Reactions of Five-Membered Zirconacyclocumulenes with Tris(pentafluorophenyl)borane: Carbon−Carbon Double Bond Cleavage and Formation of Novel Zwitterionic Complexes

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The five-membered zirconacyclocumulenes $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl, $R = Me_3Si$ **1a**, Me **1b**, Ph **1c**) each react differently with $B(C_6F_5)_3$. For **1a** ($R = Me_3Si$) a bond cleavage of the central carbon−carbon double bond of the cyclocumulene was found, and the bis-σ-alkynyl complex $Cp^*_2Zr(\sigma\text{-}C{\equiv}CSiMe_3)_2$ (**2**) was formed. This reaction occurred with 10% $B(C_6F_5)_3$, giving after 6 days a quantitative yield of complex **2**. With **1b** (R = Me) $B(C_6F_5)_3$ attacks the β-C atom of the starting cumulene and the C_4 chain remains intact, forming $Cp^*_2Zr\{\eta^3\text{-}1,3,4\text{-}C(Me)\text{-}C[B(C_6F_5)_3]\text{-}C{\equiv}CMe\}$ (**3**) with a hex-2-en-4-yn-2-yl-3-[tris(pentafluorophenyl)borate] ligand at the permethylzirconocene center. With **1c** (R = Ph) the C_4 chain also is not cleaved, but $B(C_6F_5)_3$ attacks the α-C atom of the starting cumulene and yields $Cp^*_2Zr\{\eta^3\text{-}1,2,3\text{-}C(Ph){=}C{=}C{=}C(Ph)[B(C_6F_5)_3]\}$ (**4**) with a 1,4-diphenylbuta-1,2,3-trien-1-yl-4-[tris(pentafluorophenyl)borate] ligand, coordinated at the permethylzirconocene center. The molecular structure of complex **4** was confirmed by X-ray crystallography.

Introduction

In reactions of different titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene the activation of unreactive bonds was described by us in some reviews.[1] For example, such cleavage of C−H, C−C (Cp-ring opening, cleavage of butadiynes), Si−C, P−C, N−H, N−C, N−N, Si−O, N−O, C−O, C−S, and C−B bonds gave complexes of potential applicability in stoichiometric and catalytic reactions.[1]

During the investigations concerning C−C single bond activation we obtained the five-membered metallacyclocumulenes $Cp'_2M(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$[1b] with Cp′ = Cp, Cp* and M = Ti, Zr. These are the key intermediates in both reactions of *C−C single bond cleavage* of different 1,4-substituted 1,3-butadiynes RC≡C−C≡CR to alkynyl groups (and also in the opposite reaction of *C−C single bond formation* starting from alkynyl groups under formation of 1,4-substituted 1,3-butadiynes). Depending on the nature of the metals M and ligands L, coupling or cleavage is favored, and the combination of both reactions offered the first C−C single bond metathesis in homogeneous solution. This is photocatalyzed and titanocene-mediated and proceeds via titanocene-monoalkynyl complexes.[1]

For the zirconocene(IV)-bis-alkynyl complex $Cp_2Zr(\sigma\text{-}C{\equiv}CMe)_2$ Erker and co-workers reported that catalytic amounts of strong Lewis acids such as $B(C_6F_5)_3$ promote the *C−C bond coupling* reaction of the acetylide groups. The formation of 1,3-diyne complexes $Cp_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)$, presumably via the unisolated complexes of $[MeC{\equiv}CB(C_6F_5)_3]^-$ and zirconocene(IV)-monoalkynyl cations $[Cp_2Zr(C{\equiv}CMe)]^+$ as intermediates, was observed.[2]

We found such a *C−C bond coupling* reaction, occuring in the absence of a borane, under UV irradiation of $Cp_2Ti(\sigma\text{-}C{\equiv}C\text{-}t\text{-}Bu)_2$[3a] and recently for the corresponding permethylzirconocene complexes $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$ in sunlight. In the latter case high yields of the zirconacyclocumulenes **1**, $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ with R = Ph,

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(1) (a) Ohff, A.; Pulst, S.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (b) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (c) Rosenthal, U.; Burlakov, V. V. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: New York, 2002; p 355. (d) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884. (e) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *J. Organomet. Chem.* **2003**, *670*, 84.

(2) (a) Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. *Angew. Chem.* **1994**, *106*, 1570; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480. (b) Ahlers, W.; Temme, B.; Erker, G.; Fröhlich, R.; Fox, T. *J. Organomet. Chem.* **1997**, *527*, 191. (c) Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. *J. Organomet. Chem.* **1999**, *578*, 115. (d) Ahlers, W.; Temme, B.; Erker, G.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 1440. (e) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911.

(3) (a) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1996**, *108*, 1175; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112. (b) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 8313. (c) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 81. (d) Frömberg, W. Ph.D. Thesis, University of Bochum, 1986. (e) Kirchbauer, F. G. Ph.D. Thesis, University of Rostock, 1999.

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Me, and Me_3Si, were obtained.[3b,c,e] In principle this photoreaction in the absence of a borane was described in 1986 by Frömberg,[3d] but the structure of the resulting product was not elucidated.

Additionally, the *C−C double bond cleavage* of five-membered zirconacyclocumulenes of type **1** with Lewis acids such as "Cp_2Zr" or "Cp_2Ti" was reported in which the homo- or heterobinuclear alkynyl complexes $Cp_2Zr(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2ZrCp_2$ or $Cp_2Zr(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2TiCp_2$ were obtained.[4a−f] Very recently we found that **1a** is also cleaved by $^{i}Bu_2AlH$.[4g]

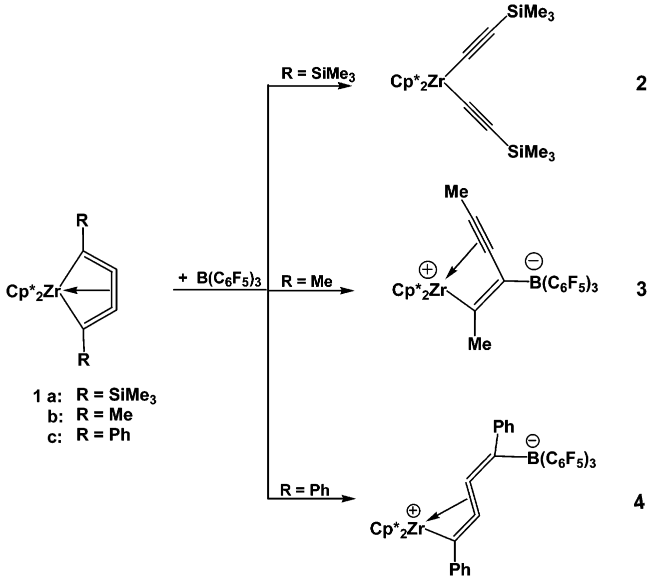
A related reaction was observed with $B(C_6F_5)_3$ at a *permethylzirconocene* system. A *C−C double bond cleavage* of a complexed diyne in $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$ with formation of the bis-alkynyl complex $Cp^*{}_2Zr(\sigma\text{-}C{\equiv}CSiMe_3)_2$ was briefly mentioned.[5a]

This is opposite Erker's results[2] with other *zirconocene* complexes noted above.

To investigate this totally different and at first sight confusing influence of $B(C_6F_5)_3$ (on one hand *C−C bond coupling* and on the other *C−C bond cleavage* reactions), we have studied the interaction of the five-membered zirconacyclocumulenes $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ (R = Me_3Si **1a**, Me **1b**, Ph **1c**) toward $B(C_6F_5)_3$.

These results extend our prior investigations about the reactivity of metallacyclopropenes $Cp'_2M(\eta^2\text{-}RC_2R)$ (M = Ti, Zr; Cp′ = Cp, Cp*; and R = Me_3Si) toward $B(C_6F_5)_3$[5b−e] to zirconacyclocumulenes $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$, which also contain two M−C σ bonds. The chemistry involving the attack of tris(pentafluorophenyl)borane on coordinated ligands in group 4 metallocene chemistry has been elaborated by several groups, mostly for the use as catalysts in olefin polymerization.[6] This area now has been developed for the special case of metallacyclocumulenes as complexes of 1,3-butadiynes.

Scheme 1



Results and Discussion

The five-membered zirconacyclocumulene $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$ (**1a**) reacts with an equimolar amount of $B(C_6F_5)_3$ in *n*-hexane with cleavage of the central carbon−carbon bond. The bis-σ-alkynyl complex $Cp^*{}_2Zr(\sigma\text{-}C{\equiv}CSiMe_3)_2$ (**2**) (Scheme 1) was formed (which was obtained earlier by "salt elimination" from $Cp^*{}_2ZrCl_2$ and $LiC{\equiv}CSiMe_3$[3b]).

Since the borane does not appear in the reaction product, we checked whether an equimolar amount of $B(C_6F_5)_3$ really is needed to convert the zirconacyclocumulene **1a** to **2**. This cleavage reaction in *n*-hexane is indeed catalyzed by 10% of $B(C_6F_5)_3$ to give, after 6 days, a quantitative yield of **2**.

Complex $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)$ (**1b**) reacts at room temperature in toluene with an equimolar amount of $B(C_6F_5)_3$, which attacks at the β-C atom of the cumulene ligand. In this reaction the C_4 chain remains intact and the product **3** containing a hex-2-en-4-yn-2-yl-3-[tris(pentafluorophenyl)borate] ligand at the permethylzirconocene center was isolated (Scheme 1). Complex **3** was investigated by IR and NMR spectroscopy and by X-ray crystallography.

In the reaction of $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}PhC_4Ph)$ (**1c**) with $B(C_6F_5)_3$ at 80 °C in toluene a complex with a 1,4-diphenylbuta-1,2,3-trien-1-yl-4-[tris(pentafluorophenyl)borate] ligand, coordinated at the permethylzirconocene center, **4**, was formed (Scheme 1). At room temperature no reaction was observed. The product **4** was the result of an unprecedented attack of the borane at the α-C atom of the cumulene ligand while the C_4 chain remained uncleaved. Complex **4** was studied by spectroscopic methods, and the molecular structure was determined by X-ray crystallography.

To explain the formation of such different products from **1a**, **1b**, and **1c** in their reactions with $B(C_6F_5)_3$, we examined the spectroscopic properties and the structural data of the starting complexes $Cp^*{}_2Zr(\eta^4\text{-}$

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(4) (a) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C 36. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Organometallics* **1994**, *13*, 2903. (c) Rosenthal, U.; Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *Organometallics* **1995**, *14*, 2961. (d) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967. (e) Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Collect. Czechoslov. Chem. Commun.* **1997**, *62*, 331. (f) Hsu, D. P.; Davis, W. M.; Buchwald, S. L *J. Am. Chem. Soc.* **1993**, *115*, 10394. (g) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 4160.

(5) (a) Rosenthal, U.; Arndt, P.; Baumann, W.; Burlakov, V. V.; Spannenberg, A. *J. Organomet. Chem.* **2003**, *670*, 84. (b) Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **2003**, *115*, 1455; *Angew. Chem., Int. Ed.* **2003**, *42*, 1414. (c) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Letov, A. V.; Lyssenko, K. A.; Korlyukov, A. A.; Strunkina, L. I.; Minacheva, M. Kh.; Shur, V. B. *Organometallics* **2001**, *20*, 4072. (d) Burlakov, V. V.; Troyanov, S. I.; Letov, A. V.; Strunkina, L. I.; Minacheva, M. Kh.; Furin, G. G.; Rosenthal, U.; Shur, V. B. J. *Organomet. Chem.* **2000**, *598*, 243. (e) Burlakov, V. V.; Pellny, P.-M.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B.; Rosenthal, U. *Chem. Commun.* **2000**, 241. (f) Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *536−537*, 293. (g) Pellny, P.-M.; Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Francke, V.; Rosenthal, U. *J. Organomet. Chem.* **1999**, *578*, 125.

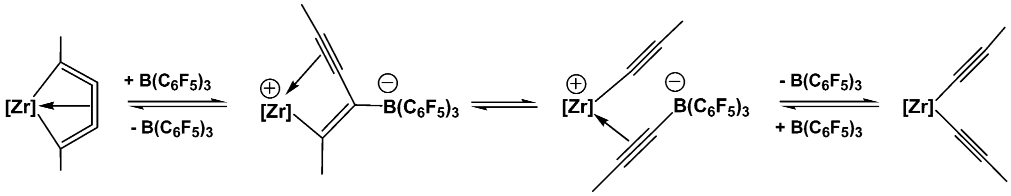
(6) Examples: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143, and references therein. (b) Janiak, C. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1998; Vol. 2, p 547. (c) Tullo, A. H. *Chem. Eng. News* **2001**, *79*, 35. (d) Jordan, R. F.; Bajgur, C. S.; Willet, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (e) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (f) Hlatky, G. G.; Turner, H. W.; Eckmann, R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (h) Piers, W. E. *Chem. Eur. J.* **1998**, 13. (i) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309. (j) Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (k) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325, and references therein.

Table 1. ^{13}C NMR Spectroscopic and Molecular Structural Comparison of the Starting Complexes $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ ($\Delta\delta$ = coordination shift)

	1a, R = Me_3Si	**1b**,[a] R = Me	**1c**, R = Ph
^{13}C NMR [ppm]			
Cα	188.0 ($\Delta\delta$ = 101.9)	171.7 ($\Delta\delta$ = 99.7)	179.4 ($\Delta\delta$ = 97.4)
Cβ	144.5 ($\Delta\delta$ = 55.1)	111.5 ($\Delta\delta$ = 46.7)	118.4 ($\Delta\delta$ = 44.1)
X-ray [Å, deg]			
Cα−Cβ	1.291(6); 1.293(6)	1.286(8); 1.283(9)	1.296(4); 1.305(5)
Cβ−Cβ'	1.337(6)	1.311(9)	1.327(4)
Zr−Cα	2.422(4); 2.426(5)	2.325(5); 2.334(5)	2.345(4); 2.357(4)
Zr−Cβ	2.305(4); 2.307(4)	2.307(5); 2.308(5)	2.328(4); 2.330(4)

[a] For **1b** bond lengths and angles for only one of the two molecules of the asymmetric unit are listed.

Scheme 2



1,2,3,4-RC$_4$R) in search of a possible reason for these remarkable differences in reaction behavior (Table 1).

Due to electronic and steric factors, we assumed electrophilic attack of the borane at the C$_\beta$ atom of the cyclocumulene to be kinetically favored in all cases. The structural data presented in Table 1 for all complexes are very similar, and NMR spectroscopic data show for all complexes a larger downfield shift for C$_\alpha$ atoms in comparison to C$_\beta$. This is more pronounced for **1a** due to the β-position of the silyl groups.[6j] For the special C−C bond cleavage in the formation of **2** via complexes of type **3**, complexes of alkynylborates $[Me_3SiC{\equiv}CB(C_6F_5)_3]^-$ with permethylzirconocene(IV)-monoalkynyl counterions $[Cp^*_2Zr(C{\equiv}CSiMe_3)]^+$ as intermediates are assumed (see Scheme 2).

Such species are stabilized by the Me_3Si group (β-effect).[5b,6k] We recently reported the first stable complex of this type for Ti(III), the zwitterionic $[rac\text{-}(ebthi)Ti]^+$-$[\eta^2\text{-}Me_3SiC_2B(C_6F_5)_3]^-$.[5b] After dissociation of $B(C_6F_5)_3$ the complex with two σ-bonded alkynyl groups **2** is formed. The tendency for *C−C single bond cleavage* of the $SiC_2{-}C_2Si$ unit by coordination with metals has been observed in many cases.[4] It is remarkable that for $Cp_2Zr(\sigma\text{-}C{\equiv}CMe)_2$ with a Cp ligand and R = Me the reaction with $B(C_6F_5)_3$ proceeds in the opposite direction to give by *C−C coupling of the acetylides* the zirconacyclocumulene $Cp_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)$.[2]

For **1b** and **1c**, with R = Me and Ph, respectively, no C−C cleavage occurred and completely different products were observed. Neither significant differences in their ^{13}C NMR spectroscopic data nor in their structural parameters could explain the formation of the different products **3** and **4** (Table 1). Nevertheless, they are formed, but interestingly at different temperatures: **3** at room temperature and **4** at higher temperature. When the reaction of **1b** with $B(C_6F_5)_3$ was carried out also at 80 °C (as with **1c**), a clean reaction did not take place. NMR investigations of the resulting oily product showed that a complicated mixture of different complexes was present. None of them could be isolated in pure form or identified.

It is well established for metallacyclocumulenes that an equilibrium between η^4 and η^2 coordination of the butadiyne ligands can exist in solution.[1b] At higher temperature the η^2 coordination is (entropically) favored due to intramolecular movement of the ligands.[3b] This means that in the case of **1c** the η^2 complex could be the reactive species instead of the η^4 complex, leading to a different reaction course. We observed evidence of such species earlier in coupling reactions of the corresponding titanacyclocumulenes $Cp_2Ti(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ for R = Ph[5f,g] and Me.[5g] However, when solutions of **1c** were investigated by ^{1}H and ^{13}C NMR spectroscopy up to 100 °C, there were no hints of such changing hapticity. The ^{1}H and ^{13}C chemical shifts exhibited only insignificant variations.

An alternative explanation may be that at the higher temperature for **1c** the thermodynamically more stable α-product is produced from the initially formed β-product. Unfortunately, dynamic NMR investigations with complexes **3** and **4** at 20−100 °C gave no answer to this question due to decomposition of the complexes.

NMR Investigations. The NMR spectroscopic data of complex **2** were published earlier.[3b] The $^{13}C\{^1H\}$ NMR data of $Cp^*_2Zr\{\eta^3\text{-}1,3,4\text{-}C(Me)\text{-}C[B(C_6F_5)_3]\text{-}C{\equiv}CMe\}$ (**3**) [100.0, 101.5 (C≡C); 240.5 (=C$_\alpha$)] correspond very well to those of the analogous Cp complexes $Cp_2M\{\eta^3\text{-}1,3,4\text{-}C(Me)\text{-}C[B(C_6F_5)_3]\text{-}C{\equiv}CMe\}$ [M = Zr:[2a] 108.5, 105.0 (C≡C); 255.0 ppm (=C$_\alpha$); M = Hf:[2b] 107.3, 96.4 (C≡C); 251.4.0 (=C$_\alpha$)], published earlier. Not unexpectedly, a signal for the boron-substituted carbon is not observable.

The comparison of the $^{13}C\{^1H\}$ NMR data of the "*trans*-cumulenic" complex **4** with those of the "*cis*-cumulenic" precursor **1c** exhibits very similar chemical shifts for C$_\alpha$ (176.8 and 179.4 ppm, respectively). Despite uncertain assignments, data for C$_\beta$ and C$_\gamma$ (122.5/171.5 vs 118.5 for **1c**) show the changing bonding mode, also in comparison to another zirconocene derivative[7] with η^3-propargyl/allenyl ligands, $Cp_2Zr(Me)(CH_2\text{-}C{\equiv}CPh)$/$Cp_2Zr(Me)(CPh{=}C{=}CH_2)$ (C(Ph) 120.5 and C(CH$_2$) 114.1 ppm). Steric restrictions are obvious for the phenyl group in the terminal position (at C4): a broad signal (which splits upon cooling) with $\delta(^1H)$ 4.47 ppm for its

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(7) (a) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994. (b) Blosser, P. W.; Galucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2000**, *597*, 125. (c) Rosenthal, U. *Angew. Chem.* **2004**, *116*, 3972; *Angew. Chem., Int. Ed.* **2004**, *43*, 3882.

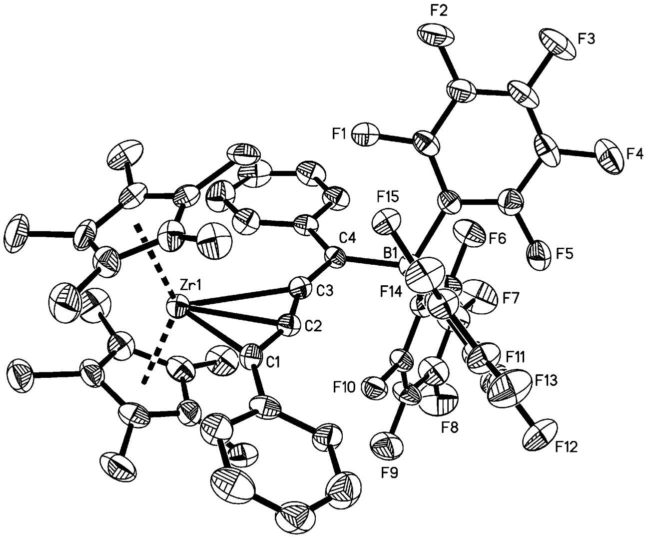


Figure 1. Crystal structure of complex **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: C1−C2 1.288(10), C2−C3 1.316(10), C3−C4 1.343(10); C1−C2−C3 153.8(8), C2−C3−C4 155.3(7), Zr−C1−C11 148.1(5), B1−C4−C5 121.8(6).

ortho-H, at extremely high field. This phenyl group must be “engulfed” by the zirconocene unit and the B(C_6F_5)$_3$ unit so that its rotation is hindered and its *ortho*-protons feel the magnetic anisotropy of an aromatic ring. A similar alk-1-en-3-yn-1-yl ligand without boron substituents also was encountered by Horton in cationic complexes of the type [Cp*$_2$Zr{η^2-CH=C(R)-C≡CR}][B(4-C_6H_4F)$_4$] (R = t-Bu) [125.3 (=C-t-Bu), 110.9 (≡C−t-Bu), 82.5 (−C≡); 210.2 ppm (=C$_\alpha$)].[8]

X-ray Crystal Structures. Complexes **2**, **3**, and **4** were investigated by X-ray crystallography.

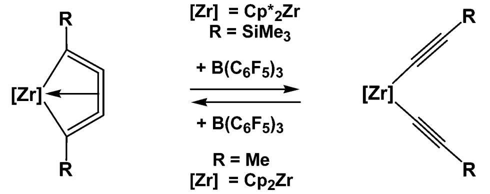
Due to strong disorders, a detailed discussion of the structure of **2** is not possible, but connectivity was reliably established. The molecular structure of the permethylzirconocene diacetylide Cp*$_2$Zr(σ-C≡CSiMe$_3$)$_2$ (**2**) is very similar to that of Cp$_2$Zr(σ-C≡CMe)$_2$.[2e]

Complex **3** displays a bent permethylzirconocene together with an additional ligand derived from complexed hex-2,4-diyne, where the attack of the borane in β position of the zirconacyclocumulene was clearly proven. Similar complexes with the hex-2-en-4-yn-2-yl-3-[tris(pentafluorophenyl)borate] ligand were often discussed, but determined as a structure only of the Hf complex Cp$_2$Hf{η^2-C(Me)-C[B(C_6F_5)$_3$]-C≡CMe} [2b] and the Zr complex (η^5-MeC$_5$H$_4$)$_2$Zr{η^2-C(Me)-C[B(C_6F_5)$_3$]-C≡CMe}.[9]

The molecular structure of complex **4** consists of a bent permethylzirconocene and the unprecedented 1,4-diphenylbuta-2,3,4-trien-1-yl-4-[tris(pentafluorophenyl)borate] ligand.

The former 1,4-diphenylbutadiyne is located between a permethylzirconocene Cp*$_2$Zr and the tris(pentafluorophenyl)borane, forming a “*trans*-cumulenic” structure [C1−C2 1.288(10); C2−C3 1.316(10); C3−C4 1.343(10) Å; C1−C2−C3 153.8(8)°; C2−C3−C4 155.3(7)°]. The bond distances are in the same range as found for the “*cis*-cumulenic” structure of the starting complex **1c** (Cα−Cβ 1.296(5) and 1.305(5); Cβ−Cβ' 1.327(4) Å; Cα−Cβ−Cβ' 148.5(4)°, 148.0(4)°). Another "*trans*-cumulenic" structure was described by Buchwald et al. in a seven-memberd zirconacyclocumulene [C1−C2 1.279(6); C2−C3 1.298(6); C3−C4 1.337(6) Å; C1−C2−C3 148.8(5)°; C2−C3−C4 160.1(5)°].[4f] Structural elements of **4** can be found also in the above-mentioned parent η^3-propargyl/η^3-allenyl complex Cp$_2$Zr(Me)(CPh=C=CH$_2$) [C(Ph)−C 1.259(4); C−C(H) 1.344(5) Å; C(Ph)−C−C(H) 155.4(3)°)].[7] The structure of **4** also is similar to that of a published dimeric zirconium complex in which the former 1,4-diphenylbutadiyne is located between two zirconium carborane complexes [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$)]$_2$Zr(NMe$_2$)$_2$, forming a “*trans*-cumulenic” structure [Cα−Cβ 1.268(17); Cβ−Cβ' 1.38(3) Å; Cα−Cβ−Cβ' 150.3(18)°].[10] There are some similarities to Teuben’s complexes[11a,b] with “zigzag-butadiyne ligands” as μ-η(1−3),η(2−4)-*trans*,*trans*-tetradehydrobutadiene moieties between two titanocene cores, e.g., for t-BuC≡C−C≡Ct-Bu [C1−C2 1.325(5); C2−C3 1.494(6); C3−C4 1.325(5) Å; C1−C2−C3 128.2(4)°; C2−C3−C4 128.2(4)°].[11c] These complexes have, in contrast to **4**, additional interactions of each of the Ti atoms with the internal C atoms of the bridging ligand, which reduces the bond order at C2−C3. Complexes of this type do not exist for Zr and were predicted by calculations only with special substituents.[11d]

Scheme 3



Conclusion

Reactions of five-membered zirconacyclocumulenes Cp′$_2$Zr(η^4-1,2,3,4-RC$_4$R) (Cp′ = Cp and Cp*) with B(C_6F_5)$_3$ are strongly influenced by the Cp′ ligands and the substituents R.

Depending on the nature of R for Cp* complexes, either a C−C bond cleavage to the bis-alkynyl complex **2** (R = Me$_3$Si) or reactions of the borane at the β-C (R = Me) and α-C atom (R = Ph) with formation of the zwitterionic complexes **3** and **4** were observed. All these products represent different steps of the C−C cleavage reaction: **4** (unproductive way), **3** (intermediate), and **2** (product).

On the basis of these findings, the catalytic influence of B(C_6F_5)$_3$ on C−C cleavage and coupling reactions may be described by an equilibrium (Scheme 2). In this the position between the zirconacyclocumulene and bis-alkynyl is determined by the choice of the Cp′ ligand system and the substituent R: for Cp/Me to the cycle and for Cp*/Me$_3$Si to the bis-alkynyl complex (Scheme 3). In summary it should be pointed out that B(C_6F_5)$_3$

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(8) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185.

(9) Erker, G.; Venne-Dunker, S.; Kehr, G.; Kleigrewe, N.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S. *Organometallics* **2004**, *23*, 4391.

(10) Wang, Y.; Wang, H.; Wang, H.; Chan, H.-S.; Xie, Z. *J. Organomet. Chem.* **2003**, *683*, 39.

(11) (a) Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87. (b) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (c) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W.; Görls, H. *J. Organomet. Chem.* **1994**, *468*, C4−C8. (d) Jemmis, E. D.; Giju, K. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 606.

can catalyze either the C−C coupling or cleavage process in such systems.

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 solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker ARX 400. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: benzene-d_6 ($\delta_H = 7.16$, $\delta_C = 128.0$). The spectra were assigned with the help of DEPT and shift correlation experiments. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 2. $B(C_6F_5)_3$ (0.026 g, 0.051 mmol) was dissolved in *n*-hexane (15 mL) under Ar, and the resulting solution was added to $Cp^*_2Zr(Me_3SiC_4SiMe_3)$[3b] (**1a**) (0.280 g, 0.503 mmol). The resulting yellow solution was allowed to stand under an argon atmosphere at room temperature. After one week the mixture was filtered, and upon cooling to −78 °C for 5 days, light yellow crystals were formed in the filtrate, which were separated from the mother liquor by decanting, washed with a small amount of cold *n*-hexane, and dried in a vacuum. Yield: 0.122 g (43,6%), mp 173−174 °C under Ar; 162−166 °C in ref 3b. Anal. Calcd for $C_{30}H_{48}Si_2Zr$: C, 64.80; H, 8.70. Found: C, 64.70; H, 9.01. MS (70 eV, *m/z*): 554 $[M]^+$, 360 $[Cp_2Zr]^+$. ^{1}H NMR and ^{13}C{^{1}H} NMR (C_6D_6, 297 K) data are identical to those given in ref 3b.

NMR Spectroscopic Investigations for the Formation of Complex 2. $B(C_6F_5)_3$ (0.020 g, 0.039 mmol) was dissolved in *n*-hexane (10 mL) under Ar. The solution was filtered, and the filtrate was added to $Cp^*_2Zr(Me_3SiC_4SiMe_3)$ (**1a**) (0.217 g, 0.390 mmol). Samples (1 mL) of the reaction mixture were taken, evaporated in a vacuum, and dissolved in C_6D_6, and the resulting solution was analyzed by ^{1}H NMR. The following results were obtained: % of **1a**/% of **2**: 86.3/13.7 (0.2 days); 55.3/44.7 (1 day); 15.3/84.7 (3 days); and 0.0/100 (6 days).

Preparation of Complex 3. $B(C_6F_5)_3$ (0.515 g, 1.01 mmol) was dissolved in warm toluene (10 mL) under Ar, and the resulting solution was added to a solution of $Cp^*_2Zr(MeC_4Me)$[3c] (**1b**) (0.450 g, 1.02 mmol) in toluene (7−8 mL). The resulting red-brownish mixture was filtered and the filtrate allowed to stand under argon atmosphere at room temperature. After 1 day dark red crystals of **3** had formed. The crystals were separated from the mother liquor by decanting, washed with toluene, and dried in a vacuum. Yield: 0.764 g (78%), mp 154−155 °C (dec) under Ar. Anal. Calcd for $C_{44}H_{36}ZrBF_{15}$: C, 55.53; H, 3.81. Found: C, 55.87; H, 4.01. ^{1}H NMR (C_6D_6, 297 K): 1.20 (s, 3H, Me); 1.50 (s, 30H, Cp*); 2.22 (s, 3H, Me). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 10.8 (Cp*); 6.9, 22.8 (CH_3); 100.0, 101.5 (C≡C); 124.2 (Cp*); 125 (br, ipso-C_6F_5) 137.4 ($^1J_{CF} = 247$ Hz, m-C_6F_5); 139.2 ($^1J_{CF} = 246$ Hz, p-C_6F_5); 148.8 ($^1J_{CF} = 240$ Hz, o-C_6F_5); 240.5 (=C_α); (=C_β)− the signal is not observed. IR (Nujol mull, cm^{-1}): 2132 (ν C≡C).

Crystals of **3** with C_6D_6 as solvate (mp 133−135 °C (dec) under Ar) suitable for X-ray analysis were grown from the filtrate of the reaction conducted with C_6D_6 as solvent.

Preparation of Complex 4. $B(C_6F_5)_3$ (0.403 g, 0.79 mmol) was dissolved in toluene (15 mL) under Ar, and the resulting solution was added to $Cp^*_2Zr(PhC_4Ph)$[3b] (**1c**) (0.440 g, 0.78 mmol). The resulting mixture was warmed to 80 °C for 6 h, filtered, and allowed to stand under argon atmosphere at −78 °C. After one week brown crystals of **4** had formed, which were separated from the mother liquor by decanting. After drying in a vacuum at 20 °C the crystals turned to an amorphous powder containing one mole of toluene per mole of **4** (found by NMR). Yield of this compound: 0.375 g (41%), mp 191−194 °C (dec) under Ar. Anal. Calcd for $C_{54}H_{40}ZrBF_{15}\cdot C_7H_8$: C, 62,73; H, 4.14. Found: C, 62,44; H, 4.07. ^{1}H NMR (C_6D_6, 297 K): δ 2.11 (s, 3H, Me, toluene); 1.57 (s, 30H, Cp*); 4.47 (d, 2H, 4-Ph *ortho*); 6.38 (d, 2H, 1-Ph *ortho*); 6.77 (t, 1H, 4-Ph *para*); 6.86 (t, 2H, 4-Ph *meta*); 6.94 (t, 1H, 1-Ph *para*); 7.10 (t, 2H, 1-Ph *meta*). ^{13}C NMR (C_6D_6, 297 K): δ 11.9 (C_5Me_5); 21.4 (Me, toluene); 122.5 (C3 or C2); 126.0 (C_5Me_5); 126.8 (4-Ph *para*); 128.6 (1-Ph *meta*); 129.3 (1-Ph *para*); 129.6 (4-Ph *meta*); 131.6 (1-Ph *ortho*); 133.1 (4-Ph *ortho*); 134.5 (1-Ph *ipso*); 146.5 (4-Ph *ipso*); 171.5 (C2 or C3); 176.8 (C1); C4 not observed. Aromatic signals for toluene were not identified.

Crystals of **4** suitable for X-ray analysis were obtained directly from the reaction as described above.

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 representation. Crystal structures of **2** and **3** suffered from extensive disorder. For **2** the Cp* ligands and the Me_3Si groups are disordered. In **3** the ligand derived from hex-2,4-diyne appeares in two different orientations, but the attack of the borane in β position of the zirconacyclocumulene could be established. Crystal data for **2**: yellow prism, monoclinic, space group $P2_1/c$, $a = 10.487(2)$ Å, $b = 19.198(4)$ Å, $c = 16.240(3)$ Å; $\beta = 95.47(3)°$; $V = 3254.7(11)$ Å^3, $Z = 4$, D_c 1.135 g cm^{-3}; 9626 reflections measured, 5193 were independent of symmetry and 3626 were observed $[(I > 2\sigma(I)]$, $R = 0.063$, $R_w{}^2$ (all data) = 0.176, 272 parameters. Crystal data for **3**: red-brown prism, triclinic, space group $P\bar{1}$, $a = 10.104(2)$ Å, $b = 12.719(3)$ Å, $c = 19.325(4)$ Å; $\alpha = 73.49(3)°$, $\beta = 79.12(3)°$, $\gamma = 70.27(3)°$; $V = 2229.4(8)$ Å^3, $Z = 2$, $D_c = 1.534$ g cm^{-3}; 4540 reflections measured, 3294 were observed $[(I > 2\sigma(I)]$, $R = 0.055$, $R_w{}^2$ (all data) = 0.129, 571 parameters.

The crystals of **4** contain a large amount of disordered solvent molecules (in total four molecules per formula unit). Crystal data for **4**: brown prism, orthorhombic, space group $Pna2_1$, $a = 26.031(5)$ Å, $b = 21.308(4)$ Å, $c = 14.864(3)$ Å; $V = 8245(3)$ Å^3, $Z = 4$, $D_c = 1.141$ g·cm^{-3}; 35 404 reflections measured, 10 417 were independent of symmetry and 7675 were observed $[(I > 2\sigma(I)]$, $R = 0.065$, $R_w{}^2$(all data) = 0.195, 776 parameters.

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

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