Metallacycloallenes

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

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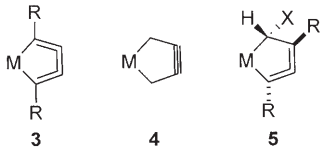
Dedicated to Professor Emanuel Vogel on the occasion of his 80th birthday

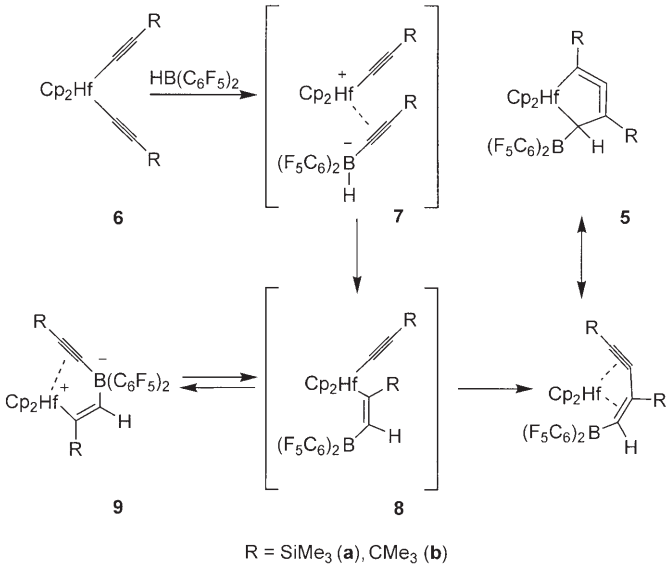
Incorporation of allenic moieties into small rings leads to unfavorable bending and planarizing distortions. The resulting strain has precluded the direct observation of 1,2-cyclopentadiene (**1**) or 1,2-cyclohexadiene (**2**) to date. Information about such highly strained cyclic allenes was derived from trapping reactions and quantum chemical calculations.[1–3] The cycloallenes **1** and **2** are chiral, with calculated enantiomerization barriers of less than 1–5 (**1**) and 14–18 kcal mol^{-1} (**2**).[1,4,5]

In view of the known tendency of Group 4 metallocene units to strongly stabilize bent cumulenes **3**[6] or even nonlinear alkynes **4**[7] in metallacyclic ring structures, it was tempting to synthesize such a metallacyclic five-membered cycloallene-type compound (**5**, Scheme 1). The preparation and characterization of first examples of this type of compound are described herein.



Scheme 1. Metallacyclocumulene (**3**), metallacyclopentyne (**4**), and the novel metallacycloallene (**5**).

$[Cp_2Hf(C{\equiv}CSiMe_3)_2]$ (**6a**, Scheme 2, $Cp = C_5H_5$) was obtained from the reaction of $[Cp_2HfCl_2]$ with $LiC{\equiv}CSiMe_3$. Treatment of **6a** with $HB(C_6F_5)_2$[8] initiated a reaction sequence through a 1,1-hydroboration.[9] This reaction is probably initiated by alkynyl abstraction (leading to **7a**) and subsequent C–H and C–Hf σ-bond formation to give the reactive intermediate **8a**. This species may then undergo reductive coupling to yield **5a** directly.



Scheme 2. Formation pathway of complexes **5**.

The reactive intermediates **7a** and **8a** were not directly observed, but we have found a sizable admixture of the typical follow-up product **9a** under kinetic control. (^{1}H NMR spectroscopy (233 K) $\delta = 7.45$ (=CH[B]), 5.42 (s, 10 H, Cp), 0.29, 0.07 ppm ($2 \times SiMe_3$); ^{13}C NMR (233 K) $\delta = 105.2$ (=C[Si]), 109.5 (=CH[B]), 201.5 ppm (=C[Hf]); ^{19}F NMR (233 K): $\delta = -134.4$ (*o*-F), −158.2 (*p*-F), −163.7 ppm (*m*-F); ^{11}B NMR: $\delta = -24$ ppm). Warming resulted in rapid conversion of **9a** ultimately to **5a** in a first-order reaction (**9a**→**5a** $\Delta G^{\neq} = 23.5 \pm 0.1$ kcal mol^{-1} at 313 K). The reaction of $[Cp_2Hf(C{\equiv}CtBu)_2]$ (**6b**) with $HB(C_6F_5)_2$ proceeded analogously to give **5b** (60 °C, 2 h). Single crystals suited for X-ray crystal structure analysis were obtained from both **5a** and **5b** (pentane/toluene).[10]

The structure of **5a** (Figure 1) features a metallacyclic five-membered ring system with all four carbon atoms in bonding distance to hafnium[10] (Hf–C1: 2.494(3) Å, Hf–C2: 2.513(3) Å, Hf–C3: 2.314(3) Å, Hf–C4: 2.340(3) Å).[11] The C4–C3 bond is short, at 1.276(4) Å. The C3–C2 bond is longer (1.356(4) Å), and the C1–C2 bond is in the C–C σ-bond range (1.490(4) Å). Carbon atom C1 features typical bond angles of a saturated carbon atom in a five-membered ring (B1-C1-C2: 129.5(3)°, B1-C1-Hf: 109.2(2)°, C2-C1-Hf: 73.4(2)°). Carbon

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Supporting information for this article (details of the synthesis, spectroscopic and structural characterization of **5a** and **5b**, and details of the quantum chemical calculations and references) is available on the WWW under http://www.angewandte.org or from the author.

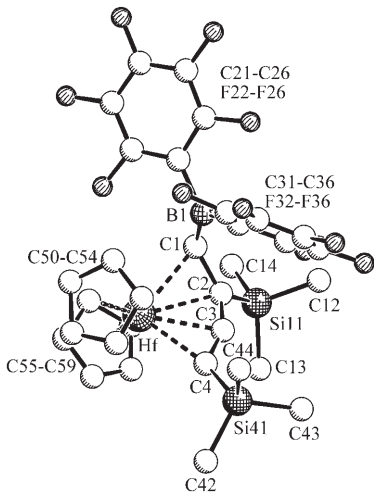


Figure 1. Molecular structure of complex **5a** (hydrogen atoms omitted for clarity).

atom C2 is planar tricoordinate (sum of the bonding angles: 359.8(3)°). The bonding angles at carbon atom C4 are 129.6(3)° (C3-C4-Si41), 73.0(2)° (C3-C4-Hf), and 150.3(2)° (Si41-C4-Hf). The system is markedly bent at carbon atom C3 (C2-C3-C4: 156.4(3)°). The central unsaturated C_3 system features a typical allenoic distortion of its substituents from planarity (dihedral angles Si41-C4···C2-Si11: 74.4°, C1-C2···C4-Hf: 43.5°). Complex **5b** shows similar structural data (see Figure 2, Table 1, and the Supporting Information).

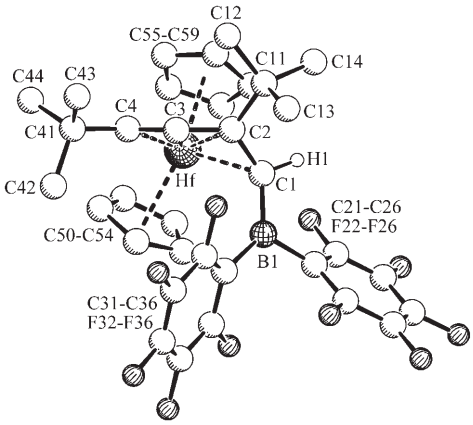


Figure 2. Molecular structure of complex **5b** (hydrogen atoms omitted for clarity, except H1).

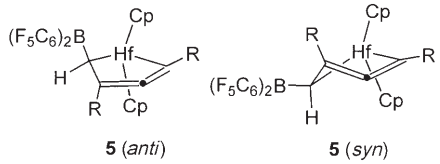
The nonplanar structure of **5a**,**b** contains a chiral center (C1) and a chiral axis. Therefore, each of the compounds **5a**,**b** should exist as a mixture of two diastereoisomers, characterized by a *syn* or *anti* relationship of the bulky $B(C_6F_5)_2$ substituent at C1 with the $SiMe_3$ (or CMe_3) group at C2. This situation was found experimentally for **5a**, which shows dynamic NMR spectra. At 363 K (600 MHz, C_7D_8) we observed only an averaged set of signals in the ^{1}H NMR spectrum. Lowering the temperature led to decoalescence (for details, see the Supporting Information), and eventually

Table 1: Comparison of computed[a] and experimental structural parameters of complex **5b**(*anti*) (R = CMe_3).[b]

	5b (calcd)	**5b** (exptl)[c]	**2b**	**10**
B–C1	150.5	149.5		
C1–C2	146.1	147.7		134.5
C2–C3	136.1	135.7	133.2	141.9
C3–C4	130.0	129.6	133.2	121.6
C1–Hf	253.0	253.6		
C2–Hf	256.5	256.0		
C3–Hf	233.0	231.8		
C4–Hf	231.0	229.5		
C(Cp)–Hf	252–256	248–255		
C2-C3-C4	155.2	155.5		
C1-C2···C4-Hf	−39.1	−39.1		

[a] PBE-D/TZVPP′, bond length in pm, angles in deg. [b] Data from the calculated structures of 1,3-dimethyl-1,2-cyclohexadiene (**2b**) and butenyne (**10**) are given for comparison. [c] Average values from two independent molecules.

to the observation of separate sets of resonances for the two diastereoisomers **5a**(*anti*) and **5a**(*syn*) in an approximately 2:1 ratio. From a line-shape analysis, a Gibbs activation energy of $\Delta G^{\ddagger}_{dia} = 14.4 \pm 0.3$ kcal mol^{-1} (273 K) was calculated for the ring-flip inversion process of the chiral cycloallene structural element in complex **5a** (Scheme 3). The major



Scheme 3. *anti* and *syn* diastereoisomers of complex **5**.

diastereomer features signals in the ^{1}H NMR spectrum at δ = 5.09, 4.93 (each s, each 5 H, Cp), and 2.36 ppm ([B]CH) and of the allenoic unit in the ^{13}C NMR spectrum at δ = 93.7 (=C[Si]), 136.2 (=C=), and 114.4 ppm (=C[Hf]). The corresponding signals of the minor diastereoisomer occur at δ = 5.31, 5.14 (^{1}H, Cp), 3.65 (^{1}H, [B]CH), 88.7 (=C[Si]), 141.5 (=C=), and 127.1 ppm (=C[Hf]), respectively (both at 233 K, 600/151 MHz, C_7D_8).

The special bonding features of **5** were analyzed by DFT calculations.[12] This approach will be exemplified by the calculations on the bis(*tert*-butyl)-substituted complexes **5b**. The DFT calculations identify two minima separated by 3.2 kcal mol^{-1}, which correspond to the diastereoisomers **5b**(*anti*) and **5b**(*syn*). The computed structure of the global minimum (Figure 3) is in excellent agreement with the X-ray crystal structure (Table 1), including the characteristic bending of the C2-C3-C4 unit and the typical C1-C2···C4-Hf dihedral angle.

The Wiberg bond orders (BO), which are expected to be 1–3 for single, double, and triple bonds, were calculated as being close to C–C double bonds for both C2–C3 (1.51) and C3–C4 (1.81; Figure 3). The small bond order of 1.12 for C1–C2 supports the interpretation of the cycloallene character of **5b**(*anti*), which is also in agreement with the computed bond

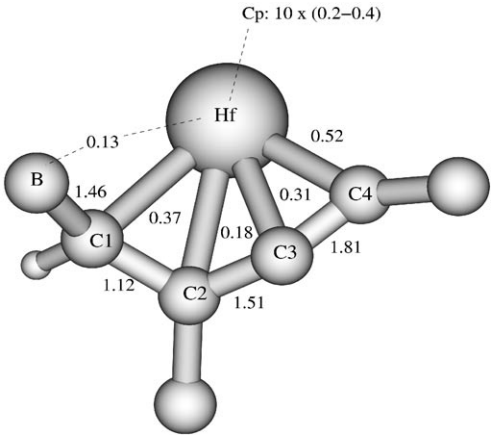


Figure 3. Calculated structure of the core of complex **5b**(*anti*) with Wiberg bond orders (PBE-D/TZVPP′ level).

lengths of **5b** and the reference data for **2** and **10** (Table 1). We also note some multiple-bond character of the B–C1 interaction (BO = 1.46). A natural bond orbital (NBO) population analysis (Table 2) features strongly occupied

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
C3–C4	1.847	π
C2–C3	1.950	σ, sp^2-sp
C2–C3	1.755	π
C2–C3	0.345	π*
B	0.445	p, lone pair
C1–C2	1.939	σ, sp^2-sp^2
B–C1	1.925	σ, sp$^{1.5}$-sp^2
Hf–C1	1.529	σ, (81% C1), d-p
Hf–C4	1.716	σ, (77% C4), d-sp^3

[a] PBE-D/TZVPP′.

localized two-center-two-electron NBOs of σ and π type for C2–C3 and C3–C4, as expected for an allene substructure. No third NBO for C3–C4, as required for a triply bonded structure, is observed. Covalent interactions in a Lewis sense between the Hf center and carbon atoms are only found for C1 and C4, although these bonds are rather polar, with about 80% population at the carbon atoms (Table 2).

This combination of experimental and computational work has shown that unique five-membered metallacyclic allenoid compounds (**5**) are readily available by a short synthetic route involving 1,1-hydroboration of a metal alkynyl complex and subsequent C–C coupling. Detailed inspection of the experimentally determined molecular geometry and the population analysis of the Kohn–Sham wave function have revealed an interesting electronic structure that can be regarded as a mixture of a distorted allene and a coordinated substituted butenyne, but it also features interactions that seem to be unique for this general type of compound.[13] These findings indicate a powerful influence of the Group 4 bent metallocene unit to internally stabilize very strained organic π systems, such as bent allene-type structures, in a unique way to yield remarkably stable isolable derivatives.

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[10] X-ray crystal structure analysis for **5a**: $C_{32}H_{29}BF_{10}HfSi_2$, $M=849.03$, yellow-orange crystal $0.50\times0.15\times0.07$ mm, monoclinic, space group $P2_1/c$ (No. 14), $a=19.4148(2)$, $b=9.8658(1)$, $c=18.8991(2)$ Å, $\beta=115.591(1)°$, $V=3264.86(6)$ Å^3, $Z=4$, $\rho_{calcd}=1.727$ g cm^{-3}, $\mu=3.348$ mm^{-1}, empirical absorption correction ($0.285\le T\le0.799$), $\lambda=0.71073$ 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 ($R_{int}=0.033$) and 6979 observed reflections [$I\ge2\sigma(I)$], 422 refined parameters, $R=0.031$, $wR^2=0.076$, max (min) residual electron density 0.85 (−1.18) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. X-ray crystal structure analysis for **5b**: $C_{34}H_{29}BF_{10}Hf$, $M=816.87$, orange crystal $0.35\times0.30\times0.10$ mm, triclinic, space group $P\bar{1}$ (No. 2), $a=9.619(1)$, $b=18.416(1)$, $c=18.506(1)$ Å, $\alpha=79.43(1)$, $\beta=76.80(1)$, $\gamma=80.25(1)°$, $V=3109.5(4)$ Å^3, $Z=4$, $\rho_{calcd}=1.745$ g cm^{-3}, $\mu=3.439$ mm^{-1}, empirical absorption correction ($0.379\le T\le0.725$), $\lambda=0.71073$ 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 [$I\ge2\sigma(I)$], 841 refined parameters, $R=0.045$, $wR^2=0.100$, max (min) 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. 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 Enzymol.* **1997**, *276*, 307–326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr. Sect. A* **2003**, *59*, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**). CCDC-664142 (**5b**) and 664143 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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