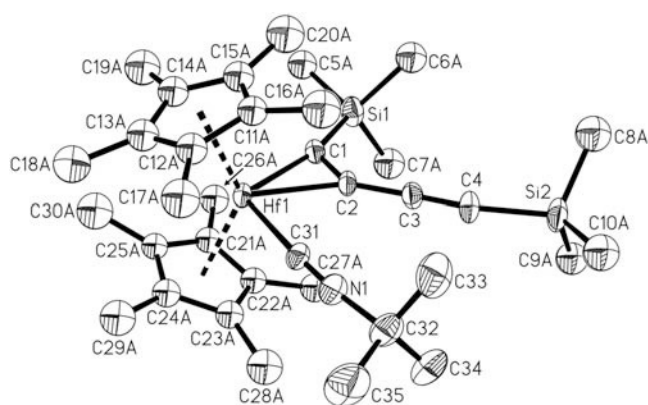


# Crystal structure of bis(pentamethylcyclopentadienyl)(1-*tert*-butylisocyanido)-2-trimethylsilyl-3-[(trimethylsilyl)ethynyl]-hafnacyclopropene, (C<sub>10</sub>H<sub>15</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>9</sub>N)Hf(C<sub>10</sub>H<sub>18</sub>Si<sub>2</sub>)

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Received January 25, 2010, accepted and available on-line February 3, 2010; CCDC no. 1267/2908



## Abstract

C<sub>35</sub>H<sub>57</sub>HfNSi<sub>2</sub>, monoclinic, *P*12<sub>1</sub>/*c*1 (no. 14), *a* = 10.7410(3) Å, *b* = 16.2302(5) Å, *c* = 21.6945(7) Å, β = 104.512(2)°, *V* = 3661.3 Å<sup>3</sup>, *Z* = 4, *R*<sub>gt</sub>(*F*) = 0.049, *wR*<sub>ref</sub>(*F*<sup>2</sup>) = 0.138, *T* = 200 K.

## Source of material

Cp\*<sub>2</sub>Hf(η<sup>4</sup>-Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub>) (0.345 g, 0.54 mmol) was dissolved in 15 mL of toluene and *tert*-butylisocyanide (0.121 mL, 1.08 mmol) was added. The deep red solution was heated to 60 °C for two hours, followed by subsequent removal of all volatiles in vacuum. The resulting dark red oily residue was allowed to stand at room temperature, giving yellow prisms after two days which were used for X-ray analysis.

## Experimental details

Both pentamethylcyclopentadienyl ligands and both trimethylsilyl groups are disordered over two sites. For clarity only the positions with higher occupancies are shown. All not fully occupied atoms are refined isotropically.

## Discussion

Recently we have reported on the interactions of 1,3-butadiynes with permethylhafnocene, resulting in the formation of five-membered hafnacyclocumulenes [1]. We were interested to investigate the reaction behaviour of these complexes especially with respect to insertion reactions, e.g. with CO<sub>2</sub> or isocyanides. For example, the zirconacyclocumulene Cp\*<sub>2</sub>Zr(η<sup>4</sup>-Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub>) reacts with carbon dioxide by twofold insertion to give a nine-membered metallacycle [2]. A similar reactivity was expected for hafnacyclocumulenes and isocyanides. Sur-

prisingly, in the reaction of Cp\*<sub>2</sub>Hf(η<sup>4</sup>-Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub>) with *tert*-butylisocyanide no insertion takes place. Instead, the terminal carbon atom of the donor coordinates to the metal center. This results in a change of the coordination mode of the butadiyne from η<sup>4</sup> in the starting complex to η<sup>2</sup> in the product. The different nature of the triple bonds can be derived from the bond lengths of C1—C2 1.331(10) and C3—C4 1.213(10) Å, with the longer bond being coordinated to the hafnium center resulting in a hafnacyclopropene structure. The exocyclic ethynyl moiety displays a nearly linear geometry with ∠C2—C3—C4 = 176.5(9)°. One reason for the coordination of the isocyanide instead of an insertion into the M—C(α) bond might be the high steric demand of the cyclopentadienyl ligand, the trimethylsilyl group and the *tert*-butyl group of the donor. However, the isocyanide coordinates at the sterically less hindered side of the molecule.

**Table 1.** Data collection and handling.

Crystal:	yellow prism, size 0.27 × 0.30 × 0.50 mm
Wavelength:	Mo <i>K</i> <sub>α</sub> radiation (0.71073 Å)
μ:	26.69 cm <sup>-1</sup>
Diffractometer, scan mode:	STOE IPDS II, ω
2θ <sub>max</sub> :	51°
<i>N</i> ( <i>hkl</i> ) <sub>measured</sub> , <i>N</i> ( <i>hkl</i> ) <sub>unique</sub> :	45456, 6682
Criterion for <i>I</i> <sub>obs</sub> , <i>N</i> ( <i>hkl</i> ) <sub>gt</sub> :	<i>I</i> <sub>obs</sub> > 2 σ( <i>I</i> <sub>obs</sub> ), 5021
<i>N</i> ( <i>param</i> ) <sub>refined</sub> :	220
Programs:	SHELXS-97 [3], SHELXL-97 [4], SHELXTL [5]

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
C(5A)	4e	0.53(4)	1.041(3)	0.741(1)	-0.026(1)	0.075(6)
H(5AA)	4e	0.53	0.9816	0.7278	-0.0670	0.113
H(5AB)	4e	0.53	1.0692	0.6898	-0.0025	0.113
H(5AC)	4e	0.53	1.1163	0.7698	-0.0335	0.113
C(6A)	4e	0.53	0.845(3)	0.870(2)	-0.040(1)	0.079(6)
H(6AA)	4e	0.53	0.7971	0.9076	-0.0196	0.118
H(6AB)	4e	0.53	0.7840	0.8324	-0.0685	0.118
H(6AC)	4e	0.53	0.8925	0.9010	-0.0654	0.118
C(7A)	4e	0.53	1.076(3)	0.881(2)	0.071(1)	0.087(6)
H(7AA)	4e	0.53	1.0320	0.9166	0.0950	0.130
H(7AB)	4e	0.53	1.1141	0.9155	0.0428	0.130
H(7AC)	4e	0.53	1.1445	0.8503	0.0999	0.130
C(5B)	4e	0.47(4)	1.090(2)	0.747(1)	0.001(2)	0.077(6)
H(5BA)	4e	0.47	1.1671	0.7491	0.0362	0.115
H(5BB)	4e	0.47	1.1093	0.7698	-0.0376	0.115
H(5BC)	4e	0.47	1.0622	0.6894	-0.0071	0.115
C(6B)	4e	0.47	0.848(4)	0.858(3)	-0.049(1)	0.086(7)

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**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
C(1)	4e	0.8697(7)	0.7511(4)	0.0706(3)	0.042(4)	0.033(3)	0.047(4)	0.004(3)	0.008(3)	0.004(3)
C(2)	4e	0.7894(7)	0.7878(4)	0.0996(3)	0.040(4)	0.026(3)	0.048(4)	0.004(3)	0.005(3)	0.001(3)
C(3)	4e	0.7458(8)	0.8680(4)	0.1038(4)	0.048(4)	0.036(4)	0.051(4)	0.008(3)	0.012(3)	0.004(3)
C(4)	4e	0.7025(8)	0.9361(4)	0.1085(4)	0.058(5)	0.029(4)	0.072(5)	0.003(3)	0.016(4)	0.002(3)
C(31)	4e	0.6559(7)	0.7177(4)	0.1733(4)	0.040(4)	0.036(4)	0.049(4)	−0.002(3)	0.007(3)	−0.007(3)
C(32)	4e	0.5171(9)	0.8126(6)	0.2259(5)	0.063(6)	0.070(6)	0.073(6)	0.003(5)	0.036(5)	−0.014(5)
C(33)	4e	0.413(1)	0.8480(7)	0.1714(7)	0.070(7)	0.089(8)	0.12(1)	0.030(6)	0.028(7)	−0.005(7)
C(34)	4e	0.608(1)	0.8804(7)	0.2593(6)	0.096(9)	0.082(7)	0.093(8)	0.002(6)	0.041(7)	−0.030(6)
C(35)	4e	0.461(2)	0.7643(9)	0.2727(7)	0.14(1)	0.11(1)	0.13(1)	−0.013(9)	0.09(1)	−0.012(8)
N(1)	4e	0.5939(7)	0.7561(4)	0.1982(3)	0.047(4)	0.053(4)	0.063(4)	0.001(3)	0.016(3)	−0.005(3)
Hf(1)	4e	0.78872(3)	0.65399(2)	0.12362(1)	0.0377(2)	0.0248(2)	0.0438(2)	0.0015(1)	0.0087(1)	−0.0007(1)
Si(1)	4e	0.9590(3)	0.8080(2)	0.0213(1)	0.070(2)	0.047(1)	0.077(2)	0.007(1)	0.036(1)	0.012(1)
Si(2)	4e	0.6677(2)	1.0455(1)	0.1060(1)	0.065(2)	0.032(1)	0.085(2)	0.008(1)	−0.004(1)	−0.010(1)

*Acknowledgment.* We would like to acknowledge funding by the Deutsche Forschungsgemeinschaft (GRK 1213)

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