# Interactions of hafnocene and zirconocene dihydrides with acetylenes. Synthesis of the first acetylene complex of hafnium

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The first acetylene complex of hafnium, $Cp_2Hf[Me_3SiC{\equiv}CHf(H)Cp_2]$, was synthesized by the reaction of hafnocene dihydride $Cp_2HfH_2$ with bis(trimethylsilyl)acetylene in benzene. The reaction is accompanied by elimination of the $Me_3Si$ group from the molecule of the initial acetylene, as a result of which the acetylenide derivative of hafnium $Cp_2Hf(C{\equiv}CSiMe_3)(H)$ acts as an acetylene ligand in the complex. Under analogous conditions, the reaction of zirconocene dihydride $Cp_2ZrH_2$ with bis(trimethylsilyl)acetylene affords an analogous acetylene complex of zirconium $Cp_2Zr[M_3SiC{\equiv}CZr(H)Cp_2]$. Reactions of $Cp_2HfH_2$ with tolane and 3-hexyne proceed differently than the reaction with bis(trimethylsilyl)acetylene. Here the corresponding hafnacyclopentadiene metallacycles are the final products.

**Key words:** zirconium, hafnium, acetylene complexes, hydrides, metallacyclopentadienes.

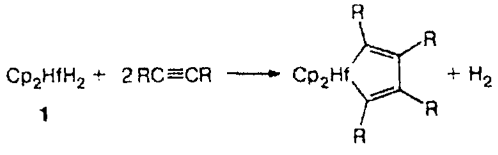
A rather large number of acetylene complexes of titanium and zirconium have been obtained to date. However, acetylene complexes of hafnium are unknown. In searching for approaches to the synthesis of such complexes, we studied interactions of different acetylenes with hafnocene dihydride $Cp_2HfH_2$ (**1**). In the solid state, this compound, like the analogous derivative of zirconocene $Cp_2ZrH_2$ (**2**), has the polymeric structure $[Cp_2HfH_2]_n$ with bridging and terminal hydride ligands.[1,2] It was believed that in the reaction of **1** with acetylenes, dihydrogen would be evolved from the initial dihydride to form the corresponding acetylene complexes of hafnocene $Cp_2Hf(RC_2R)$.

In this work, we studied interactions of compound **1** with tolane, 3-hexyne, and bis(trimethylsilyl)acetylene.* We also studied the reaction of **2** with bis(trimethylsilyl)acetylene.

## Results and Discussion

Reactions of compound **1** with tolane and 3-hexyne were carried out in benzene under an argon atmosphere with gradual increase in the reaction temperature from 20 to 60 °C followed by stirring of the mixture at 60 °C for 1—1.5 h. The molar ratio of the reagents was 1 : 1. Because of the low solubility of the initial dihydride in benzene, a suspension of **1** in benzene was introduced in the reaction with acetylenes. It turned out that under such conditions the reaction yields the corresponding hafnacyclopentadiene derivatives **3** and **4** (Scheme 1) rather than the target acetylene complexes $Cp_2Hf(RC_2R)$ (R = Ph, or Et). Because of a deficiency of acetylene, about half the amount of dihydride remained nonconsumed.

**Scheme 1**



**3, 4**

R = Et (**3**), Ph (**4**)

Complete conversion of **1** was achieved when RC≡CR and **1** were taken in a molar ratio of 2 : 1. It is worth noting that when the initial mixture of the reagents was heated from 20 to 60 °C instantly, no reaction occured (at least, during 8 h).

The resulting data may be explained by the fact that the acetylene complex $Cp_2Hf(RC_2R)$ (R = Ph, or Et) formed at the initial stages reacts rapidly with yet nonconsumed acetylene to yield the final hafnacyclopentadiene derivative. Therefore, to terminate the reac-

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tion at the stage of formation of the acetylene complex, it is necessary to hinder the reaction of this complex with free acetylene. We believed that this can be achieved if bis(trimethylsilyl)acetylene, which contains bulky $Me_3Si$ groups, is introduced in the reaction with dihydride. Actually, the reaction of **1** with bis(trimethylsilyl)acetylene afforded the acetylene complex of hafnium. However, the composition of the complex differs from what we expected.

Reactions with bis(trimethylsilyl)acetylene were carried out under conditions identical to those used in the reactions with tolane and 3-hexyne. The molar $Me_3SiC{\equiv}CSiMe_3$ : **1** ratio was varied within a range of (2—0.5) : 1. In all cases, compound **1** was gradually dissolved in the course of the reaction, and the color of the solution changed from colorless to dark-violet. When $Me_3SiC{\equiv}CSiMe_3$ and compound **1** were taken in ratios of 2 : 1 and 1 : 1, acetylene was partly nonconsumed. Complete conversion of acetylene in the reaction with **1** was observed when $Me_3SiC{\equiv}CSiMe_3$ and **1** were taken in a ratio of 1 : 2.

A dark-violet fine crystalline complex **5** was isolated from the reaction mixture. This complex is extremely sensitive to atmospheric oxygen and moisture. The complex is readily soluble in benzene and THF and less soluble in hexane.

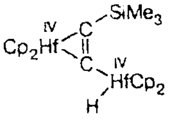
The $^1H$ NMR spectrum of complex **5** in THF-$d_8$ has two singlets of protons of nonequivalent $\eta^5$-$C_5H_5$ rings (at $\delta$ 5.73 and 5.84), singlets of methyl protons of the $SiMe_3$ group (at $\delta$ 0.01), and a singlet of the hydride proton at $\delta$ −2.25 (the ratio of intensities of the signals is close to 10 : 10 : 9 : 1). If hafnocene dideuteride $Cp_2HfD_2$ was involved in the reaction with bis(trimethylsilyl)acetylene, the signal of the hydride ligand was absent in the $^1H$ NMR spectrum of a dark-violet product. The $^{13}C$ {$^1H$} NMR spectrum of complex **5** in $C_6D_6$ shows signals of C atoms of two nonequivalent $\eta^5$-$C_5H_5$ rings (at $\delta$ 104.22 and 102.90) and of the $Me_3Si$ group (at $\delta$ 1.40) and two low intensity singlets of acetylene C atoms at $\delta$ 204.74 and 291.35. Such a large difference in the chemical shifts of acetylene C atoms was observed previously for binuclear acetylenide complexes of zirconocene $[Cp_2Zr(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CR)]_2$ (see, for example, Ref. 4). This may be indicative of the fact that complex **5** contains a trimethylsilylacetylenide group, *i.e.*, one $Me_3Si$ group of the initial acetylene is eliminated (apparently, in the form of $Me_3SiH$) in the reaction of compound **1** with bis(trimethylsilyl)acetylene.

Thus, analysis of the NMR spectra allows to suggest that complex **5** contains two nonequivalent $(\eta^5\text{-}C_5H_5)_2Hf$ groups, one trimethylsilylacetylenide ligand, and one hydride hydrogen atom. This suggestion is consistent with the data of elemental analysis, molecular weight measurements, and the results of studies of the reactions of complex **5** with HCl (in EtOH) and $H_2SO_4$.

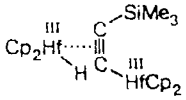
Thus, treatment of solid complex **5** with a 50% aq. $H_2SO_4$ yielded 1 mole of gaseous hydrogen (per mole of **5**). The reaction of the complex with HCl in EtOH yielded 2 moles of $Cp_2HfCl_2$ per mole of compound **5**. Based on the data of GC-MS, trimethylvinylsilane and trimethylsilylacetylene were also formed, which supports the suggestion that one $Me_3Si$ group is eliminated from the initial acetylene in the reaction with **1**. The molecular weight measured in benzene by the cryoscopic method is indicative of the monomeric form of the complex.

The IR spectrum of the complex (Nujol mulls) shows bands typical of $\eta^5$-$C_5H_5$ rings (3091, 1126, 1068, 1014, and 798 $cm^{-1}$) and of the $SiMe_3$ group (2955, 2919, 2849, 1305, 1237, and 856 $cm^{-1}$) and also a rather intense absorption band at 1636 $cm^{-1}$, which may be assigned to stretching vibrations of the coordinated CC bond of the acetylene ligand. Such a low value of $\nu$(CC) indicates that the order of this bond is close to 2. Stretching vibrations of the Hf—H bond were not detected in the IR spectrum. Deformation vibrations appear in the IR spectrum as a band at 720 $cm^{-1}$. This band is shifted to 515 $cm^{-1}$ in the spectrum of the complex obtained from $Cp_2HfD_2$. The value of this shift corresponds to the theoretically expected value of the isotopic shift ($\beta_H/\beta_D$ = 1.40).

Based on the data obtained, it is possible to suggest two structures (**5A** and **5B**) for complex **5**. According to both structures, compound **5** is the acetylene complex of hafnocene in which the trimethylsilylacetylenide derivative of hafnium acts as an acetylene ligand.



**5A**



**5B**

The structure **5A** is analogous to the known structures of the acetylene complexes of titanocene and zirconocene, which have the structures of metallacyclopropene derivatives (see, for example, Refs. 5 and 6). Both hafnium atoms in structure **5A** are in the oxidation state +4, and the order of the acetylene bond is close to 2. Unlike structure **5A**, the oxidation states of both hafnium atoms in structure **5B** are equal to +3, and therefore, in this case the CC bond of the acetylene ligand must be, apparently, closer to the triple rather than to the double bond.* Taking into account that the $\nu$(CC) band of the acetylene group in complex **5** (1636 $cm^{-1}$) is observed in the region typical of double C=C bonds, structure **5A** is, apparently, preferential.

We also studied the reaction of dihydride **2** with bis(trimethylsilyl)acetylene. Experiments were carried out under conditions identical to those used in the case of **1**.

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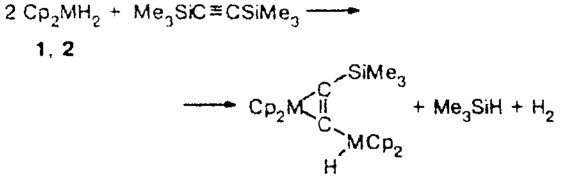
* Diamagnetism of structure **5B** could be provided by a direct antiferromagnetic interaction between $Hf^{III}$ atoms or an interaction of unpaired electrons through the acetylenide ligand.

The reaction yielded a dark-blue compound extremely sensitive to atmospheric oxygen. This compound was identified as the acetylene complex of zirconium (**6**). Unlike compound **5**, we failed to isolate **6** in the analytically pure form. However, based on the data of NMR spectroscopy, it is believed that this complex has a structure analogous to **5**. The $^1H$ NMR spectrum of complex **6** in THF-$d_8$, like the spectrum of complex **5**, has two singlets of protons of nonequivalent $\eta^5$-$C_5H_5$ rings (at δ 5.82 and 5.95), a singlet of methyl protons of the $Me_3Si$ group (at δ 0.04), and a singlet of the hydride ligand (at δ −7.25) (the ratio of the intensities of the signals is close to 10 : 10 : 9 : 1). The $^{13}C$ {$^1H$} NMR spectrum of complex **6** in $C_6D_6$, like the spectrum of **5**, contains singlets of C atoms of two nonequivalent $\eta^5$-$C_5H_5$ rings (at δ 105.15 and 104.22), a singlet of the $Me_3Si$ group (at δ 1.27), and two low-intensity singlets of acetylene C atoms (at δ 197.66 and 283.30).

Thus, based on the data obtained, it can be concluded that in the reactions of dihydrides **1** and **2** with bis(trimethylsilyl)acetylene, the $Me_3Si$ group is eliminated from the initial acetylene to form the acetylene complexes of zirconium and hafnium, $Cp_2M[Me_3SiC{\equiv}CM(H)Cp_2]$ (M = Zr, or Hf), containing the trimethylsilylacetylenide derivative $Cp_2M(C{\equiv}CSiMe_3)(H)$ as an acetylene ligand (Scheme 2).

**Scheme 2**



**5, 6**

M = Hf (**5**), Zr (**6**)

Complex **5** is the first example of the acetylene complex of hafnium.

## Experimental

Experiments were carried out under an argon atmosphere with careful exclusion of atmospheric oxygen and moisture. Solvents were purified according to standard procedures and distilled under Ar over sodium and sodium benzophenone ketyl (THF) or over sodium and calcium hydride (*n*-hexane and benzene) immediately before use. Initial dihydrides **1** and **2** were prepared according to procedures reported previously.[1,7] The IR spectra were recorded on an IFS-25 Bruker FT infrared spectrometer (resolution was 2 $cm^{-1}$) in Nujol mulls under Ar. The $^1H$ and $^{13}C$ {$^1H$} NMR spectra were recorded on a Bruker WH-400 spectrometer in THF-$d_8$ and $C_6D_6$ solutions (cyclohexane or $Me_4Si$ were used as the internal standard).

**Reaction of 1 with bis(trimethylsilyl)acetylene.** Compound **1** (1.31 g, 4.22 mmol) and benzene (60 mL) were placed in a two-neck flask under an argon atmosphere. Then $Me_3SiC{\equiv}CSiMe_3$ (0.37 g, 2.18 mmol) was added with stirring using a magnetic stirrer. The reaction mixture was gradually heated with stirring from 20 to 60 °C for 25—30 min. In the course of the reaction, compound **1** was dissolved, and the color changed from colorless to dark-violet. The mixture was stirred at 60 °C for 1—1.5 h. The dark-violet solution obtained was cooled, filtered off, and evaporated at 20 °C *in vacuo* to dryness. The residue was dried *in vacuo* at 20 °C for 4 h. Dark-violet fine crystalline complex **5** was obtained in a yield of 1.33 g (88%). Based on the data of $^1H$ NMR spectroscopy, compound **5** contains 0.25 mole of crystallization benzene per mole of the complex; m.p. 126—127 °C (with decomp., in an atmosphere of argon). Found (%): C, 42.58; H, 4.41. $C_{25}H_{30}Hf_2Si \cdot 0.25C_6H_6$. Calculated (%): C, 42.30; H, 4.39. Mol. weight (cryoscopy in $C_6H_6$), found: 800, calculated: 735. $^1H$ NMR (THF-$d_8$), δ: 5.84 (s, 10 H, $\eta^5$-$C_5H_5$); 5.73 (s, 10 H, $\eta^5$-$C_5H_5$); 0.01 (s, 9 H, Me); −2.25 (s, 1 H, HfH). $^1H$ NMR ($C_6D_6$), δ: 5.69 (s, 10 H, $\eta^5$-$C_5H_5$); 5.67 (s, 10 H, $\eta^5$-$C_5H_5$); 0.20 (s, 9 H, Me); −2.20 (s, 1 H, HfH). $^{13}C$ {$^1H$} NMR ($C_6D_6$), δ: 104.22 (s, $\eta^5$-$C_5H_5$); 102.90 (s, $\eta^5$-$C_5H_5$); 1.40 (s, Me); 204.74 (s, C≡C); 291.35 (s, C≡C). An amount of crystallization benzene in samples of complex **5** varied within 0.2—0.3 mole per mole of **5**.

**Reaction of 2 with bis(trimethylsilyl)acetylene.** The reaction of **2** with bis(trimethylsilyl)acetylene was carried out according to the procedure used for **1**. Dark-blue fine crystalline complex **6** was obtained in a yield of 1.58 g. $^1H$ NMR (THF-$d_8$), δ: 5.95 (s, 10 H, $\eta^5$-$C_5H_5$); 5.82 (s, 10 H, $\eta^5$-$C_5H_5$); 0.04 (s, 9 H, Me); −7.25 (s, 1 H, ZrH). $^{13}C$ {$^1H$} NMR ($C_6D_6$), δ: 105.15 (s, $\eta^5$-$C_5H_5$); 104.22 (s, $\eta^5$-$C_5H_5$); 1.27 (s, Me); 197.66 (s, C≡C); 283.30 (s, C≡C).

**Protolysis of complex 5.** A 10 *M* HCl solution in EtOH (1 mL) was added to a solution of complex **5** (0.24 g, 0.33 mmol) in benzene (10 mL). The dark-violet color of the solution immediately disappeared, and hydrogen was evolved. After completion of the reaction, the colorless solution was evaporated at 20 °C *in vacuo* to dryness. $Cp_2HfCl_2$ was obtained in a yield of 0.24 g (94%), m.p. 230 °C (*cf.* Ref. 8: m.p. 232 °C). The melting point of $Cp_2HfCl_2$ remained unchanged after recrystallization from $C_6H_6$.

Complex **5** (0.1298 g, 0.1814 mmol) was placed in one arm of a Rittenberg vessel, and a 50% $H_2SO_4$ aqueous solution (5 mL) was placed in the second arm. The Rittenberg vessel was connected to a high-vacuum apparatus equipped with a gas mercury burette and a Topler pump. The vessel was evacuated with cooling. Complex **5** was mixed with $H_2SO_4$. Gaseous $H_2$ was evolved. After completion of the reaction, $H_2$ was transferred into the gas burette using the Topler pump, and the volume of $H_2$ evolved was determined (4.2 mL or 0.97 moles of $H_2$ per mole of the complex).

**Reaction of 1 with tolane.** A solution of tolane (0.37 g, 2 mmol) in $C_6H_6$ (20 mL) was added to a suspension of compound **1** (0.32 g, 1 mmol) in $C_6H_6$ (20 mL). The temperature of the solution was gradually increased to 60 °C with stirring during 25—30 min. Then the mixture was stirred at this temperature for 30 min. In the course of the reaction, compound **1** was dissolved, and the solution turned yellow. The reaction mixture was cooled, filtered off, and evaporated *in vacuo* at 20 °C to dryness. Fine crystalline yellow complex **3** that formed was twice washed with hexane and dried *in vacuo*. The yield of **3** was 0.6 g (88%), m.p. 235—237 °C (in an atmosphere of argon). Found (%): C, 68.65; H, 4.75; Hf, 26.76. $C_{34}H_{34}Hf$. Calculated (%): C, 68.62; H, 4.54;

Hf, 26.82. $^1$H NMR ($C_6D_6$), δ: 5.92 (s, 10 H, $\eta^5$-$C_5H_5$); 6.68—7.09 (m, 20 H, Ph). The NMR data obtained agree well with the published data.[9]

The reaction of **1** with 3-hexyne was carried out according to an analogous procedure. The reaction yielded complex **4**, m.p. 72 °C (in an atmosphere of argon). Found (%): C, 55.78; H, 6.53; Hf, 37.96. $C_{22}H_{30}Hf$. Calculated (%): C, 55.87; H, 6.39; Hf, 37.74. $^1$H NMR ($C_6D_6$), δ: 5.85 (s, 10 H, $\eta^5$-$C_5H_5$); 0.92 (t, 6 H, Me, $J$ = 7.5 Hz); 1.02 (t, 6 H, Me, $J$ = 7.5 Hz); 2.25 (q, 4 H, $CH_2$, $J$ = 7.5 Hz); 2.45 (q, 4 H, $CH_2$, $J$ = 7.5 Hz); the spectral data agree with the published data.[9]

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