Evidence for a Carbon-Carbon Coupling Reaction To Proceed through a Planar-Tetracoordinate Carbon Intermediate

Gerhard Erker,* Sabine Venne-Dunker, Gerald Kehr, Nina Kleigrewe, Roland Fröhlich,[†] Christian Mück-Lichtenfeld,[‡] and Stefan Grimme^{*,‡}

Universität Münster, Organisch-Chemisches Institut, Corrensstrasse 40, D-48149 Münster, Germany

Received June 15, 2004

Treatment of bis(propynyl)zirconocene with $B(C_6F_5)_3$ results in a linear C–C coupling of the alkynyl ligands to form the zwitterionic complex 3. Its treatment with excess $RC \equiv N$ vields an organometallic methylenecyclopropene derivative (6). This reaction topologically requires a very endothermic substituted butenyne to methylenecyclopropene cyclization to become energetically feasible by suitable stabilization effects. A DFT study has revealed that the $\mathbf{3} \rightarrow \mathbf{6}$ conversion is probably triggered by nitrile addition to the metal with formation of a planar-tetracoordinate carbon intermediate, featuring coordination of the threemembered carbocycle through one of its carbon–carbon σ bonds.

Introduction

Planar-tetracoordinate carbon is sp² hybridized and thus contains a strongly electron deficient σ system (only six electrons making four bonds), with the remaining electron pair residing in the perpendicular p orbital. Conjugative interaction of the p electron pair plus the attachment of strongly σ donating substituents may stabilize this very unusual coordination geometry of tetravalent carbon.^{1,2} Computational studies have identified a variety of systems with favored planar-tetracoordinate carbon geometries, mostly stabilized by metal substituents or by a confinement in a rigid cage structure.³ A small number of compounds, stable at room temperature, have actually been isolated and characterized so far that feature such electronically stabilized tetracoordinate carbon atoms within an organometallic framework.^{4,5} The complexes **1** are typical examples

(1) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. J. Am. Chem. Soc.

(3) Rasmussen, D. R.; Radom, L. Angew. Chem. 1999, 111, 3052; Angew. Chem., Int. Ed. 1999, 38, 2876. Wang, Z.-X.; Schleyer, P. v. R. J. Am. Chem. Soc. 2001, 123, 994; 2002, 124, 11979.

(4) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A. Angew. Chem. **1995**, 107, 1194; Angew. Chem., Int. Ed. Engl. **1995**, 44, 1111 Hule Krasin, L. Claites, B.; Belmar, M. M.; Deurow, L. Angew. Chem. 1999, 1197, 1197, Angew. Chem., H. Lu. Eng. 1999, 34, 1111. Hyla-Kryspin, I.; Gleiter, R.; Rohmer, M.-M.; Devemy, J.; Gunale, A.; Pritzkow, H.; Siebert, W. Chem. Eur. J. 1997, 3, 294. Sahin, Y.; Präsang, C.; Hofmann, M.; Subramanian, G.; Geiseler, G.; Massa, W.; Berndt, A. Angew. Chem. 2003, 115, 695; Angew. Chem., Int. Ed. 2003, 42, 671. See also: Kickham, J. E.; Guérin, F.; Stewart, J. C.; Stephan, D. W. Angew. Chem. 2000, 112, 3406; Angew. Chem., Int. Ed. 2000, 39, 3263.

(5) Reviews: Röttger, D.; Erker, G. Angew. Chem. **1997**, 109, 840; Angew. Chem., Int. Ed. **1997**, 36, 812. Erker, G. Chem. Soc. Rev. **1999**, 28. 307.



e.g.: $L_n M^1 = Cp_2 Zr$; $L_n M^2 = AlR_2$, GaR_2 , $ZrCp_2^+$

(Scheme 1). In such systems an electron-rich carbon to metal σ bond is coordinated to a second electron-poor metal center inside a rigid framework. This results in the formation of a three-center-two-electron bonding situation in the σ plane with a conventionally stabilized π system perpendicular to it.5,6

Although an increasing number of such examples have been reported, planar-tetracoordinate carbon compounds have remained more a structural curiosity rather than being of importance as stabilized minimum structures in chemical reactions. We have now found an example where the electronic stabilization of a planar-tetracoordinate-carbon-containing reactive intermediate may have helped significantly in making an unusual carbon-carbon coupling reaction take place under rather mild conditions.

Results and Discussion

We had previously shown that bis(propynyl)zirconocene (2) and related systems react with $B(C_6F_5)_3$

^{*} To whom correspondence should be addressed. E-mail: erker@unimuenster.de (G.E.).

X-ray crystal structure analyses.

[‡] DFT calculations.

⁽¹⁾ Hormani, R., Ader, R. W., Wilcox, C. F., St. S. All, Chem. 1970, 92, 4992. Hoffmann, R. Pure Appl. Chem. 1971, 28, 181.
(2) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. J. Am. Chem. Soc. 1976, 98, 5419.
Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. Angew. Chem. 1989, 101, 1313; Angew. Chem., Int. Ed. Engl. 1989, 28, 1321. Li, X.; Zhang, H.-F.; Wang, L.-S.; Geske, G. D.; Boldyrev, A. I. Angew. Chem. 2000, 112, 3776; Angew. Chem., Int. Ed. 2000, 39, 3630. Wang, L.-S.; Boldyrev, A. I.; Li, X.; Simons, J. J. Am. Chem. Soc. 2000, 122, 7681 and references therein.

⁽⁶⁾ Erker, G.; Röttger, D. Angew. Chem. 1993, 105, 1691; Angew. Chem., Int. Ed. Engl. 1993, 32, 1623. Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R. J. Am. Chem. Soc. 1995, 117, 10503. Binger, P.; Sandmeyer, F.; Krüger, C.; Erker,
 G. *Tetrahedron* 1995, 51, 4277. Röttger, D.; Pflug, J.; Erker, G.; Kotila,
 S.; Fröhlich, R. *Organometallics* 1996, 15, 1265. Schottek, J.; Erker, G.; Fröhlich, R. Eur. J. Inorg. Chem. 1998, 551. See also: Schottek, J.; Erker, G.; Fröhlich, R. Angew. Chem. 1997, 109, 2585; Angew. 5.; Erker, G.; Fromich, R. Angew. Chem. **199**, 709, 2585; Angew. Chem., Int. Ed. **1997**, 36, 2475. Schottek, J.; Röttger, D.; Erker, G.; Fröhlich, R. J. Am. Chem. Soc. **1998**, 120, 5264. Hogenbirk, M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Schottek, J.; Fröhlich, R.; Erker, G.; Kooijman, H.; Spek, A. L. Eur. J. Inorg. Chem. **2004**, 1175.



Figure 1. Molecular structure of **3**' (experimentally determined by single-crystal X-ray diffraction). Selected bond lengths (Å) and angles (deg) (averaged over the two independent molecules), with the corresponding DFT-calculated values of **3** given in brackets for comparison: Zr-C2, 2.175(3) [2.200]; Zr-C3, 2.643(3) [2.575]; Zr-C4, 2.376(3) [2.337]; Zr-C5, 2.718(3) [2.762]; C1-C2, 1.497(4) [1.493]; C2-C3, 1.358(4) [1.367]; B1-C3, 1.684(5) [1.777]; C3-C4, 1.456(4) [1.432]; C4-C5, 1.208(5) [1.236]; C5-C6, 1.468(5) [1.463]; C1-C2-Zr, 141.0(2) [142.4]; C3-C2-Zr, 94.0(2) [89.3]; C1-C2-C3, 125.1(3) [128.3]; C2-C3-C4, 118.5(3) [122.7]; C2-C3-B, 125.2(3) [125.0]; C4-C3-B, 116.0(3) [112.1]; C3-C4-C5, 175.4(3) [178.8]; C4-C5-C6, 174.1(4) [168.2].

by rapid coupling of the alkynyl ligands to yield the zwitterionic product 3,7 A related hafnium complex was characterized by X-ray diffraction: however, not with high precision. We are now able to characterize complex 3' by an X-ray crystal structure analysis (see Figure 1). Complex 3' (R = CH₃) contains a planar central organic σ/π ligand framework, which was formed by coupling of a pair of propynyl ligands that connects the zirconocene unit with the $B(C_6F_5)_3$ moiety. Inside the μ -Me₂C₄ ligand the C4–C5 bond length is very short (1.208(5) Å), corresponding to a carbon–carbon triple bond that is unsymmetrically η^2 coordinated to zirconium (Zr-C4 = 2.376(3) Å, Zr-C5 = 2.718(3) Å). The newly formed C3-C4 bond (1.456(4) Å) is adjacent to a C2-C3 double bond (1.358(4) Å). Inside this ligand framework the C2-C3-C4 angle is close to the expected sp² value (118.5(3)°). The adjacent η^2 -acetylene unit is close to linear (C3-C4-C5 = 175.4(3)°, C4-C5-C6 = 174.1(4)°).

Complex **3** undergoes a remarkable reaction when treated with an organic nitrile reagent. A total of 2 equiv of RCN is taken up to form the methylenecyclopropene derivatives **6**. Several examples of these unusually structured compounds have been characterized by X-ray diffraction.⁸ We have now carried out a combined theoretical/experimental study that probably reveals the unusual reaction pathway that this remarkable chemical transformation takes.

Treatment of **3** with pivalonitrile in d_8 -toluene at -60 °C resulted in a spontaneous formation of a 1:1 adduct (**4a**). Its ¹³C NMR spectrum indicates that the alkyne moiety of the central μ -hexadiyne ligand in **4a** is probably no longer coordinated to the d⁰ zirconium center (¹³C NMR: $\delta(3)^7$ 108.5/105.0 (C5/4) vs $\delta(4a)$ 103.3/68.2). Slowly warming the mixture to room temperature in the dark revealed that the formation of the adduct from **3** and R¹CN was reversible and that concurrent equilibration with the metallacyclocumulene product **5**⁹ and R¹CN-B(C₆F₅)₃ occurred. Eventually out of the **3** \rightleftharpoons **4a** \rightleftharpoons **5** equilibrium mixture the irreversible and complete formation of the organometallic methyl-enecyclopropene product **6a** took place.

Treatment of the betaine **3** with excess benzonitrile at low temperature gave the adduct **4b**, which subsequently reacted further to give the metalated methylenccyclopropene derivative **6b**. For the determination of the rate of the **4b** \rightarrow **6b** conversion, the adduct **4b** was generated in situ by treatment of complex **3** with a ca. 10-fold excess of benzonitrile in *d*₈-toluene. At 243 K the consumption of **4b** was monitored under pseudofirst-order conditions using an added quantity of ferrocene as the internal standard. This gave a rate constant of $k_{\text{chem}} = k_{\text{obs}}/[\text{PhCN}]$ of $3.58 \times 10^{-3} \text{ s}^{-1} \text{ L}$ mol⁻¹, which corresponds to a Gibbs activation energy of $\Delta G^{\ddagger}_{\text{chem}}(243 \text{ K}) = 16.8 \pm 0.1 \text{ kcal mol}^{-1}$ for the secondorder reaction (**4b** \rightarrow **6b**) under standard conditions (i.e. 1 M benzonitrile).¹⁰

A detailed theoretical DFT study of the hypersurface of **3** with acetonitrile instead of PhCN has located the same types of structures as local minima. Their energies relative to the reference $3/CH_3CN$ are listed in Scheme 2 in brackets. The good agreement between the experimental (X-ray diffraction, 3') and calculated structural parameters of the betaine systems **3** shows the suitability of the DFT method for this organometallic system.

Topologically, the formation of **6** from **3** requires an intramolecular alkyne insertion into the zirconium to carbon σ bond to take place rapidly under the reaction conditions. However, calculations show that the underlying hexenyne to dimethyl-methylenecyclopropene isomerization is endothermic by ca. 26.6 kcal mol⁻¹. (DFT-BLYP; QCISD(T), +25.2 kcal mol⁻¹). Therefore, we had to identify the essential stabilizing factors that allowed this type of rearrangement to occur under the prevailing conditions of our experiment.

The DFT calculation produced a rather unusual $Cp_2Zr/B(C_6F_5)_3$ substituted methylenecyclopropene structure (8) of the direct alkyne insertion product. The Zr-C5-C4 angle in 8 is extremely reduced, namely from an expected 120° to 82°. This brings the methylenecy-

⁽⁷⁾ Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. Angew. Chem. **1994**, 106, 1570; Angew. Chem., Int. Ed. Engl. **1994**, 33, 1480. Ahlers, W.; Temme, B.; Erker, G.; Fröhlich, R.; Fox, T. J. Organomet. Chem. **1997**, 527, 191.

^{(8) (}a) Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. J. Chem. Soc., Chem. Commun. 1994, 1713. Erker, G.; Ahlers, W.; Fröhlich, R. J. Am. Chem. Soc. 1995, 117, 5853. Ahlers, W.; Erker, G.; Fröhlich, R.; Zippel, F. Chem. Ber./Recl. 1997, 130, 1079. Ahlers, W.; Erker, G.; Fröhlich, R. J. Organomet. Chem. 1998, 571, 83. Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. J. Organomet. Chem. 1999, 578, 115. Venne-Dunker, S.; Ahlers, W.; Erker, G.; Fröhlich, R. Eur. J. Inorg. Chem. 2000, 1671.
(b) For a remotely related reaction see, e.g.: Pragliola, S.; Milano, G.; Guerra, G.; Longo, P. J. Am. Chem. Soc. 2002, 124, 3502.

^{(9) (}a) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. Acc. Chem. Res. **2000**, 33, 119. Rosenthal, U.; Burlakov, V. V. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 355. (b) The state of the $\mathbf{3} = \mathbf{4} = \mathbf{5}$ equilibrium can be very dependent on the substituents at the acetylide units: Rosenthal, U.; Arndt, P.; Baumann, W.; Burlakov, V. V.; Spannenberg, A. J. Organomet. Chem. **2003**, 670, 84.

^{(10) (}a) Dahlmann, M.; Erker, G.; Bergander, K. J. Am. Chem. Soc.
2000, 122, 7986. (b) Moore, J. W.; Pearson, R. G. In Kinetics and Mechanism; Wiley: New York, 1981; pp 178–181. Robinson, P. J. J. Chem. Educ. 1978, 55, 509.



^{*a*} Legend: $R^1 = CMe_3$ (**a**), Ph (**b**), Me (**c**); ${}^{R}Cp = C_5H_5$ MeC₅H₄ (**3**'). Calculated relative energies (in kcal/mol) are given in brackets.

clopropene $C(sp^2)-C(sp^2) \sigma$ bond into a direct bonding contact with the strongly electrophilic zirconium center.^{11,12} The core of the molecule has remained completely planar. The overall bonding situation in **8** is in principle very similar to that in the organometallic systems **1**, depicted in Scheme 1, except that in **8** an electron-rich carbon–carbon σ bond from a strained all-sp²-carbon three-membered carbocycle is interacting with the available metal acceptor orbital in the metallocene σ ligand plane. The resulting very distorted structure of **8** featuring short Zr–C4 (2.396 Å) and Zr–C2 (2.609 Å) contacts consequently contains a planar-tetracoordinated carbon atom (C4) of a type similar to that found in the experimental structures of the complex types **1** (see Figure 2).

The internal σ coordination of the methylenecyclopropene carbon-carbon σ bond to the strongly electrophilic zirconium center in 8 constitutes a major stabilizing factor, making the product of internal alkyne insertion (8) more favorable by ca. 7 kcal mol⁻¹ than the hypothetical, not C4-tetracoordinated isomer 7, which could not be obtained as a stable minimum in our computations. Nevertheless, the structurally attractive system 8 is probably still too high in energy $(\Delta E(3/8) \approx +19 \text{ kcal mol}^{-1})$ to serve as a reactive intermediate in the observed reaction under the actual experimental conditions. However, we have located a similarly structured likely intermediate of the $3 \rightarrow 6$ conversion on this hypersurface, which already contained 1 equiv of the nitrile added. The DFT calculated structure of 9 (see Scheme 3 and Figure 3) is only +6.7kcal mol⁻¹ in energy above the **3** plus acetonitrile reference. It contains acetonitrile coordinated to zirconium (d(Zr-N) = 2.329 Å), and it has the completed



Figure 2. DFT-calculated structure of the internal alkyne insertion product **8**.

Scheme 3.	Possible Reactive Intermediates of t	he
	Conversion $3 \rightarrow 6^a$	



^{*a*} DFT-calculated relative energies (in kcal/mol) are given in brackets. [Zr] denotes Cp_2Zr , and [B] denotes $B(C_6F_5)_3$.

methylenecyclopropene moiety located in the central σ ligand plane of the bent metallocene unit. Again, the three-membered carbocycle is side-on coordinated to the metal center, but this essential σ -C-C coordination is much more unsymmetrical than in **8**. In **9** the Zr-C5-C4 angle amounts to 88.3° and the Zr···C2 distance has opened to 3.150 Å, but the Zr-C4 bond has remained strong at 2.496 Å. Carbon atom C4 is planar tetracoordinate. It features four close contacts in a single plane (C4-C5 = 1.356 Å, C4-C3 = 1.469 Å, C4-C2 = 1.477 Å, and C4-Zr = 2.496 Å).

It seems likely that the topologically necessary intramolecular alkyne insertion into the $C(sp^2)$ -Zr bond of **3** is triggered by nitrile, a feature that is probably thermodynamic in origin to help to overcome the enormous endothermicity of the underlying hexenyne to dimethyl-methylenecyclopropene cyclization within the zwitterionic framework of the zirconium/boron betaine system **3**. The calculated likely intermediate (**9**) of this unusual reaction seems to contain a planar-

⁽¹¹⁾ For related examples of σ interactions at unusually structured bent metallocene complexes see, e.g.: (a) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, *295*, 660. Suzuki, N.; Aihara, N.; Takahara, H.; Watanabe, T.; Iwasaki, M.; Saburi, M.; Hashizume, D.; Chihara, T. *J. Am. Chem. Soc.* **2004**, *126*, 60. (b) Lam, K. C.; Lin, Z. *Organometallics* **2003**, *22*, 3466. Jemmis, E. D.; Phukan, A. K.; Jiao, H.; Rosenthal, U. *Organometallics* **2003**, *22*, 4958.

 ⁽¹²⁾ See for a comparison: Sorger, K.; Schleyer, P. v. R.; Stalke, D. J. Chem. Soc., Chem. Commun. 1995, 2279. Sorger, K.; Schleyer, P. v. R.; Fleischer, R. S. Stalke, D. J. Am. Chem. Soc. 1996, 118, 6924. Jensen, T. R.; Marks, T. J. Macromolecules 2003, 36, 1775.





Figure 3. DFT-calculated structure of **9** featuring a planar-tetracoordinate carbon atom (C4).

tetracoordinate carbon atom. Stable organometallic systems exhibiting such unusual coordination geometries of carbon had found interest mostly because of their unusual structural and bonding features.⁵ Our example shows that forming planar-tetracoordinate carbon geometries might also help to stabilize reactive intermediates and, thus, "anti-van't Hoff/LeBel" carbon compounds may in some cases play a much more important role than previously thought.

Experimental Section

Reactions and handling of the organometallic reagents and products was carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for spectroscopic characterization) were dried and distilled under argon prior to use. For additional general information, including a list of instruments used for spectroscopic and physical characterization of the compounds, see ref 10a. The bis(propynyl)zirconocene complexes **2** (Cp₂Zr(C=CCH₃)₂) and **2'** ((MeC₅H₄)₂Zr(C=CCH₃)₂) and the betaine system **3** were prepared according to literature procedures.^{7,8}

Reaction of Bis(η^{5} -methylcylopentadienyl)bis(propynyl)zirconium (2') with Tris(pentafluorophenyl)borane: Synthesis of Complex 3'. Complex 2' (2.00 g, 6.11 mmol) was mixed with tris(pentafluorophenyl)borane (3.13 g, 6.11 mmol). At -78 °C cold toluene (20 mL) was added. After 1 h at low temperature the mixture was warmed to room temperature and stirred overnight. The precipitated orange colored product 3' was collected by filtration, washed with pentane, and dried in vacuo. Yield: 4.16 g (81%). Anal. Calcd for C₃₆H₂₀BF₁₅Zr (839.6): C, 51.49; H, 2.38. Found: C, 51.73; H, 2.60. ¹H NMR (d_6 -benzene, 200 MHz, 300 K): δ 5.23 (br, 8H, C₅H₄), 2.26 (s, 3H, CH₃), 1.39 (br s, 6H, C₅H₄CH₃), 1.09 (s, 3H, CC-CH₃). ¹¹B NMR (d_6 -benzene, 64.2 MHz, 300 K): δ -13.3.

X-ray Crystal Structure Analysis of Complex 3'. Single crystals were grown over several months from a toluene

solution. Crystal data are as follows: formula C₃₆H₂₀BF₁₅Zr, $M_{\rm r} = 839.55$, colorless crystal 0.35 \times 0.15 \times 0.10 mm, a =15.6168(1) Å, b = 20.0336(2) Å, c = 20.2833(2) Å, $\beta =$ 90.012(1)°, V = 6345.85(10) Å³, $\rho_{calcd} = 1.758$ g cm⁻³, $\mu = 4.63$ cm⁻¹, empirical absorption correction (0.855 $\leq T \leq$ 0.955), Z = 8, monoclinic (pseudo-orthorhombic with the twinning law 100, 0, -1, 0, 0, 0, -1), space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and φ scans, 48 557 reflections collected ($\pm h$, $\pm k, \pm l$, $(\sin \theta)/\lambda = 0.65 \text{ Å}^{-1}$, 13 397 independent ($R_{\text{int}} = 0.059$) and 11 026 observed reflections ($I \ge 2\sigma(I)$), 964 refined parameters, R1 = 0.038, wR2 = 0.073, maximum residual electron density 0.37 (-0.55) e Å⁻³, hydrogens calculated and refined as riding atoms, ratio of the twins refined to 0.629(1): 0.371(1), two almost identical molecules in the asymmetric unit. The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius BV, 1998), data reduction Denzo-SMN,¹³ absorption correction SORTAV,¹⁴ structure solution SHELXS-97,¹⁵ structure refinement SHELXL-97,16 graphics SCHAKAL.17 Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-229224. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code +44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk).

Reaction of the Betaine System 3 with Pivalonitrile. (a) Formation of the Adduct 4a at 213 K. An NMR tube was charged with complex **3** (5.00 mg, 6.20 μ mol). d_8 -Toluene (1 mL) was added and the solution cooled to -78 °C. At this temperature 1.40 μ L (1.03 mg, 12.4 μ mol) of pivalonitrile was added. The system was mixed and directly monitored by NMR at -60 °C. This revealed that the adduct **4a** was selectively formed under these conditions. ¹H NMR (toluene- d_8 , 599.9 MHz, 213 K): δ 5.54, 5.27 (each s, each 5H, Cp), 1.95 (s, 3H, 1-H), 1.21 (s, 3H, 6-H), 0.61 (s, 9H, 9-H). $^{13}C{^{1}H}$ NMR (toluene-d₈, 150.4 MHz, 213 K): δ 198.2 (C2), 120.5 (C7), 110.8, 110.3 (Cp), 103.3 (C5), 68.2 (C4), 28.1 (C8), 25.2 (C1), 25.0 (C9), 7.5 (C6). The one-dimensional ¹³C data are extracted from the two-dimensional GHSQC and GHMBC experiments. GHSQC (toluene-d₈, 150.4 MHz/599.9 MHz, 213 K): δ(¹³C)/δ(¹H) 110.8, 110.3/5.54, 5.27 (Cp/Cp), 25.2/1.95 (C1/1-H), 7.5/1.21 (C6/6-H), 25.0/0.61 (C9/9-H). GHMBC (toluene-d₈, 150.4 MHz/599.9 MHz, 213 K): $\delta(^{13}C)/\delta(^{1}H)$ 198.2/1.95 (C2/1-H), 120.5/0.61 (C7/ 9-H), 103.3/1.21 (C5/6-H), 68.2/1.21(C4/6-H), 28.1/0.61 (C8/9-H).

(b) Formation of the Metallacyclocumulene 5 and Subsequently of the Insertion Product 6a. The reaction mixture described above was slowly warmed to room temperature. NMR spectroscopy showed that first complex 5 was formed, which was subsequently consumed during several hours at ambient temperature to eventually give 6a. Data for complex 5 are as follows. ¹H NMR (toluene- d_8 , 599.9 MHz, 213 K): δ 5.01 (s, 10H, Cp), 2.77 (s, 6H, CH₃); borane-nitrile adduct δ 0.58 (s, 9-H, CH₃). ¹³C{¹H} NMR (toluene- d_8 , 150.4 MHz, 213 K): δ 170.1 (C1), 103.8 (C2), 102.7 (Cp), 17.6 (CH₃); borane-nitrile adduct δ 119.1 (*C*N), 26.1 (CH₃). The *C*Me₃ carbon signal was not observed.

(c) Preparation of the Pivalonitrile Insertion Product 6a. Pivalonitrile (0.25 mL, 188 mg, 2.26 mmol) was added to a suspension of 600 mg (0.74 mmol) of complex 3 in 30 mL of

⁽¹³⁾ Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.

⁽¹⁴⁾ Blessing, R. H. Acta Crystallogr. **1995**, A51, 33–37. Blessing, R. H. J. Appl. Crystallogr. **1997**, 30, 421–426.

 ⁽¹⁵⁾ Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467–473.
 (16) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany. 1997.

⁽¹⁷⁾ Keller, E. SCHAKAL; Universität Freiburg, Freiburg, Germany, 1997.

toluene at -78 °C. The mixture was slowly warmed to room temperature and then stirred for a further 6 h. Volatiles were removed in vacuo to give the product 6a (564 mg, 78%) as a yellow solid as a 4:1 mixture of two isomers. Mp 238 °C dec. Anal. Calcd for C44H34BF15N2Zr (987.9): C, 54.05; H, 3.50; N, 2.87. Found: C, 54.00; H, 3.81; N, 3.35. ¹H NMR (toluene-d₈, 599.9 MHz, 213 K): major isomer, δ 5.49 (s, 10H, Cp), 2.23 (s, 3H, 6-H), 1.62 (s, 3H, 5-H), 1.07 (s, 9H, 9-H), 0.70 (s, 9H, 12-H); minor isomer, δ 5.51 (s, 10H, Cp), 2.26 (s, 3H, 6-H), 1.77 (s, 3H, 5-H), 1.04 (s, 9H, 9-H), 0.65 (s, 9H, 12-H). ¹³C{¹H} NMR (toluene- d_8 , 150.4 MHz, 213 K): major isomer, δ 187.2 (C7), 166.0 (C1), 149.8 (C3), 145.6 (C2), 148.9 (dm, ${}^{1}J_{CF} = 244$ Hz, o-B(C₆F₅)₃), 139.5 (dm, ${}^{1}J_{CF} = 246$ Hz, p-B(C₆F₅)₃), 147.7 (dm, ${}^{1}J_{CF} = 258$ Hz, m-B(C₆F₅)₃), 141.0 (C10), 122.8 (broad, ipso-B(C₆F₅)₃), 110.3, 110.2 (Cp), 83.8 (C4), 38.9 (C8), 30.2 (C9), 28.1 (C11), 26.2 (C12), 22.5 (C6), 11.5 (C5); minor isomer, δ 187.2 (C7), 166.0 (C1), 147.9 (C3), 145.4 (C2), 140.3 (C10), 111.6, 111.5 (Cp), 82.1 (C4), 41.5 (C8), 29.9 (C9), 29.4 (C11), 26.3 (C12), 21.3 (C6), 11.5 (C5). The ¹³C resonances of C1 were not observed; the ¹³C resonances of the C₆F₅ unit were superposed. ¹¹B{¹H} NMR (toluene- d_8 , 64.2 MHz, 300 K): δ -17.3 ($v_{1/2} = 3$ Hz). ¹⁹F NMR (toluene- d_8 , 282.4 MHz, 213 K): major isomer, δ -134.3 (*o*-B(C₆F₅)₃), -163.0 (*p*-B(C₆F₅)₃), -167.5 (*m*-B(C₆F₅)₃); minor isomer, δ -133.8 (*o*-B(C₆F₅)₃), $-162.3 (p-B(C_6F_5)_3), -167.1 (m-B(C_6F_5)_3).$

Reaction of Complex 3 with Benzonitrile at 213 K. Generation of the Adduct 4b. An NMR tube was charged with 5.00 mg (6.20 μ mol) of complex 3 and 1 mL of d_8 -toluene and then cooled to -78 °C. At this temperature 1.30 μ L (1.28 mg, 1.24 μ mol) of benzonitrile was added and the system mixed and characterized by NMR spectroscopy at -60 °C. At low temperature, only the formation of the adduct 4b was observed. ¹H NMR (toluene-d₈, 599.9 MHz, 213 K): δ 6.67, 6.49 (each m, 5H, Ph), 5.62, 5.36 (each s, each 5H, 2 Cp), 1.96 (s, 3H, 1-H), 1.24 (s, 3H, 6-H). ¹³C{¹H} NMR (toluene-d₈, 150.4 MHz, 213 K): δ 198.0 (C2), 131.8, 131.8, 128.4 (Ph), 111.6 (Ph_{ipso}), 110.6, 110.3 (Cp), 106.4 (C5), 63.8 (C4), 7.5 (C1), 1.4 (C6) (C3 resonance was not observed). GHSQC (toluene-ds. 150.4 MHz/599.9 MHz, 213 K): δ(¹³C)/δ(¹H) 131.8, 131.8. 128.4/ 6.67, 6.49 (Ph/Ph), 110.6, 110.3/5.62, 5.36 (Cp/Cp), 7.5/1.96 (C1/ 1-H), 1.4/1.24 (C6/6-H). GHMBC (toluene-d₈, 150.4 MHz/599.9 MHz, 213 K): δ(¹³C)/δ(¹H) 198.0/1.96 (C2/1-H), 131.8, 128.4/ 6.67, 6.49 (Ph/Ph), 111.6/6.49 (Phipso/Ph), 110.6, 110.3/5.36, 5.62 (Cp/Cp), 106.4/1.24 (C5/6-H), 63.8/1.24 (C4/6-H).

When the mixture was warmed to room temperature, the formation of the previously described product **6b**^{7,8} was monitored. ¹H NMR (toluene- d_8 , 599.9 MHz, 298 K): δ 6.88, 6.79, 6.64 (each m, 10H, Ph), 5.52 (s, 10H, Cp), 1.85 (s, 3H, 5-H), 1.28 (s, 3H, 6-H). ¹³C{¹H} NMR (toluene- d_8 , 150.4 MHz, 213 K): δ 181.6 (C7), 173.5 (C3), 153.7 (C2), 149.0 (dm, ¹ J_{CF} = 241 Hz, *o*-B(C₆F₅)₃), 145.7 (C8), 139.6 (dm, ¹ J_{CF} = 246 Hz, *p*-B(C₆F₅)₃), 137.4 (dm, ¹ J_{CF} = 247 Hz, *m*-B(C₆F₅)₃), 133.9, 133.5, 132.8, 130.6, 129.8, 129.5, 128.5, 127.8 (Ph), 112.6 (Cp), 87.6 (C4), 15.9 (C5), 9.0 (C6). The ¹³C resonances of C1 and ipso-B(C₆F₅)₃ were not observed.

Determination of the Reaction Rate of the 3 + Benzonitrile Reaction To Yield 6b. Complex 3 was dissolved with a defined quantity of ferrocene (used as an internal standard) in d_8 -toluene at room temperature in an NMR tube. The solution was cooled to -78 °C, and 7.5 μ L of pivalonitrile was added slowly via syringe. After the system was carefully mixed inside the cooling bath, the NMR tube was transferred to the NMR spectrometer at -50 °C. The reaction was then started by raising the temperature to -30 °C, and the measurement was also started. The decrease of the concentration of the educt (which was the corresponding benzonitrile adduct 4b) was monitored using the corresponding ¹H NMR Cp resonances at δ 5.67 and 5.38 (each s, each 5H), and the increase of the concentration of the product (6b) was followed by integration of the corresponding ¹H NMR Cp resonance at δ 5.49 (s, 10H). Four independent series of measurements were carried out (for details see the Supporting Information) to give an averaged value of $\Delta G^{\ddagger}_{\text{chem}}(243 \text{ K}) = 16.8 \pm 0.1 \text{ kcal mol}^{-1}$.

DFT Calculations. All quantum-chemical calculations have been performed with the TURBOMOLE suite of programs.^{18a} The structures have been fully optimized at the density functional (DFT) level employing the B-LYP functional.^{18b} A Gaussian AO basis of valence-triple- ζ quality, including polarization functions (TZVP),^{18c} was used for heavy atoms, except for the C₆F₅ substituents, for which a split-valence basis set with polarization functions (SVP)^{18d} was used. One additional f-polarization function ($\alpha = 0.988$ 993) from the TURBOMOLE basis set library and a relativistic pseudo-potential (small core)^{18e} were employed for zirconium. The RI approximation was used for the two-electron integrals.^{18f}

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Text, tables and figures giving details of the DFT calculations, additional spectroscopic data, and details of the kinetic study and the X-ray crystal structure analysis; crystallographic data are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0495628

^{(18) (}a) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Huber, C.; Huniar, U.; Kattannek, M.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Treutler, O.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. TURBOMOLE (Version 5.3); Universität Karlsruhe, Karlruhe, Germany, 2000. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098 Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Schäfer, A. Huber, C.; Ahlrichs, R. J. Chem. Phys. **1994**, *100*, 5829. (d) Schäfer, A.; Horn, H.; Ahlrichs, R. J. Chem. Phys. **1992**, *97*, 2571. (e) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Theor. Chim. Acta **1990**, *77*, 123. (f) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Chem. Phys. Lett. **1995**, *240*, 283.