Reactions of Decamethylhafnocene with 1,3-Butadiynes: Formation of Hafnacyclocumulenes and C−H Activation at Pentamethylcyclopentadienyl Ligands

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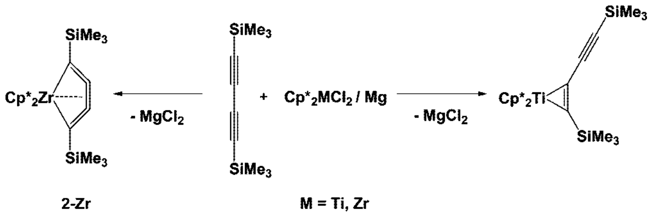
The reduction of $Cp^*_2HfCl_2$ with lithium in the presence of disubstituted butadiynes RC≡C−C≡CR (R = Ph, $SiMe_3$, *t*-Bu) in toluene leads, respectively, to the five-membered hafnacyclocumulene complexes $Cp^*_2Hf(\eta^4\text{-}1,2,3,4\text{-}PhC_4Ph)$ (**1-Hf**) and $Cp^*_2Hf(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$ (**2-Hf**) and, in the case of 1,4-bis(*tert*-butyl)butadiyne by a 2-fold activation of the methyl groups of one pentamethylcyclopentadienyl ligand, to the complex $Cp^*Hf[-C(=C=CH\text{-}t\text{-}Bu)-CH(t\text{-}Bu)CH_2-\eta^5\text{-}C_5Me_3-CH_2-]$ (**3-Hf**) containing a fulvene ligand that is coupled to the modified substrate (allenic subunit). The latter inserts 2 equiv of the isocyanide *t*-BuNC to give by coupling of the isocyanide molecules the complex $Cp^*Hf[-C(=C=CH\text{-}t\text{-}Bu)-CH(t\text{-}Bu)CH_2-\eta^5\text{-}C_5Me_3-CH_2-C(=N\text{-}t\text{-}Bu)-C(=N\text{-}t\text{-}Bu)-]$ (**4**). The structures of complexes **3-Hf** and **4** were determined by X-ray crystallography.

Introduction

In the past we investigated in detail the reactions of 1,3-butadiynes RC≡C−C≡CR with unsubstituted titanocene and zirconocene derivatives.[1] Different modes of complexation, unusual C−C single bond cleavage reactions, and a series of coupling reactions were in part unexpected results of these studies. The individually obtained products proved to be strongly dependent on the substituents R, the metals, and the stoichiometry employed in the conversions. The most interesting outcome of these reactions of the metallocenes "Cp_2M" (M = Ti, Zr) with 1,3-butadiynes was a series of stable five-membered metallacyclocumulenes $Cp_2M(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$, M = Ti, Zr.[1] Additionally, different interactions of decamethyltitanocene and -zirconocene complexes with 1,3-butadiynes RC≡C−C≡CR were described. As is well-known in organometallic chemistry, electronic and steric properties can be influenced dramatically by replacing the Cp by Cp* ligands. The increased steric bulk, solubility, and electron donor characteristics lead to different reactivities and spectral properties of these complexes compared to their Cp counterparts. Due to the short lengths of the C−H bonds and the existence of basic centers, e.g., carbanionic groups, H transfer reactions (formal "σ-bond metathesis reactions") often occur. These ligands cannot be regarded as innocent spectator ligands because sometimes one or even two of the methyl groups of the decamethylcyclopentadienyl moieties are involved in the reactions. While for zirconium five-membered zirconacyclocumulenes (η^4-complexes, 1-zirconacyclopenta-2,3,4-trienes) $Cp^*_2M(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ (M = Zr, R = Me, Ph, $SiMe_3$) predominate, for titanium no metallacyclocumulenes, but rather titanacyclopropenes (η^2-complexes) were found as products (Scheme 1). Different C−C coupling reactions of the decamethyltitanocene systems were found to be typical for both metals (Scheme 2).[2]

Scheme 1. Coordination of $Me_3SiC≡C−C≡CSiMe_3$ with Decamethylmetallocenes (M = Ti, Zr)



The first pioneering results in this area came from Brintzinger[3] and Bercaw[4] as well as from Teuben,[5] who showed that a tetramethylfulvene Ti(III) product $Cp^*Ti[C_5Me_4(CH_2)]$ is the intermediate for the subsequent C−C coupling reactions of

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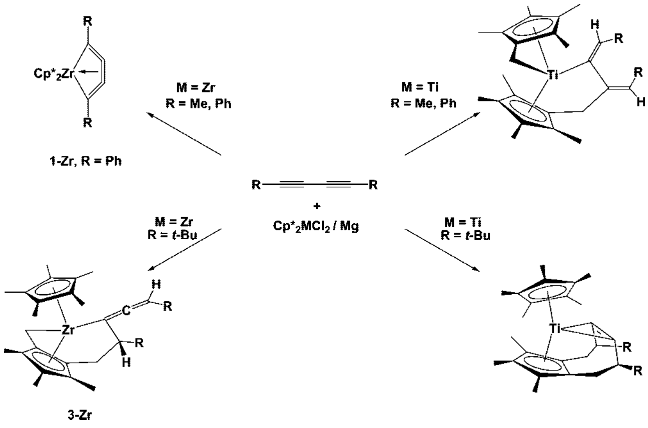
Scheme 2. C−H Bond Activations and C−C Couplings in the Coordination Sphere of Decamethylmetallocenes (M = Ti, Zr)

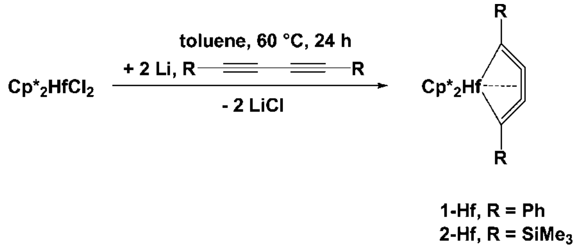


decamethyltitanocenes. A second deprotonation, leading to $Cp^*Ti[C_5Me_3(CH_2)_2]$, was described by Beckhaus[6] and Mach.[7]

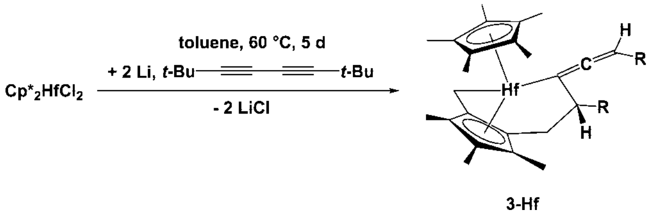
This behavior has some consequences for the interactions of decamethyltitanocene and -zirconocene complexes with 1,3-butadiynes, resulting in different C−H activations of one or of both of the pentamethylcyclopentadienyl ligands with subsequent C−C coupling reactions (Scheme 2). When using the decamethyltitanocene fragment "Cp^*_2Ti", the reaction depends strongly on the substituents R/R′. The coupling product of the butadiyne with two methyl groups of one of the pentamethylcyclopentadienyl ring systems, $Cp^*Ti[\eta^5\text{-}C_5Me_3(CH_2{-}CHR{-}\eta^2\text{-}C_2{-}CHR{-}CH_2)]$, is obtained with R = *t*-Bu. In this complex one pentamethylcyclopentadienyl ligand is anellated to an eight-membered ring with a C−C triple bond that is coordinated to the titanium center. A different activation of both pentamethylcyclopentadienyl ligands is observed for R = Me, Ph, resulting in the complexes $[\eta^5\text{-}C_5Me_4(CH_2){-}]Ti[{-}C({=}CHR){-}C({=}CHR){-}CH_2{-}\eta^5\text{-}C_5Me_4]$, which contain a fulvene as well as a butadienyl-substituted pentamethylcyclopentadienyl ligand. The influence of the size of the metal is illustrated in the reaction of $Cp^*_2ZrCl_2$ with MeC≡C−C≡CMe. Here the five-membered metallacyclocumulene complex $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)$ is obtained.

Very recently we reported that during the synthesis of $Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ several bond activation processes, e.g., ring opening of THF, Si−C bond cleavage, and tandem Si−C/C−H bond cleavage, can occur, showing the higher reactivity of hafnocene compounds compared to their titanocene and zirconocene analogues.[8] The isolation of the hafnocene complexes was possible only by substituting THF in the reduction with magnesium. Alternatively a new reduction procedure using metallic lithium in toluene for the reduction of hafnocene dichlorides was used. The enhanced reactivity of hafnocene compounds compared to zirconocenes, as shown, for example, by the Chirik group,[9] motivated us to study the reactions of decamethylhafnocene with 1,3-butadiynes and compare these with the above-mentioned results obtained in the cases of titanium and zirconium complexes.

Scheme 3. Formation of Hafnacyclocumulenes



Scheme 4. Formation of Complex 3-Hf by 2-fold Activation of One of the Cp* Ligands



Results and Discussion

The reduction of $Cp^*_2HfCl_2$ with lithium in the presence of RC≡C−C≡CR (R = Ph, $SiMe_3$) in toluene gave the five-membered hafnacyclocumulene complexes $Cp^*_2Hf(\eta^4\text{-}1,2,3,4\text{-}PhC_4Ph)$ (**1-Hf**) and $Cp^*_2Hf(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$ (**2-Hf**) (Scheme 3). These compounds were obtained as yellow-orange (**1-Hf**, 51% yield) and as dark red crystals (**2-Hf**, 59% yield), respectively. Complex **2-Hf** is highly sensitive toward air and moisture. In contrast to **2-Hf**, a crystalline sample of **1-Hf** can be exposed to air without decomposition for several minutes.

NMR spectroscopic studies of complexes **1-Hf** and **2-Hf** in benzene-d_6 revealed similarities to the corresponding Zr complexes **1-Zr** and **2-Zr**[2a] (**1-Hf**: Cβ: 118.3, Cα: 180.4; **1-Zr**: Cβ: 118.4, Cα: 179.4; **2-Hf**: Cβ: 144.9, Cα: 189.3; **2-Zr**: Cβ: 144.5, Cα: 188.0 ppm). As seen before, the $SiMe_3$ group deshields Cβ by withdrawing electron density, which causes a downfield shift compared to the Ph-substituted complexes.

In the reaction of $Cp^*_2HfCl_2$ with lithium in the presence of *t*-BuC≡C−C≡C-*t*-Bu in toluene a 2-fold activation of the methyl groups of one of the pentamethylcyclopentadienyl ligands to give the complex $Cp^*Hf[{-}C({=}C{=}CH\text{-}t\text{-}Bu){-}CH(t\text{-}Bu)CH_2{-}\eta^5\text{-}C_5Me_3{-}CH_2{-}]$ (**3-Hf**) was observed. The latter contains a fulvene ligand that is coupled to the modified substrate (allenic subunit) (Scheme 4). Complex **3-Hf** was obtained as a yellow crystalline solid in moderate yield (55%).

The molecular structure of complex **3-Hf** was confirmed by X-ray crystallography (Figure 1, Table 1). Bond lengths in the doubly C−H activated ligand of C23−C28 (1.463(4) Å) and Hf−C28 (2.326(3) Å) clearly indicate the character of a π-η^5,σ-η^1-tetramethylfulvenyl group. Moreover, the allenic subunit is nearly linear (C2−C3−C4 173.9(4)°). The C−C bonds are in the range of a double bond, indicating the allenic character.

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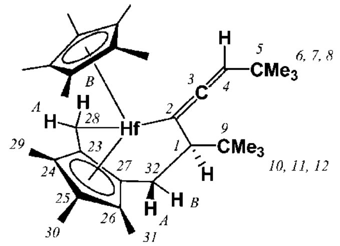
Scheme 5. Numbering Scheme of Complex 3-Hf



The different character of the methylene groups of the activated Cp* ligand (π-η^5,σ-η^1-tetramethylfulvenyl ligand) is shown by the chemical shifts of the corresponding carbon atoms; see Table 2. Whereas the signal for C28 is found to be shifted downfield to 72.3 ppm, indicating the higher s-character of this carbon atom, the signal for C32 is located at 26.8 ppm, as found before for other sp^3 carbon atoms connected to aromatic systems. An unambiguous assignment of the allenic carbon atoms C2 and C3 was not possible despite evaluation of ^{1}H−^{13}C spin–spin couplings to 4-H, 1-H, and 32-H. It is reasonable to assign 141.5 ppm to the central carbon atom of the cumulenic subunit (C3), although this differs from the expected shift for an allene (200–210 ppm), as the shift for C2 (191.0 ppm) is characteristic for a metallated sp^2 carbon atom. However, the observed wavenumber of ν(C=C=C) = 1892 cm^{-1} clearly indicates the allenic subunit of this compound.

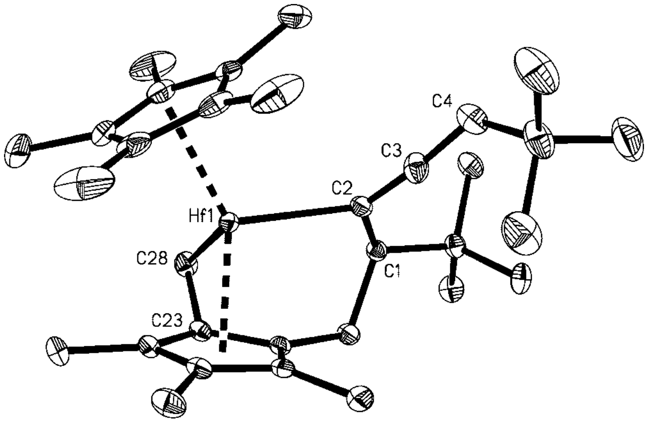


Figure 1. Molecular structure of complex **3-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Hf1−C2 2.295(2), Hf1−C28 2.326(3), C1−C2 1.538(3), C2−C3 1.295(4), C3−C4 1.333(4), C23−C28 1.463(4); C1−C2−C3 124.7(2), C2−C3−C4 173.9(4).

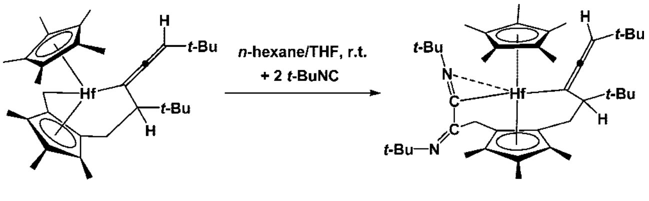
Table 1. Crystallographic Data

	3-Hf	**4**
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.1553(3)	11.4937(6)
b [Å]	10.5481(3)	13.1411(6)
c [Å]	14.5085(4)	15.2373(8)
α [deg]	99.349(2)	64.457(4)
β [deg]	90.460(3)	80.109(4)
γ [deg]	110.431(2)	66.716(4)
V [Å^3]	1433.50(7)	1907.4(2)
Z	2	2
density [g·cm^{-3}]	1.416	1.354
μ(Mo Kα) [mm^{-1}]	3.655	2.764
max., min. transmn	0.5608, 0.3174	0.5892, 0.4178
T [K]	200(2)	200(2)
no. of rflns (measd)	20 563	27 242
no. of rflns (indep)	5628 (R_{int} = 0.0371)	7508 (R_{int} = 0.0398)
no. of rflns (obsd)	5124	6861
no. of params	298	406
GOF on F^2	0.986	0.979
R1 ($I > 2\sigma(I)$)	0.0184	0.0170
wR2 (all data)	0.0415	0.0409

Table 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Data δ/ppm of Complex 3-Hf (main component 3a-Hf and side component 3b-Hf), C_6D_6 at Ambient Temperature

	functional	3a-Hf		3b-Hf	
atom no.	group	H	C	H	C
23	Cp*−C		120.85		
24	Cp*−C		116.37		
25	Cp*−C		117.68		
26	Cp*−C		125.44		
27	Cp*−C		127.84		
32	CH_2	2.50 (A)	26.80	2.42	25.43
		2.53 (B)		2.36	
1	CH	1.69	50.30		51.26
9	1−*t*-Bu$_{\text{quart}}$		35.74		36.20
10, 11, 12	1−*t*Bu CH_3	1.05	28.23 (br)		28.79
	Cp*−C		117.56		117.34
	Cp*CH_3	1.95	11.55	1.99	11.92
28	CH_2 fulvene	1.90 (A)	72.33	1.94	70.92
		1.47 (B)		1.53	
2	Hf−C		191.03		184.83
3	=C=		141.49		145.92
4	CH	4.25	91.83	4.14	91.88
5	4−*t*-Bu$_{\text{quart}}$		32.52		33.06
6, 7, 8	5−*t*Bu CH_3	1.16	31.55	1.30	31.50
29	Cp*−CH_3	1.47	10.71	1.46	10.32
30	Cp*−CH_3	1.64	10.57	1.69	10.60
31	Cp*−CH_3	2.07	13.16		

Scheme 6. Insertion and Coupling of *t*-BuNC to Form Complex 4



3-Hf **4**

Furthermore NMR investigations have shown that—similar to the corresponding zirconium complex—two isomers of this complex exist in solution (2-fold set of signals, diastereomeric ratio of **3a-Hf** to **3b-Hf** of 6:1). It is reasonable to assume that they differ in the arrangement of substituents at C4.[2b] The crystal structure shows the major isomer.

A comparison to the analogous Zr complex[2b] shows no significant differences in spectroscopic and structural features. All NMR signals for the Hf compound are similar to those found before for the Zr compound. Nevertheless they are shifted slightly downfield. X-ray data are in the same range as well; however Hf−C bonds (Hf−C2 2.295(2), Hf−C$_{\text{fulvenyl}}$ 2.326(5) Å) are slightly shorter compared to the corresponding Zr−C bonds (Zr−C17 2.332(5), Zr−C$_{\text{fulvenyl}}$ 2.389(5) Å).[2b]

Complex **3-Hf** inserts 2 equiv of the isocyanide *t*-BuNC to give the complex Cp*Hf[−C(=C=CH-*t*-Bu)−CH(*t*-Bu)CH$_2$−η^5-C$_5$Me$_3$−CH$_2$−C(=N-*t*-Bu)−C(=N-*t*-Bu)−] (**4**) as a yellow crystalline solid in a rather low yield of 29% (Scheme 6).

NMR spectra of **4** resemble those of its precursor **3-Hf**. In particular the signals for the cumulenic part of the molecule are similar. Likewise, **4** was isolated as a pair of diastereomers in a ratio of about 8:1. Differences due to the insertion of the isocyanide into the Hf−C bond are observed for the methylene group C32. The former fulvene carbon of **3-Hf** ($^2J_{\text{H,H}}$ = 8 Hz)

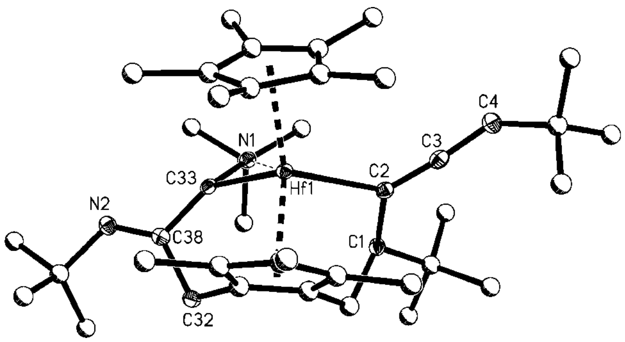
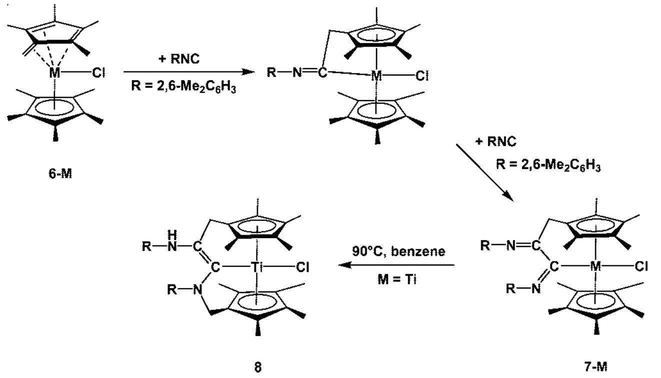


Figure 2. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. Labeled atoms are shown as thermal ellipsoids that correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Hf1−C2 2.383(2), Hf1−C33 2.190(2), Hf1−N1 2.404(2), C2−C3 1.301(3), C3−C4 1.329(3), N1−C33 1.274(3), N2−C38 1.268(3), C33−C38 1.485(3); C2−C3−C4 173.1(2), N1−C33−C38 132.5(2), N2−C38−C33 123.4(2).

Scheme 7. Isocyanide Insertion and Coupling Starting from Fulvene Complexes (M = Ti, Zr)



is converted to an sp^3 carbon ($^2J_{\mathrm{H,H}}$ = 16 Hz). A characteristic high-frequency signal is observed for the metalated diazadiene carbon atom 33 (Figure 2), which follows (if compared to its equivalents in the below discussed compounds **7-M**[5e]) the expected trend: **7-Ti** 228.2 ppm, **7-Zr** 233.5 ppm, **4** 254.2 ppm. However, only three of the *tert*-butyl groups are detected at ambient temperature. The signals due to the fourth are too broad and were found only after raising the temperature (see Experimental Section). The presence of four such bulky groups introduces steric pressure that prevents one of them from unhindered rotation.

IR measurements have shown that the allenic subunit remains intact (ν(C=C=C) of 1885 cm^{-1}). Moreover, the C−N stretching vibration ν(C=N) of 1641 cm^{-1} indicates the double-bond character in the diazabutadiene moiety. This can also be derived from the C−N bond lengths obtained by X-ray analysis (Figure 2) (N1−C33 1.274(3), N2−C38 1.268(3) Å). Furthermore the C33−C38 distance of 1.485(3) Å is similar, as found before, to those of other complexes with a diazabutadiene unit (e.g., $Cp_2Hf[-N(-t\text{-}Bu)C-C(=N-t\text{-}Bu)CH_2SiMe_2CH_2-]$ (**5**) N1−C1 1.269(6), N2−C2 1.262(7), C1−C2 1.500(7) Å[10]).

Interestingly, a similar coordination motif was found earlier by Teuben and co-workers for titanium and zirconium complexes (Scheme 7).[5e] In the reaction of the fulvene complex **6-M** with an isocycanide the terminal carbon atom is inserted into the fulvene M−C bond and coupled with a second molecule of the isocyanide to form the 1,4-diazadiene complex **7-M**. In the case of titanium (at elevated temperatures) the latter compound undergoes a second C−H activation at the intact pentamethylcyclopentadienyl ligand to give complex **8**, which contains an enediamine unit connecting both activated ligands.

The most significant difference between compound **7-M** and the above-described hafnium complex **4** is the coordination of the N1 atom to the hafnium (Hf1−N1 2.404(2) Å). Such an interaction was also found before in complex **5** (Hf1−N1 2.222(5) Å). However, in complex **4** this contact is weaker due to the steric bulk of the Cp* ligand, thus preventing a stronger Hf−N interaction.

Conclusion

The reduction of $Cp^*_2HfCl_2$ with lithium in the presence of RC≡C−C≡CR (R = Ph, SiMe$_3$, *t*-Bu) in toluene yields different products, namely, the five-membered hafnocyclocumulene complexes $Cp^*_2Hf(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ (**1-Hf**: R = Ph, **2-Hf**: R = SiMe$_3$) and, in the case of R = *t*-Bu, the butadiyne activation product $Cp^*Hf[-C(=C=CH\text{-}t\text{-}Bu)-CH(t\text{-}Bu)CH_2-\eta^5\text{-}C_5Me_3-CH_2-]$ (**3-Hf**). These are very similar to those obtained in corresponding reactions of $Cp^*_2ZrCl_2$. Interestingly, the hafnium complex can insert the isocyanide *t*-BuNC twice to form the complex $Cp^*Hf[-C(=C=CH\text{-}t\text{-}Bu)-CH(t\text{-}Bu)CH_2-\eta^5\text{-}C_5Me_3-CH_2-C(=N\text{-}t\text{-}Bu)-C(=N\text{-}t\text{-}Bu)-]$ (**4**) by coupling of both molecules of the isocyanide.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. $Cp^*_2HfCl_2$ was purchased from MCAT and used without further purification. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvent (C_6D_6) was treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^{1}H, ^{13}C) 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). The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of 1-Hf. A mixture of $Cp^*_2HfCl_2$ (1.517 g, 2.92 mmol), finely cut lithium (0.081 g, 11.68 g-atom), and 1,4-diphenylbutadiyne (0.590 g, 2.92 mmol) in 30 mL of toluene was stirred for 24 h at 60 °C. After evaporation of the solvent, the ocher residue was extracted with *n*-hexane (2 × 10 mL), followed by subsequent filtration of the solution. After evaporation of the solvent the yellow residue was recrystallized from toluene at −32 °C. After 48 h yellow-orange crystals were formed, which were isolated, washed with cold *n*-hexane, and dried in vacuum to give 0.968 g (1.49 mmol, 51%) of complex **1-Hf**, mp 192–195 °C (dec) under Ar. Anal. Calcd for $C_{36}H_{40}Hf$: C, 66.40; H, 6.19. Found: C, 64.26; H, 6.05 (despite repeated recrystallization from toluene small amounts of $Cp^*_2HfCl_2$ prevented better data). ^{1}H NMR (298 K, C_6D_6, 300 MHz): δ 1.70 (s, 30 H, Cp*), 7.13 (m, 2 H, *p*-Ph), 7.32 (m, 4 H, *m*-Ph), 8.08 (m, 4 H, *o*-Ph). ^{13}C NMR (298 K, C_6D_6, 75 MHz): δ 11.9 (s, $C_5\mathit{Me}_5$), 112.5 (s, C_5Me_5), 118.3 (s, Cβ), 127.7 (s, *p*-Ph), 128.7 (s, *m*-Ph), 134.3 (s, *o*-Ph), 137.3 (s, *i*-Ph), 180.4 (s, Cα). MS (CI, isobutane, *m/z*): 652 [M]$^+$.

Preparation of 2-Hf. A mixture of $Cp^*_2HfCl_2$ (1.217 g, 2.34 mmol), finely cut lithium (0.065 g, 9.36 g-atom), and 1,4-bis(trimethylsilyl)butadiyne (0.455 g, 2.34 mmol) in 25 mL of toluene was stirred for 24 h at 60 °C. After evaporation of the solvent the dark brown residue was extracted with *n*-hexane (3 × 15 mL), followed by subsequent filtration of the dark red solution. After evaporation of the solvent the dark red residue was recrystal-

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(10) Berg, F. J.; Petersen, J. L. *Organometallics* **1993**, *12*, 3890.

lized from toluene at −32 °C. Within 24 h dark red crystals were formed, which were isolated, washed with cold *n*-hexane, and dried under vacuum to give 0.877 g (1.38 mmol, 59%) of the highly air- and moisture-sensitive complex **2-Hf**, mp 212 °C (dec) under Ar. Anal. Calcd for $C_{30}H_{48}HfSi_2$: C, 56.01; H, 7.52. Found: C, 55.40; H, 7.67. ^{1}H NMR (298 K, C_6D_6, 300 MHz): δ 0.56 (s, 18 H, $SiMe_3$), 1.65 (s, 30 H, Cp*). ^{13}C NMR (298 K, C_6D_6, 75 MHz): δ 3.4 (s, $SiMe_3$), 11.9 (s, C_5*Me*$_5$), 111.9 (s, *C*$_5$Me$_5$), 144.9 (Cβ), 189.3 (Cα). MS (CI, isobutane, *m*/*z*): 644 $[M]^+$.

Preparation of 3-Hf. A mixture of $Cp^*{}_2HfCl_2$ (1.46 g, 2.8 mmol), finely cut lithium (0.078 g, 11.2 g-atom), and 1,4-bis(*tert*-butyl)butadiyne (0.456 g, 2.8 mmol) in 15 mL of toluene was stirred for 5 days at 60 °C. After evaporation of the solvent the residue was extracted with *n*-hexane (2 × 15 mL, 55 °C), followed by subsequent filtration of the warm solution. Upon cooling to room temperature, yellow prisms were formed, which were isolated, washed with cold *n*-hexane, and dried in vacuum to give 0.94 g (1.5 mmol, 55%) of complex **3-Hf**, mp 119 °C under Ar. Anal. Calcd for $C_{32}H_{48}Hf$: C, 62.88; H, 7.92. Found: C, 61.80; H, 7.90. IR (Nujol mull, cm^{-1}): 1892 (δ C=C=C). NMR: see Table 2. MS (CI, isobutane, *m*/*z*): 612 $[M]^+$.

Preparation of 4. Compound **3-Hf** (0.205 g, 0.34 mmol) was dissolved in 10 mL of *n*-hexane/THF (10:1). *t*-BuNC (0.038 mL, 0.34 mmol) was added to the solution at room temperature. The color of the reaction mixture immediately changed from yellow-orange to yellow. After stirring for an additional 16 h the solvent was removed under vacuum and the yellow residue was dissolved in *n*-hexane, filtered, and stored at room temperature. After several days yellow crystals had formed, which were isolated, washed with cold *n*-hexane, and dried under vacuum to give 0.076 g (0.098 mmol, 29%) of complex **4**, mp 189–191 (dec) under Ar. Anal. Calcd for $C_{42}H_{66}HfN_2$: C, 64.88; H, 8.56; N, 3.60. Found: C, 65.30; H, 8.60; N, 3.32. IR (Nujol mull, cm^{-1}): 1641 (δ C=N), 1885 cm^{-1} (δ *C*=C=C). ^{1}H NMR (major isomer only, 298 K, C_6D_6, numbering refers to Figure 2; 400 MHz): δ 1.38 (s, 9 H, N2-*t*-Bu), 1.39 (s, 9 H, 4-*t*-Bu), 1.51 (s, 9 H, N1-*t*-Bu), 1.78, 1.88, 2.07 (3s, 3 H each, Cp-Me), 1.97 (s, 15 H, Cp*), 1.98, 2.42 (2m, 1H each, 31-H), 2.35 (m, 1H, 1-H), 2.48, 3.34 (2d, 1H each, $^2J = 16.1$ Hz, 32-H), 4.21 (d, 1H, $^5J = 4.4$ Hz, 4-H). ^{13}C NMR (100 MHz): δ 11.6, 12.5, 13.5 (3 × Cp-Me), 12.2 (C_5*Me*$_5$), 24.5 (C31), 29.3 (C32), 30.7 (N2-*t*-Bu Me), 31.5 (4-*t*-Bu Me), 32.0 (N1-*t*-Bu Me), 33.2 (4-*t*-Bu C), 37.9 (1-*t*-Bu C), 55.7 (N2-*t*-Bu C), 59.2 (C1), 60.7 (N1-*t*-Bu C), 92.0 (C4), 104.9, 113.8, 119.2, 119.3, 119.6 (5 × Cp-C), 115.7 (*C*$_5$Me$_5$), 132.7 (C3), 177.2 (C38), 193.5 (*C*2), 254.5 (C33). Signals due to *t*-Bu at 330 K, δ (^{1}H, 300 MHz/^{13}C, 75 MHz): 1.29 broad/28.9 at C1, 1.36/31.5 at C4, 1.39/30.8 at N2, 1.52/32.1 at N1. MS (CI, isobutane, *m*/*z*): 778 $[M]^+$, 721 $[M - t\text{-Bu}]^+$, 695 $[M - t\text{-BuNC}]^+$, 612 $[M - 2\ t\text{-BuNC}]^+$.

X-ray Crystallographic Study of Complexes 3-Hf and 4. Diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97[11]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[12]). XP (Bruker AXS) was used for graphical representations.

Supporting Information Available: Tables of crystallographic data in cif format, including bond lengths and angles of compounds **3-Hf** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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