Reaction of Alkylzirconocene Cation Complexes with $(R-C{\equiv}C-)_2SiR_2$ Reagents: Preparation of Heterodimetallic Compounds Containing A μ-Alkynyl Ligand Bridge between Zirconium and Silicon

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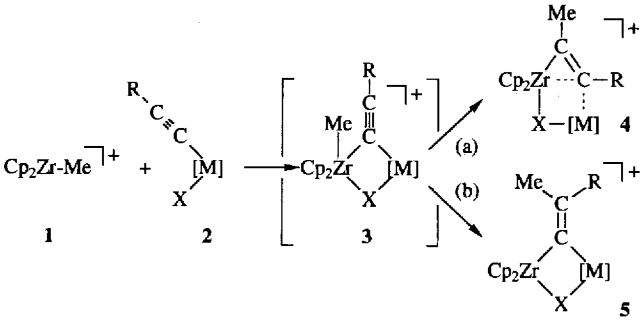
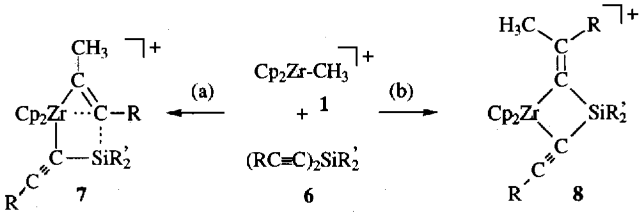
The methylzirconocene cation, employed as the $[Cp_2ZrCH_3(THF)]^+BPh_4^-$ reagent **1a** reacts with $(R'C{\equiv}C)_2SiR_2$ substrates (**6a**–**d**) by means of carbometallation of an alkynyl group to yield the mixed metal ring systems **8a**–**d**, containing both a 1,1-disubstituted μ-alkenyl and an alkynyl bridge between zirconium and silicon (e.g. shown by X-ray crystal structure analyses of complexes **8a** and **8c**). A similar addition reaction takes place upon treatment of the (butadiene)zirconocene/tris(pentafluorophenyl)-borane 1:1 addition product **9** with $(CH_3-C{\equiv}C)_2Si(CH_3)_2$ (**6c**) to give **10**. Here the incipient alkyl zirconocene cation character of the metallocene/borate betaine complex **9** shows up in the alkynyl silane carbometallation reaction.

There is evidence that alkylzirconocene cations[1] Cp_2Zr-R^+ react with alkynyl group 4 metal complexes and related reagents by means of reaction paths involving dimetallic intermediates such as **3**. Examples from our group[2] as well as work by Horton et al.[3] have revealed that **3** may undergo either of two competing subsequent reactions (a) and (b) leading to the stable products **4** and **5**, respectively as shown in the Scheme. Reaction path (a) involves a reductive coupling step at the bent metallocene unit and leads to the remarkable planar tetracoordinate carbon compounds **4**, whereas path (b) belongs to the family of the carbometallation reactions[4]. The favored coupling path depends strongly on the metals and substituents involved and on the general reaction conditions.

Scheme 1



It would be interesting to use bis(alkynyl)silane derivatives as a component in this general reaction scheme. In principle either of the competing reaction paths are viable because the reagents **6** may react either as ordinary substituted alkynes and thus become carbometallated as shown in path (b) in the Scheme or they may serve as $RC{\equiv}C-$group donors as shown in path (a). In each case, a structurally interesting type of product would result. Novel planar tetracoordinate carbon compounds (**7**) would arise from path (a)[5], whereas a novel type of main group/transition metal-containing, dimetallic, four-membered ring compounds (**8**)[6] would result from path (b).



Because it was hard to predict which of the paths would be favoured, we reacted the methylzirconocene cation with a number of bis(alkynyl)silane reagents.

Results and Discussion

The methylzirconocene cation was employed as the tetrahydrofuran-stabilized reagent $[Cp_2ZrCH_3(THF)]^+BPh_4^-$ **1a** "Jordan's cation"[1l] for this study with tetraphenylborate as the non-nucleophilic counterion. Bis(alkynyl)silane reagents $(R'C{\equiv}C)_2SiR_2$ were prepared in the usual way by reacting the respective alkynyl lithium reagents with Cl_2SiR_2 in a 2:1 molar ratio[7].

The reaction of $(PhC{\equiv}C)_2Si(CH_3)_2$ (**6a**) with $Cp_2ZrCH_3(THF)^+BPh_4^-$ (**1a**) was carried out in dichloromethane solution at ambient temperature. The initially yellow colored solution turned dark red over 24 h, and then the reaction product **8a** was isolated as a bright red solid in 75% yield. Single crystals for the X-ray crystal structure

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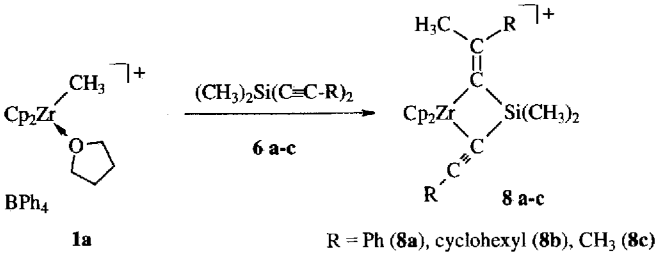
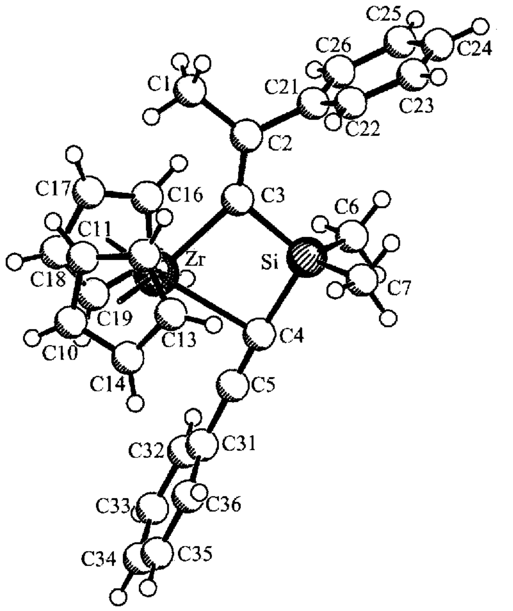
analysis of **8a** were obtained from dichloromethane/toluene. The X-ray diffraction study revealed that product formation took place under these conditions by means of a carbometallation of one of the carbon-carbon triple bonds [path (b), see above]. A main group/transition metal, heterobimetallic, four-membered ring system is obtained in which the silicon and zirconium metal centers are connected by both an alkenyl and an alkynyl bridging ligand.

The central four-membered ring is planar. The Zr–C3–Si angle inside this central ring is 95.2(3)°. Consequently, one of the remaining angles at the olefinic carbon center C3 is very large [Zr–C3–C2 140.8(6)°] whereas the other is close to the expected sp^2 carbon value [C2–C3–Si 123.9(6)°]. The corresponding angles at C2 are closer to one another in value at 114.5(6)° (C1–C2–C21), 122.5(7)° (C21–C2–C3), and 123.0(7)° (C3–C2–C1). The C2–C3 distance is typical for a C=C double bond [1.329(9) Å; C1–C2 1.495(10) Å C2–C21 1.494(10) Å]. The Zr–C3 bond length is 2.245(7) Å, and thus falls in the expected range for a σ bond between an sp^2 carbon and zirconium[8]. The four Si–C bonds are all similar [1.872(7) Å Si–C3, 1.869(8) Å Si–C4, 1.850(9) Å Si–C7, 1.861(9) Å Si–C6]. The C7–Si–C6 angle is 113.8(5)°, and the C3–Si–C4 angle is, as expected, much smaller at 100.9(3)°. A remarkable structural feature of **8a** is the μ-alkynyl bridging group between silicon and zirconium. The $Si-C{\equiv}C-C_{Ar}$ unit is linear [Si–C4–C5 173.0(6)°, C4–C5–C31 179.9(8)°] and points toward the zirconium. The Zr–C4 bond [2.462(7) Å] is in the range typical for a zirconocene-to-carbon π interaction. The Zr–C5 interaction appears to be much weaker [2.874(8) Å]. The C4–C5 bond length [1.225(9) Å] is typical for a carbon-carbon triple bond [C5–C31 1.419(10) Å]. The Zr–C4–Si angle is 88.5(3)°. Thus it appears that the alkynyl π system is not much affected by the μ-C≡C–Ar bridging in this complex (IR of **8a**: $\nu_{C\equiv C}$ = 2157 cm^{-1}). It appears that the specific bonding situation in **8a** is similar as it is encountered in many dinuclear μ-acetylide transition metal complexes[9].



The ^{1}H-NMR spectrum of **8a** (in CD_2Cl_2) shows singlets at δ = 6.39 (10H, Cp), 1.98 (3H, $C{\equiv}C-CH_3$), and 0.25 (6H, $Si(CH_3)_2$). The ^{13}C-NMR resonance of the *Zr*-alkenyl carbon atom (C3 in Figure 1) appears at the very typical value of δ = 213.7 (C2 168.9). There are four quaternary ^{13}C-NMR carbon resonances at δ = 145.9, 117.0, 108.5, and 101.6 (Cp signal at 115.5, $C{\equiv}C-CH_3$ at 33.1, and $Si(CH_3)_2$ at 0.9).

Figure 1. Molecular structure of **8a** (only the cationic part is shown); selected bond lengths and angles are discussed in the text



The reaction of **1a** with $(cyclohexyl-C{\equiv}C)_2Si(CH_3)_2$ (**6b**) gives **8b** in approximately 50% yield. It contains a single isomer that probably also arises from *cis* addition of the $Cp_2Zr-CH_3^+$ moiety to the carbon-carbon triple bond. The product **8b** shows a $\nu_{C\equiv C}$ band at 2101 cm^{-1} in the IR spectrum. The ^{13}C NMR alkenyl carbon resonances (C3, C2; nonsystematic numbering scheme as used in Figure 1) are at δ = 213.0 and 172.8. The ^{13}C-NMR carbon signals of the μ-C≡C–R ligand appear at δ = 117.9 (C5) and 93.3 ppm (C4).

Analogously, $Cp_2ZrCH_3^+$ adds to bis(propynyl)dimethylsilane (**6c**) to give **8c** [isolated in 92% yield, orange-colored solid, m.p. 150°C (dec.); ^{13}C-NMR signals at δ = 114.5 (Cp), 32.6 [(*Z*)-CH_3], 28.7 [(*E*)-CH_3]; alkenyl ^{13}C-NMR resonances at δ = 215.6 (C3) and 163.6 (C2) ppm; alkynyl resonances at δ = 108.6 (C5), 92.7 (C4), 7.0 (CH_3)]. The (*Z*)- and (*E*)-CH_3 ^{1}H-NMR signals of complex **8c** are observed at δ = 1.69 and 1.95, respectively. The δ = 1.69 resonance is missing when the corresponding deuterated reagent $Cp_2ZrCD_3^+$ is added to the silane substrate **6c** (plus the C1 ^{13}C-NMR resonance is affected). This experiment confirms that also in the case of **6c** formation the carbometallation is a *cis*-selective process.

Complex **8c** was also characterized by an X-ray structural analysis. A projection of the molecular geometry of the cation is shown in Figure 2. In this case, the accuracy of the structure determination was rather poor (R value of ~11%). Therefore, the detailed structural data of **8c** will not be discussed.

We have also treated the methylzirconocene cation with tetrakis(propynyl)silane (**6d**). The 1:1 addition product **8d** was isolated. Its IR spectrum shows $\nu_{C\equiv C}$ bands at 2183 and 2132 cm^{-1}. The ^{13}C-NMR spectrum of complex **8d** in CD_2Cl_2 shows a Cp resonance at δ = 115.1 and signals of the methyl groups at the alkenyl moiety at δ = 32.2 and 29.3. The signals of the propynyl methyl groups are found

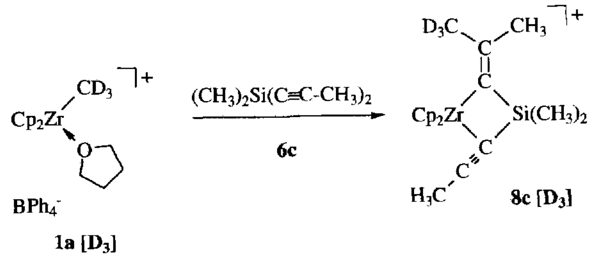
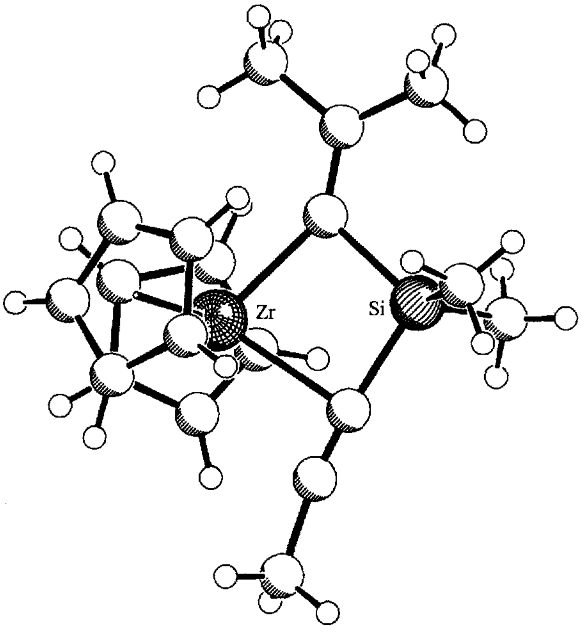


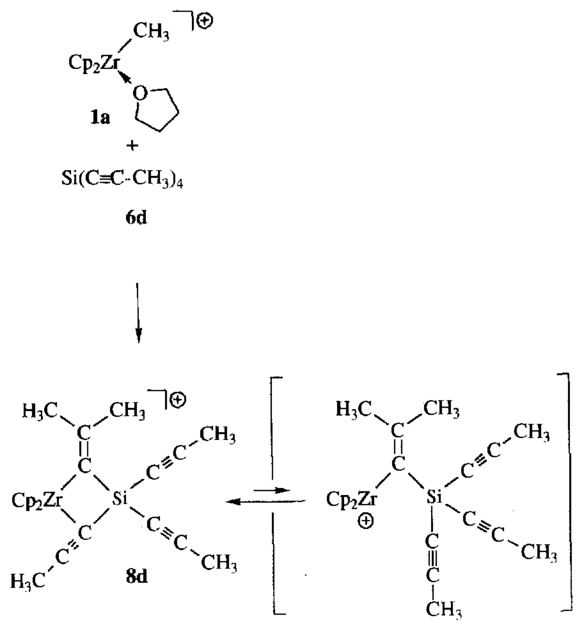
Figure 2. A view of the molecular structure of **8c** (only the cation is shown)



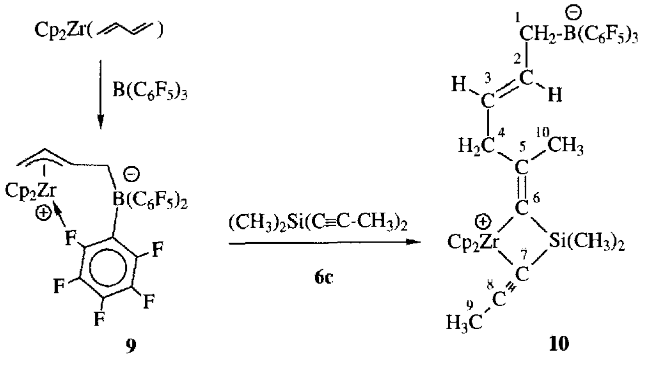
at $\delta = 6.5$ and 5.3 (double intensity). The quarternary carbon signals of the bridging alkenyl moiety are observed at $\delta = 204.6$ and 167.7; the corresponding bridging alkynyl ^{13}C-NMR resonances are at $\delta = 105.5$ and 85.5 ppm (C5, C4), those of the terminal $C{\equiv}C{-}CH_3$ groups at silicon at $\delta = 108.2$, 71.2 and 5.3 (CH_3).

The ^1H-NMR spectrum of **8d** exhibits a Cp singlet at $\delta = 6.39$ and singlets of the alkenyl methyl groups at $\delta = 2.08$ [(*E*)-CH_3] and 1.64 ppm [(*Z*)-CH_3]. But the proton NMR spectrum of complex **8d** is dynamic. In CD_2Cl_2 solution at room temperature (200 MHz), it exhibits very broad methyl resonances of the bridging as well as terminal propynyl ligands that become sharp signals at low temperature (233 K: $\delta = 2.00$ and 1.54). Apparently, opening the μ-$C{\equiv}C{-}CH_3$ bridge between zirconium and silicon affords only a rather small activation barrier, so that a rapid equilibration of all three $-C{\equiv}C{-}CH_3$ groups is easily achieved above room temperature on the ^1H-NMR time scale. This process is even faster in the coordinating solvent THF, where only a single, averaged ^1H-NMR propynyl methyl resonance is observed at ambient temperature.

We conclude that the alkynylsilane moieties in the dimetallic systems examined apparently have no tendency to undergo a complete alkynyl migration to zirconium followed by reductive carbon–carbon coupling. Instead a clean carbometallation reaction is observed which leads to a very stable cationic four-membered main group/transition metal dimetallic system that shows interesting σ-alkynyl bridging. It thus appears that this reaction pattern is typical when alkyl group 4 metallocene cation reagents and bis(alkynyl)silane derivatives are combined, and it should be possible to also use this typical behavior to characterize incipient alkyl zirconocene cation behavior in reagents and catalysts that are thought to contain hidden or protected alkylmetallocene cation character.



Such a reagent is the zirconocene/borate betaine complex **9** that we have recently described[10]. It is readily formed upon treatment of (butadiene)zirconocene with tris(pentafluorophenyl)borane. Complex **9** contains a weak fluoride coordination to zirconium. It is an active catalyst for α-olefin polymerization, and is thought to generate an active catalytic site at zirconium by simply opening the fluoride bridge. The resulting hydrocarbyl zirconocene cation center, which is part of the neutral metallocene/borate betaine complex, should then be able to react with a bis(alkynyl)silane derivate in a way similar to that described for the **1**/**6** reaction pairs above. In fact, it does.



The zirconocene/borate betaine complex **9** was prepared from (butadiene)zirconocene and $B(C_6F_5)_3$ in toluene and directly reacted with $(CH_3{-}C{\equiv}C)_2Si(CH_3)_2$. Addition of pentane to the reaction mixture led to the precipitation of the 1:1 addition product **10**. Complex **10** is formed by the addition of the butadienyl-borate ligand system to one of the propynyl groups. The resulting alkenyl ligand system is bridging between zirconium and silicon. It exhibits typical ^{13}C-NMR resonances at 216.7 (C6) and 168.2 (C5); the remaining butadiene derived carbon signals of this ligand are found at $\delta = 52.0$ ($^1J_{CH} = 124$ Hz, C4), 120.6, 140.4 (C3, C2, ^{1}H-NMR signals at 4.93 and 5.70, $^3J_{HH} = 15$ Hz), and 29.3 (broad, C1; the corresponding 1-H and 4-H ^{1}H-NMR signals are at $\delta = 2.15$ and 2.27). The $B(C_6F_5)_3$ group bonded to C1 exhibits ^{13}C-NMR resonances at $\delta = 127.5$ (ipso-C), 148.7 ($^1J_{CF} = 233$ Hz), 138.0 ($^1J_{CF} = 243$ Hz), and 136.8 ($^1J_{CF} = 235$ Hz). The ^{11}B-NMR resonance is at -14 and the ^{19}F resonances are observed at $\delta = -130$, -163, and -166. The ^{1}H/^{13}C-NMR signals of the methyl group at C5 are at $\delta = 2.06/25.6$. Complex **10** also contains a $C{\equiv}C{-}CH_3$ ligand that is σ-bridging between silicon and zirconium (typical ^{13}C-NMR signals at $\delta = 107.8$ and 92.9). The acetylide IR bond of **10** is at $\nu_{C\equiv C} = 2128$ cm^{-1}.

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Experimental

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or a drybox. Solvents were dried and distilled under argon prior to use. The following instruments were used for product characterization: Bruker AC 200 P NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{11}B, 64 MHz), Bruker ARX 300 NMR spectrometer (^{19}F, 282 MHz), VARIAN UNITY*plus* NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{29}Si NMR, 119 MHz); Nicolet 5 DXC FT IR spectrometer; DuPont 2910 DSC, STA Instruments (melting points). The starting materials **1a**[1] and **6a–d**[7] were prepared according to literature procedures. The ^{1}H/^{13}C-NMR resonances (in CD_2Cl_2) of the BPh_4^- anion were observed at 7.36–7.28 (m, 8H), 6.95–6.90 (m, 8H), 6.81–6.76 (m, 4H) and 164.3 (q, B–*C*, $^1J_{BC} = 50$ Hz), 136.4, 126.0, 122.2 (aromatic C).

Synthesis of **8a**: A mixture of 480 mg (0.76 mmol) of the methylzirconocene cation reagent **1a** and 390 mg (1.50 mmol) of the bisalkynylsilane **6a** was dissolved in 10 ml dichloromethane and stirred for 24 h. The color of the solution turned from yellow to dark red during this time. The solvent was removed in vacuo, the residue washed twice with 20 ml of toluene and dried in vacuo to give **8a** as a bright red solid. Yield 470 mg (75%), m.p. 146 °C (dec., DSC). Single crystals for the X-ray crystal structure analysis were obtained from dichloromethane/toluene. – IR (KBr): $\tilde{\nu} = 3051$, 3015, 2960, 2157 ($C{\equiv}C$), 1590, 1486, 1435, 1334, 1279, 1238, 1069, 1015, 803, 757, 698 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): $\delta = 7.73{-}7.00$ (m, 10H, aromatic), 6.39 (s, 10H, Cp), 1.98 (s, 3H, $C{=}C{-}CH_3$), 0.25 (s, 6H, $Si(CH_3)_2$). – ^{13}C NMR (CD_2Cl_2): $\delta = 213.7$ (s, C3), 168.9 (s, C2), 145.9 (*ipso*-C, aromatic), 135.0, 134.6, 131.7, 130.6, 129.0, 128.3, (aromatic C), 117.0 (s), 108.5 (s), 101.6 (s), 115.5 (Cp), 33.1 (q, C1, $^1J_{CH} = 128$ Hz), 0.9 (q, $Si(CH_3)_2$, $^1J_{CH} = 125$ Hz). – ^{29}Si NMR (CD_2Cl_2): $\delta = -60.8$ ($Si(CH_3)_2$). *X-ray crystal structure analysis of* **8a**: $C_{53}H_{49}BSiZr \cdot C_7H_8$ (908.18), 0.3 × 0.25 × 0.1 mm, $a = 11.863(1)$, $b = 14.095(2)$, $c = 15.188(2)$ Å, $\alpha = 77.14(1)$, $\beta = 82.58(1)$, $\gamma = 88.35(1)°$, $V = 2455.1(5)$ Å^3, $\rho_{calcd.} = 1.228$ g cm^{-3}, $\mu = 2.86$ cm^{-1}, empirical absorption correction, $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), Enraf-Nonius-CAD4-diffractometer, $\lambda = 0.71073$ Å, $\omega/2\Theta$ scans, 6806 reflections measured ($-h$, $\pm k$, $\pm l$), $[\sin\Theta/\lambda]_{max.} = 0.54$ Å^{-1}, 6431 independent and 3272 observed reflections [$I \leqslant 2\sigma(I)$], 572 refined parameters, $R = 0.056$, $wR^2 = 0.141$, max. residual electron density 0.35 (-0.42) eÅ^{-3}, direct methods, hydrogen atoms calculated and riding. Programs used: SHELXS 86, SHELXL 93, SCHAKAL 92. Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404332, the names of the authors, and the journal citation.

Synthesis of **8b**: To a solution of 964 mg (1.54 mmol) of the methylzirconocene cation reagent **1a** in 10 ml of dichloromethane 800 mg (2.94 mmol) of the bisalkynylsilane **6b** was added via syringe. The initially yellow-colored solution turned red over 24 h. The solvent was removed in vacuo, the residue washed twice with 20 ml toluene and dried in vacuo. Yield 640 mg (50%) of **8b**, m.p. 146 °C (dec., DSC). – IR (KBr): $\tilde{\nu} = 3052$, 3035, 3014, 2997, 2981, 2925, 2848, 2101 ($C{\equiv}C$), 1579, 1568, 1478, 1448, 1427, 1348, 1247, 1013, 811, 734, 704, 606 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): $\delta = 6.30$ (s, 10H, Cp), 2.38 (m, 1H, CH), 1.95 (m, 1H, CH), 1.93–1.20 (m, 20H, CH_2), 1.56 (s, 3H, $C{=}C{-}CH_3$), 0.57 (s, 6H, $Si(CH_3)_2$). – ^{13}C NMR (CD_2Cl_2): $\delta = 213.0$ (s, $\mathit{C}{=}C{-}CH_3$), 172.8 (s, $C{=}\mathit{C}{-}CH_3$), 117.9 ($C{\equiv}\mathit{C}{-}Si$), 114.5 (Cp), 93.3 (s, $\mathit{C}{\equiv}C{-}Si$), 54.9 (CH), 32.0 ($C{=}C{-}\mathit{C}H_3$), 31.8, 31.7, 26.4, 26.0, 25.2, 24.8 (CH_2), 25.5 (CH), 0.23 ($Si(CH_3)_2$). – ^{29}Si NMR (CD_2Cl_2): $\delta = -62.8$ ($Si(CH_3)_2$). – $C_{53}H_{61}BSiZr$ (828.19): calcd. C 76.86, H 7.42; found C 75.05, H 7.45.

Synthesis of **8c**: To a suspension of 1.14 g (1.82 mmol) of the methylzirconocene cation reagent **1a** in 10 ml of dichloromethane 400 mg (2.94 mmol) of the bisalkynylsilane **6c** was added via syringe. The initially yellow colored reaction mixture turned red during 24 h. The solvent was removed in vacuo, the residue washed twice with 20 ml of toluene and dried in vacuo. Yield 1.16 g (92%) of **8c**, m.p. 150 °C (dec., DSC). – IR (KBr): $\tilde{\nu} = 3051$, 3032, 2996, 2980, 2904, 2123, 1581, 1478, 1427, 1357, 1249, 1013, 952, 814, 704, 603 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): $\delta = 6.28$ (s, 10H, Cp), 1.95 (s, 3H, *trans* $C{=}C{-}CH_3$), 1.69 (s, 3H, *cis* $C{=}C{-}CH_3$), 1.62 (s, 3H, $C{\equiv}C{-}CH_3$), 0.55 (s, 6H, $Si(CH_3)_2$). – ^{13}C NMR (CD_2Cl_2): $\delta = 215.6$ (s, $\mathit{C}{=}C{-}CH_3$), 163.6 (s, $C{=}\mathit{C}{-}CH_3$), 114.5 (Cp), 108.6 (s, $C{\equiv}\mathit{C}{-}CH_3$), 92.7 (s, $\mathit{C}{\equiv}C{-}CH_3$), 32.6 (q, *cis* $C{=}C{-}\mathit{C}H_3$, $^1J_{CH} = 125$ Hz), 28.7 (q, *trans* $C{=}C{-}\mathit{C}H_3$, $^1J_{CH} = 126$ Hz), 7.0 (q, $C{\equiv}C{-}\mathit{C}H_3$, $^1J_{CH} = 136$ Hz), -1.0 (q, $Si(CH_3)_2$, $^1J_{CH} = 124$ Hz). – ^{29}Si NMR (CD_2Cl_2): $\delta = -64.8$ ($Si(CH_3)_2$). Compound **8c** **[D$_3$]** was prepared in a manner analogous to that for **8c**. ^{1}H-NMR resonance for the *cis* $C{=}C{-}\mathit{C}H_3$ group is missing; the ^{13}C resonance was not resolved.

Synthesis of **8d**: To a suspension of 1.26 g (2.01 mmol) of the methylzirconocene cation reagent **1a** in 40 ml of dichloromethane 500 mg (2.71 mmol) of **6d** was added. The initially yellow-colored reaction mixture turned red during 12 h. The solvent was removed in vacuo and the residue was washed with 50 ml toluene. Recrystallization from dichloromethane/toluene (1:4) gave **8d** as a red solid. Yield 1.3 g (87%) of **8d**, m.p. 65 °C (dec., DSC). – IR (KBr): $\tilde{\nu} = 3055$, 3043, 3000, 2981, 2966, 2911, 2183 ($C{\equiv}C$), 2132 ($C{\equiv}C$), 1621, 1591, 1579, 1480, 1431, 1240, 1032, 820, 735, 601, 520 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): $\delta = 6.39$ (s, 10H, Cp), 2.08 (s, 3H, *trans* $C{=}C{-}CH_3$), 2.01 (br. s, 6H, terminal $C{\equiv}C{-}CH_3$), 1.64 (br. s, 3H, bridging $C{\equiv}C{-}CH_3$), 1.64 (s, 3H, *cis* $C{=}C{-}CH_3$); ^{1}H NMR (233 K, CD_2Cl_2): $\delta = 6.36$ (s, 10H, Cp), 2.03 (s, 3H, *trans* $C{=}C{-}CH_3$), 2.00 (s, 6H, terminal $C{\equiv}C{-}CH_3$), 1.61 (s, 3H, *cis* $C{=}C{-}CH_3$), 1.54 (s, 3H, bridging $C{\equiv}C{-}CH_3$). – ^{13}C NMR (233 K, CD_2Cl_2): δ = 204.6 (s, *C*=C−CH$_3$), 167.7 (s, C=*C*−CH$_3$), 115.1 (Cp), 108.2 (s, terminal C≡*C*−CH$_3$), 105.5 (s, bridging C≡*C*−CH$_3$), 85.3 (s, bridging) *C*≡C−CH$_3$), 71.2 (s, terminal *C*≡C−CH$_3$), 32.3, 29.3 (C=C−*C*H$_3$), 6.5 (s, bridging C≡C−*C*H$_3$), 5.3 (s, terminal C≡C−*C*H$_3$). – ^1H NMR ([D$_8$]-THF): δ = 6.44 (s, 10H, Cp), 2.04 (s, 3H, *trans* $C{=}C{-}CH_3$), 1.84 (s, 9H, $C{\equiv}C{-}CH_3$), 1.55 (s, 3H, *cis* $C{=}C{-}CH_3$). – $C_{47}H_{45}BSiZr$ (739.99): calcd. C 76.29, H 6.13; found C 75.76, H 6.31.

Synthesis of **10**: 640 mg (2.32 mmol) (butadiene)zirconocene and 1.19 g (2.32 mmol) of $B(C_6F_5)_3$ were dissolved in 40 ml bromobenzene. After stirring for 10 min, 3.50 mg (2.57 mmol) of **6c** was added via syringe. The color of the reaction mixture immediately turned to red. After 1 h pentane was added to precipitate **10**, which was isolated as a yellow solid, washed with toluene and dried in vacuo. Yield: 1.14 g (53%), m.p. 80°C (dec., DSC). – IR (KBr): $\tilde{\nu}$ = 3118, 3020, 2960, 2912, 2128 (C≡C), 1641 (C=C), 1575, 1512, 1451, 1375, 1270, 1084, 974, 819, 459 cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 6.38 (s, 10H, Cp), 5.70 (dt, 1H, 2-H, $^3J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.6 Hz), 4.93 (dt, 1H, 3-H, $^3J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 6.6 Hz), 2.27 (d, 2H, 4-H, $^3J_{HH}$ = 6.6 Hz), 2.15 (d, 2H, 1-H, $^3J_{HH}$ = 7.6 Hz), 2.06 (s, 3H, 10-H), 1.65 (s, 3H, 9-H), 0.49 (s, 6H, $SiMe_2$). – ^{13}C NMR (CD_2Cl_2): δ = 216.7 (s, C6), 168.2 (s, C5), 148.7 (d, *o*-C_6F_5, $^1J_{CF}$ = 233 Hz), 140.4 (d, C2/C3, $^1J_{CH}$ = 146 Hz), 138.0 (d, *p*-C_6F_5, $^1J_{CF}$ = 243 Hz), 136.8 (d, *m*-C_6F_5, $^1J_{CF}$ = 235 Hz), 127.5 (s, *ipso*-C_6F_5), 120.6 (d, C2/C3, $^1J_{CH}$ = 153 Hz), 107.8 (s, C7/C8), 92.9 (s, C7/C8), 52.0 (t, C4, $^1J_{CH}$ = 124 Hz), 29.3 (br., C1), 25.6 (C10), 7.6 (C9), 1.06 ($Si(CH_3)_2$). – ^{29}Si NMR (CD_2Cl_2): δ = −61.3 ($Si(CH_3)_2$). – ^{19}F NMR (CD_2Cl_2): δ = −130 (m, C_6F_5), −163 (m, C_6F_5), −166 (m, C_6F_5). ^{11}B NMR (CD_2Cl_2): δ = −14 (s, $B(C_6F_5)_3$). – $C_{40}H_{28}BF_{15}SiZr$ (923.76): calcd. C 52.01, H 3.06; found C 53.07, H 3.65.

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