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Reactions of 1-Titana- and 1-Zirconacyclopent-3-ynes with Tris(pentafluorophenyl)borane[†]

Marc A. Bach, Torsten Beweries, Vladimir V. Burlakov,[§] Perdita Arndt,
Wolfgang Baumann, Anke Spannenberg, and Uwe Rosenthal*

Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V.,
Albert-Einstein-Strasse 29a, D-18059 Rostock, Germany

Werner Bonrath

DSM Nutritional Products, R&D Chemical Process Technology,
P.O. Box 3255, Bldg. 214/071, CH-4002 Basel, Switzerland

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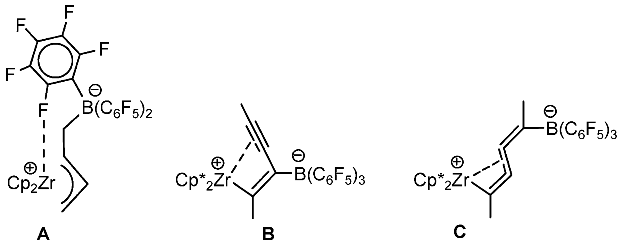
The 1-metallacyclopent-3-ynes $Cp_2Ti(\eta^4\text{-}H_2C_4H_2)$ (**1**) (Cp = η^5-cyclopentadienyl) and *rac*-(ebthi)$Zr(\eta^4\text{-}H_2C_4H_2)$ (**2**) (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl) react with $B(C_6F_5)_3$ under ring opening of the metallacycle and formation of the zwitterionic complexes $[Cp_2Ti]^+{-}CH_2C{\equiv}CCH_2{-}[B^-(C_6F_5)_3]$ (**3**) and [*rac*-(ebthi)Zr]$^+{-}CH_2C{\equiv}CCH_2{-}[B^-(C_6F_5)_3]$ (**4**). Crystal structures of **3** and **4** show a but-2-yne-1,4-diyl ligand bridging the metallocenium center and the formed boranate. Complex **4** is an active catalyst for ethylene polymerization.

Introduction

In group 4 metallocene chemistry the ability of the Lewis acid $B(C_6F_5)_3$ to abstract alkyl groups from metallocene alkyl compounds and to form coordinatively unsaturated alkylmetal cationic complexes $[Cp'_2MR]^+$ (Cp′ = substituted η^5-cyclopentadienyl) is well-documented from numerous investigations relating to Ziegler/Natta catalysts for olefin polymerization.[1] Mostly metallocene dialkyls Cp'_2MR_2 were investigated, formed after alkylation of metallocene dihalides Cp'_2MX_2 by organoaluminum compounds as activators (Cp′ = substituted or nonsubstituted η^5-cyclopentadienyl ligands).[2]

Also reactions of $B(C_6F_5)_3$ with different five-membered metallacycles such as metallacyclo*pentadienes* $Cp'_2Zr(\eta^2\text{-}C_4R_4)$,[3] metallacyclo*pentenes* $Cp'_2Zr(\eta^2\text{-}C_4R_6)$ (formation of **A**, Chart 1),[4] and metallacyclo*pentanes* $Cp'_2Zr(\eta^2\text{-}C_4R_8)$ [5] were published. Recently such reactions with $B(C_6F_5)_3$ for metallacyclo*propenes* $Cp'_2M(\eta^2\text{-}RC_2R)$[6] and the special case of unusual five-membered metalla*cyclocumulenes* (metallacyclo*pentatrienes*) $Cp'_2M(\eta^4\text{-}RC_4R)$[7] (Cp′ = Cp and Cp* = η^5-pentamethylcyclopentadienyl; formation of **B** [8a,b] and **C**,[8a] Chart 1) were reported. All these metallacycles have two metal–carbon σ-bonds like the above-mentioned dialkyl compounds, and the studies were conducted to obtain active single-component catalysts with the counteranion tethered to the end of the growing chain.

Chart 1. Examples for Zwitterionic Complexes



We report here on reactions of the metallacyclo*pentynes*, namely, the 1-titanacyclopent-3-yne $Cp_2Ti(\eta^4\text{-}H_2C_4H_2)$ (**1**)[7,9c,f] and the 1-zirconacyclopent-3-yne *rac*-(ebthi)$Zr(\eta^4\text{-}H_2C_4H_2)$ (**2**) (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl) with $B(C_6F_5)_3$ to form the novel zwitterionic boranate complexes $[Cp'_2M]^+{-}CH_2C{\equiv}CCH_2{-}[B^-(C_6F_5)_3]$ (**3**, M = Ti, Cp = Cp′; **4**, M = Zr, Cp'_2 = *rac*-(ebthi)Zr), of which the latter is an active catalyst for ethylene polymerization. The results are compared with the reactions of metalla*cyclocumulenes* (1-metallacyclopenta-2,3,4-trienes) $Cp'_2M(\eta^4\text{-}RC_4R)$ with Cp′ = Cp* and Cp.

The complexes **1** and **2** react with $B(C_6F_5)_3$ in *n*-hexane or toluene solution at room temperature under

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[†] In memory of Dr. habil Erhard Kurras, deceased June 10th, 2005.

* To whom correspondence should be addressed. E-mail: uwe.rosenthal@ifok-rostock.de.

[§] On leave from the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 117813, Moscow, Russia.

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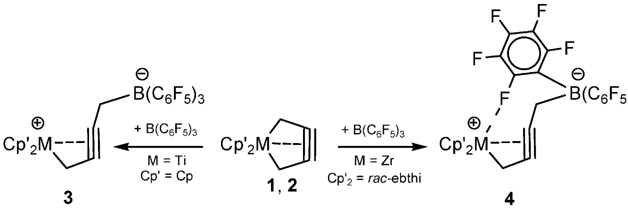
10.1021/om0507880 CCC: $30.25

Scheme 1. Reactions of Metallacyclopentynes with $B(C_6F_5)_3$



opening of the metallacycle and formation of the zwitterionic complexes **3** and **4**, in which a but-2-yne-1,4-diyl ligand is bridging the metallocenium center and the formed boranate (Scheme 1).

The extremely low solubility of the obtained zwitterionic complexes prevents obtaining ^{13}C NMR data and investigations of the molecular dynamics, as described for the type **A** complexes (Chart 1).[4] The absorption of the ν(C≡C) of the metallacyclopentynes (**1**, 2018; **2**, 2010 cm^{-1}) disappeared for the triple bond in the spectra of **3** and **4**.

The molecular structures of the titanium complex **3** and the zirconium complex **4** were confirmed by X-ray crystallography (Figures 1 and 2).

Both complexes show the typical bent metallocene parts Cp_2Ti and *rac*-(ebthi)Zr, which interact with the but-2-yne-1,4-diyl ligand similarly for both metals. The short C2−C3 bonds, extremely long M1−C3 distances, and C2−C3−C4 angles of 164.2° and 161.1° indicate only a very weak interaction of the metals with the triple bond, as expected for alkyne complexes of titanium and zirconium in higher formal oxidation state.[6a]

Some bond distances and angles of the σ-propargyl part of complex **4** are different from those of the, in principle, similar η^3-propargyl (**I**)/allenyl (**II**) complexes (Chart 2).

For example, in the complex $Cp_2Zr(Me)(\eta^3\text{-}CH_2CCPh)$ the bond lengths (Å) Zr1−C1 2.658, Zr1−C2 2.438, Zr1−C3 2.361, C1−C2 1.344, C2−C3 1.259, C3−C4 1.462 and angles (deg) Zr1−C1−C2 65.8, C1−C2−C3 155.4, C2−C3−C4 137.3 were found.[10] Nevertheless, in complex **4** the C3 atom is only 0.077 Å out of the plane Zr1−C1−C2 and differs from this point of view not very much from the planarity that is the characteristic structural feature of such η^3-propargyl/allenyl complexes. One can better compare the Zr−C distances of complex **4** with those in complexes of type **A** (Zr1−C1 2.339, Zr1−C2 2.494, Zr1−C3 2.710 Å) and **C** (Zr1−C1 2.298, Zr1−C2 2.448, Zr1−C3 2.695 Å) (Chart 1).

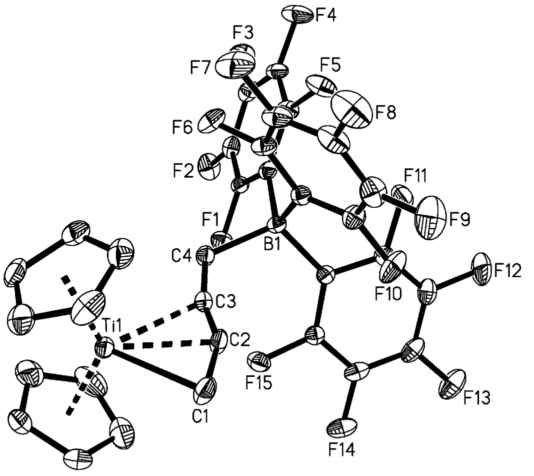


Figure 1. Molecular structure of complex **3**. Bond lengths (Å): Ti1−C1 2.277(3), Ti1−C2 2.268(3), Ti1−C3 2.420, C1−C2 1.393(4), C2−C3 1.225(4), C3−C4 1.453(4). Bond angles (deg): Ti1−C1−C2 71.80(16), C1−C2−C3 154.3(3), C2−C3−C4 164.2(3).

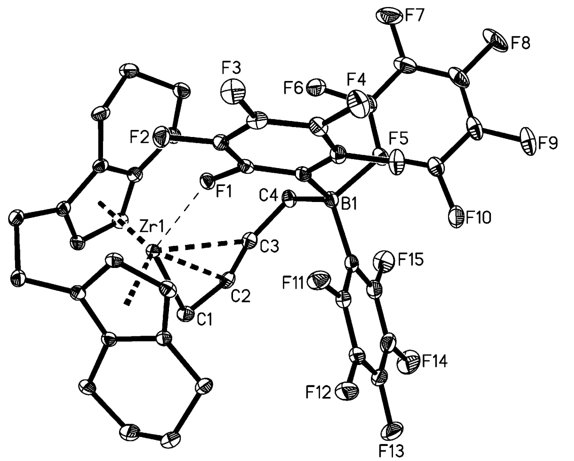
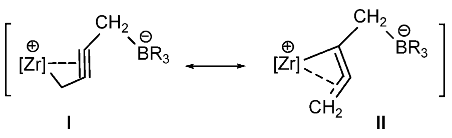
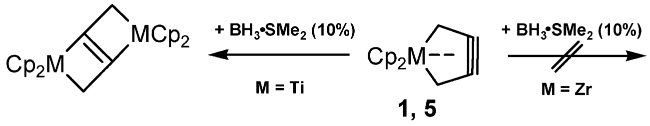


Figure 2. Molecular structure of complex **4**. Bond lengths (Å): Zr1−C1 2.371(2), Zr1−C2 2.414(2), Zr1−C3 2.600, C1−C2 1.401(3), C2−C3 1.229(3), C3−C4 1.476(3). Bond angles (deg): Zr1−C1−C2 74.67(13), C1−C2−C3 155.5(2), C2−C3−C4 161.1(2).

Chart 2 η^3-Propargyl (I) and Allenyl (II) Complexes



Scheme 2. Reactions the Metallacyclopentynes 1 and 5 with $BH_3 \cdot SMe_2$



The most important difference between the structures of the titanium complex **3** and the zirconium complex **4** is that in the latter one *ortho*-F atom of a pentafluorophenyl group coordinates to the Zr center; therefore the corresponding F−C_{ring} bond is elongated (F1−C15 1.402(2) Å) and a short Zr−F distance was found (Zr1−F1 2.442(1) Å). Compared with complex **A** (Zr1−F1 2.243 Å) this is longer and the weakness of such a coordination is evident from the ^{19}F NMR spectra in solution, giving no signal in the expected range (**A**: −213 ppm). In the titanium complex **3** there is no Ti−F coordination.

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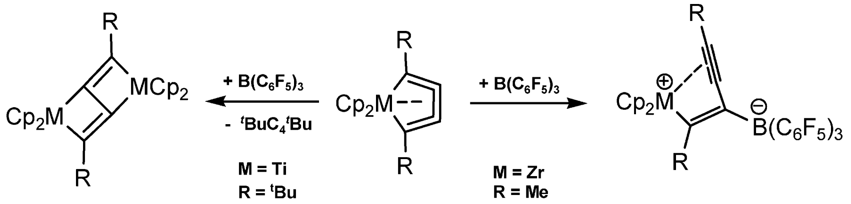
Scheme 3. Different Reactions of Five-Membered Titanacyclocumulenes with $B(C_6F_5)_3$



A different behavior was observed in the reactions of **1**[9c] and Suzuki's $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**5**)[9f] with $BH_3{\cdot}SMe_2$ (Scheme 2, left). Starting from **1**, BH_3 (10 mol %) or BPh_3 catalyzes in toluene at rt the formation of 2,2-dititanabicyclo[2.2.0]hex-1(4)-ene (M = Ti),[9c] and no zwitterionic compound was isolated. This is remarkable because in reactions of **1** and **2** with $B(C_6F_5)_3$ no such binuclear species were observed even if an excess of this borane was used and furthermore a reaction times of two weeks. It is of interest that the formation of a binuclear complex was described for **1** after a very long reaction time or very fast under the catalytic influence of Ni(0) complexes.[9g] With **5** as starting material under the same reaction conditions the analogous dinuclear zirconium complex[9f] was not obtained.

As mentioned in the Introduction, the reaction of five-membered metalla*cyclocumulenes* $Cp^*{}_2Zr(\eta^4\text{-}RC_4R)$ with $Cp' = Cp^*$ toward $B(C_6F_5)_3$ was described recently to give products **C** and **B**, from which the latter was also obtained in reactions of $Cp_2Zr(C{\equiv}CMe)_2$ with $B(C_6F_5)_3$.[8b] The corresponding complex $Cp_2Ti(\eta^4\text{-}t\text{-Bu-}C_4\text{-}t\text{-Bu})$ reacts in toluene at rt with catalytic amounts of $B(C_6F_5)_3$ to the free butadiyne *t*-Bu-C_4-*t*-Bu and the well-known complex with a bridging *trans*-1,3-butadiyne ligand $[Cp_2Ti]_2[\mu\text{-}\eta^2(1,3){:}\eta^2(2,4)\text{-}t\text{-Bu}{-}C_2C_2{-}t\text{-Bu})]$ (Scheme 3).[7]

Complexes **3** and **4** were checked in toluene solution at 40 °C as single-component catalysts for ethylene polymerization. Whereas complex **3** gave only traces of polyethylene, the activity of complex **4** was 86 kg pol./mol h. For comparison, the Cp* complex **C** (Chart 1) did not show any activity and the other Cp* complex **B** was, under the same conditions, similarly active (68 kg pol./mol h).

The herein-described zwitterionic complexes contribute to the fundamental understanding of the bonding and reactivity of five-membered metallacyclocumulenes and metallacyclopentynes as unusual small and strained metallacycles. The here-established reactivity extends the knowledge of single-component catalysts as "*intramolecular*" ion pairs that contain the counterion at the end of the growing chain. These are the first examples with a triple bond.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvent (THF-d_8) was treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker ARX 400. Chemical shifts (^1H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the solvents: benzene-d_6 ($\delta_H = 7.16$, $\delta_C = 128.0$). The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 2. *rac*-(ebthi)$ZrCl_2$ (1.02 g, 2.37 mmol) and finely devided magnesium turnings (0.115 g, 5.72 mmol) were suspended in THF (40 mL), and 1,4-dichlorobut-2-yne (0.23 mL, 2.37 mmol) was added. The reaction mixture was stirred for 12 h at room temperature, and the solvent was removed in a vacuum. The pale brown residue was extracted with *n*-hexane (3 × 15 mL), and the united *n*-hexane solutions were evaporated to half its volume. Crystallization at −78 °C yields 0.23 g (28%) of complex **2** as a light brown solid. **2** was used without further purification. ^1H NMR (C_6D_6): δ 5.75 ppm (d, 3 Hz, 2H), 3.71 ppm (d, 3 Hz, 2H), 2.95−2.87 ppm (m, 2H), 2.84−2.78 ppm (m, 2H), 2.74−2.57 ppm (m, 4H), 2.52−2.45 ppm (m, 2H), 2.43−2.36 ppm (m, 2H), 1.90−1.80 ppm (m, 4H), 1.74−1.64 ppm (m, 2H), 1.46−1.21 ppm (m, 6H). ^{13}C NMR (C_6D_6): δ 122.2 ppm (C_{quart}), 120.6 ppm (C_{quart}), 113.9 ppm (C_{quart}), 108.8 ppm (C_{alkyne}), 103.5 ppm (CH), 98.4 ppm (CH), 44.5 ppm ($CH_{2-pentyne}$), 28.7 ppm (CH_2), 24.4 (CH_2), 23.4 ppm (CH_2), 23.1 ppm (CH_2), 23.0 ppm (CH_2). IR: ν 2010 cm^{-1}.

Preparation of Complex 3. Tris(pentafluorophenyl)borane (0.22 g, 0.43 mmol) was dissolved in *n*-hexane (5 mL) and added to a solution of complex **1** (0.1 g, 0.43 mmol) in *n*-hexane (5 mL) at 20 °C. Immediately a dark green deposit was formed, which was filtered, washed with *n*-hexane (3 × 2 mL), and dried in a vacuum. Yield of complex **3**: 0.26 g (82%). Synthesis in toluene instead of *n*-hexane combined with a vibration-free storage of the reaction mixture was used to grow single crystals for X-ray diffraction analysis. MS (70 eV): *m/z* (rel intensity) 512 (100), 334(17), 178 (29), 65 (32). Anal. Calcd for $C_{32}H_{14}BF_{15}Ti$: C 51.79, H 1.90. Found: C 51.68, H 2.17.

Preparation of Complex 4. A solution of compound **2** (0.23 g, 0.57 mmol) in *n*-hexane/toluene (10:1, 40 mL) was added to a solution of tris(pentafluorophenyl)borane (0.34 g, 0.66 mmol) in *n*-hexane/toluene (10:1, 40 mL). The dark reaction mixture was stirred for 20 s and stored vibration-free. Yellow crystals of complex **4** were obtained after 4 weeks. ^1H NMR (C_6D_6): δ 1.10−2.97 ppm (24 H, CH_2, not further analyzed), 4.30 ppm (d, 3.0 Hz, 1 H, C=CH), 5.10 ppm (d, 2.8 Hz, 1 H, C=CH), 5.35 ppm (d, 3.0 Hz, 1 H, C=CH), 5.65 ppm (d, 2.8 Hz, 1 H, C=CH). Anal. Calcd for $C_{42}H_{24}BF_{15}Zr$: C 54.85, H 3.07. Found: C 54.91, H 2.68.

X-ray data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). XP (BRUKER AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in cif format, including bond lengths and angles of compound **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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