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 114.9 (s). Anal. Calcd for $C_{31}H_{34}HfNP$: C, 59.09; H, 5.44; N, 2.22. Found: C, 59.42; H, 5.27; N, 2.06.

Synthesis of [{η^5-$C_5H_4(CH_2)_2$PMes-κP}Hf(NEt_2)(allyl)] (Hf-16). The synthetic procedure was similar to that for **Hf-14**, using **Hf-1** (0.061 g, 0.10 mmol), **Hf-7** (0.10 g, 0.20 mmol), and $LiNEt_2$(0.30 mmol) prepared by the reaction of $NHEt_2$ (0.022 g, 0.30 mmol) with BuLi (0.18 mL of BuLi, 1.65 M hexane solution, 0.30 mmol) in 10 mL of THF. A brown powder of **Hf-16** was obtained (0.13 g, 82%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.02 (s, 2H, *m*-H in Mes), 6.18 (m, 1H, Cp), 5.85 (m, 1H, Cp), 5.32 (m, 1H, Cp), 4.84 (m, 2H, Cp and 2-H in allyl), 3.44−2.64 (m, 12H, CH_2CH_2, 1,3-H in allyl, and NCH_2), 2.54 (s, 6H, *o*-Me in Mes) 2.28 (s, 3H, *p*-Me in Mes), 0.86 (t, J_{HH} = 7.0 Hz, 6H, CH_2CH_3). ^{31}P NMR (121.5 MHz, C_6D_6): δ 42.7 (d, J_{PH} = 40 Hz).

Synthesis of [η^5-$CpZrCl_3(tht)_2$] (Zr-17). Tetrahydrothiophene (0.15 g, 1.68 mmol) was added slowly to a suspension of [η^5-$CpZrCl_3$][16] (0.22 g, 0.84 mmol) in 15 mL of toluene at room temperature. The colorless solution formed was stirred for 30 min, and then the solvent was removed in vacuo. The white residue obtained was washed with hexane, followed by drying it in vacuo to give a white powder of **Zr-17** (0.34 g, 92%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.36 (s, 5H, Cp), 3.44 (br-s, 8H, tht), 1.44 (m, 8H, tht). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 120.4 (s, Cp), 37.1 (br s, tht), 30.0 (s, tht). Anal. Calcd for $C_{13}H_{21}$-Cl_3S_2Zr: C, 35.57; H, 4.82. Found: C, 36.08; H, 4.24.

Synthesis of [η^5-$CpHfCl_3(tht)_2$] (Hf-17). The procedure applied is a modification of that for [$CpHfCl_3(SMe_2)_2$].[17] Tetrahydrothiophene (2.48 g, 28.20 mmol) was added to a suspension of $HfCl_4$ (4.51 g, 14.10 mmol) in 70 mL of toluene at room temperature, and then the reaction mixture was treated with $CpSn^nBu_3$ (5.01 g, 14.10 mmol) in 10 mL of toluene. After stirring overnight at 70 °C to complete the reaction, the solvent was removed in vacuo. The white residue obtained was washed with hexane/toluene (1:2) and dried in vacuo to give a white powder of **Hf-17** (4.53 g, 61%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.16 (s, 5H, Cp), 3.13 (br s, 8H, tht), 1.38 (m, 8H, tht). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 117.8 (s, Cp), 37.4 (br s, tht), 30.0 (s, tht). Anal. Calcd for $C_{13}H_{21}Cl_3HfS_2$: C, 29.67; H, 4.02. Found: C, 29.98; H, 3.74.

Synthesis of PHMeMes. MeI (7.14 g, 50.30 mmol) in 60 mL of THF was added slowly to LiPHMes (50.30 mmol) prepared from PH_2Mes[18] (7.55 g, 50.30 mmol) and BuLi (30.48

(15) Barlow, M. G.; Green, M.; Haszeldine, R. N.; Higson, H. G. *J. Chem. Soc. (C)* **1966**, 1592.

(16) Erker, G.; Berg, K.; Treschanke L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.

(17) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.

(18) Jempty, T. C.; Gogins, K. A. Z.; Mazur, Y.; Miller, L. L. *J. Org. Chem.* **1981**, *46*, 4545.

mL of BuLi, 1.65 M hexane solution, 50.30 mmol) in 200 mL of THF at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and then 100 mL of ether and 50 mL of degassed water were added to the white residue. After LiI was extracted with degassed water, the ether layer was separated and dried over $MgSO_4$. The solution was filtered, and then the filtrate was reduced in volume in vacuo. The residue was distilled under reduced pressure to give a colorless liquid of PHMeMes (5.18 g, 62%, bp 85 °C/1.5 Torr). ^{1}H NMR (300 MHz, C_6D_6): δ 6.79 (s, 2H, *m*-H in Mes), 4.32 (dm, $J_{PH} = 213.3$ Hz, 1H, PH), 2.43 (s, 6H, *o*-Me in Mes), 2.13 (s, 3H, *p*-Me in Mes) 1.05 (m, 3H, PMe). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 141.6 (d, $J_{PC} = 12.4$ Hz, aromatic-C in Mes), 137.8 (s, aromatic-C in Mes), 130.1 (d, $J_{PC} = 3.0$ Hz, aromatic-C in Mes), 129.3 (d, $J_{PC} = 3.7$ Hz, aromatic-C in Mes), 22.8 (d, $J_{PC} = 11.8$ Hz, *o*-Me in Mes), 21.0 (s, *p*-Me in Mes), 4.7 (d, $J_{PC} = 14.3$ Hz, PMe). ^{31}P NMR (121.5 MHz, C_6D_6): δ −105.6 (d, $J_{PH} = 214$ Hz).

X-ray Crystallography. The red single crystals of **Zr-13** were obtained from its THF/hexane solution. The single crystal covered with an inert oil was mounted on a glass fiber and cooled to 200 K with a cold nitrogen gas flow. The measurement was made on a Mac Science DIP2030 imaging plate area diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Indexing was performed from 180 oscillations which were exposed for 3.3 min. The crystal-to-detector distance was 100.00 mm with the detector at the zero swing position. Readout was performed in the 0.10 mm pixel mode. The data were collected up to a maximum 2θ value of 56°. Cell parameters and reflection intensities were estimated using the program package MacDENZO.[19] The structure was solved by direct methods with the SIR-92 program system[20] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and included at the final stage of refinements with fixed parameters. All calculations were carried out using the teXsan crystallographic software package from the Molecular Structure Corp.[21] The crystallographic data for **Zr-13** are summarized in Table 3.

Table 3. Crystal Data for (Zr-13)·(thf)$_{0.5}$

empirical formula	$C_{26}H_{35}Cl_2N_4O_{0.5}PZr$
fw	604.69
cryst dimens	0.50 × 0.40 × 0.05 mm
cryst syst	triclinic
lattice params	$a = 8.0490(2)$ Å
	$b = 16.4160(3)$ Å
	$c = 21.9390(6)$ Å
	$\alpha = 81.054(1)°$
	$\beta = 88.255(1)°$
	$\gamma = 89.857(1)°$
	$V = 2862.3(1)$ Å^3
space group	$P\bar{1}$ (#2)
Z value	4
D_{calc}	1.403 g/cm^3
no. of reflns measd	12 393
no. of obsd reflns ($I > 2.00\sigma(I)$, $2\theta < 50.00°$)	7776
no. of variables	622
residuals: R; R_w	0.071; 0.115
GOF	1.37

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Supporting Information Available: Tables giving positional and thermal parameters, crystallographic data, and bond lengths and angles for **Zr-13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) MacDENZO: Gewirth, D. (with the cooperation of the program authors Otwinowski, Z., and Minor, W.) In *The MacDenzo Manual−A Description of the Programs DENZO, XDISPLAYF, and SCALEPACK*; Yale University: New Haven, CT, 1995.

(20) *SIR-92*: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gurgliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M.; University of Bari: Bari, Italy, 1992.

(21) *teXsan*: Single-Crystal Structure Analysis Software, Version 1.6; Molecular Structure Corp.: The Woodlands, TX, 1993.