

Notes

Novel Ti₆, Zr₃, and Zr₆ Complexes from Branched Polyynes and Titanocene as Well as ZirconocenePaul-Michael Pellny, Vladimir V. Burlakov,[†] Wolfgang Baumann, Anke Spannenberg, Rhett Kempe, and Uwe Rosenthal*

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Received March 22, 1999

Summary: Reactions of the branched polyynes tris(*tert*-butylbutadiynyl)benzene (1,3,5-(*t*BuC≡CC≡C)₃C₆H₃) (**1**) with the metallocene sources Cp₂Ti(η²-Me₃SiC≡CSiMe₃) (**2**) and Cp₂Zr(THF)(η²-Me₃SiC≡CSiMe₃) (**3**; THF = tetrahydrofuran) led to diverse novel organometallic Ti₆ (**4**), Zr₃ (**5**), and Zr₆ (**6**) complexes depending on the metals, the polyynes, and the stoichiometries employed in the conversions. The new complexes have been characterized spectroscopically. Additionally X-ray crystal structure analyses were performed for **4** and **6**.

Branched metal complexes containing carbon–carbon triple bonds in the side chains¹ are potentially useful for building up carbon-rich networks² and nanoarchitectures for material science.³ This includes the areas of special polymers,⁴ liquid crystals,⁵ NLO systems,⁶ electron storage,⁷ etc.

After earlier investigations into disubstituted 1,3-butadiynes R(C≡C)₂R,⁸ α,ω-diyne R(C≡C)X(C≡C)R,⁹ as well as linear octatetraynes R(C≡C)₄R,¹⁰ we recently turned our attention to branched polyynes. Herein we report on the results of the reactions of tris(*tert*-butylbutadiynyl)benzene (1,3,5-(*t*BuC≡CC≡C)₃C₆H₃) (**1**) and of hexakis(*tert*-butylbutadiynyl)benzene (1,2,3,4,5,6-(*t*BuC≡CC≡C)₆C₆) with the metallocene sources

Cp₂Ti(η²-Me₃SiC≡CSiMe₃) (**2**)¹¹ and Cp₂Zr(THF)(η²-Me₃SiC≡CSiMe₃) (**3**; THF = tetrahydrofuran).¹² These conversions are highly dependent on the metals, the substituents R attached to the polyyne, and the stoichiometry employed and lead to diverse novel organometallic Ti₆, Zr₃, and Zr₆ complexes.

The triskelic^{1d} polyyne **1**, which so far has not been known, is synthesized from 1,3,5-tribromobenzene and *tert*-butylbutadiyne via a Sonogashira coupling reaction.¹³

In the reaction of **1** with 6 equiv of complex **2**, which easily releases bis(trimethylsilyl)acetylene and thus is a superb preparative source for the unstable titanocene

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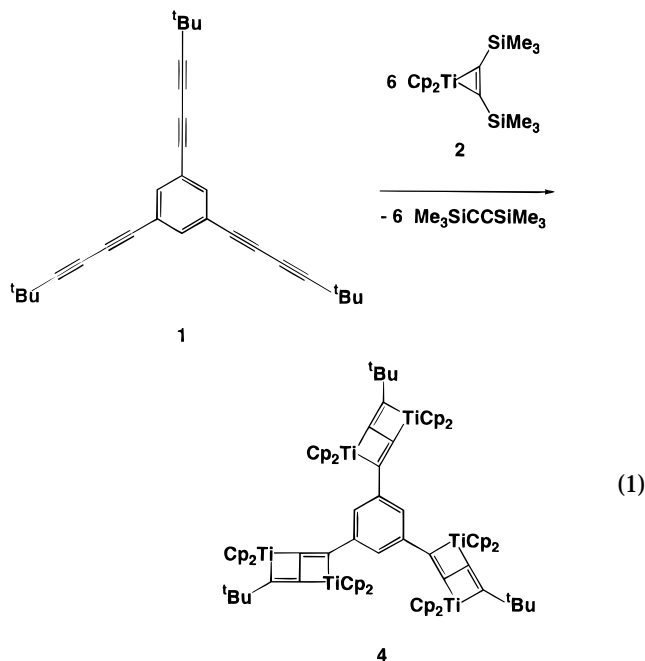
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"Cp₂Ti",¹¹ the dark green complex **4** is formed (eq 1).

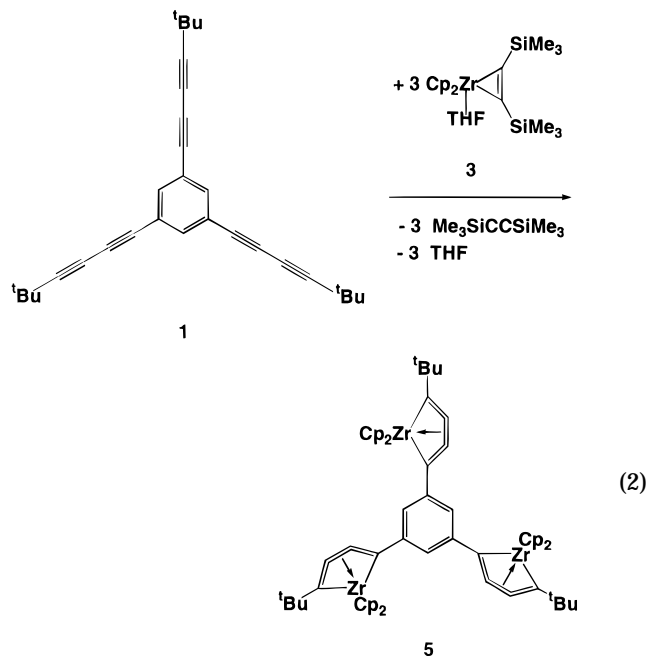


The titanium compound **4** is highly soluble in THF, slightly less soluble in benzene, and only sparingly soluble in *n*-hexane. The IR spectrum shows no band in the range expected for a complexed C–C triple bond, that is between 1900 and 1600 cm⁻¹. The ¹H [δ = 1.42 (s, 27H, CMe₃), 5.66 (s, 60H, Cp), 7.24 (s, 3H, aromatic)] and ¹³C NMR spectra [δ = 126.8, 145.7, 218.0, 240.2 (C≡C)] confirm an identical coordination of all three butadiynyl substituents by two titanocene cores each.

The crystal structure analysis of **4**¹⁴ (Figure 1) shows a central benzene ring, which is substituted by three intact 1,4-disubstituted tetrahydro- μ -(1-3- η):(2-4- η)-*trans,trans*-butadiene units¹⁰ [C11–C12, 1.332(9); C12–C13, 1.495(9); C13–C14, 1.326(10) Å] between two titanocene cores [Ti3–C11, 2.073(7); Ti3–C12, 2.331(7); Ti3–C13, 2.147(8); Ti4–C12, 2.150(8); Ti4–C13, 2.339(8); Ti4–C14, 2.105(8) Å]. Those "zigzag butadienes" are, together with the according metals, nearly planar and are connected to each other through the benzene ring. While two of these units are, in a rough approximation, coplanar to the benzene core, the third substituent is fairly explicitly tilted out of this plane. The angle between these two planes is about 96°. Sterical reasons should be assumed to explain this structural feature.

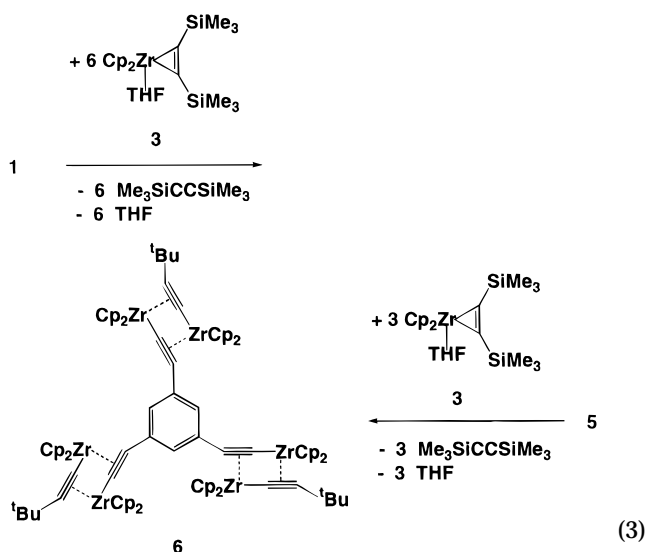
The reaction of **1** with the zirconocene source **3**¹² progresses principally in a different way. Using 3 equiv of **3**, the brownish red zirconium compound **5** is generated, as shown by eq 2. Compound **5** should be conceived as a benzene derivative substituted by three five-membered zirconacyclocumulene moieties. Metallacyclocumulenes as products of reactions of substituted butadiynes with metallocenes are well-known,^{8b,c,e} and their peculiar and surprising stability has been vali-

(14) Crystal data for **4**: triclinic, *P* $\bar{1}$, *a* = 16.654(2) Å, *b* = 17.857(2) Å, *c* = 18.487(2) Å, α = 101.40(2)°, β = 102.60(2)°, γ = 115.00(2)°, *V* = 4594.2(11) Å³, *Z* = 2, ρ = 1.263 g cm⁻³, 13 602 measured reflections, 13 602 symmetry-independent reflections, 7037 of which were considered as observed (*I* > 2 σ (*I*)), 707 refined parameters, *R*₁ = 0.086, *wR*₂ = 0.219, residual electron density 1.065 e Å⁻³ (20).



dated by theoretical calculations.¹⁵ The structural assignment follows ¹³C NMR spectroscopical investigations of **5** [105.9, 114.1 (β -C), 175.7, 193.2 (α -C)], as compared to previously isolated and spectroscopically characterized five-membered metallacyclocumulenes Cp₂M(η ⁴-1,2,3,4-RC₄R) [M = Ti, R = Ph, 103.1 (β -C), 176.8 (α -C)^{8c}; M = Ti, R = ^tBu, 94.7 (β -C), 181.9 (α -C);^{8c} M = Zr, R = ^tBu, 105.5 (β -C), 186.4 (α -C)^{8b}].

Treatment of **1** with 6 equiv of **3**, or reaction of **5** with a further 3 equiv of **3**, leads to the orange red complex **6** (eq 3). The IR spectrum of the zirconium compound **6**



shows two bands in the expected range for complexed C–C triple bonds at 1839 and 1772 cm⁻¹. The ¹H [δ = 1.65 (s, 27H, CMe₃), 5.54 (s, 60H, Cp), 8.13 (s, 3H, aromatic)] and ¹³C NMR spectra [δ = 157.7, 165.6, 214.3, 231.6 (C≡C)] confirm an identical coordination of all butadiynyl substituents, here by two zirconocene cores each.

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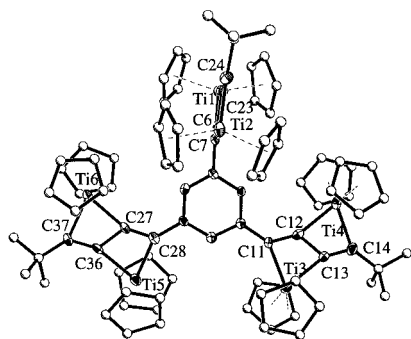


Figure 1. ORTEP view of **4** (for clarity only atoms regarded significant are drawn as 30% probability ellipsoids). Selected average bond lengths (Å) and angles (deg): C11–C12, 1.332(9); C12–C13, 1.495(9); C13–C14, 1.326(10); Ti3–C11, 2.073(7); Ti3–C12, 2.331(7); Ti3–C13, 2.147(8); Ti4–C12, 2.150(8); Ti4–C13, 2.339(8); Ti4–C14, 2.105(8); C11–C12–C13, 125.8(7); C12–C13–C14, 126.8(7); C11–Ti3–C13 73.2(3); C12–Ti4–C14, 72.8(3).

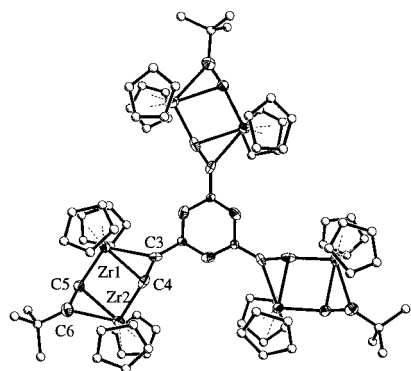


Figure 2. ORTEP view of **6** (for clarity only atoms regarded significant are drawn as 30% probability ellipsoids). Selected average bond lengths (Å) and angles (deg): Zr1–C3, 2.384(13); Zr1–C4, 2.402(12); Zr2–C5, 2.448(12); Zr2–C6, 2.443(14); Zr1–C5, 2.183(14); C4–C5, 3.003 (as determined with XP); Zr2–C4, 2.18(2); C3–C4–Zr2, 173.3(10); Zr1–C5–C6, 172.8(12); C3–Zr1–C5, 112.5(4); C4–Zr2–C6, 109.7(5).

The crystal structure analysis of **6**¹⁶ (Figure 2) provides clear evidence for the 3-fold bond cleavage of the substituents' C–C single bonds induced by the zirconocene fragments [C4–C5, 3.003 Å]. Contrasting the structure of complex **4** (as described above) an almost planar arrangement of all six zirconium atoms and the benzene linkage is verified for complex **6**.

All four Zr–C bond distances of the two π -coordinated C–C triple bonds [Zr1–C3, 2.384(13); Zr1–C4 2.402(12); Zr2–C5, 2.448(12); Zr2–C6, 2.443(14) Å] as well as both Zr–C σ -bonds [Zr1–C5, 2.183(14); Zr2–C4, 2.18(2) Å] in **6** are very much in the expected range as established by comparable compounds.¹⁰

When employing the corresponding hexakis(*tert*-butylbutadiynyl)benzene (^tBuC \equiv CC \equiv C)₆C₆¹⁷ in analogous reactions, we have so far not been able to obtain any defined complexes with either **2** or **3**, the reason assum-

ingly being sterical restrictions, which are already indicated in the structure of **4**.

Experimental Data

All research was carried out under the exclusion of oxygen and moisture. Compound **1** was prepared in analogy to ref 17.

Compound 1. In a boiling suspension of 1500 mg (4.77 mmol) of 1,3,5-tribromobenzene, 500 mg (0.72 mmol) of PdCl₂(PPh₃)₂, 270 mg (1.44 mmol) of CuI, and 80 mL of Et₃N were dissolved (in three portions in intervals of 12 h) altogether 3185 mg (30 mmol) of *tert*-butylbutadiyne.¹⁸ After refluxing for another 12 h the mixture was allowed to cool off and was filtered over celite, and the residue was washed with petrol ether. The solvents were removed under reduced pressure. Chromatographical workup on silica gel, elution with *n*-pentane, and recrystallization from ethyl acetate yielded 725 mg of **1** (39 %) as light yellow crystals; mp, 187–188 °C. Anal. Calcd for C₃₀H₃₀ (390.57): C, 92.26; H, 7.74. Found: C, 91.91; H, 7.87. NMR (Bruker-ARX-400, 297K). ¹H NMR (CDCl₃): δ = 1.30 (s, 27 H, CMe₃), 7.46 (s, 3 H, aromatic). ¹³C NMR (CDCl₃): δ = 28.3 (CMe₃), 30.4 (CMe₃), 63.5, 73.7, 75.6, 93.3 (C=C), 123.2, 135.9 (aromatic). IR (Nujol): 2238 cm⁻¹ (ν (C=C)). MS (70 eV): *m/z* 390 ([M]⁺), 375 ([M – Me]⁺).

Compound 4. A solution of 59 mg (0.15 mmol) of **1** in about 10 mL of THF was added to a solution of 316 mg (0.91 mmol) of **2** in 10 mL of THF. The color of the mixture darkened instantly, and after stirring for 48 h at room temperature the solution was dark green. All volatile material was removed under reduced pressure, and the residue was redissolved in 5 mL of THF and layered with 10 mL of *n*-hexane. After a few days at room temperature green crystals precipitated, which were washed with cold *n*-hexane and dried in vacuo to yield 220 mg (73%) of **4**; mp, >270 °C. Anal. Calcd for C₉₀H₉₀Ti₆ (1458.98): C, 74.09; H, 6.22. Found: C, 73.75; H, 6.29. NMR (Bruker-ARX-400, 297K). ¹H NMR (THF-*d*₆): δ = 1.42 (s, 27 H, CMe₃), 5.66 (s, 60 H, Cp), 7.24 (s, 3 H, aromatic). ¹³C NMR (THF-*d*₆): δ = 33.1 (CMe₃), 43.1 (CMe₃), 107.3 (Cp), 126.5 (aromatic), 126.8 (C=C), 132.1 (aromatic), 145.7, 218.0, 240.2 (C=C).

Compound 5. To a solution of 250 mg (0.54 mmol) of **3** in 5 mL THF was added a solution of 70 mg (0.18 mmol) of **1** in 5 mL of THF. The color changed within a few minutes, and stirring for 48 h at room temperature resulted in a brownish red solution. After removal of the volatile material, the residue was washed three times with cold *n*-hexane (–30 °C) and dried under vacuum. The yield was 168 mg (88%); mp, >270 °C. Anal. Calcd for C₆₀H₆₆Zr₃ (1054.80): C, 68.32; H, 5.73. Found: C, 68.29; H, 6.02. NMR (Bruker-ARX-400, 297K). ¹H NMR (THF-*d*₆): δ = 1.69 (s, 27 H, CMe₃), 5.57 (s, 30 H, Cp), 8.72 (s, 3 H, aromatic). ¹³C-NMR (THF-*d*₆): δ = 33.7 (CMe₃), 38.5 (CMe₃), 105.9, 114.1 (β -C), 137.6, 138.4 (aromatic), 175.7, 193.2 (α -C).

Compound 6. Solutions of 506 mg (1.09 mmol) of **3** and of 48 mg (0.15 mmol) of **1**, both in about 5 mL of THF, were combined. The color of the mixture immediately darkened and became dark green after 48 h at room temperature. All volatile material was removed in vacuo, the residue was redissolved in 3 mL of THF, and the concentrated solution was stored at –78 °C to induce precipitation. In a few days there appeared orange red crystals in the dark green solution. The mother liquor was decanted; the crystals were washed with cold *n*-hexane and recrystallized from warm THF to afford 190 mg

(16) Crystal data of **6**: trigonal, *R*3c, *a* = *b* = 25.010(4) Å, *c* = 36.369(7) Å, *V* = 19701(6) Å³, *Z* = 6, ρ = 1.033 g cm⁻³, 12 442 measured reflections, 3862 symmetry-independent reflections, 3384 of which were considered as observed (*I* > 2 σ (*I*)), 212 refined parameters, *R*₁ = 0.071, *wR*₂ = 0.207, residual electron density 1.095 e Å⁻³ (20).

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(90 %) of **6**; mp, >270 °C. Anal. Calcd for C₉₀H₉₀Zr₆ (1710.13): C, 62.88; H, 5.28. Found: C, 62.93; H, 5.55. NMR (Bruker-ARX-400, 297K). ¹H NMR (THF-*d*₈): δ = 1.65 (s, 27 H, CMe₃), 5.54 (s, 60 H, Cp), 8.13 (s, 3 H, aromatic). ¹³C NMR (THF-*d*₈): δ = 33.9 (CMe₃), 38.2 (CMe₃), 102.9, 103.3 (Cp), 132.5, 137.5 (aromatic), 157.7, 165.6, 214.3, 231.6 (C≡C). IR (Nujol): 1839 and 1772 cm⁻¹ (ν(C≡C) coord).

Acknowledgment. We gratefully acknowledge the financial support of the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as "supplementary publication no. CCDC-114272 and no. CCDC-114273". Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, U.K. (Fax: International code +(1223) 336-033. E-mail: deposit@ccdc.cam.ac.uk.) A figure of an ORTEP diagram and tables of crystallographic data, atom, refinement, and bond distances and angles are available free of charge via the Internet at <http://pubs.acs.org>.

OM9901980