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Synthesis of Hafnacyclopentanes from Hafnocene Alkyne Complexes: Influence of Styrene Substituents on the C–C Coupling Regioselectivity

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The alkyne complex *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1**) [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] reacts with styrene and *p*-(trifluoromethyl)styrene to give hafnacyclopentanes **2** and **3**, respectively. C–C coupling proceeds in different ways: whereas for complex **2** a hafnacyclopentane with substituents in the α,β-position is formed, in the latter case only α,α coupling was observed. Complexes **2** and **3** can be activated with B(C$_6$F$_5$)$_3$ to form active catalysts for the polymerization of ethylene.

Introduction

Titanocene and zirconocene alkyne complexes of the type Cp′$_2$M(L)(η^2-Me$_3$SiC$_2$SiMe$_3$) (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl; M = Ti, no L; M = Zr, L = thf, pyridine, acetone) are versatile starting materials for the generation of the unstable and highly reactive metallocenes "Cp′$_2$M". The application of these complexes in stoichiometric and catalytic reactions such as polymerizations or the formation of metallacycles has been reviewed extensively in the last years.[1]

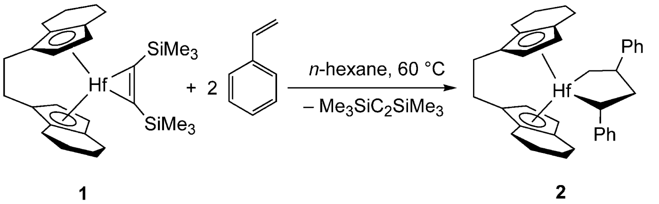
Recently, the first hafnocene alkyne complexes were synthesized, and the structural features and the reactivity of these compounds have been compared to similar titanium and zirconium complexes.[2] Moreover, some unprecedented Si–C and C–H bond-activation processes have been observed, which show the high potential of hafnocene in catalytic and stoichiometric reactions.[3,4] However, until very recently such hafnocene alkyne complexes were not found to generate "free" hafnocene. In our group, the complex *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1**) was treated with ethylene; in a two-step reaction the hafnacyclopentane *rac*-(ebthi)Hf(–CH$_2$–CH$_2$–CH$_2$–CH$_2$–) was formed via the hafnacyclopentene *rac*-(ebthi)Hf[(Me$_3$Si)C=C(SiMe$_3$)–CH$_2$–CH$_2$].[5]

Coupling reactions to give saturated metallacycles have also been observed before for zirconium compounds: the alkyne complexes Cp′$_2$Zr(L)(η^2-Me$_3$SiC$_2$SiMe$_3$) [Cp′$_2$ = *rac*-(ebthi), no L; Cp′$_2$ = Cp$_2$, L = thf] are able to couple ethylene and substituted olefins like norbornadiene[6a] or styrene[6b] to give zirconacyclopentanes. Because coupling of propene should result in the formation of a "hidden" (i.e., metal-bound) hexene, this reaction could be of interest in petrochemical-based applications. However, with propene no uniform reaction product was found.[6b] These C–C coupling reactions are an attractive tool for the functionalization of olefins. Moreover, they play an important role in olefin oligomerization; for example, metallacyclopentanes are believed to be a key intermediate in the formation of LAOs (linear alpha olefins; e.g., 1-hexene and 1-octene) from ethylene.[7]

In this communication we report on the synthesis of substituted hafnacyclopentanes from *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1**) with styrene and *p*-(trifluoromethyl)styrene, respectively.

Results and Discussion

In the reaction of the hafnocene alkyne complex **1** with styrene, the Ph-substituted hafnacyclopentane **2** is formed (Scheme 1). The compound precipitates from a warm *n*-hexane reaction mixture as a yellow crystalline solid (62% isolated yield, slow decomposition at 209 °C).



Scheme 1. α,β-Coupling of styrene to give hafnacyclopentane **2**.

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The molecular structure of this complex is depicted in Figure 1 and proves the structural motif of an α,β-substituted hafnacyclopentane. However, a detailed discussion of the bond lengths in the five-membered ring is not possible due to a disorder in the metallacycle. In the case of the similar ebthi-substituted zirconacyclopentane[6b] and in **2** the Ph rings are located in the α- and β-position, which is favoured electronically and sterically. For other zirconium complexes Negishi and coworkers described the possibility of a benzylic or agostic interaction of the substituent in the α-position.[8] The substituent in the β-position avoids steric hindrance by interaction with the ebthi ligand.[9]

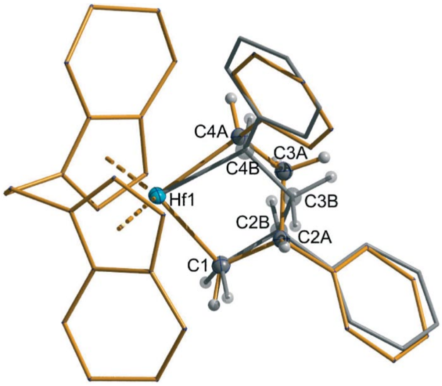
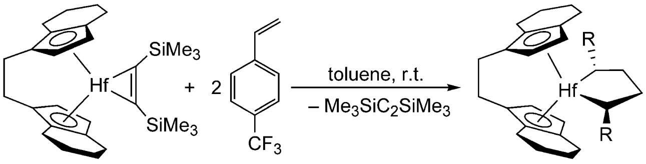


Figure 1. Molecular structure of complex **2**. Hydrogen atoms (except at C1, C2, C3 and C4) are omitted for clarity. The thermal ellipsoids correspond to 30% probability (atoms with lower occupancy are shown in grey).

In the solid state for complex **2** two species (ratio 0.64:0.36) with various configurations at C2 in comparison to the orientation of the Ph ring at C4 were observed (Figure 1). In both compounds, the styrene molecules possess a head-to-tail-connection, resulting in a metallacycle with the constitution Hf–CHPh–CH_2–CHPh–CH_2. This was also shown by NMR spectroscopic experiments; the same behaviour is assumed for the analogous zirconium complex.[6b]

Surprisingly, in a similar reaction of complex **1** with *p*-CF_3-styrene a different coupling mode is observed. Instead of an α,β orientation of the aryl groups, both substituents are in the α-position to the metal center (Scheme 2), resulting in a C_2 symmetry in solution. Hafnacyclopentane **3** crystallizes as yellow prisms (46% isolated yield), which slowly decompose at temperatures above 238 °C.



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3, R = *p*-CF_3Ph

Scheme 2. α,α-Coupling of *p*-CF_3-styrene to give hafnacyclopentane **3**.

Figure 2 shows the molecular structure of complex **3**. Both *p*-$CF_3C_6H_4$ substituents are located in the α-position to the metal center. Moreover, it becomes clear from the graphical representation that both rings are *trans* orientated to each other to minimize steric interactions among each other and with the ebthi ligand, respectively. Bond lengths in the hafnacyclopentane are as expected [C1–C2 1.541(5), C2–C3 1.524(5), C3–C4 1.542(5) Å].

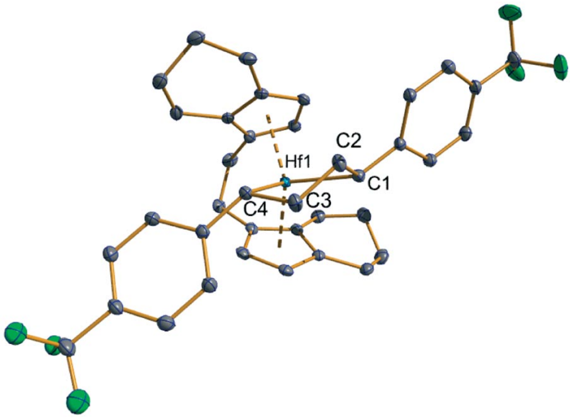


Figure 2. Molecular structure of complex **3**. Hydrogen atoms and two positions of the disordered fluorine atoms of the CF_3 group are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

In solution for complex **3** only one species is present. This may be due to the stabilizing electron-withdrawing effect of the CF_3 groups in the *para* position, leading to an enhancement in the partial negative charge at the olefinic carbon atom in the α-position to the aryl ring. This may also be the reason for the exclusive formation of a metallacycle with substituents in the α-position, probably the electronic effects superimpose the steric effects. Relative to the signal for the Cβ atom the ^{13}C NMR signal for the Cα atom of the five-membered metallacycle is shifted downfield significantly (Cα: 63.2, Cβ: 23.3 ppm) due to the deshielding influence of the metal center. As a result of the low solubility of **3**, no ^{13}C NMR signal was found for the CF_3 group, but a ^{19}F signal was located at –61.7 ppm.

Reaction of complexes **2** and **3** with $B(C_6F_5)_3$ results in the formation of active systems for the polymerization of ethylene (T = 40 °C; activity of **2**: 271 kg polymer $mol^{-1} h^{-1} bar^{-1}$; activity of **3**: only trace amounts of PE were isolated). Most likely the five-membered ring of **2** is opened by interaction with the Lewis acid similarly as found in other metallacycles[10] under generation of a zwitterionic species, which should consist of a hafnocenium centre and a boranate unit linked by the C_4 chain of the former substituted metallacyclopentane [*rac*-(ebthi)Hf]$^+$[–CHPh–CH_2–CHPh–CH_2–$B(C_6F_5)_3$]$^-$ or [*rac*-(ebthi)Hf]$^+$[–CH_2–CHPh–CH_2–CHPh–$B(C_6F_5)_3$]$^-$. However, it was not possible to isolate the assumed active species.

Conclusions

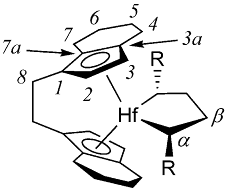
We have prepared new Ph- and $CF_3C_6H_4$-substituted hafnacyclopentanes starting from the corresponding hafnocene alkyne complex. The herein described reactions are among the first examples where the alkyne dissociates from a hafnocene alkyne complex to generate "free" hafnocene, which then undergoes formation of the hafnacycle. These findings may be the starting point for a series of applications of these complexes in hafnocene chemistry, further applications are under investigation.

Experimental Section

General: All operations were carried out under an atmosphere of argon with standard Schlenk techniques. Prior to use, solvents (including deuterated solvents) were freshly distilled from sodium tetraethylaluminate and stored under an atmosphere of argon. Styrene was purchased from Sigma Aldrich and freshly distilled prior to use. Complex **1** was prepared according to ref.[5] The starting material *rac*-(ebthi)$HfCl_2$ was purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. The following spectrometers were used: Mass spectra: MAT 95-XP; NMR spectra: Bruker AV 300/AV 400; Chemical shifts (^1H, ^{13}C) are given in ppm relative to $SiMe_4$ and are referenced to signals of the used solvent: [D_6]benzene (δ_H = 7.16 ppm, δ_C = 128.0 ppm), [D_8]thf (δ_H = 1.73 ppm, δ_C = 25.2 ppm). Coupling constants are given in Hz. The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Complex 2: Complex **1** (0.210 g, 0.34 mmol) was dissolved in *n*-hexane (10 mL). Styrene (0.078 mL, 0.68 mmol) was added to the blue green solution, and the mixture was heated to 60 °C. A slow colour change to yellow green was observed. After 2 h, yellow crystals had formed from the warm solution, which were isolated from the warm mother liquor, washed with *n*-hexane at room temperature and dried in vacuo. Yield: 0.138 g (0.21 mmol, 62%). M.p. 209 °C (decomp.) under Ar. $C_{36}H_{40}Hf$ (651.19): calcd. C 66.40, H 6.91; found C 66.39, H 6.67. Data for **2a**: ^1H NMR (400 MHz, C_6D_6, 297 K): δ = 1.07 (m, 1 H, Hf-CH_2), 1.13 (m, 1 H, Hf-CH_2), 2.08 (m, 1 H, CH_2), 2.67 (m, 1 H, Hf-CH), 2.75 (m, 1 H, CH_2), 3.08 (m, 1 H, CH), 4.77 (d, 1 H, Cp2), 4.81 (d, 1 H, Cp1), 5.64 (d, 1 H, Cp2), 6.29 (d, 1 H, Cp1), 6.91 (d, 2 H, *o*-Ph), 6.94 (m, 1 H, *p*-Ph), 7.13 (m, 1 H, *p*-Ph), 7.32 (m, 2 H, *m*-Ph), 7.35 (m, 2 H, *m*-Ph), 7.41 (d, 2 H, *o*-Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 297 K): δ = 40.5 (CH), 40.8 (CH_2), 60.4 (Hf-CH_2), 66.1 (Hf-CH), 108.2 (Cp2), 108.4 (Cp1), 113.7 (Cp2), 115.2 (Cp1), 121.1 (*p*-Ph), 124.5 (*o*-Ph), 125.4 (*p*-Ph), 126.7 (*o*-Ph), 128.1 (*m*-Ph), 128.5 (*m*-Ph), 154.9 (β-Ph, *i*-Ph), 155.7 (α-Ph, *i*-Ph) ppm. Data for **2b**: ^1H NMR (400 MHz, C_6D_6, 297 K): δ = 0.26 (m, 1 H, Hf-CH_2), 2.01 (m, 1 H, CH_2), 2.10 (m, 1 H, Hf-CH_2), 2.29 (m, 1 H, Hf-CH), 2.66 (m, 1 H, CH_2), 3.13 (m, 1 H, Hf-CH), 4.80 (d, 1 H, Cp1), 4.91 (d, 1 H, Cp2), 5.61 (d, 1 H, Cp2), 6.35 (d, 1 H, Cp1), 6.95 (m, 1 H, *p*-Ph), 7.05 (d, 2 H, *o*-Ph), 7.13 (m, 1 H, *p*-Ph), 7.32 (m, 2 H, *m*-Ph), 7.38 (m, 2 H, *m*-Ph), 7.47 (d, 2 H, *o*-Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 297 K): δ = 37.1 (CH), 38.1 (CH_2), 57.0 (Hf-CH_2), 64.0 (Hf-CH), 106.5 (Cp1), 108.8 (Cp2), 113.7 (Cp2), 114.0 (Cp1), 121.0 (*p*-Ph), 123.7 (*o*-Ph), 125.5 (*p*-Ph), 126.6 (*o*-Ph), 128.2 (*m*-Ph), 128.7 (*m*-Ph), 154.6 (β-Ph, *i*-Ph), 159.1 (α-Ph, *i*-Ph) ppm. The following ^{13}C signals of the *rac*-(ebthi) ligand were assigned to the groups; however, no assignment to species **2a** or **2b** could be made: ^{13}C NMR (100 MHz, C_6D_6, 297 K): δ = 23.4, 24.0, 24.1, 24.4 (Cp1-α-CH_2), 23.8, 23.8, 24.2, 24.6 (Cp1-β-CH_2), 22.7, 23.0, 23.0, 23.2 (Cp2-α-CH_2), 22.8, 22.8, 23.2, 23.2 (Cp2-β-CH_2), 27.2, 27.6, 28.0, 28.2 (CH_2 bridge), 120.0, 120.3, 120.7, 120.9, 123.7, 124.0 (Cp1-C_{quart}), 125.1, 125.2, 125.9, 126.0, 127.0, 127.6 (Cp2-C_{quart}) ppm. MS (EI, 70 eV): *m*/*z* = 650 $[M]^+$.

Complex 3: Complex **1** (0.490 g, 0.80 mmol) was dissolved in toluene (10 mL). *p*-(Trifluoromethyl)styrene (0.236 mL, 1.60 mmol) was then added to the blue green solution, and the mixture was kept at room temperature. The colour changed from blue green to green. After 4 h the solution was concentrated in vacuo to half its volume, filtered and slowly layered with *n*-hexane (2 mL). After standing at room temperature overnight, yellow crystals had formed, which were separated by decantation of the mother liquor, washed with cooled *n*-hexane and dried in vacuo. Yield: 0.289 (0.37 mmol, 46%). M.p. >238 °C (decomp.) under Ar. $C_{38}H_{38}F_6Hf$ (787.19): calcd. C 57.98, H 4.87; found C 57.91, H 5.07. ^1H NMR (400 MHz, [D_8]thf, 303 K): δ = 1.63 (m, 2 H, H6), 1.79 (m, 2 H, H5), 1.94 (m, 2 H, H5), 1.96 (m, 2 H, H6), 2.01 (m, 2 H, β-CH_2), 2.23 (m, 2 H, β-CH_2), 2.28 (br., 2 H, α-CH), 2.49 (ddd, $J_{H,H}$ = 16, 9, 5.5 Hz, 2 H, H7), 2.77 (ddd, $J_{H,H}$ = 16, 5.5, 5.5 Hz, 2 H, H7), 2.87 (m, 4 H, H4), 2.88 (AA′BB′, 4 H, H8), 4.82 (d, $J_{H,H}$ = 2.9 Hz, 2 H, H2), 5.36 (d, $J_{H,H}$ = 2.9 Hz, 2 H, H3), 6.92 (AA′XX′, 4 H, *o*-Ph), 7.47 (AA′XX′, 4 H, *m*-Ph) ppm. ^{13}C NMR (100 MHz, [D_8]thf, 303 K): δ = 23.3 (Cβ), 23.4 (C5), 23.7 (C6), 24.1 (C7), 24.8 (C4), 28.6 (C8), 63.2 (Cα), 110.1 (C2), 115.0 (C3), 122.3 (C7a), 123.1 (q, $J_{C,F}$ = 32.0 Hz, *p*-Ph), 124.4 (*o*-Ph), 125.1 (q, $J_{C,F}$ = 3.7 Hz, *m*-Ph), 128.1 (C1), 129.3 (C3a), 162.6 (*i*-Ph) ppm. No signal for the CF_3 group was found. ^{19}F NMR (282 MHz, [D_8]thf, 303 K):: δ = –61.7 (CF_3) ppm. MS (CI, isobutane): *m*/*z* = 787 $[M]^+$, 615 $[M - p\text{-}CF_3\text{-styrene}]^+$.



General Protocol for the Polymerization of Ethylene: The hafnium complex (0.042 mmol) and $B(C_6F_5)_3$ (0.042 mmol) were dissolved in toluene (20 mL). The solution was warmed to 40 °C and the Ar atmosphere was removed carefully in vacuo. The Schlenk tube was then flushed with ethylene (1.3 bar). After 5 min the polymerization was stopped by the addition of EtOH/H_2O/HCl (100:100:25 mL). The slurry was filtered through a paper filter; the precipitate was washed with acetone (2×) and dried in vacuo.

Crystallographic Details: Diffraction data were collected with a STOE IPDS diffractometer by using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-97[11] and SIR 2004,[12] respectively) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[11]). DIAMOND[13] was used for graphical representations.

Complex 2: $C_{36}H_{40}Hf$, M_r = 651.17, yellow crystal, $0.50 \times 0.30 \times 0.25$ mm, monoclinic, space group $P2_1/n$, a = 10.968(2) Å, b = 11.463(2) Å, c = 21.579(4) Å, β = 94.75(3)°, V = 2703.6(9) Å^3, Z = 4, $\rho_{calcd.}$ = 1.600 g cm^{-3}, T = 200 K, μ = 3.882 mm^{-1}, numerical absorption correction (max. and min. transmission: 0.4589 and 0.2696), 43564 reflections collected, 6206 independent reflections (R_{int} = 0.0363), 5283 reflections observed [$I > 2\sigma(I)$], 260 refined parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0195, wR_2 = 0.0422, R indices (all data): R_1 = 0.0270, wR_2 = 0.0434.

Complex 3: $C_{38}H_{38}F_6Hf$, M_r = 787.17, yellow crystal, $0.45 \times 0.30 \times 0.20$ mm, triclinic, space group $P\bar{1}$, a = 11.5020(4) Å,

b = 11.9687(4) Å, c = 11.9785(4) Å, α = 70.870(3)°, β = 75.645(3)°, γ = 80.241(3)°, V = 1502.27(9) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.740 g cm^{-3}, T = 200 K, μ = 3.537 mm^{-1}, numerical absorption correction (max. and min. transmission: 0.5742 and 0.3345), 28961 reflections collected, 8090 independent reflections (R_{int} = 0.0231), 7591 reflections observed [$I > 2\sigma(I)$], 418 refined parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0264, wR_2 = 0.0668, R indices (all data): R_1 = 0.0292, wR_2 = 0.0675.

CCDC-718878 (for **2**) and -718879 (for **3**) 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.

Acknowledgments

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