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

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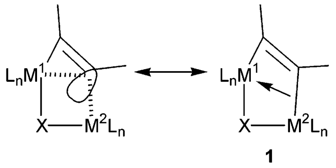
Treatment of bis(propynyl)zirconocene with $B(C_6F_5)_3$ results in a linear C−C coupling of the alkynyl ligands to form the zwitterionic complex **3**. Its treatment with excess RC≡N yields an organometallic methylenecyclopropene derivative (**6**). This reaction topologically requires a very endothermic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

Introduction

Planar-tetracoordinate carbon is sp^2 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 (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]

Scheme 1



e.g.: $L_nM^1 = Cp_2Zr$; $L_nM^2 = AlR_2, GaR_2, ZrCp_2^+$

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 $B(C_6F_5)_3$

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† X-ray crystal structure analyses.

‡ DFT calculations.

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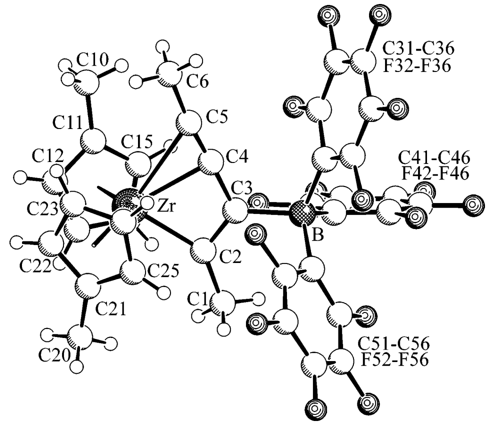

Figure 1. Molecular structure of **3′** (experimentally determined by single-crystal X-ray diffraction). Selected bond lengths (Å) and angles (deg) (averaged over the two independent molecules), with the corresponding DFT-calculated values of **3** given in brackets for comparison: Zr−C2, 2.175(3) [2.200]; 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 = CH_3) 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-Me_2C_4 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 sp^2 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 ^{13}C NMR spectrum indicates that the alkyne moiety of the central μ-hexadiyne ligand in **4a** is probably no longer coordinated to the d^0 zirconium center (^{13}C NMR: $\delta(\mathbf{3})^7$ 108.5/105.0 (C5/4) vs $\delta(\mathbf{4a})$ 103.3/68.2). Slowly warming the mixture to room temperature in the dark revealed that the formation of the adduct from **3** and R^1CN was reversible and that concurrent equilibration with the metallacyclocumulene product **5**[9] and $R^1CN{-}B(C_6F_5)_3$ occurred. Eventually out of the $\mathbf{3} \rightleftarrows \mathbf{4a} \rightleftarrows \mathbf{5}$ equilibrium mixture the irreversible and complete formation of the organometallic methylenecyclopropene 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 methylenecyclopropene derivative **6b**. For the determination of the rate of the $\mathbf{4b} \rightarrow \mathbf{6b}$ 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 pseudo-first-order conditions using an added quantity of ferrocene as the internal standard. This gave a rate constant of $k_{chem} = k_{obs}/[PhCN]$ of 3.58×10^{-3} s^{-1} L mol^{-1}, which corresponds to a Gibbs activation energy of $\Delta G^{\ddagger}{}_{chem}(243\ K) = 16.8 \pm 0.1$ kcal mol^{-1} for the second-order reaction ($\mathbf{4b} \rightarrow \mathbf{6b}$) 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-

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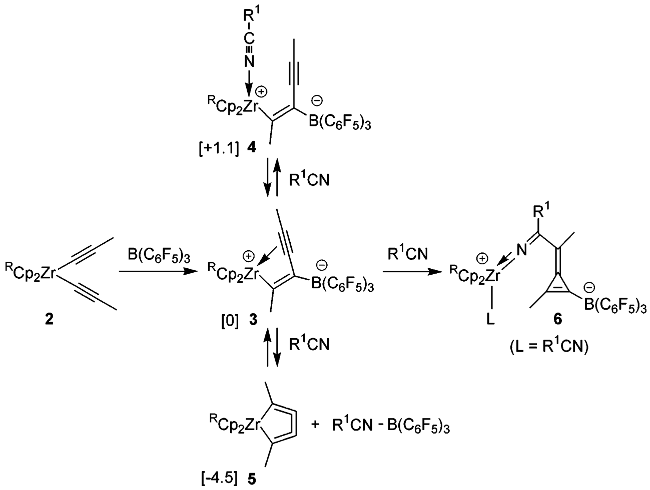
Scheme 2[a]



[a] Legend: $R^1 = CMe_3$ (**a**), Ph (**b**), Me (**c**); $^RCp = C_5H_5$ MeC_5H_4 (**3′**). Calculated relative energies (in kcal/mol) are given in brackets.

clopropene $C(sp^2)-C(sp^2)$ σ 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-sp^2-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 (ΔE(**3**/**8**) $\approx +19$ 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** → **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 +6.7 kcal 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 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).

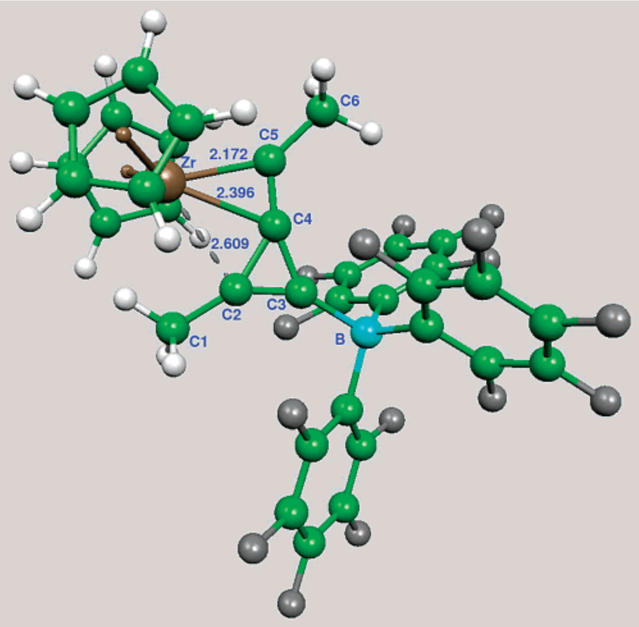
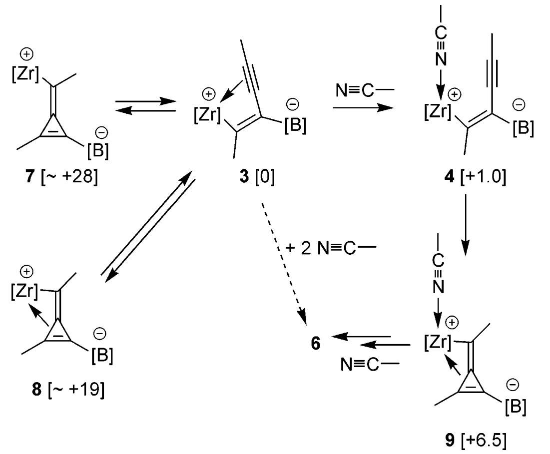


Figure 2. DFT-calculated structure of the internal alkyne insertion product **8**.

Scheme 3. Possible Reactive Intermediates of the Conversion 3 → 6[a]



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

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-

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(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.

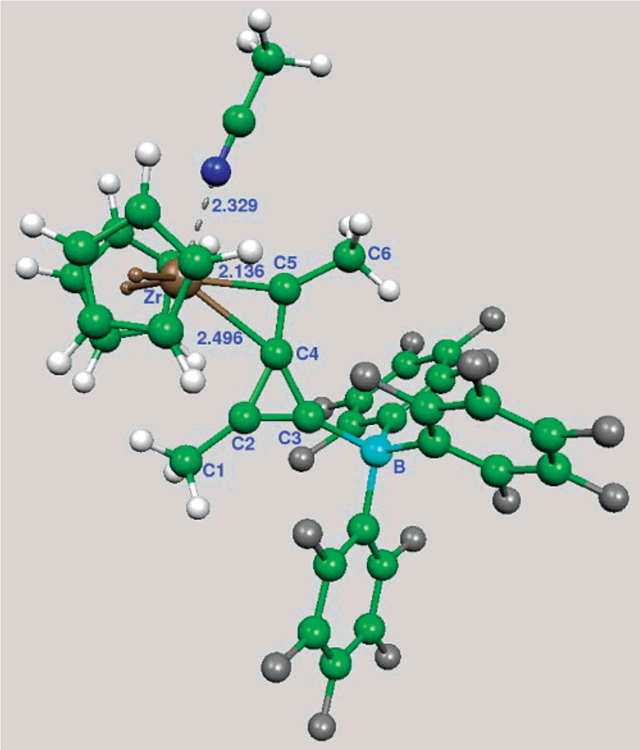

Figure 3. DFT-calculated structure of **9** featuring a planar-tetracoordinate carbon atom (C4).

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** ($Cp_2Zr(C{\equiv}CCH_3)_2$) and **2′** ($(MeC_5H_4)_2Zr(C{\equiv}CCH_3)_2$) 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 $C_{36}H_{20}BF_{15}Zr$ (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, C_5H_4), 2.26 (s, 3H, CH_3), 1.39 (br s, 6H, $C_5H_4CH_3$), 1.09 (s, 3H, $CC{-}CH_3$). ^{11}B 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 $C_{36}H_{20}BF_{15}Zr$, $M_r = 839.55$, colorless crystal 0.35 × 0.15 × 0.10 mm, $a = 15.6168(1)$ Å, $b = 20.0336(2)$ Å, $c = 20.2833(2)$ Å, $\beta = 90.012(1)°$, $V = 6345.85(10)$ Å^3, $\rho_{calcd} = 1.758$ g cm^{-3}, $\mu = 4.63$ cm^{-1}, empirical absorption correction ($0.855 \le T \le 0.955$), $Z = 8$, 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 ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.65$ Å^{-1}, 13 397 independent ($R_{int} = 0.059$) 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 μmol). d_8-Toluene (1 mL) was added and the solution cooled to −78 °C. At this temperature 1.40 μL (1.03 mg, 12.4 μmol) 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). $^{13}C\{^1H\}$ NMR (toluene-d_8, 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 ^{13}C data are extracted from the two-dimensional GHSQC and GHMBC experiments. GHSQC (toluene-d_8, 150.4 MHz/599.9 MHz, 213 K): $\delta(^{13}C)/\delta(^1H)$ 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-d_8, 150.4 MHz/599.9 MHz, 213 K): $\delta(^{13}C)/\delta(^1H)$ 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, CH_3); borane−nitrile adduct δ 0.58 (s, 9-H, CH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, 150.4 MHz, 213 K): δ 170.1 (C1), 103.8 (C2), 102.7 (Cp), 17.6 (CH_3); borane−nitrile adduct δ 119.1 (CN), 26.1 (CH_3). The CMe$_3$ 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

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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 $C_{44}H_{34}BF_{15}N_2Zr$ (987.9): C, 54.05; H, 3.50; N, 2.87. Found: C, 54.00; H, 3.81; N, 3.35. ^1H NMR (toluene-d_8, 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). $^{13}C\{^1H\}$ 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, $^1J_{CF} = 244$ Hz, *o*-$B(C_6F_5)_3$), 139.5 (dm, $^1J_{CF} = 246$ Hz, *p*-$B(C_6F_5)_3$), 147.7 (dm, $^1J_{CF} = 258$ Hz, *m*-$B(C_6F_5)_3$), 141.0 (C10), 122.8 (broad, ipso-$B(C_6F_5)_3$), 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 ^{13}C resonances of C1 were not observed; the ^{13}C resonances of the C_6F_5 unit were superposed. $^{11}B\{^1H\}$ NMR (toluene-d_8, 64.2 MHz, 300 K): δ −17.3 ($\nu_{1/2} = 3$ Hz). ^{19}F NMR (toluene-d_8, 282.4 MHz, 213 K): major isomer, δ −134.3 (*o*-$B(C_6F_5)_3$), −163.0 (*p*-$B(C_6F_5)_3$), −167.5 (*m*-$B(C_6F_5)_3$); minor isomer, δ −133.8 (*o*-$B(C_6F_5)_3$), −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 μmol) of complex **3** and 1 mL of d_8-toluene and then cooled to −78 °C. At this temperature 1.30 μL (1.28 mg, 1.24 μmol) 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-d_8, 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). $^{13}C\{^1H\}$ NMR (toluene-d_8, 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-d_8, 150.4 MHz/599.9 MHz, 213 K): $\delta(^{13}C)/\delta(^1H)$ 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-d_8, 150.4 MHz/599.9 MHz, 213 K): $\delta(^{13}C)/\delta(^1H)$ 198.0/1.96 (C2/1-H), 131.8, 128.4/6.67, 6.49 (Ph/Ph), 111.6/6.49 (Ph_{ipso}/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). $^{13}C\{^1H\}$ NMR (toluene-d_8, 150.4 MHz, 213 K): δ 181.6 (C7), 173.5 (C3), 153.7 (C2), 149.0 (dm, $^1J_{CF} = 241$ Hz, *o*-$B(C_6F_5)_3$), 145.7 (C8), 139.6 (dm, $^1J_{CF} = 246$ Hz, *p*-$B(C_6F_5)_3$), 137.4 (dm, $^1J_{CF} = 247$ Hz, *m*-$B(C_6F_5)_3$), 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 ^{13}C resonances of C1 and ipso-$B(C_6F_5)_3$ 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 μL 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 $\Delta G^{\ddagger}_{chem}(243\ K) = 16.8 \pm 0.1\ kcal\ mol^{-1}$.

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 C_6F_5 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 pseudopotential (small core)[18e] were employed for zirconium. The RI approximation was used for the two-electron integrals.[18f]

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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.

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