Formation of Hypercoordinated Carbon inside a (μ-Hydrocarbyl)bis(group 4 metallocene) Framework by a Simple Protonation Route

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Abstract: (Alkenyl)zirconocene chlorides $Cp_2Zr(Cl)(CH{=}CHR)$ (**4**, R = H, phenyl, *n*-butyl, or cyclohexyl) react with "Cp_2Zr" generated from various precursors to yield the neutral dinuclear alkenyl-bridged bis(metallocene) complexes **6** [$Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CHR)ZrCp_2$]. The complexes **6** are regioselectively protonated by treatment with ($HNMe_2Ph^+$)(BPh_4^-) (**8a**) to yield the unusually structured products **9** [$Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}\eta^1{:}\eta^2\text{-}C^1H_2C^2HR)ZrCp_2^+$], which exhibit an unsymmetrically bridged hydrocarbyl ligand containing a novel type of a hypercoordinated carbon center (C^1) inside the rigid organometallic framework. From the NMR analysis and an X-ray crystal structure determination of the example **10c** [$(MeCp)_2Zr(\mu\text{-}Cl)(\mu\text{-}C^1H_2C^2H\text{-}n\text{-butyl})Zr(MeCp)_2^+$], it is evident that the hypercarbon atom C^1 is coordinated to four close neighboring atoms (Zr^1, Zr^2, C^2, and H^{1a}) in a distorted square-planar arrangement with the remaining $C^1{-}H^{1b}$ bond being oriented perpendicular to it. H^{1b} thus marks the apex of a distorted square pyramid; the hypercarbon atom C^1 is located in the center of the basal plane. This unusual structural coordination geometry around C^1 is determined by the stereoelectronic features of the two adjacent group 4 bent metallocene units. From the dynamic features of complex **9a** (R = H), a stabilization energy of ca. 10 kcal mol^{-1} is estimated for the uncommon coordination mode of C1, which is favored here, relative to a "normal" sp^3-hybridized structure in a C_{2v}-symmetric metallacyclic framework. Part of the pronounced thermodynamic stabilization of this unusual pentacoordinate carbon geometry originates from the strong α-agostic $Zr{\cdots}H^{1a}{-}C^1$ interaction in the basal plane. From the monodeuterated derivative **9a**-C^1HD, an energy difference of 220 cal mol^{-1} between D and H favoring the bridging position was determined.

Introduction

Hypercarbon compounds show most interesting structural and chemical properties. Pure hydrocarbon systems that contain hypercoordinated carbon can be generated by protonation of various C_nH_m precursors in the strict absence of basic or nucleophilic anions. Consequently, such systems were studied extensively in superacidic media or in the gas phase.[1] Organometallic substituents have been used successfully to prepare stable compounds containing hypercoordinated carbon in various coordination geometries. Mostly such organometallic systems contain a combination of several metal substituents, and they are usually prepared by adding an electrophilic metal-containing reagent to a carbon center of a hydrocarbyl ligand of an organometallic precursor component, thereby creating an expanded coordination environment at the specific carbon center inside the chosen framework.[1a,2,3] We have now, to our knowledge for the first time, found a simple protonation route that has made hypercarbon geometries synthetically available in a dimetallic group 4 bis(metallocene) complex framework.[4] This route uses readily available neutral dimetallic (μ-alkenyl)bis(zirconocene) complexes as precursors.[5] Addition of a proton to the unsaturated alkenyl bridge leads to a saturated [$-CH_2\text{-}CH_3-$]$^+$ derived bridging ligand inside a stabilizing dimetallic framework. The newly formed hydrocarbyl ligands contain hypercoordinated carbon, apparently derived from an unusual

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Table 1. [(μ-η^1:η^2-Alkenyl)(μ-Cl)($ZrCp_2$)$_2$] Complexes **6** Obtained from Zirconocene Addition Reactions to (σ-Alkenyl)zirconocene Chloride Complexes **4**

product[a]	educt	R^1	method[a]	yield (%)	δC^1H[b]	δC^2H[b]	$^3J_{HH}$ (Hz)
6a	**4a**	H	A	22	178.8, 7.15	63.1, 3.92	17.8[c]
6a-d_1[d]	*E*-**4a**-d_1	D	B	73	*e*	*e*	*e*
6b	**4b**	Ph	A	38	170.3,[f] 7.69	84.9,[f] 4.55	18.1
6c	**4c**	*n*-Bu	A	30	183.0, 6.92	88.7, 2.99	17.9
6d	**4d**	Cy	C	46	180.6, 7.01	70.2, 2.85	17.9

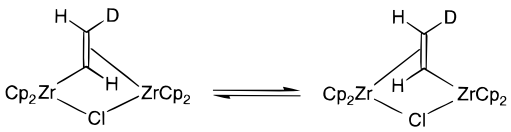
[a] See Scheme 1. [b] In benzene-d_6. [c] $^3J_{trans}$, $^3J_{cis}$ = 13.5 Hz, ^2J = 1.8 Hz. [d] 1:1 mixture of *E*/*Z*-isomers. [e] See **6a**. [f] From ref 5a.

distorted square-pyramidal CX_5 geometry. The systems are stable, and they are readily prepared by using *N*,*N*-dimethylanilinium salts with large nonnucleophilic anions (BPh_4^- or $B(C_6F_5)_4^-$) as protonating reagents.[6] A variety of typical examples is described in this article.

Results and Discussion

Preparation of the Organometallic Precursors. The dinuclear (μ-alkenyl)bis(metallocene) starting materials (**6**) for this study were prepared in the following way. The alkynes **3a**−**d** were hydrozirconated[7a] to give the (σ-alkenyl)zirconocene chloride complexes **4a**−**d**. These were then treated with in situ generated zirconocene (Cp_2Zr; or a synthetic equivalent thereof) to directly yield the [(μ-η^1:η^2-alkenyl)(μ-Cl)(Cp_2Zr)$_2$] complexes **6a**−**d**. We have used three different zirconocene generating methods, namely the "Negishi method" (treatment of zirconocene dichloride with two *n*-butyllithium equivalents),[8] photolysis of diphenylzirconocene,[9] or the reaction with (butadiene)zirconocene.[10] The latter two methods were previously used successfully by us to transfer the Cp_2Zr unit from readily available precursors. All three methods produce the dimetallic complexes **6** in reasonable yield. One example of this class of compounds, namely **6b**, had been structurally characterized by us previously.[5a]

The complexes **6** show very characteristic spectroscopic features (see Table 1). Most noteworthy for this class of compounds is the very typical ^{13}C NMR chemical shift of the $[Zr]_2(C^1H{=})$ moiety. All the (μ-alkenyl)bis(zirconocene) complexes (**6b**−**d**) that bear an aryl or alkyl substituent at the 2-position exhibit a trans-configurated $Zr^1-C^1H{=}C^2HR$ framework just like their mononuclear (σ-alkenyl)zirconocene chloride precursors **4**. Only the parent compound, the [(μ-vinyl)(μ-Cl)-($ZrCp_2$)$_2$] complex **6a** behaves differently, but this was only revealed upon introduction of a deuterium label at the 2-position. "Deuteriozirconation" of acetylene had stereoselectively generated the *Z*-configurated $Cp_2Zr(Cl)CH{=}CHD$ system **4a**-d_1 (i.e., the system that exhibits the Cp_2ZrCl substituent and the β-deuterium atom in a cis arrangement). Treatment with Cp_2-Zr(butadiene) under UV irradiation led to the formation of the dinuclear complex **6a**-d_1, but stereochemically unselective. The deuterated complex **6a**-d_1 was obtained as a 1:1 mixture of the respective *E*- and *Z*-isomers. This is probably due to an intramolecular rearrangement that leads to a connectivity exchange of the framework but is otherwise degenerate. Such equilibration by means of intramolecular μ-η^1:η^2-alkenyl migration has frequently been observed at other dinuclear metal complex frameworks.[11] In this specific case, this otherwise hidden process becomes apparent by stereochemical scrambling of the deuterium label at the 2-position.



E-/Z-**6a-d$_1$**

Treatment of the alkynes **3a**−**d** with the related hydrozirconation reagent [$(MeCp)_2Zr(H)Cl$] (**2**)[7b] yields the [(alkenyl)-(Cl)$Zr(CpMe)_2$] complexes **5a**−**d**. Addition of $(MeCp)_2Zr$, transferred from the corresponding Negishi reagent, or in situ generated by photolysis of $(MeCp)_2ZrPh_2$, led to the formation of the corresponding dinuclear alkenyl-bridged bis(zirconocene) systems **7a**−**d**. However, these four methyl-Cp bearing systems were not isolated and separately characterized but directly subjected to the protonolysis reaction (see below).

Protonation of the Dinuclear [(μ-Alkenyl)(μ-Cl)($ZrCp^R_2$)$_2$] Complexes. We have used *N*,*N*-dimethylammonium tetraphenylborate (**8a**)[6] as the reagent for protonating the (μ-alkenyl)-bis(zirconocene) complexes **6** and **7**, respectively. In a few cases we have in addition employed the same ammonium cation

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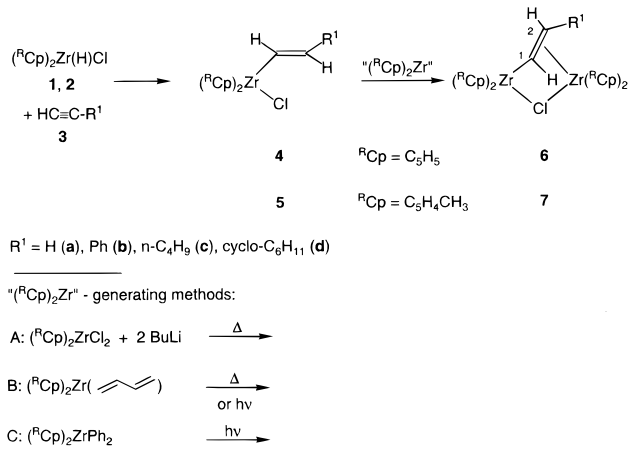
Scheme 1



as its $B(C_6F_5)_4^-$ salt (reagent **8b**), and in one case, we have used $[^2H]NMe_2Ph^+BPh_4^-$ (**8a**-d_1) to selectively transfer a deuteron instead of a proton.

Treatment of the phenyl-substituted precursor **6b** with $HNMe_2Ph^+BPh_4^-$ (**8a**) cleanly gave the product **9b**. Protonation took place completely regioselectively at carbon atom C1 of the bridging *trans*-1-styryl ligand of the dinuclear starting material.

The protonated product **9b** was isolated in >60% yield. It contains two inequivalent Cp_2Zr units whose cyclopentadienyl ligands are diastereotopic ($^1H/^{13}C$ NMR signals at δ 6.27, 6.04, 5.97, 5.38/113.6, 111.5, 109.2, and 108.6 in dichloromethane-d_2 at 203 K). The $-C^1H_2C^2HPh-$ ligand formed by H^+ addition to the former μ-$C^1H{=}C^2HPh$ moiety exhibits some rather remarkable spectroscopic features that indicate a very unsymmetrical connection of the two zirconium centers, namely a μ-(η^1-C^1):η^2-(C1,C2)-bridging mode with C^1 being pentacoordinate and one of the C^1-H bonds being bonded α-agostic to the metal center Zr1 (see below and Scheme 2). The ^1H NMR chemical shifts of the μ-η^1:η^2-$C^1H_2C^2HPh-$ ligand of **9b** are at δ 5.17 (C^2H), 4.63, and −5.55. The coupling constants amount to ^3J = 15.6 and 6.6 Hz and a geminal ^2J = 5.4 Hz coupling constant. The corresponding ^{13}C NMR features are observed at δ 86.3 (C^2) with a coupling constant of $^1J_{C^2-H}$ = 142 Hz, which is very typical for a three-membered metallacyclic "zirconacyclopropane"-type structural subunit,[12] and at δ 92.5 ppm with two very different $^1J_{C^1-H}$ coupling constants of 131 and 99 Hz. The latter values are very characteristic of a situation where one C−H bond (here at C1) exhibits a strong α-agostic bonding situation[13] with the adjacent electron-deficient metal center (here Zr1). This typically leads to a strong decrease of the $^1J_{CH}$ coupling constant of the C−H bond directly involved in the agostic interaction which is usually accompanied by an increase of the $^1J_{CH}$ value of the remaining geminal C−H moiety due to a resulting rehybridization effect.[13,14] The pronounced shifting of the corresponding C^1-H(agost.) ^1H NMR resonance to strongly negative δ values is in accord with a partial μ-hydrido character of the resulting $C^1-(\mu\text{-H})-Zr^1$ moiety.[15]

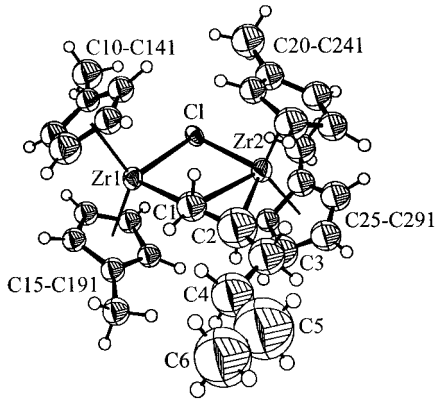


Figure 1. View of the framework of complex **10c** (only the cation is depicted); the hypercoordinated carbon atom C1 is distorted square pyramidal (H atoms on C1 are in calculated positions).

The NMR spectroscopic assignment was secured by 2D NMR measurements (GCOSY, GHMBC, GHSQC)[16] and in addition by selective deuterium labeling. For this purpose we have treated the neutral (styryl)bis(zirconocene) complex **6b** with 1 mol equiv of $DNMe_2Ph^+BPh_4^-$ (**8a**-d_1), which resulted within the accuracy of the ^1H NMR analysis in the formation of a 1:1 mixture of the isotopomeric products **9b**-d_1 (μ-H) and **9b**-d_1 (μ-D) (see Scheme 2). They show an identical set of phenyl and Cp resonances, as well as the 2-H signal (δ 5.17, 1H, ^3J = 15.6 and 6.3 Hz), but they are readily distinguished by the simplified appearance of the signals at δ −5.51 (agostic H^A, corresponding to 0.5 H intensity, ^3J = 5.3 Hz) and δ 4.63 (H^B, "0.5 H", ^3J = 15.6 Hz).

The protonation of the 2-*n*-butyl-substituted dinuclear complexes **6c** and **7c**, respectively, is noteworthy in respect of two additional observations. First, we have succeeded in obtaining single crystals of **10c**, by allowing pentane at −20 °C to slowly diffuse into a solution of its BPh_4^- salt in 1,1,2,2-tetrachloroethane, that were suited for an X-ray crystal structure analysis. Unfortunately, the quality of this diffraction analysis is only poor and the structure refinement was complicated by the presence of the included heavy-atom-containing solvent molecules. Therefore, only isotropical refinement was carried out, and the molecular structure will not be discussed in detail. However, the overall framework of complex **10c**, as it had already become apparent from the very characteristic NMR data (see above), is further supported by this analysis. The complex framework contains a distinctly unsymmetrically bridging hydrocarbyl ligand. The framework is dimetallabicyclic, and it is almost planar.[17] It is made up from two zirconium atoms, bridged by a chloride and the carbon atoms C1 and C2 of the bridging μ-1-hexylene ligand. The bridging 1-alkylene ligand is μ-η^1:η^2-bonded to the two zirconium centers. The carbon

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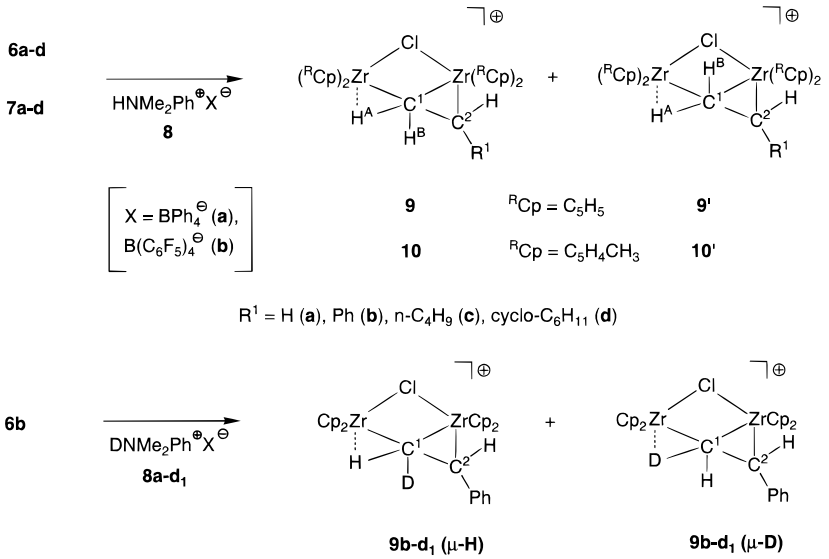
Scheme 2



center C1 is equally bonded to both metal centers Zr1 and Zr2; the Zr1−C1−C2 arrangement is far away from tetrahedral (ca. 157(2)°); consequently, the Zr1−C1 and Zr2−C1 vectors are close to orthogonal (angle Zr1−C1−Zr2 ∼ 97.3(7)°). The MeCp ring systems are oriented above and below the central plane of complex **10c**.

We have seen that one C^1−H bond at the pentacoordinate carbon center forms a strong α-agostic interaction with the adjacent metal center Zr1. Because of the specific stereoelectronic features of the group 4 bent metallocene unit—its acceptor orbital is located in the σ-ligand plane[18]—this requires that the C^1−H vector is oriented closely in plane with the heavy atom framework of the core of this complex type. This necessarily leads to a close-to-coplanar arrangement of C1 with its adjacent neighbors Zr1, Zr2, C2, and H^A(agost.). The remaining C^1−H^B bond must then be oriented almost perpendicular to this plane, making the "nonagostic" hydrogen H^B at C1 to the apex of a distorted square-pyramidal coordination polyhedron around the hypercoordinated carbon atom C1. Two stereoisomeric situations are possible for this polyhedral arrangement. The apical C^1−H^B vector can be arranged trans or cis to the C^2−H unit.

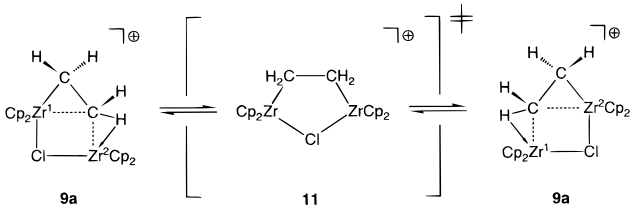
For the cationic complex **9b** (R = Ph, see above) we have only observed a single isomer. This is different for the *n*-butyl products **9c** and **10c**, respectively. In each case we have observed that a mixture of the two possible stereoisomers was formed. From the very characteristic spectroscopic data (see below and the Experimental Section), it is very clear that the protonation again had proceeded completely regioselectively. The protonation of **6c** with $HNMe_2Ph^+BPh_4^-$ (**8a**) has resulted in the formation of the two stereoisomers **9c** and **9c′** in a 90:10 ratio. The isomers show clearly distinguished sets of ^{1}H NMR Cp resonances (major isomer **9c** at δ 6.15, 5.86, 5.85, and 5.65 in dichloromethane-d_2 at 278 K; minor isomer **9c′** at δ 6.13, 5.83, 5.80, and 5.60). The isomers are most readily recognized by the pronouncedly different chemical shifts of their agostic C^1−H^A hydrogen NMR signals (**9c**: δ −5.70, ^3J = 6.6 Hz, ^2J = 4.8 Hz; **9c′**: δ −6.23, ^3J = 6.6 Hz, ^2J = 5.4 Hz). The corresponding C^2H (δ 3.69) and C^1−H^B (δ 4.04, ^3J = 15.6 Hz, ^2J = 4.8 Hz) signals of the major isomer **9c** overlap closely with the respective C^2H and C^1−H^B resonances of the minor isomer **9c′** (as was shown by the GCOSY experiment), but it is clear from the spectral appearance of this complex, and the many related analogous isomeric pairs that we found in this study (see below), that the $^3J_{(C^1-H^B)(C^2-H)}$ coupling constants (i.e., ca. 15−16 Hz) as well as the pairs of the gauche coupling constants $^3J_{(C^1-H^A)(C^2-H)}$ (ca. 5−6 Hz) are almost identical for both the major and minor isomers in this whole series. Thus, on the basis of the vicinal coupling constants, we cannot arrive at an absolute stereochemical assignment in this hypercoordinated carbon situation, namely which of the observed isomers is characterized by a cis or trans arrangement of the C^1−H^B and C^2−H vectors at the central organometallic framework. We tentatively assign the major isomer the structure **9c** with a trans arrangement between C^1−H^B and C^2−H because this might lead to sterically slightly better positioning of the hydrocarbyl substituent at C2 in a pseudoequatorial position away from the bulky ^{R}Cp substituents at the edges of the adjacent hypercoordinated square-pyramidal carbon polyhedron. But a secure absolute stereochemical assignment must await an X-ray crystal structure analysis of much better quality than the one that is only available at present.

The system derived from protonation of the related complex **7c** shows an analogous isomeric situation. Here the stereoisomers **10c** and **10c′** are found in a 80:20 ratio. The cyclohexyl-substituted systems **9d**/**9d′** and **10d**/**10d′** are also found as similar mixture of isomers. Surprisingly, protonation of the (μ-styryl)(μ-Cl)($ZrMeCp_2$)$_2$ precursor **7b** with $HNMe_2Ph^+BPh_4^-$ produced a mixture of the isomers **10b** ("agostic" C^1−*H* resonance at δ −5.75 ppm) and **10b′** (δ (C^1−H^A) at −6.24 ppm) in a 80:20 ratio, whereas only a single isomer was observed for the "parent" (μ-CH_2CHPh−)($ZrCp_2$)$_2^+$ system **9b** (see above).

The precursors **6b**−**d** were also protonated by treatment with $HNMe_2Ph^+B(C_6F_5)_4^-$ (**8b**). As expected, the cations **9b**−**d** were cleanly formed, the systems **9c** and **9d**, respectively, again as mixtures of stereoisomers. However, the two series of product salts containing the different anions BPh_4^- and $B(C_6F_5)_4^-$ were unexpectedly not completely identical in every aspect. Although most ^{1}H and ^{13}C NMR data were superimposable or even appeared identical, we noticed a slight difference of the ^{1}H and ^{13}C NMR chemical shifts of some of the Cp resonances. Whether this might be due to concentration and/or weak ion pairing effects will be explored.

(18) Brintzinger, H. H.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 1105. Lauher, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Scheme 3



Protonation of 6a and Generation and Dynamic Features of the Parent System 9a. Treatment of the (μ-vinyl)bis(zirconocene) chloride complex **4a** with *N*,*N*-dimethylanilium tetraphenylborate (**8a**) cleanly gave **9a**, which was isolated in 67% yield. Like its 2-substituted relatives, the parent cationic metallocene complex is a very sensitive compound. Its spectra can be recorded in, for example, dichloromethane solution only at low temperature, since a decomposition reaction takes place slowly above a temperature of ca. 10 °C to yield zirconocene dichloride among other as yet unidentified products.

The ^{1}H NMR spectrum of **9a** recorded at a high temperature is very simple; it contains only two singlets in a 4:20 intensity ratio. Both the methylene and the Cp resonances became broad with decreasing temperature, and eventually each separated into two sets of signals. Below the Cp-coalescence temperature, two Cp singlets are observed [^{1}H NMR (600 MHz): δ 6.02 and 5.73, each of 10H intensity]. The methylene resonances appear at δ 3.52 and -0.87 ppm with an averaged $^3J_{HH}$ coupling constant of 9.4 Hz.

Complex **9a**·BPh_4^- is only poorly soluble. The corresponding **9a**·$B(C_6F_5)_4^-$ salt, obtained by treatment of **6a** with $HNMe_2Ph^+B(C_6F_5)_4^-$ (**8b**) shows an increased solubility, which made the recording of the ^{13}C NMR spectra easier. Again, we must note a slight anion dependence of some of the ^{1}H and ^{13}C NMR data, which may be due to concentration effects, differences in the ionic strength of the solutions, or potentially weak ion pair interactions (see above), but the overall appearance of the spectra is alike. At low temperature (213 K) complex **9a**·$B(C_6F_5)_4^-$ exhibits two Cp resonances in the ^{13}C NMR spectrum (150 MHz) at δ 112.5 and 107.5 and methylene carbon signals at δ 68.5 ($^2J_{CH}$ = 150 Hz, C2) and δ 96.5 ($^2J_{CH}$ = 116 Hz, C1). Lowering the temperature further did not lead to any additional splitting of these ^{1}H and ^{13}C NMR resonances (T_{min} = 193 K).

These spectroscopic data indicate that the overall structure of the parent compound **9a** is analogous to the substituted systems **9b**−**d**, but that there are two different dynamic processes taking place in **9a**, both being characterized by rather different rate constants. First, there is an equilibration process that leads to an interchange of the C^1H_2 and C^2H_2 methylene groups inside the metallacyclic framework and, consequently, to an intramolecular positional exchange between the Cp_2Zr^1 and Cp_2Zr^2 bent metallocene moieties[19] (see Scheme 3). The equilibration process of the Cp_2ZrCH_2 moieties can be frozen out on the NMR time scale. From the Cp coalescence a Gibbs activation energy of $\Delta G^‡$ (232 K) = 10.5 ± 0.5 kcal mol^{-1} was derived for this intramolecular rearrangement process.

It is very likely that complex **9a** also contains a strong $C^1-H^A\cdots Zr^1$ agostic interaction, analogous to that shown for the related complexes **9b**−**d** in this series, only that there is a very rapid $C^1-H^A/-H^B$ equilibration taking place. This could not be frozen out on the ^{1}H or ^{13}C NMR time scale at the lowest temperatures reached, so that the corresponding spectral data of the C^1H_2 moiety, containing the pentacoordinated carbon center, correspond to averaged values of the C^1-H^A (agostic) and C^1-H^B (nonagostic) units. From a comparison of the C^1H_2 coupling constants compilated in Table 2 it can be seen that the $^1J_{(C^1H_2)}$ = 116 Hz coupling constant observed for **9a** is the expected value obtained from averaging the typical $^1J_{C^1-H^A}$ (ca. 100 Hz) and $^1J_{C^1-H^B}$ (ca. 130 Hz) values.[13,14] This means then that the observed C^1H_2 chemical shift of **9a** (δ −0.87 ppm) must also represent an averaged chemical shift value corresponding to a rapid 1:1 equilibrium situation between a basal agostic C^1-H^A and an apical (and consequently nonagostic) C^1-H^B bond at the hypercoordinated carbon atom C^1. This interpretation is supported by a deuterium-labeling experiment, making use of the different aptitudes of hydrogen and deuterium for entering into the agostic bonding situation with hydrogen preferring the bridging mode over deuterium in a direct competition.[20]

In a dynamic situation, as it is encountered in the case of **9a**, this may lead to a pronounced deviation from a 1:1 equilibrium situation and thus to an unusually large isotopic effect of the corresponding C^1HD NMR resonance.[21]

Treatment of **6a**-d_1 (1:1 mixture of *E*- and *Z*-isomer, see above) with $HNMe_2Ph^+BPh_4^-$ (**8a**) gave the monodeuterated product **9a**-d_1, which was isolated in 61% yield. Again, the product exhibits both intramolecular dynamic features as discussed above, which leads to a rapid scrambling of the deuterium label between the carbon atoms C^1 and C^2 and a completely scrambled ^{1}H NMR spectrum at high temperature. However, the presence of the chirality center introduced by the isotopic substitution (or the resulting distortion of the complex framework, respectively) is just recognized by the adjacent metallocene units[22] and leads to a very narrow separation of the 600-MHz ^{1}H NMR resonances of the four Cp ligands (δ 5.92, 5.91, 5.90, and 5.89 in dichloromethane-d_2 at 308 K, where complex **9a**-d_1 is stable for a short period of time just to allow the measurement).

At low temperature (193 K, 600 MHz), splitting into two complete sets of ^{1}H NMR signals is observed in a 1:1 ratio that corresponds to the two regioisomeric isotopomers[19a] **9a**-C^1HD and **9a**-C^2HD (four narrowly split pairs of ^{1}H NMR Cp singlets at δ 6.04, 6.00, 5.99, 5.96, 5.75, 5.73, 5.72, and 5.70). Thus, the positional equilibration (i.e., $Cp_2Zr^1(C^1HD)(C^2H_2)Zr^2Cp_2 \rightleftharpoons Cp_2Zr^1(C^1H_2)(C^2HD)Zr^2Cp_2$) was frozen on the 600-MHz ^{1}H NMR time scale at 193 K, but both the C^1H^A/H^B and the C^1H/D agostic/nonagostic interconversions were still very rapid under these conditions (see Scheme 4). This led to very characteristic ^{1}H NMR resonances for the isomers **9a**-C^1H_2 at δ 3.50 (C^2HD), −0.79, and −1.00 (C^1H_2, coupling constants $^3J_{HH}$ = 8.3 and 10.3 Hz, $^2J_{HH}$ = 4.4 Hz) and **9a**-C^1HD at δ 3.58, 3.41 (C^2H_2), and −2.18 (C^1HD, coupling constants $^2J_{HH}$ = 5.6 Hz, $^3J_{HH}$ =

(19) For related dynamic processes, see e.g.: (a) Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R. *J. Am. Chem. Soc.* **1995**, *117*, 10503. Röttger, D.; Erker, G. *Angew. Chem.* 1997, *109*, 840; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 812. Ahlers, W.; Temme, B.; Erker, G.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 1440. Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. *Chem. Ber.* **1997**, *130*, 1069. (b) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437.

(20) Wolfsberg, M. *Annu. Rev. Phys. Chem.* **1969**, *20*, 2043. Bartell, L. S.; Roskos, R. R. *J. Chem. Soc.* **1973**, *10*, 1.

(21) For a discussion of isotope effects on rapidly equilibrating systems and on their NMR spectra, see e.g.: (a) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, *23*, 63 and references therein. (b) Saunders: M.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2561. Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. Faller, J. W.; Murray, H. H.; Sauders, M. *J. Am. Chem. Soc.* **1980**, *102*, 2306.

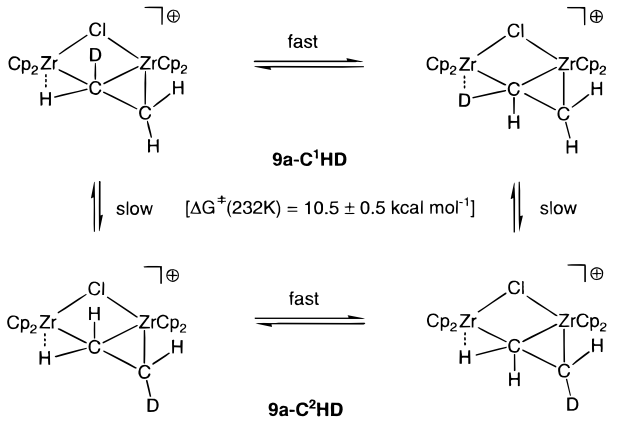
(22) Mislow, K.; Graeve, R.; Gordon, A. J.; Wahl, G. H., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1199. Mislow, K.; Graeve, R.; Gordon, A. J.; Wahl, G. H., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1733. Carter, R. E.; Melander, L. *Adv. Phys. Org. Chem.* **1973**, *10*, 1. Biali, S. E.; Rappoport, Z.; Hull, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5450.

Table 2. Characterization of the Cationic Products (**9** and **10**) Obtained by Protonation of the Neutral Precursors **6** and **7** with **8a**[a]

	R	yield[b]	*T* (K)[c]	$C^2H(R)$[d]		$C^1H^AH^B$ (major)[e]		ratio[f]	C^1H^A (minor)[g]
9a	H	67	203	67.6	3.52[h]	95.6	−0.87[h]		
9b	Ph	63	203	86.3 [142]	5.17 (15.6)	92.5 [99, 131]	−5.55, 4.63 (6.6, 5.4)	*i*	*i*
9c	*n*-Bu	54	278,[j] 253[k]	94.3 [139]	3.69 (15.6)	104.5 [97, 132]	−5.70, 4.04 (6.6, 4.8)	9:1	−6.23 (6.6, 5.4)
9d	Cy	51	278,[j] 253[k]	101.4[l]	3.50 (15.6)	101.8[l]	−5.86, 4.07 (6.2, 5.4)	9:1	−6.37 (6.7, 5.4)
10a	H	66	193	73.6	3.20[h]	97.6	−0.91[h]		
10b	Ph	60	243	86.5 [142]	4.97 (15.7)	93.5 [99, 131]	−5.75, 4.60 (6.3 5.9)	8:2	−6.24 (6.2, 5.9)
10c	*n*-Bu	69	243	94.3 [133]	3.27 (15.6)	104.5 [97, 134]	−5.88, 4.03 (6.6 5.9)	8:2	−6.40 (6.2, 5.8)
10d	Cy	44	253	101.7[l]	3.34 (15.6)	102.7[l]	−6.02, 4.08 (6.3, 5.8)	9:1	−6.54 (6.4, 5.2)

[a] BPh_4^- salts; for $B(C_6F_5)_4^-$ salts, see Experimental Section. [b] In percent. [c] NMR spectra in dichloromethane-d_2 at *T* (K). [d] $^1J_{C^2H}$ in square brackets, $^3J_{HH}$ in parentheses. [e] H^A = agostic, major isomer, $^1J_{C^1H^A}$ followed by $^1J_{C^1H^B}$ in square brackets, $^3J_{HH}$, followed by $^2J_{HH}$ in parentheses. [f] Major:minor stereoisomer ratio. [g] ^1H NMR of agostic hydrogen of the minor isomer, $^3J_{HH}$ followed by $^2J_{HH}$ in parentheses. [h] Averaged value. [i] Minor isomer not observed. [j] ^1H NMR. [k] ^{13}C NMR. [l] Not determined.

Scheme 4



6.4 and 9.5 Hz). Thus we note that the isotopic effects on the ^1H NMR chemical shift of the C^2HD and the C^2H_2 and C^1H_2 resonances are marginal, as expected, whereas the C^1HD resonance of the **9a**-C^1HD isomer shows a very large isotopic shift effect: introduction of the ^2H substituent has caused a shifting of this signal from δ −0.87 in **9a** to δ −2.18 in **9a**-C^1HD.

Similar to the ingenious analysis of the agostic situation of methyl groups at metal centers introduced by J. R. Shapley et al.,[23] which makes use of the variations of equilibrium isotope-induced shifts of the ^1H NMR resonance in the $-CH_3$, $-CH_2D$, $-CHD_2$ series of isotopomers, the equilibrium ^1H NMR chemical shifts at the C^1H_2 and C^1HD unit of **9a** and **9a**-C^1HD can be expressed by eqs 1 and 2,

$$\bar{\delta}_{C^1H_2} = (\delta_t + \delta_b)/2 \quad (1)$$

$$\bar{\delta}_{C^1HD} = (K\delta_t + \delta_b)/(K + 1) \quad (2)$$

with δ_t and δ_b denoting the chemical shift of the nonagostic (i.e., terminal) C^1-H and the agostic (i.e., bridging) C^1-H group, respectively, under limiting nonequilibrating conditions and defining $K = \exp(-\Delta E/RT)$. ΔE is the energy difference between the $C^1-(\mu\text{-D})$ and $C^1-(\mu\text{-H})$ bridged forms at the temperature *T* in this intramolecular competition situation of the regioisomer **9a**-C^1HD.

In contrast to Shapley's situation of the analysis of a rapidly equilibrating agostic/nonagostic methyl group, the analogous equilibrating methylene situation is eo ipso mathematically underdetermined as we have only two observables ($\delta_{C^1H_2}$ and δ_{C^1HD}) available to obtain the three parameters δ_t, δ_b, and *K*. Fortunately, the series of substituted analogues of **9a**, namely **9b**−**d** and **10b**−**d** give static NMR spectra, as described above, has allowed to deduce a reliable estimate of the limiting δ_b value, which has turned out to be rather substituent insensitive (see Table 2). If we use the average value of $\delta_b = -5.77$ ($\delta_{C^1-H^A}$(agostic) from complexes **9b**−**d** and **10b**−**d**), eq 1 gives $\delta_t = +4.03$ ppm, a value that is close to the $\delta_{C^1-H^B}$(nonagostic) average of the complexes **9b**−**d** and **10b**−**d** listed in Table 2. With these values of δ_b and δ_t eq 2 is solved to give an energy difference of $\Delta E \sim 220$ cal mol^{-1} between D and H in the bridging, i.e. agostic, position at the base of the hypercarbon polyhedron in **9a** ($T = 203$ K).[24]

Conclusions

Hypercarbon chemistry has in the past mostly used the available coordination sites at the element carbon and has usually extended the coordination sphere of this central atom by constructing an array of three-center−two-electron and two-center−two-electron bonds in the most favorable way.[1,2] This has in a large number of cases resulted in arrangements of ligands around the central carbon atom of rather high symmetry. Hydrocarbyl systems formed by adding one or more protons to a suited hydrocarbon and organometallic systems resulting from the analogous addition of metal-containing fragments appear to behave basically alike in this respect. The system that we have obtained here by the protonation reaction of the bis(zirconocene) complexes **6** (or **7**, respectively) seems to behave fundamentally different. Here the formation of the hypercoordinated carbon and the preferred shape of the resulting CX_5^+ polyhedron is characteristically determined by the very specific stereoelectronic properties of the two group 4 bent metallocene units that are involved. Their well-defined single σ-ligand plane[18,25] has determined the planar framework of the obtained products, and the pronounced ability of the $^RCp_2Zr$ unit to form a strong agostic interaction[26] with one of the adjacent C^1-H bonds has led to the formation of the very unusual polyhedral geometry of the resulting product, as it has become apparent from the combined structural evidence of our study. The CX_5^+ compounds **9** and **10** seem to be unique in the sense that they contain a near to coplanar CX_4 unit, bearing the hypercarbon atom in its center, which exhibits the fifth ligand at carbon (here a hydrogen atom) perpendicularly oriented to this plane to complete the unusual overall geometry. In another view, the complexes **9** and **10** can formally be thought of being con-

(23) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(24) We note that the energy difference ΔE is slightly larger for the methylene (220 cal mol^{-1}) than for the methyl situation (130 cal mol^{-1}).[23] Whether this is a general effect, which could be based on the slightly higher nucleophilic character of the methylene CH_2 bonds, or if this is specific to the hypercarbon geometry will be investigated in a separate study.

(25) Erker, G.; Rosenfeldt, F. *Angew. Chem.* **1978**, *90*, 640; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605. Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1.

structed by a distorted rectangular-pyramidal framework, consisting of two zirconium atoms, two hydrogens, and a carbon (namely C^2) to which an additional carbon center (C^1) was added face-centered to the basal Zr_2HC-containing plane.

This unique polyhedral arrangement around the carbon center C1 is apparently obtained in the protonation reaction under thermodynamic control. The obtained unique structural framework is obviously preferred over a "normal" structure, such as the dimetallamonocyclic geometry **11** (see Scheme 3) that is probably passed through as a transition state[19a] or high-lying intermediate in the degenerate rearrangement of **9**. The activation energy of this rearrangement may serve as a first approximation to evaluate the extra stabilization energy of the pentacoordinate carbon structure in this specific coordination environment. We conclude that the combined features of the involved two group 4 metallocene units have apparently made the here-found uniquely distorted CX_5^+ hypercarbon structure by ca. 10 kcal mol^{-1} more stable than any of its possible conventional structural alternatives. This is a very large stabilizing effect. It underlines the potential that organometallic substructures exhibiting specific stereoelectronic properties, such as the group 4 metallocenes, have to function as essential thermodynamically stabilizing components in the construction of compounds containing the element carbon in novel or uncommon coordination geometries.[27] The ability of using adjacent C−H bonds as "functional groups" in the construction of such organometallic frameworks and the disclosure of kinetically viable pathways, such as the protonation reaction described in this article, will probably make the use of metallocene moieties and similar groups of great value in the future construction of novel very unusually structured carbon compounds.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR measurements) were dried and distilled under argon prior to use. The following instruments were used for spectroscopic and physical characterization of the compounds: Bruker AC 200 P (^{1}H, 200 MHz; ^{13}C, 50 MHz) and Varian Unity Plus (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{19}F, 564 MHz; ^{11}B, 192 MHz) FT NMR spectrometer (in addition to the usual 1D experiments, the new compounds were usually also characterized by the following 2D NMR experiments: GHSQC (gradient pulsed heteronuclear single quantum coherence), GHMBC (gradient pulsed heteronuclear multiple bond coherence), and GCOSY (gradient pulsed correlated spectroscopy);[16] Nicolet 5DXC FT-IR spectrometer, Enraf-Nonius MACH3 diffractometer (programs used: MolEN, SHELXS-86, SHELXL-93, DIAMOND); elemental analyses: Foss Heraeus CHN-Rapid; melting points were determined by differential scanning calorimetry DSC 2010, Texas Instruments. The hydrozirconation reactions to yield **4** and **5** were carried out as described in the literature.[7] The metallocene-generating reactions were performed analogously as previously described.[8−10] Complex **6b** had been prepared by a different method and described previously.[5a] The ammonium salts **8a**,**b** were prepared according to literature procedures.[6]

(*μ*-Chloro)(*μ*-*η*^{1}:*η*^{2}-vinyl)bis(zirconocene) 6a. Zirconocene dichloride (3.5 g, 12 mmol) was dissolved in THF. At −78 °C 15.5 mL (24 mmol) of a 1.55 M *n*-butyllithium solution in hexane was added dropwise with stirring. The mixture was stirred for 1 h, then a cold (−78 °C) solution of vinylzirconocene chloride (**4a**, 3.4 g, 12 mmol) in THF was added. The mixture was allowed to warm to room temperature during 18 h. Solvent was removed in vacuo. The residue was taken up in 50 mL of toluene and filtered. The filtrate was concentrated to a volume of 10 mL in vacuo. Pentane (30 mL) was added. The product precipitated at −30 °C. It was collected by filtration, washed with pentane (3 × 30 mL), and dried in vacuo to give 1.4 g (22%) of **6a** as an orange amorphous solid, mp 204 °C (dec). ^{1}H NMR (200.1 MHz, 300 K, benzene-d_6): δ 7.15 (dd, 1H, ^3J = 13.5 Hz, ^3J = 17.8 Hz), 5.61 (s, 5 H, Cp-H), 5.32 (s, 5H, Cp-H), 5.25 (s, 5H, Cp-H), 5.07 (s, 5H, Cp-H), 3.92 (dd, 1H, 2′−H, ^3J = 13.5 Hz, ^2J = 1.8 Hz), 2.64 (dd, 1H, 2-H, ^3J = 17.8 Hz, ^2J = 1.8 Hz) ppm. ^{13}C NMR (90.6 MHz, 300 K, benzene-d_6): δ 178.8 (C1), 106.5, 105.2, 104.5, 103.6 (Cp-C), 63.1 (C2) ppm. Anal. Calcd for $C_{22}H_{23}ClZr_2$ (505.3): C, 52.29; H, 4.59. Found: C, 52.97; H, 4.66%.

Preparation of the *E*/*Z*-(*μ*-Chloro)(*μ*-*η*^{1}:*η*^{2}-CH═CHD)bis(zirconocene) Mixture (*E*/*Z*-6a-*d*$_1$). A mixture of *E*-(DHC═CH−)-$ZrCp_2Cl$ (*E*-**4a**-d_1) (300 mg, 1.05 mmol) and (butadiene)zirconocene (290 mg, 1.05 mmol) was dissolved in 10 mL of benzene-d_6. The reaction mixture was irradiated (Philipps HPK 125, Pyrex filter) for 5 h at ambient temperature. During this time the product precipitated from the solution as an orange solid. It was collected by filtration, washed with a small portion of pentane, and dried in vacuo to give a 1:1 mixture of *E*- and *Z*-**6a**-d_1; yield 390 mg (73%), mp 207 °C (dec). ^{1}H NMR (200.1 MHz, 300 K, benzene-d_6): δ 7.14 (m, 2H, 1-H partially hidden under solvent), 5.61 (s, 10H, Cp-H), 5.324/5.321 (s, each 5H, Cp-H), 5.257/5.255 (s, each 5H, Cp-H), 5.078/5.076 (s, each 5H, Cp-H), 3.92 (d, 1H, 2-H, ^3J = 13.5 Hz), 2.64 (d, 1H, 2-H, ^3J = 17.7 Hz) ppm. ^{13}C NMR (90.6 MHz, 300 K, benzene-d_6): δ 178.8 (C1), 104.7, 103.4, 103.0, 101.8 (Cp-C), 61.1, 61.0 (each t, C2, $^1J_{CD}$ = 22.6 Hz and $^1J_{CD}$ = 21.9 Hz) ppm. Anal. Calcd for $C_{22}H_{22}DClZr_2$ (506.32): C, 52.19; H, 4.59. Found: C, 51.73; H, 4.89.

(*μ*-Chloro)(*μ*-*η*^{1}:*η*^{2}-*E*-2-styryl)bis(zirconocene) 6b. A 1.55 M *n*-butyllithium solution in hexane (15.5 mL, 24 mmol) was added dropwise with stirring at −78 °C to a solution of 3.5 g (12 mmol) of Cp_2ZrCl_2 in THF. After the mixture was stirred for 1 h at −78 °C, a cold solution of 4.0 g (12 mmol) of $Cp_2Zr(Cl)(CH═CHPh)$ **4b** in THF was added. The mixture was stirred for 18 h and warmed to room temperature. Solvent was removed in vacuo, the residue extracted with 50 mL of toluene and filtered. The filtrate was concentrated to 10 mL in vacuo, pentane (30 mL) was added, and the product precipitated at −30 °C. Collection by filtration gave 1.2 g (38%) of the previously described[5a] product **6b**. ^{1}H NMR (200.1 MHz, 300 K, benzene-d_6): δ 7.69 (d, 1H, 1-H, ^3J = 18.1 Hz), 7.38−6.94 (m, 5H, Ph-H), 5.63, 5.27, 4.87 (s, each 5H, Cp-H), 4.55 (d, 1H, 2-H, ^3J = 18.1 Hz) ppm.

Generation of (*μ*-Chloro)(*μ*-*η*^{1}:*η*^{2}-*E*-1-hexenyl)bis(zirconocene) 6c. Analogously as described above, the reaction of 1.0 g (2.9 mmol) of *E*-(1-hexenyl)zirconocene chloride **4c** with 1 mol equiv of zirconocene, generated from 0.86 g (2.9 mmol) of zirconocene dichloride by treatment with 5.7 mmol of *n*-butyllithium, gave 0.49 g (30%) of **6c** as a very sensitive orange oil, DSC: 120 °C (dec). Complex **6c** was only characterized spectroscopically and then directly employed as a starting material for the protonation reaction. ^{1}H NMR (200.1 MHz, 300 K, benzene-d_6): δ 6.92 (d, 1H, 1-H, ^3J = 17.9 Hz), 5.56, 5.33, 5.22, 5.07 (s, each 5H, Cp-H), 2.99 (m, 1H, 2-H), 1.61 (m, 6H, CH_2), 0.86 (t, 3H, CH_3, ^3J = 6.5 Hz) ppm. ^{13}C NMR (50.3 MHz, 300

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K, benzene-d_6): δ 183.0 (C1), 106.1, 105.0, 104.3, 103.8 (Cp-*C*), 88.7 (C2), 44.7 (*C*H$_2$), 37.5 (*C*H$_2$), 23.3 (*C*H$_2$), 14.7 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ 3098, 2953, 2921, 2852, 1635, 1588, 1481, 1261, 1013, 799, 736 cm^{-1}.

Generation of (μ-Chloro)(μ-η^1:η^2-*E*-2-cyclohexylethenyl)bis(zirconocene) 6d. Diphenylzirconocene (0.60 g, 1.6 mmol) and **4d** (0.60 g, 1.6 mmol) were together dissolved in 15 mL of toluene and then irradiated (Philipps HPK 125, Pyrex filter) for 4 h at −78 °C. Solvent was removed in vacuo and the residue washed with pentane to give 0.43 g (46%) of **6d** as a yellow oil, DSC: 114 °C (dec). The product was spectroscopically identified and then directly used for the protonation reaction. ^{1}H NMR (200.1 MHz, 300 K, benzene-d_6): δ 7.01 (d, 1H, 1-H, ^3J = 17.9 Hz), 5.54, 5.37, 5.22, 5.06 (s, each 5H, Cp-H), 2.85 (m, 1H, 2-H), 1.77, 1.19 (m, 11H, CH$_2$, CH) ppm. ^{13}C NMR (50.3 MHz, 300 K, benzene-d_6): δ 180.6 (C1), 106.1, 105.1, 104.3, 103.7 (Cp-*C*), 70.2 (C2), 67.2 (*C*H), 52.3 (*C*H$_2$), 42.2 (*C*H$_2$), 35.3 (*C*H$_2$) ppm. IR (KBr) $\tilde{\nu}$ 3098, 2919, 2847, 1635, 1438, 1261, 1191, 1013, 798, 736 cm^{-1}.

Preparation of (μ-Chloro)(μ-η^1:η^2-ethylene)bis(zirconocene) Tetraphenylborate 9a·BPh$_4^-$. The solid reagents **6a** (320 mg, 0.63 mmol) and **8a** (350 mg, 0.79 mmol) were mixed, and then 50 mL of bromobenzene was added. The resulting suspension was stirred for 1 h, during which time the ammonium salt was completely used up. The resulting orange precipitate was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield 350 mg (67%) of **9a**·BPh$_4^-$, mp 162 °C (dec). ^{1}H NMR (200.1 MHz, 300 K, dichloromethane-d_2): δ 5.92 (s, 20H, Cp-H), 1.41 (br, 4H, CH$_2$); BPh$_4^-$: 7.40−7.30 (m, 8H, Ph-H), 7.10−7.00 (m, 8H, Ph-H), 7.00−6.85 (m, 4H, Ph-H) ppm. Above 10 °C the complex decomposed slowly in dichloromethane. ^{1}H NMR (599.9 MHz, 203 K, dichloromethane-d_2): δ 6.02 (s, 10H, Cp-H), 5.73 (s, 10H, Cp-H), 3.52 (t, 2H, 2-H, ^3J = 9.4 Hz), −0.87 (t, 2H, 1-H, ^3J = 9.4 Hz); BPh$_4^-$: 7.28 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.89 (m, 4H, Ph-H) ppm. ^{13}C NMR (150.9 MHz, 203 K, dichloromethane-d_2): δ 112.2 (Cp), 106.9 (Cp), 95.6 (C1), 67.6 (C2); BPh$_4^-$: 134.4 (Ph), 125.2 (Ph), 121.1 (Ph) ppm (*ipso*-C not observed). GCOSY (599.9 MHz, 203 K, dichloromethane-d_2): δ 3.52 (2-H)/−0.87 (1-H) ppm. GHSQC (599.9 MHz, 203 K, dichloromethane-d_2): δ 112.2/6.02 (Cp), 106.9/5.73 (Cp), 95.6/−0.87 (C1), 67.6/3.52 (C2); BPh$_4^-$: 134.4/7.28 (Ph), 125.2/7.04 (Ph), 121.1/6.89 (Ph) ppm. Coalescence of the Cp ligand signals at T_c = 232 K, $\Delta\nu$ = 174 Hz. $\Delta G^{\ddagger}$ = 10.5 ± 0.5 kcal/mol. IR (KBr): $\tilde{\nu}$ 3053, 2965, 2924, 2851, 1601, 1431, 1020, 802, 737, 704 cm^{-1}. Anal. Calcd for C$_{46}$H$_{44}$BClZr$_2$ (825.6): C, 66.93; H, 5.37. Found: C, 65.71; H, 5.33%.

(μ-Chloro)(μ-η^1:η^2-2-phenylethylene)bis(zirconocene) Tetraphenylborate 9b·BPh$_4^-$. Bromobenzene (50 mL) was added to a mixture of 366 mg (0.63 mmol) of **6b** and 350 mg (0.79 mmol) of **8a**. The suspension was stirred for 1 h at ambient temperature. The precipitate was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield 360 mg (63%) of **9b**·BPh$_4^-$, mp 130 °C (dec). The compound is very sensitive. It decomposes in CD_2Cl_2 solution within a few minutes; therefore, the spectra were recorded at 203 K. Only one stereoisomer was observed. ^{1}H NMR (599.9 MHz, 203 K, dichloromethane-d_2): δ 7.62 (m, 2H, Ph-H), 7.48 (m, 2H, Ph-H), 7.15 (m, 1H, Ph-H), 6.27, 6.04, 5.97, 5.38 (s, each 5H, Cp-H), 5.17 (dd, 1H, 2-H, ^3J = 6.6 Hz, ^3J = 15.6 Hz), 4.63 (dd, 1H, 1-H, ^2J = 5.3 Hz, ^3J = 15.6 Hz), −5.55 (dd, 1H, 1-H′, ^3J = 6.6 Hz, ^2J = 5.3 Hz); BPh$_4^-$: 7.35 (m, 8H, Ph-H), 7.06 (m, 8H, Ph-H), 6.91 (m, 4H, Ph-H) ppm. ^{13}C NMR (150.9 MHz, 203 K, dichloromethane-d_2): δ 137.9 (Ph), 127.3 (Ph), 124.5 (Ph), 113.6, 111.5, 109.2, 108.6 (Cp), 92.5 (dd, C1, $^1J_{C^1H}$ = 131 Hz, $^1J_{C^1H}$ = 99 Hz), 86.3 (d, C2, $^1J_{C^2H}$ = 142 Hz); BPh$_4^-$: 162.2 (B−C, $^1J_{BC}$ = 49 Hz), 134.7 (Ph), 133.6 (Ph), 121.1 (Ph) ppm. GCOSY (599.9 MHz, 203 K, dichloromethane-d_2): δ −5.51 (1-H′)/4.63 (1-H), −5.55, 4.63 (1-H′, 1-H)/5.17 (2-H) ppm. GHSQC (599.9 MHz, 203 K, dichloromethane-d_2): δ 137.9/7.62 (Ph), 127.3/7.48 (Ph), 124.5/7.15 (Ph), 113.6/6.27, 108.6/6.04, 111.5/5.97, 109.2/5.39 (Cp), 92.5/4.63, −5.55 (C1), 86.3/5.17 (C2); BPh$_4^-$: 134.7/7.35 (Ph), 133.6/7.06 (Ph), 121.1/6.91 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3054, 2965, 2922, 2853, 1485, 1429, 1261, 1015, 808, 735, 708 cm^{-1}. Anal. Calcd for C$_{52}$H$_{48}$BClZr$_2$ (901.7): C, 69.27; H, 5.37. Found: C, 68.20; H, 5.47%.

(μ-Chloro)(μ-η^1:η^2-1,2-hexylene)bis(zirconocene) Tetraphenylborate 9c·BPh$_4^-$. A suspension obtained from 250 mg (0.45 mmol) of complex **6c** and 259 mg (0.59 mmol) of **8a** in 50 mL of bromobenzene was stirred for 1 h at room temperature. The resulting yellow precipitate was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield 210 mg (54%) of **9c**·BPh$_4^-$, mp 111 °C (dec). A mixture of two stereoisomers was observed by ^{1}H NMR at room temperature in a 9:1 ratio. ^{1}H NMR (599.9 MHz, 278 K, dichloromethane-d_2): Major isomer **9a**: δ 6.15, 5.86, 5.85, 5.65 (s, each 5H, Cp-H), 4.04 (dd, 1H, 1-H, ^3J = 15.6 Hz, ^2J = 4.8 Hz), 3.69 (m, 1H, 2-H), 2.16 (m, 2H, CH$_2$), 1.56, 1.47 (each m, 4H, CH$_2$), 1.01 (t, 3H, CH$_3$, ^3J = 7.6 Hz), −5.70 (dd, 1H, 1-H′, ^3J = 6.6 Hz, ^2J = 4.8 Hz); BPh$_4$-: 7.30 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.90 (m, 4H, Ph-H) ppm. Minor isomer **9a′**: δ 6.13, 5.83, 5.80, 5.60 (s, each 5H, Cp-H), −6.23 (dd, 1H, 1-H′, ^3J = 6.6 Hz, ^2J = 5.4 Hz); remaining signals hidden by major isomer. ^{13}C NMR (90.6 MHz, 253 K, dichloromethane-d_2) **9a**: δ 115.0, 112.5, 112.0, 110.0 (Cp), 104.5 (dd, C1, $^1J_{C^1H}$ = 132 Hz, $^1J_{C^1H}$ = 97 Hz), 94.3 (d, C2, $^1J_{C^2H}$ = 139 Hz), 36.6, 45.8, 23.3 (each CH$_2$), 14.7 (CH$_3$); BPh$_4^-$: 165.8 (B−C, $^1J_{BC}$ = 49 Hz), 135.2 (Ph), 126.6 (Ph), 121.1 (Ph) ppm. GCOSY (599.9 MHz, 253K, dichloromethane-d_2): δ −5.70 (1-H′)/4.04 (1-H), −5.70, 4.04 (1-H′, 1-H)/3.69 (2-H), 3.69 (2-H)/1.56 (CH$_2$ of C$_4$H$_6$) ppm. GHSQC (599.9 MHz, 278 K, dichloromethane-d_2): δ 115.0/6.15, 112.5/5.86, 112.0/5.85, 110.0/5.65 (Cp), 104.5/4.04, −5.70 (C1), 94.3/3.69 (C2), 45.8/2.16, 36.6/1.56, 23.3/1.47 (CH$_2$), 14.7/1.01 (CH$_3$); BPh$_4^-$: 135.2/7.30 (Ph), 126.6/7.04 (Ph), 121.1/6.90 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3054, 2960, 2922, 2852, 1427, 1266, 1021, 809, 736, 705 cm^{-1}. Anal. Calcd for C$_{50}$H$_{52}$BClZr$_2$ (881.7): C, 68.12; H, 5.94. Found: C, 66.61; H, 5.44%.

(μ-Chloro)(μ-η^1:η^2-2-cyclohexylethylene)bis(zirconocene) Tetraphenylborate 9d·BPh$_4^-$. Complex **6d** (150 mg, 0.26 mmol) and 134 mg (0.33 mmol) of **8a** were suspended together in 20 mL of bromobenzene and stirred for 1 h. At 0 °C pentane was added dropwise to precipitate the product that was collected by filtration, washed with pentane (2 × 2 mL), and dried in vacuo to give 120 mg (51%) of **9d**·BPh$_4^-$ as an orange powdery solid (9:1 ratio of the stereoisomers **9d** and **9d′**), mp 128 °C (dec). ^{1}H NMR (599.9 MHz, 278 K, dichloromethane-d_2): Major isomer **9d**: δ 6.17, 5.86, 5.85, 5.63 (s, each 5H, Cp-H), 4.07 (dd, 1H, 1-H, ^3J = 15.6 Hz, ^2J = 5.4 Hz), 3.50 (m, 1H, 2-H), 1.83, 1.31 (each m, 11H, C$_6$H$_{11}$), −5.86 (dd, 1H, 1-H′, ^3J = 6.2 Hz, ^2J = 5.4 Hz); BPh$_4^-$: δ 7.33−7.32 (m, 8H, Ph-H), 7.24−7.03 (m 8H, Ph-H), 6.92−6.89 (m, 4H, Ph-H). Minor isomer **9d′**: δ 6.15, 5.84, 5.82, 5.59 (s, each 5H, Cp-H), −6.37 (dd, 1H, 1-H′, ^3J = 6.7 Hz, ^2J = 5.4 Hz); remaining signals under those of the major isomer. ^{13}C NMR (150.9 MHz, 253 K, dichloromethane-d_2) **9d**: δ 113.8, 111.3, 108.0, 107.8 (Cp), 101.8 (C1), 101.4 (C2), 59.7, 40.7, 26.4 (C$_6$H$_{11}$); BPh$_4^-$: 163.8 (B−C, $^1J_{BC}$ = 49 Hz), 135.8 (Ph), 125.9 (Ph), 121.9 (Ph). GCOSY (599.9 MHz, 253K, dichloromethane-d_2) δ −5.72 (1-H′)/4.10 (1-H), −5.72, 4.10 (1-H′, 1-H)/3.53 (2-H) ppm. GHSQC (599.9 MHz, 253K, dichloromethane-d_2): δ 113.8/6.17, 111.3/5.86, 108.0/5.85, 107.8/5.63 (Cp), 101.8/4.07, −5.86 (C1), 101.4/3.50 (C2); BPh$_4^-$: 135.8/7.33 (Ph), 125.9/7.03 (Ph), 121.9/6.89 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3053, 2920, 2848, 1474, 1441, 1261, 1014, 814, 732, 703 cm^{-1}. Anal. Calcd for C$_{52}$H$_{54}$BClZr$_2$ (907.7): C, 68.81; H, 6.00. Found: C, 67.85; H, 5.75%.

(μ-Chloro)(μ-η^1:η^2-ethylene)bis[bis(methylcyclopentadienyl)zirconium] Tetraphenylborate 10a·BPh$_4^-$. Generation of the Neutral (μ-Chloro)(μ-η^1:η^2-vinyl)bis[bis(methylcyclopentadienyl)zirconium] Precursor 7a. A 1.55 M *n*-butyllithium solution in hexane (3.0 mL, 4.8 mmol) was slowly added to a solution of 0.76 g (2.4 mmol) of (MeCp)$_2$ZrCl$_2$ in THF at −78 °C. The mixture was stirred at −78 °C for 1 h. Then a precooled (−78 °C) THF solution of 0.74 g (2.4 mmol) of (MeCp)$_2$Zr(Cl)(CH═CH$_2$) (**5a**) was added. The mixture was allowed to warm to room temperature and then stirred for another 2 h. Solvent was removed in vacuo, the residue taken up in 20 mL of toluene, and the remaining lithium chloride precipitate removed by filtration. Solvent was removed from the clear filtrate in vacuo. The crude reaction product (**7a**) was directly used for the protonation reaction without any further purification.

Preparation of 10a·BPh$_4^-$: 180 mg (0.32 mmol) of crude **7a**, prepared as described above, and **8a** (185 mg, 0.42 mmol) were suspended together in 50 mL of bromobenzene and stirred for 1 h at ambient temperature. The resulting orange precipitate was collected

by filtration, washed with ether (3 × 10 mL), and dried in vacuo to give 180 mg (66%) of **10a**·BPh_4^-, mp 117 °C (dec). The product tends to decompose slowly above 10 °C in dichloromethane solution to give $(MeCp)_2ZrCl_2$ among other products. ^{1}H NMR (200.1 MHz, 300 K, dichloromethane-d_2): δ 5.80, 5.71 (each m, 16H, Cp-H), 2.08 (s, 12H, Cp-CH_3), 1.35 (br, 4H, CH_2); BPh_4^-: 7.40−7.30 (m, 8H, Ph-H), 7.10−7.00 (m, 8H, Ph-H), 7.00−6.85 (m, 4H, Ph-H) ppm. ^{1}H NMR (599.9 MHz, 193 K, dichloromethane-d_2): δ 5.80−5.40 (each m, 16H, Cp-H), 3.20 (t, 2H, 2-H, ^3J = 9.6 Hz), 2.09, 2.06 (s, each 6H, Cp-CH_3), −0.91 (t, 2H, 1-H, ^3J = 9.6 Hz); BPh_4^-: 7.29 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.89 (m, 4H, Ph-H) ppm. ^{13}C NMR (150.9 MHz, 193 K, dichloromethane-d_2): δ 114.1−102.3 (Cp), 97.6 (C1), 73.6 (C2), 16.1, 15.7 (Cp-CH_3); BPh_4^-: 134.4 (Ph), 125.2 (Ph), 121.1 (Ph) ppm, ipso-C of Ph not observed. GCOSY (599.9 MHz, 193 K, dichloromethane-d_2): δ 3.22 (2-H)/−0.91 (1-H) ppm. GHSQC (599.9 MHz, 193 K, dichloromethane-d_2): δ 114.1−102.3/5.80−5.40 (Cp), 97.6/-0.91 (C1), 73.6/3.22 (C2), 16.1/2.09 (Cp-CH_3), 15.7/2.06 (Cp-CH_3); BPh_4^-: 134.4/7.29 (Ph), 125.2/7.04 (Ph), 121.1/6.89 (Ph) ppm. IR (KBr) $\tilde{\nu}$ 3054, 2960, 2925, 2850, 1590, 1479, 1432, 1261, 1035, 807, 734, 705 cm^{-1}. Anal. Calcd for $C_{50}H_{52}BClZr_2$ (881.7): C, 68.12: H, 5.94. Found: C, 68.28; H, 5.56%.

(μ-Chloro)(μ-η^1:η^2-2-phenylethylene)bis[bis(methylcyclopentadienyl)zirconium] Tetraphenylborate 10b·BPh_4^-: Generation of the Precursor 7b. Analogously as described above complex **7b** was obtained from the reaction of 2.17 g (5.6 mmol) of *E*-$(MeCp)_2Zr(Cl)$-(CH═CHPh) (**5b**) with bis(methylcyclopentadienyl)zirconium, generated by treatment of 1.76 g (5.6 mmol) of $(MeCp)_2ZrCl_2$ with 7 mL (11.2 mmol) of a 1.55 M *n*-butyllithium solution. The crude product **7b** was employed in the protonation reaction without any further purification.

Preparation of 10b·BPh_4^-: Analogously as described above, 240 mg (0.38 mmol) of the crude reagent **7b** was treated with 218 mg (0.49 mmol) of **8a** in 50 mL of bromobenzene to give compound **10b** (two isomers in a 80:20 ratio) as a red powder; yield 218 mg (60%), mp 140 °C (dec). ^{1}H NMR (599.9 MHz, 243 K, dichloromethane-d_2): major isomer **10b**: δ 7.42 (m, 2H, Ph-H), 7.18 (m, 2H, Ph-H), 7.08 (m, 1H, Ph-H), 6.29−5.11, 4.73 (each m, 16H, Cp-H), 4.97 (dd, 1H, 2-H, ^3J = 6.3 Hz, ^3J = 15.7 Hz), 4.60 (dd, 1H, 1-H, ^3J = 15.7 Hz, ^2J = 5.9 Hz), 2.25, 2.22, 2.11, 1.85 (s, each 3H, Cp-CH_3), −5.75 (dd, 1H, 1-H′, ^3J = 6.3 Hz, ^2J = 5.9 Hz); BPh_4^-: 7.30 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.89 (m, 4H, Ph-H) ppm. Minor isomer **10b′**: δ 2.30, 2.29, 2.17, 1.74 (s, each 3H, Cp-CH_3), −6.24 (dd, 1H, 1-H′, ^3J = 6.2 Hz, ^2J = 5.9 Hz); remaining signals under those of **10b**. ^{13}C NMR (150.9 MHz, 243 K, dichloromethane-d_2) **10b**: δ 127.9 (Ph), 125.8 (Ph), 123.5 (Ph), 116.0−104.0 (Cp), 93.5 (dd, C1, $^1J_{C^1H}$ = 131 Hz, $^1J_{C^1H}$ = 99 Hz), 86.5 (d, C2, $^1J_{C^2H}$ = 142 Hz), 15.8, 15.2, 15.1, 14.4 (Cp-CH_3); BPh_4^-: 163.8 (q, B−C, $^1J_{BC}$ = 49 Hz), 134.7 (Ph), 133.6 (Ph), 121.1 (Ph) ppm, ipso-C of Ph and MeCp not observed. GCOSY (599.9 MHz, 243 K, dichloromethane-d_2): δ −5.75 (1-H′)/4.60 (1-H), −5.75, 4.60 (1-H′, 1-H)/4.97 (2-H) ppm. GHSQC (599.9 MHz, 243 K, dichloromethane-d_2): δ 127.9/7.42 (Ph), 125.8/7.18 (Ph), 123.5/7.08 (Ph), 116−104/6.29−5.11, 4.73 (Cp), 93.5/4.60, −5.75 (C1), 86.5/4.97 (C2), 15.1/2.25, 15.8/2.22, 15.2/2.11, 14.4/1.85 (Cp-CH_3); BPh_4^-: 134.7/7.30 (Ph), 133.6/7.04 (Ph), 121.1/6.89 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3052, 2963, 2920, 1516, 1427, 1091, 978, 815, 733 cm^{-1}. Anal. Calcd. for $C_{56}H_{56}BClZr_2$ (957.8) C 70.23, H 5.89; found C 69.02, H 6.35.

(μ-Chloro)(μ-η^1:η^2-1,2-hexylene)bis[bis(methylcyclopentadienyl)-zirconium] Tetraphenylborate 10c·BPh_4^-: Generation of the Precursor 7c. Complex **7c** was prepared analogously as described above from 0.77 g (2.1 mmol) of *E*-$(MeCp)_2Zr(Cl)(CH{=}CH{-}C_4H_9)$ (**5c**) by treatment with the "Negishi reagent" obtained by reacting 0.67 g (2.1 mmol) of $(MeCp)_2ZrCl_2$ with 2.7 mL (4.2 mmol) of a 1.55 M *n*-butyllithium solution in hexane. The crude product **7c** was used directly without any further purification. Preparation of **10c**·BPh_4^-: Analogously as described above 155 mg (0.24 mmol) of **7c** was treated with 140 mg (0.32 mmol) of **8a** in 50 mL of bromobenzene to yield 155 mg (69%) of **10c**·BPh_4^- as a yellow solid, mp 126 °C (dec), mixture of two isomers in a 80:20 ratio. ^{1}H NMR (599.9 MHz, 243 K, dichloromethane-d_2): Major isomer **10c**: δ 6.17−5.13 (m, 16H, Cp-H), 4.03 (dd, 1H, 1-H, ^3J = 15.6 Hz, ^2J = 5.9 Hz), 3.27 (m, 1H, 2-H), 2.21, 2.18, 2.14, 2.08 (s, each 3H, Cp-CH_3) 1.88 (m, 2H, CH_2), 1.44 (m, 4H, C_2H_4), 0.95 (t, 3H, CH_3, ^3J = 7.6 Hz), −5.88 (dd, 1H, 1-H′, ^3J = 6.6 Hz, ^2J = 5.9 Hz); BPh_4^-: 7.30 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.90 (m, 4H, Ph-H) ppm. Minor isomer **10c′**: δ 2.19, 2.17, 2.12, 2.09 (s, each 3H, Cp-CH_3), −6.40 (dd, 1H, 1-H′, ^3J = 6.2 Hz, ^2J = 5.8 Hz); remaining signals under the resonances of the major isomer. ^{13}C NMR (90.6 MHz, 243 K, dichloromethane-d_2) **10c**: δ 115.5−108.7 (Cp), 104.5 (dd, C1, $^1J_{C^1H}$ = 134 Hz, $^1J_{C^1H}$ = 97 Hz), 94.3 (d, C2, $^1J_{C^2H}$ = 133 Hz), 44.9 (CH_2), 38.3, 23.1 (C_2H_4), 15.6, 15.4, 15.3, 15.1 (Cp-CH_3), 14.9 (CH_3); BPh_4-: 163.9 (B−C, $^1J_{BC}$ = 49 Hz), 135.2 (Ph), 126.6 (Ph), 121.1 (Ph) ppm. GCOSY (599.9 MHz, 243 K, dichloromethane-d_2): δ −5.88 (1-H′)/4.03 (1-H), −5.88, 4.03 (1-H′,1-H)/3.27 (2-H), 3.27 (2-H)/1.88 (CH_2 of C_4H_9) ppm. GHSQC (599.9 MHz, 243 K, dichloromethane-d_2): δ 115.5−108.7/6.17−5.13 (Cp), 104.5/4.03, −5.88 (C1), 94.3/3.27 (C2), 15.6/2.18, 15.4/2.14, 15.3/2.21, 15.1/2.08 (Cp-CH_3); BPh_4^-: 135.2/7.30 (Ph), 126.6/7.04 (Ph), 121.1/6.90 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3052, 2960, 2921, 2848, 1591, 1439, 1032, 808, 729 cm^{-1}. Anal. Calcd for $C_{54}H_{60}BClZr_2$ (937.8): C, 69.16; H, 6.45. Found: C, 68.55; H, 6.31%.

X-ray Crystal Structure Analysis of 10c. Single crystals were obtained from 1,1,2,2-tetrachloroethane/pentane by the diffusion method. Formula $C_{54}H_{60}BClZr_2 \cdot 2\ C_2H_2Cl_4$, M = 1273.39, 0.50 × 0.20 × 0.20 mm, a = 14.707(3) Å, b = 23.408(9) Å, c = 17.547(6) Å, β = 104.52(3)°, V = 5848(3) Å^3, ρ_{calc} = 1.446 g cm^{-3}, μ = 8.04 cm^{-1}, empirical absorption correction via φ scan data (0.954 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 5672 reflections collected ($\pm h$, $-k$, $-l$), [(sin θ)/λ] = 0.44 Å^{-1}, 5444 independent and 2061 observed reflections [$I \geq 2\sigma(I)$], 293 refined parameters, R = 0.070, wR^2 = 0.150, maximum residual electron density 0.54 (−0.44) e Å^{-3}, due to the small amount of observed data only the Zr and Cl atoms were refined with anisotropic thermal parameters, phenyl groups of the anion were constrained to idealized six rings, hydrogens calculated and refined as riding atoms, the hydrogens of the secondary CH_2 group at C1 were calculated omitting the Zr2−C1 bond.

(μ-Chloro)(μ-η^1:η^2-2-cyclohexylethylene)bis[bis(methylcyclopentadienyl)zirconium] Tetraphenylborate 10d·BPh_4^-: Generation of the Precursor 7d. A solution of 460 mg (1.1 mmol) of $(MeCp)_2ZrPh_2$ and 450 mg (1.1 mmol) of *E*-$(MeCp)_2Zr(Cl)(CH{=}CH$-cyclo-$C_6H_{11})$ (**5d**) in 5 mL of toluene was irradiated (Philipps HPK 125, Pyrex filter) for 12 h at −20 °C. Solvent was then removed in vacuo. The crude product **7d** was employed directly for the protonation reaction without any further purification.

Preparation of 10d·BPh_4^-: Analogously as described above 420 mg (0.65 mmol) of the crude **7d** was treated with 350 mg (0.87 mmol) of **8a** in 50 mL of bromobenzene to give 270 mg (44%) of **10d** (mixture of two isomers, 9:1 ratio) as a yellow-green oil, DSC: 140 °C (dec). The oily product mixture was only characterized spectroscopically. ^{1}H NMR (599.9 MHz, 253 K, dichloromethane-d_2): Major isomer **10d**: δ 6.52−5.45 (m, 16H, Cp-H), 4.08 (dd, 1H, 1-H, ^3J = 15.6 Hz, ^2J = 5.8 Hz), 3.34 (m, 1H, 2-H), 2.16, 2.14, 2.13, 2.07 (s, each 3H, Cp-CH_3), 1.79, 1.31 (each m, 11H, C_6H_{11}), −6.02 (dd, 1H, 1-H′, ^3J = 6.3 Hz, ^2J = 5.8 Hz); BPh_4^-: 7.36 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.93 (m, 4H, Ph-H) ppm. Minor isomer **10d′**: δ 2.11, 2.08, 2.04, 2.01 (s, each 3H, Cp-CH_3), −6.54 (dd, 1H, 1-H′, ^3J = 6.4 Hz, ^2J = 5.2 Hz); remaining signals under major isomer resonances. ^{13}C NMR (150.6 MHz, 253 K, dichloromethane-d_2): δ 117.5−108.2 (Cp), 102.7 (C1), 101.7 (C2), 53.1 (*C*H), 41.2 (*C*H_2), 34.2, 26.4, 22.5 (*C*H_2), 15.5, 15.3, 15.2, 14.1 (Cp-CH_3); BPh_4^-: 163.9 (q, B−C, $^1J_{BC}$ = 49 Hz), 135.8 (Ph), 125.9 (Ph), 121.9 (Ph) ppm. GCOSY (599.9 MHz, 243 K, dichloromethane-d_2): δ −5.89 (1-H′)/4.08 (1-H), −5.89, 4.08 (1-H′, 1-H)/3.34 (2-H), 3.34 (2-H)/1.79 (CH of C_6H_{11}) ppm. GHSQC (599.9 MHz, 243 K, dichloromethane-d_2): δ 117.5−108.2/6.52−5.45 (Cp), 102.7/4.08, −6.02 (C1), 101.7/3.34 (C2), 15.5/2.16, 15.3/2.14, 15.2/2.13, 14.1/2.07 (Cp-CH_3); BPh_4^-: 135.8/7.36 (Ph), 125.9/7.04 (Ph), 121.9/6.93 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3053, 3031, 2960, 2921, 2849, 1591, 1431, 1240, 1032, 806, 732, 703, 602 cm^{-1}.

Generation of 9a·$B(C_6F_5)_4^-$. Bromobenzene (20 mL) was added at −78 °C to a solid mixture of complex **6a** (150 mg, 0.30 mmol) and 237 mg (0.30 mmol) of **8b**. The mixture was stirred for 30 min at −78 °C, then warmed to room temperature and stirred for additional 30 min. A 5-mL portion of pentane was added at 0 °C to precipitate

the product as a yellow-green oil that was separated from the solution by decanting. The oil was washed with 10 mL of pentane, yield 220 mg (62%), DSC: 107 °C (dec). ^{1}H NMR (200.1 MHz, 300 K, dichloromethane-d_2): δ 6.01 (s, 20H, Cp-H), 1.49 (br, 4H, CH_2) ppm. ^{1}H NMR (200.1 MHz, 213 K, dichloromethane-d_2): δ 6.12 (s, 10H, Cp-H), 5.73 (s, 10H, Cp-H), 3.53 (t, 2H, 2-H, ^3J = 9.3 Hz), −0.90 (t, 2H, 1-H, ^3J = 9.3 Hz) ppm. Coalescence of the Cp resonances at 236 K, $\Delta\nu$ = 78.1 Hz. $\Delta G^{\ddagger}$ = 10.8 ± 0.5 kcal/mol. ^{13}C NMR (150.9 MHz, 213 K, dichloromethane-d_2): δ 112.5, 107.5 (d, Cp, $^1J_{CH}$ = 173 Hz), 96.5 (t, C1, $^1J_{C^1H}$ = 116 Hz), 68.3 (t, C2, $^1J_{C^2H}$ = 150 Hz); $B(C_6F_5)_4^-$: δ 147.8 (d, *o*-C−F, $^1J_{CF}$ = 239 Hz), 137.9 (d, *p*-C−F, $^1J_{CF}$ = 245 Hz), 136.1 (d, *m*−C-F, $^1J_{CF}$ = 247 Hz), 129.2 (s, *ipso*-C−B) ppm. GCOSY (599.9 MHz, 213 K, dichloromethane-d_2): δ 3.53 (2-H)/−0.90 (1-H) ppm. GHSQC (599.9 MHz, 203 K, dichloromethane-d_2): δ 112.5/6.12 (Cp), 107.5/5.73 (Cp), 96.5/-0.90 (C1), 68.3/3.53 (C2) ppm.

Generation of 9b·B(C$_6$F$_5$)$_4^-$. A solution containing 150 mg (0.26 mmol) of complex **6b** and 266 mg (0.33 mmol) of **8b** in 50 mL of bromobenzene was stirred for 1 h at 0 °C. The product was then precipitated as a red oil by the addition of 30 mL of pentane. The solution was removed by decanting. Pentane (30 mL) was added, and the oil solidified by extensive stirring. The red solid product was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield 174 mg (53%) of the product, mp 103 °C (dec), two isomers in a 95:5 ratio. ^{1}H NMR (599.9 MHz, 233 K, dichloromethane-d_2): Major isomer **9b**: δ 7.63 (m, 2H, Ph-H), 7.23 (m, 2H, Ph-H), 7.10 (m, 1H, Ph-H), 6.42, 6.13, 6.05, 5.39 (s, each 5H, Cp-H), 5.20 (dd, 1H, 2-H, ^3J = 6.6 Hz, ^3J = 15.9 Hz), 4.70 (dd, 1H, 1-H, ^3J = 15.9 Hz, ^2J = 5.4 Hz), −5.52 (dd, 1H, 1-H′, ^3J = 6.6 Hz, ^2J = 5.4 Hz) ppm. Minor isomer **9b′**: δ 6.40, 6.08, 5.93, 5.35 (s, each 5H, Cp-H), −6.06 (dd, 1H, 1-H′, ^3J = 6.4 Hz, ^2J = 5.4 Hz); remaining signals hidden under major isomer resonances. ^{13}C NMR (150.9 MHz, 233 K, dichloromethane-d_2) **9b**: δ 113.5, 111.4, 109.3, 108.7 (d, Cp, $^1J_{CH}$ = 174 Hz), 92.7 (dd, C1, $^1J_{C^1H}$ = 132 Hz, $^1J_{C^1H}$ = 100 Hz), 86.7 (d, C2, $^1J_{C^2H}$ = 142 Hz); $B(C_6F_5)_4^-$: δ 147.9 (d, *o*-C−F, $^1J_{CF}$ = 237 Hz), 138.0 (d, *p*-C−F, $^1J_{CF}$ = 244 Hz), 136.5 (d, *m*-C−F, $^1J_{CF}$ = 246 Hz), 129.5 (s, *ipso*-C−B) ppm. GCOSY (599.9 MHz, 233 K, dichloromethane-d_2): δ −5.52 (1-H′)/4.70 (1-H), −5.52, 4.70 (1-H′, 1-H)/5.20 (2-H) ppm. GHSQC (599.9 MHz, 233 K, dichloromethane-d_2): δ 113.5/6.42, 111.4/6.13, 108.7/6.05, 109.3/5.39 (Cp), 92.7/4.70, −5.52 (C1), 86.7/5.20 (C2) ppm. IR (KBr): $\tilde{\nu}$ 3122, 2962, 2919, 2850, 1644, 1514, 1463, 1274, 1088, 816, 740 cm^{-1}. Anal. Calcd for $C_{52}H_{28}BClF_{20}Zr_2$ (1261.5): C, 49.51; H, 2.24. Found: C, 49.38; H, 3.06%.

Generation of 9c·B(C$_6$F$_5$)$_4^-$. A solution containing 150 mg (0.27 mmol) of complex **6c** and 214 mg (0.27 mmol) of **8b** in 20 mL of bromobenzene was stirred for 1 h at −30 °C. The solution was then warmed to room temperature and stirred for 1 h. Pentane (30 mL) was added to precipitate the product. A red oil separated from which the solvent was decanted off. Pentane (30 mL) was added and the oily suspension stirred for 10 min. The oil was allowed to settle, and the pentane phase was removed by decanting to give 174 mg (53%) of the product as an oil, DSC: 143 °C (dec), mixture of two isomers in a ca. 95:5 ratio. ^{1}H NMR (599.9 MHz, 253 K, dichloromethane-d_2): Major isomer **9c**: δ 6.31, 6.03, 5.87, 5.65 (s, each 5H, Cp-H), 4.14 (dd, 1H, 1-H, ^3J = 15.4 Hz, ^3J = 4.9 Hz), 3.68 (m, 1H, 2-H), 1.37 (m, 2H, CH_2), 1.21 (m, 4H, CH_2), 0.93 (t, 3H, CH_3, ^3J = 6.8 Hz), −5.73 (dd, 1H, 1-H′, ^3J = 6.7 Hz , ^3J = 4.9 Hz) ppm. Minor isomer **9c′**: δ 6.00, 5.84, 5.72, 5.61 (s, each 5H, Cp-H), −6.28 (dd, 1H, 1-H′, ^3J = 6.4 Hz , ^3J = 5.9 Hz) ppm, remaining signals under the major isomer resonances. ^{13}C NMR (150.9 MHz, 253 K, dichloromethane-d_2) **9c:** δ 113.2, 111.2, 108.1, 107.8 (Cp), 104.3 (C1), 94.1 (C2), 36.8 (CH_2), 30.9 (CH_3), 27.2 (C_2H_4); $B(C_6F_5)_4$-: δ 147.6 (d, *o*-C−F, $^1J_{CF}$ = 236 Hz), 137.7 (d, *p*-C−F, $^1J_{CF}$ = 244 Hz), 136.8 (d, *m*-C−F, $^1J_{CF}$ = 246 Hz), 128.5 (s, *ipso*-C−B) ppm. GCOSY (599.9 MHz, 253 K, dichloromethane-d_2): δ −5.73 (1-H′)/4.14 (1-H), −5.73, 4.14 (1-H′, 1-H)/3.68 (2-H), 3.68 (2-H)/1.37 (CH_2 of C_4H_9) ppm. GHSQC (599.9 MHz, 253 K, dichloromethane-d_2): δ 113.2/6.31, 111.2/6.03, 108.1/5.87, 107.8/5.65 (Cp), 104.3/4.14, −5.73 (C1), 94.1/3.68 (C2), 36.8/1.37 (CH_2), 27.2/1.21 (C_2H_4), 30.9/0.93 (CH_3) ppm. ^{19}F NMR (564.3 MHz, 253 K, dichloromethane-d_2) **9c:** δ −134.7 (s, 8F, *o*-F, C_6F_5), −164.4 (s, 8F, *m*-F, C_6F_5), −168.5 (s, 4F, *p*-F, C_6F_5) ppm. IR (KBr): $\tilde{\nu}$ 3125, 2972, 2926, 2884, 1644, 1515, 1463, 1274, 1086, 978, 816 cm^{-1}.

Preparation of (μ-Chloro)(μ-η^1:η^2-CH$_2$−CHD)bis(zirconocene) Tetraphenylborate 9a-d$_1$·BPh$_4^-$. A suspension of 100 mg (0.20 mmol) of *E*/*Z*-**6a**-d_1 and 104 mg (0.26 mmol) of **8a** in 20 mL of bromobenzene was stirred for 1 h at room temperature. The resulting orange precipitate was collected by filtration, washed with ether (3 × 20 mL) and dried in vacuo to give 100 mg (61%) of the product, mp 134 °C (dec), two isomers in 50:50 ratio. ^{1}H NMR (599.9 MHz 308 K, dichloromethane-d_2): δ 5.92, 5.91, 5.90, 5.89 (s, each 5H, Cp-H), 1.30 (br, 3H, CH_2, CHD); BPh_4^-: 7.40−7.30 (m, 8H, Ph-H), 7.07−7.02 (m, 8H, Ph-H), 6.93−6.88 (m, 4H, Ph-H) ppm. ^{1}H NMR (599.9 MHz, 193 K, dichloromethane-d_2): δ 6.04, 6.00, 5.99, 5.96, 5.75, 5.73, 5.72, 5.70 (s, each 5H, Cp-H, the Cp resonances cannot be assigned to the respective isomers). **9a**-C^{1}HD: 3.58 (dd, 1H, 2-H, ^3J = 6.4 Hz, ^2J = 5.6 Hz), 3.41 (dd, 1H, 2-H′, ^3J = 9.5 Hz, ^2J = 5.6 Hz), −2.18 (dd, 1H, 1-H′, ^3J = 6.4 Hz, ^3J = 9.5 Hz); **9a**-C^{2}HD: 3.50 (dd, 1H, 2-H, ^3J = 8.3 Hz, ^3J = 10.3 Hz), −0.79 (dd, 1H, 1-H, ^3J = 10.3 Hz, ^2J = 4.4 Hz), −1.00 (dd, 1H, 1-H′, ^3J = 8.3 Hz, ^2J = 4.4 Hz); BPh_4^-: 7.30 (m, 8H, Ph-H), 7.03 (m, 8H, Ph-H), 6.89 (m, 4H, Ph-H) ppm. GCOSY (599.9 MHz, 193 K, dichloromethane-d_2) **9a**-C^{1}HD: δ 3.58 (2-H)/3.41 (2′-H), 3.58, 3.41 (2-H′, 2-H)/−2.18 (1-H′); **9a**-C^{2}HD: δ −0.78 (1-H)/−1.00 (1-H′), −0.78, −1.00 (1-H, 1-H′)/3.50 (2-H) ppm. GHSQC (^{13}C not broad band decoupled, ^{13}C chemical shifts ca. ±0.5 ppm) (599.9 MHz, 193 K, dichloromethane-d_2): δ 112.6/6.04, 112.4/6.00, 112.3/5.99, 112.1/5.96, 107.2/5.75, 107.15/5.73, 5.72, 107.12/5.70 (Cp); **9a**-C^{1}HD: 94.6 ($^1J_{C^1H}$ = 110 Hz)/−2.18 (C1), 66.8 ($^1J_{C^2H}$ = 157 Hz, $^1J_{C^2H}$ = 155 Hz)/3.58, 3.41 (C2); **9a**-C^{2}HD: 66.7 ($^1J_{C^2H}$ = 155 Hz)/3.50 (C2), 95.0 ($^1J_{C^1H}$ = 123 Hz, $^1J_{C^1H}$ = 123 Hz)/−0.78, −1.00 (C1), 67.6/3.52 (C2); BPh_4^-: 135.8/7.28 (Ph), 125.7/7.04 (Ph), 121.6/6.89 (Ph) ppm. IR (KBr): $\tilde{\nu}$ 3053, 2962, 2925, 2851, 1601, 1430, 1019, 803, 737 cm^{-1}. Anal. Calcd for $C_{46}H_{43}DBClZr_2$ (826.6): C, 66.84; H, 5.49. Found: C, 66.31; H, 5.09%.

Generation of (μ-Chloro)(μ-η^1:η^2-CHD-CHPh)bis(zirconocene) Tetraphenylborate 9b·BPh$_4^-$. Bromobenzene (20 mL) was added to a mixture of 150 mg (0.25 mmol) of **6b** and 136 mg (0.34 mmol) of $DNMe_2Ph^+BPh_4^-$ (**8a**-d_1). The mixture was stirred for 1 h at ambient temperature and then worked up as described for **9b**·BPh_4^- to give 100 mg (43%) of **9b**-d_1·BPh_4^- as a red powder, mp 127 °C (dec), two isotopomers in a 50:50 ratio. ^{1}H NMR (599.9 MHz, 233 K, dichloromethane-d_2) both isotopomers: δ 7.58 (m, 2H, Ph-H), 7.46 (m, 2H, Ph-H), 7.14 (m, 1H, Ph-H), 6.28, 6.03, 5.95, 5.37 (s, each 5H, Cp-H), 5.17 (br, 1H, 2-H); **9b**-d_1 (μ-H): −5.59 (d, 1H, 1-H, ^3J = 6.0 Hz); **9b**-d_1 (μ-D): 4.58 (d, 1H, 1-H, ^3J = 15.6 Hz); BPh_4^-: 7.31 (m, 8H, Ph-H), 7.04 (m, 8H, Ph-H), 6.89 (m, 4H, Ph-H) ppm. GCOSY (599.9 MHz, 233 K, dichloromethane-d_2) **9b**-d$_1$ (μ-H): δ −5.59 (1-H)/5.17 (2-H); **9b**-d_1 (μ-D): δ 4.58 (1-H)/5.17 (2-H) ppm. IR (KBr): $\tilde{\nu}$ 3054, 2965, 2922, 2853, 1485, 1429, 1261, 1015, 808, 735, 708 cm^{-1}.

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Supporting Information Available: Details on the X-ray crystal structure determination of complex **10c** and of the analysis of the agostic cation system **9a**-d_1 (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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