Supporting Information

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Five-membered Metallacyclic Allenoids: Synthesis and Structure of Remarkably Stable Strongly Distorted Cyclic Allene Derivatives

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Supporting Informations

All air- and moisture-sensitive compounds were prepared and handled under an argon atmosphere using standard Schlenk and glove-box techniques. Anhydrous solvents were used in all the preparations. The solvents were passed through columns under an argon atmosphere, the deuterated solvents were distilled from drying agents and stored under argon.

The physical characterization of the products was performed using the following instruments. NMR: Bruker AC 200 P-FT (¹B: 64.2 MHz), Bruker ARX 300 (¹B: 96.3 MHz), Varian Inova 500 (¹H: 499.9 MHz; ¹⁹F: 470.3 MHz; ²⁹Si: 99.5 MHz), Varian Unity Plus 600 (¹H: 599.9 MHz; ¹³C: 150.8 MHz; ¹⁹F: 564.4). Most NMR assignments were supported by additional 2D experiments. The IR spectra were obtained with a Varian 3100 FT-IR (EXCALIBUR Series) spectrometer. The mass spectrometry was performed using a direct inlet and electron impact spectrometer MAT8200. Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument. HB(C₆F₅)₂ [D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492] and **6a** [W. Ahlers, B. Temme, G. Erker, R. Fröhlich, T. Fox, *J. Organomet. Chem.* **1997**, *527*, 191] were prepared according to procedures reported in the literature.

X-ray crystal structure analysis: Data sets were collected with Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek,

W. Majewski, W. Minor, *Acta Cryst.* **2003**, A59, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**. CCDC 664142 (**5b**) & 664143 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

[Bis(η^5 -cyclopentadienyl)-bis(3,3-dimethyl-1-butynyl)]hafnium (6b**).** Hafnocenedichloride (2.00 g, 5.27 mmol) and 3,3-dimethylbutynyllithium (0.97 g, 10.54 mmol) were weighed in an Argon-filled glove-box and put in a 200 mL Schlenk flask. The flask was cooled to -30°C , and 50 mL of diethyl ether were added under Argon. The solution was allowed to warm slowly to room temperature and left stirring for 12 hours. After this time, the precipitate was separate by filtration, and the volatiles were removed from the filtrate under reduced pressure, leaving a brown powder (1.56 g, 63%). Crystals suitable for single-crystal X-ray diffraction were obtained from concentrated toluene solution at -30°C .

^1H NMR (C_6D_6 , 599.9 MHz, 298 K, TMS): δ 6.03 (s, 10 H, Cp), 1.24 (s, 9 H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.8 MHz, 298 K, TMS): δ 138.9 (C1), 136.8 (C2), 109.9 ($^1J_{\text{CH}} = 181$ Hz, Cp), 31.6 ($^1J_{\text{CH}} = 124$ Hz, C4), 28.8 (C3). $^{13}\text{C}, ^1\text{H}$ GHMBC (C_6D_6 , 150.8/599.9 MHz, 298 K): $\delta^{13}\text{C}/\delta^1\text{H}$ 136.8 (C2)/1.24 ($\text{C}(\text{CH}_3)_3$), 28.8 (C3)/1.24 ($\text{C}(\text{CH}_3)_3$). FT-IR (KBr, cm^{-1}): 3097, 2963, 2074, 1474, 1453, 1359, 1243, 1199, 1019, 900, 835, 814, 726, 555, 540, 449. $\text{C}_{20}\text{H}_{20}\text{Hf}$, $M = 470.95$ g/mol; calculated: C: 56.11, H: 5.99; found: C: 56.24, H: 5.77.

Bis(η^5 -cyclopentadienyl)-1-bis(pentafluorophenyl)boryl-2,4-bis(1,1-dimethylethyl)-hafnacyclopenta-2,3-diene (5b**).** Bis(η^5 -cyclopentadienyl)bis(3,3-dimethyl-1-butynyl)-hafnium (200 mg, 0.423 mmol), and bis(pentafluorophenyl)borane (146.5 mg, 0.423 mmol), prepared following established procedures, were weighed in an argon-filled glove-box and put into a Schlenk flask. Toluene (50 mL) was added to the flask by cannula and the resulting red solution was stirred at 60°C for 2 hours. After heating, the volatiles were removed under high vacuum. The obtained residue was washed with pentane ($2 \times 20\text{mL}$) and dried in vacuo to get a red powder (314 mg, 91%). ^1H and ^{13}C NMR analyses indicated the presence of one main

product **5b** (ca. 80%) and one minor product not identified yet [$\delta^1\text{H}$ (C_7D_8 , 600 MHz, 233 K) 5.47 (s, Cp)]. Crystals suitable for single-crystal X-ray diffraction were obtained at room temperature from a concentrated toluene solution of the compound. ^1H NMR (C_7D_8 , 600

MHz, 233 K, TMS): δ 5.29 (s, 5 H, Cp^{A}), 5.11 (s, 5 H, Cp^{B}), 4.00 (s, 1 H, 1-H), 1.08 (s, 9 H, 4- $\text{C}(\text{CH}_3)_3$), 1.05 (s, 9 H, 2- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 151 MHz, 233 K, TMS): δ 166.3 (C4), 131.8 (C3), 120.1 (C2), 117.4 (ipso- C_6F_5)^b, 115.8 (ipso- C_6F_5)^b, n.o. (C-F), 104.9 (Cp^{A}), 102.9 (Cp^{B}), 60.5 (C1)^a, 37.9, 32.8 (4- $\text{C}(\text{CH}_3)_3$), 37.4, 30.4 (2- $\text{C}(\text{CH}_3)_3$). [^a Determined by $^{13}\text{C}, ^1\text{H}$ GHSQC. ^b Determined by $^{13}\text{C}, ^1\text{H}$ GHMBC].

$^{13}\text{C}, ^1\text{H}$ GHSQC (C_7D_8 , 151 / 600 MHz, 233 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 104.9 / 5.29 (Cp^{A}), 102.9 / 5.11 (Cp^{B}), 60.5 / 4.00 (1-CH), 32.8 / 1.08 (4- $\text{C}(\text{CH}_3)_3$), 30.4 / 1.05 (2- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}, ^1\text{H}$ GHMBC (C_7D_8 , 151 / 600 MHz, 213 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 166.3 / 1.08 (C4 / 4- $\text{C}(\text{CH}_3)_3$), 131.8 / 4.00 (C3 / 1-H), 120.1 / 4.00, 1.05 (C2 / 1-H, 2- $\text{C}(\text{CH}_3)_3$), 117.4 / 4.00 (ipso- C_6F_5 / 1-H), 115.8 / 4.00 (ipso- C_6F_5 / 1-H), 104.9 / 5.29 (Cp^{A}), 102.9 / 5.11 (Cp^{B}), 37.9 / 1.08 (4- $\text{C}(\text{CH}_3)_3$), 37.4 / 4.00, 1.05 (2- $\text{C}(\text{CH}_3)_3$ / 1-H, 2- $\text{C}(\text{CH}_3)_3$), 32.8 / 1.08 (4- $\text{C}(\text{CH}_3)_3$), 30.4 / 1.05 (2- $\text{C}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 564 MHz, 233 K, CFCl_3): δ -125.5 (2 F, o-F), -153.7 (1 F, p-F), -162.9 (2 F, m-F) ($\text{C}_6\text{F}_5^{\text{A}}$), -129.2 (2 F, o-F), -153.5 (1 F, p-F), -161.8 (2 F, m-F) ($\text{C}_6\text{F}_5^{\text{B}}$). $^{19}\text{F}, ^{19}\text{F}$ COSY (C_7D_8 , 564 MHz, 233 K, CFCl_3): $\delta^{19}\text{F} / \delta^{19}\text{F}$ -125.5 / -162.9 (o- F^{A} / m- F^{A}), -129.2 / -161.8 (o- F^{B} / m- F^{B}), -153.5 / -161.8 (p- F^{B} / m- F^{B}), -153.7 / -162.9 (p- F^{A} / m- F^{A}), -161.8 / -129.2, -153.5 (m- F^{B} / o- F^{B} , m- F^{B}), -162.9 / -125.5, -153.7 (m- F^{A} / o- F^{A} , m- F^{A}).

^1H NMR (C_7D_8 , 600 MHz, 298 K, TMS): δ 5.29 (broad, 5 H, Cp^{A}), 5.17 (s, 5 H, Cp^{B}), 3.73 (broad, 1 H, 1-H), 1.11 (s, 9 H, 4- $\text{C}(\text{CH}_3)_3$), 1.01 (s, 9 H, 2- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 151 MHz, 298 K, TMS): δ 105.3 (broad, Cp^{A}), 103.1 (Cp^{B}), 38.3, 33.1 (4- $\text{C}(\text{CH}_3)_3$), 37.5, 30.9 (broad) (2- $\text{C}(\text{CH}_3)_3$), n.o. (C4, C3, C2, C1, C_6F_5). $^{13}\text{C}, ^1\text{H}$ GHSQC (C_7D_8 , 151 / 600 MHz, 298 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 105.3 / 5.29 (Cp^{A}), 103.1 / 5.17 (Cp^{B}), n.o. / n.o (1-CH), 33.1 / 1.11 (4- $\text{C}(\text{CH}_3)_3$), 30.9 / 1.01 (2- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}, ^1\text{H}$ GHMBC (C_7D_8 , 151 / 600 MHz, 298 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 105.3 / 5.29 (Cp^{A}), 103.1 / 5.17 (Cp^{B}), 38.3 / 1.01 (4- $\text{C}(\text{CH}_3)_3$), 37.5 / 1.01 (2- $\text{C}(\text{CH}_3)_3$ / 2- $\text{C}(\text{CH}_3)_3$), 33.1 / 1.11 (4- $\text{C}(\text{CH}_3)_3$), 30.9 / 1.01 (2- $\text{C}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 564 MHz, 298 K, CFCl_3): δ -126.7 (2 F), -155.0 (1 F), -163.2 (2 F) (each broad, $\text{C}_6\text{F}_5^{\text{A}}$), -129.7 (2 F), -153.9 (broad, 1 F), -162.3 (broad, 2 F) ($\text{C}_6\text{F}_5^{\text{B}}$). $^{19}\text{F}, ^{19}\text{F}$ COSY (C_7D_8 , 564 MHz, 298 K, CFCl_3): $\delta^{19}\text{F} / \delta^{19}\text{F}$ -126.7 / -163.2 (o- F^{A} / m- F^{A}), -129.7 / -162.3 (o- F^{B} / m- F^{B}), -153.9 / -162.3 (p- F^{B} / m- F^{B}), -155.0 / -163.2 (p- F^{A} / m- F^{A}), -162.3 / -129.7, -153.9 (m-

$F^B / o-F^B, m-F^B$), -163.2 / -126.7, -155.0 ($m-F^A / o-F^A, m-F^A$). $^{11}B\{^1H\}$ NMR (C_7D_8 , 64 MHz, 300 K, $BF_3 \cdot OEt_2$): δ 48 ($\nu_{1/2} = 1000$ Hz).

$C_{34}H_{29}BF_{10}Hf$ (816.9): calcd. C 49.99, H 3.58; found C 48.94, H 3.51.

X-ray crystal structure analysis for **5b**: formula $C_{34}H_{29}BF_{10}Hf$, $M = 816.87$, orange crystal 0.35 x 0.30 x 0.10 mm, $a = 9.619(1)$, $b = 18.416(1)$, $c = 18.506(1)$ Å, $\alpha = 79.43(1)$, $\beta = 76.80(1)$, $\gamma = 80.25(1)^\circ$, $V = 3109.5(4)$ Å³, $\rho_{calc} = 1.745$ g cm⁻³, $\mu = 3.439$ mm⁻¹, empirical absorption correction ($0.379 \leq T \leq 0.725$), $Z = 4$, triclinic, space group $P1bar$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 33651 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 15092 independent ($R_{int} = 0.046$) and 11114 observed reflections [$I \geq 2 \sigma(I)$], 841 refined parameters, $R = 0.045$, $wR^2 = 0.100$, max. residual electron density 2.11 (-2.98) e Å⁻³, two almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

Bis(η^5 -cyclopentadienyl)-1-bis(pentafluorophenyl)boryl-2,4-bis(trimethylsilyl)-hafna-cyclopenta-2,3-diene. (5a anti/syn). Bis(η^5 -cyclopentadienyl)bis(trimethylsilylethynyl)-hafnium (200 mg, 0.397 mmol), and bis(pentafluorophenyl)borane (137.5 mg, 0.397 mmol), both prepared following established procedures, were weighed in an argon-filled glove-box and mixed into a Schlenk flask. Toluene (50 mL) was added and the resulting red solution was stirred at 60°C for 2 hours. After heating, the volatiles were removed under high vacuum. The obtained residue was washed with pentane (2×20 mL) and dried in vacuo to get **5a** as a red powder (273 mg, 81%). ^1H , ^{13}C and ^{29}Si NMR analyses indicated the presence of two isomers [**5a**(anti), **5a**(syn)] in a 2:1 ratio.

Major Isomer. ^1H NMR (C_7D_8 , 600 MHz, 233 K, TMS): δ 5.09 (s, 5 H, Cp^A), 4.93 (s, 5 H, Cp^B), 2.36 (broad, $^3J(^{29}Si, ^1H) = 8.7$ Hz, 1 H, 1-H), 0.09 (s, $^3J(^{29}Si, ^1H) = 6.7$ Hz, 9 H, 4-Si(CH₃)₃), -0.08 (s, $^3J(^{29}Si, ^1H) = 6.3$ Hz, 9 H, 2-Si(CH₃)₃). $^{13}C\{^1H\}$ NMR (C_7D_8 , 151

MHz, 233 K, TMS): δ 136.2 (C3), 118.8 (ipso- C_6F_5)^b, 116.9 (ipso- C_6F_5)^b, 114.4 (C4), 105.7 (Cp^B), 102.5 (broad, Cp^A), 93.7 (C2), 84.8 (C1)^a, 1.3 (4-Si(CH₃)₃), 0.5 (2-Si(CH₃)₃), n.o. (C_6F_5). [^a Determined by $^{13}C, ^1H$ GHSQC. ^b Determined by $^{13}C, ^1H$ GHMBC]. $^{13}C, ^1H$ GHSQC (C_7D_8 , 151 / 600 MHz, 233 K, TMS): $\delta^{13}C / \delta^1H$ 105.7 / 4.93 (Cp^B), 102.5 / 5.09 (Cp^A), 84.8 / 2.36 (1-CH). $^{13}C, ^1H$ GHMBC (C_7D_8 , 151 / 600 MHz, 233 K, TMS): $\delta^{13}C / \delta^1H$ 136.2, 118.8, 116.9 / 2.36 (C3, ipso- C_6F_5 , ipso- C_6F_5 / 1-H), 114.4 / 0.09 (C4 / 4-Si(CH₃)₃), 105.7 / 4.93 (Cp^B), 102.5 / 5.09 (Cp^A), 93.7 / 2.36, -0.08 (C2 / 1-H, 2-

Si(CH₃)₃), 84.8 / 2.36 (1-CH), 1.3 / 0.09 (4-Si(CH₃)₃), 0.5 / -0.08 (2-Si(CH₃)₃). ¹⁹F{¹H} NMR (C₇D₈, 564 MHz, 233 K, CFCl₃): δ -126.1, -127.1 (o-F), -155.4 (p-F), -161.7, -162.3 (m-F) (each m, each 1F, C₆F₅), -129.6 (2 F, o-F), -154.4 (1 F, p-F), n.o. (broad, m-F) (each m, C₆F₅). ²⁹Si{DEPT} NMR (C₇D₈, 100 MHz, 223 K, TMS): δ -3.2 (2-Si), -6.5 (4-Si). ²⁹Si,¹H GHMQC (C₇D₈, 100 / 500 MHz, 223 K, TMS): δ²⁹Si / δ¹H -3.2 / 2.36, -0.08 (2-Si / 1-H, 2-Si(CH₃)₃), -6.5 / 0.09 (4-Si / 4-Si(CH₃)₃).

Minor Isomer. ¹H NMR (C₇D₈, 600 MHz, 233 K, TMS): δ 5.31 (s, 5 H, Cp^A), 5.14 (s, 5H, Cp^B), 3.65 (broad, 1 H, 1-H), 0.23 (s, 9 H, 2-Si(CH₃)₃), 0.00 (s, ³J(²⁹Si,¹H) = 6.5 Hz, 9 H, 4-Si(CH₃)₃). ¹³C{¹H} NMR (C₇D₈, 151 MHz, 233 K, TMS): δ 141.5 (C3)^b, 127.1 (C4), 117.4 (ipso-C₆F₅)^b, 114.5 (ipso-C₆F₅)^b, 105.0 (Cp^A), 102.6 (Cp^B), 88.7 (C2), 66.1 (C1)^a, 1.1 (4-Si(CH₃)₃), -0.6 (2-Si(CH₃)₃). [^a Determined by ¹³C,¹H GHSQC. ^b Determined by ¹³C,¹H GHMBC]. ¹³C,¹H GHSQC (C₇D₈, 151 / 600 MHz, 233 K, TMS): δ¹³C / δ¹H 105.0 / 5.31 (Cp^A), 102.6 / 5.14 (Cp^B), 66.1 / 3.65 (1-CH). ¹³C,¹H GHMBC (C₇D₈, 151 / 600 MHz, 233 K, TMS): δ¹³C / δ¹H 141.5 / 3.65 (C3 / 1-H), 127.1 / 0.00 (C4 / 4-Si(CH₃)₃), 117.4, 114.5 / 3.65 (2 × ipso-C₆F₅ / 1-H), 105.0 / 5.31 (Cp^A), 102.6 / 5.14 (Cp^B), 88.7 / 0.23 (C2 / 2-Si(CH₃)₃), 1.1 / 0.00 (4-Si(CH₃)₃), -0.6 / 0.23 (2-Si(CH₃)₃). ¹⁹F{¹H} NMR (C₇D₈, 564 MHz, 233 K, CFCl₃): δ -123.4 (broad, o-F), -153.3 (1 F, p-F), -163.0 (2 F, m-F) (each m, C₆F₅), -127.7 (2 F, o-F), -154.1 (1 F, p-F), -162.3 (2 F, m-F) (each m, C₆F₅). ²⁹Si{DEPT} NMR (C₇D₈, 100 MHz, 223 K, TMS): δ 1.4 (2-Si), -6.8 (4-Si). ²⁹Si,¹H GHMQC (C₇D₈, 100 / 500 MHz, 223 K, TMS): δ²⁹Si / δ¹H 1.4 / 3.65, 0.23 (2-Si / 1-H, 2-Si(CH₃)₃), -6.8 / 0.00 (4-Si / 4-Si(CH₃)₃).

Additional data:

¹H NMR (C₇D₈, 600 MHz, 293 K, TMS): δ 5.28, 5.16, 5.04 (each broad, Cp), 3.60, 2.29 (each broad, 1-H), 0.07, -0.06 (each broad, Si(CH₃)₃). ¹H NMR (C₇D₈, 600 MHz, 363 K, TMS): δ 5.24, 5.23 (each s, Σ 10 H, Cp), 2.82 (broad, 1 H, 1-H), 0.10 (s, ³J(²⁹Si,¹H) = 6.6 Hz, 9 H, Si(CH₃)₃), 0.01 (s, ³J(²⁹Si,¹H) = 6.1 Hz, 9 H, Si(CH₃)₃).

¹¹B{¹H} NMR (C₇D₈, 64 MHz, 300 K, BF₃·OEt₂): δ 42 (ν_{1/2} = 1100 Hz).

¹⁹F{¹H} NMR (C₇D₈, 564 MHz, 358 K, CFCl₃): δ -125.7 (2 F, o), -155.6 (1 F, p), -163.0 (2 F, m) (each m, C₆F₅), -128.9 (2 F, o), -155.0 (1 F, p), -162.6 (2 F, m) (each m, C₆F₅). ¹⁹F,¹⁹F COSY (C₇D₈, 564 / 564 MHz, 358 K, CFCl₃): δ¹⁹F / δ¹⁹F -125.7 / -163.0 (o / m), -128.9 / -162.6 (o / m), -155.0 / -162.6 (p / m), -155.6 / -163.0 (p / m), -162.6 / -128.9, -155.0 (m / o, p), -163.0 / -125.7, -155.6 (m / o, p).

FT-IR (KBr, cm^{-1}): 2959, 2900, 1854, 1816, 1646, 1517, 1463, 1379, 1248, 1086, 1022, 984, 968, 840, 815, 755. MS-EI: m/z 850.4 (22%, $[\text{M}^+]$), 407.2 (9%, $[\text{Cp}_2\text{HfC}\equiv\text{CSi}(\text{CH}_3)_3]^+$), 329.2 (93%, $[\text{Cp}_2\text{Hf-F}^+]$), 310.7 (80%, $[\text{Cp}_2\text{Hf}^+]$). $\text{C}_{32}\text{H}_{29}\text{BF}_{10}\text{HfSi}_2$ (849.0): calcd. C 45.27, H 3.44; found C 44.41, H 3.48.

Crystals suitable for single-crystal X-ray diffraction were obtained at room temperature from addition of pentane to a concentrated toluene solution of the compound.

X-ray crystal structure analysis for **5a**: formula $\text{C}_{32}\text{H}_{29}\text{BF}_{10}\text{HfSi}_2$, $M = 849.03$, yellow-orange crystal $0.50 \times 0.15 \times 0.07$ mm, $a = 19.4148(2)$, $b = 9.8658(1)$, $c = 18.8991(2)$ Å, $\beta = 115.591(1)^\circ$, $V = 3264.86(6)$ Å³, $\rho_{\text{calc}} = 1.727$ g cm⁻³, $\mu = 3.348$ mm⁻¹, empirical absorption correction ($0.285 \leq T \leq 0.799$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, ω and ϕ scans, 20262 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 8106 independent ($R_{\text{int}} = 0.033$) and 6979 observed reflections [$I \geq 2\sigma(I)$], 422 refined parameters, $R = 0.031$, $wR^2 = 0.076$, max. residual electron density 0.85 (-1.18) e Å⁻³, hydrogen atoms calculated and refined as riding atoms.

{[Bis(η^5 -cyclopentadienyl)]-[1,5-trimethylsilyl-3-borata(bis(pentafluorophenyl))-pent-1-en-4-yn]-yl}-hafnium(IV) (9a). Bis(η^5 -cyclopentadienyl)bis(trimethylsilylethynyl)hafnium^[1] (20 mg, 0.040 mmol), and bis(pentafluorophenyl)borane^[2] (13.7 mg, 0.040 mmol), both prepared following established procedures, were weighed in an argon-filled glove-box and put into a NMR tube. They were dissolved by toluene- d_8 (*ca.* 0.8 mL) and the tube was sealed

under vacuum. NMR analysis showed the presence of compound **9a**, along with **5a**. After heating at 60 °C for 2 hours, compound **9a** disappeared, and only **5a** was visible. ¹H NMR (C_7D_8 , 600 MHz, 233 K, TMS): δ 7.45 (broad, 1 H, 2-H), 5.42 (s, 10 H, Cp), 0.29 (s, 9 H, 1-Si(CH₃)₃), 0.07 (s, 9 H, 5-Si(CH₃)₃). ¹³C{¹H} NMR (C_7D_8 , 151

MHz, 233 K, TMS): δ 201.5 (C1), 109.8 (Cp), 109.5 (broad, C2), 105.2 (C5), 0.7 (1-Si(CH₃)₃), -0.5 (5-Si(CH₃)₃), n.o. (C4, C₆F₅). ¹³C, ¹H GHSQC (C_7D_8 , 151 / 600 MHz, 233 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 109.8 / 5.42 (Cp), 109.5 / 7.45 (2-H). ¹³C, ¹H GHMBC (C_7D_8 , 151 / 600 MHz, 233 K, TMS): $\delta^{13}\text{C} / \delta^1\text{H}$ 201.5 / 7.45, 0.29 (C1 / 2-H, 1-Si(CH₃)₃), 109.8 / 5.42 (Cp), 105.2 / 0.07 (C5 / 5-Si(CH₃)₃), 0.7 / 0.29 (1-Si(CH₃)₃), -0.5 / 0.07 (5-Si(CH₃)₃). ²⁹Si{DEPT} NMR (C_7D_8 , 100 MHz, 223 K, TMS): δ -0.9 (1-Si), -8.6 (5-Si). ²⁹Si, ¹H GHMQC (C_7D_8 , 100 / 500 MHz, 223 K, TMS): $\delta^{29}\text{Si} / \delta^1\text{H}$ -0.9 / 0.29 (1-Si / 1-Si(CH₃)₃), -8.6 / 0.07 (5-Si / 5-Si(CH₃)₃). ¹¹B{¹H} NMR (C_7D_8 , 64 MHz, 300 K, BF₃·OEt₂): δ -24. ¹⁹F{¹H} NMR (C_7D_8 , 564

MHz, 233 K, CFCl_3): δ -134.4 (m, 4 F, o-F), -158.2 (t, $^3J_{\text{p,m}} = 19$ Hz, 2 F, p-F), -163.7 (m, 4 F, m-F).

Kinetic Study by NMR (600 MHz Varian UnityPlus spectrometer)

Basic equations:

Formation of the product: $I = A_1 \exp(-t/\tau) + A_3$

$$[P]_t = [P]_0 \exp(-k_{\text{obs}} t)$$

$$-t/\tau = -k_{\text{obs}} t$$

$$k_{\text{obs}} = 1/\tau$$

$$\Delta G^\ddagger = -R T \ln((k_{\text{obs}} h)/(k_b T))$$

$$R = 8.31451 \text{ (m}^2 \cdot \text{kg)/(s}^2 \cdot \text{K} \cdot \text{mol)}$$

$$k_b = 1.380658 \cdot 10^{-23} \text{ J/K}$$

$$h = 6.6260755 \cdot 10^{-34} \text{ J s}$$

Consumption of the starting material: $I = -A_1 \exp(-t/\tau) + A_3 - A_1$

Kinetic experiments:

9a was generated in situ by mixing **6a** and $\text{HB}(\text{C}_6\text{F}_5)_2$. The reaction mixture was dissolved in toluene- d_8 [with a defined amount of ferrocene (as an inert, internal standard)] at room temperature. Directly, after careful mixing of the solution, the NMR tube was injected into the spectrometer which was heated to 40°C. The rearrangement of **9a** to **5a** was monitored by ^1H NMR.

Observation of decreasing of $\delta^1\text{H}$ (**9a**) = 5.46 (10H, Cp; series A + B), 0.22 (9H, SiMe_3 , series B), 0.14 (9H, SiMe_3 , series B).

Observation of increasing of $\delta^1\text{H}$ (**5a**) = 5.18 (10H, Cp, series A + B), 0.08 (9H, SiMe_3 , series B).

Series A: 313 K (**6a**: 31.7 mg (63.00 mmol); $\text{HB}(\text{C}_6\text{F}_5)_2$: 21.6 mg (62.44 mmol); ferrocene: 4.85 mg (26.07 mmol); in 0.8 ml toluene- d_8)

Series B: 313 K (**6a**: 27.5 mg (54.66 mmol); $\text{HB}(\text{C}_6\text{F}_5)_2$: 18.8 mg (54.35 mmol); ferrocene: 1.21 mg (6.50 mmol); in 0.5 ml toluene- d_8)

	series A	series B
$\tau(5.46)$	3112	3007
$k_{\text{obs}}(5.46)$	$3.2134 \cdot 10^{-4}$	$3.3256 \cdot 10^{-4}$
$\Delta G_{\text{chem}}^\ddagger(5.46)$	23.5	23.5
$\tau(0.22)$	---	3170
$k_{\text{obs}}(0.22)$		$3.1546 \cdot 10^{-4}$
$\Delta G_{\text{chem}}^\ddagger(0.22)$		23.5
$\tau(0.14)$	---	3030
$k_{\text{obs}}(0.14)$		$3.3003 \cdot 10^{-4}$
$\Delta G_{\text{chem}}^\ddagger(0.14)$		23.4
$\tau(5.18)$	3293	3212
$k_{\text{obs}}(5.18)$	$3.0367 \cdot 10^{-4}$	$3.1133 \cdot 10^{-4}$
$\Delta G_{\text{chem}}^\ddagger(5.18)$	23.5	23.5
$\tau(0.08)$	---	3093
$k_{\text{obs}}(0.08)$		$3.2331 \cdot 10^{-4}$
$\Delta G_{\text{chem}}^\ddagger(0.08)$		23.4

lineshape analysis

Experimental and simulated 600 MHz ¹H NMR spectra in toluene-d₈

lineshape analyse of **5a(anti)** / **5a(syn)** in toluene

T1/T2	T [K]	site 1		site 2		Int 1	Int 2	k(1,2) [s ⁻¹]	K = Int2/Int1	k(2,1) [s ⁻¹]	G ₁₂ [#] [kJ/mol]	G ₂₁ [#] [kJ/mol]	G ⁰ [kJ/mol]	1/T	ln(k(1,2)/T)	ln(k(2,1)/T)
0,2	353	83	-30	16	100	0,680	0,320	25000	0,471	53125	57,23	55,02	2,21	2,83E-03	4,26	5,01
0,2	343	81	-30	16	100	0,680	0,320	10000	0,471	21250	58,14	55,99	2,15	2,92E-03	3,37	4,13
0,2	333	78	-30	16	100	0,680	0,320	5000	0,471	10625	58,28	56,20	2,09	3,00E-03	2,71	3,46
0,2	323	78	-30	16	100	0,680	0,320	2500	0,471	5313	58,31	56,29	2,02	3,10E-03	2,05	2,80
0,2	313	73	-30	16	100	0,680	0,320	1000	0,471	2125	58,81	56,85	1,96	3,19E-03	1,16	1,92
0,2	303	70	-30	16	100	0,680	0,320	400	0,471	850	59,16	57,26	1,90	3,30E-03	0,28	1,03
0,2	293	67	-43	16	107	0,680	0,320	150	0,471	319	59,51	57,68	1,84	3,41E-03	-0,67	0,08
0,2	283	67	-43	16	114	0,680	0,320	50	0,471	106	59,99	58,21	1,77	3,53E-03	-1,73	-0,98
0,2	273	67	-43	14	121	0,680	0,320	18	0,471	38	60,10	58,39	1,71	3,66E-03	-2,72	-1,97
0,2	263	66	-43	12	128	0,680	0,320	7	0,471	15	59,89	58,24	1,65	3,80E-03	-3,63	-2,87
0,2	253	65	-42	10	134	0,680	0,320	3	0,471	6	59,31	57,72	1,59	3,95E-03	-4,43	-3,68
0,2	243	65	-42	10	141	0,680	0,320	2	0,471	4	57,70	56,18	1,52	4,12E-03	-4,80	-4,05

Konstanten 8,31441

1,38E-23

4.184

6,63E-34

$$\Delta G^\ddagger = RT \cdot \left[23,76 - \ln\left(\frac{k}{T}\right) \right]$$

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \left(23,76 + \frac{\Delta S^\ddagger}{R} \right)$$

$$\Delta H^\ddagger = -R \cdot \text{Steigung}$$

$$\Delta S^\ddagger = (\text{Achsenabschnitt} - 23,76) \cdot R$$

$\Delta G_{273K}^\ddagger$	60,1	kJ/mol
$\Delta H^\ddagger$	64,9	kJ/mol
$\Delta S^\ddagger$	19,4	J/mol/K

Steigung -7808,4
Achsenab. 26,089

DFT Calculations

The computed structure is in excellent agreement with that from the X-ray analysis. The largest deviation is 2 pm for the C1-C2 distance while most other bond lengths agree to within 1 pm. Also the bending angle C2-C3-C4 of the 'allene' unit and the dihedral angle C1-C2-C4-Hf agree surprisingly well. The only notable difference is the relative orientation of the Cp rings which is staggered in the computation while found to be eclipsed experimentally.

Population analysis of the wavefunction reveals an interesting electronic structure of the complex that can be regarded as a mixture of a coordinated (distorted) allene and a butenyne but also features interactions that seem to be unique for this structure. For comparison we also discuss corresponding data for the model compound 1,3-dimethyl-1,2-hexadiene ('6-ring allene') and butenyne as the other extreme.

Table 1. Comparison of computed^[a] and experimental structural parameters of complex **5b(anti)** (R = -CMe₃).^[b,c]

	5b(calcd.)	exptl.	2b	10
B-C1	150.5	149.7		
C1-C2	146.1	148.1		134.5
C2-C3	136.1	135.1	133.2	141.9
C3-C4	130.0	130.2	133.2	121.6
C1-Hf	253.0	253.6		
C2-Hf	256.5	256.5		
C3-Hf	233.0	232.5		
C4-Hf	231.0	230.1		
C(Cp)-H	252-256	250-255		
C2-C3-C4	155.2	155.4		
C1-C2...C4-Hf	-39.1	-39.5		

[a] PBE-D/TZVPP', bond length in pm, angles in deg). [b] Reference data correspond to calculated structures of compound **2b** (R = CH₃, see Scheme 1) and butenyne (**10**). [c] Dihedral angle C6-C1...C3-C4.

Figure 1: Structure of the core of complex **5b**(anti) with Wiberg bond orders (PBE-D/TZVPP') level

The Wiberg bond orders (BO) (see Figure 1) that are roughly expected to be one to three for single, double and triple-bonds, respectively, are shown for the core of the complex in Fig. 1. The values between C2-C3 and C3-C4 are 1.51 and 1.81, respectively, which is closer to two double bonds as in our model allene (where both values are 1.92) than for a single and a triple bond. These values are also in accordance with the computed and experimental bond lengths of 135-136 and 130 pm. A butenyne structure has notably different bond lengths of 135, 142 and 122 pm for the formal double, single and triple bonds, respectively. The small bond order of 1.12 between C1-C2 and the multiple bond character of the B-C1 interaction (BO=1.46) further support this interpretation. The covalent bonding interactions between Hf and the carbons C1, C3 and C4 are relatively strong and similar to those between Hf and the Cp-rings. These values and the small interaction for the Hf and C2 atoms point to an interpretation in terms of a cyclic metalla-allene-type structure. The bending angle C2-C3-C4 deviates much less from linearity (about 25 degree) than for our model allene. The allene-type torsion angle (C1-C2-C4-Hf) is about 39 degree, which is almost in between the values of 90 degree for an un-distorted allene and zero degree which can be expected for a butenyne unit. A further intriguing aspect is the relatively large BO of 0.13 between the boron and Hf atoms despite their large spatial distance of 327 pm. This is a result of a 2e-3c-bonding contribution B-C1-Hf which is obvious from an average spread-out value over atomic centers of 2.51 as obtained when the canonical molecular orbitals are localized.

This view of the electronic structure as a metalla-cyclo-allene is clearly supported by the results of a natural bond orbital (NBO) population analysis (see Table 2). Strongly occupied localized 2c-2e NBO of sigma and π type are found between C2-C3 and C3-C4 as expected for an allene substructure. No third NBO between C3-C4 as required for a triply bonded structure is observed. The distortion and special bonding situation of the allene moiety is indicated by the relatively large population of the C2-C3 π^* NBO and a localized π NBO at the boron center. Furthermore, the C1-C2 and B-C1 interactions are well characterized as single bonds. Covalent interactions in a Lewis sense between the Hf and carbon atoms are only found for C1 and C4 as required for a ring structure although it is noted, that these bonds are rather polar with about 80 % population at the carbon atoms.

Table 2. Results of a natural bond orbital (NBO) population analysis for the core of complex **5b(anti)**.^[a]

NBO	population	character
C3–C4	1.951	σ , sp-sp ^{2,3}
C3–C4	1.847	π
C2–C3	1.950	σ , sp ^{2,3} -sp
C2–C3	1.755	π
C2–C3	0.345	π^*
B	0.445	p, lone-pair
C1–C2	1.939	σ , sp ^{2,3} -sp ^{1,9}
B–C1	1.925	σ , sp ^{1,5} -sp ^{1,7}
Hf–C1	1.529	σ , (81% C1), d-p
Hf–C4	1.716	σ , (77% C4), d-sp ^{2,7}

[a]: PBE-D/TZVPP'

Theoretical Methods and Technical Details of the Computations

The quantum chemical DFT calculations have been performed with slightly modified versions of the TURBOMOLE suite of programs.^[1] As Gaussian AO basis, large triple-zeta (denoted as TZVPP') sets of Ahlrichs et al.^[2] have been employed. In standard notation these are [5s3p1d] for B, C and F and [3s1p] for H. The four atoms that belong to the allene unit are described by a larger [5s3p2p1f] (TZVPP) AO basis to improve the quality in the most important part of the molecule. For the hafnium atom, the basis set is of comparable quality (i.e., [6s3p3d1f]) and we employ a scalar relativistic pseudo-potentials^[3] for the 60 core electrons. All geometries have been fully optimized at the DFT level using the PBE density functional^[4] that also includes an empirical correction for intra-molecular dispersion (also called van der Waals) interactions^[5] (dubbed PBE-D in the following). For a detailed description of this dispersion correction, that is of great importance in studies of large molecules, including many illustrative examples see Ref. [6], for the most recent chemical applications of this method see Ref [7]. In all DFT treatments, the RI-approximation has been used^[8] for the Coulomb integrals which speeds the computations up significantly without any significant loss of accuracy. For the population analysis we use the NBO 4.0 program of Weinhold et al.^[9]

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