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Synthesis, Characterization, and Reactivity of Zirconocene and Hafnocene Silyl Hydride Complexes

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The trimethylphosphine adducts of zirconocene and hafnocene silyl hydride complexes have been prepared and the X-ray crystal structure of the zirconocene complex has been determined. In addition, the mechanism of formation of these complexes and a study of the reactivity of the zirconocene complex are presented. The complex $Cp_2Zr(H)(SiPh_3)(PMe_3)$ (2) crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.336$ (2) Å, $b = 28.863$ (8) Å, $c = 11.051$ (3) Å, $\beta = 111.11$ (2)°, and $Z = 4$; $R_w = 0.048$.

Early-transition-metal complexes containing silicon ligands are becoming increasingly important in organometallic chemistry.[2-6] Pioneering studies by Tilley[2,4] and by Harrod[3a-e] have demonstrated that group 4 metal–silicon bonds are quite reactive, undergoing insertion reactions[2] and participating in silane polymerizations[3,4] and σ-bond metathesis reactions.[4] While metallocene silyl hydride complexes have been postulated as key intermediates in the polymerization of silanes,[3d] very few of these complexes have been synthesized. To date, one Zr(IV)[3c] and two Ti(III)[3a,b] dimeric silyl hydride complexes have been prepared by Harrod and co-workers, but relatively little is known about their reactivity. We now report a new method for the synthesis of hafnocene and zirconocene silyl hydride complexes, a preliminary study of the reactivity of the zirconocene derivative, and the X-ray crystal structure of $Cp_2Zr(H)(SiPh_3)(PMe_3)$ (2).

The silyl hydride complexes were synthesized by the addition of triphenylsilane to solutions of group 4 metallocene olefin complexes, as shown in Figure 1. For example, treatment of THF solutions of $Cp_2Zr(\eta^2\text{-1-butene})PMe_3$,[7] (1) generated in situ, with 1 equiv of triphenylsilane produces the triphenylsilyl hydride complex 2. Complex 2 may be isolated as a red-brown solid in 48% yield by removing the solvent and washing with ether. The hafnocene analogue 4 may be similarly obtained in 66% yield by treating benzene solutions of $Cp_2Hf(\eta^2\text{-isobutylene})(PMe_3)$[8] (3) with 1 equiv of triphenylsilane.

Table I. Positional Parameters

atom	*x*	*y*	*z*
Zr	0.33224 (5)	0.13860 (2)	0.02559 (4)
P	0.1094 (2)	0.08193 (6)	−0.1192 (1)
Si	0.4189 (1)	0.12086 (4)	0.2840 (1)
C(1)	0.3270 (8)	0.2242 (2)	0.0327 (6)
C(2)	0.2225 (8)	0.2126 (2)	−0.0916 (6)
C(3)	0.0986 (7)	0.1900 (2)	−0.0757 (5)
C(4)	0.1255 (7)	0.1874 (2)	0.0568 (5)
C(5)	0.2663 (7)	0.2092 (2)	0.1242 (5)
C(6)	0.5212 (7)	0.0778 (2)	0.0245 (6)
C(7)	0.6064 (6)	0.1144 (2)	0.0980 (5)
C(8)	0.5912 (8)	0.1527 (2)	0.0157 (7)
C(9)	0.4969 (9)	0.1391 (3)	−0.1093 (6)
C(10)	0.4554 (8)	0.0921 (3)	−0.1037 (6)
C(11)	0.2477 (5)	0.1253 (2)	0.3412 (4)
C(12)	0.2293 (6)	0.1634 (2)	0.4097 (5)
C(13)	0.0971 (7)	0.1696 (2)	0.4387 (6)
C(14)	−0.0159 (6)	0.1362 (2)	0.4053 (6)
C(15)	0.0008 (5)	0.0974 (2)	0.3381 (5)
C(16)	0.1300 (5)	0.0925 (2)	0.3056 (5)
C(21)	0.5088 (5)	0.0607 (2)	0.3336 (4)
C(22)	0.4235 (5)	0.0203 (2)	0.2927 (5)
C(23)	0.4860 (6)	−0.0233 (2)	0.3301 (5)
C(24)	0.6385 (7)	−0.0284 (2)	0.4067 (5)
C(25)	0.7274 (6)	0.0109 (2)	0.4452 (5)
C(26)	0.6628 (5)	0.0548 (2)	0.4111 (4)
C(27)	−0.0633 (8)	0.0819 (3)	−0.0794 (7)
C(28)	0.0294 (9)	0.0895 (3)	−0.2957 (6)
C(29)	0.158 (1)	0.0203 (2)	−0.1075 (7)
C(31)	0.5654 (5)	0.1613 (2)	0.4064 (4)
C(32)	0.6352 (6)	0.1983 (2)	0.3688 (5)
C(33)	0.7385 (6)	0.2279 (2)	0.4580 (6)
C(34)	0.7708 (6)	0.2214 (2)	0.5893 (6)
C(35)	0.7031 (7)	0.1856 (2)	0.6314 (5)
C(36)	0.6028 (6)	0.1560 (2)	0.5407 (5)
H(1)	0.258 (5)	0.088 (2)	0.103 (4)

A single-crystal X-ray structure determination of 2 was performed, and the ORTEP diagram is shown in Figure 2. The hydride ligand was located on an oblique plane dif-

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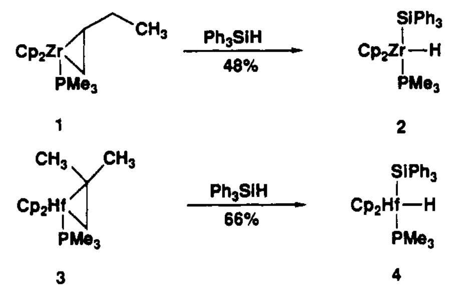

Figure 1.

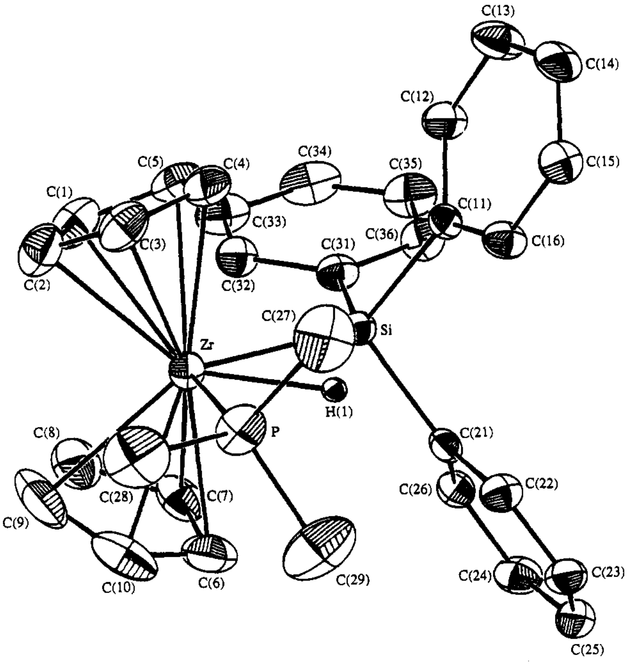

Figure 2. ORTEP diagram of 2 with thermal ellipsoids at 40% probability. The hydrogen atom was given arbitrary thermal parameters.

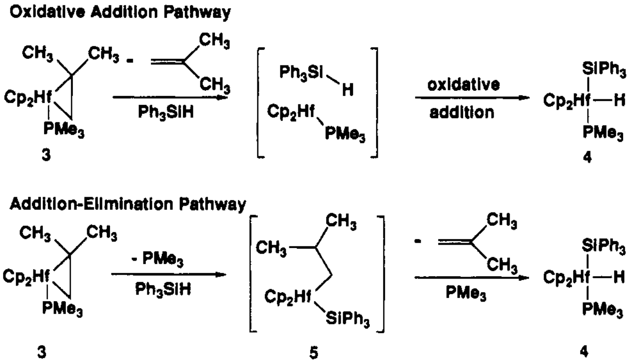

Figure 3.

ference map defined by the Zr, Si, and P atoms; its position was successfully refined. The Zr–Si bond length of 2.721 (2) Å is slightly shorter than those of previously characterized structures containing this structural unit, which exhibit an average Zr–Si bond length of 2.814 Å.[2,9] Both the Zr–PMe$_3$ and the Zr–H bond lengths are in agreement with anticipated values.[10]

Table II. Bond Distances

Zr–H(1)	1.94 (5)	C(1)–C(5)	1.394 (8)
Zr–P	2.677 (2)	C(1)–C(2)	1.409 (8)
Zr–Si	2.721 (2)	C(2)–C(3)	1.394 (9)
Zr–C(1)	2.473 (5)	C(3)–C(4)	1.396 (8)
Zr–C(2)	2.518 (6)	C(4)–C(5)	1.405 (8)
Zr–C(3)	2.541 (6)	C(6)–C(10)	1.389 (9)
Zr–C(4)	2.511 (5)	C(6)–C(7)	1.393 (8)
Zr–C(5)	2.489 (5)	C(7)–C(8)	1.405 (8)
Zr–C(6)	2.491 (6)	C(8)–C(9)	1.40 (1)
Zr–C(7)	2.491 (5)	C(9)–C(10)	1.42 (1)
Zr–C(8)	2.493 (6)	C(11)–C(12)	1.381 (6)
Zr–C(9)	2.498 (6)	C(11)–C(16)	1.394 (6)
Zr–C(10)	2.520 (6)	C(12)–C(13)	1.394 (7)
P–C(27)	1.817 (8)	C(13)–C(14)	1.379 (7)
P–C(29)	1.828 (7)	C(14)–C(15)	1.383 (7)
P–C(28)	1.832 (6)	C(15)–C(16)	1.385 (6)
Si–C(11)	1.923 (5)	C(21)–C(22)	1.393 (6)
Si–C(21)	1.921 (5)	C(31)–C(32)	1.391 (7)
Si–C(31)	1.931 (5)	C(31)–C(36)	1.405 (6)
C(21)–C(26)	1.394 (6)	C(32)–C(33)	1.396 (7)
C(22)–C(23)	1.384 (6)	C(33)–C(34)	1.385 (8)
C(23)–C(24)	1.378 (7)	C(34)–C(35)	1.377 (8)
C(24)–C(25)	1.381 (7)	C(35)–C(36)	1.392 (7)
C(25)–C(26)	1.395 (7)		

Table III. Bond Angles

P–Zr–Si	112.68 (5)	C(29)–P–Zr	115.6 (2)
H(1)–Zr–P	59 (1)	C(12)–C(11)–Si	121.0 (3)
H(1)–Zr–Si	54 (1)	C(16)–C(11)–Si	121.7 (3)
H(1)–Zr–C(1)	136 (1)	C(12)–C(11)–C(16)	117.1 (4)
H(1)–Zr–C(6)	81 (1)	C(11)–C(12)–C(13)	121.5 (5)
C(11)–Si–C(31)	101.1 (2)	C(14)–C(13)–C(12)	120.3 (5)
C(21)–Si–C(11)	107.2 (2)	C(13)–C(14)–C(15)	119.1 (4)
C(21)–Si–C(31)	102.7 (2)	C(14)–C(15)–C(16)	119.9 (4)
C(11)–Si–Zr	111.4 (1)	C(15)–C(16)–C(11)	122.0 (4)
C(21)–Si–Zr	113.8 (1)	C(22)–C(21)–Si	121.6 (3)
C(31)–Si–Zr	119.3 (2)	C(26)–C(21)–Si	122.2 (4)
C(5)–C(1)–C(2)	108.3 (6)	C(22)–C(21)–C(26)	116.1 (4)
C(3)–C(2)–C(1)	107.6 (5)	C(23)–C(22)–C(21)	122.2 (4)
C(2)–C(3)–C(4)	108.3 (5)	C(24)–C(23)–C(22)	120.9 (5)
C(3)–C(4)–C(5)	108.2 (5)	C(23)–C(24)–C(25)	118.3 (5)
C(1)–C(5)–C(4)	107.6 (5)	C(24)–C(25)–C(26)	120.7 (5)
C(10)–C(6)–C(7)	108.7 (6)	C(21)–C(26)–C(25)	121.7 (4)
C(6)–C(7)–C(8)	108.4 (5)	C(32)–C(31)–Si	123.0 (3)
C(9)–C(8)–C(7)	107.4 (6)	C(36)–C(31)–Si	121.2 (4)
C(8)–C(9)–C(10)	108.0 (6)	C(32)–C(31)–C(36)	115.7 (4)
C(6)–C(10)–C(9)	107.5 (6)	C(31)–C(32)–C(33)	122.7 (5)
C(27)–P–C(29)	101.7 (4)	C(34)–C(33)–C(32)	119.4 (5)
C(27)–P–C(28)	101.6 (3)	C(35)–C(34)–C(33)	120.2 (5)
C(29)–P–C(28)	100.8 (3)	C(34)–C(35)–C(36)	119.4 (5)
C(27)–P–Zr	114.9 (2)	C(35)–C(36)–C(31)	122.7 (5)
C(28)–P–Zr	119.6 (2)		

Two plausible pathways exist for the formation of the silyl hydride complexes. The first involves the loss of the olefin to generate a metallocene–PMe$_3$ species followed by oxidative addition of the Si–H bond. In the second, the Si–H bond directly adds across a M–C bond of the olefin complex, followed by β-H elimination and loss of alkene, as shown for the hafnium complex in Figure 3. We favor the addition–elimination pathway, since an intermediate consistent with structure 5 is observed by ^{1}H NMR spectroscopy during the reaction of 3 with triphenylsilane. The ^{1}H NMR (300 MHz, C_7D_8) spectrum of the intermediate has several characteristic features: a singlet at δ 5.66

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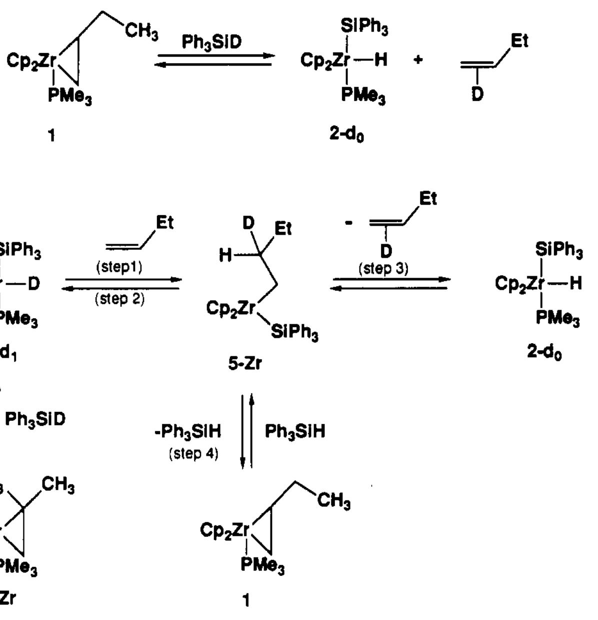

Figure 4.

(Cp hydrogens), a multiplet at δ 2.31 (J = 6.9 Hz, methine hydrogen), and a doublet at δ −0.59 (J = 6.9 Hz, methylene hydrogens, α to Hf). The methyl protons are obscured by the peaks due to PMe_3 in the mixture of **3**–**5**.

To further study the mechanism of the formation of compounds **2** and **4**, a deuterium labeling study was performed. When **1** was treated with $DSiPh_3$, a mixture of **1** and **2**-d_0 was produced (Figure 4). Presumably, the deuterium is incorporated into the 1-butene byproduct of the reaction. To determine the fate of the deuterium, the deuterium-labeled complex (**2**-d_1) was synthesized and its reaction with 1-butene was examined. Compound **2**-d_1 was synthesized by the addition of $DSiPh_3$ to the unstable zirconocene analogue of **3**. When **2**-d_1 was exposed to an excess of 1-butene, scrambling of the deuterium into the olefin was observed, as judged by the ^{2}H NMR spectrum of the 1-butene, with concommitant production of **2**-d_0. This scrambling is consistent with the reversible insertion of 1-butene into the Zr–H(D) bond of **2** to produce **5-Zr** (step 1), which then undergoes a β-hydride (deuteride) elimination to give a mixture of **2**-d_1 (step 2) and **2**-d_0 (step 3). The majority of the deuterium should be incorporated into the 1-butene due to a primary kinetic isotope effect, as well as for statistical reasons. Additional evidence for this mechanism is provided by the observation of **1** in the reaction mixture, which results from the reversible elimination of $HSiPh_3$ (or $DSiPh_3$) from the intermediate **5-Zr** (step 4). Unfortunately, the observed loss of the label from **2**-d_1 under the reaction conditions prevents a distinction from being made between the two reaction pathways shown in Figure 3 by simple labeling studies.

The reactivity of **2** with a variety of unsaturated organic substrates has been investigated, and the results are shown in Figure 5. In all cases examined, the hydride ligand participates in new bond-forming reactions; no reaction of the silyl ligand is observed. Treatment of benzene solutions of **2** with acetone, pivalonitrile, or *tert*-butyl isocyanide gives the insertion products **6**–**8**, respectively. While **6** is quite stable, the thermal instability of **7** and **8** have precluded their isolation in analytically pure form. The geometry of the iminoacyl ligand of **8** has not been determined. In contrast to the reactivity seen with heteroatom-containing substrates, the reaction of **2** with all-carbon unsaturated substrates results in the elimination of the silane. Thus, addition of excess 2-butyne to benzene

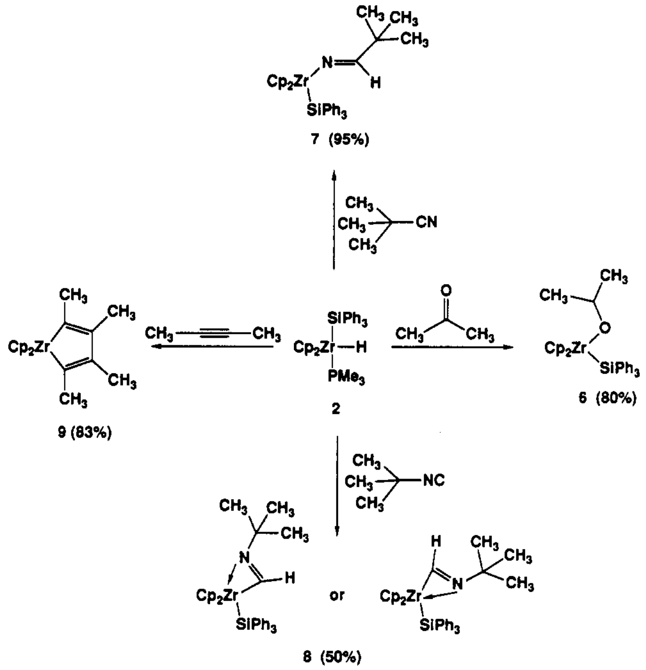

Figure 5.

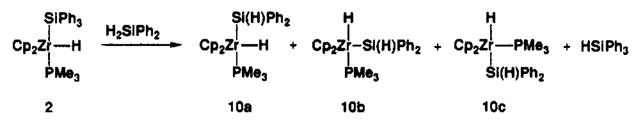

Figure 6.

solutions of **2** gives metallacycle **9**[11] in 83% yield, with the concommitant production of Ph_3SiH. This reaction is similar to that discussed above in the reaction of butene with **2**-d_1; however in this case an alkyne complex is produced by the elimination of the silane. The nascent alkyne complex subsequently inserts an additional equivalent of alkyne to produce **9**.

Complex **2** undergoes σ-bond metathesis reactions with silanes.[4] For example, when **2** is treated with 1 equiv of Ph_2SiH_2, a mixture of two geometric isomers (3.2:1) of **10** is produced quantitatively (as judged by ^{1}H NMR spectroscopy), along with Ph_3SiH (Figure 6). Based on the J_{HP} values for the Zr–H signals of the two isomers, the major isomer appears to be structurally similar to **2**, where the hydride is located between the silicon and phosphorus ligands (**10a**) (δ = 0.06, dd, J_{HP} = 69 Hz, J_{HH} = 3 Hz, Zr*H*; J_{HP} = 73 Hz for **2**) while the minor isomer, with a smaller J_{HP} value (δ = −1.11 dd, J_{HP} = 16 Hz, J_{HH} = 10Hz, Zr*H*), is tentatively assigned to be the isomer with the $Si(H)Ph_2$ ligand centered between the hydride ligand and PMe_3 (**10b**). It should be noted that the coupling constants for the minor isomer are much smaller than those of the complex $Cp_2Zr(H)(PMe_3)(Cl)$, which has the phosphine ligand bound in the central orbital,[13] in a structure similar to **10c**. Similar isomeric mixtures of **10** are formed when **1** is treated with Ph_2SiH_2.

In summary, we have developed a new route to metallocene silyl hydride complexes and have examined the reaction chemistry of these complexes. Further work is in progress to study the participation of these complexes

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in a variety of stoichiometric and catalytic processes.

Experimental Section

General Data. All reactions were performed under an atmosphere of argon using standard Schlenk techniques. Transfer and storage of all solids was done in a Vacuum Atmospheres Co. drybox under a nitrogen atmosphere. The sealable flasks used in the procedures were single-neck flasks fitted with teflon O-ring screw valves.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker WM-250, Varian XL-300, Varian Gemini 300, or a Varian VXR-500 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Mattson Cygnus Starlab 100 Fourier transform spectrometer. Electron impact mass spectra and high-resolution mass spectra were recorded on a Finnegan MAT System 8200. Elemental analyses were performed by Oneida Research Services, Whitesborough, NY.

Tetrahydrofuran, diethyl ether, and benzene were distilled under argon from sodium/benzophenone ketyl before use. Hexane was deolefinated by stirring over H_2SO_4 and stored over CaH_2 before distillation from sodium/benzophenone ketyl under argon. Cp_2ZrCl_2 and Cp_2HfCl_2 were purchased from Boulder Scientific Inc., Mead, CO, and were used without further purification. All other reagents were available from commercial sources and were used without further purification unless noted otherwise.

Prepration of (η^5-C_5H_5)$_2$Zr(H)(SiPh$_3$)(PMe$_3$) (2). Zirconocene dichloride (2.9 g, 10 mmol) was dissolved in THF (100 mL, −78 °C), *n*-BuLi (15 mL, 1.4 M in hexanes, 21 mmol) was added, and the reaction mixture was stirred for 20 min at −78 °C. At this point, chlorotrimethylsilane (0.40 mL, 3.1 mmol) was added. After 5 min, trimethylphosphine (3.2 mL, 30 mmol) and a solution of Ph_3SiH (2.6 g, 10 mmol) in THF (10 mL) were sequentially added via cannula with a THF rinse (5 mL). The reaction mixture was warmed to room temperature and was stirred for 2 h. The solvent was removed in vacuo to give a reddish oil, which was dissolved in C_6H_6 (50 mL) and cannula filtered. Trimethylphosphine (1 mL, 10 mmol) was added, and the reaction mixture was stirred for 30 min at 75 °C. The solvent was removed in vacuo to produce a sticky red-brown solid, which was rinsed with Et_2O (30 mL) to give 2.7 g of an orange-red solid (48%): ^1H NMR (300 MHz, C_6D_6) δ 0.35 (d, J_{HP} = 73 Hz, 1 H), 0.82 (d, J_{HP} = 6.2 Hz, 9 H), 4.95 (d, J_{HP} = 1.8 Hz, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 19.88 (d, J_{CP} = 32 Hz), 98.22, 126.76, 127.16, 137.18, 149.57; ^{31}P NMR (121 MHz, C_6D_6) δ 5.73; ^{29}Si NMR (60 MHz, C_6D_6) δ 39.48 (d, J_{SiP} = 15 Hz); IR (KBr, cm^{-1}) 3062, 2980, 2907, 1560 (Zr–H, confirmed by a band at 1110 for the Zr–D analogue), 1427, 1284, 1080, 948, 800, 705, 507. Anal. Calcd for $C_{31}H_{35}PSiZr$: C, 66.74; H, 6.32. Found: C, 66.28; H, 6.32.

Preparation of (η^5-C_5H_5)$_2$Hf(H)(SiPh$_3$)(PMe$_3$) (4). The complex (η^5-C_5H_5)$_2$Hf(isobutylene)(PMe$_3$)[8] (0.13 g, 0.30 mmol) was dissolved in benzene (3 mL), Ph_3SiH (0.080 g, 0.30 mmol) was added, and the reaction mixture was stirred for 12 h at room temperature. At this point, the solvent was removed in vacuo to produce 0.14 g (65% yield) of 4, which was approximately 90% pure, as judged by ^1H NMR spectroscopy. This complex appeared to be unstable in solution. ^1H NMR (300 MHz, C_6D_6): δ 0.86 (d, J_{HP} = 6.3 Hz, 9 H), 1.90 (d, J_{HP} = 74.4 Hz, 1 H), 4.88 (d, J_{HP} = 1.9 Hz, 10 H), 7.2–7.4 (broad, 9 H), 7.55–7.61 (m, 1 H), 7.9–8.2 (broad, 5 H). ^{13}C NMR (75 MHz, C_6D_6): δ 20.24 (d, J_{CP} = 23.7 Hz), 96.94, 130.02, 136.20, 137.34 (broad), 150.21 (broad). ^{31}P NMR (121 MHz, C_6D_6): δ −4.78. IR (KBr, cm^{-1}): 3052, 3009, 2130, 1427, 803, 732, 705, 508. HRMS: calcd for $C_{28}H_{26}HfPSi$ (M − C_3H_9P − H) 566.1160, Found 566.113 ± 0.003 amu. Anal. Calcd for $C_{31}H_{35}HfPSi$: C, 57.71; H, 5.47. Found (average of 4 attempts): C, 54.65; H, 5.34.

Observation of 5 by ^{1}H NMR Spectroscopy. Toluene-d_8 (0.65 mL) was added to a mixture of solid 3 (0.021 g, 0.048 mmol) and triphenylsilane (0.012 g, 0.046 mmol), and the reaction mixture was left for 6 h at −20 °C. A mixture of 3–5, along with free PMe_3 and isobutylene, was observed by ^1H NMR spectroscopy 5: ^1H NMR (300 MHz, C_7D_8) δ −0.59 (d, J = 6.9 Hz, 2 H), 2.31 (m, J = 6.9 Hz, 1 H), 5.66 (s, 10 H).

Reaction of 2 with Acetone To Produce 6. Complex 2 (0.31 g, 0.56 mmol) was dissolved in benzene (12 mL), and acetone (0.043 mL, 0.59 mmol) was added via syringe. The reaction mixture was stirred overnight at room temperature, and then the solvent was evaporated in vacuo to give 0.24 g of a yellow powder (80% yield, >95% pure). For recrystallization, complex 6 (100 mg) was washed with Et_2O (2 mL) and was then dissolved in THF (1 mL) and hexane (1 mL) was added. The material was filtered and the filtrate was slowly cooled to −78 °C to give 60 mg of a pale yellow solid. ^1H NMR (300 MHz, C_6D_6): δ 0.92 (d, J = 6.3 Hz, 6 H), 4.06 (septet, J = 6.3 Hz, 1 H), 5.71 (s, 10 H), 7.16–7.22 (m, 5 H), 7.23–7.29 (m, 5 H), 7.78 (dd, J = 1.5, 6.8 Hz, 5 H). ^{13}C NMR (75 MHz, C_6D_6): δ 26.37, 75.18, 109.07, 136.69, 145.54. IR (KBr, cm^{-1}): 3046, 2970, 2862, 1427, 1143, 1016, 803, 708, 701, 506, 490. Anal. Calcd for $C_{31}H_{32}OSiZr$: C, 68.96; H, 5.97. Found: C, 68.82; H, 5.95.

Reaction of 2 with Pivalonitrile To Produce 7. Complex 2 (0.04 g, 0.07 mmol) was dissolved in benzene-d_6 (0.65 mL) in a septum-capped NMR tube, and pivalonitrile (0.016 mL, 0.14 mmol) was added via syringe. The reaction mixture stood for 13 h. The yield of the reaction is >95%, as judged by ^1H NMR spectroscopy. At this point, the solvent was removed in vacuo to produce a yellow solid. The complex was thermally sensitive and decomposed upon attempted recrystallization. ^1H NMR (300 MHz, C_6D_6): δ 0.77 (s, 9 H), 5.57 (s, 10 H), 7.17–7.23 (m, 5 H), 7.28–7.33 (m, 5 H), 7.80 (d, J = 6.3 Hz, 5 H), 8.43 (s, 1 H). ^{13}C NMR (75 MHz, C_6D_6): δ 25.67, 38.50, 106.46, 127.27, 136.25, 136.58, 146.76, 177.86. IR (KBr, cm^{-1}): 3042, 3004, 2954, 2807, 1690, 1424, 1086, 1014, 805, 703, 502. HRMS: calcd for $C_{33}H_{35}NSiZr$ 563.1582, found 563.1578 ± 0.0006 amu. Anal. Calcd for $C_{33}H_{35}NSiZr$: C, 70.16; H, 6.24; found (average of 2 attempts): C, 68.78; H, 6.29.

Reaction of 2 with *tert*-Butyl Isocyanide To Produce 8. Complex 2 (0.34 g, 0.62 mmol) was dissolved in benzene (10 mL) and *tert*-butyl isonitrile (0.069 mL, 0.62 mmol) was added via syringe. The reaction mixture was stirred for 16 h, and the solvent was removed in vacuo. The tan solid which was produced was rinsed with Et_2O (2 mL) to give 0.17 g of 8 (50%). This material appears to be >95% pure, as judged by ^1H NMR spectroscopy, although we have been unable to obtain a satisfactory elemental analysis. ^1H NMR (300 MHz, C_6D_6): δ 0.76 (s, 9 H), 5.37 (s, 10 H), 7.16–7.23 (m, 5 H), 7.32 (t, J = 7.2 Hz, 5 H), 7.85 (dd, J = 1.5, 8 Hz, 5 H), 10.33 (s, 1 H). ^{13}C NMR (75 MHz, C_6D_6): δ 28.97, 59.29, 127.09, 136.74, 148.60, 214.43. IR (KBr, cm^{-1}): 3044, 2974, 2933, 1582, 1427, 1363, 1191, 1174, 1013, 804, 704, 503. HRMS: calcd for $C_{29}H_{26}NSiZr$ (M − C_4H_9) 506.0878, found 506.0876 ± 0.0006 amu (M$^+$ not observed). Anal. Calcd for $C_{33}H_{35}NSiZr$: C, 70.16; H, 6.24. Found (average of 3 attempts): C, 68.19; H, 6.06.

Reaction of 2 with 2-Butyne To Produce 9. Complex 2 (0.20 g, 0.36 mmol) was dissolved in benzene (8.0 mL), and 2-butyne (0.062 mL, 0.079 mmol) was added via syringe. The reaction mixture was stirred for 14 h, and the solvent was removed in vacuo. The estimated yield of 9,[11] as determined by ^1H NMR spectroscopy, was 83%. ^1H NMR (300 MHz, C_6D_6): δ 1.70 (s, 6 H), 1.85 (s, 6 H), 5.90 (s, 10 H). ^{13}C NMR (75 MHz, C_6D_6): δ 14.83, 20.10, 110.15, 110.56, 182.52.

Synthesis of (η^5-C_5H_5)$_2$Zr(H)(SiHPh$_2$)(PMe$_3$) (10). Complex 1 (500 mg, 1.39 mmol) was dissolved in THF (40 mL, −78 °C), diphenylsilane (0.26 mL, 1.39 mmol) was added, the cold bath was removed, and the reaction mixture was stirred for 1.5 h, while slowly warming to room temperature. The solvent was reduced in volume to ~10 mL, and product was precipitated by the addition of cold hexanes. The dull yellow solid obtained was washed with hexanes (5 × 5 mL) to afford 270 mg of 10 (40%) as a mixture of two geometric isomers (3.2:1.0). ^1H NMR (300 MHz, C_6D_6): major isomer δ 0.06 (dd, J = 3 Hz, J_{HP} = 69 Hz, 1 H), 0.80 (d, J_{HP} = 6 Hz, 9 H), 4.95 (d, J_{HP} = 2 Hz, 10 H), 6.22 (d, J = 3 Hz, 1 H), 8.09 (d, J = 7 Hz, 4 H); minor isomer δ −1.11 (dd, J = 10 Hz, J_{HP} = 16 Hz, 1 H), 0.96 (d, J_{HP} = 6 Hz, 9 H), 4.90 (d, J_{HP} = 2 Hz, 10 H), 5.51 (dd, J = 10 Hz, J = 13 Hz, 1 H), 8.15 (d, J = 7 Hz, 4 H); other resonances (C_6H_5) for both isomers δ 7.20 (m), 7.32 (t, J = 7 Hz). ^{13}C NMR (75 MHz, C_6D_6): major isomer δ 19.9, 97.9, 149.3; minor isomer δ 16.9, 97.2, 149.5; other resonances (C_6H_5) for both isomers δ 127.0–136.1. ^{31}P NMR (121 MHz, C_6D_6): δ 3.35 (major isomer), 2.28 (minor isomer). ^{29}Si NMR (99 MHz, C_6D_6): δ 50.46. Anal. Calcd for $ZrC_{25}H_{31}PSi$ (mixture of both isomers): C, 62.36; H, 6.49. Found: C, 61.97; H, 6.00.

Reaction of 2 with Diphenylsilane To Produce 10. Complex 2 was dissolved in benzene-d_6 (0.65 mL) in an NMR tube and diphenylsilane was added. After 1.5 h, a >95% yield of **10** was observed by ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6): major isomer δ 0.06 (dd, J = 3 Hz, J = 69 Hz, 1 H), 0.80 (d, J = 6 Hz, 9 H), 4.96 (d, J = 2 Hz, 10 H), 6.23 (d, J = 3 Hz, 1 H), 8.09 (d, J = 7 Hz, 4 H); minor isomer δ −1.12 (dd, J = 10 Hz, J = 16 Hz, 1 H), 0.96 (d, J = 6 Hz, 9 H), 4.91 (d, J = 2 Hz, 10 H), 5.51 (dd, J = 10 Hz, J = 13 Hz, 1 H), 8.15 (d, J = 7 Hz, 4 H); other resonances (C_6H_5) for both isomers 7.20 (m), 7.32 (t, J = 7 Hz).

Table IV. Crystallographic Data

formula	$C_{28}H_{26}PSiZr$
fw	481.82
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a	9.336 (2) Å
b	28.863 (8) Å
c	11.051 (3) Å
β	111.11 (2)°
Z	4
D_{calc}	1.152 g/cm^3
size	0.125 × 0.250 × 0.380 mm
$\mu_{MoK\alpha}$	4.40 cm^{-1}
diffractometer	Rigaku AFC6R
radiation	Mo Kα (λ = 0.71069 Å)
temp	−72 °C
scan type	ω
2θ range	4.0–55°
no. of reflns measd	
total	6888
unique	6506
no. of obsns ($I > 3.00\sigma(I)$)	3083
max. peak in final diff map	0.43 e/Å^3
min. peak in final diff. map	−0.34 e/Å^3
structure soln	direct methods
refinement	full-matrix least squares
R	0.038
R_w	0.048

Crystallography. Crystals were obtained from a THF/hexane mixture at room temperature. A wheat-colored rod of **2** (0.125 mm × 0.250 mm × 0.360 mm) was mounted on a glass fiber. Data were collected at −72 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation, λ = 0.71069 Å: monoclinic, space group $P2_1/c$, a = 9.336 (2) Å, b = 28.863 (8) Å, c = 11.051 (3) Å, β = 111.11 (2)°, V = 2778 (1) Å^3, Z = 4; d(calcd) = 1.152 g/cm^3. A total of 6506 unique reflections were collected (ω–2θ scan) to 2θ of 55.0°. The structure was solved by direct methods (SHELXS-86). Anisotropic refinement of all non-hydrogen atoms (fixed hydrogen parameters, d_{C-H} = 0.95 Å) and the isotropic refinement of the hydride by full-matrix least squares resulted in R = 0.038 and R_w = 0.048. Other crystallographic data are listed in Table IV.

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Registry No. **1**, 107453-01-0; **2**-d_0, 136911-78-9; **2**-d_1, 136911-79-0; **3**, 127033-21-0; **4**, 136911-80-3; **5**, 136911-81-4; **6**, 136911-82-5; **7**, 136911-83-6; **8**, 136911-84-7; **9**, 84101-39-3; **10a**, 136983-91-0; **10b**, 136983-92-1; Ph_3SiH, 789-25-3; $DSiPh_3$, 18536-60-2; 1-butene, 106-98-9; zirconocene dichloride, 1291-32-3; acetone, 67-64-1; pivalonitrile, 630-18-2; *tert*-butyl isocyanide, 7188-38-7; 2-butyne, 503-17-3; diphenylsilane, 775-12-2.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compounds **4**, **7**, and **8**, a ^{1}H NMR spectrum of a mixture of **3**, **4**, and **5**, a textual presentation of crystallographic data and procedures for **2**, ORTEP diagrams, and tables of crystal data, bond distances and angles, final positional and thermal parameters, and torsion angles and least-squares planes (35 pages); tables of structure factors (43 pages). Ordering information is given on any current masthead page.