3954 *Organometallics* **2008,** *27,* 3954–3959

Synthesis and Reactions of Cp*$_2$Hf(η^2-PhC$_2$SiMe$_3$) with Water and Carbon Dioxide[†]

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Received April 4, 2008

The complexation of phenyl(trimethylsilyl)acetylene by decamethylhafnocene gave the complex Cp*$_2$Hf(η^2-PhC$_2$SiMe$_3$) (**1-Hf**). By comparison of detailed spectroscopic and structural data as well as of some regioselective reactions of **1-Hf** to the titanium analogue Cp*$_2$Ti(η^2-PhC$_2$SiMe$_3$) (**1-Ti**) and the zirconium complex Cp*$_2$Zr(η^2-PhC$_2$SiMe$_3$) (**1-Zr**) one can try to understand how the metals interact in these complexes with differently substituted acetylenic carbon atoms. All data for **1-Hf** show an extremely strong interaction of the alkyne with hafnium compared to the analogous compounds of titanium and zirconium. Complex **1-Hf** reacted with water at the Hf−C(Ph) bond to form the complex Cp*$_2$Hf(OH)−C(SiMe$_3$)=CHPh (**2-Hf**). With carbon dioxide, a mixture of regioisomeric hafnafuranones **4a/b-Hf** was formed.

Introduction

In group 4 chemistry, the complexation of bis(trimethylsilyl)acetylene by metallocenes leads to three-membered metallacyclopropenes Cp′$_2$M(η^2-Me$_3$SiC$_2$SiMe$_3$) (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl). Such titanium and zirconium compounds show a very broad chemistry.[1] All attempts to obtain the analogous well-defined hafnium complexes failed for many years. The reason for this was assumed to be the enhanced reducing ability of hafnium compounds compared to those of zirconium. For the case of (*s-cis*-η^4-diene) metallocene complexes, Erker and co-workers described the σ to π ratio of the diene bonding to be shifted to a larger σ character for hafnium compared to zirconium, giving shorter Hf−C than Zr−C bonds.[2] Some consequences of the significantly different reactivity of hafnium compared to zirconium were shown by the Chirik group in the functionalization of molecular nitrogen with carbon dioxide in a hafnocene complex.[3]

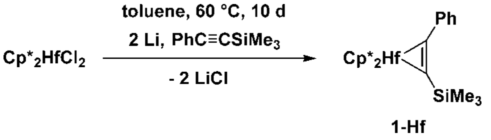
Recently, we found during the synthesis of Cp*$_2$Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) several examples of the consequences of such higher reducing ability of hafnocene compounds; e.g., ring opening of THF[4a,b] and a tandem Si−C/C−H bond cleavage[4c] can occur.

In this work, we investigated the complexation of phenyl(trimethylsilyl)acetylene by decamethylhafnocene by spectroscopic and structural methods. In general, one can tune the metal−alkyne interaction by changing the metals, the cyclopentadienyl ligands, or any additional ligands L. The observed trends, i.e., larger coordination shifts in the IR and ^{13}C NMR spectra as well as longer C−C bond distances and bending back angles of the substituents, indicate a stronger complexation of the alkyne in complexes with hafnium and/or pentamethylcyclopentadienyl ligands (compared to titanium and zirconium and/or cyclopentadienyl). If an additional ligand L is present, the interaction of the alkyne with the metal generally becomes weaker.

Results and Discussion

The reaction of decamethylhafnocene dichloride Cp*$_2$HfCl$_2$ with PhC$_2$SiMe$_3$ and lithium in toluene resulted in formation of the dark blue crystalline complex Cp*$_2$Hf(η^2-PhC$_2$SiMe$_3$) (**1-Hf**) in 49% yield (Scheme 1).

Scheme 1. Formation of Complex 1-Hf



Complex **1-Hf** is sensitive toward moisture and can be exposed to air for several minutes without decomposition. Its IR spectrum shows ν(C≡C) at 1528 cm^{-1}. As expected, there are two signals in the ^{13}C NMR spectrum at 246.8 (*C*SiMe$_3$) and 259.2 ppm (*C*Ph). Discrimination of the alkyne carbon atoms in phenyl(trimethylsilyl)acetylene was achieved by observation of the ^{13}C−^{1}H coupling patterns.[5,8d] These data indicate the strong complexation of the alkyne, leading to the hafnacyclopropene structure. The structure of complex **1-Hf** was confirmed by X-ray analysis (Figure 1). The C1−C2 bond distance of 1.334(3) Å is in the range of a C=C double bond. Moreover, the coordination mode of the alkyne is proved by the different Hf−C bond lengths of Hf1−C1 2.155(2) and Hf1−C2 2.197(2) Å. The reason for this difference can be found

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[†] This work is dedicated to Professor Günther Oehme on the occasion of his 70th birthday.

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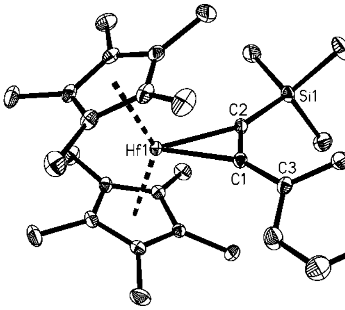
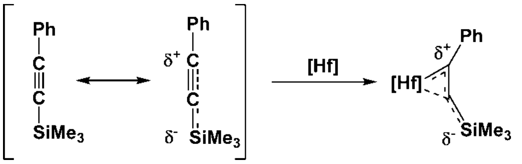


Figure 1. Molecular structure of complex **1-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−C2 1.334(3), Hf1−C1 2.155(2), Hf1−C2 2.197(2), C2−Si1 1.849(2), C1−C3 1.472(3); C1−Hf1−C2 35.69(8), C1−C2−Si1 140.1(2), C2−C1−C3 134.8(2).

in the electronic polarization in the alkyne, leading to a partial positive charge at C(Ph) and to a partial negative charge at the Si (β-effect of Me_3Si groups).[6] For this reason, the Hf−C(Ph) bond is stronger and shorter than the Hf−C($SiMe_3$) bond. Such effects have been observed before; especially for electron-rich late transition metals, this becomes even more relevant due to the high s-electron density, which is attracted by the partial positive charge of the C(Ph) of the alkyne (Scheme 2).[7]

Scheme 2. Coordination of PhC_2SiMe_3 at the Hafnocene Fragment



In contrast to what was found in the case of the bis(trimethylsilyl)acetylene complex $Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$, the synthesis of compound **1-Hf** is not accompanied by the formation of side products, i.e., vinylidene complexes or hafnacyclopentenes formed by Si−C and C−H bond activation.[4a,c] With respect to reductive coupling, no reactions with an excess of alkyne to give hafnacyclopentadienes were observed.

Another way of explaining the coordination of phenyl(trimethylsilyl)acetylene at the metal center is a combination of inductive parameters with spectroscopic data as reported previously for complexes with late transition metals such as Ni(0).[8a] A correlation of the these parameters of the substituents R with the coordination shifts in the IR and ^{13}C NMR spectra was described, e.g., for Ph larger coordination shifts of the alkyne were found (compared to $SiMe_3$).[8a] A similar result was found in the IR data for the early transition metals titanium and zirconium, but in the ^{13}C NMR spectra the reverse case was established.[8b] Thus, in the ^{13}C NMR spectra of these complexes with R = $SiMe_3$ larger shifts were observed compared to R = Ph. Unsymmetrically substituted complexes (Ph and $SiMe_3$) give upon coordination a smaller polarization of the carbon atoms for titanium and zirconium (compared to the free alkyne). This is not the case for Ni(0) complexes and was assumed to be a result of electron delocalization in the metallacyclopropenes of the early transition metals.[8c]

Table 1. Comparison of Spectroscopic Data of $L_2M(\eta^2\text{-}PhC_2SiMe_3)^a$

	M = Hf (**1-Hf**)	M = Ti (**1-Ti**)	M = Zr (**1-Zr**)	M = Ni (**1a-Ni**)
$\nu(C\equiv C)/cm^{-1}$	1528	1625	1618	1768
$\Delta\nu(C\equiv C)/cm^{-1}$	632	535	542	392
δ(CPh)/ppm	259.2	224.9	235.1	157.1
$\delta(CSiMe_3)$/ppm	246.8	213.2	222.5	128.2
$\Delta\delta$/ppm	12.4	11.7	12.6	28.9
$\Delta\delta$(CPh)/ppm	153.2	118.9	129.1	51.1
$\Delta\delta(CSiMe_3)$/ppm	152.8	119.2	128.5	34.8
$\Delta(\Delta\delta)$	0.4	−0.3	0.6	16.3
$d(C\equiv C)$/Å	1.334(3)	1.308(3)	1.340(9)	

[a] L = Cp*, M = Hf (**1-Hf**), Ti (**1-Ti**), Zr (**1-Zr**); L = Ph_3P, M = Ni (**1a-Ni**).[8d] For free alkyne: IR $\nu(C\equiv C)$ 2160 cm^{-1}; ^{13}C NMR $\delta(CSiMe_3)$ 94.0 ppm, δ(CPh) 106.0 ppm; $\Delta\delta = \delta$(CPh) 106.0 ppm − $\delta(CSiMe_3)$ 94.0 ppm = 12.0 ppm; $\Delta\Delta\delta = \Delta\delta(CPh) - \Delta\delta(CSiMe_3)$.

All spectroscopic data for **1-Hf** show a significantly stronger interaction of the alkyne with hafnium compared to the analogous compounds of titanium **1-Ti**[9] and zirconium **1-Zr**[10] as indicated by the higher shifts $\Delta\nu(C\equiv C)$, δ(CPh), and $\delta(CSiMe_3)$ in comparison to the starting alkyne (Table 1). With regard to different changes at the different substituted C-atoms, surprisingly there is no trend connected with the stronger complexation. In this respect, hafnium behaves similar to titanium and zirconium. One explanation could be the above-discussed delocalization in the three-membered ring.

The comparison of the structural data of complexes **1-Hf**, **1-Ti**, and **1-Zr** gives the same tendency for the complexation of phenyl(trimethylsilyl)acetylene as described before:[8c−e] shorter M−C(Ph) than M−C($SiMe_3$) bonds and larger C−C−Si than C−C−C_{ipso}(Ph) bending back angles. With regard to the difference in the M−C distances in the metallacyclopropene unit (Δd), unexpectedly, there is no trend which indicates a stronger complexation in the case of Hf. The stronger interaction with the alkyne in **1-Hf** compared to the Ti compound **1-Ti** can be derived from the C1−C2 bond length. The distance C1−C2 in **1-Zr** is essentially the same as the bond length in **1-Hf**, even though the spectroscopic data for **1-Hf** indicate a considerably stronger bonding of the alkyne than in **1-Zr**. This inconsistency might be clarified by DFT calculations. Compared to the alkyne complex $Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (C1−C2 1.337(4), Hf1−C1 2.188(3), Hf1−C2 2.184(3) Å), there is a clear

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Scheme 3. Formation of Complexes 2-M by Reaction of the Metallacyclopropenes 1-M with Water

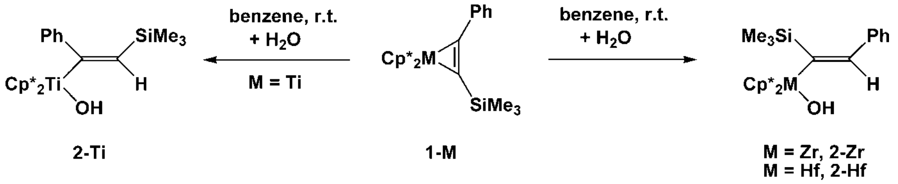


Table 2. Some NMR Parameters That Are Useful To Determine the Regiochemistry of Protonation of Coordinated PhC_2SiMe_3 to an Alkenyl Ligand

compound	=CH $\delta(^1H)$	=CH ^1J(C,H)	OH $\delta(^1H)$	$SiMe_3$ $\delta(^{13}C)$	$J(Si,H_{vinyl})$
2-Hf	8.40	155	4.25	7.7	22 (^3J)
2-Zr	8.40	153	4.58	7.3	22 (^3J)
2-Ti	4.72	131	7.98	1.1	6.0 (^2J)
$Cp_2Ti(OMe)$-C(Ph)=CH($SiMe_3$) (ref 9a)	5.51	134		0.7	6.4 (^2J)

difference in the structural parameters, showing the effect of the replacement of one Me_3Si group by a Ph group.

Reaction of 1-Hf with water to 2-Hf. 1-Hf reacted with water at the Hf−C(Ph) bond to form the complex $Cp^*_2Hf(OH)-C(SiMe_3)=CHPh$ (**2-Hf**) (Scheme 3), which was isolated as colorless needles in 71% yield.

The molecular structure of complex **2-Hf** (Figure 2) displays a hafnocene fragment coordinated with an alkenyl unit and a hydroxyl group. Unlike in similar alkenyl complexes of Ti and Zr,[11,13b] there is no agostic interaction between the hafnium center and the hydrogen atom at C2. The C1−C2 distance of 1.355(4) Å is in the range of a C=C double bond; this feature can also be derived from the IR data (ν(C≡C) 1593 cm^{-1}).

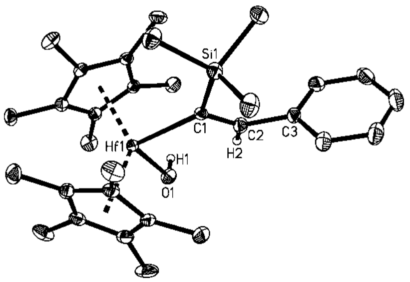


Figure 2. Molecular structure of complex **2-Hf**. Hydrogen atoms (except H1 and H2) are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−C2 1.355(4), C1−Hf1 2.319(3), Hf1−O1 1.984(2); Hf1−C1−C2 110.5(2), C1−C2−C3 130.6(3), C2−C1−Si1 115.0(2).

In the ^1H NMR spectrum, the signal for the OH group is a singlet at 4.25 ppm. The peak for the β-H is located at 8.40 ppm, compared to the similar complex $Cp_2Hf[-C(SiMe_3)=CH(SiMe_3)]_2O$ (**3-Hf**) (δ = 7.96 ppm).[12] This is in the same range; however, there is a slight shift downfield due to the different electronic properties of the alkyne substituents.

Reaction of 1-Ti and 1-Zr with Water and Comparison of the Products with 2-Hf. The reaction of **1-Ti** with water was investigated to compare the products with those obtained with **1-Hf**. **1-Ti** reacted with water at the Ti−C($SiMe_3$) bond to form the yellow complex $Cp^*_2Ti(OH)-C(Ph)=CH(SiMe_3)$ (**2-Ti**) (Scheme 3) in 53% yield. This is exactly the opposite of what was found for **1-Hf** and may be due to the high steric demand of the $SiMe_3$ group which is located in the β position to the metal center to minimize steric hindrance with the methyl groups of the permethyltitanocene fragment. The X-ray structure of **2-Ti** is shown in Figure 3.

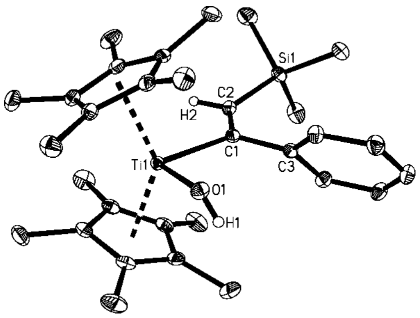


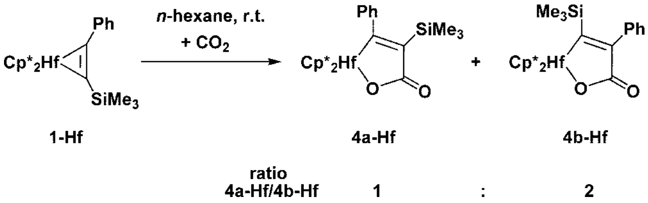
Figure 3. Molecular structure of complex **2-Ti**. Hydrogen atoms (except H1 and H2) are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−C2 1.347(2), C1−Ti1 2.211(2), Ti1−O1 1.877(1); Ti1−C1−C2 124.0(1), C3−C1−C2 116.7(1), C1−C2−Si1 131.3(1).

The bond length of C1−C2 (1.347(2) Å) is indicative of the C=C double bond character; compared to the starting complex **1-Ti**, this bond is longer (C1−C2 1.308(3) Å). As in **2-Hf**, no agostic interaction between the metal center and H2 was found. The ^1H NMR spectrum shows characteristic signals due to the OH group at 7.98 ppm and the hydrogen atom in β position at 4.72 ppm.

In contrast to **2-Ti**, the regioselectivity of the hydrolysis of **2-Zr** is the same as that of **2-Hf** (Scheme 3). Colorless needles of **2-Zr** were obtained from *n*-hexane. The spectroscopic data indicate the existence of a σ-alkenyl-complex: ^1H NMR signals at 4.58 and 8.40 ppm can be assigned to the OH group and the β-CH, respectively. The IR spectrum shows a characteristic OH absorption band at 3676 cm^{-1}.

Compared to **2-Hf**, **2-Zr** shows no significant differences in spectroscopic data. However, both complexes clearly differ from the titanium complex **2-Ti** and the related protolysis products $Cp_2Ti(OAlkyl)-C(Ph)=CH(SiMe_3)$.[13a] In the latter case, hydrolytic attack occurred at the M−C($SiMe_3$) bond. The regiochemistry of the hydrolysis of the M−C bonds in alkyne complexes can be determined safely by several NMR parameters (Table 2), but the best are the scalar coupling constants between vinylic H and ^{29}Si which is large ($^3J_{trans}$) for the α-silyl-substituted alkenyl ligands at Hf and Zr but small (^2J) for the β-silyl-substituted alkenyls at Ti (last column of Table 2).

Scheme 4. Reaction of Complex 1-Hf with CO_2 To Give 4a-Hf and 4b-Hf



Reaction of 1-Hf with Carbon Dioxide to 4-Hf. Reactions of metallocene alkyne complexes with carbon dioxide have been studied extensively.[13] These simple reactions can provide useful information with respect to the influence of the Cp ligand and the alkyne substituents on the regioselectivity of the insertion of other substrates in stoichiometric and catalytic reactions.

The alkyne complex **1-Hf** reacted with CO_2 to give a mixture of the regioisomeric hafnafuranones **4a-Hf** and **4b-Hf** (Scheme 4). From an *n*-hexane solution of this mixture, **4a-Hf** and **4b-Hf** crystallized as yellow prisms and yellow needles, respectively. Due to their similar solubility in suitable organic solvents, these complexes could not be separated. For this reason, for NMR investigations a mixture of **4a-Hf** and **4b-Hf** was used. However, only a small amount of the crystals of **4a-Hf** obtained from *n*-hexane were suitable for X-ray analysis.

This complex is a hafnafuranone (Figure 4) that contains a bent hafnocene fragment, which is similar to the zirconafuranone **4a-Zr** described earlier.[13d] The double-bond character of C1−C2 is indicated by the bond length of 1.363(3) Å.

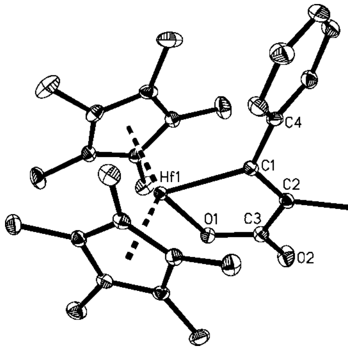


Figure 4. Molecular structure of complex **4a-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Hf1−C1 2.292(2), C1−C2 1.363(3), C2−C3 1.504(3), C3−O1 1.332(2), Hf1−O1 2.030(1), C3−O2 1.220(2), C1−Hf1−O1 76.16(6), C2−C1−C4 119.0(2), C1−C2−Si1 127.6(2).

NMR spectra and behavior of **4a/b-Hf** closely resemble those of the analogous Zr complexes[13d] that result from CO_2 addition to **1-Zr**. One remarkable feature is the hindered rotation of the trimethylsilyl group in **4b-Hf**, which is indicated by its temperature-dependent ^1H and ^{13}C NMR signals. Line broadening is perceptible even at ambient temperature. Below 240 K, two signals of intensity ratio 1:2 are registered for the three methyl groups (see the Experimental Section). The bulky trimethylsilyl group in α position of the hafnacycle is constrained between the bulky Cp* ligands; therefore, it cannot rotate freely and "locks in" with one methyl group in the mirror plane of the molecule which is represented by the metallacycle.

Both complexes **4a/b-Hf** suffer easy hydrolysis to yield the respective hafnocene carboxylates $Cp^*_2Hf(OH)OC({=}O){-}CSiMe_3{=}CHPh$ (**5a-Hf**) and $Cp^*_2Hf(OH)OC({=}O){-}CPh{=}CHSiMe_3$ (**5b-Hf**). These were not isolated but characterized in the reaction mixture (see the Experimental Section). Once again, this behavior is completely analogous to that of the zirconafuranones **4a/b-Zr**.[13d]

Conclusion

All spectroscopic and structural data for $Cp^*_2Hf(\eta^2\text{-}PhC_2SiMe_3)$ (**1-Hf**) show an extremely strong interaction of the alkyne with hafnium compared to the analogous compounds of titanium **1-Ti** and zirconium **1-Zr**. There is no directed influence of this stronger coordination on the different substituted C-atoms C(Ph) and C($SiMe_3$). Reactions of the alkyne complexes **1-M** with water gave σ-alkenyl complexes. Depending on the metal, the hydrolysis proceeds at the M−C($SiMe_3$) bond (M = Ti) or at the M−C(Ph) bond (M = Zr, Hf). Moreover, the hafnocene alkyne complex **1-Hf** was reacted with CO_2 to give by insertion into both Hf−C bonds unselectively a mixture of hafnafuranones **4a-Hf** and **4b-Hf**. This reaction behavior is in principle the same as found for **1-Zr** but in contrast to the titanium complex **1-Ti**, which gives an insertion of CO_2 at the C($SiMe_3$). We found that in both cases the titanium complex is reacting clearly different from its zirconium and hafnium analogues, which sometimes react in the same manner (this work) or differently, as shown before.[14]

Experimental Section

General Methods. All operations were carried out under argon with standard Schlenk techniques. Prior to use, nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents (C_6D_6, THF-d_8) were treated with sodium tetraethylaluminate, distilled, and stored under argon. $Cp^*_2HfCl_2$ was purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^1H, ^{13}C, ^{29}Si) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: C_6D_6 (δ_H 7.16, δ_C 128.0), THF-d_8 (δ_H 1.73, δ_C 25.2). The spectra were assigned with the help of DEPT and shift correlation experiments. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of 1-Hf. $Cp^*_2HfCl_2$ (2.06 g, 4.0 mmol) and finely cut lithium (0.110 g, 15.8 mmol) were suspended in 20 mL of toluene, and 1-phenyl-2-trimethylsilylacetylene (0.787 mL, 4.0 mmol) was added. The mixture was stirred for 10 days at 60 °C, followed by subsequent removal of all volatiles in vacuum. The blue-green residue was extracted with *n*-hexane at 55 °C (3 × 10 mL), and the blue filtrate was concentrated to half-its volume, filtered, and stored at −78 °C. After 24 h, dark blue crystals had formed, which were isolated by decanting of the mother liquor,

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washed with cold *n*-hexane, and dried in vacuum to give 1.22 g (2.0 mmol, 49%) of complex **1-Hf**: mp 187−189 °C under Ar; IR (nujol mull, $\mathrm{cm^{-1}}$) 1528 (C≡C); NMR (C_6D_6, 296 K) ^{1}H (400 MHz) δ 0.40 (s, 9H, $SiMe_3$), 1.82 (s, 30H, Cp*), 6.99 (m, 2H, *o*-Ph), 7.01 (m, 1H, *p*-Ph), 7.27 (m, 2H, *m*-Ph); ^{13}C (100 MHz) δ 4.2 ($SiMe_3$), 11.6 ($C_5\mathit{Me}_5$), 118.2 (C_5Me_5), 125.8 (*p*-Ph), 128.2 (*m*-Ph), 131.3 (*o*-Ph), 132.2 (*i*-Ph), 246.8 (*C*SiMe$_3$), 259.2 (*C*Ph); ^{29}Si (79 MHz) δ −8.0. MS (70 eV, *m*/*z*) 624 $[M]^+$. Anal. Calcd for $C_{31}H_{44}HfSi$: C, 59.74; H, 7.12. Found: C, 59.33; H, 6.82.

Preparation of 2-Hf. $Cp^*_2Hf(\eta^2\text{-}PhC_2SiMe_3)$ (**1-Hf**) (0.749 g, 1.20 mmol) was dissolved in 10 mL of benzene, and water (0.022 mL, 1.22 mmol) was added to the blue solution. The mixture was agitated and kept at room temperature. After 2 weeks, the solvent was removed in vacuum from the colorless solution. The white residue was dissolved in 5 mL of benzene, and the resulting solution was filtered and slowly concentrated in an argon flush to half-its volume. After 24 h at room temperature, colorless needles had formed, which were isolated, washed with cold *n*-hexane, and dried in vacuum to give 0.548 g (0.85 mmol, 71%) of complex **2-Hf**: mp 184−186 °C under Ar; IR (KBr, $\mathrm{cm^{-1}}$) 1239 ($SiMe_3$), 1593 (C=C), 3681 (OH); NMR (C_6D_6, 296 K) ^{1}H (300 MHz) δ 0.24 (s, 9H, $SiMe_3$), 1.91 (s, 30H, Cp*), 4.25 (s, 1H, OH), 7.10 (m, 1H, *p*-Ph), 7.23 (m, 2H, *m*-Ph), 7.34 (m, 2H, *o*-Ph), 8.40 (s, 1H, CH); ^{13}C (75 MHz) δ 7.7 ($SiMe_3$), 12.0 ($C_5\mathit{Me}_5$), 118.3 (C_5Me_5), 125.9 (*p*-Ph), 127.8 (*m*-Ph), 128.4 (*o*-Ph), 147.6 (*i*-Ph), 158.7 (*C*H-Ph), 207.4 (*C*-SiMe$_3$); MS (70 eV, *m*/*z*) 642 $[M]^+$, 625 $[M - OH]^+$. Anal. Calcd for $C_{31}H_{46}HfOSi$: C, 58.06; H, 7.23. Found: C, 57.83; H, 7.17.

Preparation of 2-Ti. $Cp^*_2Ti(\eta^2\text{-}PhC_2SiMe_3)$ (**1-Ti**) (0.463 g, 0.94 mmol) was dissolved in 15 mL of benzene, and water (0.017 mL, 0.94 mmol) was added. The dark red solution was stirred and kept at room temperature. After 10 days, the solvent was removed in vacuum from the yellow solution. The yellow residue was dissolved in 10 mL of *n*-hexane, and the solution was filtered and kept at room temperature. After 2 h, yellow crystals had formed, which were isolated, washed with cold *n*-hexane, and dried in vacuum to give 0.253 g (0.49 mmol, 53%) of complex **2-Ti**: mp 124−126 °C under Ar; IR (KBr, $\mathrm{cm^{-1}}$) 1236 ($SiMe_3$), 1588 (C=C), 3628 (OH); NMR (THF-d_8, 296 K) ^{1}H (300 MHz) δ −0.19 (s, 9H, $SiMe_3$), 1.86 (s, 30H, Cp*), 4.72 (s, 1H, CH), 6.85 (m, 1H, *p*-Ph) 6.95 (m, 4H, *o*/*m*-Ph), 7.98 (s, 1H, OH); ^{13}C (75 MHz) δ 1.1 ($SiMe_3$), 12.5 ($C_5\mathit{Me}_5$), 121.8 (C_5Me_5), 124.5 (*p*-Ph), 126.5 (*m*-Ph), 127.9 (*o*-Ph), 132.7 (*C*H-SiMe$_3$), 158.1 (*i*-Ph), 224.8 (*C*-Ph); MS (70 eV, *m*/*z*) 493 $[M - OH]^+$, 335 $[Cp^*_2TiOH]^+$. Anal. Calcd for $C_{31}H_{46}TiOSi$: C, 72.91; H, 9.08. Found: C, 72.20; H, 9.19.

Preparation of 2-Zr. $Cp^*_2Zr(\eta^2\text{-}PhC_2SiMe_3)$ (**1-Zr**) (0.365 g, 0.68 mmol) was dissolved in 8 mL of benzene, and water (0.012 mL, 0.68 mmol) was added. The blue-green solution was agitated and kept at room temperature. After 1 week, the solvent was removed in vacuum from the colorless solution. The residue was dissolved in 5 mL of warm *n*-hexane, and the resulting solution was filtered and allowed to cool to room temperature. After 24 h, colorless needles were formed, which were isolated, washed with cold *n*-hexane and dried in vacuum to give 0.253 g (0.46 mmol, 67%) of complex **2-Zr**: mp 173 °C under Ar; IR (KBr, $\mathrm{cm^{-1}}$) 1238 ($SiMe_3$), 1593 (C=C), 3676 (OH); NMR (C_6D_6, 296 K) ^{1}H (400 MHz) δ 0.25 (s, 9H, $SiMe_3$), 1.88 (s, 30H, Cp*), 4.58 (s, 1H, OH), 7.10 (m, 1H, *p*-Ph), 7.22 (m, 2H, *m*-Ph), 7.34 (m, 2H, *o*-Ph), 8.40 (s, 1H, CH). ^{13}C (100 MHz) δ 7.3 ($SiMe_3$), 12.0 ($C_5\mathit{Me}_5$), 119.3 (C_5Me_5), 125.9 (*p*-Ph), 127.8 (*m*-Ph), 128.4 (*o*-Ph), 146.2 (*i*-Ph), 155.2 (*C*H-Ph), 207.0 (*C*-SiMe$_3$); ^{29}Si (79 MHz) δ −16.0; MS (70 eV, *m*/*z*) 535 $[M - OH]^+$, 377 $[Cp^*_2ZrOH]^+$. Anal. Calcd. for $C_{31}H_{46}ZrOSi$: C, 67.21; H, 8.37. Found: C, 66.92; H, 7.82.

Preparation of 3-Hf. See ref 12: NMR (297 K, C_6D_6) ^{1}H (300 MHz) δ 0.34 (s, 18 H, α-SiMe$_3$), 0.40 (s, 18 H, β-SiMe$_3$), 6.00 (s, 20 H, Cp), 7.96 (br s, 2 H, =CH); ^{13}C (75 MHz) δ 2.3 (β-SiMe$_3$), 4.2 (α-SiMe$_3$), 110.6 (Cp), 158.6 (=CH), 235.0 (HfC).

Preparation of 4a-Hf and 4b-Hf. $Cp^*_2Hf(\eta^2\text{-}PhC_2SiMe_3)$ (**1-Hf**) (0.749 g, 1.20 mmol) was dissolved in 10 mL of *n*-hexane. The blue-green solution was filtered, the Ar atmosphere was removed in vacuum, and the Schlenk tube was flushed with dry CO_2. The color of the reaction mixture changed to yellow, and after 2 h, yellow crystals formed, which were separated by decanting of the mother liquor, washed with cold *n*-hexane, and dried in vacuum to give 0.214 g (0.32 mmol, 51%) of a mixture of complexes **4a-Hf** and **4b-Hf**. From this precipitate single yellow prisms of **4a-Hf** were selected and used for an X-ray analysis. Both species were characterized by NMR spectroscopy in THF-d_8 solution at 307 K as a mixture which contained also varying amounts of their hydrolysis products **5a-Hf**, $Cp^*_2Hf(OH)OC(=O)-C(SiMe_3)=CHPh$, and **5b-Hf**, $Cp^*_2Hf(OH)OC(=O)\text{-}CPh=CH(SiMe_3)$. Not all signals were identified. **4a-Hf**: ^{1}H (400 MHz) δ 0.02 (s, 9H, $SiMe_3$), 1.92 (s. 30H, Cp*), 6.78 (m, 2H, *o*-Ph), 7.22 (m, 2H, *m*-Ph); ^{13}C (100 MHz) δ 2.1 ($SiMe_3$), 11.3 ($C_5\mathit{Me}_5$), 122.0 (C_5Me_5), 126.5 (*p*-Ph), 128.1 (*m*-Ph), 129.4 (*o*-Ph), 158.6 (*C*-SiMe$_3$), 240.7 (*C*-Ph); ^{29}Si (79 MHz) δ −10.4. **4b-Hf**: ^{1}H (400 MHz) δ −0.12 (br s, 9H, $SiMe_3$), 2.06 (s, 30H, Cp*), 7.11 (m, 2H, *o*-Ph), 7.12 (m, 1H, *p*-Ph), 7.19 (m, 2H, *m*-Ph); ^{13}C (100 MHz) δ 5.6 ($SiMe_3$), 11.8 ($C_5\mathit{Me}_5$), 122.2 (C_5Me_5), 126.6 (*p*-Ph), 127.3 (*m*-Ph), 130.5 (*o*-Ph), 146.1 (*i*-Ph), 163.2 (CO), 165.6 (*C*-Ph), 228.6 (*C*-SiMe$_3$); ^{29}Si (79 MHz) δ −14.6. **4b-Hf at 207 K**: ^{1}H δ −0.05 (br s, 3H, $SiMe_3$), −0.22 (br s, 6H, $SiMe_3$), 2.05 (s, 30H, Cp*); ^{13}C δ 5.4 (1C $SiMe_3$), 5.5 (2C $SiMe_3$), 11.9 ($C_5\mathit{Me}_5$), 121.8 (C_5Me_5). **5a-Hf**: ^{1}H (400 MHz) δ 0.07 (s, 9H, $SiMe_3$), 1.91 (s. 30H, Cp*), 3.76 (br s, OH), 7.24 (m, 2H, *o*-Ph), 8.50 (s, 1H, CH); ^{13}C (100 MHz) δ 1.4 ($SiMe_3$), 11.2 ($C_5\mathit{Me}_5$), 118.8 (C_5Me_5), 128.5 (*m*-Ph), 128.7 (*p*-Ph), 129.1 (*o*-Ph), 139.5 (*i*-Ph), 140.2 (*C*-SiMe$_3$), 155.6 (*C*-Ph), 177.8 (CO); ^{29}Si (79 MHz) δ −7.2 ($^3J_{\mathrm{Si,H}} = 11.6$ Hz). **5b-Hf**: ^{1}H (400 MHz) δ −0.12 (s, 9H, $SiMe_3$), 1.84 (s. 30H, Cp*), 3.66 (br s, OH), 7.15 (s, 1H, CH), 7.24 (m, 2H, *o*-Ph), 7.29 (m, 2H, *m*-Ph); ^{13}C (100 MHz) δ −0.6 ($SiMe_3$), 11.0 ($C_5\mathit{Me}_5$), 118.7 (C_5Me_5), 127.9 (*p*-Ph), 128.0 (*m*-Ph), 130.5 (*o*-Ph), 140.2 (*i*-Ph), 143.0 (*C*-SiMe$_3$), 152.9 (*C*-Ph), 174.0 (CO); ^{29}Si (79 MHz) δ −8.1 ($^2J_{\mathrm{Si,H}} = 2.7$ Hz); MS for **4-Hf** (70 eV, *m*/*z*) 668 $[M]^+$.

Diffraction data were collected on a STOE IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97[15] and SIR 2004,[16] respectively) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[17]). XP (Bruker AXS) was used for graphical representations. X-ray data are shown in Table 3.

Table 3. Crystallographic Data

	1-Hf	**2-Hf**	**2-Ti**	**4a-Hf**
cryst syst	triclinic	monoclinic	triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.703(2)	15.937(1)	9.1336(4)	10.2069(5)
b (Å)	10.366(2)	11.7378(5)	10.3287(4)	17.1456(4)
c (Å)	15.583(3)	16.5513(9)	16.5723(7)	17.6053(6)
α (deg)	83.09(3)	90.00	93.569(3)	90.00
β (deg)	72.17(3)	114.011(5)	104.347(3)	105.079(3)
γ (deg)	72.66(3)	90.00	107.040(3)	90.00
V ($Å^3$)	1423.5(5)	2828.2(3)	1432.7(1)	2974.9(2)
Z	2	4	2	4
density ($g\cdot cm^{-3}$)	1.454	1.506	1.184	1.490
μ(Mo Kα) (mm^{-1})	3.722	3.752	0.361	3.573
T (K)	200(2)	200(2)	200(2)	200(2)
no. of rflns (measd)	20436	42379	21698	56772
no. of rflns (indep)	5597	5982	5936	8008
no. of rflns (obsd)	5270	4974	4713	6637
no. of params	298	321	328	338
R1 ($I > 2\sigma(I)$)	0.014	0.022	0.031	0.018
wR2 (all data)	0.037	0.050	0.086	0.039

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Acknowledgment. We thank our technical staff in particular Regina Jesse and Petra Bartels for assistance. Support by the Deutsche Forschungsgemeinschaft (SPP 1118, Project No. Ro 1269/6 and GRK 1213) and the Russian Foundation for Basic Research (project code 05-03-32515) is acknowledged.

Supporting Information Available: Crystallographic data in CIF file format, including bond lengths and angles of compound **1-Hf**, **2-Hf**, **2-Ti**, and **4a-Hf** (data). This material is available free of charge via the Internet at http://pubs.acs.org.

OM8003064