Communications

Complexation of Bis(trimethylsilyl)acetylene by Decamethylhafnocene To Give the Hafnacyclopropene Cp*$_2$Hf(η^2-Me$_3$SiC$_2$SiMe$_3$): An Unusually Strong Metal−Alkyne Interaction[†]

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Summary: The complexes Cp$_2$Hf(PMe$_3$)(η^2-Me$_3$SiC$_2$SiMe$_3$) (3) and Cp$_2$Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (4), as the first examples of well-defined hafnium alkyne complexes with a simple intact alkyne, are described; 4 displays an unusually strong interaction of the alkyne with hafnium, in comparison to analogous compounds of titanium and zirconium.*

In group 4 chemistry the complexation of bis(trimethylsilyl)-acetylene by metallocenes leads to the 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] Surprisingly, all attempts to obtain analogous well-defined hafnium complexes have failed so far. The reason for this is not obvious but might be found in the enhanced reactivity of hafnium compounds compared to those of zirconium. Erker et al. described in case of (*s-cis*-η^4-diene)metallocene complexes the σ to π ratio of the diene bonding to be shifted to a larger σ character for hafnium compared to zirconium, giving Hf−C bonds that are shorter

than Zr−C bonds.[2] Very recently the impressive consequences of such high reactivity were shown by the Chirik group, who reported the functionalization of molecular nitrogen by a hafnocene complex. In contrast, the analogous zirconocene compound did not functionalize N$_2$.[3]

To the best of our knowledge, only two well-defined hafnium alkyne complexes have been found, but neither of them bears the starting intact acetylene (Me$_3$SiC≡CSiMe$_3$ in the case of **2**) as the ligand (Chart 1).

Complex **1** was reported by the Erker group, resulting from the reaction of dipropynylhafnocene Cp$_2$Hf(C≡CMe)$_2$ with B(C$_6$F$_5$)$_3$.[4] Compound **2** was obtained by Shur and co-workers as a product of the reaction of the hydride Cp$_2$HfH$_2$ with Me$_3$SiC≡CSiMe$_3$.[5]

We report here the synthesis and characterization of the first hafnium complexes containing the original alkyne reactand, Cp$_2$-Hf(PMe$_3$)(η^2-Me$_3$SiC$_2$SiMe$_3$) (**3**)[6] (Scheme 1) and Cp*$_2$Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**4**)[7] (Scheme 2).

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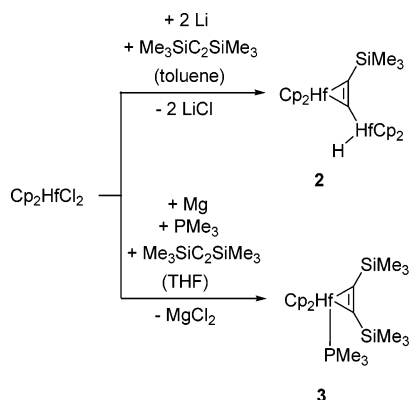
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Chart 1. Known Hafnium Alkyne Complexes 1 and 2
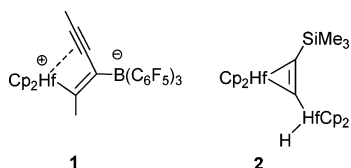
Scheme 1. Formation of the Cp Complexes 2 (by a New Method) and 3

Our first experiments showed that the method used for the successful preparation of similar titanium and zirconium complexes failed in the attempted synthesis of a hafnocene alkyne complex. The reaction of Cp_2HfCl_2 with $Me_3SiC\equiv CSiMe_3$ using magnesium as the reducing agent in THF gave a mixture of products which we could not identify. When this reaction was conducted in the presence of PMe_3, complex **3** was formed in 51% yield. When metallic lithium was used as the reducing agent in toluene without added phosphine, complex **2**, which was identical to Shur's product,[5] was obtained by a new method (Scheme 1) (see the Supporting Information).

However, when decamethylhafnocene dichloride, $Cp*_2HfCl_2$, was used, reaction with $Me_3SiC\equiv CSiMe_3$ and lithium in toluene solvent resulted in formation of the desired type of complex,

$Cp*_2Hf(\eta^2-Me_3SiC_2SiMe_3)$ (**4**) (Scheme 2). Obviously it was the presence of THF that caused the problems encountered in the attempted synthesis of the hafnium complexes using magnesium in THF.

Scheme 2. Formation of Complex 4
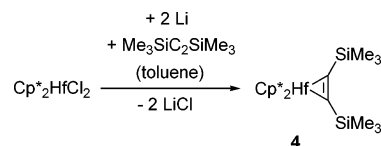
In contrast, in the synthesis of the analogous complexes $Cp*_2$-$Ti(\eta^2-Me_3SiC_2SiMe_3)$ and $Cp*_2Zr(\eta^2-Me_3SiC_2SiMe_3)$ the THF apparently acts as a stabilizing agent during the complex formation reaction. All complexes of this type were synthesized in THF.[1] Additionally, THF stabilizes the resulting alkyne complexes: e.g., in $Cp_2Zr(THF)(\eta^2-Me_3SiC_2SiMe_3)$. If the interaction of hafnocene with THF is stronger, this could lead to other reaction pathways and products.

Scheme 3. Ring-Opening Reaction of THF
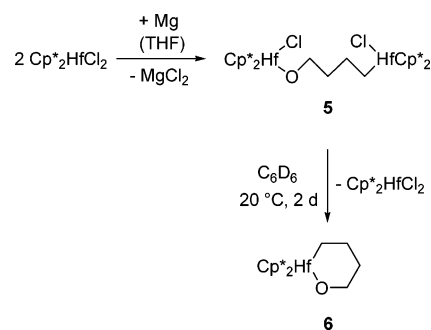
To investigate details of the THF reactions with hafnocene, the reactions of $Cp*_2HfCl_2$ with magnesium in THF with and without $Me_3SiC\equiv CSiMe_3$ were performed. Without the alkyne a ring-opening reaction of THF occurred (Scheme 3), giving the dinuclear complex $Cp*_2Hf(Cl)OCH_2CH_2CH_2CH_2(Cl)$-$HfCp*_2$ (**5**). This product was only formed in the presence of magnesium; heating of $Cp*_2HfCl_2$ in THF gave no reaction at all. In benzene solution **5** underwent disproportionation to $Cp*_2$-$HfCl_2$ and the 1-hafna-2-oxacyclohexane **6**, as indicated by NMR. This complex is very similar to the analogous 1-zircona-2-oxacyclohexane which had been prepared earlier by another procedure.[8] The compounds **5** and **6** indicate clearly that during the reaction with magnesium in THF ring opening instead of alkyne complexation takes place. This is the reason why the synthesis failed and lithium in toluene is preferred.

Complex **3** is highly sensitive toward oxygen and moisture. One can consider **3** as a hafnacyclopropene, as can be seen from its IR spectrum, which shows $\nu(C\equiv C)$ at 1551 cm^{-1}. The alkyne is coordinated unsymmetrically, showing two singlets in the ^1H NMR at 0.32 and 0.52 ppm for the $SiMe_3$ protons and two doublets in the ^{13}C NMR at 182.6 and 212.8 ppm. In the crystal structure of **3** (Figure 1) the distance between the carbon atoms of the complexed alkyne (1.311(4) Å) is in the range of a double bond and two different C−Hf distances for the alkyne ligand (2.198(3) and 2.277(3) Å) were observed.

In complex **4** the alkyne is coordinated symmetrically to the metal. The most important property of this compound is the strong interaction of the alkyne with the hafnium, which can

(6) Preparation of $Cp_2Hf(PMe_3)(Me_3SiC\equiv CSiMe_3)$ (**3**): to a suspension of Cp_2HfCl_2 (3.0 g, 7.90 mmol) and Mg turnings (0.13 g, 8.02 g atom) in 50 mL of THF were added at room temperature bis(trimethylsilyl)acetylene (1.85 mL, 8.19 mmol) and PMe_3 (8.0 mL of a 1.0 M solution in THF, 8.00 mmol). The colorless mixture became deep red as it was stirred for 16 h. All volatiles were removed under vacuum, and the residue was extracted with 4 × 15 mL of *n*-hexane. The solvent was again removed from the obtained solutions, giving the red crude product material, which was recrystallized from *n*-hexane/THF to give yellow prisms of **3**: yield 2.24 g (51%); mp 118 °C dec under Ar. Anal. Calcd for $C_{21}H_{37}HfPSi_2$ (555.15): C, 45.43; H, 6.72. Found: C, 40.27; H, 5.84 (because of partial dissociation of PMe_3, better data could not be obtained). IR (Nujol mull, cm^{-1}): 1240 ($SiMe_3$), 1551 (C≡C). NMR (400 MHz, 298 K, C_6D_6): ^1H, δ 0.32 (s, 9 H, $SiMe_3$), 0.52 (s, 9 H, $SiMe_3$), 1.12 (d, $J_{P,H}$ = 5.8 Hz, 9 H, PMe_3), 5.07 (d, $J_{P,H}$ = 1.7 Hz, 10 H, Cp); ^{13}C, δ 3.1 (s, $SiMe_3$), 3.4 (s, $SiMe_3$), 19.2 (d, $J_{P,C}$ = 18 Hz, PMe_3), 101.8 (s, Cp), 182.6 (d, $J_{P,C}$ = 8 Hz, C≡C), 212.8 (d, $J_{P,C}$ = 5 Hz, C≡C); ^{31}P, δ −8.9 (s, PMe_3). MS (70 eV, *m/z*): 480 [Cp_2-$Hf(Me_3SiC\equiv CSiMe_3)$]$^+$, 310 [$Cp_2Hf$]$^+$.

(7) Preparation of **4**: a suspension of $Cp*_2HfCl_2$ (1.773 g, 3.41 g atom), finely sliced lithium wire (0.103 g, 14.8 mmol), and bis(trimethylsilyl)-acetylene (0.80 mL, 3.56 mmol) in 15 mL of toluene was stirred for 10 days at 60 °C. The resulting dark blue solution was filtered and evaporated to dryness under vacuum. The residue was extracted with 15 mL of *n*-hexane at 55 °C. The resulting blue solution was filtered and concentrated under vacuum to a total volume of 10 mL. After the concentrated solution stood for 24 h at −78 °C, dark blue crystals formed, which were separated, washed with cold *n*-hexane, and dried under vacuum to give complex **4**: yield 0.951 g (45%); mp 242−243 °C under Ar. Anal. Calcd for $C_{28}H_{48}HfSi_2$: C, 54.30; H, 7.81. Found: C, 54.54; H, 7.97. IR (Nujol mull, cm^{-1}): 1470 (ν(C≡C)). NMR (400 MHz, 298 K, C_6D_6): ^1H, δ 0.26 (s, 18H, $SiMe_3$), 1.81 (s, 30H, Cp*); ^{13}C, δ 4.7 ($SiMe_3$), 11.6 (C_5Me_5), 118.0 (C_5Me_5), 283.4 (C≡C). MS (70 eV, *m/z*): 620 [M]$^+$.

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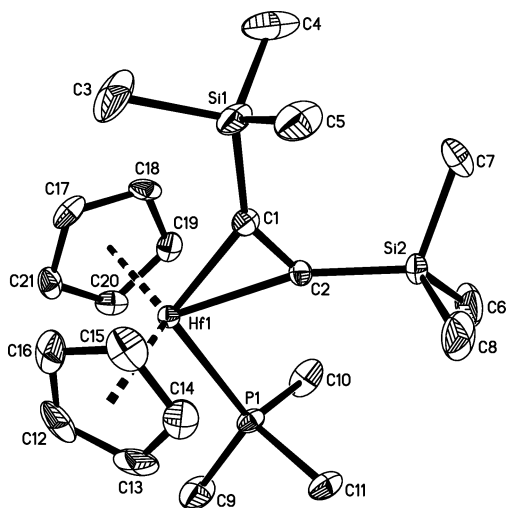
Figure 1. Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−C2 = 1.311(4), Hf1−C1 = 2.198(3), Hf1−C2 = 2.277(3), C1−Si1 = 1.850(3), C2−Si2 = 1.848(3), Hf1−P1 = 2.660(1); C1−Hf1-C2 = 34.02(9), C1−C2−Si2 = 126.8(2), C2−C1−Si1 = 143.5(2).
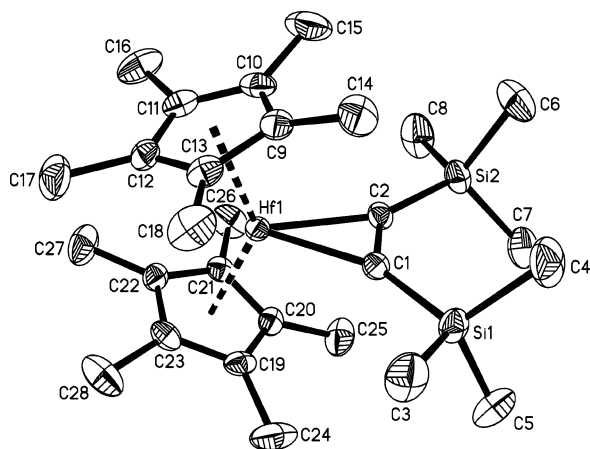

Figure 2. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−C2 = 1.337(4), Hf1−C1 = 2.188(3), Hf1−C2 = 2.184(3), C1−Si1 = 1.860(3), C2−Si2 = 1.862(3); C1−Hf1−C2 = 35.60(11), C1−C2−Si2 = 134.5(3), C2−C1−Si1 = 134.0(3).

be derived from the spectroscopic and structural data. The observed $\nu(C\equiv C)$ value of 1470 cm^{-1} for complex **4** is indicative of strong complexation of the alkyne to the metal center, resulting in the hafnacyclopropene structure ($\nu(C\equiv C)$ for the Ti analogue, 1563/1596 cm^{-1};[9] $\nu(C\equiv C)$ for the Zr analogue, 1516 cm^{-1} [10]). The ^{13}C NMR signal for the carbon

atoms of the complexed alkyne, 283.4 ppm, is shifted far downfield compared to those for the analogous titanium and zirconium complexes Cp*$_2$M(η^2-Me$_3$SiC$_2$SiMe$_3$) (Ti, 248.5 ppm;[9] Zr, 260.5 ppm[10]). The molecular structure (Figure 2) of complex **4** shows the two Cp* ligands and the alkyne coordinated at the hafnium center.

The distance of 1.337(4) Å between the alkyne carbon atoms is in the range of a double bond and also clarifies the aforementioned tendency of group 4 alkyne complexes, in which the electron density of the π system is reduced (Ti, 1.309(4) Å;[9] Zr, 1.320(3)[10] Å) compared to the free alkyne (C1−C2 = 1.208 Å).[11] For these complexes the trend of M−C(alkyne) bond distances (Ti−C = 2.122(3)/2.126(3) Å; Zr−C = 2.216(2)/2.221(2) Å; Hf−C = 2.188(3)/2.184(3) Å) is the same as that found in the complexes Cp$_2$MMe$_2$ (Ti−C = 2.181(2)/2.170(2) Å;[12] Zr−C = 2.280(5)/2.273(5) Å;[13] Hf−C = 2.240(12)/2.233-(12) Å[13]).

This approach, resulting from the comparison of the spectroscopic and structural data, also should be reflected in the chemical reactivity of these complexes. For example, in the series of complexes Cp*$_2$M(η^2-Me$_3$SiC$_2$SiMe$_3$) the titanium species did not react with boiling acetone, whereas acetone inserted into the ZrC$_2$ ring of the zirconium complex easily at room temperature.[1] On reaction with carbon dioxide, the alkyne was completely displaced from the titanium complex, whereas in the case of zirconium CO$_2$ insertion into the M−C bond of the ZrC$_2$ ring was observed.[1] On this basis interesting new insertion reactions are expected for the hafnium complex. These will be the subject of further detailed investigations.

Supporting Information Available: CIF files giving crystallographic data, including bond lengths and angles, of compounds **3** and **4** and text giving experimental details for compounds **2**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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