

Methyl-Substituted Zirconocene–Bis(trimethylsilyl)acetylene Complexes (C₅H_{5–n}Me_n)₂Zr(η²-Me₃SiC≡CSiMe₃) (n = 2–5)

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The (C₅H_{5–n}Me_n)₂Zr[η²-C₂(SiMe₃)₂] (n = 2–5; 1,3-dimethyl, 1,2,3-trimethyl) (**2C–F**) complexes were prepared by the reduction of corresponding zirconocene dichlorides with magnesium in THF in the presence of bis(trimethylsilyl)acetylene (BTMSA). All of them are stable in the absence of THF. Crystal structures of (C₅HMe₄)₂Zr[η²-C₂(SiMe₃)₂] (**2E**) and (C₅Me₅)₂Zr[η²-C₂(SiMe₃)₂] (**2F**) and of the analogous titanium complexes are isomorphous. The red shift of the ν(C≡C) vibration and the downfield shift of ¹³C δ(C≡C) indicate that BTMSA in **2C–F** is more strongly coordinated than in analogous titanocene complexes. The nonisolated complex (C₅H₄Me)₂Zr[η²-C₂(SiMe₃)₂](THF) (**2B·THF**) rearranges after the loss of THF to give the dimer [(η⁵-C₅H₄Me)(η¹-C(SiMe₃)=CH(SiMe₃)Zr(μ-η¹:η⁵-C₅H₃Me)]₂ (**3B**).

Introduction

Highly reactive early transition metal metallocenes, rapidly rearranging with the formation of additional Ti–H, C–C or Ti–C bonds,¹ can be stabilized by the coordination of carbon monoxide,² phosphanes,³ and acetylenes⁴ and/or by a combination of acetylenes with one of the former ligands.⁵ The titanocene-acetylene complexes (C₅H₅)₂Ti(R₁C≡CR₂) have been reported for R₁ = R₂ = Ph,^{4a} Me,^{4b} and SiMe₃,^{4c} R₁ = SiMe₃, R₂ = Ph,^{4d} R₂ = ^tBu, ⁿBu, and ⁿPr^{4e}, and the permethyltitanocene complexes (C₅Me₅)₂Ti(R₁C≡CR₂) for R₁ = R₂ = alkyl or Ph,^{4f} R₁ = R₂ = SiMe₃,^{4g} and R₁ = SiMe₃, R₂

= Ph.^{4d} The existence of the (C₅H₅)₂Ti(MeC≡CMe) complex^{4b} was not later confirmed.^{4h} Recently, a complete series of the (C₅H_{5–n}Me_n)₂Ti[η²-C₂(SiMe₃)₂] (n = 0–5) complexes has been obtained.⁴ⁱ The four-electron coordination bond in these complexes was inferred from large shifts of the ν(C≡C) vibration (Δν = 400–500 cm⁻¹) and a low-field shift of δ_C(C≡C) into the region 196–245 ppm.^{4e,j} The complexes of the type (C₅H₅)₂Ti(R₁C≡CR₂)(L), for instance, L = CO, R₁ = R₂ = Ph,^{5a,b} R₁ = R₂ = C₆F₅,^{5b} and L = PMe₃, R₁ = R₂ = H,^{5c} R₁ = H, R₂ = Ph,^{5d} and R₁ = R₂ = Ph,^{5e} bind, as judged from ν(C≡C), weakly the internal acetylenes (1785–1740 cm⁻¹) and strongly HC≡CH (1618 cm⁻¹) and PhC≡CPh (1590 cm⁻¹). All the complexes except those containing bis(trimethylsilyl)acetylene (BTMSA) react with excess acetylenes to give titanacyclopentadiene derivatives.^{4a,b,e,j} The BTMSA in (C₅H₅)₂Ti[η²-C₂(SiMe₃)₂] is easily replaced by other acetylenes^{4c,j,6a,b} or by 1,4-disubstituted 1,3-butadiynes.^{7a–d} It is also liberated upon interaction with alcohols and carbonyl compounds.^{4e} The reluctance of BTMSA to participate in insertion reactions, particularly with itself,⁸ makes BTMSA the ligand of choice for studies of the reactivity of titanocene species. The thermolysis of the (C₅H_{5–n}Me_n)₂Ti[η²-C₂(SiMe₃)₂] (n = 0–5) complexes thus afforded in addition to the products of titanocene rearrangements only BTMSA (for n = 0–4) or bis(trimethylsilyl)ethylenes (for n = 5).⁴ⁱ

The zirconocene–acetylene complexes were until recently obtained only with coordinated electron donor

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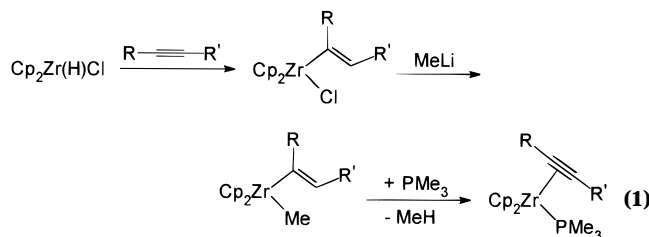
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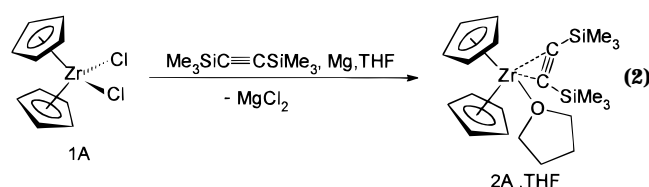
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ligands. Well-defined complexes of the type $(C_5H_5)_2Zr$ -(acetylene)(PM_e_3) were obtained for the cyclic acetylenes benzyne and cyclohexyne,^{9a–c} as well as for linear acetylenes $R_1C\equiv CR_2$ with $R_1 = H$, $R_2 = nBu$ ^{9d} and with $R_1 = R_2 = Ph$.^{9e–h} These complexes were generally synthesized from $(C_5H_5)_2ZrCl_2$ according to eq 1^{9a–d} or



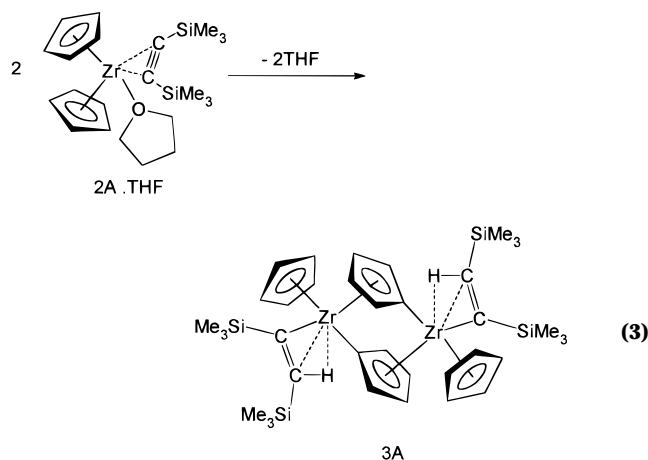
from $(C_5H_5)_2Zr(PMe_3)_2$ ^{9e} or $(C_5H_5)_2Zr(\eta^2\text{-olefin})(PMe_3)$ ^{9f,g} complexes by adding the acetylene. Addition of acetylenes in excess to these complexes^{9a} or to the dicarbonyl $(C_5H_5)_2Zr(CO)_2$ ^{9h} generally affords zirconacyclopentadiene complexes. Interestingly, such a zirconacyclopentadiene complex obtained from phenyl(trimethylsilyl)acetylene dissociates in the presence of PM_e_3 to give $(C_5H_5)_2Zr(PhC\equiv CSiMe_3)(PMe_3)$ and free acetylene.⁹ⁱ

Recently, a complex stabilized by THF, namely $(C_5H_5)_2Zr(Me_3SiC\equiv CSiMe_3)(THF)$ (**2A**·THF), has been obtained by the reduction of zirconocene dichloride by magnesium in the presence of BTMSA in THF (eq 2).^{10a} This



complex easily loses THF, e.g. under reduced pressure at room temperature and the complex $(C_5H_5)_2Zr(Me_3SiC\equiv CSiMe_3)$ undergoes a dimerization induced by a hydrogen transfer from the Cp ring to the BTMSA ligand (eq 3).

In contrast to $(C_5H_5)_2Ti(Me_3SiC\equiv CSiMe_3)$, complex **2A**·THF reacts with CO_2 , water, and acetone without elimination of BTMSA.^{10b,c} The zirconadihydrofurans resulting from the reaction with acetone^{10c} react further with acetylenedicarboxylates with elimination of acetone and BTMSA whereas a new zirconadihydrofuran



derivative is formed.^{10d} The *tert*-butyl(trimethylsilyl)acetylene complex $(C_5H_5)_2Zr(Me_3CC\equiv CSiMe_3)(THF)$ was prepared according to eq 2 and exerted the same reactivity toward the above reagents as **2A**·THF.^{10e} The BTMSA ligand is readily replaced by 1,4-dialkyl-1,3-butadiynes, and these are cleaved to give binuclear zirconocene(III) acetylides.^{7c,10f} The THF ligand in **2A**·THF can be replaced by pyridine (py) to give the more stable $(C_5H_5)_2Zr(Me_3SiC\equiv CSiMe_3)(py)$ complex,^{10g} and this, at variance with **2A**·THF, reacts with 1,4-di-*tert*-butyl-1,3-butadiyne yielding five- or seven-membered zirconacyclic cumulene complexes.^{10h} Only the reaction with ketimines resulted in the elimination of BTMSA.¹⁰ⁱ

The coordination of an electron-donating ligand which is essential for the thermal stability of all the above zirconocene acetylene complexes can, in principle, be substituted by the electron-donation effect of methyl substituents at the cyclopentadienyl ligands.¹¹ Such an effect has been clearly demonstrated in the series of methylated titanocene monohalides $(C_5H_{5-n}Me_n)_2TiX$ ($n = 0, 1, 3–5$; $X = Cl, Br, I$) by the increasing reluctance to dimerize or to coordinate THF when the number of Me substituents (n) grows from 3 to 5.¹² A note on the preparation of the thermally stable $(C_5Me_5)_2Zr[\eta^2-C_2-Ph_2]$ complex¹³ and a recent report on the preparation of *rac*-[1,2-ethylene-1,1'-bis(η^5 -tetrahydroindenyl)] $[\eta^2$ -bis(trimethylsilyl)acetylene]zirconium,¹⁴ the first struc-

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turally characterized complex without an additional ligand, encouraged us to communicate results of our investigation of the influence of methyl substituents at the cyclopentadienyl ligands on the stability of zirconocene–acetylene complexes. Here we report the synthesis of the $(C_5H_{5-n}Me_n)_2Zr[\eta^2-C_2(SiMe_3)_2]$ ($n = 2-5$) complexes which are stable in the absence of electron donor ligands and the crystal structures of the complexes for $n = 4$ and 5 and of a dimeric product of rearrangement of the labile $(C_5H_4Me)_2Zr[\eta^2-C_2(SiMe_3)_2]$ complex.

Experimental Section

General Data. All manipulations with reagents, syntheses, and most of the spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. The adjustment of single crystals into capillaries for X-ray analysis and the preparation of KBr pellets for infrared measurements were performed in an atmosphere of purified nitrogen. 1H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in C_6D_6 at 25 °C. Chemical shifts (given in the δ scale) were referenced to the solvent signal (δ_H 7.15 ppm, δ_C 128.0 ppm). Assignment of spectra of the $C_5H_{5-n}Me_n$ ligands was carried out using a delayed COSY experiment. UV–vis spectra were registered in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Mass spectra were obtained on a JEOL D-100 spectrometer at 70 eV (only important mass peaks and peaks of intensity $\geq 5\%$ are reported). Samples in capillaries were opened and inserted into the direct inlet under argon. Infrared spectra were measured on a UR-75 (Zeiss, Jena, Germany) or on a Mattson Galaxy 2020 FTIR single beam spectrometer. KBr pellets from estimated amounts of solid samples were prepared in a glovebox (mBraun labmaster 130) under purified nitrogen and were measured in a cuvette under a nitrogen atmosphere. EDX measurements were carried out with a Zeiss DSM-962 scanning electron microscope equipped with an EDAX X-ray detector. An acceleration voltage of 25 kV was used for the generation of cathodic radiation.

Chemicals. The solvents THF, hexane, toluene, and benzene- d_6 were purified by conventional methods, dried by refluxing over $LiAlH_4$, and stored as solutions of dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu-H)]_2$.¹⁵ Bis(trimethylsilyl)acetylene (BTMSA) (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and distilled into ampules. Magnesium turnings (Fluka, purum for Grignard reactions) were weighed and evacuated. Methylcyclopentadiene was obtained by cracking of the dimer (Fluka) and was immediately used for the preparation of the lithium salt. 1,3-Dimethylcyclopentadiene,¹⁶ 1,2,3-trimethylcyclopentadiene, tetramethylcyclopentadiene, and pentamethylcyclopentadiene were prepared as reported earlier.^{14d} Zirconocene dichlorides $(C_5H_{5-n}Me_n)_2ZrCl_2$ ($n = 1-5$) (**1B–1F**) were prepared by a modified general method^{17a,b} as follows. The lithium salts of the cyclopentadienes were obtained by adding BuLi in hexane (1.6 M, 52 mL, 83 mmol; Chemetall GmbH, Frankfurt a.M., Germany) to the cyclopentadiene (80 mmol) in 400 mL of toluene. After 1 h of stirring at room temperature finely powdered $ZrCl_4$ (8.4 g, 36 mmol; Merck) was added under argon and the mixture was refluxed (from minimum 4 h for C_5H_4Me to 48 h for C_5Me_5). Half the amount of toluene (200 mL) was distilled off, and after

cooling of the solution to room temperature, 50 mL of aqueous HCl was added. After standing overnight in air, light greenish crystals were filtered from a green mother liquor. The crude products were recrystallized from hot toluene to give fine needlelike crystals. The purity of the compounds was checked by MS analysis. IR spectra (regions 400–1600 cm^{-1}) are listed below.

$(C_5H_4Me)_2ZrCl_2$ (1B). The yield of colorless crystals was 7.5 g (65%); mp 182 °C (lit. mp 180 °C^{18a}). IR (KBr, cm^{-1}): 1496 s, 1455 m, 1443 m, 1414 w, 1374 s, 1352 w, 1243 m, 1074 w, 1048 s, 1042 s, 1033 s, 936 m, 880 m, 852 s, 841 vs, 816 s, 618 m.

$(C_5H_3Me_2)_2ZrCl_2$ (1C). The yield of colorless crystals was 4.6 g (37%); mp 173 °C. IR (KBr, cm^{-1}): 1507 s, 1452 s, 1440 s, 1380 s, 1277 w, 1137 w, 1050 s, 1028 m, 944w, 901 m, 847 vs, 828 s, 620 m.

$(C_5H_2Me_3)_2ZrCl_2$ (1D). The yield of colorless crystals was 4.9 g (36%); mp 252 °C. IR (KBr, cm^{-1}): 1489 s, 1474 m, 1448 s, 1374 s, 1302 w, 1196 m, 1028 s, 914 w, 904 w, 877 w, 834 s, 818 vs, 710 w, 616 w, 455 w.

$(C_5HMe_4)_2ZrCl_2$ (1E). The yield of slightly yellow crystals was 8.0 g (55%); mp 262 °C (lit. mp 211 °C^{18b}). IR (KBr, cm^{-1}): 1485 m, 1448 m, 1431 m, 1383 s, 1370 s, 1323 w, 1150 w, 1116 vw, 1024 s, 976 w, 902 m, 862 vs, 601 m.

$(C_5Me_5)_2ZrCl_2$ (1F). The yield of yellow crystals was 8.4 g (54%); mp 311 °C. IR (KBr, cm^{-1}): 1483 s, 1446 s, 1423 s, 1376 vs, 1163 w, 1062 w, 1021 s, 952 w, 805 w, 598 w. The reported NMR data for **1E**^{17a} and **1F**^{17b} agreed with our records.

Preparation of $(C_5H_{5-n}Me_n)_2Zr[\eta^2-C_2(SiMe_3)_2]$ ($n = 2-5$) Complexes **2C–2F. $(C_5H_{5-n}Me_n)_2ZrCl_2$ (**1C–1F**) (2 mmol) and Mg (0.050 g, 2.1 mmol) were charged into an ampule equipped with a Teflon-coated magnetic stirrer. The ampule was evacuated, and BTMSA (0.6 mL, 2.7 mmol) and THF (30 mL) were distilled in on a vacuum line. The mixture was frozen by liquid nitrogen, sealed off, and stirred at 60 °C until all magnesium had disappeared. Turquoise solutions were obtained from **1D–1F**, and a honey-yellow solution was obtained from **1C**. The solutions were evaporated in vacuo (the product from **1C** turned to turquoise), and the residues were extracted with hexane. In order to remove all $MgCl_2$ these solutions were evaporated and the residues were extracted by a minimum amount of hexane. Crystalline compounds **2E, 2F** were obtained by cooling of the concentrated solutions. Compounds **2C, 2D** formed amorphous solids both by cooling and by slow evaporation of hexane. They were purified by removing mother liquors at –70 °C. All the compounds were also prepared by the same procedure using a 5-fold molar excess of magnesium with respect to **1C–1F**. The reaction time was shortened to ca. 30 min at 60 °C.**

$(C_5H_3Me_2)_2Zr[\eta^2-C_2(SiMe_3)_2]$ (2C). The yield of green amorphous solid was 0.76 g (85%). 1H NMR (C_6D_6): δ 0.03 (s, 18H, SiMe₃), 1.73 (s, 12H), 5.79 (s, 4H, H-4, H-5), 6.09 (s, 2H, H-2). ^{13}C NMR (C_6D_6): δ 2.1 (q, 6C), 15.2 (q, 4C), 111.0 (d, 4C), 112.1 (d, 2C), 125.1 (s, 2C), 258.2 (s, 2C). IR (KBr): 1566 (m), 1512 (w), 1462 (m), 1445 (m), 1375 (w), 1242 (s), 1028 (w), 835 (vs, b), 748 (m), 725 (w), 685 (m), 664 (m), 638 (m), 617 (w), 598 (w), 548 (vw), 470 (w). UV–vis (hexane, green) (nm): 775 (w); THF, yellow (nm), strong absorption decreasing in intensity to 570, 750 (vw). MS (direct inlet, 70 eV, 75–80 °C, m/z (%)): 446 (M^+ , 8), 276 (100). Anal. Calcd for $C_{22}H_{36}Si_2Zr$: C, 59.0; H, 8.1. Found: C, 59.8; H, 8.3.

$(C_5H_2Me_3)_2Zr[\eta^2-C_2(SiMe_3)_2]$ (2D). The yield of green amorphous solid was 0.88 g (92%); mp 214 °C. 1H NMR (C_6D_6): δ 0.14 (s, 18H, SiMe₃), 1.78 (s, 12H), 1.89 (s, 6H), 5.52 (s, 4H). ^{13}C NMR (C_6D_6): δ 2.8 (q, 6C), 12.0 (q, 2C), 14.0 (q, 4C), 108.5 (d, 4C), 114.1 (s, 4C), 122.4 (s, 2C), 260.0 (s, 2C). IR (KBr): 1535 (m), 1487 (w), 1445 (m), 1383 (m), 1242 (s), 1024

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Table 1. Crystallographic Data and Experimental Details for **2E,F** and **3B**

	2E	2F	3B
mol formula	C ₂₆ H ₄₄ Si ₂ Zr	C ₂₈ H ₄₈ Si ₂ Zr	C ₄₀ H ₆₄ Si ₄ Zr ₂
mol wt	504.01	532.06	839.72
cryst syst	monoclinic	triclinic	triclinic
space group	C ₂ /c (No. 15)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)
cell consts			
<i>a</i> , Å	15.4388(9)	9.2206(5)	9.6327(5)
<i>b</i> , Å	10.7291(6)	10.2874(6)	10.2197(7)
<i>c</i> , Å	17.7724(13)	17.3717(7)	13.5296(8)
α, (deg)	90	79.198(8)	110.853(6)
β, (deg)	104.92(1)	75.628(5)	91.563(5)
γ, (deg)	90	72.559(5)	117.016(5)
<i>V</i> , Å ³	2844.6(3)	1511.43(13)	1079.89(11)
<i>Z</i>	4	2	1
<i>d</i> _{calcd} , g/cm ⁻³	1.177	1.169	1.291
<i>F</i> (000)	1072	568	440
μ(Mo Kα), mm ⁻¹	0.480	0.455	0.619
cryst dimens, mm	0.6 × 0.5 × 0.5	0.7 × 0.5 × 0.5	0.4 × 0.3 × 0.3
θ _{min} , θ _{max} , deg	3.07, 25.01	3.01, 4.99	3.20, 24.99
range of indices (<i>hkl</i>)	−18 to +17, 0−12, 0−21	±10, −11 to +12, 0−20	±11, −12 to +11, 0−16
rflns colld	2661	5301	4783
indepdt rflns	2514	5301	3790
data/restraints/params	2514/0/142	5300/0/297	3790/0/222
goodness-of-fit on <i>F</i> ²	1.083	1.107	1.025
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.0325, <i>wR</i> ₂ =0.0785	<i>R</i> ₁ =0.0267, <i>wR</i> ₂ =0.0766	<i>R</i> ₁ =0.0320, <i>wR</i> ₂ =0.0693
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0276, <i>wR</i> ₂ =0.0761	<i>R</i> ₁ =0.0314, <i>wR</i> ₂ =0.0794	<i>R</i> ₁ =0.0542, <i>wR</i> ₂ =0.0765
min, max resid density e Å ⁻³	−0.235, 0.272	−0.294, 0.294	−0.280, 0.326

(w), 858 (vs), 843 (vs), 781 (s), 748 (m), 683 (w), 654 (m), 617 (w), 482 (w), 459 (m) cm⁻¹. UV–vis (hexane, green) (nm): 305 (sh), 745 (ε = 220 cm² mmol⁻¹). MS (direct inlet, 70 eV, 110–115 °C, *m/z* (%)): 474 (M⁺, 6), 304 (100). Anal. Calcd for C₂₄H₄₀Si₂Zr: C, 60.5; H, 8.5. Found: C, 60.2; H, 8.6.

(C₅HMe₄)₂Zr[η²-C₂(SiMe₃)₂] (**2E**). The yield of turquoise crystals was 0.79 g (78%); mp 223 °C. ¹H NMR (C₆D₆): δ 0.14 (s, 18H, SiMe₃), 1.53 (s, 12H), 2.00 (s, 12H), 5.29 (s, 2H). ¹³C NMR (C₆D₆): δ 3.4 (q, 6C), 12.6 (q, 4C), 12.7 (q, 4C), 109.2 (d, 2C), 119.1 (s, 4C), 121.5 (s, 4C), 260.2 (s, 2C). IR (KBr): 1516 (s), 1439 (m), 1381 (m), 1238 (s), 1022 (w), 855 (vs), 828 (vs), 748 (s), 681 (w), 656 (m), 619 (w), 492 (w), 475 (m), 459 (m) cm⁻¹. UV–vis (hexane, turquoise) (nm): 338 (sh), 738 (w). MS (direct inlet, 70 eV, 115–120 °C, *m/z* (%)): 502 (M⁺, 4), 332 (100). Anal. Calcd for C₂₆H₄₄Si₂Zr: C, 62.0; H, 8.8. Found: C, 61.8; H, 8.8.

(C₅Me₅)₂Zr[η²-C₂(SiMe₃)₂] (**2F**). The yield of turquoise crystals was 0.80 g (75%); mp 241 °C. ¹H NMR (C₆D₆): δ 0.19 (s, 18H, SiMe₃), 1.76 (s, 30H). ¹³C NMR (C₆D₆): δ 4.0 (q, 6C), 11.8 (q, 10C), 118.8 (s, 10C), 260.5 (s, 2C). IR (KBr): 1516 (s), 1443 (m), 1377 (m), 1240 (s), 1024 (w), 855 (vs), 829 (s), 750 (m), 679 (w), 658 (m), 619 (w), 457 (m) cm⁻¹. UV–vis (hexane, turquoise) (nm): 360 (s), 725 (w, ε = 140 cm² mmol⁻¹). MS (direct inlet, 70 eV, 115–120 °C, *m/z* (%)): 530 (M⁺, 2), 360 (100). Anal. Calcd for C₂₈H₄₈Si₂Zr: C, 63.2; H 9.1. Found: C, 63.0; H, 9.2.

The MS spectra contain additional ions *m/z* 170, 155, 97, 73, and 70 in mutual abundances fitting to free BTMSA. The dissociation of **2C–F** probably occurs on the surface of the ionization chamber before the ionization. The intensities of M⁺ ions are therefore only tentative.

The EDX measurements of **2C–F** were carried out in order to clearly detect contents >2% of chemical elements with an atomic number >6. In all cases only sharp Kα signals of Si and Lα of Zr were visible.

Isolation of a Rearranged Dimer of 2B, [(μ-η⁵:η¹-C₅H₃Me)(η⁵-C₅H₄Me)(η¹-C₂H{SiMe₃)₂Zr(IV)]₂ (3B**).** **1B** (0.32 g, 1 mmol), Mg (0.025 g, 1.05 mmol), BTMSA (0.6 mL, 2.7 mmol), and THF (20 mL) were charged into an ampule, and this mixture was heated under stirring to 60 °C until all the magnesium had dissolved (ca. 20 h). The resulting yellow-brown solution was evaporated, and the residue was extracted by hexane to give a reddish-brown solution. The remained gray residue was further extracted until the point when only

an insoluble residue remained. The collected extracts were concentrated and cooled to −18 °C. Dirty white crystals were separated from the pale brown solution. The crystals were recrystallized from a saturated hexane solution by slow cooling. The yield of glittering white crystals was 0.18 g (43%). Suitable crystals were selected for the X-ray diffraction analysis which identified the compound to be **3B**. The solutions of **3B** in C₆D₆ were turning green at room temperature. The ¹H and ¹³C NMR spectra of such solutions indicated the presence of a mixture of compounds whose spectra could not be assigned.

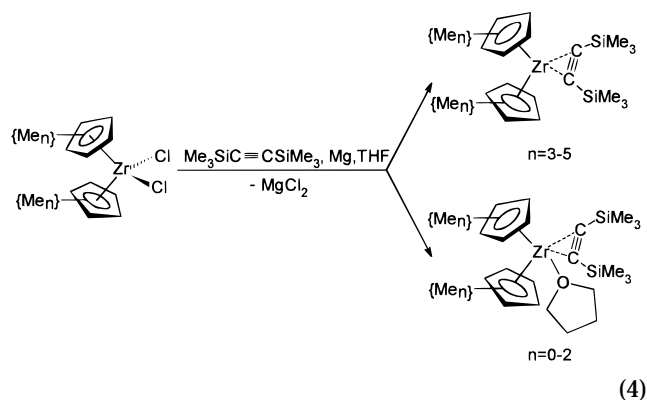
X-ray Crystal Structure Analyses of 2E, 2F, and 3B. Turquoise crystal fragments of **2E,F** and a pale green (nearly colorless) crystal fragment of **3B** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox (mBraun labmaster 130) and sealed by wax. The X-ray measurements were carried out on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ 0.710 69 Å) at room temperature. Crystal data were collected with a scan ratio 2θ/ω = 1. The structures were solved by Patterson and Fourier methods which revealed the locations of the non-hydrogen atoms. Their coordinates and anisotropic thermal parameters were refined at first using the SHELX-76 program.¹⁹ The final refinements were performed by full-matrix least-squares methods on all unique *F*_o² data using the SHELXL-93 program.²⁰ The hydrogen atom H(2) in **3B**, which was clearly located in a difference electron density map, was refined isotropically. All other hydrogen atom contributions were included using a riding model with C–H distances free to refine. The structures of **2E,F** and the structures of the corresponding Ti analogues—(C₅HMe₄)₂Ti[η²-C₂(SiMe₃)₂]⁴¹ and (C₅Me₅)₂Ti[η²-C₂(SiMe₃)₂]^{46,6a}—were found to be isomorphous. The PC ULM package¹⁹ was used for the further calculations. Crystal data are summarized in Table 1. The atomic coordinates and thermal parameters for **2E,F**, and **3B** are given in the Supporting Information.

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Results and Discussion

The reduction of the zirconocene dichlorides ($C_5H_5-nMe_n$) $_2ZrCl_2$ ($n = 1-5$) (**1B-F**) in THF by 1.05 equiv of magnesium in the presence of excess BTMSA afforded turquoise solutions for $n = 4$ and 5, a green solution for $n = 3$, and honey-yellow solutions for $n = 1$ and 2. The workup of these solutions consisting of the evaporation of the solvent in vacuum and extraction of the residue by hexane afforded turquoise crystalline compounds **2F** for $n = 5$ and **2E** for $n = 4$ and a green amorphous solid **2D** for $n = 3$. The honey-yellow solution obtained from **1C** also afforded a green amorphous solid **2C**. All these compounds were identified to be zirconocene-BTMSA derivatives ($C_5H_5-nMe_n$) $_2Zr[\eta^2-C_2(SiMe_3)_2]$ ($n = 2-5$) (**2C-F**) on the basis of X-ray crystal structure analyses of **2E,F** and 1H and ^{13}C NMR, IR, UV-vis, and MS spectra (see below). The compounds **2D-F** dissolve in THF to give green and turquoise solutions whereas **2C** gives a honey-yellow solution. This yellow color is typical of the THF adducts of the zirconocene-BTMSA complexes. The **1A**/Mg/BTMSA/THF system afforded a yellow solution from which the orange crystalline complex (C_5H_5) $_2Zr[\eta^2-C_2(SiMe_3)_2](THF)$ (**2A**·THF) has recently been isolated and its X-ray crystal structure has been determined.^{10a} The system with **1B** also yielded a dark yellow solution from which an ochre crystalline solid separated after partial evaporation of THF at room temperature. This product was not further investigated. Its conversion to **3B** after the total loss of THF in vacuum, analogous to the conversion of **2A**·THF into **3A** (see eq 3), leaves, however, no doubt that the ochre solid was **2B**·THF. These results imply that at room temperature the BTMSA complexes are generally formed according to eq 4.



The green and turquoise THF solutions of **2D,E** turned yellow when cooled to -30 and -80 °C, respectively, and the initial colors were restored after warming. No color changes occurred upon cooling of hexane and toluene solutions, and hence, the above color change apparently indicates the coordination of THF at low temperature. Only the THF solution of **2F** did not change color even when cooled to -196 °C.

Among the THF-containing complexes only **2C**·THF remained stable as **2C** after the loss of THF. The workup of the THF solution of **2B**·THF initiated by pumping off all THF in vacuum afforded a white crystalline compound as the sole product. Its X-ray crystal structure analysis proved that it is a rearranged dimer of **2B**, $[(\mu-\eta^5:\eta^1-C_5H_3Me)(\eta^5-C_5H_4Me)(\eta^1-C_2H-SiMe_3)_2Zr^{IV}]_2$ (**3B**) (see below), whose molecular struc-

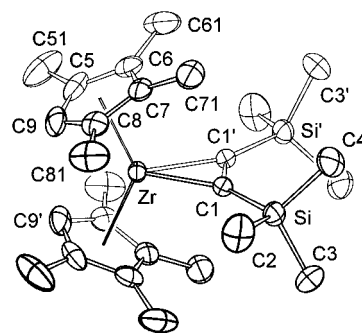


Figure 1. ORTEP drawing of **2E**, with ellipsoids drawn at the 30% probability level. Atoms Si', C(1)', C(9)', etc., are related to atoms Si, C(1), C(9), etc., by the symmetry operation $-x, y, 1/2 - z$.

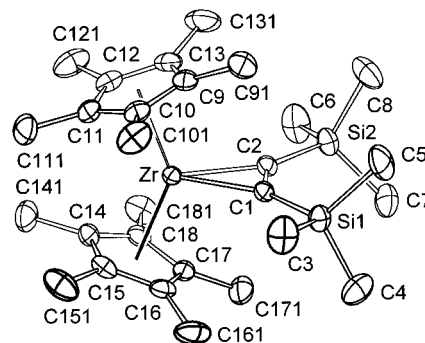


Figure 2. ORTEP drawing of **2F**, with ellipsoids drawn at the 30% probability level.

ture is very similar to that of **3A** (see eq 3). Compound **3B** appeared to be unstable as its hydrocarbon solutions slowly turned green at room temperature. This circumstance precluded its further characterization. Compound **3A** was reported to consist of two isomers in C_6D_6 solution and to dissociate in THF solution into **2A**·THF.^{10a}

Description of the Crystal Structures of 2E,F. The X-ray diffraction analysis revealed that both structures and the structures of the analogous titanium complexes (C_5HMe_4) $_2Ti[\eta^2-C_2(SiMe_3)_2]$ ⁴¹ (**4E**) and (C_5Me_5) $_2Ti[\eta^2-C_2(SiMe_3)_2]$ ^{6a} (**4F**), respectively, are isomorphous. The molecular structure of **2E** (Figure 1) is symmetrical with respect to a crystallographic 2-fold rotation axis which passes the Zr atom and bisects the acetylenic C-C bond. The overall appearance of the molecular structure of **2F** (Figure 2) is very similar to that of **2E**. The important molecular parameters of **2E,F** are listed in Table 2. The Zr-C_{ac} bond distance in **2E** is by 0.016 Å shorter than that in **2F** whereas the acetylenic C-C bond lengths are practically the same. A slightly longer Zr-C_{Cp} as well as (C-C)_{Cp} bond lengths in **2F** compared to **2E** have to be accounted for by both the electronic and steric effects of permethyl substitution. The Zr-CE vector is perpendicular to the ring plane in **2F**, and this is surprising because the steric hindrance between the C_5Me_5 ligands is clearly demonstrated by bending of the most exposed methyl carbon atoms C(111) and C(141) as much as 0.3 Å away from the ring planes farther away from the Zr atom. As a rule in metallocene structural chemistry,²¹ the M-C_{Cp} distance in **2E** is shorter for the hydrogen-bearing

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Table 2. Selected Bond Distances and Angles for 2E,F^a

	2E		2F	
(a) Bond Distances (Å)				
Zr–C(1)	2.202(2)	2.221(2)	2.216(2)	
Zr–CE(Cp ring)	2.230(3)	2.247(3)	2.253(3)	
Zr–C(Cp ring)(av)	2.529(3)	2.547(3)	2.553(3)	
C–C(Cp ring)(av)	1.402(4)	1.411(4)	1.411(4)	
C(1)–C(1'), C(1)–C(2), resp	1.316(3)	1.320(3)		
Si–C(1)	1.857(2)	1.858(2)	1.859(2)	
Si–C(2)	1.869(4)	1.871(4)	1.872(4)	
Si–C(3)	1.875(4)	1.879(4)	1.874(4)	
Si–C(4)	1.870(4)	1.882(4)	1.876(4)	
(b) Bond Angles (deg)				
CE–Zr–CE'	134.5(1)	139.0(1)		
C(1)–Zr–C(1')	34.8(1)	34.6(1)		
Zr–C(1)–C(1')	72.6(1)	72.5(1)	72.9(1)	
Si–C(1)–C(1')	135.4(2)	135.1(2)	135.9(2)	
ϕ^b	49.5	41.0		

^a One column of data is appropriate to 2E because of the symmetry. The left column for 2F is appropriate to atoms with lower numbers. ^b Dihedral angle between least-squares planes of the cyclopentadienyl rings.

Table 3. Comparison of Main Structural Parameters of 2E,F with (C₅HMe₄)₂Ti[η²-C₂(SiMe₃)₂] (4E) and (C₅Me₅)₂Ti[η²-C₂(SiMe₃)₂] (4F)^a

	2E	4E	2F	4F
Zr–C _{ac} ^b	2.202	2.106	2.219	2.124
Zr–CE ^b	2.230	2.092	2.250	2.114
C–C(Cp ring)	1.402	1.403	1.411	1.414
C _{ac} –C _{ac}	1.316	1.303	1.320	1.309
Si–C _{ac} ^b	1.857	1.853	1.859	1.856
CE–Zr–CE	134.5	134.9	139.0	138.6
Si–C(1)–C(1') ^b	135.4	135.9	135.5	135.8
ϕ^c	49.5	50.0	41.0	41.1

^a Structural data for 4E are taken from ref 4i, and those for 4F, from ref 6a. The accuracy of the diffraction measurements of all compounds was very similar. ^b Average values are taken for 2F and 4F. ^c Dihedral angle between least-squares planes of the cyclopentadienyl rings.

carbon atom (Zr–C(5) 2.509(3) Å) than for those bearing Me groups (e.g., Zr–C(7) 2.570(3) Å). This effect together with a smaller CE–Zr–CE angle in 2E (134.5°) compared to that in 2F (139.0°) brings about that the angle between planes of C₅ rings in 2E is by 8.5° larger ($\phi = 49.5^\circ$) than in 2F ($\phi = 41.0^\circ$). As a consequence, the metallocene skeleton in 2E offers a larger coordination space at the Zr atom in spite of the circumstance that the average Zr–C_{Cp} distance is by 0.02 Å shorter than in 2F. Both compounds differ from the analogous titanium compounds 4E,F mainly in the parameters controlled by a larger covalent radius and a lower electronegativity of the Zr atom (1.45 Å and 1.4 against 1.32 Å and 1.5 for Ti). The comparison of most important structural parameters of these Zr and Ti compounds is carried out in Table 3. Of these, the C_{ac}–C_{ac} bonds which are longer in 2E,F by ca. 0.01 Å than in 4E,F reflect a stronger coordination of BTMSA in the former compounds, as also follows from the comparison of spectroscopic parameters (see below). The bending of the acetylene molecule is the same in all mentioned compounds with the Si–C–C angle close to 135°. Apart from the fact that Zr–C bonds are by ca. 0.1 Å longer than the Ti–C bonds, the bent metallocene skeletons show the same CE–M–CE angles and the same dihedral angles ϕ between the cyclopentadienyl rings in pairs of C₅HMe₄ and C₅Me₅ compounds. The staggered

Table 4. NMR (δ , ppm), IR (cm⁻¹), and UV–Vis (λ , nm) Data for the BTMSA Ligand in 2C–F

Cpd	¹ H(Me)	¹³ C(Me) ^a	¹³ C(C≡C) ^a	ν (C≡C) ^b	λ
2C	0.03 s	2.1 q	258.2 s	1566	775
2D	0.14 s	2.8 q	260.0 s	1535	745
2E	0.14 s	3.4 q	260.2 s	1516	738
2F	0.20 s	4.0 q	260.5 s	1516	725

^a Chemical shifts for noncoordinated BTMSA (C₆D₆, 23 °C): ¹³C(Me) δ 0.2 q, ¹³C(C≡C) δ 113.8 s.²² ^b The band of the highest wavenumber in the relevant region.

mutual orientation of the cyclopentadienyl rings and the placement of the hydrogen atoms of the C₅HMe₄ rings in the hinge positions are the common features of these Zr and Ti compounds.^{4i,6a}

Spectroscopic Data for 2C–F. All the spectroscopic methods brought evidence of the strong coordination of BTMSA to the zirconocene moieties and confirmed that the molecular structures of all the compounds in hydrocarbon solutions do not differ from those found for 2E,F in the solid state. The EI-MS spectra registered the molecular ions in the range of intensities 2–8% and showed that the elimination of the BTMSA molecule is the main fragmentation channel. The fragmentation pattern typical of the free BTMSA molecule found in all the MS spectra, however, indicated that a thermal dissociation occurred on walls of the ionization chamber. The intensities of the molecular ions are inversely proportional to the temperature of evaporation and, hence, may reflect the degree of thermal dissociation and not the strength of the coordination bond. The sharp NMR lines and the absence of EPR signals agree with the expected diamagnetism of the Zr(II) compounds. ¹H and ¹³C NMR spectra resolved individual hydrogen and carbon atoms of the methylated cyclopentadienyl ligands and gave information on chemical shifts of the coordinated BTMSA molecule. Infrared spectra represent fingerprints of the cyclopentadienyl ligands (practically identical with the spectra of the zirconocene dichlorides), strong absorptions of the SiMe₃ groups at 828–855 cm⁻¹ and at 1240 cm⁻¹, and a strongly lowered ν (C≡C) vibration. The data pertinent to the BTMSA ligand are collected in Table 4.

All the NMR data show the dependence on the number of Me groups in compounds 2C–F. The increments per one Me group, however, vary widely. The comparison of these data with those for the analogous Ti complexes shows that shifts of δ have the same tendency although the absolute values as well as their differences differ ((C₅H_{5-n}Me_n)₂Ti[η²-C₂(SiMe₃)₂], for $n = 2-5$: ¹H(Me) δ -0.23 to +0.02, s; ¹³C(Me) δ 1.5–4.2, q; ¹³C(C≡C) δ 245.5–248.5, s).⁴ⁱ Among the NMR data, most relevant to the strength of the metal-to-BTMSA coordination is the downfield shift of the acetylenic carbon atoms, and this shows that the strength of the coordination bond increases from 2C to 2F and that the zirconocenes form even stronger complexes than the titanocenes. This is independently confirmed by the wavenumbers of the ν (C≡C) vibration. This vibration occurs in 2C–F at wavenumbers which are lower by about 100 cm⁻¹ with respect to the corresponding titanocene compounds, and the overall shift from the wavenumber of BTMSA (2107 cm⁻¹)²³ of 540–590 cm⁻¹ is the largest so far reported. It has to be mentioned that the chemical shifts found in 2C–F, as well as in

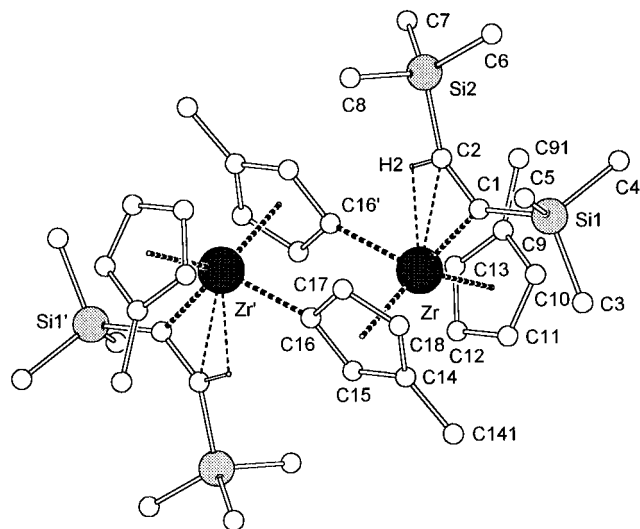


Figure 3. PLUTON²⁵ drawing of the molecular structure of **3B**. Atoms Zr', Si(1)', C(16)', etc., are related to atoms Zr, Si(1), C(16), etc., by the symmetry operation $-x, -y, -z$.

the titanocene compounds, fall into the range of values (190–270 ppm) which are assumed to be typical for alkynes acting as four-electron donors in metal complexes.^{4j,24} The donation of four π -electrons to the Zr(II) ion has to be, however, accompanied by an extensive back-donation of d^2 electrons into the LUMO of BTMSA. A widely used description of the compounds as metal-cyclopropene derivatives accounts for their reactivity in various coupling reactions^{9a} and fits to some structural features like the C–C bond distance close to the C=C bond length and the bending of the SiMe₃ substituents from the C–C vector (Table 2); however, the presence of a zirconocene Zr(IV) compound is hardly compatible with the color of the compounds. The sole absorption band in the region 440–2000 nm occurring close to 750 nm (Table 4) does not fit to the presence of either a Zr(IV) or Zr(II) ion. We suggest that it arises from a CT $\pi^* \rightarrow d$ transition in the above mentioned tentative model with the both d^2 electrons residing in a low-energy nonbonding orbital of the coordinated BTMSA. A similar absorption band was also observed in the titanocene analogues with λ_{max} in the range 920–1060 nm.⁴ⁱ The molar extinction coefficients 100–200 cm² mmol⁻¹ for these bands may correspond to their suggested nature.

Description of the Crystal Structure of $[(\mu-\eta^5: \eta^1-C_5H_3Me)(\eta^5-C_5H_4Me)(\eta^1-C_2H\{SiMe_3\}_2)Zr(IV)]_2$ (3B**).** The X-ray diffraction analysis of **3B** revealed that it is a centrosymmetric dimer bis[$(\mu-(\eta^5:\eta^1-3$ -methylcyclopentadienylyl)(η^5 -methylcyclopentadienylyl)($\eta^1-1,2$ -bis(trimethylsilyl)ethenyl)zirconium(IV)] linked via bridging methylcyclopentadienyl ligands. One hydrogen atom originating from each bridging ligand is apparently transferred to an η^2 -coordinated BTMSA to give a $\eta^1-1,2$ -bis(trimethylsilyl)ethenyl ligand. The drawing of **3B** with its atom numbering scheme is shown in Figure 3. Selected interatomic distances and valence angles are listed in Table 5. The molecular structure

Table 5. Selected Bond Distances and Angles for **3B**

(a) Bond Distances (Å)			
Zr–C(1)	2.256(3)	Zr–C(2)	2.557(3)
Zr–C(9)	2.601(4)	Zr–C(10)	2.542(5)
Zr–C(11)	2.486(5)	Zr–C(12)	2.495(5)
Zr–C(13)	2.558(4)	Zr–C(14)	2.535(4)
Zr–C(15)	2.481(3)	Zr–C(16)	2.529(3)
Zr–C(16')	2.359(3)	Zr–C(17)	2.468(3)
Zr–C(18)	2.509(4)	Zr–CE(1)	2.247(5)
Zr–CE(2)	2.197(4)	Zr–H(2)	2.150(37)
Zr'–C(16)	2.359(3)	C(1)–C(2)	1.324(5)
Si(1)–C(1)	1.859(3)	C(2)–H(2)	0.933(37)
Si(2)–C(2)	1.874(4)	Si(1)–C(Me) _{av}	1.864(5)
C–C(9–13) _{av}	1.384(7)	Si(2)–C(Me) _{av}	1.861(5)
C–C(14–18) _{av}	1.413(5)	Zr–Zr'	4.075(1)
(b) Bond Angles (deg)			
C(1)–Zr–C(2)	31.1(1)	C(1)–Zr–C(16')	120.1(1)
C(1)–Zr–H(2)	51.7(10)	C(16')–Zr–H(2)	68.7(10)
C(1)–Zr–CE(1)	102.0(1)	C(16')–Zr–CE(1)	102.2(1)
C(1)–Zr–CE(2)	103.9(1)	C(16')–Zr–CE(2)	96.6(1)
CE(1)–Zr–H(2)	109.7(10)	CE(2)–Zr–H(2)	116.2(10)
CE(1)–Zr–CE(2)	134.1(1)	C(1)–C(2)–H(2)	115.7(23)
Zr–C(1)–C(2)	87.1(2)	Si(1)–C(1)–C(2)	132.0(3)
Zr–C(2)–C(1)	61.8(2)	Si(2)–C(2)–C(1)	138.9(3)
Zr–C(2)–H(2)	54.3(23)	Si(2)–C(2)–H(2)	105.2(23)

of **3B** is very similar to the structure of the analogous compound **3A** obtained from **2A**·THF after the loss of THF.^{10a} Most of the distances and angles are the same as in **3A** within the accuracy of measurement. The most interesting feature of both these compounds is the coordination mode of the ethenyl ligand where slight differences between **3A** and **3B** are discernible. The Zr–C(1) σ -bond is the shortest Zr–C bond in the molecule but the Zr–C(2) distance falls into the range of Zr–C_{sp} π -bond lengths. The hydrogen atom H(2) at this carbon atom is inclined toward the Zr atom to attain the distance of 2.15 Å. In comparison with the structure of **3A** the Zr–C(1) distance is by 0.01 Å longer and the Zr–C(2) distance by 0.01 Å shorter. The Zr–H(2)–C(2) angle is by 9.6° larger than that in **3A**; however, the Zr–H(2) distance is virtually the same. The agostic interaction between the H(2) and Zr atoms was assumed on the basis of this distance and NMR arguments drawn from the behavior of the C(2)–H(2) fragment.^{10a} A larger difference between the Si(2)–C(2)–C(1) (138.9(3)°) and the Si(1)–C(1)–C(2) (132.0(3)°) angles is also at variance with the values of 135.3 and 133.3° found in **3A**.^{10a}

The methyl substituents in the zirconocene moieties are orientated as to minimize the steric strain arising from their presence. The Zr–CE(2) distance is by 0.05 Å shorter than the Zr–CE(1) distance in spite of a remarkable distortion of the former ring. The angle C(15)–C(16)–C(17) at the bridging carbon atom amounts to only 103.0(3)° whereas the most oblique angle in the CE(1) ring is the C(10)–C(9)–C(13) angle, equal to 106.7(4)°, at the carbon atom bearing the Me group. The bridging bond Zr'–C(16) of 2.359(3) Å length is by 0.1 Å longer than the Zr–C(1) bond but distinctly shorter than the coordination bonds to sp² carbon atoms of the C₅H₄Me rings and to C(2) of the ethenyl group.

Outlook. The stable, well-characterized methyl-substituted zirconocene–BTMSA complexes may be used as starting materials for the coupling reactions with aldehydes, ketones, olefins, nitriles and acetylenes.²⁶ Compared to the zirconocene–alkyne derivatives so far used the stabilization by the unpleasant and

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expensive PMe_3 can be avoided and the regioselectivity in the above mentioned coupling reactions can be increased by the discrimination of the coordination space at the zirconium center. A recent study of the regioselectivity and diastereoselectivity of the insertion of aldehydes into the zirconocene–alkyne complexes afforded rather poor achievements.²⁷ The use of the $(\text{C}_5\text{Me}_5)_2\text{Zr}$ and $(\text{C}_5\text{HMe}_4)_2\text{Zr}$ –BTMSA complexes gives new prospects to this type of reactions, where the selectivity is controlled by the size of the available coordination space. A dramatic change in the reactivity has been recently found in the titanocene series of the BTMSA complexes, where $(\text{C}_5\text{Me}_5)_2\text{Ti}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ has been found to be a superior catalyst for the selective linear head-to-tail dimerization of 1-alkynes whereas the $(\text{C}_5\text{HMe}_4)_2\text{Ti}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ complex was practically inactive.²⁸ In addition, the kinetics of coupling reactions of the substrates bearing a polar substituent can be influenced by the Lewis acidity of the zirconium atom

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which is controlled by the methyl substituents at the cyclopentadienyl ligands. This has been demonstrated by a decrease in affinity to THF of compounds **2C–F** with the increasing number of methyl substituents. The investigation of the catalytic activity of the new zirconocene–BTMSA complexes and its comparison to that of the titanium analogues will be an emphasis in our further research work.

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Supporting Information Available: Tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, bond distances, valence angles, least-squares planes and atomic deviations therefrom, and important intermolecular contacts and figures giving views of the unit cell for **2E,F** and **3B** (33 pages). Ordering information is given on any current masthead page.

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