Formation, Structure, and Dynamic Behavior of a Novel Dinuclear Cationic μ-2,4-Hexadiyne Bis(zirconocene) Complex[†]

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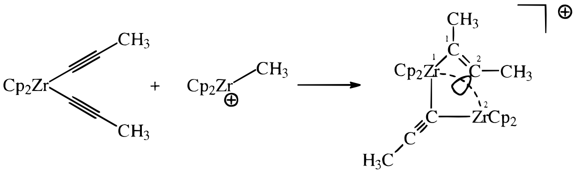
Bis(propynyl)zirconocene (**1b**) reacts with 0.5 molar equiv of trityl tetraphenylborate by a propynyl group transfer to form $Ph_3CC{\equiv}CCH_3$ and $Cp_2ZrC{\equiv}CCH_3^+$. The in-situ-generated (propynyl)zirconocene cation is not stable under the reaction conditions but instantaneously reacts with the neutral starting material **1b** to form the $[(\mu\text{-}C{\equiv}CCH_3)(\mu\text{-}CH_3C{\equiv}CC{\equiv}CCH_3)(ZrCp_2)_2{}^+][BPh_4{}^-]$ salt, **9**. Complex **9** was characterized by an X-ray crystal structure analysis. It contains an unsymmetrically bridging hexadiyne ligand and exhibits a planar-tetracoordinate carbon center that is stabilized by a three-center two-electron interaction with the two adjacent zirconocene moieties. In solution, complex **9** exhibits dynamic NMR spectra that indicate a symmetrizing exchange of the bonding situations between the two ends of the μ-hexadiyne ligand. The Gibbs activation energy of the automerization reaction of **9** is $\Delta G^{\ddagger}(190\ \text{K}) \approx 9.5\ \text{kcal mol}^{-1}$.

Introduction

The chemistry of alkyl- and hydridozirconocene cations, Cp_2ZrR^+ and Cp_2ZrH^+, respectively, has been of considerable interest due to their involvement as important reactive species in alkene polymerization reactions at homogeneous metallocene Ziegler catalysts.[1,2] In addition, an interesting stoichiometric organometallic chemistry of various Cp_2ZrR^+ cations is evolving that, among other topics, has led to the disclosure and development of a variety of novel types of organometallic compounds.[3] The formation of dimetallic systems **3** that contain a planar-tetracoordinate carbon atom is a prominent example (eq 1).[4]



(1)

1b **2** **3**

A number of interesting reactions of Cp_2ZrR^+ systems containing simple unfunctionalized hydrocarbyl σ-ligands R have been reported so far, but much less is known about the organometallic chemistry of the Cp_2ZrR^+ complexes that contain σ-alkenyl or -alkynyl groups.[1,5] There is evidence that such systems may exhibit an enhanced reactivity, and thus, it might be more difficult to isolate them. A typical example is depicted in eq 2, where the $Cp_2ZrC{\equiv}CCH_3^+$ cation is formed by a σ-ligand abstraction using the strong organometallic Lewis acid $B(C_6F_5)_3$ but evades its isolation by a very rapid subsequent insertion reaction of the functionalized borate anion to yield the stable betaine product **5**.[6]

We have now generated the reactive $Cp_2ZrC{\equiv}CR^+$ cation system in a different way, starting from the bis(alkynyl)metallocene **1**,[7] and have found yet another mode of stabilization by a subsequent CC-coupling

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[†] Dedicated to Professor Peter Welzel on the occasion of his 60th birthday.

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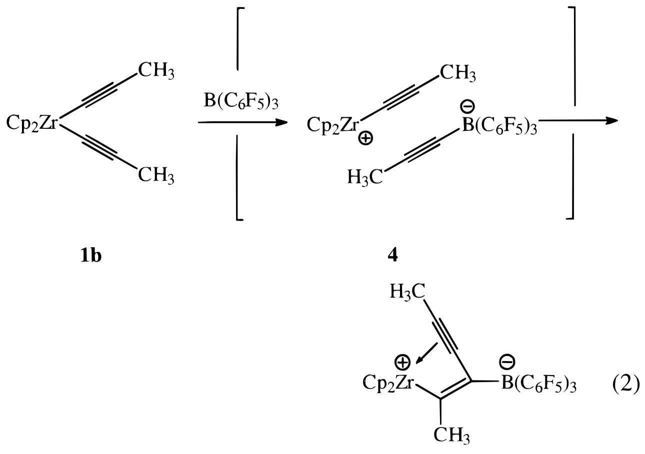


1b **4**

(2)

5

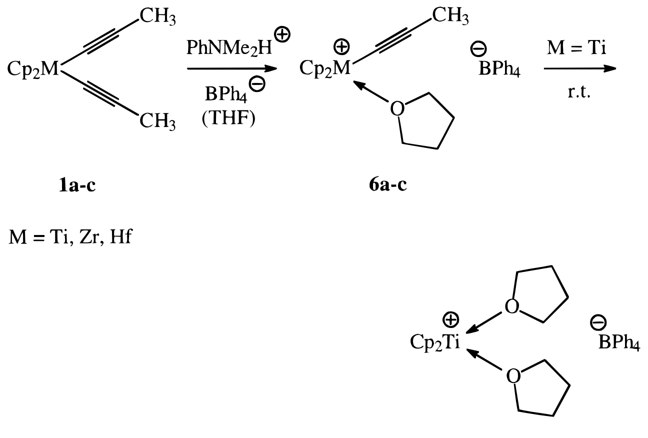
reaction that led to a novel dinuclear μ-2,4-hexadiyne bis(zirconocene) complex exhibiting interesting structural features and a dynamic behavior.

Results and Discussion

Generating Ligand-Stabilized σ-Propynyl Group 4 Metallocene Cations. We have reacted the bis(propynyl)metallocenes **1a**−**c** (M = Ti, Zr, Hf) with *N*,*N*-dimethylanilinium tetraphenylborate[8] in THF solution at low temperature. In a typical experiment $Cp_2Zr(C{\equiv}CCH_3)_2$ (**1b**) was dissolved in THF-d_8 and charged with $PhNMe_2H^+BPh_4^-$ at −78 °C. Under direct ^1H NMR monitoring, it was observed that the system started to react at −40 °C with the formation of propyne (^1H NMR: δ 2.02 (q, 1H), 1.73 (d, 3H)) and the THF-d_8-stabilized (σ-propynyl)zirconocene cation (**6b**). The latter is characterized by typical $^1H/^{13}C$ NMR resonances at δ 6.45 (10H, Cp)/115.7 and 1.94 (3H, CH_3)/5.8. The cation **6b** is only moderately stable in THF-d_8 solution. Even at −10 °C it is unspecifically decomposed during several hours. We tried to isolate the $[Cp_2Zr(C{\equiv}CCH_3)(THF)^+]BPh_4^-$ salt from THF solutions but have been unsuccessful so far.

The corresponding $Cp_2Hf(C{\equiv}CCH_3)(THF)^+$ and $Cp_2Ti(C{\equiv}CCH_3)(THF)^+$ systems **6c** and **6a** are slightly more stable than the zirconium system **6b**, but their isolation has also evaded us so far. Both were, however, characterized spectroscopically after being generated by treatment of the respective $Cp_2M(C{\equiv}CCH_3)_2$ starting materials (**1c**, **1a**) with $PhNMe_2H^+BPh_4^-$ in THF-d_8. The (σ-propynyl)$TiCp_2^+$ cation, thus, exhibits ^1H NMR signals at δ 6.47 (Cp) and 2.15 (CH_3) in a 10:3 intensity ratio and ^{13}C NMR resonances at δ 119.7 (Cp), 148.0 (α-C≡C), 77.0 (β-C≡C), and 6.5 (CH_3).

Above room temperature, the $[Cp_2Hf(C{\equiv}CCH_3)(THF)^+]BPh_4^-$ system, **6c**, decomposes unspecifically. In contrast, the (σ-propynyl)(tetrahydrofuran)$TiCp_2^+$ cation is decomposed in ca. 3 days at ambient temperature to yield the known paramagnetic titanium(III) complex $[Cp_2Ti(THF)_2^+]BPh_4^-$ (**7**).[9ac] The blue bis(cyclopentadienyl)bis(tetrahydrofuran)titanium(III) tetraphenylborate salt was isolated and identified by an X-ray crystal structure analysis. The molecular structure of the $Cp_2Ti(THF)_2^+$ cation in the crystal structure of **7** is analogous to the structures recently observed for several closely related examples ($[Cp_2Ti(THF)(acetonitrile)^+]BPh_4^-$,[9a] $[Cp_2Ti(THF)_2^+]Co(CO)_4^-$,[9b] and $[Cp_2Ti(pyridine)_2^+]BPh_4^-$ [9c]). In **7**, the (THF−oxygen)−Ti−(THF−oxygen) angle is 77.49(7)°; the corresponding Ti−O distances are 2.208(2) and 2.239(2) Å (further details about the structure of **7** are provided with the Supporting Information).



1a-c **6a-c**

M = Ti, Zr, Hf

7

We, thus, have concluded that ligand-stabilized (σ-alkynyl)metallocene cations can be generated by means of protonation reactions, employing a suitable nonnucleophilic counteranion, of course. Then we tried to use a similar technique to generate the corresponding donor ligand free $Cp_2MC{\equiv}CCH_3^+$ cations. This was not successful using the protonation reaction, but an interesting reaction sequence was found when the $Cp_2Zr(C{\equiv}CCH_3)_2$ starting material (**1b**) was treated with trityl tetraphenylborate[10] in a noncoordinating solvent.

Synthesis of a Dinuclear μ-2,4-Hexadiyne Bis(zirconocene) Cation System. Bis(propynyl)zirconocene (**1b**) was treated with trityl tetraphenylborate in toluene solution at 0 °C. A product (**9**) is formed that precipitates from the aromatic solvent and, thus, is isolated in close to quantitative yield. Recrystallization from dichloromethane at −20 °C furnished single crystals of **9** that were suitable for an X-ray crystal structure analysis.

The X-ray crystal structure analysis of **9** shows the presence of an organometallic salt with a well-separated cation and tetraphenylborate anion. The organometallic monocation of **9** contains two zirconocene units that are connected by means of two different hydrocarbyl units. One of the bridges is made up by a μ-η^1:η^1-propynyl ligand (Zr1−C30, 2.259(6) Å; Zr2−C30, 2.446(5) Å; C30−C31, 1.215(8) Å; Zr1−C30−Zr2, 103.0(2)°). These bonding features are typical of a σ-bridging acetylide ligand; a closely related molecular arrangement and

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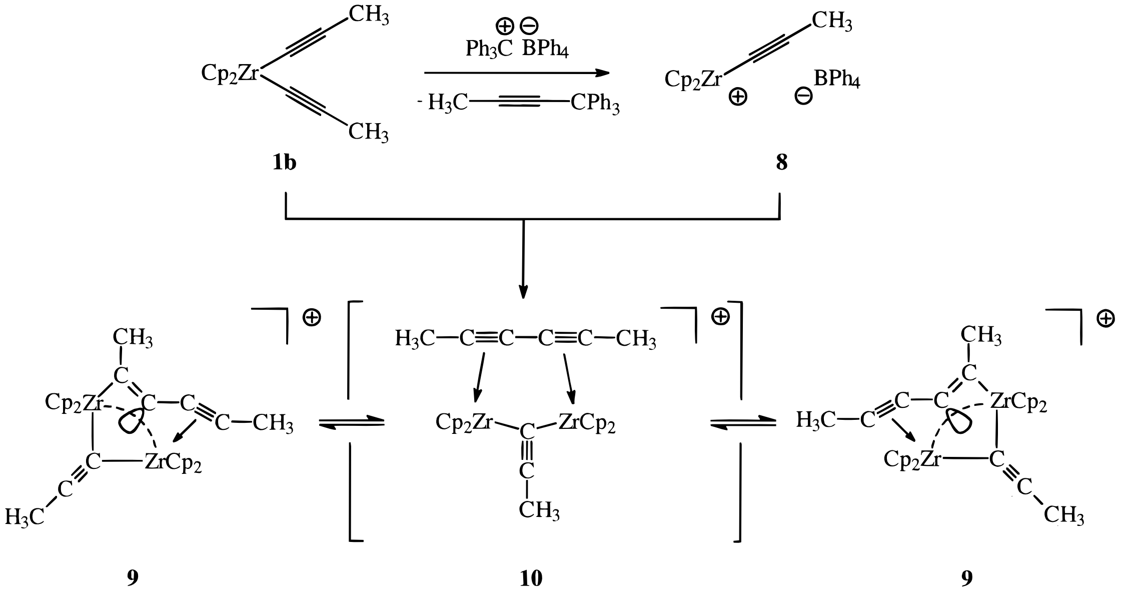
Scheme 1



similar bonding values have been observed for many dinuclear μ-acetylide complexes having a group 4 transition metal involved.[4,11,12]

It is the second hydrocarbyl bridge that makes the structure of complex **9** so noteworthy. The two zirconium centers are connected by a μ-2,4-hexadiyne ligand that has been formed by the CC-coupling of two σ-propynyl ligand at zirconium. The hexadiyne bridges the two zirconium centers unsymmetrically. The bridging function is carried out essentially by one of the triple bonds. It connects them in an η^1:η^2-fashion. The Zr2−C37 bond is very short, 2.173(5) Å. The C37−C36 linkage is in the range of a carbon−carbon double bond (1.317(8) Å). Carbon atom C36 is bonded to both Zr2 and Zr1. This connection is best described as a three-center two-electron bonding situation (Zr2−C36, 2.530(5) Å; Zr1−C36, 2.435(6) Å).[4,11] This specific connection makes carbon atom C36 planar-tetracoordinate.[13] It is bonded to four closely neighboring atoms (C37, Zr2, Zr1, C35; C36−C35, 1.401(8) Å). The respective bonding angles around C36 are 130.9(5)° (C35−C36−C37), 59.2(3)° (C37−C36−Zr2), 95.8(2)° (Zr2−C36−Zr1), and 74.1(3)° (Zr1−C36−C35). The remaining alkynyl group connected to C36 is only weakly coordinated to the electron-deficient zirconium atom Zr1 (Zr1−C35, 2.453(5) Å; Zr1−C34, 2.763(6) Å). This rather unsymmetric "π-agostic" interaction[14] leads to some distortion of this alkynyl group: the C35−C34 triple bond (1.203(8) Å) is bent toward zirconium (C36−C35−C34, 164.2(6)°), whereas the terminal methyl group is oriented away from the metal center (C35−C34−C33, 169.2(7)°) (Scheme 1).

The global minimum structure of **9** in solution is equivalent, although complex **9** exhibits dynamic NMR spectra in solution. The salt **9** is only sparingly soluble in most noncoordinating solvents. However, its solubility in CD_2Cl_2 is just sufficient enough to obtain the limiting low-temperature ^{1}H NMR spectrum. At 180 K (200 MHz), complex **9** exhibits two sharp Cp singlets at δ 5.78 and 5.70 (each of relative intensity 10). The CH_3 singlets of the μ-2,4-hexadiyne ligand appear at δ 2.84 and 2.55 (each of relative intensity 3), and the ^{1}H NMR resonance of the μ-η^1:η^1-C≡C-CH_3 ligand appears at δ 2.41 (relative intensity 3). Upon raising the monitoring temperature, the Cp signals as well as the hexadiyne methyl resonances rapidly get broad and coalesce. At high temperature (269 K), a very simple ^{1}H NMR spectrum of the rapidly equilibrating species is observed, showing three singlets at δ 5.79 (Cp), 2.75 (CH_3), and 2.45 (C≡CCH_3) in a 20:6:3 ratio. The ^{13}C NMR spectrum (in THF-d_8, 168 K) at the low-temperature limit exhibits signals at δ 219.5, 129.1, 114.1, 110.6, 106.0 and 48.8 (C), 110.4 and 110.0 (Cp), and 33.1, 10.1, 7.9 (CH_3).

It must be assumed that the reaction of $Cp_2Zr(C{\equiv}CCH_3)_2$ (**1b**) with the trityl cation is initiated by a σ-propynyl abstraction from zirconium and transfer to carbon to give $CH_3C{\equiv}CCPh_3$ (which is observed as a reaction product by ^{1}H NMR spectroscopy) and the $Cp_2ZrC{\equiv}CCH_3^+$ cation (**8**). In the absence of a suitable donor ligand, the 14e$^-$ cation **8** seems to be extremely reactive, too reactive to be observed directly under the reaction conditions and certainly too reactive to allow its isolation from the reaction mixture. Instead, the

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intermediate **8** reacts instantaneously with the neutral bis(propynyl)zirconocene starting material present in solution. The associative coupling of the organometallic reagents is probably facilitated by the high propensity of connecting the two electrophilic metal centers by means of a thermodynamically favorable $Zr_2(\mu\text{-}\eta^1{:}\eta^1\text{-alkynyl})$ linkage—such acetylide bridges seem to be among the strongest means of connecting two zirconium centers by a hydrocarbyl bridging ligand.[4,11,12] The system is then further stabilized by the subsequent carbon−carbon coupling of two of the propynyl groups present at the dinuclear zirconocene systems to form the 2,4-hexadiyne ligand, which is then stabilized by forming the unsymmetrically bridged $Zr_2[\mu\text{-}(\eta^1\text{-C}{:}\eta^2\text{-C,C}]$ dinuclear metallocene cation system (**9**), exhibiting a planar-tetracoordinate carbon atom. We had recently shown that the formation of (μ-RCCR)Zr_2 type cations containing a planar-tetracoordinate carbon center is in general very favorable. The formation of the dimetallabicyclic structure with this unusual carbon coordination geometry was found to be favored by ca. 10−12 kcal mol^{-1} over the dimetallacyclopentene.[4a] Therefore, it is not surprising to observe the analogous structural type here.

Often the alkyl substituents at C2 of the planar-tetracoordinate carbon complexes **3** form an agostic interaction with their adjacent metal center (i.e., Zr2 in **3**, see eq 1).[4,15] In the new complex **9**, such a σ-agostic interaction cannot be formed straightforwardly, since the favored regioisomer (**9**) has a $-C{\equiv}CCH_3^+$ substituent attached at its planar-tetracoordinate bridgehead carbon. Instead, the π-system of this substituent is used to diminish the electron-deficiency of the nearby zirconocene group by forming a weak π-agostic interaction.[14]

It may be that this coordinative acetylide to metal interaction facilitates the novel type of dynamic process observed to take place within the cation **9**. The parent planar-tetracoordinate carbon complexes **3** (see eq 1) are known to rapidly exchange the three-center two-electron bonding situation between the zirconium centers Zr1/Zr2 and C1/C2.[4a] This type of degenerate rearrangement (which reversibly interchanges the planar-tetracoordinate carbon bonding situation between carbon atoms C2 and C1) is prohibited in **9** because of the unsymmetrical substitution pattern. However, we observe an alternative low-energy automerization pathway ($\Delta G^{\ddagger}$(190 K) ≈ 9.5 ± 0.5 kcal mol^{-1} from the dynamic ^1H NMR experiment at the Cp coalescence temperature) that leads to a mutual exchange of the propynyl moieties of the μ-2,4-hexadiyne ligand (and hence an intramolecular equilibration of the metallocene units).[16]

Establishing the reaction pathway of this automerization reaction in detail requires additional experimental investigations and probably a thorough theoretical study, but it is likely that a symmetrical intermediate geometry (transition state or high-lying reactive intermediate) of a bis(π-alkyne)$(ZrCp_2)_2(\mu\text{-}C{\equiv}CR)$ structural type (**10**) is readily available starting from **9**.[6a,17]

Our study has again shown that planar-tetracoordinate carbon is enormously stabilized by two zirconium centers in the environment of the dimetallabicyclic framework encountered here. At the same time, it appears that the dimetallic $(Cp_2Zr)_2(\mu\text{-}C{\equiv}CR)^+$ cation fragment is formed very easily and may allow for the formation of novel types of dinuclear metallocene π-complexes that may show interesting properties when used as stoichiometric organometallic reagents or in catalysis. We are currently trying to develop the chemistry of such species experimentally.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers and equipment used for the physical characterization, see ref 4a. The following compounds and reagents were prepared according to published procedures: bis(propynyl)titanocene, -zirconocene, and -hafnocene (**1a**−**c**),[7] *N*,*N*-dimethylanilinium tetraphenylborate,[18] and trityl tetraphenylborate.[19]

Reaction of the Bis(propynyl) Group 4 Metallocenes 1a−c with *N*,*N*-Dimethylanilinium Tetraphenylborate. These reactions were carried out in deuterated solvent in a NMR tube. The products **6a**−**c** plus propyne were not isolated but only characterized spectroscopically (^1H, ^{13}C NMR). General procedure: a sample of ca. 10 mg of the respective complex **6** was mixed with an equimolar quantity of solid *N*,*N*-dimethylanilinium tetraphenylborate in a 5 mm NMR tube. Then, ca. 0.5 mL of tetrahydrofuran-d_8 was added at −50 °C. Propyne was formed at −40 °C, and the metallocene cation systems **6** were spectroscopically characterized at temperatures <0 °C to prevent rapid decomposition. Complex **6a** (prepared starting from 10 mg (39 μmol) of **1a**): ^1H NMR (THF-d_8) δ 6.47 (s, 10H, Cp), 2.15 (s, 3H, CH_3); δ 7.32 (m, 8H), 6.90 (m, 8H), 6.75 (m, 4H) (BPh_4^-); δ 7.14, 6.65 (m, 5H, Ph), 2.88 (s, 6H, CH_3) (*N*,*N*-dimethylaniline); δ 2.02 (q, 1H, CH), 1.73 (d, 3H, CH_3) (propyne). ^{13}C NMR (THF-d_8): δ 148.0, 77.0, 6.5 ($C{\equiv}C{-}CH_3$), 119.7 (Cp); δ 165.1 ($^1J_{BC}$ = 50 Hz), 137.1, 125.8, 122.0 (BPh_4^-); δ 151.6, 132.6, 117.0, 113.2, 40.5 (*N*,*N*-dimethylaniline); δ 80.0, 68.4, 2.8 (propyne). Complex **6b** (prepared starting from 10 mg (33 μmol) of **1b**): ^1H NMR (THF-d_8) δ 6.45 (s, 10H, Cp), 1.94 (s, 3H, CH_3). ^{13}C NMR (THF-d_8): δ 115.7 (Cp), 78.0, 5.8 (1 acetylide C not located). Complex **6c** (prepared starting from 8 mg (21 μmol) of **1c**): ^1H NMR (THF-d_8) δ 6.38 (s, 10H, Cp), 1.96 (s, 3H, CH_3). ^{13}C NMR (THF-d_8): δ 114.9 (Cp), 139.6, 54.2, 5.7 ($C{\equiv}CCH_3$), signals of BPh_4^-, *N*,*N*-dimethylaniline, and propyne, see above.

Formation of Bis(cyclopentadienyl)bis(tetrahydrofuran)titanium(III) Tetraphenylborate, 7. Bis(propynyl)titanocene (**1a**, 100 mg, 0.39 mmol) was mixed with 85 mg (0.195 mmol) of *N*,*N*-dimethylanilinium tetraphenylborate; then, 3 mL of THF was added. The mixture was briefly homogenized with stirring and then left for 48 h at room temperature without stirring. During that time, blue crystals of **7** were formed that were characterized by an X-ray crystal structure analysis of **7**: formula $C_{42}H_{46}O_2BTi$, M_w = 641.50, 0.6 × 0.2 × 0.1 mm, a = 13.008(3) Å, b = 13.482(3) Å, c = 20.330(7) Å, β = 106.98(2)°, V = 3410(2) Å^3, ρ_{calcd} = 1.250 g cm^{-3}, μ = 2.87 cm^{-1}, no absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73, $\omega/2\theta$ scans, 7224 reflections collected ($\pm h, -k, \pm l$), $[(\sin\theta)/\lambda]_{max}$ = 0.62 Å^{-1}, 6921 independent and 4330 observed reflections [$I > 2\sigma(I)$],

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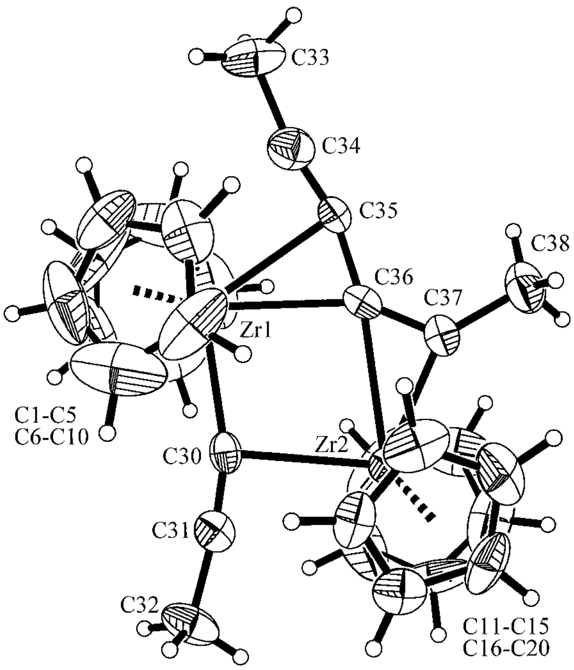

Figure 1. A view of the molecular geometry of the cation **9**; carbon atom C36 is planar-tetracoordinate. Selected bond lengths (Å) and angles (deg): Zr2−C(Cp) (av), 2.509(7); Zr1−C(Cp) (av), 2.494(7); Zr2−C30, 2.446(5); Zr1−C30, 2.259(6); C30−C31, 1.215(8); C31−C32, 1.463(8); C30−C31−C32, 173.4(6); Zr1−C30−Zr2, 103.0(2); Zr2−C30−C31, 93.6(4); Zr1−C30−C31, 163.4(5); Zr2−C37, 2.173(5); C37−C38, 1.481(8); C37−C36, 1.317(8); Zr2−C37−C38, 143.7(5); Zr2−C37−C36, 89.4(4); C36−C37−C38, 126.9(6); C36−C35, 1.401(8); C35−C34, 1.203(8); C34−C33, 1.483(9); C35−C36−C37, 130.9(5) (for additional values, see text).

415 refined parameters, R1 = 0.047, wR2 = 0.113, max residual electron density 0.38 (−0.35) e Å^{-3}, hydrogens calculated and riding. For detailed information about the structural data of **7** see the Supporting Information.

Preparation of 9. A mixture of bis(propynyl)zirconocene (**1b**, 500 mg, 1.65 mmol) and trityl tetraphenylborate (464 mg, 825 μmol) was suspended in 10 mL of dichloromethane and stirred for 2 h at room temperature. Solvent was then removed in vacuo, and the oily residue was stirred with pentane overnight to solidify. The pentane phase was decanted (1,1,1-triphenylbut-2-yne was isolated from the pentane phase: ^{1}H NMR (CDCl$_3$) δ 7.23 (m, 15H, Ph), 1.92 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 145.9 (*ipso*-C of Ph), 129.1, 127.9, 126.6 (Ph), 85.1, 80.8 (C≡C), 55.9 (*C*Ph$_3$), 3.9 (CH$_3$)), and the remaining precipitate was dried in vacuo to give 609 mg (84%) of **9**, mp 166 °C (dec). ^{1}H NMR (CDCl$_3$, 300 K): δ 5.62 (s, 20H, Cp), 2.58 (s, 6H, CH$_3$), 2.16 (s, 3H, CH$_3$); δ 7.47 (m, 8H), 7.05 (m, 8H), 6.93 (m, 4H) (BPh$_4^-$). ^{1}H NMR (THF-d_8, 168 K): δ 6.01 (s, 10H, Cp), 5.94 (s, 10H, Cp), 2.98 (s, 3H, CH$_3$), 2.53 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$). ^{13}C NMR (THF-d_8, 300 K): δ 110.2 (Cp), 129.9, 112.0, 10.0 (μ-C≡CCH$_3$), 20.2 (*C*H$_3$-C≡CC≡CCH$_3$, acetylide carbons not observed at 300 K). ^{13}C NMR (THF-d_8, 168 K): δ 110.4, 110.0 (Cp), 129.1, 110.6, 10.1 (μ-C≡CCH$_3$), 219.5, 114.1, 106.0, 48.8, 33.1, 7.9 (μ-CH$_3$-C≡CC≡CCH$_3$); δ 164.7 ($^1J_{\mathrm{BC}}$ = 49 Hz, *ipso*-C of Ph), 137.0, 125.9, 122.0 (Ph) (BPh$_4^-$). ^{1}H/^{13}C-2D NMR correlation experiments[20] (atom numbering used as in Figure 1), GHSQC-NMR (giving the immediate ^{13}C/^{1}H connection) (THF-d_8, 168 K, 150.8/599.8 MHz): δ 110.4/6.01 (Cp), 110.0/5.94 (Cp), 33.1/2.98 (38), 10.1/2.43 (32), 7.9/2.53 (33). GHMBC-NMR (providing the long-range ^{13}C/^{1}H correlation) (THF-d_8, 168 K, 150.8/599.8 MHz): δ 219.5/2.98 (C-37/38−H), 129.1/2.43 (C-30/32−H), 114.1/2.53 (C-34/33−H), 110.6/2.43 (C-31/32−H), 110.4, 110.0, 106.0/2.98 (C-36/38−H), 48.8/2.53 (C-35/33-H), 33.1, 10.1, 7.9. IR (KBr): $\tilde{\nu}$ = 3113 cm^{-1}, 3053, 3032, 2982, 2918, 2850, 2065, 1579, 1479, 1427, 1262, 1015, 809, 744, 704. UV−vis (dichloromethane): $\lambda_{\max}$ = 256 (ϵ 14 300), 285 (sh, ϵ 11 000), 314 (sh, ϵ 4500). Anal. Calcd for C$_{53}$H$_{49}$BZr$_2$ (879.2): C, 72.40; H, 5.62. Found C, 73.82; H, 5.66%. X-ray crystal structure analysis of **9**: formula C$_{53}$H$_{49}$BZr$_2$, M_{w} = 879.17, 0.6 × 0.3 × 0.25 mm, a = 15.006(2) Å, b = 15.086(4) Å, c = 19.741(3) Å, β = 111.53(1)°, V = 4157.2(14) Å^3, ρ_{calcd} = 1.405 g cm^{-3}, μ = 5.38 cm^{-1}, empirical absorption correction via ψ-scan data (0.873 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73, $\omega/2\theta$ scans, 7607 reflections collected ($-h,-k,\pm l$), $[(\sin\theta)/\lambda]_{\max}$ = 0.59 Å^{-1}, 7313 independent and 4400 observed reflections [$I > 2\sigma(I)$], 508 refined parameters, R1 = 0.053, wR2 = 0.122, max residual electron density 0.81 (−1.54) e Å^{-3}, hydrogens calculated and riding. Data were collected on an Enraf-Nonius MACH3-diffractometer. Structures were solved with the program SHELXS-86 and refined with SHELXL-93. Graphics were done with XP.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates of **7** and **9** (19 pages). Ordering information is given on any current masthead page.

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[20] Braun, S.; Kalinowski, H.; Berger, S. *100 and More Basic NMR Experiments*; VCH: Weinheim, Germany, 1996, and references cited therein.