Olefin Polymerization Catalysts

Reactions of Titanium and Zirconium Derivatives of Bis(trimethylsilyl)acetylene with Tris(pentafluorophenyl)borane: A Titanium(III) Complex of an Alkynylboranate **

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Dedicated to D. habil. Erhard Kurras
on the occasion of his 75th birthday

Special cations, formed by the formal abstraction of a methyl anion from zirconocene dimethyl complexes with the help of the strong Lewis acid $B(C_6F_5)_3$, introduced by Ewen and Marks, are highly active catalysts for the polymerization of α-olefins.[1] It has become evident that other zirconocene complexes (for example, of olefins, alkynes, butadienes) can also undergo a similar activation and thus may be suitable precursors for polymerization catalysts.[2]

Recently we described[3] that titanocene and zirconocene complexes of silylalkynes, such as $[Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (Cp' = substituted or unsubstituted $\eta^5\text{-}C_5H_5$) offer a rich chemistry of this type with boron-containing reagents. Especially interesting are the titanium complexes because dissociation of the alkyne ligands and C–H activation of the Cp ligands are possible (Scheme 1). Cationic complexes of type **A** were formed with $[HNMe_3][BPh_4]$,[3a] whereas an electrophilic substitution of an H atom of one $\eta^5\text{-}C_5H_5$ ring or of one methyl group of a Cp* ligand (Cp* = C_5Me_5) occurred with $B(C_6F_5)_3$, and paramagnetic zwitterionic Ti^{III} complexes of types **B**[3b,c] or **C**[3d,e] were formed.

Similar compounds,[2] such as $[Cp\{C_5H_4B(C_6F_5)_3\}Zr(acac)]$ (acac = 2,4-pentanedione (acetylacetone))[4] or $[Cp\{C_5H_4BH(C_6F_5)_2\}Zr\{\sigma\text{-}C(Et){=}CHEt\}]$,[5] were described also. The functionalization of the Cp* ligands is the same in reactions of Cp* silylalkyne zirconocene complexes as for the titanium compounds of type **C**. However, the alkyne does not

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Supporting information (syntheses and details of X-ray structure investigations) for this article is available on the WWW under http://www.angewandte.org or from the author.

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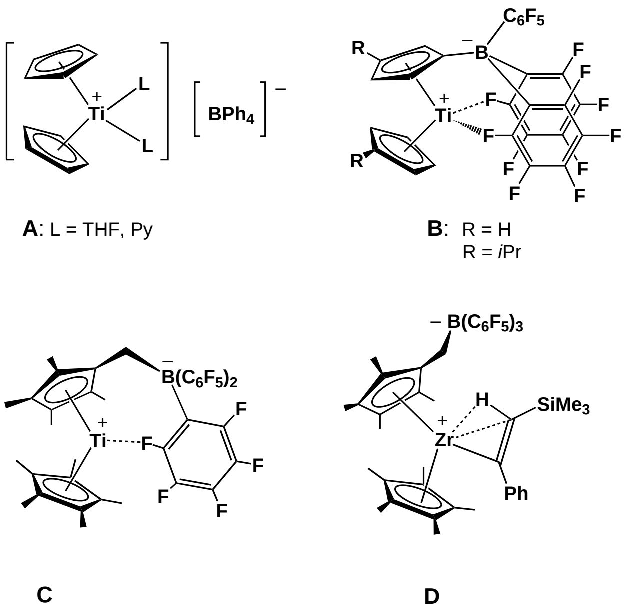


Scheme 1. Typical structures of boron-containing titanocene and zirconocene complexes

dissociate but binds the H atom under formation of an agostic alkenyl compound of type **D**.[3d]

Herein we report the reactions of complexes *rac*-[(ebthi)M(η^2-$Me_3SiC_2SiMe_3$)],[6] (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with $B(C_6F_5)_3$,[1] which proceed totally differently for Ti and Zr complexes.[7] The reaction of the Zr complex occurs as for the type **D** complexes with an electrophilic substitution at an H atom of the Cp ring to give an alkenyl compound **1** (Scheme 2). At room temperature the ^{1}H NMR spectra of **1** display at very broad resonance signals, which become sharp on cooling to 252 K and broaden again at lower temperatures. The poor solubility (crystallization upon cooling) prevents a deeper insight into the dynamics of the molecule, but at 252 K two species in a 2:1 ratio are evident. They undergo chemical exchange and exhibit the number of NMR signals expected from their solid state structures (see below). One plausible explanation of this dynamic behavior could be a hindered rotation of the alkenyl group around the C–Zr bond. A reason for the hindered rotation could be the agostic Zr-H-C interaction or the proximity of one silyl group to one C_6F_5 group.

The molecular structure of **1**[8] (Figure 1) shows the typical (ebthi)Zr-part, which is substituted in 3-position by the boranate. One *ortho* F atom coordinates to the zirconium center, therefore the corresponding F–C_{ring} bond is elongated. This coordination is also evident from the ^{19}F NMR signal which, at $\delta = -200.2$ ppm, is shifted to extremely high field.

The alkenyl group is σ bonded to the Zr center and has an additional agostic interaction,[9] indicated by the typical Zr-C14-C13 angle of 87.4 (4)°, similar to that found in **D** (86.5°).[3d] Additionally, the small coupling constant ^1J(C,H) of 91 Hz at C13 is characteristic for an agostic interaction.[9]

The preparation of complex **1** demonstrates the importance of the proper sequence when adding reagents to achieve catalytic activity. If the alkyne complex *rac*-[(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$)] is first treated with ethene to yield the zirconacyclopentane *rac*-[(ebthi)Zr(C_4H_8)] and this is subsequently activated by $B(C_6F_5)_3$, an active catalyst for polymerization results.[10a] But if the borane is added to the alkyne

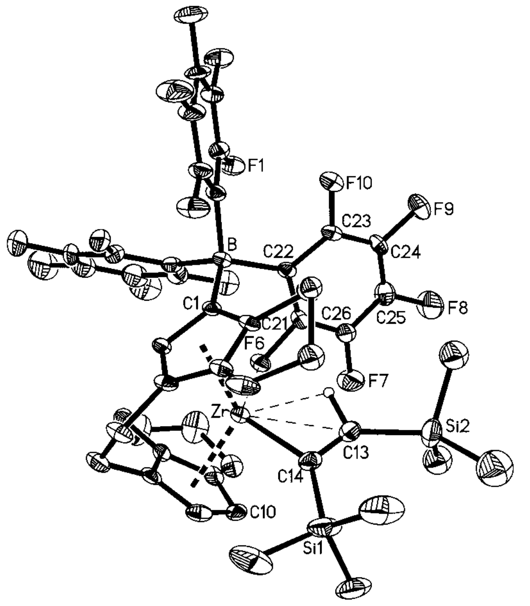
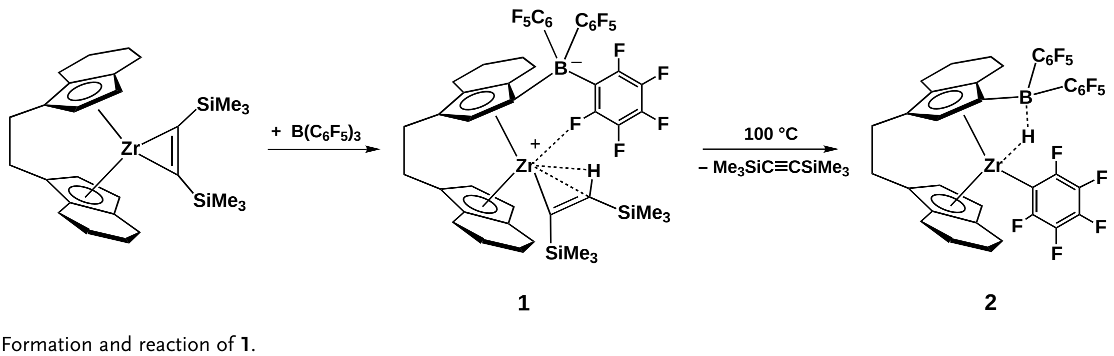


Figure 1. ORTEP plot of **1**. The thermal ellipsoids are set at 30% probability. For clarity the hydrogen atoms (with exception of H13) and one position of the disordered groups are omitted. Selected bond lengths [Å] and angles [°]: C1-B 1.640(9), Zr-F6 2.379(3), C21-F6 1.421(6), C26-F7 1.332 (8), C25-F8 1.377(8), C24-F9 1.361(7), C23-F10 1.343(7), Zr-C14 2.259(7); C1-B-C22 108.2(5), Zr-C14-C13 87.4(4).



Scheme 2. Formation and reaction of **1**.

compound first, complex **1** is formed, which does not react with ethene and, accordingly, is inactive in polymerization. The similar complex **D** is active in ethene polymerization, presumably because it has no Zr–F interaction.

If solutions of **1** are heated to 100 °C, the alkyne is eliminated and one B–C bond is cleaved with a subsequent transfer of a pentafluorophenyl group from boron to zirconium, whereupon complex **2** with one μ-H atom between boron and the zirconium center is formed (Scheme 2) Such a transfer of C_6F_5 from boron to zirconium[10b] is known, as is the μ-H atom type of structure.[10c] It is possible to describe compound **2** either as Zr^{IV} σ-C_6F_5 hydrido complex with an electroneutral borane ligand or alternatively as a zwitterionic betaine-boranate.

The resonance signal of the hydride unit is located in the same region of the ^{1}H NMR spectra as the signals of the ebthi groups and was identified only by ^{11}B-decoupling experiments ($\delta = 0.82$ ppm). During the thermal interconversion of **1** into **2** the high-field shifted ^{19}F NMR signal disappeared, which indicates that there is no F–Zr interaction in **2**.

The molecular structure of **2**[11] (Figure 2) displays the typical (ebthi)Zr-part, substituted by the diaryl boron unit $B(C_6F_5)_2$. The Zr-H-B bridge of **2** has atomic distances typical for this type of structure.[10c]

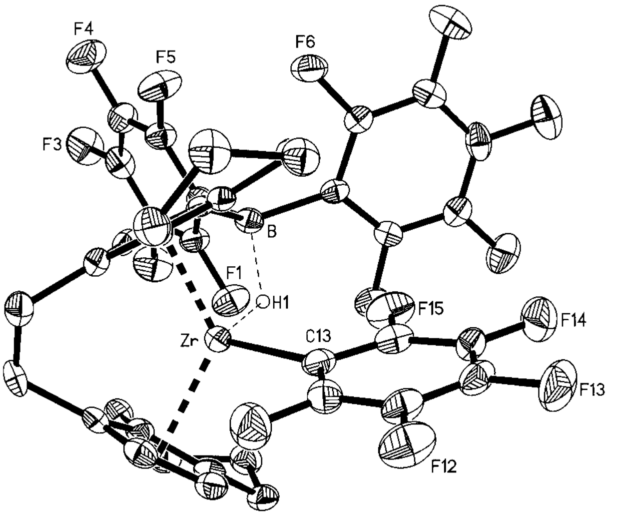
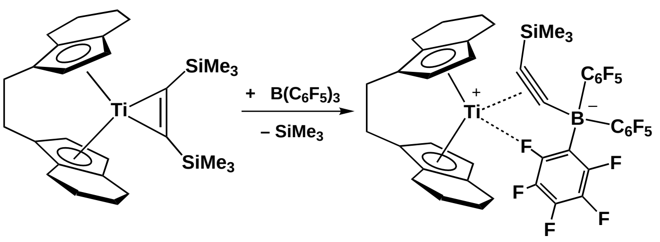


Figure 2. ORTEP plot of **2**. The thermal ellipsoids are set at 30% probability. For clarity the hydrogen atoms (with exception of H1) are omitted. Selected bond lengths [Å]: Zr-C13 2.334(6), B-H1 1.481, Zr-H1 2.113.

The Ti complex *rac*-[(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] reacts, surprisingly, in a totally different way with $B(C_6F_5)_3$ to the Zr compound (Scheme 3). Neither an electrophilic substitution of an H atom nor an elimination of the alkyne were observed, but after a C–Si bond cleavage and a subsequent B–C bond formation the first zwitterionic titanocene(III) η^2-(trimethylsilyl)alkynylboranate complex *rac*-[{(ebthi)Ti}$^+${η^2-$Me_3SiC_2B(C_6F_5)_3$}$^-$] (**3**) was obtained. Similar Si–C bond cleavage reactions of silylalkynes $Me_3SiC{\equiv}CR$ by transition-metal complexes under formation of σ-alkynyl complexes $[L_nM(SiMe_3)(C{\equiv}CR)]$ are known for late-transition-metal compounds.[12]



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Scheme 3. Conversion of *rac*-[(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] into **3**.

The green compound **3** is paramagnetic (EPR in toluene at 20 °C: $g = 1.980$, $\Delta H = 6.7$ G, $a_{Ti} = 11.0$ G). A large number of lines indicate an unpaired electron, which interacts with one or two F-atoms. The IR spectrum (nujol mull) displays the absorption for the C≡C bond at 1988 cm^{-1} which indicates very weak alkyne complexation. In the starting complex which can be described as a Ti^{II} alkyne complex or alternatively as a Ti^{IV} metallacyclopropene, this absorption was found at 1594 cm^{-1},[6] a result of stronger backbonding effects. This interpretation is also supported by the X-ray crystal structure (Figure 3).

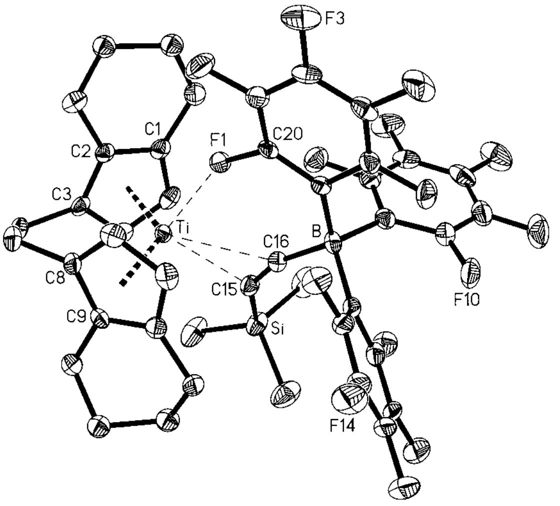

Figure 3. ORTEP plot of **3**. The thermal ellipsoids are set at 30% probability. For clarity the hydrogen atoms and one position of the disordered groups are omitted. Selected bond lengths [Å] and angles [°]: C15-C16 1.226(5), C15-Si 1.866(4), C16-B 1.617(5), Ti-C16 2.639(4), Ti-C15 2.515(4), Ti-F1 2.260(2), C20-F1 1.389(4); C15-C16-B 161.1(4), C16-C15-Si 144.3(3).

The molecular structure of **3**[13] (Figure 3) shows the typical (ebthi)Ti structure, but in contrast to **1** is unsubstituted. The $[Me_3SiC{\equiv}CB(C_6F_5)_3]^-$ ligand is complexed unsymmetrically and weakly as expected. A comparably weak coordination was also found in the dimeric σ,π-alkynyl-bridged titanocene(III) complexes $[\{Cp_2Ti(C{\equiv}CSiMe_3)\}_2]$ (C-C 1.244(3), Ti-C(Ti) 2.393(1), Ti-C(Si) 2.318(2) Å; C-C-Ti 176.4(1), C-C-Si 141.5(2)°).[14] A stronger complexation is found in $[Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (C-C 1.309(4), Ti-C 2.122(3) and 2.126(3) Å; Si-C-C 134.8(3) and 136.8(3)°).[15] One *ortho* F atom in **3** coordinates to the titanium center and

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thus lies farther from the ring carbon atoms than all the other F atoms.

Compound **3**, to our knowledge, is the first Ti^{III} alkyne complex, if one leaves out the very special cases of dimeric σ,π-alkynyl-bridged complexes $[\{Cp_2Ti(C{\equiv}CSiMe_3)\}_2]$[14] and $[\{Cp_2Ti(C{\equiv}CSnMe_3)\}_2]$.[16] In addition metallocene complexes of alkynylboranates $[RC{\equiv}C\text{-}BR_3]^-$ have not been isolated or characterized before, though they were assumed frequently as reactive intermediates.[17,18] One example for this is the $B(C_6F_5)_3$-catalyzed C–C coupling of alkynyl groups to 1,3-butadiynes from zirconocene(IV)-bisalkynyl complexes $[Cp_2Zr(C{\equiv}CR)_2]$ described by Erker et al. which was proposed to proceed via the not-isolated $[RC{\equiv}CB(C_6F_5)_3]^-$ complexes of zirconocene(IV) monoalkynyl cations $[Cp_2Zr(C{\equiv}CR)]^+$.[17] Complexes of the type $[Cp_2Zr\{\eta^2\text{-}RC_2B(C_6F_5)_2\}]$ were isolated by Piers et al. from neutral alkynylboranes $RC{\equiv}C{-}BR_2$ with metallocenes.[19] Compounds with alkynylboranates were proposed also by Wrackmeyer et al. in the reaction of stannylalkynes $Me_3SnC{\equiv}CR$ with triethylborane (BEt_3), where not-isolated intermediates, such as $[Me_3Sn]^+[RC{\equiv}CBEt_3]^-$ react under formation of stannylolefines $Me_3SnC(Et){=}CR(BEt_2)$.[18]

The reaction which generates **3** may be understood as an oxidative Si–C bond cleavage in $Me_3SiC{\equiv}CSiMe_3$ (in analogy to ref. [12]) under formation of the σ-alkynyl complex *rac*-$[(\text{ebthi})Ti(SiMe_3)(C{\equiv}CSiMe_3)]$, which gives (by reduction) Me_3Si radicals and the dimeric σ,π-alkynyl-bridged complex *rac*-$[\{(\text{ebthi})Ti(C{\equiv}CSiMe_3)\}_2]$ (in analogy to ref. [14]). With $B(C_6F_5)_3$, this complex would generate **3**. Similar reaction steps were described for $Me_3SnC{\equiv}CSnMe_3$, via $[Cp_2Ti(SnMe_3)(C{\equiv}CR)]$, to Me_3Sn radicals and $[\{Cp_2Ti(C{\equiv}C\text{-}SnMe_3)\}_2]$.[16] An NMR-spectroscopy investigation of the reaction was prevented by the presence of paramagnetic complexes, and the fate of the Me_3Si group remains unknown. Pure complex **3** crystallizes from the mixture but after evaporation of all the *n*-hexane, only amorphous mixtures of undefined compounds remained.

With utmost exclusion of moisture,[20a] the green complex **3** was formed in a yield of approximately 35% along with trace amounts of blue crystals, which are a mixture of *rac*-$[\{(\text{ebthi})Ti\}^+\{HO\text{-}B(C_6F_5)_3\}]^-$ (**4**) and *rac*-$[\{(\text{ebthi})Ti\}^+\{H\text{-}B\text{-}(C_6F_5)_3\}]^-$ (**5**).[20b] If water is present (as the Brönsted acid $B(C_6F_5)_3{\cdot}H_2O$[21]), **4** and **5** were isolated as the only products,[20b] and bis(trimethylsilyl)acetylene was detected in the reaction solution by NMR spectroscopy. Complex **3** was not formed in the reaction of *rac*-$[(\text{ebthi})Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ with a mixture of **4** and **5** in *n*-hexane.

The compounds described here form a series of complexes of the type *rac*-$[\{(\text{ebthi})Ti\}^+\{X\text{-}B(C_6F_5)_3\}^-]$ ($X = C{\equiv}CSiMe_3$ (**3**), OH (**4**) or H (**5**)). To date, we failed to synthesize similar complexes by the reaction of the recently published stable permethyltitanocene monoalkynyl complexes $[Cp^*_2Ti\text{-}C{\equiv}C\text{-}t\text{Bu}]$[22] with $B(C_6F_5)_3$. Whether this is because of the specific properties of the Cp ligands (Cp* vs. ebthi) or of the alkynyl substituents (Me_3Si vs. *t*Bu) or because of the reaction path itself is being investigated.

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[8] Crystal structure of **1**: crystal size 0.4 × 0.3 × 0.2 mm, colorless prism, space group $P\bar{1}$, triclinic, $a = 13.186(3)$, $b = 13.822(3)$, $c = 16.300(3)$ Å, $\alpha = 85.44(3)$, $\beta = 88.65(3)$, $\gamma = 83.00(3)°$, $V = 2939.0(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.270\ g\,cm^{-3}$, 7137 reflections measured, 7137 were independent of symmetry and 3913 were observed ($I > 2\sigma(I)$), $R1 = 0.058$, wR^2 (all data) = 0.178, 633 parameters.

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[11] Crystal structure of **2**: crystal size 0.4 × 0.3 × 0.2 mm, yellow prism, space group $P2_1/n$, monoclinic, $a = 9.331(2)$, $b = 21.371(4)$, $c = 18.188(4)$ Å, $\beta = 95.04(3)°$, $V = 3612.9(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.635\ g\,cm^{-3}$, 12779 reflections measured, 4514 were independent of symmetry and 2629 were observed ($I > 2\sigma(I)$), $R1 = 0.044$, wR^2 (all data) = 0.112, 515 parameters.

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[13] Crystal structure of **3**: crystal size 0.5 × 0.4 × 0.4 mm, dark green prism, space group $P2_1/n$, monoclinic, $a = 13.373(3)$, $b = 12.206(2)$, $c = 24.584(5)$ Å, $\beta = 102.72(3)°$, $V = 3914.4(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.564\ g\,cm^{-3}$, 11406 reflections measured, 5892 were independent of symmetry and 3358 were observed ($I > 2\sigma(I)$), $R1 = 0.048$, wR^2 (all data) = 0.112, 546 parameters. CCDC-195461 (**1**), CCDC-195462 (**2**), CCDC-195463 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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