Synthesis and Isolation of Di-*n*-butylhafnocene and Its Application as a Versatile Starting Material for the Synthesis of New Hafnacycles

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The previously described hafnocene alkyne complexes are of limited applicability for the generation of the hafnocene fragment in stoichiometric and catalytic reactions. For this reason di-*n*-butylhafnocene (**1-Hf**) was fully characterized and used as a hafnocene source in reactions with alkynes and diynes. With bis(trimethylsilyl)acetylene and pyridine the alkyne complex Cp₂Hf(py)(η^2 -Me₃SiC₂SiMe₃) (**2-Hf**) was obtained and coordination of di-*tert*-butylbutadiyne yielded the first structurally characterized hafnacyclocumulene, Cp₂Hf(η^4 -*t*-BuC₄-*t*-Bu) (**4-Hf**). By the coupling of 2 equiv of the 1,3-butadiyne RC₄R at the hafnocene center, hafnacyclopentadienes were formed regioselectively (R = *t*-Bu, **5-***t***-Bu-Hf**; R = SiMe₃, **5-SiMe₃-Hf**). In the case of 1,4-diphenylbutadiyne the hafnocene-substituted [4]radialene **6-Hf** was formed. Treatment of the latter with acid gave the free [4]radialene **7**. In the reaction of **4-Hf** with diphenylacetylene, the alkyne inserted into the Hf-C_α bond to give the hafnacyclopentadiene **8**.

Introduction

The investigation of hafnocene complexes with respect to their spectroscopic and structural properties and the application of such compounds in unusual bond activation reactions has been a topic of current interest in group 4 organometallic chemistry. For example, Chirik and co-workers have reported dinitrogen functionalizations promoted by hafnocene complexes.¹ Moreover, in our group, the first hafnocene alkyne complexes of type Cp'₂Hf(L)(η^2 -RC₂SiMe₃) (Cp' = substituted or unsubstituted cyclopentadienyl; R = SiMe₃, Ph; L = PMe₃) have been synthesized and investigated.² During the formation of Cp*₂Hf(η^2 -Me₃SiC₂SiMe₃) unprecedented C–H and Si–C bond activations occurred which have not been observed for the titanium and zirconium analogues.³

However, in contrast to the corresponding alkyne complexes of titanocene and zirconocene, hafnocene alkyne complexes cannot be used as hafnocene sources, due to the strong complexation of the alkyne to the metal atom, as evidenced by spectroscopic and structural data. In the case of zirconium, the Negishi system Cp₂ZrCl₂/n-BuLi has found numerous applications as a Zr(II) source: e.g., in organic and organometallic coupling reactions. In the reaction of Cp₂ZrCl₂ with *n*-BuLi at -78 °C, the dialkyl complex Cp₂Zr(*n*-Bu)₂ (**1-Zr**)⁴ is formed, which eliminates butane and 1-butene to give the free zirconocene. This then can undergo further reactions. This chemistry has been reviewed in numerous articles and books.⁴ Only two applications of the corresponding system Cp2HfCl2/ *n*-BuLi have been reported.⁵ However, as in the case of Cp₂Zr(*n*- Bu_{2} , the complex $Cp_{2}Hf(n-Bu_{2})$ had not been isolated and fully characterized. This now has been achieved by our group.

Metallocene sources such as the Negishi reagent or group 4 metallocene alkyne complexes can be used for the preparation of a variety of metallacycles. Complexes with rather unusual structural motifs, such as five-membered metallacyclocumulenes (i.e., 1-metallacyclopenta-2,3,4-trienes) and 1-metallacyclopent-3-ynes, have been prepared in our group and by Suzuki and co-workers.⁶ The first zirconacyclocumulene was prepared by reaction of the alkyne complex **2-Zr** with di-*tert*-butylbutadiyne (eq 1).⁷



We recently prepared the first five-membered hafnacyclocumulenes by reduction of $Cp_{2}^{*}HfCl_{2}$ by metallic lithium in the

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presence of the 1,3-butadiyne RC_4R (R = Ph, SiMe₃) (eq 2).⁸ Spectroscopic investigations of these complexes revealed similarities to the corresponding zirconium species. However, a characterization of these complexes by X-ray crystallography was not possible.



In the reaction of the zirconocene alkyne complex **2-Zr** with 2 equiv of 1,3-butadiynes, Me_3SiC_4R (R = SiMe₃, *t*-Bu), sevenmembered zirconacyclocumulenes were formed. Most likely the second molecule of the diyne inserts into the five-membered zirconacyclocumulene, which was formed as an intermediate by prior coordination of the first 1,3-butadiyne molecule (Scheme 1).⁷ Another possibility was described by Buchwald and co-workers, who prepared this complex with R = SiMe₃ starting from the Negishi reagent.⁹

Scheme 1. Seven-Membered Zirconacyclocumulenes



For titanium, no such insertion was found to take place. Instead, with the alkyne complex $Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$ as

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starting material, two molecules of the 1,3-butadiyne $Me_3SiC_4SiMe_3$ were coupled to give a titanacyclopentadiene (eq 3).¹⁰



Results and Discussion

Di-*n*-butylhafnocene was prepared by reaction of Cp₂HfCl₂ with *n*-BuLi (eq 4) at room temperature as a pale yellow solid, which melts at 32–33 °C. The NMR spectrum displays a signal for the Cp protons at 5.67 ppm. Moreover, a characteristic multiplet for the α -CH₂ group can be found at 0.12 ppm. Hence, complex **1-Hf** was isolated in analytically pure form for the first time and its existence was established by ¹H and ¹³C NMR. The observed signal for the Cp protons in the ¹H NMR is the same as found before by Negishi et al.;⁵ thus, the previously suggested presence of this complex in solution was proved by our investigations.



Remarkably, formation of 1-Hf proceeds at room temperature and reactions with substrates take place at 100 °C (see below).¹¹ Brubaker and co-workers found that thermolysis of this compound at 60 °C yields 1-butene and butane as well as traces of methane and ethylene.¹² These observations are in contrast to the behavior of $Cp_2Zr(n-Bu)_2$, which is formed at -78 °C and generates the Negishi reagent Cp₂Zr(1-butene) by elimination of butane at temperatures around -40 °C. Therefore, the system Cp₂ZrCl₂/n-BuLi can be used as a versatile in situ source of Zr(II) in organometallic and organic coupling reactions. However, its limited stability at temperatures above -40 °C is a disadvantage. The decomposition of Cp2Zr(1-butene) was investigated by Dioumaev and Harrod.¹³ Also, THF must be used as the solvent. These obstacles have been overcome by the use of the zirconocene alkyne complex $Cp_2Zr(py)(\eta^2 -$ Me₃SiC₂SiMe₃) (2-Zr), which can be stored at room temperature, can be used in a definite stoichiometry, and generates the metallocene under mild conditions by dissociation of the alkyne. A similar, stable reagent is now available for hafnium.



Complex **1-Hf** can be used for the generation of the pyridinestabilized hafnocene alkyne complex **2-Hf** (eq 5). Reaction of

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⁽¹¹⁾ For our investigations we used a reaction temperature of 100 °C to minimize the reaction time. According to Brubaker and co-workers¹² elimination of butane and 1-butene already takes place at 60 °C.

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Scheme 2. Reactions of 1-Hf with Butadiynes



the Cp₂HfCl₂/*n*-BuLi system with bis(trimethylsilyl)acetylene and pyridine at 100 °C in toluene followed by extraction with *n*-hexane gave **2-Hf** as dark purple crystals (32%), mp 121–123 °C. Longer heating results in decomposition of **2-Hf** to a mixture of unidentified products; therefore, it is essential that the reaction time does not exceed 3–4 h. This reaction protocol is an alternative to the previously described preparation of hafnocene alkyne complexes in which magnesium or lithium is used as a reducing agent.^{2a}

The IR spectrum of **2-Hf** shows an intense band at 1548 cm⁻¹, but a definite assignment to the coordinated alkyne is not possible, due to the stretching vibration of pyridine which is also found in this region. A comparison with the corresponding values for similar complexes suggests that this assignment makes sense $(Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)^{14}$ (**2-Zr**), 1579/1599 cm⁻¹; $Cp_2Hf(PMe_3)(\eta^2-Me_3SiC_2SiMe_3)^{2a}$ (**3**), 1551 cm⁻¹). Moreover, a slightly stronger complexation of the alkyne to the metal in **2-Hf** compared to that in **2-Zr** becomes evident.

NMR spectroscopic measurements at variable temperature revealed similarities to **2-Zr**. At room temperature, due to the fast rotation of the alkyne at the metal, only one signal was observed for the SiMe₃ group (see Figure S1 in the Supporting Information). This pseudosymmetry was removed after cooling; at -6 °C two signals arise from the broad room-temperature signal, and at -56 °C these signals appear sharp at 0.18 and 0.52 ppm. Similar observations were made in the ¹³C NMR spectra. Signals due to the alkyne carbon atoms—both appeared at -16 °C—were observed at 207.0 and 233.0 ppm at -56 °C. Moreover, this downfield shift clearly identifies **2-Hf** as a hafnacyclopropene (**2-Zr**, 195.3 and 220.5 ppm).

Upon reaction of $Cp_2Hf(n-Bu)_2$ (**1-Hf**) with di-*tert*-butylbutadiyne in toluene the first structurally characterized hafnacyclocumulene, **4-Hf**, was formed (reported earlier in a preliminary communication¹⁵) (Scheme 2). After recrystallization from *n*-hexane yellow crystals (71%) were isolated, mp 192–193 °C.

¹³C NMR spectroscopic data for the ring carbon atoms resemble those of the corresponding titanium¹⁰ and zirconium⁷

complexes (**4-Hf**, C_{α} 188.1 and C_{β} 105.9 ppm; **4-Ti**, C_{α} 181.9 and C_{β} 94.7 ppm; **4-Zr**, C_{α} 186.4 and C_{β} 105.5 ppm) and show the expected behavior: i.e., the downfield shift of the signal for C_{α} compared to C_{β} .

The molecular structure of **4-Hf** is depicted in Figure 1. Bond lengths and angles are similar to those found earlier for **4-Zr**.⁷ The central double bond is elongated, due to the interaction of the in-plane π orbitals of this bond with the metal d(π) orbitals (C1-C2 = 1.288(5), C2-C3 = 1.334(5), C3-C4 = 1.298(5) Å). This feature has been described before for the analogous titanium and zirconium complexes. It was investigated theoretically by Jiao and Jemmis, who found these complexes to be "in-plane aromatic" with a (η^2 - σ , σ) + (η^2 - π , π) coordination of the 1,3-butadiyne.¹⁶



Figure 1. Molecular structure of complex **4-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Hf1-C1 = 2.281(4), C1-C2 = 1.288(5), C2-C3 = 1.334(5), C3-C4 = 1.298(5), Hf1-C4 = 2.308(4); C1-Hf1-C4 = 99.20(14), Hf1-C1-C2 = 74.2(2), C1-C2-C3 = 146.3(4), C2-C3-C4 = 147.1(4), C3-C4-Hf1 = 73.2(2).

The reaction of **1-Hf** with bis(trimethylsilyl)butadiyne over 5 h results in the formation of the hafnacyclopentadiene **5-SiMe₃-Hf** in 66% yield (Scheme 2). This complex is obtained

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irrespective of the ratio of the reagents used. The formation of the corresponding hafnacyclocumulene was not observed.

NMR data are in the expected range. The nature of the SiMe₃ substituents can be derived from the downfield shift of the signals for corresponding adjacent C_{α} atoms in the ¹³C NMR spectrum (225.1 ppm) compared to the signal for the alkynyl-substituted C_{α} of the hafnacyclopentadiene (196.4 ppm). The IR spectrum displays characteristic bands due to the stretching vibrations of the alkynyl group at 2075 and 2121 cm⁻¹.

The molecular structure of **5-SiMe₃-Hf** is comparable with that of the complex **5-t-Bu-Hf**, which will be discussed below. Therefore, an ORTEP representation is given in the Supporting Information (Figure S2). Characteristic bond lengths for a metallacyclopentadiene with the central bond significantly longer than the other two bonds were observed (C1–C2 = 1.369(3), C2–C3 = 1.495(3), C3–C4 = 1.378(3) Å).

To the best of our knowledge, there are only three examples of structurally characterized hafnacyclopentadienes.¹⁷ The characteristic bond distances in the hafnacyclopentadiene in **5-SiMe₃-Hf** are similar to those found earlier (e.g., in Cp₂Hf- $[C(Ph)=C(Ph)C(Ph)=C(Ph)]^{17a}$).

In comparison to the reactions of **2-Zr** with Me₃SiC₄R (R = SiMe₃, *t*-Bu), which gave seven-membered zirconacyclocumulenes as described above, an insertion of a second molecule of the diyne did not occur. Instead, in the reaction of **1-Hf** with two molecules of the diyne coupling was the exclusive process. In fact, the reaction of the hafnium complex is similar to the aforementioned formation of the titanacyclopentadiene starting from the corresponding alkyne complex.¹⁰

In the reaction of **1-Hf** with diphenylbutadiyne a totally different and unexpected outcome is observed. Instead of the formation of a five-membered metallacycle similar to **4-Hf** and **5-SiMe₃-Hf**, the dinuclear hafnocene-substituted radialene **6-Hf** was obtained (Scheme 2).

Complex **6-Hf** is sparingly soluble in organic solvents; therefore, complete ¹³C NMR data in solution could not be obtained. Signals due to the Cp ligands were observed at 6.01 (¹H) and 109.2 (¹³C) ppm, respectively. However, the existence of this complex was proved unequivocally by mass spectral studies, which showed the molecular ion $[M]^+$ at m/z 1022.

The molecular structure of **6-Hf** is depicted in Figure 2. Bond lengths and angles for the central radialene unit are similar to those found earlier for a similar titanium complex with η^{5} -MeC₅H₄ ligands (**6-Ti-Me**).^{18a} The data obtained for **6-Hf** are comparable to those in the cyclobutane ring of the tricyclic

[4]radialene,18b which formed by dimerization of cyclohepta-1,2,3-triene (corresponding data for 6-Ti-Me in brackets): C2-C3 = 1.535(3) [1.528(4)], C2-C3A = 1.499(3) [1.525(4)],C3-C4 = 1.352(3) [1.344(4)], C1-C2 = 1.347(3) [1.336(4)]Å; C1-C2-C3 = 128.0(2) [127.5(3)], C2-C3-C4 = 127.6(2) [127.6(3)], C2-C3-C2A = 90.1(2) [89.8(2)], C3-C2-C3A= 89.9(2) [90.2(2)], C4-C3-C2A = 142.0(2) [142.6(3)], $C1-C2-C3A = 141.9(2) [142.3(3)]^{\circ}$. Further data for the fused hafnacyclopentadiene 6-Hf are as follows: C1-Hf1 = 2.219(2), C4-Hf1 = 2.223(2) Å; C2-C1-Hf1 = 95.6(2), C3-C4-Hf1 $= 95.5(2)^{\circ}$. The cyclobutane ring C2, C3, C2A, C3A is planar and nearly coplanar with the two fused hafnacyclopentadiene ring systems (mean deviation from the best plane defined by Hf1, C1, C2, C3, C4, Hf1A, C1A, C2A, C3A, C4A 0.081 Å). The planes of the phenyl groups bound to one hafnacyclopentadiene ring are twisted with respect to each other $(16.2(2)^{\circ})$ and show angles of 42.0(2) and $45.3(2)^{\circ}$ to the plane of the central four-membered ring.



Figure 2. Molecular structure of complex **6-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C2–C3 = 1.535(3), C2–C3A = 1.499(3), C3–C4 = 1.352(3), C1–C2 = 1.347(3), C1–Hf1 = 2.219(2), C4–Hf1 = 2.223(2); C1–C2–C3 = 128.0(2), C2–C3–C4 = 127.6(2), C2–C3–C2A = 90.1(2), C3–C2–C3A = 89.9(2), C4–C3–C2A = 142.0(2), C1–C2–C3A = 141.9(2), C2–C1–Hf1 = 95.6(2), C3–C4–Hf1 = 95.5(2).

In addition to this dinuclear complex **6-Hf**, a number of other species were formed in the reaction of **1-Hf** with diphenylbutadiyne. The identification of this species was not successful and will be subject of further investigations. However, it is reasonable to assume a constitution as observed earlier for the byproducts of the reaction of Cp₂Ti(η^2 -Me₃SiC₂SiMe₃) with 1,4-diphenylbutadiyne.^{18a}

In the case of the titanium complex **6-Ti** protolysis with hydrochloric acid led to the formation of an acyclic hydrocarbon.^{18a} This conversion is very fast, and we are not sure whether it proceeds via a free radialene. In contrast, after protolysis of the hafnium complex **6-Hf** a free [4]radialene (7)

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was obtained (Scheme 3). Whereas **6-Ti** reacted very quickly upon treatment with acid, the conversion of **6-Hf** to Cp_2HfCl_2 and the free [4]radialene **7** required reaction times of more than 30 min.

The mass spectrum of **7** displayed the molecular ion at m/z 408; therefore, a compound of the expected composition $C_{32}H_{24}$ should be present. The NMR spectrum revealed the existence of a [4]radialene. A symmetric data set was observed, and in comparison to other symmetrical [4]radialenes, the NMR spectroscopic data are in good agreement (¹³C NMR for the cyclobutane ring carbon atoms of **7**, 142.1; for C_4 (=CMe₂)₄, 138.3;^{19a} for C_4 (=CPh₂)₄, 139.3 ppm^{19b}). Unfortunately, the organic [4]radialene **7** has not been isolated in analytically pure form, as in solution it slowly decomposes.

Compounds with structural motifs similar to those of **4-Hf**, **5-SiMe₃-Hf**, and **6-Hf** have been reported earlier. In fact, the formation of the same series of complexes was shown for titanium.^{10,18a} Surprisingly, for zirconium the formation of metallacyclopentadienes ($R = SiMe_3$) or radialenes (R = Ph) was not observed. Instead, in similar reactions the corresponding seven-membered-ring systems ($R = SiMe_3$; see Scheme 1) or dinuclear complexes (R = Ph) were found. Hence, in these cases titanium and hafnium behave similarly, whereas zirconium differs significantly from its group 4 analogues.

Additionally, we were interested in investigating the reactions of the new hafnacyclocumulene **4-Hf** toward alkynes. Thus, **4-Hf** was reacted with di-*tert*-butylbutadiyne and diphenylacetylene, respectively. As a result, by a change of the coordination mode in the five-membered hafnacy-clocumulene from η^4 to η^2 followed by insertion of the corresponding alkyne into the Hf–C_{α} bond of the intermediate π complex the hafnacyclopentadienes **5-t-Bu-Hf** (64%) and **8** (90%) were formed (Scheme 4).

Scheme 4. Insertion of Alkynes into the $Hf-C_{\alpha}$ Bond of 4-Hf



NMR data of the complexes are in the expected range and are similar to those of **5-SiMe₃-Hf** ($C_{\alpha}(t-Bu)$, 223.4 ppm; $C_{\alpha}(alkynyl)$, 164.8 ppm). In the IR spectra a characteristic band for the alkynyl fragment was seen at 2153 cm⁻¹. In the IR spectrum of **8** no band was found in the region 1700–2500 cm⁻¹, which normally would indicate the existence of a C–C triple bond. The constitution of this compound was determined by NMR spectral measurements and by MS (molecular ion [M]⁺ at *m*/*z* 650).

The molecular structure of **5-***t***-Bu-Hf** is depicted in Figure 3. Bond lengths in the five-membered metallacycle of complex **5-***t***-Bu-Hf** are similar to those in the aforementioned **5-SiMe₃-Hf** (**5-***t***-Bu-Hf**, Hf1-C1 = 2.230(2), C1-C2 = 1.355(3), C2-C3 = 1.516(3), C3-C4 = 1.375 (3), Hf1-C4 = 2.257(2) Å; **5-SiMe₃-Hf**, Hf1-C1 = 2.240(2), C1-C2 = 1.369(3), C2-C3 = 1.495(3), C3-C4 = 1.378(3), Hf1-C4 = 2.227(2) Å).

Conclusion

The complex $Cp_2Hf(n-Bu)_2$ which generates the free metallocene at elevated temperatures can serve as an excellent



Figure 3. Molecular structure of complex **5-***t***-Bu-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Hf1-C1 = 2.230(2), C1-C2 = 1.355(3), C2-C3 = 1.516(3), C3-C4 = 1.375(3), Hf1-C4 = 2.257(2), C5-C6 = 1.209(3), C15-C16 = 1.198(3); C1-Hf1-C4 = 77.01(8), Hf1-C1-C2 = 115.6(2), C1-C2-C3 = 115.3(2), C2-C3-C4 = 120.2(2), C3-C4-Hf1 = 111.2(2).

hafnocene source for stoichiometric reactions with unsaturated organic substrates. In reactions of $Cp_2Hf(n-Bu)_2$ with alkynes and 1,3-butadiynes, respectively, metallacyclopropenes, metallacyclocumulenes, and metallacyclopentadienes are formed. In the reactions with 1,3-butadiynes the obtained products depend on the substituents of the diyne: whereas for *t*-Bu substituents the obtained hafnacyclocumulene is the first structurally characterized example for a compound of this type, for Ph substituents a dinuclear hafnocene-substituted radialene was formed.

Experimental Section

General Considerations. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents (including deuterated solvents benzene- d_6 , toluene- d_8 , and THF- d_8) were freshly distilled from sodium tetraethylaluminate and stored under argon. Cp₂HfCl₂ was purchased from Sigma Aldrich and MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. The following spectrometers were used: mass spectra, MAT 95-XP and Finnigan Polaris Q; NMR spectra, Bruker AV 300, AV 400, and AMX 400. Chemical shifts (¹H, ¹³C) are given relative to SiMe4 and are referenced to signals of the solvent used: benzene- d_6 ($\delta_{\rm H}$ 7.16, $\delta_{\rm C}$ 128.0), toluene- d_8 ($\delta_{\rm H}$ 2.03, $\delta_{\rm C}$ 20.4), and THF- d_8 ($\delta_{\rm H}$ 1.73, $\delta_{\rm C}$ 25.2). The spectra were assigned with the help of DEPT. Melting points were determined with sealed capillaries on a Büchi 535 apparatus. Elemental analyses were carried out on a Leco CHNS-932 elemental analyzer.

Diffraction data were collected on a STOE IPDS diffractometer and on a Bruker APEX II CCD diffractometer using graphitemonochromated Mo K α radiation. The structures were solved by direct methods (SHELXS-97²⁰) and refined by full-matrix leastsquares techniques on F^2 (SHELXL-97²⁰). XP (Bruker AXS) and DIAMOND²¹ were used for graphical representations. For **4-Hf** and **5-SiMe₃-Hf** disorder in one Cp ligand and for **5-t-Bu-Hf** disorder in one *t*-Bu group were observed. Only one position of these groups is depicted in the graphical representations. The crystals of **6-Hf** contained benzene- d_6 as lattice solvent. Crystallographic data for **4-Hf**, **5-SiMe₃**, **5-t-Bu-Hf**, and **6-Hf** are given in Table 1.

Di-n-butylhafnocene

 Table 1. Crystallographic Data for 4-Hf, 5-SiMe₃, 5-t-Bu-Hf, and

 6-Hf

		*		
	4-Hf	5-SiMe ₃ -Hf	5-t-Bu-Hf	6-Hf
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_{1}2_{1}2_{1}$	Pbca	C2/c	$P2_1/n$
a (Å)	9.0260(3)	11.12668(15)	22.069(2)	7.8491(2)
b (Å)	13.9022(5)	19.9661(4)	15.6389(15)	26.7157(5)
<i>c</i> (Å)	15.2615(6)	30.5895(4)	20.097(2)	11.3534(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	119.753(2)	102.212(2)
γ (deg)	90.00	90.00	90.00	90.00
$V(Å^3)$	1915.03(12)	6795.7(2)	6021.8(10)	2326.88(10)
Ζ	4	8	8	2
density (g cm ⁻³)	1.633	1.364	1.397	1.681
μ (Mo K α) (mm ⁻¹)	5.445	3.227	3.483	4.501
T (K)	100(2)	200(2)	100(2)	200(2)
no. of measd rflns	15 608	90 282	36 087	27 477
no. of indep rflns	5092	6674	8013	4912
no. of obsd rflns	4853	5230	7080	4270
no. of params	180	308	345	286
GOF on F^2	1.039	0.925	1.061	0.969
R1 $(I > 2\sigma(I))$	0.0226	0.0195	0.0221	0.0173
wR2 (all data)	0.0502	0.0446	0.0509	0.0388

Preparation of Cp₂Hf(n-Bu)₂ (1-Hf). To a suspension of Cp₂HfCl₂ (2.016 g, 5.31 mmol) in 20 mL of *n*-hexane was added 6.7 mL (10.72 mmol) of a 1.6 M solution of n-BuLi in n-hexane. The mixture was stirred for 30 min at room temperature, resulting in a yellow solution which was filtered and concentrated under vacuum to half its volume and stored at -78 °C. After 1 day a pale yellow precipitate had formed, which was isolated by decanting of the mother liquor, washed with cold n-hexane, and dried under vacuum to give complex 1-Hf: yield 1.579 g (3.73 mmol, 70%). Mp: 32-33 °C under Ar. Anal. Calcd for C18H28Hf (422.90 g mol⁻¹): C, 51.12; H, 6.67. Found: C, 50.86; H, 6.43. NMR (297 K, benzene- d_6): ¹H, δ 0.12 (m, 4 H, α -CH₂), 1.02 (t, 3 H, CH₃), 1.34 (m, 4 H, γ -CH₂), 1.46 (m, 4 H, β -CH₂), 5.67 (s, 10 H, Cp); ¹³C, δ 14.2 (CH₃), 31.0 (γ -CH₂), 34.8 (β -CH₂), 58.6 (α -CH₂), 109.9 (Cp). The signal for the Cp protons in the ¹H NMR at 5.67 ppm is the same as found before and reported by Negishi et al. in ref 5b. MS (EI, 70 eV): m/z 365 [M – Bu – 2 H]⁺, 311 [Cp₂HfH]⁺, 310 $[Cp_2Hf]^+$.

Preparation of the Alkyne Complex 2-Hf. To a solution of 1-Hf (1.351 g, 3.19 mmol) in 10 mL of toluene was added bis(trimethylsilyl)acetylene (0.72 mL, 3.19 mmol) and pyridine (0.60 mL, 4.33 mmol). The reaction mixture was filtered and stirred at 100 °C. After 3.5 h all volatiles were evaporated from the dark purple solution and the residue was extracted with 20-25 mL of n-hexane at 55 °C. The solution was filtered, concentrated under vacuum to 7-8 mL, and stored at -78 °C. After 1 h dark purple crystals had formed which were isolated by decanting of the mother liquor, washed with cold *n*-hexane, and dried under vacuum to give complex **2-Hf**: yield 0.786 g (1.41 mmol, 44%). Mp: 121–123 °C under Ar. Anal. Calcd for C₂₃H₃₃HfNSi₂ (558.18 g mol⁻¹): C, 49.49; H, 5.96; N, 2.51. Found: C, 49.29; H, 6.00; N, 2.71. NMR at 217 K (toluene- d_8): ¹H, δ 0.18 (s, 9 H, SiMe₃), 0.52 (s, 9 H, SiMe₃), 5.29 (s, 10 H, Cp), 6.17 (m, 2 H, m-Py), 6.63 (m, 1 H, p-Py), 8.84 (m, 2 H, *o*-Py); ¹³C, δ 2.6 (SiMe₃), 2.7 (SiMe₃), 105.3 (Cp), 123.0 (*m*-Py), 136.3 (*p*-Py), 154.3 (*o*-Py), 207.0 (C≡C), 233.0 (C≡C); ²⁹Si, δ -7.7 (SiMe₃), -5.1 (SiMe₃). NMR at 297 K (toluene-*d*₈): ¹H, δ 0.24 (s, 18 H, SiMe₃), 5.28 (s, 10 H, Cp), 6.40 (m, 2 H, *m*-Py), 6.82 (m, 1 H, *p*-Py), 8.94 (m, 2 H, *o*-Py); ¹³C, δ 2.8 (SiMe₃), 105.6 (Cp), 123.2 (m-Py), 136.5 (p-Py), 154.6 (o-Py). Signals for the coordinated triple bond were not observed due to exchange broadening. IR (Nujol mull, cm⁻¹): 1548 (C≡C). MS (CI, isobutane): m/z 481 [M - Py]⁺, 171 [Me₃SiC₂SiMe₃]⁺.

Preparation of the Hafnacyclocumulene 4-Hf. Di-tert-butylbutadiyne (0.374 g, 2.30 mmol) was dissolved in 15 mL of toluene, and this solution was added to solid $Cp_2Hf(n-Bu)_2$ (0.974 g, 2.30 mmol). The obtained solution was filtered, and the filtrate was heated to 100 °C. After 5 h all volatiles were removed under vacuum and the residue was extracted with 8-10 mL of n-hexane at 55 °C. The yellow solution was filtered and stored at -78 °C. After 1 day yellow crystals had formed, which were isolated by decanting of the mother liquor, washed with cold n-hexane, and dried under vacuum to give complex 4-Hf: yield 0.808 g (1.72 mmol, 75%). Mp: 192-193 °C under Ar. Anal. Calcd for C₂₂H₂₈Hf (470.95 g mol⁻¹): C, 56.11; H, 5.99; Hf, 37,90. Found: C, 56.26; H, 6.21; Hf, 37.60. NMR (297 K, benzene- d_6): ¹H, δ 1.53 (s, 18 H, *t*-Bu), 5.18 (s, 10 H, Cp); ¹³C, δ 33.3 (C(CH₃)), 37.6 (C(CH₃)₃), 103.1 (Cp), 105.9 (β -C), 188.1 (α -C). MS (EI, 70 eV): m/z 472 [M]⁺.

Preparation of the Hafnacyclopentadiene 5-SiMe₃-Hf. Cp₂Hf(n-Bu)₂ (0.750 g, 1.77 mmol) was dissolved in 10 mL of toluene, and the yellow solution was added to bis(trimethylsilyl)butadiyne (0.690 g, 3.55 mmol). The solution was filtered and warmed to 100 °C. After 5 h all volatiles were removed from the dark yellow-brown solution under vacuum. The residue was dissolved in 10-15 mL of n-hexane at 55 °C, followed by filtration of the yellow-orange solution. The filtrate was stored at -78 °C; after 1 day yellow crystals had formed, which were isolated by decanting of the mother liquor, washed with cold *n*-hexane, and dried under vacuum to give complex 5-SiMe₃-Hf: yield 1.040 g (1.49 mmol, 84%). Mp: 170-172 °C under Ar. Anal. Calcd for C₃₀H₄₆HfSi₄ (697.52 g mol⁻¹): C, 51.66; H, 6.65. Found: C, 51.83; H 6.75. NMR (296 K, benzene- d_6 ; numbering according to the atom labeling in the molecular structure, see Figure S2 in the Supporting Information): ¹H, δ 0.22 (s, 9 H, C4-SiMe₃), 0.26 (s, 9 H, C6-SiMe₃), 0.28 (s, 9 H, C14-SiMe₃), 0.69 (s, 9 H, C2-SiMe₃), 5.97 (s, 10 H, Cp); ¹³C, $\delta = 0.2$ (C15/16/17), 0.5 (C7/8/9), 0.8 (C18/19/20), 2.8 (C10/11/ 12), 93.3 (C14), 107.7 (C5), 111.1 (Cp), 111.5 (C13), 123.4 (C6), 135.3 (C3), 161.4 (C2), 196.4 (C1), 225.1 (C4); ²⁹Si, δ –20.6 (Si1), -19.8 (Si3), -13.3 (Si4), -5.5 (Si2). IR (Nujol mull, cm⁻¹): 2075, 2121 (C=C). MS (EI, 70 eV): m/z 698 [M]⁺, 504 [M - $Me_3SiC_4SiMe_3$ ⁺, 310 [Cp₂Hf]⁺.

Preparation of Complex 6-Hf. A solution of Cp₂Hf(*n*-Bu)₂ (1.582 g, 3.74 mmol) in 10 mL of toluene was added to a solution of 1,4-diphenylbutadiyne (0.690 g, 3.55 mmol) in 10 mL of toluene. The mixture was filtered and warmed to 100 °C. After 6 h the resulting red-brown solution was cooled to room temperature. Dark red crystals were isolated by decanting of the mother liquor, washed four times with toluene, and dried under vacuum to give complex **6-Hf**: yield 0.436 g (23%). Mp: 396–397 °C under Ar. Anal. Calcd for C₅₂H₄₀Hf₂ (1021.85 g mol⁻¹): C, 61.12; H, 3.95. Found: C, 61.12; H, 4.02. NMR (296 K, THF-*d*₈): ¹H, δ 6.01 (s, 20 H, Cp), 6.68 (m, 8 H, Ph), 6.74 (m, 12 H, Ph); ¹³C, δ 109.2 (Cp). Due to the low solubility in common NMR solvents, no ¹³C signals for the Ph substituents and for the central C₈ unit were observed. MS (EI, 70 eV): *m/z* 1022 [M]⁺, 820 [M – PhC₄Ph – H₂]⁺, 511 [¹/₂M]⁺, 411 [Cp₂Hf-C₂Ph]⁺, 310 [Cp₂Hf]⁺.

Protolysis of Complex 6-Hf to Compound 7. Complex **6-Hf** (0.448 g, 0.438 mmol) was dissolved in 10 mL of THF, and HCl (3 mL of a 2 M solution in diethyl ether, 1.752 mmol) was added. The resulting mixture was stirred, and after 30 min the dark red precipitate of **6-Hf** dissolved. After 45 min all volatiles were removed under vacuum and the residue was analyzed by NMR, indicating a mixture of compound $7/Cp_2HfCl_2$ in a ratio of 1:2. Compound 7 is unstable in solution and decomposes within several days. Attempts to isolate the free [4]radialene from Cp_2HfCl_2 by recrystallization were not successful, and column chromatography on sililca gel led to decomposition. Hence, no analytically pure samples of compound 7 were obtained. NMR (296 K, benzene- d_6): ¹H, δ 6.77 (m, 8 H, *m*-Ph), 6.89 (m, 4 H, *p*-Ph), 6.93 (s, 4 H,

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C=CH), 6.94 (m, 8 H, *o*-Ph); 13 C, δ 116.8 (C=*C*H), 127.2 (*m*-Ph), 127.2 (*p*-Ph), 129.3 (*o*-Ph), 137.0 (*i*-Ph), 142.1 (*C*=CH). MS (EI, 70 eV): m/z 408 [M]⁺, 329 [M - Ph - 2H]⁺, 317 [M - PhCH₂]⁺, 302 [M - PhCH₂CH₂]⁺, 203 [PhC₄Ph + H]⁺.

Preparation of the Hafnacyclopentadiene 5-t-Bu-Hf. A solution of di-tert-butylbutadiyne (0.225 g, 1.39 mmol) in 5-7 mL of toluene was added to solid complex 4-Hf (0.653 g, 1.39 mmol). The obtained yellow solution was filtered and heated to 100 °C. After 3 days all volatiles were removed from the yellow solution and the residue was extracted with 15 mL of n-hexane at 55 °C. The yellow-brown solution was filtered, concentrated under vacuum to a volume of 5 mL, and stored at -78 °C. After 1 day yellow crystals had formed, which were isolated by decanting of the mother liquor, washed with cold *n*-hexane, and dried under vacuum to give the complex 5-t-Bu-Hf: yield 0.654 g (1.03 mmol, 75%). Mp: 178-180 °C under Ar. Anal. Calcd for C₃₄H₄₆Hf (634.22 g mol⁻¹): C, 64.49; H, 7.32. Found: C, 64.34; H, 7.22. NMR (296 K, benzene d_6 ; numbering according to the atom labeling in the molecular structure, see Figure S3 in the Supporting Information): 1 H, δ 1.23 (s, 9 H, C6-CMe₃), 1.24 (s, 9 H, C4-CMe₃), 1.31 (s, 9 H, C16–CMe₃), 1.85 (s, 9 H, C2–CMe₃), 6.06 (s, 10 H, Cp); 13 C, δ 28.6 (C17), 29.5 (C7), 30.5 (C18/19/20), 30.5 (C22/23/24), 31.5 (C8/9/10), 32.6 (C12/13/14), 41.2 (C21), 42.7 (C11), 81.1 (C5 or C15), 85.4 (C5 or C15), 103.6 (C16), 110.5 (Cp), 121.3 (C6), 127.1 (C3), 155.7 (C2), 164.8 (C1), 223.4 (C4). IR (Nujol mull, cm⁻¹): 2153 (C=C). MS (EI, 70 eV): m/z 634 [M]⁺, 310 [Cp₂Hf]⁺.

Preparation of the Hafnacyclopentadiene 8. A solution of diphenylacetylene (0.270 g, 1.51 mmol) in 5–7 mL of toluene was added to solid **4-Hf** (0.711 g, 1.51 mmol). The obtained light yellow solution was filtered and warmed to 100 °C. After 3 days all volatiles were removed from the resulting yellow-orange solution under vacuum. The residue was dissolved in 10 mL of *n*-hexane, and the solution was filtered and stored at -78 °C. After 1 day yellow crystals had formed, which were isolated by decanting of the mother liquor, washed with cold *n*-hexane, and dried under vacuum to give complex **8**: yield 0.885 g (1.36 mmol, 90%). Mp: 194–196 °C under Ar. Anal. Calcd for C₃₆H₃₈Hf (649.18 g mol⁻¹):

C, 66.61; H, 5.90. Found: C, 66.92; H, 6.18. NMR (296 K, benzene*d*₆): ¹H, δ 1.00 (s, 9 H, *t*-Bu at C3), 1.40 (s, 9 H, *t*-Bu at C4), 5.93 (s, 10 H, Cp), 6.73 (m, 1 H, p-Ph at C1), 6.78 (m, 2 H, o-Ph at C1), 6.91 (m, 1 H, p-Ph at C2), 7.00 (m, 2 H, m-Ph at C1), 7.03 (m, 2 H, *m*-Ph at C2), 7.13 (m, 2 H, *o*-Ph at C2); 13 C, δ 28.1 (${}^{2}J_{C,H}$ = 5 Hz, C=CCMe₃), 30.5 (${}^{1}J_{C,H}$ = 127 Hz, ${}^{3}J_{C,H}$ = 5 Hz, C=CCMe₃), 30.9 (${}^{1}J_{C,H} = 125 \text{ Hz}$, ${}^{3}J_{C,H} = 6 \text{ Hz}$, CMe₃), 41.1 (${}^{2}J_{C,H}$ = 4 Hz, CMe₃), 82.7 (C=C-t-Bu), 104.9 (${}^{3}J_{C,H}$ = 7 Hz, C=C-t-Bu), 110.6 (${}^{1}J_{C,H} = 173$ Hz, Cp), 120.9 (C3), 123.2 (*p*-Ph at C1), 125.0 (p-Ph at C2), 126.6 (m-Ph at C2), 127.1 (o-Ph at C1), 127.7 (m-Ph at C1), 131.0 (o-Ph at C2), 136.0 (C2), 143.3 (i-Ph at C2), 150.0 (*i*-Ph at C1), 192.8 (C1), 216.3 (${}^{3}J_{C,H} = 5$ Hz, C4). IR (Nujol mull): the stretching vibration for the exocyclic C=C fragment was not observed in the region $1700-2500 \text{ cm}^{-1}$. MS (EI, 70 eV): m/z650 $[M]^+$, 593 $[M - t-Bu]^+$, 488 $[M - t-BuC_4t-Bu]^+$, 472 $[M - t-BuC_4t-Bu]^+$, 472 [M - t-Bu $PhC_2Ph]^+$, 415 $[M - PhC_2Ph-t-Bu]^+$, 310 $[Cp_2Hf]^+$, 178 $[PhC_2Ph]^+$.

Numbering scheme for complex 8:



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Supporting Information Available: Figures giving temperaturedependent ¹H NMR spectra of **2-Hf** and an ORTEP drawing of **5-SiMe₃-Hf** and CIF files giving crystallographic data for compounds **4-Hf**, **5-SiMe₃-Hf**, **5-t-Bu-Hf**, and **6-Hf**. This material is available free of charge via the Internet at http://pubs.acs.org.

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